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Ni, Pd, Pt, and Ru Complexes of Phosphine-Borate Ligands

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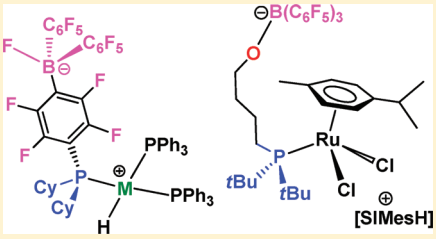
Supporting Information

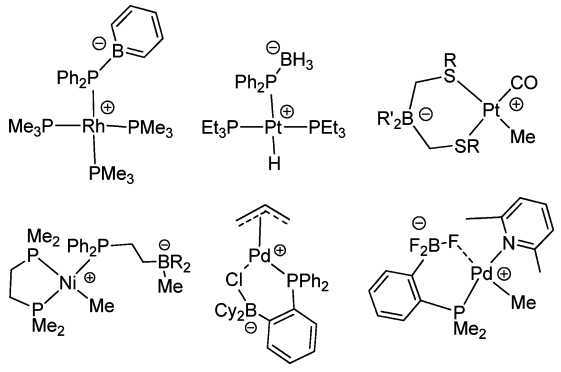
ABSTRACT: The species $Cy_2PHC_6F_4BF(C_6F_5)_2$ reacts with $Pt(PPh_3)_4$ to yield the new product *cis*-$(PPh_3)_2PtH(Cy_2PC_6F_4BF(C_6F_5)_2)$ **1** via oxidative addition of the P−H bond of the phosphonium borate to Pt(0). The corresponding reaction with $Pd(PPh_3)_4$ affords the Pd analogue of **1**, namely, *cis*-$(PPh_3)_2PdH(Cy_2PC_6F_4BF(C_6F_5)_2)$ **3**; while modification of the phosphonium borate gave the salt $[(PPh_3)_3PtH][(tBu_2PC_6F_4BF(C_6F_5)_2)]$ **2**. Alternatively initial deprotonation of the phosphonium borate gave $[tBu_3PH][Cy_2PC_6F_4BF(C_6F_5)_2]$ **4**, $[SIMesH][Cy_2PC_6F_4BF(C_6F_5)_2]$ **5** which reacted with $NiCl_2(DME)$ yielding $[BaseH]_2[trans\text{-}Cl_2Ni(Cy_2PC_6F_4BF(C_6F_5)_2)_2]$ (Base = tBu_3P **6**, SIMes **7**) or with $PdCl_2(PhCN)_2$ to give $[BaseH]_2[trans\text{-}Cl_2Pd(Cy_2PC_6F_4BF(C_6F_5)_2)_2]$ (Base = tBu_3P **8**, SIMes **9**). While $[C_{10}H_6N_2(Me)_4H][tBu_2PC_6F_4BF(C_6F_5)_2]$ **10** was also prepared. A third strategy for formation of a metal complex of anionic phosphine-borate derivatives was demonstrated in the reaction of $(COD)PtMe_2$ with the neutral phosphine-borane $Mes_2PC_6F_4B(C_6F_5)_2$ affording $(COD)PtMe(Mes_2PC_6F_4BMe(C_6F_5)_2)$ **11**. Extension of this reactivity to $tBu_2PH(CH_2)_4OB(C_6F_5)_3)$ was demonstrated in the reaction with $Pt(PPh_3)_4$ which yielded *cis*-$(PPh_3)_2PtH(tBu_2P(CH_2)_4OB(C_6F_5)_3)$ **12**, while the reaction of $[SIMesH][tBu_2P(CH_2)_4OB(C_6F_5)_3]$ **13** with $NiCl_2(DME)$ and $PdCl_2(PhCN)_2$ afforded the complexes $[SIMesH]_2[trans\text{-}Cl_2Ni(tBu_2PC_4H_8OB(C_6F_5)_3)_2]$ **14** and $[SIMesH]_2[trans\text{-}PdCl_2(tBu_2P(CH_2)_4OB(C_6F_5)_3)_2]$ **15**, respectively, analogous to those prepared with **4** and **5**. Finally, the reaction of **7** and **13** with $[(p\text{-cymene})RuCl_2]_2$ proceeds to give the new orange products $[SIMesH][(p\text{-cymene})RuCl_2(Cy_2PC_6F_4BF(C_6F_5)_2)]$ **16** and $[SIMesH][(p\text{-cymene})RuCl_2(tBu_2P(CH_2)_4OB(C_6F_5)_3)]$ **17**, respectively. Crystal structures of **1**, **6**, **10**, **11**, **12**, and **16** are reported.



INTRODUCTION

Neutral phosphine ligands are ubiquitous in transition metal chemistry. On the other hand, anionic phosphine donors have also garnered some attention. For example, a variety of hybrid donor ligands including those incorporating phosphine-carbon,[1] phosphine-alkoxide,[1e,2] phosphine-amide,[3] phosphine-sulfonate[4] or phosphine-thiolate[5] donors have been exploited in a range of coordination chemistry and in some cases, catalysis. Anionic phosphines which provide a pendant noncoordinating anion have also been explored as the proximity of the anion to a metal center impacts not only on solubility but also on the subsequent reactivity. Several strategies to such ligands have been reported, and the subsequent chemistry of such complexes has been explored. For example, sulfonated triphenylphosphine has been employed to exploit the chemistry of metal complexes in catalysis in water.[6] In other efforts to phosphines with pendant anions, Fu and co-workers[7] have developed the chemistry of diphenylphosphidoboratabenzene, $[Ph_2PBC_5H_5]^-$ to prepare zwitterionic Zr, Fe, and Rh complexes (Scheme 1). In related work, Manners and co-workers have described Pt complexes of phosphine-borane anions of the form $[R_2PBH_3]^-$ and $[RHPBH_3]^-$ (Scheme 1).[8] In a different approach, Peters and co-workers have developed a family of complexes derived from the use of *bis*- and *tris*-(phosphino)borates[9] where these ligands provide a remote borate anion (Scheme 1). Alternatively another strategy is based on the use of neutral ambiphilic phosphine-borane species[10] to abstract a halide or an alkyl group from a metal thus generating the pendant anion. For example, Bourissou et al. have exploited this approach in the reaction of $iPr_2PC_6H_4BCy_2$ with $[(Allyl)PdCl]_2$ to give Pd−P and B−Cl bonds (Scheme 1),[10h] while Tilley and co-workers have described the reactions of phosphinoethylboranes with Ni-methyl species to give zwitterionic phosphine-methylborate complexes (Scheme 1).[11] Very recently Piers and Jordan have described similar species derived from the coordination of the anionic BF_3 moiety adjacent the phosphine donors in the anionic phosphine of the form $F_3BC_6H_4PR_2$(Scheme 1).[12]

Scheme 1. Examples of Complexes Containing Anionic Phosphine Ligands



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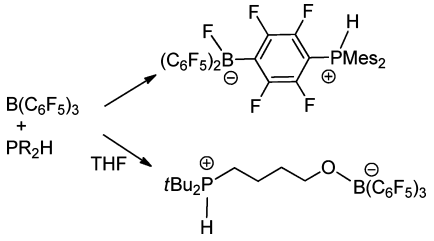
Recently we have developed the chemistry of frustrated Lewis pairs (FLPs); while most notably, these systems activate H_2, they have also been shown to activate a variety of molecules, including: B−H bonds,[13] disulfides,[14] CO_2,[15] alkenes,[16] dienes,[17] alkynes,[18] CO, azides,[19] N_2O,[20] and most recently NO.[21] This work was initiated based on the synthesis of zwitterions of the form $R_2PH(C_6F_4)BF(C_6F_5)_2$ which are readily prepared from the combination of sterically bulky secondary phosphines and $B(C_6F_5)_3$ (Scheme 2). Analogous

Scheme 2. FLP Routes to Zwitterionic Phosphonium Borates



zwitterionic species are derived from reactions of such P/B FLPs with THF or lactones resulting in ring opened products (Scheme 2).[22] These zwitterions are readily accessible in high yields from commercially available precursors and provide easy access to anionic phosphine donors. In this paper, we demonstrate that these materials can be used to prepare a series of zwitterionic phosphine-borate complexes of Ni, Pd, Pt, and Ru. This work demonstrates that exploiting this FLP chemistry provides a convenient avenue to anionic phosphines with pendent noncoordinating anions.

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, toluene, hexane, and pentane) were purified employing a Grubbs' type column system manufactured by Innovative Technology. ^1H, ^{11}B, $^{13}C\{^1H\}$, ^{19}F, 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, ^{11}B, ^{19}F and ^{31}P resonances were referenced externally to 85% H_3PO_4, $BF_3(Et_2O)$, and $CFCl_3$, respectively. ^1H-^{13}C HSQC and HMBC experiments were carried out using conventional pulse sequences to aid in the assignment of peaks in the $^{13}C\{^1H\}$ NMR spectra. Coupling constants (J) are reported as absolute values. Spectral simulations of selected second order ^{31}P spectra were performed using the software package MestReNova. 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. UV−visible spectra were collected as 10^{-6} M solutions on a Agilent Technology UV−visible spectrometer. ε is quoted in mol^{-1} cm^{-1}. All chemicals were purchased from Aldrich Chemical Co. or Strem Chemical Co. and used without further purification. C_6D_6 and cyclohexane were vacuum transferred from Na/benzophenone, and freeze−pump−thaw degassed (×3). CD_2Cl_2 and C_6D_5Br were vacuum transferred from CaH_2, 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. $R_2PHC_6F_4BF(C_6F_5)_2$ (R = Cy, *t*Bu), $tBu_2PH(CH_2)_4OB(C_6F_5)_3$,[23] $Mes_2PC_6F_4B(C_6F_5)_2$,[24] and SIMes[25] were prepared by literature methods. $(COD)PtMe_2$ were purchased from the Aldrich Chemical Co.

Synthesis of *cis*-$(PPh_3)_2PtH(Cy_2PC_6F_4BF(C_6F_5)_2)$ 1, $[(PPh_3)_3PtH][(tBu_2PC_6F_4BF(C_6F_5)_2)]$ 2, *cis*-$(PPh_3)_2PdH(Cy_2PC_6F_4BF(C_6F_5)_2)$ 3, and *cis*-$(PPh_3)_2PtH(tBu_2P(CH_2)_4OB(C_6F_5)_3)$ 12. These compounds were prepared in a similar fashion using analogous precursors and thus only one preparation is detailed. A cloudy white solution of $Cy_2PHC_6F_4BF(C_6F_5)_2$ (0.114 g, 0.161 mmol) in toluene (5 mL) was added to an orange solution of $Pt(PPh_3)_4$ (0.200 g, 0.161 mmol) in toluene (5 mL). The reaction mixture was stirred at room temperature overnight. The resulting cloudy orange solution was concentrated via vacuum to 2 mL. Ten milliliters of pentane were added to precipitate a pale peach solid. The solvent was decanted, and the solid washed with 3 × 5 mL of pentane and dried under vacuum.

1. Pale peach powder. Yield 198 mg (86%). Crystals suitable for X-ray diffraction were grown from a layered C_6D_6 /cyclohexane solution. ^1H NMR (CD_2Cl_2): 7.34−7.11 (br m, 30H, $P\{C_6H_5\}_3$), 2.33−1.16 (br m, 22H, $P\{C_6H_{11}\}_2$), −6.73 (ddd, $^1J_{H-Pt}$ = 778 Hz, $^2J_{H-P}$ = 160, 17, 13 Hz, 1H, Pt-*H*). ^{11}B NMR (CD_2Cl_2): −0.78 (br). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) partial: 134.53 (d, J_{C-P} = 12 Hz, Ar−C, $P\{C_6H_5\}_3$), 131.55 (d, J_{C-P} = 10 Hz, Ar−C, $P\{C_6H_5\}_3$), 128.87 (d, J = 11 Hz, Ar−C, $P\{C_6H_5\}_3$), 30.82 (m, $P\{C_6H_{11}\}_2$), 27.16 (d, J_{C-P} = 7 Hz, $P\{C_6H_{11}\}_2$), 27.03 (d, J_{C-P} = 6 Hz, $P\{C_6H_{11}\}_2$), 26.45 (s, $P\{C_6H_{11}\}_2$). ^{19}F NMR (CD_2Cl_2): −130.41 (br s, 2F, C_6F_4), −132.83 (br m, $^3J_{F-F}$ = 12 Hz, 2F, C_6F_4), −135.38 (br m, 4F, *o*-C_6F_5), −162.35 (t, $^3J_{F-F}$ = 20 Hz, 2F, *p*-C_6F_5), −166.81 (tm, $^3J_{F-F}$ = 20 Hz, 4F, *m*-C_6F_5), −192.65 (br s, 1F, B-*F*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 28.98 (dd, $^1J_{P-Pt}$ = 2805 Hz, $^3J_{P-P}$ = 341, 19 Hz, *P*Cy_2), 22.01 (dd, $^1J_{P-Pt}$ = 2290 Hz, $^3J_{P-P}$ = 20, 19 Hz, *trans* HPt*P*Ph_3), 18.16 (dd, $^1J_{P-Pt}$ = 2779 Hz, $^3J_{P-P}$ = 341, 20 Hz, *cis* HPt*P*Ph_3). Anal. Calcd for $C_{66}H_{53}BF_{15}P_3Pt$: C, 55.44; H, 3.74; Found: C, 55.17; H, 3.91.

2. Pale peach powder. Yield 173 mg (78%). ^1H NMR (CD_2Cl_2): 7.41−7.05 (br m, 45H, $P\{C_6H_5\}_3$), 1.22 (d, $^3J_{H-P}$ = 13 Hz, 18H, $P\{C(CH_3)_3\}_2$), −5.76 (ddd, $^1J_{H-Pt}$ = 773 Hz, $^2J_{H-P}$ = 164, 18, 13 Hz, 1H, Pt-*H*). ^{11}B NMR (CD_2Cl_2): −0.54 (br d, $^1J_{B-F}$ = 69 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) partial: 134.27 (t, J_{C-P} = 6 Hz, $P\{C_6H_5\}_3$), 131.84 (br d, J_{C-P} = 6 Hz, $P\{C_6H_5\}_3$), 131.42 (d, J_{C-P} = 2 Hz, $P\{C_6H_5\}_3$), 129.40 (s, $P\{C_6H_5\}_3$), 129.24 (t, J_{C-P} = 5 Hz, $P\{C_6H_5\}_3$), 128.95 (d, J = 10 Hz, $P\{C_6H_5\}_3$), 128.58 (s, $P\{C_6H_5\}_3$), 125.66 (s, $P\{C_6H_5\}_3$), 30.61 (dd, $^1J_{C-P}$ = 19 Hz, $^4J_{C-F}$ = 3 Hz, $P\{C(CH_3)_3\}_2$), 21.56 (s, $P\{C(CH_3)_3\}_2$). ^{19}F NMR (CD_2Cl_2): −124.68 (br s, 1F, C_6F_4), −132.34 (br dm, $^3J_{F-P}$ = 109 Hz, 1F, C_6F_4), −135.48 (br m, 6F, 2F C_6F_4 and 4F *o*-C_6F_5), −163.04 (t, $^3J_{F-F}$ = 20 Hz, 2F, *p*-C_6F_5), −167.17 (t, $^3J_{F-F}$ = 20 Hz, 4F, *m*-C_6F_5), −191.84 (br s, 1F, B-*F*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 23.14 (t, $^1J_{P-Pt}$ = 2220 Hz, $^3J_{P-P}$ = 19 Hz, *trans* HPt(PPh_3)$_3$), 22.90 (d, $^1J_{P-Pt}$ = 2819 Hz, $^3J_{P-P}$ = 19 Hz, *cis* HPt(PPh_3)$_3$), 20.28 (br d, $^3J_{P-F}$ = 110 Hz, *Pt*Bu_2). Anal. Calcd for $C_{80}H_{64}BF_{15}P_4Pt$: C, 58.58; H, 3.93; Found: C, 58.19; H, 4.49.

3. white powder. Yield 57 mg (64%). ^1H NMR (CD_2Cl_2): 7.36−7.16 (br m, 30H, $P\{C_6H_5\}_3$), 2.21−1.16 (br m, 22H, $P\{C_6H_{11}\}_2$), −8.05 (ddd, $^2J_{H-P}$ = 175, 13, 6 Hz, 1H, Pd-*H*). ^{11}B NMR (CD_2Cl_2): −0.55 (br). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) partial: 133.77 (br t, Ar−C, $P\{C_6H_5\}_3$), 130.94 (br s, Ar−C, $P\{C_6H_5\}_3$), 130.86 (br s, Ar−C, $P\{C_6H_5\}_3$), 128.47 (br d, Ar−C, $P\{C_6H_5\}_3$), 30.32 (m, $P\{C_6H_{11}\}_2$), 26.17 (br d, $P\{C_6H_{11}\}_2$), 26.12 (s, $P\{C_6H_{11}\}_2$). ^{19}F NMR (CD_2Cl_2): −131.85 (br s, 2F, C_6F_4), −133.71 (br m, $^3J_{F-P}$ = 12 Hz, 2F, C_6F_4), −136.39 (br m, 4F, *o*-C_6F_5), −163.36 (t, $^3J_{F-F}$ = 20 Hz, 2F, *p*-C_6F_5), −167.83 (tm, $^3J_{F-F}$ = 20 Hz, 4F, *m*-C_6F_5), −193.40 (br s, 1F, B-*F*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 31.09 (ddt, $^3J_{P-P}$ = 343, 28 Hz, $^3J_{F-P}$ = 12 Hz, *P*Cy_2), 24.02 (dd, $^3J_{P-P}$ = 343, 29 Hz, *cis* HPd*P*Ph_3) 20.45 (ddt, $^3J_{P-P}$ = 29, 28 Hz, *trans* HPd*P*Ph_3). Anal. Calcd for $C_{66}H_{53}BF_{15}P_3Pd$: C, 59.10; H, 3.98; Found: C, 57.27[26]; H, 4.09.

12. pale peach powder. Yield 71 mg (84%). Crystals suitable for X-ray diffraction were grown from a layered C_6D_6/pentane solution. ^1H NMR (CD_2Cl_2): 7.40−7.05 (br m, 30H, $P\{C_6H_5\}_3$), 2.88 (br s, 2H, CH_2CH_2O), 1.54 (br s, 4H, $CH_2CH_2CH_2O$), 1.28 (d, $^3J_{H-P}$ = 14 Hz, 18H, $P\{C(CH_3)_3\}_2$), 0.87 (br s, 2H, PCH_2CH_2), −6.92 (ddd, $^1J_{H-Pt}$ = 786 Hz, $^2J_{H-P}$ = 162, 14, 14 Hz, 1H, Pt-*H*). ^{11}B NMR (CD_2Cl_2): −2.94 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) partial: 134.34 (br d, J_{C-P} = 40 Hz, Ar−C, $P\{C_6H_5\}_3$), 131.33 (br d, J_{C-P} = 26 Hz,

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Ar−C, P{C_6H_5}$_3$), 129.11 (d, J_{C-P} = 10 Hz, Ar−C, P{C_6H_5}$_3$), 128.83 (d, J_{C-P} = 11 Hz, Ar−C, P{C_6H_5}$_3$), 63.14 (s, CH_2CH_2O), 37.18 (d, $^1J_{C-P}$ = 27.5 Hz, P{$C(CH_3)_3$}$_2$), 34.08 (d, $^1J_{C-P}$ = 16 Hz, PCH_2CH_2), 30.01 (br d, P{$C(CH_3)_3$}$_2$), 23.23 (s, CH_2CH_2O), 21.16 (s, PCH_2CH_2). ^{19}F NMR (CD_2Cl_2): −133.80 (d, $^3J_{F-F}$ = 25 Hz, 6F, *o*-C_6F_5), −163.96 (t, $^3J_{F-F}$ = 20 Hz, 3F *p*-C_6F_5), −167.43 (t, $^3J_{F-F}$ = 19 Hz, 6F, *m*-C_6F_5). ^{31}P{^{1}H} NMR (CD_2Cl_2): 56.52 (dd, $^1J_{P-Pt}$ = 2729 Hz, $^3J_{P-P}$ = 314, 17 Hz, *Pt*Bu_2), 21.58 (dd, $^1J_{P-Pt}$ = 2247 Hz, $^3J_{P-P}$ = 20, 17 Hz, *trans* HPt*P*Ph_3), 18.38 (dd, $^1J_{P-Pt}$ = 2569 Hz, $^3J_{P-P}$ = 314, 20 Hz, *cis* HPt*P*Ph_3). Anal. Calcd for $C_{66}H_{57}BF_{15}OP_3Pt$: C, 55.13; H, 4.02; Found: C, 55.19; H, 4.32.

Synthesis of [BaseH][$Cy_2PC_6F_4BF(C_6F_5)_2$] (Base = *t*Bu_3P 4, SIMes 5). These compounds were prepared in a similar fashion and thus only one preparation is detailed. A clear, colorless solution of *t*-Bu_3P (0.057 g, 0.282 mmol) in toluene (4 mL) was added to a white slurry of $Cy_2PHC_6F_4BF(C_6F_5)_2$ (0.200 g, 0.282 mmol) in toluene (4 mL). The resulting reaction mixture was stirred at room temperature overnight. All volatiles were removed via vacuum from the clear, colorless solution. The residue was washed with 4 × 5 mL of pentane and dried via vacuum.

4. white powder. Yield 240 mg (93%). ^{1}H NMR (C_6D_6): 6.09 (d, $^1J_{H-P}$ = 472 Hz, 1H, *H*-P{$C(CH_3)_3$}$_3$), 2.39−1.08 (br m, 22 H, P{C_6H_{11}}$_2$), 0.79 (d, $^3J_{H-P}$ = 15 Hz, 18H, H−P{$C(CH_3)_3$}$_3$). ^{11}B NMR (C_6D_6): 0.16 (br). ^{13}C{^{1}H} NMR (CD_2Cl_2): 37.86 (d, $^1J_{C-P}$ = 28 Hz, P{$C(CH_3)_3$}$_3$), 30.41 (s, P{$C(CH_3)_3$}$_3$), 27.58 (s, P{C_6H_{11}}$_2$), 27.53 (d, J_{C-P} = 6 Hz, P{C_6H_{11}}$_2$), 27.41 (d, P{C_6H_{11}}$_2$), 26.87 (s, P{C_6H_{11}}$_2$). ^{19}F NMR (C_6D_6): −132.42 (br m, 2F, C_6F_4), −134.21 (br m, 2F, C_6F_4), −134.54 (m, 4F, *o*-C_6F_5), −160.87 (t, 2F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −165.72 (td, 4F, $^3J_{F-F}$ = 21, 8 Hz, *m*-C_6F_5), −181.13 (br s, 1F, B-*F*). ^{31}P{^{1}H} NMR (C_6D_6): 48.99 (s, 1P, H*Pt*Bu_3), −10.37 (t, $^3J_{P-F}$ = 38 Hz, 1P, *P*Cy_2). Anal. Calcd for $C_{42}H_{50}BF_{15}P_2$: C, 55.28; H, 5.52; Found: C, 55.45; H, 5.63.

5. white powder. Yield 660 mg (92%). ^{1}H NMR (CD_2Cl_2): 8.19 (s, 1H, NC*H*N), 7.01 (s, 4H, *m*-MesAr-*H*), 4.42 (s, 4H, NCH_2CH_2N), 2.32 (s, 18H, Mes-CH_3), 2.20−1.12 (br m, 22 H, P{C_6H_{11}}$_2$). ^{11}B NMR (CD_2Cl_2): −0.49 (br). ^{13}C{^{1}H} NMR (CD_2Cl_2) partial: 160.36 (s, NCHN), 141.77 (s, *ipso*-MesAr-*C*-N), 135.40 (s, *o*-MesAr-*C*), 130.61 (s, *m*-MesAr-*C*), 130.30 (s, *p*-MesAr-C), 51.96 (s, NCH_2-CH_2N), 32.44 (br m, P{C_6H_{11}}$_2$), 29.81 (s, P{C_6H_{11}}$_2$), 28.98 (s, P{C_6H_{11}}$_2$), 27.75 (br m, P{C_6H_{11}}$_2$), 27.56 (br m, P{C_6H_{11}}$_2$), 26.81 (s, P{C_6H_{11}}$_2$), 21.29 (s, Mes-*p*-CH_3), 17.91 (s, Mes-*o*-CH_3). ^{19}F NMR (CD_2Cl_2): −133.80 (m, 2F, C_6F_4), −135.81 (m, 2F, C_6F_4), −135.67 (m, 4F *o*-C_6F_5), −162.64 (t, 2F, $^3J_{F-F}$ = 21 Hz, *p*-C_6F_5), −166.92 (td, 4F, $^3J_{F-F}$ = 21, 4.75 Hz, *m*-C_6F_5), −189.90 (br s, 1F, B-*F*). ^{31}P{^{1}H} NMR (CD_2Cl_2): −10.69 (t, $^3J_{P-F}$ = 35 Hz, *P*Cy_2). Anal. Calcd for $C_{51}H_{49}BF_{15}N_2P$: C, 60.25; H, 4.86; N, 2.76; Found: C, 60.51; H, 5.21; N, 3.18.

Synthesis of [BaseH]$_2$[*trans*-$Cl_2Ni(Cy_2PC_6F_4BF(C_6F_5)_2)_2$] (Base = *t*$Bu_3$P 6, SIMes 7). These compounds were prepared in a similar fashion and thus only one preparation is detailed. A solution of **4** (0.075 g, 0.082 mmol) in CH_2Cl_2 (4 mL) was added to a solution of $NiCl_2$(DME) (0.0099 g, 0.045 mmol) in CH_2Cl_2 (4 mL). The reaction mixture was stirred at room temperature overnight to give an opaque pink/purple solution. The mixture was filtered through glass wool, and the resulting clear pink/purple solution was concentrated to 1 mL via vacuum. Twelve milliliters of pentane were added to precipitate a pink solid, which was washed with 5 mL of pentane and dried via vacuum.

6. Pink powder. Yield 58 mg (73%). Crystals suitable for X-ray diffraction were grown from a layered CH_2Cl_2/pentane solution. ^{1}H NMR (CD_2Cl_2): 5.48 (d, $^1J_{H-P}$ = 445 Hz, 2H, *H*-P{$C(CH_3)_3$}$_3$), 2.20−1.29 (br m, 44H, P{C_6H_{11}}$_2$), 1.54 (d, $^3J_{H-P}$ = 16 Hz, 54H, H−P{$C(CH_3)_3$}$_3$). ^{11}B NMR (CD_2Cl_2): δ −0.76 (br). ^{13}C{^{1}H} NMR (CD_2Cl_2) partial: 37.55 (d, $^1J_{C-P}$ = 27 Hz, P{$C(CH_3)_3$}$_3$), 30.34 (s, P{$C(CH_3)_3$}$_3$), 29.96 (s, P{C_6H_{11}}$_2$), 29.28 (s, P{C_6H_{11}}$_2$), 27.88 (d, $^3J_{C-P}$ = 7 Hz, P{C_6H_{11}}$_2$), 27.02 (s, P{C_6H_{11}}$_2$). ^{19}F NMR (CD_2Cl_2): −128.05 (br m, 4F, C_6F_4), −134.65 (br s, 4F, C_6F_4), −135.25 (br s, 8F *o*-C_6F_5), −162.44 (br m, 4F, *p*-C_6F_5), −166.81 (br s, 8F, *m*-C_6F_5), −188.99 (br s, 2F, B-*F*). ^{31}P{^{1}H} NMR (CD_2Cl_2): 56.33 (s, 2P, H-*Pt*Bu_3), 10.17 (s, 2P, *P*Cy_2). Anal. Calcd for $C_{84}H_{100}B_2Cl_2F_{30}NiP_4$: C, 51.61; H, 5.16; Found: C, 50.76;[18] H, 5.40. UV−vis: λ_{max} (ε)/nm 382 (6096).

7. Pink powder. Yield 119 mg (75%). ^{1}H NMR (CD_2Cl_2): 7.76 (s, 2H, NC*H*N), 6.98 (s, 8H, *m*-MesAr-*H*), 4.25 (s, 8H, NCH_2CH_2N), 2.44−1.29 (br m, 4H, P{C_6H_{11}}$_2$), 2.29 (s, 12H, Mes-*p*-CH_3), 2.23 (s, 24H, Mes-*o*-CH_3). ^{11}B NMR (CD_2Cl_2): −0.76 (br). ^{13}C{^{1}H} NMR (CD_2Cl_2) partial: 158.90 (s, NCHN), 141.65 (s, *ipso*-MesAr−C-N), 135.22 (s, *o*-MesAr−C), 130.42 (s, *m*-MesAr−C), 129.93 (s, *p*-MesAr−C), 51.70 (s, NCH_2CH_2N), 32.33 (br s, P{C_6H_{11}}$_2$), 29.75 (br s, P{C_6H_{11}}$_2$), 28.94 (br s, P{C_6H_{11}}$_2$), 27.51 (br s, P{C_6H_{11}}$_2$), 21.09 (s, Mes-*p*-CH_3), 17.59 (s, Mes-*o*-CH_3). ^{19}F NMR (CD_2Cl_2): −134.75 (br m, 8F, C_6F_4), −135.52 (br m, 8F, *o*-C_6F_5), −162.35 (t, $^3J_{F-F}$ = 20 Hz, 4F, *p*-C_6F_5), −166.82 (br m, 8F, *m*-C_6F_5), −191.01 (br s, 2F, B-*F*).^{31}P{^{1}H} NMR (CD_2Cl_2): 10.60 (br s, *P*Cy_2). Anal. Calcd for $C_{102}H_{98}B_2Cl_2F_{30}N_4NiP_2$: C, 56.64; H, 4.57; N, 2.59; Found: C, 55.94;[18] H, 4.78; N, 2.47. UV−vis: λ_{max} (ε)/nm 382 (8525).

Synthesis of [*t*Bu_3PH]$_2$[*trans*-$Cl_2Pd(Cy_2PC_6F_4BF(C_6F_5)_2)_2$] 8, [SIMesH]$_2$[*trans*-$PdCl_2(Cy_2PC_6F_4BF(C_6F_5)_2)_2$] 9, and [SIMesH]$_2$-[*trans*-$PdCl_2$(*t*$Bu_2P(CH_2)_4OB(C_6F_5)_3)_2$] 15. These compounds were prepared in a similar fashion and thus only one preparation is detailed. A solution of $PdCl_2(PhCN)_2$ (0.014 g, 0.037 mmol) in dichloromethane (3 mL) was added to a solution of **5** (0.0668 g, 0.073 mmol) in dichloromethane (3 mL). The reaction mixture was stirred at room temperature overnight to give a clear, bright yellow solution. The reaction mixture was concentrated to 1 mL under vacuum. Ten milliliters of pentane were added to precipitate a yellow solid. The solvent was decanted, and the solid washed with a further 5 mL of pentane and dried under vacuum. The final product was a pale yellow powder.

8. Yield 59 mg (81%). ^{1}H NMR (CD_2Cl_2): 5.55 (d, $^1J_{H-P}$ = 446 Hz, 2H, *H*-P{$C(CH_3)_3$}$_3$), 2.30−1.19 (br m, 44H, P{C_6H_{11}}$_2$), 1.56 (d, $^3J_{H-P}$ = 16 Hz, 54H, H−P{$C(CH_3)_3$}$_3$). ^{11}B NMR (CD_2Cl_2): −0.32 (br). ^{13}C{^{1}H} NMR (CD_2Cl_2) partial: 37.40 (d, $^1J_{C-P}$ = 27 Hz, P{$C(CH_3)_3$}$_3$), 29.96 (s, P{$C(CH_3)_3$}$_3$), 32.75 (s, P{C_6H_{11}}$_2$), 29.51 (s, P{C_6H_{11}}$_2$), 28.83 (s, P{C_6H_{11}}$_2$), 27.27 (d, J_{C-P} = 7 Hz, P{C_6H_{11}}$_2$), 26.51 (s, P{C_6H_{11}}$_2$). ^{19}F NMR (CD_2Cl_2): −129.30 (br s, 4F, C_6F_4), −135.42 (br dm, 4F, C_6F_4), −136.19 (br m, 8F, *o*-C_6F_5), −163.37 (t, 4F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −167.76 (t, 8F, $^3J_{F-F}$ = 20, 7 Hz, *meta*-C_6F_5), −189.45 (br s, 2F, B-*F*). ^{31}P{^{1}H} NMR (CD_2Cl_2): 55.96 (s, 2P, *Pt*Bu_3), 25.75 (s, 2P, *P*Cy_2). Anal. Calcd for $C_{84}H_{100}B_2Cl_2F_{30}P_4Pd$: C, 50.38; H, 5.03; Found: C, 50.67; H, 5.37.

9. Beige powder. Yield 77 mg (47%). ^{1}H NMR (CD_2Cl_2): 7.85 (s, 2H, NC*H*N), 6.98 (s, 8H, *m*-MesAr-*H*), 4.33 (s, 8H, NCH_2CH_2N), 2.77 (br m, 4H, P{C_6H_{11}}$_2$), 2.30 (s, 12H, Mes-*p*-CH_3), 2.26 (s, 24H, Mes-*o*-CH_3), 2.14−1.67 (br m, 40 H, P{C_6H_{11}}$_2$). ^{11}B NMR (CD_2Cl_2): −0.82 (br). ^{13}C{^{1}H} NMR (CD_2Cl_2) partial: 158.91 (s, NCHN), 141.65 (s, *ipso*-MesAr−C-N), 135.37 (s, *o*-MesAr−C), 130.46 (s, *m*-MesAr−C), 130.07 (s, *p*-MesAr−C), 51.82 (s, NCH_2-CH_2N), 32.96 (m, P{C_6H_{11}}$_2$), 29.75 (d, J_{C-P} = 3 Hz, P{C_6H_{11}}$_2$), 28.99 (d, J_{C-P} = 3 Hz, P{C_6H_{11}}$_2$), 27.52 (s, P{C_6H_{11}}$_2$), 21.14 (s, Mes-*p*-CH_3), 17.66 (s, Mes-*o*-CH_3). ^{19}F NMR (CD_2Cl_2): −134.62 (br s, 8F, C_6F_4), −135.52 (br m, 8F *o*-C_6F_5), −162.35 (t, 4F, $^3J_{F-F}$ = 20 Hz, *p*-C_6F_5), −167.17 (dt, 8F, $^3J_{F-F}$ = 20, 5 Hz, *m*-C_6F_5), −191.26 (br s, 2F, B-*F*). ^{31}P{^{1}H} NMR (CD_2Cl_2): 26.05 (s, *P*Cy_2). Anal. Calcd for $C_{102}H_{98}B_2Cl_2F_{30}N_4P_2Pd$: C, 55.42; H, 4.47; N, 2.53; Found: C, 55.86; H, 4.51; N, 2.63.

15. Pale yellow powder. Yield 77 mg (47%). ^{1}H NMR (CD_2Cl_2): 8.00 (s, 2H, NC*H*N), 7.03 (s, 8H, *m*-MesAr-*H*), 4.44 (s, 8H, NCH_2CH_2N), 3.01 (br s, 4H, CH_2CH_2O), 2.33 (s, 24H, Mes-*o*-CH_3), 2.31 (s, 12H, Mes-*p*-CH_3), 1.76 (br s, 8H, $PCH_2CH_2CH_2$), (1.61 (br s, 4H, PCH_2CH_2), 1.37 (t, 36H, $^3J_{H-P}$ = 6 Hz, P{$C(CH_3)_3$}$_2$). ^{11}B NMR (CD_2Cl_2): −3.02 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2) partial: 160.76 (s, NCHN), 141.90 (s, *ipso*-MesAr−C-N), 135.13 (s, *o*-MesAr−C), 130.60 (s, *m*-MesAr−C), 130.01 (s, *p*-MesAr−C), 63.93 (d, $^2J_{C-B}$ = 7 Hz, CH_2CH_2O), 61.04 (d, $^1J_{C-P}$ = 10 Hz, PCH_2CH_2), 51.87 (s, NCH_2CH_2N), 30.85 (br m, P{$C(CH_3)_3$}$_2$), 30.76 (br d, P{$C(CH_3)_3$}$_2$), 23.44 (s, CH_2CH_2O), 22.77 (s, PCH_2CH_2), 21.15 (s, Mes-*p*-CH_3), 17.79 (s, Mes-*o*-CH_3). ^{19}F NMR (CD_2Cl_2): −133.80 (br d, $^3J_{F-F}$ = 22 Hz, 4F, *o*-C_6F_5), −163.90 (t, $^3J_{F-F}$ = 20 Hz, 2F, *p*-C_6F_5), −167.29 (t, $^3J_{F-F}$ = 20 Hz, 4F, *m*-C_6F_5). ^{31}P{^{1}H} NMR

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(CD_2Cl_2): 40.61 (br s, $PtBu_2$). Anal. Calcd for $C_{102}H_{106}B_2Cl_2F_{30}N_4O_2P_2Pd$: C, 54.43; H, 4.75; N, 2.49; Found: C, 54.19; H, 4.95; N, 2.41.

Synthesis of $[C_{10}H_6N_2(Me)_4H][tBu_2PC_6F_4BF(C_6F_5)_2]$ 12. To a slurry of $tBu_2PH(C_6F_4)BF(C_6F_5)_2$ (0.050 g, 0.076 mmol) in benzene (2 mL) was added a solution of proton sponge (0.016 g, 0.075 mmol) in benzene (1 mL). The reaction was allowed to stir for 30 min at which time all volatiles were removed in vacuo to give a white solid. Yield 60 mg (91%). Crystals suitable for X-ray diffraction were grown via slow evaporation of a concentrated benzene solution at 25 °C. ^{1}H NMR (C_6D_6): 18.16 (s, 1H, N*H*), 7.39 (d, $^3J_{H-H}$ = 8 Hz, 2H, $C_{10}H_6$), 7.08 (t, $^3J_{H-H}$ = 8 Hz, 2H, $C_{10}H_6$), 6.84 (d, $^3J_{H-H}$ = 8 Hz, 2H, $C_{10}H_6$), 2.31 (s, 12H, $\{N(CH_3)_2\}_2$), 1.25 (d, $^1J_{H-P}$ = 14 Hz, 18H, $P\{C(CH_3)_3\}_2$). $^{11}B\{^1H\}$ NMR (C_6D_6): −0.78 (br). $^{13}C\{^1H\}$ NMR (C_6D_6) partial: 149.20 (dm, $^1J_{C-F}$ = 230 Hz, *C*F), 148.76 (dm, $^1J_{C-F}$ = 240 Hz, *C*F), 147.37 (dm, $^1J_{C-F}$ = 240 Hz, *C*F), 143.74 (s, quaternary, $C_{10}H_6N_2(CH_3)_4H$), 139.48 (dm, $^1J_{C-F}$ = 245 Hz, *C*F), 137.10 (dm, $^1J_{C-F}$ = 250 Hz, *C*F), 135.68 (s, quaternary, $C_{10}H_6N_2(CH_3)_4H$), 129.43 (s, *o*-$C_{10}H_6N_2(CH_3)_4H$), 126.97 (s, *m*-$C_{10}H_6N_2(CH_3)_4H$), 120.81 (s, *p*-$C_{10}H_6N_2(CH_3)_4H$), 118.68 (s, quaternary, $C_{10}H_6N_2(CH_3)_4H$), 45.29 (s, $N(CH_3)_2$), 32.71 (d, $^1J_{C-P}$ = 28 Hz, $P\{C(CH_3)_3\}_2$), 30.55 (d, $^2J_{C-P}$ = 20 Hz, $P\{C(CH_3)_3\}_2$). ^{19}F NMR (C_6D_6): −123.92 (ddd, 1F, $^3J_{F-F(D)}$ = 38 Hz, $^3J_{F-P}$ = 21 Hz, $^4J_{F-F(B)}$ = 14 Hz, C_6F_4 A), −130.99 (ddd, 1F, $^3J_{F-P}$ = 110 Hz, $^3J_{F-F(C)}$ = 24 Hz, $^4J_{F-F(A)}$ = 14 Hz C_6F_4 B), −134.56 (ddd, 1F, $^3J_{F-F(B)}$ = 24 Hz, $^4J_{F-P}$ = 14 Hz, $^4J_{F-P}$ = 7 Hz, C_6F_4 C), −134.91 (m, 1F, C_6F_4 D), −134.91 (dm, 4F, $^3J_{F-F}$ = 15 Hz, *o*-C_6F_5), −161.51 (t, 2F, $^3J_{F-F}$ = 20 Hz , *p*-C_6F_5), - 166.17 (ddd, 4F, $^3J_{F-F}$ = 20 Hz, $^3J_{F-F}$ = 15 Hz, $^6J_{F-F}$ = 9 Hz *meta*-C_6F_5), −190.63 (br s, 1F, $Ar^F{}_3BF$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 21.67 (dddd, $^3J_{P-F(B)}$ = 110 Hz, $^3J_{P-F(A)}$ = 21 Hz, $^5J_{P-F(C)}$ = 7 Hz, $^5J_{P-F(D)}$ = 5 Hz). Anal. Calcd. for $C_{40}H_{37}BF_{15}N_2P$: C, 55.06; H, 4.27; N, 3.21. Found: C, 55.11; H, 4.37; N, 3.07%.

Synthesis of $(COD)PtMe(Mes_2PC_6F_4BMe(C_6F_5)_2)$ 11. To a vial charged with $(COD)PtMe_2$ (0.026 g, 0.078 mmol) and C_6D_5Br (0.5 mL) was added $Mes_2P(C_6F_4)B(C_6F_5)_2$ (0.060 g, 0.078 mmol) dissolved in C_6D_5Br (0.5 mL). The mixture was shaken for 5 min and transferred to an NMR tube for analysis. Quantitative formation of **10** was observed by NMR spectroscopy. After solvent removal under vacuum, **10** was obtained as a cream colored solid in 81% yield (70 mg). Crystals suitable for X-ray diffraction were grown by slowly adding pentane to the above sample and letting stand 24 h. ^{1}H NMR (C_6D_5Br, −25 °C): 7.25−7.67 (br m, 4H, $P(C_6H_2)_2$), 5.90 (br s, 1H, COD), 5.16 (br s, 1H, COD), 4.92 (br s, 2H, COD), 3.10 (br s, 3H, $P(C_6H_2Me\text{-}4)$), 2.88 (br s, 3H, $P(C_6H_2Me\text{-}4)$), 2.41−2.10 (br m, 18H, $P(C_6H_2Me\text{-}2,6)_2$, COD), 1.54 (br s, 2H, COD), 1.25 (br m, 3H, B*Me*), 0.44 (br s, 3H, Pt*Me*). $^{11}B\{^1H\}$ NMR (C_6D_5Br): −14.60 (br). $^{13}C\{^1H\}$ NMR (C_6D_5Br) partial: 148.87 (dm, $^1J_{C-F}$ = 250 Hz, *C*F), 145.10 (dm, $^1J_{C-F}$ = 250 Hz, *C*F), 142.50 (br, quat), 141.45 (dm, $^1J_{C-F}$ = 245 Hz, *C*F), 137.30 (dm, $^1J_{C-F}$ = 250 Hz, *C*F), 130.83 (s, *p*-C_6H_2), 111.68 (br, COD), 108.01 (m, COD), 30.03 (br, COD), 29.37 (br, COD), 24.50 (br, $C_6H_2Me\text{-}4$), 20.94 (br, $C_6H_2Me\text{-}2,6$), 11.33 (br, B*Me*), 5.39 (br, Pt*Me*). ^{19}F NMR (C_6D_5Br): −128.70 (m, $^3J_{F-F}$ = 20 Hz, 1F, C_6F_4), −129.28 (m, 1F, C_6F_4), −130.04 (m, 1F, C_6F_4), −132.21 (m, $^3J_{F-F}$ = 22 Hz, 1F, C_6F_4), −132.57 (m, $^3J_{F-F}$ = 24 Hz, 4F, *o*-C_6F_5), −163.81 (m, $^3J_{F-F}$ = 21 Hz, 2F, *p*-C_6F_5), - 166.65 (m, $^3J_{F-F}$ = 22 Hz, 4F, *m*-C_6F_5). $^{31}P\{^1H\}$ NMR (C_6D_5Br): −11.33 (d, $^1J_{P-Pt}$ = 3831 Hz, $P(Mes)_2$). Anal. Calcd for $C_{46}H_{40}BF_{14}PPt$: C, 50.43; H, 3.68; Found: C, 50.27; H, 3.41.

Synthesis of $[SIMesH][tBu_2P(CH_2)_4OB(C_6F_5)_3]$ 13. To a solution of $tBu_2PH(CH_2)_4OB(C_6F_5)_3$ (0.500 g, 0.685 mmol) in toluene (5 mL) a solution of SIMes (0.2157 g, 0.685 mmol) in toluene (3 mL) was added. The resulting clear, yellow solution was stirred at room temperature for 1 h. All volatiles were removed via vacuum. The yellow oil was washed with 4 × 5 mL of pentane and dried under vacuum. The final product was a white powder. Yield 682 mg (96%). ^{1}H NMR (CD_2Cl_2): 7.96 (s, 1H, NC*H*N), 7.06 (s, 4H, *m*-MesAr-*H*), 4.44 (s, 4H, NCH_2CH_2N), 3.43 (br m, 2H, CH_2CH_2O), 2.34 (s, 12H, Mes-*o*-CH_3), 2.33 (s, 6H, Mes-*p*-CH_3), 1.53 (br m, 2H, CH_2CH_2OB), 1.46 (br m, 2H, PCH_2CH_2), 1.26 (br m, 2H, PCH_2CH_2), 1.03 (d, 18H, $^1J_{H-P}$ = 10.65 Hz, $P\{C(CH_3)_3\}_2$). ^{11}B NMR (CD_2Cl_2): −3.00 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) partial: 159.31 (s, NCHN), 142.07 (s, *ipso*-MesAr−C-N), 135.01 (s, *o*-MesAr−C), 130.68 (s, *m*-MesAr−C), 129.76 (s, *p*-MesAr−C), 51.86 (s, NCH_2CH_2N), 64.43 (s, CH_2CH_2O), 34.91 (d, $^1J_{C-P}$ = 12 Hz, PCH_2CH_2), 21.64 (s, CH_2CH_2O), 21.46 (d, $^2J_{C-P}$ = 5 Hz, PCH_2CH_2), 31.21 (d, $^1J_{C-P}$ = 21 Hz, $P\{C(CH_3)_3\}_2$), 29.68 (d, $^1J_{C-P}$ = 14 Hz, $P\{C(CH_3)_3\}_2$), 21.10 (s, Mes-*p*-CH_3), 17.76 (s, Mes-*o*-CH_3). ^{19}F NMR (CD_2Cl_2): −133.86 (br d, $^3J_{F-F}$ = 22 Hz, 6F, *o*-C_6F_5), −164.05 (t, $^3J_{F-F}$ = 20 Hz, 3F, *p*-C_6F_5), −167.39 (br t, $^3J_{F-F}$ = 20 Hz, 6F, *m*-C_6F_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 28.46 (s, 1P, $PtBu_2$). Anal. Calcd for $C_{51}H_{53}BF_{15}N_2OP$ + 0.6 equiv of toluene: C, 60.71; H, 5.33; N, 2.56; Found: C, 60.63; H, 5.52; N, 2.69.

Synthesis of $[SIMesH]_2[trans\text{-}Cl_2Ni(tBu_2P(CH_2)_4OB(C_6F_5)_3)_2]$ 14. A solution of $NiCl_2$(DME) (0.011 g, 0.049 mmol) in CH_2Cl_2 (3 mL) was added to a solution of **13** (0.100 g, 0.096 mmol) in CH_2Cl_2 (3 mL). After stirring at room temperature for 10 min, the reaction mixture began to change color from yellow to green. Stirring was continued overnight to give an opaque blue solution. The solution was filtered through glass wool to remove any unreacted $NiCl_2$(DME). Volatiles were removed from the filtrate via vacuum. The blue oily residue was washed with 2 × 5 mL of pentane, redissolved in 2 mL of toluene and precipitated with 10 mL of pentane. The residue was again dissolved in 5 mL of CH_2Cl_2, filtered through glass wool, and all volatiles were removed via vacuum to give a blue oil. Five milliliters of hexane were added, and the mixture stored in the freezer at −35 °C. The final product was a blue powder. Yield 78 mg (72%). ^{1}H NMR (CD_2Cl_2): δ 9.37 (s, 2H, NC*H*N), 7.20 (s, 8H, *m*-MesAr-*H*), 5.37 (s, 8H, NCH_2CH_2N), 3.34 (br s, 4H, CH_2CH_2O), 2.83 (br s, 4H, CH_2CH_2O), 2.61 (s, 12H, Mes-*p*-CH_3), 2.43 (s, 24H, Mes-*o*-CH_3), 2.27 (br s, 4H, PCH_2CH_2), 1.81 (br s, 4H, PCH_2CH_2), 1.61 (d, 36H, $^3J_{H-P}$ = 16 Hz, $P\{C(CH_3)_3\}_2$). ^{11}B NMR (CD_2Cl_2): δ −2.41 (s), −2.93 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) partial: δ 168.50 (s, 2C, NCHN), 142.06 (s, *ipso*-MesAr−C-N), 136.18 (s, *p*-MesAr−C), 131.53 (s, *m*-MesAr−C and *o*-MesAr−C), 64.34 (br d, PCH_2CH_2), 63.84 (br d, CH_2CH_2O), 33.63 (s, CH_2CH_2O), 33.28 (s, PCH_2CH_2), 28.49 (s, Mes-*p*-CH_3), 27.01 (d, $^1J_{C-P}$ = 14 Hz, $P\{C(CH_3)_3\}_2$), 26.51 (d, $^3J_{C-P}$ = 5 Hz, $P\{C(CH_3)_3\}_2$), 21.68 (s, Mes-*o*-CH_3). ^{19}F NMR (CD_2Cl_2): δ 133.19 (d, $^3J_{F-F}$ = 23 Hz, 2F, *o*-C_6F_5), −135.10 (d, $^3J_{F-F}$ = 23 Hz, 2F, *o*-C_6F_5), −164.13 (t, $^3J_{F-F}$ = 20 Hz, 1F, *p*-C_6F_5), −164.36 (t, $^3J_{F-F}$ = 20 Hz, 2F, *p*-C_6F_5), −167.56 (dd, $^3J_{F-F}$ = 20, 19 Hz, 2F, *m*-C_6F_5), −167.84 (dd, $^3J_{F-F}$ = 20, 19 Hz, 2F, *m*-C_6F_5). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 54.02 (s, $PtBu_2$). UV−vis: λ_{max} (ε)/nm 343 (1155). Anal. Calcd for $C_{102}H_{106}B_2Cl_2F_{30}N_4NiO_2P_2$: C, 55.16; H, 4.85; N, 2.54; Found: C, 52.78; H, 4.93; N, 1.95.

Synthesis of $[SIMesH][(p\text{-cymene})RuCl_2(Cy_2PC_6F_4BF(C_6F_5)_2)]$ 16, $[SIMesH][(p\text{-cymene})RuCl_2(tBu_2P(CH_2)_4OB(C_6F_5)_3)]$ 17. These compounds were prepared in a similar fashion and thus only one preparation is detailed. A solution of $[(p\text{-cymene})RuCl_2]_2$ (0.0753 g, 0.123 mmol) in CH_2Cl_2 (6 mL) was added to a solution of **6** (0.250 g, 0.246 mmol) in CH_2Cl_2 (9 mL) to give a clear, deep red solution. The reaction mixture was stirred at room temperature overnight. The resulting solution was concentrated under vacuum to approximately 1 mL. Fifteen milliliters of pentane were added to precipitate the product. The orange powder was washed with a further 2 × 4 mL of pentane and dried under vacuum.

16. Orange powder. Yield 300 mg (92%). Crystals suitable for X-ray diffraction were grown from slow diffusion of pentane into a concentrated CH_2Cl_2 solution. ^{1}H NMR (CD_2Cl_2): 8.63 (s, 1H, NC*H*N), 7.05 (s, 4H, *m*-MesAr-*H*), 4.98 (d, $^3J_{H-H}$ = 6 Hz, 2H, *p*-cymene C_6H_4), 4.58 (d, $^3J_{H-H}$ = 6 Hz, 2H, *p*-cymene C_6H_4), 4.40 (s, 4H, NCH_2CH_2N), 2.81 (br s, 2H, $P\{C_6H_{11}\}_2$), 2.46 (septet, 1H, $^3J_{H-H}$ = 7 Hz, *p*-cymene $CH\{CH_3\}_2$), 2.38 (s, 12H, Mes-*o*-CH_3), 2.32 (s, 6H, Mes-*p*-CH_3), 2.28−1.12 (br m, 20H, $P\{C_6H_{11}\}_2$), 1.83 (s, 3H, *p*-cymene-*p*-CH_3), 1.00 (d, $^3J_{H-H}$ = 7 Hz, 6H, *p*-cymene $CH\{CH_3\}_2$). ^{11}B NMR (CD_2Cl_2): −0.52 (br). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) partial: 160.76 (s, NCHN), 141.68 (s, *ipso*-MesAr−C-N), 135.45 (s, *o*-MesAr−C), 130.58 (s, *m*-MesAr−C), 130.43 (s, *p*-MesAr−C), 108.03 (s, *p*-cymene C_6H_4), 94.63 (br s, *p*-cymene C_6H_4), 85.84 (br s, *p*-cymene C_6H_4), 30.80 (s, *p*-cymene $CH\{CH_3\}_2$), 29.79 (s, $P\{C_6H_{11}\}_2$), 28.65 (d, J_{C-P} = 11 Hz, $P\{C_6H_{11}\}_2$), 28.02 (d, J_{C-P} = 13 Hz, $P\{C_6H_{11}\}_2$),

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Table 1. Crystallographic Parameters

	1	6	10	11	12	16
formula	$C_{84}H_{83}BF_{15}P_3Pt$	$C_{84}H_{100}B_2Cl_2F_{30}NiP_4$	$C_{40}H_{37}BF_{15}N_2P$	$C_{46}H_{40}BF_{14}PPt$	$C_{66}H_{57}BF_{15}OP_3Pt$	$C_{61}H_{63}BCl_2F_{15}N_2PRu$
FW	1676.31	1954.75	872.50	1095.65	1449.93	1322.88
cryst. system	triclinic	triclinic	monoclinic	monoclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	13.6554(8)	11.6221(6)	13.5325(14)	9.031(5)	14.3247(11)	11.7251(9)
b (Å)	17.3383(10)	13.0066(7)	12.9076(13)	19.620(11)	14.9512(12)	12.7188(10)
c (Å)	17.5183(11)	16.1921(9)	23.869(3)	23.802(13)	16.0283(13)	20.8837(16)
α (deg)	75.178(3)	89.881(2)	90		86.229(4)	106.730(4)
β (deg)	67.214(3)	81.754(2)	99.999(1)	95.685(9)	64.236(4)	102.730(4)
γ (deg)	82.180(3)	66.233(2)	90		87.839(4)	90.302(4)
V (Å^3)	3693.5(4)	2212.7(2)	4106.0(7)	4197(4)	3084.7(4)	2901.4(4)
Z	2	1	4	4	2	2
d_{calc} (g cm^{-3})	1.507	1.467	1.411	1.734	1.561	1.514
μ (mm^{-1})	2.048	0.459	0.167	3.478	2.440	0.480
total data	94061	37124	38674	39136	47708	42750
R_{int}	0.0336	0.0512	0.0254	0.1113	0.0465	0.0724
$F_o^2 > 2\sigma(F_o^2)$	24500	6542	5071	3726	11929	6843
parameters	941	560	546	558	788	748
R_1	0.0282	0.0520	0.0548	0.0855	0.0379	0.0495
wR_2	0.0697	0.1308	0.1422	0.2591	0.0948	0.1225
GOF	1.028	1.007	1.045	1.076	1.022	1.008

26.77 (s, P{C_6H_{11}}$_2$), 21.91 (br m, P{C_6H_{11}}$_2$), 21.68 (s, Mes-*p*-CH_3), 21.20 (s, *p*-cymene CH{CH_3}$_2$), 18.28 (s, Mes-*o*-CH_3), 17.51 (s, *p*-cymene-*p*-CH_3). ^{19}F NMR (CD_2Cl_2): −130.76 (br s, 2F, C_6F_4), −133.86 (br m, 2F, C_6F_4), −136.51 (br m, 4F, *o*-C_6F_5), −163.23 (t, $^3J_{F-F}$ = 20 Hz, 2F, *p*-C_6F_5), −167.70 (m, 4F, *m*-C_6F_5), −192.52 (br s, 1F, B-*F*). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 37.55 (br s, *P*Cy_2). Anal. Calcd for $C_{61}H_{63}BCl_2F_{15}N_2PRu$: C, 55.38; H, 4.80; N, 2.12 Found: C, 53.48;[18] H, 4.87; N, 2.28.

17. Orange powder. Yield 282 mg (87%). ^{1}H NMR (CD_2Cl_2): 9.42 (s, 1H, NC*H*N), 7.03 (s, 4H, *m*-MesAr-*H*), 5.00 (br s, 4H, *p*-cymene, C_6H_4), 4.34 (s, 4H, NCH_2CH_2N), 3.12 (br m, 4H, CH_2CH_2O), 2.62 (septet, $^3J_{H-H}$ = 7 Hz, 1H, *p*-cymene *CH*{CH_3}$_2$), 2.41 (s, 12H, Mes-*o*-CH_3), 2.32 (s, 6H, Mes-*p*-CH_3), 2.08 (br s, 4H, CH_2CH_2OB), 1.94 (br s, 4H, PCH_2CH_2), 1.78 (s, 3H, *p*-cymene *p*-CH_3), 1.52 (br m, 4H, PCH_2CH_2), 1.13 (d, $^3J_{H-H}$ = 7 Hz, 6H, *p*-cymene CH{CH_3}$_2$), 1.09 (d, $^3J_{H-P}$ = 13 Hz, 18H, P{C(CH_3)$_3$}$_2$). ^{11}B NMR (CD_2Cl_2): −2.93 (s). ^{13}C{^{1}H} NMR (CD_2Cl_2) partial: 161.57 (s, NCHN), 141.39 (s, *ipso*-MesAr−C-N), 135.77 (s, *o*-MesAr−C), 130.72 (s, *m*-MesAr−C), 130.37 (s, *p*-MesAr−C), 103.93 (s, *p*-cymene C_6H_4), 94.29 (s, *p*-cymene C_6H_4), 87.99 (br s, *p*-cymene C_6H_4), 87.03 (br s, *p*-cymene C_6H_4), 63.21 (br s, CH_2CH_2O), 51.60 (s, NCH_2CH_2N), 38.01 (d, $^1J_{C-P}$ = 12 Hz, P{*C*(CH_3)$_3$}$_2$), 36.07 (d, $^1J_{C-P}$ = 10 Hz, PCH_2CH_2), 30.93 (d, $^3J_{C-P}$ = 3 Hz, P{C(CH_3)$_3$}$_2$), 29.09 (s, CH_2CH_2O), 23.70 (d, $^3J_{C-P}$ = 3 Hz, PCH_2CH_2), 30.25 (s, *p*-cymene *CH*{CH_3}$_2$), 21.95 (s, *p*-cymene CH{CH_3}$_2$), 21.13 (s, Mes-*p*-CH_3), 18.20 (s, Mes-*o*-CH_3), 17.14 (s, *p*-cymene-*p*-CH_3). ^{19}F NMR (CD_2Cl_2): −134.61 (d, $^3J_{F-F}$ = 23 Hz, 4F *o*-C_6F_5), −165.01 (t, $^3J_{F-F}$ = 20 Hz, 2F, *p*-C_6F_5), −168.24 (br m, 4F, *m*-C_6F_5). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 41.54 (s, *Pt*Bu_2). Anal. Calcd for $C_{61}H_{67}BCl_2F_{15}N_2OPRu$: C, 54.56; H, 5.03; N, 2.09; Found: C, 55.16; H, 5.40; N, 2.59.

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 (Table 1). 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.[47] 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 σ 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 as well as the magnitude of the residual electron densities in each case were of no chemical significance. Additional details are provided in the Supporting Information.

RESULTS AND DISCUSSION

The species $Cy_2PHC_6F_4BF(C_6F_5)_2$ reacts with $Pt(PPh_3)_4$ to yield the new product **1** which was isolated in 86% yield. The ^{11}B resonance of **1** was observed at −0.78 ppm. The corresponding ^{19}F NMR signals at −130.41 and −132.83 ppm were attributable to the C_6F_4 fragment while the resonances at −135.38, −162.35, and −166.81 ppm arose from the C_6F_5 groups. Retention of the borate portion of the phosphonium-borate was reasoned because of the unique resonance at −192.65 ppm, attributable to a B-*F* unit. The ^{31}P{^{1}H} NMR spectrum of **1** showed three doublet of doublets at 28.98, 22.01, and 18.16 ppm with P−P coupling constants of 341, 19, and 20 Hz. These signals also exhibit Pt satellites with Pt−P coupling constants of 2805, 2290, and 2779 Hz, respectively. These spectral features exhibited some degree of second order character and thus the above coupling constant and chemical shift data were derived from an iterative process of spectral simulation (Figure 1). The ^{31}P{^{1}H} NMR data are consistent with the coordination of three chemically inequivalent phosphorus centers to Pt, inferring that two

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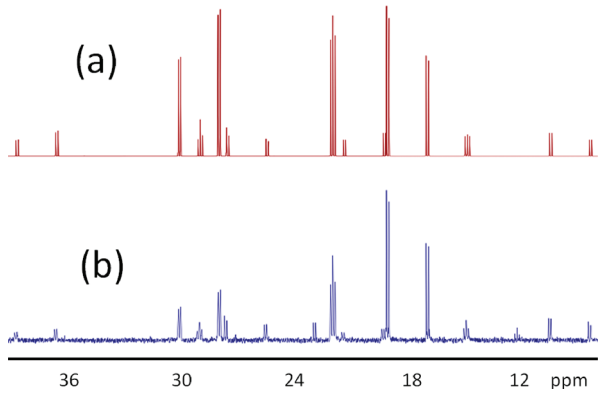

Figure 1. (a) Simulated and (b) experimental $^{31}P\{^{1}H\}$ NMR spectra for **1**.

PPh_3 units remain bound to Pt, but are in distinct environments. The ^{1}H NMR spectrum of **1** shows the expected resonances due to the phenyl and cyclohexyl groups consistent with a ratio of the PPh_3/phosphine-borate of 2:1. In addition, a doublet of doublet of doublets is seen at −6.73 ppm with P−H couplings of 160, 17, and 13 Hz, typical of a Pt-hydride in a P_3PtH square planar coordination sphere.[27] As well, this signal exhibits Pt satellites with a Pt−H coupling of 778 Hz (Figure 2).

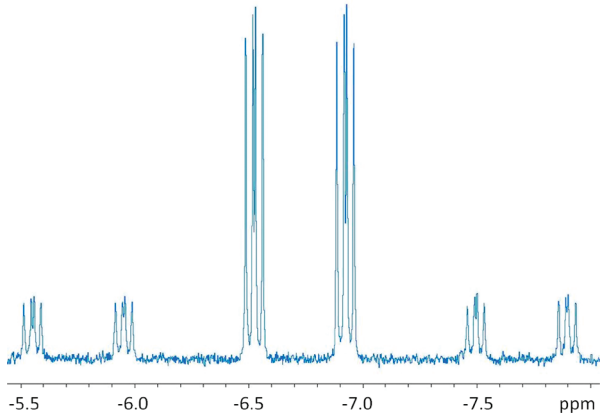

Figure 2. Hydride resonance observed in ^{1}H NMR spectrum of **1**.

The data is consistent with the formulation of **1** as *cis*-$(PPh_3)_2$-$PtH(Cy_2PC_6F_4BF(C_6F_5)_2)$, but stands in contrast to those previously reported for cations of the form $[(R_3P)_3MH]^+$ (M = Ni, Pd) which are reported to be stereochemically nonrigid.[28] Thus it can be inferred that oxidative addition of the P−H bond of the phosphonium borate occurs resulting in the *cis*-disposition of the Pt-hydride and the coordinated PCy_2 fragment of the phosphine-borate.

The formulation of **1** was confirmed via a crystallographic study (Figure 3), affirming the anticipated pseudosquare planar coordination geometry about Pt with a *cis*-disposition of the Pt-hydride and the coordinated phosphine-borate. The Pt−P distances for phosphine-borate and the PPh_3 groups *cis* and *trans* to the hydride were found to be 2.3188(4) Å, 2.3195(5) Å, and 2.3460(5) Å, respectively. The longest of these Pt−P distances is consistent with the strong *trans* influence of the hydride. The refined Pt−H distance was determined to be 1.71(3) Å. The coordination sphere of Pt is distorted from that of an ideal square plane as the *trans*-P−Pt−P angle is 156.047(16)°, while the *trans*-P−Pt−H angle is 174.1(11)°.

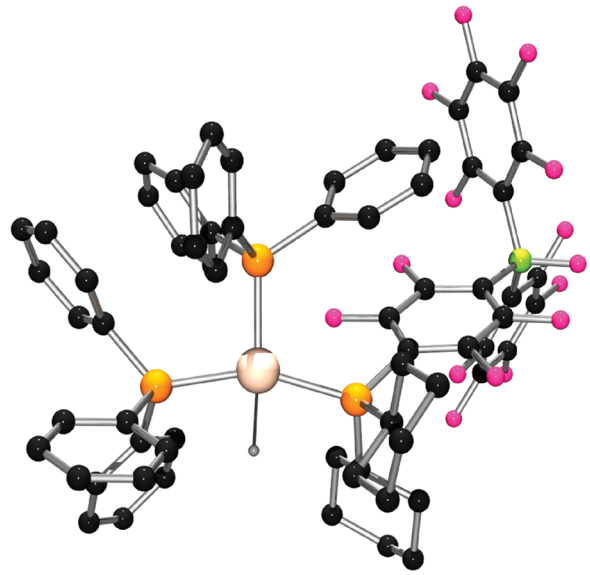

Figure 3. Pov-ray depictions of **1**; C, black; P, orange; F, pink; Pt, light-wood; B, yellow-green; H, gray.

The corresponding *cis*-P−Pt−P angles are 105.741(15)° and 98.138(16)°, while the *cis*-P−Pt−H angles are 77.9(10)° and 78.5(10)°. These distortions of the coordination sphere toward the hydride are not unexpected due to the steric demands of the phosphine ligands about the formally cationic Pt center.

The corresponding reaction of $tBu_2PHC_6F_4BF(C_6F_5)_2$ with $Pt(PPh_3)_4$ afforded a product **2** in 78% yield. In contrast to **1**, this species exhibits ^{11}B, ^{31}P, and ^{19}F NMR spectra consistent with the presence of the anion $[(tBu_2PC_6F_4BF(C_6F_5)_2)]$ (**10**, vide infra). In addition, the overlapping $^{31}P\{^{1}H\}$ NMR triplet and doublet resonances at 23.14 and 22.90 ppm with a P−P coupling of 19 Hz and Pt−P couplings of 2220 and 2819 Hz were observed. Together with the ^{1}H NMR doublet of doublet of doublets at −5.76 ppm, these data are consistent with the formulation of **2** as $[(PPh_3)_3PtH][(tBu_2PC_6F_4BF(C_6F_5)_2)]$ (Scheme 3). The inability of the anion to displace PPh_3, in this case, is attributed to steric issues.

While modification of the phosphonium borate results in altered reactivity, the reaction of $Cy_2PHC_6F_4BF(C_6F_5)_2$ with $Pd(PPh_3)_4$ affords the Pd analogue of **1**, namely *cis*-$(PPh_3)_2$-$PdH(Cy_2PC_6F_4BF(C_6F_5)_2)$ **3**, in 64% isolated yield (Scheme 3). The ^{11}B, ^{19}F, and ^{31}P NMR spectral parameters are analogous to those of **1**. The ^{1}H NMR spectrum of **3** was similar to that of **1**, exhibiting the characteristic hydride resonance at −8.05 ppm. It is also noteworthy that a small portion of an additional hydride complex is formed in the reaction affording **3**. The hydride signal for this species is slightly upfield from **3**. Although this species could not be isolated, it is proposed that the additional product is the isomer in which the hydride is *trans* to the phosphine-borate. Attempts to extend this oxidative addition approach to yield Ni-hydride complexes via reaction of the phosphonium borate with $Ni(PPh_3)_4$ led only to an inseparable mixture of products.

An alternative strategy to the reaction of the phosphonium borate with transition metal precursors involves initial deprotonation. Deprotonation of $Cy_2PHC_6F_4BF(C_6F_5)_2$ with tBu_3P proceeds as the latter phosphine is more basic than the P center in the phosphonium-borate. This afforded ready access to $[tBu_3PH][Cy_2PC_6F_4BF(C_6F_5)_2]$ **4** in 93% isolated yield as a white powder (Scheme 3). The ^{1}H NMR spectrum of **4** confirms the protonation of the tBu_3P as evidenced by the

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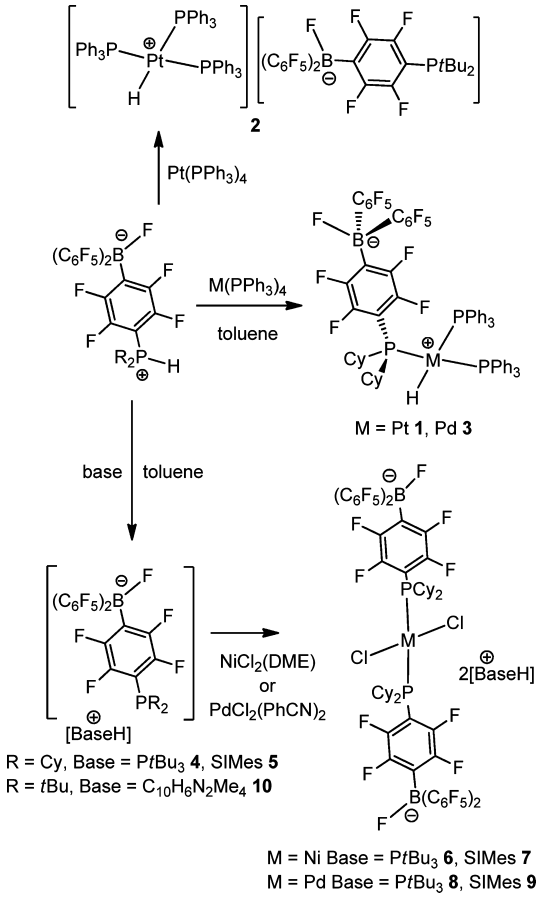
Scheme 3. Synthesis of Complexes 1−10



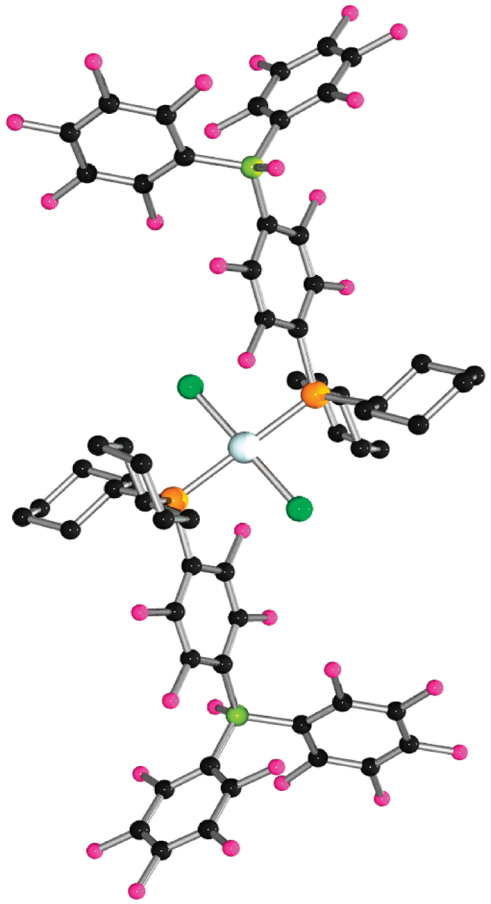


Figure 4. Pov-ray depiction of anion of **6**; C, black; P, orange; F, pink; Ni, light-blue; B, yellow-green.

doublet at 6.09 ppm with a P−H coupling constant of 472 Hz. Furthermore, the $^{31}P\{^{1}H\}$ resonances at 48.99 ppm and −10.37 ppm are attributable to the phosphonium cation [tBu$_3$PH] and the PCy_2 fragment, respectively. The ^{11}B and ^{19}F signals exhibit only minor changes as a result of this deprotonation. In a completely analogous fashion this deprotonation can be accomplished by employing the N-heterocyclic carbene, SIMes affording the corresponding salt [SIMesH][$Cy_2PC_6F_4BF(C_6F_5)_2$] **5** in 92% isolated yield. Subsequent reaction of **4** or **5** with $NiCl_2$(DME) yielded the pink powders **6** and **7** in 73 and 75% yield, respectively. The ^{11}B and ^{19}F NMR spectra of these products are only slightly perturbed from those of the precursor salts. The $^{31}P\{^{1}H\}$ NMR of **6** shows signals at 56.33 and 10.17 ppm in a 1:1 ratio consistent with two phosphonium cations and two phosphines bound to Ni. The corresponding salt **7** showed only a single $^{31}P\{^{1}H\}$ resonance at 10.60 ppm. These data suggest the formulations of **6** and **7** as [BaseH]$_2$[*trans*-$Cl_2Ni(Cy_2PC_6F_4BF(C_6F_5)_2)_2$] (Base = tBu$_3$P **6**, SIMes **7**) (Scheme 3). In the case of **6**, this formulation was confirmed crystallographically (Figure 4). The dianionic nature of nickel center in **6** results from the two coordinated chlorine atoms and the two pendant borate centers on the coordinated phosphines. The Ni center sits on a crystallographic 2-fold with Ni−Cl and Ni−P distances of 2.1672(7) Å and 2.2292(7) Å, respectively. The Ni coordination sphere is essentially square planar as the Cl−Ni−P angles are 90.54(3)° and 89.46(3)°, while the Cl−Ni−Cl and P−Ni−P angles are 180.0° and 179.999(1)°, respectively. The UV−vis spectra for both **6** and **7** show a single absorption peak at 382 nm with a molar absorptivity coefficient of 6096 and 8525 L mol^{-1} cm^{-1}, respectively.

The corresponding reactions of **4** or **5** with $PdCl_2(PhCN)_2$ provide facile access to the analogous salts [BaseH]$_2$[*trans*-$Cl_2Pd(Cy_2PC_6F_4BF(C_6F_5)_2)_2$] (Base = tBu$_3$P **8**, SIMes **9**) which were isolated as pale yellow powders in 81% and 47% yields, respectively (Scheme 3). These products exhibit NMR parameters analogous to **6** and **7**. Efforts to extend the chemistry to salts of [$tBu_2PC_6F_4BF(C_6F_5)_2$] were undertaken with the isolation of [$C_{10}H_6N_2(Me)_4H$][$tBu_2PC_6F_4BF(C_6F_5)_2$] **10** (Scheme 3), as well as with the analogous phosphonium and imidazolium salts. The spectroscopic and crystallographic data (Figure 5) confirmed the formulation of **10**. Nonetheless, combination of **10** and $NiCl_2$(DME) led to no reaction, presumably a result of the additional steric demands of this derivative.

A third strategy for formation of a metal complex of anionic phosphine-borate derivatives was demonstrated in the reaction of (COD)$PtMe_2$ with the neutral phosphine-borane $Mes_2PC_6F_4B(C_6F_5)_2$. The combination of these species results in an immediate reactions affording the new species **11** which was isolated in 81% yield as a cream colored solid. The $^{11}B\{^{1}H\}$ NMR spectrum of **11** shows a peak at −14.60 ppm, consistent with the formation of a methyl-borate center. The ^{1}H NMR spectrum suggests a dissymmetric environment for the coordinated COD. In addition methyl resonances at 1.25 and 0.44 ppm are attributable to the boron-bound and Pt-bound methyl groups. The corresponding $^{13}C\{^{1}H\}$ NMR resonances for these methyl groups are seen at 11.33 and 5.39 ppm,

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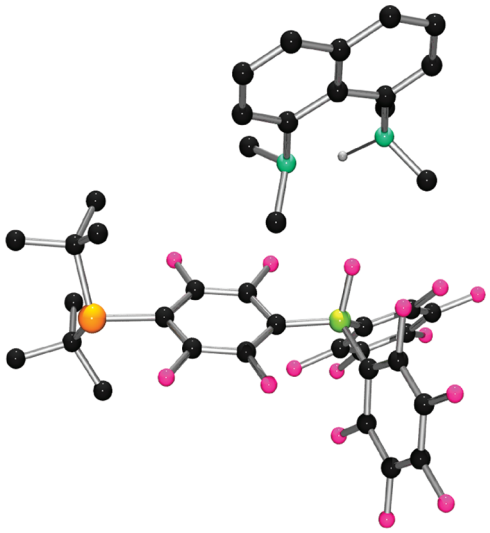
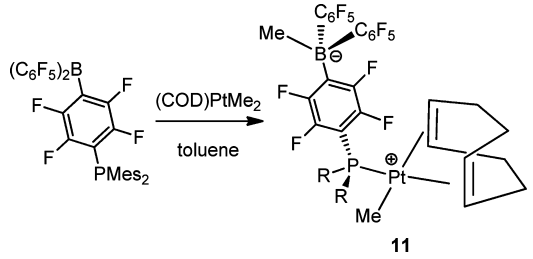


Figure 5. Pov-ray depiction of **10**; C, black; P, orange; F, pink; N, light-blue; B, yellow-green; H, gray.

respectively. The ^{19}F NMR resonances are as expected, with a gap between the signals for the *meta* and *para* fluorines of the C_6F_5 groups of 2.9 ppm, indicative of formation of a methyl borate. The presence of four separate resonances for the fluorines of the C_6F_4 bridge indicate restricted rotation about the P−C_6F_4 bond not seen in the starting phosphine-borane or previously discussed phosphine borate complexes. The $^{31}P\{^1H\}$ NMR spectrum consists of a single resonance at −11.33 ppm, which exhibits Pt-satellites and a Pt−P coupling constant of 3831 Hz. Based upon these data, **11** is best formulated as (COD)PtMe($Mes_2PC_6F_4BMe(C_6F_5)_2$) (Scheme 4). The solid

Scheme 4. Synthesis of Complex 11



11

state structure of **11** was determined by X-ray crystallography (Figure 6) confirming the zwitterionic nature resulting from the pendant methyl borate anion and the phosphine-stabilized cationic platinum center. The geometry about platinum is distorted square planar. The Pt−P bond length of 2.348(4) Å is typical for related phosphorus−platinum complexes.[29] Interestingly, addition of a second equivalent of the phosphino-borane did not result in a second methyl abstraction or displacement of the cycloctadiene ligand. The formation of **11** demonstrates the ability of the present phosphino-boranes to act as an ambiphilic ligands effecting methyl abstraction and subsequent coordination of the phosphine to the resulting vacant coordination site. This reactivity is reminiscent of the reactions of Ni-methyl derivatives with phosphinoethylboranes described by Tilley et al.[11]

This approach to anionic-phosphine-ligand complexes can be extended to other products derived from FLP chemistry. For example, the product of THF ring-opening $tBu_2PH(CH_2)_4OB(C_6F_5)_3$ reacts with $Pt(PPh_3)_4$ resulting in the oxidative

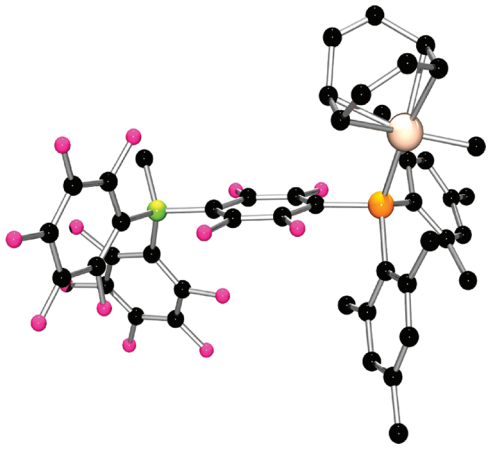
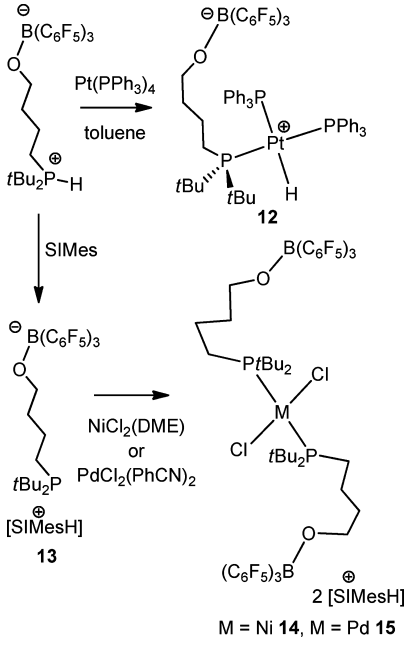


Figure 6. Pov-ray depiction of **11**; C, black; P, orange; F, pink; Pt, light-wood; B, yellow-green.

addition of the P−H bond to Pt affording the species, *cis*-$(PPh_3)_2PtH(tBu_2P(CH_2)_4OB(C_6F_5)_3)$ **12** in 84% yield (Scheme 5). This species is characterized by a ^{11}B NMR

Scheme 5. Synthesis of 12−15



resonance at −2.94 ppm and ^{19}F NMR signals typical of an anionic borate. The $^{31}P\{^1H\}$ NMR data for **12** shows multiplets at 56.56, 21.57, and 18.06 ppm consistent with coordination of the anionic phosphine to a square planar Pt with two PPh_3 ligands. The most diagnostic peak in the ^1H NMR spectrum of **12** is the resonance attributable to the hydride which is seen as a multiplet at −6.92 ppm with P−H couplings of 162 and 14 Hz. It is noteworthy that this resonance is close to that described above for **1**. This signal also exhibits Pt-satellites with a Pt−H coupling of 786 Hz (Figure 7). The formulation of **12** was also confirmed crystallographically (Figure 8). The geometry about Pt in **12** is very similar to that seen in **1**. The Pt−P distances in **12** for the phosphine-borate, and the PPh_3 groups that are *cis* and *trans* to the hydride are 2.3142(9) Å, 2.3208(9) Å, and 2.3543(10) Å, respectively. The shortest of these Pt−P

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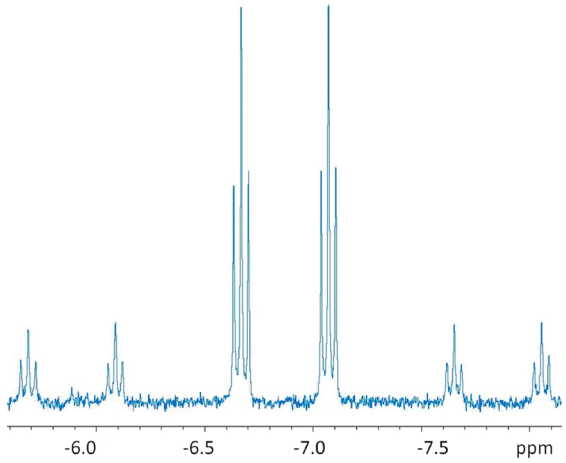


Figure 7. Hydride resonance observed in ^{1}H NMR spectrum of **12**.

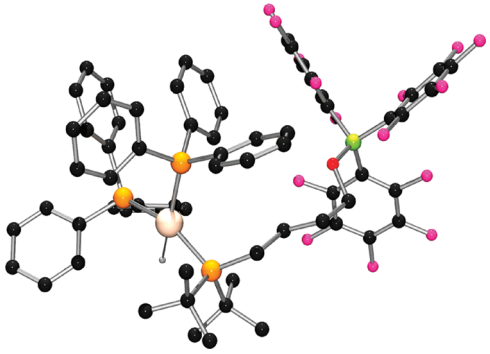


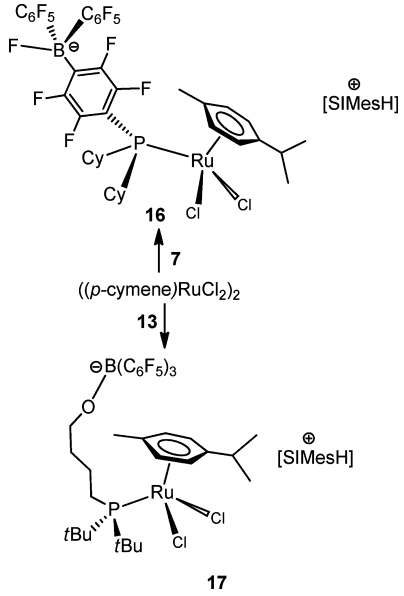
Figure 8. Pov-ray depiction of **12**; C, black; P, orange; F, pink; Pt, light-wood; B, yellow-green; H, gray.

bond length results from the phosphine-borate consistent with the greater donor ability of the trialkylphosphine center of this anionic moiety. The distortions from square planarity are similar to those in **1** with *trans*-P−Pt−P angle of 156.88(4)° and cis-P−Pt−P angles of 105.62(3)° and 97.49(3)°.

In contrast to the fluoro-arene phosphonium borate, tBu$_2$PH(CH$_2$)$_4$OB(C$_6$F$_5$)$_3$ could not be deprotonated with PtBu$_3$ or proton sponge. This is consistent with the great basicity of the P center in tBu$_2$PH(CH$_2$)$_4$OB(C$_6$F$_5$)$_3$. Nonetheless, the phosphonium borate tBu$_2$PH(CH$_2$)$_4$OB(C$_6$F$_5$)$_3$ is readily deprotonated via reaction with SIMes. In this fashion, [SIMesH][tBu$_2$P(CH$_2$)$_4$OB(C$_6$F$_5$)$_3$] **13** was prepared in 96% isolated yield (Scheme 5). In a fashion analogous to that employed to prepare **7** and **9**, subsequent reaction with NiCl$_2$(DME) and PdCl$_2$(PhCN)$_2$ afforded the analogous complexes [SIMesH]$_2$[*trans*-Cl$_2$Ni(tBu$_2$PC$_4$H$_8$OB(C$_6$F$_5$)$_3$)$_2$] **14** and [SIMesH]$_2$[*trans*-PdCl$_2$(tBu$_2$P(CH$_2$)$_4$OB(C$_6$F$_5$)$_3$)$_2$] **15**, respectively (Scheme 5). These products were isolated as blue and yellow powders, respectively, in yields of 72 and 47%. The ^{31}P{^{1}H} NMR spectral data for **14** and **15** were analogous to those of **7** and **9**, respectively, with the characteristic resonances at 54.02 and 40.61 ppm, respectively. The ^{11}B and ^{19}F NMR spectra for **15** indicate that both phosphine borates coordinated to Pd are chemically equivalent. However, **14** exhibits two ^{11}B resonances at −2.41 and −2.93 ppm in a 1:1 ratio. Also, the presence of six multiplets in the ^{19}F NMR spectrum corresponding to two sets of inequivalent C$_6$F$_5$ groups, suggests that inhibited rotation about P−Ni bonds affords two rotomers of this species. This blue complex exhibits a maximum absorption at 343 nm, blue-shifted compared to **6** and **7** due to the greater donor ability of this phosphine borate ligand. The molar absorptivity coefficient is 1155 L mol^{-1} cm^{-1}.

Finally, reaction of **7** and **13** with [(*p*-cymene)RuCl$_2$]$_2$ proceeds to give the new orange products **16** and **17** in 92 and 87% isolated yield, respectively. These species show the ^{11}B and ^{19}F NMR spectra characteristic of the coordination of the respective anion phosphine-borates as well as ^{31}P NMR resonances at 37.55 and 41.54 ppm respectively. The ^{1}H spectra are as expected with resonances attributable to the *p*-cymene, cyclohexyl, and imidiazolium protons. These data support the formulation of **16** and **17** as [SIMesH][(*p*-cymene)RuCl$_2$(Cy$_2$PC$_6$F$_4$BF(C$_6$F$_5$)$_2$)] and [SIMesH][(*p*-cymene)RuCl$_2$(tBu$_2$P(CH$_2$)$_4$OB(C$_6$F$_5$)$_3$)], respectively (Scheme 6). These formulations were further validated by the

Scheme 6. Synthesis of 16−17



X-ray crystallographic study of **16** (Figure 9). The Ru adopts a pseudotetrahedral, "piano-stool" type geometry with a η^6-bound

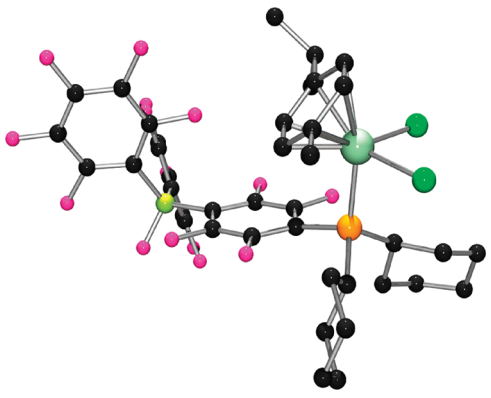


Figure 9. Pov-ray depiction of anion of **16**; C, black; P, orange; F, pink; Cl, green; Ru, light-green; B, yellow-green.

p-cymene acting as the "seat" of the stool. The "legs" of the stool are derived from the Ru−P and two Ru−Cl bonds which were found to be 2.3996(11) Å, 2.4076(12) Å, and 2.4172(12) Å, respectively. The nature of **16** is similar to that seen for

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(*p*-cymene)$RuCl_2$($Ph_2PCH_2CH_2$(9-BBN)] reported by Bourissou and co-workers.[10a]

CONCLUSIONS

Herein we have demonstrated the utility of the phosphonium borates derived from FLP chemistry in the formation of zwitterionic phosphine complexes. These observations illustrate that FLP chemistry offers convenient access to unique anionic phosphine ligands that can be employed with a variety of transition metal precursors. While this aspect has not been the primary target of FLP chemistry, the present report suggests that FLP chemistry provides a unique and facile strategy for the ligand design and synthesis of anionic phosphines. To this end we are exploring the potential of such ligands complexes in applications in catalysis.

ASSOCIATED CONTENT

Supporting Information

Crystallographic information files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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