Dalton Transactions

Cite this: *Dalton Trans.*, 2011, **40**, 4918

www.rsc.org/dalton

PAPER

Mononuclear and dinuclear palladium and nickel complexes of phosphinimine-based tridentate ligands†

Renan Cariou, Fatme Dahcheh, Todd W. Graham and Douglas W. Stephan*

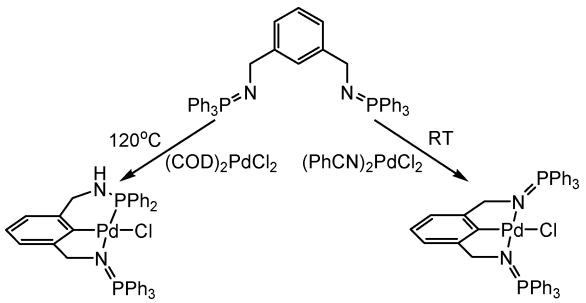
Received 22nd January 2011, Accepted 22nd February 2011
DOI: 10.1039/c1dt10131e

The tridentate *bis*-phosphinimine ligands O(1,2-$C_6H_4N{=}PPh_3)_2$ **1**, HN(1,2-$C_2H_4N{=}PR_3)_2$ (R = Ph **2**, *i*Pr **3**), MeN(1,2-$C_2H_4N{=}PPh_3)_2$ **4** and HN(1,2-$C_6H_4N{=}PPh_3)_2$ **5** were prepared. Employing these ligands, monometallic Pd and Ni complexes O(1,2-$C_6H_4N{=}PPh_3)_2PdCl_2$ **6**, RN(1,2-$CH_2CH_2N{=}PPh_3)_2PdCl][Cl]$ (R = H **7**, Me **8**), [HN(1,2-$CH_2CH_2N{=}PiPr_3)_2PdCl][Cl]$ **9**, [MeN(1,2-$CH_2CH_2N{=}PPh_3)_2PdCl][PF_6]$ **10**, [HN(1,2-$CH_2CH_2N{=}PPh_3)_2NiCl_2]$ **11**, [HN(1,2-$CH_2CH_2N{=}PR_3)_2NiCl][X]$ (X = Cl, R = *i*Pr **12**, X = PF_6, R = Ph **13**, *i*Pr **14**), and [HN(1,2-$C_6H_4N{=}PPh_3)_2Ni(MeCN)_2][BF_4]Cl$ **15** were prepared and characterized. While the ether-*bis*-phosphinimine ligand **1** acts in a bidentate fashion to Pd, the amine-*bis*-phosphinimine ligands **2–5** act in a tridentate fashion, yielding monometallic complexes of varying geometries. In contrast, initial reaction of the amine-*bis*-phosphinimine ligands with base followed by treatment with $NiCl_2$(DME), afforded the amide-bridged bimetallic complexes N(1,2-$CH_2CH_2N{=}PR_3)_2Ni_2Cl_3$ (R = Ph **16**, *i*Pr **17**) and N(1,2-$C_6H_4N{=}PPh_3)_2Ni_2Cl_3$ **18**. The precise nature of a number of these complexes were crystallographically characterized.

Introduction

Complexes of tridentate or pincer ligands have attracted great interest as ligand variations affords tunable reactivity. Group 10 metal complexes bearing pincer ligands have found applications in diverse areas of chemistry such as sensors, switches and catalysts.[1] Although PCP pincer type ligands have attracted the most interest,[2] PNP type ligands, which offer electronic and steric flexibility, have proven to be able to stabilize highly reactive species, such as group IV alkylidene, phosphinidene,[3] metal hydrides,[4,5] and three coordinate complexes.[6,7] In addition, PNP pincer complexes display interesting reactivity such as oxidative addition of C-Halogen bonds,[8,9] C–H bond activation,[5] N_2 activation and homolytic cleavage of H_2.[7]

In targeting new ligand systems that might also find applications in catalysis, we are developing strategies based on the notion that steric protection of an active site can be provided by appropriate ligand design. To this end, we sought to employ phosphinimine donors in tridentate ligands as the N atoms are basic and the inclusion of phosphinimine substituents would sterically shield the adjacent coordination site. While mono- and bidentate phosphinimide and phosphinimine ligands have been employed to access a variety of complexes and catalyst precursors,[10–12,13–15] tridentate ligands incorporating phosphinimine donors have received very limited attention.[16] We have recently communicated the unusual rearrangement reactivity of phosphinimine-arene-based pincer ligands in Pd complexes (Scheme 1).[17] Nonetheless, these early data demonstrate the predicted pocketing provided by such ligands. Herein, we explore related ligand systems that incorporate ether and amine central donors in tridentate *bis*-phosphinimine ligands. The variety of Ni and Pd coordination geometries accessible employing these ligands are demonstrated and the implications for future chemistry is considered.



Scheme 1 Reactions of *bis*-phosphinimine ligands with Pd complexes.

Experimental Section

General Remarks

All manipulations were carried out under an atmosphere of dry, O_2-free N_2 employing an Innovative Technology glove box and

Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada, M5S 3H6. E-mail: dstephan@chem.utoronto.ca; Tel: 416-946-3294

† CCDC reference numbers 809529–809536. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c1dt10131e

a Schlenk vacuum-line. Solvents were purified with a Grubbs-type column system manufactured by Innovative Technology and dispensed into thick-walled Schlenk glass flasks equipped with Teflon-valve stopcocks (pentane, toluene, CH_2Cl_2), or were dried over the appropriate agents and distilled. All solvents were thoroughly degassed after purification (repeated freeze-pump-thaw cycles). Deuterated solvents were dried over the appropriate agents, vacuum-transferred into storage flasks with Teflon stopcocks and degassed accordingly (CD_2Cl_2). Toluene and pentane were stored over potassium mirrors, while bromobenzene and dichloromethane were stored over 4 Å molecular sieves. ^1H, ^{13}C and ^{31}P NMR spectra were recorded at 25 °C on Varian 400 MHz and Bruker 400 MHz spectrometers. Chemical shifts are given relative to $SiMe_4$ and referenced to the residue solvent signal (^1H, ^{13}C) or relative to an external standard (^{31}P: 85% H_3PO_4). Chemical shifts are reported in ppm and coupling constants as scalar values in Hz. Combustion analyses were performed in house employing a Perkin–Elmer CHN Analyzer. $HN(1,2\text{-}C_6H_4NH_2)_2$ was synthesized according to literature procedure.[18] In several cases, repeated attempts to obtain suitable carbon analysis were unsuccessful. This is thought to result from the formation of metal-carbides during combustion. $O(1,2\text{-}C_6H_4NH_2)_2$, $HN(CH_2CH_2NH_2)_2$ were purchased from Aldrich and $Me(CH_2CH_2NH_2)_2$ from TCI. Liquids were degassed and stored over 4 Å molecular sieves.

Synthesis of $O(1,2\text{-}C_6H_4N{=}PPh_3)_2$ 1

A solution of PPh_3Br_2 (4.22 g, 9.99 mmol) in 50 mL CH_2Cl_2 was added dropwise at 0 °C to a solution of $O(1,2\text{-}C_6H_4NH_2)_2$ (1.00 g, 4.99 mmol) in 50 mL CH_2Cl_2 and 15 mL Et_3N. The suspension was stirred and allowed to warm to 25 °C and was then stirred for one hour further. The solvent was removed *in vacuo* to afford a white solid. The product was extracted into THF and filtered through Celite to remove the $HNEt_3Br$ salt. The solvent was then removed *in vacuo* to afford an off-white solid. Yield: 3.42 g (95%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 2.5. ^1H NMR (CD_2Cl_2): 7.69–7.65 (m, 12H, *o*-Ar*H*); 7.46–7.41 (m, 6H, *p*-Ar*H*); 7.34–7.30 (m, 12H, *m*-Ar*H*); 6.68–6.62 (m, 2H, OAr*H*); 6.61–6.59 (m, 2H, OAr*H*); 6.39–6.34 (m, 2H, OAr*H*); 6.27–6.25 (m, 2H, OAr*H*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 149.9 (d, 1,2-C_6H_4, J_{CP} = 17 Hz); 141.3 (1,2-C_6H_4); 132.6 (d, C_6H_5, J_{CP} = 10 Hz); 131.5 (C_6H_5); 131.2 (d, C_6H_5, J_{CP} = 3 Hz); 128.3 (d, C_6H_5, J_{CP} = 12 Hz); 123.4 (d, 1,2-C_6H_4, J_{CP} = 14 Hz); 122.3 (1,2-C_6H_4); 118.4 (1,2-C_6H_4), 117.1 (1,2-C_6H_4).

Synthesis of $HN(1,2\text{-}CH_2CH_2N{=}PR_3)_2$ R = Ph 2, *i*Pr 3

These compounds were prepared in a similar fashion with the variations noted. Thus only one preparation is detailed. Ph_3PBr_2 (10.0 g, 23.7 mmol) in *ca.* 200 mL of CH_2Cl_2 was added at 0 °C to a solution of $HN(CH_2CH_2NH_2)_2$ (1.27 mL, 11.8 mol) in 60 mL of 1 : 1 CH_2Cl_2/NEt_3. The mixture was stirred at room temperature for 1 h and then the solvent was removed in *vacuo*. The residue was suspended in THF (100 mL) and cooled to 0 °C. $K[N(SiMe_3)_2]$ (4.71 g, 23.6 mmol) in THF (50 mL) was added, stirred at room temperature for 30 min and the volatiles removed *in vacuo*. The residue was redissolved in THF and the second deprotonation was repeated in the same way. The solution was filtered through Celite and the solvent was removed. The residue was triturated with ether (*ca.* 100 mL), the resulting solid was collected filtered and dried *in vacuo*. **2**: Yield: 5.20 g (70%).^1H NMR (C_6D_6): 7.78 (m, 12 H, C_6H_5); 7.01 (M, 18 H, C_6H_5); 3.68 (dt, $^3J_{HP}$ = 14.6 Hz, $^3J_{HH}$ = 5.7 Hz, CH_2); 3.28 (t, $^3J_{HH}$ = 5.7 Hz, CH_2). $^{31}P\{^1H\}$ NMR (C_6D_6): 5.9. $^{13}C\{^1H\}$ NMR (C_6D_6): 134.0 (*C*q), 132.6 (d, *C*H, J_{CP} = 12 Hz), 130.6 (d, *C*H, J_{PC} = 4 Hz), 128.8 (d, *C*H, J_{CP} = 15 Hz), 55.4 (d, CH_2, $^2J_{CP}$ = 29 Hz), 45.6 (d, CH_2, $^3J_{CP}$ = 7 Hz). +ESI-MS(*m*/*z*): 624 $[M+H]^+$. Anal. Calcd. for $C_{40}H_{39}N_3P_2$: C, 77.03; H, 6.30; N, 6.74. Found: C, 76.61; H, 6.90; N, 6.72., **3**: Yield: 1.04 g (80%). ^1H NMR (C_6D_6): 3.61 (dt, 4H, $HNCH_2CH_2$, $^3J_{HH}$ = 6 Hz, $^4J_{HP}$ = 12 Hz), 3.08 (t, 4H, $HNCH_2CH_2$, $^3J_{HH}$ = 6 Hz), 2.69 (s broad, 1H, N*H*), 2.14 (dq, 6H, CH^iPr, $^3J_{HH}$ = 7 Hz, $^2J_{HP}$ = Hz), 1.26 (dd, 36H, CH_3 *i*Pr, $^3J_{HH}$ = 7 Hz, $^3J_{HP}$ = 13 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): 27.9. $^{13}C\{^1H\}$ NMR (C_6D_6): 56.6 (d, $NHCH_2CH_2$, J_{CP} = 18 Hz), 46.6 (d, $HNCH_2CH_2$, J_{CP} = 6 Hz), 24.6 (d, CH^iPr, J_{CP} = 57 Hz), 17.4 (d, CH_3 ^iPr, J_{CP} = 3 Hz). +ESI-MS(*m*/*z*): 420 $[M+H]^+$. Anal. Calcd. for $C_{22}H_{51}N_3P_2$: C, 62.97; H, 12.25; N, 10.01. Found: C,62.42; H, 12.06; N, 9.88.

Synthesis of $MeN(1,2\text{-}CH_2CH_2N{=}PPh_3)_2$ 4

A solution of PPh_3Br_2 (2.00 g, 6.25 mmol) in 50 mL CH_2Cl_2 was added dropwise at 0 °C to a solution of $MeN(CH_2CH_2NH_2)_2$ (0.32 g, 3.11 mmol) in 50 mL CH_2Cl_2 and 15 mL Et_3N. The suspension was stirred and allowed to warm to 25 °C and then was left stirring for one hour. The solvent was removed *in vacuo* to afford a white solid. A solution of $K[N(SiMe_3)_2]$ (1.25 g, 6.25 mmol) in 5 mL THF was added dropwise at −35 °C to a suspension of the white solid in 50 mL THF at −35 °C. The suspension was stirred and allowed to warm to 25 °C. The solvent was removed *in vacuo* to afford a white solid. The same step was repeated to afford the product as a white solid. Yield: 1.04 g (80%).^1H NMR (C_6D_6): 7.75 (m, 12 H, C_6H_5); 7.03 (m, 18H, C_6H_5); 3.72 (m, 4H, CH_2); 3.07 (t, 4H, $^3J_{HH}$ = 7 Hz CH_2), 2.41 (s, 3H, N–CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6): 6.0. $^{13}C\{^1H\}$ NMR (C_6D_6): 132.7 (d, *C*H, J_{CP} = 8.8 Hz), 130.6 (d, *C*H, J_{CP} = 2.7 Hz), 128.2 (Cq), 127.7 (d, *C*H, J_{CP} = 24.4 Hz) 64.9 (d, CH_2, $^2J_{CP}$ = 21.1 Hz), 44.6 (d, CH_2, $^3J_{CP}$ = 4.9 Hz), 44.0 (*N*-CH_3). Anal. Calcd. for $C_{41}H_{41}N_3P_2$ (637.73): C, 77.22; H, 6.48; N, 6.59. Found: C, 77.02; H, 6.22; N, 6.34.

Synthesis of $HN(1,2\text{-}C_6H_4N{=}PPh_3)_2$ 5

A solution of Ph_3PBr_2 (2.15 g, 5.10 mmol) in of CH_2Cl_2 (100 mL) was added slowly to a solution of $HN(1,2\text{-}C_6H_4NH_2)_2$ (0.508 g, 2.55 mmol) in CH_2Cl_2 (10 mL) and NEt_3 (7 mL) at 0 °C. The reaction was stirred 15 min at this temperature and allowed to warm up to room temperature for 30 min. Volatiles were evaporated under *vacuum* and the residue extracted with THF (150 mL) and filtered through a pad of Celite. Solvents were evaporated to dryness to afford a green solid. Recrystallisation from CH_2Cl_2–Et_2O. Yield: 1.62 g (88%). ^1H NMR (CD_2Cl_2): 8.63 (s br, 1H, N*H*), 7.83 (m, 12H, Ar*H*), 7.44 (dt, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.4 Hz, 8H, ArH), 7.27 (dt, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 2.9 Hz, 12H, ArH), 6.64 (td, 2H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.5 Hz, C_6H_4), 6.46 (dt, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.3 Hz, 2H, C_6H_4), 6.40 (td, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, 2H, C_6H_4), $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 3.8. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 140.1 (*C*q),138.5 (d, *C*H, J_{CP} = 21 Hz), 133.0 (d, *C*H, J_{CP} = 10 Hz), 131.9 (d, *C*H, J_{CP} = 3 Hz), 131.8 (*C*H), 130.8 (*C*H), 128.4 (d, *C*H, J_{CP} = 12 Hz), 120.2 (d, *C*H, J_{CP} =

10 Hz), 118.6 (*C*H), 117.9 (*C*H), 113.4 (*C*H). +ESI-MS(*m*/*z*): 720 $[M+H]^+$. Anal. Calcd for $C_{48}H_{39}N_3P_2$ (719.79): C, 80.09; H, 5.46; N, 5.84. Found: C, 79.98; H, 5.89; N, 5.80.

Synthesis of O(1,2-C_6H_4N=PPh_3)$_2PdCl_2$ 6

A solution of $Pd(CH_3CN)_2Cl_2$ (0.090 g, 0.347 mmol) in 3 mL CH_2Cl_2 was added dropwise to a solution of **1** (0.250 g, 0.347 mmol) in 5 mL CH_2Cl_2. A color change from light orange to dark orange/red was observed when left stirring for an hour. The solution was concentrated and product recrystallized upon addition of Et_2O yielding an orange powder. Yield: 0.271 g (87%). ^{1}H NMR (CD_2Cl_2): 8.19 (br s, 4H, P*Ph*$_3$); 7.96 (m, 2H, 1,2-C_6H_4); 7.64 (br s, 4H, P*Ph*$_3$); 7.45 (m, 10H, P*Ph*$_3$); 7.19 (m, 6H, P*Ph*$_3$); 6.92 (m, 6H, P*Ph*$_3$); 6.50 (t, 4H, 1,2-C_6H_4), 5.67 (dt, 2H, 1,2-C_6H_4). ^{31}P{^{1}H} NMR (CD_2Cl_2): 37.1. ^{13}C NMR (CD_2Cl_2): 150.1 (d, J_{CP} = 9 Hz); 137.3; 136.4 (d, J_{CP} = 3 Hz); 134.4 (d, J_{CP} = 11 Hz); 132.7; 130.2 (d, J_{CP} = 14 Hz); 128.0; 124.8 (d, J_{CP} = 3 Hz); 123.1 (d, J_{CP} = 3 Hz); 120.6 (d, J_{CP} = 2 Hz). Anal. Calcd. for $C_{48}H_{38}N_2P_2OPdCl_2$: C, 64.19; H, 4.26; N, 3.12. Found: C, 62.19; H, 4.34; N, 3.32.

Synthesis of [RN(1,2-CH_2CH_2N=PPh_3)$_2PdCl$][Cl] (R = H 7, Me 8)

These compounds were prepared in a similar fashion with the variations noted. A solution of $Pd(CH_3CN)_2Cl_2$ (0.042 g, 0.160 mmol) in 5 mL CH_2Cl_2 was added dropwise to a solution of **2** (0.10 g, 0.160 mmol) in 5 mL CH_2Cl_2. A color change from yellow to light orange was observed when left stirring for one hour. The solution was concentrated and the product recrystallized by the addition of Et_2O yielding a yellow powder. **7**: Yield: 0.104 g (81%). ^{1}H NMR (CD_2Cl_2): 8.94 (t, 1H, *NH*, $^3J_{HH}$ = 10 Hz); 7.88–7.83 (m, 12H, C_6H_5); 7.63–7.59 (m, 6H, C_6H_5); 7.54–7.49 (m, 12H, C_6H_5); 3.46 (m, 2H, HNCH$_2$*CH*$_2$); 2.85 (m, 2H, HN*CH*$_2$CH$_2$); 2.70 (m, 2H, HN*CH*$_2$CH$_2$); 2.47 (m, 2H, HNCH$_2$*CH*$_2$). ^{31}P{^{1}H} NMR (CD_2Cl_2): 34.0. ^{13}C NMR (CD_2Cl_2): 133.8 (d, J_{CP} = 10 Hz); 132.2; 128.8 (d, J_{CP} = 10 Hz); 128.2 (d, J_{CP} = 13 Hz); 56.7 (HN*C*H$_2$CH$_2$); 54.7 (HNCH$_2$*C*H$_2$). Repeated attempts to obtain EA were unsuccessful.

8: Yield: 0.200 g (78%). ^{1}H NMR (400 MHz, CD_2Cl_2): 7.66 (m, 12H,C_6H_5); 7.63 (m, 6H, C_6H_5); 7.55 (m, 12H, C_6H_5); 3.64 (dt, 2H, MeNCH$_2$*CH*$_2$, $^3J_{HH}$ = 6 Hz, J_{HP} = 18 Hz); 3.31 (tt, 2H, MeN*CH*$_2$CH$_2$, $^3J_{HH}$ = 3 Hz, J_{HP} = 12 Hz); 3.14 (s, 3H, *Me*NCH$_2$CH$_2$); 2.81 (m, 2H, MeN*CH*$_2$CH$_2$), 2.75 (m, 2H, MeNCH$_2$*CH*$_2$). ^{31}P{^{1}H} NMR (CD_2Cl_2): 35.4. ^{13}C NMR (100 MHz, CD_2Cl_2): 134.3 (d, Ar–C, J_{CP} = 15 Hz); 133.0 (Ar–C); 128.8 (d, Ar–C, J_{CP} = 13 Hz); 127.2 (d, Ar–C, J_{CP} = 102 Hz); 66.7 (d, MeNCH$_2$*C*H$_2$, J_{CP} = 15 Hz); 53.1 (MeN*C*H$_2$CH$_2$); 45.6 (*Me*NCH$_2$CH$_2$). Anal. Calcd. for $C_{41}H_{41}N_3P_2PdCl_2$: C, 60.42; H, 5.07; N, 5.16. Found: C, 56.30; H, 5.32; N, 5.03.

Synthesis of [HN(1,2-CH_2CH_2N=P*i*Pr$_3$)$_2PdCl$][Cl] 9

A suspension of $Pd(CH_3CN)_2Cl_2$ (0.120 g, 0.462 mmol) in 5 mL THF was added to a solution of **3** (0.200 g, 0.476 mmol) in 5 mL THF. The resulting mixture was heated at 60 °C in a sealed Schlenk bomb for two hours. The solvent was removed *in vacuo* and the product was extracted into CH_2Cl_2 and the mixture was then filtered. The filtrate was concentrated and the pale brown product was obtained by the addition of Et_2O. Yield: 0.217 g (76%). ^{1}H NMR (400 MHz, CD_2Cl_2): 8.46 (broad s, 1H, NH); 3.44 (m, 2H, HNCH$_2$*CH*$_2$); 3.07 (m, 2H, HNCH$_2$*CH*$_2$); 2.95 (septet, 6H, C*H*(CH$_3$)$_2$, $^3J_{HH}$ = 7 Hz); 2.63 (m, 4H, HN*CH*$_2$CH$_2$); 1.46 (dd, 18H, CH(*CH*$_3$)$_2$, $^3J_{HH}$ = 7 Hz, J_{HP} = 15 Hz); 1.40 (dd, 18H, CH(*CH*$_3$)$_2$, $^3J_{HH}$ = 7 Hz, J_{HP} = 15 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2): 63.4. ^{13}C NMR (101 MHz, CD_2Cl_2): 56.6 (d, HN*CH*$_2$CH$_2$, J_{CP} = 11 Hz); 53.8 (d, HNCH$_2$*CH*$_2$, J_{CP} = 4 Hz); 25.6 (d, *C*H(CH$_3$)$_2$, J_{CP} = 2 Hz); 17.7 (d, CH(*CH*$_3$)$_2$, J_{CP} = 4 Hz); 16.5 (d, CH(*CH*$_3$)$_2$, J_{CP} = 54 Hz). Anal. Calcd. for $C_{22}H_{51}N_3P_2PdCl_2$: C, 44.27; H, 8.61; N, 7.04. Found: C, 44.04; H, 8.58; N, 7.46.

Synthesis of [MeN(1,2-CH_2CH_2N=PPh_3)$_2PdCl$][PF_6] 10

$NaPF_6$ (0.025 g, 0.015 mmol) was added to a stirring solution of **8** (0.100 g, 0.012 mmol) in 10 ml CH_2Cl_2. The solution was left stirring for one hour and was then filtered over Celite. The filtrate was concentrated and the product isolated as a yellow powder by adding Et_2O. Yield: 0.101 g (89%). ^{1}H NMR (400 MHz, CD_2Cl_2): 7.76 (m, 12H,C_6H_5); 7.66 (m, 6H, C_6H_5); 7.56 (m, 12H, C_6H_5); 3.61 (ddd, 2H, MeNCH$_2$*CH*$_2$, $^3J_{HH}$ = 6 Hz, J_{HP} = 18 Hz); 3.29 (dt, 2H, MeN*CH*$_2$CH$_2$, $^3J_{HH}$ = 3 Hz, J_{HP} = 12 Hz); 3.04 (s, 3H, *Me*NCH$_2$CH$_2$); 2.81 (m, 2H, MeN*CH*$_2$CH$_2$); 2.56 (m, 2H, MeNCH$_2$*CH*$_2$). ^{31}P{^{1}H} NMR (CD_2Cl_2): 35.6; –143.4. ^{19}F{^{1}H} NMR (377 MHz, CD_2Cl_2): –73.2. ^{13}C NMR (100 MHz, CD_2Cl_2): 134.3 (d, Ar–C, J_{CP} = 10 Hz); 133.4 (Ar–C); 129.2 (d, Ar–C, J_{CP} = 13 Hz); 127.4 (d, Ar–C_q, J_{CP} = 102 Hz); 66.9 (d, MeNCH$_2$*C*H$_2$, J_{CP} = 15 Hz); 53.3 (MeN*C*H$_2$CH$_2$); 45.8 (*Me*NCH$_2$CH$_2$). Anal. Calcd. for $C_{41}H_{41}N_3P_2PdClPF_6$: C, 53.26; H, 4.47; N, 4.54. Found: C, 53.05; H, 5.06; N, 4.38.

Synthesis of [HN(1,2-CH_2CH_2N=PPh_3)$_2NiCl_2$] 11, [HN(1,2-CH_2CH_2N=P*i*Pr$_3$)$_2$NiCl][Cl] 12

These compounds were prepared in a similar fashion, thus only one preparation is detailed. $NiCl_2$(DME) (0.350 g, 1.592 mmol) was added to **2** (1.0 g, 1.603 mmol) in THF (5 mL) and the mixture was stirred overnight. After cooling to –35 °C, the yellow solid was collected by vacuum filtration on a plug of Celite and was washed with cold THF (2 mL) and then dried *in vacuo*. The yellow solid dissolved in CH_2Cl_2 (*ca.* 10 mL) and then the purple solution was filtered through Celite. Ether (*ca.* 20 mL) was added dropwise resulting in the precipitation of a lemon yellow solid. The suspension was cooled to –35 °C, and the solid was collected by vacuum filtration and dried *in vacuo*. Yield: 0.980 g (82%). **11**: μ_{eff} = 3.13 BM. Anal. Calcd. for $C_{40}H_{39}Cl_2N_3NiP_2$: C, 63.78; H, 5.22; N, 5.58. Found: C, 63.98; H, 5.50; N, 6.01. **12**: pink solid. Yield: 85%. μ_{eff} = 3.08 BM. Anal. Calcd. for $C_{22}H_{51}Cl_2N_3NiP_2$: C, 48.11; H, 9.36; N, 7.65. Found: C,45.37; H,8.86; N,7.92. IR (CH_2Cl_2) ν: 3442 (NH).

Synthesis of [HN(1,2-CH_2CH_2N=PR_3)$_2$NiCl][PF_6] R = Ph 13, *i*Pr 14

These compounds were prepared in a similar fashion, thus only one preparation is detailed. (0.147 g, 0.875 mmol) of $NaPF_6$ was added to **11** (0.100 g, 0.133 mmol) of in *ca.* 2 mL of CH_2Cl_2. The mixture was stirred overnight and was then filtered through Celite. 10 mL of ether was added dropwise to precipitate a purple solid that was triturated for one hour. The solvent was decanted and the solid was washed with 2 × 5 mL of ether and dried *in vacuo*. **13**:

Yield: 0.077 g (67%). Recrystallization of **13** from CH_2Cl_2 afforded purple crystals of **13a**; recrystallization of **13** from BrC_6H_5 afforded **13b**. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 40.1, –141.3. μ_{eff} = 3.23 BM. Anal. Calcd. for $C_{40}H_{39}ClF_6N_3NiP_3$: C, 55.68; H, 4.56; N, 4.87. Found: C, 53.77; H, 4.66; N, 4.90. **14**: Yield: 0.054 g (91%). μ_{eff} = 3.08 BM, Anal. Calcd. for $C_{22}H_{51}ClF_6N_3NiP_3$: C, 40.11; H, 7.80; N, 6.38. Found: C, 41.09; H, 7.57; N, 6.81.

Synthesis of [HN(1,2-$C_6H_4N{=}PPh_3)_2Ni(MeCN)_2$][$BF_4$]Cl 15

A solution of **5** (0.153 g, 0.21 mmol) in THF (4 mL) was added to [Ni(MeCN)$_6$][BF_4)$_2$] (0.102 g, 0.21 mmol) in THF (2 mL). The resulting suspension was stirred at room temperature overnight. Volatiles were evaporated *in vacuo* and the solid was crystallized from CH_2Cl_2–Et_2O. Yield: 0.210 g (96%), $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 37.1. μ_{eff} = 3.17 BM. Anal. Calcd (%) for $C_{52}H_{44}BF_4Cl\,N_5NiP_2$: C, 63.55; H, 4.61; N, 7.13. Found: C, 61.43; H, 4.88; N, 7.27.

Synthesis of N(1,2-$CH_2CH_2N{=}PR_3)_2Ni_2Cl_3$ R = Ph 16, *i*Pr 17 and HN(1,2-$C_6H_4N{=}PPh_3)_2Ni_2Cl_3$ 18

These compounds were prepared in a similar fashion, thus only one preparation is detailed. A solution of K[N($SiMe_3$)$_2$] (0.066 g, 0.33 mmol) in THF (2 mL) was added dropwise to a solution of **2** (0.205 g, 0.33 mmol) in THF (3 mL) at –35 °C and was left stirring for 30 min. The mixture was left stirring at room temperature for 30 min. A suspension of $NiCl_2$(DME) (0.145 g, 0.66 mmol) in THF (3 mL) was added to the ligand mixture and was stirred overnight and a color change from yellow to dark purple/blue was oberved. The solvent was removed *in vacuo* and solid extracted into CH_2Cl_2 and filtered. The solvent was then removed *in vacuo* yielding a blue solid. Yield: 0.230 g (83%). **16**: $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 51.0. μ_{eff} = 4.97 BM, Anal. Calcd. for $C_{40}H_{38}Cl_3N_3Ni_2P_2$: C, 56.76; H, 4.53; N, 4.96. Found: C, 54.89; H, 4.90; N, 4.99 **17**: Yield: 0.073 g (55%).$^{31}P\{^1H\}$ NMR (CD_2Cl_2): 79.3. μ_{eff} = 4.63 BM. Anal. Calcd for $C_{22}H_{50}Cl_3N_3Ni_2P_2$: C, 41.14; H, 7.85; N, 6.54. Found: C, 40.92; H, 7.42; N, 6.06. **18**: Yield: 0.274 g (75%). μ_{eff} = 5.02 BM. +ESI-MS (*m*/*z*): 881 [M-$NiCl_2$]$^+$. Anal. Calcd. for $C_{48}H_{38}Cl_3N_3Ni_2P_2$: C, 61.17; H, 4.06; N, 4.46. Found: C, 59.49; H, 4.74; N, 4.70.

X-ray Data Collection, Reduction, Solution and Refinement

Single crystals were coated in Paratone-N oil in the glove-box, mounted on a MiTegen Micromount and placed under an N_2 stream. The data were collected on a Bruker Apex II diffractometer. The data were collected at 150(±2) K for all crystals. Data reduction was performed using the SAINT software package and an absorption correction applied using SADABS. The structures were solved by direct methods using XS and refined by full-matrix least-squares on F^2 using XL as implemented in the SHELXTL suite of programs.[19] All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were placed in calculated positions using an appropriate riding model and coupled isotropic temperature factors (see Table 1 and supplementary data†). In the case of compounds **7** and **11**, disorder of the halides were modeled by initial refinement of the site occupancy factors.

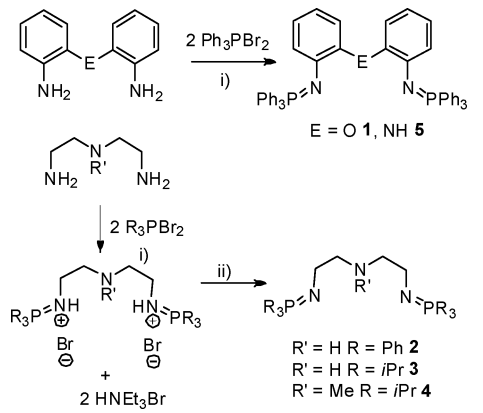
Results and Discussion

Ligand Synthesis

The ligand O(1,2-$C_6H_4N{=}PPh_3)_2$ **1** was synthesized in 95% yield using a modified literature procedure *via* condensation of prepared Ph_3PBr_2 and 2,2′-oxydianiline in the presence of NEt_3.[20] Related amino-*bis*-phosphinimine ligands are also readily synthesized by the reaction of the corresponding triamine with two equivalents of either Ph_3PBr_2 or iPr_3PBr_2 in the presence of NEt_3 (Scheme 2). In this fashion the ligands HN(1,2-$C_2H_4N{=}PR_3)_2$ (R = Ph **2**, *i*Pr **3**), MeN(1,2-$C_2H_4N{=}PR_3)_2$ **4** and HN(1,2-$C_6H_4N{=}PPh_3)_2$ **5** were prepared. While the synthesis of **2**, **3** and **4** requires deprotonation with a comparatively strong base such as *t*BuOK or K[N($SiMe_3$)$_2$], the latter procedure is preferred as deprotonation with *t*BuOK yields small amounts of phosphine oxide contamination. In the

Table 1 Crystallographic data

	6	**7**·2CH_2Cl_2	**9**	**11**	**12**	**13a**	**13b**	**18**·C_6H_6
Formula	$C_{50}H_{41}Cl_2N_3OP_2Pd$	$C_{42}H_{43}Cl_6N_3P_2Pd$	$C_{22}H_{51}Cl_2N_3P_2Pd$	$C_{40}H_{39}\,Br_{0.5}Cl_{1.5}N_3NiP_2$	$C_{22}H_{51}Cl_2N_3NiP_2$	$C_{40}H_{39}ClF_6N_3NiP_3$	$C_{40}H_{40}ClF_6N_3NiP_3$	$C_{59}H_{50}Cl_3N_3Ni_2P_2$
wt	939.10	970.83	596.90	775.52	549.21	862.81	863.82	1086.73
Cryst. syst.	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Triclinic	Monoclinic
Space grp	$P2_1/c$	*Ibca*	$P2_1/n$	$P2_1/n$	$P2_1/n$	$Pmn2_1$	$P\bar{1}$	$C2/c$
a/Å	20.2104(7)	12.260(4)	8.6503(2)	12.0407(13)	8.6286(6)	21.7288(9)	10.0118(7)	33.823(3)
b/Å	24.1180(10)	20.121(6)	26.8756(5)	22.977(3)	32.013(2)	7.6413(3)	13.1874(10)	8.9261(9)
c/Å	20.0246(8)	35.895(11)	12.0880(3)	13.4590(14)	10.8902(8)	11.6265(5)	16.4704(12)	23.968(2)
α (°)	90.00	90.00	90.00	90.00	90.00	90.00	67.100(4)	90.00
β (°)	118.446(2)	90.00	93.1560(10)	97.437(5)	99.150(2)	90.00	89.195(4)	133.969(4)
γ (°)	90.00	90.00	90.00	90.00	90.00	90.00	77.437(4)	90.00
V/Å^3	8582.2(6)	8855(5)	2805.98(11)	3692.3(7)	2969.9(4)	1930.42(14)	1949.2(2)	5207.9(9)
Z	8	8	4	4	4	2	2	4
d(calc) g cm^{-1}	1.454	1.456	1.413	1.395	1.228	1.484	1.472	1.386
R(int)	0.0783	0.0646	0.0381	0.0759	0.0322	0.0391	0.0993	0.0901
μ/cm^{-1}	0.674	0.887	0.981	1.295	0.955	0.759	0.752	0.980
Total data	139535	67942	21416	74014	22133	54670	27269	21713
$>2\sigma(F_o^2)$	15098	5096	4934	8424	5222	7697	10660	5929
Variables	1063	262	271	441	271	247	491	317
R ($>2\sigma$)	0.0353	0.0647	0.0368	0.0436	0.0408	0.0420	0.0732	0.0670
R_w	0.0816	0.1644	0.0862	0.1016	0.0922	0.1217	0.1994	0.2239
GOF	1.011	1.177	1.032	1.008	1.133	1.043	0.971	0.892

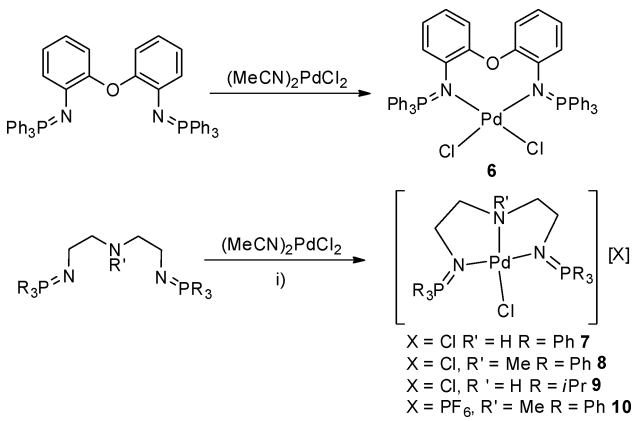


Scheme 2 Synthesis of *bis*-phosphinimine ligands. i) CH_2Cl_2, NEt_3. ii) 2×2 K[N(SiMe$_3$)$_2$], THF.

case of **1** and **5**, NEt_3 is sufficiently basic to effect deprotonation of the phosphiniminium salt. These new ligands **2–5** give rise to ^{31}P resonances at 5.9, 27.9, 6.0 and 3.8 ppm respectively.[16]

Pd-Complexes

Addition of $(MeCN)_2PdCl_2$ to a solution of **1** in CH_2Cl_2 proceeds cleanly with the formation of a single product **6** which was isolated in 87% yield (Scheme 3). This species exhibited a $^{31}P\{^1H\}$ NMR signal at 37.1 ppm inferring a symmetric disposition of the phosphinimine fragments. X-ray crystallography revealed the formulation of **6** as O(1,2-$C_6H_4N{=}PPh_3)_2PdCl_2$ (Fig. 1) in which the Pd occupies a square planar coordination sphere with the phosphinimine nitrogens bound in a *cis* orientation. The ligand was bound to the metal centre in a bidentate mode. The non-bonded Pd–O distance is 4.110(2) Å. The bite angle for the bidentate *bis*-phosphinimine fragment, that is the N(1)–Pd–N(2) is 85.8°.



Scheme 3 Synthesis of Pd-complexes of *bis*-phosphinimine ligands, (i) anion exchange required for **10**.

In contrast, reaction of ligands **2–4** with $(MeCN)_2PdCl_2$ in CH_2Cl_2 led to the formation of the complexes formulated as [HN($CH_2CH_2N{=}PR_3)_2$PdCl][Cl] (R = Ph **7**, R = *i*Pr **9**) and [MeN($CH_2CH_2N{=}PPh_3)_2$PdCl][Cl] **8**. These species were spectroscopically similar. In the case of **7**, the $^{31}P\{^1H\}$ NMR spectrum showed a resonance at 34.0 ppm and the ^{1}H NMR spectrum showed the expected resonances for the ethylene backbone at

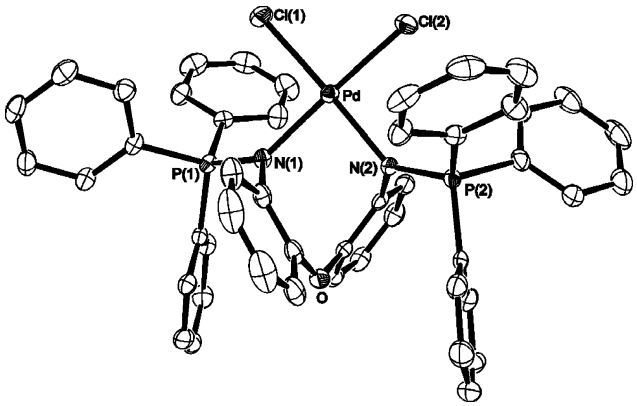


Fig. 1 ORTEP drawing of **6**, hydrogen atoms are omitted for clarity.

3.46, 2.85, 2.70, and 2.47 ppm. A single crystal of compound **7** was obtained and the X-ray structure (Fig. 2) shows a distorted square planar geometry around the palladium centre with the amine proton at an angle about 94° to the plane formed by the N_3-ligand and the metal centre. The bond length Pd–N(2) in **7** is 2.008(9) Å which is slightly shorter than the phosphinimine nitrogen-Pd bonds of 2.043(1) and 2.046(1) Å for Pd–N(1) and Pd–N(3), respectively. The source of the bromide counter-ion is likely residual $HNEt_3Br$ as purification of the ligand **2** proved challenging. This was not the case for ligand **3**.

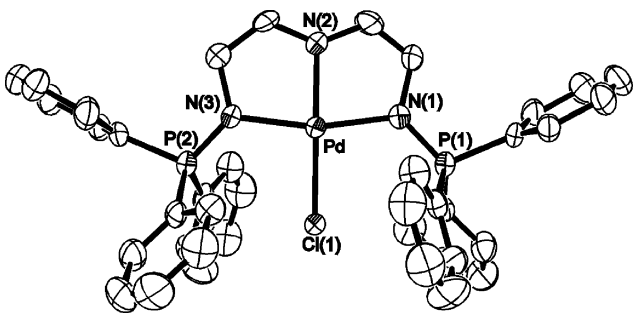


Fig. 2 ORTEP drawing of the cation of **7**, hydrogen atoms and bromide anion are omitted for clarity.

X-ray crystallographic characterization of compound **9** was also performed. The geometry about Pd is similar to that seen in **7**. The Pd–N bond distances for the phosphinimine groups are slightly shorter at 2.054(3) Å and 2.066(3) Å for Pd–(N1) and Pd–(N3) respectively, while the central Pd–N distance in **9** was found to be 2.019(3) Å (Fig. 3). An interesting feature of these molecules is the generation of the protective pocket about the Cl-site on Pd generated by the phosphine-substituent of the phosphinimine fragments.

Subsequent reaction of **8** with $NaPF_6$ resulted in anion exchange and isolation of [MeN($CH_2CH_2N{=}PPh_3)_2$PdCl][PF_6] **10**. The product was isolated in 89% yield and showed two resonances in the $^{31}P\{^1H\}$ NMR spectrum at 35.6 and −143.4 ppm attributable to the cation and anion respectively. In addition the $^{19}F\{^1H\}$ NMR spectrum showed the typical resonance for the PF_6 anion at −73.2 ppm.

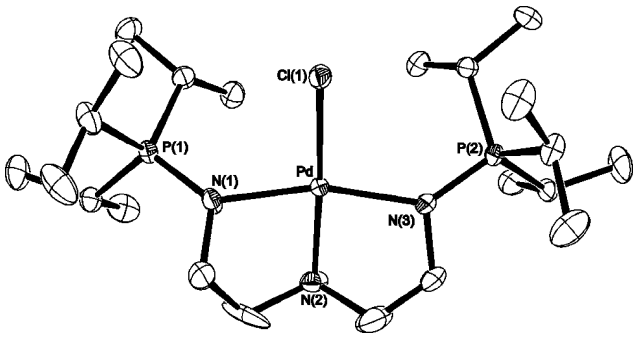


Fig. 3 ORTEP drawing of the cation of **9**, hydrogen atoms are omitted for clarity.

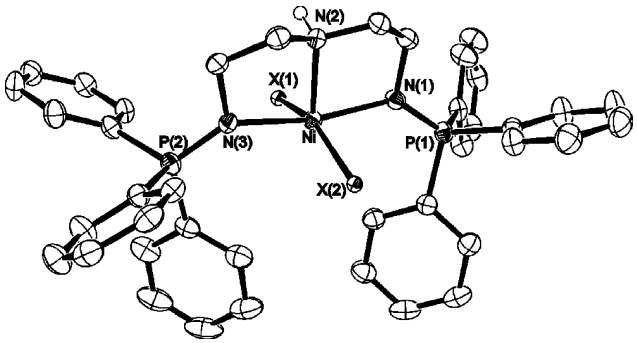
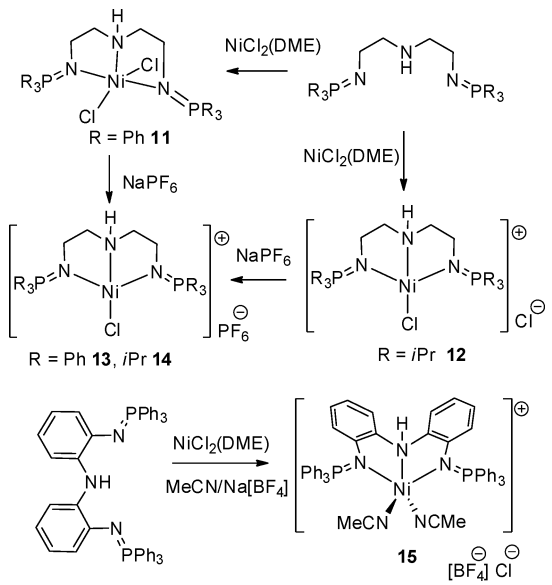


Fig. 4 ORTEP drawing of **11**, all hydrogen atoms except the NH are omitted for clarity, X = disordered Br/Cl.

Ni-Complexes

The formation of **6–10** suggests that the diaryl-ether fragment of ligand **1** is insufficiently basic to afford chelation in the tridentate fashion seen with the amine linked analogs. It is for this reason that the exploration of Ni chemistry focused on these latter ligands. The reactions of **2** and **3** with $NiCl_2$(DME) in THF afford the corresponding mononuclear complexes **11** and **12** in good yields (Scheme 4). Complexes are paramagnetic with magnetic moments of 3.13 and 3.08 BM for **11** and **12**, respectively. The values are in agreement with the spin only value of 2.82 BM expected for two unpaired electrons. Single crystals of **11** and **12** were grown from C_6H_5Br. X-Ray analysis of yellow crystals of **11** revealed a five coordinate Ni centre with the ligand adopting a meridional coordination mode (Fig. 4). The halide ions were shown to be a disordered mixture of Br and Cl with an approximate X(1)–Ni–X(2) angle of 155.6°. As with the Pd complex, **7**, the Br is derived from the difficulties of complete separation of the ligand from Et_3NHBr. The distorted trigonal bypyramid geometry (τ = 0.18),[21] at Ni results in N(1)–Ni–N(3) angle of 166.4(2)°. The Ni–N(2) bond length is of 2.013(5) Å which is significantly shorter than the nickel-phosphinimine bonds Ni–N(1) and Ni–N(3) of 2.127(5) Å and 2.113(5) Å, respectively, presumably the impact of both steric and electronic effects.



Scheme 4 Synthesis of Ni-complexes of *bis*-phosphinimine ligands.

In contrast, the Ni cation in **12** has a distorted pseudo-tetrahedral geometry at Ni with N(3)–Ni–N(1) and N(2)–Ni–Cl(1) angles of 125.45(10)° and 142.85(8)° (Fig. 5). The phosphinimine-nickel bond lengths, Ni–N(1) and Ni–N(3) are 1.993(2) Å and 1.989(2) Å, respectively while the Ni–Cl(1) bond length of 2.2547(8) Å is about 0.2 Å shorter than the Ni–Cl distances in **11**. These shorter distances in **12** are consistent with the four coordinate cationic character of **12**. However, it is noteworthy that the Ni–N(2) bond of 2.069(2) Å is lengthened by about 0.06 Å compared to that in **11**, most likely a result of the presence of stronger electron donor NP*i*Pr$_3$ groups in **12**.

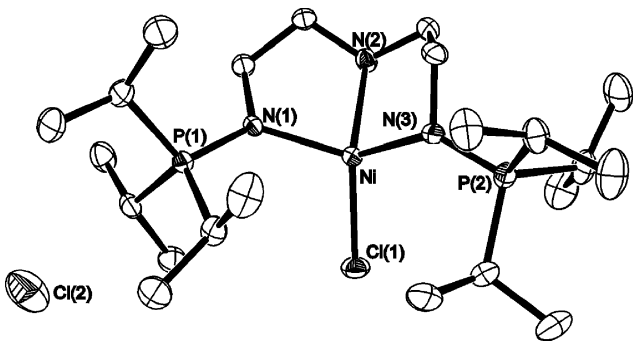


Fig. 5 ORTEP drawing of **12**, hydrogen atoms are omitted for clarity.

The corresponding PF_6 salts of complexes **13** and **14**, were synthesised by salt metathesis using $NaPF_6$ in CH_2Cl_2 (Scheme 3) and isolated as purple solids. These products **13** and **14** were paramagnetic with μ_{eff} of 3.23 and 3.28 BM, respectively. In the case of **13**, two crystal forms were obtained. Purple crystals of **13a** were obtained by recrystallization from CH_2Cl_2. Single crystals analysis of **13a** reveals a distorted two fold symmetric square planar geometry at the Ni center (Fig. 6(a)) with the N(2)–Ni–N(2)′ and N(1)–Ni–Cl(1) angles of 166.2(1)° and 165.5(2)°, respectively. The Ni–N(1) is 1.922(2) Å, while the Ni–N(2) bond distance is found to be 1.926(1) Å. The latter as well as the Ni–Cl(1) bond distance of 2.1657(6) Å, are slightly shorter than those in **12**. In contrast, recrystallization of the purple solution of **13** in bromobenzene, afforded yellow crystals of **13b** (Fig. 6(b)). In this case, the Ni cation adopts a pseudo-tetrahedral geometry with Ni–N(1), Ni–N(2), Ni–N(3) and Ni–Cl(1) distances of 1.942(4) Å, 2.026(4) Å, 1.980(4) Å and 2.2781(12) Å, respectively. The observation of these two forms of **13** is consistent with subtle solvation effects that result in an equilibrium mixture of

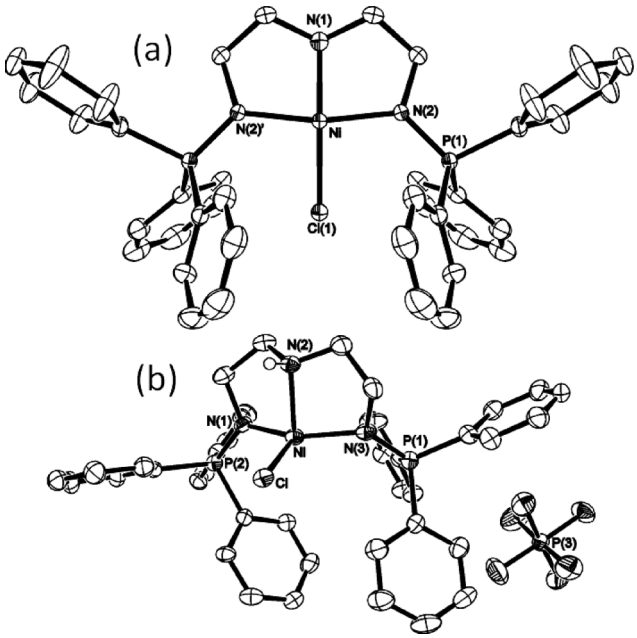


Fig. 6 ORTEP drawings of (a) the cation of **13a**, (b) **13b**; hydrogen atoms except the NH are omitted for clarity.

presumably diamagnetic and paramagnetic geometries, **13a** and **13b** as dissolution of either crystalline product results in the generation of the mixture.

A mononuclear complex **15** bearing ligand **5** was synthesized from the reaction of **5** with $[Ni(MeCN)_6][(BF_4)_2]$ generated from $NiCl_2$ (Scheme 3). This species was isolated in 96% yield and observed to have a magnetic moment of 3.17 BM, consistent with a mononuclear Ni complex of formula $[HN(1,2\text{-}C_6H_4N{=}PPh_3)_2Ni(MeCN)_2][BF_4]Cl$ **15**. Attempts to characterize **15** by X-Ray analysis afforded only preliminary data. While the geometry about the Ni of **15** was confirmed to be five coordinate trigonal bipyramidal Ni(II) centre, disorder of the anions and included solvent, preclude a publishable solution. Nonetheless, the two phosphinimine-fragments of the N_3-ligand are bound in the equatorial plane while the central amine donor of the N_3-ligand is bound in one of the axial positions with two acetonitrile molecules completing the coordination sphere (Fig. 7). The poor crystal quality precludes discussion of the metric parameters.

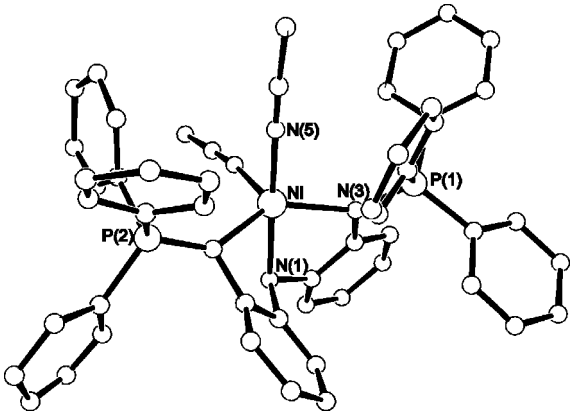
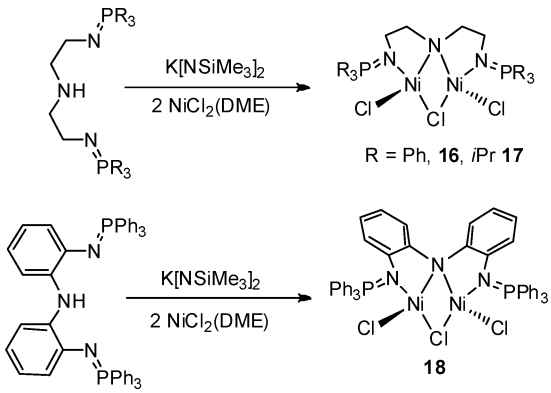


Fig. 7 PLUTO drawing of the cation of **15**.

Interestingly, treatment of ligands **2**, **3** and **5** with $K[N(SiMe_3)_2]$ prior to the reaction $NiCl_2(DME)$ did not lead to the expected mononuclear nickel amide complexes. Rather, unusual dinuclear complexes formulated as $N(1,2\text{-}CH_2CH_2N{=}PR_3)_2Ni_2Cl_3$ R = Ph **16**, *i*Pr **17** and $N(1,2\text{-}C_6H_4N{=}PPh_3)_2Ni_2Cl_3$ **18** were formed (Scheme 5). Even if the ligand to metal ratio was equimolar, the dinuclear species were obtained in 50% yield as determined by ^1H NMR spectroscopy. An additional equivalent of unreacted protonated ligand (**3**.HCl) was detected. Subsequent treatment of this mixture with one equivalent of base and $NiCl_2(DME)$ led to the full conversion to the dinuclear complex. These complexes **16**–**18** are paramagnetic, a feature attributable to pseudo-tetrahedral environments at the Ni centers. Magnetic moments are in the range 4.63–5.02 BM representing a total of four unpaired electrons, consistent with two unpaired electrons per d^8 Ni centre.



Scheme 5 Syntheses of dinuclear Ni(II) complexes.

The precise nature of the geometries of these dinuclear species were probed by X-ray analysis. In the case of **18**, the data confirmed the dinuclear formulation with two pseudo-tetrahedral Ni centres bridged by the ligand and a chlorine atom (Fig. 8). The bridging nature of the ligand is unusual and unexpected and suggests that the phosphinimine moiety is labile. To our knowledge only a few examples of Ni complexes with bridging amides are reported in the literature.[22–26] The nickel-amide bond Ni–N(2) (2.014(2) Å) is slightly longer than nickel-phosphinimine bonds Ni–N(1) of 1.981(5) Å. The angle Ni(1)–N(2)–Ni(2) is of 88.21(27)° and the two Ni centers are separated by 2.803 Å. The terminal Ni–Cl bond distance of 2.2029(17) Å was found to be significantly shorter than the bridging Ni–Cl distances of 2.2964(18) Å.

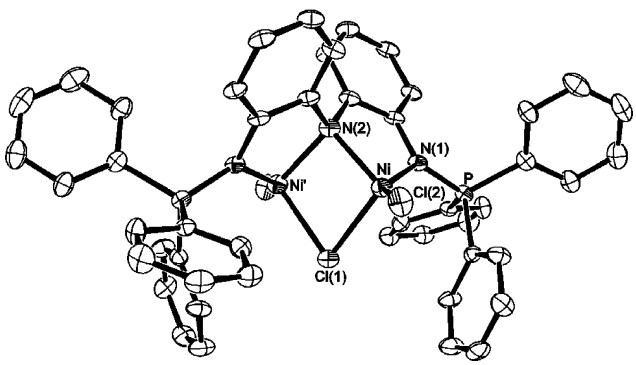


Fig. 8 ORTEP drawing of **18**.

The contrasting nature of the monometallic and bimetallic chemistry derived from the tridentate *bis*-phosphinimine ligands resulting from treatment with base is an interesting aspect and presumably results from the propensity of Ni amides to bridge two metal centers. This provides a facile control over the formation of mono *versus* bimetallic complexes.

Conclusions

In summary, new types of pincer ligands containing phosphinimine fragments have been synthesized and used to complex Pd and Ni. The Pd chemistry supports the view that amino-*bis*-phosphinimines provides convenient access to cationic square planar complexes, where the phosphinimine-substituents sterically shelter the metal-bound halide site. In the case of Ni, both mononuclear and dinuclear complexes are derived from variation in the ligand precursor. This synthetic chemistry sets the stage for an investigation of these and related systems in various applications. The reactivity of the sterically protected pocket of the mono-metallic systems as well as the cooperative reactivity of amide bridged bimetallic systems are now the subject of exploration. These results will be reported in due course.

Acknowledgements

The financial support of NSERC of Canada and LANXESS Corp is gratefully acknowledged. DWS is also grateful for the award of a Killam Research Fellowship.

Notes and references

1 M. Albrecht and G. v. Koten, *Angew. Chem., Int. Ed.*, 2001, **40**, 3750–3781.
2 M. E. van der Boom and D. Milstein, *Chem. Rev.*, 2003, **103**, 1759–1792.
3 B. C. Bailey, J. C. Huffman, D. J. Mindiola, W. Weng and O. V. Ozerov, *Organometallics*, 2005, **24**, 1390–1393.
4 O. V. Ozerov, C. Guo, L. Fan and B. M. Foxman, *Organometallics*, 2004, **23**, 5573–5580.
5 L.-C. Liang, P.-S. Chien and Y.-L. Huang, *J. Am. Chem. Soc.*, 2006, **128**, 15562–15563.
6 H. Fan, B. Fullmer, C. M. Pink and K. Caulton, *Angew. Chem., Int. Ed.*, 2008, **47**, 9112–9114.
7 M. Ingleson, H. Fan, M. Pink, J. Tomaszewski and K. G. Caulton, *J. Am. Chem. Soc.*, 2006, **128**, 1804–1805.
8 L. Fan, S. Parkin and O. V. Ozerov, *J. Am. Chem. Soc.*, 2005, **127**, 16772–16773.
9 S. Gatard, R. Çelenligil-Çetin, C. Guo, B. M. Foxman and O. V. Ozerov, *J. Am. Chem. Soc.*, 2006, **128**, 2808–2809.
10 K. Dehnicke, M. Krieger and W. Massa, *Coord. Chem. Rev.*, 1999, **182**, 19–65.
11 K. Dehnicke and F. Weller, *Coord. Chem. Rev.*, 1997, **158**, 103–169.
12 D. W. Stephan, *Organometallics*, 2005, **24**, 2548.
13 E. W. Abel and S. A. Mucklejohn, *Phosphorus Sulfur Relat. Elem.*, 1981, **9**, 235–266.
14 M. T. Reetz, E. Bohres and R. Goddard, *Chem. Commun.*, 1998, 935.
15 M. Sauthier, F. Leca, R. F. d. Souza, K. Bernardo-Gusmao, L. F. T. Queiroz, L. Toupet and R. Reau, *New J. Chem.*, 2002, **26**, 630–635.
16 R. Bielsa, R. Navarro, T. Soler and E. P. Urriolabeitia, *Dalton Trans.*, 2008, 1787–1794.
17 M. J. Sgro and D. W. Stephan, *Dalton Trans.*, 2011, DOI: 10.1039/C0DT01623C.
18 J. H. Gorvin, *J. Chem. Soc., Perkin Trans. 1*, 1988, 1331.
19 G. M. Sheldrick, Bruker AXS Inc., Madison, WI, 2000.
20 P. Molina, M. Alajarin, P. Sanchez-Andrada, J. Elguero and M. L. Jimeno, *J. Org. Chem.*, 1994, **59**, 7306–7315.
21 A. W. Addison, T. Nageswara Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349.
22 A. R. Fout, F. Basuli, H. Fan, J. Tomaszewski, J. C. Huffman, M.-H. Baik and D. J. Mindiola, *Angew. Chem., Int. Ed.*, 2006, **45**, 3291–3295.
23 D. Adhikari, S. Mossin, F. Basuli, B. R. Dible, M. Chipara, H. Fan, J. C. Huffman, K. Meyer and D. J. Mindiola, *Inorg. Chem.*, 2008, **47**, 10479–10490.
24 K. K. Kamar, S. Das, C. Hung, A. Castiñeiras, M. D. Kuz,′min, C. Rillo, J. Bartolomé and S. Goswami, *Inorg. Chem.*, 2003, **42**, 5367–5375.
25 S. B. Harkins and J. C. Peters, *J. Am. Chem. Soc.*, 2005, **127**, 2030–2031.
26 H. Hope, M. M. Olmstead, B. D. Murray and P. P. Power, *J. Am. Chem. Soc.*, 1985, **107**, 712–713.