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New group 10 complexes of the bulky iminophosphine ligands [$Ph_2PCH_2C(Ph)$═$N(2,6\text{-}R_2C_6H_3)$], where R = Me, ^{i}Pr

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New neutral and cationic complexes [$NiBr_2$(**L1**)] (**1**), [$NiBr_2(OPHPh_2)$(**L1**)] (**2**), [$NiMe_2$(**L1**)] (**3**), [NiBr(PMe_3)(**L1**)](Br) (**4**), [$Ni(CH_3CN)(PMe_3)$(**L1**)]$(BF_4)_2$ (**5**), [$PdBr_2$(**L2**)] (**6**), [PdI_2(**L1**)] (**7**), [PtMeCl(**L1**)] (**8**), [$PtMe_2$(**L1**)] (**9**), [$Pt(CH_3CN)_2$(**L1**)]$(BF_4)_2$ (**10**), [Pt(**L1**)$_2$]$(X)_2$ [X = Cl (**11a**), Br (**11b**)], [PtX(**L1**)$_2$](X) [X = Cl (**12a**), Br (**12b**)], where **L1**: [$Ph_2PCH_2C(Ph)$═$N(2,6\text{-}Me_2C_6H_3)_2$] and **L2**: [$Ph_2PCH_2C(Ph)$═$N(2,6\text{-}{}^iPr_2C_6H_3)_2$], have been prepared and characterised. The molecular structures of **1**, **2**, **6**, **7** and **9** have been determined. The complexes [$PdBr_2$(**L2**)] (**6**), [$PdBr_2$(**L1**)] and [PdMeCl(**L1**)] have been found to catalyse the Heck coupling of 4-bromoacetophenone with *n*-butyl acrylate under aerobic conditions.

Introduction

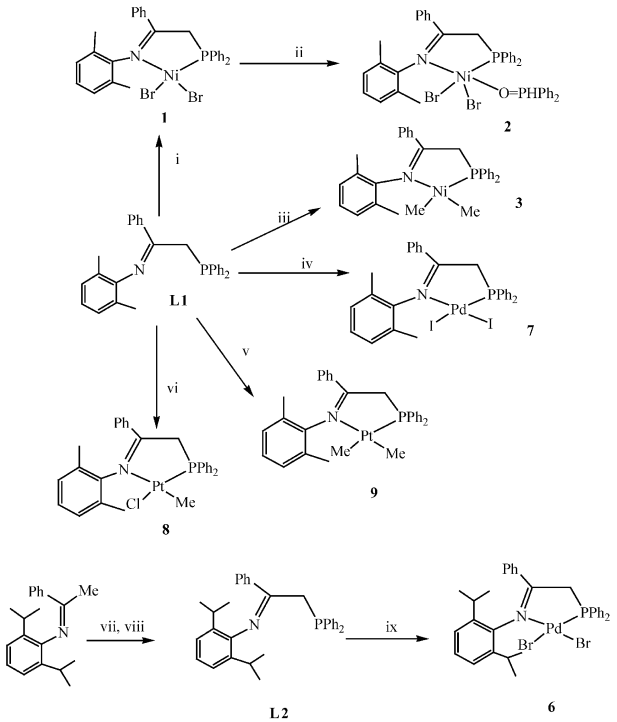
Group 10 transition metals with diimine-based donor ligands have been found to catalyse the polymerisation of ethene and propene, giving rise to a new generation of polymers.[1] Hybrid N/P ligands containing phosphine and imine donor atoms can exhibit hemi-labile character. Such behaviour is of interest in homogeneous catalysis and in the activation of small molecules since it facilitates the formation and stabilisation of intermediate species.[2–7] The coordination chemistry and catalytic properties of N/P ligands with late transition metals continue to attract attention owing to the possibility of tailoring the steric and electronic properties of the different donor groups.[8–23] Hybrid ligands are believed to enhance the catalytic activity for Heck reactions by use of cooperative effects.[24,25] However, complexes containing mixed nitrogen and phosphorus ligands, where the imine acts as a π acceptor and the phosphine as a good σ donor, have rarely been investigated as catalysts for the Heck reaction.[24]

Here, we describe the preparation of neutral and cationic Ni(II), Pd(II) and Pt(II) complexes of the chelating bidentate iminophosphines [$Ph_2PCH_2C(Ph)$═$N(2,6\text{-}Me_2C_6H_3)$] (**L1**) and [$Ph_2PCH_2C(Ph)$═$N(2,6\text{-}{}^iPr_2C_6H_3)$] (**L2**) (Scheme 1). We report that the Pd(II) complexes [$PdBr_2$(**L2**)] **6**, [$PdBr_2$(**L1**)][26] and [PdMeCl(**L1**)][26] catalyse the Heck coupling of 4-bromoacetophenone with *n*-butyl acrylate under aerobic conditions.

Results and discussion

The phosphine-imine ligands **L1** and **L2** were prepared using established procedures.[18,26] We have previously shown that iminophosphine ligands of this family predominantly exist in solution as the *E* isomer, although they are able to interconvert between the *E* and *Z* isomers.[26,27] Thus, ligand-exchange reactions using [$MMe_2(L_2)$] complexes (where M = Ni, Pd and Pt; L_2 = a bidentate ligand such as bpy, tmeda or cod) provide a convenient route to a large variety of dimethyl metal complexes.[28,29]

New neutral and cationic Group 10 complexes of bulky heteroditopic N/P ligands have been prepared and are shown in Schemes 1 and 2. All these complexes were characterised by mass spectrometry (FAB), elemental analysis and ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectroscopy, with the aid of ^{1}H{^{31}P} NMR, NOE difference, ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, and ^{1}H-^{13}C HMBC experiments. ^{1}H NMR spectra of all compounds show resonances specific to metal-coordinated ligands **L1** or **L2** with



Scheme 1 Formation of neutral compounds **1–3** and **6–9**: (i) [$NiBr_2$(dme)], THF; (ii) $Ph_2P(H)$═O, CH_2Cl_2; (iii) [$NiMe_2$(tmeda)], toluene; (iv) [3,5-$(CF_3)_2C_6H_3$]I, [$Pd(dba)_2$], THF; (v) [$PtMe_2$(cod)], THF, −78 °C to room temperature; (vi) [PtMeCl(cod)], THF; (vii) LDA, THF, −78 °C; (viii) Ph_2PCl, THF, −78 °C to room temperature; (ix) $PdBr_2$.

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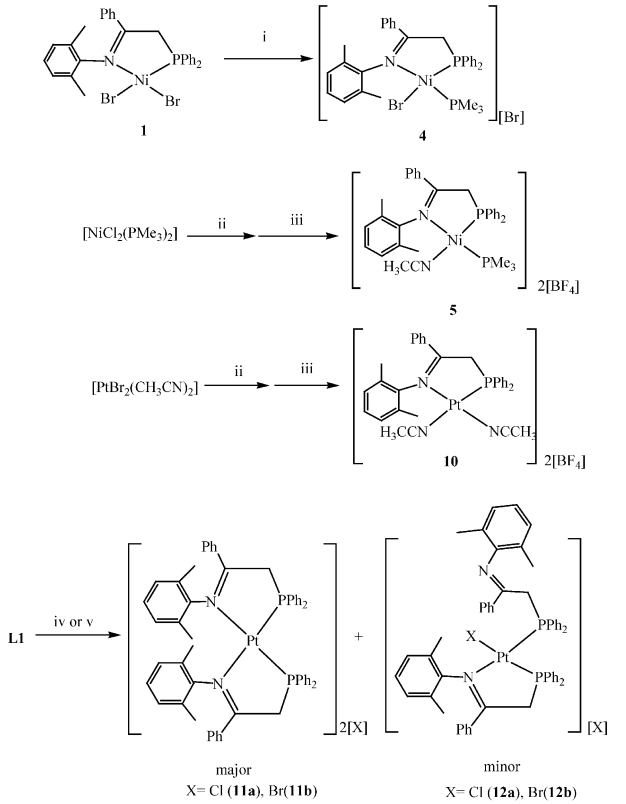

Scheme 2 Formation of mono- and dicationic complexes **4**, **5**, **10**, **11a, 11b** and **12a, 12b**: (i) 2 PMe_3, THF; (ii) 2 $AgBF_4$, CH_3CN; (iii) **L1**, CH_3CN; (iv) $[PtCl_2(cod)]$; (v) $[PtBr_2(CH_3CN)_2]$.

the correct integration ratios. Spectroscopic data for all new compounds are given in Table 1 and the main NMR features are discussed below. Complexes **1**, **2**, **6**, **7** and **9** were also characterised by X-ray diffraction and relevant molecular parameters are given in Table 2.

Compounds **1**, **2**, **6** and **7** are air-stable in the solid state and moderately sensitive to oxygen and moisture in solutions. The metal-alkyl systems **3**, **8** and **9** and the mono- and dicationic complexes **4**, **5**, **10**, **11a, 11b** and **12a, 12b** are especially air- and moisture-sensitive. Compound **2** was found thermally unstable above 0 °C. All mono- and dicationic complexes are insoluble in nonpolar solvents, relatively stable towards decomposition in CH_2Cl_2 or THF, and decompose rapidly in MeOH and $CHCl_3$. Solutions of **9** in CD_2Cl_2 or d^8-THF decompose upon standing for *ca.* 2 h at room temperature. Although **9** is somewhat more stable towards decomposition in solution and the solid state than its analogous Ni and Pd complexes, the low solubility and rapid decomposition at room temperature prevented characterisation by $^{13}C\{^1H\}$ NMR spectroscopy and catalysis testing for Heck reactions.

Syntheses

Nickel(II) complexes. The complexes $[NiX_2(\mathbf{L1})]$, where X = Br (**1**) and Me (**3**), were prepared *via* reaction of $[NiBr_2(dme)]$ and $[NiMe_2(tmeda)]$, respectively, with **L1** (Scheme 1). Red crystals of **1**, suitable for X-ray structure determination, were obtained by allowing a concentrated CH_2Cl_2 solution to stand for 1 week at −20 °C, under a nitrogen atmosphere. Both nickel(II) complexes **1** and **3** are sensitive to moisture. However, **3** is additionally thermally sensitive and decomposes (presumably through elimination) to afford the free ligand **L1**, after storage for 12 h at room temperature under N_2, as shown by ^1H and $^{31}P\{^1H\}$ NMR spectroscopies. To further explore the coordination chemistry of **1** under aerobic conditions, this was exposed to one equivalent of $O{=}PHPh_2$ in CH_2Cl_2, resulting in the formation of $[NiBr_2(O{=}PHPh_2)(Ph_2PCH_2C(Ph){=}N(2,6\text{-}Me_2C_6H_3)]$ (**2**) in low yields (<10%). Complex **2** was identified by single-crystal X-ray diffraction. The Ni(II) monocationic complex $[NiBr(PMe_3)\{Ph_2PCH_2C(Ph){=}N(2,6\text{-}Me_2C_6H_3)\}]Br$ (**4**) was prepared by reacting complex **1** with 2 equivalents of PMe_3. Traces of **L1** and $[Ni(PMe_3)_2Br_2]$ were also identified by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, suggesting facile displacement of the N/P ligand by PMe_3. The Ni(II) dicationic complex $[Ni(CH_3CN)(PMe_3)\{Ph_2PCH_2C(Ph){=}N(2,6\text{-}Me_2C_6H_3)\}][BF_4]_2$ (**5**) was obtained by reacting $[Ni(MeCN)_2(PMe_3)_2][BF_4]_2$ with one equivalent of **L1**.

Palladium(II) complexes. The iminophosphine ligand **L2** was reacted with $PdBr_2$ to afford the complex $\{PdBr_2[Ph_2PCH_2C(Ph){=}N(2,6\text{-}^iPr_2C_6H_3)]\}$ (**6**). The neutral complex $\{PdI_2[Ph_2PCH_2C(Ph){=}N(2,6\text{-}Me_2C_6H_3)]\}$ (**7**) was prepared by an oxidative addition reaction between $\{[3,5\text{-}(CF_3)_2C_6H_3]I\}$ and $[Pd(dba)_2]$ (dba = dibenzylidenacetone) in the presence of **L1** (Scheme 1). Although Pd(II) complexes of the type [PdRI(N/N)], where R = 3,5-$(CF_3)_2C_6H_3$) and N/N = $Me_2N(CH_2)_2NMe_2$,[30] or [PdRI(N/P)], where R = Me or Ph and N/P = 2-(diisopropylphosphinomethyl)-1-methylimidazole,[14] have previously been prepared by this method, no traces of the monoaryl complex $[PdI\{3,5\text{-}(CF_3)_2C_6H_3\}(\mathbf{L1})]$ were found. The formation of dihalide complex **7** instead of the expected complex $[PdI\{3,5\text{-}(CF_3)_2C_6H_3\}(\mathbf{L1})]$ was presumably a consequence of unfavourable steric interactions between the iminophosphine ligand and the bulky aryl group 3,5-$(CF_3)_2C_6H_3$ in the latter. Crystals of **6** and **7** suitable for single-crystal X-ray diffraction were obtained from concentrated CH_2Cl_2 solutions layered with pentane and stored at −20 °C.

Platinum(II) complexes. The neutral complexes $[PtMeCl(\mathbf{L1})]$ (**8**) and $[PtMe_2(\mathbf{L1})]$ (**9**) were isolated from the reaction of [PtMeCl(cod)] (cod = 1,5-cyclooctadiene) and $[PtMe_2(cod)]$ with **L1**, respectively. Crystals suitable for X-ray diffraction studies were grown for **9** from a 1 : 4 mixture of toluene and pentane at −20 °C. The dicationic complex $[Pt(CH_3CN)_2\{Ph_2PCH_2C(Ph){=}N(2,6\text{-}Me_2C_6H_3)\}][BF_4]_2$ (**10**) was obtained by treating $[Pt(CH_3CN)_4][BF_4]_2$ with a CH_3CN solution of **L1**. Interestingly, reaction between $[PtCl_2(cod)]$ and **L1** carried out at room temperature in THF afforded a mixture of two products in a 5 : 1 ratio as determined by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Similarly, the reaction between **L1** and *cis*-$[PtBr_2(CH_3CN)_2]$ carried out in CH_2Cl_2 gave a mixture of two products in the 3 : 2 ratio (as shown by integration in the ^1H NMR spectrum). In both cases, the products could not be separated by crystallisation and chromatography on silica led to decomposition. NMR, elemental analysis and FAB mass spectrometry shown that, in each case, the products contained two components, with the stoichiometry Pt : **L1** : X of 1 : 2 : 2. Thus, the formation of complexes $[Pt(\mathbf{L1})_2][X]_2$, X = Cl (**11a**) and Br (**11b**), and $[PtX(\mathbf{L1})_2]X$, X = Cl (**12a**) and Br (**12b**), are proposed. Variable temperature NMR experiments in CD_2Cl_2 did not confirm the presence of an equilibrium between the two complexes.

NMR and magnetic data

Room temperature ^1H NMR spectroscopy of **1** showed broad signals between δ −5 and 25. The $^{31}P\{^1H\}$ NMR spectrum recorded at the same temperature showed no signal from the phosphorus nucleus. This is indicative of a paramagnetic complex, consistent with Ni(II) in a tetrahedral geometry. The dynamic behaviour of this species in solution was studied by variable temperature NMR spectroscopy. ^1H- and $^{31}P\{^1H\}$ NMR spectroscopy (CD_2Cl_2) at −80 °C and below showed

Table 1 Data characterising compounds **L-2**, **1–12**

	Compound data	NMR data
L2	**[$Ph_2PCH_2C(Ph)$═$N(2,6\text{-}^iPr_2(C_6H_3)$]** $C_{32}H_{36}NP$ MW 463.60 Air and moisture sensitive, oily light-yellow solid $\nu_{C=N}$ 1640 cm^{-1}	^1H NMR (500 MHz, CD_2Cl_2) Minor isomer (*Z*):1.02 (d, CH_3CHCH_3, 12H, $^3J_{HH} = 6.8$), 2.09 (h, CH_3CHCH_3, 2H), 3.80 (d, CH_2-P, 2H, $^2J_{PH} = 1$); Major isomer (*E*): 1.44 (d, CH_3CHCH_3, 12H, $^3J_{HH} = 6.6$), 3.37 (h, CH_3CHCH_3, 2H, $^3J_{HH} = 6.6$), 3.43 (d, CH_2-P, 2H, $^2J_{PH} = 1.7$), 7.96–7.10 (multiple resonances, aromatic protons) $^{31}P\{^1H\}$ NMR data (202.4 MHz, toluene): Minor isomer (*Z*): −19.2 (s), Major isomer (*E*): −12.6 (s) $^{31}P\{^1H\}$ NMR (202.4 MHz, CD_2Cl_2): Minor isomer (*Z*): −21.0 (s), Major isomer (*E*): −14.9 (s)
1	**[$NiBr_2${$Ph_2PCH_2C(Ph)$═$N(2,6\text{-}Me_2C_6H_3)$}]** $C_{28}H_{26}Br_2NNiP$ MW 625.99 Air-stable red-brown crystals. Elemental analysis: % calculated (found) C 53.47 (53.72), H 4.21 (4.18), N 2.23 (2.23), Ni 8.91 (9.38) Mass spectrometry: FAB^+: *m*/*z* 626.0 (15) $[M]^+$, 546 (100) $[M - Br]^+$ IR: $\nu_{C=N}$ 1584 cm^{-1}	^1H NMR (500 MHz, CD_2Cl_2, − 90 °C) 2.24 (s, 6H, $Me_2C_6H_3$), 4.09 (b, CH_2–P, 2H), 6.50 (b, 1H, *p*-H of $Me_2C_6H_3$), 6.85 (b, 2H, *m*-H of $Me_2C_6H_3$), 7.15-7.40 (b, 5H, *o, p, m*-H of *Ph*), 7.57 (b, 4H, *m*-H of PPh_2), 7.67 (b, 4H, *p*-H of PPh_2), 7.99 (b, 2H, *o*-H of PPh_2) $^{31}P\{^1H\}$ NMR (202.4 MHz, CD_2Cl_2, −90 °C): 41.9 (s)
2	**[$NiBr_2(O$═$HPPh_2)${$Ph_2PCH_2C(Ph)$═$N(2,6\text{-}Me_2C_6H_3)$}]** $C_{40}H_{37}Br_2NNiOP$ Mw 828.18 Air and moisture sensitive brown crystals Elemental analysis % found (Calc.) C 57.34 (58.01), H 5.20 (4.50), N 1.63 (1.69) Mass spectrometry: FAB^+: *m*/*z* 829.0 (14) $[M]^+$, 749.0 (20) $[M\text{-}Br]^+$, 626.0 (100) $[M\text{-}(OHPPh_2)]^+$ IR: $\nu_{C=N}$ 1560 cm^{-1}, ν_{PH} 2370, 2340 cm^{-1} , $\nu_{P=O}$ 1238 cm^{-1}	^1H NMR (500 MHz, CD_2Cl_2) paramagnetic, 15 broad resonances between δ −4 and −21
3	**[$NiMe_2${$Ph_2PCH_2C(Ph)$═$N(2,6\text{-}Me_2C_6H_3)$}]** $C_{30}H_{32}NNiP$ MW 496.26 Air and moisture sensitive red powder Elemental analysis: % Found (Calc.) C 69.1 (72.6), H 5.9 (6.5), N 2.3 (2.8) Mass spectrometry: FAB^+: *m*/*z* 496.3 (10) $[M]^+$, 481.3 (30) $[M - Me]^+$, 466.2 (100) $[M - Ni - 2Me]^+$	^1H NMR (500 MHz, d^8-toluene): 0.06 (d, 3H, Ni-*Me trans*-P, $^3J_{PH} = 4.7$), 0.49 (d, 3H, Ni-*Me*, *cis*-P, $^3J_{PH} = 12.3$), 2.09 (s, 6H, $Me_2C_6H_3$), 3.31 (d, CH_2-P, 2H, $^2J_{PH} = 6.7$), 7.9 (b, 4H, *o*-H of PPh_2), 7.67 (b, 4H, *m*-H of PPh_2), 7.40 (b, 2H, *p*-H of PPh_2), 7.4-6.6 (multiple resonances, 8H, aromatic protons) $^{31}P\{^1H\}$ NMR (202.4 MHz, d^8-toluene) 30.8(s) $^{13}C\{^1H\}$ NMR (125.7 MHz, d^8-toluene) −12.0 (d, Ni-*Me*, $^2J_{PC} = 226$), 3.8 (d, Ni-*Me*, $^2J_{PC} = 89$), 21.5 (s, $Me_2C_6H_3N$), 39.7 (d, CH_2-P, $^1J_{PC} = 6$), 142.2 (s, *i-C* of $Me_2C_6H_3N$), 169.4 (d, *C*═N, $^3J_{PC} = 15$), 128.0 (d, *i*-C of PPh_2, $^3J_{PC} = 27$), 127.9 (d, *m*-C of PPh_2, $^3J_{PC} = 13$), other aromatic C-resonances 132.7, 127.5, 125.0, 124.4, 123.0, 122.3, 119.3
4	**[$NiBr(PMe_3)${$Ph_2PCH_2C(Ph)$═$N(2,6\text{-}Me_2C_6H_3)$}][Br]** $C_{31}H_{35}Br_2NNiP_2$ MW 702.07 Air and moisture sensitive purple powder Elemental analysis: % Found (Calc.) C 53.2 (53.0), H 5.2 (5.02), N 1.0 (2.00), Ni 8.0 (8.3), Br 26.1 (22.7) Mass spectrometry: FAB^+: *m*/*z* 619.2 (20) $[M - Br]^+$, 546.1 (70) $[M - Br - PMe_3]^+$	^1H NMR (300 MHz, CD_2Cl_2) 1.16 (b, 9H, P*Me*$_3$), 1.96 (s, 6H, $Me_2C_6H_3$), 4.67 (d, 2H, CH_2-P, $^2J_{PH} = 21.5$), 6.88 (t, 1H, *p*-H of $Me_2C_6H_3$), 7.18 (d, 2H, *m*-H of $Me_2C_6H_3$), 7.00 (m, 2H, *o*-H of *Ph*), 7.09 (m, 2H, *m*-H of *Ph*), 7.17 (m, 1H, *p*-H of *Ph*), 7.46 (m, 4H, *o*-H of PPh_2, $^3J_{P\text{–}Pho} = 13.4$), 7.93 (b, 4H, *m*-H of PPh_2), 7.79 (b, 2H, *p*-H of PPh_2) $^{31}P\{^1H\}$ NMR data (121.51 MHz, CD_2Cl_2): 34.2 (d, *P*Ph$_2$, $^2J_{PP} = 218$) −22.9 (d, *P*Me$_3$ $^2J_{PP} = 218$) $^{13}C\{^1H\}$ NMR data (75.5 MHz, CD_2Cl_2): 14.5 (b, P*Me*$_3$), 17.6 (s, $Me_2C_6H_3N$), 149.4 (s, *i-C* of $Me_2C_6H_3N$), 125.2 (s, *o*-C of $Me_2C_6H_3N$), 128.2 (s, *m*-C of $Me_2C_6H_3N$), 130.2 (s, *p*-C of $Me_2C_6H_3N$), 162.0 (b, N═*C*), 138.8 (b, *i*-C of *Ph*), 131.0 (s, *o*-C of *Ph*), 130.2 (s, *m*-C of *Ph*), 128.0 (s, *p*-C of *Ph*), 135.4 (b, i-C of PPh_2), 131.6 (b, o-C of PPh_2), 130.8 (b, m-C of PPh_2), 128.4 (b, p-C of PPh_2)
5	**[$Ni(CH_3CN)(PMe_3)${$Ph_2PCH_2C(Ph)$═$N(2,6\text{-}Me_2C_6H_3)$}][BF_4]$_2$** $C_{33}H_{38}B_2F_8N_2NiP_2$ MW 756.93 Air and moisture sensitive orange powder Elemental analysis: % Found (Calc.) C 51.5 (52.3), H 5.31 (5.06), N 3.7 (3.7) Mass spectrometry: FAB^+: *m*/*z* 583.4(70) $[M - 2BF_4]^{2+}$, 540.9(15) $[M - 2BF_4 - CH_3CN]^{2+}$, 507.2 (100) $[M - 2BF_4 - PMe_3]^{2+}$ IR: $\nu_{C=N}$ 1634, ν_{BF} 906 –1250 cm^{-1} (broad), ν_{CH_3CN} 2004–2300 cm^{-1} (broad)	^1H NMR (500 MHz, CD_2Cl_2): 1.22 (dd, 9H, P*Me*$_3$ *cis*-*P*Ph$_2$, $^2J_{PH} = 12$, $^4J_{PH} = 1$), 1.83 (dd, 3H, *Me*CN *trans*-*P*Ph$_2$, $^2J_{PH} = 13.5$, $^4J_{PH} = 1$), 2.17 (s, 6H, $Me_2C_6H_3$), 4.51 (dd, 2H, CH_2-P, $^2J_{PH} = 12$, $^4J_{PH} = 1.5$), 6.90 (t, 1H, *p*-H of $Me_2C_6H_3$, $^3J_{HH} = 7.5$), 6.97 (d, 2H, *m*-H of $Me_2C_6H_3$, $^3J_{HH} = 7.5$), 7.18 (m, 2H, *o*-H of *Ph*), 7.02 (m, 2H, *m*-H of *Ph*), 7.34 (m, 1H, *p*-H of *Ph*), 7.99 (m, 4H, *o*-H of PPh_2, $^3J_{PH} = 12.9$), 7.81 (m, 4H, *m*-H of PPh_2, $^4J_{PH} = 2.5$), 7.62 (m, 2H, *p*-H of PPh_2, $^5J_{PH} = 2$) $^{31}P\{^1H\}$ NMR data (202.4 MHz, CD_2Cl_2) 51.2 (d, *P*Ph$_2$, $^2J_{PP} = 102$), −8.2 (d, *P*Me$_3$, $^2J_{PP} = 102$) $^{11}B\{^1H\}$ NMR (160.4 MHz, CD_2Cl_2) −0.6 (s) ^{19}F NMR (282.45 MHz, CD_2Cl_2) −146.3 (s) $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2): 14.7 (d, *Me*CN *trans*-P, $^2J_{PC} = 71$), 15.9 (d, P*Me*$_3$ *cis*-P, $^2J_{PC} = 36$), 19.5 (s, $Me_2C_6H_3N$), 48.2 (b, CH_2-P), 145.3 (s, *i-C* of $Me_2C_6H_3N$), 128.2 (s, *m*-C of $Me_2C_6H_3N$), 128.6 (s, *o*-C of *Ph*), 127.9 (s, *m*-C of Ph), 127.4 (s, *p*-C of *Ph*), 134.2 (b, i-C of PPh_2), 133.5 (d, o-C of PPh_2, $^2J_{PC} = 11$), 130.7 (d, m-C of PPh_2, $^3J_{PC} = 11$), 130.9 (b, p-C of PPh_2), other aromatic C-resonances: 132.3, 127.4, 124.5

Table 1 (*continued*)

	Compound data	NMR data
6	**[$PdBr_2${$Ph_2PCH_2C(Ph)$=$N(2,6\text{-}^iPr_2C_6H_3)$}]** $C_{32}H_{36}Br_2NPPd$ MW 731.85 Air stable red-orange powder Elemental analysis: % Found (Calc.) C 52.2 (52.2), H 5.2 (4.9), N 1.8 (1.9), Br 21.1 (21.8) Mass spectrometry: FAB^+: *m/z* 729(3) $[M]^+$, 649(10) $[M - Br]^+$, 567(20) $[M - 2Br]^+$ IR: $\nu_{C=N}$ 1592 cm^{-1}	^1H NMR (500 MHz, CD_2Cl_2) 0.47 (d, CH_3CHCH_3, 6H, $^2J_{HH} = 6.6$), 1.40 (d, CH_3CHCH_3, 6H, $^3J_{HH} = 6.6$), 2.88 (h, CH_3CHCH_3, 6H, $^3J_{HH} = 6.8$), 4.45 (d, CH_2-P, 2H, $^2J_{PH} = 13.5$), 7.01 (t, 1H, p-H of $^iPr_2C_6H_3$), 7.03 (d, 2H, m-H of $^iPr_2C_6H_3$), 7.05 (m, 2H, o-H of *Ph*), 7.21 (m, 2H, m-H of *Ph*), 7.37 (m, 1H, p-H of *Ph*), 7.90 (m, 4H, o-H of PPh_2, $^3J_{PH} = 8.5$), 7.58 (m, 4H, m-H of PPh_2, $^4J_{PH} = 2.8$), 7.68 (m, 2H, p-H of PPh_2, $^5J_{PH} = 2.5$) $^{31}P\{^1H\}$ NMR (202.4 MHz, CD_2Cl_2) 45.0 (s) $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_2Cl_2) 23.0 (s, CH_3CHCH_3), 24.5 (s, CH_3CHCH_3), 25.9 (s, CH_3CHCH_3), 48.4(d, CH_2-P, $^1J_{PC} = 18$), 144.6 (s, *i-C* of $^iPr_2C_6H_3N$), 140.0 (s, *o*-C of $^iPr_2C_6H_3N$), 128.3 (s, *m*-C of $^iPr_2C_6H_3N$), 124.1 (s, *p*-C of $^iPr_2C_6H_3N$), 179.3 (b, N=*C*), 132.9 (b, *i-C* of *Ph*), 132.5(s, *o*-C of *Ph*), 129.6 (s, *m*-C of *Ph*), 128.9 (s, *p*-C of *Ph*), 126.4 (d, *i*-C of PPh_2, $^1J_{PC} = 34$), 133.5 (d, *o*-C of PPh_2, $^2J_{PC} = 7$), 129.7 (d, *m*-C of PPh_2, $^3J_{PC} = 7$), 133.1 (s, *p*-C of PPh_2)
7	**[PdI_2{$Ph_2PCH_2C(Ph)$=$N(2,6\text{-}Me_2C_6H_3)$}]** $C_{28}H_{26}I_2NPPd$ MW 767.72 Air stable red-brown powder Elemental analysis: % Found (Calc.) C 44.5 (43.8), H 3.7 (3.4), N 2.0 (1.8) Mass spectrometry: FAB^+: *m/z* 640.31 (100) $[M - I]^+$, 407(20) $[M - PdI_2]^+$ IR: $\nu_{C=N}$ 1570 cm^{-1}	^1H NMR (500 MHz, CD_2Cl_2) 2.03 (s, 6H, $Me_2C_6H_3$), 4.35 (d, 2H, CH_2-P, $^2J_{PH} = 13.2$), 6.81 (t, 1H, *p*-H of $Me_2C_6H_3$), 6.89 (d, 2H, *m*-H of $Me_2C_6H_3$), 6.95 (m, 2H, *o*-H of *Ph*), 7.13 (m, 2H, *m*-H of *Ph*), 7.27 (m, 1H, *p*-H of *Ph*), 7.90 (m, 4H, *o*-H of PPh_2, $^3J_{PH} = 12.7$), 7.58 (m, 4H, *m*-H of PPh_2, $^4J_{PH} = 2.7$), 7.66 (m, 2H, *p*-H of PPh_2, $^5J_{PH} = 1.95$) $^{31}P\{^1H\}$ NMR (202.4 MHz, CD_2Cl_2) 43.1 (s) $^{13}C\{^1H\}$ NMR (125.7 MHz, CD_2Cl_2) 19.6 (s, $Me_2C_6H_3N$), 49.8 (d, CH_2-P, $^1J_{PC} = 27$), 180.6 (d, N=*C*, $^2J_{PC} = 7.6$), 148.2 (s, *i-C* of $Me_2C_6H_3N$), 133.4 (d, *o*-C of PPh_2, $^2J_{PC} = 10$), 129.5 (d, *m*-C of PPh_2, $^3J_{PC} = 11$), 132.9 (d, *p*-C of PPh_2, $^4J_{PC} = 3$), other aromatic C-resonances, assignable to *Ph*-CN and $Me_2C_6H_3N$: 131.7, 130.4, 128.8, 128.1, 127.7, 127.4, 127.2
8	**[PtMeCl{$Ph_2PCH_2C(Ph)$=$N(2,6\text{-}Me_2C_6H_3)$}]** $C_{29}H_{29}ClNPPt$ MW 653.06 Air stable white-yellow powder Elemental analysis: % Found (Calc.) C 52.1 (53.3), H 4.7 (4.5), N 2.03 (2.1) Mass spectrometry: FAB^+: *m/z* 652.0(10) $[M]^+$, 638.0(100) $[M - Me]^+$, 617.1(30) $[M - Cl]^+$, 601.1(50) $[M - Cl - Me]^+$	^1H NMR data (500 MHz, CD_2Cl_2): 0.68 (d, 3H, Pt-*Me cis*-P, $^3J_{PH} = 3.5$, $^1J_{PtH} = 73$), 2.08 (s, 6H, $Me_2C_6H_3$), 3.97 (d, CH_2-P, 2H, $^2J_{PH} = 11$), 6.92 (d, 3H, *m*-H of $Me_2C_6H_3$), 7.02 (t, 2H, *p*-H of $Me_2C_6H_3$), 7.19 (m, 2H, *o* + *m*-H of *Ph*), 7.37 (m, 2H, *p*-H of *Ph*), 7.84 (m, 4H, *o*-H of PPh_2), 7.55 (m, 4H, *m*-H of PPh_2), 7.67 (m, 2H, *p*-H of PPh_2) $^{31}P\{^1H\}$ NMR data (202.4 MHz, CD_2Cl_2) 22.6 ($^1J_{PtP} = 4670$) $^{13}C\{^1H\}$ NMR data (125.7 MHz, CD_2Cl_2) 1.0 (b, Pt-*Me*), 18.5 (s, $Me_2C_6H_3N$), 48.1 (d, CH_2-P, $^1J_{PC} = 37$), 176.2 (b, N=*C*), 135.6 (d, *i*-C of *Ph*, $^3J_{PC} = 8$), 145.7 (d, *i*-C of $Me_2C_6H_3$, $^1J_{PC} = 23$), 133.2 (d, *o*-C of PPh_2, $^2J_{PC} = 12$), 129.2 (d, *m*-C of PPh_2, $^3J_{PC} = 12$), 131.1 (d, *p*-C of PPh_2), other aromatic C-resonances: 131.5, 130.6, 128.5, 127.5, 126.5, 126.3, 126.1
9	**[$PtMe_2${$Ph_2PCH_2C(Ph)$=$N(2,6\text{-}Me_2C_6H_3)$}]** $C_{30}H_{32}NPPt$ Mw 632.64 Air and moisture sensitive light-yellow powder Elemental analysis: % Found (Calc.) C 57.1 (56.9), H 5.2 (5.1), N 2.3 (2.2) m/z Mass spectrometry: FAB^+: *m/z* 632.3 (15) $[M]^+$, 617.6 (15) $[M - Me]^+$, 602.3 (100) $[M - 2Me]^+$	^1H NMR (500 MHz, CD_2Cl_2) −0.23 (d, 3H, Pt-*Me trans*-P, $^3J_{PH} = 8.2$, $^1J_{PtH} = 67.1$), 0.84 (d, 3H, Pt-*Me*, *cis*-P, $^3J_{PH} = 7.5$, $^1J_{PtH} = 89.5$), 1.98 (s, 6H, $Me_2C_6H_3$), 3.76 (d, 2H, CH_2-P, $^2J_{PH} = 8.8$), 6.62 (b, 2H, *m*-H of $Me_2C_6H_3$), 6.85 (b, 1H, p-H of $Me_2C_6H_3$), 6.93 (m, 2H, *o*-H of *Ph*), 7.15 (b, 4H, *m* + *p*-H of *Ph*), 7.20 (b, 4H, *m*-H of PPh_2), 7.62 (b, 4H, *o*-H of PPh_2), 7.70 (b, 2H, *p*-H of PPh_2) $^{31}P\{^1H\}$ NMR (202.4 MHz, d^8-THF) 17.2 (s, $^1J_{PtP} = 1995$)
10	**[$Pt(CH_3CN)_2${$Ph_2PCH_2C(Ph)$=$N(2,6\text{-}Me_2C_6H_3)$}][BF_4]$_2$** $C_{32}H_{32}B_2F_8N_3PPt$ MW 858.29 Air and moisture sensitive brown-yellow powder Elemental analysis: % Found (Calc.) C 43.7 (44.7), H 4.03 (3.8), N 5.36 (4.9), P 3.20 (3.60), B 2.4 (2.5) Mass spectrometry (FAB^+): *m/z* 684.3 $[M - 2BF_4]^+$	^1H NMR (500 MHz, CD_2Cl_2) 1.95 (b, 3H, CH_3CN *trans*-P), 2.19 (s, 6H, $Me_2C_6H_3$), 2.37 (b, 3H, CH_3CN *cis*-P), 4.87 (d, 2H, CH_2-P, $^2J_{PH} = 12.7$), 7.15 (t, 1H, *p*-H of $Me_2C_6H_3$, $^2J_{HH} = 7.3$), 7.09 (d, 2H, *m*-H of $Me_2C_6H_3$, $^2J_{HH} = 7.3$), 7.30 (m, 4H, *o* + *m*-H of *Ph*), 7.46 (m, 1H, *p*-H of *Ph*), 7.99 (m, 4H, *o*-H of PPh_2, $^3J_{PH} = 8.5$), 7.73 (m, 4H, *m*-H of PPh_2, $^4J_{PH} = 3.4$), 7.82 (m, 2H, *p*-H of PPh_2, $^5J_{PH} = 2.2$) $^{31}P\{^1H\}$ NMR (202.4 MHz, CD_2Cl_2) 18.3 ($^1J_{PtP} = 3613$) $^{11}B\{^1H\}$ NMR (160.4 MHz, CD_2Cl_2) −0.9 (s) ^{19}F NMR (282.45 MHz, CD_2Cl_2) −151.5 (s) $^{13}C\{^1H\}$ NMR data (125.7 MHz, CD_2Cl_2) 17.8 (s, $Me_2C_6H_3N$),18.9 (b, CH_3CN *trans*-P), 30.8 (b, CH_3CN *cis*-P), 45.7 (d, CH_2-P, $^1J_{PC} =$ 107),144.8 (s, *i*-C of $Me_2C_6H_3N$), 195.9 (b, N=*C*), 121.3 (d, CH_3CN *cis*-P, $^2J_{PC} = 72$), 116.9 (b, CH_3CN *trans*-P), 134.0 (d, *i*-C of PPh_2, $^1J_{P-Phi} = 55$), 133.4 (d, *o*-C of PPh_2, $^2J_{P-Pho} = 11$), 131.3 (d, *m*-C of PPh_2, $^3J_{P-Phm} = 12$), 130.3 (b, *p*-C of PPh_2), other aromatic-C resonances 135.5, 134.8, 133.4, 130.4, 130.0, 129.9, 129.6, 129.3, 123.1
11a and **12a**	$C_{56}H_{52}Cl_2NPtP_2$ Air stable white powder Elemental analysis:% found (Calc.) C 61.4 (62.2) H 4.3 (4.8) N 1.8 (2.6) Mass spectrometry (FAB): *m/z* 1045.1(65) $[M - Cl]^+$, 1008.2(90) $[M - 2Cl]^+$	***cis*-[Pt{$Ph_2PCH_2C(Ph)$=$N(2,6\text{-}Me_2C_6H_3)$}$_2$][Cl]$_2$** ^1H NMR (CD_2Cl_2): 2.15 (s, $Me_2C_6H_3$, 12H), 3.99 (d, CH_2-P, $^3J_{PH} = 11.5$ Hz, 4H), 7.96 (m, *o*-Ph_2P, 8H), 7.78 (*m, p*-Ph_2P, 4H), 7.62 (m, *m*-Ph_2P, 8H) $^{31}P\{^1H\}$NMR (CD_2Cl_2): 14.2 ($^1J_{PPt} = 3781$ Hz) ***cis*-[PtCl{$Ph_2PCH_2C(Ph)$=$N(2,6\text{-}Me_2C_6H_3$)}$_2$][Cl]** ^1H NMR (CD_2Cl_2): 2.18 (b, $Me_2C_6H_3$, 6H), 1.95 (b, $Me_2C_6H_3$, 6H), 4.30 (broad d, CH_2-P, $^3J_{PH} = 11.0$ Hz, 2H), 5.20 (broad d, CH_2-P, $^3J_{PH} = 11.0$ Hz, 2H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2):29.0 (d, $^1J_{PPt} = 3683$ Hz, $^1J_{PP} = 15$ Hz), −4.0 (d, $^1J_{PPt} = 3683$ Hz, $^1J_{PP} = 15$ Hz). 7.47–6.95 (multiple resonances of aromatic protons)

Table 1 (*continued*)

	Compound data	NMR data
11b and **12b**	$C_{56}H_{52}Br_2NPtP_2$ Air stable light yellow powder Elemental analysis:% found (Calc.) C 56.2 (57.5) H 4.1 (4.5) N 1.9 (2.4) Mass spectrometry (FAB): *m*/*z* 1090.1 (5) $[M - Br]^+$, 1010.2(15) $[M - 2Br]^+$	***cis*-[Pt{$Ph_2PCH_2C(Ph)$=N(2,6-$Me_2C_6H_3$)}$_2$][Br]$_2$** ^{1}H NMR (CD_2Cl_2): 2.23 (s, $Me_2C_6H_3$, 12H), 4.01 (d, CH_2-P, $^3J_{PH}$ = 12.0 Hz, 4H), 7.96 (m, o-Ph_2P, 8H, $^3J_{PH}$ = 13.2), 7.78 (m, m-Ph_2P, 8H, $^4J_{PH}$ = 2.9 Hz), 7.66 (m, p-Ph_2P, 4H, $^5J_{P-H}$ = 2.0 Hz) $^{31}P\{^1H\}$NMR (CD_2Cl_2): 18.4 ($^1J_{PPt}$ = 3653 Hz) ***cis*-[PtBr{$Ph_2PCH_2C(Ph)$=N(2,6-$Me_2C_6H_3$)}$_2$][Br]** ^{1}H NMR (CD_2Cl_2): 2.23 (s, $Me_2C_6H_3$, 12H), 1.90 (b, $Me_2C_6H_3$, 6H), 4.80 (broad d, CH_2-P, $^3J_{PH}$ = 11.0 Hz, 2H), 4.43 (broad d, CH_2-P, $^3J_{PH}$ = 11.0 Hz, 4H). 7.50–6.90 (multiple resonances of aromatic protons) $^{31}P\{^1H\}$NMR (CD_2Cl_2): 34.2 (d, $^1J_{PPt}$ = 3672 Hz, $^2J_{PP}$ = 11 Hz), −4.0 (d, $^1J_{PPt}$ = 3672 Hz, $^2J_{PP}$ = 11 Hz)

resonances characteristic for a diamagnetic complex incorporating the ligand **L1**. The ^{1}H resonances of **1** were still broad at −90 °C and signals due to paramagnetic species are still observable in the baseline. Below −80 °C, the $^{31}P\{^1H\}$ NMR spectrum showed a broad signal at δ 41.9, which sharpened up upon further cooling. Surprisingly, single crystal X-ray diffraction (150 K) showed that the solid-state geometry of complex **1** is a distorted square-planar one (*vide infra*). It is known that nickel dibromide complexes with chelating bulky diimines such as[$NiBr_2${(2,6-RR′C_6H_3)N=C(R″)–C(R″)=N(2,6-RR′C_6H_3)}], where R, R′ = H, CH_3, CF_3, or C_6H_5, R″ = 1,8-naphthadiyl, Et, Me, or Cy, are tetrahedral and paramagnetic in the solid state.[31] In contrast, with chelating bis-phosphines, nickel dihalide complexes can be either in a distorted square-planar or tetrahedral geometry, depending on the nature of the phosphine ligand and/or the nature of the halides.[32] Complexes containing mixed alkyl and phenyl phosphines may either be in a square-planar or tetrahedral geometry, depending on the number of phenyl groups attached to the phosphorus atom. The equilibrium between square-planar (diamagnetic) and tetrahedral (paramagnetic) geometries of Ni(II) dihalides has been studied extensively.[33–40]

We have investigated the magnetism of **1** in the solid state by variable temperature SQUID magnetometry from 5–350 K, and in solution by Evan's method (between 190–293 K in CD_2Cl_2). The magnetic moment estimated for **1** using the SQUID and Evan's method is *ca.* 2.5 B.M. Magnetic moments of 0 (no unpaired electrons and square-planar geometry) or 3.3 BM (two unpaired electrons, tetrahedral) were expected. Intermediate values indicate a mixture of the two forms in equilibrium. Both methods point towards a spin-equilibrium system whereby the diamagnetic (square-planar) form is favoured at low temperature and the paramagnetic (tetrahedral) form is favoured at high temperature. However, the transition is gradual and there is an appreciable concentration of the tetrahedral form at all of the temperatures studied, thus no sharp spin-crossover point was observed. Variable temperature (VT) NMR experiments in CD_2Cl_2, which followed the change in chemical shift of both the paramagnetic and diamagnetic sets of resonances with temperature, did not lead to meaningful thermodynamic parameters for the tetrahedral/square-planar equilibrium in solution. These observations support the presence of a dynamic equilibrium slower than the NMR timescale for **1**, consistent with the presence in the NMR spectra of two separate sets of resonances due to the diamagnetic and paramagnetic isomers at all temperatures.

The room temperature ^{1}H NMR spectrum of **2** (CD_2Cl_2) also showed broad resonances in the range δ −4 to 21, indicating that this complex is not diamagnetic in solution at room temperature. Proton NMR spectroscopy of paramagnetic pentacoordinate-Ni(II) N/P complexes usually shows signals in the range δ −14 to 20.[13] The room temperature $^{31}P\{^1H\}$ NMR spectroscopy of **2** showed no resonances. A variable temperature NMR between −80 and 20 °C did not show any conclusive evidence to support diamagnetic-paramagnetic dynamic behaviour for **2**. The ability of Ni(II) to form both charged and neutral pentacoordinate complexes is well-documented in the literature.[32] Thus, numerous high-spin distorted trigonal-bipyramidal and square-pyramidal complexes are known, usually containing hard donor sites.[41]

The ^{1}H NMR spectroscopy of **3** showed doublets at δ 0.06 ($^3J_{PH}$ = 4.7 Hz) and at δ 0.49 ($^3J_{PH}$ = 12.3 Hz) assigned to the $NiCH_3$ protons trans and cis to the PPh_2 moiety, respectively. $^{31}P\{^1H\}$ NMR spectroscopy in d^8-toluene of **3** exhibited a singlet at δ 30.8, showing that the Ni-coordinated phosphine is considerably deshielded compared to free **L1**.

The cationic complexes **4** and **5** are both diamagnetic, as shown by ^{1}H and $^{31}P\{^1H\}$ NMR spectroscopy in CD_2Cl_2. The broad signal at δ 1.16 in the ^{1}H NMR spectrum of **4** was assigned to the PMe_3 protons. The cis arrangement of PMe_3 relative to the PPh_2 group of the chelating ligand was assigned on the basis of a strong NOE between the methyl groups of the PMe_3 ligand and the ortho protons of the PPh_2 unit. This configuration is probably favoured since it minimizes the steric repulsions between the 2,6-$Me_2C_6H_3$ unit and the PMe_3 group. The $^{31}P\{^1H\}$ NMR spectrum of **4** showed two doublets of equal intensity, at δ 34.2 (assigned to the PPh_2 group) and at δ −22.9 (assigned to the PMe_3 group), with the coupling constant $^2J_{PP}$ = 218 Hz. The ^{1}H NMR spectrum (CD_2Cl_2) of **5** shows a double doublet at δ 1.83 ($^3J_{PH}$ = 13.5 Hz, $^4J_{PH}$ = 1 Hz), assignable to the protons of the CH_3CN group trans to phosphorus, and a double doublet at δ 1.22 ($^3J_{PH}$ = 12 Hz, $^5J_{PH}$ = 1 Hz) assigned to the $P(CH_3)_3$ group cis to the PPh_2 moiety. A strong NOE between the $P(CH_3)_3$ and the H_{ortho} from Ph_2P (δ = 7.99) indicates a cis coordination of the PMe_3 and PPh_2 to the metal centre. $^{31}P\{^1H\}$ NMR spectroscopy (CD_2Cl_2) of **5** showed two doublets of equal intensities, at δ 51.2 (assigned to PPh_2) and at δ −8.2 (assigned to PMe_3) with $^2J_{PP}$ = 102 Hz. As expected, the coordinated phosphorus nuclei are considerably deshielded compared to those of the free ligands.

The ^{1}H NMR spectrum of **6** exhibits two doublets at δ 0.47 and 1.40 ($^3J_{HH}$ = 6.6 Hz), corresponding to the two prochiral methyl groups and a heptet (δ 2.88) for the two CH protons of the equivalent ^{i}Pr groups, but only one doublet for the CH_2 protons of the ligand backbone (δ 4.45, $^2J_{PH}$ = 13.5). This indicates that rotation around the imine N–aryl bond is fast on the NMR timescale. However in the X-ray diffraction of **6** one ^{i}Pr group is placed above the plane defined by the imine group and the other below this plane, suggesting some degree of steric hindrance against free rotation. For the analogous complex **7**, only one sharp resonance corresponding to the protons of the 2,6-$Me_2C_6H_3$ unit was observed in the aliphatic region of the ^{1}H spectrum (δ 2.03), as well as one methine doublet (δ 4.35 **7**, $^2J_{PH}$ = 13.2 Hz). The effect of metal coordination on the ^{1}H NMR chemical shifts are especially noticeable in the case of the CH_2 resonances, which changed from δ 3.80 ($^2J_{PH}$ = 1 for the free *Z* isomer of **L2**) or 3.81 ($^2J_{PH}$ = 1.1 for the free *Z* isomer

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1**, **2**, **6**, **7** and **9**

1			
Ni(1)–Br(1)	2.349(2)	Br(1)–Ni(1)–Br(2)	93.09(9)
Ni(1)–Br(2)	2.315(2)	Ni(1)–N(1)–C(2)	120.1(10)
Ni(1)–P(1)	2.140(5)	P(1)–C(1)–C(2)	105.9(10)
Ni(1)–N(1)	1.925(11)	Br(1)–Ni(1)–P(1)	170.76(17)
P(1)–C(1)	1.852(16)	Br(2)–Ni(1)–P(1)	86.07(13)
P(1)–C(3)	1.78(2)	P(1)–Ni(1)–N(1)	86.1(4)
P(1)–C(9)	1.802(17)	Br(1)–Ni(1)–N(1)	95.9(4)
N(1)–C(2)	1.304(19)	Br(2)–Ni(1)–N(1)	169.1(4)
N(1)–C(21)	1.45(2)	Ni(1)–P(1)–C(1)	99.5(6)
C(1)–C(2)	1.46(2)		
2			
Ni(1)–Br(1)	2.4736(13)	Br(1)–Ni(1)–Br(2)	113.38(5)
Ni(1)–Br(2)	2.4634(12)	Br(1)–Ni(1)–P(1)	95.27(6)
Ni(1)–P(1)	2.329(2)	Br(2)–Ni(1)–P(1)	93.56(6)
Ni(1)–N(1)	2.111(6)	Br(1)–Ni(1)–N(1)	150.44(15)
Ni(1)–O(1)	2.041(5)	Br(2)–Ni(1)–N(1)	96.04(15)
P(1)–C(1)	1.824(9)	P(1)–Ni(1)–N(1)	79.34(16)
P(1)–C(3)	1.839(6)	Br(1)–Ni(1)–O(1)	89.86(15)
P(1)–C(9)	1.816(8)	Br(2)–Ni(1)–O(1)	92.44(14)
N(1)–C(2)	1.295(8)	P(1)–Ni(1)–O(1)	169.84(15)
N(1)–C(21)	1.439(9)	N(1)–Ni(1)–O(1)	91.9(2)
C(1)–C(2)	1.518(11)	Ni(1)–O(1)–P(2)	122.4(3)
		O(1)–P(2)–C(29)	111.2(3)
		O(1)–P(2)–C(35)	113.7(3)
		C(29)–P(2)–C(35)	107.4(3)
		O(1)–P(2)–H(1)	116(4)
6			
Pd(1)–Br(1)	2.5029(11)	Br(1)–Pd(1)–Br(2)	92.20(4)
Pd(1)–Br(2)	2.4289(10)	Br(1)–Pd(1)–N(1)	94.89(14)
Pd(1)–N(1)	2.095(5)	Br(2)–Pd(1)–N(1)	171.01(14)
Pd(1)–P(1)	2.2158(18)	Br(1)–Pd(1)–P(1)	173.08(5)
N(1)–C(2)	1.293(9)	Br(2)–Pd(1)–P(1)	92.45(6)
N(1)–C(3)	1.433(8)	N(1)–Pd(1)–P(1)	81.00(15)
P(1)–C(1)	1.837(7)		
P(1)–C(21)	1.814(7)		
P(1)–C(27)	1.820(8)		
C(1)–C(2)	1.502(10)		
7 (Molecule 1)			
Pd(1)–I(1)	2.6260(6)	I(1)–Pd(1)–I(2)	89.695(19)
Pd(1)–I(2)	2.5768(5)	I(1)–Pd(1)–P(1)	173.17(4)
Pd(1)–P(1)	2.2293(14)	I(2)–Pd(1)–P(1)	93.97(4)
Pd(1)–N(1)	2.110(5)	I(1)–Pd(1)–N(1)	95.72(12)
P(1)–C(2)	1.843(6)	I(2)–Pd(1)–N(1)	173.09(12)
P(1)–C(17)	1.808(6)	P(1)–Pd(1)–N(1)	81.08(12)
P(1)–C(23)	1.797(6)		
N(1)–C(1)	1.282(7)		
N(1)–C(3)	1.444(7)		
C(1)–C(2)	1.501(8)		
7 (Molecule 2)			
Pd(2)–I(3)	2.6334(5)	I(3)–Pd(2)–I(4)	93.525(16)
Pd(2)–I(4)	2.5803(5)	I(3)–Pd(2)–P(2)	167.91(4)
Pd(2)–P(2)	2.2276(13)	I(4)–Pd(2)–P(2)	92.77(4)
Pd(2)–N(2)	2.112(4)	I(3)–Pd(2)–N(2)	94.13(11)
P(2)–C(30)	1.833(5)	I(4)–Pd(2)–N(2)	169.72(11)
P(2)–C(45)	1.811(5)	P(2)–Pd(2)–N(2)	80.99(12)
P(2)–C(51)	1.802(5)		
N(2)–C(29)	1.288(6)		
N(2)–C(31)	1.440(6)		
C(29)–C(30)	1.502(7)		
9			
Pt(1)–P(1)	2.2411(9)	P(1)–Pt(1)–N(1)	80.87(9)
Pt(1)–N(1)	2.162(3)	P(1)–Pt(1)–C(3)	174.03(12)
Pt(1)–C(3)	2.091(4)	N(1)–Pt(1)–C(3)	94.10(14)
Pt(1)–C(4)	2.057(4)	P(1)–Pt(1)–C(4)	98.50(13)
P(1)–C(2)	1.844(4)	N(1)–Pt(1)–C(4)	178.92(14)
P(1)–C(19)	1.822(4)	C(3)–Pt(1)–C(4)	86.59(17)
P(1)–C(25)	1.836(4)		
N(1)–C(5)	1.443(4)		
N(1)–C(1)	1.297(5)		
C(1)–C(2)	1.522(5)		

of **L1**). ^{31}P NMR spectra (CD_2Cl_2) showed singlet resonances at δ 45.0 (for **6**) and 43.1 (for **7**), significantly downfield compared to that of free **L2** and **L1**, found at δ −21.0 and −19.8, respectively.

The ^{1}H NMR spectrum of **8** (CD_2Cl_2) showed a centred doublet assignable to the MePt group at δ 0.68 ($^{3}J_{PH}$ = 3.5 Hz), with the corresponding satellites due to coupling with ^{195}Pt ($^{2}J_{PtH}$ = 75 Hz). The strong NOE between Pt–methyl protons of **8** and the ortho protons of PPh_2 indicated that this methyl group is coordinated to the platinum cis to the phosphorus nuclei. NMR spectroscopy also confirmed that this is the only isomer present in solution. The ^{31}P{^{1}H} NMR spectrum (CD_2Cl_2) of [PtMeCl(**L1**)] **8** showed a centred singlet at δ 22.6. ^{195}Pt satellites are observed and the coupling constant ($^{1}J_{PtP}$ = 4670 Hz) is larger than that observed for [$PtMe_2$(**L1**)] **9** (δ 17.2, $^{1}J_{PtP}$ = 1995 Hz). The ^{1}H NMR spectrum (CD_2Cl_2) of **9** showed a centred pair of doublets assignable to the MePt groups at δ 0.84 (cis to PPh_2, $^{3}J_{PH}$ = 7.5) and δ −0.23 (trans to PPh_2, $^{3}J_{PH}$ = 8.2). As expected, the Pt–H coupling is larger for the MePt cis to PPh_2 ($^{2}J_{PtH}$ = 89.5) than for the MePt trans to P ($^{2}J_{PtH}$ = 67.0). The ^{1}H NMR spectrum of **10** (CD_2Cl_2) showed broad signals at δ 1.95 and 2.37 assignable to the protons of the MeCN groups trans and cis to phosphorus respectively. The ^{31}P{^{1}H} NMR spectrum (CD_2Cl_2) of **10** showed a centred singlet with ^{195}Pt satellites at δ 18.3 ($^{1}J_{PtP}$ = 3613 Hz).

X-Ray data

ORTEP views of complexes **1** and **2** are shown in Figs. 1–3. For both complexes **1** and **2**, the N and P donors of the ligand **L1** are coordinated to the metal, forming 5-membered rings. Single crystal X-ray diffraction showed that the structure of [$NiBr_2$(**L1**)] (**1**) in the solid state is in a distorted square-planar geometry. The geometry around the Ni centre in [$NiBr_2$(O=$PHPh_2$)(**L1**)] (**2**) is closer to a distorted square-pyramid than to a trigonal bipyramid. In the latter complex, the P(1) centre is pulled slightly towards Ni, the Br(2) atom is placed axial and the pyramid base, formed by N(1), P(1), Br(1) and O(1), is almost planar. The bite angle N(1)–Ni(1)–P(1) for compound **1** is 86.1(4)°, which is similar to those of numerous nickel(II) chelating bis-phosphine complexes, which incorporate a two-carbon atom, P,P′ linkage, such as 1,2-bis(diphenylphosphino)ethane (dppe). In these latter complexes, angles are found in the range 85–90°.[42] The corresponding N(1)–Ni(1)–P(1) bite angle for compound **2** is 79.34(16)°, that is, considerably smaller than that of **1**, probably due to the more puckered structure of the chelate ring. As a consequence of the differences in the overall geometries of the complexes, the Br(1)–Ni–Br(2) angle for **1**, 93.09(9)°, is considerably smaller than that for **2** [113.38(5)°]. The sum of the angles at N(1) in complexes **1** and **2** are indicative of sp^2 hybridisation. The geometry of the

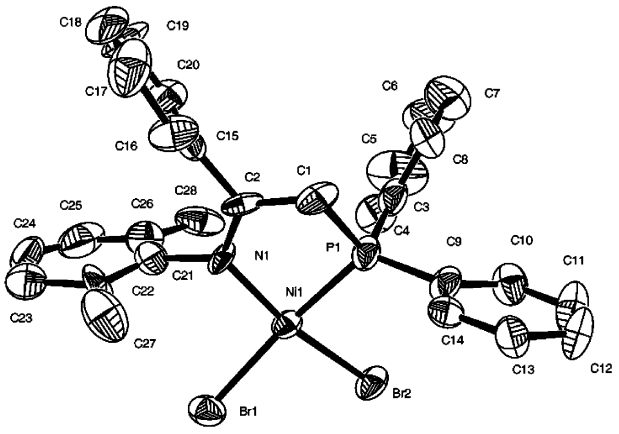

Fig. 1 ORTEP diagram of the molecular structure of complex **1**.

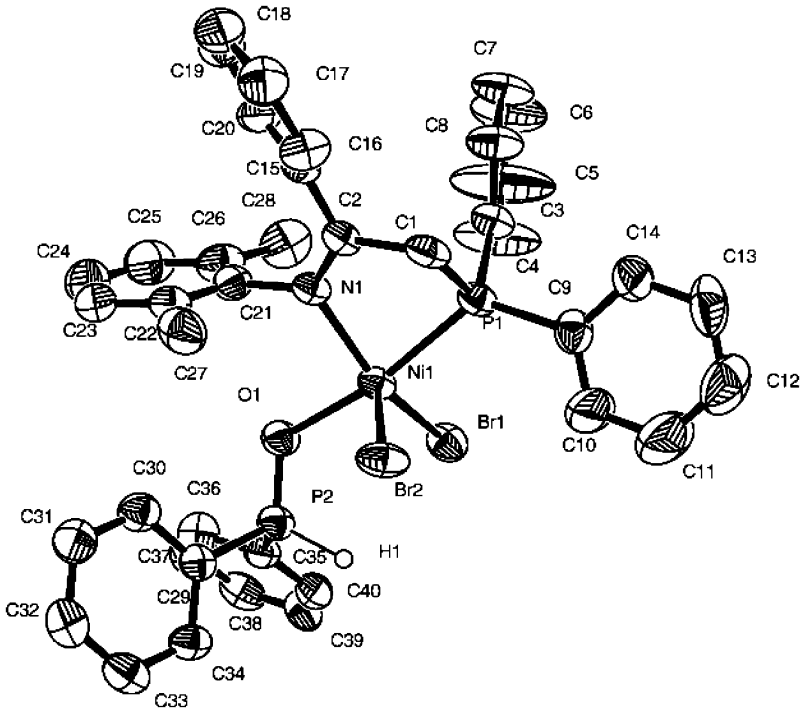

Fig. 2 ORTEP diagram of the molecular structure of complex **2**.

nickel atom in **1** is distorted square-planar, with the chelating ligand inducing a cis arrangement of the bromine atoms. In **1**, the Ni(1)–Br(1) and Ni(1)–Br(2) distances are 2.349(2) Å and 2.315(2) Å, respectively, with the slightly elongated metal-halide bond situated *trans* to the phosphine unit. The carbon-carbon distances C(1)–C(2) for the ligand backbones of 1.46(2) (**1**) and 1.518(11) (**2**) Å are within the range expected for the imine form of the ligand and close to the values observed for Pd(II) complexes and for the free ligand **L1**, reported by us earlier.[26] The N(1)–C(2) separations [of 1.304(19) (**1**) and 1.295(8) (**2**) Å] are slightly larger than that found in the free ligand **L1** [1.273(2) Å]. The atom H(1) was located, using a Fourier map during the structure refinement, at the P(2) centre of the O=P(H)Ph_2 group, which exhibits a distorted tetrahedral geometry. This determination is also supported by the infrared spectrum, which showed two bands, assignable to ν_{PH} (at 2370 and 2340 cm^{-1}) and a broad band (at 1238 cm^{-1}) assignable to the P=O stretch.

ORTEP diagrams of complexes **6** and **7** are shown in Figs. 4 and 5, respectively. These Pd(II) complexes have similar structures in the solid state and in solution, with the ligand in its iminophosphine form and square-planar geometry at the Pd centre. The N–Pd–P bite angles for [$PdBr_2$(**L2**)] **6** is 81.00(15)°, that is, somewhat smaller than that for the isostructural [$PdBr_2$(**L1**)], 82.91(6)°.[26] This is due to the increased bulk of the isopropyl groups serving to increase the distance of the N (and P) donor atoms from the Pd centre, which in turn decreases the bite angle. The palladium–halogen bond lengths for **6** and **7** are in the range expected for Pd(II) complexes,[42] with the longer metal–halogen bond always trans to the phosphorus atom due to the greater trans influence. The Pd–P separation slightly increases across the series, from 2.1845(12) Å for [$PdCl_2$(**L1**)][26] to 2.2119(19) Å for [$PdBr_2$(**L1**)],[26] 2.2158(18) Å for [$PdBr_2$(**L2**)] (**6**), and 2.2293(14) and 2.2276(13) Å for [PdI_2(**L1**)] (**7**; molecules 1 and 2, respectively, since two independent molecules are present in the asymmetric unit). This variation occurs as a result of the increasing trans influence in the halide series: Cl < Br < I. In general, little variation in the bond lengths of **L1** can be observed upon chelation to Pd(II), although the C=N carbon–

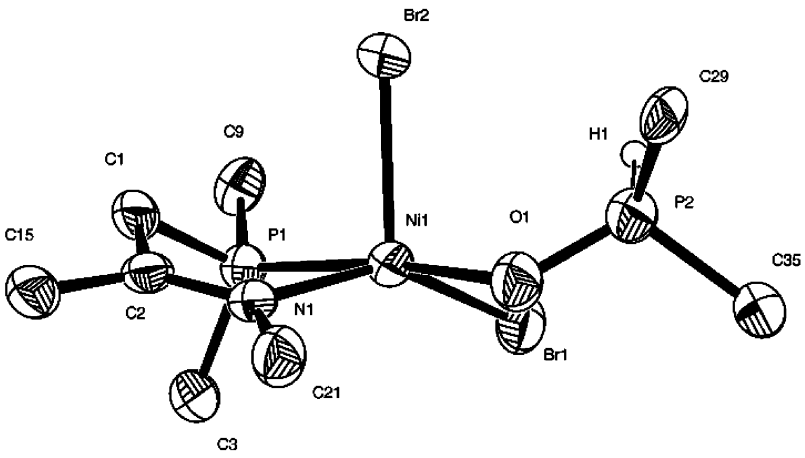

Fig. 3 Alternative view of the molecular structure of complex **2**, showing the distorted square-pyramid geometry around the Ni(II) centre (for clarity only the ipso carbons from the aryl rings are shown).

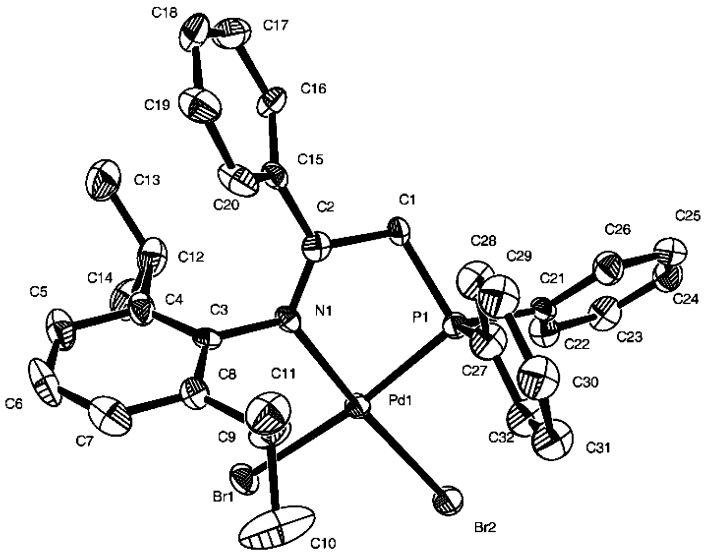

Fig. 4 ORTEP diagram of the molecular structure of complex **6**.

nitrogen separation increases upon coordination, from 1.273(2) Å for the free ligand to 1.282(7) Å and 1.288(6) Å for **7** (N.B. two independent molecules in the asymmetric unit). The ligand backbone carbon–carbon distances for complexes **6** and **7** (Table 2) are comparable with that of free **L1** [1.504(2) Å].

An ORTEP diagram of complex **9** is shown in Fig. 6. X-Ray structure determination confirmed that this complex exhibits the same structure in the solid state as in solution, and is isostructural with [$PdMe_2$(**L1**)].[26] In the solid state, this complex also exhibits a pseudo square-planar geometry around the metal centre. The P(1)–Pt(1)–N(1) bite angle is 80.87(9)°, which is only slightly larger than that of complex [$PdMe_2$(**L1**)],[26] at 80.2(2)°. The Pt–C bond length for the methyl group situated trans to phosphorus is 2.091(4) Å. This is close to that of the methyl cis to PPh_2 [2.057(4) Å], although the slight increase is expected because of the greater trans influence of phosphorus compared to nitrogen. The difference between these interatomic separations is comparable to that found between the corresponding cis and trans Pd–Me distances of complex [$PdMe_2$(**L1**)] [2.045(11) and 2.09(1) Å, respectively]. The ligand backbone carbon–carbon distance for complex **9** [1.522(5) Å] is comparable to that of related Pd complexes and somewhat larger than that of the free **L1** [1.504(2) Å].

Heck reaction tests

In recent years, palladium complexes of hybrid nitrogen and phosphorus ligands have received attention as Heck catalysts,[24] due to the possibility of enhanced reactivity by cooperative effects. However, to date, no estimation of the activity in Heck processes of Pd complexes of ligands with a flexible backbone, such as **L1** and **L2**, has been reported. We have shown that [PdMeCl(**L1**)] shows moderate activity in another C–C coupling reaction, that is, the CO/ethylene copolymerisation reaction.[26]

The complex [$PdBr_2$(**L2**)] (**6**), as well as two of our previously reported complexes, [$PdBr_2$(**L1**)] and [PdMeCl(**L1**)],[26,27] were tested as pre-catalysts for the Heck coupling of 4-bromoacetophenone with *n*-butyl acrylate under aerobic conditions. A mixture of 4-bromoacetophenone and 1.4 equiv. of *n*-butyl acrylate was heated at 130 °C for 20 h in *N*,*N*-dimethylacetamide in the presence of a base (sodium acetate), and 0.5 mol % of the pre-catalyst. $(n\text{-Bu})_4$NOAc was added, as it has been shown that the presence of a soluble base significantly reduces the induction time required to form the catalytically active species.[43] For the catalysts used, quantitative conversion into the corresponding olefin was achieved

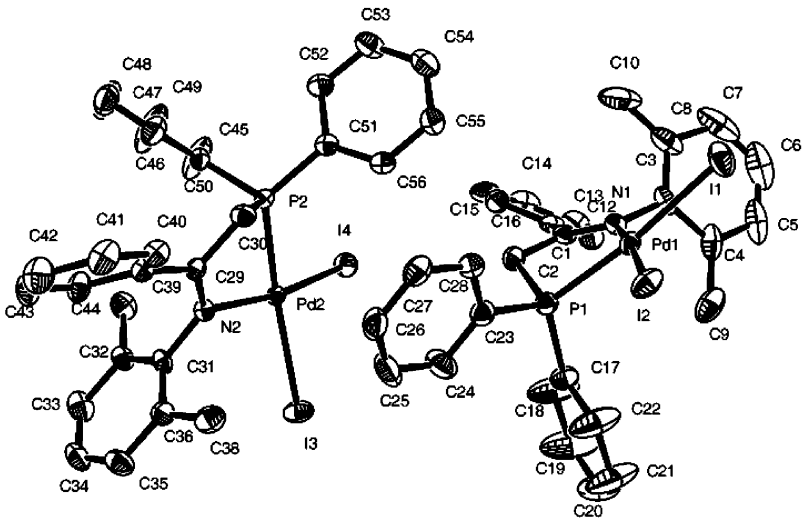

Fig. 5 ORTEP diagram of the molecular structure of complex **7**.

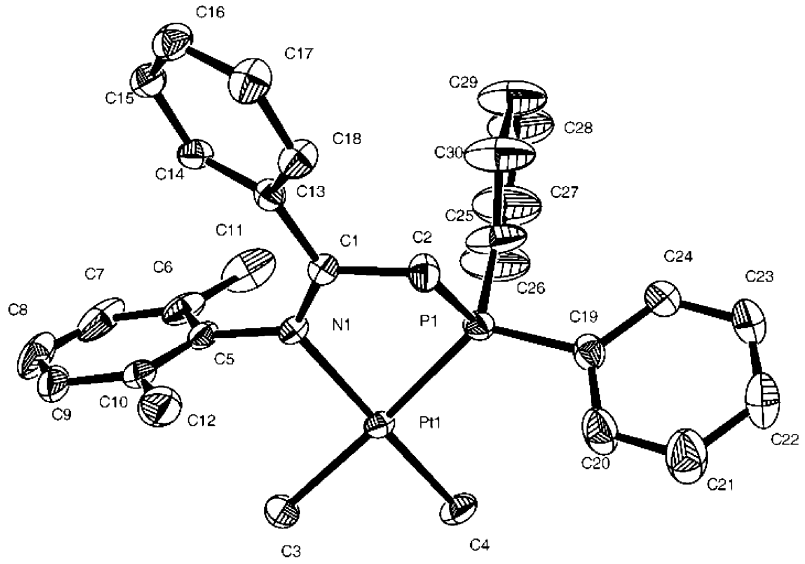

Fig. 6 ORTEP diagram of the molecular structure of complex **9**.

Table 3 Yield percentages and TON from the Heck coupling of 4-bromoacetophenone and *n*-butyl acrylate with different pre-catalysts

Pre-catalyst (130 °C, 20 h)	% Yield	TON/mol product per mol Pd
None (blank run)	0	0
[$PdBr_2$(**L2**)] (**6**)	100	200
[$PdBr_2$(**L1**)][26,27]	93	186
[PdMeCl(**L1**)][26,27]	74	148

under the conditions used. Yields and TON are given in Table 3. With [$PdBr_2$(**L1**)], , the conversion yield (determined by GC-MS, based on 4-bromoacetophenone) was 93% and the turnover number 186 mol product per mol Pd. With [$PdBr_2$(**L2**)] (**6**), a 100% conversion yield (turnover number 200) was obtained. Using the pre-catalyst [PdMeCl(**L1**)],[26,27] the yield (determined by GC-MS, based on 4-bromoacetophenone) was 74% and the turnover number 148 (estimated as mol product per mol catalyst). In all cases, the reaction time was 20 h. The slightly lower yield could be explained by the thermal decomposition of the methyl–Pd pre-catalyst during the induction period.

In all cases, although the yields were extremely high and comparable to those obtained using Pd(II) complexes of the ligands *o*-[$PPh_2C_6H_4NH_2$] and *o*-[$PPh_2C_6H_4N{=}CHPh$)] under similar reaction conditions,[24] the turnover numbers so far are significantly lower and further studies to improve these are under way.

Conclusions

New nickel(II), palladium(II) and platinum(II) *cis*-dimethyl and monomethyl monohalide complexes of bulky iminophosphine ligands have been prepared and characterised. In contrast to the reaction of [PtX_2(cod)] (X = Cl, Br) with **L1**, which leads to a mixture of products, treatment of [$PtMe_2$(cod)] or [PtMeCl(cod)] with one equivalent of **L1** affords in both cases the corresponding chelating complexes cleanly. The pre-catalysts [$PdBr_2$(**L2**)] **6**, [$PdBr_2$(**L1**)] and [PdMeCl(**L1**)] have been found to be active in the Heck coupling of 4-bromoacetophenone with *n*-butyl acrylate. The attractive features of these catalytic systems—high yields and air and moisture stability—approach those of industrial interest and open future perspectives for their use in other palladium-catalysed organic reactions.

Experimental

General methods and materials

All manipulations of air- and/or moisture-sensitive materials were performed under an inert atmosphere of pure argon or dry N_2 using standard Schlenk line techniques, or in an inert atmosphere dry-box. Inert gases were purified firstly by passage through columns filled with activated molecular sieves (4 Å) and then either manganese(II) oxide suspended on vermiculite, for the Schlenk line, or BASF catalyst, for the dry-box. Celite was purchased from Fluka Chemie and oven-dried at 150 °C prior to use for filtration. Solvents were pre-dried over activated 4 Å molecular sieves and then distilled under N_2 atmosphere from NaK alloy (light petroleum ether, b.p. 40–60 °C, diethyl ether, pentane), from sodium (toluene), from potassium (THF), or from calcium hydride (dichloromethane). Deuterated NMR solvents (Aldrich, Goss Scientific) were refluxed and distilled from potassium metal (d^8-toluene) or from calcium hydride (CD_2Cl_2), distilled and degassed prior to use. Microanalyses were performed by the microanalytical laboratory of the Inorganic Chemistry Laboratory, University of Oxford, and FAB^+ mass spectra by the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea, UK.

NMR spectra were recorded using either a Varian Mercury-VX 300 (^{1}H 300 MHz, ^{13}C 75.5 MHz, ^{19}F 282.3 MHz, ^{31}P 121.6 MHz) or a Varian UNITY plus (^{1}H 500 MHz, ^{11}B 160.4 MHz, ^{13}C 125.7 MHz, ^{31}P 202.4 MHz) spectrometer and were at room temperature unless otherwise stated. The spectra were referenced internally relative to the residual protio solvent (^{1}H) and solvent (^{13}C) resonances relative to tetramethylsilane (^{1}H, ^{13}C, $\delta = 0$) or externally to $BF_3 \cdot Et_2O$ (^{11}B, $\delta = 0$); H_3PO_3 (^{31}P, $\delta = 0$) or $CFCl_3$ (^{19}F, $\delta = 0$). Chemical shifts (δ) are expressed in ppm and coupling constants (J) in Hz.

GC-MS chromatograms and spectra were recorded using a Hewlett Packard 5890 gas chromatograph fitted with a non-polar column connected to a Trio-1000 mass spectrometer operating in electron impact (EI, 70 eV) and chemical ionisation (CI; NH_3) modes and detecting positively charged species. The temperature profile for the GC was: 100 °C for 3 min, then 10 °C min^{-1} ramp to 280 °C (held for 10 min).

The reagents *n*-BuLi, PMe_3, [$NiBr_2$(dme)], [Pd(dba)$_2$], $AgBF_4$, $PdBr_2$, [3,5-$(CF_3)2C_6H_3$]I, 4-bromoacetophenone, diethylene glycol, di-*n*-butyl ether, *n*-butyl acrylate and *N*,*N*-dimethylacetamide were purchased from Aldrich and used as received. Ph_2PCl, $^iPr_2NH$ and 2,6-$^iPr_2C_6H_3NH_2$ were pur-

chased from Strem and purified by vacuum distillation before use. The compounds $[PtMe_2(cod)]$,[44] $[PtClMe(cod)]$,[45] $[NiMe_2(tmeda)]$,[46] $[NiCl_2(PMe_3)_2]$[47] and **L1**[18,26] were prepared according to literature procedures.

Syntheses

Spectroscopic data for all new compounds are given in Table 1.

[PhMeC=N(2,6-^{i}Pr$_2$C$_6$H$_3$)]. The synthesis was adapted from the method of Okamoto *et al.*[48] A mixture of acetophenone (25.75 g, 21.45 mmol), 2,6-diisopropylphenylamine (36.98 g, 21.45 mmol) and *p*-tolylsulfonic acid (*ca.* 1 g) in a round-bottomed flask fitted with a Soxhlet extractor containing about 20 g anhydrous $CaSO_4$ was refluxed in 200 ml toluene for 24 h. During this time, water was removed using activated molecular sieves (4 Å), which were contained in the round-bottomed flask. The reaction mixture was subsequently filtered through Celite. After removal of volatile compounds, the brown residue was distilled under reduced pressure (0.6×10^{-3} bar). The unreacted starting materials were collected between 80–115 °C, and the imine was collected at 140 °C as a yellow oil, which solidified at room temperature to give a yellow powder. Yield: 14.25 g, 24%. IR (CsI): $\nu_{C=N} = 1645\ cm^{-1}$. Anal. calcd (%): C 85.9, H 9.0, N 5.0; found: C 85.2, H 9.7, N 4.9.

[Ph$_2$PCH$_2$C(Ph)=N(2,6-^{i}Pr$_2$C$_6$H$_3$)] (L2). To a pre-cooled solution of dry ^{i}Pr$_2$NH (1.81 g, 17.90 mmol) in 50 ml THF, a 1.6 M solution *n*-BuLi in hexanes (1.14 g, 17.90 mmol) was added dropwise at −78 °C. The mixture was allowed to warm up to room temperature and stirred for 30 min. A cold solution of **13** (5.00 g, 17.90 mmol) in 25 ml THF was added dropwise at −78 °C under stirring. The mixture was stirred for 2 h at −78 °C and the formation of the lithium salt of the imine, a bright yellow precipitate, was observed. A cold solution of Ph_2PCl (4.94 g, 17.9 mmol) in 25 ml THF was transferred to the reaction mixture dropwise. The yellow precipitate gradually disappeared and the solution turned to a lighter yellow. The mixture was stirred for 12 h at room temperature before removal of the volatile compounds under reduced pressure. The resulting white residue was extracted with 50 ml toluene, and removal of the solvent under reduces pressure gave a yellow oil. Attempts to purify the product by extraction with pentane, 40–60 °C petroleum ether or 100–120 °C petroleum ether were unsuccessful because of the high solubility of the yellow oil in all these solvents. Recrystallisation from pentane at −20 °C resulted in the formation of a crystalline material shown by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy to be mainly the expected product, [Ph$_2$PCH$_2$C(Ph)=N(2,6-^{i}Pr$_2$C$_6$H$_3$)] (**L2**) as a mixture of the two *E*/*Z* isomers in a 2 : 1 ratio (by integration), together with starting materials and oxidation products. Attempts to separate the components of this mixture by column chromatography (on Kieselgur, using mixtures of Et_2O and petroleum ether 40–60 °C, in various ratios) were unsuccessful. Further attempts to isolate this ligand were not undertaken. Instead, the ligand was prepared *in situ* and used directly for the synthesis of **6**.

[NiBr$_2$(L1)] (1), from the reaction of L1 with [NiBr$_2$(dme)]. **L1** (1.00 g, 2.46 mmol) was dissolved in 50 ml THF and added to a suspension of $[NiBr_2(dme)]$ (0.76 g, 2.46 mmol) in 50 ml THF. The mixture was stirred for 12 h at room temperature. Volatile compounds were removed under reduced pressure and the resulting brown residue was washed with pentane. Recrystallisation from CD_2Cl_2 and Et_2O at −20 °C afforded air stable dark-red needle-like crystals of **1**, which were isolated by filtration. Yield: 1.05 g, 70%.

[NiBr$_2$(O=PHPh$_2$)(L1)] (2). The exposure of complex **1** (0.05 g, 0.06 mmol) to one equivalent of O=PHPh$_2$ (0.012 g, 0.06 mmol) in 50 ml CH_2Cl_2 for 12 h at room temperature resulted in the formation of a small amount of **2** as air and moisture sensitive brown, square-shaped crystals (yield < 10%). The product was characterised by X-ray crystallography as $[NiBr_2(O{=}PHPh_2)(\mathbf{L1})]$ (**2**).

[NiMe$_2$(L1)] (3): NMR-scale reaction between L1 and [NiMe$_2$(tmeda)]. d^8-Toluene (0.6 ml) was condensed onto a solid mixture of $[NiMe_2(tmeda)]$ (0.015 g, 0.086 mmol) and **L1** (0.035 g, 0.0857 mmol) at −173 °C in a Young's NMR tube fitted with a Teflon valve. The mixture was warmed to −78 °C and the reaction monitored by ^{1}H NMR spectroscopy over 4 h, allowing it to equilibrate at each of the following temperature steps: −75, −50, −40, −30, −20, −10, 0, +10, +25 °C and +25 °C after 24 h. **3** was identified between −10 and +25 °C {^{1}H NMR: $\delta = -0.213$ (d, 3H, PdCH_3, *cis*-P, $^3J_{PH} = 3.5$ Hz), 0.222 (d, 3H, PdCH_3, *trans*-P, $^3J_{PH} = 11.5$ Hz), 1.879 [s, 6H, (CH_3)$_2$C$_6$H$_3$], 3.062 (d, 2H, CH$_2$P, $^3J_{PH} = 6$ Hz), 7.427–6.443 (multiple resonances of aromatic protons, 18H). ^{31}P{^{1}H} NMR: $\delta = 30.75$} at various low concentrations relative to free tmeda [^{1}H NMR: $\delta = 1.94$ (s, 12H), 5.24 (s, 4H)], the formation of which was also only observed above −10 °C, unreacted **L1** and $[NiMe_2(TMEDA)]$ [^{1}H NMR: $\delta = -0.639$ (s, 6H), 1.443 (s, 4H), 1.94 (s, 12H)]. After 24 h at +25 °C the product $[NiMe_2(\mathbf{L1})]$ (**3**) could not be observed in the ^{1}H and ^{31}P{^{1}H} NMR spectra.

[NiMe$_2$(L1)] (3). The compounds $[NiMe_2(tmeda)]$ (0.065 g, 0.37 mmol) and **L1** (0.15 g, 0.37 mmol) were mixed in a Schlenk tube and 100 ml toluene was added. The mixture was stirred for 6 h at room temperature, after which volatile compounds were removed under reduced pressure. The resulting red solid was washed twice with pentane and residual volatiles were removed under reduced pressure to yield **3** as an air- and moisture-sensitive red microcrystalline solid. Yield: 0.05 g, 29%.

[NiBr(PMe$_3$)(L1)][Br] (4), from the reaction of 1 with PMe$_3$. Compound **1** (0.40 g, 0.64 mmol) was dissolved in 50 ml THF at room temperature and PMe_3 (0.09 g, 1.28 mmol) in 20 ml THF was added *via* a syringe. The solution turned blue after addition and was left stirring for 5 h. Volatile compounds were removed under reduced pressure to give a blue residue. Pentane (20 ml) was added to the residue, giving a deep-blue precipitate and a purple supernatant. The mixture was stirred for a further 30 min, prior to separation as described below.

Fraction 1: a deep-blue powder was isolated by filtration, washed with pentane and the residual volatiles removed under reduced pressure. The air- and moisture-sensitive powder was identified as **4**. Yield: 0.18 g, 63%.

Fraction 2. Volatile compounds were removed from the purple pentane filtrate under reduced pressure and the resulting purple residue was recrystallised from a 1 4mixture of toluene and pentane at −20 °C. A small amount of white microcrystalline precipitate was isolated by filtration and identified as **L1** (yield < 5%). Purple crystals of an additional product (*ca.* 0.040 g) were isolated from the filtrate and identified as $[NiBr_2(PMe_3)_2]$.

[Ni(CH$_3$CN)(PMe$_3$)(L1)][BF$_4$]$_2$ (5). The solids $[Ni(PMe_3)_2Cl_2]$ (0.10 g, 0.35 mmol) and $AgBF_4$ (0.14 g, 0.70 mmol) were mixed in a Schlenk tube and 50 ml of CH_3CN were added. The mixture was stirred at room temperature under N_2 for 30 min. Formation of a white precipitate and an orange supernatant was observed. The orange supernatant was filtered into a second Schlenk tube, which contained **L1** (0.14 g, 0.35 mmol) dissolved in 20 ml of CH_3CN. The reaction mixture was stirred

for 12 h, filtered and the residual volatiles removed under reduced pressure to give an orange residue. This was further recrystallised from CH_2Cl_2 and pentane to give **5** as an air- and moisture-sensitive orange powder. Yield: 0.09 g, 36%.

[$PdBr_2$(L2)] (6). Reaction between the imine [PhMeC=N(2,6-$^iPr_2C_6H_3$] (5.00 g, 17.90 mmol) and LDA (1.92 g, 17.9 mmol), prepared *in situ*, and Ph_2PCl (4.94 g, 17.90 mmol) in 200 ml THF was performed as described above. The toluene extract was added to a suspension of $PdBr_2$ (4.76 g, 17.90 mmol) in 50 ml THF, and the reaction mixture immediately turned red. After 10 min of stirring at ambient temperature, an orange precipitate was formed, the colour of the supernatant remaining red-brown. The mixture was stirred for a further 2 h, the solid isolated by filtration, and the residual volatiles removed under reduced pressure. The brown powder was recrystallised from CH_2Cl_2 and pentane giving **6** as a microcrystalline air-stable red-orange solid. Yield: 7.20 g, 55%.

[PdI_2(L1)] (7). To a stirred solution of [Pd(dba)$_2$] (0.195 g, 0.21 mmol) in THF (50 ml), a THF (20 ml) solution of **L1** (0.1 g, 0.21 mmol) was added dropwise. After stirring for 10 min, 0.5 ml of [3,5-$(CF_3)_2C_6H_3$]I in 20 ml THF was added and the reaction mixture was refluxed for 2 h, then stirred at room temperature for a further 2 h. The resulting solution was then filtered in order to remove the trace amount of Pd black. The solvent was removed from the filtrate under reduced pressure and the brown residue washed several times with Et_2O. Recrystallisation of the residual solid from CH_2Cl_2 and pentane gave complex **7** as air-stable red block-shaped crystals. Yield: 0.049 g, 30%.

[PtClMe(L1)] (8). To a mixture of **L1** (0.058 g, 0.14 mmol) and [PtMeCl(cod)] (0.050 g, 0.14 mmol), 100 ml THF was added under stirring. The reaction mixture was stirred for 12 h at room temperature. The resulting white solid was isolated by filtration, washed with 20 ml of cold pentane and the residual volatiles removed under reduced pressure. The white powder obtained was recrystallised from a 1 : 4 mixture of CH_2Cl_2 and pentane at −20 °C to give **8** as air-stable white-yellow crystals. Yield: 0.048 g, 52%.

[$PtMe_2$(L1)] (9). A −78 °C THF (20 ml) solution of **L1** (50 mg, 0.150 mmol) was added to a −78 °C THF solution of [$PtMe_2$(cod)] and left to reach room temperature whilst stirring. Volatiles were removed under reduced pressure and the light-yellow residue was washed with 20 ml pentane. The residual volatiles were removed under reduced pressure to give a yellow powder. Yield of crude product: 60.7 mg, 64%. Recrystallisation from a 1: 4 mixture of toluene and pentane at −20 °C gave yellow crystals of **9**.

[$Pt(CH_3CN)_2$(L1)][BF_4]$_2$ (10). The solids [*cis*-$PtBr_2(CH_3CN)_2$] (0.10 g, 0.23 mmol) and $AgBF_4$ (89.24 mg, 0.457 mmol) were mixed in a Schlenk tube and 50 ml CH_3CN was added. The mixture was stirred at room temperature for 30 min. Formation of a white precipitate was observed. **L1** (0.09 g, 0.23 mmol) was dissolved in 20 ml CH_3CN and was added to the mixture whilst stirring. The resulting orange-coloured mixture was left stirring overnight in darkness. After isolating the supernatant by filtration, volatiles were removed under reduced pressure to give a dark-orange residue, which was washed with 20 ml pentane to give **10** as an air- and moisture-sensitive brown-yellow powder. Yield: 0.15 g, 76.5%.

***cis*-[Pt(L1)$_2$][Cl]$_2$ (11a) and *cis*-[PtCl(L1)$_2$][Cl] (12a), from the reaction of L1 with [$PtCl_2$(cod)].** The solids [$PtCl_2$(cod)] (0.09 g, 0.25 mmol) and **L1** (0.10 g, 0.25 mmol) were mixed in a Schlenk tube and 50 ml THF were added. After stirring at room temperature for 12 h, no colour change occurred. Subsequently, volatiles were removed under reduced pressure. The resulting yellow solid was recrystallised from a 1 : 4 mixture of CH_2Cl_2 and pentane, which gave a light-yellow microcrystalline solid, identified as a mixture of **11a** and **12a** in a 5 : 1 ratio by integration. Crude yield: 0.05 g, 43%.

***cis*-[Pt(L1)$_2$][Br]$_2$ (11b) and *cis*-[PtBr(L1)$_2$][Br] (12b), from the reaction of L1 with [*cis*-$PtBr_2(CH_3CN)_2$].** The solids [*cis*-$PtBr_2(CH_3CN)_2$] (0.10 g, 0.228 mmol) and **L1** (0.093 g, 0.228 mmol) were mixed in a Schlenk tube and 100 ml CH_2Cl_2 were added. After stirring for 12 h at room temperature, volatiles were removed under reduced pressure and the resulting yellow solid was recrystallised from CH_2Cl_2 at −20 °C, affording an inseparable mixture containing **11b** and **12b** (3 : 2 ratio by integration), as a light-yellow microcrystalline powder. Crude yield: 0.047 g, 35%.

Heck coupling of 4-bromoacetophenone and *n*-butyl acrylate using [$PdBr_2$(L2)] (6), [$PdBr_2$(L1)] and [PdClMe(L1)] as pre-catalysts

Sodium acetate (2.25 g, 27.4 mmol), 4-bromoacetophenone (4.98 g, 25.0 mmol), diethylene glycol di-*n*-butyl ether (0.50 g, 2.9 mmol, G.C. standard), *n*-butyl acrylate (4.486 g, 35.0 mmol) and a *N*,*N*-dimethylacetamide solution (10 ml) of the pre-catalyst (0.5 mol %, based on 4-bromoacetophenone) were added to *N*,*N*-dimethylacetamide (20 ml) in a 100 ml 3-necked flask equipped with a thermometer and a reflux condenser. Tetrabutylammonium acetate (2.26 g, 7.5 mmol) was also added to the reaction mixture, as a completely soluble base. The mixture was refluxed at the appropriate reaction temperature for 20 h. The reaction mixture was worked-up by adding it at room temperature to an excess of water, extracting with diethyl ether and drying with magnesium sulfate. The extracted material was analysed by GC-MS. The yield was calculated by integration of the chromatographic peak of the product against 4-bromoacetophenone and against the GC standard peak for diethylene glycol di-*n*-butyl ether.

Crystal structure determination‡

Crystals were isolated by filtration, and a specimen crystal selected under an inert atmosphere, covered with polyfluoroether, and mounted on the end of a nylon loop. Crystal data are summarised in Table 4. All data were collected at 150 K except for compound **9**, which was collected at 190 K. Data collection was performed on an Enraf-Nonius DIP2000 for **1** and **2**, and on a Nonius KappaCCD for **6**, **7** and **9**, using graphite-monochromated MoKα radiation (λ = 0.71073 Å). The images were processed with the DENZO and SCALEPACK programs.[49] The crystal structures were solved by direct methods using the program SIR92.[50] The refinement and graphical calculations were performed using the CRYSTALS[51] and CAMERON[52] software packages. The structures were refined by full-matrix least-squares procedure on *F*. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located in Fourier maps and their positions adjusted geometrically (after each cycle of refinement) with isotropic thermal parameters. Chebychev weighting schemes and empirical absorption corrections were applied.[53]

For complex **1**, the largest peaks and deepest troughs of the difference Fourier map lie close to the Br atoms, suggesting that these may be disordered. However, attempts to model this

‡ CCDC reference numbers 236196 and 236200. See http://www.rsc.org/suppdata/nj/b4/b412391c/ for crystallographic data in .cif or other electronic format.

Table 4 Summary of crystallographic data

	1	2	6	7	9
Empirical formula	$C_{28}H_{26}Br_2NNiP$	$C_{40}H_{37}Br_2NNiOP_2 + 1.24CH_2Cl_2$	$C_{32}H_{34}Br_2NPPd$	$C_{28}H_{26}I_2NPPd$	$C_{30}H_{32}NPPt$
Formula weight	626.01	936.10	729.81	767.71	632.66
Temperature/K	150	150	150(2)	150	190
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$Pcab$	$P2_1cn$	$P2_1$	$C2/c$
a/Å	11.576(1)	13.535(1)	9.9766(2)	10.4664(2)	39.359(1)
α/°	90	90	90	90	90
b/Å	23.162(3)	23.464(2)	13.5588(3)	16.3356(3)	9.388(1)
β/°	117.85(1)	90	90	99.3449(9)	107.83(1)
c/Å	11.171(1)	27.850(3)	21.8426(7)	16.3526(3)	14.772(1)
γ/°	90	90	90	90	90
U/Å^3	2648.3	8844.7	2954.7	2758.8	5196.1
Z	4	8	4	4	8
ρ (calcd)/mg m^{-3}	1.570	1.406	1.641	1.848	1.62
Absorption coefficient/mm^{-1}	3.827	2.503	3.409	2.985	5.48
$F(000)$	1256	3775.3	1456	1472	2488
θ range for data collection	2.0 to 26.7	4.1 to 26.4	1 to 27	5.0 to 27.5	1 to 27.5
Reflections collected	9456	49653	6291	44207	47816
Independent reflections	5338	8500	4082	12405	5063
R_{int}	0.110	0.087	0.093	0.046	0.03
Data/parameters	2572/298	3915/512	4082/334	10511/596	5063/317
Goodness-of-fit	1.0865	1.2474	1.0579	1.0807	1.1085
R [$I > 3\sigma(I)$]	0.1178	0.0581	0.0394	0.0306	0.0279
wR [$I > 3\sigma(I)$]	0.1040	0.0658	0.0344	0.0336	0.0328

did not lead to substantial improvements in the agreement of calculated and observed structure factors. The large anisotropic thermal parameters of several of the C atoms may also be indicative of unresolved disorder, but in view of the paucity of observed diffraction data, it is not possible to model this meaningfully. For complex **2**, three distinct solvent sites were located in difference Fourier maps and the coordinates, anisotropic thermal parameters and site occupancies of the C and Cl atoms were subsequently refined. The P–H hydrogen atom was located in a difference Fourier map and its coordinates and isotropic thermal parameter subsequently refined.

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References

1 G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem., Int. Ed.*, 1999, **38**, 428.
2 E. Lindner, S. Pautz and M. Haustein, *Coord. Chem. Rev.*, 1996, **155**, 145.
3 A. Bader and E. Lindner, *Coord. Chem. Rev.*, 1991, **108**, 27.
4 W. Keim, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 235.
5 W. Keim, *New J. Chem.*, 1994, **18**, 93.
6 P. Braustein, Y. Chauvin, S. Mercier, L. Saussine, A. DeCian and J. Fischer, *J. Chem. Soc., Chem. Commun.*, 1994, 2203.
7 J. Pietsch, P. Braunstein and Y. Chauvin, *New J. Chem.*, 1998, **22**, 467.
8 C. M. Killian, J. P. McDevitt, P. B. Mackenzie, L. S. Moody and J. A. Ponasik, Jr., *Catalyst composition for the polymerisation of olefins*, WO9840420, USA, 1998.
9 Z. Guan, *Bidentate ligand catalysts for polymerisation of ethylene*, WO2000059956, USA, 2000.
10 P. Braunstein, J. Pietsch, Y. Chauvin, S. Mercier, L. Saussine, A. DeCian and J. Fischer, *J. Chem. Soc., Dalton Trans.*, 1996, 3571.
11 V. C. Gibson, A. Tomov, A. J. P. White and D. J. Williams, *Chem. Commun.*, 2001, 719.
12 X. Liu, K. F. Mok and P.-H. Leung, *Organometallics*, 2001, **20**, 3918.
13 M. A. Jalil, S. Fujinami and H. Nishikawa, *J. Chem. Soc., Dalton Trans.*, 1999, 3499.
14 M. A. Jalil, S. Fujinami and H. Nishikawa, *J. Chem. Soc., Dalton Trans.*, 2001, 1091.
15 O. Daugulis and M. Brookhart, *Organometallics*, 2002, **21**, 9.
16 A. Baceiredo, G. Bertrand, P. Dyer, J. Kawcett, N. Griep-Raming, O. Guerret, M. J. Hanton, D. R. Russel and A.-M. Williamson, *New J. Chem.*, 2001, **25**, 591.
17 A. Apfelbacher, P. Braunstein, L. Brissieux and R. Welter, *J. Chem. Soc., Dalton Trans.*, 2003, 1669.
18 G. Muller, M. Klinga, P. Osswald, M. Leskela and B. Rieger, *Z. Naturforsch. B*, 2002, **57**, 803.
19 Z. Guan and W. J. Marshall, *Organometallics*, 2002, **21**, 3580.
20 X. Liu, T. K. W. Ong, S. Selvaratnam, J. J. Vittal, A. J. P. White, D. J. Williams and P.-H. Leung, *J. Organomet. Chem.*, 2002, **643**, 4.
21 M. Koprowski, R.-M. Sebastian, V. Maraval, M. Zablocka, V. Cadiemo, B. Donnadieu, A. Igau, A.-M. Caminade and J.-P. Majoral, *Organometallics*, 2002, **21**, 4680.
22 D. B. Grotjahn, D. Combs, S. Van, G. Aguirre and F. Ortega, *Inorg. Chem.*, 2000, **39**, 2080.
23 M. A. Jalil, S. Fujinami, H. Senda and H. Nishikawa, *J. Chem. Soc., Dalton Trans.*, 1999, 1655.
24 K. R. Reddy, K. Surekha, G. H. Lee, S. M. Peng and S. T. Liu, *Organometallics*, 2000, **19**, 2637.
25 D. Morales-Morales, R. Redon, Y. Zheng and J. R. Dilworth, *Inorg. Chim. Acta*, 2002, **328**, 39.
26 K. S. Coleman, M. L. H. Green, S. I. Pascu, N. H. Rees, A. R. Cowley and L. H. Rees, *J. Chem. Soc., Dalton Trans.*, 2001, 3384.
27 S. I. Pascu, *Nickel(II), Palladium(II), Platinum(II) and Rhodium(I) Complexes of Iminophosphine Ligands*, D. Phil. Thesis, University of Oxford, Oxford, 2002.
28 S. H. de Graaf, J. Boersma and G. van Koten, *J. Organomet. Chem.*, 1988, **358**, 545.
29 S. H. de Graaf, J. Boersma, W. J. J. Smeets, S. A. L. and G. van Koten, *Organometallics.*, 1989, **8**, 2907.
30 T. Yagyu, M. Hamada, K. Osakada and T. Yamamoto, *Organometallics*, 2001, **20**, 1087.
31 D. P. Gates, S. A. Svejda, E. Onate, C. M. Killian, L. K. Johnson, P. S. White and M. Brookhart, *Macromolecules*, 2000, **33**, 2320.
32 L. Sacconi, F. Mani and A. Bencini, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, Pergamon Press, Oxford, 1987, vol. 5, p. 116.
33 C. Ercolani, J. V. Quagliano and L. M. Vallarino, *Inorg. Chim. Acta*, 1973, **9**, 413.
34 L. H. Pignolet Jr., W. W. Horrocks and R. H. Holm, *J. Am. Chem. Soc.*, 1970, **92**, 1855.
35 R. G. Hayter and S. Humiec, *Inorg. Chem.*, 1965, **4**, 1701.
36 E. Alyea, G. Ferguson, B. L. Ruhl and R. Shakya, *Polyhedron*, 1965, **4**, 1701.
37 J. C. Cloyd, Jr. and D. W. Meek, *Inorg. Chim. Acta*, 1972, **12**, 607.

38 G. Booth and J. Chatt, *J. Chem. Soc.*, 1965, 3238.
39 L. Que, Jr. and L. H. Pignolet, *Inorg. Chem.*, 1973, **12**, 156.
40 K. K. Chow and C. A. MacAuliffe, *Inorg. Chim. Acta*, 1974, **10**, 197.
41 L. Crociani, G. Bandoli, A. Dolmella, M. Basato and B. Corain, *Eur. J. Inorg. Chem.*, 1998, 1811.
42 F. H. Allen, J. E. Davies, J. J. Galloy, O. Johnson, O. Kennard, C. F. Macrae, E. M. Mitchell, G. F. Mitchell, J. M. Smith and D. G. Watson, *J. Chem. Inf. Comput. Sci.*, 1991, **31**, 187.
43 W. A. Herrmann, M. Elison, J. Fischer, C. Köcher and G. R. J. Artus, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2371.
44 E. Costa, P. Pringle and M. Ravetz, *Inorg. Synth.*, 1997, **31**, 284.
45 F. T. Lapido and G. K. Anderson, *J. Organomet. Chem.*, 1994, **13**, 303.
46 W. Kaschube, K. R. Poerschke and G. Wilke, *J. Organomet. Chem.*, 1988, **355**, 525.
47 O. Dahl, *Acta Chem. Scand.*, 1969, **23**, 2342.
48 H. Okamoto, K. Shozo, M. Ogasawara, M. Konnai and T. Takematsu, *Agric. Biol. Chem.*, 1991, **55**, 2733.
49 Z. Otwinowski and W. Minor, in *Methods in Enzymology*, eds. C. N. Carter, Jr. and R. M. Sweet, Academic Press, London, 1996, vol. **276**,p. 307.
50 A. Altomare, G. Carascano, C. Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **26**, 343.
51 (*a*) D. J. Watkin, C. K. Prout, J. R. Carruthers and P. W. Betteridge, *CRYSTALS*, Oxford, UK, 1996; (*b*) P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl. Crystallogr.*, 2003, **36**, 1487.
52 D. J. Watkin, C. K. Prout and L. J. Pearce, *CAMERON*, Oxford, UK, 1996.
53 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A.*, 1983, **39**, 158.