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SYNTHÈSE ET RÉACTIVITÉ DE COMPLEXES DU NICKEL(II) COMPORTANT DES LIGANDS CARBÈNE N-HÉTÉROCYCLIQUE. DES RÉACTIONS DE COUPLAGE C–C CROISÉ À L'ACTIVATION DE LIAISONS C–H

Soutenue le 27 septembre 2010 devant la commission d'examen :

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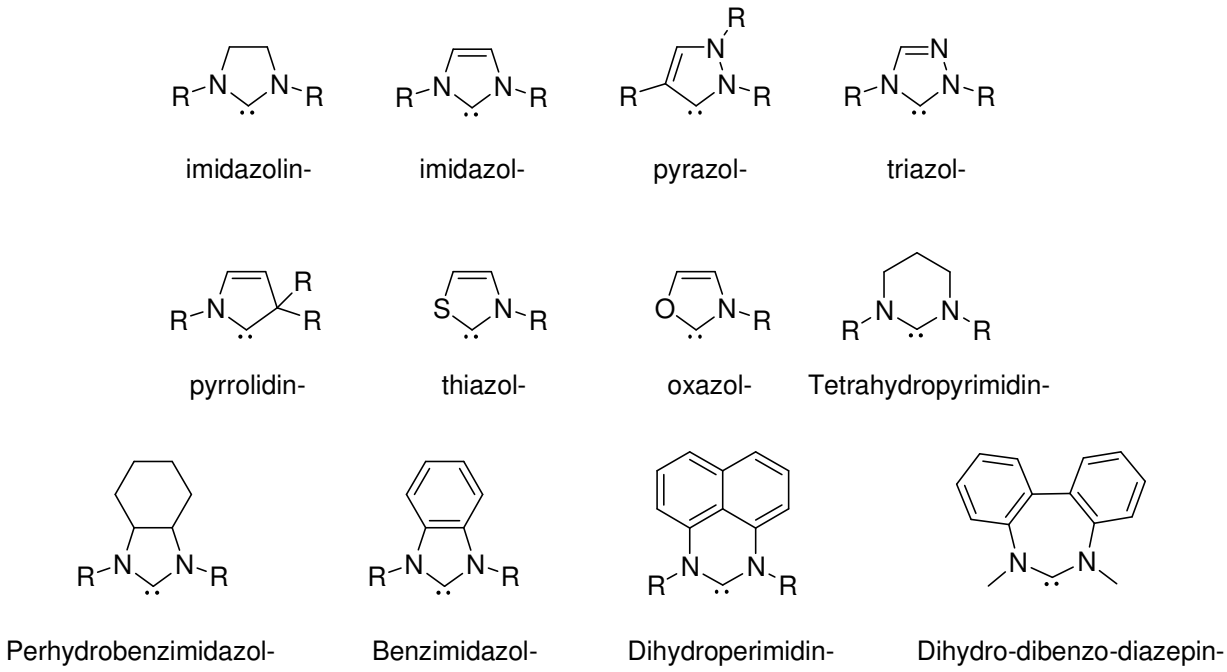
Table of Contents

Chapter 1

N-Heterocyclic Carbenes as Ligands in Nickel-Catalyzed Organic Transformations

1. Introduction

N-heterocyclic carbenes (NHCs), which contain at least one α-amino substituent have become essential ligands in the field of organometallic chemistry and in particular in homogeneous catalysis.[1] The most cited subclasses of NHCs are illustrated in Scheme 1.

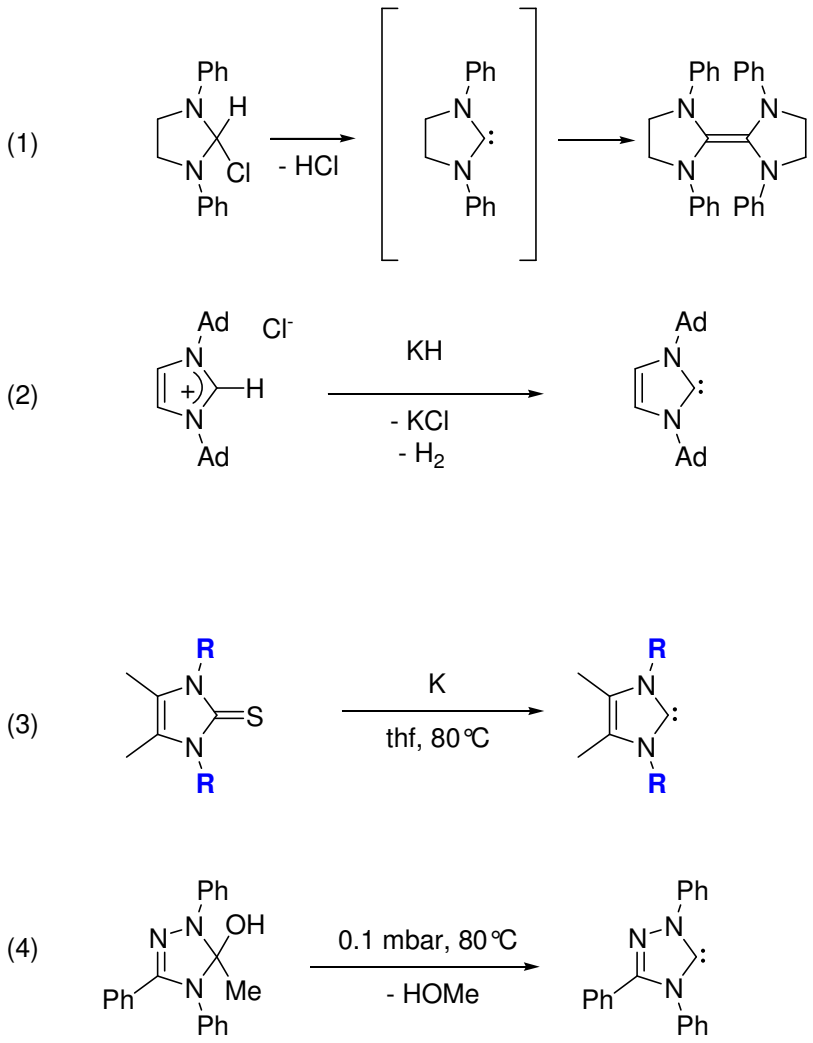


Scheme 1 : Most cited subclasses of NHCs. The suffix "ylidene" should be added to each subclass.

Over the last fifty years, they have evolved from being elusive intermediates, for which Wanzlick[2] could show only indirect evidence in the form of decomposition fragments (Eq. 1, Scheme 2), to stable species from the reaction of *N*-substituted imidazolium salts with potassium hydroxide (Eq. 2, Scheme 2) by Arduengo.[3] Further pioneering work was reported by Kuhn who prepared the desired imidazol-*2*-ylidene from the appropriate imidazol-*2*-thione and potassium in refluxing thf (Eq. 3, Scheme 2),[4] as well as Enders who synthesized the first nowadays

[1] some recent reviews: (a) O. Kuehl, *Chem. Soc. Rev.* **2007**, *36*, 592. (b) W. A. Herrmann, *Angew. Chem. Int. Ed.* **2002**, *41*, 1290.
[2] (a) H. W. Wanzlick, H. J. Schönherr, *Liebigs Ann. Chem.* **1970**, *731*, 176; (b) H. J. Schönherr, H. W. Wanzlick, *Chem. Ber.* **1970**, *103*, 1037; (c) H. W. Wanzlick, F. Esser, H. J. Kleiner, *Chem. Ber.* **1963**, *96*, 1208; (d) H. W. Wanzlick, H. J. Kleiner, *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 75.
[3] A. J. Arduengo III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361.
[4] N. Kuhn, T. Kratz, *Synthesis* **1993**, 561.

commercially available NHC by thermal decomposition of the adequate 5-methoxytriazoline precursor via α-elimination of methanol in vacuo (Eq. 4, Scheme 2).[5]



Scheme 2

The exceptional stability of these nucleophilic singlet carbenes arises from the combined π-electron donating and σ-electron withdrawing properties of the α-nitrogen atoms.[6,7,8] Indeed, the mesomeric and inductive effects formally preserve the electronic neutrality of the carbene centre by

[5] D. Enders, K. Breuer, G. Raabe, J. Runsink, J. H. Teles, J. P. Melder, K. Ebel, S. Brode, *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1021
[6] W. A. Herrmann, C. Köcher, *Angew. Chem. Int. Ed.* **1997**, *36*, 2163.
[7] D. Bourissou, O. Guerret, F. P. Gabbat, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39.
[8] (a) J. F. Lehmann, S. G. Urquhart, L. E. Ennios, A. P. Hitchcock, K. Hatano, S. Gupta, M. K. Denk, *Organometallics* **1999**, *18*, 1862; (b) C. Boehme, G. Frenking, *J. Am. Chem. Soc.* **1996**, *118*, 2039; (c) C. Heinemann, T. Müller, Y. Apeloig, H. Schwarz, *J. Am. Chem. Soc.* **1996**, *118*, 2013; (d) A. J. Arduengo III, H. V. R. Dias, D. A. Dixon, R. L. Harlow, W. T. Klooster, T. F. Koetzle, *J. Am. Chem. Soc.* **1994**, *116*, 6812; (e) A. J. Arduengo III, H. Bock, H. Chen, M. Denk, A. D. Dixon, J. C. Green, W. A. Herrmann, N. L. Jones, M. Wagner, R. West, *J. Am. Chem. Soc.* **1994**, *116*, 1641; (f) D. A. Dixon, A. J. Arduengo III, *J. Phys. Chem.* **1991**, *95*, 4180.

electronic push-push [Figure 1, A] and pull-pull [Figure 1, B] mechanisms and lead to an increase in the singlet-triplet gap, thereby stabilizing the singlet over the more reactive triplet state. These effects also make the normally vacant π orbital on the carbenoid carbon less available for attacks of electrophiles and thus increase not only the thermodynamic - but also the kinetic stability of the singlet state. Steric effects in contrast only contribute marginally to the stability of the NHCs.[8b,d-g]

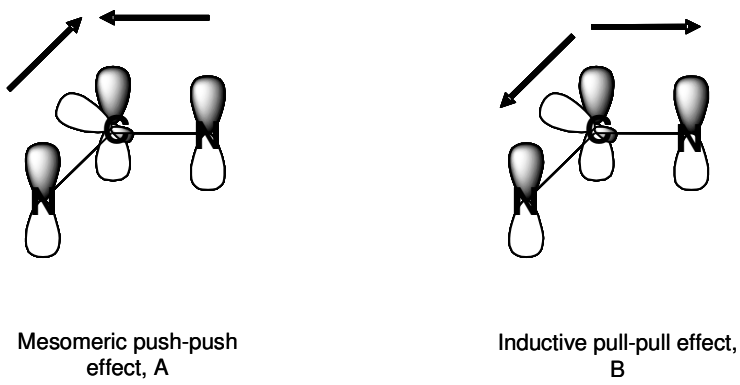


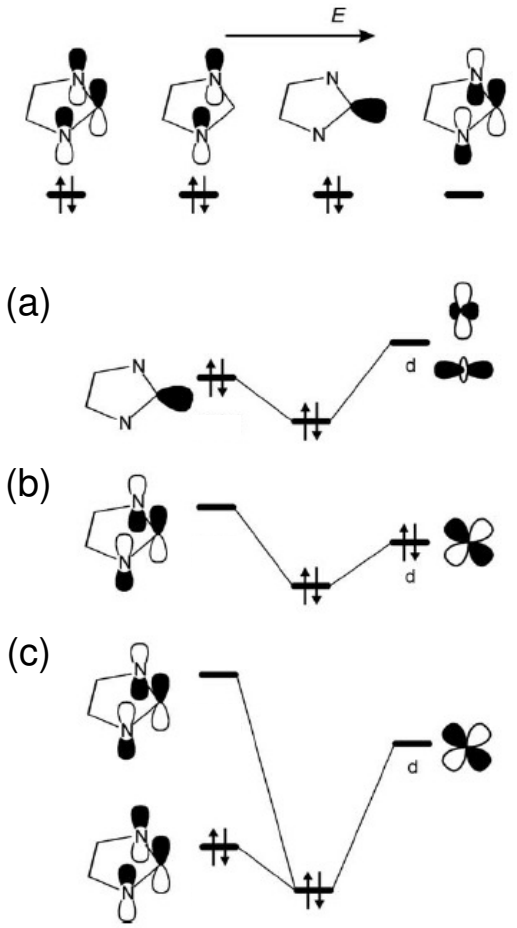
Figure 1

Rapidly, the realization of their outstanding potential of NHCs as support ligands for homogeneous catalysis, notably by Herrmann,[9] Enders[10] as well as Dixneuf and Çetinkaya[11] converted these laboratory curiosities into "broadly catalytically useful ligands comparable with cyclopentadienyls and phosphines".[12] Indeed, many TM-NHC complexes have proven to be more efficient catalysts than TM-PR_3 compounds.[1b,13]

Currently, imidazol-*2*-ylidenes and imidazolin-*2*-ylidenes represent the dominant architecture of the stable cyclic diaminocarbenes (Scheme 1).[14,15] The success of NHCs is generally attributed to their strong σ-donating properties which allow very strong NHC-TM bonds.[16,17,18] Nevertheless, three interactions of the NHC–TM bond should be considered when trying to fully understand the strength of the NHC-TM bonding (Scheme 9): **(a)** σ-donation from the NHC σ-donor orbital to a

[9] W. A. Herrmann, M. Elison, J. Fischer, C. Köcher, G. R. J. Artus, *Ang. Chem., Int. Ed. Engl.* **1995**, *34*, 2371.
[10] D. Enders, H. Gielen, G. Raabe, J. Rusinke, J. H. Teles, *Chem. Ber.* **1996**, *129*, 4483.
[11] H. Kücükbay, B. Çetinkaya, S. Guesmi, P. H. Dixneuf, *Organometallics* **1996**, *15*, 2434.
[12] As stated by R. H. Crabtree in 2005, see: R. H. Crabtree, *J. Organomet. Chem.* **2005**, *690*, 5451.
[13] (a) F. Glorius (Ed.) Topics in Organometallic Chemistry 21 (*N*-Heterocyclic Carbenes in Transition Metal Catalysis) Springer Berlin/Heiderlberg, Germany, 2007; (b) A. J. Arduengo III, *Acc. Chem. Res.* **1999**, *32*, 913; (c) N. M. Scott, S. P. Nolan, *Eur. J. Inorg. Chem.* **2005**, 1815; (d) Special issue: *Coord. Chem. Rev.* **2006** ,*251*, 595 ff.
[14] A. J. Arduengo III, H. V. R. Dias, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1992**, *114*, 5530.
[15] A. J. Arduengo III US Patent 5077414 A2, 1992.
[16].S. Diéz-González, S. P. Nolan, *Coord. Chem. Rev.* **2007**, *251*, 874.
[17] W. A. Herrmann, *Organometallics* **1995**, *14*, 1085.
[18] S.-T. Liu, R.-Z. Ku, C.-Y. Liu, F. M. Kiang, *J. Organomet. Chem.* **1997**, *543*, 249.

TM acceptor orbital,[19] **(b)** π-backdonation from an occupied TM d_π orbital into the NHC carbon p_π orbital and **(c)** delocalization of the NHC π-system into an unoccupied TM d_π (p_π) orbital (thus, π–donation).[20] In particular, electron-rich Ni(0)$(NHC)_2$ complexes are suggested to gather high amounts of ligand π-donation which would reach up to 43 % of the total NHC-Ni orbital energy for Ni(0)$(H_4\text{-NHC})_2$ (H_4-NHC = tetrahydroimidazol-*2*-ylidene) complexes.[21].



Scheme 3

Ni(0)-NHC systems generally receive less publicity than their palladium based counterparts. However, despite (i) the high importance that are found in natural products,[22] drugs,[23] or

[19] A. R. Chianese, X. Li, M. C. Janzen, J. W. Faller, R. H. Crabtree, *Organometallics* **2003**, *22*, 1663.
[20] (a) E. F. Penka, C. W. Schläpfer, M. Anatasov, M. Albrecht, C. Daul, *J. Organom. Chem.* **2007**, *692*, 5709; (b) D. M. Khramov, V. M. Lynch, C. W. Bielawski, *Organometallics* **2007**, *26*, 6042; (c) S. Fantasia, J. L. Petersen, H. Jacobsen, S. P. Nolan, *Organometallics* **2007**, *26*, 5880; (d) H. Jacobsen, A. Correa, C. Costabile, L. Cavallo, *J. Organomet. Chem.* **2006**, *691*, 4350; (e) N. M. Scott, R. Dorta, E. D. Stevens, A. Correa, L. Cavallo, S. P. Nolan, *J. Am. Chem. Soc.* **2005**, *127*, 3516; (f) R. Dorta, E. D. Stevens, N. M. Scott, C. Costabile, L. Cavallo, C. D. Hoff, S. P. Nolan, *J. Am. Chem. Soc.* **2005**, *127*, 2485; (g) J. Huang, H.-J. Schanz, E. D. Stevens, S. P. Nolan, *Organometallics* **1999**, *18*, 2370.
[21] U. Radius, F. M. Bickelhaupt, *Coord. Chem. Rev*. **2009**, *253*, 678.
[22] G. Bringmann, D. Menche, *Acc. Chem. Res.* **2001**, *34*, 625.
[23] P. J. Hadjuk, M. Bures, J. Praestgaard, S. W. Fesik, *J. Med. Chem.* **2000**, *43*, 3443.

materials,[24] (ii) the much lower cost and easier removal of nickel from the products[25] (with respect to its more widely used d^{10} counterpart, palladium), and the unique properties of NHC ligands in comparison to phosphines,[1] examples of Ni(0)-NHC catalysts remain scarce. Nevertheless, these species have already found many applications in a vast variety of organic transformations and the steadily increasing number of communications testifies the potential of these species.

In this chapter, we describe the present state of nickel-NHC mediated catalytic organic transformations. First, we focus on coupling reactions which generate C–C, C–N and C–S bonds by catalytic sp^2-C–X bond activation. This section will include Kumada-Corriu, Negishi and Suzuki-Miyaura cross-couplings of aryl halides or pseudohalides with organometallic reagents. Furthermore, Mizoroko-Heck cross-couplings of aryl halides with alkenes, aryl animations and aryl thiolations as well as one example of Ullmann homocoupling of aryl halides are described.

Next, we target those C–C bonds which are generated by catalytic sp^2-C–H bond activation such as Michael additions, alkylation of imidazolium halides and recently, ketone arylation. We complete this section with the Ni-NHC catalyzed hydrothiolation of alkynes and recent investigations of catalytic and stoechiometric of sp^2-C–F bond activation.

The third part of Chapter describes inter- or intramolecular π-component activation including [2+2+2] and [2+2] cycloadditions and rearrangement reactions of vinyl cyclopropanes, vinyl azirides, cyclopropylen-ynes and aziridinylen-yne as well as *three* component couplings of unsaturated hydrocarbons with aldehydes and metal hydrides. Finally we briefly describe Ni-NHC catalyzed polymerization in the fourth and last section of this chapter. For all reaction types, we have considered both well defined Ni-NHC complexes and in situ procedures using either NHCs or azolium salts. The catalytic dehydrogenation reactions of aryl halides,[26] and imines,[27] as well as the Ni-NHC catalyzed hydrosilylation[28] are not included in this chapter.

2. Catalytic C–C, C–N, and C–S Bond Formation Reactions via sp^2-C–X (X = Halide, Pseudo Halide) Activation

2.1. Cross-Coupling Reactions

The cross-coupling reactions of organometallic reagents with organic electrophiles in the presence of group 8 – 10 metal catalysts, notably nickel and palladium complexes, is the method of

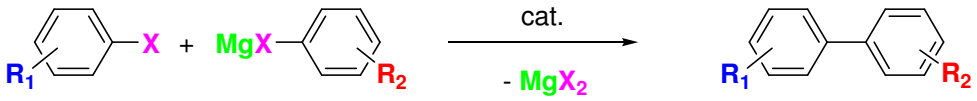
[24] T. Yamamoto, *Synlett* **2003**, 425.
[25] C. E. Tucker, J. G. de Vries, *Top. Catal.* **2002**, *19*, 111.
[26] C. Desmarets, S. Kuhl, R. Schneider, Y. Fort, *Organometallics* **2002**, *21*, 1554.
[27] S. Kuhl, R. Schneider, Y. Fort, *Organometallics* **2003**, *22*, 4184.
[28] M. R. Chaulgain, G. M. Mahandru, J. Montgomery, *Tetrahedron* **2009**, *62*, 7560.

choice for a wide range of C–C, C–N, C–S or C–M bond forming process. Whereas Pd-NHC systems have shown outstanding activity for these reactions, Ni-NHC catalysts have shown only moderate activity. Nevertheless, some procedures have shown the potential of Ni-NHCs for the activation unless reactive sp^2-C–Cl and in particular of sp^2-C–F bonds.

This section summarizes the present state of Ni-NHC catalyzed C–C, C–N and C–S cross-coupling reactions, which have been described since the discovery of NHCs as highly efficient supporting ligands in homogeneous catalysis.[9-12] First, we will focus on Kumada-Corriu cross-coupling, Negishi coupling and then Suzuki-Miyaura cross-coupling reactions. In the second part, we will target Ni-NHC mediated C–N and C–S cross-couplings.

2.1.1. Kumada-Corriu Cross-Coupling

The Kumada-Corriu cross-coupling reaction promotes C–C bond formation between an sp^2-hybridized carbon-halide (or carbon-pseudohalide) and a vinyl- or aryl-Grignard reagent (Scheme 4).[29] Even if Grignard reagents are air and moisture sensitive, they are crucial coupling partners as most boronic acids, organozincs and stannanes are derived from these compounds. It is not surprising that in particular Pd-NHCs have been receiving much attention in association with NHCs.[30] Nevertheless, these systems generally require high reaction temperatures.[31] Rapidly, Ni-NHC catalysts have shown their outstanding potential as catalysts in Kumada-Corriu cross-coupling of aryl chlorides and even unreactive aryl fluorides at room temperature. Even though some key *in situ* procedures staring $Ni(acac)_2$ (acac = acetylacetonate) and azolium salts or from zero valent $Ni(cod)_2$ and the free carbene, mainly well–defined Ni(II)-NHC complexes have been studied.

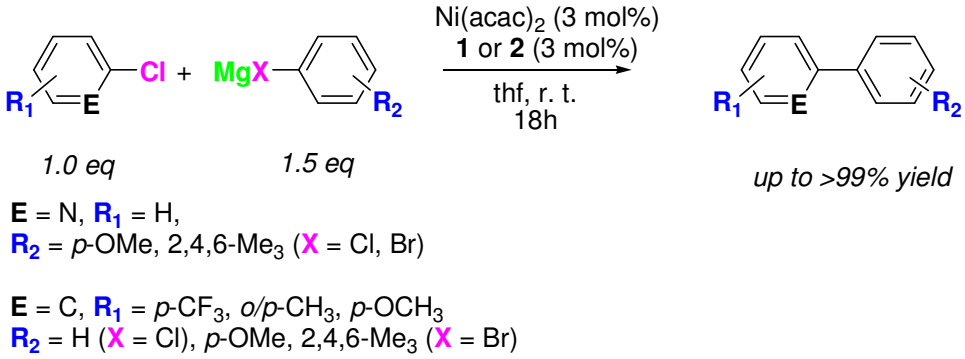


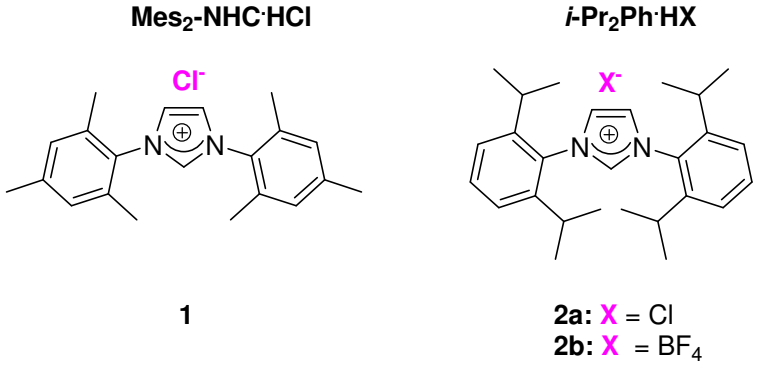
Scheme 4

[29] (a) K. Tamao; K. Sumitani, M. Kumada, *J. Am. Chem. Soc.* **1972**, *94*, 4374; (b) R. J. P. Corriu, J. P. Masse, *J. Chem. Soc., Chem. Commun.* **1972**, 144.
[30] As a recent review on Pd-NHC mediated Cross-Coupling reactions, see: N. Marion, S. P. Nolan, *Acc. Chem. Res.* **2008**, *41*, 1440.
[31] (a) C. Wolf, H. Xu, *J. Org, Chem* **2008**, *73*, 162; (b) R. Martin, S. L. Buchwald, *J. Am. Chem. Soc.* **2007**, *129*, 3844; (c) L. Ackermann, C. J. Gschrei, A. Althammer, M. Riederer, *Chem. Commun.* **2006**, 1419; (d) J. Huang, S. P. Nolan, *J. Am. Chem. Soc.* **1999**, *121*, 9889.

2.1.1.1. Monocarbene Systems

Almost ten years ago, Herrmann and co-workers ensured the success of Ni-NHC as efficient catalytic systems for Kumada-Corriu cross-coupling reactions by the *in situ* generated active species from $Ni(acac)_2$ and (2,4,6-trimethylphenyl)imidazolium chloride (Mes_2-NHC·HCl), **1**, and (2,6-diisopropylphenyl)imidazolium chloride {(i-$Pr_2Ph)_2$-NHC·HCl}, **2a** (Scheme 2).[32]





Scheme 5

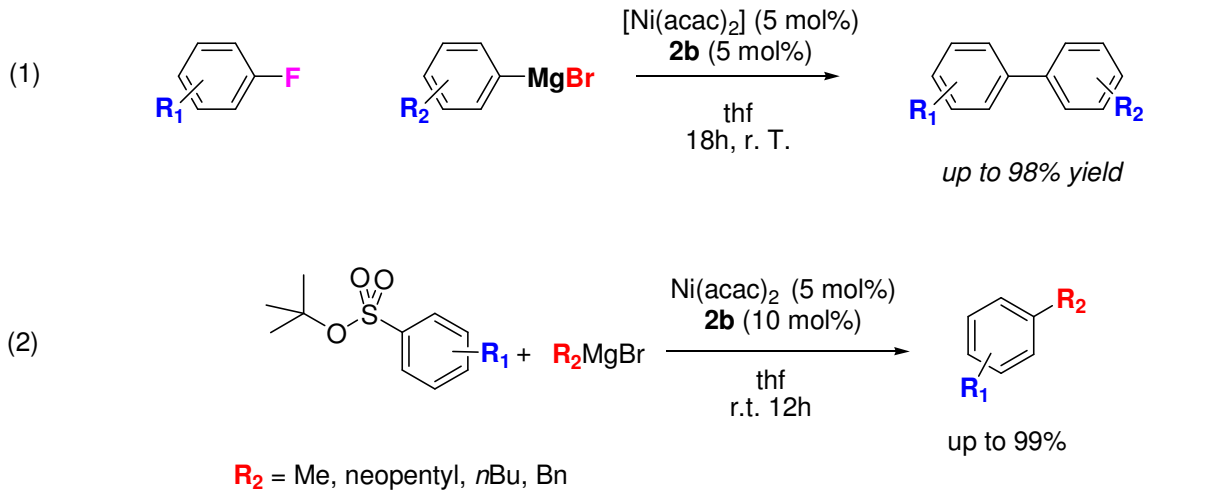
Thus, a vast number of functionalized biaryls was synthesized in good to excellent yield from organomagnesium bromide or chloride derivatives and electronically activated as well as deactivated aryl chlorides. Among these substrates electron-poor arenes displayed the highest reactivity.

Moreover, generally unreactive aryl *fluorides* were discovered as good coupling partners by employing an Ni{(i-$Pr_2Ph)_2$-NHC} species generated *in situ* from $Ni(acac)_2$ and **2b** (Eq. 1, Scheme 6).[33] Under standard conditions[32], activated electron-poor as well as deactivated electron-rich aryl fluorides were both converted in high yield. Using fluorides, the steric congestion of the Grignard did impact the activity of the active species and lowered the conversion rate. In contrast, coupling

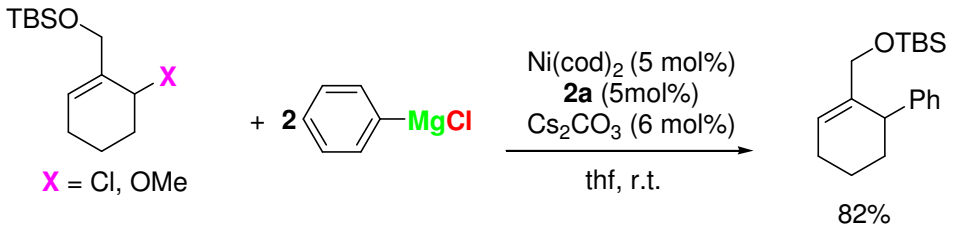
[32] V. P. W. Böhm, T. Weskamp, C. W. K. Gstöttmayr, W. A. Herrmann, *Angew. Chem. Int. Ed.* **2000**, *39*, 1602.
[33] V. P. W. Böhm, C. W. K. Gstöttmayr, T. Weskamp, W. A. Herrmann, *Angew. Chem., Int. Ed.* **2001**, *40*, 3387.

of aryl chlorides was insensitive to steric congestion of the organometallic reagent. This system notably permitted the preparation of tri-*ortho*-substituted biaryl compounds, a result not matched yet by subsequent reports.

Finally, pseudo halides such as arenesulfonates[34] (Eq. 2, Scheme 6) and less familiar aryltitanium(IV) alkoxides[35] (Eq. 3, Scheme 6) as well as 2-substituted cyclohexene derivatives (Scheme 7) were found to be suitable coupling partners for Grigands by employing the *in situ* generated Ni{(*i*-$Pr_2Ph)_2$-NHC}.[36]



Scheme 6

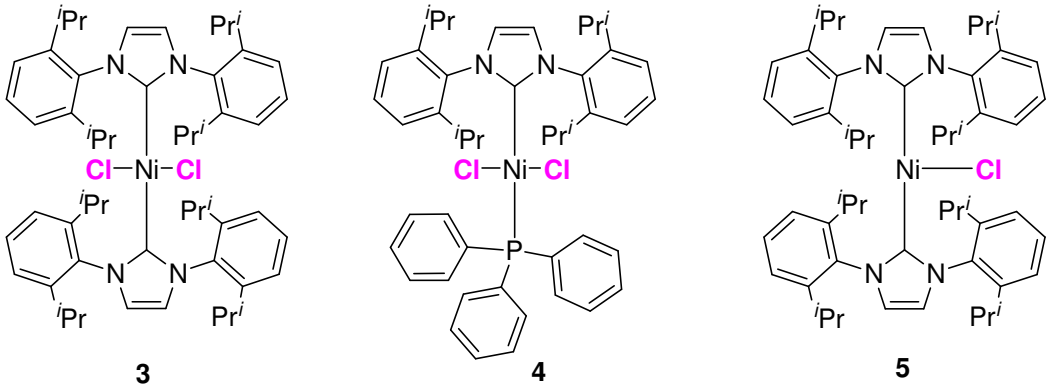


Scheme 7

A comparison of the complexes $[NiCl_2(PPh_3)_2]$, $[NiCl_2\{i\text{-}Pr_2Ph)_2\text{-NHC}\}_2]$[37], **3**, and mixed $[NiCl_2\{i\text{-}Pr_2Ph)_2\text{-NHC}\}PPh_3]$, **4**, as a pre-catalyst for Kumada-Corriu cross coupling has been

[34] C.-B. Kim, H. Jo, B.-K. Ahn, C. K. Kim, K. Park, *J. Org. Chem.* **2009**, *74*, 9566.
[35] G. Manolikakes, N. Dastbaravardeh, P. Knochel, *Synlett* **2007**, *13*, 2077.
[36] T. Yamazaki, Y. Sato, *Synthesis* **2008**, *17*, 2830.
[37] W. A. Herrmann, G. Gerstberger, M. Spiegler, *Organometallics* **1997**, *16*, 2209.

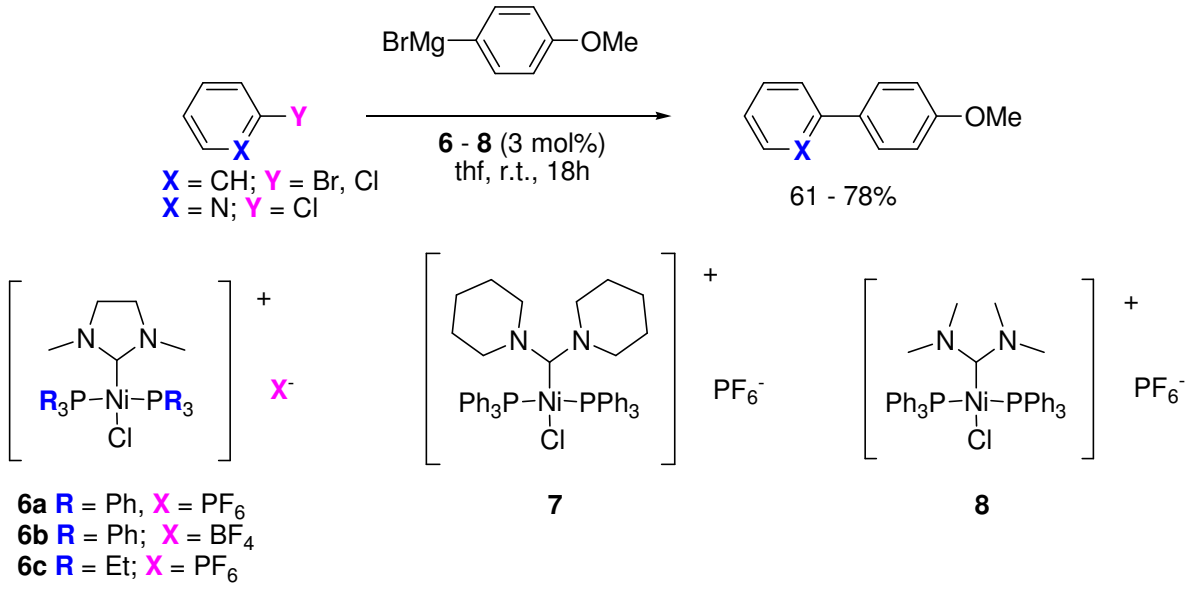
reported by Matsubara (Scheme 8).[38] Compared to **3**, the mixed complex **4** showed the highest activity with respect to the conversion of PhMgCl and aryl chlorides. Mechanistic investigation on the catalytic intermediates of the cross-coupling reaction allowed the identification of the T-shaped nickel(I)-NHC_2 intermediate, **5**.[39] In the presence of free *i*-Pr_2Ph_2-NHC, **5** was selectively formed and isolated by the reaction of zero-valent [Ni(*i*-$Pr_2Ph)_2$-$NHC)_2$] with chloroarenes and appeared to promote cross-coupling involving 4-bromoanisole or 4-bromobiphenyl and PhMgCl in almost quantitative yield after 18 hours. As the reaction proceeded in similar manner starting from **3**[37,38] the authors postulate that the Ni(I) species **5** is a possible intermediate in the catalytic reaction using **3** as a pre-catalyst.



Scheme 8

Saturated 1,3-methylimidazolin-*2*-ylidene-, **6a**, as well as acyclic diaminocarbene-nickel-phosphine complexes, **7** and **8**, were also identified as good pre-catalysts for the Kumada-Corriu cross-coupling reaction involving *p*-methoxyphenylmagnesium bromide and chloro-, bromobenzene or 2-chloropyridine (Scheme 5).[40] The related biaryls were isolated in good yields (61 – 78 %).

[38] K. Matsubara, K. Ueno, Y. Shibata, *Organometallics* **2006**, *25*, 3422.
[39] S. Miyazaki, Y. Koga, T. Matsumoto, K. Matsubara, *Chem. Commun*. **2010**, *46*, 1932.
[40] D. Kremzov, G. Seidel, C. W. Lehmann, A. Fürstner, *Chem. Eur. J.* **2005**, *11*, 1833.

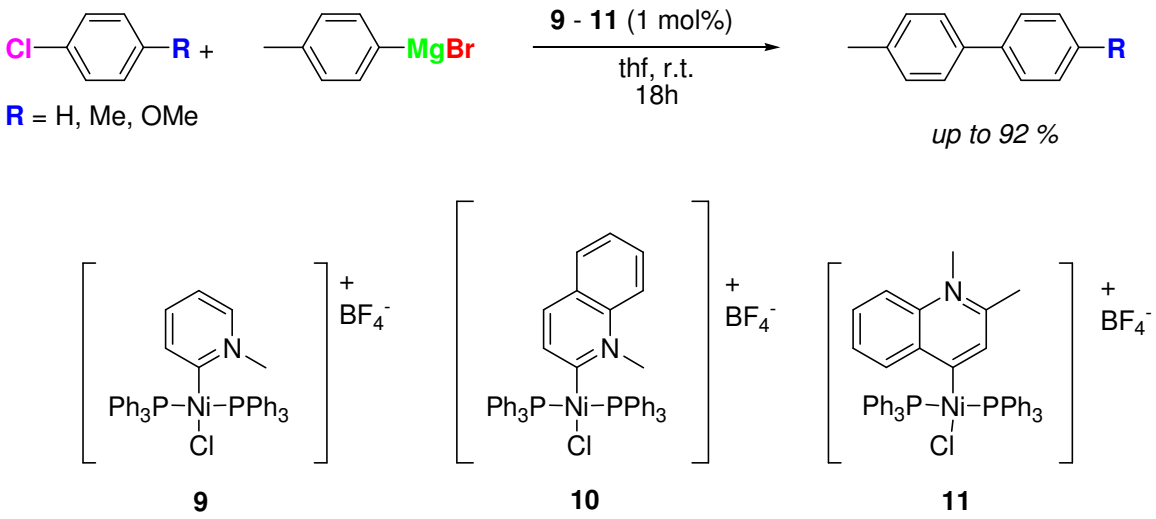


Scheme 9

1-*N*-Pyridyl based NHCs were found to show analogous activity for Kumada-Corriu cross-coupling involving chloroarenes and BrMgPh.[41] Herrmann postulated that this family of ligands might show even stronger σ-interaction with the metal centre and thus, efficiently promote C–C bond formation.

The series of cationic 1-*N*-pyridyl- and quinolidyl- ligand precursors have been synthesized from the appropriate commercially available chloropyridine and chloroquinoline derivatives by alkylation with the Meerwein salt[42] in overall high yield.[41a,43] The corresponding cationic nickel(II) complexes **9**, **10** and **11** have been formed by employing [Ni(PPh$_3$)$_4$] as a metal source and isolated as yellow crystals, that reveal a distorted square planar coordination sphere around the nickel atom. The reaction pattern for Kumada-Corriu cross-coupling appeared to be similar to that of imidazol-*2*-ylidene based nickel species, although selectivity towards cross-coupling was slightly decreased and undesirable homocoupling was observed (Scheme 10).

[41] (a) S. K. Schenider, G. R. Julius, C. Loschen, H. G. Raubenheimer, G. Frenking, W. A. Herrmann, *Dalton Trans.* **2006**, 1226; (b) S. K. Schenider, P. Roembke, G. R. Julius, C. Loschen, H. G. Raubenheimer, G. Frenking, W. A. Herrmann, *Eur. J. Inorg. Chem.* **2005**, 2973.
[42] P. J. Fraser, W. R. Roper, F. G. A. Stone, *Dalton Trans.* **1974**, 102.
[43] W. H. Meyer, M. Deetlefs, M. Pohlmann, R. Scholz, M. W. Esterhuyser, G. R. Julius, H. G. Raubenheimer, *Dalton Trans.* **2003**, 413.

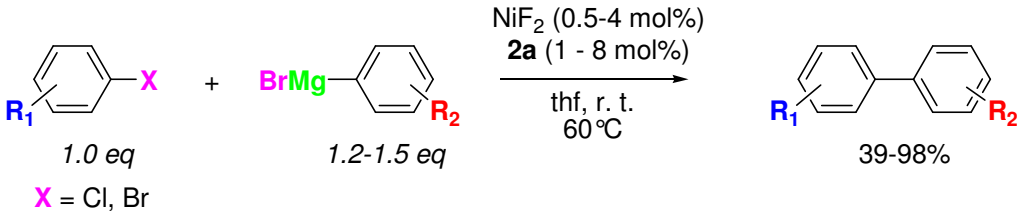


Scheme 10

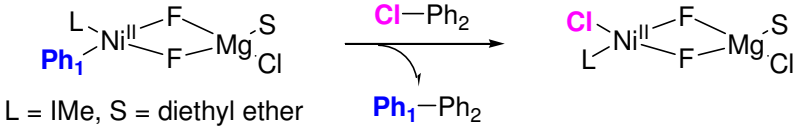
Finally, metal fluorides $MF_x \cdot yH_2O$ (M = Fe, Co and Ni) in association with NHCs efficiently promote the Kumada cross-coupling reaction of a broad range of aryl and heteroaryl halides with excellent yield and selectivity (Eq. 1, Scheme 11).[44] The catalytic system generated *in situ* from two equivalents of **2a**-**b** and $NiF_2 \cdot 4H_2O$ showed good tolerance for functional groups and bulky substituents in both the Grignard and the aryl halide. Multiple arylation reaction of polychloroarenes was achieved in good yield. Strong coordination of the fluoride ion onto the nickel atom should suppress the conventional transmetallation-reductive elimination process of classical Ni(0)-Ni(II) systems resulting in lower selectivity and higher amounts of homocoupling of the aryl halide reagent (Eq. 2, Scheme 11). Computational DFT calculations for the simplified Ni-IMe (IMe = 1,3-dimethylimidazol-*2*-ylidene) system proposed that the catalytic pathway should occur by a metalate mechanism involving a high-valent heteroleptic nickel(IV) key complex, **I**, (Eq. 3, Scheme 11) rather that via a classical Ni(0)-Ni(II) catalytic cycle.[45,46]

[44] T. Hatakeyama, S. Hashimoto, K. Ishizuka, M. Nakamura, *J. Am. Chem. Soc.* **2009**, *131*, 11949.
[45] (a) M. Carnes, D. Buccella, J. Y.-C. Chen, A. P. Ramirez, N. J. Turro, C. Nuckolls, M. Steigerwald, *Angew. Chem. Int. Ed.* **2009**, *48*, 290; (b) V. Dimitrov, A. Linden, *Angew. Chem. Int. Ed.* **2003**, *42*, 2631; (c) E. K. Byrne, K. H. Theopold, *J. Am. Chem. Soc.* **1989**, *111*, 3887; (d) B. K. Bower, H. G. Tennet, *J. Am. Chem. Soc.* **1972**, *94*, 2462.
[46] As some other examples of metalate mechanism for nickel catalysts, see: (a) J. Terao, H. Todo, H. Watanabe, A. Ikumi, N. Kambe, *Angew. Chem. Int. Ed.* **2004**, *43*, 6180; (b) J. Terao, H. Watanabe, A. Ikumi, H. Kuniyasu, N. Kambe, *J. Am. Chem. Soc.* **2002**, *124*, 4222.

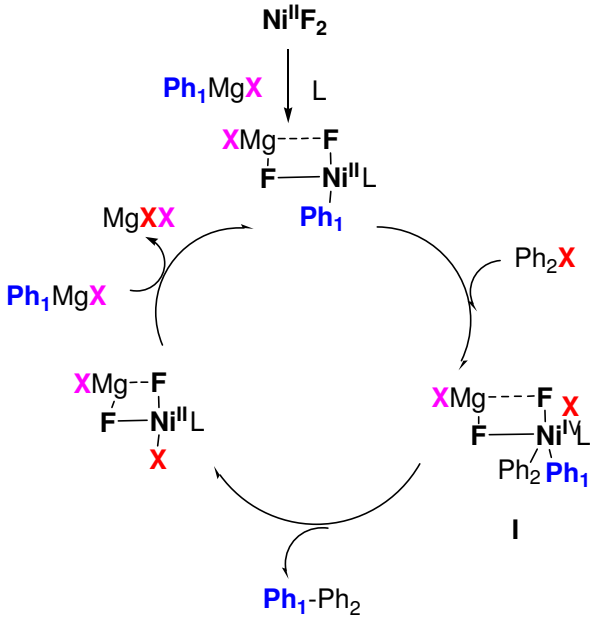
(1)



(2)



(3)



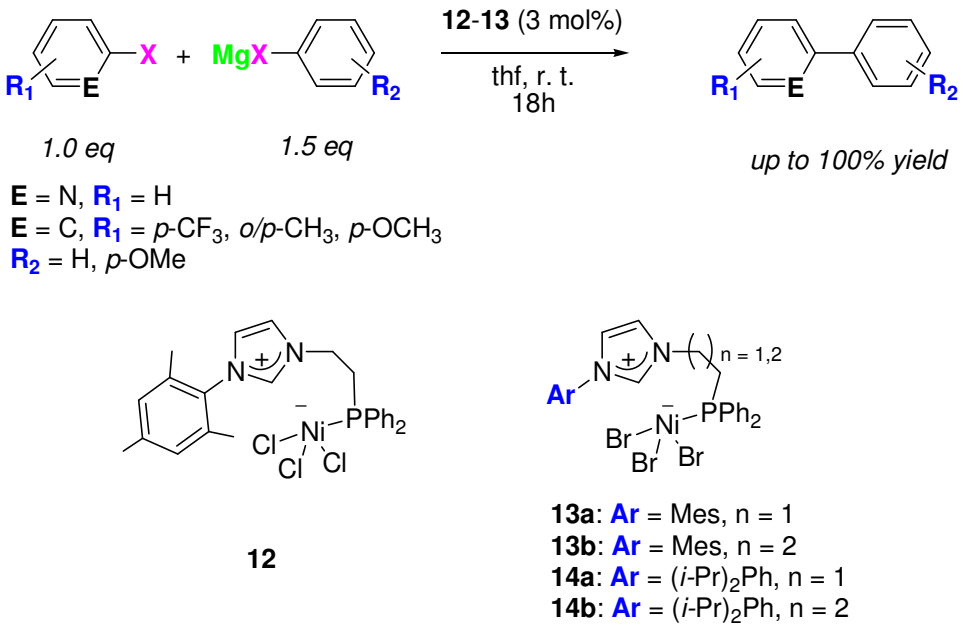
Scheme 11

2.1.1.2. Bidentate carbene systems

A series of imidazolium tethered, Ni-PPh_2R (R = $(CH_2)_n$(NHC), n = 1, 2) complexes **12**-**14** rapidly promoted quantitative coupling of 4-chloroanisole and PhMgCl (Scheme 12).[47,48] The pendant imidazolium moiety would be deprotonated by the Grignard reagent and thus, generate the corresponding carbene complex which catalytic activity is almost comparable to Herrmann's pioneer work.[32,33] However, all catalysts showed decreasing selectivity using highly electronically deactivated *p*-$CF_3(C_6H_4)Cl$ leading to increasing undesirable homocoupling and dehalogenation of the aryl halide. Moreover, their performance appeared to be related to the length of the carbon

[47] J. Wolf, A. Labande, J.-C. Daran, R. Poli, *J. Organomet. Chem.* **2006**, *691*, 433.
[48] J. Wolf, A. Labande, M. Natella, J.-C. Daran, R. Poli, *J. Mol. Catal. A: Chem.* **2006**, *259*, 205.

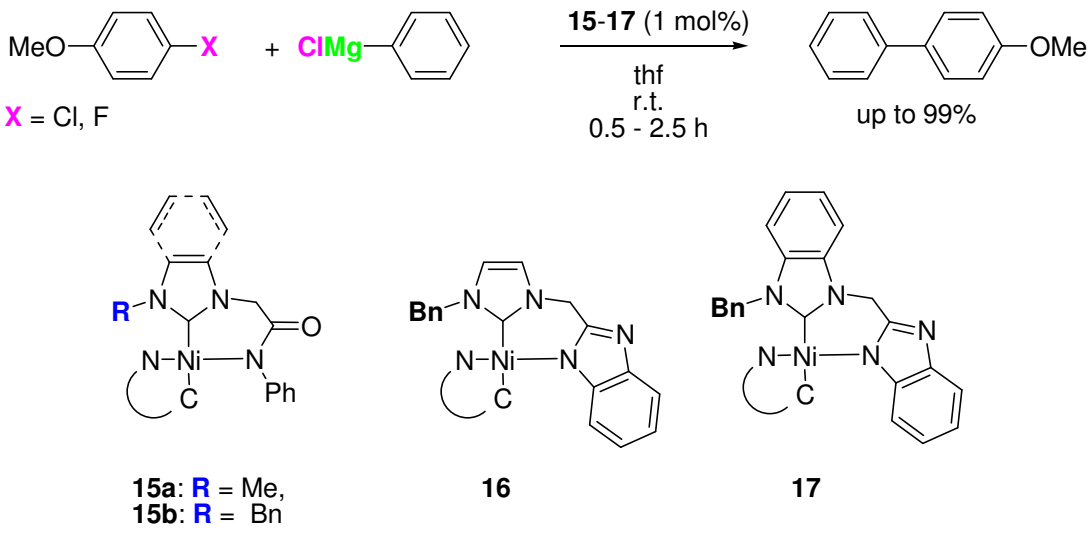
linker between the NHC moiety and the Ni-PPh_2 centre. Correspondingly, **13a** and **14a** showed better activity than **13b** and **14b**.



Scheme 12

Very recently, a series of bidentate Ni-NHC_2 complexes, **15**-**17**, that bear *anionic N*-donor moieties has been reported to show outstanding catalytic activity for Kumada-Corriu cross-coupling.[49] The benzimidazolato-functionalized catalyst **17** has shown even better activity than Herrmann's pioneering system[32,33] (Scheme 13). Thus, coupling involving electronically deactivated chloroanisole and almost unreactive fluoroanisole were completed after only 30 and 150 minutes respectively. The authors postulated that interactions of the hemilabile anionic amido moieties with *in situ* generated cationic $MgCl^+$ lead to a potential stabilization of coordinatively unsaturated intermediates by interaction during the catalytic cycle.

[49] J. Berding, T. F. van Dijkman, M. Lutz, A. L. Spek, E. Bouwman, *Dalton Trans.* **2009**, *35*, 6948.

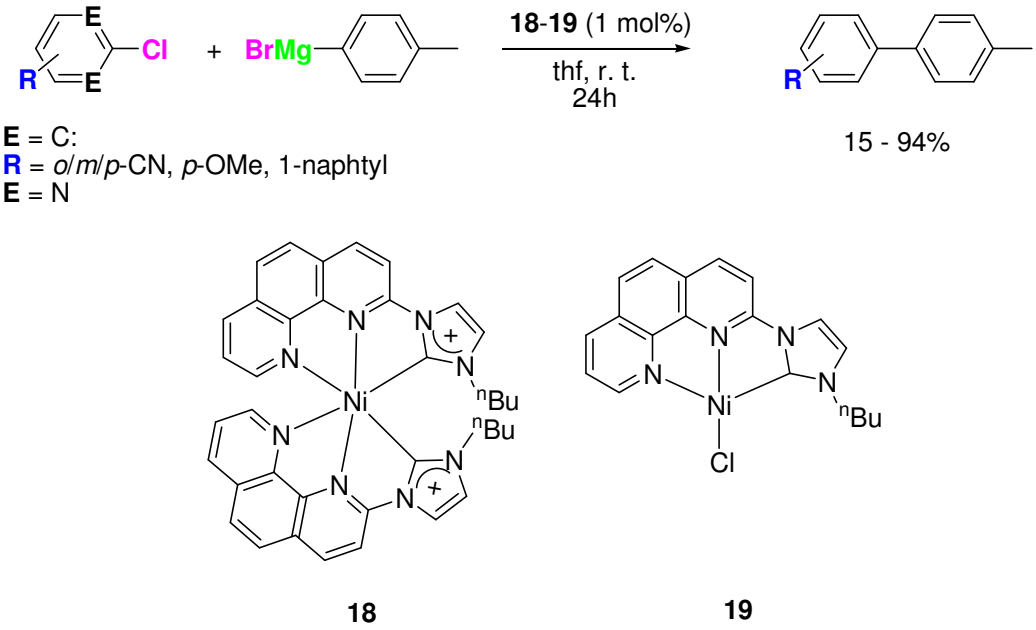


Scheme 13

2.1.1.3. Tridentate Carbene Systems

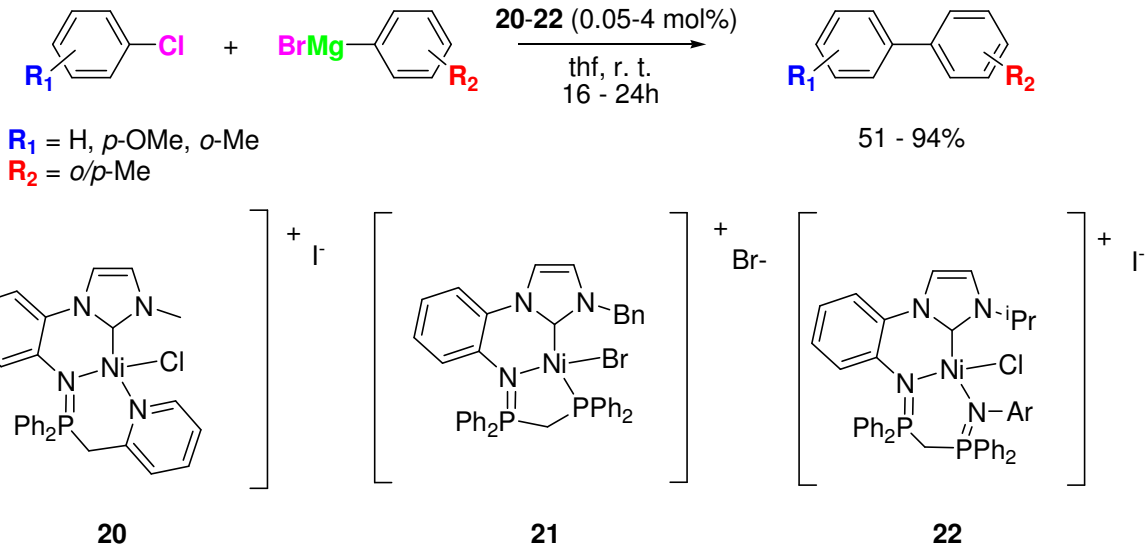
Chen and co-workers have synthesized two unsymmetrically shaped [*N*,*N*,*C*] pincer complexes of the type [Ni{[*N*,*N*,*C*]}Cl]$^{+}$ PF_6^{-}, **18**, and [Ni{[*N*,*N*,*C*]}$_2$]$^{2+}$ $2PF_6^{-}$, **19** (Scheme 14) which were active catalysts for the Kumada-Corriu cross-coupling in moderate to high yields.[50] The authors postulate that the lower catalytic activity observed for **18** stems from the generation of the unsaturated active species which should be more difficult for the octahedral 20-electron species **18** than for the square planar 16-electron complex **19**.

[50] S. Gu, W. Chan, *Organometallics* **2009**, *28*, 909.



Scheme 14

Furthermore, three [*C*,*N*,*N*] and [*C*,*N*,*P*] pincer type complexes **20** – **22**, bearing unsymmetrically substituted alkyl- and benzoyl- *N*,*N'*- 1-(2-azidophenyl)imidazol-2-ylidenes were reported as highly efficient catalysts with electronically deactivated aryl chlorides (Scheme 15). Nevertheless, comparing to **20** and **21**, lower activity was observed with complex **22**, which was attributed to less efficient dynamic dissociation of the hemilabile σ-donor moiety.[51]

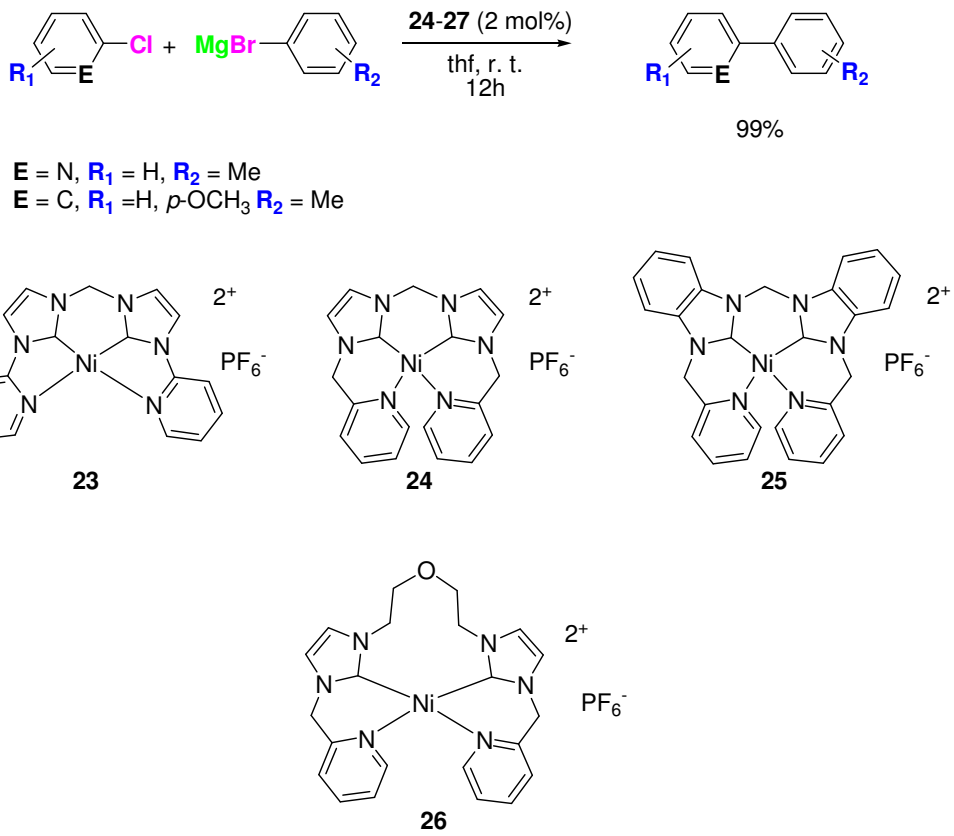


Scheme 15

[51] C. Zhang, Z.-X. Wang, *Organometallics* **2009**, *28*, 6507.

2.1.1.4.Tetradentate Carbene Species

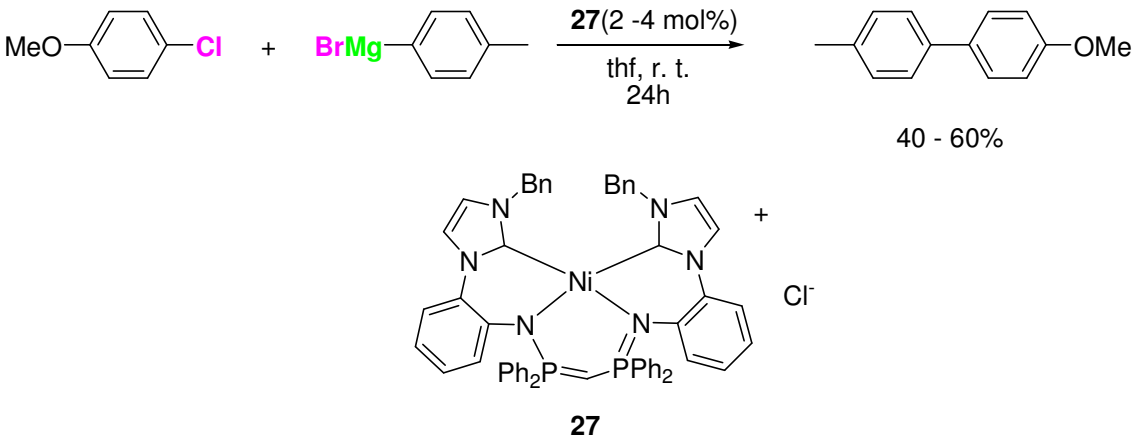
Four tetradentate pyridine-functionalized nickel(II)-NHC_2 complexes, **23–26**, were reported as excellent pre-catalysts for the Kumada-Corriu cross-coupling involving PhMgBr or *p*-tolyl-MgBr and various aryl, vinyl and heteroaryl chlorides as well as aryl dichlorides (Scheme 16).[52] The stabilization of coordinatively unsaturated intermediates by dissociation of the corresponding labile Ni–N bond appears highly efficient for the *bis*-carbene ligand backbones of **23–26** which carry the linker between the two strongly bonded carbene moieties.



Scheme 16

In contrast, the *bis*-diphenylphosphine linker between the two labile nitrogen atoms of the ligand framework of complex **27** should act as a barrier and hence hinder efficient substrate coordination during the catalytic cycle. Hence, only moderate yields were observed with electronically deactivated reagents by employing this catalyst (Scheme 17).[51]

[52] Z. Xi, B. Liu, W. Chen, *J. Org. Chem.* **2008**, *73*, 3954.



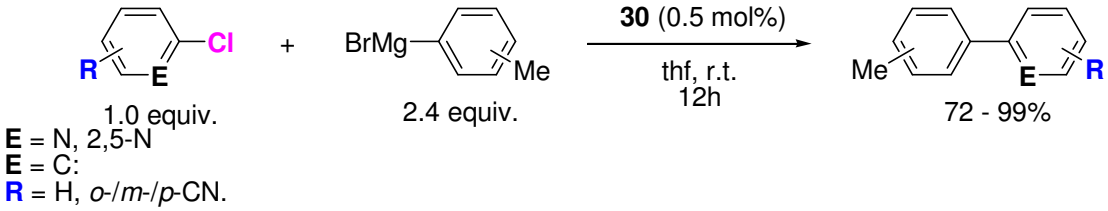
Scheme 17

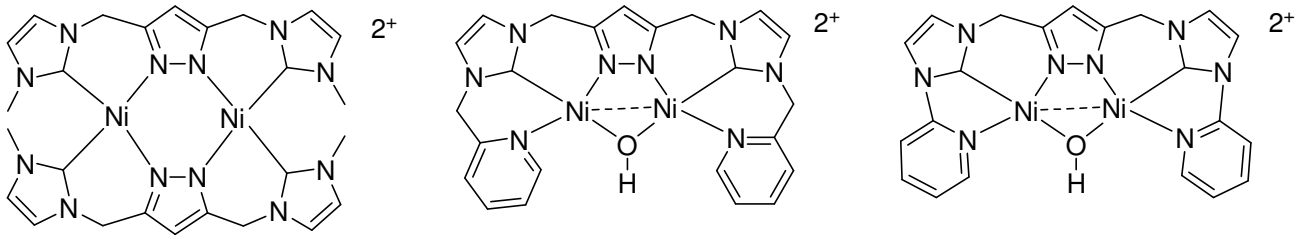
2.1.1.5. Di-nickel(II) Complexes

Some dinickel(II) complexes bearing multidentate *poly*-carbene NHC ligands have been tested as pre-catalysts for Kumada-Corriu cross-couplings of aryl chlorides and tolyl magnesium bromide (Scheme 18).[53] The framework of the strongly σ-donating NHCs was based on an anionic pyrazolate moiety, as this motif should bind the two metal centres within a single Ni–Ni bond distance which would promote bimetallic cooperative catalysis between the two nickel centres.[54,55]

Complex **28** was isolated as a dimeric cationic complex with square planar nickel(II) centres. As expected, the two nickel atoms are held together by the tetradentate 3,5-bis (*N*-methylimidazolylidenylmethyl)pyrazolate ligand, fashioning a *six*-membered Ni_2N_2 metallacyclic ring. Furthermore, both **29** and **30** formed a *five*-membered nickelacycle in which both nickel atoms were bridged by pyrazolate and hydroxide ligands and were effective catalyst for the coupling of *p*-chlorotoluene and *p*-PhMgBr (67 % compared to 98 % and > 99 % yield respectively) compared to **28**. Finally, the reaction scope was studied with **30** and revealed that this catalyst shows notably high functional group tolerance to nitrile substituted chloroaryl derivatives and heteroarenes. Regrettably, only formations of mono-*ortho*-substituted biaryls were tested.

[53] Y. Zhou, Z. Xi, W. Chen, D. Wang, *Organometallics* **2008**, *27*, 5911.
[54] as a review for bimetallic cooperative catalysis, see: (a) C. Schneider, *Angew. Chem. Int. Ed.* **2009**, *48*, 2084. (b) M. Shibasaki, S. Matsunaga, N. Kumagai, *Synlett* **2008**, 1583; (c) S. Matsunaga, M. Shibasaki, *Bull. Chem. Soc. Jpn.* **2008**, *81*, 60.
[55] Y. Zhou, W. Chen, *Organometallics* **2007**, *26*, 2742.





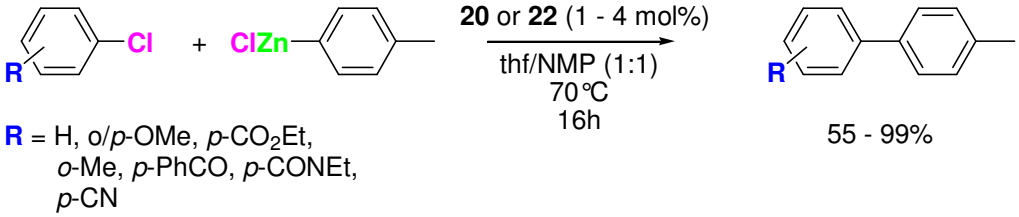
28 **29** **30**

Scheme 18

2.1.2. Negishi Coupling

The Negishi cross-couplings generate sp^2-C–C bonds from an aryl halide or pseudo halide and an organozinc compound, are analogous to the Kumada-Corriu cross-coupling reaction. To our knowledge, to date activity for Negishi coupling has only been tested with the previously described complexes **20** and **22** (active in Kumada–Corriu cross-coupling, Scheme 15).

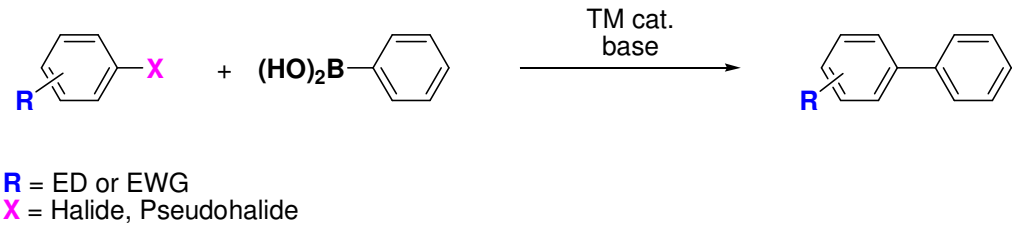
Thus, a variety of unactivated aryl chlorides, heterocyclic chlorides and vinyl chlorides with organozinc reagents were coupled by these catalysts in good yields at 70 °C (Scheme 19).[51] However, in contrast to Kumada-Corriu cross-couplings, the catalytic reactions proceeded only slowly at room temperature.



Scheme 19

2.1.3. Suzuki-Miyaura Cross-Coupling

Suzuki-Miyaura cross-coupling reactions[56,57,] are probably the most famous synthetic method to access a wide range of biaryls starting from organic halides with ready available boronic reagents (Scheme 20).[58] Whereas Pd-NHCs are outstanding catalysts for this reaction,[59] the Ni-based complexes have generally shown moderate activities. In particular, bi- and tridentate well defined Ni(II)-NHC complexes were tested. For these species, the essential reduction of the Ni(II) to an zero valent Ni(0) species is generally supposed to occur by homocoupling of the organometallic reagent.[33]



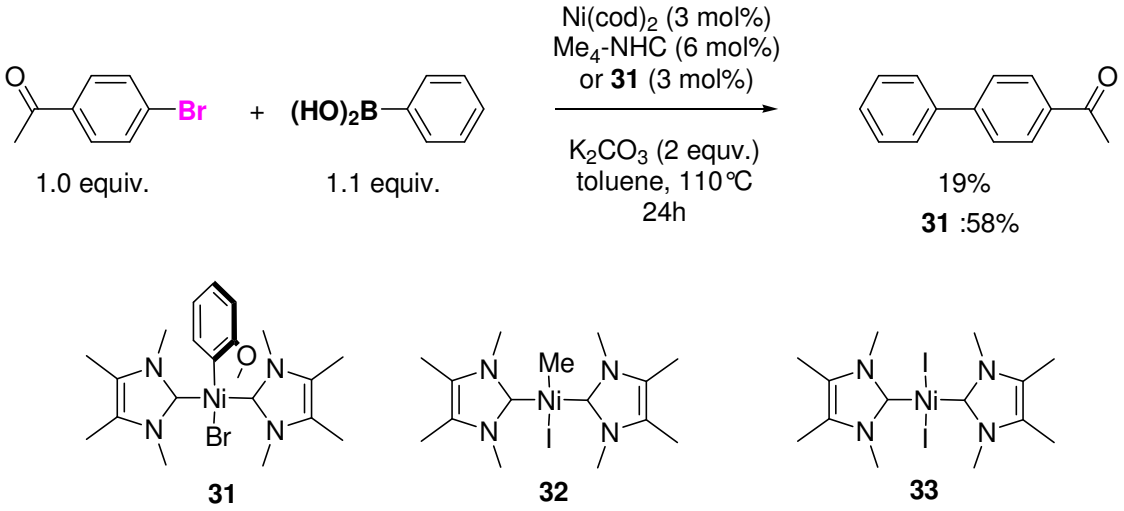
Scheme 20

2.1.3.1. Monodentate Ni-NHC Catalysts

Some *in situ* procedures have been reported that start from zero-valent [Ni(cod)$_2$] and two molar equivalents of monodentate NHCs. Whereas coupling of 4'-bromoacetophenone and phenyl boronic acid yielded poor amounts of the desired biphenyl derivative by employing an *in situ* generated [Ni(0)(Me$_4$-NHC)$_2$] (Me$_4$-NHC = 2,3,4,5-tetramethylimidazol-2-ylidene) catalyst (Scheme 21), the oxidative addition of stoechiometric amounts of a small range of organic halides onto this *in situ* generated species allowed some insight into the mechanism of Ni-NHC catalyzed cross-coupling reactions.[60] Thus, the respective Ni(II) compounds *trans*-Ni(Me$_4$-NHC)$_2$(*o*-tolyl)Br, **31**, *trans*-Ni(Me$_4$-NHC)$_2$(Me)I, **32**, and *trans*-Ni(Me$_4$-NHC)$_2$I$_2$, **33**, were isolated. Furthermore, by employing **31** as a pre-catalyst, even better yields of the desired biphenyl compound were observed. These results suggested that **31** would be an intermediate in the catalytic pathway for Suzuki-Miyaura cross-coupling of aryl halides with boronic acids.

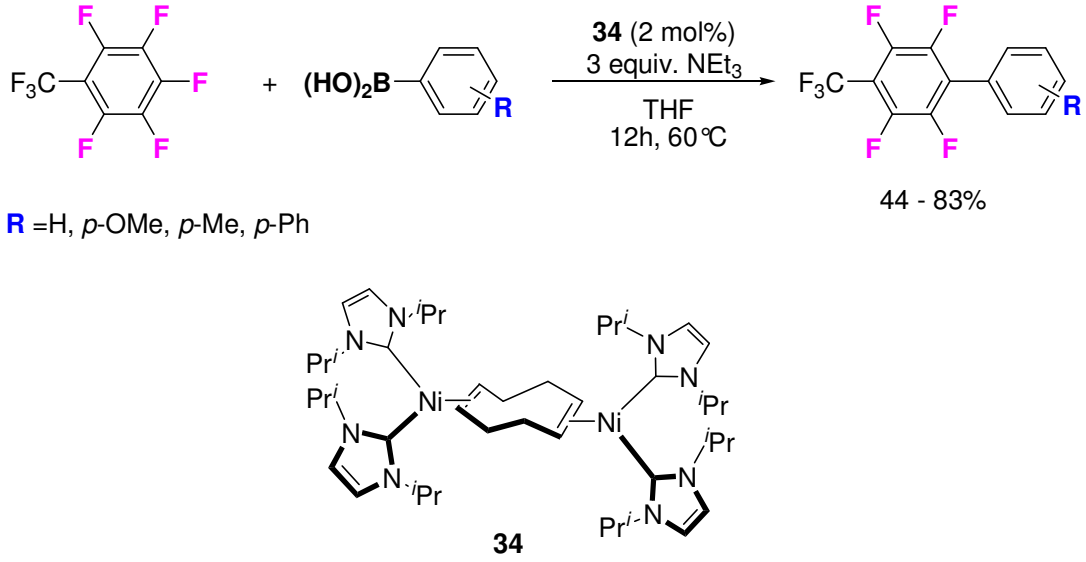
---

[56] (a) N. Miyaura, *Tetrahedron Lett.* **1979**, 3437; (b) N. Miyaura, A. Suzuki, *Chem. Commun.* **1979**, 866.
[57] (a) A. Suzuki, *Pure Appl. Chem.* **1994**, *63*, 419; (b) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995** *95* 2457; (c) N. Miyaura, A. Suzuki, *J. Organomet. Chem.* **1999**, *576*, 147.
[58] A. F. Indolese, A. Schynder, T. B. Aemmer, R. B. Portm32ann, M. B. Uebelhart, Ed. By W. A. Herrmann, *Synthetic Methods of Organometallic and Inorganic Chemistry* **2002**, *10*, 105.
[59] O. Navarro, N. Marion, J. Mei, S. P. Nolan, *Chem. Eur. J.* **2006**, *12*, 5142 and references therein.
[60] D. S. McGuinness, K. J. Cavell, *Organometallics* **1999**, *18*, 1596.



Scheme 21

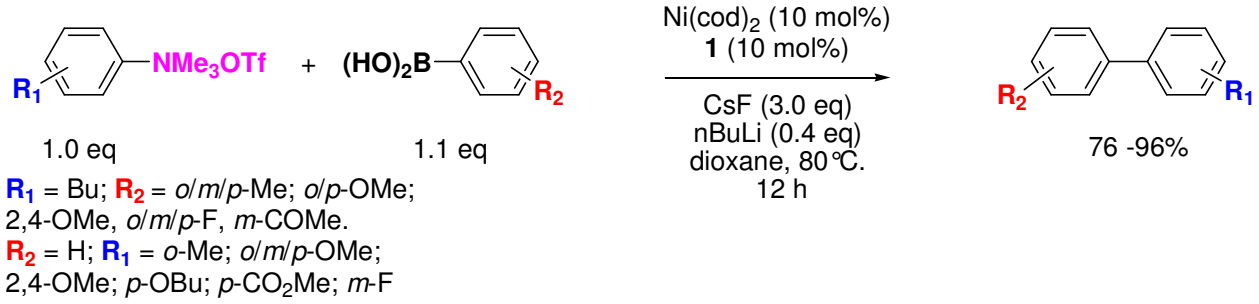
Moreover, the coupling of unreactive perfluorotoluene and boronic acids was achieved in a highly chemo- and regioselective manner and in respectable yields by employing the *in situ* generated dinuclear cod-bridged complex [Ni_2(*i*-Pr_2-NHC)$_4$(cod)], **34** (Scheme 22).[61,62] Thus, only the *trans* coupling-product was isolated and no multiple coupling was observed. It noteworthy that the activity of this system was best when NEt_3 was used as a base and a drastic decrease was noticed with inorganic bases such as K_2CO_3 or KF.



Scheme 22

[61] T. Schaub, M. Backes, U. Radius, *J. Am. Chem. Soc.* **2006**, *128*, 15964.
[62] T. Schaub, U. Radius, *Chem. Eur. J.* **2005**, *11*, 5024.

Whereas only traces of the coupling product were observed when phosphine nickel-complexes ($Ni(dppp)Cl_2$ and $Ni(dppf)Cl_2$) (dppf = 1,1-bis(diphenylphosphino)ferrocene) were employed, successful coupling of boronic acids, boronate esters and alkenylboronates with trimethylammonium salts was observed with a catalyst generated *in situ* from a 1:1 mixture of $Ni(cod)_2$ and Mes_2-NHC, **1** (Scheme 23).[63] Similar to the catalyst **34**,[61,62] the activity of the [Ni(0)(Mes_2-NHC)] species appeared to be highly base dependent as much lower conversions were observed by employing K_3PO_4 (5 %) and KF (57 %) as a base compared to CsF (98 %). Moreover, this catalytic system showed high functional group tolerance with respect to the substituents on both the aryl trimethylammonium triflate and the boronic acid and electronically activated, deactivated and sterically hindered substrates underwent Suzuki-Miyaura coupling in excellent yields (76 – 96 %).



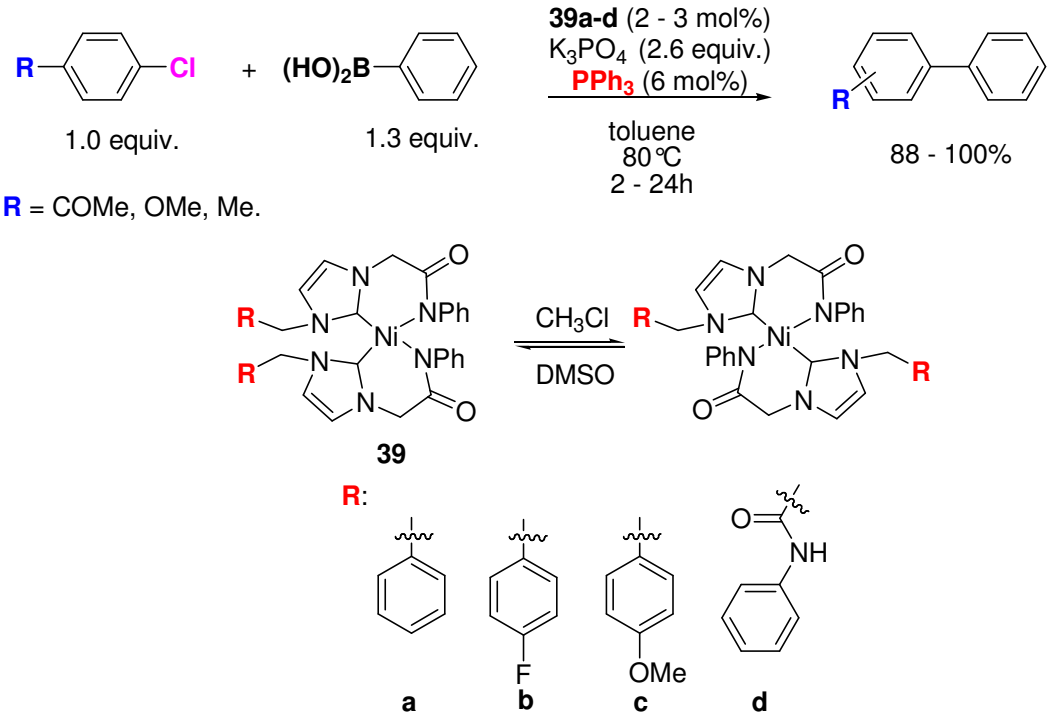
Scheme 23

2.1.3.2.Polydentate Ni-NHC_2 Systems

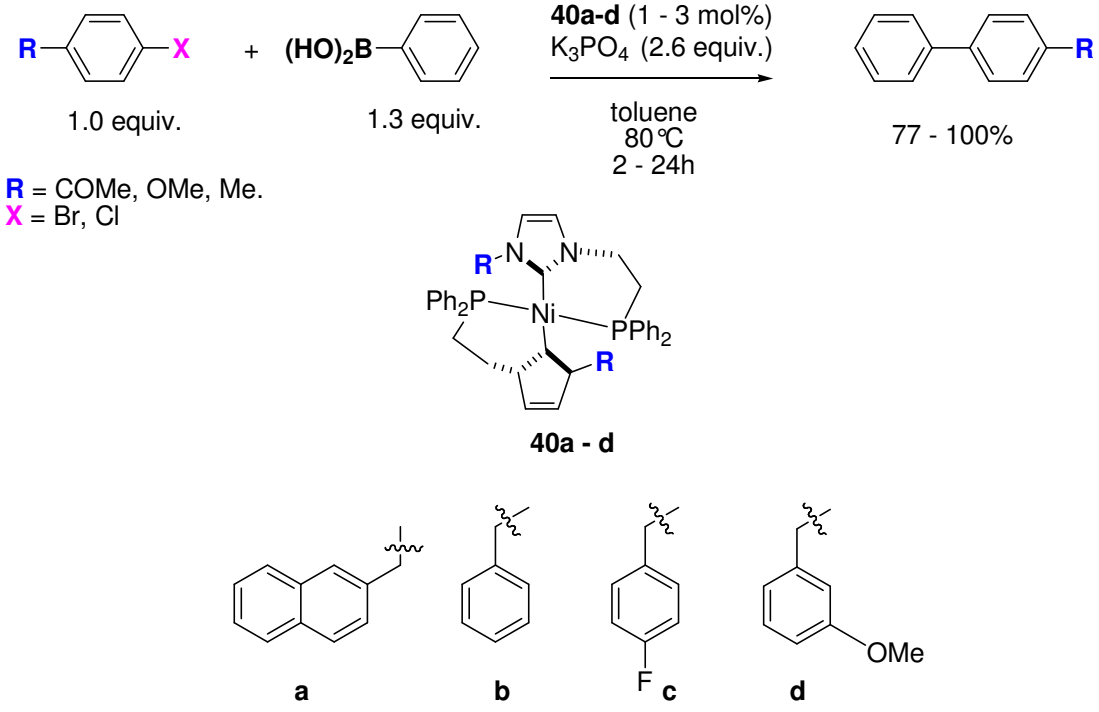
The series of nickel(II) complexes **39** (Eq. 1, Scheme 24) carrying two amido-functionalized bidentate NHC ligands as well as that of their phosphine functionalized counterparts **40** (Scheme 25) were reported to mediate Suzuki cross-coupling of a range of activated aryl chlorides and $PhB(OH)_2$ with K_3PO_4 as a base.[64,65] By employing **39**, generally lower conversions were observed with electronically deactivated substrates. Nevertheless, the activity of these species was substantially improved by the addition of triphenylphosphine as a co-catalyst. For catalysts **40**, containing a phosphane ligand the need of additional phosphine was restricted to the most challenging chlorides. Nevertheless, generally lower reactivity was noticed when the catalyst loading was diminished from 3 mol% to 1 mol%: a 77 % yield of the cross-coupled product of

[63] S. B. Blakey, D. W. MacMillan, *J. Am. Chem. Soc.* **2003**, *125*, 6046.
[64] (a) C.-Y. Liao, K.-T. Chan, Y.-C. Chang, C.-Y. Chen, C.-Y. Tu, C.-H. Hu, H. M. Lee, *Organometallics* **2007**, *26*, 5826; (b) C.-Y. Liao, K.-T. Chan, J.-Y. Zeng, C.-H. Hu, C.-Y. Tu, H. M. Lee, *Organometallics* **2007**, *26*, 1692.
[65] C.-C. Lee, W.-C. Ke, K.-T. Chan, C.-L. Lai, C.-H. Hu, H. M. Lee, *Chem. Eur. J.* **2007**, *13*, 582.

chloroanisole and $PhB(OH)_2$ was observed without addition of phosphine, whereas 92 % conversion was achieved by addition of two equivalents of PPh_3.

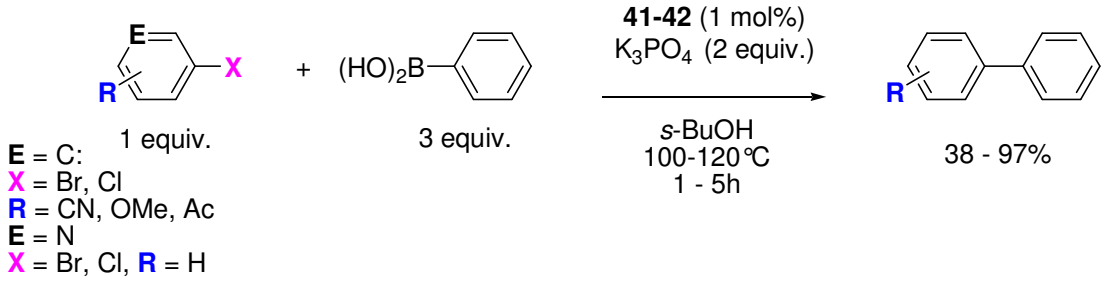


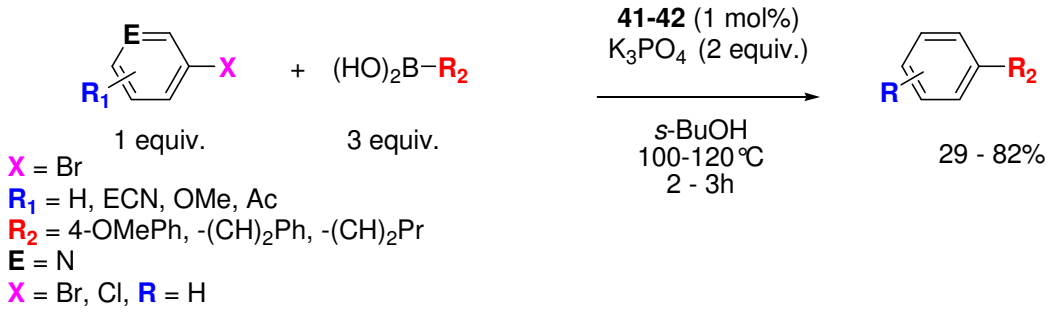
Scheme 24

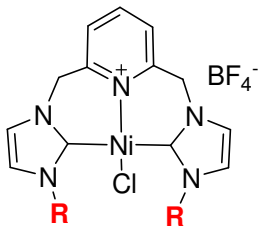


Scheme 25

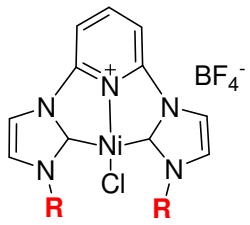
Similar to the bidentate systems **39** and **40**, the series of nickel(II) [*C*,*N*,*C*] pincer-type pre-catalysts, **41**–**42**, has produced biphenyls from electronically activated aryl bromides and chlorides in overall good yields although the influence of phosphine as co-catalyst has not been considered for these species (Scheme 26).[66] The *five*-membered nickelacycles **42** were reported to be notably faster catalysts than their *six*-membered counterparts **41** suggesting that the more sterically hindered metal centre of the *five*-membered ring would facilitate the reductive elimination of the biaryl product.







41a : **R** = Mes
41b: **R** = *i*-Pr$_2$Ph



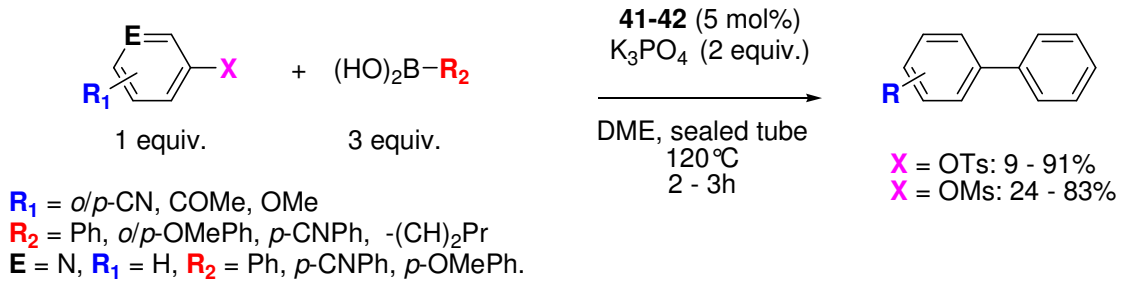
42a : **R** = Mes
42b: **R** = *i*-Pr$_2$Ph

Scheme 26

Moreover, a series of electronically activated aryl as well as heteroaryl tosylate derivatives appeared to be good coupling partners by employing **41**-**42** as catalysts, whereas only poor

[66] Inamoto K., J.-I. Kuroda, E. Kwon, K. Hiroya, T. Doi, *J. Organomet. Chem.* **2009**, *694*, 389.

conversions were achieved with electron-rich and bulky reagents (Scheme 27).[67] Generally lower conversions were observed using the cheaper aryl mesylate derivatives. In contrast to the coupling involving aryl *halides*, using tosylates and mesylates, the complex **41** was reported to generate the better active species.

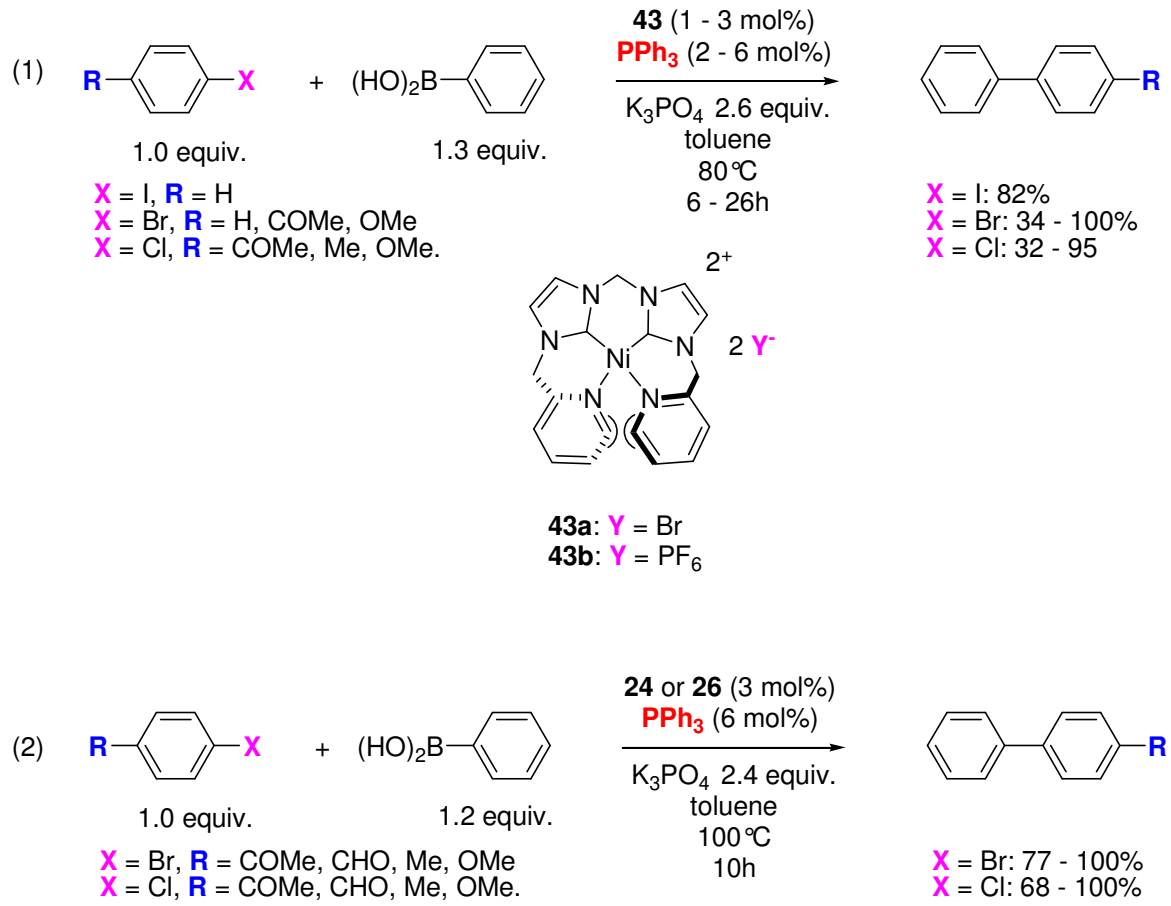


Scheme 27

Finally, a range of tetradentate pyridine-functionalized *bis*-carbene Ni(II)-NHC complexes, **43**, was reported to generate efficient catalysts for Suzuki-Miyaura cross-couplings (Eq. 1, Scheme 28).[68] Nevertheless, similar to the previously described bidentate complexes **39** and **40**, bearing hemilabile amido- and phosphane-functionalities, the catalytic activity of **43** was highly dependent on the addition of triphenylphosphine. Thus, reactions involving activated 4'-chloroacetophenone were almost completed after 24 hours by employing **43** but this conversion dramatically diminished to 19 % with the absence of the co-catalyst.

Analogously, the Ni(II)-NHC pre-catalysts **24** and **26**, (Scheme 16) bearing hemilabile pyridine functions, only poorly converted electronically deactivated aryl chlorides and bromides into desired biphenyl derivatives whereas reaction yields were dramatically increased by addition of 2 molar equivalents of triphenylphosphine (Eq. 2, Scheme 28).[69] It noteworthy that even in the presence of additives, the reactivity of the active species remained highly solvent dependent.

[67] J.-I. Kuroda, K. Inamoto, K. Hiroya, T. Doi, *Eur. J. Org. Chem.* **2009**, 2246.
[68] P. L. Chiu, C.-L. Lai, C.-F. Chang, C.-H. Hu, H. M. Lee, *Organometallics* **2005**, *24*, 6169.
[69] Z. Xi, X. Zhang, W. Chen, S. Fu, D. Wang, *Organometallics* **2007**, *26*, 6636.



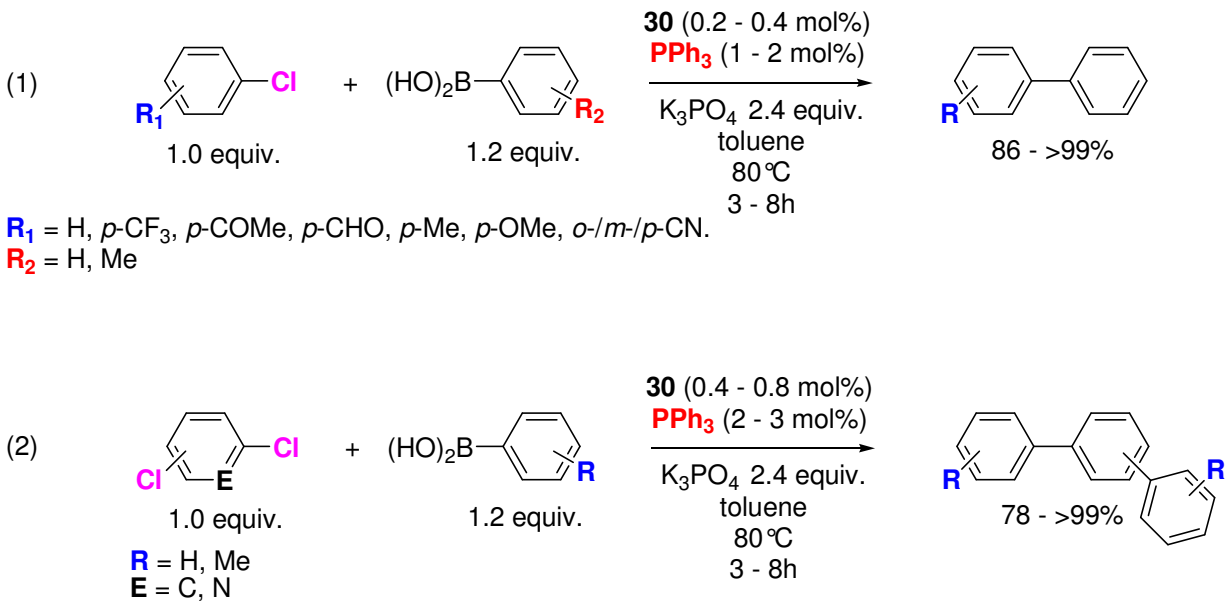
Scheme 28

2.1.3.3. Dinuclear Poly-Carbene Systems

The dinickel(II) complexes **29** - **30** (Scheme 18), which were previously described as good catalysts for Kumada-Corriu reactions, also generated active species for Suzuki-Miyaura cross-couplings (Scheme 30).[68] Nevertheless, similar to the other pyridine functionalized pre-catalysts, **24**-**26** and **43**, significant lower catalytic activity was observed without addition of tripehnylphosphine as co-catalyst. Thus, coupling of both electronically activated and deactivated aryl halides afforded the related biphenyls in only moderate to good yield (40 – 88 %) and poor conversion was obtained for deactivated 4-chlorotoluene and –anisole (11 – 20 %).[70] As expected, excellent conversions were achieved by the addition of 5 molar equivalents of PPh_3 with respect to the catalyst loading and terphenyl- and diarylpyridine derivatives could also be synthesized from the appropriate aryl- or heteroaryl dichlorides in almost quantitative yield. However, very low

[70] M. Robins, J. Liu, *Org. Lett.* **2005**, *7*, 1149.

catalyst loading (0.2 – 0.8 mol%) was employed, a result not matched yet by other Ni-NHC systems.

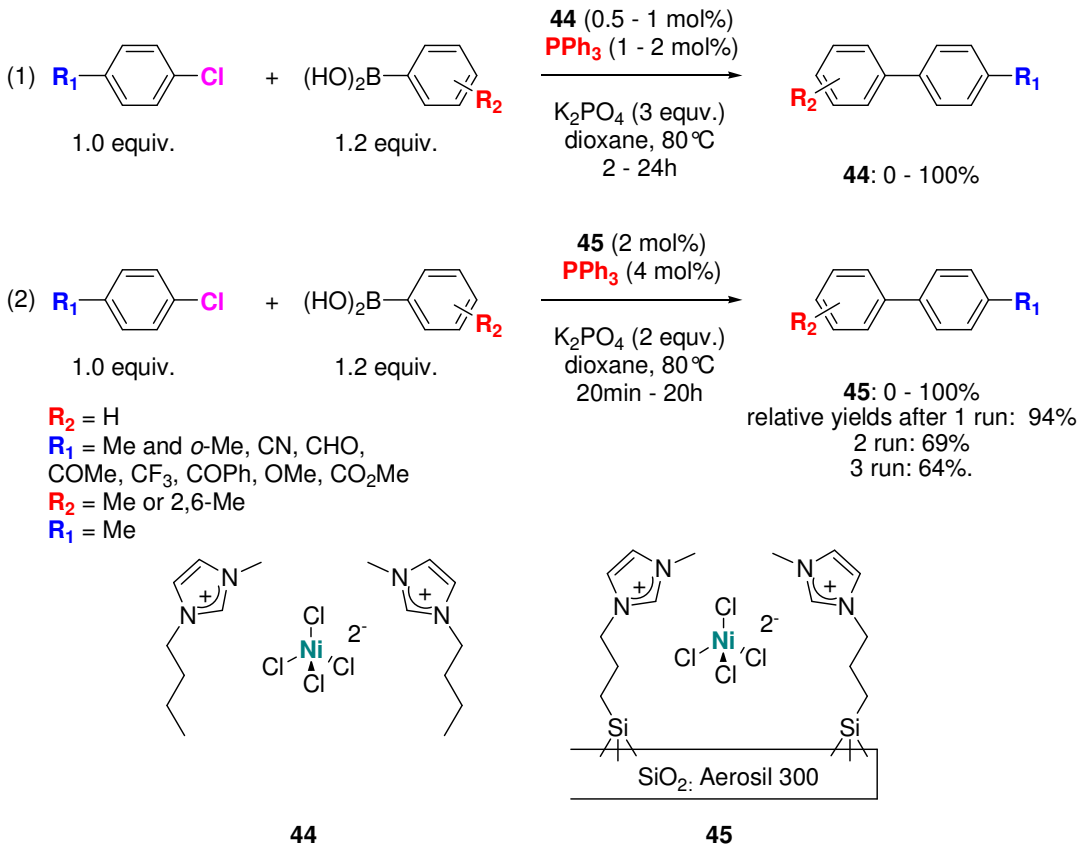


Scheme 29

2.1.3.4. Surface Immobilized Ni(II)-NHC Catalysts

Finally, a nickel-ion containing ionic liquid salt, **44**, and its silica-grafted derivative, **45**, were reported to be highly active for Suzuki-Miyaura cross-coupling (Scheme 30).[71] High to quantitative yield was observed with both species for cross-coupling reactions involving electronically activated reagents with 2 molar equivalents of PPh_3 as a co-catalyst. Sterically hindered boronic acids were observed as unreactive. The catalytic system appeared to be highly solvent and phosphine dependent as the reactivity dramatically decreases when polar solvents, lower substrate concentrations or PCy_3, $P(NMe_2)_3$ or dppf instead of PPh_3 were employed. It worth mentioning that much shorter reaction times were required for reagents carrying a deactivating electron-donor group with the silica immobilized **45** with respect to **44**. The heterogeneous pre-catalyst **45** could be recycled once without significant activity loss.

[71] (a) T. Sasaki, M. Tada, C. Zhong, T. Kume, Y. Iwasawa, *J. Mol. Catal. A: Chem.* **2008** *279* 200; (b) C. Zhong, T. Sasaki, M. Tada, Y. Iwasawa, *J. Catal.* **2006** *242* 364.



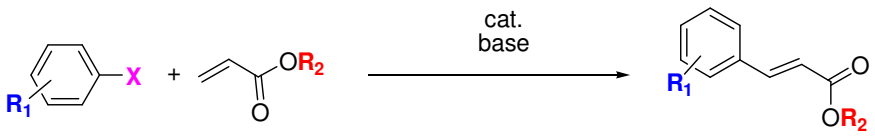
Scheme 30

2.1.4. Mizoko-Heck Reactions

The Mizoroko-Heck reaction is another powerful tool for the formation of a new C–C bond employing aryl halides and alkenes by activation of a sp^2-C–X bond of the aryl halide (Scheme 31).[72,73,74] Traditionally, these reactions are carried out using a palladium based catalytic system such as phosphapalladacycles,[30,75] Pd-[*P*,*C*,*C*] and Pd-[*P*,*C*,*P*] pincer complexes,[76] and Pd/*t*-Bu_3P compounds.[77] First attempts at nickel catalyzed Heck reactions employing a $Ni(PPh_3)_2Cl_2$ based

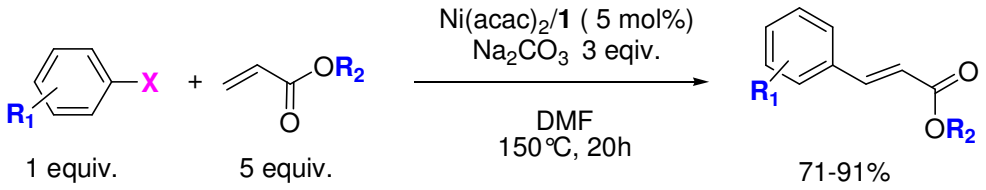
[72] R. F. Heck, J.-P. Jr. Nolley, *J. Org. Chem.* **1972**, *37*, 2320.
[73] T. Mizoroko, K. Mori, A. Ozaki, *Bull. Chem. Soc. Jap.* **1971**, *44*, 581.
[74] R. F. Heck, *Org. React.* **1982**, *27*, 345.
[75] E.-I. Neghishi, *Handbook of Organopalladium Chemistry for Organic*; Wiley: New York **2002**
[76] (a) W. A. Herrmann, C. Brossmer, C.-P. Reisinger, T. H. Reirmeier, K. Oefele, M. Beller, *Chem. – Eur. J.* **1997**, *3*, 1357; (b) M. Ohff, A. Ohff, M. E. van der Boom, D. Milstein, *J. Am. Chem. Soc.* **1997**, *119*, 11687.
[77] (a) K. Salvakumar, A. Zapf, M Beller, *Org. Lett.* **2004**, *6*, 3031; (b) E. Peris, J. A. Loch, J. Mata, R. H. Crabtree, *Chem. Commun.* **2001**, 210; (c) C. Yang, H. M. Lee, S. P. Nolan, *Org. Lett.* **2001**, *3*, 1461; (d) W. A. Herrmann, C.-P. Reisinger, M. Spiegler, *J. Organomet. Chem.* **1998**, *557*, 93; (e) W. A. Herrmann, M. Elison, J. Fischer, C. Kocker, G. R. Artus, *Angew. Chem., Int. Ed.* **1995**, *34*, 2371.

system resulted in poor selectivity and required stoechiometric amounts of Zn as a reductant in the reaction medium.[78] Only moderate coupling was achieved using $Ni[P(OPh_3)]_4$ and $Ni[P(OEt_3)]_4$.[79]



Scheme 31

To our knowledge, to date, only one example of Ni-NHC promoted Heck coupling was reported. The combination of $Ni(acac)_2$ and $(Mes_2\text{-NHC})\cdot HCl$, **1**, allowed for the coupling of both electron-rich and electron–poor aryl iodides and bromides at 150 °C (Scheme 34).[80] Under these reaction conditions, only traces of the product were observed using a $[Ni(PPh_3)]$ or [Ni(dppf)] pre-catalyst. Interestingly, the reaction turned out to be highly ligand dependent as moderate to poor yields were obtained with $\{(i\text{-}Pr_2Ph)_2\text{-NHC}\}\cdot HCl$, **2a**, and $\{SMes_2\text{-NHC}\}\cdot HBF_4$ as a ligand precursor, respectively.



X = Br
R1 = H, CN, CO_2Bu, CHO
R2 = Bu

X = I
R1 = Me, COMe, CO_2Me, *m/p*-OMe
R2 = Me

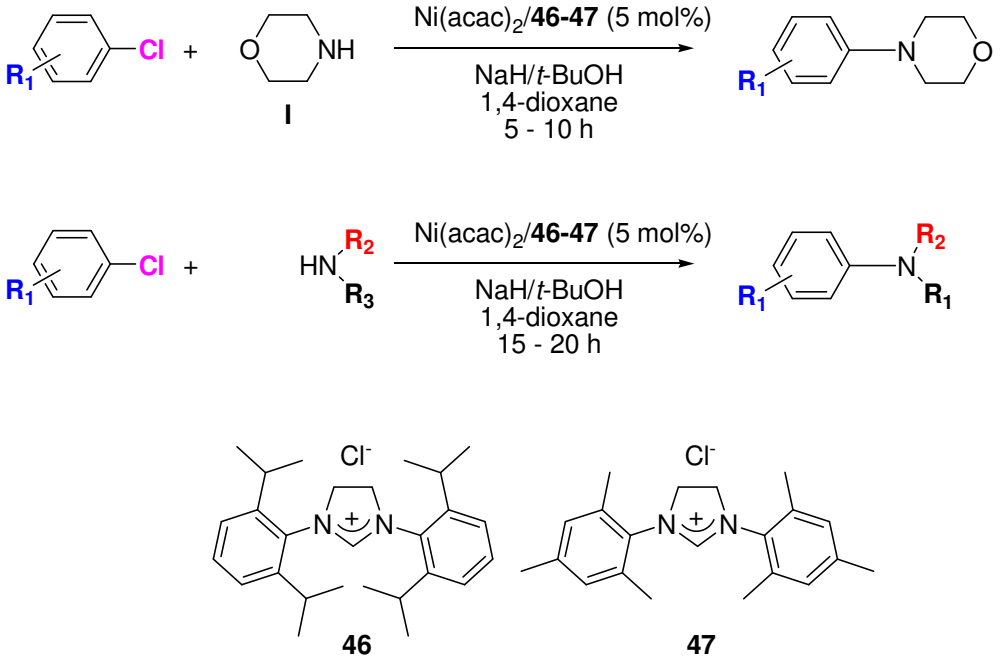
Scheme 32

[78] (a) R. Sustmann, P. Hopp, P. Holl, *Tetrahedron Lett.* **1989**, *30*, 689; (b) S. A. Lebedev, V. S. Lopatina, E. S. Petrov, I. P., Beletskaya, *J. Organomet. Chem.* **1988**, *344*, 253 ; (c) G. P. Boldrini, D. Savolia, E. Tagliavini, C. Trombini, A. U. Ronchi, *J. Organomet. Chem.* **1986**, *301*, C62.
[79] S. Iyer, C. Ramash, A. Ramani, *Tetrahedron Lett.* **1997**, *38*, 8533.
[80] K. Inamoto, J.-i. Kuroda, T. Danjo, T. Sakamoto, *Synlett* **2005**, *10*, 1624.

2.1.5. Carbon–Heteroatom Bond Forming Cross-Coupling Reactions

2.1.5.1. Aryl Amination

Initial research on the coupling of chlorobenzene and morpholine, **I**, showed that *in situ* generated catalyst systems prepared from 1:2 mixtures of $Ni(acac)_2$, {S(*i*-Pr_2Ph_2)-NHC}·HCl (**46**), *t*-BuOH and sodium hydride afforded benzylmorpholine in nearly quantitative yield (Scheme 33).[81d] This system transformed secondary cyclic amines and acyclic amines in good to excellent yields under relatively mild conditions. This catalyst showed low sensibility to steric congestion of the aryl chloride;[81c] for aniline derivatives instead, deactivating electron-withdrawing groups had a major impact on the reactivity of the active species. It worth mentioning that *N*,*N'*-diarylation could be selectively achieved with 2.4 molar equivalents of the aryl chloride.[81a]



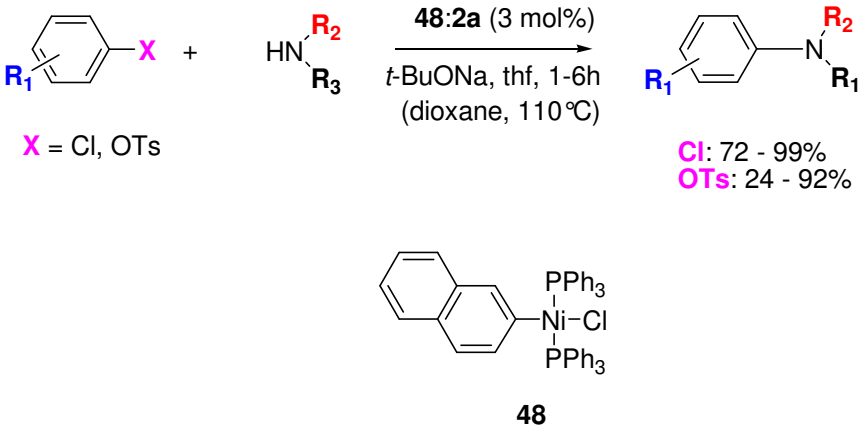
Scheme 33

Moreover, quantitative reaction of aryl chlorides with secondary cyclic amines or aniline derivatives was also obtained with an *in situ* generated catalyst from 1:2 mixtures of the nickel(II)-aryl complex **48** and **2a** without any addition of a reducing agent (Scheme 34).[82] The reactivity of this catalyst was notably faster compared to the precedent system (1-6 h instead of 5–24 h). The reactivity appeared to depend on the bulk of the NHC ligand as lower conversions were obtained by

[81] (a) S. Kuhl, Y. Fort, R. Schneider, *J. Organomet. Chem.* **2005**, *690*, 6169; (b) R. Omar-Amrani, A. Thomas, E. Brenner, R. Schneider, Y. Fort, *Org. Lett.* **2003**, *5*, 2311; (c) C. Desmarets, R. Schneider, Y. Fort, *J. Org. Chem.* **2002**, *67*, 3029; (d) B. Gradel, E. Brenner, R. Schneider, Y. Fort, *Tetrahedron Lett.* **2001**, *42*, 5689.
[82] C. Chen, L.-M. Yang, *J. Org. Chem.* **2007**, *72*, 6324.

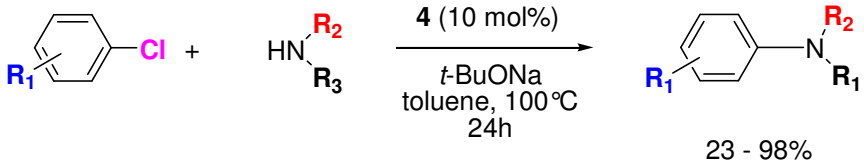
employing Mes_2-NHC·HCl, **1**. In contrast to the catalytic system which was generated from $Ni(acac)_2$,[81] the 1:1 combination of **48** and the unsaturated counterpart of **2a**, {S*i*-$Pr_2Ph)_2$-NHC}, **47**, was much less effective for this reaction.

Furthermore, this catalyst allowed for the unprecedented amination of tosylates.[83] The reactions were surprisingly fast when compared with precedent systems (15-30 min instead of 5–12 h for), although heating was still required. The obtained yields were usually high even if the undesirable O–S cleavage of the starting tosylate was competitive in all entries.



Scheme 34

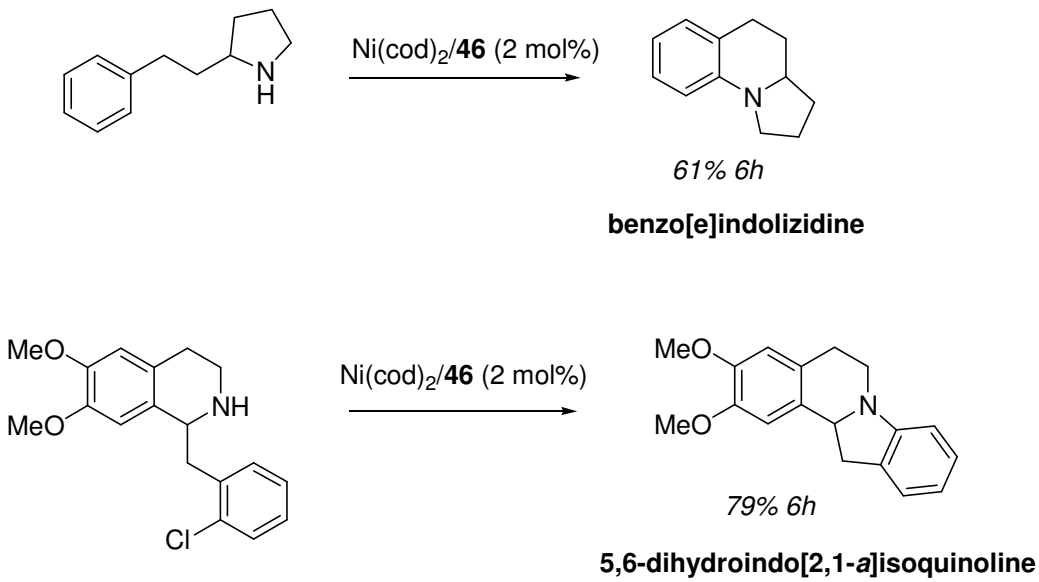
Effective *N*-arylation of secondary cyclic amines and aniline derivatives was also promoted by the mixed {(*i*-$Pr_2Ph)_2$-NHC}-phosphine nickel(II) complex **4** (Scheme 4) in high yield (Scheme 35).[84] Though, contrary to the $Ni(acac)_2$/**46** and $Ni(cod)_2$/**46** catalytic systems[81] neither *N*-arylation of morpholine nor *N*,*N*-diarylation was observed with **4**. Furthermore, catalytic experiments showed that homoleptic nickel(0) complexes are certainly very close to the active catalyst in this amination reaction.



Scheme 35

[83] C.-Y. Gao, L.-M. Yang, *J. Org. Chem.* **2008**, *73*, 1624.
[84] K. Matsubara, K. Ueno, Y. Koga, K. Hara, *J. Org. Chem.* **2007**, *72*, 5069.

Finally, it worth mentioning that intramolecular C–N bond formation between sp^2-C–Cl and amine can be achieved with (1:1) mixtures of [Ni(cod)$_2$] and **46**.[81c] Under these reaction conditions 5-, 6- and 7-membered fused ring systems have been prepared and the synthesis of larger structures such as benzo[e]indolizidine and 5,6-dihydroindo[2,1-*a*]isoquinoline was achieved in high yield (Scheme 36).



Scheme 36

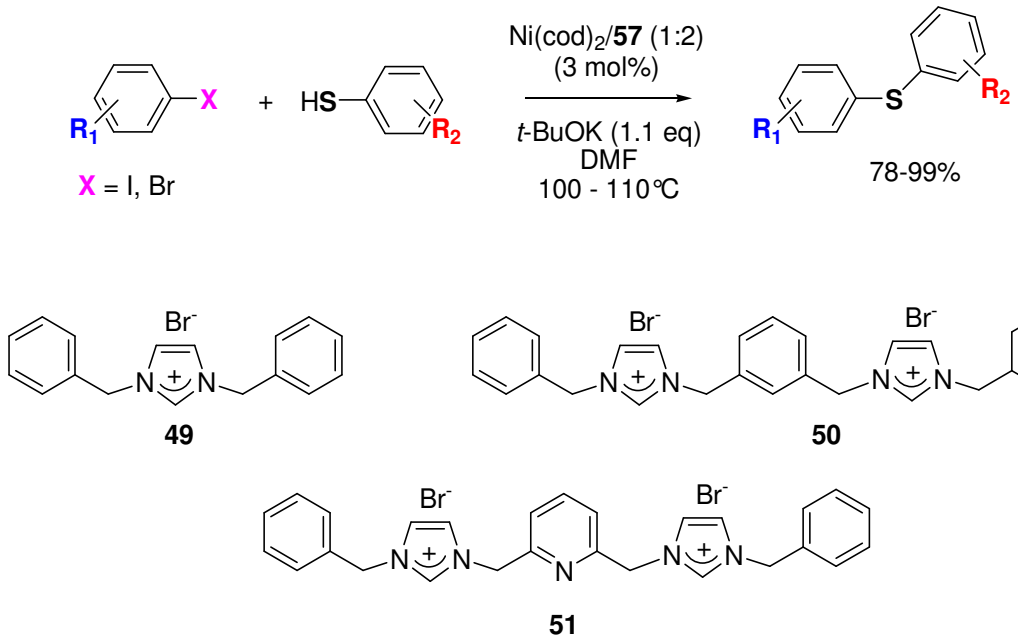
2.1.5.2. Aryl Thiolation

Organosulphur chemistry has been receiving increasing interest, since sulphur containing groups are an important auxiliary function in organic synthetic sequences,[85] but examples of Ni-NHC-catalyzed C–S cross-couplings are extremely scarce.

Efficient coupling of aryl iodides and - bromides with thiols was reported to be catalyzed by a zero-valent Ni(0)-NHC$_2$ system which was prepared *in situ* from 1:2 mixtures of [Ni(cod)$_2$], the appropriate NHC precursor and potassium *t*-butoxide (KO*t*-Bu) (Scheme 37).[86] Among the variety of imidazolium and imidazolinium salts that have been screened, **49**, **50** as well as the [*C*,*N*,*C*] pincer ligand precursor **51** proved to be the ligands of choice. Although the use of bidentate

[85] For general reviews on sulfides, see: *Comprehensive Organic Chemistry* Vol. 3; D. N. Jones, Ed. Pergamon Press: Oxford, **1979**.
[86] Y. Zhang, K. C. Ngeow, J. Y. Ying, *Org. Lett.* **2007**, *9*, 3495.

catalysts did not show significant increases in activity, they demonstrated greater stability compared to the monodentate system.

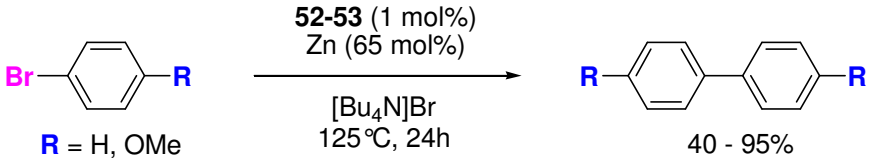


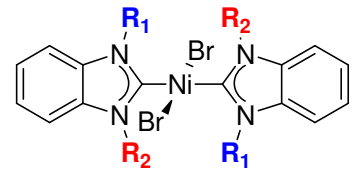
Scheme 37

2.2. Homocoupling of sp^2-C–X Bonds: the Ullmann Coupling of Aryl Halides

Only one example of Ullmann homocoupling of aryl halides has been reported to date. The activity of a range of benzannulated *trans*-[$NiBr_2(NHC)_2$] type compounds has been studied for the homocoupling of aryl bromides in the presence of zinc as reductant (Scheme 38).[87] The compounds **52**–**53**, carrying benzimidazol-*2*-ylidene ligands with increasing steric demands promoted the homocoupling of both bromotoluene and bromoanisole in moderate to high yield. The use of ionic liquid ([Bu_4N]Br) as a solvent appeared to be necessary since no conversion was detected in traditional polar solvents such as DMF.

[87] H. V. Huynh, L. R. Wong, P. S. Ng, *Organometallics* **2008**, *27*, 2231.





$R_1 = R_2$
52a: CH_2Ph,
52b: *i*-Pr,
52c: $CHPh_2$,
52d: *i*-Bu

$R_1 = CH_2Ph$
53a: R_2 = *i*-Pr,
53b: $R_2 = CHPh_2$

Scheme 38

3. C–C Coupling via sp^2- and sp^3-C–H Bond Activation

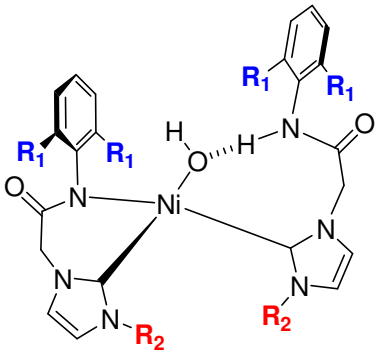
Nickel mediated C–H bond activation reactions are quite rare.[88] To our knowledge, only three examples for Ni-NHC catalyzed coupling reactions via C–H bond activation have been reported.

3.1. Michael Additions

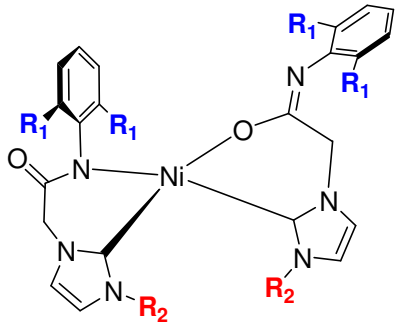
A series of nickel(II) complexes of N/O-functionalized NHCs, **54**–**57**, were reported to be efficient pre-catalysts for the Michael reactions of β-dicarbonyl, β-ketoester, β-diester and α-cyano ester compounds with activated olefins in air and at ambient temperature under the much preferred base-free conditions, which avoids the unwanted side reactions that usually arise in classical Michael conditions (i. e. in strongly basic conditions).[89]

[88] a) Chattopadhyay et al. *Eur. J. Inorg. Chem.* **2007**, 4263; b) P. T. Wolczanski et al. *J. Organomet. Chem.* **2007**, *692*, 4774; c) Bercaw et al. *Polyhedron* **2004**, *23*, 2797; d) Milstein et al., *Inorg. Chim. Acta* **2004**, *357*, 4015; e) Zargorian et al. *Organometallics* **2006**, *25*, 602; f) Haenel et al. *Chem. Ber.* **1991**, 124, 333; g) Rimml et al. *J. Organomet. Chem.* **1983**, *259*, C6; h) Shaw et al. *J. Chem. Soc., Dalton Trans.* **1976**, 1020; i) Barinov et al. *J. Organomet. Chem.* **1971**, *29*, C53; j) Barinov et al. *J. Organomet. Chem* **1970**, *23*, 546; k) Dubeck et al. *J. Am. Chem. Soc.* **1963**, *85*, 1544.
[89] (a) K. M. Samanataray, M. M. Shaikh, P. Ghosh, *Organometallics* **2008**, *28*, 2267; (b) S. Ray, M. M. Shaikh, P. Ghosh, *Eur. J. Inorg. Chem.* **2009**, 1932.

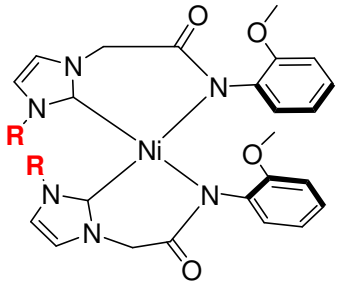
The square planar diamagnetic catalyst precursors **54**-**57** were all synthesized by reaction of $NiCl_2 \cdot 6H_2O$ with aryl acetamido-*N*-substituted NHC salts in presence of K_2CO_3. It is note worthy that with the isopropylphenyl-substituted acetamido-NHC, rare examples of NHC-Ni complexes bearing a terminal OH ligand were isolated (Scheme 39).



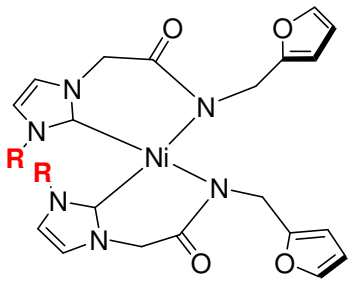
54a: R_1 = *i*-Pr_2Ph; R_2 = *i*-Pr (47%)
54b: R_1 = *i*-Pr_2Ph; R_2 = CH_2Ph (43%)



55a: R_1 = Me; R_2 = CH_2Ph (49%)
55b: R_1 = Et; R_2 = CH_2Ph (55%)



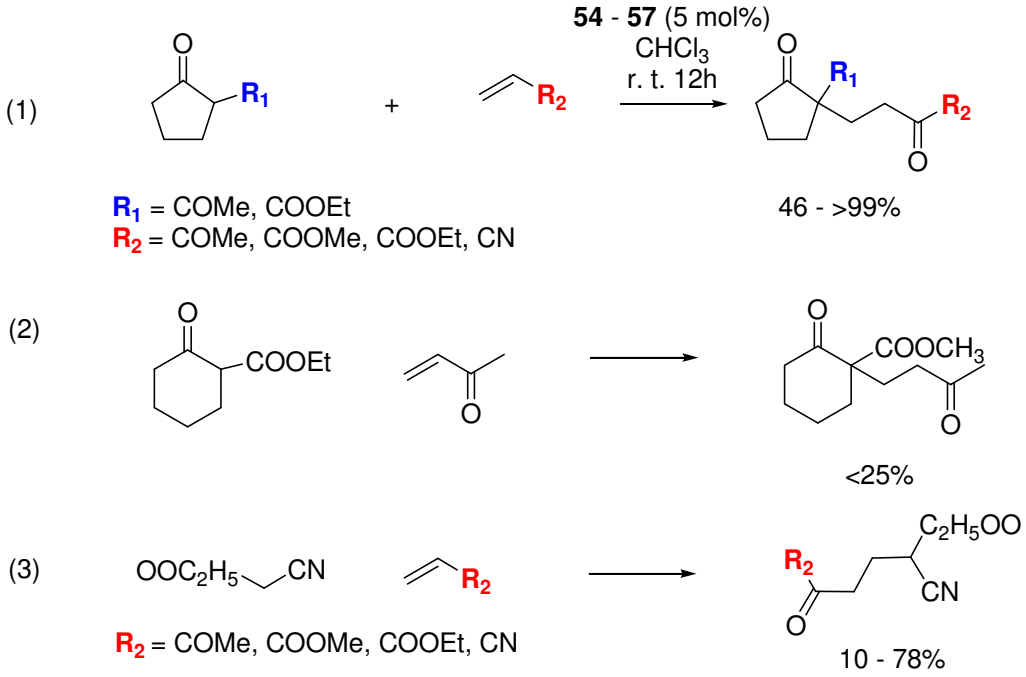
56a: R = Me (61%)
56b: R = *i*-Pr (63%)
56c: R = CH_2Ph (63%)



57a: R = Me (63%)
57b: R = CH_2Ph (66%)

Scheme 39

Compounds **54**-**56** promoted the base-free Michael addition of a wide range of substrates by ligand assisted activation of α-C–H bonds by the anionic amido-functionalized NHC (Scheme 38). Better conversion was observed employing **54a** and **55** as pre-catalysts. Across activated olefins especially *five*-membered substrates appeared to be excellent coupling partners (Eq. 1. Scheme 40). In contrast, only moderate conversion could be achieved employing *six*-membered cyclohexanone derivatives and acyclic substrates (Eq. 2 & Eq. 3, Scheme 40).



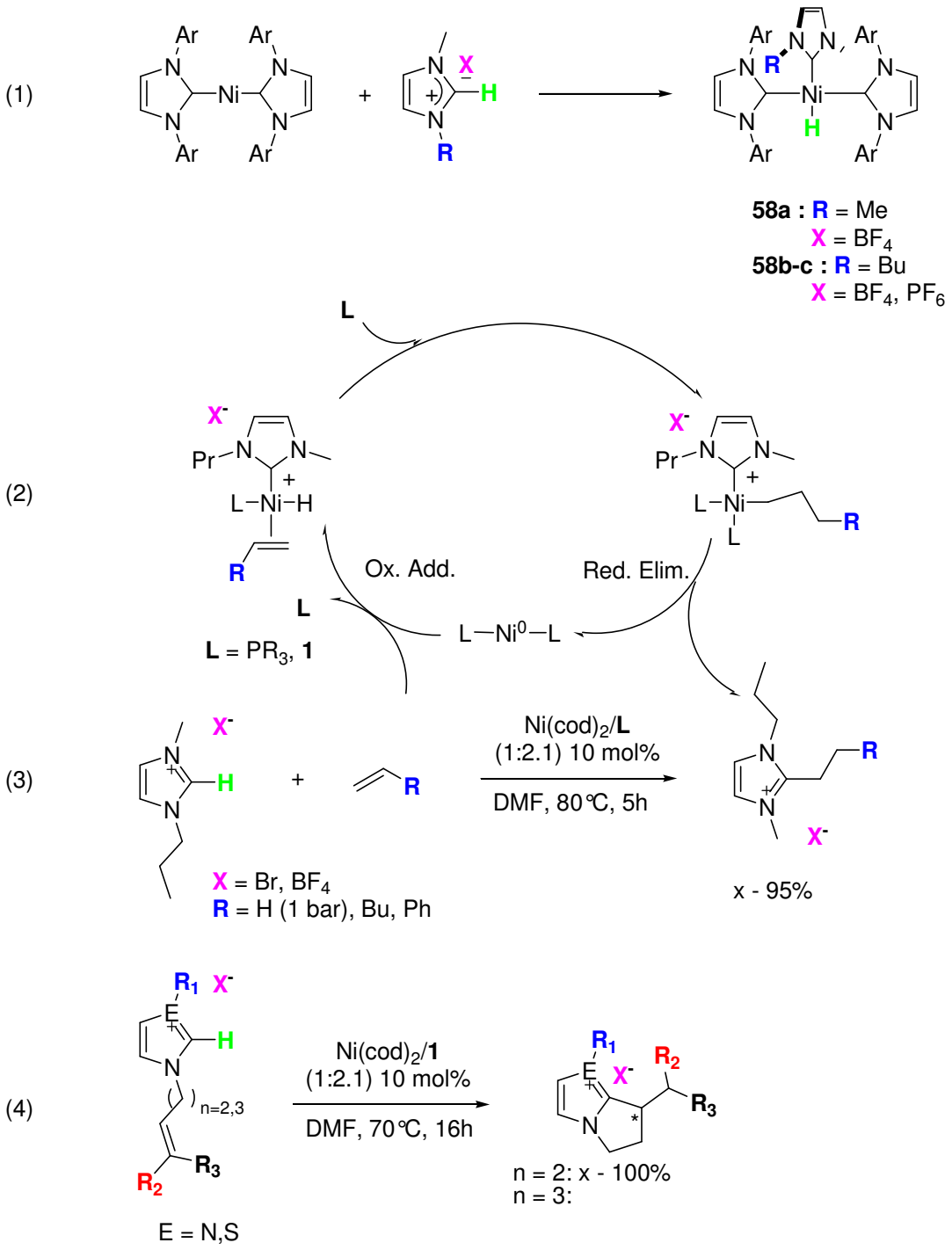
Scheme 40

3.2. Annulations of Heterocycles

Cavell and co-workers have well documented that group 10 metal complexes of type $[(R)(NHC)ML_2]^+$ where R is usually an alkyl, aryl or an acyl substituent, undergo facile reductive elimination to generate M(0) species and 2-R-substituted azolium salts as products.[90] They further demonstrated that 2-*H*-azolium salts will oxidatively add to M(0) complexes to afford reactive NHC-M-hydride complexes (Eq. 1, Scheme 41).[91] By combining the two half-reactions in the presence of an alkenyl chain, they established a nickel catalyzed alkylation of 2-*H*-imidazolium salts via catalytic C–H bond activation and subsequent C–C bond formation (Eq. 2 & 3, Scheme 41).[92] A range of olefins and azolium salts has been employed as substrates providing a library of C(2) substituted compounds. The latter reaction was extended to the intramolecular catalytic annulation of heterocycles by reaction of imidazolium or thiazolium salts with *N*-butenyl, *N*-

[90] (a) D. S. McGuinness, K. J. Cavell, *Organometallics* **2000**, *19*, 4918 ; (b) D. S. McGuinness, N. Saending, B. F. Yates, K. J. Cavell, *J. Am. Chem. Soc.* **2001**, *123*, 4029 ; (c) K. J. Cavell *Dalton Trans.* **2008**, 6676.
[91] (a) N. D. Clement, K. J. Cavell, C. Jones, C. J. Elsevier, *Angew. Chem. Int. Ed.* **2004**, *43*, 1277; (b) M. A. Duin, N. D. Clement, K. J. Cavell, C. J. Elsevier, *Chem. Commun.* **2003**, 400; (c) D. S. McGuinness, K. J. Cavell, B. F. Yates, *Chem. Commun.* **2001**, 355; (d) D. S. McGuinness, K. J. Cavell, B. F. Yates, B. W. Skelton, A. H. White, *J. Am. Chem. Soc.* **2001**, *123*, 8317.
[92] (a) A. T. Normand, K. J. Hawkes, N. D. Clement, K. J. Cavell, B. F. Yates, *Organometallics* **2007**, *26*, 5352; (b) N. D. Clement, K. J. Cavell, *Angew. Chem, Int. Ed.* **2004**, *43*, 3845.

substituted butenyl and *N*-pentenyl substituents (Eq. 4, Scheme 41). The resulting *five-* or *six-*membered fused-ring systems were obtained in excellent yields.[93]

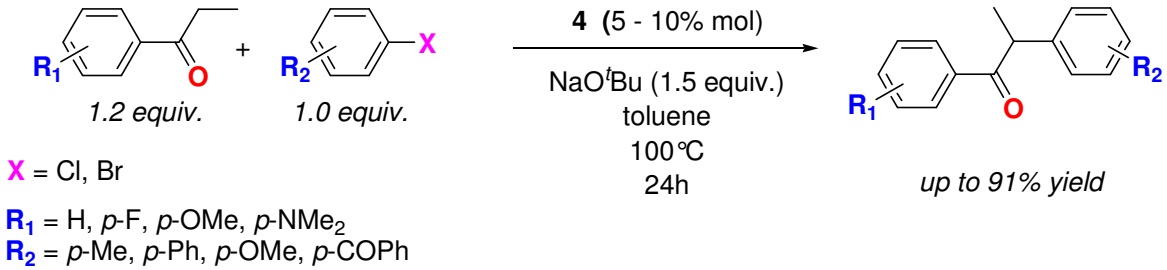


Scheme 41

[93] A. T. Normand, .S. K. Yen, H. V. Huynh, T. S. Andy Hor, K. J. Cavell, *Organometallics* **2008**, *27*, 3153.

3.3. Ketone arylation Reactions

α-Arylation of acyclic ketones was allowed by employing the mixed phosphine-NHC-Ni(II) complex **4** under relatively mild conditions.[84] At 100 °C, in presence of NaO*t*-Bu as a base, **4** achieved the arylation reaction with a range of aryl halides (Cl, Br) and propriophenone in moderate to good yield (Scheme 42).



Scheme 42

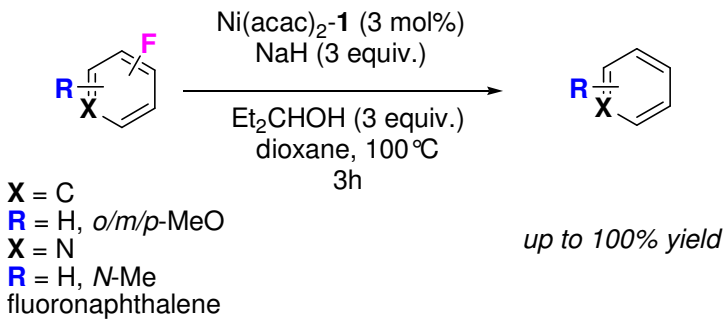
4. Miscellaneous Nickel-NHC Catalyzed sp^2-C–X Bond Activation

4.1. sp^2-C–F Bond Activation

4.1.1. Catalytic sp^2-C–F Bond Activation

The Ni-NHC catalyst generated *in situ* from [Ni(acac)$_2$], **1** (Scheme 5) and NaH in a 1:1:1 molar ratio was reported to promote hydrogenolysis of fluoronaphthalene in quantitative yield (Scheme 43). Interestingly, *4*-fluoroanisole appeared to act as a poor reagent whereas its sterically congested counterpart, *2*-fluoroanisole, was transformed almost quantitatively. It noteworthy that in contrast to an *in situ* generated Ni(0)/PEt$_3$ species[94] the Ni-NHC catalyst was inactive for *2*-fluoropyridine.

[94] (a) L. Cronin, C. L. Higgitt, R. Karch, R. N. Perutz, *Organometallics* **1997**, *16*, 4920; (b) S. Burling, P. I. P. Elliott, N. A. Jasmin, R. J. Lindup, J. McKenna, R. N. Perutz, S. J. Archibald, A. C. Whitwood, *Dalton Trans.* **2005**, 3686.



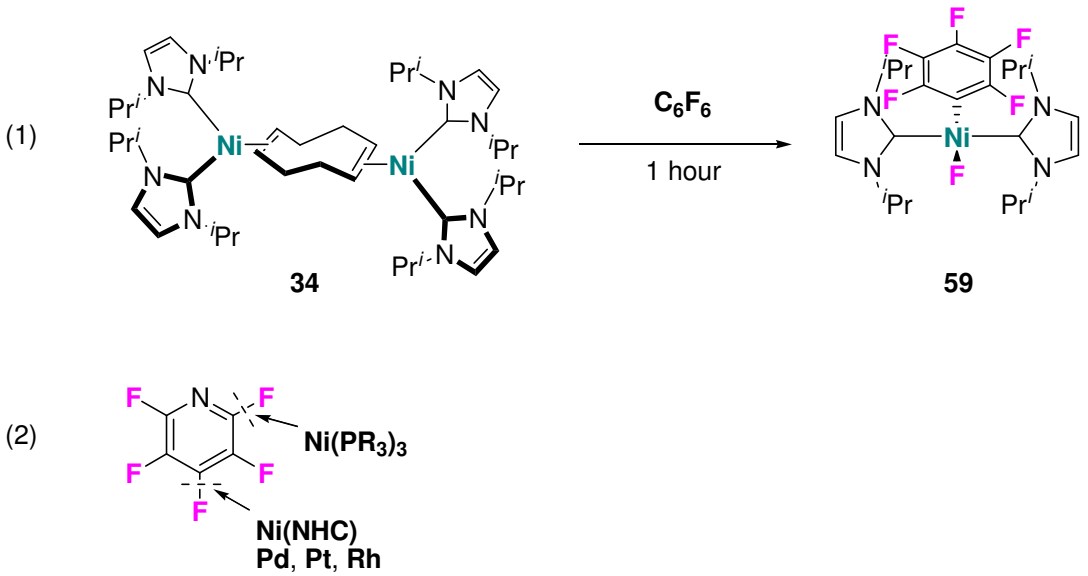
Scheme 43

4.1.2. Stoechiometric sp^2-C–F Bond Activation in Aromatic Fluorides[95]

Catalytic activation of C–F bonds by Ni-NHC species is well known as fluoroarenes have become common reagents in Ni-NHC promoted C–C bond formation reactions;[33,61,62] defluorination has also been observed.[96] Furthermore, reaction of the complex $[Ni_2(cod)\{(i\text{-}Pr)_2\text{-}NHC\}_4]$, **34**, smoothly promotes oxidative addition of hexafluorobenzene in quantitative yield under mild conditions (Eq. 1, Scheme 44).[97] Similar to the oxidative addition of aryl iodides onto *in situ* generated zero-valent $Ni(Me_4\text{-}NHC)_2$ species[60] the resulting nickel(II) complex, **59**, adopted a square-planar geometry with a *trans* alignment of the NHC ligands. Furthermore, displacement of the fluoride ligand was achieved using a variety of silylated reagents as well as organolithium compounds; the formation of the very strong Si–F bond and of lithium fluoride being excellent thermodynamic forces.[98] Furthermore, analysis of the oxidative addition reactions of a range of fluorinated arenes to **34** revealed that the metal insertion regioselectively proceeded at the C(4)-position of the fluoroarene ring as observed for Pt and Rh mediated C–F bond activation.[99] This is contrary to what is observed in the *in situ* generated and electronically analogous $Ni(0)/PEt_3$ species, that insert sp^2-C–F bonds at the C(2)-position (Eq. 2, Scheme 44).[94] The activation of sp^2-C–F bonds predominated with respect to sp^2-C–H bond activation, and this was rationalized by

[95] for a review on Ni-mediated C–F bond activation, see: T. Braun, R. N. Perutz, *Chem. Commun.* **2002**, 2749.
[96] S. Kuhl, R. Schneider, Y. Fort, *Adv. Synth. Catal.* **2003**, *345*, 341.
[97] (a) T. Schaub, M. Backes, U. Radius, *Eur. J. Inorg. Chem.* **2008**, 2680; (b) T. Schaub, P. Fischer, A. Steffen, T. Braun, U. Radius, *J. Am. Chem. Soc.* **2008**, *130*, 9304; (c) T. Schaub, M. Backes, U. Radius, *Organometallics* **2006**, *25*, 4196; (d) T. Schaub, U. Radius, *Chem. Eur. J.* **2005**, *11*, 5024.
[98] T. Schaub, M. Backes, U. Radius, *Eur. J. Inorg. Chem.* **2008**, 2680.
[99] (a) A. Nova, S. Erhardt, N. A. Jasmin, R. N. Perutz, S. A. MacGregor, J. E. McGrady, A. C. Whitwood, *J. Am. Chem. Soc.* **2008**, *130*, 15499; (b) T. Schaub, P. Fischer, A. Steffen, T. Braun, U. Radius, *J. Am. Chem. Soc.* **2008**, *130*, 9304; (c) N. A. Jasmin, R. N. Perutz, A. C. Whitwood, T. Braun, J. Inzundu, B. Neumann, S. Rothfeld, H.-G. Stammler, *Organometallics* **2004**, *23*, 6140; (d) D. Noveski, T. Braun, B. Neumann, A. Stammler, H.-G. Stammler, *Dalton Trans.* **2004**, 4106.

comparing the weak Ni–H bond energy with respect to the much stronger Ni–F bond energy of the corresponding nickel(II) species.[100]

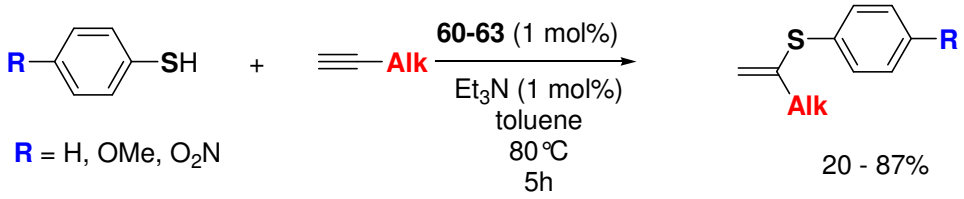


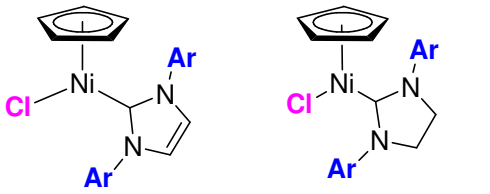
Scheme 44

4.2. Hydrothiolation of terminal alkynes

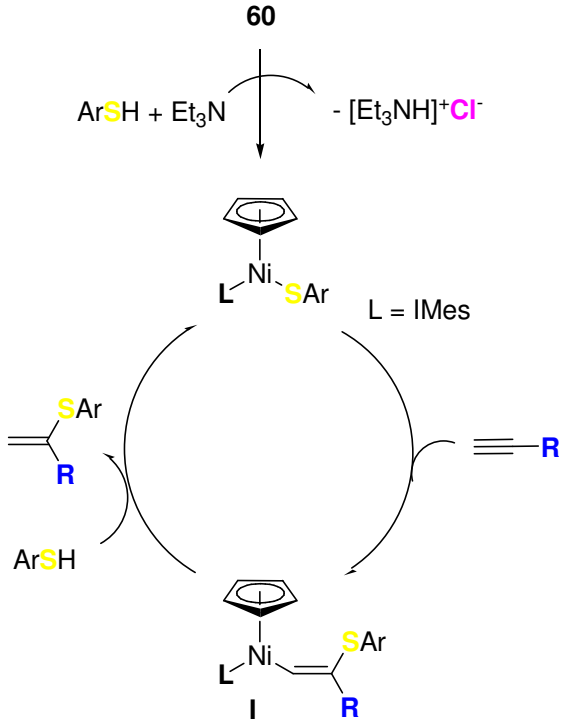
A series of Ni(II) half-sandwich complexes, [Ni(Mes$_2$-NHC)ClCp], **60**, and [Ni{(*i*-Pr$_2$Ph)$_2$-NHC}ClCp], **61**, as well as their imidazolin-*2*-ylidene binded counterparts [Ni (SMes$_2$-NHC)ClCp], **62**, and [Ni{S(*i*-Pr$_2$Ph)$_2$-NHC}ClCp], **63**, were reported to be efficient pre-catalysts for the regioselective hydrothiolation of terminal alkynes on the more hindered carbon atom (Scheme 45).[101] Among the tested compounds, **60** proved to be the best pre-catalyst and a large range of vinylsulfide derivatives could be isolated in high yield (61 – 87 %) with high regioselectivity.

[100] M. Reinhold, J. E. McGrady, R. N. Perutz, *J. Am. Chem. Soc.* **2004**, *126*, 5268.
[101] D. A. Malyshev, N. M. Scott, N. Marion, E. D. Stevens, V. P. Ananikov, I. P. Betelskaya, S. P. Nolan, *Organometallics* **2006**, *25*, 4462.





60: **Ar** = Mes
61: **Ar** = (*i*-Pr)$_2$Ph
62: **Ar** = Mes
63: **Ar** = (*i*-Pr)$_2$Ph



Scheme 45

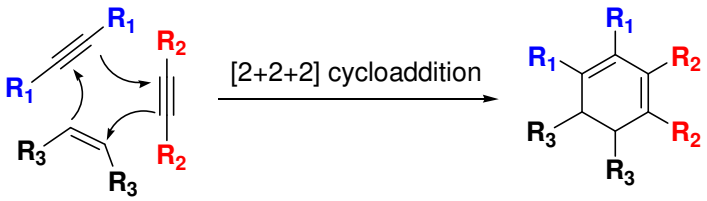
It is noteworthy that the homogeneous behaviour of the active species allowed the authors to have insights into the reaction pathway, which could be followed by NMR analysis. The following path was proposed: (i) displacement of the chloride ligand by a ArS^- group, (ii) subsequent alkyne

insertion into the Ni–S bond to form the □-allyl Ni(II) intermediate, **I**, and finally, (iii) protonolysis of the Ni–C bond.

5. π-Component Activation

5.1. Cycloadditions

Cycloadditions are pericyclic chemical reactions in which two or more intra- or intermolecular π-components, involving 4n + 2 (n = 0, 1, 2…) π-electrons, combine to form a cyclic adduct in which there is a net reduction of the bond multiplicity. In particular, transition-metal-catalyzed cycloadditions[102] are intensively studied for the quick construction of complex cyclic systems under mild conditions. Recent reports of nickel phosphine catalytic systems for the synthesis of pyrones[103],[104] pyrans[105], isoquinolines[106] and pyridines[107] from simple, acyclic precursors have incited the use of NHC-type nickel species for cyclization reactions. Ni-NHC catalysts have been extensively studied for [2+2+2] Cycloadditions (Scheme 46)[108] and for rearrangement reactions.



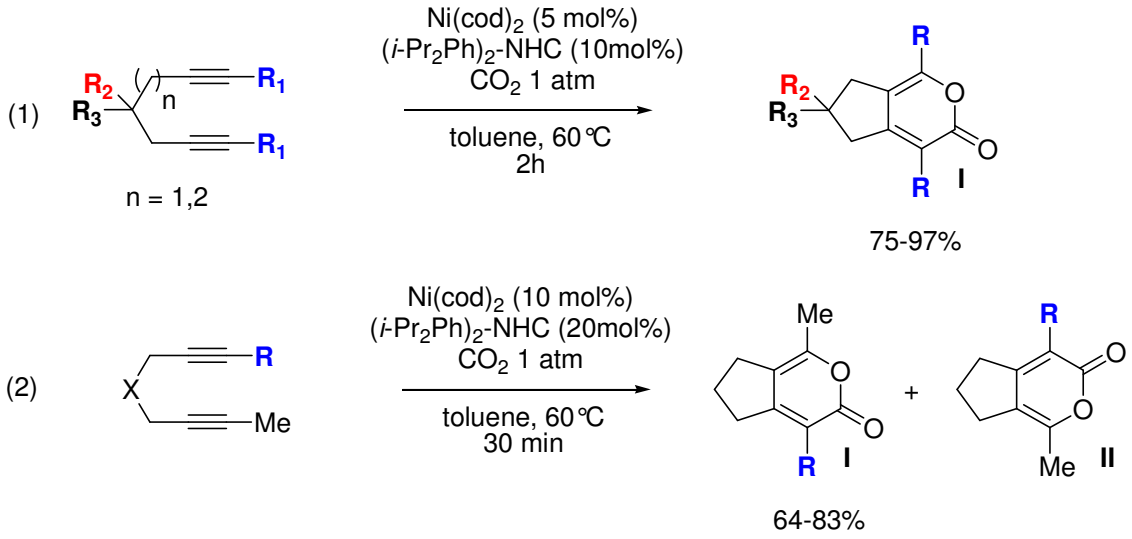
Scheme 46

5.1.1. [2+2+2] Cycloadditions

[102] as a review for Ni-mediated reactions, see: (a) J. Montgomery, *Angew. Chem., Int. Ed.* **2004**, *43,* 3890; (b) J. Houpis, J. Lee, *Tetrahedron* **2000**, *56*, 817; (c) J. Montmogery, *Acc. Chem. Res.* **2000**, *33*, 467; (d) H. Buchholz, P. Heimbach, H. J. Hey, H. Selbeck, W. Wiese, *Coord. Chem. Rev.* **1972**, *8*, 129.
[103] (a) T. Tsuda, M. Shohei, N. Hasagawa, T. Saesuga, *J. Org. Chem.* **1990**, *55*, 2978; (b) T. Tsuda, S. Morikawa, T. Saegusa, *J. Chem. Soc., Chem. Commun.* **1989**, 9; (c) T. Tsuda, S. Morikawa, T. Saegusa, *Synth. Commun.* **1989**, *19*, 1575, (d) T. Tsuda, S. Morikawa, R. Sumiya, T. Saegusa, *J. Org. Chem.* **1988**, *53*, 3140; (e) Tsuda, R. Sumiya, T. Saegusa, *Synth. Commun.* **1987**, *17*, 147.
[104] Y; Kishimoto, I. Mitani, *Synlett* **2008**, 2141.
[105] I. Kogama, T. Kurahashi, S. Matsubara, *J. Am. Chem. Soc.* **2009**, *131*, 1350.
[106] (a) T. Iwayama, Y. Sato, *Heterocycles* **2010**, *80*, 917; (b) T. Iwayama, Y. Sato, *Chem. Commun.* **2009**, 5345; (c) Y. Sato, T. Nishima, M. Mori, *Heterocycles* **1997**, *44*, 443; (d) Y. Sato, T. Nishima, M. Mori, *J. Org. Chem.* **1994**, *59*, 6133.
[107] (a) H. Hoberg, G. Burkhart, *Synthesis* **1982**, 324, (b) H. Hoberg, G. Burkhart, *Synthesis* **1979**, 525.
[108] as a recent review, see: J. A. Vela, C. Saa, *Synlett* **2008**, 2571; b) P. R. Chopade, J. Louie, *Adv. Synth. & Catal.* **2006**, *348*, 2307; c) S. Kotha, E. Brahmachary, K. Lahiri, *Eur. J. Org. Chem.* **2005**, 2741.

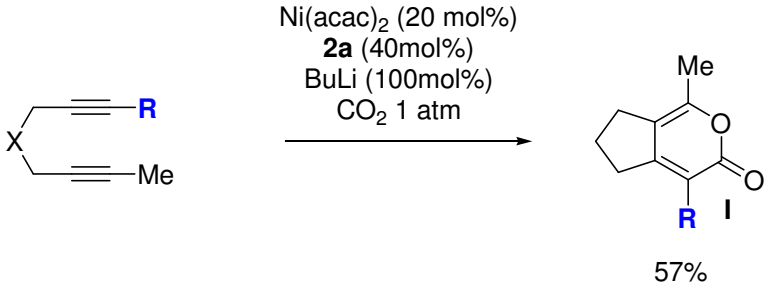
5.1.1.1. [2+2+2] Cycloaddition of diynes and CO_2

The catalytic system generated by the equilibrium of the zero-valent complex [Ni(cod)$_2$] with (*i*-Pr$_2$Ph)$_2$-NHC [(2,6-diisopropylphenyl)imidazol-2-ylidene] in a 1:2 ratio catalyzes the [2+2+2] cycloaddition of CO_2 and diynes to afford pyrones under mild conditions (Eq. 1, Scheme 47).[109] Good to excellent yields were observed with 5 mol% of the Ni(0)-NHC$_2$ system at 60 °C under 1 atmosphere of CO_2, and a variety of substrates was transformed with good functional group tolerance. Regiomeric mixtures of pyrone derivatives **I** and **II** were obtained when asymmetrical diynes were reacted with CO_2 in the presence of a catalyst generated from Ni(cod)$_2$ and Mes$_2$-NHC (2,4,6-trimethylphenylimidazol-2-ylidene) (Eq. 2, Scheme 47).[110] Regioselectivity for these substrates could be significantly improved with the larger (*i*-Pr$_2$Ph)$_2$-NHC ligand. Analogously, pyrone derivatives have been synthesized employing Ni(acac)$_2$ and **2a** in a 1:2 molar ration in the presence of *n*-BuLi as either a deprotonating and a reducing agent (Scheme 48).[111] However, under these reaction conditions, only moderate conversion was observed.



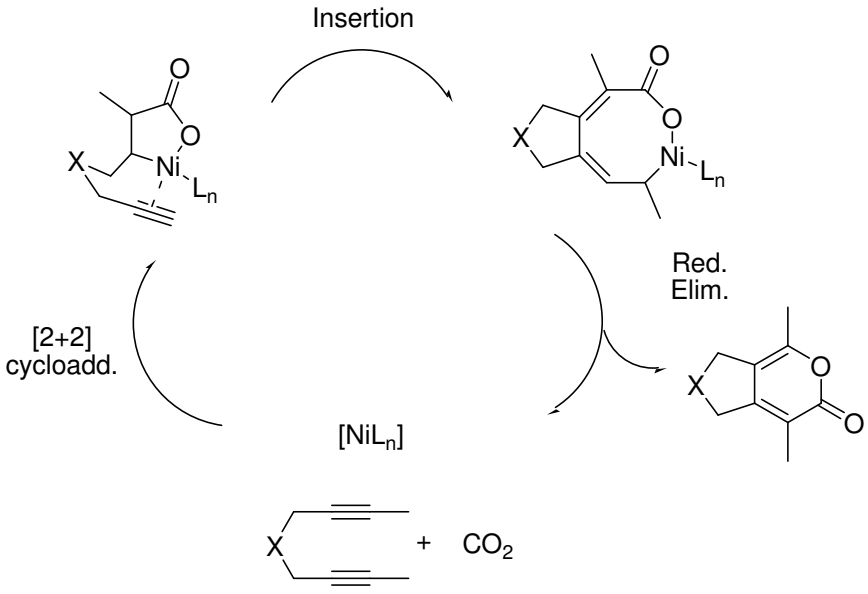
Scheme 47

[109] J. Louie, J. E. Gibby, M. V. Farnworth, T. N. Tekavec, *J. Am. Chem. Soc.* **2002,** *124*, 14688.
[110] T. N. Tekavec, A. M. Arif, J. Louie, *Tetrahedron* **2004**, *60*, 7431.
[111] T. N. Tekavec, G. Zuo, K. Simon, J. Louie, *J. Org. Chem.* **2006**, *71*, 5834.



Scheme 48

These results, coupled with some NMR studies and a couple of control experiments, allowed some insight into the catalytic cycle. The mechanism was proposed to involve an initial [2+2] cycloaddition of CO_2 with the less sterically demanding alkynyl moiety. Subsequent insertion of the second pendant alkynyl unit followed by a carbon-oxygen bond-forming reductive elimination would then release the pyrone product and regenerate the catalyst (Scheme 49). As expected, according to the proposed mechanism, no conversion for sterically hindered diynes was observed.

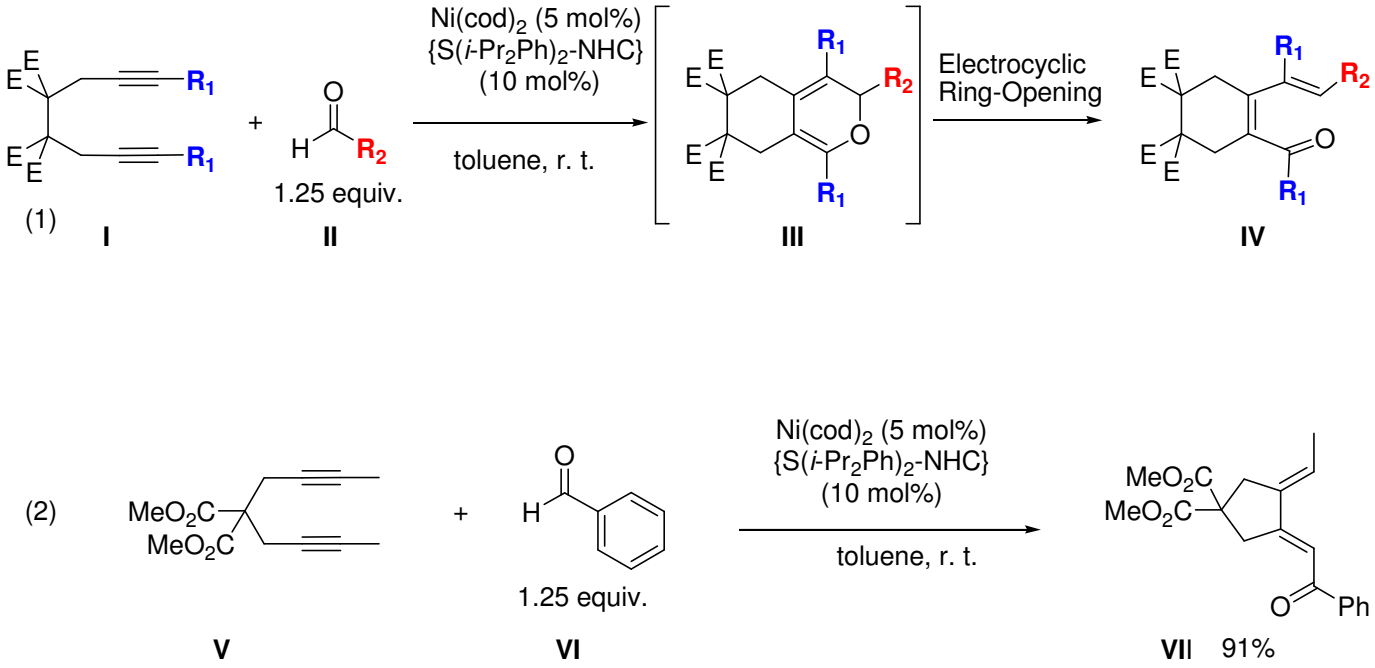


Scheme 49

5.1.1.2. [2+2+2] Cycloaddition of Diynes and Carbonyl Derivatives

5.1.1.2.1. Aldehydes

The combination of $Ni(cod)_2$ and unsaturated $S(i\text{-}Pr_2Ph)_2$-NHC in a 1:2 ratio did also show high activity for the [2+2+2] cycloaddition involving diynes and aldehydes.[112] Thus, $[Ni\{S(i\text{-}Pr_2Ph)_2\text{-NHC}\}_2]$ cleanly afforded dienone **IV**, derived from electrocyclic ring-opening of the initial pyran **III** by reaction of diyne **II** and aldehyde **I** (Eq. 1, Scheme 50). Diynes which possess a three carbon linkage between the alkyne units also undergo clean cycloaddition with benzaldehyde (Eq. 2, Scheme 50). Interestingly, the connectivity of these dienones was different from those obtained for diynes possessing a four-carbon linkage.

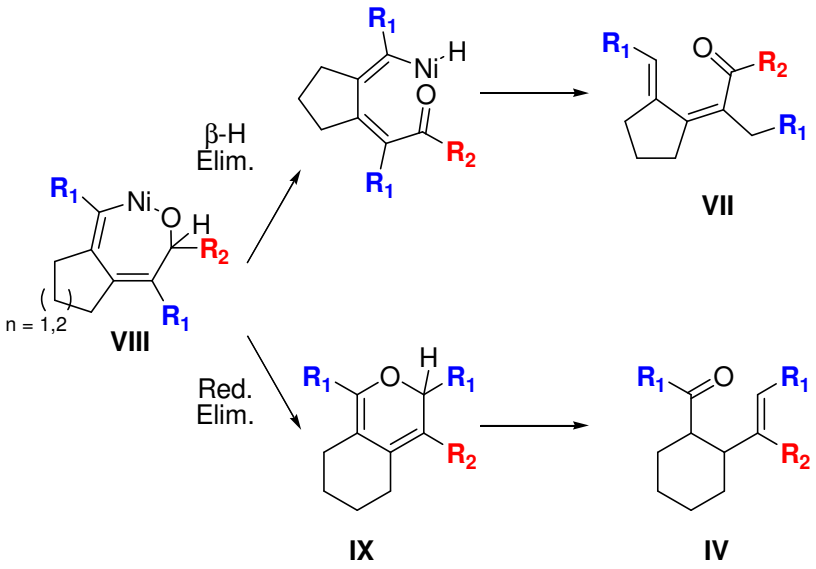


Scheme 50

Specifically, the Ph group of benzaldehyde remains connected to the carbonyl in dienones of type **VI** while this bond has been cleaved in dienones of type **IV**. The authors attributed this difference in the reactivity of diynes **V**, n = 2, to a slow rate of reductive elimination, relative to β-hydride elimination from nickelacycle **VIII** to form a strained fused [5,6] ring system (Scheme 51). For diynes **I**, n = 1, the rate of reductive elimination from the less strained [6,6] ring system, **IX**, is more facile. The same catalytic system also allowed unactivated ketones to cleanly react with

[112] T. N. Tekavec, J. Louie, *Org. Lett.* **2005**, *7*, 4037.

diynes to afford pyrans in good yield. With $Ni(acac)_2$, **2a** and *n*-BuLi in a 1:2:5 molar ratio as a catalyst precursor, only poor yields of pyrane **IV** were obtained.[112]

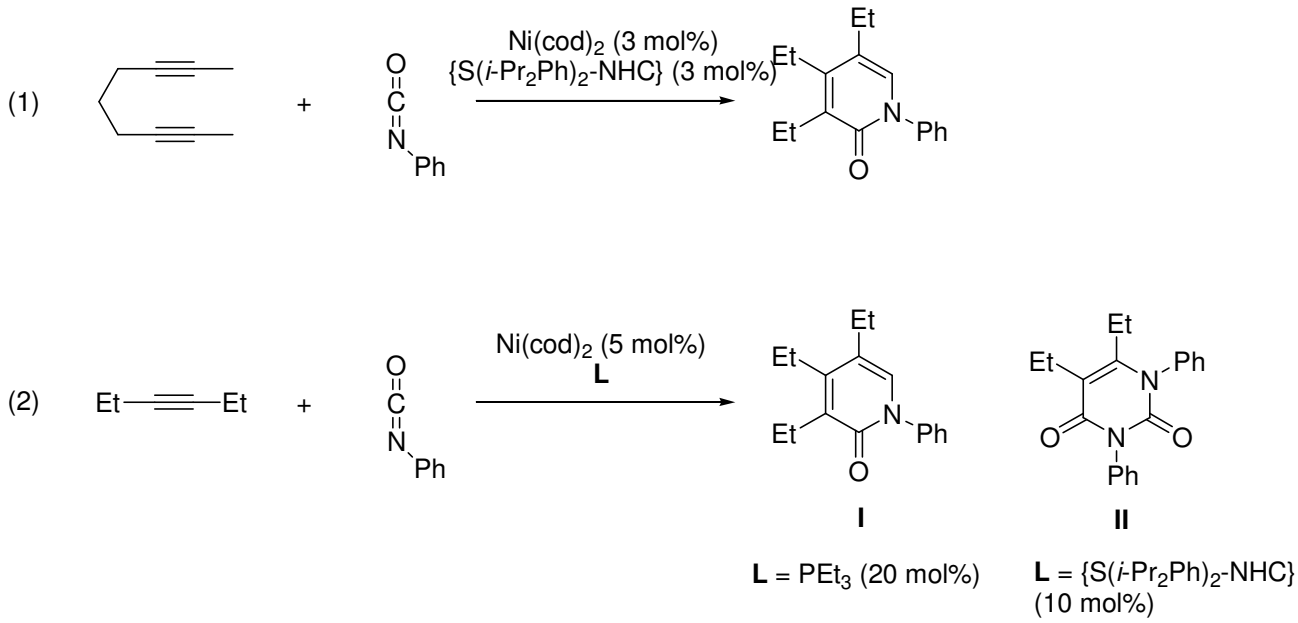


Scheme 51

5.1.1.2.2. Isocyanates

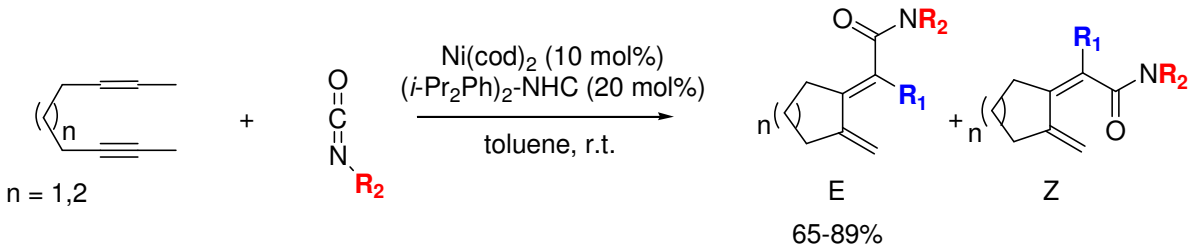
[2+2+2] cycloadditions involving alkyl-substituted diynes with 3-, 4-, or 5-carbon linkages and aryl- and alkyl-substituted isocyanates to afford 2-pyridiones were reported to be mediated by $Ni(cod)_2$ and $S(i\text{-}Pr_2Ph)_2$-NHC in a 1:1 molar ratio at room temperature (Eq. 1, Scheme 52).[113] Higher reaction temperatures were required with arylisocyanates bearing electron-withdrawing groups. Surprisingly, pyrimidinedione rather than 2-pyridione was formed from isocyanates and asymmetrically substituted alkynes with (1:2) mixtures of $Ni(cod)_2$ and $S(i\text{-}Pr_2Ph)_2$-NHC (Eq. 2, Scheme 52).[114] It worth note that the desired 2-pyridiones were obtained with high regioselectivity from cycloaddition of isocyanates and alkynes catalyzed by the electronically related system of $Ni(cod)_2$ and PEt_3 in a 1:2 molar ratio.[113]

[113] H. A. Duong, M. J. Cross, J. Louie, *J. Am. Chem. Soc.* **2004**, *126*, 11438.
[114] H. A. Duang, J. Louie, *Organomet. Chem.* **2005**, *690*, 5098.



Scheme 52

Furthermore, dienamides that contain [5] or [6]-membered rings are formed with good enantioselectivity by [2+2+2] cycloadditions of enynes and isocyantates from a (1:2) combination of zero-valent $Ni(cod)_2$ and $(i\text{-}Pr_2Ph)_2$-NHC (Scheme 53).[115] Under these conditions, alkyl *N*-substituted isocyantates are transformed in good yields; dienamides having a bicyclic ring system could also be formed. In contrast, aryl-isocyanates reacted more sluggishly and required more forcing conditions. It worth mentioning that dienamides were not obtained from $Ni(cod)_2$ in association with phosphine ligands or with less bulky NHCs.

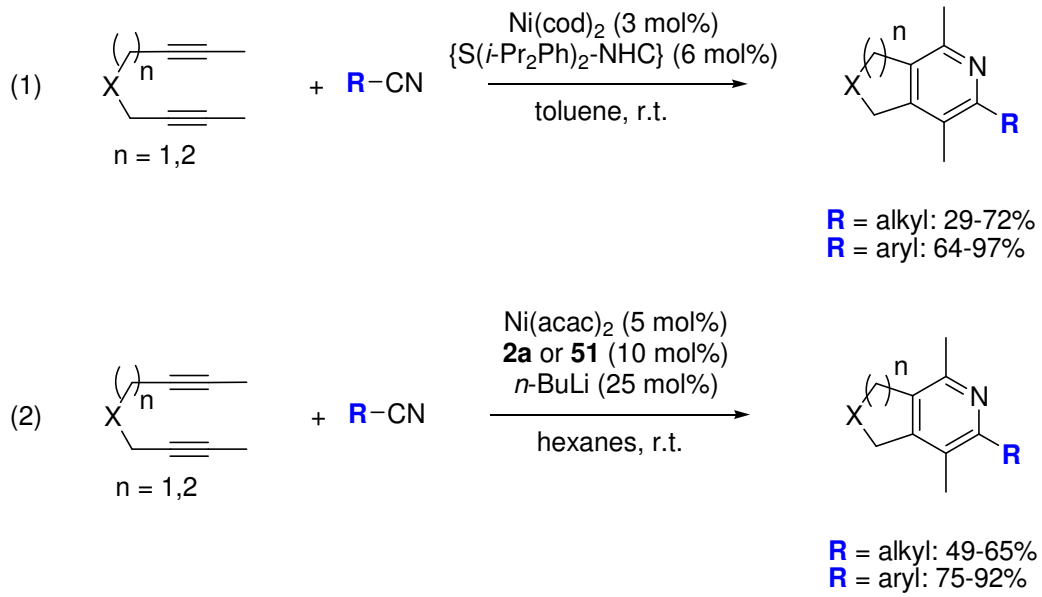


Scheme 53

[115] B. R. D'Souza, J. Louie, *Org. Lett.* **2009**, *11*, 4168.

5.1.1.3. [2+2+2] Cycloadditions of Diynes and Nitriles

[5,6]-membered fused ring pyridines could be obtained at room temperature from cycloadditions of diynes and nitriles with a catalyst generated *in situ* from $Ni(cod)_2$ and $S(i\text{-}Pr_2Ph)_2$-NHC (Eq. 1, Scheme 54).[116] Both aryl- and alkylnitriles as well as heteroarylnitriles were readily converted to the respective pyridines, although alkylnitriles gave slightly diminished yields. It worth mentioning that [7,6]-membered pyridines could be obtained, although in moderate yield, from diynes which have a 5-carbon linkage. In a reaction similar to the [2+2+2] cycloadditions of diynes and CO_2, cycloaddition of diynes and nitriles was also promoted by a catalyst generated *in situ* from $Ni(acac)_2$, **2a** or **46** and *n*-BuLi with a 1:2:5 molar ratio, in good to excellent yield (Eq. 2, Scheme 54).[112]

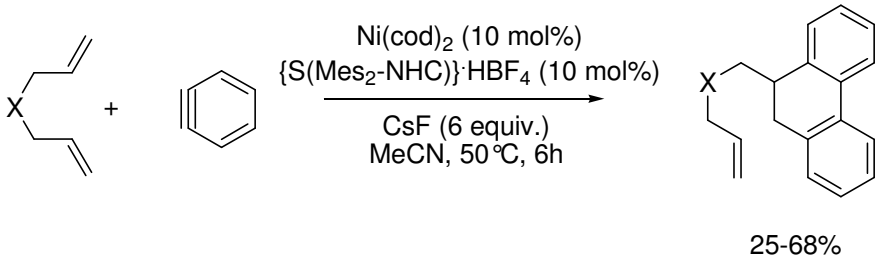


Scheme 54

5.1.1.4. Cycloaddition of Dienes and Alkynes

$Ni(cod)_2$ in association with $(SMes_2\text{-NHC})\cdot HBF_4$ in a 1:1 molar ratio was reported to cyclize terminal dienes and alkynes in the presence of CsF with gentle heating (Scheme 55).[117] The corresponding 9,10-dihydrophenanthrene compounds were isolated in moderate yields with good enantioselectivity.

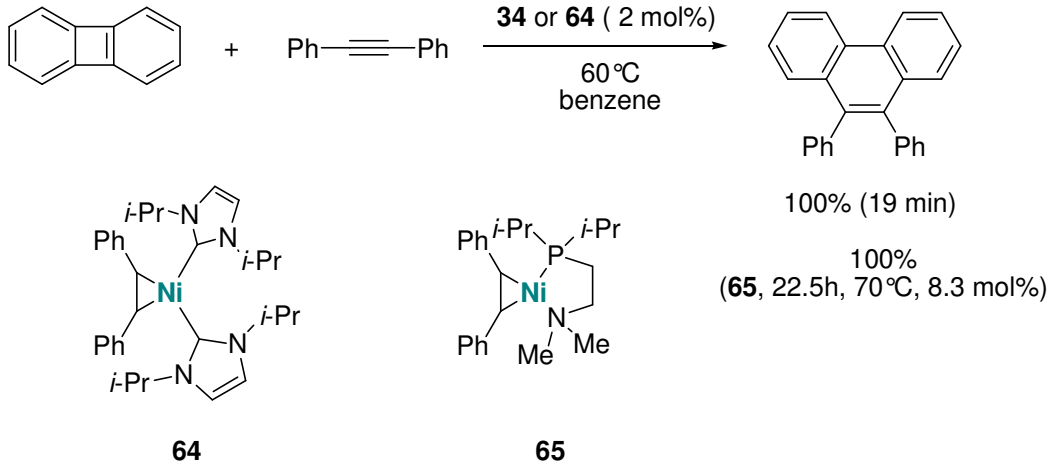
[116] M. M. McCornick, H. A. Duong, G. Zuo, J. Louie, *J. Am. Chem. Soc.* **2005**, *127*, 5030.
[117] N. Saito, K. Shiotani, A. Kinbora, Y. Sato, *Chem. Commun.* **2009**, 4284.



Scheme 55

5.1.2. [2+2] Cycloadditions

The catalytic insertion of internal alkynes into the 2,2'-bond of biphenylene has been reported by employing [Ni_2(cod){(i-Pr)$_2$-NHC}$_4$], **34**, (Scheme 22) and [Ni{(i-Pr)$_2$-NHC}$_2${η^2-C_2(Ph_2)}], **64**, as catalysts (Scheme 56). The synthesis of the desired 9,10-diphenylphenanthrene compound was completed after only 19 minutes at 60 °C in benzene with the catalysts **34** and **64**.[118] In comparison, the catalyst [Ni{(i-Pr_2P)-C_2H_4-(NMe_2)}(η^2-C_2Ph_2)], **65**, required 22.5 hours at 70 °C to form this compound quantitatively.[119]



64 **65**

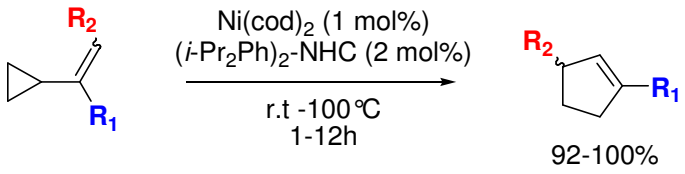
Scheme 56

[118] T. Schaub, U. Radius, *Chem. Eur. J.* **2005**, *11*, 5024.
[119] C. Müller, R. J. Lachicotte, W. D. Jones, *Organometallics* **2002**, *20*, 5745.

5.2. Rearrangement Reactions

$Ni(cod)_2$/NHC catalytic systems turned out to be active for the rearrangement of viniyl-cyclopropanes,[120] cyclopropylen-ynes,[121] vinyl aziridines, and aziridinylen-ynes[122] to afford cyclopentane- and cycloheptene-based products. In all cases, $Ni(cod)_2/PR_3$ bases catalytic systems were ineffective.

The catalyst generated *in situ* from zero-valent $Ni(cod)_2$ and $(i\text{-}Pr_2Ph)_2$-NHC in a 1:2 molar ratio rearranges unactivated vinyl-cyclopropanes (VCPs) into cyclopentanes under mild conditions (Scheme 57).[120] Substrates possessing electron-withdrawing, heteroatom or phenyl groups on the cyclopropane ring underwent rapid isomerization and afforded high yields of the corresponding cyclopentane. Slightly elevated temperatures were necessary for the isomerization of trisubstituted olefins. It worth mentioning that good reactivity was obtained in a variety of hydrocarbon solvents but was completely inhibited in acetonitrile and dichloromethane. Finally, under the same reaction conditions, significantly lower VCP rearrangement conversions were observed by employing Mes_2-NHC as a ligand (49 % and 100 % respectively). This preliminary result was completed by theoretical and experimental studies of the [1,3]-sigmatropic rearrangement of VCP into cyclopentane. The bulkiness of the NHC ligand revealed to be decisive for effective metal-product dissociation.[123]

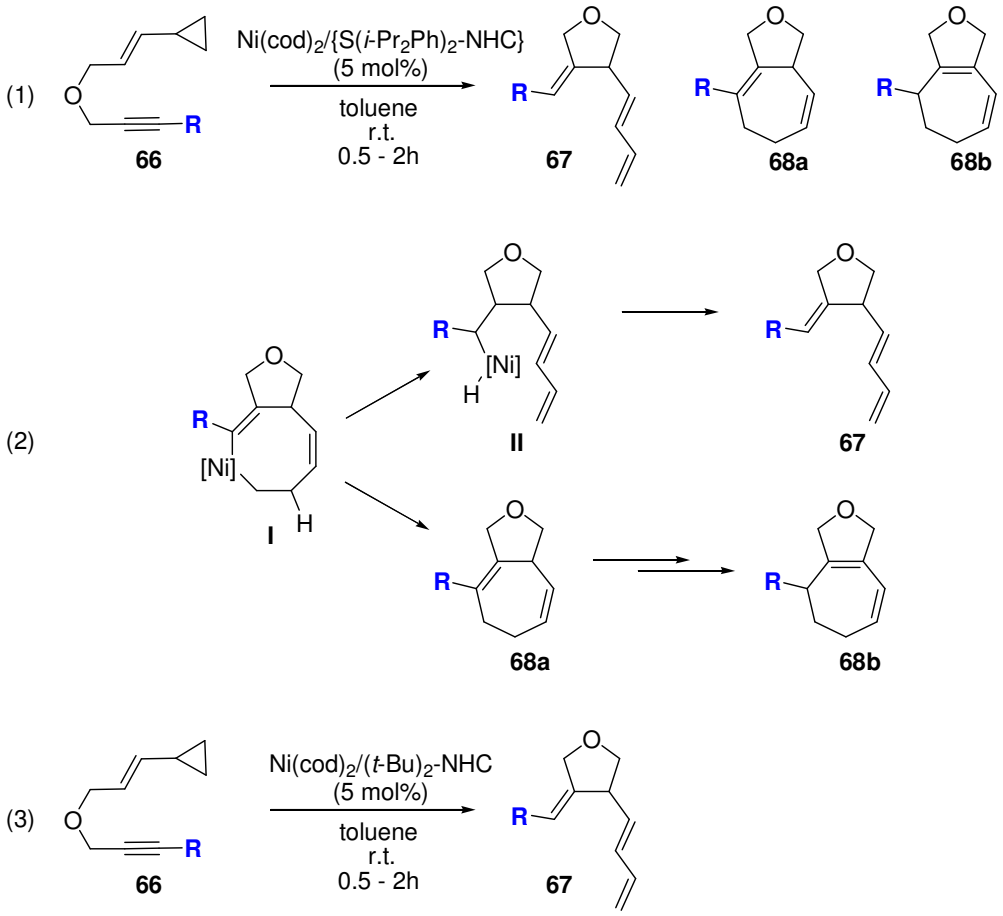


Scheme 57

Furthermore, (1:2) mixtures of $Ni(cod)_2$ and $S(i\text{-}Pr_2Ph)_2$-NHC mediated catalytic isomerization of cyclopropylen-ynes, **66**, in high yield (Eq. 1, Scheme 58).[121] It was established that for small R (e.g. R = Me), tetrahydrofuran **67** was obtained as a sole product. As R became larger (R = Et, *i*-Pr), a mixture consisting of **67** and [5,7]-membered fused ring cycloheptadienes, **68**, was obtained. Finally, when R = *t*-Butyl or TMS, **68** was observed in good yields (82 – 88 %). These results suggested a mechanism that diverges at a common eight-membered intermediate **I** (Eq. 2,

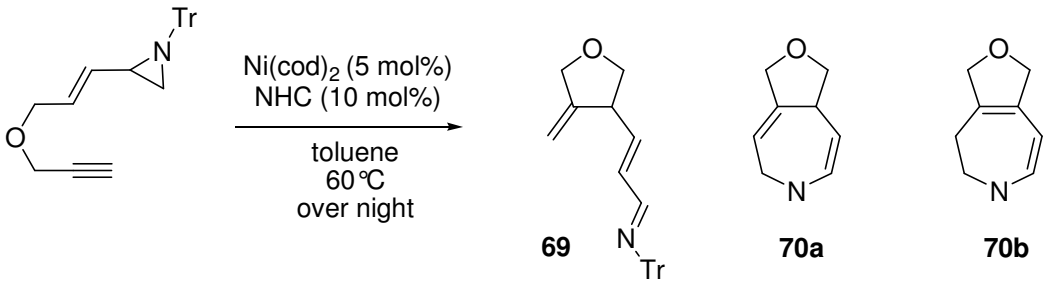
[120] G. Zuo, J. Louie, *Angew. Chem. Int. Ed.* **2004**, *43*, 2277.
[121] G. Zuo, J. Louie, *J. Am. Chem. Soc.*, **2005**, *127*, 5798.
[122] G. Zuo, J. Louie, *Tetrahedron Lett.* **2008**, *49,* 6797.
[123] S. C. Wang, D. M. Troast, M. Conda-Sheridan, G. Zuo, D. LaGarde, J. Louie, D. J. Trantillo, *J. Org. Chem.* **2009**, *74*, 7822.

Scheme 58). **I** would undergo *β*-hydride elimination (**II**) followed by reductive elimination to afford the cycloheptadiene product **68**. Steric hindrance induced by large substrate substituants would inhibit the *β*-hydride elimination step and direct reductive elimination of the eight-membered intermediate would afford **68a** and subsequently **68b** by isomerization. The desired tetrahydrofuran compound **67** could be selectively formed from a large scale of cyclopropylen-yne substrates, regardless of substituent size and under very mild conditions, by employing *t*-Bu_2-NHC (*t*-Bu_2-NHC = 1,3-bis-*tert*-butylimidazol-2-ylidene) as a ligand (Eq. 3, Scheme 58).



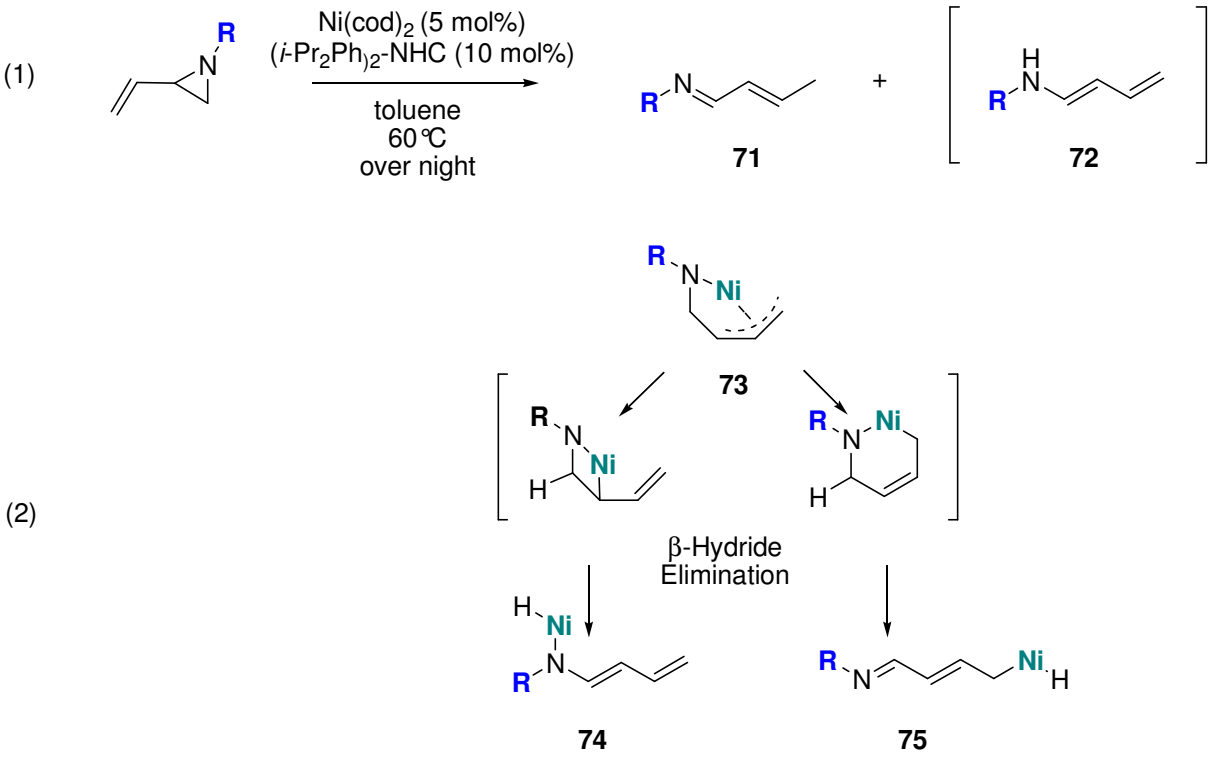
Scheme 58

Similarly, catalytic isomerization of vinyl aziridinylen-ynes with a (1:2) mixture of $Ni(cod)_2$ and NHC formed tetrahydrofuran **69** and bicyclic cycloheptadienes, **70,** (Scheme 59).[122] By employing the bulky (*i*-$Pr_2Ph)_2$-NHC as a ligand, the formation of the azepine compounds **70b** was favoured, whereas smaller Mes_2-NHC selectively isomerized the vinyl aziridines into azepines **70a**. [Ni{(*t*-$Bu)_2$-NHC}] selectively formed the unsaturated imine **69**. These results are consistent with rearrangement of cyclopropylen-yne



Scheme 59

Furthermore, the 1:2 combination of $Ni(cod)_2$ and $(i\text{-}Pr_2Ph)_2$-NHC efficiently catalyzed the isomerization of vinyl aziridine to α,β-unsaturated imines, **71**, or 1,3-butadienylamine, **72** (Eq. 1, Scheme 60). The isomerization to imines or 1,3-butadienylamines can be rationalized by the formation of a key π-allyl-Ni complex. Due to the difficulty of reductive elimination of the sp^3-C–N bond this π-allyl-Ni complex **73** undergoes β-hydride elimination followed by reductive elimination. 1,3-Butadienylamine **72** and imine **71** arise from a metallazetidine intermediate **74** and a metallapiperidine intermediate **75**, respectively (Eq. 2, Scheme 60).



Scheme 60

5.3. *Three* Component Coupling Reactions

Transition metal catalyzed reductive couplings have seen extensive developments in recent years and have been demonstrated with a broad array of catalysts and substrate combinations. In reactions of this type, π-systems such as aldehydes, enones, alkynes, dienes or allenes are typically combined with a reducing agent such as elemental hydrogen, silanes, boranes or organozincs. During the coupling event, the π-systems are joined via C–C bond formation and undergo a net electron oxidation.[124] Ni-NHC catalytic systems, in particular, allow the synthesis of allylic, homoallylic or cyclic alcohol derivatives via the intra- or intermolecular coupling of alkene, 1,3-diene, alkyne or allene moieties with aldehydes and silanes.

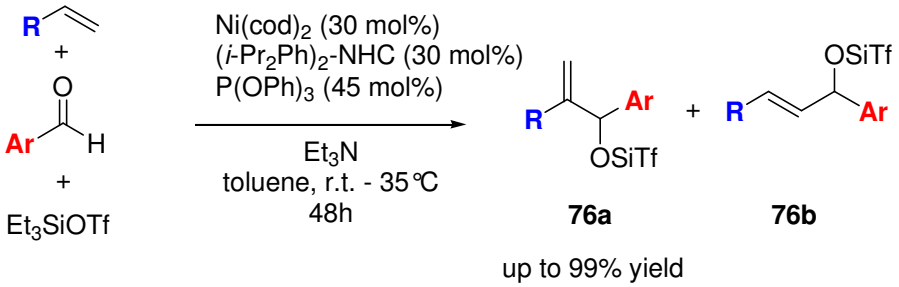
5.3.1. sp^2-C hydrocarbon, Aldehyde and Silane

5.3.1.1. Alkene, Aldehyde and Silane

NHC-nickel(0) catalyzed *three* component coupling reactions involving α-olefins, aldehydes and silyl triflates have been documented by Jameson and co-workers.[125] The combination of $[Ni(cod)_2]$, $(i\text{-}Pr_2Ph)_2$-NHC and electron-withdrawing phosphite $P(OPh)_3$ as a co-catalyst in the presence of triethylamine afforded a large variety of allylic alcohol derivatives **76a** in excellent yield with high regioselectively (Scheme 61). Contrary to the $(i\text{-}Pr_2Ph)_2$-NHC-Ni(0) catalyst, nickel(0) in association with $EtOPPh_2$ or Ph_3P selectively afforded the complementary homoallylic alcohol derivatives **76b**.[126] It is believed by the authors that this impressive selectivity and efficiency is the result of a synergistic relationship between the strong σ-donor $(i\text{-}Pr_2Ph)_2$-NHC and the strong π-acceptor $P(OPh)_3$. The electron-withdrawing phosphite would lower the strong electron-donating ability of the NHC ligand at a specific point in the catalytic cycle: this consequently accelerates the reductive elimination of the desired product and suppresses undesirable side-reactions. It noteworthy, that no turnover was observed by employing this catalyst for the reaction of aldehydes, alkynes and silane triflates without any phosphite additive.[127]

---

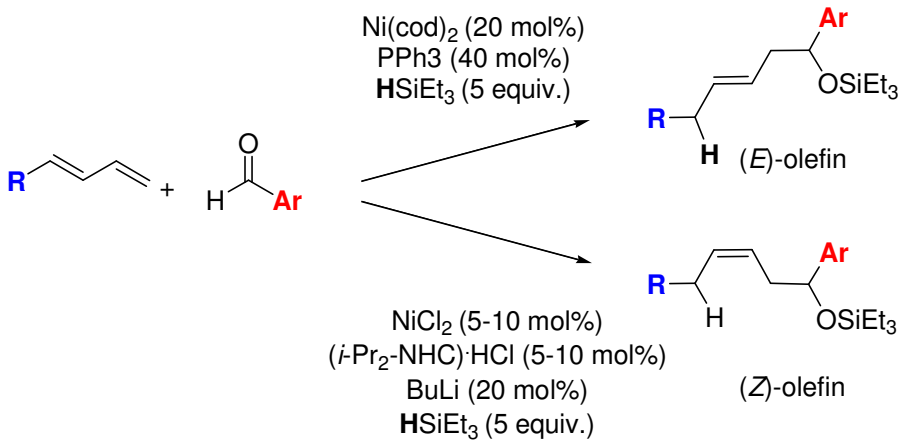
[124] For reviews on Ni(0) catalyzed multicomponent coupling, see: a) J. Montgomery, *Angew. Chem. Int. Ed.* **2004**, *43*, 3890; b) S.-I. Ikeda, *Angew. Chem. Int. Ed.* **2003**, *42*, 4620; c) J. Montgomery, *Acc. Chem. Res.* **2000**, *33*, 467.
[125] C.-Y. Ho, T. F. Jamison, *Angew. Chem., Int. Ed.* **2007**, *46*, 782.
[126] a) C.-Y. Ho, S.-S. Ng, T. F. Jamison, *J. Am. Chem. Soc.* **2006**, *128*, 5362; b) S.-S. Ng, C.-Y. Ho, T. F. Jamison, *J. Am. Chem. Soc.* **2006**, *128*, 11463.
[127] (a) S.-S. Ng, T. F. Jamison, *Tetrahedron* **2006**, *62* 11350; (b) S.-S. Ng, T. F. Jamison, *J. Am. Chem. Soc.* **2005** *127* 7320.



Scheme 61

5.3.1.2. 1,3-Diene, Aldehyde and Silane

The nickel(0) catalyzed reductive coupling of 1,3-dienes with aldehydes in presence of a silane appeared to be ligand controlled and highly region- and stereoselective (Scheme 62).[128] Thus, the (*E*)-olefin was obtained as the sole product using (1:2) mixtures of $Ni(cod)_2$ and PPh_3.[128c] Selective synthesis of the (*Z*)-isomer was promoted by the catalytic system generated *in situ* from (1:1) combinations of $NiCl_2$, {(*i*-Pr)$_2$-NHC}·HCl in the presence of BuLi as either a reducing agent and a base, although undesirable hydrosilylation of the 1,3-diene was detected as a side reaction.[128b]

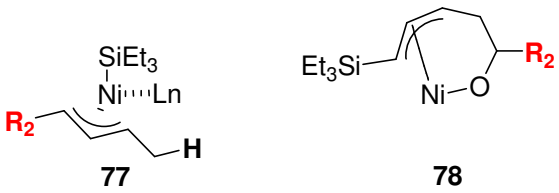


Scheme 62

Furthermore, regio- and stereoselectivity for this reaction involving 1,3-diene, aldehyde and silane could be considerably improved by employing (1:2) mixtures of $Ni(cod)_2$, Mes_2-NHC·HCl, in the presence of Cs_2CO_3 as a base and PPh_3 as a stabilizer for the active Ni-NHC species.[128a] The

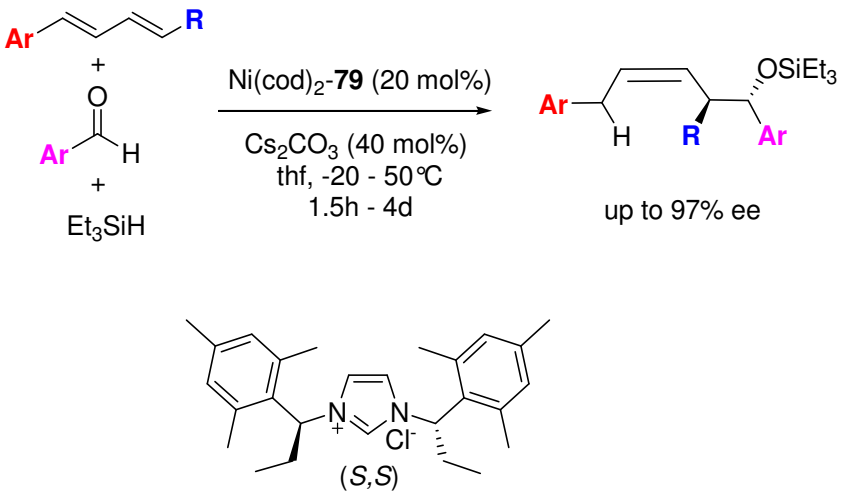
[128](a) R. Sawaki, Y. Sato, M. Mori, *Org. Lett.* **2004**, *6*, 1131; (b) Sato Y., Sawaki R., Mori M., *Organometallics* **2001**, *20*, 5460; (c) Takimoto M. Hiraga Y. Sato Y. Miro M., *Tetrahedron Lett.* **1998**, 4543.

authors postulate that the reverse stereoselectivity that is observed for phosphine and NHC ligands hints two different key allylnickel intermediates (Scheme 63). The (*E*)-geometry is believed to be directed by a *syn*-π-allylnickel intermediate, **77**, whereas the (Z)-isomer is generated from a π-allyloxanickel species, **78**.



Scheme 63

Finally, highly enantio- and diastereoselective asymmetric *three* component coupling these substrated has been realized using the C_2-symmetric chiral *N*-heterocyclic carbene, **79**,[129] as a ligand (Scheme 64).[130]



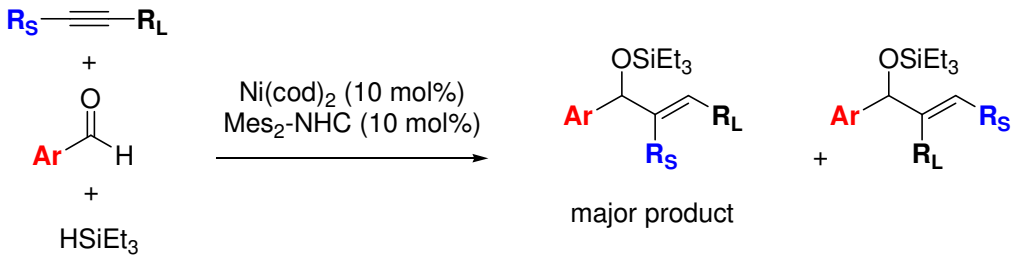
Scheme 64

[129] W. A. Herrmann, L. J. Goossen, C. Köcher, G. R. J. Artus, *Angew. Chem. Int. Ed.* **1996**, *35*, 2805.
[130] Y. Sato, Hinata Y., Seki R. , Y. Oonishi, N. Saito, *Org. Lett.* **2007**, *9*, 5596.

5.3.2. *Sp*-C-Hydrocarbons, Aldehyde and Silane

5.3.2.1. Alkyne, Aldehyde and Silane

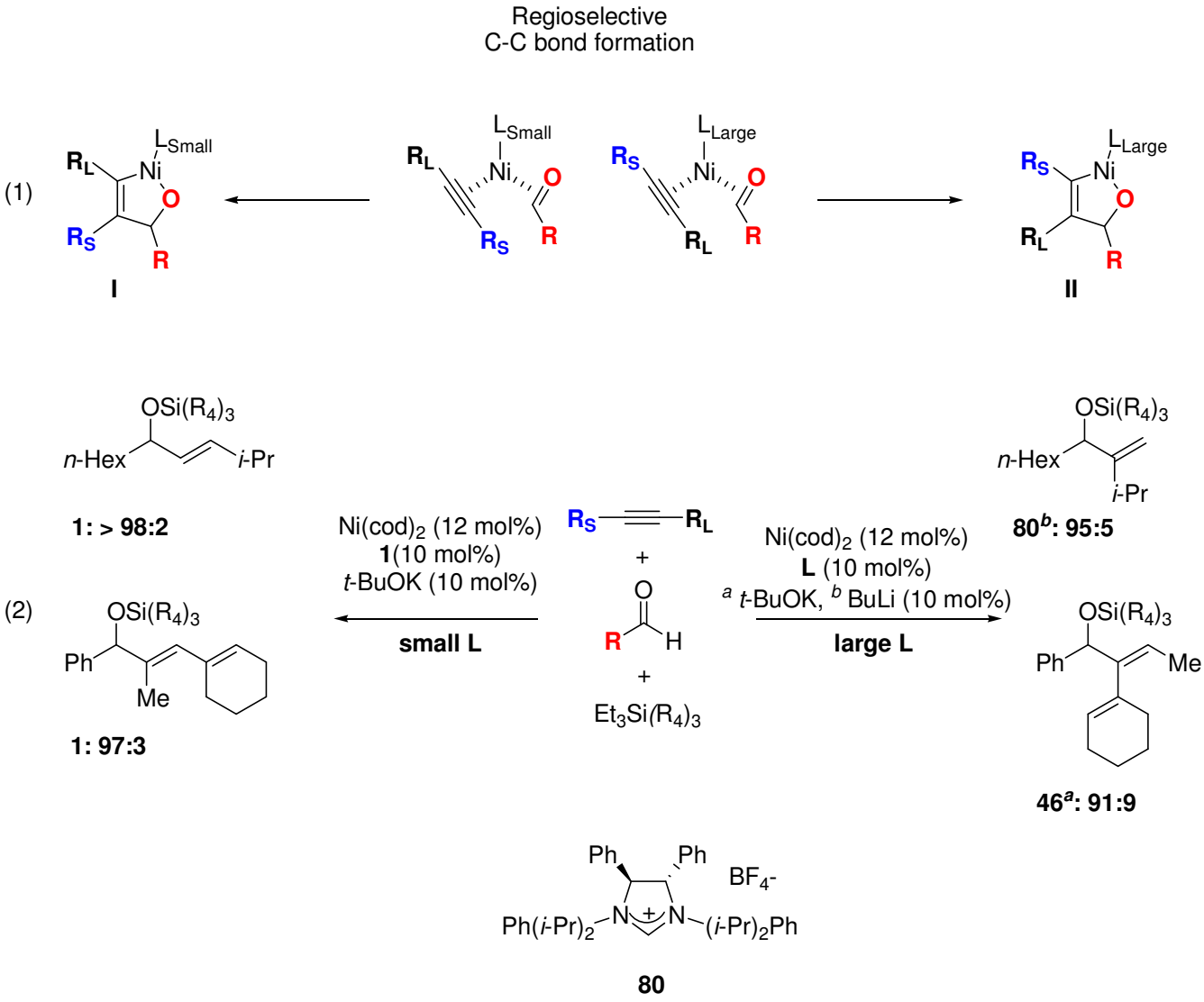
The intermolecular reductive coupling involving *sp*-hybridized alkyne derivatives, bearing one small (R_S) and one large (R_L) terminal substituent, aldehydes and silanes has been widely studied as an entry to stereodefined allylic alcohols (Scheme 63). The 1:1 combination of [Ni(cod)$_2$] and Mes$_2$-NHC provided the corresponding allylic silane derivatives with good to excellent yield and regioselectivity for the less encumbered product.[131] A deuterium labelling cross-over experiment allowed some insight into the mechanism accounting for these results.



Scheme 65

Moreover, it was suggested that the size of the NHC ligand would give high stereocontrol of the allylic silane product (Eq. 1, Scheme 66).[132] Indeed, by employing the much bulkier 1,3-di-isopropylphenyl-4,5-diphenyl-imidazolium tetraborate **80**[133] as a ligand precursor, the regioselectivity of the allylic silane was reversed with respect to that of the smaller (Mes$_2$-NHC)·HCl, **1**, (Eq. 2, Scheme 66). Computational studies hinted that phosphine ligands in association with [Ni(cod)$_2$] and borane as a reducing agent only show minimal impact on the regioselectivity of the coupling product.[134] With HSiEt$_3$ instead for this catalytic reaction, only poor reactivity of Ni(0)-P(Bu)$_3$ was detected.[131]

[131] G. M. Mahandru, G. Liu, J. Montgomery, *J. Am. Chem. Soc.* **2004**, *126*, 3698.
[132] H. A. Malik, G. J. Sormunen, J. Montgomery, *J. Am. Chem. Soc.* **2010**, *132*, 5304.
[133] T. W. Funk, J. M. Berlin, R. H. Grubbs, *Angew. Chem., Int. Ed.* **2006**, *45*, 6652.
[134] (a) P. Liu, P. McCarren, P. H. Y. Cheong, T. F. Jamison, K. N. Houk, *J. Am. Chem. Soc.* **2010**, *132*, 2050; (b) W. S. Huang, J. Chan,. T. F. Jamison, *Org. Lett.* **2000**, *2*, 4221.

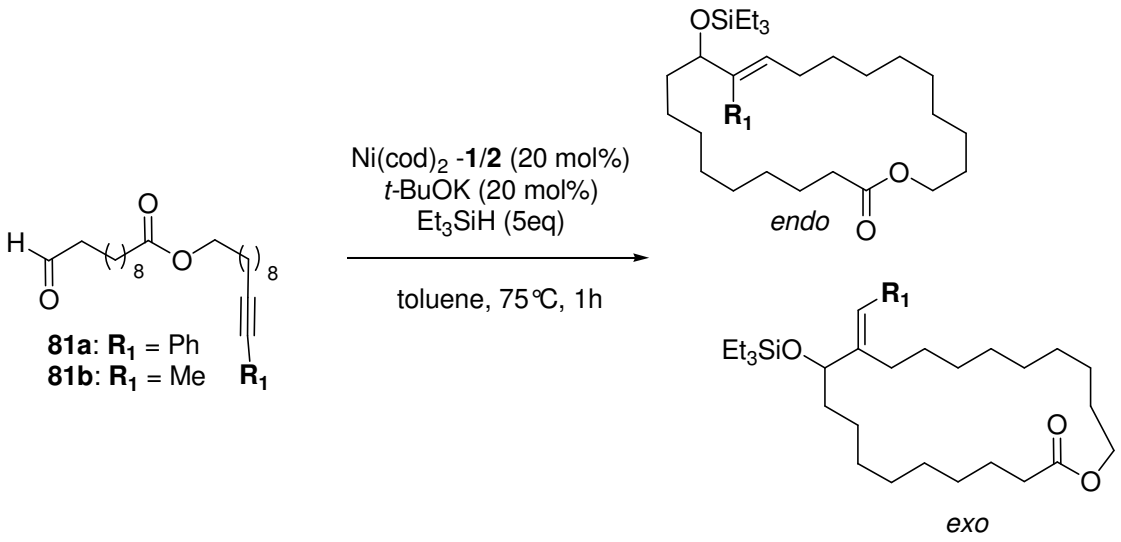


Scheme 66

Furthermore, under the optimized reaction conditions the combination of [Ni(cod)$_2$] and **1** or {(*i*-Pr$_2$Ph)$_2$-NHC}·HCl, **2a**, as a ligand precursor promoted intramolecular reductive coupling of ynals for the synthesis of either macrocyclic *endo*- and/or *exo*cyclic allylic alcohols (Scheme 67).[135] Accordingly, the Ni(0)-(Mes$_2$-NHC) system selectively promoted the cyclization resulting in *endo*-marcocylces varying in size from 14- to 22-membered rings. Under the same reaction conditions, macrocyclization of the phenyl substituted internal alkyne **81a** provided the sole *exo*cyclic product. In contrast, cyclization of the methyl-substituted substrate **81b** resulted in a (1:1) mixture of products. Similar to the intermolecular reductive coupling,[131] this intramolecular version appeared to be highly sensitive to the ligand size as switching to the bulkier (*i*-Pr$_2$Ph)$_2$-NHC carbene provided

[135] B. Knapp-Reed, G. M. Mahandru, J. Montgomery, *J. Am. Chem. Soc.* **2005**, *127*, 13156.

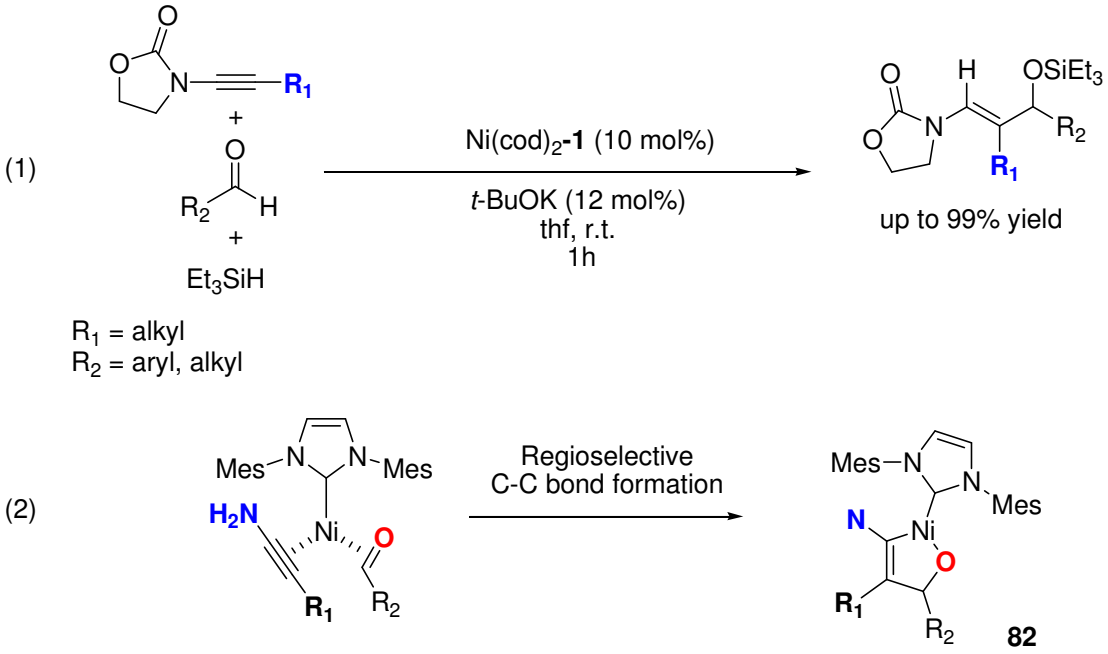
the *exo*cyclic olefin as the major product. It noteworthy, that this is the first example of Ni-catalyzed macrocyclization of ynal containing terminal alkynes and the first example of ligand-controlled reversal in regioselection with internal alkynes.



Scheme 67

Finally, by employing (1:1) mixtures of [Ni(cod)$_2$], **1** and *n*-BuLi, also reductive coupling of ynamide, aldehyde and silane was achieved in a highly selective manner (Eq. 1, Scheme 68).[136] Good yields of the desired compounds were isolated with electron poor aryl aldehydes. Generally lower conversions were obtained with alkyl substituted aldehydes. The stereoselective synthesis of γ-silyloxyenamide derivatives was reported to proceed in up to quantitative yield. Suppression of undesired side reactions like hydrosilylation and polymerization of the ynamide was achieved by slow addition (7 h) of a thf solution of the ynamide into the catalytic medium. The coupling was believed to occur by σ-bond metathesis of a regioselective obtained oxanickelacycle intermediate, **82**, with Et_3SiH to afford a nickel hydride and finally the γ-silyloxyenamide derivative after a final reductive elimination step (Eq. 2, Scheme 68).

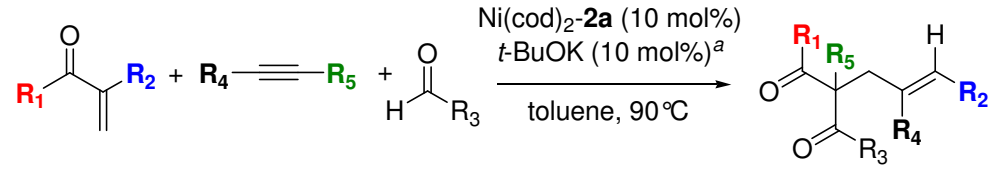
[136] N. Saito, T. Katamaya, Y. Sato *Organic Lett.* **2008**, *10*, 3829.



Scheme 68

5.3.2.2. Alkyne, Enone and Aldehyde

The highly chemoselective reductive coupling of alkyne, enone and aldehyde derivatives without the addition of a reducing agent such as borane or silane was obtained with (1:n:1) mixtures of [Ni(cod)$_2$], (*i*-Pr$_2$Ph)$_2$-NHC (n = 1) or PCy$_3$ (n = 2) and KO*t*-Bu (Scheme 69).[137] Similar to the π-component coupling of dienes, aldehydes and silanes,[128] reverse selectivity was observed between the sterically congested (*i*-Pr$_2$Ph)$_2$-NHC and the comparatively small PCy$_3$ ligand.



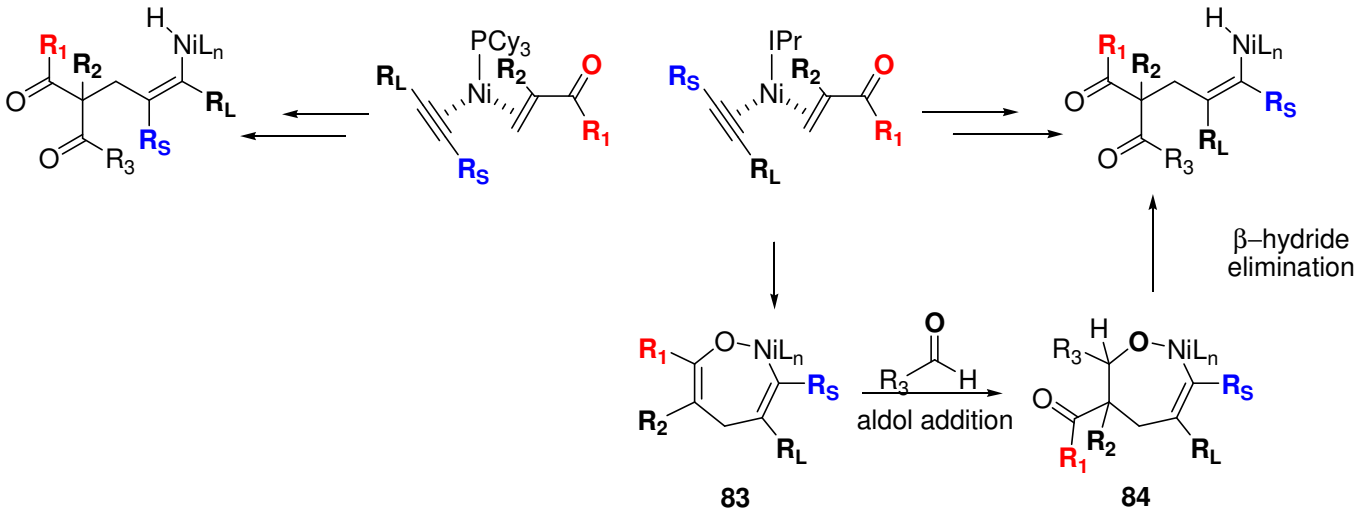
R$_1$ = Me, *n*-pent, Et
R$_2$ = H, Me
R$_3$ = Ph, Furyl, *i*-Pr, Cy
R$_4$ = H, Me, Et, Ph
R$_5$ = H, Me, Et, Ph

[a] PCy$_3$ variant: PCy$_3$ (20 mol%), Ni(cod)$_2$ (10 mol%)

Scheme 69

[137] A. Herath, W. Li, J. Montgomery, *J. Am. Chem. Soc.* **2008**, *130*, 468.

Some insight into the mechanism accounting for the formation of the 1,3-diketone derivative was obtained by deuterium labelling analysis. The unusual high degree of chemoselectivity for this reaction involving three π-components is believed to stem from a key cyclic nickel enolate intermediate, **83** (Scheme 70). Aldol addition of **84** to the aldehyde, subsequent *β*-hydride elimination and reductive elimination finally forms the corresponding 1,3-diketone product. Functional group substitution was tolerated at the α-position to the ketone contrary to *β*-substitution. It noteworthy, that catalytic reactions had to be carried out in aprotic solvents to avoid undesirable enolate protonation leading to the γ,δ-unsaturated ester derivatives.[138]

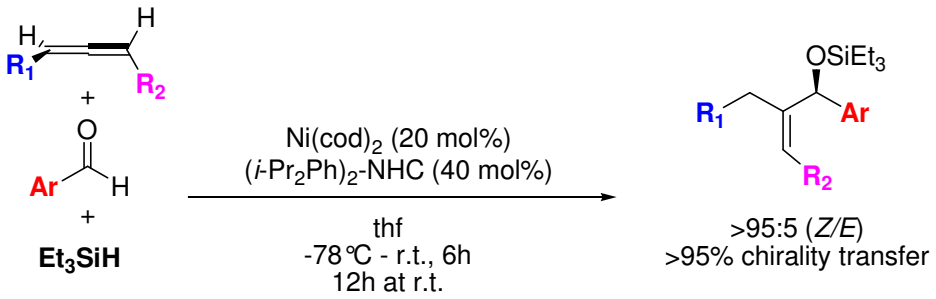


Scheme 70

5.3.2.3. Allene, Aldehyde, Silane[139]

A rare example of intermolecular addition of electrophiles to a central *sp*-hybridized and least nucleophilic carbon of an unactivated allene was reported to be catalyzed by (1:2) mixtures of $Ni(cod)_2$ and {(*i*-$Pr_2Ph)_2$-NHC}(Scheme 71).[140] Moreover, the Ni(0)-NHC catalyst performed the reaction regioselectively on the more hindered C=C bond and the transfer of the axial *trans* chirality of the allene to the allylic alcohol derivative was achieved with high fidelity. By employing (1:1) mixtures of $Ni(cod)_2$ and PCy_3 a significant decrease of the enantiomeric purity was detected.

[138] A. Herath, B. B. Thompson, J. Montgomery, *J. Am. Chem. Soc*. **2007**, *129*, 8712.
[139] For a review about transition-metal catalyzed *three* component coupling of allenes, see: M. Jeganmohan, C.-H. Cheng, *Chem. Commun.* **2008**, 3101.
[140] S.-G. Ng, T. F. Jamison *J. Am. Chem. Soc.* **2005**, *127*, 7320.

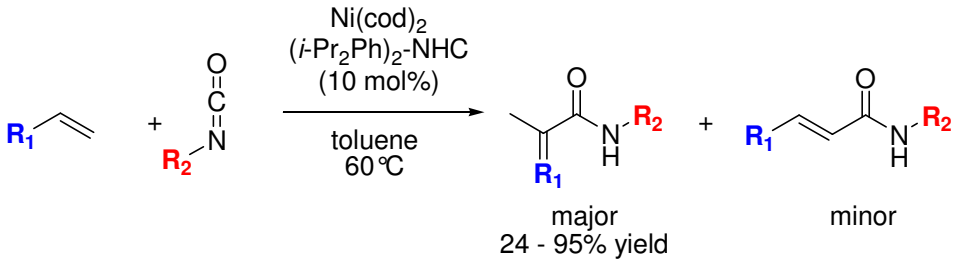


R_1 = R_2 = *n*-Pr
R_1 = Me, R_2 = Cy, *t*-Bu

Scheme 71

5.3.2.4. Isocyanates and α-Olefins

The (1:1) combination of [Ni(cod)$_2$] and (*i*-Pr$_2$Ph)$_2$-NHC further selectively catalyzed two π-component couplings of a vast number α-olefins and isocyanates, yielding *N*-alkylated acrylamides (Scheme 72).[141] The C–C bond formation occurred exclusively at the 2-position of the alkene and formed the desired *cis*-distributed α,β-unsaturated amides in high degree of selectivity. A final acid treatment converted the *N*-alkylated acrylamides to free amides.

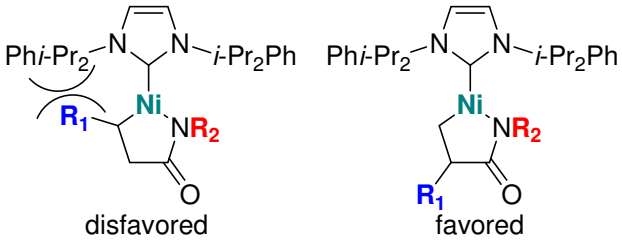


R_1 = *n*-hex, Cy, Bz..
R_2 = Cy, *t*-Bu

Scheme 72

Reverse selectivity, which was further attributed to a preference for the substituent on the α-olefin to be oriented away from the bulky NHC ligand (Scheme 73), was noted using the electronically analogous trialkylphosphine additives. Good conversion and high selectivity was observed for aliphatic olefins with branching at the allylic or homoallylic position whereas the reaction scope for the isocyanate appeared to be limited to bulky electron-rich derivatives.

[141] K. D. Schleicher, T. F. Jamison, *Org. Lett.* **2007,** *9*, 875.



R$_1$ = *n*-hex, Cy, Bz..
R$_2$ = Cy, *t*-Bu

Scheme 73

6. Polymerization

The use of Ni-NHC systems as polymerization catalysts has first been tested in the dimerization of 1-butene.[142] However, the [Ni(NHC)$_2$I$_2$] complex was found to be far more reactive than the [Ni(PCy$_3$)$_2$Cl$_2$] analogue[143] at room temperature, although the selectivity in terms of branched dimmers was disappointingly low. Furthermore, the Ni-NHC system suffered from catalyst deactivation by 1,2-alkyl migration for monodentate NHC systems.[60]

Furthermore, a small number of well-defined Ni(II)-NHC complexes has been tested for catalytic activity in the polymerization of styrene and norbornene.

Half-sandwich nickel complexes bearing mono- or bidentate NHC ligands were reported to be efficient catalyst precursors for styrene polymerization. The complexes [Ni(Mes$_2$-NHC)ClCp], **60** (Scheme 45) showed good activity for styrene polymerization in the presence of MAO via a cationic mechanism.[144] In contrast, lower activity was reported for the corresponding half-sandwich nickel(II) complex **61** (Scheme 45) bearing the bulkier (*i*-Pr$_2$Ph)$_2$-NHC ligand.[145] Similar to these half-sandwich species, a mixture of NaBPh$_4$ as a activation agent, styrene and the related indenyl-nickel(II) complexes **85** or **86** (Scheme 75) in a 300:7:1 molar ratio formed polystyrene in good yield.[146]

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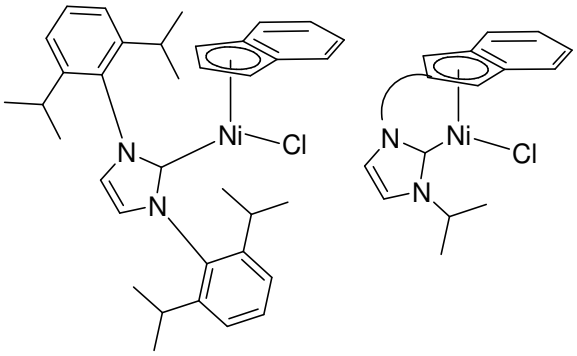
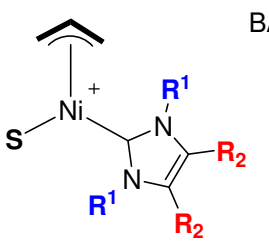
[142] D. S. MacGuiness, W. Mueller, P. Wasserscheid, K. J. Cavell, *Organometallics* **2002**, *21*, 175.
[143] A. L. MacKinnon, M. C. Baird, *J. Organomet. Chem.* **2003**, *683*, 114.
[144] W. Buchowicz, A. Kozioł, L. B. Jerzykiewicz, T. Lis, S. Pasynkiewicz, A. Pęcherzewska, A. Pietrzykowski, *J. Mol. Catal. A: Chem.* **2006**, *257*, 118.
[145] T. A. Huber, *Organometallics* **1997**, *16*, 5811.
[146] (a) L.-Z. Xie, H.-M. Sun, D.-M. Hu, Z.-H. Liu, Q. Shen, Y. Zhang, *Polyhedron* **2009**, *28*, 2585; (b) H.-M. Sun, D.-M. Hu, Y.-S. Wang, Q. Shen, Y. Zhang, *J. Organomet. Chem.* **2007**, *692*, 903.



85 **86**

Scheme 74

Cámpora and co-workers have studied the catalytic activity of cationic π-allylic nickel(II) complexes, **87a**–**c**, stabilized by a single monodentate NHC ligand as well as a labile aquo or acetonitrile ligand (Scheme 75).[147] The aquo-complexes **87a** showed moderate activity for polymerization, affording poly(*cis*-1,4-butadiene) and atactic polystyrene in small yields without any addition of co-catalyst. Polymerization was thought to be promoted by a "naked" allyl-nickel complex. Although the complexes **87a** and **87b** allowed to the general increase of the product molecular weight, these species showed notably lower catalytic activity.



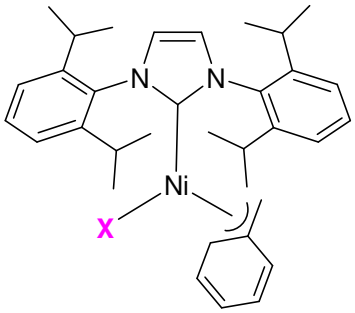
87a: S = H_2O, R^1 = *i*-Pr_2Ph R_2 = H
87b: S = MeCN, R^1 = 2,6-(*i*-Pr)C_6H_4, R_2 = H
87c: S = MeCN, R^1 = R_2 = Me

Ar^F = 3,5-$C_6H_3(CF_3)_2$

Scheme 75

The closely related η^3-benzylnickel complexes **88** have been tested as catalysts for the polymerization of norbornene (Scheme 76).[148] Good activity for polymerization has been observed with complexes **88** without any addition of MAO. So far, this is the only *neutral* Ni-NHC catalyst ever reported that did not require the addition of an external activator.

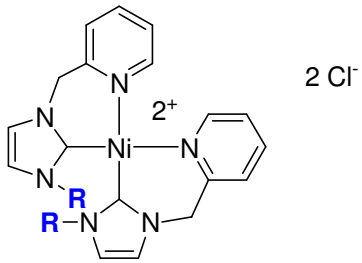
[147] J. Cámpora, L. Ortiz de la Tabla, P. Palma, E. Álvarez, F. Lahoz, K. Mereiter, *Organometallics* **2006**, *25*, 3314.
[148] S. Sujith, E. K. Noh, B. Y. Lee, J. W. Han, *J. Organomet. Chem.* **2008**, *693*, 2171.



X = **88a** CF_3CO_2,
88b CF_3SO_3

Scheme 76

Several polydentate [*N,C*]-type as well as *[O,C]*-type ligand precursors have been designed as the authors believed that chelating NHCs would enhance the stability of the catalytically active species. The resulting neutral or cationic nickel(II) complexes have shown moderate activity for the polymerization of ethylene, styrene, norbornene and propylene. Furthermore, the cationic nickel complexes **89**, carrying two picolyl-functionalized NHCs the appeared to be catalyze the polymerization of ethylene and norbornene in the presence of MAO (Scheme 77).[149] At 80 °C, the resulting polynorbornene presented a high molecular weight, although with a moderate molecular weigh distribution indicating that polymerization occurred exclusively via a vinyl addition pathway. However, the catalytic activity of **89** remained lower than that observed with complex **88**.[148]

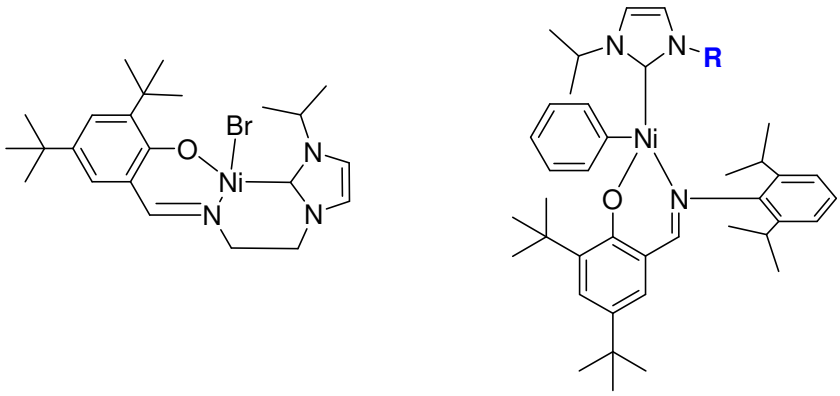


R = **89a** Me (80%)
89b Bn (62%)

Scheme 77

[149] X. Wang, S. Liu, G. X. Jin, *Organometallics* **2004**, *23*, 6002.

Based on the encouraging results obtained with the previously described chelating Ni-complex, several anionic salicylaldimidine-functionalized imidazolium salts were designed and the related neutral square planar nickel(II) complexes **90**-**91** tested for catalytic activity in the polymerization of styrene and ethylene (Scheme 78)[150]. Complex **90** appeared to show the best activity compared to other Ni-NHC catalyst for styrene polymerization. Under optimized reaction conditions, polystyrene could be quantitatively formed with a number average molecular weight of 17 600 after 12 h of reaction at 80 °C in toluene in the presence of $NaBPh_4$ as an activator. In contrast, **91b** showed only modest ethylene dimerization activity. Very fast β-elimination of the dimer-intermediate was believed to inhibit any further insertion to afford longer chains.



90

R = **91a** Bn (80 %)
91b *i*-Pr (82 %)

Scheme 78

Inspired by the interesting activity of dialkylphosphinoenolate Ni(II) complexes for ethylene polymerization,[151] an enolate-moiety based bidentate anionic NHC ligand has been synthesized.[152] The resulting [*C,O*] type nickel(II) complexes **92** appeared to catalyze both ethylene and propylene polymerization without the addition of any co-catalyst in toluene solutions at 40 – 60 °C (Scheme 79). Linear atactic polymer chains carrying α-olefin end groups were isolated in good yield. Polymerization was believed to proceed via a coordination-insertion mechanism. Although the lifetime of the active species were revealed to be very short, their activities were comparable to those of SHOP-type (*S*hell *H*igher *O*lefin *P*rocess) catalysts.

[150] (a) W. F. Li, *J. Organomet. Chem.* **2008**, *693*, 2047; (b) W. Li, H. Sun, M. Chen, Z. Wang, D. Hu, Q. Shen, Y. Zhang, *Organometallics* **2005**, *24*, 5925.
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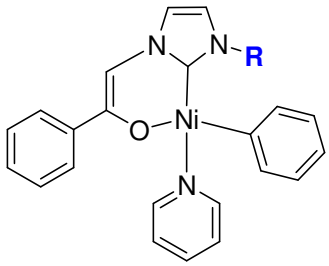
[152] B.E. Ketz, X. G. Ottenwaelder, R. M. Waymouth, *Chem. Commun.* **2005**, 5693.



R = **92a** *i*-Pr_2Ph
92b Mes

Scheme 79

The Ni(II)-NHC complexes **35a**, **36**, **61** and **85-91** have shown moderate to good activity for the polymerization of ethylene, propylene, styrene or norbornene. As a general trend, these species reacted via a cationic polymerization mechanism and were dependent on MAO or $NaBPh_3$ as additive. Nevertheless, the Ni(II)-NHC complexes **92** bearing an amido-functionalized bidentate NHC ligand catalyzed the polymerization of ethylene and propylene via a coordination-insertion mechanism without any additive.

7. Conclusion

Ni-NHC complexes prove to be efficient catalysts in a wide range of important organic transformations. Notably cross-coupling reactions, π-component couplings and polymerization have been receiving much attention in the last decade. Generally, either *in situ* procedures starting form of Ni(0)$(cod)_2$ or Ni(II)$(acac)_2$ and the appropriate NHC ligand, or well defined air stable Ni(II) complexes bearing amido, phosphine or pyridine functionalized NHCs as ligands have been tested.

The most efficient Ni-NHC catalyzed cross-coupling was undoubtedly the Kumada-Corriu reaction. Generally, catalysts prepared from *in situ* processes showed better activity compared to the range of well defined mono- or polydentate Ni(II)-NHC catalyst precursors. The Ni-NHC catalysts have demonstrated great functional group tolerance and a vast number of biphenyl compounds could be synthesized at room temperature and in good yields from electronically activated and deactivated aryl chlorides. Also more “exotic” partners such as aryl sulfonates, aryltitanium(IV)

alkoxides, cyclohexene compounds and notably unreactive aryl fluorides were coupled with Grignard reagents in good yields. The best results were observed by employing a benzimidazolato-functionalized NHC-Ni catalyst (Scheme 13); Coupling of chloroanisole and almost unreactive fluoroanisole with phenylmagnesium chloride were completed after only 30 and 150 minutes respectively at room temperature (1 mol% of catalyst).

When compared to Pd(NHC) catalysts, the nickel based counterparts have shown only moderate activity for the Suzuki-Miyaura cross-coupling of aryl halides. Mainly well defined bi- and tridentate Ni(II) species were tested as catalysts generated from *in situ* procedures have only showed moderate catalytic activity for this reaction. A major part of these pre-catalysts required the use of a tertiary phosphine (generally PPh_3) as co-ligand to ensure good conversions for aryl bromides, chlorides and notably for the electron rich version of these substrates. For catalysts bearing a phosphane-sidearm, the need of additional PPh_3 was limited to the most challenging aryl chlorides. Compared to Pd-NHC catalysts, generally, relatively high reaction temperatures (80–120 °C) were required. All these systems were particularly sensitive to hindrance, and only mono-ortho-substituted biphenyl products could be prepared. Good results were observed employing aryl tosilates, mesitylates or ammonium salts as coupling partners.

Far less interest focussed the study of Heck-Mizoko, Negishi or heterobond-forming cross-coupling reactions. Generally, relatively high catalyst loadings (2-10 mol%) and high reaction temperatures (70-110 °C) were required; for the Heck-Mizoko reaction respectable results could only be obtained with aryl iodides at 150 °C. In contrast, Ni(II)-NHC complexes have demonstrated excellent activity towards catalytic arylations of ketones, alkylations and annulations of imidazoles as well as towards Michael additions under mild conditions. Notably the Michael Addition reactions could be carried out in air, at room temperature and without the addition of a base.

Furthermore, extensive effort has focussed the scope and breadth of Ni(0)-NHC catalysed π-component coupling reactions. The combination of $[Ni(cod)_2]$ and the appropriate NHC demonstrated to catalyze in a highly selective manner [2+2+2] cycloadditions of a variety of π-components with CO_2, carbonyl or nitrile compounds, the rearrangement of cyclopropylenes, cyclopropyl-ynes, vinyl azirides and aziridinyl-ynes as well as *three* component reductive couplings of unsaturated hydrocarbons, aldehydes and metal hydrides. In some cases, the highly air sensitive $Ni(cod)_2$ could be replaced by air stable $Ni(acac)_2$ in the presence of a external reducing agent, though generally higher catalyst loadings were required. [Ni(0)-NHC]-based systems did not only effectively catalyze the coupling of π-components, aldehydes and silanes, but did also demonstrate strongly ligand-controlled reversal regioselectivity for a vast number of unsaturated hydrocarbon

substrates. The Ni-NHC catalyzed coupling of 1,3-diene and aldehyde also provides the corresponding homoallylic silyl ether compound with reversed *E*/*Z* selectivity when compared to the phosphine-based systems.

Some Ni(II)-NHC complexes have shown moderate to good activity in polymerization reactions of ethylene, propylene, styrene and norbornene in the presence of MAO or $NaBPh_3$ as activators.

Finally, Ni-NHC systems have shown outstanding activity in the activation of C–F bonds, a particularly challenging process due to their chemical inerty. Notably the Kumada-Corriu reaction of aryl fluorides and Grignards was achieved at room temperature and in good yields. A small number of recent discoveries testify that Ni-NHC systems are capable of activating small molecules such as CO_2,[153,154] oxygen,[155] or ammonia borane,[156] that is considered as a chemical hydrogen storage agent. All show the high potential of Ni-NHCs as an alternative to palladium, iridium and ruthenium in homogeneous catalysis.

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[156] (a) X. Yang, M. B. Hall, *J. Am. Chem. Soc.* **2008**, *130*, 1798; (b) R. J. Keaton, J. M. Blacquiere, R. T. Baker, *J. Am. Chem. Soc.* **2006**, *129*, 1844.

Chapter 2

Synthesis and Catalytic Activity of Half-Sandwich Nickel(II) Complexes Bearing Asymmetrically *N*,*N*'-Substituted *N*-Heterocyclic Carbenes

1. Introduction

Since the first isolation of stable imidazol-2-ylidene[1], *N*-heterocyclic carbenes (NHCs) have become a very important class of ligands in organometallic chemistry and in transition metal-catalyzed reactions.[2] As seen in the previous chapter, NHCs behave like typical strong σ-donor ligands[3] with non-negligible π-acceptor abilities,[4] this last characteristic being particularly true for nickel species.[5] These electronic characteristics are similar to those of tertiary phosphines and they show similar abilities in stabilizing the various oxidation states and coordinatively unsaturated intermediates that appear in transition metal-catalyzed reactions.[1,6] However, NHCs show superior performance over traditional trialkyl- or triaryl phosphine ligands in many aspects, including structure versatility, facile preparation, thermal, air and moisture stability of the carbene precursor, as well as non-toxicity. In addition, NHCs exhibit better resistance to ligand dissociation[7] and degradative cleavage[8] both of which are less likely as compared to tertiary phosphines.[9] Both properties lead to a higher complex stability of TM-NHCs complexes. Moreover, carbene complexes have shown unprecedented catalytic activity under homogeneous conditions in many important organic reactions.[2]

In the Chapter 1, we have described the potential of Ni-NHC complexes as active catalysts for a variety of important organic transformations. In most systems, an active zero valent nickel species was generated *in situ* from a Ni(0) compound such as $Ni(cod)_2$ and a NHC ligand or from a Ni(II) species, a NHC ligand and an excess of reductant. The major disadvantages of these systems are the

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[1] A. J. Arduengo III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361.
[2] Recent reviews in NHC ligands and their applications in catalysis include: (a) Special issues 5-6 of *Coord. Chem. Rev.* **2007**, *246*, 595; (b) O. Kuhl, *Chem. Soc. Rev.* **2007**, *36*, 592; (c) V. César, S. Bellemin-Laponnaz, L. Gade, *Chem. Soc. Rev.* **2004**, *33*, 619; (d) W. A. Herrmann, *Angew. Chem. Int. Ed.* **2002**, *41*, 1290; (e) D. Bourissou, O. Guerret, F. P. Gabbat, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39.
[3] (a) R. Dorta, E. D. Stevens, N. M. Scott, C. Costabile, L. Cavallo, C. D. Hoff, S. P. Nolan, *J. Am. Chem. Soc.* **2005**, *127*, 2485; (b) A. R. Chianese, X. Li, M. C. Janzen, J. W. Faller, R. H. Crabtree, *Organometallics* **2003**, *22*, 1663.
[4] (a) E. F. Penka, C. W. Schläpfer, M. Anatasov, M. Albrecht, C. Daul, *J. Organomet. Chem.* **2007**, *692*, 5709; (b) D. M. Khramov, V. M. Lynch, C. W. Bielawski, *Organometallics* **2007**, *26*, 6042; (c) S. Fantasia, J. L. Petersen, H. Jacobsen, S. P. Nolan, *Organometallics* **2007**, *26*, 5880.
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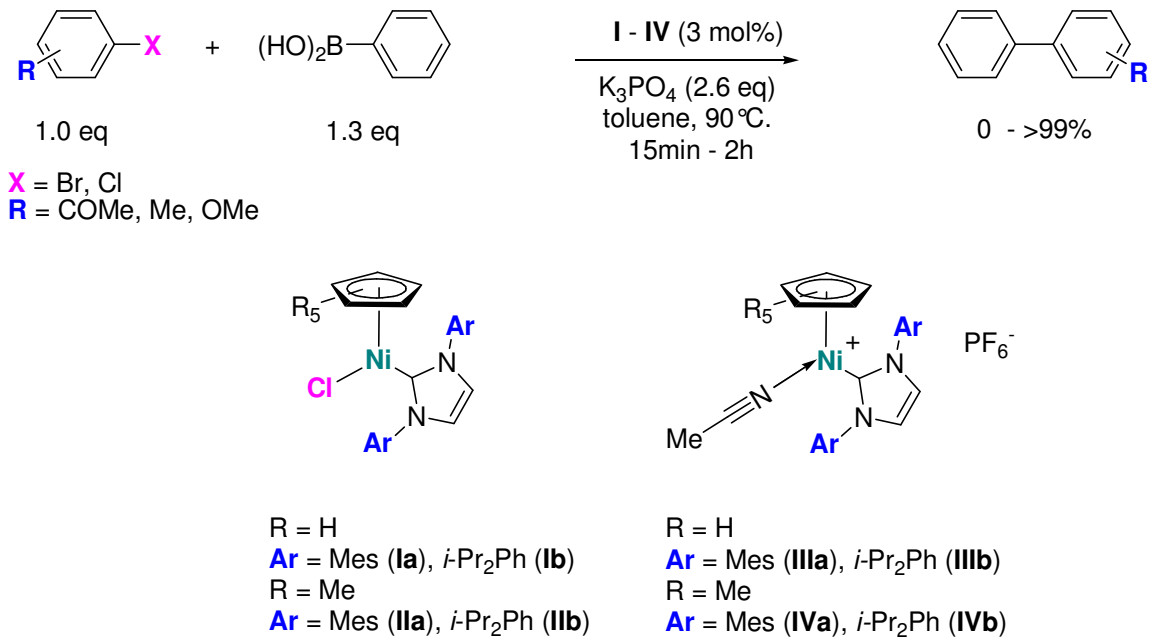
[8] (a) S. H. Hong, A. Chlenov, M. W. Day, R. H. Grubbs, *Angew. Chem. Int. Ed.* **2007**, *46*, 4648; (b) B. R. Galan, M. Gembicky, P. M. Dominiak, J. B. Keister, S. T. Diver, *J. Am. Chem. Soc.* **2005**, *127*, 15702; (c) J. A. Cabeza, I. del Río, D. Miguel, M. G. Sánchez-Vega, *Chem. Commun.* **2005**, 3956; (d) S. Caddick, F. G. N. Cloke, P. B. Hitchcock, A. K. Lewis, *Angew. Chem. Int. Ed.* **2004**, *43*, 5824; (e) R. F. Jazzar, S. A. Macgregor, M. F. Mahon, S. P. Richards, M. K. Whittlesey, *J. Am. Chem. Soc.* **2002**, *124*, 4944.
[9] Phosphines are often subject to P-C bond cleavage *(a)* or orthometalation *(b)*: (a) J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, 2nd Ed.; University Science: Mill Valley, CA, 1987; (b) P. E. Garrou, *Chem. Rev.* **1985**, *85*, 171.

air sensitivity of the Ni(0) species and/or the necessity of an excess of reductant, which generates supplementary inorganic waste products. To overcome this inconvenience, much effort has been devoted to design well-defined, air-stable electron-rich Ni(II)-NHC complexes, which are able to catalyze organic reactions without an external reductant. Such species catalyze a small number of reactions, where no organometallic partner is involved (see Chapter 1, Section 2.3., Section 3., Section 4.2., Section 5. and Section 6.), as well as cross-coupling reactions, in which the organometallic reagent is known to help reduce the Ni(II) to Ni(0) (see Chapter 1, Section 2.1.1 to Section 2.1.3, and Section 2.2.).[10,11] Nevertheless, despite the much lower cost and easier removal of nickel from the product with respect to palladium[12] and the unique properties of NHC ligands in comparison to phosphines, examples of Ni(II)-NHC-based catalysts for cross-coupling reactions remain scarce.

In this context, our group has recently reported the efficient Suzuki-Miyaura coupling of aryl bromides and chlorides by neutral [Ni(Ar_2-NHC)ClCp†] [Cp† = η^5-C_5H_5 (Cp), η^5-$C_{10}H_{15}$ (Cp*)] **I**,[13,14] and **II**[15] and cationic [Ni(Ar_2-NHC)(CH_3CN)Cp†]$^+$(PF_6)$^-$ (Cp† = Cp, **III**, Cp*, **IV**) complexes (Scheme 80).[16] The half-sandwich Ni(II)-NHC complexes **II** and **IV**, bearing the bulky and electron-rich Cp* ring, were shown to display one of the highest rates for Ni(II)-based catalysts in the absence of co-catalyst or reductant. The coupling of 4'-bromoacetophenone and phenylboronic acid with K_3PO_4 as the sole additive was indeed almost quantitative after only 10-15 minutes at 90 °C with 3 mol% of the sterically encumbered species **IIb** and its cationic counterpart **IVb**.

[10] For palladium(II) catalysts, see: M. Moreno-Mañanaz, M. Pérez, R. Pleixats, *J. Org. Chem.* **1996**, *61*, 2346.
[11] For nickel(II) catalysts, see: (a) C. Chen, L.-M. Yang, *Tetrahedron Lett.* **2007**, *48*, 2427; (b) V. Percec, G. M. Golding, J. Smidkral, O. Weichold, *J. Org. Chem.* **2004**, *69*, 3447; (c) D. Zim, V. R. Lando, J. Dupont, A. L. Monteiro, *Org. Lett.* **2001**, *3*, 3049; (d) K. Inada, N. Miyaura, *Tetrahedron* **2000**, *56*, 8657; (e) A. F. Indolese, *Tetrahedron Lett.* **1997**, *38*, 3515.
[12] C. E. Tucker, J. G. de Vries, *Top. Catal.* **2002**, *19*, 111.
[13] C. D. Abernethy, A. H. Cowley, R. A. Jones, *J. Organomet. Chem.* **2000**, *596*, 3.
[14] R. A. Kelly III, N. M. Scott, S. Díez-González, E. D. Stevens, S. P. Nolan, *Organometallics* **2005**, *24*, 3442.
[15] (a) V. Ritleng, C. Barth, E. Brenner, S. Milosevic, M. J. Chetcuti, *Organometallics* **2008**, *27*, 4223; (b) V. Ritleng, E. Brenner, M. J. Chetcuti, *J. Chem. Educ.* **2008**, *85*, 1646.
[16] V. Ritleng, A. M. Oertel, M. J. Chetcuti, *Dalton Trans.* **2010**, *39*, 8153.



Scheme 80

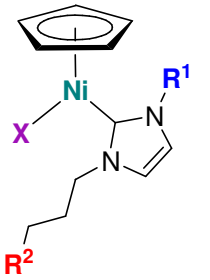
On the other hand the relative dearth of effective, non-polluting, truly recyclable and inexpensive catalysts for the syntheses of fine organic chemicals on large scales[12,17] generates an increasing demand for supported versions of homogeneous catalysts.[18] Indeed, despite high activity and selectivity, homogeneous catalysis has shown some disadvantage in industry.[19] This disadvantage is mainly due to the difficulty of separating the soluble catalyst from the reaction product, which in turn may lead to economical and environmental problems especially in the case of expensive and toxic metal catalysts. Among the possible practical strategies for separating and recycling active catalysts,[20] the immobilization of homogeneous catalysts on solid supports appears particularly attractive because it should combine the advantages of heterogeneous catalysis (i.e. high throughput techniques, continuous flow reactors, easy product isolation and catalyst recycling) with the versatility of homogeneous catalysis. Compared to expensive organic polymers,[21] inorganic metal oxide materials are common supports for the heterogenization of molecular catalysts due to their excellent thermal and chemical stability. They have rigid structures that are not deformed by solvent swelling during catalytic reactions, they can be used at both high and low

[17] J. G. de Vries, *Can. J. Chem.* **2001**, *79*, 1086.
[18] See special issue 10 of *Chem. Rev.* **2002**, *102*, 3215.
[19] J. Hagen, Industrial Catalysis: A practical Approach, Wiley-VHC, Weinheim, 1999.
[20] D. J. Cole-Hamilton, *Science* **2003**, *299*, 1702.
[21] (a) N. E. Leadbeater, M. Marco, *Chem. Rev.* **2002**, *102*, 3217; (b) C. A. McNamara, M. J. Dixon, M. Bradley, *Chem. Rev.* **2002**, *102*, 3275.

temperatures and at high pressures.[22] In addition, they possess high surface areas and organic groups can be robustly anchored to the surface silanol groups.

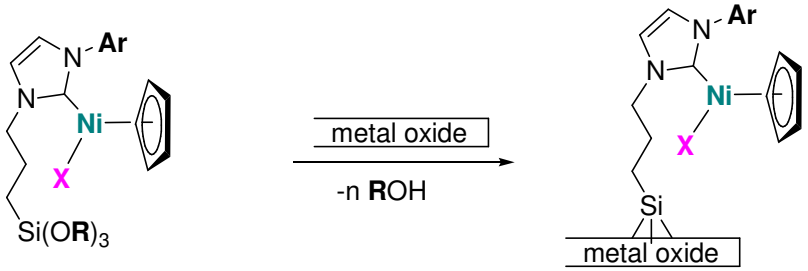
As a butyl side arm could serve as a model for a three-carbon linker between the carbene ring and a trialkoxysilane function (Eq. Scheme 81), which would give easy access to a heterogenized version of the [Ni(R^1-NHC-R^2)XCp†] complexes by simple condensation of the alkoxide moiety with the surface silanol groups that are present on common metal oxides (Eq. 2, Scheme 81), we thus thought of (i) replacing one of the NHC-aryl-substituent by a *n*-butyl group and study its influence on the catalytic activity of the resulting complexes, and (ii) if the results were satisfying of indeed heterogenizing our complexes.

(1)



R^1 = Ar, Alk
R^2 = Me, Si(OR)$_3$

(2)



Scheme 81

Thus, in this Chapter, we describe the synthesis of the *N*,*N*'-unsymmetrically disubstituted 1-aryl and 1-alkyl-3-*n*-butyl-imidazolium salts and briefly compare their electronic properties to those of their symmetrically substituted counterparts. Next, we present the synthesis of the corresponding

[22] M. Chabanas, C. Copéret, J. M. Basset, *Chem.-Eur. J.* **2003**, *9*,971; (b) J. S. Kingsbury, S. B. Garber, J. M. Giftos, B. L. Gray, M. M. Okamoto, R. A. Farrer, J. T. Fourkas, A. H. Hoveyda, *Angew. Chem. Int. Ed.* **2001**, *40*, 4251.

half-sandwich complexes [Ni(Ar-NHC-*n*-Bu)ICp†] (Ar = Ph, Mes, *i*-Pr$_2$Ph; Cp† = Cp, Cp*) and [Ni(R-NHC-*n*-Bu)ClCp] (R = Me, *i*-Pr) and discuss their structural and electronic properties. We complete this section by the catalytic study of the new complexes in the Suzuki-Miyaura cross-coupling of aryl bromides with phenylboronic acid and compare the obtained results to those reported for the related symmetrically substituted [Ni(R$_2$-NHC)XCp†] catalysts, **I**, **II**, **III** and **IV**.[16]

The extension of the variety of *N*,*N'*-unsymmetrically substituted imidazolium salts to a range of compounds, which carry trialkoxysilane substituents instead of a *n*-butyl group is then presented, followed by a brief discussion of their synthesis and compare of their electronic properties with respect to their *n*-butyl analogues. This part continues with the synthesis of the corresponding complexes [Ni(Ar-NHC-TMS)ICp†], [Ni(Ar-NHC-TES)ClCp†]) and [Ni(R-NHC-TMS)ClCp] (Ar = Ph, Mes, *i*-Pr$_2$Ph; R = Me, *i*-Pr; TMS = trimethoxysilylpropyl; TES = triethoxysilylpropyl). Finally, we present the immobilization of one TES-functionalized Ni-NHC compound onto alumina and compare the catalytic activity of the heterogenized catalyst for the Suzuki-Miyaura cross-coupling of 4'-bromoacetophenone and phenylboronic acid to that of the its *n*-butyl homogeneous analogue.

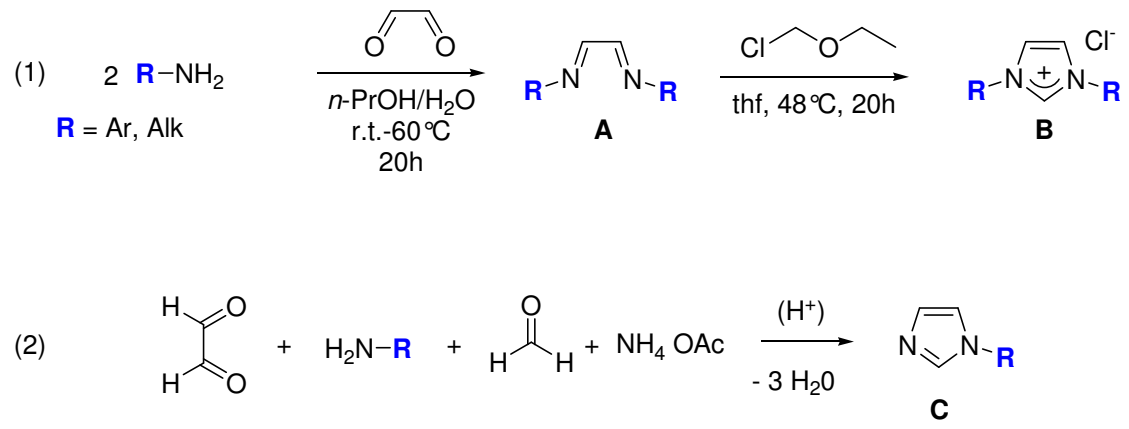
2. Results and discussion

2.1. Synthesis and characterization of the *n*-butyl substituted imidazolium salts

Currently, imidazol-*2*-ylidenes and imidazolin-*2*-ylidenes represent the dominant architecture of stable diaminocarbenes.[2] Generally, they are prepared by Arduengo's method from a *N,N'*-symmetrically disubstituted or *N,N'*-unsymmetrically disubstituted imidazolium salt and a strong base.[23,24]

The *N,N'*-symmetrically disubstituted imidazolium salts **B** are generally formed from a diimine precursor **A**, which is prepared by the acid catalyzed condensation of glyoxal with two equivalents of an amine (Eq. 1, Scheme 82).[25] The final ring closing step was traditionally achieved by employing formaldehyde,[1,26] but a major improvement was realized by using chloromethylethylether instead (Eq. 1, Scheme 82).[27] The thus obtained crude reaction products are indeed sufficiently pure to be used in subsequent reactions without the need of further recrystallization or purification.

Similarly, a wide range of *five*-membered *N*-monosubstituted imidazoles **C** can be easily prepared from the cyclocondensation involving glyoxal, formaldehyde and one molar equivalent of a primary amine (Eq. 2, Scheme 82).[28]

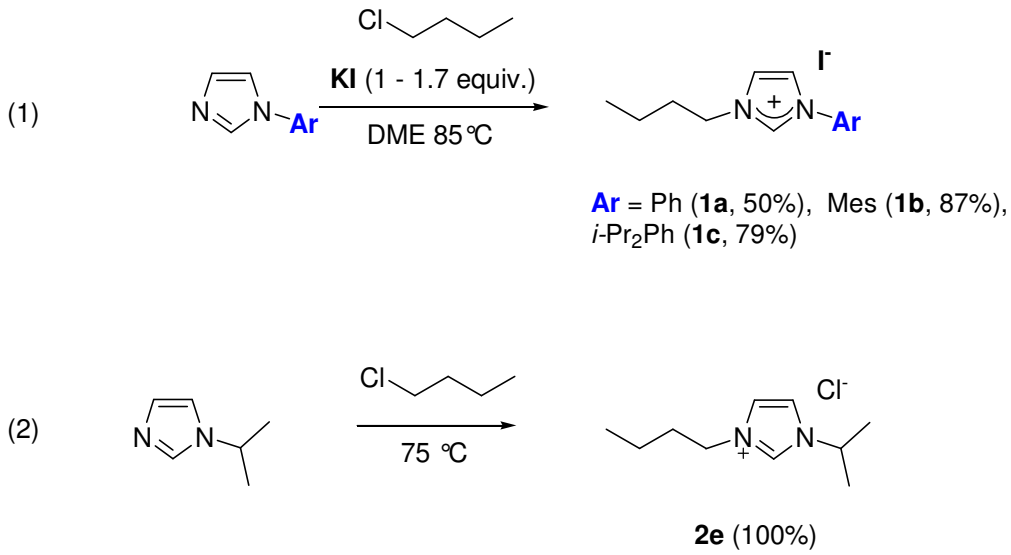


Scheme 82

[23] A. J. Arduengo III, H. V. R. Dias, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1992**, *114*, 5530.
[24] A. J. Arduengo III US Patent 5077414 A2, 1992.
[25] M. Zettlitzer, H. tom Dieck, E. T. K. Haupt, L. Stamp, *Chem. Ber.* **1986**, *119*, 1868.
[26] (a) H.-W. Wanzlick, W. Löchel, *Chem. Ber.* **1953**, *86*, 1463, (b) L. Jaenicke, E. Brode, *Liebigs Ann. Chem.* **1959**, *624*, 120.
[27] A. J. Arduengo III, R. Krafczyk, R. Schmutzler, *Tetrahedron* **1999**, *55*, 14523.
[28] J. Wallach, *Ber. Dtsch. Chem. Ges.* **1925**, *15*, 645.

The most obvious route for the synthesis of *N*-alkyl-*N'*-aryl-substituted NHC precursors seemed us to be the *N'*-alkylation of *N*-arylated imidazoles of type **C**. However, alkyl chlorides being often poorly reactive and requiring forcing reaction conditions,[29,30] the only synthetic routes that had been reported involved expensive alkyl iodides[31,32] or bromides.[33] We thus developed an easy, one pot synthesis of *N*-alkyl-*N'*-aryl substituted imidazolium salts from commercially available, cheaper alkyl chlorides.[34]

Hence, 1-*n*-butyl-3-phenyl-, 1-*n*-butyl-3-(2,4,6-trimethylphenyl)-, and 1-*n*-butyl-3-(2,6-diisopropylphenyl)imidazolium iodide **1a-c** could be prepared from 1-chlorobutane and the corresponding arylimidazoles[35,36,37] in 1,2-dimethoxyethane (DME) in the presence of an equimolar or larger quantity of potassium iodide (Eq. 1, Scheme 83). The addition of KI leads to the formation by precipitation of the sparingly soluble KCl from the reaction medium. The large *N*,*N'*-disubstituted imidazolium cations are presumably better stabilized in the solid state with a big I^- counter anion.



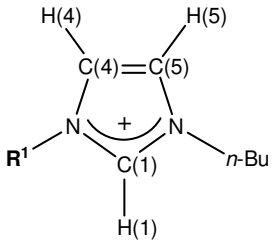
Scheme 83

29 K. Koehler, K. Weigl, WO 2005016940, **2005**.
[30] M. V. Jiménez, J. J. Pérez-Torrente, M. I. Bartolomé, V. Gierz, F. J. Lahoz, L. A. Oro, *Organometallics* **2008**, *27*, 224.
[31] C. S. J. Cazin, M. Veith, P. Braunstein, R. B. Bedford, *Synthesis* **2005**, 622.
[32] V. Polshettiwar, P. Hesemann, J. J. E. Moreau, *Tetrahedron Lett.* **2007**, *48*, 5363.
[33] (a) W. Buchowicz, W. Wojtczak, A. Pietrzykowski, A. Lupa, L. B. Jerzykiewicz, A. Makal, K. Woźniak, *Eur. J. Inorg. Chem.* **2010**, 648; (b) A. Fürstner, L. Ackermann, B. Gabor, R. Goddard, C. W. Lehmann, R. Mynott, F. Selzer, O. R. Thiel, *Chem.- Eur. J.* **2001**, *7*, 3236; (c) J. Wolf, A. Labande, M. Natella, J.-C. Daran, R. Poli, *J. Mol. Catal. A: Chem.* **2006**, *259*, 205.
[34] A. M. Oertel, V. Ritleng, M. Chetcuti, *Synthesis* **2009**, 1647.
[35] O. V. Starikova, G. V. Doglushin, L. I. Larina, T. N. Komarova, V. A. Lopyrev, *ARKIVOK* **2003**, *13*, 119.
[36] J. Liu, J. Chen, J. Zhao, Y. Zhao, L. Li, H. Zhang, *Synthesis* **2003**, 2661.
[37] G. Occhipinti, H.-R. Bjørsvik, K. W. Törnroos, A. Fürstner, V. R. Jensen, *Organometallics* **2007**, *26*, 4383.

The preparation of *N*,*N'*-dialkylimidazolium salt derivatives from the more reactive *N*-methyl- and *N*-isopropylimidazole does not require the addition of KI. Thus, while 1-*n*-butyl-3-methylimidazolium chloride **2d** was prepared as reported in the literature,[38] the preparation of 1-*n*-butyl-3-*i*-propylimidazolium chloride **2e** does not even require any solvent addition, as simply refluxing neat *N*-isopropylimidazole with 1 molar equivalent of 1-chlorobutane affords **2e** in quantitative yield (Eq. 2, Scheme 83).

All the imidazolium salts **1** - **2** described here are hygroscopic solids. In addition, the iodide salts **1a** - **c** appear to liberate traces of free iodine in the presence of light, which makes the salts appear cream coloured, or even pale yellow unless very pure and/or freshly prepared. Good spectroscopic data (^{1}H, ^{13}C{^{1}H} and ^{13}C DEPT NMR and HRMS) were obtained for all described salts. ^{1}H NMR chemical shifts of the imidazolium ring protons are listed in Table 1.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of the imidazolium iodide, **1**, and chloride, **2**, salts are straightforward at ambient temperature. They show the presence of the imidazole ring protons, those of the *n*-butyl group and those of the aryl or alkyl group. The *N*-bound *n*-butyl group is expected to exert a greater electron donating inductive effect compared to an *N*-bound aryl, methyl or *i*-propyl group.[39] Accordingly, the H(5) protons, which are in α of the *n*-butyl group are slightly down field shifted compared to the H(4) protons, which are in α of the aryl, methyl or *i*-propyl groups (Scheme 84 and Table 1), and except for R^1 = phenyl (**1a**), a larger chemical shift difference Δ between H(4) and H(5) is observed when R^1 = aryl (Δ_{mean} = 0.65 ppm, **1b,c**) than when R^1 = alkyl (Δ_{mean} = 0.14 ppm, **2d,b**). This is most probably due to the fact than when R^1 = aryl, the difference of electron donating inductive effect is larger than when R^1 = alkyl.[39] The observed variations of the H(1) protons chemical shifts are most probably due to salt concentration and solvent effects rather than to any substituent induced inductive electronic effect.[39,40]



Scheme 84

[38] J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willhauer, G. A. Broker, R. D. Rogers, *Green Chem.* **2001**, *3*, 156.
[39] S.-T. Lin, M.-F. Ding, C.-W. Chang, S.-.S Lue, *Tetrahedron* **2004**, *60*, 9441.
[40] K. Seidman, G. E. Maciel, *J. Am. Chem. Soc.* **1977**, *99*, 659.

Table 1 : Selected ^{1}H NMR ($CDCl_3$) data for the *n*-butyl substituted imidazolium salts **1-2**

	NC*H(1)*N	NC*H(5)*=NC*H(4)*	Δ (ppm)
1a	10.59	7.73, 7.68	0.05
1b	10.06	7.82, 7.21	0.61
1c	10.14	7.88, 7.21	0.67
2d	10.57	7.61, 7.45	0.17
2e	10.80	7.58, 7.48	0.10

The $^{13}C\{^{1}H\}$ NMR chemical shifts observed for these asymmetrically substituted imidazolium salts (see experimental section) are similar to those of previously reported imidazolium salts and do not deserve any special comment.[41]

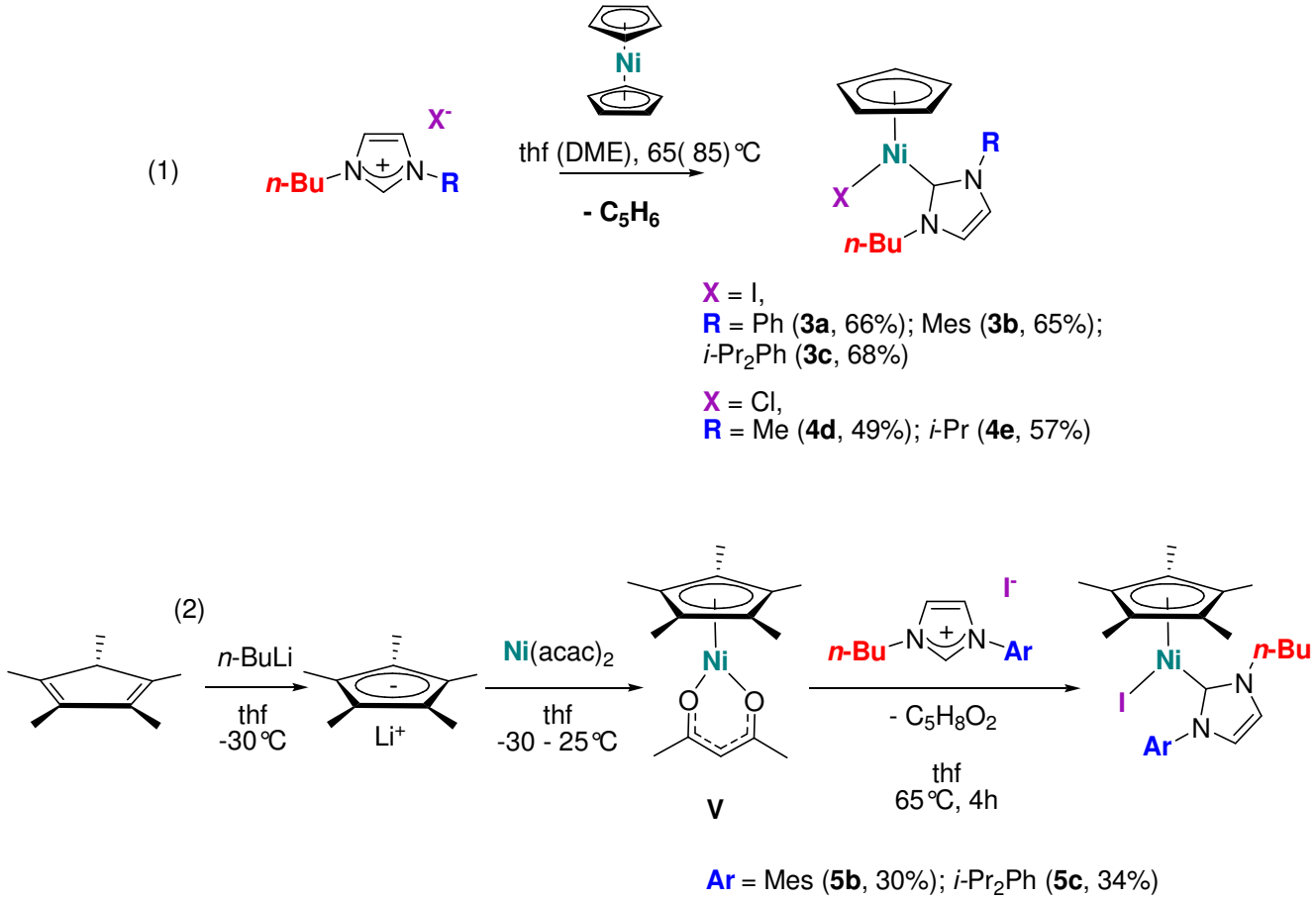
2.2. Syntheses of [Ni(Ar-NHC-*n*-Bu)ICp†] (Cp† = Cp, Cp*) and [Ni(R-NHC-*n*-Bu)ClCp] complexes

Most common methods of attaching a NHC onto a metal centre require prior synthesis of either the free carbene[42,43,44] or a NHC silver complex[2,44,45,46] before subsequent complexation or transmetallation. These tedious procedures can be avoided by the direct addition of the imidazolium salt onto a nickel precursor that is carrying a basic ligand such as cyclopentadienyl or acetylacetonate that will play the role of a hydrogen acceptor. In this way, a variety of *N*,*N'*-symmetrically disubstituted half-sandwich [Ni(**R$_2$**-NHC)XCp†] (Cp† = Cp, Cp*; X = Cl, Br, I) complexes was synthesized by Abernethy, **I**,[13] Nolan, **III**,[14] and more recently by our group, **IV**[15,16] (see Scheme 80). Using similar procedures, we have synthesized a variety of [Ni(Ar-NHC-*n*-Bu)ICp†] [Cp† = Cp, (**3**) Cp*(**5**)] and [Ni(R-NHC-*n*-Bu)ClCp] (**4**), bearing the *N*,*N'*-unsymmetrically disubstituted NHCs derived from the previously synthesized imidazolium salts **1a-c** and **2d,e** (Scheme 6).

Thus, the Cp-complexes [Ni(Ph-NHC-*n*-Bu)ICp] **3a**, Ni(Mes-NHC-*n*-Bu)ICp] **3b**, [Ni(*i*-Pr$_2$Ph-NHC-*n*-Bu)ICp] **3c**, [Ni(Me-NHC-*n*-Bu)ClCp] **4d**, and [Ni(*i*-Pr-NHC-*n*-Bu)ClCp] **4e**, have been synthesized by the addition of nickelocene to the appropriate imidazolium halide salt (Eq. 1,

[41] D. Tapu, D. A. Dixon, C. Roe, *Chem. Rev.* **2009**, *109*, 3385 and references therein.
[42] L. Jafarpour, S. P. Nolan, *Organometallics* **2000**, *19*, 2055.
[43] W. A. Herrmann, M. Elison, J. Fischer, C. Köcher, G. R. L. Artus, *Chem.-Eur. J.* **1996**, *2*, 772.
[44] E. Peris, *Top. Organomet. Chem.* **2007**, *21*, 83.
[45] A. R. Chianese, X. Li, M. C. Jansen, J. W. Faller, R. H. Crabtree, *Organometallics* **2003**, *22*, 1663.
[46] H. M. Wang, I. J. B. Lin *Organometallics* **1998**, *17*, 972.

Scheme 85).[13-15] The reactions were carried out in refluxing tetrahydrofurane (thf) or DME depending on the solubility of the imidazolium salt in these solvents and complexes **3**,**4** were isolated as dark red solids in good yields (49–68 %). The Cp*-complexes [Ni(Mes-NHC-*n*-Bu)ICp*] **5b** and [Ni(*i*-Pr_2Ph-NHC-*n*-Bu)ICp*] **5c** were obtained from the reaction in refluxing thf of the appropriate imidazolium iodide salt with *in situ* prepared [Ni(acac)Cp*] **V**[47] according to the route developed in our laboratory (Eq. 2, Scheme 85).[15a] Complexes **5** were isolated as dark red crystals in moderate yields (30–34 %).



Scheme 85

Good ^{1}H and ^{13}C{^{1}H} NMR spectroscopic data could be obtained for all complexes **3**-**5**. 2D COSY and HSQC NMR spectra were recorded for the complexes **5** in order to help in the signal assignment. Satisfying elemental analyses (**3a**, **3b** and **5c**) or ES-MS spectrometric data (**3c** and **4d,e**) were obtained for most compounds. Single crystals suitable for single crystal X-ray diffraction studies were obtained for all complexes except **3a**.

[47] E. E. Brunel, L. Valle, J. M. Manriquez, *Organometallics* **1985**, *4*, 1680.

2.2.1. Structural studies

The solid state structures of the complexes [Ni(Mes-NHC-*n*-Bu)ICp], **3b**, [Ni(*i*-Pr_2Ph-NHC-*n*-Bu)ICp], **3c**, [Ni(Me-NHC-*n*-Bu)ClCp], **4d**, [Ni(*i*-Pr-NHC-*n*-Bu)ClCp], **4e**, as well as [Ni(Mes-NHC-*n*-Bu)ICp*], **5b**, [Ni(*i*-Pr_2Ph-NHC-*n*-Bu)ICp*], **5c**, have been unambiguously determined by single crystal X-ray diffraction studies. All molecular structures are shown in Figure 2. There are two crystallographically independent molecules in the asymmetric unit of **4e**, but the general geometric features of the two molecules are the same, and therefore only one of them is shown in Figure 2. Crystals were grown from cold solutions of toluene and pentane for all complexes. Crystallographic data and data collection parameters for all compounds **3**-**5** are listed in Table 7, which is placed in the experimental part of this chapter. A list of selected bond lengths and bond angles appears in Table 2 for complexes **3** and **5** and in Table 3 for complexes **4**. The *N*-aryl substituted complexes **3b** and **3c** crystallize in the P_{-1} space group. Their Cp* bonded counterparts **5b** and **5c**, as well as the alkyl substituted complexes **4d** and **4e** crystallize in the space group $P2_1/c$.

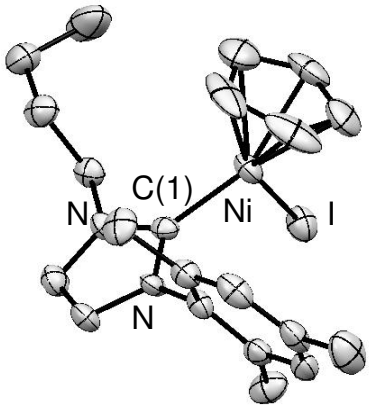
For all complexes **3**–**5** of general formula [Ni(R-NHC-*n*-Bu)X$Cp^{\dagger}$] if the $Cp^{\dagger}$ centroid is considered as one ligand, the geometry at the nickel is trigonal-planar [Σ(angles at Ni) ~ 360°± 1° for all structures]. There are however significant departures from the idealized 120° angles of trigonal planar structures. Compared to the large C(1)–Ni–$Cp^{\dagger}_{cent}$ (127.7–137.0°) and $Cp^{\dagger}_{cent}$–Ni–X (127.1–134.8°) angles, the C(1)–Ni–X angle is considerably smaller (93.7–97.3°). These compounds may thus be referred as "two-legged piano stool" complexes like the closely related complexes [Ni(Mes_2-NHC)ClCp] **Ia**[13], [Ni{(*i*-Pr_2Ph)$_2$-NHC}ClCp] **Ib**[14], [Ni(Mes_2-NHC)ClCp*] **IIa**[15] and [Ni{(*i*-Pr_2Ph)$_2$-NHC}ClCp*] **IIb**[16] for which similar angles have been reported: [132.4(2), 129.2(2), 98.4(2)°], [134.8(8), 131.0(8), 93.86(3)°], [142.0, 122.7, 95.27(9)°] and [143.0, 123.1, 93.85(13)°], respectively. Hence, the dangling *n*-butyl group of compounds **3**-**5** does not create significant distortion of the nickel coordination sphere compared to that of [Ni(R_2-NHC)X$Cp^{\dagger}$] type compounds.[13-16]

The Ni–C(1) bond distance [C(1) = the carbenoid carbon atom, Figure 2] lies in the range of 1.884(3)-1.891(4) Å for the complexes whit R = aryl and 1.863(5)-1.886(6) Å for the complexes with R = alkyl (Table 2 and Table 3). These values are comparable to those reported for **Ia**, 1.917 Å,[13] **Ib**, 1.8748(11) Å,[14] **IIa**, 1.906(3) Å,[15] **IIb**, 1.900(4) Å,[16] as well as for [Ni(Me_2-NHC)ClCp], 1.880(4) Å.[15]

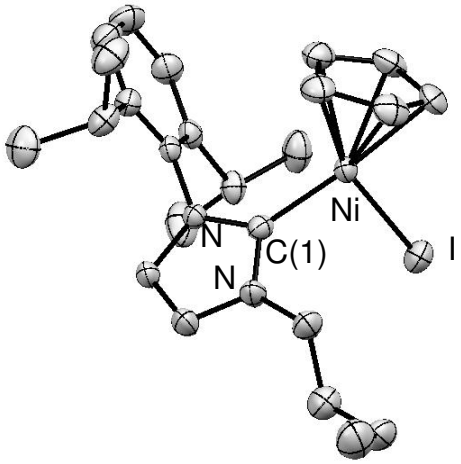
In all complexes the $Cp^{\dagger}$ ring exhibits structural distortions as there are small variations [*av*. 0.0728 Å; *min*. 0.05 Å (for **5c**); *max*. 0.09 Å (for **3b**)] in the C–C bond lengths. Such variations have been previously observed in NiCp* systems and arise from "allyl-ene" or "diene" distortions

in the Cp* ring.[16,48] In contrast to the closely related symmetrically substituted complex [Ni{(*i*-$Pr_2Ph)_2$-NHC}ClCp*] **IIb**[16] for which "allyl-ene" distortions have been pointed out,[16] the $Cp^{\dagger}$ rings of complexes **3c**, **5a**, **5b**, **4d** and **4e** show rather diene distortions, as these systems show two non-adjacent equally short C–C bonds that differ by 0.01 Å or less ($\Delta_{na} < 0.01$ Å) (Scheme 86). Allyl-ene distortions are indeed generally considered when two adjacent C–C bonds are equally short and differ by less than 0.01 Å ($\Delta_a < 0.01$ Å). Thus, complex **3b** shows intermediate distortion ("in between") of its Cp group (see Scheme 86). Note that intermediate C–C bond distortion has also been observed in the Cp* ring of [Ni(PEt_3)(OMe)Cp*].[48a]

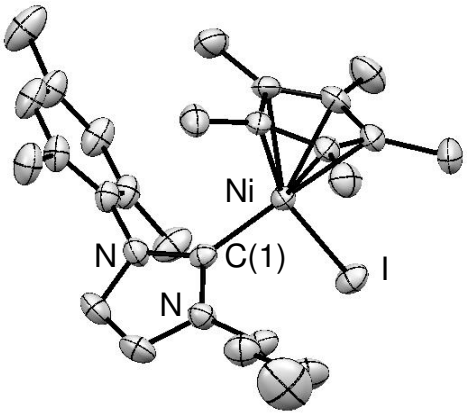
[48] (a) P. L. Holland, M. E. Smith, R. A. Andersen, R. G. Bergman, *J. Am. Chem. Soc.* **1997**, *119*, 12815; (b) M. E. Smith, R. A. Andersen, *J. Am. Chem. Soc.* **1996**, *118*, 11119. (c) R. J. Cross, R. W. Hoyle, A. R. Kennedy, L. Manojlovic-Muir, K. W. Muir, *J. Organomet. Chem.* **1994**, *468*, 265; (d) C. C. Carmona, S. Clapham, M. Gonidec, V. Ritleng, P. Braunstein, R. Welter, M. J. Chetcuti, *Eur. J. Inorg. Chem.* **2010**, 403-409.



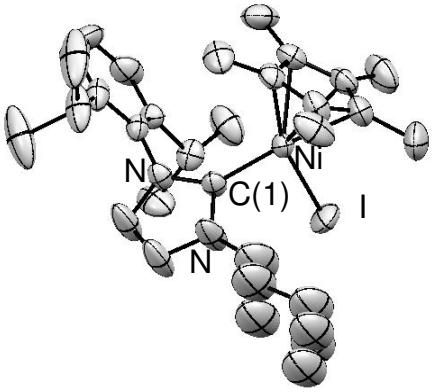
[Ni(Mes-NHC-*n*-Bu)ICp], 3b



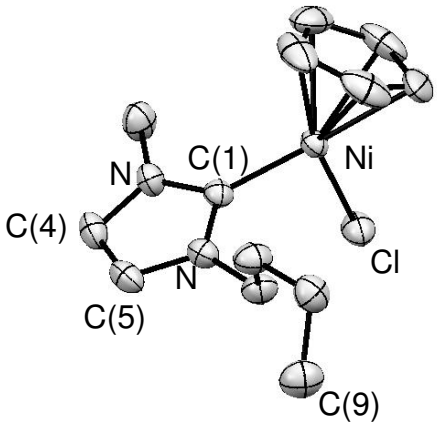
[Ni(*i*-Pr$_2$Ph-NHC-*n*-Bu)ICp], 3c



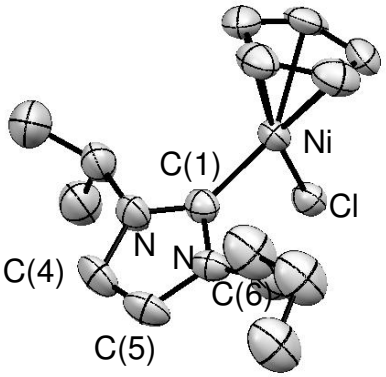
[Ni(Mes-NHC-*n*-Bu)ICp*], 5b



[Ni(*i*-Pr$_2$Ph-NHC-*n*-Bu)ICp*], 5c



[Ni(Me-NHC-*n*-Bu)ClCp], 4d



[Ni(*i*-Pr-NHC-*n*-Bu)ClCp], 4e

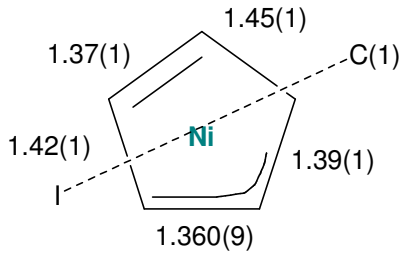
Figure 2: ORTEP plot of the complexes **3b**, **3c**, **5b**, **5c**, **4d** and **4e**. Key atoms are labelled. Ellipsoids are shown at the 50 % probability level. Hydrogen atoms are omitted for clarity. Only one of the two crystallographically independent molecules of the asymmetric unit of **4e** is shown.

Table 2 : Selected bond length (Å) and angles (°) for the complexes **3b**, **3c**, **5b** and **5c**

	3b	**3c**	**5b**	**5c**
Ni–C(1)	1.886(4)	1.884(3)	1.891(4)	1.887(6)
Ni–I	2.5221(9)	2.5099(6)	2.5186(5)	2.537(1)
Ni–C_{Cp} (*av*)	*2.144*	*2.131*	*2.139*	*2.138*
min, max	2.055(9), 2.153(5)	2.055(4), 2.183(3)	2.041(4), 2.172(4)	2.038(8), 2.191(7)
Ni–Cp_{cent}	1.761	1.759	1.761	1.765
C_{Cp}–C_{Cp} (*av*)	*1.398*	*1.417*	*1.428*	*1.419*
min, max	1.360(9), 1.450(1)	1.380(6), 1.453(4)	1.390(6), 1.460(5)	1.39(1), 1.440(1)
C(1)–Ni–I	97.3(1)	95.5(1)	96.4(1)	95.2(2)
C(1)–Ni–Cp_{cent}	134.8	134.7	135.7	137.0
I–Ni–Cp_{cent}	127.9	129.7	127.5	127.1

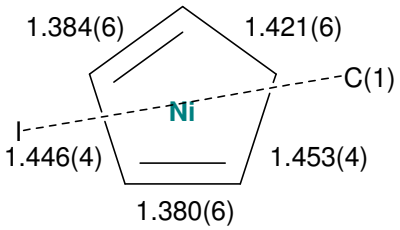
Table 3 : Selected bond length (Å) and angles (°) for the complexes **4d** and **4e**

	4d	**4e**	
Ni–C(1)	1.878(2)	1.886(6)	1.863(5)
Ni–Cl	2.1947(6)	2.193(1)	2.186(2)
Ni–C_{Cp} (*av*, min, max)	*2.126*, 2.035(3), 2.155(3)	*2.128,* 2.038(6), 2.189(7)	*n.r.*
Ni–Cp_{cent}	1.768	1.769	1.759
C_{Cp}–C_{Cp} (*av*, min, max)	*1.389*, 1.354(4), 1.426(5)	*1.390,*1.373(9), 1.43(1)	*n.r.*
C(1)–Ni–Cl	95.27(7)	93.7(2)	93.8(2)
C(1)–Ni–Cp_{cent}	132.8	132.4	131.9
Cl–Ni–Cp_{cent}	131.9	133.8	134.2



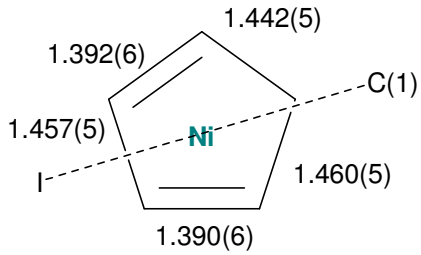
"in between"

[Ni(Mes-NHC-*n*-Bu)ICp], **3b**



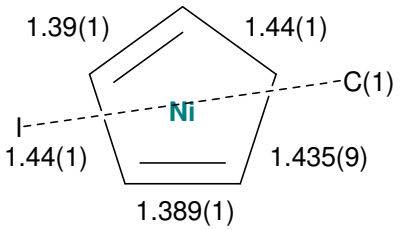
"diene"

[Ni(*i*-Pr$_2$Ph-NHC-*n*-Bu)ICp], **3c**



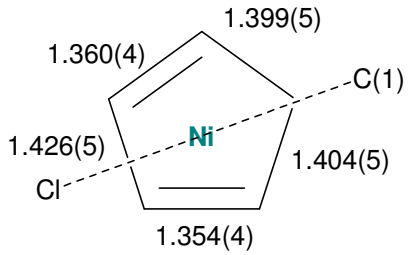
"diene"

[Ni(Mes-NHC-*n*-Bu)ICp*], **5b**



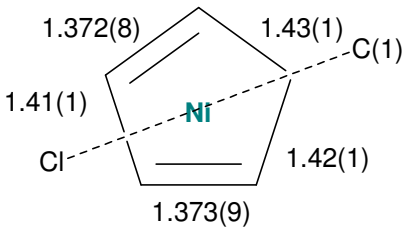
"diene"

[Ni(*i*-Pr$_2$Ph-NHC-*n*-Bu)ICp*], **5c**



"diene"

[Ni(Me-NHC-*n*-Bu)ClCp], **4d**



"diene"

[Ni(*i*-Pr-NHC-*n*-Bu)ClCp], **4e**

Scheme 86: Cp† rings of **3b,c**, **5b,c** and **4d,e** shown in a similar orientation, i.e.: perpendicular to the plane defined by the halide, the nickel and the carbenoid carbon atom C(1).

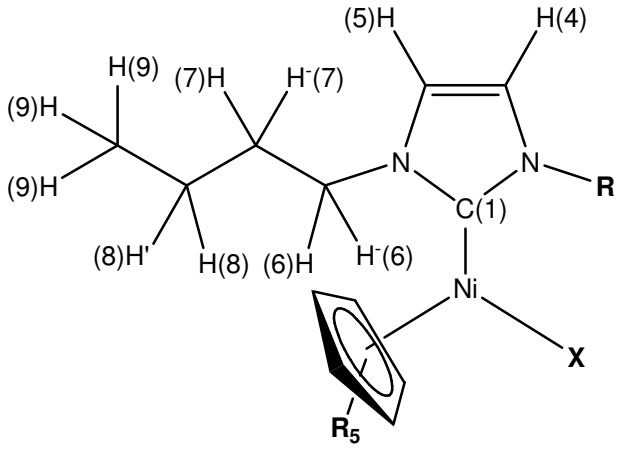
As seen for the [Ni(Mes$_2$-NHC)ClCp*] complex **IV**,[15a] the space-filling molecular models of the complexes **3b** and **5b** on one side and of **3c** and **5c** on the other side suggest that complete rotation about the mesityl–nitrogen bond for **3b** and **5a**, as well as around the *i*-Pr$_2$Ph–nitrogen bond

for **3c** and **5b**, is not allowed without severe molecular deformations, due to the steric bulk of the Cp or Cp* ring and of the big iodine ligand as well as their interactions with the NHC group.

It is worth to mention that some short contact interactions have been noticed for compounds **4d,e** and **5a** in the solid state. Thus, hydrogen bonds of 2.8149(7) Å and 2.626(1) Å are observed between the H(4) proton of the imidazole ring of complexes **4d** and **4e**, respectively, and the chloride of an adjacent molecule. A short contact of 2.449 Å is observed between the H(4) proton and one Cp* ring proton of an adjacent molecule in the case of **5a**.

2.2.2. Spectroscopic studies

The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of *N*-alkyl substituted complexes [Ni(Me-NHC-*n*-Bu)ClCp] **4d** and [Ni(*i*-Pr-NHC-*n*-Bu)ClCp] **4e** and of the *N*-phenyl substituted complex [Ni(Ph-NHC-*n*-Bu)ICp] **3a** are well resolved at ambient temperature. They show the Cp group, the imidazole ring, the *n*-butyl group as well as the *N*-alkyl or *N*-phenyl substituent, which is in accord with the molecular structure of these complexes (Scheme 87). Nevertheless, three pairs of multiplets, that each show a 1:1 integrated ratio, are observed for the methylene protons H(6) and H'(6), H(7) and H'(7), H(8) and H'(8) of these complexes, which shows that they are all diastereotopic at the NMR time scale at room temperature. In contrast, the set of H(9) protons resonates as an apparent binominal triplet suggesting that the protons of the terminal methyl group are equivalent on the NMR time scale.



Scheme 87

The ^{1}H NMR as well as the $^{13}C\{^{1}H\}$ NMR spectra of the Cp* complexes **5b** and **5c** reveal that neither the *ortho*-substituents nor the *meta* protons of the aromatic rings are equivalent at the NMR time scale at room temperature. Indeed, the ^{1}H NMR spectrum of **5b** display four singlets in a 3:3

and 1:1 relative integrated ratio for, respectively, the *ortho*-methyl groups and the *meta*-hydrogen atoms of the mesityl ring. Similarly the ^{1}H NMR spectrum of **5c** displays four doublets and two pseudoseptets in a 3:3:3:3 and 1:1 integrated ratio for the *ortho*-isopropyl groups and two doublets in a 1:1 integrated ratio for *meta*-hydrogen atoms. Finally, as for the complexes **4d,e** and **3a**, the protons of each -CH_2- unit of the *n*-butyl group are not equivalent at the NMR time scale at ambient temperature. These results suggest that at room temperature, rotation about the Ni–C(1) and the N–C_{Aryl} bonds are frozen on the NMR time scale for complexes **5b,c**.

The ^{1}H NMR spectra of complexes **3b** and **3c** are even more complex at room temperature. For all these complexes, the H(6), H'(6), H(7), H'(7), H(8) and H'(8) protons of the butyl chain appear as three pairs of broad and unresolved multiplets at ambient temperature. Furthermore, the signals of the *meta*-protons and the *ortho*-substituents of the aromatic ring are observed as broad signals as well, suggesting a slightly less hampered dynamic process than in compounds **5b,c**. Low temperature ^{1}H NMR experiments were thus performed on $CDCl_3$ solutions of **3b** and **3c** to freeze the dynamic process at the NMR time scale.

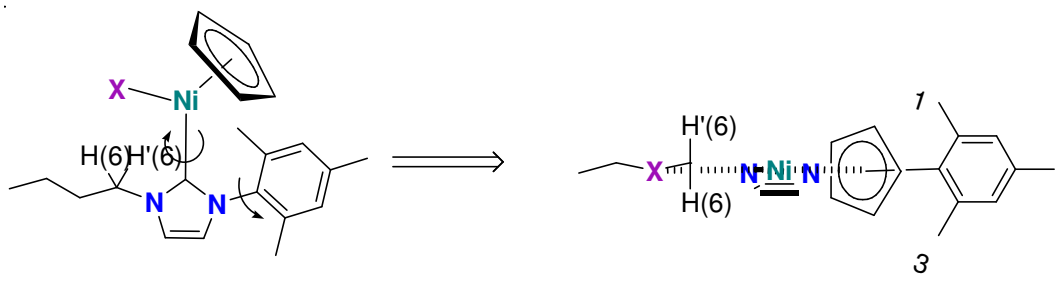
At 263 K the *meta*-protons of the aromatic ring of **3b** resonate as two separate singlets in a 1:1 integrated ratio. Similarly, the signals of the methyl groups at the *ortho*- and the *para*-position of the aromatic ring are observed as three separate singlets in a 3:3:3 relative integrated ratio. In the case of **3c**, all the signals are sharp at 253 K (Figure 3). The two isopropyl groups are displayed as four doublets in a 3:3:3:3 integrated ratio and two pseudoseptets in a 1:1 relative integrated ratio (for the C*H* protons). For both compounds, the H(6), H'(6), H(7), H'(7), H(8) and H'(8) methylene protons resonate as three pairs of well-resolved multiplets at these temperatures.

Variable-temperature experiments were then performed on $C_2D_2Cl_4$ solutions of **3b** and **3c** between 298 and 368 K. As the temperature was increased, the signals of the *meta*-protons and of the *ortho*-methyl groups of **3b** became even broader and coalesced at a temperature (T_C) of *ca.* 303 and 323 K, respectively. The free energy of activation ($\Delta G^{\neq}$) for this fluxional process (based on the T_C of the *ortho*-methyl groups and, independently, of the *meta*-aromatic protons) is 62 ± 2 kJ.mol^{-1}.[49] Coalescence of the H(6) and H'(6) protons of **3b** was observed at *ca.* 323 K. The $\Delta G^{\neq}$ for this fluxional process was calculated to be of 61 ± 2 kJ.mol^{-1} as well. This strongly suggests that all three coalescences are linked to the same dynamic process in **3b**. Similarly, in the case of **3c**, coalescence of the *meta*-aromatic ring protons (at 303 K), the isopropyl groups (at 289 and 303 K) and of the H(6) protons (at 313 K) all gave the same free energy of activation $\Delta G^{\neq}$ of *ca.* 60 ± 2 kJ.mol^{-1}, which strongly suggests that all four coalescences are linked to the same process in **3c**, as

[49] H. S. Gutowsky, C. H. Holm, *J. Chem. Phys.* **1956**, *25*, 1228.

well. Finally one will note that the activation energies of the dynamic processes for complexes **3b** and **3c** are essentially the same.

The most likely dynamic process that could account for these signal equivalences on the ^{1}H NMR time scale at elevated temperature is free rotation about the Ni-C(1) bond. Indeed, rotation of the Ni–C(1) bond would generate an effective symmetry plane that would bisect these molecules in solution. The illustration, **3b-sym** (Scheme 88), of this plane is shown for the complex **3b**. Only the H(6) and H'(6) methylene protons are labelled for clarity. The mirror plane would contain the halogen, the nickel, the Cp† ring centroid and imidazole ring atoms as well as those of the aliphatic chain.



3b **3b-sym**

Scheme 88

Similar dynamic behaviour was previously observed for the symmetrically-substituted Cp* complexes [Ni(Mes$_2$-NHC)ClCp*] **IIa** and [Ni{(*i*-Pr$_2$Ph)$_2$-NHC}ClCp*] **IIb**,[15a] which show a barrier to Ni–C(1) bond rotation of 65-67 kJ.mol^{-1}. However, the analogous Cp complexes [Ni(Mes$_2$-NHC)ClCp] **Ia** and [Ni{(*i*-Pr$_2$Ph)$_2$-NHC}ClCp] **Ib** did not show any barrier to Ni–C(1) bond rotation at room temperature.[13,14,15b] Thus, in the case of **3b,c**, we believe that it is the presence of the voluminous iodide and its steric interaction with the *n*-butyl-NHC-Mes group that hampers the free rotation about the Ni–C(1) bond and renders it more difficult with respect to that about the Ni–C(1) bond of [Ni(Mes$_2$-NHC)ClCp], which bears a smaller chloride ligand.

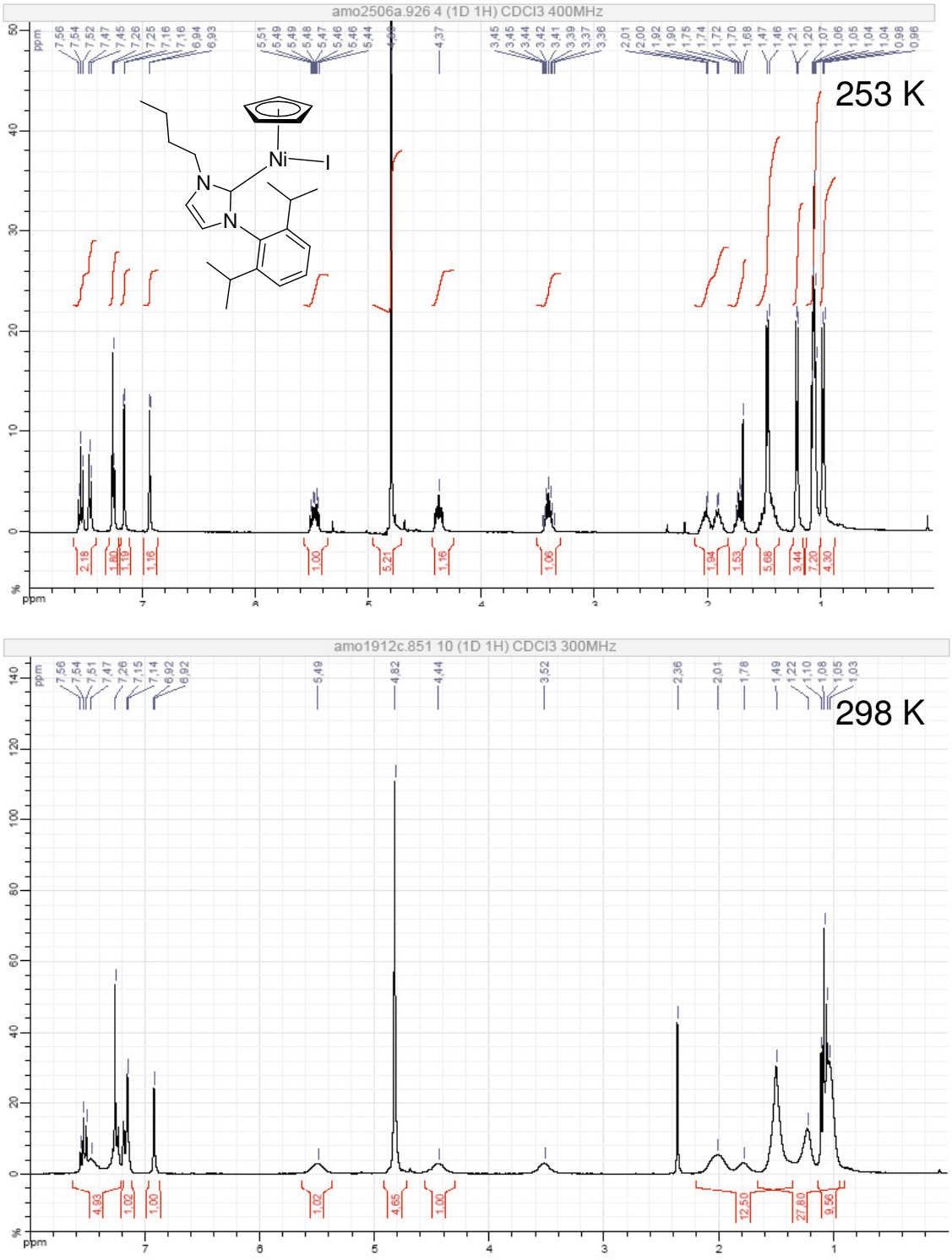


Figure 3 : ^{1}H NMR spectra of [Ni(*i*-Pr$_2$Ph-NHC-*n*-Bu)ICp], **3c**, at 253 and 298 K ($CDCl_3$, 400.14 MHz).

In previous studies, the barrier to the metal–carbene bond rotation observed in numerous M-NHC complexes was mainly attributed to steric effects, as the metal–carbene bond was believed to

have predominantly single-bond character.[50] However, more recent studies of the electronic effects in [M(NHC)$_n$] (M = Ni, Pd, Pt; n = 2, 3) type complexes, and especially in Ni(0)-NHC$_2$ compounds, suggest that the part of the π-contribution in Ni-NHC bonds is significantly higher than thought earlier and could reach up to 43 % in a zero-valent nickel D$_{2d}$-[Ni(H$_2$-NHC)$_2$] complex.[4c,5] Thus, the barrier to the rotation about the Ni–C(1) bond observed in complexes **3b,c** and **5b,c** may not only be due to steric effects but also to electronic effects, i.e.: the inductive electron-donating effect of the *n*-butyl chain.

2.3. Suzuki-Miyaura cross-coupling of aryl halides

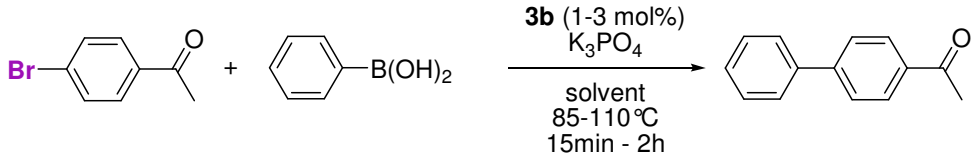
The complexes [Ni(Mes-NHC-*n*-Bu)ICp] **3b**, [Ni(*i*-Pr$_2$Ph-NHC-*n*-Bu)ICp] **3c**, [Ni(Me-NHC-*n*-Bu)ClCp] **4d**, and [Ni(*i*-Pr-NHC-*n*-Bu)ClCp] **4e**, as well as [Ni(*i*-Pr$_2$Ph-NHC-*n*-Bu)ICp*] **5c**, were then tested for their catalytic activity in Suzuki-Miyaura cross-coupling reactions to check the influence of the *n*-butyl group as well as that of the voluminous iodide ligand (when present) on the reaction yields and rates.

Initial studies focussed on the reaction of 4'-bromoacetophenone with various amounts of phenylboronic acid and K$_3$PO$_4$ in the presence of **3b** (1-3 mol%) under various solvent and temperature conditions to optimize the reaction conditions, and were carried out by using Schlenk techniques (Table 4, entries 1-7). As for the reactions catalyzed by the symmetrically substituted analogues,[16] all reactions were run *without any additive such as PPh$_3$*. The first runs were conducted in refluxing DME with 3 mol% of catalyst loading (Table 4, entries 1-3). Low conversion (44 %) was observed with 1.1 equiv. (equiv. = molar equivalent) of PhB(OH)$_2$ and 2.2 equiv. of K$_3$PO$_4$ (entry 1). Increasing of the amount of PhB(OH)$_2$ and K$_3$PO$_4$ to 1.2 and 2.4 equiv., respectively, significantly improved the reaction yield (entry 2). No further significant improvement was observed when the amounts of PhB(OH)$_2$ and K$_3$PO$_4$ were raised to 1.3 and 2.6 equiv., respectively (entry 3). However, under these conditions, toluene proved to be the solvent of choice since a similar yield could be obtained in only 60 minutes (entry 4). Increasing the temperature to 110 °C (entry 5) and the reaction time to 120 min (entry 6) further increased the yield to reach 94%. Very interestingly, decreasing the catalyst loading to 1 mol% did not affect the reaction yield and

[50] (a) T. Weskamp, W. C. Schattenmann, M. Spiegler, W. A. Herrmann, *Angew. Chem. Int. Ed.* **1998**, *37*, 2490; (b) E. F. Penka, C. W. Schläpfer, M. Atanasov, M. Albrecht, C. Daul, *J. Organomet. Chem.* **2007**, *692*, 5709; (c) C. P. Newman, R. J. Deeth, G. J. Clarkson, J. P. Rourke, *Organometallics* **2007**, *26*, 6225. (d) L. C. Silva, P. T. Gomes, L. F. Veiros, S. I. Pascu, M. T. Duarte, S. Namorado, J. R. Ascenso, A. R. Dias, *Organometallics* **2006**, *25*, 4391; (e) D. Enders, H. Gielen, *J. Organomet. Chem.* **2001**, *617*, 70; (f) M. J. Doyle, M. F. Lappert, *J. Chem. Soc., Chem. Commun.* **1974**, 679.

91% conversion could be observed after 60 min with 1 mol % of **3b** (entry 7). This is in sharp contrast to what had been observed with the symmetric species **I-IV** (Scheme 80) bearing a smaller chloride or acetonitrile ligand instead of the big iodide and for which fast deactivation of the active species occurred.[16]

Table 4 : Optimization of the reaction conditions for the Suzuki–Miyaura cross–coupling of 4'-bromoacetophenone with phenylboronic acid catalyzed by **3b**.[a]



entry	solvent	mol%	$PhB(OH)_2$ (equiv.)	K_3PO_4 (equiv.)	T (°C)	t (min)	yield (%) [b,c]
1	DME	3	1.1	2.2	85	120	44
2	DME	3	1.2	2.4	85	120	72
3	DME	3	1.3	2.6	85	120	73
4	Tol	3	1.3	2.6	90	60	78
5	Tol	3	1.3	2.6	110	60	86
6	Tol	3	1.3	2.6	110	120	94
7	Tol	1	1.3	2.6	110	60	91
8	Tol	1	1.3	2.6	110	15	88[d]
9	Tol	1	1.3	2.6	110	60	>99[d]

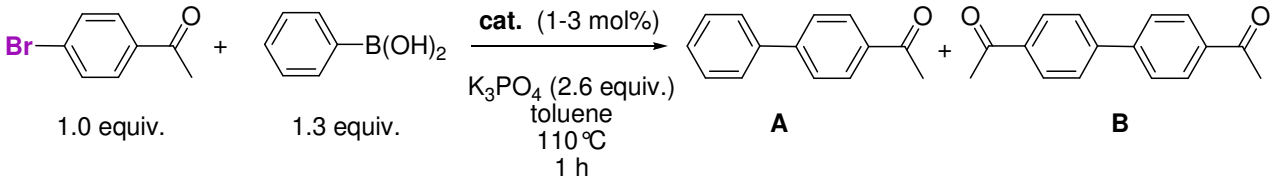
[a]**Reaction conditions** : bromoacetophenone (199 mg, 1.0 mmol), phenylboronic acid (1.1–1.3 mmol), K_3PO_4 (2.2 –2.6 mmol), solvent (3.0 mL), catalyst **3b** (1–3 mol%); 85 – 110 °C; 15–120 min; [b] NMR yield; [c] Average value for three runs; [d] The reactors have been loaded in a glovebox with $H_2O < 0.5$ ppm, $O_2 < 0.5$ ppm.

When carrying these condition optimization experiments, we observed significant variations of the reaction yields between each of the three catalytic runs that were conducted under the same reaction condition. We believed that these variations were due to small amounts of O_2 that entered the catalytic reactor when the solvent was injected in the reaction medium by a syringe through a septum (cf. experimental section). Indeed, the thus entered small amount of O_2 would then progressively deactivate the highly air sensitive Ni(0) active species. To prevent such O_2 contamination, we then decided to load the catalytic reactors with both substrates, K_3PO_4 and 1 mol% toluene solutions of the catalyst **3b** in a glovebox with H_2O and O_2 levels < 0.5 ppm (Table 4, entries 8 & 9). To our delight, we did not observe any irregular yield variations anymore under

these conditions, and we even observed significant improvements. Thus, conversion was almost quantitative after 60 min (entry 9), and even 88 % of conversion was observed after *only 15 min* of reaction (entry 8) leading to a turnover frequency (TOF) of 352 h^{-1}, which is even better than the TOF of 190 h^{-1} observed with [Ni(*i*-Pr_2Ph)$_2$-NHC)(NCMe)Cp*](PF$_6$)[16] and is the best TOF observed so far in Suzuki-Miyaura cross-coupling catalyzed by a Ni(II) complex *in the absence of reductant and co-catalyst* (See Chapter 1, Section 2.3).[51]

The catalytic activities of the Cp complexes [Ni(*i*-Pr_2Ph-NHC-*n*-Bu)ICp], **3c**, [Ni(Me-NHC-*n*-Bu)ICp], **4d**, and [Ni(*i*-Pr-NHC-*n*-Bu)ICp], **4e**, as well as of the Cp* species [Ni(*i*-Pr_2Ph-NHC-*n*-Bu)ICp*], **5c**, were next examined under the standard conditions established with **3b** (Table 5).

Table 5 : Suzuki–Miyaura cross-coupling of 4'-bromoacetophenone with phenylboronic acid catalyzed by **3c**, **4d,e** and **5c**.[a]



entry	cat.	mol%	yield (%)[b]	selectivity (A/B)
1	**3c**	3	88	(100/0)
2	**5c**	1	88	(100/0)
3	**4d**	1	81[c]	(80/19)
4	**4e**	1	87[c]	(79/20)

[a]**Reaction conditions** : bromoacetophenone (199 mg, 1.0 mmol), phenylboronic acid (1.3 mmol), K_3PO_4 (2.6 mmol), toluene (3.0 mL), catalyst (1–3 mol%), 110 °C; 1h. [b]average NMR yield of three runs; [c] The reactors were loaded in a glovebox with H_2O < 0.5 ppm, O_2 < 0.5 ppm.

All complexes are catalytically active and give the desired 4-acetylbiphenyl coupling product in good yield. However, in contrast to [Ni{(*i*-Pr_2Ph)$_2$-NHC}ClCp] **Ib**, which bears the bulkier *i*-Pr_2Ph substituents on the imidazole ring and gave better results than [Ni(Mes$_2$-NHC)ClCp] **Ia**,[16] no improvement was observed with **3c**, which also bears one *i*-Pr_2Ph group instead of a mesityl group (entry 1). In addition, in contrast to the Cp* symmetric complexes **II**, which gave much better results than the symmetric Cp complexes **I**, we also did not observe any improvement with the Cp* complex **5c** (entry 2). Finally, a greatly decreased selectivity was observed with the alkyl-

[51] For an example of high but lower TOF, see: K. Inamoto, J.-i. Kuroda, E. Kwon, K. Hiroya and T. Doi, *J. Organomet. Chem.*, **2009**, *694*, 389.

substituted [Ni(R-NHC-*n*-Bu)ClCp] species **4d** (R = Me) and **4e** (R = *i*-Pr), as significant amounts of the homocoupling product 4,4'-acetylbiphenyl were detected with these catalysts (entries 3 & 4).

The precise reaction mechanism remains to be elucidated. Nevertheless, a few comments can be made. The catalyst deactivation that was observed when a small amount of O_2 accidentally entered the reactor further sustains that the catalytically active species is a highly air sensitive Ni(0) complex, as it was thought for the symmetric catalysts.[16] The significant stabilization of the active species, which allowed to decrease the catalyst loading from 3 mol% to 1 mol% with complexes **3b**,**c** and **5b**,**c** with respect to the symmetric catalysts **II** and **IV** that bear either a chloride or an acetonitrile ligand, may be attributed to the presence of the voluminous iodide ligand rather than to that of the *n*-butyl arm, the latter being most probably too far of the metal centre to exert much influence.[52] Moreover, the absence of improvement observed with **3c** and **5c** (with respect to **3b**) shows that neither a faster reduction from the starting Ni(II) complex to the active Ni(0) species (as expected with the Cp* species)[16] nor a better steric protection of the catalytically active centre (as expected with a *i*-Pr_2Ph-substituent instead of a Mes-substituent and/or a Cp* ligand instead of a Cp ligand),[16] do play a significant role anymore in presence of the highly protecting iodide ligand. This observation further hints that Cp slippage would generate the active catalyst rather than Ni–halide dissociation as this would explain why the substitution of a Cp by a bulkier Cp* would not procure higher stability to the active species. The presence of a Cp* may show influence exclusively on the reduction of Ni(II) to the active Ni(0) species as M–Cp* bonds are known to be less robust than M–Cp bonds.[53]

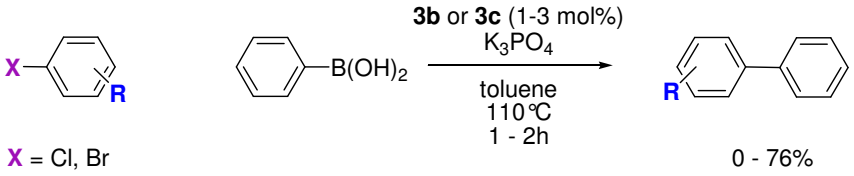
The reaction scope of the [Ni(Ar-NHC-*n*-Bu)ICp] catalysts **3b**,**c** has next been examined with a short series of aryl bromides and chlorides bearing electron-withdrawing and electron-donating substituents (Table 6). Good yields of 4,4'-acetylbiphenyl were obtained from 4'-chloroacetophenone with both catalysts (entries 1 & 2). The electron-donating substrates 4-bromotoluene and 4-chlorotoluene were however converted to the desired coupling products in lower yields (entries 3 & 4), and even lower yields of the desired biphenyl derivatives were detected with sterically hindered 2-bromo- and 2-chlorotoluene (entries 5 & 6), which is rather disappointing since other Ni(II)-NHC species convert these substrates very efficiently (See Chapter I, Section 2.3). Nevertheless, good conversion was obtained for the coupling of bromonaphthalene, although a longer reaction time was necessary (entry 9). A significantly decreased selectivity was noticed for

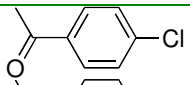
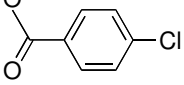
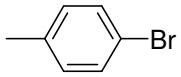
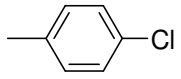
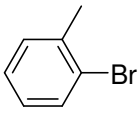
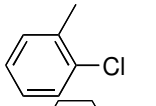
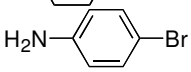
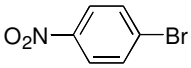
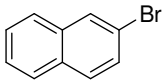
[52] As no substantial significant difference was observed between the neutral [Ni(Ar_2-NHC)ClCp†] and the cationic [Ni(Ar_2-NHC)(NCMe)Cp†](PF_6) complexes, which contain a labile acetonitrile ligand, the necessary generation of a vacant site was postulated to arise through Cp or Cp* slippage rather than by dissociation of the halide or acetonitrile ligand. See ref. 16. The iodide ligand is thereof supposed to stay on the active species.

[53] M. J. Chetcuti, L. A. DeLiberato, P. E. Fanwick, B. E. Grant, *Inorg. Chem.* **1990**, *29*, 1295 and references therein.

the cross-coupling of 4'-bromoaniline (entry 7), as major amounts of biphenyl (22 %) – resulting from the homocoupling of phenylboronic acid – and of aniline (12 %) – resulting from the dehalogenation of the heteroaryl bromide – were observed. Finally, no reaction was detected with the electronically deactivated 1-bromo-4-nitrobenzene (entry 8).

Table 6 : Suzuki–Miyaura coupling of aryl chlorides and bromides with phenylboronic acid catalyzed by **3b** and **3c**.[a]



entry	cat.	mol%	X-Ar-R_1	R_2	t (min)	yield (%)[b]
1	3b	3		H	60	76
2	3c	3		H	60	77
3	3b	1		H	60	46
4	3b	1		H	60	23
5	3b	1		H	60	27
6	3c	1		H	60	10[c]
7	3b	1		H	60	28[c,d]
8	3b	3		H	60	0
9	3b	1		H	120	67[e,f]

[a]**Reaction conditions** : Aryl halide (1.0 mmol), phenylboronic acid (1.3 mmol), K_3PO_4 (2.6 mmol), cat. (1-3 mol %), toluene (3 mL), 110 °C. [b]NMR yields; [c]isolated yield; [d]22% of homocoupling of phenyl boronic acid; [e]12% of dehalogenation product; [f]GC-MS yield.

This short series of electronically activated and deactivated aryl halides shows that the reaction scope of the [Ni(Ar-NHC-*n*-Bu)ICp] catalysts **3b** and **3c** is of the same order than that of the related symmetric complexes [Ni(Ar_2-NHC)LCp*] (Ar = Mes, *i*-Pr_2Ph; L = Cl^-, NCMe PF_6^-) **I-IV** species.[16] Thus, although **3b** and **3c** were slightly less active for the coupling of 4'-chloroacetophenone, good yields and high selectivity were obtained in all cases with 4'-

bromoacetophenone and 4'-chloroacetophenone bearing the electron-withdrawing acetyl group. Moreover, a decreased activity was noticed with the electron-donating substrates for both types of complexes. Nevertheless, compared to the active species generated by the symmetric catalysts **II** and **IV** bearing either a chloride or an acetonitrile ligand, those formed by the *n*-butyl compounds **3b**,**c** bearing a voluminous iodide ligand are much more stable and active and allow to reduce the catalyst loading, which is crucial in the perspective of an heterogenized version. These species even allowed to observe *in the absence of co-catalyst and reductant* – which is also crucial in the perspective of an heterogenized version – the highest TOF ever observed for Ni(II)-catalyzed Suzuki-Miyaura cross-coupling of 4'-bromoacetophenone and phenylboronic.

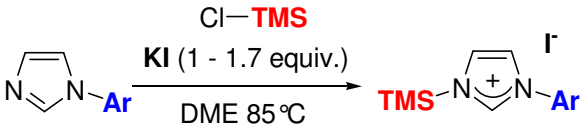
2.4. Synthesis and characterization of the trialkoxysilylpropyl-substituted imidazolium salts

A series of trimethoxysilylpropyl (TMS) tethered imidazolium salts has been synthesized *via* the same synthetic route that was discussed for their *n*-butyl counterparts in Section 2.1 (Eq 1, Scheme 4).[34] Hence, 1-phenyl-3-[3-(trimethoxysilyl)propyl]-, 1-(2,4,6-trimethylphenyl)-3-[3-(trimethoxysilyl)propyl]- and 1-(2,6-diisopropylphenyl)-3-[3-(trimethoxysilyl)propyl]-imidazolium iodide, **6a–c**, were obtained in good yields from the appropriate *N*-substituted imidazole and (3-chloropropyl)trimethoxysilane with an equimolar amount of KI (Eq. 1, Scheme 89). The 1-isopropyl-3-[3-(trimethoxysilyl)propyl]-imidazolium chloride, **7e**, could be obtained in moderate yield by simple reflux of *N*-*i*-propylimidazole with (3-chloropropyl)trimethoxysilane in the absence of KI (Eq. 2, Scheme 89).

The triethoxysilylpropyl (TES) functionalized imidazolium chlorides; 1-(2,4,6-trimethylphenyl)-3-[3-(triethoxysilyl)propyl]-, **6'b**, 1-(2,6-diisopropylphenyl)-3-[3-(triethoxysilyl)propyl]-, **6'c**, and 1-[(3-trimethoxysilyl)propyl]-3-methyl-imidazolium chloride, **7d**, were prepared according to a slightly modified version of a microwave assisted procedure that has been reported for the synthesis of other silane tethered imidazolium halides.[54] Hence, **6'b**, **6'c** and **7d** were synthesized in good to quantitative yields from equimolar thf solutions of the appropriate imidazole and (3-chloropropyl)alkoxysilane in a sealed vessel at 175 °C (Eq. 3, Scheme 89).

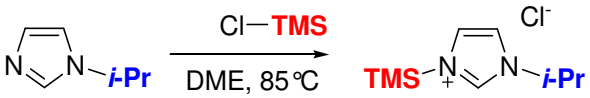
[54] (a) S.-K. Fu, S.-T. Liu, *Synth. Commun.* **2006**, *36*, 2059; (b) M. Deetlefs, K. R. Seddon, *Green Chem.* **2003**, *5*, 181.

(1)



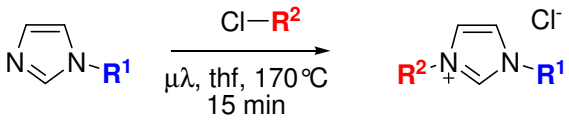
Ar = Ph (**6a**, 76%), Mes (**6b**, 87%), *i*-Pr_2Ph (**6c**, 64%)

(2)



7e, 34%

(3)



R^2 = TMS
R^1 = Me (**7d**, >99%) (No solvent)
R^2 = TES
R^1 = Mes (**6'b**, 70%), *i*-Pr_2Ph (**6'c**, 58%)

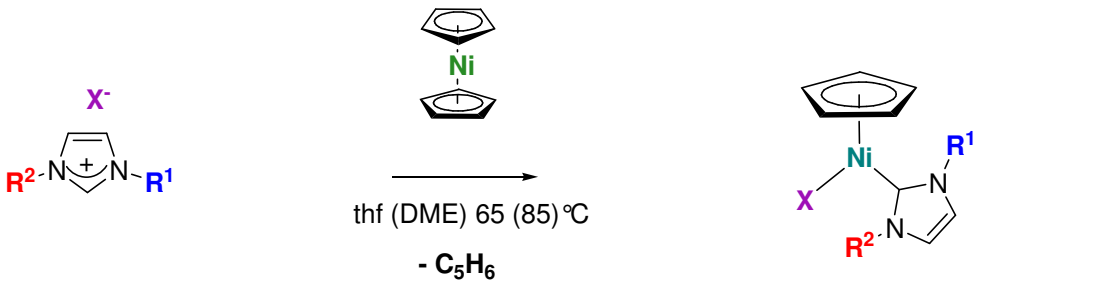
Scheme 89

The TMS-functionalized salts **6a-c** and **7d**,**e** were isolated as hygroscopic solids or non-volatile oils, that often appear slightly coloured. These oils are difficult to purify and sometimes contain traces of the (3-chloropropyl)trialkoxysilane and its hydrolysis products. The TES-functionalized salts **6'b** and **6'c** were isolated as a white solid of satisfying purity. Nevertheless good spectroscopic data [^{1}H, ^{13}C{^{1}H} and ^{13}C DEPT NMR, HRMS (MALDI TOF)] were obtained for all imidazolium salts.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of the compounds **6**, **6'** and **7** are straightforward at ambient temperature. All show the presence of the imidazole ring, the trialkoxysilane arm and the aryl or alkyl substituent. No significant chemical shift differences were observed for the chemical shifts of the imidazole ring protons compared to those of their *n*-butyl analogues **1a-c** and **2d,e** (Table 1). The terminal silane function should thus have no major impact on the electronic properties of the imidazole ring.

2.5. Syntheses of [Ni(Ar-NHC-TMS)XCp] and [Ni(Ar-NHC-TES)ClCp] complexes

The complexes [Ni(Ph-NHC-TMS]ICp], **8a**, [Ni(Me-NHC-TMS)ClCp] **9d**, and [Ni(*i*-Pr-NHC-TMS]ClCp], **9e**, [Ni(Mes-NHC-TES)ClCp], **8'b**, and [Ni(*i*-Pr_2Ph-NHC-TES)ClCp], **8'c** were synthesized according to the same procedure than their *n*-butyl counterparts **3**,**4**, i.e.: by direct reaction of the appropriate imidazolium salt with nickelocene (Scheme 90).[21]



X = I, **R²** = TMS
R¹ = Ph (**8a**, 43%); Mes (**8b**, n.r.); *i*-Pr_2Ph (**8c**, n.r.)

X = Cl, **R²** = TES
R¹ = Mes (**8'b**, 71%); *i*-Pr_2Ph (**8'c**, 38%)

X = Cl, **R²** = TMS
R¹ = Me (**9a**, 49%); *i*-Pr (**9b**, 57%)

Scheme 90

The TES-functionalized complexes **8'b** and **8'c** were isolated in good yields (63-71%) as pink oils of satisfying purity after column chromatography. Purification of the TMS-functionalized **9d**,**e** and more particularly of the *N*-aryl substituted compounds **8a-c** revealed to be much more difficult as neither crystallization nor column chromatography could be employed for these species; the complexes remain immobilized onto the silica or alumina by condensation of the trimethoxysilyl groups with the surface silanols. Thus, of the *N*-aryl substituted compounds **8a-c**, only **8a** could be obtained with an interpretable ^{1}H NMR spectrum. The ^{1}H NMR spectra of **8b**,**c** always revealed important traces of the ligand precursor, the hydrolysis product, as well as other decomposition products. Therefore, complexes **8a-c** will not be further commented.

Good spectroscopic ^{1}H and ^{13}C{^{1}H} NMR data could be obtained for complexes **8'b**, **8'c** and **9d,e**. They show the presence of one Cp ligand, the imidazole ring and its *N,N'*-substituents. In contrast to their *n*-butyl counterparts **3b** and **3c**, which bear a bulky iodide ligand, complexes **8'b** and **8'c**, which carry a smaller chloride ligand, show a greatly reduced barrier to the Ni–C(1) bond rotation at room temperature on the NMR time scale. Indeed, in contrast to **3b**,**c**, which NMR

spectra display broad but split signals for the *ortho*-substituents of the aryl rings (i.e.: before coalescence), the NMR spectra of **8'b** and **8'c** display broad non-split signals for the *ortho*-substituents of the aryl rings (i.e.: after coalescence). This result confirms the prevalent role played by the voluminous iodide ligand in hampering free rotation about the nickel-carbene bond in complexes **3b**,**c** (and of course in complexes **5b,c**). It also shows that despite its position far off the nickel, the very bulky triethoxysilylpropyl arm is non-innocent regarding to the dynamic processes in **8'b** and **8'c** since the symmetric compounds [Ni(Ar_2-NHC)ClCp] did not show any rotation barrier at all on the NMR time scale at room temperature. [13,14,15b]

Variable-temperature ^{1}H NMR data, from 223 to 298 K, were collected on a $CDCl_3$ solution of **8'c**. All signals are sharp and doubled at 223 K. The free energy of activation ($\Delta G^{\neq}$) was determined to be of *ca.* 51 ± 2 kJ.mol^{-1}, which is lower than that determined for complex **3c** (60 ± 2 kJ.mol^{-1}), as expected.

2.6. Immobilization of [Ni(Mes-NHC-TES)ClCp] onto alumina

The complex [Ni(Mes-NHC-TES)ClCp], **8'b**, was covalently grafted onto alumina[55] by condensation of the triethoxysilyl groups with the surface silanols (Scheme 2) by refluxing **8'b** in toluene with alumina for 4h. The pink colour of the solid obtained after volatiles removal and thorough washings directly suggested that successful immobilization of **8'b** had occurred. To confirm it, the surface of the hybrid material **10** was analyzed by ^{1}H MAS solid state NMR (Figure 3) and Diffuse Reflection Infrared Fourier Transform (DRIFT) spectroscopy (Figure 3), and the amount of nickel was determined by Atomic Emission Spectroscopy (ICP-AES).

[55] Alumina was chosen among the variety of metal oxides for practical means.

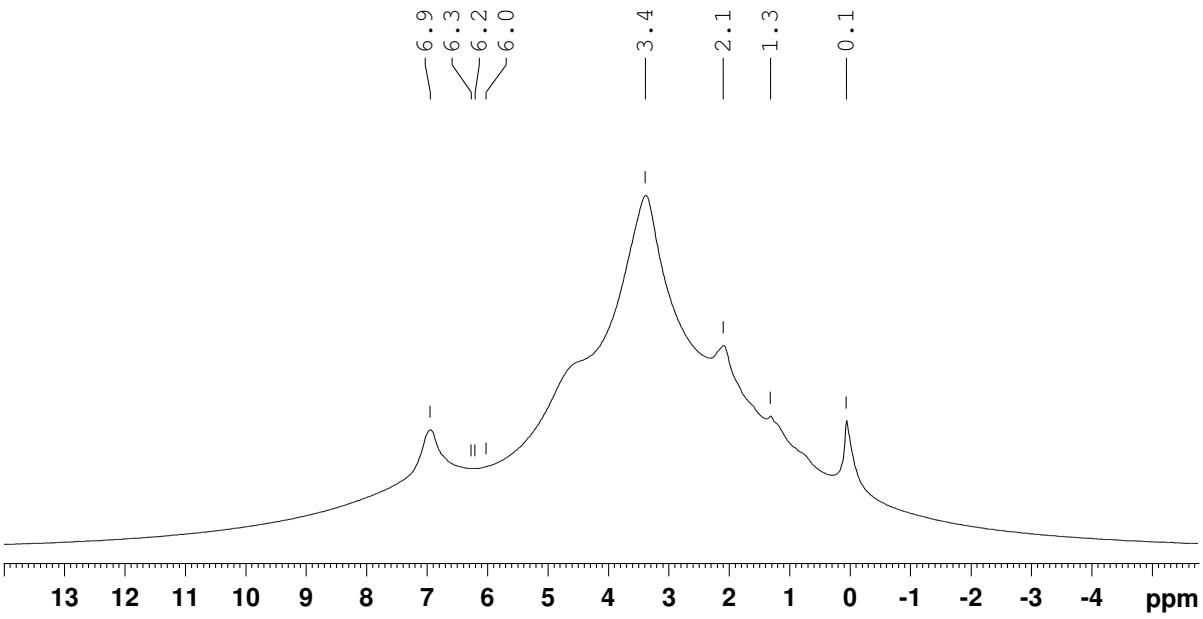


Figure 4

The interpretation of a solid state ^{1}H MAS spectrum is similar to that of a solution ^{1}H NMR spectrum. However, very broad signals are usually observed and couplings are not resolved. The ^{1}H MAS spectrum (Figure 4) further suggested that complex **8'c** had been successfully immobilized onto alumina surface as the resonance signal for the NHC ligand (6.9 ppm), the Cp ring (3.6 ppm) and the three carbon linker are observed (2.1 and 1.3 ppm). The peak at 0.1 ppm may originate from silicon grease. The DRIFTS spectrum of the organic-inorganic hybrid material **10** further suggested that **8'c** had well been grafted onto alumina's surface (Figure 5). The DRIFTS spectrum indeed shows the presence sp^2-C–H, sp^3-C–H (ν = 3131-3089 cm^{-1} and 2979-2830 cm^{-1}) bonds and perhaps (as these bands are very weak) also of sp^2-C=N bonds (ν = 1545-1609 cm^{-1}). Finally, ICP-AES data allowed to evaluate the amount of nickel to 2.84 mg for 1 g of the hybrid material **10**, i.e.: 0.05 mmol.g^{-1}. This value is 10 times lower than that reported for a silica immobilized system tested in Suzuki-Miyaura cross-coupling (Chapter 1, Section 2.1.3.4.).[56] However, the percentage is in accord with theoretical values, calculated on the base of the specific surface of the alumina and the surface that would occupy one mol of the complex **8'b**.

[56] C. Zhong, T. Sasaki, M. Tada, Y. Iwasawa, *J. Catal.* **2006**, *242*, 357.

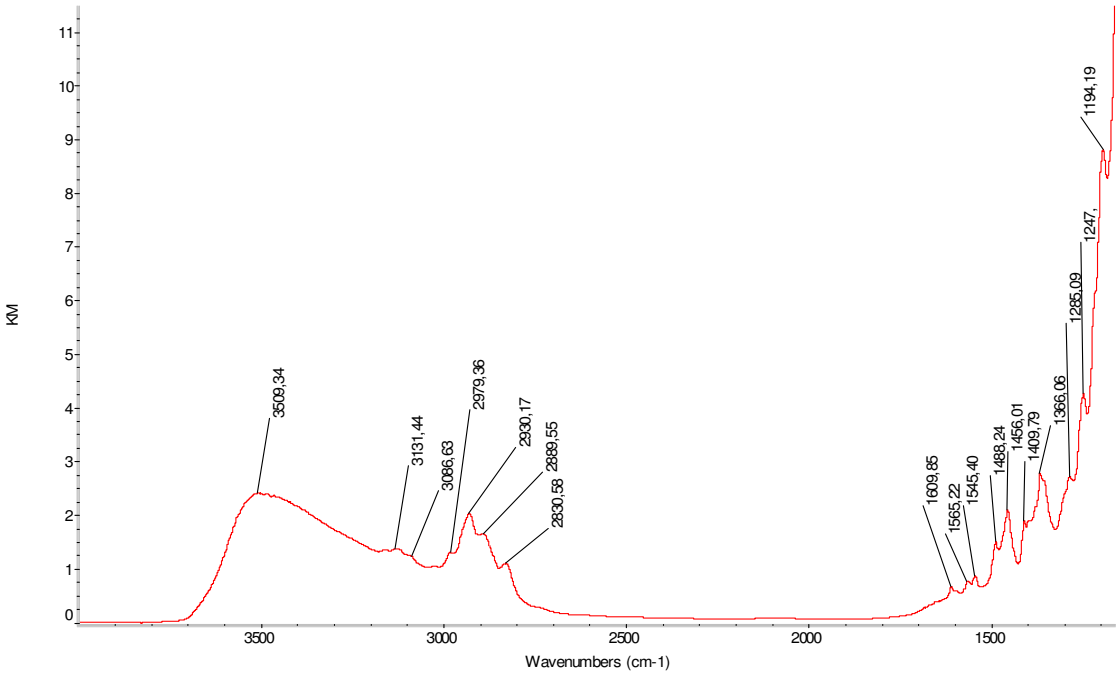
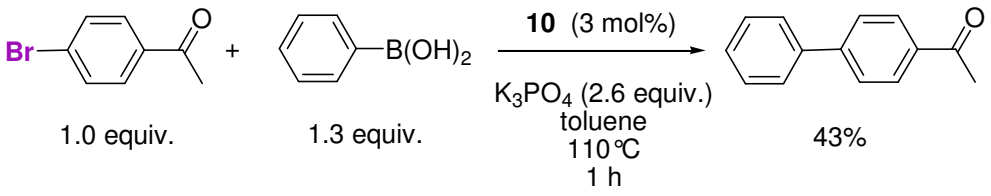


Figure 5

2.7. Suzuki-Miyaura cross-coupling catalyzed by the immobilized complex

The catalytic activity in Suzuki-Miyaura cross-couplings of the hybrid material **10** was evaluated for the coupling of 4'-bromoacetophenone with phenylboronic acid under the standard conditions established for its non-grafted analogues. Only 43% of the desired biphenyl derivative was detected with 3 mol% of nickel after 1 h of reaction (Scheme 91), which is markedly low compared to the nearly quantitative yield observed with 1 mol% of its closest analogue **3b**. Grafting of our catalysts onto alumina seems thus highly detrimental to their catalytic activity. However, at this stage, it is unclear to what extent this activity drop is due to the heterogenization itself or to the presence of a small chloride on **8'c** instead of a the highly protecting iodide on **3c**. To answer that question, at least partially, the activity of **8'c** should be tested prior grafting, and a complex bearing an iodide should be immobilized and tested.



Scheme 91

3. Conclusion

A series of *N*,*N'*-unsymmetrically disubstituted imidazolium salts, **1**-**2**, bearing a *N*-bound *n*-butyl arm, was prepared from the appropriate *N*-alkylimidazole and 1-chlorobutane or from the appropriate *N*-arylimidazole and 1-chlorobutane in the presence of one molar equivalent of potassium iodide. A series of analogous trialkoxysilylpropyl tethered imidazolium salts, **6**-**7** were also prepared by using similar synthetic routes or by microwave irradiation.

Direct reaction of these imidazolium salts with nickelocene or [Ni(acac)Cp*] allowed to prepare the corresponding [Ni(R-NHC-*n*-Bu)XCp†] (Cp† = Cp, Cp*; R = Me, *i*-Pr, Ph, Mes, *i*-Pr$_2$Ph; X = Cl, I), **3-5**, [Ni(R-NHC-TMS)XCp] (R = Me, *i*-Pr, Ph; X = Cl, I), **8-9**, and [Ni(Ar-NHC-TES)ClCp] (Ar = Mes, *i*-Pr$_2$Ph), **8'**, complexes in good yields.

Single-crystal X-ray diffraction studies of complexes **3b,c**, **4d,e** and **5b,c** revealed that these compounds have geometric features common to all 18-electron NiCp†L$_2$ (Cp† = Cp, Cp*) complexes and, in particular, to [Ni(R$^2_2$-NHC)XCp] compounds. Moreover, no significant distortion of the coordination sphere around the nickel atom with respect to that of closely related symmetric [Ni(Ar$_2$-NHC)ClCp†] complexes was noticed. Nevertheless, ^{1}H NMR data revealed that the replacement of the chloride ligand by the much bulkier iodide ligand hampers the rotation about the nickel–carbene bond at room temperature whatever the nature of the Cp† ligand: Cp or Cp*. Thus, in contrast to [Ni(Ar$_2$-NHC)ClCp] (Ar = Mes, *i*-Pr$_2$Ph) species, complexes [Ni(Ar-NHC-*n*-Bu]ICp] **3b** (Ar = Mes) and **3c** (Ar = *i*-Pr$_2$Ph) show a barrier to nickel-carbene bond rotation ($\Delta G^{\#}$ = 60-61 ± 2 kJ.mol^{-1}) that was elucidated by VT ^{1}H NMR studies. The barrier is believed to be predominantly steric in nature but electronic contribution to this barrier can not be ruled out.

Accordingly, in contrast to **3b** and **3c**, which bear a bulky iodide ligand, the triethoxysilylpropyl tethered complexes [Ni(Ar-NHC-TES)ClCp] **8'b** (Ar = Mes) and **8'c** (Ar = *i*-Pr$_2$Ph), which carry a smaller chloride ligand, show a reduced barrier to the Ni–C(1) bond rotation at room temperature on the NMR time scale ($\Delta G^{\neq}$ = 51 ± 2 kJ.mol^{-1}). This result confirms the prevalent role played by the voluminous iodide ligand in hampering free rotation about the nickel-carbene bond in complexes **3b**,**c**, and shows that despite its position far off the nickel centre, the very bulky triethoxysilylpropyl arm is non innocent regarding to the dynamic processes in **8'b** and **8'c**.

As the symmetric [Ni(Ar$_2$-NHC)XCp†] (X = Cl$^-$; NCMe, PF$_6^-$) complexes, all [Ni(R-NHC-*n*-Bu)XCp†] complexes **3**-**5** appeared to be highly active catalyst for the Suzuki-Miyaura cross-coupling of 4'-bromoacetophenone and phenylboronic acid *in the absence of reductant and co-catalyst*. Thus, the substitution of one aryl group by a *n*-butyl chain does not affect the catalytic

activity of half-sandwich Ni(II)-NHC complexes for Suzuki-Miyaura cross-couplings. Moreover, by employing **3b** for these substrates, a notably higher turnover frequency (TOF) than with [Ni(*i*-$Pr_2Ph)_2$-NHC)(NCMe)Cp*](PF_6) was observed; TOF of 352 h^{-1} and 190 h^{-1}, respectively. So far, such a TOF has not been matched by other Ni(II)-NHC catalytic systems. Complexes **3b,c** are active with both aryl bromides and chlorides. However, as for the symmetric species [Ni(Ar_2-NHC)XCp†] (X = Cl^-; NCMe, PF_6^-), the substrate scope is more or less limited to aryl halides bearing electron-withdrawing groups.

The significant stabilization of the active species, which allowed to decrease the catalyst loading from 3 mol% to 1 mol% with complexes **3-5** with respect to the symmetric catalysts, that bear either a chloride or an acetonitrile ligand, was attributed to the presence of the voluminous iodide ligand rather than to that of the *n*-butyl arm, the latter being most probably too far off the metal centre to exert such an influence. The lack of improvement observed with **3c** and **5b** (with respect to **3b**) shows that in presence of the highly protecting iodide ligand, neither a faster reduction from the starting Ni(II) complex to the active Ni(0) by an electron-rich Cp* nor a better steric protection by a Cp* ring or NHC aryl-substituents do play a significant role anymore in contrast to what was observed with the symmetric complexes. These results further hint that the coordinatively unsaturated intermediate that may appear during the catalytic cycle should be generated by Cp† ring slippage rather than by decoordination of the halide (or acetonitrile) ligand.[16]

The complex [Ni(Mes-NHC-TES)ClCp], **8'b**, was covalently grafted onto alumina and the resulting hybrid material **10** was analyzed by ^{1}H MAS solid state NMR, DRIFT and ICP-AES. A significant decrease of activity was observed for the Suzuki-Miyaura cross-coupling of 4'-bromoacetophenone and phenylboronic acid. However, at this stage, it is unclear to what extent this activity drop is due to the immobilization itself or to the presence of a small chloride instead of the highly protecting iodide.

The investigation of the catalytic activity of the "free" silyl-functionalized catalyst **8'b** probably clarifies the latter point. Furthermore, the immobilization of a iodo-Ni(II)-NHC complex as well as the study of the catalytic activity of this heterogenized version could also be considered. Furthermore, substitution of the chloride by a iodide ligand in symmetric [Ni(Ar_2-NHC)XCp†] complexes might show even better catalytic activities that the asymmetric *n*-butyl counterparts.

4. Experimental

General comments. All reactions were carried out using standard Schlenk techniques under an atmosphere of dry argon. Solvents were distilled from appropriate drying agents under argon

prior to use. Solution NMR were recorded at 298 K, unless otherwise specified, on FT-Bruker Ultra Shield 300 and FT-Bruker Spectrospin 400 spectrometers operating at 300.13 or 400.14 MHz for ^{1}H and at 75.47 MHz or 100.61 MHz for ^{13}C{^{1}H}. DEPT ^{13}C spectra were obtained for all complexes to help in the ^{13}C signal assignments. Supplementary 2D COSY and HBQC spectra were obtained for **3a** and **3b**. The chemical shifts are referenced to residual deuterated solvent peaks. Chemical shifts (δ) and coupling constants (*J*) are expressed in ppm and Hz, respectively. The ^{1}H NMR variable-temperature experiments were recorded at 400.14 MHz from 298 to 368 K in $C_2D_2Cl_4$ for complexes **3b**, **3c** and from 223 to 298 K in $CDCl_3$ for **8'b**. HRMS were recorded on a MALDI-TOF Biflex Bruker mass spectrometer for the compounds. ES-MS were recorded on a MicrOTOF 66 mass spectrometer. Elemental analysis were performed by the Service d'Analyses, de Mesures Physiques et de Spectroscopie Optique, UMR CNRS 7177, at the Institut de Chimie, Université de Strasbourg. DRIFTS and ^{1}H MAS data collection were performed by Dr. R. Gauvin, Unité de Catalyse et de Chimie du Solide, UMR CNRS 8181, Villeneuve d'Asq. ICP-AES was performed by the Laboratoire de Chimie Analytique et Minérale, UMR CNRS 7178, Institut Pluridisciplinaire Hubert Curien (IPHC), Université de Strasbourg. Commercial compounds were used as received. 1-Isopropyl-1*H*-imidazole,[35] 1-phenyl-1*H*-imidazole,[36] 1-mesityl-1*H*-imidazole,[37] 1-(2,6-diisopropylphenyl)-1*H*-imidazole,[36] 1-methyl-3-butylimidazolium chloride **2e**,[38] and bis(2,4-pentanedionato)nickel(II)[47] were prepared according to published methods. 1-Methyl-3-[3-(trimethoxysilyl)propyl]imidazolium chloride **7d** was synthesized by a modified micro-wave assisted synthesis route.[29]

Synthesis of 1-butyl-3-phenylimidazolium iodide (1a). A suspension of 1-phenyl-*1H*-imidazole (0.720 g, 4.99 mmol), 1-chlorobutane (0.470 g, 0.530 mL, 5.07 mmol) and KI (0.830 g, 5.00 mmol) in DME (10 mL) was vigorously stirred at 75 °C for 18 h. The mixture was cooled to r.t. and the solvent removed under vacuum. The residue was extracted with acetonitrile (10 mL), filtered over a Celite pad, and rinsed with acetonitrile (2 x 5 mL). The acetonitrile was evaporated, the residue washed with toluene (5 x 3 mL) and crystallized (toluene, 3 mL, r.t., 3 h). The crystals were washed with toluene (3 x 2 mL) and diethyl ether (3 x 2 mL), and dried in vacuo. **1a** was obtained as a light brown solid (0.825 g, 2.50 mmol, 50 %). HRMS (MALDI TOF): *m/z* $[M]^+$ calcd for $C_{13}H_{17}N_2$: 201.1403; *found*: 201.1386. ^{1}H NMR ($CDCl_3$; 300.13 MHz): δ = 10.59 (br s, 1H, NC*H*N), 7.80 (m, 2H, Ph), 7.73 and 7.68 (t, ^{3}J = 1.8, 1H, NC*H*), 7.55 (m, 3H, Ph), 4.59 (t, ^{3}J = 7.4, 2H, NCH_2), 1.98 (tt, ^{3}J = 7.4, ^{3}J = 7.8, 2H, NCH_2CH_2), 1.44 (qt, ^{3}J = 7.8, ^{3}J = 7.4, 2H, CH_2CH_3), 0.97 (t, ^{3}J = 7.4, 3H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ = 135.4 (N*C*HN), 134.5 (*ipso*-

C_{Ar}), 130.8 (*o*-C_{Ar}), 130.6 (*p*-C_{Ar}), 123.4 and 121.0 (N*C*H), 122.2 (*m*-C_{Ar}), 50.6 (N*C*H_2), 32.4 (NCH$_2$*C*H_2), 19.7 (*C*H_2CH$_3$), 13.7 (*C*H_3).

Synthesis of 1-butyl-3-(2,4,6-trimethylphenyl)imidazolium iodide (1b). A suspension of 1-mesityl-1*H*-imidazole (1.856 g, 9.97 mmol), 1-chlorobutane (2.816 g, 3.20 mL, 30.62 mmol) and KI (2.800 g, 16.9 mmol) in DME (40 mL) was vigorously stirred at 75 °C for 48 h. The mixture was cooled to r.t. and the solvent removed under vacuum. The residue was extracted with acetonitrile (30 mL) and filtered over Celite, which was rinsed with acetonitrile (2 x 10 mL). Acetonitrile was evaporated and the resulting dense yellow oil was crystallized (toluene, 3 mL, r.t. 1 h). The crystals were washed with toluene (3 x 2 mL) and diethyl ether (3 x 2 mL) and dried in vacuo. **1b** was obtained as a white solid (3.221 g, 8.70 mmol, 87 %). HRMS (MALDI TOF): *m/z* $[M]^+$ calcd for $C_{16}H_{23}N_2$: 243.1862; *found*: 243.1856. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 10.06 (bs, 1H, NC*H*N), 7.82 and 7.21 (d, ^3J = 1.7, 1H, NC*H*), 6.99 (s, 2H, *m*-H), 4.71 (t, ^3J = 7.3, 2H, NCH_2), 2.33 (s, 3H, *p*-Me), 2.07 (s, 6H, *o*-Me), 1.97 (tt, ^3J = 7.3, ^3J = 7.8, 2H, NCH$_2$CH_2), 1.42 (qt, ^3J = 7.8, ^3J = 7.3, 2H, CH_2CH$_3$), 0.97 (t, ^3J = 7.3, 3H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ = 141.5 (*p*-C_{Ar}), 137.4 (N*C*HN), 134.3 (*o*-C_{Ar}), 130.6 (*ipso*-C_{Ar}), 130.0 (*m*-C_{Ar}), 123.4 and 123.3 (N*C*H), 50.5 (N*C*H_2), 32.6 (NCH$_2$*C*H_2), 21.2 (*p*-Me), 19.5 (*C*H_2CH$_3$), 18.0 (*o*-Me), 13.7 (*C*H_3).

Synthesis of 1-butyl-3-(2,6-diisopropylphenyl)imidazolium iodide (1c). A suspension of 1-(2,6-diisopropylphenyl)-1*H*-imidazole (2.310 g, 10.12 mmol), 1-chlorobutane (3.367 g, 3.80 mL, 36.37 mmol) and KI (2.800 g, 16.87 mmol) in DME (40 mL) was vigorously stirred at 75 °C for 50 h. The mixture was cooled to r.t. and the solvent removed under vacuum. The residue was extracted with acetonitrile (20 mL), filtered over Celite, and rinsed with acetonitrile (3 x 3 mL). Acetonitrile was evaporated; the residue was washed with toluene (3 x 3 mL) and crystallized (toluene, 3 mL, r.t., 2 h). The crystals were washed with toluene (3 x 2 mL) and diethyl ether (3 x 2 mL) and dried in vacuum. **1c** was obtained as a pale yellow solid (3.291 g, 7.98 mmol, 79 %). HRMS (MALDI TOF): *m/z* $[M]^+$ calcd for $C_{19}H_{29}N_2$: 285.2325; *found*: 285.2321. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ =10.14 (bs, 1H, NC*H*N), 7.88 (d, ^3J = 1.7, 1H, NC*H*), 7.54 (t, ^3J = 8.0, 1H, *p*-H), 7.31 (d, ^3J = 8.0, 2H, *m*-H), 7.21 (d, ^3J = 1.7, 1H, NC*H*), 4.80 (t, ^3J = 7.2, 2H, NCH_2), 2.29 (hept, ^3J = 6.8, 2H, C*H*), 2.00 (tt, ^3J = 7.2, ^3J = 7.6, 2H, NCH$_2$CH_2), 1.43 (qt, ^3J = 7.6, ^3J = 7.4, 2H, CH_2CH$_3$), 1.24 (d, ^3J = 6.8, 6H, CH*Me*$_2$), 1.15 (d, ^3J = 6.8, 6H, CH*Me*$_2$), 1.00 (t, ^3J = 7.4, 3H, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ = 145.5 (*o*-C_{Ar}), 137.6 (N*C*HN), 132.1 (*p*-C_{Ar}), 130.0 (*ipso*-C_{Ar}), 124.9 (*m*-

C_{Ar}), 124.4 and 123.4 (N*C*H), 50.5 (N*C*H_2), 32.7 (NCH$_2$*C*H$_2$), 28.9 (*C*HMe$_2$), 24.7 (CH*Me*$_2$), 24.3 (CH*Me*$_2$), 19.4 (*C*H_2CH$_3$), 13.7 (*C*H_3).

Synthesis of 1-butyl-3-isopropylimidazolium chloride (2d). 1-Isopropyl-1*H*-imidazole (0.575 g, 5.22 mmol) was added to 1-chlorobutane (0.930 g, 1.05 mL, 10.0 mmol). The mixture was stirred at 75 °C for 12 h. The mixture was cooled to r.t. and excess 1-chlorobutane was removed under reduced pressure. The resultant oil was further dried in vacuo (30 °C, 2 h). **2d** was obtained as a colourless oil in quantitative yield (1.062 g. 5.26 mmol). HRMS (MALDI TOF): *m/z* $[M]^+$ calcd for $C_{10}H_{19}N_2$: 167.1543; *found*: 167.1528. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 10.80 (bs, 1H, NC*H*N), 7.58 and 7.48 (d, ^3J = 1.8, 1H, NC*H*), 4.85 (hept, ^3J = 6.7, 1H, C*H*Me$_2$), 4.30 (t, ^3J = 7.5, 2H, NC*H*$_2$), 1.83 (tt, ^3J = 7.5, ^3J = 7.6, 2H, NCH$_2$C*H*$_2$), 1.54 (d, ^3J = 6.7, 6H, CH*Me*$_2$), 1.30 (qt, ^3J = 7.6, ^3J = 7.4, 2H, C*H*$_2$CH$_3$), 0.87 (t, ^3J = 7.4, 3 H, C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ = 136.7 (N*C*HN), 122.2 and 120.1 (N*C*H), 53.2 (*C*HMe$_2$), 49.7 (N*C*H_2), 32.3 (NCH$_2$*C*H$_2$), 23.3 (CH*Me*$_2$), 19.6 (*C*H_2CH$_3$), 13.5 (*C*H_3).

Synthesis of [Ni{Ph-NHC-*n*-Bu}ICp] (3a). To a suspension of **1a** (213 mg, 0.65 mmol) in thf (12 mL) was added nickelocene (123 mg, 0.65 mmol). The resulting suspension was heated at 85 °C under vigorous stirring for 18 h during which time the solution colour slowly turned from dark green to dark red. The resulting solution was cooled to r.t. and the solvent was evaporated under vacuum. The residue was crystallized in cold solutions of toluene and pentane (1: 4), washed with pentane (3 x 3 mL) and **3a** was obtained as red crystals in 66 % yield (194 mg,0.43 mmol). *Anal.* calcd for $C_{18}H_{21}IN_2Ni$: C: 47.94, H: 4.69, N: 6.21; *found*: C: 48.00, H: 4.820, N: 6.055. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 8.09 (m, 2H, Ph), 7.57 (m, 3H, Ph), 7.14 and 7.11 (d, ^3J = 1.9, 1H, NC*H*), 5.17 and 4.58 (m, 1H, NC*H*$_2$), 4.90 (s, 5H, η^5-C$_5$*H*$_5$), 2.01 and 1.90 (m, 1H, NCH$_2$C*H*$_2$), 1.55 (m, 2H, MeC*H*$_2$), 1.07 (t, ^3J = 7.3, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ = 165.9 (N*C*N), 140.9 (*ipso*-C_{Ar}), 129.1 (*o*-/*m*-C_{Ar}) and 126.5 (*m*-/*o*-C_{Ar}), 128.6 (*p*-C_{Ar}), 123.7 and 122.6 (N*C*H), 92.0 (η^5-*C*$_5$H$_5$), 53.2 (N*C*H_2), 32.9 (*C*H_2), 20.3 (*C*H_2CH$_3$), 14.1 (*C*H_3).

Synthesis of [Ni(Mes-NHC-*n*-Bu)ICp] (3b). To a suspension of **1b** (1.250 g, 3.03 mmol) in DME (40 mL) was added nickelocene (566 mg, 3.03 mmol). The mixture was refluxed for 39 h, during which time the solution colour slowly turned from dark green to dark red. The mixture was cooled to r.t., the solvent was then removed under vacuum and excess nickelocene was extracted

with pentane (3 x 5 mL). Column chromatography over neutral silica with diethyl ether/pentane (7: 3) as eluent afforded **3b** as a deep red-violet solid after solvent evaporation (1.06 g, 1.98 mmol, 65 %). ES-MS: *m/z* $[M]^+$ calcd for $C_{21}H_{27}N_2Ni$: 365.152; *found*: 365.150. ^1H NMR ($CDCl_3$, 263 K, 400.14 MHz): δ = 7.16 (s, 2H, *m*-H), 6.99 and 6.87 (s, 1H, NC*H*), 5.47 and 4.36 (m, 1H, NCH_2), 4.88 (s, 5H, η^5-C_5H_5), 2.47 (s, 3H, *o*-Me), 2.42 (s, 3H, *o*-Me), 2.01 and 1.90 (m, 1H, NCH_2CH_2), 1.74 (s, 3H, *p*-Me), 1.49 and 1.44 (2m, 2 x 1H, CH_2CH_3), 1.05 (t, 3H, CH_2CH_3, ^3J = 7.3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.47 MHz): δ = 166.4 (N*C*N), 139.1 (*p*-C_{Ar}), 137.9 and 134.4 (*o*-C_{Ar}), 136.9 (*ipso*-C_{Ar}), 130.1 and 128.66 (*m*-C_{Ar}), 124.4 and 122.5 (N*C*H), 91.8 (η^5-C_5H_5), 53.6 (NCH_2), 33.1 (NCH_2CH_2), 21.3 (*p-Me*), 20.1 (CH_2CH_3), 18.0 and 17.9 (*o-Me*), 14.1 (CH_2CH_3).

Synthesis of [Ni(*i*-Pr$_2$Ph-NHC-*n*-Bu)ICp] (3c). To a suspension of **1c** (1.25 g, 3.03 mmol) in DME (40 mL) was added nickelocene (566 mg, 3.03 mmol). The mixture was stirred at 85 °C for 39 h during which time the solution colour slowly turned from dark green to dark red. The solvent was then removed under vacuum and excess nickelocene was extracted with pentane (4 x 5 mL). Column chromatography over neutral silica with diethyl ether/pentane (7: 3) as eluent afforded **3c** (1.103 g, 2.06 mmol, 68 %) as a pink solid afer solvent evaporation and drying under reduced pressure. ES-MS: *m/z* $[M]^+$ calcd for $C_{24}H_{33}N_2Ni$: 407.199; *found*: 407.195. ^1H NMR ($CDCl_3$, 253 K, 400.14 MHz): δ = 7.54 (m, 1H, *p*-H), 7.46 (d, ^3J = 6.8, 1H, *m*-H), 7.26 (d, 1H, ^3J n.r, *m*-H), 7.16 and 6.93 (d, 1H, ^3J = 1.7, NC*H*), 5.47 and 4.37 (m, 1H, NCH_2), 4.80 (s, 5H, η^5-C_5H_5), 3.41 (sept, 1H, ^3J = 6.8, C*H*$(Me)_2$), 2.01 and 1.90 (m, 1H, NCH_2CH_2), 1.72 (sept, 1H, ^3J = 6.8, C*H*$(Me)_2$), 1.46 (d, 3H, ^3J = 6.8, CH*Me*$_2$, and m, 2H, CH_2CH_3), 1.20 (d, 3H, ^3J = 6.8, CH*Me*$_2$), 1.05 (d, 3H , ^3J = 6.8, CH*Me*$_2$, and t, 3H, ^3J = 7.2, CH_2CH_3), 0.97 (d, 3H, ^3J = 6.8, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.47 MHz): δ = 167.9 (N*C*N), 148.4 and 145.5 (b, *o*-C_{Ar}), 136.7 (*ipso*-C_{Ar}), 130.2 (*p*-C_{Ar}), 126.1 and 122.0 (N*C*H), 124.9 and 123.4 (b, *m*-C_{Ar}), 91.6 (η^5-C_5H_5), 54.0 (NCH_2), 33.1 (NCH_2CH_2), 28.7 and 28.2 (b, *C*HMe_2), 26.9, 26.1, 23.7 and 22.6 (b, CH*Me*$_2$), 20.1 (CH_2CH_3), 14.1 (CH_2CH_3).

Synthesis of [Ni(Me-NHC-*n*-Bu)ClCp] (4d). To a suspension of **2d** (339 mg, 1.92 mmol) in thf (20 mL) was added nickelocene (553 mg, 2.93 mmol). The reaction medium was stirred at 65 °C for 2 h, cooled to r.t. and the solvent was evaporated under vacuum. The residue was extracted with hot toluene (3 x 5 mL), filtered over Celite and the solvent was evaporated under vacuum to *ca.* 1 mL. Column chromatography over neutral silica with ethyl acetate/pentane (8.5:1.5) as eluent afforded **4d** (282 g, 0.94 mmol, 49 %) as dark red needles from cold solutions of toluene/pentene.

ES-MS: *m/z* $[M]^+$ calcd for $C_{13}H_{19}N_2Ni$: 261.089; *found*: 261.090. ^1H NMR ($CDCl_3$, 300.13 MHz): δ = 6.91 (bs, 2H, NC*H*), 5.22 (s, 5H, η^5-C_5H_5), 4.75 (bs, 2H, NCH_2), 4.33 (s, 3H, *Me*), 1.94 (bs, 2H, NCH_2CH_2), 1.51 (m, 2H, CH_2CH_3), 1.05 (t, ^3J = 7.35, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.47 MHz): δ = 159.6 (N*C*N), 123.5 and 121.8 (N*C*H), 91.7 (η^5-C_5H_5), 51.7 (NCH_2), 38.9 (*Me*), 33.2 (NCH_2CH_2), 20.2 (CH_2CH_3), 14.0 (CH_2CH_3).

Synthesis of [Ni(*i*-Pr-NHC-*n*-Bu)ClCp] (4e). To a suspension of **2e** (189 mg, 0.93 mmol) in DME (9 mL) was added nickelocene (176 mg, 0.93 mmol). The green suspension was stirred at 65 °C for 2 h. The resulting dark red solution was cooled to r.t. and the solvent was reduced under vacuum to *ca.* 1 mL. The solution was purified by chromatography over neutral silica with diethyl ether, the solvent was then evaporated under vacuum and **4e** was obtained as dark red crystals (175 mg, 0.54 mmol, 57 %). ES-MS: *m/z* $[M]^+$ calcd for $C_{15}H_{23}N_2Ni$: 289.122; *found*: 289.121. ^1H NMR ($CDCl_3$, 300.13 MHz) : δ = 6.96 and 6.94 (d, ^3J = 2.1, 1H, NC*H*), 6.47 (pseudoseptet, ^3J = 6.8, 1H, C*H*), 5.22 (s, 5H, η^5-C_5H_5), 4.90 and 4.70 (m, 1H, NCH_2), 2.00 and 1.89 (m, 1H, NCH_2CH_2), 1.54 (d, ^3J = 6.8, 6H, $CH(Me)_2$) and (m, 2H, CH_2Me), 1.06 (t, ^3J = 7.5, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.47 MHz): δ = 158.2 (N*C*N), 122.2 and 118.1 (N*C*H), 91.8 (η^5-C_5H_5), 53.7 (*C*H), 51.7 (NCH_2), 33.3 (NCH_2CH_2), 23.8 ($CHMe_2$), 20.3 (CH_2CH_3), 14.0 (CH_2CH_3).

Synthesis of [Ni(Mes-NHC-*n*-Bu)ICp*] (5b). *n*-Butyllithium (0.530 mL, 1.6 M solution in hexanes, 0.85 mmol) was added dropwise at –30 °C to a solution of pentamethylcyclopentadiene (0.140 mL, 0.85 mmol) in thf (2 mL). The resulting white suspension of LiCp* was stirred at this temperature for 5 min. A green solution of *bis*-(2,4-pentanedionato)nickel(II) (218 mg, 0.85 mmol) in thf (2 mL) was added and the resulting mixture was stirred at –30 °C for 5 more minutes. The reaction mixture was then allowed to reach r.t. and was stirred for 1 h to afford a dark red suspension of [NiCp*(acac)]. To that suspension was added **1b** (315 mg, 0.85 mmol) in a single portion and the reaction mixture was stirred at reflux for 3 h. The resulting red-violet suspension was cooled to r.t. and the solvent evacuated under vacuum. The residue was dissolved in toluene (5 mL) and filtered over silica, which was rinsed with toluene (4 x 5 mL) till the washings were colourless. The mixture was concentrated to *ca.* 1 mL under vacuum, then, pentane (5 mL) was added and the solution was crystallized overnight at -32 °C. **5b** (145 mg, 0.260 mmol, 30 %) was isolated as a dark red solid which was washed with pentane (3 x 3 mL) and dried under vacuum for 2 h. ^1H NMR (C_6D_6, 400.14 MHz): δ = 6.88 (s, 1H, *m*-H), 6.66 (s, 1H, *m*-H), 6.40 and 6.01 (d, ^3J = 1.6, 1H, NC*H*), 4.94 (m, 2H, NCH_2), 2.95 (s, 3H, *o*-Me), 2.14 (s, 3H, *p*-Me), 1.75 (m, 1H,

NCH_2CH_2), 1.57 (s, 3H, *o*-Me), 1.46 (s, 15H, C_5Me_5), 1.39 (m, 1H and 2H, CH_2CH_2 and CH_2CH_3), 0.94 (t, ^3J = 7.2, 3H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.47 MHz): δ = 175.4 (N*C*N), 138.1 and 137.8 (*o*-C_{Ar}), 136.6 (*ipso*-C_{Ar}), 134.6 (*p*-C_{Ar}), 130.1 and 128.3 (*m*-C_{Ar}), 124.6 and 119.9 (N*C*H), 101.3 (C_5Me_5), 53.7 (NCH_2), 32.7 (NCH_2CH_2), 23.7 (*o*-Me), 20.6 (*p*-Me), 20.3 (CH_2CH_3), 18.4 (*o*-Me), 13.9 (CH_2CH_3), 10.7 (C_5Me_5).

Synthesis of [Ni(*i*-Pr$_2$Ph-NHC-*n*-Bu)ICp*] (5c). *n*-Butyllithium (0.600 mL, 1.6 M solution in hexanes, 1.00 mmol) was added dropwise at –30 °C to a solution of pentamethylcyclopentadiene (0.160 mL, 1.00 mmol) in thf (5 mL). The resulting white suspension of LiCp* was stirred at this temperature for 5 min. A green solution of *bis*-(2,4-pentanedionato)nickel(II) (257 mg, 1.00 mmol) in thf (5 mL) was added and the resulting mixture was stirred at –30 °C for 5 more minutes. The reaction mixture was then allowed to reach r.t. and was stirred for 1 h to afford a dark red suspension of [NiCp*(acac)]. To that suspension was added **1c** (323 mg, 0.780 mmol) in a single portion and the reaction mixture was stirred at reflux for 3 h. The resulting red-violet suspension was cooled to r.t. and the solvent evacuated under vacuum. The residue was dissolved in toluene (10 mL) and filtered through silica, which was rinsed with toluene (3 x 10 mL) till the washings were colourless. The mixture was concentrated to *ca.* 1 mL under vacuum, then, pentane (10 mL) was added and the solution was crystallized overnight at -32 °C. **5c** (160 mg, 0.260 mmol, 34 %) was isolated as a dark red solid which was washed with pentane (3 x 3 mL) and dried under vacuum for 2 h. *Anal.* calcd for $C_{29}H_{43}IN_2Ni$: C: 57.54, H: 6.628, N: 7.161; *found*: C: 57.62, H: 4.281, N: 7.064. ^1H NMR ($CDCl_3$, 300.13 MHz): δ = 7.44 (m, 2H, *m*-H), 7,21 (d, ^3J = 6.4, 1H, *p*-H), 7.13 and 6.87 (d, ^3J = 1.8, 1H, NC*H*), 5.38 and 4.78 (m, 1H, NCH_2), 4.28 (sept., ^3J = 6.8, 1H, C*H*Me$_2$-A), 2.06 and 1.83 (m, 1H, NCH_2CH_2), 1.98 (sept., ^3J = 6.8, 1H, C*H*Me$_2$-B), 1.59 (m, 2H, CH_2CH_3), 1.42 and 0.87 (d, ^3J = 6.8, 3H, CHMe_2-A), 1.30 (s, 15H, C_5Me_5), 1.24 and 1.12 (d, ^3J = 6.8, 3H, CHMe_2-B), 1.08 (t, ^3J = 7.4, 3H, CH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.47 MHz): δ = 148.4 and 145.8 (*o*-C_{Ar}), 136.4 (*ipso*-C_{Ar}), 129.9 and 125.2 (*m*-C_{Ar}), 126.8 (N*C*H'), 123.7 (*p*-C_{Ar}), 119.2 (N*C*H), 101.8 (C_5Me_5), 54.7 (NCH_2), 33.2 (NCH_2CH_2), 29.3 (*C*HMe$_2$ A), 28.2 (*C*HMe$_2$ B), 28.0 and 23.0 (CHMe_2-B), 25.9 and 23.2 (CHMe_2-A), 20.6 (CH_2CH_3), 14.3 (CH_2CH_3), 10.8 (C_5Me_5).

Synthesis of 1-phenyl-3-[3-(trimethoxysilyl)propyl]imidazolium iodide (6a). A suspension of 1-phenyl-*1H*-imidazole (1.586 g, 11.00 mmol), (3-chloropropyl)trimethoxysilane (2.15 g, 2.00 mL, 10.97 mmol) and KI (3.100 g, 18.67 mmol) in DME (40 mL) was vigorously stirred at 85 °C for 63 h. The reaction mixture was cooled to r.t. and the solvent removed under vacuum. The

residue was extracted with acetonitrile (20 mL) and filtered over Celite and rinsed with acetonitrile (2 x 10 mL). Acetonitrile was evaporated and the residue was washed with toluene (4 x 5 mL) and dried in vacuum for 3 h. **6a** was obtained as a brown oil (3.631 g, 8.40 mmol, 76 %), that was contaminated with small quantities of (3-chloropropyl)trimethoxysilane. HRMS (MALDI TOF): *m/z* $[M]^+$ calcd for $C_{15}H_{23}N_2O_3Si$: 307.1472; *found*: 307.1457. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 10.57 (s, 1H, NC*H*N), 7.80 – 7.54 (m, 7H, Ph and 2 NC*H*), 4.60 (t, ^3J = 7.3, 2H, NCH_2), 3.57 (s, 9H, Si(OCH_3)$_3$), 2.10 (m, ^3J = 8.1, ^3J = 7.3, 2H, CH_2), 0.74 – 0.69 (m, 2H, SiCH_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ = 135.3 (N*C*N), 134.5 (*ipso*-C, Ph), 130.8 and 122.2 (*o*/*m*-C_{Ar}, Ph), 130.6 (*p*-C_{Ar}, Ph), 123.5 and 121.0 (N*C*H), 52.5 (N*C*H_2), 51.0 (Si(O*C*H_3)$_3$), 24.3 (*C*H_2), 6.1 (*C*H_2Si).

Synthesis of 1-(2,4,6-trimethylphenyl)-3-[3-(trimethoxysilyl)propyl]imidazolium iodide (6b). A suspension of 1-mesityl-1*H*-imidazole (0.923 g, 4.96 mmol), (3-chloropropyl)trimethoxysilane (1.003 g, 0.92 mL, 5.05 mmol) and KI (0.996 g, 6.00 mmol) in DME (20 mL) was vigorously stirred at 85 °C for 60 h. The mixture was cooled to r.t. and the solvent removed under vacuum. The residue was extracted with acetonitrile (12 mL), filtered over Celite, and rinsed with acetonitrile (3 x 4 mL). Acetonitrile was evaporated and the residue was washed with hot toluene (3 x 3 mL) and dried in vacuo. **6b** was obtained as a pale yellow solid (2.212 g, 4.67 mmol, 94 %). HRMS (MALDI TOF): *m/z* $[M]^+$ calcd for $C_{18}H_{29}N_2O_3Si$: 349.1942; *found*: 349.1940. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 9.99 (bs, 1H, NC*H*N), 7.76 (d, ^3J = 1.7, 1H, NC*H*), 7.21 (d, ^3J = 1.7, 1H, NC*H*), 6.99 (s, 2H, *m*-H), 4.70 (t, ^3J = 7.2, 2H, NCH_2), 3.56 (s, 9H, Si(OCH_3)$_3$), 2.33 (s, 3H, *p*-Me), 2.10 (tt, ^3J = 7.2, ^3J = 7.9, 2H, CH_2), 2.08 (s, 6H, *o*-Me), 0.68 (m, ^3J = 7.9, 2H, CH_2Si). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ = 141.6 (*p*-C_{Ar}), 137.5 (N*C*N), 134.4 (*o*-C_{Ar}), 130.7 (*ipso*-C_{Ar}), 130.1 (*m*-C_{Ar}), 123.4 (N*C*H), 52.4 (N*C*H_2), 51.0 (Si(O*C*H_3)$_3$), 24.6 (*C*H_2), 21.3 (*p*-Me), 18.0 (*o*-Me), 5.8 (*C*H_2Si).

Synthesis of 1-(2,4,6-trimethylphenyl)-3-[3-(triethoxysilyl)propyl]imidazolium chloride (6'b). 1-Mesityl-1*H*-imidazole (559 mg, 3.0 mmol), (3-chloropropyl)triethoxysilane (0.72 mL, 3.0 mmol) and thf (1 mL) were mixed in a 10-mL sealed vessel and placed in a Discover CEM S-class microwave oven operating at 2450 MHz. The mixture was heated rapidly and kept at 180 °C for 20 min while stirring magnetically. The reaction medium was cooled at 60 °C and taken out of the microwave reactor. **6'b** (978 mg, 2.3 mmol, 76 %) was obtained as a white solid after washings with toluene (2 x 3 mL) and pentane (2 x 5 mL) and drying under vacuum for 2 h. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 10.70 (s, 1H, NC*H*N), 7.69 and 7.16 (t, ^3J = 1.6, 1H, NC*H*), 6.96 (s, 2H, *m*-H),

4.72 (t, ^3J = 7.0, 2H, NCH_2), 3.80 (q, ^3J = 7.1, 6H, Si(CH_2CH$_3$)$_3$), 2.31 (s, 3H, *p*-Me), 2.08 (m, 2H, CH_2), 2.04 (s, 6, *o*-Me), 1.19 (t, ^3J = 7.1, 9H, Si(CH$_2$CH_3)$_3$). ^{13}C{^{1}H} NMR (CDCl$_3$, 75.47 MHz): δ = 141.4 (*ipso*/*p*-C$_{Ar}$), 139.2 (N*C*N), 134.4 (*o*-C$_{Ar}$), 131.0 (*p*/*ips*o-C$_{Ar}$), 130.0 (*m*-C$_{Ar}$), 123.1 and 122.7 (N*C*H), 58.8 (Si(O*C*H$_2$CH$_3$)$_3$), 52.2 (N*C*H$_2$), 24.8 (*C*H$_2$), 21.3 (*p*-Me), 18.5 (*o*-Me), 17.8 (Si(CH$_2$*C*H$_3$)$_3$), 7.2 (*C*H$_2$Si).

Synthesis of 1-(2,6-diisopropylphenyl)-3-[3-(trimethoxysilyl)propyl]imidazolium iodide (6c). A suspension of 1-(2,6-diisopropylphenyl)-1*H*-imidazole (2.288 g, 10.02 mmol), 3-chloropropyltrimethoxysilane (1.94 g, 1.80 mL, 9.76 mmol) and KI (1.999 g, 12.04 mmol) in DME (40 mL) was vigorously stirred at 85 °C for 47 h. The mixture was cooled to r.t. and the solvent was removed under vacuum. The residue was extracted with acetonitrile (15 mL) and filtered over Celite. Volatiles were evaporated under reduced pressure and the residue was washed with hot toluene (3 x 3 mL) followed by drying in vacuum for 2 h at 30 °C. **6c** was obtained as a pale yellow solid (3.271 g, 6.31 mmol, 63 %). HRMS (MALDI TOF): *m/z* [M]$^+$ calcd for C$_{21}$H$_{35}$N$_2$O$_3$Si: 391.2423; *found*: 391.2411. ^{1}H NMR (CDCl$_3$, 300.13 MHz): δ = 9.90 (bs, 1H, NC*H*N), 8.02 (d, ^3J = 1.7, 1H, NC*H*), 7.48 (t, ^3J = 7.8, 1H, *p*-*H*), 7.26 (t, ^3J = 1.7, 1H, NC*H*), 7.24 (d, ^3J = 7.8, 2H, *m*-*H*), 4.69 (t, ^3J = 7.0, 2H, NCH_2), 3.50 (s, 9H, Si(OCH_3)$_3$), 2.22 (hept., ^3J = 6.8, 2H, C*H*Me$_2$), 2.06 (tt, ^3J = 7.0, ^3J = 8.1, 2H, CH_2), 1.16 (d, ^3J = 6.8, 6H, CH*Me*$_2$), 1.09 (d, ^3J = 6.8, 6H, CH*Me*$_2$), 0.62 (m, 2H, CH_2Si). ^{13}C{^{1}H} NMR (CDCl$_3$, 75.47 MHz): δ = 145.3 (*o*-C$_{Ar}$), 137.2 (N*C*HN), 131.9 (*p*-C$_{Ar}$), 129.9 (*ipso*-C$_{Ar}$), 124.7 (*m*-C$_{Ar}$), 124.5 and 123.7 (N*C*H), 52.0 (N*C*H$_2$), 50.8 (Si(O*C*H$_3$)$_3$), 28.7 (*C*HMe$_2$), 24.5 (CH*Me*$_2$ and *C*H$_2$), 24.1 (CH*Me*$_2$), 5.5 (*C*H$_2$Si).

Synthesis of 1-(2,6-diisopropylphenyl)-3-[3-(triethoxysilyl)propyl]imidazolium chloride (6'c). 1-(2,6-diisopropylphenyl)-1*H*-imidazole (228 mg, 1.00 mmol), (3-chloropropyl)triethoxysilane (0.36 mL, 1.5 mmol) and thf (1 mL) were mixed in a 10-mL sealed vessel and placed in a Discover CEM S-class microwave oven operating at 2450 MHz. The mixture was heated rapidly and kept at 180 °C for 20 min while stirring magnetically. The reaction medium was cooled at 60 °C and taken out of the microwave reactor. **6'b** (359 mg, 0.6 mmol, 61 %) was obtained as a white solid after washings with diethyl ether (4 x 3 mL) and pentane (2 x 5 mL) followed by drying under vacuum for 2 h. ^{1}H NMR (CDCl$_3$, 300.13 MHz): δ = 10.68 (s, 1H, NC*H*N), 7.80 and 7.14 (t, ^3J = 1.5, 1H, NC*H*), 7.30 (m, 2H, *m*-H), 4.85 (t, ^3J = 6.8, 2H, NCH_2), 3.84 (q, ^3J = 7.0, 6H, Si(OCH_2CH$_3$)$_3$), 2.26 (m, 2H, C*H*Me$_2$), 2.10 (m, 2H, CH_2), 1.22 (t, ^3J = 7.0, 9H, Si(OCH$_2$CH_3)$_3$), 1.15 and 1.13 (d, ^3J = 3.2, 6H, CH*Me*$_2$), 0.66 (m, 2H, CH_2Si). ^{13}C{^{1}H} NMR

($CDCl_3$, 75.47 MHz): δ = 145.6 (*o*-C_{Ar}), 139.45 (N*C*N), 132.0 (*p*-C_{Ar}), 130.5 (*ipso*-C_{Ar}), 124.8 (*m*-C_{Ar}), 124.1 and 122.9 (N*C*H), 58.9 (Si(O*C*H_2CH$_3$)$_3$), 52.3 (N*C*H_2), 29.0 (*C*HMe$_2$), 24.8 (*C*H_2), 24.5 and 24.4 (CH*Me*$_2$), 18.5 (Si(CH$_2$C*H*$_3$)$_3$), 7.0 (C*H*$_2$Si).

Synthesis of 1-[3-(trimethoxysilyl)propyl]-3-methylimidazolium chloride (7d). A neat mixture of 1-methyl-1*H*-imidazole (82 μL, 1.0 mmol) and 3-chloropropyltrimethoxysilane (0.24 mL, 1.0 mmol) were mixed in a 10-mL sealed vessel and placed in a Discover CEM S-class microwave oven operating at 2450 MHz. The mixture was heated rapidly and kept at 180 °C for 20 min while stirring magnetically. **7d** was obtained as a dense orange oil in quantitative yield (295 mg, 1.0 mmol, quant.). ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ= 10.17 (s, 1H, NC*H*N), 7.57 and 7.27 (bs, 1H, NC*H*), 4.05 (t, ^3J = 8.1, 2H, NCH_2), 3.85 (s, 3H, Me), 3.27 (s, 9H, Si(OCH_3)$_3$), 1.73 (m, 2H, CH_2), 0.34 (m, 2H, CH_2Si).

Synthesis of 1-isopropyl-3-[3-(trimethoxysilyl)propyl]imidazolium chloride (7e). A solution of 1-isopropyl-1*H*-imidazole (1.093 mg, 9.92 mmol) and (3-chloropropyl)trimethoxysilane (2.017 mg, 1.85 mL, 10.15 mmol) in DME (20 mL) was stirred at 85 °C for 96 h. The mixture was cooled to r.t., and the solvent was removed under vacuum. The oily residue washed with toluene (5 x 3 mL) and dried in vacuo. **7e** was obtained as a colourless oil (1.071 g, 3.4 mmol, 35 %). HRMS (MALDI TOF): *m/z* $[M]^+$ calcd for $C_{12}H_{25}N_2O_3Si$: 273.1629; *found*: 273.1594. ^{1}H NMR ($CDCl_3$, 300.16 MHz): δ = 10.96 (s, 1H, NC*H*N), 7.79 (t, ^3J = 1.8, 1H, NC*H*), 7.33 (t, ^3J = 1.8, 1H, NC*H*), 4.90 (hept., ^3J = 6.8, 1H, C*H*), 4.34 (t, ^3J = 7.3, 2H, NCH_2), 3.52 (s, 9H, Si(OCH_3)$_3$), 1.96 (m, 2H, CH_2), 1.58 (d, ^3J = 6.8, CH*Me*$_2$), 0.61 (m, SiCH_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ = 136.43 (N*C*HN), 121.88 and 120.19 (N*C*H), 53.00 (N*C*H_2), 51.48 (*C*HMe$_2$), 50.52 (Si(O*C*H$_3$)$_3$, 24.00 (*C*H_2), 23.01 (CH*Me*$_2$), 5.86 (*C*H$_2$Si).

Synthesis of [Ni(Ph-NHC-TMS)ICp] (8a). To a suspension of **6a**, (865 mg; 2.00 mmol) in DME (20 mL) was added nickelocene (376 mg; 2.00 mmol). The resulting green suspension was heated at 85 °C for 18 h under vigorous stirring. The resulting red solution was cooled to r.t. and the solvent was evaporated under vacuum. The residue was extracted with toluene until the washings became colourless and filtered on a celite pad, which was rinsed with toluene (4 x 10 mL). The toluene was evaporated, the residue dissolved in acetonitrile (10 mL) and the solution extracted with pentane (8 x 10 mL). Acetonitrile was evaporated under vacuum and **8a** was obtained as a red

oil in 43 % yield (480mg, 0.86 mmol). ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 8.08 and 7.55 (m, 5H, Ph), 7.13 (s, 2H, NC*H*), 5.13 and 4.59 (m, 1H, NCH_2), 4.91 (s, 5H, η^5-C$_5H_5$), 3.63 (s, 9H, Si(OCH_3)$_3$, 23.10 (m, 2H, NCH$_2$CH_2), 0.83 (m, 2H, SiCH_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ = 166.1 (N*C*N), 140.9 (*ipso*-C$_{Ar}$), 129.1 and 126.4 (*o*/*m*-C$_{Ar}$), 128.6 (*p*-C$_{Ar}$), 123.6 and 122.8 (NC*H*), 92.0 (η^5-*C*$_5$H$_5$), 55.4 (NCH_2), 50.9 (Si(O*C*H$_3$)$_3$), 24.3 (NCH$_2$CH_2), 6.7 (CH_2Si).

Synthesis of [Ni(Mes-NHC-TES)ClCp] (8'b). To a suspension of **6'b** (285 mg, 0.67 mmol) in DME (10 mL) was added nickelocene (126 mg, 0.67 mmol). The resulting suspension was vigorously stirred at 85 °C for 30 min, while the solution colour slowly turned from dark green to dark red. The solvent was cooled to r.t. and then, evaporated under reduced pressure. Column chromatography over neutral silica with diethyl ether/pentane (7: 3) as eluent afforded **8'b** (261 mg, 0.47 mmol, 71 %) as a dark pink oil after solvent evaporation and drying under reduced pressure. ES-MS: *m/z* [M]$^+$ calcd for $C_{26}H_{39}N_2NiO_3Si$: 513.208; *found*: 513.206. ^{1}H NMR ($CDCl_3$, 400.14 MHz): δ = 7.17 (bs, 1H, NC*H*), 7.08 (s, 2H, *m*-H), 6.82 (bs, 1H, NC*H*), 5.00 (bs, 2H, NCH_2), 4.72 (s, 5H, η^5-C$_5H_5$), 3.87 (q, ^{3}J = 6.9, 6H, Si(OCH_2CH$_3$)$_3$), 2.43 (s, 3H, *p*-Me), 2.25 (tt, ^{3}J =8.0, J = 6.8, 2H, CH_2), 2.11 (bs, 6H, *o*-Me), 1.26 (t, ^{3}J = 6.9, 9H, Si(OCH$_2$CH_3)$_3$), 0.79 (m, ^{3}J = 8.0, 2H, CH_2Si). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ = 162.9 (N*C*N), 139.3 (o-C$_{Ar}$), 137.1 and 136.2 (*ipso*- and *p*-C$_{Ar}$), 129.3 (*m*-C$_{Ar}$), 123.4 and 123.2 (N*C*H), 91.8 (η^5-*C*$_5$H$_5$), 58.8 (Si(O*C*H$_2$CH$_3$)$_3$), 54.4 (N*C*H$_2$), 25.2 (*C*H$_2$), 21.4 (*p*-Me), 18.6 (Si(OCH$_2$*C*H$_3$)$_3$), 18.5 (*o*-Me), 7.9 (*C*H$_2$Si).

Synthesis of [Ni(*i*-Pr$_2$Ph-NHC-TES)ClCp] (8'c). To a suspension of **6'c** (518 mg; 1.00 mmol) in DME (20 mL) was added nickelocene (189 mg; 1.00 mmol). The mixture was stirred at 85 °C for 2 h. The resulting red solution was cooled to r.t. and the solvent was evaporated under vacuum. The residue was extracted with toluene (3 x 10 mL) and filtered through Celite, which was rinsed with toluene (3 x 5 mL). The solvent was evaporated under vacuum for 2 h. The oily residue was washed with diethyl ether (3 x 5 mL) and dried under vacuum for 2 h. **8'c** was obtained as a dark red oil (373 mg; 0.63 mmol, 63 %). ^{1}H NMR ($CDCl_3$, 400.14 MHz, 223 K): δ = 7.57 (m, 2H, *m*-H), 7.28 (s, 1H, *p*-H), 7.18 and 6.91 (s, 1H, NC*H*), 5.65 (m, 1H, NCH_2), 4.66 (s, 5H, η^5-C$_5H_5$), 4.23 (m, 1H, NCH_2), 3.87 (q, ^{3}J = 7.0, 6H, Si(OCH_2CH$_3$)$_3$), 3.18 (pseudoseptet, ^{3}J = 6.1, 1H, C*H*Me$_2$), 2.18 (m, 2H, CH_2), 1.76 (pseudoseptet, ^{3}J = 6.1, 1H, C*H*Me$_2$), 1.53 (d, ^{3}J = 6.1, 3H, CH*Me*), 1.26 (t, ^{3}J = 7.0, 9H, Si(OCH$_2$CH_3)$_3$), 1.14 (d, ^{3}J = 6.1, 3H, CH*Me*), 1.07 (d, ^{3}J = 6.1, 3H, CH*Me*), 0.96 (d, ^{3}J = 6.1, 3H, CH*Me*), 0.82 (m, 2H, CH_2Si). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz):

δ = 163.5 (N*C*N), 146.9 (*o*-C_{Ar}), 136.5 (*ipso*-C_{Ar}), 130.2 (*p*-C_{Ar}), 124.9 (N*C*H), 124.0 (*m*-C_{Ar}), 122.6 (N*C*H), 91.6 (η^5-C_5H_5), 58.6 (Si(O*C*H_2*C*H_3)$_3$), 54.4 (N*C*H_2), 28.3 (CH*Me*), 26.4 (*C*HMe_2), 25.1 (*C*H_2), 22.8 (CH*Me*), 18.4 (Si(OCH$_2$*C*H$_3$)$_3$), 7.8 (*C*H_2Si).

Synthesis of [Ni(Me-NHC-TMS)ClCp] (9d). 7d (950 mg, 3.38 mmol) was dried in a Schlenk-tube for 30 minutes under vacuum. Nickelocene (638 mg, 3.38 mmol) was added and the reactives were dissolved in DME (20 mL). The resulting solution was heated at 85 °C for 16 h under vigorous stirring. The solution turned rapidly from green to bright red. The solution was cooled to r.t. and the solvent was then evaporated under vacuum. The residue was extracted with 30 mL of hot toluene and filtered through Celite which was rinsed with toluene (10 mL). Toluene was evaporated under vacuum and the resulting dense, red oil was precipitated at r.t. in ether/ pentane (3: 8). **9d** was obtained as a red solid in 35 % yield. ES-MS: *m/z* $[M]^+$ calcd for $C_{15}H_{25}N_2NiO_3Si$: 365.089; *found*: 365.083. ^{1}H NMR ($CDCl_3$, 300.16 MHz): δ = 6.93 and 6.91 (d, ^3J = 1.9, 1H, NC*H*), 5.23 (s, 5H, η^5-C_5H_5), 4.75 (m, 2H, NCH_2), 4.33 (s, 3H, CH_3), 3.61 (s, 9H, Si(OCH_3)), 2.10 (tt, ^3J = 6.8, ^3J = 8.2, 2H, CH_2), 0.80 (m, 2H, CH_2Si). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ = 160.04 (N*C*N), 123.40 and 121.98 (N*C*H), 91.72 (η^5-C_5H_5), 53.96 (N*C*H_2), 50.75 (Si(O*C*H_3)), 38.92 (*C*H_3), 24.60 (*C*H_2), 6.57 (*C*H_2Si).

Synthesis of [Ni(*i*-Pr-NHC-TMS)ClCp] (9e). To a suspension of **7e** (190 mg, 0.6 mmol) in thf (12 mL) was added nickelocene (116 mg, 0.6 mmol) and the resulting green suspension was stirred at 65 °C for 18 h. The solvent was evaporated under vacuum, the residue extracted with hot toluene (3 x 5 mL) and filtered through Celite, which was rinsed with toluene until the washings were colourless. The solvent was evaporated under vacuum and the red oily residue washed with pentane (4 x 5 mL). **9e** (190 mg, 0.44 mmol, 73 %) was obtained as a red oil after drying under vacuum for 2 h. ES-MS: *m/z* $[M]^+$ calcd for $C_{17}H_{29}N_2NiO_3Si$: 395.130; *found*: 395.133. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 6.97 and 6.95 (d, ^3J = 2.1, 1H, NC*H*), 6.46 (pseudoseptet, ^3J = 6.9, 1H, C*H*(Me)$_2$), 5.23 (s, 5H, η^5-C_5H_5), 4.93 and 4.68 (m, 1H, NCH_2), 3.62 (s, 9H, Si(OCH_3)), 2.10 and 2.05 (m, 1H, CH_2), 1.57 and 1.59 (bd, 6H, CH(Me)$_2$), 0.82 (m, 2H, CH_2Si). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ = 155.01 (N*C*N), 120.40 and 116.06 (N*C*H), 89.14 (η^5-C_5H_5), 51.45 (N*C*H_2), 50.88 (*C*H), 48.63 (Si(O*C*H_3)), 22.03 (*C*H_2), 21.46 (*C*H_3), 4.06 (*C*H_2Si).

Immobilization of [Ni(Mes-NHC-TES)ClCp], 8'c, onto alumina. Alumina (3.700 g, 36.29 mmol) was introduced in a Schlenk tube and degassed under vacuum for 1 night at 110 °C. **8'b** (200 mg, 0.33 mmol) in toluene (15 mL) was added and the resulting suspension was heated at 100 °C for 3 h with vigorous stirring. After cooling the suspension to r.t., the solvent was removed by syringe and the solid residue rinsed with hot CH_2Cl_2 (6 x 10 mL). The residue was dried over night in vacuo and the supported complex **10** was isolated as a pink solid was dried under vacuum for 3 h. ICP-AES: 2.84 mg/g of nickel was detected for 1 g of hybrid material **10**. ^{1}H MAS (400.14 MHz, 14 kHz, 128 transients): δ = 6.9 (NC*H* and *m*-H), 4.6 (Cp and NCH_2), 3.4 (*o*-Me, *p*-Me and $SiOEt_{3-n}$), 2.1 (CH_2CH_2Si) and 1.3 (CH_2CH_2Si). DRIFT (64 scans): 3131 and 3086 cm^{-1} ν(sp^2 C-H); 2979 - 2831 cm^{-1}, ν(sp^3 C-H); 1610 - 1366 cm^{-1}, ν(C=C).

General procedure for Suzuki-Miyaura cross-coupling reactions using standard Schlenk techniques. A Schlenk tube equipped with a septum was charged with aryl halide (1.0 mmol), phenyl boronic acid (1.3 mmol), K_3PO_4 (2.6 mmol) and catalyst (1 – 3 mol%) before being put under an atmosphere of argon. Toluene (3 mL) was injected and the mixture immediately heated with vigorous stirring by putting the Schlenk into an oil bath at 85 – 110 °C. After 1 – 2 h, the reaction was stopped by allowing air to enter the Schlenk tube. GC yields were calculated by using tetradecane as an internal standard. NMR yields were determined by removing a sample with a syringe, drying it under vacuum, extracting the residue with $CDCl_3$ and filtering the sample in a NMR tube. In a standard work up, the solvent was completely removed under vacuum. The residue was extracted with a 1:1 mixture of diethyl ether/water (20 mL). The organic phase was separated and the aqueous layer extracted with another 10 mL portion of diethyl ether. The combined organic layers were dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude material was purified by column chromatography over SiO_2 with pentane/ethyl acetate as eluent to give the desired product. All yields are the average values of at least three runs.

General procedure for Suzuki-Miyaura cross-coupling reactions using standard glovebox techniques. In a glovebox with levels of H_2O and O_2 < 0.5 ppm, a Schlenk tube equipped with a glass stopper was charged with aryl halide (1.0 mmol), phenyl boronic acid (1.3 mmol), K_3PO_4 (2.6 mmol) and a toluene solution containing 1 – 3 mol% of catalyst (3 mL). The Schlenk tube was then taken outside the glovebox and the mixture was immediately heated at 110 °C with vigorous stirring by putting the Schlenk into an oil bath at 110 °C. After 15 – 120 min, the reaction

was stopped by allowing air to enter the Schlenk tube. GC and NMR yields were determined as for the reactions carried out under standard Schlenk techniques.

General procedure for Suzuki-Miyaura cross-coupling reactions catalyzed by the supported complex 10. In a glovebox with levels of H_2O and O_2 < 0.5 ppm a Schlenk tube was charged with aryl halide (1.0 mmol), phenyl boronic acid (1.3 mmol), K_3PO_4 (2.6 mmol) and the hybrid catalyst **10** (620 mg, 3 mol% of Ni). Toluene (3 mL) was added and the Schlenk tube was closed with a greased glass stopper. The Schlenk tube was taken outside the glovebox and the mixture was immediately heated at 110 °C with vigorous stirring by putting the Schlenk into a hot oil bath at 110 °C. After 15 – 120 min, the reaction was stopped by allowing air to enter the Schlenk tube. GC and NMR yields were determined as for the reactions carried out under standard Schlenk techniques.

X-ray Diffraction Studies. Structure Determination and Refinement. Single crystals of **3b**, **3c**, **4d**, **4e**, **5b** and **5c** suitable for X-ray diffraction studies were selected from batches of crystals obtained for toluene/pentane solutions at -32 °C for all compounds. Diffraction data for all crystals were collected on a Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). A summary of crystal data, data collection parameters and structure refinements is given in Table 8. Cell parameters were determined from reflections taken from one set of 10 frames (1.0° steps in phi angle), each at 20 s exposure. The structures were solved using direct methods (SHELXS97) and refined against F2 for all reflections using the SHELXL97 software. Multiscan absorptions corrections (MULscanABS in PLATON) were applied. All non-hydrogen atoms were refined anisotropically in structures. The *n*-butyl group of **5b** exhibits disorder. Hydrogen atoms in all structures were generated accordingly to stereochemistry and refined as fixed contributors using a riding model in SHEL97.[57,58]

[57] *Kappa CCD Operation Manual* ; Delft, The Netherlands, 1997.
[58] G. M. Sheldrick, *SHELXL97, Program fro the refinement of crystal structures* ; University of Göttingen, Germany, 1997.

Table 7: X-ray crystallographic data and data collection parameters for complexes **3**, **4** and **5**

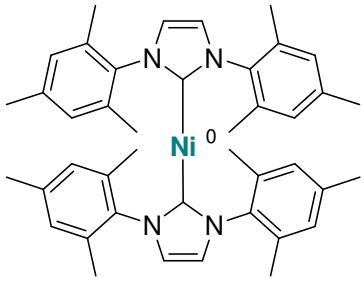
Compound	**3b**	**3c**	**4d**	**4e**	**5a**	**5b**
Formula	$C_{21}H_{27}IN_2Ni$	$C_{24}H_{33}IN_2Ni$	$C_{13}H_{19}ClN_2i$	$C_{15}H_{23}ClN_2i$	$C_{26}H_{37}IN_2Ni$	$C_{29}H_{43}IN_2Ni$
Formula weight	493.06	535.13	297.46	325.51	563.19	605.26
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P_{-1}	P_{-1}	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	8.5246(5)	8.1838(2)	13.1632(7)	11.2294(4)	12.7615(3)	9.9126(5)
b (Å)	11.9988(9)	10.9585(5)	10.3986(7)	15.0015(8)	13.5249(5)	14.0043(4)
c (Å)	12.1499(9)	15.6604(7)	10.5106(5)	20.9173(10)	15.9132(6)	21.5414(10)
α(°)	102.649(4)	99.404(2)				
β(°)	106.289(4)	91.338(2)	106.876(3)	111.534(3)	105.607	104.799(2)
γ(°)	109.11(4)	108.408(2)				
V (Å^3)	1058.98(13)	1311.22(9)	1376.72(14)	3277.7(3)	2645.32(15)	2891.2(2)
Z	2	2	4	8	4	4
D_x (Mg.m^{-3})	1.546	1.355	1.435	1.319	1.414	1.391
Absorp. coeff. (mm^{-1})	2.38	1.93	1.58	1.34	1.92	1.76
T (K)	173	173	173	173	173	173
Crystal form, colour	Block, red	Block, red	Block, red	Prism, red	Prism, red	Block, red
Crystal size (mm)	0.20 x 0.15 x 0.10	0.40 x 0.35 x 0.30	0.40 x 0.25 x 0.15	0.30 x 0.20 x 0.15	0.25 x 0.25 x 0.23	0.30 x 0.07 x 0.05
h,k,l$_{max}$	11, 15, 12	10, 14, 20	16, 12, 12	12, 19, 27	15, 17, 14	10, 14, 27
T_{min}, T_{max}	0.623, 0.776	0.475, 0.548	0.574, 0. 727	0.714, 0.784	0.595, 0.823	0.638, 0.713
Reflns collected	10120	13016	8274	23167	15282	18312
R (reflections)	0.044 (3412)	0.041 (5982)	0.032 (3136)	0.057 (3271)	0.039 (6058)	0.069 (6622)
wR^2 (reflections)	0.127 (4819)	0.115 (4645)	0.083 (2648)	0.190 (7520)	0.120 (4489)	0.225 (3586)
GOF on F^2	1.09	1.06	1.08	0.94	1.09	1.06

Chapter 3

Synthesis and reactivity of half-sandwich nickel complexes bearing two different NHC ligands

1. Introduction

An important number of Ni-NHC catalyzed reactions are promoted by *in situ* generated nickel(0)-NHC catalysts (See Chapter 1). Among the variety of the thus generated active species, several systems seem to be promoted by a *bis*-NHC metal complex, although the precise form of the active catalyst often remains unclear (See Chapter 1). Some elegant studies have targeted the isolation of the catalytically active Ni(0)-NHC species in order to gain a better understanding of the mechanism, that is involved in the activation of sp^2-C–X bonds, and in particular of sp^2-C–F bonds (Chapter I, Section 4.1.2), and hence, in the cross-coupling reactions of aryl halides with organometallic reagents (Chapter 1, Section 2.1.1.1 and Section 2.1.3.1). Generally, the method of choice has focussed on the interaction mode of the aryl halide with a well-defined Ni(0)-NHC complex, that is supposed to be structurally close to the active species. All these mechanistic investigations hint a key *trans*-[$Ni^0(R_2\text{-NHC})_2$] intermediate, analogous to the complex, [$Ni^0(Mes_2\text{-NHC})$] **I**, (Scheme 92) that was first isolated by Arduengo.[1,2]



I

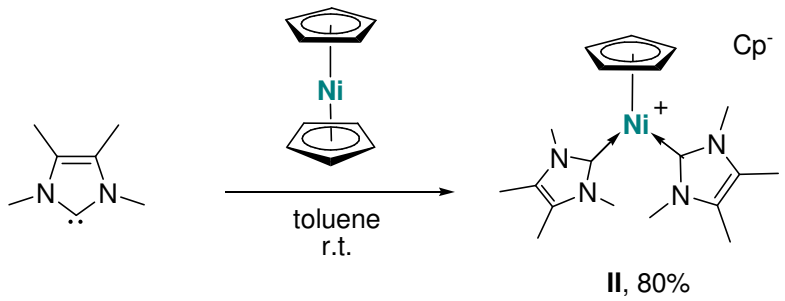
Scheme 92

As already outlined in Chapter 2, our group has recently prepared and intensively studied neutral [Ni(Ar_2-NHC)Cl$Cp^\dagger$], and cationic [Ni(Ar_2-NHC)(CH_3CN)$Cp^\dagger$]$^+PF_6^-$ (Ar = Mes, *i*-Pr_2Ph, $Cp^\dagger$ = Cp, Cp*) complexes that are able to catalyse the Suzuki-Miyaura cross-coupling of aryl bromides and chlorides with phenylboronic acid without the addition of a reductant or a co-catalyst.[3] In this context, we have introduced a variety of new [Ni(Ar-NHC-*n*-Bu)I$Cp^\dagger$] (Ar = Mes, *i*-Pr_2Ph, $Cp^\dagger$ = Cp, Cp*) complexes, which revealed to be highly catalytically active for this

[1] A. J. Arduengo III, S. F. Gamper, C. Calabrese, F. Davidson, *J. Am. Chem. Soc.* **1994**, *116*, 4391.
[2] (a) S. Miyazaki, Y. Koga, T. Matsumoto, K. Matsubara, *Chem. Commun.* **2010**, *46*, 1932; (b) T. Schaub, M. Backes, U. Radius, *Eur. J. Inorg. Chem.* **2008**, 2680; (c) D. S. McGuinness, K. J. Cavell, *Organometallics*, **1999**, *18*, 1596.
[3] (a) V. Ritleng, A. M. Oertel, M. J. Chetcuti, *Dalton Trans.* **2010**, *39*, 8153; (b) V. Ritleng, C. Barth, E. Brenner, S. Milosevic, M. J. Chetcuti, *Organometallics*, **2008**, *27*, 4223; (c) V. Ritleng, E. Brenner, M. J. Chetcuti, *J. Chem. Educ.* **2008**, *85*, 1646.

coupling reaction as well (See Chapter 2, Section 2.3.). However, during these studies we have noticed that the *in situ* generated active Ni(0) species is highly air sensitive and hence, rather unstable. We thus decided to develop a synthetic route for new half-sandwich nickel(II) catalysts, that would carry two NHC ligands, as we believed that a second NHC unit should improve the stability of a coordinatively unsaturated Ni(0) species that may appear during the catalytic reaction.

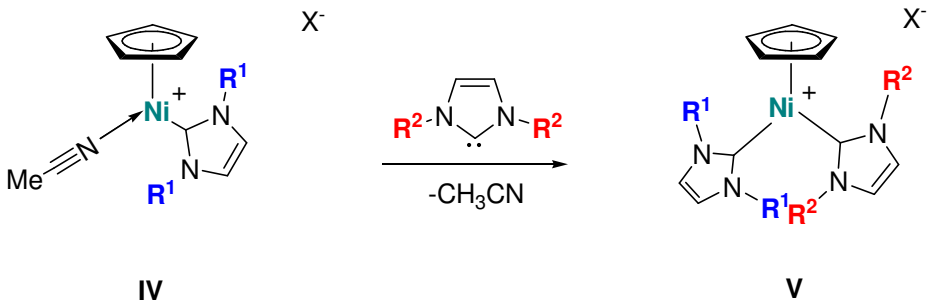
To our knowledge, only one approach has yet been documented for the synthesis of half-sandwich *bis*-NHC metal complexes. Thus, a variety of carbene adducts of Ca, Mg, Sr, Ba and Zn displaying one or two carbene ligands was formed by displacing a labile ligand of the corresponding metallocene (usually solvents such as diethyl ether or thf) with an equimolar amount of Me_4-NHC (Me_4-NHC = 1,2,3,4-*tetra*-methylimidazol-*2*-ylidene).[4] Following this method, the complex $[Ni(Me_4\text{-NHC})_2Cp]^+Cp^-$, **II**, was prepared in good yield by Abernethy *et al*. from equimolar toluene solutions of the small Me_4-NHC and of nickelocene (Scheme 93)[5]



Scheme 93

Based on these results, we thought that the acetonitrile ligand of the cationic complexes $[Ni(Mes_2\text{-NHC})(CH_3CN)Cp]^+PF_6^-$, **IV**, which was demonstrated to be labile,[3b] should be easily displaced by a strongly σ-bonding carbene to form cationic *bis*-carbene complexes of general formula $[Ni(R^1{}_2\text{-NHC})(R^2{}_2\text{-NHC})Cp]^+X^-$, **V** (Scheme 94). The formation of a strong σ-bond should indeed favour the cationic *bis*-NHC species over the cationic acetonitrile complexes.[4] In addition, such a strategy seemed particularly attractive to us, as it should allow introducing successively two *different* NHC units. This has to our knowledge never been done. Moreover, removal of the Cp ring from the half sandwich *bis*-NHC compounds would further allow us to generate new square planar *bis*-NHC nickel(II) species bearing two different NHCs.

[4] A. J. Arduengo III, F. Davidson, R. Krafczyk, W. J. Marshall, M. Tamm, *Organometallics*, **1998** ,*17*, 3375.
[5] C. D. Abernethy, J. A. C. Clyburne, A. H. Cowley, R. A. Jones, *J. Am. Chem. Soc.* **1999**, *121*, 2329.



IV **V**

Scheme 94

In this chapter, we will describe how we achieved the synthesis of $[Ni(R^1_2\text{-NHC})(R^2_2\text{-NHC})Cp]^+X^-$ complexes by the reaction of cationic acetonitrile $[Ni(R_2\text{-NHC})(CH_3CN)Cp]^+PF_6^-$ complexes with the appropriate free carbene. The molecular structure of the *bis*-NHC complex $[Ni(Mes_2\text{-NHC})(Me_2\text{-NHC})Cp]^+PF_6^-$ will be presented and compared to those of the cationic *mono*-carbene half-sandwich nickel(II) compounds, $[Ni(R_2\text{-NHC})(CH_3CN)Cp]^+PF_6^-$ [R = Me (**11**), Mes, (**12a**)], and of the related *bis*-NHC species **II** (Scheme 2). Next, we will present the catalytic activity of these species for the Suzuki-Miyaura cross-coupling of 4'-bromoacetophenone and phenylboronic acid and show that the second NHC unit does indeed dramatically stabilize the nickel centre compared to the *mono*-carbene compounds. Finally, we will complete this chapter with the synthesis of a new square planar *bis*-NHC nickel(II) complex bearing one Me_2-NHC and one *i*-Pr-NHC-Me ligand. This complex was generated by abstraction of the Cp ring from the appropriate cationic half-sandwich *bis*-NHC nickel complex with acid solutions of acetonitrile.

2. Results and discussion

2.1. Synthesis of $[Ni(R^1_2\text{-NHC})(R^2_2\text{-NHC})Cp]^+X^-$ complexes

The cationic acetonitrile species $[Ni(Mes_2\text{-NHC})(CH_3CN)Cp]^+PF_6^-$, **12a**, was prepared from the reaction of an acetonitrile solution of the neutral halide complex, $[Ni(Mes_2\text{-NHC})ClCp]$,[3b,6] with KPF_6 according to the method recently published by our group.[3a] The complex $[Ni(Me_2\text{-NHC})(CH_3CN)Cp]^+BF_4^-$, **11**, was prepared from reaction of an acetonitrile solution of the $[Ni(Me_2\text{-NHC})ICp]$[3b] with $AgBF_4$ (Scheme 95). The molecular structures of these complexes, as well as their ^1H/ $^{13}C\{^1H\}$ NMR data, will be used for a comparison purpose with that of the new cationic

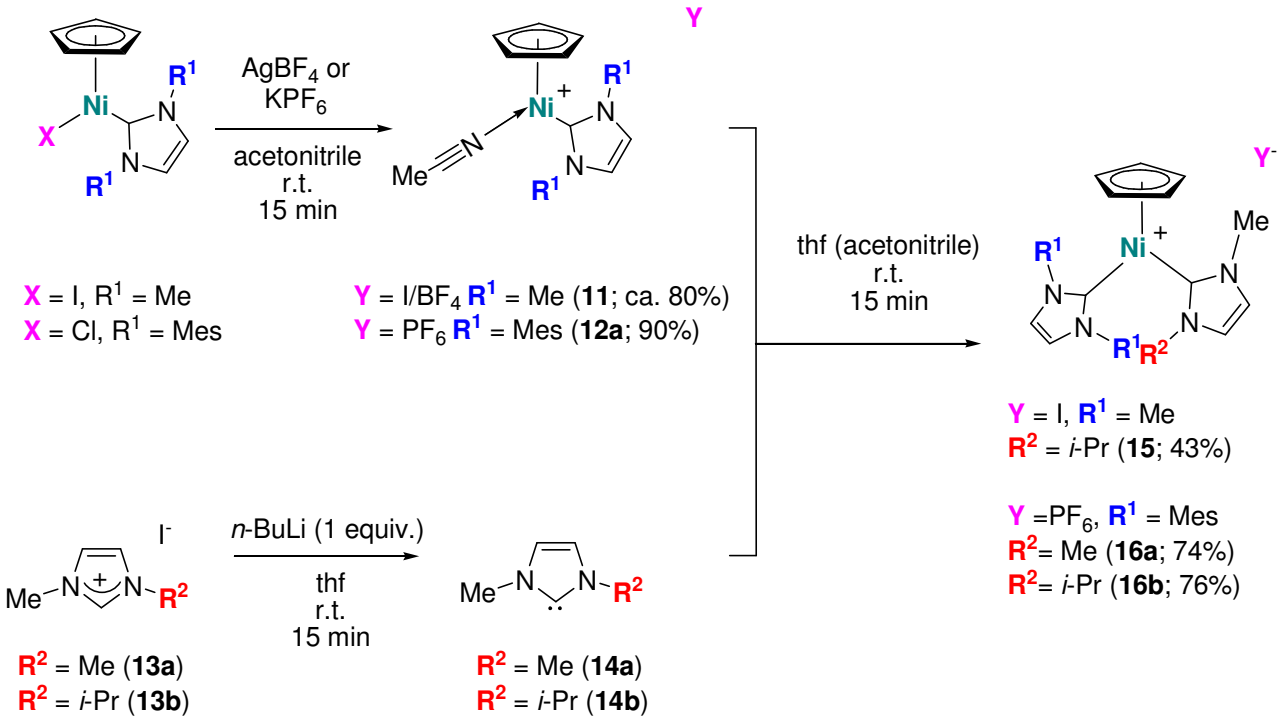
[6] C. D. Abernethy, A. H. Cowley, R. A. Jones, *J. Organomet. Chem.* **2000**, *596,* 3.

bis-NHC species (*vide infra*), but their synthesis will not be further commented in this chapter as this is done in Chapter 4.

The free NHCs, **14**, were prepared by treating thf suspensions of the appropriate imidazolium iodide salt, Me_2-NHC·HI, **13a**, or *i*-Pr-NHC-Me·HI, **13b**, with an equimolar amount of *n*-butyllithium at room temperature for 15 minutes. The resulting white mixtures were filtered through Celite (which was previously dried at 110 °C for at least 24 h) and directly added to the solution containing the cationic acetonitrile complexes **11** and **12a** without further purification or isolation (Scheme 95).

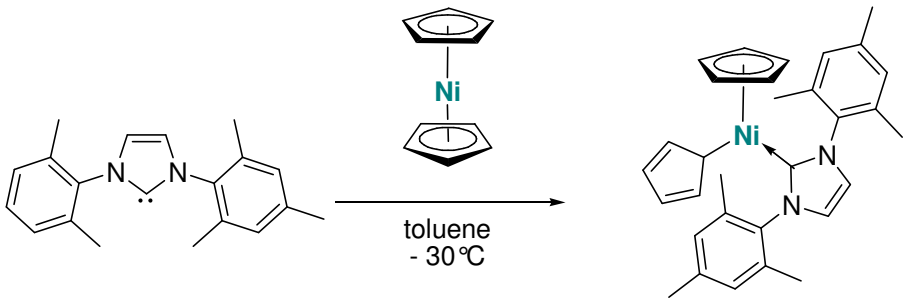
Thus, the cationic half-sandwich nickel(II) complex $[Ni(Me_2\text{-NHC})(i\text{-Pr-NHC-Me})Cp]^+I^-$,[7] **15**, was synthesized by treating a thf/acetonitrile (1:5) solution of $[Ni(Me_2\text{-NHC})(CH_3CN)Cp]^+I^-/BF_4^-$, **11**,[7] with a freshly prepared equimolar thf solution of *i*-Pr-NHC-Me, **13b**, at room temperature. Analogously, the complexes $[Ni(Mes_2\text{-NHC})(Me_2\text{-NHC})Cp]^+PF_6^-$, **16a**, and $[Ni(Mes_2\text{-NHC})(i\text{-Pr-NHC-Me})Cp]^+PF_6^-$, **16b**, were prepared by treating thf solutions of $[Ni(Mes_2\text{-NHC})(CH_3CN)Cp]^+PF_6$, **12**, with a freshly prepared equimolar thf solution of Me_2-NHC, **14a**, or *i*-Pr-NHC-Me, **14b**, respectively. In this way, the acetonitrile was abstracted and the desired *bis*-NHC complexes **15** and **16a,b** were isolated as green air stable solids in 43 % to 76 % yields (Scheme 95). Good ^1H and $^{13}C\{^1H\}$ NMR spectroscopic data and elemental analyses data were collected for all complexes. Crystals suitable for single-crystal X-ray diffraction studies could be obtained for **16a** (*vide infra*).

[7] Unsatisfactory elemental analyses were repeatedly obtained for complex **11**, and its anion is believed to be a mixture of I^- and BF_4^-. In addition, elemental analyses for **15** demonstrated that its anion was I^- and not BF_4^-. The origin of the iodide counterion of **15** may thus either arise from **11** and/or from the thf solution of free *i*-Pr-NHC-Me, which is generated from the corresponding imidazolium salt, (Me-NHC-*i*-Pr)·HI, and an equimolar amount of *n*-butyllithium. Some LiI would remain dissolved in the resulting mixture and hence would not be removed by filtration. The strong σ-bond, which is generated between the nickel atom and the carbene carbon of the second NHC ligand would prevent re-coordination of the iodide onto the nickel to regenerate the neutral iodo-complex $[Ni(Me_2\text{-NHC})ICp]$.



Scheme 95

During this study, several attempts were undertaken to bind a second bulky Mes_2-NHC ligand onto $[Ni(Mes_2\text{-NHC})(CH_3CN)Cp]^+PF_6$, **12a**. They were all unfruitful, suggesting that two bulky Mes_2-NHCs cannot bind simultaneously to half-sandwich nickel complexes. This behaviour was also observed by Abernethy as only one Mes_2-NHC coordinated to the nickel atom when equimolar toluene solutions of nickelocene were treated with Mes_2-NHC. In this case and in contrast to the reaction of nickelocene with the smaller Me_4-NHC ligand, the *mono*-carbene adduct $[Ni(Mes_2\text{-NHC})(\eta^1\text{-}C_5H_5)(\eta^5\text{-}C_5H_5)]$, **III**, instead of the expected *bis*-NHC species was isolated (Scheme 96).[5]



III, 45%

Scheme 96

In addition, we further observed that with the already sterically congested nickel complex **12a**, a second bulky Mes_2-NHC carbene rather acts as a base, as small amounts of Mes_2-NHC·HPF_6

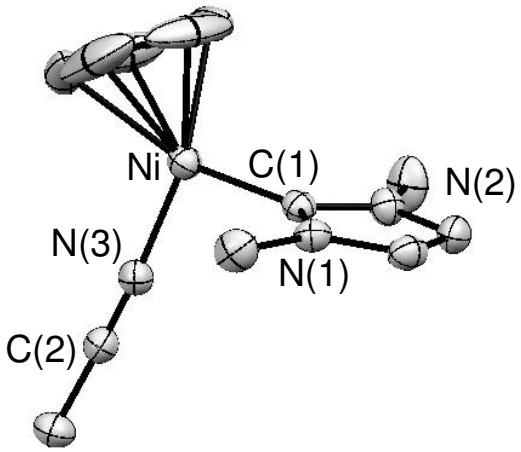
and of a neutral cyanomethyl complex, [Ni(Mes_2-NHC)(CH_2CN)Cp], were isolated, as the result of an acid/base reaction between the acetonitrile ligand of **12a** and the added second bulky carbene. This reaction is discussed in Chapter 4 and will not be further commented here.

2.1.1. Structural studies

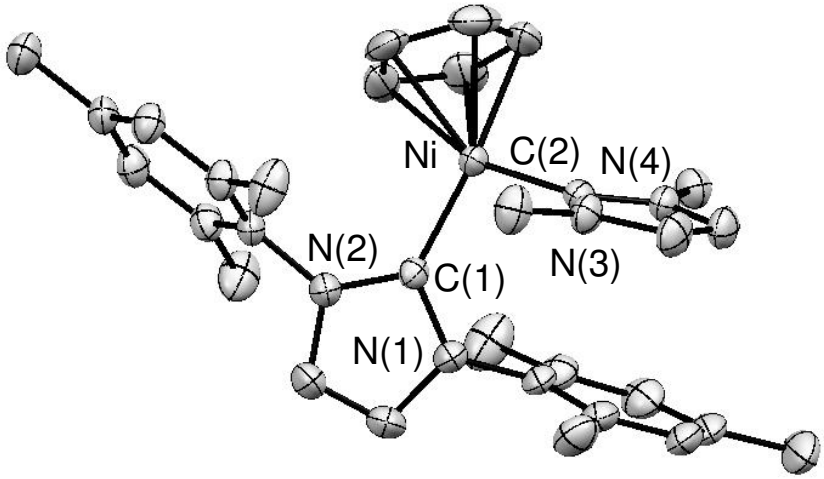
Crystals suitable for X-ray diffraction studies for the cationic acetonitrile complex [Ni(Me_2-NHC)(CH_3CN)Cp]$^+BF_4^-$, **11**, and for the cationic *bis*-carbene complex [Ni(Mes_2-NHC)(Me_2-NHC)Cp]$^+PF_6^-$, **16a** were grown from cold solutions of acetonitrile/diethyl ether and CH_2Cl_2/diethyl ether, respectively. Crystallographic data and data collection parameters for both complexes are listed in Table 12 (see Experimental Section). The molecular structures of the cationic parts of **11** and **16a** are shown in Figure 1. The molecular structure of the cationic part of **12a** is presented in Chapter 4.[8] Selected bond lengths and angles of **11**, **12a** and **16a** appear in Table 8. Other bond lengths and angles of **16a** appear in Table 4. Structural data of the cationic parts of **11** and **12a** are used for comparison purpose only.

The molecular structure of **16a** display the Cp ring, the bulky [Mes_2-NHC], as well as the [Me_2-NHC] ligand and adopts a two-legged piano stool geometry, which is the common geometry for 18-electron $NiCpL_2$ complexes.[9] In particular, the molecular structure of **16a** is similar to that of the closely related *bis*-NHC nickel(II) complex [Ni(Me_4-NHC)$_2$Cp]$^+Cp^-$, **II**, reported by Abernethy.[5] Thus, the C(1)–Ni–C(2) angle of **16a** (96.9°) and **II** (97.0°)[5] are remarkably close, and the distances between the nickel atom and both carbene carbon atoms are similar, [1.906(2) Å and 1.899(3) Å for **16a** and 1.883(2) Å for **II**[5]]. Moreover, the Ni–C_{NHC} bond lengths of **16a** are similar to those of their respective cationic *mono*-carbene counterparts **12a** [1.902(2) Å][7] and **11** [1.888(2) Å], see Table 8. Finally, the angles between the Cp ring centroid, the nickel atom and the carbene carbon of the each NHC moiety are of the same order than those of complexes **11** and **12a**; C(1)–Ni–Cp_{cent} = 136.0° (**16a**), 131.8°, (**12a**); C(2)–Ni–Cp_{cent} = 126.0° (**16a**), 131.3° (**11**) (Table 8). Thus, the coordination of the second NHC ligand to the nickel atom would not induce major distortions compared to the *mono*-carbene species.

[8] A. M. Oertel, V. Ritleng, L. F. Veiros, M. J. Chetcuti, *J. Am. Chem. Soc.* **2010**, DOI: 10.102/ja105368p.
[9] R. A. Kelly III, N. M. Scott, S. Díez-González, E. D. Stevens, S. P. Nolan, *Organometallics*, **2005**, *24*, 3442.



[Ni(Me$_2$-NHC)(CH$_3$CN)Cp]$^+$BF$_4^-$, 11



[Ni(Mes$_2$-NHC)(Me$_2$-NHC)Cp]$^+$PF$_6^-$, 16a

Figure 6 : ORTEP plot of the cationic parts of [Ni(Me$_2$-NHC)(CH$_3$CN)Cp]$^+$BF$_4^-$, **11**, and [Ni(Mes$_2$-NHC)(Me$_2$-NHC)Cp]$^+$PF$_6^-$, **16a**. Ellipsoids are shown at the 50 % probability level. Key atoms are labelled and hydrogen atoms are omitted for clarity.

It is noteworthy that as for the [Ni(R-NHC-*n*-Bu)ICp†] complexes (see Chapter 2), small differences are observed for the Ni–C$_{Cp}$ bond - [2.096(3) Å (min), 2.172(3) Å (max)] and in

particular for the C_{Cp}–C_{Cp} bond distances [1.379(5) Å (min), 1.434(5) Å (max)], see Table 11. These variations arise from "diene" distortions of the Cp ring.[10]

Table 8 : Selected bond lengths (Å) and angles (°) for complexes **16a**, **11** and **12a**[7].

	16a	**11**	**12a**[7]
Ni–C(1)	1.906(2)	-	1.902(2)
Ni–C(2)	1.899(3)	1.888(2)	-
C(n)–Ni–L[a]	96.9(1)	98.87(7)	96.94(8)
C(1)–Ni–Cp_{cent}	136.0	-	131.8
C(2)–Ni–Cp_{cent}	126.9	131.3	-

[a] n = 1, L = C(2) for **16a**; n = 2, L = CH_3CN for **11**; n = 1, L = CH_3CN for **12a**.

2.1.2. Spectroscopic studies

The ^1H and $^{13}C\{H\}$ NMR spectra of the cationic half-sandwich *bis*-NHC complexes [Ni(Me_2-NHC)(*i*-Pr-NHC-Me)Cp]$^+BF_4^-$, **15**, [Ni(Mes_2-NHC)(Me_2-NHC)Cp]$^+PF_6^-$, **16a**, and [Ni(Mes_2-NHC)(*i*-Pr-NHC-Me)Cp]$^+PF_6^-$, **16b**, are straightforward at ambient temperature. They all show the signals of one Cp ring and of the two NHC ligands.

It is noteworthy that, for the Cp protons, no difference of chemical shift is observed between the cationic *mono*-carbene complex [Ni(Mes_2-NHC)(CH_3CN)Cp]$^+PF_6^-$, **12a**,[7] and the complexes **16a,b**, which contain the same aryl-substituted Mes_2-NHC unit. Similarly, no difference of chemical shift is observed between the Cp protons of the mono-carbene complex [Ni(Me_2-NHC)(CH_3CN)Cp]$^+PF_6^-$, **11**, and of the *bis*-carbene complex **15**, which contain the same alkyl-substituted Me_2-NHC moiety. Finally, the Cp ring protons of **15** and its closely related analogue [Ni(Me_4-NHC)$_2$Cp]$^+Cp^-$, **II**,[5] are identical (Table 9).

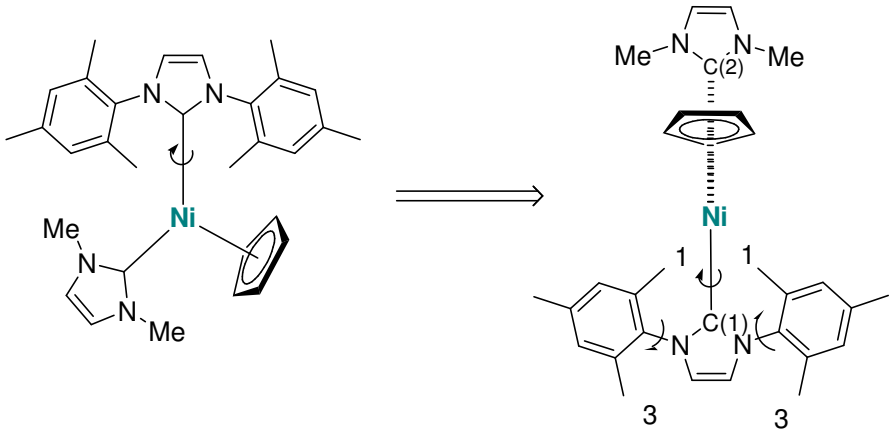
Table 9 : ^1H NMR chemical shift (ppm) of the Cp ring protons for complexes **II**, **11**, **12a**, **15** and **16a,b**

11[a]	**15**[a]	**II**[b,5]	**16a**[c]	**16b**[c]	**12a**[c,7]
5.44	5.45	5.45	4.76	4.72	4.76

[a] in CD_3CN. [b] in C_6D_6. [c] in $CDCl_3$.

[10] P. L. Holland, M. E. Smith, R. A. Andersen, R. G. Bergman, *J. Am. Chem. Soc.* **1997**, *119*, 12815.

In the *bis*-NHC complex **16a**, the methyl groups and the alkene protons of the imidazole ring of the Me_2-NHC ligand are, respectively, equivalent on the NMR time scale and resonate as two singlets in a 1:3 relative integrated ratio. The alkene protons of the Mes_2-NHC moiety, as well as the *ortho*-methyls and *meta*-hydrogens of the mesityl groups are also equivalent, respectively. There is thus an effective plane of symmetry present in solution that bisects the molecule, as well as free rotation about the Ni–C(1) and Ni–C(2) bonds at room temperature on the NMR time scale. This mirror plane, generated by rotation about the Ni–C(1) and Ni–C(2) bonds, would contain both carbene carbon atoms C(1) and C(2), the nickel centre and the Cp ring centroid (see conformation **16a-sym** in Scheme 97).



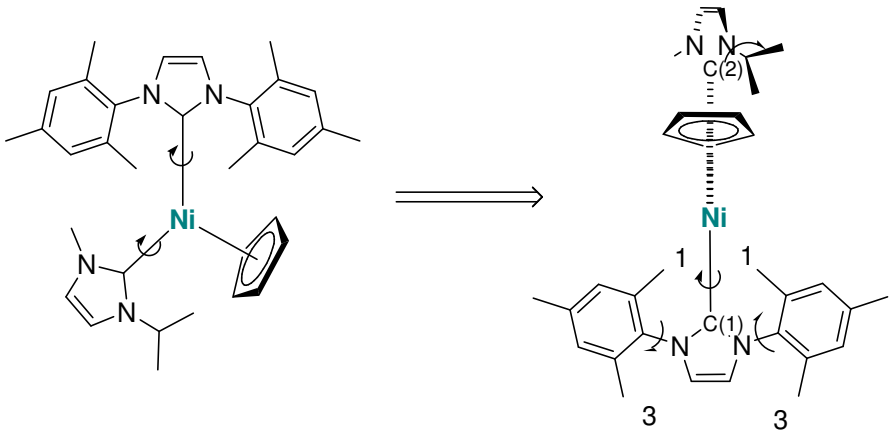
16a **16a-sym**

Scheme 97

In contrast, the ^{1}H NMR spectrum of [Ni(Mes_2-NHC)(*i*-Pr-NHC-Me)Cp]$^+PF_6^-$, **16b**, reveals that the *meta*-hydrogen atoms and the *ortho*-methyl groups resonate as four separate singlets in a 1:1:3:3 relative integrated ratio. Moreover, the isopropyl group of Me-NHC-*i*-Pr resonates as two doublets with in a 3:3 integrated ratio. Accordingly, complete rotation about the Ni–C(1), Ni–C(2), N–Mes and N–*i*-Pr bonds should be frozen on the NMR time scale at ambient temperature, which shows that substitution of one of the N-methyls of **16a** by an isopropyl as in **16b** has a major impact on the dynamic behaviour of the *bis*-NHC complex.[11] Nevertheless, the two alkene protons of the Mes_2-NHC are isochronous, indicating that a molecular mirror plane is present on the NMR time scale. This mirror plane, that can be generated by small rotations about the Ni–C(1) and/or Ni–C(2) bonds (if one consider **16b**), contains the carbene carbon atom C(1), the nickel atom, the Cp ring

[11] The steric bulk of the *i*-Pr-NHC-Me ligand must therefore be comparable to that of an iodide as hampered rotation of the nickel–carbene bond is also observed for [Ni(Ar-NHC-*n*-Bu)ICp] (Ar = Mes, *i*-Pr_2Ph) species (see Chapter 2, Section 1).

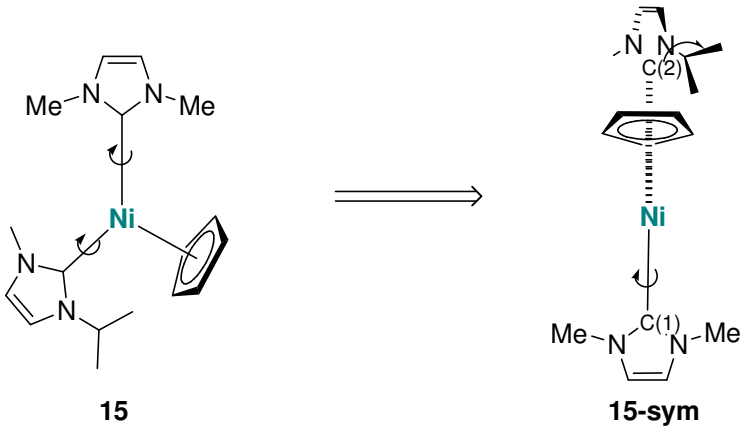
centroid, the plane defined by the *i*-Pr-NHC-Me ligand, the C*H* proton of the *i*-Pr group, that it bisects (see conformation **16b-sym** in Scheme 98).



16b **16b-sym**

Scheme 98

Finally, the ^{1}H NMR spectrum of **15** does not show any barrier to the nickel–carbene bond rotation for both NHC ligands and reveals that a molecular mirror plane is present on the NMR time scale at room temperature. The methyl groups of the Me_2-NHC ligand, as well as the isopropyl methyl groups of the *i*-Pr-NHC-Me ligand are isochronous and resonate as one singlet and one doublet, respectively. The mirror plane that bisects the molecule is depicted in **15-sym** (Scheme 99) and contains the same atoms than in **16b-sym**.



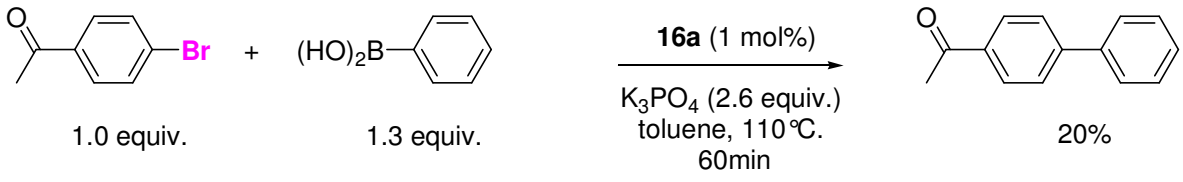
15 **15-sym**

Scheme 99

These results clearly illustrate the major impact that would have two big NHC units on the resulting half-sandwich *bis*-NHC nickel complex; substitution of one of the methyl group in **16a** by an *i*-propyl leads to major perturbations of the dynamic processes of the resulting species, **16b**. Hence, a second Mes_2-NHC ligand, which is much more voluminous than an *i*-Pr-NHC-Me ligand, can not bind to a CpNi(Mes_2-NHC) moiety without severe molecular deformations, and the energy required for such deformations must be much higher than the stabilizing σ-donation from the Mes_2-NHC ligand, which explains why a $[Ni(Mes_2\text{-NHC})_2Cp]^+$ complex could not be synthesized.

2.2. Catalytic behaviour of the half-sandwich $[Ni(R^1{}_2\text{-NHC})(R^2{}_2\text{-NHC})Cp]^+X^-$ complexes in Suzuki-Miyaura cross-coupling

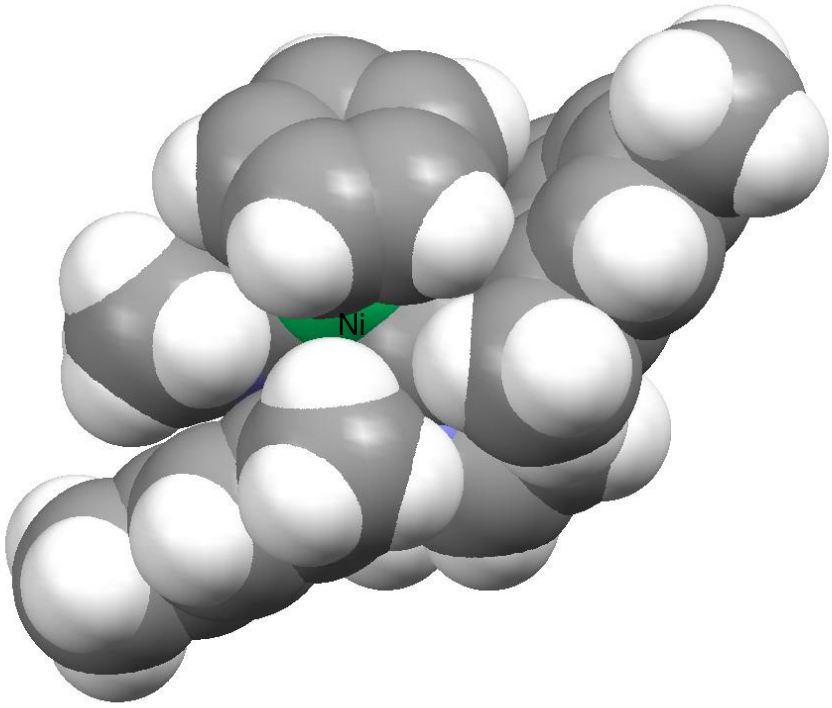
The catalytic activity of $[Ni(Mes_2\text{-NHC})(Me_2\text{-NHC})Cp]^+PF_6^-$, **16a**, was studied for the Suzuki-Miyaura cross-coupling of 4'-bromoacetophenone and phenylboronic acid (Scheme 100). Although the complex was found to be catalytically active, only 20 % yield of the desired 4-acetylbiphenyl was detected after 60 min in refluxing toluene with 1 mol% of catalyst loading. Compared to the outstanding turnover frequencies observed with the related *mono*-carbene half-sandwich catalysts $[Ni\{(i\text{-}Pr_2Ph)_2\text{-NHC}\}(NCMe)Cp^*]^+PF_6^-$ [3a] and [Ni(Mes-NHC-*n*-Bu)ICp] (Chapter 2, Section 2.3.), this result was clearly disappointing. Thus, in contrast to what we expected, the coordination of a second NHC ligand onto the nickel atom does not stabilize the active species, but instead dramatically stabilizes the catalyst precursor!



Scheme 100

The space filling plot of **16a** (Figure 2) illustrates one possible origin of the great stability of this complex. Indeed, the nickel centre is almost totally shielded by the bulky Mes_2-NHC, the smaller Me_2-NHC and the Cp ring. If the necessary creation of a vacant site on the active species arises through Cp ring displacement, another possible reason is that **16a** may well generate an active Ni(0) species, that features a structure similar to that arising from the square planar $[Ni(NHC)_2X_2]$ complexes, which have shown similar activity for the Suzuki-Miyaura cross-

coupling of 4'-bromoacetophenone and phenylboronic acid (see Chapter 1, Section 2.1.3.1).[12] These results hint that the efficient active catalyst resulting from our [Ni(NHC)LCp†] complexes is most probably a *mono*-NHC-Ni species.



[Ni(Mes$_2$-NHC)(Me$_2$-NHC)Cp]$^+$PF$_6^-$, 16a

Figure 7 : Space filling plot of the molecular structure of the cationic part of [Ni(Mes$_2$-NHC)(Me$_2$-NHC)Cp]$^+$PF$_6^-$, **16a**. The nickel atom is labelled**.**

2.3. Synthesis of [Ni(R$^1_2$-NHC)(R$^2_2$-NHC)X$_2$] complexes

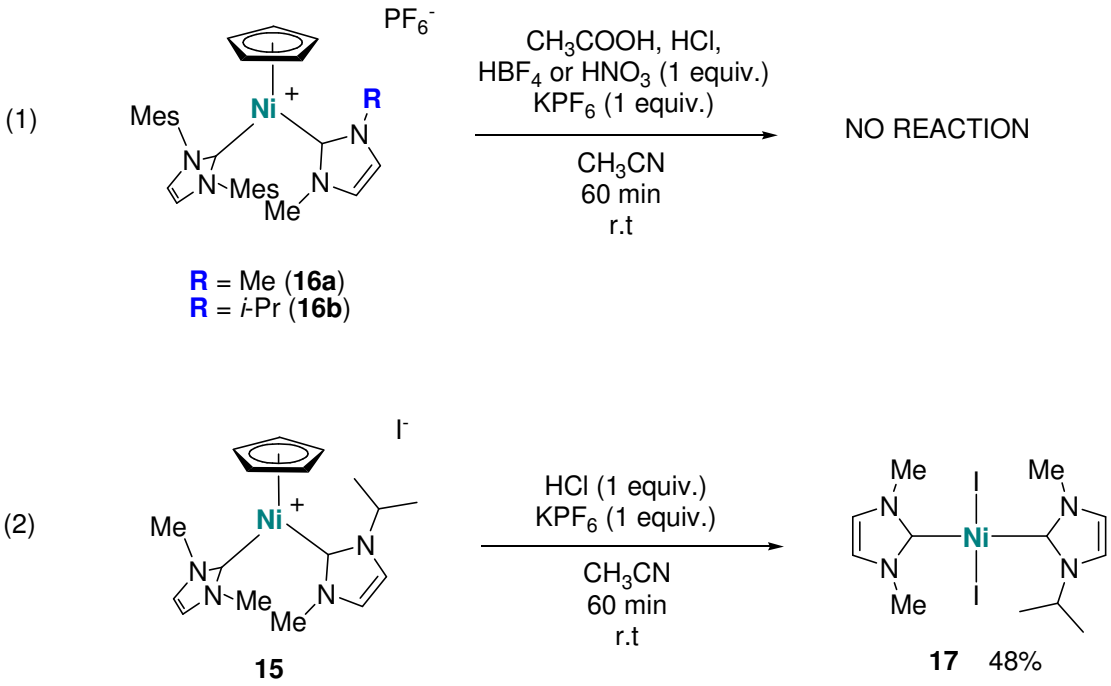
In the last section of this chapter, we were interested in the lability of the Ni–Cp bonds of **15** and **16a,b** in order to generate square planar *bis*-NHC nickel complexes carrying two different NHCs that we hoped to be *cis*.

For that purpose, we chose to first study the lability of the Ni–Cp bond of [Ni(Mes$_2$-NHC)(Me$_2$-NHC)Cp]$^+$PF$_6^-$, **16a**, and [Ni(Mes$_2$-NHC)(*i*-Pr-NHC-Me)Cp]$^+$PF$_6^-$, **16b** by treating them with solutions of an acid in acetonitrile in the presence of KPF$_6$. We indeed believed that an acid in a coordinating solvent such as acetonitrile could protonate the anionic Cp ligand to generate cyclopentadiene and, in the presence of a second equivalent of PF$_6^-$, a *cis* square planar dicationic complex of general formula [Ni(Mes$_2$-NHC)(Me-NHC-R)(CH$_3$CN)$_2$](PF$_6$)$_2$. Attempts employing

[12] D. S. McGuinness, K. J. Cavell, *Organometallics*, **1999**, *18*, 1596.

0.01 M solutions of acetic acid, HCl, HBF_4 or HNO_3 in acetonitrile in the presence of 1 equivalent of KPF_6 were however all unfruitful (Eq. 1, Scheme 101). Astonishingly, these complexes were "solid as rocks" towards protonation, as neither reaction nor decomposition of the green complexes was observed (as indicated by the absence of colour change)! Thus, both the Ni–Cp and the Ni–NHC bonds of these compounds are remarkably inert.

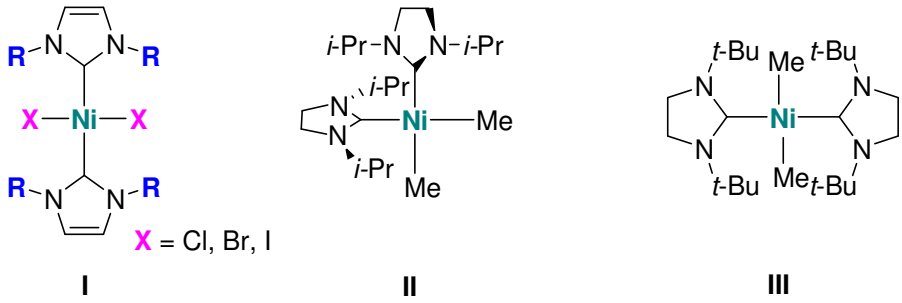
We then studied the reactivity of the *bis*-NHC complex [Ni(Mes-NHC)(*i*-Pr-NHC-Me)Cp]$^+$I$^-$, **15**, that bears two small NHC ligands, and possesses an iodide as counterion instead of hexafluorophosphate. In this case removal of the Cp ring could be achieved by treating it for 1 h at ambient temperature with an equimolar amount of a 0.01 M solution of HCl in acetonitrile in the presence of an 1 equivalent of KPF_6 (Eq. 2, Scheme 101). The resulting complex **17** was isolated as pink crystals in 48 % and was characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, as well as by a single-crystal X-ray diffraction study (*vide infra*), which revealed that **17** was a neutral square planar complex carrying two iodide ligands in *trans*-positions. The presence of iodide in the reaction medium (as the counterion of **15**) may thus have been one of the driving force of the reaction, although the influence on the reactivity of the smaller size of the NHCs of complex **15** compared to those of complexes **16a,b** cannot be ruled out.



Scheme 101

To our knowledge, such *bis*-NHC-nickel complexes are unprecedented. Indeed, the methodologies, that have been reported for the formation of square planar *bis*-NHC nickel

complexes to date, are limited to species, which carry two identical NHC ligands.[13,14] Among these methods, complexes *trans*-[Ni(R_2-NHC)$_2$X]$_2$, **I**, (Scheme 102) are generally prepared from [Ni(PPh_3)$_2X_2$] (X= Cl, Br) or [Ni(thf)$_2X_2$] (X= Cl, Br), the appropriate NHC precursor and a base (Scheme 2).[13,15] The complex *trans*-[Ni(Me_2-NHC)$_2I_2$] was however prepared by employing anhydrous [Ni(OAc)$_2$]. The use of this precursor allowed avoiding the addition of a base into the reaction medium, but required drastic reaction conditions (150 °C, vacuum, no solvent).[13] *Cis*- or *trans*-[Ni(R_2-NHC)$_2Me_2$] complexes **II** and **III** were prepared by employing [Ni(tmed)(Me)$_2$] (tmed = *N*,*N*'-tetramethylethylenediamine) as a precursor.[14]



I **II** **III**

Scheme 102

2.3.1. Structural studies

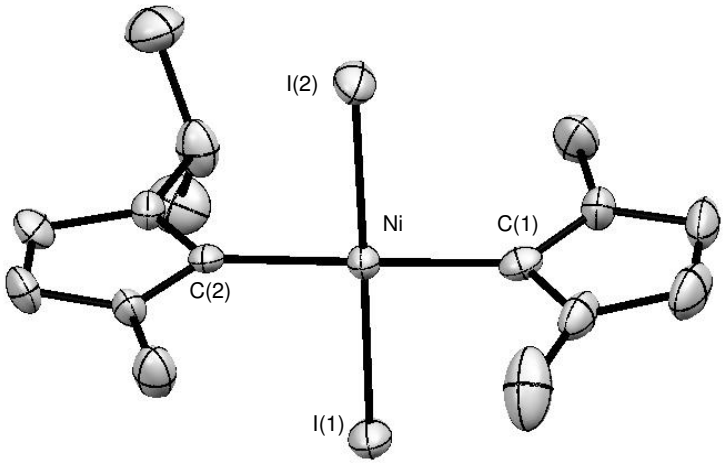
Unambiguous determination of the molecular structure of the new complex [Ni(Me_2-NHC)(*i*-Pr-NHC-Me)I_2], **17**, was determined by a single crystal X-ray diffraction study. Crystals suitable for single-crystal X-ray diffractions were grown from cold solutions of CD_3Cl and diethyl ether. Crystallographic data and data collection parameters are listed in Table 12 (see experimental section). A list of selected bond lengths and angles appears in Table 10. The molecular structure of **17** is shown in Figure 8 and shows one Me_2-NHC and one *i*-Pr-NHC-Me ligand, as well as two iodides in a square planar *trans* array around the nickel centre.

The majority of the reported square planar *bis*-NHC-Ni complexes bearing monodentate ligands and, in particular, those complexes bearing voluminous bromides or iodides, feature a *trans* geometry.[2,13,15,16] In presence of small methyl groups instead of halide ligands, the NHC-ligand size

[13] W. A. Herrmann, G. Gerstberger, M. Spiegler, *Organometallics*, **1997**, *16*, 2209.
[14] A. A. Danopoulos, D. Pugh, *Dalton Trans.* **2008**, 30.
[15] K. Matsubara, K. Ueno, Y. Shibata, *Organometallics*, **2006**, *25*, 3422.
[16] R. Jothibasu, K.-W. Huang, H. V. Huynh, *Organometallics*, **2010**, DOI 10.1021/om100241v.

controls the geometry of the complex; a *cis*-geometry was thus observed with *i*-Pr_2-NHCs while a *trans*-geometry was observed with bulkier *t*-Bu_2-NHCs (See **II** and **III**, Scheme 102).[14]

The Ni–C(1) [1.910(1) Å] and the Ni–C(2) [1.909(9) Å] bond distances of [Ni(Me_2-NHC)(*i*-Pr-NHC-Me)I_2], **17**, are similar to those observed for the Ni–C_{NHC} bonds in the related *trans*-[Ni(Me_4-NHC)$_2I_2$][2c] and *trans*-[Ni(Cy-NHC)$_2Cl_2$][13] complexes [1.897(3) and 1.911(2) Å, respectively]. The Ni–I bond lengths of **17** [2.508(2), 2.497(2) Å] are in accord with the value reported for *trans*-[Ni(Me_4-NHC)$_2I_2$] [2.5180(3) Å],[2c] and the angles between the carbene carbons, the nickel atom and the iodides are all close to 90° (see Table 10). Hence, the presence of a *different second NHC ligand* only causes minor distortion to the idealized square planar geometry of *trans*-[Ni(R_2-NHC)$_2X_2$] complexes bearing two *identical* NHC moieties.



Ni[(Me_2-NHC)(*i*-Pr-NHC-Me)I_2], 17

Figure 8 : ORTEP plot for the molecular structure of the complex [Ni(Me_2-NHC)(*i*-Pr-NHC-Me)I_2], **17**. Ellipsoids are shown at the 50 % probability level. Key atoms are labelled and hydrogen atoms are omitted for clarity.

Table 10 : Selected bond lengths (Å) and angles (°) for complex **17**.

	17
Ni–C(1)	1.910(1)
Ni–C(2)	1.909(9)
Ni–I(1)	2.497(2)
Ni–I(2)	2.508(2)
C(1)–Ni–I(1)	88.8(3)
C(1)–Ni–I(2)	92.1(3)
C(2)–Ni–I(1)	89.8(3)
C(2)–Ni–I(2)	89.3(3)

2.3.2. Spectroscopic studies

The ^{1}H NMR spectra of **17** is straightforward at ambient temperature and shows the Me_2-NHC and the *i*-Pr-NHC-Me ligands. No major difference between the chemical shifts of the NHC-ring protons of **17** (Me_2-NHC, 6.75 ppm and *i*-Pr-NHC-Me, 6.80 and 6.79 ppm) are observed and that of [Ni(Me_2-NHC)$_2$I$_2$] (6.73 ppm).[2c] Furthermore, **17** exhibits characteristic chemical shifts for the carbene carbons C(1) and C(2) at 174.1 ppm and 172.2 ppm, that are close to those reported for *trans*-[Ni(Cy_2-NHC)$_2$Cl$_2$],[13] *trans*-[Ni(Cy_2-NHC)$_2$Br$_2$][13] and *trans*-[Ni(Me_2-NHC)$_2$I$_2$][2c]: 169.3, 170.6 and 173.9 ppm, respectively.

Although complex **17** is almost identical to *trans*-[Ni(R_2-NHC)$_2$X$_2$] (X= Br, I) complexes, it is the first example of a square planar *bis*-NHC complex bearing two different NHC ligands to date. Furthermore, its synthesis shows that in some cases, the Ni–Cp bond is not as strong as generally accepted.[17]

3. Conclusion

We have developed a methodology for the synthesis of cationic half-sandwich Ni(II)-complexes bearing two *different* NHC ligands. The compounds were generated by ligand displacement of the labile acetonitrile ligand from cationic acetonitrile CpNi-(NHC) complexes and the appropriate *N*,*N'*-alkyl substituted "free" NHC. Thus, [Ni(Me_2-NHC)(*i*-Pr-NHC-Me)Cp]$^{+}$I^{-}, **15**, [Ni(Mes_2-NHC)(Me_2-NHC)Cp]$^{+}$$PF_6^{-}$, **16a**, and [Ni($Mes_2$-NHC)(*i*-Pr-NHC-Me)Cp]$^{+}$$PF_6^{-}$, **16b,** were

[17] M. J. Chetcuti, L. A. DeLiberato, P. E. Fanwick, B. E. Grant, *Inorg. Chem.* **1990**, *29*, 1295 and references therein.

isolated in respectable to good yields from the reaction of cationic half-sandwich complexes [Ni(Me_2-NHC)(CH_3CN)Cp]$^+BF_4^-$, **11**, or [Ni(Mes_2-NHC)(CH_3CN)Cp]$^+PF_6^-$, **12a**, with equimolar thf solutions of "free" Me_2-NHC or *i*-Pr-NHC-Me.

The molecular structure of **16a** revealed that cationic CpNi-(*bis*-NHC) complexes feature a piano stool geometry with a trigonal planar geometry around the nickel atom, as seen for a related [Ni(Me_4-NHC)$_2$Cp]$^+Cp^-$ complex. Furthermore, no major distortion of the coordination sphere of **16a** with respect of that of its cationic acetonitrile precursors [Ni(Me_2-NHC)(CH_3CN)Cp]$^+BF_4^-$, **11**, and [Ni(Mes_2-NHC)(CH_3CN)Cp]$^+PF_6^-$, **12a** was noticed. ^{1}H NMR studies have shown the apparition of a barrier about the Ni–C_{NHC} bond rotation at ambient temperature on the NMR time scale by the substitution of the Me_2-NHC ligand in **16a** by the *i*-Pr-NHC-Me ligand in **16b**. These results clearly illustrate that a second Mes_2-NHC ligand, which is much more voluminous than an *i*-Pr-NHC-Me, would not bind to a CpNi(Mes_2-NHC) moiety without severe molecular deformations. The energy required for this process must be much higher than the stabilizing σ-donation from the Mes_2-NHC ligand. Accordingly, only CpNi-(NHC)(NHC)' complexes bearing at least one small NHC ligand could be synthesized.

Compared to the outstanding turnover frequencies observed with the related *mono*-carbene half-sandwich catalysts, the catalytic activity of [Ni(Mes_2-NHC)(Me_2-NHC)Cp]$^+PF_6^-$, **16a**, for the Suzuki-Miyaura cross-coupling of 4'-bromoacetophenone and phenylboronic acid was dramatically lower, which suggests that the efficient active catalyst resulting from our [Ni(NHC)LCp†] complexes is most probably a *mono*-NHC-Ni species.

The robustness of the Ni–Cp and Ni–C_{NHC} bonds of the *bis*-NHC complexes **16a,b** that bear a bulky Mes_2-NHC ligand and have PF_6^- as counter-ion was demonstrated by the inertness of these species under acid conditions. The Ni–Cp bonds of complex **15**, that bears two small alkyl-substituted NHC ligands and an iodide as counter-ion are less robust, and the Cp ring could be removed by treating acetonitrile solutions of **15** with equimolar amounts of HCl. The presence of iodide in the reaction medium of **15** may however well be the reason of the apparent difference of reactivity between **15** and **16a,b**, as the resulting square planar complex *trans*-[Ni(Me_2-NHC)(*i*-Pr-NHC-Me)I_2] **17** has two iodide ligands. Complex **17** is the first example of a square planar TM(II)-NHC_2 metal complex bearing *two different* NHC ligands.

4. Experimental

General comments. All reactions were carried out using standard Schlenk techniques under an atmosphere of dry argon. Solvents were distilled from appropriate drying agents under argon

prior to use. Solution NMR spectra were recorded on FT-Bruker Ultra Shield 300 and FT-Bruker Spectrospin 400 spectrometers operating at 300.13 or 400.14 MHz for ^{1}H and at 75.47 or 100.61 MHz for $^{13}C\{^{1}H\}$. DEPT ^{13}C spectra were obtained for all complexes to help in the ^{13}C signal assignments. Supplementary 2D COSY and HSBQ spectra were obtained for **16b** and **17**. The chemical shifts are referenced to residual deuterated solvent peaks. Chemical shifts (δ) and coupling constants (*J*) are expressed in ppm and Hz, respectively. Elemental analysis for **15** and **16a,b** were performed by the Service d'Analyses, de Mesures Physiques et de Spectroscopie Optique, UMR CNRS 7177, at the Institut de Chimie, Université de Strasbourg. Commercial compounds were used as received. 1-Isopropyl-1*H*-imidazole,[18] 1,3-*bis*-(2,4,6-trimethylphenyl)imidazolium chloride,[19] [Ni(Mes_2-NHC)ClCp)],[3c,6] [Ni(Me_2-NHC)ICp][3b] and [Ni(Mes_2-NHC)(CH_3CN)Cp]$^{+}PF_6^{-}$, **12a**,[3a] were prepared according to published methods.

Synthesis of [Ni(Me_2-NHC)(CH_3CN)Cp]$^{+}I^{-}/BF_4^{-}$ (11). $AgBF_4$ (263 mg, 1.35 mmol) was added to a solution of [Ni(Me_2-NHC)ICp] (466 mg, 1.35 mmol) in acetonitrile (30 mL) under vigorous stirring. The colour immediately changed from red to green. The resulting mixture was filtered through Celite, which was rinsed with acetonitrile (4 x 5 mL) and the solvent was evaporated under vacuum. **11** was crystallized overnight from solutions of acetonitrile/diethyl ether at –32 °C. The overlaying solution was removed by syringe and the solid washed with diethyl ether (3 x 5 mL). **11** was obtained as green crystals in 80 % yield (730 mg, 2.1 mmol). ^{1}H NMR (CD_3CN, 300.13 MHz): δ = 7.20 (s, 2H, NC*H*), 5.44 (s, 5H, η^5-C_5H_5), 4.07 (s, 6H, CH_3). $^{13}C\{^{1}H\}$ NMR (CD_3CN, 75.47 MHz): δ = 156.2 (N*C*N), 125.8 (N*C*H), 93.8 (η^5-C_5H_5), 39.2 (CH_3).

Synthesis of 1,3-*bis*-methylimidazolium iodide (13a). Iodomethane (1.64 mL, 20.0 mmol) was added to a solution of 1-methyl-1*H*-imidazole (1.6 mL, 20.0 mmol) in toluene (80 mL). The mixture was stirred at 50°C overnight. The overlaying solution was removed by syringe, the resulting white solid was washed with diethyl ether (3 x 7 mL) and dried in vacuo for 2 h. **13a** was obtained as a white solid in 97 % yield (4.37 g, 19.5 mmol). ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 10.01 (s, 1H, NC*H*N), 7.41 (s, 2H, NC*H*), 4.09 (s, 6H, CH_3).

Synthesis of 1-isopropyl-(3-methyl)imidazolium iodide (13b). Iodomethane (1.42 g, 0.62 mL, 10.0 mmol) was added dropwise over a period of 5 min to a solution of 1-isopropyl-1*H*-imidazole (1.102 g, 10.0 mmol) in toluene (20 mL). The solution was heated at 50°C and stirred at

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this temperature for 8 h. The overlaying solution was removed by syringe, the resulting white solid was washed with diethyl ether (3 x 7 mL) and dried in vacuo for 2 h. **13b** was obtained as a white solid in 95 % yield (2.40 g, 9.5 mmol). ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 10.20 (s, 1H, NC*H*N), 7.43 and 7.40 (s, 1H, NC*H*), 4.83 (septet, ^{3}J = 6.6, 1H, C*H*), 4.13 (s, 3H, CH_3), 1.66 (d, ^{3}J = 6.6, CH*Me*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ = 136.0 (N*C*HN), 123.9 and 120.2 (N*C*H), 53.6 (*C*H), 37.2 (CH_3), 23.3 (CH*Me*$_2$).

Synthesis of [Ni(Me$_2$-NHC)(*i*-Pr-NHC-Me)Cp]$^{+}$I^{-} (15). *n*-Butyllithium (1 mL, 1.60 mmol, 1.6 M in hexanes) was added dropwise to a suspension of **13b** (403 mg, 1.60 mmol) in thf (16 mL) and stirred for 10 min at r.t.. The reaction mixture was filtered through Celite and the resulting carbene solution, **14b**, was added to a solution of **11** (540 mg, 1.55 mmol) in acetonitrile (20 mL) under vigorous stirring. The mixture was stirred at this temperature for 15 min and progressively, took a more reddish colour. Volatiles were evaporated under vacuum. The residue was then dissolved in acetonitrile (5 mL) and filtered on alumina, which was rinsed with acetonitrile (3 x 5 mL). The solvent was evaporated under vacuum and **15** was precipitated at r.t. from a solution of acetonitrile and diethyl ether to afford a green powder in 43 % yield (290 mg, 0.67 mmol). *Anal. calcd* for $C_{17}H_{25}IN_4Ni$: C, 43.35; H, 5.35, N; 11.90. *Found*: C, 43.08; H, 5.38; N, 12.05. ^{1}H NMR (CD_3CN, 300.13 MHz): δ = 7.17 and 7.15 (d, ^{3}J = 1.98, 1H, NC*H*), 7.07 (s, 2H, NC*H*), 5.45 (s, 5H, η^5-C_5H_5), 5.41 (pseudoseptet, ^{3}J = 6.77, 1H, C*H*), 3.98 (s, 3H, CH_3), 3.85 (s, 6H, CH_3), 1.20 (d, ^{3}J = 6.77, 6H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (CD_3CN, 75.47 MHz): δ = 164.2 and 162.5 (N*C*N), 126.4 and 120.0 (N*C*H(5)), 125.4 (N*C*H(4)), 92.3 (η^5-*C*$_5$H$_5$), 54.2 (*C*H), 39.7 (*C*H$_3$), 39.3 (*C*H$_3$), 23.1 (CH(C*H*$_3$)$_2$).

Synthesis of [Ni(Mes$_2$-NHC)(Me$_2$-NHC)Cp]$^{+}$PF$_6^{-}$ (16a). *n*-Butyllithium (0.20 mL, 0.32 mmol, 1.6 M in hexanes) was added dropwise to a suspension of **13a** (222 mg, 0.32 mmol) in thf (3 mL) and stirred for 10 min at r.t.. The reaction mixture was filtered through Celite and the resulting carbene solution, **14a**, was added to a solution of **12a** (211 mg, 0.32 mmol) in thf (5 mL) under vigorous stirring. The mixture was stirred at this temperature for 15 min and then, the volatiles were evaporated under vacuum. The residue was extracted with CH_2Cl_2 (3 x 5 mL) and filtered through Celite, which was rinsed with CH_2Cl_2 (3 x 5 mL). The solvent was evaporated under vacuum and **16a** crystallized from a cold solution of CH_2Cl_2 and diethyl ether. **16a** was isolated as green crystals in 74 % yield (170 mg, 0.25 mmol). *Anal. calcd* for $C_{31}H_{37}F_6N_4NiP$: C, 55.63; H, 5.57; N, 8.37. *Found*: C, 55.48; H, 5.62; N, 8.38. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 7.03 (s, 4H, *m*-H), 6.98 (s,

2H, NC*H*), 6.93 (s, 2H, NC*H*), 4.76 (s, 5H, η^5-C_5H_5), 3.42 (s, 6H, CH_3), 2.39 (s, 6H, *p*-Me), 1.98 (s, 12H, *o*-Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.47 MHz): δ = 168.2 (N*C*N) and 160.3 (N*C*'N), 140.0 (*ispo*/*p*-C_{Ar}), 136.3 (*p*/*ipso*-C_{Ar}), 135.1 (*o*-C_{Ar}), 129.8 (*m*-C_{Ar}), 125.8 (N*C*H), 124.8 (N*C*H'), 91.9 (η^5-C_5H_5), 38.9 (CH_3), 21.2 (*p*-Me), 18.1 (*o*-Me).

Synthesis of [Ni(Mes$_2$-NHC)(*i*-Pr-NHC-Me)Cp]$^+$PF$_6^-$ (16b). *n*-Butyllithium (0.3 mL, 0.48 mmol, 1.6 M in hexanes) was added dropwise to a suspension of **13b** (109 mg, 0.43 mmol) in thf (5 mL) and stirred for 10 min at r.t. The reaction mixture was filtered through Celite and the resulting carbene solution, **14b**, was added to a solution of **12a** (267 mg, 0.43 mmol) in thf (5 mL) under vigorous stirring. The mixture was stirred at this temperature for 15 min and then, the volatiles were evaporated under vacuum. The residue was dissolved in CH_3CN (5 mL) and filtered through alumina, which was rinsed with CH_3CN (3 x 10 mL). The solvent was evaporated under reduced pressure and **16b** was crystallized from a cold solution of thf and pentane. **16b** was isolated as green crystals in 76 % yield (228 mg, 0.33 mmol). *Anal. calcd* for $C_{33}H_{41}F_6N_4NiP$: C, 56.84; H, 5.93; N, 8.03. *Found*: C, 56.74; H, 6.17; N, 7.97. ^1H NMR ($CDCl_3$, 300.13 MHz): δ = 7.15 (bs, *m*-H), 7.05 and 6.97 (d, ^3J = 2.1, 1H, NC*H*), 7.00 (s, 2H, NC*H*), 6.94 (bs, 2H, *m*-H), 5.42 (pseudo-septet, ^3J = 6.8, 1H, C*H*), 4.72 (s, 5H, η^5-C_5H_5), 2.87 (s, 3H, CH_3), 2.40 (s, 6H, *o*-Me), 2.28 (s, 6H, *p*-Me), 1.58 (s, 6H, *o*-Me), 1.30 and 1.28 (d, ^3J = 6.8, 3H, CH(CH_3)). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.47 MHz): δ = 168.1 [N*C*N(A)][a], 158.1 [N*C*N(B)][a], 140.3 (*p*/*ipso*-C_{Ar}), 136.2 (*ipso*/*p*-C_{Ar}), 135.4 and 135.3 (*o*-C_{Ar}), 129.9 and 129.6 (*m*-C_{Ar}), 126.1 [N*C*H(A)], 125.7 and 119.5 [N*C*H(B)], 91.8 (η^5-C_5H_5), 53.2 ($CH(CH_3)_2$), 37.3 (CH_3), 24.5 and 22.8 (CH(CH_3), 21.1 (*p*-Me), 18.5 (*o*-Me), 17.4 (*o*-Me).

[a] A = Mes$_2$-NHC, B = *i*-Pr-NHC-Me.

Synthesis of *trans*-[Ni(Me$_2$-NHC)(*i*-Pr-NHC-Me)I$_2$] (17). A solution of HCl in CH_3CN (0.01 M, 2.0 mL) was added drop-wise to a suspension of **15** (80 mg, 0.19 mmol) in CH_3CN (15 mL) in the presence of an equimolar amount of KPF_6 (35 mg, 0.19 mmol). The resulting mixture was stirred at r.t. for 1 h. The initially green mixture turned progressively to red. Volatiles were evaporated under vacuum and then, the solid residue was dissolved in thf (10 mL) and stirred at the same temperature for 1 h. The mixture was filtered through silica and volatiles were evaporated to dryness. **17** was crystallized from a cold solution of CH_2Cl_2 and pentane, washed with pentane and dried in vacuo for 2 h. **17** was isolated as a red solid in 48 % yield (40 mg, 0.11 mmol). ^1H NMR ($CDCl_3$, 300.13 MHz): δ = 6.80 and 6.79 (s, 1H, NC*H*), 6.75 (s, 2H, NC*H*), 6.25 (pseudoseptet, ^3J = 6.77, 1H, C*H*), 4.25 (bs, 6H, CH_3), 4.24 (s, 3H, CH_3), 1.60 (d, ^3J = 6.77, CHCH_3). $^{13}C\{^1H\}$ NMR

($CDCl_3$, 75.47 MHz): δ = 174.1 and 172.2 (N*C*N), 123.7 and 117.1 (N*C*H'), 123.0 (N*C*H), 52.3 (*C*H), 38.0 and 37.9 (CH_3), 22.9 (CHCH_3).

Procedure for the Suzuki-Miyaura cross-coupling reaction. In a glovebox with levels of H_2O and O_2 < 0.5 ppm, a Schlenk tube equipped with a glass stopper was charged with 4'-bromoacetophenone (1.0 mmol), phenylboronic acid (1.3 mmol), K_3PO_4 (2.6 mmol), **16a** (7 mg, 7 x 10^{-5} mol, *ca.* 1 mol%) and toluene (3 mL). The Schlenk tube was taken outside the glovebox and the mixture was immediately heated at 110 °C with vigorous stirring by putting the Schlenk tube into an oil bath at 110 °C. After 60 min, the reaction was stopped by allowing air to enter the Schlenk tube. NMR yields were determined by removing a sample with a syringe, drying it under vacuum, extracting the residue with $CDCl_3$ and filtering the sample in a NMR tube. The obtained yield (20 %) is the average value of three runs.

X-ray Diffraction Studies. Structure Determination and Refinement. Single crystals of **11**, **16a** and **17** suitable for X-ray diffraction studies were selected from batches of crystals obtained at –32 °C from acetonitrile/diethyl ether solutions for **11**, and CH_2Cl_2/diethyl ether solutions for **16a**. Single crystals of **17** were obtained by slow diffusion of diethylether in solutions of **17** in $CDCl_3$ at room temperature. Diffraction data for all crystals were collected on a Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). A summary of crystal data, data collection parameters and structure refinements is given in Table 5. Cell parameters were determined from reflections taken from one set of 10 frames (1.0° steps in phi angle), each at 20 s exposure. The structures were solved using direct methods (SHELXS97) and refined against F^2 for all reflections using the SHELXL97 software. Multiscan absorptions corrections (MULscanABS in PLATON) were applied. All non-hydrogen atoms were refined anisotropically in structures. Hydrogen atoms in all structures were generated accordingly to stereochemistry and refined as fixed contributors using a riding model in SHELXL97.[20,21]

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Table 11 : Selected bond lengths (Å) and angles (°) for complex **16a**

	16a
Ni–C(1)	1.906(2)
Ni–C(2)	1.899(3)
Ni–Cp_{cent}	1.772
Ni–C_{Cp} (*av.*,min, max)	*2.136*, 2.096(3), 2.172(3)
C_{Cp}–C_{Cp} (*av.*,min, max)	1.4028, 1.379(5), 1.434(5)
C(1)–Ni–L	96.9(1)
C(1)–Ni–Cp_{cent}	136.0
C(2)–Ni–Cp_{cent}	126.9

Table 12: X-ray crystallographic data and data collection parameters for **11**, **16a** and **17**

	11	**16a**	**17**
Empiric formula	$C_{12}H_{16}N_3Ni{\cdot}BF_4$	$C_{31}H_{37}N_4Ni{\cdot}F_6P$	$C_{12}H_{20}I_2N_4Ni$
Formula weight	347.80	669.33	532.83
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P_{-1}	$P2_1/c$	$P2_1/c$
a (Å)	6.8787(6)	9.1782(2)	15.769(3)
b (Å)	10.1410(8)	18.5195(6)	8.9194(15)
c (Å)	10.8037(9)	18.6420(6)	13.135(2)
α (°)	97.351(2)	-	-
β (°)	93.501(2)	97.070(2)	107.207(3)
γ (°)	93.098(2)	-	-
V (Å^3)	744.59(11)	3144.59(16)	1764.8(5)
Z	2	4	4
D_x (Mg.m^{-3})	1.551	1.414	2.004
Absorp. Coeff. (mm^{-1})	1.34	0.73	4.59
Temperature (K)	174	173	173
Crystal Form, colour	Block, green	Prism, green	Prism, red
Crystal Size	0.48 x 0.40 x 0.30	0.46 x 0.22 x 0.15	0.30 x 0.30 x 0.10
h,k,l max	*9, 14, 12*	*11, 24, 24*	*20, 10, 17*
Tmin, Tmax	*0.566, 0.689*	-	*0.340*, *0.657*
Reflns collected	10183	23130	10047
R (reflections)	0.039(10183)	0.051(5568)	0.075(2921)
wR^2 (reflections)	0.099(4363)	0.145(7155)	0.173(3977)
GOF on F^2	1.06	1.04	1.29

Chapter 4

Base-Assisted sp^3-C–H Bond Activation at $Cp^{\dagger}$Ni-NHC Centres: Synthesis and Reactivity of New Alkyl-Ni(II) Complexes and Nickelacycles

1. Introduction

In the past two decades, much effort has targeted the catalytic sp^2-C–H bond functionalization of arenes and heteroarenes. This field is now recognized as an economically and environmentally attractive alternative to the traditional cross-coupling reactions involving aryl halides and organometallic reagents which generate undesirable inorganic waste.[1,2]

The activation of sp^3-C–H bonds represents a significantly bigger challenge owing to the large HOMO–LUMO gap between the sp^3-C–H σ and σ* orbitals, and less success has been achieved here.[1b,3] In particular, the functionalization of sp^3-C–H bonds in molecules with reactive functional groups, such as nitriles, is somewhat restricted, as these functional groups are often much more reactive towards the metal centre.

Recent research of our group has focussed the synthesis of new [Ni(R^1_2-NHC)(R^2_2-NHC)Cp] type complexes from the cationic acetonitrile complex [Ni(Mes_2-NHC)(CH_3CN)]$^+PF_6^-$ and an equimolar amount of the appropriate NHC (Chapter 3). Though, by employing the Mes_2-NHC carbene as a reagent, instead of the desired *bis*-NHC complex, we isolated small amounts of a cyanomethyl Ni(II) complex, [Ni(Mes_2-NHC)(η^1-CH_2CN)Cp]. We believe that the cyanomethyl complex arises from deprotonation of the *N*-coordinated acetonitrile ligand by the bulky carbene that in this particular case, acts as a base (Scheme 103). It should be mentioned here that the metallation of acetonitrile (pK_a = 25)[4] to give TM-CH_2CN complexes is not only rare in general, but is unknown for nickel species and has been observed virtually exclusively in complexes with group 8 or group 9 metals[5,6] and in a few homo- or heterobimetallic species.[7]

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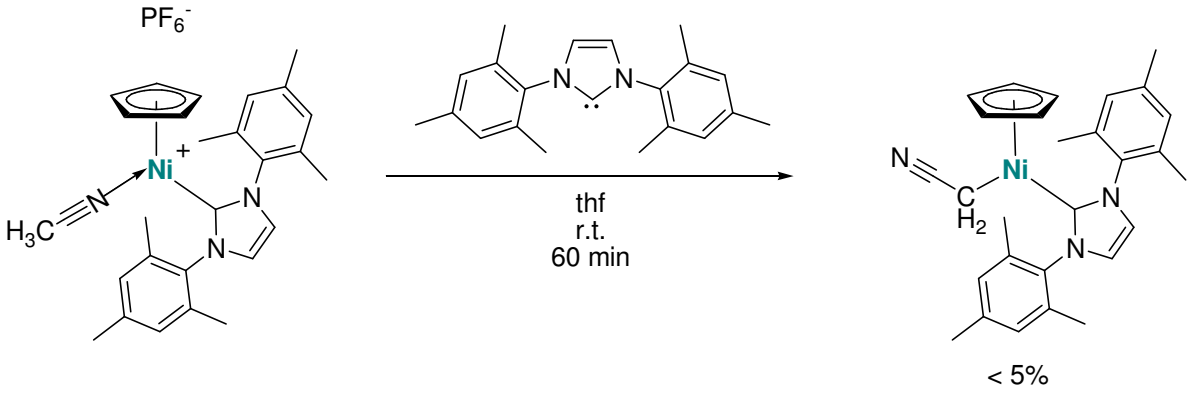

Scheme 103

In fact, metal coordinated acetonitrile can be considered as an easily substituted labile inert ligand. Therefore, acetonitrile-containing complexes are often used as a source of coordinatively unsaturated species, thus providing convenient precursors in organometallic syntheses and catalysis.[8] Indeed, we have applied this property of the acetonitrile ligand for the synthesis of cationic half-sandwich *bis*-NHC nickel compounds (See Chapter 3).

However, late TM coordinated nitrile ligands are not always considered as inert.[9] The acetonitrile ligand itself can undergo nucleophilic attack and subsequent metallation by metathesis in the presence of a strong base, to form the corresponding cyanomethyl TM complex.[5,7] Moreover, in some Ni-NHC species, unusual C–C bond cleavage of organonitriles was reported.[10]

To that effect, we were pleased that we could isolate the desired cyanomethyl-Ni(II) compound in excellent yields when $[Ni(Mes_2\text{-}NHC)(CH_3CN)Cp]^+PF_6^-$ was treated with potassium *t*-butoxide (KO*t*-Bu). Furthermore, we were wondering if the scope for the reactivity of the C–H bond α to the nitrile function of acetonitrile ligand on a Ni(II)-NHC-centre could be generalized to carbonyl functions (Scheme 104) as some Ni(II)-NHC complexes have shown to activate CO_2.[11,12]

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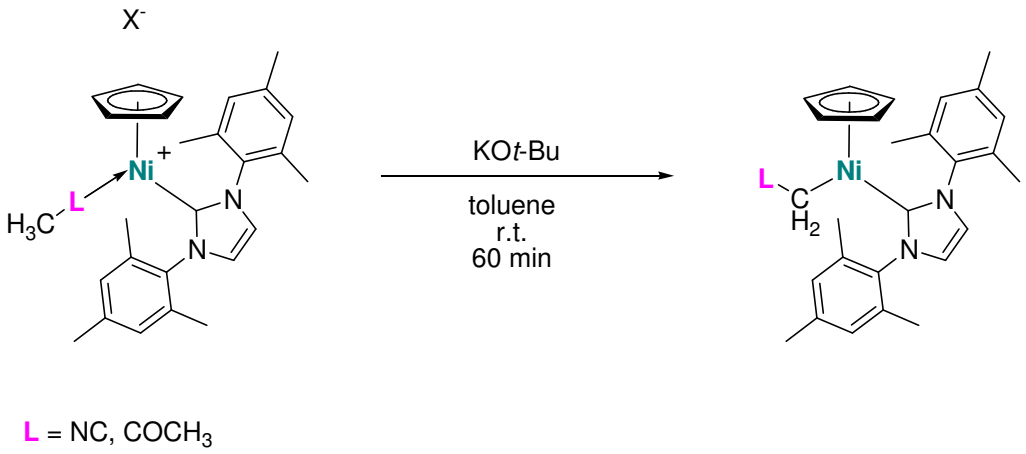
[11] (a) J. Li, Z. Lin, *Organometallics* **2009**, *28*, 4231; (b) B. R. Dible, M. S. Sigman, A. M. Arif, *Inorg. Chem.* **2005**, *44*, 3774.

[12] (a) T. N. Tekavec, G. Zuo, K. Simon, J. Louie, *J. Org. Chem.* **2006**, *71*, 5834; (b) T. N. Tekavec, A. M. Arif, J. Louie, *Tetrahedron* **2004**, *60*, 7431; (c) J. Louie, J. E. Gibby, M. V. Farnworth, T. N. Tekavec, *J. Am. Chem. Soc.* **2002,** *124*, 14688.



Scheme 104

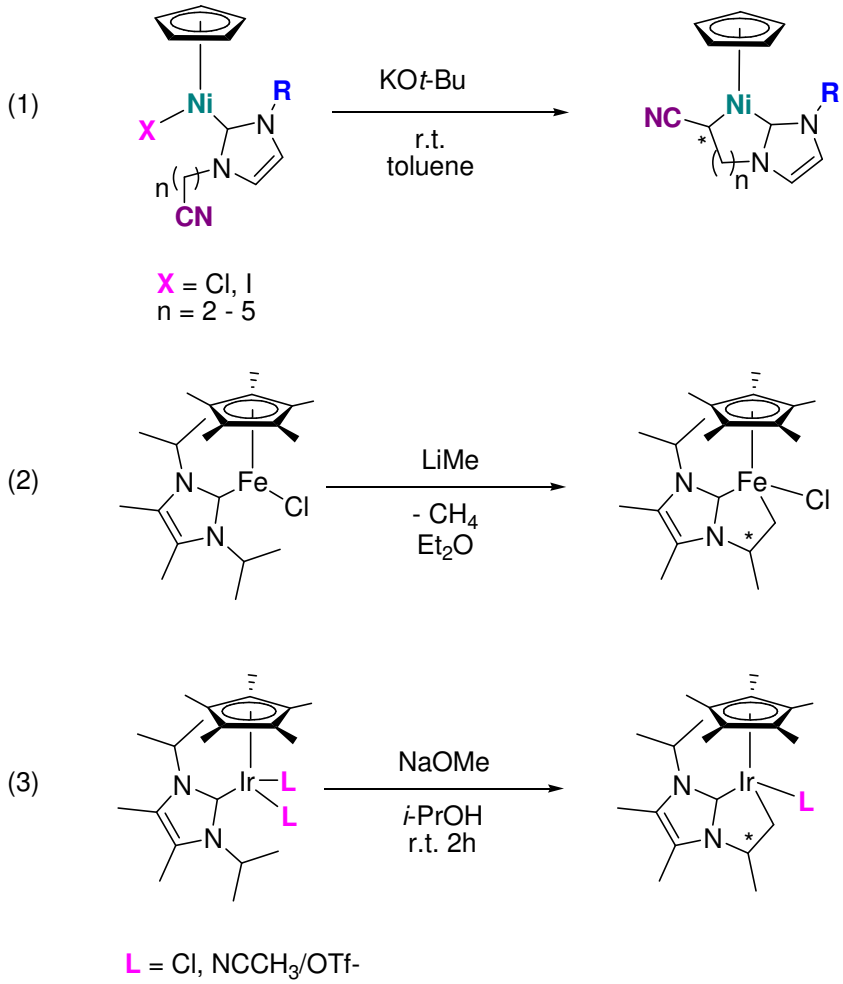
Furthermore, the recent discovery of intramolecular sp^2-C as well as sp^3-C–H bond activation by some late TMs such as iron,[13] rhodium, ruthenium[14] and iridium[15] bearing NHC ligands has opened a synthetic route for a new family of TM-NHC complexes bearing a [C,C']-chelating NHC ligand. The cyclometallation of iron, iridium and ruthenium complexes generally aroused from steric interactions of a branched alkyl *N*-substituent and a strongly alkaline ligand. Thus, the desired cyclometallations could be achieved by methane[13] (Eq. 2, Scheme 105) or ethane[16] elimination or by base-assisted C–H bond activation of the *N*-alkyl substituent with an alkoxide (Eq. 3, Scheme 105)[14c,15a-c]; a classical TM promoted C–H bond activation process has also been observed.[15e]

Finally, the reaction of the cationic *bis*-NHC species **15** with acid solutions of acetonitrile has shown that in half-sandwich Ni(II)-NHC complexes, the Ni–Cp bond could be

[13] Y. Ohki, T. Hatanaka, K. Tatsumi, *J. Am. Chem. Soc.*, **2008**, *130*, 17174.
[14] for Ruthenium, see : (a) A E. W. Ledger, M. F. Mahon, M. K. Whittlesey, J. M. J. Williams, *Dalton Trans.* **2009**, 6941; (b) C. Zhang, Y. Zhao, B. Li, H. Song, S. Xu, B. Wang, *Dalton Trans.* **2009**, 5182; (c) S. Burling, B. M. Paine, D. Nama, V. S. Brown, M. F. Mahon, T. J. Prior, P. S. Pregosin, M. K. Whittlesey, J. M. J. Williams, *J. Am. Chem. Soc.* **2007**, *129*, 1987; (d) S. Burling, M. F. Mahon, B. M. Plaine, M. K. Whittlesey, J. M. J. Williams, *Organometallics* **2004**, *23*, 4537.
[15] for Iridium, see : (a) Y. Tanabe, F. Hanasaka, K.-i. Fujita, R. Yamaguchi, *Organometallics* **2007**, *26*, 4618; (b) F. Hanasaka, Y. Tanabe, K.-i. Fujita, R. Yamaguchi, *Organometallics* **2006**, *25*, 826; (c) R. Corberán, M. Sanaú, E. Peris, *Organometallics* **2006**, *25*, 4002;(d) R. Corberán, M. Sanaú, E. Peris, *J. Am. Chem. Soc.* **2006**, *128*, 3974; (e) N. M. Scott, R. Dorta, E. D. Stevens, A. Correa, L. Cavallo, S. P. Nolan, *J. Am. Chem. Soc.* **2005**, *127*, 3516; (f) A. A. Danopoulos, S. Winston, M. B. Husrthouse, *J. Chem. Soc., Dalton Trans.* **2002**, 3090; (g) M. Prinz, M. Grosche, E. Herdtweck, W. A. Herrmann, *Organometallics* **2000**, *19*, 1692.
[16] for platin, see: G. C. Fortman, N. M. Scott, A. Linden, E. D. Stevens, R. Dorta, S. P. Nolan, *Chem. Commun.* **2010**, *46*, 1050.

less robust that commonly admitted (See Chapter 3).[17] This discovery lead to a methodology for new square planar Ni(II)-NHC_2 compounds.

All these results have convinced us to study the scope for sp^3-C–H bond activation generated by a Ni(II)-NHC centre with those C–H bonds, which are i) α to a *N*-bounded acetonitrile ligand, ii) α to a *O*-coordinated carbonyl compound such as acetone and 4'-methoxyacetophenone and iii) α to an intramolecular nitrile functionality of a *N*,*N*'-asymmetrically substituted NHC ligand (Eq. 1, Scheme 105).



Scheme 105

[17] Only few examples of M–Cp bond cleavage have been reported to date: (a) C. P. Casey, J. M. O'Connor, K. J. Haller, *J. Am. Chem. Soc.* **1985**, *107*, 1241; (b) K. Jonas, *Adv. Organomet. Chem.* **1982**, *19*, 97. Examples of M–Cp* bond cleavage is less rare due to the greater steric bulk of these ligands and have been observed notably for hetero-bimetallic species: (d) M. J. Chetcuit, B. E. Grant, *J. Am. Chem. Soc.* **1989** *111* 2743; (e) M. J. Chetcuti, L. A. DeLiberato, P. E. Fanwick, B. E. Grant, *Inorg. Chem.* **1990**, *29*, 1295.

In the first part of this chapter we target sp^3-C–H bond activation of C–H bonds which are α to a polar functional group. We describe how we obtained the first examples of C–H bond activation of a labile acetonitrile ligand on a nickel(II) centre. The reaction consists in the ligand formally loosing one hydrogen atom and doing a flip to give the corresponding metallated product. Structural data of the initial *N*-bound cationic acetonitrile nickel(II) complex [Ni(Mes$_2$-NHC)(CH$_3$CN)Cp†] (Cp† = Cp, Cp*) and the final cyanomethyl nickel(II) complex [Ni(Mes$_2$-NHC)(CH$_2$CN)Cp] are presented. Furthermore, we have focussed on sp^3-C–H bonds α to a carbonyl function. The synthesis of the cationic acetone Ni(II) complex [Ni(Mes$_2$-NHC){(CH$_3$)$_2$CO}Cp] as well as the reaction of this cationic complex with KO*t*-Bu is presented. The reaction scope of these sp^3-C–H bond activations is further investigated by employing 4'-methoxyacetophenone as a substrate. The cationic *O*-bound acetone nickel(II) complex and the final (post C–H activation) acetonyl nickel(II) complexes [Ni(Mes$_2$-NHC)(CH$_2$COCH$_3$)Cp] as well as [Ni(Mes$_2$-NHC){CH$_2$CO(*p*-C$_6$H$_4$-OMe)}Cp] were fully characterized by NMR spectroscopy. In addition, single crystal X-ray diffraction studies of the complex [Ni(Mes$_2$-NHC){CH$_2$CO(*p*-C$_6$H$_4$-OMe)}Cp] were obtained.

In the second part, we target the synthesis of neutral halo-nickel(II) complexes, [Ni{NC(CH$_2$)$_3$-NHC-Me}ICp] and [Ni{NC(CH$_2$)$_n$-NHC-Mes}XCp] (n = 3, X = Cl; n = 4, X = I, n = 5, X = Br), as well as of some of their cationic acetonitrile counterparts [Ni{NC(CH$_2$)$_n$)-NHC-Mes}(CH$_3$CN)Cp]$^+$PF$_6^-$ (n = 3, 5) and [Ni{NC(CH$_2$)$_4$)-NHC-Mes}(CH$_3$CN)Cp]$^+$BF$_4^-$, bearing an *N*-alkyl nitrile substituted NHC ligand. All complexes were fully characterized by standard spectroscopic techniques and the structures of the neutral complexes [Ni{NC(CH$_2$)$_3$-NHC-Mes}ClCp] and of [Ni{NC(CH$_2$)$_2$-NHC-Me}ICp] were established by single crystal X-ray diffraction studies. Furthermore, we describe how we have achieved the synthesis of cyanoalkyl-Ni(II) nickelacycles [Ni{CHCN(CH$_2$)$_2$-NHC-Me}Cp] and [Ni{CH(CN)CH$_2$)$_n$-NHC-Mes}Cp] (n = 3 – 5) by activation of the C–H bond α to the nitrile group in both the neutral and the cationic compounds. All compounds were fully characterized by NMR and by IR spectroscopy and the molecular structures of [Ni{CHCN(CH$_2$)$_2$-NHC-Mes}Cp] and [Ni{CHCN(CH$_2$)$_4$-NHC-Mes}Cp] were determined by single crystal X-ray diffraction studies.

Finally, we have investigated the strength of the Ni–Cp bond. We will briefly present the reactivity of these complexes as catalysts in the Suzuki-Miyaura cross-coupling of 4'-bormoacetophenone and phenyl boronic acid. We close this chapter by the synthesis of square planar [Ni{CHCN(CH$_2$)$_n$-NHC-R}(acac)] (n = 2, R = Me and n = 3, R = Mes; acac = acetonyl

acetonate) complexes which have been obtained by removal of the Cp ligand from acid acetonitrile solutions of the nickelacycles and HCl.

2. Results and Discussion

2.1. Base assisted C–H bond activation α to polar functional groups

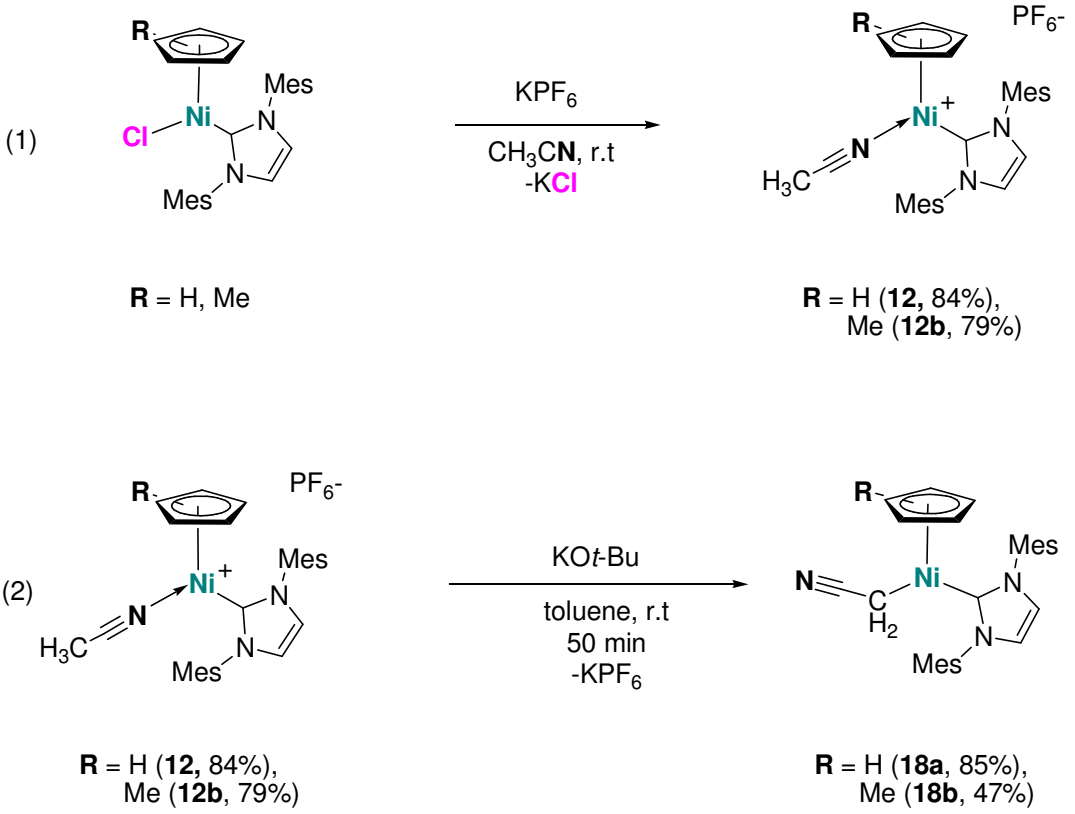
2.1.1. Synthesis of [Ni(Mes$_2$-NHC)(CH$_2$R)Cp] (R = CN, COMe, CO(*p*-C$_4$H$_6$-OMe) complexes

2.1.1.1. Base-assisted *sp*^{3}-C–H bond activation of acetonitrile

Recent research of our group has focussed on Cp and Cp* complexes of nickel bearing NHC ligands. We have described the chemistry and dynamic behaviour of complexes [Ni(Ar$_2$-NHC)XCp†] (Cp† = Cp, Cp*; X = Cl, I; Ar = Mes, *i*-Pr$_2$Ph)[18] and some aspects of their catalytic behaviour as well as that of their cationic [Ni(Ar$_2$-NHC)(CH$_3$CN)Cp†]$^+$PF$_6^-$ counterparts.[19]

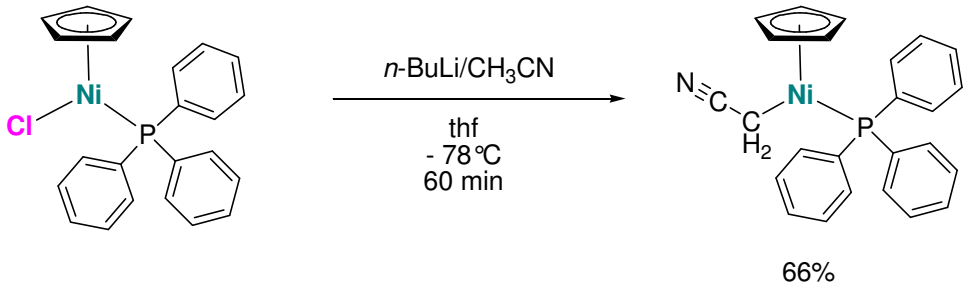
The cationic *N*-bound nickel(II) complexes [Ni(Mes$_2$-NHC)(CH$_3$CN)Cp†] (Cp† = Cp, Cp*), **12**, were synthesized in good yields from the reaction of the chloro-nickel(II) compound [Ni(Mes$_2$-NHC)ClCp][20] with equimolar acetonitrile solutions of KPF$_6$ (or AgBF$_4$) (Eq. 1, Scheme 106).[19] Furthermore, when toluene suspensions of **12** were stirred with 1 equivalent KO*t*-Bu for 50 minutes at room temperature, ^{1}H NMR data indicated that a rapid and quantitative deprotonation of the acetonitrile ligand had occurred (Eq. 2, Scheme 106). Moreover, during this process the initially insoluble green-yellow complex progressively gave way to a brownish solution. The resulting cyanomethyl group coordinated to the nickel atom was subsequently isolated as [Ni(Mes$_2$-NHC)(CH$_2$CN)Cp], **18a**, a neutral cyanomethyl complex in 85 % yield. The related Cp* complex [Ni(Mes$_2$-NHC)(CH$_2$CN)Cp], **12b**, also generates the corresponding **18b** complex, though in much lower yield as shown in Equation 2 of Scheme 106. Attempts to carry the reaction with a weaker base such as potassium carbonate failed.

[18] (a) V. Ritleng, C. Barth, E. Brenner, S. Milosevic, M. J. Chetcuti, *Organometallics* **2008**, *27*, 4223; (b) V. Ritleng, E. Brenner, M. J. Chetcuti, *J. Chem. Edu.* **2008**, 1646.
[19] V. Ritleng, A. M. Oertel, M. J. Chetcuti, *Dalton Trans.* **2010**, *39*, 8153.
[20] C. D. Abernethy, A. H. Cowley, R. A. Jones, *J. Organomet. Chem.* **2000**, *596*, 3.



Scheme 106

Generally cyanomethyl TM complexes are obtained by oxidative addition of $ClCH_2CN$ to a late TM phosphine complex or, under strictly alkaline reaction conditions, by metathesis of the appropriate halo-TM complex with $LiCH_2CN$ (*n*-BuLi/CH_3CN) at -78 °C.[21] In particular, the electronically related phosphine-coordinated counterpart, [Ni(PPh_3)(CH_2CN)Cp], was synthesized by the former method in 66 % yield (Scheme 107).[22]



Scheme 107

[21] (a) T. A. Atesin, T. Li, S. Lachaize, W. W. Brennessel, J. J. Garcia, W. D. Jones, *J. Am. Chem. Soc.*, **2007**, *129*, 7562 ; (b) K. D. Tau, D. W. Meek, *Inorg. Chem.*, **1979**, *18*, 3574; (c) R. Ros, R. Bataillard, R. Roulet, *J. Organomet. Chem.,* **1076**, *118*, C53 ; (d) R. Ros, J. Renaud, R. Roulet, *Helv. Chim. Acta*, **1975**, *58*, 133; (e) K. Suzuki, H. Yamamoto, *J. Organomet. Chem.*, **1973**, *54*, 385.

[22] J. G. Davidson, E. K. Barefield, D. G. Van Derveer, *Organometallics*, **1985**, *4*, 1178.

2.1.1.2. Base-assisted sp^3-C–H bond activation of carbonyl compounds

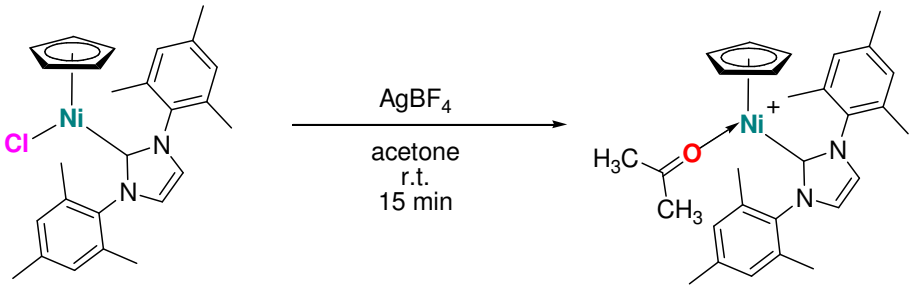
We were pleased to extend the synthesis of the cationic acetonitrile Ni(II)-NHC species to cationic acetone complexes.[19] Even though direct metallation of ketones has already been obtained by employing acetone solutions of the appropriate TM complex carrying basic ligands (in particular for complexes of Pt and Au[23]) to our knowledge, this method has not yet been observed for nickel-complexes.

When acetone solutions of the neutral complex [Ni(Mes$_2$-NHC)ClCp][20] were treated with an equimolar amount of $AgBF_4$, the chloride was abstracted and the cationic acetone complex [Ni(Mes$_2$-NHC)(CH$_3$(CO)Cp]$^+BF_4^-$, **19**, was isolated in good yield (Eq. 1, Scheme 108). Furthermore, the corresponding α-C–H bond activation product [Ni(Mes$_2$-NHC)(CH$_2$COCH$_3$)Cp], **20**, was synthesized by treating acetone solutions of the cationic complex **19** with an equimolar amount of KO*t*-Bu although compared to the cyanomethyl complex **18**, only moderate yields of **20** were isolated (Eq. 2, Scheme 108). Interestingly, a mixture of the complex **20** and another product was observed in the ^{1}H NMR spectrum. This second compound was identified as the dinuclear nickel complex [Ni$_2$(Mes$_2$-NHC)$_2${(CH$_2$)$_2$CO}Cp], **21**, which could be isolated in moderate yields from the reaction of equimolar toluene suspensions of **19** and KO*t*-Bu (Eq. 3, Scheme 108). The initially reddish suspension progressively dissolved to generate a brownish solution, analogous to that what was observed for the synthesis of the cyanomethyl-Ni(II) complex.

Finally, we have isolated 31 % of the C–H bond activation product [Ni(Mes$_2$-NHC)(CH$_2$CO(*p*-C$_6$H$_4$-OMe)Cp], **22**, from toluene mixtures of 4'-methoxyacetophenone, [Ni(Mes$_2$-NHC)ClCp] and KO*t*-Bu (Eq. 4, Scheme 108).

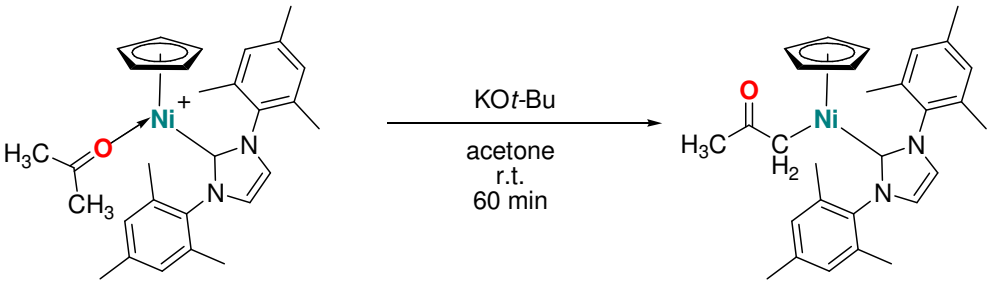
[23] (a) L. R. Falvello, R. Garde, E. M. Miqueleiz, M. Tomas, E. P. Urriolabeitia, *Inorg. Chim. Acta*, **1997**, *264*, 297; (b) J. Vicente, M. D. Bermudez, J. Escribano, M. P. Carrillo, P. G. Jones, *J. Chem. Soc., Dalton Trans.*, **1990**, 3083; (c) J. Vicente, M. D. Bermudez, M. T. Chicote, M. J. Sanchez-Santano, *J. Chem. Soc., Dalton Trans.*, **1990**, 1945; (d) J. Vicente, M. D. Bermudez, M. T. Chicote, M. J. Sanchez-Santano, *J. Chem. Soc., Chem. Commun.*, **1989**, 141; (e) Y. Aoyama, A. Yamagishi, Y. Tanaka, H. Toi, H. Ogoshi, *J. Am. Chem. Soc.*, **1987**, *109*, 4735.

(1)



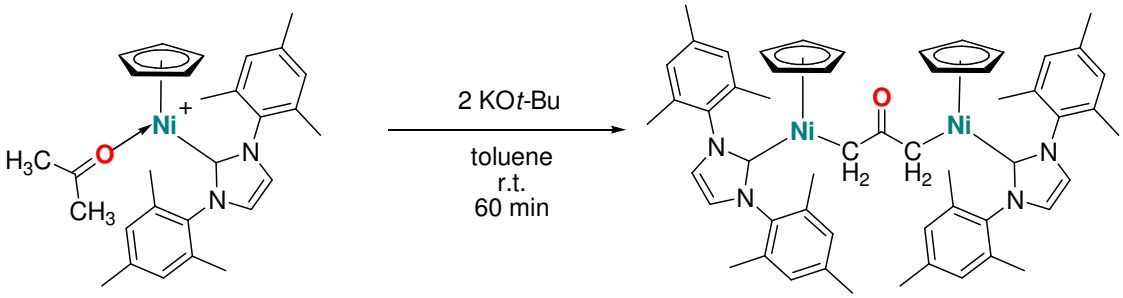
19, 90%

(2)



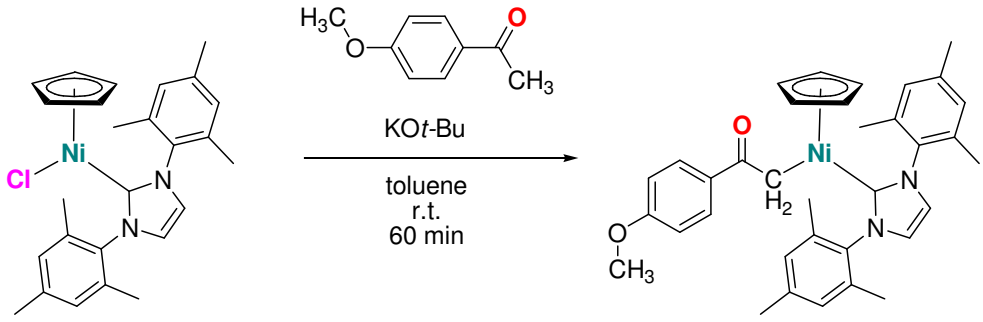
20, 31%

(3)



21, 20%

(4)



22, 31%

Scheme 108

Good ^{1}H and $^{13}C\{^{1}H\}$ NMR data could be obtained for all complexes expect **22**, for which was collected only ^{1}H NMR data. Crystals suitable for single crystal X-ray diffraction studies could be obtained for the complexes **21** and **22** from cold mixtures of thf/pentane.

2.1.2. Structural studies

2.1.2.1. [Ni(Mes$_2$-NHC)(η^1-CH$_2$CN)Cp]

Crystals of the cationic complex [Ni(Mes$_2$-NHC)(CH$_3$CN)Cp]$^+$BF$_4^-$, **12a**, and of its cyanomethyl derivative [Ni(Mes$_2$-NHC)(CH$_2$CN)Cp], **18a**, were grown from (1:3:1) mixtures of acetonitrile/diethyl ether/pentane and from (1:3) solutions of thf/pentane respectively. Crystallographic data and data collection parameters are listed in Table 22. A list of selected bond length and angles for both complexes appears in Table 13. The molecular structure of the cationic part of **12a** and that of **18a** are shown in a similar orientation in Figure 1-A and 1-B respectively.

The molecular structure of **12a** displays the Cp ring, the Mes$_2$-NHC ligand, the *N*-bound acetonitrile ligand all bound to nickel, and one PF_6 counter anion. **12a** adopts a two legged piano stool geometry with the acetonitrile nitrogen atom N(1) and the carbenoid carbon C(1) subtending an angle of 96.5° at the nickel atom.[24] In all aspects, the molecular structure does not substantially differ from those of the 18-electron ML_2Cp complexes and notably from that of its neutral halo-counterparts [Ni(Mes$_2$-NHC)ClCp].[20]

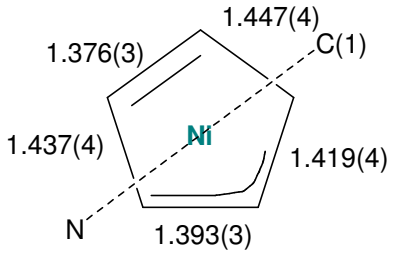
Furthermore, the acetonitrile ligand is linear [N–C(3)–C(2) = 178.5(3)°] but the Ni–N bond is nevertheless not perfectly co-linear with this axis [NiN(1)C(2) = 174.5(2)°]. The sum of all the angles subtended by the Cp centroid, the NHC carbenoid carbon atom C(1) and the acetonitrile nitrogen N(3) is equal 360°, so that the nickel coordination geometry is strictly trigonal planar. Distortions of the Cp ligand C–C bonds, which are intermediate ($\Delta_{na} > 0.01$Å) between those detected for "ene-allyl" and "diene" distortions are observed for the compound **12a** (Scheme 109).[25] Such "in between" distortions of the C–C bond distances of the Cp ligand have been previously observed for [Ni(Mes-NHC-*n*-Bu]ICp] (See Chapter 2).

Similarly, **18a** features a two legged piano stool geometry in which the cyanomethyl ligand bends away from both the Cp and the NHC ligand. Thus, the transformation of the *N*-

[24] N. M. Scott, S. P. Nolan, *Eur. J. Inorg. Chem*, **2005**, 1815.
[25] (a) S. Milosevic, E. Brenner, V. Ritleng, M. J. Chetcuti, *Dalton Trans*. **2008**, 1973, (b) D. P. Allen, C. M. Crudden, L. A. Calhoun, R. Wang, *J. Organomet. Chem.* **2004**, *689*, 3203; (c) R. Dorta, E. D. Stevens, C. D. Hoff, S. P. Nolan, *J. Am. Chem. Soc.* **2002**, *125*, 10490; (d) R. W. Simms, M. J. Drewitt, M. J. Baird, *Organometallics* **2002**, *21*, 2958; (e) P. L. Holland, M. E. Smith, R. A. Andersen, R. G. Bergman, *J. Am. Chem. Soc.* **1997**, *119*, 12815.

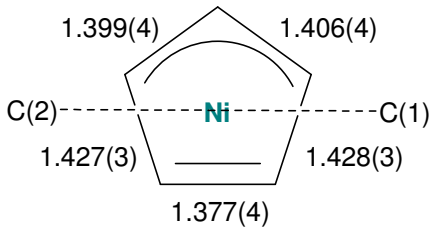
coordinated CH_3CN into a *C*-bounded η^1-CH_2CN group results in a now Ni–C(2)–C(3) angle of 112.5(2)° which is similar to the Ru–C–C angle of 112.81(19)°] seen in the complex $Ru(PPh_3)_2(CH_2CN)(\eta^5$-indenyl)][6a] displaying a similar geometry.

Interestingly, in contrast to the cationic acetonitrile compound **12a** the Cp ring of the cyanomethyl-nickel complex **18** exhibits now "ene-allyl" C–C bond distortions. Thus, the [C(1)–Ni–C(2)] plane bisects the two longest C–C bonds of the Cp ring and the two adjacent short C–C bonds (1.399(4) Å and 1.406(4) Å) are opposite to the shortest C–C bond (1.377(4) Å). The "ene-allyl" distortion of the Cp ligand of **18a** is illustrated in Scheme 109. In this manuscript, "ene-allyl" distortions have been defined as those distortions in which the two adjacent short C–C bonds differ from less than 0.01 Å ($\Delta_a < 0.01$ Å).



"in between"

[Ni(Mes$_2$-NHC)(CH_3CN)Cp]$^+PF_6^-$, **12**



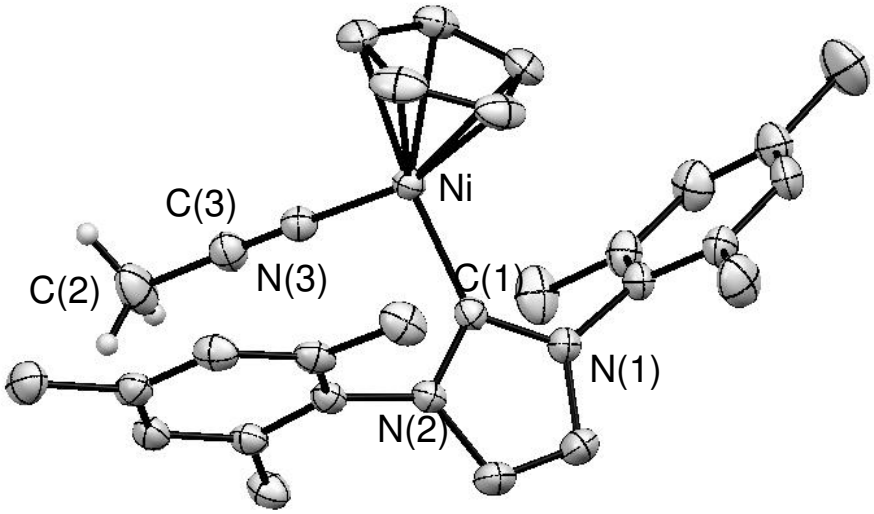
"ene-allyl"

[Ni(Mes$_2$-NHC)(η^1-CH_2CN)Cp], **18a**

Scheme 109

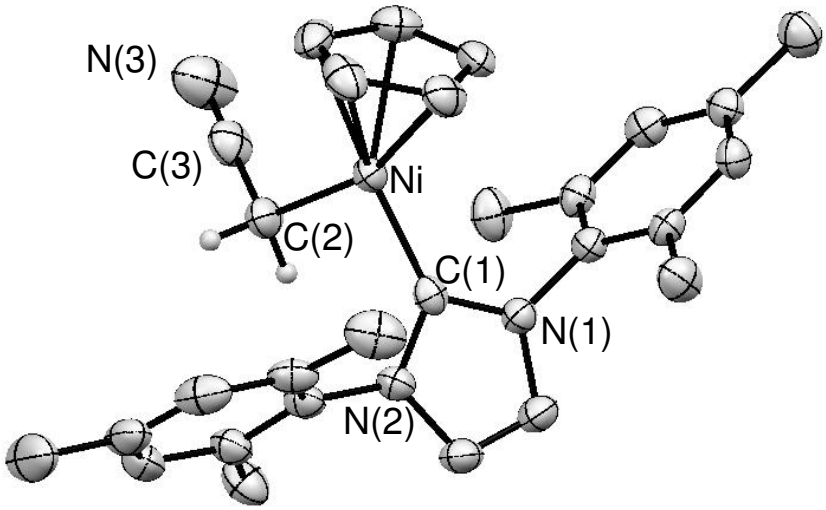
The Ni–C(2) bond distance of the cyanomethyl group [1.961(3) Å] is smaller than the Ni–C bond distance reported for the related methyl–nickel(II) carbene compound (2.033(3) Å),[20] though similar to that reported for [Ni(PEt_3)(Me)Cp*] (1.96(4) Å)[25e] bearing the strongly electron donating Cp* ligand. Unfortunately, no crystallographic data was reported for [Ni(PEt_3)(CH_2CN)Cp].[22]

A



[Ni(Mes$_2$-NHC)(CH$_3$CN)Cp]$^+$, 12

B



[Ni(Mes$_2$-NHC)(η^1-CH$_2$CN)Cp], 18a

Figure 9 : A, ORTEP plot of the cationic part of the complex [Ni(Mes$_2$-NHC)(CH$_3$CN)Cp]$^+$BF$_4^-$, **12a**. B, ORTEP plot of the complex [Ni(Mes$_2$-NHC)(η^1-CH$_2$CN)Cp], **18a**. Ellipsoids are shown at the 50 % probability level. Key atoms are labelled. Only hydrogen atoms of the acetonitrile ligand and of the cyanomethyl group are shown for clarity.

Table 13 : Selected bond length (Å) and angles (°) of **12a** and **18a**

	12a	**18a**
Ni–C(1)	1.902(2)	1.877(2)
Ni–L[a]	1.869(2)	1.961(3)
C≡N	1.138(3)	1.146(4)
Ni–Cp_{cent}	1.760	1.778
Ni–C_{Cp} (*av*, min, max)	*2.1306*, 2.022(3), 2.200(3)	2.1424, 2.083(2), 2.189(2)
C_{Cp}–C_{Cp} (*av*, min, max)	*1.4144*, 1.376(3), 1.447(4)	1.4074, 1.377(4), 1.428(3)
C(1)–Ni–L	96.94(8)	91.9(1)
C(1)–Ni–C_{cent}	131.8	137.5
L–Ni–C_{cent}	131.2	130.5
Ni–N≡C	174.5(2)	112.5(2)
N≡C–C	177.9(3)	178.5(3)

[a] L = N for **12a**, L = C(2) for **18**.

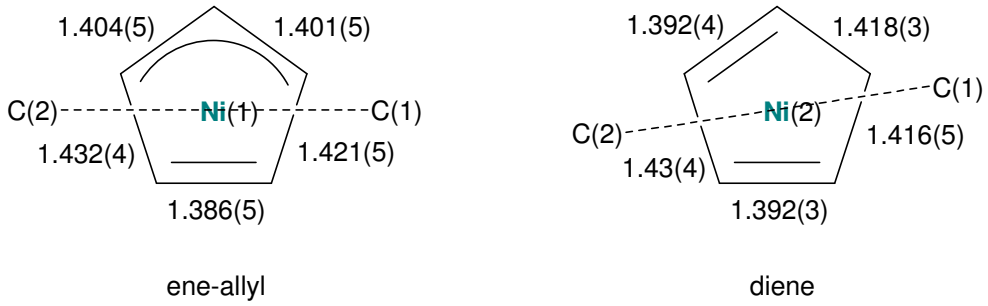
2.1.2.2. $[Ni_2(Mes_2\text{-}NHC)_2\{\eta^1,\eta^1\text{-}(CH_2)_2\}Cp_2]$ and $[Ni(Mes_2\text{-}NHC)(\eta^1\text{-}CH_2(p\text{-}C_6H_4\text{-}OMe)Cp]$

Single crystals of the complexes $[Ni_2(Mes_2\text{-}NHC)_2\{(CH_2)_2CO\}Cp_2]$, **21**, and $[Ni(Mes_2\text{-}NHC)(CH_2CO(p\text{-}C_6H_4\text{-}OMe)Cp]$, **22**, were grown in cold solutions of thf and pentane. Crystallographic data and data collection parameters are listed in Table 22. The molecular structures of **21** and **22** are shown in Figure 2-A and Figure 2-B respectively.

The molecular structure of the binuclear complex **21** shows the two Cp nickel Mes_2-NHC fragments bridged by a η^1,η^1–$(CH_2)_2CO$ ligand as well as one Cp ring and one Mes_2-NHC bonded to each nickel. The complex features a two legged piano stool geometry for each of the nickel atoms with a trigonal planar nickel coordination geometry [∑angles) = 359.9]. In addition, the two halves of the molecule of **21** (Figure 2-A) are not crystallograpically related but are effectively equivalent as shown by the very similar geometrical parameters which are observed. The bridging η^1,η^1-$(CH_2)_2CO$ group displays a non-linear angle with each nickel atom [Ni–C(2)–C(3) = 112.9(2)° and 111.3(4)°] and bents away from both the two Cp rings and the Mes_2-NHC groups.

The Ni–C(1) values average 1.882 Å [1.878(2) Å and 1.888(2) Å] and are similar to those observed for [Ni(Mes$_2$-NHC)ClCp].[20] The Ni–C(2) bonds average 1.976 Å [1.975(3) Å and 1.977(3) Å] and are comparable to those of the cyanomethyl-Ni(II) compound [Ni(Mes$_2$-NHC)(η^1-CH$_2$CN)Cp], **18a** (1.961(3) Å, Table 13) though, still smaller than that of the methyl-Ni(II) complex [Ni(Mes$_2$-NHC)(Me)Cp] (2.033(3) Å).[20] Furthermore, the C=O bond lengths of acetonyl-metal compounds seems insensitive to the nature of the TM since the distance observed for **21** [1.235(3) Å] is analogous to those noted for other acetonyl-metal complexes [1.227(9) Å has been reported for a gold(III)[26] complex and 1.238(14) Å has been observed for a platinum(II) compound].[27]

Interestingly, the Cp group which is bounded to the Ni(1) atom features "ene-allyl" distortions (Δ_a < 0.01 Å) in contrast to that bound to the Ni(2) which displays "diene" distortions (Δ_{na} < 0.01 Å). An illustration of the Cp ligand distortions of the dinickel complex **21** featuring the C–C bond lengths of each ring is shown in Scheme 110.



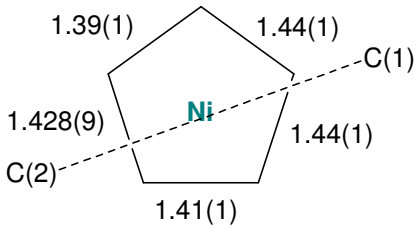
Scheme 110

It noteworthy, that an intermolecular short contact is observed between one imidazole ring proton and the carbonyl oxygen atom of a neighbouring complex [2.134(2) Å]. Finally, the large distance which separates the nickel atoms [5.3503(5) Å] suggests that complete rotation of the Ni–C(1) bonds in solution would be allowed without major structural distortion.

The molecular structure of the complex [Ni(Mes$_2$-NHC)(η^1-CH$_2$CO(*p*-C$_6$H$_4$-OMe)Cp], **22**, displays one nickel atom surrounded by one Cp ring, the NHC and the ketonyl ligand in a piano stool geometry which is similar to that of each nickel atom in the previously described ketonyl-complex **21** (Figure 2-B).

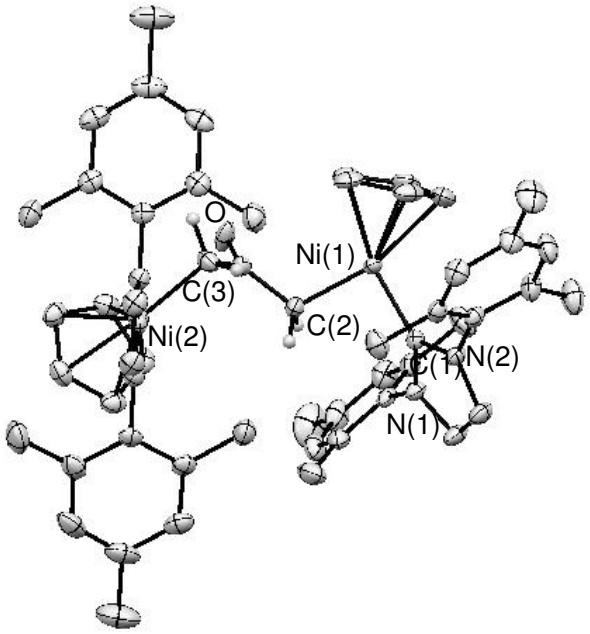
[26] D. Fan, E. Mendélez, J. D. Ranford, P. F. Lee, J. J. Vittal, *J. Organomet. Chem.* **2004**, *689*, 2969.
[27] L. R. Falvello, R. Garde, E. M. Miqueleiz, M. Tomás, E. P. Urriolabeita, *Inorg. Chim. Acta* **1997**, *264*, 297.

Generally, no significant distortion of the coordination sphere of the nickel atom in the complex **22** is observed compared to that of both nickel atoms of **21** or related half-sandwich Ni(II) complexes. The Ni–C(2)–C(3) angle [111.5(5)°] is similar to those observed for the ketonyl bridge and both Ni atoms of **21** as well as to the angle between the nickel and the cyanomethyl ligand in the complex **18a**. Moreover, the Ni–C(1) and Ni–C(2) bond distances [1.864(7) and 1.990(7) Å respectively] are similar to those observed for **21**. Nevertheless, a slight decrease of the C=O bond length is detected whit respect to that of **21** which should be induced by the aromatic ring system α to the carbonyl bond. Finally, it noteworthy, that the C–C bond lengths of the Cp ligand of **22** do not show any real evidence for Cp ligand distortions (Scheme 111).



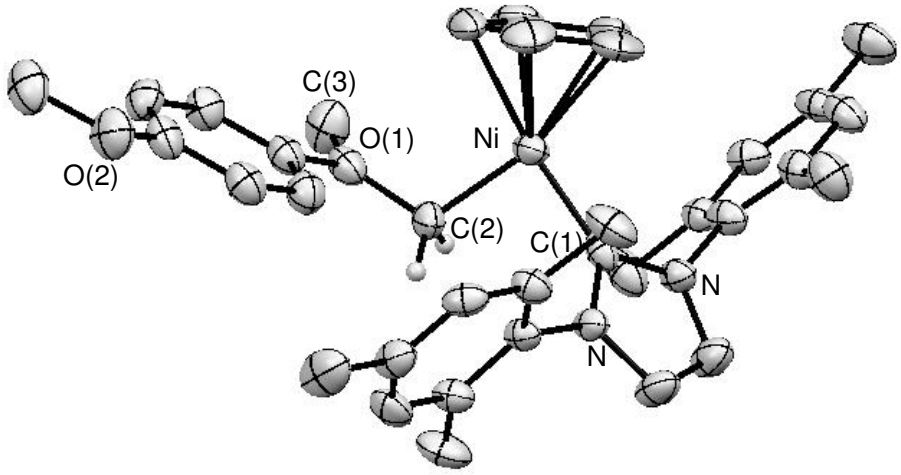
Scheme 111

A



$[Ni_2(Mes_2\text{-}NHC)_2\{\eta^1,\eta^1\text{-}(CH_2)_2CO\}Cp_2]$, 21

B



$[Ni(Mes_2\text{-}NHC)(\eta^1\text{-}CH_2CO(p\text{-}C_6H_4\text{-}OMe)Cp]$, 22

Figure 10 : ORTEP plot of the complex $[Ni_2(Mes_2\text{-}NHC)(\eta^1,\eta^1\text{-}(CH_2)_2CO)Cp_2]$, **21**, and of the complex $[Ni(Mes_2\text{-}NHC)\{\eta^1\text{-}CH_2CO(p\text{-}C_6H_4\text{-}OMe)\}Cp]$, **22**. Ellipsoids are shown at the 50 % probability level. Key atoms are labelled. Only hydrogen atoms of the ketonyl ligands of **21** and **22** are shown for clarity.

Table 14 : Selected bond length (Å) and angles (°) of complexes **21** and **22**.

	21		**22**
	Ni(1)	Ni(2)	
Ni–C(1)	1.878(2)	1.888(2)	1.864(7)
Ni–C(2)	1.975(3)	1.977(3)	1.990(7)
Ni–C_{cent}	1.790	1.794	1.779
Ni–C_{Cp} (*av*)	*2.208*	*2.158*	*2.150*
min, max	2.111(2), 2.189(3)	2.108(3), 2.210(2)	2.104(9), 2.198(7)
C_{Cp}–C_{Cp} (*av*)	*1,409*	*1.410*	*1.422*
min, max	1.386(5), 1.432(4)	1,392(3), 1.430(4)	1,39(1), 1.44(1)
C=O		1.235(3)	1.214(8)
C(3)–CO	1.477(4)	1.483(4)	1.45(1)
C_{cent}–Ni–C(1)	136.9	137.1	136.0
C_{cent}–Ni–C(2)	130.6	128.6	131.0
C(1)–Ni–C(2)	92.5(1)	94.4(1)	92.5(3)
Ni–C(2)–C(3)	112.9(2)	111.3(2)	111.5(5)

2.1.3. Spectroscopic data studies

2.1.3.1.[Ni(Mes$_2$-NHC)(η^1-CH$_2$CN)Cp]

The ^{1}H NMR spectra of the cationic complexes [Ni(Mes$_2$-NHC)(CH$_3$CN)Cp], **12a**, and [Ni(Mes$_2$-NHC)(CH$_3$CN)Cp*], **12b**, are straightforward at ambient temperature and show the imidazole ring protons as well as the aryl *N*-substituents, and the Cp or Cp* ring (Table 15). ^{1}H NMR spectroscopic data confirm that the acetonitrile ligand is labile, as free exchange is observed between free CD$_3$CN and coordinated CH$_3$CN in CD$_3$CN solutions for these complexes. For samples of **12** a surprisingly weak ν(C≡N) stretch is observed at 2299 (or 2294) cm^{-1}.[28]

The ^{1}H NMR spectra of [Ni(Mes$_2$-NHC)(CH$_2$CN)Cp] **18a** and [Ni(Mes$_2$-NHC)(CH$_2$CN)Cp*) **18b** are in accord with their proposed structures. Both show the resonance signals of the imidazole ring protons and those of the *N*-substituents, those of the

[28] This value is consistent with those reported for nickel–*N*-bound acetonitrile complexes. A. E. Wickenden, R. A. Krause, *Inorg. Chem.* **1965**, *4*, 404.

Cp or Cp* as well as those of the cyanomethyl group (Table 15). There is a minor chemical shift difference between the resonance signals of the methylene protons of complexes **18** (-0.08 ppm and -0.07 ppm) and that of the complex [Ni(PPh_3)(CH_2CN)Cp], **I**, (0.07 ppm) (Scheme 107).[22] However, the α-nitrile group causes a down field shift of these protons with respect to that of the Ni-Me group of [Ni(Mes_2-NHC)(Me)Cp] (-0.62 ppm).[29] This shift may be generated by the electron attracting nitrile group, which pulls the electrons from the strongly σ-donating NHC ligand directly into the cyanomethyl ligand. This is also hinted by the slight high field shift of the imidazole ring protons compared to that of the *halo*-counterparts bearing a Cp (6.99 and 7.16 ppm)[20] of Cp* (6.08 and 6.64 ppm).[19]

Table 15 : Selected ^{1}H NMR data for compounds **12** and **18** (300.13 MHz).

	NC*H*=C*H*N	Cp/Cp*	Aryl	CH_3CN	CH_2CN
12a[a]	7.20	4.76	7.13 (*m*-H), 2.43 (*p*-Me), 2.11 (*o*-Me)	2.11	-
12b[a]	7.30	0.96	7.17 (*m*-H), 2.40 (*p*-Me), 2.12 (*o*-Me)	1.94	-
18a[b]	6.99	4.60	7.07 (*m*-H), 2.41 (*p*-Me), 2.11 (*o*-Me)	-	-0.08
18b[c]	6.08	1.40	6.84 (*m*-H), 2.29 (*o*-Me), 2.16 (*p*-Me), 1.93 (*o*-Me)	-	-0.07

[a] CD_3CN; [b] $CDCl_3$; [c] C_6D_6

The methylene carbon atoms appear at -42.0 ppm (**18a**) and -29.8 ppm (**18b**) in their $^{13}C\{^1H\}$ NMR spectra which are a high field shift with respect to acetonitrile, though similar (though slightly high field shifted for **18a**) to that of the Ni-Me group in [Ni(Mes_2-NHC)(Me)Cp].[29] Unfortunately, no $^{13}C\{^1H\}$ NMR data was collected for the complex [Ni(PPh_3)(CH_2CN)Cp].[22] The C≡N vibrational stretches are now observed as strong bands at 2188 cm^{-1} (**18a**) and 2179 cm^{-1} (**18b**) in their IR spectrum.

[29] W. Buchowicz, A. Kozioł, L. B. Jerzykiewicz, T. Lis, S. Pasynkiewicz, A. Pęcherzewska, A. Pietrzykowski, *J. Mol. Cat. A: Chem.* **2006**, *257*, 118.

2.1.3.2. [Ni(CH_2COCH_3)Cp], [Ni_2(Mes_2-NHC)$_2${$(CH_2)_2CO$}Cp_2] and [Ni(Mes_2-NHC)(CH_2CO(*p*-C_6H_4-OMe)Cp]

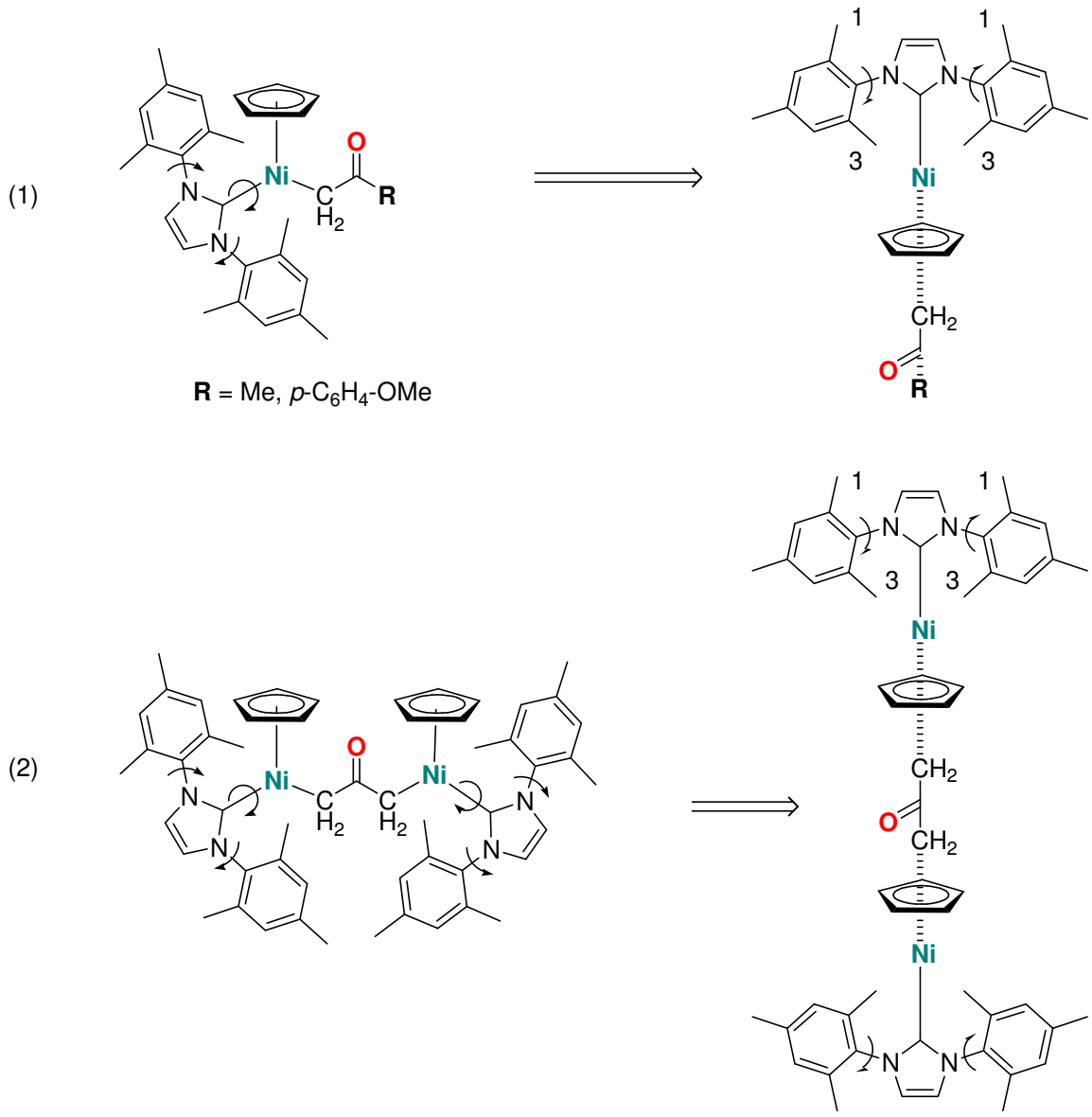
The ^{1}H and ^{13}C{^{1}H} NMR spectra of **19** are straightforward at ambient temperature and show the both the Cp ring and the Mes_2-NHC ligand. Furthermore, free acetone that would result from exchange with acetone-d_6 in solutions of acetone-d_6 in is observed in the ^{1}H and ^{13}C{^{1}H} NMR spectra of **19** suggesting that the acetone ligand is actually labile.[19]

The ^{1}H and ^{13}C{H} NMR spectra of [Ni(CH_2COCH_3)Cp], **20**, show the resonance signals of the Cp ring, the Mes_2-NHC ligand and the acetonyl group. The protons of the *ortho*-methyl groups of the Mes_2-NHC ligand are isochronous on the NMR time scale, which shows that free rotation of the Ni–C(1) bond is allowed at this temperature; an effective symmetry plane that bisects the molecule exists in solution on the NMR time scale. This mirror plane contains the carbenoid carbon atom C(1), the nickel, the Cp ring centroid as well as the C=O and *C*H_3 of the acetonyl ligand [Eq. 1, with R = Me, Scheme 112]. Furthermore, the methylene protons of the acetonyl ligand resonate as a singlet at 1.07 ppm; a down field shift compared to the cyanomethyl methylene protons of **18a**. The carbonyl carbon atom resonates now at 217.1 ppm.

The ^{1}H and the ^{13}C{^{1}H} NMR spectra of the dinickel complex **21** are in accord with the molecular structure and show that the two halves of the molecule are isochronous on the NMR time scale at room temperature. Thus, also **21** features a symmetry plane that bisects the molecule in solution on the NMR time scale. This plane is illustrated in Equation 2 of Scheme 112. This mirror plane would be easily generated by small oscillations of both Ni–CH_2 bonds coupled to small twist of the mesityl groups.

An up field shift is observed for the signal of the CH_2 protons of the complex **20** compared to that of the dinickel complex **21** (0.67 and 1.07 ppm respectively). The carbonyl carbon atom resonated now at 231.0 ppm (down field shifted compared to that of **20**.)

Finally, also the ^{1}H NMR spectrum of the complex **22** is straightforward at ambient temperature and shows the Mes_2-NHC ligand, the Cp and the (*p*-methoxyphenyl)ketonyl ligand. Similar to **20**, **22** displays a mirror plane that bisects the complex in solution on the NMR time scale [Eq. 1, with R = *p*-C_6H_4-OMe, Scheme 112]. The up field shift observed for the resonance signal of the methylene protons of complex **22** compared to that of complex **20** (1.57 and 1.07 ppm respectively) should be attributed to the aromatic ring $\tilde{\alpha}$ to the C=O bond.



Scheme 112

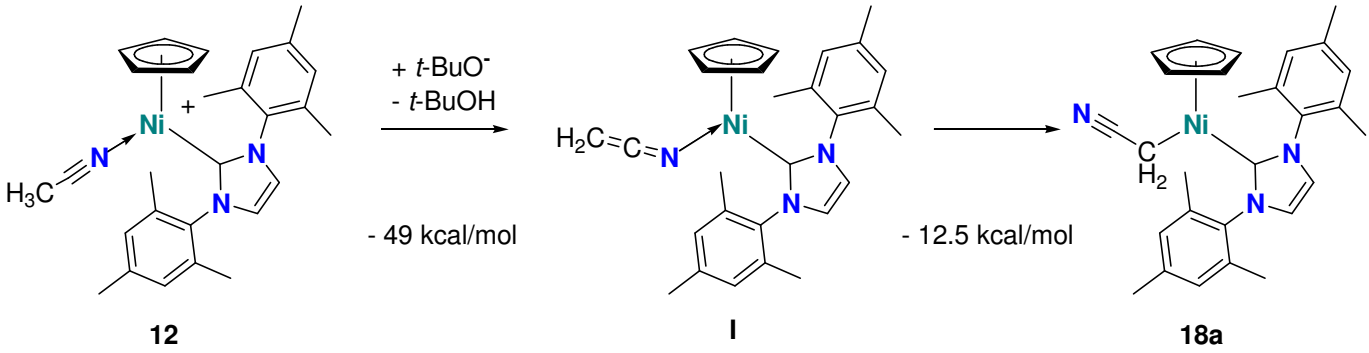
Table 16 : Selected ^{1}H NMR data ($CDCl_3$, 300.13 MHz) f or complexes **20**, **21** and **22**

	NC*H*=C*H*N	Cp	Aryl	CH_2
19[a]	7.69	4.68	7.21 (*m*-H), 2.44 (*p*-Me), 2.19 (*o*-Me)	-
20	6.99	4.45	7.07 (*m*-H), 2.40 (*p*-Me), 2.13 (*o*-Me)	1.07
21	6.88	4.34	7.00 (*m*-H), 2.39 (*p*-Me), 2.18 (*o*-Me)	0.67
22	7.01	4.32	7.12 (*m*-H), 2.46 (*p*-Me), 2.18 (*o*-Me)	1.57

[a] acetone-d_6

2.1.4. DFT calculations and mechanistic pathway

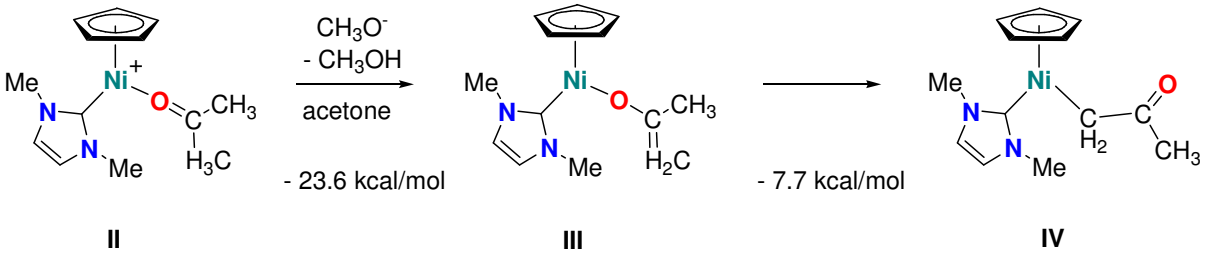
Preliminary theoretical analysis based on density functional theory (DFT) calculations was used to investigate the mechanism of the reaction, screening possible intermediates. All attempts to optimize a side bound π-coordinated acetonitrile complex failed, resulting always in the *N*-coordinated reagent, **12a**. Thus, the existence of a η^2-$NCCH_3$ intermediate in the reaction seems unlikely although some examples of side bound R–CN species in Ni-NHC complexes are also known.[30] Instead, the calculations point towards a two-step path with deprotonation of **12a** yielding an intermediate with an *N*-coordinated cyanomethyl anion (H_2C=C=N) ligand, **I**, and, then, rearrangement of this ligand from *N*- to *C*-coordinated. The calculated energy values indicate that both steps are favorable, from the thermodynamic point of view (Scheme 113).



Scheme 113

For the mechanism of the reaction of acetone we have chosen to focus on a simplified system composed of the related cationic complex [Ni(Me_2-NHC){$(CH_3)_2CO$}Cp]$^+$ **II**, MeO- as a base and acetone as a solvent. Deprotonation of the labile *O*-coordinated π-acetone intermediate **III** via a classical acid-base mechanism[31] to form the *O*-coordinated η^1-enolate compound **IV** similar to the mechanism seen for acetonitrile is in accord with the DFT calculation data (Scheme 114). A favourable energy balance of –23.6 kcal/mol was found for this system. Subsequent rearrangement of **III** should generate the observed *C*-coordinated η^1-acetonylnickel(II) complex **IV.** This mechanism is similar to that described by Aoyama for rhodium(III) and gold(III) complexes.[23]

[30] T. Schaub, C. Döring, U. Radius, *Dalton Trans.* **2007**, 1993.
[31] D. P. Arnold, M. A. Bennett, *J. Organomet. Chem.* **1980**, *199*, 119 and references therein.

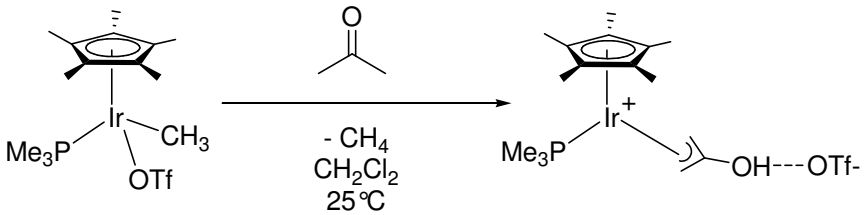


II **III** **IV**

Scheme 114

We were surprised to discover that lower yields were observed for the metallation of acetone compared to those obtained of the metallation of acetonitrile (31 and 80 % respectively). In fact, the lower pKa of acetone (pK_a = 19.3)[4] compared to acetonitrile (pK_a = 25)[4] suggest that the contrary should be observed. Moreover, in contrast to the relatively clean reaction of acetonitrile, significantly more decomposition products are observed when acetone is employed. Generally, nitriles are suggested to have stronger coordination abilities compared to carbonyl compounds.[32] Hence, decomposition of the acetonyl-nickel(II) complex **20** could arise from the lower stability of the *O*-bonded neutral intermediate, **II**, with respect to **I**, which would be observed for the metallation of acetonitrile. Moreover, we have observed that the acetonyl-nickel(II) complex **20** slowly transforms into the related chloro-nickel(II) compound [Ni(Mes_2-NHC)ClCp] in solutions of $CDCl_3$ (which generally generate free HCl). This observation hints that even the final acetonyl-Ni(II) species is less stable than **18a** as no such evolution is observed for this cyanomethyl-Ni(II) complex.

To our knowledge, to date, the double metallation of acetone has not yet been observed before as we could only find one example of a pseudo double C–H bond activation of acetone. Nevertheless, direct comparison with the dinickel complex **21** is not possible since the cationic η^3-hydroxyallyl iridium(III) complex [IrCp*(PMe_3){$(CH_2)_2$COH}]$^+$OTf$^-$ features π-bonding between the metal centre and the ligand, and rearrangement to the corresponding "*mono*activation" η^1-enolate complex was observed (Scheme 115).[15c].



Scheme 115

[32] H. Takaya, M. Ito, S.-i. Murahashi, *J. Am. Chem. Soc.* **2009**, *131*, 10824.

We believe that the formation of the ketonyl-bridged dinickel complex **21** is independent of that of compound **20** and does not arise from a acid-base mechanism (Scheme 114). Preliminary ^{1}H NMR studies in solution of C_6D_6 have shown that both species are present in a *ca.* equimolar ratio after only 5 minutes of reaction time. Moreover, a low chemical shift resonance signal of a possible nickel hydride was observed at -9.8 ppm although no evidence for any hydride intermediate could be found by DFT calculations for the formation of the metallation product **IV**. We suggest that this signal hints to a classical C–H bond activation process for the formation of the dinickel species. However, at this stage, a mechanistic pathway for the synthesis of the dinickel complex **21** remains strictly speculative.

Finally, the low reaction yields that were observed for the metallation of Ni(II) coordinated acetone might not only stem from the moderate stability of the acetonyl-nickel(II) complex **21**, but also from the competition between these two totally different reaction mechanisms.

2.2. Intramolecular base-assisted C–H bond activation

2.2.1. *N*-Alkylnitrile substituted Ni(II)-NHC complexes

2.2.1.1. Synthesis of *N*-alkylnitrile substituted ligands

The recent research of our group which has focused on the preparation of *N*-aryl-*N'*-alkyl substituted NHC ligands (See Chapter 2, Section 2.1 and 2.2), leaded us to the synthesis of alkylnitrile functionalized NHCs with the objective of stabilizing [Ni(NHC)XCp†] catalysts in Suzuki-Miyaura cross-coupling reactions.[33]

The *N*-nitrile-*N'*-mesityl substituted NHC ligand precursors **23a** – **23c** were synthesized according to the procedure described in Chapter 1, i.e.: by mixing 1-mesityl-1*H*-imidazole[34] with the appropriate commercially available cyanoalkyl chloride in refluxing DME (Scheme 116).[35] One equivalent of KI was added for the synthesis of **4c**.[36] The imidazolium salts **23a** – **23c** were isolated as white or creamy, hygroscopic powders in good yield.

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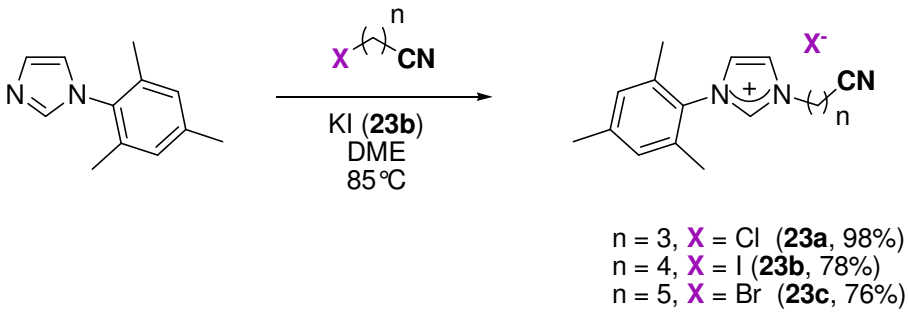
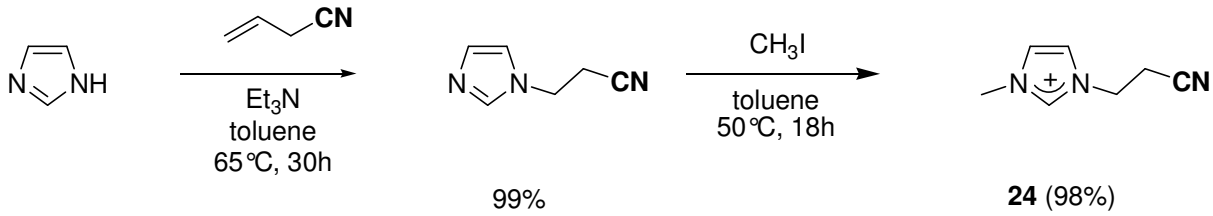
[33] A. Fürstner, H. Krause, L. Ackermann, C. W. Lehmann, *Chem. Commun.* **2001**, 2240.
[34] G. Occhipinti, H.-R. Bjørsvik, K. W. Törnroos, A. Fürstner, V. R. Jensen, *Organometallics* **2007**, *26,* 4383.
[35] (a) Z. Fei, D. Zhao, D. Pieraccini, W. H. Ang, T. J. Geldbach, R. Scopelliti, C. Chiappe, P. J. Dyson, *Organometallics* **2007**, *26*, 1588; (b) D. Zhao, Z. Fei, R. Scopelliti, P. J. Dyson, *Inorg. Chem.* **2004**, *43*, 2197; (c) W. A. Herrmann, L. J. Goossen, M. Spiegler, *Organometallics* **1998**, *17*, 2162; (d) P. A. Z. Suarez, J. E. L. Dullius, S. Einloft, R. F. de Souza, J. Dupont, *Polyherdon* **1996**, *15*, 1217; (e) P. B. Hitchcock, K. R. Seddon, T.



Scheme 116

Although successful synthesis of {1-NC$(CH_2)_2$-NHC-3-Me}·HCl, **24**, has been reported by reacting 3-chloropropionitrile with 1-methyl-1*H*-imidazole,[33c] this procedure did not work in our hands. Thus **24** has been synthesized via a modified procedure from iodomethane and 2-(*1H*-1-imidazolyl)ethylcarbonitrile which was previously prepared from acrylonitrile and imidazole in the presence of triethylamine[37] (Scheme 117). **24** was obtained as a white hygroscopic solid in nearly quantitative yield.



Scheme 117

Good ^{1}H and ^{13}C {^{1}H} NMR spectroscopic data could be obtained for all ligand precursors. The assignment of the chemical shift resonance signals for all of the compounds was straightforward and does not deserve particular comment. The halide salts **23a–c** as well as **24** showed C≡N stretching frequencies of 2243–2250 cm^{-1}. These values are similar to those reported for other *N*-akylnitrile substituted imidazolium salts.[38,33a,b]

Welton, *J. Chem. Soc., Dalton Trans.* **1993**, 2639; (f) P. A. Z. Suarez, J. E. L. Dullius, S. Einloft, R. F. de Souza, J. Dupont, *Polyherdon* **1996**, *15* 1217.

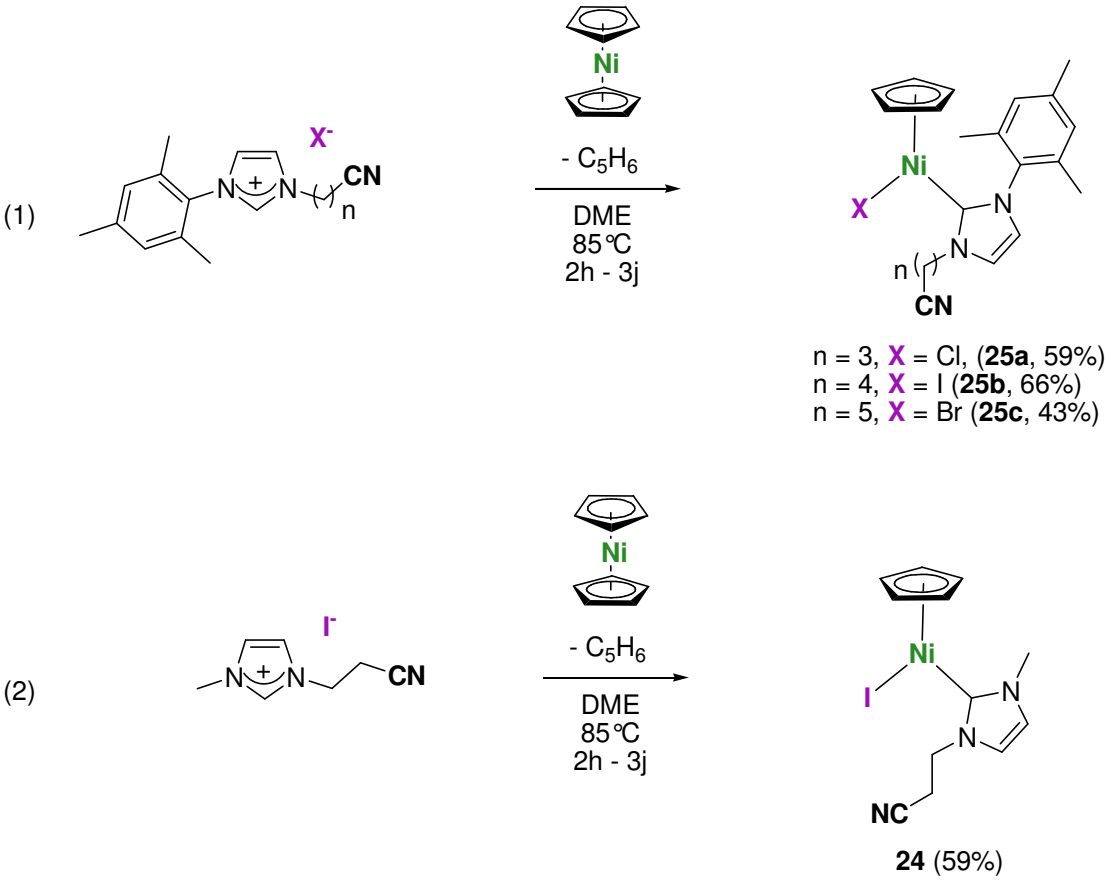
[36] A. M. Oertel, V. Ritleng, M. J. Chetcuti, *Synthesis* **2009**, 1647.

[37] F. Z. Macaev, K. Gavrilov, V. Muntyanu, E. Styngach, L. Vlad, L. Bets, S. Pogrebnoi, A. Barba, *Chemistry of Natural Compounds* **2007**, *43*, 136.

[38] H. V. Huynh, J. Wu, *J. Organomet. Chem.* **2009**, *694*, 323.

2.2.1.2. Synthesis of *N*-alkylnitrile substituted Ni(II)-NHC complexes

The *N*-alkyl substituted Ni(II)-NHC complexes [Ni{Mes-NHC-$(CH_2)_3$CN}ClCp], **25a**, [Ni{Mes-NHC-$(CH_2)_4$CN}ICp], **25b**, [Ni{Mes-NHC-$(CH_2)_5$CN}BrCp], **25c** (Eq. 1, Scheme 118) as well as the complex [Ni{Me-NHC-$(CH_2)_2$CN}ICp], **26**, (Eq. 2, Scheme 118) were synthesized as violet to red solids in good yields (43 – 66 %) following the methodology described in Chapter 2. This consists in treating nickelocene directly with the appropriate imidazolium halide in refluxing thf or DME, with one of the Cp rings playing the role of the proton acceptor.[18-20] Under these reaction conditions, no undesired base catalyzed C–CN bond cleavage of the tethered nitrile function was observed for compounds **25**-**26**. This was reported for the synthesis of [Pd{Mes-NHC-$(CH_2)_2$CN}$_2$Br] which was prepared by treating [$Pd(OAc)_2$] with [Mes-NHC-$(CH_2)_2$CN]·HCl in refluxing DMSO.[38] Good ^{1}H and ^{13}C{^{1}H} NMR and IR spectroscopic data as well as elemental analysis could be obtained for all compounds. Moreover, the molecular structures of the complexes **25a** and **26** were established by single crystal X-ray diffraction studies.



Scheme 118

Crystals of **25a** and **26** suitable for single-crystal X-ray diffraction studies could be obtained from cold solutions CH_2Cl_2/diethylether and solutions of toluene and the molecular structures of these compounds are shown in Figure 3 in a similar orientation. Crystallographic data and data collection parameters are listen in Table 23. Selected bond lengths and angles are shown in Table 17. It noteworthy, that there are two crystallographically independent molecules of **26** (**26-A** and **26-B**), but their general geometric features are the same.

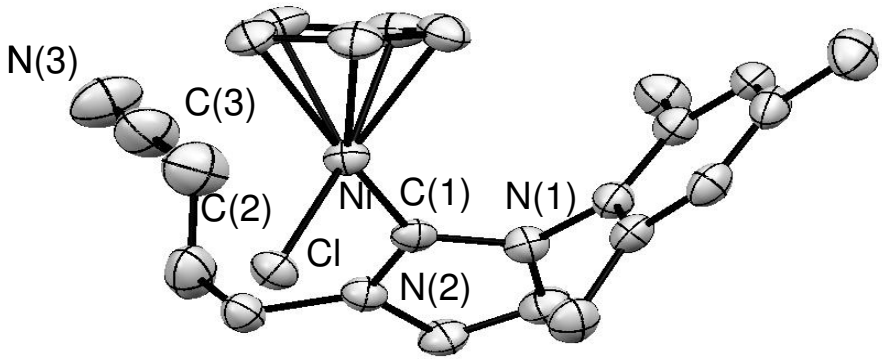
The molecular structures of **25a** and **26** feature the Cp ring, the halide and the nitrile tethered NHC ligand. The two legged piano stool geometry of the central nickel atom is similar to those of the *N*-butyl,*N*-aryl substituted nickel(II) complexes which have been described in Chapter 2 and will not be further commented here. As seen for the butyl-substituted counterpart [Ni(Mes-NHC-*n*-Bu)ICp] **3b**, the Cp ligand of **25a** features "diene" distortions (Δ_{na} < 0.01 Å).[39] The distortions observed for the C–C bond lengths in the Cp ring of **26** were not concluding (Scheme 119).

Table 17 : Selected bond length (Å) and angles (°) for **25a** and **26** (molecule A and B)

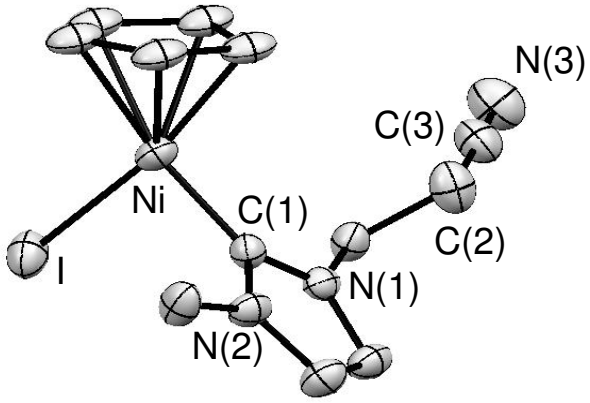
	25a	**26-A**	**26-B**
Ni–C(1)	1.882(3)	1.884(6)	1.866(7)
Ni–X	2.2140(8)	2.5083(10)	2.4979(10)
C≡N	1.098(5)	1.145(12)	1.145(11)
$Ni–Cp_{cent}$	1.773	1.775	[b]1.748
$Ni–C_{Cp}$ (*av*)	*2.141*	*2.126*	[b]*2.125*
min, max	2.058(3), 2.175(3)	2.102(8), 2.166(8)	2.043(17), 2.170(17)
$C_{Cp}–C_{Cp}$ (*av*)	*1.412*	*1.375*	[b]*1.42*
min, max	1.387(5), 1.439(5)	1.335(16), 1.448(17)	1.54(3), 1.27(3)
C(1)–Ni–X	98.41(9)	93.5(2)	92.9(2)
$C(1)–Ni–Cp_{cent}$	132.2	134.1	[b]135.8
$X–Ni–Cp_{cent}$	129.3	132.2	[b]131.2

[a] **1a**, X = I; **1b**, X = Cl. [b] The Cp ring in molecule 26-B is rotationally disordered over two equally populated sites and the positional esds are relatively large; centroid based on all ten Cp carbon atoms.

[39] P. L. Holland, M. E. Smith, R. A. Andersen, R. G. Bergman, *J. Am. Chem. Soc.* **1997**, *119*, 12815.

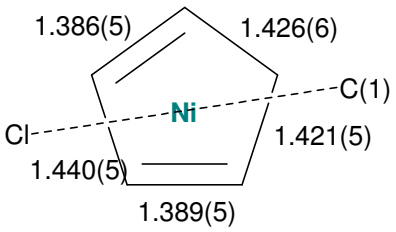


[Ni{Mes-NHC-$(CH_2)_3$CN}ClCp], 25a



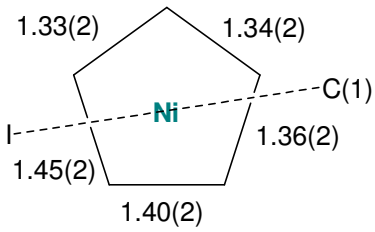
[Ni{Me-NHC-$(CH_2)_2$CN}ICp], 26

Figure 11 : ORTEP plot of complex [Ni(Mes-NHC-$(CH_2)_3$CN}ClCp], **25a**, and of complex [Ni(Me-NHC-$(CH_2)_2$CN}ICp], **26**. Ellipsoids are shown at the 50 % probability level. Key atoms are labelled and hydrogen atoms are omitted for clarity.



diene

[Ni(Mes-NHC-$(CH_2)_3$CN}ClCp], 25a



n.r.

[Ni(Me-NHC-$(CH_2)_2$CN}ICp], 26

Scheme 119

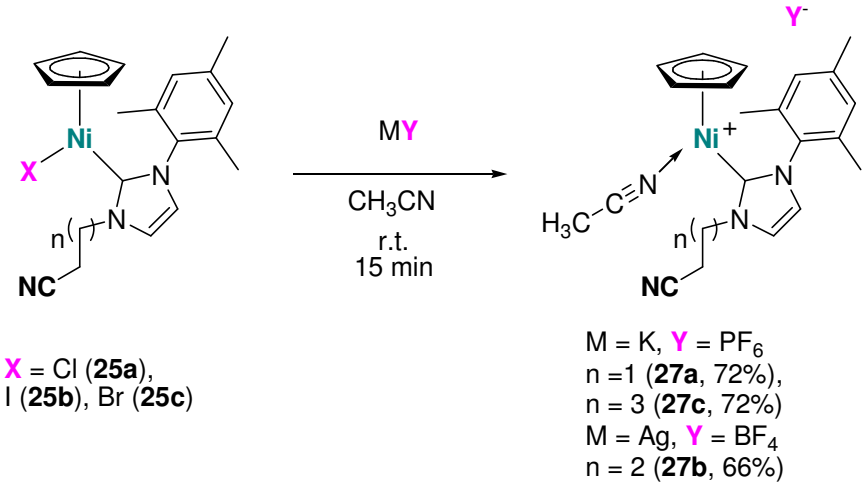
^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopic data of **25a–c** and those of **26** are in accord with the proposed molecular structures. The rotation of the N–C(1) bond is hampered at room temperature for the compounds **25b**, **25c** and **26**, bearing bulky bromide (**25c**) and iodide (**25b**, **26**) ligands. This has been previously observed for the butyl *N*-substituted counterpart [Ni(Mes-NHC-*n*-Bu)ICp] **3b**, which was described in Chapter 2.

Variable temperature (VT) ^{1}H NMR data was collected for **25b** in solutions of $CDCl_3$ from 243 K to 333 K. The free energy $\Delta G^{\#}$ calculated for the rotation barrier to the Ni–C(1) bond rotation of **25b** carrying a iodide ligand, based on the coalescence temperatures of the *meta*-aromatic protons and independently on that of the NCH_2 methylene protons was found of 58 ± 2 kJ.mol^{-1}. This value is similar to that determined for complex **3b** (60 ± 2 kJ.mol^{-1}, See Chapter 2, Section 2.2.2).

In contrast, the ^{1}H NMR spectrum of **25a**, bearing the small chloride ligand shows only minor perturbation of the Ni–C(1) bond rotation. These results further hint at that the size of the halide ligand as the major factor determining the solution dynamics of half-sandwich halo-Ni(II)-NHC complexes.The C≡N stretching frequencies of the complexes **25**-**26** were similar to those of the imidazolium halide salts **23**-**24**.

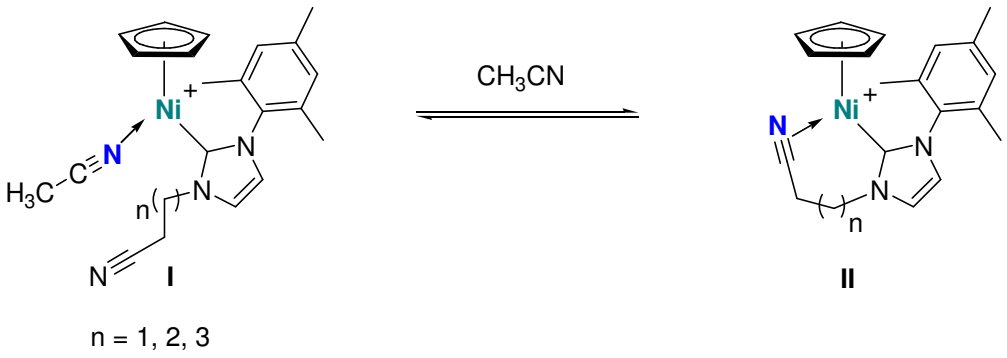
2.2.2. Synthesis of cationic *N*-alkylnitrile substituted Ni(II)-NHC complexes

The synthesis method used for the cationic acetonitrile bound counterparts of [Ni(Mes$_2$-NHC)ClCp†] complexes could be successfully employed for compounds **25**.[19] Thus, the cationic acetonitrile species [Ni{Mes-NHC-$(CH_2)_2$CN}(CH_3CN)Cp]$^{+}PF_6^{-}$ **27a**, and [Ni{Mes-NHC-$(CH_2)_3$CN}(CH_3CN)Cp]$^{+}BF_4^{-}$ **27c** were obtained from equimolar acetonitrile solutions of **25a**, and **25c** potassium hexafluorophosphate (KPF_6) at room temperature. [Ni{Mes-NHC-$(CH_2)_2$CN}(CH_3CN)Cp]$^{+}PF_6^{-}$ **27b** was prepared from equimolar acetonitrile solutions of **25b** and silver tetrafluoroborate ($AgBF_4$). Good spectroscopic data (^{1}H, $^{13}C\{^{1}H\}$ NMR and IR) could be obtained for all compounds.



Scheme 120

Very weak bands are observed for the C≡N vibrational stretches of the cationic complexes **27a**–**c** and the C≡N stretching frequencies are similar those of the neutral halo-nickel(II) counterparts **25a**-**c**. Moreover, a second very weak band is observed at *ca.* 2290 cm^{-1} for the cationic complexes **27a** and **27b**. These results hint that at the solid state, acetonitrile would be coordinated to the central nickel atom.[28] Though, only unsatisfactory elemental analysis of these species has been obtained (either calculated for a non-coordinated nitrile and thus, bearing a acetonitrile ligand or a coordinated nitrile function) suggesting that there would be a mixture of the acetonitrile coordinated, **I**, and the cyclic side-arm bonded species, **II**, in the solid state (Scheme 121). Unfortunately, no single crystals could be grown to confirm or refute this suggestion.



Scheme 121

The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were straightforward at room temperature for all cationic acetonitrile complexes and in accord with their proposed molecular structures. As

seen in the cationic acetonitrile counterparts **12a**, substitution of the halide by the smaller and linear acetonitrile ligand results in unhampered rotation of the Ni–C(1) bond on the NMR time scale.[19] This observation further suggests that the rotation barrier to the Ni—C(1) bond rotation arises from the bulk of the halide (and/or Cp*) and is only slightly affected by the alkyl pendant arm of the asymmetrically *N*-aryl,*N'*-alkyl substituted NHC ligand (see also Chapter 2).

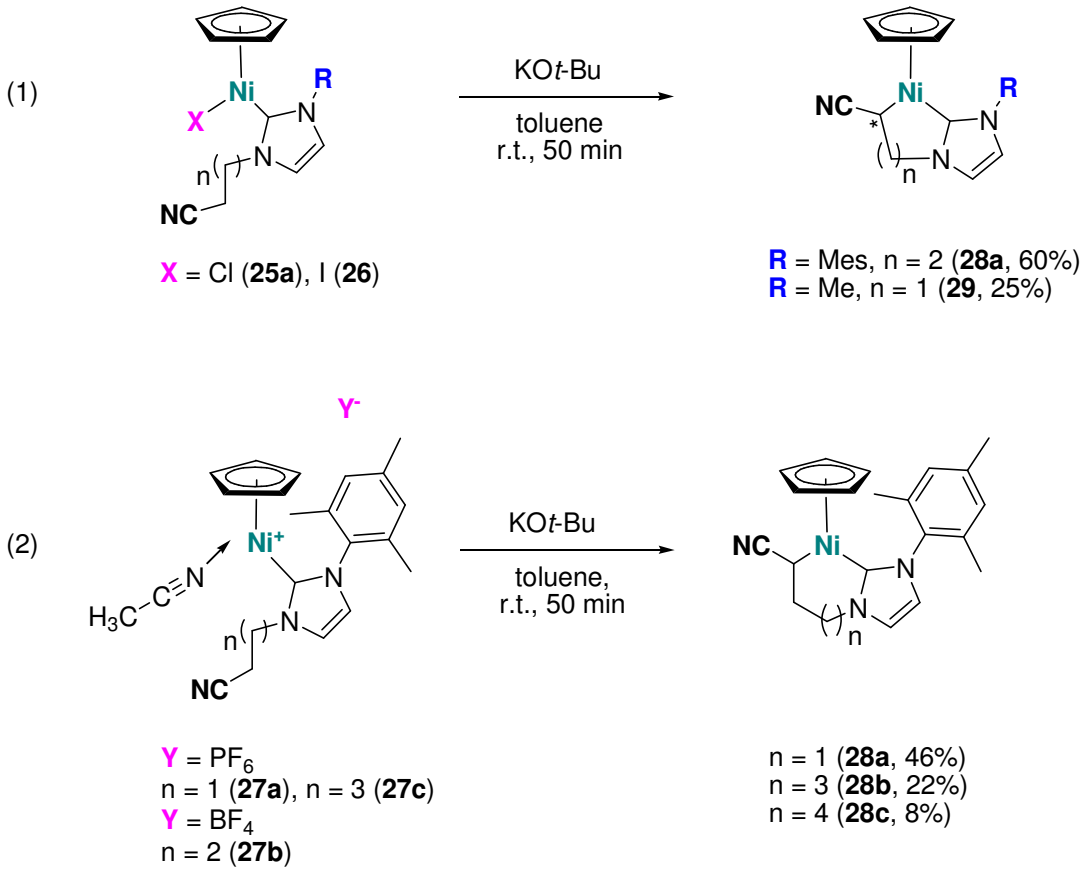
As we have observed a second weak C≡N stretching band in the IR spectra of **27** suggesting the presence of the acetonitrile ligand, we were surprised that we could not observe any exchange of labile acetonitrile with CD_3CN in CD_3CN solutions of the cationic acetonitrile complexes **27** as seen for $[Ni(Ar_2\text{-NHC})(CH_3CN)Cp^*]^+PF_6^-$ **12**.[19] Furthermore, low temperature ^1H NMR data collection (228 K) of CD_3CN solutions of **27c** have not shown evidence for a *N*-coordinated pendant arm. The dynamic process of the coordination and de-coordination of the nitrile function in solutions of CD_3CN might be to fast to be detected on the NMR time scale or it does not take place.

2.2.3. Synthesis of half-sandwich nickelacycles by intramolecular sp^3-C–H bond activation

When toluene solutions of the neutral halo-nickel(II) complexes **25a** and **26** were reacted with an equimolar amount of KO*t*-Bu, one methylene proton α to the nitrile was abstracted and a racemic mixture of the resulting nickelacycles [Ni{Mes-NHC-$CHCN(CH_2)_2$}Cp] **28a**, and [Ni{Me-NHC-$CHCN(CH_2)_1$}Cp] **29** were isolated in respectable yields (Eq. 1, Scheme 122).

Moreover, when toluene suspensions of the *cationic* acetonitrile species **27a**–**27c** were reacted with KO*t*-Bu in toluene, a racemic mixture of the nickelacycles [Ni{Mes-NHC-$CHCN(CH_2)_2$}Cp] **28a**, [Ni{Mes-NHC-$CHCN(CH_2)_3$}Cp] **28b** and of [Ni{Mes-NHC-$CHCN(CH_2)_4$}Cp] **28c** was isolated in moderate to good yield (Eq. 2, Scheme 122). It worth note that the cationic compounds **27**, gave no evidence for deprotonation of acetonitrile, which would result in the generation of the corresponding cyanomethyl complexes [Ni{Mes-NHC-$(CH_2)_nCN$}(□^{1}-CH_2CN)Cp] (n = 2, 3, 4). This was deducted by analysis of the ^1H NMR spectra of the reaction crude product.

Good ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopic data could be obtained for all of the complexes. IR spectroscopic data was obtained for the compounds **28a**, **28b** and **29**. Crystallographic data could be collected from single crystals of **28a** and **28c**.



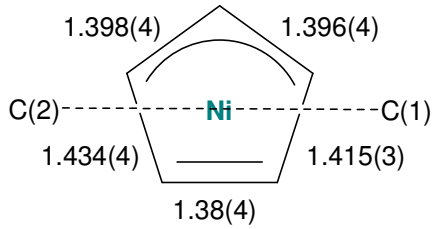
Scheme 122

2.2.3.1. Structural studies

Single crystals suitable for single-crystal X-ray diffraction studies of **28a** and **28c** were grown from cold mixtures of thf/pentane. Crystallographic data and data collection parameters are listed in Table 22. A list of selected bond length and angles appears in Table 6. The molecular structure of **28a** and **28c** are shown in Figure 4.

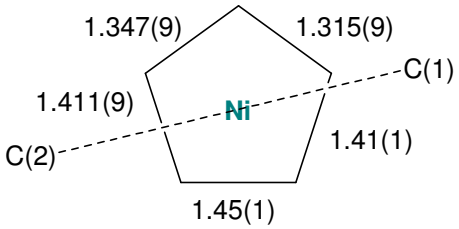
The molecular structures of the complexes **28a** and **28c** display one Cp ring and the bidentate NHC ligand in a two legged piano stool geometry featuring a trigonal planar coordination sphere geometry around the central nickel(II) atom [Σ(angles) = 357°]. A set of each enantiomer (*R*) and (*S*) is present in the unit cell of both compounds.

In contrast to the acyclic precursors **25a** bearing a *N*-propylnitrile substituent, the nickelacycle **28a** displays "ene-allyl" distortions[39] of the Cp ring C–C bonds which are similar to the cyanomethyl complex **18a** (Scheme 123). Furthermore, the Ni–C(1) bond distances observed for **28a** and **28c** [1.856(2) Å and 1.866(4) Å respectively] are slightly shorter than that observed for **18a**, **25a** and **26**. In contrast, the Ni–C(2) bond lengths [1.972(2) Å and 1.987(7) Å] are longer than that of the $NCCH_2$-Ni(II) group in **18a** [1.906(6) Å]. Finally, no significant difference of the C≡N bond lengths was noticed between **28a**, **28c** and of **18a** [1.142(2), 1.127(7) and 1.146(4) Å respectively] or the complex [Pd{Me-NHC-$(CH_2)_3$CN}$_2$$Cl_2$] [1.145(3) Å and 1.129(5)].[33a]



"ene-allyl"

[Ni{Mes-NHC-CHCN$(CH_2)_2$}Cp], **28a**



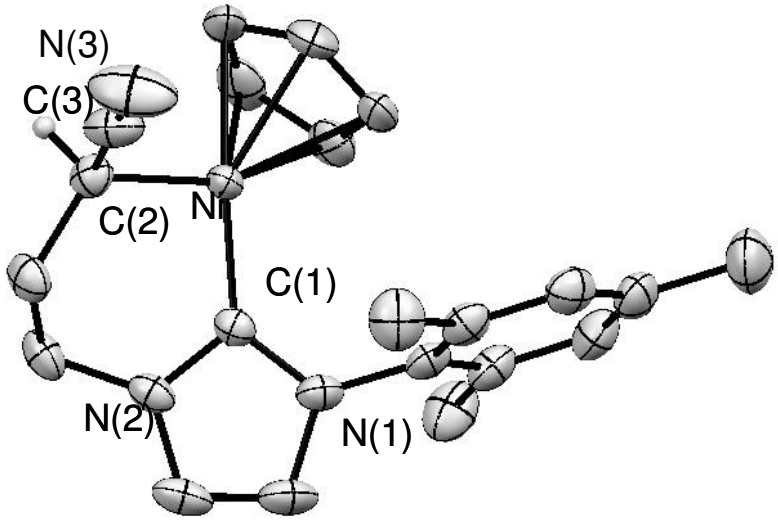
n.r.

[Ni{Mes-NHC-CHCN$(CH_2)_4$}Cp], **28c**

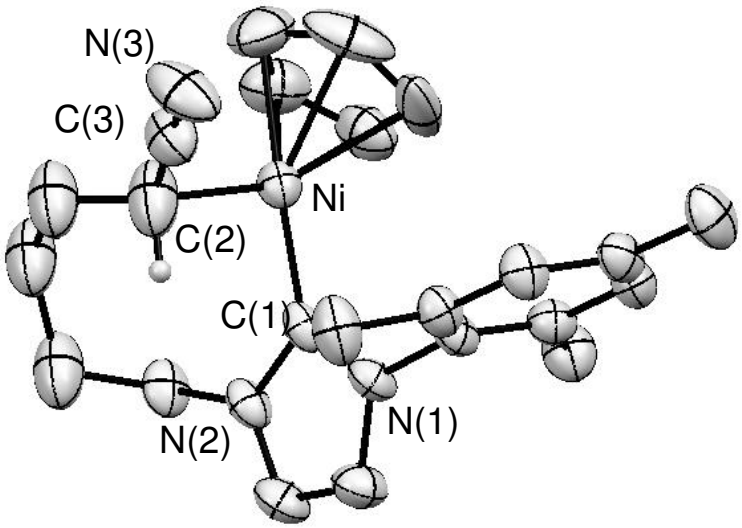
Scheme 123

Table 18 : Selected bond length (Å) and angles (°) for **28a** and **28c**

	28a	**28c**
Ni–C(1)	1.856(2)	1.866(4)
Ni–C(2)	1.972(2)	1.987(7)
Ni–C_{cent}	1.768	1.765
Ni–C_{Cp} (*av*, min, max)	*2.133*, 2.096(3), 2.160(3)	*2.123*, 2.079(7), 2.156(5)
C_{Cp}–C_{Cp} (*av*, min, max)	*1.404*, 1.380(4), 1.434(4)	*1.387*, 1.315(9), 1.45(1)
C≡N	1.142(2)	1.127(7)
C(1)–Ni–C(2)	93.96(9)	90.1(2)
Cp_{cent}–Ni–C(1)	131	137
Cp_{cent}–Ni–C(2)	135	132.5
Ni–C(2)–C(3)	106.9(2)	106.5(4)
C(2)–C(3)–N(3)	177.7(3)	177.0(6)



(*R*)-[Ni{Mes-NHC-CHCN(CH$_2$)$_2$}Cp], 28a



(*R*)-[Ni{Mes-NHC-CHCN(CH$_2$)$_4$}Cp], 28c

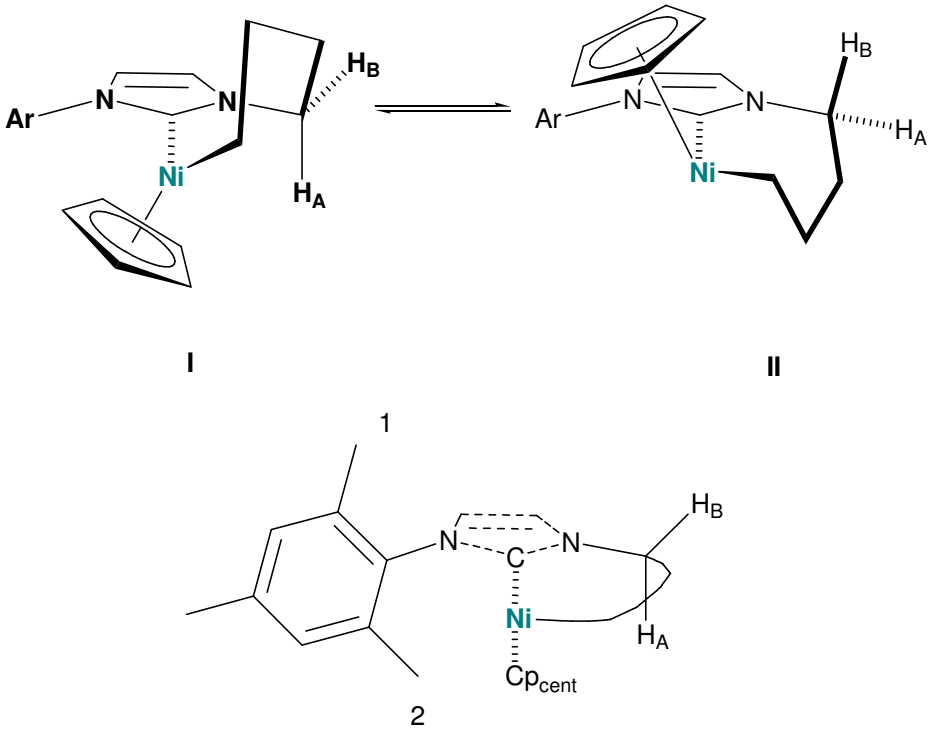
Figure 12 : ORTEP plot of the complexes (*R*)-[Ni{Mes-NHC-CHCN(CH$_2$)$_2$}Cp], **28a**, and (*R*)-[Ni{Mes-NHC-CHCN(CH$_2$)$_4$}Cp], **28c**. Ellipsoids are shown at the 50 % probability level. Key atoms are labelled and hydrogen atoms are omitted for clarity.

2.2.3.2. Spectroscopic data

The C≡N stretching frequencies of the cyclic compounds **28a**, **28b** and **29** (2179, 2176 and 2179 cm^{-1} respectively) are lower compared to that of the acyclic precursors **25a**, **25b** and **26** which average 2250 cm^{-1}. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of the nickelacycles **28a** and **29** are straightforward at ambient temperature and show the signal of the Cp ring protons and those of the bidentate NHC ligand. A significant down field shift of the proton α to the nitrile group of **29,28a,b,c,** (2.70, 2.15, 1.54 and .130 ppm respectively) is observed when compared to the chemical shift of the NCCH_2-Ni(II) group in complex **18a** (-0.08 ppm). No symmetry plane is observed in solution for complex **28a** and **29** and their respective spectra do not need further comment.

The signal of the NCH_2 protons of the seven-membered nickelacycle **28b** is coalescent at ambient temperature suggesting that conformational fluctuations of the cyclic system are possible (the limiting conformations **I** and **II** are shown in Scheme 124). These fluctuations would generate a mirror plane in solution that would contain the nickel atom, the carbenoid carbon, the Cp ring centroid and the cyclic carbon atoms (**28b-sym**, Scheme 124). To that effect, ^{1}H VT-NMR data was collected from 208 K to 333 K in solutions of $CDCl_3$ for the metallacycles **28b**. At 208 K, the *ortho* and the *para* methyl groups of the aromatic ring resonate as three sharp singlets in a 1:1:1 integrated ratio. As the temperature increases, these signals broaden and become eventually coalescent at 273 K (T_C). Similar coalescence was observed for the *meta*-aromatic ring protons at 278 K and for the aliphatic NCH_2 protons at 288 K. The free energy of activation ($\Delta G^{\#}$) calculated for this fluxional process (based on the T_C of these protons) was 53 ± 1 $kJ.mol^{-1}$.

Conformational fluctuations are also observed in the ^{1}H NMR spectra of **28b**. Though, ^{1}H VT-NMR data collections of **28c** in $CDCl_3$ solutions from 208 to 333 K did not reveal any presence of an analogous mirror plane in solution and the signal of the NCH_2 protons, the *ortho*-methyl groups and the aromatic *meta*-protons remained split.



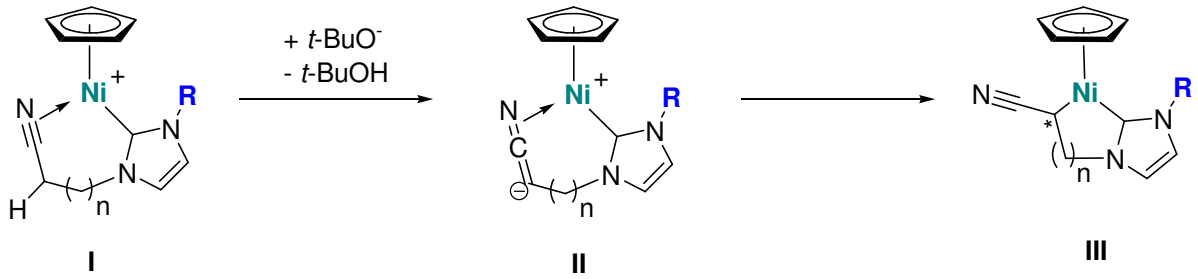
28b-sym

Scheme 124

2.2.3.3. Mechanistic pathway

Up to now, the exact pathway of the cyclometallation has not been elucidated by DFT calculations. Nevertheless, the following speculative reaction pathway for the generation of cyclic species from acyclic *N*-alkylnitrile substituted NHC-Ni(II) complexes could be reasonably understood in terms of a stepwise sequence involving (i) *N*-coordination of the nitrile group to the nickel(II) atom, (ii) deprotonation of the proton α to the nitrile group and (iii) rearrangement of the resulting *N*-coordinated anionic group into the [C,C']-chelating species (Scheme 125).

By employing the neutral halo-nickel complexes **25a** and **26**, the initial *N*-coordination step might be assisted by the abstraction of the halide by the potassium cation of KO*t*-Bu fallowed by the precipitation of the resulting potassium halide salt which would be less soluble in toluene than the initial alkoxide.

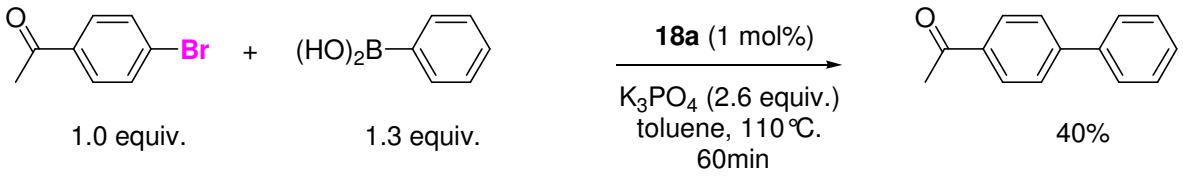


R = Me, n = 1
R = Mes, n = 2, 3, 4

Scheme 125

2.2.3.4. Reactivity of the half-sandwich nickelacycles

Compound [Ni(Mes_2-NHC)(CH_2CN)Cp] **18a** was catalytically active for the Suzuki-Miyaura cross-coupling of 4'-bromoacetophenone and phenyl boronic acid and the desired biphenyl compound was formed in 40 % yield after 60 min in refluxing toluene (Scheme 126). Compared to the half-sandwich cationic *bis*-NHC-Ni(II) complex **16a**, **18a** showed higher reactivity for Suzuki-Miyaura cross-coupling. In contrast, compared to the excellent activity observed for the [Ni(Ar-NHC-*n*-Bu)Cp] type complexes **3b** and **3c** (Chapter 1) the activity of this catalyst was rather disappointing.



Scheme 126

These results suggest that the coordinatively unsaturated active species that is generated from Ni-cyanomethyl complexes would be more active than that furnished by a CpNi-(*bis*-NHC) compound. (The latter may resemble to the (moderately) active species generated by square-planar Ni-NHC_2 complexes; See Chapter 3, Section 2.2. and Chapter 1, Section 2.1.3.1 for square-planar Ni-NHC_2 complexes in Suzuki-Miyaura cross-couplings). Furthermore, the substitution of a iodide ligand by a cyanomethyl leads to the formation of a notably less active catalyst than that generated by the [Ni(Ar-NHC-*n*-Bu)ICp†] complexes (See Chapter 2, Section 2.3.). As seen for the symmetric chloro- or acetonitrile complexes,[19] the significant

decrease in activity may arise from the lower steric protection by the small cyanomethyl ligand when compared to the much bulkier iodide. Notably the acetonitrile ligand might show similar steric protection to the active species than the cyanomethyl ligand. Hence, the increase of the catalyst loading from 1 to 3 mol% would confirm or reject this suggestion as analogous yields of the desired biphenyl compound would be obtained (or not) by employing 3 mol% of the cyanomethyl complex.

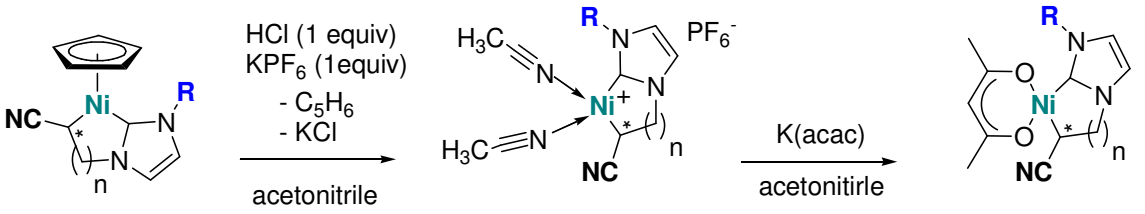
2.3. Square-planar [C,C']-chelating Ni(II)-NHC complexes

2.3.1. Synthesis of [Ni{R-NHC-CHCN$(CH_2)_n$}Cp] (R = Me, Mes; n = 1, 2) type complexes

We have studied the lability of the Ni–Cp and Ni-cyanoalkyl bonds of complexes **28a** and **29** under acid conditions. We were convinced that as seen for the *bis*-NHC complex **15** (Chapter 3, Section 3), the Ni–NHC bond would remain inert under these conditions.

When the nickelacycles **28a** and **29** are treated with 0.01 M acid solutions of HCl in acetonitrile in the presence of an equimolar amount of KPF_6, the initially green solutions immediately changed to a bright yellow colouration. The ^1H NMR spectra of the reaction crude-product only revealed the signals of the bidentate NHC ligand. Thus, under acid conditions, the Ni–Cp bond and not the Ni–cyanoalkyl bond showed lability. Accordingly, when acetonitrile solutions of **28a** and **29** are treated with an equimolar amount of HCl (0.01 M in acetonitrile) in the presence of an equimolar amount of KPF_6, the Cp ring was abstracted and the corresponding cationic complexes [Ni{Mes-NHC-CHCN$(CH_2)_2$}$(CH_3CN)_2$]$^+PF_6^-$ **30a** and [Ni{Me-NHC-CHCN(CH_2)}$(CH_3CN)_2$]$^+PF_6^-$ **31** are formed, respectively. Subsequent reaction of these compounds with potassium acetonyl acetonate leaded to the formation of the corresponding neutral *six*-membered metallacycle [Ni{Mes-NHC-CHCN$(CH_2)_2$}(acac)] **32a** and *five*-membered nickelacycle [Ni{Me-NHC-CHCN(CH_2)}(acac)], **33**, respectively (Scheme 127). The complexes **32a** and **33** were isolated as green-yellow diamagnetic solids in good yields. Only the cationic intermediate **30** was isolated for spectroscopic analysis.

Good ^1H and $^{13}C\{^1H\}$ NMR as well as IR spectroscopic data was obtained for the complex **30a**, **32a** and **33**. Single crystals suitable for single crystal X-ray diffraction studies of compound **32a** were obtained from cold solutions of CH_2Cl_2 and diethyl ether by slow evaporation under reduced pressure. Crystallographic data and data collection parameters are listed in Table 23. Selected bond length and bond angles are shown in Table 19.



R = Mes, n = 2 (**28a**)
R = Me, n = 1 (**29**)

R = Mes, n = 2 (**30a**, n.r.)
R = Mes,n = 1 (**31**, n.r.)

R = Mes, n = 2 (**32a**, 89%)
R = Mes, n = 1 (**33**, 83%)

Scheme 127

2.3.2. Structural studies

The molecular structure of the complex **32a** shows a square planar nickel atom [Σ(angles around nickel atom) ≈ 360°] which is bound to the [C,C']-chelating NHC and the bidentate acetonyl acetonate ligand; 1/2 of a thf molecule is present in the unit cell. To date, this is the first example of a square-planar Ni(II) complex carrying a [C,C']-chelating cyanoalkyl NHC ligand.[40] Indeed, the variety of square-planar [C,C]-chelating nickel complexes is limited to bidentate *bis*-NHC complexes. To that effect, direct comparison of the bond length observed for this species to that detected in analogous species was infeasible. We have thus chosen to compare the values observed for the complex **32a** to those reported for *cis*-Ni(II)-NHC_2.[41]

The Ni–C(1) bond is shorter compared to that observed for square planar *bis*-NHC Ni(II) complexes *cis*-[Ni{(Me-NHC)$_2$-$(CH_2)_2$}$(CH_3)_2$],[41] **I**, and *cis*-[Ni(*i*-$Pr_2(Me_2)$-NHC)$_2Me_2$, **II**] [1.869(2), 1.907(5), 1.911(6), 1.910(2) and 1.930(9) respectively].[42] Whereas the Ni–C(2) bond appears similar to that reported for these species (1.961(2), 1,972(6), 1.962(6), 1.966(2) and 1.975(3) Å respectively). No significant differences between these bond lengths as well as that of the C≡N bond [1.145(3) Å] of **32a** and those observed previously for the piano stool shaped precursor **28a** are noticed (Table 18).

[40] A [C,C',C] Ni-NHC pincer has been reported in which the nickel is bound to a sp^2-C atom: A. Liu, X. Zhang, W. Chen, *Organometallics* **2009**, *28*, 4868.
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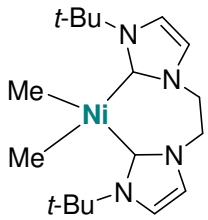
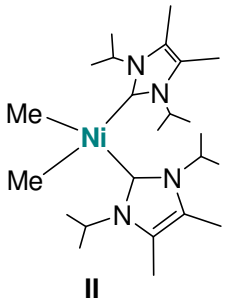
[42] (a) A. A. Danopoulos, D. Pugh, *Dalton Trans.* **2007**, 30.



I



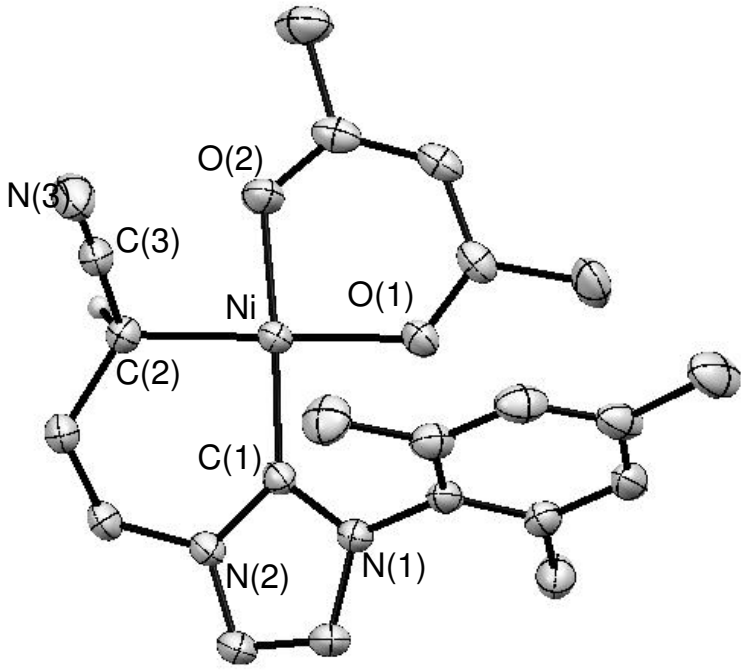
II

Scheme 128

The molecular structure of the complex **32a** suggests that for this species no effective mirror plane would be generated in solutions of this compounds as the cyanomethyl group points out of the plane which contains the NHC ring atoms, the nickel, the carbon C(2) as well as the acetyl acetonate ligand.

Table 19 : Selected bond length (Å) and bond angles (°) of compound **32a**

	32a
Ni–C(1)	1.869(2)
Ni–C(2)	1.961(2)
Ni–O	1.897(1), 1.884(2)
C–O	1.278(3), 1.270(2)
C≡N	1.145(3)
C(2)–C(3)–N	178.0(2)
C(1)–Ni–O(1)	89.71(7)
C(2)–Ni–O(2)	84.97(7)
O(1)–Ni–O(2)	93.29(6)



(*R*)-[Ni{Mes-NHC-CHCN(CH$_2$)$_2$}(acac)], 32a

Figure 13 : ORTEP plot of complex [Ni{Mes-NHC-CHCN(CH$_2$)$_2$}(acac)], **32a**. Ellipsoids are shown at the 50% probability level. Key atoms are labelled and hydrogen atoms as well as the thf are omitted for clarity.

2.3.3. Spectroscopic data

The ^{1}H and ^{13}C{^{1}H} NMR spectra of the new nickelacycles **32a** and **33** show the signals of the bidentate NHC ligand and the acetonyl acetonate ligand. The ^{1}H and ^{13}C{^{1}H} NMR spectra of the reaction intermediate **30a** only show the signals of the bidentate NHC ligand. Curiously, no evidence for the nitrile carbon signal could be detected in the ^{13}C{^{1}H} NMR spectra of complexe **30a**. Probably, this signal would be hidden by the signal of a aromatic carbon atom (notably a *p*-/*ipso*-C$_{Ar}$) of the mesityl group which would display a similar chemical shift.

The abstraction of the Cp ring and generation of the cationic acetonitrile complex **30a** leads to a high frequency shift of the C≡N stretching frequency with respect to that of the half-sandwich counterpart **28a** (2235 and 2176 cm^{-1} respectively). A broad and moderately strong band is observed hinting that the CN starching frequency of the cyano group and the

acetonitrile ligands[28] might be superposed. In contrast, the C≡N stretching frequencies of the acetyl acetone bound neutral species **32a** and **33** are similar to those of **28a** and **29** (2186, 2185, 2181 and 2179 cm^{-1} respectively).

The up field shift of the C*H* proton α to the nitrile of the square planar complexes **32a** and **33** with respect to those the half-sandwich nickelacycles **28a** and **29** is noticed (Table 20). Similarly, the signals of the carbenoid carbon C(1) (Table 21), of the complexes **30a**, **32a** and **33** (155.6, 163.0 and 160.8 ppm respectively) were high field shifted with respect to those observed for the Cp bounded precursors **28a** and **29** (171.3 and 173.5 ppm respectively) as well as to that detected for the square-planar *bis*-NHC complex **17** (174.1 and 172.2 ppm Chapter 3, Section 4).

Table 20 : Selected ^{1}H NMR (CD_3CN, 300.13 MHz) data for **30a**, **32a** and **33**

	NC*H*=C*H*N	**C*H***	**R** [a]
30a	7.32, 7.03, (d)	2.37 (t)	7.24, 7.05 (H_{Ar}); 2.56, 2.03 (*o*-Me); 2.37 (*p*-Me)
32a	7.21, 6.83, (d)	1.76 (t)	7.07, 6.94 (H_{Ar}); 2.51, 2.08 (*o*-Me); 2.31 (*p*-Me)
33	6.78, 6.59, (d)	3.79, (dd)	3.72 (Me)

[a] R = Me (**33**), Mes (**30, 32**)

Table 21 : Selected $^{13}C\{^{1}H\}$ NMR (CD_3CN, 300.13 MHz) data for **30a**, **32a** and **33**

	NCN	***C*H**	***C*N**	**R** [a]
30a	155.6	-2.5	n.r	139.8 (*ipso*/*p*-C_{Ar}); 136.1 (*p*/*ipso*-C_{Ar}); 135.7, 135.2 (*o*-C_{Ar}); 129.9, 129.5 (*m*-C_{Ar}); 20.7 (*p*-Me); 18.7, 17.8 (*o*-Me)
32	163.0	-2.4	n.r.	138.7 (*ipso*/*p*-C_{Ar}); 137.3 (*p*/*ipso*-C_{Ar}); 136.2, 135.6 (*o*-C_{Ar}); 129.5 (*m*-C_{Ar}); 25.1, 20.9 (*o*-Me); 26.8 (*p*-Me)
33	160.8	4.0	n.r	35.5

[a] R = Me (**33**), Mes (**30, 32**)

3. Conclusion

We have shown that CpNi-NHC centres activate sp^3-C–H bonds α to organic functional groups under relatively mild conditions. Thus, activation of a C–H bond of the labile acetonitrile ligand was achieved by treating toluene suspension the cationic acetonitrile complex $[Ni(Mes_2\text{-}NHC)(CH_3CN)Cp^{\dagger}]^+PF_6^-$ **12a** with equimolar amounts of KO*t*-Bu. The resulting cyanomethyl-nickel complex $[Ni(Mes_2\text{-}NHC)(CH_2CN)Cp]$ was obtained in good yields whereas lower yields were isolated starting from the cationic Ni-Cp* complex. The reaction resulted in the ligand formally loosing one proton and doing a sharp flip to bind the nickel atom by the sp^3-carbon. Analogously, when toluene suspensions (or acetone solutions) of the cationic acetone complex $[Ni(Mes_2\text{-}NHC)\{(CH_3)_2CO\}Cp]^+BF_4^-$ were treated with equimolar amounts, the desired acetonyl-Ni(II) $[Ni(Mes_2\text{-}NHC)\{CH_2C(O)CH_3\}Cp]$ compound was formed, although comparing to the cyanomethyl product much lower yields were obtained. This was mainly attributed to the co-generation of a second acetone activation product; indeed, low yields of a dinickel complex $[Ni_2(Mes_2\text{-}NHC)_2\{(CH_2)_2C(O)\}Cp_2]$, featuring two CpNi-NHC units linked by a bridging $\{\eta^1,\eta^1\text{-}(CH_2)_2(CO)\}$ ligand, were also isolated form the reaction crude product. Finally, the desired ketonyl compound was also formed from toluene solutions of $[Ni(Mes_2\text{-}NHC)ClCp]$ and 4'-methoxyacetophenone in the presence of one molar equivalent of KO*t*-Bu. Theoretical analyses based on DFT calculations have demonstrated that the deprotonation of these ligands should occur via a two-step mechanism in which the *N*/*O*-bound ligand was first deprotonation by BuO^- and then re-arranges to generate the sp^3-C–Ni bond. At this stage, the mechanism for the formation of the acetone *bis*-activation product remains unclear. Single crystal X-ray diffraction studies have shown that the CpNi(II)-alkyl complexes show common two-legged piano stool geometry with a strictly trigonal planar geometry around the nickel atom. The cyanomethyl nickel complex showed only moderate activity for Suzuki-Miyaura cross-coupling of 4'-bromoacetophenone and phenylboronic acid when compared to their CpNi-iodo counterparts. At this stage, it is unclear to what extend the difference seen for this two species is due to steric reasons.

The reaction scope of α-C–H bond activation by the CpNi(II)-NHC centre was extended by the activation of a C–H bond α- to a nitrile in NHC-attached sidearms. In this way, a series of five- to eight-membered half-sandwich nickelacycles was synthesized in respectable yields. Single X-ray diffraction studies of the six- and the eight-membered metallacycles revealed

that these compounds featured the common two-legged piano stool geometry and puckered non-planar metallacyclic rings.

Furthermore, as seen for the CpNi-(*bis*-NHC) compound bearing two small NHC ligands, the Ni–Cp bond, and not the Ni–NHC or the Ni-cyanoalkyl bonds, was labile under acid conditions. Thus, by treating acetonitrile solutions of the appropriate nickelacycle in the presence of an equimolar amount of KPF_6 and HCl, and subsequent reaction with potassium acetonyl acetonate generated a series of new square-planar Ni(II) complexes bearing a [C,C']-chelating NHC ligand. In contrast, the Ni–ketonyl bond showed less stability than the Ni–Cp bond in CpNi-acetonyl complexes as slow re-generation of the chloro-nickel complex was observed in (slightly acid) solutions of this complex in $CDCl_3$.

The activation of C–H bonds α to nitrile and carbonyl functions as well as the recent disclosure of nickel(II) catalyzed C–H arylations of arenes and heteroarenes, in the presence of *t*-BuO^- as a base,[43,44,45] hints at the growing potential of nickel complexes in the transition-metal catalyzed C–H bond functionalization.[46] Furthermore, the synthesis routes for chiral TM-NHC complexes[47] are more or less limited to the attachment of homochiral substituents on either the nitrogen atom or on the carbon atoms at position 4 and/or 5 of the imidazole ring,[48] or to the coordination to the metal via *anionic* NHC-attached sidearms centred at group 15 atoms.[49] The synthesis scope for half-sandwich nickelacycles, bearing a [C,C']-chelating ligand should by investigated for the generation of atropochiral complexes as these species bear a stereogenic centre directly bound onto the nickel atom.

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4. Experimental

General comments. All reactions were carried out using standard Schlenk techniques under an atmosphere of dry argon. Solvents were distilled from appropriate drying agents under argon prior to use. Solution NMR spectra were recorded at 298 K unless otherwise specified on FT-Bruker Ultra Shield 300 or FT Bruker-Spectrospin 400 spectrometers operating at 300.13 or 400.14 MHz for ^{1}H, and at 75.47 or 100.61 MHz for ^{13}C{^{1}H}. DEPT ^{13}C spectra were recorded for all compounds to help in the ^{13}C signal assignments. Supplementary 2D COSY spectra were obtained for [Ni{Mes-NHC-CHCN$(CH_2)_2$}Cp], **28a**, [Ni{Mes-NHC-CHCN$(CH_2)_4$}Cp], **28c**, [Ni{Mes-NHC-CHCN$(CH_2)_2$}$(CH_3CN)_2$]$^{+}PF_6^{-}$, **30**, [Ni{Mes-NHC-CHCN$(CH_2)_2$}(acac)], **32**, and [Ni{Me-NHC-CHCNCH_2}(acac)], **33**. A supplementary HSQC spectrum was obtained for **32**. The ^{1}H NMR variable-temperature experiments were recorded at 400.14 MHz in $CDCl_3$, from 208 K to 333 K for complexes [Ni{Mes-NHC-CHCN$(CH_2)_3$}Cp], **28b** and [Ni{Mes-NHC-CHCN$(CH_2)_4$}Cp], **28c**. The chemical shifts are referenced to the residual deuterated solvent peaks. Chemical shifts (δ) and coupling constants (*J*) are expressed in ppm and Hz respectively. IR spectra of solid samples of **23a**, and of the complexes **25a**, **28a**, **28b**, **29**, **30**, **32**, and **33** were recorded on a FT-IR Nicolet 380 spectrometer equipped with a diamond SMART iTR ATR. IR spectra of solid samples of **23b**, **23c**, **26**, **27c** were recorded on a Nicolet 380 spectrometer equipped with a Ge SMART iTR ATR. IR spectra of the samples **25b**, **25c**, **27a**, and **27b** were recorded on a FT-IR Nicolet 380 spectrometer with KBr pellets. Vibrational frequencies are expressed in cm^{-1}. Elemental analyses were performed by the Service d'Analyses, de Mesures Physiques et de Spectroscopie Optique, UMR CNRS 7177, Institut de Chimie, Université de Strasbourg. Commercial compounds were used as received. 1-mesityl-1*H*-imidazole,[34] and 1-(propylnitrile)-1*H*-imidazole,[37] as well as [Ni(Mes_2-NHC]ClCp][20] and [Ni(Mes_2-NHC)(CH_3CN)Cp]$^{+}PF_6^{-}$, **12a**,[19] and [Ni(Mes_2NHC)(CH_3CN)Cp*](PF_6), **12b**,[19] were prepared according to published methods.

Synthesis of [Ni(Mes_2-NHC)(CH_2CN)Cp] (18a). [Ni(Mes_2-NHC)(CH_3CN)Cp]$^{+}PF_6^{-}$, **12a**, (430 mg, 0.700 mmol) was added to a suspension of KO*t*-Bu (79 mg, 0.704 mmol) in toluene (7 mL) at r.t.. Dissolution of the complex was observed in *ca.* 20 min, thus leading to a dark green solution containing a white salt. After 1 h, the reaction medium was filtered through Celite, which was rinsed with toluene (3 × 5 mL), and concentrated to dryness. Crystallization from a (4:15) mixture of toluene/pentane afforded **18a** as a dark green solid

that was washed with pentane (3 × 3 mL) and dried in vacuo (280 mg, 0.598 mmol, 85 %). *Anal. calcd* for $C_{28}H_{31}N_3Ni$: C, 71.82; H, 6.67; N, 8.97. *Found*: C, 72.18; H, 6.67; N, 8.74. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 7.07 (s, 4H, *m*-H), 6.99 (s, 2H, NC*H*), 4.60 (s, 5H, η^5-C_5H_5), 2.41 (s, 6H, *p*-Me), 2.11 (s, 12H, *o*-Me), –0.08 (s, 2H, CH_2CN). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.61 MHz): δ = 177.8 (N*C*N), 139.2 (*p*-/*ipso*-C_{Ar}), 136.6 (*ipso*-/*p*-C_{Ar}), 135.3 (*o*-C_{Ar}), 132.7 (CH_2*C*N), 129.4 (*m*-C_{Ar}), 123.9 (N*C*H), 91.4 (η^5-*C*$_5$H$_5$), 21.3 (*p*-Me), 18.4 (*o*-Me), –42.0 (*C*H$_2$CN). FT-IR [ATR Ge]: ν(C_{sp2}-H) 3162 (w), 3128 (w), 3097 (w); ν(C_{sp3}-H) 2955 (m), 2918 (m), 2859 (w); ν(CN) 2188 (s).

Synthesis of [Ni(Mes$_2$-NHC)(CH$_2$CN)Cp*] (18b). To a suspension of [Ni(Mes$_2$-NHC)(CH_3CN)Cp*]$^+$$PF_6^-$, **12b** (206 mg, 0.301 mmol) in toluene (5 mL) was added to at r.t. KO*t*-Bu (40 mg, 0.357 mmol). Dissolution of the complex was observed in *ca.* 30 min, thus leading to a dark brown solution containing a white salt. After 3 h, the solvent was removed under vacuum; then, the residue was extracted with thf (10 mL), filtered through alumina and concentrated to dryness. Crystallization from a (4:15) mixture of thf/pentane afforded **18b** as a brown solid that was washed with pentane (3 × 3 mL) and dried in vacuo (76 mg, 0,141 mmol, 47 %). ^{1}H NMR (C_6D_6, 300.13 MHz): δ = 6.84 (br. s, 4H, *m*-H), 6.08 (s, 2H, NC*H*), 2.29 (br. s, 6H, *o*-Me), 2.16 (s, 6H, *p*-Me), 1.93 (br. s, 6H, *o*-Me), 1.40 (s, 15H, C$_5$*Me*$_5$), –0.07 (s, 2H, CH_2CN). ^{13}C{^{1}H} NMR (C_6D_6, 75.47 MHz): δ = 184.8 (N*C*N), 138.5 (*p*-C_{Ar}), 137.5 (*ipso*-C_{Ar}), 136.1 and 135.3 (*o*-C_{Ar}), 130.2 and 129.1 (*m*-C_{Ar}), 129.5 (CH_2*C*N), 123.9 (N*C*H), 99.4 (η^5-*C*$_5$Me$_5$), 21.0 (*p*-Me), 19.0 (*o*-Me), 9.8 (η^5-C$_5$*Me*$_5$), –29.8 (*C*H$_2$CN). IR [ATR]: ν(C_{sp2}-H) 3169 (w), 3130 (w), 3104 (w); ν(C_{sp3}-H) 2945 (m), 2911 (m), 2853 (m); ν(CN) 2179 (s).

Synthesis of [Ni(Mes$_2$-NHC){(CH$_3$)$_2$CO}Cp]$^+$BF$_4^-$ (19). $AgBF_4$ (195 mg, 1.0 mmol) was added to a solution of [Ni(Mes$_2$-NHC)ClCp] (1.0 mmol, 463 mg) in acetone (10 mL). The resulting suspension immediately turned bright red and was stirred at r.t. for 10 min. The mixture was filtered through Celite, which was rinsed with acetone (3 x 3 mL) and then the solvent was evaporated to dryness. **19** (516 mg, 0.9 mmol, 90 %) was crystallized from a (1:3) solution of acetone/ether at –32°C and obtained as red crystals. *Anal. calcd* for $C_{29}H_{35}BF_4N_2NiO$: C, 55.18; H, 5.589; N, 4.438. *Found*: C, 54.95; H, 5.517; N, 4.604. ^{1}H NMR (acetone-d_6, 300.16 MHz): δ = 7.69 (s, 2H, NC*H*), 7.27 (s, 4H, *m*-H), 4.68 (s, 5H, η^5-C_5H_5), 2.44 (s, 6H, *p*-Me), 2.19 (s, 12H, *o*-Me). ^{13}C{^{1}H} NMR (acetone-d_6, 75.47 MHz):

δ = 160.8 (N*C*N), 140.8 (*p*-C_{Ar}), 137.1 (*ipso*-C_{Ar}), 136.4 (*o*-C_{Ar}), 130.5 (*m*-C_{Ar}), 126.1 (N*C*H), 94.0 (η^5-*C*$_5$H$_5$), 21.1 (*p*-Me), 18.16 (*o*-Me).

Synthesis of [Ni(Mes$_2$-NHC){CH$_2$(CO)CH$_3$}Cp] (20). To a solution of **19** (162 mg, 0.26 mmol) in acetone (3 mL) was added KO*t*-Bu (39 mg, 0.35 mmol) under vigorous stirring. The red mixture was stirred at r.t. for 1 h. The resulting brownish solution was evaporated to dryness, dissolved in CH_2Cl_2 (10 mL) and filtered through alumina, which was rinsed with CH_2Cl_2 until the washings were colourless. Volatiles were evaporated under vacuum and the residue crystallized in a (1:4) solution of thf/pentane at –32°C to obtain **20** as brown crystals in 31 % yield (40 mg, 0.08 mmol). ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 7.07 (s, 4H, *m*-H), 6.99 (s, 2H, NC*H*), 4.45 (s, 5H, η^5-C$_5$*H*$_5$), 2.40 (s, 6H, *p*-Me), 2.13 (s, 12H, *o*-Me), 1.60 (s, 3H, COC*H*$_3$), 1.07 (s, 2H, C*H*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ = 217.1 (*C*O), 177.8 (N*C*N), 139.1 (*p*-C_{Ar}), 137.0 (*ipso*-C_{Ar}), 135.5 (*o*-C_{Ar}), 129.4 (*m*-C_{Ar}), 123.9 (N*C*H), 91.3 (η^5-*C*$_5$H$_5$), 29.0 (CO*C*H$_3$), 21.3 (*p*-Me), 18.5 (*o*-Me), 3.6 (*C*H$_2$).

Synthesis of [Ni$_2$(Mes$_2$-NHC)$_2${(CH$_2$)$_2$CO}Cp$_2$] (21). To a suspension of **19** (573 mg, 1.0 mmol) in toluene (3 mL) was added KO*t*-Bu (224 mg, 2.0 mmol) under vigorous stirring. The suspension was stirred at r.t. for 4 h. The solvent was evaporated to dryness and the residue was then dissolved in CH_2Cl_2 and filtered through alumina, which was rinsed with thf until the washings were colourless. The solvent was evaporated under vacuum and the brown residue crystallized in a mixture of thf/pentane to afford **21** as brown crystals in 20 % yield (93 mg, 0.10 mmol). ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 7.00 (s, 8H, *m*-H), 6.88 (s, 4H, NC*H*), 4.34 (s, 10H, η^5-C$_5$*H*$_5$), 2.39 (s, 12H, *p*-Me), 2.18 (s, 24H, *o*-Me), 0.67 (s, 4H, C*H*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ = 231.0 (*C*O), 180.5 (N*C*N), 138.6 (*p*-C_{Ar}), 137.3 (*ipso*-C_{Ar}), 135.7 (*o*-C_{Ar}), 129.3 (*m*-C_{Ar}), 123.4 (N*C*H), 90.8 (η^5-*C*$_5$H$_5$), 21.4 (*p*-Me), 19.1 (*o*-Me), 1.42 (*C*H$_2$).

Synthesis of [Ni(Mes$_2$-NHC){CH$_2$CO(*p*-C$_6$H$_4$-OMe)}Cp] (22). To a solution of [Ni(Mes$_2$-NHC)ClCp] (161 mg, 0.34 mmol) in thf (4 mL) was added KO*t*-Bu (39 mg, 0.34 mmol) with vigorous stirring. The resulting suspension was stirred for 2.5 h and then filtered through alumina, which was rinsed with thf until the washings were colourless. The solvent was evaporated under reduced pressure and **22** (61 mg, 0.105 mmol) was obtained as a brown solid which was rinsed with pentane (2 x 3 mL) and dried under vacuum in 31 % yield from a

cold (1:4) mixture of thf/pentane. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 7.41 (d, ^{3}J = 9.1, 2H, *o*-/*m*-H), 7.12 (s, 4H, *m*-H), 7.01 (s, 2H, NC*H*), 6.61 (d, ^{3}J = 9.1, 2H, *o*-/*m*-H), 4.32 (s, 5H, η^5-C_5H_5), 3.82 (s, 3H, OCH_3), 2.46 (s, 6H, *p*-Me), 2.17 (s, 12H, *o*-Me), 1.57 (s, 2H, CH_2).

Synthesis of 1-(2,4,6)-trimethylphenyl-(3-butylnitrile)imidazolium chloride (23a). A solution of 1-mesityl-1*H*-imidazole (500 mg, 2.68 mmol) and 4-chlorobutyronitrile (0.27 mL, 2.82 mmol) in DME (10 mL) was refluxed for 3 days. The biphasic mixture was cooled to r.t. and the supernatant DME removed by syringe. The resulting colourless oil was washed with hot DME (5 mL) and dried under high vacuum to give **23a** as a white powder in 98 % yield (762 mg, 2.63 mmol). *Anal. calcd* for $C_{16}H_{20}N_3Cl\bullet{}^1/_4H_2O$: C, 65.30; H, 7.02; N, 14.27. *Found*: C, 65.01; H, 7.08; N, 14.22. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 10.70 (s, 1H, NC*H*N), 8.04 (t, ^{3}J = 1.8, 1H, NC*H*), 7.17 (t, ^{3}J = 1.8, 1H, NC*H*), 7.00 (s, 2H, *m*-H), 4.99 (t, ^{3}J = 6.9, 2H, NCH_2), 2.77 (t, ^{3}J = 6.9, 2H, CH_2CN), 2.48 (quintet, ^{3}J = 6.9, 2H, CH_2), 2.34 (s, 3H, *p*-Me), 2.07 (s, 6H, *o*-Me). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ = 141.4 (*p*-/*ipso*-C_{Ar}), 138.7 (N*C*HN), 134.3 (*o*-C_{Ar}), 130.8 (*ipso*-/*p*-C_{Ar}), 130.0 (*m*-C_{Ar}), 123.8 and 123.4 (N*C*H), 118.9 (*C*N), 48.9 (NCH_2), 26.6 (CH_2), 21.2 (*p*-Me), 17.8 (*o*-Me), 14.5 (CH_2). FT-IR [ATR C, cm^{-1}]: ν(C_{sp2}-H) 3150 (m), 3132 (m), 3068 (s); ν(C_{sp3}-H) 2973 (m), 2935 (m), 2915 (m), 2868 (w); ν(C≡N) 2248 (m).

Synthesis of 1-(2,4,6)-trimethylphenyl-(3-pentylnitrile)imidazolium iodide (23b). A suspension of 1-mesityl-1*H*-imidazole (1.449 g, 7.78 mmol), (5-chloropentane)nitrile (2.0 mL, 17.8 mmol) and KI (1.970 g, 11.9 mmol) in DME (20 mL) was vigorously stirred at 80 °C for 22 h. The brown reaction mixture was cooled to r.t. and the solvent removed under vacuum. The brown residue was extracted with acetonitrile (15 mL) and filtered through Celite, which was rinsed with acetonitrile (20 mL) till the washings were colourless. Evaporation of the solvent followed by addition of DME (3 mL) to the resulting brown oil allowed crystallization of a white solid after 5 h at -18 °C. The solid was filtered, washed with DME (2 x 2 mL) and dried in vacuum to give **23b** as white crystals in 78 % yield (2.402 g, 6.08 mmol). *Anal. calcd* for $C_{17}H_{22}N_3I$: C, 51.65; H, 5.61; N, 10.63. *Found*: C, 51.23; H, 5.32; N, 10.64. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 9.94 (s, 1H, NC*H*N), 8.11 (t, ^{3}J = 1.7, 1H, NC*H*), 7.20 (t, ^{3}J = 1.7, 1H, NC*H*), 6.99 (s, 2H, *m*-H), 4.79 (t, ^{3}J = 7.5, 2H, NCH_2), 2.55 (t, ^{3}J = 7.1, 2H, CH_2CN), 2.32 (s, 3H, *p*-Me), 2.23 (m, 2H, CH_2), 2.06 (s, 6H, *o*-Me), 1.83 (m, 2H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ = 141.6 (*p*-/*ipso*-C_{Ar}), 137.1 (N*C*HN), 134.2 (*o*-

C_{Ar}), 130.6 (*ipso-*/*p*-C_{Ar}), 130.0 (*m*-C_{Ar}), 123.8 and 123.5 (N*C*H), 119.5 (*C*N), 49.3 (N*C*H_2), 29.7 (*C*H_2), 22.1 (*C*H_2), 21.2 (*p*-Me), 17.9 (*o*-Me), 17.1 (*C*H_2). FT-IR [ATR Ge, cm^{-1}]: ν(C_{sp2}-H) 3104 (w), 3053 (m); ν(C_{sp3}-H) 2967 (m), 2941 (m); ν(C≡N) 2247 (w).

Synthesis of 1-(2,4,6)-trimethylphenyl-(3-hexylnitrile)imidazolium bromide (23c). A solution of 1-mesityl-1*H*-imidazole (1.126 g, 6.05 mmol) and (6-bromohexane)nitrile (95 %) (1.2 mL, 8.60 mmol) in DME (20 mL) was refluxed for 22 h, affording a yellow suspension that was cooled to r.t. and filtered on a glass frit. The resulting solid was washed with DME (2 x 1 mL) and dried in vacuum to give **23c** as white crystals in 76 % yield (1.673 g, 4.62 mmol). *Anal. calcd* for $C_{18}H_{24}N_3Br$: C, 59.67; H, 6.68; N, 11.60. *Found*: C, 59.40; H, 6.77; N, 11.66. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 10.25 (s, 1H, NC*H*N), 8.10 (t, ^3J = 1.5, 1H, NC*H*), 7.17 (t, ^3J = 1.5, 1H, NC*H*), 6.95 (s, 2H, *m*-H), 4.72 (t, ^3J = 7.2, 2H, NCH_2), 2.38 (t, ^3J = 6.9, 2H, CH_2CN), 2.29 (s, 3H, *p*-Me), 2.10 (m, 2H, CH_2), 2.02 (s, 6H, *o*-Me), 1.73 (m, 2H, CH_2), 1.54 (m, 2H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ = 141.3 (*p-*/*ipso*-C_{Ar}), 137.8 (N*C*HN), 134.2 (*o*-C_{Ar}), 130.7 (*ipso-*/*p*-C_{Ar}), 129.9 (*m*-C_{Ar}), 123.5 and 123.3 (N*C*H), 119.7 (*C*N), 49.7 (N*C*H_2), 29.7 (*C*H_2), 25.0 (*C*H_2), 24.6 (*C*H_2), 21.1 (*p*-Me), 17.7 (*o*-Me), 17.1 (*C*H_2).FṮIR [ATR Ge, cm^{-1}]: ν(C_{sp2}-H) 3131 (w), 3056 (m); ν(C_{sp3}-H) 2939 (m), 2869 (w); ν(C≡N) 2243 (w).

Synthesis of 1-propylnitrile-(3-methyl)imidazolium iodide (24). A solution of 1-(propylnitrile)-1*H*-imidazole (1.11 g, 9.2 mmol) and iodomethane (0.62 mL, 10.0 mmol) in DME (20 mL) was stirred at 60 °C for 20 h. The resulting biphasic mixture was cooled to r.t. and the solvent was removed by syringe. The solid residue was washed with dry toluene (4 x 10 mL) and dried under vacuum for 2 h to afford **24** as a white solid in 98 % yield (2.36 g, 9.0 mmol). ^{1}H NMR (D_2O, 300.13 MHz): δ = 8.91 (s, 1H, NC*H*N), 7.61 (t, ^3J = 1.5, 1H, NC*H*), 7.52 (t, ^3J = 1.5, 1H, NC*H*), 4.58 (t, ^3J = 6.3, 2H, NCH_2), 3.93 (s, 3H, CH_3), 3.17 (t, ^3J = 6.3, 2H, CH_2CN). FT-IR (cm^{-1}): ν̣C_{sp2}–H), 3244; ν̣C_{sp3}–H), 2916, 2788, 2700; ν(C≡N), 2250; ν(C=N) 1720 (m).

Synthesis of [Ni{Mes-NHC-$(CH_2)_3$CN}ClCp] (25a). Nickelocene (325 mg, 1.72 mmol) and **23a** (548 mg, 1.89 mmol) were refluxed for 4 h in thf (20 mL). The solution colour turned from dark green to violet in *ca.* 2 h. The mixture was cooled to r.t. and solvent was then removed under reduced pressure and the residue extracted with hot toluene (10 mL)

and filtered through Celite, which was rinsed with toluene till the washings were colourless. The resulting purple-red solution was concentrated under vacuum to 1 - 2 mL and allowed to stand at -28 °C for a couple of hours to afford **25a** as violet crystals (468 mg, 1.13 mmol, 66 %) that were washed with pentane (3 x 2 mL) and dried under vacuum. *Anal. calcd.* for $C_{21}H_{24}N_3NiCl$: C, 61.13; H, 5.86; N, 10.18. *Found*: C, 61.50; H, 5.90; N, 9.85. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 7.21 (d, ^3J = 1.8, 1H, NC*H*), 7.10 (s, 2H, *m*-H), 6.91 (d, ^3J = 1.8, 1H, NC*H*), 5.16 (bt, ^3J = 7.2, 2H, NCH_2), 4.74 (s, 5H, η^5-C$_5H_5$), 2.59 (b, 4H, (CH_2)$_2$CN), 2.43 (s, 3H, *p*-Me), 2.12 (s, 6H, *o*-Me). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ = 164.2 (N*C*N), 139.3 (*p*-/*ipso*-C$_{Ar}$), 136.6 (*ipso*-/*p*-C$_{Ar}$), 135.8 (*o*-C$_{Ar}$), 129.2 (*m*-C$_{Ar}$), 124.1 and 122.7 (N*C*H), 119.0 (*C*N), 91.8 (η^5-*C*$_5$H$_5$), 50.3 (N*C*H$_2$), 26.8 (*C*H$_2$), 21.2 (*p*-Me), 18.3 (*o*-Me), 14.8 (*C*H$_2$CN). FT-IR [ATR C, cm^{-1}]: ν(C$_{sp2}$-H) 3169 (w), 3132 (w), 3100 (w); ν(C$_{sp3}$-H) 2940 (m), 2863 (w); ν(C≡N) 2250 (m).

Synthesis of [NiCp{Mes-NHC-(CH$_2$)$_4$CN}ICp] (25b). Nickelocene (830 mg, 4.39 mmol) and **23b** (1.333 g, 3.37 mmol) were refluxed for 70 h in thf (20 mL). The solution colour slowly turned from dark green to purple-red. The mixture was cooled to r.t., the solvent was then removed under reduced pressure and the residue extracted with hot toluene (10 mL) and filtered through Celite, which was rinsed with toluene till the washings were colourless. The resulting purple-red solution was concentrated under vacuum to *ca.* 2 mL and allowed to stand at -28 °C for a couple of hours to afford **25b** as a violet powder (750 mg, 1.45 mmol, 43 %) that was washed with pentane (3 x 2 mL) and dried under vacuum. *Anal. calcd* for $C_{22}H_{26}N_3NiI$: C, 51.00; H, 5.06; N, 8.11. *Found*: C, 51.09; H, 5.30; N, 7.96. ^{1}H NMR ($CDCl_3$, 243 K, 400.14 MHz): δ = 7.20 (s, 1H, NC*H*), 7.16 (s, 1H, *m*-H), 7.01 (s, 1H, *m*-H), 6.91 (s, 1H, NC*H*), 5.25 (m, 1H, NCH_2), 4.86 (s, 5H, η^5-C$_5H_5$), 4.68 (m, 1H, NCH_2), 2.57 (m, 2H, CH_2CN), 2.46 (s, 3H, *o*-Me), 2.42 (s, 3H, *p*-Me), 2.19 (m, 2H, CH_2), 1.86 (m, 2H, CH_2), 1.75 (s, 3H, *o*-Me). ^{1}H NMR ($CDCl_3$, 400.14 MHz): δ = 7.17 (d, ^3J = 1.6, 1H, NC*H*), 7.07 (b, 2H, *m*-H), 6.88 (d, ^3J = 1.6, 1H, NC*H*), 5.19 (vb, 1H, NCH_2), 4.88 (s, 5H, η^5-C$_5H_5$), 4.79 (vb, 1H, NCH_2), 2.52 (b, 2H, CH_2CN), 2.42 (vb, 3H, *o*-Me), 2.42 (s, 3H, *p*-Me), 2.23 (b, 2H, CH_2), 1.85 (m, 2H, CH_2), 1.77 (s, 3H, *o*-Me). ^{1}H NMR ($CDCl_3$, 333 K, 400.14 MHz): δ = 7.18 (s, 1H, NC*H*), 7.07 (s, 2H, *m*-H), 6.88 (s, 1H, NC*H*), 5.00 (b, 2H, NCH_2), 4.90 (s, 5H, η^5-C$_5H_5$), 2.52 (m, 2H, CH_2CN), 2.42 (s, 3H, *p*-Me), 2.26 (m, 2H, CH_2), 2.13 (vb, 6H, *o*-Me), 1.89 (m, 2H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ = 167.6 (N*C*N), 139.4 (*p*-/*ipso*-C$_{Ar}$), 136.8 (*ipso*-/*p*-C$_{Ar}$), 129.4 (b, *m*-C$_{Ar}$), 124.9 and 122.4 (N*C*H), 119.5

(*C*N), 92.0 (η^5-C_5H_5), 52.8 (N*C*H_2), 29.8 (*C*H_2), 22.9 (*C*H_2), 21.3 (*p*-Me), 17.4 (*C*H_2CN). IR [KBr, cm^{-1}]: ν(C_{sp2}-H) 3169 (m), 3149 (m), 3116 (m), 3091 (m); ν(C_{sp3}-H) 2942 (s), 2927 (s), 2868 (m); ν(C≡N) 2247 (m).

Synthesis of [NiCp{Mes-NHC-$(CH_2)_5$CN}BrCp] (25c). Nickelocene (152 mg, 0.805 mmol) and **23c** (280 mg, 0.773 mmol) were refluxed for 20 h in thf (10 mL). The solution colour progressively turned from dark green to purple-red. The mixture was cooled to r.t. solvent was then removed under reduced pressure and the residue extracted with hot toluene (10 mL) and filtered through Celite, which was rinsed with toluene till the washings were colourless. The resulting solution was concentrated to dryness and crystallized from a mixture of acetone/pentane to afford **25c** as a violet powder (264 mg, 0.545 mmol, 71 %) that was washed with pentane (3 x 2 mL) and dried under vacuum. *Anal. calcd*. for $C_{23}H_{28}N_3NiBr$: C, 56.95; H, 5.82; N, 8.66. *Found*: C, 56.31; H, 5.77; N, 8.52. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 7.16 (d, ^3J = 1.7, 1H, NC*H*), 7.07 (bs, 2H, *m*-H), 6.86 (d, ^3J = 1.7, 1H, NC*H*), 5.02 (b, 2H, NCH_2), 4.78 (s, 5H, η^5-C_5H_5), 2.45 (t, ^3J = 6.6, 2H, CH_2CN), 2.42 (s, 3H, *p*-Me), 2.24-1,99 (vb, 8H, CH_2 and *o*-Me), 1.83 (m, 2H, CH_2), 1.68 (m, 2H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ = 164.1 (N*C*N), 139.2 (*p*-/*ipso*-C_{Ar}), 136.8 (*ipso*-/*p*-C_{Ar}), 135.9 (b, *o*-C_{Ar}), 129.2 (*m*-C_{Ar}), 124.1 and 122.4 (N*C*H), 119.6 (*C*N), 91.8 (η^5-C_5H_5), 52.2 (N*C*H_2), 30.2 (CH_2), 25.9 (*C*H_2), 25.1 (*C*H_2), 21.3 (*p*-Me), 18.7 (b, *o*-Me), 17.3 (*C*H_2CN). IR [KBr, cm^{-1}]: ν(C_{sp2}-H) 3150 (m), 3117 (m), 3091 (m); ν(C_{sp3}-H) 2946 (s), 2927 (s), 2916 (w), 2863 (m); ν(C≡N) 2239 (m).

Synthesis of [Ni{Me-NHC-$(CH_2)_2$CN}ICp] (26). To a solution of **24** (789 mg, 3.0 mmol) in DME was added nickelocene (567 mg, 3.0 mmol). The resulting mixture was stirred at 85 °C for 4 days. The solution was cooled to r.t. and the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (5 mL) and separated through silica gel column employing CH_2Cl_2 as eluent. The eluent was evaporated under vacuum and **26** was crystallized at r.t. from a mixture of CH_2Cl_2/pentane to give dark red needles (467 mg, 1.8 mmol, 59 %) which were rinsed with pentane (3 x 5 mL) and dried under vacuum. X-Ray quality crystals were obtained from a CH_2Cl_2/diethyl ether (1 : 3) solution at – 28 °C. *Anal. calcd* for $C_{12}H_{14}N_3NiI$: C, 37.35; H, 3.66; N, 10.89. *Found*: C, 37.18; H, 4.04; N, 10.81. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 7.15 (s, 1H, NC*H*), 7.01 (s, 1H, NC*H*), 5.36 (s, 5H, η^5-C_5H_5), 5.15 (m, 1H, NCH_2), 4.71 (m, 1H, NCH_2), 4.19 (s, 3H, Me), 3.25 (m, 2H, CH_2CN).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.47 MHz): δ = 167.3 (N*C*N), 124.6 and 122.6 (N*C*H), 117.5 (*C*N), 92.0 (η^5-*C*$_5H_5$), 47.9 (N*C*H_2), 39.8 (Me), 19.6 (*C*H_2*C*N). FT-IR [ATR Ge, cm^{-1}]: ν(C_{sp2}-H) 3155 (m), 3119 (m), 3101 (m); ν(C_{sp3}-H) 2980 (w), 2945 (m), 2921 (m); ν(C≡N) 2251 (m).

Synthesis of [Ni{Mes-NHC-(CH$_2$)$_3$CN}(CH$_3$CN)Cp]$^+$PF$_6^-$ (27a). KPF_6 (211 mg, 1.15 mmol) was added to a solution of **25a** (468 mg, 1.13 mmol) in acetonitrile (10 mL). The colour changed instantly from violet to dark yellow. After 45 min., the reaction medium was filtered through Celite and then concentrated to dryness. Crystallization from an acetonitrile/toluene mixture then afforded **27a** as a yellow solid that was washed with diethyl ether (3 x 2 mL), and dried under vacuum (458 mg, 0.813 mmol, 72 %). ^1H NMR (CD_3CN, 300.13 MHz): δ = 7.52 (d, ^3J = 2.0, 1H, NC*H*), 7.22 (d, ^3J = 2.0, 1H, NC*H*), 7.16 (s, 2H, *m*-H), 5.01 (s, 5H, η^5-C$_5H_5$), 4.78 (t, ^3J = 7.4, 2H, NCH_2), 2.61 (t, ^3J = 6.9, 2H, CH_2CN), 2.41 (s, 3H, *p*-Me), 2.38 (m, 2H, CH_2), 1.99 (s, 6H, *o*-Me). $^{13}C\{^1H\}$ NMR (CD_3CN, 75.47 MHz): δ = 159.1 (N*C*N), 140.7 (*p*-/*ipso*-C_{Ar}); 137.1 (*ipso*-/*p*-C_{Ar}), 136.5 (*o*-C_{Ar}), 130.2 (*m*-C_{Ar}), 126.8 and 125.0 (N*C*H), 120.5 (*C*N), 93.9 (η^5-*C*$_5H_5$), 51.3 (N*C*H_2), 27.3 (*C*H_2), 21.2 (*p*-Me), 18.1 (*o*-Me), 15.3 (*C*H_2CN). IR [KBr, cm^{-1}]: ν(C_{sp2}-H) 3176 (m), 3147 (m); ν(C_{sp3}-H) 2957 (m), 2925 (m), 2862 (w); ν(C≡N) 2294 (w), 2249 (w); ν(P-F) 840 (s).

Synthesis of [NiCp{Mes-NHC-(CH$_2$)$_4$CN}(CH$_3$CN)]$^+$BF$_4^-$ (27b). $AgBF_4$ (31.3 mg, 0.161 mmol) was added to a solution of **25b** (83.5 mg, 0.161 mmol) in acetonitrile (10 mL). The colour changed instantly from violet to dark yellow. After 1 h, the reaction medium was filtered through Celite and concentrated to dryness. The resulting yellow solid was washed with diethyl ether (3 x 2 mL), and dried under vacuum to afford **27b** in 66 % yield (55 mg, 0.106 mmol). ^1H NMR (CD_3CN, 300.13 MHz): δ = 7.51 (d, ^3J = 2.1, 1H, NC*H*), 7.20 (d, ^3J = 2.1, 1H, NC*H*), 7.16 (s, 2H, *m*-H), 5.00 (s, 5H, η^5-C$_5H_5$), 4.70 (t, ^3J = 7.4, 2H, NCH_2), 2.56 (t, ^3J = 7.1, 2H, CH_2CN), 2.41 (s, 3H, *p*-Me), 2.14 (m, 2H, NCH$_2$*C*H_2), 1.98 (s, 6H, *o*-Me), 1.78 (m, 2H *C*H_2CH$_2$CN). $^{13}C\{^1H\}$ NMR (CD_3CN, 75.47 MHz): δ = 158.3 (N*C*N), 140.7 (*p*-/*ipso*-C_{Ar}), 137.1 (*ipso*-/*p*-C_{Ar}), 136.5 (*o*-C_{Ar}), 130.1 (*m*-C_{Ar}), 126.7 and 125.0 (N*C*H), 121.1 (*C*N), 93.8 (η^5-*C*$_5H_5$), 51.9 (N*C*H_2), 30.7 (*C*H_2), 23.5 (*C*H_2), 21.2 (*p*-Me), 18.1 (*o*-Me), 17.5 (*C*H_2CN). IR [KBr, cm^{-1}]: ν(C_{sp2}-H) 3167 (m), 3132 (m), 3101 (m); ν(C_{sp3}-H) 2926 (m), 2871 (m); ν(C≡N) 2291(w), 2248 (w); ν(B-F) 1063 (s).

Synthesis of [Ni{Mes-NHC-$(CH_2)_5$CN}(CH_3CN)Cp]$^+PF_6^-$ (27c). KPF_6 (211 mg, 1.15 mmol) was added to a solution of **25c** (468 mg, 1.13 mmol) in acetonitrile (10 mL). The colour changed instantly from violet to dark yellow. After 45 min., the reaction medium was filtered through Celite and concentrated to dryness. Crystallization from a mixture of acetonitrile - toluene then afforded **27c** as a yellow solid that was washed with diethyl ether (3 x 2 mL), and dried under vacuum (458 mg, 0.813 mmol, 72 %). ^{1}H NMR (CD_3CN, 300.13 MHz): δ = 7.50 (d, ^3J = 2.0, 1H, NC*H*), 7.20 (d, ^3J = 2.0, 1H, NC*H*), 7.16 (s, 2H, *m*-H), 4.99 (s, 5H, η^5-C_5H_5), 4.68 (t, ^3J = 7.4, 2H, NCH_2), 2.47 (t, ^3J = 7.1, 2H, CH_2CN), 2.41 (s, 3H, *p*-Me), 2.03 (m, 2H, CH_2), 1.98 (s, 6H, *o*-Me), 1.76 (m, 2H, CH_2), 1.57 (m, 2H, CH_2). ^{13}C{^{1}H} NMR (CD_3CN, 75.47 MHz): δ = 158.0 (N*C*N); 140.6 (*p-/ipso*-C_{Ar}), 137.1 (*ipso-/p*-C_{Ar}), 136.5 (*o*-C_{Ar}), 130.1 (*m*-C_{Ar}), 126.6 and 124.9 (N*C*H), 121.2 (*C*N), 93.8 (η^5-C_5H_5), 52.4 (N*C*H_2), 30.8 (*C*H_2), 26.4 (*C*H_2), 25.7 (*C*H_2), 21.2 (*p*-Me), 18.1 (*o*-Me), 17.5 (*C*H_2CN). FT-IR [ATR Ge cm^{-1}]: ν(C_{sp2}-H) 3165 (w), 3134 (w); ν(C_{sp3}-H) 2935 (m), 2865 (w); ν(C≡N) n.r. (w); ν(P-F) 832 (s).

Synthesis of [Ni{Mes-NHC-CHCN$(CH_2)_2$}Cp] (28a) from 25a. KO*t*-Bu (42 mg, 0.374 mmol) was added to a solution of **25a** (154 mg, 0.373 mmol) in toluene (7.4 mL) at r.t.. The solution colour quickly turned from violet to dark green. After 2 h, the reaction medium was filtered through alumina, which was rinsed with thf (3 × 20 mL), and concentrated to dryness. Crystallization from a thf/pentane (1:3) solution afforded **28a** as dark green crystals (78 mg, 0.207 mmol, 56 %) that were washed with pentane (3 x 2 mL) and dried under vacuum. *Anal. calcd* for $C_{21}H_{23}N_3Ni$: C, 67.06; H, 6.16; N, 11.17. *Found*: C, 67.14; H, 5.96; N, 11.35. ^{1}H NMR ($CDCl_3$, 400.14 MHz): δ = 7.04 (d, ^3J = 1.6, 1H, NC*H*), 7.04 (s, 1H, *m*-H), 6.98 (s, 1H, *m*-H), 6.64 (d, ^3J = 1.6, 1H, NC*H*), 4.69 (s, 5H, η^5-C_5H_5), 3.98 and 3.83 (m, 1H, NCH_2), 2.36 (s, 3H, *p*-Me), 2.18 (s, 3H, *o*-Me), 2.15 (t, ^3J = 6.6, 1H, C*H*CN), 1.99 (s, 3H, *o*-Me), 1.67 and 1.41 (m, 1H, CH_2CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.61 MHz): δ = 171.3 (N*C*N), 139.3 (*p-/ipso*-C_{Ar}), 137.2 (*ipso-/p*-C_{Ar}), 136.5 and 135.3 (*o*-C_{Ar}), 132.6 (*C*N), 129.4 and 129.0 (*m*-C_{Ar}), 122.2 and 121.6 (N*C*H), 91.2 (η^5-C_5H_5), 50.1 (N*C*H_2), 30.0 (*C*H_2), 21.3 (*p*-Me), 18.5 and 18.0 (*o*-Me), –25.3 (*C*HCN). FT-IR [ATR C, cm^{-1}]: ν(C_{sp2}-H) 3172 (w), 3146 (w), 3112 (w); ν(C_{sp3}-H) 2922 (m), 2897 (m), 2850 (m); ν(C≡N) 2181 (s).

Synthesis of [Ni{Mes-NHC-CHCN(CH$_2$)$_2$}Cp] (28a) from 27a. **28a** was also synthesized in 46 % yield (60 mg, 0.16 mmol) by employing **27a** instead of **25a** as a reagent: from **27a** (191 mg, 0.34 mmol) and KO*t*-Bu (38 mg, 0.34 mmol) in toluene (7.4 mL).

Synthesis of [Ni{Mes-NHC-CHCN(CH$_2$)$_3$}Cp] (28b). **27b** (200 mg, 0.39 mmol) was added portion-wise to a suspension of KO*t*-Bu (50 mg, 0.45 mmol) in toluene (9 mL) over a period of 30 min and stirred for further 40 min. The resulting green mixture was filtered through alumina, which was rinsed with thf (60 mL). Volatiles were evaporated under vacuum and the residue was dried for 2 h. **28b** (40 mg, 0.1 mmol, 22 %) was crystallized from a (1:3) mixture of thf/pentane and obtained as green crystals. *Anal. calcd* for $C_{23}H_{27}N_3Ni$: C, 68.36; H, 6.688; N, 10.40. *Found*: C, 68.01; H, 6.813; N, 10.66. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 7.05 (d, ^3J = 1.7, 1H, NC*H*) and (s, 2H, *m*-H), 6.79 (d, ^3J = 1.7, 1H, NC*H*), 4.70 (s, 5H, η^5-C$_5$*H*$_5$), 2.39 (s, 3H, *p*-Me), 2.10 (bs, 6H, *o*-Me), 2.00 and 1.69 (m, 1H, C*H*$_2$), 1.61 (vb, 1H, C*H*), 1.15 and 0.97 (vb, 1H, C*H*$_2$CH). ^{1}H NMR ($CDCl_3$, 400.14 MHz, 333 K): δ = 7.05 (s, 3H, NC*H* and *m*-H), 6.79 (s, 1H, NC*H*), 4.84 and 4.60 (bm, 1H, NC*H*$_2$), 4.71 (s, 5H, η^5-C$_5$*H*$_5$), 2.40 (s, 3H, *p*-Me), 2.10 (bs, 6H, *o*-Me), 2.00 and 6.69 (m, 1H, C*H*$_2$), 1.53 (m, 1H, C*H*), 1.29 and 1.18 (m, 1H, C*H*$_2$CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ = 174.30 (N*C*N), 138.16 and 135.88 (*ipso/p*-C$_{Ar}$), 134.80 and 134.75 (*o*-C$_{Ar}$), 132.52 (*C*N), 128.42 and 128.27 (*m*-C$_{Ar}$), 122.21 and 120.68 (N*C*H), 90.07 (η^5-*C*$_5$H$_5$), 47.53 (N*C*H$_2$), 27.20 (*C*H$_2$), 25.97 (*C*H$_2$CH), 20.35 (*p*-Me), 17.46 and 17.31 (*o*-Me), -27.10 (*C*H). FT-IR [ATR C cm^{-1}]: ν(C$_{sp2}$-H) 3147 (w), 3117 (w); ν(C$_{sp3}$-H) 2945 (m), 2856 (w); ν(C≡N) 2176 (m).

Synthesis of [Ni{Mes-NHC-CH(CN)(CH$_2$)$_4$}Cp] (28c). To a suspension of KO*t*-Bu (48 mg, 0.43 mmol) in toluene (9 mL) (stirred for 10 min) was added **27c** (210 mg, 0.43 mmol) was added portion-wise over a period of 10 min and stirred for further 1 h 10 min. The resulting brown mixture was filtered over alumina, which was rinsed with thf (60 mL), then concentrated under vacuum and the residue dried for 2 h. **7d** (15 mg, 0.04 mmol, 8 %) was crystallized from thf and obtained as a brown yellow solid. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ = 7.09 (d, ^3J = 1.9, 1H, NC*H*), 7.07 and 7.04 (bs, 1H, *m*-H), 6.85 (d, ^3J = 1.9, 1H, NC*H*), 5.23 and 4.47 (m, 1H, NC*H*$_2$), 4.85 (s, 5H, η^5-C$_5$*H*$_5$), 2.41 (s, 3H, *p*-Me), 2.20 and 1.93 (m, 1H, C*H*$_2$), 2.01 and 1.89 (s, 3H, *o*-Me), 1.51 (m, 2H, C*H*$_2$), 1.30 (td, ^3J = 7.7, ^3J = 2.8, C*H*), 1.11 and 0.94 (m, 1H, C*H*$_2$CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ = 177.29 (N*C*N), 139.04 and 136.77 (*ipso/p*-C$_{Ar}$), 135.76 and 135.48 (*o*-C$_{Ar}$), 134.17 (*C*N), 129.37 and 129.17 (*m*-C$_{Ar}$),

124.07 and 121.90 (N*C*H), 91.41 (η^5-C_5H_5), 52.38 (NCH_2), 31.00 (CH_2), 29.87 (CH_2), 27.60 (CH_2CH), 21.29 (*p*-Me), 18.24 and 18.13 (*o*-Me), -18.68 (*C*H).

Synthesis of [Ni{Me-NHC-CH(CN)CH$_2$}Cp] (29). To a suspension of KO*t*-Bu (193 mg, 0.50 mmol) in toluene (2.5 mL) was added **26**, (56 mg, 0.50 mmol) under vigorous stirring over a period of 20 minutes. The mixture was stirred for further 40 minutes and filtered over alumina, which was rinsed with thf (80 mL). The solvent was evaporated under vacuum and **29** (32 mg, 0.13 mmol, 25 %) was crystallized from a (1:4) mixture of thf/pentane at r.t. and then dried under vacuum for 2 h. *Anal. calcd.* for $C_{12}H_{13}N_3Ni$: C, 55.87; H, 5.080; N, 16.29. *Found*: C, 55.69; H, 5.071; N, 16.58. ^{1}H NMR ($CDCl_3$, 400.14 MHz): δ = 6.77 and 6.63 (s, 1H, NC*H*), 5.35 (s, 5H, η^5-C_5H_5), 3.74 (m, 2H, CH_2), 3.34 (s, 3H, CH_3), 2.70 (dd, ^3J = 6.0, ^3J = 5.9, 1H, C*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.47 MHz): δ = 173.50 (N*C*N), 131.31 (*C*N), 122.63 and 117.24 (N*C*H), 90.21 (η^5-C_5H_5), 53.85 (NCH_2), 37.74 (CH_3), -11.56 (*C*H). FT-IR [ATR C, cm^{-1}]: ν(C_{sp2}-H) 3156 (w), 3130 (w) 3093 (w); ν(C_{sp3}-H) 2932 (m), 2875 (w); ν(C≡N) 2179 (m).

Synthesis of [Ni{Mes-NHC-CHCN(CH$_2$)$_2$}(CH$_3$CN)$_2$]$^+$PF$_6^-$ (30). A solution of a HCl in acetonitrile (1.92 mL, 0.51 mmol, 0.01 M) was added under vigorous stirring to a solution of **28a** (200 mg, 0.51 mmol) in the presence of an equimolar amount of KPF_6 (94 mg, 0.51 mmol). The green mixture turned immediately yellow and was stirred for 10 min at r.t. and was then filtered through Celite which was rinsed with acetonitrile until the washings became colourless. Volatiles were evaporated under vacuum and the resulting solid was dried for 2 h. **30** was obtained as a yellow powder (249 mg, 0.46 mmol, 93 %) which was rinsed with pentane (3 x 5 mL). ^{1}H NMR (CD_3CN, 300.13 MHz): δ = 7.32 and 7.03 (d, ^3J = 1.7, 1H, NC*H*), 7.24 and 7.05 (s, 1H, *m*-H), 4.12 and 4.02 (m, 1H, NCH_2), 2.56 (s, 3H, *o*-Me), 2.37 (s, 3H, *p*-Me), 2.33, (m, 1H, C*H*), 2.03 (s, 3H, *o*-Me), 1.96 (s, 6H, CH_3CN), 1.68 and 1.09 (m, 1H, CH_2). ^{13}C{^{1}H} NMR (CD_3CN, 75.47 MHz): δ = 155.6 (N*C*N); 139.8 (*ipso*/*p*-C_{Ar}); 135.7 (*p*-/*ipso*-C_{Ar} and *C*N), 136.1 and 135.2 (*o*-C_{Ar}), 129.9 and 129.5 (*m*-C_{Ar}), 124.9 and 123.1 (N*C*H), 50.1 (NCH_2), 28.7 (CH_2), 20.7 (*p*-Me), 18.7 and 17.8 (*o*-Me), -2.5 (*C*H). FT-IR [ATR C, cm^{-1}]: ν(C_{sp2}-H) 3174 (w); ν(C_{sp3}-H) 2922 (w); ν(C≡N) 2235 (m); ν(P–F) 826 (s).

Synthesis of [Ni{Mes-NHC-CHCN(CH$_2$)$_2$}(acac)] (32): A solution of HCl in acetonitrile (5.3 mL, 0.53 mmol, 0.01 M) was added drop-wise under vigorous stirring to a

solution of 28a (200 mg, 0.53 mmol) in acetonitrile (5 mL) in the presence of an equimolar amount of KPF_6 (86 mg, 0.53 mmol). The initially dark green solution immediately turned bright yellow. The resulting mixture was stirred for further 10 min, filtered through Celite and added to a suspension of K(acac) (73 mg, 0.53 mmol) in acetonitrile (5 mL). The mixture was stirred for further 10 min and filtered through Celite, which was rinsed until the washings became colourless. The solvent was evaporated to dryness and 32 (210 mg, 0.24 mmol, 89 %) was obtained from cold solutions of thf/pentane, washed with cold pentane (3 x 5 mL) dried in vacuo for 2 h. ^{1}H NMR (CD_3CN, 300.13 MHz): δ = 7.22 and 6.83 (d, ^3J = 1.8, 1H, NC*H*), 7.07 and 6.94 (s, 1H, *m*-H), 5.15 (s, 1H, COC*H*), 4.08 (m, 2H, NCH_2), 3.64 (thf), 2.51 (s, 3H, *o*-Me), 2.31 (s, 3H, *p*-Me), 2.08 (s, 3H, *o*-Me), 1.80 (thf), 1.76 (m, 1H, C*H*), 1.70 and 1.31 (s, 6H, 2 x $COCH_3$) 1.68 and 1.02 (m, 1H, CH_2). $^{13}C\{^1H\}$ NMR (CD_3CN, 75.47 MHz): δ = 188.1 and 187.1 (*C*O), 163.4 (N*C*N), 139.2 (*ipso*-/*p*-C_{Ar}), 137.1 (*C*N), 136.7 (*p*-/*ipso*-C_{Ar}), 136.0 (*o*-C_{Ar}), 129.9 (*m*-C_{Ar}), 124.7 and 122.8 (N*C*H), 101.1 (*C*HCO), 68.7 (thf), 51.2 (NCH_2), 31.1 (CH_2), 27.3 and 25.5 (2 x $COCH_3$), 26.8 (thf), 21.3 (*p*-Me), 19.2 (*o*-Me), -2.1 (*C*H). FT-IR [ATR C, cm^{-1}]: ν(C_{sp2}-H) 3346 (w), 3124 (w); ν(C_{sp3}-H) 2961 (w), 2291 (m), 2859 (w); ν(C≡N) 2186 (m)); ν(C=O) 1395 (s).

Synthesis of [Ni{Me-NHC-CHCNCH$_2$}(acac)] (33). A solution of HCl in acetonitrile (3.3 mL, 0.33 mmol, 0.01 M) was added drop-wise at r.t. and under vigorous stirring to a solution of 29 (86 mg, 0.33 mmol) in acetonitrile (3 mL) in the presence of KPF_6 (61 mg, 0.33 mmol). The initially dark green solution immediately turned bright yellow. The resulting mixture was stirred for 10 min at this temperature, filtered through Celite and added to a suspension of K(acac) (46 mg, 0.33 mmol) in acetonitrile (3 mL). The mixture was stirred for further 10 min and filtered through Celite, which was rinsed until the washings became colourless. The solvent was evaporated to dryness and 33 (80 mg, 0.27 mmol, 83 %) was obtained as a yellow powder, which was washed with cold pentane (3 x 5 mL) dried in vacuo for 2 h. ^{1}H NMR (CD_3CN, 300.13 MHz): δ = 6.77 and 6.58 (d, ^3J = 1.8, 1H, NC*H*), 5.38 (s, 1H, COC*H*), 3.78 (dd, ^3J = 12.1, ^3J = 8.0, 1H, NCH_2), 3.74 (s, 3H, CH_3), 3.51 (dd, ^3J = 8.0, ^3J = 3.2, 1H, NCH_2), 2.20 (dd, ^3J = 12.1, ^3J = 3.2, 1H, NCH_2), 1.88 and 1.84 (s, 6H, 2 x $COCH_3$). $^{13}C\{^1H\}$ NMR (CD_3CN, 75.47 MHz): δ = 187.5 and 185.9 (*C*O), 160.8 (N*C*N), 136.3 (w, *C*N), 123.8 and 117.3 (N*C*H), 101.2 (CO*C*H), 52.4 (NCH_2), 35.5 (CH_3), 27.2 and 26.6 (2 x $COCH_3$), 4.0 (*C*H). FT-IR [ATR C, cm^{-1}]: ν(C_{sp2}-H) 3147 (w) 3115 (w); ν(C≡N) 2185 (m); ν(C=O) 1377 (s).

Crystal Structure Determination of Complexes 12, 18a, 21, 22, 25a, 26, 28a, 28c and 32. Single crystals of **12**, **18a**, **21** and **22** suitable for X-ray diffraction studies were selected from batches of crystals obtained at -32 °C from (1:3:1) mixtures of acetonitrile/diethyl ether/pentane (**12**), (1:3) mixtures of toluene/pentane (**18a**) and (1:3) mixtures of thf/pentane (**21** and **22**). Furthermore, single crystals of **25a**, **26**, **28a**, **28c** as well as **32** suitable for X-ray diffraction studies were selected from batches of crystals obtained at -32 °C from (1:4) mixtures of thf/pentane (**25a**, **26**, **28a**), thf (**28c**) and from slow diffusion of pentane in cold solutions of **32** in CH_2Cl_2 in vacuo. Diffraction data for all crystals were collected at 173(2) K on a Nonius Kappa-CCD area detector diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). A summary of crystal data, data collection parameters and structure refinements is given in Table 10. Cell parameters were determined from reflections taken from one set of ten frames (1.0° steps in phi angle), each at 20s exposure. All structures were solved using direct methods with SHELXS-97 and refined against F^2 for all reflections using the SHELXL-97 software. Multiscan absorption corrections (MULscanABS in PLATON) were applied. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were generated according to stereochemistry and refined as fixed contributors using a riding model in SHELXL-97.[50,51]

[50] *Kappa CCD Operation Manual* , Delft, The Netherlands, 1997.
[51] G. M. Sheldrick, *SHELXL97, Program fro the refinement of crystal structures* , University of Göttingen, Germany, 1997.

Table 22 : Crystallographic data and data collection parameters for the complexes **12**, **18a**, **21** and **22**

	12	**18a**	**21**	**22**
Empirical formula	C28H32N$_3$Ni.BF4	$C_{28}H_{31}N_3Ni$	$C_{55}H_{62}N_4Ni_2O$	$C_{35}H_{38}N_2NiO_2$
Formula weight	556.09	468.27	912.51	577.38
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	P_{-1}	$P2_1/c$	$P2_1/c$	P_{-1}
a (Å)	8.2527(2)	14.0902(4)	16.2310(4)	9.806(2)
b (Å)	8.7456(2)	11.4279(5)	16.2709(4)	11.596(2)
c (Å)	18.6585(5)	16.0073(6)	20.3051(5)	14.753(3)
α(°)	88.573(2)	90	90	95.317(4)
β(°)	84.141(1)	110.029(2)	115.830(2)	96.846(5)
γ(°)	85.407(2)	90	90	113.015(4)
V (Å^3)	1335.15(6)	2421.63(16)	4826.7(2)	1515.3(6)
Z	2	4	4	2
D_x (Mg.m^{-3})	1.383	1.284	1.256	1.265
Abs. Coeff. (mm^{-1})	0.78	0.82	0.82	0.67
Temperature (K)	173	173	173	173
Crystal Form, color	Block, green	Block, green	Plate, brown	Block, brown
Crystal Size	0.50 x 0.48 x 0.25	0.32 x 0.16 x 0.14	0.40 x 0.18 x 0.10	0.24 x 0.14 x 0.12
h,k,l max	8, 11, 23	18, 13, 15	20, 20, 26	12, 14, 19
T_{min}, T_{max}	0.681, 0.884	-	0.733, 0.922	0.617, 0.746
Reflns collected	14996	14183	31486	11703
R (reflections)	0.042 (?)	0.042 (4135)	0.043 (8210)	0.074 (3231)
wR^2 (reflections)	0.128 (6087)	0.094 (5541)	0.099 (10751)	0.299 (6576)
GOF on F^2	1.10	1.01	1.04	1.00

Table 23 : Crystallographic data and data collection parameters for the complexes **25a**, **26**, **28a**, **28c** and **32**

Complex	**25a**	**26**	**28a**	**28c**	**32**
Empirical formula	$C_{21}H_{24}ClN_3Ni$	$C_{12}H_{14}IN_3Ni$	$C_{21}H_{23}N_3Ni$	$C_{23}H_{27}N_3Ni$	$2(C_{21}H_{25}N_3NiO_2)\cdot C_4H_8O$
Formula weight	412.59	385.87	376.13	404.19	892.40
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Tetragonal
Space group	$P2_1/c$	$P2_1$*	$P2_1/c$	$P2_1/c$	I_{-4}
a (Å)	12.5973(7)	9.1418(4)	13.7797(6)	11.6933(5)	18.4575(4)
b (Å)	10.5420(3)	17.7148(8)	9.5135(5)	10.5431(5)	13.1542(4)
c (Å)	15.9021(9)	9.2110(3)	16.2298(6)	16.9450(8)	
β (°)	110.575(2)	109.206(2)	117.249(3)	107.026(2)	
V ($Å^3$)	1977.10(17)	1408.65(10)	1891.50(15)	1997.48(16)	4481.36(19)
Z	4	4	4	4	4
D_x ($Mg.m^{-3}$)	1.386	1.819	1.321	0.98	1.323
Abs. coeff. (mm^{-1})	1.13	3.55	1.03	1.03	0.89
T (K)	173	173	173	173	173
Crystal form, color	Prism, red	Block, red	Prism, green	Prism, brown	Block, yellow
Crystal size (mm)	0.25 × 0.25 × 0.25	0.25 × 0.15 × 0.15	0.50 x 0.44 x 0.30	0.50 x 0.50 x 0.30	0.20 x 0.15 x 0.10
h, k, l_{max}	16, 13, 18	10, 23, 11	17, 12, 16	15, 13, 18	24, 23, 17
T_{min}, T_{max}	–	0.494, 0.588	0.587, 0.736	0.566, 0.858	0.842, 0.916
Reflns collected	13633	12365	11227	18673	29009
R (reflections)	0.048 (3143)	0.039 (5003)	0.034 (3624)	0.071 (3617)	0.026 (4775)
wR^2 (reflections)	0.150 (4537)	0.121 (5948)	0.109 (4328)	0.207 (4539)	0.068 (5149)
GOF (on F^2)	1.062	1.078	1.176	1.041	1.05

General Conclusion

The research in this thesis has targeted some aspects of the chemistry of half-sandwich nickel(II)-*N*-heterocyclic carbene (NHC) complexes. In this context, a series of *N*,*N'*-asymmetrically disubstituted imidazolium salts bearing a *N*-bound *n*-butyl arm, was prepared from the appropriate *N*-alkylimidazole and 1-chlorobutane or from the appropriate *N*-arylimidazole and 1-chlorobutane in the presence of one equivalent of potassium iodide.

Direct reaction of these imidazolium salts with nickelocene or [Ni(acac)Cp*] allowed the preparation of the corresponding [Ni(R-NHC-*n*-Bu)XCp†] (Cp† = Cp, Cp*; R = Me, *i*-Pr, Ph, Mes, *i*-Pr$_2$Ph; X = Cl, I). These complexes were targeted as models for future heterogenized versions of these complexes by employing (3-trialkoxysilylpropyl)imidazolium halides. All complexes were fully characterized by standard spectroscopic techniques [^{1}H/^{13}C{^{1}H} NMR spectroscopy, 2D NMR spectroscopy when appropriate and MS and/or elemental analyses]. The most representative complexes were further analyzed by single-crystal X-ray diffraction studies and confirmed that these compounds display a two-legged piano stool geometry common to all 18-electron NiCp†L$_2$ (Cp† = Cp, Cp*) complexes.

When compared to their closely related symmetric [Ni(Ar$_2$-NHC)ClCp†] counterparts, no significant distortion of their geometric features by the *n*-butyl sidearm was noticed. Nevertheless, ^{1}H NMR data revealed that the substitution of the chloride ligand by the much bulkier iodide ligand perturbs the rotation about the nickel–carbene bond at room temperature whatever the nature of the Cp† ligand: Cp or Cp*. The rotational barrier to nickel–carbene bond rotation ($\Delta G^{\#}$ = 60-61 ± 2 kJ.mol^{-1}) was elucidated by VT ^{1}H NMR studies and is believed to be predominantly steric in nature but electronic contribution to this barrier can not be ruled out.

As seen for the symmetric [Ni(Ar$_2$-NHC)XCp†] (X = Cl$^-$; NCMe, PF$_6^-$) species, all [Ni(R-NHC-*n*-Bu)XCp†] complexes appeared to generate highly active Ni(0)-catalysts for the Suzuki-Miyaura cross-coupling of 4'-bromoacetophenone and phenylboronic acid *in the absence of reductant and co-catalyst*. Thus, the catalytic activity was unaltered by the replacement of one aryl group by a *n*-butyl group. Moreover, substitution of the small chloride by the much bulkier iodide ligand seemed to furnish significantly better steric protection to the active species, compared to the bulky mesityl or diisopropylphenyl *N*-substituents of the imidazole rings of the symmetric complexes, which might be too far from the active metal centre to exert much influence. This major

impact on the catalyst's stability of the bulky iodide ligand, hints at $Cp^{\dagger}$ ring slippage rather than halide dissociation for the necessary generation of a coordinatively unsaturated intermediate during the catalytic cycle. Thus lower catalyst loadings were required with the [Ni(R-NHC-*n*-Bu)I$Cp^{\dagger}$] complexes; 1 mol% instead of 3 mol% with the symmetric complexes, and among the best TOFs reported for Ni(II)-catalyzed Suzuki cross-coupling reactions under similar conditions were observed.

These particularly encouraging results drove us to indeed prepare a heterogenized version of the complexes by covalent grafting onto alumina of a complex bearing a (3-triethoxysilylpropyl)-sidearm instead of a *n*-butyl group: [Ni(Mes-NHC-TES)ClCp]. Unfortunately, its catalytic activity in the Suzuki-Miyaura coupling of 4'-bromoacetophenone and phenylboronic acid appeared to be greatly reduced compared to those of its homogenous analogues. However, at this stage, it is unclear to what extent this activity drop is due to the immobilization itself or to the presence of a small chloride on this species instead of a highly protecting iodide.

In the prospect of studying effect of the presence of a second strongly σ-donating NHC unit on the active species stability, we have developed an original methodology for the synthesis of unprecedented half-sandwich Ni(II) complexes bearing *two different* NHC ligands. The compounds were prepared by the displacement of the labile acetonitrile ligand of the cationic [Ni(R_2-NHC)(CH_3CN)Cp]$^+X^-$ (R = Mes, Me; X = PF_6, BF_4) complexes with a free NHC. It was demonstrated that only species bearing at least one small NHC ligand could be prepared, most probably for steric reasons. The resulting cationic *bis*-NHC-Ni compounds were fully characterized by standard spectroscopic techniques [$^1H/^{13}C\{^1H\}$ NMR spectroscopy, 2D NMR spectroscopy when appropriate and elemental analyses]. Single crystal X-ray diffraction studies of [Ni(Mes_2-NHC)(Me_2-NHC)Cp]$^+BF_4^-$ showed that it displays geometric features analogous to its *mono*-carbene CpNi-(NHC) counterparts. Nevertheless, it demonstrated poor activity for the Suzuki-Miyaura cross-coupling of 4'-bromoacetophenone and phenylboronic acid, hinting the crucial role of the halide ligand for the active species.

The final chapter presents a novel reaction in which the base-promoted activation of sp^3-hybridized C–H bonds α- to functional organic groups at $Cp^{\dagger}$Ni-NHC centres was achieved. The scope and breadth of this reaction was demonstrated by the activation of acetonitrile, acetone and other ketones under relatively mild conditions to give the corresponding cyanomethyl-, acetonyl- or ketonyl-[Ni-(NHC)] complexes. The activation of acetonitrile occurred cleanly from toluene suspensions of the cationic acetonitrile complexes [Ni(Mes_2-NHC)(CH_3CN)$Cp^{\dagger}$]$^+PF_6^-$ and potassium *t*-butoxide and in good yields. In contrast, under similar reaction conditions, the

activation of acetone featuring two sets of α-C–H bonds on the carbonyl group, gave much lower yields. This was attributed to two simultaneous reactions in which the *mono*- and a *bis*-activation product of acetone (containing a remarkable {(η^1,η^1)-$(CH_2)_2C(O)$}-bridging unit between to CpNi-(NHC) moieties) were formed. Possible mechanistic pathways for these reactions have been the subject of theoretical DFT analyses. The activation of acetonitrile and the *mono*-activation of acetone were thus attributed to a deprotonation of nickel-bound acetonitrile or acetone followed by a rearrangement to the final cyanomethyl or acetonyl complexes. The remarkable *bis*-activation product of acetone may however arise via a different reaction pathway. The activation of C–H bonds α-to nitriles in NHC-attached sidearms gave rise to a series of new half-sandwich nickelacycles. All C–H activation products were fully characterized by standard spectroscopic techniques. Single X-ray diffraction studies of representative compounds revealed that these compounds featured the common two-legged piano stool geometry and puckered non-planar metallacyclic rings.

When CpNi-(*bis*-NHC) complexes or CpNi metallacycles were treated with HCl, nickel complexes, carrying a [C,C']-chelating ligand or two different NHCs and no Cp ring were fully characterized by standard spectroscopic techniques. Single-crystal X-ray diffraction studies of representative complexes confirmed the square-planar geometry of the nickel atom in these species Thus, the Ni–NHC and Ni–cyanoalkyl bonds of these complexes are much more robust than Ni–Cp bonds, and seem completely inert, even under acid conditions.

Prospective reactions: [Ni(Ar-NHC-*n*-Bu)ICp] complexes have shown outstanding reactivity as catalysts for the Suzuki-Miyaura cross-coupling or aryl halides and phenylboronic acid. The substitution of the chloride ligand by a much bulkier iodide would act against the rapid decomposition of the active species, which is observed for the *in situ* generated active catalyst of symmetric [Ni(Ar_2-NHC)ClCp†] species. We thus suppose that [Ni(Ar_2-NHC)ICp*] bearing a more labile Cp* ligand, might show even better activities in Suzuki-Miyaura cross-coupling.

The activation of C–H bonds α– to organic functional groups, as well as the recent disclosure of nickel(II) catalyzed C–H arylations of arenes and heteroarenes, in the presence of *t*-BuO^- as a base, hints at the growing potential of nickel complexes in the transition-metal catalyzed C–H bond functionalization, rather than those of more expensive palladium or ruthenium species. Furthermore, the synthesis scope of half-sandwich nickelacycles, bearing a [C,C']-chelating ligand could be investigated. These species bear a stereogenic centre, which is directly bound onto the nickel atom. Although many chiral systems containing NHCs have been described, examples of

NHC ligands presenting an atropostereogenic axis are still rare and are all limited to examples of phosphonium ylide ligands. Thus the synthesis of *N,N'*-asymmetrically substituted NHC ligands bearing a 1,1-binaphthyl backbone and a terminal nitrile function would lead to a methodology for the synthesis series of atropochiral complexes from the base-assisted α-C–H bond activation by CpNi-(NHC) centres. These complexes may give access to Ni-NHC asymmetric catalysis. Finally, the nickel-alkyl complexes could be the subject of Ni–C insertion reactions towards CO or alkenes.

Publications

C–H Activation of Acetonitrile at Nickel: Ligand Flip and Conversion of *N*-bound Acetonitrile into a *C*-bound Cyanomethyl Ligand.

Anna Magdalena Oertel, Vincent Ritleng, Michael J. Chetcuti

J. Am. Chem. Soc. **2010**, DOI:10.1021/ja105368p.

Half-sandwich NHC-nickel(II) complexes as pre-catalysts for the fast Suzuki coupling of aryl halides: a comparative study.

Vincent Ritleng*, Anna Magdalena Oertel, Michael J. Chetcuti*

Dalton Trans. **2010**, *39*, 8153.

***N'*-Activation of *N*-Arylimidazoles: Facile Syntheses of *N*-Alkyl-*N'*-aryl imidazolium Iodides from Less Expensive Chloro Substrates.**

Anna Magdalena Oertel, Vincent Ritleng, Michael J. Chetcuti*

Synthesis, **2008**, 1647

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C−H Activation of Acetonitrile at Nickel: Ligand Flip and Conversion of N-Bound Acetonitrile into a C-Bound Cyanomethyl Ligand

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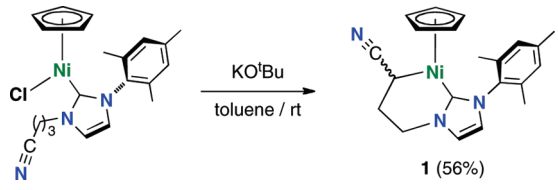
Abstract: Nickel joins the fairly exclusive list of metals that can activate nitrile C−H bonds. We report the first example of the C−H activation of an acetonitrile ligand on a nickel center. The acetonitrile ligand formally loses a proton and undergoes a sharp flip to give a cyanomethyl ligand that is coordinated to the nickel atom. Structures of an initial N-bound acetonitrile−nickel complex and of a final cyanomethyl−nickel complex are both presented.

The activation of C−H bonds has emerged as a potent tool for the functionalization of organic molecules.[1] As sp^3-hybridized C−H bonds are much less reactive than most other bonds, their activation when they are proximal to other functional groups is nontrivial. Herein, we describe the first example of the C−H activation of a labile acetonitrile ligand on a nickel center. The ligand formally loses a proton and does a sharp flip to give a cyanomethyl−nickel complex. Structural data for an initial CpNi N-bound acetonitrile species, a final CpNi−CH_2CN complex,[2] and some DFT calculations are presented.

Our recent research has focused on nickel Cp and Cp* complexes with N-heterocyclic carbene (NHC) ligands. We have described the chemistry and some aspects of the catalytic behavior of [Ni(NHC)XCp†] (X = Cl, I) complexes.[3] In this context, we now report a [Ni(NHC)ClCp] complex in which the NHC ligand bears a $-(CH_2)_3CN$ side-chain group on one nitrogen atom and a mesityl group on the other. Upon treatment with KO*t*Bu, a C−H bond α to the nitrile group underwent an intramolecular activation to give the nickelacyclic species **1** (Scheme 1; see the Supporting Information).

Scheme 1. Formation of Nickelacycle **1** by Activation of a C−H Bond α to a Nitrile Group in a Side Chain Linked to the NHC Ligand



1 (56%)

The extension of this reaction to CH_3CN was of interest, as acetonitrile metalation to M−CH_2CN complexes is not only rare in general (it is a challenge to selectively cleave C−H bonds in the presence of other functional groups) but also completely unknown for nickel species.[4] Such activation has been observed virtually exclusively for group 8 and group 9 metal complexes.[5] X-ray data are also very limited for cyanomethyl complexes, and to our knowledge, no structural data for a CH_3CN complex and its corresponding cyanomethyl derivative have been reported.

We have shown that when CH_3CN solutions of the neutral complexes [Ni{(Mes_2)NHC}ClCp†] are treated with KPF_6, chloride abstraction affords the cationic complexes [Ni{(Mes_2)NHC}-$(NCCH_3)$Cp†]$^+$[PF_6^-] [Cp† = Cp (**2**), Cp* (**2***)] in high yield. The CH_3CN ligands in complexes **2** and **2*** are labile.[3c] An X-ray diffraction study of the cation of **2**, which is presented here (Figure 1), shows that the CH_3CN ligand is essentially linear but that the Ni−N bond is not perfectly collinear with this axis.

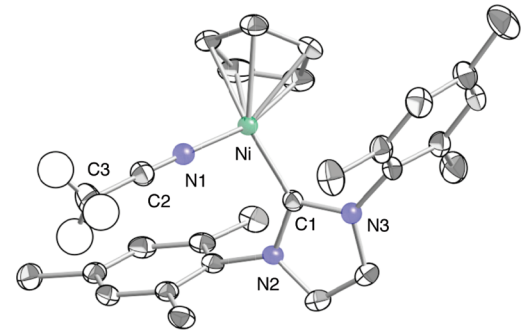
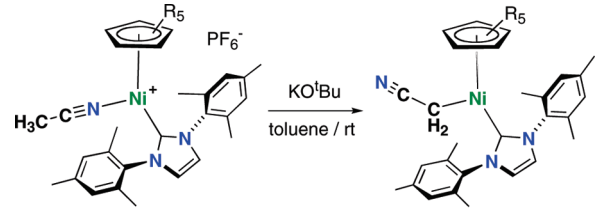


Figure 1. Molecular structure of the cation of **2**. Key atoms are labeled. Only H atoms of acetonitrile are shown (as isotropic spheres). Selected distances (Å) and angles (deg): Ni−C1, 1.902(2); Ni−N1, 1.8685(19); C2−N1, 1.138(3); Ni−N1−C2, 174.52(19); N1−C2−C3, 177.9(2); N1−Ni−C1, 96.93(8).

When **2** was reacted with KO*t*Bu, ^{1}H NMR data indicated the rapid, quantitative deprotonation of the CH_3CN ligand. The resulting cyanomethyl group coordinated to the nickel atom, leading to the isolation of the neutral species [Ni{$(Mes)_2$NHC}(CH_2CN)Cp] (**3**). The Cp* species **2*** similarly generated complex **3*** (Scheme 2).

Scheme 2. Base-Promoted C−H Activation of Coordinated CH_3CN



2, R = H
2*, R = Me

3, R = H (85%)
3*, R = Me (47%)

Spectroscopic data for **3** and **3*** (see the Supporting Information) are in accord with their proposed structures. The structure of **3** was confirmed by X-ray diffraction (Figure 2). The transformation of

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10.1021/ja105368p

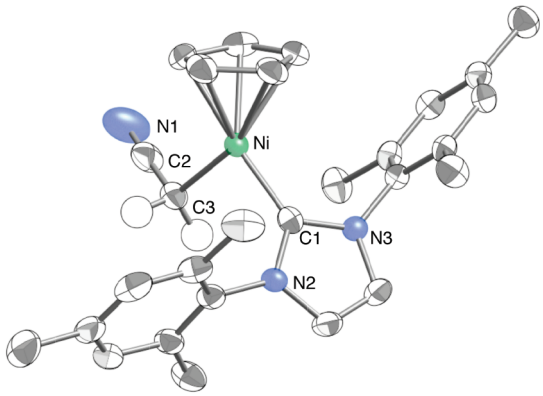


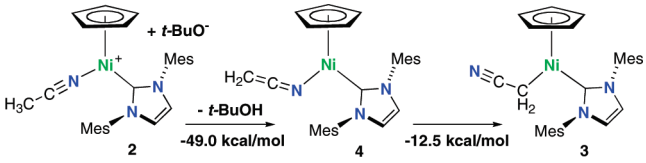
Figure 2. Molecular structure of **3**. Key atoms are labeled. Only H atoms of the cyanomethyl ligand are shown (as isotropic spheres). Selected distances (Å) and angles (deg): Ni−C1, 1.877(2); Ni−C3, 1.961(2); C2−C3, 1.429(3); C2−N1, 1.147(3); Ni−C3−C2, 112.5(2); C3−C2−N1, 178.5(6); C1−Ni−C3, 91.9(1).

the CH_3CN ligand into a CH_2CN group resulted in a nonlinear Ni−C3−C2 angle of 112.5(2)°.

Much effort has targeted the C−H functionalization of arenes and heteroarenes,[6] and this field is now recognized as an economically and environmentally attractive alternative to the traditional cross-coupling reactions with organometallic reagents. The activation of C(sp^3)−H bonds represents a significantly greater challenge because of the large HOMO−LUMO gap between the C−H σ and σ^* orbitals, and less success has been achieved here.[7] In particular, C(sp^3)−H bond functionalization in molecules with reactive functional groups is somewhat restricted, as these groups are often much more reactive toward the metal center.

The reaction mechanism has not yet been fully established. The N-coordination of CH_3CN seen in the solid state is probably strongly favored and retained in solution, but a weaker side-bound π-(κ^1-*C*, κ^1-*N*) coordination mode could a priori be envisaged as a minor, higher-energy state.[8] Nevertheless, preliminary density functional theory (DFT) calculations[9] to investigate mechanistic details of the reaction by screening possible intermediates indicated that a side-bound ligand was unlikely. Indeed, all attempts to optimize a side-bound π-coordinated CH_3CN species failed, resulting instead in the N-coordinated reagent **2**. The calculations instead suggested a two-step pathway: deprotonation of **2** to yield an intermediate with an N-coordinated $H_2C{=}C{=}N$ ligand (**4**, Scheme 3) followed by a

Scheme 3. DFT-Calculated Energy Balance for the Reaction



ligand flip from the N- to the final C-bound species. The calculated energies indicated that both steps are thermodynamically favorable.

The recent disclosure of Ni(II)-catalyzed C−H arylations of arenes and heteroarenes in the presence of tBuO$^-$ as a base[10] hints at the growing potential for use of nickel species (as opposed to more expensive palladium or ruthenium species) in transition-metal-catalyzed C−H bond functionalization.

C−H bonds α to other functional groups can also be activated at Cp†Ni(NHC) centers. Our recent results show that α-C−H bonds of ketones are activated to give [Ni(NHC){$CH_2C(O)R$}Cp] species.[11] We continue to investigate the scope and breadth of these activation reactions.

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Supporting Information Available: Full details of the synthesis and characterization of all new compounds; X-ray data (CIF) for **1**, **2**, and **3**; and full DFT computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(2) Abbreviations: Cp = η^5-C_5H_5; Cp* = η^5-C_5Me_5; Cp† = Cp or Cp*; Mes = 2,4,6-$C_6H_2Me_3$.

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Half-sandwich NHC-nickel(II) complexes as pre-catalysts for the fast Suzuki coupling of aryl halides: a comparative study† ‡

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Cationic half-sandwich nickel complexes of general formula [Ni(NHC)(NCMe)(η^5-C_5R_5)](PF_6) [NHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) **a**, 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene (IMes) **b**; R = H, Me] were prepared from the reaction of their neutral homologues [Ni(NHC)Cl(η^5-C_5R_5)] with 1 equiv. of KPF_6 in acetonitrile at room temperature. The new cationic complexes [Ni(IPr)(NCMe)(η^5-C_5Me_5)](PF_6) **3a**, [Ni(IMes)(NCMe)(η^5-C_5Me_5)](PF_6) **3b** and [Ni(IMes)(NCMe)(η^5-C_5H_5)](PF_6) **4b** were obtained in high yield and were fully characterized by ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy, elemental analyses, and in the case of **3a** by a single-crystal X-ray diffraction study. The neutral analogue of **3a**, [Ni(IPr)Cl(η^5-C_5Me_5)] **1a** was also structurally characterized. Their geometries were compared and no significant structural differences were observed. Nevertheless solution NMR spectroscopy established that the acetonitrile ligand of the cationic species is labile in solution. This results in the absence of any rotational significant barrier about the nickel–carbene carbon bond at ambient temperature in solution in the sterically congested cationic complexes **3a** and **3b**, in contrast to their neutral analogues **1a** and [Ni(IMes)Cl(η^5-C_5Me_5)] **1b**. The neutral and the cationic complexes catalyzed the cross-coupling of phenylboronic acid with aryl halides in the absence of co-catalysts or reductants. Surprisingly, the neutral or cationic nature of the complexes proved to have almost no influence on the reaction yields and rates. However, complexes bearing the bulky electron-rich pentamethylcyclopentadienyl ligand were much more active than those bearing the cyclopentadienyl ligand, and TOF of up to 190 h^{-1}, a high rate for nickel(II) complexes under similar conditions, were observed with these species.

Introduction

Since the first isolation of a stable imidazol-2-ylidene,[1] N-heterocyclic carbenes (NHCs) have become a very important class of ligands in organometallic chemistry.[2] NHCs behave like typical strong σ-donor[3] ligands with non-negligible π-acceptor abilities.[4] These electronic characteristics are similar to those of tertiary phosphines, and they show similar abilities to stabilize the various oxidation states and coordinatively unsaturated intermediates that appear in catalytic reactions.[2,5] However, NHCs show superior performances in many aspects over traditional trialkyl- and triarylphosphine ligands, including versatility, ready preparation, thermal-, air- and moisture-stability, as well as non-toxicity. In addition, NHCs exhibit superior qualities regarding ligand dissociation[6] and degradative cleavage,[7] both of which are less likely as compared to tertiary phosphines.[8] Both properties lead to a higher complex stability. Moreover, carbene complexes have shown unprecedented catalytic activity under homogeneous conditions in many important organic reactions.[2]

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‡ Throughout this manuscript, Cp = η^5-C_5H_5, Cp* = η^5-C_5Me_5, IPr = **a** = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, IMes = **b** = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene.

The chemistry of Ni-NHC complexes has been much less investigated than that of Pd-, Ru- or even Rh-NHC complexes.[2] However, the last decade has seen the emergence of a number of NHC-Ni(0) systems, generally generated *in situ* from a Ni(0) compound such as $Ni(COD)_2$ and a NHC ligand, or from a Ni(II) compound, a NHC ligand and an excess of reductant. These species were shown to be efficient catalysts in the amination of aryl chlorides,[9] C–S couplings,[10] cross-coupling reactions of fluorinated arenes,[11] three-component couplings of unsaturated hydrocarbons, aldehydes and silyl derivatives,[12] and [2+2+2] cycloadditions.[13,14,15] The major disadvantages of these systems are the air-sensitivity of the Ni(0) species and/or the necessity of an excess of reductant,[9b–d,12f,13d] which generates large amounts of waste. To overcome this inconvenience, much recent effort has been devoted to the development of well-defined air-stable Ni(II) complexes bearing electron-rich NHC ligands[3a,16] that are able to catalyze organic reactions without external reductants. Such species catalyze the amination of aryl halides,[17] the hydrothiolation of alkynes,[18] the base-free Michael addition[19] and the α-arylation of acyclic ketones[17a] (where no organometallic partner is involved), as well as Suzuki,[20] Kumada[20c,21] and Negishi[22] C–C cross-couplings reactions, in which the organometallic reagent ($ArB(OH)_2$, ArMgX, ArZnX) is known to help reduce Ni(II) to Ni(0).[23,24]

However, despite (i) the high importance of developing efficient syntheses of biaryl compounds that are found in natural products,[25] drugs[26] or materials,[27] (ii) the much lower cost and easier removal of nickel from the product[28] (with respect to its

Table 1 ^{1}H NMR data of the cationic complexes **3a**, **3b** and **4b** and of their neutral counterparts **1a**, **1b** and **2b**[a]

	Cp§	NC*H*=C*H*N	Ar	Ref.
1a[b]	1.12 (Cp*)	6.64	7.39 (d, 2H, *m*-H, ^3J = 7.6), 7.30 (t, 2H, *p*-H), 7.08 (d, 2H, *m*-H), 4.19 (m, 2H, C*H*Me$_2$), 2.29 (m, 2H, C*H*Me$_2$), 1.61 (d, 6H, CH*Me*$_2$, ^3J = 6.8), 1.23 (d, 6H, CH*Me*$_2$, ^3J = 6.8), 1.06 (d, 6H, CH*Me*$_2$, ^3J = 6.8), 0.88 (d, 6H, CH*Me*$_2$, ^3J = 6.8)	29
3a[c]	0.88 (Cp*)	7.51	7.62 (m, 2H, *p*-H), 7.50 (d, 4H, *m*-H, ^3J = 7.5), 2.60 (br, 4H, C*H*Me$_2$), 1.37 (d, 12H, CH*Me*$_2$, ^3J = 6.9), 1.13 (d, 12H, CH*Me*$_2$, ^3J = 6.9)[d]	This work
1b[e]	1.17 (Cp*)	6.22	6.92 (br, 2H, *m*-*H*), 6.80 (br, 2H, *m*-*H*), 2.69 (br s, 6H, *o*-*Me*), 2.21 (s, 6H, *p*-*Me*), 1.81 (br s, 6H, *o*-*Me*)	29
3b[c]	0.96 (Cp*)	7.30	7.17 (s, 4H, *m*-H), 2.40 (s, 6H, *p*-Me), 2.12 (br s, 12H, *o*-Me)[d]	This work
2b[f]	4.56 (Cp)	7.09	7.12 (s, 4H, *m*-H), 2.45 (s, 6H, *p*-Me), 2.18 (s, 12H, *o*-Me)	30
4b[f]	4.76 (Cp)	7.20	7.13 (s, 4H, *m*-H), 2.43 (s, 6H, *p*-Me), 2.12 (s, 3H, NC*Me*), 2.11 (s, 12H, *o*-Me)	This work

[a] δ in ppm and *J* in Hz. [b] In toluene-d_8 at 263 K. [c] In acetonitrile-d_3. [d] Free CH_3CN that results from exchange with CD_3CN is seen as a singlet (at 1.96 ppm) on the downfield side of the multiplet due to residual CHD_2CN observed at 1.94 ppm. [e] In toluene-d_8. [f] In chloroform-d_1.

more widely used d^{10} counterpart, palladium), and (iii) the unique properties of NHC ligands in comparison to phosphines,[2] examples of NHC-Ni(II)-based catalysts for C–C coupling reactions remain scarce.[20,21,22]

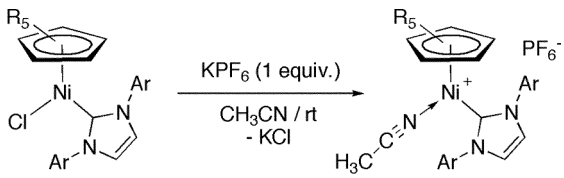
Following our ongoing interest in NHC-Ni(II) compounds,[6a] we have recently described the synthesis and dynamic behavior of air and moisture stable neutral complexes [Ni(NHC)ClCp§] (Cp§ = Cp, Cp*)‡ that bear aryl substituents on both NHC-nitrogen atoms.[29,30] Herein we report the high yield syntheses of some of their cationic derivatives, [Ni(NHC)(NCMe)Cp§](PF$_6$) by reaction of the corresponding neutral species with KPF_6 in acetonitrile. The structure of one of these cationic complex was established by a single-crystal X-ray diffraction study and was compared to that of its neutral counterpart. No remarkable structural differences were observed in the solid state but solution NMR spectroscopy did reveal that the acetonitrile ligand in the cations is labile; this might lead to differences in the catalytic behaviour. Having all these complexes in hand, we thus decided to check the respective influence of (i) their cationic or neutral nature and (ii) the presence of the bulky electron-rich pentamethylcyclopentadienyl ligand or of the less bulky and electron poorer cyclopentadienyl on their activity in Suzuki–Miyaura couplings.

All the complexes catalyzed the cross-coupling of aryl halides with phenyl boronic acid in the absence of co-catalysts or reductants. Surprisingly, the neutral or cationic nature of the complexes proved to have almost no influence on the reaction yields and rates. However, complexes bearing the bulky electron-rich pentamethylcyclopentadienyl ligand proved to be much more active than those bearing the cyclopentadienyl ligand, and among the best TOFs reported for Ni(II)-catalyzed Suzuki cross-coupling reactions under similar conditions were observed with these complexes.[20]

Results and discussion

Synthesis and characterization of the cationic complexes [Ni(NHC)(NCMe)Cp§]$^+$PF$_6^-$

When acetonitrile solutions of the neutral complexes, [Ni(NHC)ClCp§] (Cp§ = Cp*, NHC = IPr, **1a**; Cp§ = Cp*, NHC = IMes, **1b**; Cp§ = Cp, NHC = IMes, **2b**)‡ were treated with 1 equivalent of KPF_6, the chloride was abstracted and the cationic complexes, [Ni(NHC)(NCCH$_3$)Cp§]$^+$PF$_6^-$ (Cp§ = Cp*, NHC = IPr, **3a**; Cp§ = Cp*, NHC = IMes, **3b**; Cp§ = Cp, NHC = IMes, **4b**) were isolated as yellow to green air-stable solids in 71–84% yield (eqn (1)). All complexes were fully characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy (Tables 1 and 2), IR spectroscopy and elemental analyses.



(1)

1a: R = Me; Ar = 2,6-C$_6$H$_3$*i*-Pr$_2$ — **3a**: 71 %
1b: R = Me; Ar = 2,4,6-C$_6$H$_2$Me$_3$ — **3b**: 79 %
2b: R = H; Ar = 2,4,6-C$_6$H$_2$Me$_3$ — **4b**: 84%

The ^{1}H and ^{13}C{^{1}H} NMR spectra of the cationic complexes **3a**, **3b** and **4b** at ambient temperature are straightforward: all show the presence of one η^5-Cp* or -Cp group and of the IPr or IMes ligand. As for the neutral complexes **1a**,[29] **1b**[29] and **2b**,[16e,30] the spectra reveal that an effective plane of symmetry that bisects the molecule exists in solution on the NMR time scale. This effective mirror plane contains the acetonitrile ligand, the nickel and the NHC carbene carbon atom, as well as the Cp* or Cp ring centroid.

Nevertheless, in contrast to the sterically congested neutral Cp* species **1a** and **1b**, which possess a rotation barrier of 65–67 kJ mol^{-1} about the nickel–carbene carbon bond,[29] the corresponding cationic complexes **3a** and **3b** show a greatly reduced rotation barrier at room temperature. Thus, the ^{1}H NMR spectrum of **1b** at ambient temperature displays two singlets in a 1 : 1 integrated ratio for the four *meta*-hydrogen atoms of the two mesityl groups, as well as three singlets, in a 3 : 3 : 3 relative integrated ratio, for the four *ortho*- and the two *para*-methyl groups.[29] In contrast, its cationic analogue **3b** displays only one singlet for all the *meta*-hydrogen atoms and two singlets in a 3 : 6 relative integrated ratio for the *ortho*- and *para*-methyl groups (the bigger signal being slightly broadened, Table 1). Similarly, the ^{1}H NMR spectrum of **3a** displays only one doublet for the *meta* aromatic ring protons, one broad signal for the C*H* protons of the isopropyl groups and two doublets for the isopropyl methyls (the central carbon of each isopropyl group is diastereotopic). All these signals are doubled in the ^{1}H NMR spectrum of **1a** (Table 1). This doubling of the aryl substituent signals of **1a** and **1b** is also observed in their ^{13}C NMR spectra (Table 2). The ^{1}H and ^{13}C NMR spectra of the less bulky Cp species **2b** and **4b** are similar.

Table 2 $^{13}C\{^{1}H\}$ NMR data of the cationic complexes **3a**, **3b** and **4b** and of their neutral counterparts **1a**, **1b** and **2b**[a]

	Cp[δ]	NCN	NCH=CHN	Ar	Ref.
1a[b]	102.1 (C_5), 10.1 (Me_5)	180.0	123.1	149.6 and 145.8 (*o*-C_{Ar}), 138.0 (*ipso*-C_{Ar}), 130.1 and 125.9 (*m*-C_{Ar}), 125.7 (*p*-C_{Ar}), 28.7 ($CHMe_2$), 27.2 and 26.9 ($CHMe_2$), 23.9 and 22.7 ($CHMe_2$)	29
3a[c]	105.6 (C_5), 9.8 (Me_5)	172.3	128.6	147.6 (*o*-C_{Ar}), 137.0 (*ipso*-C_{Ar}), 131.6 (*p*-C_{Ar}), 125.4 (*m*-C_{Ar}), 29.5 ($CHMe_2$), 27.1 and 22.9 ($CHMe_2$)[d]	This work
1b[b]	102.2 (C_5), 9.9 (Me_5)	177.2	124.1	138.6 and 134.8 (*o*-C_{Ar}), 138.4 (*p*-C_{Ar}), 137.8 (*ipso*-C_{Ar}), 130.5 and 129.3 (*m*-C_{Ar}), 21.4 (*o*-*Me*), 20.6 (*p*-*Me*), 18.6 (*o*-*Me*)	29
3b[c]	105.6 (C_5), 9.5 (Me_5)	170.2	126.8	140.4 (*ipso*-C_{Ar} or *p*-C_{Ar}), 137.0 (*p*-C_{Ar} or *ipso*-C_{Ar}), 136.4 (*o*-C_{Ar}), 130.3 (*m*-C_{Ar}), 21.1 (*p*-Me), 18.9 (*o*-Me)[d]	This work
2b[e]	92.3 (C_5H_5)	167.2	124.6	139.3 (*p*-C_{Ar} or *ipso*-C_{Ar}), 136.8 (*ipso*-C_{Ar} or *p*-C_{Ar}), 136.1 (*o*-C_{Ar}), 129.4 (*m*-C_{Ar}), 21.4 (*p*-Me), 18.6 (*o*-Me)	This work
4b[c]	94.3 (C_5H_5)	160.2	127.1	140.9 (*p*-C_{Ar} or *ipso*-C_{Ar}), 136.9 (*ipso*-C_{Ar} or *p*-C_{Ar}), 136.4 (*o*-C_{Ar}), 130.3 (*m*-C_{Ar}), 21.3 (*p*-Me), 18.4 (*o*-Me)[d]	This work

[a] δ in ppm. [b] In benzene-d_6. [c] In acetonitrile-d_3. [d] Free CH_3CN that results from exchange with CD_3CN is seen as two singlets (at 1.77 and 118.3 ppm) overlapping with the multiplet due to residual CHD_2CN at 1.32 ppm and with the singlet due to CD_3CN at 118.3 ppm. [e] In chloroform-d_1.

Neither of them shows an observable rotational barrier at ambient temperature.

These results suggest that substitution of a bulky chloride by a smaller acetonitrile molecule would reduce the steric congestion in the cationic complexes bearing the bulky Cp* and allow free rotation about the nickel–carbene carbon bond at ambient temperature. However a comparison of the molecular structures of **1a** and **3a** shows that they are very similar (*vide infra*). We thus tend to believe that this observed free rotation at room temperature in the cationic species is the direct result of ligand exchange and a dynamic process rather than of a purely dynamic process. Indeed, free CH_3CN that results from exchange with CD_3CN is seen in the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of **3a**, **3b**, and **4b**, indicating that the acetonitrile ligand of the cationic species is labile in solution. A dynamic rotational process would be much more facile for the two coordinate intermediate presumably present during the acetonitrile ligand exchange.

It is noteworthy that the carbene carbon atoms in complexes **3a**, **3b** and **4b** appear at 172.3, 170.2 and 160.2 ppm (in CD_3CN), respectively, in the ^{13}C NMR spectrum of these complexes. These signals are slightly upfield of the signals seen at 180.0, 177.2 (both in C_6D_6) and 167.2 ppm (in $CDCl_3$), respectively, for their neutral derivatives (Table 2). The apparent absence of a significant rotational barrier about the nickel–carbene carbon bond in the cationic Cp* species **3a** and **3b** at ambient temperature is thus probably mainly due to the lability of acetonitrile in solution, but there may also be a minor electronic component.[29]

The IR spectra of the cationic complexes are rather surprising as weak ν(CN) stretches are observed for solid samples of all three complexes at 2281 (**3a**), 2294 (**3b**) and 2299 cm^{-1} (**4b**). These values are consistent with those reported for other Ni(II)–*N*-bound acetonitrile complexes.[31]

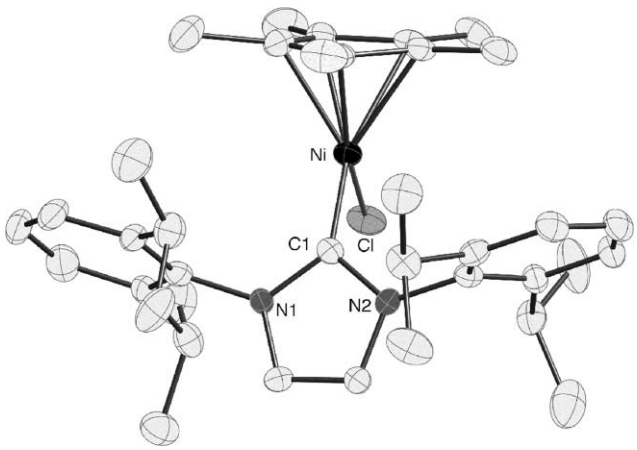


Fig. 1 Molecular structure of **1a** showing all non-H atoms. Ellipsoids are shown at the 50% probability level and key atoms are labelled.

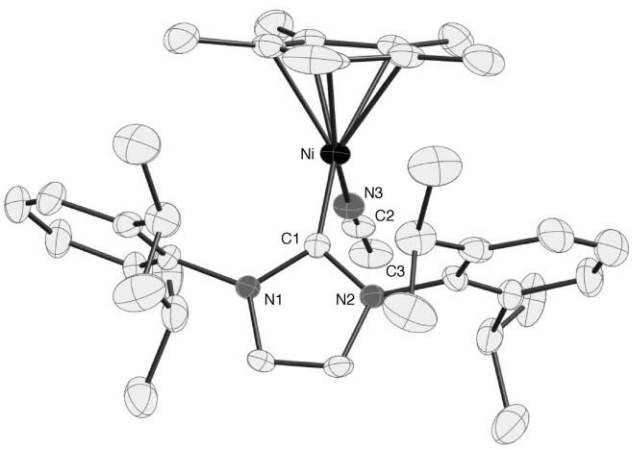


Fig. 2 Molecular structure of the cationic part of **3a** showing all non-H atoms. Ellipsoids are shown at the 50% probability level and key atoms are labelled.

Structural studies of complexes 1a and 3a

Crystals of the cationic complex **3a** and of its neutral precursor **1a** suitable for X-ray structure determination were grown from cold acetonitrile–toluene (**3a**) and toluene (**1a**) solutions. The molecular structures of **1a** and of the cationic part of **3a** are shown in similar orientations in Fig. 1 and 2, respectively. Crystallographic data and data collection parameters are listed in Table 3, and a list of selected bond lengths and angles for both complexes appear in Table 4.

The molecular structure of these complexes are strikingly similar. Both feature a nickel atom bonded to a η^5-Cp* group, a IPr moiety, and a chloride (**1a**) or an acetonitrile (**3a**) ligand

Table 3 X-Ray crystallographic data and data collection parameters for complexes **1a** and **3a**

Compound	**1a**	**3a**
Empirical formula	$C_{37}H_{51}ClN_2Ni$	$C_{39}H_{54}N_3Ni{\cdot}F_6P$
M_r	617.96	768.53
Crystal system	Monoclinic	Orthorhombic
Space group	*Cc*	*Pnma*
a/Å	11.9474(8)	13.7019(5)
b/Å	31.263(3)	18.0171(7)
c/Å	10.6055(5)	16.5430(7)
β/°	93.510(4)	90
V/Å^3	3953.8(5)	4083.9(3)
Z	4	4
D_c/Mg m^{-3}	1.038	1.250
μ/mm^{-1}	0.581	0.571
T/K	173(2)	173(2)
Crystal form, colour	Prism, red	Block, dark yellow
Crystal size/mm	0.30 × 0.10 × 0. 05	0.20 × 0.18 × 0.15
h, k, l_{max}	11, 37, 13	17, 23, 21
T_{min}, T_{max}	—	0.568, 0.784
Reflns collected	14280	26294
R (reflections)	0.0597 (5068)	0.0698 (3025)
w$R2$ (reflections)	0.1499 (7141)	0.1316 (4829)
GOF on F^2	0.965	1.090

Table 4 Selected bond lengths (Å) and angles (°) for **1a** and **3a**

	1a	**3a**
Ni–C(1)	1.900(4)	1.911(4)
Ni–L[a]	2.2094(13)	1.881(4)
Ni–C(Cp*) (av)	2.155	2.143
Ni–C(Cp*) (min)	2.061(5)	2.063(5)
Ni–C(Cp*) (max)	2.202(5)	2.166(3)
C(Cp*)–C(Cp*) (av)	1.430	1.429
C(Cp*)–C(Cp*) (min)	1.399(7)	1.392(5)
C(Cp*)–C(Cp*) (max)	1.471(8)	1.466(7)
Ni–N(3)–C(2)	—	170.1(4)
N(3)–C(2)–C(3)	—	179.4(5)
C(1)–Ni–L	93.85(13)	97.54(17)
C(1)–Ni–Cp*$_{cent}$	143.0	140.0
L–Ni–Cp*$_{cent}$	123.1	122.5

[a] L = Cl for **1a** and N(3) for **3a**.

in a two-legged piano stool geometry. If one considers the Cp* group as a single ligand, the nickel atom lies at the centre of a trigonal plane formed by the ring centroid, the carbenoid carbon atom C(1) of the NHC ligand, and the chloride Cl or the nitrogen N(3) of the acetonitrile ligand; the sum of all angles subtended by these atoms is equal to 360° in both structures. However there are significant departures from the idealized 120° angles of a trigonal structure. The carbenoid carbon C(1) and the chloride atom Cl of **1a** subtend an angle of 93.8(1)° at the nickel atom, and similarly the carbenoid carbon C(1) and the nitrogen atom N(3) of **3a** subtend a slightly larger angle of 97.5(2)°. These angles are in the range of those observed for the closely related neutral mesityl analogue **1b**,[29] for its Cp derivative **2b**[16e] and for the Cp derivative of **1a**, [Ni(IPr)ClCp] **2a**,[17b] for which values of 95.3(1), 98.4(2) and 93.86(3)° have been registered, respectively. The Cp complexes **2a** and **2b**, which show the biggest difference for this angle (4.5°), both do not show an observable rotation barrier about the nickel–carbene carbon bond in solution at ambient temperature. Hence, the difference of 3.6° between the C(1)–Ni–L angle in **1a** (L = Cl) and in **3a** [L = N(3)] does not appear to be correlated to the rotation barrier variation.

The C(1)–Ni–Cp$^{\S}_{cent}$ angle spans the range of 142 ± 0.5° for the Cp* species **1a** and **1b**,[29] which show a rotation barrier about the nickel–carbene carbon bond. In contrast, the Cp species **2a**,[17b] **2b**[16e] and [Ni(1,3-dimethylimidazol-2-ylidene)ICp],[29] as well as the Cp* complex, [Ni(1,3-dimethylimidazol-2-ylidene)ICp*], exhibit a smaller angle of 134.2 ± 1.8° and do not show an observable rotation barrier.[29] This angle seems thus to be correlated to the presence or absence of a rotation barrier about the nickel–carbene carbon bond. However, despite the C(1)–Ni–Cp*$_{cent}$ angle of 140.0° (Table 4) measured in the cationic derivative **3a**, a greatly reduced rotational barrier is observed in this complex, but as discussed earlier, this behaviour is probably due to acetonitrile ligand dissociation.

The nickel–carbene carbon bond lengths are not significantly different from each other [Ni–C(1) = 1.900(4) Å (**1a**); 1.911(4) (**3a**)]. These value are comparable to those reported for the closely related neutral mesityl analogue **1b** [1.906(3) Å][29] and for its Cp derivative **2b** [1.917(9) Å],[16e] but are somewhat longer than that reported for **2a** [1.8748(11) Å].[17b] The Ni–Cl distance of 2.2094(13) Å in **1a** is close to the Ni–Cl distance observed in **1b**, where a value of 2.1962(9) has been registered,[29] but is slightly longer than those reported for the neutral Cp derivatives **2a** and **2b**, where values of 2.1876(3)[17b] and 2.185(2) Å[16e] have been observed, respectively. The acetonitrile ligand of **3a** is linear [N(3)–C(2)–C(3) = 179.4(5)°] but the Ni–N(3) bond is nevertheless not perfectly co-linear with this axis [Ni–N(3)–C(2) = 170.1(4)°].

The plane that contains the imidazol-2-ylidene ring is almost orthogonal to the Cl–Ni–Cp*$_{cent}$ plane and makes an angle of 86.3° with it in the neutral complex **1a**. The two halves of the molecule are thus not related by a mirror plane, bur are not too far off from mirror symmetry, and the two aryl groups approximately eclipse each other. In contrast a crystallographically imposed mirror plane bisects the cation of **3a** and the PF_6^- anion, so this angle is precisely 90° in **3a**.

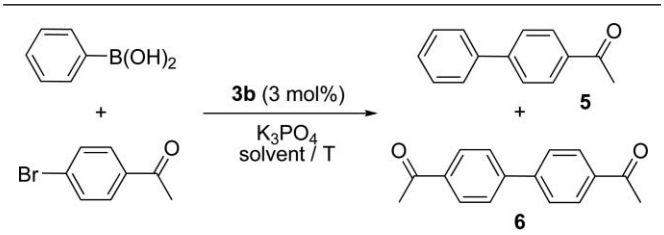
Both aryl rings in **1a** are close to perpendicular to the imidazolylidene ring (the plane of all aromatic carbon atoms in each aryl ring makes angles of 83.1 and 86.3° with the carbene plane). The corresponding angle in **3a** is 85.7°.

In both complexes, the Cp* ring exhibits structural distortions, as there are significant variations in the Ni–Cp* carbon distances, which range from 2.061(5) to 2.202(5) Å in **1a** and from 2.063(5) to 2.166(3) Å in **3a**, as well as fluctuations in the aromatic C–C distances, which extend from 1.3991(7) to 1.471(8) Å in **1a** and from 1.392(5) to 1.466(7) Å in **3a**. Such variations arise from "allyl–ene" distortions in the Cp* ligand and have been previously observed in other Cp*Ni systems.[32]

There are no abnormally short non-bonded contacts or unusual packing features in molecule **1a**. However, all the acetonitrile methyl protons in **3a** interact with fluorine atoms of the PF_6^- anion: the hydrogen atom on the mirror plane undergoes two C–H···F interactions of 2.441 Å, while the two other protons each interact with one fluorine atom of another PF_6^- group (each C–H···F = 2.571 Å).

In conclusion, there appear to be no significant structural differences between **1a** and **3a** that might explain the low rotation barrier in **3a**. This behaviour is thus more likely due to the labile nature of the acetonitrile ligand in solution (*vide supra*).

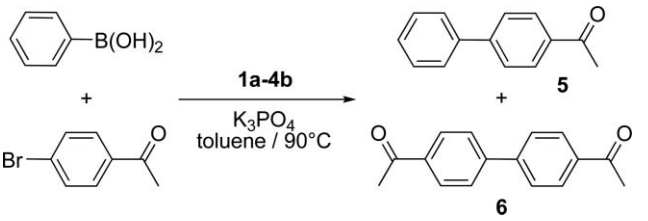
Table 5 Optimization of reaction conditions for the Suzuki–Miyaura cross-coupling of 4′-bromoacetophenone with phenylboronic acid catalyzed by **3b** [a]



Entry	Solvent	$PhB(OH)_2$ (equiv.)	K_3PO_4 (equiv.)	T/°C	t/min	Conv.[b] (%)	Select.[b] (**5**/**6**)
1	DME	1.1	2.2	25	60	22	100/0
2	DME	1.1	2.2	82	120	82	100/0
3	DME	1.3	2.6	82	120	90	100/0
4	CH_3CN	1.3	2.6	85	120	32	100/0
5	Toluene	1.3	2.6	90	120	100	96/4
6	Toluene	1.3	2.6	90	40	100	96/4

[a] *Reaction conditions*: 4′-bromoacetophenone (1 mmol), phenylboronic acid (1.1–1.3 mmol), K_3PO_4 (2.2–2.6 mmol) as base, **3b** (3 mol%), solvent (3 mL). [b] According to NMR.

Table 6 Suzuki–Miyaura cross-coupling of 4′-bromoacetophenone with phenylboronic acid catalyzed by **1a–4b** [a]



Entry	Cat. (mol%)	t/min	Conv.[b] (%)	Select.[b] (**5**/**6**)
1	**1a** (3)	15	92	93/7
2	**3a** (3)	10	95	94/6
3	**3a** (3)	15	98	92/8
4	**1b** (3)	15	92	95/5
5	**3b** (3)	15	89	94/6
6	**2a** (3)	15	79	100/0
7	**2a** (3)	30	87	100/0
8	**2b** (3)	15	54	100/0
9	**2b** (3)	30	68	100/0
10	**4b** (3)	15	55	100/0
11	**4b** (3)	30	68	100/0
12	**1b** (1)	60[c]	63	99/1
13	**3a** (1)	60[c]	61	98/2

[a] *Reaction conditions*: 4′-bromoacetophenone (1 mmol), phenylboronic acid (1.3 mmol), K_3PO_4 (2.6 mmol) as base, **1a–4b** (1–3 mol%), toluene (3 mL), 90 °C. [b] According to NMR. [c] Run at 110 °C.

Catalytic Suzuki–Miyaura coupling reactions

Initial studies focussed on the reaction of 4′-bromoacetophenone with various amounts of phenylboronic acid and K_3PO_4 in the presence of the cationic Cp* complex **3b** (3 mol%) under various solvent and temperature conditions to optimize the reaction conditions (Table 5). All reactions were run *without* any additive such as PPh_3 as is often the case.[20c–f,i,23a,c]

The first runs were conducted in DME. Low conversion to the coupling product **5** was observed with 1.1 equiv. of $PhB(OH)_2$ and 2.2 equiv. of K_3PO_4 at room temperature (Table 5, entry 1). Increasing the temperature to 82 °C greatly improved the yield (entry 2), and increasing the $PhB(OH)_2$ and K_3PO_4 loadings to 1.3 and 2.6 equiv., respectively, led to an even better conversion of 90% after 2 h (entry 3). Under these conditions, acetonitrile was not effective (entry 4), whereas toluene proved to be the best solvent. Full conversion was indeed observed in this solvent, though with a slightly decreased selectivity, as small amounts of the homocoupling product 4,4′-acetylbiphenyl **6** were detected (entry 5). In the latter solvent, it even proved to be possible to decrease the reaction time to only 40 min to reach full conversion (entry 6).

The catalytic activities of the various half-sandwich NHC-nickel(II) complexes **1–4** were next examined under the standard conditions established with complex **3b**, *i.e.*: with 1.3 equiv. of $PhB(OH)_2$ and 2.6 equiv. of K_3PO_4 in toluene at 90 °C (Table 6). All complexes are catalytically active and give the desired product **5** in moderate to excellent yield in *15 min*, which is a very fast reaction time for nickel-catalyzed Suzuki couplings. Typical reactions times, indeed, usually range under similar conditions from 1–2 h at best to 12–24 h at worst.[20,23]

Surprisingly, the neutral or cationic nature of the complexes had almost no influence on the reaction yields and rates (Table 6, entries 1, 4, 8 and 9 *vs.* 3, 5, 10 and 11, respectively). A marked difference is observed between the Cp-complexes **2a** and **2b** (entries 6–9), which may be explained by the better steric protection of the active site by the more bulky IPr ligand. Although still present, this influence is less prominent with the more bulky, electron-rich Cp* complexes **1** and **3**. These latter species gave much better results overall in terms of rates and conversions, but with a slightly decreased selectivity, as the Cp species did not produce the homocoupling product **6** (entries 1–5 *vs.* 6–11). Conversions up to 95% were obtained in the case of **2a** after only 10 min, and 98% after 15 min, leading to turnover frequencies (TOF) of 190 and 131 h^{-1} (entries 2 and 3). These are among the best TOFs observed so far in Suzuki–Miyaura cross-coupling catalyzed by a Ni(II) complex in the *absence* of reductant and co-catalyst.[20,23] We are indeed aware of only one example where a higher TOF of 261 h^{-1} has been observed (with a pincer-type bis-NHC-nickel(II) catalyst), for the coupling of 4-bromobenzonitrile with phenylboronic acid.[20a,33]

Longer reaction times with the Cp species **2** and **4** afforded only slightly improved conversions (entries 7, 9 and 11). Attempts to decrease the catalyst loadings of the Cp* species **1b** and **3a** to 1 mol% led to only 63 and 61% conversion, respectively, after 1 h at 110 °C (entries 12 and 13). These results indicate fast catalyst deactivation.

The precise reaction mechanism remains to be elucidated. Nevertheless, a few comments can be made. The absence of significant reactivity difference between the cationic and the neutral complexes suggest that the necessary creation of a vacant site might arise through Cp or Cp* ring slippage rather than acetonitrile or chloride dissociation. We have indeed observed many cases of Cp* ring slippage in NiCp* complexes,[34] and our recent work with CpNi–NHC complexes has also shown that Cp ligands are much more labile than expected in such systems.[6a] In addition, it is noteworthy that traces of biphenyl were observed in all cases. This suggests initial reduction of the Ni(II) precursor to a Ni(0) active species by the homocoupling of phenylboronic acid *via* a mechanism previously postulated for related Pd(II) species[24] and

for other nickel based systems.[23] Initial reduction to an unstable Ni(0) species is further corroborated by the very high air sensitivity of the active species, and the fast colour change of the reaction medium (after only 1–2 min at 90 °C).

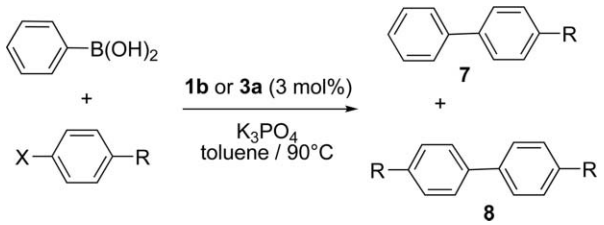
To get some further insight into the roles played by the different reactive species present in the medium and in particular by the phenylboronic acid, we conducted a series of control experiments. The first one was carried out in the absence of the phenylboronic acid but in otherwise unchanged conditions. No reaction was observed, nor was there any colour change of the reaction medium. The 4′-bromoacetophenone and the catalyst precursor were found to be unchanged by ^{1}H NMR analysis of the crude mixture. A second control experiment was run in the absence of 4′-bromoacetophenone. In this case, the colour of the reaction medium changed in a couple of minutes as observed during the typical catalytic runs. Unfortunately ^{1}H NMR analysis of the medium gave a complicated spectrum that could not be interpreted. Finally a last control experiment was run in the absence of base. A rapid colour change was observed, and signals of the catalyst precursor were not observable any more by ^{1}H NMR; nevertheless no coupling had occurred. These control experiments demonstrate the crucial role played by phenylboronic acid in the generation of the catalytically active species (presumably a Ni(0) species as discussed above), as well as the necessary presence of K_3PO_4 for this nickel complex to achieve the cross-coupling reaction.

The better results observed with complexes **1** and **3** bearing the bulky Cp* ligand, as compared to the Cp species **2** and **4**, may be explained by a better stabilization of the coordinatively unsaturated sites through steric protection and electronic donation and/or by a faster or more efficient reduction of the initial Ni(II) species by the electron-rich ligand.

As the cationic Cp* species **3a** presents the best results in terms of rate (Table 6, entries 2 and 3) and the neutral Cp* species **1b**, the best results in terms of rate *vs.* selectivity (entry 4), the reaction scopes of these two complexes have been examined with a short series of aryl bromides and chlorides bearing electron-withdrawing and electron-donating substituents. Results are presented in Table 7.

Excellent yields of 4-acetylbiphenyl were obtained from 4′-chloroacetophenone with both catalysts (Table 7, entries 1 and 2). In addition, a remarkable increase of selectivity was observed with **1b** compared to the result obtained with 4′-bromoacetophenone (Table 6, entry 4 *vs.* Table 7, entry 2). It is noteworthy that excellent selectivity was also observed with 4-bromotoluene (entries 7 and 8). Electron-donating substrates were however converted to the desired coupling products in lower yields (entries 3–8) and, excepting 4-bromoanisole, which was converted to 4-methoxybiphenyl in 70% by **3a** and only 21% by **1b**, the neutral catalyst precursor was slightly more active with these substrates.

Table 7 Suzuki–Miyaura cross-coupling of aryl bromides and chlorides with phenylboronic acid catalyzed by **1b** and **3a** [a]



Entry	Cat.	R	X	Conv.[b] (%)	Select.[b] (**7**/**8**)
1	**3a**	COMe	Cl	92	93/7
2	**1b**	COMe	Cl	91	100/0
3	**3a**	OMe	Br	70	90/10
4	**1b**	OMe	Br	21	88/12
5	**3a**	OMe	Cl	0	—
6	**1b**	OMe	Cl	12[c]	92/8
7	**3a**	Me	Br	31[d,e]	100/0
8	**1b**	Me	Br	49[d,e]	100/0

[a] *Reaction conditions*: aryl halide (1 mmol), phenylboronic acid (1.3 mmol), K_3PO_4 (2.6 mmol) as base, **1b** or **3a** (3 mol%), toluene (3 mL), 90 °C, 1 h. [b] According to NMR. [c] Isolated yield. [d] Run at 110 °C. [e] GC yield.

Conclusions

In summary, cationic Ni(II)-NHC complexes of formula [Ni(NHC)(NCCH$_3$)Cp§](PF$_6$) (Cp§ = Cp*, NHC = IPr **3a**; Cp§ = Cp*, NHC = IMes **3b**; Cp§ = Cp, NHC = IMes **4b**) were isolated in high yields from the reaction of their neutral counterparts [Ni(NHC)ClCp§] **1a**, **1b** and **2b** with KPF$_6$ in acetonitrile. Single-crystal X-ray diffraction studies established the molecular geometries of the neutral and cationic analogues **1a** and **3a**. No remarkable structural differences were observed. Nevertheless, solution NMR spectroscopy established that in contrast to the sterically congested neutral Cp* species **1a** and **1b**, the corresponding cationic complexes **3a** and **3b** show a greatly reduced barrier to the nickel–carbene bond rotation at ambient temperature. In addition, NMR spectroscopy also established that the acetonitrile ligand of the cationic species is labile in solution. Hence, the absence of a rotation barrier in **3a** and **3b** is most probably due to the labile nature of the acetonitrile ligand in solution rather than to the smaller size of acetonitrile as compared to the chloride.

The neutral and the cationic complexes [Ni^{II}(NHC)LCp§] (L = Cl$^-$ or NCMe, PF$_6^-$) **1–4** catalyse the Suzuki–Miyaura cross-couplings of aryl halides and phenylboronic acid in the presence of K_3PO_4 as the sole additive. The bulky electron-rich Cp* species are much more efficient than the Cp complexes, and one of the highest rates for nickel(II)-based catalysts in the absence of a co-catalyst or reductant was observed for the coupling of phenylboronic acid and 4′-bromoacetophenone with **3a**. Although the novel cationic species possess a labile acetonitrile ligand, no substantial benefit was observed during the catalytic reactions. The necessary creation of a vacant site might arise through Cp or Cp* ring slippage rather than acetonitrile or chloride dissociation. The high rates observed with the Cp* complexes is believed to be derived at least partially from the presence of the bulky electron-rich Cp* ligand, which may both facilitate the probable initial reduction to Ni(0) by phenylboronic acid and stabilize the coordinatively unsaturated sites through steric protection and electronic donation. Mechanistic studies are currently under way to try to confirm these hypotheses. Catalytic studies with other half-sandwich Ni-NHC complexes that bear a weakly coordinating dangling arm that may stabilize the coordinatively unsaturated active site (and hence allow for a better catalyst stability) are also underway.

Experimental

General

All reactions were carried out using standard Schlenk techniques under an atmosphere of dry argon. Solvents were distilled from appropriate drying agents under argon prior to use. Solution NMR spectra were recorded at 298 K on a FT-Bruker Ultra Shield 300 spectrometer operating at 300.13 MHz for ^{1}H, and at 75.47 MHz for ^{13}C $\{^{1}H\}$. DEPT ^{13}C spectra were recorded for all complexes to help in the ^{13}C signal assignments. The chemical shifts are referenced to the residual deuterated solvent peaks. Chemical shifts (δ) and coupling constants (J) are expressed in ppm and Hz respectively. IR spectra of complexes **3a**, **3b** and **4b** were recorded on a FT-IR Nicolet 380 spectrometer with KBr pellets. Vibrational frequencies are expressed in cm^{-1}. Elemental analyses were performed by the Service d'Analyses, de Mesures Physiques et de Spectroscopie Optique, UMR CNRS 7177, Institut de Chimie, Université de Strasbourg. Commercial compounds were used as received. Complexes [Ni(IPr)ClCp*] **1a**,[29] [Ni(IMes)ClCp*] **1b**,[29] [Ni(IPr)ClCp] **2a**[17b] and [Ni(IMes)ClCp] **2b**[16e,30] were prepared according to published methods.

Synthesis of [Ni(IPr)(NCMe)Cp*](PF$_6$) (3a)

KPF_6 (94 mg, 0.511 mmol) was added to a suspension of **1a** (316 mg, 0.511 mmol) in acetonitrile (5 mL). The mixture was stirred for 1 h at room temperature. During the first 15 min, the colour changed from violet to dark yellow. The reaction medium was filtered through Celite, concentrated to *ca.* 1 mL, and treated with diethyl ether (3 mL) to yield an orange–brown solid after standing at −28 °C for 1 h. The mother-liquor was removed by syringe, and the solid washed with diethyl ether (3 × 1 mL), and dried under vacuum to give **3a** (280 mg, 0.364 mmol, 71%). Anal. Calc. for $C_{39}H_{54}F_6N_3NiP$: C, 60.95; H, 7.08; N, 5.47. Found: C, 61.37; H, 7.22; N, 5.41%. ^{1}H NMR (CD_3CN, 300.13 MHz): see Table 1. $^{13}C\{^{1}H\}$ NMR (CD_3CN, 75.47 MHz): see Table 2. FT-IR: ν(CN) 2281 (w), ν(P–F) 838 (s).

Synthesis of [Ni(IMes)(NCMe)Cp*](PF$_6$) (3b)

Complex **3b** was prepared from [Ni(IMes)ClCp*] **1b** by a procedure similar to that used for **3a**, and was isolated as an analytically pure yellow–brown solid in 79% yield. Anal. Calc. for $C_{33}H_{42}F_6N_3NiP$: C, 57.92; H, 6.19; N, 6.14. Found: C, 57.80; H, 6.19; N, 6.02%. ^{1}H NMR (CD_3CN, 300.13 MHz): see Table 1. $^{13}C\{^{1}H\}$ NMR (CD_3CN, 75.47 MHz): see Table 2. FT-IR: ν(CN) 2294 (w); ν(P–F) 839 (s).

Synthesis of [Ni(IMes)(NCMe)Cp](PF$_6$) (4b)

Complex **4b** was prepared from [Ni(IMes)ClCp] **2b** by a procedure similar to that used for **3a**, and was isolated as an analytically pure green solid in 84% yield. Anal. Calc. for $C_{28}H_{32}F_6N_3NiP$: C, 54.75; H, 5.25; N, 6.84. Found: C, 54.67; H, 5.03; N, 6.70%. ^{1}H NMR ($CDCl_3$, 300.13 MHz): see Table 1. $^{13}C\{^{1}H\}$ NMR (CD_3CN, 75.47 MHz): see Table 2. FT-IR: ν(CN) 2299 (w); ν(P–F) 842 (s).

General procedure for the Suzuki coupling reactions

A Schlenk tube equipped with a septum was charged with aryl halide (1.0 mmol), phenylboronic acid (1.3 mmol), K_3PO_4 (2.6 mmol) and catalyst (1.0–3.0 mol%) before being put under an atmosphere of argon. Toluene (3 mL) was injected and the mixture immediately heated with vigorous stirring by putting the Schlenk tube in an oil-bath at 90 °C. After 10–60 min, the reaction was stopped by cooling the reaction to room temperature and allowing air to enter in the Schlenk tube. GC yields were calculated by using tetradecane as internal standard. NMR yields were determined by removing a sample with a syringe, drying it under high vacuum, extracting the residue with $CDCl_3$ and filtering the solution in the NMR tube. In a standard work up, the solvent was removed completely under vacuum. The residue was extracted with a 1 : 1 mixture of diethyl ether–water (20 mL). The organic layer was separated and the aqueous layer extracted with another 10 mL portion of diethyl ether. The combined extracts were washed with water (2 × 10 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the crude material was purified by column chromatography over SiO_2 with pentane–ethyl acetate as eluent to give the desired product. All yields are the average value of at least two runs.

X-Ray diffraction studies. Structure determination and refinement

Single crystals of **1a** and **3a** suitable for X-ray diffractions studies were selected from batches of crystals obtained at –28 °C from toluene (**1a**) and acetonitrile–toluene (**3a**) solutions. Diffraction data for all crystals were collected at 173(2) K on a Nonius Kappa-CCD area detector diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). A summary of crystal data, data collection parameters, and structure refinements is given in Table 1. Cell parameters were determined from reflections taken from one set of ten frames (1.0° steps in phi angle), each at 20 s exposure. All structures were solved using direct methods with SHELXS-97 and refined against F^2 for all reflections using the SHELXL-97 software.[35] Multiscan absorption corrections (MULscanABS in PLATON) were applied.[36] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were generated according to stereochemistry and refined as fixed contributors using a riding model in SHELXL-97.

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N′-Activation of *N*-Arylimidazoles: Facile Syntheses of *N*-Alkyl-*N*′-aryl-imidazolium Iodides from Less Expensive Chloro Substrates

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Abstract: A series of N,N′-asymmetrically substituted imidazolium iodide salts have been synthesized, starting from *N*-arylimidazoles and the less expensive, but less reactive, 1-chlorobutane or (3-chloropropyl)trimethoxysilane. The addition of potassium iodide and the use of 1,2-dimethoxyethane as a solvent lead to multigram quantities of these salts becoming readily available, in yields ranging from 50% to 94%. Direct combination of (3-chloropropyl)trimethoxysilane with 1-mesityl-1*H*-imidazole was also effected, in good yield, by using a microwave oven at 180 °C. The synthesis of two 1-alkyl-3-isopropylimidazolium chlorides is also presented herein.

Key words: arylimidazoles, imidazolium salts, trimethoxysilyl, chloroalkyls, N-heterocyclic carbenes

N,N′-Disubstituted imidazolium salts are important intermediates in the synthesis of transition metal complexes that contain N-heterocyclic carbene (NHC) ligands.[1] Complexes with NHC ligands have become increasingly important in homogeneous[2] and, more recently, in heterogeneous catalysis.[3] N,N′-Disubstituted imidazolium salts have also found applications in their own right as ionic liquids and 'green' solvents.[4]

We have developed an interest in the synthesis and catalytic properties of the nickel NHC complexes [Ni(η^5-C_5R_5)(NHC)X] [R = H (Cp) or Me (Cp*); X = Cl, I].[5] These complexes may be prepared in a straightforward manner by reaction of NiCp or Cp* species with imidazolium salts. We are investigating the homogeneous catalytic properties of such species[6] and are also looking into grafting them with trimethoxysilyl-substituted NHC ligands onto solid supports for heterogeneous catalytic applications.[7]

The repertoire of commercially available imidazolium salts is limited. Herein we describe the easy syntheses of N,N′-asymmetrically substituted imidazolium salts, which are either new (**1b**, **2a**, **3a**, **3b**, **4b**) or for which no convenient route has been described (**1a**,[8] **2b**,[9] **4a**[10]). All the prepared imidazolium salts contain either an N-bound butyl group **1a**–**4a** or else, an N-bound 3-(trimethoxysilyl)propyl [$CH_2CH_2CH_2Si(OMe)_3$] group **1b**–**4b** (Equation 1, Table 1).[7] Most contain *N*-arylimidazolium moieties and have iodide as the anion.

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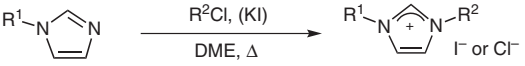
Known synthetic procedures for *N*-alkyl-*N*′-arylimidazolium salts often require the use of alkyl iodides[3b,11] or bromides[12] when starting from the less reactive arylimidazoles. The chlorides are often inert or require forcing conditions.[9,13] We present here a simple new synthetic method to prepare not easily accessible *N*-alkyl-*N*′-arylimidazolium cations from the less reactive alkyl chlorides, under moderate conditions.



R^1 = Ph, 2,4,6-$Me_3C_6H_2$, 2,6-*i*-$Pr_2C_6H_3$, *i*-Pr
R^2 = *n*-BuCl, $(MeO)_3SiCH_2CH_2CH_2Cl$

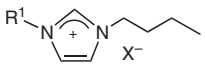
Equation 1 Synthesis of *N*,*N*′-asymmetrically substituted imidazolium salts **1**–**4**

All the *N*-alkyl-*N*′-arylimidazolium salts were synthesized by direct reaction of 1-chlorobutane or (3-chloropropyl)trimethoxysilane with the readily available corresponding *N*-arylimidazoles using (i) 1,2-dimethoxyethane as a solvent, and simultaneously (ii) an equimolar (or larger) quantity of potassium iodide (Equation 1).[14] The addition of potassium iodide leads to the formation by precipitation of the sparingly soluble potassium chloride from the reaction medium. The large N,N′-disubstituted imidazolium cations are presumably better stabilized in the solid state with a big (I^-) counteranion.

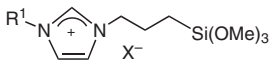
Preparations of the *N*-alkyl-*N*′-isopropylimidazolium derivatives **4a** and **4b** from the more reactive 1-isopropyl-1*H*-imidazole do not require the addition of potassium iodide. Moreover, **4a** does not even require any solvent addition, as simply refluxing neat 1-isopropyl-1*H*-imidazole with an equimolar quantity of 1-chlorobutane affords **4a** in good yield. The synthesis of **4b** is similar, but 1,2-dimethoxyethane was added to slightly raise the reflux temperature.

The chloride salt of **2b**, **2b′**, could be synthesized by heating 1-mesityl-1*H*-imidazole and (3-chloropropyl)trimethoxysilane in a microwave oven; the addition of potassium iodide was not needed to form the cation, and the chloride salt of **2b** was obtained this way in 82% yield, after 20 minutes of reaction time at 180 °C. Higher temperatures led to decomposition, while addition of potassium iodide or shorter reaction times produced less of the desired cation.

Table 1 Preparation of *N*,*N*′-Imidazolium Salts **1**–**4**[a]



1a–4a



1b–4b

Entry	Product	R^1	X	Yield (%)
1	**1a**	Ph	I	50
2	**1b**	Ph	I	76
3	**2a**	2,4,6-$Me_3C_6H_2$	I	87
4	**2b**	2,4,6-$Me_3C_6H_2$	I	94
5	**2b′**	2,4,6-$Me_3C_6H_2$	Cl	82[b]
6	**3a**	2,6-*i*-$Pr_2C_6H_3$	I	79
7	**3b**	2,6-*i*-$Pr_2C_6H_3$	I	64
8	**4a**	*i*-Pr	Cl	quant.[c]
9	**4b**	*i*-Pr	Cl	35[d]

[a] Conditions: R^1Cl, KI, DME, heat; unless otherwise stated.
[b] Microwave irradiation.
[c] R^1Cl, heat.
[d] R^1Cl, DME, heat.

All the butylimidazolium iodide salts described here are hydroscopic solids that appear to liberate traces of free iodine, in the presence of light, which makes the salts appear cream colored, or even pale yellow unless very pure and/or freshly prepared. The [3-(trimethoxysilyl)propyl]imidazolium salts are nonvolatile oils that also often appear slightly yellow colored. These oils are difficult to purify as they sometimes contain traces of (3-chloropropyl)trimethoxysilane and its hydrolysis products. Nevertheless good spectroscopic data (^1H, $^{13}C\{^1H\}$ and ^{13}C DEPT NMR and HRMS) were obtained for all the described salts.

All reactions were carried out using standard Schlenk techniques under an atmosphere of dry argon. Solvents were distilled from appropriate drying agents under argon prior to use. Solution NMR spectra were recorded on a FT-Bruker Ultra Shield 300 spectrometer operating at 300.13 MHz for ^1H NMR, and at 75.47 MHz for $^{13}C\{^1H\}$ NMR. DEPT ^{13}C spectra were obtained for all compounds to help in the ^{13}C signal assignments. Chemical shifts are referenced to the residual deuterated solvent peaks. HRMS were recorded on a MALDI-TOF Biflex Bruker mass spectrometer. Commercial compounds were used as received. 1-Isopropyl-1*H*-imidazole,[15] 1-phenyl-1*H*-imidazole,[16] 1-mesityl-1*H*-imidazole,[17] and 1-(2,6-diisopropylphenyl)-1*H*-imidazole[16] were synthesized according to published methods.

1-Butyl-3-phenylimidazolium Iodide (1a)
A suspension of 1-phenyl-1*H*-imidazole (0.720 g, 4.99 mmol), 1-chlorobutane (0.470 g, 0.530 mL, 5.07 mmol), and KI (0.830 g, 5.00 mmol) in DME (10 mL) was vigorously stirred at 75 °C for 18 h. The mixture was cooled to r.t. and the solvent removed under vacuum. The residue was extracted with MeCN (10 mL), filtered over a Celite pad, and rinsed with MeCN (2 × 5 mL). The MeCN was evaporated, the residue washed with toluene (5 × 3 mL), and crystallized (toluene, 3 mL, r.t., 3 h). The crystals were washed with toluene (3 × 2 mL) and Et_2O (3 × 2 mL) and dried in vacuo. The product was obtained as a light brown solid (0.825 g, 50%).

^1H NMR: δ = 10.59 (br s, 1 H, NCHN), 7.80 (m, 2 H, Ph), 7.73 (dd, *J* = 1.8 Hz, 1 H, NCH), 7.68 (t, *J* = 1.8 Hz, 1 H, NCH), 7.55 (m, 3 H, Ph), 4.59 (t, *J* = 7.4 Hz, 2 H, NCH_2), 1.98 (tt, *J* = 7.4, 7.8 Hz, 2 H, NCH_2CH_2), 1.44 (qt, *J* = 7.8, 7.4 Hz, 2 H, CH_2CH_3), 0.97 (t, *J* = 7.4 Hz, 3 H, CH_3).

^{13}C NMR: δ = 135.4 (NCHN), 134.5 (*ipso*-C_{Ar}), 130.8 (*o*-C_{Ar}), 130.6 (*p*-C_{Ar}), 123.4 and 121.0 (NCH), 122.2 (*m*-C_{Ar}), 50.6 (NCH_2), 32.4 (NCH_2CH_2), 19.7 (CH_2CH_3), 13.7 (CH_3).

HRMS (MALDI TOF): *m*/*z* $[M]^+$ calcd for $C_{13}H_{17}N_2$: 201.1403; found: 201.1386.

1-Phenyl-3-[3-(trimethoxysilyl)propyl]imidazolium Iodide (1b)
A suspension of 1-phenyl-1*H*-imidazole (1.586 g, 11.00 mmol), (3-chloropropyl)trimethoxysilane (2.180 g, 2.00 mL, 10.97 mmol), and KI (3.100 g, 18.67 mmol) in DME (40 mL) was vigorously stirred at 85 °C for 63 h. The mixture was cooled to r.t. and the solvent removed under vacuum. The residue was extracted with MeCN (20 mL), filtered over Celite, and rinsed with MeCN (2 × 10 mL). The MeCN was evaporated and the residue was washed with toluene (4 × 5 mL) and dried in vacuo for 3 h. The product was obtained as a brown oil (3.631 g, 76%), that was contaminated with small quantities of (3-chloropropyl)trimethoxysilane.

^1H NMR: δ = 10.57 (1 H, NCHN), 7.80–7.54 (m, 7 H, Ph, 2 NCH), 4.60 (t, *J* = 7.3 Hz, 2 H), 3.57 (9 H, Me), 2.10 (m, *J* = 8.1, 7.3 Hz, 2 H, NCH_2CH_2), 0.74–0.69 (m, 2 H, $SiCH_2$).

^{13}C NMR: δ = 135.3 (NCN), 134.5 (*ipso*-C, Ph), 130.8 and 122.2 (*o*-C, *m*-C, Ph), 130.6 (*p*-C, Ph), 123.5 and 121.0 (NCH), 52.5 (NCH_2), 51.0 (Me), 24.3 (NCH_2CH_2), 6.1 ($SiCH_2$).

HRMS (MALDI TOF): *m*/*z* $[M]^+$ calcd for $C_{15}H_{23}N_2O_3Si$: 307.1472; found: 307.1457.

1-Butyl-3-(2,4,6-trimethylphenyl)imidazolium Iodide (2a)
A suspension of 1-mesityl-1*H*-imidazole (1.856 g, 9.97 mmol), 1-chlorobutane (2.835 g, 3.20 mL, 30.6 mmol), and KI (2.800 g, 16.9 mmol) in DME (40 mL) was vigorously stirred at 75 °C for 48 h. The mixture was cooled to r.t. and the solvent removed under vacuum. The residue was extracted with MeCN (30 mL), filtered over a Celite pad, and rinsed with MeCN (2 × 10 mL). MeCN was evaporated, the resulting dense yellow oil was crystallized (toluene, 3 mL, r.t., 1 h). The crystals were washed with toluene (3 × 2 mL) and Et_2O (3 × 2 mL) and dried in vacuo. The product was obtained as a white solid (3.221 g, 87%).

^1H NMR: δ = 10.06 (br s, 1 H, NCHN), 7.82 (dd, *J* = 1.7 Hz, 1 H, NCH), 7.21 (dd, *J* = 1.7 Hz, 1 H, NCH), 6.99 (s, 2 H, *m*-*H*), 4.71 (t, *J* = 7.3 Hz, 2 H, NCH_2), 2.33 (s, 3 H, *p*-Me), 2.07 (s, 6 H, *o*-Me), 1,97 (tt, *J* = 7.3, 7.8 Hz, 2 H, NCH_2CH_2), 1.42 (qt, *J* = 7.8, 7.3 Hz, 2 H, CH_2CH_3), 0.97 (t, *J* = 7.3 Hz, 3 H, CH_3).

^{13}C NMR: δ = 141.6 (*p*-C_{Ar}), 137.5 (NCHN), 134.4 (*o*-C_{Ar}), 130.7 (*ipso*-C_{Ar}), 130.1 (*m*-C_{Ar}), 123.4 and 123.3 (NCH), 50.6 (NCH_2), 32.7 (NCH_2CH_2), 21.3 (*p*-Me), 19.5 (CH_2CH_3), 18.0 (*o*-Me), 13.8 (CH_3).

HRMS (MALDI TOF): *m*/*z* $[M]^+$ calcd for $C_{16}H_{23}N_2$: 243.1862; found: 243.1856.

1-[3-(Trimethoxysilyl)propyl]-3-(2,4,6-trimethylphenyl)imidazolium Iodide (2b) by Thermal Synthesis
A suspension of 1-mesityl-1*H*-imidazole (0.923 g, 4.96 mmol), (3-chloropropyl)trimethoxysilane (1.003 g, 0.92 mL, 5.05 mmol), and KI (0.996 g, 6.00 mmol) in DME (20 mL) was vigorously stirred at 85 °C for 60 h. The mixture was cooled to r.t. and the solvent removed under vacuum. The residue was extracted with MeCN (12 mL), filtered over Celite, and rinsed with MeCN (3 × 4 mL). MeCN

was evaporated and the residue was washed with hot toluene (3 × 5 mL) and dried in vacuo. The product was obtained as a pale yellow solid (2.212 g, 94%).

^{1}H NMR: δ = 9.99 (br s, 1 H, NCHN), 7.76 (dd, *J* = 1.7 Hz, 1 H, NCH), 7.21 (dd, *J* = 1.7 Hz, 1 H, NCH), 6.99 (s, 2 H, *m*-H), 4.70 (t, *J* = 7.2 Hz, 2 H, NCH_2), 3.56 (s, 9 H, OMe), 2.33 (s, 3 H, *p*-Me), 2.10 (tt, *J* = 7.2, 7.9 Hz, 2 H, NCH_2CH_2), 2.08 (s, 6 H, *o*-Me), 0.68 (m, *J* = 7.9 Hz, 2 H, CH_2Si).

^{13}C NMR: δ = 141.6 (*p*-C_{Ar}), 137.5 (NCN), 134.4 (*o*-C_{Ar}), 130.7 (*ipso*-C_{Ar}), 130.1 (*m*-C_{Ar}), 123.4 (2 NCH), 52.4 (NCH_2), 51.0 (OMe), 24.6 (NCH_2CH_2), 21.3 (*p*-Me), 18.0 (*o*-Me), 5.8 (CH_2Si).

HRMS (MALDI TOF): *m*/*z* [M]$^+$ calcd for $C_{18}H_{29}N_2O_3Si$: 349.1942; found: 349.1940.

1-[3-(Trimethoxysilyl)propyl]-3-(2,4,6-trimethylphenyl)imidazolium Chloride (2b′) by Microwave Synthesis

1-Mesityl-1*H*-imidazole (186 mg, 1.00 mmol) and (3-chloropropyl)trimethoxysilane (204 mg, 0.19 mL, 1.03 mmol) were mixed in a 10-mL sealed vessel and placed in a Discover CEM S-class microwave oven operating at 2450 MHz. The mixture was heated rapidly and kept at 180 °C for 20 min while stirred magnetically. The resinous product was purified following procedures described in the thermal synthesis for **2b** and was formed in 82% yield (by NMR).

1-Butyl-3-(2,6-diisopropylphenyl)imidazolium Iodide (3a)

A suspension of 1-(2,6-diisopropylphenyl)-1*H*-imidazole (2.310 g, 10.12 mmol), 1-chlorobutane (3.367 g, 3.80 mL, 36.37 mmol), and KI (2.800 g, 16.87 mmol) in DME (40 mL) was vigorously stirred at 75 °C for 50 h. The mixture was cooled to r.t. and the solvent removed under vacuum. The residue was extracted with MeCN (20 mL), filtered over Celite, and rinsed with MeCN (3 × 3 mL). MeCN was evaporated, the residue was washed with toluene (3 × 3 mL), and crystallized (toluene, 3 mL, r.t., 2 h). The crystals were washed with toluene (3 × 2 mL) and Et_2O (3 × 2 mL) and dried in vacuo. The product was obtained as a pale yellow solid (3.291 g, 79%).

^{1}H NMR: δ = 10.14 (br s, 1 H, NCHN), 7.88 (dd, *J* = 1.7 Hz, 1 H, NCH), 7.54 (t, *J* = 8.0 Hz, 1 H, *p*-H), 7.31 (d, *J* = 8.0 Hz, 2 H, *m*-H), 7.21 (dd, *J* = 1.7 Hz, 1 H, NCH), 4.80 (t, *J* = 7.2 Hz, 2 H, NCH_2), 2.29 (hept, *J* = 6.8 Hz, 2 H, C*H*Me_2), 2.00 (tt, *J* = 7.2, 7.6 Hz, 2 H, NCH_2CH_2), 1.43 (qt, *J* = 7.6, 7.4 Hz, 2 H, CH_2CH_3), 1.24 (d, *J* = 6.8 Hz, 6 H, CHMe_2), 1.15 (d, *J* = 6.8 Hz, 6 H, CHMe_2), 1.00 (t, *J* = 7.4 Hz, 3 H, CH_3).

^{13}C NMR: δ = 145.5 (*o*-C_{Ar}), 137.7 (NCHN), 132.2 (*p*-C_{Ar}), 130.2 (*ipso*-C_{Ar}), 124.9 (*m*-C_{Ar}), 124.5 and 123.5 (NCH), 50.6 (NCH_2), 32.7 (NCH_2CH_2), 29.0 (C*H*Me_2), 24.7 (CHMe_2), 24.4 (CHMe_2), 19.5 (CH_2CH_3), 13.8 (CH_3).

HRMS (MALDI TOF): *m*/*z* [M]$^+$ calcd for $C_{19}H_{29}N_2$: 285.2325; found: 285.2321.

1-(2,6-Diisopropylphenyl)-3-[3-(trimethoxysilyl)propyl]imidazolium Iodide (3b)

A suspension of 1-(2,6-diisopropylphenyl)-1*H*-imidazole (2.288 g, 10.02 mmol), (3-chloropropyl)trimethoxysilane (1.962 g, 1.80 mL, 9.87 mmol), and KI (1.999 g, 12.04 mmol) in DME (40 mL) was vigorously stirred at 85 °C for 47 h. The mixture was cooled to r.t. and the solvent removed under vacuum. The residue was extracted with MeCN (20 mL), filtered over Celite, and rinsed with MeCN (3 × 5 mL). MeCN was evaporated, the residue was washed with hot toluene (3 × 5 mL) and dried in vacuo (30 °C, 2 h). The product was obtained as a pale yellow solid (3.271 g, 64%).

^{1}H NMR: δ = 9.90 (br s, 1 H, NCHN), 8.02 (dd, *J* = 1.7 Hz, 1 H, NCH), 7.48 (t, *J* = 7.8 Hz, 1 H, *p*-H), 7.26 (t, *J* = 1.7 Hz, 1 H, NCH), 7.24 (d, *J* = 7.8 Hz, 2 H, *m*-H), 4.69 (t, *J* = 7.0 Hz, 2 H, NCH_2), 3.50 (s, 9 H, OMe), 2.22 (hept, *J* = 6.8 Hz, 2 H, C*H*Me_2), 2.06 (tt, *J* = 7.0, 8.1 Hz, 2 H, NCH_2CH_2), 1.16 (d, *J* = 6.8 Hz, 6 H, CHMe_2), 1.09 (d, *J* = 6.8 Hz, 6 H, CHMe_2), 0.62 (m, *J* = 8.1 Hz, 2 H, CH_2Si).

^{13}C NMR: δ = 145.4 (*o*-C_{Ar}), 137.3 (NCHN), 132.0 (*p*-C_{Ar}), 130.0 (*ipso*-C_{Ar}), 124.7 (*m*-C_{Ar}), 124.6 and 123.8 (NCH), 52.1 (NCH_2), 50.8 (OMe), 28.8 (C*H*Me_2), 24.5 (CHMe_2 and NCH_2CH_2), 24.2 (CHMe_2), 5.6 (CH_2Si).

HRMS (MALDI TOF): *m*/*z* [M]$^+$ calcd for $C_{21}H_{35}N_2O_3Si$: 391.2423; found: 391.2411.

1-Butyl-3-isopropylimidazolium Chloride (4a)

1-Isopropyl-1*H*-imidazole (0.575 g, 5.22 mmol) was added to 1-chlorobutane (0.930 g, 1.05 mL, 10.0 mmol). The mixture was stirred at 75 °C for 12 h. The mixture was cooled to r.t. and excess 1-chlorobutane was removed under vacuum. The resultant oil was further dried in vacuo (30 °C, 2 h). The product was obtained as a colorless oil (1.059 g, quant.).

^{1}H NMR: δ = 10.80 (br s, 1 H, NCHN), 7.58 (dd, *J* = 1.8 Hz, 1 H, NCH), 7.48 (dd, *J* = 1.8 Hz, 1 H, NCH), 4.85 (hept, *J* = 6.7 Hz, 1 H, C*H*Me_2), 4.30 (t, *J* = 7.5 Hz, 2 H, NCH_2), 1.83 (tt, *J* = 7.5, 7.6 Hz, 2 H, NCH_2CH_2), 1.54 (d, *J* = 6.7 Hz, 6 H, CHMe_2), 1.30 (qt, *J* = 7.6, 7.4 Hz, 2 H, CH_2CH_3), 0.87 (t, *J* = 7.4 Hz, 3 H, CH_3).

^{13}C NMR: δ = 136.7 (NCHN), 122.2 and 120.1 (NCH), 53.2 (C*H*Me_2), 49.7 (NCH_2), 32.3 (NCH_2CH_2), 23.3 (CHMe_2), 19.6 (CH_2CH_3), 13.5 (CH_3).

HRMS (MALDI TOF): *m*/*z* [M]$^+$ calcd for $C_{10}H_{19}N_2$: 167.1543; found: 167.1528.

1-Isopropyl-3-[3-(trimethoxysilyl)propyl]imidazolium Chloride (4b)

A solution of 1-isopropyl-1*H*-imidazole (1.093 g, 9.92 mmol) and (3-chloropropyl)trimethoxysilane (2.017 g, 1.85 mL, 10.15 mmol) in DME (10 mL) was stirred at 85 °C for 96 h. The mixture was cooled to r.t. and the solvent removed under vacuum. The resulting oil was washed with toluene (5 × 3 mL) and dried in vacuo. The product was obtained as a colorless oil (1.071 g, 35%).

^{1}H NMR: δ = 10.96 (br s, 1 H, NCHN), 7.49 (dd, *J* = 1.7 Hz, 1 H, NCH), 7.33 (dd, *J* = 1.7 Hz, 1 H, NCH), 4.90 (hept, *J* = 6.7 Hz, 1 H, C*H*Me_2), 4.34 (t, *J* = 7.4 Hz, 2 H, NCH_2), 3.52 (s, 9 H, OMe), 1.98 (tt, *J* = 7.4, 8.1 Hz, 2 H, NCH_2CH_2), 1.58 (d, *J* = 6.7 Hz, 6 H, CHMe_2), 0.61 (m, *J* = 8.1 Hz, 2 H, CH_2Si).

^{13}C NMR: δ = 136.6 (NCHN), 122.1 and 120.4 (NCH), 53.2 (C*H*Me_2), 51.7 (NCH_2), 50.7 (OMe), 24.2 (NCH_2CH_2), 23.2 (CHMe_2), 6.1 (CH_2Si).

HRMS (MALDI TOF): *m*/*z* [M]$^+$ calcd for $C_{12}H_{25}N_2O_3Si$: 273.1629; found: 273.1594.

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Synthesis and Reactivity of Nickel(II) Complexes bearing *N*-Heterocyclic Carbene Ligands: From C–C Cross-Coupling Reactions to sp^3-C–H Bond Activation

Abstract: The research in this thesis targets some aspects of the chemistry of nickel-*N*-heterocyclic carbene (NHC) complexes. A series of half-sandwich nickel(II) complexes, [Ni(R-NHC-*n*-Bu]XCp†] (Cp† = Cp, Cp*, X = Cl, I), bearing a *N*-bound *n*-butyl sidearm NHC ligands has been synthesized from the appropriate imidazolium halides and nickelocene or [Ni(acac)Cp*] as models for heterogenized versions of these complexes. All these complexes were fully characterized by standard spectroscopic techniques [^{1}H and ^{13}C{^{1}H}NMR spectroscopy, 2D spectroscopy when appropriate, MS, and elemental analyses]. Furthermore, many representative complexes were the subject of single-crystal X-ray diffraction studies. All these complexes feature a two-legged piano stool geometry common for 18-electron MCp†L$_2$ compounds with a trigonal planar geometry around the central nickel atom. The [Ni(Ar-NHC-*n*-Bu)ICp] compounds are highly active catalysts for the Suzuki cross-coupling of aryl bromides or chlorides with phenylboronic acid *in the absence of any reductant or co-catalyst* and show higher turnover frequencies (TOF) than seen in their closely related symmetric [Ni(Ar$_2$-NHC)LCp†] counterparts. The origin of the improved stability of the *in situ* generated active species is discussed. A heterogenized version of these complexes onto alumina has been prepared by employing 3-(trialkoxysilylpropyl)imidazolium halides and tested in Suzuki cross-coupling.

In the prospect of enhancing the longevity of the active species, unprecedented half-sandwich Ni(II) complexes bearing two *different* NHC ligands were prepared by displacement of the labile acetonitrile ligand from [Ni(Ar$_2$-NHC)(CH$_3$CN)Cp]$^+$X$^-$ with a "free" NHC. The resulting cationic *bis*-(NHC)-nickel complexes [Ni(NHC)(NHC')Cp]$^+$X$^-$ show remarkable stability, and thus low acitivity in Suzuki couplings. The Ni–NHC bonds are particularly robust as can be demonstrated by the displacement of the Cp, and not of a NHC ligand, when these *bis*-NHC Cp complexes are protonated.

The final chapter presents a novel reaction in which the base-promoted activation of sp^3-hybridized C–H bonds α- to functional organic groups at Cp†Ni-NHC centres was achieved. The scope and breadth of this activation is demonstrated by the activation of acetonitrile, acetone and other ketones under relatively mild conditions to give a range of new nickel alkyls. A remarkable double activation of acetone was notably demonstrated. The activation of C–H bonds α-to nitriles in NHC-attached sidearms to give a series of new half-sandwich nickelacycles was also achieved. Possible mechanistic pathways for these reactions have been the subject of theoretical DFT analyses. Similarly to the *bis*-NHC species, the nickelacycles show great robustness of the NHC– and alkyl–Ni bonds.

Key-words: Nickel, *N*-heterocyclic carbene (NHC), two-legged piano stool geometry, Suzuki-Miyaura Cross-Coupling, *bis*-NHC-nickel complexes, base-promoted C–H bond activation, nickel–alkyl bond, nickelacycles.