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PAPER

# Ni(II), Pd(II) and Pt(II) complexes of PNP and PSP tridentate amino–phosphine ligands†

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The ligands D($(CH_2)_2NHPiPr_2)_2$ (D = NH **1**, S **2**) react with (dme)$NiCl_2$ or $(PhCN)_2MCl_2$ (M = Pd, Pt) to give complexes of the form [D($(CH_2)_2NHPiPr_2)_2$MX]X (X = Cl, I; M = Ni, Pd, Pt) which were converted to corresponding iodide derivatives by reaction with $Me_3SiI$. Reaction of **1** or **2** with (COD)PdMeCl affords facile routes to [$\kappa^3$*P,N,P*-NH($(CH_2)_2NHPiPr_2)_2$PdMe]Cl (**8a**) and [$\kappa^3$*P,S,P*-S-($(CH_2)_2NHPiPr_2)_2$PdMe]Cl (**9a**) in high yields. An alternative synthetic approach involves oxidative addition of MeI to a M(0) precursor yielding [$\kappa^3$*P,N,P*-HN($CH_2CH_2NHPiPr_2)_2$NiMe]I (**10**), [$\kappa^3$*P,N,P*-HN-($CH_2CH_2NHPiPr_2)_2$MMe]I (M = Pd **8b** Pt **11**) and [$\kappa^3$*P,S,P*-S($CH_2CH_2NHPiPr_2)_2$MMe]I (M = Pd **9b**, Pt **12**). Alternatively, use of $NEt_3HCl$ in place of MeI produces the species [$\kappa^3$*P,N,P*-HN-($CH_2CH_2NHPiPr_2)_2$MH]X (X = Cl, M = Ni **13a**, Pd **14a**, Pt **16a**). The analogs containing **2**; [$\kappa^3$*P,S,P*-S($(CH_2)_2NHPiPr_2)_2$MH]X (M = Pd, X = $PF_6$ **15**: M = Pt, X = Br, **17a**, $PF_6$ **17b**) were also prepared in yields ranging from 74–93%. In addition, aryl halide oxidative addition was also employed to prepare [$\kappa^3$*P,N,P*-HN($CH_2CH_2NHPiPr_2)_2$M$C_6H_4$F]Cl (M = Ni **18**, Pd **19**) and [$\kappa^3$*P,S,P*-S($(CH_2)_2NHPiPr_2)_2$-Pd($C_6H_4$F)]Cl (**20**). Crystal structures of **3a**, **4a**, **5a**, **6a**, **8a**, **9a**, **14b** and **16b** are reported.

## Introduction

Tridentate ligand complexes have received considerable interest over the past decade as the number of possible variations afford applications in catalyst, sensor and switch technologies.[1] Phosphine-based PCP[2] and PNP[3] type ligands have garnered the most attention demonstrating electronic and steric tunability, thus rendering highly reactive species stable.[4–8] In addition, such complexes have displayed interesting reactivity including oxidative addition of C–halogen bonds,[7,9] C–H bond activation,[6] $N_2$ activation and homolytic cleavage of $H_2$.[8,10] Recent work has demonstrated that Group 10 complexes containing tridentate ligands, specifically those species containing M–X bonds (M = Ni, Pd; X = H, alkyl, aryl), are of particular importance as they are often implicated as intermediates in catalytic transformations and have interesting reactivity. The nucleophilic M–X bonds of these complexes have been shown to insert $CO_2$, and in some cases allow for its reduction into value-added products.[11–16] In addition, the insertion of olefins into the M–X bonds serves as the (re)initiation step in olefin polymerization, making the isolation of these species desirable as they may serve as active catalysts.[17–20] More recently, Milstein *et al.* have focused attention on dissymmetric pincer ligands as such systems appear to employ the non-innocence of the ligand to generate unique reactivity.[21–23]

In our own efforts to develop new pincer ligand chemistry, we have developed the chemistry of tridentate bis-phosphinimine ligands demonstrating that such ligands provide access to both mono- and bimetallic systems.[24–27] In exploring related ligand systems, we have recently focused on amino-phosphine ligands. While such ligands are easy to prepare, studies of the chemistry of metal complexes with bidentate ligands containing these donors has garnered limited attention.[28–33] We have very recently explored the complexation chemistry of related bidentate amino-phosphines demonstrating that this functionality can in some instances provide three-membered NPM rings.[34,35] Related studies of tridentate ligands incorporating aminophosphine donors have received very limited attention[36–38] prompting us to explore synthetic routes to complexes of tridentate bis-amino-phosphine ligands with central NH or S donors. In exploring the chemistry of these ligands we have previously communicated that while the ligand $HN(CH_2CH_2NHPiPr_2)_2$ (**1**) provides access to Ni(II) products *via* subsequent reaction with acid, alkyl or aryl halides the ligand $S(CH_2CH_2NHPiPr_2)_2$ (**2**) undergoes oxidative addition to Ni(0) to effect ligand cleavage[39] (Scheme 1). In this full report, we describe the direct synthetic routes to ligand–metal halide cations, as well as oxidative addition routes to alkyl, aryl and hydride complexes of Ni(II), Pd(II) and Pt(II) incorporating these tridentate aminophosphine ligands.

## Experimental section

All preparations were performed under an atmosphere of dry, $O_2$-free $N_2$ employing both Schlenk line techniques and inert atmosphere glove boxes. Solvents (THF, $CH_2Cl_2$, $Et_2O$ hexane

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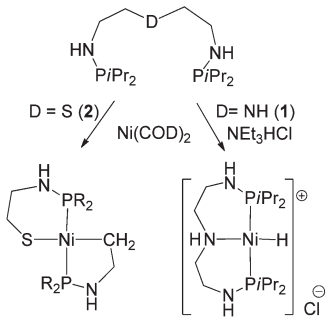



**Scheme 1** Reactions of aminophosphine tridentate ligands with Ni(COD)$_2$ and substrates.



and pentane) were purified employing a Grubbs' type column system manufactured by Innovative Technology. Solvents were stored in the glove box over 4 Å molecular sieves. $^{1}$H, $^{13}$C{$^{1}$H}, $^{19}$F{$^{1}$H} and $^{31}$P{$^{1}$H} NMR spectra were acquired on a Bruker Avance 400 MHz spectrometer or a Varian Mercury 400 MHz spectrometer. $^{1}$H and $^{13}$C NMR were internally referenced to $CD_2Cl_2$ relative to $SiMe_4$. NMR samples were prepared in the glove box, capped and sealed with parafilm. $^{19}$F resonances were referenced externally to $CFCl_3$ and $^{31}$P resonances were referenced externally to 85% $H_3PO_4$. $^{1}$H–$^{13}$C HSQC experiments were carried out using conventional pulse sequences to aid in the assignment of peaks in the $^{13}$C{$^{1}$H} NMR spectroscopy. Coupling constants (*J*) are reported as absolute values in Hz. All glassware was dried overnight at 120 °C and evacuated for 1 hour prior to use. Combustion analyses were performed in-house employing a Perkin Elmer 2400 Series II CHNS Analyzer. $CD_2Cl_2$ was purchased from the Cambridge Isotope Laboratories and was dried over $CaH_2$, distilled, degassed and stored under $N_2$ in a glove box. Ni(COD)$_2$, Pd(PPh$_3$)$_4$, Pt(PPh$_3$)$_4$, (dme)NiCl$_2$, PhCN$_2$PdCl$_2$, PhCN$_2$PtCl$_2$, NiI$_2$, PdI$_2$ and PtI$_2$ were obtained from Strem Chemicals Inc. iPr$_2$PCl, Et$_3$N, HN(CH$_2$CH$_2$NH$_2$)$_2$, [NH$_4$][PF$_6$], MeI and 1-Cl-2-F-C$_6$H$_4$ were obtained from Aldrich Chemical Co. S(CH$_2$CH$_2$NH$_2$)$_2$ was obtained from TCI America. All of the reagents from Aldrich Chemical Co., TCI America and Strem Chemical Inc. were used without further purification. Hyflo Super Cel® (Celite) was purchased from Aldrich and dried for at least 12 h in a vacuum oven or on a Schlenk line prior to use. Molecular sieves (4 Å) were purchased from Aldrich and dried at 100 °C under vacuum using a Schlenk line. Compound **1** and **2** were prepared as previously reported.[39]

### Synthesis of NH((CH$_2$)$_2$NHPiPr$_2$)$_2$·HCl (1·HCl)

A 250 mL round bottom Schlenk flask was charged with **1** (1 g, 2.981 mmol) and 50 mL of Et$_2$O and stirred under nitrogen. A solution of HCl in Et$_2$O (2 M, 1.49 mL, 2.981 mmol) was added dropwise over 5 min giving an immediate change from a clear colorless solution to a cloudy white mixture. The reaction was stirred for 30 min before being filtered through a fine porosity filter frit. The white solid was washed with Et$_2$O (5 mL × 3 times) and dried *in vacuo*. The product was obtained as a waxy white solid in 90% (998 mg, 2.683 mmol) yield. $^{1}$H ($CD_2Cl_2$) 7.66 (b, 1H, CH$_2$N*H*CH$_2$), 3.21 (d of t, 4H, $^{3}J_{HH}$ 6, $^{3}J_{HP}$ 9, C*H*$_2$N), 2.82 (t, 4H, $^{3}J_{HH}$ 6 Hz, (NH)–C*H*$_2$), 2.11 (br, 2H, NH), 1.60 (sept, 4H, $^{3}J_{HH}$ 7 Hz, Me$_2$C*H*), 0.99 (m, 24H, Me$_2$CH). $^{13}$C{$^{1}$H} ($CD_2Cl_2$) 52.38 (d, $^{3}J_{CP}$ 6 Hz, *C*H$_2$), 46.21 (d, $^{2}J_{CP}$ 29 Hz, *C*H$_2$N), 27.02 (d, $^{1}J_{CP}$ 12 Hz, Me$_2$*C*H), 19.81 (d, $^{2}J_{CP}$ 21 Hz, Me$_2$CH), 17.95 (d, $^{2}J_{CP}$ 8 Hz, Me$_2$CH)). $^{31}$P{$^{1}$H} ($CD_2Cl_2$) 70.73 (s).

### Synthesis of [κ$^3$*P,N,P*-NH((CH$_2$)$_2$NHPiPr$_2$)$_2$NiCl]Cl (3a), [κ$^3$*P,S,P*-S((CH$_2$)$_2$NHPiPr$_2$)$_2$NiCl]Cl (5a)

These complexes were prepared in a similar fashion and thus only one preparation is detailed. A solution of **1** (100 mg, 0.298 mmol) in $CH_2Cl_2$ (2 mL) was added to a yellow-orange suspension of (dme)NiCl$_2$ (66 mg, 0.298 mmol) and $CH_2Cl_2$ (2 mL) in a scintillation vial equipped with a stir bar giving an immediate change to a clear orange solution. The reaction mixture was stirred for 4 hours at which point the orange solution was dried to a bright orange solid. The solid was washed with hexane (3 × 4 mL) and the solution was decanted of the solid before it was dried *in vacuo*. The product was recrystallized from the diffusion of pentane into a DCM solution. The orange product was obtained in 90% yield (125 mg, 0.268 mmol).

**3a**: $^{1}$H ($CD_2Cl_2$) 4.73 (bs, 1H, NH), 3.57 (bm, 2H, CH$_2$), 3.25 (bm, 2H, CH$_2$), 2.95 (bm, 2H, CH$_2$), 2.69 (bm, 2H, CH$_2$), 2.45 (bs, 2H, NH), 2.28 (sept, 4H, $^{3}J_{HH}$ 7 Hz, C*H*Me$_2$), 1.55 (m, 12H, $^{3}J_{HH}$ 7 Hz, CH*Me*$_2$), 1.32 (m, 6H, $^{3}J_{HH}$ 7 Hz, CH*Me*$_2$), 1.19 (m, 6H, $^{3}J_{HH}$ 7 Hz, CH*Me*$_2$). $^{13}$C{$^{1}$H} ($CD_2Cl_2$) 52.26 (bs, CH$_2$), 42.19 (bs, CH$_2$), 27.69 (vt, $^{1}J_{CP}$ 15 Hz, Me$_2$*C*H), 27.36 (vt, $^{1}J_{CP}$ 14 Hz, Me$_2$*C*H), 19.72 (d, $^{2}J_{CP}$ 5 Hz, *Me*$_2$CH), 18.27 (s, *Me*$_2$CH), 16.83 (s, *Me*$_2$CH). $^{31}$P{$^{1}$H} ($CD_2Cl_2$) 62.62 (s). Anal. Calc. for C$_{16}$H$_{39}$N$_3$P$_2$NiCl$_2$: C, 41.30; H, 8.46; N, 9.04. Found: C, 41.06; H, 8.44; N, 9.17.

**5a**: Starting with **2** (100 mg, 0.284 mmol) and dmeNiCl$_2$ (62 mg, 0.284 mmol), the orange product was obtained in 93% yield (127 mg, 0.263 mmol). $^{1}$H ($CD_2Cl_2$) 3.99 (m, 2H, N*H*P$^{i}$Pr$_2$), 3.42 (m, 4H, $^{3}J_{HH}$ 5 Hz, C*H*$_2$NHPiPr$_2$), 2.65 (t, 4H, $^{3}J_{HH}$ 5 Hz, SC*H*$_2$), 2.45 (sept, 4H, $^{3}J_{HH}$ 7 Hz, C*H*Me$_2$), 1.51 (m, 12H, $^{3}J_{HH}$ 7 Hz, CH*Me*$_2$), 1.34 (m, 12H, $^{3}J_{HH}$ 7 Hz, CH*Me*$_2$). $^{13}$C{$^{1}$H} ($CD_2Cl_2$) 43.22 (s, CH$_2$), 34.31 (s, CH$_2$), 28.22 (vt, $^{1}J_{CP}$ 115 Hz, Me$_2$*C*H), 19.75 (s, *Me*$_2$CH), 17.54 (s, *Me*$_2$CH). $^{31}$P{$^{1}$H} ($CD_2Cl_2$) 68.54 (s). Anal. Calc. for C$_{16}$H$_{38}$N$_2$P$_2$SNiCl$_2$: C, 39.85; H, 7.95; N, 5.81. Found: C, 39.93; H, 8.00; N, 6.10.

### Synthesis of [κ$^3$*P,N,P*-NH((CH$_2$)$_2$NHPiPr$_2$)$_2$NiI]I (3b), [κ$^3$*P,S,P*-S((CH$_2$)$_2$NHPiPr$_2$)$_2$NiI]I (5b)

These complexes were prepared in a similar fashion and thus only one preparation is detailed. A solution of **1** (54 mg, 0.160 mmol) in $CH_2Cl_2$ (2 mL) was added to a black slurry of NiI$_2$ (50 mg, 0.160 mmol) and $CH_2Cl_2$ (2 mL) in a scintillation vial equipped with a stir bar. No immediate color change was observed. The reaction mixture was stirred for 12 hours at which point the purple solution was dried to a red-purple solid. The solid was washed with hexane (3 × 4 mL) and the solution was decanted of the solid before it was dried *in vacuo*. The product was recrystallized from the diffusion of pentane into a $CH_2Cl_2$ solution. The purple product was obtained in 83% yield

(86 mg, 0.133 mmol). **3b**: $^{1}$H ($CD_2Cl_2$) 3.49 (bm, 2H, $CH_2$), 3.44 (bs, 1H, NH), 3.34 (bm, 2H, $CH_2$), 3.01 (bm, 2H, $CH_2$), 2.91 (bm, 2H, $CH_2$), 2.52 (sept, 2H, $^{3}J_{HH}$ 7 Hz, C*H*Me$_2$), 2.46 (sept, 2H, $^{3}J_{HH}$ 7 Hz, C*H*Me$_2$), 2.23 (bs, 2H, NH), 1.55 (m, 12H, $^{3}J_{HH}$ 7 Hz, CH*Me*$_2$), 1.47 (m, 6H, $^{3}J_{HH}$ 7 Hz, CH*Me*$_2$), 1.35 (m, 6H, $^{3}J_{HH}$ 7 Hz, CH*Me*$_2$). $^{13}$C{$^{1}$H} ($CD_2Cl_2$) 48.06 (vt, $J_{CP}$ 4 Hz, $CH_2$), 41.08 (vt, $J_{CP}$ 2 Hz, $CH_2$), 31.55 (t, $^{1}J_{CP}$ 16 Hz, Me$_2$*C*H), 28.73 (t, $^{1}J_{CP}$ 15 Hz, Me$_2$*C*H), 20.17 (d of t, $^{2}J_{CP}$ 7 Hz, $^{2}J_{CP}$ 2 Hz, *Me*$_2$CH), 18.16 (s, *Me*$_2$CH), 17.51 (s, *Me*$_2$CH). $^{31}$P{$^{1}$H} ($CD_2Cl_2$) 78.20 (s). Anal. Calc. for $C_{16}H_{39}N_3P_2NiI_2$: C, 29.64; H, 6.07; N, 6.49. Found: C, 29.85; H, 5.86; N, 6.81.

**5b**: Starting with **2** (56 mg, 0.160 mmol) and $NiI_2$ (50 mg, 0.160 mmol), the red product was obtained in 87% yield (92 mg, 0.139 mmol). $^{1}$H ($CD_2Cl_2$) 3.47 (m, 4H, $^{3}J_{HH}$ 5 Hz, $CH_2$), 2.82 (m, 4H, $^{3}J_{HH}$ 5 Hz, $CH_2$), 2.77 (m, 2H, NH), 2.72 (m, 4H, $^{3}J_{HH}$ 7 Hz, C*H*Me$_2$), 1.50 (m, 12H, $^{3}J_{HH}$ 7 Hz, CH*Me*$_2$), 1.32 (m, 12H, $^{3}J_{HH}$ 7 Hz, CH*Me*$_2$). $^{13}$C{$^{1}$H} ($CD_2Cl_2$) 43.13 (vt, $J_{CP}$ 2 Hz, $CH_2$), 34.84 (vt, $J_{CP}$ 3 Hz, $CH_2$), 31.97 (t, $^{1}J_{CP}$ 16 Hz, Me$_2$*C*H), 20.37 (t, $^{2}J_{CP}$ 2 Hz, *Me*$_2$CH), 18.14 (d, $^{2}J_{CP}$ 2 Hz, *Me*$_2$CH). $^{31}$P{$^{1}$H} ($CD_2Cl_2$) 78.42 (s). Anal. Calc. for $C_{16}H_{38}N_2P_2SNiI_2$: C, 28.88; H, 5.76; N, 4.21. Found: C, 28.49; H, 5.76; N, 4.36.

### Synthesis of [κ$^3$*P,N,P*-NH((CH$_2$)$_2$NHPiPr$_2$)$_2$PdCl]Cl (4a), [κ$^3$*P,S,P*-S((CH$_2$)$_2$NHPiPr$_2$)$_2$PdCl]Cl (6a)

These complexes were prepared in a similar fashion to **3a** and **5a** and thus only the amounts of starting materials are detailed.

**4a**: Starting with **1** (100 mg, 0.298 mmol) and $(PhCN)_2PdCl_2$ (114 mg, 0.298 mmol) the yellow product was obtained in 94% yield (144 mg, 0.280 mmol). $^{1}$H ($CD_2Cl_2$) 6.43 (bs, 1H, NH), 3.62 (m, 2H, $^{3}J_{HH}$ 7 Hz, $CH_2$), 3.26 (m, 2H, $^{3}J_{HH}$ 7 Hz, $CH_2$), 2.97 (m, 2H, $CH_2$), 2.75 (m, 2H, $CH_2$), 2.50 (bs, 2H, NH), 2.47 (d of sept, 2H, $^{3}J_{HH}$ 7 Hz, C*H*Me$_2$), 2.39 (d of sept, 2H, $^{3}J_{HH}$ 7 Hz, C*H*Me$_2$), 1.36 (m, 18H, $^{3}J_{HH}$ 7 Hz, CH*Me*$_2$), 1.23 (m, 6H, $^{3}J_{HH}$ 7 Hz, CH*Me*$_2$). $^{13}$C{$^{1}$H} ($CD_2Cl_2$) 55.06 (vt, $J_{CP}$ 3 Hz, $CH_2$), 44.09 (vt, $J_{CP}$ 2 Hz, $CH_2$), 28.31 (vt, $^{1}J_{CP}$ 15 Hz, Me$_2$*C*H), 27.58 (vt, $^{1}J_{CP}$ 16 Hz, Me$_2$*C*H), 19.40 (s, *Me*$_2$CH), 17.68 (s, *Me*$_2$CH), 16.83 (s, *Me*$_2$CH). $^{31}$P{$^{1}$H} ($CD_2Cl_2$) 71.62 (s). Anal. Calc. for $C_{16}H_{39}N_3P_2PdCl_2$: C, 37.46; H, 7.67; N, 8.20. Found: C, 37.92; H, 7.92; N, 8.17.

**6a**: Starting with **4** (100 mg, 0.284 mmol) and $(PhCN)_2PdCl_2$ (109 mg, 0.160 mmol), the yellow product was obtained in 92% yield (138 mg, 0.261 mmol). $^{1}$H ($CD_2Cl_2$) 3.95 (bs, 2H, NHP$^{i}$Pr$_2$), 3.47 (m, 4H, $^{3}J_{HH}$ 5 Hz, C*H*$_2$NHPiPr$_2$), 2.87 (t, 4H, $^{3}J_{HH}$ 5 Hz, SC*H*$_2$), 2.58 (sept, 4H, $^{3}J_{HH}$ 7 Hz, C*H*Me$_2$), 1.35 (m, 12H, $^{3}J_{HH}$ Hz, CH*Me*$_2$), 1.28 (m, 12H, $^{3}J_{HH}$ 7 Hz, CH*Me*$_2$). $^{13}$C{$^{1}$H} ($CD_2Cl_2$) 45.72 (vt, $J_{CP}$ 3 Hz, $CH_2$), 36.10 (vt, $J_{CP}$ 2 Hz, $CH_2$), 28.03 (t, $^{1}J_{CP}$ 15 Hz, Me$_2$*C*H), 19.04 (d, $^{2}J_{CP}$ 2 Hz, *Me*$_2$CH), 17.35 (s, *Me*$_2$CH). $^{31}$P{$^{1}$H} ($CD_2Cl_2$) 76.97 (s). Anal. Calc. for $C_{16}H_{38}N_2P_2SPdCl_2$: C, 36.26; H, 7.23; N, 5.29. Found: C, 36.82; H, 7.40; N, 5.41.

### Synthesis of [κ$^3$*P,N,P*-NH((CH$_2$)$_2$NHPiPr$_2$)$_2$PdI]I (4b), [κ$^3$*P,S,P*-S((CH$_2$)$_2$NHPiPr$_2$)$_2$PdI]I (6b)

These complexes were prepared in a similar fashion and thus only one preparation is detailed. A solution of **1** (47 mg, 0.139 mmol) in $CH_2Cl_2$ (2 mL) was added to a black slurry of $PdI_2$ (50 mg, 0.139 mmol) in $CH_2Cl_2$ (2 mL) in a scintillation vial equipped with a stir bar. No immediate change is observed but after 12 h a cloudy yellow solution is obtained. The reaction mixture was stirred for 12 hours at which point the cloudy yellow solution was filtered through Celite to remove black particulate before being dried to a bright yellow solid. The solid was washed with hexane (3 × 4 mL) and the solution was decanted of the solid before it was dried *in vacuo*. The product was recrystallized from the diffusion of pentane into a $CH_2Cl_2$ solution. The yellow product was obtained in 85% yield (82 mg, 0.118 mmol).

**4b**: $^{1}$H ($CD_2Cl_2$) 4.85 (bs, 1H, NH), 3.53 (m, 2H, $CH_2$), 3.26 (m, 2H, $CH_2$), 3.13 (m, 2H, $CH_2$), 2.82 (m, 2H, $CH_2$), 2.64 (m, 2H, $^{3}J_{HH}$ 7 Hz, C*H*Me$_2$), 2.58 (m, 2H, $^{3}J_{HH}$ 7 Hz, C*H*Me$_2$), 2.44 (bs, 2H, NH), 1.39 (m, 18H, $^{3}J_{HH}$ 7 Hz, CH*Me*$_2$), 1.24 (m, 6H, $^{3}J_{HH}$ 7 Hz, CH*Me*$_2$). $^{13}$C{$^{1}$H} ($CD_2Cl_2$) 53.71 (vt, $J_{CP}$ 2 Hz, $CH_2$), 43.15 (vt, $J_{CP}$ 2 Hz, $CH_2$), 30.05 (t, $^{1}J_{CP}$ 19 Hz, Me$_2$*C*H), 28.80 (t, $^{1}J_{CP}$ 19 Hz, Me$_2$*C*H), 19.56 (d, $^{2}J_{CP}$ 2 Hz, *Me*$_2$CH), 19.22 (d, $^{2}J_{CP}$ 2 Hz, *Me*$_2$CH), 18.08 (s, *Me*$_2$CH), 17.03 (s, *Me*$_2$CH). $^{31}$P{$^{1}$H} ($CD_2Cl_2$) 77.8 (s). Anal. Calc. for $C_{16}H_{39}N_3P_2PdI_2$: C, 27.61; H, 5.65; N, 6.04. Found: C, 28.08; H, 5.35; N, 5.97.

**6b**: Starting with **2** (49 mg, 0.139 mmol) and $PdI_2$ (50 mg, 0.139 mmol), the yellow product was obtained in 81% yield (80 mg, 0.113 mmol). $^{1}$H ($CD_2Cl_2$) 3.46 (m, 4H, $^{3}J_{HH}$ 5 Hz, $CH_2$), 3.10 (m, 2H, NH), 2.93 (m, 4H, $^{3}J_{HH}$ 5 Hz, $CH_2$), 2.76 (sept, 4H, $^{3}J_{HH}$ 7 Hz, C*H*Me$_2$), 1.50 (m, 12H, $^{3}J_{HH}$ 7 Hz, CH*Me*$_2$), 1.32 (m, 12H, $^{3}J_{HH}$ 7 Hz, CH*Me*$_2$). $^{13}$C{$^{1}$H} ($CD_2Cl_2$) 45.60 (vt, $J_{CP}$ 3 Hz, $CH_2$), 36.25 (vt, $J_{CP}$ 2 Hz, $CH_2$), 31.33 (t, $^{1}J_{CP}$ 16 Hz, Me$_2$*C*H), 19.73 (t, $^{2}J_{CP}$ 2 Hz, *Me*$_2$CH), 17.86 (s, *Me*$_2$CH). $^{31}$P{$^{1}$H} ($CD_2Cl_2$) 77.88 (s). Anal. Calc. for $C_{16}H_{38}N_2P_2SPdI_2$: C, 26.95; H, 5.38; N, 3.93. Found: C, 27.38; H, 5.69; N, 4.04.

### Synthesis of [κ$^3$*P,S,P*-S((CH$_2$)$_2$NHPiPr$_2$)$_2$PtCl]Cl (7a)

This product was prepared in a similar fashion to **6a** starting with **2** (100 mg, 0.284 mmol) and $(PhCN)_2PtCl_2$ (134 mg, 0.284 mmol). The white product was obtained in 88% yield (155 mg, 0.250 mmol). $^{1}$H ($CD_2Cl_2$) 4.10 (bs, 2H, NHP$^{i}$Pr$_2$), 3.47 (m, 4H, C*H*$_2$NHPiPr$_2$), 3.07 (m, 4H, SC*H*$_2$), 2.66 (m, 4H, C*H*Me$_2$), 1.29 (m, 24H, CH*Me*$_2$). $^{13}$C{$^{1}$H} ($CD_2Cl_2$) 45.55 (vt, $J_{CP}$ 3 Hz, $CH_2$), 37.17 (vt, $J_{CP}$ 3 Hz, $CH_2$), 27.33 (vt, $^{1}J_{CP}$ 15 Hz, Me$_2$*C*H), 19.47 (bs, *Me*$_2$CH). $^{31}$P{$^{1}$H} ($CD_2Cl_2$) 66.09 (t, $^{2}J_{PPt}$ 2312 Hz). Anal. Calc. for $C_{16}H_{38}N_2P_2SPtCl_2$: C, 31.06; H, 6.19; N, 4.53. Found: C, 30.78; H, 6.14; N, 4.41.

### Synthesis of [κ$^3$*P,S,P*-S((CH$_2$)$_2$NHPiPr$_2$)$_2$PtI]I (7b)

This product was prepared in a similar fashion to **6b** starting with **2** (37 mg, 0.111 mmol) and $PtI_2$ (50 mg, 0.111 mmol). The off-white product was obtained in 77% yield (67 mg, 0.085 mmol). $^{1}$H ($CD_2Cl_2$) 3.50 (bm, 4H, $CH_2$), 3.22 (bm, 2H, NH), 3.10 (bm, 4H, $CH_2$), 2.87 (sept, 4H, $^{3}J_{HH}$ 7 Hz, C*H*Me$_2$), 1.33 (m, 12H, $^{3}J_{HH}$ 6 Hz, CH*Me*$_2$), 1.27 (m, 12H, $^{3}J_{HH}$ 7 Hz, CH*Me*$_2$). $^{13}$C{$^{1}$H} ($CD_2Cl_2$) 45.09 (vt, $J_{CP}$ 2 Hz, $CH_2$), 37.22 (vt, $J_{CP}$ 2 Hz, $CH_2$), 30.08 (vt, $^{1}J_{CP}$ 19 Hz, Me$_2$*C*H), 19.19

(vt, $^2J_{CP}$ 5 Hz, *Me*$_2$CH), 17.57 (bs, *Me*$_2$CH). $^{31}P\{^1H\}$ ($CD_2Cl_2$) 64.08 (t, $^1J_{PPt}$ 2277 Hz). Anal. Calc. for $C_{16}H_{38}N_2P_2SPdI_2$: C, 23.97; H, 4.78; N, 3.50. Found: C, 23.98; H, 5.10; N, 3.41.

### Alternative synthesis of 3b, 4b, 5b, 6b, 7b

These complexes were prepared in a similar fashion and thus only one preparation is detailed. An orange suspension of **2a** in $CH_2Cl_2$ (50 mg, 0.107 mmol; 2 mL) was prepared in a 4 dram vial equipped with a stir bar. Neat $Me_3SiI$ (31 μL, 0.215 mmol) was added giving an immediate change to a clear deep purple solution. The reaction mixture was stirred for 2 h at which point $^{31}P\{^1H\}$ indicated quantitative conversion to **2b**. The volatiles were removed and the purple solid was redissolved in $CH_2Cl_2$ (1 mL) and layered with pentane. The product was obtained in 93% yield (64 mg, 0.100 mmol).

**3b**: Starting with **3a** (50 mg, 0.097 mmol) and $Me_3SiI$ (28 μL, 0.215 mmol), the yellow product was obtained in 91% yield (61 mg, 0.088 mmol).

**5b**: Starting with **5a** (50 mg, 0.103 mmol) and $Me_3SiI$ (30 μL, 0.207 mmol), the yellow product was obtained in 92% yield (63 mg, 0.095 mmol).

**6b**: Starting with **6a** (50 mg, 0.094 mmol) and $Me_3SiI$ (27 μL, 0.189 mmol), the yellow product was obtained in 96% yield (64 mg, 0.090 mmol).

**7b**: Starting with **7a** (50 mg, 0. 081 mmol) and $Me_3SiI$ (23 μL, 0.162 mmol), the off white product was obtained in 89% yield (58 mg, 0.072 mmol).

### Synthesis of [κ$^3$*P,N,P*-NH((CH$_2$)$_2$NHPiPr$_2$)$_2$PdMe]Cl (8a), [κ$^3$*P,S,P*-S((CH$_2$)$_2$NHPiPr$_2$)$_2$PdMe]Cl (9a)

These complexes were prepared in a similar fashion and thus only one preparation is detailed. A solution of **1** in THF (127 mg, 0.377 mmol; 2 mL) was added to an off-white slurry of (COD)PdMeCl and THF (100 mg, 0.377 mmol; 2 mL) in a scintillation vial equipped with a stir bar. An off-white precipitate immediately forms in a colorless solution. The reaction mixture was stirred for 4 hours at which point it was dried to a pale yellow-white solid. The crude product was washed with hexane (3 × 4 mL) and the solution was decanted off before the product was dried *in vacuo*. The product was recrystallized from the diffusion of pentane into a $CH_2Cl_2$ solution. The off-white product was obtained in 87% yield (161 mg, 0.328 mmol).

**8a**: $^1H$ ($CD_2Cl_2$) 3.89 (bs, 1H, NH), 3.30 (m, 4H, $CH_2$), 3.03 (m, 4H, C*H*$_2$), 2.57 (m, 2H, NH), 2.23 (sept, 2H, $^3J_{HH}$ 7 Hz, C*H*Me$_2$), 2.12 (sept, 2H, $^3J_{HH}$ 7 Hz, C*H*Me$_2$), 1.31 (m, 6H, $^3J_{HH}$ 7 Hz, CH*Me*$_2$), 1.23 (m, 18H, $^3J_{HH}$ 7 Hz, CH*Me*$_2$), 0.19 (t, 3H, $^3J_{HP}$ 7 Hz, PdMe). $^{13}C\{^1H\}$ ($CD_2Cl_2$) 54.49 (vt, $J_{CP}$ 2 Hz, $CH_2$), 45.35 (vt, $J_{CP}$ 4 Hz, $CH_2$), 26.93 (vt, $^1J_{CP}$ 14 Hz, CHMe$_2$), 26.68 (vt, $^1J_{CP}$ 14 Hz, *C*HMe$_2$), 19.03 (vt, $^2J_{CP}$ 3 Hz, CH*Me*$_2$), 18.87 (vt, $^2J_{CP}$ 3 Hz, CH*Me*$_2$), 17.61 (s, CH*Me*$_2$), 16.69 (s, CH*Me*$_2$), −13.02 (t, $^2J_{CP}$ 7 Hz, PdMe). $^{31}P\{^1H\}$ ($CD_2Cl_2$) 79.80 (s). Anal. Calc. for $C_{17}H_{42}ClN_3P_2PdCl$: C, 41.45; H, 8.60; N, 8.54; Found: C, 41.10; H, 8.63; N, 8.04.

**9a**: Starting with **2** (133 mg, 0.377 mmol) and (COD)PdMeCl (100 mg, 0.377 mmol), the white product was obtained in 89% yield (170 mg, 0.333 mmol). $^1H$ ($CD_2Cl_2$) 3.73 (bt, 2H, $^3J_{HH}$ 7 Hz, NH), 3.38 (m, 4H, $^3J_{HH}$ 5 Hz C*H*$_2$), 2.82 (t, 4H, $^3J_{HH}$ 5 Hz, SC*H*$_2$), 2.27 (sept, 4H, $^3J_{HH}$ 7 Hz, C*H*Me$_2$), 1.25 (m, 12H, $^3J_{HH}$ 7 Hz, CH*Me*$_2$), 1.18 (m, 12H, $^3J_{HH}$ 7 Hz, CH*Me*$_2$), 0.51 (t, 3H, $^3J_{HP}$ 7 Hz, Pd–CH$_3$). $^{13}C\{^1H\}$ ($CD_2Cl_2$) 46.97 (vt, $J_{CP}$ 4 Hz, $CH_2$), 38.83 (s, $CH_2$), 26.75 (vt, $^1J_{CP}$ 15 Hz, *C*HMe$_2$), 18.79 (vt, $^2J_{CP}$ 3 Hz, CH*Me*$_2$), 17.11 (s, CH*Me*$_2$), −6.15 (t, $^2J_{CP}$ 6 Hz, PdMe). $^{31}P\{^1H\}$ ($CD_2Cl_2$) 81.12 (s). Anal. Calc. for $C_{17}H_{41}ClN_2P_2PdS$: C, 40.07; H, 8.12; N, 5.50; Found: C, 39.87; H, 7.55; N, 5.46.

### Synthesis of [κ$^3$*P,N,P*-NH((CH$_2$)$_2$NHPiPr$_2$)$_2$PdMe]I (8b) and [κ$^3$*P,S,P*-S((CH$_2$)$_2$NHPiPr$_2$)$_2$PdMe]I (9b)

These complexes were prepared in a similar fashion and thus only one preparation is detailed. A solution of **1** in THF (58 mg, 0.173 mmol; 2 mL) was added to a yellow slurry of $(PPh_3)_4Pd$ and THF (200 mg, 0.173 mmol; 2 mL) in a scintillation vial equipped with a stir bar. The solution was stirred for 30 min yielding no observable change before iodomethane (25 mg, 0.173 mmol; neat) was added. A white precipitate forms almost immediately. The reaction mixture was stirred for 12 hours at which point it was concentrated before hexane was added to precipitate a fluffy white powder. The supernatant was removed and the white powder was dried. The crude product was washed with hexane (3 × 4 mL) and the solution was decanted off before the product was dried *in vacuo*. The product was recrystallized from the diffusion of pentane into a $CH_2Cl_2$ solution. The white product was obtained in 88% yield (89 mg, 0.152 mmol).

**8b**: $^1H$ ($CD_2Cl_2$) 3.40 (bs, 1H, NH), 3.37 (m, 2H, $CH_2$), 3.30 (m, 2H, $CH_2$), 3.10 (m, 2H, $CH_2$), 2.58 (m, 2H, $CH_2$), 2.49 (bt, 2H, $^3J_{HH}$ 5 Hz, NH), 2.22 (sept, 2H, $^3J_{HH}$ 7 Hz, C*H*Me$_2$), 2.13 (sept, 2H, $^3J_{HH}$ 7 Hz, C*H*Me$_2$), 1.31 (m, 6H, $^3J_{HH}$ 7 Hz, CH*Me*$_2$), 1.22 (m, 18H, $^3J_{HH}$ 7 Hz, CH*Me*$_2$), 0.22 (t, 3H, $^3J_{HP}$ 7 Hz, PdMe). $^{13}C\{^1H\}$ ($CD_2Cl_2$) 54.61 (vt, $J_{CP}$ 2 Hz, $CH_2$), 45.19 (vt, $J_{CP}$ 4 Hz, $CH_2$), 27.05 (vt, $^1J_{CP}$ 15 Hz, *C*HMe$_2$), 26.68 (vt, $^1J_{CP}$ 13 Hz, *C*HMe$_2$), 18.98 (vt, $^2J_{CP}$ 3 Hz, CH*Me*$_2$), 18.89 (vt, $^2J_{CP}$ 3 Hz, CH*Me*$_2$), 17.79 (s, CH*Me*$_2$), 16.74 (s, CH*Me*$_2$), −12.66 (t, $^2J_{CP}$ 7 Hz, PdMe). $^{31}P\{^1H\}$ ($CD_2Cl_2$) 79.62 (s). Anal. Calc. for $C_{17}H_{42}N_3P_2PdI$: C, 34.95; H, 7.25; N, 7.20; Found: C, 35.07; H, 7.12; N, 7.11.

**9b**: Starting with **2** (58 mg, 0.173 mmol), $(PPh_3)_4Pd$ (100 mg, 0.173 mmol), and $CH_3I$ (25 mg, 0.173 mmol) the white solid was obtained in a 76% yield. $^1H$ ($CD_2Cl_2$) 3.40 (m, 4H, $^3J_{HH}$ 5 Hz $CH_2$), 2.91 (bt, 2H, NH), 2.86 (t, 4H, $^3J_{HH}$ 5 Hz, S–$CH_2$), 2.26 (sept, 4H, $^3J_{HH}$ 7 Hz, C*H*Me$_2$), 1.24 (m, 12H, $^3J_{HH}$ 7 Hz, CH*Me*$_2$), 1.19 (m, 12H, $^3J_{HH}$ 7 Hz, CH*Me*$_2$), 0.52 (t, 3H, $^3J_{HP}$ 7 Hz, PdMe). $^{13}C\{^1H\}$ ($CD_2Cl_2$) 46.76 (vt, $J_{CP}$ 4 Hz, $CH_2$), 38.33 (s, $CH_2$), 26.76 (vt, $^1J_{CP}$ 15 Hz, *C*HMe$_2$), 18.77 (vt, $^2J_{CP}$ 3 Hz, CH*Me*$_2$), 17.15 (s, CH*Me*$_2$), −6.00 (t, $^2J_{CP}$ 6 Hz, PdMe). $^{31}P\{^1H\}$ ($CD_2Cl_2$) 81.65 (s). Anal. Calc. for $C_{17}H_{41}IN_2P_2PdS$: C, 33.97; H, 6.88; N, 4.66; Found: C, 33.79; H, 6.77; N, 4.91.

### Synthesis of [κ$^3$*P,N,P*-NH((CH$_2$)$_2$NHPiPr$_2$)$_2$PtMe]I (11), [κ$^3$*P,S,P*-S((CH$_2$)$_2$NHPiPr$_2$)$_2$PtMe]I (12)

These complexes were prepared in a similar fashion to **8b** and **9b** and thus only the amounts of starting materials are detailed.

**11**: Starting from **1** (54 mg, 0.161 mmol), $(PPh_3)_4Pt$ (200 mg, 0.161 mmol) and iodomethane (23 mg, 0.161 mmol), the white product was obtained in 86% yield (93 mg, 0.138 mmol). $^1H$ ($CD_2Cl_2$) 4.05 (bs, 1H, NH), 3.42 (m, 2H, $CH_2$), 3.34 (m, 4H, $CH_2$), 2.77 (m, 2H, $CH_2$), 2.67 (bt, 2H, NH), 2.35 (sept, 2H, $^3J_{HH}$ 7 Hz, C*H*Me$_2$), 2.25 (sept, 2H, $^3J_{HH}$ 7 Hz, C*H*Me$_2$), 1.32 (m, 6H, $^3J_{HH}$ 7 Hz, CH*Me*$_2$), 1.23 (m, 18H, $^3J_{HH}$ 7 Hz, CH*Me*$_2$), 0.38 (t, 3H, $^3J_{HP}$ 7 Hz, $^2J_{HPt}$ 76 Hz, PtMe). $^{13}C\{^1H\}$ ($CD_2Cl_2$) 54.83 (vt, $J_{CP}$ 2 Hz, $CH_2$), 45.01 (vt, $J_{CP}$ 2 Hz, $^2J_{CPt}$ 37 Hz $CH_2$), 27.04 (vt, $^1J_{CP}$ 18 Hz, *C*HMe$_2$), 26.48 (vt, $^1J_{CP}$ 18 Hz, *C*HMe$_2$), 18.67 (vt, $^2J_{CP}$ 2 Hz, CH*Me*$_2$), 18.43 (vt, $^2J_{CP}$ 2 Hz, CH*Me*$_2$), 17.57 (s, $^3J_{CPt}$ 23 Hz, CH*Me*$_2$), 16.63 (s, $^3J_{CPt}$ 21 Hz, CH*Me*$_2$), −27.19 (t, $^2J_{CP}$ 8 Hz, PtMe). $^{31}P\{^1H\}$ ($CD_2Cl_2$) 73.95 (t, $^1J_{PPt}$ 2842Hz). Anal. Calc. for $C_{17}H_{42}N_3P_2PtI$: C, 30.35; H, 6.30; N, 6.25; Found: C, 30.39; H, 6.50; N, 6.45.

**12**: Starting with **2** (57 mg, 0.161 mmol), $(PPh_3)_4Pt$ (200 mg, 0.161 mmol), and $CH_3I$ (23 mg, 0.161 mmol) the white solid was obtained in a 77% yield (85 mg, 0.123 mmol). $^1H$ ($CD_2Cl_2$) 3.42 (m, 4H, $^3J_{HH}$ 5 Hz $CH_2$), 3.25 (bt, 2H, NH), 3.00 (t, 4H, $^3J_{HH}$ 5 Hz, S–$CH_2$), 2.39 (sept, 4H, $^3J_{HH}$ 7 Hz, C*H*Me$_2$), 1.24 (m, 12H, $^3J_{HH}$ 7 Hz, CH*Me*$_2$), 1.20 (m, 12H, $^3J_{HH}$ 7 Hz, CH*Me*$_2$), 0.62 (t, 3H, $^3J_{HP}$ 7 Hz, $^2J_{HPt}$ 74 Hz, PtMe). $^{13}C\{^1H\}$ ($CD_2Cl_2$) 46.58 (t of vt, $J_{CP}$ 3 Hz, $J_{CPt}$ 51 Hz $CH_2$), 38.13 (t, $J_{CP}$ 7 Hz, $CH_2$), 26.53 (vt, $^1J_{CP}$ 18 Hz, *C*HMe$_2$), 18.34 (t of vt, $^2J_{CP}$ 2 Hz, $J_{CPt}$ 15 Hz CH*Me*$_2$), 16.98 (s, $J_{CPt}$ 21 Hz, CH*Me*$_2$), −15.06 (t, $^2J_{CP}$ 8 Hz, PtMe). $^{31}P\{^1H\}$ ($CD_2Cl_2$) 71.51 (t, $^2J_{PPt}$ 2707 Hz). Anal. Calc. for $C_{17}H_{41}IN_2P_2PtS$: C, 29.60; H, 6.00; N, 4.06; Found: C, 29.65; H, 6.10; N, 4.02.

### Synthesis of [κ$^3$*P,N,P*-HN(CH$_2$CH$_2$NHPiPr$_2$)$_2$NiH]PF$_6$ (13b)

For this procedure the product from **13a** was used without purification. To a stirring orange solution of **13a** (50 mg, 0.116 mmol) in $CH_2Cl_2$ (2 mL) was added a suspension of $NaPF_6$ in DCM (20 mg, 0.116 mmol; 2 mL). The mixture was stirred for 12 hours yielding a slightly cloudy pale orange solution. The reaction mixture was filtered through Celite and dried to a pale orange solid. The product was recrystallized from the diffusion of diethyl ether into a $CH_2Cl_2$ solution of the crude product. **13b** was obtained as orange crystals in 71% yield (45 mg, 0.082 mmol). $^1H$ NMR ($CD_2Cl_2$) 3.33 (m, 4H, $CH_2$), 2.90 (m, 2H, $CH_2$), 2.79 (m, 2H, $CH_2$), 2.46 (bt, 1H, $^2J_{HH}$ 11.5 Hz, NH), 1.84 (m, 6H, (4H) $^3J_{HH}$ 7.1 Hz, C*H*Me$_2$, (2H), NH), 1.21 (m, 24H, $^3J_{HH}$ 7.1 Hz, CH*Me*$_2$), −21.10 (t, $^2J_{HP}$ 80.7 Hz, Ni–H). $^{13}C\{^1H\}$ NMR ($CD_2Cl_2$) 56.91 (vt, $J_{CP}$ 4.4 Hz, $CH_2$), 44.91 (vt, $J_{CP}$ 3.7 Hz, $CH_2$), 30.45 (vt, $^1J_{CP}$ 15.4 Hz, *C*HMe$_2$), 27.99 (vt, $^1J_{CP}$ 20.6 Hz, *C*HMe$_2$), 19.14 (vt, $^2J_{CP}$ 2.2 Hz CH*Me*$_2$), 18.52 (vt, $^2J_{CP}$ 2.2 Hz CH*Me*$_2$), 17.07 (s, CH*Me*$_2$). $^{19}F\{^1H\}$ ($CD_2Cl_2$) −73.83 (d, $^1J_{FP}$ 711.4 Hz). $^{31}P\{^1H\}$ ($CD_2Cl_2$) 79.28 (s), −144.42 (sept, $^1J_{PF}$ 711.4 Hz, $PF_6$). Anal. Calc. for $C_{16}H_{40}ClN_3P_3NiF_6$: C, 35.56; H, 7.47; N, 7.78; Found: C, 35.70; H, 7.69; N, 7.80.

### Synthesis of [κ$^3$*P,N,P*-NH((CH$_2$)$_2$NHPiPr$_2$)$_2$PdH]Cl (14a)

A solution of **1** (81 mg, 0.216 mmol) in THF (2 mL) was added to a bright yellow slurry of $Pd(PPh_3)_4$ (250 mg, 0.216 mmol) and THF (2 mL) in a scintillation vial equipped with a stir bar immediately giving a cloudy pale yellow mixture. The reaction mixture was allowed to stir for 30 min at which point there was no observable change. A suspension of $NEt_3HCl$ (30 mg, 0.216 mmol) and THF (2 mL) was combined with the reaction mixture giving a very pale yellow solution. The reaction mixture was stirred for 12 hours at which point it was dried to a pale-yellow solid. The crude product was washed with hexane (3 × 4 mL) and the solution was decanted off before the product was dried *in vacuo*. The white product was obtained in 93% yield (96 mg, 0.201 mmol). $^1H$ ($CD_2Cl_2$) 5.47 (bs, 1H, NH), 3.68 (t, 2H, $^3J_{HH}$ 11 Hz, $CH_2$), 3.32 (m, 2H, $CH_2$), 3.01 (m, 2H, $^3J_{HH}$ 11 Hz, $CH_2$), 2.69 (m, 2H, $^3J_{HH}$ 11 Hz, $CH_2$), 2.30 (bs, 2H, NHiPr), 1.94 (m, 2H, $^3J_{HH}$ 7 Hz, C*H*Me$_2$), 1.87 (m, 2H, $^3J_{HH}$ 1 Hz, C*H*Me$_2$), 1.20 (m, 12H, $^3J_{HH}$ 7 Hz, CH*Me*$_2$), 1.15 (m, 12H, $^3J_{HH}$ 7 Hz, CH*Me*$_2$), −13.24 (bt, 1H, PdH). $^{13}C\{^1H\}$ ($CD_2Cl_2$) 57.23 (vt, $J_{CP}$ 3 Hz, $CH_2$), 45.48 (vt, $J_{CP}$ 4 Hz, $CH_2$), 30.64 (vt, $^1J_{CP}$ 13 Hz, *C*HMe$_2$), 27.86 (vt, $^1J_{CP}$ 18 Hz, *C*HMe$_2$), 19.31 (bs, CH*Me*$_2$), 18.51 (bs, CH*Me*$_2$), 17.35 (vt, $^2J_{CP}$ 12 Hz, CH*Me*$_2$). $^{31}P\{^1H\}$ ($CD_2Cl_2$) 84.61 (s). Anal. Calc. for $C_{16}H_{40}ClN_3P_2Pd$: C, 40.16; H, 8.43; N, 8.79; Found: C, 40.36; H, 8.11; N, 8.79.

### Synthesis of [κ$^3$*P,N,P*-NH((CH$_2$)$_2$NHPiPr$_2$)$_2$PdH]PF$_6$ (14b)

A solid sample of $NaPF_6$ (17.6 mg, 0.104 mmol) was added to a colorless solution of **14a** (50 mg, 0.104 mmol; 2 mL) giving a cloudy mixture. The mixture was stirred over night and filtered through Celite to a clear colorless solution. The solution was dried to a white solid. The product was obtained in 77% yield (47 mg, 0.080 mmol). $^1H$ ($CD_2Cl_2$) 3.41 (m, 2H, $CH_2$), 3.32 (m, 2H, $CH_2$), 3.04 (m, 2H, $CH_2$), 2.79 (m, 3H, (2H) $CH_2$, (1H) NH), 2.10 (bs, 2H, NH$^i$Pr), 1.92 (m, 4H, $^3J_{HH}$ 7 Hz, C*H*Me$_2$), 1.20 (m, 24H, $^3J_{HH}$ 7 Hz, CH*Me*$_2$), −13.42 (bt, 1H, PdH). $^{13}C\{^1H\}$ ($CD_2Cl_2$) 58.14 (vt, $J_{CP}$ 3 Hz, $CH_2$), 46.28 (vt, $J_{CP}$ 3 Hz, $CH_2$), 31.44 (vt, $^1J_{CP}$ 18 Hz, *C*HMe$_2$), 18.38 (vt, $^2J_{CP}$ 2 Hz, CH*Me*$_2$), 17.22 (bs, CH*Me*$_2$), 17.09 (bs, CH*Me*$_2$). $^{19}F\{^1H\}$ ($CD_2Cl_2$) −74.07 (d, $^1J_{PF}$ 711 Hz). $^{31}P\{^1H\}$ ($CD_2Cl_2$) 84.00 (s, $^i$Pr$_2$P), −144.47 (sept, $^1J_{PF}$ 711 Hz). Anal. Calc. for $C_{16}H_{40}N_3P_3PdF_6$: C, 32.67; H, 6.86; N, 7.15; Found: C, 32.85; H, 7.26; N, 7.21.

### Synthesis of [κ$^3$*P,S,P*-S((CH$_2$)$_2$NHPiPr$_2$)$_2$PdH]PF$_6$ (15)

A solution of **2** (61 mg, 0.173 mmol) in THF (2 mL) was added to a yellow slurry of $Pd(PPh_3)_4$ (200 mg, 0.173 mmol) and THF (2 mL) in a scintillation vial equipped with a stir bar. The reaction mixture was allowed to stir for 30 min at which point there was no observable change. A slurry of $NH_4PF_6$ (28 mg, 0.173 mmol) and THF (2 mL) was combined with the reaction mixture giving a white cloudy solution. The reaction mixture was stirred for 12 hours at which point it was dried to a pale-yellow solid. The crude product was washed with hexane (3 × 4 mL) and the solution was decanted off before the product was dried *in vacuo*. The solid was recrystallized from a mixture of $CH_2Cl_2$, benzene and diethyl ether giving a white product in 79% yield (80 mg, 0.137 mmol). $^1H$ ($CD_2Cl_2$) 3.44 (m, 4H, $CH_2$), 2.86 (m, 4H, $CH_2$), 2.22 (bs, 2H, NH), 2.00 (sept, 4H, $^3J_{HH}$ 7 Hz, C*H*Me$_2$), 1.15 (m, 24H, $^3J_{HH}$ 7 Hz, CH*Me*$_2$),

−9.17 (bs, 1H, Pd–H). $^{13}C\{^1H\}$ ($CD_2Cl_2$) 46.91 (vt, $J_{CP}$ 4 Hz, $CH_2$), 38.32 (vt, $J_{CP}$ 2 Hz, $J_{PtC}$ 13 Hz, $CH_2$), 29.66 (vt, $^1J_{CP}$ 16 Hz, *C*HMe$_2$), 18.73 (vt, $^2J_{CP}$ 4 Hz, CH*Me*$_2$), 17.06 (s, CH*Me*$_2$). $^{19}F$ $\{^1H\}$ ($CD_2Cl_2$) −74.06 (d, $^1J_{PF}$ 710 Hz, $PF_6$). $^{31}P\{^1H\}$ ($CD_2Cl_2$) 89.25 (s), −144.24 (sept, $^1J_{PF}$ 710 Hz, $PF_6$). Anal. Calc. for $C_{16}H_{39}N_2P_3SPdF_6$: C, 31.76; H, 6.50; N, 4.63; Found: C, 32.22; H, 6.59; N, 4.73.

### Synthesis of [κ$^3$*P,N,P*-NH((CH$_2$)$_2$NHPiPr$_2$)$_2$PtH]Cl (16a)

This complex was prepared in a similar fashion to **14a** starting with **1** (75 mg, 0.201 mmol), $Pt(PPh_3)_4$ (250 mg, 0.201 mmol) and $NEt_3HCl$ (28 mg, 0.201 mmol). The pale-yellow product was obtained in 90% yield (103 mg, 0.181 mmol). $^1H$ ($CD_2Cl_2$) 6.24 (bs, 1H, NH), 3.79 (m, 2H, $^3J_{HH}$ 12 Hz, $CH_2$), 3.27 (m, 4H, C*H*$_2$NHP), 2.80 (m, 2H, $^3J_{HH}$ 11 Hz, $CH_2$), 2.35 (m, 2H, N*H*), 2.04 (m, 2H, $^3J_{HH}$ 7 Hz, C*H*Me$_2$), 1.95 (m, 2H, $^3J_{HH}$ 7 Hz, C*H*Me$_2$), 1.21 (m, 12H, $^3J_{HH}$ 7 Hz, CH*Me*$_2$), 1.14 (m, 12H, $^3J_{HH}$ 7 Hz, CH*Me*$_2$), −16.79 (tt, 1H, $^2J_{HP}$ 18 Hz, $^1J_{HPt}$ 1025 Hz, Pd–H). $^{13}C\{^1H\}$ ($CD_2Cl_2$) 58.08 (vt, $J_{CP}$ 3 Hz, $CH_2$), 46.02 (vt, $J_{CP}$ 3 Hz, $CH_2$), 31.45 (vt, $^1J_{CP}$ 18 Hz, *C*HMe$_2$), 28.73 (vt, $^1J_{CP}$ 23 Hz, *C*HMe$_2$), 19.13 (vt, $^2J_{CP}$ 2 Hz, CH*Me*$_2$), 18.41 (vt, $^2J_{CP}$ 2 Hz, CH*Me*$_2$), 17.39 (d, $^2J_{CP}$ 12 Hz, CH*Me*$_2$). $^{31}P\{^1H\}$NMR ($CD_2Cl_2$) 79.92 (t, $^1J_{PPt}$ 2787 Hz). Anal. Calc. for $C_{16}H_{40}ClN_3P_2Pt$: C, 33.87; H, 7.11; N, 7.41; Found: C, 33.39; H, 6.96; N, 7.22.

### Synthesis of [κ$^3$*P,N,P*-NH((CH$_2$)$_2$NHPiPr$_2$)$_2$PtH]PF$_6$ (16b)

This complex was prepared in a similar fashion to **14a** starting with $NaPF_6$ (15 mg, 0.088 mmol) and **16a** (50 mg, 0.088 mmol). The product was obtained in 80% yield (48 mg, 0.071 mmol). $^1H$ ($CD_2Cl_2$) 3.39 (m, 5H, (4H) $CH_2$, (1H) NH), 3.24 (m, 2H, $CH_2$), 2.92 (m, 2H, $CH_2$), 2.30 (m, 2H, NH), 2.05 (m, 2H, $^3J_{HH}$ 7 Hz, C*H*Me$_2$), 1.99 (m, 2H, $^3J_{HH}$ 7 Hz, C*H*Me$_2$), 1.16 (m, 24H, $^3J_{HH}$ 7 Hz, CH*Me*$_2$), −17.21 (tt, 1H, $^2J_{HP}$ 18 Hz, $^1J_{HPt}$ 1069 Hz, Pt–H). $^{13}C\{^1H\}$ ($CD_2Cl_2$) 57.24 (vt, $J_{CP}$ 3 Hz, $CH_2$), 45.82 (vt, $J_{CP}$ 4 Hz, $CH_2$), 30.65 (vt, $^1J_{CP}$ 13 Hz, *C*HMe$_2$), 27.93 (vt, $^1J_{CP}$ 18 Hz, *C*HMe$_2$), 19.13 (vt, $^2J_{CP}$ 4 Hz, CH*Me*$_2$), 18.49 (vt, $^2J_{CP}$ 4 Hz, CH*Me*$_2$), 17.25 (s, CH*Me*$_2$), 16.92 (s, CH*Me*$_2$). $^{19}F$ $\{^1H\}$ ($CD_2Cl_2$) −74.07 (d, $^1J_{PF}$ 712 Hz). $^{31}P\{^1H\}$NMR ($CD_2Cl_2$) 80.73 (t, $^1J_{PPt}$ 2761 Hz), −144.49 (sept, $^1J_{PF}$ 712 Hz). Anal. Calc. for $C_{16}H_{40}N_3P_3PtF_6$: C, 28.39; H, 5.96; N, 6.21; Found: C, 28.53; H, 6.20; N, 6.12.

### Synthesis of [κ$^3$*P,S,P*-S((CH$_2$)$_2$NHPiPr$_2$)$_2$PtH]Br (17a)

A solution of **2** in THF (71 mg, 0.201 mmol; 2 mL) was added to a yellow-orange slurry of $Pt(PPh_3)_4$ and THF (250 mg, 0.201 mmol; 2 mL) in a scintillation vial equipped with a stir bar giving no immediate change. A slurry of $PPh_3HBr$ and THF (69 mg, 0.201 mmol; 2 mL) was then added and the mixture was transferred to a bomb and heated for 12 h at 65 °C. The white reaction mixture was dried to an off-white solid. The crude product was washed with hexane (3 × 4 mL) and the solution was decanted off before the product was dried *in vacuo*. The white product was obtained in 83% yield (105 mg, 0.166 mmol). $^1H$ ($CD_2Cl_2$) 3.81 (m, 2H, NH), 3.49 (m, 4H, $CH_2$), 3.00 (m, 4H, $CH_2$), 2.16 (sept, 4H, $^3J_{HH}$ 7 Hz, C*H*Me$_2$), 1.18 (m, 24H, $^3J_{HH}$ 7 Hz, CH*Me*$_2$), −10.11 (t of t, 1H, $^2J_{HP}$ 16 Hz, $^1J_{HPt}$ 1221 Hz, Pt–H). $^{13}C\{^1H\}$ ($CD_2Cl_2$) 46.84 (t of vt, $J_{CP}$ 3 Hz, $J_{PtC}$ 47 Hz, $CH_2$), 38.15 (t of vt, $J_{CP}$ 2 Hz, $J_{PtC}$ 14 Hz, $CH_2$), 30.32 (vt, $^1J_{CP}$ 20 Hz, *C*HMe$_2$), 18.62 (t of vt, $^2J_{CP}$ 2 Hz, $^3J_{PtC}$ 24 Hz, CH*Me*$_2$), 17 (d, $^3J_{PtC}$ 26 Hz, CH*Me*$_2$). $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$) 79.48 (t, $^1J_{PPt}$ 2623 Hz). Anal. Calc. for $C_{16}H_{39}BrN_2P_2SPt$: C, 30.56; H, 6.26; N, 4.46; Found: C, 31.02; H, 6.29; N, 4.25.

### Synthesis of [κ$^3$*P,S,P*-S((CH$_2$)$_2$NHPiPr$_2$)$_2$PtH]PF$_6$ (17b)

This complex was prepared in a similar fashion to **14a** starting with $NaPF_6$ (13 mg, 0.080 mmol) and **17a** (50 mg, 0.080 mmol). The product was obtained in 74% yield (41 mg, 0.059 mmol). $^1H$ ($CD_2Cl_2$) 3.48 (m, 4H, $CH_2$), 3.25 (m, 2H, NH), 3.00 (m, 4H, $CH_2$), 2.13 (sept, 4H, $^3J_{HH}$ 7 Hz, C*H*Me$_2$), 1.17 (m, 24H, $^3J_{HH}$ 7 Hz, CHMe$_2$), −10.10 (t of t, 1H, $^2J_{HP}$ 16 Hz, $^1J_{HPt}$ 1216 Hz, Pt–H). $^{13}C\{^1H\}$ ($CD_2Cl_2$) 46.92 (t of vt, $J_{CP}$ 3 Hz, $J_{PtC}$ 45 Hz, $CH_2$), 38.14 (t of vt, $J_{CP}$ 2 Hz, $J_{PtC}$ 14 Hz, $CH_2$), 30.34 (vt, $^1J_{CP}$ 20 Hz, *C*HMe$_2$), 18.61 (t of vt, $^2J_{CP}$ 2 Hz, $^3J_{PtC}$ 24 Hz, CHMe$_2$), 17.33 (d, $^3J_{PtC}$ 26 Hz, CHMe$_2$). $^{19}F$ $\{^1H\}$ ($CD_2Cl_2$) −73.26 (d, $^1J_{PF}$ 711 Hz). $^{31}P\{^1H\}$ ($CD_2Cl_2$) 79.82 (t, $^1J_{PPt}$ 2637 Hz), −144.49 (sept, $^1J_{PF}$ 712 Hz). Anal. Calc. for $C_{16}H_{39}BrN_2P_3SPtF_6$: C, 28.39; H, 5.96; N, 6.21; Found: C, 28.53; H, 6.20; N, 6.12.

### Synthesis of 13a, 14a and 16a using 1HCl

These complexes were prepared in a similar fashion and thus only one preparation is detailed. **14a**: A solution of **1HCl** in THF (81 mg, 0.216 mmol; 2 mL) was added to a bright yellow slurry of $Pd(PPh_3)_4$ and THF (250 mg, 0.216 mmol; 2 mL) in a scintillation vial equipped with a stir bar immediately giving a cloudy pale yellow mixture. The reaction mixture was stirred for 2 hours at which point it was dried to a pale-yellow solid. The crude product was washed with hexane (3 × 4 mL) and the solution was decanted off before the product was dried *in vacuo*. The white product was obtained in 93% yield (96 mg, 0.201 mmol).

(**13a**): Starting with **1HCl** (68 mg, 0.182 mmol), $(COD)_2Ni$ (50 mg, 0.182 mmol), the orange product was obtained in 88% yield (69 mg, 0.160 mmol).

(**16a**): Starting with **1HCl** (75 mg, 0.201 mmol), $(PPh_3)_4Pd$ (100 mg, 0.173 mmol), the pale yellow product was obtained in 90% yield (103 mg, 0.181 mmol).

### Synthesis of [κ$^3$*P,N,P*-NH((CH$_2$)$_2$NHPiPr$_2$)$_2$Pd(C$_6$H$_4$F)]Cl (19) and [κ$^3$*P,S,P*-S((CH$_2$)$_2$NHPiPr$_2$)$_2$Pd(C$_6$H$_4$F)]Cl (20)

These complexes were prepared in a similar fashion and thus only one preparation is detailed. A solution of **1** (58 mg, 0.173 mmol) in THF (2 mL) was added to a yellow slurry of $Pd(PPh_3)_4$ (200 mg, 0.173 mmol) and THF (2 mL) in a scintillation vial equipped with a stir bar. The reaction mixture was allowed to stir for 30 min at which point a clear yellow solution was obtained. A solution of *o*-$ClFC_6H_4$ and THF (0.5 mL; 2 mL) was combined with the reaction mixture giving no

immediate change. The reaction mixture was transferred to a 100 mL tube bomb and stirred for 12 hours at 65 °C at which point it was dried to an orange solid. The crude product was washed with hexane (3 × 4 mL) and the solution was decanted off before the product was dried *in vacuo*. The off-white solid was dissolved in $CH_2Cl_2$ and benzene and diethyl ether were layered on top of the $CH_2Cl_2$ layer. The mixture was allowed to slowly mix overnight giving colorless crystals and a pale-yellow solution. The solution was decanted off and the crystals were dried. The white product was obtained in 64% yield (63 mg, 0.110 mmol).

**19**: $^1$H ($CD_2Cl_2$) 7.33 (m, 2H, ArH $C_6$, [a/b]), 7.00 (m, 2H, ArH $C_3$, [a/b]), 6.93 (m, 2H, ArH $C_5$, [a/b]), 6.76 (m, 2H, ArH $C_4$, [a/b]), 4.48 (bs, 1H, $R_2NH$ [b]), 4.15 (bs, 1H, $R_2NH$ [a]), 3.44 (m, 4H, $CH_2$ [a/b]), 3.34 (m, 4H, $CH_2$ [a/b]), 3.25 (s, 2H, NH [a/b]), 3.14 (m, 2H, $CH_2$ [a or b]), 3.09 (m, 2H, $CH_2$ [a or b]), 3.00 (s, 2H, NH [a/b]), 2.76 (m, 2H, $CH_2$ [a or b]), 2.00 (m, 4H, $^3J_{HH}$ 6 Hz, C*H*Me$_2$ [a/b]), 1.87 (m, 2H, $^3J_{HH}$ 6 Hz, C*H*Me$_2$ [a/b]), 1.78 (m, 2H, $^3J_{HH}$ 6 Hz, C*H*Me$_2$ [a/b]), 1.30 (m, 12H, $^3J_{HH}$ 6 Hz, CH*Me*$_2$ [a/b]), 1.19 (m, 12H, $^3J_{HH}$ 6 Hz, CH*Me*$_2$ [a/b]), 1.10 (m, 12H, $^3J_{HH}$ 6 Hz, CH*Me*$_2$ [a/b]), 0.99 (m, 12H, $^3J_{HH}$ 6 Hz, CH*Me*$_2$ [a/b]). $^{13}$C{$^1$H} ($CD_2Cl_2$) partial: 139.93 (d of t, $J_{CF}$ 16 Hz, $J_{CP}$ 2.44 Hz, Ar), 139.51 (d of t, $J_{CF}$ 16 Hz, $J_{CP}$ 3 Hz, Ar), 126.05 (m, overlapping Ar), 124.33 (bs, Ar), 124.10 (bs, Ar), 123.85 (m, $C_{ipso}$), 123.27 (m, $C_{ipso}$), 114.60 (m, overlapping Ar), 53.25 (m, $CH_2$ obscured by $CH_2Cl_2$), 52.79 (bs, $CH_2$), 44.81 (vt, $J_{CP}$ 3 Hz, $CH_2$), 44.29 (vt, $J_{CP}$ 3 Hz, $CH_2$), 29.38 (vt, $^1J_{CP}$ 14 Hz, *C*HMe$_2$), 28.79 (vt, $^1J_{CP}$ 15 Hz, *C*HMe$_2$), 28.08 (vt, $^1J_{CP}$ 14 Hz, *C*HMe$_2$), 27.80 (vt, $^1J_{CP}$ 15 Hz, *C*HMe$_2$), 18.69 (bs, CH*Me*$_2$), 18.00 (bs, CH*Me*$_2$), 17.84 (bs, CH*Me*$_2$), 17.30 (bs, CH*Me*$_2$), 16.98 (bs, CH*Me*$_2$), 16.48 (bs, CH*Me*$_2$), 15.94 (bs, CH*Me*$_2$). $^{19}$F {$^1$H} ($CD_2Cl_2$) −85.38 (t, $^4J_{FP}$ 6 Hz, [b]), −85.85 (t, $^4J_{FP}$ 6 Hz, [a]). $^{31}$P{$^1$H} ($CD_2Cl_2$) 75.00 (d, $^4J_{PF}$ 6 Hz, [a]), 74.68 (d, $^4J_{PF}$ 6 Hz, [b]). Anal. Calc. for $C_{22}H_{43}N_3P_2PdClF$: C, 46.14; H, 7.57; N, 7.34; Found: C, 45.94; H, 7.62; N, 7.42.

**20**: Starting with **2** (61 mg, 0.173 mmol), $(PPh_3)_4Pd$ (200 mg, 0.173 mmol), and *o*-$ClFC_6H_4$ (0.5 mL) the white product was obtained in 58% yield (59 mg, 0.100 mmol). $^1$H ($CD_2Cl_2$) 7.33 (m, 1H, ArH $C_6$), 7.04 (m, 1H, $^3J_{HH}$ 8 Hz, ArH $C_3$), 6.94 (t, 1H, $^3J_{HH}$ 7.82 Hz, ArH $C_5$), 6.77 (t, 1H, $^3J_{HH}$ 8 Hz, ArH $C_4$), 3.96 (bs, 2H, NH), 3.56 (m, 2H, $CH_2$), 3.33 (m, 2H, $CH_2$), 2.96 (m, 2H, $CH_2$), 2.73 (m, 2H, $CH_2$), 1.91 (m, 2H, $^3J_{HH}$ 8 Hz, C*H*Me$_2$), 1.84 (m, 2H, $^3J_{HH}$ 8 Hz, C*H*Me$_2$), 1.21 (m, 6H, $^3J_{HH}$ 8 Hz, CH*Me*$_2$), 1.11 (m, 12H, $^3J_{HH}$ 8 Hz, CH*Me*$_2$), 0.92 (m, 6H, $^3J_{HH}$ 8 Hz, CH*Me*$_2$). $^{13}$C{$^1$H} ($CD_2Cl_2$) 164.52 (d of t, $^1J_{CF}$ 227 Hz, $^3J_{CP}$ 3 Hz, $ArC_2$ CF), 139.47 (d of t, $J_{CF}$ 17 Hz, $J_{CP}$ 3 Hz, $ArC_6$), 127.68 (d of t, $^2J_{CF}$ 42 Hz, $^2J_{CP}$ 10 Hz, $ArC_1$ C–F), 126.72 (d of t, $J_{CF}$ 7 Hz, $J_{CP}$ 2 Hz, $ArC_3$), 124.68 (s, $ArC_5$), 114.73 (d, $J_{CF}$ 29 Hz, $ArC_4$), 46.24 (vt, $J_{CP}$ 3 Hz, $CH_2$), 37.55 (s, $CH_2$), 29.33 (vt, $^1J_{CP}$ 15 Hz, *C*HMe$_2$), 28.52 (vt, $^1J_{CP}$ 14 Hz, *C*HMe$_2$), 18.89 (s, CH*Me*$_2$), 17.65 (m, CH*Me*$_2$), 17.57 (bs, CH*Me*$_2$), 16.40 (bs, CH*Me*$_2$). $^{19}$F {$^1$H} ($CD_2Cl_2$) −83.56 (t, $^4J_{FP}$ 5 Hz). $^{31}$P{$^1$H} ($CD_2Cl_2$) 74.55 (s). Anal. Calc. for $C_{22}H_{42}N_2P_2SPdClF$: C, 44.81; H, 7.18; N, 4.75; Found: C, 44.66; H, 7.30; N, 5.01.

X-ray data collection, reduction, solution and refinement single crystals were coated in Paratone-N oil in the glovebox, mounted on a MiTegen Micromount and placed under an $N_2$ stream. The data were collected on a Bruker Apex II diffractometer and data collection strategies were determined employing Bruker provided Apex software. 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.[40] 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.

## Results and discussion

A solution of **1** in $CH_2Cl_2$ was added to a yellow suspension of dmeNi$Cl_2$ in $CH_2Cl_2$ giving a clear orange solution. After work-up, **3a** was obtained in 90% yield. The $^{31}$P{$^1$H} NMR spectrum displayed a single resonance at 62.6 ppm, consistent with a symmetric coordination of the phosphine donors. The solid state structure was determined crystallographically (Fig. 1(a)) confirming the pseudo-square planar geometry about the Ni cation of formula [κ$^3$*P*,*N*,*P*-NH((CH$_2$)$_2$NHPiPr$_2$)$_2$NiCl]Cl. The P–Ni bond lengths are 2.2275(7) Å and 2.2529(7) Å, the N–Ni bond length is 1.949(2) Å and the Ni–Cl bond length is 2.1664(7) Å. The P–Ni–P and N–Ni–Cl bond angles are 171.90 (2)° and 177.16(6)°, respectively, consistent with a slightly distorted square planar geometry.

Complex **3a** is only sparingly soluble in most solvents, and thus halide exchange was used to improve solubility. The conversion of **3a** to [κ$^3$*P*,*N*,*P*-NH((CH$_2$)$_2$NHPiPr$_2$)$_2$NiI]I (**3b**) was completed by the addition of two equivalents of $Me_3SiI$ to a $CH_2Cl_2$ solution of **3a**. A sharp color change from orange to purple is observed, and **3b** was obtained quantitatively following manipulation. While the $^1$H NMR spectrum remains similar to that observed in **3a**, aside from an up-field shift of the central NH proton resonance from 4.73 to 3.44 ppm, the $^{31}$P{$^1$H} signal is shifted downfield by 15.6 ppm to 78.2 ppm for **3b**. This species was also prepared directly in high yields from the reaction of **1** with $NiI_2$ in $CH_2Cl_2$.

The analogous reaction of a $CH_2Cl_2$ solution of **1** and a yellow-orange suspension of $(PhCN)_2PdCl_2$ afforded a clear yellow solution which ultimately gave the product [κ$^3$*P*,*N*,*P*-NH((CH$_2$)$_2$NHPiPr$_2$)$_2$PdCl]Cl (**4a**) in 94% yield. The $^{31}$P{$^1$H} NMR spectrum shows a singlet at 71.6 ppm and the $^1$H NMR spectral data was consistent with a symmetrically bound tridentate ligand. X-ray quality crystals of **4a** confirmed the structure (Fig. 1(b)). The two P–Pd, N–Pd and Pd–Cl bond lengths are 2.3172(19) Å and 2.3387(19) Å, 2.097(5) Å and 2.2913(17) Å, respectively, while the N–Pd–Cl and P–Pd–P bond angles are 170.48(6)° and 177.1(2)° indicative of a distorted square planar geometry. To improve solubility, the analogous [κ$^3$*P*,*N*,*P*-NH((CH$_2$)$_2$NHPiPr$_2$)$_2$PdI]I (**4b**) was prepared either quantitatively *via* the reaction of **4a** with two equivalents of $Me_3SiI$ or in 85% yield from the reaction of $PdI_2$ with **1**. While the major spectroscopic characteristics of **4b** are similar to **4a**, the $^{31}$P{$^1$H} NMR resonance of **4b** is downfield at 79.7 ppm while the $^1$H resonance for the central NH shifts upfield to 4.85 ppm.

**Table 1** Crystallographic data

| | **2a** | **3a** | **5a** | **6a** | **8a** | **9a** | **14b** | **16b** |
|---|---|---|---|---|---|---|---|---|
| Formula | $C_{16}H_{39}Cl_2N_3NiP_2$ | $C_{16}H_{39}Cl_2N_3P_2Pd$ | $C_{17}H_{40}Cl_4N_2NiP_2S$ | $C_{17}H_{40}Cl_4N_2P_2PdS$ | $C_{17}H_{42}ClN_3P_2Pd$ | $C_{18}H_{43}Cl_3N_2P_2PdS$ | $C_{16}H_{39}F_6N_3P_3Pd$ | $C_{16}H_{40}F_6N_3P_3Pt$ |
| Form. wt | 465.05 | 512.74 | 567.02 | 614.71 | 492.33 | 594.29 | 586.81 | 676.51 |
| Cry. sys. | Triclinic | Orthorhombic | Triclinic | Triclinic | Monoclinic | Triclinic | Monoclinic | Triclinic |
| Space grp | $P\bar{1}$ | *Pna*2(1) | $P\bar{1}$ | $P\bar{1}$ | *C*2/*c* | $P\bar{1}$ | *P*2(1)/*n* | $P\bar{1}$ |
| *a* (Å) | 15.6535(9) | 23.205(6) | 8.4687(10) | 8.4324(4) | 21.040(3) | 8.4214(15) | 10.5371(4) | 10.4144(5) |
| *b* (Å) | 18.4051(10) | 10.981(2) | 11.3598(13) | 11.4053(6) | 8.6683(9) | 11.430(2) | 8.8800(4) | 10.5406(6) |
| *c* (Å) | 27.970(2) | 8.9992(19) | 15.5241(18) | 15.4027(8) | 27.228(3) | 15.337(3) | 27.0360(9) | 12.3384(7) |
| $\alpha$ (°) | 104.784(3) | 90.00 | 82.318(7) | 81.069(2) | 90.00 | 81.066(8) | 90.00 | 84.575(2) |
| $\beta$ (°) | 97.910(3) | 90.00 | 74.896(7) | 74.771(2) | 104.473(9) | 74.944(8) | 93.029(2) | 67.522(2) |
| $\gamma$ (°) | 109.773(2) | 90.00 | 68.538(6) | 68.760(2) | 90.00 | 69.118(8) | 90.00 | 88.505(2) |
| *V* (Å$^3$) | 7106.6(8) | 2293.2(9) | 1340.7(3) | 1329.25(12) | 4808.2(10) | 1328.7(4) | 2526.21(17) | 1245.85(12) |
| *Z* | 12 | 4 | 2 | 2 | 8 | 2 | 4 | 2 |
| Temp (K) | 150(2) | 150(2) | 150(2) | 150(2) | 150(2) | 150(2) | 150(2) | 150(2) |
| *d*(calc) (g cm$^{-1}$) | 1.304 | 1.485 | 1.405 | 1.536 | 1.360 | 1.485 | 1.543 | 1.803 |
| *R*(int) | 0.0409 | 0.0686 | 0.0627 | 0.0287 | 0.0506 | 0.0349 | 0.0281 | 0.0240 |
| $\mu$ (mm$^{-1}$) | 1.184 | 1.187 | 1.327 | 1.307 | 1.021 | 1.207 | 0.976 | 5.877 |
| Total data | 117 303 | 16 227 | 15 080 | 22 016 | 21 062 | 21 331 | 17 068 | 17 256 |
| # indpndt reflns | 32 132 | 4271 | 4503 | 6060 | 5482 | 6094 | 4447 | 4376 |
| Reflns $F_0 > 2\sigma(F_0)$ | 23 501 | 3147 | 2723 | 5230 | 4002 | 5046 | 3948 | 4217 |
| Flack param. | — | 0.14(5) | — | — | — | — | — | — |
| Variables | 1297 | 217 | 244 | 256 | 217 | 244 | 262 | 266 |
| *R* (>2$\sigma$) | 0.0397 | 0.0464 | 0.0566 | 0.0244 | 0.0394 | 0.0297 | 0.0400 | 0.0155 |
| $R_w$ (all data) | 0.0998 | 0.1001 | 0.1568 | 0.0577 | 0.0845 | 0.0710 | 0.1033 | 0.0358 |
| GOF | 1.013 | 1.047 | 1.049 | 1.019 | 1.028 | 1.019 | 1.026 | 1.039 |

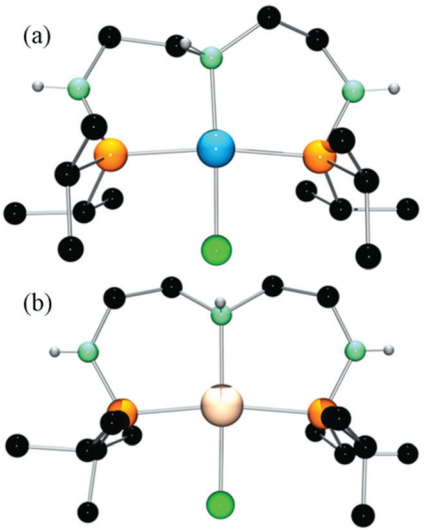



**Fig. 1** POV-Ray depiction of the cations (a) **3a** and (b) **4a**: C: black, N: aquamarine, P: orange, Cl: green, Ni: sky blue, Pd: lightwood. Hydrogen atoms, except for NH, are omitted for clarity. Counter-ion also omitted for clarity.

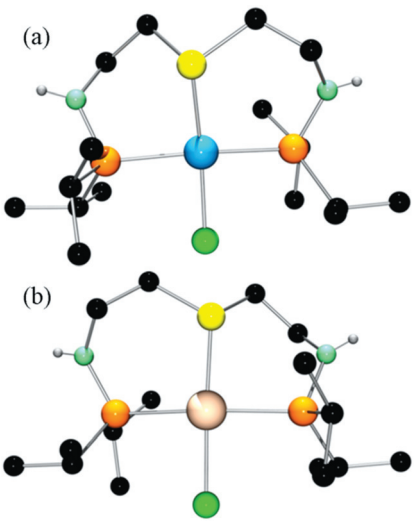



**Fig. 2** POV-Ray depiction of (a) **5a** and (b) **6a**: C: black, N: aquamarine, S: yellow, P: orange, Cl: green, Ni: sky blue, Pd: lightwood. Hydrogen atoms except for NH are omitted for clarity. Counter-ion also omitted for clarity.

Syntheses of analogous products incorporating the ligand $S((CH_2)_2NHPiPr_2)_2$ (**2**) were also undertaken. Reaction of **2** with $dmeNiCl_2$ in $CH_2Cl_2$ gives a red-orange solution that upon work-up yields [$\kappa^3$*P,S,P*-$S((CH_2)_2NHPiPr_2)_2NiCl$]Cl (**5a**) as an orange solid. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 68.5 ppm and the $^1H$ NMR is consistent with the formulation. The four coordinate geometry at the Ni center of the cation was also confirmed crystallographically (Fig. 2(a)). The P–Ni, S–Ni and Ni–Cl bond lengths are 2.2371(16) Å and 2.2578(16) Å, 2.1702(18) Å and 2.1617(19) Å, respectively, while the S–Ni–Cl and P–Ni–P bond angles are 168.48(8)° and 172.23(7)°, indicative of a distorted square planar geometry.

The solid state structure of **5a** stands in contrast to $\kappa^3$*P,S,P*-$S((CH_2)_3PPh_2)_2NiCl_2$ as previously reported by Cheng *et al.*[41] which adopted a square pyramidal geometry with a meridional tridentate ligand and a chloride anion occupying the apical position. This difference in complex geometry presumably results from the more electron rich nature of the Ni-center in **5a** compared to that in $\kappa^3$*P,S,P*-$S((CH_2)_3PPh_2)_2NiCl_2$ reflecting the strong donor ability of the dialkyl-aminophosphine ligand **2**.

As with the formation of **3b**, the synthesis of [$\kappa^3$*P,S,P*-$S((CH_2)_2NHPiPr_2)_2NiI$]I (**5b**) was achieved either *via* direct reaction of $NiI_2$ and **2**, or by reaction of **5a** with $Me_3SiI$. Both procedures gave high yields. The $^{31}P\{^1H\}$ NMR spectrum of **5b** showed a shift downfield to 78.4 ppm upon replacement of the halide with I.

The reaction of **2** with $(PhCN)_2PdCl_2$ or $PdI_2$ gives [$\kappa^3$*P,S,P*-$S((CH_2)_2NHPiPr_2)_2PdCl$]Cl (**6a**) and [$\kappa^3$*P,S,P*-$S((CH_2)_2NHPiPr_2)_2PdI$]I (**6b**), both as yellow solids, in high yields. In both cases, the $^{31}P\{^1H\}$ NMR spectrum shows a singlet, at 76.9 ppm and 77.8 ppm, respectively, consistent with symmetric coordination of the ligand. The connectivity of **6a** was further confirmed crystallographically, where again a square planar geometry is observed with the P–Pd bond distances being 2.3316(5) Å and 2.3476(5) Å, the S–Pd bond distance being 2.2963(5) Å, and the Pd–Cl bond distance being 2.3089(5) Å (Fig. 2(b)).

Attempts to prepare Pt analogs *via* reactions of **1** and $(PhCN)_2PtCl_2$ or $PtI_2$ in $CH_2Cl_2$ gave only a mixture or impure products. However the analogous reactions of **2** with $(PhCN)_2PtCl_2$ gave colorless solutions that after work-up yields [$\kappa^3$*P,S,P*-$S((CH_2)_2NHPiPr_2)_2PtCl$]Cl (**7a**) as a fluffy white solid. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 66.1 ppm with Pt satellites showing a $^1J_{P-Pt}$ coupling constant of 2313 Hz. Likewise, the reaction of **2** with $PtI_2$ gave [$\kappa^3$*P,S,P*-$S((CH_2)_2NHPiPr_2)_2PtI$]I (**7b**) as an off-white solid that exhibits a $^{31}P\{^1H\}$ resonance at 64.1 ppm with Pt satellites showing a $^1J_{P-Pt}$ of 2277 Hz.

Reaction of **1** or **2** with (COD)PdMeCl affords facile routes to [$\kappa^3$*P,N,P*-$NH((CH_2)_2NHPiPr_2)_2PdMe$]Cl (**8a**) and [$\kappa^3$*P,S,P*-$S((CH_2)_2NHPiPr_2)_2PdMe$]Cl (**9a**) in high yields (Scheme 2). The compounds **8a** and **9a**, both off-white solids, exhibited a single resonance in the $^{31}P\{^1H\}$ NMR spectra at 79.8 and 81.1 ppm, respectively, as well as diagnostic upfield triplets at 0.19 and 0.51 ppm in the $^1H$ NMR spectra, typical for the Pd–methyl fragments.[42] Both complexes were characterized crystallographically (Fig. 3). In **8a**, the Pd–C, and Pd–P bond lengths are 2.065 (3) Å, 2.3168(9) Å and 2.3181(9) Å, respectively, while in **9a** the same analogous lengths are 2.071(3) Å, 2.3091(8) Å and 2.3230(7) Å, respectively. In both cases, the Pd–Me bond is similar in length to that previously reported for $\kappa^3$*P,N,P*-$NH((CH_2)_2PiPr_2)PdMeCl$ (2.075 Å), and the P–Pd bond lengths in **8a** and **9a** are also similar to those reported for $\kappa^3$*P,N,P*-$NH((CH_2)_2PiPr_2)_2PdMeCl$ (2.2960–2.2970 Å).[42]

### Oxidative additions to give M-alkyl, hydride and aryl derivatives

We have previously communicated the synthesis of [$\kappa^3$*P,N,P*-$HN(CH_2CH_2NHPiPr_2)_2NiMe$]I (**10**) from the reaction of $Ni(COD)_2$, **1** and MeI in 79% yield.[39] In a similar fashion, Pd–alkyl analogues incorporating the ligands **1** or **2** were prepared *via* the reaction with $Pd(PPh_3)_4$ and MeI. Notably, there is no

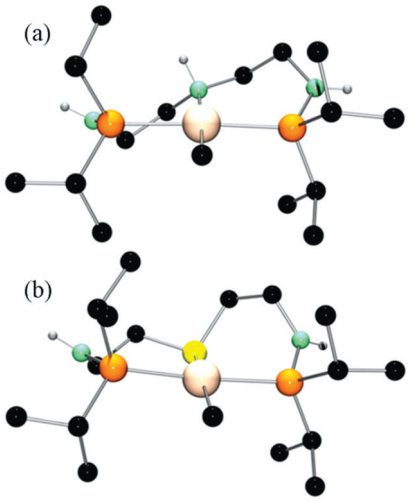
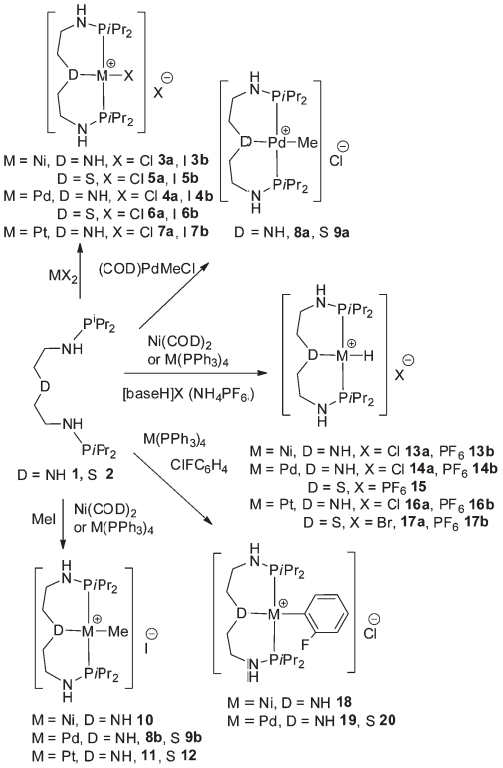



**Fig. 3** POV-Ray depictions of (a) **8a** and (b) **9a**: C: black, N: aquamarine, S: yellow, P: orange, Cl: green, Pd: lightwood. Hydrogen atoms, except for NH, are omitted for clarity. Counter-ion also omitted for clarity.




**Scheme 2** Synthesis of PNP and PSP Ni, Pd and Pt complexes.

reaction between **1** or **2** and $Pd(PPh_3)_4$, even with prolonged heating. However, addition of MeI to solutions of **1** or **2** and $Pd(PPh_3)_4$ in THF results in the *in situ* generation of $(PPh_3)_2PdMeI$[43] which reacts with the tridentate ligands. Subsequent work-up in both cases afforded white powders, $[\kappa^3P,N,P\text{-HN}(CH_2CH_2NHPiPr_2)_2PdMe]I$ (**8b**) and $[\kappa^3P,S,P\text{-S}(CH_2CH_2NHPiPr_2)_2PdMe]I$ (**9b**), respectively. The $^{31}P\{^1H\}$ NMR spectra for **8b** and **9b** show singlets at 79.6 ppm and 81.7 ppm, respectively. Both $^1H$ NMR and $^{13}C\{^1H\}$ NMR spectra reveal diagnostic upfield resonances consistent with the presence of a Pd–Me fragment (**8b**: $^1H$: 0.22 ppm, $^{13}C\{^1H\}$: −12.66 ppm; **9b**: $^1H$: 0.52 ppm, $^{13}C\{^1H\}$: −6.00 ppm).[42]

The analogous reactions were also carried out using $Pt(PPh_3)_4$ as a platinum source. The addition of a THF solution of **1** to an off-white solution of $Pt(PPh_3)_4$ gives no immediate change. Upon addition of one equivalent of MeI, a white precipitate formed. After work-up to remove free phosphine, $[\kappa^3P,N,P\text{-NH}((CH_2)_2NHPiPr_2)_2PtMe]I$ (**11**) was obtained in 86% yield. The $^{31}P\{^1H\}$ NMR spectrum contains a signal at 74.0 ppm with Pt satellites having a $^1J_{Pt-P}$ coupling constant of 2842 Hz. The $^1H$ NMR spectrum shows a triplet at 0.38 ppm with $^{195}Pt$ satellite signals with P–H and Pt–H couplings of 7 Hz and 76 Hz, respectively. A diagnostic signal attributable to the metal-bound carbon atom is observed in the $^{13}C\{^1H\}$ spectrum at −27.19 ppm with a C–P coupling constant of 8 Hz. Similarly, the reaction of **2** with $Pt(PPh_3)_4$ followed by the addition of MeI results in the formation of $[\kappa^3P,S,P\text{-S}((CH_2)_2NHPiPr_2)_2PtMe]I$ (**12**) as a white solid, which exhibits a $^{31}P\{^1H\}$ signal centered at 71.5 ppm with Pt-satellites and a Pt–P coupling constant of 2707 Hz. As was the case with **11**, a triplet of triplets is observed in the $^1H$ NMR at 0.62 ppm with the corresponding $^{13}C$ resonance at −15.06 ppm, confirming the presence of the Pt–methyl fragment.

We have also previously described the synthesis of analogous Ni–hydride complexes employing a similar methodology.[39] Thus, oxidative addition reaction involving $Ni(COD)_2$, the ligand **1** and $NEt_3HCl$ afforded $[\kappa^3P,N,P\text{-HN}(CH_2CH_2NHPiPr_2)_2NiH]Cl$ (**13a**) in 87% yield. The characteristic hydride triplet resonance was seen in the $^1H$ NMR spectrum at −20.90 ppm with P–H coupling of 81 Hz while the $^{31}P\{^1H\}$NMR spectrum showed a singlet at 80.00 ppm. Straightforward anion metathesis affords $[\kappa^3P,N,P\text{-HN}(CH_2CH_2NHPiPr_2)_2NiH]PF_6$ (**13b**) as orange crystals in 71% yield. The structure of **13b** was previously described. This same strategy can be employed to access Pd and Pt analogues using $Pd(PPh_3)_4$ and $Pt(PPh_3)_4$ as synthons. In this manner, $[\kappa^3P,N,P\text{-NH}((CH_2)_2NHPiPr_2)_2MH]X$ (M = Pd, X = Cl **14a**, $PF_6$ **14b**; M = Pt, X = Cl **16a**, $PF_6$ **16b**) and $[\kappa^3P,S,P\text{-S}((CH_2)_2NHPiPr_2)_2MH]X$ (M = Pd, X = $PF_6$ **15**: M = Pt, X = Br **17a**, $PF_6$ **17b**) were prepared in yields ranging from 74–93% yield. These species exhibit typical hydride resonance in the range of −9 to −17 ppm. Compounds **14b** and **16b** were crystallographically characterized (Fig. 4) confirming the pseudo-square planar geometry about the metals although the hydride could not be found in **14b**. In the case of **16b** the Pt–H bond length was found to be 1.693 Å, which is significantly elongated compared to that reported for *trans*-$[(iPr_3P)_2Pt(H)(OEt_2)]^+$ (1.53 Å).[44] As all of these reactions required the use of an external proton source, initial protonation of either **1** or **2** avoids the need for the additional reagent. Thus addition of a solution of HCl in diethylether to a solution of **1** gave **1HCl** as a waxy solid. The most noticeable spectroscopic change was the downfield shift of the $^{31}P\{^1H\}$ NMR singlet to 70.7 ppm. This allowed for **13a**, **14a**, **16a** to be prepared *via* the reactions employing **1HCl** and the appropriate metal (0) starting material. In these cases the ligand itself acts as the proton source for hydride formation.

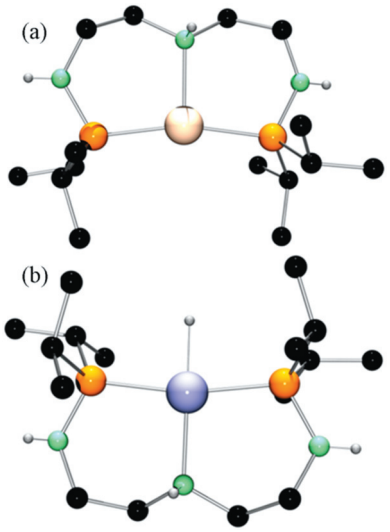
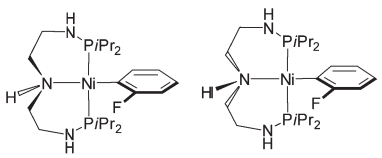



**Fig. 4** POV-Ray depictions of (a) **14b** and (b) **16b**; C: black, N: aquamarine, S: yellow, P: orange, Cl: green, Pd: lightwood. Pt: light steel blue, Hydrogen atoms, except for NH and Pt–H, are omitted for clarity. Counter-ion also omitted for clarity.



**Scheme 3** The rotational isomers of the cation of **18**.

Employing this oxidative addition strategy, the combination of **1** and $Ni(COD)_2$, 1-Cl-2-$FC_6H_4$ was shown to afford [$\kappa^3$*P,N,P*-$HN(CH_2CH_2NHPiPr_2)_2Ni(o\text{-}C_6H_4F)$]Cl (**18**) in 86% yield. The $^{19}F\{^1H\}$ NMR spectrum of **18** shows resonances at −84.11 and −84.23 ppm, while the $^{31}P\{^1H\}$ NMR spectra gave rise to signals at 70.58 and 69.53 ppm. These data, together with analogous $^1H$ NMR data were consistent with the presence of two conformational isomers, attributable to the relative orientation of the *ortho*-F and the NH fragments (Scheme 3). Similarly, the analogous reactions of $Pd(PPh_3)_4$ afforded no reactions at room temperature. However, on heating to 65 °C for 48 hours, the species [$\kappa^3$*P,N,P*-$NH((CH_2)_2NHPiPr_2)_2Pd(o\text{-}C_6H_4F)$]Cl (**19**) and [$\kappa^3$*P,S,P*-$S((CH_2)_2NHPiPr_2)_2Pd(o\text{-}C_6H_4F)$]Cl (**20**) were isolated in 64% and 58% yield, respectively. Despite extensive efforts to extend the reactions of 1-Cl-2-$FC_6H_4$ to the analogous Pt species, no clean products could be obtained even on heating to 65 °C for extended periods (24–72 hours). Similar to **18**, the $^{31}P\{^1H\}$, $^{19}F\{^1H\}$ and $^1H$ NMR data for **19** were consistent with the presence of two isomeric forms again attributable to the possible orientation of the *ortho*-F relative to the central NH of the tridentate ligand, inferring restricted rotation about the Pd–C bond. In contrast, only one resonance is observed in the $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectra for **20** at 74.6 and −83.6 ppm, respectively. Similarly the $^1H$ and $^{13}C\{^1H\}$ data infer free rotation about the Pt–C bond. Weaker sigma donation by the S in **20** relative to NH in **19** presumably diminishes back-bonding from Pd to the aryl group, lengthening the Pd–C bond length in **20** than that in **19**, thus allowing free rotation about the Pd–C bond. In addition, weaker donor from S in **20** presumably facilitates inversion of the chiral S by a dissociation–re-association mechanism.

## Conclusion

In summary, we have described the syntheses and characterized a series of Ni(II), Pd(II) and Pt(II) complexes incorporating tridentate bis-aminophosphine ligands. Employing an oxidative addition strategy metal hydride, alkyl and aryl derivatives are readily accessible. It is these latter species that are the subject of on-going reactivity studies that will be reported in due course.

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