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Synthesis of nickel phenyl complexes with new chelating κ^2-*P*,*N* ligands derived from α-iminoazatriphenylphosphoranes[1]

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Abstract

Reactions of the phosphorus ylide $Ph_3P{=}NC({=}NPh)Ph$ (**3**), conveniently prepared in high yield from Ph_3PNLi and $ClC({=}NPh)Ph$, with $[Ni(COD)_2]$ in the presence of a tertiary phosphine yielded the complexes $[NiPh\{Ph_2PN{=}C(NPh)Ph\}\{NPh[{=}CPh(N{=}PPh_3)]\}]$ (**5**) and $[NiPh\{Ph_2PN{=}C(NPh)Ph\}(PR_3)]$ ($PR_3 = PMe_3$ (**6a**), PMe_2Ph (**6b**), $PMePh_2$ (**6c**)) which result from oxidative addition of a P–Ph bond to the Ni(0) centre. When $PTol_3$ was used, only **5** could be isolated, whereas the other phosphines led to the corresponding complexes **6a–c** together with varying amounts of **5** depending on their steric demand. Reaction of the *N*-methylated phosphorus ylide $Ph_3P{=}N{-}C[{=}N(o\text{-}C_6H_4)NMe]$ (1-methyl-2-(triphenylphosphoranylideneamino)benzimidazole (**7**)) with $[Ni(COD)_2]$ in the presence of $PTol_3$ gave the complex $[NiPh\{Ph2PN{=}C[N(o\text{-}C_6H_4)NMe]\}(PTol_3)]$ (**9**). No such reaction was observed for the non-methylated analogue $Ph_3P{=}N{-}C[{=}N(o\text{-}C_6H_4)NH]$ (2-(triphenylphosphoranylideneamino)benzimidazole (**8**)), but a dinuclear complex with *N*,*N* bridging ligands formulated as $[Ni_2\{Ph_3P{=}N{-}C[{=}N(o\text{-}C_6H_4)N]\}_4$ (**10**) was formed. Experiments to study the potential of the nickel compounds as catalysts for ethylene oligomerization were disappointing and only the formation of styrene and minor amounts of low molecular weight linear α-olefins was observed. The structure of $[Ph_3P{=}NC({=}NPh)Ph]\cdot HCl$ (**3**·HCl) has been determined by X-ray diffraction: monoclinic, space group $P2_1/n$, 13.137(3), $b = 14.942(4)$, $c = 13.9444(4)$ Å, $\beta = 90.13(2)°$, $V = 2737.2$ Å^3, $Z = 4$. The structure was solved (direct methods) by using 2209 reflections with $I > 3\sigma$ (I) out of 6028 unique reflections and refined (full-matrix least-squares) to $R(F) = 0.048$, $Rw(F) = 0.068$. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Phosphorus ylides; Azaphosphoranes, P–C bond activation; (*P*,*N*)-chelates; Ethylene insertion; Crystal structure; Imidazole; Bridging ligand

1. Introduction

Whereas nickel complex containing chelating *P*,*O* or *O*,*O* ligands are well-known catalysts for olefin oligomerization [3–6], polymerization [6–8] and co-polymerization [8,9], only few systems with an *N* donor group in the chelate have been investigated up to now [10]. Previously we have shown that the oxidative addition of an α-iminophosphorus ylide to $[Ni(COD)_2]$ in the presence of a two-electron donor ligand leads to the formation of square planar complexes of the type $[NiPh\{Ph_2PCH{=}C(NPh)PH\}(L)]$ ($L = NPh[{=}CPh(CH{=}PPh_3)]$ (**1a**), PMe_3 (**1b**), PMe_2Ph (**1c**), $PMePh_2$ (**1d**)) [1]. This reaction is analogous to that used by Keim [3,4] for the synthesis of complexes such as $[NiPh\{Ph_2PCH{=}C(O)Ph\}(PPh_3)]$ (**2**) from the corresponding α-ketophosphorus ylides and an Ni(0) com-

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[1] Complexes with functional phosphines. Previous papers, see Refs [1,2].

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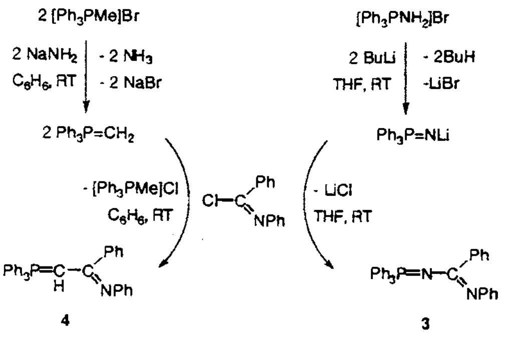
pound. Complex **2** belongs to a family of molecules considered to be precursors of the active species involved in the catalytic oligomerization of ethylene into linear α-olefins in the Shell Higher Olefins Process (SHOP) [11]. The activity and selectivity (α-olefin distribution) of these catalysts can be influenced by variation of the heteroatoms, the electronic and steric effects of the substituents, the ring size of the chelate and the nature of the two-electron donor ligand [7,8,10,12,13]. These results prompted us to modify the environment of the nickel centre, using as ligand precursors the α-(*N*-phenyl,benzylimino)azatriphenylphosphorane $Ph_3P{=}NC({=}NPh)Ph$ (**3**) and the two benzimidazole derivatives 1-methyl-2-(triphenylphosphoranylideneamino)benzimidazole $Ph_3P{=}N{-}C[{=}N(o\text{-}C_6H_4)NMe]$ (**7**) and 2-(triphenylphosphoranylideneamino)benzimidazole $Ph_3P{=}N{-}C[{=}N(o{-}C_6H_4)NH]$ (**8**), respectively.

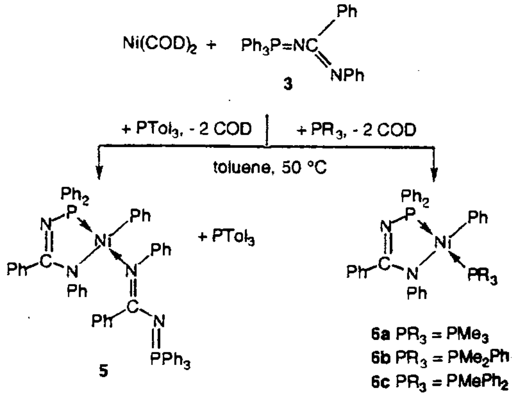
2. Results and discussion

The synthesis of (α-acyl)azatriphenylphosphoranes $Ph_3P{=}NC({=}O)R$ (R = Me, Et, Bu, Ph, CCl_3, $CClF_2$, CF_3) from the *N*-lithiated triphenylphosphine imide and a carbonyl reagent has been recently developed, making use of the high reactivity of the in situ generated $Ph_3P{=}NLi$ towards the acyl compound [14]. The yields obtained in this reaction typically range from 70 to 90%. Employing a modified procedure, the α-(*N*-phenyl,benzylimino)triphenylphosphorane $Ph_3P{=}NC({=}NPh)Ph$ (**3**) was obtained in a manner similar to that used for its isoelectronic analogue $Ph_3P{=}CHC({=}NPh)Ph$ (**4**) [15]. This procedure yielded **3** in a much more convenient manner and in higher yield than reported before (see Scheme 1, [16]).

At the end of the reaction, the destruction of residual BuLi with aqueous 10% HBr led to the formation of the hydrobromide adduct of the phosphorus ylide **3**, which was isolated as bright yellow crystals from CH_2Cl_2/pentane. Analytically pure **3** was obtained from **3**·HBr by treatment with solid NaOH. In addition to their characterization by elemental analysis, ^1H and ^{31}P NMR spectroscopy, the molecular structure of **3**·HCl was determined by X-ray diffraction. Crystals of the latter were formed after slow crystallization from $CHCl_3$/pentane, during which time Cl for Br exchange occurred. Obviously, **3**·HCl may also be formed directly from **3**.



Scheme 1.



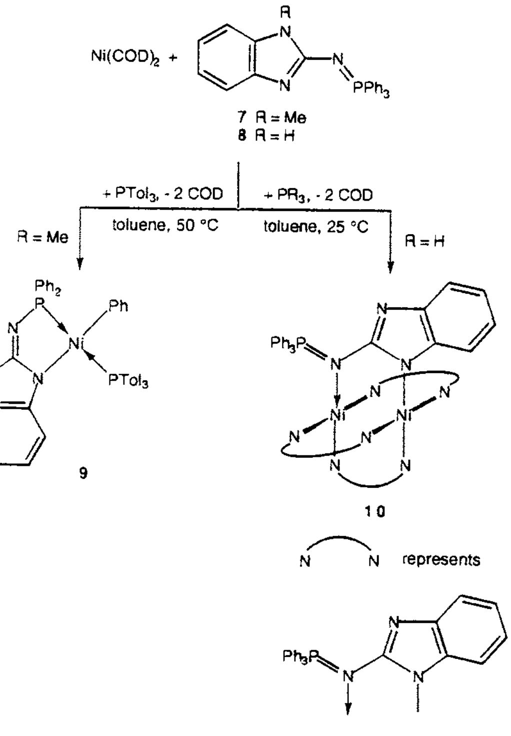
Scheme 2.

Reaction of **3** with equivalent amounts of $[Ni(COD)_2]$ and $PTol_3$ in toluene under the usual conditions [3,4] gave the yellow complex $[NiPh\{Ph_2PN{=}C(NPh)Ph\}\{NPh[{=}CPh(N{=}PPh_3)]\}]$ (**5**) after work-up. Recrystallization from a toluene/pentane mixture gave the product in 45% yield. It was characterized by ^1H and ^{31}P NMR spectroscopy as well as mass spectroscopy and elemental analysis. These data are in agreement with the results found previously for the reaction of **4** under similar conditions [1], but the singlet in the ^{31}P NMR spectrum assigned to the PPh_2 donor group of the chelate is remarkably downfield shifted at δ 78.9 in **5** compared with δ 27.5 in **1a**. In agreement with recent unexpected findings [1], the tris(*p*-tolyl)phosphine ligand was not present in the complex, but was replaced by an intact ylide molecule. Coordination of this ligand to the nickel centre occurs via the nitrogen atom of the imino moiety, as was observed for **1a**. The nearly quantitative formation, based on the phosphorus ylide, of **5** may be due to the good solubility of **3** in toluene, which is not the case for the related $Ph_3P{=}CHC({=}NPh)Ph$ (**4**), thus leading to side reactions in the heterogeneous reaction mixture (see Scheme 2).

In analogous reactions, the nickel complexes $[NiPh\{Ph_2PN{=}C(NPh)Ph\}(PR_3)]$ ($PR_3 = PMe_3$ (**6a**), PMe_2Ph (**6b**), $PMePh_2$ (**6c**)) were synthesized from equimolar amounts of **3**, $[Ni(COD)_2]$ and PR_3 ($PR_3 = PMe_3$, PMe_2Ph, $PMePh_2$) in yields up to 50%. As already observed for the phosphorus ylide **4**, the increasing cone angles of these phosphines [17] were directly reflected in the increasing amount of **5** that was formed during the reaction. The competition between **3** and PR_3 for coordination to the Ni centre, which leads to **5** or **6** respectively, is therefore strongly dependent on steric factors. Complexes **6a–c** were characterized by their ^{1}H and ^{31}P NMR spectra, mass spectroscopy and elemental analysis. Their ^{31}P NMR spectra exhibit typical AB patterns with coupling constants in the range 280–290 Hz. The signals due to the PPh_2 donor goup of the chelates appear around 70 ppm. This value is smaller than that observed for **5**, owing to the stronger σ-donor capacity of the phosphine ligands compared with **3**. The phosphorus donor of the isoelectronic chelate in complex **1b–d** resonates at ca. 17 ppm [1], thus indicating significant changes in the electronic structure of the metallacycle in **5** and **6a–c** compared with that in **1**.

In contrast to the reactions between the phosphorus ylides **3** or **4**, $[Ni(COD)_2]$ and bulky phosphines PPh_3 or $PTol_3$, the *N*-methylated benzimidazole derivative $Ph_3P{=}N{-}C[{=}N(o\text{-}C_6H_4)NMe]$ (**7**) yielded the complex $[NiPh\{Ph_2PN{=}C[N(o\text{-}C_6H_4)NMe]\}(PTol_3)]$ (**9**) which contains the phosphine ligand. This would be consistent with the *N*(sp^2) donor function part of the imidazole ring being a weaker ligand than **3**. Unfortunately, attempts to crystallize complex **9** only gave crystals of insufficient quality for X-ray diffraction (see Scheme 3).

When the non-methylated benzimidazole derivative $Ph_3P{=}N{-}C[{=}N(o\text{-}C_6H_4)NH]$ (**8**) was used as reagent, no complex similar to **9** could be observed. ^{31}P NMR and mass spectroscopy data tentatively allowed the identification of a binuclear nickel compound $[Ni_2\{Ph_3P{=}N{-}C[{=}N(o\text{-}C_6H_4)N]\}_4]$ (**10**) formed by oxidative addition of NH groups to the Ni(0) centres and presumably bridged by *N*,*N* bidentate ligands. This oxidative addition reaction requires the presence of a phosphine, e.g. PPh_3, in the reaction mixture, although this ligand is not incorporated in the final product. Related observations have been made previously for the synthesis of **1a** [1]. Compound **10** was not formed by the reaction of a solution of two equivalents of **8** or $K[Ph_3P{=}N{-}C\{{=}N(o\text{-}C_6H_4)N\}]$ with an Ni(II) salt, e.g. $Ni(MeCO_2)(BuEtCHCO_2)$, in methanol at room temperature. At the end of the reaction, only the starting materials were recovered.



Scheme 3.

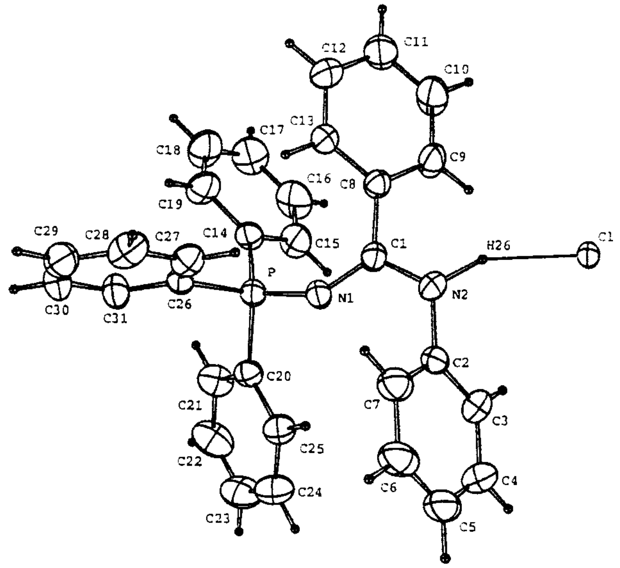


Fig. 1. View of the molecular structure of $[Ph_3P{=}NC({=}NPh)Ph]\cdot HCl$ ($3\cdot HCl$).

Complexes **5**, **6a**, **6b** and **9** were reacted with ethylene under the usual conditions [12], but the results obtained were disappointing. However, that insertion of ethylene into the Ni–Ph bond had occurred could be deduced from the styrene found in the liquid phase together with traces of low molecular weight olefins (greater than 98% linear α-olefins; C_4–C_6 olefins), thus indicating an extremely low catalytic activity. Taking into account recent observations [1], this should be due to the instability of the catalytically active nickel hydride.

2.1. *Crystal structure of* **3**·*HCl*

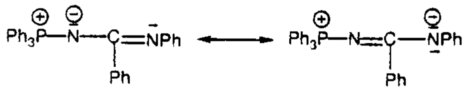
A view of the molecular structure is shown in Fig. 1 and selected distances and angles are given in Table 1.

The P=N(1)–C(1)=N(2) system is almost planar (torsion angle 158.4(4)°) and adopts an s-*trans* conformation. It is interesting to compare this structure with that of the recently reported isoelectronic ligand $Ph_3P{=}CHC({=}NPh)Ph$ [1]. In the latter, the almost planar P=C–C=N system adopts an s-*cis* conformation, not encountered here probably because of the presence of the N(2)···H(26)···Cl moiety. The P–N(1) and C(1)–N(2) distances of 1.590(3) and 1.341(5) Å, respectively clearly indicate the double bond character of these

Table 1
Selected bond distances (Å) and angles (deg) for **3**·HCl

P	N1	1.590 (3)	
P	C14	1.785 (4)	
P	C20	1.800 (4)	
P	C26	1.793 (4)	
N1	C1	1.308 (5)	
C1	N2	1.341 (5)	
C1	C8	1.483 (6)	
N2	C2	1.436 (5)	
N1	P	C14	118.4 (2)
N1	P	C20	106.1 (2)
N1	P	C26	107.4 (2)
C14	P	C20	105.3 (2)
C14	P	C26	110.2 (2)
C20	P	C26	109.1 (2)
P	N1	C1	136.2 (3)
N1	C1	N2	118.2 (3)
N1	C1	C8	124.1 (4)
N2	C1	C8	117.6 (4)
C1	N2	C2	122.4 (3)

Numbers in parentheses are estimated S.D. in the least significant digits.



Scheme 4.

bonds. The former is shorter than the corresponding P=CH distance in the Ph_3P=CHC(=NPh)Ph (1.708(2)Å), as expected in view of the greater electronegativity of nitrogen. Similarly, the N(1)–C(1) distance of 1.308(5)Å is shorter than the corresponding =CH–C distance in Ph_3P=CHC(=NPh)Ph (1.411(3)Å). The longer C(1)–N(2) distance compared with that in Ph_3P=CHC(=NPh)Ph (1.313(3)Å) reflects the protonation of N(2). Proton H(26) was found by Fourier differences and the H(26)–Cl distance is 2.112(1)Å whereas the N(2)···Cl separation is 3.174(4)Å. Phosphorus ylides having an electron-withdrawing group in the α-position are stabilized because the negative charge is delocalized by resonance (see Scheme 4).

This simple picture is also clearly consistent with the site of protonation observed for **3**.

3. Experimental

3.1. 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 at 81 MHz on a Bruker CXP 200. All spectra were recorded at room temperature. ^1H and ^{31}P shifts are given relative to internal TMS and external H_3PO_4, respectively. A positive sign denotes a shift downfield from that of the reference. 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 analyzed 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 form 35–270°C. BuLi (1.6 mol l^{-1}) and the phosphines were purchased from Aldrich and used as received except for degassing of the liquid phosphines. High purity ethylene was purchased from Air Liquide and used without further purification.

3.2. Synthesis

[Ni(COD)$_2$] [18], [Ph_3PNH_2]Br [14], ClC(NPh)Ph [19], Ph_3P=N–C[=N(*o*-C_6H_4)NMe] (**7**) [20] and Ph_3P=N–C[=N(*o*-C_6H_4)NH] (**8**) [20] were synthesized according to the published methods.

*3.2.1. [Ph$_3$P=NC(=NPh)Ph]·HBr(**3**·HBr)*

A volume of 12.6 ml (20.2 mmol) ^{n}BuLi in hexane was added slowly to a stirred suspension of 3.61 g (10.1 mmol) [Ph_3PNH_2]Br in 120 ml THF at −10°C. After stirring for 1 h at −10°C, the pale yellow clear solution was treated with a cold solution of 2.18 g (10.1 mmol) ClC(=NPh)Ph in 30 ml THF. The resulting orange solution was allowed to warm to ambient temperature and stirred under exclusion of light for 40 h. Then 7.4 g (20.2 mmol) 10% HBr was added dropwise to the light yellow solution at 0°C (exothermic reaction!). Subsequently, the cloudy mixture was treated with 45 ml CH_2Cl_2 and 70 ml H_2O, the layers separated and the aqueous phase was washed with 2 × 45 ml CH_2Cl_2. The combined organic extracts were washed with 2 × 60 ml sat. NaBr, dried over Na_2SO_4 and evaporated. The crude product was recrystallized from CH_2Cl_2/petane to yield **3**·HBr as bright yellow crystals, which were washed with 2 × 10 ml pentane and dried in vacuo, Yield 4.52 g (83%). Anal. Found: C, 69.35; H, 5.37; N, 5.22; P, 5.92. $C_{31}H_{26}BrN_2P$ (537.4) Calc.: C, 69.28; H, 4.88; N, 5.21; P, 5.76%. ^1H NMR ($CDCl_3$): δ 12.5 (br, 1H, NH), 8.1–6.7 (25H, aromatic H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 16.6 (s).

*3.2.2. [Ph$_3$P=NC(=NPh)Ph]·HCl (**3**·HCl)*

Single crystals suitable for X-ray diffraction were first obtained, unexpectedly, by slow recrystallization of **3**·HBr from $CHCl_3$/pentane. The were reproducibly obtained by slow addition of excess 10% HCl to a solution of **3** (see below) in THF. Anal. Found: C, 74.3;

H, 5.2; N, 5.0. $C_{31}H_{26}ClN_2P$ (493.0) Calc.: C, 75.53; H, 5.31; N, 5.68%. Spectroscopic data are identical with those of **3**·HBr.

3.2.3. Ph_3P=NC(=NPh)Ph (**3**)

A solution of 2.83 g (5.3 mmol) **3**·HBr in 25 ml CH_2Cl_2 was stirred with 0.68 g (17.0 mmol) powdered NaOH for 4 h at ambient temperature. After filtration, the solvent was removed in vacuo to give the analytically pure product. Yield 2.45 g (> 98%). Anal. Found: C, 80.86; H, 5.50; N, 6.03; P, 6.83. $C_{31}H_{25}N_2P$ (456.5) Calc.: C, 81.56; H, 5.52; N, 6.14; P, 6.78%. ^1H NMR ($CDCl_3$): δ 8.2–6.1 (aromatic H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 14.9 (s).

3.2.4. [NiPh{Ph_2PN=C(NPh)Ph}{NPh[=CPh(N=PPh_3)]}] (**5**)

A cold solution of 0.30 g (1.1 mmol) [Ni(COD)$_2$] in 20 ml toluene was added slowly to a solution of 0.33 g (1.1 mmol) $PTol_3$ and 0.50 g (1.1 mmol) Ph_3P=NC(=NPh)Ph in 15 ml toluene at 0°C. The mixture became dark red immediately. After stirring for 16 h at room temperature, the clear red solution was heated to 50°C for 2 h and subsequently the solvent was removed in vacuo. The dark residue was taken up in 10 ml toluene, the brown solution filtered and 100 ml pentane was added. The fluffy yellow precipitate was filtered off, washed with 2 × 5 ml pentane and dried in vacuo. A second crop of **5** could be isolated from the solution after cooling to − 18°C. Yield 0.46 g (45%). ^1H NMR (C_6D_6): 8.4–6.1 (aromatic H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 78.9 (s), 3.4 (s). MS (EI): *m*/*e* 971 [M^+], 894 [M^+ − Ph], 515 [M^+−**3**], 438 [M^+−Ph−**3**], 456 (**3**$^+$).

3.2.5. [NiPh{Ph_2PN=C(NPh)Ph}(PMe_3)] (**6a**)

A cold solution of 0.51 g (1.9 mmol) [Ni(COD)$_2$] in 30 ml toluene was added slowly to a solution of 197 µl (1.9 mmol) PMe_3 and 0.87 g (1.9 mmol) Ph_3P=NC(=NPh)Ph in 20 ml toluene at 0°C. The mixture became yellow/orange immediately and acquired an intense orange tint within 1 h. After 16 h stirring at room temperature, the clear yellow/brown solution was heated to 50°C for 2 h and subsequently the solvent was removed in vacuo The orange residue was taken up in 5 ml toluene, the brown solution filtered and 80 ml pentane was added. The fluffy yellow solid was filtered off and discarded. At − 18°C, orange crystals were precipitated from the solution. These were isolated, washed with 2 × 5 ml pentane and dried in vacuo. Yield 0.27 g (26%). Anal. Found: C, 68.34; H, 5.92; N, 4.52; P, 10.3. $C_{34}H_{34}N_2P_2Ni$ (591.3) Calc.: C, 69.06; H, 5.80; N, 4.74; P, 10.48%. ^1H MNR (C_6D_6): δ 8.3–6.1 (25H, aromatic H), 0.23 (d, $^2J_{PH} = 7.9$, 9H, PMe_3). $^{31}P\{^1H\}$ MNR (C_6D_6): AB spin system δ_A 68.7, δ_B −25.7 ($^2J_{AB} = 290.8$). MS (EI): *m*/*e* 591 [M^+], 514 [M^+−Ph], 515 [M^+−PMe_3], 438 [M^+−Ph−PMe_3].

3.2.6. [NiPh{Ph_2PN=C(NPh)Ph}(PMe_2Ph)] (**6b**)

As described for **6a**, 0.38 g (1.4 mmol) [Ni(COD)$_2$] in 25 ml toluene was reacted with a solution of 199 µl (1.4 mmol) PMe_2Ph and 0.64 g (1.4 mmol) Ph_3P=NC(=NPh)Ph in 20 ml toluene. The residue obtained at the end of the reaction was treated with 10 ml toluene and the suspension filtered. The solid was washed with 2 × 5 ml pentane and dried in vacuo to afford pure **6b**. Yield 0.45 g (50%). Anal. Found: C, 70.90; H, 5.65; N, 4.32; P, 9.27. $C_{39}H_{36}N_2P_2$ Ni (653.4) Calc.: C, 71.69; H, 5.55; N, 4.29; P, 9.48%. ^1H NMR (C_6D_6): δ 8.5–7.3 (30H, aromatic H), 1.42 (d, br, $^2J_{PH} \approx 8$, 6H, PMe_2Ph). $^{31}P\{^1H\}$ NMR (C_6D_6): AB spin system δ_A 68.4, δ_B − 12.9 ($^2J_{AB} = 285.3$). MS (EI): *m*/*e* 653 [M^+], 576 [M^+ − Ph], 515 [M^+−PMe_2Ph], 438 [M^+−Ph−PMe_2Ph].The by-product **5** could be precipitated from the solution by addition of 80 ml pentane. Yield 0.15 g (14%).

3.2.7. [NiPh{Ph_2PN=C(NPh)Ph}($PMePh_2$)] (**6c**)

As described for **6a**, 0.38 g (1.4 mmol) [Ni(COD)$_2$] in 25 ml toluene was reacted with a solution of 260 µl (1.4 mmol) $PMePh_2$ and 0.64 g (1.4 mmol) Ph_3P=NC(=NPh)Ph in 20 ml toluene. **6c** was obtained as the minor product in a mixture with **5**. $^{31}P^1H$ MNR (C_6D_6): AB spin system δ_A 66.0, δ_B 1.4 ($^2J_{AB} = 282.9$).

3.2.8. [NiPh{Ph_2PN= C[N(*o*-C_6H_4)NMe]}($PTol_3$)] (**9**)

As described for **6a**, 0.41 g (1.5 mmol) [Ni(COD)$_2$] in 30 ml toluene was reacted with a solution of 0.47 g (1.5 mmol) $PTol_3$ and 0.55 g (1.3 mmol) Ph_3P=N–C[=N(*o*-C_6H_4)NMe] in 20 ml toluene. Recrystallization from toluene/pentane gave the product, which still contained some of the starting phosphorane and $PTol_3$ due to their similar solubility properties. ^1H NMR (C_6D_6): δ 8.4–6.3 (aromatic H), 3.28 (s, br, NMe), 1.90 (s, br, PC_6H_4Me). $^{31}P\{^1H\}$ NMR (C_6D_6): AB spin system δ_A 67.6, δ_B 22.5 ($^2J_{AB} = 280.7$). MS (EI): *m*/*e* 770 [M^+], 693 [M^+ − Ph], 466 [M^+ − $PTol_3$], 389 [M^+ − Ph − $PTol_3$], 304 [$PTol_3^+$].

3.2.9. [Ni_2{Ph_3P=N–C[=N(*o*-C_6H_4)N]}$_4$] (**10**)

A cold soltion of 0.48 g (1.7 mmol) [Ni(COD)$_2$] in 30 ml toluene was added slowly to a suspension of 0.45 g (1.7 mmol) PPh_3 and 0.67 g (1.7 mmol) Ph_3P=N − C[=N(*o* − C_6H_4)NH] in 20 ml toluene at 0°C. The mixture became orange/brown immediately. After stirring for 24 h at room temperature, the brown mixture was filtered, the bright yellow solid washed with 2 × 5 ml pentane and dried in vacuo. Owing to similar solubility properties of some unidentified minor impurities, the product was not obtained in a pure form. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 68.0 (br). MS (EI): *m*/*e* 1684 [$Ni_2L_4^+$, not observed], 1160 [$Ni_2L_4^+$ − $2PPh_3$], 1292 [$Ni_2L_3^+$], 900 [$Ni_2L_2^+$], 842 [NiL_2^+], 392 [L^+].

3.2.10. *Reactions with ethylene*

About 0.1 mmol of the nickel complexes **5**, **6**, **6b** or **9** was dissolved in 20 ml toluene, transferred via a cannula to the autoclave and stirred under 0.5 MPa ethylene for 16 h. Then temperature and pressure were increased to the standard conditions 80–90°C and 6 MPa. After 4–5 h, the autoclave was cooled to ambient temperature, the pressure released and the products analyzed by gas phase chromatography.

3.3. *Collection of the X-ray data and structure determination for [Ph$_3$P=NC(=NPh)Ph)]·HCl (**3**·HCl)*

Single crystals suitable for X-ray diffraction were obtained from CHCl$_3$/pentane. Data were collected on a Nonius MACH-3 diffractometer using Mo–K$_\alpha$ $\theta/2\theta$ scans. The structure was solved using direct methods and refined against $|F|$. Hydrogen atoms were introduced as fixed contributors. Absorption corrections computed from the psi scans of four reflections. For all computations the Nonius MolEN package [21] was used.

3.3.1. *Crystal data for **3**·HCl*

Colourless crystals data collected at room temperature (crystal dimensions, $0.25 \times 0.25 \times 0.20$ mm^3): C$_{31}$H$_{26}$N$_2$PCl, $M = 493.0$, monoclinic, space group $P2_1/n$, $a = 13.137(3)$, $b = 14.942(4)$, $c = 13.944(4)$ Å, $\beta = 90.13(2)°$, $V = 2737.2$ Å^3, $Z = 4$, $D_c = 1.196$ g cm^{-3}, μ(Mo–K$_\alpha$) $= 2.154$ cm^{-1}. A total of 6026 reflections was collected, $2° < \theta < 26°$, 2209 reflections having $I > 3\sigma$(I). Absorption factors 0.96/1.00. 316 parameters. Final results R(F) $= 0.048$, Rw(F) $= 0.068$, GOF $= 0.251$, maximum residual electronic density 0.06 e Å^{-3}. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were introduced as fixed contributors ($d_{C-H} = 0.95$ Å, $B_H = 1.3B_{equiv}$(C) Å^2), with the exception of the NH proton located in a difference map. Atomic coordinates with their estimated standard deviations corresponding to the final least-squares refinement are given in Table 2.

Table 2
Positional parameters and their estimated S.D.

Atom	x	y	z	B (Å^2)
P	0.7817 (1)	0.06437 (9)	0.82636 (9)	3.34 (3)
N1	0.7204 (3)	0.0401 (3)	0.9210 (3)	3.68 (9)
C1	0.7037 (4)	0.0782 (3)	1.0040 (3)	3.5 (1)
N2	0.6759 (3)	0.0260 (3)	1.0778 (3)	3.9 (1)
C2	0.6689 (4)	−0.0696 (3)	1.0698 (3)	3.7 (1)
C3	0.7315 (5)	−0.1234 (4)	1.1240 (4)	5.2 (1)
C4	0.7220 (6)	−0.2151 (4)	1.1152 (4)	6.7 (2)
C5	0.6534 (6)	−0.2530 (4)	1.0559 (5)	6.6 (2)
C6	0.5908 (5)	−0.1991 (4)	1.0023 (4)	5.8 (2)
C7	0.5976 (4)	−0.1073 (4)	1.0092 (4)	4.8 (1)
C8	0.7086 (4)	0.1761 (3)	1.0209 (3)	3.5 (1)
C9	0.7485 (5)	0.2115 (4)	1.1049 (4)	5.2 (1)
C10	0.7538 (6)	0.3028 (4)	1.1168 (4)	6.6 (2)
C11	0.7195 (6)	0.3604 (4)	1.0479 (4)	6.7 (2)
C12	0.6791 (5)	0.3249 (4)	0.9645 (4)	5.8 (2)
C13	0.6743 (5)	0.2342 (4)	0.9519 (4)	4.4 (1)
C14	0.8597 (4)	0.1622 (3)	0.8268 (4)	3.7 (1)
C15	0.9361 (5)	0.1676 (4)	0.8953 (4)	5.4 (1)
C16	0.9973 (5)	0.2439 (5)	0.8995 (5)	6.9 (2)
C17	0.9820 (5)	0.3131 (4)	0.8363 (5)	7.1 (2)
C18	0.9072 (6)	0.3078 (4)	0.7695 (5)	7.0 (2)
C19	0.8458 (5)	0.2334 (4)	0.7652 (4)	5.4 (1)
C20	0.8679 (4)	−0.0274 (3)	0.8062 (4)	3.6 (1)
C21	0.9549 (4)	−0.0172 (4)	0.7518 (4)	5.2 (1)
C22	1.0177 (5)	−0.0901 (5)	0.7361 (5)	7.0 (2)
C23	0.9936 (5)	−0.1724 (4)	0.7733 (5)	6.6 (2)
C24	0.9088 (5)	−0.1833 (4)	0.8262 (5)	6.1 (2)
C25	0.8460 (4)	−0.1111 (4)	0.8443 (4)	4.8 (1)
C26	0.6918 (4)	0.0693 (3)	0.7296 (3)	3.3 (1)
C27	0.5879 (4)	0.0706 (3)	0.7494 (4)	4.1 (1)
C28	0.5174 (4)	0.0739 (4)	0.6772 (4)	5.3 (1)
C29	0.5506 (5)	0.0777 (4)	0.5829 (4)	6.0 (2)
C30	0.6511 (5)	0.0756 (4)	0.5618 (4)	5.9 (2)
C31	0.7228 (4)	0.0718 (4)	0.6350 (4)	4.7 (1)
C1	0.71064 (9)	0.05432 (8)	1.30104 (7)	2.88 (2)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter (4/3) $[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\ \text{gamma})\beta(1,2) + ac(\cos\ \text{beta})\beta(1,3) + bc(\cos\ \text{alpha})\beta(2,3)]$.

4. Supplementary material available

Additional material available from the Cambridge Crystallographic Data Centre comprises H atom coordinates, thermal parameters and remaining bond lengths and angles.

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