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par

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Modulation des Propriétés Electroniques et Stériques de Nouvelles Phosphines Chélatantes. Applications en Oligomérisation et Polymérisation de l'Ethylène.

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La pensée ne doit jamais se soumettre, ni à un dogme, ni à un parti, ni à une passion, ni à un intérêt, ni à une idée préconçue, ni à quoi que ce soit, si ce n'est aux faits eux-mêmes, parce que, pour elle se soumettre, ce serait cesser d'exister.

Henri Poincaré

Un grand Merci à tous celles et ceux qui ont rendu possible ce travail, ou qui ont, directement ou indirectement, continuellement ou sporadiquement, contribué à sa réalisation.

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Contents

CHAPTER 1:

CHAPTER 2:

CHAPTER 3:

CHAPTER 4:

CHAPTER 5:

CHAPTER 6:

CHAPTER 7:

General Introduction and objectives

General Introduction

Transition metals are at the core of a wide range of catalyst systems.[1] In comparison to main group metals, they possess more orbitals available for interactions, and with different symmetry. Additionally, transition metals can combine specific functions, e.g. Lewis acidity, substrate activation, red/ox chemistry and polar bonds. This diversity is a key factor in imparting catalytic properties to transition metals and their complexes. The ability to bind inert spectator ligands in addition to reactive moieties forms the basis for innovative transition metal catalyst design. These ancillary ligands primarily control the configuration and conformation of reactive coordinated substrates, and thus catalyst reactivity. Variation of the properties, either electronic or steric or both, of such ligands offers the opportunity to tune catalyst properties. The wide range of possible spectator ligands, metal oxidation states and coordination numbers provides a near infinite array of potential catalysts.

The unique character of the metal-carbon bond is another important element of (transition) metal-based catalysts that has been exploited in many catalytic (and stoichiometric) metal-mediated transformations.[2] The wide range of available organometallic metal-alkyl species offers a broad spectrum of reactivity with various substrates to allow interesting opportunities for C-C, C-H, C-O, C-N and C-X bond formation. A very important application of C-C bond formation with organometallic catalysts is the polymerisation and copolymerisation of olefins and the closely related oligomerization of olefins.

The production of polyolefins is one of the most important area of chemical industry, which estimated worldwide annual production of 80 million tons (in 2000) has witnessed a 100% increase in production volume over the past decade only.[3]

The first oligomerisation process was developed by Ziegler (Alfen process) in the early 50's. During extensive studies on organoaluminium compounds, Ziegler discovered the *Aufbaureaktion,*[4] a series of sequential repetitive olefin insertions into the Al-C bond (Fig. 1, Eq. 1), which takes place under high ethylene pressure (100-400 bar) and moderate temperatures (100-150°C). Relevant for the production of linear α-olefins was the observation that the insertion of ethylene into an Al-H bond is reversible (Fig1, Eq. 2),[5] indicating that olefin elimination can occur.

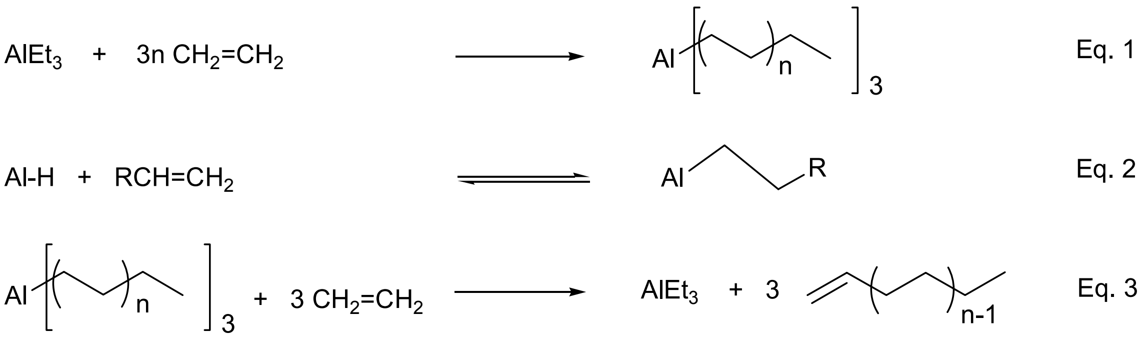


Figure 1.

Upon variation of the pressure, temperature and reaction time, it was possible to induce the displacement of olefins (*Verdrängung*) affording triethylaluminum and three equivalents of α-olefins (Fig. 1, Eq. 3), achieved at high temperature (250-400°C) and low ethylene pressure (10 bar).[6]

Several processes still involve alkyl-aluminum compounds for the production of α-olefins (Gulf/Chevron,[7,8] Ethyl Corporation[9]).

The most important discovery made by Ziegler in 1952 was that in the presence of nickel salts, the alkyl-aluminum catalysed *Aufbaureaktion* is directed to yield mainly butenes.[4a,6] This phenomenon is often referred to as the “nickel effect”.[10] These findings initiated an intensive investigation into organo-nickel chemistry.[11] Wilke was the first to observe ligand effects on selectivity in nickel-catalyzed reactions.[12] Most of the nickel complexes that were used were called “bare” or “naked” as the nickel atom is coordinated to ligands that could be quantitatively displaced by substrates or bind to only a few ligands.[12]

During the late 60’s, upon extension of the ligand variations to bidentate [*P*,*O*] chelators, Keim discovered highly active ethylene oligomerisation catalysts that produce linear α-olefins with excellent selectivity (Fig. 2).[13,14]

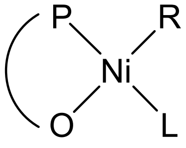


Figure 2.

This type of catalysts forms the basis of the SHOP-process (Shell Higher Olefin Process), which accounts for about 35% of the annual worldwide production of α-olefins made through ethylene oligomerisation.[15,16] With an annual production of about 1 million tons, the SHOP is the largest *single feed* industrial application of homogeneous catalysis.[15,16]

Table 1. Comparison of different processes that produce α-olefins. Product distributions (wt.-%) of C_6-C_{18} α-olefins.[17]

	Wax-cracking	Gulf/Chevron	Ethyl	SHOP
α-olefins	83-89	91-97	63-98	96-98
Branched olefins	3-12	2-8	2-29	1-3
Paraffins	1-2	1,4	0,1-0,8	0,1
Dienes	3-6	-	-	-
Mono-olefins	92-95	99	>99	99,9

Interestingly, it was found that these catalyst systems are also able to produce linear polyethylene under certain conditions.[13] This constituted the first example of *single site* catalysed olefin polymerisation using late transition metal catalyst.[18]

However, Ziegler had already discovered in 1955 that the polymerization of ethylene to high molecular weight linear polyethylene could be achieved with heterogeneous $TiCl_4/AlEt_2Cl$ catalysts.[19] A little later, Natta showed that it is possible to stereoselectively polymerise propylene to isotactic polypropylene with a closely related catalyst system.[20] Since these initial discoveries, the development of homogeneous olefin polymerization catalysts has mainly focused on group IV metals, resulting in an explosion of new catalysts in the 80's.[21] As a matter of fact, nickel-based catalysts were, at this time, less efficient and were only able to produce polyethylene with moderate molecular weights.

After the discovery, in the early 90's, that cationic SHOP-like catalysts are able to oligomerise ethylene with high activities at lower temperature and ethylene pressure,[22,23] highly active cationic nickel catalysts based on α-diimine ligands were found to also catalyse this reaction.[24]

Since then, the interest for such metal complexes for the production of polyolefins has continuously grown.[25] Indeed, they present several advantages over group IV metal complexes including easy complex synthesis, low preparation cost for first series metal complexes, low ecological impact, etc.

The interest for these catalysts further arises from their decreased oxophilicity and greater functional group tolerance, that would make them ideal for the copolymerisation of olefins with polar comonomers,[25,26] or the polymerization of olefins in aqueous media under mild conditions.[27] The discovery of these features has notably played a crucial role in the development of the SHOP, for which the oligomerisation reaction is performed in 1,4-butanediol.[18]

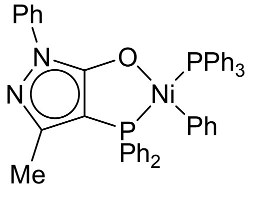
Thus, more recently several highly efficient nickel polymerisation (as well as oligomerisation) catalysts based on [*P*,*P*],[28] [*P*,*N*][29] or [*N*,*O*][30] chelators have been reported, together with some other chelate complexes based on other metals such as iron, cobalt, etc.[25]

Functional phosphine ligands, by their modular character are ligands which are perfectly suited for late transition metals.[31] Though they are only rarely involved in *in-vivo* metallo-catalyzed reactions,[32] they are at the core of numerous man-made catalytic systems, that some of which display important industrial spin-offs.[33]

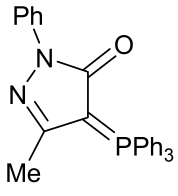
Objectives

The present thesis focuses on the synthesis of new nickel complexes based on modified diphosphine and phosphinoenolate chelators. These modifications were of three major types: electronic and steric through ligand backbone substitution, and backbone size. Catalytic properties of these complexes were investigated in ethylene oligomerisation and polymerisation.

The work is divided into seven chapters. In *chapter 1*, a literature overview describes the structure-reactivity relationship of [Ni-(*P,O*)] based catalysts. *Chapter 2* describes the synthesis and ethylene oligomerisation properties of the new electron-poor SHOP-type complex **A**, in which the strongly electron-withdrawing pyrazol substituent induces an unprecedented shift of the oligomerization products to short α-olefins. Subsequently, *Chapter 3* displays a study of the coordination properties of the phosphorus-ylide **B**, which can be seen as a procatalyst similar as **A**, involving the coordination of the pyridine-like nitrogen atom. With the aim to get better knowledge of the impact of electron-withdrawing substituents on product chain-length, a comparative study of three electron-poor [Ni-(*P,O*)] complexes is presented in *Chapter 4*.

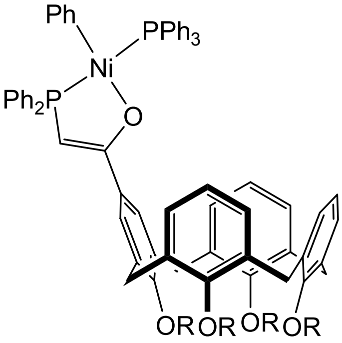


A



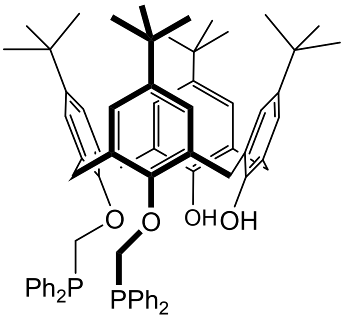
B

Chapter 5 deals with SHOP-like catalysts anchored on the upper-rim of a bulky calix[4]arene platform (**C**).



C

The ability of this macrocycle to achieve an efficient steric crowding of the [Ni-(*P,O*)] moiety has been investigated, together with its preorganisation ability for bimetallic catalyst systems. Further, *Chapter 6* reports the study of new diphosphine-nickel complexes based on a calix[4]arene proximally substituted by two -OCH_2PPh_2 podand arms (**D**). Finally, *Chapter 7* is devoted to the NMR study of an asymmetric analogue of **D**, which displays a rare P-P' coupling constant.



D

References

[1] a) C. Masters, *Homogeneous Transition-Metal Catalysis*, Chapman and Hall, London, UK, **1981**; b) G. W. Parshall, S. D. Ittel, Homogeneous catalysis, Wiley & Sons Inc., New York, USA, 1992; c) W. A. Herrmann, B. Cornils, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1048 ; d) D. Seebach, *Angew. Chem. Int. Ed. Engl.* **1990**, *29(11)*, 1320-1367.

[2] a) P. M. Maitlis, *The Organic chemistry of Palladium*, Academic Press Inc., London, **1971**; b) *Homogeneous Catalysis with Metal Phosphine complexes* (Ed. L. H. Pignolet), Plenum Press, New York, **1983**; c) *Metal-Catalysed Cross-coupling Reactions* (Eds. F. Diederich, P. J. Stang), Wiley-VCH, Weinheim, **1998**; *Transition Metals for Organic Synthesis* (Ed. M. Beller, C. Bolm), Wiley-VCH, Weinheim, **2004**.

[3] *Chem. Eng. News* **2001**, *79(26)*, *June 25*, p. 44.

[4] a) K. Ziegler, H. G. Gellert, H. Kühlhorn, H. Martin, K. Meyer, K. Nagel, H. Sauer, K. Zoser, *Angew. Chem.* **1952**, 64, 323; b) K. Ziegler, E. Holzkamp, H. Breil, H. Martin, *Angew. Chem.* **1955**, 67, 54; c) K. Ziegler, H. G. Gellert, K. Zosel, E. Holzkamp, J. Schneider, M. Söll, W. R. Kroll, *Liebigs Ann. Chem.* **1960**, *629*, 121.

[5] K. Ziegler, W. R. Kroll, W. Larbig, O. W. Steudel, *Liebigs Ann. Chem.* **1960**, *629*, 53.

[6] K. Ziegler, H. G. Gellert, E. Holzkamp, G. Wilke, E. W. Duck, W. R. Kroll, *Liebigs Ann. Chem.* **1960**, *629*, 172.

[7] H. B. Fernald, B. H. Gwynn, A. N. Kresge, US 3482000 (Gulf R. & D. Comp.), **1969**.

[8] a) H. B. Fernald, B. H. Gwynn, A. N. Kresge, DE 1443927 (Gulf R. & D. Comp.), **1961**; b) H. B. Fernald, B. H. Gwynn, A. N. Kresge, GB 186610 (Gulf R. & D. Comp.), **1970**.

[9] a) W. T. Davis, M. F. Gautreaux, US 3391219 (Ethyl Corp.), **1968**; b) C. W. Lanier, US 3906053 (Ethyl Corp.), **1975**.

[10] G. Wilke, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 185.

[11] W. Keim, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 235-244.

[12] G. Wilke, B. Bogdanovic, P. Hardt, P. Heimbach, W. Keim, M. Kröner, W. Oberkirch, K. Tanaka, *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 151.

[13] a) P. W. Glockner, W. Keim, R. F. Mason, US 3647914 (Shell), **1972**; b) R. S. Bauer, H. Chung, P. W. Glockner , W. Keim, H. van Zwet, US 3635937 (Shell), **1972**; c) R. Bauer, H. Chung, K.W. Barnett, P. W. Glockner , W. Keim, H. van Zwet US 3686159 (Shell), **1972**; d) D.M. Singleton, P. W. Glockner, W. Keim, GB 1364870 (Shell), **1974**; e) R. S. Bauer, H. Chung, D. Camel, W. Keim, H. van Zwet, US 3637636 (Shell), **1972**; f) R. Bauer, P. W. Glockner , W. Keim, H. van Zwet, H. Chung, US 3644563 (Shell), **1972**; g) H. van Zwet, R. Bauer, W. Keim, US 3644564 (Shell), **1972**; h) R. Bauer, P. W. Glockner,W. Keim, R. F. Mason, US 3647915 (Shell), **1972**; i) R. S. Bauer, H. Chung, W. Keim, H. van Zwet, US 3661803 (Shell), **1972**; j) R. F. Mason,

(Shell) US 3676523, **1972**; US 3686351, **1972**; US 3737475, **1993**; k) A.J. Berger, US 3726938 (Shell), **1973**; l) E.F. Lutz, US 3825615, **1974**; US 4528416, **1985**.

[14] W. Keim, F. H. Kowalt, R. Goddard, C. Krüger, *Angew. Chem. Int. Ed. Engl.* **1978**, *17(6)*, 466-467.

[15] P. M. Morse, *Chem. Eng. News* **1999**, *77(11)*, *March 15*, p. 22.

[16] J. Skupinska, *Chem. Rev.* **1991**, *91*, 613-648.

[17] A. M. Al-Jarallah, J. A. Anabtawi, M. A. B. Aitani, A. W. Al-Sadoun, *Catal. Today* **1992**, *14*, 1.

[18] W. Keim, *Green Chemistry* **2003**, *5*, 105-111.

[19] a) K. Ziegler, E. Holzkamp, H. Breil, H. Martin, *Angew. Chem.* **1955**, 67, 541; b) K. Ziegler, *Angew. Chem.* **1964**, 76, 545.

[20] a) G. Natta, *Angew. Chem.* **1956**, 68, 393; b) G. Natta, *Angew. Chem.* **1964**, 76, 553.

[21] a)P. C. Möhring, N.J. Coville, *J. Organomet. Chem.* **1994**, *479*, 1-29; b) M. Bochmann, *J. Chem. Soc. Dalton Trans.* **1996**, 255-270; c) H. H. Brintzinger, D. Fisher, R. Mülhaupt, B. Rieger, R. M. Waymouth, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1143-1170; d) V. K. Gupta, S. Satish, I. S. Bhardwaj, *Rev. Macromol. Chem. Phys. C* **1994**, *34*, 439-514; e) Y. Imanishi, N. Naga, *Prog. Polym. Sci.* **2001**, *26*, 1147-1198; f) W. Kaminsky, *J. Chem. Soc. Dalton Trans.* **1998**, 1413-1418; g) K. Soga, T. Shiono, *Prog. Polym. Sci.* **1997**, *22*, 1503-1546; h) R. F. Jordan, *Adv. Organomet. Chem.* **1991**, *32*, 325-387.

[22] S. Mecking, *Coord. Chem. Rev.* **2000**, *203*, 325-351.

[23] M. C. Bonnet, F. Dahan, A. Ecke, W. Keim, R. P. Schulz, I. Tkatchenko, *J. Chem. Soc. Chem. Comm.* **1994**, 615-616.

[24] a) L. K. Johnson, C. M. Killian, M. Brookhart, *J. Am. Chem. Soc.* **1995**, *117*, 6414-6415; b) L. K. Johnson, C. M. Killian, S. D. Arthur, J. Feldman, E. F. McCord, S. J. McLain, K. A. Kreutzer, M. A. Bennett, E. B. Coughlin, S. D. Ittel, A. Parthasarathy, D. J. Tempel, M. Brookhart, WO-A 96/23010 (DuPont), **1996**.

[25] a) V. C. Gibson, S.K. Spitzmesser, *Chem. Rev.* **2003**, *103*, 283-315; b) S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169-1204; c) G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem. Int. Ed. Engl.* **1999**, 38, 428-447.

[26] M. J. Yanjarappa, S. Sivaram, *Prog. Polym. Sci.* **2002**, *27*, 1347-1398.

[27] S. Mecking, A. Held, F. M. Bauers, *Angew. Chem. Int. Ed. Engl.* **2002**, 41, 544-561.

[28] a) N. A. Cooley, S. M. Green, D. F. Wass, K. Heslop, A. Orpen, P. G. Pringle, *Organometallics* **2001**, *20*, 4769-4771; b) M. Lejeune, D. Semeril, C. Jeunesse, D. Matt, F. Peruch, P. J. Lutz, L. Ricard, *Chem. Eur. J.* **2004**, *10(21)*, 5354-5360.

[29] P. Braunstein, *J. Organomet. Chem.* **2004**, *689(24)*, 3953-3967.

[30] K. A. Ostoja Starzewski, T. R. Younkin, E. F. Connor, J. I. Henderson, S. K. Friedrich, R. H. Grubbs, D. A. Bansleben, *Science* **2000**, 288, 1749-1751.

[31] R. Mason, D. W. Meek, *Angew. Chem. Int. Ed. Engl.* **1978**, *17(3)*, 183-194.

[32] W. Keim, *J. Mol. Catal. A: Chem.* **2004**, *224(1-2)*, 11-16.

[33] a) J. Ansell, M. Wills, *Chem. Soc. Rev.* **2002**, *31(5)*, 259-268; b) W. Keim, *J. Mol. Catal. A: Chem.* **2004**, *224(1-2)*, 11-16; c) W. S. Knowles, *Angew. Chem. Int. Ed. Eng.* **2000**, *41(12)*, 1998-2007; d) B. L. Feringa, *Acc. Chem. Res.* **2000**, *33(6)*, 346-353; e) A. Bader, E. Lindner, *Coord. Chem. Rev.* **1991**, *108*, 27-110.

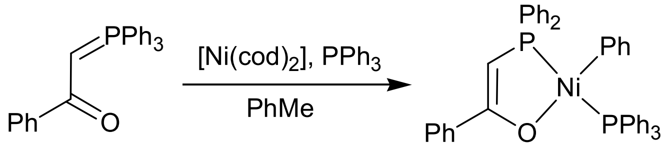
Chapter 1

Structure-Reactivity Relationships for [Ni(*P,O*)R(L)] Complexes, a Class of Versatile Catalysts for the Oligomerisation and Polymerisation of Ethylene

I. Introduction

During the early 70's, inspired by the work of Ziegler and Wilke, Keim introduced novel, homogeneous catalysts suitable for the oligomerisation of ethylene. The catalytic systems, which resulted from the combination of a nickel compound and a *P,O* chelator were found to be very efficient for the selective production of linear α-olefins.[1-7] The SHOP process (SHOP = Shell Higher Olefin Process) to which these catalysts were applied for the production of α-olefins constitutes one of the most important industrial application of homogeneous catalysis.[8,9] The original catalysts were generated *in situ*, by mixing keto-phosphorus ligands and "naked nickel" complexes. Their discovery follows a blossoming period in organic phosphorus chemistry.[10]

In 1978, Keim published the first synthesis of a complex of the general formula [Ni(*P,O*)Ph(PPh$_3$)], that is of a complex that may typically be employed in the SHOP process (Scheme 1). Interestingly, the complex was obtained via oxidative addition of a keto-stabilised phosphorus ylide to [Ni(cod)$_2$], a reaction that involves transfer of a phenyl group from the phosphorus to the nickel atom.[11] Other synthetic routes involving phosphines instead of phosphorus ylides were reported later.[12-14] Another important discovery made by Keim in the 70's was that catalysts of this family are also able to produce linear polyethylene under certain conditions, for example by operating in alkanes.[15-19]



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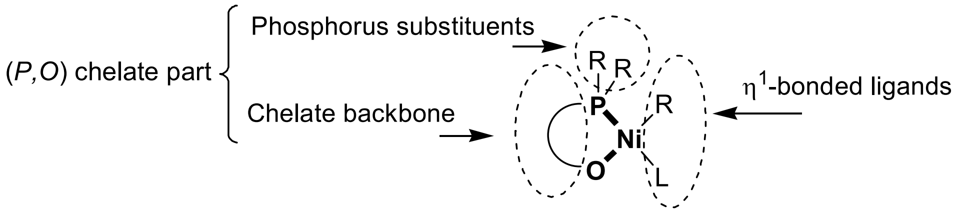
Scheme 1. Synthesis of a SHOP-type catalyst from a keto stabilised phosphorus ylide

The impact of a number of parameters on the catalytic properties of the complexes of this family has been investigated (nature of the substituents, backbone size, solvent for catalysis, use of cocatalysts, etc.). Considering their general structure, depicted in Scheme 2, two major types of structural variations can be envisaged: those involving the η^1-coordinated ligands (R and L) and those modifying the *P,O* chelate part. From the latter, two minor types of variations can be distinguished: at the phosphorus atom and at the chelate carbon atoms.



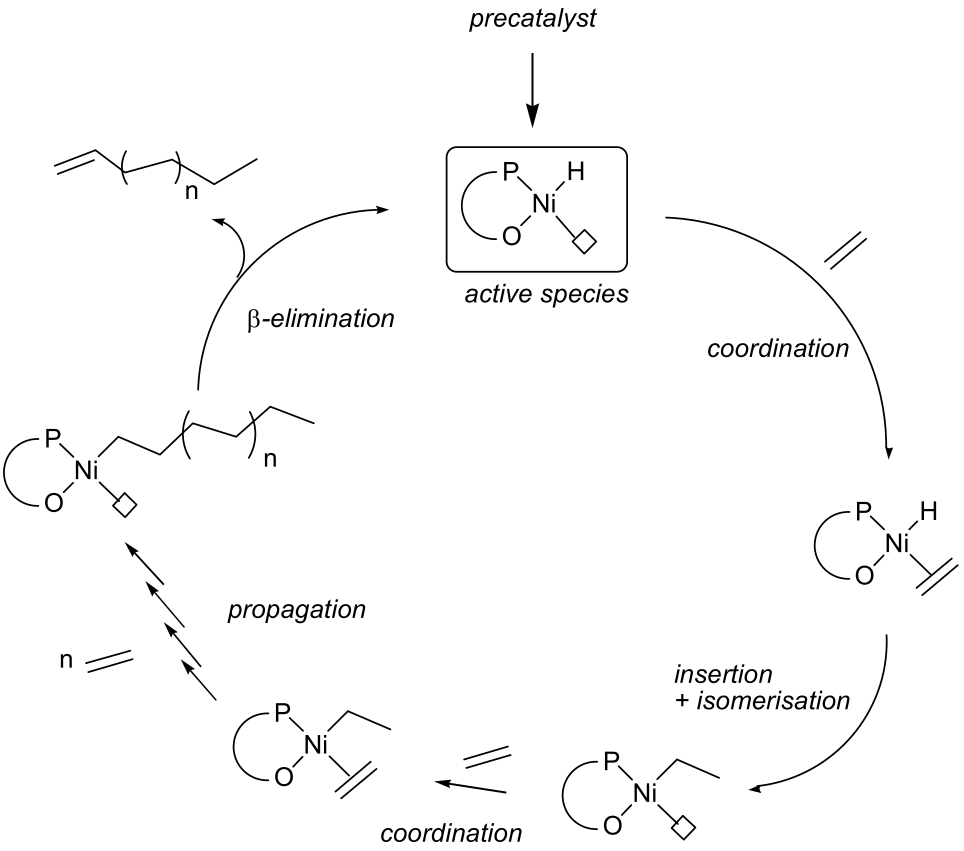
Scheme 2. Structural decomposition of [Ni(*P,O*)R(L)] complexes

The present chapter gives an overview of the main advances made in the field of ethylene oligomerisation and polymerisation using "Ni(*P,O*)" complexes in the last three decades. We arbitrarily choose to give all catalyst activities (TOFs) and productivities (TONs), respectively in mol(C_2H_4) mol(cat)$^{-1}$ h^{-1} and mol(C_2H_4) mol(cat)$^{-1}$.

II. General properties of [Ni(*P,O*)R(L)] complexes

A. Description of the catalytic cycle

The generally accepted mechanism follows a step growth process starting from a nickel-hydride complex that results from activation of the precatalytic species (Scheme 3).[20] After coordination of ethylene, a migratory insertion takes place to generate a Ni-alkyl species, which positions the alkyl chain in the position trans to the phosphorus atom. As the alkyl chain is assumed to be more strongly coordinated in the position *trans* to the oxygen atom, an isomerisation step is supposed to occur before the following ethylene coordination step. It is generally admitted that chain termination occurs via a β-elimination mechanism affording back the nickel-hydride species with concomittant release of an α-olefin. The whole mechanism is of the Michaelis-Menten type.[21] This is also the case when a strong monodentate donor ligand, *e. g.* a phosphine, is present, but only at ethylene pressures higher than 30 bar.[21,22] At lower pressures, at least two different active species are present (*vide infra*).[22] The insertion of ethylene as shown in Scheme 3 (chain propagation) was found to be the rate-limiting step.[20-22]



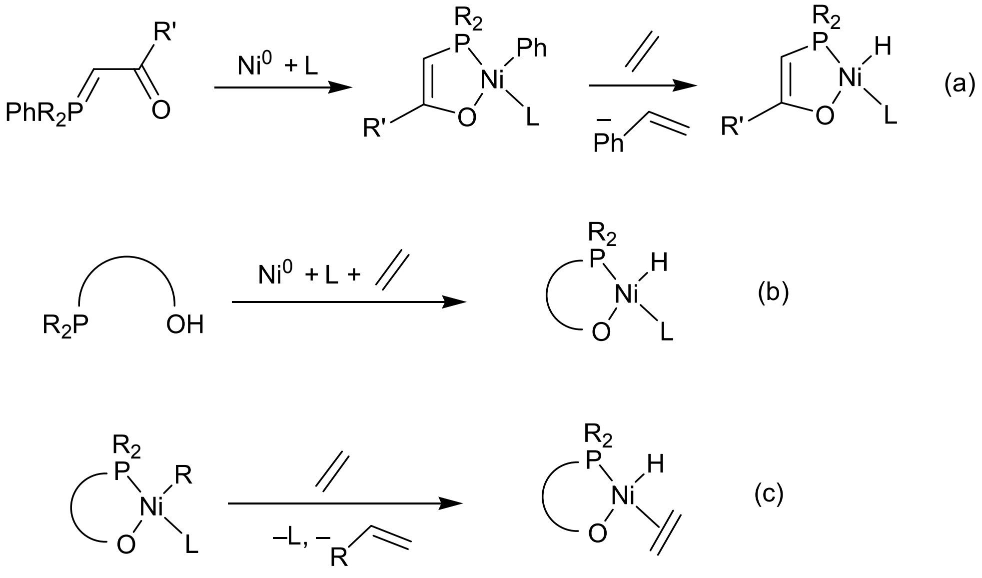
Scheme 3. Catalytic cycle in the absence of a strong monodentate donor ligand.

From such a chain-growth process a Schulz-Flory type distribution is obtained which can be described by the β value (β = termination rate/propagation rate). Lower β values correspond to longer chains. In practice, the product composition is determined using the α value (α = mol fraction C_{n+2}-alkene/mol fraction C_n-alkene, $\alpha = (1 + \beta)^{-1}$).[23-25] If polyethylene is produced, a Schulz-Flory type distribution leads to a polydispersity index (M_w/M_n) of 2.[26]

B. Synthesis of the active species

The active nickel hydride species can be generated in different ways. It is usually formed *in situ* according to a two-step sequence: (*i*) oxidative addition of a keto-stabilised phosphorus ylide or a phosphanyl-hydroxy ligand on a nickel(0) complex such as [Ni(cod)$_2$]; (*ii*) reaction with ethylene (Scheme 4, eq. a and b). An alternative method consists in reacting ethylene with a procatalytic complex, that is a complex in which the anionic, chelating *P,O* unit is already present. For a number of such complexes, the R/L couple is eliminated after reaction with ethylene, resulting then in a complex of formula [Ni(*P,O*)H(ethylene)] (Scheme

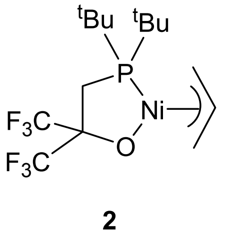
4, c). This is, for example, the case for R/L = Ph/olefin, η^3-allyl or η^5-Cp.[27] According to the nature of the R/L couple, the activation temperature and induction time may change. While the allyl moiety of [Ni(Ph_2PCH=C(O)Ph)(allyl)] is displaced at 50°C within 5 minutes, activation of [Ni(Ph_2PCH=C(O)Ph)(Cp)] requires about 20 minutes at 120°C.[27]



Scheme 4. Generating the active nickel hydride complex.

In some cases, activation of [Ni(*P,O*)allyl] complexes, e. g. **2**, was carried out using a borane cocatalyst (Table 1).[28,29]

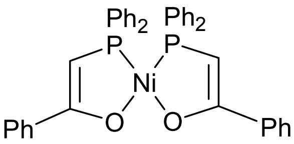
Table 1. Borane cocatalyst effect on allylic catalysts.

 **2**	Cocatalyst	TON	M_w (g/mol)	$M_\mathrm{w}/M_\mathrm{n}$
	none	0	/	/
	BPh_3 (5 equiv.)	7300	737800	3.5
	$B(C_6F_5)_3$ (5 equiv.)	3400	134300	60.2

Conditions: 64 bar C_2H_4, 25°C, 18 h, 0.05 mmol cat., 5 mL PhCl

C. Deactivation pathways

Klabunde et al. have investigated the reaction mixtures obtained after completion of the catalytic runs performed with an analogue of **1** (L = pyridine). The authors isolated the bis(phosphanylenolato) nickel(II) complex **3**, which proved to be catalytically inactive.[30,31] Gibson proposed that the formation of Ni(*P,O*)$_2$ complexes of this type is likely induced by coordination of the oxygen atom of a Ni(*P,O*) moiety to a second nickel centre belonging to an unsaturated 14 electron "Ni(*P,O*)R" species, but a detailed mechanism was not proposed.[32] Note, the formation of *O*-stabilised dimers such as **4** was demonstrated by Klabunde.



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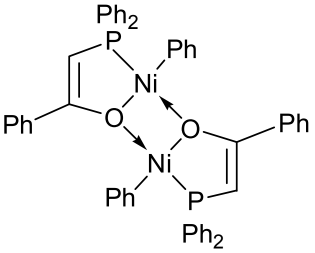
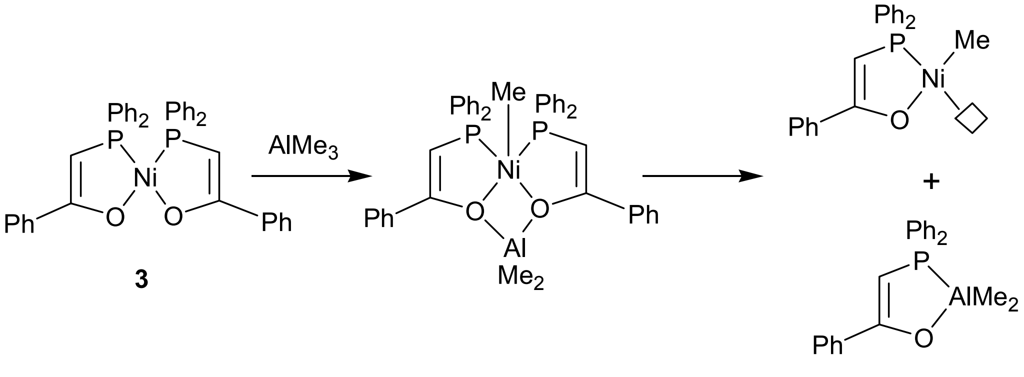


4

Interestingly, it was found that the activity of Ni(*P,O*) catalysts can be increased by adding aluminium alkyl cocatalysts.[30,31,33-36] The latter probably reactivate complexes of type **3** according to Scheme 5, hence improving the catalyst's lifetime.[30,31]



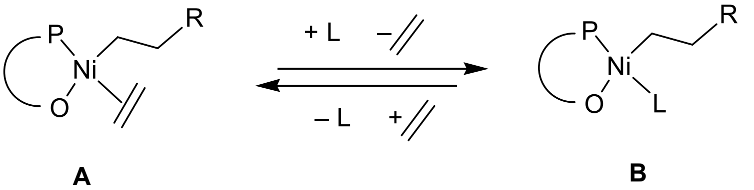
Scheme 5. Proposed reactivation pathway by aluminium alkyl cocatalysts

However, using such activators either affords a dramatic drop of selectivity in α-olefins or broadens the polyethylene molecular weight distributions.

An effective way to avoid deactivation through a binuclear mechanism can been achieved by catalyst immobilisation. Several types of heterogeneisation have been reported, e.g. using inorganic supports (Celite,[30,31] alumina;[37,38] silice,[37-40] magnesium hydrides[37]) or polymer matrices (adsorption on polyethylene,[19] covalent linkage on polystyrene[39,41,42] and dendrimers[43]).

III. Influence of the L ligand

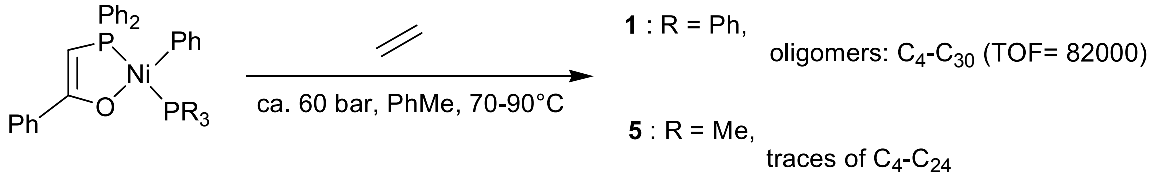
While the R group plays only an important role in procatalysts activation, the presence of a strong L ligand is able to induce important changes in reactivity. In solution, this two-electron donor ligand is able to bind the different nickel-alkyl intermediates, and thus compete with ethylene. This can be rationalised by an equilibrium, at each stage of the chain growth, between two types of catalytic species, one having coordinated ethylene (**A**), and the other L as ligand (**B**) (Eq. 1).[21,22,36,44] Since structure **A**, unlike **B**, exactly prefigures the insertion step, it is reasonable to admit that the probability of β-elimination is lower for **A** than for **B**.[21,22,36,44] This could explain why in the presence of a L ligand the chain termination is favoured over chain propagation. However, the way L acts for initiating a chain termination step remains unclear. Recent studies (*vide infra*) have shown that its role is not simply restricted to a lowering of the chain growth rate.



(1)

A. Influences of the nature of L.

As already mentioned, the direct consequence of the competitive coordination of **L** is a decrease of the chain propagation rate. If the equilibrium represented by eq. 1 is entirely displaced toward the formation of **B**, ethylene coordination and its subsequent insertion can no longer take place. This was shown by replacing PPh_3 in **1** by the more basic PMe_3 ligand (Fig. 6).[36] Addition of the latter results in an almost complete inhibition of the catalytic reaction.

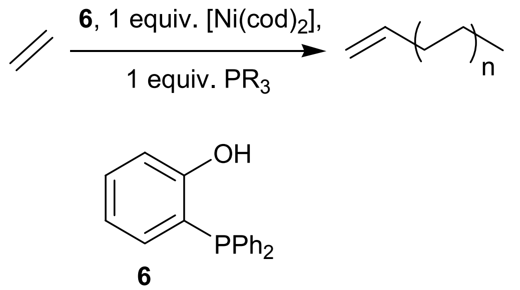


Scheme 6. Effect of an alkyl phosphine ligand *vs.* that of PPh_3.

On the other hand, upon abstraction of the PPh_3 ligand by addition of a phosphine sponge such as $[Ni(cod)_2]$, the catalyst produces linear polyethylene instead of C_4-C_{20} α-olefins.[30,31] The same behaviour is observed when the ligand is only weakly coordinating like, *e. g.*, $Ph_3P=O$ or pyridine.[30,31]

An interesting recent study, carried out with phosphanylphenolato complexes, has clearly established that the activities and the polyolefin distribution are closely related to the coordination ability of the phosphine ligand (L) (Table 2).[45] In keeping with eq. 1, the better the coordination ability of the ligand, the higher the equilibrium concentration of **B**-type complexes; this in turn lowers the ethylene insertion rate and leads to higher β values.

Table 2. Influence of PR_3 substituents.

	PR_3	pKa	Ω^* (°)	C_4 (g)	Oligomers (g)	Wax (g)
 **6**	Me_3P	8.65	118	>3.8	1.5	/
	Et_3P	8.69	132	>4.8	6.8	/
	Ph_3P	2.73	145	2.5 (and C_6)	2.8	8.6
	p-Tol_3P	3.83	145	>1.1	5.8	/
	o-Tol_3P	/	194	/	0.1	6.5 (HDPE)
	Mes_3P	/	212	/	0.1	9.2 (HDPE)
	Cy_3P	9.7	170	/	0.5	11.1

Conditions : cat. 0.1 mmol, 16 mL PhMe, 100°C, ca. 15 h. * cone angle

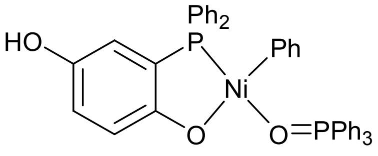
Thus, the combination of nickel phosphanylphenolates with the strongly coordinating phosphines PMe_3 or PEt_3 results in the production of much shorter oligomers (C_4-C_{14}) than those formed with PPh_3 (note, unlike the nickel-phosphanylenolates analogues, nickel-phosphanylphenolates remain active in the presence of PMe_3).

On the other hand, if the coordination ability of the L ligand is lower than that of PPh_3, the chain growth rate increases and the oligomers produced become longer. This is notably the case for the phosphines $P(o\text{-}Tol)_3$, $PMes_3$, and PCy_3,[45] which, because of their bulkiness are, less coordinating than PPh_3. The same holds for less basic triarylphosphines, for example $P(p\text{-}C_6H_4Cl)_3$ and $P(p\text{-}C_6H_4F)_3$).[36] It must be noted that the measured productivities do not follow the same trend, since a good coordinating L ligand plays a stabilisation role for the active species, thus enhancing the catalyst's life time. In fact, its coordination disfavours the formation of an inactive $Ni(P,O)_2$ complex via a bimetallic intermediate analogous to **4**. Thus, when the coordination ability of the L ligand decreases, the initial activity is higher, but the measured productivity may decrease with time. This was clearly inferred from a kinetic study.[45]

As a general trend, polar, coordinating solvents (DMF, acetone, THF, alcools, …) exert an influence comparable to that of a phosphine ligand. First, they result in lower-weighted material, but in a moderate way in comparison to PPh_3.[46] Further, the activities are lowered with respect to experiments carried out in non-coordinating solvents,[30,31,46] though the active species may be stabilised by the solvent coordination.[46] In fact, one has to be careful in interpreting such solvents effects, since the rather low solubility of ethylene in some protic solvents may severely contribute to lower the activity.[47]

The effects of water have also been investigated. In a toluene/water slurry, lowered activities[46] or total catalyst inhibition[30,31] were observed, whereas the addition of water to THF induced higher activities. In the latter case, increased molecular weights were also observed.[46] Biphasic catalysis in aqueous media was also found to be efficient.[47-50] Recent applications of Ni(*P,O*) complexes include their use in emulsion polymerisation. To date, emulsion polymerisation is achieved by a free-radical technique. It constitutes an important industrial polymerisation process for the production of stable polymer lattices, *i. e.* of stable colloidal aqueous dispersions of polymer particles of about 50 nm to 1µm.[51] As an alternative route, Mecking et al. have shown that some nickel phosphanylphenolates are very efficient for the production of aqueous dispersions of extraordinarily small polyethylene nanoparticles.[51]

Finally, it should be mentioned that apolar solvents such as alkanes result in a considerable increase of the molecular weight of the polyethylene formed.[11] Molecular weights as high as 1.07 10^6 g mol^{-1} were obtained using catalyst **7** in cyclohexane.[52]



7

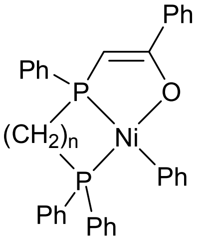
B. Influence of the L:Ni ratio.

The influence of the PPh_3-stoechiometry on the catalytic properties of systems derived from the phosphinophenol **6** were investigated by Heinicke et al (P_{init} = 50bar, T = 100°C, toluene).[45] The authors showed that, as expected, the catalyst lifetime and the TON are higher in the presence of PPh_3 than in its absence. The TON was found roughly constant for PPh_3:Ni ratios comprised between 1 and 15. For higher ratios the TONs significantly decreased, probably because the equilibria represented by eq. 1 are strongly shifted towards the right side.

Several studies have unambiguously established that increasing the L:Ni ratio also increases the proportion of lower-weighted polyolefins.[21,22,45] For example, using ligand **6**, resulted in β values of 0.6, 0.9 and 1.4, for PPh_3:Ni ratios of respectively 5, 7 and 10. Interestingly, this enhancement is not associated with an activity decrease (up to a given amount of PPh_3), unlike the observations made with ligands displaying a stronger coordinating ability.

Overall, monodentate tertiary phosphines (PR_3) constitute valuable additives for tuning the chain length of the α-olefins. On the basis of a kinetic study, de Souza et al. have shown that, beside the **A**-type complexes, PR_3-containing intermediates must be directly involved in the catalytic cycle, but no precise mechanism was proposed. Other authors came more recently to the same conclusion.[36,45]

The only examples where the L ligand is covalently linked to the *P,O* moiety are those of complexes **8**-**13**, which were generated *in situ*.[53] These catalysts produce mainly waxes (M_w = 1850, M_w/M_n = 1.7), representing 52-90 wt% of the polyolefins produced. Although the catalytic behaviour of these ligands could not be fully explained, these results illustrate the potential of *P,O* chelators with appended functional groups. Ligands of this family, in particular those bearing hemilabile subunits, will certainly receive increasing attention in the future.[54-56]



8-13 (n = 1-6)

IV. Variation of the *P,O* chelate part

A. Variation of the $P_{chelate}$-substituents

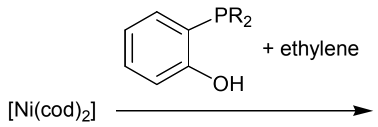
Changes in the $P_{chelate}$ substituents may induce important modifications in the catalytic behaviour of Ni(*P,O*) complexes. In the normal case, the $P_{chelate}$ atom is coordinated trans to the L ligand and therefore any modification in its substituents may modify the coordinating properties of L via the trans effect. Since this interplay may lead to an intricate catalytic behaviour, we will first discuss the case of L-free catalysts.

1. In the absence of L ligand.

Heinicke et al. have investigated the behaviour of the nickel phosphanylphenolates derived from **6**, and **14-17**, which differ only by the P substituents, in the absence of any additional donor ligand (Table 3).[46] The productivity of the catalyst was shown to increase with the phosphorus basicity, but the observed variations are rather weak. The influence on the chain length is more pronounced. The latter increases in the order R = Ph < ^{t}Bu ≈ Et < ^{i}Pr < Cy, that is, in first approximation, in the order of increasing basicity. To explain this effect, the authors invoked the higher trans influence exerted by the more basic PR_2 moieties, which disfavors the agostic interaction with the β-C*H* atom of the growing alkyl chain and hence the chain termination step.[46] In fact, as can be deduced from the results obtained for the $P(^tBu)_2$-

derivative **16** (leading to lower average molecular weights), a second effect seems to operate, namely one related to the steric encumbrance of the PR_2 group.

Table 3. Influence of the $P_{chelate}$-substituents in the absence of L.



R	Ω [a] (°)	TON	M_w (g mol^{-1})	M_n (g mol^{-1})	M_w/M_n
Ph (**6**)	145	2960	5510	4430	1.2
Et (**14**)	136	3670	21800	7940	2.7
^{i}Pr (**15**)	155	2890	25800	6230	4.2
^{t}Bu (**16**)	162	4210	14000	2330	6.0
Cy (**17**)	170	3920	59000	26500	2.2

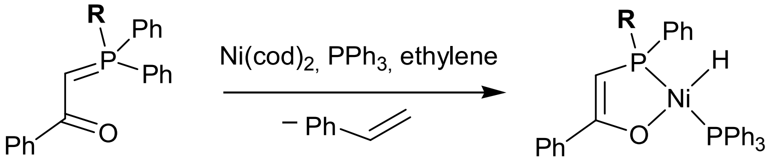
Conditions: cat. 0.1 mmol, 20 mL PhMe, 15 h, 50 bar (batch), 100°C; [a] cone angle values of the corresponding PR_2Ph ligands.

The authors proposed that bulky P-substituents favour conformations of the polymer chain with the β-CH closer to the *trans* position of the phosphanyl group. Note that the polydispersities also display a strong dependence toward the bulkiness of the substituents (Table 3).

2. In the presence of L

If the catalyst is associated with an L ligand, *e. g.* a tertiary phosphine, the impact of the $P_{chelate}$ substituents is more difficult to predict. Intuitively, one may anticipate that with a moderately coordinating L ligand, the catalytic behaviour will be similar to that described above in the absence of L. Indeed Keim showed that in the presence of PPh_3, variations within the $P_{chelate}$-substituents only weakly affect the activity of enolato nickel complexes. On the other hand, important changes were found in the product distribution (Table 4): as expected

Table 4. Influence of the $P_{chelate}$ substituents on the chain length.



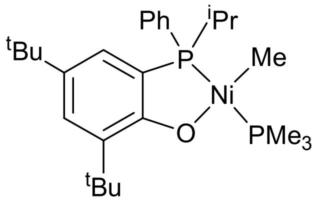
R	solid (wt.-%)	M_n (g mol^{-1})	M_w (g mol^{-1})	M_w/M_n
Ph (**1**)	0	/	/	/
Me (**18**)	47	520	1330	2,55
Et (**19**)	74	650	1830	2,80
Cy (**20**)	81	480	1550	3,20
Menthyl (**21**)	93	860	5470	6,35

Conditions: 100°C, 10 h, 40 bar, 20 mL PhMe, ylide 0.05 mmol, $Ni(cod)_2$ 0.05 mmol, PPh_3 0.05 mmol)

(see above), more basic $P_{chelate}$ moieties result in longer chains.[57] The same holds when the steric encumbrance of the $P_{chelate}$ substituents is increased. As in the case without L, the polydispersity increases with increasing basicity and bulkiness of the $R_2P_{chelate}$ moiety.

Similar results were found by Heinicke et al. for phosphanylphenolate-based catalysts.[45] These authors also studied the catalytic behaviour of different nickel $(R_2P{\sim}O)_{phenolato}$ complexes in the presence of basic PR_3 ligands. Molecular weights are in general lower with $Ph_2P{\sim}ONi$ than with $Cy_2P{\sim}ONi$, whatever the phosphine additive used, hence reflecting the better labilising effect induced by the Cy_2P moiety on the trans-positioned phosphine. However, with certain basic phosphines, such as P(*p*-tolyl)$_3$ or P(*m*-tolyl)$_3$ the α-olefin selectivity drops, suggesting that steric effects may lower the stability of the P,O chelate. Surprisingly, in the presence of PMe_3 the distribution of the oligomers produced with the $^iPr_2P$-phenolato complex **15** is shifted toward molecular weights lower than those of the olefins formed with the less electron-rich Ph_2P-analogue **14** (Table 5).[44] This behaviour contrasts with that of related Ni(*P,O*) complexes not associated with a phosphine ligand.[46] The authors have proposed that, in this particular case, the β-elimination step occurs on a PMe_3-coordinated intermediate, and that the higher β-elimination rate found for **15** is due to a higher electron density at the nickel centre in comparison of **14**.[44] It should be recalled that Ni(II) readily forms pentacoordinated complexes with PMe_3, unlike other phosphines.

Table 5. Influence of the $P_{chelate}$ substituents on chain length and activity.



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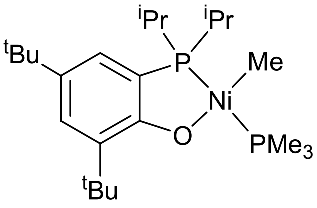


23

TON 257 2174

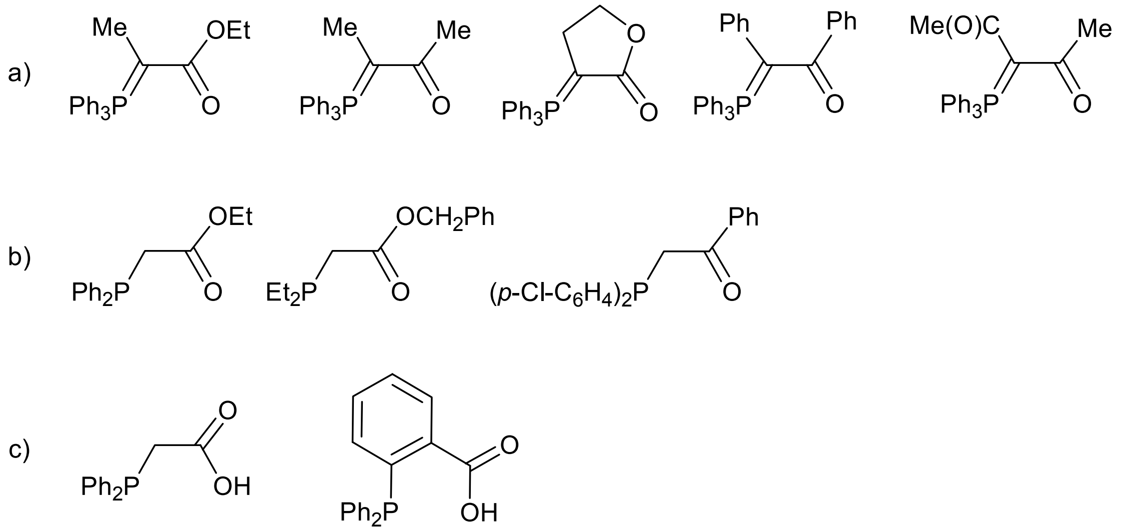
Oligomer distribution (wt.-%)	C_4	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{14+}
22	3.0	8.2	10.3	11.2	11.6	11.6	44.1
23	8.0	19.2	19.5	15.1	3.9	0.9	33.3

Conditions: 0.1 mmol cat., 12 mL PhMe, 35 bar, 6-10 h.

Overall, it seems that the $P_{chelate}$ substituents largely influence the β-elimination rate, in the absence and in the presence of phosphines of moderate basicity (such as PPh_3), but exert only a weak influence on the chain propagation rate. However, in the presence of a strongly coordinating L ligand, the rate-limiting step can switch to ethylene coordination, the activity of the catalyst being then mainly tuned by the donor properties of the $P_{chelate}$ atom through its trans influence.

B. Variation of the *P,O* backbone

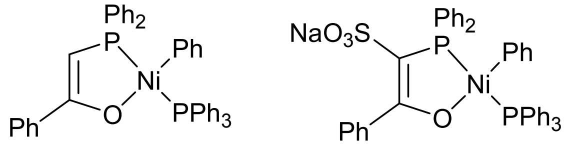
The chelate part is the one that allows the most variation opportunities. Indeed, it is possible to change its substituents, its size (i.e. the number of atoms between the P and O atoms) and its charge. Furthermore, by anchoring another [Ni(*P,O*)] moiety onto the *P,O* backbone, bimetallic complexes may be obtained. Most of the studies that aimed at tuning the catalyst activity through backbone variations have only appeared recently, even if the patents published in the early 70's have already cover a great variety of catalyst precursors (Scheme 7).[1-7,15-19]



Scheme 7. Examples of organic precursors of Ni(*P,O*) catalysts patented in the early 70's: a) β-keto phosphorus ylides, b) β-(carbonyl)phosphines, c) phosphino carboxylic acids

1. Electronic effects of substituents positioned on the $C_{\alpha\text{-P}}$ and $C_{\beta\text{-P}}$ atoms

The first example of a drastic activity enhancement through chelate modification of Keim's catalyst **1** was reported by Klabunde et al. in 1987 (Scheme 8).[30,31] The authors showed that anchoring an electron-withdrawing sulfonato substituent at the $C_{\alpha\text{-P}}$ atom of catalyst **16** led to an activity increase of two orders of magnitude.

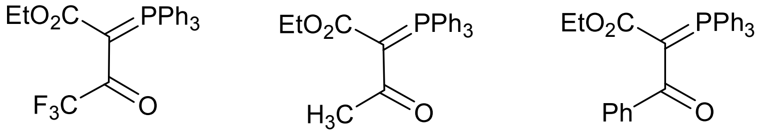


	1	**24**
TOF	6000	515000
M_w (g/mol) (M_w/M_n)	ca. 6000 (2)	133000 (10.2)

Scheme 8. Effect of a sulfonato substituent on the $C_{\alpha\text{-P}}$ atom. Conditions: PhMe, excess [Ni(cod)$_2$], 4 bar C_2H_4, 60°C (**1**) or 28°C (**24**).

The averaged molecular weight of the polyethylene formed also considerably increased, going from M_w = 6000 in the presence of **1** to M_w = 133000 with **24**. Catalyst **24** was also found to be active in ethylene/polar monomers copolymerisation[30] and ethylene/α-olefin cooligomerisation[33-35].

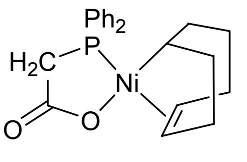
More recently, Claverie et al. have reported a highly active catalyst based on the β-keto phosphorus ylide **25**, which contains two electron withdrawing substituents, namely a CF_3 and a CO_2Et group (Scheme 9).[58] According to the authors, the activity of this catalyst reaches that of early transition metal polymerisation catalysts. The CF_3 group adjacent to the oxygen atom, which is a much stronger electron-withdrawing group than the CO_2Et group, seems to be crucial for the activity increase, as the related catalyst systems based on **26** and **27** display considerably lower activities. Interestingly, **25** results in polyethylene chains that are shorter than those obtained with **26** and **27**, unambiguously demonstrating the effect of a strong electron withdrawing group positioned on the $C_{\beta\text{-P}}$ atom. Note, this effect strongly contrasts with that of the SO_3Na group positioned on the $C_{\alpha\text{-P}}$ atom of **24**. Overall, these findings suggest that the olefin distribution may be influenced by the position of the electron-withdrawing substituent on the *P,O* backbone.



	25	**26**	**27**
TOF max.	> 4.2×10^6	21000	73000
M_w (g/mol)	3500	10000	8000
M_w/M_n	2.7	3.1	2.9

Scheme 9. β-keto phosphorus ylides bearing electron withdrawing substituents which were used in the nickel catalysed polymerisation of ethylene (conditions: PhMe 400 mL, 3 bar C_2H_4, 70°C)

Other electron-withdrawing substituents were found to strongly enhance chain termination over chain propagation. The most striking examples are the catalysts **28**[21] and **29**[13,59]. These catalysts, which display good activities, are able to produce a high content of lower α-olefins even in the absence of a phosphine ligand.



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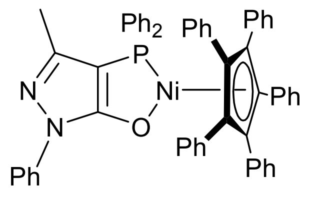
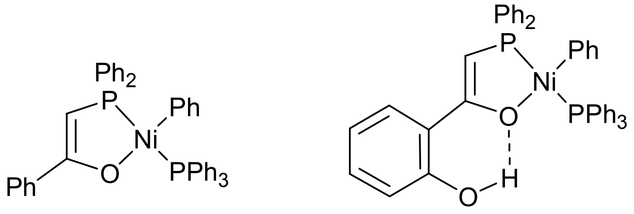


29

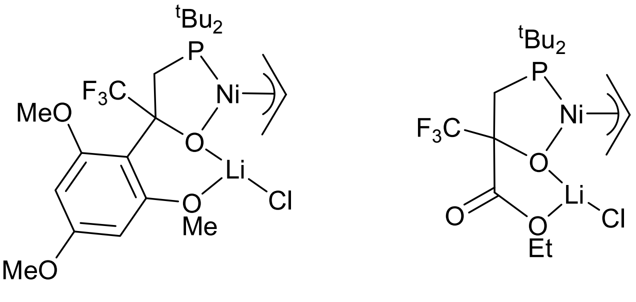
A similar effect was found in ethylene oligomerisation with the phosphine-containing catalyst **30** (Scheme 10).[60,61] In this case, the electron-withdrawing effect results from hydrogen bonding between the oxygen atom of the *P,O* chelate and the phenolic OH. In comparison to **1**, complex **30** significantly shifts the α-olefin distribution toward lower oligomers, the activity remaining unchanged.



	1	**30**
TOF	5700	5700
α	0.70	0.48

Scheme 10. Compared catalytic behaviour of **1** and **30** (Conditions: 0.10 mmol cat., 20 mL PhMe, 60-80°C, 1.5 h, P = 55 bar).

The idea to use Ni(*P,O*) catalysts combining an electron-rich phosphorus atom with an oxygen atom being bonded to second metal ion was exploited by researcher at Du Pont. Thus, complexes **31** and **32**, in which the oxygen atom of the chelate coordinates to LiCl, proved to be efficient ethylene polymerisation catalysts (Scheme 11).[29,62]

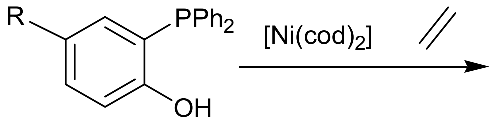


	31	**32**
TON	27700	17300
M_w	13900	30500
M_w/M_n	4.9	18.3

Scheme 11. Catalytic behaviour of **31** and **32** in ethylene polymerisation (Conditions: 0.02 mmol cat., 10 mL 1,3,5-$C_6H_3Cl_3$, 25°C, 18 h, P = 69 bar, 10 equiv. $B(C_6F_5)_3$).

Heinicke et al. have investigated a series of diphenylphosphanylphenolates in which the phenol ring contains a substituent (R = H, Me, OMe, F) located on the *p*-OH carbon atom (Table 6).[46] The study shows that the R groups used have only a modest impact on the molecular weights. Among the catalysts tested, the highest catalytic activity was observed for R = OMe.

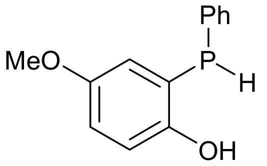
Table 6. Influence of substituents on phosphanylphenolato ligands.



R	TON	M* (g mol^{-1})
H (**6**)	2960	2000
Me (**33**)	3140	1560
OMe (**34**)	4570	2340
F (**35**)	2960	2840

Conditions : 0.1 mmol cat., PhMe 20 mL, 50 bar C_2H_4 (batch), 100°C, 15 h;
* determined by ^{1}H NMR.

The authors have also investigated the behaviour of P(alkyl)$_2$-analogues of **6** and **33**-**35** . They found that the corresponding TON variations parallel those reported for the PPh$_2$-compounds. However, in this case the MeO- and F-derivatives result in polyethylene with significantly shorter chains than those formed for R = H.[46] A totally different behaviour was found for catalysts having a secondary phosphine (Scheme 1 2).[46,62] In this case, the introduction of a methoxy substituent induces a drastic increase of the molecular weight of the formed polyethylene.



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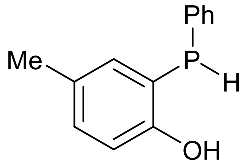
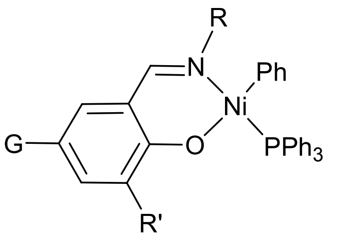


37

	36	37
TOF	227000	149000
M_w	696800	16360

Scheme 12. Catalytic behaviour of phosphanylphenolate based catalysts containing a secondary P (conditions: ca. 0.1 mmol ligand, 1 equiv. [Ni(cod)$_2$], 50 bar, 20 mL PhMe, 80°C (**36**) or 120°C (**37**), 15 h).

Salicylaldiminato nickel complexes, which constitute *N,O*-analogues of phosphanylphenolato nickel complexes (Scheme 13), have recently also been assessed as ethylene oligomerisation and polymerisation catalysts.[63,64] It was shown that introduction of electron withdrawing substituents (*e.g.* G = NO_2) on the para position of the phenolate ligand in complexes of the type shown in Scheme 13 results in an activity increase. This is in accord with a theoretical study which established that such substituents increase the ethylene insertion rate as a result of an electron density decrease of the phenolate oxygen atom.[65] Electron-releasing groups, such as OMe, produce the opposite effect. These results contrast somewhat with those reported by Heinicke for **34**/Ni, but fit well with the general observation made for Ni(*P,O*) catalysts, that tethering electron withdrawing substituents at the chelate increases the activity of the catalyst.



G = H, OMe, NO_2
R = Ph, 2,6-$(^iPr)_2C_6H_3$
R' = H, ^tBu, 9-anthracenyl

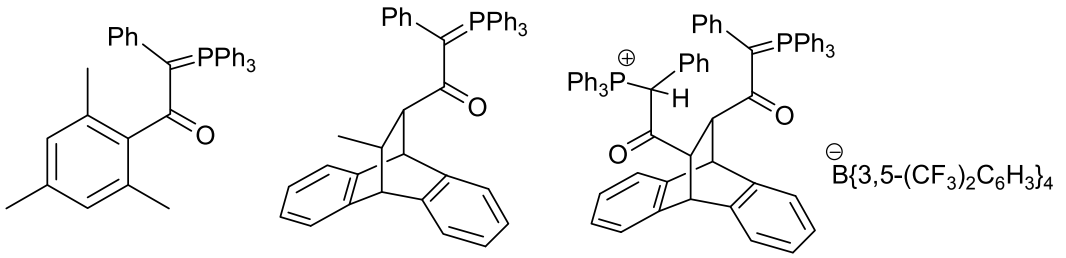
Scheme 13. Salicylaldimine-based nickel catalysts.

Further studies that aim at understanding the electronic influence of chelate substituents on the catalytic centre (in the absence and in the presence of a phosphine ligand) are still needed. An idea that is emerging is that substituents which exert a selective electronic influence on either the phosphorus or the oxygen atom could allow a better tuning of the catalytic outcome. In this regard, only few studies have been dealing with the influence of substituents directly connected to the carbon atoms of the *P,O* arm.

2. Steric effects of substituents positioned on the $C_{\alpha\text{-P}}$ and $C_{\beta\text{-P}}$ atoms

It is well known that steric shielding of the metal centre (actually of the axial coordination sites) in α-diimine and salicylaldiminato nickel complexes allows production of high molecular weighted polymers.[66] Interestingly, to date, there a no studies about similarly crowded Ni(*P,O*) complexes. This is rather surprising, since such structures could easily be achieved, for instance by substituting the $P_{chelate}$ atom by *o*-functionalised aryl rings.

Gibson et al. have studied the beneficial role of bulky substituents directly linked to the carbonyl group. Thus, catalysts formed from ylides **39** and **40** are considerably more active in ethylene polymerisation than that derived from the less bulky **38** (Scheme 14).[32] The bulky anthracenyl group in these ylides possibly protects the nickel from binding of potentially poisoning donor groups, and also disfavours the coordination of another nickel centre to the oxygen atom which would result in a catalytically inactive Ni(*P,O*)$_2$ complex[31] (*vide supra*).



	38	**39**	**40**
TOF	14300	54200	527600
M_n (g/mol)	4200	5200	9900

Scheme 14. Ethylene polymerisation with keto-phosphorus ylides bearing a bulky substituent (conditions: for **38** and **39**: ca. 5 mmol ylide, 5 equiv. [Ni(cod)$_2$], P =1 bar, 70°C, PhMe, 15 min; for **40**: P = 4 bar, 2.5 mmol ylide, 12 equiv. [Ni(cod)$_2$], PhMe, 50°C)

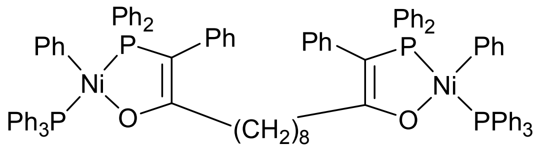
As expected, increasing the steric crowding of one of the keto substituents has only a moderate impact on the polyethylene molecular weight distribution.

Finally, it is noteworthy that these catalysts were found suitable for the production of methylmethacrylate end-functionalised polyethylene.[67]

3. Bimetallic catalysts

In the mid 90's, Kurtev and Tomov published a series of molecular catalysts containing two identical Ni(*P,O*) subunits separated by spacers of different length and flexibility (**41**-**47**). The complexes, which were generated from the appropriate bis(ylide), were assessed in ethylene oligomerisation and polymerisation[68,69] as well as in propylene dimerisation[70]. The study revealed that the selectivity in linear olefins of the bimetallic catalysts **41**-**43**, when used as oligomerisation catalysts, is much lower than that of comparable mononuclear systems

(Table 7). Thus, beside the expected α-olefins, internal olefins as well as co-oligomerisation products such as 2-ethyl-1-butene are formed. The authors proposed that the mechanism of co-oligomerization could include intramolecular substrate transfer involving both metal centres. The oligomerisation activities vary in the order **43** > **42** > **41**. The reason for the higher activity of **43** remains unclear, but, according to the authors, possibly relates to a steric effect.



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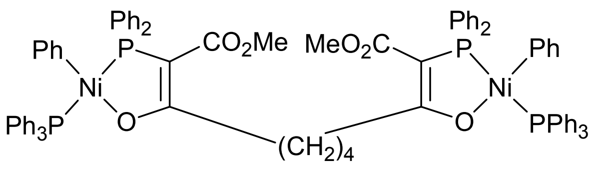

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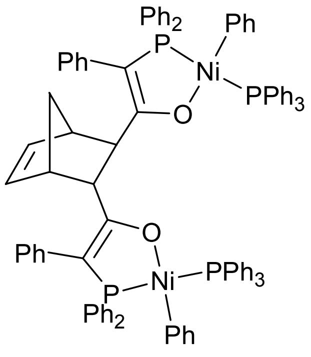

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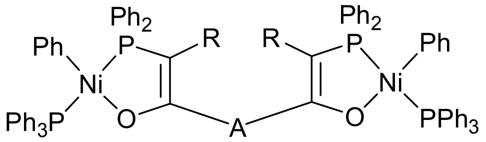


44 R = Ph; A = 1,3-C_6H_4
45 R = H; A = 1,4-C_6H_4
46 R = Ph; A = $(CH_2)_8$
47 R = Ph; A = 1,1'-(η^5-C_5H_4)$_2$Fe

Table 7. Ethylene oligomerisation with bimetallic catalysts **41**-**43**.

Cat.	TOF	Linearity (wt.-%)	α-portion (wt.-%)	2-ethyl-1-butene (wt.-%)
41	2135	85.4	80.3	9.2
42	2930	70.8	71.6	29.0
43	3035	86.7	72.3	11.2

Conditions: 0.01 mmol cat., PhMe 100 mL, 1-6 h, 70°C, 23 bar C_2H_4.

The authors further assessed the bis-nickel complexes **41**-**47** in the polymerisation of ethylene (Table 8).[69] They found that the presence of a phosphine scavenger is not needed with **44** nor **45**, but is required in all other cases. The highest activity was again observed for the system derived from **43**. The authors showed that the activity correlates with the variation of the P=C force constant between the ylide and the corresponding complex, as well as that of the C=O force constant. The observed differences were taken as a measure of the ethylene coordination strength (and accordingly its activation) in the catalytic complex. It is likely that because of steric repulsions between the norbornene part and the individual *P,O* chelates of **43**, the electron distribution within the *P,O* chelate is modified and results in a better activation of the coordinated ethylene, which accordingly leads to an increased activity.

Table 8. Ethylene polymerisation with Ni/bis-ylide catalysts **41**-**47**.

Cat.	A	P (atm)	TOF
41	-$(CH_2)_8$-	25	4000
42	-$(CH_2)_4$-	17	11500
43		5.4	14600
44	1,3-C_6H_4	5.5	2100
45	1,4-C_6H_4	4.2	5700
46	-$(CH_2)_8$-	25	1900
47	1,1'-$(\eta^5\text{-}C_5H_4)_2Fe$	25	1700

Conditions: 10-150 mg cat., excess [Ni(cod)$_2$], 50°C, PhMe 100 mL.

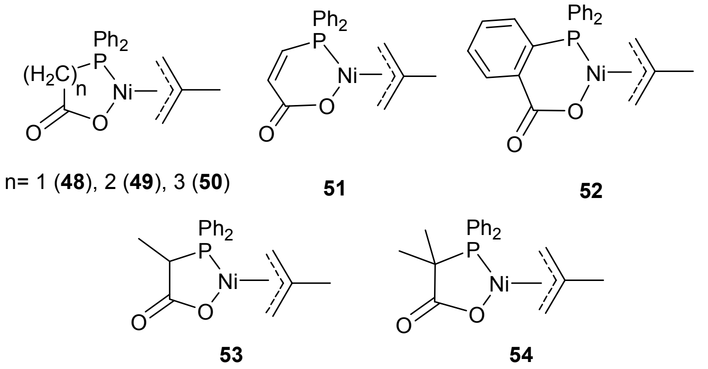
It should be noted here that the method used by Kurtev for obtaining information about the electron density at the metal centre contrasts with that used by Keim et al. for other Ni(*P,O*) complexes, the latter being based on X-ray photoelectron spectroscopy (ESCA).[18]

In conclusion, bimetallic Ni(*P,O*) catalysts are promising systems. In view of the results outlined above, sophistication of such systems could find specific applications in cooligomerisation or copolymerisation reactions, or for increasing the content of branched compounds in ethylene polymerisation. Finally, it should be mentioned that such effects were recently observed with bimetallic metallocene catalysts.[71]

4. Changing the length of the chelate backbone

Most of the Ni(*P,O*) polymerisation catalysts that have been studied so far are based on a rigid, five-membered metallacycle. It was observed that larger metallacycles usually result in a dramatic activity drop. This was shown in a study by Keim et al. on the phosphanylcarboxylato nickel complexes **48-54** (Table 9).[72]

Table 9. Influence of the backbone size and flexibility.


n= 1 (**48**), 2 (**49**), 3 (**50**)
51
52
53
54

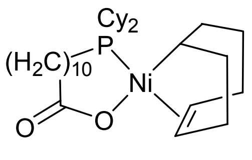
Cat.	TON	C_{max}
48	3740	waxes
49	143	C_{20}
50	107	C_6
51	582	C_{34}
52	2912	waxes
53	5276	waxes
54	4920	waxes

Conditions: 0.15 mmol cat., PhMe 30 mL, 50 bar, 12h.

On going from **48** to **49,** that is by introducing an additional CH_2 unit in the backbone, the productivity is divided by a factor 25. This is due to an increase of the backbone flexibility, as the replacement of the ethylenic group of **49** by a C=C double bond (as in complexes **51** and **52**) leads to higher productivities. The lengthening of the backbone is associated with an increase of the ligand basicity, which in turn increases the activity. This is clearly shown by comparing the TONs of catalysts **48** with those of **53** and **54** in which methyl groups have been grafted on the backbone.[72] Thus, electronic factors can be excluded to explain the activity drop. The correlation between backbone flexibility and activity may be attributed to an equilibrium between square planar and tetrahedral complexes, the formation of the latter being favoured for longer backbones. It is assumed that only the square planar form is active.[72] Such equilibria are well known for $[\{R_2P(CH_2)_nPR_2\}NiX_2]$ complexes with n > 3.[73] Note, a recent study on polymerisation catalysts of the latter type revealed a similar correlation between activity and backbone length.[74]

Lengthening of the *P,O* backbone further induces the formation of considerably lower weighted material, but this effect was not explained. A similar effect was observed with cationic Ni(*P,O*) complexes.[75]

The longest *P,O* chelators used to date are those found in the carboxylato complexes **55**-**57**. The latter oligomerise ethylene to α-olefins, but at rates lower than those observed for **1**.[76]



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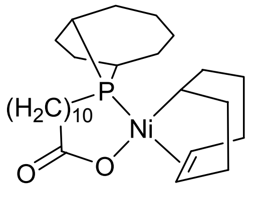

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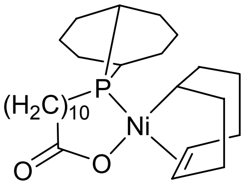

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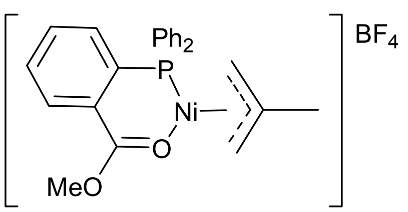
5. Neutral vs. anionic *P,O* chelators

The discovery that cationic nickel(II) complexes containing a neutral *P,O* chelate can also be employed in ethylene oligomerisation was only made in 1994.[77] The late introduction of such complexes is rather surprising considering that cationic nickel-allyl complexes have been employed for many years in catalytic C-C coupling reactions.[78] Catalyst **58**, for example, was found to be considerably more active than the related neutral complex **52** (TON(**58**) = 770; 0.1 mmol Ni; 3 bar; 0°C; TON(**52**) = 340; 0.05 mmol Ni; 40 bar; 100°C).



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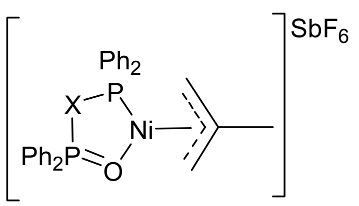
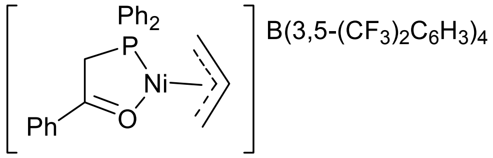


59 X = o-C_6H_4
60 X = NH
61 X = CH_2

The products formed consisted in a mixture of linear and branched oligomers, indicating that the catalysts are also active in ethylene/α-olefins copolymerisation.[77] This ability (or this lack of selectivity) was explained by the labile character of the oxygen atom.[75] Thus, substitution of the ester group by a phosphine-oxide moiety, which behaves as a better donor ligand (in *e.g.* complexes **59-61**), resulted in an increase of the selectivity in linear olefins.[75] However, with such complexes, owing to olefin isomerisation, the α-olefin selectivity remains low.[75]

As a general trend, cationic catalysts present very high β-elimination rates. For example, with **59** no olefins longer than C_{34} were detected. A typical example is catalyst **62,** which may be regarded as cationic version of **1**, and which produces only a mixture of butenes (Table 10).[79]

Table 10. Effect of phosphorus substituents on cationic ethylene oligomertisation/ polymerisation catalysts.



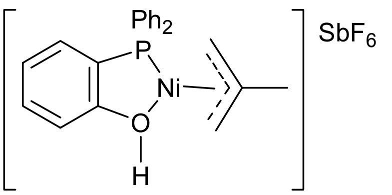
62 R = Ph
63 R = 2,4,6-$(CH_3)_3C_6H_2$
64 R = ^tBu

Cat.	P (bar)	t (min)	TOF	Products
62	13.8	15	$1.3\ 10^6$	1-butene (85%) 2-butene (15%)
63	13.8	30	$1.1\ 10^6$	PE (M_n = 860)
64	13.6	60	$2.4\ 10^5$	PE (M_n = 3700)

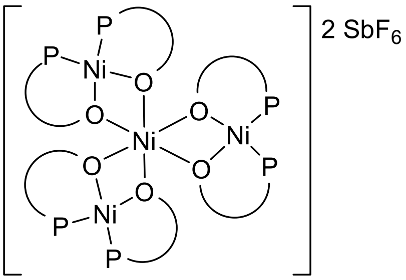
Conditions: ca. 2 µmol of cat., 25 °C, ca. 100 mL PhMe.

However, using of a more basic phosphine moiety can reduce the β-elimination rate. For example, with catalysts **63** or **64**, containing respectively $P(mesityl)_2$ and $P(^tBu)_2$ groups, linear polyethylene is produced.[79,80] All catalysts shown in Table 10 exhibit remarkably high TOFs, which are comparable to those of early transition metal catalysts.[80] It should be noted that the catalyst stability is strongly dependent upon the nature of the phosphorus substituents. Thus, while **62** is completely deactivated after 15 min, **64** is still active after 1 h.

Heinicke et al. recently reported the cationic phosphino-phenol complexes **65** and **66**, which were shown to be rather unstable, their decomposition leading to tetranuclear complexes of type **67**.[81] Despite their restricted stability, both complexes proved to be highly active catalysts for the conversion, at room temperature, of ethylene into isomeric mixtures of butenes, hexenes and lower amounts of higher olefins. The C_6 fraction consisted mainly of branched and internal olefins.



65 R= Ph
66 R= Cy



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V. Conclusion

In the last three decades, many examples of highly efficient SHOP-like catalysts appeared in the literature. Their study helped to gain insight into the factors that govern their reactivity and also largely contributed to the understanding of particular aspects of the mechanism leading to polyolefin production.

It was clearly established that beside the (*P,O*) chelate, the monodentate tertiary phosphine present in such complexes plays a key role for tuning the α-olefin distribution. Provided this phosphine is able to reversibly bind the metal centre during the catalytic process, the better its coordination strength, the higher the β-elimination rate. The most recent studies illustrating the relevance of the monodentate phosphine led to the conclusion that there are at least two mechanisms leading to chain termination.

Many studies have shown that variation of the $P_{chelate}$ properties allows for tuning the molecular weight distribution. Thus, the higher the basicity of this phosphorus atom, the higher the molecular weights of the polyolefins produced. On the other hand, increasing the bulkiness of the P-substituents was found to induce the opposite effect.

The introduction of electron-withdrawing substituents on the chelate backbone of anionic *P,O* ligands was shown to drastically increase the rate of ethylene insertion. As expected, the same effect is observed when using a cationic complex containing a neutral *P,O* chelator.

Some recently reported SHOP-like catalysts displayed activities that compare with those of early transition metal polymerisation catalysts. The impact of electron-withdrawing substituents, both on the catalyst activity and on the chain length of the polyolefins produced, is sometimes difficult to predict. Further studies showing how their nature and their position on the chelate backbone may influence the catalytic outcome will certainly help to rationalise the observed effects.

The presence of steric groups in close proximity to the oxygen atom of the chelate were shown to effectively stabilise the active species, and hence to improve the catalysts productivities. Interestingly, the effects of bulky $P_{chelate}$-substituents able to protect the axial positions of the nickel centre have not been investigated yet. These could, in principle, favour the formation of higher polymers.

Finally, one may anticipate that in the forthcoming years modified SHOP-complexes, especially bimetallic ones, will find new applications in various ethylene copolymerisation reactions.

References

[1] R. Mason, (Shell Oil Co.), US 3737475, **1973**.

[2] H. van Zwet, R. Bauer and W. Keim, (Shell Oil Co.), US 3644564, **1972**.

[3] P. W. Glockner, W. Keim and R. F. Mason, (Shell Oil Co.), US 3647914, **1972**.

[4] R. Bauer, P. W. Glockner, W. Keim, H. van Zwet and H. Chung, (Shell Oil Co.), US 3644563, **1972**.

[5] R. Bauer, P. W. Glockner, W. Keim and R. F. Mason, (Shell Oil Co.), US 3647915, **1972**.

[6] R. F. Mason, (Shell Oil Co.), US 3676523, **1972**.

[7] R. F. Mason, (Shell Oil Co.), US 3686351, **1972**.

[8] P. M. Morse, *Chem. & Eng. News* **1999**, *77*, 19-25.

[9] J. Skupinska, *Chem. Rev.* **1991**, *91*, 613-648.

[10] O. Kolodiazhnyi, *Phosphorus Ylides*, Wiley-VCH, Weinheim, **1999**.

[11] W. Keim, F. H. Kowaldt, R. Goddard and C. Krüger, *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 466-467.

[12] D. Matt, M. Huhn, J. Fischer, A. De Cian, W. Kläui, I. Tkatchenko and M. C. Bonnet, *Dalton Trans.* **1993**, 513-524.

[13] M. Huhn, M. Burgard, D. Matt and J. Steiner, (EEHEICS), DE 4415725, **1994**.

[14] M. D. Fryzuk, X. Gao and S. J. Rettig, *Can. J. Chem.* **1995**, *73*, 1175-1180.

[15] R. S. Bauer, H. Chung, P. W. Glockner and W. Keim, (Shell Oil Co.), US 3635937, **1972**.

[16] R. Bauer, H. Chung, W. Keim and H. Van Zwet, (Shell Oil Co.), US 3661803, **1972**.

[17] R. Bauer, H. Chung, L. G. Cannell, W. Keim and H. Van Zwet, (Shell Oil Co.), US 3637636, **1972**.

[18] R. Bauer, H. Chung, K. W. Barnett, P. W. Glockner, W. Keim and H. van Zwet, (Shell Oil Co.), US 3686159, **1972**.

[19] D. M. Singleton, P. W. Glockner and W. Keim, (Shell Int. Res.), GB 1364870, **1974**.

[20] U. Müller, W. Keim, C. Krüger and P. Betz, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1011-1013.

[21] M. Peuckert and W. Keim, *Organometallics* **1983**, *2*, 594-597.

[22] A. L. Monteiro, M. O. de Souza and R. F. de Souza, *Polymer Bulletin* **1996**, *36*, 331-336.

[23] P. J. Flory, *J. Am. Chem. Soc.* **1940**, *62*, 1561-1565.

[24] G. V. Schulz, *Z. Physik. Chem.* **1939**, *B43*, 25-46.

[25] G. V. Schulz, *Z. Physik. Chem.* **1935**, *B30*, 379-388.

[26] M. Fortuny, M. Nele, P. A. Melo and J. C. Pinto, *Macromol. Theory Simul.* **2004**, *13*, 355-364.

[27] W. Keim, *New J. Chem.* **1987**, *11*, 531-534.

[28] L. K. Johnson and L. Wang, (Du Pont), WO 03031485, **2003**.

[29] L. Wang, E. Hauptman, L. K. Johnson, E. Forrester McCord, Y. Wang and S. D. Ittel, (Du Pont), US 2002032289, **2002**.

[30] U. Klabunde and S. D. Ittel, *J. Mol. Catal.* **1987**, *41*, 123-134.

[31] U. Klabunde, R. Mulhaupt, T. Herskovitz, A. H. Janovicz, J. Calabrese and S. D. Ittel, *J. Polym. Sci. Part A: Polym. Chem.* **1987**, *25*, 1989-2003.

[32] V. C. Gibson, A. Tomov, A. J. P. White and D. J. Williams, *Chem. Commun.* **2001**, 719-720.

[33] Y. V. Kissin, *J. Polym. Sci. Part A: Polym. Chem.* **1989**, *27*, 605-621.

[34] Y. V. Kissin, *J. Polym. Sci. Part A: Polym. Chem.* **1989**, *27*, 623-637.

[35] Y. V. Kissin and D. L. Beach, *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 147-155.

[36] J. Pietsch, P. Braunstein and Y. Chauvin, *New J. Chem.* **1998**, *22*, 467-472.

[37] G. A. Nesterov, G. Fink and V. A. Zakharov, *Macromol. Rapid Commun.* **1989**, *10*, 669-673.

[38] G. A. Nesterov, V. A. Zakharov, G. Fink and W. Fenzl, *J. Mol. Catal.* **1991**, *69*, 129-136.

[39] M. Peuckert, W. Keim, S. Storp and R. S. Weber, *J. Mol. Catal.* **1983**, *20*, 115-127.

[40] G. A. Nesterov, V. A. Zakharov, G. Fink and W. Fenzl, *J. Mol. Catal.* **1991**, *66*, 367-372.

[41] G. Braca, M. Di Girolamo, A. M. Raspolli Galletti, G. Sbrana, M. Brunelli and G. Bertolini, *J. Mol. Catal.* **1992**, *74*, 421-431.

[42] G. Braca, M. Di Girolamo, A. M. Raspolli Galletti, G. Sbrana, R. Silla and P. Ferrarini, *J. Mol. Catal. A: Chem.* **1995**, *96*, 203-213.

[43] C. Müller, L. J. Ackerman, J. N. H. Reek, P. C. J. Kamer and P. W. N. M. van Leeuwen, *J. Am. Chem. Soc.* **2004**, *126*, 14960-14963.

[44] J. Heinicke, M. He, A. Dal, H. F. Klein, O. Hetche, W. Keim, U. Flörke and H.-J. Haupt, *Eur. J. Inorg. Chem.* **2000**, 431-440.

[45] J. Heinicke, M. Köhler, N. Peulecke and W. Keim, *J. Catal.* **2004**, *225*, 16-23.

[46] J. Heinicke, M. Köhler, N. Peulecke, M. He, M. K. Kindermann, W. Keim and G. Fink, *Chem. Eur. J.* **2003**, *9*, 6093-6107.

[47] A. Held, S. Mecking and F. M. Bauers, *Chem. Commun.* **2000**, 301-302.

[48] S. Mecking and F. M. Bauers, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2000**, *41*, 209-210.

[49] S. Mecking and F. M. Bauers, *Macromolecules* **2001**, *34*, 1165-1171.

[50] S. Mecking, A. Held and F. M. Bauers, *Angew. Chem. Int. Ed.* **2002**, *41*, 544-561.

[51] L. Kolb, V. Monteil, R. Thomann and S. Mecking, *Angew. Chem. Int. Ed. Engl.* **2005**, *44*, 429-432.

[52] K. A. O. Starzewski and J. Witte, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 63-64.

[53] W. Keim and R. Nücker, *Chem. Ing. Tech.* **1994**, *66*, 950-951.

[54] A. Bader and E. Lindner, *Coord. Chem. Rev.* **1991**, *108*, 27-110.

[55] W. Keim, *J. Mol. Catal. A: Chem.* **2004**, *224*, 11-16.

[56] P. Braunstein, *Chem. Rev.* **2006**, *106*, 134-159.

[57] K. Hirose and W. Keim, *J. Mol. Catal.* **1992**, *73*, 271-276.

[58] R. Soula, J. P. Broyer, M. F. Llauro, A. Tomov, R. Spitz, J. Claverie, X. Drujon, J. Malinge and T. Saudemont, *Organometallics* **2001**, *34*, 2438-2442.

[59] D. Matt, M. Huhn, M. Bonnet, I. Tkatchenko, U. Englert and W. Kläui, *Inorg. Chem.* **1995**, *34*, 1288-1291.

[60] P. Braunstein, Y. Chauvin, S. Mercier and L. Saussine, *C. R. Chimie* **2005**, *8*, 31-38.

[61] P. Braunstein, Y. Chauvin, S. Mercier, L. Saussine, A. De Cian and J. Fischer, *J. Chem. Soc., Chem. Commun.* **1994**, 2203-2204.

[62] O. Kristen, J. Heinicke, W. Keim, M. Köhler and M. He, (BASF AG), DE 19947519, **2001**.

[63] C. Wang, S. Friedrich, T. R. Younkin, R. T. Li, R. H. Grubbs, D. A. Bansleben and M. W. Day, *Organometallics* **1998**, *17*, 3149-3151.

[64] T. Younkin, E. F. Connor, J. I. Henderson, S. K. Friedrich, R. H. Grubbs and D. A. Bansleben, *Science* **2000**, *287*, 460-462.

[65] M. S. W. Chan, L. Deng and T. Ziegler, *Organometallics* **2000**, *19*, 2741-2750.

[66] S. D. Ittel, L. K. Johnson and M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169-1204.

[67] V. C. Gibson and A. Tomov, *Chem. Commun.* **2001**, 1964-1965.

[68] K. Kurtev and A. Tomov, *J. Mol. Catal.* **1994**, *88*, 141-150.

[69] K. Kurtev and A. Tomov, *J. Mol. Catal. A: Chem.* **1995**, *103*, 95-103.

[70] M. Mitkova, A. Tomov and K. Kurtev, *J. Mol. Catal. A: Chem.* **1996**, *110*, 25-32.

[71] L. Li, M. V. Metz, H. Li, M.-C. Chen, T. J. Marks, L. Liable-Sands and A. L. Rheingold, *J. Am. Chem. Soc.* **2002**, *124*, 12725-12741.

[72] W. Keim and R. P. Schulz, *J. Mol. Catal.* **1994**, *92*, 21-33.

[73] L. Sacconi and J. Gelsomini, *Inorg. Chem.* **1968**, *7*, 291-294.

[74] I. Albers, E. Alvarez, J. Campora, C. M. Maya, P. Palma, L. J. Sanchez and E. Passaglia, *J. Organomet. Chem.* **2004**, *689*, 833-839.

[75] I. Brassat, W. Keim, S. Killat, M. Möthrath, P. Mastrorilli, C. F. Nobile and G. P. Suranna, *J. Mol. Catal. A: Chem.* **2000**, *157*, 41-58.

[76] H. K. Luo and D. G. Li, *Applied Organomet. Chem.* **2000**, *14*, 389-393.

[77] M. C. Bonnet, F. Dahan, A. Ecke, W. Keim, R. P. Schulz and I. Tkatchenko, *J. Chem. Soc. Chem. Commun.* **1994**, 615-616.

[78] R. B. A. Pardy and I. Tkatchenko, *J. Chem. Soc. Chem. Commun.* **1981**, 49-50.

[79] J. M. Malinoski and M. Brookhart, *Organometallics* **2003**, *22*, 5324-5335.

[80] W. Liu, J. M. Malinoski and M. Brookhart, *Organometallics* **2002**, *21*, 2836-2838.

[81] J. Heinicke, M. Köhler, N. Peulecke, M. K. Kindermann, W. Keim and M. Köckerling, *Organometallics* **2005**, *24*, 344-352.

Chapter 2

An Efficient Keim-Type Catalyst Based on an Electron-Poor P,O-Chelate; Tuning the Selectivity of Ethylene Oligomerisation towards Short α-Olefins.

Abstract

The tertiary phosphane Ph_2P-pzONa, in which the phosphorus atom is substituted by an electron-withdrawing pyrazolonato unit, reacts with *trans*-[$NiPhCl(PPh_3)_2$] to afford quantitatively *trans*-*P*,*P*'-[$NiPh(Ph_2P\text{-}pzO)(PPh_3)$] (**4**), the first Keim-type catalyst derived from an amide. In the absence of any cocatalyst, complex **4** converts ethylene in high selectivity and activity into linear α-olefins. The product distribution is drastically shifted towards lower oligomers when compared to the outcome of the reaction carried out with the conventional SHOP catalyst. Thus, when operating at 1 bar, over 99 wt.-% of the oligomers formed are C_4–C_{16} oligomers. In ethylene-free solvents, **4** was shown to slowly undergo reductive elimination to produce the stabilised phosphorus ylide Ph_3P-pzO (**5**). Both compounds (**4** and **5**) were characterised by single-crystal X-ray diffraction analyses.

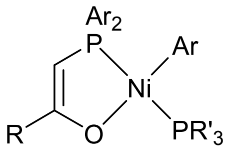
Résumé

Le 4-diphénylphosphanyl-1-phényl-3-méthyl-2-pyrazol-5-onate de sodium (**3**·Na), ligand combinant une unité PPh_2 à un groupement électroattracteur pyrazolonate, réagit avec le complexe *trans*-[$NiPhCl(PPh_3)_2$] pour former quantitativement *trans*-*P*,*P*'-[NiPh(**3**)(PPh_3)] (**4**), premier complexe de type Keim dérivé d'un amide. En l'absence de cocatalyseurs, **4** convertit sélectivement l'éthylène en α-oléfines linéaires avec une activité comparable à celle du complexe [$NiPh(Ph_2PCH{=}C(O)Ph(PPh_3)$] (**1a**), utilisé dans le procédé SHOP. La caractéristique principale de ce catalyseur, par comparaison avec **1a**, réside dans son aptitude à déplacer la distribution des produits vers des oligomères courts. Ainsi, en opérant à 1 bar, 99 % en masse des produits formés sont des oligomères C_4–C_{16}. En solution et en l'absence

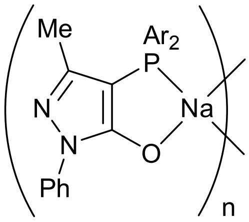
d'éthylène, **4** se décompose lentement selon une réaction d'élimination réductrice conduisant à un ylure de phosphore stabilisé, la 4-triphénylphosphoranylidène-1-phényl-3-méthyl-pyazol-5-one (**5**). Les composés **4** et **5** ont été caractérisés par une étude de diffraction des rayons-X.

Introduction

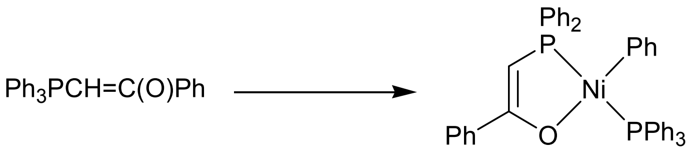
Square-planar nickel(II) complexes of the general formula trans-*P,P'*-$NiAr\{Ar_2PCH{=}C(O)R'\}(PR_3)]$ (**1**; R,R' = aryl, alkyl) have been extensively studied over the last 25 years, mainly because of their ability to oligomerise ethylene into α-olefins under mild conditions.[1-7] The discovery of this catalyst type stretches back to the early seventies, when researchers at SHELL discovered that mixing Ni^0 complexes with phosphorus ylides, e.g. $Ph_3PCH{=}C(O)Ph$ (**2**), produced highly active oligomerisation catalysts.[8] Later, Keim et al. showed that reaction of **2** with $Ni(cod)_2$ in the presence of PPh_3 resulted in an oxidative addition reaction with cleavage of a P-Ph(ylide) bond and subsequent formation of the phosphanyl-enolato complex $[NiPh\{Ph_2PCH{=}C(O)Ph\}(PPh_3)]$ (**1a**), known as Keim's oligomerisation catalyst.[9] Since Keim's pioneering studies, a number of related *P,O*-nickel complexes (*P,O* = 3-electron chelate) have been prepared and studied, but surprisingly little is known about variants in which the *P,O*-chelate behaves as an electron-poor donor, although the complex $[NiH\{Ph_2PCH_2C(CF_3)_2O\}PCy_3]$ was reported to be inactive. Note that several recent publications have focussed on nickel complexes with electron-rich *P,O*-chelates,[10,11] while a few nickel complexes in which the *P,O* ligand behaves as a neutral 4-electron donor have also been studied.[12]



1 : R = alkyl, aryl



$[Na(Ph2P\text{-}pzO)]_n$ (**3·Na**)$_n$



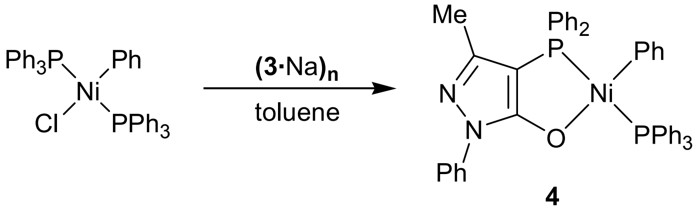
2 **1a**

We now describe the convenient, direct synthesis of the new Keim-type catalyst **4** starting from a P^{III} derivative, namely the sodium pyrazolonato-phosphane Ph_2P-pzONa (**3**·Na).[13] Our investigations show how the presence of the strong electron-withdrawing pyrazolonato ring,[14] known to be stronger than CF_3, drastically drives the product distribution towards shorter olefins. The present study furthers demonstrates that "Keim catalysts" may undergo reductive elimination with formation of a phosphorus ylide. The reported complex **4** is the first example of a Keim-type catalyst derived from an amide.

Results and discussion

Synthesis

Reaction of $[NiPhCl(PPh_3)_2]$ with one equiv. of Ph_2P-pzONa in toluene afforded complex **4** in ca. 90 % yield. It is noteworthy that this reaction constitutes a rare case in which a **1a**-analogue was obtained from a phosphanylenolate rather than a phosphorus ylide.



4

The ^{31}P NMR spectrum of **4** displays an AB quartet (δ_A/δ_B = 20.2/–8.6 ppm) with a J(PP') coupling constant of 280 Hz, typical for *trans*-arranged phosphorus atoms. The phosphorus signal of the P-enolato moiety (δ = –8.6 ppm) is strongly shifted to high field with respect to that of other diphenylphosphanylenolates reported in the literature, thus reflecting the high electron-withdrawing nature of the pyrazolonato ring. The solid-state structure of **4** was elucidated by an X-ray diffraction study (Figure 1), which reveals a significant deviation from the usual square-planar coordination geometry observed in other [NiPh(*PO*)PPh_3] complexes. Thus, while the C(23) and oxygen atoms lie on one side of the mean-squares coordination plane, the two P atoms are turned towards the other side [distances to the plane: C(23) –0.154(1);O –0.160(1); P1 +0.184(1); P2 +0.185(1) Å]. Consistent with the electronic features of the pyrazolonato ring, the Ni-O and the Ni-P(1) bonds [1.955(1) Å and 2.210(1) Å, respectively] are somewhat longer than their counterparts in **1a** (1.914 Å; 2.168 Å). The shortness of the P(1)-C(2) bond [1.770(2) Å] is in keeping with electron delocalisation within the *PO* chelate.

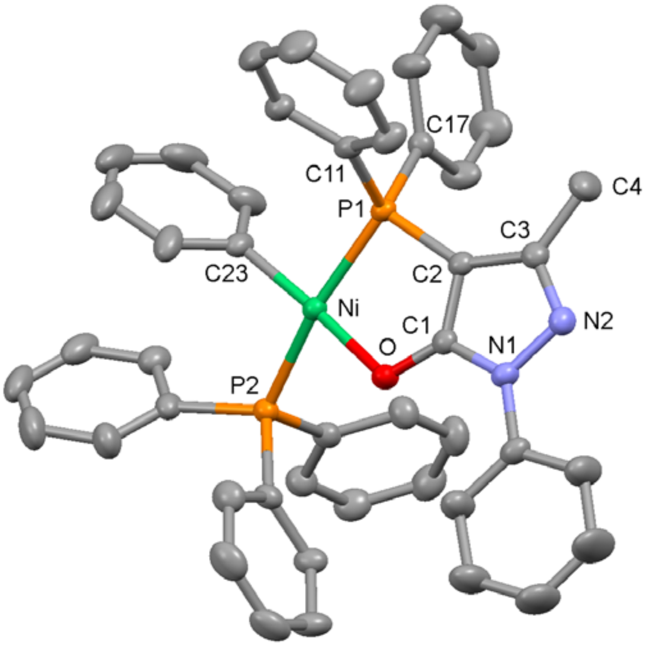
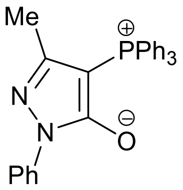


Figure 1. Molecular structure of complex **4**. Important distances [Å] and angles [°]: NiC(23) 1.885(2); NiO 1.955(1); NiP(1) 2.210(1); NiP(2) 2.224(1); P(1)C(2) 1.770(2); P(1)C(17) 1.820(2); P(1)C(11) 1.823(2); OC(1) 1.296(2); C(2)C(1) 1.393(2); C(2)C(3) 1.419(3); N(1)C(1) 1.370(2); N(1)N(2) 1.400(2) P(1)NiP(2) 167.26(2); C(23)NiO 173.83(7).

Interestingly, we noted that on standing, colourless crystals slowly formed from toluene solutions containing **4**.



5

An X-ray analysis of the product reveals the formation of the phosphorus ylide **5** (Figure 2). Surprisingly, a similar reductive elimination reaction had not been reported for **1a**. A careful reinvestigation of the latter complex showed that, in fact, **1a** undergoes the same slow transformation in toluene, resulting in the formation of $Ph_3PCH{=}C(O)Ph$. Possibly, this transformation is triggered by the presence of trace amounts of air, since we found that bubbling air through a C_6D_6 solution of **4** rapidly produced **5**.

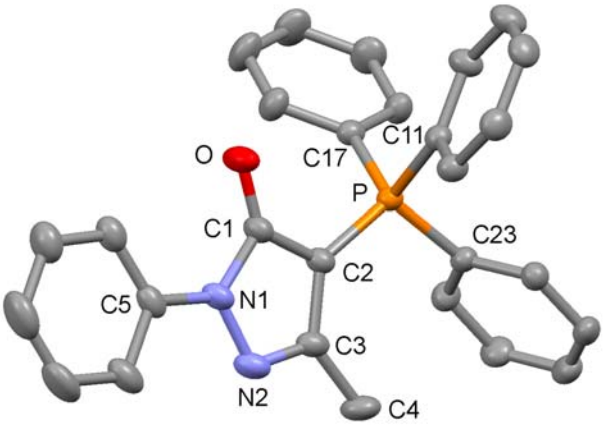


Figure 2. Molecular structure of the phosphorus ylide **5**. Important distances [Å]: P(1)C(2) 1.736(2); P(1)C(23) 1.797(3); P(1)C(17) 1.806(2); P(1)C(11) 1.808(2); OC(1) 1.249(3); C(2)C(1) 1.430(3); C(2)C(3) 1.429(3); N(1)C(1) 1.400(3); N(1)N(2) 1.395(3).

Catalytic study

Typically for a Keim-type catalyst, complex **4** displays high activity in the low-pressure oligomerisation of ethylene without requiring any activating agent to trigger the reaction. Turnover frequencies (TOF) as high as 6600 $\mathrm{mol_{ethylene}{\cdot}mol_{Ni}^{-1}{\cdot}h^{-1}}$ were observed when operating in toluene at 70 °C under a constant ethylene pressure of 5 bar and a nickel concentration of 0.25 μmol/mL (cf. TOF = 7500 for **1a**) [2 h experiments]. At this pressure, the selectivity in the α-olefins surpassed 95 % (Table 1).

The most striking feature of **4** involves the product distribution that considerably shifts towards lower oligomers in comparison with the outcome of Keim's catalyst. Thus, under the conditions outlined above, ca. 72 wt.-% of the oligomers produced after 60 min were C_4-C_{16} olefins; this fraction represents only 15 wt.-% of the total amount of oligomers produced with **1a** in the same period of time. When applying a constant ethylene pressure of 1 bar, this ratio rose to 99 wt.-% (versus 60 % for **1a**). The performances of **4** and **1a** were also compared with those in batch experiments carried out at higher pressures. Thus, when applying an initial pressure of 20 bar ([Ni] = 0.25 μmol/mL), the amount of C_4-C_{16} olefins produced with **4** after 1 h was 25 wt.-% of the total amount of oligomers, versus only 9.6 % for **1a**.

Table 1. Ethylene oligomerisation with **1a** and **4**. General conditions: toluene 30 mL, 70°C, calibrated on heptane.

Ni complex (7.5 μmol)[a]	$P(C_2H_4)$ [bar]	Time [h]	BF_3 [μmol]	TOF [$mol_{ethylene}\ mol_{Ni}^{-1}\ h^{-1}$]	C_4-C_{16} distribution [wt.-%]
1a	1	2		3400	60.2
1a	5	2		7500	15.3
1a	5	1		15500	15.3
1a[a]	20	1		19900	9.6
1a[a]	20	1	7.5	9400	9.6
4	1	2		1800	98.9
4	5	2		6600	45.2
4	5	1		9700	72.5
4[a]	20	1		6600	25.1
4[a]	20	1	7.5	3800	97.0

[a] Batch experiments, toluene 20 mL, 70 °C.

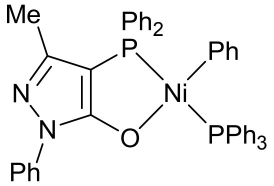
It must be mentioned here that a SHOP catalyst in which the oxygen atom was involved in hydrogen bonding has been reported to also favour βelimination, hence the formation of shorter oligomers, but not to such an extent.[2] Interestingly, the observed effect can be drastically enhanced by using BF_3 as an additive. For example, in experiments where stoichiometric amounts of BF_3 were used (batch autoclave, $P_{initial}$ = 20 bar, [**4**] = 0.25 μmol/mL), the fraction of C_4-C_{16} olefins obtained after 1 h represented 97 % of all oligomers formed. It appears plausible that the BF_3 unit binds to the pyrazole ring, probably through a nitrogen atom,[15] hence increasing the electron deficiency of the nickel atom. Overall, the effect observed by adding BF_3 is reminiscent of the properties of $[Ni\{Ph_2PC_6H_4C(O)O\}(Me\text{-}2\text{-}allyl)]$,[16] which upon addition of $B(C_6F_5)_3$ shifts ethylene oligomerisation towards the formation of low-weight olefins (butene and hexene).[17]

Finally, we noted that mixing complex **4** with $Ni(cod)_2$ in excess afforded, as expected,[11,18,19] a catalyst which polymerises ethylene. Its activity compares with that of **1a**, but analysis of the polymer reveals that the polyethylene chains are considerably shorter (M_w = 650 g mol^{-1}) than those obtained with **1a** (M_w = 4500 g mol^{-1}) under similar conditions. These findings confirm the remarkable electronic properties of the phosphanyl-pyrazolonato ligand. Further investigations are in progress which aim at the use of electron poor *P*,*O* chelators that allow the controlled production of industrially relevant α-olefins in the absence of any cocatalyst.

Experimental section

General.

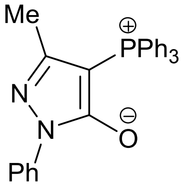
All manipulations were performed in Schlenk-type flasks under dry nitrogen. Solvents were dried by conventional methods and distilled immediately prior to use. $CDCl_3$ was passed down a 5 cm-thick alumina column and stored under nitrogen over mo-lecular sieves (4 Å). IR spectra were measured with a Perkin-Elmer 1605 spectrometer. Routine ^1H and $^{31}P\{^1H\}$ spectra were recorded with FT Bruker instruments (AC-300 or Bruker AM-400). $^{13}C\{^1H\}$ were recorded with an FT Bruker AC-200 spectrometer. ^1H NMR spectra are referenced to residual protonated solvents ($\delta = 7.16$ ppm for C_6D_6 and 7.26 ppm for $CDCl_3$); ^{13}C chemical shifts are reported relative to deuterated solvents ($\delta =128.0$ ppm for C_6D_6 and 77.0 ppm for $CDCl_3$); ^{31}P NMR spectroscopic data are given relative to external H_3PO_4. The catalytic solutions were analysed with a Varian 3900 gas chromatograph equipped with a WCOT fused silica column (25 m, 0.32 mm inside diameter, 0.25 mm film thickness). High temperature size exclusion chromatography (HT SEC) measurements were performed at 150 °C with a "PL220" apparatus (Column set HT-MixedB-TCB-01) in 1,2,4-trichlorobenzene (with 0.2 % Irganox). Calibration was made with linear PS samples. Ph_2P-pzONa[13] and $[NiPhCl(PPh_3)_2]$[20,21] are reported according to procedures reported in the literature.



[NiPh{Ph₂P-pzO}(PPh₃)] (4).

To a stirred suspension of Ph_2P-pzONa (0.766 g, 2.14 mmol) in toluene (30 mL) was added a solution of $[NiPhCl(PPh_3)_2]$ (1.491 g, 2.14 mmol) in toluene (40 mL). After stirring for 4 h, the mixture was filtered through Celite in order to remove NaCl. The solution was concentrated to ca. 10 mL. On standing, dark yellow crystals formed overnight. After removal of the supernatant solution, the crystals were washed successively with cold toluene (5 mL) and pentane (10 mL), and then dried in vacuo. Yield: 1.088 g, 60 %. Addition of pentane to the mother liquor afforded further amounts of **4** as a yellow powder, which increases the yield to 90 %. $C_{46}H_{38}N_2NiOP_2{\cdot}C_7H_8$ ($M_r = 755.46 + 92.14 = 847.60$): calcd. C 75.1, H 5.47, N 3.31; found C 74.6, H 5.39, N 3.34. IR (KBr): 1592.6 (m), 1515.5 (s), 1495.0 (s), 1425.8 s cm^{-1}. ^1H

NMR (300 MHz, C_6D_6): δ = 8.25-6.44 (35 H, arom. H), 2.02 (s, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ = 140.76-118.06 (arom. C), 89.83 (d, *J*(P,C) = 63 Hz, *C*(PPh_2)), 14.77 (s, CH_3) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ = 20.2 and –8.6 (AB spin system, *J*(PP') = 280 Hz).



Ph_3P-pzO (5).

[NiPh{Ph_2P-pzO}(PPh_3)] (**4**; 0.100 g, 0.13 mmol) was dissolved in toluene (5 mL). Upon standing in air, crystals of Ph_3P-pzO appeared after 48 h. The supernatant was removed by suction, and the crystals were dried under high vacuum. Yield: 0.056 g, 70 %. $C_{28}H_{23}N_2OP$ (M_r = 434.48): calcd. C 77.41, H 5.34, N 6.45; found C 77.49, H 5.38, N, 6.41. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ= 10.6 ppm (lit.: 12.6[22]).

X-ray Crystal Structure Determination of 4·toluene.

Single crystals of **4** suitable for X-ray diffraction analysis were obtained from a concentrated toluene solution of the complex. Data were collected on a Nonius KappaCCD diffractometer (graphite Mo-K_α radiation, λ = 0.71073 Å). The structure was solved by direct methods with the SHELXS-97 program and refined by full-matrix least-squares techniques (SHELXL-97) on F^2.[23] Hydrogen atoms were located by using the geometric method. The crystal data and structural refinement details are listed in Table 2. The compound was found to crystallise with one molecule of toluene (CCDC 242626).

X-ray Crystal Structure Determination of 5·benzene.

Single crystals of **5** suitable for X-ray diffraction analysis were obtained from a toluene solution of the complex on standing in air. Data collection and structure solution were as for compound **4**. The compound crystallised with one molecule of benzene. The benzene molecules occupy special positions (–1). CCDC-242627 and CCDC-242626 contain the supplementary crystallographic data.

Table 2. Crystallographic data for **4**·toluene and **5**·benzene**.**

Formula	**$C_{46}H_{38}N_2NiOP_2 \cdot C_7H_8$ (4·toluene)**	**$C_{28}H_{23}N_2OP \cdot C_6H_6$ (5·benzene)**
Formula weight	847.57	512.56
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
a [Å] b [Å] c [Å]	10.939(1) 13.283(1) 16.156(1)	29.361(5) 9.314(1) 22.758(5)
α [°] β [°] γ [°]	72.29(5) 75.29(5) 87.71(5)	90 119.06(5) 90
V [Å^3]	2161.2(3)	5440(3)
Z	2	8
$D_{calcd.}$ [g cm^{-3}]	1.302	1.252
μ (Mo-$K\alpha$) [mm^{-1}]	0.565	0.131
F(000)	888	2160
Crystal Size [mm]	0.08 × 0.10 × 0.13	0.06 × 0.07 × 0.09
Temperature [K]	173(2)	173(2)
Radiation Mo-$K\alpha$ [Å]	0.71069	0.71069
θmin/max [°]	1.4/30.0	1.6/30.0
Data set	–15/15; –17/18; –22/21	–41/36; 0/13; 0/32
Total, Unique data, R(int)	34952, 12654 0.035	7963, 7962 0.036
Observed data [$I > 2.0\sigma(I)$]	9904	5436
Number of reflections, Number of parameters	12654 532	7962 333
R_1, wR_2, S	0.0442, 0.1468, 0.993	0.0781, 0.2297, 1.156
Min. and max. residual density [e Å^{-3}]	–0.664, 0.453	–0.864, 1.829

Catalytic runs

Ethylene oligomerisation: The low-pressure catalytic runs (≤5 bar) were carried out at constant ethylene pressure in a Büchi miniclave (200 mL) equipped with a Teflon-coated magnetic stirrer. The higher pressure experiments were carried out under batch mode in a stainless steel autoclave was used (100 mL). Both reactors were dried under vacuum at 100 °C for 1 h before use. In a typical procedure, a Schlenk flask was charged with the complex (7.5 µmol) and toluene (10 mL). The resulting solution was injected into the autoclave together with additional toluene (20 mL). The autoclave was then pressurised with ethylene and heated at 70 °C. After completion of the reaction, the autoclave was cooled with an ice bath and depressurized over 1 h. The solution was analysed by GC. Heptane (200 µL) was used as internal reference. For details see Tables 3-5.

Ethylene Polymerisation: Polymerisations were carried out in a mini-Büchi glass reactor (200 mL), equipped with a Teflon-coated magnetic stirrer and heating (temperature-controlled oil bath), at constant ethylene pressure. The autoclave was heated at 100 °C under vacuum for 1 h before use and purged with ethylene. The reaction temperature refers to the bath temperature.

In a typical run, the reactor was charged at ambient temperature under an ethylene atmosphere, with a solution of catalyst (7.5 µmol) in toluene (15 mL), followed by a solution of $Ni(cod)_2$ (75 µmol) in toluene (15 mL). The autoclave temperature was raised to 70 °C, and pressurised to 5 bar. Venting the autoclave quenched the reaction, and the reaction mixture was subsequently poured into a stirring solution of methanol (300 mL) and concentrated HCl (10 mL) to precipitate the polymer. The white powder was isolated by filtration, washed with methanol, and dried in vacuo at 50 °C. By using Keim's catalyst (**1a**), 1.80 g of a polymer was obtained and was characterised by M_w = 4500 g mol^{-1} and M_w/M_n = 1.87 (Catalyst activity: 240 g•mmol$_{\mathrm{cat}}^{-1}$•h^{-1}). The polymer (1.51 g) obtained with **4** has the following characteristics: M_w = 650 g mol^{-1} and M_w/M_n = 1.31 (Activity: 201 g•mmol$_{\mathrm{cat}}^{-1}$•h^{-1}).

Table 3. Ethylene oligomerisation using Keim-type complex (**1a**)[a]

<table>
<tr><th>run</th><th>Ni (μmol)</th><th colspan="2">P(C_2H_4) (bar)</th><th colspan="2">time (h)</th><th>α[b]</th><th>β[b]</th><th colspan="4">TOF (mol C_2H_4)/(mol Ni·h)</th><th colspan="3">m(C_2H_4 consumed)(g)</th><th>solid[c] (g)</th></tr>
<tr><td rowspan="4">1</td><td>7.5</td><td colspan="2">5</td><td colspan="2">2</td><td>0.92</td><td>0.09</td><td colspan="4">7500</td><td colspan="3">3.15</td><td>1.078</td></tr>
<tr><td rowspan="2">distribution (wt-%)</td><td>C_4</td><td>C_6</td><td>C_8</td><td>C_{10}</td><td>C_{12}</td><td>C_{14}</td><td>C_{16}</td><td>C_{18}</td><td>C_{20}</td><td>C_{22}</td><td>C_{24}</td><td>C_{26}</td><td>C_{28}</td><td>C_{30+}</td></tr>
<tr><td>1.19</td><td>1.64</td><td>2.01</td><td>2.31</td><td>2.55</td><td>2.74</td><td>2.88</td><td>2.98</td><td>3.05</td><td>3.08</td><td>3.10</td><td>3.08</td><td>3.06</td><td>66.32</td></tr>
<tr><td>α-olefin (%)</td><td>98.9</td><td>98.1</td><td>97.8</td><td>98.4</td><td>98.5</td><td>98.3</td><td>98.3</td><td>97.7</td><td>97.4</td><td>95.7</td><td>95.1</td><td>88.5</td><td>77.1</td><td></td></tr>
<tr><td rowspan="4">2</td><td>15</td><td colspan="2">5</td><td colspan="2">2</td><td>0.92</td><td>0.09</td><td colspan="4">7400</td><td colspan="3">6.21</td><td>n d</td></tr>
<tr><td rowspan="2">distribution (wt-%)</td><td>C_4</td><td>C_6</td><td>C_8</td><td>C_{10}</td><td>C_{12}</td><td>C_{14}</td><td>C_{16}</td><td>C_{18}</td><td>C_{20}</td><td>C_{22}</td><td>C_{24}</td><td>C_{26}</td><td>C_{28}</td><td>C_{30+}</td></tr>
<tr><td>1.19</td><td>1.64</td><td>2.01</td><td>2.31</td><td>2.55</td><td>2.74</td><td>2.88</td><td>2.98</td><td>3.05</td><td>3.08</td><td>3.10</td><td>3.08</td><td>3.06</td><td>66.32</td></tr>
<tr><td>α-olefin (%)</td><td>99.7</td><td>99.8</td><td>98.8</td><td>98.7</td><td>98.6</td><td>98.5</td><td>98.0</td><td>97.0</td><td>95.2</td><td>91.6</td><td>81.4</td><td>76.0</td><td>64.7</td><td></td></tr>
<tr><td rowspan="4">3</td><td>7.5</td><td colspan="2">5</td><td colspan="2">0.5</td><td>0.89</td><td>0.12</td><td colspan="4">29600</td><td colspan="3">3.11</td><td>0.863</td></tr>
<tr><td rowspan="2">distribution (wt-%)</td><td>C_4</td><td>C_6</td><td>C_8</td><td>C_{10}</td><td>C_{12}</td><td>C_{14}</td><td>C_{16}</td><td>C_{18}</td><td>C_{20}</td><td>C_{22}</td><td>C_{24}</td><td>C_{26}</td><td>C_{28}</td><td>C_{30+}</td></tr>
<tr><td>2.18</td><td>2.91</td><td>3.45</td><td>3.84</td><td>4.10</td><td>4.26</td><td>4.33</td><td>4.44</td><td>4.29</td><td>4.20</td><td>4.08</td><td>3.93</td><td>3.77</td><td>50.30</td></tr>
<tr><td>α-olefin (%)</td><td>94.4</td><td>97.2</td><td>98.4</td><td>98.4</td><td>98.3</td><td>97.6</td><td>97.0</td><td>96.3</td><td>95.5</td><td>92.6</td><td>90.6</td><td>86.1</td><td>75.8</td><td></td></tr>
<tr><td rowspan="4">4</td><td>7.5</td><td colspan="2">5</td><td colspan="2">1</td><td>0.92</td><td>0.09</td><td colspan="4">15500</td><td colspan="3">3.25</td><td>0.737</td></tr>
<tr><td rowspan="2">distribution (wt-%)</td><td>C_4</td><td>C_6</td><td>C_8</td><td>C_{10}</td><td>C_{12}</td><td>C_{14}</td><td>C_{16}</td><td>C_{18}</td><td>C_{20}</td><td>C_{22}</td><td>C_{24}</td><td>C_{26}</td><td>C_{28}</td><td>C_{30+}</td></tr>
<tr><td>1.19</td><td>1.64</td><td>2.01</td><td>2.31</td><td>2.55</td><td>2.74</td><td>2.88</td><td>2.98</td><td>3.05</td><td>3.08</td><td>3.10</td><td>3.08</td><td>3.06</td><td>66.32</td></tr>
<tr><td>α-olefin (%)</td><td>99.1</td><td>99.1</td><td>98.7</td><td>98.5</td><td>98.4</td><td>98.2</td><td>98.2</td><td>98.0</td><td>97.6</td><td>97.3</td><td>93.4</td><td>88.7</td><td>83.3</td><td></td></tr>
<tr><td rowspan="4">5</td><td>7.5</td><td colspan="2">1</td><td colspan="2">2</td><td>0.78</td><td>0.28</td><td colspan="4">3400</td><td colspan="3">1.44</td><td>traces</td></tr>
<tr><td rowspan="2">distribution (wt-%)</td><td>C_4</td><td>C_6</td><td>C_8</td><td>C_{10}</td><td>C_{12}</td><td>C_{14}</td><td>C_{16}</td><td>C_{18}</td><td>C_{20}</td><td>C_{22}</td><td>C_{24}</td><td>C_{26}</td><td>C_{28}</td><td>C_{30+}</td></tr>
<tr><td>7.93</td><td>9.28</td><td>9.65</td><td>9.41</td><td>8.81</td><td>8.02</td><td>7.15</td><td>6.27</td><td>5.43</td><td>4.66</td><td>3.97</td><td>3.35</td><td>2.82</td><td>13.23</td></tr>
<tr><td>α-olefin (%)</td><td>98.5</td><td>98.3</td><td>98.1</td><td>98.2</td><td>98.2</td><td>98.1</td><td>98.1</td><td>98.2</td><td>98.0</td><td>97.4</td><td>96.8</td><td>n d</td><td>n d</td><td></td></tr>
</table>

[a] General conditions: toluene 30 mL, P(C_2H_4) constant during the reaction, 70°C, [b] Schulz-Flory parameters $\alpha = n(C_{n+2})/n(C_n)$, $\beta = (1-\alpha)/\alpha$, [c] after precipitation of the reaction solution into 200 mL of MeOH/HCl.

Table 4. Ethylene oligomerisation using complex **4**[a]

run	Ni (µmol)	time (h)	P(C_2H_4) (bar)			α[b]	β[b]		TOF (mol C_2H_4)/(mol Ni·h)				m(C_2H_4 consumed) (g)		
1	7.5	2	1			0.44	1.27		1800				0.76		
	distribution (wt %)	C_4	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{24}	C_{26}	C_{28}	C_{30+}
		40.20	26.54	15.57	8.56	4.52	2.32	1.17	0.58	0.28	0.14	0.06	0.03	0.01	0.01
	α-olefin (%)	94.2	89.0	88.3	86.0	83.2	86.0	85.0	n d	n d	n d	n d	n d	n d	
2	7.5	2	2.5			0.60	0.67		4200				1.76		
	distribution (wt %)	C_4	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{24}	C_{26}	C_{28}	C_{30+}
		22.86	20.57	16.46	12.34	8.89	6.22	4.27	2.88	1.92	1.27	0.83	0.54	0.35	0.62
	α-olefin (%)	98.1	97.7	95.2	94.8	93.7	93.9	90.6	88.3	85.6	81.7	n d	n d	n d	
3	7.5	2	5			0.83	0.20		6600				2.77		
	distribution (wt %)	C_4	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{24}	C_{26}	C_{28}	C_{30+}
		4.94	6.15	6.80	7.06	7.03	6.81	6.46	6.03	5.56	5.08	4.60	4.14	3.70	25.63
	α-olefin (%)	97.9	97.0	96.4	95.3	95.2	95.0	94.6	93.8	91.7	86.1	n d	n d	n d	
4	7.5	0.5	5			0.69	0.45		14400				1.51		
	distribution (wt %)	C_4	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{24}	C_{26}	C_{28}	C_{30+}
		14.67	15.18	13.97	12.04	9.98	8.03	6.33	4.91	3.77	2.86	2.15	1.61	1.20	3.26
	α-olefin (%)	97.6	97.5	97.6	96.2	95.6	95.3	93.8	93.2	92.8	91.1	67.8	61.4	n d	
5	7.5	1	5			0.73	0.37		9700				2.04		
	distribution (wt %)	C_4	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{24}	C_{26}	C_{28}	C_{30+}
		11.48	12.57	12.24	11.16	9.78	8.33	6.95	5.71	4.63	3.72	2.96	2.34	1.84	6.29
	α-olefin (%)	97.4	96.4	95.5	95.4	94.9	94.2	92.8	92.2	89.1	85.9	81.0	78.3	n d	
6[c]	7.5	1	5			0.66	0.51		1100				0.23		
	distribution (wt %)	C_4	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{24}	C_{26}	C_{28}	C_{30+}
		17.25	17.08	15.03	12.40	9.82	7.56	5.70	4.23	3.11	2.25	1.62	1.16	0.82	1.94
	α-olefin (%)	96.7	97.2	97.3	97.2	97.2	96.2	95.2	93.6	88.1	n d	n d	n d	n d	

[a] General conditions toluene 30 mL, P(C_2H_4) constant during the reaction, 70°C, [b] Schulz-Flory parameters $\alpha = n(C_{n+2})/n(C_n)$, $\beta = (1-\alpha)/\alpha$, [c] addition of 7.5 µmol BF_3.

Table 5. Ethylene oligomerisation at higher pressure[a]

run	complex	time (h)	$P(C_2H_4)$ (bar)		T (°C)		α[b]	β[b]	TOF (mol C_2H_4)/(mol Ni·h)			$m(C_2H_4$ consumed) (g)			Solid[c] (g)
1	**1a**	3	40		90		0.96	0.04	4600			2.89			2.29
	distribution	C_4	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{24}	C_{26}	C_{28}	C_{30+}
	(wt %)	0.34	0.48	0.62	0.74	0.86	0.96	1.05	1.14	1.21	1.28	1.34	1.39	1.44	87.14
	α-olefin (%)	98.1	97.7	97.0	96.3	96.6	96.7	96.6	96.0	94.8	92.6	87.6	82.7	74.4	
2	**1a**	1	20		70		0.94	0.06	19900			4.18			1.24
	distribution	C_4	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{24}	C_{26}	C_{28}	C_{30+}
	(wt %)	0.69	0.97	1.22	1.43	1.61	1.77	1.90	2.01	2.10	2.17	2.23	2.27	2.30	77.33
	α-olefin (%)	n d	98.0	98.2	98.1	97.9	97.8	98.0	97.9	97.7	97.3	94.7	93.5	87.0	
3[d]	**1a**	1	20		70		0.94	0.06	9400			1.97			0.14
	distribution	C_4	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{24}	C_{26}	C_{28}	C_{30+}
	(wt %)	0.69	0.97	1.22	1.43	1.61	1.77	1.90	2.01	2.10	2.17	2.23	2.27	2.30	77.33
	α-olefin (%)	97.3	96.7	97.0	97.0	97.4	97.6	97.4	97.3	97.2	96.6	96.3	96.0	82.8	
4[e]	**1a**	1	20		70		0.05	19.00	9700			2.04			0
	distribution	C_4	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{24}	C_{26}	C_{28}	C_{30+}
	(wt %)	92.56	6.94	0.46	0.03	/	/	/	/	/	/	/	/	/	/
	α-olefin (%)	n d	58.3	28.9	n d										
5	**4**	3	40		90		0.92	0.09	4100			2.62			0.15
	distribution	C_4	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{24}	C_{26}	C_{28}	C_{30+}
	(wt %)	1.19	1.64	2.01	2.31	2.55	2.74	2.88	2.98	3.05	3.08	3.10	3.08	3.06	66.32
	α-olefin (%)	96.4	95.0	93.8	93.4	93.1	92.2	91.4	90.7	88.9	85.3	76.7	66.8	52.2	
6	**4**	1	20		70		0.89	0.12	6600			1.39			traces
	distribution	C_4	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{24}	C_{26}	C_{28}	C_{30+}
	(wt %)	2.18	2.91	3.45	3.84	4.10	4.26	4.33	4.34	4.29	4.20	4.08	3.93	3.77	50.30
	α-olefin (%)	96.7	95.8	96.4	95.8	95.4	95.5	95.3	95.1	94.6	93.5	84.6	79.2	68.5	
7[d]	**4**	1	20		70		0.51	0.96	3800			0.80			0
	distribution	C_4	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{24}	C_{26}	C_{28}	C_{30+}
	(wt %)	32.23	24.65	16.76	10.69	6.54	3.89	2.27	1.30	0.74	0.41	0.23	0.13	0.07	0.08
	α-olefin (%)	95.9	93.5	93.4	93.0	92.5	91.9	91.9	89.9	86.0	82.1	n d	n d	n d	
8[e]	**4**	1	20		70		0.34	1.94	1000			0.21			0
	distribution	C_4	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	C_{22}	C_{24}	C_{26}	C_{28}	C_{30+}
	(wt %)	52.48	26.77	12.13	5.16	2.10	0.83	0.32	0.12	0.05	0.02	0.01	/	/	/
	α-olefin (%)	98.6	90.1	88.9	86.6	85.4	84.2	81,8	77.5	n d	n d	n d			

[a] General conditions: Ni complex 7.5 μmol, toluene 20 mL, $P(C_2H_4)$ charged at r.t., [b] Schulz-Flory parameters $\alpha = n(C_{n+2})/n(C_n)$, $\beta = (1-\alpha)/\alpha$, [c] after precipitation of the reaction solution into 200 mL of MeOH/Hcl, [d] addition of 7.5 μmol BF_3, [e] addition of 75 μmol BF_3.

References

[1] W. Keim , *Angew. Chem. Int. Ed. Engl.* 1990, **29**, 235 -244.

[2] P. Braunstein, Y. Chauvin, S. Mercier, L. Saussine , A. De Cian , J. Fischer , *J. Chem. Soc. Chem. Commun.* 1994, 2203 -2204.

[3] K. Kurtev, A. Tomov , *J. Mol. Catal.* 1994, **88**, 141 -150.

[4] A. L. Monteiro, M. O. de Souza, R. F. de Souza, *Polym. Bull.* 1996, **36**, 331 -336.

[5] G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem. Int. Ed.* 1999, **38**, 428 -447.

[6] S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* 2000, **100**, 1169 -1204.

[7] V. C. Gibson, S. K. Spitzmesser, *Chem. Rev.* 2003, **103**, 283 -315 .

[8] P. W. Glockner, W. Keim, R. F. Mason, U. S. Patent 3.647.914 Shell Oil Co., **1971** [Chem. Abstr. 1971, 75, 88072g].

[9] W. Keim, F. H. Kowaldt, R. Goddard, C. Krüger, *Angew. Chem. Int. Ed. Engl.* 1978, **17**, 466 -467.

[10] K. Hirose, W. Keim, *J. Mol. Catal.* 1992, **73**, 271 -276.

[11] J. Heinicke, M. Koesling, R. Brüll, W. Keim, H. Pritzkow, *Eur. J. Inorg. Chem.* 2000, 299 -305.

[12] J. M. Malinowski, M. Brookhart, *Organometallics* 2003, **22**, 5324 -5335.

[13] D. Matt, N. Sutter-Beydoun, J.-P. Brunette, F. Balegroune, D. Grandjean, *Inorg. Chem.* 1993, **32**, 3488 -3492.

[14] E. C. Okafor, *Spectrochim. Acta Part A* 1987, **37**, 939.

[15] L. Komorowski, W. Maringgele, A. Meller, K. Niedenzu, J. Serwatowski, *Inorg. Chem.* 1990, **29**, 3845 -3849.

[16] M. C. Bonnet, M. C. Dahan, A. Ecke, W. Keim, R. P. Schultz, I. Tkatchenko, *J. Chem. Soc. Chem. Commun.* 1994, 615 -616.

[17] Z. J. A. Komon, X. Bu, C. G. Bazan, *J. Am. Chem. Soc.* 2000, **122**, 12379 -12380.

[18] U. Klabunde, R. Mulhaupt, T. Herskovitz, A. H. Janowicz, J. Calabrese, S. D. Ittel, *J. Polymer. Sci. Part A Polym. Chem.* 1987, **25**, 1989 -2003.

[19] R. Soula, J. P. Broyer, M. F. Llauro, A. Tomov, R. Spitz, J. Claverie, X. Drujon, J. Malinge, T. Saudemont, *Macromolecules* 2001, **34**, 2438 -2442.

[20] A. Zeller, E. Herdtweck, T. Strassner, *Eur. J. Inorg. Chem.* 2003, **9**, 1802 -1806.

[21] M. Hiodai, T. Kashiwagi, T. Ikeuchi, Y. Uchida, *J. Organomet. Chem.* 1971, **30**, 279 -282.

[22] F. Palacios, A. M. Ochoa de Retana, J. Pagalday, *Tetrahedron* 1999, **55**, 14451 -14458.

[23] G. M. Sheldrick, *SHELX-97, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

Chapter 3

Can Weak Interactions Modify the Binding Properties of a Strong Nitrogen Donor? Unusual N-Coordination of a Phosphoranylidene-Substituted Pyrazolone Unit Towards Palladium(II) Centres: an Experimental and Theoretical Study

Abstract

Selective N(2)-binding of 3-methyl-1-phenyl-4-(triphenylphosphoranylidene)-2-pyrazolin-5-one (**L**) has been found in two palladium(II) complexes, [$PdCl_2\mathbf{L}_2$] (**2**) and [$Pd(o\text{-}C_6H_4CH_2NMe_2)Cl\mathbf{L}$] (**3**). X-Ray diffraction studies show that the pyrazole rings lie almost perpendicular to the coordination plane. In both complexes the metal atom is located out of the plane defined by the pyrazole ring(s) (dihedral angle between the plane and the Pd–N vector ~30°). To investigate the origin of this distortion, a theoretical study was carried out on a simplified model of complex **2**, where a single pyrazolone ligand was replaced by NH_3.[*] From this study it could be inferred that the out-of-plane distortion mainly involves weak, electrostatic interactions between a chlorine atom and an *ortho*-aromatic H atom of the N(1)-linked phenyl group, as well as between the other chlorine atom and an *ortho*-aromatic H atom of the PPh_3 group.

Résumé

Dans ce chapitre, nous avons étudié les propriétés complexantes d'un ylure de phosphore stabilisé, précurseur potentiel d’un catalyseur de type SHOP, la 4-(triphénylphosphoranylidène)-3-méthyl-1-phényl-2-pyrazolin-5-one (**L**). Ce composé comporte un noyau pyrazolonato connecté par le carbone 4 à une entité PPh_3. La réactivité de **L** vis-à-vis du palladium se distingue du comportement habituel des ylures de phosphore céto-

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[*] carried out by Antonio J. Mota and Alain Dedieu (*Laboratoire de Chimie Quantique, UMR 7551 CNRS, Université Louis Pasteur, 4 rue Blaise Pascal, 67070, Strasbourg)*

stabilisés, connus pour se comporter soit en *C*- soit en *O*-nucléophiles. En effet, la réaction de **L** avec [$PdCl_2(PhCN)_2$] et [$Pd(o\text{-}C_6H_4CH_2NMe_2)Cl]_2$ conduit uniquement à des complexes où l'un des atomes d'azote du cycle pyrazolyle, N(2), est coordiné. Des études par diffraction des rayons X réalisés pour [$PdCl_2$**L_2**] (**2**) et [$Pd(o\text{-}C_6H_4CH_2NMe_2)Cl$**L**] (**3**) ont montré que tous les cycles pyrazolyles sont orientés quasi perpendiculairement au plan de coordination. Dans chaque complexe, l'atome métallique est situé en dehors du plan défini par le cycle azoté, l'angle dièdre entre le vecteur Pd-N et le plan pyrazolyle étant de 26° dans **2** (pour les deux cycles présents) et 21° dans **3**. Pour déterminer l'origine de cette distorsion, une étude théorique a été menée sur un modèle simplifié du complexe **2**, où un des deux ligands pyrazolyle a été remplacé par NH_3.[*] Cette étude montre que la distorsion observée résulte principalement d'interactions électrostatiques faibles, en particulier entre un atome de chlore et un proton *ortho*-aromatique du groupement phényle porté par l'azote N(1) ainsi qu'entre l'autre atome de chlore et un proton *ortho*-aromatique du groupement PPh_3. Ce travail constitue par ailleurs une preuve que l'atome d'azote N(2) peut effectivement servir d'atome coordinateur vis-à-vis d'un acide de Lewis, renforçant ainsi l'idée que l'addition de BF_3 au catalyseur [NiPh(4-diphénylphosphoranyl-1-phényl-3-méthyl-2-pyazol-5-onate)(PPh_3)] (voir chapitre 2) peut conduire à un appauvrissement électronique du cycle pyrazolyle via formation d'un adduit $N(2)\rightarrow BF_3$.

Introduction

Pyrazolone units have been extensively employed in ligand design, especially for the synthesis of highly efficient extracting agents such as 4-acylpyrazole-5-ones.[1–7] In most of these ligands, the planar pyrazole ring serves as an effective electron-withdrawing function, while the carbonyl group behaves as a coordinating group. Some recent studies have clearly established that one of the two nitrogen atoms, namely the pyridine-like donor, N(2), may also coordinate metal ions, but to date only two pyrazolone derivatives have been reported where the sole metal-binding atom is the N(2) atom.[8,9] Other studies have shown that this pyridinic nitrogen atom may sometimes be involved in weak, supramolecular bonding interactions, thereby influencing the whole structure of the metal derivatives.[3,10]

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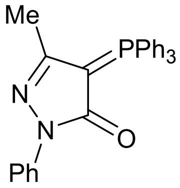


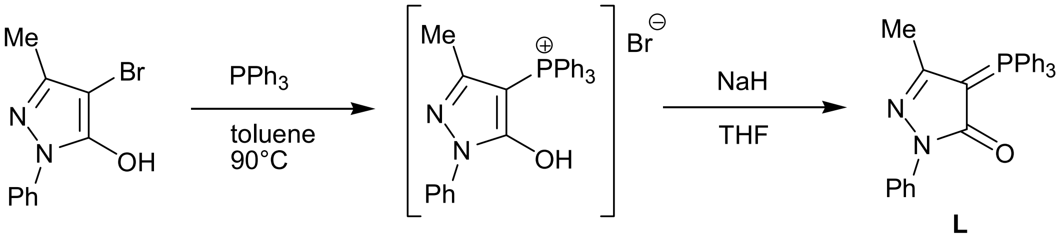
L

We now report on the coordinative properties of the pyrazolone-derived phosphorus ylide **L**, which, unlike other β-keto-stabilized phosphorus ylides, does not behave as a C-[11,12] or O-donor[13,14] towards transition metals. This study describes the first examples of N(2)-binding of a pyrazolone unit to a palladium centre. Further, a theoretical study provides a rationale for the observed out-of-plane binding of the palladium atom with respect to the pyrazole ring.

Results and discussion

Synthesis

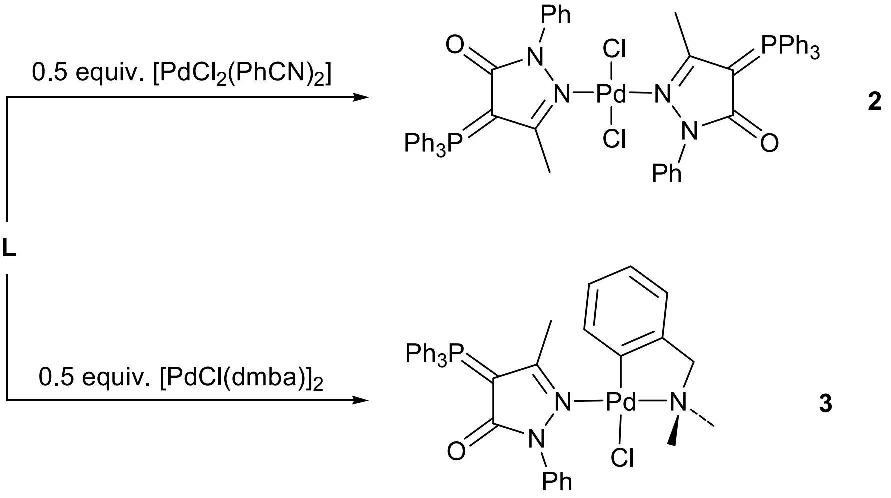
The phosphorus ylide **L** was obtained in two steps according to Scheme 1: (i) reaction of the bromo-enol **1** with one equivalent of triphenylphosphine in toluene at 90 °C; (ii) deprotonation of the resulting phosphonium salt with NaH/THF. The ^{31}P NMR spectrum of **L** displays a singlet at 10.6 ppm, while the IR spectrum shows a strong and broad carbonyl band at 1603 cm^{-1}. Note that a more costly synthesis of **L**, which involves the preparation of a nickel-phosphinoenolate, has been reported recently, together with the X-ray structure of **L**.[15]



Scheme 1. Two-step synthesis of **L**.

Keto-stabilized phosphorus ylides are ambidentate ligands that usually behave either as C- or O-donor ligands. In the present case, the β-keto ylide unit is fused to a pyrazole ring, resulting in additional conjugation of the ylidic electron pair. The strong electron withdrawing character of the pyrazole ring has been demonstrated in a number of studies,[16] and this feature has also recently been exploited for the synthesis of electron poor P,O-chelating phosphines for use in catalysis.[15] We wondered whether the presence of the pyrazole ring in **L** could totally "neutralise" the binding/nucleophilic properties of the keto-ylidic fragment and therefore investigated its reaction towards palladium(II) centres. Palladium(II) was chosen because this metal is known to bind carbonyl-stabilised ylides either through the C- or the O-bonding mode.[12,14]

Reaction of $[PdCl_2(PhCN)_2]$ with 2 equiv. of **L** afforded complex **2** in 55% yield. The chemical shift of the phosphorus atom (10.9 ppm) as well as the $^1J(PC_{pyrazole})$ coupling constant are almost unchanged with respect to that of **L**. In contrast, the chemical shift of the pyrazole carbon atom linked to the phosphorus atom has undergone a significant downfield shift of *ca.* 5.2 ppm, indicating an important electronic perturbation of the pyrazole ring upon complexation. Bonding of the pyridinic N(2) atoms was inferred from an X-ray diffraction study (*vide infra*). Similarly, reaction of 2 equiv. of **L** with $[Pd(o\text{-}C_6H_4CH_2NMe_2)Cl]_2$ gave quantitatively the *N*-coordinated complex **3**. The NMR data of the ylidic ligand of **3** are very close to those found in complex **2** (see Experimental section). The ^1H NMR spectrum of **3** shows two NMe signals, in keeping with a pyrazolone ligand that does not freely rotate about the coordination bond. For both complexes, the IR spectrum shows a strong carbonyl absorption at 1624 cm^{-1} (*vs.* 1603 cm^{-1} in **L**), a value which, *a priori*, justified exclusion of the *O*-bonding mode.



In the solid state, the complex **2** (Fig. 1) has a centrosymmetric structure, the Pd atom having an almost ideal square planar environment, with N–Pd–Cl(1) and N–Pd–Cl(2) angles of

88.6(2) and 91.4(2)°, respectively. The Pd–Cl (2.315(2) Å) and Pd–N distances (2.013(6) Å) lie in the range expected for such bonds. The most important structural modification observed on going from free **L** to its coordinated form is that of the N–C(Me) bond, which undergoes a lengthening of 0.055 Å. Each pyrazole ring is strongly inclined with respect to the coordination plane, the interplanar dihedral angle being 79°.

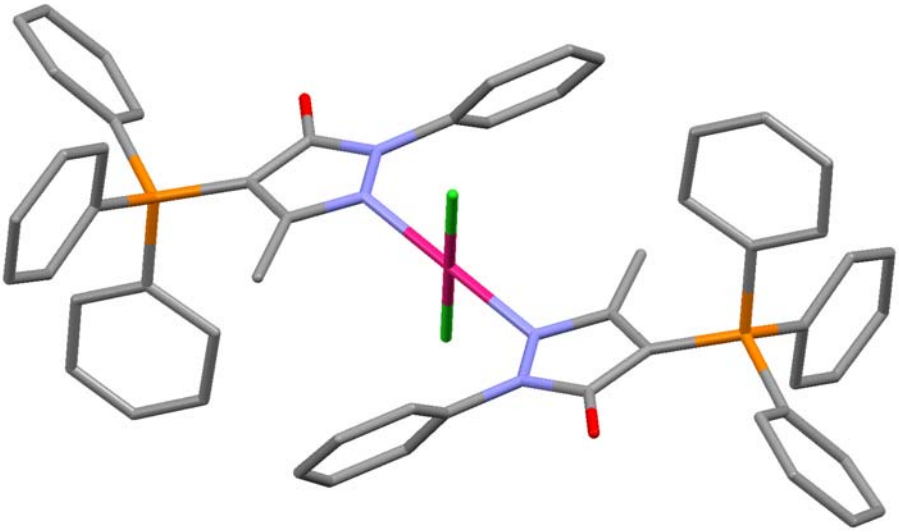


Figure 1. Molecular structure of [$PdCl_2L_2$] (**2**). The solvent molecules have been omitted for clarity.

An intriguing feature of this structure is the out-of-pyrazole-plane coordination of the palladium atom. The distance of the metal atom to the plane defined by the pyrazolone rings is 0.83(1) Å, which corresponds to an angle between the N–Pd and N–G vectors of 164° (G being the pyrazole barycentre).A similar bonding mode was found in complex **3**, the structure of which was also determined by an X-ray diffraction study (Fig. 2). Here, the angle between the N–Pd and N–G vectors is 159°, while the distance of the metal to the pyrazolone plane is 0.71 Å. Clearly, there is a degree of pyramidalisation of N(2). An explanation for this unexpected behaviour is given below. We note that in complex **3**, the pyrazole plane also adopts an almost orthogonal orientation to the metal plane (interplanar angle 89°). Intermolecular interactions which would explain the stereochemical distortion about the N(2) atom can be excluded in both structures.

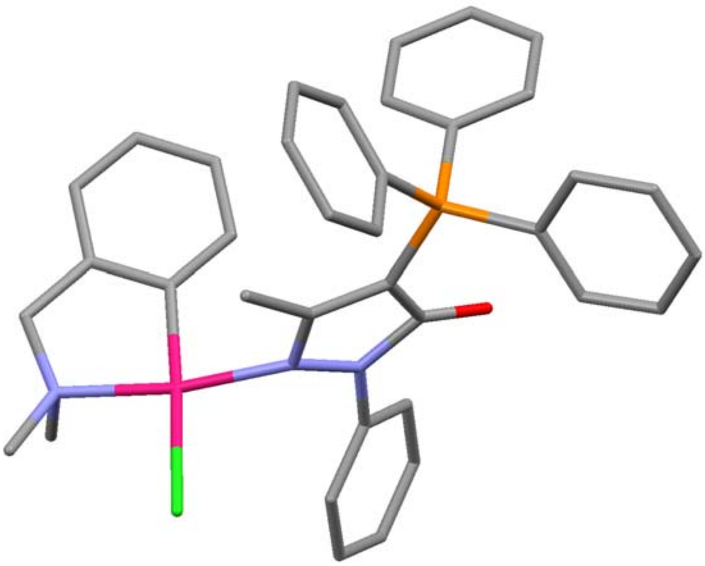
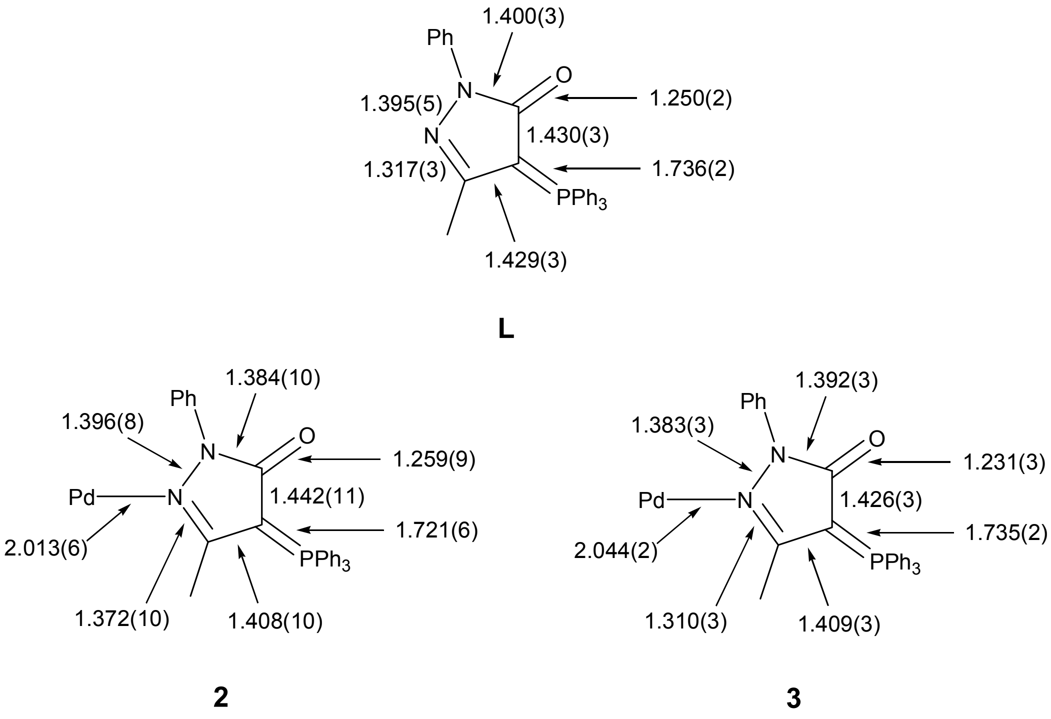


Figure 2. Molecular structure of $[Pd(o\text{-}C_6H_4CH_2NMe_2)Cl]_2$ (**3**). Only one conformation of the disordered metallomacrocycle is shown.

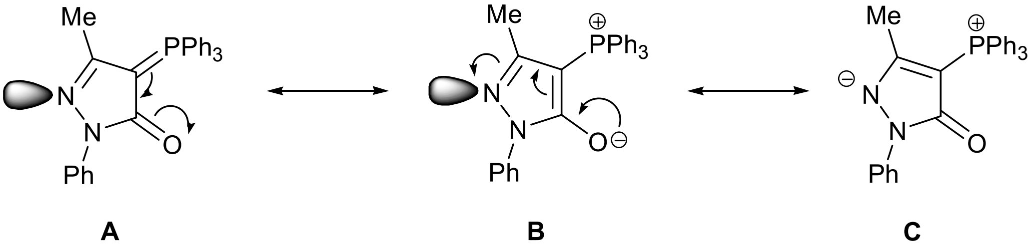
Important structural data for the complexes compared to those of **L** are given in Scheme 2.



Scheme 2. Important structural data of complexes **2** and **3**, compared with those of **L**.

Theoretical study

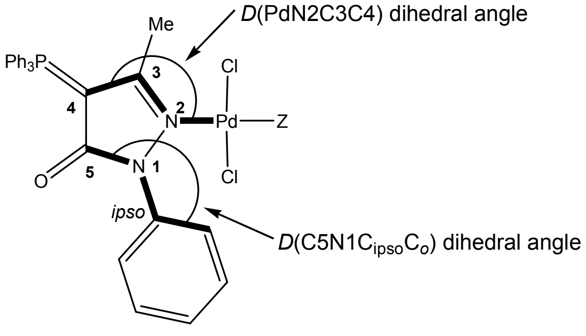
That the Pd atom is significantly displaced out of the plane defined by the pyrazolone ring is somewhat astonishing because a closely related example of copper coordination shows a perfectly planar metal–pyrazolone system,[9] as is expected if we consider an ideal aromatic system with a pure sp^2 orbital on the coordinating nitrogen atom (resonance forms **A** and **B** in Scheme 3). *A priori*, several electronic effects may account for the distortion encountered in the Pd complexes treated here (**2** and **3**). In particular, a lack of delocalisation in the pyrazolone ring, which would result in the pyramidalisation of the coordinating nitrogen atom (resonance form **C** in Scheme 3) could satisfactorily explain this occurrence. On the other hand, it is well established that weak intramolecular interactions may also significantly modify the metal's first coordination sphere.[17]



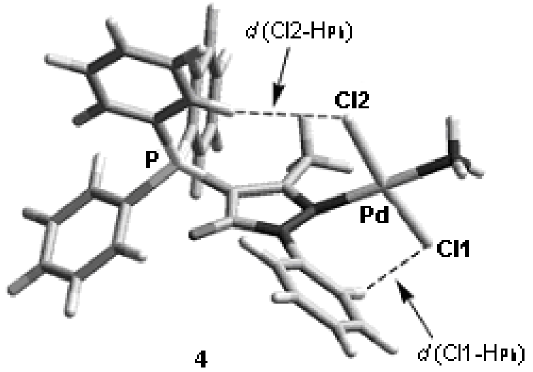
Scheme 3. Possible resonance forms with a significant contribution.

The theoretical analysis was performed by quantum mechanics calculations carried out at the DFT level, using a simplified version of the X-ray structure of **2** as the starting geometry (see computational details). One of the two pyrazolone ligands was replaced by NH_3 in order to obtain structure **4** (Table 1). This was considered justifiable since the *trans* arrangement of the nitrogen ligands in **2** should result in negligible steric interactions between the two organic moieties. In fact, it proved to be an acceptable approximation when comparing the geometries obtained by both X-ray and DFT calculations (see Table 1). The rest of the complex was unchanged. An additional molecular mechanics calculation (see computational details), accounting for steric and electrostatic interactions, was also carried out in order to establish, by comparison with the DFT calculations, the origin of the out-of-plane distortion of Pd in this complex.

Table 1. Experimental and calculated values for selected geometrical parameters.[a,b,c]



2 Z = pyrazolone ligand (**L**)
4 Z = NH_3



4

Entry	Parameter	X-Ray	DFT	MM
1	*d*(Pd–N2)	2.013(6)	2.067	1.963
2	*d*(N1–N2)	1.396(8)	1.407	1.366
3	*d*(N2–C3)	1.372(10)	1.344	1.417
4	*d*(C3–C4)	1.408(10)	1.426	1.466
5	*d*(C4–C5)	1.442(11)	1.452	1.463
6	*d*(C5–N1)	1.384(10)	1.399	1.415
7	*d*(C5–O)	1.259(9)	1.268	1.389
8	*d*(C4–P)	1.721(8)	1.750	1.756
9	*d*(H_{Ph}–Cl1)	2.949	2.796	3.039
10	*d*(Cl2–H_{Ph})	3.359	3.246	3.075
11	*D*(PdN2C3C4)	−150.4	−147.3	−147.0
12	*D*(C5N1$C_{ipso}C_o$)	+130.1	+140.9	+141.1

[a] *d* for distance in angstroms (Å). *D* for dihedral in degrees (°). [b] X-Ray and MM calculation refer to compound **2**. DFT calculations refer to structure **4**. [c] *D*(PdN2C3C4) reflects the out-of-plane Pd distortion whereas *D*(C5N1$C_{ipso}C_o$) measures the torsion of the phenyl group with respect to the pyrazolone ring.

Although the MM geometry is not very accurate, the global shape of complex **2** is well reproduced if compared to both the X-ray structure and the calculated DFT geometry for **4** (Fig. 3). Most interestingly, the value for the *D*(PdN2C3C4) dihedral angle (which is a measure of the out-of-plane Pd distortion) given by MM coincides with the experimental and DFT ones. This means that the deviation from planarity of the Pd/pyrazolone system could have its origin in other factors than the electronic properties of the pyrazolone ring, *viz.*, steric and electrostatic interactions.

From all these calculations, it can be concluded that the Pd atom always prefers to be located out of the plane defined by the pyrazolone ring, independently of the calculation method chosen, in agreement with the crystal structure. Some significant geometrical parameters derived from the X-ray crystallographic data, from the DFT and the MM calculation are shown in Table 1.

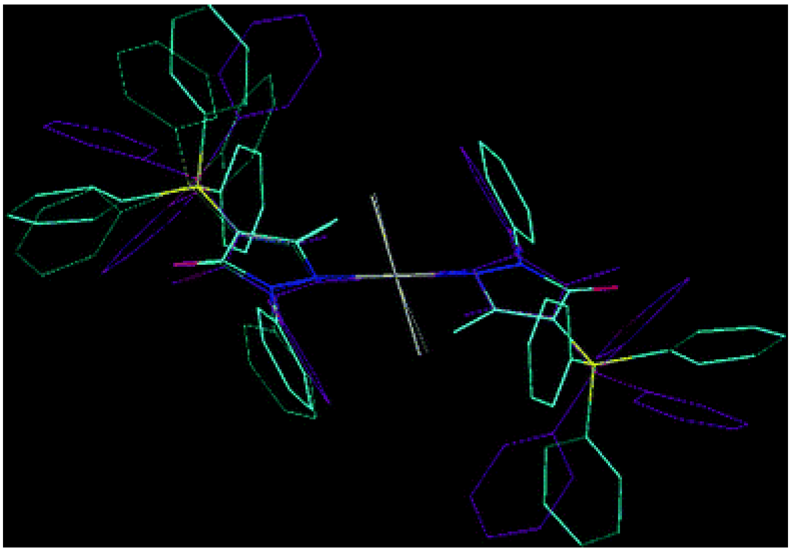


Figure 3. X-Ray crystal (thick line, blue) and molecular mechanics (magenta) structures of compound **2**. The DFT structure (thin line, blue) is calculated for **4**. Hydrogens have been omitted for clarity.

The bond distances within the pyrazolone ring shown by the X-ray structures of **L** and **2** (see Scheme 2) are indicative of a slight contribution of resonance form **C** in the complex. Thus, the *d*(N2–C3) distance in **2** has increased and the *d*(C3–C4) distance has decreased when compared to the values found in free **L** (Scheme 2). The same trend becomes apparent in the DFT calculations on **4**: thus, on going from **L** to **4** the *d*(N2–C3) distances vary from 1.329 to 1.344 Å, and the *d*(C3–C4) distances from 1.445 to 1.426 Å. However, for both structures only slight differences can be found in the Mulliken charges. Moreover, the NBO analysis gives approximately the same charge distribution for **L** and **4** and almost the same bond contribution and hybridization type for all atoms in the pyrazole ring.

Due to the MM calculation, which account for the experimental *D*(PdN2C3C4) dihedral angle, as well as the similarities of **L** and **4** as established by NBO analysis, we considered that the out-of-plane distortion of the Pd atom could have its origin in steric and electronic factors instead of an electronic distribution effect in the pyrazolone ring. In order to prove this hypothesis, several DFT calculations, in which system **4** was *structurally* modified, were carried out. Thus, when the phenyl group located at N(1) was replaced by a methyl group, the Pd atom became completely coplanar with the pyrazolone ring (the *D*(PdN2C3C4) dihedral angle changed to –177.5°, see entry 11, Table 1). However, when the same phenyl group was replaced by the smaller pyrrolyl ring (attachment through a C_α carbon atom),[18] the distortion was approximately the same (the D(PdN2C3C4) dihedral angle changing to –146.2°), but the torsion of the pyrrolyl ring drastically diminished ($D(\mathrm{C5N1}C_{ipso}C_o)$ dihedral angle: +159.3°) with respect to that of the phenyl ring (entry 12, Table 1). In fact, the calculation points to important $H_{aromatic}\cdots Cl(1)$ attractive electrostatic interactions (entry 9, Table 1) that favour the palladium displacement in both **4** and the pyrrolyl substituted system: indeed the $d(H_{Ph}–Cl1)$ distance is significantly smaller (2.796 Å in **4** and 2.867 Å in the pyrrolyl substituted system) than the sum of the van der Waals radii (~3.0 Å). Obviously, the more planar orientation of the pyrrolyl ring increases its conjugation with the pyrazolone moiety. Overall, the inclination of an N-bonded aromatic ring with respect to the pyrazolyl plane results from a balance between three factors: (i) attractive electrostatic $H_{aromatic}\cdots Cl$ interactions; (ii) steric constraints (which become most apparent in the case of the phenyl ring); (iii) stabilisation by conjugation. In keeping with this assumption, we observe that when N(2) is not coordinated (as in **L**) the phenyl ring becomes coplanar with the pyrazolone ring, maximizing the π-delocalization.

Careful analysis of the DFT calculations shows that there exists an additional, but weaker attractive electrostatic interaction that amplifies the out-of plane shift of the metal. The latter is established between the other chlorine atom and one of the phenyl rings of the phosphonium moiety ($Cl(2)\cdots H_{aromatic}$, entry 10, Table 1). This is best examplified by the substitution in **4** of the PPh_3 unit by PH_3 (which suppresses this interaction). In this case the D(PdN2C3C4) dihedral angle value changes back to –165.3°, which corresponds to a less important out-of-plane displacement (distortion decrease: 18°). Note that each of these electrostatic $H_{aromatic}\cdots Cl$ interactions occurs twice in the experimental system because of the symmetry of the structure (Fig. 4).

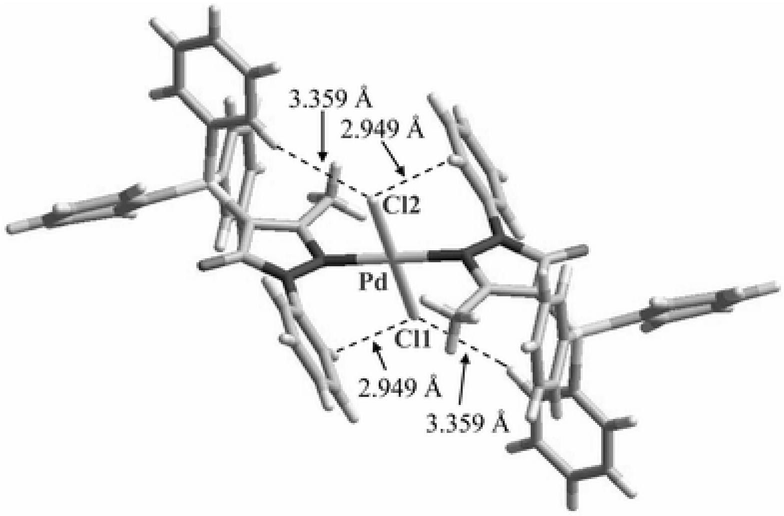


Figure 4. The four main electrostatic interactions found in complex **2**.

Those electrostatic interactions are the main contributing factors for the out-of-plane palladium shift can also be inferred from substitutions made on the metallic moiety. For instance, when the chlorine atoms were substituted by methyl groups (which have a similar van der Waals radii but avoid possible attractive electrostatic interactions), the $D(\mathrm{C5N1C}_{ipso}\mathrm{C}_{o})$ dihedral angle varied only slightly, $D = +137.7°$, whereas the D(PdN2C3C4) dihedral angle became –166.3°. Note that the torsion of the N-linked phenyl group did not vary because there was no change in the steric component. However, the out-of-plane distortion of the Pd atom became much smaller due to the elimination of the two electrostatic $\mathrm{H}_{\mathrm{aromatic}}\cdots\mathrm{Cl}$ interactions. Finally, the clearest evidence for the presence of such electrostatic interactions consisted in the substitution of the two chlorine atoms for the smaller but more electronegative fluorine atoms. The consequences of this modification are quite significant: the D(PdN2C3C4) dihedral angle became –132.9° (thus, the Pd out-of-plane shift drastically increased) and the distances $d(\mathrm{H}_{\mathrm{Ph}}–\mathrm{Cl1})$ and $d(\mathrm{Cl2}–\mathrm{H}_{\mathrm{Ph}})$ decreased to 2.063 and 2.144 Å, respectively (the sum of the Van der Waals radii of H and F amounts 2.55 Å) (Fig. 5).

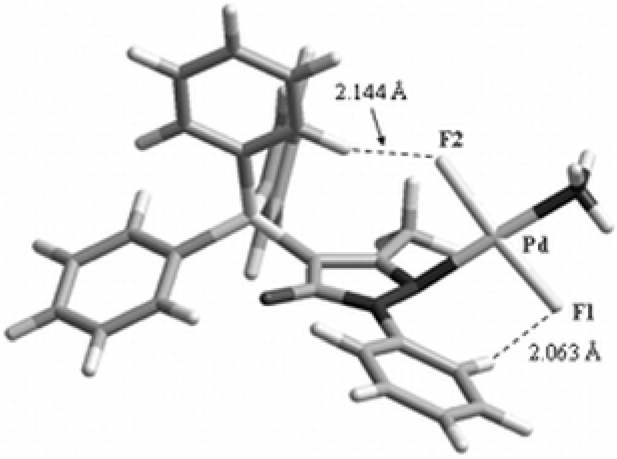


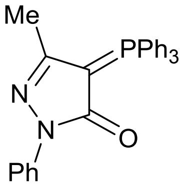
Figure 5. DFT structure of the complex obtained by replacement of the chlorine atoms in **4** by fluorine atoms.

In that case the N-linked phenyl ring becomes more conjugated to the pyrazolone system, the $D(\text{C5N1C}_{ipso}\text{C}_o)$ dihedral angle changing to +159.2°. This is a direct consequence of an increased electrostatic $\text{H}_{\text{aromatic}}\cdots$halide interaction as well as a decrease of the steric hindrance between the phenyl ring and the halide.

Taking into account the calculations presented above, it can be concluded that the main contribution to the observed out-of-plane Pd displacement arises from the attractive electrostatic interactions established between the chlorine atoms and hydrogen atoms of the closest phenyl groups: as shown by DFT-B3LYP calculations, substitution of either the phenyl group at N(1) or of the chloride ligands by methyl groups leads to an almost in-plane coordination of the palladium atom. Conversely, substitution of the chlorine atoms by fluorine atoms results in a more distorted palladium complex with strong, attractive electrostatic $\text{H}_{\text{aromatic}}\cdots\text{F}$ interactions. Furthermore, replacement in **4** of the Ph_3P unit by H_3P leads to a more planar system owing to the suppression of the weaker $\text{H}_{\text{aromatic}}\cdots\text{Cl}$ interaction. Finally, when the N-bonded phenyl ring is replaced by the smaller pyrrolyl group, the out-of-plane Pd distortion (which should diminish if steric factors were predominant) does not change, but is associated merely with a more conjugated pyrrolyl-pyrazolone system.[19] Overall, this study is a further confirmation that weak intramolecular interactions can significantly modify the binding properties of a strong donor.

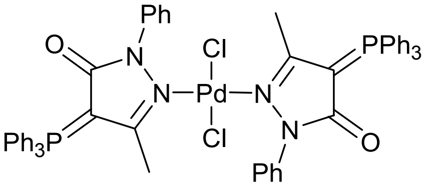
Experimental section

General: All syntheses were performed in Schlenk-type flasks under dry nitrogen. Solvents were dried by conventional methods and distilled immediately prior to use. $CDCl_3$ was passed down a 5 cm-thick alumina column and stored under nitrogen over molecular sieves (4Å). Routine ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ spectra were recorded with an AC-200 Bruker FT instruments. ^1H NMR spectra were referenced to residual protonated solvents (7.26 ppm for $CDCl_3$ and 5.32 for CD_2Cl_2), ^{13}C chemical shifts are reported relative to deuterated solvents (77.0 ppm for $CDCl_3$ and 53.8 ppm for CD_2Cl_2), and the ^{31}P NMR data are given relative to external H_3PO_4. $[PdCl_2(PhCN)_2]$,[20] $[Pd(o\text{-}C_6H_4CH_2NMe_2)Cl]_2$[21] and the bromo-enol **1**[22] were prepared using a literature procedure.



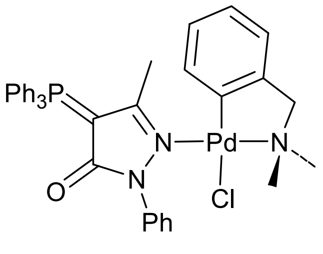
3-Methyl-1-phenyl-4-triphenylphosphoranylidene-2-pyrazolin-5-one (L).

To a stirred solution of 3-methyl-1-phenyl-4-bromo-2-pyrazolin-5-one **1** (10.000 g, 39.50 mmol) in toluene (150 cm^3) was added a solution of PPh_3 (10.360 g, 39.50 mmol) in toluene (200 cm^3). After 0.5 h, a white precipitate appeared. The resulting suspension was then warmed up to 90 °C and stirred for 15 h. After cooling, the supernatant solution was removed and the residue was washed with cold toluene (2 × 20 mL). The residue was then treated with NaH (60% in mineral oil, 1.600 g, 40.0 mmol) in THF (200 cm^3). After stirring for 15 h, the solvent was removed in *vacuo*, upon which the residue was redissolved in toluene (200 cm^{-3}). The solution was filtered through Celite, then concentrated to 20% of its initial volume. Addition of Et_2O afforded a white microcrystalline powder. Yield: 7.720 g, 45%; IR (KBr, cm^{-1}): ν(C=O) 1603s. ^1H NMR (300 MHz, $CDCl_3$): δ 8.12–8.09 (m, 2H, ArH), 7.80–7.51 (m, 15H, ArH), 7.33–7.28 (m, 2H, ArH), 7.05–6.99 (m, 1H, ArH), 1.43 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 167.50 (d, C(O), $^2J(PC)$ = 18.5 Hz), 149.50–119.12 (aryl-C and quat.-C), 65.98 (d, PC_{pyrazo}, $J(PC)$ = 130 Hz), 16.02 (s, CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 10.6 (s). Found: C, 77.49; H, 5.38; N, 6.41. Calc. for $C_{28}H_{23}N_2OP$ (M_r = 434.469): C, 77.40; H, 5.31; N, 6.45%.



trans-Dichloro-bis(3-methyl-1-phenyl-4-triphenylphosphoranylidene-2-pyrazolin-5-one) palladium(II) (2).

To a stirred solution of 3-methyl-1-phenyl-4-triphenylphosphoranylidene-2-pyrazolin-5-one **L** (0.200 g, 0.50 mmol) in chloroform (10 cm^3) was added a solution of [$PdCl_2(PhCN)_2$] (0.096 g, 0.25 mmol) in chloroform (10 cm^3). The pale orange solution was stirred for 1 h at room temperature, then heated for a further 15 h under reflux. The solution was concentrated to *ca.* 5 cm^3. Upon cooling overnight at –20 °C, an orange crystalline solid precipitated, which was collected by filtration, washed successively with cold chloroform (5 cm^3) and pentane (10 cm^3), and eventually dried in *vacuo*. Yield: 0.144 g, 55%; IR (KBr, cm^{-1}): ν(C=O) 1624s. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.03–8.01 (m, 4H, ArH), 7.77–7.70 (m, 18H, ArH), 7.64–7.61 (m, 12H, ArH), 7.46–7.41 (m, 4H, ArH), 7.27–7.21 (m, 2H, ArH), 1.67 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): δ 165.56 (d, C(O), ^2J(PC) = 15 Hz), 155.17–121.48 (aryl-C and C_{quat}), 71.20 (d, PC_{pyrazo}, J(PC) = 133 Hz), 16.31 (s, CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ 10.9 (s). Found: C, 64.08; H, 4.56; N, 5.28. Calc. for $C_{56}H_{46}Cl_2N_4O_2P_2Pd$ (M_r = 1046.27): C, 64.29; H, 4.43; N, 5.35%. Monitoring the reaction by ^{31}P NMR shows the quantitative formation of an intermediate at an early stage of the reaction, which was not characterized (singlet at 10.6 ppm). Presumably this compound corresponds to the *cis* isomer.



Chloro(*o*-dimethylaminomethylphenyl)(3-methyl-1-phenyl-4-triphenylphosphoranylidene-2-pyrazolin-5-one)palladium(II) (3).

To a stirred solution of 3-methyl-1-phenyl-4-triphenylphosphoranylidene-2-pyrazolin-5-one **L** (0.200 g, 0.50 mmol) in toluene (10 cm^3) was added a solution of [$Pd(o\text{-}C_6H_4CH_2NMe_2)Cl]_2$ (0.138 g, 0.25 mmol) in toluene (10 cm^3). A pale yellow precipitate formed immediately.

After stirring for 0.5 h, the precipitate was collected by filtration, washed first with toluene (5 cm^3), then pentane (10 cm^3) before being dried in *vacuo*. Yield: 0.327 g, 92%; IR (KBr, cm^{-1}): ν(C=O) 1624s. ^1H NMR (300 MHz, $CDCl_3$): δ 8.10 (pseudo d, 2H, ArH), 7.80–7.55 (m, 15H, ArH), 7.35–7.30 (m, 2H, ArH), 7.17–7.10 (m, 1H, ArH), 6.91–6.75 (m, 3H, ArH), 6.26 (d, 1H, ArH, J = 7.1 Hz), 3.73 and 3.58 (AB spin system, 2H, NCH_2, ^2J = 14.0 Hz), 2.77 and 2.68 (2s, 2 × 3H, NCH_3), 1.95 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 165.97 (d, C(O), ^2J(PC) = 15.6 Hz), 152.92–122.90 (aryl-C and C-pyrazole), 73.75 (s, NCH_2), 69.90 (d, PC_{pyrazo}, J(PC) = 132 Hz), 52.48 and 52.22 (2s, NCH_3), 18.08 (s, CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 11.4 (s). Found: C, 62.41; H, 4.77; N, 5.84. Calc. for $C_{37}H_{35}ClN_3OPPd$ (M_r = 710.54): C, 62.55; H, 4.97; N, 5.91%.

X-Ray crystallography

Crystal data for 2.

Crystals suitable for X-ray diffraction were obtained by slow evaporation of a chloroform solution. $C_{56}H_{46}Cl_2N_4O_2P_2Pd\cdot 4CHCl_3$, M = 1523.78, triclinic, space group $P\bar{1}$, yellow prisms, a = 10.4860(4), b = 11.1350(5), c = 18.4870(8) Å, α= 76.56(5), β = 87.92(5), γ = 67.80(5)°, V = 1940.57(14) Å^3, Z = 1, μ = 0.801 mm^{-1}, F(000) = 768, D_c = 1.304 g cm^{-3}. Crystals of the compound were glued to a glass fibre and mounted on a Nonius Kappa CCD. X-Ray diffraction measurements were made using graphite-monochromated Mo-Kα radiation (λ = 0.71073Å) at 173 K. Data collection was carried out using the Nonius collect suite. 8556 Reflections collected ($1.13 < \theta < 27.41°$), 5324 data with $I > 2\sigma(I)$. The structure was solved by direct methods with SHELXS-97 and refined with SHELXL-97.[23] Hydrogen atoms were included and refined using a riding model in SHELX-97. Final results: R_1 = 0.0915, wR_1 = 0.219, goodness of fit = 0.835, 376 parameters, largest difference peak = 0.996 e Å^{-3}. Important bond lengths and angles are given in Table 1.

Crystal data for 3.

Crystals suitable for X-ray diffraction were obtained by slow evaporation of a dichloromethane solution: $C_{37}H_{35}ClN_3OPPd$, M = 710.54, monoclinic, space group $P2_1$, orange plates, a = 9.5561(1), b = 16.2957(2), c = 11.0233(1) Å, β= 110.4610(7)°, V = 1608.29(3) Å^3, Z = 2, μ = 0.744 mm^{-1}, F(000) = 728. Crystals of the compound were mounted on a Nonius Kappa CCD. Data collection with Mo-K_α radiation (λ = 0.71073 Å) was carried out at 173 K using the Nonius collect suite.[24] 71068 reflections were collected ($3.2 < \theta < 27.5°$), 7233

being found to be unique (merging *R* = 0.096). The structure was solved by direct methods with the program SIR92.[25] Least squares refinement was carried out using the program CRYSTALS.[26,27] Hydrogen atoms are in calculated positions. Final results: $R(F) = 0.0236$ ($I > 3\sigma(I)$), $wR(F) = 0.0281$ (all data), goodness of fit = 1.0672, residual electron density minimum/maximum = –0.67/0.77 e Å $^{-3}$. A disorder over two positions was found for the Me_2NCH_2 group. Important bond lengths are given in Scheme 1.
CCDC reference numbers 271195 and 271196.

Computational details

The calculations were carried out at the DFT-B3LYP level[28–30] with the Gaussian 03 program.[31] We used as starting geometries those provided by the X-ray structure. Owing to the symmetry of the crystal structure, we have replaced one organic molecule by the amino group. The geometries were fully optimized by the gradient technique with the following basis: For Pd the LANL2DZ basis set was modified following the prescription of Couty and Hall.[32] In this modified basis the innermost core electrons (up to 3d) are described by the relativistic orbital-adjusted effective core potential of Hay and Wadt[33] and the remaining outer core and valence electrons by a [341/541/31] basis set where the two outermost 5p functions of the standard LANL2DZ basis set have been replaced by a[41] split of the 5p function optimized by Couty and Hall. The carbon, oxygen, nitrogen and hydrogen atoms[34] were described by the standard 6-31G basis set, whereas we used for the phosphorus and halogen atoms the polarized 6-31G* basis set.[35] The DFT *d*(Pd–N2) distance values obtained with this basis set are in agreement with those of experimental pyrazole–palladium complexes.[36–38] The molecular mechanics calculation was performed using the MM+ force field (improved MM2) implemented on the Hyperchem program.[39]

References

[1] E. C. Okafor, *Polyhedron* **1983**, *2*, 309.

[2] K. Torkestani, G. J. Goetz-Grandmont, J.-P. Brunette, *Solv. Extr. Ion Exch.* **1997**, *15*, 819.

[3] F. Marchetti, C. Pettinari, A. Cingolani, D. Leonesi, A. Drozdov, S. I. Troyanov, *J. Chem. Soc., Dalton Trans.* **1998**, 3325.

[4] B. A. Uzoukwu, K. Gloe, O. Rademacher, *Z. Anorg. Allg. Chem.* **2001**, *627*, 108.

[5] F. Marchetti, C. Pettinari, A. Cingolani, A. Drozdov, S. Troyanov, *J. Chem. Soc., Dalton Trans.* **2002**, 2616.

[6] H. Mukai, S. Umetani, M. Matsui, *Solv. Extr. Ion Exch.* **2003**, *21*, 73.

[7] R. Meera and M. L. P. Reddy, *Solv. Extr. Ion Exch.* **2004**, *22*, 761.

[8] A. Cingolani, F. Marchetti, C. Pettinari, R. Pettinari, B. W. Skelton, A. H. White, *Inorg. Chem. Commun.* **2004**, *7*, 235.

[9] V. I. Sokol, V. V. Davidov, N. Y. Merkur'eva, O. A. Al-Saleh, M. A. Ryabov, V. S. Sergienko, Y. V. Shklyaev, *Russ. J. Inorg. Chem.* **2002**, *47*, 409.

[10] C. Pettinari, F. Marchetti, A. Cingolani, D. Leonesi, S. Troyanov, A. Drozdov, *J. Chem. Soc., Dalton Trans.* **1999**, 1555.

[11] P. Bravo, G. Fronza, C. Ticozzi, *J. Organomet. Chem.* **1976**, *111*, 361.

[12] J. Vicente, M. T. Chicote and J. Fernandez-Baeza, *J. Organomet. Chem.* **1989**, *364*, 407.

[13] R. Usón, R. Forniés, R. Navarro, P. Espinet, C. Mendivil, *J. Organomet. Chem.* **1985**, *290*, 125.

[14] D. Soulivong, C. Wieser, M. Marcellin, D. Matt, A. Harriman, L. Toupet, *J. Chem. Soc., Dalton Trans.* **1997**, 2257.

[15] P. Kuhn, D. Sémeril, C. Jeunesse, D. Matt, P. Lutz, R. Welter, *Eur. J. Inorg. Chem.* **2005**, 1477.

[16] S. Umetani, Y. Kawase, T. H. L. Le, M. Matsui, *J. Chem. Soc., Dalton Trans.* **2000**, 2787.

[17] J. Harrowfield, D. Matt, *J. Incl. Phenom. Macrocycl. Chem.* **2004**, *50*, 133.

[18] This group was chosen because it is the smallest uncharged aromatic group. It was attached to the pyrazolone ring through a C_α atom carbon in order to avoid alteration of the electronic character of the pyrazolone ring. Fixing the orientation of the NH group

towards the oxygen atom of the carbonyl group resulted in $H_{aromatic}\cdots Cl(1)$ interactions similar to those observed in 4.

[19] Replacing the N-linked phenyl group by the more bulky *tert*-butyl group, the out-of-plane distortion slightly increased, the *D*(PdN2C3C4) dihedral angle changing to –144.5°. Although steric repulsion between the *tert*-butyl group and the palladium centre may come into play, we note that the attractive electrostatic $Cl(2)\cdots H_{aromatic}$ interaction is still present (the *d*(Cl2–HPh) distance changed from 3.246 Å to an even smaller value, 3.054 Å, see entry 10, Table 1). Moreover, there are some other attractive interactions that result from the out-of-plane Pd distortion: these involve (i) the Pd atom, which interacts with two hydrogen atoms, one originating from the *tert*-butyl group and sitting apically above the metal (Pd ···H 2.539 Å), the other one belonging to the C(3)-methyl group (Pd ···H 2.729 Å); (ii) the Cl(1) atom, which interacts with H atoms of the same alkyl groups (Cl(1) ···H distances: 3.043 and 2.905 Å, respectively).

[20] F. R. Hartley, *The Chemistry of Platinum and Palladium*, Wiley, New York, **1973**.

[21] A. C. Cope, E. C. Friedrich, *J. Am. Chem. Soc.* **1968**, *90*, 909.

[22] G. Westöö, *Acta Chem. Scand.* **1952**, *6*, 1499.

[23] G. M. Sheldrick, *SHELXL-97, Program for the refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

[24] *COLLECT Software*, Nonius BV, **1997–2001**.

[25] A. Altomare, G. Cascarano, A. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 435.

[26] D. J. Watkin, C. K. Prout, J. R. Carruthers, P. W. Betteridge, R. I. Cooper, *CRYSTALS, Issue 11*, Chemical Crystallography Laboratory, Oxford, UK, **2001**.

[27] J. R. Carruthers, D. J. Watkin, *Acta Crystallogr. Sect. A* **1979**, *35*, 698.

[28] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098.

[29] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.

[30] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

[31] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Y. Ayala,

K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *GAUSSIAN 03 (Revision C.02)*, Gaussian, Inc., Wallingford, CT, **2004**.

[32] M. Couty, M. B. Hall, *J. Comput. Chem.* **1996**, *17*, 1359.

[33] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299.

[34] W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257.

[35] P. C. Hariharan, J. A. Pople, *Mol. Phys.* **1974**, *27*, 209.

[36] A. V. Godoy Netto, A. E. Mauro, R. C. G. Frem, A. M. Santana, R. H. A. Santos, J. R. Zoia, *J. Coord. Chem.* **2001**, *54*, 129.

[37] V. I. Sokol, M. A. Porai-Koshits, T. O. Vardosanidze, V. N. Voropaev, E. S. Domnina, G. G. Skvortsova, *Koord. Khim.* **1983**, *9*, 1539.

[38] S. Kingsley, V. Chandrasekhar, C. D. Incarvito, M. K. Lam, A. L. Rheingold, *Inorg. Chem.* **2001**, *40*, 5890.

[39] Hyperchem™ release 7.51. Hypercube, Inc., 1115 NW 4th Street, Gainesville, FL 32601, USA.

Chapter 4

Ethylene oligomerisation and polymerisation with nickel phosphanylenolates bearing electron-withdrawing substituents. Structure-reactivity relationships.

Abstract

Three SHOP-type catalysts in which the C=C(O) double bond is substituted by electron withdrawing substituents, [Ni{$Ph_2PC(R^1)=C(R^2)O$}Ph(PPh_3)] (**2**, R^1,R^2 = –C(Me)=NN(Ph)–; **3**, R^1 = CO_2Et, R^2 = Ph; **4**, R^1 = CO_2Et, R^2 = CF_3) have been assessed as ethylene oligomerisation and polymerisation catalysts and compared to Keim's complex, [Ni{$Ph_2PCH=C(Ph)O$}Ph(PPh_3)] (**1**). A rationale of the influence of the double bond substituents of the *P,O*-chelate unit on the catalytic properties is proposed, on the basis of X-ray diffraction studies, spectroscopic data and DFT-B3LYP calculations.* Whatever their relative electron-withdrawing strength, the R^1 and R^2 substituents induce an activity increase with respect to catalyst **1**. For those systems in which the basicity of the oxygen atom is decreased relative to that of the phosphorus atom, the chain propagation rate increases with respect to that for catalyst **1**. Reduction of the basicity of the P relative to that of the O, however, induces higher chain termination rates.

Résumé

Ce chapitre est consacré à l'étude de la réactivité en oligomérisation et polymérisation de l'éthylène de trois catalyseurs de type SHOP dont la double liaison C=C(O) a été substituée par des groupements électroattracteurs, [Ni{$Ph_2PC(R^1)=C(R^2)O$}Ph(PPh_3)] (**2**, R^1,R^2 = –C(Me)=NN(Ph)–; **3**, R^1 = CO_2Et, R^2 = Ph; **4**, R^1 = CO_2Et, R^2 = CF_3). Leurs performances ont été comparées à celles du complexe de référence [Ni{$Ph_2PCH=C(Ph)O$}Ph(PPh_3)] (**1**). Les propriétés catalytiques de ces complexes ont été corrélées aux propriétés électroniques et stériques des substituants de la double liaison, en faisant appel à des études de diffraction des

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* Calculations were made by Antonio J. Mota,University of Grenada, Spain

rayons-X, aux données spectroscopiques des complexes ainsi qu'à des calculs théoriques DFT-B3LYP.* Quel que soit leur pouvoir électroattracteur, les substituants R^1 et R^2 induisent une augmentation d'activité par rapport au catalyseur **1**. Pour les chélates *P,O* dont la basicité de l'atome d'oxygène est diminuée par rapport à celle de l'atome de phosphore, la vitesse de propagation de chaîne augmente par rapport à celle du catalyseur **1**. Une réduction de la basicité de l'atome de phosphore relativement à celle de l'oxygène entraîne quant à elle des vitesses de terminaison de chaîne plus élevées. Pour la première fois, les performances de catalyseurs de type SHOP ont été reliées au caractère différencié des atomes coordinateurs du chélate *P,O*.

Introduction

The use of *late* transition metal complexes as single site ethylene oligomerisation and polymerisation catalysts was first achieved industrially in the early 70's when *in situ*-generated phosphanylenolato-nickel complexes were employed for the selective production of linear α-olefins (SHOP process).[1-4] Since then, the interest in such complexes as catalysts for the production of polyolefins has continually increased.[5-8] Regarding polymerisation reactions, late transition metal complexes present several advantages over the classical group IV metal catalysts, including easy complex synthesis, low cost for the preparation of the first-series-metal-derivatives, low environmental impact, functional group tolerance, etc.[9] Nowadays, their development is driven by three main goals: (*i*) the selective production of C_4-C_{10} α-olefins, the demand for which for copolymerisation purposes is growing rapidly;[10] (*ii*) the production of ethylene/polar monomer copolymers which represent one of the most promising development areas of polyolefin industry;[11-13] (*iii*) the production of polymer lattices (*i.e.* stable colloidal aqueous dispersions of polymer particles) through aqueous emulsion polymerisation under mild conditions.[14]

The SHOP catalysts, which contain anionic, phosphanylenolato chelates (Scheme 1) proved to be suited for all these purposes. While such complexes, when used without any additive, usually function as ethylene oligomerisation catalysts, their combination with a phosphine scavenger (*e.g.,* [Ni(cod)$_2$] (cod = 1,5-bis(cyclooctadiene))), allowing removal of the neutral phosphine ligand (PR'$_3$ in **A**) results in a polymerisation catalyst.[15,16] The original SHOP catalysts, once deprived of the unidentate phosphine ligand, displayed only modest

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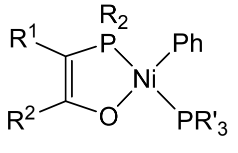
* Les calculs ont été effectués par Antonio J. Mota,Université de Grenade, Espagne

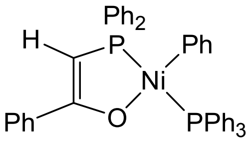
activities in ethylene polymerisation. In fact, highly efficient systems may be obtained through modification of the *P,O* chelator.



A

Scheme 1. General formula of SHOP-type catalysts.

It appears that introduction of *electron-withdrawing* substituents on the *P,O* backbone (which here are referred to as "Z" substituents) significantly increases the rate of ethylene polymerisation.[15-17] Complex **B** for example, which contains a sulphonato substituent on the P-C_α carbon atom, shows an activity, which under optimised conditions, is two orders of magnitude higher than that of prototype **1**.[15,16] Interestingly, the –SO_3Na substituent of **B** further induces the formation of polymer chains longer than those formed with **1** (when operating as a polymerisation catalyst). Careful examination of the literature reveals that the presence of Z substituents does not systematically result in higher polyolefins. In a recent paper, we have shown that the strongly electron-withdrawing pyrazole ring of complex **2** causes a dramatic shift of the polyolefin distribution towards the formation of shorter olefins.[18] In fact, **2** is the only phosphanylenolato nickel complex which, under typical polymerisation conditions (*i.e.* after removal of the neutral phosphine ligand), is able to produce significant amounts of short oligomers with good activities.[19,20] Note that the phosphanylacetato complex **C** was found to behave similarly.[21,22] Intuitively, these observations suggest that the properties of SHOP catalysts containing electron-poor *P,O* chelates are strongly dependent on the way the Z group modifies the relative donor properties of the P and the O atoms of the chelate, *i.e.* to what extent the basicity of the donor atoms is modified. To gain greater insight into the intimate factors that govern the properties of such complexes, we decided to compare the structural and catalytic properties of three phosphanylenolato nickel complexes, namely **2**-**4**, in which



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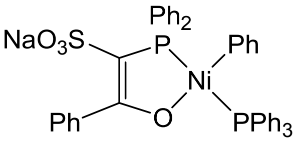
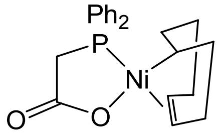
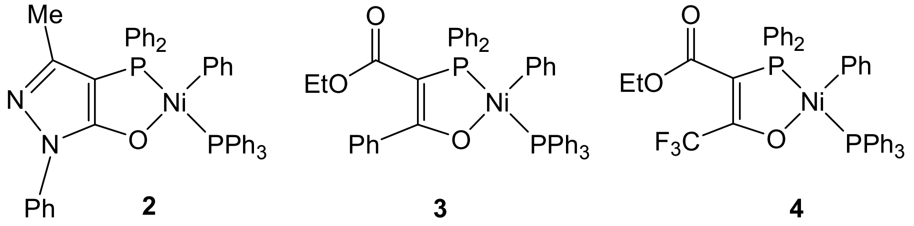


B



C

the two carbon atoms of the *P,O* chelates are substituted by Z groups of unequal strength (Scheme 2). Their catalytic properties were assessed with respect to both ethylene oligomerisation and polymerisation, and compared with those of **1**. It is worth mentioning here that the chelating *P,O*-ligands of **3** and **4** were recently assessed by other authors, but only for polymerisation using *in situ*-generated complexes.[17] A synthesis of **2**, together with some preliminary catalytic results, was reported by us recently.[18]

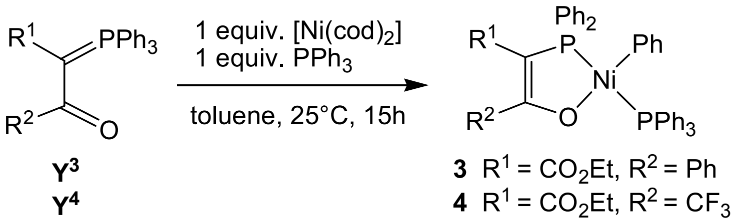


Scheme 2. The electron-poor Ni(*P,O*) complexes used in this study.

Results

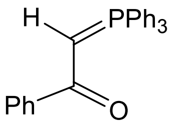
Synthesis of the complexes

The new complexes **3** and **4** were synthesised in good yields by reaction of [Ni(cod)$_2$] with the appropriate phosphorus ylide in the presence of PPh$_3$ (Scheme 3).

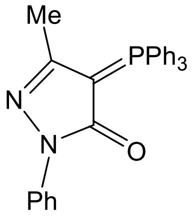


Scheme 3. Preparation of complexes **3** and **4** using phosphorus ylides.

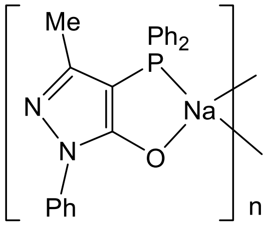
We found that this methodology, originally applied by Keim for the preparation of **1** (starting from $\mathbf{Y^1}$, where $R^1 = H$, $R^2 = Ph$),[4] could also be applied to the synthesis of complex **2** using the phosphorus ylide $\mathbf{Y^2}$. Nevertheless, the previously reported preparation of **2**, which relies on the sodium phosphanylpyrazolonate **5**, requires fewer synthetic steps and in practice turns out to give readier access to **2**.[18]



Y¹



Y²



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Complexes **3** and **4** could be isolated as dark yellow crystals upon slow diffusion of hexane into a toluene solution of the complex. Addition of hexane to a concentrated toluene solution of **4** precipitated a powder, which spontaneously converted to monocrystals upon standing. The two complexes were characterised by elemental analysis, ^{1}H, ^{31}P and ^{13}C NMR and X-Ray analysis (*vide infra*). The ^{31}P NMR spectra both exhibit an AB system, with *J*(AB) values (276 Hz (**3**) and 277 Hz (**4**)) in accord with *trans*-positioned phosphorus atoms (cf. 284 Hz and 280 Hz for **1** and **2**, respectively). On going from **3** to **4**, that is, upon replacement of a Ph by a CF_3 group, the charge distribution on the C=C double bond is strongly perturbed, as can be seen from the chemical shift variations of the corresponding carbon atoms, $\Delta(\delta C_{\beta-P}) = -17.6$ ppm, $\Delta(\delta C_{\alpha-P}) = +3.3$ ppm. Owing to the conjugation of the $C{=}O_{ester}$ bond with the C=C bond of the chelating unit, the $\nu(C{=}O)_{ester}$ frequency (1670 cm^{-1}) of complex **3** is lowered with respect to that of conventional, non-conjugated esters. In keeping with the strong inductive effect of the CF_3 group, which lowers the conjugation between the C=C bond and the CO_2 group, however, the carbonyl band of **4** appears at a higher wavenumber than in **3**, namely 1699 cm^{-1}. The two IR spectra further exhibit strong, characteristic $\nu(C{=}C) + \nu(C{-}O)$ combination bands, at 1459 cm^{-1} for **3** and 1517 cm^{-1} for **4**. That of **3** is somewhat lower than expected (cf. 1506 cm^{-1} for **1**[23]), suggesting a structural distortion within the PCCO arm (*vide infra*). The solid state structures of **3** and **4** were determined by single crystal X-ray diffraction studies (Figures 1 and 2; for structural data see Table 1). Together with that of **2**, they constitute the only reported structures of SHOP-type catalysts having an electron-deficient *P,O* chelate. It should be mentioned that the NBO charge analysis at the DFT–B3LYP/6-31G* level (see supporting information) shows that the positive global charge of the NiPCCO ring (+ 0.755 (**3**); + 0.681 (**4**)) in both complexes is considerably higher than in **1** (+ 0.478). For comparison, the corresponding charge in **2** is + 0.808.

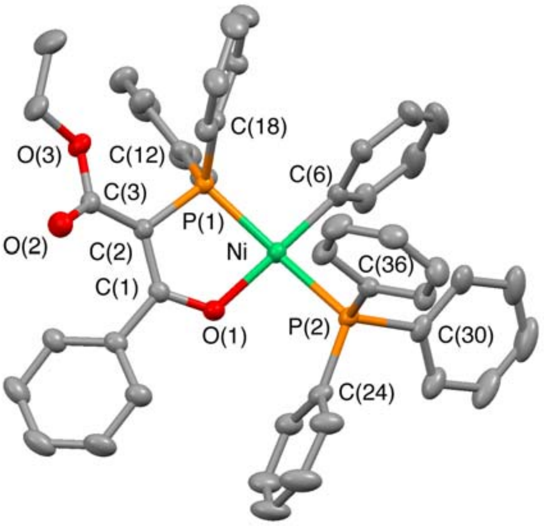


Figure 1. Molecular structure of **3**.

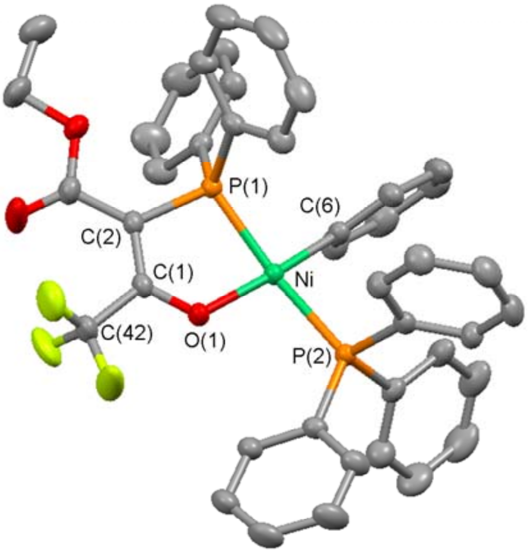


Figure 2. Molecular structure of **4.**

As previously observed for **2**,[18] the coordination environment of **3** deviates slightly from an ideal square planar geometry. Thus, while P(1) and P(2) lie on the same side of the mean square coordination plane, C(12) and O(1) are turned towards the other side of this plane (P(1)NiP(2) = 161.7°; C(6)NiO(1) = – 177.9°). A similar "Td-oriented" distortion was also found in **4** (P(1)NiP(2) = 170.3°; C(6)NiO(1) = – 170.6°). Comparison of the structural data of **1**[4,24] and **3** shows that substitution of the enolate H atom of **1** by an ethoxycarbonyl group has only a minor impact on the four bond lengths involving the nickel centre. On the other hand, in keeping with the IR data discussed above, the carbonyl group of **3** induces a lengthening of the conjugated C(1)=C(2) bond with respect to **1** (Table 1). An interesting feature of this complex is that the metallacyclic unit deviates significantly from planarity (distance of P(1) to the plane defined by Ni, O(1), C(1), C(2): 0.277(2) Å). In fact, the observed distortion results from an important steric interaction between the carbonyl group and the neighbouring phenyl ring, as revealed by the C(6)C(1)–C(2)C(3) torsion angle of 22.7° (Figure 3).

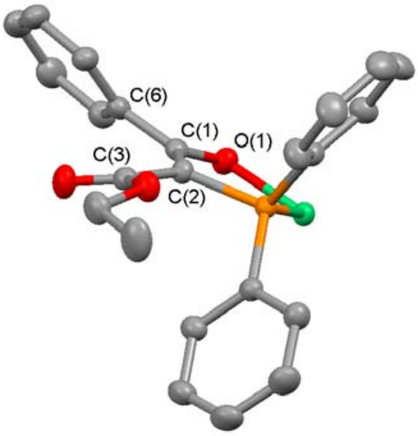


Figure 3. Partial view of **3** showing the distortion about the C(1)=C(2) double bond.

Surprisingly, the presence of the CF_3 group in **4** induces only a slight lengthening of the Ni–P_{chel} and Ni–O bonds with respect to those of **3** (Table 1). Nevertheless, the NBO charge analysis shows that the negative charge on the oxygen atom of the metallacycle undergoes a significant variation, namely from –0.730 in **3** to –0.705 in **4** (*cf.* –0.781 in **1**). Moreover, the whole charge of the nickel-bonded phenyl group also decreases, going from –0.391 to –0.377, while the charge on each phosphorus atom remains practically unchanged. Thus, should **3** and **4** display important differences in their catalytic behaviour, this could then be due to the charge differences along the O–Ni–C(Ph) axis. As far as the X-ray structure is concerned, the strong *–I* effect of the CF_3 group is best seen in the C=C bond length of **4** (1.374(2) Å), which is significantly shorter than the corresponding one in **3** **(**1.395(2) Å).

As reported in a preliminary work, the presence of the electron-withdrawing pyrazolyl ring in **2** induces a marked lengthening of both, the Ni–P and Ni–O bonds. In this case, the Ni–O and Ni–P bonds are respectively 0.056 Å and 0.065 Å longer than the corresponding bonds in **1**, showing that the electron-withdrawing effect of the pyrazolyl ring of **2** is not only strong, but also nearly symmetrically distributed over the *P,O* chelate. Interestingly, the charge of the oxygen atom in **2** as well as that of the P_{chel} atom are almost identical to those of **1**, as inferred from DFT calculations. We note, however, that the charge of the metallated aryl ring has changed from –0.399 in **1** to –0.375 in **2**, thus reflecting the strong inductive effect of the pyrazolyl ring.

Previously, we have shown that the pyrozolonato complex **2** may undergo reductive elimination, both in solution and in the solid state, resulting in formation of ylide $\mathbf{Y^2}$.[18] A similar transformation was also observed for **4**, but at a considerably lower rate. Overall, the rate of reductive elimination varies in the order **2** > **4** > **3** ≈ **1**, *i.e.,* it follows the same variation as the Ni–P$_{chelate}$ bond length.

Table 1. Selected structural data for complexes **1-4** (bond lengths [Å], angles [°]).

Compound	P–C$_{chelate}$	C–O	C=C$_{chelate}$	Ni–PPh$_2$	Ni–PPh$_3$	Ni–O	Ni–C	PNiO
1(DAGBES)[a]	1.76(2)	1.30(2)	1.34(2)	2.154(4)	2.275(6)	1.89(1)	1.90(2)	88.0(4)
1(PBZMNI) [a]	1.768	1.313	1.365	2.167	2.230	1.913	1.892	86.49
2	1.770(2)	1.296(2)	1.393(2)	2.210(1)	2.224(1)	1.955(1)	1.885(2)	89.33(6)
3	1.792(2)	1.295(2)	1.395(2)	2.168(1)	2.232(1)	1.907(1)	1.891(2)	85.99(4)
4	1.810(2)	1.286(2)	1.374(2)	2.1754(5)	2.2565(5)	1.921(1)	1.894(2)	85.56(4)

[a] DAGBES and PBZMNI differ in their space group. Standard deviations are not available for PBZMNI

Ethylene oligomerisation

The catalytic tests were carried out in toluene at 70°C, at constant pressures, using a 200 mL glass reactor. For comparison, complex **1** was also tested under these conditions. As expected, the complexes **2-4** catalyse the oligomerisation of ethylene, producing, like **1**, oligomers which are linear to 99%. The selectivity for α-olefins, determined on the C_4-C_{16} fraction (5 bar experiments), is higher than 96% for complexes **1-3** and drops, owing to isomerisation, to 81% for complex **4** (Table 2, entries 1, 4, 7 and 10). The olefins are present in a Schulz-Flory distribution.[25] The α values decrease significantly on going from **1** and **3** (α = 0.92 and 0.93, respectively) to **2** and **4** (α = 0.73 and 0.78, respectively), *viz.* strongly electron-withdrawing Z groups favour the formation of shorter oligomers. The shift towards shorter oligomers is remarkable in the case of complex **2** (Figure 4). Thus, when operating at 5 bar, the C_4-C_{16} fraction obtained with this complex represents ca. 73 wt.-% of the total amount of olefins produced (Table 2, entry 4), while it represents only 15 wt.-% when using **1** under similar conditions. It is interesting to note that the ability of the complexes **2** and **4** to shift the product distribution towards shorter olefins does not correlate with the observed reaction rates. Indeed, these vary in the order **2** < **1** < **4** < **3**, complex **3** operating 7 times faster than **2** (Table 2, compare entries 1, 4, 7, 10).

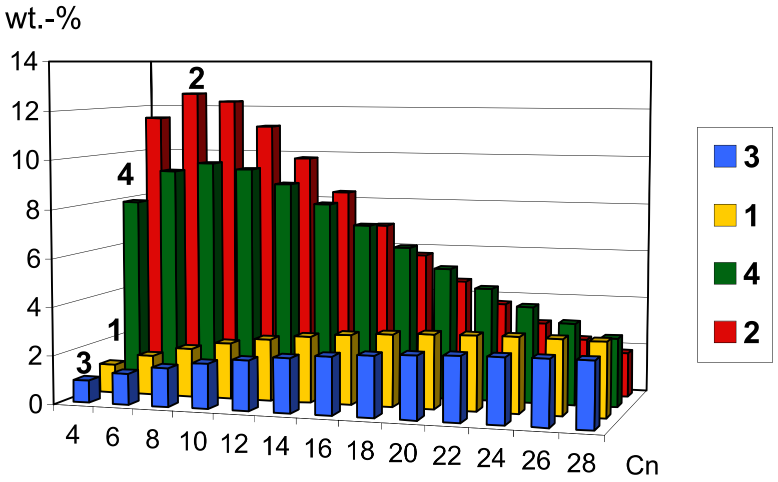


Figure 4. Ethylene oligomerisation. Product distribution using catalysts **1-4** (5 bar, 1 h).

Thus, the factors that govern the activity and the product distribution of SHOP-type catalysts containing electron-poor chelators cannot be attributed solely to the electron withdrawing strength of the Z substituents.

Table 2. Ethylene oligomerisation using complexes **1-4** under a constant ethylene pressure.[a]

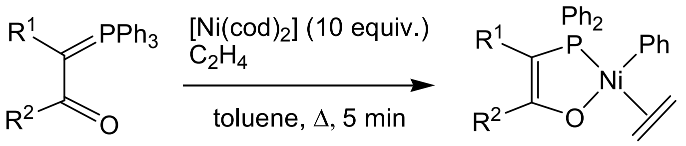
run	catal.	P [bar]	t [h]	TOF [mol(C_2H_4) mol(Ni)$^{-1}$ h^{-1}]	α[b]	C_2H_4 consum. [g]	C_4-C_{16} [wt.-%]	α-olefin[c] [wt.-%]
1	**1**	5	1	15500	0.92	3.25	15.3	98.6
2	**1**	5	2	7500	0.92	3.15	15.3	98.3
3	**1**	5	0.5	29600	0.89	3.11	25.1	97.3
4	**2**	5	1	9700	0.73	2.04	72.5	95.9
5	**2**	5	2	6600	0.83	2.77	45.2	95.2
6	**2**	5	0.5	14400	0.69	1.51	80.2	96.2
7	**3**	5	1	68000	0.93	14.32	12.3	95.8
8	**3**	2.5	2	14800	0.87	6.23	31.9	92.3
9	**3**	2.5	1	27600	0.86	5.81	37.0	92.6
10	**4**	5	1	32600	0.78	6.87	60.2	81.5
11	**4**	2.5	1	26500	0.72	5.58	75.2	75.8

[a] 200 mL glass reactor filled with 7.5 μmol cat. in 30 mL PhMe, 70°C (external oil bath temperature); [b] Schulz-Flory parameter $\alpha = \text{mol}(C_{n+2})/\text{mol}(C_n)$; [c] for the C_4-C_{16} fraction

Recent work has already shown that the outcome of ethylene oligomerisation by SHOP catalysts markedly depends on the relative electronic (and steric) properties of the two P(III) centres.[26-35] Logically, an understanding of the intrinsic properties of the Ni-*P,O* metallacycles described in this work is required to assess the catalytic systems lacking the PPh_3 ligand. We therefore decided to generate catalytic systems of the types **1a**-**4a** (see next section). In keeping with a number of polymerisation studies on SHOP-type catalysts, we anticipated that this approach would result in the formation of polyolefins of higher molecular weight.[16]

Ethylene polymerisation

Two methods were, *a priori*, available to generate *in situ* complexes of the types **1a**-**4a**: a) treatment of one of the complexes described above with a phosphine scavenger such as $[Ni(cod)_2]$ or $[Rh(acac)(C_2H_4)_2]$; b) reaction of the appropriate phosphorus ylide with $[Ni(cod)_2]$ in toluene. In order to get catalytic systems that were rigorously PPh_3-free, the latter method was preferred (Scheme 4). The runs were carried out under constant pressure and stopped after 0.5 h. The temperature of the reaction was kept constant (Table 3). The results are summarised in Table 3.



Y¹ **1a** $R^1 = H, R^2 = Ph$
Y² **2a** $R^1,R^2 = –C(Me)=N–N(Ph)–$
Y³ **3a** $R^1 = CO_2Et, R^2 = Ph$
Y⁴ **4a** $R^1 = CO_2Et, R^2 = CF_3$

Scheme 4. *In situ* generation of the catalytic systems **1a**-**4a**.

The experiments revealed that the pyrazolone derivative **2a** is the most active catalyst, its performance slightly surpassing that of **4a**, which was previously regarded as the most active neutral, SHOP-derived polymerisation catalyst. Overall, the activity of the complexes follows the order: **1a** < **3a** < **4a** < **2a**. In other words, the higher the electron deficiency of the *P,O* chelate, the higher the reaction rate. For the three electron-poor systems **2a**-**4a**, the maximum activity was found for a reaction temperature of ca. 80°C when the runs carried out at 5 bar. The optimised activity of **1a** was not determined, but obviously requires temperatures above 90°C. As expected, increasing the pressure from 5 to 10 bar increases the activity of the catalysts (Table 3, entries 4, 8, 12, 16).

The influence of the electron-withdrawing Z group(s) on the chain length of the polyethylene is remarkable. While **3a** produces polyethylene characterised by an M_w higher than that obtained with **1a** (Table 3, entries 1 and 9), the chains produced with **2a** and **4a** are shorter. Analysis of the reaction solutions by GC revealed that the outcome of the **2a**-catalysis differs from all others, this catalyst being the only one producing significant amounts of light oligomers.

Table 3. Ethylene polymerisation using *in situ*-generated catalysts **1a**- **4a**.[a]

Entry	Cat.	Cat. amount (μmol)	P (bar)	T[b] (°C)	PE[c] (g)	Activity (g $\text{mmol}_{\text{cat.}}^{-1}$ h^{-1})	M_w[d] (g mol^{-1})	PDI[e]	T_m[f] (°C)
1	**1a**	4	5	70	1.12	560	6600	2.5	127.0
2	**1a**	4	5	80	1.87	940	/	/	126.7
3	**1a**	4	5	90	2.27	1140	3900	1.8	124.0
4	**1a**	2	10	80	2.83	2830	4100	1.8	127.4
5	**2a**	4	5	70	3.37 4.5[g]	1690 2200	1100	1.6	97.9[h]
6	**2a**	4	5	80	3.46 4.4[g]	1730 2200	/	/	96.2[h]
7	**2a**	4	5	90	2.59 3.8[g]	1300 1900	1200	1.3	95.7[h]
8	**2a**	2	10	80	3.81 4.3[g]	3810 4300	1500	1.5	98.1[h]
9	**3a**	4	5	70	0.61	300	9500	2.0	129.7
10	**3a**	4	5	80	2.75	1370	/	/	128.7
11	**3a**	4	5	90	2.37	1190	7100	1.9	127.8
12	**3a**	2	10	80	4.42	4420	8200	1.9	128.0
13	**4a**	4	5	70	2.96	1480	5200	1.9	124.5
14	**4a**	4	5	80	4.29	2150	/	/	121.5
15	**4a**	4	5	90	4.27	2140	4300	1.8	119.6
16	**4a**	2	10	80	4.11	4110	4600	1.7	124.3

[a] conditions: 100 mL stainless steel autoclave, 20 mL PhMe, 0.5 h reaction time, 10 equiv. [Ni(cod)_2]; [b] temperature inside the autoclave; [c] after precipitation of the reaction mixture with 200 mL MeOH/HCl; [d] determined by SEC-HT *vs.* polystyrene standard uncorrected; [e] PDI (polydispersity index) = M_w/M_n; [f] measured by DSC; [g] total amount of products, including soluble oligomers; [h] very broad DSC curve.

It turned out that ca. 25 wt.-% of the oligomers formed are soluble in methanol. In keeping with this observation, the polydispersity of the polymeric material obtained after precipitation was lower than that of the polymer formed with the three other catalysts (Table 3, entries 5-8). The low values of the corresponding melting temperatures (T_m) are also consistent with these findings.

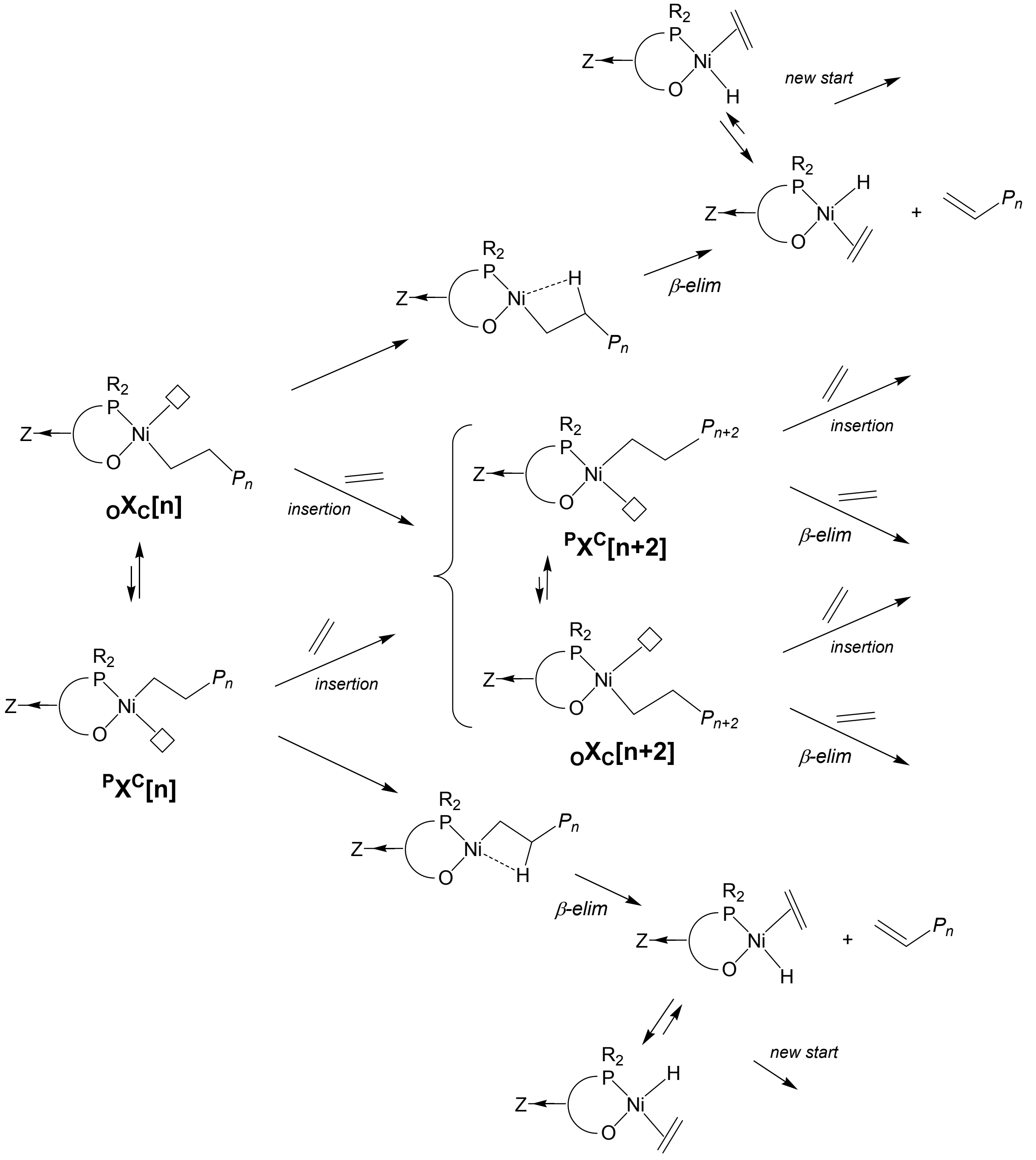
Discussion

The results presented above clearly show that under "polymerisation conditions", *i.e.* in the absence of PPh_3, the *P,O*-chelators substituted by electron-withdrawing groups (**2a**-**4a**) gave catalysts all more active than system **1a**. These findings do not parallel the observations made under oligomerisation conditions. Thus, complex **2** was found to be a little less active than **1**, and **4** less active than **3**. Taking again **1** (or **1a**) as reference compound, whatever the conditions used, the pyrazolonato ligand of **2**/**2a** and the CF_3/CO_2Et-substituted enolate of **4**/**4a** shift the product distribution towards compounds with lower molecular weights. In contrast, system **3a** where the *P,O* chelate is Ph/CO_2Et-substituted gave compounds with increased molecular weight. Note, polymers with much higher molecular weights were obtained with the related Ph/SO_3Na-substituted complex **B** reported by Klabunde et al.[16]

In order to understand the effects exerted by Z substituents, one has to bear in mind the recent studies by Heinicke and Keim showing that a selective increase of the basicity of the P_{chel} atom increases the activity of the catalyst under polymerisation conditions.[32] This strongly suggests that the systematic activity increase observed with SHOP-catalysts having Z-substituted *P,O* arms must arise from a decrease of the basicity of the oxygen atom. The latter was shown, by theoretical calculations, to induce an electron density decrease along the ONiC(Ph) axis. This is also in line with the recent calculations made by Ziegler for *N,O*-chelated Ni catalysts who showed that an electron density decrease on the O atom reduces the ethylene insertion barrier.[36] It should be noted here that the Ni–O bonds in **2** (1.955(1) Å) and **4** (1.921(1) Å), which are the two complexes with the strongest electron-withdrawing substituents and the highest activities, are significantly longer than those of **3** (1.907(1) Å) and **1** (1.89(1) Å).

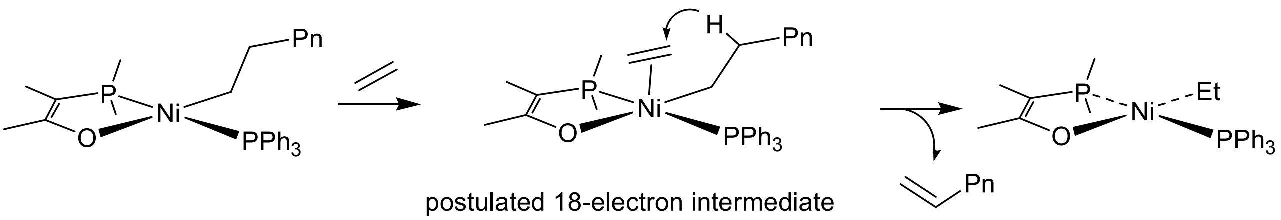
It is further known that the electronic properties of the P_{chel} atom markedly influences the product distribution.[32] Using phosphanylphenolato complexes, Heinicke *et al.* found that replacement of the PPh_2 moiety by $P(alkyl)_2$ groups favours the formation of longer chains under polymerisation conditions. The authors proposed that with more basic PR_2 groups the nickel becomes less electropositive and, accordingly, the barrier for the *β-elimination* step is increased. This suggests that in the general case the C–H activation preferentially occurs in an intermediate having a *cis*-P,alkyl structure (abbreviated $\mathbf{{}^{P}X^{C}[n+2]}$ in Scheme 5) rather than a *trans*-P,alkyl one (noted $\mathbf{{}_{O}X_{C}[n+2]}$**)**, *i.e.*, the hydride is formed on the coordination site trans to the phosphorus atom. On the other hand, in keeping with calculations made by Ziegler for *N,O*-chelated complexes,[36] it seems reasonable to consider that the *ethylene insertion barrier* is lower for a complex of the $\mathbf{{}_{O}X_{C}[n]}$-type than for a $\mathbf{{}^{P}X^{C}[n]}$ complex (see Scheme 5). Therefore, isomerisation of $\mathbf{{}^{P}X^{C}[n]}$ alkyl complexes into $\mathbf{{}_{O}X_{C}[n]}$ ones occurs, in the general case, before the insertion step. Z groups that decrease the donor properties of the P atom only should logically facilitate the β-elimination step in the intermediates of the $\mathbf{{}^{P}X^{C}[n+2]}$-type (originating from a $\mathbf{{}_{O}X_{C}[n]}$-type complex). If the Z group is also able to decrease the basicity of the oxygen atom, then β-elimination should also be favoured in $\mathbf{{}_{O}X_{C}[n+2]}$ structures. One may envisage that in complexes in which the basicity of both the P and the O atom have been considerably decreased, the β-CH activation process becomes favoured on both coordination sites, trans to P and trans to O, and not just trans to P. Overall the role of Z groups exerting a *strong* withdrawing effect on both coordinating atoms, as in **2**, is to allow CH activation on two sites, which in turn increases the probability of chain termination.

Complex **4a** is an interesting case where the CF_3/CO_2Et couple exerts a larger influence on the oxygen atom than on the P_{chel} atom (*vide supra*, structure of **4**). Here, the distribution shift towards lower olefins is less pronounced than with **2a** as a consequence of the higher electron density on the P_{chel} atom, which makes β-elimination in intermediates of the $\mathbf{{}^{P}X^{C}[n+2]}$-type somewhat less favourable. The rate of β-elimination nevertheless remains high, possibly because it is strongly favoured in the $\mathbf{{}_{O}X_{C}[n+2]}$-type intermediates (the position trans to the electron deficient O atom having a high activation efficiency). One may wonder why catalyst **3a**, the activity of which compares with that of **1a**, results in polymers that are longer than those obtained with **1a**. It is likely that this relates directly to the observed metallocycle puckering (see above) induced by the steric interaction between the neighbouring phenyl and CO_2Et groups. Electron delocalisation within the PCCO arm of **3** becomes then less efficient than in **1**, and accordingly makes the phosphorus a better donor, thus disfavouring β-elimination. Note that one of the two ^{31}P-phosphorus signals of **3** has undergone a significant low-field shift, of over 10 ppm, with respect to its counterpart in **1** (for details, see experimental section).



Scheme 5. Possible insertion and β-elimination steps during ethylene polymerisation.

Are these interpretations consistent with the observations made under oligomerisation conditions, that is when the PPh_3 ligand is present ? The effect of PR_3 ligands has been investigated by several authors.[27,33] It is now well established that strongly coordinating PR_3 ligands decrease the activity of the complex, displacement of this phosphine by the incoming ethylene molecule being more difficult. Interestingly, PR_3 ligands have also an impact on the product distribution. An increase of the phosphine basicity usually induces a drop of the molecular weight of the oligomers formed. A rationale of this observation, in mechanistic terms, has not been given yet. Monteiro et al. have suggested that beside the conventional *β*-elimination from a $\mathbf{^{P}X^{C}[n+2]}$-type intermediate (Scheme 5), a second termination mechanism must occur, in this case involving a PR_3 complex.[37] Chauvin and Braunstein came recently to a similar conclusion.[38] However, the intimate mechanism leading to olefin release was not elucidated. Such an elimination could, for example, occur within an 18-electron ethylene/phosphine complex by transfer of a *β*-H atom to the coordinated ethylene (Scheme 6). Of course, an electron poor *P,O*-chelate making the Ni atom electron-deficient should favour coordination of ethylene, resulting in the 18-electron species shown in Scheme 6.



Scheme 6. One of the possible chain termination steps during oligomerisation taking into account of the presence of a PR_3 ligand.

The most active oligomerisation catalyst is complex **3**. This result implies the presence of a PPh_2 moiety having a relatively high trans influence that facilitates the labilisation of the PPh_3 ligand. It is further consistent with the rather long chains formed under polymerisation conditions (see above). Thus, although the CO_2Et group of this complex acts as an electron-attracting group through conjugation, it reduces, via steric interactions with the neighbouring Ph substituent, the electron delocalisation of P electrons within the chelating unit. In contrast, the pyrazolonato complex **2** is the less active one of the four complexes studied. This is in accord with the strong electron-withdrawing effect exerted by the pyrazole ring on the P_{chel} atom, which incidentally makes the Ni–PPh_3 coordination stronger, hence making phosphine substitution by ethylene more difficult. On the other hand, complex **4** is, like under polymerisation conditions, more active than **1**, confirming that the P_{chel} atom is only weakly affected by the presence of the CF_3 group.

Finally, it should be emphasized that an enforced PPh_3 binding is not the only criterion for shifting the olefin distribution towards shorter oligomers. This is clearly shown by considering the fact that **4**, in which the PPh_3 ligand is expected to be more labile than in **2**, also induces a significant distribution shift towards lower olefins ($\alpha = 0.78$). This observation strongly suggests that the basicity of the O atom may also play a key role with respect to the production of such short olefins. A possible mechanism consistent with this finding involves the 18-electron intermediate shown in Scheme 6, although chain termination via a *β*-agostic interaction at an apical site of a [Ni(*P,O*)(alkyl)PPh_3] intermediate cannot formally be excluded.

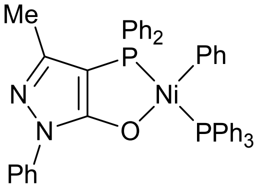
Conclusion

In the present study we have examined the impact of electron-withdrawing substituents anchored at the C=C double bond of nickel phosphanylenolates on their structural and catalytic properties. From the structural and theoretical studies undertaken in this work, it appears that such groups induce a significant lengthening of both the Ni–O and Ni–P_{chel} bonds, the amplitude of the lengthening being a good indication of the attracting power of the backbone substituents. While replacement of the *H*(C=C) atom of **1** by a CO_2Et group (leading to **3**) does not induce important bond changes in the first coordination sphere (the CO_2Et group mainly perturbing the electron delocalisation within the PCCO moiety), the CF_3 group of **4** exerts its electron-withdrawing influence primarily on the O-Ni-C(Ph) rod. On the other hand, the pyrazol ring, which is by far the best acceptor, exerts a strong, but balanced influence on the Ni–P_{chel} and Ni–O bond lengths. Our catalytic studies clearly show that, under polymerisation conditions: *i*) Z substituents increase the insertion rate whatever the relative acceptor strength of the two enolate substituents, this effect probably being propagated through the oxygen atom; *ii*) Z substituents shift the product distribution towards short chains, this effect being propagated essentially via the P atom, although a less basic oxygen atom may also facilitate the *β*-CH activation process trans to the oxygen atom. Under oligomerisation conditions, the introduction of Z substituents on the C=C double bond necessarily increases the reaction rate, provided the Z groups exert a global effect more directed towards the oxygen atom than towards the phosphorus atom. Should the donor properties of the P_{chel} atom also be significantly lowered (as in **2**), then the binding of the trans-bonded PPh_3 ligand increases and accordingly makes olefin coordination more difficult. The factors that govern the product distribution are more subtle. Possibly, *strong* electron withdrawing substituents, whatever their directional properties, favor the formation of a pentacoordinated [Ni(*P,O*)(alkyl)PPh_3(C_2H_4)] intermediate from which termination occurs. This termination route would then occur concomitantly with the conventional *β*-elimination route involving a 14 electron [Ni(*P,O*)(alkyl)] intermediate. Further mechanistic studies aimed at confirming these conclusions are currently under investigation.

Experimental section

General considerations: All syntheses were performed in Schlenk-type flasks under dry nitrogen. Solvents were dried by conventional methods and distilled immediately prior to use. Routine ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ spectra were recorded with an AC-200 Bruker FT instruments. ^1H NMR spectra were referenced to residual protonated solvents (7.16 ppm for C_6D_6), ^{13}C chemical shifts are reported relative to deuterated solvents (128.0 ppm for C_6D_6), and the ^{31}P NMR data are given relative to external H_3PO_4. The catalytic solutions were analysed with a Varian 3900 gas chromatograph equipped with a WCOT fused silica column (25 m, 0.32 mm inside diameter, 0.25 mm film thickness). High temperature size exclusion chromatography (HT SEC) measurements were performed at 150 °C with a PL220 apparatus (Column set HT-Mixed B-TCB-01) in 1,2,4-trichlorobenzene (with 0.2% Irganox). Calibration was made with linear PS samples. $\mathbf{Y^1}$,[39] $\mathbf{Y^2}$,[40] $\mathbf{Y^3}$,[41] $\mathbf{Y^4}$,[42] and the complexes [Ni(cod)$_2$],[23] **1**[4] and **2**[18] were prepared according to literature procedures. The chemical shifts of the phosphorus atoms of **1** and **2** are as follows: δ (C_6D_6) 21.5 and 19.9 ppm for **1** and 20.2 and –8.6 ppm for **2**.

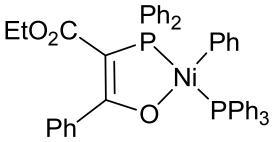
Synthesis



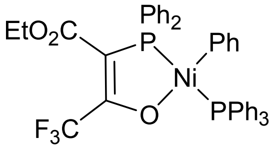
[Ni{Ph$_2$PC(Me)=NN(Ph)C(O)}(Ph)PPh$_3$] (2).

To a cold suspension (0°C) of 3-methyl-1-phenyl-4-triphenylphosphoranylidene-2-pyrazolin-5-one ($\mathbf{Y^2}$) (0.500 g, 1.15 mmol) and PPh_3 (0.303 g, 1.15 mmol) in toluene (20 mL) was added a cold solution (0°C) of [Ni(cod)$_2$] (0.316 g, 1.15 mmol) in toluene (20 mL). The mixture was stirred for 15 h, after which the solution was concentrated to ca. 5 mL. Slow diffusion of hexane into this solution afforded yellow crystals of **2**. Yield: 0.591 g, 68 %. IR (KBr): 1592.6 (m), 1515.5 (s), 1495.0 (s), 1425.8 (s) cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ = 8.25–6.44 (35 H, arom. H), 2.02 (s, 3 H, CH_3) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6): δ = 140.76–118.06 (arom. C), 89.83 (d, $J(P,C)$ = 63 Hz, PC_{pyrazo}), 14.77 (s, CH_3) ppm. $^{31}P\{^1H\}$

NMR (121 MHz, C_6D_6): $\delta = 20.2$ and -8.6 (AB spin system, J(PP') = 280 Hz). Found: C, 74.6; H, 5.39; N, 3.34; calc. for $C_{46}H_{38}N_2NiOP_2$ (Mr = 755.46): C, 75.10; H, 5.47; N, 3.34.%.



[Ni{$Ph_2PC(CO_2Et)=C(Ph)O$}(Ph)PPh_3] (3): To a cold suspension (0°C) of ethyl-(2-benzoyl-2-triphenylphosphoranylidene)acetate (**Y^3**) (0.500 g, 1.19 mmol) and PPh_3 (0.315 g, 1.2 mmol) in toluene (20 mL) was added a cold solution (0°C) of [Ni(cod)$_2$] (0.330 g, 1.20 mmol) in toluene (20 mL). The mixture was stirred for 15 h and then concentrated to ca. 5 mL. Slow diffusion of hexane to this solution afforded yellow crystals. Yield: 0.63 g, 74 %; IR (KBr, cm^{-1}): ν(C=O) = 1670s, ν(C=C) + ν(C–O) = 1459s cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 7.83-7.78 (4 H, arom. H), 7.50-7.44 (m, 8 H, arom. H), 7.15-6.88 (m, 20 H, arom. H), 6.58 (t, 1 H, arom. H, $J = 7.0$ Hz), 6.48 (t, 2 H, arom. H, $J = 7.3$ Hz), 3.74 (q, 2H, CH_2, $^3J = 7.1$ Hz), 0.54 (t, 3H, CH_3, $^3J = 7.1$ Hz). $^{13}C\{^1H\}$ NMR (125.8 MHz, C_6D_6): δ 195.01 (d, C(O)Ph, ^2J(PC) = 24 Hz), 165.53 (s, CO_2Et), 137.77-121.34 (arom. C), 90.73 (d, $C_\alpha PPh_2$, J(PC) = 50 Hz), 58.45 (s, CH_2), 13.91 (s, CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6): δ 31.60 and 20.08 (AB spin system, J(PP') = 276 Hz). Attempts to assign the ^{31}P signals through selective ^{13}C[28] experiments have failed, probably because the ^{31}P signals relax too fast. Found: C, 73.25; H, 5.43; calcd. for $C_{47}H_{40}NiO_3P_2$ (M_r = 773.46): C, 72.98; H, 5.21%.



[Ni{$Ph_2PC(CO_2Et)=C(CF_3)O$}(Ph)PPh_3] (4): To a cold (0°C) solution of ethyl-(2-trifluoroacetyl-2-triphenylphosphoranylidene)acetate (**Y^4**) (0.200 g, 0.45 mmol) and PPh_3 (0.118 g, 0.45 mmol) in toluene (20 mL) was added a solution of [Ni(cod)$_2$] (0.124 g, 0.45 mmol) in toluene (10 mL). The mixture was stirred at room temperature for 15 h. The solution was then concentrated to ca. 0.5 mL and hexane (20 mL) was added affording a yellow precipitate. Upon standing, the yellow powder slowly transformed into dark yellow crystals. Yield: 0.23 g, 67 %; IR (KBr, cm^{-1}): ν(C=O) = 1699s, ν(C=C) + ν(C–O) = 1517s cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ 7.66-7.60 (m, 4 H, arom. H), 7.44 (t, 6 H, arom. H, $J = 8.4$ Hz), 7.03-6.95 (15 H, arom. H), 6.76 (d, 2H, arom. H, $J = 7.4$ Hz), 6.52 (t, 1H, arom. H, $J = 7.0$

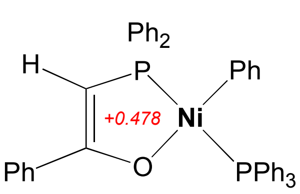
Hz), 6.40 (t, 2H, arom. H, *J* = 7.3 Hz), 3.78 (q, 2H, CH_2, ^3J = 7.1 Hz), 0.65 (t, 3H, CH_3, ^3J = 7.1 Hz). $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): δ 177.45 (dq, *C*(O)CF_3, $^2J(PC)$ = 27 Hz, $^4J(FC)$ = 35 Hz), 163.07 (s, *C*O_2Et), 137.42-121.30 (arom. C), 93.82 (d, $C_\alpha PPh_2$, *J*(PC) = 45 Hz), 59.13 (s, CH_2), 13.51 (s, CH_3). $^{31}P\ \{^1H\}$ NMR (121 MHz, C_6D_6): δ 30.58 and 18.84 (AB spin system, *J*(PP') = 277 Hz). $^{19}F\ \{^1H\}$ NMR (282 MHz, C_6D_6): δ – 67.76. Found: C, 65.73; H, 4.63; calc. for $C_{42}H_{35}F_3NiO_3P_2$ (M_r = 765.362): C, 65.91; H, 4.61%.

X-ray Crystal Structure Determination of 3 and 4: Single crystals of **3** and **4** (dark orange prisms) suitable for X-ray diffraction analysis were obtained from slow diffusion of hexane into a toluene solution of the corresponding complex. Crystals of the compounds were mounted on a Nonius Kappa CCD. Data collection was carried out using the Nonius collect suite.[43] The structures were solved by direct methods with the program SIR92.[44] Least squares refinements were carried out using the program CRYSTALS.[45,46] Hydrogen atoms are in calculated positions. Complex **3** crystallized with 0.5 molecule of toluene. Final results are given in Table 4. CCDC reference numbers 299905 (**4**) and 299906 (**3**)

Computational details

The calculations were carried out at the DFT-B3LYP level[47-49] with the Gaussian 03 program.[50] As starting geometries we used those provided by the X-ray structures. The geometries were fully optimized by the gradient technique with the following basis: the LANL2DZ basis set for Ni, the standard 6-31G basis set for C, H, N and O,[51] and the corresponding polarized 6-31G* basis set for P and F.[52]

Global NBO charge of the metallacyclic unit



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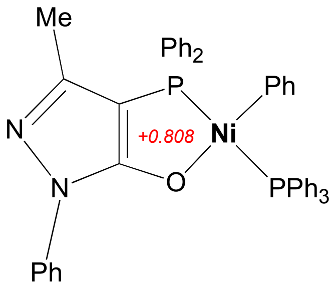

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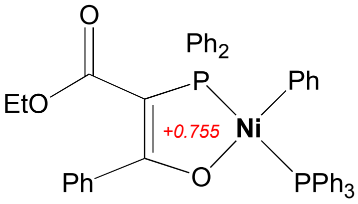

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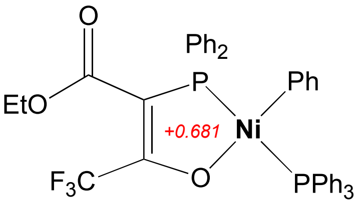
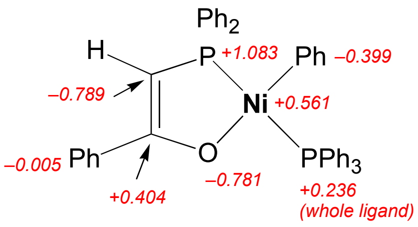


4

Significant NBO charge distribution within the complexes 1-4



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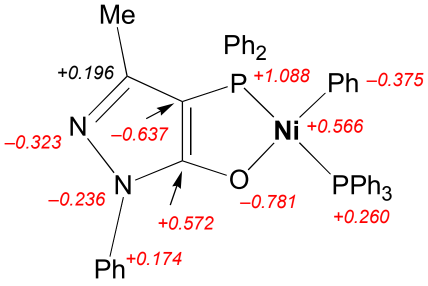

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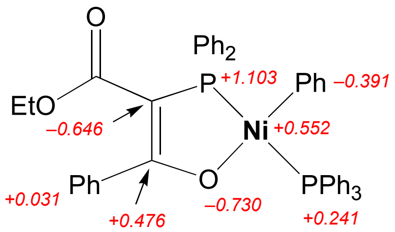

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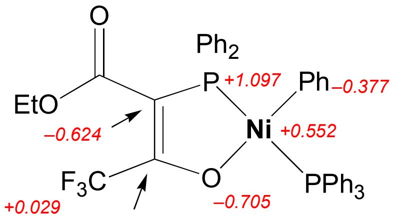
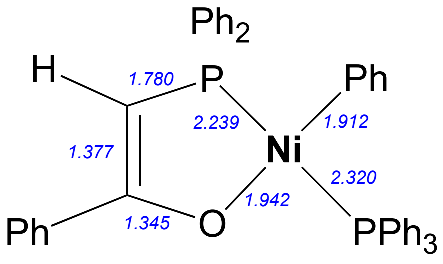


4

Relevant, calculated bond lengths in 1-4



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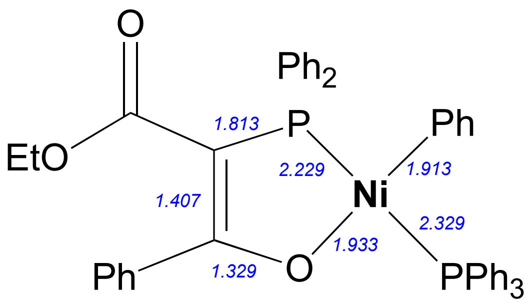

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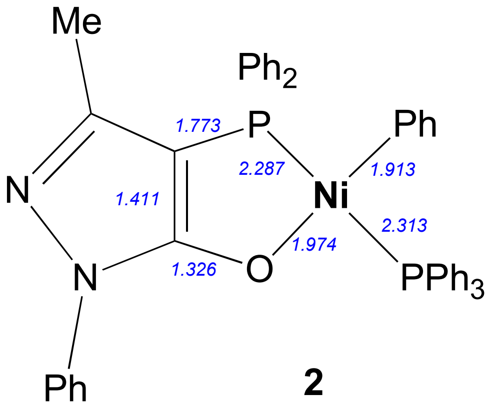

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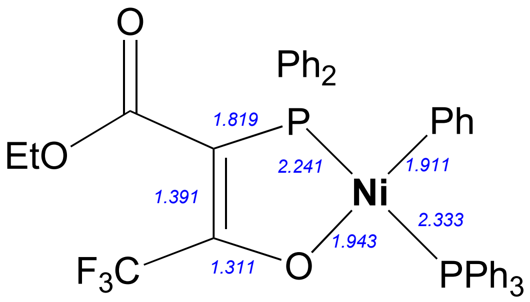


4

Table 4. Crystallographic data for **3** and **4**.

Formula	$C_{47}H_{40}NiO_3P_2$ (**3**)•0.5 (C_7H_8)	$C_{42}H_{35}F_3NiO_3P_2$ (**4**)
Formula weight	819.56	765.39
Crystal system	Monoclinic	Monoclinic
Space group	$P2/a$	$P2_1/n$
a (Å)	18.0407(2)	14.3693(2)
b (Å)	11.3007(1)	13.3818(1)
c (Å)	20.6002(2)	18.8392(2)
α (°)	90	90
β (°)	97.5760(5)	90.3555(6)
γ(°)	90	90
V (Å^3)	4163.16(7)	3622.47(7)
Z	4	4
D(calcd.) (g•cm^{-3})	1.308	1.403
μ(Mo-$K\alpha$) (mm^{-1})	0.586	0.679
F(000)	1716	1584
Crystal size (mm)	0.13×0.22×0.40	0.10×0.10×0.30
Temperature (K)	173	173
Radiation, λ(Mo-$K\alpha$) (Å)	0.71073	0.71073
θmin./max. (°)	2.0/28.7	1.8/30.1
Data set (h; k; l)	−24/24; −15/15; −27/27	−20/19; −18/18; −26/26
Total, unique data, R(int.)	42232, 10735, 0.117	36903, 7160, 0.064
Obsd. data with $I > 2.0\sigma(I)$	6676	7134
$N_{\text{reflections}}$, $N_{\text{parameters}}$	6676, 535	7134, 460
$R1$, $wR2$, S	0.0336, 0.0604, 1.09	0.0324, 0.0461, 0.99
Min., max. residual electron density (e•Å^{-3})	−0.62, 0.61	−0.49, 0.41

Catalytic runs

Ethylene oligomerisation: Low pressure catalytic runs were carried out in a Büchi miniclave (200 mL), equipped with a Teflon-coated magnetic stirrer, at constant ethylene pressure. The reactor was dried under vacuum at 100 °C for 1 h before use. In a typical procedure, a Schlenk flask was charged with the complex (7.5 μmol) and toluene (10 mL). The resulting solution was injected into the autoclave together with additional toluene (20 mL). The autoclave was then pressurised with ethylene and heated at the desired temperature. The temperature refers to the external oil bath. After completion of the reaction, the autoclave was cooled with an ice bath and depressurised over 1 h. The solution was analysed by GC. Heptane was used as internal reference.

Ethylene Polymerisation: Polymerisations were carried out at constant ethylene pressure in a Parr stainless steel autoclave (100 mL), equipped with a mechanical stirrer, a heating device, and an internal temperature probe. The autoclave was heated at 100 °C under vacuum for 1 h before use and purged with ethylene. In a typical run, the reactor was charged at ambient temperature under an ethylene atmosphere, with a solution of the ylide in toluene (10 mL), followed by a solution of [Ni(cod)$_2$] (10 equiv.) in toluene (10 mL). The autoclave was then pressurised, and heated to the desired temperature. The reaction exothermicity was controlled by means of an ice bath. Venting the autoclave quenched the reaction and the mixture was subsequently poured into a stirred solution of acidified methanol (200 mL of 10% HCl) to precipitate the polymer. The white powder was isolated by filtration, washed with methanol, and dried in vacuo at 50 °C.

References

[1] R. Bauer, H. Chung, K. W. Barnett, P. W. Glockner, W. Keim and H. van Zwet, (Shell Oil Co.), US 3686159, **1972**.

[2] R. S. Bauer, H. Chung, P. W. Glockner and W. Keim, (Shell Oil Co.), US 3635937, **1972**.

[3] D. M. Singleton, P. W. Glockner and W. Keim, (Shell Int. Res.), GB 1364870, **1974**.

[4] W. Keim, F. H. Kowaldt, R. Goddard and C. Krüger, *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 466-467.

[5] G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 428-447.

[6] S. D. Ittel, L. K. Johnson and M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169-1204.

[7] R. Spitz and C. Boisson, *L'actualité chimique* **2002**, 54-58.

[8] V. C. Gibson and S. K. Spitzmesser, *Chem. Rev.* **2003**, *103*, 283-315.

[9] S. Mecking, A. Held and F. M. Bauers, *Angew. Chem. Int. Ed. Engl.* **2002**, *41*, 544-561.

[10] F. Speiser, P. Braunstein and L. Saussine, *Acc. Chem Res.* **2005**, *38*, 784-793.

[11] S. Y. Desjardins, K. J. Cavell, J. L. Hoare, B. W. Skelton, A. N. Sobolev, A. H. White and W. Keim, *J. Organometal. Chem.* **1997**, *544*, 163-174.

[12] L. S. Boffa and B. M. Novak, *Chem. Rev.* **2000**, *100*, 1479-1494.

[13] M. J. Yanjarappa and S. Sivaram, *Prog. Polym. Sci.* **2002**, *27*, 1347-1398.

[14] L. Kolb, V. Monteil, R. Thomann and S. Mecking, *Angew. Chem. Int. Ed. Engl.* **2005**, *44*, 429 - 432.

[15] U. Klabunde and S. D. Ittel, *J. Mol. Catal.* **1987**, *41*, 123-134.

[16] U. Klabunde, R. Mulhaupt, T. Herskovitz, A. H. Janovicz, J. Calabrese and S. D. Ittel, *J. Polym. Sci. Part A: Polym. Chem.* **1987**, *25*, 1989-2003.

[17] R. Soula, J. P. Broyer, M. F. Llauro, A. Tomov, R. Spitz, J. Claverie, X. Drujon, J. Malinge and T. Saudemont, *Macromolecules* **2001**, *34*, 2438 -2442.

[18] P. Kuhn, D. Sémeril, C. Jeunesse, D. Matt, P. Lutz and R. Welter, *Eur. J. Inorg. Chem.* **2005**, 1477-1481.

[19] M. Huhn, M. Burgard, D. Matt and J. Steiner, (EEHEICS), DE 4415725, **1994**.

[20] D. Matt, M. Huhn, M. Bonnet, I. Tkatchenko, U. Englert and W. Kläui, *Inorg. Chem.* **1995**, *34*, 1288 - 1291.

[21] W. Keim and R. P. Schulz, *J. Mol. Catal.* **1994**, *92*, 21-33.

[22] M. Peuckert and W. Keim, *Organometallics* **1983**, *2*, 594-597.

[23] T. M. Gomes Carneiro, J. Dupont, M. Luke and D. Matt, *Quimica Nova* **1988**, *11*, 215-217.

[24] H. Qichen, X. Minzhi, Q. Yanlong, X. Weihua, S. Meicheng and T. Youqi, *J. Organomet. Chem.* **1985**, *287*, 419-426.

[25] P. J. Flory, *J. Am. Chem. Soc.* **1940**, *62*, 1561-1565.

[26] K. Hirose and W. Keim, *J. Mol. Catal.* **1992**, *73*, 271-276.

[27] J. Pietsch, P. Braunstein and Y. Chauvin, *New J. Chem.* **1998**, *22*, 467-472.

[28] J. Heinicke, M. He, A. Dal, H. F. Klein, O. Hetche, W. Keim, U. Flörke and H.-J. Haupt, *Eur. J. Inorg. Chem.* **2000**, 431-440.

[29] J. Heinicke, M. Koesling, R. Brüll, W. Keim and H. Pritzkow, *Eur. J. Inorg. Chem.* **2000**.

[30] O. Kristen, J. Heinicke, W. Keim, M. Köhler and M. He, (BASF AG), DE 19947519 **2001**.

[31] J. M. Malinoski and M. Brookhart, *Organometallics* **2003**, *22*, 5324 -5335.

[32] J. Heinicke, M. Köhler, N. Peulecke, M. He, M. K. Kindermann, W. Keim and G. Fink, *Chem. Eur. J.* **2003**, *9*, 6093 - 6107.

[33] J. Heinicke, M. Köhler, N. Peulecke and W. Keim, *J. Catal.* **2004**, *225*, 16-23.

[34] J. Heinicke, M. Köhler, N. Peulecke, M. K. Kindermann, W. Keim and M. Köckerling, *Organometallics* **2005**, *24*, 344 -352.

[35] J. Heinicke, M. Köhler, N. Peulecke, M. He and W. Keim, *J. Organomet. Chem.* **2005**, *690*, 2449-2457

[36] M. S. W. Chan, L. Deng and T. Ziegler, *Organometallics* **2000**, *19*, 2741 -2750.

[37] A. L. Monteiro, M. O. de Souza and R. F. de Souza, *Polymer Bulletin* **1996**, *36*, 331-336.

[38] P. Braunstein, Y. Chauvin, S. Mercier and L. Saussine, *C. R. Chimie* **2005**, *8*, 31-38.

[39] F. Ramirez and S. Dershowitz, *J. Org. Chem.* **1957**, *22*, 41-45.

[40] A. J. Mota, A. Dedieu, P. Kuhn, D. Matt, R. Welter and M. Neuburger, *Dalton Trans.* **2005**, 3155-3160.

[41] P. A. Chopard, R. J. G. Searle and F. H. Devitt, *J. Org. Chem.* **1965**, *30*, 1015-1019.

[42] B. C. Hamper, *J. Org. Chem.* **1988**, *53*, 5558-5562.

[43] *COLLECT Software, Nonius BV, 1997-2001.*

[44] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 435-436.

[45] D. J. Watkin, C. K. Prout, P. W. Carruthers, P. W. Betteridge and R. I. Cooper, *CRYSTALS, Issue 11, Chemical Crystallography Laboratory, Oxford, UK, 2001.*

[46] J. R. Carruthers and D. J. Watkin, *Acta Crystallogr. Sect. A* **1979**, *35*, 698.

[47] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098.

[48] C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.

[49] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.

[50] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03 (Revision C.02), Gaussian Inc., Wallingford, CT, 2004.*

[51] W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257.

[52] P. C. Hariharan and J. A. Pople, *Mol. Phys.* **1974**, *27*, 209.

Chapter 5

Catalytic applications of keto-stabilised phosphorus ylides based on a macrocyclic scaffold: calixarenes with one or two pendant Ni(*P,O*)-subunits as ethylene oligomerisation and polymerisation catalysts

Abstract

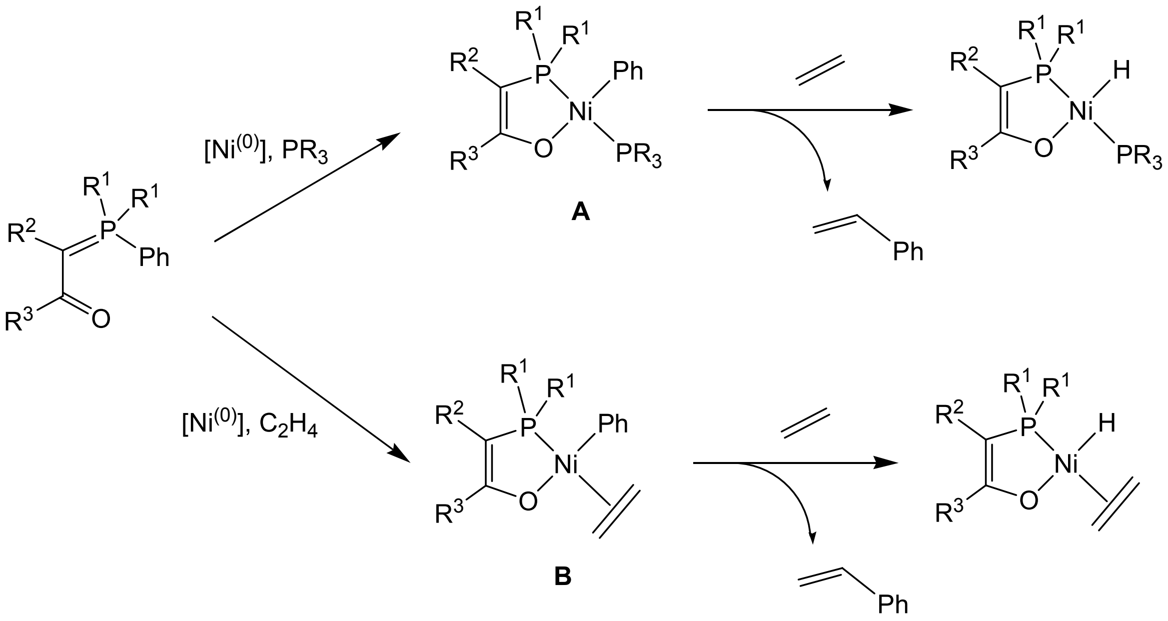
Four calix[4]arenes containing either one or two ylidic – C(O)CH=PPh_3 moieties anchored at *p*-phenolic carbon atoms were prepared starting from c*one*-25,27-dipropoxy-calix[4]arene (**1**): *1,3-alternate*-5,17-bis(2-triphenylphosphoranylideneacetyl)-25,26,27,28tetrapropoxycalix[4]arene (**12),** *1,3-alternate*-5-(2-triphenylphosphoranylideneacetyl)-25,26,27,28-tetrapropoxycalix[4]arene (**13**), *cone*-5-(2-triphenylphosphoranylideneacetyl)-25,27-dihydroxy-26,28-dipropoxycalix[4]arene (**14**), *cone*-5,17-bis(2-triphenylphosphoranylideneacetyl)-25,27-dihydroxy-26,28-dipropoxycalix[4]arene (**15**). All the ylides were shown to be suitable for the preparation of SHOP-type complexes, *i.e.* of molecules containing [NiPh{Ph_2PCH=C(O)R}PPh_3] subunits (R = calixarene fragment). The monometallic complexes, namely those obtained from the monophosphorus ylides **13** and **14**, proved to be efficient ethylene oligomerisation or polymerisation catalysts. They display significantly better activities than the prototype [NiPh{Ph_2PCH=C(O)Ph}PPh_3], hence reflecting the beneficial role of the bulky calixarene substituent. The systems derived from the two ylides **12** and **15**, both containing two convergent ylidic moieties, resulted in lower activities, the proximity of the two catalytic centres facilitating an intramolecular deactivation pathway during the period of catalyst activation. For the first time, the solid state structure of a complex containing *two* "NiPh(*P,O*)PPh_3" units as well as that of a SHOP-type complex having two *linked* phosphorus units were determined.

Résumé

Ce chapitre est consacré à la synthèse d'ylures de phosphore stabilisés, substitués au niveau du groupement carbonyle par un fragment très encombré de type calix[4]arène. Quatre calixarènes ont été étudiés. Ils comportent soit un, soit deux fragments –$C(O)CH{=}PPh_3$ greffés sur des positions para phénoliques: le 5,17-bis(2-triphénylphosphoranylidèneacétyl)-25,26,27,28-tétrapropoxycalix[4]arène (*conformation 1,3-alternée*) (**12**), le 5-(2-triphénylphosphoranylidèneacétyl)-25,26,27,28-tétrapropoxycalix[4]arène (*1,3-alterné*) (**13**), le 5-(2-triphénylphosphoranylidèneacétyl)-25,27-dihydroxy-26,28-dipropoxycalix[4]arène (*cône*) (**14**), et le 5,17-bis(2-triphénylphosphoranylidèneacétyl)-25,27-dihydroxy-26,28-dipropoxycalix[4]arène (*cône*) (**15**). Ces ylures ont pu être utilisés pour la préparation de complexes de type SHOP, c'est-à-dire de molécules contenant le fragment $[NiPh\{Ph_2PCH{=}C(O)R\}PPh_3]$ (R = fragment calixarene). Les complexes monométalliques dérivés des ylures **13** et **14** se sont avérés être des catalyseurs efficaces d'oligomérisation et de polymérisation de l'éthylène. Ils présentent des activités significativement plus grandes que le complexe de référence $[NiPh\{Ph_2PCH{=}C(O)Ph\}PPh_3]$, reflétant ainsi le rôle bénéfique du groupement encombré *calixarène* qui retarde la désactivation du catalyseur. Les systèmes dérivés des deux ylures **12** et **15**, contenant chacun deux ylures convergents, présentent des activités inférieures à celle des mono-ylures. Ici, la proximité des deux centres catalytiques peut conduire à un processus de désactivation. Une étude approfondie réalisée avec le bis-ylure **12**, montre qu'au cours de la phase d'activation du système, une partie des molécules se transforme en un complexe mononucléaire inactif, comportant une entité phosphinoénolate chélatante ainsi qu'une entité P-monodentate. Celles-ci sont toutes deux liées au calixarène. Une synthèse rationnelle de ce complexe a été effectuée à partir d'un bis-phosphinoénolate dérivé de **12**. Ce travail décrit la première structure cristallographique d'un complexe contenant deux entités "NiPh(*P,O*)PPh_3" ainsi que celle d'un complexe de type SHOP où les deux atomes de phosphore sont reliés entre eux.

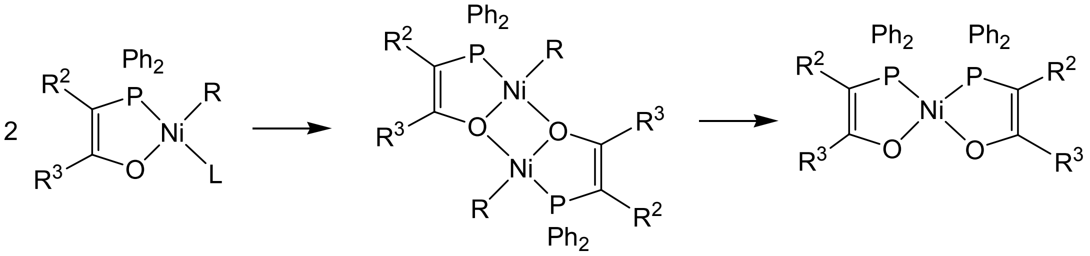
Introduction

Nickel(II) phosphanylenolates with the general formula [NiPh(*P,O*)L] (L = tertiary phosphine; *P,O* = chelating phospanylenolato ligand) (**A**) constitute valuable precursors for highly efficient oligomerisation catalysts suitable for the selective production of linear α-olefins.[1-5] The same complexes, which are frequently referred to as SHOP catalysts, can also be used as ethylene polymerisation catalysts if pre-treated with a phosphine sponge to remove the neutral phosphine ligand (L).[6,7] Their synthesis is usually achieved via oxidative addition of a keto-stabilised phosphorus ylide to a nickel(0) complex[8] in the presence of a tertiary phosphine (Scheme 1), or by reacting of a phosphanylenolate with an appropriate Ni(II) precursor.[9-11] It is noteworthy that active oligomerisation catalysts based on such complexes can directly be generated *in situ*.[12] This can also be done for forming a polymerisation catalyst (complex of type **B**), the oxidative addition being then carried out in the presence of ethylene instead of a tertiary phosphine.[13-15]



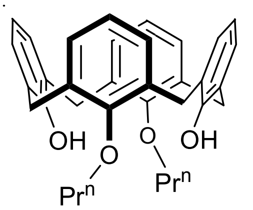
Scheme 1. Synthesis of typical SHOP oligomerisation (**A**) and polymerisation (**B**) catalysts.

Owing to their relatively high functional group tolerance, complexes of type **B** represent interesting precatalysts for the copolymerisation of ethylene with polar monomers, which is one of the most promising fields of polyolefin industry.[16-18] Other applications include their use as ethylene polymerisation catalysts in aqueous media.[19-21] A major drawback of **B**-type polymerisation catalysts arises from their low intrinsic activity in comparison to the highly active group 4-metal catalysts. This is in part possibly due to the formation during catalysis of a inactive [Ni(*P,O*)$_2$] complex, which may result from the formation of a transient dimer (Scheme 2).[6,7] A logical way to prevent such a catalyst deactivation is to introduce bulky substituents in the vicinity of the oxygen atom.



Scheme 2. A typical deactivation pathway of SHOP catalysts.

In fact, only one publication using this approach has been reported to date,[14] although there is a parallel with *P,O*-chelates grafted to a dendrimeric unit.[22] In the present work, we describe the first syntheses of keto-stabilized phosphorus ylides and β-ketophosphines tethered to a calix[4]arene platform that may play the role of a bulky substituent. It should be recalled here that calix[4]arenes are large scaffolds, the size of which is not only easily tunable through functionalisation, but also variable due to their intrinsic conformational mobility.[23,24] The new phosphorus compounds were used for the preparation of SHOP-type complexes and assessed in ethylene oligomerisation and polymerisation. The first X-ray structure determination for a molecular catalyst containing two "Ni(*P,O*)" subunits forms part of this work. Assignments of the calixarene conformations were made using well-established rules based on ^{13}C and ^{1}H NMR spectroscopy.[25,26] All compounds were obtained starting from 25,27-dipropoxy-calix[4]arene (**1**).[27]



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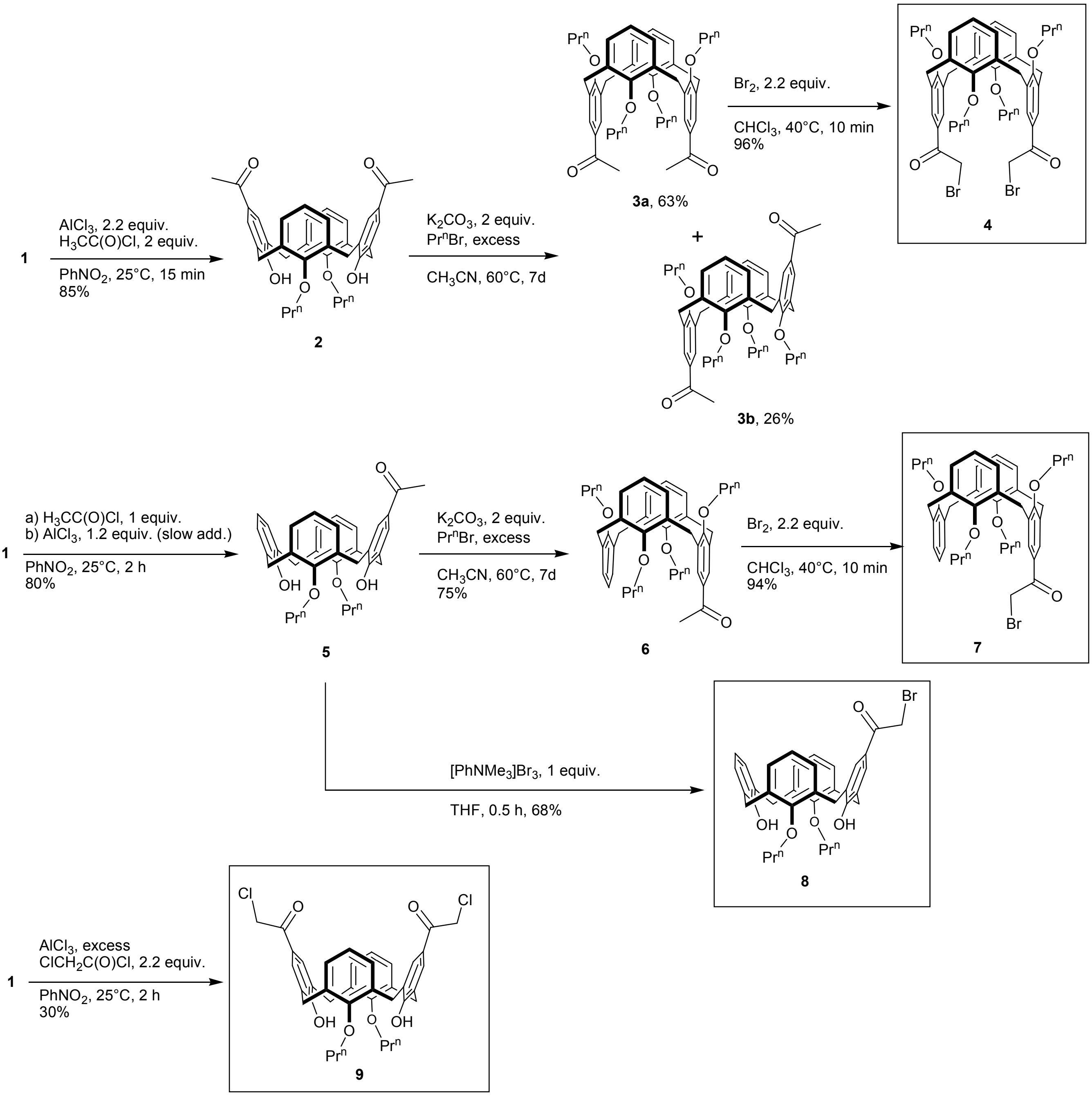
Results and discussion

Ligand synthesis

Preparation of haloacetylated precursors. The new compounds were obtained through upper-rim functionalisation of appropriate calix[4]arene precursors. The preparation of the phosphorus ylides **12**-**15** required the synthesis of the haloacetylated precursors **4**, **7**, **8**, and **9**, respectively. Compounds **4**, **7**, and **8** were obtained via Friedel-Crafts acetylation of **1** in nitrobenzene at room temperature followed by a conventional bromination reaction (Scheme 3). The chloro derivative **9** was obtained in a one-step reaction using $AlCl_3/ClCH_2C(O)Cl$. It is interesting to note that the acetylation reaction leading to **2** is fast (reaction time < 15 min) in comparison to the recently reported 12-hour diacetylation of the 25,27-dimethoxy analogue of **1**.[28,29]

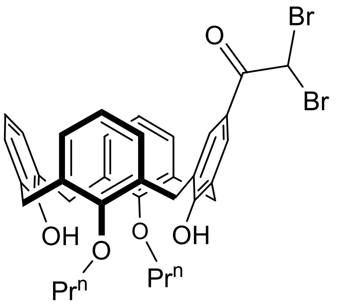


Scheme 3. Stepwise buildup of haloacetylated calixarenes suitable for the preparation of phosphorus ylides.

To restrict the functionalisation of **1** to a selective monoacetylation, the $AlCl_3$ solution was added dropwise over two hours to a calixarene/$CH_3C(O)Cl$ 1:1 mixture. Further, we observed that when the acetylations were carried out using an $CH_3C(O)Cl$:calix ratio larger than 3:1, acetylation of the propylated phenoxy rings also occurred, but at a slower rate (products not described in this paper). The yield of the reaction leading to **9** did not exceed 30%, unidentified side-products being formed in this case. Finally, it is worth mentioning that the Friedel-Crafts acetylation products **2**, **5** and **9** adopt a cone conformation, as unambiguously deduced from the corresponding ^{13}C NMR spectra (see experimental part), in which the Ar*C*H_2 signal appears near 31.4 ppm, that is, in a range typical for $ArCH_2Ar$ units having *syn*-oriented aryl rings.[26]

Compound **4** could be obtained from **2** in two steps: (*i*) alkylation with K_2CO_3/Pr^nBr, affording the *1,3-alternate* conformer **3a** as the major compound (yield: 63%; partial cone-**3b** was isolated in 26% yield); (*ii*) bromination of **3a** with Br_2 to yield quantitatively the bis-bromoacetylated compound **4**. Compound **7** was synthesised similarly in good yield starting from **5**. We found that direct bromination of **5** with $[PhNMe_3]Br_3$ gave **8** in 68% yield, a transformation in which the cone conformation was maintained.

Chromatographic purification of the product revealed that the dibrominated compound **10** was also formed (see experimental part). When the bromination of **5** was carried out with Br_2, a mixture of compounds was formed for which chromatographic separation proved difficult.



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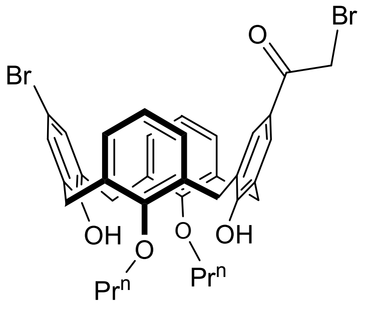

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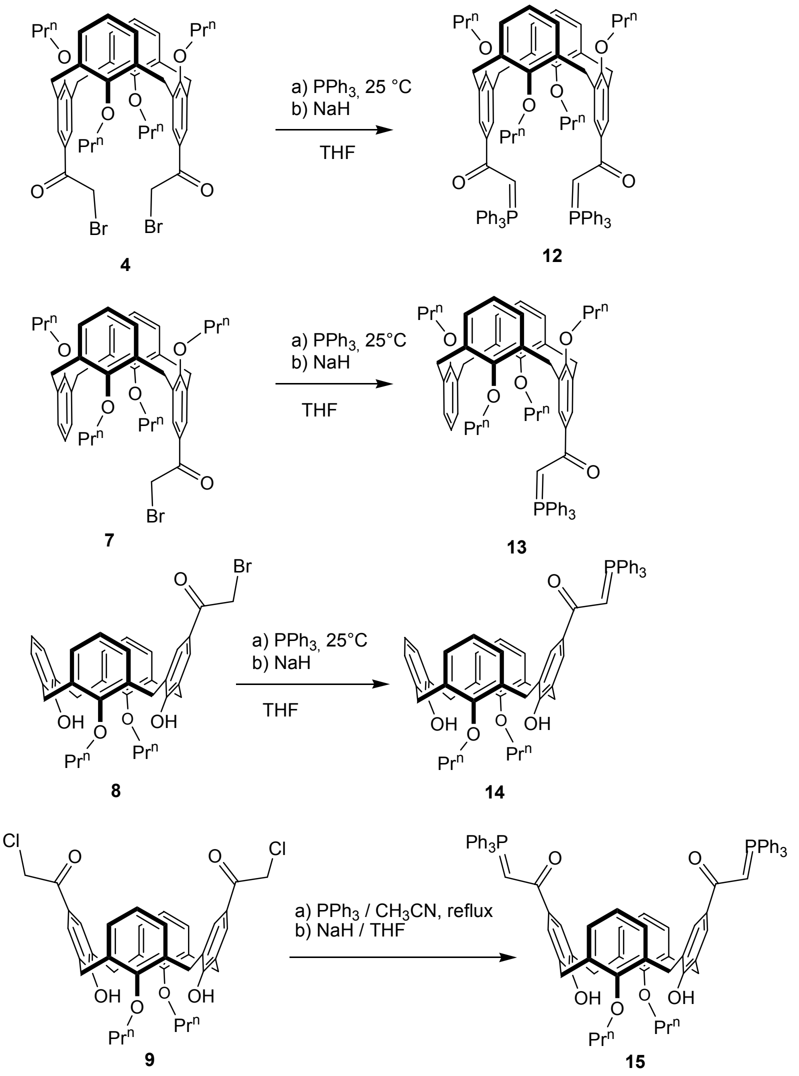
Only **11**, for which an optimised preparation is described in the experimental part, could be isolated.

Preparation of the phosphorus ylides. The four phosphorus ylides **12-15** were eventually prepared in nearly quantitative yield according to the following sequence: (*i*) reaction of PPh_3 with the appropriate



Scheme 4. Synthesis of the phosphorus ylides **12-15**.

haloacetylated calixarene; (*ii*) deprotonation of the resulting phosphonium salt with NaH (Scheme 4). For each ylide, the ^{31}P NMR spectrum exhibits a singlet near 16.5 ppm. In the IR spectra, the ν(C=O) stretching bands appear in the range 1507-1518 cm^{-1}. The molecular structure of ylide **15** was confirmed by an X-ray diffraction study (Fig. 1). In the solid state, the calixarene core exhibits a typical flattened cone conformation, with dihedral angles between the facing phenoxy rings of respectively 35° and 82°. The distance between the two phosphorus atoms is ca. 15 Å. The P=C bond lengths of the ylide moieties are respectively 1.721(4) and 1.713(4) Å (cf. 1.804(5) Å for the shortest P–C(aryl) bond).

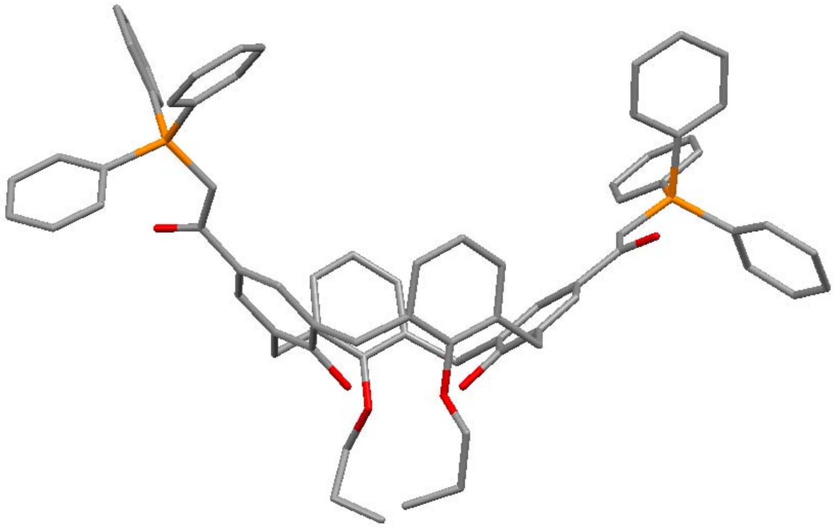
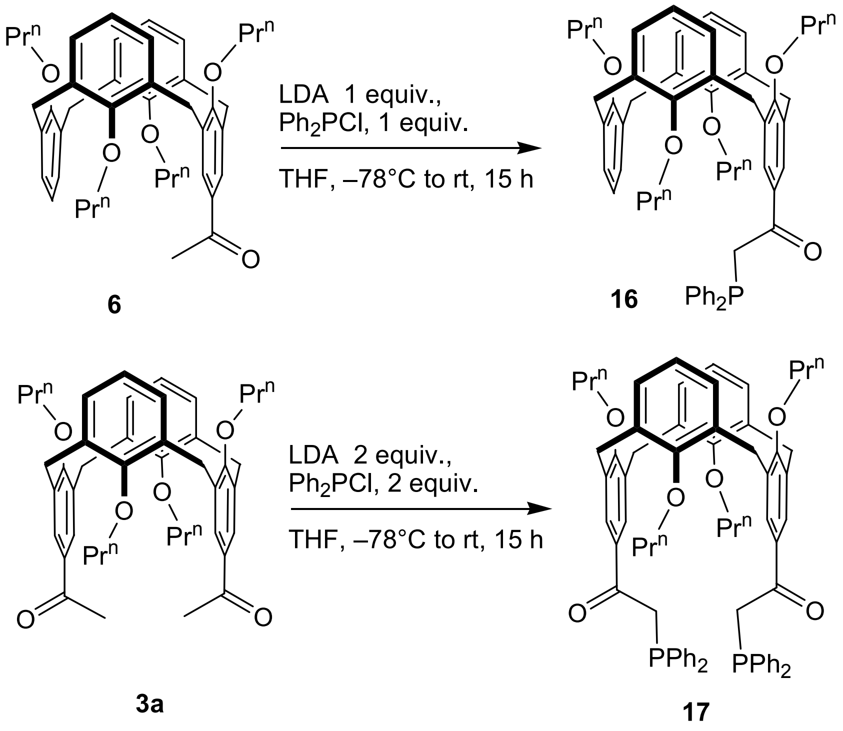


Figure 1. X-ray structure of bis-ylide **15**. P···P separation: 15.14(1) Å. The compound crystallises with two molecules of MeOH and half a molecule of CH_2Cl_2 (not shown)

For the preparation of SHOP-type catalysts, it is sometimes of advantage to start from a β-ketophosphine instead of a phosphorus ylide.[30] We therefore also prepared the two phosphines **16** and **17**.

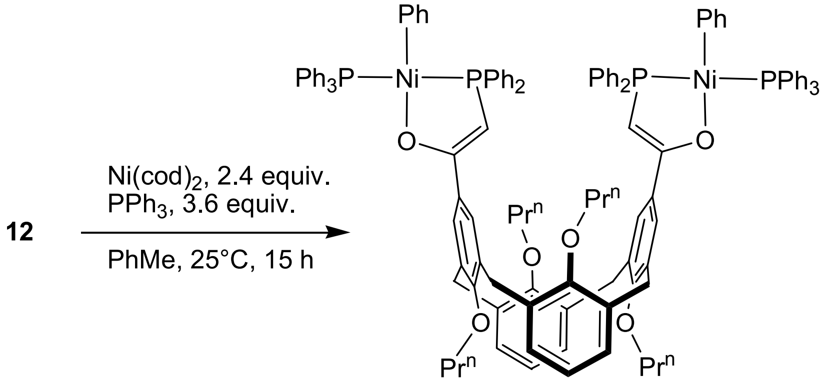


Scheme 5. Synthesis of the β-ketophosphines **16** and **17**.

These were obtained in high yields using a well-established procedure, namely by deprotonation of the appropriate acetyl derivative with $LiNPr^i_2$ (LDA), followed by reaction with PPh_2Cl (Scheme 5).[31] The corresponding phosphorus signals appear as singlets at –19.4 and –16.2 ppm, respectively, for **16** and **17**.

Synthesis of catalytic precursors

In the present study, all catalytic precursors were generated in situ from [Ni(cod)$_2$], either in the presence of PPh_3/ethylene (for the preparation of oligomerisation catalysts) or ethylene alone (for the preparation of polymerisation catalysts). NMR studies revealed that the reaction of **12** with [Ni(cod)$_2$] in toluene at 60°C occurs readily, affording a single product (^{31}P NMR signal at 20.5 ppm) which can be used as such for the catalytic studies. The same observation holds for the bis-ylide **15**. In order to prove that a bimetallic catalyst precursor does form, we isolated the product formed by reacting **12** with [Ni(cod)$_2$] in the presence of PPh_3. This reaction gave complex **18** (Scheme 6). We found that upon standing **18** straightforwardly undergoes reductive elimination at both nickel sites, hence reforming **12**. To avoid back formation of the ylide, it turned out to be advantageous to carry out the reaction leading to **18** in the presence of a slight excess of [Ni(cod)$_2$] and PPh_3 as well. The ^{31}P NMR spectrum of **18** shows an AB system, with a *J*(PP') coupling constant of 283 Hz, typical of trans-positioned P atoms. In the ^{1}H NMR spectrum, the PCH protons appear as a broad singlet at 5.17 ppm.



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Scheme 6. Synthesis of the "bis-SHOP" complex **18**.

The solid state structure of **18** was determined by a single crystal X-ray diffraction study (Fig. 2). It represents the first X-ray crystal structure of a bimetallic SHOP-catalyst. In a strict sense, the molecule has C_1 symmetry, but it may be regarded as possessing a pseudo plane of symmetry containing the C(29), O(3), and O(4) atoms. The two Ni–PPh$_3$ vectors are nearly parallel and oriented in the same direction. The calixarene adopts a 1,3-alternate conformation, each distal pair of phenol rings defining an open cavity. The interplanar angle between the rings linked to O(1) and O(2) atoms is 35°, while that between the other two distal rings is ca. 55°. In fact, the O(4) atom comes closer to the centre of the cavity than the O(3) atom, thereby minimising the steric interactions between the two PPh$_3$ ligands and the propyl chain substituting O(4). We note that the shortest C(116)$\cdots$O(enolate) separation (3.42(1) Å) involves the O(5) atom. Both nickel atoms lie in an almost square-planar coordination environment, as usually observed in related structures.[32-34] The two metallacyclic units are structurally very similar and may be considered planar. In accord with some electron delocalisation within the PCCO chelate arms, the P–CH bond lengths (both of 1.754(4) Å) are slightly shorter than those of the corresponding P–C(aryl) bonds (≥ 1.816(5) Å),

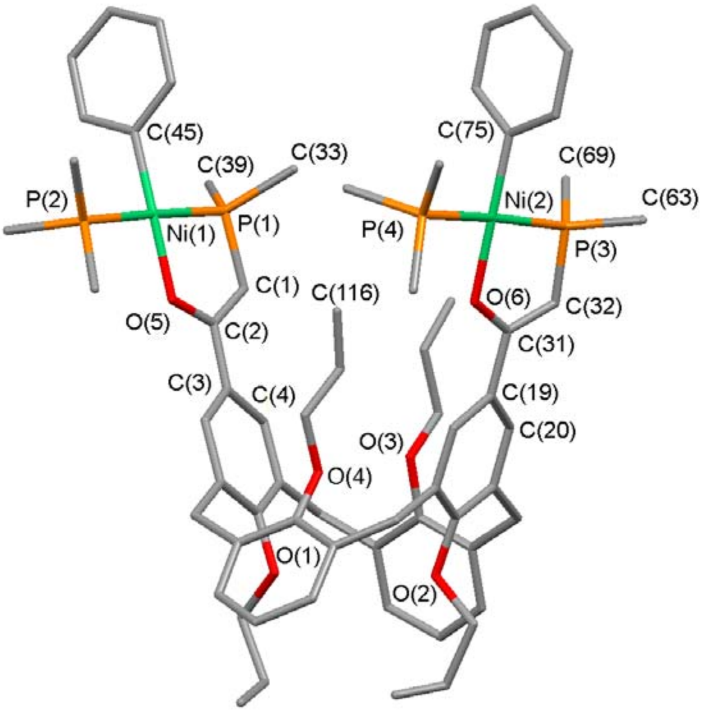


Figure 2. X-ray structure of **18**. For clarity, only the C$_{ipso}$ carbon atoms of the PPh units are shown.

Table 1. Important bond lengths and angles in complex **18**.

C(2)-O(5)	1.308(4)	C(31)-O(6)	1.304(4)
C(1)-P(1)	1.754(3)	C(32)-P(3)	1.754(4)
Ni(1)-O(5)	1.919(2)	Ni(2)-O(6)	1.910(3)
Ni(1)-P(1)	2.1730(9)	Ni(2)-P(3)	2.1645(12)
Ni(1)-P(2)	2.2255(9)	Ni(2)-P(4)	2.1995(12)
Ni(1)-C(45)	1.893(3)	Ni(2)-C(75)	1.890(5)
C(1)-C(2)	1.371(5)	C(31)-C(32)	1.367(5)
P(1)Ni(1)O(6)	86.48(7)	P(3)Ni(2)O(5)	86.60(8)
P(1)Ni(1)P(2)	176.78(4)	P(3)Ni(2)P(4)	174.39(5)

Both "Ni(*P,O*)" moieties and the phenoxy rings to which they are linked are nearly coplanar (D(C1C2C3C4) = –10.7(5)°; D(C20C19C31C32) = –18.6(5)°), thus reflecting the good conjugation between these rings (Table 1). The distance between the two nickel atoms is 8.71(1) Å. Finally, it is worth mentioning that the reaction of **15** with [Ni(cod)$_2$] in the presence of PPh$_3$ leads also to the formation of a bimetallic complex having two SHOP-subunits, as shown by ^{31}P and ^{1}H NMR experiments (see experimental part). In this reaction the cone conformation is maintained.

Ethylene polymerisation

The polymerisation tests were carried out in toluene under constant ethylene pressure, the ylide Ph$_3$P=CHC(O)Ph (**19**) serving as a reference compound. Temperatures higher than 60°C were necessary to start the reaction. All four ylides catalyse, when associated to nickel(0), the polymerisation of ethylene to linear polyethylene. Surprisingly, the bis-ylides **12** and **15** showed significantly lower activities than **19** (Table 2). This contrasts with the observations made by Kurtev and Tomov on bimetallic SHOP complexes with divergent catalytic centres which were found to be remarkably active compared to related, monometallic systems.[35,36]

Table 2. Ethylene polymerisation using ylides **12-15** and $Ph_3P=CHC(O)Ph$ (**19**)[a]

Entry	Ylide	Amount (μmol)	P (bar)	T (°C)	t (h)	PE[b] (g)	TOF[c] (h^{-1})	M_w[d] ($g\ mol^{-1}$)	M_n[d] ($g\ mol^{-1}$)	M_w/M_n	T_m[e] (°C)
1	**19**	4	5	70	0.5	1.12	20000	6600	2600	2.5	127.0
2	**19**	4	5	80	0.5	1.87	33300	-	-	-	126.7
3	**19**	4	5	90	0.5	2.27	40500	3900	2200	1.8	124.0
4	**19**	2	10	70	0.5	1.06	37800	-	-	-	-
5	**12**	2	5	70	0.25	0.47	16800	4100	2300	1.8	126.6
6	**12**	2	5	80	0.25	0.74	35600	5300	2000	2.6	124.8
7	**12**	2	5	70	1	0.86	7700	-	-	-	132.8
8	**12**	2	10	70	0.25	1.11	39600	4000	2000	2.0	126.5
9	**13**	2	5	70	0.25	0.70	49900	3300	2000	1.6	124.8
10	**13**	2	5	80	0.25	1.12	79800	2700	1800	1.5	123.7
11	**13**	2	5	70	1	1.47	26200	3300	2000	1.6	125.3
12	**13**	2	10	70	0.25	1.20	85500	3300	2000	1.6	125.3
13	**14**	2	5	70	0.25	0.30	21400	7000	3300	2.1	128.7
14	**14**	2	5	80	0.25	0.89	63400	4900	2800	1.7	128.0
15	**14**	2	5	70	1	0.65	11600	5400	3000	1.8	
16	**14**	2	10	70	0.25	0.59	42100	5500	3000	1.8	129.0
17	**15**	2	5	70	0.25	0.18	6400	5700	3000	1.9	
18	**15**	2	5	80	0.25	0.52	18500	6000	2500	2.4	126.9
19	**15**	2	5	70	1	0.58	5200	-	-	-	128.9
20	**15**	2	10	70	0.25	0.66	23500	5700	2800	2.0	129.1

[a] General conditions: PhMe 20 mL, 0.5 h, $[Ni(cod)_2]$ / ylide unit = 10. [b] After precipitation of the reaction mixture with acidified (HCl) methanol (200 mL). [c] In ($molC_2H_4$) (mol*P,O*-chelated Ni units)$^{-1}$ h^{-1}. [d] determined by SEC-HT *vs.* polystyrene standard, uncorrected. [e] measured by DSC.

Our findings suggest the occurrence of an intramolecular deactivation mechanism involving the two ylidic centres (*vide infra*). On the other hand, the mono-ylides **13** and **14** were about two times more active than **19**,[37] strongly suggesting that the calixarene moiety behaves as a sufficiently bulky substituent for preventing a deactivation pathway according to scheme 2 (with formation of a bis-phosphanylenolato complex). The polyethylenes obtained with the two ylides containing a phenolic function, **14** and **15**, exhibited higher molecular weights (M_w = 6000-7000) than those obtained with the other two ylides (M_w = 3000-4000). This observation is in line with the better donor properties of the *p*-ArOH substituents of **14** and **15**, which push some electron density into the corresponding metallacycles. Electron rich Ni(*P,O*) metallacycles are known to favour chain growth over β-elimination.[13,38-41] Analysis of the ^{13}C NMR spectra revealed that the polyethylene samples do not show any significant branching.

Ethylene oligomerisation

In these tests a 1:1 Ni/PPh$_3$ ratio was used. The results of the oligomerisation tests are summarised in Table 3. All catalysts produce, like the system obtained from **19**, highly linear oligomers, for which the α-olefin content is 98-99% over the C_4-C_{16} range. As in the polymerisation reactions described above, the systems based on the ylides **12** and **15** displayed significantly lower activities than that of the reference compound **19**, while those obtained from the mono-ylides **13** and **14** resulted in higher activities (Table 3). For example, at 5 bar, the activity of **14** is ca. 30% higher than that of **19**, while that of **12** is ca. 35% lower. Thus, it is likely again that with the bis-ylidic systems, a deactivation mechanism takes place. The protecting effect exerted by the calixarene fragment of the monoylidic systems is logically less pronounced here than under polymerisation, because of the competing stabilising effect also exerted by PPh$_3$.[42] As inferred from the α values, the electronic properties of the chelates formed from **12**-**15** compare well with that formed with **19**.

Table 3. Ethylene oligomerisation using ylides **12-15** and **19**[a]

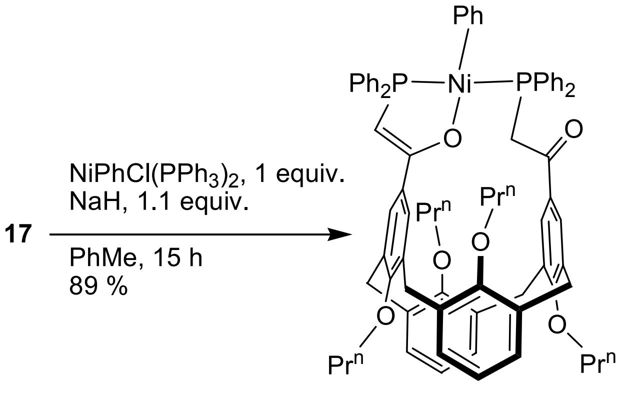
Entry	Ylide	[Ni(cod)$_2$] (μmol)	PPh$_3$ (μmol)	P (bar)	TOF (mol(C_2H_4) mol(Ni)$^{-1}$ h^{-1})	α[b]	C_2H_4 consumption[c] (g)
1	**19**	5	5	5	41800	0.94	8.79
2	**19**	5	5	10	50400	0.95	10.60
3	**12**	10	10	5	34700	0.92	9.74
4	**12**	10	10	10	36700	0.95	10.29
5	**13**	5	5	5	54000	0.96	15.15
6	**13**	5	5	10	63400	0.96	17.80
7	**14**	5	5	5	55800	0.95	15.64
8	**14**	5	5	10	67500	0.96	18.95
9	**15**	10	10	5	28700	0.94	8.04
10	**15**	10	10	10	35100	0.95	9.83

[a] General conditions: ylide 5 μmol, PhMe 20 mL, 70°C, 1 h, 100 mL autoclave. [b] Schulz-Flory parameter $\alpha = n(C_{n+2})/n(C_n)$. [c] calculated value using heptane as internal standard.

Overall, the calixarene fragment of **13** and **14** is of significant, but moderate efficiency, probably because the Ni(*P,O*) ring can freely rotate about the C(O)–calix axis, hence temporarily displacing the catalytic centre away from the bulky substituent and therefore limiting its protecting role.

Possible deactivation pathway of the bis-nickel complexes

The ^{31}P NMR spectra of the solutions obtained after ethylene polymerisation with **12** revealed the presence of several species. Among them, a compound, which corresponded to ca. 50% of the other species, exhibited a characteristic AB system (δ_A = 16.2 , δ_B = 10.8 ppm), with *J*(AB) = 291 Hz, which is a good indication for the presence of two trans-arranged phosphorus atoms. This product could not be separated from the reaction mixture. We surmised that the "double-SHOP catalyst" initially formed had partially converted into a monometallic species containing trans-bonded phosphorus atoms. It turned out that this compound could be obtained quantitatively by reacting diphosphine **17** with [NiCl(Ph)(PPh_3)$_2$] in the presence of NaH (Scheme 7). It is noteworthy that the resulting complex, **20**, forms selectively even in the presence of an excess of nickel and base at 80°C. Interestingly, we found no indication for the transient formation of complex **18** during this synthesis. Consistent with the presence of a free ketone function, the IR spectrum of **20** shows a strong absorption band at 1671 cm^{-1}. The IR spectrum further shows a strong absorption at 1495 cm^{-1} that may be assigned to the enolate system. In the ^{1}H NMR spectrum, the PCH proton of the enolate appears as a doublet at 4.83 ppm (^2J(PH) = 2.2 Hz).



20

Scheme 7.

The crystal structure of **20** was elucidated by an X-ray diffraction study (Fig. 3). Complex **20** constitutes the first characterized example of a SHOP-type complex in which the two P(III) ligands are linked together.[43] The nickel atom adopts a slightly distorted square planar coordination geometry, the P(1)NiP(2) and C(69)NiO(1) angles being respectively 172.7°(1) and 173.4°(1). In contrast to those of **18**, the four *p*-C atoms of the phenoxy rings are oriented towards the calixarene axis. The dihedral angles between the coordination plane and the C(15)- and the C(37)- rings are respectively 51° and 58°. It is interesting to note that the P(2), C(56), C(55), and O(6) atoms define a plane which is nearly coplanar with the C(37)-phenoxy ring. In other terms, one PCH_2 hydrogen atom lies inside the virtual tube defined by the calixarene moiety, the other points away. The inequivalence of the two PCH_2 protons was not evident in the ^1H NMR spectrum, since these protons give rise, at room temperature, to a broad signal centred at 4.22 ppm, suggesting a fast oscillation of the coordination plane about the calixarene axis as shown in Scheme 8.

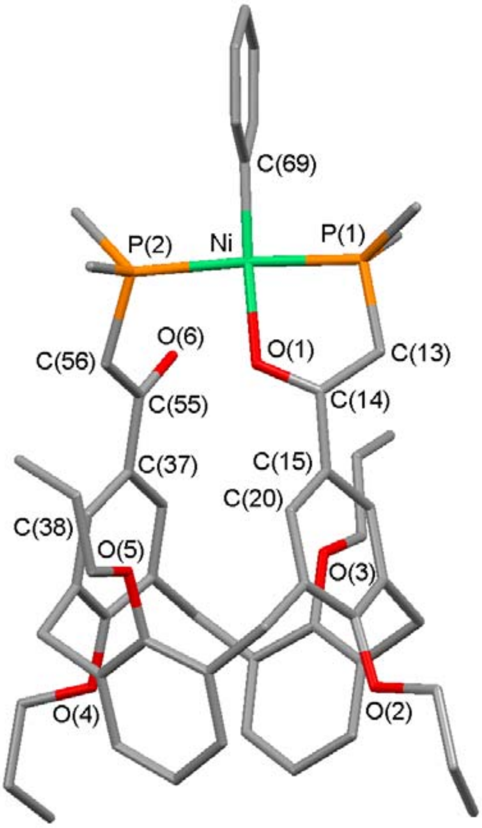
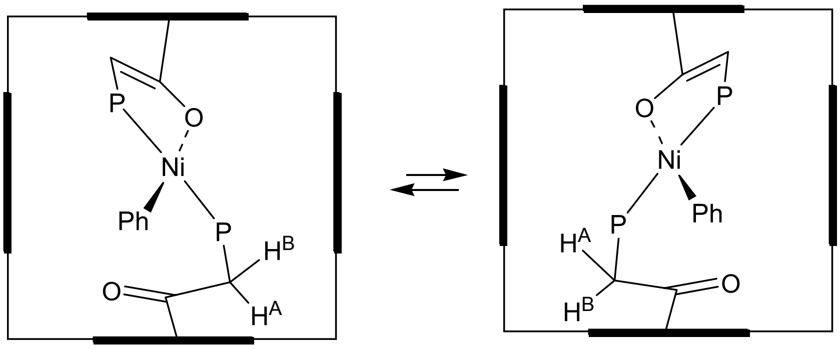


Fig. 3 X-ray structure of **20**.



Scheme 8. Postulated dynamics of complex **20** (view along the calixarene axis).

It turned out that **20** is not active, neither in oligomerisation nor polymerisation, even when operating at 30 bar and at 90°C. Since substantial amounts of this complex were always found in the catalytic solutions after completion of the reaction, the activity of the Ni-**12** system as inferred from the data shown in Table 2 is underestimated. Careful investigations revealed that the formation of **20** requires the presence of ethylene and that **20** forms during the first minutes following addition of ethylene (1 bar) to a solution of [Ni(cod)$_2$]/**12** maintained at 70°C. The question whether its formation can be avoided cannot be answered at this stage of our investigations.

Conclusion

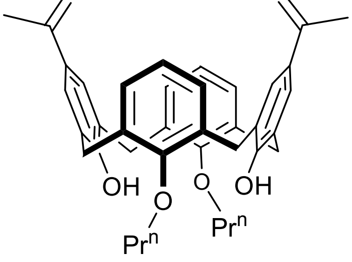
The present works describes the first examples of calixarenes having keto-stabilized phosphorus ylides tethered to *p*-phenolic carbon atoms of the macrocyclic core. These may be straightforwardly converted into SHOP-type complexes. The monometallic complexes obtained from the corresponding monophosphorus ylides provided efficient ethylene oligomerisation or polymerisation catalysts displaying better activities than the prototype **19**, hence reflecting the protecting role of the bulky calixarene substituent against catalyst deactivation. The systems derived from the bis-ylides **12** and **15** resulted in lower activities, the proximity of the two (potential) catalytic centres facilitating an intramolecular deactivation pattern during catalyst activation. Further studies will concentrate on the way such a deactivation may be prevented.

Experimental section

General procedures

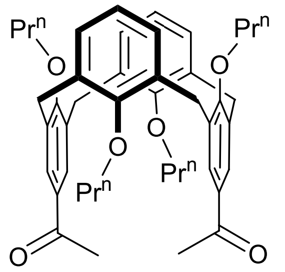
Solvents were dried over suitable reagents and freshly distilled under dry nitrogen before use. $CDCl_3$ was passed through a 5 cm-thick alumina column and stored under N_2 over molecular sieves (4 Å). All reactions were carried out using Schlenk tube techniques under a dry nitrogen atmosphere. IR spectra were recorded on a Perkin-Elmer 1600 spectrometer (KBr pellets, 4000-400 cm^{-1}) or a VERTEX 70 FT-IR spectrometer (pure, unmodified sample). Routine ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker AC-300 (^1H: 300.1 MHz; ^{31}P: 121.5 MHz) and ARX-500 (^1H: 500.1 MHz) spectrometers. Proton chemical shifts are reported relative to residual protonated solvents (C_6D_6, δ 7.16; $CHCl_3$, δ 7.26). The ^{13}C chemical shifts are referenced relative to deuterated solvents (C_6D_6, δ 128.02; $CDCl_3$, δ 77.0) and the ^{31}P NMR data are given relative to external H_3PO_4. For column chromatography Geduran SI (E. Merck, 0.040-0.063 mm) silica was used. Routine thin-layer chromatography analyses were carried out by using plates coated with Merck Kieselgel 60 GF_{254}. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie, Strasbourg. Melting points were determined with a Büchi 535 capillary melting-point apparatus and are uncorrected. High temperature size exclusion chromatography (HT SEC) measurements were performed at 150 °C with a "PL220" apparatus (Column set HT-MixedB-TCB-01) in 1,2,4-trichlorobenzene (with 0.2% Irganox). Calibration was made with linear polystyrene samples. DSC measurements were made using a Perkin Elmer DSC4 apparatus with a heating rate of 10°C/min. The catalytic solutions were analysed with a Varian 3900 gas chromatograph equipped with a WCOT-fused silica column (25 m, 0.32 mm inside diameter, 0.25 mm film thickness). The calixarene **1**,[27] **19**,[44] $[Ni(cod)_2]$,[44] $[NiPhCl(PPh_3)_2]$,[45] and $PhNMe_3Br_3$[46] were prepared according to literature procedures.

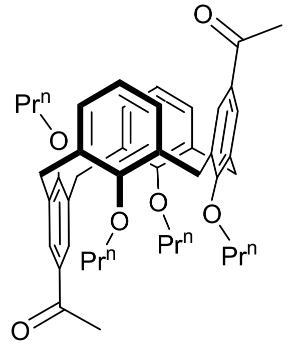
Acetylated calixarenes



5,17-Diacetyl-25,27-dipropoxy-26,28-dihydroxycalix[4]arene (*cone*) (2).

To a solution of 25,27-dihydroxy-26,28-dipropoxycalix[4]arene (*cone*) (**1**) (8.100 g, 15.93 mmol) in nitrobenzene (250 mL) was added $AlCl_3$ (9.55g, 71.66 mmol). Acetyl chloride (2.62 g, 33.45 mmol) was slowly added, and the resulting brownish solution was stirred for 0.25 h (a longer reaction time results in formation of the triacetylated compound). The reaction was quenched with 2N HCl (150 mL). The organic phase was separated and washed with water (100 mL). The solvent was removed in *vacuo* at ca. 120°C affording a brown residue. Recrystallisation from a CH_2Cl_2-MeOH mixture afforded pure **2** as a white powder. Yield: 8.02 g, 85 %; mp >250°C; IR (KBr, cm^{-1}): ν(C=O) = 1666, s. ^1H NMR (300 MHz, $CDCl_3$): δ 9.04 (s, 2H, OH), 7.75, (s, 4H, *m*-ArH), 6.97 (d, 4H, *m*-ArH, $^3J = 7.6$ Hz), 6.79 (t, 2H, *p*-ArH, $^3J = 7.6$ Hz), 4.31 and 3.48 (AB spin system, 8H, $ArCH_2Ar$, $^2J = 12.8$ Hz), 4.01 (t, 4H, OCH_2, $^3J = 6.2$ Hz), 2.55 (s, 6H, $C(O)CH_3$), 2.08 (m, 4H, OCH_2CH_2), 1.33 (t, 6H, CH_2CH_3, $^3J = 7.4$ Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 196.90 (s, C(O)), 158.39, 151.75, 132.69, 129.58, 129.30, 128.89, 127.95 and 125.60 (8s, aryl C), 78.54 (s, OCH_2), 31.42 (s, $ArCH_2Ar$), 26.28 (s, $C(O)CH_3$), 23.51 (s, OCH_2CH_2), 10.92 (s, CH_2CH_3). Found: C, 77.05; H, 6.91. Calc. for $C_{38}H_{40}O_6$ ($M_r = 592.73$) C, 77.00; H, 6.80%.



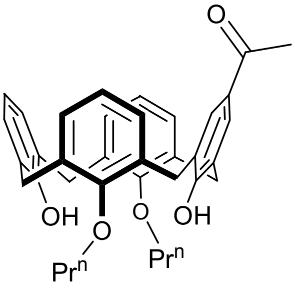


5,17-Diacetyl-25,26,27,28-tetrapropoxycalix[4]arene (*1,3-alternate* (3a) and *partial cone* (3b)).

K_2CO_3 (0.467 g, 3.38 mmol) was added to a solution of **1** (1.000 g, 1.69 mmol) in refluxing acetonitrile (100 mL). After 1 h, *n*-PrBr (0.624 g, 5.07 mmol) was added and the suspension was maintained under reflux. The reaction was monitored by TLC ($R_f = 0.7$ (**3b**), $R_f = 0.4$ (**3a**), SiO_2, AcOEt-CH_2Cl_2, 5:95, *v/v*) and heating was stopped after 7 d. After filtration the solution was evaporated to dryness and the two isomers were separated by column chromatography on silica gel using AcOEt-CH_2Cl_2 (5:95 v/v) as eluant.

(**3a**) Yield: 0.721 g, 63 %; mp 223-226°C; IR (KBr, cm^{-1}): ν(C=O) = 1676, s. ^1H NMR (300 MHz, $CDCl_3$): δ 7.64 (s, 4H, *m*-ArH of acylated Ar), 6.99 (d, 4H, *m*-ArH, $^3J = 7.5$ Hz), 6.65

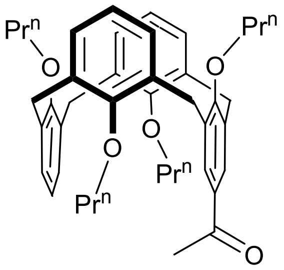
(t, 2H, *p*-ArH, ^3J = 7.5 Hz), 3.71-3.65 (8H, OCH_2), 3.61 and 3.54 (AB spin system, 8H, Ar*CH₂*Ar, ^2J = 13.4 Hz), 2.47 (s, 6H, $C(O)CH_3$), 1.95-1.79 (8H, CH_2CH_3), 1.09-1.01 (12H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 197.69 (s, C(O)), 160.85-121.77 (aryl and quat.-C), 74.80 (s, OCH_2), 35.37 (s, $ArCH_2Ar$), 26.40 (s, $C(O)CH_3$), 23.92 (s, CH_2CH_3), 10.64 (s, CH_2CH_3). Found: C, 77.88; H, 8.02. Calc. for $C_{44}H_{52}O_6$ (M_r = 676.89): C, 78.07; H, 7.74%.
(**3b**) Yield: 0.314 g, 26 %; mp 224-226°C; IR (KBr, cm^{-1}): ν(C=O) = 1677s. ^1H NMR (300 MHz, $CDCl_3$): δ 7.93 and 7.74 (2s, 2H each, *m*-ArH of acylated Ar), 6.94 (d, 2H, *m*-ArH, ^3J = 7.5 Hz), 6.45 (two overlapping d, 2H, *p*-ArH, $^3J = {^3J'}$ = 7.5 Hz), 6.25 (d, 2H, *m*-ArH, ^3J = 7.5 Hz), 4.08 and 3.14 (AB spin system, 4H, $ArCH_2Ar$, ^2J = 13.4 Hz), 3.85-3.80 (m, 4H, OCH_2), 3.74 and 3.67 (AB spin system, 4H, $ArCH_2Ar$, ^2J = 12.7 Hz), 3.55 (m, 2H, OCH_2), 3.30 (m, 2H, OCH_2), 2.63 and 2.62 (2s, 3H each, $C(O)CH_3$), 2.00-1.89 (6H, CH_2CH_3), 1.35-1.27 (m, 2H, CH_2CH_3), 1.13-1.05 (9H, CH_2CH_3), 0.62 (t, 3H, CH_2CH_3 ^3J = 7.5 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 197.69 and 197.27 (2s, C(O)), 162.19-121.80 (aryl and quat.-C), 76.36, 75.70 and 75.01 (3s, OCH_2), 35.82 and 30.52 (2s, $ArCH_2Ar$), 26.62 and 26.48 (2s, $CH_3C(O)$), 24.16, 23.87 and 22.12 (3s, CH_2CH_3), 10.88, 10.63 and 9.31 (3s, CH_2CH_3). Found: C, 78.03; H, 7.80. Calc. for $C_{44}H_{52}O_6$ (M_r = 676.89): C, 78.07; H, 7.74%.



5-Acetyl-25,27-dipropoxy-26,28-dihydroxycalix[4]arene (*cone*) (5).

To a solution of **1** (3.000 g, 5.90 mmol) in nitrobenzene (250 mL) was added acetyl chloride (0.467 g, 5.95 mmol). A solution of $AlCl_3$ (0.790 g, 5.95 mmol) in nitrobenzene (50 mL) was then added dropwise over 2 hours. The resulting brownish solution was stirred for a further 10 min and then quenched with 2N HCl (200 mL). The organic phase was separated and washed with water (2 x 100 mL). Removal of the solvent in *vacuo* under heating at 120°C gave a residue, which was purified by column chromatography using AcOEt-CH_2Cl_2 (2:98, *v/v*) as eluant (R_f = 0.5, SiO_2, AcOEt-CH_2Cl_2, 2:98, *v/v*). Yield: 2.920 g, 90 %; mp > 250°C. IR (KBr, cm^{-1}): ν(C=O) = 1671, s. ^1H NMR (300 MHz, $CDCl_3$): δ 9.13 (s, 1H, OH), 8.27 (s, 1H, OH), 7.76 (s, 2H, *m*-ArH of acylated ring), 7.08 (d, 2H, *m*-ArH, ^3J = 7.4 Hz), 6.96 (d, 4H, *m*-ArH, ^3J = 7.5 Hz), 6.78 (t, 2H, *p*-ArH, ^3J = 7.6 Hz), 6.67 (t, 1H, *p*-ArH, ^3J = 7.4 Hz), 4.34 and 3.48

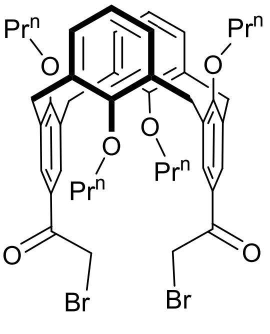
(AB spin system, 4H, ArCH_2Ar, ^2J = 13.0 Hz), 4.34 and 3.41 (AB spin system, 4H, ArCH_2Ar, ^2J = 13.0 Hz), 4.01 (t, 4H, OCH$_2$, ^3J = 6.2 Hz), 2.56 (s, 3H, C(O)CH$_3$), 2.08 (m, 4H, OCH$_2$CH_2), 1.34 (t, 6H, CH$_2$CH_3, ^3J = 7.4 Hz). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 196.94 (s, C(O)), 158.54-119.08 (aryl and quat.-C), 78.45 (s, OCH$_2$), 31.48 and 31.44 (2s, ArCH$_2$Ar), 26.29 (s, C(O)CH$_3$), 23.54 (s, OCH$_2$CH$_2$), 10.96 (s, CH$_2$CH$_3$). Found: C, 78.16; H, 6.84. Calc. for $C_{36}H_{38}O_5$ (M_r = 550.69): C, 78.52; H, 6.96%.



5-Acetyl-25,26,27,28-tetrapropoxycalix[4]arene (*1,3-alternate*) (6).

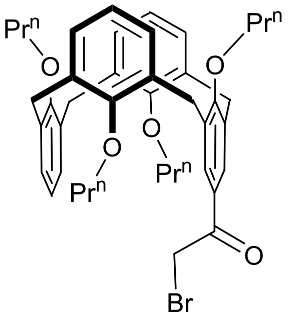
A suspension of K_2CO_3 (0.467 g, 3.38 mmol) and 5-acetyl-25,27-dipropoxy-26,28-dihydroxycalix[4]arene (*cone*) (**5**) (1.000 g, 1.69 mmol) was stirred in refluxing acetonitrile (100 mL) for 1h. Then *n*-PrBr (0.624 g, 5.07 mmol) was added and the suspension was further stirred at 60°C for 1 week. Product formation was monitored by TLC (R_f = 0.6, SiO$_2$, AcOEt-CH$_2$Cl$_2$, 2:98, v/v). After filtration, the solution was evaporated to dryness. The product was recrystallised from CH$_2$Cl$_2$/MeOH. Yield: 0.805 g, 75 %; mp 156-158°C; IR (KBr, cm^{-1}): ν(C=O) = 1680, s. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.70 (s, 2H, *m*-ArH of acylated Ar), 7.03-6.97 (6H, *m*-ArH,), 6.65 (t, 2H, *p*-ArH, ^3J = 7.5 Hz), 6.54 (pseudo t, 1H, *p*-ArH, ^3J = 7.5 Hz), 3.69-3.56 (16H, OCH$_2$ and ArCH_2Ar), 2.58 (s, 3H, C(O)CH$_3$), 1.87-1.74 (8H, CH_2CH$_3$), 1.07-1.02 (12H, CH$_2$CH_3). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 197.78 (s, C(O)), 160.76-121.24 (aryl and quat.-C), 74.79, 74.59 and 74.39 (3s, OCH$_2$), 35.41 and 35.38 (2s, ArCH$_2$Ar), 26.52 (s, C(O)CH$_3$), 23.88 and 23.85 (2s, CH$_2$CH$_3$), 10.69 (s, CH$_2$CH$_3$). Found: C, 79.54; H, 7.93. Calc. for $C_{42}H_{50}O_5$ (M_r = 634.86): C, 79.46; H, 7.94%.

2-haloacetylated calixarenes

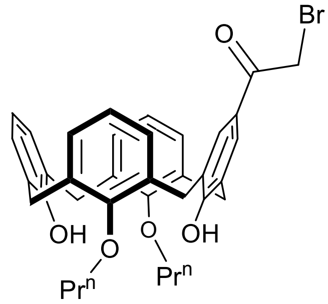


5,17-Bis(2-bromoacetyl)-25,26,27,28-tetrapropoxycalix[4]arene(*1,3-alternate*) (4).

To a solution of 5,17-diacetyl-25,26,27,28-tetrapropoxycalix[4]arene (**3a**) (4.000 g, 5.91 mmol) in $CHCl_3$ (30 mL) at 40°C was slowly added a solution of Br_2 (1.940 g, 12.11 mmol) in $CHCl_3$ (10 mL). After being stirred for 5 min the solution was washed successively with 10% Na_2SO_3 (10 mL) and 10% $NaHCO_3$ (20 mL), then dried with $MgSO_4$, and concentrated. Addition of MeOH afforded a white microcrystalline powder. Yield: 4.73 g, 96 %; mp 123-126°C; IR (KBr, cm^{-1}): ν(C=O) = 1668, s. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 (s, 4H, *m*-ArH), 6.98 (d, 4H, *m*-ArH, ^3J = 7.5 Hz), 6.63 (t, 2H, *p*-ArH, ^3J = 7.5 Hz), 4.36 (s, 4H, $C(O)CH_2Br$), 3.74 (t, 4H, OCH_2, ^3J = 7.0 Hz), 3.73 (t, 4H, OCH_2, ^3J = 7.3 Hz), 3.57 and 3.52 (AB spin system, 8H, $ArCH_2Ar$, ^2J = 13.1 Hz), 2.09-1.97 (m, 4H, CH_2CH_3), 1.97-1.83 (m, 4H, CH_2CH_3), 1.16 (t, 6H, CH_2CH_3, ^3J = 7.4 Hz), 1.10 (t, 6H, CH_2CH_3, ^3J = 7.4 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 191.04 (s, C(O)), 161.49-121.96 (aryl and quat.-C), 75.40 (s, OCH_2), 34.78 (s, $ArCH_2Ar$), 31.44 (s, $C(O)CH_2Br$), 24.15 and 24.08 (2s, CH_2CH_3), 10.79 and 10.74 (2s, CH_2CH_3). Found: C, 63.19; H, 5.89. Calc. for $C_{44}H_{50}Br_2O_6$ (M_r = 834.69): C, 63.32; H, 6.04%.



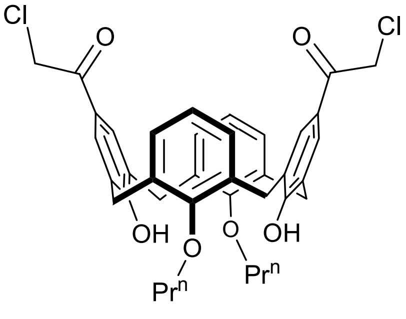
5-(2-Bromoacetyl)-25,26,27,28-tetrapropoxycalix[4]arene (*1,3-alternate*) (7). To a stirred solution of 5-acetyl-25,26,27,28-tetrapropoxycalix[4]arene (**6**) (2.00 g, 3.15 mmol) in CH_2Cl_2 (30 mL) was added slowly a solution of Br_2 (0.50 g, 3.15 mmol) in CH_2Cl_2 (20 mL). After the addition was completed the solution was washed successively with 10% Na_2SO_3 (10 mL) and 10% $NaHCO_3$ (20 mL), dried over $MgSO_4$ and concentrated. Addition of MeOH afforded a white precipitate. Yield: 2.110 g, 94 %; mp 105-109°C; IR (KBr, cm^{-1}): ν(C=O) =1678, s. ^1H NMR (300 MHz, $CDCl_3$): δ 7.73 (s, 2H, *m*-ArH), 7.03 (dd, 2H, *m*-ArH, *J* = 7.6 Hz, *J'* = 1.7 Hz), 6.97 (d, 4H, *m*-ArH, *J* = 7.5 Hz), 6.64 (pseudo t, 2H, *p*-ArH, ^3J = 7.5 Hz), 6.52 (t, 1H, *p*-ArH, ^3J = 7.5 Hz), 4.50 (s, 2H, $C(O)CH_2Br$), 3.72-3.54 (16H, OCH_2 and $ArCH_2Ar$), 1.93-1.82 (8H, CH_2CH_3), 1.11-1.03 (12H, CH_2CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 190.32 (s, C(O)), 161.38-121.07 (aryl and quat.-C), 75.20, 74.99 and 74.66 (3s, OCH_2), 35.12 and 35.02 (2s, $ArCH_2Ar$), 32.13 (s, CH_2Br), 23.99 and 23.96 (2s, CH_2CH_3), 10.76 (s, CH_2CH_3). Found: C, 70.61; H, 6.96. Calc. for $C_{42}H_{49}BrO_5$ (M_r = 713.15): C, 70.68; H, 6.92%.



5-(2-Bromoacetyl)-25,27-dihydroxy-26,28-dipropoxycalix[4]arene (*cone*) (8).

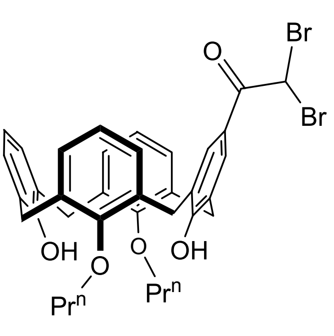
To a solution of 5-acetyl-25,27-dihydroxy-26,28-dipropoxycalix[4]arene (**5**) (3.00 g, 5.45 mmol) in THF (100 mL) was added dropwise a solution of $PhNMe_3Br_3$ (2.05 g, 5.45 mmol) in THF (50 mL). The mixture was stirred until complete discolouration. After filtration the solution was evaporated to dryness. The residue was purified by column chromatography on silica gel using a cyclohexane-dichloromethane mixture (1:4) as eluent (R_f = 0.2, SiO_2, cyclohexane-CH_2Cl_2, 1:4, *v/v*). 5-(2,2-Dibromoacetyl)-25,27-dihydroxy-26,28-dipropoxycalix[4]arene (**10**) eluted first (R_f = 0.4, SiO_2, cyclohexane-CH_2Cl_2 1:4, *v/v*). Yield: 2.33 g, 68%; mp 223-227°C (dec); IR (KBr, cm^{-1}): ν(C=O) = 1683, s. ^1H NMR (300 MHz, $CDCl_3$): δ 9.34 (s, 1H, OH), 8.27 (s, 1H, OH), 7.80, (s, 2H, *m*-ArH), 7.08 (d, 2H, *m*-ArH, ^3J = 7.5 Hz), 6.99-6.94 (4H, *m*-ArH), 6.78 (pseudo t, 2H, *p*-ArH, ^3J = 7.6Hz), 6.67 (t, 1H, *p*-ArH, ^3J = 7.4 Hz), 4.41 (s, 2H, $C(O)CH_2Br$), 4.33 and 3.49 (AB spin system, 4H, $ArCH_2Ar$, ^2J = 13.1 Hz), 4.33 and 3.41 (AB spin system, 4H, $ArCH_2Ar$, ^2J = 13.0 Hz), 4.04-3.98 (m, 4H,

OCH_2), 2.14-2.06 (m, 4H, OCH_2CH_2), 1.34 (t, 6H, CH_2CH_3, $^3J = 7.4$ Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 190.03 (s, C(O)), 159.46-119.12 (aryl and quat.-C), 78.49 (s, OCH_2), 31.47 and 31.44 (2s, $ArCH_2Ar$), 30.79 (s, $C(O)CH_2Br$), 23.54 (s, OCH_2CH_2), 10.97 (s, CH_2CH_3). Found: C, 68.60; H, 5.85. Calc. for $C_{36}H_{37}O_5Br$ ($M_r = 629.59$): C, 68.68; H, 5.92%.



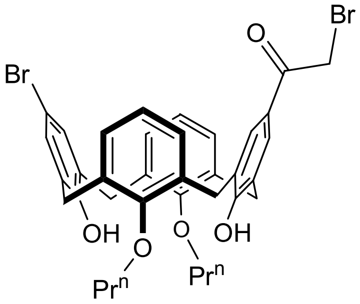
5,17-Bis(chloroacetyl)-25,27-dipropoxy-26,28-dihydroxycalix[4]arene (*cone*) (9).

To a solution of **1** (8.100 g, 15.93 mmol) in nitrobenzene (250 mL) was first added $AlCl_3$ (9.550 g, 71.66 mmol), then a solution of $ClCH_2C(O)Cl$ (3.780 g, 33.45 mmol) in nitrobenzene (20 mL). The resulting brownish solution was stirred for 2 h and then quenched with 2N HCl (150 mL). The organic phase was separated and washed with water (2 x 50 mL). Removal of the solvent in *vacuo* at 120°C gave a residue, which was chromatographed on silica gel using CH_2Cl_2 as eluent ($R_f = 0.2$, SiO_2, CH_2Cl_2). Yield: 3.160 g, 30 %; mp > 250°C; IR (KBr, cm^{-1}): ν(C=O) = 1678, s. ^1H NMR (300 MHz, $CDCl_3$): δ 9.25 (s, 2H, OH), 7.77 (s, 4H, *m*-ArH), 6.97 (d, 4H, *m*-ArH, $^3J = 7.5$ Hz), 6.80 (t, 2H, *p*-ArH, $^3J = 7.5$Hz), 4.66 (s, 4H, CH_2Cl), 4.31 and 3.50 (AB spin system, 8H, $ArCH_2Ar$, $^2J = 13.1$ Hz), 4.02 (t, 4H, OCH_2, $^3J = 6.2$ Hz), 2.15-2.03 (m, 4H, OCH_2CH_2), 1.34 (t, 6H, CH_2CH_3, $^3J = 7.4$ Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 189.74 (s, C=O), 159.25, 151.72, 132.45, 129.93, 129.43, 128.37, 125.73 and 125.71 (8s, arom. C), 78.65 (s, OCH_2), 45.70 (s, CH_2Cl), 31.39 (s, $ArCH_2Ar$), 23.52 (s, OCH_2CH_2), 10.95 (s, CH_2CH_3). Found: C, 68.97; H, 5.81. Calc. for $C_{38}H_{38}Cl_2O_6$ ($M_r = 661.62$): C, 68.98; H, 5.79 %.



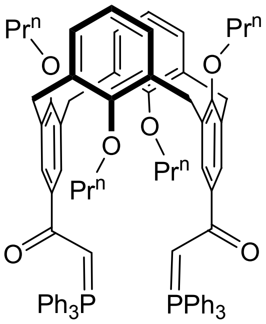
5-(2,2-Dibromoacetyl)-25,27-dihydroxy-26,28-dipropoxycalix[4]arene (*cone*) (10).

To a solution of 5-acetyl-25,27-dihydroxy-26,28-dipropoxycalix[4]arene (**5**) (3.000 g, 5.45 mmol) in THF (100 mL) was added dropwise a solution of $PhNMe_3Br_3$ (4.100 g, 10.90 mmol) in THF (50 mL). The mixture was stirred until complete discolouration, and was then filtered and evaporated to dryness. The residue was recrystallised from CH_2Cl_2-MeOH. Yield: 3.44 g, 89%; mp 208-212°C (dec.); IR (KBr, cm^{-1}): ν(C=O) = 1685, s. ^1H NMR (300 MHz, $CDCl_3$): δ 9.50 (s, 1H, OH), 8.29 (s, 1H, OH), 7.92, (s, 2H, *m*-ArH), 7.09 (d, 2H, *m*-ArH, $^3J = 7.3$ Hz), 6.99-6.94 (4H, *m*-ArH), 6.79 (pseudo t, 2H, *p*-ArH, $^3J = 7.5$ Hz), 6.74 (s, 1H, C(O)$CHBr_2$), 6.68 (t, 1H, *p*-ArH, $^3J = 7.4$ Hz), 4.33 and 3.51 (AB spin system, 4H, ArCH_2Ar, $^2J = 13.1$ Hz), 4.33 and 3.43 (AB spin system, 4H, ArCH_2Ar, $^2J = 13.0$ Hz), 4.10-3.90 (m, 4H, OCH_2), 2.25-2.00 (m, 4H, OCH_2CH_2), 1.35 (t, 6H, CH_2CH_3, $^3J = 7.3$ Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 184.65 (s, C(O)), 160.05-119.16 (aryl and quat.-C), 78.52 (s, OCH_2), 40.38 (s, C(O)$CHBr_2$), 31.48 and 31.45 (2s, ArCH_2Ar), 23.54 (s, OCH_2CH_2), 10.98 (s, CH_2CH_3). Found: C, 60.91; H, 5.06. Calc. for $C_{36}H_{36}O_5Br_2$ ($M_r = 708.49$): C, 61.03; H, 5.12%.



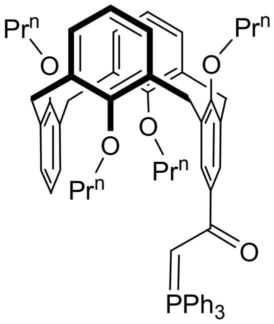
5-(2-bromoacetyl)-17-bromo-25,27-dihydroxy-26,28-dipropoxycalix[4]arene (*cone*) (11). To a solution of 5-acetyl-25,27-dihydroxy-26,28-dipropoxycalix[4]arene (**5**) (4.500 g, 8.17 mmol) in $CHCl_3$ (50 mL) at 60°C was added dropwise over 5 min a solution of Br_2 (2.60 g, 16.34 mmol) in $CHCl_3$ (20 mL). The mixture was stirred for 0.5 h and washed successively with 10% Na_2SO_3 (10 mL) and 10% $NaHCO_3$ (20 mL), dried over $MgSO_4$, filtered and concentrated to ca. 5 mL. Addition of hexane afforded a white precipitate. Yield: 5.99 g, 94 %; mp 231-234°C; IR (KBr, cm^{-1}): ν(C=O) = 1680, s. ^1H NMR (300 MHz, $CDCl_3$): δ 9.28 (s, 1H, OH), 8.42 (s, 1H, OH), 7.81, (s, 2H, *m*-ArH), 7.20 (s, 2H, *m*-ArH), 7.00-6.95 (4H, *m*-ArH), 6.82 (t, 2H, *p*-ArH, $^3J = 7.5$ Hz), 4.42 (s, 2H, C(O)CH_2Br), 4.32 and 3.50 (AB spin system, 4H, ArCH_2Ar, $^2J = 13.1$ Hz), 4.29 and 3.36 (AB spin system, 4H, ArCH_2Ar, $^2J = 13.1$ Hz), 4.01 (t, 4H, OCH_2, $^3J = 6.2$ Hz), 2.15-2.03 (m, 4H, C$H_2$$CH_3$), 1.34 (t, 6H, CH_2CH_3, $^3J = 7.4$ Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 190.04 (s, C(O)), 159.34-110.49 (aryl and quat.-C), 78.59 (s, OCH_2), 31.44 and 31.20 (2s, ArCH_2Ar), 30.79 (s, C(O)CH_2Br), 23.52 (s, OCH$_2$*C*H$_2$), 10.95 (s, CH$_2$*C*H$_3$). Found: C, 60.91; H, 5.23. Calc. for $C_{36}H_{36}O_5Br_2$ (M_r = 708.49): C, 61.03; H, 5.12%.

Keto-stabilzed ylides



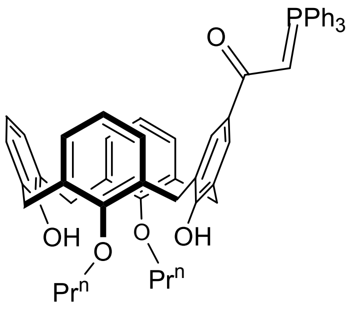
5,17-Bis(2-triphenylphosphoranylideneacetyl)-25,26,27,28-tetrapropoxycalix[4]arene (*1,3-alternate*) (12).

To a solution of 5,17-bis(2-bromoacetyl)-25,26,27,28-tetrapropoxycalix[4]arene (**4**) (4.000 g, 4.79 mmol) in THF (30 mL) was added PPh$_3$ (2.52 g, 9.58 mmol). The solution was stirred for 15 h uponwhich NaH (60% in mineral oil, 0.240 g, 10 mmol) was added. After stirring for 5 h, the mixture was filtered through Celite and the resulting solution concentrated to ca. 5 mL. Addition of Et$_2$O yielded the ylide as a white powder. Yield: 4.930 g, 86 %; mp 236-240°C (dec.); IR (KBr, cm^{-1}): 1515, s. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.74-7.67 (12H, PPh$_3$), 7.67 (s, 4H, *m*-ArH), 7.49-7.35 (18H, PPh$_3$), 7.01 (d, 4H, *m*-ArH, ^3J = 7.4 Hz), 6.78 (t, 2H, *p*-ArH, ^3J = 7.5 Hz), 4.40-4.28 (2H, PCH), 3.89 and 3.81 (AB spin system, 8H, ArC*H*$_2$Ar, ^2J = 15.8 Hz), 3.34 (t, 4H, OCH$_2$, ^3J = 7.3 Hz), 3.30 (t, 4H, OCH$_2$, ^3J = 7.3 Hz), 1.36-1.20 (8H, C*H*$_2$CH$_3$), 0.65 (t, 6H, CH$_2$C*H*$_3$, ^3J = 7.5 Hz), 0.58 (t, 6H, CH$_2$C*H*$_3$, ^3J = 7.5 Hz). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 185.18 (d, C(O), ^2J(PC) = 3.0 Hz), 158.45-121.95 (aryl and quat.-C), 71.90 and 71.61 (2s, OCH$_2$), 49.12 (d, PCH, *J*(PC) = 114.0 Hz), 38.55 (s, Ar*C*H$_2$Ar), 22.82 and 22.37 (2s, *C*H$_2$CH$_3$), 10.37 and 10.17 (2s, CH$_2$*C*H$_3$). ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$): δ 16.31 (s). Found: C, 79.99; H, 6.68. Calc. for $C_{80}H_{78}O_6P_2$ (M_r= 1197.44): C, 80.24; H, 6.56%.



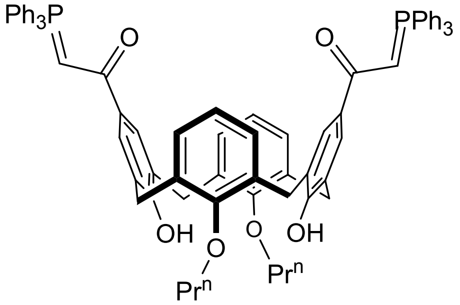
5-(2-triphenylphosphoranylideneacetyl)-25,26,27,28-tetrapropoxycalix[4]arene (*1,3-alternate*) (13).

A mixture of 5-(2-bromoacetyl)-25,26,27,28-tetrapropoxycalix[4]arene (**7**) (1.000 g, 1.4 mmol) and PPh_3 (0.37 g, 1.4 mmol) in THF (20 mL) was stirred at ambient temperature for 15 h. NaH (60% in mineral oil, 0.056 g, 1.4 mmol) was then added, and the suspension was stirred for 5 h. The solvent was removed *in vacuo*, and the residue was treated with toluene. After filtration through celite, the resulting solution was concentrated to ca. 5 mL. Addition of hexane afforded a white microcrystalline powder. Yield: 1.04 g, 83 %; mp 112-115°C; IR (ATR sampling, cm^{-1}): 1518s. ^1H NMR (300 MHz, $CDCl_3$): δ 7.84-7.77 (6H, PPh_3), 7.66 (s, 2H, *m*-ArH), 7.61-7.47 (9H, PPh_3), 7.05-7.01 (6H, *m*-ArH), 6.72 (pseudo t, 2H, *p*-ArH, ^3J = 7.5 Hz), 6.69 (t, 1H, *p*-ArH, ^3J = 7.5 Hz), 4.31 (d, 1H, PCH, ^2J(PH) = 26.2 Hz), 3.77-3.65 (8H, $ArCH_2Ar$), 3.60-3.44 (8H, OCH_2), 1.69-1.50 (8H, CH_2CH_3), 0.91 (t, 3H, CH_2CH_3, ^3J = 7.5 Hz), 0.90 (t, 3H, CH_2CH_3, ^3J = 7.6 Hz), 0.82 (t, 6H, CH_2CH_3, ^3J = 7.4 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 185.90 (d, C(O), ^2J(PC) = 2.9 Hz), 158.00-121.64 (aryl and quat.-C), 73.44, 73.35 and 73.31 (3s, OCH_2), 49.28 (d, PCH, J(PC) = 112.8 Hz), 36.86 and 36.72 (2s, $ArCH_2Ar$), 23.52 and 23.35 (2s, CH_2CH_3), 10.59, 10.54 and 10.47 (3s, CH_2CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 16.22 (s). Found: C, 80.38; H, 6.91. Calc. for $C_{60}H_{63}O_5P$ (M_r = 895.13): C, 80.51; H, 7.09%.



5-(2-triphenylphosphoranylideneacetyl)-25,27-dihydroxy-26,28-dipropoxycalix[4]arene (*cone*) (14).

A mixture of 5-(2-bromoacetyl)-25,27-dihydroxy-26,28-dipropoxycalix[4]arene (**8**) (2.000 g, 3.18 mmol) and PPh_3 (0.833 g, 3.18 mmol) in THF (100 mL) was stirred for 15 h. NaH (60% in mineral oil, 0.127 g, 3.18 mmol) was then added, and the white suspension was stirred for a further 5 h. The mixture was filtered through Celite upon which it was concentrated. Addition of Et_2O afforded a white powder. Yield: 2.35 g, 91%; mp >250°C; IR (ATR sampling, cm^{-1}): 1511s. ^1H NMR (300 MHz, $CDCl_3$): δ 8.55 (s, 1H, OH), 8.30 (s, 1H, OH), 7.83 (s, 2H, *m*-ArH), 7.79-7.72 (6H, PPh_3), 7.48-7.43 (9H, PPh_3), 7.08 (d, 2H, *m*-ArH, ^3J = 7.5 Hz), 7.03 (A part of ABX, dd, 2H, *m*-ArH, ^4J(AB) = 1.5 Hz, ^3J(AX) = 7.5 Hz), 6.92 (B part of ABX, dd, 2H, *m*-ArH, ^4J(AB) = 1.5 Hz, ^3J(BX) = 7.5 Hz), 6.71 (X part of ABX, pseudo t, 2H, *p*-ArH, ^3J(AX) = ^3J(BX) = 7.5 Hz), 6.67 (t, 1H, *p*-ArH, ^3J = 7.5 Hz), 4.44-4.35 (signal overlapping with $ArCH_2$, 1H, PCH), 4.37 and 3.51 (AB spin system, 4H, $ArCH_2Ar$, ^2J = 13.0 Hz), 4.37 and 3.36 (AB spin system, 4H, $ArCH_2Ar$, ^2J = 12.9 Hz), 4.07-3.97 (m, 4H, OCH_2), 2.17-2.06 (m, 4H, CH_2CH_3), 1.36 (t, 6H, CH_2CH_3, ^3J = 7.5 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 184.73 (s, C(O)), 155.24-119.04 (aryl and quat.-C), 78.33 (s, OCH_2), 48.95 (d, PCH, *J*(PC) = 115 Hz), 31.61 and 31.49 (2s, $ArCH_2Ar$), 23.59 (s, OCH_2CH_2), 11.02 (s, CH_2CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 16.6 (s). Found: C, 80.14; H, 6.19. Calc. for $C_{54}H_{51}O_5P$ (M_r = 810.97): C, 79.98; H, 6.34%.

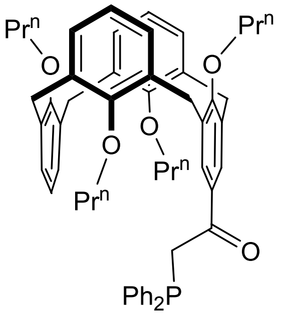


5,17-Bis(2-triphenylphosphoranylideneacetyl)-25,27-dihydroxy-26,28-dipropoxycalix[4] arene (*cone*) (15).

To a solution of 5,17-bis(2-chloroacetyl)-25,27-dihydroxy-26,28-dipropoxycalix[4]arene (**9**) (2.000 g, 3.02 mmol) in acetonitrile (30 mL) was added PPh_3 (1.762 g, 6.04 mmol). The solution was stirred for 15 h under reflux, and then concentrated to ca. 10 mL. Addition of Et_2O afforded quantitatively the corresponding phosphonium salt as a white powder which was dried in *vacuo* for 0.5 h. The phosphonium salt was then suspended in THF (50 mL) and NaH (60% in mineral oil, 0.242 g, 6.04 mmol) was added. After 5 h the solution was filtered through Celite, then concentrated to ca. 20 mL. Addition of Et_2O yielded the ylide as a white powder. Yield: 2.960 g, 88 %; mp >250°C; IR (KBr, cm^{-1}): 1507s. ^1H NMR (300 MHz,

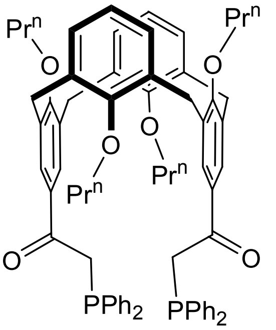
$CDCl_3$): δ 8.36 (s, 2H, OH), 7.77-7.64 (12H, PPh_3 and 4H, *m*-ArH), 7.56-7.44 (18H, PPh_3), 6.97 (d, 4H, *m*-ArH, $^3J = 7.6$ Hz), 6.69 (t, 2H, *p*-ArH, $^3J = 7.5$ Hz), 4.40-4.27 (2H, PCH), 4.30 and 3.44 (AB spin system, 8H, ArC*H*$_2$Ar, $^2J = 12.9$ Hz), 3.97 (t, 4H, OCH_2, $^3J = 6.2$ Hz), 2.12-2.01 (m, 4H, C*H*$_2$CH$_3$), 1.30 (t, 6H, CH$_2$C*H*$_3$, $^3J = 7.4$ Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 184.86 (d, C(O), ^2J(PC) = 3 Hz), 155.19-125.21 (aryl and quat.-C), 76.68 (s, OCH_2), 48.79 (d, PCH, *J*(PC) = 113 Hz), 31.53 (s, Ar*C*H$_2$Ar), 23.53 (s, *C*H$_2$CH$_3$), 10.92 (s, CH$_2$*C*H$_3$). $^{31}P\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 16.5. Found: C, 79.65; H, 5.83. Calc. for $C_{74}H_{66}O_6P_2$ (M_r = 1113.28): C, 79.84; H, 5.98%.

Calixarenes bearing β-ketophosphine units



5-Diphenylphosphinoacetyl-25,26,27,28-tetrapropoxycalix[4]arene (*1,3-alternate*) (16). To a solution of $HNPr_2^i$ (0.184 g, 1.82 mmol) in THF (10mL), maintained at −78°C, was slowly added a 1.6M solution of *n*-BuLi in hexane (1.13 mL, 1.81 mmol). The mixture was stirred for 0.5 h, and a solution of 5-acetyl-25,26,27,28-tetrapropoxycalix[4]arene (**6**) (1.150 g, 1.81 mmol) in THF (20 mL) was subsequently added, with the temperature kept at −78°C. After stirring the mixture for 1 h, a solution of Ph_2PCl (0.399 g, 1.81 mmol) in THF (5 mL) was slowly added. The temperature was then raised to 25°C, and the mixture was stirred for a further 15 h. After removal of the solvent *in vacuo*, the residue was treated with toluene and the resulting suspension was filtered through celite in order to remove LiCl. The filtered solution was evaporated to dryness. Recrystallisation from CH_2Cl_2-MeOH gave **16** as a pure white solid. Yield: 1.379 g, 93 %; mp 139-141 °C; IR (KBr, cm^{-1}): ν(C=O) = 1667, s. ^1H NMR (300 MHz, $CDCl_3$): δ 7.74 (s, 2H, *m*-ArH), 7.57-7.51 (3H, ArH), 7.42-7.37 (5H, ArH), 7.03-6.95 (6H, ArH), 6.65 (pseudo t, 2H, *p*-ArH, $^3J = 7.4$ Hz), 6.57 (t, 1H, *p*-ArH, $^3J = 7.4$ Hz), 3.80 (s, 2H, PCH_2), 3.71-3.54 (16H, OCH_2 and ArC*H*$_2$Ar), 1.89-1.69 (8H, C*H*$_2$CH$_3$), 1.06 (t, 3H, CH$_2$C*H*$_3$, $^3J = 7.4$ Hz), 1.03 (t, 3H, CH$_2$C*H*$_3$, $^3J = 7.4$ Hz), 0.91 (t, 6H, CH$_2$C*H*$_3$, $^3J = 7.4$ Hz). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 196.20 (d, C(O), ^2J(PC) = 8.7 Hz), 160.92-

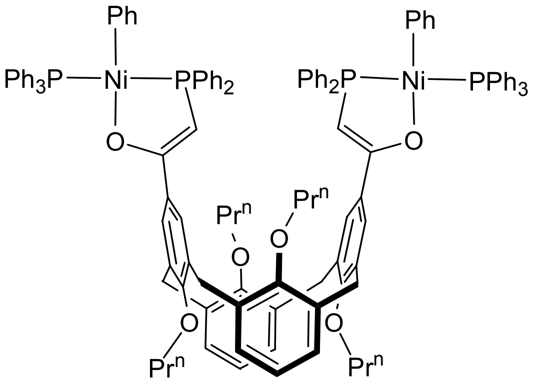
121.35 (aryl and quat.-C), 74.86, 74.69 and 74.47 (3s, OCH$_2$), 40.68 (d, PCH$_2$, ^1J(PC)= 18.6 Hz), 35.31 (s, Ar*C*H$_2$Ar), 23.92 and 23.89 (2s, *C*H$_2$CH$_3$), 10.71 and 10.60 (2s, CH$_2$*C*H$_3$). ^{31}P {^{1}H} NMR (121 MHz, CDCl$_3$): δ –19.4 (s). Found: C, 79.11; H, 7.51. Calc. for $C_{54}H_{59}O_5P$ (M_r = 819.04): C, 79.19; H, 7.26%.



5,17-Bis(diphenylphosphinoacetyl)-25,26,27,28-tetrapropoxycalix[4]arene (*1,3-alternate*) (17).

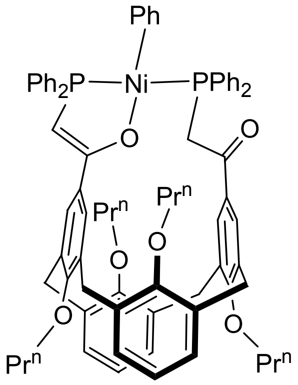
To a solution of HNPr$^i_2$ (0.101 g, 1.00 mmol) in THF (10mL) at −78°C was slowly added a 1.5M solution of *n*-BuLi (0.67 mL, 1.00 mmol). The mixture was stirred for 0.5 h, and a solution of 5,17-diacetyl-25,26,27,28-tetrapropoxycalix[4]arene (**3a**) (0.340 g, 0.50 mmol) in THF (20 mL) was subsequently added, with the temperature kept at −78°C. After stirring the solution for 1 h, a solution of Ph$_2$PCl (0.221 g, 1.00 mmol) was slowly added. The temperature was then raised to 25°C, and the mixture was stirred for 15 h. After removal of the solvent *in vacuo*, the residue was treated with toluene and the resulting suspension was filtered through Celite in order to remove LiCl. The filtered solution was evaporated to dryness and the product was recrystallised from CH$_2$Cl$_2$-MeOH, yielding **17** as a pure white solid. Yield: 0.470g, 90 %; mp 155°C; IR (KBr, cm^{-1}): ν(C=O) = 1667, s. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.68 (s, 4H, *m*-ArH), 7.58-7.33 (20H, PPh$_2$), 6.97 (d, 4H, *m*-ArH, ^3J = 7.6 Hz), 6.63 (pseudo t, 2H, *p*-ArH, ^3J = 7.5 Hz), 3.77 (s, 4H, PCH$_2$, ^2J(PH) = 0 Hz), 3.69 (t, 4H, OCH$_2$, ^3J = 7.1 Hz), 3.59 (t, 4H, OCH$_2$, ^3J = 7.6 Hz), 3.52 (s br, 8H, ArC*H*$_2$Ar), 1.90-1.71 (8H, C*H*$_2$CH$_3$), 1.06 (t, 6H, CH$_2$C*H*$_3$, ^3J = 7.4 Hz), 0.79 (t, 6H, CH$_2$C*H*$_3$, ^3J = 7.4 Hz). ^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ 196.31 (d, C(O), ^2J(PC) = 8.3 Hz), 160.96-121.75 (aryl and quat.-C), 74.84 and 74.78 (2s, OCH$_2$), 40.00 (d, PCH$_2$, ^1J(PC) = 20.1 Hz), 35.28 (s, Ar*C*H$_2$Ar), 24.06 and 23.98 (2s, *C*H$_2$CH$_3$), 10.67 and 10.40 (2s, CH$_2$*C*H$_3$). ^{31}P {^{1}H} NMR (121 MHz, CDCl$_3$): δ –16.2 (s). Found: C, 78.01; H, 6.76. Calc. for $C_{68}H_{70}O_6P_2$ (M_r = 1045.25): C, 78.14; H, 6.75%.

Nickel complexes



Complex 18.

A solution of 5,17-bis(2-triphenylphosphoranylideneacetyl)-25,26,27,28-tetrapropoxy calix[4]arene **12** (1.197 g, 1.00 mmol), PPh_3 (0.944 g, 3.60 mmol) and $[Ni(cod)_2]$ (0.660 g, 2.40 mmol) in toluene (50 mL) was stirred at room temperature for 15 h. The red solution was then concentrated to ca. 10 mL. Slow diffusion of hexane (70 mL) into this solution afforded yellow crystals suitable for X-ray diffraction study. After removal of the supernatant the crystals were washed with hexane and dried under vacuum. Yield: 0.331 g, 18 %. Note, sometimes **18** crystallises with some red crystals of $[Ni(PPh_3)_4]$. The latter can easily be removed mechanically. ^1H NMR (300 MHz, C_6D_6): δ 7.90-6.62 (70H, ArH), 5.17 (s, 2H, PCH), 3.76 (s br, 8H, $ArCH_2Ar$), 3.33 (4H, OCH_2), 3.06 (4H, OCH_2), 1.40-1.10 (8H, CH_2CH_3), 0.88 (t, 6H, CH_2CH_3, $^3J \sim 7$ Hz), 0.72 (t, 6H, CH_2CH_3, $^3J \sim 7$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 21.8 and 19.4 ppm (AB spin system, J(PP') = 283 Hz). Found: C, 75.43; H, 5.87. Calc. for $C_{116}H_{108}Ni_2O_6P_4$ (M_r = 1839.32): C, 75.75; H, 5.92%.



Complex 20.

To a solution of 5,17-diphenylphosphinoacetyl-25,26,27,28-tetrapropoxycalix[4]arene (**17**) (0.200 g, 0.19 mmol) and $[NiPhCl(PPh_3)_2]$ (0.132 g, 0.19 mmol) in THF (20mL) was added

NaH (0.010 g, 0.42 mmol). After stirring for 4 h, the suspension was filtered through Celite and the resulting yellow solution was concentrated to ca. 2 mL. Addition of hexane (ca. 20 mL) afforded 20 as a yellow powder. Yield: 0.200 g, 89 %; IR (KBr, cm^{-1}): ν(C=O) = 1671, s. ^{1}H NMR (300 MHz, C_6D_6): δ 8.09-6.62 (35H, ArH), 4.83 (d, 1H, PCH, ^2J(PH) = 2.2 Hz), 4.22 (s br, 2H, PCH_2), 3.68-3.49 (16H, ArCH_2Ar and OCH_2), 1.80-1.73 (8H, CH_2CH_3), 1.00 (t, 3H, CH_2CH_3, ^3J = 7.4 Hz), 0.95 (t, 3H, CH_2CH_3, ^3J = 7.4 Hz), 0.70 (s br, 6H, CH_2CH_3). ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ 193.39 (s, CH_2C=O, ^2J(PC) = 0 Hz), 160.53-120.62 (aryl and quat.-C), 79.16 (d, PCH, ^1J(PC) = 50 Hz), 75.80, 75.76 and 75.34 (3s, OCH_2), 40.13 (d, PCH_2, ^1J(PC) = 29 Hz), 34.47 and 34.41 (2s, ArCH_2Ar), 24.21, 24.14 and 24.04 (3s, CH_2CH_3), 10.69, 10.63 and 10.49 (3s, CH_2CH_3). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): δ 16.2 and 10.8 (AB spin system, J(PP') = 291 Hz). Found: C, 75.12; H, 6.24. Calc. for $C_{74}H_{74}NiO_6P_2$ (M_r= 1180.04): C, 75.32; H, 6.32%.

Reaction of 15 with [Ni(cod)$_2$].

To a cold (0°C) solution of 5,17-bis(2-triphenylphosphoranylideneacetyl)-25,27-dihydroxy-26,28-dipropoxycalix[4]arene (*cone*) (1.000 g, 0.90 mmol) and PPh_3 (0.685 g, 2.6 mmol) in toluene (20mL) was added a cold solution (0°C) of [Ni(cod)$_2$] (0.550 g, 2.00 mmol) in toluene (20 mL). The mixture was stirred for 15 h, then concentrated to ca. 5 mL. Addition of hexane precipitated a yellow powder. Yield: 2.960 g, 67 %. ^{1}H NMR (300 MHz, C_6D_6): δ 8.48 (s, 2H, OH), 7.72-6.23 (70H, ArH), 5.32 (s, 2H, PCH), 4.35 and 3.22 (AB spin system, 8H, ArCH_2Ar, ^2J = 13.0 Hz), 3.64 (s br, 4H, OCH_2), 1.77 (s br, 4H, CH_2CH_3), 1.16 (s br, 6H, CH_2CH_3). ^{31}P{^{1}H} NMR (121 MHz, C_6D_6): δ 22.6 and 20.0 (AB spin system, J(AB) = 284 Hz). $C_{110}H_{96}Ni_2O_6P_4$ (M_r= 1755.217).

X-ray crystallography

Crystal data for 15.

Crystals of **15** suitable for X-ray diffraction were obtained by slow diffusion of methanol into a dichloromethane solution of the compound. $C_{74}H_{66}O_6P_2$•0.5(CH_2Cl_2)•2(CH_3OH), M = 1219.75, triclinic, space group $P\bar{1}$, colourless prisms, a = 10.127(2), b = 16.167(2), c = 20.818(4) Å, α = 86.82(5), β = 83.22(5), γ = 78.40(5)°, V = 3313.6(1) Å^3, Z = 2, μ = 0.162 mm^{-1}, F(000) = 1290, D_c = 1.222 g cm^{-3}. Crystals of the compound were glued to a glass fibre and mounted on a Nonius Kappa CCD instrument. X-Ray diffraction measurements were made using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 173 K. Data collection was carried out using the Nonius collect suite[47] 19356 Reflections collected ($1.00 < \theta < 30.03°$), 10532 data with $I > 2\sigma(I)$. The structure was solved by direct methods with SHELXS-97 and refined with SHELXL-97.[48] Hydrogen atoms were included and refined using a riding model in SHELX-97. Final results: $R_1 = 0.0927$, $wR_2 = 0.237$, goodness of fit = 0.96, 769 parameters, residual electron density min/max = –0.97/1.02 e Å^{-3}.

Crystal data for 18.

Crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a toluene solution. Data collection and structure solution were as for compound **15**. $C_{116}H_{108}Ni_2O_6P_4$, $M = 1839.32$, monoclinic, spacegroup $P2_1/c$, yellow prisms, $a = 18.498(2)$, $b = 28.088(2)$, $c = 18.725(2)$ Å, $\beta = 98.181(3)$, $V = 9630.0(2)$ Å^3, $Z = 4$, $\mu = 0.514$ mm^{-1}, $F(000) = 3872$, $D_c = 1.269$ g cm^{-3}. Crystals of the compound were glued to a glass fibre and mounted on a Nonius Kappa CCD. X-Ray diffraction measurements were made using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 173 K. Data collection and structure solution was as for **18**. 28035 Reflections collected ($1.32 < \theta < 30.05°$), 17204 data with $I > 2\sigma(I)$. Final results: $R_1 = 0.0839$, $wR_2 = 0.2572$, goodness of fit = 0.94, 1137 parameters, residual electron density min/max = –1.094/2.051 e Å^{-3}.

Crystal data for 20.

Crystals suitable for X-ray diffraction were obtained by slow diffusion of hexane into a toluene solution of the compound. $C_{74}H_{74}NiO_6P_2$, $M = 1180.06$, monoclinic, spacegroup $P2_1/n$, yellow prisms, $a = 17.548(7)$, $b = 19.597(6)$, $c = 18.816(8)$ Å, $\beta = 104.88(3)$ Å, $V = 6254(4)$ Å^3, $Z = 4$, $\mu = 0.415$ mm^{-1}, $F(000) = 2496$, $D_c = 1.253$ g cm^{-3}. Crystals of the compound were glued to a glass fibre and mounted on a STOE IPDS diffractometer. X-Ray diffraction measurements were made using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 173 K. Data collection was carried out using the STOE IPDS software. 48066 reflections were collected ($1.5 < \theta < 26.9°$), 13324 being found to be unique (merging R = 0.069). The structure was solved by direct methods with the program SIR92.[49] Least squares refinement was carried out using the program CRYSTALS.[50,51] Hydrogen atoms are in calculated positions. Final results: $R_1 = 0.0678$ ($I > 1.4\sigma(I)$), $wR_2 = 0.0547$ (all data), goodness of fit = 1.20, residual electron density minimum/maximum = –1.05/1.35 eÅ^{-3}.

CCDC reference numbers 294726-294728.

Catalytic runs

The catalytic runs were carried out in a stainless steel autoclave (100 mL) equipped with a mechanical stirrer, a heating device, and an internal temperature probe. The reactor was dried under vacuum at 100 °C for 1 h before use. In a typical procedure, a solution of the ylide in toluene (10 mL) was added by injection at ambient temperature followed by a toluene solution (10 mL) either containing 1 equiv. of [Ni(cod)$_2$] and 1 equiv. of PPh$_3$ (for oligomerisation runs) or an excess of [Ni(cod)$_2$] (for polymerisation runs). The autoclave was then pressurised with ethylene and heated up to the desired temperature. If necessary, the evolution of heat was controlled by means of an ice bath. After completion of the oligomerisation runs, the autoclave was cooled with an ice bath and depressurised over 1 h. The solution was analysed by GC. Heptane (200 µL/10 mL of catalytic solution) was used as internal reference. For the polymerisation runs, the reaction was quenched by venting the autoclave, and the reaction mixture was subsequently poured into a stirred solution (200 mL) of acidified methanol (10% HCl) to precipitate the polymer. The white powder was isolated by filtration, washed with methanol, and dried in *vacuo* at 50 °C.

References

[1] W. Keim, *Angew. Chem., Int. Ed.* **1990**, *29*, 235-244.

[2] W. Keim, F. H. Kowaldt, R. Goddard and C. Krüger, *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 466-467.

[3] J. Skupinska, *Chem. Rev.,* **1991**, *91*, 613-648.

[4] G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 428-447.

[5] V. C. Gibson and S. K. Spitzmesser, *Chem. Rev.* **2003**, *103*, 283-315.

[6] U. Klabunde and S. D. Ittel, *J. Mol. Catal.* **1987**, *41*, 123-134.

[7] U. Klabunde, R. Mulhaupt, T. Herskovitz, A. H. Janovicz, J. Calabrese and S. D. Ittel, *J. Polym. Sci. Part A: Polym. Chem.* **1987**, *25*, 1989-2003.

[8] W. Keim, *New J. Chem.* **1987**, *11*, 531-534.

[9] D. Matt, M. Huhn, M. Bonnet, I. Tkatchenko, U. Englert and W. Kläui, *Inorg. Chem.* **1995**, *34*, 1288-1291.

[10] D. Matt, M. Huhn, J. Fischer, A. De Cian, W. Kläui, I. Tkatchenko and I. Bonnet, *J. Chem. Soc., Dalton Trans.* **1993**, 1173-1178.

[11] R. C. J. Atkinson, V. C. Gibson, N. J. Long, A. J. P. White and D. J. Williams, *Dalton Trans.* **2004**, 1823-1826.

[12] K. Hirose and W. Keim, *J. Mol. Catal.* **1992**, *73*, 271-276.

[13] K. A. Ostoja Starzewski and J. Witte, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 63-64.

[14] V. C. Gibson, A. Tomov, A. J. P. White and D. J. Williams, *Chem. Commun.* **2001**, 719-720.

[15] R. Soula, J. P. Broyer, M. F. Llauro, A. Tomov, R. Spitz, J. Claverie, X. Drujon, J. Malinge and T. Saudemont, *Macromolecules* **2001**, *34*, 2438-2442.

[16] L. S. Boffa and B. M. Novak, *Chem. Rev.* **2000**, *100*, 1479-1494.

[17] S. D. Ittel, L. K. Johnson and M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169-1204.

[18] M. J. Yanjarappa and S. Sivaram, *Prog. Polym. Sci.* **2002**, *27*, 1347-1398.

[19] S. Mecking, A. Held and F. M. Bauers, *Angew. Chem. Int. Ed. Engl.* **2002**, *41*, 544-561.

[20] W. Keim, *Green Chem.* **2003**, *5*, 105-111.

[21] L. Kolb, V. Monteil, R. Thomann and S. Mecking, *Angew. Chem. Int. Ed. Engl.* **2005**, *44*, 429-432.

[22] C. Müller, L. J. Ackerman, J. N. H. Reek, P. C. J. Kamer and P. W. N. M. van Leeuwen, *J. Am. Chem. Soc.* **2004**, *126*, 14960-14963.

[23] V. Böhmer, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 713-745.

[24] C. Jeunesse, D. Armspach and D. Matt, *Chem. Commun.* **2005**, 5603-5614.

[25] C. Dieleman, S. Steyer, C. Jeunesse and D. Matt, *Dalton Trans.* **2001**, 2508-2517.

[26] C. Jaime, J. de Mendoza, P. Prados, P. M. Nieto and C. Sánchez, *J. Org. Chem.* **1991**, *56*, 3372-3376.

[27] A. Casnati, A. Pochini, R. Ungaro, F. Ugozzoli, F. Arnaud, S. Fanni, M.-J. Schwing, R. J. M. Egberink, F. de Jong and D. N. Reinhoudt, *J. Am. Chem. Soc.* **1995**, *117*, 2767-2777.

[28] Z.-T. Huang and G.-Q. Wang, *J. Chem. Soc., Perkin Trans. 1* **1993**, 167-168.

[29] Z.-T. Huang and G.-Q. Wang, *Chem. Ber.* **1994**, *127*, 519-523.

[30] P. Kuhn, D. Sémeril, C. Jeunesse, D. Matt, P. Lutz and R. Welter, *Eur. J. Inorg. Chem.* **2005**, 1477-1481.

[31] D. Matt and A. van Dorsselaer, *Polyhedron* **1991**, *10*, 1521-1526.

[32] H. Qichen, X. Minzhi, Q. Yanlong, X. Weihua, S. Meicheng and T. Youqi, *J. Organomet. Chem.* **1985**, *287*, 419-426.

[33] K. A. Ostoja Starzewski and L. Born, *Organometallics* **1992**, *11*, 2701-2704.

[34] M. D. Fryzuk, Xiaoliang Gao and S. J. Rettig, *Can. J. Chem.* **1995**, *73*, 1175-1180.

[35] K. Kurtev and A. Tomov, *J. Mol. Catal.* **1994**, *88*, 141-150.

[36] A. Tomov and K. Kurtev, *J. Mol. Catal. A: Chem.* **1995**, *103*, 95-103.

[37] To be pertinent, the activity of **12-15** should have been compared to that of $Ph_3P{=}CHC(O)(p\text{-}ArOR)$ (R = H or alkyl) rather than to that of **19**. In fact, it is well known that Ni(*P,O*) catalysts bearing electron donating substituents are less active than their unsubstituted homologues.

[38] J. Heinicke, M. Koesling, R. Brüll, W. Keim and H. Pritzkow, *Eur. J. Inorg. Chem.* **2000**, 299-305.

[39] J. Heinicke, M. Köhler, N. Peulecke, M. He, M. K. Kindermann, W. Keim and G. Fink, *Chem. Eur. J.* **2003**, *9*, 6093-6107.

[40] J. Heinicke, M. Köhler, N. Peulecke, M. He and W. Keim, *J. Organomet. Chem.* **2005**, *690*, 2449-2457

[41] P. Kuhn, D. Sémeril, C. Jeunesse, D. Matt, M. Neuburger and A. Motta, unpublished results.

[42] J. Heinicke, M. Köhler, N. Peulecke and W. Keim, *J. Catal.* **2004**, *225*, 16-23.

[43] W. Keim and R. Nücker, *Chem.-Ing.-Tech.* **1994**, *66*, 950-951.

[44] T. M. Gomes Carneiro, J. Dupont, M. Luke and D. Matt, *Quimica Nova* **1988**, *11*, 215-217.

[45] A. Zeller, E. Herdtweck and T. Strassner, *Eur. J. Inorg. Chem.* **2003**, *9*, 1802-1806.

[46] J. Jacques and A. Marquet, *Organic Syntheses, Coll. Vol. 6*, p.175 (**1988**); *Vol. 53*, p.111 (**1973**).

[47] COLLECT Software, Nonius BV, **1997-2001**.

[48] G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, **1997**.

[49] A. Altomare, G. Cascarano, A. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 435.

[50] D. J. Watkin, C. K. Prout, J. R. Carruthers, P. W. Betteridge and R. I. Cooper, *CRYSTALS,* Issue 11, Chemical Crystallography Laboratory, Oxford, UK, **2001**.

[51] J. R. Carruthers and D. J. Watkin, *Acta Crystallogr. Sect. A* **1979**, *35*, 698-699.

Chapter 6

Coordination Chemistry of Large Diphosphanes - Directional Properties of a Calix[4]arene Proximally Substituted by Two -OCH_2PPh_2 Podand Arms

Abstract

The proximally-functionalised calixarene 5,11,17,23-tetra-*tert*-butyl-25,26-bis(diphenylphosphanylmethoxy)-27,28-dihydroxycalix[4]arene (**1**), a large diphosphane in which the P^{III} centres are separated by 10 bonds, behaves as a chelating ligand towards NiX_2 moieties (X = Cl, Br). As shown by three X-ray studies carried out on complexes of the type [NiX_2·**1**], the diphosphane is able to accommodate either tetrahedral or strongly distorted tetrahedral coordination geometries, but not a square planar one. In all structures, the ligand positions the nickel atom away from the calixarene axis. In the presence of methylaluminoxane (MAO), [$NiCl_2$·**1**] effectively catalyses the oligomerisation of ethylene, affording C_4-C_{12} oligomers.

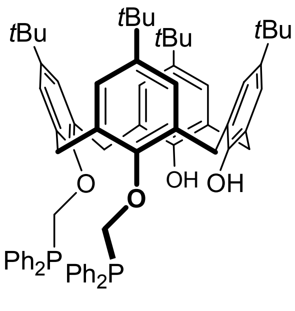
Résumé

Ce chapitre décrit la synthèse et les propriétés complexantes et catalytiques d'un calix[4]arène comportant deux entités phosphines –CH_2PPh_2 ancrées sur des atomes d'oxygène phénoliques proximaux, le 5,11,17,23-tétra-*tert*-butyl-25,26-bis(diphénylphosphinométhoxy)-27,28-dihydroxycalix[4]arène (**1**). La longueur relativement courte des podands ainsi que la rigidité marquée du fragment reliant les deux atomes de phosphore laissait prévoir la formation de complexes chélates où une coordination *trans* serait impossible. Des études cristallographiques réalisées pour trois complexes paramagnétiques du type [NiX_2·**1**] (X = Cl, Br), montrent que cette diphosphine de grande taille, où les atomes de phosphore sont séparés par 10 liaisons, peut effectivement former des complexes chélates. Dans l'un des complexes, l'atome de nickel est tétraédrique, l'angle de chélation étant proche de 119°. Dans les deux autres, la stéréochimie du nickel s'éloigne d'une géométrie tétraédrique idéale, sans toutefois pouvoir atteindre une géométrie *plan-carré*. Dans ces cas, l'angle de chélation est légèrement

inférieur à 160°, confirmant ainsi nos prévisions. Une telle stéréochimie, entre *plan-carré* et tétraédrique, est très rare pour des complexes du type [NiX_2P_2]. En présence de méthylaluminoxane (MAO), [$NiCl_2$·**1**] catalyse l'oligomérisation de l'éthylène, produisant des oligomères C_4-C_{12} avec une activité comparable à celle du complexe [$NiCl_2${1,2-bis-(diphénylphosphino)éthane}]. Ce comportement tranche avec celui d'autres grandes diphosphines, qui en présence de nickel conduisent à des activités nettement plus faibles.

Introduction

Calix[4]arenes locked in the cone conformation are remarkable building blocks for the preparation of multifunctional ligands.[1-5] They are frequently used as preorganising platforms allowing control of the orientation of podands anchored to one of the rims and hence for imposing a particular coordination geometry upon a complexed metal ion.[6,7] Depending upon their nature, length and flexibility, convergent binding sites tethered at the same rim may not only result in high complexation selectivities but also produce metal complexes with unconventional catalytic properties.[8-18] In a recent paper, we reported the coordination chemistry of the diphosphane **1** and have shown that this conical calixarene,[19] as well as some derivatives,[20,21] forms square planar Pt^{II} chelate complexes (**A**) exclusively in the *cis* configuration in which the P-M vectors are oriented away from the calixarene axis, thus positioning the metal outside the conical domain defined by the macrocycle. The ligand bite angle in *cis*-[$PtCl_2$·**1**], as revealed by an X-ray study, is 103.4(1)°. In order to further substantiate the directional properties of this diphosphane, we have now investigated its coordination behaviour towards $NiCl_2$ and $NiBr_2$ units, two versatile fragments known to form either tetrahedral or square planar [NiX_2(phosphane)$_2$] metal complexes.



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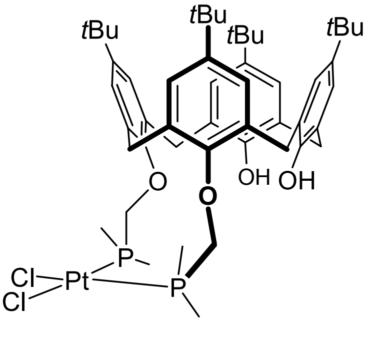


A

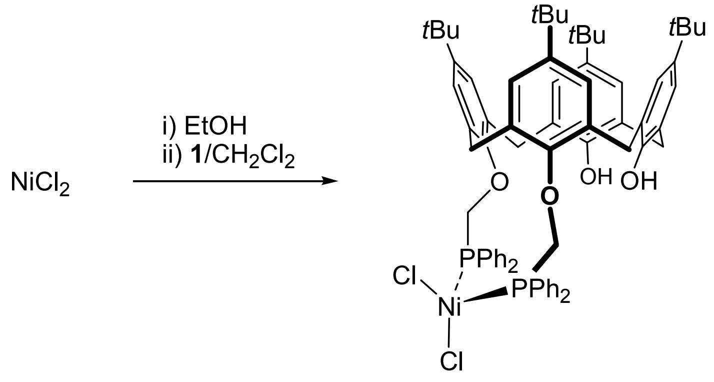
The present study describes the syntheses and structures of three paramagnetic nickel(II) complexes based on **1** and illustrates that the ligand bite angle may undergo major variation, hence enabling the metal centre to approach closer to the calixarene core.

Results and discussion

Synthesis

From our previous study it appears that despite its considerable length, diphosphane **1** is sufficiently preorganised to readily form chelate complexes with the $PtCl_2$ moiety.[19] Complexation of this fragment results in formation of a compound in which the platinum atom is oriented outwards from the cone defined by the calixarene. The same complexation behaviour towards $PtCl_2$ was observed when using analogues of **1** in which the phenol rings bear substituents.[19,21] Inverting the orientation of the P lone pairs is a challenging goal that would lead to complexes where the metal is brought closer to the calixarene axis, thus favouring interactions between the coordination centre and the bulky calixarene core. In order to study whether **1** gives access to such structures, we decided to investigate the coordination properties of **1** towards the nickel(II) centre which has a greater stereoflexibility than platinum(II).

The preparation of complex **2** required a two-step procedure consisting of (*i*) dissolution of anhydrous $NiCl_2$ in small amounts of EtOH to form an unidentified species which, unlike $NiCl_2$, is soluble in CH_2Cl_2 and (*ii*) treatment of the thus formed species with a solution of **1** in CH_2Cl_2 (Equation 1). A direct synthesis in CH_2Cl_2 was impossible due to the insolubility of $NiCl_2$ in this solvent, while attempted synthesis in pure EtOH did not result in phosphane coordination. We found that the best $EtOH/CH_2Cl_2$ ratio was ca. 1:10.



(1)

2

The dark blue complex **2** is paramagnetic and was characterised by elemental analysis and an X-ray diffraction study. Its molecular structure is shown in Figure 1. The shape of the calixarene core deviates only slightly from an ideal cone. Thus, the "centroid-centroid" separations between the distal phenol units are 6.45 and 6.93 Å, respectively, while the dihedral angles between the calixarene reference plane [defined as the mean plane of the bridging C atoms, here C(12), C(23), C(34), C(45)] and those of the four phenol rings are 115° (C2), 103° (C18), 134° (C29) and 124° (C40). Hydrogen bonds involving the hydroxy groups and the neighbouring phenolic oxygen atoms may contribute to this structure, as indicated by the rather short O(1)···O(3) [2.78(2) Å], O(2)···O(4) [2.87(2) Å] and O(3)···O(4) [2.67(2) Å] separations (cf. O(1)···O(2) [3.46(2) Å]). The compound crystallises with two dichloromethane molecules, one of them lying inside the calixarene basket. The shortest contacts of the latter with the aromatic walls are between H(71b) and C(27) (2.83 Å), and H(71b) and C(28) (2.84 Å). Note, considerably shorter contacts have been found in other calixarenes with CH_2Cl_2 guests.[22] The Ni atom is slightly bent towards the exterior of the cavity and its coordination geometry may be regarded as being between square planar and tetrahedral. By considering the PNiP and ClNiCl angles of 158.45(3)° and 158.29(4)°, one gets the impression that the ligand is attempting unsuccessfully to behave as a *trans* spanning ligand. Clearly, complexation results in a strained chelate ring, as shown by the C(1)P(1)Ni and C(46)P(2)Ni angles of 109.9(1)° and 108.1(1)°, respectively, which are about 10° smaller than the other CPNi angles. It should be remembered here that, as shown in previous studies, calix[4]arenes having at least two proximal -OCH_2PPh_2 units display a marked propensity to form *cis*-chelated structures, no *trans* complexes having been reported to date. The NiP bond lengths [2.220(1), 2.247(1) Å] lie in the range found for complexes of the general formula *trans*-$[NiCl_2(PPh_2R)_2]$.[23-25]

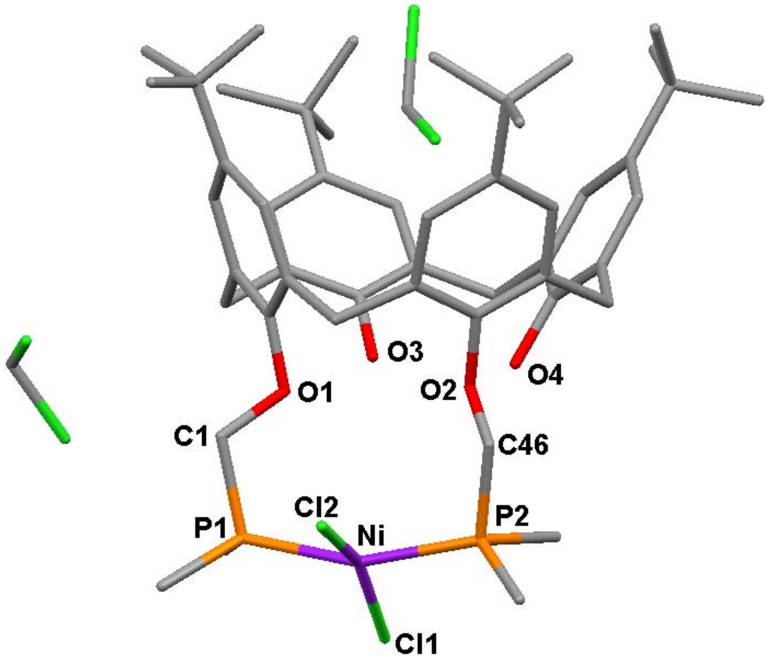
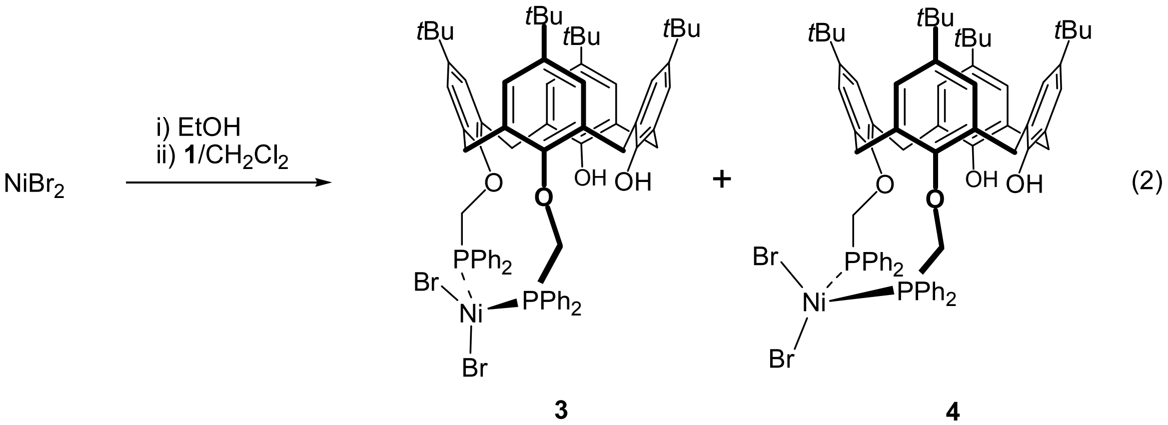


Figure 1. Molecular structure of the blue complex [$NiCl_2$·**1**]·$2CH_2Cl_2$ (**2**·$2CH_2Cl_2$); only the C_{ipso} atoms of the P-phenyl rings are shown.

Complexes **3** and **4** were obtained as a binary mixture, but could be separated mechanically after crystallisation. They were prepared similarly to the method outlined above for **2**, but starting from anhydrous $NiBr_2$ (Equation 2). Crystallisation from dichloromethane/heptane afforded a mixture of crystals of turquoise **3** and red-brown **4**.



3 **4** (2)

Obtaining this crystal mixture is easily reproducible. It appears likely that both compounds exist in equilibrium in solution, since dissolving crystals of either of them afforded the same green solution (toluene or CH_2Cl_2). The two molecular structures were determined by single-crystal X-ray diffraction studies (Figure 2 and 3). Again, both calixarenes adopt the shape of a cone having a "circular" cross section and both cavities host a dichloromethane molecule. As found in **2**, hydrogen bonds involving the hydroxy groups appear to stabilise the whole calixarene geometry (Table 1). The coordination geometry of **3** is close to that found in **2**, as can be seen from the PNiP and BrNiBr angles of 158.58(3)° and 152.19(2)°, respectively. In contrast, **4** has a conventional tetrahedral stereochemistry with considerably smaller PNiP [118.6(3)°] and BrNiBr [138.55(5)°] angles. Incidentally, the metallomacrocyclic unit of **4** is less strained than those of **2** and **3**. For example, the values of the NiPC$_\alpha$ angles in this unit are 119.0(1)° and 117.6(1)°. We note that in all three complexes, the Ni atom is orientated away from the calixarene axis. In each structure, a halogen atom approaches the axial H(12) atom but weak interactions with this methylene H are likely to occur in **2** and **3** [H$_{axial}$(12)···X distances (Å): 2.77, 2.84 and 3.00, respectively, for **2**, **3** and **4**]. These weak interactions could explain why the Ni-X(2) bonds of **2** and **3** are slightly but significantly longer than the corresponding Ni-X(1) bonds. Involvement of ArCH$_{axial}$ hydrogen atoms in weak bonding have recently been found in other calixarenes, in particular in some agostic CH···M interactions.[21] Finally, it is noteworthy that there is no indication in the syntheses outlined above of oligomer formation, illustrating the high degree of preorganisation of calixarene **1**.

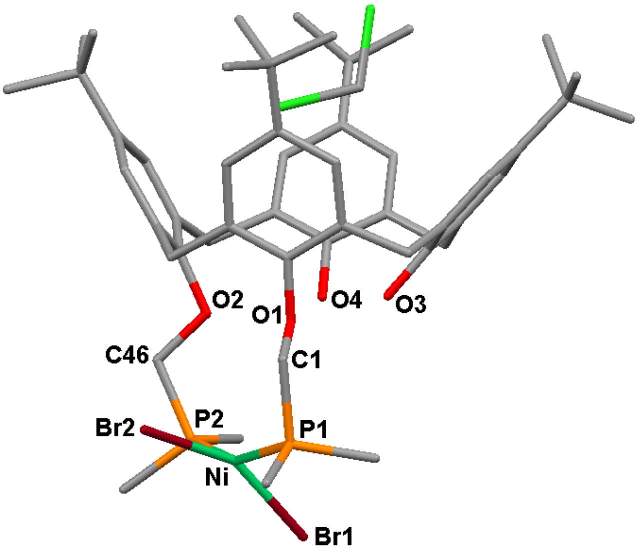


Figure 2. Molecular structure of the turquoise complex [NiBr$_2$·**1**]·2CH$_2$Cl$_2$ (**3**·2CH$_2$Cl$_2$); for clarity, only the C$_{ipso}$ atoms of the P-phenyl rings are shown.

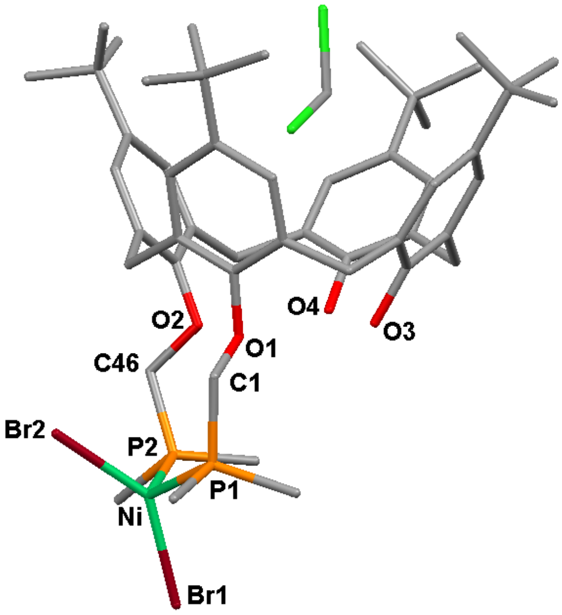


Figure 3. Molecular structure of the red brown complex [NiBr$_2$·**1**]·1.75CH$_2$Cl$_2$ (**4**·1.75CH$_2$Cl$_2$); for clarity, only the C$_{ipso}$ atoms of the P-phenyl rings are shown.

Table 1. Relevant structural parameters for **2**, **3** and **4** in the solid state

Distances (Å)	**2**	**3**	**4**
O1···O2	3.46(2)	3.47(2)	3.30(2)
O1···O3	2.78(2)	2.78(2)	2.74(2)
O1···O4	3.96(2)	3.98(2)	4.11(2)
O2···O3	3.96(2)	3.98(2)	4.11(2)
O2···O4	2.87(2)	2.89(2)	3.05(2)
O3···O4	2.67(2)	2.68(2)	2.63(2)
Ni-P1	2.247(1)	2.235(1)	2.290(9)
Ni-P2	2.220(1)	2.215(1)	2.303(9)
Ni-X1	2.150(2)	2.286(1)	2.320(6)
Ni-X2	2.168(2)	2.308(1)	2.338(6)
Angles (°)			
PNiP	158.45(3)	158.58(3)	118.6(3)
XNiX	158.29(4)	152.19(2)	138.55(5)
Dihedral angles (°) between the phenol rings and the calixarene reference plane			
(C2)	115(1)	115(1)	114(1)
(C18)	103(1)	104(1)	110(1)
(C29)	134(1)	136(1)	122(1)
(C40)	124(1)	124(1)	133(1)

Ethylene oligomerisation

It is well known that [$NiCl_2$(phosphane)$_2$] complexes constitute good precatalysts for the oligomerisation or polymerisation of olefins, the outcome of the reaction being strongly dependent on the nature of the phosphane.[26,27] Thus for example, [$NiCl_2(PCy_3)_2$] activated with $AlEt_2Cl$ becomes a highly selective ethylene dimerisation catalyst.[28] A typical activity for this complex is 1600 mol(C_2H_4)·mol(Ni)$^{-1}$·h^{-1}.[29] Other complexes, for instance [$NiBr_2\{Ar_2PN(Me)PAr_2\}$] (Ar = *o*-*i*Pr$C_6H_4$), display a high ethylene polymerisation activity [with activities as high as 79000 mol(C_2H_4)·mol(Ni)$^{-1}$·h^{-1}] producing high molecular weight polymers.[30] Recent work on [$NiCl_2$(chelate)] complexes has clearly underlined that a subtle combination of backbone rigidity and partial steric protection of the nickel centre is the determining factor for product distribution control.[31,32] It is also worth mentioning that to date, long chain diphosphanes having a backbone containing more than six carbon atoms have not been studied in olefin oligomerisation/polymerisation systems.[27,33] Reports dealing with generic calix[4]arenes that were employed in olefin polymerisation have appeared in the literature, but these remain scarce.[34-37]

In view of the fact that ligand **1** possesses a flexible bite angle, we decided to assess the role of complex **2** in ethylene oligomerisation. The runs were performed in toluene ([catalyst] = 0.3 mmol/dm^3) using methylaluminoxane (MAO) (1500 equiv.) as the activator. Operating under an ethylene pressure of 10 bar and stopping the reaction after 1 h, produced C_4 to C_{12} oligomers. The observed activity was 3100 mol(C_2H_4)·mol(Ni)$^{-1}$·h^{-1}. The product distribution is typically of the Schulz-Flory type, with α about 0.2 (Table 2).

Table 2. Ethylene oligomerisation with **2** (conditions: complex **2** (6 μmol), MAO (0.500 g), toluene (20 mL), initial temperature 25 °C)

P(C_2H_4) (bar)	α	TOF (mol C_2H_4)/(mol [Ni]·h)	Activity g C_2H_4/(mmol [Ni]·h·bar)	Olefin distribution (wt.-%)					
				C_4	C_6	C_8	C_{10}	C_{12}	C_{14}
10	0.18	3100	8.7	73.9	19.9	4.8	1.1	0.3	/
30	0.22	9800	9.1	68.4	22.6	6.6	1.8	0.5	0.1

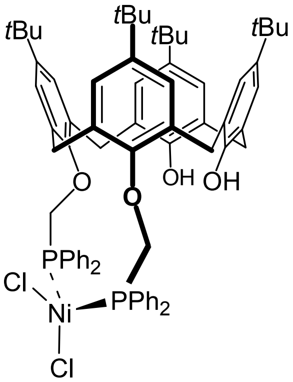
Applying a pressure of 30 bar increased the activity up to 9800 mol(C_2H_4)·mol(Ni)$^{-1}$·h^{-1} without modifying the product distribution. Interestingly, no catalyst deactivation was observed during these 1 h experiments. As shown by the study outlined above, diphosphane **1** is able to undergo large bite angle variations but this has only little impact on the catalyst activity. For comparison, in terms of activity and selectivity, the catalyst performance compares with that of [$NiCl_2(Ph_2PCH_2PPh_2)$], a complex in which the chelating unit is much more strained than that in **2**.[38] The structural studies revealed that, whatever the coordination geometry of nickel complexes containing **1**, the bulky calixarene core is remote from the nickel centre, resulting in a rather un-crowded metal environment and hence facilitating reductive elimination steps.

Conclusion

In this study we have shown that in the presence of NiX_2 moieties the large diphosphane **1** straightforwardly forms chelate complexes, thus confirming the good preorganisation of the ligand. While previous studies have shown that **1** and its congeners act exclusively as *cis*-chelators towards the $PtCl_2$ moiety, we have discovered that **1** is also able to adapt to various tetrahedral coordination geometries, some of them being extremely distorted. Thus, **1** gives access to bite angles lying in the range 103.4°-158.6°. The fact that to date no complex could be synthesised in which **1** behaves as a genuine *trans* chelator obviously arises from the rigidity of the spacer that links the P^{III} atoms as well as the shortness of the two phosphorus arms. The present work further demonstrates that ligand **1** is able to bring the metal centre closer to the calixarene axis than was previously observed in Pt^{II} complexes, although the PM vectors remain oriented outwards. Activation of **2** with MAO afforded a good ethylene oligomerisation catalyst resulting selectively in C_4-C_{12} oligomers. The formation of short oligomers suggests that during catalysis the nickel environment is slightly encumbered hence favouring reductive elimination over chain propagation. The formation of polymers could possibly be forced by orientating the PM vectors towards the calixarene axis so as to ensure partial protection of the metal. Further studies are aimed at exploiting the bite angle flexibility of diphosphane **1** in catalytic reactions.

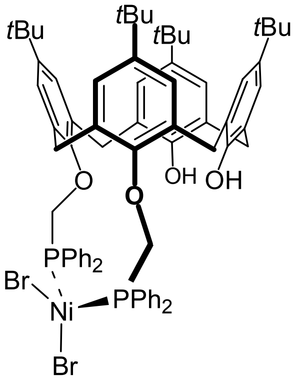
Experimental section

General Conditions: Solvents were dried with suitable reagents and freshly distilled under dry nitrogen before use. All reactions were carried out using modified Schlenk techniques under a dry nitrogen atmosphere. Elemental analyses were performed by the Service de Microanalyse, Centre de Recherche Chimie, Université Louis Pasteur, Strasbourg. 5,11,17,23-Tetra-*tert*-butyl-25,26-bis(diphenylphosphanylmethoxy)-27,28-dihydroxycalix[4]arene (**1**) was prepared according to the previously reported method.[19] MAO 10 wt.-% (Aldrich) was used as a white powder which was obtained after evaporation of the solvent (60 °C, 3 h). This treatment reduces the amount of residual trimethylaluminium to ca. 3%.



Dichloro-{5,11,17,23-tetra-tert-butyl-25,26-bis(diphenylphosphanylmethoxy)-27,28-dihydroxycalix[4]arene}nickel(II) (2).

Anhydrous $NiCl_2$ (0.019 g, 0.15 mmol) was dissolved in hot ethanol (0.5 mL) whereupon a solution of **1** (0.153 g, 0.15 mmol) in CH_2Cl_2 (5 mL) was added. During addition the pale yellow solution turned deep blue. After 0.25 h, the solvent was removed in vacuo. The residue was treated with a small volume of pentane (5 mL) and the resultant suspension filtered through a glass frit. Cooling to -30 °C precipitated a dark blue powder, which was dried in vacuo. Yield: 0.070 g, 40%. $C_{70}H_{78}Cl_2NiO_4P_2$ (M_r = 1174.93): calcd. C 71.56, H 6.69; found C 71.66, H 6.90. Single-crystals suitable for X-ray diffraction were obtained by slow diffusion at room temperature of hexane into a CH_2Cl_2 solution of the complex.



Dibromo-{5,11,17,23-tetra-*tert*-butyl-25,26-bis(diphenylphosphanylmethoxy)-27,28-dihydroxycalix[4]arene}nickel(II), Isomers 3 and 4.

Anhydrous $NiBr_2$ (0.041 g, 0.19 mmol) was dissolved in hot ethanol (0.5 mL) resulting in a pale orange solution. A solution of **1** (0.200 g, 0.19 mmol) in CH_2Cl_2 (5 mL) was then added and the mixture turned green. After 0.25 h, the solution was evaporated to dryness. The residue was redissolved in CH_2Cl_2 (ca. 1 mL), whereupon pentane was added to precipitate a pale green powder, which was recovered by filtration. Yield: 0.197 g, 82%. The green powder was then dissolved in CH_2Cl_2. Slow diffusion of heptane into the resultant intense green solution afforded crystals of **3** (turquoise colour) and **4** (red brown), which were separated mechanically. Elemental analyses were carried out on both isomers after drying in high vacuum: $C_{70}H_{78}Br_2NiO_4P_2$ (M_r = 1263.83): calcd. C 66.53, H 6.22; found for **3**: C 66.22; H 5.75; found for **4**: C 66.50; H 6.42.

Crystal Structure Determination of 2·2CH_2Cl_2.

Single crystals of **2** suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of the complex. Data were collected with a Nonius KappaCCD diffractometer (graphite-monochromated Mo-K_α radiation, λ= 0.71073 Å). The structure was solved by direct methods using the SHELXS-97 program and refined by full-matrix least-squares techniques (SHELXL-97) on F^2.[39] Hydrogen atoms were located using the geometric method. The crystal data and structural refinement details are listed in Table 3. The compound was found to crystallise with two molecules of dichloromethane, one of them lying inside the cavity. CCDC-234357 contains the supplementary crystallographic data for this structure.

Table 3. Crystal and structure refinement data for **2**, **3** and **4**

Formula	$C_{70}H_{78}Cl_2NiO_4P_2$ $\cdot 2CH_2Cl_2$	$C_{70}H_{78}Br_2NiO_4P_2 \cdot 2CH_2Cl_2$	$C_{70}H_{78}Br_2NiO_4P_2$ $\cdot 1.75CH_2Cl_2$
Molecular mass	1344.73	1433.65	1387.97
Crystal system	triclinic	triclinic	monoclinic
Space group	P_1	P_1	$P2_1/n$
a (Å)	12.7590(10)	12.736(5)	18.868(2)
b (Å)	16.7150(10)	16.895(5)	14.1060(10)
c (Å)	18.4130(10)	18.441(5)	29.853(3)
α(°)	110.11(5)	110.599(5)	90
β(°)	104.31(5)	104.026(5)	105.62(5)
γ(°)	100.36(5)	100.257(5)	90
V (Å^3)	3418(2)	3448.8(19)	7651.8(12)
Z	2	2	4
D(calcd.) (g·cm^{-3})	1.307	1.380	1.205
μ(Mo-K_α) (mm^{-1})	0.612	1.688	1.470
F(000)	1412	1484	2882
Crystal size (mm)	0.08 × 0.10 × 0.13	0.05 × 0.07 × 0.08	0.06 × 0.07 × 0.08
Temperature (K)	173	173	173
Radiation, λ(Mo-K_α) (Å)	0.71069	0.71069	0.71069
$\theta_{min.,max.}$ (°)	1.3, 30.0	1.8, 30.0	1.0, 30.0
Data set (h; k; l)	–17/17; –23/22; 0/25	–17/17; –23/23; –25/24	–21/26; –19/19; –34/42
Total, unique data, R(int.)	19905, 19905, 0.035	41543, 20069, 0.050	36106, 20421, 0.073
Obsd. data with $I > 2.0\sigma(I)$	14740	15013	10790
$N_{reflections}$, $N_{parameters}$	19905, 766	20069, 766	20421, 748
$R1$, $wR2$, S	0.0712, 0.1863, 1.05	0.0663, 0.1496, 1.03	0.0989, 0.3089, 1.02
Min., max. residual electron density (e·Å^{-3})	–1.07, 1.17	–1.13, 1.29	–1.25, 1.56

Crystal Structure Determination of $3 \cdot 2CH_2Cl_2$ and $4 \cdot 1.75CH_2Cl_2$.

Single crystals of **3** and **4** were obtained simultaneously by slow diffusion of heptane into a solution of [$NiBr_2 \cdot$**1**]. Data collection and structure solution were carried out as above for **2** (Table 3). The poorer quality of the structure of **4** is due to disordered solvent molecules, whether they lie inside or outside the cavity. CCDC-234358 (for **3**) and CCDC-234359 (for **4**).

Oligomerisation of Ethylene.

The catalytic runs were carried out in a 100 mL glass-lined stainless steel autoclave containing a magnetic stirring bar. In a typical run, a solution of complex **2** (0.007 g, 6 µmol) in toluene (15 mL) was introduced under nitrogen into the autoclave whereupon a solution of

MAO (0.500 g) in toluene (5 mL) was added. After stirring for ca. 1 min the autoclave was pressurised with ethylene and the pressure (10 or 30 bar) was maintained at a constant value. During the runs described in this work, the temperature raised from 25 °C to 37 °C when operating at 10 bar and up to 42 °C under 30 bar. After 1 h, the autoclave was cooled to 7 °C and then depressurised over a period of 1 h. Heptane (200 µL), which serves as internal reference for the GC analysis, was then added to the reaction mixture. The liquid phase was analysed with a VARIAN 3900 gas chromatograph equipped with a WCOT fused silica column (25 m, 0.32 mm inside diameter, 0.25 mm film thickness).

References

[1] V. Böhmer, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 713 -745.

[2] C. D. Gutsche, *Calixarenes Revisited*, Monographs in Supramolecular Chemistry (Ed.: J. F. Stoddart), The Royal Society of Chemistry, Cambridge, **1998**.

[3] P. J. A. Kenis, O. F. J. Noordman, H. Schönherr, E. G. Kerver, B. H. M. Snellink-Ruël, G. J. van Hummel, S. Harkema, C. van der Vorst, J. Hare, S. J. Picken, J. F. J. Engbersen, N. F. van Hulst, G. J. Vancso, D. N. Reinhoudt, *Chem. Eur. J.* **1998**, *4*, 1225 -1234.

[4] *Calixarenes in Action* (Ed.: L. Mandolini, R. Ungaro), Imperial College Press, **2000**.

[5] S. Steyer, C. Jeunesse, D. Armspach, D. Matt, J. Harrowfield, in *Calixarene 2001* (Eds.: Z. Asfari, V. Böhmer, J. Harrowfield, J. Vicens), Kluwer, Dordrecht, pp. 513-535.

[6] C. Wieser, C. Dieleman, D. Matt, *Coord. Chem. Rev.* **1997**, *165*, 93 -161.

[7] P. D. Harvey, *Coord. Chem. Rev.* **2002**, *233 -234*, 289-309.

[8] C. Wieser, D. Matt, J. Fischer, A. Harriman, *J. Chem. Soc., Dalton Trans.* **1997**, 2391 -2402.

[9] R. Paciello, L. Siggel, M. Röper, *Angew. Chem. Int. Ed.* **1999**, *38*, 1920 -1923.

[10] C. J. Cobley, D. D. Ellis, A. G. Orpen, P. G. Pringle, *J. Chem. Soc., Dalton Trans.* **2000**, 1109 -1112.

[11] C. J. Cobley, D. D. Ellis, A. G. Orpen, P. G. Pringle, *J. Chem. Soc., Dalton Trans.* **2000**, 1101 -1107.

[12] F. J. Parlevliet, C. Kiener, J. Fraanje, K. Goubitz, M. Lutz, A. L. Spek, P. C. J. Kamer, P. W. N. M. van Leewen, *J. Chem. Soc., Dalton Trans.* **2000**, 1113 -1122.

[13] C. Jeunesse, C. Dieleman, S. Steyer, D. Matt, *J. Chem. Soc., Dalton Trans.* **2001**, 881 -892.

[14] X. Fang, B. L. Scott, J. G. Watkin, C. A. G. Carter, G. J. Kubas, *Inorg. Chim. Acta* **2001**, *317*, 276 -281.

[15] C. Kunze, D. Selent, I. Neda, M. Freytag, P. G. Jones, R. Schmutzler, W. Baumann, A. Börner, *Z. Anor. Allg. Chem.* **2002**, *628*, 779 -787.

[16] S. Steyer, C. Jeunesse, D. Matt, R. Welter, M. Wesolek, *Dalton Trans.* **2002**, 4264 -4274.

[17] F. Plourde, K. Gilbert, J. Gagnon, P. D. Harvey, *Organometallics* **2003**, *22*, 2862 -2875.

[18] M. Frank, G. Maas, J. Schatz, *Eur. J. Org. Chem.* **2004**, 607 -613.

[19] C. B. Dieleman, C. Marsol, D. Matt, N. Kyritsakas, A. Harriman, J.-P. Kintzinger, *J. Chem. Soc., Dalton Trans.* **1999**, 4139 -4148.

[20] C. Dieleman, S. Steyer, C. Jeunesse, D. Matt, J. *Chem. Soc., Dalton Trans.* **2001**, 2508 - 2517.

[21] C. Dieleman, C. Jeunesse, D. Matt, Z. Kristallog. *NCS* **2001**, *216*, 435 -438.

[22] C. Dieleman, D. Matt, P. G. Jones, H. Thönnessen, *Acta Crystallogr.*, *Sect. C* **2003**, *59*, o247 -o249.

[23] P. Braunstein, D. Matt, D. Nobel, F. Balegroune, S.-E. Bouaoud, D. Grandjean, J. Fischer, *J. Chem. Soc., Dalton Trans.* **1988**, 353 -361.

[24] J. Sletten, J. A. Kovacs, *J. Crystallogr. Spectrosc. Res.* **1993**, *23*, 239.

[25] S. J. Coles, P. Faulds, M. B. Hursthouse, D. G. Kelly, G. C. Ranger, N. M. Walker, *J. Chem. Res.* **1999**, *418*, 1811.

[26] S. Muthukumaru Pillai, M. Ravindranathan, S. Sivaram, *Chem. Rev.* **1986**, *86*, 353 -399.

[27] V. C. Gibson, S. K. Spitzmesser, *Chem. Rev.* **2003**, *103*, 283 -315.

[28] D. Commereuc, Y. Chauvin, G. Léger, J. Gaillard, *Rev. Inst. Fr. Pet.* **1982**, *37*, 639 - 649.

[29] F. Speiser, P. Braunstein, L. Saussine, *Organometallics* **2004**, *23*, 2625 -2632.

[30] N. A. Cooley, S. M. Green, D. F. Wass, K. Heslop, A. G. Orpen, P. G. Pringle, *Organometallics* **2001**, *20*, 4769 -4771.

[31] M. Sauthier, F. Leca, R. F. de Souza, K. Bernardo-Gusmão, L. F. Trevisan Queiroz, L. Toupet, R. Réau, *New J. Chem.* **2002**, 630 -635.

[32] C. Bianchini, L. Gonsalvi, W. Oberhauser, D. Sémeril, P. Brüggeller, R. Gutman, *Dalton Trans.* **2003**, 3869 -3875.

[33] P.-G. Lassahn, V. Lozan, B. Wu, A. S. Weller, C. Janiak, *Dalton Trans.* **2003**, 4437 - 4450.

[34] R. A. Kemp, D. S. Brown, M. Lattman, J. Li, *J. Mol. Cat. A: Chem.* **1999**, *149*, 125 - 133.

[35] V. C. Gibson, C. Redshaw, M. R. J. Elsegood*, J. Chem. Soc., Dalton Trans.* **2001**, 767 - 769.

[36] C. Capacchione, P. Neri, A. Proto, *Inorg. Chem. Commun.* **2003**, *6*, 339 -342.

[37] C. Huang, J. Ahn, S. Kwon, J. Kim, J. Lee, Y. Han, H. Kim, *Applied Catal. A* **2004**, *258*, 173 -181.

[38] C. Bianchini, unpublished results.

[39] G. M. Sheldrick, SHELXL-97, *Program for Crystal Structure Refinement*, University of Göttingen: Göttingen, Germany, **1997**.

Chapter 7

Phosphorus-phosphorus coupling in a diphosphine with a ten bond P•••P separation.

Abstract

The ^{31}P NMR spectrum of the large, unsymmetrical diphosphine in which the phosphorus atoms are separated by ten bonds, reveals a J(PP') coupling constant of 8.0 Hz; in the solid state, the distance between the two P atoms is 5.333(1) Å.

Résumé

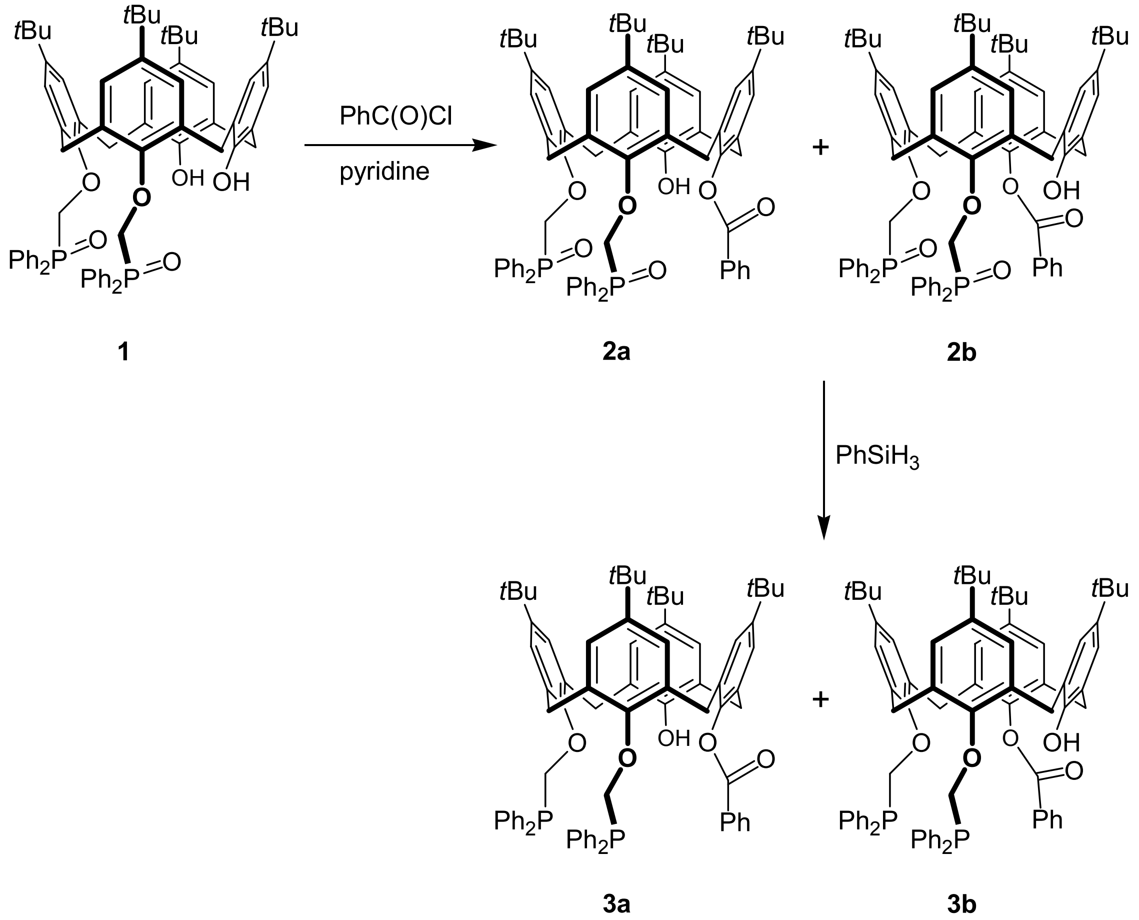
Dans ce chapitre, nous décrivons la synthèse et la structure cristallographique d'une variante asymétrique de la diphosphine décrite au chapitre 6, le 5,11,17,23-tétra-*tert*-butyl-25,26-bis(diphénylphosphinométhoxy)-27-benzoyl-28-hydroxycalix[4]arène. Une propriété remarquable de cette diphosphine est l'existence d'une constante de couplage J(PP') de 8.0 Hz. Il s'agit de la diphosphine la plus longue pour laquelle un tel couplage a été observé. Celui-ci résulte vraisemblablement d'une interaction à travers l'espace.

Introduction

Long range coupling constants, which conventionally are related to systems where an interacting pair of nuclei is separated by more than four bonds, are often used as source of information concerning a molecular structure.[1,2] Despite continuous interest in P(III)-containing ligands in organometallic chemistry and catalysis for over 50 years,[3,4] relatively few data are available for $J(\mathrm{P^{III}P^{III}})$ long range coupling constants, even though many diphosphines where the phosphorus centres occupy remote sites on large molecular frameworks are known.[5,6] Thus, for example, the question whether rigidification of a backbone allows for very remote phosphorus-phosphorus coupling remains open. One reason for this lack of information arises from the fact that the observation of long range couplings requires the phosphorus atoms to be anisochronous, in other words, to occupy inequivalent molecular sites. While both ${}^{8}J$(PP')[7,8] and ${}^{9}J$(PP')[9] coupling constants (27.5 Hz and 10.3 Hz, respectively) were recently reported for new diphosphanes, the lack of accompanying crystal structure determinations prevented any assessment of possible correlations of the coupling constant values with particular structural features of the molecule, such as, for example, a constrained spatial proximity which would favor direct "through space" coupling. The issue is a focus of the present discussion.

Results and discussion

As part of an ongoing programme aimed at the synthesis of calixarene P(III)-podands,[10,11] we have prepared a new, inherently chiral calix[4]arene, **L**, in which two proximal phenol rings are substituted by $–CH_2PPh_2$ ligands, the two P atoms being separated by ten bonds. The ${}^{1}H$, ${}^{31}P$ and ${}^{13}C$ spectra all reveal long range couplings involving both phosphorus atoms. Diphosphine **L** was obtained from **1** according to the two-step synthesis shown in Scheme 1. Mono-acylation of **1** with ClC(O)Ph in excess afforded **2** in 68% yield as a racemic mixture of **2a** and **2b**, which differ only by the position of the benzoyl substituent on the calixarene skeleton. Subsequent reduction with $PhSiH_3$/toluene gave diphosphine **L** (racemic mixture of **3a** and **3b**) in 87% yield.



The solid state structure of **L** was determined from X-ray diffraction data (Fig. 1). The space group is such that both enantiomeric forms of **L** are present in the unit cell. The calixarene skeleton adopts an elliptically distorted ("pinched") cone conformation in which the acylated phenol ring and its distal counterpart (*i.e.* the ring bearing P(1)) are almost parallel. The centroid separations between opposed rings of the macrocyclic unit are respectively 5.62(1) Å and 7.48(1) Å. The O(4)•••O(5) and O(4)•••O(2) distances, respectively 3.070(1) and 2.909(2) Å, indicate that the hydroxy group is hydrogen-bonded to one of the neighbouring phenoxy oxygen atoms. In fact, the position of H(4) could be inferred from the X-ray data, and it was found to be at a distance of 2.26(1) Å from O(2). The phosphorus lone pairs are not directed towards the centre of the ligand cavity formed by the pendent substituents, though P(1) is closer to an appropriate orientation than is P(2), the separation between the two P atoms being 5.333(1) Å, with an approximate alignment of the two P-(lone pair) dipoles. Another factor possibly influencing the solid state orientation of P(2) is a π–π interaction between the phenacyl ring and the C(60)-phenyl group, these rings being nearly parallel and separated by only 3.7 Å.

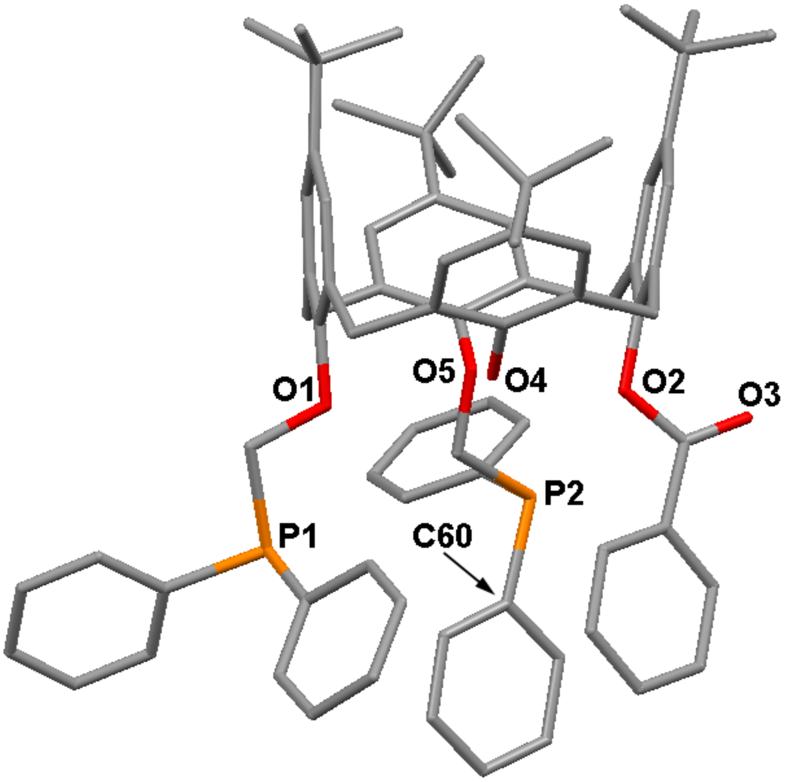
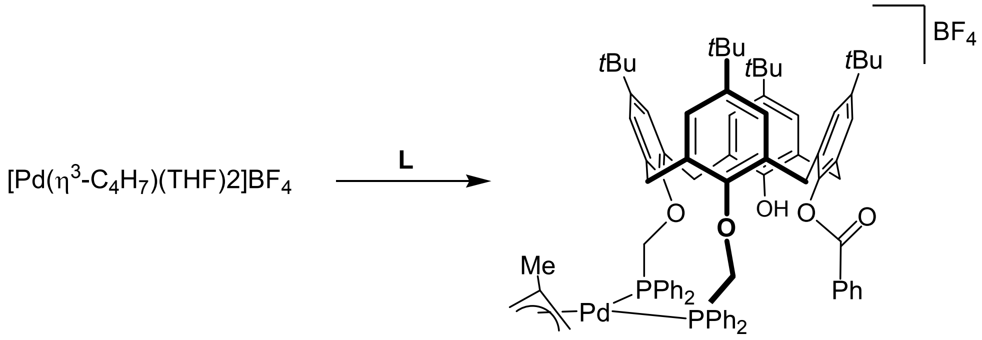


Figure 1. Solid state structure of **L.**

The $^{31}P\{^{1}H\}$ NMR spectrum (121.5 Hz, $CDCl_3$, 20 °C) of **L** displays two doublets, centered at –20.1 and –22.2 ppm, respectively, with a ten-bond P–P coupling of 8.0 Hz. The existence of coupling between the two P atoms was demonstrated by measuring the spectrum in $CDCl_3$ at different fields and by carrying out a 2D Homonuclear ^{31}P COSY experiment (Figure 2). When the experiments were repeated in CD_3OD, the magnitude of the coupling did not change. While this coupling, in principle, might arise from either "through-space" or "through-bond" interactions, a pure "through-bond" ^{10}J(PP') coupling in a non-conjugated system such as **L** is expected to be nearly zero. Even in a highly conjugated naphthyl-derived diphosphine, a ^{9}J(PP') of barely 4.0 Hz has been reported.[12] If "through bond" interactions are negligible, significant coupling is still possible via "through space" effects involving transmission of spin-spin interactions via the lone pairs of electrons on the phosphorus atoms.[13] As pendent groups on the calixarene skeleton, the phosphine substituents are brought into relatively close proximity, though interactions involving the P centres must depend strongly on the ligand conformations and their dynamics. As revealed by a 2D ROESY experiment, the calixarene core displays high flexibility, the unsubstituted phenolic ring flipping rapidly through the calixarene annulus, while there is clearly considerable flexibility in the pendent arms. Thus, it is certainly possible for the phosphorus centres to come into close contact temporarily. The spatial proximity of the two phosphorus atoms was further demonstrated by the ease of forming cis-chelate complexes with **L**, such as e.g. **4** which was obtained quantitatively by reacting **3** with $[Pd(\eta^3\text{-}C_3H_4Me)(THF)_2]BF_4$ (THF = tetrahydrofuran). Finally, a variable temperature NMR study revealed that the *J*(PP) coupling constant increases significantly when lowering the temperature (varying from 8.0 Hz at 283K to 10.5 Hz at 183K), an observation which is consistent with a longer period of overlap of the lone pairs as a result of slower molecular dynamics.[13]



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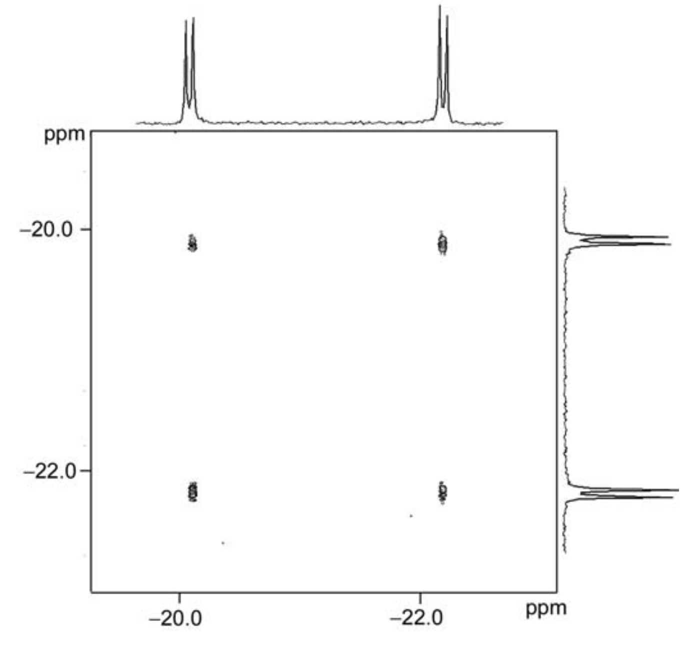
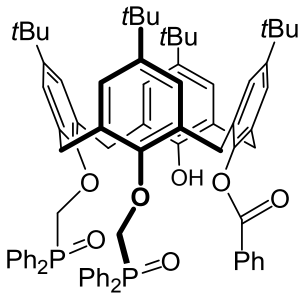


Figure 2. COSY ^{31}P-^{31}P spectrum of **L.**

In the solid state the separation between the two phosphorus atoms is well-defined. Unfortunately, solid state NMR required the use of a powdered sample, which led to the dissolvation of the crystals and detection of several species. Nevertheless, coupling between the P atoms within the resolution of the measurements (< 150 Hz) was not detectable.

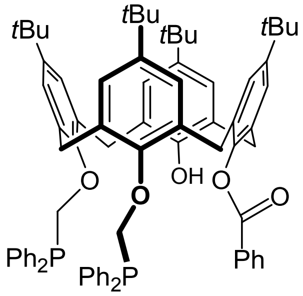
Overall the present study describes the first example of *J*(PP') coupling in a diphosphine where the phosphorus atoms are separated by ten chemical bonds. Further studies aiming at the understanding of the mechanism of such remote coupling, in particular their dependency on internal backbone dynamics are currently underway.

Experimental section



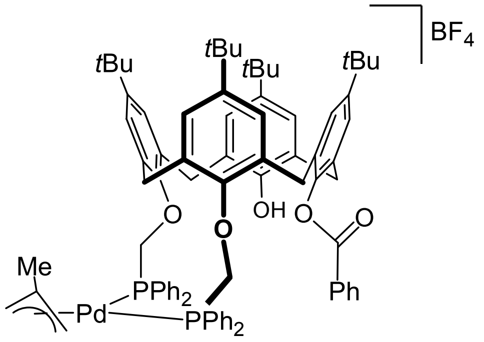
5,11,17,23-Tetra-*tert*-butyl-25,26-bis(diphenylphosphinoylmethoxy)-27(or 28)-benzoyloxy-28(or 27)-hydroxy-calix[4]arene (2).

A solution containing 5,11,17,23-tetra-*tert*-butyl-25,26-bis(diphenylphosphinoylmethoxy)-27,28-bis(hydroxy)calix[4]arene (**1**) (3.230 g, 3.00 mmol) and benzoyl chloride (0.878 g, 6.20 mmol) in pyridine (100 mL) was stirred for 15 h at room temperature. After evaporation of the solvent the solid residue was taken up in CH_2Cl_2. Addition of MeOH and partial removal under *vacuo* of CH_2Cl_2 afforded **2** as a white precipitate. Yield: 2.410 g, 68 %; mp > 240°C; IR (KBr, cm^{-1}): ν(C=O) 1726s; ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 8.47-8.44 (m, 2H, ArH), 7.95-7.85 (m, 4H, ArH), 7.60-7.10 (m, 19H, ArH), 7.07 and 7.02 (AB system, 2H, *m*-ArH, ^4J = 2.2 Hz), 6.87 and 6.66 (AB system, 2H, *m*-ArH, ^4J = 2.4 Hz), 6.54 (s br , 2H, *m*-ArH), 6.45 and 6.42 (AB system, 2H, *m*-ArH, ^4J = 2.3 Hz), 5.65 and 4.75 (ABX system with X = P, 2H, P(O)CH_2, ^2J (AB) = 14.8 Hz, ^2J (AX) = 4.1 Hz, ^2J (BX) = 0 Hz), 5.27 (s, 1H, OH), 5.22 and 4.67 (ABX system with X=P, 2H, P(O)CH_2, ^2J (AB) = 13.9 Hz, ^2J (AX) = 4.1 Hz, ^2J (BX) = 0 Hz), 4.79 and 2.91 (AB system, 2H, ArCH_2Ar, ^2J(AB) = 13.0 Hz), 4.55 and 3.23 (AB system, 2H, ArCH_2Ar, ^2J(AB) = 13.4 Hz), 4.38 and 3.19 (AB system, 2H, ArCH_2Ar, ^2J(AB) = 13.2 Hz), 4.19 and 3.19 (AB system, 2H, ArCH_2Ar, ^2J(AB) = 13.2 Hz), 1.31 and 1.23 (2s, 2×9H, $C(CH_3)_3$), 0.80 (s, 18H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 166.15 (s, C(O)), 152.26-124.97 (aryl C), 74.24 (d, P(O)CH_2, ^1J(PC) = 80.2 Hz), 70.73 (d, P(O)CH_2, ^1J(PC) = 73.4 Hz), 33.98, 33.91, 33.75 and 33.71 (4s, $C(CH_3)_3$), 33.10, 31.81 and 31.67 (3s, ArCH$_2$Ar), 33.10, 31.81 and 31.67 (3s, $C(CH_3)_3$). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): δ 25.9 (s), 23.2 (s). Found: C, 78.19; H, 6.96. Calc. for $C_{77}H_{82}O_7P_2$ (M_r = 1181.46): C, 78.28; H, 7.00%.



5,11,17,23-Tetra-*tert*-butyl-25,26-bis(diphenylphosphinomethoxy)-27(or 28)-benzoyloxy –28(or 27)-hydroxy-calix[4]arene (racemate) (L).

A mixture of 5,11,17,23-tetra-*tert*-butyl-25,26-bis(diphenylphosphinoylmethoxy)-27(28)-benzoyloxy-28(27)-hydroxy-calix[4]arene (0.300 g, 0.25 mmol) and $PhSiH_3$ (0.230 g, 2.12 mmol) in toluene (10 mL) was stirred for 7 d at 90°C. The solution was evaporated to dryness, upon which the residue was taken up in CH_2Cl_2. Addition of methanol followed by slow evaporation of CH_2Cl_2 afforded **L** as a white precipitate. Yield: 0.260 g, 87 %; mp > 240°C; IR (KBr, cm^{-1}): ν(C=O) = 1726 s; ^1H NMR (300.1 MHz, $CDCl_3$): δ 8.59-8.57 (m, 2H, ArH), 7.56-7.10 (m, 20H, ArH), 7.03-6.89 (m, 5H, ArH), 6.77-6.75 (m, 2H, ArH), 6.60-6.55 (m, 4H, ArH), 5.75 (s, 1H, OH), 5.55 and 4.90 (ABX system with X=P, 2H, PCH_2, ^2J (AB) = 12.6 Hz, ^2J (AX) = 4.0 Hz, ^2J (BX) = 0 Hz), 4.75 and 4.58 (ABX system with X=P, 2H, PCH_2, ^2J (AB) = 11.7 Hz, ^2J (AX) = 5.5 Hz, ^2J (BX) = 0 Hz), 4.58 and 3.01 (AB system, 2H, ArCH_2Ar, ^2J(AB) = 12.8 Hz), 4.29 and 3.21 (AB system, 2H, ArCH_2Ar, ^2J(AB) = 13.0 Hz), 4.18 and 3.23 (AB system, 2H, ArCH_2Ar, ^2J(AB) = 13.5 Hz), 4.14 and 3.13 (AB system, 2H, ArCH_2Ar, ^2J(AB) = 13.4 Hz), 1.32, 1.30, 0.87 and 0.81 (4s, 4x9H, $C(CH_3)_3$. $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ 166.41 (s, C=O), 152.89-124.90 (Aryl C), 78.74 (d, PCH_2, ^1J(PC) = 7.4 Hz), 75.79 (dd, PCH_2, ^1J(PC) = 11.2 Hz, J(P'C) = 3.6 Hz), 34.23, 34.04, 33.93 and 33.87 (4s, $C(CH_3)_3$), 33.21 (d, ArCH$_2$Ar, ^5J(PC) = 7.2 Hz), 32.51 (dd, ArCH$_2$Ar, ^5J(PC) = 6.8 Hz, ^5J(P'C) = 2.4 Hz), 32.24 (d, ArCH$_2$Ar, ^5J(PC) = 2.8 Hz), 31.90 (s, ArCH$_2$Ar), 31.86 and 31.78 (2s, $C(CH_3)_3$), 31.09 (broad, $C(CH_3)_3$). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$): –20.1 and –22.2 (AB system, J(PP') = 8.0 Hz). Found: C, 80.34; H, 7.10. Calc. for $C_{77}H_{82}O_5P_2$ (M_r = 1149.46): C, 80.46; H, 7.19%.



(η^3-2-Methylallyl)-(*P,P'*)-{5,11,17,23-*tetra-tert*-butyl-25,26-bis(diphenylphosphinomethoxy)-27 (or 28)-benzoyl-28 (or 27-hydroxy)-calix[4]arene}palladium(II) tetrafluoroborate (4).

To a solution of $[Pd(\eta^3\text{-}C_4H_7)Cl]_2$ (0.037 g, 0.093 mmol) in CH_2Cl_2 (10 mL) was added a solution of $AgBF_4$ (0.036 g, 0.186 mmol) in THF (1 mL). After 5 min., the solution was decanted in order to eliminate AgCl. The supernatant was filtered through Celite and added to a solution of **L** (0.214 g, 0.186 mmol) in CH_2Cl_2 (300 mL). After 1 h, the solution was concentrated to *ca.* 5 mL and addition of pentane afforded a yellow precipitate. Yield: 0.207 g, 85 %; mp > 199°C (dec.). In keeping with two possible orientations of the Me-allyl group, the ^{1}H and ^{31}P NMR spectra revealed the presence of two isomers present in a ca. 1:3 ratio. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 20.47 and 12.90 (AB system, ^2J(PP') = 37.9 Hz), 19.50 and 10.93 (AB system, ^2J(PP') = 37.8 Hz). ES mass spectrum *m/z* 1309.6 $[M-BF_4]^+$. Found: C, 65.21; H, 5.97. Calc. for $C_{81}H_{89}O_5P_2PdBF_4\cdot 1.5\ CH_2Cl_2$ (M_r = 1397.76 + 127.39): C, 64.97; H, 6.08%.

X-ray Crystal Structure Determination of 3.

Single crystals were obtained by slow diffusion of methanol into a dichloromethane solution of **3.** $C_{77}H_{82}O_5P_2\cdot 1/2CH_2Cl_2$, *M*r = 1191.83, triclinic, *P*-1, *a* = 10.637(1), *b* = 15.234(1), *c* = 21.083(1) Å, α = 99.840(1), β = 96.1300(10), γ = 90.940(1) *V* = 3344.8(4) Å^3, *Z* = 2, D_X = 1.183 mg.m^{-3}, λ(MoKα) = 0.71069Å, μ = 0.156 cm^{-1}, *F*(000) = 1270, *T* = 150 K. Diffraction data were collected on a NONIUS Kappa CCD using graphite-monochromated MoKα radiation. Crystal dimensions 0.20x0.18x0.18mm. Total reflections collected 24414 and 11996 with $I > 2\sigma(I)$. Goodness of fit on F^2 = 0.127; $R(I > 2\sigma(I))$ = 0.052, *wR*2 = 0.1777 (all data), 821 parameters; maximum/minimum residual density 0.76(6) / -0.77(6) e-Å^{-3}. The crystal structure was solved with SIR97[14] and refined with SHELXL97[15] by full matrix least-squares using anisotropic thermal displacement parameters for all non-hydrogen atoms;

hydrogen atoms were included in the riding mode. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-237221.

References

[1] R. H. Contreras and J. E. Peralta, *Prog. Nucl. Magn. Res. Spec.* **2000**, *37*, 321-425.

[2] J.-C. Hierso, A. Fihri, V. V. Ivanov, B. Hanquet, N. Pirio, B. Donnadieu, B. B. Rebière, R. Amardeil and P. Meunier, *J. Am. Chem. Soc.* **2004**, *126*, 11077-11087.

[3] T. J. Colacot, *Chem. Rev.* **2003**, *103*, 3101-3118.

[4] V. V. Grushin, *Chem. Rev.* **2004**, *104*, 1629-1662.

[5] C. A. Bessel, P. Aggarwal, A. C. Marschilok and K. J. Takeuchi, *Chem. Rev.* **2001**, *101*, 1031-1066.

[6] M. R. Eberhard, K. M. Heslop, A. G. Orpen and P. G. Pringle, *Organometallics* **2005**, *24*, 335-337.

[7] S. D. Pastor, S. P. Shum, R. K. Rodebaugh, A. D. DeBellis and F. H. Clarke, *Helv. Chim. Acta* **1993**, *76*, 900-914.

[8] S. D. Pastor, S. P. Shum, A. D. DeBellis, L. P. Burke and R. K. Rodebaugh, *Inorg. Chem.* **1996**, *35*, 949-958.

[9] Y. T. Wong, C. Yang, K.-C. Ying and G. Jia, *Organometallics* **2002**, *21*, 1782-1787.

[10] M. Lejeune, D. Sémeril, C. Jeunesse, D. Matt, F. Perruch, P. J. Lutz and L. Ricard, *Chem. Eur. J.* 2004, *10*, 5354-3360.

[11] C. Jeunesse, D. Armspach and D. Matt, *Chem. Comm.* **2005**, 5603-5614.

[12] L. Ernst, *J. C. S. Chem. Comm.* **1977**, 375-376.

[13] S. A. Reiter, S. D. Nogai, K. Karaghiosoff and H. Schmidbaur, *J. Am. Chem. Soc.* **2004**, *126*, 15833-15843.

[14] A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, SIR97: a new tool for crystal structure determination and refinement. *J. Appl. Crystallogr.* **1999**, *32*, 115-119.

[15] G. M. Sheldrick, *SHELX-97. Program for the refinement of crystal structures.* University of Göttingen, Germany, **1997**.

General Conclusion

The present thesis focuses on the synthesis of new nickel complexes based on modified diphosphine and phosphinoenolate chelators. The modifications were of three major types: electronic and steric through ligand backbone substitution, and backbone size. Catalytic properties of these complexes were investigated in ethylene oligomerisation and polymerisation.

In *Chapter 2*, the reactivity of the complex $[Ni\{Ph_2PC(R^1)=C(R^2)O\}Ph(PPh_3)]$ (R^1,R^2 = –C(Me)=NN(Ph)–), in which the *P,O* chelate is substituted by an electron-withdrawing pyrazolyl unit, has been investigated in ethylene oligomerisation. In the absence of any cocatalyst, it converts ethylene in high selectivity and activity into α-olefins. The product distribution is drastically shifted towards lower oligomers when compared to the outcome of the reaction carried out with the conventional SHOP catalyst $[Ni\{Ph_2PCH=C(Ph)O\}Ph(PPh_3)]$. Further, the electron-withdrawing strength of the pyrazol unit can be enhanced through coordination of the N(2) atom to Lewis acids such as BF_3. In ethylene-free solvents, the pyrazole derived complex was shown to slowly undergo reductive elimination to produce the stabilised phosphorus ylide 3-methyl-1-phenyl-4-(triphenylphosphoranylidene)-2-pyrazolin-5-one (**L**).

Selective N(2)-binding of this phosphorus ylide has been found in two palladium(II) complexes, $[PdCl_2(\mathbf{L})_2]$ and $[Pd(o\text{-}C_6H_4CH_2NMe_2)Cl(\mathbf{L})]$. X-Ray diffraction studies have shown that in both complexes the metal atom is located out of the plane defined by the pyrazole ring(s) (dihedral angle between the plane and the Pd–N vector ~30°). To investigate the origin of this distortion, a theoretical study presented in *Chapter 3* was carried out on a simplified model of complex $[PdCl_2(\mathbf{L})_2]$, where a single pyrazolone ligand was replaced by NH_3. From this study, it could be inferred that the out-of-plane distortion mainly involves weak, electrostatic interactions between a chlorine atom and an *ortho*-aromatic H atom of the N(1)-linked phenyl group, as well as between the other chlorine atom and an *ortho*-aromatic H atom of the PPh_3 group.

In *Chapter 4*, the three SHOP-type catalysts in which the C=C(O) double bond is substituted by electron withdrawing substituents, [Ni{$Ph_2PC(R^1)=C(R^2)O$}Ph(PPh_3)] (R^1,R^2 = –C(Me)=NN(Ph)–; R^1 = CO_2Et, R^2 = Ph; R^1 = CO_2Et, R^2 = CF_3) have been assessed as ethylene oligomerisation and polymerisation catalysts and compared to the reference complex [Ni{$Ph_2PCH=C(Ph)O$}Ph(PPh_3)]. A rationale of the influence of the double bond substituents of the *P,O*-chelate unit on the catalytic properties was proposed, on the basis of X-ray diffraction studies, spectroscopic data and DFT-B3LYP calculations. Whatever their relative electron-withdrawing strength, the R^1 and R^2 substituents induce an activity increase with respect to the reference catalyst. For those systems in which the basicity of the oxygen atom is decreased relative to that of the phosphorus atom, the chain propagation rate increases. Reduction of the basicity of the P relative to that of the O, however, induces higher chain termination rates.

In *Chapter 5*, four calix[4]arenes containing either one or two ylidic – C(O)CH=PPh_3 moieties anchored at *p*-phenolic carbon atoms were prepared starting from c*one*-25,27-dipropoxy-calix[4]arene: *1,3-alternate*-5,17-bis(2-triphenylphosphoranylideneacetyl)-25,26,27,28tetrapropoxycalix[4]arene**,** *1,3-alternate*-5-(2-triphenylphosphoranylidene acetyl)-25,26,27,28-tetrapropoxyca lix[4]arene, *cone*-5-(2-triphenylphosphoranylidene acetyl)-25,27-dihydroxy-26,28-dipro poxycalix[4]arene, *cone*-5,17-bis(2-triphenylphosphoranylidene acetyl)-25,27-dihydroxy-26,28-dipropoxycalix[4]arene. All the ylides were shown to be suitable for the preparation of SHOP-type complexes, *i.e.* of molecules containing [NiPh{$Ph_2PCH=C(O)R$}PPh_3] subunits (R = calixarene fragment). The monometallic complexes derived from the monophosphorus ylides, proved to be efficient ethylene oligomerisation or polymerisation catalysts. They display significantly better activities than the prototype [NiPh{$Ph_2PCH=C(O)Ph$}PPh_3], hence reflecting the beneficial role of the bulky calixarene substituent. The systems derived from the two other ylides, both containing two convergent ylidic moieties, resulted in lower activities, the proximity of the two catalytic centres facilitating an intramolecular deactivation pathway during the period of catalyst activation. For the first time, the solid state structure of a complex containing *two* "NiPh(*P,O*)PPh_3" units as well as that of a SHOP-type complex having two *linked* phosphorus units were determined.

The proximally-functionalised calixarene 5,11,17,23-tetra*tert*-butyl-25,26-bis(diphenylphosphanylmethoxy)-27,28-dihydroxycalix[4]arene (**L'**), a large diphosphane in which the PIII centres are separated by 10 bonds, behaves as a chelating ligand towards NiX_2 moieties (X = Cl, Br), as presented in *Chapter 6*. As shown by three X-ray studies carried out on complexes of the type [NiX_2·**L'**], the diphosphane is able to accommodate either tetrahedral or strongly distorted tetrahedral coordination geometries, but not a square planar one. In all structures, the ligand positions the nickel atom away from the calixarene axis. In the presence of methylaluminoxane (MAO), [$NiCl_2$·**L'**] effectively catalyses the oligomerisation of ethylene, affording $\tilde{C}_4C_{12}$ oligomers with activities comparable to the complex [$NiCl_2$(dppe)].

Finally, *Chapter 7* reports on the study of the large, unsymmetrical diphosphine 5,11,17,23-tetra-*tert*-butyl-25,26-bis(diphenylphosphanylmethoxy)-27-benzoyl-28-hydroxycalix[4]arene, in which the phosphorus atoms are separated by ten bonds. Its ^{31}P NMR spectrum revealed an unexpected *J*(PP') coupling constant of 8.0 Hz possibly due to a through space interaction; in the solid state, the distance between the two P atoms is 5.333(1) Å.

Conclusion générale

Le présent travail est consacré à la synthèse et l'étude de complexes du nickel originaux basés sur deux types de phosphines chélatantes: (*a*) des diphosphines construites sur un squelette capable de donner naissance à de grands métallomacrocycles et d'imposer une tension aux chélates formés; (*b*) des ligands phosphinoénolates modifiés, notamment substitués par des groupes électro-attracteurs ou encombrés. L'ensemble des complexes synthétisés a fait l'objet d'une évaluation en oligomérisation et/ou polymérisation d'éthylène.

Le *chapitre 2* est consacré à l'étude d’un ligand phosphine combinant une unité PPh_2 à un fragment électroattracteur pyrazolonate, le 4-diphénylphosphanyl-1-phényl-3-méthyl-2-pyrazol-5-onate de sodium. Celui-ci réagit avec le complexe *trans*-$[NiPhCl(PPh_3)_2]$ pour former quantitativement *trans-P*,*P*’-[NiPh(4-diphénylphosphanyl-1-phényl-3-méthyl-2-pyrazol-5-onate)(PPh_3)], premier complexe de type Keim dérivé d’un amide. En l’absence de cocatalyseurs, il convertit sélectivement l’éthylène en α-oléfines linéaires avec une activité comparable à celle du complexe de référence $[NiPh(Ph_2PCH{=}C(O)Ph(PPh_3)]$, utilisé dans le procédé SHOP. La caractéristique principale de ce catalyseur réside dans son aptitude à déplacer la distribution des produits vers les oligomères courts par rapport au catalyseur de référence. Ainsi, en opérant à 1 bar, 99 % en masse des produits formés sont des oligomères C_4–C_{16}. En solution et en l’absence d’éthylène, le complexe se décompose lentement selon une réaction d’élimination réductrice conduisant à un ylure de phosphore stabilisé, la 4-triphénylphosphoranylidène-1-phényl-3-méthyl-pyrazol-5-one.

Dans le *chapitre 3*, nous avons étudié les propriétés complexantes d'un ylure de phosphore stabilisé, précurseur potentiel d’un catalyseur de type SHOP, la 4-(triphénylphosphoranylidène)-3-méthyl-1-phényl-2-pyrazolin-5-one (**L**). Ce composé comporte un noyau pyrazolonato connecté par le carbone 4 à une entité PPh_3. La réactivité de **L** vis-à-vis du palladium se distingue du comportement habituel des ylures de phosphore céto-stabilisés, connus pour se comporter soit en *C*- soit en *O*-nucléophiles. En effet, la réaction de **L** avec $[PdCl_2(PhCN)_2]$ et $[Pd(o\text{-}C_6H_4CH_2NMe_2)Cl]_2$ conduit uniquement à des complexes où l'un des atomes d'azote du cycle pyrazolyle, N(2), est coordiné. Des études de diffraction des rayons X réalisées pour $[PdCl_2(\mathbf{L})_2]$ et $[Pd(o\text{-}C_6H_4CH_2NMe_2)Cl\mathbf{L}]$ ont montré que tous les cycles pyrazolyles sont orientés quasi perpendiculairement au plan de coordination. Dans chaque complexe, l'atome métallique est situé en dehors du plan défini par le cycle azoté, l'angle dièdre entre le vecteur Pd-N et le plan pyrazolyle étant de 26° dans [$PdCl_2$(**L**)$_2$] (pour les deux cycles présents) et 21° dans [Pd(*o*-$C_6H_4CH_2NMe_2$)Cl**L**]. Pour déterminer l'origine de cette distorsion, une étude théorique a été menée sur un modèle simplifié du complexe [$PdCl_2$**L**$_2$], où un des deux ligands pyrazolyle a été remplacé par NH_3. Cette étude montre que la distorsion observée résulte principalement d'interactions électrostatiques faibles, en particulier entre un atome de chlore et un proton *ortho*-aromatique du groupement phényle porté par l'azote N(1) ainsi qu'entre l'autre atome de chlore et un proton *ortho*-aromatique du groupement PPh_3. Ce travail constitue par ailleurs une preuve que l'atome d'azote N(2) peut effectivement servir d'atome coordinateur vis-à-vis d'un acide de Lewis, renforçant ainsi l'idée que l'addition de BF_3 au catalyseur [NiPh(4-diphénylphosphoranyl-1-phényl-3-méthyl-2-pyazol-5-onate)(PPh_3)] du chapitre 2, peut conduire à un appauvrissement électronique du cycle pyrazolyle via formation d'un adduit N(2)→BF_3.

Le *chapitre 4* est une étude de la réactivité en oligomérisation et polymérisation de l'éthylène de trois catalyseurs de type SHOP dont la double liaison C=C(O) a été substituée par des groupements électroattracteurs, [Ni{$Ph_2PC(R^1)=C(R^2)O$}Ph(PPh_3)] (R^1,R^2 = –C(Me)=NN(Ph)–; R^1 = CO_2Et, R^2 = Ph; R^1 = CO_2Et, R^2 = CF_3). Leurs performances ont été comparées à celles du complexe de référence [Ni{$Ph_2PCH=C(Ph)O$}Ph(PPh_3)]. Les propriétés catalytiques de ces complexes ont été corrélées aux propriétés électroniques et stériques des substituants de la double liaison, en faisant appel à des études de diffraction des rayons-X, aux données spectroscopiques des complexes ainsi que des calculs théoriques DFT-B3LYP. Quel que soit leur pouvoir électroattracteur, les substituants R^1 et R^2 induisent une augmentation d'activité par rapport au catalyseur de référence. Pour les chélates *P,O* dont la basicité de l'atome d'oxygène est diminuée par rapport à celle de l'atome de phosphore, la vitesse de propagation de chaîne augmente par rapport à celle du catalyseur de référence. Une réduction de la basicité de l'atome de phosphore relativement à celle de l'oxygène entraîne quant à elle des vitesses de terminaison de chaîne plus élevées. Pour la première fois, les performances de catalyseurs de type SHOP ont été reliées au caractère différencié des atomes coordinateurs du chélate *P,O*.

Le *chapitre 5* est consacré à la synthèse d'ylures de phosphore stabilisés, substitués au niveau du groupement carbonyle par un fragment très encombré de type calix[4]arène. Quatre calixarènes ont été étudiés. Ils comportent soit un, soit deux fragments –C(O)CH=PPh_3 greffés sur des positions para phénoliques: le 5,17-bis(2-triphénylphosphoranylidèneacétyl)-25,26,27,28-tétrapropoxycalix[4]arène (*conformation 1,3-alternée*), le 5-(2-triphénylphosphoranylidèneacétyl)-25,26,27,28-tétrapropoxycalix[4]arène (*1,3-alterné*), le 5-(2-triphénylphosphoranylidèneacétyl)-25,27-dihydroxy-26,28-dipropoxycalix[4]arène (*cône*), et le 5,17-bis(2-triphénylphosphoranylidèneacétyl)-25,27-dihydroxy-26,28-dipropoxycalix[4]arène (*cône*). Ces ylures ont pu être utilisés pour la préparation de complexes de type SHOP, c'est-à-dire de molécules contenant le fragment [NiPh{Ph_2PCH=C(O)R}PPh_3] (R = fragment calixarene). Les complexes monométalliques dérivés des mono-ylures se sont avérés être des catalyseurs efficaces d'oligomérisation et de polymérisation de l'éthylène. Ils présentent des activités significativement plus grandes que le complexe de référence [NiPh{Ph_2PCH=C(O)Ph}PPh_3], reflétant ainsi le rôle bénéfique du groupement encombré *calixarène* qui retarde la désactivation du catalyseur. Les systèmes dérivés des deux bis-ylures présentent des activités inférieures à celle des mono-ylures. Ici, la proximité des deux centres catalytiques peut conduire à un processus de désactivation. Une étude approfondie réalisée avec le bis-ylure 5,17-bis(2-triphénylphosphoranylidèneacétyl)-25,26,27,28-tétrapropoxycalix[4]arène, montre qu'au cours de la phase d'activation, une fraction des molécules se transforment en un complexe mononucléaire inactif, comportant une entité phosphinoénolate chélatante ainsi qu'une entité P-monodentate. Celles-ci sont toutes deux liées au calixarène. Une synthèse rationnelle de ce complexe a été effectuée à partir d'une bis-phosphinocétone. Ce travail décrit la première structure cristallographique d'un complexe contenant deux entités "NiPh(*P,O*)PPh_3" ainsi que celle d'un complexe de type SHOP où les deux atomes de phosphore sont reliés entre eux.

Le *chapitre 6* décrit la synthèse et les propriétés complexantes et catalytiques d'un calix[4]arène comportant deux entités phosphines –CH_2PPh_2 ancrées sur des atomes d'oxygène phénoliques proximaux, le 5,11,17,23-tétra-*tert*-butyl-25,26-bis(diphénylphosphinométhoxy)-27,28-dihydroxycalix[4]arène (**L'**). La longueur relativement courte des podands ainsi que la rigidité marquée du fragment reliant les deux atomes de phosphore laissait prévoir la formation de complexes chélates où une coordination *trans* serait impossible. Des études cristallographiques réalisées pour trois complexes paramagnétiques du type [NiX_2•**L'**] (X = Cl, Br), montrent que cette diphosphine de grande taille, où les atomes de phosphore sont séparés par 10 liaisons, peut effectivement former des complexes chélates. Dans l'un des complexes, l'atome de nickel est tétraédrique, l'angle de chélation étant proche de 119°. Dans les deux autres, la stéréochimie du nickel s'éloigne d'une géométrie tétraédrique idéale, sans toutefois pouvoir atteindre une géométrie *plan-carré*. Dans ces cas, l'angle de chélation est légèrement inférieur à 160°, confirmant ainsi nos prévisions. Une telle stéréochimie, entre *plan-carré* et tétraédrique, est très rare pour des complexes du type [NiX_2P_2]. En présence de méthylaluminoxane (MAO), [$NiCl_2$·**L'**] catalyse l'oligomérisation de l'éthylène, produisant des oligomères C_4-C_{12} avec une activité comparable à celle du complexe [$NiCl_2${1,2-bis-(diphénylphosphino)éthane}]. Ce comportement tranche avec celui d'autres grandes diphosphines, qui en présence de nickel conduisent à des activités nettement plus faibles.

Enfin, dans le *chapitre 7*, nous décrivons la synthèse et la structure cristallographique d'une variante asymétrique de la diphosphine décrite au chapitre 6, le 5,11,17,23-tétra-*tert*-butyl-25,26-bis(diphénylphosphinométhoxy)-27-benzoyl-28-hydroxycalix[4]arène. Une propriété remarquable de cette diphosphine est l'existence d'une constante de couplage *J*(PP') de 8.0 Hz. Il s'agit de la diphosphine la plus longue pour laquelle un tel couplage a été observé. Celui-ci résulte vraisemblablement d'une interaction à travers l'espace.

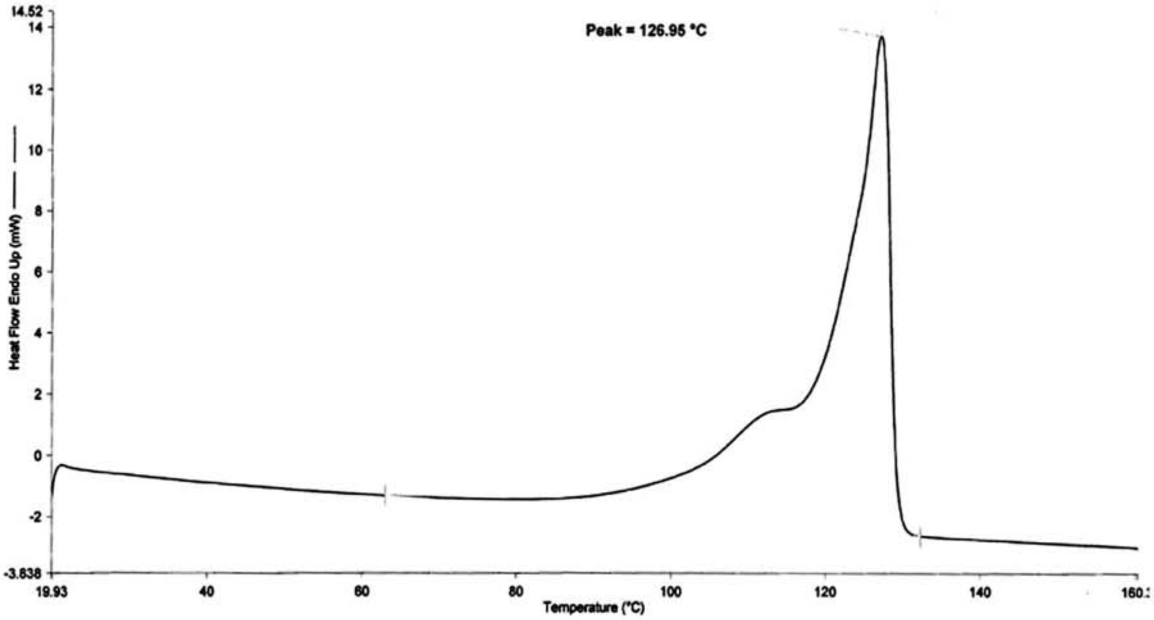
Perspectives de ce travail:

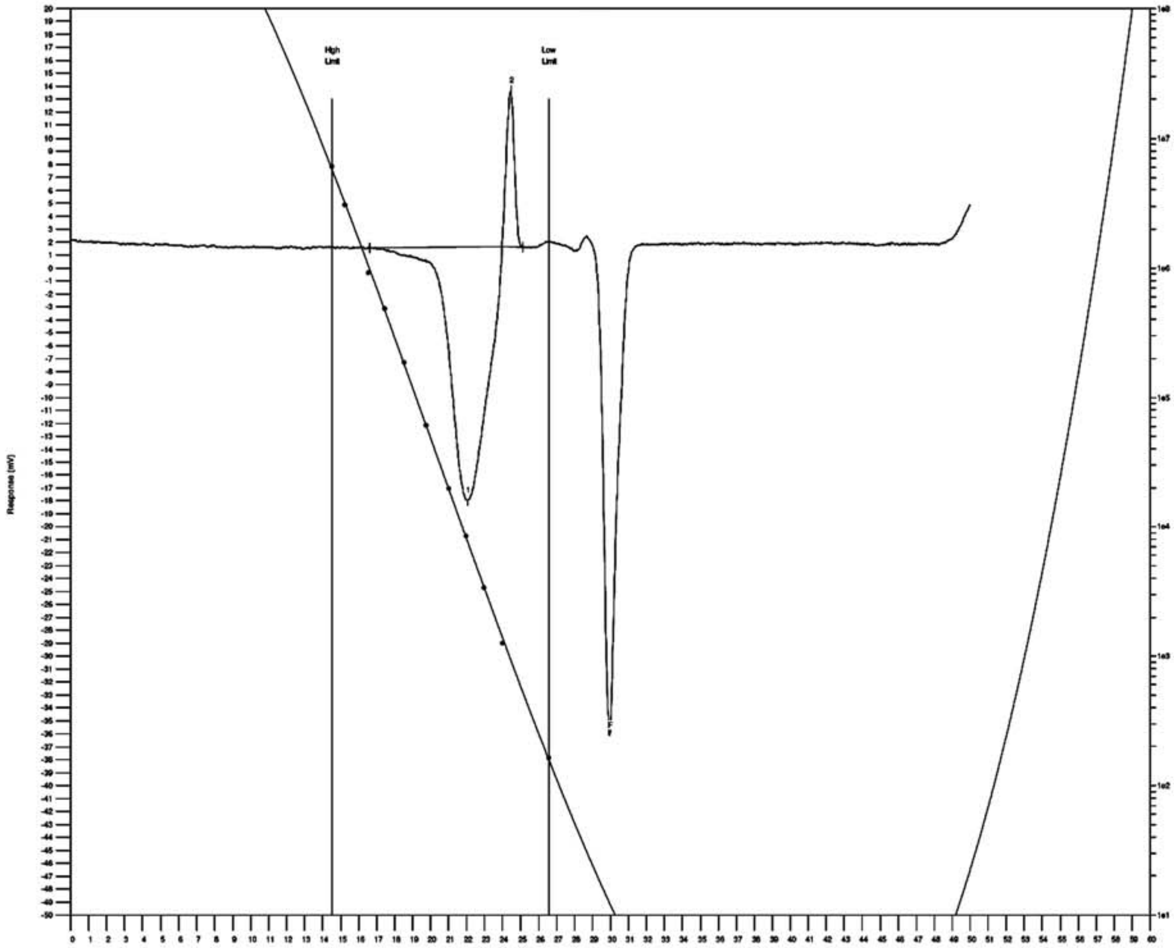
- la mise au point de catalyseurs de type SHOP contenant un ligand phosphino-pyrazolonate où l'atome d'azote N(2) est impliqué dans une coordination avec un acide de Lewis.
- la synthèse de nouveaux catalyseurs de type SHOP comportant un groupement très électroattracteur sur le carbone en position α du phosphore
- la préparation de catalyseurs de type SHOP construits sur une plateforme calixarène, et où l'atome de nickel est orienté vers le centre de la cavité

Annex

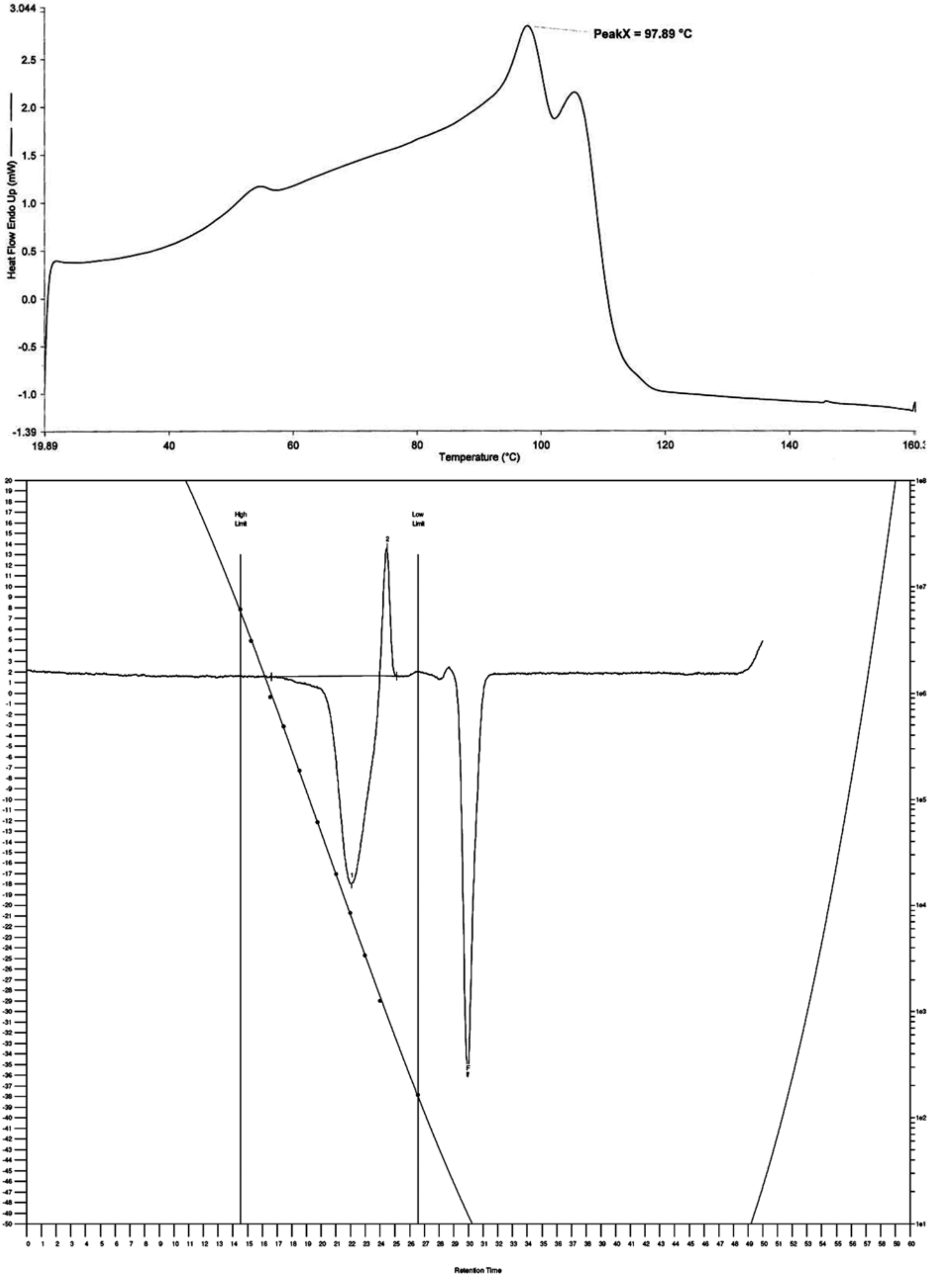
Selected DSC and SEC-HT traces representative of the polythylene formed with some catalysts

PE of Keim's catalyst (5 bar C_2H_4, 70°C)

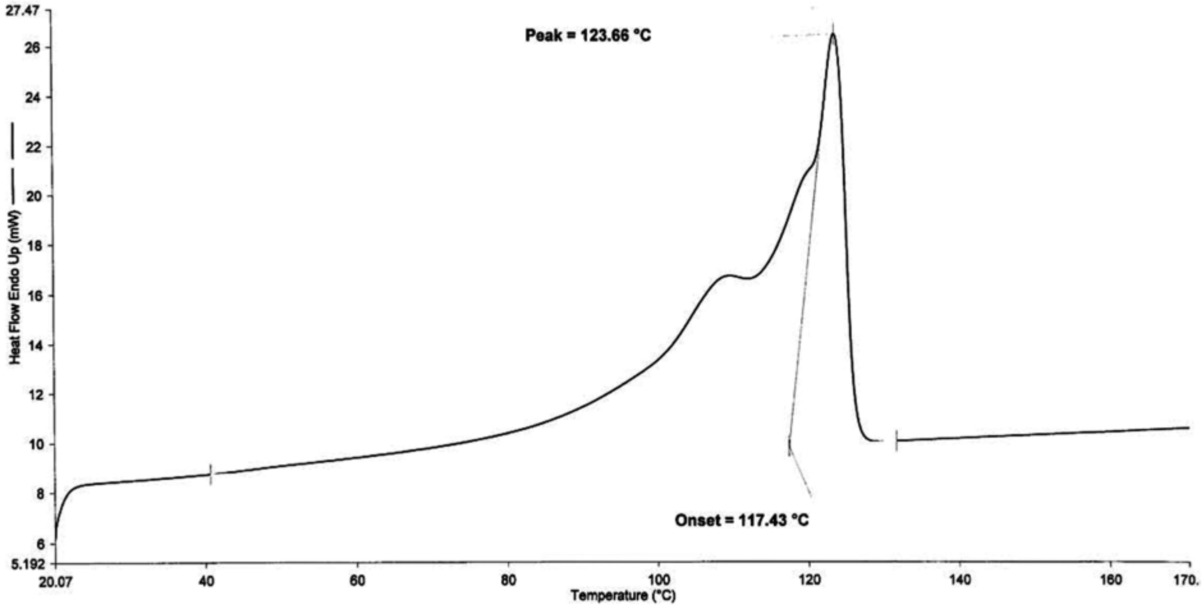


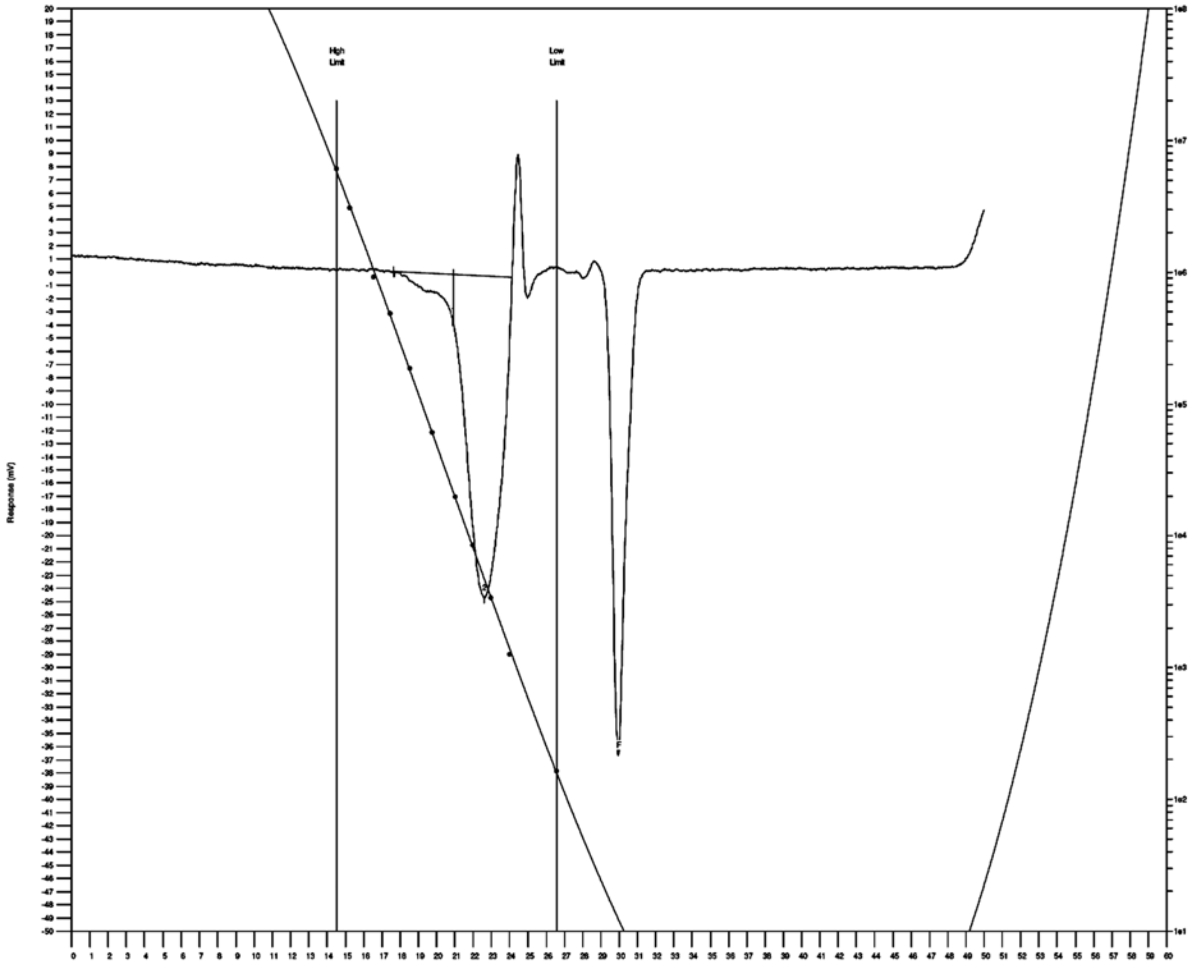


PE of the pyrazolone derivated catalyst (5 bar C_2H_4, 70°C)



PE of the terapropoxy-calixarene derivated mono-ylide precatalyst (5 bar C_2H_4, 80°C, 0.25 h)





PE of the terapropoxy-calixarene derivated bis-ylide precatalyst (5 bar C_2H_4, 70°C)