Preliminary communication / Communication

Influence of intramolecular N–H⋯O–Ni hydrogen bonding in nickel(II) diphenylphosphinoenolate phenyl complexes on the catalytic oligomerization of ethylene

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Abstract

Nickel(II) diphenylphosphinoenolate complexes have been prepared from (*ortho*-HX-substituted benzoylmethylene)triphenyl phosphoranes (X = NMe, NPh) and [Ni(1,5-cod)$_2$] in the presence of a tertiary phosphine (PPh$_3$ or P(p-C$_6$H$_4$F)$_3$). An X-ray diffraction study of the complexes [NiPh{Ph$_2$PCH⋯C(⋯O)(o-C$_6$H$_4$NHMe)}(PPh$_3$)] **10** and [NiPh{Ph$_2$PCH⋯C(⋯O)(o-C$_6$H$_4$NHPh)}{P(p-C$_6$H$_4$F)$_3$}] **16** establishes the presence of strong intramolecular hydrogen bonding between the enolate oxygen and the N–H function, as originally found in [NiPh{Ph$_2$PCH⋯C(⋯O)(o-C$_6$H$_4$NHPh)}(PPh$_3$)] **11.** This feature favours the formation of the desired shorter-chain-length products in the catalytic oligomerisation of ethylene. *To cite this article: P. Braunstein et al., C. R. Chimie 8 (2005)*.
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Résumé

Des complexes diphénylphosphinoénolate du Ni(II) ont été préparés par réaction entre des (benzoylméthylène)triphénylphosphoranes substitués en *ortho* par un groupe HX (X = NMe, NPh) et [Ni(1,5-cod)$_2$] en présence d'une phosphine tertiaire (PPh$_3$ ou P(p-C$_6$H$_4$F)$_3$). La structure des complexes [NiPh{Ph$_2$PCH⋯C(⋯O)(o-C$_6$H$_4$NHMe)}(PPh$_3$)] **10** et [NiPh{Ph$_2$PCH⋯C(⋯O)(o-C$_6$H$_4$NHPh)}{P(p-C$_6$H$_4$F)$_3$}] **16**, déterminée par diffraction des rayons X, permet de mettre en évidence une liaison hydrogène intramoléculaire forte entre l'oxygène de l'énolate et la fonction N–H, comme ce fut le cas dans [NiPh{Ph$_2$PCH⋯C(⋯O)(o-C$_6$H$_4$NHPh)}(PPh$_3$)] **11**. Ceci favorise la formation souhaitée de chaînes plus courtes dans l'oligomérisation catalytique de l'éthylène. *Pour citer cet article : P. Braunstein et al., C. R. Chimie 8 (2005)*.
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1. Introduction

Processes leading to linear α-olefins have gained much commercial significance owing to their various applications, in particular in the fields of plasticizers and detergents [1,2]. New grades of linear low-density polyethylene (LLDPE) have been developed, which are obtained by copolymerization of ethylene with a light α-olefin, such as 1-butene, 1-hexene or 1-octene. Current processes for the synthesis of linear α-olefins are based on the oligomerisation of ethylene and the ability to modulate the carbon-chain length remains a central issue [3]. Typical distributions cover the C_4–C_{28} (Ethyl Corporation) and C_4–C_{50} ranges (Chevron, Shell). Although modulation of chain length can be achieved by a subsequent olefin metathesis reaction, it remains important to develop catalysts able to oligomerize ethylene selectively in α-olefins in the C_4–C_8 range.

Nickel(II) complexes containing specific phosphorus–oxygen chelating ligands are very efficient catalysts for the oligomerisation of ethylene to linear α-olefins [4–8]. The combined soft and hard donor character of the chelating P,O ligand plays a key role in determining the properties of these catalysts that have led to the industrial Shell Higher Olefin Process (SHOP) for the selective production of liquid linear α-olefins, which is one of the largest applications of homogeneous catalysis [8]. The structurally characterized complex [Ni(Ph){Ph₂PCH⋯C(⋯O)Ph}(PPh₃)] (**1a**) [9], which contains both a Ni-carbon σ-bond and a bidentate, three-electron-donor P∩O chelating ligand, catalyzes the oligomerisation of ethylene at 50 bar and 50 °C, and is regarded as a suitable model for the SHOP catalyst [7,8].
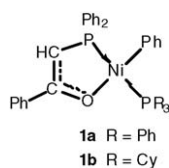
Such square planar Ni(II) complexes are typically prepared by oxidative addition of (benzoylmethylene)triphenylphosphoranes Ph₃P=CHC(=O)R to Ni(0) complexes such as [Ni(cod)₂] (cod = 1,5-cyclooctadiene), in the presence of a two-electron-donor phosphine ligand. It is remarkable that the oxidative addition of a P-phenyl bond across the zerovalent metal centre has so far remained limited to nickel. To access Pd(II) complexes analogous of the Ni-based SHOP catalysts, we therefore had to develop another approach, which consisted in the coordination of a functional phosphine of the type Ph₂PCH₂C(=O)R to a Pd(II) aryl complex, followed by deprotonation of the coordinated phosphine to generate the phosphinoenolate complex [10]. Since subtle variations of the ligands may be sufficient to change significantly the catalytic properties of these complexes, we were interested in modifying the stereoelectronic environment of the nickel centre. We could show that the α-iminophosphorus ylide Ph₃P=CHC(=NPh)Ph **2** also oxidatively adds to [Ni(cod)₂] and affords P,N analogues of the P,O systems. Depending upon the nature of the added two-electron-donor phosphine ligand, coordination of the latter or of an intact ylide molecule was observed, as in **3** or **4**, respectively (Scheme 1) [11].
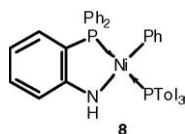
Similar observations were made with isoelectronic azaphosphoranes (Scheme 2) [11b].
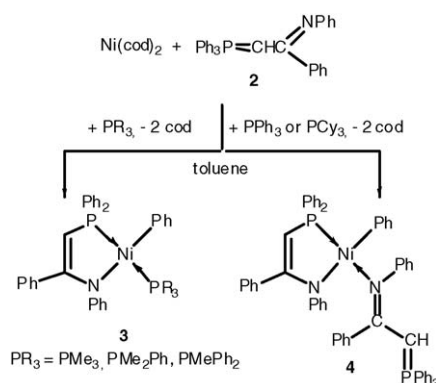
Scheme 1.

Scheme 2.
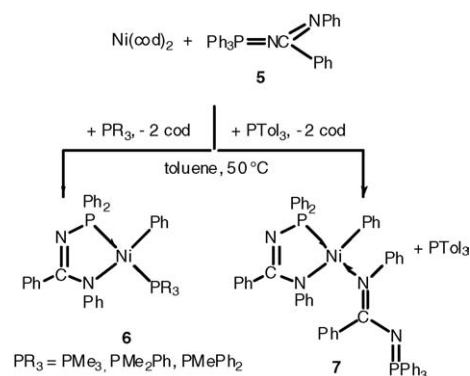
The presence of a nitrogen donor atom in **3**, **6** or [Ni(Ph){Ph$_2$P(o-C$_6$H$_4$NH}(PTol$_3$)] (**8**) instead of oxygen in the three electron donor chelate was found to be detrimental for the catalytic activity [7,11a].

However, recent results have shown that Ni(II) complexes containing neutral, four-electron-donor P,N chelates (P = phosphine, phosphonite or phosphinite moiety; N = pyridine or oxazoline donor) are efficient and selective dimerisation or oligomerisation catalysts in the presence of MAO or small amounts of AlEtCl$_2$ as cocatalyst [12].

The activity and selectivity (α-olefin distribution) of complexes of type **1** are strongly dependent on the electronic and steric properties of the substituents, the ring size of the chelate and the nature of the two-electron-donor ligand. As shown in Scheme 3, dissociation of the phosphine ligand enables coordination of an ethylene molecule that can then undergo insertion into the Ni–Ph (initiation step), Ni–H or Ni-alkyl bond and this leads to chain growth.

There have been numerous attempts to modify the molecular weight distribution of the resulting oligomers by changing the structure of the phosphinoenolate ligand and/or the ancillary phosphine [8a,13]. With the aim of facilitating β-hydrogen elimination during the growing step (Scheme 3) and thus favour low-molecular-weight products, we have attempted to modify the electronic density at the nickel centre by favouring the occurrence of an additional intramolecular bonding interaction between the enolate oxygen atom and an ortho-substituent on the aromatic ring of the P,O chelate, as shown with **9–11** [5].

Scheme 3.
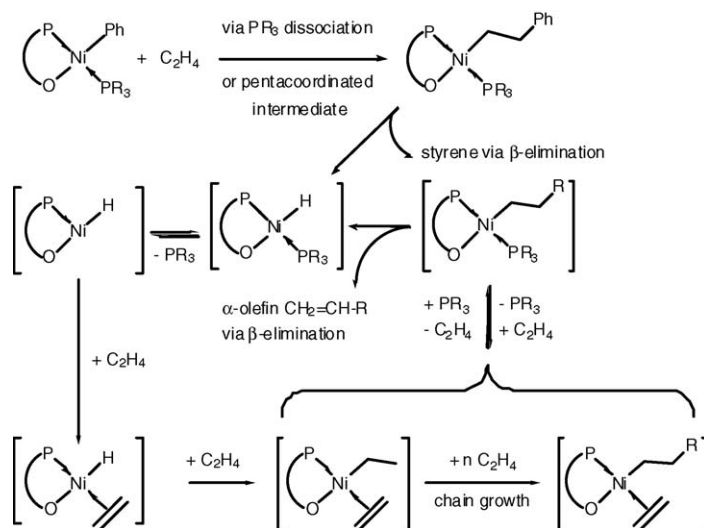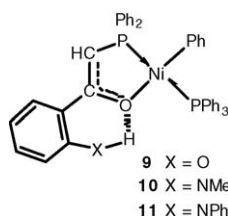
Here we report further studies on the influence of the substituents at X = N and of the phosphine PR_3 on the structural and catalytic properties of the corresponding Ni(II) complexes. We also compare the crystal structures of the new complex [NiPh{Ph₂PCH⋯C(⋯O)(o-C₆H₄NHPh)}{P(p-C₆H₄F)₃}] **16,** which contains a $P(p\text{-}C_6H_4F)_3$ ligand, with those of the PPh₃ complexes [NiPh{Ph₂PCH⋯C(⋯O)(o-C₆H₄NHMe)}(PPh₃)] **10** and [NiPh{Ph₂PCH⋯C(⋯O)(o-C₆H₄NHPh)}(PPh₃)] **11**.

2. Results and discussion

Reaction of the (*ortho*-substituted benzoylmethylene)triphenylphosphoranes **12a–c**, prepared in a manner similar to related ylides [14], with one equivalent each of [Ni(cod)₂] and triarylphosphine in toluene, afforded the respective Ni(II) complexes under similar conditions to those described previously for complex **11** (Scheme 4) [5,9]. The new yellow complexes were isolated analytically pure by precipitation with pentane. The trans arrangement of the P atoms gives rise in the ³¹P{¹H} NMR spectrum to an AB pattern with typical coupling constants.

A view of the crystal structures of complexes **10** and **16** is shown in Figs. 1 and 2, respectively, and selected bond distances and angles are given in Table 1. The square-planar coordination around the Ni(II) centre is
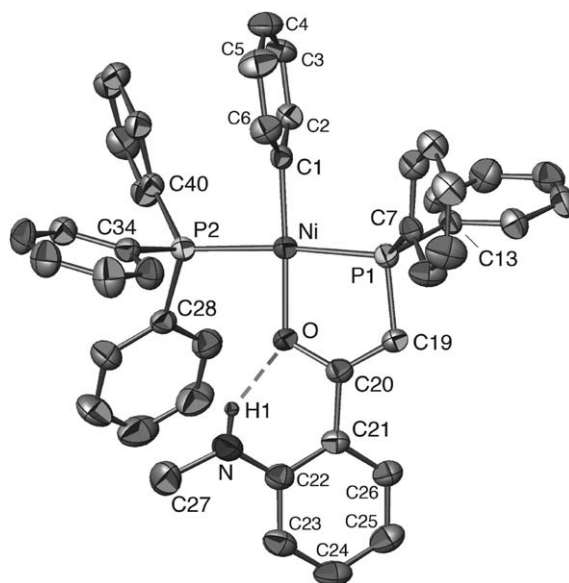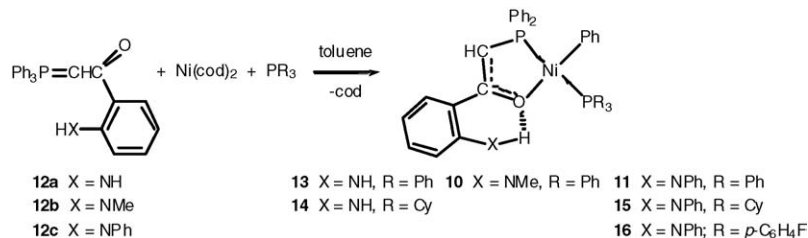
Fig. 1. Molecular structure of complex **10** in **10**·2 (C₇H₈). Except for N–H(1), the H atoms are not represented.

only slightly distorted and the five-membered Ni–P–C–C–O cycle is nearly planar, owing to electron delocalisation within the enolate moiety. The relatively short Ni–Ph distance is consistent with the electron affinity of the P,O chelating ligand. Since the first step in the catalytic cycle is the insertion of ethylene into the Ni-phenyl bond, which is followed by β-H elimination, the strength of this bond influences the catalyst's activation temperature [8a]. The most notable feature in these structures is the strong intramolecular N–H⋯O hydrogen bonding: the calculated distance between the NH hydrogen atom and the oxygen atom of the enolate ligand is rather short: 2.18(5) Å in **10**·2 (C₇H₈) and 2.00(5) Å in **16**·1/2 (C₆H₆), respectively [15,16].

The coordination geometry around the nitrogen atom in complexes **10**·2 (C₇H₈) and **16**·1/2 (C₆H₆) is planar, with the sum of their valency angles being 360.0(5)° and 359.7(5)°, respectively. This was also observed in
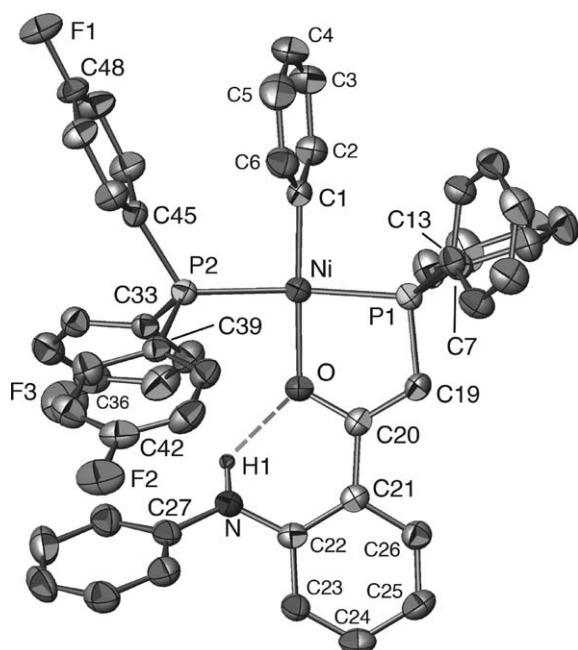

Scheme 4.

Fig. 2. Molecular structure of complex **16** in **16**·1/2 (C$_6$H$_6$). Except for N–H(1), the H atoms are not represented.

Table 1
Selected bond lengths (Å) and angles (deg) in complexes **10**·2 (C$_7$H$_8$) and **16**·1/2 (C$_6$H$_6$), compared with those for **11** [5]

	10·2 (C$_7$H$_8$)	**16**·1/2 (C$_6$H$_6$)	**11**
Ni–C(1)	1.899(6)	1.893(5)	1.886(3)
Ni–P(1)	2.183(2)	2.161(2)	2.180(1)
Ni–P(2)	2.223(2)	2.213(2)	2.214(1)
Ni–O	1.908(4)	1.929(4)	1.923(2)
P(1)–C(19)	1.772(6)	1.762(5)	1.766(4)
C(19)–C(20)	1.354(8)	1.360(8)	1.345(4)
C(20)–C(21)	1.497(8)	1.489(7)	1.498(5)
C(21)–C(22)	1.410(8)	1.415(8)	1.413(4)
C(22)–N	1.371(8)	1.381(7)	1.396(5)
N–C(27)	1.441(9)	1.409(7)	1.400(4)
C(20)–O	1.315(7)	1.327(6)	1.332(4)
P(1)–Ni–P(2)	174.60(7)	172.43(6)	159.78(4)
C(1)–Ni–O	175.7(2)	178.5(2)	170.1(1)
O–Ni–P(1)	85.8(1)	86.3(1)	86.20(6)
P(1)–C(19)–C(20)	113.3(4)	114.7(4)	113.6(2)
C(19)–C(20)–C(21)	122.9(5)	123.1(5)	123.1(3)
C(19)–C(20)–O	121.7(5)	120.3(5)	122.4(3)
C(20)–O–Ni	119.8(3)	119.0(3)	117.9(2)
C(21)–C(22)–N	120.8(5)	121.8(5)	119.8(3)
C(22)–N–C(27)	122.2(6)	125.4(5)	128.3(3)

the structure of **11** and is probably due to the combined influence of electronic and steric interactions resulting from the hydrogen bonding which leads to a stabilised, six-membered ring. The ^{1}H NMR data are typical for NH···O protons [5]. To evaluate the consequences of changing one parameter at a time in the ligand system on the main bonding parameters, a comparison of the structural data for complexes **10**·2 (C$_7$H$_8$), **11** and **16**·1/2 (C$_6$H$_6$) is provided in Table 1. Only minor variations are observed when the nitrogen substituent is Me or Ph (compare **10** and **11**) or when the PPh$_3$ ligand is replaced with the less electron donor P(p-C$_6$H$_4$F)$_3$ (compare **11** and **16**). However, we will see that the effects are more pronounced when looking at the catalytic properties of these complexes.

The distribution of oligomers obtained with the various catalyst precursors is shown in Fig. 3 and selected catalytic data are presented in Table 2. Complexes **9–11** and **13–16** display high activity and selectivity in ethylene oligomerisation to linear α-olefins (20 ml toluene, 0.10 mmol catalyst, 60–80 °C, 55 bar ethylene, 1.5–6 h), with a marked shift of the product distribution to lower molecular weights when compared to **1a** under similar experimental conditions. A comparison between the complexes containing the PPh$_3$ ligand shows that the effect of hydrogen bonding on product distribution is more pronounced for **9** and **11** than for **10** and **13**. Comparing pre-catalysts **11**, **15** and **16** shows that the influence of the phosphine ligand on the mass distribution appears modest, except in the C$_4$ fraction whose selectivity increases to 37% in the case of the P(p-C$_6$H$_4$F)$_3$ derivative **16**, in contrast to its larger influence on the productivity and TOF values (see Table 2). Complex **15** yielded a broader mass distribution and heavier olefins were obtained (waxes).

We have previously observed that replacing PPh$_3$ with PCy$_3$ in complexes of type **1** leads to an increase of the TON from 82 000 to 180 000 mol C$_2$H$_4$ converted·(mol catalyst h)$^{-1}$ [7]. A similar trend is observed here when comparing the data between **13** and **14** or **11** and **15**.

The high selectivity observed for linear α–olefins is consistent with the ethylene pressure used, which provides a high-enough concentration in solution to limit efficiently consecutive, codimerisation reactions. The complex analogous to **9** with a methoxy group in *ortho* position instead of a OH group yielded a productivity of 2.2 kg C$_2$H$_4$ (g Ni h)$^{-1}$ and a TOF of
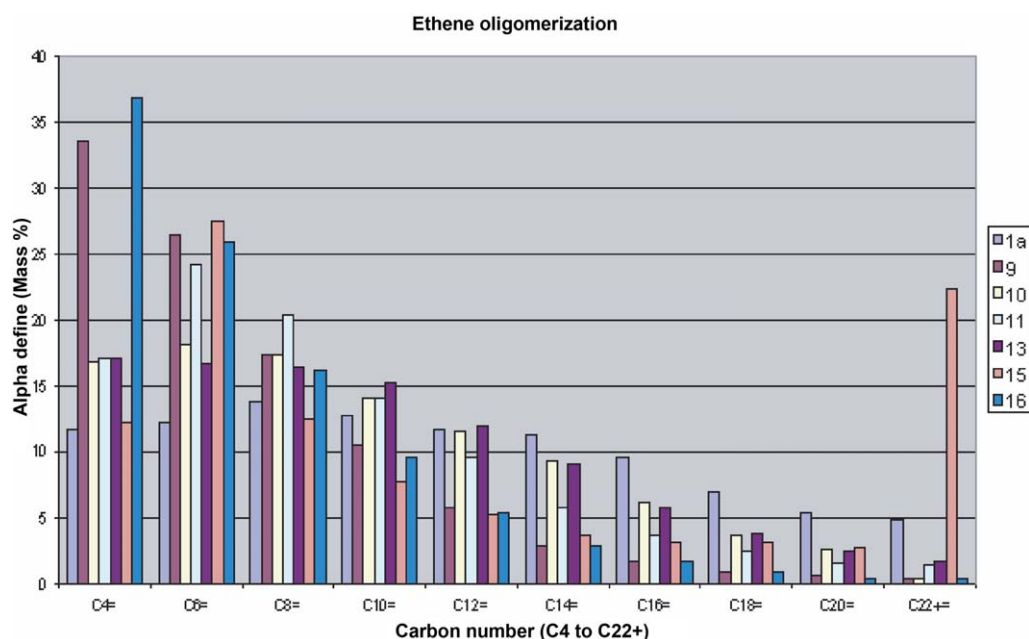
Ethene oligomerization

Fig. 3. Selectivity in mass% of the oligomers formed in the catalytic reactions. For each carbon fraction, the sequence of complexes is: **1a**, **9**, **10**, **11**, **13**, **15** and **16**.

Table 2
Catalytic data of the nickel complexes in the oligomerisation of ethylene

Complex	T (°C)	Time (h)	k_α (SF)[a]	Productivity[b]	TOF[c]	Selectivity (%)[d]
1a	60	1.5	0.7	2.7	5700	98
9	60	1.5	0.48	2.7	5700	89–92
10	70	4	0.62	1.3	2700	96–98
11	80	3.5	0.56	2.9	6100	97–99
13	60	5.5	0.61	2.3	4800	98–99
14	80	6	0.88	5.3	11 100	nd[e]
15	70	4	0.82	6.3	13 200	nd[e]
16	67	1.5	0.47	4.2	8800	97–98

[a] The k_α factor is calculated without considering the butenes.
[b] kg of C_2H_4 (g Ni h)$^{-1}$.
[c] mol of C_2H_4 (mol Ni h)$^{-1}$.
[d] Selectivity for linear α-olefins (C_4 to C_8).
[e] Partial loss of light olefins during the dissolution of the waxes.

4600 mol C_2H_4 (mol Ni h)$^{-1}$, slightly lower than **9**, but gave a maximum mass distribution for the C_8 and C_{10} fractions, similar to that observed with **1a**, suggesting no significant electronic influence of the MeO substituent. Obviously, the intramolecular hydrogen bonding in these new catalytic precursors allows a fine tuning of their selectivity; it favours β-hydrogen elimination and thus the formation of C_4–C_8 olefins, of which 95–99% are linear α-olefins. Further work is still needed

to fully evaluate and rationalize the catalytic implications of such intramolecular ligand effects.

3. Experimental section

3.1. Reagents and physical measurements

All operations were performed in Schlenk-type flasks under high-purity argon, using vacuum line tech-

niques. The solvents were purified and dried under argon by conventional methods. The ^{1}H NMR spectra were recorded at 200 MHz on a Bruker AC 200 F, the ^{31}P{^{1}H} NMR spectra at 81 MHz on a Bruker CXP 200 and at 122 MHz on a Bruker AC300 instrument. The spectra were recorded at room temperature and the ^{1}H and ^{31}P shifts are given relative to internal TMS and external H$_3$PO$_4$, respectively. A positive sign denotes a shift downfield from that of the reference. Coupling constants are given in Hz. The electron impact mass spectra (EI, 70 eV) were recorded on a Fisons ZAB-HF spectrometer. Reactions with ethylene were performed in a 130-ml double-walled stainless steel autoclave, fitted with a manometer, a septum inlet and a magnetic stirrer. The products were analysed by gas phase chromatography with a Hewlett Packard 5890 Series II instrument on a PONA column (methylsilicone, diameter: 0.22 mm, length: 50 m, temperature program from 35–270 °C) for the C$_{4=}$–C$_{30=}$ fraction, and on a capillary Supelco Polywax SPB1 column (diameter: 0.53 mm, length: 30 m, 'on-column injection', 3 min at 5 °C, then temperature program 10 °C min^{-1} up to 380 °C) for the C$_{4=}$–C$_{100=}$ fraction. The highest mass detected corresponded to C$_{100=}$. High-purity ethylene was purchased from Air Liquide and used as received.

3.2. Synthesis

The complexes [Ni(cod)$_2$] [17], **10** and **11** [5] were synthesized according to the literature and complexes **13**–**16** were prepared according to Scheme 4 by following the method used for **10** and **11**. Satisfactory elemental analyses were obtained for the new complexes. The phosphine P(p-C$_6$H$_4$F)$_3$ was purchased from Strem and used as received.

Selected data for **10**: IR (KBr): 1600w, 1580w, 1510s, 1470w cm^{-1}. ^{1}H NMR (200 MHz, C$_6$D$_6$) δ: 1.90 (s, 3H, NMe), 5.05 (s, 1H, PCH). ^{31}P{^{1}H} NMR (81 MHz, C$_6$D$_6$): 16.4 (d, ^2J(PP) = 280 Hz, PPh$_3$), 19.5 (d, P,O).

13: R (KBr): 1600w, 1555w, 1475w cm^{-1}. ^{1}H NMR (200 MHz, C$_6$D$_6$) δ: 5.60 (2H, br s, NH$_2$), 6.10 (s, 1H, PCH). ^{31}P{^{1}H} NMR (81 MHz, C$_6$D$_6$): 15.6 (d, ^2J(PP) = 281 Hz, PPh$_3$), 20.4 (d, P,O).

14: ^{1}H NMR (200 MHz, C$_6$D$_6$) δ: 5.60 (2H, br s, NH$_2$), 6.10 (s, 1H, PCH). ^{31}P{^{1}H} NMR (81 MHz, C$_6$D$_6$): 13.9 (d, ^2J(PP) = 265 Hz, PCy$_3$), 17.9 (d, P,O).

15: IR (KBr): 1585w, 1565, 1510s, 1495w, 1455w cm^{-1}. ^{1}H NMR (200 MHz, C$_6$D$_6$) δ: 5.60 (2H, br s, NH$_2$), 6.10 (s, 1H, PCH). ^{31}P{^{1}H} NMR (81 MHz, C$_6$D$_6$): 13 (d, ^2J(PP) = 266 Hz, PCy$_3$), 17.4 (d, P,O).

16: IR (KBr): 1590w, 1570w, 1495s, 1455w cm^{-1}. ^{1}H NMR (200 MHz, C$_6$D$_6$) δ: 5.10 (s, 1H, PCH), 6.35–7.75 (m, 36H, aromatic), 8.80 (s, 1H, NHPh). ^{31}P{^{1}H} NMR (81 MHz, C$_6$D$_6$): 16 (d, ^2J(PP) = 284 Hz, P(p-C$_6$H$_4$F)$_3$), 17.2 (d, P,O).

3.3. Crystallography

Single crystals suitable for X-ray diffraction were obtained by recrystallisation of **10** and **16** from toluene/hexane or benzene/hexane, which afforded **10**·2 (C$_7$H$_8$) and **16**·1/2 (C$_6$H$_6$), respectively. Diffraction data were collected on a Philips PW1100/16 diffractometer the using Cu Kα graphite monochromated radiation (λ = 1.54184 Å) by θ/2θ flying step-scan. The structures were solved using SHELXS-97 and full-matrix least-square refinements were carried out using the SHELXL-97 program [18]. All non-hydrogen atoms were refined with anisotropic parameters. The hydrogen atoms were included in their calculated positions and refined with a riding model. The benzene molecule found in **16**·1/2 (C$_6$H$_6$) was disordered. For both structures, atomic coordinates, bond lengths and angles, and thermal parameters have been deposited within the Cambridge Crystallographic Data Centre, CCDC 248694 and 248970.

3.3.1. Crystal data for compound **10**·2 (C$_7$H$_8$)

Yellow crystals from toluene/hexane. C$_{45}$H$_{39}$NNiOP$_2$·2 C$_7$H$_8$, M = 914.8; monoclinic; space group $P21/n$ (No. 14); a = 20.9190(10), b = 14.7780(10), c = 15.7050(10) Å, β = 97.22(5), V = 4816.6(7) Å^3, Z = 4, D_c = 1.261 g cm^{-3}, μ = 1.523 mm^{-1}, F(000) = 1928, T = 173 K; 5058 unique reflections (θ = 3.3–51.1 °), of which 4359 with $I > 2\,\sigma(I)$ were used for structure solution; R = 0.0726, $wR2$ = 0.2061.

3.3.2. Crystal data for compound **16**·1/2 (C$_6$H$_6$)

Yellow crystals from benzene/hexane. C$_{50}$H$_{38}$F$_3$NNiOP$_2$·1/2C$_6$H$_6$, M = 885.52; triclinic; space group $P\bar{1}$ (No. 2); a = 12.248(2), b = 17.882(2), c = 10.365(2) Å, α = 101.67(5), β = 103.12(5),

References

[1] B. Rieger, L. Saunders Baugh, S. Kacker, S. Striegler (Eds.), Late Transition Metal Polymerization Catalysis, Wiley-VCH, Weinheim, 2003.

[2] (a) G.R. Lappin, J.D. Sauer, Alpha Olefins Applications Handbook, Marcel Dekker Inc., New-York, 1989; (b) A. Hennico, J. Léonard, A. Forestière, Y. Glaize, Hydrocarbon Process. 69 (1990) 73.

[3] (a) D. Vogt, Oligomerization of Ethylene to Higher Linear α-Olefins, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Complexes; VCH: Weinheim, Germany, 2002, pp. 240–253; (b) H. Olivier-Bourbigou, L. Saussine, Dimerization and Codimerization, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Complexes, VCH, Weinheim, Germany, 2002, pp. 253–265.

[4] (a) P. Wasserscheid, C. Hilgers, W. Keim, J. Mol. Catal. A: Chem. 214 (2004) 83; (b) J. Heinicke, M. Köhler, N. Peulecke, W. Keim, J. Catal. 225 (2004) 16; (c) J. Heinicke, M. Köhler, N. Peulecke, M. He, M. K. Kindermann, W. Keim, G. Fink, Chem. Eur. J. 9 (2003) 6093; (d) D. Vogt, SHOP Process, in: B. Cornils, W.A. Herrmann (Eds.), Aqueous Phase Organometallic Catalysts, Concepts and Applications, VCH, Weinheim, Germany, 1998, pp. 541–547; (e) U. Klabunde, S.D. Ittel, J. Mol. Catal. 41 (1987) 123.

[5] P. Braunstein, Y. Chauvin, S. Mercier, L. Saussine, A. DeCian, J. Fischer, J. Chem. Soc., Chem. Commun. (1994) 2203.

[6] J.M. Malinoski, P.S. White, M. Brookhart, Organometallics 22 (2003) 621.

[7] J. Pietsch, P. Braunstein, Y. Chauvin, New J. Chem. 22 (1998) 467.

[8] (a) A. Ostoja Starzewski, L. Born, Organometallics 11 (1992) 2701; (b) W. Keim, New J. Chem. 11 (1987) 531; (c) W. Keim, Angew. Chem. Int. Ed. Engl. 29 (1990) 235; (d) W. Keim, New J. Chem. 18 (1994) 93.

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

[10] (a) J. Andrieu, P. Braunstein, C. R. Acad. Sci. Paris, Ser. IIb 320 (1995) 661; (b) J. Andrieu, P. Braunstein, F. Naud, R.D. Adams, R. Layland, Bull. Soc. Chim. Fr. 133 (1996) 669.

[11] (a) P. Braunstein, J. Pietsch, Y. Chauvin, S. Mercier, L. Saussine, A. DeCian, J. Fischer, J. Chem. Soc., Dalton Trans. (1996) 3571; (b) P. Braunstein, J. Pietsch, Y. Chauvin, A. DeCian, J. Fischer, J. Organomet. Chem. 529 (1997) 387.

[12] (a) F. Speiser, P. Braunstein, L. Saussine, R. Welter, Organometallics 23 (2004) 2613; (b) F. Speiser, P. Braunstein, L. Saussine, Organometallics 23 (2004) 2625; (c) F. Speiser, P. Braunstein, L. Saussine, Organometallics 23 (2004) 2633; (d) F. Speiser, P. Braunstein, L. Saussine, Dalton Trans. (2004) 1539; (e) F. Speiser, P. Braunstein, L. Saussine, R. Welter, Inorg. Chem. 43 (2004) 1649.

[13] K. Hirose, W. Keim, J. Mol. Catal. 73 (1992) 271.

[14] G. Baldoli, E. Licandro, S. Maiorana, E. Menta, A. Papagni, Synthesis (1986) 288.

[15] R. Taylor, O. Kennard, J. Am. Chem. Soc. 104 (1982) 5063.

[16] V. Bertolasi, L. Nanni, P. Gilli, V. Ferretti, G. Gilli, Y.M. Issa, et al., New J. Chem. 18 (1994) 251.

[17] R.A. Schunn, S.D. Ittel, M.A. Cushing, Inorg. Synth. 28 (1990) 94.

[18] G.M. Sheldrick, SHELXL97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.