Metallated triphenylphosphinimine complexes

Pingrong Wei, Katie T. K. Chan and Douglas W. Stephan *

Department of Chemistry & Biochemistry, University of Windsor, Windsor, Ontario, Canada N9B3P4. E-mail: stephan@uwindsor.ca

The reagent [(o-C$_6$H$_4$PPh$_2$NSiMe$_3$)Li]$_2$·Et$_2$O **1** reacted with BCl$_3$ affording (o-C$_6$H$_4$PPh$_2$NSiMe$_3$)BCl$_2$ **4**. Similarly reaction of **1** with Me$_2$AlCl resulted in a 1 : 1 mixture of (o-C$_6$H$_4$PPh$_2$NSiMe$_3$)AlMe$_2$ **5** and (o-C$_6$H$_4$PPh$_2$NSiMe$_3$)-Al(Me)Cl **6** while the analogous reaction of **1** with GaCl$_3$ gave (o-C$_6$H$_4$PPh$_2$NSiMe$_3$)$_2$Ga(o-C$_6$H$_4$PPh$_2$NH) **7**. The analogous compound [Li(o-C$_6$H$_4$PPh$_2$NPh)]$_2$·Et$_2$O **2** was used to make (o-C$_6$H$_4$PPh$_2$NPh)GaCl$_2$ **8**, while reaction of **2** with Me$_2$AlCl gave a mixture of [(o-C$_6$H$_4$PPh$_2$NPh)AlCl$_2$ **9** and the salt [(o-C$_6$H$_4$PPh$_2$NPh)$_2$Al][AlMeCl$_3$] **10**. The compound **2** also reacts with PdCl$_2$(COD) affording [Pd(o-C$_6$H$_4$PPh$_2$NPh)(μ-Cl)]$_2$ **11** and [Pd(o-C$_6$H$_4$PPh$_2$NPh)$_2$] **12**. Similarly, the complexes [Ni(o-C$_6$H$_4$PPh$_2$NPh)$_2$] **13** and [Ni(o-C$_6$H$_4$PPh$_2$N(3,5-C$_6$H$_3$Me$_2$))$_2$] **14** were prepared. The compounds **4–14** have been structurally characterized by X-ray methods.

Introduction

The current interest in diimine ligands and the use of related late transition metal complexes in olefin polymerization catalysis[1–14] has prompted our efforts to probe the coordination and organometallic chemistry of related phosphinimide and phosphinimine based ligand complexes. While our efforts in the chemistry of early transition metal phosphinimides have resulted in the development of new commercially viable olefin polymerization catalysts,[15,16] our studies in related late metal phosphinimine systems are just beginning to appear. In recent work we have described the development of phosphinimine-pyridine and phosphinimine-imidazole chelate complexes of Fe and Ni.[17] In recent papers, Stalke and co-workers have also described Sn, Pb[18] and Zn[19] complexes of the *ortho*-metallated triphenylphosphinimines. In very recent work we have described related Rh complexes as well as similar imidazolate-phosphinimine complexes.[20] Such ligand variations have been shown to alter the course of facile oxidative addition reactions of CH$_2$Cl$_2$ at Rh. In efforts to broaden the range of compounds accessible for future study, we have explored synthetic pathways to main group and transition metal complexes of metallated phosphinimines. In this manuscript we describe the preparation and structure of these species. The implications of this chemistry are considered.

Experimental

General data

All preparations were done under an atmosphere of dry, O$_2$-free N$_2$ employing both Schlenk line techniques and a Vacuum Atmospheres inert atmosphere glove box. Solvents were purified employing a Grubbs' type solvent purification system manufactured by Innovative Technology. All organic reagents were purified by conventional methods. ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectra were recorded on Bruker Avance-300 and -500 spectrometers. All spectra were recorded in C$_6$D$_6$ at 25 °C unless otherwise noted. Trace amounts of protonated solvents were used as references and chemical shifts are reported relative to SiMe$_4$. For ^{31}P{^{1}H} NMR spectra they were referenced to external 85% H$_3$PO$_4$. Combustion analyses were done in-house employing a Perkin Elmer CHN Analyzer. Ph$_3$PNPh was purchased from the Aldrich Chemical Company. The compounds [(o-C$_6$H$_4$PPh$_2$NSiMe$_3$)Li]$_2$·Et$_2$O **1**, [(o-C$_6$H$_4$PPh$_2$NPh)Li]$_2$·Et$_2$O **2** and [Li(o-C$_6$H$_4$PPh$_2$N(3,5-C$_6$H$_3$Me$_2$))$_2$]$_2$·Et$_2$O **3** were prepared by reaction of the precursor phosphinimine with MeLi or PhLi, with minor modifications to known methods.[17,21–23]

Synthesis of (o-C$_6$H$_4$PPh$_2$NSiMe$_3$)BCl$_2$ 4. To a stirred solution of BCl$_3$ (1.0 M, 0.163 mL, 0.163 mmol) in toluene (10 mL) was added **1** (0.064 g, 0.082 mmol) in toluene (5 mL). The resulting solution was stirred overnight at 25 °C and filtered through Celite. Colorless crystals were isolated upon the evaporation of solvent. Yield 0.030 g, 43%. ^{31}P{^{1}H} NMR δ: 46.5 (s). ^{31}P{^{1}H} NMR δ: 47.12 (s). ^{1}H NMR δ: 8.31–8.28 (br, 1H, Ph), 7.64–7.57(br, 4H, Ph), 7.19 (br, 1H, Ph), 6.98–6.77 (br, 8H, Ph), 0.37 (s, 9H, SiMe$_3$). ^{13}C{^{1}H} NMR δ: 133.9 (br, Ph), 133.8 (s, Ph), 132.2 (s, Ph), 132.0 (s, Ph), 129.6 (s, Ph), 129.5 (s, Ph), 126.9 (s, Ph), 126.0 (s, Ph), 125.8 (s, Ph), 125.6 (s, Ph), 3.4 (s, SiMe$_3$). Anal. Calcd. (found) for C$_{21}$H$_{23}$NPSiBCl$_2$: C, 58.63 (59.19); H, 5.39 (5.60); N, 3.26 (3.33%).

Synthesis of (o-C$_6$H$_4$PPh$_2$NSiMe$_3$)AlMe$_2$ 5 and (o-C$_6$H$_4$PPh$_2$NSiMe$_3$)Al(Me)Cl 6. To a stirred solution of Me$_2$AlCl (1.0 M, 0.183 mL, 0.183 mmol) in toluene (10 mL) was added the lithiated iminophosphorane **1** (0.072 g, 0.092 mmol) in toluene (5 mL). The resulting solution was stirred overnight at 25 °C and filtered through Celite. Colorless crystals of **5/6** were obtained from toluene. Efforts to separate these products were futile, however, these compounds co-crystallized. X-Ray crystallography showed that these species were (o-C$_6$H$_4$PPh$_2$-NSiMe$_3$)AlMe$_2$ **5** and (o-C$_6$H$_4$PPh$_2$NSiMe$_3$)Al(Me)Cl **6**. Yield 0.040 g, 54%. ^{31}P{^{1}H} NMR δ: 34.1, 33.7. ^{1}H NMR δ: 8.05–7.99 (br, 2H, Ph), 7.70–7.44 (br, 8H, Ph), 7.28–7.20 (br, 1H, Ph), 7.06–7.02 (br, 1H, Ph), 6.98–6.85 (br, 16H, Ph), 0.24 (s, 3H, Me), 0.16 (s, 9H, SiMe$_3$), 0.12 (s, 9H, SiMe$_3$), 0.06 (s, 6H, Me). ^{13}C{^{1}H} NMR δ: 136.7 (d, Ph), 136.5 (s, Ph), 136.4 (s, Ph), 133.7 (s, Ph), 133.5 (s, Ph), 133.4 (s, Ph), 133.2 (s, Ph), 132.8 (d, Ph), 131.8 (d, Ph), 131.3 (s, Ph), 131.1 (d, Ph), 130.1 (s, Ph), 129.6 (s, Ph), 129.4 (s, Ph), 129.2 (s, Ph), 129.1 (s, Ph), 127.45 (s, Ph), 127.3 (s, Ph), 3.5 (d, SiMe$_3$), 3.4 (d, SiMe$_3$), −5.2 (d, Me), −5.4 (d, Me). Anal. Calcd. (found) for C$_{45}$H$_{55}$N$_2$P$_2$Si$_2$Al$_2$Cl: C, 65.00 (64.79); H, 6.67 (6.86); N, 3.37 (3.37%).

Synthesis of (o-C$_6$H$_4$PPh$_2$NSiMe$_3$)$_2$Ga(o-C$_6$H$_4$PPh$_2$NH) 7. To a stirred solution of GaCl$_3$ (0.025 g, 0.142 mmol) in Et$_2$O (10 mL) was added the lithiated iminophosphorane **1** (0.162 g, 0.206 mmol) in Et$_2$O (5 mL). The resulting solution was stirred overnight at room temperature. The volatiles were removed under vacuum. Colorless crystals were obtained from toluene. Yield 0.050 g, 34%. ^{31}P{^{1}H} NMR δ: 27.3, 20.9. ^{1}H NMR δ: 7.77–7.69 (br, 12H, Ph), 7.16–7.00 (br, 30H, Ph), 0.39 (s, 18H, SiMe$_3$). ^{13}C{^{1}H} NMR δ: 137.1 (s, Ph), 135.8 (s, Ph), 134.1 (s, Ph), 133.9 (s, Ph), 132.8 (s, Ph), 132.6 (s, Ph), 131.2 (s, Ph), 4.8 (s, SiMe$_3$). Anal. Calcd. (found) for C$_{60}$H$_{61}$N$_3$P$_3$Si$_2$Ga: C, 69.10 (68.65); H, 5.90 (6.59); N, 4.03 (3.66%).

Synthesis of (*o*-C₆H₄PPh₂NPh)GaCl₂, 8. To a stirred solution of GaCl₃ (0.022 g, 0.125 mmol) in toluene (10 mL) was added the lithiated iminophosphorane **2** (0.054 g, 0.068 mmol) in toluene (5 mL). The resulting solution was stirred overnight at room temperature and filtered through Celite. Colorless crystals of **8** were obtained from a mixture of toluene/hexane. Yield 0.020 g, 32%. $^{31}P\{^1H\}$ NMR δ: 25.6. ^1H NMR δ: 7.84–7.81 (br, 1H, Ph), 7.49–7.42 (br, 6H, Ph), 7.08–7.03 (br, 1H, Ph), 6.95–6.73 (br, 11H, Ph). $^{13}C\{^1H\}$ NMR δ: 137.0 (s, Ph), 136.3 (s, Ph), 136.2 (s, Ph), 135.8 (s, Ph), 133.8 (s, Ph), 133.7 (s, Ph), 133.3 (s, Ph), 129.8 (s, Ph), 129.6 (s, Ph), 126.6 (s, Ph), 126.5 (s, Ph), 124.4 (s, Ph). Anal. Calcd. (found) for C₂₄H₁₉NPGaCl₂: C, 58.47 (58.20); H, 3.88 (3.92); N, 2.84 (2.90%).

Synthesis of (*o*-C₆H₄PPh₂NPh)AlCl₂ 9 and [(*o*-C₆H₄PPh₂-NPh)₂Al][AlMeCl₃] 10. To a stirred solution of Me₂AlCl (1.0 M, 0.125 mL, 0.125 mmol) in toluene (10 mL) was added the lithiated iminophosphorane **2** (0.054 g, 0.068 mmol) in toluene (5 mL). The resulting solution was stirred overnight at room temperature and filtered through Celite. A mixture of colorless crystals of **9** and **10** were obtained from toluene/hexane. These species were not separable except by crystal selection. **9/10**: Yield 0.02 g, 33%. $^{31}P\{^1H\}$ NMR δ: 33.4, 31.9. ^1H NMR δ: 8.08–8.05, 7.86–7.83, 7.71–7.64, 7.39–7.25, 7.08–6.62 (br, Ph), 0.08 (s, Me). $^{13}C\{^1H\}$ NMR δ: 142.9 (d, Ph), 140.4 (d, Ph), 137.6 (s, Ph), 137.3 (s, Ph), 134.7 (d, Ph), 133.9 (s, Ph), 133.7 (m, Ph), 133.4 (d, Ph), 130.5 (d, Ph), 130.1 (m, Ph), 129.7 (m, Ph), 126.4 (d, Ph), 124.5 (s, Ph), 123.7 (s, Ph), −7.7 (s, Me). Anal. Calcd. (found) for C₇₃H₆₀N₃P₃Al₃Cl₅: C, 65.90 (65.81); H, 4.55 (5.39); N, 3.16 (2.83%).

Synthesis of [Pd(*o*-C₆H₄PPh₂NPh)(μ-Cl)]₂ 11 and [Pd(*o*-C₆-H₄PPh₂NPh)₂] 12. A solution of **2** (0.23 g, 0.28 mmol) and PdCl₂(COD) (0.08 g, 0.28 mmol) was dissolved in THF (5 mL). The mixture was stirred at 25 °C for 6 h during which time a fine grayish green solid precipitated from solution. The heterogeneous mixture was stirred overnight, and then filtered through Celite and the solvent removed *in vacuo*. The yellow residue was dissolved in CH₂Cl₂ and recrystallized to afford tiny orange crystals of **11**. Yield: 0.04 g, 14%. The yellow filtrate was concentrated to *ca*. 1 mL and benzene slowly added. A yellow precipitated after standing overnight. The yellow powder was isolated by filtration and dissolved in CH₂Cl₂ and cooled to −20 °C affording crystals of **12** Yield: 0.12 g, 52%. **11**: ^1H NMR(CD₂Cl₂) δ: 7.83–7.79 (m, 8H, PPh₂), 7.61–7.59 (m, 6H, PPh₂), 7.50 (m, 2H, PC₆H₄), 7.49–7.47 (m, 8H), 7.27 (dd, 2H, $^3J_{H–H}$ = 8 Hz, PC₆H₄), 7.07–6.99 (m, 4H, NPh), 6.93–6.91 (m, 4H, NPh), 6.86 (d, 2H, $^3J_{H–H}$ = 7 Hz, PC₆H₄), 6.82–6.79 (m, 2H, NPh). $^{13}C\{^1H\}$ NMR(CD₂Cl₂) δ: 149.2 (d, $^2J_{P–C}$ = 18 Hz, PC₆H₄), 147.1 (s, PC₆H₄), 142.2 (s, PPh₂), 135.4 (s, PPh₂), 133.2 (d, $^2J_{P–C}$ = 10 Hz, PPh₂), 133.0 (s, PPh₂), 129.9 (s, NPh), 127.9 (s, NPh), 127.5 (s, PC₆H₄), 126.9 (s, NPh), 126.3 (d, $^2J_{P–C}$ = 11 Hz, PC₆H₄), 125.2 (s, NPh), 124.3 (s, PC₆H₄), 121.5 (s, PC₆H₄). $^{31}P\{^1H\}$ NMR(CD₂Cl₂) δ: 45.5 (s). Anal. Calcd. (found) for C₄₈H₃₈P₂N₂Cl₂Pd₂: C, 58.32 (57.12); H, 3.87 (3.85); N, 2.83 (2.64%). **12**: ^1H NMR δ: 8.27(d, 1H, $^3J_{H–H}$ = 8 Hz, P(C₆H₄)), 7.69 (m, 4H, $^3J_{P–H}$ = 11 Hz, $^3J_{H–H}$ = 7 Hz, PPh₂(*o*-H)), 7.23 (m, 1H, $^3J_{H–H}$ = 8 Hz, P(C₆H₄)), 7.02 (dt, 2H, $^3J_{H–H}$ = 7 Hz, $^4J_{P–H}$ = 1 Hz, NPh), 6.95 (dt, 4H, $^3J_{H–H}$ = 8 Hz, $^4J_{P–H}$ = 2 Hz, PPh₂), 6.80 (m, 4H), 6.75–6.72 (dd, 2H, $^3J_{H–H}$ = 8 Hz, PPh₂(*p*-H)), 6.62 (dd, 1H, $^3J_{H–H}$ = 7 Hz, NPh). $^{13}C\{^1H\}$ NMR δ: 171.2 (d, $^2J_{P–C}$ = 20 Hz, P(C₆H₄Pd)), 148.9(s, P(C₆H₄)(*ipso*-C)), 144.9 (s, PPh), 143.0 (s, PPh), 140.9 (s), 133.8 (d, $^2J_{P–C}$ = 10 Hz, PPh₂), 131.6 (s), 131.1 (s), 130.0 (s), 129.9 (s, NPh), 127.2(s, NPh), 125.9 (d, $^2J_{P–C}$ = 12 Hz, P(C₆H₄)), 121.9(s), 121.8 (s, P(C₆H₄)), 119.1 (s, P(C₆H₄)). $^{31}P\{^1H\}$ NMR δ: 27.8 (s). Anal. Calcd. (found) for C₄₈H₃₈P₂N₂Pd: C, 71.07 (70.62); H, 4.72 (4.39); N, 3.45 (3.08%).

Synthesis of [Ni(*o*-C₆H₄PPh₂NPh)₂] 13 and [Ni(*o*-C₆H₄PPh₂N-(3,5-C₆H₃Me₂))₂] 14. These compounds were prepared by

similar methods and thus only one preparation is detailed. A solution of **2** (0.13 g, 0.16 mmol) and NiBr₂(PPh₃)₂ (0.12 g, 0.16 mmol) was dissolved in THF (5 mL) at −20 °C. The reddish solution was stirred overnight at 25 °C, and then the solvent was removed *in vacuo*. The residue was washed with pentane and recrystallized from benzene to afford red crystals of **13**. Yield: 0.17 g, 74%. ^1H NMR δ: 8.02 (dd, 1H, $^3J_{H–H}$ = 8 Hz, P(C₆H₄)), 7.62 (m, 4H, $^3J_{P–H}$ = 11 Hz, $^3J_{H–H}$ = 8 Hz, PPh₂), 6.98 (m, 9H), 6.86 (m, 1H, P(C₆H₄)), 6.74 (m, 1H, P(C₆H₄)), 6.67 (m, 3H, NPh, P(C₆H₄)). $^{13}C\{^1H\}$ NMR δ: 170.4 (d, $^2J_{P–C}$ = 24 Hz, P(C₆H₄Ni)(*ipso*-C)), 149.6 (s, P(C₆H₄)(*ipso*-C)), 143.8 (s, PPh), 143.5 (s, P(C₆H₄)), 141.7 (s, PPh), 133.6 (d, $^2J_{P–C}$ = 10 Hz, PPh₂), 132.7 (s), 131.5 (s, P(C₆H₄)), 131.3 (s), 130.4 (s, NPh), 121.8 (s, P(C₆H₄)), 120.1 (s, P(C₆H₄)). $^{31}P\{^1H\}$ NMR δ: 33.7 (s). Anal. Calcd. (found) for C₄₈H₃₈P₂N₂Ni: C, 75.51 (74.97); H, 5.02 (5.27); N, 3.67 (3.51%). **14**: Yield : 0.08 g, 58 %. The molecule **14** co-crystallizes with benzene and the by-product NiBr(PPh₃)₃ in the following ratio NiBr(PPh₃)₃·0.5C₆H₆·0.5**14**. ^1H NMR δ: 8.04 (d, 2H, $^3J_{H–H}$ = 8 Hz, PC₆H₄), 7.74–7.62 (m, 8H, PPh₂), 7.08–6.95 (m, 14H), 6.92–6.83 (m, 2H, PC₆H₄), 6.81–6.73 (m, 2H, PC₆H₄), 6.64 (s, 4H, C₆H₃Me₂), 6.26 (s, 2H, C₆H₃Me₂), 1.90 (s, 12H, Me). $^{13}C\{^1H\}$NMR δ: 169.7 (d, $^2J_{P–C}$ = 25 Hz, PC₆H₄), 149.5 (s, PC₆H₄), 144.3 (s, PPh₂), 142.8 (s, PC₆H₄), 141.7 (s, PPh₂), 135.6 (s, PPh₂), 133.3 (d, $^2J_{P–C}$ = 10 Hz, PPh₂), 132.0 (s), 131.4 (s, PC₆H₄), 129.1 (s, C₆H₃Me₂), 126.6 (d, $^2J_{P–C}$ = 14 Hz, PC₆H₄), 122.4 (s), 121.7 (s, C₆H₃Me₂), 20.9 (s, Me). $^{31}P\{^1H\}$NMR δ: 35.4 (s). Anal. Calcd. (found) for C₅₂H₄₆P₂N₂Ni: C, 76.20 (76.08); H, 5.66 (5.34); N, 3.42 (3.21%).

Crystallography

X-Ray data collection and reduction. Crystals were manipulated and mounted in capillaries in a glove box, thus maintaining a dry, O₂-free environment for each crystal. Diffraction experiments were performed on a Siemens SMART System CCD diffractometer. The data were collected in a hemisphere of data in 1329 frames with 10 second exposure times. The observed extinctions were consistent with the space groups in each case. The data sets were collected (4.5°<2θ<45–50.0°). A measure of decay was obtained by re-collecting the first 50 frames of each data set. The intensities of reflections within these frames showed no statistically significant change over the duration of the data collections. The data were processed using the SAINT and XPREP processing packages.[37] An empirical absorption correction based on redundant data was applied to each data set. Subsequent solution and refinement was performed using the SHELXTL[37] solution package operating on a Pentium computer. See Table 1 for crystallographic details.

Structure solution and refinement. Non-hydrogen atomic scattering factors were taken from the literature tabulations.[24] The heavy atom positions were determined using direct methods employing the SHELXTL[37] direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least squares techniques on F, minimizing the function $\omega(|F_o| - |F_c|)^2$ where the weight ω is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases atoms were treated isotropically. C–H atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C–H bond length of 0.95 Å. H-atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the C-atom to which they are bonded. The H-atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the resi-

Table 1 Crystallographic data

|	4	5/6	7	8	9	11	12·CH$_2$Cl$_2$	13·1.5C$_6$H$_6$	Ni(PPh$_3$)$_3$Br·0.5C$_6$H$_6$·0.5 14
Formula	C$_{21}$H$_{23}$BCl$_2$NPSi	C$_{45}$H$_{55}$Al$_2$ClN$_2$P$_2$Si$_2$	C$_{60}$H$_{61}$GaN$_3$P$_3$Si$_2$	C$_{24}$H$_{19}$GaCl$_2$NP	C$_{24}$H$_{19}$Cl$_2$GaNP	C$_{48}$H$_{38}$Cl$_2$N$_2$ P$_2$Pd$_2$	C$_{49}$H$_{40}$Cl$_2$N$_2$P$_2$Pd	C$_{57}$H$_{47}$N$_2$NiP$_2$	C$_{83}$H$_{71}$BrNP$_4$Ni$_{1.5}$
M	430.17	831.44	1042.93	450.25	492.99	988.44	896.07	880.62	1374.26
a/Å	9.264(6)	20.492(12)	10.210(5)	9.746(5)	9.696(5)	12.509(8)	14.543(9)	11.703(7)	15.719(10)
b/Å	14.245(8)	9.113(5)	14.196(7)	17.166(9)	17.260(9)	14.847(9)	10.026(6)	13.353(8)	13.700(8)
c/Å	17.380(10)	26.214(16)	22.407(12)	14.235(8)	14.120(8)	22.963(13)	29.194(17)	17.039(10)	35.49(2)
α/°	90.00	90.00	78.956(10)	90.00	90.00	90.00	90.00	108.071(12)	90
β/°	90.035(11)	90.00	79.552(9)	100.233(11)	100.220(10)	99.363(12)	95.731(11)	92.150(14)	90.364(12)
γ/°	90.00	90.00	73.884(11)	90.00	90.00	90.00	90.00	108.907(11)	90
Crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	P2$_1$/n	Pna2$_1$	P1̄	P2$_1$/n	P2$_1$/n	C2/c	P2$_1$/c	P1̄	P2/c
V/Å^3	2293(2)	4895(5)	3034(3)	2344(2)	2325(2)	4208(4)	4235(4)	2366(2)	7643(8)
d$_{calc}$/g cm^{-1}	1.246	1.128	1.142	1.275	1.408	1.560	1.405	1.236	1.194
Z	4	4	2	4	4	4	4	2	4
μ/cm^{-1}	0.411	0.259	0.609	0.393	1.492	1.094	0.677	0.517	0.0613
Data collected	9762	19914	13176	9772	9644	8873	17288	10265	31881
Data F$_o^2$>3σ(F$_o^2$)	3289	5764	8673	3311	3306	3008	6030	6701	10886
Variables	244	487	622	289	289	253	505	559	816
R	0.0452	0.0562	0.0681	0.0859	0.0569	0.0193	0.0333	0.0519	0.0548
R$_W$	0.0810	0.1370	0.1511	0.2454	0.1149	0.0367	0.0648	0.0473	0.1731
GOF	1.018	0.818	0.830	0.967	1.049	1.056	0.957	0.809	1.021

dual electron densities in each case were of no chemical significance.

CCDC reference numbers 211243–211251.

See http://www.rsc.org/suppdata/dt/b3/b305877h/ for crystallographic data in CIF or other electronic format.

Results and discussion

The reagent [(o-C$_6$H$_4$PPh$_2$NSiMe$_3$)Li]$_2$·Et$_2$O **1** was prepared *via* literature methods [23] and reacted with BCl$_3$ to give colorless crystals of (o-C$_6$H$_4$PPh$_2$NSiMe$_3$)BCl$_2$ **4** in 43% yield (Scheme 1). The NMR data were as anticipated and an X-ray study confirmed this formulation (Fig. 1). The pseudo-tetrahedral coordination sphere about B is comprised of the aryl-C, the phosphinimine-N and the two Cl atoms. The B–N distance is 1.576(4) Å which is much longer than the B–N seen in the phosphinimide derivative [(t-Bu$_3$PN)$_2$B]Cl (1.258(5) Å) [25] or [B(NPPh$_3$)$_3$] (1.446(8) Å). [26] The B–C bond is slightly longer at 1.597(5) Å, while the B–Cl distances average 1.893(6) Å. The P–N distance is typical at 1.624(3) Å. The bite angle of the anionic metallated-phosphinimine chelate is 106.1(3)° similar to the Cl–B–Cl angle of 106.8(2)°. The B–N–P angle is 110.0(2)°, typical of trigonal planar N donors.
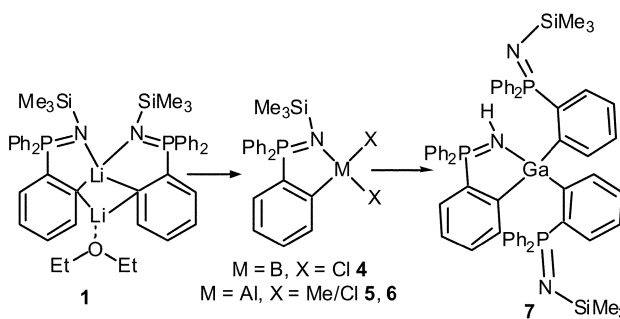
Scheme 1

A similar reaction of **1** with Me$_2$AlCl resulted in a 1 : 1 mixture of two products as evidenced by the ^{31}P{^{1}H} NMR signals at 34.1 and 33.7 ppm. Efforts to separate these products were futile, however, these compounds co-crystallized. X-Ray crystallography showed that these species were (o-C$_6$H$_4$PPh$_2$-NSiMe$_3$)AlMe$_2$ **5** and (o-C$_6$H$_4$PPh$_2$NSiMe$_3$)Al(Me)Cl **6** (Scheme 1). While the general geometry of these species was similar to that observed for **4**, a detailed discussion of the metric parameters is not possible due to the disordered methyl and chloride ligands.

The analogous reaction of **1** with GaCl$_3$ also resulted in colorless crystals however, ^{31}P{^{1}H} NMR data showed two resonances at 27.3 and 20.9 ppm consistent with different phosphinimine ligands in a 2 : 1 ratio. ^{1}H NMR spectra showed only one resonance for the SiMe$_3$ groups. X-Ray diffraction revealed the formulation of **7** as (o-C$_6$H$_4$PPh$_2$NSiMe$_3$)$_2$Ga(o-C$_6$H$_4$PPh$_2$-NH) (Fig. 2, Scheme 1). In this molecule two phosphinimine ligands **1** are bound to Ga only through the aryl-C atoms. A third ligand chelates to the Ga center where the SiMe$_3$ on N has been replaced by H.

The resulting geometry about Ga is that of a distorted tetrahedron. The bite angle for the chelating ligand is 86.8(3)° considerably less than that seen above in **4**. The remaining angles about Ga range from 101.0(2)° to 127.3(3)°. The average Ga–C distance is 2.026(8) Å while the Ga–N distance is 2.007(6) Å. The P–N distance in the chelating metallated phosphinimine (NH) is slightly longer (1.585(6) Å) than those seen in the pendant ligands (1.550(5) Å, 1.564(6) Å).

Clearly the replacement of SiMe$_3$ by proton reduces the steric congestion about Ga allowing chelation to occur. However the source of the proton could not be identified. Nonetheless it is perhaps a bit surprising that this metallated ligand does not
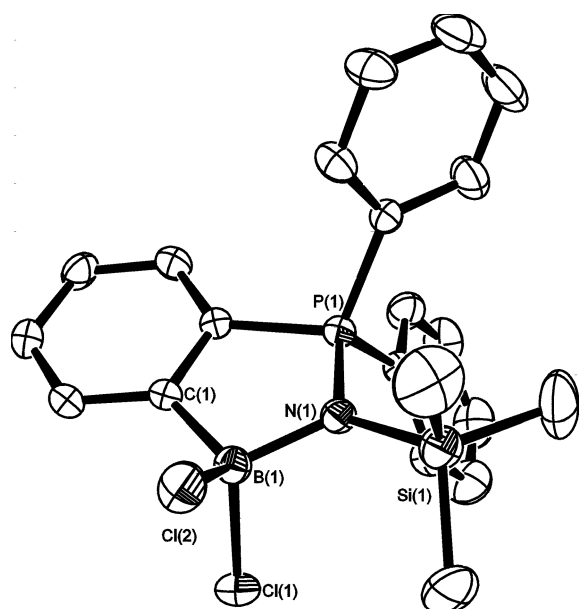
Fig. 1 ORTEP[37] drawing of **4**, 30% thermal ellipsoids are shown, hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): B(1)–N(1) 1.576(4), B(1)–C(1) 1.597(5), B(1)–Cl(2) 1.877(4), B(1)–Cl(1) 1.909(4), P(1)–N(1) 1.624(3); N(1)–B(1)–C(1) 106.1(3), N(1)–B(1)–Cl(2) 111.7(3), C(1)–B(1)–Cl(2) 112.7(3), N(1)–B(1)–Cl(1) 110.3(2), C(1)–B(1)–Cl(1) 109.3(3), Cl(2)–B(1)–Cl(1) 106.8(2), B(1)–N(1)–P(1) 110.0(2).
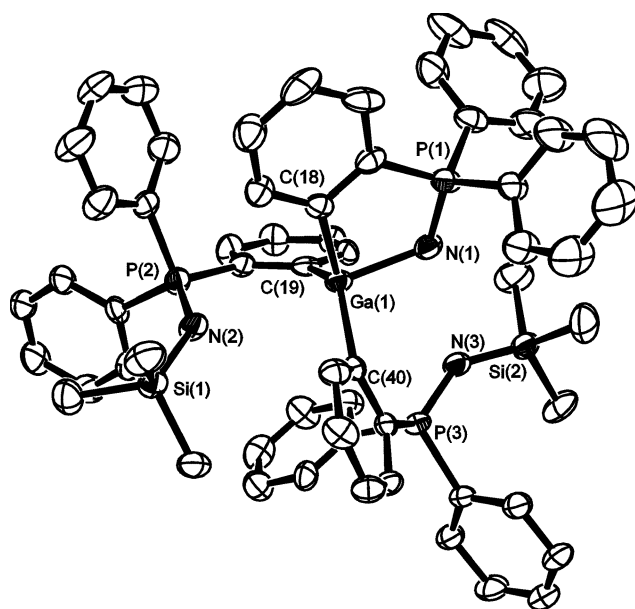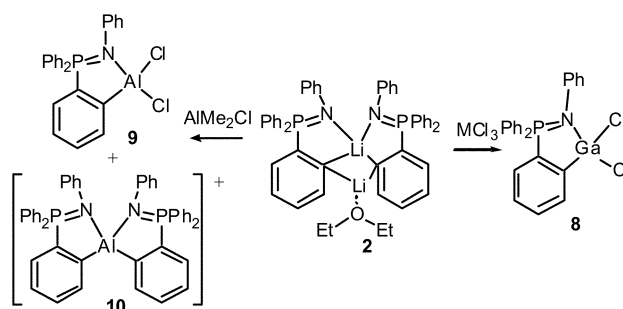

Fig. 2 ORTEP drawing of **7**, 30% thermal ellipsoids are shown, hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ga(1)–N(1) 2.007(6), Ga(1)–C(40) 2.019(6), Ga(1)–C(19) 2.028(7), Ga(1)–C(18) 2.033(8), P(1)–N(1) 1.585(6), P(2)–N(2) 1.550(5), P(2)–C(24) 1.797(7), P(3)–N(3) 1.564(6), Si(1)–N(2) 1.683(6), Si(2)–N(3) 1.680(6); N(1)–Ga(1)–C(40) 101.0(2), N(1)–Ga(1)–C(19) 102.6(3), C(40)–Ga(1)–C(19) 127.3(3), N(1)–Ga(1)–C(18) 86.8(3), C(40)–Ga(1)–C(18) 114.2(3), C(19)–Ga(1)–C(18) 113.5(3), P(1)–N(1)–Ga(1) 118.1(3), P(2)–N(2)–Si(1) 136.6(4), P(3)–N(3)–Si(2) 140.5(4).
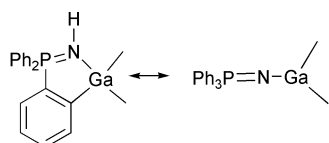
Scheme 2

appear to rearrange to the Ph₃PN⁻ tautomer (Scheme 2). A number of N-bound complexes of Ph₃PN⁻ have been previously reported.[27,28]

The phosphinimine Ph₃PNPh is commercially available and is readily lithiated to give [Li(o-C₆H₄PPh₂NPh)]₂·Et₂O **2** using a method analogous to that previously reported.[21] This species reacted with GaCl₃ to give a complex of formula (o-C₆H₄-PPh₂NPh)GaCl₂ **8** in moderate yields (Scheme 3). This compound was also characterized crystallographically (Fig. 3). In this case, similar disorder models were required. These models involved 50 : 50 disorders of the P, N and M atoms. This unusual disorder appears to arise because of the approximately co-planar nature of the metallated-arene ring and the N-bound phenyl group which allows the PC₆H₄ and PNPh to disorder. Again, more detailed comments on the metric parameters are precluded by this disorder.
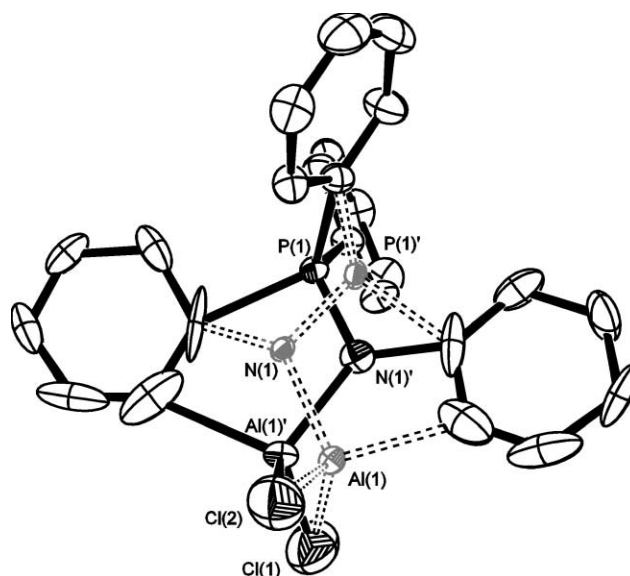

Scheme 3

Fig. 3 ORTEP drawing of **9**, 30% thermal ellipsoids are shown, hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): **9**: Al(1)–N(1) 1.944(9), Al(1)–Cl(2) 2.076(5), Al(1)–Cl(1) 2.101(5), Al(1)–C(1) 2.133(13); N(1)–Al(1)–Cl(2) 108.5(3), N(1)–Al(1)–Cl(1) 110.1(3), Cl(2)–Al(1)–Cl(1) 113.3(2). **8**: Ga(1)–N(1) 1.636(10), Ga(1)–C(1) 2.004(9), Ga(1)–Cl(2) 2.157(2), Ga(1)–Cl(1) 2.241(2); N(1)–Ga(1)–C(1) 65.4(6), N(1)–Ga(1)–Cl(2) 125.7(4), C(1)–Ga(1)–Cl(2) 120.3(3), N(1)–Ga(1)–Cl(1) 118.8(4), C(1)–Ga(1)–Cl(1) 112.7(3), Cl(2)–Ga(1)–Cl(1) 107.84(9).

Interestingly in a reaction, reminiscent of that affording **5** and **6**, reaction of **2** with Me₂AlCl also gave a mixture of products. Although the two products could not be separated by solubility, crystal selection afforded X-ray studies. In the crystal structure of product **9** a formulation and disorder structure analogous to **8** confirmed the formulation as (o-C₆H₄PPh₂-NPh)AlCl₂ **9**. The second species, **10** was obtained only as poor quality crystals. X-Ray studies confirmed this material was a salt. While the cation refined nicely, the disordered nature of the anion could not be resolved. Thus, based on X-ray and elemental analyses data, **10** was formulated as [(o-C₆H₄PPh₂-NPh)₂Al][AlMeCl₃]. As only the gross structural features of **10** were ascertained, the solution is not publishable.[29]

In extending the chemistry of these metallated phosphin-imines attempts were made to react **1** with various Ni(II), Pd(II) or Pt(II) reagents under a variety of reaction conditions. In all cases no products could be isolated. Similarly, attempts to first brominate **1** and then effect oxidative addition to Ni(0) species failed to give isolable arylated phosphinimine complexes. In contrast, reaction of **2** with PdCl$_2$(COD) in a 1 : 1 ratio in THF afforded a low yield (14%) of a compound formulated on the basis of NMR and EA data as [Pd(*o*-C$_6$H$_4$PPh$_2$NPh)-(µ-Cl)]$_2$ **11** (Scheme 4). Crystallographic data confirmed the two-fold symmetry of this dimeric formulation (Fig. 4). The two Pd centers are bridged by two Cl atoms. Each Pd atom has a slightly distorted square planar coordination environment. However, the Pd–Cl distances were found to be 2.3502(12) Å and 2.5130(13) Å. This dissymmetry arises as a result of greater *trans* influence of C *versus* the N-donor atoms. The Pd–C distance in **11** is 1.992(2) Å while the Pd–N distance is 2.047(2) Å with a chelate bite angle of 85.45(10)°. The bridging Pd–Cl–Pd′ angle is 77.46(4)° while the angle between Pd-coordination planes is 83.5°. This results in a Pd–Pd′ separation of 3.0453(17) Å.
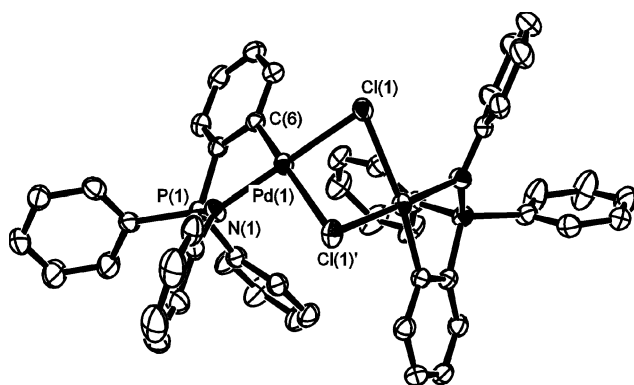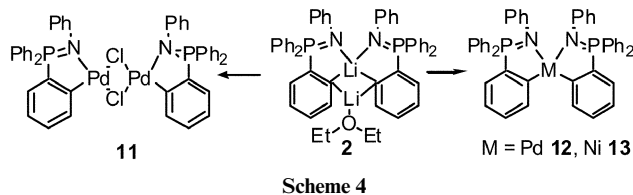
Scheme 4

Fig. 4 ORTEP drawing of **11**, 30% thermal ellipsoids are shown, hydrogen atoms have been omitted for clarity. Atoms that are marked with primes refer to equivalent positions ($-x, y, 0.5 - z$). Selected bond distances (Å) and angles (°): Pd(1)–C(6) 1.992(2), Pd(1)–N(1) 2.047(2), Pd(1)–Cl(1) 2.3502(12), Pd(1)–Cl(1) 2.5130(13), Pd(1)–Pd(1) 3.0453(17), P(1)–N(1) 1.614(2); C(6)–Pd(1)–N(1) 85.45(10), C(6)–Pd(1)–Cl(1) 96.09(8), N(1)–Pd(1)–Cl(1) 177.79(6), C(6)–Pd(1)–Cl(1) 166.98(7), N(1)–Pd(1)–Cl(1) 94.04(7), Cl(1)–Pd(1)–Cl(1) 84.81(4), Pd(1)–Cl(1)–Pd(1) 77.46(4), C(19)–N(1)–P(1) 125.01(17), C(19)–N(1)–Pd(1) 122.32(16), P(1)–N(1)–Pd(1) 110.84(11), C(5)–C(6)–Pd(1) 126.39(19), C(1)–C(6)–Pd(1) 116.50(18).

Attempts to improve the yield of **11** were unsuccessful. However, reaction of **2** with PdCl$_2$(COD) afforded a product form-ulated as [Pd(*o*-C$_6$H$_4$PPh$_2$NPh)$_2$] **12** in about 50% yield (Scheme 4). The upfield ^{31}P resonance observed for **12** compared to that of **11** was consistent with the presence of a second strong donor ligand on Pd. The structure was confirmed crystallographically (Fig. 5). The geometry about Pd is approximately square planar in which the two aryl C atoms are *cis* to one another. The Pd–C distances in **12** are 2.004(3) Å and 2.011(3) Å while the Pd–N distances in **12** are 2.146(3) Å and 2.172(3) Å. Both are longer than those seen in **11**, consistent with the presence of the strong donor ligands. The Pd–C bonds are longer than those seen in [Pd(C$_6$H$_5$)Br(PMe$_3$)CPh(NEt$_2$)] (2.016(5) Å),[30] [PdBr{*o*-C$_6$-H$_4$B(pin)}(PCy$_3$)$_2$] (pin = pinacolato) (2.026(5) Å),[31] and *trans*-[PdCl{C$_6$H$_3$(CO$_2$H)$_2$-2,5}(PPh$_3$)$_2$] (2.000(3) Å).[32] In contrast,
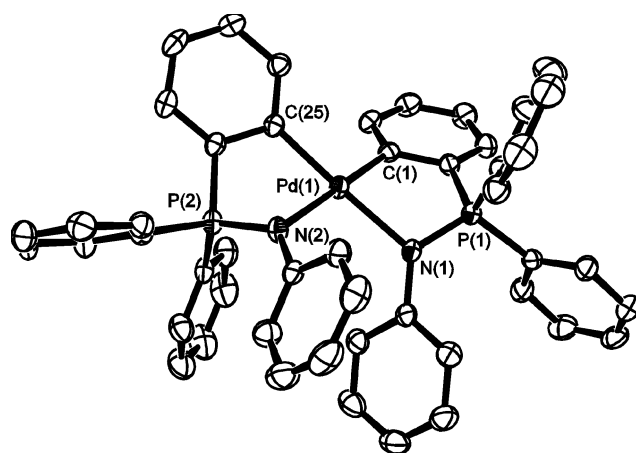
Fig. 5 ORTEP drawing of **12**, 30% thermal ellipsoids are shown, hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Pd(1)–C(25) 2.004(3), Pd(1)–C(1) 2.011(3), Pd(1)–N(1) 2.146(3), Pd(1)–N(2) 2.172(3), Pd(1)–P(2) 2.9729(19), N(1)–P(1) 1.599(3), N(2)–C(43) 1.404(5), N(2)–P(2) 1.607(3); C(25)–Pd(1)–C(1) 94.27(14), C(25)–Pd(1)–N(1) 176.57(12), C(1)–Pd(1)–N(1) 86.30(12), C(25)–Pd(1)–N(2) 84.70(12), C(1)–Pd(1)–N(2) 176.58(12), N(1)–Pd(1)–N(2) 94.92(11), C(25)–Pd(1)–P(2) 61.61(10), C(1)–Pd(1)–P(2) 145.22(10), N(1)–Pd(1)–P(2) 119.33(7), N(2)–Pd(1)–P(2) 31.83(8), C(7)–N(1)–P(1) 126.1(2), C(7)–N(1)–Pd(1) 126.4(2), P(1)–N(1)–Pd(1) 105.41(15), C(43)–N(2)–P(2) 126.9(2), C(43)–N(2)–Pd(1) 127.4(2), P(2)–N(2)–Pd(1) 102.71(15), C(6)–C(1)–Pd(1) 128.2(3), C(2)–C(1)–Pd(1) 115.4(3), C(30)–C(25)–Pd(1) 128.9(2), C(26)–C(25)–Pd(1) 115.0(2).

the bite angles of the chelates in **12** of 86.30(12)° and 84.70(12)° are in the same range as that seen in **11**.

Compound **12** was observed to be light sensitive, decompos-ing to a black solid. While **11** is stable to light, the sensitivity of **12** suggests that reductive coupling of the aryl rings could be photochemically induced although this was not confirmed. This notion inferred a *cis* arrangement of the arene rings, a structural feature that was subsequently confirmed by the growth of X-ray quality crystals of **12** by recrystallization at −20 °C in the dark. In a similar sense Stalke *et al.*[19] observed that reaction of **1** with CuCl$_2$ resulted in the reductive coupling product [(*o*-C$_6$H$_4$PPh$_2$NSiMe$_3$)$_2$].

Using the starting material NiBr$_2$(PPh$_3$)$_2$ attempts to prepare related Ni complexes resulted only in the isolation of the Ni-analog of **12**, [Ni(*o*-C$_6$H$_4$PPh$_2$NPh)$_2$] **13** (Scheme 4). Using optimized stoichiometry this species was isolated in 74% yield. The compound was diamagnetic and the NMR data suggested a structure similar to **12**, an inference that was confirmed by an X-ray structural study of **13** (Fig. 6). The distorted square planar geometry about Ni is similar to that seen in **12** with Ni–C distances of 1.898(5) Å and 1.910(5) Å and Ni–N 1.982(4) Å and 2.018(3) Å respectively. The Ni–C distances are longer than those found in [NiBr{*o*-C$_6$H$_4$B(pin)}-(PPh$_3$)$_2$] (1.894(3) Å),[31] [NiCl(C$_6$H$_2${CH$_2$NMe$_2$}$_2$-2,6-SiMe$_3$-4)] (1.8850(16) Å)[33] and in *trans*-(Me$_3$P)BrNi(η^2-C(NBu^t)CH$_2$-*o*-C$_6$H$_4$)NiBr(PMe$_3$)$_2$ (1.90(2) Å).[34] The C–Ni–N bite angles in **13** (89.98(19)°, 89.23(19)°) were found to be slightly greater than those in **12**. The average P–N bond length in **13** (1.616(4) Å), is only slightly longer than that seen in **12** (1.604(3) Å) and the parent phosphinimine Ph$_3$PNPh (1.602(3) Å).[35]

A similar synthetic approach has also been employed to react [Li(*o*-C$_6$H$_4$PPh$_2$N(3,5-C$_6$H$_3$Me$_2$))$_2$]·Et$_2$O **3** with NiBr$_2$(PPh$_3$)$_2$. While this reaction yields orange X-ray quality crystals, a side-product is also obtained. Fortunately, X-ray diffraction studies confirmed the co-crystallization of the two-fold symmetric species [Ni(*o*-C$_6$H$_4$PPh$_2$N(3,5-C$_6$H$_3$Me$_2$))$_2$] **14** (Fig. 7) with a two symmetry benzene of crystallization and the by-product NiBr(PPh$_3$)$_3$. The geometry of NiBr(PPh$_3$)$_3$ was as previously reported.[36] The structure of the latter by-product is identical to that previously reported, while the structure of **14** is similar to
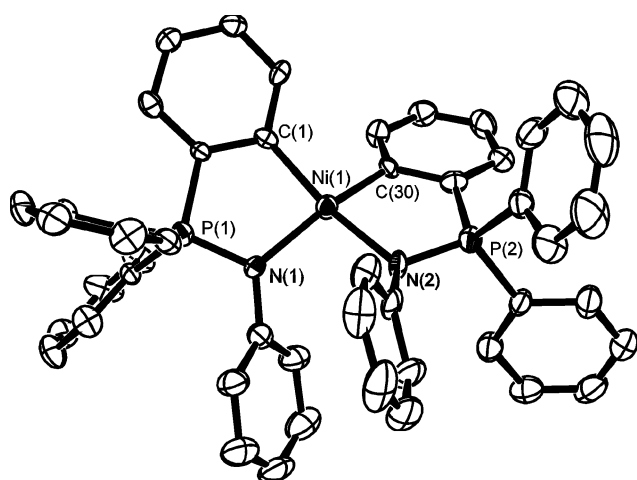
Fig. 6 ORTEP drawing of **13**, 30% thermal ellipsoids are shown, hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ni(1)–C(30) 1.898(5), Ni(1)–C(1) 1.910(5), Ni(1)–N(1) 1.982(4), Ni(1)–N(2) 2.018(3), P(1)–N(1) 1.616(3); C(30)–Ni(1)–C(1) 93.8(2), C(30)–Ni(1)–N(1) 160.33(16), C(1)–Ni(1)–N(1) 89.98(19), C(30)–Ni(1)–N(2) 89.23(19), C(1)–Ni(1)–N(2) 160.86(16), N(1)–Ni(1)–N(2) 93.47(16), C(19)–N(1)–P(1) 118.9(4), C(19)–N(1)–Ni(1) 122.4(3), P(1)–N(1)–Ni(1) 114.9(2), C(43)–N(2)–P(2) 116.4(3), C(43)–N(2)–Ni(1) 123.5(3), P(2)–N(2)–Ni(1) 112.9(2), C(2)–C(1)–Ni(1) 127.0(4), C(6)–C(1)–Ni(1) 117.1(4), C(29)–C(30)–Ni(1) 127.2(4), C(25)–C(30)–Ni(1) 118.6(4).
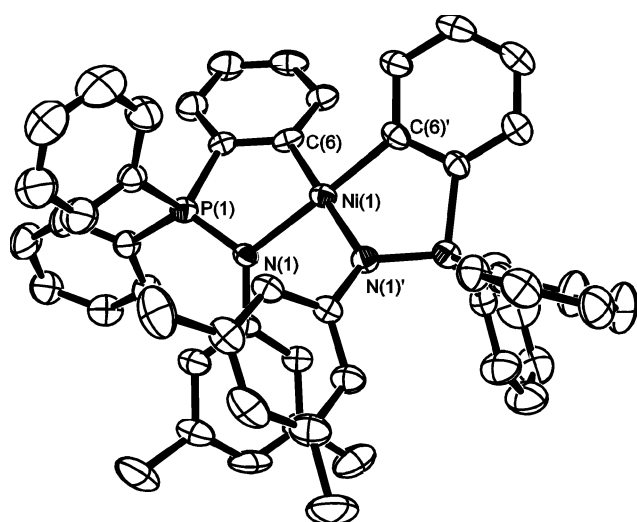

Fig. 7 ORTEP drawing of **14**, 30% thermal ellipsoids are shown, hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Ni(1)–C(6) 1.920(5), Ni(1)–C(6) 1.920(5), Ni(1)–N(1) 2.020(4), Ni(1)–N(1) 2.020(4), N(1)–C(19) 1.433(6); C(6)–Ni(1)–C(6) 94.3(4), C(6)–Ni(1)–N(1) 177.73(19), C(6)–Ni(1)–N(1) 85.4(2), C(6)–Ni(1)–N(1) 85.4(2), C(6)–Ni(1)–N(1) 177.73(19), N(1)–Ni(1)–N(1) 95.0(2), P(1)–N(1)–Ni(1) 108.5(2).

that described above for **13**. The geometry of **14** is two-fold symmetry as the Ni sits on a crystallographic special position. Approximate π-stacking of the N-bound aryl groups in **14** is similar to that seen in **13** and results in a slightly distorted square planar geometry about Ni. The Ni–C and Ni–N distances in **14** of 1.920(5) Å and 2.020(4) Å respectively are similar to those seen in **13** as is the C–Ni–N angle (85.4(2)°).

The fortuitous co-crystallization of the Ni(I) by-product NiBr(PPh₃)₃, in the formation of **14**, suggests that some degree of metal reduction by the Li reagents may account for the only moderate yields in these syntheses of transition metal species **11**–**14**. In a related sense, Stalke and co-workers have seen evidence of oxidative ligand coupling.[19] In addition, in the syntheses described herein, it is generally observed for both the main group and transition metal derivatives that more than one metallated phosphinimine ligand are readily incorporated.

Similar phenomena have been observed for related Sn, Pb[18] and Zn[19] compounds. This is thought to be an artifact of solubility and electronic effects. The mono-ligated species are more soluble than the halide precursors and at the same time incorporation of the strong donor aryl and phosphinimine ligands acts to labilize the remaining halides prompting further substitution. Efforts to utilize these strong donor ligands and their complexes are the subject of on-going studies.

Acknowledgements

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