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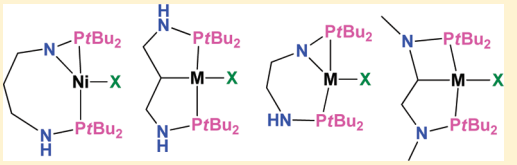
# Nickel(II) and Palladium(II) Bis-Aminophosphine Pincer Complexes

Erin A. Gwynne and Douglas W. Stephan*

Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada M5S 3H6

Supporting Information

**ABSTRACT:** The aminophosphine ligands $CH_2(CH_2NHPtBu_2)_2$ (**1**), $(CH_2NHPtBu_2)_2$ (**2**), and $(CH_2NMePtBu_2)_2$ (**3**) were prepared from the corresponding amines and $ClPtBu_2$. The ligand **1** reacts with $PdI_2$ to give the pincer complex ($\kappa^3$*P,C,P*-$CH(CH_2NHPtBu_2)_2$)PdI (**4**). The analogous reaction of **1** with $NiCl_2$(dme) gave a the purple product ($\kappa^3$*P,N,P*-$tBu_2PNH(CH_2)_3NPtBu_2$)NiCl (**5**), which contains a strained three-membered P−N−Ni ring. Subsequent reaction of **5** with $B(C_6F_5)_3$ resulted in conversion to ($\kappa^3$*P,C,P*-$CH(CH_2NHPtBu_2)_2$)NiCl (**6**). The related reaction of the aminophosphine ligand **2** with $PdI_2$ and with $NiCl_2$(dme) led, in both cases, to the complexes ($\kappa^3$*P,N,P*-$tBu_2PNH(CH_2)_2NPtBu_2$)MX (MX = PdI (**7**), NiCl (**8**)), respectively, whereas the reaction of **3** with $PdX_2$ gave ($\kappa^3$*P,C,P*-$tBu_2PN(Me)CHCH_2N(Me)PtBu_2$)PdX (X = I (**9**), Br (**10**), Cl (**11**)). The analogous reaction of **3** with $NiCl_2$(dme) afforded $[(tBu_2PH)(NMe)(CH_2)_2(NMe)(tBu_2P)NiCl_3]$, (**12**), which upon treatment with $B(C_6F_5)_3$ afforded the species ($\kappa^3$*P,C,P*-$tBu_2PN(Me)CHCH_2N(Me)PtBu_2$)NiCl (**13**). Crystallographic studies of **4**−**6**, **8**, **9**, **11**, and **12** are reported. The implications of these results are considered.




## INTRODUCTION

Chelating ligands have proven instrumental in the development of new catalysts; furthermore trans-chelating "pincer" ligands have garnered considerable attention over the years.[1−13] The most extensively investigated pincer complexes feature ligands based on a meta-substituted arene skeleton (PCP). Variations of the PCP-pincer framework have been shown to alter the electronic and steric properties of the corresponding metal complexes, resulting in unique reactivity.[14,15]

Aminophosphine chelating ligands of the form (linker)-$(NR'PR_2)_2$ have also garnered attention, as such ligands are readily prepared from diamines and chlorophosphines.[5,16] While linked diaminophosphine ligands such as $(CH_2N(R')PR_2)_2$ (R′ = H, alkyl; R = alkyl, aryl) have been reported by Wollins,[17] Gusev,[9] Vogt,[16] and others,[18−21] investigations of PCP aminophosphine-based pincer ligand complexes have received less attention.[10] We were drawn to these systems, as such ligands offer adjacent P and N donors, suggesting the possibility of unique binding modes and thus subsequent reactivity. In this regard, the only report in which the N atom of an aminophosphine has been shown to participate in binding to a metal was recently reported by Palacios et al. In this case a bis-aminophosphine ligand was shown to bind to Ru via both P atoms as well as one of the amino NH groups, affording the Ru cation $[Cp^*Ru(\kappa^3P,N,P\text{-}(iPr_2PNH)_2C_6H_{10}]^+$.[21] In this paper, we describe the synthesis and characterization of Ni and Pd complexes of bis-aminophosphine chelating ligands. Interestingly, these ligands are shown to readily adopt two tridentate binding modes. Participation of the secondary N adjacent to P affords $\kappa^3$*P,N,P* ligands that incorporate three-membered NPM metallacycles. Alternatively, metalation of the alkyl chain in the ligand backbone affords $\kappa^3$*P,C,P* pincer complexes.

## EXPERIMENTAL SECTION

All preparations were performed under an atmosphere of dry, $O_2$-free $N_2$ employing both Schlenk line and inert-atmosphere glovebox techniques. Solvents ($CH_2Cl_2$, $Et_2O$, and pentane) were purified employing a Grubbs type column system manufactured by Innovative Technology. $^1H$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were acquired on a Bruker Avance 400 MHz spectrometer, a Varian Mercury 300 MHz spectrometer, or a Varian Mercury 400 MHz spectrometer. $^1H$ NMR resonances were referenced internally to the residual protonated solvent resonances, $^{13}C$ resonances were referenced internally to the deuterated solvent resonances, and $^{31}P$ resonances were referenced externally to 85% $H_3PO_4$. $^1H-^{13}C$ HSQC experiments were carried out using conventional pulse sequences to aid in the assignment of peaks in $^{13}C\{^1H\}$ NMR spectroscopy. Coupling constants ($J$) are reported as absolute values. All glassware was dried overnight at 120 °C and evacuated for 1 h prior to use. Combustion analyses were performed in house employing a Perkin-Elmer 2400 Series II CHNS Analyzer. All diamines were purchased from Aldrich and degassed prior to use. $tBu_2PCl$ was purchased from Strem Chemical Co. All other chemicals were purchased from Aldrich Chemical Co. and used without further purification. THF-$d_8$ was purchased in 1 g ampules and dried over 4 Å activated molecular sieves prior to use. $C_6D_6$ and toluene-$d_8$ were vacuum-distilled from Na/benzophenone and freeze−pump−thaw degassed (×3). 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.

**Synthesis of $CH_2(CH_2NHPtBu_2)_2$ (1).**[9]. A solution of 1,3-diaminopropane (695 mg, 9.38 mmol) and triethylamine (2.0 g, 19.8 mmol) was stirred in THF (5 mL). To this was added a solution of $ClPtBu_2$

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(1.4 equiv, 2.43 g, 13.4 mmol) in THF (15 mL). After the mixture was stirred overnight, the white salt precipitate was allowed to settle and the clear supernatant was filtered through Celite. THF and unreacted diamine were removed under vacuum to give a colorless liquid (2.36 g, 97%). $^1$H NMR ($C_6D_6$): $\delta$ 3.00 (m, 4H, $CH_2$), 1.56 (dt, $^2J_{H-P}$ = 7 Hz, $^3J_{H-H}$ = 7 Hz, 2H, NH), 1.06 (d, $^3J_{H-P}$ = 11 Hz, 36H, C($CH_3$)$_3$). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ 78.8. $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 48.53 (d, $^2J_{C-P}$ = 29 Hz, 2C, $NCH_2CH_2$), 37.67 (t, $^3J_{C-P}$ = 7 Hz, 1C, $CCH_2C$), 34.48 (d, $^1J_{C-P}$ = 22 Hz, 4C, $C(CH_3)_3$), 28.98 (d, $^2J_{C-P}$ = 15 Hz, C($CH_3$)$_3$). Anal. Calcd for $C_{19}H_{44}N_2P_2$: C, 62.95; H, 12.23; N, 7.73. Found: C, 63.07; H, 12.12; N, 7.43.

**Synthesis of ($CH_2NHPtBu_2$)$_2$ (2).** A solution of Cl$Pt$Bu$_2$ (2.00 g, 11.1 mmol) in THF (15 mL) was added with stirring to a solution of ethylenediamine (500 mg, 8.32 mmol) and triethylamine (2.0 g, 19.8 mmol) in THF (5 mL). After the mixture was stirrred overnight, the white salt precipitate was allowed to settle and the clear supernatant was filtered through Celite. THF and unreacted diamine were removed under vacuum, and the resulting oily solid was recrystallized from hexanes at −40 °C to give a white crystalline solid (3.24 g, 84%). $^1$H NMR ($C_6D_6$): $\delta$ 3.04 (m, 4H, $CH_2$), 1.24 (br d, $^2J_{P-H}$ = 11 Hz, 2H, NH), 1.09 (d, $^3J_{P-H}$ = 11 Hz, 36H, C($CH_3$)$_3$). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ 78.3. $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 53.83 (dd, $^2J_{C-P}$ = 27 Hz, $^3J_{C-P}$ = 7 Hz, 2C, $CH_2$), 34.46 (d, $^1J_{C-P}$ = 21 Hz, 4C, $C(CH_3)_3$), 28.91 (d, $^2J_{C-P}$ = 15 Hz, C($CH_3$)$_3$). Anal. Calcd for $C_{18}H_{42}N_2P_2$: C, 62.04; H, 12.15; N, 8.04. Found: C, 62.07; H, 12.12; N, 8.13.

**Synthesis of ($CH_2NMePtBu_2$)$_2$ (3).**[22]. *n*-BuLi (22.66 mmol, 1.7 M in THF, 13.3 mL) was added dropwise to a solution of *N*,*N*′-dimethylethylenediamine (1.0 g, 11.34 mmol) in THF (20 mL). After 3 h of stirring, a solution of Cl$Pt$Bu$_2$ (2.40 g, 22.7 mmol) in THF (15 mL) was added slowly to the lithiated diamine and the mixture was stirred at room temperature for 6 h. The mixture was filtered to remove LiCl, and volatiles were removed from the filtrate under vacuum. The resulting white waxy solid was recrystallized from pentane to give a colorless crystalline solid (3.46 g, 81%). $^1$H NMR ($C_6D_6$): $\delta$ 3.34 (m, $CH_2$), 2.71 (6H, d, $^3J_{H-P}$ = 6 Hz, $NCH_3$), 1.23 (d, $^3J_{H-P}$ = 12 Hz, 36H, C($CH_3$)$_3$). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ 108.0, 104.8, 104.0. $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 60.7 (d, $^2J_{C-P}$ = 41 Hz), 39.1 (br s), 36.1 (d, $^1J_{C-P}$ = 28 Hz, P$C$(CH$_3$)$_3$), 30.1 (d, $^2J_{C-P}$ = 17 Hz, PC($CH_3$)$_3$). Anal. Calcd for $C_{20}H_{46}N_2P_2$: C, 63.80; H, 12.31; N, 7.44. Found: C, 63.78; H, 12.34; N, 7.41.

**Synthesis of ($\kappa^3$*P,C,P*-CH($CH_2NHPtBu_2$)$_2$)PdI (4).** A solution of $PdI_2$ (100 mg, 0.278 mmol) in THF (6 mL) was added dropwise with stirring to a solution of $CH_2$(($CH_2$)$_2$P$t$Bu$_2$)$_2$ (100 mg, 0.277 mmol) in THF (5 mL). Stirring overnight led to formation of a red solution, which was filtered through Celite. THF was removed under vacuum to give 98 mg (62%) of a pale red solid. $^1$H NMR ($C_6D_6$): $\delta$ 3.37 (m, 1H, $H$CPd), 2.84 (m, 4H, $CH_2$N), 1.46 (br s, 2H, NH), 1.37 (vt, $J_{H-P}$ = 7 Hz, PC($CH_3$)$_3$), 1.31 (vt, $J_{H-P}$ = 7 Hz, PC($CH_3$)$_3$). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ 130. $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 61.2 (t, $^2J_{C-P}$ = 5 Hz, H$C$Pd), 55.3 (t, $^2J_{C-P}$ = 7 Hz, $NCH_2$), 40.2 (t, $^1J_{C-P}$ = 6 Hz, P$C$(CH$_3$)$_3$), 37.6 (t, $^1J_{C-P}$ = 12 Hz, P$C$(CH$_3$)$_3$), 29.1 (t, $^2J_{C-P}$ = 3 Hz, PC($CH_3$)$_3$), 28.5 (t, $^2J_{C-P}$ = 3 Hz, PC($CH_3$)$_3$). Anal. Calcd for $C_{19}H_{43}N_2P_2PdI$: C, 38.36; H, 7.29; N, 4.71. Found: C, 37.88; H, 7.17; N, 4.61.

**Synthesis of ($\kappa^3$*P,N,P*-*t*Bu$_2$PNH($CH_2$)$_3$NP*t*Bu$_2$)NiCl (5).** A suspension of $NiCl_2$(dme) (108 mg, 0.554 mmol) in THF (6 mL) was added with stirring to a solution of **2** (200 mg, 0.552 mmol) in THF (4 mL) in the presence of triethylamine. The resulting green-brown solution was stirred overnight to give a purple mixture, which was then filtered through Celite to give a bright fuchsia solution. Volatiles were removed under vacuum, and the purple solid was recrystallized from pentane. Yield: 197 mg, 78%. $^1$H NMR (toluene-$d_8$): $\delta$ 3.05 (m, 2H, $CCH_2C$), 2.54 (m, 2H, $CH_2$N), 2.09 (m, 2H, $CH_2$N), 1.44 (d, $^3J_{H-P}$ = 12 Hz, 18H, PC($CH_3$)$_3$), 1.37 (d, $^3J_{H-P}$ = 15 Hz, 18H, PC($CH_3$)$_3$. $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ 106, −29 (d, $^2J_{P-P}$ = 261 Hz). $^{13}$C{$^1$H} NMR (toluene-$d_8$): $\delta$ 41.7 (d, $^2J_{C-P}$ = 16 Hz, $CH_2$N), 40.7 (d, $^2J_{C-P}$ = 5, $CCH_2C$), 38.1 (dd, $^1J_{C-P}$ = 10 Hz, $^3J_{C-P}$ = 3.5 Hz, $C(CH_3)_3$), 34.4 (dd, $^1J_{C-P}$ = 6 Hz, $^3J_{C-P}$ = 2 Hz, $C(CH_3)_3$), 29.0 (dd, $^2J_{C-P}$ = 4 Hz, $^4J_{C-P}$ = 1.0 Hz), 28.8 (d, $^2J_{C-P}$ = 5 Hz), 27.46 (s). Anal. Calcd for $C_{19}H_{43}ClN_2NiP_2$: C, 50.08; H, 9.51; N, 6.15. Found: C, 49.70; H, 9.87; N, 5.75.

**Synthesis of ($\kappa^3$*P,C,P*-CH($CH_2NHPtBu_2$)$_2$)NiCl (6).** To a purple solution of **5** (20 mg, 0.044 mmol) in toluene (2 mL) was added a colorless solution of B($C_6F_5$)$_3$ (22 mg, 0.044 mmol) in toluene (4 mL). After 10 min of stirring at room temperature, the solution turned yellow and a small amount of green oil had formed. The yellow solution was decanted from the green oil, and toluene was removed under vacuum to afford a yellow crystalline solid (isolated yield 48%). Yellow crystals suitable for X-ray diffraction were grown from hexanes. $^1$H NMR ($C_6D_6$): $\delta$ 3.10 (m, 2H, $CH_2$), 3.01 (m, 4H, $CH_2$), 1.45 (d, $J$ = 7 Hz, 1H, N$H$), 1.44 (d, $J_{P-H}$ = 7 Hz, 1H, N$H$), 1.38 (d, $J_{P-H}$ = 6 Hz, 18H, PC($CH_3$)$_3$), 1.37 (d, $J_{P-H}$ = 6 Hz, 18H, PC($CH_3$)$_3$). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ 119.0. $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 55.0 (vt, $J_{C-P}$ = 10.3 Hz, 2C, $CH_2$NP), 42.3 (vt, $J_{C-P}$ = 12 Hz, 1C, HCNi), 39.0 (vt, $J_{C-P}$ = 5 Hz, 2C, $C(CH_3)_3$), 38.0 (vt, $J_{C-P}$ = 12 Hz, 2C, $C(CH_3)_3$), 28.4 (vt, $J_{C-P}$ = 3 Hz, 6C, C($CH_3$)$_3$), 27.9 (vt, $J_{C-P}$ = 3 Hz, 6C, C($CH_3$)$_3$). Anal. Calcd for $C_{19}H_{43}ClN_2NiP_2$: C, 50.08; H, 9.51; N, 6.15. Found: C, 50.10; H, 9.63; N, 6.05.

**Synthesis of ($\kappa^3$*P,N,P*-*t*Bu$_2$PNH($CH_2$)$_2$NP*t*Bu$_2$)PdI (7) and ($\kappa^3$*P,N,P*-*t*Bu$_2$PNH($CH_2$)$_2$NP*t*Bu$_2$)NiCl (8).** These compounds were prepared in a similar fashion, and thus only one preparation is detailed. On addition of an orange suspension of (dme)$NiCl_2$ (60 mg, 0.287 mmol) in THF (6 mL) to a clear solution of **1** (100 mg, 0.287 mmol) in THF (5 mL) with stirring, the reaction mixture turned dark red. After 15 min, all (dme)$NiCl_2$ had dissolved and the solution was dark fuchsia. The solution was stirred for 4 h and then filtered through a plug of Celite to remove a forest green precipitate, affording a bright fuschia solution. The solvent was removed under vacuum to give the purple crystalline solid **8** (65 mg, 54%).

Data for **7** are as follows. Yield: 66%. $^1$H NMR ($C_6D_6$): $\delta$ 2.71 (m, 2H, $CH_2$), 2.63 (m, 2H, $CH_2$), 1.17 (d, $^3J_{P-H}$ = 14 Hz, 18H, PC($CH_3$)$_3$), 1.05 (d, $^3J_{P-H}$ = 16 Hz, 18H, PC($CH_3$)$_3$). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ 86.5, 17.7 (d, $^2J_{P-P}$ = 372 Hz). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 52.3 (t, $^2J_{C-P}$ = 9 Hz, $NCH_2$), 47.4 (dd, $^2J_{C-P}$ = $NCH_2$), 37.8 (dd, $^3J_{C-P}$ = 10 Hz, $^1J_{C-P}$ = 6 Hz, PC($CH_3$)$_3$), 37.2 (dd, $^3J_{C-P}$ = 10 Hz, $^1J_{C-P}$ = 4 Hz, PC($CH_3$)$_3$), 29.0 (d, $^2J_{C-P}$ = 3 Hz, PC($CH_3$)$_3$), 28.3 (d, $^2J_{C-P}$ = 7 Hz, PC($CH_3$)$_3$). Anal. Calcd for $C_{18}H_{41}N_2P_2PdI$: C, 37.22; H, 7.12; N, 4.82. Found: C, 35.86; H, 7.18; N, 5.17.[23]

Data for **8** are as follows. Yield: 54%. $^1$H NMR ($C_6D_6$): $\delta$ 2.56 (br m, 2H, $NCH_2$), 2.18 (br m, 2H, $NCH_2$), 1.45 (d, $^3J_{P-H}$ = 13 Hz, 18H, PC($CH_3$)$_3$), 1.28 (d, $^3J_{P-H}$ = 15 Hz, 18H, PC($CH_3$)$_3$). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ 98, −19 (d, $^2J_{P-P}$ = 262 Hz). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 48.7 (dd, $^3J_{C-P}$ = 9 Hz, $^2J_{P-C}$ = 4 Hz, $NCH_2CH_2$), 43.7 (dd, $^3J_{C-P}$ = 16 Hz, $^2J_{C-P}$ = 5 Hz, $NCH_2CH_2$), 38.0 (dd, $^1J_{C-P}$ = 14 Hz, $^3J_{C-P}$ = 4 Hz, PC($CH_3$)$_3$), 35.2 (dd, $^1J_{C-P}$ = 6 Hz, $^3J_{C-P}$ = 4 Hz, PC($CH_3$)$_3$), 29.4 (dd, $^2J_{C-P}$ = 6 Hz, $^4J_{C-P}$ = 2 Hz, C($CH_3$)$_3$), 28.7 (dd, $^2J_{C-P}$ = 6 Hz, $^4J_{C-P}$ = 1 Hz, C($CH_3$)$_3$). Anal. Calcd for $C_{18}H_{41}ClN_2NiP_2$: C, 48.95; H, 9.36; N, 6.34. Found: C, 49.21; H, 9.89; N, 6.49.

**Synthesis of ($\kappa^3$*P,C,P*-*t*Bu$_2$PN(Me)CHCH$_2$N(Me)P*t*Bu$_2$)PdX (X = I (9), Br (10), Cl (11)).** These compounds were prepared in a similar fashion, and thus only one preparation is detailed. A solution of $PdI_2$ (285 mg, 0.792 mmol) in THF (6 mL) was added dropwise with stirring to a solution of **3** (300 mg, 0.796 mmol) in THF (6 mL) in the presence of $Et_3N$. The dark solution was stirred overnight and then filtered through Celite. Volatiles were removed under vacuum, and the resulting golden brown solid was extracted into toluene and filtered again through Celite. Removal of the toluene under vacuum gave a yellow solid (417 mg, 86% yield).

**Table 1. Crystallographic Parameters**

| | 4 | 5 | 6 | 8 | 9 | 11 | 12·2$CH_2Cl_2$ |
|---|---|---|---|---|---|---|---|
| formula | $C_{19}H_{43}N_2P_2PdI$ | $C_{19}H_{43}N_2P_2NiCl$ | $C_{19}H_{43}N_2P_2NiCl$ | $C_{18}H_{41}N_2P_2NiCl$ | $C_{20}H_{45}N_2P_2PdI$ | $C_{20}H_{45}N_2P_2PdCl$ | $C_{22}H_{51}N_2P_2NiCl_7$ |
| fw | 594.79 | 455.65 | 455.65 | 441.63 | 608.82 | 517.37 | 712.45 |
| cryst syst | monoclinic | orthorhombic | monoclinic | monoclinic | hexagonal | monoclinic | orthorhombic |
| space group | $P2_1/n$ | $P2_12_12_1$ | $P2_1/n$ | $P2_1/m$ | $P\bar{4}2_1m$ | $P2_1/c$ | $Pna2_1$ |
| $a$ (Å) | 15.454(2) | 11.646 (1) | 11.8428(8) | 8.024(1) | 11.7919(4) | 8.7937(3) | 10.8771(6) |
| $b$ (Å) | 10.741(1) | 14.188(1) | 14.4447(9) | 14.249(2) | 11.7919(4) | 11.7012(4) | 20.2402(12) |
| $c$ (Å) | 16.245(2) | 15.041(1) | 14.715(1) | 10.444(1) | 9.4299(3) | 24.3196(9) | 15.8448(11) |
| α (deg) | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| $\beta$ (deg) | 112.477(4) | 90.00 | 103.688(4) | 99.858(9) | 90.00 | 90.332(2) | 90.00 |
| $\gamma$ (deg) | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| $V$ (Å$^3$) | 2491.6(6) | 2485.3(4) | 2445.7(3) | 1176.4(3) | 1311.20(6) | 2502.37(15) | 3488.3(4) |
| $Z$ | 4 | 4 | 4 | 2 | 2 | 4 | 4 |
| $d_{calcd}$ (g cm$^{-3}$) | 1.586 | 1.218 | 1.238 | 1.247 | 1.542 | 1.373 | 1.357 |
| $\mu$ (mm$^{-1}$) | 2.188 | 1.022 | 1.022 | 1.078 | 2.015 | 0.981 | 1.199 |
| total no. of data | 21 720 | 40 754 | 49 993 | 18 769 | 47 434 | 42 913 | 39 600 |
| $R_{int}$ | 0.0288 | 0.1284 | 0.0872 | 0.0622 | 0.0612 | 0.0356 | 0.0452 |
| $F_o^2 > 3\sigma(F_o^2)$ | 5716 | 5706 | 5626 | 4858 | 3212 | 9802 | 10343 |
| no. of params | 226 | 226 | 226 | 160 | 75 | 271 | 307 |
| R1 | 0.0228 | 0.0482 | 0.0529 | 0.0546 | 0.0415 | 0.0381 | 0.0554 |
| wR2 | 0.0591 | 0.998 | 0.1434 | 0.1550 | 0.0980 | 0.996 | 0.1544 |
| GOF | 0.978 | 1.005 | 1.025 | 1.074 | 1.093 | 1.022 | 1.048 |

Data for **9** are as follows. $^1$H NMR ($C_6D_6$): $\delta$ 2.98 (m, 1H, NC(H)*H*), 2.84 (m, H, *H*CPd), 2.74 (m, 1H, NC(H)*H*), 2.52 (d, $^3J_{H-P}$ = 4 Hz, 3H, NC*H*$_3$), 2.30 (d, $^3J_{H-P}$ = 9 Hz, 3H, NC*H*$_3$), 1.49 (d, $^3J_{H-P}$ = 14 Hz, 9H, PC(C*H*$_3$)$_3$), 1.35 (d, $^3J_{H-P}$ = 9 Hz, 9H, PC(C*H*$_3$)$_3$), 1.33 (d, $^3J_{H-P}$ = 14 Hz, 9H, PC(C*H*$_3$)$_3$), 1.31 (d, $^3J_{H-P}$ = 8 Hz, 9H, PC(C*H*$_3$)$_3$). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ 132.6, 15.2 (d, $^2J_{P-P}$ = 388 Hz). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 67.4 (dd, $^2J_{C-P}$ = 19 Hz, $^2J_{C-P}$ = 9 Hz, HCPd), 46.4 (dd, $^2J_{C-P}$ = 10 Hz, $^3J_{C-P}$ = 7 Hz, $H_2C$), 39.6 (d, $^2J_{C-P}$ = 4 Hz, $CH_2N(CH_3)P$), 38.7 (d, $^2J_{C-P}$ = 7 Hz, CHN(*C*H$_3$)P), 30.5 (dd, $^2J_{C-P}$ = 7, $J_{C-P}$ = 1 Hz, PC(*C*H$_3$)$_3$), 30.3 (dd, $^2J_{C-P}$ = 6 Hz, $J_{C-P}$ = 1 Hz, PC(*C*H$_3$)$_3$), 29.8 (dd, $^2J_{C-P}$ = 6 Hz, $J_{C-P}$ = 1.3 Hz, PC(*C*H$_3$)$_3$), 28.7 (d, $^2J_{C-P}$ = 5 Hz, PC(*C*H$_3$)$_3$). Anal. Calcd for $C_{20}H_{45}N_2P_2PdI$: C, 39.45; H, 7.45; N, 4.60. Found: C, 38.98; H, 7.09; N, 4.47.

Data for **10** are as follows. Yellow solid. Yield: 26 mg (22%). $^1$H NMR ($C_6D_6$): $\delta$ 2.98 (td, $^3J_{H-P}$ = 10 Hz, $^3J_{H-P}$ = 2 Hz, 1H, PdC*H*), 2.76 (m, 1H, C*H*H), 2.68 (m, 1H, CH*H*), 2.51 (d, $^3J_{H-P}$ = 4 Hz, 3H, NC*H*$_3$), 2.30 (d, $^3J_{H-P}$ = 9 Hz, 3H, NC*H*$_3$), 1.49 (d, $^3J_{H-P}$ = 14 Hz, 9H, PC(C*H*$_3$)$_3$), 1.35 (d, $^3J_{H-P}$ = 14 Hz, 9H, PC(C*H*$_3$)$_3$), 1.32 (d, $^3J_{H-P}$ = 14 Hz, 9H, PC(C*H*$_3$)$_3$), 1.32 (d, $^3J_{H-P}$ = 14 Hz, 9H, PC(C*H*$_3$)$_3$). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ 129.3, 19.0 (d, $^2J_{P-P}$ = 397 Hz). Anal. Calcd for $C_{20}H_{45}N_2P_2PdBr$: C, 42.75; H, 8.07; N, 4.99. Found: C, 42.29; H, 8.09; N, 4.87.

Data for **11** are as follows. Pale yellow crystalline solid. Recrystallization from dichloromethane and hexanes (1:1) afforded light yellow crystals suitable for X-ray diffraction (29 mg, 21%). $^1$H NMR ($CD_2Cl_2$): 3.05 (m, 1H, PdC*H*), 2.97 (m, 1H, PdC(H)C*H*H), 2.77 (m, 1H, PdC(H)CH*H*), 2.82 (d, $^3J_{H-P}$ = 4 Hz, 3H, NC*H*$_3$), 2.62 (d, $^3J_{H-P}$ = 9 Hz, 3H, NC*H*$_3$), 1.39 (d, $^3J_{H-P}$ = 14 Hz, 9H, PC(C*H*$_3$)$_3$), 1.33 (d, $^3J_{H-P}$ = 14 Hz, 9H, PC(C*H*$_3$)$_3$), 1.32 (d, $^3J_{H-P}$ = 15 Hz, 9H, PC(C*H*$_3$)$_3$), 1.28 (d, $^3J_{H-P}$ = 14 Hz, 9H, PC(C*H*$_3$)$_3$). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ 128.9, 22.9 (d, $^2J_{P-P}$ = 403 Hz). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 67.3 (dd, $^2J_{C-P}$ = 19 Hz, $^2J_{C-P}$ = 9 Hz, HCPd), 43.0 (dd, $^2J_{C-P}$ = 11 Hz, $^3J_{C-P}$ = 6 Hz, $H_2C$), 39.9 (d, $^2J_{C-P}$ = 7 Hz, $CH_2N(CH_3)P$), 38.6 (d, $^2J_{C-P}$ = 4 Hz, CHN(*C*H$_3$)P), 29.7 (dd, $^2J_{C-P}$ = 8, $J_{C-P}$ = 1.2 Hz, PC(*C*H$_3$)$_3$), 29.4 (dd, $^2J_{C-P}$ = 6 Hz, $J_{C-P}$ = 1 Hz, PC(*C*H$_3$)$_3$), 29.3 (dd, $^2J_{C-P}$ = 6 Hz, $J_{C-P}$ = 1 Hz, PC(*C*H$_3$)$_3$), 28.7 (d, $^2J_{C-P}$ = 6 Hz, PC(*C*H$_3$)$_3$). Anal. Calcd for $C_{20}H_{45}ClN_2P_2Pd$: C, 46.43; H, 8.77; N, 5.41. Found: C, 46.32; H, 8.69; N, 5.43.

**Alternative Synthesis of 11.** A solution of $PdCl_2(MeCN)_2$ (0.5 equiv) and $Pd_2(dba)_3$ (0.25 equiv) in THF (8 mL) was added dropwise to a clear colorless solution of **3** in THF (5 mL). The mixture was stirred overnight to produce a dark yellow-green mixture. Removal of an olive green precipitate via filtration left a golden solution which upon removal of volatiles afforded **11** as the exclusive product. Yield: 95%.

**Synthesis of (*t*Bu$_2$P(H)N(Me)CH$_2$CH$_2$N(Me)P*t*Bu$_2$)NiCl$_3$ (12).** A solution of **3** (100 mg, 0.265 mmol) in THF (4 mL) was added to a suspension of (dme)$NiCl_2$ in THF (6 mL) and stirred at 25 °C for 4 h to give a green solution. Filtration of the mixture through Celite and evaporation of the solvent under vacuum afforded a blue-green crystalline solid. Yield: 95%. The paramagnetic species was determined to be **12** by X-ray crystallography. $^{31}$P NMR ($CD_2Cl_2$): 53.3 ($^1J_{P-H}$ = 508 Hz). Anal. Calcd for $C_{20}H_{47}N_2P_2NiCl_3$: C, 44.27; H, 8.73; N, 5.16. Found: C, 44.70; H, 8.35; N, 5.56.

**Synthesis of ($\kappa^3$-*P,C,P*-*t*Bu$_2$PN(Me)CHCH$_2$N(Me)P*t*Bu$_2$)NiCl (13).** Addition of $B(C_6F_5)_3$ to a suspension of **12** in $C_6D_6$ immediately produced a green oil and yellow solution. Decanting the solution to separate the oil gave a bright yellow solution which was revealed by NMR spectroscopy to contain exclusively the PCP pincer complex. Slow addition of hexane afforded **13** in 85% yield. $^1$H NMR ($C_6D_6$): $\delta$ 2.49 (d, $^3J_{H-P}$ = 4 Hz, 3H, NC*H*$_3$), 2.33 (m, 1H, *H*CNi), 2.31 (m, 2H, $H_2$CC), 2.23 (d, $^3J_{H-P}$ = 9 Hz, 3H, NC*H*$_3$), 1.56 (d, $^3J_{H-P}$ = 13 Hz, 9H, PC(C*H*$_3$)$_3$), 1.46 (d, $^3J_{H-P}$ = 14 Hz, 9H, PC(C*H*$_3$)$_3$), 1.44 (d, $^3J_{H-P}$ = 13 Hz, 9H, PC(C*H*$_3$)$_3$), 1.41 (d, $^3J_{H-P}$ = 13 Hz, 9H, PC(C*H*$_3$)$_3$). $^{31}$P{$^1$H} NMR ($C_6D_6$): $\delta$ 120.7, 31.9 (d, $^2J_{P-P}$ = 289 Hz). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta$ 58.6 (dd, $^2J_{C-P}$ = 19 Hz, $^2J_{C-P}$ = 9 Hz, HCNi), 41.1 (dd, $^2J_{C-P}$ = 10 Hz, $^3J_{C-P}$ = 5 Hz, $H_2C$), 39.1 (d, $^2J_{C-P}$ = 7 Hz, $CH_2N(CH_3)P$), 38.2 (d, $^2J_{C-P}$ = 4 Hz, CHN(*C*H$_3$)P), 28.8 (dd, $^2J_{C-P}$ = 8, $J_{C-P}$ = 1 Hz, PC(*C*H$_3$)$_3$), 28.7 (dd, $^2J_{C-P}$ = 6 Hz, $J_{C-P}$ = 1 Hz, PC(*C*H$_3$)$_3$), 28.5 (dd, $^2J_{C-P}$ = 6 Hz, $J_{C-P}$ = 1 Hz, PC(*C*H$_3$)$_3$), 28.4 (d, $^2J_{C-P}$ = 6 Hz, PC(*C*H$_3$)$_3$). $^{11}$B NMR: $\delta$ −7.2. $^{19}$F NMR: $\delta$ −131.66 (d, $^3J_{F-F}$ = 17, 6F, *o*-F), −163.41 (t, $^3J_{F-F}$ = 20 Hz, 3F, *p*-F),


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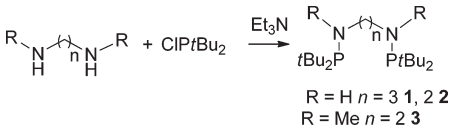
**Scheme 1. Synthesis of Ligands 1−3**




−167.71 (t, $^3J_{F-F}$ = 18 Hz, 6F, *m*-F). Anal. Calcd for $C_{20}H_{45}ClN_2NiP_2$: C, 51.14; H, 9.66; N, 5.96. Found: C, 51.07; H, 9.28; N, 5.83.

**DFT Calculations.** Preliminary calculations were performed with Gaussian03[24,25] using density functional theory (DFT). The geometries of compounds **6** and **7** were optimized by starting from the X-ray data using the B3LYP exchange-correlational functional with the 6-311-G(d,p) basis set. Optimizations were performed without (symmetry) constraints, and the resulting structures were confirmed to be minima on the potential energy surface by frequency calculations (the number of imaginary frequencies is zero). Visualization of the computed structures and molecular orbitals was achieved using the program WebMO.

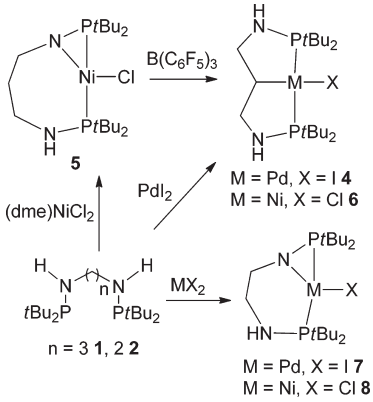
**X-ray Data Collection and Reduction.** Crystals were coated in Paratone-N oil in the glovebox, mounted on a MiTegen Micromount, and placed under a $N_2$ stream, thus maintaining a dry, $O_2$-free environment for each crystal. The data for crystals of **10** were collected on a Nonius Kappa-CCD diffractometer; for crystals of **4**, **6**, **7**, and **8**, data were collected on a Bruker Apex II diffractometer. The data were collected at 150(2) K for all crystals. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the empirical multiscan method (SADABS).

**Structure Solution and Refinement.** Non-hydrogen atomic scattering factors were taken from the literature tabulations. The heavy-atom positions were determined using direct methods employing the SHELXTL direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on *F*, minimizing the function $\sigma(F_o - F_c)^2$, where the weight $\sigma$ is defined as $4F_o^2/2\sigma(F_o^2)$ and $F_o$ and $F_c$ are the observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases, atoms were treated isotropically. C−H atom positions were calculated and allowed to ride on the carbon to which they were bonded, assuming a C−H bond length of 0.95 Å. H atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the C atom to which they were bonded. The H atom contributions were calculated but not refined. The locations of the largest peaks in the final difference Fourier map calculation and the magnitude of the residual electron densities in each case were of no chemical significance. In the case of compound **8**, disorder of the ligand backbone carbons and one *t*Bu group was modeled. For **9** and **11** some degree of full-molecule disorder was evident. The models were refined by employing only the positions of the Pd and halide atoms, as the remainder of the disordered molecule could not be located. Additional details are provided in the Supporting Information. Crystallographic parameters for **4**−**6**, **8**, **9**, **11**, and **12** are given in Table 1.

## RESULTS AND DISCUSSION

N,N′-substituted diamine-based ligands were prepared using the appropriate substituent and a minor modification of the known methodology for such ligands.[26−28] Reaction of the diamines with 2 equiv of $ClPtBu_2$ afforded the corresponding bis(aminophosphine) compounds in good yield. In this fashion $CH_2(CH_2NHPtBu_2)_2$ (**1**), $(CH_2NHPtBu_2)_2$ (**2**), and

**Scheme 2. Synthesis of Ni and Pd Complexes of 1 and 2**



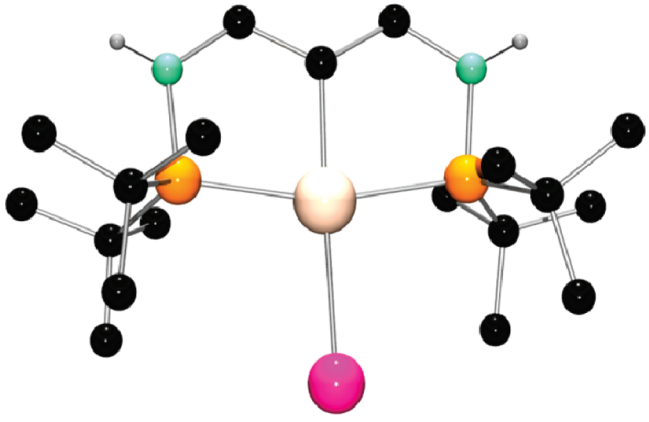



**Figure 1.** Pov-ray depiction of **4**: (black) C; (blue-green) N; (orange) P; (pink) I; (light wood) Pd. Hydrogen atoms, except for NH, are omitted for clarity.

$(CH_2NMePtBu_2)_2$ (**3**) were prepared from 1,3-diaminopropane, *N*,*N*′-ethylenediamine, and dimethylethylenediamine, respectively, and each were fully spectroscopically characterized (Scheme 1). The ligands **1** and **2** gave rise to $^{31}P$ NMR resonances at 78.8 and 78.3 ppm and were isolated in 97 and 84% yields, respectively. In the case of the bis-aminophosphine derived from the secondary diamine, this required deprotonation with an alkyllithium reagent. In this fashion $(CH_2NMePtBu_2)_2$ (**3**) was prepared and isolated as a crystalline solid in 81% yield. The $^{31}P$ NMR spectrum reflects the steric demands of the ligand, as one broad resonance at 50 ppm is observed and, on heating to 50 °C, this signal becomes a sharp singlet. On cooling to −30 °C, three sharp signals are observed at 108.0, 104.8, and 104.0 ppm. These signals are attributed to diastereomers of **3** resulting from steric inhibition of inversion about the pyramidal nitrogen atoms.

The bis-aminophosphine ligand **1** reacts with $PdI_2$ in THF at room temperature to give the symmetrical PCP-pincer complex **4**, which is characterized by the appearance of a single resonance in the $^{31}P$ NMR spectrum at 130 ppm and a pattern of virtual triplets for the *tert*-butyl groups in the $^1H$ and $^{13}C\{^1H\}$ NMR spectra. The phosphorus chemical shift of 130 ppm is in accordance with the more electron-rich environment provided by the amino groups. These data support the formulation of **4** as the symmetric pincer complex $CH(CH_2NHPtBu_2)_2PdI$, in which the central carbon of the chelate is metalated (Scheme 2). This was confirmed crystallographically (Figure 1). This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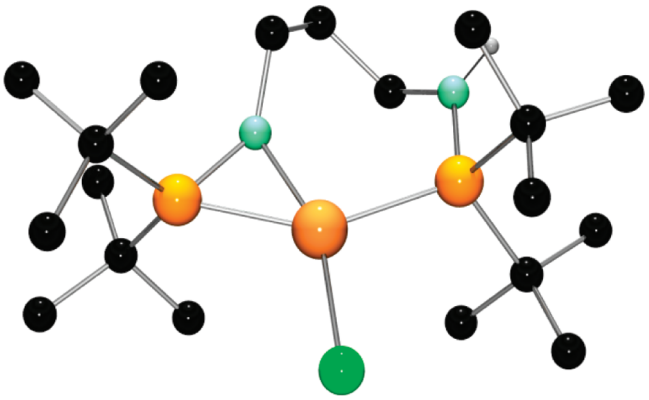

**Figure 2.** Pov-ray depiction of **5**: (black) C; (blue-green) N; (orange) P; (green) Cl; (burnt orange) N. Hydrogen atoms, except for NH, are omitted for clarity.

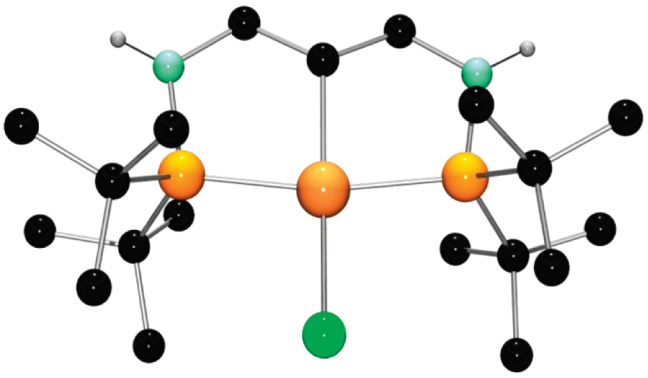

**Figure 3.** Pov-ray depiction of **6**: Hydrogen atoms, except for NH, are omitted for clarity. C: black, N: blue-green, P: orange: Cl: green, Ni: burnt orange.

geometry is reminiscent of the known species ($\kappa^3$*P,C,P*-CH((CH$_2$)$_2$P*t*Bu$_2$)$_2$)PdI.[29−31] Structural data for **4** reveal a square-planar Pd center with a Pd−C distance of 2.061(3) Å while the Pd−P and Pd−I distances are 2.3089(6) and 2.3191(6) Å and 2.7227(3) Å, respectively, with a P−Pd−P angle of 164.42(2)°. The C−Pd−I angle of 173.9(2)° is bent slightly out of the plane defined by the P$_2$PdI atoms. The Pd−P distances in **4** are slightly longer than those reported by Kirchner and co-workers in the pyridyl bis-aminophosphine cation [($\kappa^3$*P,N,P*-(C$_5$H$_3$N)(NHP*t*-Bu$_2$)$_2$)PdCl]$^+$ (2.2987(5), 2.2985(5) Å).[32] The P−N bond lengths in **4** are ca. 1.67 Å, typical of P−N bonds.[33]

The corresponding reaction of **1** with NiCl$_2$(dme) gave a reaction mixture from which the purple solid **5** was obtained. Repetition of the reaction in the presence of NEt$_3$ was found to enhance the isolated yield of **5** to 78% (Scheme 2). The $^{31}$P{$^1$H} NMR spectrum of **5** showed two resonances at 106 and −29 ppm, each showing a coupling constant of 261 Hz, while the $^1$H NMR data revealed two resonances attributable to the *t*Bu groups at 1.44 and 1.37 ppm. These data are consistent with a trans disposition of inequivalent phosphine fragments. The nature of **5** was unambiguously confirmed as ($\kappa^3$*P,N,P*-*t*Bu$_2$PNH-(CH$_2$)$_3$NP*t*Bu$_2$)NiCl by X-ray crystallography (Figure 2). These data show a four-coordinate nickel center in which the coordination sphere about Ni is comprised of two P atoms, a Cl atom, and a N atom. The resulting strained three-membered P−N−Ni ring results in a significant distortion of the pseudo-square-planar geometry about Ni and presumably accounts for the dramatic difference in $^{31}$P chemical shift between the two P atoms. The inequivalence of the P environments is reflected in the Ni−P distances of 2.161(1) and 2.222(1) Å, the former being the P in the three-membered NiPN metallacycle ring. The latter Ni−P distance in **5** is only slightly longer than the Ni−P bond lengths in the pyridyl bis-aminophosphine cation [($\kappa^3$-*P,N,P*-(C$_5$H$_3$N)-(NHP*t*Bu$_2$)$_2$)NiCl]$^+$ (2.2067(4), 2.2062(4) Å);[32] this is perhaps a reflection of the strained geometry. The corresponding Ni−N distance in the ring is 1.891(3) Å. Similarly, the P−N bond lengths differ quite significantly, as the P−N bond length within the NiPN three-membered ring was found to be 1.603(3) Å, while the other P−N bond in the ligand was significantly longer at 1.679(3) Å. The Ni−Cl distance was found to be 2.1989(11) Å. The P−Ni−P, N−Ni−Cl, and P−Ni−Cl angles in **5** were found to be 145.94(4), 157.11(10), and 111.20(4)°, respectively. The constraint in the NiPN metallacycle is reflected in the Ni−P−N angle of 58.08(12)°. This dissymmetric binding mode for an aminophosphine fragment is rare. In a 1993 report a geometrically related NPCo fragment was reported in the complex (Ph$_2$PNPPh$_2$NPPh$_2$)$_2$Co,[34] while Valerga and co-workers[21] have more recently reported the Ru cation [Cp*Ru($\kappa^3$-*P,N,P*-(*i*Pr$_2$PNH)$_2$C$_6$H$_{10}$)]$^+$, in which the amine N adjacent to P coordinates to Ru. This latter species exhibits a single $^{31}$P resonance at 92.3 ppm in solution,[21] as the binding of the NH in the Ru cation appears to be fluxional. In contrast, the N atom in the present NPNi metallacycle **5** is deprotonated and thus the nitrogen binding is not fluxional in solution. To our knowledge this amido-phosphine binding represents an unprecedented form of binding for a PNP pincer ligand.

In an effort to probe the inherent stability of this strained NPNi metallacycle, we reasoned that interaction with a Lewis acid could prompt ring opening. To this end, we examined the subsequent reaction of **5** with B(C$_6$F$_5$)$_3$. This resulted in the initially purple solution becoming yellow, with separation of a green oil. Separation of this oil and subsequent recrystallization ultimately afforded the yellow crystalline product **6** in an isolated yield of 48% (Scheme 2). In contrast to the case for **5**, this species shows a single $^{31}$P{$^1$H} NMR signal at 119.0 ppm and $^1$H and $^{13}$C{$^1$H} NMR resonances consistent with a symmetric ligand and metalation at the central C of the ligand backbone. X-ray diffraction confirmed the formulation of **6** as ($\kappa^3$*P,C,P*-CH-(CH$_2$NHP*t*Bu$_2$)$_2$)NiCl (Figure 3). The metalation of the central carbon results in two adjacent five-membered rings, with a Ni−C bond length of 1.974(4) Å and Ni−P bond lengths of 2.1908(10) and 2.1941(10) Å. In this pseudo-square-planar complex, the P−Ni−P angle in **6** is 168.09(4)°, while the C−Ni−Cl angle is 171.93(17)°. DFT calculations performed at the B3LYP/6311-G(d,p) level for the optimized structures of **5** and **6** revealed a small energy difference, with the C−H activated complex **6** being lower in energy than the N−H activated complex **5** by $\Delta G$ = 9.96 kcal mol$^{-1}$. While this observation suggests that **5** is a kinetic product, the nature of the conversion to **6** via a boron-mediated process remains the subject of speculation. It is reasonable to suggest that a reversible interaction of B with either the NPNi metallacycle or possibly Ni-bound halide could generate a site of unsaturation, prompting activation of the alkyl C−H bond and thus proton migration from the central C to N.

The related reactions of amino-phosphine ligand **2** with PdI$_2$ and with NiCl$_2$(dme) led, in both cases, to the complexes $\kappa^3$-*P,N,P*-(*t*Bu$_2$PNH(CH$_2$)$_2$NP*t*Bu$_2$)PdI (**7**) and $\kappa^3$-*P,N,*


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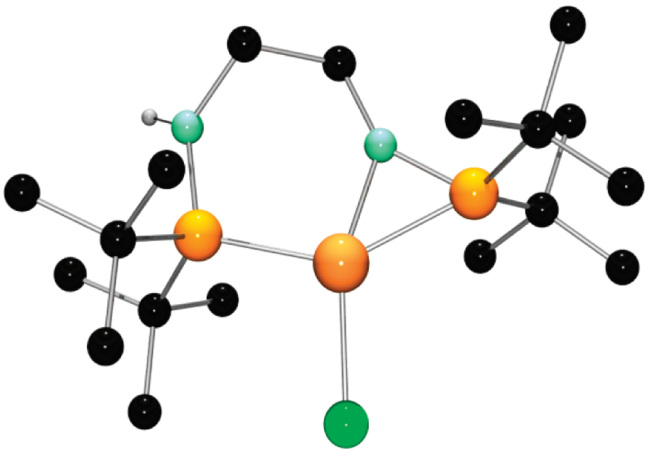


**Figure 4.** Pov-ray depiction of **8**: (black) C; (blue-green) N; (orange) P; (green) Cl; (burnt orange) Ni. Hydrogen atoms, except for NH, are omitted for clarity.

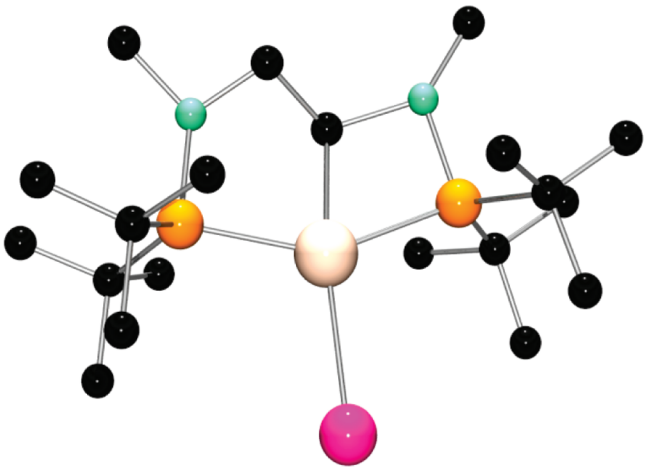
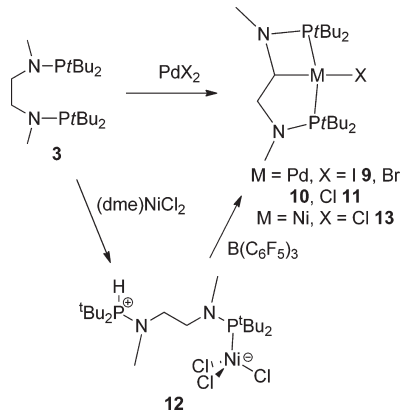


**Figure 5.** Pov-ray depiction of **9**: (black) C; (blue-green) N; (orange) P; (pink) I; (light wood) Pd. Hydrogen atoms are omitted for clarity.

**Scheme 3. Synthesis of Ni and Pd Complexes of 3**



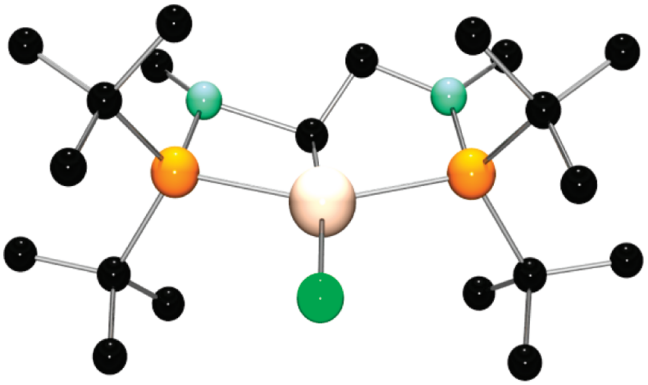



**Figure 6.** Pov-ray depiction of **11**: (black) C; (blue-green) N; (orange) P; (green) Cl; (light wood) Pd. Hydrogen atoms are omitted for clarity.

*P*-($t$Bu$_2$PNH(CH$_2$)$_2$NP$t$Bu$_2$)NiCl (**8**), respectively (Scheme 2). Both species are characterized by the presence of two coupled phosphorus species in the $^{31}$P NMR spectra. The chemical shifts of these doublets in the spectrum for **7** were observed at 85 and −32 ppm ($\Delta$ = 117 ppm) with a $^2J_{P-P}$ of 262 Hz, while for **8** the chemical shifts were seen at 87 and 18 ppm ($\Delta$ = 69 ppm) and $J_{P-P}$ of 372 Hz. The $^1$H NMR spectrum also revealed inequivalent *t*-butyl environments, consistent with some dissymmetry of the coordination sphere about the metals. The backbone methylene protons give rise to two multiplets, consistent with molecular dissymmetry. The solid-state structure of **8** was determined *via* X-ray crystallography (Figure 4), confirming the geometries of these species in which the pseudosquare planar coordination sphere comprised of three- (NPNi) and six- (NC$_2$NPNi) membered rings. The Ni−P bond lengths are 2.1844(8) and 2.1850(8) Å while the Ni−N distance was found to be 1.825(2) Å. The P−Ni−P angle of **8** was found to be 141.49(3)° while the N−Ni−P in the NNiP three membered ring was found to be 45.34(8)°.

To probe the effect of substitution at nitrogen, complexation of **3** with Pd and Ni was investigated (Scheme 3). When **3** was treated with PdI$_2$, the new product **9** gave rise to a $^{31}$P NMR spectrum comprised of two doublets at 132.6 and 15.2 ppm with a large P−P coupling of 388 Hz. This is consistent with two inequivalent phosphorus environments that are oriented trans to one another. The corresponding $^1$H NMR spectrum revealed four distinct *tert*-butyl environments, giving further support to the existence of two separate phosphorus environments and also suggesting that some degree of rigidity exists in the ligand backbone. These data are consistent with the formulation of **9** as ($\kappa^3$*P,C,P*-$t$Bu$_2$PN(Me)CHCH$_2$N(Me)P$t$Bu$_2$)PdI, in which CH activation of the ligand backbone occurs to yield the asymmetric pincer. This binding mode stands in contrast to that observed for related group VI and Pd and Pt complexes where bis-aminophosphine ligands are observed to be simple bidentate ligands.[18] In a similar fashion, the species ($\kappa^3$-*P,C,P*-$t$Bu$_2$PN(Me)CHCH$_2$N(Me)P$t$Bu$_2$)PdX (X = Br (**10**), Cl (**11**)) were prepared. Compounds **9** and **11** were characterized by X-ray diffraction studies (Figures 5 and 6, respectively). The Pd center in each adopts a distorted-square-planar geometry defined by the P atoms, the metalated C atom, and the halide. Pd−P distances were determined to be 2.298(1) Å in **9** and 2.2847(8) and 2.3023(8) Å in **11**. The Pd−C bond distances were found to be 2.062(8) Å in **9**, while the disorder in **11** generates some uncertainty in the Pd−C bond lengths. The P−Pd−P bond angle is 149.62(6)° in **9** and 149.50(3)° in **11**, which deviate significantly from the typical square-planar angle of 180°. These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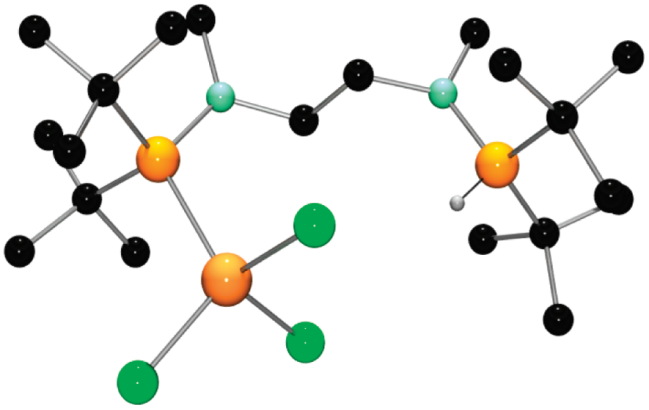

**Figure 7.** Pov-ray depiction of **12**: (black) C; (blue-green) N; (orange) P; C(green) Cl; (burnt orange) Ni. Hydrogen atoms, except for PH, are omitted for clarity.

distortions result from the constraints associated with the four-membered ring.

In attempts to prepare Ni analogues of **9**−**11**, **3** was reacted with $NiCl_2$(dme), yielding a bright turquoise product. Broad NMR spectra suggested the formation of a paramagnetic species and thus a tetrahedral geometry. Despite the poor solubility, a broad signal was observed in the $^{31}$P NMR spectrum at 53.3 ppm ($^1J_{P-H}$ = 508 Hz) indicative of the presence of a phosphonium fragment. Light green crystals were crystallographically characterized as the zwitterionic nickel phosphonium complex $[(t\mathrm{Bu}_2\mathrm{PH})(\mathrm{NMe})(\mathrm{CH}_2)_2(\mathrm{NMe})(t\mathrm{Bu}_2\mathrm{P})\mathrm{NiCl}_3]$, (**12**) (Figure 7), in which phosphine acts as a monodentate ligand binding to a $NiCl_3$ anionic moiety. The source of proton that gives rise to the counter phosphonium cation is unclear but could arise from adventitious moisture or residual base-HCl in the ligand. The geometry at Ni is pseudotetrahedral with a Ni−P distance of 2.372(1), Ni−Cl distances of 2.250(1), 2.267(1), and 2.270(1) Å, and P−Ni−Cl angles of 112.72(4), 106.50(4), and 111.66(4)°. An intermolecular interaction in the solid state between Cl and the PH proton is also evident at a distance of 3.053 Å. A similar zwitterionic by-product was observed by Zargarian and co-workers in their efforts to isolate Ni-pincer complexes incorporating $t\mathrm{Bu}_2\mathrm{P}(\mathrm{CH}_2)_5\mathrm{P}t\mathrm{Bu}_2$.[35] In this case, further protonation gave the salt $[(t\mathrm{Bu}_2\mathrm{PH}(\mathrm{CH}_2)_2)_2\mathrm{CH}_2][\mathrm{NiCl}_4]$.

Attempts to abstract HCl with triethylamine, tri-*tert*-butylphosphine, or Proton Sponge from **12** failed, yielding only intractable mixtures. However, treatment of **12** with $B(C_6F_5)_3$ afforded the species **13**, which exhibited the appearance of the characteristic doublets in the $^{31}$P NMR spectrum at 120.7 and 31.9 ppm with a P−P coupling of 289 Hz. This observation is consistent with a trans arrangement of the P atoms. Subsequent isolation of **13** confirmed removal of the anion, presumably as the acid salt. The formulation of **13** was spectroscopically confirmed as $(\kappa^3P,C,P\text{-}t\mathrm{Bu}_2\mathrm{PN}(\mathrm{Me})\mathrm{CHCH}_2\mathrm{N}(\mathrm{Me})\mathrm{P}t\mathrm{Bu}_2)\mathrm{NiCl}$ and supported by preliminary structural data. However, the poor crystal data and apparent full molecular disorder precluded the presentation of these data. The $^{11}$B NMR spectrum of the reaction mixture showed a singlet resonance at −6.7 ppm, consistent with the formation of the anion $[\mathrm{ClB}(\mathrm{C}_6\mathrm{F}_5)_3]^-$.[36] Formally, the conversion of **12** to **13** involves both loss of HCl and $\mathrm{H}[\mathrm{ClB}(\mathrm{C}_6\mathrm{F}_5)_3]$ presumably prompted by halide abstraction from Ni, although the mechanistic details of this reaction have not been elucidated.

The results above indicate that in the case of Ni complexes of the three-carbon chain secondary diamino-phosphine ligand **1**, amido-phosphine metallacycles constituting an unprecedented form of a PNP-pincer ligand are obtained. This PNP binding mode isomerizes to the PCP binding mode which is observed directly in the case of analogous Pd complexes. Shortening the alkyl chain or alkylation of the N in the ligand resulted in PCP-type pincer complexes. In addition, the chelating nature of these ligands dictates the close proximity of the resulting electron-rich metal center to C−H and N−H bonds, prompting activation of one of the N−H or C−H bonds.

## CONCLUSIONS

In conclusion, we have described the synthesis of a series of Ni and Pd complexes of seemingly bidentate bis-aminophosphine ligands. In all cases the resulting products incorporate tridentate bound ligands in which the N−H or an alkyl C−H bond has been activated, affording either PNP- or PCP-pincer complexes. The utility of these unusual species in subsequent chemistry is the subject of current investigations.

## ASSOCIATED CONTENT

**Supporting Information.** CIF files giving crystallographic data for **4**−**6**, **8**. **9**, **11**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

## AUTHOR INFORMATION

**Corresponding Author**

*E-mail: dstephan@chem.utoronto.ca. Tel: 416-946-3294.

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