Phenyl nickel complexes with a chelating P,N ligand. Structures of $Ph_3P{=}CHC({=}NPh)Ph$ and $[NiPh\{Ph_2PCH{\cdots}C({\cdots}NPh)Ph\}\{Ph_3P{=}CHC({=}NPh)Ph\text{-}N\}]$*

Pierre Braunstein,[a] **Jörg Pietsch,**[a,b] **Yves Chauvin,**[b] **Sophie Mercier,**[b] **Lucien Saussine,**[b] **André DeCian**[c] **and Jean Fischer**[c]

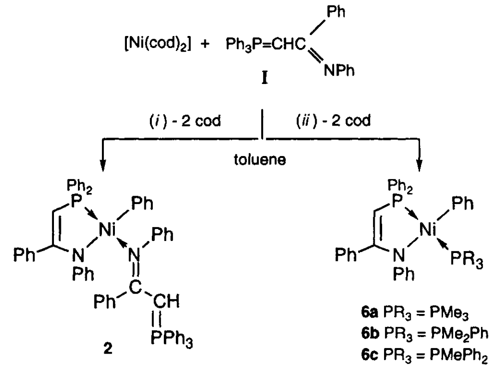
[a] *Laboratoire de Chimie de Coordination, Associé au CNRS (URA 416), Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg Cédex, France*
[b] *Institut Français du Pétrole, BP 311, F-92506 Rueil-Malmaison, France*
[c] *Laboratoire de Cristallochimie et de Chimie Structurale, Associé au CNRS (URA 424), Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg Cédex, France*

The complexes $[NiPh\{Ph_2PCH{\cdots}C({\cdots}NPh)Ph\}\{Ph_3P{=}CHC({=}NPh)Ph\text{-}N\}]$ and $[NiPh\{Ph_2PCH{\cdots}C({\cdots}NPh)Ph\}(PR_3)]$ (PR_3 = PMe_3, PMe_2Ph or $PMePh_2$) were prepared starting from $[Ni(cod)_2]$ (cod = cycloocta-1,5-diene) and the phosphorus ylide $Ph_3P{=}CHC({=}NPh)Ph$ **I** in the presence of a tertiary phosphine. Surprisingly, only the first complex was isolated when PPh_3 and $P(C_6H_{11})_3$ were used, whereas the other phosphines led to the corresponding PR_3 complexes together with variable amounts of the first depending on their steric demand. The known synthesis of **I** has been optimized to yields close to 90%. Experiments carried out to study the potential of the nickel compounds as catalysts for ethylene oligomerization showed the stoichiometric formation of styrene and minor amounts of low-molecular-weight linear α-olefins. The molecular structures of **I** and the first complex have been determined by X-ray diffraction. In the nickel complex the co-ordination around the metal is distorted square planar, with P(1)–Ni–C(1) and N(1)–Ni–N(2) angles of 90.30(8) and 97.18(8)°, respectively.

The oxidative addition of α-ketophosphorus ylides $Ph_3P{=}CR'C({=}O)R''$ to nickel(0) complexes such as $[Ni(cod)_2]$ (cod = cycloocta-1,5-diene), in the presence of a two-electron donor phosphine ligand, represents a key step in reactions leading to square-planar complexes containing both a Ni–C σ bond and a bidentate, three-electron donor P,O chelating ligand as in $[NiPh\{Ph_2PCH{\cdots}C({\cdots}O)Ph\}(PPh_3)]$ **1**.[2] This and related compounds are convenient precursors of the active species responsible for the catalytic oligomerization of ethylene into linear α-olefins, as in the Shell higher olefins process (SHOP).[2,3] The activity and selectivity (α-olefin distribution) of complexes of type **1** are strongly dependent on the electronic and steric effects of the substituents, the ring size of the chelate and the nature of the two-electron-donor ligand.[4] Since subtle modifications may be sufficient to change significantly the catalytic properties of these complexes, we were interested in modifying the environment of the nickel centre by using an α-iminophosphorus ylide reagent.

Results and Discussion

The α-iminophosphorus ylide $Ph_3P{=}CHC({=}NPh)Ph$ **I** (see Fig. 1) was prepared according to a published method,[5] which was modified to optimize the yield. Apparently, addition of methanol to the reaction mixture enhanced the reactivity of the sodium amide used to deprotonate the intermediate phosphonium salt and consequently led to yields of *ca.* 90%. In contrast to the published data, the signal for the CH proton appears in the ^1H NMR spectrum as a well resolved doublet with a coupling constant $^2J_{PH}$ of 26.9 Hz. The $^{31}P\text{-}\{^1H\}$ NMR signal was found at δ 11.1. Reaction of **I** with 1 equivalent of $[Ni(cod)_2]$ and 1 equivalent of PPh_3 or $P(C_6H_{11})_3$ in toluene under conventional conditions[2] gave a yellow-ochre product after usual work-up (see Scheme 1).



Scheme 1 (*i*) $+PPh_3$ or $P(C_6H_{11})_3$; (*ii*) PR_3

Recrystallization from a toluene–pentane mixture yielded the complex $[NiPh\{Ph_2PCH{\cdots}C({\cdots}NPh)Ph\}\{Ph_3P{=}CHC({=}NPh)Ph\text{-}N\}]$ **2** that was characterized by ^1H and ^{31}P NMR as well as by mass spectroscopy. The data are consistent with the result of the X-ray analysis (see Fig. 2). Unexpectedly, the tertiary phosphine ligand was not present in the slightly distorted square-planar complex, but instead an intact ylide molecule was bound to the nickel centre *via* the nitrogen atom of the imino moiety. When the reaction was conducted in the absence of PPh_3 or $P(C_6H_{11})_3$ compound **2** was not observed, but the starting materials were recovered and some decomposition occurred. A two-fold excess of the phosphorus ylide **I**, either in the presence or the absence of a phosphine, did not favour the formation of **2**. However, the presence of a two-electron donor other than a phosphine, *e.g.* pyridine (py), led to the formation of a small amount of **2**. A second minor compound was tentatively assigned to the expected $[NiPh\{Ph_2PCH{\cdots}C({\cdots}NPh)Ph\}(py)]$ **3**, but most of the starting phosphorane was recovered.

The formation of complex **2** instead of the corresponding

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* Complexes with functional phosphines. Previous papers, see ref. 1.

PPh_3 complex could suggest a better σ-donor capacity for the imino group in **I**, which would prevent co-ordination of the phosphine. This is, however, unlikely to be the case with the more basic $P(C_6H_{11})_3$ and is also not consistent with the following reactions which were monitored with ^{31}P NMR spectroscopy. Whereas PMe_3 instantaneously and quantitatively replaced the phosphine ligand in $[\overline{\text{NiPh}\{\text{Ph}_2\text{PCH}{\cdots}\text{C}({\cdots}\text{O})}\text{Ph}\}(\text{PR}_3)]$ [$PR_3 = PPh_3$ **1** or $P(C_6H_{11})_3$ **4**] at room temperature to form yellow $[\overline{\text{NiPh}\{\text{Ph}_2\text{PCH}{\cdots}\text{C}({\cdots}\text{O})}\text{Ph}\}(\text{PMe}_3)]$ **5**, no such substitution could be observed with the phosphorus ylide **I**, even at 45 °C. Furthermore, the ylide ligand in **2** was easily displaced by PMe_3 at room temperature to give unco-ordinated **I** and a mixture of uncharacterized products.

Thus the preferred formation of compound **2** in the presence of PPh_3 or $P(C_6H_{11})_3$ should be explained on steric grounds: these bulky phosphine ligands do not compete favourably with **I** for co-ordination to the nickel(II) centre. Since a phosphine ligand, including PPh_3 or $P(C_6H_{11})_3$, is always required for the reaction of **I** with $[Ni(cod)_2]$ to proceed, an essential step preliminary to the oxidative addition of the ylide to the nickel(0) compound must occur. This could be the generation of a reactive intermediate such as $[Ni(cod)(PR_3)_2]$,[6] capable of leading to P–C bond cleavage of **I**.

The reaction between equimolar amounts of compound **I**, $[Ni(cod)_2]$ and a phosphine PR_3 (PMe_3, PMe_2Ph or $PMePh_2$) under the conditions used for the synthesis of **2** yielded the corresponding nickel complexes $[\overline{\text{NiPh}\{\text{Ph}_2\text{PCH}{\cdots}\text{C}({\cdots}\text{N}}\text{Ph})\text{Ph}\}(\text{PR}_3)]$ ($PR_3 = PMe_3$ **6a**, PMe_2Ph **6b** or $PMePh_2$ **6c**) and, as a side product, **2**. The increasing cone angles of these phosphines[7] were directly reflected in the increasing amount of **2** that was formed during the reaction. The ^{31}P NMR spectra of the complexes **6** exhibit typical AB patterns with relatively high coupling constants of the order of 300 Hz.

The reactions of complexes **2**, **6a** and **6b** with ethylene under conventional conditions[4a] to form linear α-olefins as oligomerization products were disappointing. However, that quantitative insertion of ethylene into the Ni–Ph bond had occurred could be deduced from the styrene quantity found in the liquid phase together with traces of low-molecular-weight olefins (> 98% linear α-olefins; C_4–C_8 olefins, but oligomers up to C_{26} were observed for **6b**), thus indicating a very low catalytic activity. This could be due to an enhanced instability of the catalytically active nickel hydride species, which leads to rapid deactivation of the catalyst. This was also suggested by the following results. When a solution of **2** was treated with ethylene at room temperature in an NMR tube the typical resonances of olefinic oligomerization products could be observed in the ^1H NMR spectrum after 4 h. The reaction was finished after *ca.* 20 h, leaving most of the ethylene unreacted. The ^{31}P-{^1H} NMR spectrum of the final reaction mixture did not show any signal for the starting complex **2** or for any other nickel compound formed during oligomerization or decomposition. Instead, a dark precipitate formed in the NMR tube, which could not be identified, but was believed to contain the nickel introduced in the form of a compound (or mixture of compounds) insoluble in the solvent C_6D_6 and thus inactive for oligomerization reactions.

Crystal structure of $Ph_3P{=}CHC({=}NPh)Ph$ I

A view of the structure is shown in Fig. 1 and selected distances and angles are listed in Table 1. The crystal structure consists of discrete molecular units, separated by normal van der Waals contacts. The P–C(19) distance of 1.708(2) Å is much shorter than the P–Ph distances, consistent with an ylidic double-bond character. This value is also slightly shorter than in the related α-keto ylide $Ph_3P{=}CHC({=}O)Ph$ [1.716(5) and 1.723(5) Å].[8] The N–C(20) distance of 1.313(3) Å similarly reflects a double-bond character. The bond angles in the molecule are unexceptional, that at C(19) being 121.6(2)° and at N 122.1(2)°. The torsion angle P–C(19)–C(20)–N is 5.5(3)°.

Table 1 Selected bond lengths (Å) and angles (°) for compound **I**

P–C(1)	1.811(2)	C(19)–C(20)	1.411(3)
P–C(7)	1.820(2)	C(20)–N	1.313(3)
P–C(13)	1.801(2)	C(20)–C(27)	1.498(3)
P–C(19)	1.708(2)	N–C(21)	1.399(3)
C(1)–P–C(7)	105.1(1)	P–C(19)–C(20)	121.6(2)
C(1)–P–C(13)	108.7(1)	C(19)–C(20)–N	119.2(2)
C(1)–P–C(19)	113.2(1)	C(19)–C(20)–C(27)	117.4(2)
C(7)–P–C(13)	105.8(1)	N–C(20)–C(27)	123.4(2)
C(7)–P–C(19)	118.0(1)	C(20)–N–C(21)	122.1(2)
C(13)–P–C(19)	105.5(1)	N–C(21)–C(22)	123.8(2)

Numbers in parentheses are estimated standard deviations in the least significant digits.

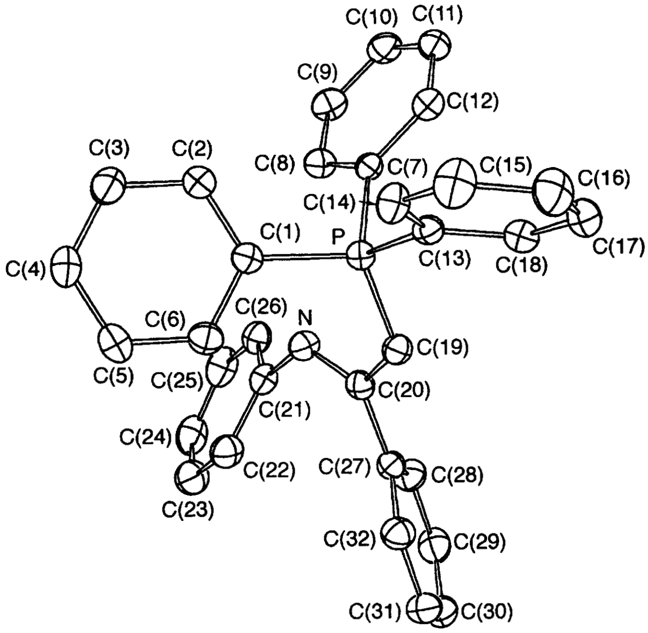

Fig. 1 View of the molecular structure of $Ph_3P{=}CHC({=}NPh)Ph$ **I**

Crystal structure of $[\overline{\text{NiPh}\{\text{Ph}_2\text{PCH}{\cdots}\text{C}({\cdots}\text{N}}\text{Ph})\text{Ph}\}\{\text{Ph}_3\text{P}{=}\text{CHC}({=}\text{NPh})\text{Ph-}N\}]$ 2

A view of the structure is shown in Fig. 2 and selected distances and angles are listed in Table 2. The crystal structure consists of discrete molecular units, separated by normal van der Waals contacts. The square-planar co-ordination around nickel is only slightly distorted and the metal is situated out of the plane defined by C(1), N(1), N(2) and P by 0.0709(4) Å; the five-membered $\overline{\text{Ni–P–C–C–N}}$ ring is nearly planar, owing to electron delocalization within the enamide moiety. The Ni–Ph distance of 1.906(3) Å is slightly longer than in $[\overline{\text{NiPh}\{\text{Ph}_2\text{PCH}{\cdots}\text{C}({\cdots}\text{O})}\{o\text{-C}_6\text{H}_4\text{NHPh}\}(\text{PPh}_3)]$ [1.886(3) Å], probably because of a stronger electron affinity of the P,O chelate in the latter complex.[4a] This effect was already proposed to explain an analogous shortening of the Ni–Ph bond in $[\overline{\text{NiPh}\{\text{Ph}_2\text{PCH}{\cdots}\text{C}({\cdots}\text{O})}\text{Ph}\}(\text{PPh}_3)]$ (1.893 Å) compared with related Ni–Ph compounds (1.96–2.00 Å).[2a] The phenyl ring makes an angle of 93.46(7)° with the metal co-ordination plane. The C(19)–C(20) and C(20)–N(1) distances are almost identical, which together with a short P(1)–C(19) bond, indicate π delocalization of the electrons within the metallacycle. An intact ylide molecule is co-ordinated *trans* to P(1), through the nitrogen atom N(2). The Ni–N(2) bond distance of 1.965(2) Å is not significantly different (within 3σ) from that of 1.974(2) Å for the Ni–N(1) bond. This

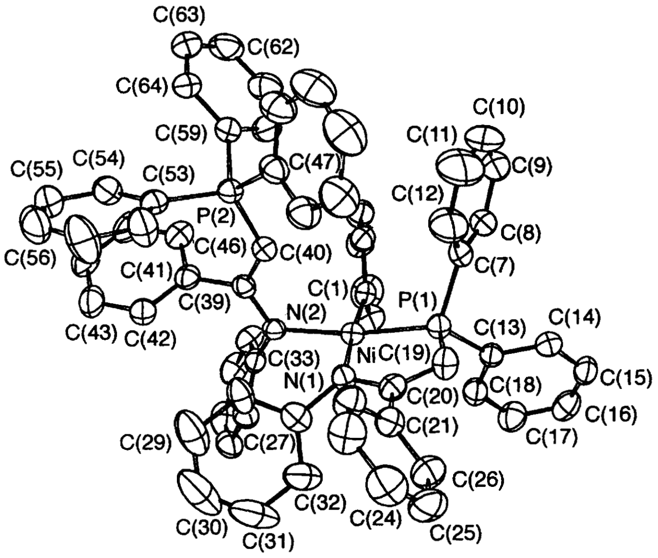

Fig. 2 View of the molecular structure of [NiPh{Ph_2PCH⋯C(⋯N-Ph)Ph}{Ph_3P=CHC(=NPh)Ph-*N*}] **2**

Table 2 Selected bond lengths (Å) and angles (°) for compound **2**

Ni–P(1)	2.1192(7)	C(20)–N(1)	1.358(3)
Ni–C(1)	1.906(3)	N(1)–C(27)	1.424(3)
Ni–N(1)	1.974(2)	P(2)–C(40)	1.705(3)
Ni–N(2)	1.965(2)	C(40)–C(39)	1.404(3)
P(1)–C(19)	1.748(3)	C(39)–N(2)	1.324(3)
C(19)–C(20)	1.368(4)	N(2)–C(33)	1.428(3)
P(1)–Ni–C(1)	90.30(8)	N(1)–Ni–N(2)	97.18(8)
P(1)–Ni–N(1)	85.62(6)	P(1)–C(19)–C(20)	113.5(2)
P(1)–Ni–N(2)	171.88(6)	C(19)–C(20)–N(1)	120.2(2)
C(1)–Ni–N(1)	175.92(9)	C(20)–N(1)–Ni	118.0(2)
C(1)–Ni–N(2)	86.85(9)		

suggests a strong co-ordination to the metal centre, although the NPh donor group of the chelate is characterized by a larger steric demand compared to that of a phosphinoenolate oxygen donor in related nickel complexes.[2a,4a] The N(2)–C(39) bond of 1.324(3) Å retains a strong double-bond character and is not significantly (within 3σ) elongated when compared to the free ylide [1.313(3) Å]. As expected, the P(2)–C(40) distance of 1.705(3) Å is similar to that in the free ylide [1.708(2) Å]. The N(2) and P(2) atoms are oriented differently about the C(39)–C(40) axis than in the free ylide. This is probably the result of steric effects. The C(39)–N(2)–Ni plane makes an angle of 9.8(4)° with the P(2)–C(40)–C(39) plane and of 89.9(1)° with the metal co-ordination plane.

Experimental

Reagents and physical measurements

All operations were performed in Schlenk-type flasks under high-purity argon, using vacuum-line techniques. The solvents were purified and dried under argon by conventional methods. The ^1H NMR spectra were recorded at 200 MHz on a Bruker AC 200 F, the ^{31}P-{^1H} NMR spectra at 81 MHz on a Bruker CXP 200 spectrometer. All spectra were recorded at room temperature. The ^1H and ^{31}P shifts are given relative to internal $SiMe_4$ and external H_3PO_4, respectively. A positive sign denotes a shift downfield from that of the reference. The electron-impact (EI) mass spectrum (70 eV, *ca.* 1.12 × 10^{-17} J) of compound **2** was recorded on a Fisons ZAB-HF spectrometer. Reactions with ethylene were performed in a double-walled stainless-steel autoclave (130 cm^3), 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) using a temperature program from 35 to 270 °C. The phosphines were obtained from Aldrich and used without further purification except degassing of the liquid ones. High-purity ethylene from Air Liquide was used as received.

Synthesis

The complexes [Ni(cod)$_2$][9] and [NiPh{Ph_2PCH⋯C(⋯O)Ph}-(PPh_3)][2a] were prepared according to the literature.

Ph_3P=CHC(=NPh)Ph I. The salt [$PMePh_3$]Br (14.2 g, 39.8 mmol) and $NaNH_2$ (4.29 g, 110 mmol) were suspended in benzene (150 cm^3) and two or three drops of absolute methanol were added. The mixture was stirred at ambient temperature for 24 h, filtered and the evolved NH_3 removed *in vacuo*. The yellow solution of Ph_3P=CH_2 was treated with ClC(NPh)Ph (3.72 g, 17.2 mmol) in benzene (30 cm^3) and stirred for 2 h, while moderate warming and the precipitation of a solid were observed. Subsequent addition of charcoal, filtration and evaporation of the solvent afforded the crude product, which was redissolved in boiling $CHCl_3$ (90 cm^3). After addition of pentane (350 cm^3), the mixture was cooled to -18 °C and the yellow, air-stable solid was isolated, washed with pentane (2 × 25 cm^3) and dried *in vacuo*. Yield: 6.89 g (88%) (Found: C, 84.0; H, 5.6; N, 2.9. $C_{32}H_{26}NP$ requires C, 84.40; H, 5.75; N, 3.05%). NMR ($CDCl_3$): ^1H, δ 7.9–6.1 (25 H, aromatic H) and 3.25 (d, 1 H, $^2J_{PH}$ = 26.9 Hz, P=CH); ^{31}P-{^1H}, δ 11.1 (s).

[NiPh{Ph_2PCH⋯C(⋯NPh)Ph}{Ph_3P=CHC(=NPh)Ph-*N*}] 2. A cold solution of [Ni(cod)$_2$] (0.43 g, 1.6 mmol) in toluene (30 cm^3) was added slowly to a suspension of PPh_3 (0.42 g, 1.6 mmol) and Ph_3P=CHC(=NPh)Ph (0.73 g, 1.6 mmol) in toluene (20 cm^3) at 0 °C. The suspension became immediately dark red and acquired a dark brown tint within 1–2 h. After stirring at room temperature for 20 h the mixture was heated to 50 °C for 2 h and subsequently the solvent was removed *in vacuo*. The dark residue was taken up in toluene (10 cm^3), the brown solution filtered and then pentane (180 cm^3) was added. A precipitate was isolated from the cooled (-18 °C) solution, washed with pentane (2 × 25 cm^3) and dried *in vacuo*, affording the yellow-ochre product **2**. Single crystals suitable for X-ray diffraction were obtained from toluene–pentane. Yield: 0.43 g (28%) (Found: C, 78.2; H, 5.2; N, 2.5; Ni, 5.7; P, 7.6. $C_{64}H_{52}N_2NiP_2$ requires C, 79.30; H, 5.40; N, 2.90; Ni, 6.05; P, 6.40%). NMR (C_6D_6): ^1H, δ 8.0–6.1 (50 H, aromatic H), 4.57 (br, 1 H, PCH) and 3.52 (d, 1 H, $^2J_{PH}$ = 25.2 Hz, P=CH); ^{31}P-{^1H}, δ 27.5 (s, Ph_2P) and 7.4 (s, Ph_3P=). Mass spectrum (EI): *m/z* 968 (M^+), 891 (M^+ − Ph), 513 (M^+ − **I**), 436 (M^+ − Ph − **I**) and 455 (**I**$^+$).

[NiPh{Ph_2PCH⋯C(⋯O)Ph}{P(C_6H_{11})$_3$}] 4. As described for the synthesis of compound **2**, **4** was obtained from the reaction of [Ni(cod)$_2$] (0.42 g, 1.6 mmol), P(C_6H_{11})$_3$ (0.45 g, 1.6 mmol) and Ph_3P=CHC(=O)Ph (0.62 g, 1.6 mmol) in toluene. Yield: 1.08 g (94%) (Found: C, 72.9; H, 7.4. $C_{44}H_{54}NiOP_2$ requires C, 73.45; H, 7.55%). NMR (C_6D_6): ^1H, δ 8.2–6.6 (20 H, aromatic H), 5.18 (s, 1 H, PCH) and 2.2–1.0 [33 H, P(C_6H_{11})$_3$]; ^{31}P-{^1H}, AB spin system, δ_A 19.7 (d, Ph_2P) and δ_B -14.1 [d, P(C_6H_{11})$_3$], $^2J_{AB}$ = 270 Hz.

[NiPh{Ph_2PCH⋯C(⋯O)Ph}(PMe_3)] 5. About 80 μmol of [NiPh{Ph_2PCH⋯C(⋯O)Ph}(PR_3)] [PR_3 = PPh_3 **1** or P(C_6H_{11})$_3$ **4**] were dissolved in C_6D_6 (1.5 cm^3) and the ^{31}P NMR spectrum recorded. Then an equimolar amount of PMe_3 was added at room temperature and the spectrum of the resulting mixture was recorded. The signals of the starting materials had disappeared, while those of **5** together with the signals of free PPh_3 and $P(C_6H_{11})_3$, respectively, could be observed. $^{31}P\text{-}\{^1H\}$ NMR (C_6D_6): δ 16.3 (br, Ph_2P) and −16.3 (br, PMe_3).

$[\overline{NiPh\{Ph_2PCH\cdots C(\cdots NPh})Ph\}(PR_3)]$ ($PR_3 = PMe_3$ 6a, PMe_2Ph 6b or $PMePh_2$ 6c). As described for compound **2**, $[Ni(cod)_2]$ was treated with equimolar amounts of the phosphine and $Ph_3P{=}CHC({=}NPh)Ph$ in toluene and the work-up was performed as described above. The impure products were isolated as yellow powders. Compound **6a**: NMR (C_6D_6), ^1H, δ 8.1–6.3 (aromatic H), 4.42 (br, PCH) and 0.33 (d, br, $^2J_{PH} \approx 9$, PMe_3); $^{31}P\text{-}\{^1H\}$, AB spin system, δ_A 16.6 (d, Ph_2P) and δ_B −25.9 (d, PMe_3), $^2J_{AB} = 296$. Compound **6b**: $^{31}P\text{-}\{^1H\}$ NMR (C_6D_6), AB spin system, δ_A 17.1 (d, Ph_2P) and δ_B −12.9 (d, PMe_2Ph), $^2J_{AB} = 300$. Compound **6c**: $^{31}P\text{-}\{^1H\}$ NMR (C_6D_6), AB spin system, δ_A 16.6 (d, Ph_2P) and δ_B −0.9 (d, $PMePh_2$), $^2J_{AB} = 301$ Hz.

Reactions with ethylene

About 50 μmol of the nickel complexes **2**, **6a** or **6b** were dissolved in toluene (20 cm^3), transferred by cannula to an autoclave and stirred under 0.5 MPa ethylene for 16 h. The temperature and pressure were then increased to the standard conditions 80–90 °C and 6 MPa. After 2–3 h the autoclave was cooled to ambient temperature, the pressure released and the products analysed.

A solution of compound **2** (*ca.* 15 μmol) in C_6D_6 (0.5 cm) was transferred to a NMR tube equipped with a pressure-inlet valve and 0.5 MPa ethylene was introduced at ambient temperature. Proton NMR spectra were recorded and showed the slow appearance of characteristic signals of olefinic oligomers. At the end of the reaction the ^{31}P NMR spectrum was recorded overnight. No signals of complex **2** or new nickel compounds could be observed. The light brown solution contained a dark precipitate, which could not be identified.

Crystallography

For both compounds **I** and **2** data were collected on a Philips PW 1100/16 diffractometer using Cu-Kα graphite-monochromated radiation (λ = 1.5418 Å), by flying step-scan. The structures were solved using direct methods and refined against $|F|$. Hydrogen atoms were introduced as fixed contributors. Empirical absorption corrections. For all computations the Enraf-Nonius MOLEN package[10] was used.

Crystal data for compound I. Yellow crystals, data collected at −100 °C (crystal dimensions 0.12 × 0.14 × 0.20 mm), $C_{32}H_{26}NP$, $M = 455.5$, monoclinic, space group $C2/c$, $a = 27.156(8)$, $b = 9.027(3)$, $c = 22.231(7)$ Å, $\beta = 118.51(2)°$, $U = 4788.8$ Å^3, $Z = 8$, $D_c = 1.264$ g cm^{-3}, μ(Cu-Kα) = 11.444 cm^{-1}.

A total of 2734 reflections was collected, $6 < 2\theta < 100°$, 2007 having $I > 3\sigma(I)$. Transmission factors: 0.85, 1.00. 307 Parameters. Final $R(F) = 0.027$, $R'(F) = 0.045$, goodness of fit = 1.042, maximum residual electron density = 0.06 e Å^{-3}.

Crystal data for compound 2. Orange crystals, data collected at −100 °C (crystal dimensions 0.24 × 0.32 × 0.38 mm), $C_{64}H_{52}N_2NiP_2$, $M = 969.8$, monoclinic, space group $P2_1/c$, $a = 11.499(3)$, $b = 20.758(6)$, $c = 22.216(7)$ Å, $\beta = 98.89(2)°$, $U = 5239.2$ Å^3, $Z = 4$, $D_c = 1.229$ g cm^{-3}, μ(Cu-Kα) = 14.094 cm^{-1}.

A total of 5912 reflections was collected, $6 < 2\theta < 102°$, 4710 having $I > 3\sigma(I)$. Transmission factors: 0.66, 1.00. 622 Parameters. Final $R(F) = 0.032$, $R'(F) = 0.054$, goodness of fit = 1.268, maximum residual electron density = 0.08 e Å^{-3}.

For both structures, all non-hydrogen atoms were refined anisotropically. The hydrogen atoms were calculated and fixed in idealised positions ($d_{C\text{-}H} = 0.95$ Å, $B_H = 1.3\ B_{equiv}$ for the carbon to which it was attached). Full least-squares refinements; $w = 1/\sigma^2(F^2)$; $\sigma^2(F^2) = \sigma^2_{counts} + (pI)^2$.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/165.

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