THESE

Présentée à

l'Université Louis Pasteur de Strasbourg

Pour obtenir le grade de

DOCTEUR

Spécialité : **CHIMIE**

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Synthèse de nouveaux complexes de nickel et de fer : Application en catalyse d'oligomérisation de l'éthylène

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Soutenue le 25 juin 2007 devant la commission d'examen :

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Remerciements

Ce travail a été réalisé au Laboratoire de Chimie de Coordination, UMR 7177 du CNRS, de l'Université Louis Pasteur, Strasbourg.

Je tiens tout d'abord à remercier mon directeur de thèse le Dr. Pierre Braunstein, Directeur de Recherche au CNRS et membre de l'Académie des Sciences en France, pour m'avoir accueilli au sein de son laboratoire, pour avoir encadré ce travail, et pour sa confiance et sa disponibilité.

Je remercie les membres de mon jury, Messieurs M. Chetcuti, P. Espinet, R. Réau, R. Welter et Madame H. Oliver-Bourbigou, qui ont accepté de juger mon travail.

Merci aussi à tous ceux qui ont contribué à ce travail notamment Dr. Roberto Pattacini, Dr. M. Agostinho, Dr. Qing-Zheng Yang et Dr. Olivier Siri.

Mes remerciements vont également à nos collaborateurs notamment Pr. Richard Welter et Dr. André DeCian pour la partie cristallographique, Dr Jean-Paul Collin pour les études électrochimiques et Dr Dominique Mandon pour les études UV-Vis à basses températures et pour ses conseils sur la chimie du fer. Je remercie également R. Graff, J-D Sauer, M. Coppe et L. Allouche du service de RMN, C. Desvignes du service de microanalyse et l'ensemble du service de spectrométrie de masse.

Un très grand merci à Anne Dégremont pour son travail, son aide et son soutient et un gigantesque merci à Marc Mermillon-Fournier (le pauvre, il a souffert avec moi) pour tout son travail, son acharnement, ses mails obscènes, ses barbecues et sa disponibilité de tous les jours.

Un remerciement spécial à Patty et Falk, mes deux stagiaires, pour avoir fait de moi un « jefe malo ».

Je remercie chaleureusement tous les membres du Laboratoire de Chimie de Coordination: Abdelatif, Matthieu, Bipro, Günter, Sabrina, Christophe, Sarah, Elisabeth, Farba, Jonathan, Lisa, Mireia, Anja, Fredy, Shuanming, Nadia, Aude, Nicola, Adel, Suyun... Merci aux membres permanents du LCC : Jacky, Catherine, Olivier, Robi, Soumia et Xavier.

Un merci aussi pour les amis du 6eme nord (JB, Mili, Pape, Alexandre, Nico, Jérôme…).

Enfin, j’adresse un merci à mes parents, ma sœur Elodie, ma grand-mère qui m’ont soutenu tout au long de cette thèse malgré les difficultés et les kilomètres.

« Avec confiance, grâce et bonne humeur,
vous verrez le bout de vos peines »
Louis-Ferdinand Céline

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Composition du document et organisation de la bibliographie

Ce document se divise en dix sections : une introduction générale, sept chapitres, un résumé et une conclusion générale.

L'introduction générale est rédigée en français et dispose de sa propre bibliographie.

Le chapitre I est présenté sous forme de publication au format du journal *Organometallics.*
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Le résumé et la conclusion générale sont rédigés en français.

Introduction générale

L'intérêt commercial des α-oléfines linéaires (LAO) est considérable et leur production est un sujet majeur pour l'industrie pétrochimique.[1-4, 5 2004] La majeure partie des LAO est produite par oligomérisation de petites oléfines comme l'éthylène, le propylène ou le butène grâce à des procédés catalytiques basés sur des métaux de transition.[6-8]

Les LAO sont des matériaux de base pour la synthèse de nombreux produits et la longueur de leur chaîne carbonée est déterminante pour leurs applications industrielles (Schéma 1).[4, 8] Les oléfines légères dans la gamme C_4-C_8 sont utilisées comme comonomères de l'éthylène pour la synthèse de polyéthylènes basse densité. Ces oléfines servent aussi à la formation de polymères haute densité ou de plastifiants. Les oléfines moyennes de la gamme C_{10}-C_{14} sont très intéressantes pour la production de détergents alcools alors que les oléfines plus lourdes de la gamme C_{16}-C_{20} sont principalement utilisées pour la production d'huiles synthétiques et d'additifs lubrifiants. La production de cires synthétiques est réalisée à partir d'oléfines lourdes possédants plus de vingt carbones (Schéma 1).

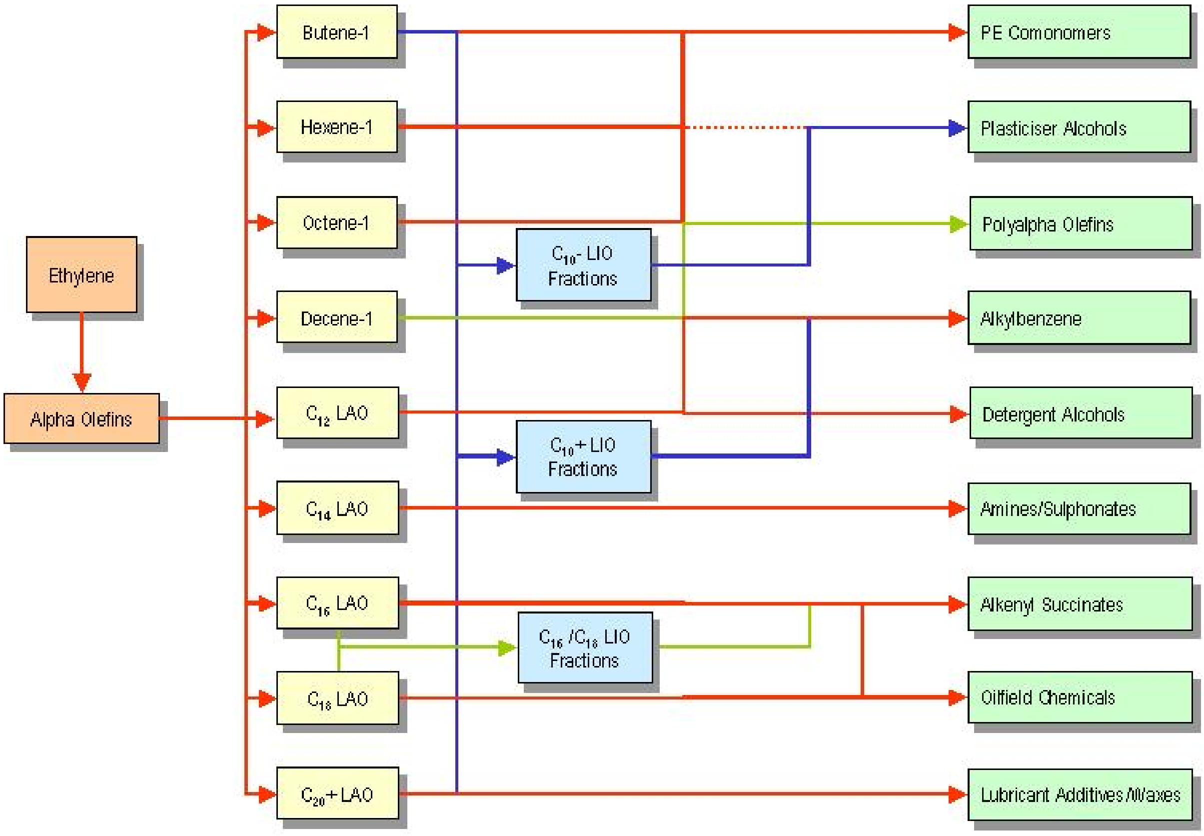


Schéma 1. Applications Industrielles des Différentes LAO

La dynamique économique des LAO est majeure puisque leur demande globale était de 3,4 millions de tonnes en 2002 et qu'elle progresse d'environ 4,9 % par an.[5 2004] L'importance des enjeux économiques et industriels force les plus grands groupes pétrochimiques à investir et développer de nouveaux procédés plus innovants et plus performants.

Dans les années 1950, les travaux de Karl Ziegler et de Giulio Natta ont largement contribué au développement de la réaction catalytique de polymérisation et d'oligomérisation des oléfines.[9] Ziegler a décris les premiers catalyseurs hétérogènes de polymérisation (Schéma 2).[10, 11] Ces catalyseurs étaient des chlorures métalliques du groupe IV ($TiCl_3$) qui, alkylés par des alkylaluminiums, transformaient l'éthylène en polyéthylène.[12]

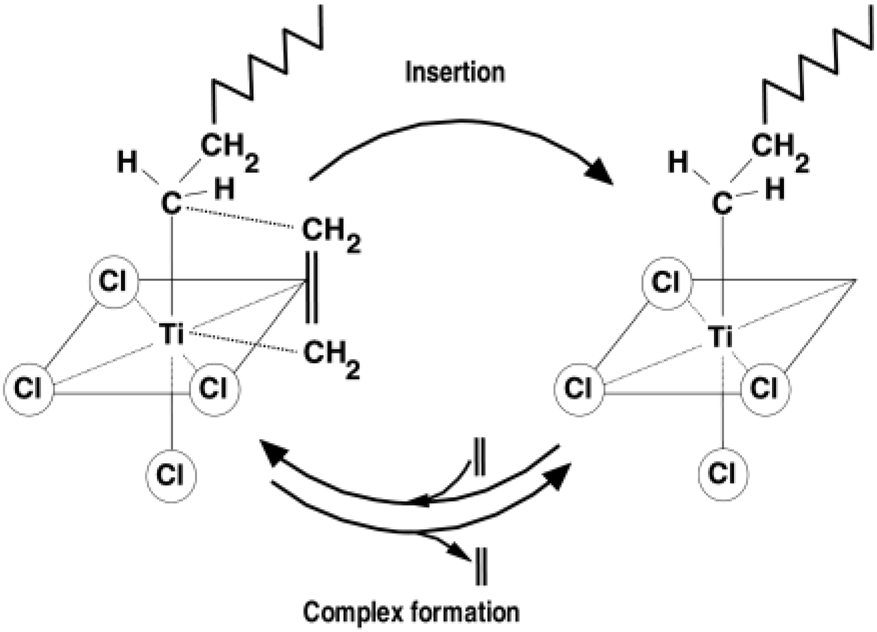


Schéma 2. Polymérisation de l'éthylène par les complexes hétérogènes de Ziegler

Ces composés du groupe IV ont ensuite évolués pour former des catalyseurs homogènes de type [Cp_2ZrCl_2] plus efficaces mais l'alkylation par des alkylaluminiuns, des chloroalkylaluminiums ou par methylaluminoxane (MAO) reste la clé pour l'activation des complexes.[13-17]

Le développement des catalyseurs de type Ziegler-Natta avec des ligands imides a permis de créer une nouvelle famille: les catalyseurs « post-métallocenes » qui ont des propriétés catalytiques très intéressantes en polymérisation des oléfines.[18-25]

L’utilisation des alkylaluminiums de Ziegler comme catalyseur a permis de développer des procédés industriels d’oligomérisation très importants comme le procédé Ethyl (Ineos) ou le procédé Gulf (Chevron Philips Chemical). Ces procédés travaillent sous haute pression d’éthylène et à haute température (pression d’éthylène de 1000 psig et température de 400 F pour le procédé Ethyl). Les LAO sont produites dans une gamme large allant de C_6-C_{18} avec une distribution de masse de type Schulz-Flory pour le procédé Gulf et dans une gamme plus serrée C_6-C_{10} avec une distribution Pseudo-Poisson pour le procédé Ethyl. Malheureusement la consommation très importante en alkylaluminiums de ces procédés diminue leur rentabilité. L’institut français du pétrole a développé le procédé Alphabutol basé sur le système $Ti(OR)_4/AlEt_3$. Ce procédé est très efficace pour la dimérisation de l’éthylène en 1-butène.[26]

En 1954, Ziegler décrivit la dimérisation de l’éthylène en 1-butène par des complexes du nickel et le baptisa « l’effet nickel » (« nickel effekts »).[9, 27, 28] Cette découverte va ouvrir de nouveaux axes de recherche vers des catalyseurs d’oligomérisation et de polymérisation à base de complexes de nickel et aussi de palladium, fer, cobalt ou de chrome.[29-34]

Les réactions catalytiques d’oligomérisation et de polymérisation de l’éthylène peuvent être décrites par un même cycle catalytique représentant les principales étapes élémentaires (Schéma 3).[8]

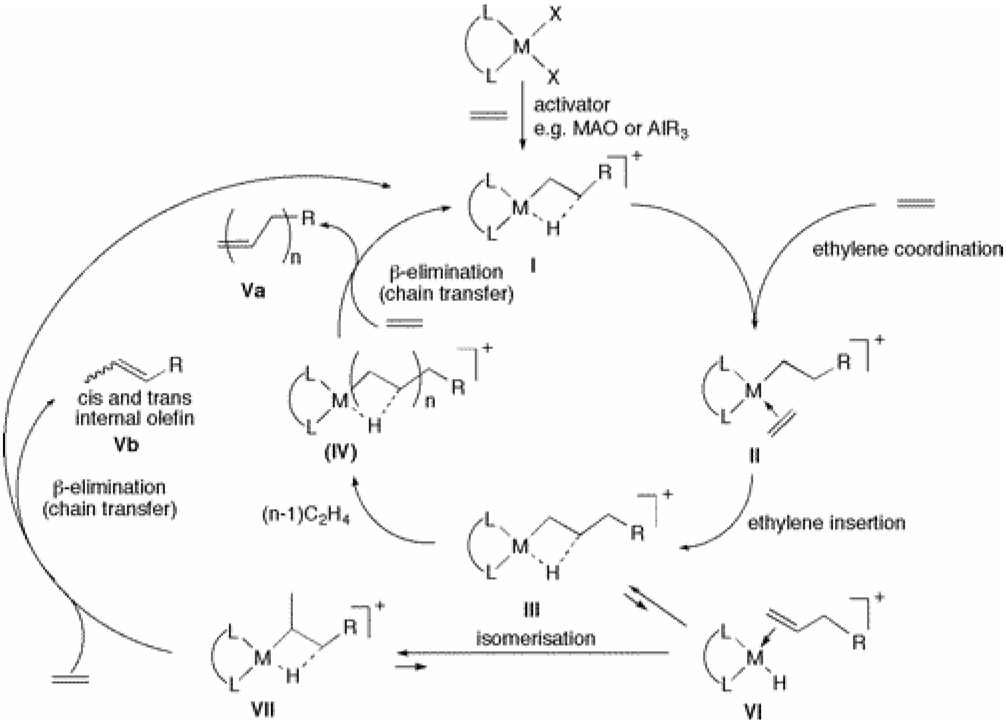


Schéma 3. Cycle catalytique d’oligomérisation ou polymérisation de l’éthylène

La première étape consiste à former l'espèce active **I** par alkylation du centre métallique du complexe halogéné. Celle-ci, sous forme cationique, est stabilisée par une interaction agostique après insertion d'une molécule d'éthylène.[35-40] Certain cycles catalytiques d'oligomérisation ou polymérisation désignent l'espèce active sous la forme hydrure métallique.[41-45] Le cycle se poursuit pour une succession coordination/insertion de molécules d'éthylène (espèces **II** et **III**) jusqu'à l'étape de l'élimination β (transfert de chaîne) qui va libérer l'oléfine **Va** et reformer l'espèce active initiale **I**. La capacité du catalyseur à retarder le transfert de chaîne pendant le cycle catalytique va être déterminante pour la longueur de la chaîne carbonée des produits finaux.[46-48] Lorsque celui-ci favorise énormément le transfert de chaîne devant la propagation de chaîne, la dimérisation de l'éthylène devient la réaction principale de la catalyse et le 1-butene le produit majoritaire.[40]

La formation de produits secondaires comme des oléfines internes ou des oligomères branchés est souvent rapportée lorsque des complexes de nickel sont utilisés comme précatalyseurs.[49-52] Pendant le cycle catalytique, des interactions agostiques entre le centre métallique et des hydrogènes internes de l'oléfines peuvent se former (espèce **VII**) et qui, après une élimination β, libèrent des oléfines internes.[48, 51, 53] Ces oléfines internes peuvent être réinsérées dans le cycle catalytique et des nouvelles oléfines internes ou des oligomères branchés sont alors libérés.[52]

Le deuxième mécanisme réactionnel présenté ci-dessous (Schéma 4) peut aussi schématiser le cycle catalytique d'oligomérisation et expliquer la sélectivité en 1-butene ou 1-hexene de certains systèmes catalytiques.[54, 55] Ce mécanisme montre le Couplage oxydant de deux molécules d'éthylène coordinées sur le centre métallique pour former un métallacyclopentane **I**. Une molécule de 1-butène peut être alors libérée par élimination réductrice ou l'insertion d'une nouvelle molécule d'éthylène conduira à la formation d'un métallacycloheptane **II** qui libéra une molécule de 1-hexène.[56]

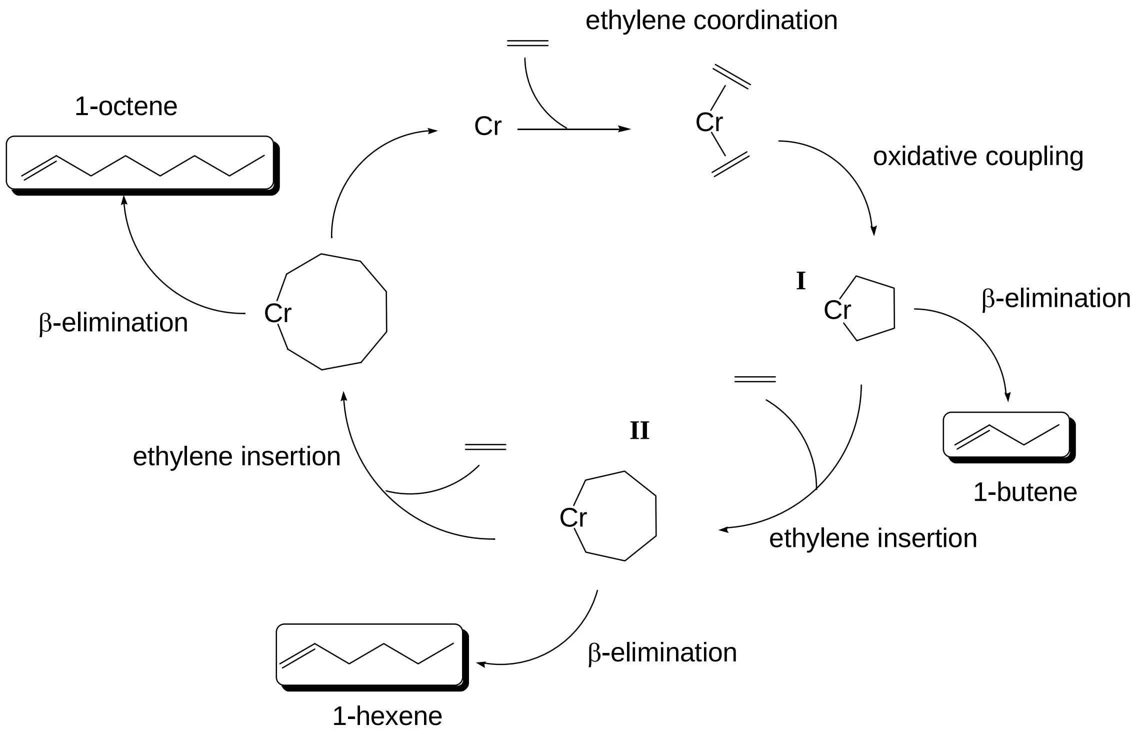


Schéma 4. Mécanisme d'oligomérisation de l'éthylène par des intermédiaires métallocycliques

Ce mécanisme réactionnel est associé aux réactions de dimérisation, trimérisation et tétramérisation de l'éthylène rapportées pour les systèmes à base de complexes de chrome comme le procédés Philips avec des ligands pyrrolides,[57] le procédé SASOL (SASOL mixed heteroatomic system) avec des ligands tridentes type P,N,P[58, 59] ou S,N,S[60, 61], le système BP avec des ligands type P,N,P[62] et autres (Schéma 5).[56, 63-67]

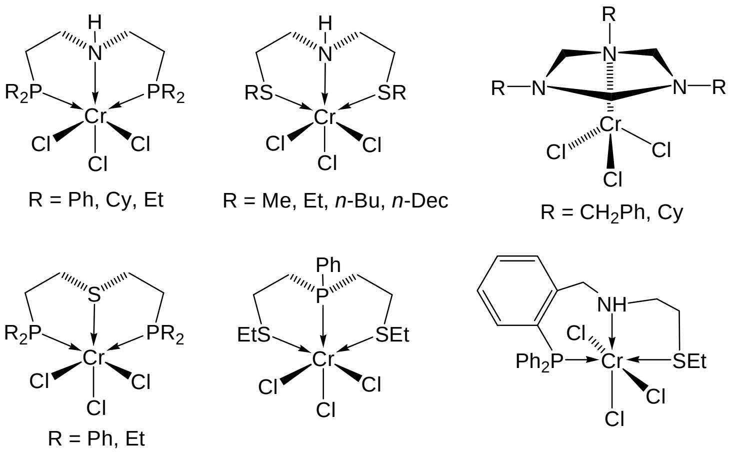


Schéma 5. Exemples de complexes de Cr(III) utilisés en oligomérisation

Des mécanismes similaires ont été rapportés pour des systèmes à base de titane,[26, 68-70] tantale[71] et nickel.[72]

Il existe trois grands procédés d'oligomérisation à base de complexes de Nickel : le procédé Dimersol développé par IFP, le procédé SHOP développé par le SHELL Oil Company et le procédé Versipol développé par DuPont.

Le procédé Dimersol a été développé par Chauvin au sein de l'IFP et permet la dimérisation du propène en isohexène et du butène en isooctène.[41, 73, 74] Les produits synthétisés sont utilisés pour fabriquer des additifs pour carburant et des plastifiants PVC.

Le procédé SHOP (Shell Higher Olefin Process) a été développé par la SHELL Oil Company et consiste à l'association de trois réactions catalytiques : oligomérisation, isomérisation et métathèse (Schéma 6).[7, 41, 75, 76]

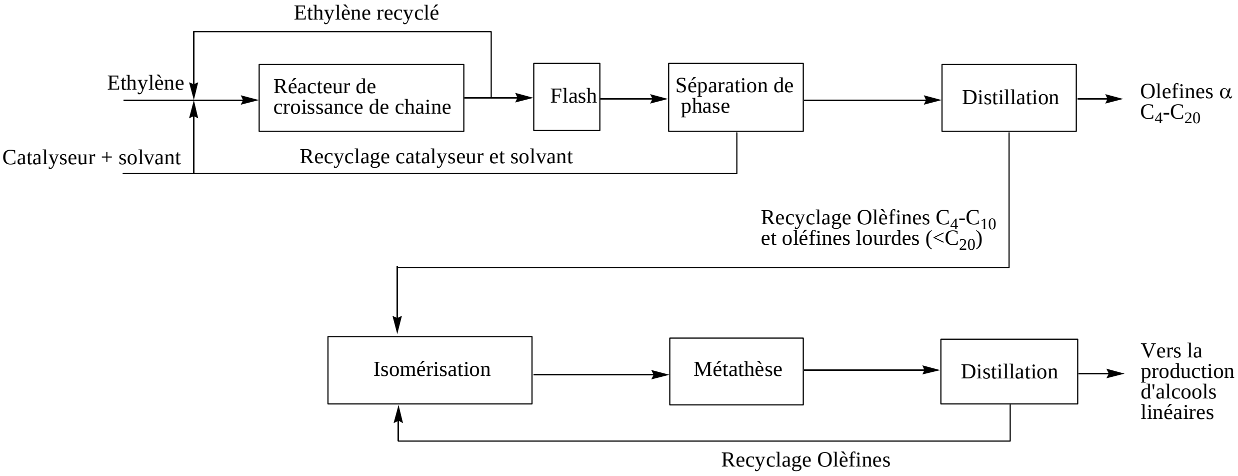


Schéma 6. Procédé SHOP

Les deux réactions suivantes, isomérisation et métathèse, servent à recycler une partie des oléfines synthétisées par oligomérisation et, après hydroformylation, ces oléfines produisent des alcools linéaires.

La synthèse des oligomères est réalisée par un complexe de nickel coordiné par un chélate de type P,O (Schéma 7) et ce système offre une très grande sélectivité en oléfines α et une distribution de masse de type Schulz-Flory.

La synthèse de ce complexe est réalisée par addition oxydante d'un ylure phosphorane sur Ni(COD)$_2$ (COD = cyclooctadiène) en présence d'une phosphine pour stabilisé le complexe (Schéma 7).[77, 78]

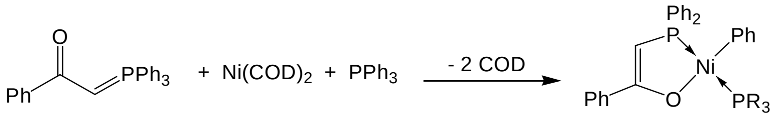
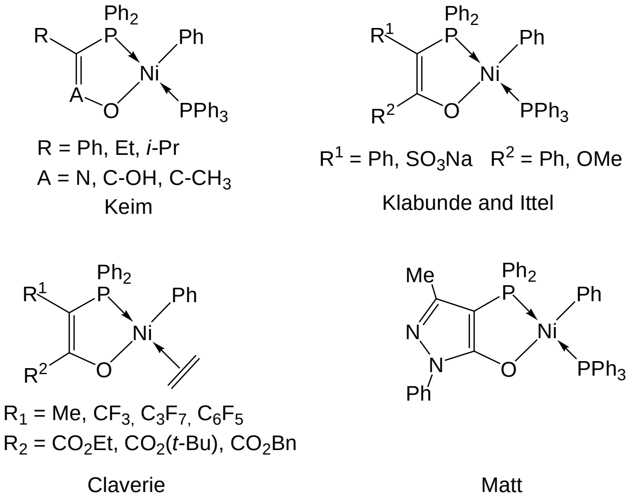


Schéma 7. Synthèse du complexe SHOP

La coordination d'un aryle sur le centre métallique assure l'activation du système catalytique ce qui, contrairement aux catalyseurs de Ziegler, rend l'utilisation de cocatalyseurs inutile.[34] Les complexes de type SHOP peuvent aussi être des catalyseurs de polymérisation lorsqu'un ligand moins donneur est utilisé à la place d'une phosphine (pyridine) ou lorsqu'un extracteur de phosphine est ajouté au milieu réactionnel.[79-83]

L'influences des substituents du chélate P,O ont été particulièrement étudiées par les groupes de Keim,[43, 84-87] Klabunde,[81, 82] Claverie,[88] Matt[89, 90] et autres (Schéma 8).[80, 91-93]



R = Ph, Et, *i*-Pr
A = N, C-OH, C-CH$_3$
Keim

R^1 = Ph, SO$_3$Na R^2 = Ph, OMe
Klabunde and Ittel

R_1 = Me, CF$_3$, C$_3$F$_7$, C$_6$F$_5$
R_2 = CO$_2$Et, CO$_2$(*t*-Bu), CO$_2$Bn
Claverie

Matt

Schéma 8. Exemples de complexes de type SHOP

La synthèse de complexes type SHOP avec des ligands allyliques a été rapportée et ces composés, neutres ou anioniques, ont montré des activités intéressantes en oligomérisation et polymérisation (Schéma 9).[33, 45, 94-99]

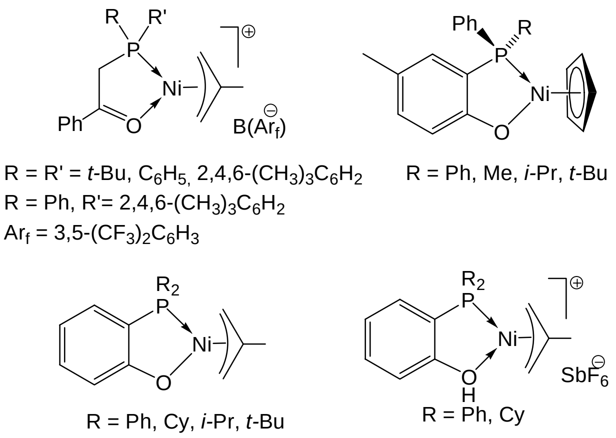


Schéma 9. Exemples de complexes type SHOP à ligands allyliques

Les catalyseurs de type SHOP continue d’évoluer et de récents travaux ont montrés l’efficacité en catalyse de complexes à chélates N,O. Les synthétises et réactivités de complexes de nickel ont été rapportées par Grubbs[100-102] et Mecking[103, 104] avec des ligands salicylaldimines et par Brookhart avec des ligands anilinotropones[105-108] ou anilinoperinaphthenones (Schéma 10).[109]

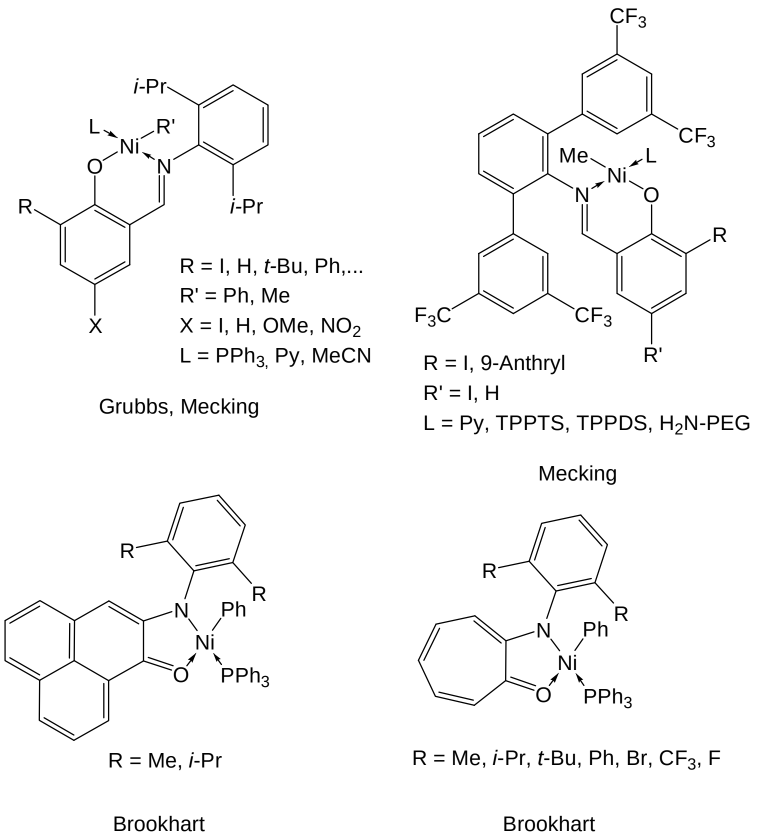
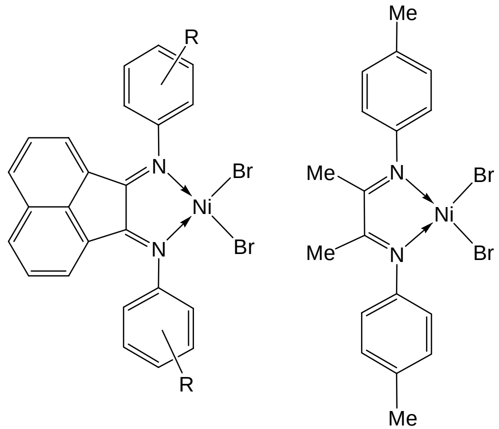


Schéma 10. Exemples de complexes type SHOP à ligands type N,O

Le procédé Versipol a été développé par DuPont sur la base de complexes de nickel ou palladium coordinés par des ligands diimine (Schéma 11).[30, 32, 34, 110]

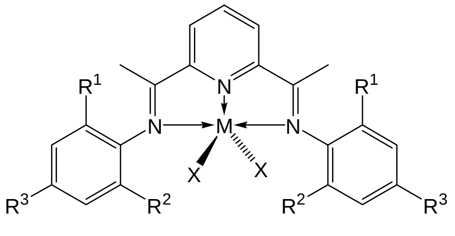


R = H, Me, *i*-Pr

Schéma 11. Complexes Ni(II) coordinés par des ligands diimines

Brookhart est le premier à avoir rapporté les très fortes activités en polymérisation de ces complexes lorsqu'ils sont activés par des alkylaluminiums.[35, 111-113] L'incorporation de substituents stériquement moins encombrants sur les groupements phényles du ligand modifie le caractère du catalyseur en catalyseur d'oligomérisation avec une distribution des oléfines de type Schulz-Flory.[49, 114]

Des complexes de fer et cobalt contenants des ligands diimines ont montré des résultats catalytiques intéressants en polymérisation.[115, 116] L'utilisation en catalyse de complexes de fer et cobalt avec des ligands tridentes pyridinediimines ont été développés parallèlement par Gibson et Brookhart (Schéma 12).



M = Fe, Co
X = Cl, Br
R^1 = H, Me, *i*-Pr, *t*-Bu, CF_3
R^2 = H, F, Me, *i*-Pr, CF_3
R^3 = H, F

Schéma 12. Complexes Fe(II) et Co(II) coordiné par des ligands pyridinediimines

Activés par des alkylaluminiums comme MAO ou $AlEtCl_2$, ces complexes se sont montrés d'excellents catalyseurs de polymérisation de l'éthylène avec formation de polymères de haut poids moléculaire.[117-121] Par modification des propriétés stériques des ligands, ces complexes ont formé des catalyseurs d'oligomérisation.[122-128]

Au sein de notre laboratoire, une importante famille de complexes de nickel à ligands hétéroditopiques P,N ont été synthétisés et évalués en oligomérisation catalytique de l'éthylène avec MAO et $AlEtCl_2$ comme cocatalyseurs.[8, 129] La basicité du groupement phosphoré a été modifiée par l'utilisation de fonctions phosphines,[130-132] phosphinites[133] ou phosphonites[134] et le groupement azoté était représenté par un hétérocycle pyridine ou oxazoline (schéma 13).

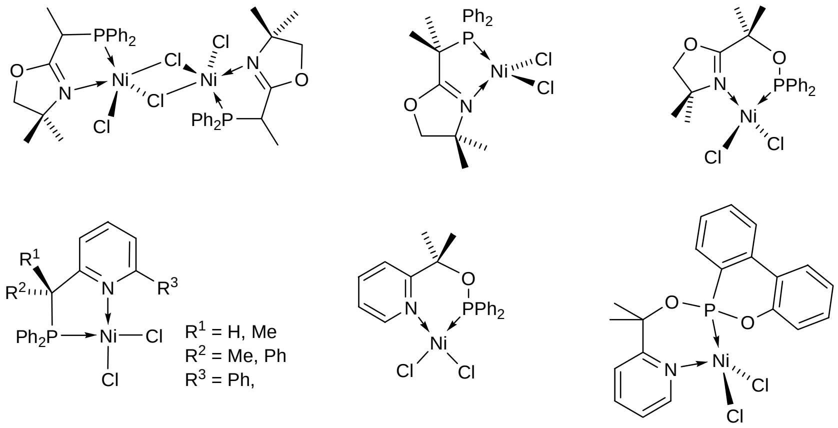


Schéma 13. Complexes de nickel à ligands type P,N

Ces complexes ont montré de fortes activés en oligomérisation de l'éthylène avec des TOF (turnover frequency) allant jusqu'à 61000 mol C_2H_4/(mol Ni·h) avec 6 equiv de $AlEtCl_2$ et 22800 mol C_2H_4/(mol Ni·h) avec 800 equiv de MAO. Ces catalyseurs avaient un fort caractère dimérisant et avaient des sélectivités en oléfines C_4 comprises entre 54 et 92% avec $AlEtCl_2$ et entre 69 et 94% avec MAO. Mais, en favorisant l'isomérisation du 1-butène en 2-butène (cis et trans), ces systèmes catalytiques ont montré des sélectivités en 1-butène modestes comprises entre 3 et 25% lorsque $AlEtCl_2$ était utilisé comme cocatalyseur et entre 33 et 38% avec MAO comme cocatalyseur.

Notre laboratoire s'est aussi attaché à étudier en oligomérisation des complexes dinucléaires de nickel coordinés par des alcools pyridine ou oxazoline[135] ainsi que des complexes de nickel coordinés par des ligands *N*,*O*-benzoquinonemonoimine (Schéma 14).[136]

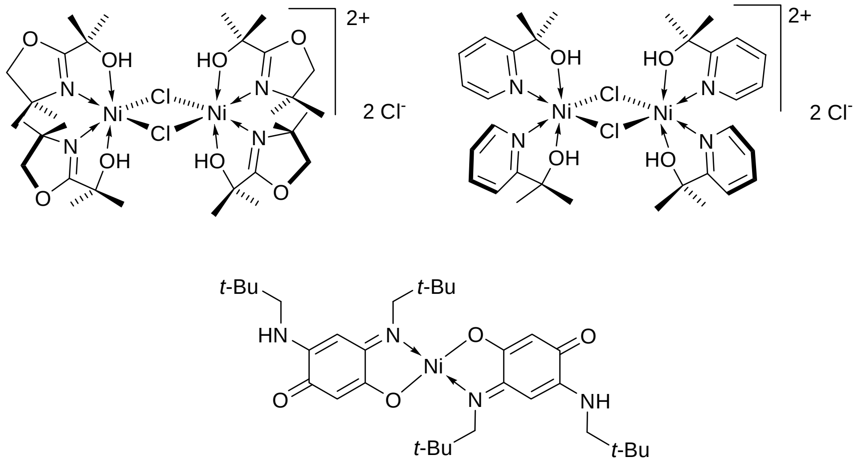


Schéma 14. Complexes de nickel à ligands type N,O

Les complexes dinucléaires à ligands alcools ont montré de très fortes activités jusqu'à 174300 mol C_2H_4/(mol Ni·h) avec 6 equiv de $AlEtCl_2$ et jusqu'à 28300 mol C_2H_4/(mol Ni·h) avec 800 equiv de MAO. Leurs sélectivités en oléfines C_4 étaient comprises entre 64 et 70% avec $AlEtCl_2$ et 77 et 88% avec MAO. Lorsque MAO est utilisé comme cocatalyseur, ces complexes dinucléaires ont montré des sélectivités intéressantes en 1-butène comprises entre 39 et 61%.

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Chapitre I

Nickel Complexes with Functional Zwitterionic *N,O*-Benzoquinonemonoimine-type Ligands: Synthesis, Structures and Catalytic Oligomerization of Ethylene

Ce chapitre est présenté sous forme de publication au format du journal *Organometallics* et a fait l'objet d'une publication dont la référence est donnée ci-dessous.

Mon travail dans cette publication a été de tester les différents complexes en réaction d'oligomérisation de l'éthylène et d'analyser les résultats obtenus.

Organometallics **2006**, 25, 5518-5527

Nickel Complexes with Functional Zwitterionic *N,O*-Benzoquinonemonoimine-type Ligands: Synthesis, Structures and Catalytic Oligomerization of Ethylene.

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Abstract

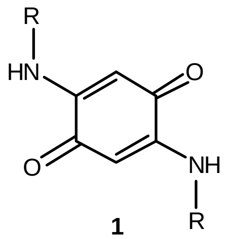
Zwitterionic *N,N'*-dialkyl-2-amino-5-alcoholate-1,4-benzoquinonemonoiminium derivatives $[C_6H_2(\overset{\cdots}{-}NHCH_2CH_2X)_2(\overset{\cdots}{-}O)_2]$ (X = NMe_2, **9**; X = NHEt, **10**; X = OMe, **11**), previously prepared from 4,6-diaminoresorcinol by a transamination reaction, and **12** (X = $N(CH_2CH_2)_2O$) behave as tridentate ligands when reacted with $[Ni(acac)_2]$ and form the corresponding octahedral Ni(II) 2:1 complexes $[Ni\{C_6H_2(=NCH_2CH_2X)O(=O)(NHCH_2CH_2X)\}_2]$ (**13**-**16**), respectively. Ligand **9** reacted with $NiCl_2{\cdot}6H_2O$ in a tandem-like manner to afford the stabilized Ni(II) zwitterionic organometalate complex $[NiCl_2\{C_6H_2(=NCH_2CH_2NMe_2)O(=O)(NHCH_2CH_2NHMe_2)\}]$ (**17**). The bonding parameters of complexes **13**$\cdot H_2O\cdot CH_2Cl_2$ and **17**, determined by X-ray diffraction, and the conformation of the ligands around the nickel center as well as the supramolecular arrangements are discussed and compared with those of their previously reported Zn(II) analogs. Complexes **13-17** were tested in the catalytic ethylene oligomerization with MAO and $AlEtCl_2$ as cocatalysts. Complex **17** yielded the highest turnover frequencies, with values up to 20 300 mol C_2H_4/(mol Ni)·h and 48 200 mol C_2H_4/(mol Ni)·h, in the presence of 400 equiv of MAO and 10 equiv of $AlEtCl_2$, respectively. Selectivities for ethylene dimers were slightly higher when using MAO, 94% (**14** in the presence of 100 equiv of MAO) and 90% (**14** in the presence of 6 equiv of $AlEtCl_2$). The selectivities for 1-butene within the C_4 fraction were much higher when using MAO as cocatalyst, with values up to 68% (**15** in the presence of 100 equiv of MAO). The fact that **17,** which contains only one tridentate ligand per nickel center, leads to higher activities than **13-16** underlines the importance of the metal center accessibility in the catalytic process.

1. Introduction

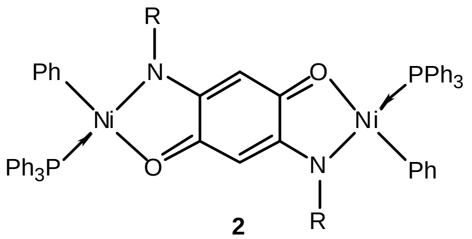
Recent review articles have illustrated the important role played by nickel complexes in the catalytic oligomerization and polymerization of olefins.[1-3] The competition between olefin insertion and chain transfer processes accounts for the occurrence of oligomerization or polymerization reactions, respectively. Obviously, this is function of a number of parameters, including the nature of the ligands and the structure of the precatalyst. With the exception of SHOP-type systems which are based on neutral phenyl complexes,[4-7] activation of the nickel precatalyst by a cocatalyst, such as MAO and $AlEtCl_2$, is generally required. The choice of the cocatalyst is crucial to the activity and selectivity of the system.[8,9] Brookhart *and coll.* have reported very active and selective α–diimine nickel complexes for ethylene polymerization and oligomerization.[10] This work has inspired the synthesis of a number of new nickel complexes with *N,N*-type ligands as precatalysts, using MMAO,[11] MAO,[12] $B(C_6F_5)_3$,[13] or $Al_2Et_3Cl_5$[14] as cocatalysts. Difunctional *P,N*-type ligands can also lead to very interesting Ni(II) precatalysts, some of them being very active and highly selective for dimerization and trimerization of ethylene in the presence of MAO or $AlEtCl_2$.[3]

Considerable research effort has been devoted over the past few years to the design of new chelating *N,O* ligands and their nickel complexes have shown very high catalytic activity for olefin oligomerization and polymerization.[15-22] Efficient ethylene polymerization catalysts with *N,O*-type ligands were developed by Grubbs *and coll.*[23-25]and Brookhart *and coll.*[26-28] which are based on salicylaldimine and anilinotropone ligands, respectively, and do not require the use of a cocatalyst. Other Ni(II) complexes with *N,O* chelates catalytically oligomerize ethylene only in the presence of a cocatalyst, such as MAO,[29,30] $AlEt_3$,[31] $B(C_6F_5)_3$,[32] and ethylaluminum sesquichloride.[33] We have shown that nickel complexes prepared from oxazoline- and pyridine-alcohols and activated by MAO or $AlEtCl_2$ are very effective and lead to high selectivities for C_4 and C_6 products.[34]

Although *N,O*-type ligands have recently been applied in coordination chemistry to the synthesis of porphyrin dimers and oligomers connected by metal ions,[35,36] only few examples of mono- or polynuclear metal complexes based on *N,O* ligands supported by a quinonoid core have been reported.[37-39] A series of 2,5-disubstituted amino-*p*-benzoquinone ligands of the *N,O,N,O* type **1** has been used recently by Zhang and coworkers for the preparation of Ni(II) complexes of type **2**, which were active as single-component catalysts in ethylene polymerization.[40]



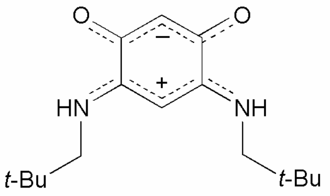
1



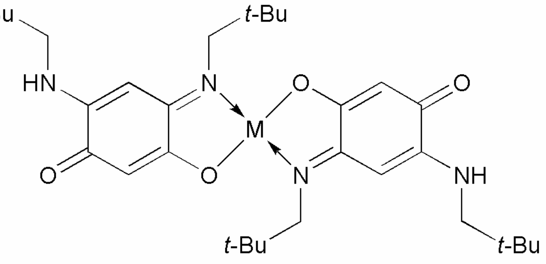
2

We recently reported the synthesis and electronic structure of the zwitterionic benzoquinonemonoimine ligand **3** from 4,6-diaminoresorcinol dihydrochloride[41] Assembling of two of these benzoquinonemonoimines around the metal center by a metalation reaction using [M(acac)$_2$] (M = Ni, Zn, Cu) afforded complexes **4-6**.[41] Precatalyst **4** was active in ethylene oligomerization and favored the dimerization and trimerization of ethylene when activated with AlEtCl$_2$.[42]

Therefore, the screening of other functional ligands of type **3** with substituents which could lead for example to potentially hemilabile behaviour,[43] should be of particular interest in coordination chemistry and homogeneous catalysis.



3

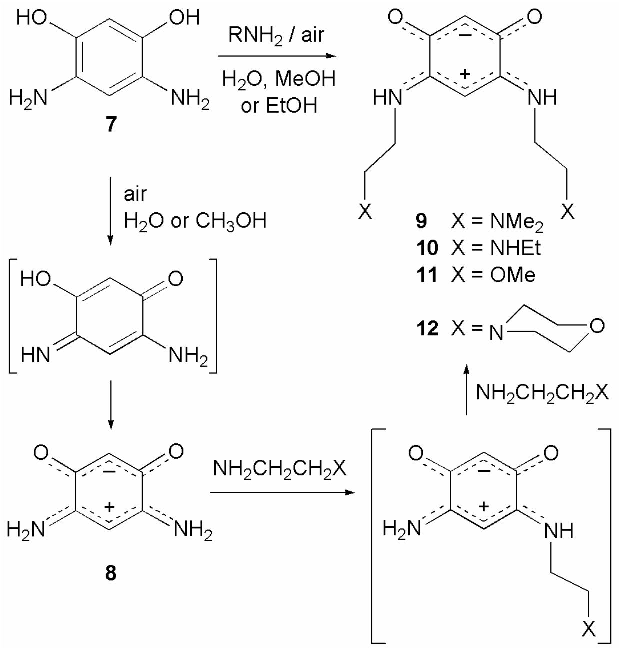


4 M = Ni
5 M = Zn
6 M = Cu

The industrial demand for C_4-C_{20} linear α-olefins has triggered research towards their selective synthesis and the fast growing needs for linear α-olefins in the C_4-C_{10} range (a *ca.* 2.5x10^6 tons/year market) explains why their selective formation from ethylene has become a topic of major fundamental and applied importance.[44] As part of our interest for new ethylene oligomerization Ni(II) catalysts for the production of short chain oligomers in the presence of only small quantities of AlEtCl$_2$ or MAO, we have extended our preliminary studies on Ni(II) complexes supported by a benzoquinonemonoimine *N,O* chelate and have now evaluated complexes **13-17**.

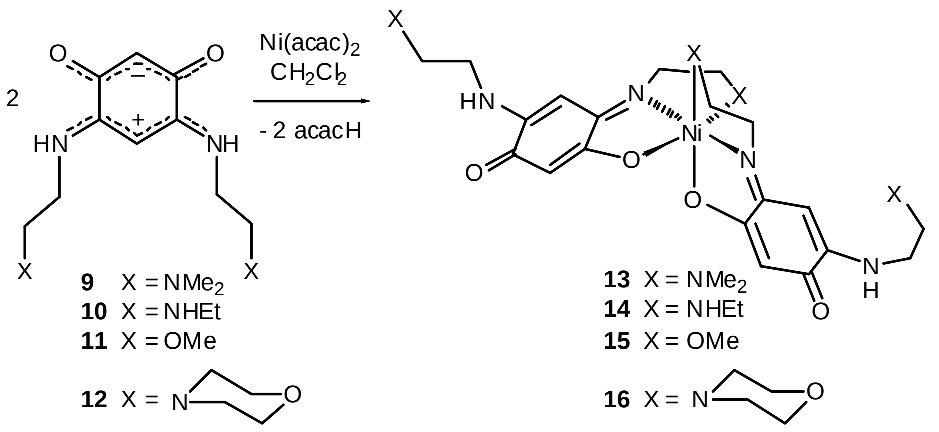
2. Results and Discussion

Ligands and Complexes. The *N*-substituted, 6π+6π electron zwitterionic benzoquinonemonoimine ligands **9-11** have been previously obtained from **7**·2HCl, via the parent zwitterion **8**, by using a new and efficient procedure which involved the first transamination reactions in quinonoid chemistry.[45,46] The new ligand **12** has now been prepared in a similar manner (Scheme 1).



Scheme 1. One pot synthesis of the zwitterions **9-12**.

These ligands react at room temperature with [Ni(acac)$_2$] in a 2:1 ligand/metal molar ratio to afford the octahedral complexes **13-16** in high yields (Scheme 2). Owing to their paramagnetism, compounds **13-16** were only characterized by mass spectrometry and elemental analysis. Single crystals of **13**·H_2O·CH_2Cl_2 suitable for X-ray diffraction were obtained by slow diffusion of pentane into a CH_2Cl_2 solution of the complex (which contained adventitious water) (see below Figure 1, Tables 1 and 2). Coordination of the pendant amino (ligands **9**, **10** and **12**) or ether (ligand **11**) function leads to hexacoordinated nickel centers.



Scheme 2. Reactions of ligands **9-12** affording the octahedral Ni(II) complexes **13-16**.

As shown in Figure 1, the octahedral geometry around the metal center in complex **13**$\cdot H_2O\cdot CH_2Cl_2$ results from the coordination of two tridentate, monometalated ligands, with their 2 electron donors imine nitrogen atoms N(1) and N(5) in mutual trans position and the covalently bound oxygens O(1) and O(3) are trans to the X donors N(3) and N(7) respectively.

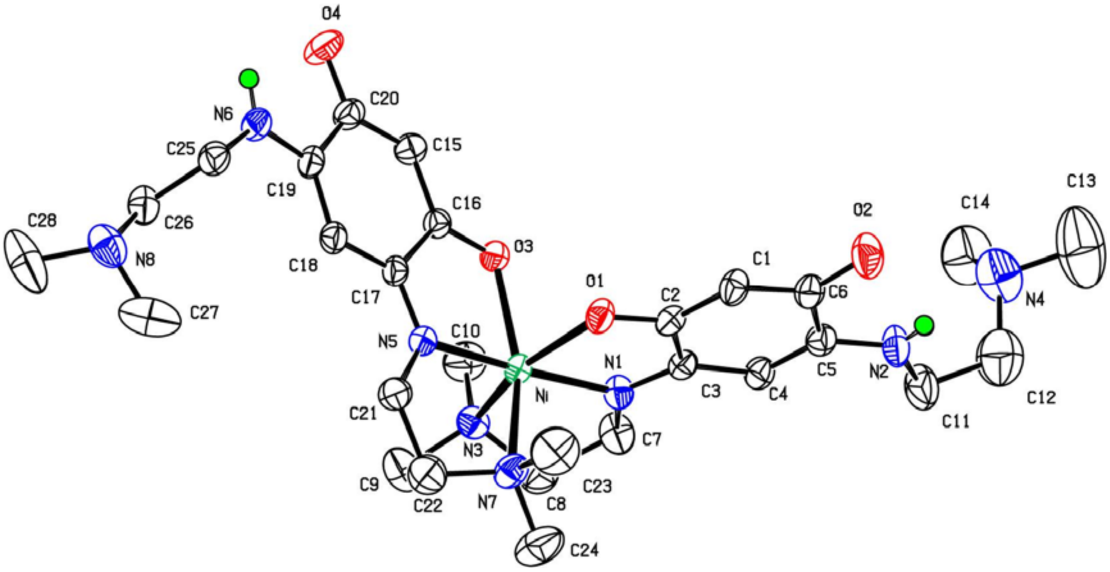


Figure 1. ORTEP view of the crystal structure of **13** in **13**$\cdot H_2O\cdot CH_2Cl_2$ (ellipsoids drawn at the 50% probability level).

The Ni-O and Ni-N bond distances in complex **13** (Table 1) are only slightly shorter than those of its zinc analog (corresponding values: Zn-N1 2.021(4), Zn-N3 2.330(5), Zn-N5 2.037(4), Zn-N7 2.442(5), Zn-O1 2.123(4), Zn-O3 2.134(4) (Å)),[46] which parallels the differences in metal radii (1.246 and 1.333 for Ni and Zn, respectively)[47]. Interatomic C-O, C-C and C-N distances within the quinonemonoimine core of complex **13** indicate an alternation of single and double bonds, which is consistent with a localized π system, as previously observed for the analogous zinc complex,[46] whereas in the free ligand[45] and all related crystallographic structures,[41,42,45,46,48]a perfectly delocalized form is present.

Examination of the crystal packing of complex **13**$\cdot H_2O\cdot CH_2Cl_2$ reveals intermolecular interactions (N2···O2 = 2.971(6) and N6···O1 = 2.897(6) Å) which lead to a one-dimensional wavelike chain arrangement in the solid (Figures 2 and 3). This arrangement also allows stabilizing π-π interactions between quinone rings, with a C15···C18 distance of 3.650(6) Å. A similar arrangement was also observed in its Zn(II) analog[45,46] However in the present case, the complex crystallized with a molecule of water and of dichloromethane. The H_2O molecules interact through hydrogen bonding, with O2···O(H_2O) and N4···O(H_2O) distances of 2.994(15) and 2.954(12) Å respectively. The CH_2Cl_2 molecules are placed between the wavelike chains, interacting with O4 (O4···Cl2 3.248(2) Å).

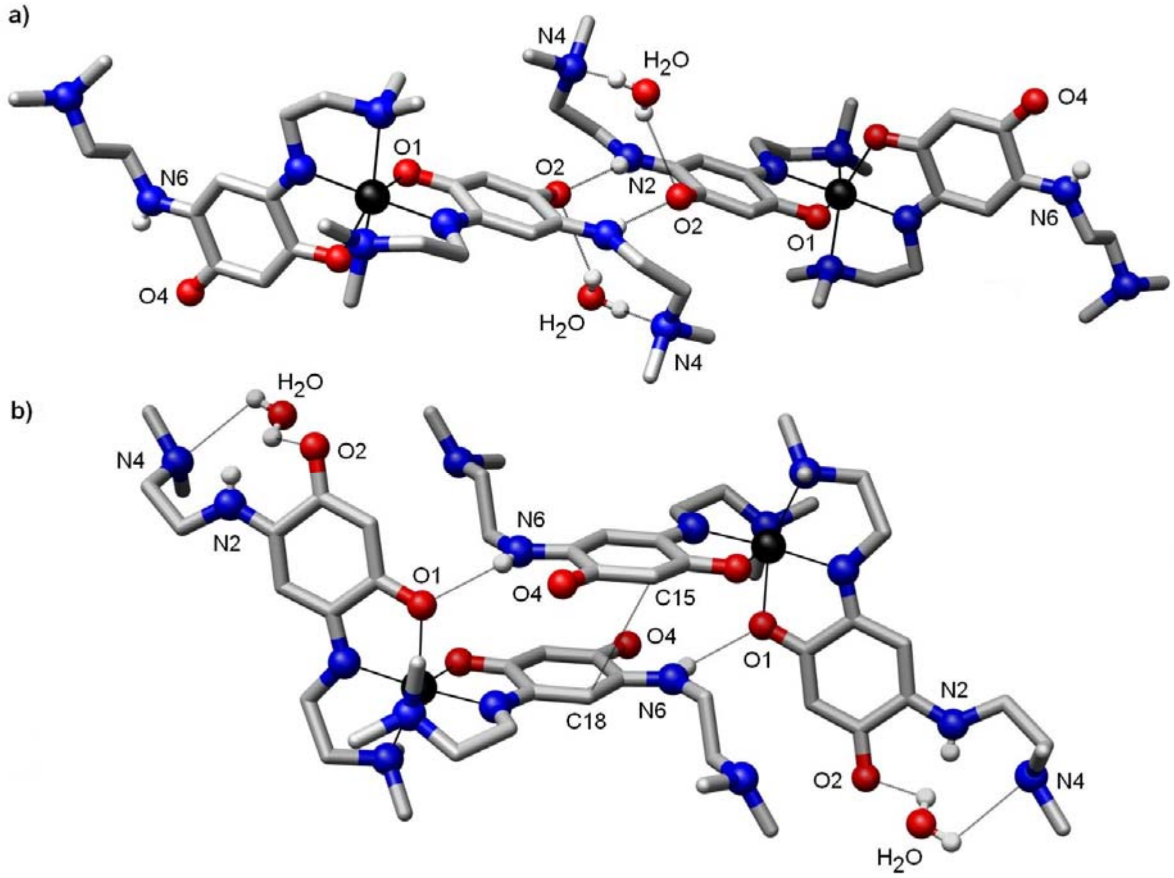


Figure 2. Hydrogen bonding in complex **13**·H_2O·CH_2Cl_2 (CH_2Cl_2 solvent molecules omitted for clarity). a) between N2 and O2, b) between N6 and O1. Color coding: nitrogen, blue; oxygen, red; nickel, black.

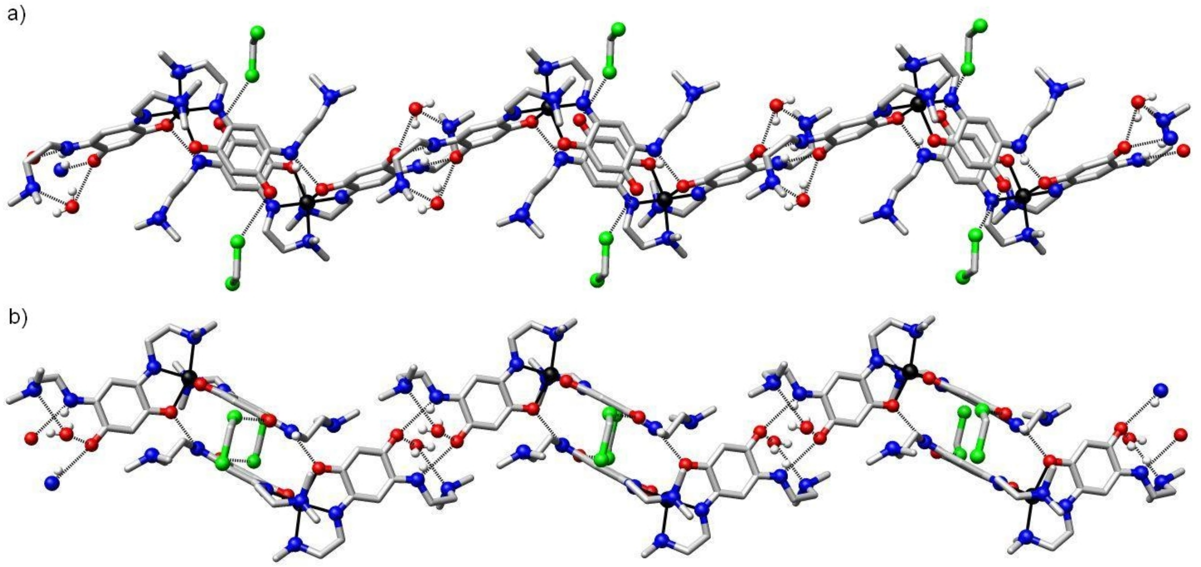
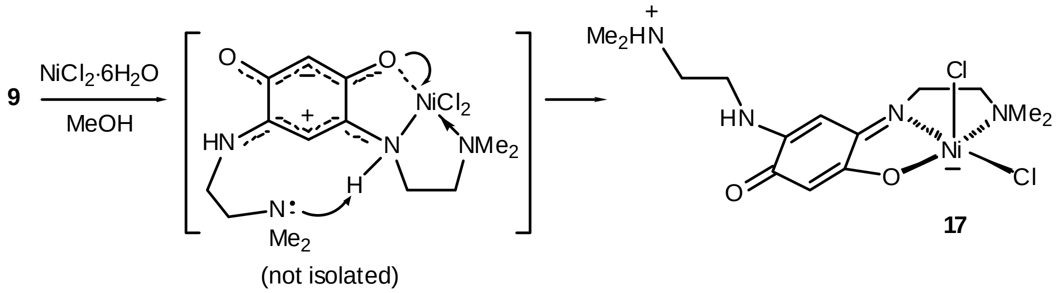


Figure 3. Views of the supramolecular array generated by **13**·$H_2O·CH_2Cl_2$ in the solid state. a) Top view, and b) side view. Color coding: nitrogen, blue; oxygen, red; chloride, green; nickel, black.

When ligand **9** was reacted with $NiCl_2·6H_2O$ in a 1:1 molar ratio at room temperature in MeOH, it afforded the mononuclear complex **17** (Scheme 3). Its molecular structure was determined by X-ray diffraction (Figure 4, Tables 1 and 2). Like its Zn(II) analog[45] complex **17** presents a zwitterionic structure, where the negative charge of the metalate moiety is balanced by the ammonium cation resulting from an intramolecular proton shift.



Scheme 3. Reaction of ligand **9** with $NiCl_2·6H_2O$ affording the pentacoordinated complex **17**. The negative charge shown for clarity on the Ni(II) center is of course partly delocalized on the ligands.

This zwitterionic complex contains only one tridentate ligand per nickel center and the pentacoordination about the metal results in a slightly distorted square base pyramidal geometry (Figure 4). The base is formed by the three ligand donor sites (N1, N3 and O1) and Cl2 while Cl1 completes the coordination sphere in the apical position of the pyramid. The nickel is at a distance of 0.3536(3) Å from the mean plane passing through N1, N3, O1 and Cl2.

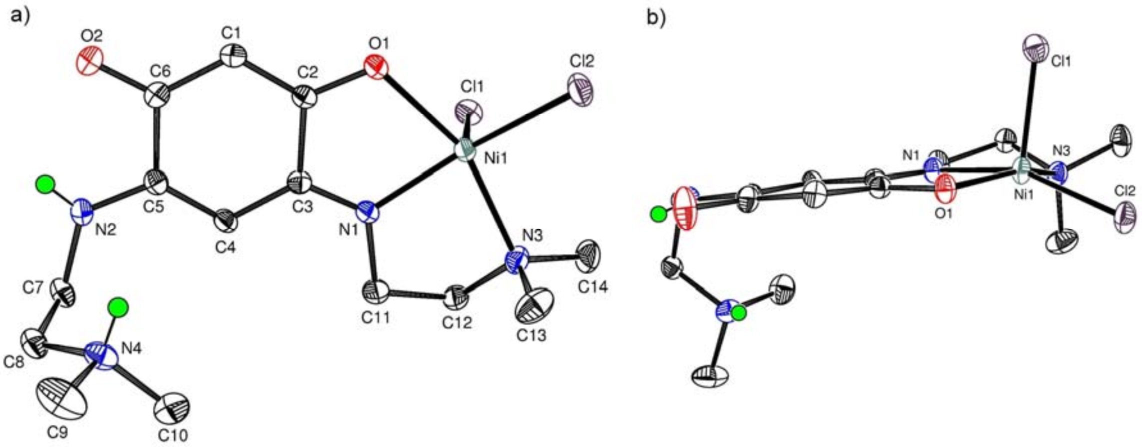


Figure 4. ORTEP view of the structure of **17** (ellipsoids drawn at the 50% probability level). a) view from the bottom of the square-base pyramid, and b) side view. Color coding: nitrogen, blue; oxygen, red; N-*H*, green; nickel, black. The C-*H* atoms are not shown.

As observed with its Zn(II) analog,[45] complex **17** forms in the solid state a pseudodimer which is stabilized by the N4-H···O1 interaction (N4···O1 = 2.810(2) Å) and π-π stacking with a C1···C4 distance of 3.542(3) Å (Figure 5). These pseudo-dimers are in turn organized along chains, in an alternate A-A'-A-A' manner, where dimer A is rotated by 88.92(4)° around the chain axis with respect to A' (Figure 6). There are no short contacts between these pseudo-dimers.

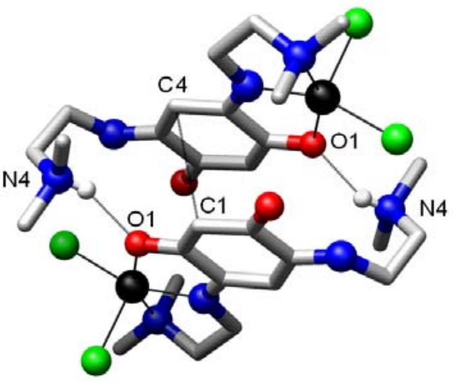


Figure 5. Hydrogen bonding in the pseudo-dimers formed by the zwitterionic Ni(II) complex **17** in the solid state. Color coding: nitrogen, blue; oxygen, red; chloride, green; nickel, black.

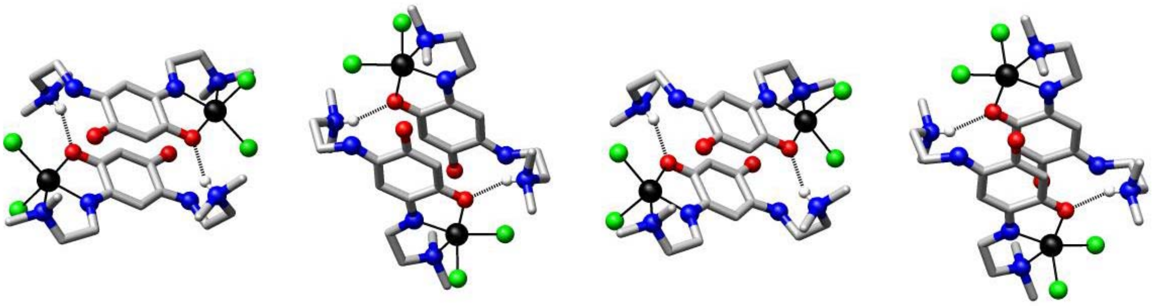


Figure 6. View of the array generated by the pseudo-dimers formed by the zwitterionic Ni(II) complex **17** in the solid state. Color coding: nitrogen, blue; oxygen, red; chloride, green; nickel, black.

Table 1. Selected bond distances (Å) in complexes **13**·H_2O·CH_2Cl_2 and **17**

	13·H_2O·CH_2Cl_2	**17**
Ni-N1	2.001(4)	1.975(1)
Ni-N3	2.238(4)	2.138(1)
Ni-N5	1.989(4)	
Ni-N7	2.264(4)	
Ni-O1	2.105(3)	2.142(1)
Ni-O3	2.116(3)	
Ni-Cl1		2.3337(5)
Ni-Cl2		2.3037(5)
O1-C2	1.284(5)	1.289(2)
C2-C1	1.380(6)	1.373(2)
C1-C6	1.407(7)	1.422(2)
C6-O2	1.256(6)	1.240(2)
N1-C3	1.299(6)	1.295(2)
C3-C4	1.422(6)	1.420(2)
C4-C5	1.366(7)	1.371(2)
C5-N2	1.337(6)	1.343(2)
C2-C3	1.506(6)	1.511(2)
C5-C6	1.511(7)	1.514(2)

Table 2. Selected bond angles (°) in complexes **13**$\cdot H_2O\cdot CH_2Cl_2$ and **17**

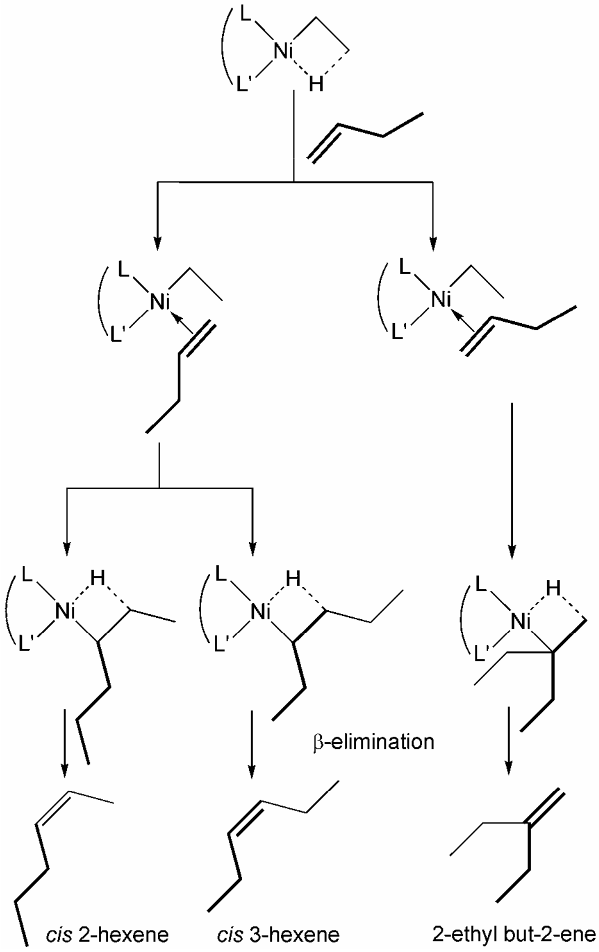
	13$\cdot H_2O\cdot CH_2Cl_2$	**17**
N5-Ni-N1	175.7(1)	
N5-Ni-O3	78.5(1)	
N1-Ni-O3	100.6(1)	
N5-Ni-O1	97.4(1)	
N1-Ni-O1	78.3(1)	77.96(5)
O1-Ni-O3	86.7(1)	
N5-Ni-N7	79.3(2)	
N1-Ni-N7	101.0(2)	
O3-Ni-N7	156.6(1)	
O1-Ni-N7	89.0(2)	
N5-Ni-N3	104.6(2)	
N1-Ni-N3	79.6(2)	81.58(6)
O1-Ni-N3	156.9(1)	156.73(5)
N3-Ni-N7	101.7(2)	
Cl1-Ni-Cl2		103.43(2)
Cl1-Ni-N1		97.78(4)
Cl2-Ni-N1		157.78(5)
Cl2-Ni-O1		98.28(3)
Cl2-Ni-N3		96.47(4)
Cl1-Ni-N3		95.79(4)
Cl1-Ni-O1		98.15(4)

3. **Catalytic Oligomerization of Ethylene**

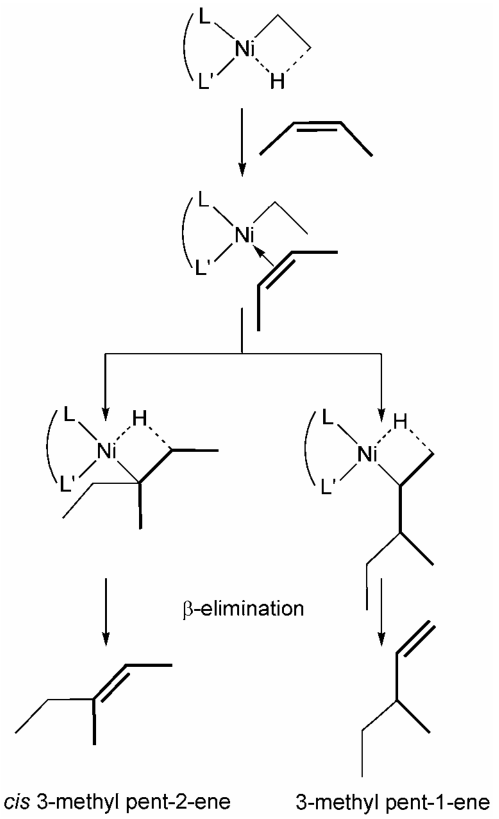
The precatalysts **13-17** have been tested in the presence of variable amounts of $AlEtCl_2$ or MAO as cocatalyst and showed high activities for the dimerization and trimerization of ethylene (Tables 3 and 4).The results were compared with those obtained with $NiCl_2(PCy_3)_2$, a typical α-olefin dimerization catalyst.[49,50]

It was interesting to determine the fractions of the different C_6 oligomers formed by chain growth or by reinsertion of 1-butene or 2-butene (Tables 5 and 6). Depending on the nature of their insertion (2,1- or 1,2-insertion) and on which C-H bond undergoes agostic interaction with the metal,[51-54] two schemes can explain the formation of *cis*- and *trans*-2-hexene, *cis*- and *trans*-3-hexene and 2-ethylbut-2-ene from 1-butene (Scheme 4) and the formation of *cis*- and *trans*-3-methylpent-2-ene and 3-methylpent-1-ene from 2-butene (Scheme 5). 1-Hexene is formed by a chain growth mechanism its Ni-catalyzed isomerization leads to 2-hexene and 3-hexene.[55]

A comparison of the various catalytic results should indicate the influence of (*i*) the nature of the donor function in the complexing ligand arm, (*ii*) the increase in metal coordination number resulting from the presence of the complexing arm, by comparison with the properties of **4**, (*iii*) the metal coordination geometry, (*iv*) the nature of the cocatalyst and (*v*) the lifetime of the catalyst.



Scheme 4. Hexenes resulting from the reinsertion of 1-butene. The stereochemical information is not illustrated: agostic interactions with diastereotopic CH_2 protons afford the cis or trans isomers.



Scheme 5. Pentenes resulting from the reinsertion of 2-butene. The stereochemical information is not illustrated.

(i) Influence of the donor function in the arm. Complexes **13-16** display hexacoordinated geometry around the metal center, with the ligand coordinating arm endowed with different donor functions. Precatalysts **13-15** afforded similar results with $AlEtCl_2$, with turnover frequency (TOF) values between 24300 and 24400 or between 35600 and 37200 mol C_2H_4/mol Ni·h, obtained with 6 or 10 equiv of cocatalyst, respectively (Table 3). Complex **16** showed a slightly lower activity (23000 mol C_2H_4/mol Ni·h with 10 equiv of $AlEtCl_2$). The selectivities for C_4 olefins observed with **13-16** were very similar and close to 89% or 82% in the presence of 6 or 10 equiv $AlEtCl_2$, respectively. However the selectivities for α-butene were lower than 9%.

With MAO as cocatalyst, the activities and selectivities of **13-15** were of similar orders of magnitude. Their activities were in the range 1300-2900 mol C_2H_4/mol Ni·h with 100 equiv of MAO, 7400-10300 with 200 equiv and the activity of **13** was found to be 14600 mol C_2H_4/mol Ni·h in the presence of 400 equiv MAO (Table 4). The selectivities for C_4 olefins were nearly 92% with 100 equiv and 85% for 200 equiv of MAO. With **13-15,** the selectivity for 1–butene was up to 68% with 100 equiv and 47% with 200 equiv MAO. Under these conditions, precatalyst **16** showed a higher activity but a lower selectivity in C_4 products and 1-butene than **13-15**.

A comparison between the four different functions available in the complexing arm shows that with both cocatalysts, the tertiary amine (precatalyst **13**), the secondary amine (precatalyst **14**) and the ether function (precatalyst **15**) led to similar catalytic results in ethylene oligomerization but the morpholine function (precatalyst **16**) led to a less active catalyst with $AlEtCl_2$ but a more active catalyst with MAO.

(ii) Influence of the Ligand Coordinating Arm. In contrast to **4**, complexes **13-17** have a coordinating arm which could display either static chelation or potentialy hemilabile behavior and therefeore influence the catalytic results. A comparison of the results obtained with **4** and **13-16**, in which the nickel center is coordinated by two ligands, is provided in Table 3. The activity of **4** (28500 and 45000 mol C_2H_4/mol Ni·h with 6 and 10 equiv of $AlEtCl_2$, respectively) and its selectivity for 1-butene were higher (14%) than those of **13-16**. However the selectivity for C_4 olefins was only 51% with **4** but up to 90% with **13-16**. This suggests that the presence of the coordinating arm in the 18 electron complexes **13-16** disfavors both the insertion of ethylene and the reinsertion mechanism which leads to the C_6 oligomers (see below).

(iii) Influence of the Coordination Geometry of the Metal. One of the objectives of the study was to determine the influence on the catalytic properties of hexacoordination in complexes with two tridentate benzoquinonemonoimine ligands and of pentacoordination in complexes containing only one benzoquinonemonoimine ligand and two chlorides. This can be done by comparing the performances of compounds **13** and **17**. Precatalyst **17** led to higher activities than **13** with $AlEtCl_2$ or MAO as cocatalyst, up to 48200 mol C_2H_4/mol Ni·h with $AlEtCl_2$ and 20300 mol C_2H_4/mol Ni·h with MAO (Table 4). In the presence of MAO or $AlEtCl_2$, the most active precatalyst in the series was **17**. The difference of activity between **17** and **13** could be due to an easier generation of the active species by nickel alkylation in the former case than with **13** where it probably requires the loss of a chelating *N,O* ligand. However, its selectivity for C_4 products and for 1-butene was lower than with **13**.

The catalyst ability to reinsert the primary C_4 products has a clear impact on product selectivity (Schemes 4 and 5). Data in Table 5 show that the fraction of branched C_6 oligomers formed from 2-butene was *ca*. 60% for **17** and *ca*. 53% for **13** with $AlEtCl_2$. A similar observation was made with MAO as cocatalyst. Consequently, precatalyst **17**, which is more active than **13** and reinserts 2-butene more readily than **13** to form C_6 products, leads to a lower selectivity for butenes.

(iv) Influence of the Cocatalyst. The use of $AlEtCl_2$ or MAO as cocatalyst influenced the catalytic results presented in Tables 3 and 4: the activities (up to 48200 mol C_2H_4/mol Ni·h) were higher with $AlEtCl_2$ as cocatalyst than with MAO, but MAO led to a higher selectivity for C_4 olefins (94% for **14**, with 100 equiv MAO). The precatalysts activated by $AlEtCl_2$ afforded strongly isomerising systems so that the fraction of 2-butene is very high (up to 95%). The reinsertion of 2-butene to form C_6 oligomers being more difficult than that of 1-butene, this explains the high selectivity in C_4 olefins. In contrast, MAO associated with **13-17** favored chain growth, as indicated by the quantities of 1-butene (up to 68%), 1-hexene (up to 20%), 2- and 3-hexenes (up to 61%) and C_8 oligomers (up to 9%) and led to a higher selectivity in C_4 olefins than $AlEtCl_2$.

The amount of cocatalyst has an important influence on the catalytic results, in particular with MAO. Increasing the amounts of MAO resulted in increased activity for **13-17** but decreased selectivity in both 1- and 2-butenes (Table 4). Reinsertion of 1-butene results in the formation of higher oligomers (the selectivity for 1-butene decreased from 49% to 24% with **13** for example). The increased percentage of C_6 oligomers from 2-butene (from 11% with 100 equiv. of MAO to 32% with 400 equiv. with **13** for example) shows that the reinsertion of 2-butene is also favored by increasing amounts of MAO.

(v) Lifetime of the Catalyst. To study the lifetime of the catalysts, complex **17**, the most active precatalyst, was tested with 10 equiv. of $AlEtCl_2$ with a reaction time increased to 200 minutes. The robustness of the catalyst was indicated by a constant activity during catalysis (the consumption of C_2H_4 was constant, no plateau of activity was observed and the final activity was 20500 mol C_2H_4/mol Ni·h). Selectivities were similar to those observed under standard conditions (Table 3).

4. Conclusion

New Ni(II) complexes have been synthesized with tridentate zwitterionic benzoquinonemonoimine ligands. The complexation with 2 equiv of the ligands **9**, **10, 11** and **12** led to the formation of **13**, **14**, **15** and **16**, respectively, with a hexacoordinated nickel center and the reaction of 1 equiv of **9** with $NiCl_2·6H_2O$ afforded the zwitterionic complex **17** with a pentacoordinated nickel center.

The precatalyst **13-17** have been tested in oligomerization of ethylene with different amounts of $AlEtCl_2$ or MAO as cocatalyst. The results showed that $AlEtCl_2$ led to more active and less selective systems in α-olefins than MAO. Increasing amounts of MAO or $AlEtCl_2$ as cocatalyst resulted in more active but less selective systems. The influence of the complexing arm of **9-12** was evaluated by comparing **4** with **13-16**. It was found that its presence led to lower activities but better selectivity in C_4 oligomers because it disfavored butene reinsertion. The comparison of **13-16** showed that the different complexing functions of the arm have no significant consequences on the catalytic results. Only **16** showed higher activities and lower selectivities with MAO as cocatalyst and lower activities with $AlEtCl_2$ as cocatalyst than **13-15**. The influence of the geometry of the complexes has been determined by the comparison between **13** and **17** and it was found that pentacoordination favored the insertion of olefins and led to higher activity but lower selectivity.

Table 3. Comparative Catalytic Data for Complexes **13-17** in the Oligomerization of Ethylene with $AlEtCl_2$ as Cocatalyst.[a, b]

	$AlEtCl_2$ (equiv)	**Selectivity (mass %)**		**Productivity [g C_2H_4/(g Ni·h)]**	**TOF [mol C_2H_4/(mol Ni·h)]**	**α-olefin (C_4) (mol %)**	**k_α[c]**
		C_4	**C_6**				
13	6	88	12	11700	24400	5.8	<0.10
13	10	82	18	17700	37200	5.3	0.15
14	6	90	10	11600	24300	9.4	<0.10
14	10	80	20	17500	36900	6.3	0.16
15	6	89	11	11600	24300	8.3	<0.10
15	10	80	20	17000	35600	4.6	0.16
16	10	83	16	10900	23000	7.1	0.13
17	6	72	28	20600	43300	4.5	0.26
17	10	76	23	23000	48200	5.7	0.20
17[d]	10	76	24	10000	20500	6.2	0.22
4[42]	6	49	45	13500	28500	14.0	0.60
4	10	51	43	21500	45000	7.0	0.57
Ref[e]	6	59	34	27600	57800	11.2	0.38
Ref	10	65	31	24400	51500	9.8	0.32

[a] Conditions: T = 30 °C, 10 bar of C_2H_4, 35 min, $4 \cdot 10^{-5}$ mol Ni complex, solvent 12 mL of chlorobenzene and 3 ml of cocatalyst solution in toluene, or 10 of mL chlorobenzene and 5 ml of cocatalyst solution in toluene, for 6 or 10 equivalents of $AlEtCl_2$, respectively. [b] No C_8-C_{10} oligomers were detected. [c] k_α = hexenes (mol)/butenes (mol). [d] Reaction time = 200 min. [e] Ref: $NiCl_2(PCy_3)_2$.

Table 4. Comparative Catalytic Data for Complexes **13-17** in the Oligomerization of Ethylene with MAO as Cocatalyst.[a, b]

	MAO (equiv)	**Selectivity (mass %)**			**Productivity [g C_2H_4/(g Ni·h)]**	**TOF [mol C_2H_4/(mol Ni·h)]**	**α-olefin (C_4) (mol %)**	**k_α[c]**
		C_4	**C_6**	**C_8**				
13	100	92	7	<1	1400	2900	49	<0.10
13	200	87	14	2	3600	7600	47	0.11
13	400	65	29	5	7300	15400	24	0.30
14	100	94	5	<1	600	1300	61	<0.10
14	200	86	12	2	3500	7400	45	0.11
15	100	93	6	<1	1300	2700	68	<0.10
15	200	82	17	1	4800	10300	37	0.14
16	100	86	12	2	2400	5000	50	<0.10
16	200	69	26	5	6100	13000	28	0.25
16	400	63	29	7	8800	18500	22	0.32
17	100	77	21	2	5500	11600	27	0.18
17	200	71	24	5	7400	16100	22	<0.10
17	400	55	35	9	9700	20300	19	0.42
Ref[d]	200	74	18	8	600	1200	76	0.16
Ref	400	70	26	4	3000	6400	72	0.24

[a] Conditions: $T = 30$ °C, 10 bar of C_2H_4, 35 min, $4 \cdot 10^{-5}$ mol Ni complex; solvent 12 mL chlorobenzene and 4, 8 or 16 mL of cocatalyst solution in toluene for 100, 200 or 400 equivalents of MAO, respectively. [b] Traces of C_{10} oligomers were detected when using 400 equivalents of MAO. [c] k_α = hexenes (mol)/butenes (mol). [d] Ref: $NiCl_2(PCy_3)_2$.

Table 5. Catalytic Data and Distribution of the C_6 Alkenes for Complexes **13-17** in the Oligomerization of Ethylene using $AlEtCl_2$ as Cocatalyst.[a]

	$AlEtCl_2$ (equiv)	**Selectivity (mass %)**			
		1-hexene	**linear C_6[b]**	**C_6[c] from 1-butene**	**C_6[d] from 2-butene**
13	6	0	40	10	52
13	10	0	39	7	54
14	6	0	42	13	45
14	10	0	43	7	50
15	6	0	46	11	43
15	10	0	43	6	51
16	10	<1[e]	46	3	50
17	6	0	36	6	58
17	10	0	36	4	60

[a] Conditions: *T* = 30 °C, 10 bar of C_2H_4, 35 min, $4 \cdot 10^{-5}$ mol Ni complex, solvent 12 mL of chlorobenzene and 3 ml of cocatalyst solution in toluene, or 10 of mL chlorobenzene and 5 ml of cocatalyst solution in toluene, for 6 or 10 equivalents of $AlEtCl_2$, respectively. [b] Sum of 3-*cis*-hexene, 3-*trans*-hexene, 2-*cis*-hexene and 2-*trans*-hexene. [c] Corresponds to 2-ethyl-1-butene. [d] Sum of 3-methyl-1-pentene, 3-methyl-2-*cis*-pentene and 3-methyl-2-*trans*-pentene. [e] Only in this case was 1-hexene detected.

Table 6. Catalytic Data for Complexes **13-17** and Distributon of the C_6 Alkenes in the Oligomerization of Ethylene using MAO as Cocatalyst.[a]

	MAO (equiv)	**Selectivity (mass %)**			
		1-hexene	**linear C_6[b]**	**C_6[c] from 1-butene**	**C_6[d] from 2-butene**
13	100	18	58	13	11
13	200	9	61	13	20
13	400	5	50	13	32
14	100	20	54	12	14
14	200	9	59	12	20
15	100	20	58	11	9
15	200	7	57	13	23
16	100	10	57	13	20
16	200	6	52	12	30
16	400	4	51	11	34
17	100	5	54	12	29
17	200	4	51	11	36

17	400	4	50	11	35

[a] Conditions: $T = 30$ °C, 10 bar of C_2H_4, 35 min, $4 \cdot 10^{-5}$ mol Ni complex; solvent 12 mL chlorobenzene and 4, 8 or 16 mL of cocatalyst solution in toluene for 100, 200 or 400 equivalents of MAO, respectively. [b] Sum of 3-*cis*-hexene, 3-*trans*-hexene, 2-*cis*-hexene and 2-*trans*-hexene. [c] Corresponds to 2-ethyl-1-butene. [d] Addition of 3-methyl-1-pentene, 3-methyl-2-*cis*-pentene and 3-methyl-2-*trans*-pentene.

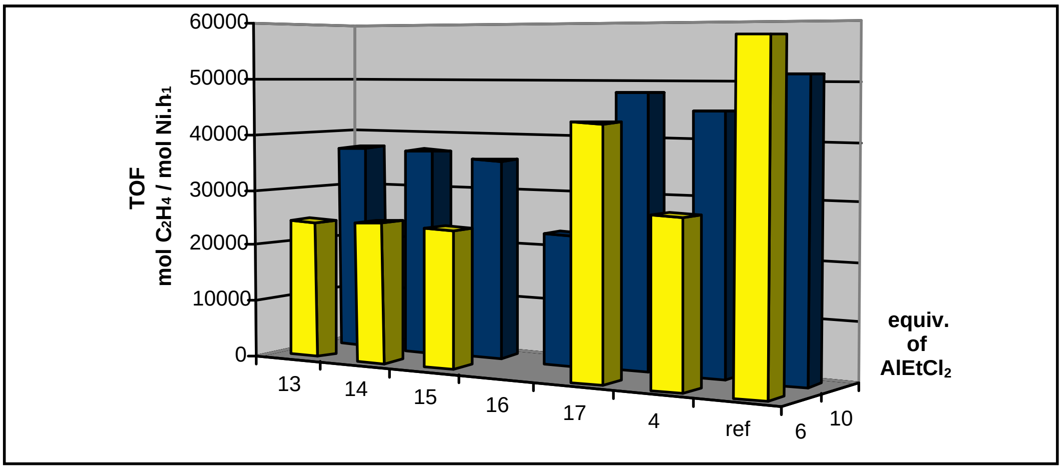


Figure 7. Catalytic activities of the complexes **13-17** and **4** in the oligomerization of ethylene using $AlEtCl_2$ as cocatalyst, Ref: $NiCl_2(PCy_3)_2$.

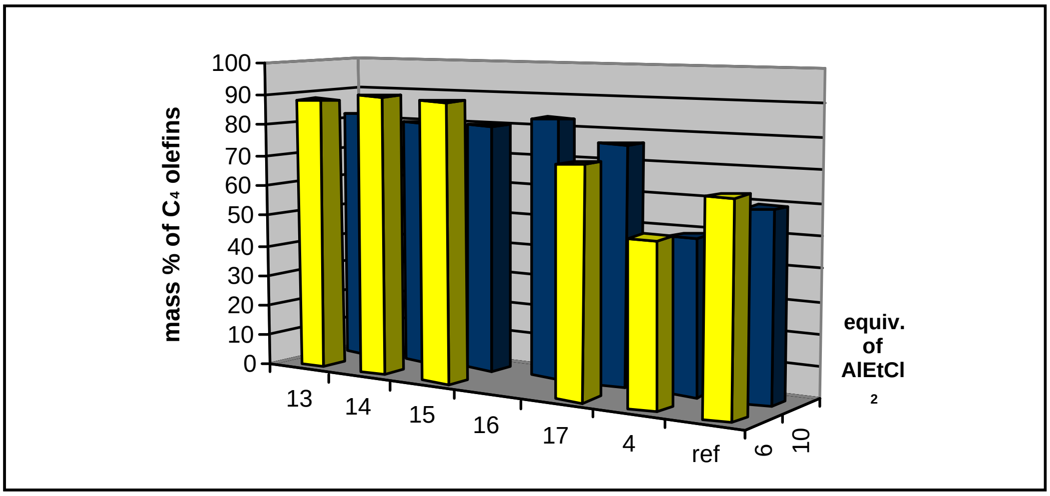


Figure 8. Selectivity of the complexes **13-17** and **4** for C_4 compounds

(1-butene and 2-butene), Ref: $NiCl_2(PCy_3)_2$

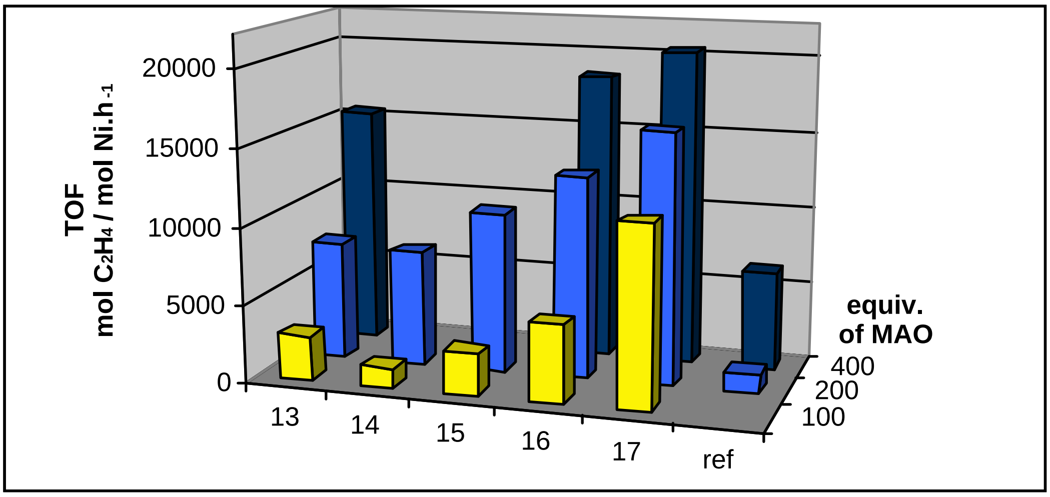


Figure 9. Catalytic activities of the complexes **13-17** in the oligomerization of ethylene using MAO as cocatalyst, Ref: $NiCl_2(PCy_3)_2$.

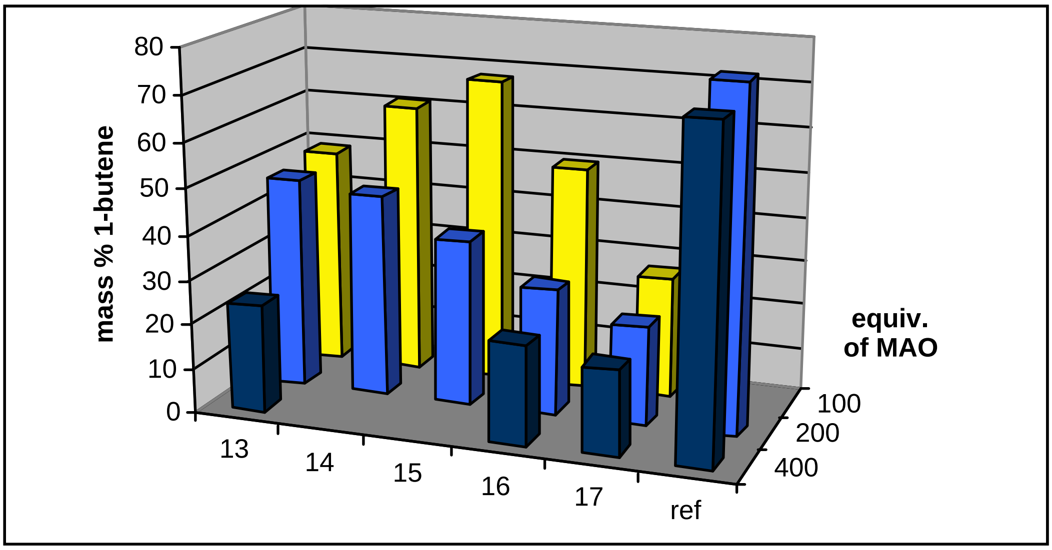


Figure 10. Selectivity of the complexes **13-17** for 1-butene, Ref: $NiCl_2(PCy_3)_2$

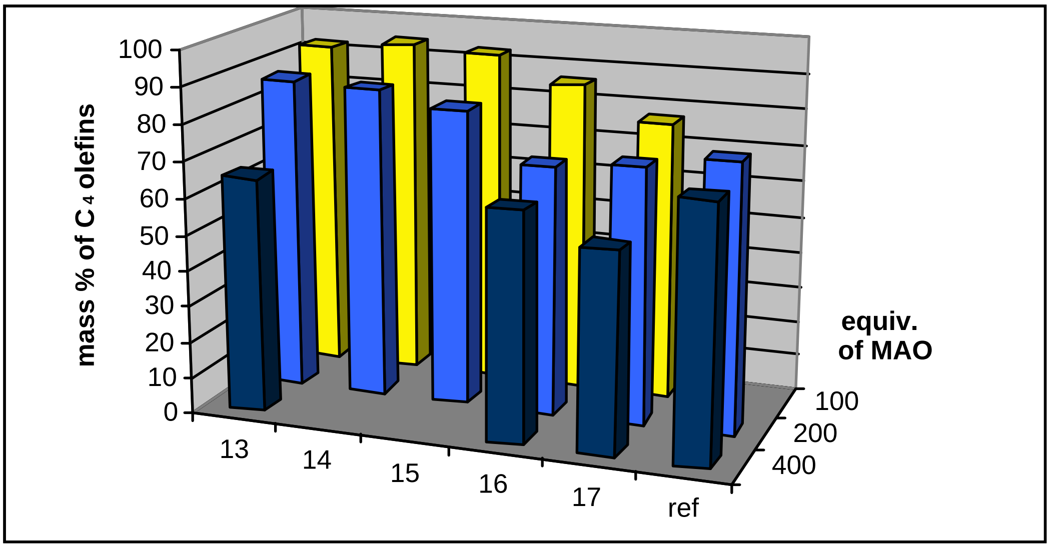


Figure 11. Selectivity of the complexes **13-17** for C_4 olefins (1-butene and 2-butene), Ref: $NiCl_2(PCy_3)_2$

5. Experimental Section

General consideration. All solvents were dried and freshly distilled under nitrogen prior to use using common techniques. All manipulations were carried out using Schlenk techniques. ^1H (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker AC300 instrument. MALDI-TOF mass spectra were recorded on a Biflex III Bruker mass spectrometer. Elemental analyses were performed by the “Service de Microanalyse, Université Louis Pasteur (Strasbourg, France)”. 4,6-Diaminoresorcinol dihydrochloride and the functional amines were commercially available. Ligands **9–11** have been prepared according to the literature.[45,46]

Ligand 12. To a stirred solution of diaminoresorcinol dihydrochloride (2.13 g, 10 mmol) in water (30 ml) was added 4-(2-aminoethyl)morpholine (9.76 g, 75 mmol) and the reaction mixture was extracted with CH_2Cl_2 after 2 h. The organic layer was collected, dried with $MgSO_4$, filtered and concentrated to ca. 30 ml. Pentane was added to the solution and the pale grey precipitate was isolated by filtration. Yield: 74%. Mass spect. (MALDI-TOF$^+$): m/z = 365.2 $[M+1]^+$; ^1H NMR (300 MHz, $CDCl_3$): δ = 2.50 (t, ^3J = 4.5 Hz, 8H, NCH_2CH_2O), 2.71 (t, ^3J = 6.1 Hz, 4H, $NHCH_2CH_2N$), 3.42 (t, ^3J = 6.1 Hz, 4H, $NHCH_2$), 3.73 (t, ^3J = 4.5 Hz, 8H, OCH_2), 5.10 (s, 1H, N$\cdots$C$\cdots$CH), 5.44 (s, 1H, O$\cdots$C$\cdots$CH), 8.48 (br s, 2H, NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 39.48 (s, NCH_2CH_2O), 53.29 (s, $NHCH_2CH_2N$), 55.42 (s, $NHCH_2$), 66.84

(s, OCH_2), 81.27 (s, $\mathrm{N}\overset{\cdots}{-}\mathrm{C}\overset{\cdots}{-}C$), 99.01 (s, $\mathrm{O}\overset{\cdots}{-}\mathrm{C}\overset{\cdots}{-}C$), 156.79 (s, $\mathrm{N}\overset{\cdots}{-}\mathrm{C}$), 172.23 (s, $\mathrm{O}\overset{\cdots}{-}\mathrm{C}$); Anal. Calcd. for $C_{18}H_{28}N_4O_4{\cdot}0.5H_2O$: C, 57.89; H, 7.83; N, 15.00. Found: C, 57.75; H, 7.80; N, 15.36.

Complex 13. Ligand **9** (1.12 g, 4.0 mmol) was dissolved in dichloromethane (200 ml) and 0.5 equiv solid $[Ni(acac)_2]$ (0.55 g, 2.0 mmol) was then added to the solution in one portion. After the solution was stirred at room temperature for 3 h, the solvent was concentrated to ca. 20 ml under vacuum and the red crystalline complex **13** was obtained by precipitation from a mixture of dichloromethane and pentane. Yield: 92%. Mass spect. (MALDI-TOF$^+$): *m/z* = 617.3[*M*+1]$^+$; Anal. Calcd. for $C_{28}H_{46}N_8NiO_4{\cdot}H_2O{\cdot}CH_2Cl_2$: C, 48.35; H, 7.00; N, 15.56. Found: C, 48.65; H, 7.12; N, 15.78.

Complex 14. The synthetic procedure was similar to that described for complex **13** but using ligand **10** instead of **9**. Yield: 88%. Mass spect. (MALDI-TOF$^+$): *m/z* = 617.3 [*M*+1]$^+$; Anal. Calcd. for $C_{28}H_{46}N_8NiO_4{\cdot}0.5H_2O\ {\cdot}0.5CH_2Cl_2$: C, 51.18; H, 7.23; N, 16.75. Found: C, 51.06; H, 7.28; N, 17.04.

Complex 15. The synthetic procedure was similar to that described for complex **13** but using ligand **11** instead of **9**. Yield: 91%. Mass spect. (MALDI-TOF$^+$): *m/z* = 565.2 [*M*+1]$^+$; Anal. Calcd. for $C_{24}H_{34}N_4NiO_8$: C, 51.00; H, 6.06; N, 9.91. Found: C, 50.91; H, 6.03; N, 9.85.

Complex 16. The synthetic procedure was similar to that described for complex **13** but using ligand **12** instead of **9**. Yield: 93%. Mass spect. (MALDI-TOF$^+$): *m/z* = 785.3 [*M*+1]$^+$; Anal. Calcd. for $C_{36}H_{54}N_8NiO_8{\cdot}0.5H_2O$: C, 54.42; H, 6.98; N, 14.10. Found; C, 54.37; H, 7.03; N, 13.91.

Complex 17. To a solution of ligand **9** (0.28 g, 1.0 mmol) in methanol (30 ml) was added 1 equiv $NiCl_2{\cdot}6H_2O$ (0.24 g, 1.0 mmol) and the reaction mixture was stirred for 3 h. Complex **17** was obtained as a purple crystalline solid by slow diffusion of ether into the reaction mixture. Yield: 71%. Ms (MALDI-TOF$^-$): m/z: 409.1 [M-1]$^-$; Anal. Calcd. for $C_{14}H_{24}Cl_2N_4NiO_2$: C, 41.02; H, 5.90; N, 13.67. Found: C, 40.81; H, 6.11; N, 13.33.

Oligomerization of Ethylene: All catalytic reactions were carried out in a magnetically stirred (900 rpm) 145 ml stainless steel autoclave. A 125 ml glass container was used to protect the inner walls of the autoclave from corrosion. All catalytic tests were started at 30 °C, and no cooling of the reactor was done during the reaction. After injection of the catalytic solution and of the cocatalyst under a constant low flow of ethylene, the reactor was pressurized to 10 bars. A temperature increase was observed which resulted solely from the exothermicity of the reaction. The 10 bar working pressure was maintained during the experiments through a continuous feed of ethylene from a reserve bottle placed on a balance to allow continuous monitoring of the ethylene uptake. In all of the catalytic experiments 4×10^{-2} mmol of Ni complex was used. The oligomerization products and remaining ethylene were only collected from the reactor at the end of the catalytic experiment. At the end of each test (35 min.) a dry ice bath, and in the more exothermic cases also liquid N_2, was used to rapidly cool down the reactor, thus stopping the reaction. When the inner temperature reached 0 ºC the ice bath was removed allowing the temperature to slowly rise to 10 ºC. The gaseous phase was then transferred into a 10 L polyethylene tank filled with water. An aliquot of this gaseous phase was transferred into a Schlenk flask, previously evacuated, for GC analysis. The products in the reactor were hydrolyzed in situ by the addition of ethanol (1 mL), transferred into a Schlenk flask, and separated from the metal complexes by trap-to-trap evaporation (20 °C, 0.3 mm Hg) into a second Schlenk flask previously immersed in liquid nitrogen in order to avoid any loss of product. For GC analyses, 1-heptene was used as an internal reference. $AlEtCl_2$ was used as cocatalyst, depending on the amount used, 2, 6 or 10 equiv, the required quantity of Ni(II) complex was dissolved in 14, 12 or 10 mL of chlorobenzene, respectively, and injected into the reactor. The cocatalyst solution, 1, 3 or 5 mL corresponding to 2, 6 or 10 equiv respectively, was then added. Therefore the total volume of the solution inside the reactor, for all the tests performed with $AlEtCl_2$, was of 15 mL. In the cases where MAO was used as cocatalyst, the Ni(II) complex was always dissolved in 12 ml of chlorobenzene and after injection of this solution, the desired amount of cocatalyst was added. The total volume of the solution inside the reactor at the beginning of each test was therefore dependant of the amount of cocatalyst used. Total volumes of 16, 20 and 28 ml correspond to 100, 200 and 400 equiv of MAO respectively.

Crystal Structure Determinations. Diffraction data were collected on a Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) (Table 7). Data were collected using phi-scans and the structures were solved by direct methods using the SHELX 97 software,[56,57] and the refinement was by full-matrix least squares on F^2. No absorption correction was used. All non-hydrogen atoms were refined anisotropically with H atoms introduced as fixed contributors ($d_{C\text{-}H}$ = 0.95 Å, U_{11} = 0.04). Crystallographic data (excluding structure factors) have been deposited in the Cambridge Crystallographic Data Centre as Supplementary publication n° CCDC 615435 and 615436. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

We thank the Centre National de la Recherche Scientifique (CNRS), the Ministère de l'Education Nationale et de la Recherche (Paris), the Institut Français du Pétrole (IFP), Clariant, and the European Commission (Palladium Network HPRN–CT-2002–00196 and COST program) for support. We also thank Dr. A. DeCian and Prof. R. Welter (ULP Strasbourg) for the crystal structure determinations and M. Mermillon-Fournier (LCC Strasbourg) for technical assistance.

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Chapitre II

Synthesis of Nickel Complexes with Bidentate *N,O* Type ligands and Application in the Catalytic Oligomerization of Ethylene

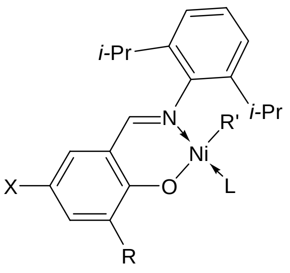
Abstract

The dinuclear complexes [Ni(μ-Cl)$_2${(4,5-dihydro-4,4-dimethyloxazol-2-yl)methanol}$_2$]$_2$Cl$_2$ **14** and [Ni(μ-Cl)$_2${(pyridin-2-yl)methanol}$_2$]$_2$Cl$_2$ **15** have been synthesized in high yields by reaction of $NiCl_2$ with 2 mol. equiv. of the ligands 4,5-dihydro-4,4-dimethyloxazol-2-yl)methanol **13** or (pyridin-2-yl)methanol, respectively. The reaction of $NiCl_2$ with 3 mol. equiv. of (pyridin-2-yl)methanol afforded in high yield the mononuclear, octahedral [Ni{(pyridin-2-yl)methanol}$_3$Cl$_2$] complex **17**. The reaction of **15** with NaH led to the deprotonation of one of the pyridine alcohol ligands to form the new complex [Ni{(pyridin-2-yl) methanol}{(pyridin-2-yl)methanolate}Cl] **20** in which the metal is coordinated by one pyridine alcohol and one pyridine alcoholate ligand. The crystal structures of the dinuclear, chloride-bridged octahedral complexes in **14**·C_6H_{12} and in **15**·$3CH_2Cl_2$ and of the mononuclear, octahedral complex **17** in **17**·CH_2Cl_2 have been determined by X-ray diffraction. In the latter case, intermolecular OH···Cl bonding interactions generate a centrosymmetric pseudo-dimer. Complexes **14**, **15** and **20** have been tested in ethylene oligomerization with $AlEtCl_2$ (Al/Ni ratios of 2, 4 or 6) or MAO (50, 100 or 200 equiv.) as cocatalysts under 10 bar of ethylene. Complex **15** in the presence of 6 equiv. of $AlEtCl_2$ proved to be the most active system with a turnover frequency (TOF) up to 187500 C_2H_4/(mol Ni·h). It was also the most selective for C_4 olefins (up to 79%) and for 1-butene (up to 79%) with 2 equiv of $AlEtCl_2$. Complex **15** with 200 equiv. of MAO was also the most active, with TOF up to 104300 C_2H_4/(mol Ni·h) under 30 bar of ethylene. It showed the highest selectivities for C_4 olefins (up to 94%) and 1-butene (up to 64%) with only 50 equiv. of MAO. The results showed that a decrease of the precatalyst concentration and an increase of the ethylene pressure lead to a system which is more efficient and selective for C_4 olefins and 1-butene.

1. Introduction

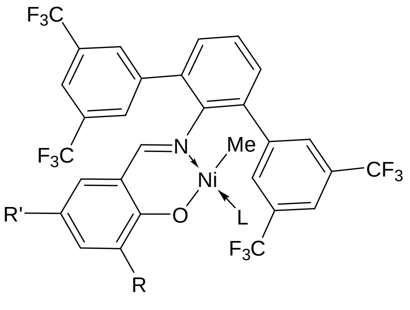
Olefin polymerization catalyzed by late transition metal complexes has been intensively developed for the production of low-density polyethylene (LDPE) and high-density polyethylene (HDPE).[1-5] However, the discovery of the « nickel effect » in catalytic olefin chemistry highlighted the oligomerizing character of nickel catalysts which favour chain transfer over chain growth.[6,7] The high industrial demand for linear α-olefins (LAO), particularly in the C_4-C_{20} range, has emphasized the key role of nickel complexes as catalysts.[8-10] The use of heteroditopic ligands, including bidentate P,O ,[11,12] P,N [13] and N,O [14,15] type ligands, allows a fine tuning of the catalytic properties of their Ni(II) complexes in olefin oligomerization.

The high activity and selectivity in LAO of the SHOP process[16-18] has generated a considerable interest for nickel complexes with a P,O-type ligands in catalytic ethylene oligomerization.[11,19-24] This system, based on a neutral phenyl nickel complex, produces a Schulz-Flory mass distribution of the α-olefins and it has inspired the synthesis of numerous nickel catalysts with P,N-[25-27] and N,O-[28] type ligands. Neutral nickel catalysts with N,O-type ligands proved to be active for ethylene polymerization without cocatalyst and these include complexes described by Grubbs (type **1**),[14,15,29] Mecking[30-32] (type **2**) and others[33-37] with salicylaldimine ligands or by Brookhart with anilinotropone ligands (type **3**) or anilinoperinaphthenone ligands (type **4**).[38-40]



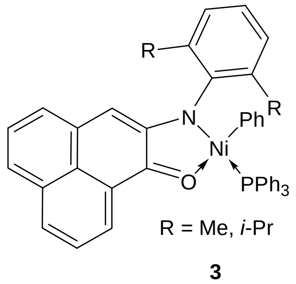
R = I, H, *t*-Bu, Ph,...
R' = Ph, Me
X = I, H, OMe, NO_2
L = PPh_3, Py, MeCN

1



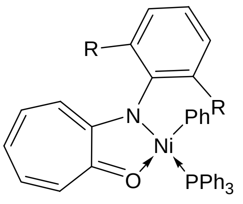
R = I, 9-anthryl
R' = I, H
L = Py, TPPTS, TPPDS, H_2N-PEG

2



R = Me, *i*-Pr

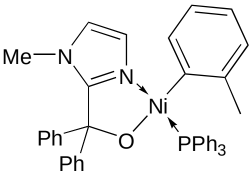
3



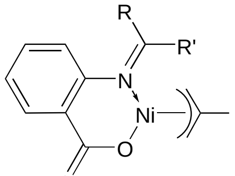
R = Me, *i*-Pr, *t*-Bu, Ph, F, Br, CF_3

4

Other neutral nickel complexes with anionic N,O^- ligands, such as the imidazole-alcoholate complexes **5**,[41] iminocarboxamide complexes **6**[42] and 2-(alkylideamino)benzoate complexes **7**,[43] form active catalysts for the oligomerization or polymerization of ethylene without any cocatalyst. In these cases, ethylene insertion in the Ni-aryl or Ni-alkyl bond represents the first step of the reaction and is followed by β-H migration, leading to olefin elimination and formation of a nickel-hydride complex, which is the active species.

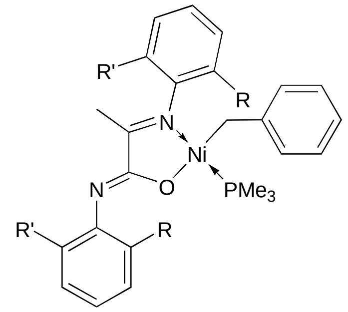


5



R = H, Et
R' = Et, *t*-Bu

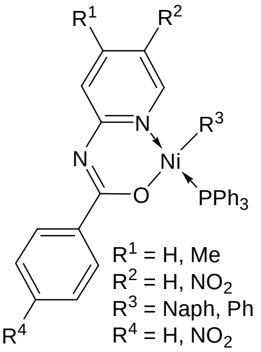
7



R = R' = Me, Et, *i*-Pr

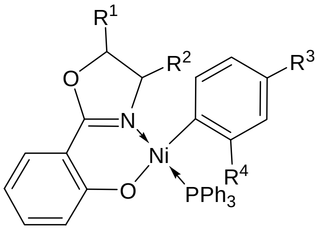
6

However, many nickel precatalysts with N,O-type ligands have to be activated with a cocatalyst, such as alkylaluminiums or $B(C_6F_5)_3$. This is the case with the ligands salicylaldimines,[44-49] N-(2-pyridyl)benzamides (in **8**),[50] 2-oxazolinylphenolates (in **9**),[51,52] or β-ketiminates (in **10**).



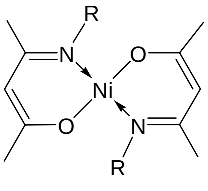
R^1 = H, Me
R^2 = H, NO_2
R^3 = Naph, Ph
R^4 = H, NO_2

8



R^1 = H, Me
R^2 = H, Ph
R^3 = H, Me
R^4 = H, Me

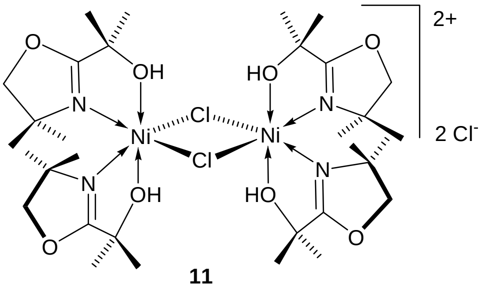
9

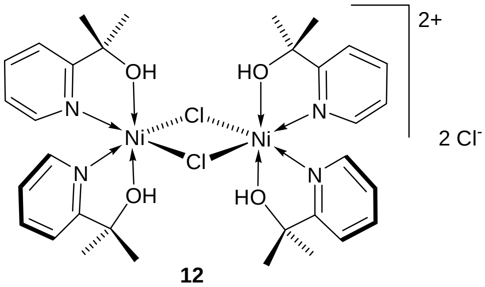


R = Ph, 2-Me-Ph, *t*-Bu

10

We reported recently the synthesis of Ni(II) precatalysts with zwitterionic N,O-benzoquinonemonoimine-type ligands which presented good activities in oligomerization of ethylene with $AlEtCl_2$ or MAO as a cocatalyst. They favoured the dimerization and trimerization of ethylene and the formation of the C_6 olefins resulted from chain growth and/or reinsertion of 1-butene or 2-butene.[53] We have also used pyridine alcohols and oxazoline alcohols to synthesise the Ni(II) complexes **11** and **12** of which the dinuclear structures were established by X-ray diffraction.[54]

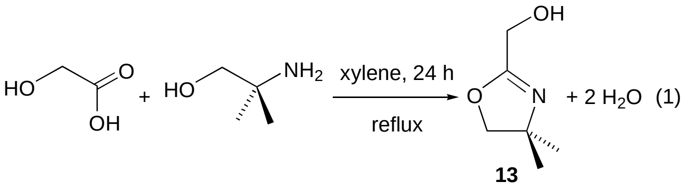

11


12

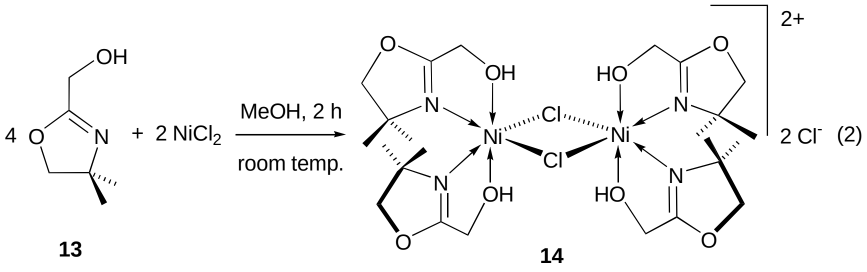
Even in the presence of small amounts of $AlEtCl_2$ or MAO as a cocatalyst, these complexes showed high activities in ethylene oligomerization (turnover frequencies (TOF) up to 174300 mol C_2H_4/(mol Ni·h) with only 6 equiv. of $AlEtCl_2$), giving mostly C_4 olefins and 1-butene. Since relatively small changes in the substitution pattern of the chelating ligand may have significant consequences on the structure and the catalytic properties of their Ni(II) complexes,[13] we wished to evaluate the possible influence of the *gem*-dimethyl substituents of the alcohol ligands and prepared the new Ni(II) complexes **14** and **15** to evaluate them for the catalytic oligomerization of ethylene, with MAO or $AlEtCl_2$ as cocatalyst.

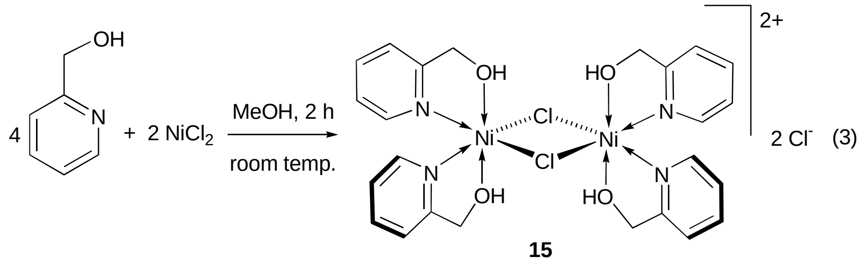
2. Results and discussion

The (4,5-dihydro-4,4-dimethyloxazol-2-yl)methanol ligand **13** was prepared according to the literature[55] by double condensation of glycolic acid with 2-amino-2-methyl-1-propanol in xylene at reflux during 24 h [eqn (1)]. Additional characterizations by ^1H NMR and $^{13}C\{^1H\}$ NMR spectroscopy are reported in the Experimental.



Complexes **14** and **15** were synthesized at room temperature by reaction of a methanol solution of $NiCl_2$ with 2 mol. equiv. of ligand **13** or of (pyridin-2-yl)methanol, respectively, and after work-up, they were isolated as green powders in almost quantitative yields [eqn (2) and (3)].





These two dicationic complexes are paramagnetic and have been characterized by IR and elemental analysis and X-ray diffraction. The dinuclear centrosymmetric structures of **14**·C_6H_{12} and **15**·$3CH_2Cl_2$ are shown in Figures 1 and 2 and selected bond distances and bond angles are given in Table 1.

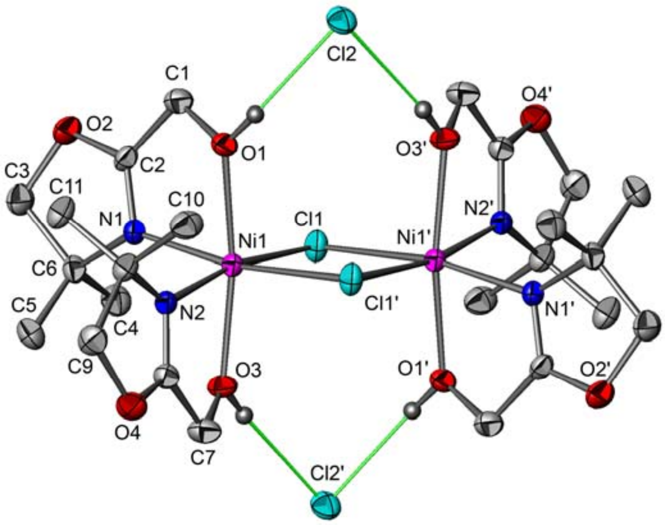


Fig. 1 ORTEP view of the structure of the oxazoline alcohol complex **14** in **14**·C_6H_{12} with thermal ellipsoids drawn at the 50% probability level, symmetry operation generating equivalent atoms: -x, -y, -z+1.

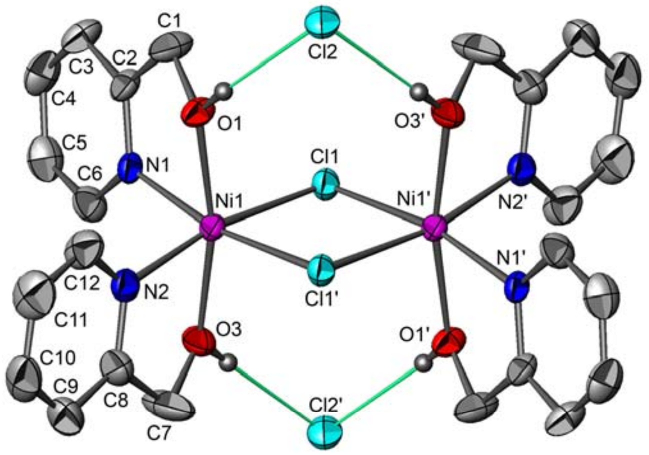


Fig. 2 ORTEP view of the structure of the pyridine alcohol complex **15** in **15**·3CH_2Cl_2 with thermal ellipsoids drawn at the 50% probability level, symmetry operation generating equivalent atoms: -x, -y+1, -z.

Table 1. Selected bond distances and bond angles in **13**·C_6H_{12} and in **14**·1.5CH_2Cl_2.

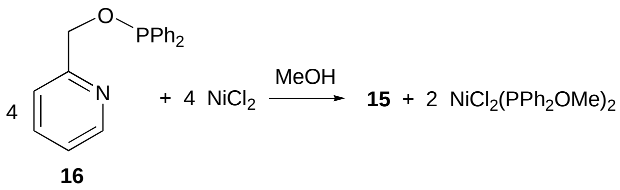
Distances (Å)	**13**	**14**
Ni1-Cl1	2.397(2)	2.4195(14)
Ni1-Cl1′	2.404(2)	2.409(2)
Ni-O1	2.107(5)	2.062(4)
O1-C1	1.420(6)	1.431(7)
C1-C2	1.489(9)	1.51(1)
C2-O2	1.338(6)	_
C2-N1	1.270(8)	1.330(8)
N1-Ni1	2.061(4)	2.062(5)
Ni1-O3	2.117(5)	2.059(5)
O3-C7	1.421(6)	1.433(9)
C7-C8	1.49(1)	1.50(1)
C8-O4	1.340(6)	_
C8-N2	1.269(8)	1.334(8)
N2-Ni1	2.064(4)	2.064(4)
Ni-Cl2	4.713(3)	4.535(2)
Ni-Cl2′	4.702(3)	4.552(2)
Angles (°)	**13**	**14**
O1-Ni1-N1	77.51(17)	77.83(18)
O1-Ni1-Cl1	93.79(12)	95.44(13)
O1-Ni1-Cl1′	92.52(10)	93.39(13)
O1-Ni1-O3	171.46(17)	167.61(17)
O1-Ni1-N2	96.51(18)	94.13(18)
N1-Ni1-Cl1	91.51(14)	88.53(14)
N1-Ni1-Cl1′	169.79(12)	168.85(14)
N1-Ni1-N2	92.89(17)	98.0(2)
N1-Ni1-O3	96.65(19)	93.8(2)

N2-Ni1-Cl1	169.45(12)	89.35(15)
N2-Ni1-Cl1′	90.48(12)	169.36(13)
O3-Ni1-Cl1	92.57(12)	93.41(13)
O3-Ni1-Cl1′	93.51(12)	95.95(15)
Cl1-Ni1-Cl1′	86.84(8)	85.48(5)
Ni1-Cl1-Ni1	93.16(8)	93.90(5)
N2-Ni1-O3	77.40(18)	77.87(19)
O1-C1-C2	106.3(4)	109.1(6)
C1-C2-N1	123.1(5)	116.8(6)
C2-N1-Ni1	114.0(4)	115.8(4)
Ni1-O3-C7	113.8(4)	113.7(4)
O3-C7-C8	106.4(5)	109.6(7)
C7-C8-N2	123.3(5)	115.9(6)
C8-N2-Ni1	113.6(4)	116.1(4)

The dications in **14**·C_6H_{12} and in **15**·3CH_2Cl_2 form centrosymmetric dimers and their Ni(II) centres adopt a distorted octahedral coordination geometry, very similar to those of **11** and **12** which contain *gem*-dimethyl substituents in α-position to the OH donor.[54] Each Ni(II) is surrounded by two N,O chelates, whose N and OH donor groups are cis and trans to each other, respectively, and by two bridging chlorides which are trans to the nitrogen atoms. The crystal structure of **15**·3CH_2Cl_2 revealed two independent but almost identical molecules in the unit cell. In both **14** and **15**, the two chloride counter anions do not interact with the metal centres and are at 4.702(3) and 4.713(3) Å for **14** and 4.535(2) and 4.552(2) Å for **15** from a Ni(II) centre. However, interactions between the chloride counter anions and the hydrogen atoms of the OH functions are observed, with O1-H1···Cl2 and O3'-H3'···Cl2 distances of 2.984(4) and 2.994(4) Å (Table S1†), for **14** and 2.993(4) and 2.972(5) Å (Table S2†), for **15**, respectively (calculated O1-H1···Cl2 and O3'-H3'···Cl2 angles of 158 and 158 ° for **14** (Table S1†) and 157 and 162 °, for **15**, respectively (Table S2†). As shown by the O1-Ni-O2 angle of 171.7(2)° for **14**·C_6H_{12} against 168.2(2)° for **11**, the metal centre in **14**·C_6H_{12} has a coordination geometry less distorted than in **11**. Compared to **11**, **14**·C_6H_{12} presents slightly shorter Ni-N and Ni-Cl distances.

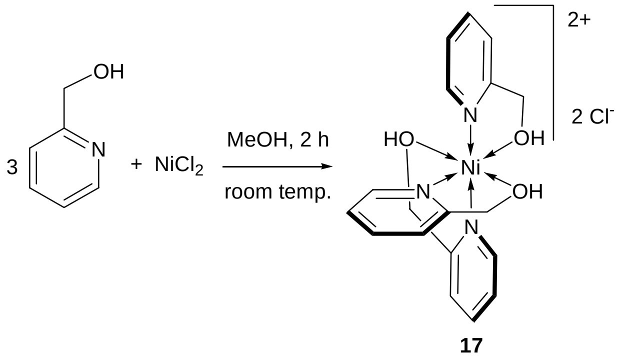
Complex **15** has similar structural characteristics to **12** and these will therefore not be discussed in detail. The structure of a nickel complex coordinated by two (pyridin-2-yl)methanol ligands has been described recently but the coordination of two water molecules led instead to a mononuclear structure with an octahedral nickel centre.[56]

Complex **15** has been obtained recently in a less convenient way by reaction of the phosphinitopyridine ligand **16** with $NiCl_2$ in MeOH. This reaction led to the cleavage of the P-O bond and formation of **15** and [$NiCl_2(PPh_2OMe)_2$] [eqn (4)].[57]



(4)

When $NiCl_2$ was reacted with more than 3 mol. equiv. of (pyridin-2-yl)methanol, the octahedral nickel complex **17** was formed quantitatively and isolated as a blue powder. The reaction of complex **15** with (pyridin-2-yl)methanol in methanol in a 1:2 ratio also led to the formation of this complex, as indicated by a colour change of the solution from green to blue [eqn (5)].



(5)

The crystal structure of **17**·CH_2Cl_2 has been determined by X-ray diffraction. An ORTEP view of the molecular structure is shown in Figure 3 and selected bond distances and bond angles are given in Table 2.

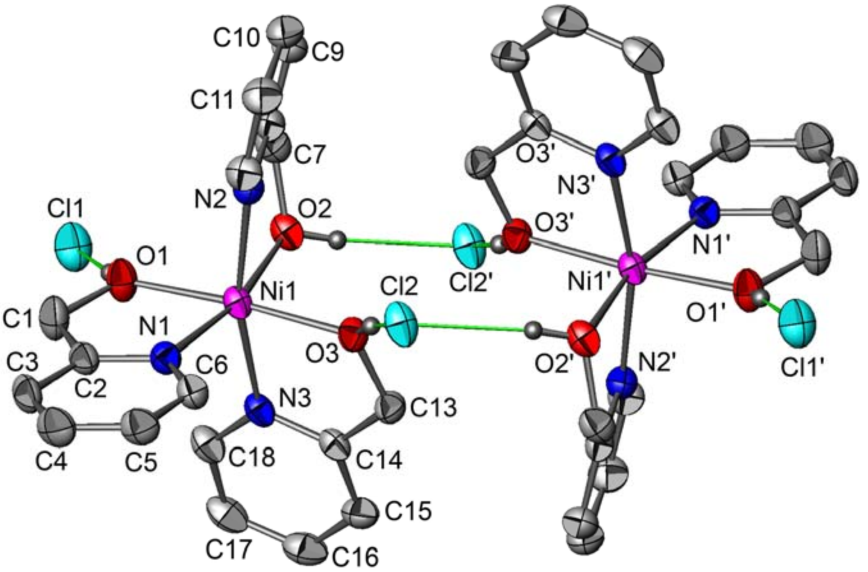


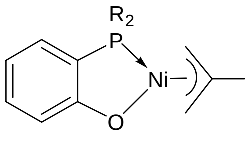
Fig. 3 ORTEP view of the structure of the oxazoline alcohol complex **17** in **17**·CH_2Cl_2 with thermal ellipsoids drawn at the 50% probability level, symmetry operation generating equivalent atoms ('): -x+1, -y+2, -z+1.

Table 2. Selected bond distances and bond angles in **17**·CH_2Cl_2

Distance (Å)			
Ni-O1	2 .043(2)	Ni-O3	2.044(2)
O1-C1	1.421(4)	O3-C13	1.423(3)
C1-C2	1.498(6)	C13-C14	1.494(6)
C2-N1	1.340(4)	C14-N3	1.433(4)
N1- Ni	2.055(2)	N3-Ni	2.075(2)
Ni-O2	2.078(2)	Ni-Cl1	4.384(1)
O2-C7	1.434(3)	Ni-Cl2	4.3280(8)
C7-C8	1.509(5)	N2-Ni	2.083(2)
C8-N2	1.339(4)		
Angle (°)			
O1-Ni-O2	89.03(8)	O3-Ni-N1	100.53(8)
O1-Ni-O3	175.07(8)	O3-Ni-N2	89.99(9)
O1-Ni-N1	79.17(8)	O3-Ni-N3	78.45(8)
O1-Ni-N2	94.93(9)	N1-Ni-N2	96.41(9)
O1-Ni-N3	96.66(9)	N1-Ni-N3	95.62(9)
O2-Ni-O3	91.63(8)	N2-Ni-N3	164.7(1)
O2-Ni-N1	167.31(8)	O2-Ni-N3	90.31(8)
O2-Ni-N2	79.85(9)		

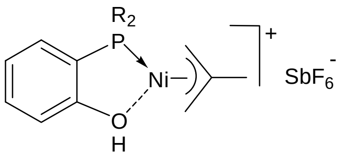
In the crystals of **17**·CH_2Cl_2, three molecules of (pyridin-2-yl)methanol chelate the metal centre in a distorted octahedral geometry (Table 2) and form a mononuclear asymmetric molecule with a meridional coordination of the three nitrogen atoms and of the three oxygens. The Ni1-N2 and Ni1-N3 bonds are in trans position and of similar length (2.084(2) and 2.072(2) Å, respectively). The trans influence of the nitrogen N1 trans to oxygen O2 makes the Ni1-O2 distance slightly longer (2.085(2) Å) than Ni1-O1 and Ni1-O3 (2.052(2) and 2.051(2) Å, respectively). The Ni1-Cl1 (4.488(1) Å) and Ni1-Cl2 (4.3280(8) Å) distances are too long to represent any significant bonding interaction. The counter anions Cl1 and Cl2 form hydrogen bonds with the hydrogen atoms H1 and H3, respectively (Figure 3), as indicated by the O1-H1···Cl1 and O3-H3···Cl2 distances of 2.922(3) and 2.934(3) Å, respectively (calculated distances H1···Cl1 and H3···Cl2: 2.08 and 2.10 Å and calculated angles O1-H1···Cl1 and O3-H3···Cl2: 176 and 169 °, respectively, Table S3†). Interestingly, the atom Cl2 connects two cations by hydrogen bonding, as depicted in Figure 3 (O2'-H2'···Cl2 distance: 2.986(2) Å, calculated O2'-H2'···Cl2 angle: 172 °, Table S3†).

We also considered converting a dative HO→Ni bond of complex **15** into a covalent Ni-O bond by deprotonation of at least one of the pyridine alcohol ligands with NaH, in order to study the catalytic properties of the resulting complex. Heinicke *et al.* have shown that whereas the neutral methallylnickel phosphanylphenolate complexes **18** catalyze the polymerization of ethylene, the corresponding, protonated cationic methallylnickel phosphinophenol complexes **19** catalyze its oligomerization.[20,58]



R = Ph, *cyclo*-Hex

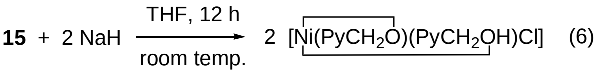
18



R = Ph, *cyclo*-Hex

19

The reaction of complex **15** with NaH in THF formed **20** which has been characterized by elemental analysis and IR spectroscopy [eqn (6)].



$$\mathbf{15} + 2\ \mathrm{NaH} \xrightarrow[\text{room temp.}]{\text{THF, 12 h}} 2\ \underset{\mathbf{20}}{[\mathrm{Ni(PyCH_2O)(PyCH_2OH)Cl}]} \quad (6)$$

Complex **20** proved to be paramagnetic in solution and its magnetic moment, determined by the Evans method in CD_2Cl_2,[59-62] was 2.7 μ_B. This value is similar to those recently reported for other Ni(II) complexes with P,N-type ligands.[63,64]

3. Catalytic oligomerization of ethylene

The complexes **14**, **15** and **20** have been evaluated in the catalytic oligomerization of ethylene with different amounts of $AlEtCl_2$ or MAO as cocatalyst and the complex $[NiCl_2\{P(n\text{-}Bu)_3\}_2]$ was used as a reference catalyst. This is convenient since it is easier to check its purity by NMR techniques, in contrast to the case of paramagnetic $[NiCl_2(PCy_3)_2]$. Furthermore, $[NiCl_2\{P(n\text{-}Bu)_3\}_2]$ has well-established catalytic properties for this reaction.[70] A comparison of the catalytic results between **14** and **15** will show the influence of the basicity of the nitrogen and that between **15** and **20** the impact of an anionic ligand vs. a neutral ligand on the oligomerization of ethylene. In order to study the influence of the concentration of the precatalysts and to compare the data with previous results obtained with Ni(II) complexes coordinated by P,N-type ligands,[13] we used 1.05×10^{-2} or 4×10^{-2} mmol of precatalyst dissolved in a total volume of 15 mL of chlorobenzene and toluene.

3.1 Use of $AlEtCl_2$ as cocatalyst

The precatalysts **14**, **15** and **20** were evaluated with 2, 4 or 6 equiv. of $AlEtCl_2$ as cocatalyst (Al/Ni ratios of 2, 4 or 6, respectively) (Table 3, Figure 4). In all cases, **15** afforded the highest turnover frequencies: 52300 and 187500 mol C_2H_4/(mol Ni·h) with 4×10^{-2} mmol and 1.05×10^{-2} of precatalyst, respectively, with 6 equiv. of $AlEtCl_2$. However, the low solubility of **15** in chlorobenzene could explain its very low activity with 2 equiv. of cocatalyst (less than 1000 mol C_2H_4/(mol Ni·h)). Indeed, more than 2 equiv. of $AlEtCl_2$ are needed to form sufficiently soluble, active species in the catalytic solution.

In contrast to **15**, complexes **14** and **20** were soluble in chlorobenzene and showed high activities with 2, 4 or 6 equiv. of $AlEtCl_2$ (Table 3). The highest activities were observed with 6 equiv. of $AlEtCl_2$: 187500 and 99800 mol C_2H_4/(mol Ni·h) with 1.05×10^{-2} mmol of complexes **15** and **20**, respectively. The selectivities for C_4 olefins and 1-butene with complexes **14**, **15** and **20** decreased with increasing catalytic activity (Table 4). Complex **15** presented the best selectivities for C_4 olefins (up to 87%) and for 1-butene (up to 97%) with 2 equiv. of $AlEtCl_2$ (Figure 5). The isomerization of 1-butene to 2-butene became more important with increasing activities. However, a decrease of the concentration of catalyst from 4×10^{-2} to 1.05×10^{-2} mmol had a beneficial impact on the selectivity for 1-butene, as shown with **20** where the selectivity increased from 6% to 29%.

The low selectivity for C_4 olefins with very active catalytic systems could be explained by the competing reinsertion of 1-butene to form 2-hexene, 3-hexene and 2-ethyl-1-butene and the reinsertion of 2-butene to form 3-methyl-1-pentene and 3-methyl-2-pentene.[53] Table 4 shows that with 1.05×10^{-2} mmol of precatalyst, less branched oligomers are formed than with 4×10^{-2} mmol of precatalyst, suggesting that a lower catalyst concentration disfavored the reinsertion of olefins. Accordingly, increasing the amount of cocatalyst favored the reinsertion of olefins and resulted in an increase of the C_6 fraction (Table 3), in particular of the C_6 oligomers formed from 2-butene (Table 4).

Table 3. Comparative Catalytic Data for Complexes **13**, **14** and **20** in the Oligomerization of Ethylene with $AlEtCl_2$ as cocatalyst[a]

	quantity of complexe (10^{-5} mol)	**EADC (equiv)**	**Time (min)**	**Selectivity[b]**			**Productivity g C_2H_4/(g Ni·h)**	**TOF mol C_2H_4/(mol Ni·h)**	**1-butene (% mol)**	**k_α[c]**
				C4	**C6**	**C8**				
13	1.05	2	35	92	8	0	9900	20700	62	<0.10
13	1.05	4	35	63	31	6	46400	97400	20	0.33
13	1.05	6	35	64	29	7	73900	155000	16	0.30
14	4	2	35	97	3	<1	<500	<1000	79	<0.10
14	4	4	35	68	30	2	16700	35200	11	0.29
14	4	6	35	69	27	4	24900	52300	6	0.27
14	1.05	2	35	95	5	<1	<1000	<1000	87	<0.10
14	1.05	4	35	81	17	2	20500	42900	39	0.14
14	1.05	6	35	70	25	5	89400	187500	10	0.23
20	4	2	35	78	21	1	9900	20700	16	0.18
20	4	4	35	68	29	3	16100	33700	9	0.29
20	4	6	35	69	28	3	19300	40500	6	0.27
20	1.05	2	35	77	19	4	12100	25300	43	0.19
20	1.05	4	35	72	23	5	35900	75300	32	0.21
20	1.05	6	35	62	32	6	47600	99800	29	0.34
ref[d]	4	2	35	83	15	2	4000	8400	13	0.12
ref	4	4	35	60	35	5	35300	74100	3	0.39
ref	4	6	35	61	34	5	35000	73600	3	0.37

[a] Conditions: T = 25-30 °C, 10 bar C_2H_4. [b] No C_{10} oligomers were detected. [c] k_α = hexenes [mol]/butenes [mol].
[d] reference: $[NiCl_2(P(n\text{-}Bu)_3)_2]$.

Table 4. Catalytic Data and Distribution of the C_6 oligomers for Complexes **13**, **14** and **20** in the Oligomerization of Ethylene with $AlEtCl_2$ as Cocatalyst[a]

	Quantity of Complex (10^{-5} mol)	$AlEtCl_2$ (equiv)	Selectivity (mass %)			
			1-hexene	2- and 3-hexene[b]	C_6[c] from 1-butene	C_6[d] from 2-butene
13	1.05	2	16	76	<1	7
13	1.05	4	3	54	12	31
13	1.05	6	3	44	3	50
14	4	4	2	43	7	48
14	4	6	<1	32	4	63
14	1.05	4	8	63	9	20
14	1.05	6	3	50	2	45
20	4	2	3	48	8	41
20	4	4	<1	33	5	61
20	4	6	1	40	6	53
20	1.05	2	14	74	2	10
20	1.05	4	3	53	11	33
20	1.05	6	3	44	5	48

[a] Conditions: T = 25-30 °C, 10 bar C_2H_4, 35 min. [b] Sum of 2-*cis*-hexene, 2-*trans*-hexene, 3-*cis*-hexene and 3-*trans*-hexene. [c] Corresponding to 2-ethyl-1-butene. [d] Sum of 3-methyl-1-pentene, 3-methyl-2-*cis*-pentene and 3-methyl-2-*trans*-pentene.

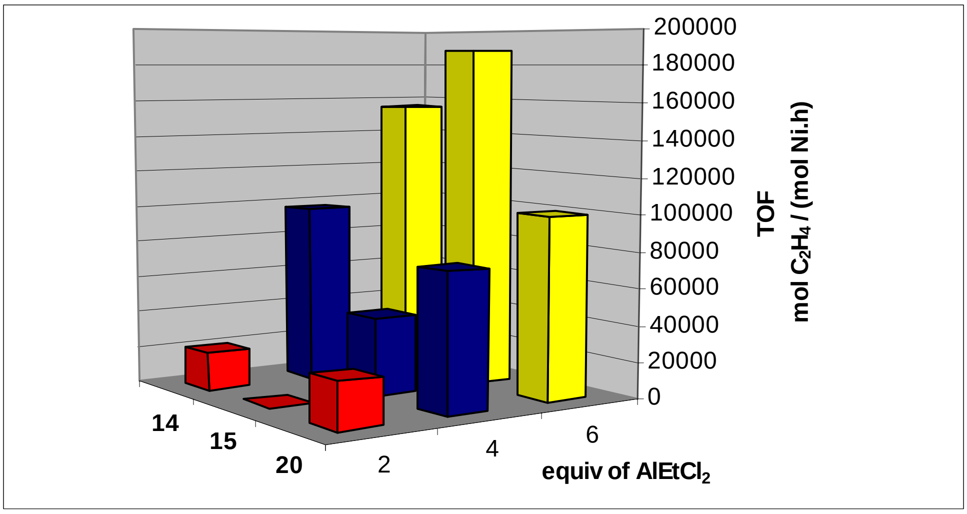


Fig. 4 Catalytic activities of the complexes **14**, **15**, and **20** (quantity of complex: $1.05{\cdot}10^{-2}$ mmol) in the oligomerization of ethylene using $AlEtCl_2$ as cocatalyst.

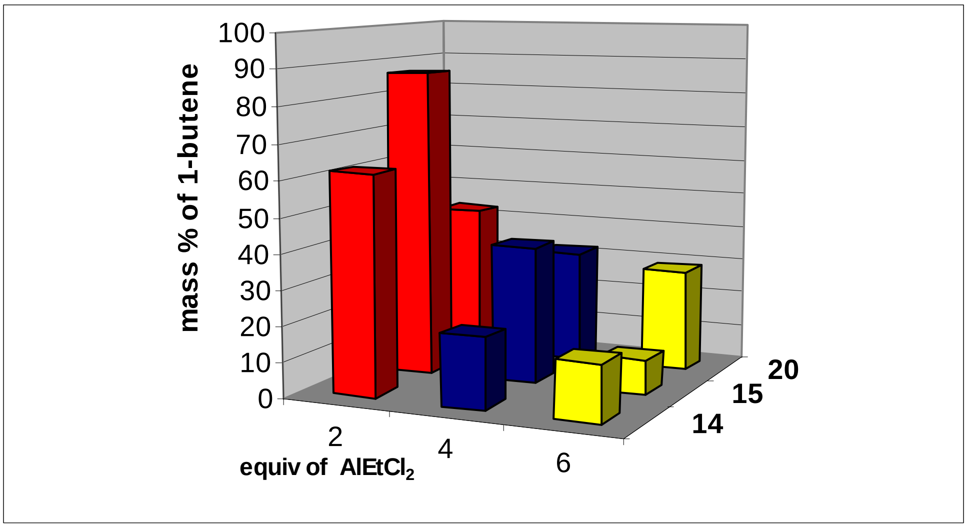


Fig. 5 Selectivity for 1-butene in the C_4 fraction for the complexes **14**, **15**, and **20** (quantity of complex: $1.05 \cdot 10^{-2}$ mmol) in the oligomerization of ethylene using $AlEtCl_2$ as cocatalyst.

3.2 Use of MAO as cocatalyst

The precatalysts **14**, **15** and **20** (1.05×10^{-2} mmol) have been evaluated in the presence of MAO (50, 100 or 200 equiv.) and all the complexes were active (Tables 5 and 6, Figures 6 and 7). Complexes **14** and **15** have similar activities, between 11100 and 12000 mol C_2H_4/(mol Ni·h) with 50 equiv. of MAO, between 24200 and 27000 mol C_2H_4/(mol Ni·h) with 100 equiv. and between 36300 and 37100 mol C_2H_4/(mol Ni·h) with 200 equiv. MAO. These complexes presented similar selectivities for C_4 olefins (up to 91%) and for 1-butene (up to 61%). Complex **20** was less active than **14** and **15** (Figure 6) with 200 equiv. of MAO but it was more selective for C_4 oligomers (up to 92%) and for 1-butene (up to 61%). A pressure increase from 10 to 30 bar led to a very high increase of catalytic activity for complexes **14** and **15** (Table 5). Whereas **15** displayed the highest activity of 104300 mol C_2H_4/(mol Ni·h), **14** presented the best selectivities for C_4 olefins (92%) and for 1-butene (61%). The pressure increase had a beneficial but modest impact on the selectivities for 1-hexene, which increased from 7% to 11% with **14** and from 6% to 9% with **15**. Table 6 shows the decrease of the C_6 fraction formed by reinsertion of 2-butene.

Two different concentrations were used for precatalyst **15** (1.05×10^{-2} and 4×10^{-2} mmol in a total volume of 10 mL of solution). If very high activities were obtained with 1.05×10^{-2} mmol of precatalyst (vide supra), better selectivities for C_4 olefins (79% with 100 equiv. of MAO and 75% with 200 equiv.) and for 1-butene (40% with 100 equiv. of MAO and 34% with 200 equiv.) were observed when 4×10^{-2} mmol of complex was used.

Table 5. Comparative Catalytic Data for Complexes **13**, **14** and **20** in the Oligomerization of Ethylene with MAO as Cocatalyst[a]

	Amt of complex (10^{-5} mol)	**Amt of MAO (equiv)**	**Selectivity**				**Productivity**	**TOF**	**1-butene**	**k_α[b]**
			C4	**C6**	**C8**	**>C8**	**g C_2H_4/(g Ni·h)**	**mol C_2H_4/(mol Ni·h)**	**(% mol)**	
13	1.05	50	85	11	3	0	5300	11100	57	<0.10
13	1.05	100	70	24	5	<1	12900	27000	36	0.23
13	1.05	200	75	20	4	1	17300	36300	35	0.18
13[d]	1.05	200	92	7	1	0	26400	55300	61	<0.10
14	4	50	94	6	<1	0	1000	2200	64	<0.10
14	4	100	74	22	4	<1	4700	9800	28	0.20
14	4	200	66	29	5	<1	6700	14100	23	0.29
14	1.05	50	91	8	1	0	5700	12000	61	<0.10
14	1.05	100	79	18	3	0	11600	24200	40	0.15
14	1.05	200	75	20	4	<1	17700	37100	34	0.18
14[d]	1.05	200	85	13	2	<1	49700	104300	51	0.11
20	1.05	50	92	7	1	0	2800	5900	61	<0.10
20	1.05	100	81	17	2	0	9900	20700	45	0.14
20	1.05	200	80	17	3	<1	11000	23000	42	0.14
ref[c]	4	50	43	46	8	3	18600	40000	3	0.72
ref	4	100	25	54	14	7	19200	41300	3	1.47
ref	4	200	26	52	16	6	17600	36900	3	1.31
ref	4	400	41	45	10	4	18900	39600	4	0.72

[a] Conditions: T = 25-30 °C, 10 bar C_2H_4. [b] k_α = hexenes [mol]/butenes [mol]. [c] reference: $[NiCl_2(P(n\text{-}Bu)_3)_2]$.
[d] pressure: 30 bar.

Table 6. Catalytic Data and Distribution of the C_6 oligomers for Complexes **13**, **14** and **20** in the Oligomerization of Ethylene with MAO as Cocatalyst[a]

	Quantity of Complex (10^{-5} mol)	MAO (equiv)	Selectivity (mass %)			
			1-hexene	2- and 3-hexene[c]	C_6 from 1-butene[d]	C_6 from 2-butene[e]
13	1.05	50	13	60	12	15
13	1.05	100	7	56	12	25
13	1.05	200	7	54	12	27
13[e]	1.05	200	11	63	13	14
14	4	50	15	59	13	13
14	4	100	5	53	12	30
14	4	200	4	53	12	31
14	1.05	50	16	59	13	12
14	1.05	100	8	58	12	22
14	1.05	200	6	54	12	28
14[e]	1.05	200	9	58	12	21
20	1.05	50	17	58	12	13
20	1.05	100	10	58	12	20
20	1.05	200	8	60	12	20

[a] Conditions: T = 25-30 °C, 10 bar C_2H_4, 35 min. [b] Sum of 2-*cis*-hexene, 2-*trans*-hexene, 3-*cis*-hexene and 3-*trans*-hexene. [c] Corresponding to 2-ethyl-1-butene. [d] Sum of 3-methyl-1-pentene, 3-methyl-2-*cis*-pentene and 3-methyl-2-*trans*-pentene. [e] presure 30 bar

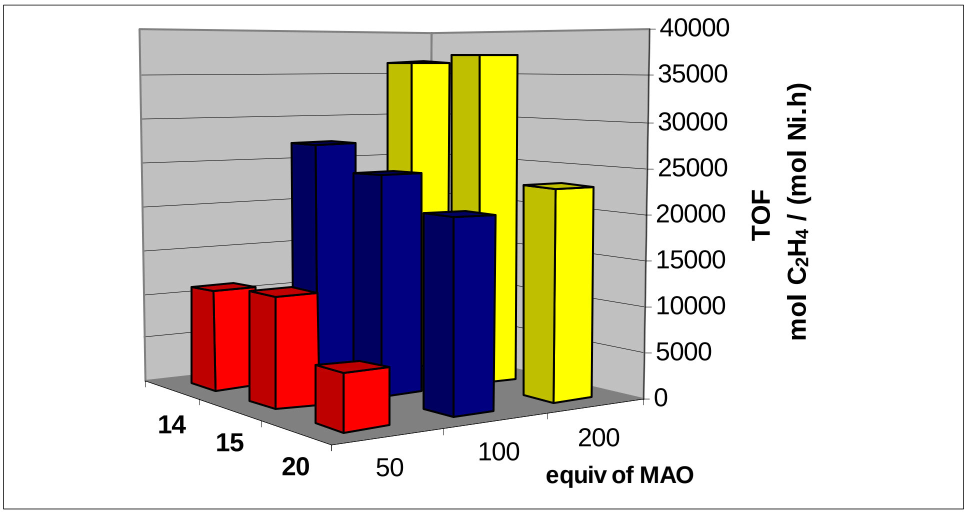


Fig. 6 Catalytic activities of the complexes **14**, **15** and **20** (quantity of complex: $1.05 \cdot 10^{-2}$ mmol) in the oligomerization of ethylene using MAO as cocatalyst.

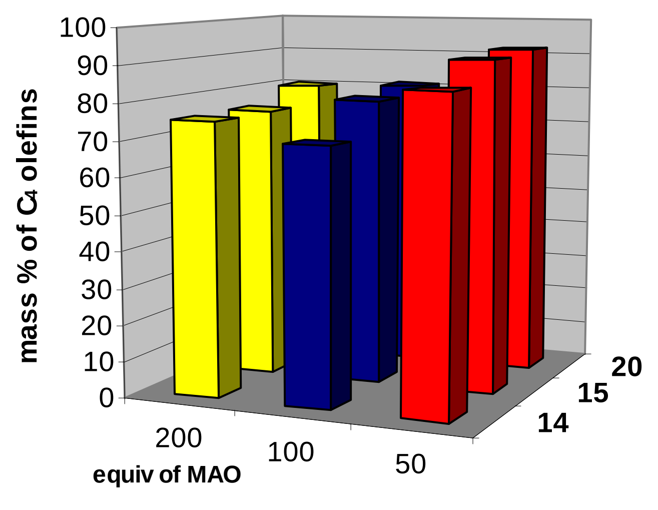


Fig. 7 Selectivity in C_4 olefins for the complexes **14**, **15**, and **20** (quantity of complex: $1.05 \cdot 10^{-2}$ mmol) in the oligomerization of ethylene using MAO as cocatalyst.

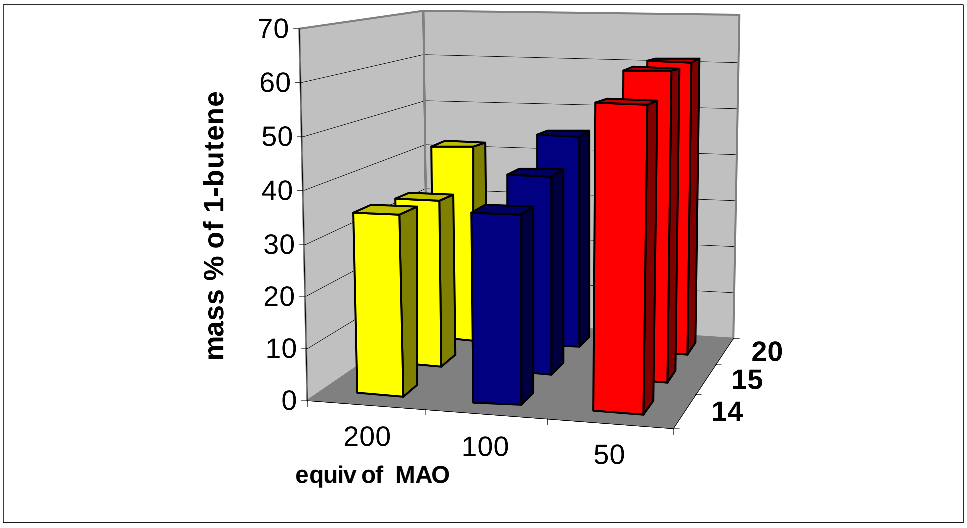


Fig. 8 Selectivity for 1-butene in the C_4 fraction with complexes **14**, **15** and **20** (quantity of complex: $1.05 \cdot 10^{-2}$ mmol) in the oligomerization of ethylene using MAO as cocatalyst.

4. Conclusion

The reaction of $NiCl_2$ with 2 mol. equiv. of the oxazoline alcohol **13** or of (pyridin-2-yl)methanol led to the formation of the corresponding complexes **14** or **15** in high yield. Single-crystal X-ray diffraction studies showed that **14** and **15** have dinuclear structures with octahedral metal coordination, very similar to those of the dinuclear complexes **11** and **12** with oxazoline alcohol or pyridine alcohol ligands bearing *gem*-dimethyl substituents in α position to the donor oxygen atom.[54] The reaction of $NiCl_2$ with 3 mol. equiv. of (pyridin-2-yl)methanol led to the octahedral, mononuclear complex **17** which can also be formed by reaction of **15** with the pyridine alcohol in a 1:2 ratio. Deprotonation of one of the two pyridine alcohol ligands of **15** with NaH afforded complex **20**.

The complexes **14**, **15** and **20** have been evaluated in the catalytic oligomerization of ethylene with 50, 100 and 200 equiv of MAO or with 2, 4 and 6 equiv of $AlEtCl_2$ as cocatalyst. When 1.05×10^{-2} mmol of complex was used, **15** presented the best activities, up to 187500 mol C_2H_4/(mol Ni·h) with only 6 equiv of $AlEtCl_2$ and the best selectivities for C_4 olefins (up to 97%) and for 1-butene (up to 79%). Under these conditions, **14** and **15** showed activities and selectivities with $AlEtCl_2$ similar to those of complexes **11** or **12** but, in contrast to previous observations made with related complexes, the pyridine alcohol ligands led here to more active complexes than the oxazoline alcohol ligands.[54] This emphasises the difficulty in generalising the observations made with one system. When 4×10^{-2} mmol of precatalysts was used in the presence of $AlEtCl_2$, **15** and **20** showed similar activities compared to those obtained with Ni(II) complexes bearing P,N type ligands.[13]

With MAO, precatalysts **14**, **15** and **20** were very active and **15** presented the highest activities up to 37100 mol C_2H_4/(mol Ni·h) with 200 equiv of MAO and selectivities for C_4 olefins (up to 94%) and 1-butene (up to 64%) with 50 equiv. of MAO. Precatalysts **14**, **15** and **20** in the presence of MAO showed higher activities than **11** and **12** (with 1.05×10^{-2} mmol of complex) and Ni(II) complexes bearing P,N type ligands (with 4×10^{-2} mmol of complex). The increase of the ethylene pressure to 30 bar resulted in more active complexes **14** and **15** (the TOF of **15** increased 104300 mol C_2H_4/(mol Ni·h)) and more selective for C_4 olefins (selectivity increase for **14** from 75% to 92%) and for 1-butene (selectivity increase for **14** from 35% to 61%). In view of the considerable importance of the nature and bonding mode of the chelating ligands on the catalytic properties of the metal complexes, further studies are required to improve these catalytic systems.

5. Experimental

The ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at 300.13 and 75.5 MHz on a Bruker AC300 instrument. Elemental analyses were performed by the "Service de Microanalyse, Université Louis Pasteur (Strasbourg, France)". IR spectra in the range of 4000-400 cm^{-1} were recorded on a Bruker IFS28FT. Mass spectra were recorded with a Bruker Daltonics microTOF (ESI; positive mode; capillary voltage: 4.8 kV; nebulizer pressure: 0.2 bar; desolvation temperature: 180 °C; desolvation gas flow rate: 4.5 L/min). Commercial $NiCl_2·6H_2O$ was dried by heating at 160 °C overnight under vacuum to give anhydrous $NiCl_2$. Magnetic moments were determined by the Evans method in CD_2Cl_2 using a solution of CH_3NO_2 in CD_2Cl_2 (20:80, v/v) as reference.[59-62] The commercial (pyridin-2-yl)methanol was distilled at 115 °C. Gas chromatographic analyses were performed on a Thermoquest GC8000 Top series gas chromatograph using a HP Pona column (50 m, 0.2 mm diameter, 0.5 μm film thickness).

Synthesis of (4,5-dihydro-4,4-dimethyloxazol-2-yl)methanol (13)

To a solution of glycolic acid (4.08 g, 53.7 mmol) in 100 mL of xylene, was added 5 mL of 2-amino-2-methyl-1-propanol (53.7 mmol) and the mixture was stirred at reflux for 24 h. After evaporation of the solvent under reduced pressure, the resulting yellow oil was distilled under reduced pressure (160 °C, 0.8 mbar) and **13** was obtained as a white powder by placing the oil in a refrigerator (Mp of **13** is around 15 °C).

Yield: 4.24 g (62%). ^{1}H NMR ($CDCl_3$): $\delta = 1.30$ (s, 6H, CH_3), 4.05 (s, 2H, CH_2), 4.26 (s, 2H, CH_2OH). ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 28.2$ (s, CH_3), 56.9 (s, CH_2OH), 66.6 (s, $\mathit{C}CH_3$), 79.7 (s, CH_2), 166.9 (s, NCO).

Synthesis of [Ni(μ-Cl)$_2${(4,5-dihydro-4,4-dimethyloxazol-2-yl)methanol}$_2$]$_2$Cl$_2$ (14)

A solution of 2 mol. equiv. of (pyridin-2-yl)methanol (1.22 g, 9.6 mmol) in 20 mL of methanol was added to a solution of anhydrous $NiCl_2$ (0.61 g, 4.8 mmol) in 50 mL of methanol and the reaction mixture was stirred overnight at room temperature. After reaction, the methanol was removed under reduced pressure, the residue was washed with diethylether, dried under reduced pressure and **14** was isolated as a green powder. Yield: 1.65 g (90%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of petroleum ether into a CH_2Cl_2 solution of **14**. Anal. Calcd. for $C_{24}H_{44}Cl_4N_4Ni_2O_8$: C, 37.15; H, 5.72; N, 7.22. Found: C, 36.97; H, 6.13; N, 6.68. IR (KBr): 1674 (s), 1637(vs), 1508 (w), 1467 (m), 1450 (m sh), 1406(m), 1371 (m), 1281 (s), 1209 (m), 1185 (w sh), 1063 (vs), 952 (s), 843 (w) cm^{-1}.

Synthesis of [Ni(μ-Cl)$_2${(pyridin-2-yl) methanol}$_2$]$_2$Cl$_2$ (15)

Complex **15** was prepared by reaction of $NiCl_2$ (0.86 g, 6.6 mmol) and (4,5-dihydro-4,4-dimethyloxazol-2-yl)methanol (1.44 g, 13.2 mmol) by following the same procedure described for **14** and it was isolated as a green powder. Yield: 2.18 g (95%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of petroleum ether into a CH_2Cl_2 solution of **15**. Anal. Calcd. for $C_{24}H_{28}Cl_4N_4Ni_2O_4$: C, 41.43; H, 4.06; N, 8.05. Found: C, 41.25; H, 4.48; N, 7.61. HRMS: Mass Calcd for $C_{12}H_{14}ClN_2NiO_2$: 311.0092. Found: 311.0099 $(Ni(N,O)_2Cl)^+$. IR (KBr): 1608 (vs), 1571 (s), 1483 (s), 1444 (s), 1440 (s sh), 1349 (w), 1286 (s), 1237 (m), 1156 (s), 1065 (s sh), 1050 (s sh), 1033 (vs), 778 (s sh), 765 (s), 727 (m), 648 (m), 626 (w) cm^{-1}.

Synthesis of [Ni{(pyridin-2-yl)methanol}$_3$Cl$_2$] (17)

To a solution of $NiCl_2$ (0.70 g, 5.4 mmol) in 30 mL of methanol was added a solution of 4 equiv. of (pyridin-2-yl)methanol (2.00 g, 21.6 mmol) in 5 mL of methanol and the reaction mixture was stirred overnight at room temperature. At the end of the reaction, the methanol was removed under reduced pressure and the residue was washed with diethylether (3x20 mL) to eliminate unreacted (pyridin-2-yl)methanol and dried under reduced pressure. The product was isolated as a blue powder. Yield: 2.05 g (93%). Single crystals of **17**·CH_2Cl_2 suitable for X-ray diffraction were obtained by slow diffusion of pentane into a CH_2Cl_2 solution. Anal. Calcd. for $C_{18}H_{21}Cl_2N_3NiO_3$: C, 47.31; H, 4.63; N, 9.20. Found: C, 47.10; H, 4.96; N, 8.51. IR (KBr): 1608 (vs), 1571 (s), 1483 (s), 1444 (s), 1440 (s sh), 1349 (w), 1286 (s), 1237 (m), 1156 (s), 1065 (s sh), 1050 (s sh), 1033 (vs), 778 (s sh), 765 (s), 727 (m), 648 (m), 626 (w) cm^{-1}.

Synthesis of [Ni{(pyridin-2-yl) methanol}{(pyridin-2-yl) methanolate}Cl] (20)

To a suspension of **15** (1.50 g, 4.3 mmol) in THF was added excess NaH (1.00 g, 41.7 mmol) and the mixture was stirred for 24 h at room temperature. At the end of the reaction, the solvent was removed under reduced pressure and 20 mL of CH_2Cl_2 was added. The green solution obtained was filtered to eliminate unreacted NaH and **15**. After removing the solvent under reduced pressure, **20** was washed with diethylether, dried under vacuum and isolated as a dark green powder. Yield: 0.97 g (72%). Anal. Calcd. for $C_{12}H_{13}ClN_2NiO_2$: C, 46.29; H, 4.21; N, 9.00. Found: C, 45.92; H, 4.57; N, 8.64. IR (KBr): 1632 (vs), 1597 (vs), 1569 (s sh), 1479 (w), 1438 (s), 1371 (vs), 1282 (m), 1244 (w), 1153 (w), 1077 (s), 1049 (s), 848 (m), 761 (vs), 729 (w), 704 (m), 643 (w) cm^{-1}.

Oligomerization of Ethylene

All catalytic reactions were carried out in a magnetically stirred (900 rpm) 145 mL stainless steel autoclave. A 125 mL glass container was used to protect the inner walls of the autoclave from corrosion. The preparation of the catalytic solution of the precatalyst is depended of the nature and the amount of the cocatalyst.

With $AlEtCl_2$, $4x10^{-2}$ mmol of Ni complex were dissolved in 14, 13 or 12 mL of cholorobenzene depending on the amount of the cocatalyst and injected into the reactor under an ethylene flux. Then 1, 2 or 3 mL of a cocatalyst solution, corresponding to 2, 4 or 6 equiv. respectively, is added to form a total volume of 15 mL with the precatalyst solution. When $1.05x10^{-2}$ mmol of precatalyst was used, a solution of the complex in 14 mL of chlorobenzene was injected into the reactor, followed by 0.26, 0.52 or 0.75 mL of a solution of the cocatalyst corresponding to 2, 4 or 6 equiv of $AlEtCl_2$ respectively.

With MAO, $1.05x10^{-2}$ or $4x10^{-2}$ mmol of Ni complex was dissolved in 10 mL in chlorobenzene and injected into the reactor under an ethylene flux. Then 2, 4 or 8 mL (for a complex amount of $4x10^{-2}$ mmol) or 0.51, 1.05 or 2.10 mL (for a complex amount of $1.05x10^{-2}$ mmol) of a cocatalyst solution, corresponding to 50, 100 or 200 equiv. of MAO respectively, was added.

All catalytic tests were started between 25 and 30 °C, and no cooling of the reactor was done during the reaction. After injection of the catalytic solution and of the cocatalyst under a constant low flow of ethylene, the reactor was pressurized to 10 bar. A temperature increase was observed which resulted solely from the exothermicity of the reaction. The 10 bar working pressure was maintained during the experiments through a continuous feed of ethylene from a reserve bottle placed on a balance to allow continuous monitoring of the ethylene uptake. At the end of each test (35 min) a dry ice bath, and in the more exothermic cases also liquid N_2, was used to rapidly cool down the reactor, thus stopping the reaction. When the inner temperature reached 0 ºC the ice bath was removed allowing the temperature to slowly rise to 10 ºC. The gaseous phase was then transferred into a 10 L polyethylene tank filled with water. An aliquot of this gaseous phase was transferred into a Schlenk flask, previously evacuated, for GC analysis. The products in the reactor were hydrolyzed in situ by the addition of ethanol (1 mL), transferred into a Schlenk flask, and separated from the metal complexes by trap-to-trap evaporation (20 °C, 0.8 mbar) into a second Schlenk flask previously immersed in liquid nitrogen in order to avoid any loss of product.

Crystal Structure Determinations

Diffraction data were collected on a Kappa CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) (Table 7). Data were collected using phi-scans and the structures were solved by direct methods using the SHELX 97 software,[71,72] and the refinement was by full-matrix least squares on F^2. No absorption correction was used. All non-hydrogen atoms were refined anisotropically with H atoms introduced as fixed contributors ($d_{\text{C-H}}$ = 0.95 Å, U_{11} = 0.04). Crystallographic data (excluding structure factors) have been deposited in the Cambridge Crystallographic Data Centre as Supplementary publication n° CCDC ******. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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7. Supporting information

Table S1. Analysis of Potential Hydrogen Bonds For **14**·C_6H_{12} (Å and °)

Donor --H....Acceptor	[ARU]	D-H	H.A	D.A	D-H.A
O1–H1...Cl2	[-]	0.84	2.19	2.984(4)	158
O3–H3...Cl2	[a]	0.84	2.20	2.994(4)	158
C1–H13A ...O4	[b]	0.99	2.47	3.200(7)	131

Translation of ARU-code to Equivalent Position Code

[a] = -x,-y,1-z
[b] = 1-x,1-y,-z

Table S2. Analysis of Potential Hydrogen Bonds For **15**·$3CH_2Cl_2$ (Å and °)

Donor --H....Acceptor	[ARU]	D-H	H.A	D.A	D-H.A
O1 –H1...Cl2	[a]	0.84	2.20	2.993(4)	157
O2 –H2...Cl4	[b]	0.84	2.15	2.978(4)	166
O3 –H3...Cl2	[-]	0.84	2.16	2.972(5)	162
O4 –H4...Cl4	[-]	0.84	2.18	3.017(5)	172
C3 –H3...Cl4	[c]	0.95	2.72	3.607(7)	156
C6 – H6...O3	[-]	0.95	2.57	3.123(9)	117
C7 – H7A...Cl8	[-]	0.99	2.69	3.473(13)	136
C12 – H12...O1	[-]	0.95	2.59	3.140(9)	117
C15 – H15...Cl9	[d]	0.95	2.67	3.305(15)	125
C1 – H18 ..O4	[-]	0.95	2.57	3.148(8)	120
C21 – H21 ..Cl9	[e]	0.95	2.81	3.515(9)	132
C24 – H24 ..O2	[-]	0.95	2.59	3.140(8)	117
C25 – H25B ..Cl2	[f]	0.99	2.68	3.535(18)	144
C27 – H27B ..Cl2	[g]	0.99	2.59	3.527(16)	157

Translation of ARU-code to Equivalent Position Code

[a] = -x,1-y,-z
[b] = 1-x,2-y,1-z
[c] = 1-x,2-y,-z
[d] = 1-x,1-y,1-z
[e] = -x,2-y,1-z
[f] = x,1+y,z
[g] = -x,1-y,1-z

Table S3. Analysis of Potential Hydrogen Bonds For **17**·CH_2Cl_2 (Å and °)

Donor – H....Acceptor	[ARU]	D-H	H.A	D.A	D-H.A
O1 – H1 ..Cl1	[-]	0.84	2.08	2.922(3)	176
O2 – H2 ..Cl2	[-]	0.84	2.15	2.986(2)	172
O3 – H3 ..Cl2	[a]	0.84	2.10	2.934(3)	169
C3 – H3 ..Cl1	[b]	0.95	2.76	3.702(3)	170
C6 – H6 ..Cl2	[a]	0.95	2.77	3.652(3)	156
C17 – H17 ..Cl2	[c]	0.95	2.65	3.560(4)	160
C19 – H19A ..Cl2	[d]	0.99	2.55	3.467(4)	154
C19 – H19B ..Cl1	[b]	0.99	2.82	3.809(5)	172

Translation of ARU-code to Equivalent Position Code

[a] = 1-x,2-y,1-z
[b] = 1-x,1-y,-z
[c] = 2-x,2-y,1-z
[d] = x,y,-1+z

Chapitre III

Unprecedented Tetranuclear Complexes with 20-Electron NiII Centers: The Role of Pressure and Temperature on Their Solid-State and Solution Fragmentation

Ce chapitre est présenté sous forme de publication au format du journal *Angewandte Chemie International Edition* et a fait l'objet d'une publication dont la référence est donnée ci-dessous.

Mon travail dans cette publication a été de synthètiser les différents complexes de nickel avec l'aide de Patricia Chavez Vasquez et d'isoler les différents isomères présentés. J'ai mesuré le moment magnétique de ces composés en solution par la méthode Evans.

Angew. Chem. Int. Ed. **2007**, 46, 6438

Unprecedented Tetranuclear Complexes with 20-Electron NiII Centers: The Role of Pressure and Temperature on Their Solid-State and Solution Fragmentation

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Abstract

Reactions of 2-diphenylphosphino-methyl-2-thiazoline (PN_{th}) and 2-diphenylphosphino-methyl-2-oxazoline (PN_{ox}) with anhydrous $NiCl_2$ afforded red solutions in CH_2Cl_2 which upon slow evaporation at 25 °C yielded red powders of $[NiCl_2(PN_{th})]$ (**1**) and $[NiCl_2(PN_{ox})]$ (**2**), respectively. These mononuclear complexes are similar to their dibromo analogs $[NiBr_2(PN_{th})]$ (**3**) and $[NiBr_2(PN_{ox})]$ (**4**) which have been shown by X-ray diffraction to have a distorted square planar structure. However, rapid precipitation from the red CH_2Cl_2 solutions of **1** or **2** yielded green powders with the same formula. Green single crystals of **1** were shown by X-ray diffraction to correspond to the formulation $[NiCl_2(PN_{th})]_4\cdot 2CH_2Cl_2$ (**1a**$\cdot 2CH_2Cl_2$). The structure of this complex shows an unprecedented, centrosymmetric Ni_4Cl_8 core. This tetranuclear complex undergoes a unique pressure-induced isomerization to the square planar monomers $[NiCl_2(PN_{th})]$, which is in equilibrium with the tetramer in solution. Similar observations were made with the PN_{ox} ligand. The magnetic properties of $[NiCl_2(PN_{th})]_4\cdot 2CH_2Cl_2$ (**2a**) are consistent with the presence of four octahedral Ni(II) ions.

Ligands combining phosphorus and nitrogen or oxygen donor atoms allow a fine-tuning of the structural properties and of the reactivity (stoichiometric and catalytic) of their metal complexes.[1] In particular, complexes bearing diversely substituted phosphino- or phosphinito-oxazolines have been studied for their dynamic behavior and catalytic activity in a number of reactions (e.g. ethylene oligomerization, hydrogenation of ketones, ethylene/CO co-polymerization, cyclopropanation, Diels-Alder reaction and allylic substitutions).[1c,2]

Since we recently found that phosphinothiazolines may display unique reactivity,[3] we became interested in comparing the ligands 2-diphenylphosphino-methyl-2-thiazoline (PN_{th}) and 2-diphenylphosphino-methyl-2-oxazoline (PN_{ox}). When PN_{th} and PN_{ox} were reacted with anhydrous $NiCl_2$, red CH_2Cl_2 solutions were formed and their slow evaporation at 25 °C afforded red powders of $[NiCl_2(PN_{th})]$ (**1**) and $[NiCl_2(PN_{ox})]$ (**2**), respectively. However, rapid precipitation from these solutions afforded green powders (see Supporting Information) and green single crystals were grown from a solution of **1** which correspond to $[NiCl_2(PN_{th})]_4\cdot 2CH_2Cl_2$ (**1a**$\cdot 2CH_2Cl_2$) (Figure 1).

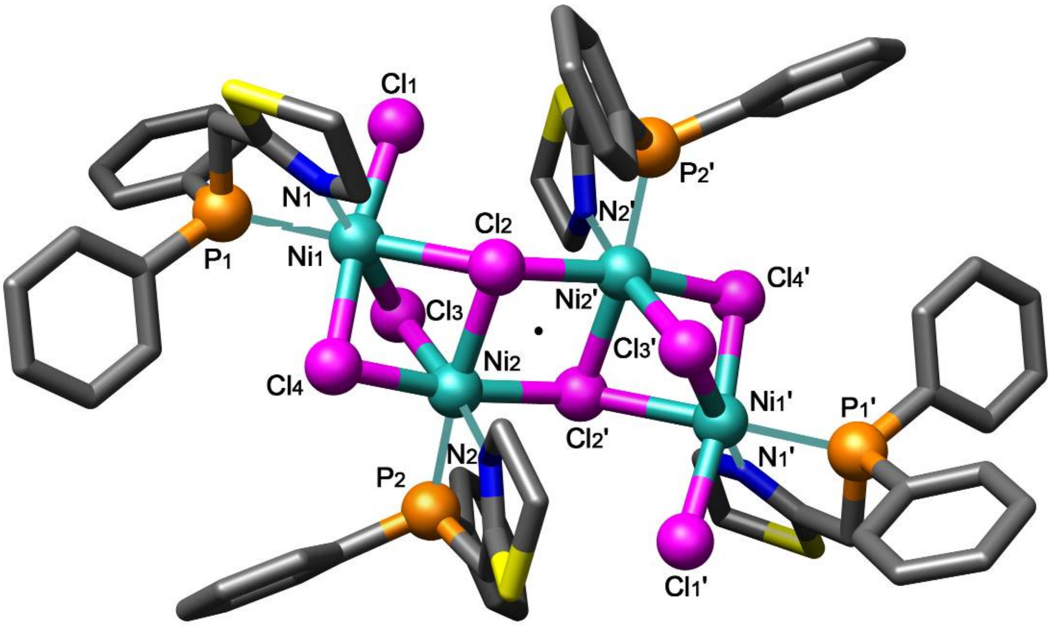


Figure 1. Solid state molecular structure of **1a** in **1a**$\cdot 2CH_2Cl_2$ with partial labeling scheme. The hydrogen atoms are omitted for clarity. The black dot represents the inversion center of the molecule. An ORTEP view with thermal ellipsoids is provided in the Supporting Information (Fig. S-1). Selected bond distances (Å) and angles (°): Ni1···Ni2 3.0951(5), Ni1-Cl1 2.3357(7), Ni1-Cl2 2.6148(8), Ni1-Cl3 2.3870(8), Ni1-Cl4 2.4265(7), Ni2-Cl2 2.4534(8), Ni2-Cl2’ 2.4307(8), Ni2-Cl3 2.4480(8), Ni2-Cl4 2.3972(8), Ni2-Cl2-Ni2’ 93.79(3), Ni1-Cl2-Ni2’ 134.50(3), Ni1-Cl2-Ni2 75.20(2), Ni1-Cl3-Ni2 79.59(3), Ni1-Cl4-Ni2 79.83(2). Symmetry operations generating equivalent atoms (’): -x, -y, -z.

In the centrosymmetric, tetranuclear structure of molecule **1a**, each metal centre has a slightly distorted octahedral coordination geometry defined by a chelating PN_{th} ligand and four chlorine atoms. Cl1 is terminally bonded to Ni1 but Ni1 and Ni2 are symmetrically bridged by Cl3 and Cl4 while Cl2 asymmetrically caps three metal centres. The Ni1···Ni2 distance of 3.0951(5) Å indicates the absence of strong metal-metal interactions.

The Ni_4Cl_8 core of **1a** is unprecedented since no complex with a M_4X_8 (X = halogen) stoichiometry appears to have been reported for group 10 metals. Furthermore, the geometry of this Ni_4Cl_8 core is new for any combination of transition metals with halogens. It is also noteworthy that **1a** represents the first complex in which a phosphine is coordinated to a $NiCl_4$ moiety. Only one example of a phosphine bound to a NiX_4 fragment (X = halogen) has been reported in the literature (X = Br).[5]

A green complex analogous to **1a**, $[NiCl_2(PN_{ox})]_4$ (**2a**), was obtained under similar conditions with the ligand PN_{ox} instead of PN_{th} and identified by X-ray powder diffraction (See Supporting Information). Complexes **1a** and **2a** undergo a pressure-induced structural modification, their color changing from green to deep red (25-35 kbar) (Scheme 1). Their high pressure forms and the red powders obtained by slow solvent evaporation were identified as the mononuclear complexes $[NiCl_2(PN_{th})]$ (**1b**) and $[NiCl_2(PN_{ox})]$ (**2b**), respectively, by comparison of their FTIR spectra with those of the corresponding bromides (Figures 2 and S-2, see Supporting Information).

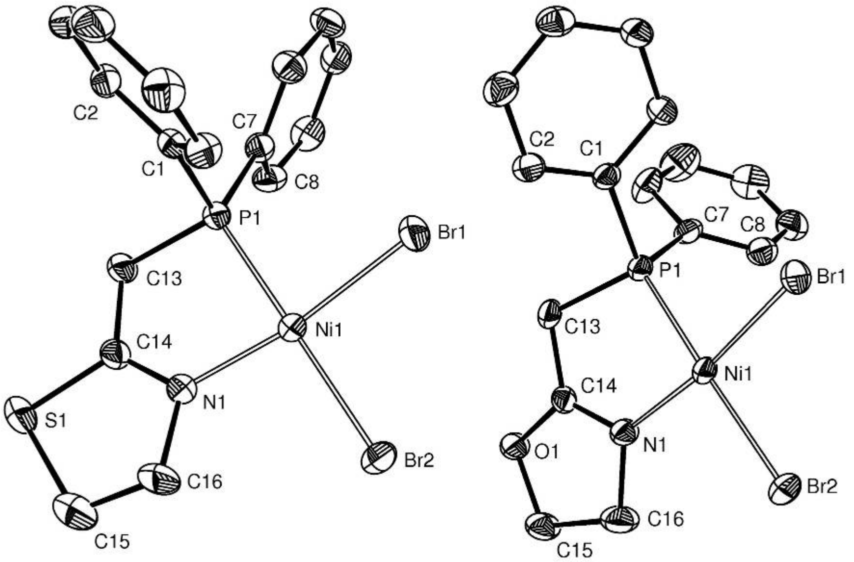
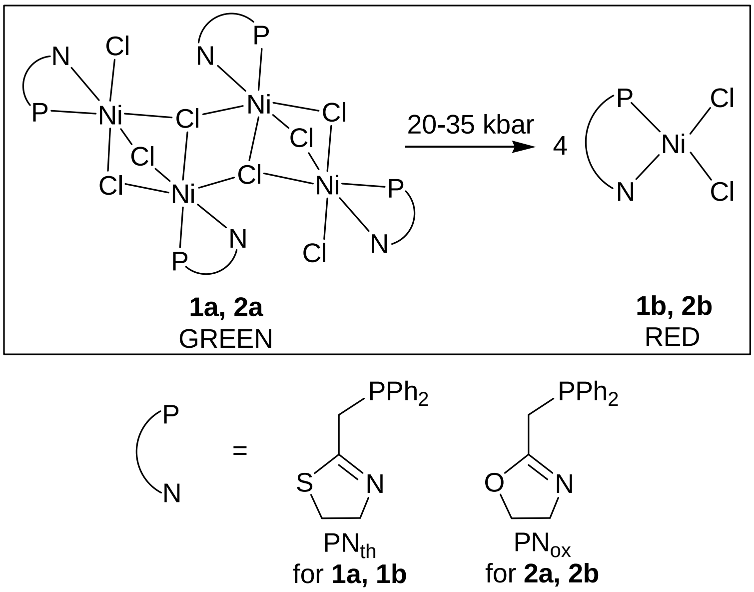


Figure 2. ORTEP views of the molecular structures of **3** and **4** with partial labeling scheme. Ellipsoids enclose 50% of the electron density. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°) for **3**: Ni1-P1 2.147(1), Ni1-N1 1.910(3), Ni1-Br1 2.3095(6), Ni1-Br2 2.3665(6); N1-Ni1-P1 84.4(1), P1-Ni1-Br1 87.75(3), N1-Ni1-Br2 95.1(1), Br1-Ni1-Br2 92.72(2). For **4**: Ni1-P1 2.158(1), Ni1-N1 1.905(3), Ni1-Br1 2.2983(7), Ni-Br2 2.3602(7), N1-Ni1-P1 85.0(1), P1-Ni1-Br1 87.73(4), N1-Ni1-Br2 94.0(1), Br1-Ni1-Br2 93.37(3).

The slightly distorted square planar complexes **3** and **4** contain the chelate ligands PN_{th} and PN_{ox} and two terminal bromides. As expected, the trans influence of the phosphorus donor results in longer Ni1-Br2 bonds compared to Ni1-Br1. Both ligands show analogous coordination geometries and structural parameters. The Ni-N and Ni-P distances in **3** are much shorter than those observed in **1a.** Although satisfactory elemental analyses data were obtained, attempts to record good quality NMR spectra failed. Consistently, red solutions of compounds **3** and **4** were found to be paramagnetic by the Evans method,[4] displaying magnetic moments of ca. 1.3 and 1.0 μB, respectively. These data point to the presence of a paramagnetic isomer in equilibrium with the square planar one(see below).



Scheme 1.

A comparison between the FTIR spectra of **2a** and **2b** is shown in Figure S-3 (Supporting Information). When compared to **2b**, the low pressure form **2a** displays several split absorptions, as a result of the presence of two symmetry-independent ligands. In contrast to **1a** but similarly to **3** and **4**, only one independent ligand is likely to be present in the unit cell of **1b**.

Few examples of nickel complexes undergoing a fully characterized pressure induced isomerization have been reported, e.g. the conversion from tetrahedral to dinuclear, square-pyramidal structures,[6] or from mononuclear to tetrahedral square planar arrangements.[7] A structurally characterized square-planar to octahedral isomerization was recently reported for a Pd thioether species.[8] Our system represents, however, a more dramatic structural isomerization, involving at the same time (i) the entropically favored fragmentation of a tetranuclear complex in four distinct square planar molecules and (ii) an octahedral to square-planar rearrangement. The former is associated with an overall denser unit cell of the mononuclear form (estimated density from X-ray powder diffraction data for **2a**·$2CH_2Cl_2$: 1.41 and for **2b**, based on data for **4**: 1.55, see Supporting Information).

The magnetic properties of **2a** in the solid state were investigated in the 300-1.8 K temperature range with an applied field of 5 kOe. The Curie constant $C = 4.64$ emu·K·mol^{-1}, determined from the fit of the $1/\chi = f(T)$ curve with the Curie-Weiss law in the high temperature region (150-300 K), is as expected for four octahedral Ni(II) ions (with a g value of 2.15).[9] Upon cooling, the χT product exhibits a regular decrease from 4.54 emu·K·mol^{-1} at 300 K to 3.47 emu·K·mol^{-1} at 20 K, indicating the occurrence of at least one intramolecular antiferromagnetic interaction. Below 20 K, the small increase of the χT product up to 3.49 emu·K·mol^{-1} at 14 K and the final decrease below 14 K are most probably due to a complicated interaction scheme and to the presence of competing intramolecular interactions (Figures 3 and S-5) as well as to zero-field splitting and intermolecular interactions. So far, no analytical fitting by full diagonalization of the complete spin Hamiltonian was successful in the whole temperature range and further studies are in progress to determine the magnitude and sign of the different exchange constants and the characteristics of the ground state.

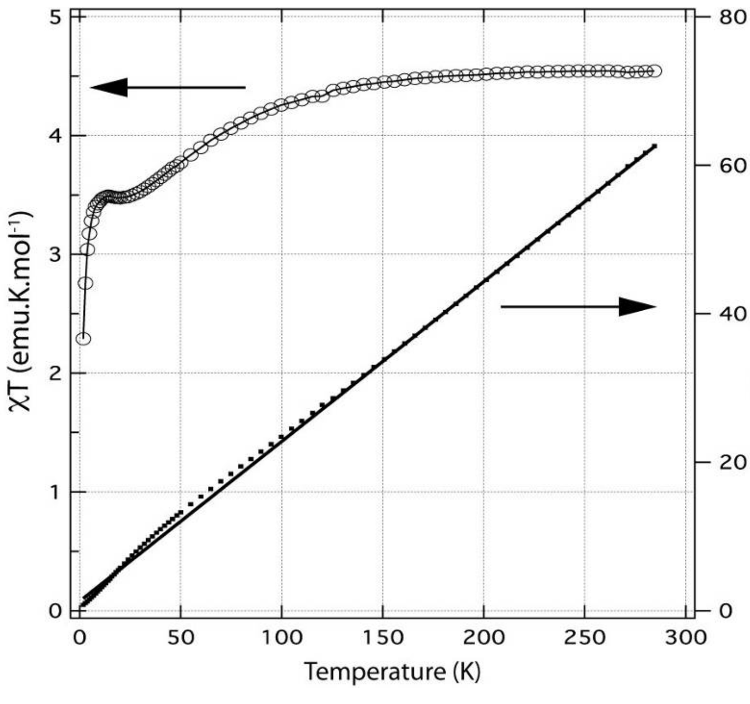


Figure 3. χT(open circles) and 1/χ (open squares) for **2a** as a function of temperature. Full line corresponds to the fit of the $1/\chi = f(T)$ curve by a Curie-Weiss law in the high temperature region (see text).

As mentioned above, solutions of **1a/b** and **2a/b** in chlorinated solvents are red at room temperature. However, at low temperatures, a color change to green is detected. Variable temperature UV-vis. spectra are shown in Figure 4.

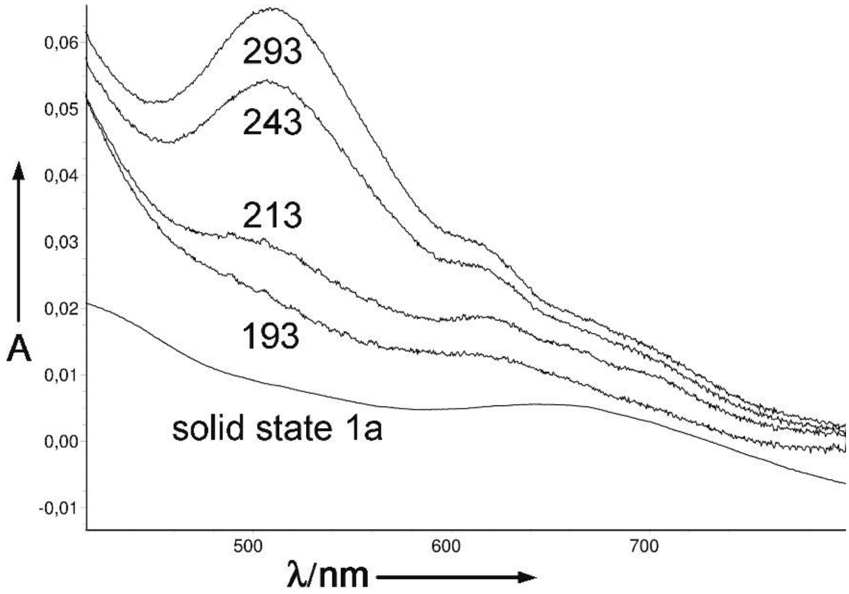


Figure 4. Visible spectra (400-800 nm) of **1a/b** in MeCN/CH$_2$Cl$_2$ (5:2) recorded in the 293-193 K range and compared to that of solid **1a**.

A strong absorption centered at 517 nm dominates the visible spectrum recorded at 293 K but two weak bands centered at 615 and 700 nm were also detected. Upon decreasing the temperature, the main absorption gradually disappears, while the two minor ones remain almost unchanged. The absorption pattern of the 193 K spectrum is similar to that of the solid state form **1a**. It can therefore be envisaged that **1a** is present in solution and favored at low temperature, being thermodynamically stabilized with respect to **1b**. The equilibrium was fully restored when the system was allowed to reach 293 K.

The presence of two distinct species in equilibrium in solution is consistent with the paramagnetism detected by NMR (Evans method). The values of 2.8 and 2.3 □B for **1** and **2** in CD$_2$Cl$_2$, respectively, are not consistent with either a square-planar or an octahedral coordination. The paramagnetic NMR data recorded for **1-4** could thus result from an equilibrium between a mononuclear diamagnetic complex and a polynuclear, probably tetranuclear, paramagnetic one. An equilibrium between square planar and octahedral Ni complexes in solution is not uncommon and previous examples involve solvent molecules entering the coordination sphere,[9] and hemilability.[10] Other examples include tetrahedral-square planar isomerisms.[11] However, the equilibrium between mononuclear and polynuclear Ni complexes remains rare. Recently, an irreversible nuclearity decrease from 6 to 4 was observed, induced by coordinating solvents.[12] The tetranuclear form is more stabilized in the case of PN$_{th}$ than of PN$_{ox}$, as observed by (i) the Evans method and (ii) the solid state isomerization pressure.

In conclusion, the situations encountered in this work reveal many unprecedented features and indicate that subtle differences result from the presence of oxygen or sulfur in PN_{ox} and PN_{th}, respectively. Further studies are in progress.

Experimental

Crystal data for **1a**: $C_{64}H_{64}Cl_8N_4Ni_4P_4S_4 \cdot 2CH_2Cl_2$, T = 193 K, M = 1829.60, triclinic P-1, a = 11.248(1), b = 11.518(1), c = 14.843(2) Å, α = 91.811(3), β = 94.041(3), γ = 97.161(3)°, V = 1901.6(3) Å^3, Z = 1, D_c = 1.598 g·cm^{-3}, μ(Mo-Kα) = 1.63 mm^{-1}, F(000) = 932, 2θ_{max} (°) = 60, R_1 = 0.0485, wR_2 = 0.1107, R(int) = 0.0369 parameters = 420, obs. Refl. = 7468(17720 meas.). CCDC N° 641491. For **3**: $C_{16}H_{16}NSPNiBr_2$, T = 193 K, M = 503.86, triclinic P-1, a = 8.6595(3), b = 8.6983(2), c = 12.9457(4) Å, α = 91.476(1), β = 98.175(1), γ = 111.337(1)°, V = 895.86(5) Å^3, Z = 2, D_c = 1.868 g·cm^{-3}, μ(Mo-Kα) = 5.74 mm^{-1}, F(000) = 496, 2θ_{max} (°) = 57.4, R_1 = 0.0438, wR_2 = 0.0965, R(int) = 0.0380 parameters = 199, obs. Refl. = 3318 (6954 meas.). CCDC N° 641489; For **4**: $C_{16}H_{16}NOPNiBr_2$, T = 193 K, M = 503.86, triclinic P-1, a = 8.6330(3), b = 8.7360(3), c = 11.8890(4) Å, α = 104.2010(17), β = 96.7060(17), γ = 96.3230(12)°, V = 854.28(5) Å^3, Z = 2, D_c = 1.896 g·cm^{-3}, μ(Mo-Kα) = 5.90 mm^{-1}, F(000) = 480, 2θ_{max} (°) = 58.2, R_1 = 0.0464, wR_2 = 0.1194, R(int) = 0.0429 parameters = 199, obs. Refl. = 2768 (6589 meas.). CCDC N° 641490. Supplementary crystallographic data (excluding structure factors) can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax (+44)1223-336-033 or deposit@ccdc.cam.ac.uk).

Notes and references

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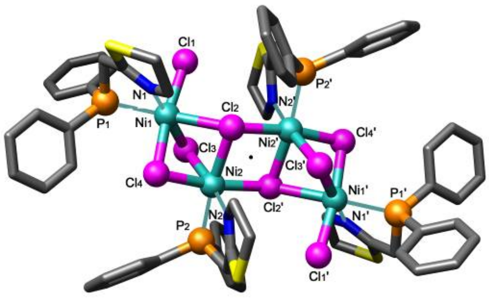
Keywords: magnetism; nickel; polynuclear complexes; PN ligands; pressure-induced isomerization.

For the Table of Contents

Complexes under pressure! The tetranuclear complexes $[NiCl_2(PN)]_4$ (PN = 2-diphenylphosphino-methyl-2-oxazoline or 2-diphenylphosphino-methyl-2-thiazoline) have an unprecedented, centrosymmetric Ni_4Cl_8 core and undergo a pressure-induced isomerization to the mononuclear, square planar complexes $[NiCl_2(PN)]$, which are in equilibrium with the respective tetramer in solution.



SUPPORTING INFORMATION FOR

Unprecedented Tetranuclear Complexes with 20-Electron NiII Centers: The Role of Pressure and Temperature on Their Solid-State and Solution Fragmentation.**

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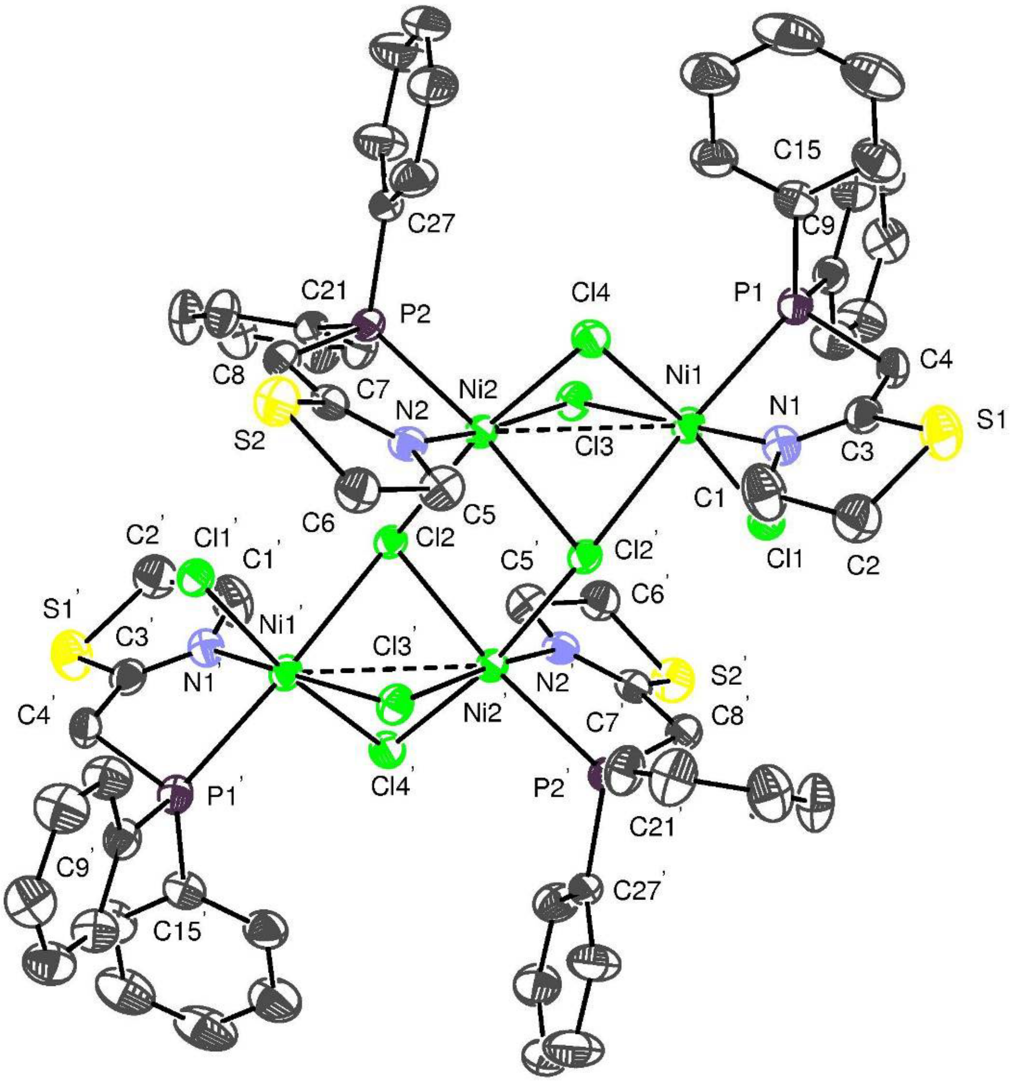

Figure S-1: ORTEP plot of the molecular structure of **1a** in **1a**·2CH_2Cl_2 together with partial numbering scheme. Ellipsoids include 30% of the electron density. Hydrogen atoms and solvent molecules are omitted for clarity.

1. Experimental

General Considerations

All manipulations were carried out under inert dinitrogen atmosphere, using standard Schlenk-line conditions and dried and freshly distilled solvents. The ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra were recorded unless otherwise stated on a Bruker Avance 300 instrument at 300.13, 75.47 and 121.49 MHz, respectively, using TMS, or H_3PO_4 (85% in D_2O) as external standards with downfield shifts reported as positive. FT-IR spectra in the range of 4000-650 cm^{-1} were recorded on a Nicolet Nexus FT-IR spectrometer coupled with a Continuum microspectrometer, operating in diffuse reflectance. Elemental C, H, N analyses were performed by the "Service de microanalyses", Université Louis Pasteur, Strasbourg. The solid state visible spectrum of **1a** was recorded on a CCD detector using a Nikon TE microscope (40 X; N.A. 0.45) and decomposed by an Acton/Princeton Instruments monochromator. The variable temperature spectra of **1a/b** were recorded on a VARIAN Cary05E, equipped with a OXFORD INSTRUMENTS DN1704 cryostat. Mass spectra were recorded with a Bruker Daltonics microTOF [ESI(+) capillary voltage: 4.8 kV; nebulizer pressure: 0.2 Bar; desolvation temperature: 180 °C; desolvation gas flow rate: 30 L/h]. Magnetic measurements were performed at the Institut de Physique et Chimie des Matériaux de Strasbourg (UMR CNRS-ULP 7504) using a Quantum Design MPMS-XL SQUID magnetometer. The susceptibility measurement was performed in the 300-1.8 K temperature range with an applied field of 5 kOe. Magnetization measurements at different fields at room temperature confirm the absence of ferromagnetic impurities. Data were corrected for the sample holder and diamagnetism was estimated from Pascal constants. 2-[(diphenylphosphino)methyl]oxazoline (PN_{ox}) was prepared according to literature procedures.[S-1] Anhydrous $NiCl_2$ was prepared by dehydration of $NiCl_2 \cdot 6H_2O$ at 150°C under vacuum prior to use. Other chemicals were commercially available and used as received.

2. Synthesis

2.1 Preparation and Spectroscopic Data for 2-[(diphenylphosphino)methyl]thiazoline (PN_{th}).

20 mL (32.0 mmol) of a 1.6 M *n*-BuLi solution was added dropwise to a solution of liquid 2-methyl-2-thiazoline (3.06 mL, 3.23 g, 32.0 mmol) in 100 mL of THF at –78 °C. The pale red reaction mixture was stirred for 1 h at –78 °C. Pure Me_3SiCl (8.09 mL, 6.95 g, 64.0 mmol) was then added dropwise and stirring was continued at -78°C for 2h. Pure PPh_2Cl (5.89 mL, 7.06 g, 32.0 mmol) was added dropwise to the colourless solution at –78 °C. The reaction mixture was allowed to reach at room temperature overnight. The volatiles were removed under reduced pressure, resulting in a yellow oily crude product which was dissolved in CH_2Cl_2 (50 mL). LiCl was removed

by filtration. The solvent was evaporated, yielding pure PN_{th} as a pale yellow powder. Yield: 7.03 g, 68%.

^{1}H NMR ($CDCl_3$) δ: 3.25 (t, 2H, $^3J_{H\text{-}H}$ = 8.4 Hz, SCH_2), 3.32 (s, 2H, PCH_2), 4.14 (tt, 2H, $^3J_{H\text{-}H}$ = 8.4 Hz, $^5J_{H\text{-}H}$ = 0.7 Hz, NCH_2), 7.32-7.48 (m, 10H, aromatic). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 34.6 (d, $^4J_{P\text{-}C}$ = 2.0 Hz, SCH_2), 35.1 (d, $^1J_{P\text{-}C}$ = 17.1 Hz, PCH_2), 64.5 (s, NCH_2), 128.5-137.6 (m, aromatic, PPh_2), 167.7 (d, $^2J_{P\text{-}C}$ = 12.2 Hz, C=N). ^{31}P{^{1}H} NMR ($CDCl_3$) δ: -15.5 (s). Anal. Calcd. for $C_{16}H_{16}NPS$ (285.34): C, 67.35; H, 5.65; N, 4.91. Found: C, 67.06; H, 5.94; N, 4.99.

2.2 Preparation and Spectroscopic Data for $[Ni(PN_{th})Cl_2]_4$ (1a).

0.73 g of solid **1b** (see below) was dissolved in a minimum amount of CH_2Cl_2. To this, petroleum ether was quickly added (three times the volume of CH_2Cl_2). **1a** precipitated as a pale green powder. Yield: 0.71 g, 98%.

FTIR (cm^{-1}) selected absorptions: 3071w, 3058w, 3038w, 3005w, 2984w, 2947w, 2932w, 2919w, 2904w, 2887w, 20870w, 2859w, 2854w, 1603vs, 1585m(sh), 1572m, 1483s, 1434s, 1397w(sh), 1382s, 1342w, 1324w, 1315w, 1277w, 1254m(sh), 1238s, 1190w, 1183w(sh), 1169w, 1159w, 1137w, 1128w, 1100s, 1093s(sh), 1071w, 1028vs, 1024vs(sh), 1004m(sh), 984w(sh), 949m, 907w, 862w, 853w, 841w, 827m(sh), 820m, 770m(sh), 764m(sh), 754m(sh), 739vs, 693vs, 690vs(sh), 672m. Anal. Calcd. for $C_{64}H_{64}N_4Cl_8Ni_4P_4S_4$ (M = 1651.8): C, 46.49; H, 3.90; N, 3.39. Found: C, 46.13; H, 3.66; N, 3.40.

2.3 Preparation and Spectroscopic Data for $[Ni(PN_{th})Cl_2]$ (1b).

A solution of PN_{th} (0.51 g, 1.8 mmol) in methanol (10 mL) was added to a solution of $NiCl_2$ (0.23 g, 1.8 mmol) in methanol (100 mL), resulting in a green reaction mixture. Stirring was continued for one hour at room temperature. The volatiles were removed under reduced pressure and the green solid obtained was left under vacuum for 12 h, yielding **1b** as a red amorphous solid. Yield: 0.73 g, 1.75 mmol, 98%.

FTIR (cm^{-1}) selected absorptions: 3051w, 2986w, 2947w, 2905w, 2861w, 1603vs, 1483m, 1435vs, 1386m, 1315w, 1275w, 1240s, 1189w, 1159w, 1100s, 1029vs, 1000w, 948w, 821w, 741vs, 693vs. ESI$^+$: [M-Cl]$^+$ 377.9779 (calcd. For $[C_{16}H_{16}NClNiPS]^+$: 377.9778). Anal. Calcd. for $C_{16}H_{16}NCl_2NiPS$ (M = 412.9): C, 46.49; H, 3.90; N, 3.39. Found: C, 46.07; H, 3.91; N, 4.23.

2.4 Preparation and Spectroscopic Data for $[Ni(PN_{ox})Cl_2]_4$ (2a).

Complex **2b** (1.20 g, 3.0 mmol, see below) was dissolved in a minimum amount of CH_2Cl_2. To this, petroleum ether was quickly added (three times the volume of CH_2Cl_2). **2a** precipitated as a

pale green powder. Yield: 1.10 g, 92%. Alternatively **2a** can be obtained by evaporating under vacuum, and at ca. -15°C, a solution of **2b** in a 2:1 CH_2Cl_2/heptane mixture. Yield: 1.18 g, 98%.
FTIR (cm^{-1}) selected absorptions: 3076w, 3058w, 3035w, 2991w, 2960w, 2933w, 2901w, 1667vs(sh), 1663vs, 1585w, 1574w, 1485s, 1475m, 1454w, 1442m(sh), 1438s(sh), 1434s, 1401s, 1372s, 1334m, 1270vs(sh), 1265vs, 1231w, 1199w, 1190w, 1166s, 1148w, 1104s, 1095w(sh), 1071w, 1045s, 1036s, 999m, 970w, 965w(sh), 938m, 926m, 820w, 814w, 752m(sh), 744vs, 737vs, 704m(sh), 695vs, 688vs(sh). Anal. Calcd. for $C_{64}H_{64}N_4Cl_8Ni_4P_4O_4$ (M = 1587.8): C, 48.37; H, 4.06; N, 3.53. Found: C, 48.29; H, 3.88; N, 3.65.

2.5 Preparation and Spectroscopic Data for [Ni(PN_{ox})Cl_2] (2b).

A solution of PN_{ox} (1.66 g, 6.2 mmol) in methanol (10 mL) was added to a solution of $NiCl_2$ (0.80 g, 6.2 mmol) in methanol (50 mL), resulting in a green reaction mixture. Stirring was continued for one hour at room temperature. The volatiles were removed under reduced pressure and the green solid obtained was left under vacuum for 12 h, yielding **2b** as a red amorphous solid. Yield: 2.40 g, 97 %
FTIR (cm^{-1}) selected absorptions: 3054w, 2985w, 2914w, 1654vs, 1622vs(sh), 1484s, 1435vs, 1403s, 1371s, 1355m, 1268vs, 1190w(sh), 1169m, 1135w, 1101m, 1072w, 1029m, 999m, 971w, 931m, 829m, 742s, 693s, 665w. ESI^+: $[M-Cl]^+$ 3619984 (calcd. For $[C_{16}H_{16}NClNiPO]^+$: 362.0006). Anal. Calcd. for $C_{16}H_{16}NCl_2NiPO$ (M = 397.0): C, 48.37; H, 4.03; N, 3.53. Found: C, 47.93; H, 4.31; N, 3.69.

2.6 Preparation and Spectroscopic Data for [Ni(PN_{th})Br_2] (3).

A solution of solid PN_{th} (0.86 g, 3.0 mmol) in 5 mL of methanol was added to a solution of $NiBr_2$ (0.66 g, 3.0 mmol) in 40 mL of methanol and the dark red solution obtained was stirred for one hour at room temperature. Evaporation of the volatiles under reduced pressure yielded a deep red residue which was dissolved in 30 mL of CH_2Cl_2. $NiBr_2$ was filtered off and a red powder was precipitated with petroleum ether (80 mL). Drying under vacuum yielded **3** as a ruby red powder. Yield: 1.39 g, 2.8 mmol, 92%.
FTIR (cm^{-1}): selected absorptions: 3052w, 2926w, 2883w, 1600m, 1558s, 1483w, 1435vs, 1382m, 1310w, 1249m, 1186w, 1160w, 1103s, 1039m, 1029m(sh), 998w, 962w, 835w, 787w, 747vs, 736vs(sh), 689vs, 672m(sh). Anal. Calcd. for $C_{16}H_{16}NBr_2NiPS$ (M = 503.84): C, 38.14; H, 3.20; N, 2.78. Found: C, 37.89; H, 3.25; N, 2.51

2.7 Preparation and Spectroscopic Data for [Ni(PN_{ox})Br_2] (4).

4 was prepared following the same procedure described above for the synthesis of **3**. 0.61 g of PN_{ox} (2.3 mmol) and 0.50 g of $NiBr_2$ (2.3 mmol) were used. **4** was obtained as a deep red powder. Yield: 1.00 g, 2.05 mmol, 89%

FTIR (cm^{-1}) selected absorptions: 3066w, 2954w, 2911w, 1628vs, 1587w, 1573w, 1478m, 1453w, 1435vs, 1426s(sh), 1370m, 1339m, 1312w, 1268s, 1198w, 1178m, 1160w, 1133w, 1100s, 1071w, 1047m, 1027m(sh), 998m, 974w, 928m, 829m, 752m(sh), 742s, 712w(sh), 690s. Anal. Calcd. for $C_{16}H_{16}NBr_2NiPO$ (M = 487.78): C, 39.40; H, 3.31; N, 2.87. Found: C, 39.10; H, 3.56; N, 2.88

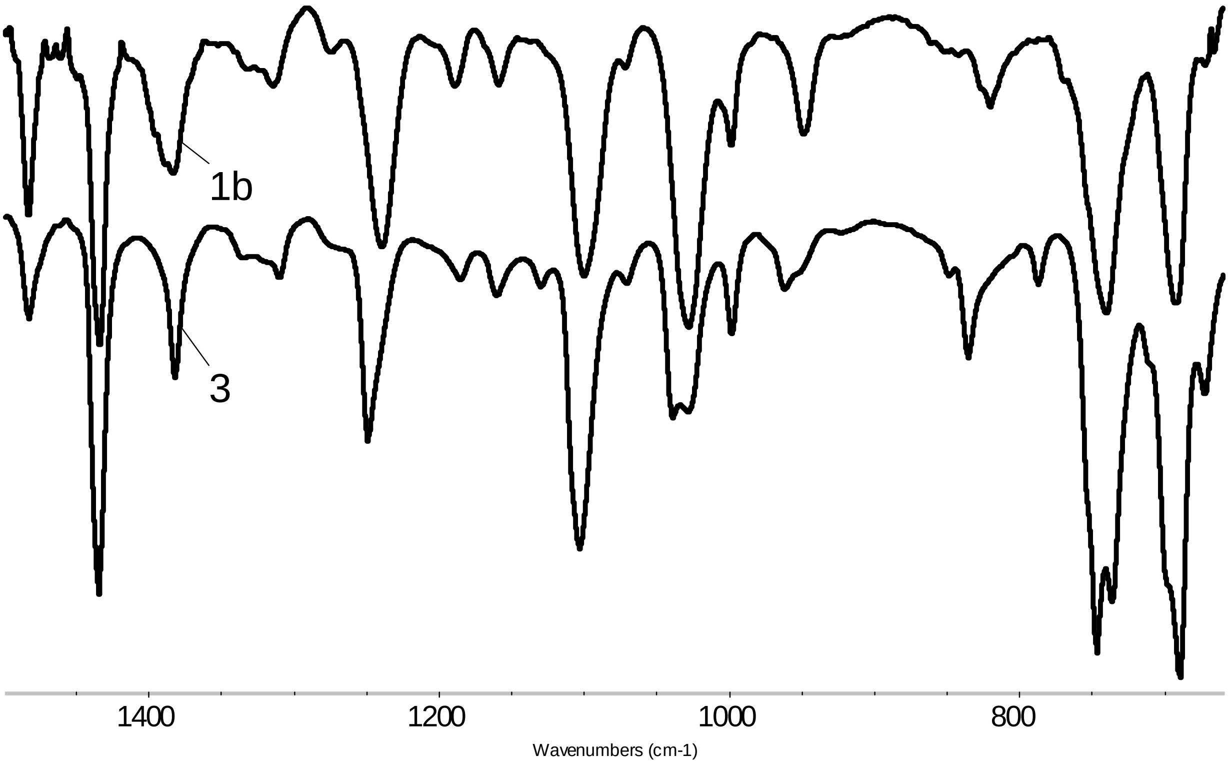

Figure S-2. Comparison between the FTIR spectra of **1b** and **3,** emphasizing the spectroscopic similarity between the two complexes.(reflectance mode, 1500-650 cm^{-1} region).

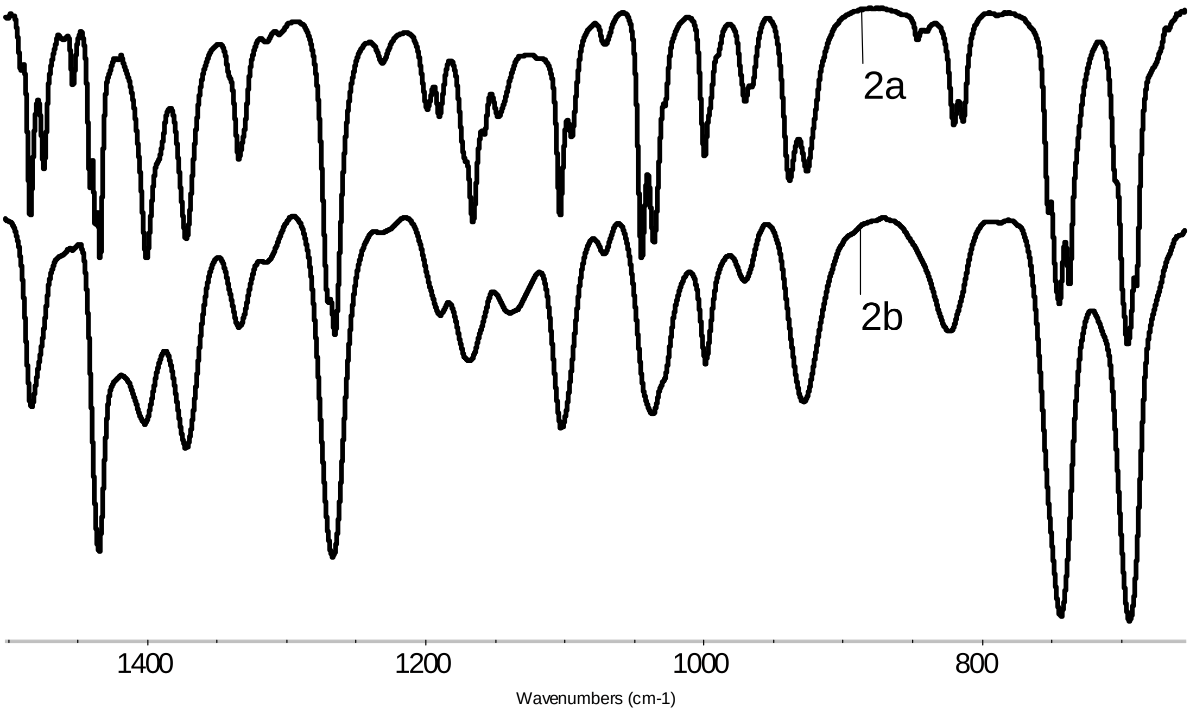

Figure S-3. Comparison between the FTIR spectra of **2a** and **2b** (reflectance mode, 1500-750 cm^{-1} region).

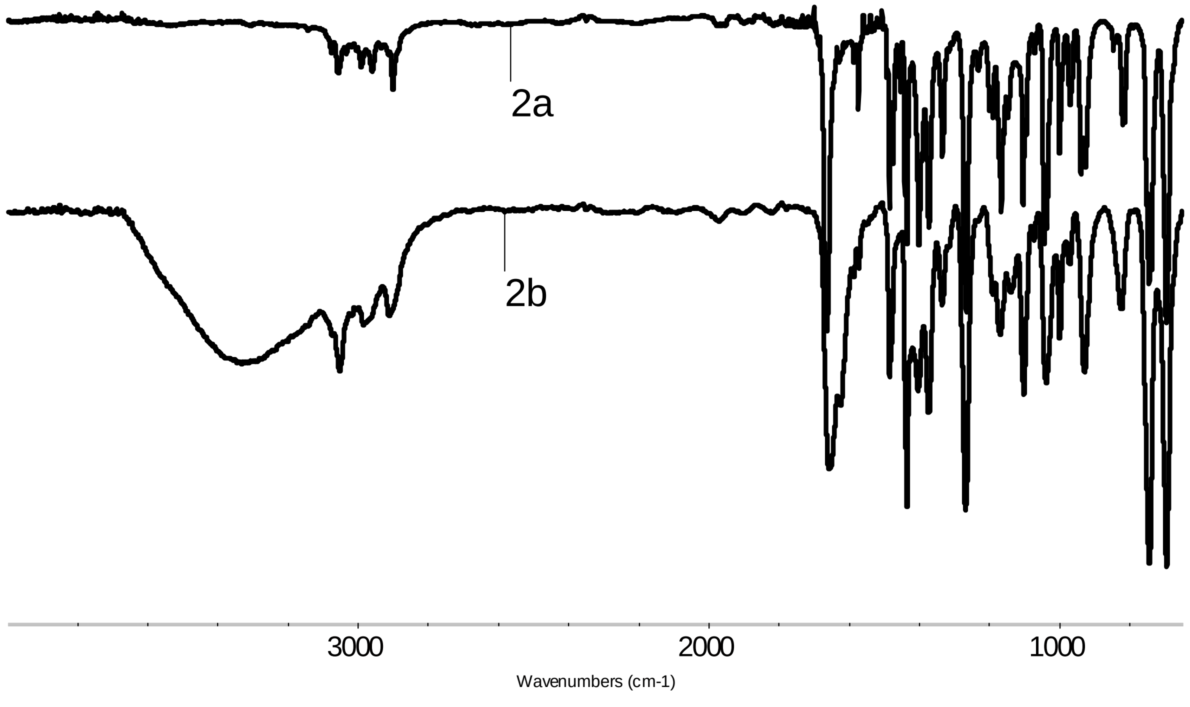

Figure S-4. FTIR spectrum (4000-650 cm^{-1} region) of **2a** (upper spectrum) recorded by FTIR microscopy immediately after isomerization from dry **2b** (lower spectrum) on a metallic support, with the aid of a spatula. The 3320 cm^{-1} absorption emphasizes its hygroscopicity.

3. Evans method[S-2]

A solution of paramagnetic species in CD_2Cl_2 (5 mg in 0.3 mL) was placed in a NMR tube and an inner narrow-bore NMR tube, containing a solution of CH_3NO_2 (20% Vol.) in CD_2Cl_2, was installed. The υ_{CH3} (Hz) is measured by ^{1}H NMR on a Bruker Avance 300 MHz instrument operating at 300.13 MHz, respectively, using TMS as external standard. $\upsilon°_{CH3}$ is measured in the same way, using pure CD_2Cl_2 instead of the sample solution. The simplified mathematic formula (1) is used to calculate the mass susceptibility χ_p which can was used to calculate the magnetic moment μ in Bohr Magnetons (BM) with formula (2).

(1) $\chi_p = \chi_0 + (3000.\Delta\upsilon)/(4\Pi.\upsilon_0.C.M)$

[$\chi_0 = \chi_{CD2Cl2} = -0.58\cdot10^{-6}$ (cm^3/l); $\upsilon_0 = 300013$ Hz; $\Delta\upsilon = \upsilon_{CH3}-\upsilon°_{CH3}$ C = Concentration of the paramagnetic compound (mol/l); M = Molar mass of the paramagnetic compound (g/mol)]

(2) $\mu = 2.84\cdot\sqrt{}(\chi_p\cdot M\cdot T)$

[T = Temperature].

4. Magnetic Study

The magnetic properties of **2a** were investigated in the 300-1.8 K temperature range with an applied field of 5 kOe. The Curie constant $C = 4.64$ emu·K·mol^{-1}, determined from the fit of the $1/\chi = f(T)$ curve with the Curie-Weiss law in the high temperature region (150-300 K), is in accordance with what is expected for four octahedral Ni(II) ions (with a g value of 2.15).[S3]

Upon cooling, the χT product exhibits a regular decrease from 4.54 emu·K·mol^{-1} at 300 K to 3.47 emu·K·mol^{-1} at 20 K, indicating the occurrence of at least one intramolecular antiferromagnetic interaction. Below 20 K, the small increase of the χT product up to 3.49 emu·K·mol^{-1} at 14 K and the final decrease below 14 K are most probably due to the complicated interaction scheme and to the presence of competing intramolecular interactions (Fig. S-5) as well as zero-field splitting and intermolecular interactions.

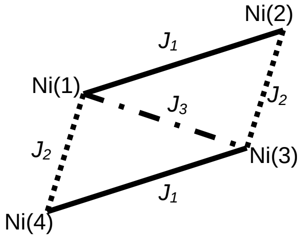

Figure S-5. Spin and interaction topology considered for Ni_4.

Considering the spin topology described in Figure S-5 and assuming each pairwise interaction is describable in terms of the Heisenberg Hamiltonian of the form $\hat{\mathbf{H}} = -J_{ij}\,\hat{\mathbf{S}}_i\cdot\hat{\mathbf{S}}_j$, the complete spin Hamiltonian for Ni_4 is given in eq. 1

$$\hat{\mathbf{H}} = -J_1\,\hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_2 - J_2\,\hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_4 - J_3\hat{\mathbf{S}}_1\cdot\hat{\mathbf{S}}_3 - J_2\,\hat{\mathbf{S}}_2\cdot\hat{\mathbf{S}}_3 - J_1\,\hat{\mathbf{S}}_3\cdot\hat{\mathbf{S}}_4 \qquad (1)$$

As explained by Griffith and by Hendrickson, the existence of three different exchange constants for this peculiar spin topology prevents the use of the Kambe vector-coupling approach.[S4,S5,S6] Unfortunately, in the present case, no analytical fitting by full diagonalization of the complete spin Hamiltonian was successful in the whole temperature range. This may infirm the hypothesis of Heisenberg type interactions.

The magnetic properties of this compound require further studies, for instance by neutron diffraction, neutron scattering, or high-field EPR spectroscopy, in order to precise the amplitude and sign of the different exchange constants and the characteristics of the ground state (spin value, anisotropy).

5. Crystallographic

5.1 X-ray data collection, structure solution and refinement for 1a·$2CH_2Cl_2$, 3 and 4.

Suitable crystals for X-ray analysis of compounds **1a**·$2CH_2Cl_2$, **3** and **4** were obtained by layering hexane on dichloromethane solutions. The intensity data was collected at 173(2) K on a Kappa CCD diffractometer[S-7] (graphite monochromated MoK_α radiation, $\lambda = 0.71073$ Å). Crystallographic and experimental details for the structures are summarized in Table S-1. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares procedures (based on F^2, SHELXL-97)[S-8] with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions and refined *riding* on the corresponding parent atoms. For **1a**, C2 and C6 were found disordered in two positions with equal occupancy factors and their position was refined isotropically. CCDC-641489 (**3**), 641490 (**4**) and 641491 (**1a**·$2CH_2Cl_2$) contain the supplementary crystallographic data that can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax (+44)1223-336-033 or deposit@ccdc.cam.ac.uk). Figure 1 was produced using the UCSF Chimera package from the Computer Graphics Laboratory, University of California, San Francisco: C.C. Huang, G.S. Couch, E.F. Pettersen, T.E. Ferrin, "Chimera: An Extensible Molecular Modeling

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Table S-1: X-ray data collection and refinement parameters for compounds **1a**·$2CH_2Cl_2$, **3** and **4**.

Compound	**1a·$2CH_2Cl_2$**	**3**	**4**
Formula	$C_{64}H_{64}Cl_8$ $N_4Ni_4P_4S_4 \cdot 2CH_2Cl_2$	$C_{16}H_{16}NSPNiBr_2$	$C_{16}H_{16}NOPNiBr_2$
FW	1829.60	503.86	503.86
Crystal System	Triclinic	Triclinic	Triclinic
Space Group	*P-1*	*P-1*	*P-1*
***a*, Å**	11.248(1)	8.6595(3)	8.6330(3)
***b*, Å**	11.518(1)	8.6983(2)	8.7360(3)
***c*, Å**	14.843(2)	12.9457(4)	11.8890(4)
α, °	91.811(3)	91.476(1)	104.2010(17)
β, °	94.041(3)	98.175(1)	96.7060(17)
γ,°	97.161(3)	111.337(1)	96.3230(12)
***V*, $Å^3$**	1901.6(3)	895.86(5)	854.28(5)
Z	1	2	2
D_{calcd}, g cm^{-3}	1.598	1.868	1.896
***F*(000)**	932	496	480
Crystal size (mm)	0.14 × 0.14 × 0.10	0.10 × 0.10 × 0.10	0.12 × 0.11 × 0.10
μ, cm^{-1}	1.634	5.74	5.90
Rflns. collected	17720	6954	6589
Rflns. unique	10978	4612	4548
Rflns. observed [$I > 2\sigma(I)$]	7468	3318	2768
Parameters	420	199	199
***R* Indices [I>2σ(I)]**	*R1* = 0.0485 *wR2* = 0.1107	*R1* = 0.0438, *wR2* = 0.0965	*R1* = 0.0464, *wR2* = 0.0985
***R* Indices (all data)**	*R2* = 0.0858, *wR2* = 0.1263	*R1* = 0.0743, *wR2* = 0. 1089	*R2* = 0.0999, *wR2* = 0.1194

5.2 X-ray powder data collection and cell refinement for compound 2a. Density estimation of 2a and 2b.

Powder X-Ray data for **2a** were obtained by using a Bragg-Brentano Siemens D5000 (CuKα1, λ = 1.54051 Å) diffractometer equipped with a primary beam monochromator. The cell parameters were determined with the program DICVOL04[S-9] and refined by profile fitting procedures with the program Fullprof2000.[S-10] The experimental and calculated diffraction profiles are depicted in Figure S-6, together with the trace of their difference (measured–calculated). Refined cell parameters: a = 11.379(4), b = 11.945(3), c = 15.479(5) Å, α = 83.58(3), β = 84.84(3), γ = 88.02(3)°, V = 2081(1) Å^3. Fitting refinement parameters: Bragg R: 0.0362, R_f = 0.04; χ^2: 1.22 GoF: 1.1.

The refined volume of V = 2081(1) Å^3 for **2a** results in a calculated density of 1.41 g/cm^3, considering **2a**·2CH_2Cl_2 as the cell content. The density of 1.55 g/cm^3, estimated for **2b** is calculated by considering its cell volume similar to that of **4** [854.28(5) Å^3].

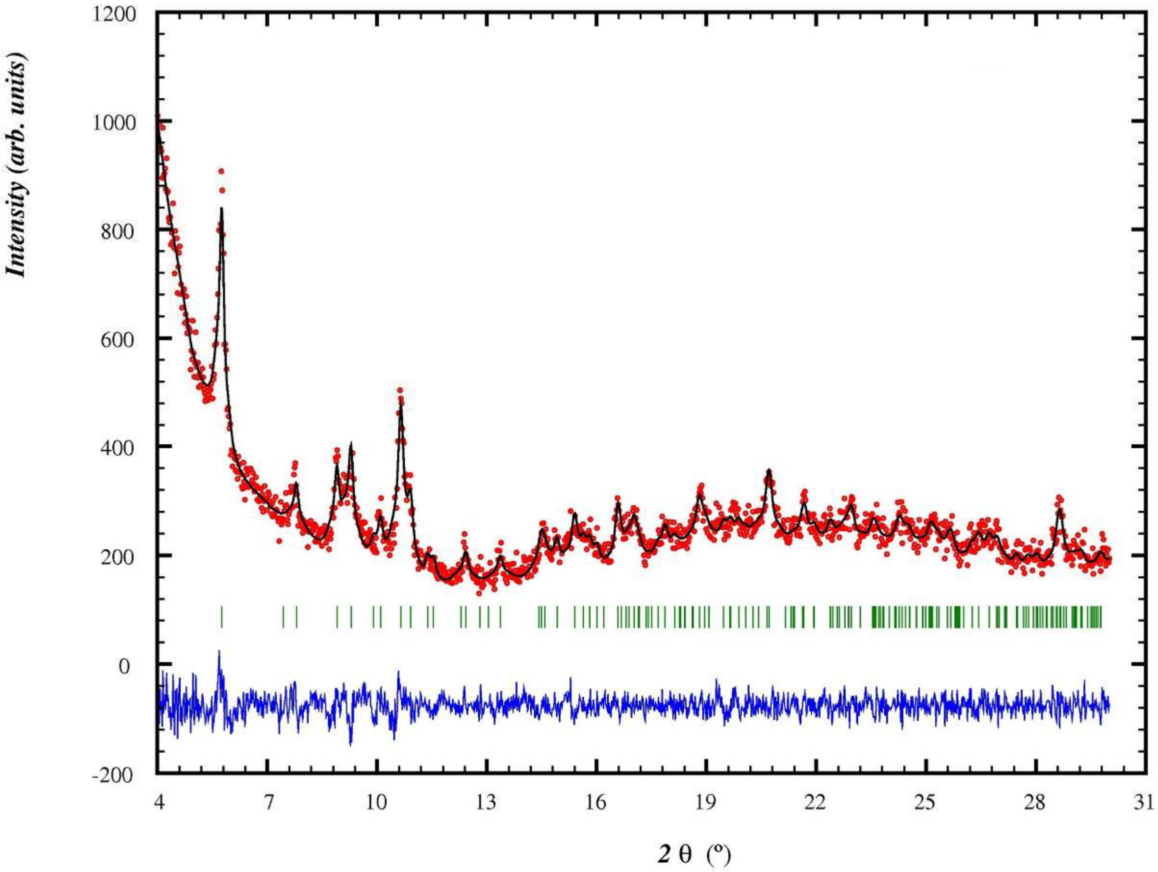

Figure S-6: Superimposition of the experimental (red dots) and fitted (black line) X-ray diffractions patterns of compound **2a**. The difference trace is reported in blue. Bragg positions are reported in green.

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Chapitre IV

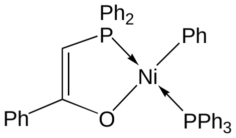
Mono- and Dinuclear Nickel Complexes with Phosphinopyridine, Phosphinitopyridine and Phosphonitopyridine Ligands: Synthesis, Structures and Catalytic Oligomerization of Ethylene.

Abstract

The P,N-type ligands 2-[(diphenylphosphino)methyl]pyridine **12,** 2-[2-(diphenylphosphino)ethyl]pyridine **13,** 2-methyl-oxy-(diphenylphosphino)pyridine **14**, 2-methyl-oxy-(dibenzyl-1,2-oxa-phosphorino)pyridine **15** and 2-methyl-oxy-(di-*tert*-butylphosphino)pyridine **16** have been prepared in good yields and **12** and **13** have been used to synthesize Ni(II) complexes of formula [Ni(P,N)Cl_2] **17** (P,N = **12**) and **18** (P,N = **13**) by reaction with $NiCl_2$ in methanol. The crystal structure of **18** has been determined by X-ray diffraction to be dinuclear with a distorted square-base pyramidal geometry around the Ni(II) centers. To examine the possible influence of the nature of the spacer link between the P and N donor atoms, we compared ligand **13**, with a CH_2CH_2 spacer, with **14** and **16** which have a isosteric CH_2-O spacer. Reactions of the phosphinitopyridine ligands **14** and **16** and of the phosphonitopyridine **15** with [NiX_2(DME)] (X = Cl or Br) afforded the complexes [Ni(P,N)Cl_2] **20** (X = Cl; P,N = **14**), **21** (X = Br; P,N = **14**), **22** (X = Cl; P,N = **16**) and **23** (X = Cl; P,N = **15**), respectively. The mononuclear structure of complex **22** has been established by X-ray diffraction and showed a distorted tetrahedral geometry around the metal center. Complexes **17**, **18** and **20-22** have been evaluated as precatalysts in the oligomerization of ethylene, with $AlEtCl_2$ or MAO as cocatalyst, in order to evaluate the influence of the stereoelectronic properties of the phosphorus substituents. With 6 equivalents of $AlEtCl_2$ as cocatalyst, complex **18** was the most active with turnover frequencies (TOF) up to 91200 C_2H_4/(mol Ni·h) and **20** with 2 equivalents of $AlEtCl_2$ showed the highest selectivities for ethylene dimers (up to 97%) and in 1-butene (up to 72%). With only 25 equivalents of MAO as cocatalyst, complex **18** was again the most active, with TOF values up to 20600 C_2H_4/(mol Ni·h). Despite the high selectivity for C_4 olefins of **17**, **18**, **20** and **21** (up to 93% for **20**), **22** presented the best selectivities for 1-butene (up to 73%) with MAO as cocatalyst and its high reactivity for the reinsertion of 1-butene resulted in 2-ethyl-1-butene to be the main product of the catalytic reaction (up to 91%).

1. Introduction

The catalytic production of linear α−olefins (LAO) has enjoyed major industrial developments since the seminal works of Ziegler and Natta on the oligomerization and polymerization of ethylene with metal catalysts activated by alkylaluminiums.[1-4] By favoring chain transfer over propagation during the catalytic cycle, late transition metals such as Ni, Pd, Co and Fe are good candidates for the formation of oligomerization catalysts.[5-9] The discovery of the “nickel effect” by Ziegler in 1953 proved the preference of this metal for the oligomerization of ethylene[10] and many systems based on nickel complexes with P,O,[11-18] N,N,[19-21] N,O,[22-27] P,P,[28] and P,N[8] chelating ligands have provided very interesting catalytic results. The SHOP process which is based on neutral phenyl nickel complexes of type **1** and does not require any cocatalyst, remains a reference in oligomerization of ethylene with its remarkable selectivity for LAO and Schulz-Flory distribution.[11,12] The α-diimine Ni(II) complexes **2** and **3** also form very active and selective catalysts for LAO when activated by a cocatalyst like methylalumoxane (MAO).[20,21]



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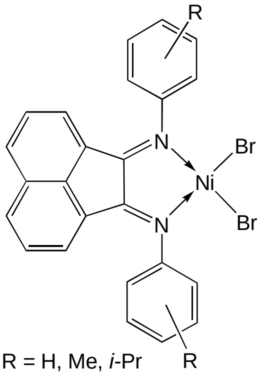

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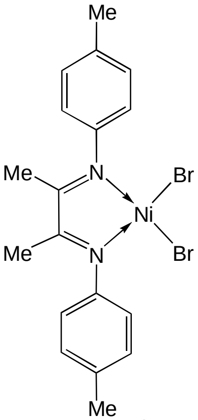
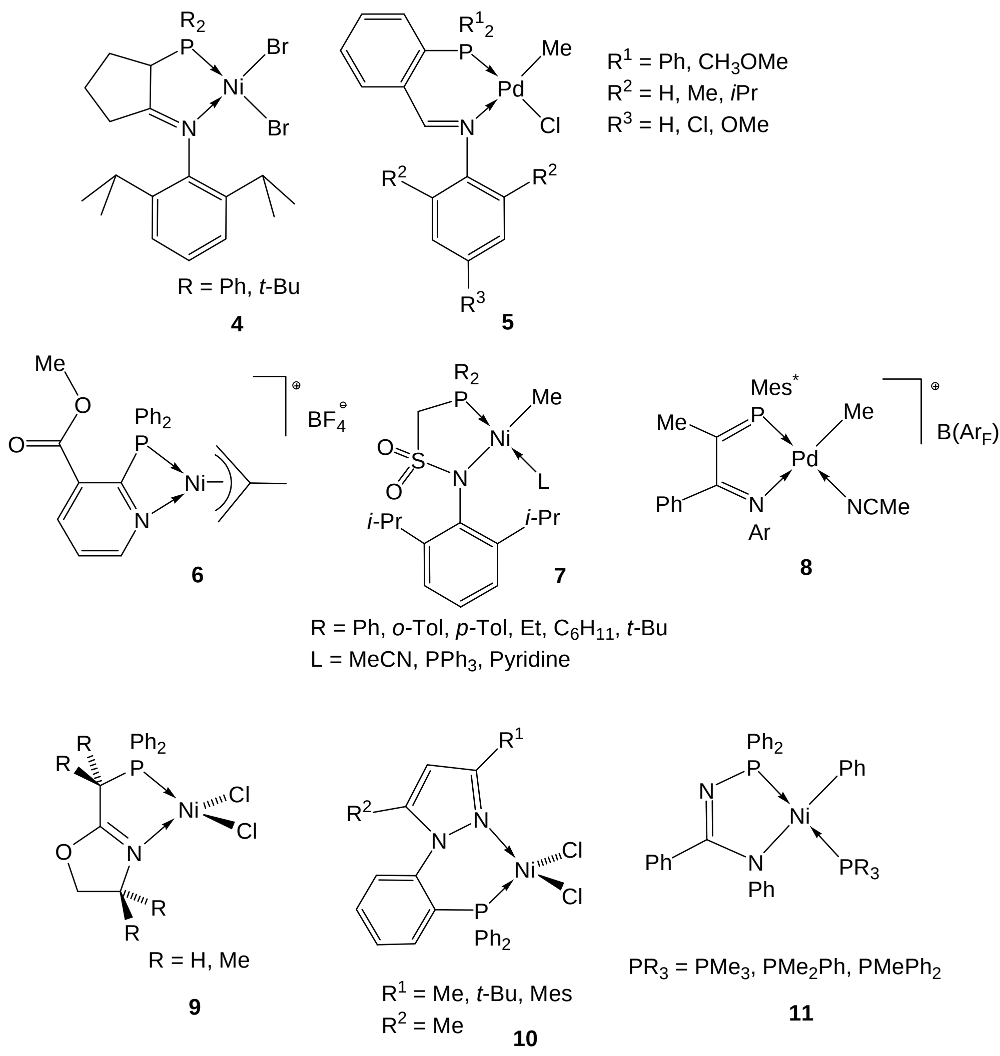


3

In combinaison with divalent nickel or palladium, P,N-type ligands, such as phosphinoimines in **4** and **5**,[29,30] phosphinonicotine-methyl-esters in **6**,[31] phosphinosulfonamides in **7**,[32] phosphinidine-imines in **8**,[33] phosphinooxazolines in **9**,[34,35] phosphinopyrazole in **10**,[36] or derived from α-iminoazatriphenylphosphoranes in **11**,[37] result in active catalysts for ethylene oligomerization or polymerization (Scheme 1).

Scheme 1. Complexes with P,N-type ligands for the catalytic oligomerization or polymerization of ethylene (references given in the text)



The properties and applications of transition metal complexes with phosphinopyridine ligands have been reviewed[38-41] and some of their Ni(II) complexes catalyze the oligomerization of ethylene in the presence of MAO[42-45] or $AlEtCl_2$[46] as cocatalyst. We have recently reported Ni(II) complexes with phosphinopyridine ligands which led to high selectivities for the dimerization of ethylene but modest selectivities for α–olefins, and some ethylene trimerization was also noted.[47-50] We were therefore interested in the synthesis of new Ni(II) catalyst precursors based on phosphinopyridine ligands with different substituents on phosphorus to modify its electronic and steric effects and examine the consequences for this catalytic reaction. Introducing *t*-butyl substituents on phosphorus will result in ligands with a larger cone angle[51] and their influence on the stability of the complexes and their catalytic properties has now been investigated.

2. Results and Discussion

2.1 Synthesis of the ligands

The ligand 2-[(diphenylphosphino)methyl]pyridine **12** was prepared by deprotonation of 2-methylpyridine with *n*-BuLi, followed by reaction with excess chlorotrimethylsilane at -78 °C and reaction with 1 equivalent of chlorodiphenylphosphine at –78 °C.[52] This procedure is crucial for a high yield synthesis of the corresponding ligand because the direct reaction of the carbanion with PPh_2Cl gives rise to byproducts. The ligand 2-[2-(diphenylphosphino)ethyl]pyridine **13** was synthesized by reaction of 2-(pyridine)ethanol with $SOCl_2$ to give 2-chloroethylpyridine which was then reacted with $NaPPh_2$.[53,54] The ^1H NMR spectrum of **13** was analyzed using the MestRec software[55] by considering an AA'BB'X spin system for the P-CH_2 and Py-CH_2 protons (Figure 1). The reaction of (pyridin-2-yl)methanol with 1 equivalent of PPh_2Cl or chloro(dibenzyl-1,2-oxa)phosphorine in the presence of excess triethylamine (to neutralize the HCl liberated) afforded the new ligands 2-methyl-oxy-(diphenylphosphino)pyridine **14**[56] and 2-methyl-oxy(dibenzyl-1,2-oxa-phosphorino)pyridine **15**, respectively. Their properties are similar to those of their methyl derivatives containing a $POCMe_2$ instead of a $POCH_2$ moiety.[50]

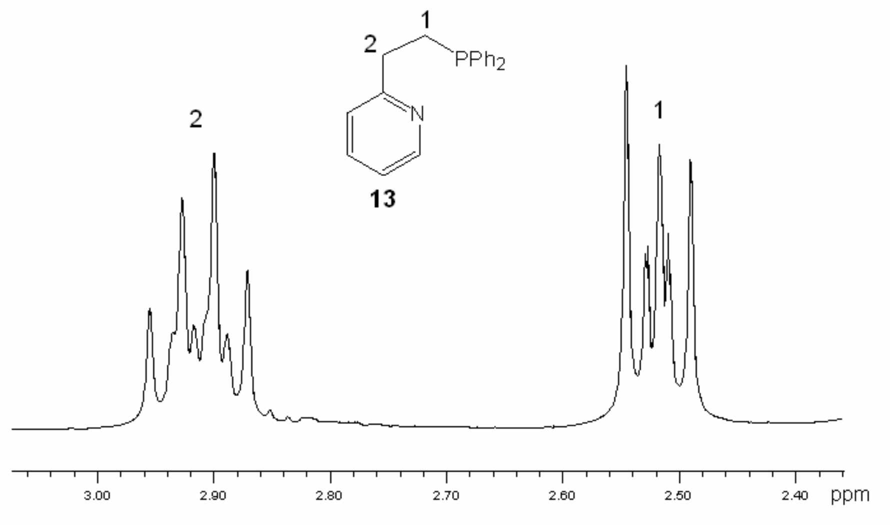
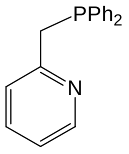


Figure 1. ^1H NMR spectrum (300 MHz) of **13** showing the P-CH_2 and the Py-CH_2 protons.



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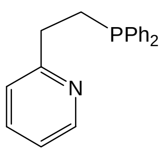
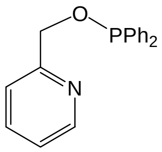


13



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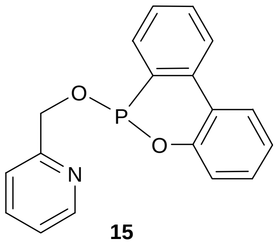
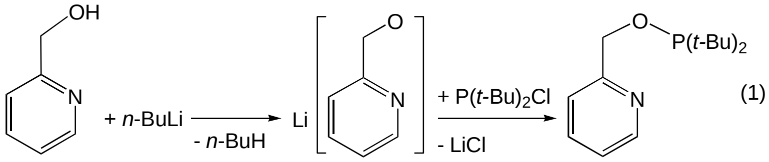


15

For the synthesis of 2-methyl-oxy-(di-*tert*-butylphosphino) pyridine **16**, 2-(pyridine)ethanol had first to be deprotonated and reacted with di-*tert*-butyl(chloro)phosphine (eq 1), because the phosphine is not electrophilic enough to react directly with a pyridine-alcohol owing to the electron donor effect of the two *tert*-butyl substituents.

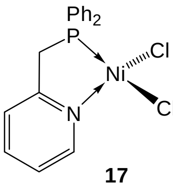


16

All the ligands have been characterized by ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, COSY, HMBC and HMQC NMR spectroscopy. We note the high ^{31}P{^{1}H} chemical shifts of **16** (δ 166.3 ppm) compared to that of the phosphinite **14** (δ 117.7 ppm) which results from the steric effect of the *tert*-butyl substituents.

2.2 Synthesis of the Ni(II) complexes

To examine the possible influence of the nature of the spacer link between the P and N donor atoms, we compared ligand **13**, which contains a CH_2-CH_2 spacer, with **14** and **16** which have a isosteric CH_2-O spacer. The Ni(II) phosphinopyridine complexes **17** and **18** were prepared by reaction of one equivalent of the corresponding phosphine with $NiCl_2$ in methanol. The immediate color change, from green to red, indicated a fast reaction. After work-up, grey and green powders of **17** and **18** were obtained in 83% and 80% yields, respectively. Slow diffusion of pentane into a CH_2Cl_2 solution of **18** afforded single crystals suitable for X-ray diffraction, which established its dinuclear structure (see below). A red-violet complex has been reported from the reaction of **13** with $NiCl_2$ in refluxing *n*-butanol.[57]



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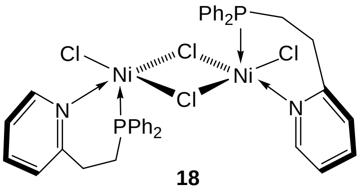
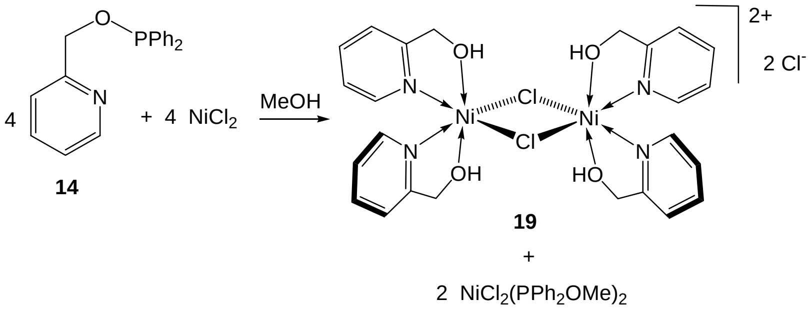


18

The complexation of $NiCl_2$ by ligand **14** in methanol led to cleavage of the phosphinite P-O bond and substituent exchange at the phosphorus to form $[Ni(\mu\text{-}Cl)_2(2\text{-pyridine ethanol})_2]Cl_2$ **19** and $[NiCl_2(PPh_2OMe)_2]$ (eq 2). The very low solubility of **19** in CH_2Cl_2 facilitated separation of the Ni(II) complexes. This reaction is consistent with the sensitivity of phosphonites to the presence of alcohols,[58] and the breaking of the P-O bond does not necessarily requires the presence of a metal cation. Complex **19** has been obtained directly from (pyridin-2-yl)methanol and $NiCl_2$ and was shown by X-ray diffraction to have a dinuclear structure.[59]



14

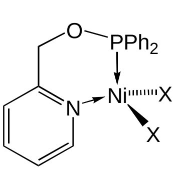
19

+

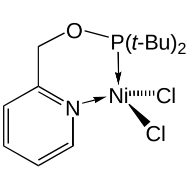
2 $NiCl_2(PPh_2OMe)_2$

(2)

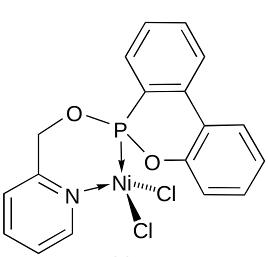
The use of methanol for metal complexation with phosphinites **14** or **16** and phosphonite **15** should therefore be avoided but other solvents (MeCN, THF or CH_2Cl_2) led to poor yields owing to the very low solubility of $NiCl_2$. However, reaction of $[NiCl_2(DME)]$ or $[NiBr_2(DME)]$ in CH_2Cl_2 with **14-16** led to the high yield formation of the Ni(II) complexes **20-23,** respectively (up to 92%). Their colors in the solid state are respectively grey, green, red or maroon but all complexes afforded red CH_2Cl_2 solutions. Red single crystals of **22** suitable for X-ray diffraction were obtained by slow diffusion of pentane into a solution of the complex in chlorobenzene and **22** presented a mononuclear structure (see below).



20 X = Cl
21 X = Br



22



23

Although some nickel complexes with P,N- or P,N,P-type ligands are diamagnetic in solution,[60] complexes **17, 18**, **20**, **22** and **23** proved to be paramagnetic in $CDCl_3$, CD_2Cl_2, CD_3CN, CD_3CD_2OD or CD_3OD solution. Their magnetic moments per Ni atom, determined by the Evans method in CD_2Cl_2,[61-64] were 2.2 (**17**), 2.7 (**18**), 2.8 (**20**), 3.0 (**22**) and 1.9 (**23**) μ_B respectively.[65,66] These values are similar to those recently reported for other Ni(II) complexes with P,N-type ligands.[34,47-50]

These complexes have also been characterized by IR, elemental analysis and mass spectrometry. High Resolution Mass Spectrometry (HRMS) with the ElectroSpray Ionisation method afforded spectra where the main peak corresponds to $[Ni(P,N)Cl]^+$. The structures of **18** and **22** are shown in Figures 2 and 3 and selected bond distances and angles are given in Tables 1 and 2.

Table 1. Selected Bond Lengths (Å) and Angles (deg) in **18**

Ni-P	2.305(1)	C6-C7	1.543(5)
Ni-N	2.061(3)	C5-C6	1.500(5)
Ni-Cl1	2.291(1)	C5-N	1.357(4)
Ni-Cl2	2.4227(9)	P-C8	1.821(4)
Ni-Cl3	2.3508(9)	P-C14	1.818(4)
P-C7	1.822(4)		
Cl1-Ni-Nl2	158.69(4)	Cl3-Ni-N	162.92(9)
Cl1-Ni-Cl3	92.09(4)	Cl3-Ni-P	100.18(3)
Cl1-Ni-N	87.97(8)	N-Ni-P	96.18(9)
Cl1-Ni-P	106.28(4)	Ni-P-C7	105.5(1)
Cl2-Ni-Cl3	84.53(3)	C7-C6-C5	113.4(3)
Cl2-Ni-N	89.23(8)	C6-C5-N	118.5(3)
Cl2-Ni-P	95.03(3)	C5-N-Ni	126.8(3)

Table 2. Selected Bond Lengths (Å) and Angles (deg) in complex **22**

Ni-P	2.304(1)	P-O	1.626(3)
Ni-N	2.005(3)	O-C6	1.454(6)
Ni-Cl1	2.217(2)	C5-C6	1.505(6)
Ni-Cl2	2.227(1)	C5-N	1.350(5)
P-C7	1.865(5)	P-C11	1.860(5)
N-Ni-P	92.2(1)	N-Ni-Cl1	102.9(1)
Ni-P-O	105.9(1)	N-Ni-Cl2	108.3(1)
P-O-C1	118.8(2)	Cl1-Ni-Cl2	123.47(5)
O-C1-C2	112.1(3)	Cl1-Ni-P	112.74(5)
C1-C2-N	116.8(4)	Cl2-Ni-P	111.77(5)
C2-N-Ni	122.5(3)		

Complex **18** has a dinuclear structure with pentacoordinated metal centers and six-membered ring chelates. The cisoid coordination of the two pyridine functions with respect to the Ni-Ni axis makes the structure non centrosymmetric but it possesses a C_2 symmetry axis passing through Cl2 and Cl3. The coordination geometry around the metals is distorted square-pyramidal, with the square base being formed by N and the three chlorides (Scheme 2). The Ni atom is out of this plane by 0.3777(1) Å.

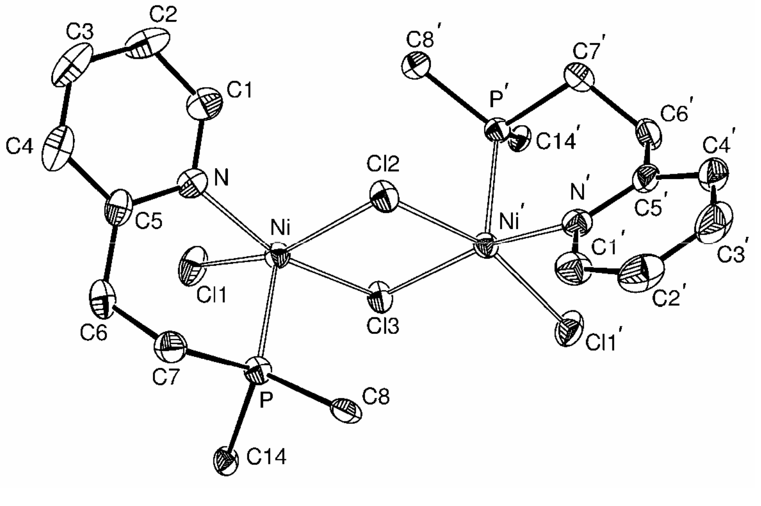
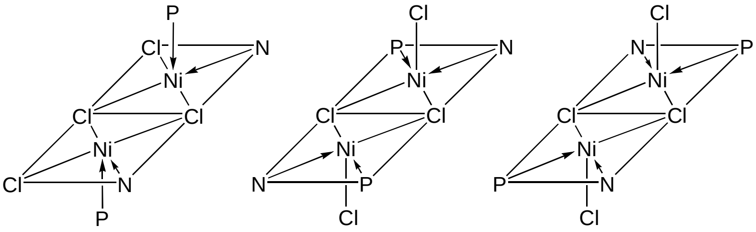


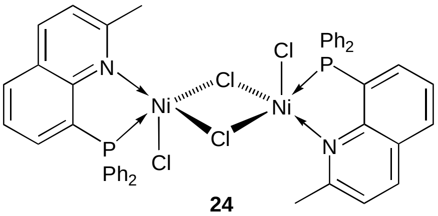
Figure 2. ORTEP view of the molecular structure of **18** (ellipsoids enclose of 50% electronic density, only the phenyl *ipso* carbons are shown and the H atoms are omitted for clarity).

Scheme 2. Representation of the square-pyramidal coordination geometries around the metals in **18**, **24** and **25**

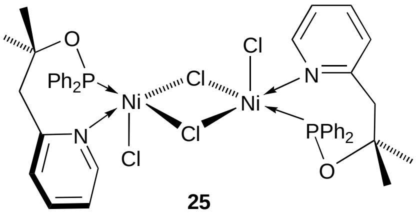


18 **24** **25**

It is interesting to compare the structure of **18** with those of the distorted square-pyramidal dinuclear Ni(II) complexes **24** and **25** which contain five- and seven-membered ring P,N chelates.[42,50]



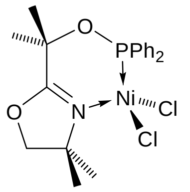
24



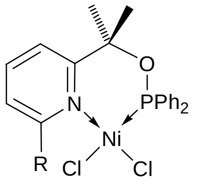
25

In contrast to **18**, complexes **24** and **25** have centrosymmetric structures and their square bases contained the atoms P, N and the 2 bridging chlorides Cl(1) and Cl(1a) (Scheme 2). The larger N-Ni-P coordination angle (96.18(9)°, Table 1) of **18** compared to **24** (84.48(9)°) or **25** (85.37(5)°) leads to the apical position being occupied by the phosphorus donor atom instead of a chloride ligand. The Ni-P and Ni-N distances in **18**, of 2.305(1) and 2.061(3) Å, respectively, are similar to those in the dinuclear complexes **24** and **25** but are longer than in related mononuclear Ni(II) complexes.[50]

Complex **22** has a mononuclear structure with a distorted tetrahedral geometry similar to that of complex **26**, in contrast to the square-planar geometry of complexes **27** and **28** (Figure 3).[50] The Ni-P and Ni-N distances of **22**, 2.304(1) and 2.006(3) Å (Table 2), are significantly longer than in complexes **26-28**. The large Cl-Ni-Cl angle (123.47(5)°) and the small N-Ni-P angle (92.1(1)°, Table 2) result in complex **22** adopting a distorted tetrahedral geometry instead of a square-planar geometry. The steric properties of the *tert*-butyl substituents on phosphorus probably explain the tetrahedral coordination in **22**. Tetrahedral Ni(II) complexes coordinated by phosphinopyridine[43,44] or phosphinoimine ligands[30] have been used previously in ethylene oligomerization and we shall now examine the catalytic properties of complexes **17**, **18** and **20-22** in this reaction.



26



27 R = H
28 R = Me

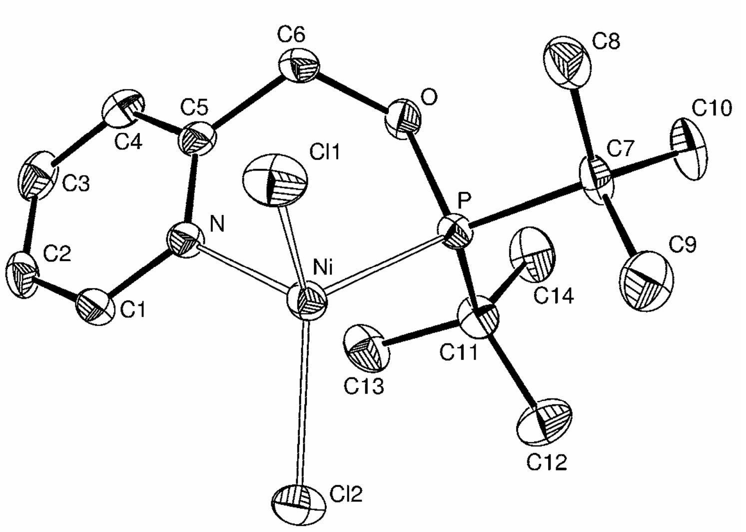


Figure 3. ORTEP view of the molecular structure of **22** (ellipsoids enclose of 50% electronic density, H atoms are omitted for clarity).

This structural study emphasizes the influence of sometimes seemingly minor variations in the stereoelectronic properties of the ligands on the structure of their corresponding Ni(II) complexes. With related phosphino-oxazoline and –thiazoline ligands, it was recently found that tetranuclear Ni(II) complexes are formed and a dramatic effect of pressure was evidenced which results in its breaking into four mononuclear complexes.[67]

3. Catalytic oligomerization of ethylene

Complexes **17**, **18** and **20-22** have been tested as precatalysts in the oligomerization of ethylene with variable amounts of $AlEtCl_2$ or MAO as cocatalyst. In previous studies, $[NiCl_2(PCy_3)_2]$, which is a typical α-olefin dimerization catalyst,[68] was used to compare the catalytic results but considering the sensitivity of this complex, we choose another reference compound, $[NiCl_2\{P(n\text{-}Bu_3)\}_2]$ which is diamagnetic and thus readily amenable to purity check by NMR spectroscopy and is also highly active in oligomerization with $AlEtCl_2$.[69]

The analysis of the different C_6 oligomers was performed in order to differentiate between a chain growth mechanism and the reinsertion of butenes. The formation of 2-hexene, 3-hexene and 2-ethyl-1-butene by reinsertion of 1-butene and the formation of 3-methyl-2-pentene and 3-methyl-1-pentene by reinsertion of 2-butene depending on the insertion mode (2,1- or 1,2-insertion) has been discussed previously.[27] Isomerization of 1-hexene leads to the formation of 2-hexene and 3-hexene.

3.1 Use of $AlEtCl_2$ as cocatalyst.

Complexes **17**, **18** and **20-22** have been tested in the presence of 2, 4 or 6 equivalents of $AlEtCl_2$ (Al/Ni ratios of 2, 4 or 6, respectively) and the catalytic results are presented in Table 3 and shown in Figures 4-6.

The highest activities were obtained for complex **18** with turnover frequencies (TOF) of 78200 and 91200 mol C_2H_4/(mol Ni·h), either with 4 or 6 equivalents of $AlEtCl_2$, respectively. Complexes **17**, **20**, **21** and **22** had similar activities (Figure 4), which increased with the amount of cocatalyst, between 17000 and 20400 mol C_2H_4/(mol Ni·h) with 2 equivalents of $AlEtCl_2$, 43500 and 46700 mol C_2H_4/(mol Ni·h) with 4 equivalents and 56600 and 63600 with 6 equivalents However, **20** showed very low activity with 2 equivalents of $AlEtCl_2$ (1100 mol C_2H_4/(mol Ni·h)).

The selectivity for 1-butene was modest and less than 17% for all the complexes except for **20** with 2 equivalents of $AlEtCl_2$ (72%, Figure 6). The high concentration of 2-butene indicates that isomerization of 1-butene is largely favored. The exothermicity of the catalytic reaction (temperature up to 115 °C) with very active systems is most likely responsible for the lower selectivity in 1-butene.[70] The selectivities for C_4 olefins were between 97% and 50% for complexes **17**, **18** and **20-22** (Figure 5) and this showed that dimerization is much favored over chain growth. The second largest is constituted by the hexenes (Table 3) with the reinsertion of 1-butene and 2-butene being very significant on the basis of the branched olefins formed (Table 4).

Increasing the amount of $AlEtCl_2$ had a significant influence on the catalytic results by forming a more active but less selective system. Higher activities were associated with an increasing isomerization of 1-butene to 2-butene. With **18**, for example, the fraction of 1-butene decreased from 13% to 2%. The higher concentration of 2-butene favored its reinsertion to give C_6 oligomers (Table 4).

Table 3. Comparative Catalytic Data for Complexes **17**, **18** and **20**-**22** in the Oligomerization of Ethylene with $AlEtCl_2$ as Cocatalyst[a]

	quantity of complex (10^{-5} mol)	$AlEtCl_2$ (equiv)	Time (min)	Selectivity[b] (%)			Productivity g C_2H_4/(g Ni·h)	TOF mol C_2H_4/(mol Ni·h)	1-butene[c] (%)	k_α[d]
				C4	C6	C8				
17	4	2	35	87	12	<1	9700	20400	17	<0.10
17	4	4	35	71	28	<1	22300	46700	14	0.26
17	4	6	35	55	43	2	30300	63600	7	0.53
18	4	2	35	76	21	3	8400	17600	13	0.19
18	4	4	35	52	44	4	37300	78200	3	0.57
18	4	6	35	50	43	7	43500	91200	2	0.59
18	1	6	35	69	30	1	99000	207600	1	0.31
18	1	6	120	70	28	2	49700	104100	9	0.27
20	4	2	35	97	2	<1	500	1100	72	<0.10
20	4	4	35	75	24	1	20700	43500	5	0.21
20	4	6	35	63	35	2	27900	58500	3	0.38
20	1	6	35	71	27	2	71600	150100	11	0.24
20	1	6	120	72	27	1	39700	83100	14	0.25
21	4	4	35	74	24	2	21100	44100	6	0.21
21	4	6	35	59	38	3	24800	56600	4	0.43
22	4	2	35	85	14	1	8200	17000	16	0.11
22	4	4	35	68	28	4	21500	45100	6	0.27
22	4	6	35	66	31	3	27200	57000	6	0.31
ref[e]	4	2	35	83	15	2	4000	8400	13	0.12
ref	4	4	35	60	35	5	35300	74100	3	0.39
ref	4	6	35	61	34	5	35000	73600	3	0.37

[a] Conditions: T = 25-30 °C, 10 bar C_2H_4, solvent 14 mL chlorobenzene and 1 mL of cocatalyst solution in toluene, 13 mL chlorobenzene and 2 ml of cocatalyst solution and 12 mL chlorobenzene and 3 mL of cocatalyst solution for 2, 4 or 6 equivalents of $AlEtCl_2$, respectively. [b] No C_{10} oligomers were detected. [c] within the C_4 fraction. [d] k_α = hexenes [mol]/butenes [mol]. [e] reference: $[NiCl_2\{P(n\text{-}Bu)_3\}_2]$.

To study the influence of the concentration of the complexes on the oligomerization of ethylene, precatalyst **18** and **20** have been tested with only 1×10^{-5} mol complex in 15 mL of solution instead of 4×10^{-5} mol for the standard procedure. The catalytic results with 6 equivalents of $AlEtCl_2$ showed that the complexes are more active and selective for C_4 oligomers under these conditions (Table 3).

Table 4. Catalytic Data and Distribution of the C_6 oligomers for Complexes **17**, **18**, **20**-**22** in the Oligomerization of Ethylene with $AlEtCl_2$ as Cocatalyst[a]

	$AlEtCl_2$ (equiv)	Selectivity (mass %)			
		1-hexene	Linear C_6[b]	C_6[c] from 1-butene	C_6[d] from 2-butene
17	2	3	37	17	43
17	4	1	37	20	42
17	6	1	30	14	55
18	2	1	27	15	57
18	4	<1	19	13	67
18	6	<1	19	13	67
18[e]	6	<1	18	14	67
18[e,f]	6	1	22	15	62
20	2	67	15	15	3
20	4	1	29	14	56
20	6	<1	25	11	63
20[e]	6	1	40	6	53
20[e,f]	6	3	45	6	46
21	4	2	22	13	63
21	6	3	26	9	62
22	2	18	49	11	22
22	4	1	32	7	60
22	6	1	31	7	61

[a] Conditions: T = 25-30 °C, 10 bar C_2H_4, 35 min, $4{\cdot}10^{-5}$ mol of complex, solvent 14 mL chlorobenzene and 1 mL of cocatalyst solution in toluene, 13 mL chlorobenzene and 2 ml of cocatalyst solution and 12 mL chlorobenzene and 3 mL of cocatalyst solution for 2, 4 or 6 equivalents of $AlEtCl_2$, respectively. [b] Sum of 2-*cis*-hexene, 2-*trans*-hexene, 3-*cis*-hexene and 3-*trans*-hexene. [c] Corresponding to 2-ethyl-1-butene. [d] Sum of 3-methyl-1-pentene, 3-methyl-2-*cis*-pentene and 3-methyl-2-*trans*-pentene. [e] 1.10^{-5} mol of complex. [f] time reaction: 120 min.

To determine the robustness of the P-O bond of complex **20** and the lifetime of the catalyst, we increased the reaction time to 120 min and compared the catalytic results with those for complex **18** (Table 3). The high and constant activities during the catalytic run (the ethylene consumption was constant, no plateau of activity was observed and the final activities were 104100 and 83100 mol C_2H_4/(mol Ni·h) for **18** and **20**, respectively) suggested a reasonable lifetime for the catalysts. The lower TOF values calculated for these experiments compared with those where the reaction time was 35 min are due to the non-linearity of the ethylene consumption as a function of time.

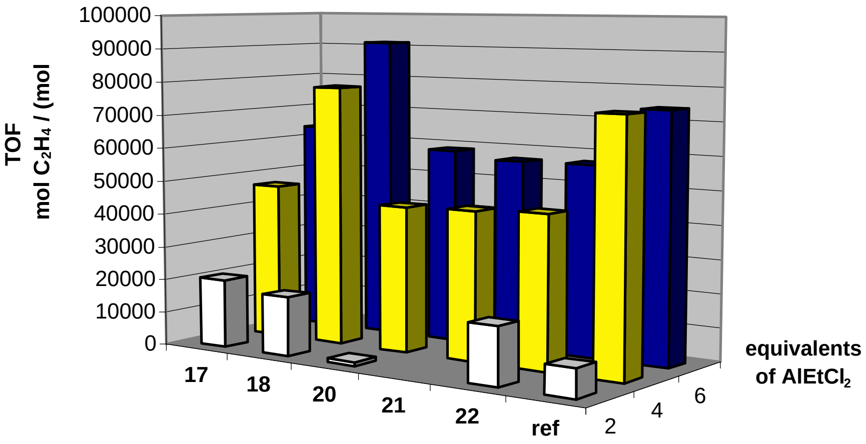


Figure 4. Catalytic activities of the complexes **17**, **18** and **20-22** in the oligomerization of ethylene using $AlEtCl_2$ as cocatalyst, Ref: $[NiCl_2\{P(n\text{-}Bu)_3\}_2]$.

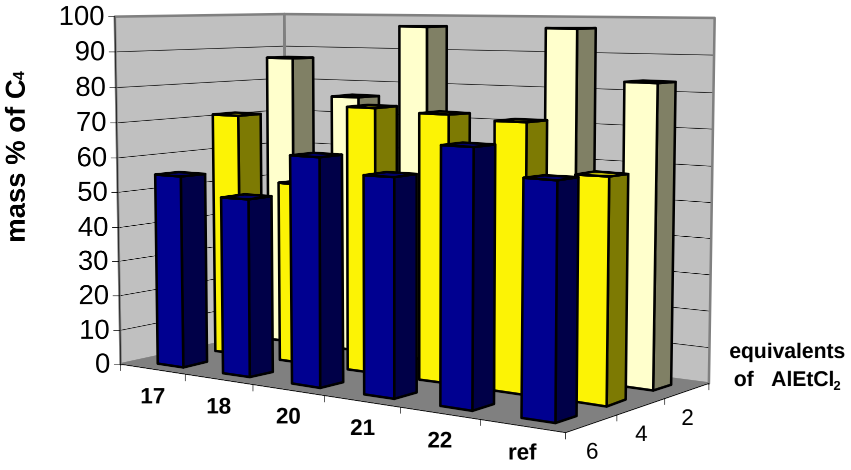


Figure 5. Selectivity of the complexes **17**, **18** and **20-22** for C_4 compounds using $AlEtCl_2$ as cocatalyst (1-butene and 2-butene), Ref: $[NiCl_2\{P(n\text{-}Bu)_3\}_2]$.

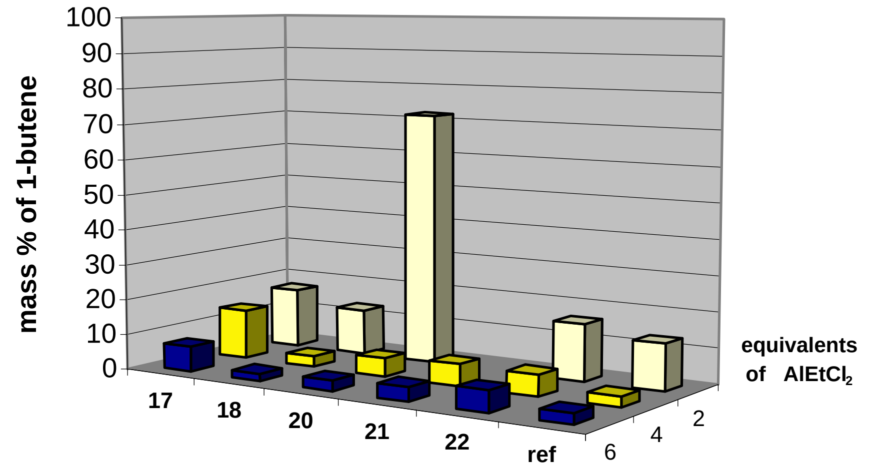


Figure 6. Selectivity of the complexes **17**, **18** and **20-22** for 1-butene using $AlEtCl_2$ as cocatalyst, Ref: $[NiCl_2\{P(n\text{-}Bu)_3\}_2]$.

3.2 Use of MAO as cocatalyst.

Complexes **17**, **18** and **20-22** have also been evaluated in the presence of 12.5, 25, 50, 100 and 200 equivalents of MAO as cocatalyst and the catalytic results are given in Tables 5 and 6 and shown in Figures 7-10.

In contrast to analogous Ni(II) complexes with pyridine-phosphine and pyridine-phosphinite ligands tested under similar conditions,[8] the precatalysts **17**, **18** and **20-22** presented high activities with very small amounts of MAO (Figures 7-9). In particular, **18** showed activities up to 18400 and 20600 mol C_2H_4/(mol Ni·h) with only 12.5 and 25 equivalents of MAO, respectively. The use of fresh MAO under strict conditions could explain these high activities of **17**, **18** and **20-22**, respectively, since MAO is known to be very sensitive to air and moisture and can rapidly evolve to a poor cocatalyst.[71] Increasing the amount of cocatalyst did not have a major impact on the catalytic results. Precatalysts **17**, **18** and **20-22** had similar activities, between 14100 and 19600 mol C_2H_4/(mol Ni·h). The precatalyst **16** with a smaller bite angle ligand than **18-22** presented slightly lower activities but better selectivities for 1-butene.

Table 5. Comparative Catalytic Data for Complexes **17**, **18**, **20**-**22** in the Oligomerization of Ethylene with MAO as Cocatalyst[a]

	Amount of complex (10^{-5} mol)	Amt of MAO (equiv)	Selectivity (%)				Productivity g C_2H_4/(g Ni·h)	TOF mol C_2H_4/(mol Ni·h)	1-butene[b] (%)	k_α[c]
			C4	C6	C8	>C8				
17	4	50	89	10	1	0	1300	2800	35	<0.10
17	4	100	61	32	6	<1	5700	12000	19	0.36
17	4	200	64	29	6	0	6800	14300	19	0.31
17	4	400	72	23	5	0	5700	12000	25	0.21
18	4	12.5	70	28	2	0	8800	18400	10	0.27
18	4	25	69	30	1	0	9800	20600	8	0.29
18	4	50	72	23	4	<1	8300	17300	11	0.21
18	4	100	65	28	6	<1	8400	17600	14	0.29
18	4	200	64	28	7	<1	8200	17300	16	0.30
20	4	25	79	17	4	0	8400	17600	11	0.14
20	4	50	72	22	5	<1	7000	14800	10	0.21
20	4	100	75	20	5	0	6700	14100	11	0.18
20	4	200	72	21	6	1	9400	19600	9	0.19
20	1	100	84	13	2	<1	14300	30100	13	0.10
20[e]	1	100	93	6	1	0	17500	36800	34	<0.10
21	4	200	65	30	4	1	9000	18900	11	0.49
22	4	25	17	52	20	11	7000	14800	38	2.00
22	4	50	20	49	22	9	7900	16600	42	1.60
22	4	100	23	52	20	5	6500	13600	42	1.50
22	1	100	26	47	17	10	11500	24200	56	1.18
22[e]	1	100	27	50	15	8	21700	45500	73	1.22
Ref[d]	4	50	43	46	8	3	18600	40000	3	0.72
ref	4	100	25	54	14	7	19200	41300	3	1.47
ref	4	200	26	52	16	6	17600	36900	3	1.31
ref	4	400	41	45	10	4	18900	39600	4	0.72

[a] Conditions: T = 25-30 °C, 10 bar C_2H_4, solvent 10 mL of chlorobenzene and 0.5, 1, 2, 4 or 8 mL of cocatalyst solution in toluene for 12.5, 25, 50, 100 or 200 equivalents of MAO, respectively. [b] within the C_4 fraction. [c] k_α = hexenes [mol]/butenes [mol]. [d] reference: $[NiCl_2\{P(n\text{-}Bu)_3\}_2]$. [e] pressure: 30 bar.

Table 6. Catalytic Data and Distribution of the C_6 oligomers for Complexes **17**, **18**, **20**-**22** in the Oligomerization of Ethylene with MAO as Cocatalyst[a]

	MAO (equiv)	Selectivity (mass %) 1-hexene	Linear C_6[b]	C_6[c] from 1-butene	C_6[d] from 2-butene
17	50	14	37	17	43
17	100	3	43	10	44
17	200	4	46	10	40
17	400	5	47	11	37
18	12.5	<1	38	15	47
18	25	<1	46	14	39
18	50	2	40	10	38
18	100	3	42	9	36
18	200	3	45	10	42
20	25	1	17	15	67
20	50	1	29	14	56
20	100	1	20	11	68
20	200	2	29	10	60
20[e]	100	2	25	12	61
20[e,f]	100	8	27	12	53
21	200	1	14	10	76
22	25	2	5	77	16
22	50	1	3	75	21
22	100	1	3	75	21
22[e]	100	3	5	83	9
22[e,f]	100	5	2	91	2

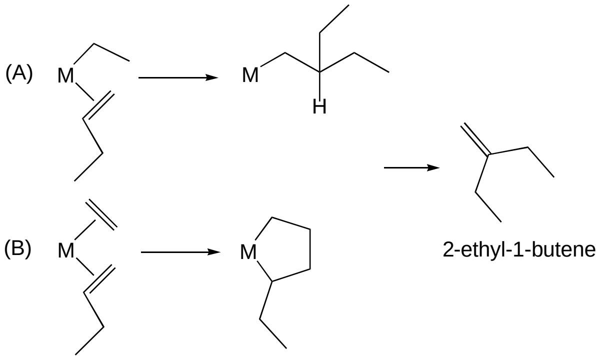
[a] Conditions: T = 25-30 °C, 10 bar C_2H_4, 35 min, $4x10^{-5}$ mol of complex, solvent 10 mL chlorobenzene and 0.5, 1, 2, 4, 8 mL of cocatalyst solution in toluene for 12.5, 25, 50, 100 or 200 equivalents of MAO, respectively. [b] Sum of 2-*cis*-hexene, 2-*trans*-hexene, 3-*cis*-hexene and 3-*trans*-hexene. [c] Corresponding to 2-ethyl-1-butene. [d] Sum of 3-methyl-1-pentene, 3-methyl-2-*cis*-pentene and 3-methyl-2-*trans*-pentene. [e] $1x10^{-5}$ mol of complex. [f] pressure: 30 bar.

In contrast to complex **20** which has phenyl substituents on the phosphorus atom, complex **22** has *tert*-butyl groups and their steric and electronic donor effects significantly affected the catalytic results. Under standard conditions, precatalyst **20** led to a low selectivity for 1-butene (less than 11% of the C_4 fraction), which is characteristic of an isomerizing catalyst, and to a high concentration of C_6 oligomers formed by reinsertion of 2-butene (up to 68%, Table 6). In contrast, **22** did not favor the isomerization of 1-butene and had a selectivity up to 42**%** for 1-butene within the C_4 fraction**.** However **22** led overall to a low selectivity in C_4 products (less than 23%) owing to the reinsertion of 1-butene to form 2-ethyl-1-butene (up to 77%, Table 6) and presented a very different mass distribution of oligomers compared to **20** (Figure 10). Heinicke *et al.* have observed similar effects with cationic methallylnickel phosphinophenol complexes where cyclohexyl substituents on the phosphorus donor function favored the formation of 2-ethyl-1-butene, in contrast to the phenyl substituents which favored the formation of *cis*-3-methyl-2-pentene.[72]

When the quantity of precatalyst **20** and **22** was decreased to 10^{-5} mol, very high activities were still observed. Under these conditions, **20** showed a slightly better selectivity for C_4 products and **22** a slightly higher selectivity for 1-butene.

Increasing the pressure to 30 bar resulted in increased catalytic activities with **20** and **22**, from 30100 to 36800 mol C_2H_4/(mol Ni·h) with **20** and from 24200 to 45500 mol C_2H_4/(mol Ni·h) with **22**. It has been shown with related systems that TOF can be independent or not on ethylene pressure.[20,70] In the former case, the alkyl olefin species is the catalyst resting state.[73] According to the literature,[20] a higher ethylene concentration favors the formation of α-olefins and the selectivities for 1-butene with **20** (34%) and **22** (73%) were indeed higher. The selectivity for C_4 products with **20** increased to 93% (Table 5) but the mass distribution of the oligomers produced by **22** did not change. The high concentration of 1-butene resulted in a marked increase of the concentration in 2-ethyl-1-butene (up to 91%). These rather surprising results with **22** suggest that the *tert*-butyl substituents on the P donor atom favor the formation of 1-butene and that its isomerization to 2-butene is disfavored with respect to formation of the C_6 product 2-ethyl-1-butene. One could envisage that the latter originates from unselective insertion of 1-butene into the Ni-ethyl bond of a primarily formed intermediate[72] (Scheme 3, route A) or by β-elimination of a metallacyclic intermediate resulting from the coupling of 1-butene with ethylene (Scheme 3, route B). Ni(II) metallacyclic compounds have been previously considered in olefin chemistry.[74]

Scheme 3. Proposed pathways to explain the formation of 2-ethyl-1-butene



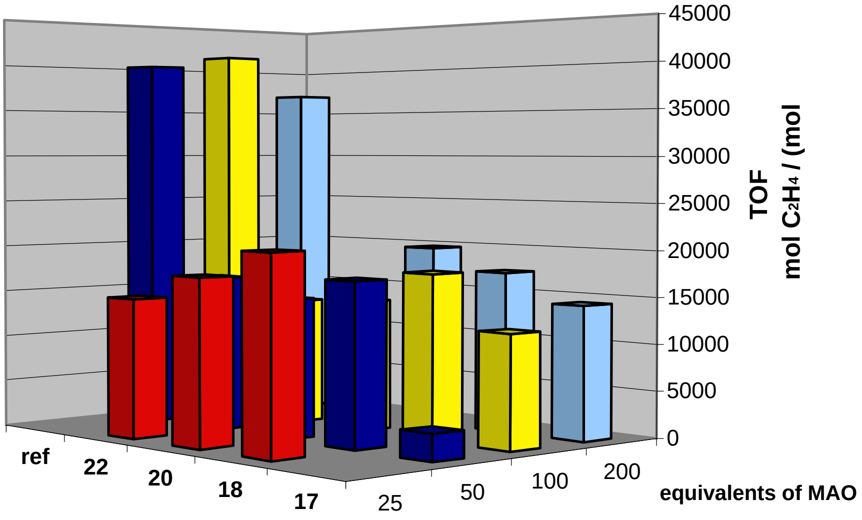


Figure 7. Catalytic activities with **17**, **18**, **20** and **22** in the oligomerization of ethylene using MAO as cocatalyst, Ref: $[NiCl_2\{P(n\text{-}Bu)_3\}_2]$.

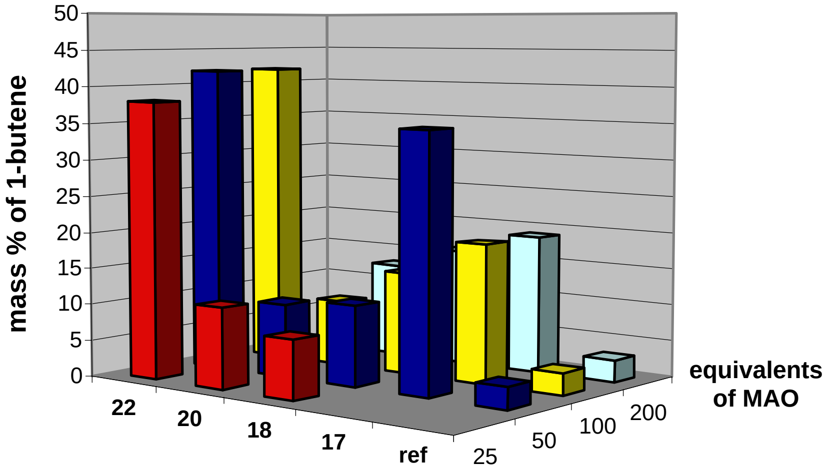


Figure 8. Selectivity of **17**, **18**, **20** and **22** for 1-butene using MAO as cocatalyst (1-butene and 2-butene), Ref: $[NiCl_2\{P(n\text{-}Bu)_3\}_2]$.

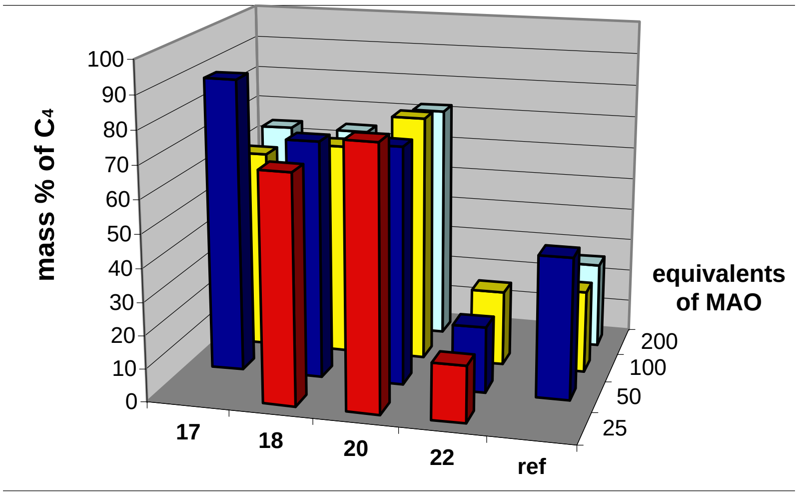


Figure 9. Selectivity of **17**, **18**, **20** and **22** for C_4 compounds using MAO as cocatalyst (1-butene and 2-butene), Ref: $[NiCl_2\{P(n\text{-}Bu)_3\}_2]$.

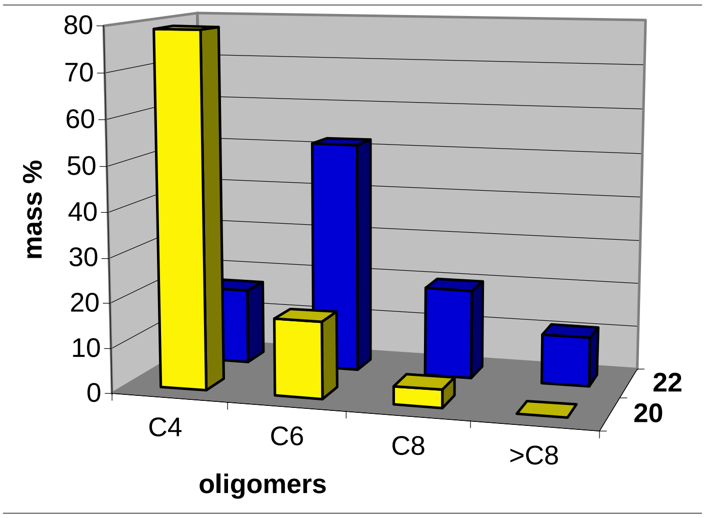


Figure 10. Mass distribution of the oligomers produced by **20** and **22** ($4{\cdot}10^{-5}$ mol of complex, 25 equivalents of MAO, 10 bar, 35 min).

4. Conclusion

New P,N ligands with a pyridine function have been synthesized in good yields and characterized by ^{1}H, $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectroscopy. These ligands present various bite angles and phosphorus functions (phosphine, phosphinite or phosphonite functions) with different substituents on the phosphorus atom (phenyl or *tert*-butyl groups). The Ni(II) complexes **17**, **18** and **20-22**, prepared in 70-92% yields from ligands **12-16**, respectively, were characterized by IR, elemental analysis and high resolution mass spectroscopy. Whereas complex **18** was shown by X-ray diffraction to have a dinuclear structure with a distorted square base pyramidal geometry, **22** in which a CH_2 group of the spacer between the pyridine and the phosphorus has been replaced with an oxygen and the phenyls on phosphorus by *t*-Bu substituents, has a mononuclear structure with a distorted tetrahedral geometry. Related Ni(II) with phosphino-oxazoline and –thiazoline ligands have been recently investigated and found to be tetranuclear, which illustrates the considerable diversity of this chemistry. A dramatic effect of pressure on the solid was evidenced which results in its breaking into four mononuclear complexes.[67]

The precatalysts **17**, **18** and **20-22** have been evaluated in the catalytic oligomerization of ethylene with $AlEtCl_2$ or MAO as cocatalyst. All the complexes presented high activities with $AlEtCl_2$ as cocatalyst and the most active was **18** (91200 mol C_2H_4/(mol Ni·h)) with 6 equivalents $AlEtCl_2$. **20** with 2 equivalents of $AlEtCl_2$ showed the best selectivities in butenes (97%) and in 1-butene (72%). The high activities of **18** and **20** when the reaction time was increased to 120 min suggested a good stability of the catalysts. Precatalysts **17**, **18** and **20-22** favored the dimerization and trimerization of ethylene but the high proportions of branched oligomers suggested a significant contribution of 1-butene and 2-butene reinsertion. The generally modest selectivity for 1-butene is consistent with the isomerizing character of **17**, **18** and **20-22**.

The precatalysts **17**, **18** and **20-22** presented high activities already with small amounts of MAO as cocatalyst. Complex **18** was the most active under 10 bar of ethylene with 25 equivalents (20600 C_2H_4/(mol Ni·h)) and **17** the most selective in C_4 oligomers (89%) and in 1-butene (35**%)** in the presence of 50 equivalents of MAO**.** In contrast to **17**, **18**, **20** and **21**, complex **22**, with *tert*-butyl substituents on phosphorus, largely favored 1-butene reinsertion over isomerization and afforded 2-ethyl-1-butene as the main product. Increasing the pressure to 30 bar made the precatalysts **20** and **22** more active and increased their selectivity for C_4 products and for 1-butene.

5. Experimental Section

General Considerations. All solvents were dried and freshly distilled under nitrogen prior to use using common techniques. All manipulations were carried out using Schlenk techniques. The ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectra were recorded at 300.13, 121.5 and 76 MHz, respectively, on a Bruker AC300 instrument. Elemental analyses were performed by the "Service de Microanalyse, Université Louis Pasteur (Strasbourg, France)". IR spectra in the range of 4000-400 cm^{-1} were recorded on a Bruker IFS28FT. Mass spectra were recorded with a Bruker Daltonics microTOF (ESI; positive mode; capillary voltage: 4.8 kV; nebulizer pressure: 0.2 bar; desolvation temperature: 180 °C; desolvation gas flow rate: 4.5 L/min). Magnetic moments were determined by the Evans method in CD_2Cl_2 using a solution of CH_3NO_2 in CD_2Cl_2 (20:80, v/v) as reference.[61-64] The complexes $NiCl_2{\cdot}6H_2O$ and $NiBr_2{\cdot}6H_2O$ were dried by heating at 160 °C overnight under vacuum to give anhydrous $NiCl_2$ and $NiBr_2$. The commercial compounds 2-picoline and (pyridin-2-yl)methanol were distilled at 130 °C and 115 °C, respectively, and degassed with nitrogen before use. A solution of $NaPPh_2$ was prepared according to the literature,[75] by addition of PPh_2Cl (7.40 g, 6 mL, 33.4 mmol) to a suspension of Na (4.00 g, 174.0 mmol) in THF (100 mL). After the mixture was stirred at reflux for 4 h, the solution became red and a grey precipitate of NaCl appeared. The salt and unreacted Na were eliminated by filtration through a canula and the compound was kept in THF. Gas chromatographic analyses were performed on a Thermoquest GC8000 Top series gas chromatograph using a HP Pona column (50 m, 0.2 mm diameter, 0.5 μm film thickness). Details of the synthesis and analytical data for known compounds are given below because of slight modifications or new data introduced.

2-[(trimethylsilyl)methyl]pyridine.[76]

A solution of *n*-BuLi (96.0 mmol, 1.6 M in hexane) was added dropwise over 15 minutes to a solution of 2-picoline (8.94 g, 96.0 mmol) in 100 mL of THF at -78 °C. After complete deprotonation, the red anion precipitated and after further stirring for 1 h at -78 °C, degassed chlorotrimethylsilane (TMSCl, 14.00 g, 112.0 mmol) was added dropwise to the solution. The brown mixture was allowed to reach at room temperature overnight and the solvents and unreacted TMSCl were evaporated under reduced pressure. The residue was distilled (120 °C, 12 mbar) to afford pure, liquid 2-[(trimethylsilyl)methyl]pyridine. Yield: 6.61 g, 42%. ^{1}H NMR ($CDCl_3$): δ 0.00 (s, 9H, $Si(CH_3)$], 2.32 (s, 2H, $SiCH_2$), 6.93 (m, 2H, Py), 7.45 (m, Py), 8.39 (d, 1H, $^3J_{H\text{-}H}$ = 4.2 Hz, HCN). ^{13}C{^{1}H} NMR ($CDCl_3$): δ -1.7 (s,

$SiCH_3$), 30.25 (s, $SiCH_2$), 119.04 (s, Py), 122.06 (s, Py), 135.72 (s, Py), 148.94 (s, Py), 161.28 (s, HCN).

2-[(diphenylphosphino)methyl]pyridine 12.[52]

To a solution of 2-[(trimethylsilyl)methyl]pyridine (4.21 g, 25.5 mmol) in 50 mL THF was added 4.70 mL of PPh_2Cl (5.62 g, 25.5 mmol) at -78 °C and the mixture was stirred overnight at room temperature. THF was eliminated under reduced pressure and dietylether was added to precipitate the LiCl formed during the reaction. After filtration and evaporation of diethylether under reduced pressure, **12** was isolated as a colorless oil. Yield: 5.60 g, 79%. Spectroscopic data are consistent with the literature values.

2-(2-chloroethyl)pyridine.[53,54]

Pure $SOCl_2$ (4.10 g, 2.5 mL, 34.2 mmol) was added to a solution of 2-pyridine-ethanol (2.50 g, 20.3 mmol) in THF and stirred at reflux for 2 h. After reaction, the THF was removed under reduced pressure and 2-(2-chloroethyl)pyridine was extracted with 50 mL of CH_2Cl_2 and washed with water saturated with $NaHCO_3$ (3×20 mL). After elimination of CH_2Cl_2 under reduced pressure, 2-(2-chloroethyl)pyridine was isolated as a dark oil. Yield: 2.40 g, 84%. ^1H NMR ($CDCl_3$): δ 3.24 (t, 2H, $^3J_{HH}$ = 6.8 Hz, $SiCH_2$), 3.92 (t, 2H, $^3J_{HH}$ = 6.8 Hz, Py-CH_2), 6.97 (d, 1H, $^3J_{HH}$ = 7.8 Hz, Py), 7.22 (m, 2H, Py), 7.65 (t, 1H, $^3J_{HH}$ = 5.8 Hz, Py), 8.55 (d, 1H, $^3J_{HH}$ = 5.4 Hz, NCH).

2-[2-(diphenylphosphino)ethyl]pyridine 13.[53,54]

A solution of 2-(2-chloroethyl)pyridine (2.40 g, 17.0 mmol) in 30 mL of THF was added to a solution of $NaPPh_2$ in THF (100 mL, 33.4 mmol) and stirred overnight. After reaction, NaCl was eliminated by filtration and THF was removed under reduced pressure. Compound **13** was purified by column chromatography (length of the stationary phase 50 cm, column diameter 2.5 cm) over silica gel using a mixture pentane/ethylacetate (3:1 and 5% diethylamine) and was isolated as a white powder. Yield: 2.17 g, 45%. ^1H NMR ($CDCl_3$): δ AA'BB'X spin system (A = A' = B = B' = H, X = P) 2.51 (m, 2H, $^2J_{AA'}$ = 13.5 Hz, $^2J_{AB}$ = 5.2 Hz, $^2J_{AB'}$ = 11 Hz, $^2J_{A'B}$ = 11 Hz, $^2J_{AB'}$ = 5.2 Hz, $^2J_{AP}$ = 0.7 Hz, $^2J_{A'P}$ = 0.7 Hz, PCH_2), 2.90 (m, 2H, $^2J_{BB'}$ = 13.5 Hz, $^2J_{AB}$ = 5.2 Hz, $^2J_{AB'}$ = 11 Hz, $^2J_{A'B}$ = 11 Hz, $^2J_{AB'}$ = 5.2 Hz, $^2J_{BP}$ = 8.5 Hz, $^2J_{A'P}$ = 8.5 Hz, CH_2Py), 7.10 (d, 2H, $^3J_{HH}$ = 7.0 Hz, Py) 7.26 (m, 6H, Ph), 7.33 (m, 4H, Ph), 7.45 (dt, 1H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 2.0 Hz, Py), 8.52 (d, 1H, $^3J_{HH}$ = 4.5

Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 28.0 (d, $^1J_{PC}$ = 12.5 Hz, PCH_2), 28.0 (d, $^2J_{PC}$ = 18.0 Hz, $PyCH_2$),121.2 (s, Py), 122.8 (s, Py), 128.5 (d, $^3J_{PC}$ = 14.1 Hz, *m*-Ph), 128.5 (s, *p*-Ph), 132.8 (d, $^2J_{PC}$ = 18.5 Hz, *o*-Ph), 136.4 (s, Py), 138.4 (d, $^1J_{PC}$ = 13.0 Hz, *ipso*-Ph), 149.4 (s, Py), 161.8 (d, $^3J_{PC}$ = 13.4 Hz, N*C*CH); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -14.2 (s).

Synthesis of 2-methyl-oxy-(diphenylphosphino)pyridine 14.[56]

To a solution of (pyridin-2-yl)methanol (3.04 g, 27.9 mmol) in THF containing 3 equivalents of triethylamine (12 mL, 85.0 mmol), was added 5 mL of PPh_2Cl (6.15 g, 27.9 mmol) at -78 °C. The solution was stirred for 2 h from -78 °C to room temperature and all volatiles were removed under reduced pressure. The residue was dissolved in diethylether to precipitate triethylammonium chloride. After filtration, the solvents were removed under reduced pressure and **14** was isolated as a pale yellow oil. Yield: 7.52 g, 92%. ^1H NMR ($CDCl_3$): δ 2.50 (t, 2H, $^3J_{HH}$ = 8.7 Hz, PCH_2), 7.17 (dd, 1H, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 4.8 Hz, C*H*CHN), 7.36(m, 6H, Ph), 7.47 (d, 1H, $^3J_{HH}$ = 7.6 Hz CCH), 7.55(m, 4H, Ph), 7.67(dt, 1H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.8 Hz, CHC*H*CH), 8.53 (d, 1H, $^3J_{HH}$ = 4.8 Hz, CHN); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 72.2 (d, $^2J_{PC}$ = 16.2 Hz, $POCH_2$), 121.2 (s, Py), 122.4 (s, Py), 128.4 (d, $^3J_{PC}$ = 6.9 Hz, *m*-Ph), 129.6 (s, *p*-Ph), 130.6 (d, $^2J_{PC}$ = 21.9 Hz, *o*-Ph), 136.7 (s, Py), 141.4 (d, $^1J_{PC}$ = 18.3 Hz, *ipso*-Ph), 149.1 (s, Py), 158.7 (d, $^2J_{PC}$ = 8.8 Hz, N*C*CH); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 117.7 (s); IR (KBr) 1592 (s), 1477 (m), 1435 (s), 1096 (s), 1050 (s), 751 (s), 697 (s) cm^{-1}.

2-methyl-oxy-(dibenzyl-1,2-oxa-phosphorino)pyridine 15.

To a solution of (pyridin-2-yl)methanol (1.08 g, 10.0 mmol) in THF containing 3 equivalents of triethylamine (4.2 mL, 30.0 mmol) was added chloro(dibenzyl-1,2-oxa)phosphorine (2.34 g, 10.0 mmol) at -78 °C. The solution was stirred for 2 h from -78 °C to room temperature and then the volatiles were removed under reduced pressure. The residue was dissolved in diethylether to precipitate triethylammonium chloride. After filtration, the solvents were removed under reduced pressure and **15** was isolated as a pale yellow oil. Yield: 2.70 g, 88%. ^1H NMR ($CDCl_3$): δ ABX spin system (A, B, X = P) 4.86 (1H, dd, J_{AB} = 13.8 Hz, $^2J_{XB}$ = 8.7 Hz, $POCH_2$) and 4.93 (1H, dd, J_{AB} = 13.8 Hz, $^2J_{XA}$ = 10.2 Hz, $POCH_2$), 7.04 (d, 1H, $^3J_{HH}$ = 7.8 Hz), 7.10 (t, 2H, $^3J_{HH}$ = 5.1 Hz), 7.19 (dt, 1H, $^3J_{HH}$ = 7.5 Hz, J_{PH} = 1.5 Hz), 7.30 (m, 1H,), 7.50 (m, 2H), 7.64 (m, 1H), 7.98 (dd, 1H, $^3J_{HH}$ = 7.8 Hz, J_{PH} = 1.8 Hz), 8.02 (d, 1H, $^3J_{HH}$ = 7.8 Hz), 8.46 (dq, 1H, $^3J_{HH}$ = 3.9 Hz, J_{PH} = 0.9 Hz, Py); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 70.6 (d, $^2J_{PC}$ = 10.8 Hz, $POCH_2$), 120.6 (s, Ph), 120.8 (s, Py), 122.3 (s, Py), 122.5 (d, ${}^2J_{PC}$ = 6.2 Hz, PC*C*C), 123.4 (s, Ph), 123.5 (s, Ph), 124.9 (s, Ph), 127.7 (d, ${}^3J_{PC}$ = 13.4 Hz, PCCHCH), 129.6 (s, Ph), 131.5 (d, ${}^2J_{PC}$ = 48.2 Hz, PC*C*H), 131.7 (s, Ph), 131.9 (s, Ph), 132.2 (d, ${}^3J_{PC}$ = 2.8 Hz, POC*C*), 136.5 (s, Py), 141.9 (s, Py), 149.7 (d, ${}^2J_{PC}$ = 9.3 Hz, POC Ph), 158.1 (d, ${}^2J_{PC}$ = 4.7 Hz, N*C*CH$_2$); ^{31}P{^{1}H} NMR (CDCl$_3$): δ 130.5 (s).

Chloro-di-*tert*-buytlphosphine.[77]

It was synthesized according to the literature[77] by dropwise addition of a solution of *n*-BuLi (60.0 mL, 102.0 mmol, 1.7 M in hexane) to a solution of PCl$_3$ (7.00 g, 51.0 mmol) in 100 mL of pentane at -78 °C. The mixture was stirred overnight from -78 °C to room temperature. LiCl was removed by filtration and pentane was slowly removed under reduced pressure. The residue was distilled under reduced pressure (70 °C, 10 mbar) and chloro-di-*tert*-butylphosphine was isolated as a colorless liquid. Yield: 2.90 g, 32%. ^{1}H NMR (CDCl$_3$): δ 1.24 (d, 18H, ${}^3J_{PH}$ =12.1 Hz, CH$_3$); ^{31}P{^{1}H} NMR (CDCl$_3$): δ 148.0 (s).

2-methyl-oxy-(di-*tert*-butylphosphino)pyridine 16.

A solution of *n*-BuLi (4.00 mL, 6.7 mmol, 1.7 M in hexane) was added to a solution of (pyridin-2-yl)methanol (0.725 g, 6.7 mmol) in 30 mL of THF at -78 °C. The solution became red and was stirred for 30 min. Di-*tert*-butylchlorophosphine (1.20 g, 6.7 mmol) in 20 mL of THF was added to the mixture to afford a pale yellow solution which was stirred overnight from -78 °C to room temperature. THF was removed under reduced pressure and diethylether was added to precipitate LiCl. After filtration and removal of the solvents under reduced pressure, **16** was isolated as a pale yellow oil. Yield: 1.52 g, 89%. ^{1}H NMR (CDCl$_3$): δ 1.13 (d, 18H, ${}^3J_{PH}$ = 11.7 Hz, CH$_3$), 4.93 (d, 2H, ${}^3J_{PH}$ = 5.7 Hz, CH$_2$), 7.18 (m, 1H, Py), 7.55 (d, 1H, ${}^3J_{HH}$ = 7.8 Hz, Py), 7.70 (dt, 1H, ${}^3J_{HH}$ = 7.5 Hz ${}^4J_{HH}$ = 1.8 Hz, Py), 8.53 (d, 1H, ${}^3J_{HH}$ = 4.8 Hz, Py); ^{13}C{^{1}H} NMR (CDCl$_3$): δ 27.4 (d, ${}^2J_{PC}$ = 15.1 Hz, CH$_3$), 35.4 (d, ${}^2J_{PC}$ = 24.3 Hz, PC), 76.1 (d, ${}^2J_{PC}$ = 21.7 Hz, OCH$_2$), 120.9 (s, Py), 122.1 (s, Py), 136.6 (s, Py), 149.0 (s, Py), 159.5 (d, ${}^3J_{PC}$ = 10.6 Hz, N*C*CH); ^{31}P{^{1}H} NMR (CDCl$_3$): δ 166.3 (s).

[NiCl$_2$(DME)].[78]

NiCl$_2$ (100 g, 771.6 mmol) was dissolved in a mixture of 300 mL of methanol and 50 mL of trimethylorthoformate and stirred at reflux overnight. After reaction, unreacted NiCl$_2$

was eliminated by filtration and 80% of the solution was removed under reduced pressure to obtain a green gel. It was dissolved in a minimum of methanol and 300 mL of DME was added. The solution was stirred at reflux overnight. A yellow powder of [$NiCl_2$(DME)] precipitated and was isolated by filtration through a canula. The powder was washed with pentane and dried under a nitrogen flux. Yield: 135.0 g, 80%. Anal. Calcd. for $C_4H_{10}Cl_2NiO_2$: C, 21.87; H, 4.59. Found: C, 21.26; H, 4.68.

[$NiBr_2$(DME)].[78]

This compound was prepared using a method similar to that described for [$NiCl_2$(DME)] starting from of $NiBr_2$ (10.0 g, 45.8 mmol). It was isolated as an orange powder. Yield: 12.3 g, 87%. Anal. Calcd. for $C_4H_{10}Br_2NiO_2$: C, 15.57; H, 3.27. Found: C, 15.72; H, 3.73.

[Ni{2-{(diphenylphosphino)methyl}pyridine}Cl_2] 17.

A solution of **12** (1.36 g, 4.9 mmol) in methanol was added to a solution of $NiCl_2$ (0.63 g, 4.9 mmol) at room temperature. The solution became red and was stirred for 1 h. Methanol was removed under reduced pressure and the residue was dissolved in 30 mL of CH_2Cl_2. Unreacted $NiCl_2$ was eliminated by filtration. The solution was concentrated to 10 mL and 40 mL of pentane was added to precipitate **17**. After filtration, **17** was washed with 20 mL of diethylether, dried under vacuum and isolated as a grey powder. Yield: 1.66, 84%. Anal. Calcd. for $C_{18}H_{16}Cl_2NNiP$: C, 53.13; H, 3.96; N, 3.44. Found: C, 53.39; H, 4.11; N, 3.45. HRMS : Mass Calcd. for $C_{18}H_{16}ClNNiP$: 362.0006. Found: 361.9984 $[Ni(P,N)Cl]^+$. IR (KBr): 1604 (vs), 1566 (w), 1476 (vs), 1435 (vs), 1310 (m), 1158 (s), 1101 (vs), 1021 (m), 998 (m), 843 (s), 743 (vs), 692 (vs), 603 (w), 522 (m), 487 (m) cm^{-1}.

[Ni(μ-Cl)$_2${2-{2-(diphenylphosphino)ethyl}pyridine}$_2$]$_2$$Cl_2$ 18.

This compound was prepared using a method similar to that described for **17** by reaction of ligand **13** (2.17 g, 6.0 mmol) with $NiCl_2$ (0.78 g, 6.0 mmol). **18** was isolated as a green powder. Yield: 2.19 g (80%). Anal. Calcd. for $C_{38}H_{36}Cl_4N_2Ni_2P_2$: C, 54.21; H, 4.31; N, 3.33. Found: C, 53.92; H, 4.39; N, 3.10. HRMS: Mass Calcd for $C_{19}H_{18}ClNNiP$: 384.0213. Found: 384.0227 $[Ni(P,N)Cl]^+$. IR (KBr): 1605 (vs), 1484 (vs), 1437 (vs), 1377 (m), 1158 (m), 1101 (s), 1025 (m), 998 (m), 869 (m), 757 (s sh), 743 (s), 718 (m), 698 (vs), 526 (s), 500 (m), 475 (m) cm^{-1}.

$[Ni(\mu\text{-}Cl)_2\{(pyridin\text{-}2\text{-}yl)\ methanol\}_2]_2Cl_2$ 19 and $[Ni\{POMe(Ph)_2\}_2Cl_2]$.

A MeOH solution of ligand **14** (0.89 g, 3.0 mmol) was added to a MeOH solution of $NiCl_2$ (0.39 g, 3.0 mmol). The resulting red solution was stirred at reflux for 1 h. After reaction, the solvent was removed under vacuum and 20 mL of CH_2Cl_2 was added. A green precipitate was isolated from the red solution by filtration and was identified as $[Ni(\mu\text{-}Cl)_2\{(pyridin\text{-}2\text{-}yl)methanol\}_2]_2Cl_2$ **19**. Yield: 0.52 g, 98%. Anal. Calcd. for $C_{24}H_{28}Cl_4N_4Ni_2O_4$: C, 41.43; H, 4.06; N, 8.05. Found: C, 41.82; H, 4.37; N, 7.86. HRMS: Mass Calcd for $C_{12}H_{14}ClN_2O_2Ni$: 311.0092. Found. 311.0099 $[Ni(N,O)_2Cl]^+$. IR(KBr): 1608 (s), 1571 (m), 1483 (m), 1444 (s), 1286 (m), 1237 (m), 1156 (m), 1033 (s), 765 (s), 727 (m) cm^{-1}.

All the volatiles of the red solution were removed under reduced pressure and the residue was dissolved in 20 mL of diethylether. 80 mL of pentane was added to the solution and a red powder precipitated which was characterized as $[Ni\{P(OMe)Ph_2\}_2Cl_2]$. Yield: 0.71 g, 84%. Anal. Calcd. for $C_{26}H_{26}Cl_2NiO_2P_2$: C, 55.56; H, 4.66. Found: C, 55.40; H, 4.69.

$[Ni\{2\text{-}methyl\text{-}oxy\text{-}(diphenylphosphino)pyridine\}Cl_2]$ 20.

Solid $[NiCl_2(DME)]$ (2.51 g, 11.5 mmol) was added to a solution of **14** (3.21 g, 11.0 mmol) in 30 mL of CH_2Cl_2. The solution became red and was stirred during 2 h. After reaction, unreacted $[NiCl_2(DME)]$ was eliminated by filtration. The solution was concentrated to 10 mL and 40 mL of pentane was added to precipitate **20**. After filtration, **20** was washed with diethylether, dried under vacuum and isolated as a green powder. Yield: 4.28 g, 92%. Anal. Calcd. for $C_{18}H_{16}Cl_2NNiOP$: C, 51.12; H, 3.81; N, 3.31. Found: C, 50.81; H, 4.04; N, 3.00. HRMS: Mass Calcd. for $C_{18}H_{16}ClNNiOP$: 386.0006. Found: 386.0007 $[Ni(P,N)Cl]^+$. IR (KBr) : 1606 (s), 1571 (m), 1484 (s), 1438 (vs), 1380 (w), 1313 (m), 1232 (w), 1185 (w), 1158 (m), 1130 (m), 1010 (vs), 833 (w), 741 (vs), 696 (vs) 618 (m), 539 (s), 486 (s) cm^{-1}.

$[Ni\{2\text{-}methyl\text{-}oxy\text{-}(diphenylphosphino)pyridine\}Br_2]$ 21.

This compound was prepared using a method similar to that described for **20** by reaction of $[NiBr_2(DME)]$ (0.77 g, 2.6 mmol) with ligand **14** (0.65 g, 2.6 mmol). **21** was isolated as a green powder. Yield: 0.92 g, 72%. Anal. Calcd. for $C_{14}H_{24}Br_2NNiOP$: C, 42.24; H, 3.15; N, 2.74. Found: C, 42.05; H, 3.33; N, 2.68. IR (KBr): 1605 (s), 1484 (s), 1438 (s), 1157 (m), 1131 (m), 1102 (s), 758 (s), 696 (s) cm^{-1}.

[Ni{2-methyl-oxy-(di-*tert*-butylphosphino)pyridine}Cl$_2$] 22.

This compound was prepared using a method similar to that described for **20** by reaction of [NiCl$_2$(DME)] (0.57 g, 2.6 mmol) with ligand **17** (0.65 g, 2.6 mmol). **22** was isolated as a red powder. Yield: 0.70 g (70%). Anal. Calcd. for $C_{14}H_{24}Cl_2NNiOP$: C, 43.91; H, 6.32; N, 3.66. Found: C, 43.25; H, 6.37; N, 3.62. HRMS: Mass Calcd. for $C_{14}H_{24}ClNNiOP$: 346.0632. Found: 346.0677 [Ni(P,N)Cl]$^+$. IR (KBr) : 1607 (s), 1479 (s), 1438 (m sh), 1370 (m), 1315 (m), 1060 (w), 1026 (vs), 999 (vs), 808 (m), 780 (s), 764 (s), 743 (m), 622 (s) cm^{-1}.

[Ni{2-methyl-oxy-(dibenzyl-1,2-oxa-phosphorino)pyridine}Cl$_2$] 23.

This compound was prepared using a method similar to that described for **20** by reaction of [NiCl$_2$(DME)] (1.93 g, 8.8 mmol) with ligand **15** (2.70 g, 8.8 mmol). **23** was isolated as a maroon powder (2.88 g, 6.6 mmol). Yield: 2.88 g, 75%. Anal. Calcd. for $C_{14}H_{24}Cl_2NNiOP$: C, 49.49; H, 3.23; N, 3.21. Found: C, 47.64; H, 4.27; N, 2.90 (despite several attempts, better analysis were not obtained). HRMS: Mass Calcd for $C_{14}H_{24}ClNNiOP$: 399.9804. Found: 399.9815 [Ni(P,N)Cl]$^+$. IR (KBr): 1675 (s sh), 1638 (s), 1608 (vs), 1583 (m sh), 1560 (w), 1476 (vs), 1443 (m), 1430 (s), 1278 (m), 1203 (vs), 1116 (s), 1060 (vs), 913 (s), 758 (vs), 716 (m), 619 (m), 605 (m), 531 m) cm^{-1}.

Oligomerization of Ethylene. All catalytic reactions were carried out in a magnetically stirred (900 rpm) 145 mL stainless steel autoclave. A 125 mL glass container was used to protect the inner walls of the autoclave from corrosion. The preparation of the solution of the precatalyst is depended of the nature and the amount of the cocatalyst.

When AlEtCl$_2$ was used as a cocatalyst, 4x10^{-2} mmol of Ni complex were dissolved in 14, 13 or 12 mL of cholorobenzene depending of the amount of the cocatalyst and injected into the reactor under an ethylene flux. Then 1, 2 or 3 mL of a cocatalyst solution, corresponding to 2, 4 or 6 equivalents respectively, was added to form a total volume of 15 mL with the precatalyst solution. When 10^{-2} mmol of precatalyst was used, a solution of the complex in 14 mL of chlorobenzene was injected into the reactor, followed by 0.75 mL of a solution of the cocatalyst (6 equivalents).

With MAO as a cocatalyst, 1x10^{-2} or 4x10^{-2} mmol of Ni complex were dissolved in 10 mL in chlorobenzene and injected into the reactor under an ethylene flux. Then 0.5, 1, 2, 4, 8 or 16 mL of a cocatalyst solution, corresponding to 12.5, 25, 50, 100 (4 mL for 4 x 10^{-2}

mmol of Ni complex or 1 mL for 10^{-2} mmol of Ni complex), 200 or 400 equivalents of MAO respectively, was added.

All catalytic tests were started between 25 and 30 °C, and no cooling of the reactor was done during the reaction. After injection of the catalytic solution and of the cocatalyst under a constant low flow of ethylene, the reactor was pressurized to 10 or 30 bar. A temperature increase was observed which resulted solely from the exothermicity of the reaction. The 10 or 30 bar working pressure was maintained during the experiments through a continuous feed of ethylene from a reserve bottle placed on a balance to allow continuous monitoring of the ethylene uptake. At the end of each test (35 or 120 min.) a dry ice bath, and in the more exothermic cases also liquid N_2, was used to rapidly cool down the reactor, thus stopping the reaction. When the inner temperature reached 0 ºC, the ice bath was removed allowing the temperature to slowly rise to 10 ºC. The gaseous phase was then transferred into a 10 L polyethylene tank filled with water. An aliquot of this gaseous phase was transferred into a Schlenk flask, previously evacuated, for GC analysis. The products in the reactor were hydrolyzed in situ by the addition of ethanol (1 mL), transferred into a Schlenk flask, and separated from the metal complexes by trap-to-trap evaporation (20 °C, 0.8 mbar) into a second Schlenk flask previously immersed in liquid nitrogen in order to avoid any loss of product.

Crystal Structure Determinations. Diffraction data were collected on a Kappa CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) (Table 7).

(insert Table 7)

Data were collected using phi-scans and the structures were solved by direct methods using the SHELX 97 software,[79,80] and the refinement was by full-matrix least squares on F^2. No absorption correction was used. All non-hydrogen atoms were refined anisotropically with H atoms introduced as fixed contributors ($d_{C\text{-}H}$ = 0.95 Å, U_{11} = 0.04). Crystallographic data (excluding structure factors) have been deposited in the Cambridge Crystallographic Data Centre as Supplementary publication n° CCDC ******. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 7. Crystallographic Data for Complexes **18** and **22**

	18	**22**
Chemical formula	$C_{38}H_{36}Cl_4N_2Ni_2P_2$	$C_{14}H_{24}Cl_2NNiOP$
M_r	841.85	382.92
Cell setting, space group	Monoclinic, $C2/c$	Monoclinic, $P2_1/n$
Temperature (K)	173 (2)	173 (2)
a (Å)	20.4250 (8)	8.8770 (3)
b (Å)	15.5080 (7)	17.1160 (6)
c (Å)	11.9040 (6)	12.0180 (5)
β (°)	103.913 (2)	102.7270 (12)
V (Å^3)	3660.0 (3)	1781.14 (11)
Z	4	4
D_x (Mg m^{-3})	1.528	1.428
Radiation	Mo-$K\alpha$	Mo-$K\alpha$
F(000)	1728	800
μ (mm^{-1})	1.44	1.47
Crystal size (mm)	0.12 × 0.03 × 0.02	0.12 × 0.10 × 0.08
No. of measured, indept and obsd reflect.	9382, 5331, 3826	7317, 4076, 3133
Criterion for obsd reflect.	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.078	0.064
θ_{max} (°)	30.0	27.5
data set (h; k; l)	-28/28; -19/21; -16/16	-11/11; -22/20; -15/15
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.096, 0.116, 1.21	0.083, 0.117, 1.19
No. of relections	5331	4076
No. of parameters	218	181

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Chapitre V

Synthesis and catalytic studies in the oligomerization of ethylene of Ni(II), Fe(II), Pd(II) and Co(II) complexes coordinated by new N,P,N Type ligands

Abstract

The N,P,N type ligands bis(2-oxazoline-2-ylmethyl)phenylphosphine **1**, bis(2-oxazolin-2,5,5-trimethyl)phenylphosphine **2**, phenyl-bis(2-picolyl)phosphine **3** and bis((pyridin-2-yl)methyl) phenylphosphonite **4** were synthesized and characterized by ^{1}H, ^{13}C {^{1}H} and ^{31}P{^{1}H} NMR. They were used to synthesize the corresponding Ni(II) complexes [Ni{bis(2-oxazoline-2-ylmethyl)phenylphosphine}Cl_2] **6**, [Ni{bis(2-oxazolin-2,5,5-trimethyl)phenylphosphine}Cl_2] **7**, [Ni{phenyl-bis(2-picolyl)phosphine}Cl_2] **8** and [Ni{bis((pyridin-2-yl)methyl) phenylphosphonite}Cl_2] **9**, respectively. The iron complexes [Fe{phenyl-bis(2-picolyl)phosphine}$_2${$FeCl_3OFeCl_3$}] **10**, [Fe{bis(2-oxazoline-2-ylmethyl)phenylphosphine}$_2${$FeCl_3OFeCl_3$}] **11** and [Fe{bis(2-oxazolin-2,5,5-trimethyl)phenylphosphine}Cl_2] **12**, synthesized by reaction of $FeCl_2{\cdot}4H_2O$ with ligands **1**-**3**, respectively, have been characterized by X-ray diffraction. The crystal structures of the octahedral complexes **10** and **11** show that two tridentate ligands are facially coordinated to the metal centre and the dianion (μ-oxo)bis[trichloroferrate(III)] compensates the doubly positive charge. In contrast to **10** and **11**, the crystal structure of **12** revealed a tetrahedral geometry with the N,N coordination of one ligand and the P-Fe distance of 4.336(1) Å establishes that of the phosphorus atom is not coordinated to the metal centre. The complexes [Pd(Me){Bis(2-oxazolin-2,5,5-trimethyl)phenylphosphine}Cl] **13**, [Pd{Bis(2-oxazolin-2,5,5-trimethyl)phenylphosphine}Cl_2] **14** and [Pd($NCCH_3$){bis(2-oxazolin-2,5,5-trimethyl)phenylphosphine}$(BF_4)_2$] **15** were prepared by reaction of ligand **2** with [Pd(Me)Cl(COD)] (COD = cyclooctadiene), [$PdCl_2(NCPh)_2$] or [$Pd(MeCN)_4(BF_4)_2$], respectively. In contrast to complex **11**, the IR and NMR studies of complexes **13** and **14** established the coordination of the phosphorus atom and of one of the two oxazoline moieties to the metal centre and the tridentate coordination of **3** in complex **15**. The cobalt complexes [Co{bis[1-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-1-ethylethyl]phenylphosphonite}Cl_2] **16**, [Co{Bis(2-oxazoline-2-ylmethyl)phenylphosphine}Cl_2] **17**, [Co{Bis(2-oxazolin-2,5,5-trimethyl)phenylphosphine}Cl_2] **18** and [Co{phenyl-bis(2-picolyl)phosphine}Cl_2] **19** were prepared by reaction of anhydrous $CoCl_2$ with the ligands NOPON^{Me2} (bis(oxazolinyl)phenylphosphonite), **1**, **2** or **3**, respectively. The crystal structure of **16** has been determined by X-ray diffraction and showed a distorted tetrahedral coordination geometry involving the phosphorus atom and one of the two oxazoline functions. In contrast

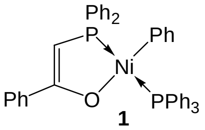
to **16**, the IR spectrum of **17** showed the coordination of the pyridine functions to the metal centre.

The complexes **7-9**, **10-12** and **16** have been evaluated in the catalytic oligomerization of ethylene with $AlEtCl_2$ or MAO as cocatalyst. The nickel complex **8** proved to be the most active precatalyst in the series with a turnover frequency (TOF) of 61800 mol C_2H_4/(mol Ni·h) with 10 equiv. of $AlEtCl_2$ and 12200 mol C_2H_4/(mol Ni·h) with 200 equiv. of MAO. For the nickel complexes, **7** presented the best selectivities in C_4 olefins (up to 90% with 6 equiv of $AlEtCl_2$ and up to 92% with 400 equiv of MAO) and the best selectivities in 1-butene were obtained with **7** with $AlEtCl_2$ as cocatalyst (up to 31% with 6 equiv) and **9** with MAO as cocatalyst (up to 72% with 200 equiv). The iron complexes were not significantly active with $AlEtCl_2$ or MAO as cocatalyst. Complex **16** with 6 equiv of $AlEtCl_2$ showed a TOF up to 17700 mol C_2H_4/(mol Co·h) at 80°C and under a pressure of 30 bars. **16** presented high selectivities in C_4 oligomers (up to 99%) and in 1-butene (up to 96%). However it did not show any significant activity with MAO as cocatalyst.

1. Introduction

Since the works of Ziegler and Natta, the search for effective olefin polymerization or oligomerization catalysts with transition metal complexes activated by alkylaluminums became of high academic and industrial interest.[1-10]

Nickel complexes became important for the catalytic ethylene oligomerization after the discovery of the Shell Higher Olefin Process (SHOP) which involves neutral Ni(II) complexes bearing a bidentate P,O type ligand (Scheme 1).[11, 12] This system has a remarkable selectivity for linear α-olefin and presents a Schulz-Flory mass distribution.



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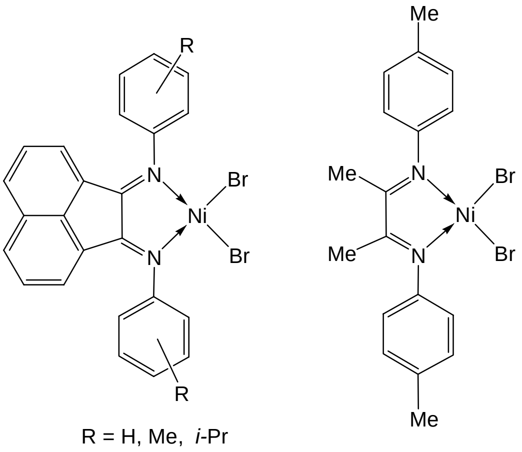
Scheme 1. SHOP-type catalyst

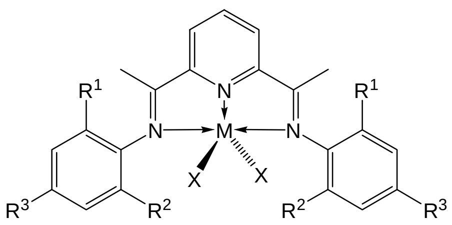
Brookhart showed that Ni(II) α-diimine complexes are effective catalysts in polymerization of ethylene (scheme 2).[6, 7, 13-17] Depending of the steric effect of the substituents of the α-diimine ligands, the [$NiCl_2$(α–diimine)] precursors form effective catalysts in ethylene oligomerization with high turnover frequencies (TOF) and a Schulz-Flory mass distribution.[18, 19]



Scheme 2. α-diimine nickel complexes

Recently we reported the synthesis of nickel complexes bearing P,N-phosphino-pyridine or -oxazoline ligands which are highly active in the catalytic ethylene oligomerization in the presence of small amounts of $AlEtCl_2$ or MAO as cocatalyst.[20]

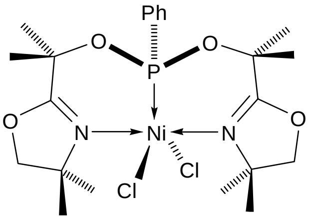
Gibson and Brookhart have described highly active olefin polymerization catalysts based on Fe(II) and Co(II) complexes coordinated by tridentate bis(imino)pyridine ligands and activated by MAO (Scheme 3).[21-25] The catalytic behavior of these Fe(II) and Co(II) bis(imino)pyridine complexes could be changed into oligomerization catalysts by using less bulky aryl substituents on the ligands.[26-30] These results inspired a considerable number of studies.[17, 31-34] (for recent examples: 31-34)



M = Fe, Co
X = Cl, Br
R^1 = H, Me, *i*-Pr, *t*-Bu, CF_3
R^2 = H, F, Me, *i*-Pr, CF_3
R^3 = H, F

Scheme 3. Typical 2,6-bis(imino)pyridyl iron or cobalt complexes

Only few phosphine or phosphonite tridentate ligands have led to effective oligomerization Ni(II) catalyst.[35, 36] The use of bis(oxazolinyl)phenylphosphonite NOPON^{Me2} has led to the pentacoordinated mononuclear nickel complex [$NiCl_2$(NOPON^{Me2})] which is an effective precatalyst with selectivities in C_4 olefins higher than 90% when activated with $AlEtCl_2$ (Scheme 4).[37]



Scheme 4. $NiCl_2$(NOPON^{Me2}) complex

The tridentate ligands NOPON^{Me2} and NOPON^{iPr} afforded active ruthenium complexes for the catalytic transfer hydrogenation and the asymmetric cyclopropanation of olefins[38] and displayed variable coordination behaviors with palladium complexes depending on the nature of counteranion and the solvent.[39, 40]

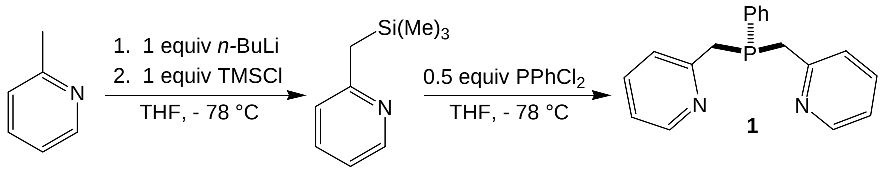
N,P,N-type phosphine ligands on ruthenium complexes displayed interesting hemilabile properties and good results for the catalytic transfer hydrogenation of ketones.[40, 41]

Only few nickel complexes coordinated by N,P,N ligands have been synthesized in the past[42] although they might have promising properties in oligomerization of ethylene. Also the synthesis of iron and cobalt complexes with new tridentate N,P,N ligands could provide interesting ethylene oligomerization catalysts. Furthermore, a story of the influence of the metal centers on the coordination behavior of such ligands should be a considerable interest.

2. Results and discussion

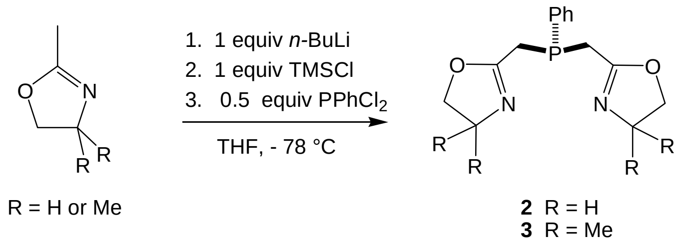
2.1 Synthesis of the ligands

Ligand **1** was prepared similarly to the literature[43] but the yield was increased if 2-picolinetrimethylsilane was isolated by distillation before $PPhCl_2$ was added (eq 1). This afforded the pure ligand in yields up to 68% and it has been characterized by ^{1}H, $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectroscopy.



(1)

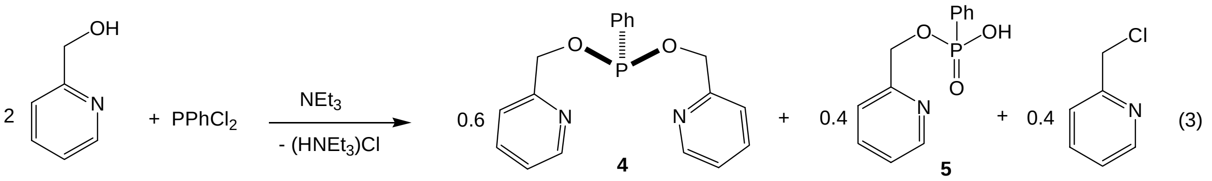
Ligand **2** was prepared according to the literature by deprotonation of the oxazoline precursor followed first by addition of chlorotrimethylsilane and then addition of 0.5 equiv of $PPhCl_2$ at –78 °C (eq 2).[41] The new ligand **3** was synthesized using the same method described for **2** (eq 2). Ligand **2** was isolated as a white powder in 83% yield and ligand **3** as a yellow oil in 41% yield and both ligands have been characterized by ^{1}H, $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectroscopy.



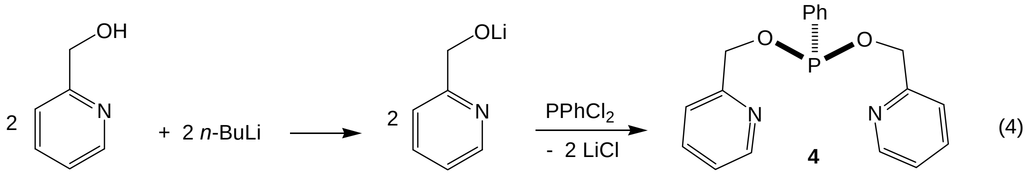
(2)

Owning to the presence of the prochiral P centre, the CH_2 protons in α position to the phosphorous atom of ligand **2** reveal a ABMX spin system (A = B = M = H, X = P)[41] and the signals of the CH_2 protons of **1** and **3** correspond to ABX spin system (A = B = H, X = P).

The sensitivity of phosphonites to the presence of HCl[37] prevents the synthesis of **4** by direct reaction of $PPhCl_2$ with (pyridine-2-yl)methanol which led to phosphonate **5** and 2-(chloromethyl)pyridine byproducts despite the presence of NEt_3 (eq 3).

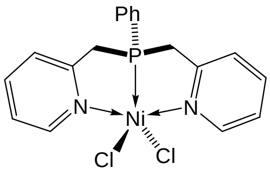


However the use of two equiv of pyridine alcoholate with one equiv of $PPhCl_2$ at -78 °C in THF yielded the tridentate pyridine phosphonite (eq 4). Its ^1H NMR spectrum showed a ABX spin system (A = B, X = P) for the CH_2 protons.

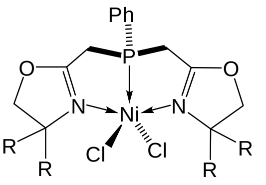


2.2 Synthesis of nickel complexes

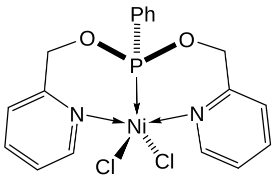
The Ni(II) phenylphosphinobis(picoline) complex **6** and the Ni(II) phenylphosphinobis(oxazoline) complexes **7** and **8** were prepared by the reaction of equimolar amounts of $NiCl_2$ and N,P,N ligands **1**-**3**, respectively, in MeOH and isolated in yields of 96%, 61% and 77%, respectively.



6



7 R = H
8 R = Me



9

Complex **9** was synthesized by stirring one equiv of ligand with one equiv of $[NiCl_2(DME)]$ (DME = 1,2-dimethoxylethane) in CH_2Cl_2 at room temperature. The nickel complexes **6**-**9** are paramagnetic in solution and their magnetic moments, determined by the Evans method[44-47] in CD_2Cl_2, were 3.1, 2,7, 2,8 and 2,7 μ_B respectively. These values are in the range found for Ni(II) complexes coordinated by P,N type ligands.[37, 48-51]

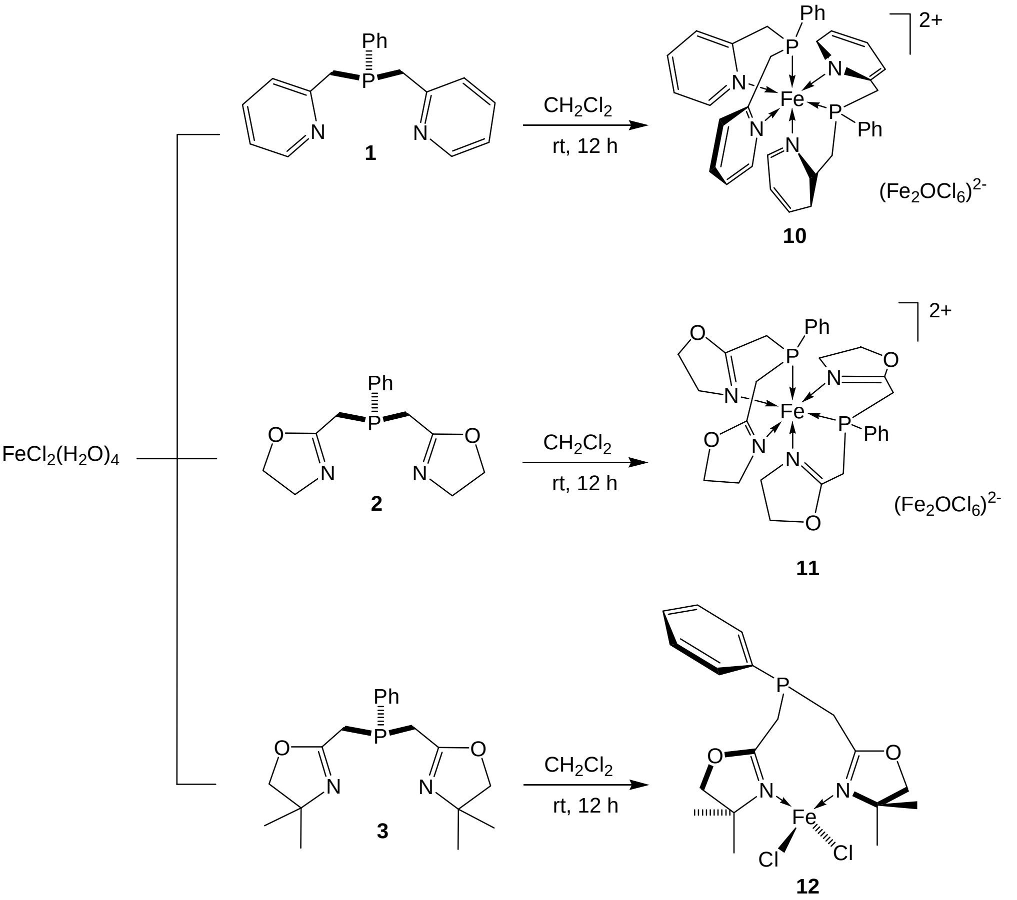
Complexes **6**-**9** were characterized by IR spectroscopy and elemental (C,H,N) analysis and their green color is comparable with that of related complexes.[37]

Ligand coordination to the metal can be confirmed by IR spectroscopy with the strong band corresponding to the C=N vibrations at 1658, 1635, 1600 and 1603 cm^{-1} respectively for **6**-**9**. The IR spectra of **6**-**9** did not show the presence of uncoordinated pyridine or oxazoline functions and this suggested a tridentate behavior for ligands **1**-**4** as described for

[Ni(NOPON^{Me2})Cl$_2$].[37] The presence of the CH$_3$ substituents of the oxazoline function can be observed by the strong band at 1270 cm^{-1} for **7** which shifts to 1321 cm^{-1} for **8**.

2.3 Synthesis of the iron complexes

The iron complexes **10-12** were prepared by reaction of one equiv of FeCl$_2$·4H$_2$O with ligands **1-3** , respectively, in CH$_2$Cl$_2$ at room temperature (Scheme 5).



Scheme 5. Synthesis of iron complexes **10-12**

The iron complexes **10** and **11** precipitated instantaneously in CH$_2$Cl$_2$ and, after work-up, they were isolated as red powders in 62% and 58% yield, respectively. The IR spectrum of complex **10** was similar to that of the corresponding Ni complex **6**. The strong IR band for the C=N vibration of **11** at 1639 cm^{-1} is shifted compared to that of its corresponding nickel complex **7** (1658 cm^{-1}).

Slow diffusion of heptane into a solution of the complexes **10** and **11** in a mixture CH_2Cl_2/MeCN (1/1) gave crystals suitable for X-ray diffraction. ORTEP views of their crystal structures are presented in Figures 1 and 2 and selected bond distances and angles are given in Tables 2 and 3, respectively.

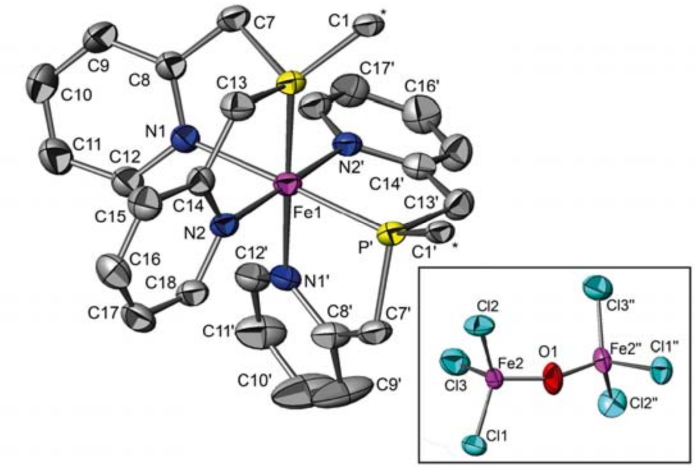


Figure 1. ORTEP view of the structure of **10** in **10**·½CH_2Cl_2 with thermal ellipsoids drawn at the 50% probability level, symmetry operator for the generation equivalent position: -x + 1/2, -y + 1/2, z (′) and –x + 1/2, -y + 3/2, z (″).

Table 1. Selected bond distances and bond angles of **10**

Bond distances (Å)			
Fe1-P	2.1654(16)	C7-P	1.831(6)
Fe1-N1	2.097(4)	P-C13	1.823(6)
Fe1-N2	2.022(4)	C13-C14	1.506(8)
N1-C8	1.355(7)	C14-N2	1.356(7)
C8-C7	1.506(8)	Fe2-O1	1.754(2)
Bond angles (°)			
P-Fe1-N1	81.43(13)	N1-Fe1-P′	177.50(13)
P-Fe1-N1′	177.50(13)	N2-Fe1-N1′	96.69(18)
P-Fe1-N2	85.60(12)	N2-Fe1-N2′	176.91(16)
P-Fe1-N2′	96.40(12)	N2-Fe1-P′	96.40(12)
P-Fe1-P′	99.32(5)	N1′-Fe1-N2′	81.26(18)
N1-Fe1-N1′	07.91(18)	N1′-Fe1-P′	81.43(13)
N1-Fe1-N2	81.26(18)	N2′-Fe1-P′	85.60(12)
N1-Fe1-N2′	96.69(18)	Fe2-O1-Fe2″	154.1(5)

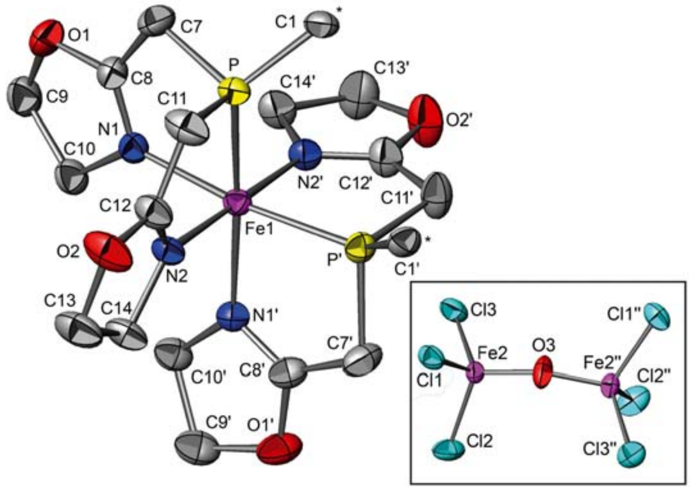


Figure 2. ORTEP view of the structure of **11** in **11**·4MeCN with thermal ellipsoids drawn at the 50% probability level, symmetry operator for the generation equivalent position: -x, y, -z +1/2 (′) and –x + 1, y, -z + 1/2 (″).

Table 2. Selected bond distances and bond angles of **11**

Bond distances (Å)			
Fe1-P	2.1842(6)	C7-P	1.841(2)
Fe1-N1	2.0416(16)	P-C11	1.836(2)
Fe1-N2	1.989(2)	C11-C12	1.474(3)
N1-C8	1.276(3)	C12-N2	1.274(3)
C8-C7	1.486(3)	Fe2-O3	1.7600(5)
Bond angles (°)			
P-Fe1-N1	82.95(5)	N1-Fe1-P′	170.61(5)
P-Fe1-N1′	170.61(5)	N2-Fe1-N1′	88.44(7)
P-Fe1-N2	82.40(5)	N2-Fe1-N2′	170.03(7)
P-Fe1-N2′	98.25(5)	N2-Fe1-P′	98.25(5)
P-Fe1-P′	96.26(2)	N1′-Fe1-N2′	90.93(7)
N1-Fe1-N1′	99.33(6)	N1′-Fe1-P′	82.95(5)
N1-Fe1-N2	88.44(7)	N2′-Fe1-P′	82.40(5)
N1-Fe1-N2′	90.93(7)	Fe2-O3-Fe2″	162.00(16)

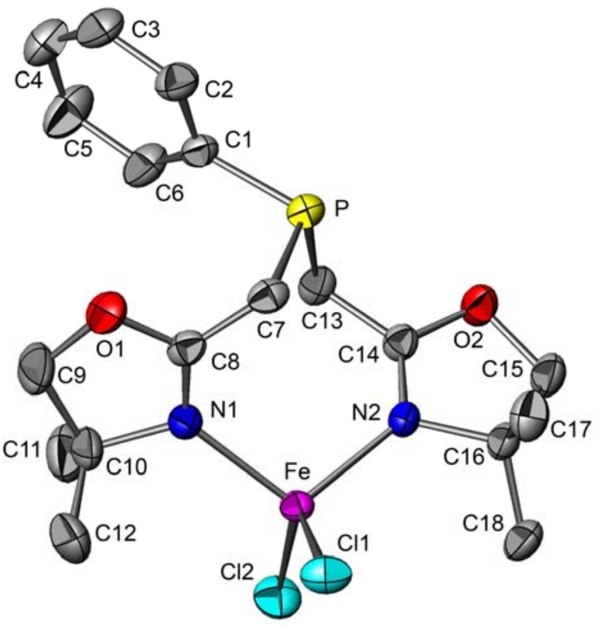


Figure 3. ORTEP view of the structure of **12** with thermal ellipsoids drawn at the 50% probability level.

Table 3. selected bond distances and bond angles of **12**

Bond distances (Å)			
Fe-Cl1	2.2607(8)	C8-C7	1.479(4)
Fe-Cl2	2.2586(8)	C7-P	1.854(3)
Fe-N1	2.088(2)	P-C13	1.857(3)
Fe-N2	2.094(2)	C13-C14	1.491(4)
N1-C8	1.279(4)	C14-N2	1.277(4)
Fe-P	4.336(1)		
Bond angles (°)			
N1-Fe-N2	105.80(9)	Fe-N1-C8	123.8(2)
N1-Fe-Cl1	104.79(8)	N1-C8-C7	126.5(3)
N1-Fe-Cl2	113.21(7)	C8-C7-P	114.1(2)
N2-Fe-Cl1	110.91(7)	C7-P-C13	100.76(13)
N2-Fe-Cl2	104.39(8)	P-C13-C14	108.00(18)
Cl1-Fe-Cl2	117.29(3)	C13-C14-N2	126.1(2)
C14-N2-Fe	128.75(19)		

The X-ray structure showed octahedral complexes with a *fac*-coordination of two tridentate ligands in contrast to the situation where only one tridentate N,P,N ligand is coordinated to the metal centre observed for ruthenium complexes with ligands **2** or NOPON^{Me2}.[38, 41] The doubly positive charge of the metal centre is compensated by the dianion (μ-oxo)bis[trichloroferrate(III)] $(Fe_2OCl_6)^{2-}$ which results from the partial oxidation of the Fe(II) precursor.[52-55] The stoichiometry of three iron atoms for two ligands in complexes **10** and **11** suggested the lost of 33% of the ligands **1** and **2** after reaction. The complexes adopted a distorted octahedral geometry as shown by the values of the P-Fe1-N1′ and N2-Fe-N2′ angles (177.50(13) and 176.91(16)°, respectively, for complex **10** and 179.61(5) and 170.03(7)°, respectively, for complex **11**). The phosphorus atoms are coordinated to the Fe(II) ion trans to a nitrogen atom and the dications have a C_2 symmetry axis passing through the metal centre. For **11**, the Fe1-N1 bond distance (2.0416(16) Å), slightly longer than the Fe1-N2 bond distance (1.989(2) Å), results from the trans influence of the phosphorous atom on N1 (Table 1). This is also noted in complex **10** with the slightly longer Fe1-N1 distance (2.097(4) Å) compared to Fe1-N2 (2.022(4) Å).

In contrast to complexes **10** and **11** where the formation of the oxo-bridged dianion $(Fe_2OCl_6)^{2-}$ was observed, Fe(II) complexes coordinated by two tridentate ligands around the metal centre have been described with a $(FeCl_4)^{2-}$counterion.[56-60] However, traces of oxygen could contaminate the solution during the synthesis of **10** and **11** and initiate the formation of $(Fe_2OCl_6)^{2-}$. Since its first description in 1978, this ferric dianion has been studied for its magnetic or structural properties and its tetraalkyl ammonium derivatives $(R_4N)_2(Fe_2OCl_6)$ are convenient starting materials for the synthesis of polynuclear iron complexes.[61-65] Tri-iron complex salts with $(Fe_2OCl_6)^{2-}$ as counter anion formed by oxidation of a Fe(II) specie have been reported.[52-54, 66-69] Compound $(Fe_2OCl_6)^{2-}$ could be easily formed by autoxidation of the metal center of Fe(II) complexes.[55] The key for the formation of $(Fe_2OCl_6)^{2-}$ could be the formation of an intermediate Fe(II) anion which rapidly autoxidizes in the presence of oxygen.[53, 65-68]

Despite the similar Fe2-O distances for **10** and **11** (1.7600(5) and 1.754(2) Å, respectively), the Fe2-O1-Fe2″ bond angle of **10** (154.1(5)°) is smaller than the Fe2-O3-Fe2″ angle of **11** (162.00(16)°). According to the literature, the Fe-O distance of the dianion $(Fe_2OCl_6)^{2-}$ is always around 1.76 Å but the Fe-O-Fe angle can be found between 147.7 and 180.0°.[63, 68]

Complex **12** was soluble in CH_2Cl_2 and, after work-up, gave a white powder in 87% yield. A magnetic moment of 4.2 μ_B has been determined for **12** by the Evan’s method[44, 46, 47, 51] in CD_2Cl_2 and, according to the literature, this value is slightly lower than expected for Fe(II) high spin complexes.[24, 29] The C=N vibration band was shifted from 1636 cm^{-1} for the nickel complex **8** to 1624 cm^{-1} for the iron complex **12**. The crystal structure of **12** has been determined X-ray diffraction. An ORTEP view is shown in Figure 3 and selected bond distances and angles are given in Table 3. The crystal structure of **12** showed a distorted tetrahedral geometry around the metal (the N1-Fe-N2 and Cl1-Fe-Cl2 bond angles are 105.80(9) and 117.29(3)°, respectively) with the coordination of the two nitrogen atoms of the tridentate ligand but without the expected coordination of the phosphorus to the iron centre. The Fe-P distance of 4.340(2) Å is very long and the phosphorus lone pair is not properly oriented to coordinate the metal center. The N,N chelating mode of **3** on the metal center formed, according to the Cambridge database, the first tetrahedral iron complex with an eight membered chelate. The N1-Fe and N2-Fe distances of 2.088(2) and 2.094(2) Å respectively, are similar than in tetrahedral iron complexes coordinated by N,N bidentate ligands and used in oligomerization or polymerization.[70-73]

Complexes **10-12** have been studied by cyclic voltammetry. The cyclic voltammograms of **10** and **11** showed two reversible redox couples attributed to the reduction of the dianion $(Fe_2OCl_6)^{2-}$ (-0.237 mV for **10** and -0.198 mV for **11** vs. SCE) and to the oxidation of the Fe(II) center of the complex (0.668 mV for **10** and 0.521 mV for **11** vs. SCE) (Figure 4). Coordinated by pyridine functions, the more electron rich **10** had a redox potential for the Fe(II) center shifted to more positive values compared to **11** and this indicates a higher stability of Fe(II) in **10** than in **11**. However, compared to Fe(II) complexes coordinated by two N,N,N tridentate ligands containing pyridine functions and with redox potentials between 0.785 and 1.06 mV vs. SCE, the redox potential of **10** is at less positive values.[74, 75]

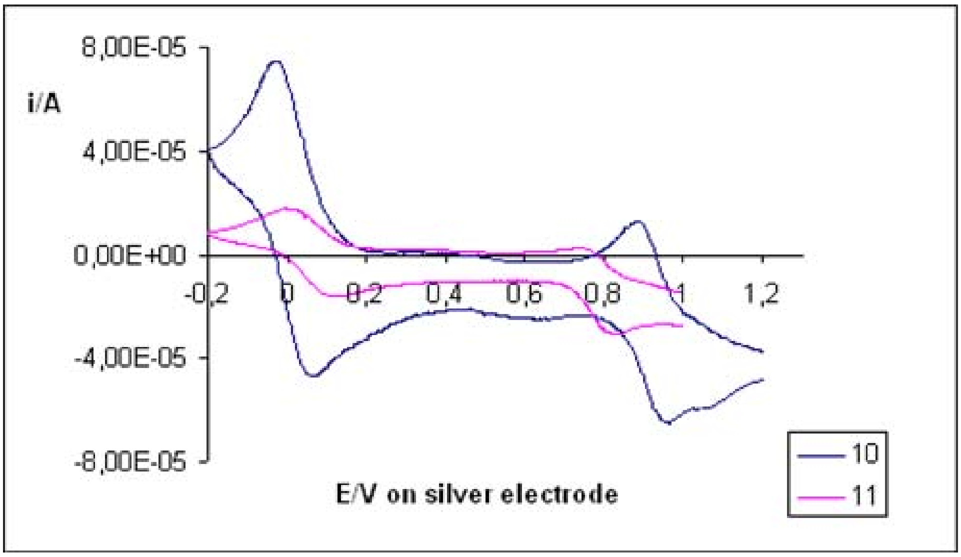


Figure 4. Cyclic voltammograms of **10** and **11** in anhydrous MeCN (0.1 M N-(*n*-Bu)$_4$PF$_6$) at a rate of 100 mV s^{-1}

The cyclic voltammogram of **12** showed a reversible redox couple at -0.168 mV vs. SCE attributed to the oxidation of Fe(II) atom and an irreversible process at 0.65 mV (Figure 5). This potential is slightly more negative than in Fe(II) complexes coordinated by α-diimine ligands.[70]

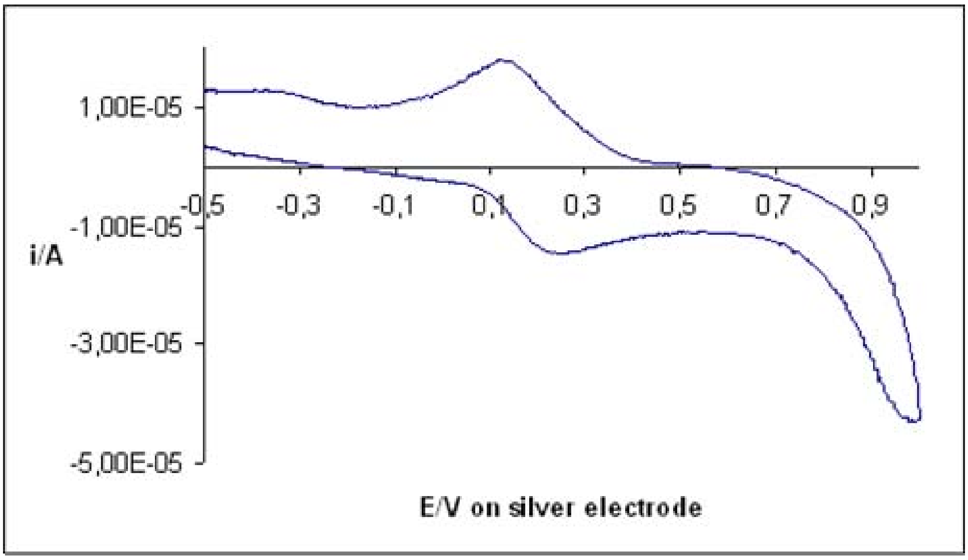
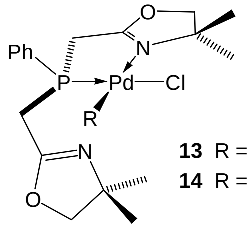


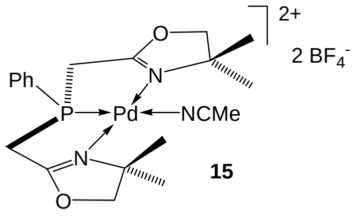
Figure 5. Cyclic voltammograms of 12 in anhydrous CH_3CN (0.1 M N-(nBu)$_4PF_6$) at a rate of 100 mV s^{-1}

2.4 Synthesis of the palladium complexes

In order to study the coordination properties of ligand **3**, we first synthesized Pd(II) complexes by reaction of one equiv of [Pd(Me)Cl(COD)] (COD = 1,5-cyclooctadiene), [$PdCl_2(CNPh)_2$] or [$Pd(MeCN)_4(BF_4)_2$] with one equiv of **3** in CH_2Cl_2.



13 R = Me
14 R = Cl



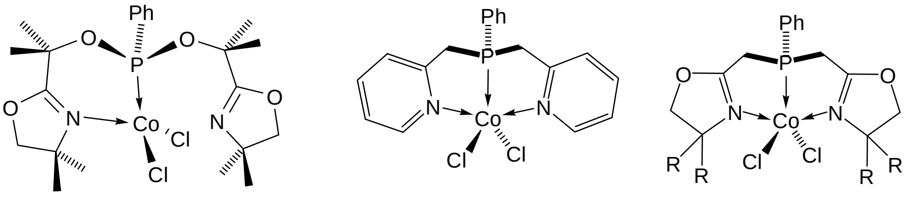
15

The reaction afforded complexes **13-15** in 87%, 82% and 90% yields, respectively. The IR spectra of **13** and **14** present two bands for the C=N vibrations of the uncoordinated and coordinated oxazoline at 1659 and 1630 cm^{-1} for **13** and 1659 and 1614 for **14**, respectively. The $^{31}P\{^1H\}$ NMR spectra clearly indicate the coordination of the phosphorus atom to the metal centre by the shift from -24.83 ppm for the free ligand to 26.56 ppm for the coordinated ligand in complex **13** and 19.93 ppm in complex **14**. The $^{13}C\{^1H\}$ NMR spectra of **13** and **14** contain two signals for the C=N oxazoline: a doublet at 169.6 ppm ($^2J_{PC}$ of 18.5 Hz, complex **13**) and 173.9 ppm ($^2J_{PC}$ of 23.9 Hz, complex **14**) corresponding to a coordinated oxazoline and singlet at 159.4 ppm (complex **13**) or a doublet at 158.2 ppm ($^2J_{PC}$ of 7.6 Hz, complex **14**) corresponding to an uncoordinated oxazoline. The ^1H NMR spectra of the complexes showed two distinct ABX spin systems (A = H, B = H, X = P) at 2.98 and 3.78 ppm (ABX spin system 1) and 3.06 and 3.23 ppm (ABX spin system 2) for **13** and 3.23 and 4.04 ppm (ABX spin system 1) and 3.49 and 3.57 ppm (ABX spin system 2) for **14** integrating for two protons each and corresponding to the signals of PCH_AH_B of the coordinated oxazoline and the free oxazoline. According to the HMBC NMR spectrum of **14**, the signal at 3.23 and 4.04 ppm correspond to the PCH_AH_B protons of the coordinated oxazoline moiety. In the ^{1}H NMR spectra of **13** and **14**, the methyl protons appear as four singlets and the OCH_2 protons form two distinct AB spin systems. The mutual *cis*-coordination of the phosphorus and the methyl group complex **13** is indicated by the doublet at 0.78 ppm with a $^3J_{PH}$ of 3.6 Hz.

In contrast to **13** and **14**, the $^{13}C\{^1H\}$ NMR spectrum of **15** contains a singlet for the C atoms in α position to the methyls at 68.4 ppm, a singlet for the OCH_2 carbon atoms at 83.4 ppm, a doublet for C=N at 174.7 ppm ($^2J_{PC}$ = 19.8 Hz) and a doublet for the PCH_2 carbon atoms at 29.6 ppm ($^1J_{PC}$ = 41.8 Hz). Its ^{1}H NMR spectrum shows an AB spin system for the OCH_2 protons at 4.44 and 4.57 ppm (J_{AB} = 8.9 Hz) and an ABX spin system for the PCH_2 protons at 3.54 and 4.35 ppm. Its $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 43.92 ppm. The IR spectrum of **15** presents an unique band for the C=N vibrations at 1613 cm^{-1}. According to the NMR and IR spectra, we conclude that ligand **3** coordinates the metal center in a tridentate fashion and that the molecule has a mirror plane passing through the P,Pd and the N_{MeCN} atoms . The coordination of a MeCN molecule stabilizes the complex.[39]

2.5 Synthesis of the cobalt complexes

In order to study the coordination of the tridentate ligands (NOPON^{Me2}), **1-3** to a cobalt centre, complexes **16-19** have been synthesized, respectively (Scheme 6). The three complexes were obtained in high yield by reaction of the corresponding ligands with anhydrous $CoCl_2$ in THF at room temperature.



16 **17** **18** R = H
19 R = Me

Scheme 6. Co(II) complexes **16-19**

Complexes **16-19** proved to be paramagnetic in solution and their magnetic moments of 3.8, 4.1, 4.0 and 4.0 μ_B, respectively, were determined by the Evans method in CD_2Cl_2.[44, 46, 47] These values are slightly lower than expected for high spin d^7 Co(II).[24, 29] Complex **17** was isolated as a green powder and complexes **16**, **18** and **19** as blue powders. The IR $\nu_{(C=N)}$ vibrations of uncoordinated oxazoline and coordinated oxazoline are at 1682 and 1627 cm^{-1}, respectively.

The IR spectrum of **17** suggested the coordination of both nitrogen atoms with an unique band for $\nu_{(C=N)}$ vibration at 1603 cm^{-1}.

The structure of **16** has been determined by X-ray diffraction and its structure is presented in Figure 6 and selected bond distances and angles are given in Table 4.

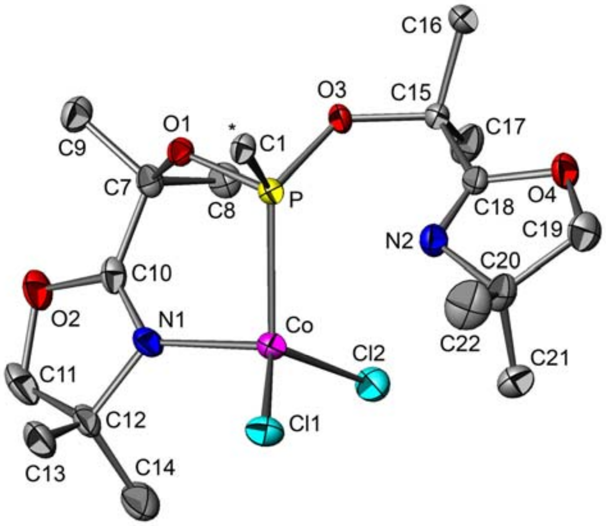


Figure 6. ORTEP view of the structure of **16** in **16**·0.5 $C_6H_5CH_3$ with thermal ellipsoids drawn at the 50% probability level.

Table 4. Selected bond distances and bond angles of **16**

Bond distances (Å)			
Co-N1	2.038(3)	C7-O1	1.449(4)
Co-P	2.3581(11)	O1-P	1.636(2)
Co-Cl1	2.2384(11)	P-O3	1.612(2)
Co-Cl2	2.2397(11)	O3-C15	1.441(4)
N1-C10	1.280(5)	C15-C18	1.505(5)
C10-C7	1.509(5)	C18-N2	1.251(5)
Bond angles (°)			
N1-Co-P	92.93(9)	N1-C10-C7	127.7(3)
N1-Co-Cl1	109.18(10)	C10-C7-O1	109.8(3)
N1-Co-Cl2	108.38(10)	C7-O1-P	123.6(2)
P-Co-Cl1	113.44(4)	O1-P-O3	97.03(12)
P-Co-Cl2	112.95(4)	P-O3-C15	132.1(2)
Cl1-Co-Cl2	117.06(4)	O3-C15-C18	110.1(3)
Co-N1-C10	129.2(2)	C15-C18-N2	126.7(3)

This establishes the coordination of the phosphorus and only one of the two oxazoline moieties of the tridentate ligand. The metal center adopts a distorted tetrahedral geometry with a Cl1-Co-Cl2 angle of 117.06(4)° and a N1-Co-P angle of 92.93(9)°. The Co-Cl1 (2.2384(11) Å), Co-Cl2 (2.2397(11) Å) and Co-N1 (2.038(3) Å) distances are similar to those in Co(II) complexes with a distorted tetrahedral geometry and containing diimine ligands.[72, 73] The hemilability of the oxazoline arms of the tridentate NOPON^{Me2} ligand has been studied on Pd complexes by variable-temperature NMR spectroscopy.[39] In contrast to the corresponding $NiCl_2$ and $RuCl_2$ complexes, NOPON^{Me2} formed tetracoordinated $CoCl_2$ and PdX_2 (X = Cl or I) complexes.[37, 38]

3. Catalytic oligomerization of ethylene

The complexes **6**, **8**-**12** and **16** have been evaluated in the catalytic oligomerization of ethylene with different amounts of $AlEtCl_2$ or MAO as cocatalyst and $NiCl_2(P(n\text{-}Bu)_3)_2$ was used as reference catalyst.

Ni complexes **6**, **8** and **9** proved to be active in oligomerization of ethylene when activated with 2, 4, 6 or 10 equiv of $AlEtCl_2$ (Table 5) or with 200 or 400 equiv of MAO (Table 6). In contrast to **6**, **8** and **9** did not have significant catalytic activities with 100 equiv of MAO. Complex **6** presented the highest activities (Figure 7) with a turnover frequency (TOF) of 61800 mol C_2H_4/(mol Ni·h) with 10 equiv. of $AlEtCl_2$ and 12200 mol C_2H_4/(mol Ni·h) with 200 equiv. of MAO) but **8** showed the best selectivities in C_4 olefins (up to 90% with 6 equiv of $AlEtCl_2$ and up to 92% with 400 equiv of MAO) and in 1-butene with $AlEtCl_2$ as cocatalyst (up to 31% with 6 equiv of $AlEtCl_2$) and **9** showed the best selectivity in 1-butene with MAO as cocatalyst (up to 72% with 200 equiv of MAO) of the nickel complexes. Similarly to Ni(II) complexes with P,N type ligands, complexes **6** and **9** coordinated by pyridine functions presented better activities than **8** and than Ni(NOPON^{Me2})Cl_2[37] coordinated by oxazoline functions with $AlEtCl_2$ or MAO as cocatalyst.

The choice of the cocatalyst has a clear impact on the catalytic results: MAO makes the system less active than $AlEtCl_2$ but more selective in 1-butene and in C_4 olefins. The amount of cocatalyst is important too because in all cases increasing the quantity of cocatalyst makes the system more active but less selective.

The catalytic results, presented in Table 5, showed that increasing the amount of cocatalyst produced more active systems but less selective in C_4 olefins and in 1-butene. Very active system the isomerization of 1-butene in 2-butene and favored the reinsertion of 1-butene and 2-butene to form C_6 oligomers.[76]

Some tetrahedral iron(II) complexes have shown good activities in oligomerization and polymerization of ethylene[72, 73] and it was therefore interesting to test **12** with different cocatalysts and study its reactivity. However, activities of **12** with 200 equiv. of MAO or 6 equiv. of $AlEtCl_2$ were very low and only traces of butenes were detected by gas chromatography. The hexacoordinated mononuclear iron complexes **10** and **11** containing two ligands around the metal centre showed no activity with MAO or $AlEtCl_2$ as cocatalyst, perhaps because the coordination sphere of the iron center in saturated which disfavors ethylene coordination to the metal centre. A similar situation was observed with other inactive iron complexes containing two C,N,C pincer ligands.[77, 78]

Table 5. Comparative Catalytic Data for Complexes **6**, **8** and **9** in the Oligomerization of Ethylene with $AlEtCl_2$ as Cocatalyst.[a, b]

	EADC (equiv)	**Selectivity (mass %)**			**Productivity [g C_2H_4/(g Ni·h)]**	**TOF [mol C_2H_4/(mol Ni·h)]**	**α-olefin (C_4) (mol %)**	**k_α**[b]
		C_4	**C_6**	**C_8**				
6	6	53	43	4	26400	55600	8	0.57
6	10	54	42	4	29500	61800	9	0.55
8	6	90	10	<1	4200	8800	31	<0.10
8	10	76	23	1	18000	37700	11	0.20
9	2	89	11	<1	1600	3400	11	<0.10
9	4	77	21	2	14900	31300	11	0.18
9	6	53	41	6	23800	49900	13	0.51
9	10	53	43	4	27800	58200	8	0.57
Ref[C]	6	60	35	5	38800	81400	3	0.40

[a] Conditions: $T = 30$ °C, 10 bar of C_2H_4, 35 min, $4 \cdot 10^{-5}$ mol Ni complex; solvent 10 mL chlorobenzene and 3 or 5 mL of cocatalyst solution in toluene 6 or 10 equivalents of $AlEtCl_2$, respectively. [b] k_α = hexenes (mol)/butenes (mol).[C] Ref = $[NiCl_2(Pn\text{-}Bu_3)_2]$.

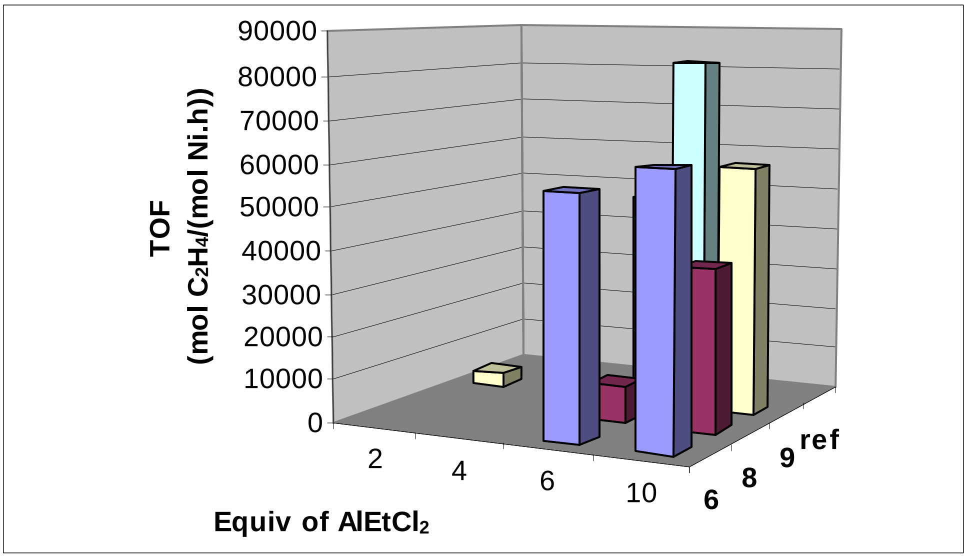


Figure 7. Catalytic activities of the complexes **6**, **8** and **9** in the oligomerization of ethylene using $AlEtCl_2$ as cocatalyst, Ref: $[NiCl_2(Pn\text{-}Bu_3)_2]$.

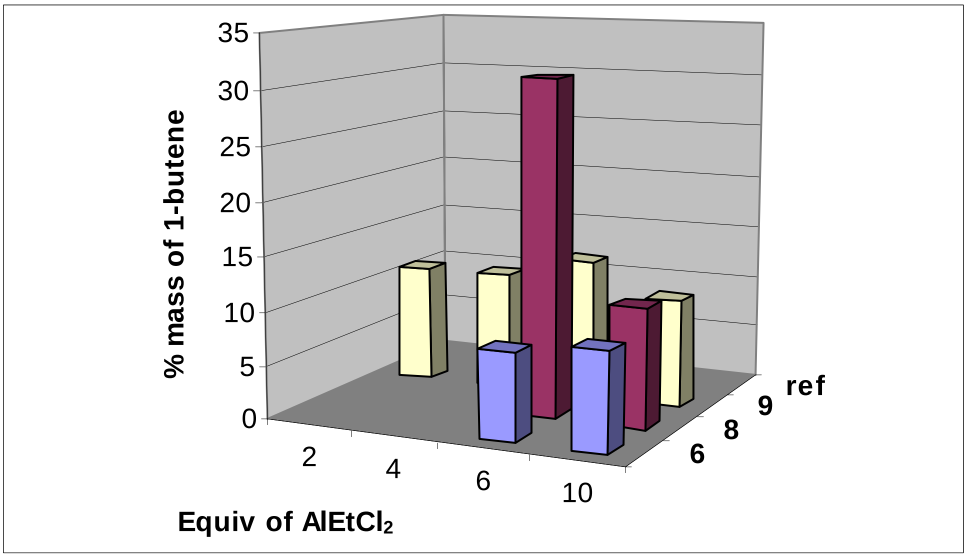


Figure 8. Selectivity of the complexes **6**, **8** and **9** for 1-butene using $AlEtCl_2$ as cocatalyst, Ref: $[NiCl_2(Pn\text{-}Bu_3)_2]$.

Table 6. Comparative Catalytic Data for Complexes **6**, **8** and **9** in the Oligomerization of Ethylene with MAO as Cocatalyst.[a, b]

	MAO (equiv)	**Selectivity (mass %)**			**Productivity [g C_2H_4/(g Ni·h)]**	**TOF [mol C_2H_4/(mol Ni·h)]**	**α-olefin (C_4) (mol %)**	**k_{α}**[c]
		C_4	**C_6**	**C_8**				
6	100	71	26	3	3900	9300	24	0.24
6	200	69	25	6	5800	12200	24	0.24
8	200	91	8	<1	500	1200	56	<0.10
8	400	92	7	<1	700	1500	59	<0.10
9	200	91	8	<1	700	1500	72	<0.10
9	400	77	20	3	1600	3400	62	0.17

[a] Conditions: $T = 30$ °C, 10 bar of C_2H_4, 35 min, $4 \cdot 10^{-5}$ mol Ni complex; solvent 12 mL chlorobenzene and 4, 8 or 16 mL of cocatalyst solution in toluene for 100, 200 or 400 equivalents of MAO, respectively. [b] Traces of C_{10} oligomers were detected when using 400 equivalents of MAO. [c] k_{α} = hexenes (mol)/butenes (mol).

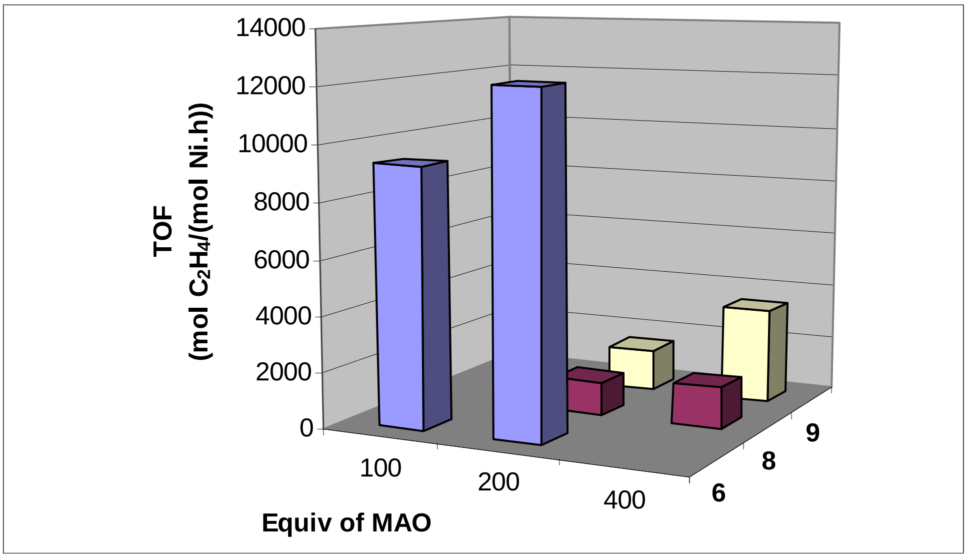


Figure 10. Catalytic activities of the complexes **6**, **8** and **9** in the oligomerization of ethylene using MAO as cocatalyst.

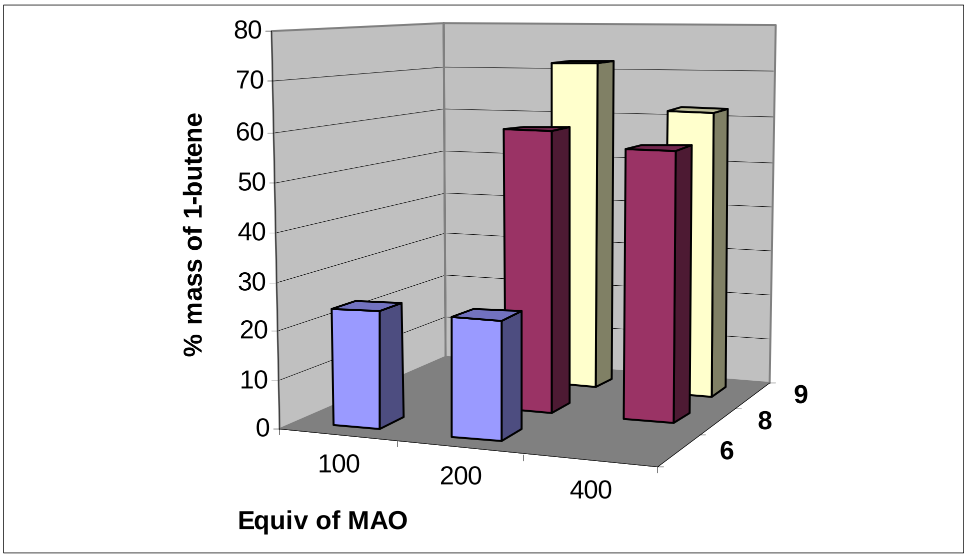


Figure 11. Selectivity of the complexes **6**, **8** and **9** for 1-butene using MAO as cocatalyst.

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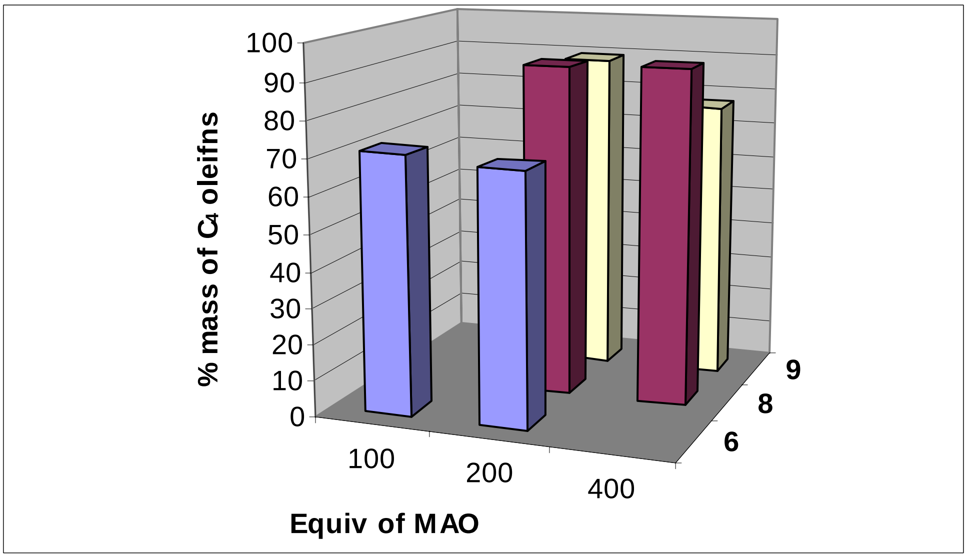

Figure 12. Selectivity of the complexes **6**, **8** and **9** for C_4 compounds using MAO as cocatalyst (1-butene and 2-butene).

Different concentrations of complex **16** (10^{-5} or $4{\cdot}10^{-5}$ mol of complex dissolved in a total volume of 15 ml) have been tested in ethylene oligomerization with 6 and 12 equiv of $AlEtCl_2$ (Table 7). In both cases, the complex presented modest activities but high selectivities for the dimerization of ethylene into 1-butene with $AlEtCl_2$ as cocatalyst. To obtain better activities, we heated the catalytic solution at 80 °C and increased the ethylene pressure to 30 bar. Under these conditions, the TOF was up to 17700 mol C_2H_4/(mol Co·h) and the system remained selective in C_4 olefins (97%) but the isomerization increased and the selectivity in 1-butene was 48%. With MAO as cocatalyst, **16** did not present any significant catalytic activity.

Table 7. Catalytic Data for Complex **16** in the Oligomerization of Ethylene with $AlEtCl_2$ as Cocatalyst.[a, b]

EADC (equiv)	Quantity of 16	P (bar)	Productivity [g C_2H_4/(g Co·h)]	TOF [mol C_2H_4/(mol Ni·h)]	α-olefin (C_4) (mol %)	C_4 olefins (mol%)	k_α[c]
6	$4 \cdot 10^{-5}$	10	700	1400	73	98	<0.1
6	10^{-5}	10	3700	7600	96	99	<0.1
12	10^{-5}	10	3200	6700	93	99	<0.1
6[b]	10^{-5}	30	8500	17700	48	97	<0.1

[a] Conditions: T=30°C, 35 min, solvent: chlorobenzene, total volume (X mL of complex solution in chlorobenzene + Y mL of cocatalyst solution in toluene) = 15 mL. [b] T=80°C.[c] k_α = hexenes (mol)/butenes (mol).

4. Conclusion

The phosphine oxazoline ligand **2** has been synthesized according to the literature and the new phosphine oxazoline ligand **1** and the phosphine pyridine ligand 3 were prepared similarly.[41] The ligand **4** has been synthesized by reaction of $PPhCl_2$ with 2 equiv of its corresponding pyridine alcoholate at low temperature.

The nickel complexes **6**-**9** were prepared in good yields by reaction of their corresponding ligands **1-4** with $NiCl_2$ in methanol or [$NiCl_2$(DME)] in CH_2Cl_2. The IR spectra of **6**-**9** suggested the coordination of the two nitrogens of the tridentate ligands **1-4**.

Complexes **6**, **8** and **9** were evaluated as precatalysts in oligomerization of ethylene using $AlEtCl_2$ or MAO as cocatalyst. Complex **6** showed the highest activities within the series with a TOF of 61800 mol C_2H_4/(mol Ni·h) with 10 equiv of $AlEtCl_2$ and a TOF of 12200 mol C_2H_4/(mol Ni·h) with 200 equiv of MAO. Precatalyst **8** showed the highest selectivities in C_4 olefins up to 90 % with 6 equiv of $AlEtCl_2$ and up to 92 % with 400 equiv of MAO. The more active systems favored the isomerization of 1-butene and the reinsertion of C_4 olefins to form C_6 oligomers. In all cases, the activity in ethylene oligomerization led to increased when more cocatalyst was used and $AlEtCl_2$ as cocatalyst form more active but less selective systems than MAO.

The ligands **1**-**3** were used for the preparation of iron complexes **10**-**12**. The crystal structures of **10** and **11** have been determined by X-ray diffraction and showed a distorted octahedral geometry with the *fac*-coordination of the two tridentate ligands **1** or **2** around the Fe(II) atom and the formation of a dianion (μ-oxo)bis[trichloroferrate(III)] to compensate the doubly positive charge. The crystal structure of **12** showed the coordination of a tridentate ligand **3** but, unexpectedly, without the coordination of the phosphorus atom on the metal center. The cyclic voltammograms of **10** and **11** showed two reversible redox couples attributed to the reduction of the dianion $(Fe_2OCl_6)^{2-}$ (-0.237 mV for **10** and -0.198 mV for **11** vs. SCE) and to the oxidation of the Fe(II) ion of the complex (0.668 mV for **10** and 0.521 mV for **11** vs. SCE). The cyclic voltammogram of **12** showed a reversible redox couple at -0.168 mV vs. SCE assigned to the oxidation of Fe(II) atom and an irreversible process at 0.65 mV. The complexes **10-12** did not show significant activities in ethylene oligomerization with $AlEtCl_2$ or MAO as cocatalyst.

Complexes **13** and **14** were synthesized by reaction of **3** with [Pd(Me)Cl(COD)] or $[PdCl_2(NCPh)_2]$, respectively. The presence of coordinated oxazoline function and uncoordinated oxazoline functions was confirmed by $^{13}C\{^1H\}$ and ^1H NMR spectroscopy and IR spectroscopy. Complex **15**, synthesized by reaction of **3** with $[Pd(MeNC)_4(BF_4)_2]$, showed the tridentate coordination of **3** to the metal center.

The cobalt complexes **16-19** have been synthesized by reaction of anhydrous $CoCl_2$ with the ligands ($NOPON^{Me2}$), **1**, **2** and **3**, respectively. The crystal structure of **16** showed a distorted tetrahedral geometry with the coordination of the phosphorus and one of the two oxazoline functions of the ligand. The presence of a coordinated and uncoordinated oxazoline ligand was still confirmed by the presence of two C=N vibration bands in its IR spectrum. In contrast to **16**, the IR spectrum of the green complex **17** showed only the presence of coordinated pyridine functions. Precatalyst **16** has been evaluated in oligomerization of ethylene with MAO or $AlEtCl_2$ as cocatalyst but it did not present significant activity with 400 equiv of MAO. However, at 80 °C and under a pressure of 30 bar, **16** showed an activity of 17700 mol C_2H_4/(mol Co·h) with 6 equiv of $AlEtCl_2$.

5. Experimental section

General consideration: All reactions were performed under purified nitrogen. Solvents were purified and dried under nitrogen by conventional methods. The ^1H NMR spectra were recorded at 300 MHz, $^{31}P\{^1H\}$ NMR spectra were recorded at 121.5 MHz, and $^{13}C\{^1H\}$ NMR spectra were recorded at 75.5 MHz on a FT Bruker AC300 instrument. IR spectra in the range of 4000-400 cm^{-1} were recorded on a Bruker IFS28FT. Gas chromatographic analyses were performed on a Thermoquest GC8000 Top Series gas chromatograph using a HP Pona column (50 m, 0.2 mm diameter, 0.5 μm film thickness). Magnetic moments were determined by the Evans method in CD_2Cl_2 using a solution of CH_3NO_2 in CD_2Cl_2 (20:80, v/v) as reference. Mass spectra were recorded with a Bruker Daltonics microTOF (ESI; positive mode; capillary voltage: 4.8 kV; nebulizer pressure: 0.2 bar; desolvation temperature: 180 °C; desolvation gas flow rate: 4.5 L/min).

The ligands and complexes NOPON^{Me}, **2**, [Pd(Me)Cl(COD)], [PdCl$_2$(NCPh)$_2$], [Pd(MeCN)$_4$(BF$_4$)$_2$] have been synthesized according to the literature.[39, 41, 79, 80]

Synthesis of phenyl-bis(2-picolyl)phosphine 1

A *n*-BuLi solution (96.0 mmol, 1.6 M in hexane) was added drop wise to a degassed solution of 2-picoline (8.94 g, 96.0 mmol) in 100 mL of THF at -78 °C. After complete deprotonation, the red anion precipitated out and after further 1 h of stirring at -78 °C, degassed chlorotrimethylsilane (10.43 g, 96.0 mmol) was added drop wise to the solution. The brown mixture was allowed to reach room temperature overnight and the THF was evaporated under reduced pressure. The residue was distilled at 120 °C and 12 mbar to obtain the pure liquid picolyltrimethylsilane compound (yield: 6.61 g, 40.0 mmol, 42%).

^{1}H NMR (300 MHz, CDCl$_3$): δ 0,00 (s, 9H, Si(CH$_3$)], 2,32 (s, 2H, SiCH$_2$), 6,93 (t, $^2J_{H\text{-}H}$ = 7,65 Hz, 2H, Py), 7,45 (td, 1H, $^2J_{H\text{-}H}$ = 1,85 Hz, $^2J_{H\text{-}H}$ = 7,65 Hz, Py), 8,39 (d, 1H, $^3J_{H\text{-}H}$ = 4,17, HCN). ^{13}C{^{1}H} NMR (CDCl$_3$, 75.5 MHz): δ -1,7 (s, SiCH$_3$), 30,2 (s, SiCH$_2$), 119,0 (s, C of Py), 122,1 (s, C of Py), 135,7 (s, C of Py), 148,9 (s, C of Py), 161,3 (s, C of Py).

Pure picolyltrimethylsilane (6.61 g, 40.0 mmol) was dissolved in a mixture of 50 mL THF and 50 mL diethylether cooled down to -78 °C and PPhCl$_2$ (3.58 g, 20.0 mmol) was added. The reaction mixture was allowed to reach room temperature overnight, the solvents were evaporated under reduced pressure and the resulting orange oil was dried in vacuum at 60 °C (yield: 4.02 g, 13.6 mmol, 68%).

^{1}H NMR (300 MHz, CDCl$_3$): δ ABX spin system (A = B = H, X = P) 3.24 (2H, dd, J_{AB} = 13.3 Hz, $^2J_{XB}$ = 1.8 Hz) 3.31 (2H, d, J_{AB} = 13.3 Hz, $^2J_{XA}$ = 0.0 Hz), 3.78 (4H, s), 6.93 – 6.89 (4H, m, aromatic H), 7.15 – 7.22 (3H, m, aromatic H), 7.30 – 7.39 (4H, m, aromatic H), 8.33 – 8.35 (2H, m, aromatic H); ^{13}C{^{1}H} NMR (75.5 MHz, CDCl$_3$): δ 37.65 (d, $^1J_{PC}$ = 18.4 Hz, P-CH$_2$), 120.8 (s, CH of Pyridyl (substitution)), 123.6 (d, $^3J_{PC}$ = 5.1 Hz, CH of Pyridyl), 128.25 (d, $^3J_{PC}$ = 6.9 Hz, *m*-CH of Aryl), 129.1 (s, *p*-CH of aryl), 132.6 (d, $^2J_{PC}$ = 19.9 Hz, *o*-CH of aryl), 136.0 (s, CH of Pyridyl), 136.7 (d, $^1J_{PC}$ = 18.4 Hz, C-P of aryl), 149.15 (s, CH of pyridyl), 158.1 (d, $^2J_{PC}$ = 5.7 Hz, N*C*-CH$_2$ of pyridyl); ^{31}P{^{1}H} NMR (121.5 MHz, CDCl$_3$): δ -12.55.

HRMS : Mass Calcd for $C_{18}H_{18}N_2P$: 293.1208. Found. 293.1247 [(N,P,N)+H]$^+$.

Synthesis of bis(2-oxazolin-2,5,5-trimethyl)phenylphosphine 3

A *n*-BuLi solution (64.0 mmol, 1.6 M in hexane) was added drop wise to a degassed solution of 2,5,5-trimethyl-2-oxazoline (7.24 g, 64.0 mmol) in 100 mL of THF at a constant temperature of -78 °C. After the pale yellow mixture was stirred for 1 h at -78 °C, degassed chlorotrimethylsilane (6.95 g, 64.0 mmol) was added drop wise and stirring for 2 h. Liquid $PPhCl_2$ (5.73 g, 32.0 mmol) was added to the colourless solution at -78 °C. The liquid was allowed to reach room temperature overnight and a mixture of diethylether and toluene was added to the yellow solution to precipitate the LiCl which was removed by filtration. Solvents were evaporated and the remaining yellow oil was dried for several hours under vacuum at 40 °C. This afforded the pure ligand as a yellow oil (yield: 4.4 g, 13.25 mmol, 41 %).

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.12 and 1.13 (6H, 2s, CH_3), ABX spin system (A = B = H, X = P) 2.80 (2H, dd, J_{AB} = 14.1 Hz, $^2J_{XB}$ = 0.9 Hz, P-CH_2) 2.92 (2H, dd, J_{AB} = 14.1 Hz, $^2J_{XA}$ = 4.6 Hz, P-CH_2), 3.78 (4H, s, O-CH_2), 7.31 – 7.35 (3H, m, aromatic H) and 7.48 – 7.53 (2H, m, aromatic H); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 26.9 (d, $^1J_{PC}$ = 22.0 Hz, P-CH_2), 28.32 (s, CH_3), 28.41 (s, CH_3), 67.1 (s, O-CH_2), 79.2 (s, *C*-CH_3), 128.35 (d, $^3J_{PC}$ = 6.9 Hz, *m*-CH of aryl), 129.4 (s, *p*-CH of aryl), 132.2 (d, $^2J_{PC}$ = 20.2 Hz, *o*-CH of aryl), 135.2 (d, J_{PC} = 20.2 Hz, C-P of aryl), 162.4 (d, $^2J_{PC}$ = 4.7 Hz, *C*=N); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ -24.83. HRMS : Mass Calcd for $C_{18}H_{26}N_2O_2P$: 333.1732. Found. 333.1656 $[(N,P,N)+H]^+$.

Synthesis of bis((pyridin-2-yl)methyl)phenylphosphonite 4

Liquid (pyridin-2-yl)methanol (1.39 g, 12.7 mmol) was dissolved in 30 ml of THF and cooled at -78 °C. 1 equiv of *n*-BuLi (12.7 mmol in solution in 8 ml of hexane) was added drop wise and the solution was stirred for 1h. After reaction 0.5 equiv of $PPhCl_2$ (0.87 ml, 6.35 mmol) was added drop wise at -78 °C and stirred overnight to room temperature. The solvent was removed under reduced pressure and 20 ml of a mixture diethylether/CH_2Cl_2 was added to precipitate LiCl. The yellow solution was filtered with a canula and the solvents were removed under reduced pressure. The resulting yellow oil was dried under vacuum at 60 °C overnight (Yield: 1.75 g, 5.4 mmol, , 86%).

^{1}H NMR (300 MHz, $CDCl_3$): δ ABX spin system (A = B = H, X = P) 4.90 (2H, dd, J_{AB} = 13.8 Hz, $^2J_{XB}$ = 7.2 Hz) 5.07 (2H, dd, J_{AB} = 13.8 Hz, $^2J_{XA}$ = 8.4 Hz), 7.15 – 7.17 (2H, m, aromatic H), 7.44 – 7.46 (5H, m, aromatic H), 7.62 – 7.67 (2H, m, aromatic H), 7.71 – 7.76 (2H, m, aromatic H) 8.50 – 8.52 (2H, m, aromatic H); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): δ 69.3 (d, $^2J_{PC}$ = 9.7 Hz, OCH_2), 121.1 (s, C of Py), 122.4 (s, C of Py) 128.45 (d, $^3J_{PC}$ = 5.5 Hz, *m*-CH of aryl), 129.8 (s, *p*-CH of aryl), 130.2 (d, $^2J_{PC}$ = 23.9 Hz, *o*-CH of aryl), 136.7 (s, Pyridyl), 140.15 (d, $^1J_{PC}$ = 19.6 Hz, P-C of aryl), 149.1 (s, C of Py), 158.4 (d, $^2J_{PC}$ = 5.4 Hz, C=N of Py); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 161.91.

(pyridin-2-yl)methyl hydrogen phenylphosphonate 5

To a THF solution of (pyridin-2-yl)methanol (3.21 g, 29.4 mmol) containing 10 mL of Net_3, was added 2 mL of $PPhCl_2$ (2.64 g, 14.7 mmol) at -78 °C. The mixture was stirred overnight to room temperature. All volatiles were removed under reduced pressure and the residue was dissolved in diethylether. The solution was filtered and the solvent was removed under reduced pressure to yield a yellow oil. Yield: 40% (the yield was evaluated by ^{1}H NMR monitoring of the chemical shifts of the C-H_2 protons of **4** and **5**). ^{1}H NMR (300 MHz, $CDCl_3$): δ ABX spin system (A = B = H, X = P) 5.16 (1H, dd, J_{AB} = 13.0 Hz, $^2J_{XB}$ = 9.1 Hz) 5.26 (1H, dd, J_{AB} = 13.0 Hz, $^2J_{XA}$ = 9.1 Hz), 7.15 – 8.51 (9H, m, aromatic H); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 27.6 (s).

Synthesis of [Ni{phenyl-bis(2-picolyl)phosphine}Cl_2] 6

A solution of 1.40 g (4.8 mmol) phenyl-bis(2-picolyl)phosphine **1** in 50 mL of methanol was stirred while 0.62 g (4.8 mmol) $NiCl_2$ in 50 mL of methanol was added drop wise to the solution. After several hours the solvent was evaporated and 10 mL of CH_2Cl_2 was added to the red oil. Petroleum ether was added to the solution to precipitate the green complex. After treating the suspension with ultrasound for 1 h, the complex was filtered and washed several times with diethylether. The complex was dried several hours in vacuum (yield: 2.0 g, 4.6 mmol, 96 %).

IR (KBr): 1600 (vs), 1566 (m), 1477 (s), 1435 (vs), 1386 (w), 1311 (w), 1155 (m), 1107 (m), 1055 (w), 1016 (w), 820 (w), 745 (s), 694 (m), 482 (m) cm^{-1} (m). Anal. Calc. for $C_{18}H_{17}Cl_2N_2NiP$: C, 51.24; H, 4.06; N, 6.64. Found: C, 51.70; H, 4.57; N, 6.32.

Synthesis of [Ni{bis(2-oxazoline-2-ylmethyl)phenylphosphine}Cl_2] 7

A solution of 0.90 g (3.25 mmol) bis(2-oxazoline-2-ylmethyl)phenylphosphine **2** in 50 mL of methanol was stirred while 0.42 g (3.25 mmol) $NiCl_2$ in 50 mL of methanol was added drop wise to the solution. After several hours the solvent was evaporated and 10 mL of dried and degassed CH_2Cl_2 was added to the red oil. Petroleum ether was added to the solution to precipitate the green complex. After treating the suspension with ultrasound for 1 h, the complex was filtered and washed several times with diethylether. The green complex was dried several hours in vacuum (yield: 0.80 g, 2.0 mmol, 61 %).

IR (KBr): 1658 (vs), 1478 (w), 1437 (m), 1402 (s), 1374 (m), 1339 (w), 1270 (s), 1168 (s), 1108 (w), 1034 (s), 999 (w), 972 (w), 932 (m), 868 (w), 749 (m), 694 (m) cm^{-1}.
Anal. Calc. for $C_{14}H_{17}Cl_2N_2NiO_2P$: C, 41.43; H, 4.22; N, 6.90. Found: C, 40.43; H, 4.42; N, 6.52.

Synthesis of [Ni{bis(2-oxazolin-2,5,5-trimethyl)phenylphosphine}Cl$_2$] 8

A solution of 2.42 g (7.3 mmol) bis(2-oxazolin-2,5,5-trimethyl)phenylphosphine **3** in 50 mL of Methanol was stirred while 0.94 g (7.3 mmol) $NiCl_2$ in 50 mL of methanol was added drop wise to the solution. After several hours the solvent was evaporated and 10 mL of dried and degassed CH_2Cl_2 was added to the red oil. Petroleum ether was added to the solution to precipitate the green complex. After treating the suspension with ultrasound for 30 minutes the complex was filtered and washed several times with diethylether. Green complex **8** was dried several hours in vacuum (yield: 2.60 g, 5.6 mmol, 77 %).
IR (KBr): 1636 (vs), 1464 (m), 1437 (m), 1403 (m), 1369 (s), 1320 (vs), 1162 (s), 1107 (m), 1028 (w), 999 (s), 955 (s), 863 (w), 840 (w), 747 (s), 695 (s) cm^{-1}.
Anal. Calc. for $C_{18}H_{25}Cl_2N_2NiO_2P$: C, 46.80; H, 5,45; N, 6.06. Found: C, 46.51; H, 5.58; N: 5.77. Mass Calcd for $C_{18}H_{25}ClN_2NiO_2P$: 425.0696. Found. 425.0641 [Ni(N,P,N)Cl]$^+$.

Synthesis of [Ni{bis((pyridin-2-yl)methyl)phenylphosphonite}Cl$_2$] 9

To a solution of ligand bis((pyridin-2-yl)methyl)phenylphosphonite **4** in 30 mL of CH_2Cl_2 (0.42 g, 1.3 mmol) was added 0.30 g (1.3 mmol) of [$NiCl_2$(DME)]. The dark green solution was stirred overnight at room temperature. After complexation, the solution was concentrated to 5 ml and filtered. 50 mL of petroleum ether was added to the solution to precipitate the complex. After filtration by canula, the green complex was washed with 20 ml of diethylether and dried under vacuum overnight (yield: 0.51 g, 1.2 mmol, 87 %).
IR (KBr) : 1603 (vs), 1571 (m), 1483 (s), 1463 (s), 1445 (vs), 1385 (w), 1315 (s), 1231 (m), 1164 (m), 1115 (m), 1026 (vs), 995 (vs sh), 836 (s), 800 (s), 770 (s), 734 (s), 713 (m), 691 (m), 626 (s),548 (s), 485 (m), 431 (m) cm^{-1}. Anal. Calcd.: for $C_{18}H_{17}Cl_2N_2NiO_2P$: C, 47.63; H, 3.77; N, 6.17. Found: C, 47.98; H, 4.21; N, 5.85. HRMS : Mass Calcd for $C_{18}H_{17}ClN_2NiO_2P$: 417.0064. Found. 417.0070 [Ni(N,P,N)Cl]$^+$.

Synthesis of [Fe{phenyl-bis(2-picolyl)phosphine}$_2${FeCl$_3$OFeCl$_3$}] 10

To a solution of phenyl-bis(2-picolyl)phosphine **1** (2.40 g, 8.2 mmol) in 50 mL of CH_2Cl_2 was added a CH_2Cl_2 solution of $FeCl_2 \cdot 4H_2O$ (1.63 g, 8.2 mmol) and the mixture was stirred at room temperature overnight. After reaction the brown precipitate was filtered and washed with diethylether. Complex **10** was dried several hours under vacuum (yield: 1.70 g, 1.7 mmol, 62 %).

IR (KBr): 1600 (s), 1471 (vs), 1434 (vs), 1396 (w), 1311 (m), 1155 (m), 1106 (s), 861 (vs), 820 (w), 804 (m), 753 (s), 744 (s sh), 707 (m), 692 (m), 603 (w), 504 (m), 492 (s) cm^{-1}.Anal. Calcd.: for $C_{36}H_{34}Cl_6Fe_3N_4OP_2$: C, 44.08; H, 3.49; N, 5.71. Found: C, 43.96; H, 4.02; N, 6.09

Synthesis of [Fe{bis(2-oxazoline-2-ylmethyl)phenylphosphine}$_2${$FeCl_3OFeCl_3$}] 11

To a solution of bis(2-oxazoline-2-ylmethyl)phenylphosphine **2** (0.43 g, 1.55 mmol) in 50 mL of CH_2Cl_2 was added a CH_2Cl_2 solution of $FeCl_2{\cdot}4H_2O$ (0.31 g, 1.55 mmol) and the mixture was stirred at room temperature overnight. After reaction the violet precipitate was filtered and washed with diethylether. Complex **11** was dried several hours under vacuum (yield: 0.28 g, 0.3 mmol, 58 %).

IR (KBr): 1639 (s), 1481 (w), 1435 (w), 1406 (m), 1373 (m), 1269 (vs), 1171 (m), 1108 (w), 999 (w), 933 (m), 858 (w), 745 (m), 694 (m) cm^{-1}. Anal. Calcd.: for $C_{28}H_{34}Cl_6Fe_3N_4O_5P_2$: C, 35.44; H, 3.61; N, 5.91. Found: C, 35.76; H, 4.39; N, 5.98. HRMS : Mass Calcd for ($C_{28}H_{34}FeN_4O_4P_2$)/2 : 304.0697. Found. 346.0673 [Fe(N,P,N)]$^{2+}$.

Synthesis of [Fe{bis(2-oxazolin-2,5,5-trimethyl)phenylphosphine}Cl_2] 12

To a solution of bis(2-oxazolin-2,5,5-trimethyl)phenylphosphine **3** (1.99 g, 6.0 mmol) in 50 mL of CH_2Cl_2 was added a CH_2Cl_2 solution of $FeCl_2{\cdot}4H_2O$ (1.19 g, 6.0 mmol) and the mixture was stirred at room temperature overnight. After reaction the solvent was eliminated under reduced pressure and 50 mL of diethylether was added to precipitate the white complex. Complex **12** was filtered, washed with diethylether and dried under vacuum (yield: 2.40 g, 5.2 mmol, 87 %). The crystal structure of **12** has been determined after formation of white crystals suitable for X-ray diffraction by slow diffusion of heptane into a CH_2Cl_2 solution of the complex.

IR (KBr): 1624 (vs), 1460 (w), 1448 (w), 1433 (w), 1423 (w), 1371 (s), 1319 (s), 1220 (w), 1178 (m), 1133 (m), 1004 (m), 954 (m), 744 (m), 698 (m) cm^{-1}.

Anal. Calcd.: for $C_{18}H_{25}Cl_2FeN_2O_2P$: C, 47.09; H, 5.45; N, 6.10. Found: C, 46.51; H, 5.58; N, 5.57.

Synthesis of [Pd(Me){bis(2-oxazolin-2,5,5-trimethyl)phenylphosphine}Cl] 13

To a solution of (2-oxazolin-2,5,5-trimethyl)phenylphosphine **3** (1.05 g, 3.15 mmol) in $\mathrm{CH_2Cl_2}$ was added [Pd(Me)Cl(COD)] (0.84 g, 3.15 mmol) at room temperature and the pale yellow solution was stirred overnight. After elimination of the solvent under reduced pressure, a pale yellow powder was obtained. Complex **13** was washed with diethylether and dried under vacuum (yield: 1.34 g, 2.7 mmol, 87%).

IR (KBr): 1659 (s), 1630 (s), 1463 (m), 1435 (m), 1366 (s), 1320 (s), 1261 (s), 1159 (s), 1103 (s), 951 (m), 801 (s), 747 (m), 692 (m) $\mathrm{cm^{-1}}$.

^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ 0.74 (3H, s, Pd-$\mathrm{CH_3}$) 1.27 (3H, s, $\mathrm{CCH_3}$) 1.30 (3H, s, $\mathrm{CCH_3}$) 1.56 (3H, s, $\mathrm{CCH_3}$) 1.58 (3H, s, $\mathrm{CCH_3}$), ABX spin system 1 (A = B = H, X = P) 2.98 (1H, $^{2}j_{\mathrm{AB}}$ = 18.0 Hz, $^{2}J_{\mathrm{PA}}$ = 11.1 Hz, $\mathrm{PC}H_A\mathrm{H_B}$), ABX spin system 2 (A = B = H, X = P) 3.06 (1H, $^{2}J_{\mathrm{AB}}$ = 14.4 Hz, $^{2}j_{\mathrm{PA}}$ = 7.5 Hz, $\mathrm{PC}H_A\mathrm{H_B}$), ABX spin system 2 (A = B = H, X = P) 3.23 (1H, $^{2}J_{\mathrm{AB}}$ = 14.4 Hz, $^{2}J_{\mathrm{PB}}$ = 12.9 Hz, $\mathrm{PCH_A}H_B$), ABX spin system 1 (A = B = H, X = P) 3.78 (1H, $^{2}J_{\mathrm{AB}}$ = 18.0 Hz, $^{2}j_{\mathrm{PB}}$ = 11.1 Hz, $\mathrm{PCH_A}H_B$), AB spin system 3.97 and 4.01 (2H, $^{2}J_{\mathrm{AB}}$ = 8.1 Hz, overlapping signal of $\mathrm{OCH_AH_B}$), AB spin system 4.13 and 4.16 (2H, $^{2}J_{\mathrm{AB}}$ = 8.1 Hz, overlapping signal of $\mathrm{OCH_AH_B}$), 7.67 – 7.84 (5H, m, aromatic H); ^{13}C{^{1}H} NMR (75.5 MHz, $\mathrm{CDCl_3}$): δ -4.3 (s, Pd-$\mathrm{CH_3}$), 26.1 (d, $^{1}J_{\mathrm{PC}}$ = 25.1 Hz, $\mathrm{PCH_2}$), 27.6 (s, C-$C\mathrm{H_3}$), 27.9 (s, C-$C\mathrm{H_3}$), 28.2 (s, C-$C\mathrm{H_3}$), 28.6 (s, C-$C\mathrm{H_3}$), 30.0 (d, $^{1}J_{\mathrm{PC}}$ = 30.0 Hz, $\mathrm{PCH_2}$), 67.9 (s, $\mathrm{N}C\mathrm{CH_3}$), 68.4 (s, $\mathrm{N}C\mathrm{CH_3}$), 79.6 (s, $\mathrm{OCH_2}$), 83.5 (s, $\mathrm{OCH_2}$), 129.2 (d, $^{2}J_{\mathrm{PC}}$ = 11.3 Hz, *m*-CH of aryl), 129.3 (d, $^{1}J_{\mathrm{PC}}$ = 48.6 Hz, C-P of aryl), 132.1 (s, *p*-CH of aryl), 132.7 (d, $^{3}J_{\mathrm{PC}}$ = 13.5 Hz, *o*-CH of aryl), 159.4 (s, C=N from uncoordinated oxazoline), 169.5 (d, $^{2}J_{\mathrm{PC}}$ = 18.5 Hz, C=N from coordinated oxazoline); ^{31}P{^{1}H} NMR (121.5 MHz , $\mathrm{CDCl_3}$): δ 26.56.

Synthesis of [Pd{bis(2-oxazolin-2,5,5-trimethyl)phenylphosphine}$\mathrm{Cl_2}$] 14

To a solution of (2-oxazolin-2,5,5-trimethyl)phenylphosphine **3** (0.80 g, 2.4 mmol) in $\mathrm{CH_2Cl_2}$ was added 0.92 g (2.4 mmol) of [$\mathrm{PdCl_2(NCPh)_2}$] at room temperature and the red solution was stirred overnight. After elimination of the solvent under reduced pressure, a yellow powder was obtained. After washing with 20 mL of THF, the pale yellow powder was dried overnight under vacuum (yield: 1.01 g, 2.0 mmol, 83%).

IR (KBr): 1659 (s), 1630 (s), 1463 (m), 1435 (m), 1419 (w), 1366 (s), 1320 (s), 1261 (s), 1159 (s), 1103 (s), 951 (m), 801 (s), 747 (m), 692 (m) $\mathrm{cm^{-1}}$.

^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ 1.22 (3H, s, $\mathrm{CCH_3}$) 1.28 (3H, s, $\mathrm{CCH_3}$) 1.67 (3H, s, $\mathrm{CCH_3}$) 1.71 (3H, s, $\mathrm{CCH_3}$) ABX spin system 1 (A = B = H, X = P) 3.23 (1H, $^{2}J_{\mathrm{AB}}$ = 18.7 Hz, $^{2}J_{\mathrm{PA}}$ = 12.7 Hz, $\mathrm{PC}H_A\mathrm{H_B}$ of coordinated oxazoline), ABX spin system 2 (A = B = H, X = P) 3.49 (1H, J_{AB} = 16.4 Hz, $^{2}J_{\mathrm{PA}}$ = 12.4 Hz, $\mathrm{PC}H_A\mathrm{H_B}$ of uncoordinated oxazoline), ABX spin system 2

(A = B = H, X = P), 3.57 (1H, $^2J_{AB}$ = 16.4 Hz, $^2J_{PB}$ = 11.0 Hz, $\mathrm{PCH_A}H_B$ of uncoordinated oxazoline), AB spin system 3.89 and 3.98 (1H, J_{AB} = 8.1 Hz, overlapping signal of $\mathrm{OCH_AH_B}$), ABX spin system 1 (A = B = H, X = P) 4.04 (1H, $^2J_{AB}$ = 18.7 Hz, $^2J_{PB}$ = 11.7 Hz, $\mathrm{PCH_A}H_B$ of coordinated oxazoline), AB spin system 4.25 and 4.34 (1H, $^2J_{AB}$ = 8.4 Hz, overlapping signal of $\mathrm{OCH_AH_B}$), 7.67 – 7.84 (5H, m, aromatic H); ^{13}C{^{1}H} NMR (75.5 MHz , $CDCl_3$): δ 26.0 (d, $^1J_{PC}$ = 35.9 Hz, PCH_2), 27.4 (s, C-*C*H_3), 27.8 (s, C-*C*H_3), 28.2 (s, C-*C*H_3), 28.5 (s, C-*C*H_3), 29.1 (d, $^1J_{PC}$ = 33.3 Hz, PCH_2), 68.0 (s, N*C*CH_3), 69.9 (s, N*C*CH_3), 79.5 (s, OCH_2), 84.2 (s, OCH_2), 125.8 (d, $^1J_{PC}$ = 56.7 Hz, C-P of aryl), 129.3 (d, $^2J_{PC}$ = 12.0 Hz, *o*-CH of aryl), 132.5 (s, *p*-CH of aryl), 132.7 (d, $^3J_{PC}$ = 8.1 Hz, *m*-CH of Aryl), 158.2 (d, $^2J_{PC}$ = 7.6 Hz, C=N from uncoordinated oxazoline), 173.9 (d, $^2J_{PC}$ = 51.6 Hz, C=N from coordinated oxazoline); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ 19.40.

Anal. Calc. for $C_{18}H_{25}Cl_2N_2O_2PPd$: C, 42.42; H, 4.94; N, 5.50. Found: C, 41.84; H, 4.59; N, 5.45.

Synthesis of [Pd($NCCH_3$){bis(2-oxazolin-2,5,5-trimethyl)phenylphosphine}(BF_4)$_2$] 15

To a solution of (2-oxazolin-2,5,5-trimethyl)phenylphosphine **3** (0.45 g, 1.4 mmol) in CH_2Cl_2 was added 0.61 g (1.4 mmol) of [$Pd_2(MeCN)_4(BF_4)$] at room temperature and the red solution was stirred overnight. After elimination of the solvent under reduced pressure, an orange powder was obtained which was washed with 20 mL of diethylether and dried overnight under vacuum (yield: 0.82 g, 1.25 mmol, 90%).

IR (KBr): 1613 (vs), 1465 (m), 1438 (w), 1422 (m), 1376 (m), 1329 (m), 1060 (vs), 864 (m), 748 (m), 691 (m) cm^{-1}.

^{1}H NMR (300 MHz, acetonitrile-d_3): δ 1.40 (6H, s, CCH_3) 1.45 (6H, s, CCH_3), ABX spin system (A = B = H, X = P) 3.54 (2H, $^2J_{AB}$ = 18.3 Hz, $^2J_{PA}$ = 16.0 Hz, $\mathrm{PC}H_A\mathrm{H_B}$), ABX spin system (A = B = H, X = P) 4.35 (2H, $^2J_{AB}$ = 18.3 Hz, $^2J_{PB}$ = 14.2Hz, $\mathrm{PCH_A}H_B$), AB spin system 4.44 (2H, J_{AB} = 8.9 Hz, $\mathrm{OCH_A}H_B$), AB spin system 4.57 (2H, J_{AB} = 8.9 Hz, $\mathrm{OC}H_A\mathrm{H_B}$), 7.65 – 8.04 (5H, m, aromatic H); ^{13}C{^{1}H} NMR (75.5 MHz, acetonitrile-d_3): δ 26.0 (s, C-*C*H_3), 26.5 (s, C-*C*H_3), 29.6 (d, $^1J_{PC}$ = 41.8 Hz, PCH_2), 68.4 (s, *C*$(CH_3)_2$), 83.4 (s, OCH_2), 121.7 (d, $^1J_{PC}$ = 66.7 Hz, C-P of aryl), 130.1 (d, $^2J_{PC}$ = 13.6 Hz, *o*-CH of aryl), 132.7 (d, $^3J_{PC}$ = 12.0 Hz, *m*-CH of Aryl), 134.8 (d, $^4J_{PC}$ = 3.3 Hz, *p*-CH of Aryl), 174.7 (d, $^2J_{PC}$ = 19.8 Hz, C=N); ^{31}P{^{1}H} NMR (121.5 MHz, acetonitrile-d_3): δ 43.92.

Anal. Calc. for $C_{20}H_{28}B_2F_8N_3O_2PPd$: C, 36.76; H, 4.32; N, 6.43. Found: C, 37.04; H, 4.56; N, 6.33.

Synthesis of [Co{bis(1-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-1-ethylethyl)phenylphosphonite}Cl$_2$] 16

Anhydrous CoCl$_2$ (0.14 g, 1.1 mmol) was added to a solution of NOPON^{Me2} (0.46 g, 1.1 mmol) in 30 mL of THF. The blue solution was for stirred 3 h at room temperature. After elimination of THF under reduced pressure, the blue powder was dried overnight under vacuum. Complex **16** was obtained as a blue powder without further purification (yield: 0.58 g, 1.05 mmol, 97%). The structure of **16** has been determined by X-ray diffraction on single crystals obtained by low diffusion of toluene into a CH$_2$Cl$_2$ solution. IR (KBr): 1682 (s), 1627 (vs), 1465 (m), 1437 (m), 1366 (m), 1313 (m), 1258 (w), 1144 (s), 1177 (w), 1142 (m), 1119 (vs), 1021 (s), 979 (vs), 913 (m), 865 (w), 741 (s), 714 (w), 698 (w), 576 (w), 562 (w) cm^{-1}. Anal. Calc. for C$_{22}$H$_{33}$Cl$_2$CoN$_2$O$_4$P: C, 48.01; H, 6.04; N, 5.09. Found: C, 48.06; H, 5.92; N, 4.84.

Synthesis of [Co{phenyl-bis(2-picolyl)phosphine}Cl$_2$] 17.

Anhydrous CoCl$_2$ (0.12 g, 0.9 mmol) was added to a solution of phenyl-bis(2-picolyl)phosphine **1** (0.27 g, 0.9 mmol) in 20 mL of MeOH. The green solution was stirred overnight at room temperature. After elimination of MeOH under reduced pressure, the residue was dissolved in 5 mL of CH$_2$Cl$_2$ and the solution was filtered. After elimination of the solvent under reduced pressure, the green complex **17** was washed with 20 mL of diethylether and dried overnight under vacuum (yield: 0.34 g, 0.8 mmol, 87%).

IR (KBr): 1603 (s), 1478 (s), 1437 (s), 1315 (s), 1164 (m), 1107 (m), 749 (s), 694 (m) cm^{-1}. Anal. Calcd.: for C$_{18}$H$_{17}$Cl$_2$CoN$_2$P: C, 51.21; H, 4.06; N, 6.64. Found: C, 50.45; H, 4.29; N, 5.92.

Synthesis of [Co{bis(2-oxazoline-2-ylmethyl)phenylphosphine}Cl$_2$] 18

Anhydrous CoCl$_2$ (0.14 g, 1.1 mmol) was added to a solution of (2-oxazoline-2-ylmethyl)phenylphosphine **2** (0.305 g, 1.1 mmol) in 30 mL of THF. Complex **18** precipitated as a blue powder and the solution was stirred overnight at room temperature. After elimination of THF under reduced pressure, the blue powder was dried overnight under vacuum. Complex **18** was obtained as a blue powder without further purification (yield: 0.43 g, 1.05 mmol, 96%). IR (KBr): 1644 (vs), 1620 (vs sh), 1478 (m), 1435 (s), 1420 (s), 1384 (s), 1330 (m), 1264 (s), 1200 (m), 1190 (m sh), 1143 (m), 1130 (m sh), 1020 (w sh), 1002 (s), 933 (s), 855 (w), 795 (w), 749 (m), 697 (w) cm^{-1}.

Anal. Calcd.: for $C_{14}H_{17}Cl_2CoN_2O_2P$: C, 41.40; H, 4.22; N, 6.90. Found: C, 41.85; H, 3.97; N, 6.58

Synthesis of [Co{bis(2-oxazolin-2,5,5-trimethyl)phenylphosphine}Cl$_2$] 19

Anhydrous $CoCl_2$ (0.24 g, 1.9 mmol) was added to a solution of bis(2-oxazolin-2,5,5-trimethyl)phenylphosphine **3** (0.62 g, 1.9 mmol) in 40 mL of THF. Complex **19** precipitated as a blue powder and the solution was stirred overnight at room temperature. After elimination of THF under reduced pressure, the blue powder was dried overnight under vacuum. Complex **19** was obtained as a blue powder without further purification (yield: 0.86 g, 1.9 mmol, 99%). IR (KBr): 1628 (vs), 1613 (vs sh), 1476 (w), 1462 (w), 1433 (w), 1422 (m), 1372 (s), 1321 (s), 1252 (w), 1222 (m), 1184 (m), 1136 (m), 1119 (m), 1012 (s), 1002 (s sh), 959 (vs), 924 (w), 839 (w), 798 (w), 773 (w), 744 (s), 699 (m) cm^{-1}.

Anal. Calcd.: for $C_{18}H_{25}Cl_2CoN_2O_2P$: C, 46.77; H, 5.45; N, 6.06. Found: C, 46.47; H, 5.23; N, 5.70

Oligomerization of Ethylene: All catalytic reactions were carried out in a magnetically stirred (900 rpm) 145 mL stainless steel autoclave. A 125 mL glass container was used to protect the inner walls of the autoclave from corrosion. The preparation of the catalytic solution of the precatalyst is depended of the nature and the amount of the cocatalyst.

With $AlEtCl_2$, 4 x 10^{-2} mmol of Ni complex were dissolved in 14, 13 or 12 mL of cholorobenzene depending of the amount of the cocatalyst and injected in the reactor under an ethylene flux. Then 1, 2 or 3 mL of a cocatalyst solution, corresponding to 2, 4 or 6 equiv respectively, is added in the reactor to form a total volume of 15 mL with the precatalyst solution. When 10^{-2} mmol of precatalyst were used, a solution of the complex in 14ml of chlorobenzene was injected and then 0.75 mL (for 6 equiv of $AlEtCl_2$) or 1.50 mL (for 12 equiv of $AlEtCl_2$) of cocatalyst solution was added in the reactor.

With MAO, 1 or 4 x 10^{-2} mmol of Ni complex were dissolved in 10 mL in chlorobenzene and injected in the reactor under an ethylene flux. Then 0.5, 1, 2, 4, 8 or 16 mL of a cocatalyst solution, corresponding to 12.5, 25, 50, 100 (4 mL for 4 x 10^{-2} mmol of Ni complex or 1 mL for 10^{-2} mmol of Ni complex), 200 or 400 equiv of MAO respectively, is added.

All catalytic tests were started between 25 and 30 °C, and no cooling of the reactor was done during the reaction. After injection of the catalytic solution and of the cocatalyst under a constant low flow of ethylene, the reactor was pressurized to 10 or 30 bar. A temperature increase was observed which resulted solely from the exothermicity of the reaction. The 10 or

30 bar working pressure were maintained during the experiments through a continuous feed of ethylene from a reserve bottle placed on a balance to allow continuous monitoring of the ethylene uptake. At the end of each test (35 min) a dry ice bath, and in the more exothermic cases also liquid N_2, was used to rapidly cool down the reactor, thus stopping the reaction. When the inner temperature reached 0 ºC the ice bath was removed allowing the temperature to slowly rise to 10 ºC. The gaseous phase was then transferred into a 10 L polyethylene tank filled with water. An aliquot of this gaseous phase was transferred into a Schlenk flask, previously evacuated, for GC analysis. The products in the reactor were hydrolyzed in situ by the addition of ethanol (1 mL), transferred into a Schlenk flask, and separated from the metal complexes by trap-to-trap evaporation (20 °C, 0.8 mBar) into a second Schlenk flask previously immersed in liquid nitrogen in order to avoid any loss of product.

Crystal Structure Determinations. Diffraction data were collected on a Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) (Table 7). Data were collected using phi-scans and the structures were solved by direct methods using the SHELX 97 software,[81, 82] and the refinement was by full-matrix least squares on F^2. No absorption correction was used. All non-hydrogen atoms were refined anisotropically with H atoms introduced as fixed contributors ($d_{C\text{-}H} = 0.95$ Å, $U_{11} = 0.04$). Crystallographic data (excluding structure factors) have been deposited in the Cambridge Crystallographic Data Centre as Supplementary publication n° CCDC ******. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgment

We thank the Centre National de la Recherche Scientifique (CNRS), the Ministère de l’Education Nationale et de la Recherche (Paris), the Institut Français du Pétrole (IFP), and and Clariant for support. We also thank Dr. A. DeCian and Prof. R. Welter (ULP Strasbourg) for the crystal structure determinations and M. Mermillon-Fournier (LCC Strasbourg) for technical assistance.

Crystal data	**10**	**11**	**12**	**16**
Chemical formula	$C_{36}H_{34}FeN_4P_2.0.5(CH_2Cl_2).Fe_2OCl_6$	$C_{28}H_{34}FeN_4O_5P_2.4(C_2H_3N).Fe_2Cl_6O$	$C_{18}H_{25}Cl_2FeN_2O_2P$	$C_{22}H_{33}Cl_2CoN_2O_4P.0.5(C_7H_8)$
M_r	1023.33	1113.00	459.12	596.37
Cell setting, space group	Orthorhombic, *Pccn*	Monoclinic, *C*2/*c*	Monoclinic, $P2_1/c$	Triclinic, *P*-1
Temperature (K)	173 (2)	173 (2)	173 (2)	173 (2)
a, b, c **(Å)**	12.6010 (3), 16.6710 (5), 20.3170 (6)	15.3270 (7), 21.8930 (12), 15.4880 (9)	12.7240 (13), 12.3190 (15), 15.5250 (19)	9.1010 (4), 9.1930 (4), 17.5460 (9)
α, β, γ (°)		90.00, 110.368 (2), 90.00	90.00, 113.772 (5), 90.00	79.9750 (15), 84.2710 (15), 83.173 (3)
V **(Å^3)**	4268.0 (2)	4872.1 (4)	2227.0 (4)	1430.62 (11)
Z	4	4	4	2
D_x **(Mg m^{-3})**	1.593	1.517	1.369	1.384
Radiation type	Mo *K*α	Mo *K*α	Mo *K*α	Mo *K*α
μ (mm^{-1})	1.55	1.32	1.00	0.88
Crystal form, colour	Prism, orange	Prism, red	Prism, colorless	Prism, blue
Crystal size (mm)	0.12 × 0.10 × 0.10	0.14 × 0.12 × 0.10	0.16 × 0.14 × 0.10	0.14 × 0.12 × 0.08
F(000)	2068	2272	952	624
No. of measured,	9257,	12328,	10818,	10153,
independent and	4894,	7114,	6465,	6620,
observed reflections	3202	5370	4953	4065
R_{int}	0.070	0.033	0.029	0.044
θ_{max} **(°)**	27.5	30.0	30.1	27.8
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.088, 0.168, 1.15	0.050, 0.090, 1.06	0.057, 0.162, 1.08	0.061, 0.180, 1.01
No. of relections	4894 reflections	7114 reflections	6465 reflections	6620 reflections
No. of parameters	247	272	235	302
H-atom treatment	Constrained to parent site	Constrained to parent site	Constrained to parent site	Constrained to parent site

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Chapitre VI

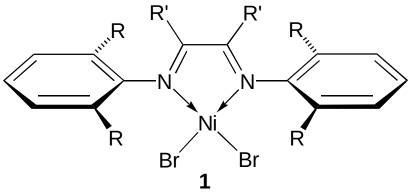
SHOP-type nickel complexes with alkyl substituents on phosphorus, synthesis and catalytic ethylene oligomerization

Abstract

The β-keto phosphorus ylids $(n\text{-Bu})_3\mathrm{P{=}CHC(O)Ph}$ **6**, $(t\text{-Bu})_2\mathrm{PhP{=}CHC(O)Ph}$ **7**, $(t\text{-Bu})\mathrm{Ph_2P{=}CHC(O)Ph}$ **8**, $(n\text{-Bu})_2\mathrm{PhP{=}CHC(O)Ph}$ **9**, $(n\text{-Bu})\mathrm{Ph_2P{=}CHC(O)Ph}$ **10**, $\mathrm{Me_2PhP{=}CHC(O)Ph}$ **11** and $\mathrm{Ph_3P{=}CHC(O)}(o\text{-OMe-C}_6\mathrm{H}_4)$ **12** have been synthesized in 80-96% yields. The Ni(II) complexes $[\overline{\mathrm{NiPh\{Ph_2PCH\underline{\cdots}C(\underline{\cdots}O}})(o\text{-OMe-C}_6\mathrm{H}_4)\}(\mathrm{PPh}_3)]$ **13**, $[\overline{\mathrm{NiPh\{Ph}(t\text{-Bu})\mathrm{PCH\underline{\cdots}C(\underline{\cdots}O}})\mathrm{Ph\}(PPh_3)}]$ **15**, $[\overline{\mathrm{NiPh\{}(n\text{-Bu})_2\mathrm{PCH\underline{\cdots}C(\underline{\cdots}O}})\mathrm{Ph\}(PPh_3)}]$ **16** and $[\overline{\mathrm{NiPh\{Ph}(n\text{-Bu})\mathrm{PCH\underline{\cdots}C(\underline{\cdots}O}})\mathrm{Ph\}(PPh_3)}]$ **17** have been prepared by reaction of equimolar amounts of $[\mathrm{Ni(COD)_2}]$ and $\mathrm{PPh_3}$ with the β-keto phosphorus ylids **12** or **8**-**10**, respectively, and characterized by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. NMR studies and the crystal structure determination of **13** indicated a bonding interaction between the hydrogen atom of the C-H group α to phosphorus and the ether function. The complexes $[\overline{\mathrm{NiPh\{Ph_2PCH\underline{\cdots}C(\underline{\cdots}O}})\mathrm{Ph\}(Py)}]$ **18**, $[\overline{\mathrm{NiPh\{Ph}(t\text{-Bu})\mathrm{PCH\underline{\cdots}C(\underline{\cdots}O}})\mathrm{Ph\}(Py)}]$ **19**, $[\overline{\mathrm{NiPh\{}(n\text{-Bu})_2\mathrm{PCH\underline{\cdots}C(\underline{\cdots}O}})\mathrm{Ph\}(Py)}]$ **20**, $[\overline{\mathrm{NiPh\{Ph}(n\text{-Bu})\mathrm{PCH\underline{\cdots}C(\underline{\cdots}O}})\mathrm{Ph\}(Py)}]$ **21** and $[\overline{\mathrm{NiPh\{Me_2PCH\underline{\cdots}C(\underline{\cdots}O}})\mathrm{Ph\}(Py)}]$ **22** have been isolated from the reactions of $[\mathrm{Ni(COD)_2}]$ and excess pyridine with the β-keto phosphorus ylids $\mathrm{Ph_3PCH{=}C(O)Ph}$ **3** or **8**-**11**, respectively, and characterized by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. Ligands **3**, **8**, **10** and **12** have been used to prepare in situ oligomerization catalysts by reaction with one equiv. of $[\mathrm{Ni(COD)_2}]$ and $\mathrm{PPh_3}$ under an ethylene pressure of 30 or 60 bar. The catalyst prepared in situ from **12**, $[\mathrm{Ni(COD)_2}]$ and $\mathrm{PPh_3}$ was the most active of the series with a TON of 12700 mol $\mathrm{C_2H_4}$/(mol Ni) under 30 bar ethylene. When the β-keto phosphorus ylid **8** was reacted in situ with three equiv. of $[\mathrm{Ni(COD)_2}]$ and one equiv. of $\mathrm{PPh_3}$ under 30 bar of ethylene, ethylene polymerization was observed with a TON of 5500 mol $\mathrm{C_2H_4}$/(mol Ni).

1. Introduction

The commercial interest for high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE) and linear α-olefins triggers research in ethylene polymerization and oligomerization. Since the works of Ziegler and Natta, alkylation of the metal centre with aluminum alkyls became the key for the formation of active catalysts in polymerization and oligomerization.[1-3] This activation process applies well to nickel precatalysts[4-6] and Brookhart *et al.* have described α-diimines nickel complexes **1** which are highly active in ethylene polymerization in the presence of MAO (methylaluminoxane) as cocatalyst.[7-10]

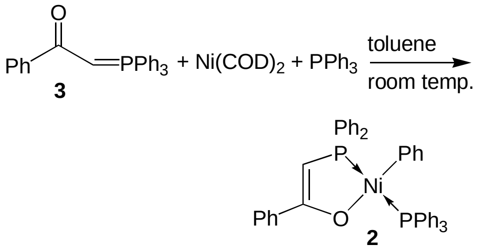


1

R = *i*-Pr
R' = H, Me, or 1,8-naphth-diyl

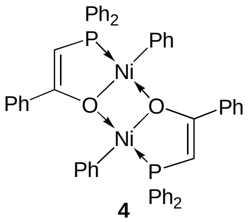
The nature of the chelating ligand is crucial for the catalyst performances and the use of α-diimine ligands with less bulky substituents turned their nickel complexes into ethylene oligomerization rather than polymerization catalysts. In this case, they showed a high selectivity for linear α-olefins with a Schulz-Flory mass distribution of the oligomers.[11,12] These results have inspired the synthesis of many nickel precatalysts coordinated by N,N-,[10-12] N,O-,[13-16] or P,N-[17,18] type ligands and activated by various alkylaluminum derivatives such as MAO, MMAO (modified MAO), $AlEtCl_2$, $AlEt_3$, $AlMe_3$, etc. With the N,O chelating ligands salicylaldimines,[13,19-22] anilinotropones[23-25] or anilinoperinaphthenones,[26] it was observed that very bulky groups retard chain transfer and lead to high molecular weight polyethylenes.[27-30]

Nickel catalysts for ethylene oligomerization are applied in the Shell Higher Olefin Process (SHOP) without any cocatalyst,[31] and lead to linear α-olefins with remarkable selectivity. The known SHOP-type catalyst **2** is synthesized by oxidative-addition of the β-keto phosphorus ylid **3** on a zerovalent nickel compound, such as $[Ni(COD)_2]$ (COD = 1,5-cyclooctadiene), in the presence of a 2 electron donor ligand, in general a phosphine such as PPh_3, to stabilize the resulting neutral Ni(II) complex [eqn (1)][32,33] (throughout this paper, the drawings will indicate a localized C=C bond for the enolate moiety but electronic delocalization involves the C-O bond).[17,18]



(1)

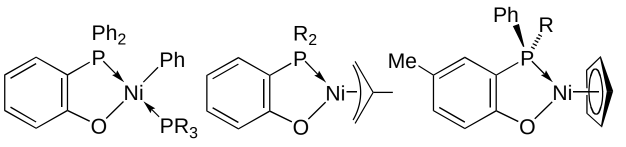
The stabilizing donor ligand plays a crucial role in the catalyst behaviour[34] and the use of more weakly bound ligands, such as pyridine, or of a catalyst promoter in excess, such as [Ni(COD)$_2$] or [Rh(acac)(C$_2$H$_4$)$_2$], which can scavenge the donor ligand, turns these nickel complexes from oligomerization into polymerization catalysts.[35] In the absence of a coligand, a dinuclear complex **4** forms as a result of the stabilization by coordination of the oxygen atom to another metal centre.[35,36]



4

Various substituents have been incorporated into the P,O chelate to modify its stereo-electronic properties and the electrophilicity of the metal centre and examine their impact on the catalyst properties and the nature of the products formed.[37-42]

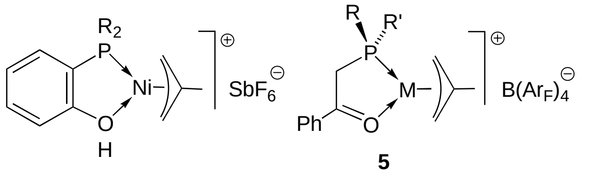
Neutral phosphino-phenolate nickel complexes are known to form ethylene oligomerization and polymerization catalysts (Scheme 1).[43-48] Heinicke, Keim *et al.* have observed that an increase of the basicity of the phosphorus donor atom improves the catalytic activity, modifies the mass distribution of the products and favors the formation of long chain polyethylenes.[44-47]



R = Ph, Me, Cy   R = Ph, Cy, *i*-Pr, *t*-Bu   R = Ph, Me, *i*-Pr, *t*-Bu

Scheme 1 Phosphino-phenolate nickel catalysts

Cationic nickel complexes derived from this ligand family have also been studied (Scheme 2) and it was found that the effect of an increased P-basicity on the molecular weight of the oligomers was much lower than in the case of the neutral, phosphino-phenolate systems.[49] Furthermore, cationic Ni(II) or Pd(II) complexes **5** with phenacyldi-*tert*-buytlphosphine or phenacyldiarylphosphine ligands catalyze ethylene polymerization and bulky phosphorus substituents tend to retard chain transfer and produce high molecular weight polyethylenes.[50,51]



5

R = Ph, Cy

M = Ni, Pd
R = R' = *t*-Bu, Ph, 2,4,6-$Me_3C_6H_2$
R = Ph, R'= 2,4,6-$Me_3C_6H_2$
Ar_F = 3,5-$(CF_3)_2C_6H_3$

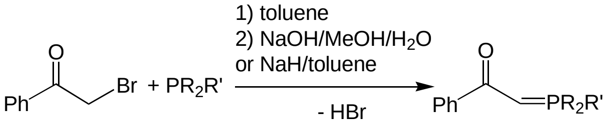
Scheme 2 Cationic phosphino-phenol and keto-phosphine catalysts

Since fewer studies have appeared on the influence of electron-donating and steric properties of the phosphorus substituents in neutral SHOP-type catalysts on the oligomer distribution,[52] and encouraged by the positive effect on catalytic activity of donor substituents in the phosphino-phenolate systems,[44-47] we decided to synthesize new β-keto phosphorus ylids with alkyl substituents on the phosphorus atom and to evaluate their corresponding nickel complexes in the catalytic oligomerization of ethylene.

2. Results and discussion

2.1 Synthesis of the β-keto phosphorus ylids

The ylids were prepared in two steps: synthesis of the phosphonium salt followed by its deprotonation.[53] The reaction of tri(*n*-butyl)phosphine with α-bromoacetophenone in toluene at room temperature afforded the phosphonium salt which, after dissolution in a mixture MeOH/H_2O (1/1) containing NaOH, afforded the corresponding β-keto phosphorus ylid **6**, which was characterized by ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy [eqn (2)].



(2)

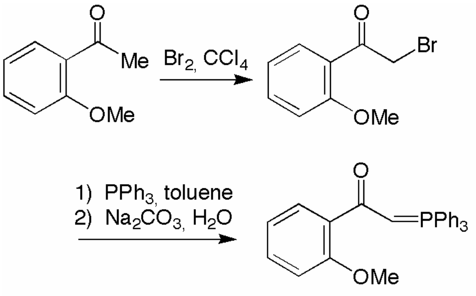
6 R = R' = *n*-Bu
7 R = *t*-Bu, R' = Ph
8 R = Ph, R' = *t*-Bu
9 R = *n*-Bu, R' = Ph
10 R = Ph, R' = *n*-Bu
11 R = Me, R' = Ph

However, reaction of **6** to [Ni$(COD)_2$] in the presence of PPh_3 did not yield the expected complex and only decomposition to nickel metal was observed. There was no indication for the migration of a *n*-butyl substituent from the phosphorus atom to the metal centre.[54]

The synthesis of β-keto phosphorus ylids from mixed alkyl/phenyl phosphonium salts could provide an access to SHOP-type nickel complexes having alkyl or mixed alkyl/phenyl substituents on the P atom of the P,O chelate. Such mixed salts were prepared by reaction of PPh_2Cl with one equiv. of *n*-BuLi or *t*-BuLi or by reaction of $PPhCl_2$ with two equiv. of *n*-BuLi or *t*-BuLi at low temperature,[55] followed by reaction with α-bromoacetophenone and deprotonation. The β-keto phosphorus ylids **7** and **8,** with *t*-butyl substituents, precipitated as white powders but **9** and **10,** with *n*-butyl substituents, formed a pale red oil.

We did not succeed in deprotonating methyl-substituted phosphonium salts using a $MeOH/H_2O$ (1/1) solution of NaOH but the β-keto phosphorus ylid **11** was obtained in toluene using NaH.

The intermediate 2-bromo-1-(2-methoxyphenyl)ethanone was synthesized by reaction of 1-(2-methoxyphenyl)ethanone with Br_2 in CCl_4 and used to prepare the β-keto phosphorus ylid **12** by reaction with PPh_3 and deprotonation with Na_2CO_3 [eqn (3)].[56]



12

(3)

2.2 Synthesis of the complexes

The nickel complex $[\mathrm{NiPh\{Ph_2PCH{\cdots}C({\cdots}O)(}\mathit{o}\mathrm{\text{-}OMe\text{-}C_6H_4)\}(PPh_3)}]$ **13** has been briefly described earlier[56] and was obtained in high yield by reaction of the β-keto phosphorus ylid **12** with equimolar amounts of $[Ni(COD)_2]$ and PPh_3 in toluene at room temperature (see Experimental). The $^{31}P\{^1H\}$ NMR spectrum of this complex should display a typical AB pattern for the trans coordinated phosphorus atoms but the small chemical shift difference between the two P resonances resulted in two intense signals at 23.6 and 23.4 ppm instead of the two doublets expected. The hydrogen atom of the C-H group α to the phosphine moiety is characterized in ^1H NMR spectroscopy by a chemical shift of 5.97 ppm, at significantly higher value than in similar complexes.[57,58] This suggested an intramolecular bonding interaction between this hydrogen atom and the ether function in ortho position to the phenyl group. A 2D NOESY spectrum confirmed this hypothesis by showing a spatial interaction between the hydrogen atom and the methyl hydrogens of the ether function.

Single crystals of **13** suitable for X-ray diffraction have been obtained by slow diffusion of heptane on a toluene solution. An ORTEP view of the molecular structure of **13** is shown in Figure 1 and selected bond distances and bond angles are given in Table 1. The metal centre adopts a slightly distorted square-planar geometry as shown by the P(2)-Ni-P(1) and O(1)-Ni-C(10) bond angles of 172.90(2) and 174.58(6), respectively (Table 1). The metal-ligand distances (Table 1) are comparable with those found in SHOP-type complexes.[31,32,58,59] The structure of **13** revealed a specific orientation of the ether group with its oxygen atom pointing toward the hydrogen atom of the C(1)H(1) group α to the phosphorus atom (Fig. 1). This orientation confirms the hydrogen bonding interaction between these two atoms with a calculated distance H(1)···O(1) of 2.28 Å (Table 2). A second intramolecular hydrogen bonding interaction H(4)···O(1) is observed with a calculated distance of 2.34 Å (Table 2).

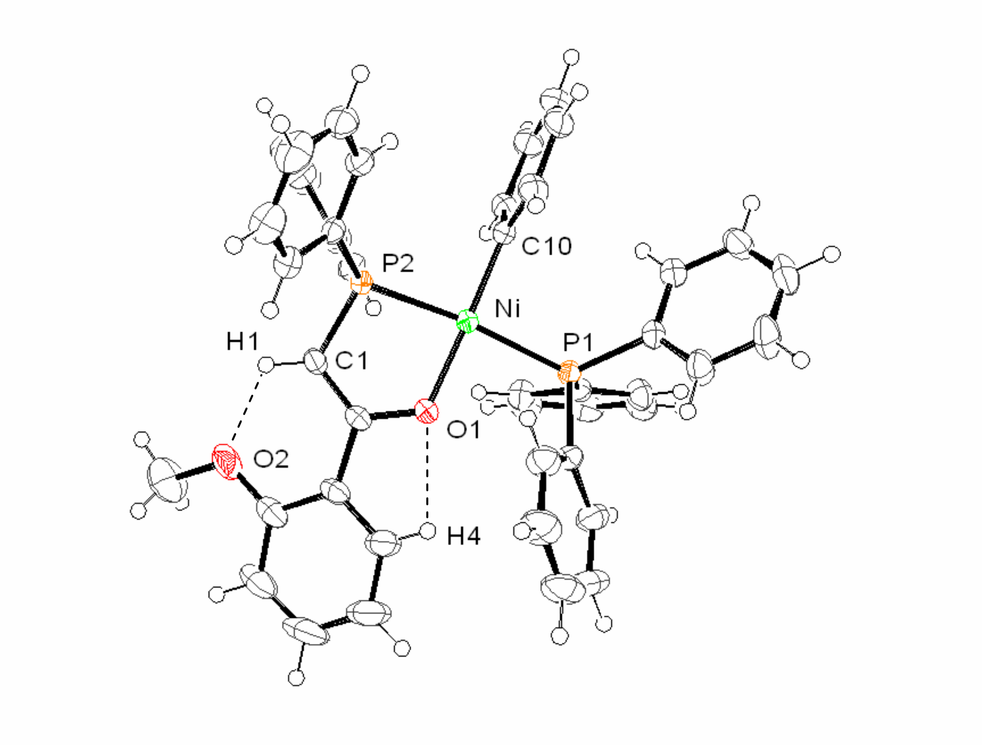


Fig. 1 ORTEP view of the molecular structure of **13** with ellipsoids drawn at the 50% probability level.

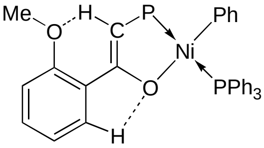
Table 1 Selected bond distances (Å) and bond angles [°] in **13**

Ni-P1	2.2167(4)
Ni-C10	1.887(2)
Ni-P2	2.1665(4)
Ni-O1	1.905(1)
P2-C1	1.768(2)
C1-C2	1.363(2)
C2-O1	1.318(2)
C2-C3	1.497(2)
O2-H1	2.283(2)
C10-Ni-P1	93.67(5)
C10-Ni-P2	92.36(5)
O1-Ni-P2	85.78(3)
O1-Ni-P1	87.88(3)

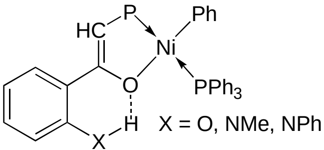
Table 2 Hydrogen bonding in **13** (Å and °)

Donor—H···Acceptor	D—H	H···A	D···A	D—H···A
C1—H···O2	0.95	2.28	2.813(2)	114
C4—H4···O1	0.95	2.34	2.676(2)	100

We have described previously the nickel complexes **14** which display an intramolecular bonding interaction between the oxygen atom coordinated to the metal centre and an hydrogen atom of an ortho-substituent on the aromatic ring of the P,O ligand.[58,60] This interaction modifies sufficiently the electronic density at the metal to shift the mass distribution of the oligomers formed toward the desired, shorter chain α-olefins.



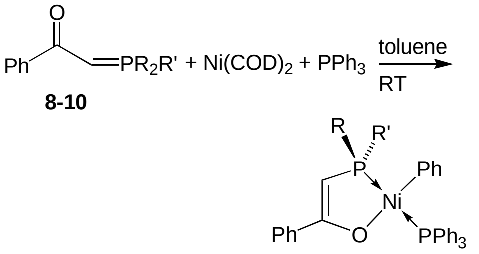
13



14

Noteworthy is the contrasting H-bonding behaviour of the P,O ligand in **13** and **14** which functions as both a donor and an acceptor in the former and acceptor in the latter. The Ni-O(1) bond of **13** should therefore be less perturbed by the H-bonding interaction involving O(2) than in **14**, and the catalytic properties of the complex should remain similar to those of the SHOP-type catalyst **2**.

The reaction of ylids **8-10** with equimolar amounts of [Ni(COD)$_2$] and PPh$_3$ at room temperature only afforded the desired complexes **15-17** in low yield [eqn (4)].

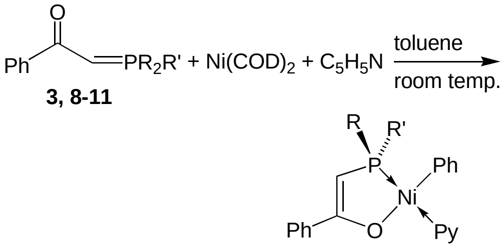


(4)

15 R = Ph, R' = *t*-Bu
16 R = R' = *n*-Bu
17 R = Ph, R' = *n*-Bu

A significant fraction of the PPh$_3$ reacted with the nickel precursor to form [Ni(PPh$_3$)$_4$], which gave rise in ^{31}P NMR spectroscopy to a broad peak around 26.1 ppm, and it was therefore not available to form the desired product. This led to only partial reaction and the low yield was evaluated by ^{1}H NMR monitoring of the chemical shifts of the C-H proton α to the phosphorus in the ligand and in the complex, or by evaluating unreacted [Ni(COD)$_2$].[38] In ^{31}P{^{1}H} NMR spectroscopy, the two trans-coordinated phosphorus atoms of complexes **15-17** form the expected AB pattern with $^2J_{PP}$ coupling constants of 278, 280 and 282 Hz, respectively. All attempts made to isolate these nickel complexes led to increased decomposition. In the case of the β-keto phosphorus ylids **7** and **11**, the formation of the complexes was not observed. Performing the complexation reactions at 60 °C with the hope to increase the yield resulted only in decomposition of [Ni(COD)$_2$].

To avoid the competition between the formation of [Ni(PPh$_3$)$_4$] and of the desired complexes by oxidative addition of the ylid, we used a pyridine ligand which is less nucleophilic than a phosphine. However, pyridine was not as reactive as PPh$_3$ and a large excess had to be used. The reaction of the ylids **3** and **8-11** with one equiv. of [Ni(COD)$_2$] and an excess of pyridine at room temperature led to the formation of the desired complexes **18-22**, which have been characterised in ^{1}H and ^{31}P{^{1}H} NMR [eqn (5)].



(5)

18 R = R' = Ph
19 R = Ph, R' = *t*-Bu
20 R = R' = *n*-Bu
21 R = Ph, R' = *n*-Bu
22 R = Me, R' = Ph

However, the reactions were not quantitative and unreacted [Ni(COD)$_2$] and β-keto phosphorus ylids were detected in the ^{1}H and ^{31}P{^{1}H} NMR spectra. Moreover **7**, remained unreactive toward [Ni(COD)$_2$] and an excess of pyridine, in contrast to **11**. Here too, an increase of the reaction temperature to 60 °C led to decomposition of the products and formation of nickel metal.

3 Catalytic oligomerization of ethylene

The catalytic tests have been performed with in situ-prepared catalysts by stirring equimolar amounts of the β-keto phosphorus ylids, [Ni(COD)$_2$] and PPh$_3$ under ethylene pressure (30 or 60 bar) and the results are given in Table 3.

Ylids **3**, **8**, **10** and **12** formed active species for ethylene oligomerization whereas catalytic tests with **7** and **9** were unsuccessful. The catalytic results with the mass distributions for the C$_4$-C$_8$ olefins are given in Table 3. Catalytic tests with **8** and **10** showed low activities, with TON of 1500 and 800 mol C$_2$H$_4$/(mol Ni) after consumption of 8.4 g and 4.5 g of ethylene in 24 h, respectively, but very high selectivities for 1-hexene, 99% with **10** and 99% with **8** (Table 3). The β-keto phosphorus ylids **3** and **12** formed more active catalysts than **8** and **10** with TON of 11000 and 12700 mol C$_2$H$_4$/(mol Ni), respectively, and both showed a similar selectivity of 98% for 1-hexene.

Catalysis with **3** and **12** have also been performed under an ethylene pressure of 60 bar during a period of 1.5 and 2 h and at 50 and 82 °C, respectively. Under these conditions, **3** and **12** consumed 15.9 g of ethylene (TON of 5700) in 1.5 h and 12.9 g (TON of 4600) in 2 h, respectively.[56] Comparing the results obtained under similar catalytic conditions between isolated complexes **12** and **14** shows that the former presents higher activities and K values.[56]

Catalytic polymerization conditions were applied to **8** by using three equiv. of [Ni(COD)$_2$] for one equiv. of β-keto phosphorus ylid and of PPh$_3$ under an ethylene pressure of 30 bar. After a reaction time of 70 h, 31.2 g of polyethylene was obtained, corresponding to a TON of 5500 mol C_2H_4/(mol Ni), higher than under oligomerization conditions (Table 3).

Table 3 Catalytic results with β-keto phosphorus ylids **3**, **8**, **10** and **12**.[a]

ligand	**3**	**3**[b]	**8**	**8**[c]	**10**	**12**	**12**[d]
C_2H_4 consumed [g]	61.7	15.9	8.4	31.2	4.5	70.8	12.9
Activity [g C_2H_4/(g Ni)]	5300	2700	700	2600	400	6000	2200
TON [mol C_2H_4/(mol Ni)]	11000	5700	1500	5500	800	12700	4600
reaction time (h)	24	1.5	24	70	24	24	2
% C_4[e] (% 1-olefin)	13 (93)	14	21 (81)	_	13 (84)	19 (95)	14
% C_6[e] (% 1-olefin)	9 (98)	15 (98)	13 (99)	_	5 (99)	11 (98)	17 (96)
% C_8[e]	6	15	9	_	3	8	15
% < C_8[e]	72	56	57	100	79	62	54
K [C_6 (mol)/C_4 (mol)]	0.44	0.69	0.41	_	0.25	0.40	0.81

[a] Conditions: T = 25 °C; 30 bar of C_2H_4; 24 h; 0.2 mmol of ylid, [Ni(COD)$_2$] and PPh_3; solvent 20 mL toluene. [b] Conditions: T = 50 °C; 60 bar of C_2H_4; 0.1 mmol of ylid; [Ni(COD)$_2$] and PPh_3; solvent: 20 mL toluene.[56,58] [c] Conditions: T = 25 °C; 70 h; 0.2 mmol of ylid and PPh_3; 0.6 mmol of [Ni(COD)$_2$]. [d] Conditions: T = 82 °C; 60 bar of C_2H_4; 0.1 mmol of ylid; [Ni(COD)$_2$] and PPh_3; solvent: 20 mL toluene.[56,58] [e] Mass %.

4. Conclusion

The β-keto phosphorus ylids **6-12** with alkyl substituents on the phosphorus atom have been synthesized in high yield. The reaction of **8**-**10** and **12** with equimolar amounts of [Ni(COD)$_2$] and PPh$_3$ yielded the complexes **13** and **15**-**17** in which an aryl substituent of the ylid phosphorus atom has migrated to the metal centre. Migration of an alkyl group to zerovalent nickel is much less favourable than that of an aryl group and was never observed. Thus, the presence of three alkyl groups on the P atom of β-keto phosphorus ylids did not allow the formation of the desired Ni(II) complexes. In such cases, alternative synthetic approaches to such SHOP-type catalyst are necessary (e.g. reaction of a sodium phosphinoenolate with a aryl, halide Ni(II) complex).[54] Such an approach has been used in the case of Pd(II) analogues to the SHOP-type catalysts since the β-keto phosphorus ylid route does not apply to other metals but nickel.[61]

^{1}H NMR studies on **13** indicated an intramolecular bonding interaction between the H atom of the C-H group α to phosphorus and the ether function, which was confirmed by X-ray diffraction (calculated O-H distance of 2.28 Å). Complexes **18-22** have been synthesized by reaction of β-keto phosphorus ylids **3** and **8-11** with an equimolar amount of [Ni(COD)$_2$] and an excess of pyridine and have been characterized by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy.

Active catalysts for ethylene oligomerization were prepared in situ by stirring equimolar amounts of β-keto phosphorus ylids **3**, **8**, **10** or **12**, [Ni(COD)$_2$] and PPh$_3$ under 30 or 60 bar of ethylene. TON up to 12700 mol C_2H_4/(mol Ni) were obtained with **12** under 30 bar of ethylene and the selectivity for linear α-olefins was between 95% and 98%. The influence of the *o*-methoxy group on the enolate-bound aryl appears beneficial for catalyst activity. Catalysis with one equiv. of **8** and PPh$_3$ and three equiv. of [Ni(COD)$_2$] under 30 bar of ethylene led only to the formation of polyethylene with a TON of 5500 mol C_2H_4/(mol Ni).

We also noted that the presence of two alkyl groups on the P atom of the P,O chelate in the complexes is detrimental with regard to catalytic activity. Therefore, a subtle balance has to be found concerning the nature of the P-substituents in order to optimize the catalytic properties of these catalysts.

5. Experimental

General Considerations. All solvents were dried and freshly distilled under nitrogen and degased under argon prior to use using common techniques. All manipulations were carried out using Schlenk techniques under argon atmosphere. The ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded at 300.13, 121.5 and 75.5 MHz , respectively, on a Bruker AC300 instrument. Gas chromatographic analyses were performed on a Thermoquest GC8000 Top series gas chromatograph using a HP Pona column (50 m, 0.2 mm diameter, 0.5 µm film thickness). The compounds $[Ni(COD)_2]$[62] and ylid **3**[53] were prepared according to the literature. Some details of the synthesis and analytical data for known compounds are given below because of slight modifications or new data introduced.

Synthesis of diphenyl(*t*-butyl)phosphine[63]

3.05 mL (17.00 mmol) of PPh_2Cl were dissolved in 40 mL of a mixture pentane/THF (3/1) and cooled to -78 °C. 10 mL of a *t*-BuLi solution in pentane (1.7 $mol \cdot L^{-1}$, 17.00 mmol) were slowly added and the solution was stirred overnight from -78 °C to room temperature. The white precipitate of LiCl was eliminated by filtration with a canula and the solvents were removed under reduced pressure. The brown oil obtained was distilled under reduced pressure (140 °C, 0.8 mBar). The phosphine was isolated as a colorless liquid. Yield: 2.630 g, 64%. ^1H NMR (300 MHz, $CDCl_3$): δ 1.22 (9H, d, $^3J_{PH}$ = 12.6 Hz, CH_3), 7.36 (3H, m, aromatic H) and 7.60 (2H, m, aromatic H); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 19.1 (s)

Synthesis of diphenyl(*n*-butyl)phosphine[64]

4.60 mL (25.60 mmol) of PPh_2Cl were dissolved in 30 mL of diethylether and cooled to -78 °C. 16 mL of a *t*-BuLi solution in pentane (1.6 $mol \cdot L^{-1}$, 25.60 mmol) were slowly added and the solution was stirred overnight from -78 °C to room temperature. The white precipitate of LiCl was eliminated by filtration with a canula and the solvents were removed under reduced pressure. The yellow oil obtained was distilled under reduced pressure (135 °C, 0.8 mBar). The phosphine was isolated as a colorless liquid. Yield: 4.270 g, 73%. ^1H NMR (300 MHz, $CDCl_3$): δ 0.90 (3H, d, $^3J_{PH}$ = 7.7 Hz, CH_3), 1.44 (4H, m, CH_2-CH_2), 2.04 (2H, m, P-CH_2), 7.31 – 7.46 (5H, m, aromatic H); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ -14.8 (s)

Synthesis of phenyldi(*t*-butyl)phosphine[65]

2.28 mL (17.00 mmol) of $PPhCl_2$ were dissolved in 40 mL of pentane and cooled to -78 °C. 20 mL of a *t*-BuLi solution in pentane (1.7 $mol \cdot L^{-1}$, 34.00 mmol) were slowly added and the solution was stirred for 3 h from -78 °C to room temperature. The white precipitate of LiCl was eliminated by filtration with a canula and the pentane was removed under reduced pressure. The white oil obtained was distilled under reduced pressure (110 °C, 0.8 mbar). The phosphine was isolated as a colorless liquid. Yield: 1.560 g, 40%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.20 (18H, d, $^3J_{PH}$ = 11.7 Hz, CH_3), 7.34 – 7.38 (3H, m, aromatic H) and 7.64 – 7.72 (2H, m, aromatic H); ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ 40.5 (s)

Synthesis of phenyldi(*n*-butyl)phosphine[55]

4.34 mL (32.00 mmol) of $PPhCl_2$ were dissolved in 60 mL of pentane and cooled to -78 °C. 40 mL of a *n*-BuLi solution in pentane (1.6 $mol \cdot L^{-1}$, 64.00 mmol) were slowly added and the solution was stirred for 3 h from -78 °C to room temperature. The white precipitate of LiCl was eliminated by filtration with a canula and the pentane was removed under reduced pressure. The white oil obtained was distilled under reduced pressure (120 °C, 0.8 mbar). The phosphine was isolated as a colorless liquid. Yield: 5.180 g, 73%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 0.91 (6H, t, $^3J_{HH}$ = 6.9 Hz, CH_3), 1.41 (8H, m, CH_2-CH_2), 1.79 (4H, br m, P-CH_2), 7.40 (3H, m, aromatic H) and 7.55 (2H, m, aromatic H); ^{31}P{^{1}H} NMR (CD_2Cl_2, 121.5 MHz): δ -20.0 (br s).

Synthesis of (benzoylmethylene)tri(*n*-butyl)phosphorane 6

3.700 g (18.60 mmol) of α-bromoacetophenone were added to a solution of 3.760 g (18.60 mmol) of tri(*n*-butyl)phosphine in 30 mL of toluene and stirred for 24 h at room temperature. The phosphonium salt was then filtered with a canula, washed with toluene (40 mL) and dried under vacuum (the phosphonium salt has not been characterized by ^{31}P{^{1}H} NMR or ^{1}H NMR). The dried salt was dissolved in a mixture of 60 mL of distilled water and 60 mL of MeOH and, an aqueous solution of NaOH (2.0 M) was added to the solution until pH 8 was reached. The solution became cloudy and the phosphorane **6** settled overnight as a red oil and the solution was eliminated with a canula. **6** was washed with water and dried under vacuum overnight. Yield: 5.400 g, 91%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.92 (9H, t, $^3J_{HH}$ = 7.2 Hz, CH_3), 1.45 (12H, m, CH_2-CH_2), 2.04 (6H, m, P-CH_2), 3.72 (1H, d, $^2J_{PH}$ = 22.8 Hz), 7.31 (3H, m, aromatic H), 7.85 (2H, m, aromatic H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 13.7 (s, CH_3), 21.5 (d, $^1J_{PC}$ = 55.1 Hz, P-CH_2), 24.1 (d, $^2J_{PC}$ = 15.0 Hz, P-CH_2-$\mathit{C}H_2$), 24.3 (d, $^3J_{PC}$ = 3.9 Hz, $\mathit{C}H_2$-CH_3), 47.8 (d, $^1J_{PC}$ = 104.3 Hz, P-CH), 126.5 (s, aromatic CH), 127.7

(s, aromatic CH), 128.9 (s, *p*-C of Ph), 141.4 (d, $^3J_{PC}$ = 13.6 Hz, *C*-CO of Ph), 185.1 (d, $^2J_{PC}$ = 3.3 Hz, CO); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 21.2.

Synthesis of (benzoylmethylene)phenyldi(*t*-butyl)phosphorane 7

1.340 g (6.70 mmol) of α-bromoacetophenone were added to a solution of 1.50 g (6.70 mmol) of phenyldi(*t*-Butyl)phosphine in 20 mL of toluene and stirred for 24 h at room temperature. The solution was removed with a canula and the phosphonium salt was then washed with toluene (20 mL) and dried under vacuum. ^1H NMR (300 MHz, MeOD): δ 1.51 (18H, d, $^3J_{PH}$ = 14.7 Hz, CH_3) 3.31 (2H, quint, *J* = 1.5 Hz, CH_2), 7.36 (3H, m, aromatic H), 7.55-7.64 (3H, m, aromatic H), 7.80 (2H, m, aromatic H), 7.90-7.98 (2H, m, aromatic H); $^{31}P\{^1H\}$ NMR (MeOD, 121.5 MHz): δ 41.8.

The dried salt was dissolved in a mixture of 20 mL of distilled water and 20 mL of MeOH and an aqueous solution of NaOH (2.0 M) was added to the solution until pH 8 was reached. The phosphorane **7** precipitated as a white powder and the solvent was removed with a canula. **7** was washed with water and dried under vacuum overnight. Yield: 2.120 g, 93%. ^1H NMR (300 MHz, $CDCl_3$): δ 1.50 (18H, d, $^3J_{PH}$ = 14.7 Hz), 3.93 (1H, d, $^2J_{PH}$ = 17.7 Hz), 7.36 (3H, m, aromatic H), 7.44-7.57 (3H, m, aromatic H), 7.86-7.96 (4H, m, aromatic H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 29.0 (s, CH_3), 35.7 (d, $^1J_{PC}$ = 45.8 Hz, P-*C*-CH_3), 48.1 (d, $^1J_{PC}$ = 97.9 Hz, P-CH), 123.7 (d, $^1J_{PC}$ = 72.3 Hz, C-P of P-Ph), 126.7 (s, CH of OC-Ph), 127.7 (s, CH of OC-Ph), 128.3 (d, $^2J_{PC}$ = 10.8 Hz, *o*-C of P-Ph), 128.7 (s, *p*-C of OC-Ph) 131.7 (d, $^4J_{PC}$ = 2.6 Hz, *p*-C of P-Ph), 134.4 (d, $^3J_{PC}$ = 7.9 Hz, *m*-C of P-Ph), 143.5 (d, $^3J_{PC}$ = 15.9 Hz, *ipso*-C of OC-Ph), 183.4 (s, CO); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 42.4.

Synthesis of (benzoylmethylene)diphenyl(*t*-butyl)phosphorane 8

This compound was prepared using a method similar to that described for **7** by reaction of 1.350 g (6.70 mmol) of α-bromoacetophenone with 1.60 g (6.70 mmol) of diphenyl(*t*-butyl)phosphine (the phosphonium salt has not been characterized by ^{31}P NMR or ^1H NMR). Yield: 2.300 g, 96%. ^1H NMR (300 MHz, $CDCl_3$): δ 1.35 (9H, d, $^3J_{PH}$ = 15.0 Hz), 4.22 (1H, d, $^2J_{PH}$ = 23.1 Hz), 7.36 (3H, m, aromatic H), 7.46-7.58 (6H, m, aromatic H), 7.91–7.99 (6H, m, aromatic H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 27.1 (s, CH_3), 32.3 (d, $^1J_{PC}$ = 54.5 Hz, P-*C*-CH_3), 47.4 (d, $^1J_{PC}$ = 107.4 Hz, P-CH), 124.6 (d, $^1J_{PC}$ = 83.1 Hz, C-P of P-Ph), 126.9 (s, C of OC-Ph), 127.7 (s, C of OC-Ph), 128.7 (d, $^2J_{PC}$ = 11.6 Hz, *o*-C of P-Ph), 129.1

(s, *p*-C of OC-Ph), 131.8 (s, *p*-C of P-Ph), 133.6 (d, $^3J_{PC}$ = 8.9 Hz, *m*-C of P-Ph), 142.0 (d, $^3J_{PC}$ = 14.0 Hz, *ipso*-C of OC-Ph), 184.4 (s, CO); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 30.9.

Synthesis of (benzoylmethylene)phenyldi(*n*-butyl)phosphorane 9

4.300 g (21.60 mmol) of α-bromoacetophenone were added to a solution of 4.800 g (21.60 mmol) of phenyldi(*n*-butyl)phosphine in 30 mL of toluene and stirred for 24 h at room temperature. The solvent was then removed with a canula and the phosphonium salt was washed with toluene (40 mL) and dried under vacuum (the phosphonium salt has not been characterized by ^{31}P NMR or ^1H NMR). The dried salt was dissolved in a mixture of 100 mL of distilled water and 50 mL of MeOH and an aqueous solution of NaOH (2.0 M) was added to the solution until pH 8 was reached. The solution became cloudy and **9** settled overnight as a red oil, it was washed with water and dried under vacuum overnight. Yield: 6.900 g, 94 %. ^1H NMR (300 MHz, $CDCl_3$): δ 0.87 (6H, t, $^3J_{HH}$ = 6.9 Hz, CH_3), 1.43 (8H, m, CH_2-CH_2), 1.32 (4H, m, P-CH_2), 3.99 (1H, d, $^2J_{PH}$ = 22.6 Hz), 7.36 (2H, m, aromatic H), 7.49-7.55 (3H, m, aromatic H), 7.70-7.77 (3H, m, aromatic H), 7.91-7.95 (2H, m, aromatic H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 13.7 (s, CH_3), 23.6 (d, $^1J_{PC}$ = 57.0 Hz, P-CH_2), 24.0 (d, $^2J_{PC}$ = 15.6 Hz, P-CH_2-CH_2), 24.4 (d, $^3J_{PC}$ = 3.6 Hz, CH_2-CH_3), 46.0 (d, $^1J_{PC}$ = 108.1 Hz, P-CH), 126.5 (d, $^1J_{PC}$ = 82.0 Hz, *ipso*-C of P-Ph), 126.6 (s, CH of OC-Ph), 127.8 (s, CH of OC-Ph), 129.1-129.3 (overlapping s of CH of OC-Ph and d of *o*-C of P-Ph), 131.2 (d, $^3J_{PC}$ = 8.7 Hz, *m*-C of P-Ph), 131.9 (d, $^4J_{PC}$ = 2.6 Hz, *p*-C of P-Ph), 141.5 (d, $^3J_{PC}$ = 13.7 Hz, *ipso*-C of OC-Ph), 185.15 (d, $^4J_{PC}$ = 3.5 Hz, CO); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 19.5.

Synthesis of (benzoylmethylene)diphenyl(*n*-butyl)phosphorane 10

This compound was prepared using a method similar to that described for **9** by reaction of 1.680 g (8.40 mmol) of α-bromoacetophenone with 2.040 g (8.40 mmol) of diphenyl(*n*-butyl)phosphine (the phosphonium salt has not been characterized by ^{31}P NMR or ^1H NMR). Yield: 2.800 g, 92%. ^1H NMR (300 MHz, $CDCl_3$): δ 0.88 (3H, t, $^3J_{HH}$ = 7.2 Hz, CH_3), 1.40-1.60 (4H, m, CH_2-CH_2), 1.78 (2H, m, P-CH_2), 4.23 (1H, d, $^2J_{PH}$ = 23.4 Hz), 7.35 (3H, m, aromatic H), 7.45-7.56 (6H, m, aromatic H), 7.70-7.78 (4H, m, aromatic H) and 7.95 (2H, m, aromatic H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 13.7 (s, CH_3), 24.1 (d, $^1J_{PC}$ = 110.9 Hz, P-CH_2), 24.2 (d, $^2J_{PC}$ = 16.7 Hz, P-CH_2-CH_2), 24.7 (d, $^3J_{PC}$ = 3.1 Hz, CH_2-CH_3), 47.9 (d, $^1J_{PC}$ = 47.9 Hz, P-CH), 126.9 (s, CH of OC-Ph), 127.8 (s, *p*-C of OC-Ph), 128.6 (d, $^1J_{PC}$ = 88.0 Hz, *ipso*-C of P-Ph), 129.0 (d, $^2J_{PC}$ = 11.6 Hz, *m*-C of P-Ph), 129.3 (s, CH of OC-

Ph), 131.9 - 132.1 (overlapping s and d, *p*-C and *o*-C of P-Ph), 141.2 (d, $^3J_{PC}$ = 11.3 Hz, *ipso*-C of OC-Ph), 185.2 (s, CO); ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ 17.0.

Synthesis of (benzoylmethylene)phenyldimethylphosphorane 11

3.200 g (16.10 mmol) of α-bromoacetophenone were added to a solution of 2.200 g (16.10 mmol) of phenyldimethylphosphine in 20 mL of toluene and stirred for 24 h at room temperature. The solvent was removed was filtered with a canula and the phosphonium salt washed with toluene (20 mL) and dried under vacuum. ^{1}H NMR (300 MHz, MeOD): δ 2.38 (6H, d, $^2J_{PH}$ = 14.7 Hz, CH_3), 3.31 (2H, quint, *J* = 1.5 Hz, CH_2), 7.52-7.57 (2H, m, aromatic H), 7.67-7.72 (3H, m, aromatic H), 7.75-7.81 (1H, m, aromatic H), 7.96-8.05 (4H, m, aromatic H); ^{31}P{^{1}H} NMR (MeOD, 121.5 MHz): δ 23.3.

NaH was added to a suspension of the phosphonium salt in toluene and the mixture was stirred overnight at room temperature. The solution was transferred with a canula to eliminate NaBr and unreacted NaH. The solvent was removed under reduced pressure and a pale yellow powder was obtained which dried under vacuum overnight. Yield: 3.800 g, 92%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.03 (6H, t, $^2J_{PH}$ = 13.5 Hz, CH_3), 4.23 (1H, d, $^2J_{PH}$ = 25.8 Hz, P-CH), 7.35 (3H, m, aromatic H), 7.52 (3H, m, aromatic H), 7.77 (2H, m, aromatic H) and 7.91 (2H, m, aromatic H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 12.4 (d, $^1J_{PC}$ = 62.1 Hz, CH_3), 51.0 (d, $^1J_{PC}$ = 111.7 Hz, P-CH), 126.6 (s, CH of OC-Ph), 127.8 (s, CH of OC-Ph), 128.9 (d, $^1J_{PC}$ = 87.0 Hz, *ipso*-C of P-Ph), 129.2 (d, $^2J_{PC}$ = 11.9 Hz, *o*-C of P-Ph), 129.5 (s, *p*-C of OC-Ph), 130.4 (d, $^3J_{PC}$ = 10.2 Hz, *m*-C of P-Ph), 132.0 (d, $^4J_{PC}$ = 2.7 Hz, *p*-C of P-Ph), 140.8 (d, $^3J_{PC}$ = 13.4 Hz, *ipso*-C of OC-Ph), 185.2 (d, $^2J_{PC}$ = 2.9 Hz, CO); ^{31}P{^{1}H} NMR ($CDCl_3$, 121.5 MHz): δ 7.4.

Synthesis of *ortho*-(methoxy)phenylcarbonylmethylene(triphenylphosphorane) 12[56]

Synthesis of 2-bromo-1-(2-methoxyphenyl)ethanone[66]

To solution of 15.000 g (100.00 mol) of 1-(2-methoxyphenyl)ethanone in 200 mL of CCl_4 at reflux, was added a solution of Br_2 (5.5 mL, 100.00 mol) over a period of 50 min. After reaction, the solvents were removed under reduced pressure and the solid residue was dissolved in 100 mL of a mixture of diethylether/pentane (1/1). The solution was cooled at 0 °C to precipitate 2-bromo-1-(2-methoxyphenyl)ethanone which was filtered and dried. The pale green solid product proved to be sensitive and was used immediately (yield: 60%).

To a solution of 13.000 g (57.00 mmol) of 2-bromo-1-(2-methoxyphenyl)ethanone in 100 mL of toluene, was added a solution of triphenylphosphine (14.900 g, 57.00 mmol) in 100 mL of toluene and the solution was stirred for 2 h at reflux. The white phosphonium salt precipitated rapidly. After reaction, it was filtered and dried under vacuum. Yield: 26.600 g, 95%. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 3.99 (3H, s, OCH_3), 5.83 (2H, d, P-CH_2), 6.95–7.10 (2H, m, aromatic H), 7.50-8.00 (17H, m, aromatic H). This phosphonium salt (13.500 g, 27.50 mmol) was dissolved in a saturated water solution of Na_2CO_3 and the solution was stirred for a few minutes. **12** was extracted with chloroform (3× 50 mL) and, after elimination of the solvents, dried under vacuum to afford an orange oil which was dissolved in 30 mL of toluene and precipitated to form a pale yellow powder. Yield: 9.000 g, 80%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.93 (3H, s, OCH_3), 4.55 (1H, d, $^2J_{PH}$ = 28.3 Hz), 6.96-7.01 (2H, m, aromatic H), 7.32 (1H, m, aromatic H), 7.53 (6H, m, aromatic H), 7.62 (3H, m, aromatic H) and 7.78 (7H, m, aromatic H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.5 MHz): δ 55.3 (d, $^1J_{PC}$ = 106.6 Hz, P-CH), 55.9 (s, OCH_3), 111.5 (s, CH of OC-Ph), 120.3 (s, CH of OC-Ph), 126.7 (s, CH of OC-Ph), 128.0 (s, CH of OC-Ph), 128.8 (d, $^3J_{PC}$ = 12.2 Hz, *m*-C of P-Ph), 129.7 (d, $^1J_{PC}$ = 13.0 Hz, *ipso*-C of P-Ph), 131.9 (d, $^4J_{PC}$ = 2.6 Hz, *p*-C of P-Ph), 132.0 (d, $^3J_{PC}$ = 14.2 Hz, *ipso*-C of OC-Ph), 133.2 (d, $^2J_{PC}$ = 10.0 Hz, *o*-C of P-Ph), 157.4 (s, OCH_3), 184.0 (s, CO); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121.5 MHz): δ 16.0.

[NiPh{Ph$_2$PCH$\underline{\cdots}$C($\underline{\cdots}$O)(*o*-OMe-C$_6$H$_4$)}(PPh$_3$)] 13

A solution of 0.170 g (0.62 mmol) of [Ni(COD)$_2$] in 30 mL of toluene was added to a solution of 0.160 g (0.62 mmol) of PPh_3 and 0.250 g (0.62 mmol) of **12** in 50 mL of toluene and the mixture was stirred for 24 h at room temperature. The red solution was evaporated under reduced pressure to afford complex **13** as a yellow powder. The ^{1}H NMR spectrum indicated a yield of 90% based on **12**. ^{1}H NMR (300 MHz, C_6D_6): δ 3.42 (3H, s, OCH_3), 5.97 (1H, s, P-CH), 6.50-6.77 (5H, m, aromatic H), 6.91-7.15 (18H, br m, aromatic H), 7.45 (1H, m, aromatic H), 7.59 (5H, br m, aromatic H), 7.75 (5H, br m, aromatic H); $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz): AB spin system with the appearance of two singlets at δ 23.6 and 23.4 ppm.

[NiPh{Ph(*t*-Bu)PCH$\underline{\cdots}$C($\underline{\cdots}$O)Ph}(PPh$_3$)] 15

A solution of 0.073 g (0.27 mmol) of [Ni(COD)$_2$] in 5 mL of toluene was added to a solution of 0.071 g (0.27 mmol) of PPh_3 and 0.098 g (0.27 mmol) of **8** in 5 mL of toluene and the mixture was stirred overnight at room temperature. After reaction, the red solution was evaporated under reduced pressure to afford the pale yellow complex **15**. The ^{1}H NMR spectrum indicated a yield of 83% based on [Ni(COD)$_2$]. ^{1}H NMR (300 MHz, C_6D_6): δ 1.22 (9H, br d, $^{3}J_{PC}$ = 13.5 Hz, CH_3), 5.11 (1H, br s, P-CH), 6.7-7.8 (30H, br m, aromatic H); ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz): AB spin system δ_A 31.4 (d, PPh(*t*-Bu), $^{2}J_{AB}$ = 278 Hz), δ_B 22.4 (d, PPh_3, $^{2}J_{AB}$ = 278 Hz).

[NiPh{(*n*-Bu)$_2$PCH···C(···O)Ph}(PPh$_3$)] 16

A solution of 0.890 g (3.24 mmol) of [Ni(COD)$_2$] in 50 mL of toluene was added to a solution of 0.850 g (3.24 mmol) of PPh_3 and 1.102 g (3.24 mmol) of **9** in 50 mL of toluene at 0 °C and the mixture was stirred for 3 days at room temperature. After reaction, the brown solution was evaporated under reduced pressure to afford complex **16** as a brown oil. The ^{1}H NMR spectrum indicated a yield of 84% based on [Ni(COD)$_2$]. ^{1}H NMR (300 MHz, C_6D_6): δ 0.86 (6H, t, $^{3}J_{HH}$ = 7.2 Hz, CH_3), 1.67 (12H, br m, CH_2), 4.60 (1H, s, PCH), 6.78-7.83 (25H, br m, aromatic H); ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz): AB spin system δ_A 22.6 (d, PPh(*t*-Bu), $^{2}J_{AB}$ = 280 Hz), δ_B 21.4 (d, PPh_3, $^{2}J_{AB}$ = 280 Hz).

[NiPh{Ph(*n*-Bu)PCH···C(···O)Ph}(PPh$_3$)] 17

A solution of 0.078 g (0.28 mmol) of [Ni(COD)$_2$] in 5 mL of toluene was added to a solution of 0.073 g (0.28 mmol) of PPh_3 and 0.104 g (0.28 mmol) of **10** in 5 mL of toluene at 0 °C and the mixture was stirred overnight at room temperature. After reaction, the yellow solution was evaporated under reduced pressure to afford complex **17** as a pale yellow powder. The ^{1}H NMR spectrum indicated a yield of 43% based on **10**. ^{1}H NMR (300 MHz, C_6D_6): δ 0.70-1.75 (9H, broad signals corresponding of the *n*-butyl substituents), 4.90 (1H, s, PCH), 6.78-7.99 (25H, br m, aromatic H), 8.39 (5H, br s, aromatic H); ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz): AB spin system δ_A 22.3 (d, PPh(*t*-Bu), $^{2}J_{AB}$ = 282 Hz), δ_B 20.4 (d, PPh_3, $^{2}J_{AB}$ = 282 Hz).

[NiPh{Ph$_2$PCH···C(···O)Ph}(Py)] 18[36]

A solution of 0.092 g (0.33 mmol) of [Ni(COD)$_2$] in 5 mL of toluene was added to a solution of 0.127 g (0.33 mmol) of **3** and 1 mL of pyridine (12.66 mmol) in 5 mL of toluene and the mixture was stirred overnight at room temperature. After reaction, the complex **18** was isolated as a pale yellow powder after filtration of the dark suspension and elimination of the solvents under reduced pressure. The ^{1}H NMR spectrum indicated a yield of 77% based on **3**. ^{1}H NMR (300 MHz, C_6D_6): δ 5.04 (1H, s, PCH), 6.32 (2H, br s, aromatic H), 6.61 (1H, br s, aromatic H), 6.78-7.36 (11H, br m, aromatic H), 7.52 (2H, br s, aromatic H), 7.71 (5H, br s, aromatic H), 8.13 (2H, br d, J_{PH} = 6.3 Hz aromatic H), 8.45 (2H, br s, aromatic H); ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz): δ 24.4 (s, PPh_2).

[NiPh{Ph(*t*-Bu)PCH$\underline{\cdots}$C($\underline{\cdots}$O)Ph}(Py)] 19

A solution of 0.093 g (0.34 mmol) of [Ni(COD)$_2$] in 5 mL of toluene was added to a solution of 0.096 g (0.34 mmol) of **8** and 1 mL of pyridine (12.66 mmol) in 5 mL of toluene and the mixture was stirred overnight at room temperature. After reaction, complex **19** was isolated as pale a yellow powder after elimination of the solvents under reduced pressure. The ^{1}H NMR spectrum indicated a yield of 94% based on **8**. ^{1}H NMR (300 MHz, C_6D_6): δ 1.28 (9H, d, $^3J_{HH}$ = 14.7 Hz, CH_3), 4.94 (1H, s, PCH), 6.3 (1H, br s, aromatic H), 6.6 (1H, br s, aromatic H), 6.9-7.3 (13H, br m, aromatic H), 7.6 (2H, br s, aromatic H), 7.7 (1H, br s, aromatic H), 8.06 (2H, d, J_{PH} = 7.2, aromatic H); ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz): δ 35.5 (s, PPh(*t*-Bu)).

[NiPh{(*n*-Bu)$_2$PCH$\underline{\cdots}$C($\underline{\cdots}$O)Ph}(Py)] 20

A solution of 0.092 g (0.33 mmol) of [Ni(COD)$_2$] in 5 mL of toluene was added to a solution of 0.114 g (0.33 mmol) of **9** and 1 mL of pyridine (12.66 mmol) in 5 mL of toluene and the mixture was stirred overnight at room temperature. After reaction, the complex **20** was isolated as pale yellow powder after elimination of the solvents under reduced pressure. The ^{1}H NMR spectrum showed a yield of 24% based on **9**. ^{1}H NMR (300 MHz, C_6D_6): δ 0.81 (6H, br s, CH_3), 1.52-1.75 (12H, br m, CH_2), 4.81 (1H, br s, PCH), 6.51-7.68 (10H, br m, aromatic H), 8.00-8.41 (5H, br s, aromatic H); ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz): δ 23.2 (s, P(*n*-Bu)$_2$).

[NiPh{Ph(*n*-Bu)PCH$\underline{\cdots}$C($\underline{\cdots}$O)Ph}(Py)] 21

A solution of 0.119 g (0.43 mmol) of [Ni(COD)$_2$] in 5 mL of toluene was added to a solution of 0.156 g (0.43 mmol) of **10** and 1 mL of pyridine (12.66 mmol) in 5 mL of toluene and the mixture was stirred overnight at room temperature. After reaction, complex **21** was isolated as a pale yellow powder after elimination of the solvents under reduced pressure. The ^{1}H NMR spectrum indicated a yield of 81% based on [Ni(COD)$_2$]. ^{1}H NMR (300 MHz,

C_6D_6): δ 0.79 (3H, br s, CH_3), 1.45-1.67 (6H, br m, CH_2), 4.81 (1H, br s, PCH), 6.28 (2H, br s, aromatic H), 6.71 (1H, br s, aromatic H), 6.93-7.35 (12H, br m, aromatic H), 8.06 (2H, br s, aromatic H), 8.37 (1H, br s, aromatic H), 8.55 (2H, br s, J_{PH} = 7.2 Hz, aromatic H); $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz): δ 22.0 (s, PPh(*n*-Bu)).

$[\overline{\mathrm{NiPh\{Me_2PCH}\underline{\cdots}\mathrm{C(}\underline{\cdots}\mathrm{O}}\mathrm{)Ph\}(Py)]}$ 22

A solution of 0.072 g (0.26 mmol) of $[Ni(COD)_2]$ in 5 mL of toluene was added to a solution of 0.067 g (0.26 mmol) of **11** and 1 mL of pyridine (12.66 mmol) in 5 mL of toluene and the mixture was stirred overnight at room temperature. After reaction, complex **22** was isolated as a pale yellow powder after elimination of the solvents under reduced pressure. The ^1H NMR spectrum indicated a yield of 83% based on $[Ni(COD)_2]$. ^1H NMR (300 MHz, C_6D_6): δ 0.87 (6H, d, $^3J_{PH}$ = 8.4 Hz, CH_3), 4.63 (1H, br s, PCH), 6.41 (2H, br s, aromatic H), 6.72 (1H, br s, aromatic H), 6.93-7.33 (7H, br m, aromatic H), 7.56 (2H, br s, aromatic H), 8.11 (1H, br s, aromatic H), 8.66 (2H, br s, aromatic H); $^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz): δ 4.0 (s, $P(Me)_2$).

Oligomerization of ethylene. All catalytic reactions were carried out in a magnetically stirred (900 rpm) 145 mL stainless steel autoclave. A 125 mL glass container was used to protect the inner walls of the autoclave from corrosion. 0.20 mmol of $[Ni(COD)_2]$ (0.055 g) was dissolved in10 mL of toluene and the solution was added to a 10 mL toluene solution containing 0.20 mmol (0.052 g) of PPh_3 and 0.20 mmol of ylid. The mixture was immediately injected into the reactor under a constant low flow of ethylene and the reactor was pressurized to 30 bar. The 30 bar working pressure were maintained during the experiments through a continuous feed of ethylene from a reserve bottle. At the end of each test, the gaseous phase was transferred into a 10 L polyethylene tank filled with water. An aliquot of this gaseous phase was transferred into a Schlenk flask, previously evacuated, for GC analysis. The products in the reactor were transferred into a Schlenk flask, and all volatiles were separated from high weight oligomers or polymers and the metal complexes before GC analysis by trap-to-trap evaporation (20 °C, 0.3 mm Hg) into a second Schlenk flask previously immersed in liquid nitrogen in order to avoid any loss of product. Ethylene consumption was calculated by addition of the mass of oligomers from the gas layer, the mass of oligomers from the volatile liquid layer and the mass non-volatile products minus the mass of complex.

Crystal Structure Determination. Diffraction data were collected on a Kappa CCD diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) (Table 4). Data were collected using phi-scans and the structures were solved by direct methods using the SHELX 97 software,[67,68] and the refinement was by full-matrix least squares on F^2. No absorption correction was used. All non-hydrogen atoms were refined anisotropically with H atoms introduced as fixed contributors ($d_{C\text{-}H}$ = 0.95 Å, U_{11} = 0.04). Crystallographic data (excluding structure factors) have been deposited in the Cambridge Crystallographic Data Centre as Supplementary publication n° CCDC ******. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 4. Summary of crystallographic data for **13**

Formula	$C_{45}H_{38}NiO_2P_2$
M_r	731.40
Crystal system	Triclinic
Space group	P-1
a, b, c (Å)	10.6130 (1), 13.4690 (2), 14.0310 (3)
α, β, γ (°)	76.3300 (8), 82.2130 (8), 74.847 (1)
V (Å^3)	1875.29 (5)
Z	2
ρ (calculated) (g cm^{-3})	1.295
μ (Mo-Kα) (mm^{-1})	0.64
Measd, independ., obsd reflections	15910, 10885, 8098
R_{int}	0.021
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.099, 1.04
No. of relections	10885 reflections
No. of parameters	451
R_1 $[I > 2\sigma(I)]$	0.0392
wR_2	0.0895

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Chapitre VII

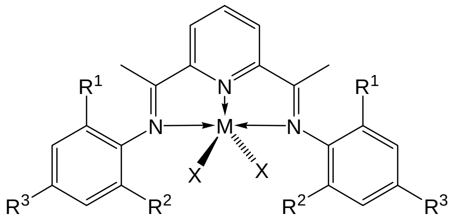
Réarrangement type Arbuzov observé sur un complexe de fer coordiné par des ligands bis(oxyde-phosphine)pyridine

Abstract

Ce chapitre présente les résultats préliminaires obtenus sur l'étude de la complexation du ligand 2,6-bis((diphenylphosphinito)methyl)pyridine **1** avec des précurseurs de nickel et de fer. La réaction du ligand **1** avec [$NiCl_2$(DME)] a permis de synthétiser le complexe [Ni{2,6-bis((diphenylphosphinito)methyl)pyridine}Cl_2] **2** qui a été caractérisé par spectrométrie de masse. La réaction de **1** avec $FeCl_3$ a formé le complexe inattendu [Fe{2,6-bis({diphenyl}oxyde-phosphine)methyl)pyridine}$_2$($FeCl_4$)] **3.** Ce complexe, identifié par diffraction des rayons X et spectrométrie de masse, montre la réduction de Fe(III) en Fe(II) et un réarrangement original du ligand en bis(oxyde-phosphine)pyridine. Un mécanisme apparenté au réarrangement Arbuzov a été proposé pour expliquer la formation de **3**. Une étude en voltamètrie cyclique à été commencée sur le complexe **3**.

1. Introduction

Brookhart et Gibson ont rapporté d'excellents résultats catalytiques d'oligomérisation et de polymérisation obtenus avec des complexes de fer et de cobalt coordinés par des ligands tridentes (bis-imino)pyridyl (Schéma 1).[1-5] Leurs travaux ont inspiré de nombreux laboratoires pour le développement de nouveaux catalyseurs d'oligomérisation et de polymérisation à base de fer et de cobalt.[6, 7]



M = Fe, Co
X = Cl, Br
R^1 = H, Me, *i*-Pr, *t*-Bu, CF_3
R^2 = H, F, Me, *i*-Pr, CF_3
R^3 = H, F

Schéma 1. Complexes typiques de Fe(II) et Co(II) avec ligand (bis-imino)pyridyl

Récemment, de très fortes sélectivités pour la dimérisation et trimérisation de l'éthylène ont été rapporté pour des systèmes catalytiques à base de complexes de chrome. Les complexes de chrome sont coordinés par des ligands tridentes et font l'objet d'importantes recherches de la part de plusieurs groupes industriels comme Philips qui développe des complexes à ligands pyrrolides,[8] le procédé SASOL (SASOL mixed heteroatomic system) avec des ligands tridentes type P,N,P[9, 10] ou S,N,S[11, 12], le système BP avec des ligands type P,N,P[13] et autres (Schéma 2).[14-19]

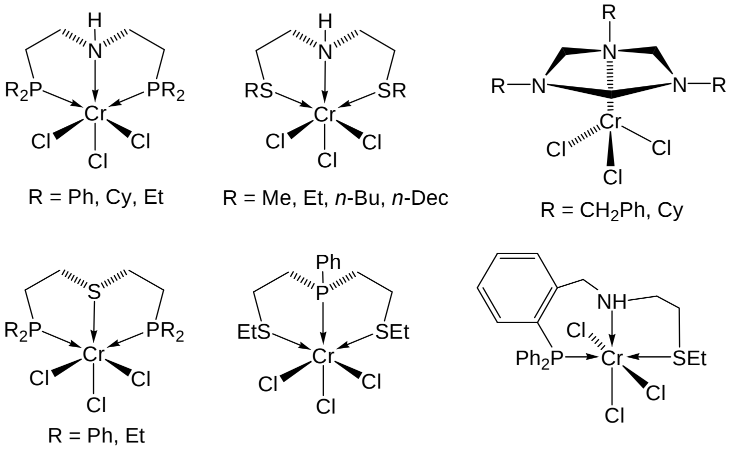


Schéma 2. Exemples de complexes de Cr(III) utilisés en oligomérisation

Par ailleurs des exemples de catalyses d'oligomérisation et de polymérisation ont été rapportés avec des complexes de Ni(II), Co(II) et Fe(II) coordinés par des ligands tridentes type P,N,P.[20, 21]

Récemment notre laboratoire a publié des résultats catalytiques d'oligomérisation intéressants obtenus avec des complexes de nickel coordinés par des ligands bidentes phosphinite-pyridine (Schéma 3).[22] Ces précatalyseurs ont montré de très fortes activités en dimérisation de l'éthylène avec des TOF (tunover frequency) allants jusqu'à 49900 mol C_2H_4/(mol Ni·h) lorsqu'ils sont activés par $AlEtCl_2$ comme cocatalyseur.

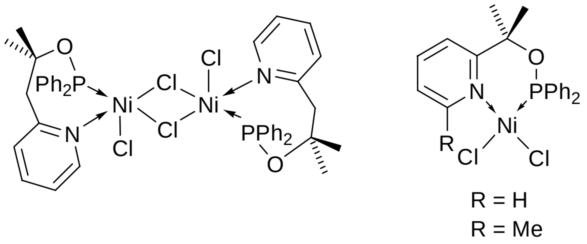
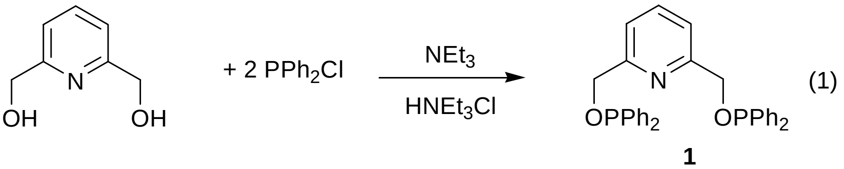


Schéma 3. Complexes de nickel coordinés par des ligands phosphinite-pyridine

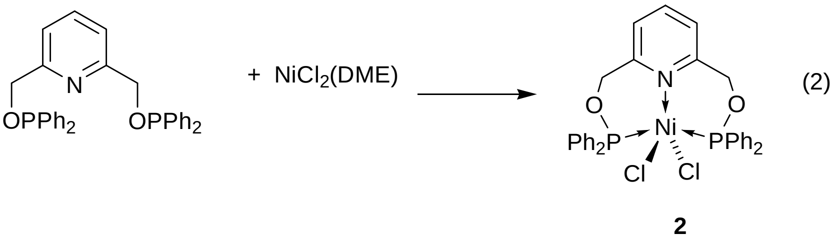
Afin de poursuivre l'étude de nouveaux systèmes d'oligomérisation de l'éthylène à base de ligands phosphinite-pyridine, nous avons entrepris de synthétiser de nouveaux complexes de nickel et fer avec le ligand 2,6-bis((diphenylphosphinito)methyl)pyridine **1**. Des résultats intéressants en hydrogénation catalytique d'imines avaient été rapportés par des complexes de Ir(I) et Rh(I) contenants le ligand **1**.[23]

2. Résultats et discussion

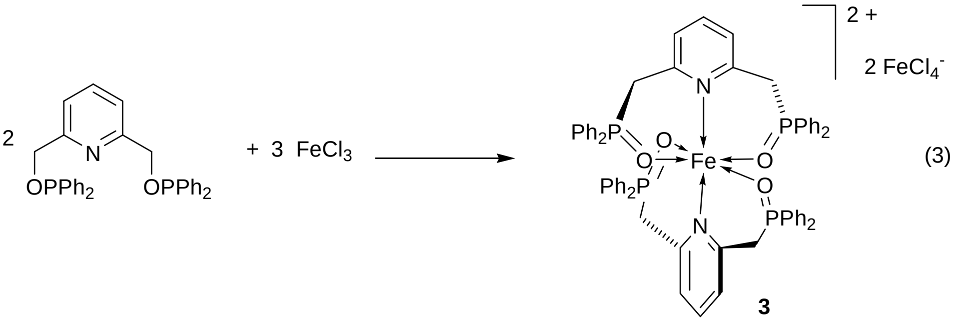
Le ligand **1** a été synthétisé par réaction de deux équiv de PPh_2Cl sur 2,6-(dimethanol)pyridine en présence de NEt_3 afin de neutraliser HCl produit pendant la réaction (eq 1). Il a été caractérisé par spectrométrie RMN ^1H, $^{13}C\{^1H\}$et $^{31}P\{^1H\}$.



Le complexe **2** a été préparé par réaction de $[NiCl_2(DME)]$ avec **1** en solution dans CH_2Cl_2 (eq 2) et il a été caractérisé sur la forme $[Ni(PNP)Cl]^+$ par spectrométrie de masse en mode ESI. Le spectre IR de **2** est très similaire à celui enregistré pour le complexe [Ni{2-methyl-oxy-(diphenylphosphino)pyridine}Cl_2].[24]



La réaction de **1** avec un équiv de $FeCl_3$ dans CH_2Cl_2 donna, après traitement, une poudre kakie (eq 3)



. La diffraction des rayons X sur des monocristaux a permis d'obtenir la structure cristalline du complexe **3** dans **3**·CH_2Cl_2. L'affinement de la structure de **3**·CH_2Cl_2 n'étant pas achevée, une vue préliminaire est proposée en Figure 1 mais une discussion sur les angles et distances de la molécule ne sera pas développée.

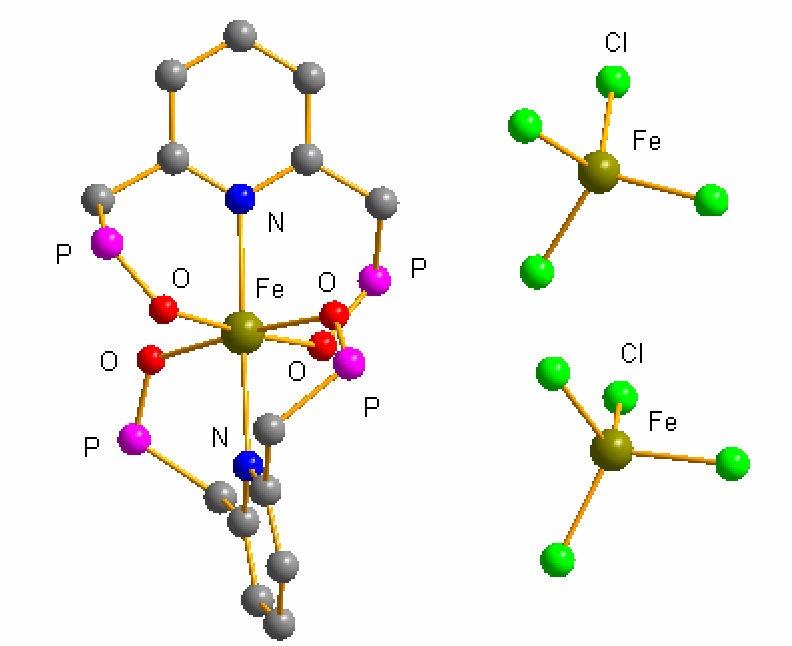


Figure 1. Vue de **3** dans **3**·CH_2Cl_2 (pour clarifier la vue, les atomes d'hydrogènes et les groupements aromatiques ont été omis)

Cette structure montre la coordination méridionale de deux ligands tridentes bis(oxyde-phosphine)pyridine autour d'un centre Fe(II) avec une géométrie octaédrique et la présence de deux contre-anions $FeCl_4^-$ pour compenser la double charge positive. Le cation $[Fe(N,P,N)_2]^{2+}$ a été caractérisé par spectrométrie de masse en mode ESI. La coordination de deux ligands tridentes sur un centre Fe(II) et la capture des ions Cl^- formant les anions $FeCl_4^-$ est souvent rapportée.[25-29]

Ce complexe inattendu montre deux points extrêmement intéressants: la réduction du Fe(III) en Fe(II) et le réarrangement des deux fonctions phosphinite de **1** en oxyde de phosphine. Un exemple de réduction de Fe(III) en Fe(II) a été rapportée en milieu alcoolique au cours d'une réaction de complexation de $FeCl_3$ par un ligand hexadente mais cependant, ce type de réduction est marginale.[30] La réduction de $FeCl_3$ peut être amorcée lorsque celui-ci réagit sur des alcynes en formant des chloro-alcènes et $FeCl_2$.[31, 32] Appuyé par les données bibliographiques, nous proposons le mécanisme suivant (schéma 4) par expliquer la réarrangement du ligand **1** et la formation du complexe **3**.

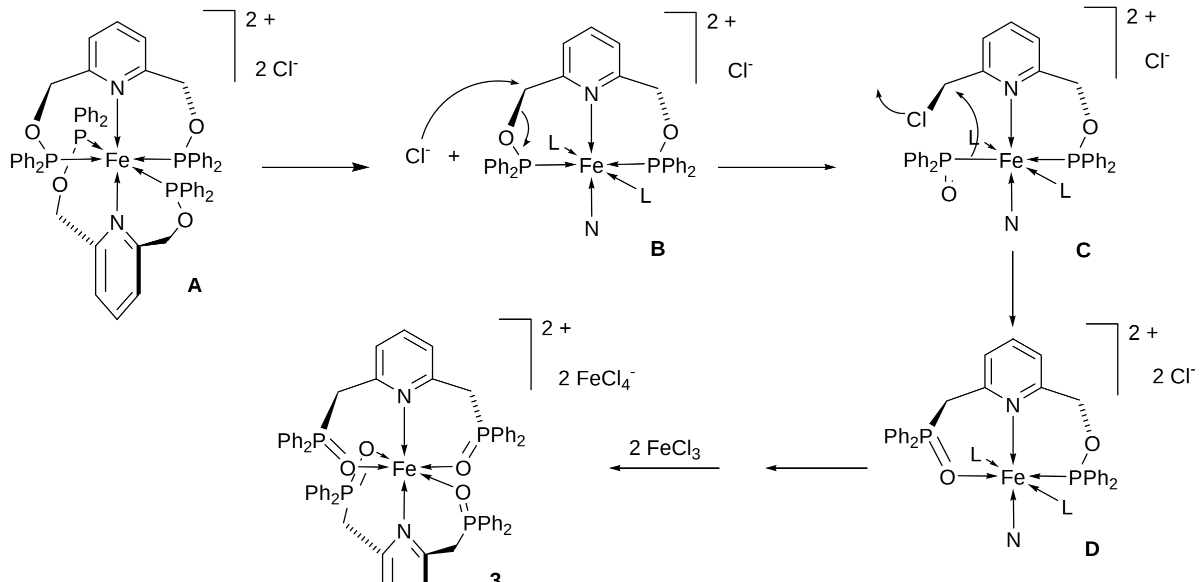
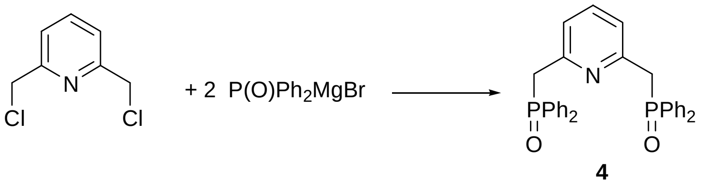


Schéma 4. Mécanisme proposé par la formation de **3**

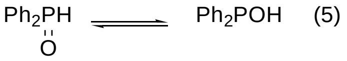
La coupure de la liaison O-CH_2 du composé **A** (Schéma 4) en présence d'ions Cl^- pour former l'intermédiaire **C** pourrait être la première étape du réarrangement. Ceci entraînerait la coordination d'un anion $(O{=}PPh_2)^-$ sur le centre métallique ce qui a été rapportée pour des complexes de niobium, tantale et de fer.[33, 34] La formation de chloro-méthane par un mécanisme apparenté à la réaction d'Arbuzov en présences d'anions halogénures a été décrite sur des complexes de Pt(II) complexés par des ligands phosphites.[35] Le ligand $(O{=}PPh_2)^-$ pourrait amorcer une réaction de substitution nucléophile sur le chloro-alkyl (intermédiaire C, Schéma 4) et finalement former le complexe **3**. La réaction de substitution nucléophile sur 2,6-bis(chloromethyl)pyridine par deux équiv de $P(O)Ph_2MgBr$ a été décrite pour la synthèse de **4** (eq 4).[36] Le mécanisme proposé (Schéma 4) s'apparente à un mécanisme de type Arbuzov.



4

(4)

Une autre hypothèse peut aussi expliquer le réarrangement observé. En effet les fonctions phosphinite sont fragiles et peuvent facilement s'hydrolysées. L'hydrolyse de **1** conduirait à la formation de 2,6-(dimethanol)pyridine et de oxyde de diphénylphosphine. L'espèce diphénylphosphinite en équilibre avec oxyde de diphénylphosphine (eq 5) pourrait réagir avec l'alcool de pyridine et former le complexe **3**.



$$\underset{\overset{\|}{O}}{Ph_2PH} \rightleftharpoons Ph_2POH \quad (5)$$

Des études sont actuellement en cours pour essayer de vérifier ces hypothèses.

Des études préliminaires en voltamètrie cyclique ont été réalisées sur le complexe **3**. Le voltammogramme obtenu (Figure 2) montre une réaction irréversible au potentiel redox de -1.664 mV vs. SCE et un couple redox réversible à -0.207 mV vs. SCE.

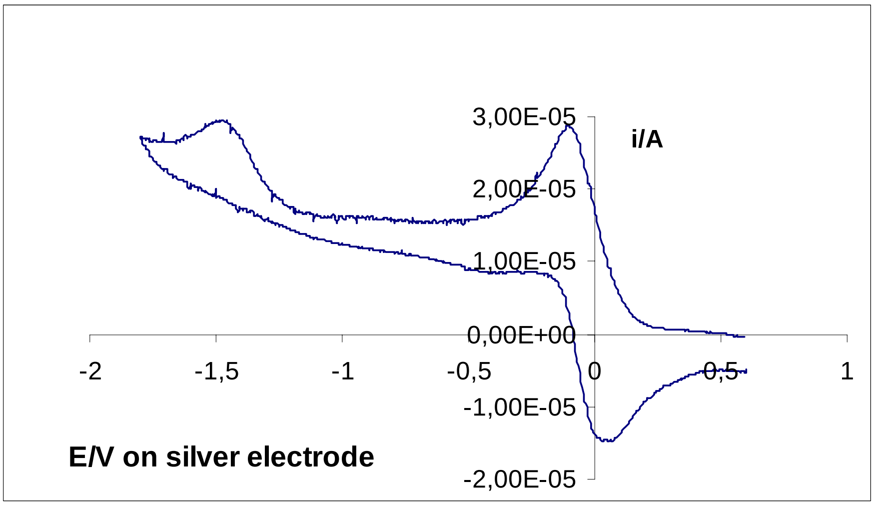


Figure 2. Voltammogramme cyclique de **3** dans MeCN anhydre (0.1 M N-(*n*-Bu)$_4$PF$_6$, at a rate of 100 mV s^{-1})

3. Conclusion

La réaction du ligand **1** sur [$NiCl_2$(DME)] a conduit à la synthèse du complexe **2** caractérisé par spectrométrie de masse et IR. La complexation de **1** sur $FeCl_3$ a conduit à la formation inattendue du complexe **3** caractérisé par diffraction des rayons X sur monocristal. La structure cristalline de **3** montre la réduction du centre métallique et le réarrangement du ligand **1** en ligand bis(oxyde-phosphine)pyridine **4**. Le mécanisme proposé pour expliquer ce réarrangement montre la coupure de la liaison O-CH_2 pour former le ligand anionique $[P(O)Ph_2]^-$qui par attaque nucléophile sur le chloro-alkyle forme le ligand bis(oxyde-phosphine)pyridine. Des études complémentaires sont en cour afin d'isoler les intermédiaires réactionnels et de compléter le mécanisme. Les études en voltamètrie cyclique de **3** montrent une réaction irréversible à -1.664 mV vs .SCE et un couple redox réversible à -0.207 mV vs. SCE. Des études complémentaires doivent être menées pour attribuer ces potentiels redox.

4. Partie expérimentale

Tous les solvants ont été séchés et distillés sont atmosphère d'azote. Toutes les manipulations ont été effectuées en utilisant la technique de Schlenk sous atmosphère d'azote. Les spectres RMN ^1H, $^{13}C\{^1H\}$et $^{31}P\{^1H\}$ ont été enregistrés sur un instrument Bruker AC300 à 300.13, 121.5 et 75.5 MHz, respectivement.

Synthèse de 2,6-bis((diphenylphosphinito)methyl)pyridine 1

Sur une solution de 2,6-(dimethanol)pyridine (3.85 g, 27.7 mmol) dans 100 mL de THF est ajouté 20 mL de NEt_3 et le mélange est refroidi à -78 °C. Un volume de 10 mL de PPh_2Cl (55.4 mmol) est alors ajouté lentement à -78 °C et le mélange est agité pendant 3 h en laissant la température remontée jusqu'à température ambiante. Après réaction, le précipité blanc de $HNEt_3Cl$ est éliminé par filtration. Les solvants sont éliminés par évaporation sous pression réduite et le résidu est redissout dans 50 mL de diethylether. Après filtration, les solvants sont éliminés sous pression réduite et le résidu est séché plusieurs heures sous vide pour donner une huile jaune. Rendement : 12.90 g, 92%. RMN ^1H ($CDCl_3$) δ: 4.94 (4H, d, $^3J_{PH}$ = 9.2 Hz, CH_2), 7.34-7.87 (23H, m, aromatic H); RMN $^{13}C\{^1H\}$ ($CDCl_3$): δ 72.1 (d, $^2J_{PC}$ = 18.9 Hz, CH_2), 119.8 (s, *C*H-CH-*C*H of pyridyl), 128.4 (d, $^3J_{PC}$ = 6.9 Hz, *m*-CH of aryl), 129.5 (s, *p*-CH of aryl), 130.8 (d, $^2J_{PC}$ = 21.7 Hz, *o*-CH of aryl), 137.3 (s, CH-*C*H-CH of pyridyl), 141.4 (d, $^1J_{PC}$ = 18.1 Hz, P-C), 158.1 (d, $^3J_{PC}$ = 8.5 Hz, C-N of pyridyl); RMN $^{31}P\{^1H\}$ ($CDCl_3$): δ 118.1.

[Ni{2,6-bis((diphenylphosphinito)methyl)pyridine}Cl_2] 2.

[$NiCl_2$(DME)] (1.09 g, 4.95 mmol) est ajouté à température ambiante à une solution de **1** (2.51 g, 4.95 mmol) dans 100 mL de CH_2Cl_2. Le mélange devient rouge immédiatement et est agité 3 h à température ambiante. Le mélange est filtré et la solution est concentrée à 40 mL sous pression réduite. 80 mL de pentane sont ajoutés pour précipiter le complexe. Après filtration, celui-ci est lavé avec plusieurs fractions de 20 mL de diéthyléther et séché une nuit sous vide pour donner une poudre rouge. Rendement : 1.95 g, 62%. HRMS : Masse théo. pour $C_{31}H_{27}ClNNiO_2P_2$: 600.0570, trouvé: 600.0550 $[Ni(N,P,N)Cl]^+$; IR (KBr) : 1607 (s), 1577 (w), 1484 (s), 1436 (vs), 1381 (w), 1311 (w), 1264 (w), 1163 (m), 1103 (s), 1016 (vs), 745 (vs), 697 (vs) 638 (w), 527 (m), 490 (s) cm^{-1}.

[Fe{2,6-bis({diphenyl}oxyde-phosphonato)methyl)pyridine}$_2$($FeCl_4$)] 3.

$FeCl_3$ (0.95 g, 5.8 mmol) est ajouté à température ambiante à une solution de **1** (3.25 g, 6.4 mmol) dans 100 mL de CH_2Cl_2. Un précipité marron apparaît rapidement et le mélange est agité pendant 48 h. Après réaction, le précipité est éliminé par filtration et la solution est concentrée à 50 mL sous pression réduite. 100 mL d'éther de pétrole sont ajoutés pour précipiter le complexe qui forme alors une huile marron collant aux parois du tube de Schlenk. La solution incolore surnageante est éliminée et l'huile est lavée par plusieurs fractions de 20 mL de diéthyléther jusqu'à l'obtention d'une poudre kakie. Rendement : 0.51 g, 12%. Des monocristaux de **3** ont été obtenus par diffusion lente de pentane sur une solution de **3** dans CH_2Cl_2. HRMS : Masse théo. pour $(C_{62}H_{27}NO_2P_2Fe)/2$: 535.1187, trouvé: 535.1193 $[Fe(N,P,N)_2]^{2+}$; IR (KBr) : 1591 (w), 1571 (w), 1453 (m), 1438 (s), 1129 (vs), 1090 (s sh), 1038 (m), 1020 (m), 996 (m), 834 (w), 798 (w), 833 (w), 741 (s), 692 (s), 526 (s) cm^{-1}.

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Résumé

et

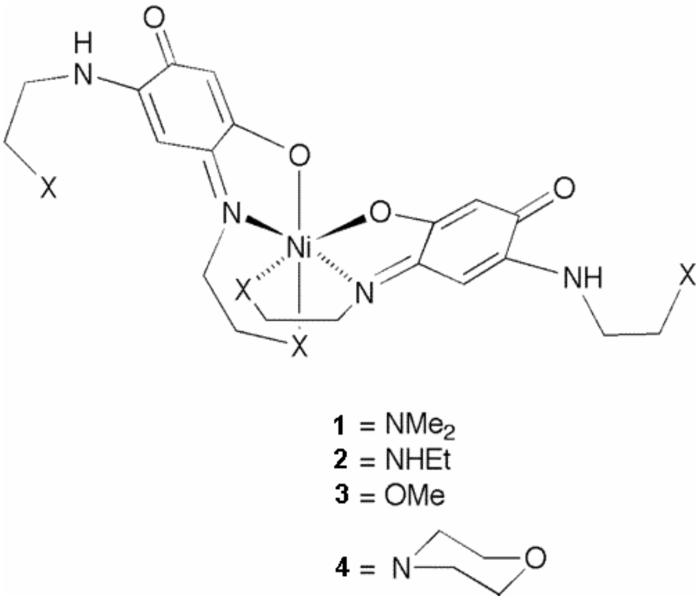
Conclusion générale

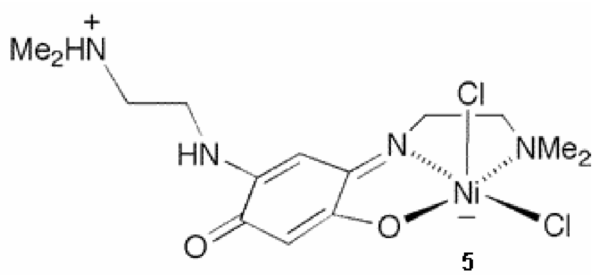
Résumé

L’étude des complexes de métaux de transition en catalyse homogène représente une part majeur de la chimie des organométalliques. Cette chimie s’appuie sur les propriétés stéréro-électroniques des ligands sur les centres métalliques afin d’optimiser l’efficacité des catalyseurs. Parmi les nombreuses réactions catalytiques, nous nous sommes attachés à l’étude de la réaction d’oligomérisation de l’éthylène qui le premier procédé industriel pour la production des oléfines alpha linéaires et qui représente des enjeux économiques considérables. Nous avons étudier la catalyse d’oligomérisation avec des complexes de nickel, fer et cobalt coordinés par des ligands type N,O, P,N, N,P,N, P,O et P,N,P. L’étude structurale de ces complexes a permis de mettre en évidence des comportements et des modes de coordination originaux. Ces complexes, activés par des cocatalyseurs comme MAO ou $AlEtCl_2$, ont montré des résultats intéressants en oligomérisation de l’éthylène avec de fortes activités et une grande sélectivité pour les oléfines C_4.

Chapitre I

Les complexes hexacoordinés **1-4** et le complexe pentacoordiné **5** ont été évalués en oligomérisation d’éthylène avec différentes quantités de MAO ou $AlEtCl_2$ comme cocatalyseur. Ces complexes ont montré un fort caractère dimérisant (sélectivité en oléfines C_4 comprise entre 94 et 51%) avec des activés fortes notamment **5** qui, avec des TOF de 20 300 mol C_2H_4/(mol Ni)·h et 48 200 mol C_2H_4/(mol Ni)·h en présence de 400 équiv de MAO et 10 équiv de $AlEtCl_2$, respectivement, a montré les activités plus élevées. La présence d’atomes donneurs sur la bras lié à l’azote du fragment benzoquinonemonoimine des complexes **1-4** entraînait une diminution de l’activé mais avec une meilleur sélectivité en oléfines C_4. Cependant les différentes fonctions (amine ou éther) formant ce bras n’apportèrent pas de modifications significatives sur les résultats catalytiques. Les résultats catalytiques ont montré que le cocatalyseur $AlEtCl_2$ formait des systèmes plus actifs que MAO mais moins sélectifs en oléfines alpha linéaires. L’augmentation du nombre d’équivalents de cocatalyseur (MAO ou $AlEtCl_2$) entraînait une hausse des activités catalytiques mais favorisait l’isomérisation des oléfines alpha en oléfines internes. Nous avons aussi noté que les systèmes les plus actifs favorisaient la réinsertion du 1-butène et 2-butène pour former des oligomères C_6.





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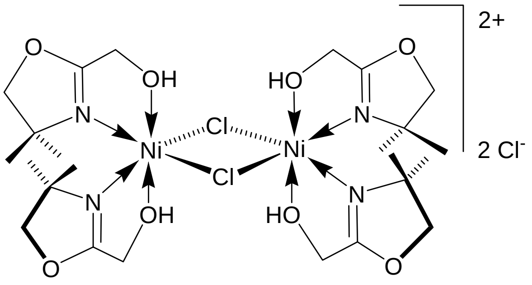
Chapitre II

Les nouveaux complexes **6** et **7** ont été synthétisés par réaction de $NiCl_2$ avec deux équiv de leur alcool correspondant. Leurs structures cristallines, déterminées par diffraction des rayons X, montrent la formation de complexes dinucléaires avec deux atomes Cl pontants. **8** a été synthétisé par réaction de $NiCl_2$ avec trois équiv de carbinol et sa structure cristalline a été déterminée par diffraction des rayons X. Le complexe **9** a été préparé par réaction du complexe **7** avec un excès de NaH.

Les propriétés catalytiques des complexes **6**, **7** et **9** ont été évaluées en oligomérisation de l'éthylène avec différentes quantités de MAO ou $AlEtCl_2$ comme cocatalyseur et une pression d'éthylène de 10 ou 30 bar. Les trois complexes favorisaient la dimérisation de l'éthylène avec des sélectivités en oléfines C_4 comprises entre 97 et 62% et des sélectivités en 1-butène comprises entre 79 et 6%. Le précatalyseur **7** a montré les meilleures activités avec des TOF jusqu'à 187500 C_2H_4/(mol Ni·h) avec 6 équiv de $AlEtCl_2$ et 104300 C_2H_4/(mol Ni·h) avec 200 équiv de MAO. Les systèmes les plus actifs favorisaient l'isomérisation du 1-butene en 2-butène mais l'augmentation de la pression d'éthylène de 10 à 30 bar améliorait la sélectivité en oléfines alpha.



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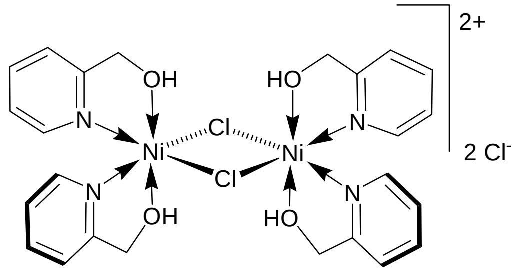

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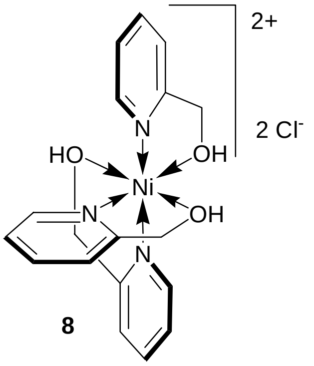

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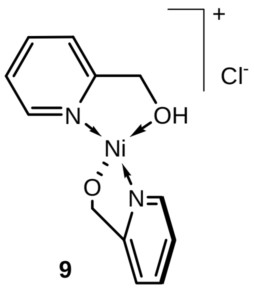

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Chapitre III

Les complexes $[NiCl_2(P,N_{th})]$ **10**, $[NiCl_2(P,N_{ox})]$ **11**, $[NiBr_2(P,N_{th})]$ **12** et $[NiBr_2(P,N_{ox})]$**13** (P,N_{th} = 2-diphenylphosphino-methyl-2-thiazoline, P,N_{ox} = diphenylphosphino-methyl-2-oxazoline) ont été synthétisés par réaction de $NiCl_2$ ou $NiBr_2$ avec un équiv de ligand phosphine-oxazoline ou phosphine-thiazoline. Les complexes **12** et **13** ont montré des structures mononucléaires carré-planes (Figure 1) déterminées par diffraction des rayons X sur monocristaux.

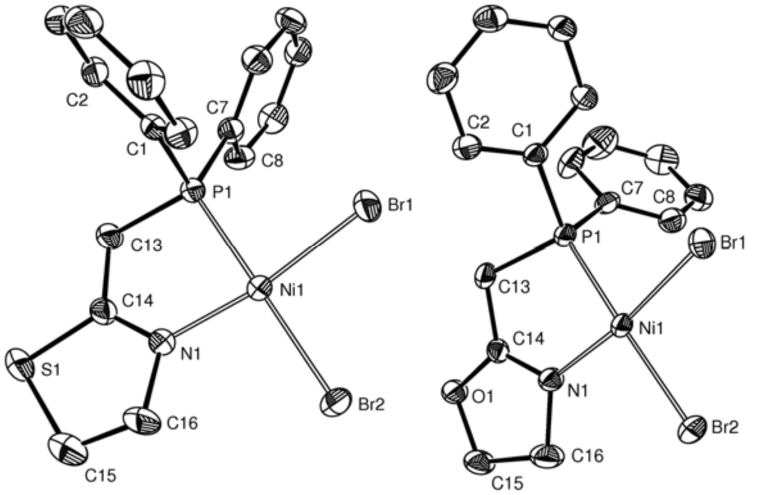


Figure 1. Vues ORTEP des structures moléculaires à l'état solide de **12** et **13** (les atomes d'hydrogène ne sont pas représentés pour simplifier la figure).

Par contre la structure de **10**, déterminée par diffraction des rayons X, montre la formation d’un complexe tétranucléaire possédant deux atomes Cl triplement pontants, quatre atomes Cl doublement pontants et deux atomes Cl terminaux (Figure 2).

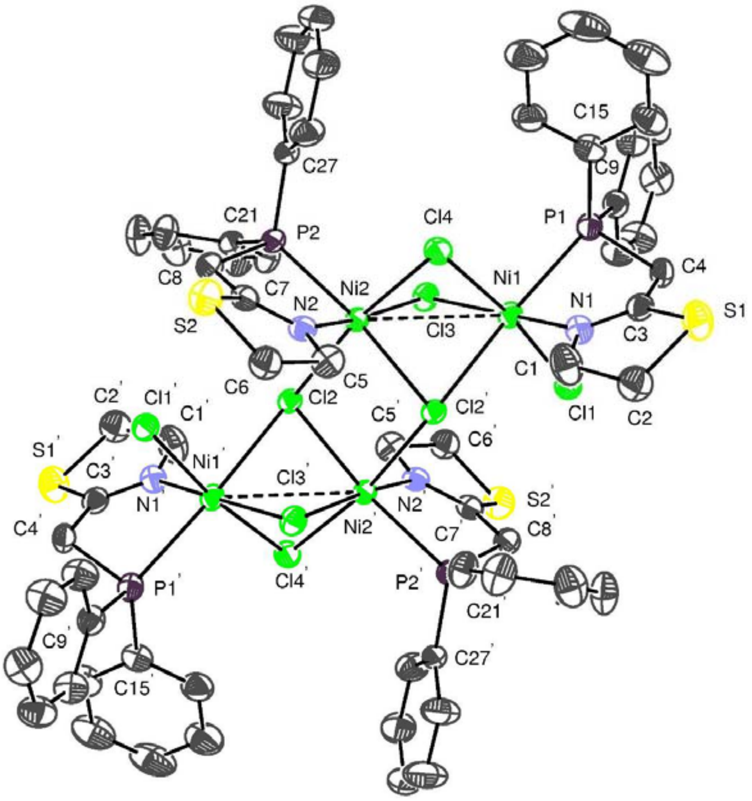
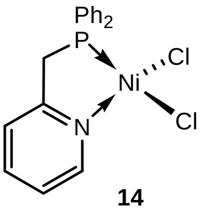


Figure 2. Vue ORTEP de la structure moléculaire à l’état solide de **10** dans **10**·2CH_2Cl_2 (les atomes d’hydrogène ne sont pas représentés pour simplifier la figure).

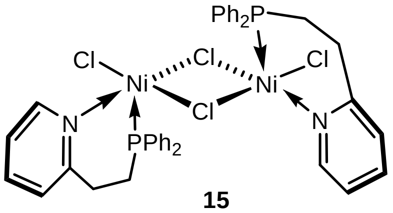
Une étude de diffraction sur poudre du complexe **11** nous a permis de l’identifier comme un complexe tétranucléaire. Les complexes **10** et **11** ont été isolés sous forme de poudres rouges par évaporation lente d’une solution de MeOH ou CH_2Cl_2 ou précipités sous forme de poudres vertes par ajout d’heptane sur une solution de CH_2Cl_2. L’étude UV-Vis à différentes températures d’une solution du complexe **10** a permis de mettre en évidence la présence d’un équilibre entre une forme [$NiCl_2$(P,N)] rouge et une forme [$NiCl_2$(P,N)]$_4$ verte. L’application d’une pression mécanique de 30 Kbar sur les complexes **10** et **11** sous la forme verte [$NiCl_2$(P,N)]$_4$ induit une isomérisation sous la forme [$NiCl_2$(P,N)] rouge. Une étude magnétique de **11** sous la forme tétranucléaire a été commencée afin de déterminer les différentes interactions ferro ou antiferro qui lient les atomes de Ni.

Chapitre IV

Les complexes **14-19** ont été synthétisés par réaction de $NiCl_2$, $NiBr_2$ ou $[NiCl_2(DME)]$ avec un équiv de ligand phosphine-pyridine, phosphonite-pyridine ou phosphinite-pyridine afin d'évaluer l'influence des fonctions phosphorées des ligands en oligomérisation de l'éthylène. Les structures cristallines des complexes **15** et **18** ont été déterminées par diffraction des rayons X. **18** montre une structure tétraédrique mononucléaire alors que **15** montre une structure dinucléaire avec une géométrie pyramide à base carrée. Les complexes **14-18** ont été testés en réaction catalytique d'oligomérisation de l'éthylène avec différentes quantités de MAO ou $AlEtCl_2$ comme cocatalyseur et avec une pression d'éthylène de 10 ou 30 bar. Le complexe **15** a montré la plus forte activité avec un TOF de 207600 C_2H_4/(mol Ni·h) avec 6 équiv de $AlEtCl_2$. Avec MAO comme cocatalyseur, le complexe **18** possédant des fonction *tert*-Butyl a montré la meilleure activité avec un TOF de 45500 C_2H_4/(mol Ni·h) avec 100 équiv de MAO et une pression de 30 bar. Ce même complexe a montré des sélectivités intéressantes en 1-butène jusqu'à 73% mais sa capacité à la réinsertion du 1-butène pour former 2-éthyl-1-butène diminue sa sélectivité en oléfines C_4 comprise entre 17 et 27%.



14



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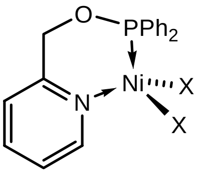
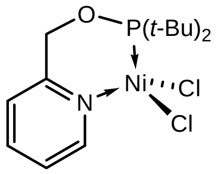


16 X = Cl
17 X = Br



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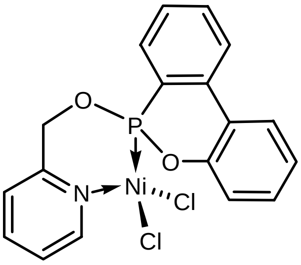

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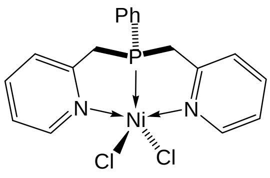
Chapitre V

Les complexes de nickel **20-23**, les complexes de fer **24-26** et les complexes de cobalt **27-30** ont été synthétisés par réaction des précuseurs $NiCl_2$, $FeCl_2{\cdot}4H_2O$ ou $CoCl_2$ avec des ligands tridentates type N,P,N comportant des fonctions oxazoline ou pyridine. Les structures cristallines de **24-27** ont été determinées par diffraction des rayons X. Les structures de **24** et **25** montrent la *fac*-coordination de deux ligands autour du centre Fe(II) et formation d'un dianion $(Fe_2OCl_6)^{2-}$ compensant la double charge positive. Contrairement à **24** et **25**, la structure de **26** montre la coordination chélatante des deux atomes d'azote du ligand et l'inattendue non coordination de l'atome de phosphore. Ces trois complexes ont été étudiés par voltammographie cyclique. La structure de **27** montre une géométrie tétraédrique du complexe avec coordination de l'atome de phosphore et la coordination d'une seule des deux fonctions oxazoline du ligand.



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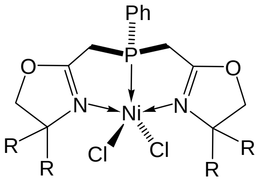
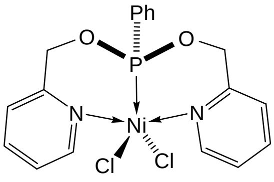


21 R = H
22 R = Me



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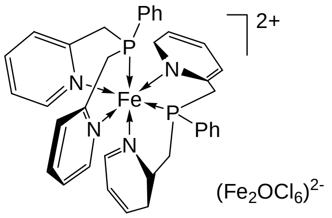

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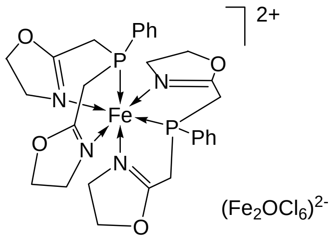

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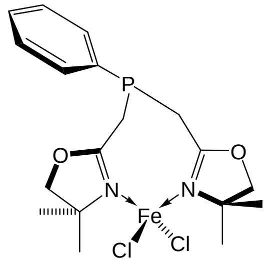

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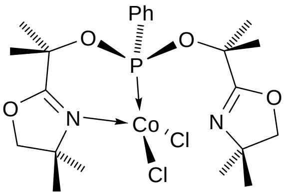

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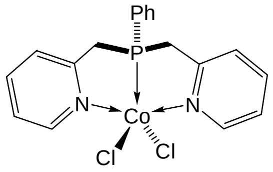

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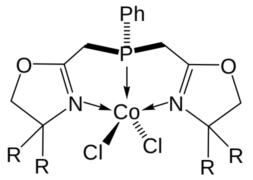
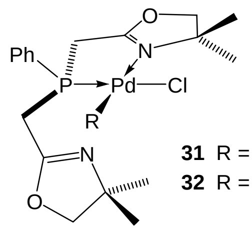
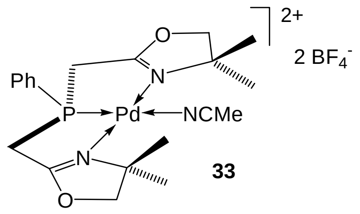


29 R = H
30 R = Me

Afin d'étudier le mode de coordination de ces ligands N,P,N, les complexes de palladium **31-33** ont été synthétisés et leurs spectres RMN et IR ont montré des modes de coordination bidentes ou tridentes en fonction du contre-ion du précurseur métallique.



31 R = Me
32 R = Cl



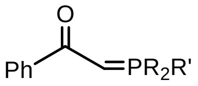
33

Les complexes **20-27** ont été évalués en réaction d'oligomérisation de l'éthylène avec MAO ou $AlEtCl_2$ comme cocatalyseur. Les complexes de nickel se sont montrés les plus actifs en particulier **20** avec un TOF de 61800 mol C_2H_4/(mol Ni·h) avec dix équiv de $AlEtCl_2$. Les trois complexes de fer **24-26** n'ont pas montré d'activité significative avec MAO ou $AlEtCl_2$

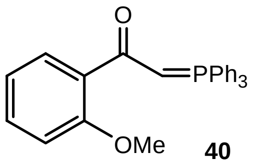
et le complexe de cobalt **27** a montré des activités modérées avec $AlEtCl_2$ jusqu'à 17700 mol C_2H_4/(mol Ni·h) sous 30 bar d'éthylène.

Chapitre VI

Une série de nouveaux ylures phosphorane **34-40** avec différents substituants alkyl et aryl sur l'atome de phosphore (*n*-Butyl, *t*-Butyl, méthyl, phényl) ont été synthétisés par réaction de phosphines mixtes alkyl/aryl avec α-bromoacétophénone.

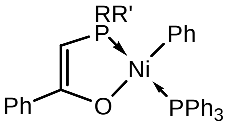


34 R = R' = *n*-Bu
35 R = *t*-Bu, R' = Ph
36 R = Ph, R' = *t*-Bu
37 R = *n*-Bu, R' = Ph
38 R = Ph, R' = *n*-Bu
39 R = Me, R' = Ph

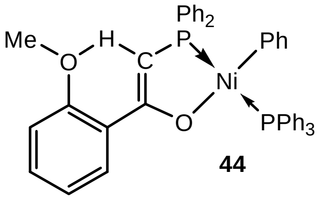


40

Les ylures **34**, **35**, **38** et **40** ont permis synthétiser les nouveaux complexes **41-44** par réaction de un équiv de $Ni(COD)_2$ avec un équiv de PPh_3. La structure cristalline de **44**, déterminée par diffraction des rayons X, montre la formation d'une liaison hydrogène entre l'atome d'oxygène de la fonction éther et l'atome d'hydrogène du groupe CH en position α du phosphore.

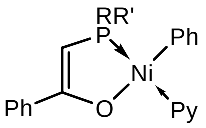


41 R = Ph, R' = *t*-Bu
42 R = R' = *n*-Bu
43 R = Ph, R' = *n*-Bu



44

L'utilisation d'un équivalent de pyridine à la place de PPh_3 a permis de synthétiser les complexes **45-49**.

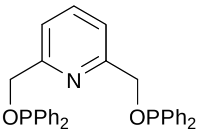


45 R = R' = Ph
46 R = Ph, R' = *t*-Bu
47 R = R' = *n*-Bu
48 R = Ph, R' = *n*-Bu
49 R = Me, R' = Ph

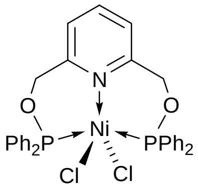
Des testes catalytiques d'oligomérisation par formation in situ du catalyseur ont été réalisés avec les ylures **35**, **37** ou **40**, PPh_3 et $[Ni(COD)_2]$ sous 30 bar d'éthylène et 24 h de temps de réaction. Ces catalyses ont montré des activités modestes avec des TON compris entre 800 et 5700 mol C_2H_4/(mol Ni) mais des sélectivités en oléfines α linéaires supérieures à 98%. L' ylure **40**, sous 60 bar a donné une activité de 4600 mol C_2H_4/(mol Ni) après 2 h de réaction. La catalyse avec l'ylure **35** et trois équiv de $[Ni(COD)_2]$ et un équiv de PPh_3 forma un catalyseur de polymérisation avec un TON de 5500 mol C_2H_4/(mol Ni).

Chapitre VII

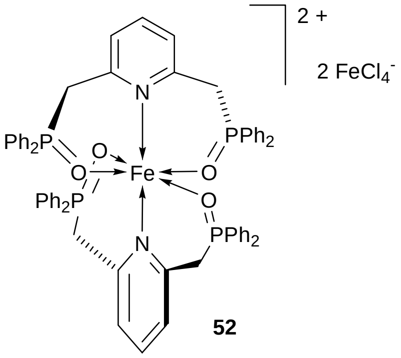
Ce chapitre présente les résultats préliminaires obtenus sur l’étude de la complexation du ligand 2,6-bis((diphenylphosphinito)methyl)pyridine **50** avec des précurseurs de nickel et de fer. La réaction du ligand **50** avec [$NiCl_2$(DME)] a permis de synthétisé le complexe [Ni{2,6-bis((diphenylphosphinito)methyl)pyridine}Cl_2] **51** qui a été caractérisé par spectrométrie de masse. La réaction de **50** avec $FeCl_3$ a formé le complexe inattendu [Fe{2,6-bis({diphenyl} oxyde-phosphine)methyl)pyridine}$_2$($FeCl_4$)] **52.** Ce complexe, identifié par diffraction des rayons X et spectrométrie de masse, montre la réduction de Fe(III) en Fe(II) et un réarrangement original du ligand en bis(oxyde-phosphine)pyridine. Un mécanisme apparenté au réarrangement Arbuzov a été proposé pour expliquer la formation de **52**. Une étude en voltamètrie cyclique à été commencée sur le complexe **52**.



50



51



52

Conclusion générale

Ce travail de thèse s'est attaché à synthétiser de nouveaux complexes de métaux de transition et de les étudier en réaction catalytique d'oligomérisation de l'éthylène. Il était intéressant de lier structures cristallines, comportement en solution et propriétés catalytiques de ces complexes.

L'étude des complexes de nickel coordinés par des ligands bidentates P,N ou N,O nous ont permis de mettre en évidence la formation de complexes mononucléaires, dinucléaires et tétranuclaires guidées par les propriétés stéréo-électroniques des ligands. Notamment l'étude en solution de complexes de nickel coordinés par des ligands phosphine-oxazoline et phosphine-thiazoline nous a montré un équilibre entre la forme mononucléaire et tétranucléaire de ces complexes en solution.

Ces complexes ont montré des activés élevées en oligomérisation lorsqu'ils sont activés par MAO ou $AlEtCl_2$ comme cocatalyseur et une sélectivité importante pour la dimérisation de l'éthylène. Les catalyses réalisées sur les complexes de nickel à ligands P,N ont clairement montré l'influence des substituants alkyl du phosphore sur les sélectivités en oléfines α linéaires. Nous avons aussi noté l'importance de la réinsertion du 1-butène et du 2-butène pendant la réaction de catalyse et qui conduit à la formation d'oligomères C_6.

Les réactions de ligands type N,P,N sur des précurseurs de Ni(II), Fe(II), Co(II) et Pd(II) ont mis en évidence des comportements de coordination fascinants. La nature du centre métallique et des contre-anions guide la coordination des ligands vers des modes bidentates ou tridentates originaux.

Nous nous sommes aussi intéressé à la préparation de nouveaux ylures phosphorane avec des substituants alkyl sur l'atome de phosphore enfin de synthétiser de nouveaux complexes de type catalyseur SHOP. Malheureusement ces complexes se sont montrés peu stables et la formation in situ de catalyseurs avec ces ylures n'apporta que des activités modérées en oligomérisation de l'éthylène.

Enfin notre étude sur la complexation du ligand (diphenylphosphinito)methyl)pyridine avec $FeCl_3$ nous a permis de mettre en évidence un réarrangement inattendu et originale de la fonction phosphinite du ligand en oxyde de phosphine et réduction du centre métallique Fe(III) en Fe(II). Un mécanisme apparenté à Arbuzov a été proposé pour ce réarrangement.