Synthesis and characterization of Co and Ni complexes stabilized by keto- and acetamide-derived P,O-type phosphine ligands†

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The coordination properties of the β-keto phosphine ligands $R_2PCH_2C(O)Ph$ (**HL¹**, R = *i*-Pr; **HL²**, R = Ph), of the new acetamide-derived phosphine ligand $(i\text{-Pr})_2PNHC(O)Me$ (**HL³**) and of $Ph_2PNHC(O)Me$ (**HL⁴**) have been examined towards Ni(II) complexes. Comparisons are made between systems in which the PCH_2 function of the ketophosphine has been replaced with an isoelectronic PNH group in amide-derived ligands, or the PCH functionality of phosphinoenolates with a PN group in phosphinoiminolate complexes. Furthermore, ligands **HL²** and **HL⁴** reacted with $[(\eta^5\text{-}C_5H_5)CoI_2(CO)]$ to afford the phosphine mono-adducts $[(\eta^5\text{-}C_5H_5)CoI_2\{Ph_2PCH_2C(O)Ph\}]$ (**1**) and $[(\eta^5\text{-}C_5H_5)CoI_2\{Ph_2PNHC(O)Me\}]$ (**3**), respectively, which upon reaction with excess NEt_3 yielded the phosphinoenolate complex $[(\eta^5\text{-}C_5H_5)CoI\{Ph_2PCH\cdots C(\cdots O)Ph\}]$ (**2**) and the phosphinoiminolate complex $[(\eta^5\text{-}C_5H_5)CoI\{Ph_2PN\cdots C(\cdots O)Me\}]$ (**4**), respectively. The complexes *cis*-$[Ni\{(i\text{-Pr})_2PN\cdots C(\cdots O)Me\}_2]$ (**6**) and *cis*-$[Ni\{Ph_2PN\cdots C(\cdots O)Me\}_2]$ (**7**) were obtained similarly from $NiCl_2$ and **HL³** and **HL⁴**, respectively, in the presence of a base. The phosphinoenolate complex $[Ni\{(i\text{-Pr})_2PCH\cdots C(\cdots O)Ph\}_2]$ (**5**) exists in ethanol as a mixture of the *cis* and *trans* isomers, in contrast to *cis*-$[Ni\{(Ph_2PCH\cdots C(\cdots O)Ph\}_2]$, and the solid-state structure of the *trans* isomer of **5** was established by X-ray diffraction. The structures of the ligand **HL³** and of the complexes **1**, **3** in **3**·3/2CH_2Cl_2, **4**, **6** and **7** have also been determined by X-ray diffraction and are compared with those of related complexes. Complexes **4**, **6** and **7** contain a five-membered heteroatomic metallocyclic moiety, which is constituted by five different chemical elements. The structural consequences of the steric bulk of the P substituents and of the electronic characteristics of the P,O chelates are discussed.

Introduction

The synthesis of functional phosphine ligands of the P,O-type and their complexation to transition metals has been much investigated during the last few years and their relevance to catalytic reactions is well documented.[1–8] With softer metal ions, P-coordination is invariably observed, with or without interaction of the neutral oxygen donor, in a chelating or, much more rarely, a bridging mode, as found in some Fe–Cd complexes.[9] In exceptional cases, the P,O ligand interacts with the metal solely *via* the oxygen function, as in Nb(V), Ta(V) and Mo(V) complexes of the acetamide-derived phosphine $Ph_2PNHC(O)Me$.[10] In addition to the possible occurrence of hemilabile behaviour and enhanced catalytic reactivity,[6] P,O or P,N chelates can also lead to reactivity of their metal complexes different from that observed with symmetrical P,P chelates.[11–15]

The monoanionic, enolate form obtained from the ketophosphine ligand $Ph_2PCH_2C(O)Ph$ generally chelates the metal centre in a P,O mode but monodentate behaviour *via* the oxygen atom has been observed with early transition metals, such as Ti(IV) and Zr(IV).[16] A few examples of bridging situations have also been encountered, in homo- and heterometallic chemistry.[3] The replacement of the PCH_2 group of such ketophosphines with an isoelectronic PNH group in amide-derived ligands, or of the PCH functionality of phosphinoenolates with a PN group in iminolate phosphines, can bring about very interesting electronic and geometric effects in their respective metal complexes.[3,17–21]

Here, we report the synthesis and characterization of Co(III) and Ni(II) complexes containing the neutral β-ketophosphine ligands $(i\text{-Pr})_2PCH_2C(O)Ph$ (**HL¹**) and $Ph_2PCH_2C(O)Ph$ (**HL²**)[22] or the acetamide-derived phosphine ligand $(i\text{-Pr})_2PNHC(O)Me$ (**HL³**), prepared similarly to $Ph_2PNHC(O)Me$ (**HL⁴**),[18] or the deprotonated form of these ligands.

Results and discussion

Synthesis and characterization of the ligands

The ligands $R_2PCH_2C(O)Ph$ (**HL¹**, R = *i*-Pr; **HL²**, R = Ph) were obtained in high yields by the previously reported procedure,[1,22] which consists of the reaction of $PhCOCH_2Li$ with the corresponding chlorophosphine in THF at low temperature (Scheme 1). In contrast to **HL²**, which was obtained as a white solid,[22] **HL¹** is an

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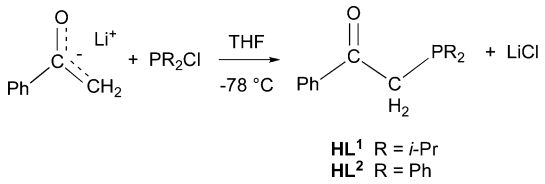
† Electronic supplementary information (ESI) available: Additional details concerning the crystal structures of complexes **1**, **4**, *trans*-**5**, **6** and **7**. CCDC reference numbers 698954–698960. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b814284j

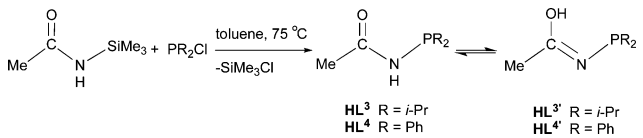


Scheme 1 Synthesis of ligands **HL**[1] and **HL**[2].

orange liquid that can be exposed to air for short periods of time, but is best kept under an inert atmosphere (see Experimental).[1]

In the ^{1}H NMR spectrum of **HL**[1], the PCH_2 protons appear as a doublet (Table 1) and the CH protons of the *i*-Pr substituents as a septet of doublets (see Experimental), as in the related phosphinooxazoline ligand $(i\text{-Pr})_2PCH_2$(oxazoline).[15] The $^{31}P\{^1H\}$ NMR spectrum consists of a singlet at δ 9.9 ppm and the characteristic ν_{CO} absorption band appears in the IR spectrum at 1673 cm^{-1}. Comparative spectroscopic data are presented in Table 1.

The acetamido-phosphine $(i\text{-Pr})_2PNHC(O)Me$ **HL**[3] has been synthesized by a similar procedure to that used for $Ph_2PNHC(O)Me$ (**HL**[4]),[18] by condensation of *N*-trimethylsilylacetamide with the corresponding chlorophosphine in toluene (Scheme 2).



Scheme 2 Synthesis of the ligands **HL**[3] and **HL**[4].

In contrast to **HL**[1] and **HL**[2], the $^{31}P\{^1H\}$ NMR ($CDCl_3$) spectrum of **HL**[3] contains two signals at δ 47.7 and 57.5 ppm (ratio 20 : 80). This is explained by the existence of a tautomeric equilibrium between the acetamido and the iminol forms **HL**[3] and **HL**[3′], respectively (Scheme 2). The N=C double bond having a deshielding effect on the adjacent atoms, the $^{31}P\{^1H\}$ signal of **HL**[3′] is expected to occur at lower field than that of **HL**[3]. We therefore assign the signal at δ 57.5 ppm (major tautomer, *ca.* 80%) to the iminol form **HL**[3′]. An equilibrium of this type has already been observed for **HL**[4],[18] however, in that case the major tautomer in $CDCl_3$ solution was the acetamido form **HL**[4] (60%). The suggested tautomeric equilibrium is solvent dependent: in acetone-d_6 the acetamido forms **HL**[3] and **HL**[4] are favoured, **HL**[4] is even the only isomer observed. The ^{1}H NMR signals for the CH_3 protons of **HL**[3] and **HL**[3′] occur at δ 2.0 and 2.18 ppm, respectively (Table 1). The ^{13}C NMR signal of the HN–C=O moiety in **HL**[3] was observed at δ 172.8 ppm and that of N=C–OH in **HL**[3′] at δ 177.3 ppm, the latter showing a $^2J_{PC}$ coupling of 18.8 Hz. Two different signals were observed for the carbon atom of the methyl group, a doublet at δ 21.8 ($^3J_{PC} = 14.8$ Hz) and a singlet at 22.7 ppm, corresponding each to one of the tautomeric forms of the ligand (tentative assignment in the Experimental).

The solid-state structure of **HL**[3] has been determined by single-crystal X-ray diffraction. An ORTEP view and a packing diagram showing the unique hydrogen bond detected[24] in this compound (d_{H1-O}: 2.37(3) Å, N–H1–O: 161(3)°) are presented in Fig. 1 and 2, respectively. The refined crystal structure clearly shows that only the **HL**[3] tautomer was present in the crystal. The H(1) hydrogen is unambiguously observed by Fourier differences, whereas no hydrogen atoms can be stabilized (from spatial position and electronic density points of view) around the O atom (Fig. 1).

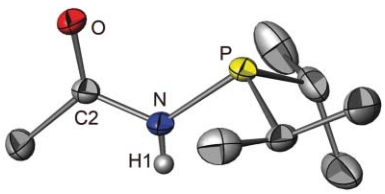


Fig. 1 ORTEP view of ligand **HL**[3] (hydrogen atoms have been omitted for clarity, except H(1) on the nitrogen atom found by Fourier differences). Displacement ellipsoids are drawn at 50% probability level.

Cobalt complexes

The reaction between $[(\eta^5\text{-}C_5H_5)CoI_2(CO)]$ and $Ph_2PCH_2C(O)Ph$ (**HL**[2]) in toluene resulted in the cleavage of the Co–CO bond to

Table 1 Selected, comparative IR and NMR data for the ligands and complexes

		NMR[c]	
	IR	^{1}H	$^{31}P\{^1H\}$
HL[1]	1673[b] (s, ν_{CO})	3.11 (d, $^2J_{PH} = 1.3$ Hz, 2H, PCH_2)	9.9
HL[2]	1670[a] (s, ν_{CO})	3.80 (s, 2H, PCH_2)	−17.1
HL[3]	1695[a] (s, ν_{CO})	2.00 (s, 3H, MeC(=O)), 5.54 (br, 1H, NH)	47.7
HL[3′]	—	2.18 (d, $^4J_{PH} = 2.7$ Hz, MeC(OH)), 2.08 (br, 1H, OH)	57.5
HL[4]	1715[b] (s, ν_{CO})	2.13 (s, 3H, MeC(=O)), 6.15 (br, 1H, NH)	21.6
HL[4′]	—	2.30 (s, 3H, MeC(OH)), OH not observed	31.1
1	1671[a] (s, ν_{CO})	4.54 (d, $^2J_{PH} = 9.7$ Hz, 2H, PCH_2)	34.6
2	1518[a] (s, ν_{CC+CO})	5.02 (s, 1H, PCH)	60.6
3	1699[a] (s, ν_{CO})	1.20 (s, 3H, Me), 6.30 (d, $^2J_{PH} = 16.7$ Hz, 1H, NH)	70.7
4	1487[a] (s, ν_{CN+CO})	2.19 (s, 3H, Me)	111.1
cis-Ni(**L**[2])$_2$[23]	1515[a] (s, ν_{CC+CO})	4.55 (s, 2H, PCH)	28.2
5	1517[a] (s, ν_{CC+CO})	—	—
6	1519 (s, ν_{CN+CO})	1.26 (dd, $^3J_{PH} = 14.5$ Hz, $^3J_{HH} = 7$ Hz, 12H, Me *i*-Pr) 1.38 (dd, $^3J_{PH} = 17.1$ Hz, $^3J_{HH} = 7.2$ Hz, 12H, Me *i*-Pr), 2.16 (s, MeCO)	115.9
7	1439[a] (s, ν_{CN+CO})	3.76 (d, $^4J_{PH} = 11.1$ Hz, 6H, Me)	34.4

[a] In KBr. [b] In CH_2Cl_2, cm^{-1}. [c] In $CDCl_3$, ppm, *J* in Hz.

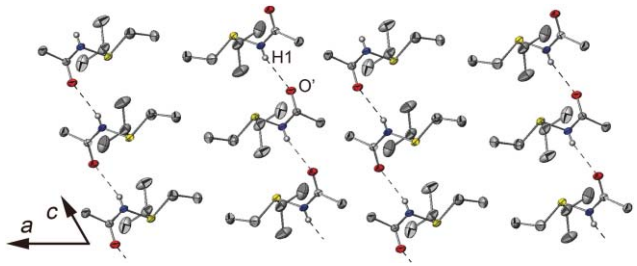
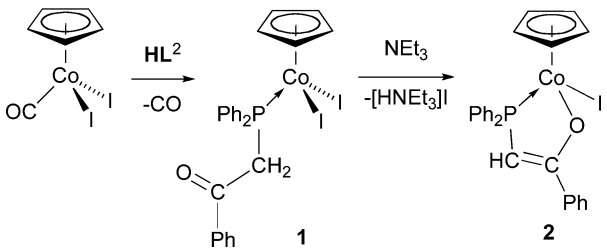


Fig. 2 Crystal packing diagram of ligand **HL**[3] showing the N–H···O hydrogen bonding. Symmetry code for equivalent positions: $x, -y + 1/2, z - 1/2$. Dashed lines indicate the hydrogen bonds.

afford the phosphine mono-adduct $[(\eta^5\text{-}C_5H_5)CoI_2(\mathbf{HL^2})]$ (**1**), as a dark blue solid (Scheme 3).



Scheme 3 Synthesis of complexes **1** and **2**.

The $^{31}P\{^1H\}$ NMR spectrum of **1** displays a resonance at δ 34.6 ppm, shifted *ca.* 52 ppm downfield of the free phosphine (δ −17.1 ppm),[22] consistent with the coordination of the phosphorus to a cobalt centre.[25] The methylene protons were observed to be magnetically equivalent, giving rise to a doublet in the ^1H NMR spectrum ($\delta = 4.54$, $^2J_{PH} = 9.7$, Table 1). The IR spectrum confirmed that the carbonyl group of the ketophosphine was not coordinated to the metal centre ($\nu_{CO} = 1671\ cm^{-1}$ for **1** *vs.* $1670\ cm^{-1}$ for the free ligand, Table 1).[22] The solid-state structure of **1** was determined by X-ray diffraction and an ORTEP view is shown in Fig. 3 (selected distances and angles are given in the caption). The distance of 3.74(1) Å between the centroids of the C(3)–C(8) and C(9)–C(14) phenyl rings and the dihedral angle of 21(1)° between the least-squares planes through these phenyl rings are consistent

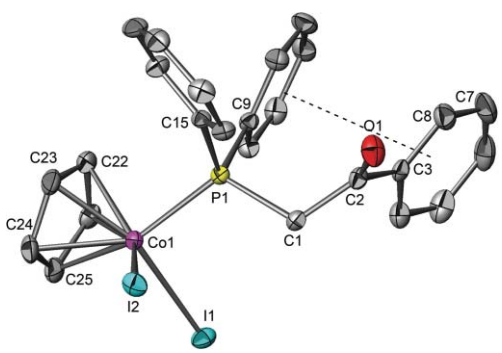
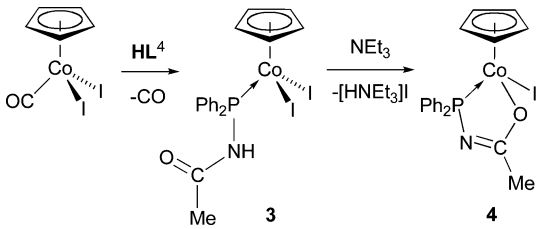


Fig. 3 ORTEP view of complex **1** (the hydrogen atoms have been omitted for clarity). Displacement ellipsoids are drawn at the 50% probability level. Selected distances (Å) and angles (°): Co1–I1, 2.593(1), Co1–I2, 2.569(1), Co1–P1, 2.231(1), P1–C1, 1.85(1), C1–C2, 1.51(1), O1–C2, 1.21(1); P1–Co1–I2, 88.9(1), C1–P1–Co1, 114.4(1), C9–P1–C15, 105.6(1).

with a π–π interaction between them (see dashed line in Fig. 3). Intermolecular interactions are given in the ESI.†

The treatment of **1** with excess triethylamine yielded the phosphinoenolate complex $[(\eta^5\text{-}C_5H_5)CoI(\mathbf{L^2})]$ (**2**) as a dark solid (Scheme 3). The IR spectrum confirmed the coordination of the oxygen enolate to the metal center ($\nu_{CC+CO} = 1518\ cm^{-1}$). The $^{31}P\{^1H\}$ NMR resonance of **2** at δ 60.6 ppm is shifted 26 ppm downfield to that for the corresponding phosphine complex **1**.

The reaction between $[(\eta^5\text{-}C_5H_5)CoI_2(CO)]$ and the (diphenylphosphino)acetamide ligand **HL**[4] in toluene resulted in the cleavage of the Co–CO bond and afforded the P mono-aduct complex $[(\eta^5\text{-}C_5H_5)CoI_2(\mathbf{HL^4})]$ (**3**), as a dark purple crystalline solid (Scheme 4).



Scheme 4 Synthesis of complexes **3** and **4**.

Its IR spectrum confirmed that the acetamide group was not coordinated to the metal centre ($\nu_{CO} = 1699\ cm^{-1}$ for **3** *vs.* $1715\ cm^{-1}$ for the free ligand).[18] The $^{31}P\{^1H\}$ NMR spectrum of **3** shows a peak at δ 70.7 ppm, which corresponds to a downfield shift of 49 ppm relative to the free ligand (δ 21.6 ppm).[18] The acetamide NH proton was observed in the ^1H NMR spectrum at δ 6.30 ppm and the methyl protons at δ 1.20 ppm (Table 1). The solid-state structure of **3** was determined by X-ray diffraction and an ORTEP view is shown in Fig. 4 (selected distances and angles are given in the caption).

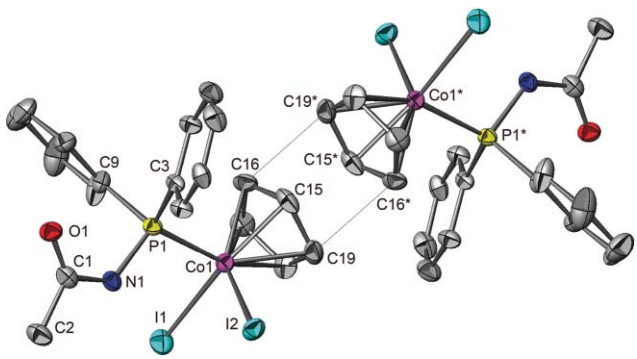


Fig. 4 ORTEP view of a pseudo-dimer of complexes **3** in **3**·3/2(CH_2Cl_2) (the hydrogen atoms have been omitted for clarity). Displacement ellipsoids are drawn at 50% probability level. Symmetry operator * for equivalent positions: $2 - x, -1 - y, 1 - z$. Selected distances (Å) and angles (°): Co1–I1, 2.596(1), Co1–I2, 2.577(1), Co1–P1, 2.198(2), P1–N1, 1.71(1), N1–C1, 1.36(1), C1–O1, 1.22(1); I1–Co1–I2, 93.3(1), N1–P1–Co1, 109.8(2), C9–P1–C3, 106.2(3).

Two quasi-identical molecules of complex **3** crystallize in the asymmetric unit. Only one of them is described (more information concerning this crystal structure is available from the cif file given in the ESI†). The dihedral angle between the least squares planes through the phenyl rings C(3)–C(8) and C(9)–C(14) is 62(1)°, a

value very close to that found in complex **1**. A π–π intermolecular interaction is observed between the two cyclopentadienyl rings C(15)–C(19) with a distance between the centroids of 3.31(1) Å. This situation allows us to describe this crystal structure as that of pseudo-dimers, as shown in Fig. 4. These pseudo-dimers are connected to each other by some CH–π interactions and numerous van der Waals contacts but no classical hydrogen bond has been found in this structure.

Treatment of **3** with excess triethylamine yielded the chelated phosphinoiminolate complex [(η^5-C_5H_5)CoI(**L**^{4})] (**4**) as a dark solid (Scheme 4). The IR spectrum confirmed that the oxygen atom was now coordinated to the metal centre ($\nu_{CN+CO} = 1487\ cm^{-1}$, Table 1). The solid state structure of **4** was also determined by X-ray diffraction and an ORTEP view of its molecular structure is shown in Fig. 5 (selected distances and angles are given in the caption).

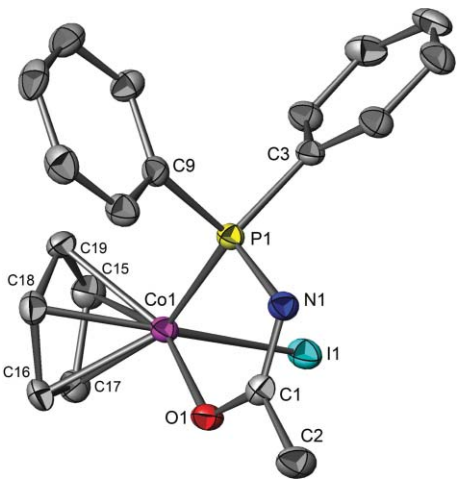


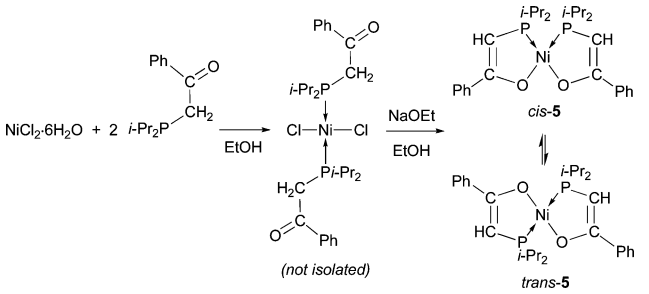
Fig. 5 ORTEP view of complex **4** (hydrogen atoms omitted for clarity). Displacement ellipsoids are drawn at 50% probability level. Selected distances (Å) and angles (°): Co1–I1, 2.572(1), Co1–O1, 1.924(2), Co1–P1, 2.190(1), P1–N1, 1.676(2), N1–C1, 1.32(1), C1–O1, 1.29(1); O1–Co1–P1, 82.6(1), I1–Co1–P1, 94.45(2), N1–P1–Co1, 102.2(1), C9–P1–C3, 102.1(2).

The crystal structure confirms that a five-membered heteroatomic ring has been formed which contains five different chemical elements. This ring is almost planar with a maximum deviation out of the ring of 0.03 Å for Co(1) and P(1). Additional structural information is provided in the ESI.†

Nickel complexes

Complex [Ni(**L**^{1})$_2$] (**5**) was obtained from **HL**^{1} as a mixture of the *cis* and *trans* isomers, which are in equilibrium in solution (Scheme 5).[26]

The formation of both isomers can be explained by opposite steric and electronic effects, the former favouring the *trans*-arrangement and the latter a *cis*-arrangement owing to the de-stabilizing effect on each other of two mutually *trans* soft phosphorus donor atoms.[27,28] The *cis* isomer has been shown to be a precursor to heterometallic complexes when acting as an O,O-chelate toward Co(II) ions.[26] Slow diffusion of hexane into a CH_2Cl_2 solution of the isomers afforded crystals suitable for X-diffraction, which revealed to be those of the *trans*-**5** isomer. An



Scheme 5 Synthesis of complex **5** and solution equilibrium between the *cis* and *trans* isomers.

ORTEP view is shown in Fig. 6 and selected bond distances and angles are given in the caption.

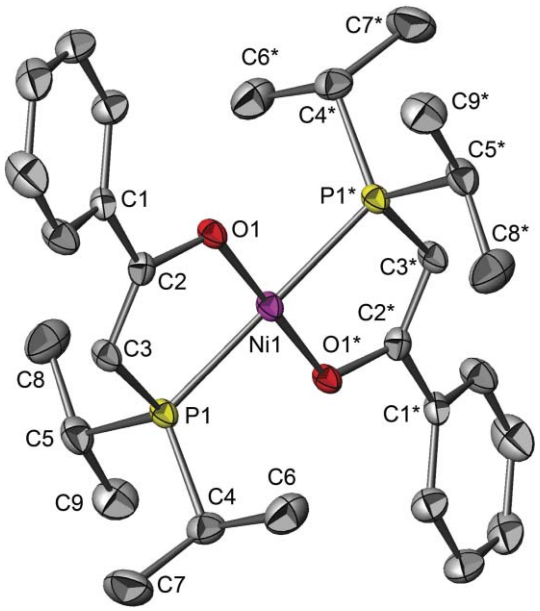


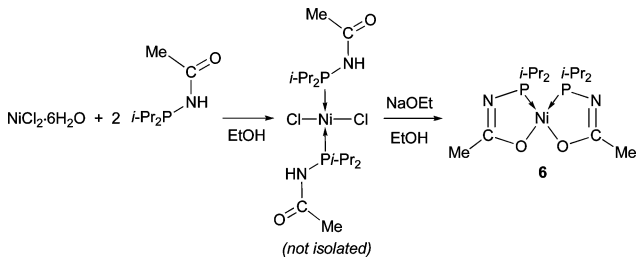
Fig. 6 ORTEP view of complex *trans*-**5** (the hydrogen atoms have been omitted for clarity). Displacement ellipsoids are drawn at the 50% probability level. Symmetry code for equivalent positions *: $-x$, $2-y$, $-z$. Selected distances (Å) and angles (°): Ni1–O1, 1.850(1), Ni1–P1, 2.199(1), P1–C3, 1.769(2), C2–C3, 1.354(3), C2–O1, 1.32(1), C2–C1, 1.49(1), P1–C4, 1.836(2), P1–C5, 1.841(2); O1–Ni1–P1, 87.0(1); O1–Ni1–O1*, 180.0(1), C3–P1–Ni1, 97.9(1), C2–O1–Ni1, 119.4(2), O1–C2–C3, 123.0(2).

The crystal structure clearly reveals the square planar coordination environment of the nickel centre, which lies on the crystallographic inversion centre. The five-membered heteroatomic ring Ni(1)–P(1)–C(3)–C(2)–O(1) is almost planar, with a maximum deviation out of the least-squares plane of +0.31(1) Å and –0.30(1) Å for Ni(1) and P(1), respectively. Other structural data are given in the ESI.†

In contrast to the equilibrium found with **5**, the *t*-Bu-substituted analogue [Ni{(*t*-Bu$_2$PCH···C(···O)Ph}$_2$] was observed only as the *trans* isomer, but no crystal structure was reported,[29] whereas the phenyl derivative [Ni{(Ph$_2$PCH···C(···O)Ph}$_2$] forms the *cis* isomer.[23,30] The latter was also obtained by reacting the ylide Ph$_3$PCHC(O)Ph with [Ni(COD)$_2$] in the presence of AsPh$_3$.[30] The complex [Ni{(Ph$_2$PCH···C(···O)Ph}$_2$] corresponds to the deactivated form of SHOP-type catalysts but can be converted

to an active ethylene homo-polymerization catalyst by alkylation with trimethylaluminum.[31,32]

The reaction of **HL**[3] with $NiCl_2 \cdot 6H_2O$ in ethanol followed by the addition of NaOEt afforded *cis*-[Ni(**L**[3])$_2$] (**6**) (Scheme 6). Its IR spectrum confirmed that the oxygen atom was coordinated to the metal centre ($\nu_{CN+CO} = 1519\ cm^{-1}$, Table 1). The $^{31}P\{^1H\}$ NMR spectrum displayed a single resonance at $\delta = 115.9$ ppm, indicating the presence of only one isomer. As expected, the CH_3 protons of the *i*-Pr substituents of the phosphorus appear as two doublets of doublets. The multiplet assigned to the *i*-Pr*CH* was not sufficiently well resolved to allow a determination of the J_{HH} and J_{PH} coupling constants. A crystal structure determination established the *cis* geometry of **6**, although steric effects were expected to favour a *trans*-arrangement. Electronic effects favouring the *cis*-arrangement appear in this case to be dominant.[28,33]



Scheme 6 Synthesis of complex **6**.

An ORTEP view of *cis*-[Ni(**L**[3])$_2$] (**6**) is shown in Fig. 7 and selected distances and angles are given in the caption. The nickel atom is in a square-planar coordination environment and lies on the crystallographic twofold axis (space group *C*2/*c*). The five-membered heteroatomic ring Ni(1)–O(1)–C(2)–N(1)–P(1) is almost planar with a maximum deviation out of the least-squares plane of +0.027(1) and –0.026(2) for Ni(1) and O(1), respectively (some CH–π interactions are provided in the ESI†).

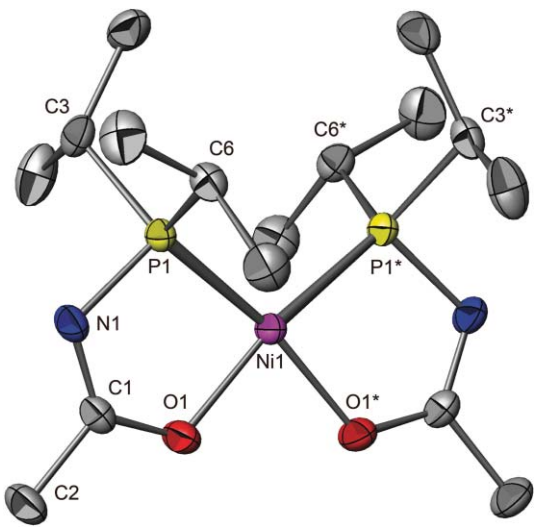
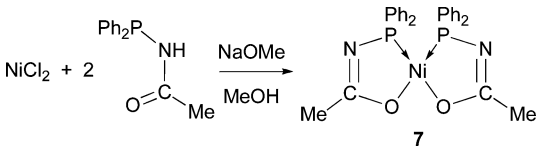


Fig. 7 ORTEP view of complex **6** (hydrogen atoms omitted for clarity). Displacement ellipsoids are drawn at the 50% probability level. Symmetry code for equivalent positions *: $-x + 2$, y, $-z + 3/2$. Selected distances (Å) and angles (°): Ni1–O1, 1.887(2), Ni1–P1, 2.175(1), P1–C3, 1.831(2), P1–C6, 1.841(2), P1–N1 1.690(2), C1–O1, 1.291(2), C1–C2, 1.502(3), C1–N1, 1.302(3); P1–Ni1–P1* 109.4(1), O1–Ni1–O1*, 85.2(1), P1–Ni1–O1, 166.2(1), C1–O1–Ni1, 118.5(1), O1–C1–N1, 125.7(2).

The reaction of **HL**[4] with $NiCl_2$ in methanol, in the presence of NaOMe, afforded *cis*-[Ni(**L**[4])$_2$] (**7**) (Scheme 7). Its $^{31}P\{^1H\}$ NMR resonance is shifted *ca.* 13 ppm downfield of that of the free ligand (δ 21.6 ppm).[18] The IR spectrum confirmed that the iminolate oxygen atom is coordinated to the metal centre ($\nu_{CN+CO} = 1439\ cm^{-1}$, Table 1).



Scheme 7 Synthesis of complex **7**.

The solid-state structure of **7** was determined by single-crystal X-ray diffraction, an ORTEP view of its molecular structure is shown in Fig. 8 and selected distances and angles are given in the caption.

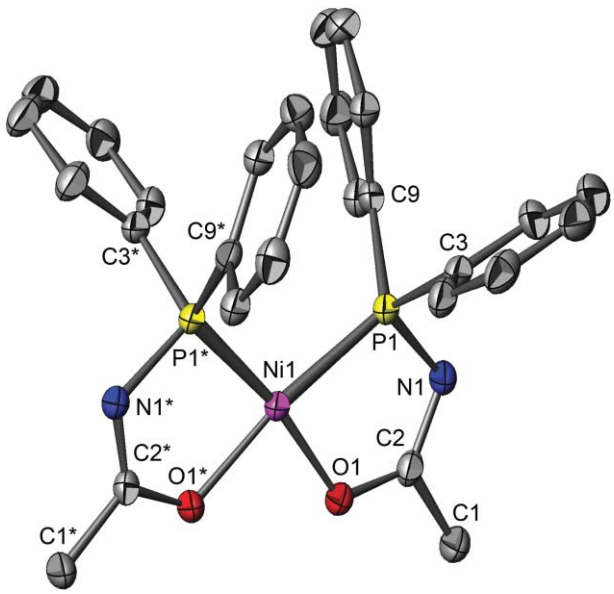


Fig. 8 ORTEP view of complex **7** (the hydrogen atoms have been omitted for clarity). Displacement ellipsoids are drawn at the 50% probability level. Symmetry code for equivalent positions *: $1 - x$, y, $1/2 - z$. Selected distances (Å) and angles (°): Ni1–O1, 1.891(1); Ni1–P1, 2.153(1), P1–C3, 1.816(2); P1–C9, 1.805(2); P1–N1, 1.686(2); C2–O1, 1.299(2); C1–C2, 1.497(3); C2–N1, 1.313(3); P1–Ni1–P1*, 105.2(1); O1–Ni1–O1*, 87.8(1); P1–Ni1–O1, 171.3(1); C2–O1–Ni1, 118.0(1); O1–C2–C1, 125.0(2).

The nickel atom has a square planar coordination and lies on the crystallographic twofold axis. The five-membered heteroatomic ring Ni(1)–O(1)–C(2)–N(1)–P(1) is almost planar with a maximum deviation out of the least-squares plane of +0.065(1) and –0.071(1) for Ni(1) and P(1), respectively. Three significant CH–π interactions (and their equivalents by symmetry operators) have been identified in the crystal packing and are given in Table 2.

Table 2 Significant CH–π interactions in *cis*-[Ni($\mathbf{L}^4$)$_2$] (**7**)

X–H	→Ring	[Equiv. position]	H···Centroid/Å	X–H···Centroid/°
C(4)–H(4)	C(9)/C(14)	[1 − *x*, *y*, 1/2 − *z*]	2.954	113.23
C(6)–H(6)	Ni(1)/P(1)	[1/2 + *x*, −1/2 + *y*, *z*]	2.848	159.57
C(12)–H(12)	C(3)/C(8)	[−1/2 + *x*, −1/2 + *y*, *z*]	2.860	136.78

Conclusion

We have performed a comparative study of the coordination properties of neutral functional phosphine ligands containing a ketone or an amide function and of the corresponding anionic P,O ligands obtained by deprotonation of the CH_2 or the NH group in α-position to the P donor, respectively. We have also examined the steric influence of the P substituents, phenyl or isopropyl, on the structure of the resulting complexes. The known β-ketophosphine ligands $R_2PCH_2C(O)Ph$ (**HL**^{1}, R = *i*-Pr; **HL**^{2}, R = Ph) and the new acetamide-derived phosphine ligand $(i\text{-Pr})_2PNHC(O)Me$ (**HL**^{3}), prepared similarly to $Ph_2PNHC(O)Me$ (**HL**^{4}) allowed systematic comparisons to be made. Ligands **HL**^{2} and **HL**^{4} reacted with the cobalt cyclopentadienyl complex $[(\eta^5\text{-}C_5H_5)CoI_2(CO)]$ to afford the phosphine mono-adducts $[(\eta^5\text{-}C_5H_5)CoI_2\{Ph_2PCH_2C(O)Ph\}]$ (**1**) and $[(\eta^5\text{-}C_5H_5)CoI_2\{Ph_2PNHC(O)Me\}]$ (**3**), respectively. No chelation of the neutral P,O ligands was observed but the treatment of these complexes with excess NEt_3 yielded the chelated phosphinoenolate and phosphinoiminolate complexes $[(\eta^5\text{-}C_5H_5)\overline{CoI\{Ph_2PCH\cdots C(\cdots O)Ph\}}]$ (**2**) and $[(\eta^5\text{-}C_5H_5)\overline{CoI\{Ph_2PN\cdots C(\cdots O)Me\}}]$ (**4**), respectively. The chelate ring of the latter contains five different chemical elements. Both **HL**^{3} and **HL**^{4} reacted with $NiCl_2$ in the presence of base to give the *cis* isomers of the square-planar phosphinoiminolate complexes *cis*-$[\overline{Ni\{(i\text{-Pr})_2PN\cdots C(\cdots O)Me\}_2}]$ (**6**) and *cis*-$[\overline{Ni\{Ph_2PN\cdots C(\cdots O)Me\}_2}]$ (**7**), respectively. In contrast, the phosphinoenolate complex $[\overline{Ni\{(i\text{-Pr})_2PCH\cdots C(\cdots O)Ph\}_2}]$ (**5**) exists in solution as a mixture of *cis* and *trans* isomers and a crystal structure of the *trans* isomer was determined by X-ray diffraction.

Previous work has shown that transition metal complexes containing a phosphino-enolate or iminolate function react with electrophilic metal centres at the $C_{enolate}$ or $N_{iminolate}$ atoms, respectively, leading to heterometallic complexes and unique coordination polymers.[3,20,21] The complexes reported in this work, therefore represent interesting candidates to extend such studies.

Experimental

The ^{1}H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded at 300.13, 75.48 and 121.49 MHz, respectively, on a FT Bruker AC300 Avance 300 instrument, unless otherwise stated. Coupling constants are given in absolute values. IR spectra, in the range 4000–400 cm^{-1}, were recorded on a Bruker IFS66FT or a Perkin Elmer 1600 Series FTIR. Elemental analyses were performed by the Service de Microanalyse, Université Louis Pasteur (Strasbourg, France). All reactions were carried out under purified N_2, using Schlenk techniques, and the solvents were freshly distilled under nitrogen prior to use. The ligands **HL**^{2},[22] and **HL**^{4},[18,34] were prepared according to literature procedures, as were the complexes $[(\eta^5\text{-}C_5H_5)CoI_2(CO)]$[35] and $[\overline{Ni\{(i\text{-Pr})_2PCH\cdots C(\cdots O)Ph\}_2}]$ (**5**).[26] Other chemicals were commercially available and used as received.

Preparation and spectroscopic data for $(i\text{-Pr})_2PCH_2C(O)Ph$ (HL^1)

Ligand **HL**^{1} was prepared similarly to $Ph_2PCH_2C(O)Ph$ (**HL**^{2}),[22] but starting from acetophenone and $(i\text{-Pr})_2PCl$, and was obtained as a clear orange liquid. Additional analytical data to those initially reported:[1] IR (CH_2Cl_2) ν/cm^{-1}: 1673 (s, ν_{CO}) cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$, room temp.) δ/ppm: 1.08 [dd, $^3J_{PH}$ = 5.7 Hz, $^3J_{HH}$ = 7.1 Hz, 6H, $(CH(CH_3)(CH_3))_2$], 1.12 [dd, $^3J_{PH}$ = 3.3 Hz, $^3J_{HH}$ = 7.1 Hz, 6H, $(CH(CH_3)(CH_3))_2$], 1.83 [septd, $^2J_{PH}$ = 1.0 Hz, $^3J_{HH}$ = 7.1 Hz, 2H, $(CH(CH_3)_2)_2$], 3.11 (d, $^2J_{PH}$ = 1.3 Hz, 2H, PCH_2), 7.40–7.55 (complex m, 3H, aromatic), 7.91–8.02 (m, 2H, aromatic). $^{13}C\{^1H\}$ ($CDCl_3$, room temp.) δ/ppm: 18.8 [d, $^2J_{PC}$ = 10.5 Hz, $(CH(CH_3)(CH_3))_2$], 19.6 [d, $^2J_{PC}$ = 15.5 Hz, $(CH(CH_3)(CH_3))_2$], 24.1 [d, $^1J_{PC}$ = 15.3 Hz, $(CH(CH_3)_2)_2$], 34.6 (d, $^1J_{PC}$ = 29.8 Hz, PCH_2), 128.3–137.0 (aromatics), 199.5 [d, $^2J_{PC}$ = 8.2 Hz, C(O)]. $^{31}P\{^1H\}$ NMR ($CDCl_3$, room temp.) δ/ppm: 9.9 (s).

Preparation and spectroscopic data for $(i\text{-Pr})_2PNHC(O)Ph$ (HL^3)

$P(i\text{-Pr})_2Cl$ (0.882 g, 5.78 mmol) was added to a solution of $MeC(O)NHSiMe_3$ (0.759 g, 5.78 mmol) in toluene (20 mL), and the mixture was placed under vacuum for 30 s, before being heated to 60 °C. The mixture was placed under vacuum for 10 s every 5 min in order to eliminate $SiClMe_3$, which was formed. After 30 min, the solution was allowed to cool to ambient temperature. The solvent was then evaporated under reduced pressure and the residue thus obtained was dried under vacuum overnight. A crystalline material with a melting point close to room temperature was obtained, keeping this material at 5 °C overnight afforded suitable crystals for X-ray diffraction. Overall yield: 0.700 g (69%). **HL**^{3} is soluble in most common organic solvents (including petroleum ether) and therefore it was difficult to purify, however, the crude product could be used for metal complexation and the resulting complexes were easier to purify. IR (KBr) ν/cm^{-1}: 1695 (s, ν_{CO}). ^{1}H NMR ($CDCl_3$, room temp.) δ/ppm: 1.02 [dd, $^3J_{PH}$ = 0.9 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, $(CH(CH_3)(CH_3))_2$], 1.07 [dd, $^3J_{PH}$ = 4.2 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, $(CH(CH_3)(CH_3))_2$], 1.72 [septd, $^2J_{PH}$ = 2.4 Hz, $^3J_{HH}$ = 7.0 Hz, 2H, $(CH(CH_3)_2)_2$], 2.00 [s, $CH_3C(=O)$], 2.08 (br, OH), 2.18 [d, $^4J_{PH}$ = 2.7 Hz, $CH_3C(OH)$], 5.54 (br, NH), see text. $^{13}C\{^1H\}$ ($CDCl_3$, room temp.) δ/ppm: 16.9 [d, $^2J_{PC}$ = 7.8 Hz, $(CH(CH_3)(CH_3))_2$], 18.3 [d, $^2J_{PC}$ = 19.8 Hz, $(CH(CH_3)(CH_3))_2$], 21.8 [d, $^3J_{PC}$ = 14.8 Hz, $CH_3C(OH)$], 22.7 [s, $CH_3C(=O)N$], 25.9 [d, $^1J_{PC}$ = 12.1 Hz, $(CH(CH_3)_2)_2$], 172.8 [s, C(O)], 177.3 [d, $^2J_{PC}$ = 18.8 Hz, NC(OH)]. $^{31}P\{^1H\}$ NMR ($CDCl_3$, room temp.) δ/ppm: 47.7 (s, minor isomer 20% **HL**^{3}), 57.5 (s, major isomer 80%, **HL**$^{3'}$).

Preparation and spectroscopic data for [(η⁵-C_5H_5)CoI_2{$Ph_2PCH_2C(O)Ph$}] (1)

The complex [(η⁵-C_5H_5)CoI_2(CO)] (0.750 g, 1.85 mmol) was suspended in toluene (50 mL) and **HL²** (0.560 g, 1.84 mmol) was added. The reaction mixture was stirred at room temperature for 1 h. The solvent was then evaporated under reduced pressure affording a dark blue residue. The latter was washed with diethylether (5 mL) and pentane (2 × 10 mL) and dried under vacuum (dark blue powder, 1.16 g, 92%). IR (KBr) ν/cm^{-1}: 1671 (s, ν_{CO}). ^{1}H NMR ($CDCl_3$, room temp.) δ/ppm: 4.54 (d, $^2J_{PH}$ = 9.7 Hz, 2H, PCH_2), 5.06 (s, 5H, C_5H_5), 7.17 (t, J = 7.6 Hz, 2H, aromatic), 7.31–7.45 (complex m, 7H, aromatic), 7.57 (d, J = 7.6 Hz, 2H, aromatic), 8.07 (t, J = 8.9 Hz, 4H, aromatic). ^{31}P{^{1}H} NMR ($CDCl_3$, room temp.) δ/ppm: 34.6 (s). Anal. calcd for $C_{25}H_{22}CoI_2OP$: C 44.02, H 3.25. Found: C 44.30, H 3.30.

Preparation and spectroscopic data for [(η⁵-C_5H_5)$\overline{CoI\{Ph_2PCH\cdots C(\cdots O)Ph\}}$] (2)

To a solution of complex **1** (0.124 g, 0.18 mmol) in toluene (20 mL) was added excess NEt_3 (1.00 mL, 7.12 mmol). The reaction mixture was stirred at room temperature for 1 h. The solution was then filtered through dry Celite and the solvent evaporated under reduced pressure. The residue was washed with diethylether (5 mL) and pentane (2 × 10 mL) and dried under vacuum overnight. Complex **2** was obtained as a black solid (0.074 g, 73%). IR (KBr) ν/cm^{-1}: 1518 (s, ν_{CC+CO}). ^{1}H NMR ($CDCl_3$, room temp.) δ/ppm: 5.02 (s, 1H, PCH), 5.16 (s, 5H, C_5H_5), 7.26–7.29 (m, 2H, aromatic), 7.44–7.52 (complex m, 7H, aromatic), 7.63–7.73 (m, 4H, aromatic), 7.82–7.88 (m, 2H, aromatic). ^{31}P{^{1}H} NMR ($CDCl_3$, room temp.) δ/ppm: 60.6 (s). Anal. calcd for $C_{25}H_{21}CoIOP$: C 54.18, H 3.82. Found: C 53.89, H 3.97.

Preparation and spectroscopic data for [(η⁵-C_5H_5)CoI_2{$Ph_2PNHC(O)Me$}] (3)

Complex **3** was obtained using a similar procedure to that described above for **1**, starting from [(η⁵-C_5H_5)CoI_2(CO)] (0.120 g, 0.30 mmol) and **HL⁴** (0.073 g, 0.30 mmol). It was obtained as a dark purple crystalline solid (0.151 g, 81%). IR (KBr) ν/cm^{-1}: 1699 (s, ν_{CO}). ^{1}H NMR ($CDCl_3$, room temp.) δ/ppm: 1.20 (s, 3H, CH_3), 5.08 (s, 5H, C_5H_5), 6.30 (d, $^2J_{PH}$ = 16.7 Hz, 1H, NH), 7.47–7.57 (complex m, 6H, aromatic), 8.07–8.16 (complex m, 4H, aromatic). ^{31}P{^{1}H} NMR ($CDCl_3$, room temp.) δ/ppm: 70.7 (s). Anal. calcd for $C_{19}H_{19}CoI_2NOP$: C 36.74, H 3.08, N 2.26. Found: C 36.84, H 3.10, N 2.20.

Preparation and spectroscopic data for [(η⁵-C_5H_5)$\overline{CoI\{Ph_2PN\cdots C(\cdots O)Me\}}$] (4)

Complex **4** was obtained using a similar procedure to that described above for **2**, starting from **3** (0.176 g, 0.28 mmol) and NEt_3 (1.00 mL, 7.12 mmol). It was obtained has a dark purple solid (0.113 g, 81%). IR (KBr) ν/cm^{-1}: 1487 (s, ν_{CN+CO}). ^{1}H NMR ($CDCl_3$, room temp.) δ/ppm: 2.19 (s, 3H, CH_3), 5.09 (s, 5H, η⁵-C_5H_5), 7.45–7.55 (complex m, 8H, aromatic), 7.93–8.01 (complex m, 2H, aromatic). ^{31}P{^{1}H} NMR ($CDCl_3$, room temp.) δ/ppm: 111.1 (s). Anal. calcd for $C_{18}H_{19}CoINOP$: C 46.27, H 3.68, N 2.84. Found: C, 46.00 H, 3.90, N 2.60.

Preparation and spectroscopic data for *cis*-[$\overline{Ni(i\text{-}Pr)_2PN\cdots C(\cdots O)Me\}_2$] (6)

A mixture of $NiCl_2\cdot 6H_2O$ (0.200 g, 0.85 mmol) and **HL³** (0.300 g, 1.71 mmol) was dissolved in ethanol (20 mL) to give a dark green solution. After it was stirred for 1 h, a solution of NaOEt (prepared from 0.040 g of Na and 10 mL of ethanol) was slowly added (20 min) and the colour changed to light green-yellow. After further stirring for 1 h, the colour of the solution changed to yellow-orange. The solvent was removed under reduced pressure and the orange solid was extracted with dry toluene to give an orange solution, which was filtered in order to remove NaCl, and pentane was added. The mixture was left in the fridge overnight to give compound **6** as yellow crystals (0.210 g, 0.515 mmol, 60%). IR ν/cm^{-1}: 1519 (s, ν_{CN+CO}). ^{1}H NMR ($CDCl_3$, room temp.) δ/ppm: 1.26 (dd, $^3J_{PH}$ = 14.5 Hz, $^3J_{HH}$ = 7 Hz, 12H, $(CH(CH_3)(CH_3))_2$), 1.38 (dd, $^3J_{PH}$ = 17.1 Hz, $^3J_{HH}$ = 7.2 Hz, 12H, $(CH(CH_3)(CH_3))_2$, 1.97–2.07 (m, 4H, *i*-PrCH), 2.16 (s, 6H, MeC=N). ^{31}P{^{1}H} NMR (121.49 MHz, $CDCl_3$, room temp.) δ/ppm: 115.9 (s). Anal. calcd for $C_{16}H_{34}N_2NiO_2P_2\cdot 1/2H_2O$: C 46.18, H 8.48, N 6.73. Found: C 46.16, H 8.32, N 6.53.

Preparation and spectroscopic data for *cis*-[$\overline{Ni\{Ph_2PN\cdots C(\cdots O)Me\}_2}$] (7)

NaOMe (0.030 g, 0.564 mmol) was dissolved in the minimum amount of methanol and a solution of **HL⁴** (0.135 g, 0.555 mmol) in dichloromethane (15 mL) was added. Anhydrous $NiCl_2$ (0.036 g, 0.278 mmol) was then added and the yellow solution thus obtained was stirred at ambient temperature for 48 h. After removal of the solvent under reduced pressure, the yellow residue was treated with toluene, and the solution was filtered in order to remove NaCl. The toluene was then evaporated under reduced pressure and the complex washed with cold petroleum ether (0.132 g, 0.243 mmol, 87%). IR (KBr) ν/cm^{-1}: 1439 (s, ν_{CN+CO}). ^{1}H NMR ($CDCl_3$, room temp.) δ/ppm: 3.76 (d, $^4J_{PH}$ = 11.1 Hz, 6H, CH_3), 7.42–7.56 (complex m, 6H, aromatic), 7.77–7.85 (m, 4H, aromatic). ^{31}P{^{1}H} NMR ($CDCl_3$, room temp.) δ/ppm: 34.4 (s). Anal. calcd for $C_{28}H_{26}N_2NiO_2P_2$: C 61.92, H 4.82, N 5.16. Found: C 62.11, H 4.95, N 4.99.

Crystal structure determinations

Crystals of **HL³** suitable for X-ray diffraction were obtained by placing a Schlenk tube with the ligand at 5 °C overnight. Crystals of **1**, **3**·3/2(CH_2Cl_2), **4**, **5** and **7** were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of the respective complex at 5 °C. Crystals of **6** were obtained from a mixture of toluene–pentane at −25 °C overnight. Diffraction data were collected on a Kappa CCD diffractometer using graphite-monochromated MoKα radiation (λ = 0.71073 Å) (Table 3). Data were collected using phi-scans and the structures were solved by direct methods using the SHELXL-97 software,[36–38] and the refinement was performed by full-matrix least squares on F^2. The absorption was not corrected. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereochemistry and refined using a riding model in SHELXL-97.

Table 3 Crystal data and X-ray refinement details for ligand **HL**^{3}, and complexes **1**, **3**·3/2(CH_2Cl_2), **4**, *trans*-**5**, **6** and **7**

Compound	**HL**^{3}	**1**	**3**·3/2(CH_2Cl_2)	**4**	*trans*-**5**	**6**	**7**
Formula	$C_8H_{18}NOP$	$C_{25}H_{22}CoIOP$	2($C_{19}H_{18}CoI_2NOP$), 3/2(CH_2Cl_2)	$C_{19}H_{18}CoINOP$	$C_{28}H_{40}NiO_2P_2$	$C_{16}H_{34}N_2NiO_2P_2$	$C_{28}H_{26}N_2NiO_2P_2$
Formula weight/g mol^{-1}	175.20	682.13	1367.48	493.14	529.25	407.10	543.16
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$C2/c$	$C2/c$
a/Å	15.5860(5)	10.2740(2)	8.0520(3)	12.6820(2)	8.3590(2)	12.4880(9)	15.5110(8)
b/Å	7.8790(4)	8.19200(10)	15.4070(5)	8.3580(2)	10.0440(4)	9.9680(7)	8.9890(12)
c/Å	9.1420(12)	28.0720(6)	19.8740(7)	17.9100(4)	10.1440(3)	17.9220(12)	19.733(3)
α/°	90.00	90.00	89.393(2)	90.00	63.3780(16)	90.00	90.000(7)
β/°	105.741(2)	94.9260(8)	82.027(2)	100.1030(13)	66.9910(16)	108.706(3)	112.010(9)
γ/°	90.00	90.00	76.3740(14)	90.00	80.8330(14)	90.00	90.000(5)
V/Å^3	1080.55(16)	2353.94(7)	2372.33(14)	1868.95(7)	700.67(4)	2113.1(3)	2550.8(5)
Z	4	4	2	4	1	4	4
D_{calcd}/g cm^{-3}	1.077	1.925	1.914	1.753	1.254	1.280	1.414
μ/mm^{-1}	0.209	3.435	3.573	2.661	0.828	1.079	0.915
F(000)	384	1312	1306	968	282	872	1128
T/K	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
$\theta_{min-max}$/°	1.36–29.15	1.46–30.02	1.36–30.07	1.63–30.00	2.27–30.03	2.40–26.37	2.83–29.11
Data set [h, k, l]	–21/21, –8/10, –12/12	–14/14, –10/11, –39/39	–11/11, –21/20, –27/25	–17/17, –10/11, –25/25	–11/11, –13/14, –14/14	–15/15, –12/11, –15/22	–21/21, –12/10, –26/26
Total, unique data, R_{int}	5114, 2898, 0.0466	11 181, 6859, 0.0288	19 144, 13 854, 0.0342	9352, 5456, 0.0298	5962, 4082, 0.0303	4974, 2097, 0.0556	5084, 3377, 0.0253
Observed data $I > 2\sigma(I)$	1559	4838	8377	4025	2681	1899	2742
Reflections, parameters.	2898, 104	6859, 271	13 854, 506	5456, 217	4082, 151	2097, 105	3377, 159
R_1 (all), R_1 (obs), wR_2 (all), wR_2 (obs), GOF	0.1227, 0.0568, 0.1650, 0.1410, 1.040	0.0622, 0.0337, 0.0688, 0.0602, 1.014	0.1162, 0.059, 0.1971, 0.1627, 0.912	0.0591, 0.0358, 0.0886, 0.0793, 1.046	0.0821, 0.0418, 0.1085, 0.0933, 1.019	0.0436, 0.0356, 0.1065, 0.1027, 1.198	0.0576, 0.0408, 0.1110, 0.1039, 1.139
Max. and av. shift/error	0.020, 0.001	0.002, 0.000	0.001, 0.000	0.003, 0.000	0.001, 0.000	0.001, 0.000	0.001, 0.000
Min., Max./e Å^{-3}	–0.259, 0.320	–0.925, 0.846	–1.592, 1.977	–1.093, 0.892	–0.562, 0.501	–0.683, 0.472	–0.697, 0.453

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References

1 P. Braunstein, Y. Chauvin, J. Nähring, A. DeCian, J. Fischer, A. Tiripicchio and F. Ugozzoli, *Organometallics*, 1996, **15**, 5551.
2 E. Lindner, S. Pautz and M. Haustein, *Coord. Chem. Rev.*, 1996, **155**, 145.
3 P. Braunstein, *Chem. Rev.*, 2006, **106**, 134–159.
4 C. S. Slone, D. A. Weinberger and C. A. Mirkin, *Prog. Inorg. Chem.*, 1999, **48**, 233–350.
5 E. Lindner, T. Schneller, F. Auer and H. A. Mayer, *Angew. Chem., Int. Ed.*, 1999, **38**, 2154.
6 P. Braunstein and F. Naud, *Angew. Chem., Int. Ed.*, 2001, **40**, 680–699.
7 P. Kuhn, D. Semeril, D. Matt, M. J. Chetcuti and P. Lutz, *Dalton Trans.*, 2007, 515.
8 A. Kermagoret and P. Braunstein, *Dalton Trans.*, 2008, 822.
9 F. Balegroune, P. Braunstein, L. Douce, Y. Dusausoy, D. Grandjean, M. Knorr and M. Strampfer, *J. Cluster Sci.*, 1992, **3**, 275.
10 X. Morise, M. L. H. Green, P. Braunstein, L. H. Rees and I. C. Vei, *New J. Chem.*, 2003, **27**, 32–38.
11 G. Helmchen and A. Pfaltz, *Acc. Chem. Res.*, 2000, **33**, 336.
12 P. Braunstein, C. Frison and X. Morise, *Angew. Chem., Int. Ed.*, 2000, **39**, 2867–2870.
13 F. Speiser, P. Braunstein and L. Saussine, *Acc. Chem. Res.*, 2005, **38**, 784–793.
14 M. Agostinho and P. Braunstein, *Chem. Commun.*, 2007, 58–60.
15 M. Agostinho and P. Braunstein, *C. R. Chimie*, 2007, **10**, 666–676.
16 C. Mattheis, P. Braunstein and A. Fischer, *J. Chem. Soc., Dalton Trans.*, 2001, 800.
17 T. Q. Ly, A. M. Z. Slawin and J. D. Woollins, *Polyhedron*, 1999, **18**, 1761–1766.
18 P. Braunstein, C. Frison, X. Morise and R. D. Adams, *J. Chem. Soc., Dalton Trans.*, 2000, 2205–2214.
19 P. Bhattacharyya, T. Q. Ly, A. M. Z. Slawin and D. J. Woollins, *Polyhedron*, 2001, **20**, 1803–1808.
20 P. Braunstein, C. Frison, N. Oberbeckmann-Winter, X. Morise, A. Messaoudi, M. Bénard, M.-M. Rohmer and R. Welter, *Angew. Chem., Int. Ed.*, 2004, **43**, 6120–6125.
21 N. Oberbeckmann-Winter, P. Braunstein and R. Welter, *Organometallics*, 2005, **24**, 3149–3157.
22 S. E. Bouaoud, P. Braunstein, D. Grandjean, D. Matt and D. Nobel, *Inorg. Chem.*, 1986, **25**, 3765–3770.
23 P. Braunstein, D. Matt, D. Nobel, F. Balegroune, S. E. Bouaoud, D. Grandjean and J. Fischer, *J. Chem. Soc., Dalton Trans.*, 1988, 353–361.
24 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7–13.
25 S. J. Landon and T. B. Brill, *Inorg. Chem.*, 1984, **23**, 1266–1271.
26 J. Andrieu, P. Braunstein, M. Drillon, Y. Dusausoy, F. Ingold, P. Rabu, A. Tiripicchio and F. Ugozzoli, *Inorg. Chem.*, 1996, **35**, 5986–5994.
27 R. G. Pearson, *Inorg. Chem.*, 1973, **12**, 712–713.
28 J. N. Harvey, K. M. Heslop, A. G. Orpen and P. G. Pringle, *Chem. Commun.*, 2003, 278–279.
29 C. J. Moulton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1980, 299–301.
30 H. Qichen, X. Minzhi, Q. Yanlong, X. Weihua, S. Meichen and T. Youqui, *J. Organomet. Chem.*, 1985, **287**, 419–426.
31 U. Klabunde and S. D. Ittel, *J. Mol. Catal. A: Chem.*, 1987, **41**, 123–134.
32 U. Klabunde, R. Mühlhaupt, T. Herskowitz, A. H. Janowicz, J. Calabrese and S. D. Ittel, *J. Polym. Sci. Part A: Polym. Chem.*, 1987, **25**, 1989–2003.
33 R. G. Pearson, *Inorg. Chem.*, 1973, **12**, 712–713.
34 P. Braunstein, C. Frison and X. Morise, *C. R. Chimie*, 2002, **5**, 131–135.
35 R. F. Heck, *Inorg. Chem.*, 1965, **4**, 855–857.
36 B. V. Nonius, *Kappa CCD Operation Manual*, Delft, The Nederlands, 1997.
37 R. Welter, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2006, **62**, s252.
38 G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.

