# Preparation of Four-membered Phosphonickelocycles. Unusual Facile Stabilization of Five-co-ordinate Complexes†

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Three different types of organometallic compounds $[Ni\{C_6Cl_4(PR_2)\text{-}2\}_2]$ (R = Ph **1** or Et **1′**), $[NiCl\{C_6Cl_4(PR_2)\text{-}2\}L]$ (R = Ph **2** or Et **2′**) and $[NiCl\{C_6Cl_4(PR_2)\text{-}2\}L_2]$ (R = Ph **3** or Et **3′**) have been obtained from 1 equivalent of $PR_2(C_6Cl_5)$ (R = Ph or Et), $[Ni(cod)_2]$ (cod = *cis,cis*-cycloocta-1,5-diene), and L = $PMe_2Ph$ **a**, $PEt_3$ **b**, $P(CH_2Ph)_3$ **c** or $PPh_3$ **d**. Complexes **2** evolve in solution, either to **1** and $[NiCl_2L_2]$, or to **3** by breaking of the Ni–P bond of the four-membered ring by free phosphine. The selective preparation of compounds **1** or **3** can be achieved by performing the oxidative-addition reaction in the absence or with 2 equivalents of L respectively. When 1 equivalent of a diphosphine was used in the oxidative-addition reaction a mononuclear five-co-ordinate complex was obtained, $[NiX\{C_6Cl_4(PR_2)\text{-}2\}(L\text{-}L)]$ **4** [L–L = $Ph_2P(CH_2)_nPPh_2$, $n = 2$ or 3]. However, dppm ($Ph_2PCH_2PPh_2$) acts as a monodentate ligand to give the five-co-ordinate compound $[NiCl\{C_6Cl_4(PPh_2)\text{-}2\}(dppm)_2]$. Complexes **2**, **2′** show preferentially a *cis* geometry, **1′** is *trans*, and **3**, **3′** have the L ligands in *trans* position. Insertion of CO or alkynes into the Ni–C bond was not observed. Compounds **1** and **1′** in the presence of neutral ligands L = CO or $PR_3$ ($PR_3$ = $PMe_2Ph$ **a** or $PEt_3$ **b**) gave five-co-ordinate complexes $[Ni\{C_6Cl_4(PPh_2)\text{-}2\}_2L]$ without cleavage of the Ni–P bond of the ring. Stabilization of the four-membered ring is achieved when two bidentate ligands are present or in the five-co-ordinate compound $[NiCl\{C_6Cl_4(PPh_2)\text{-}2\}(dppm)_2]$. Two bidentate ligands are also needed to stabilize the formation of five-co-ordinate complexes. The molecular structures of complexes **1′**, **3b**, and $[Ni\{C_6Cl_4(PPh_2)\text{-}2\}_2(PEt_3)]$ were determined by single-crystal X-ray diffraction.

The insertion reactions of $d^8$ square-planar organometallic compounds usually involves five-co-ordinate intermediates since associative activation typically occurs. The stabilization of such species involves several factors. Ligands which possess both σ-donor and π-acceptor abilities are believed to be important.[1] Natile and co-workers[2] have described a group of platinum complexes containing N–N bidentate ligands exhibiting a range from square-planar to five-co-ordinate geometries which was related to the contribution of the ligand π-acid character. Unexpectedly from the bite angle of the ligands,[3] in these complexes the bidentate ligand occupies an equatorial position in a trigonal-bipyramidal structure.

The preference for specific sites in trigonal-bipyramidal geometries is important for the activation requirements of insertion/β-elimination reactions.[4] With A,B chelating ligands the preference for a certain bite angle A–M–B could determine the ligand distribution and therefore the reactivity pattern of the complexes.

Organonickel compounds containing P,O bidentate ligands are precursors of active catalytic species in olefin oligomerization–polymerization processes.[5] We are interested in the preparation of nickel compounds containing $P,C^-$ chelates because of their potential applications in catalytic systems when preservation of the chelate part Ni(P–C) is possible, and in the study of the contribution of bidentate ligands to the stabilization of five-co-ordinate complexes. In compounds like $[Ni(C_6H_2Me_3\text{-}2,4,6)(o\text{-}C_6H_4CH_2PPh_2)\{P(CH_2Ph)_3\}]$ the reactivity of the Ni–C (chelate) bond is lower than that of the Ni–C (aryl) bond but not enough to allow their use under an atmosphere of ethylene. The stabilization of the Ni–C (chelate) bond could be achieved increasing by the electronegativity and the steric crowding of the organic fragment.

In this paper we report the reactions of $PR_2(C_6Cl_5)$ and $[Ni(cod)_2]$ (cod = *cis,cis*-cycloocta-1,5-diene) alone or in the presence of different phosphines to give a group of different nickelocycles $[NiCl\{C_6Cl_4(PR_2)\text{-}2\}L]$, $[Ni\{C_6Cl_4(PR_2)\text{-}2\}_2]$, and $[NiCl\{C_6Cl_4(PR_2)\text{-}2\}L_2]$ (R = Ph or Et; L = a phosphine). The phosphines $PR_2(C_6Cl_5)$, R = Ph or Et, were used to prepare phosphonickelocycles with a strong nickel–carbon bond which would be inert toward insertion reactions, as for the Ni–$C_6Cl_5$ bond in the presence of CO.[7] Four-membered phosphometallocycles derived from phenyl, $MC_6H_4P$,[8] and from alkyl phosphines, $MC_2H_nP$,[9] are known for a variety of metals, but only the nickel compound $[(\eta\text{-}C_5H_5)NiW(CO)_5\{\eta\text{-}MePCPh{=}CPhNi(\eta\text{-}C_5H_5)\}]$[10] has been structurally characterized. Other attempts to obtain compounds such as $[Ni\{PR_2(CH_2)_n\}(\eta\text{-}C_5H_5)]$ with $n = 2$ failed probably because of the ring strain induced in the metallocycle.[11]

## Results

*Synthesis of Nickelocycles.*—The reaction of $[Ni(cod)_2]$ with $PR_2(C_6Cl_5)$, R = Ph or Et, in the presence of 1 equivalent of free monodentate phosphines [L = $PMe_2Ph$ **a**, $PEt_3$ **b**, $P(CH_2Ph)_3$ **c** or $PPh_3$ **d**] gave a mixture of four compounds, as detected by $^{31}P$ NMR spectroscopy, three containing the $PR_2(C_6Cl_4)$ ligand and $[NiCl_2L_2]$ (Scheme 1). The organo-

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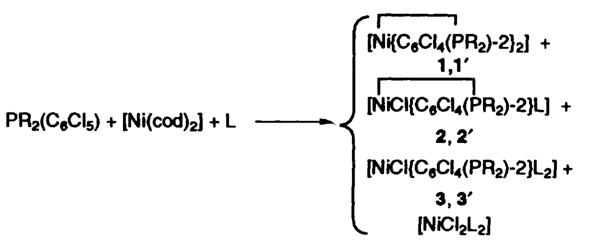
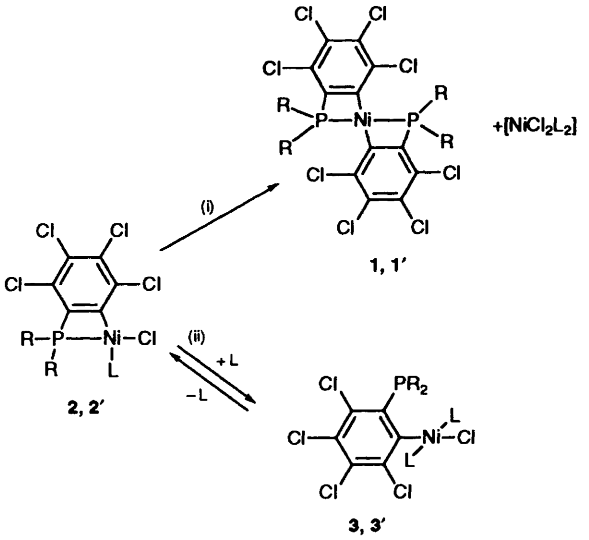
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.
*Non-SI unit employed:* $\mu_B \approx 9.27 \times 10^{-24}$ J $T^{-1}$.



**Scheme 1** R = Ph **1**–**3** or Et **1'**–**3'**



**Scheme 2**

metallic compounds were not easy to separate since an equilibrium between them is operative. However, complexes **1** and **3** were prepared directly. When the oxidative-addition reaction was performed in absence of free phosphine, the compounds $[\mathrm{Ni\{C_6Cl_4(PR_2)\text{-}2\}_2}]$ **1**, **1'** were obtained. The reaction in the presence of 2 equivalents of free phosphine with respect to Ni gave $[\mathrm{NiCl\{C_6Cl_4(PR_2)\text{-}2\}L_2}]$ [R = Ph, L = $\mathrm{PMe_2Ph}$ **3a**, $\mathrm{PEt_3}$ **3b**, $\mathrm{P(CH_2Ph)_3}$ **3c**, or $\mathrm{PPh_3}$ **3d**; R = Et, L = $\mathrm{P(CH_2Ph)_3}$ **3c'**]. The third type of organometallic compound $[\mathrm{NiCl\{C_6Cl_4(PR_2)\text{-}2\}L}]$ was difficult to isolate as a pure solid. Only the complex **2c** containing $\mathrm{P(CH_2Ph)_3}$ gave satisfactory elemental analyses; **2a**, **2b**, **2d** and those containing $\mathrm{PR_2(C_6Cl_5)}$ were observed by $^{31}$P NMR spectroscopy in solution but, as solids, were obtained as mixtures. All the compounds were air-stable as dry solids or in solution under $N_2$. Complexes **2** evolved irreversibly in solution *via* a symmetrization reaction to **1** and $[\mathrm{NiCl_2L_2}]$, or to **3** reversibly by breakage of the Ni–P bond of the four-membered ring by free phosphine [(*i*) in Scheme 2]. This equilibrium can be displaced in both senses by addition of a phosphine scavenger or free phosphine [(*ii*) in Scheme 2].

*Complexes* **1**.—The structure and geometry of the yellow complexes **1** were assigned from their elemental analyses, $^{31}$P NMR spectra and crystal-structure determination. Evidence in support of the four-membered ring was provided by the $^{31}$P NMR data, the phosphorus signal being expected in the range $\delta$ −30 to −60 for a ring of this size[12] (Table 1). The compound of stoichiometry $\mathrm{Ni\{C_6Cl_4(PPh_2)\text{-}2\}_2}$ **1** precipitates readily from its solutions as a fine yellow-orange dust. This solid was very insoluble and showed unexpected magnetic properties. Susceptibility measurements of the yellow powder were performed from 4 to 295 K, showing ferromagnetic behaviour. A maximum in susceptibility was observed near 20 K, beyond which further decreases in temperature led to a sharp decrease in the susceptibility. The values of the susceptibility of different preparations were not reproducible; the highest $\mu_{\mathrm{eff}}$ value observed was 5 $\mu_B$. Similar magnetic properties have been observed for well defined tetrameric $\mathrm{Ni_4O_4}$ compounds[13a–c] or linear chains with thiocyanate bridges.[13d] Therefore the formation of a polymeric material with Ni–P–C–Ni bridges may be assumed. However, $[\mathrm{Ni\{C_6Cl_4(PEt_2)\text{-}2\}_2}]$ **1'** showed properties expected for a square-planar mononuclear complex. The *trans* geometry was confirmed from the molecular structure determination.

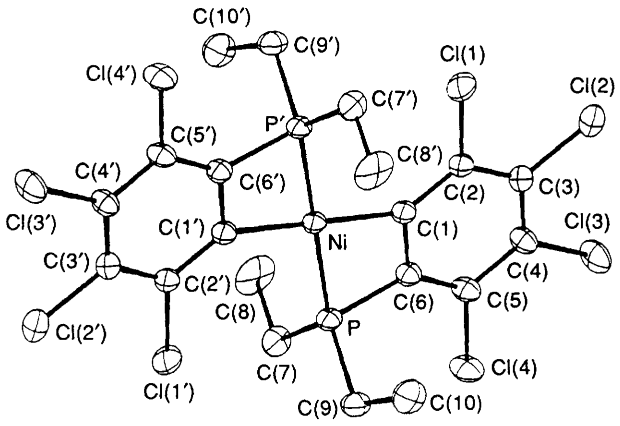


**Fig. 1** View of the structure of $[\mathrm{Ni\{C_6Cl_4(PEt_2)\text{-}2\}_2}]$ **1'** showing the atom labelling scheme. Hydrogen atoms have been omitted for clarity

**Table 1** $^{31}\mathrm{P}\text{-}\{^1\mathrm{H}\}$ NMR data for the compounds $[\mathrm{Ni\{C_6Cl_4(P^aR_2)\text{-}2\}_2}]$ (R = Ph **1** or Et **1'**) and $[\mathrm{Ni\{C_6Cl_4(P^aR_2)\text{-}2\}_2L^b}]$ **7**, **7'**

| Compound | L | δ P$^a$ | δ P$^b$ | $^2J$(P–P)/Hz |
|---|---|---|---|---|
| **1** | | −45 | | |
| **1'** | | −35 | | |
| **7a** | $\mathrm{PMe_2Ph}$ | −53.6 | −22.5 | 205.4 |
| **7b** | $\mathrm{PEt_3}$ | −56.25 | −7.1 | 201.3 |
| **7h** | CO | −57.2 | | |
| **7i** | py | −57.3 | | |
| **7a'** | $\mathrm{PMe_2Ph}$ | −56.4 | −21.2 | 170.5 |
| **7h'** | CO | −42.2 | | |

*Molecular Structure of Complex* **1'**.—The molecular and crystal structure of *trans*-$[\mathrm{Ni\{C_6Cl_4(PEt_2)\text{-}2\}_2}]$ **1'** was determined by X-ray diffraction. The crystal structure consists of discrete molecules (Fig. 1). Selected bond lengths and angles are listed in Table 2. The complex exhibits a planar arrangement of the atoms of the co-ordination sphere NiPP'C(1)C(1'), required by the space group, and each NiPCC ring is almost planar. The following displacements (Å) are observed from the least-squares plane of the NiPC(1)C(6) ring: Ni, −0.070; P, 0.0075; C(1), 0.0111; C(6), −0.0116 Å. The angle between the (NiPP'C(1)C(1') plane and that of the ring NiP(1)C(1)C(6) is 0.58°, and that of the former with the plane defined by the six carbon atoms of the tetrachlorophenyl group is 1.52°.

However, the co-ordination sphere exhibits a distorted square-planar geometry reflected in the P(1)–Ni–C(1) bite angle of 72.9(1)° [P(1)–Ni–C(1') 107.1(1)°]. Similar values have been found for P–Ni–P [72.3(3)°] in $[\mathrm{Ni(dppm)_2][BF_4]_2}$[14] (dppm = $\mathrm{Ph_2PCH_2PPh_2}$) and for C–Ni–P [72.9(2)°] in $[(\eta\text{-}\mathrm{C_5H_5})\mathrm{NiW(CO)_5}\{\eta\text{-}\mathrm{MePCPh{=}CPhNi}(\eta\text{-}\mathrm{C_5H_5})\}]$.[10] The strain in the four-membered ring is reflected in the C(1)–C(6)–P and C(6)–C(1)–Ni angles [100.7(2) and 103.6(2)° respectively] of the sp$^2$ carbon atoms of the benzene ring. The special behaviour of the analogous compound containing the $\mathrm{PPh_2(C_6Cl_4)}$ ligand must be related to the steric requirements for the accommodation of the phenyl rings, which probably result in ring opening and the formation of Ni–P–C–Ni bridges.

*Complexes* 3.—Elemental analyses and $^{31}P$ NMR spectra (Table 3) of compounds **3** were compatible with three different structures **A**–**C**. The presence of two monodentate ligands by each $PPh_2C_6Cl_4$ group and the $AB_2$ pattern in the $^{31}P$ NMR spectra with coupling constants of 25–45 Hz suggested a *cis* arrangement in the system. However, the **A** form could be excluded since no signal in the range expected for four-membered metallocycles was observed (Table 3). The $^{31}P$ NMR signals of free $PPh_2(C_6Cl_5)$ and $PEt_2(C_6Cl_5)$ appear at δ 10.7 and 12.2 respectively, close to the range for the $PR_2(C_6Cl_4)$ ligand. The coupling constant observed between phosphorus atoms in ylidenickel complexes $P_a$–Ni=C–$P_b$, where no direct interaction can be considered between Ni and $P_b$, was 7 Hz.[15] So, the coupling constants observed and the sensitivity towards the monodentate phosphine suggest a structure **C**. This type of $MPC_6H_4M$ bridge has been described in compounds of Pt, Rh and Os.[16]

The reaction of compounds **3a**–**c** with $AgBF_4$ in tetrahydrofuran (thf) gave AgCl and solutions showing the same $^{31}P$ NMR pattern as those of the starting neutral compounds (see Table 3). This was as expected for the five-co-ordinate structure **C** but not for **B**, since it could be assumed that $[\overline{Ni\{C_6Cl_4(P}R_2)\text{-}2\}L_2]^+$ cations would be formed with completely different $^{31}P$ NMR spectra. The FAB spectra of the compound of stoichiometry $NiCl\{C_6Cl_4(PPh_2)\text{-}2\}(PEt_3)_2$ **3b** showed a group of signals centered at *m*/*z* 1127 $[NiCl\{C_6Cl_4(PPh_2)\text{-}2\}_2(PEt_3)_2]$, 1020 $[Ni_2Cl\{C_6Cl_4(PPh_2)\text{-}2\}(PEt_3)_4]$, 854 $[Ni\{C_6Cl_4(PPh_2)\text{-}2\}_2]$, and 728 $[NiCl\{C_6Cl_4(PPh_2)\text{-}2\}(PEt_3)_2]$ with a reasonable isotopic pattern. The ion corresponding to the dinuclear species was not observed. Nevertheless, dimerization processes have been detected for similar complexes[17] in the ionization chamber. So, in order to establish unambiguously the nature of the products '$NiCl\{C_6Cl_4(PR_2)\text{-}2\}L_2$', the molecular and crystal structure of complex **3b** were determined by X-ray diffraction.

**Table 2** Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for $[\overline{Ni\{C_6Cl_4(P}Et_2)\text{-}2\}_2]$ **1′**

| | | | |
|---|---|---|---|
| P–Ni | 2.200(1) | C(2)–C(1) | 1.392(3) |
| C(1)–Ni | 1.952(2) | C(3)–C(2) | 1.390(4) |
| C(6)–P | 1.794(2) | C(4)–C(3) | 1.402(4) |
| C(7)–P | 1.822(3) | C(5)–C(4) | 1.392(4) |
| C(9)–P | 1.824(2) | C(6)–C(5) | 1.389(3) |
| C(1)–C(6) | 1.405(3) | | |
| P–Ni–C(1) | 72.9(1) | C(6)–P–Ni | 82.8(1) |
| P–Ni–P′ | 180.0(1) | C(1)–C(6)–P | 100.7(2) |
| C(1)–Ni–C(1′) | 180.0(1) | C(2)–C(1)–Ni | 140.5(2) |
| C(1′)–Ni–P | 107.1(1) | C(1)–C(2)–Cl(1) | 120.1(2) |
| C(6)–C(1)–Ni | 103.6(2) | C(5)–C(6)–P | 135.6(2) |

*Molecular Structure of Complex* **3b**.—The crystal structure of $[NiCl\{C_6Cl_4(PPh_2)\text{-}2\}(PEt_3)_2]$ (Fig. 2) showed the presence of discrete mononuclear molecules, separated by van der Waals distances, without a Ni–P bond closing the four-membered ring NiCCP. However, the P(1)–Ni distance was 3.018 Å, less than the sum of van der Waals radii (3.45 Å). Selected bond lengths and angles are listed in Table 4; all the bond distances are in the range expected. The complex exhibits a distorted square-planar geometry. The following displacements (Å) are observed from the least-squares plane defined by the atoms of the co-

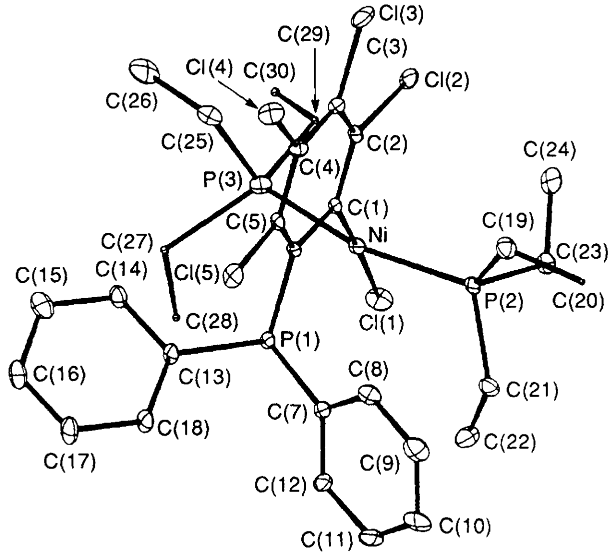
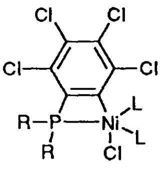
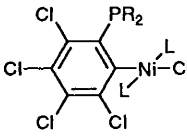


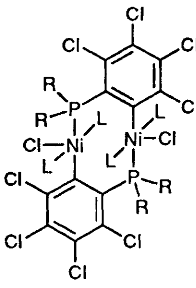
**Fig. 2** View of the structure of $[NiCl\{C_6Cl_4(PPh_2)\text{-}2\}(PEt_3)_2]$ **3b** showing the atom labelling scheme



**A**



**B**



**C**

**Table 3** $^{31}P\text{-}\{^1H\}$ NMR data[a] for the compounds $[NiX\{C_6Cl_4(P^aR_2)\text{-}2\}L^b{}_2]$ **3**, **3′**

| | | δ(P) | | | |
|---|---|---|---|---|---|
| Compound | R, L, X | $P^a$ | $P^b$ | $^2J$(P–P)/Hz | Solvent, *T*/K |
| **3a** | Ph, $PMe_2Ph$, Cl | −9.8 | | | thf, 220 |
| **3b** | Ph, $PEt_3$, Cl | 3.4 | 1.4 | 25 | $C_6H_5Me$, 220 |
| | | 2.1 | 0.8 | 27 | $C_6H_5Me$, 298[b] |
| **3c** | Ph, $P(CH_2Ph)_3$, Cl | 6.7 | −1.9 | 34 | $C_6H_5Me$, 220 |
| **3d** | Ph, $PPh_3$, Cl | 10.6 | −7.2 | 45 | $C_6H_5Me$, 220 |
| **3b′** | Et, $PEt_3$, Cl | 6.5 | −3.5 | 28 | $C_6H_5Me$, 220 |
| **3c′** | Et, $P(CH_2Ph)_3$, Cl | 6.5 | −10.2 | 40 | $C_6H_5Me$, 220 |
| **3d′** | Et, $PPh_3$, Cl | 14.1 | −11.1 | 44 | $C_6H_5Me$, 220 |
| | Ph, $PMe_2Ph$, $MeCN(BF_4^-)$ | −6.1 | −14.7 | 24 | thf, 220 |
| | Ph, $P(CH_2Ph)_3$, $MeCN(BF_4^-)$ | 6.5 | −2.6 | 42 | thf, 220 |
| | Ph, $PEt_3$, $MeCN(BF_4^-)$ | 11.9 | 1.7 | 30 | thf, 220 |

[a] Bruker WP80 SY; 32.4 MHz. [b] Varian XL-200; 81 Mz.

ordination sphere NiP(2)P(3)C(1)Cl(1) (plane A): Ni, −0.0883; P(2), 0.1820; P(3), 0.1842; C(1), −0.1468; Cl(1), −0.1311 Å. Very small displacements from the least-squares plane C(1)C(2)C(3)C(4)C(5)C(6)Cl(2)Cl(3)Cl(4)Cl(5) (plane B) were observed for the atoms of the whole tetrachlorophenyl group; Ni and P(1) show displacements of −0.1099 and −0.1979 Å. The angle between the normal to the planes AB is 86.63°, showing the perpendicular arrangement of the tetrachlorophenyl group with respect to the co-ordination sphere.

Therefore, assuming the same structure in solution, the coupling constants observed ($AB_2$ pattern) in the $^{31}$P NMR spectra are transmitted by a small Ni–P interaction.

*Complexes* **2**.—When the oxidative-addition reaction was performed with an equimolar amount of free phosphine, the compounds $[\overline{\mathrm{NiCl\{C_6Cl_4(P}}\mathrm{R_2)\text{-}2\}L}]$ **2** were observed in solution. The substitution lability of the co-ordinated phosphine precludes the stabilization of these compounds and their obtention as pure solids. Their $^{31}$P NMR spectra were observed only at low temperatures (220–240 K); formation of a four-membered ring is suggested by a signal present at high fields (Table 5). The lability may be related to the steric crowding in the co-ordination sphere, since the *o*-chlorine of the $NiC_6Cl_4P$ ring is directed towards the ligand *trans* to the phosphorus atom of the ring as observed in the structure of compound **1′** (Fig. 1). So the chlorine atom hinders co-ordination, enforcing the *cis* geometry and leading to the labile compounds **2** and **2′**.

When 1 equivalent of the bidentate phosphines dppe [1,2-bis(diphenylphosphino)ethane] or dppp [1,3-bis(diphenylphosphino)propane] was used, either in the oxidative-addition reaction or in toluene solutions of type **3** compounds, the green five-co-ordinate complexes $[\overline{\mathrm{NiCl\{C_6Cl_4(P}}\mathrm{Ph_2)\text{-}2\}(L\text{–}L)}]$ (L–L = dppe **4f** or dppp **4g**) were obtained (Scheme 3).

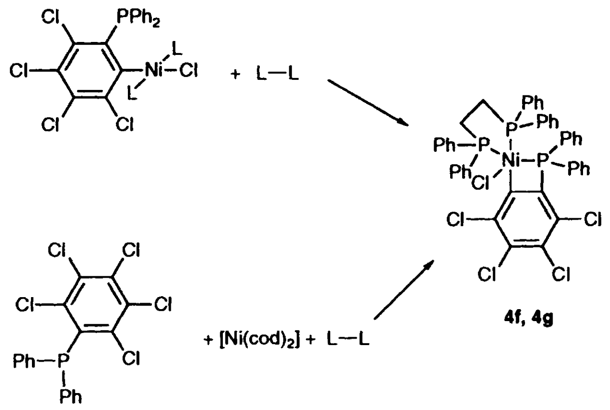
The $^{31}$P NMR signals showed three different phosphorus atoms with coupling constants in accord with a trigonal-bipyramidal geometry. The diphosphine is located in axial–equatorial position, and the phosphorus atom of the P–C ligand is in an equatorial position (Table 6). Addition of $AgBF_4$ to thf solutions of **4f** and **4g** gave brown $[\overline{\mathrm{Ni\{C_6Cl_4(P}}\mathrm{Ph_2)\text{-}2\}(L\text{–}L)}]BF_4$ compounds; only that with dppe **5f** was isolated as a pure solid. The availability of the fifth co-ordination position in **5f** was demonstrated by the further co-ordination of $PMe_2Ph$ to give $\overline{\mathrm{Ni\{C_6Cl_4(P}}\mathrm{Ph_2)\text{-}2\}(dppe)(PMe_2Ph)}]BF_4$ **6**, with four different phosphorus atoms as could be deduced from 16 signals in the $^{31}$P NMR spectrum tentatively assigned after computer simulation [$\delta_{\mathrm{PC\ ring}} = -38.1$, $\delta_{\mathrm{dppe\ ax}} = 45.2$, $\delta_{\mathrm{dppe\ eq}} = 49.3$, $\delta_{\mathrm{PMe}} = -14.2$ $J(\mathrm{P_{ring}\text{–}P}) \approx 98$, $J(\mathrm{P_{ring}\text{–}P_{ax}}) \approx 22$, $J(\mathrm{P_{ring}\text{–}P_{eq}}) \approx 137$, $J(\mathrm{P_{ax}\text{–}P_{eq}}) \approx 36$, $J(\mathrm{P_{ax}\text{–}P}) \approx 50$, $J(\mathrm{P_{eq}\text{–}P}) \approx 172$ Hz]. This spectrum is compatible with a trigonal-bipyramidal geometry with Ni–C and Ni–P (chelate) bonds in axial positions and shows similar *J* values to those observed for $[NiMe(PMe_3)_2(dppe)]BF_4$.[18]

**Table 4** Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses for $[NiCl\{C_6Cl_4(PPh_2)\text{-}2\}(PEt_3)_2]$ **3b**

| | | | |
|---|---|---|---|
| P(2)–Ni | 2.238(2) | C(7)–P(1) | 1.825(6) |
| P(3)–Ni | 2.231(2) | C(13)–P(1) | 1.838(6) |
| C(1)–Ni | 1.882(5) | C(6)–C(1) | 1.416(7) |
| Cl(1)–Ni | 2.250(2) | C(1)–C(2) | 1.403(7) |
| C(6)–P(1) | 1.836(5) | C(2)–Cl(2) | 1.739(6) |
| C(1)–Ni–P(2) | 91.2(2) | P(2)–Ni–P(3) | 165.77(8) |
| P(2)–Ni–Cl(1) | 89.84(7) | C(6)–C(1)–Ni | 119.0(4) |
| C(1)–Ni–P(3) | 91.8(2) | C(1)–C(6)–P(1) | 112.1(4) |
| P(3)–Ni–Cl(1) | 87.79(7) | C(2)–C(1)–Ni | 124.9(4) |
| C(1)–Ni–Cl(1) | 177.1(2) | C (1)–C(2)–Cl(2) | 118.2(4) |

The stabilization of five-co-ordinate compounds **4** and **6** when two bidentate ligands C–P and P–P are present suggested that similar 18-electron complexes might be prepared starting from compounds **1** and **1′**. When carbon monoxide was bubbled through toluene suspensions of **1** the solid dissolved immediately. The $^{31}$P NMR signal shifted to higher fields (Table 1) but the solid compound recovered was **1**. Insertion of CO in the Ni–C bond was not observed, as already reported with $Ni(C_6Cl_5)$ complexes.[7] Other neutral ligands, pyridine (py), $PMe_2Ph$ and $PEt_3$, were tested with **1**, and CO and $PMe_2Ph$ with **1′**. Analytically pure samples of $[\overline{\mathrm{Ni\{C_6Cl_4(P}}\mathrm{Ph_2)\text{-}2\}L}]$ (L = $PMe_2Ph$ **7a** or $PEt_3$ **7b**) were obtained (Scheme 4); the solids are green and red respectively, but orange in solution. Their $^{31}$P NMR spectra showed an $AB_2$ system with coupling constants around 200 Hz indicating the phosphorus atoms in the equatorial plane of a trigonal-bipyramidal structure. Alkynes RCCR (R = COMe or Ph) did not show any interaction with the nickel complexes.

In order to confirm the geometry and firmly establish the values of the coupling constants of the five-co-ordinate compounds, the molecular and crystal structure of complex **7b** was determined by X-ray diffraction. The crystal structure consists of discrete molecules (Fig. 3) separated by van der



**Scheme 3** L–L = dppe **f** or dppp **g**

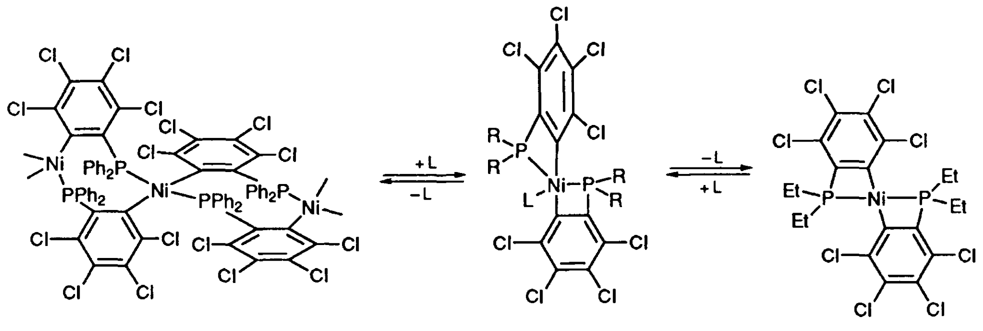
**Table 5** $^{31}$P-{$^1$H} NMR data for the compounds $[\overline{\mathrm{NiCl\{C_6Cl_4(P^a}}\mathrm{R_2)\text{-}2\}L^b}]$ (R = Ph **2** or Et **2′**) in toluene at 220 K

| Compound | L | δ(P) P$^a$ | δ(P) P$^b$ | $^2J$(P$^a$–P$^b$)/Hz |
|---|---|---|---|---|
| **2a** | $PMe_2Ph$ | −54.4 | −13.2 | 46 |
| **2c** | $P(CH_2Ph)_3$ | −48.6 | 15.4 | 65 |
| **2d** | $PPh_3$ | −58.2 | 17.5 | 42 |
| **2** | $PPh_2(C_6Cl_5)$ (*trans*) | −65 | 27 | 333 |
| **2c′** | $P(CH_2Ph)_3$ | −49.5 | 11.5 | 46 |
| **2d′** | $PPh_3$ | −49 | 14 | 44 |
| **2′** | $PEt_2(C_6Cl_5)$ (*cis*) | −42.6 | 18.5 | 67 |
| **2′** | $PEt_2(C_6Cl_5)$ (*trans*) | −56 | 35 | 314 |

**Table 6** $^{31}P$-{$^1H$} NMR data for the compounds [$NiX\{C_6Cl_4(P^aPh_2)$-2}(L–L)] **4** and [$Ni\{C_6Cl_4(PPh_2)$-2}(L–L)]X **5** in toluene at 220 K

| | | δ | | | $^2J$/Hz | | |
|---|---|---|---|---|---|---|---|
| Compound | L–L, X | $\delta_a$ | $\delta_b$ | $\delta_c$ | $P^aP^b$ | $P^aP^c$ | $P^bP^c$ |
| **4f** | dppe, Cl | −32.7 | 43.1 | 39.0 | 165.9 | −13.1 | 40.8 |
| **4g** | dppp, Cl | −55.6 | 3.3 | −10.3 | 221.6 | 31.3 | 74.4 |
| **5f** | dppe, $BF_4^-$ | −55.3 | 58.4 | 54.8 | 231.2 | 76.5 | 36.5 |
| **5g** | dppp, $BF_4^-$ | −69.7 | −3.3 | −2.8 | 294.4 | 70 | 82 |

$\delta_b$, Equatorial co-ordination; $\delta_c$ = axial co-ordination.



**1** **1′**

| | R | L |
|---|---|---|
| **7a** | Ph | $PMe_2Ph$ |
| **7a′** | Et | $PMe_2Ph$ |
| **7b** | Ph | $PEt_3$ |
| **7h** | Ph | CO |
| **7h′** | Et | CO |
| **7i** | Ph | py |

**Scheme 4**

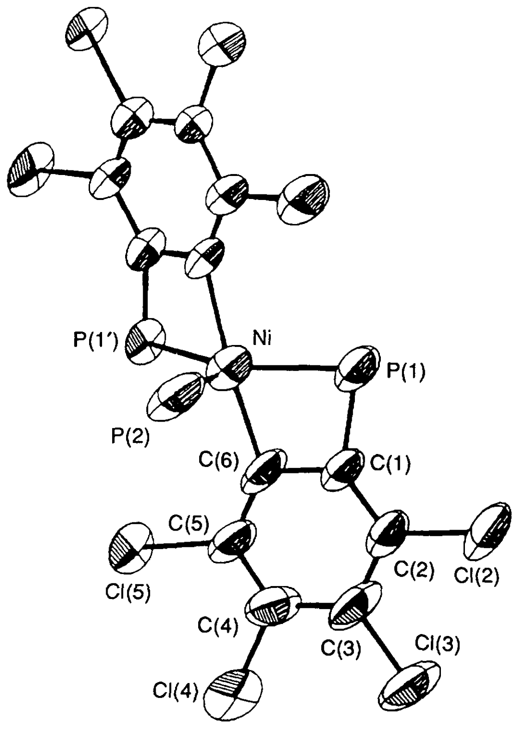


**Fig. 3** View of the structure of [$Ni\{C_6Cl_4(PPh_2)$-2}$_2(PEt_3)$] **7b** showing the atom labelling scheme. Phenyl and ethyl groups have been omitted for clarity

Waals distances. Selected bond lengths and angles are listed in Table 7. The bond distances are in the range expected. The complex exhibits a distorted trigonal-bipyramidal geometry. The trigonal plane is formed by the atoms NiP(1)P(1′)P(2) (plane A, no displacements). The following displacements (Å) are observed from the least-squares plane defined by the four-membered ring NiP(1)C(1)C(6) (plane B) or NiP(1′)C(1′)C(6′) (plane C): Ni, −0.1027(3); P(1), 0.1734(4); C(1), −0.4586(4); C(6), 0.3879(6) Å. These values are larger than those observed for the four-membered ring of complex **1′** because of the larger steric requirements in a five-co-ordinate environment and the presence of phenyl groups in the phosphine. To evaluate the displacements with respect to the whole tetrachlorophenyl ligand the plane C(1)C(2)C(3)C(4)C(5)C(6)Cl(1)Cl(2)Cl(3)-Cl(4) (plane D) was also considered; Ni and P(1) showed displacements of −0.1739 and 1.4016 Å. The angles between the normals to the planes AB, AC, AD, BC, BD, and CD are 113.30, 66.70, 87.07, 59.61, 44.36 and 20.24° respectively.

Different compounds were prepared in the oxidative addition of $PPh_2(C_6Cl_5)$ to [$Ni(cod)_2$] according to the type of phosphine used. In the presence of 2 equivalents of monodentate phosphines, four-co-ordinated square-planar compounds **3** were isolated. However, five-co-ordinated compounds **4** were obtained with bidentate phosphines (dppe or dppp). Furthermore, a bridging $PPh_2(C_6Cl_4)$ ligand may be present in compound **1** (solid state). However, when the oxidative-addition reaction was performed with different amounts of dppm [bis(diphenylphosphino)methane] the same violet compound [$NiCl\{C_6Cl_4(PPh_2)$-2}$(dppm)_2$] **8** was always obtained. Here the diphosphine acts as a monodentate ligand giving a five-co-ordinate complex. The structure was deduced from the $^{31}P$ NMR spectrum (Fig. 4) which consists of an ABB′CC′ system what can be tentatively assigned from a computer simulation [$\delta_{A(ring)} = -49.5$, $\delta_B = -18.9$, $\delta_C \approx -8.2$; $J_{AB} \approx 181$, $J_{AC} \approx 0$, $J_{BB'} \approx 12$, $J_{BC} \approx J_{B'C'} \approx 13.5$, $J_{BC'} \approx J_{B'C} \approx 0$, $J_{CC'} \approx 0$ Hz). Further attempts to co-ordinate the free phosphorus atoms of the complex failed. Monodentate

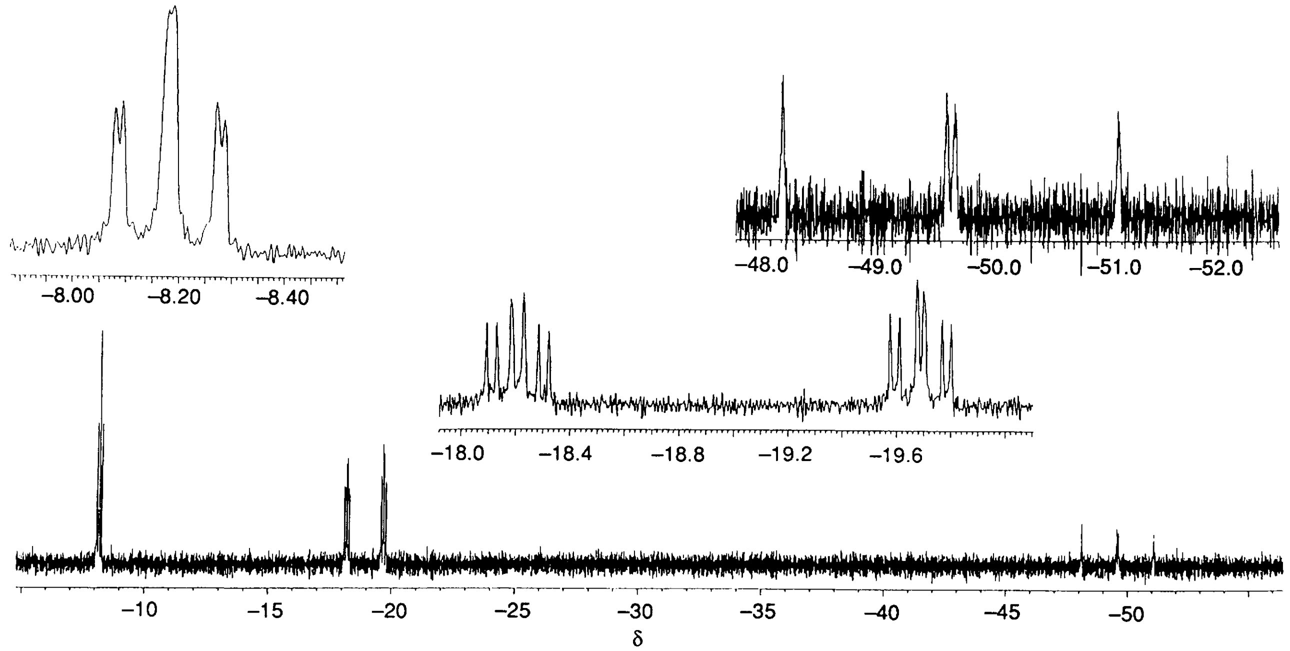
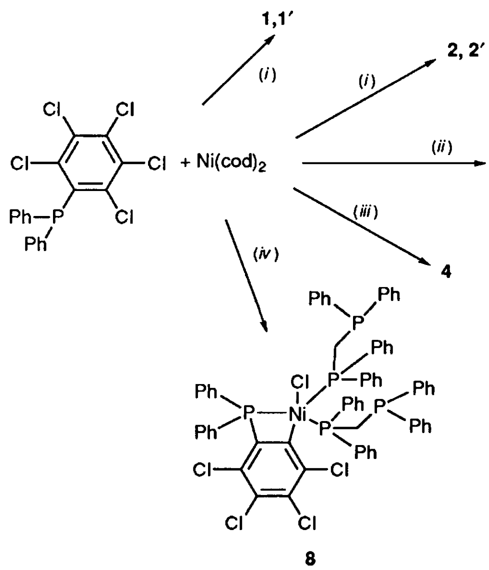


**Fig. 4** The $^{31}P$ NMR spectrum (121.4 MHz) of $[NiCl\{C_6Cl_4(PPh_2)\text{-}2\}(dppm)_2]$ **8** in $C_6D_6$ at 300 K



**Scheme 5** (*i*) $PR'_3$; (*ii*) $2PR'_3$; (*iii*) $Ph_2P(CH_2)_nPPh_2$, $n$ = 2 or 3; (*iv*) dppm

co-ordination of dppm is not unusual,[19] the small bite and steric bulk of the ligand probably preclude both bridge formation and chelation with the sterically demanding $NiC_6Cl_4PPh_2$ ring. Such a finely tuned steric dependence has been observed in $Ni(PMe_3)$ complexes where dmpm ($Me_2PCH_2PMe_2$) or dppm give bridged or chelated complexes respectively in the same substitution reactions.[20] Furthermore, cationic complexes containing chelating ligands $[NiMe(PMe_3)_2(L\text{–}L)]BF_4$ were obtained with dppe, 2,2′-bipyridyl or 1,10-phenanthroline, although no product was isolated with dppm.[18]

## Discussion

A wide range of compounds has been obtained by the oxidative addition of $PPh_2(C_6Cl_5)$ to $[Ni(cod)_2]$, depending on the nature and proportion of the phosphine as reflected in Scheme 5. Compounds **2** are the expected products in the presence of 1 equivalent of phosphine. The *cis* geometry of these compounds can be related to the steric hindrance of the *o*-chlorine atom of the tetrachlorophenyl ligand located near the co-ordination plane, thus labilizing the adjoining co-ordination site. This labilization may be responsible for their easy evolution to compounds **1** or **3**. The stabilization of four-membered metallocycles was achieved when two bidentate ligands were present (compounds **1** and **4**–**7**) but dppm acted only as a monodentate ligand (**8**). Moreover, the formation of five-co-ordinate complexes (**4**, **6** and **7**) was only possible with two bidentate ligands (except for **8**) which were co-ordinated in axial–equatorial positions.

**Table 7** Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses for $[Ni\{C_6Cl_4(PPh_2)\text{-}2\}_2(PEt_3)]$ **7b**

| | | | |
|---|---|---|---|
| P(1)–Ni | 2.266(3) | C(2)–C(1) | 1.378(14) |
| P(2)–Ni | 2.303(3) | C(3)–C(2) | 1.411(12) |
| C(1)–Ni | 1.941(10) | C(4)–C(3) | 1.393(14) |
| C(6)–P(1) | 1.786(8) | C(5)–C(4) | 1.390(14) |
| C(7)–P(1) | 1.804(8) | C(6)–C(5) | 1.398(11) |
| C(6)–C(1) | 1.417(12) | | |
| P(1)–Ni–C(1) | 102.1(3) | C(6)–P(1)–Ni | 82.0(3) |
| P(1)–Ni–P(2) | 117.2(1) | C(6)–C(1)–Ni | 104.9(8) |
| C(1)–Ni–P(2) | 96.8(2) | C(2)–C(1)–Ni | 138.1(7) |
| C(1)–Ni–P(1′) | 71.6(3) | C(5)–C(6)–P(1) | 137.4(5) |
| P(1)–Ni–P(1′) | 126.4(1) | C(1)–C(6)–P(1) | 100.6(5) |

The steric crowding of compounds **2** may be avoided partially by adopting a *cis* geometry, or by the formation of five-co-ordinate species. The stabilization in the solid state of **1′** is related to the small size of the ethyl group, since the solid compound **1** is probably not formed by discrete molecules. However, it is possible to obtain a four-co-ordinate ionic complex **5**, where the bidentate phosphine is co-ordinated in both *cis* and *trans* positions, which is more stable in solution than are compounds **2**. So the presence of bidentate ligands has a stabilizing effect in at least two aspects: a greater inertness towards reorganization reactions and the capacity to stabilize five-co-ordinate species.

The inherent stability of the four-membered ring is greater than expected, since type **1** compounds, in the presence of ligands like $PMe_2Ph$ or CO, gave stable five-co-ordinate complexes **7**, without ring opening or expansion. The ligand geometry in **7a** or **7b**, with the three phosphorus atoms in the equatorial plane, is that proposed for the intermediates of the substitution reactions. The lack of reactivity towards insertion reactions of CO or alkynes demonstrates the inertness of the Ni–$C_6Cl_4$ bond which may be related to the high electronegativity and steric crowding of the ligand, as expected.[7]

In the five-co-ordinate compounds **4**, **6**, and **7** the bidentate ligands forming four- and five-membered rings showed an expected preference for low-bite-angle sites. This means that they adopt axial–equatorial positions in an ideal trigonal-bipyramidal structure and with the most electronegative atoms in apical position according to theoretical models.[3,4]

The sum of electronic aspects and steric bulk limitations which results in the stabilization of five-co-ordinate species involves a chelate contribution. For instance, in the presence of an excess of free monodentate phosphine the four-membered ring of compounds **2** is opened, giving four-co-ordinated complexes **3**, even with the smaller phosphine $PMe_2Ph$ which stabilizes five-co-ordinate complexes $[NiMe_2(PMe_2Ph)_3]$[21] or $[\overline{NiCl(o\text{-}C_6H_4CH_2P}Ph_2)(PMe_2Ph)_2]$[6] containing a five-membered bridge. However, when a bidentate ligand is used, the substitution process is not observed and five-co-ordinate complexes are obtained, *e.g.* with diphosphines like dppe with a definite steric bulk ($PPh_2CH_2$) (cone angle $\theta = 125°$; $pK_a = 3.86$) which can be compared with the more or less basic or bulkier monodentate phosphines $PMe_2Ph$ ($\theta = 122$; $pK_a = 6.50$), $PEt_3$ ($\theta = 132$; $pK_a = 8.69$), $P(CH_2Ph)_3$ ($\theta = 165$) and $PPh_3$ ($\theta = 145$; $pK_a = 2.73$).[22,23] Similar diphosphine stabilization of five-co-ordinate allylnickel complexes was reported by Kurosawa *et al.*[24]

**Table 8** Final atomic coordinates ($\times 10^4$; $\times 10^5$ for Ni, Cl, and P) of $[\overline{Ni\{C_6Cl_4(P}Et_2)\text{-}2\}_2]$ **1′**

| Atom | *X*/*a* | *Y*/*b* | *Z*/*c* |
|---|---|---|---|
| Ni | 0 | 0 | 0 |
| P | −17 979(8) | −24 623(7) | −15 419(6) |
| Cl(1) | 37 849(13) | 29 296(9) | −10 012(8) |
| Cl(2) | 40 199(12) | 16 357(11) | −38 921(9) |
| Cl(3) | 12 009(13) | −18 542(11) | −58 735(7) |
| Cl(4) | −18 944(11) | −41 896(9) | −49 132(7) |
| C(1) | 827(3) | −46(3) | −1 609(2) |
| C(2) | 2 182(3) | 943(3) | −2 064(2) |
| C(3) | 2 310(3) | 394(3) | −3 361(3) |
| C(4) | 1 050(4) | −1 190(3) | −4 268(2) |
| C(5) | −320(3) | −2 214(3) | −3 846(2) |
| C(6) | −407(3) | −1 627(3) | −2 543(2) |
| C(7) | −1 490(4) | −4 412(3) | −1 628(3) |
| C(8) | 547(5) | −4 188(6) | −1 284(5) |
| C(9) | −4 290(3) | −3 077(4) | −2 249(3) |
| C(10) | −4 738(6) | −1 595(7) | −2 332(7) |

So, when the size of the ligands is small enough to allow five-co-ordination, their multidentate character plays a major role in the stabilization of its resulting complexes.

## Experimental

All manipulations of the organonickel compounds were carried out using Schlenk techniques under a nitrogen atmosphere. All solvents were dried and degassed by standard methods. Tetrahydrofuran was distilled over sodium–benzophenone under nitrogen before use. Phosphines were obtained commercially or prepared according to procedures described elsewhere.[25] The complex $[Ni(cod)_2]$ was prepared as reported[26] with small modifications.

Proton NMR spectra were recorded on Gemini 200 or Unity 300 Varian instruments, $^{31}P$ NMR spectra at different temperatures with a Bruker WP80SY instrument (32.38 MHz). Chemical shifts for $^1H$ NMR spectra were referenced to $SiMe_4$ by using peaks of the deuteriated solvent as secondary references. The reference for $^{31}P$ NMR spectra was 85% $H_3PO_4$ with $P(OMe)_3$ as secondary reference. All chemical shifts were reported downfield from standards. All $^{31}P$ NMR spectra were proton decoupled. The solvents used were $C_6D_6$ and $[^2H_8]$toluene for $^1H$ NMR, and toluene or thf with a 5 mm coaxial insert tube containing $[^2H_6]$acetone–$P(OMe)_3$ for $^{31}P$ spectra. The $^{31}P$ NMR spectral simulations were performed by using the PANIC 92 program.[27] Infrared spectra were recorded on a Nicolet 520 FT-IR instrument. Mass spectra were recorded on a Fisons VG quattro spectrometer. The samples were introduced in a matrix of 2-nitrobenzyl alcohol for FAB analysis and then subjected to bombardment with caesium atoms. Elemental analyses were carried out at the Servei d'anàlisis elementals at the University of Barcelona using an Eager 1108 micro-analyzer.

**Table 9** Final atomic coordinates ($\times 10^4$; $\times 10^5$ for Ni, Cl, and P) of $[NiCl\{C_6Cl_4(PPh_2)\text{-}2\}(PEt_3)_2]$ **3b**

| Atom | *X*/*a* | *Y*/*b* | *Z*/*c* |
|---|---|---|---|
| Ni | 1 540(1) | 7 509(1) | 7 029(1) |
| P(1) | 1 796(2) | 6 705(1) | 8 787(1) |
| P(2) | 3 600(2) | 6 624(1) | 6 358(1) |
| P(3) | −481(2) | 8 626(1) | 7 389(1) |
| Cl(1) | 422(2) | 6 444(2) | 6 447(2) |
| Cl(2) | 2 833(2) | 9 848(1) | 6 214(1) |
| Cl(3) | 4 195(2) | 11 217(2) | 7 205(2) |
| Cl(4) | 4 468(2) | 10 379(2) | 9 008(2) |
| Cl(5) | 3 559(2) | 8 111(2) | 9 783(1) |
| Cl(6) | 10 687(4) | 2 449(3) | 6 048(2) |
| Cl(7) | 8 051(5) | 3 749(4) | 6 690(3) |
| C(1) | 2 439(5) | 8 361(4) | 7 570(3) |
| C(2) | 2 960(6) | 9 367(4) | 7 228(4) |
| C(3) | 3 601(6) | 9 982(4) | 7 663(4) |
| C(4) | 3 737(6) | 9 607(5) | 8 438(4) |
| C(5) | 3 270(5) | 8 595(4) | 8 812(4) |
| C(6) | 2 590(5) | 7 992(4) | 8 390(3) |
| C(7) | 3 258(7) | 5 620(5) | 8 840(4) |
| C(8) | 4 653(7) | 5 792(6) | 8 672(5) |
| C(9) | 5 684(9) | 4 907(8) | 8 618(6) |
| C(10) | 5 399(12) | 3 826(8) | 8 745(6) |
| C(11) | 4 053(13) | 3 641(6) | 8 917(6) |
| C(12) | 2 944(9) | 4 521(5) | 8 964(5) |
| C(13) | 945(6) | 6 923(5) | 9 900(4) |
| C(14) | 68(7) | 7 910(6) | 10 093(5) |
| C(15) | −651(9) | 8 096(9) | 10 913(6) |
| C(16) | −516(10) | 7 258(9) | 11 559(5) |
| C(17) | 309(9) | 6 298(8) | 11 373(5) |
| C(18) | 1 047(8) | 6 118(6) | 10 555(4) |
| C(19) | 1 179(8) | 7 223(6) | 6 375(6) |
| C(20) | 6 616(20) | 6 533(17) | 5 994(14) |
| C(20′) | 6 480(21) | 6 844(18) | 5 687(15) |
| C(21) | 4 088(8) | 5 142(6) | 6 686(5) |
| C(22) | 3 000(10) | 4 375(7) | 6 741(7) |
| C(23) | 3 710(9) | 6 541(6) | 5 259(4) |
| C(24) | 3 430(13) | 7 665(8) | 4 773(5) |
| C(25) | −494(8) | 9 913(6) | 7 878(6) |
| C(26) | −1 854(10) | 10 702(9) | 8 111(8) |
| C(27) | −1 745(27) | 8 028(24) | 8 508(19) |
| C(27′) | −2 096(15) | 8 032(12) | 7 829(11) |
| C(28) | −2 131(26) | 6 933(24) | 8 429(19) |
| C(28′) | −2 064(19) | 7 471(17) | 8 773(15) |
| C(29) | −735(23) | 9 208(18) | 6 259(16) |
| C(29′) | −1 615(21) | 8 954(16) | 6 736(14) |
| C(30) | −2 126(22) | 9 621(17) | 6 171(14) |
| C(30′) | −820(43) | 9 548(34) | 5 939(29) |
| C(31) | 9 636(13) | 3 687(9) | 5 896(9) |

**Table 10** Final atomic coordinates ( × $10^4$; × $10^5$ for Ni, Cl, and P) of $[\mathrm{Ni}\{\mathrm{C_6Cl_4(PPh_2)\text{-}2}\}_2(\mathrm{PEt_3})]$ **7b**

| Atom | *X*/*a* | *Y*/*b* | *Z*/*c* |
|---|---|---|---|
| Ni | 0 | 14 024(7) | 75 000 |
| P(1) | 10 761(25) | 19 598(11) | 67 954(12) |
| P(2) | 0 | 1 639(16) | 75 000 |
| Cl(1) | 27 821(27) | 11 603(13) | 83 624(13) |
| Cl(2) | 33 038(29) | 13 569(14) | 100 662(14) |
| Cl(3) | 15 696(28) | 18 798(15) | 109 698(12) |
| Cl(4) | −7 184(29) | 21 642(14) | 101 886(13) |
| C(1) | 770(10) | 1 526(4) | 8 491(5) |
| C(2) | 1 777(10) | 1 411(4) | 8 859(5) |
| C(3) | 2 037(9) | 1 513(4) | 9 630(5) |
| C(4) | 1 261(11) | 1 745(5) | 10 039(4) |
| C(5) | 243(10) | 1 882(4) | 9 684(5) |
| C(6) | 7(8) | 1 784(4) | 8 918(4) |
| C(7) | 1 246(8) | 2 919(4) | 6 904(5) |
| C(8) | 1 318(10) | 3 199(4) | 7 626(6) |
| C(9) | 1 359(10) | 3 933(5) | 7 734(6) |
| C(10) | 1 301(9) | 4 399(5) | 7 162(7) |
| C(11) | 1 178(12) | 4 139(6) | 6 447(8) |
| C(12) | 1 171(11) | 3 402(5) | 6 320(6) |
| C(13) | 2 276(12) | 1 624(6) | 6 491(6) |
| C(14) | 2 290(16) | 1 030(8) | 6 050(8) |
| C(15) | 3 258(23) | 741(11) | 5 892(13) |
| C(16) | 4 136(20) | 1 044(16) | 6 127(12) |
| C(17) | 4 173(15) | 1 637(10) | 6 548(8) |
| C(18) | 3 199(14) | 1 917(8) | 6 730(7) |
| C(19A) | −1 149(11) | −393(8) | 7 691(11) |
| C(19B) | −963(13) | −254(7) | 6 745(8) |
| C(19C) | −889(14) | −185(8) | 8 167(8) |
| C(20A) | 854(18) | −1 165(8) | 7 694(12) |
| C(20B) | −521(20) | −263(11) | 5 968(11) |
| C(20C) | −364(24) | −192(11) | 8 987(11) |

*Crystallographic Studies.*—Crystals of $[\mathrm{Ni}\{\mathrm{C_6Cl_4(PEt_2)\text{-}2}\}_2]$ **1′** $[\mathrm{Ni}\{\mathrm{C_6Cl_4(PPh_2)\text{-}2}\}_2(\mathrm{PEt_3})]$ **7b** $[\mathrm{NiCl}\{\mathrm{C_6Cl_4(PEt_2)\text{-}2}\}(\mathrm{PEt_3})_2]$ **3b** were grown from dichloromethane–ethanol mixtures by cooling to −20 °C. A prismatic crystal was selected and mounted on an Enraf–Nonius CAD4 diffractometer. Unit-cell parameters were determined from the automatic centring of 25 reflections ($12 \leqslant \theta \leqslant 21°$) and refined by the least-squares method. The atomic coordinates of the compounds **1′**, **3b**, and **7b** are reported in Tables 8, 9 and 10 respectively.

*Crystal data for complex* **1′**. $C_{20}H_{20}Cl_8NiP_2$, $M = 664.66$, triclinic, space group $P\bar{1}$, $a = 7.6943(4)$, $b = 9.0180(6)$, $c = 11.1264(9)$ Å, $\alpha = 109.04(1)$, $\beta = 95.76(6)$, $\gamma = 108.86(1)°$, $U = 672.1(1)$ Å$^3$, $Z = 1$, $D_c = 1.643$ g cm$^{-3}$, $F(000) = 334.0$, $\mu$(Mo-K$\alpha$) = 16.34 cm$^{-1}$.

Intensities were collected with graphite-monochromatized Mo-K$\alpha$ radiation ($\lambda$ 0.710 69 Å) by the $\omega$–$2\theta$ scan technique. A total of 3911 reflections were measured in the range $2 \leqslant \theta \leqslant 30°$, 2988 of which were assumed as observed by applying the condition $I \geqslant 2.5\sigma(I)$; $R_{int}$ (on $F$) was 0.012. Three reflections were measured every 2 h as orientation and intensity control; significant intensity decay was not observed. Lorentz-polarization, but not absorption, corrections were applied.

The structure was solved by Patterson synthesis, using the SHELXS computer program and refined by full-matrix least squares with SHELX 76.[28] The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(F_o) + 0.004(F_o)^2]^{-1}$; $f, f'$ and $f''$ were taken from ref. 29. The positions of all H atoms were computed from a difference synthesis, and refined with an overall isotropic thermal parameter. The final $R$ factor was 0.040 ($R' = 0.048$) for all observed reflections. Number of parameters 173. Maximum shift/e.s.d. = 0.1; maximum and minimum peaks in the final difference synthesis 0.3 and −0.3 e Å$^{-3}$ respectively.

*Crystal data for complex* **7b**. $C_{42}H_{35}Cl_8NiP_3$ **7b**, $M = 975.00$, monoclinic, space group $C2/c$, $a = 12.776(3)$, $b = 18.596(4)$, $c = 16.243(4)$ Å, $\beta = 98.42(2)°$, $U = 4287(3)$ Å$^3$, $Z = 4$, $D_c = 1.510$ g cm$^{-3}$, $F(000) = 1984.0$, $\mu$(Mo-K$\alpha$) = 10.89 cm$^{-1}$.

Intensities were collected as above but by the $\omega$ scan technique. A total of 4312 reflections were measured ($\pm h$, $\pm k$, $l$) in the range $2 \leqslant \theta \leqslant 25°$, 1975 having $I \geqslant 2.5\sigma(I)$; $R_{int}$ (on $F$) was 0.056. Significant intensity decay was not observed. Corrections were made as above.

The structure was solved as for complex **1′** except that $w = [\sigma^2(F_o) + 0.0024(F_o)^2]^{-1}$. The positions of the C atoms of the triethylphosphine ligand were affected by disorder. Occupancy factors of 0.5 were assumed according to the heights of the peaks observed in the Fourier synthesis. The positions of five H atoms were located from a difference synthesis and five more were computed. All were refined with an overall isotropic thermal parameter using a riding model. The final $R$ factor was 0.066 ($R' = 0.069$) for all observed reflections. Number of parameters 287. Maximum shift/e.s.d. = 0.1; maximum and minimum peaks in the final difference synthesis 0.3 and −0.3 e Å$^{-3}$ respectively.

*Crystal data for complex* **3b**. $C_{30}H_{40}Cl_5NiP_3{\cdot}CH_2Cl_2$, $M = 814.48$, triclinic, space group $P\bar{1}$, $a = 9.958(2)$, $b = 12.125(3)$, $c = 16.468(3)$ Å, $\alpha = 83.93(2)$, $\beta = 102.05(3)$, $\gamma = 81.45(2)°$, $U = 1895(1)$ Å$^3$, $Z = 2$, $D_c = 1.427$ g cm$^{-3}$, $F(000) = 840.0$, $\mu$(Mo-K$\alpha$) = 11.47 cm$^{-1}$.

Intensities were collected as for complex **7b**. A total of 9741 reflections were measured ($\pm h$, $\pm k$, $l$) in the range $2 \leqslant \theta \leqslant 25°$, 9432 were independent and 5378 were assumed as observed [$I \geqslant 2.5\sigma(I)$]; $R_{int}$ (on $F$) was 0.019. Significant intensity decay was not observed. Lorentz-polarization and extinction [coefficient = 0.005(2)], but not absorption, corrections were made.

The structure was solved by Patterson synthesis, using the SHELXS[28] computer program and refined by full-matrix least squares with SHELX 93.[30] The function minimized was $\Sigma w[|F_o| - |F_c|]^2$, where $w = [\sigma^2(F_o) + (0.1254P)^2 + 2.1781P]^{-1}$, and $P = (F_o^2 + 2F_c^2)/3$.

The positions of five carbon atoms of the triethylphosphine ligand were disordered; occupancy factors of 0.5 were assumed according to the heights of the peaks observed in the Fourier synthesis. Disordered atoms were only refined isotropically. The positions of 24 hydrogen atoms were computed from a difference synthesis. All were refined with an overall isotropic thermal parameter using a riding model. The final $R$ factor was 0.068 ($R' = 0.070$) for all observed reflections. Number of parameters 379. Maximum shift/e.s.d. = 0.1; maximum and minimum peaks in the final difference synthesis 0.6 and −0.6 e Å$^{-3}$ respectively.

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

*Preparations.*—$[\mathrm{Ni}\{\mathrm{C_6Cl_4(PR_2)\text{-}2}\}_2]$ (R = Ph **1** or Et **1′**). To a stirred suspension of [Ni(cod)$_2$] (1.38 g, 5 mmol) in toluene (50 cm$^3$) at −78 °C was added $PPh_2(C_6Cl_5)$ (2.17 g, 5 mmol) or $PEt_2(C_6Cl_5)$ (1.69 g, 5 mmol). The reaction mixture was allowed to warm to room temperature and maintained overnight. The brown solid complex **1** was filtered off, and **1′** was obtained after the addition of hexane. The products were washed with water, cold methanol and dried under vacuum (**1**, 1.72 g, 80%; **1′**, 0.66 g, 40%) (Found: C, 49.75; H, 2.50. Calc. for $C_{36}H_{20}Cl_8NiP_2$ **1**: C, 50.35; H, 2.35. Found: C, 36.05; H, 3.40. Calc. for $C_{20}H_{20}Cl_8NiP_2$ **1′**: C, 36.15; H, 3.05%).

$[\mathrm{NiCl}\{\mathrm{C_6Cl_4(PPh_2)\text{-}2}\}\{\mathrm{P(CH_2Ph)_3}\}]$ **2c**. To a suspension of [Ni(cod)$_2$] (0.55 g, 2 mmol) in toluene (50 cm$^3$) at −78 °C was added $P(CH_2Ph)_3$ (0.61 g, 2 mmol) and (pentachlorophenyl)diphenylphosphine (0.87 g, 2 mmol). The reaction mixture was allowed to warm to room temperature and maintained for 6 h. The mixture was filtered to separate the $[Ni\{C_6Cl_4(PPh_2)-2\}_2]$ formed. On cooling and adding absolute ethanol $[NiCl_2\{P(CH_2Ph)_3\}_2]$ was filtered off. The solvent was partially removed under vacuum and the red complex was precipitated on adding hexane (0.4 g, 25%) (Found: C, 57.2; H, 3.95. Calc. for $C_{39}H_{31}Cl_5NiP_2$: C, 58.65; H, 3.90%).

$[NiCl\{C_6Cl_4(PR_2)-2\}L_2]$ [R = Ph, L = $PMe_2Ph$ **3a**, $PEt_3$ **3b**, $P(CH_2Ph)_3$ **3c**, or $PPh_3$ **3d**; R = Et, L = $P(CH_2Ph)_3$ **3c′**]. To a suspension of $[Ni(cod)_2]$ (0.69 g, 2.5 mmol) in toluene (50 $cm^3$) at −78 °C was added L [$PPh_3$, $P(CH_2Ph)_3$, $PMe_2Ph$, or $PEt_3$; 5 mmol] and $PPh_2(C_6Cl_5)$ (1.08 g, 2.5 mmol) or $PEt_2(C_6Cl_5)$ (0.85 g, 2.5 mmol). The reaction mixture was allowed to warm to room temperature and maintained for 6 h. The solvent was partially removed under vacuum and after addition of absolute ethanol the orange complexes were collected (70–80%) (Found: C, 48.2; H, 5.50. Calc. for $C_{30}H_{40}Cl_5NiP_3$ **3b**: C, 49.40; H, 5.55. Found: C, 53.25; H, 4.10. Calc. for $C_{34}H_{32}Cl_5NiP_3$ **3a**: C, 53.10; H, 4.20. Found: C, 65.20; H, 4.85. Calc. for $C_{60}H_{47}Cl_5NiP_3$ **3c**: C, 65.35; H, 4.75. Found: C, 62.4; H, 3.90. Calc. for $C_{54}H_{35}Cl_5NiP_3$ **3d**: C, 63.80; H, 3.95. Found: C, 61.5; H, 5.30. Calc. for $C_{52}H_{52}Cl_5NiP_3$ **3c′**: C, 62.10; H, 5.20%).

$[NiCl\{C_6Cl_4(PPh_2)-2\}(L-L)]$ (L–L = dppe **4f** or dppp **4g**). To a suspension of $[Ni(cod)_2]$ (0.55 g, 2 mmol) in toluene (40 $cm^3$) at −78 °C was added $Ph_2P(CH_2)_2PPh_2$ (dppe) or $Ph_2P(CH_2)_3PPh_2$ (dppp) (2 mmol) and $PPh_2(C_6Cl_5)$ (0.87 g, 2 mmol). The reaction mixture was allowed to warm to room temperature and maintained overnight. The solvent was partially removed and the green complexes were precipitated on adding hexane (**4f**, 1.25 g, 70%; **4g**, 1.09 g, 60%) (Found: C, 59.70; H, 3.90. Calc. for $C_{44}H_{34}Cl_5NiP_3$ **4f**: C, 59.35; H, 3.85. Found: C, 62.4; H, 4.75. Calc. for $C_{45}H_{36}Cl_5NiP_3$ **4g**: C, 59.70; H, 4.00%). $^1H$ NMR (298 K) of **4f**: δ 2.52 (d, $J \approx 30$ Hz, $P_{ax}CH_2$) and 2.03 (m, $P_{eq}CH_2$).

$[Ni\{C_6Cl_4(PPh_2)-2\}(dppe)]BF_4$ **5f**. A solution of complex **4f** (0.89 g, 1 mmol) in thf (25 $cm^3$) was stirred with $TlBF_4$ (0.32 g, 1.1 mmol) for 3 h at room temperature. After separation of TlCl through Kieselguhr, thf was partially removed. Toluene was added and the solution was kept at −5° for 12 h. A yellow-brown dust was precipitated (0.7 g, 75%) (Found: C, 54.9; H, 3.70. Calc. for $C_{44}H_{34}BCl_4F_4NiP_3$ **5f**: C, 56.05; H, 3.65%). $^1H$ NMR (298 K): δ 2.44 (m), 2.32 (m) ($CH_2$).

$[Ni\{C_6Cl_4(PPh_2)-2\}(dppe)(PMe_2Ph)]BF_4$ **6**. The phosphine $PMe_2Ph$ (0.14 g, 1.1 mmol) was added to a solution of complex **5f** (0.94 g, 1 mmol) in thf (10 $cm^3$). An orange-red solution was obtained. After 30 min of stirring, toluene (20 $cm^3$) was added and mixture was left to crystallise at −15 °C to give a brown-red powder of **6** (0.70 g, 65%) (Found: C, 56.0; H, 4.2. Calc. for $C_{52}H_{45}BCl_4F_4NiP_4$: C, 57.75; H, 4.20%). $^1H$ NMR (220 K): δ 1.24 (br, $PMe_2$); 1.6–2.2 (m) ($CH_2CH_2$).

$[Ni\{C_6Cl_4(PPh_2)-2\}_2L]$ (L = $PMe_2Ph$ **7a** *or* $PEt_3$ **7b**). To a suspension of $[Ni\{C_6Cl_4(PPh_2)-2\}_2]$ (0.86 g, 1 mmol) in toluene (40 $cm^3$) was added L ($PEt_3$ or $PMe_2Ph$; 1 mmol) at room temperature. The mixture was stirred until the solid had completely dissolved. After the addition of ethanol, dark green **7a** and red solid **7b** were obtained in quantitative yield (Found: C, 53.80; H, 3.35. Calc. for $C_{44}H_{31}Cl_8NiP_3$ **7a**: C, 54.80; H, 3.25. Found: C, 52.6; H, 3.80. Calc. for $C_{42}H_{35}Cl_8NiP_3$ **7b**: C, 53.40; H, 3.75%). δ $^1H$ NMR (220 K) of **7a**: δ 1.3 (d) and 1.4 (d) ($PMe_2$).

$[NiCl\{C_6Cl_4(PPh_2)-2\}(dppm)_2]$ **8**. To a suspension of $[Ni(cod)_2]$ (0.55 g, 2 mmol) in toluene (40 $cm^3$) at −78 °C was added dppm (0.77 g, 4 mmol) and $PPh_2(C_6Cl_5)$ (0.87 g, 2 mmol). The reaction mixture was allowed to warm to room temperature and maintained overnight. The solvent was partially removed under vacuum and after addition of ethanol a purple solid was collected (1.89 g, 75%). $^1H$ NMR ($C_6D_6$, 20 °C): δ 0.90 (t, $^2J_{HP}$ = 6 Hz, $PCH_2P$) (Found: C, 61.30; H, 4.30. Calc. for $C_{68}H_{54}Cl_5NiP_5$: C, 64.70; H, 4.30%).

## Acknowledgements

Financial support from Dirección General de Investigación Científica y Técnica (PB 90-0058) is gratefully acknowledged.

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*Received* 5*th May* 1994; *Paper* 4/02679I