Supplementary Information To:

The Synthesis and Exchange Chemistry of Frustrated Lewis Pair-Nitrous Oxide Complexes

Rebecca C. Neu, Edwin Otten, Alan Lough and Douglas W. Stephan*

Experimental Section

General Considerations. All manipulations were carried out under an atmosphere of dry, O_2-free N_2 employing standard Schlenk-line and glovebox techniques. Solvents (pentane, hexanes, CH_2Cl_2) were dried by employing a Grubbs-type column system (Innovative Technology), degassed and stored under N_2. Cyclohexane was distilled under N_2 from Na/benzophenone and bromobenzene was distilled under N_2 from CaH_2. CD_2Cl_2 was vacuum transferred from CaH_2 and C_4H_8O was vacuum transferred from Na/benzophenone. Both solvents were subsequently degassed and stored under N_2. $^tBu_3P$ (Strem Chemicals), Cy_3P (Strem Chemicals), $[Ph_3C][B(C_6F_5)_4]$ (Strem Chemicals), N_2O (Sigma-Aldrich; 99%) and $^{15}N_2O$ (Cambridge Isotope Laboratories; 99.9%, 98.8% ^{15}N enriched) were used as received. The reagents $PhB(C_6F_5)_2$,[1] $MesB(C_6F_5)_2$,[2] $(C_6F_5)_2BOC_6F_5$,[3] $B(C_6F_4$-*p*-$H)_3$,[4] $B(C_6H_4$-*p*-$F)_3$,[5] 1,4-$(C_6F_5)_2BC_6F_4B(C_6F_5)_2$,[6] $Cp^*_2Zr(OMe)Me$[7], Cp_2ZrMe_2[8] and Cp_2TiMe_2[9] were prepared according to literature procedures. ^1H, ^{11}B, ^{13}C, ^{15}N, ^{19}F and ^{31}P NMR spectra were recorded at 25 °C on a Varian NMR System 400 MHz or Bruker Avance III 400 MHz spectrometer, and were referenced using (residual) solvent resonances relative to $SiMe_4$ (^1H, ^{13}C), or relative to an external standard (^{11}B: $(Et_2O)BF_3$; ^{19}F: $CFCl_3$; ^{31}P: 85% H_3PO_4; ^{15}N: NH_3(l) via the ^{15}N resonance of 90% formamide in DMSO-d_6 at 112 ppm).[10] Chemical shifts are reported in ppm and coupling constants as scalar values in Hz. Combustion analyses were performed in house employing a Perkin-Elmer CHN Analyzer.

Synthesis of $^{t}Bu_3P(N_2O)B(C_6F_5)_2R$ (R = C_6F_5 1, Ph 2). These compounds were prepared in a similar fashion and thus only one preparation is detailed. A solution of $B(C_6F_5)_3$ (0.200 g, 0.391 mmol) and $^{t}Bu_3P$ (0.079 g, 0.391 mmol) in C_6H_5Br (5 mL) was stirred under an atmosphere of N_2O for a day, resulting in the precipitation of a colorless product. Hexanes (15 mL) were added and the resulting precipitate was allowed to settle. The supernatant was decanted and the white residue was recrystallized by diffusion of hexanes into a CH_2Cl_2 solution to give **1** as a white microcrystalline material. Yield: 0.225 g (76 %). **1:** ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 1.46 (d, $^{3}J_{P-H}$ = 14.5 Hz). ^{11}B NMR (128 MHz, CD_2Cl_2, 25 °C): δ 0.4 (s). ^{13}C NMR (101 MHz, CD_2Cl_2, 25 °C): δ 148.5 (d, J_{F-C} = 240 Hz, *o*-C_6F_5), 139.9 (d, J_{F-C} = 246 Hz, *p*-C_6F_5), 137.5 (d, J_{C-F} = 248 Hz, *m*-CF), 121.2 (br, *ipso*-C_6F_5), 41.8 (d, J_{P-C} = 29 Hz, P*C*Me$_3$), 29.7 (PC*Me*$_3$). ^{15}N NMR (40.6 MHz, CD_2Cl_2, 25 °C): δ 566.6 (dd, $^{2}J_{P-N}$ = 19.6 Hz, $^{1}J_{N-N}$ = 15.6 Hz, N*N*O), 381.7 (dd, $^{1}J_{P-N}$ = 58.7 Hz, $^{1}J_{N-N}$ = 15.6 Hz, *N*NO).^{19}F NMR (377 MHz, CD_2Cl_2, 25 °C): δ -133.8 (dd, 6F, $^{1}J_{F-F}$ = 23.9 Hz, $^{2}J_{F-F}$ = 6.9 Hz, *o*-F), -160.3 (t, 3F, *J* = 20.2 Hz, *p*-F), -166.0 (m, 6F, *m*-F). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 °C): δ 68.5 (dd, $^{1}J_{P-N}$ = 58.7 Hz, $^{2}J_{P-N}$ = 19.6 Hz). Anal. Calcd for $C_{30}H_{27}BF_{15}N_2OP$: C, 47.52; H, 3.59; N, 3.69. Found: C, 47.78; H, 3.96; N, 3.47 %. **2:** Yield: 0.144 g (76 %). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 7.40 (d, 2H, $^{3}J_{H-H}$ = 7 Hz, *o*-C_6H_5), 7.17 (t, 2H, $^{3}J_{H-H}$ = 8 Hz, *m*-C_6H_5), 7.09 (t, 1H, $^{3}J_{H-H}$ = 8 Hz, *p*-C_6H_5), 1.44 (d, 27H, $^{3}J_{H-P}$ = 14Hz, P{C(CH$_3$)$_3$}). ^{11}B{^{1}H} NMR (128 MHz, CD_2Cl_2, 25 °C): δ 3.27 (s). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 25 °C): δ 148.25 (br d, $^{1}J_{C-F}$ = 240 Hz, *o*-C_6F_5), 139.68 (br d, $^{1}J_{C-F}$ = 218 Hz, *p*-C_6F_5), 137.23 (br d, $^{1}J_{C-F}$ = 226 Hz, *m*-C_6F_5), 132.31 (s, *p*-C_6H_5), 127.35 (s, *o*-C_6H_5), 125.77 (s, *m*-C_6H_5), 41.64 (d, $^{1}J_{C-P}$ = 30 Hz, P{*C*(CH$_3$)$_3$}), 29.71 (s, CH$_3$). ^{15}N NMR (40.6 MHz, CD_2Cl_2, 25 °C): δ 577.72 (dd, $^{2}J_{N-P}$ = 19.1 Hz, $^{1}J_{N-N}$ = 16.0 Hz, PN*N*O), 377.03 (dd, $^{1}J_{N-P}$ = 59.5 Hz, $^{1}J_{N-N}$ = 16.0 Hz, P*N*NO). ^{19}F NMR (376 MHz, CD_2Cl_2, 25 °C): δ -131.87 (dd, 4F, $^{3}J_{F-F}$ = 25 Hz, $^{4}J_{F-F}$ = 9 Hz, *o*-C_6F_5), -161.71 (t, 2F, $^{3}J_{F-F}$ = 20 Hz, *m*-C_6F_5), -166.45 (td, 4F, $^{3}J_{F-F}$ = 23 Hz, $^{4}J_{F-F}$ = 8 Hz *m*-C_6F_5). ^{31}P{^{1}H}

NMR (162 MHz, CD_2Cl_2, 25 °C): δ 67.20 (dd, $^1J_{P\text{-}N}$ = 59.5 Hz, $^2J_{P\text{-}N}$ = 19.1 Hz). Anal. Calcd for $C_{30}H_{32}BF_{10}N_2OP$: C, 53.83; H, 4.97; N, 4.18. Found: C, 54.06; H, 4.94; N, 4.27 %.

Synthesis of ^{t}Bu$_3$P(N$_2$O)B(C$_6$F$_5$)$_2$R (R = Mes 3, OC$_6$F$_5$ 4). These compounds were prepared in a similar fashion and thus only one preparation is detailed. A 50 mL schlenk tube was charged with $MesB(C_6F_5)_2$ (0.103 g, 0.222 mmol) and $^tBu_3P$ (0.045 g, 0.222 mmol) in bromobenzene (5 mL). The reaction was degassed and backfilled with 1 bar of N_2O. The solution was left stirring for 12 hours at room temperature. At this time, the solution was clear and colorless. Pentane (10 mL) was added precipitating a white solid. The solid was isolated by filtration, washed with pentane (3 x 5 mL) and dried *in vacuo* for 2 hours. Yield: 0.133 g (84 %). Crystals, although not suitable for X-ray diffraction, were grown from a layered dichloromethane/cyclohexane solution at 25 °C. **3:** ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 6.56 (s, 2H, $(CH_3)_3C_6H_2$), 2.18 (s, 3H, *p*-CH_3), (s, 6H, *o*-CH_3), 1.43 (d, 27H, $^3J_{H\text{-}P}$ = 14 Hz, P{C$(CH_3)_3$}). ^{11}B{^{1}H} NMR (128 MHz, CD_2Cl_2, 25 °C): δ 3.56 (s). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 25 °C) partial: δ 148.42 (br d, $^1J_{C\text{-}F}$ = 235 Hz, *o*-C_6F_5), 141.69 (s, *o*-$(CH_3)_3C_6H_2$), 139.59 (br d, $^1J_{C\text{-}F}$ = 227 Hz, *p*-C_6F_5), 137.19 (br d, $^1J_{C\text{-}F}$ = 227 Hz, *m*-C_6F_5), 134.85 (s, *p*-$(CH_3)_3C_6H_2$), 129.78 (s, *m*-$(CH_3)_3C_6H_2$), 41.59 (d, $^1J_{C\text{-}P}$ = 30 Hz, P{*C*$(CH_3)_3$}), 29.72 (s, P{C(*C*$H_3)_3$}), 27.49 (s, *o*-(*C*$H_3)_3C_6H_2$), 24.85 (s, *p*-(*C*$H_3)_3C_6H_2$). ^{15}N NMR (40.6 MHz, CD_2Cl_2, 25 °C): δ 574.19 (dd, $^2J_{N\text{-}P}$ = 20 Hz, $^1J_{N\text{-}N}$=15 Hz, PN*N*O), 375.33 (dd, $^1J_{N\text{-}P}$ = 59 Hz, $^1J_{N\text{-}N}$ = 15, P*N*NO). ^{19}F NMR (376 MHz, CD_2Cl_2, 25 °C): δ -132.70 (dd, 4F, $^3J_{F\text{-}F}$ = 23 Hz, $^4J_{F\text{-}F}$ = 7 Hz, *o*-C_6F_5), -162.10 (t, 2F, $^3J_{F\text{-}F}$ = 20 Hz, *m*-C_6F_5), -166.71 (td, 4F, $^3J_{F\text{-}F}$ = 24 Hz, $^4J_{F\text{-}F}$ = 8 Hz, *p*-C_6F_5). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 °C): δ 67.07 (dd, $^1J_{P\text{-}N}$ = 59 Hz, $^2J_{P\text{-}N}$ = 20 Hz). Anal. Calcd. for $C_{33}H_{38}BF_{10}N_2OP$: C, 55.79; H, 5.39; N, 3.94. Found: C, 55.88; H, 5.75; N, 3.65 %. **4:** Yield: 0.121 g (85%). ^{1}H NMR (400MHz, CD_2Cl_2, 25 °C): δ 1.50 (d, $^3J_{H\text{-}P}$ = 14 Hz, P{C$(CH_3)_3$}). ^{11}B{^{1}H} NMR (128 MHz, CD_2Cl_2, 25 °C): δ 6.43 (s). ^{13}C{^{1}H} NMR (101 MHz,

CD_2Cl_2, 25 °C): δ 148.77 (br d, $^1J_{C\text{-}F}$ = 255 Hz, *o*-C_6F_5), 142.25 (br d, $^1J_{C\text{-}F}$ = 244 Hz, *o*-OC_6F_5), 140.40 (br d, $^1J_{C\text{-}F}$ = 250 Hz, *p*-C_6F_5), 138.23 (br d, $^1J_{C\text{-}F}$ = 239 Hz, *p*-OC_6F_5), 137.50 (br d, $^1J_{C\text{-}F}$ = 255 Hz, *m*-C_6F_5), 135.62 (br d, $^1J_{C\text{-}F}$ = 244 Hz, *m*-OC_6F_5), 119.38 (br s, *ipso*-C_6F_5), 115.23 (br s, *ipso*-OC_6F_5), 41.93 (d, $^1J_{C\text{-}P}$ = 29 Hz, P{*C*(CH_3)$_3$}), 29.75 (s, P{C(*C*H_3)$_3$}). ^{15}N NMR (40.6 MHz, CD_2Cl_2, 25 °C): δ 572.49 (dd, $^2J_{N\text{-}P}$ = 20 Hz, $^1J_{N\text{-}N}$ = 16 Hz, PN*N*O), 389.37 (dd, $^1J_{N\text{-}P}$ = 59 Hz, $^1J_{N\text{-}N}$ = 16 Hz, P*N*NO). ^{19}F NMR (376 MHz, CD_2Cl_2, 25 °C): δ -134.05 (d, 4F, $^3J_{F\text{-}F}$ = 16 Hz, *o*-C_6F_5), -157.72 (d, 2F, $^3J_{F\text{-}F}$ = 19 Hz, *o*-OC_6F_5), -159.03 (t, 2F, $^3J_{F\text{-}F}$ = 20 Hz, *p*-C_6F_5), -165.47 (td, 4F, $^3J_{F\text{-}F}$ = 23 Hz, $^4J_{F\text{-}F}$ = 9 Hz, *m*-C_6F_5), -166.96 (t, 1F, $^3J_{F\text{-}F}$ = 20 Hz, *p*-OC_6F_5), -170.29 (tt, 2F, $^3J_{F\text{-}F}$ = 22 Hz, $^4J_{F\text{-}F}$ = 6 Hz, *m*-OC_6F_5). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 °C): δ 68.98 (dd, $^1J_{P\text{-}N}$ = 59 Hz, $^2J_{P\text{-}N}$ = 20 Hz). Anal. Calcd. for $C_{30}H_{27}BF_{15}N_2O_2P$: C, 46.54; H, 3.51; N, 3.62. Found: C, 46.63; H, 3.47; N, 3.47 %.

Synthesis of $R_3P(N_2O)B(C_6F_4$-*p*-H$)_3$ (R = ^{t}Bu 5, Cy 8). These compounds were prepared in a similar fashion and thus only one preparation is detailed. A 50 mL schlenk tube was charged with B(C_6F_4-*p*-H)$_3$ (0.130 g, 0.284 mmol) and ^{t}Bu$_3$P in C_6H_5Br (5 mL). The resulting yellow solution was degassed and backfilled with N_2O. The reaction was left stirring under an atmosphere of N_2O for 12 hours. At this time, the solution was clear and colourless. Pentane (10 mL) was added precipitating a white solid. The product was collected by filtration, washed with pentane (3 x 5 mL) and dried *in vacuo* for 2 hours. Yield: 0.181 g (91 %). Crystals suitable for X-ray diffraction were grown from a layered bromobenzene/cyclohexane solution at 25 °C. **5:** ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 6.86 (m, 1H, C_6F_4H), 1.44 (d, 27H, $^3J_{H\text{-}P}$ = 14 Hz). ^{11}B{^{1}H} NMR (128 MHz, CD_2Cl_2, 25 °C): δ 0.69 (s). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 25 °C) partial: δ 149.58 (br d, $^1J_{C\text{-}F}$ = 238 Hz, *m*-C_6F_4H), 144.91 (br d, $^1J_{C\text{-}F}$ = 240 Hz, *o*-C_6F_4H), 103.61 (t, $^2J_{C\text{-}F}$ = 23 Hz, *p*-C_6F_4H), 41.74 (d, $^3J_{H\text{-}P}$ = 29, P{*C*(CH_3)$_3$}), 29.69 (s, P{C(*C*H_3)$_3$}). ^{15}N NMR (40.6 MHz, CD_2Cl_2, 25 °C): δ 588.75 (dd, $^2J_{N\text{-}P}$ = 20 Hz, $^1J_{N\text{-}N}$ = 16 Hz,

PN*N*O), 367.61 (dd, $^{1}J_{N\text{-}P}$ = 59 Hz, $^{1}J_{N\text{-}N}$ = 16 Hz, P*N*NO). ^{19}F NMR (376 MHz, CD_2Cl_2, 25 °C): δ -134.27 (m, 6F, *o*-C_6F_4H), -143.10 (m, 6F, *m*-C_6F_4H). $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2, 25 °C): δ 68.33 (dd, $^{1}J_{P\text{-}N}$ = 59 Hz, $^{2}J_{P\text{-}N}$ = 20 Hz). Anal. Calcd. for $C_{30}H_{30}BF_{12}N_2OP$: C, 51.16; H, 4.29; N, 3.98. Found: C, 51.24; H, 4.59; N, 4.02 %. **8:** Yield: 0.101 g (59 %). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): 6.87 (m, 1H, C_6F_4H), 2.37 (q, $^{3}J_{H\text{-}H} \approx {}^{2}J_{P\text{-}H} \approx$ 12.6 Hz, 1H, Cy α-CH), 1.81 (m, 5H, Cy), 1.42 (m, 2H, Cy), 1.23 (m, 3H, Cy). ^{11}B NMR (128 MHz, CD_2Cl_2, 25 °C): δ 0.8 (s). $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2, 25 °C): δ 148.2 (d, $^{1}J_{F\text{-}C}$ = 228 Hz, *o*-C_6F_4H), 145.8 (d, $^{1}J_{C\text{-}F}$ = 235 Hz, *m*-C_6F_4H), 128.0 (br, *ipso*-C C_6F_4H), 103.4 (t, $^{2}J_{C\text{-}F}$ = 23 Hz, *p*-C_6F_4H), 32.3 (d, $J_{P\text{-}C}$ = 43 Hz, Cy α-C), 26.7 (d, $J_{P\text{-}C}$ = 12 Hz, Cy β-C), 26.0 (d, $J_{P\text{-}C}$ = 4 Hz, Cy γ-C), 25.6 (d, $J_{P\text{-}C}$ = 1 Hz, Cy δ-C). ^{15}N NMR (40.6 MHz, CD_2Cl_2, 25 °C) δ 573.0 (dd, $^{2}J_{P\text{-}N}$ = 22.2 Hz, $^{1}J_{N\text{-}N}$ = 15.6 Hz, N*N*O), 376.1 (dd, $^{1}J_{P\text{-}N}$ = 52.5 Hz, $^{1}J_{NN}$ = 15.6 Hz, *N*NO). ^{19}F NMR (377 MHz, CD_2Cl_2, 25 °C): δ -134.2 (m, 6F, *o*-C_6F_4H), -143.0 (ddd, 6F, $^{3}J_{F\text{-}F}$ = 23 Hz, $^{3}J_{H\text{-}F}$ = 11 Hz, $^{4}J_{F\text{-}F}$ = 11 Hz, *m*-C_6F_4H). $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2, 25 °C) δ 56.4 (dd, $^{1}J_{P\text{-}N}$ = 52.5 Hz, $^{2}J_{P\text{-}N}$ = 22.2 Hz). Anal. Calcd. for $C_{36}H_{36}BF_{12}N_2OP$: C, 55.26; H, 4.64; N, 3.58. Found: C, 55.07; H, 4.54; N, 3.60 %.

Synthesis of ^{t}Bu$_3$P(N$_2$O)B(C$_6$H$_4$-*p*-F)$_3$ (6). A 50 mL schlenk tube was charged with B(C_6H_4-*p*-F)$_3$ (0.212 g, 0.716 mmol) and $^{t}Bu_3P$ (0.145 g, 0.717 mmol) in bromobenzene (10 mL). The pale yellow solution was subjected to 3 freeze-pump-thaw cycles using liquid nitrogen to degas the solution. The solution was left stirring under an atmosphere of N_2O for 12 hours at room temperature. At this time, the solution was cloudy and pale yellow. Pentane (10 mL) was added precipitating a white solid. The solid was isolated by filtration, washed with pentane (3 x 5 mL) and dried *in vacuo* for 2 hours. Yield: 0.312 g (80 %). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 7.33 (m, 6H, *o*-C_6H_4F), 6.87 (m, 6H, *m*-C_6H_4F), 1.38 (d, 27H, $^{3}J_{H\text{-}P}$ = 14 Hz). $^{11}B\{^{1}H\}$ NMR (128 MHz, CD_2Cl_2, 25 °C): δ 6.69 (s). $^{13}C\{^{1}H\}$

NMR (101 MHz, CD_2Cl_2, 25 °C) partial: δ 161.25 (br d, $^1J_{C\text{-}F}$ = 247 Hz, *p*-C_6H_4F), 135.54 (br s, *m*-C_6H_4F), 113.50 (br s, *o*-C_6H_4F), 41.31 (d, $^1J_{C\text{-}P}$ = 31 Hz, P{*C*$(CH_3)_3$}), 29.85 (s, P{C(*C*$H_3)_3$}. ^{15}N NMR (40.6 MHz, CD_2Cl_2, 25 °C): δ 588.75 (dd, $^2J_{N\text{-}P}$ = 19 Hz, $^1J_{N\text{-}N}$ = 18 Hz, PN*N*O), 367.61 (dd, $^1J_{N\text{-}P}$ = 61 Hz, $^1J_{N\text{-}N}$ = 18 Hz, P*N*NO). ^{19}F NMR (376 MHz, CD_2Cl_2, 25 °C): δ -120.87 (s). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 °C): δ 64.27 (dd, $^1J_{P\text{-}N}$ = 61 Hz, $^2J_{P\text{-}N}$ = 19 Hz). Anal. Calcd. for $C_{30}H_{39}BF_3N_2OP$: C, 66.43; H, 7.25; N, 5.16. Found: C, 66.25; H, 7.27; N, 5.17 %.

Synthesis of ^{t}Bu$_3$P(N$_2$O)B(C$_6$F$_5$)$_2$C$_6$F$_4$(C$_6$F$_5$)$_2$B(ON$_2$)P^{t}Bu$_3$ (7). A 50 mL schlenk tube was charged with 1,4-$(C_6F_5)_2BC_6F_4B(C_6F_5)_2$ (0.100 g, 0.119 mmol) and ^{t}Bu$_3$P (0.048 g, 0.237 mmol) in bromobenzene (5 mL). The pale yellow slurry was degassed and backfilled with N_2O. The solution was left stirring under an atmosphere of N_2O for 12 hours at room temperature. At this time, the solution was opaque. Pentane (10 mL) was added precipitating a white solid. The solid was isolated by filtration, washed with pentane (3 x 5 mL) and dried *in vacuo* for 2 hours. Yield: 0.144 g (91 %). Crystals suitable for x-ray diffraction were grown from a layered bromobenzene/cyclohexane solution at 25 °C. ^{1}H NMR (400MHz, CD_2Cl_2, 25 °C): δ 1.46 (d, 27H, $^3J_{H\text{-}P}$ = 14 Hz). ^{11}B{^{1}H} NMR (128 MHz, CD_2Cl_2, 25 °C): δ 0.67 (s). ^{13}C{^{1}H} NMR (101 MHz, C_4D_8O, 25 °C): δ 149.22 (br d, $^1J_{C\text{-}F}$ = 238 Hz, C_6F_4); 148.94 (br d, $^1J_{C\text{-}F}$ = 240 Hz, *o*-C_6F_5); 140.03 (br d, $^1J_{C\text{-}F}$ = 233 Hz, *p*-C_6F_5); 137.58 (br d, $^1J_{C\text{-}F}$ = 229 Hz, *m*-C_6F_5); 128.01 (br s, *ipso*-C_6F_4); 123.76 (br s, *ipso*-C_6F_5); 41.87 (d, $^1J_{C\text{-}P}$ = 29 Hz, P{*C*$(CH_3)_3$}); 29.51 (s, P{C(*C*$H_3)_3$}). ^{15}N NMR (40.6 MHz, CD_2Cl_2, 25 °C): δ 571.04 (dd, $^2J_{N\text{-}P}$ = 20 Hz, $^1J_{N\text{-}N}$ = 15 Hz, PN*N*O), 381.31 (dd, $^1J_{N\text{-}P}$ = 59 Hz, $^1J_{N\text{-}N}$ = 15 Hz, P*N*NO). ^{19}F NMR (376 MHz, CD_2Cl_2, 25 °C): δ -133.57 (d, 8F, $^3J_{F\text{-}F}$ = 17 Hz, *o*-C_6F_5), -137.48 (s, 4F, C_6F_4), -161.80 (t, 4F, $^3J_{F\text{-}F}$ = 21 Hz, *p*-C_6F_5), -166.82 (t, 8F, $^3J_{F\text{-}F}$ = 18 Hz, *m*-C_6F_5). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 °C): δ

68.37 (dd, $^{1}J_{P\text{-}N}$ = 59 Hz, $^{2}J_{P\text{-}N}$ = 20 Hz). Anal. Calcd. for $C_{54}H_{54}B_2F_{24}N_4O_2P_2$: C, 48.71; H, 4.09; N, 4.21. Found: C, 48.50; H, 4.20; N, 3.80 %.

Synthesis of $(Cy_3P{=}O)B(C_6H_4\text{-}p\text{-}F)_3$ (9). A 50 mL schlenk tube was charged with $B(C_6H_4\text{-}p\text{-}F)_3$ (0.205 g, 0.692 mmol) and Cy_3P (0.194 g, 0.692 mmol) in C_6H_5Br (5 mL). The pale yellow solution was degassed and backfilled with N_2O. The solution was left stirring under an atmosphere of N_2O for 12 hours at room temperature. At this time, the solution was faint yellow in color. Pentane (10 mL) was added precipitating a microcrystalline solid. The solid was isolated by filtration, washed with pentane (3 x 5 mL) and dried *in vacuo* for 2 hours. Yield: 0.320 g (78 %). Crystals suitable for x-ray diffraction were grown from a layered dichloromethane/pentane solution at -35 °C. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 7.38 (m, 6H, *o*-C_6H_4F), 6.97 (m, 6H, *m*-C_6H_4F), 1.90-1.16 (m, 30H, Cy). $^{11}B\{^{1}H\}$ NMR (128 MHz, CD_2Cl_2, 25 °C): δ 26.39 (s). $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2, 25 °C) partial: δ 163.64 (d, $^{1}J_{C\text{-}F}$ = 246 Hz, *p*-C_6H_4F), 146.06 (br s, *ipso*-C_6F_4H), 138.16 (d, $^{3}J_{C\text{-}F}$ = 7 Hz, *o*-C_6H_4F), 114.34 (d, $^{2}J_{C\text{-}F}$ = 20 Hz, m-C_6H_4F), 35.91 (d, $^{1}J_{C\text{-}P}$ = 59.77 Hz, Cy_3P), 27.31 (d, $^{2}J_{C\text{-}P}$ = 12 Hz, *o*-C_6H_{10}), 26.78 (d, $^{3}J_{C\text{-}P}$ = 3 Hz, *m*-C_6H_{10}), 26.46 (d, $^{4}J_{C\text{-}P}$ = 1 Hz, *p*-C_6H_{10}). ^{19}F NMR (376 MHz, CD_2Cl_2, 25 °C): δ -116.52 (s). $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2, 25 °C): δ 62.58 (s). Anal. Calcd. for $C_{36}H_{44}BF_3PCl_2O$: C, 65.27; H, 6.69. Found: C, 65.25; H, 7.12 %.

Synthesis of $[^{t}Bu_3P(N_2O)C(C_6H_5)_3][B(C_6F_5)_4]$ (10). A 20 mL scintillation vial was charged with **6** (0.081 g, 0.149 mmol) in C_6H_5Br (5 mL). A separate vial was charged with $[C(C_6H_5)_3][B(C_6F_5)_4]$ (0.136 g, 0.149 mmol) in C_6H_5Br (5 mL). The latter solution was added slowly to the first. The reaction was noted to change from a deep orange to a bright yellow within the first 30 seconds. The reaction was allowed to stir for a period of 12 hours at room temperature. Pentane was added (15 mL)

precipitating a yellow solid. The product was isolated by filtration and was subsequently washed with pentane (3 x 5 mL) and dried *in vacuo* for 2 hours. Yield: 0.165 g (96 %). Crystals suitable for X-ray diffraction were grown from a layered CH_2Cl_2/cyclohexane solution at 25 °C. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 7.37 (m, 15H, C_6H_5), 1.41 (d, $^3J_{H\text{-}P}$ = 15 Hz, P{C(CH_3)$_3$}$_3$). ^{11}B NMR (128 MHz, CD_2Cl_2, 25 °C): δ -16.68 (s). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 25 °C): δ 148.74 (br d, $^1J_{C\text{-}F}$ = 235 Hz, *o*-C_6F_5), 142.73 (s, *ipso*-C_6H_5), 138.81 (br d, $^1J_{C\text{-}F}$ = 242 Hz, *p*-C_6F_5), 136.90 (br d, $^1J_{C\text{-}F}$ = 241 Hz, *m*-C_6F_5), 128.45 (s, *ipso*-C_6F_5), 129.18 (s, *p*-C_6H_5), 129.09 (s, *m*-C_6H_5), 129.04 (s, *o*-C_6H_5), 98.30 (s, *C*(C_6H_5)$_3$), 42.69 (d, $^3J_{H\text{-}P}$ = 24 Hz, P{*C*(CH_3)$_3$}), 29.63 (s, P{C(*C*H_3)$_3$}). ^{15}N NMR (40.6 MHz, CD_2Cl_2, 25 °C): δ 548.42 (dd, $^2J_{N\text{-}P}$ = 20 Hz, $^1J_{N\text{-}N}$ = 15 Hz, PN*N*O), 412.30 (dd, $^1J_{N\text{-}P}$ = 58 Hz, $^1J_{N\text{-}N}$ = 15 Hz, P*N*NO). ^{19}F NMR (376 MHz, CD_2Cl_2, 25 °C): δ -133.04 (m, 8F, *o*-C_6F_5), -163.71 (t, 4F, $^3J_{F\text{-}F}$ = 21, *p*-C_6F_5), -167.52 (m, 8F, $^3J_{F\text{-}F}$ = 18, *m*-C_6F_5). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 °C): δ 77.31 (dd, $^1J_{P\text{-}N}$ = 58 Hz, $^2J_{P\text{-}N}$ = 20 Hz). Anal. Calcd. for $C_{55}H_{42}BF_{20}N_2OP$: C, 56.52; H, 3.62; N, 2.40. Found: C, 56.40; H, 4.02; N, 2.29 %.

Synthesis of [^{t}Bu$_3$P(N$_2$O)Zr(Me)Cp$_2$][MeB(C$_6$F$_5$)$_3$] (M = Zr 11, Ti 12). These compounds were prepared in a similar fashion and thus only one preparation is detailed. A 20 mL scintillation vial was charged with Cp_2ZrMe_2 (0.076 g, 0.260 mmol) in toluene (2 mL). A second 10 mL vial was charged with $B(C_6F_5)_3$ (0.133 g, 0.260 mmol) in toluene (5 mL). The borane solution was slowly added to the solution of Cp_2ZrMe_2 at room temperature. The resulting solution was bright yellow and was allowed to stir for an additional 5 minutes. At this time, **6** (0.141 g, 0.260 mmol) was added resulting in an opaque pale yellow solution. The reaction was allowed to stir for a period of one hour. Pentane was added (10 mL) precipitating a beige oil. The oil was taken up in CH_2Cl_2 (2 mL) and triturated with pentane (15 mL). The solvent was then decanted from the solid. The product was washed with

pentane (3 x 5 mL) and dried *in vacuo* for 2 hours. Yield: 0.226 g (83 %). Crystals suitable for X-ray diffraction were grown from a layered CH_2Cl_2/pentane solution at -35 °C. **11:** ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 6.30 (s, 10H, C_5H_5), 1.60 (d, 27H, $^3J_{H\text{-}P}$ = 14, P{C(CH_3)$_3$}$_3$), 0.48 (br s, 3H, $H_3CB(C_6F_5)_3$), 0.46 (s, 3H, $ZrCH_3$). ^{11}B NMR (128 MHz, CD_2Cl_2, 25 °C): δ -14.96 (s). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 25 °C): δ 148.88 (br d, $^1J_{C\text{-}F}$ = 238 Hz, *o*-C_6F_5), 138.07 (br d, $^1J_{C\text{-}F}$ = 241 Hz, *p*-C_6F_5), 136.94 (br d, $^1J_{C\text{-}F}$ = 244 Hz, *m*-C_6F_5), 129.10 (s, *ipso*-C_6F_5), 113.39 (s, C_5H_5), 42.07 (d, $^1J_{C\text{-}P}$ = 29 Hz, P{*C*(CH_3)$_3$}), 29.94 (s, P{C(*C*H_3)$_3$}), 10.59 (br s, H_3*C*B(C_6F_5)$_3$). ^{15}N NMR (40.6 MHz, CD_2Cl_2, 25 °C): δ 587.60 (dd, $^2J_{N\text{-}P}$ = 16 Hz, $^1J_{N\text{-}N}$ = 17 Hz, PN*N*O), 398.46 (dd, $^1J_{N\text{-}P}$ = 61 Hz, $^1J_{N\text{-}N}$ = 17 Hz, P*N*NO). ^{19}F NMR (376 MHz, CD_2Cl_2, 25 °C): δ -133.11 (d, 6F, $^3J_{F\text{-}F}$ = 20 Hz, *o*-C_6F_5), -165.25 (t, 3F, $^3J_{F\text{-}F}$ = 21 Hz, *p*-C_6F_5), -167.81 (m, 6F, *m*-C_6F_5). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 °C): δ 67.06 (dd, $^1J_{P\text{-}N}$ = 61 Hz, $^1J_{P\text{-}N}$ = 16 Hz). Anal. Calcd. for $C_{42}H_{43}BF_{15}N_2OPZr$: C, 49.96; H, 4.29; N, 2.77. Found: C, 49.83; H, 4.50; N, 2.54 %. **12:** Yield: 0.232 g (81 %). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 6.30 (s, 10H, C_5H_5); 1.58 (d, 27 H, $^3J_{H\text{-}P}$ = 14 Hz, P{C(CH_3)$_3$}$_3$); 1.06 (s, 3H, $TiCH_3$); 0.47 (br s, 3H, $H_3CB(C_6F_5)_3$). ^{11}B NMR (128MHz, CD_2Cl_2, 25 °C): δ 14.93 (s). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 25 °C): δ 148.88 (br d, $^1J_{C\text{-}F}$ = 240 Hz, *o*-C_6F_5); 138.11 (br d, $^1J_{C\text{-}F}$ = 244 Hz, *p*-C_6F_5); 136.99 (br d, $^1J_{C\text{-}F}$ = 244 Hz, *m*-C_6F_5); 129.62 (br s, *ipso*-C_6F_5); 116.43 (s, *C*$_5H_5$); 42.07 (d, $^1J_{C\text{-}P}$ = 29 Hz, P{*C*(CH_3)$_3$}), 29.93 (s, P{C(*C*H_3)$_3$}), 10.54 (br s, H_3*C*B(C_6F_5)$_3$). ^{19}F NMR (376 MHz, CD_2Cl_2, 25 °C): δ 132.21 (d, 6F, $^3J_{F\text{-}F}$ = 20 Hz, *o*-C_6F_5), 164.42 (t, 3F, $^3J_{F\text{-}F}$ = 20 Hz, *p*-C_6F_5), 166.97 (m, 6F, *m*-C_6F_5). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 25 °C): δ 64.36 (s). Anal. Calcd. for $C_{52}H_{43}BF_{15}N_2OPTi$: C, 52.17; H, 4.49; N, 2.90. Found: C, 52.02; H, 4.25; N, 2.80 %.

Synthesis of [^{t}Bu$_3$P(N$_2$O)Zr(OMe)Cp*$_2$][B(C$_6$F$_5$)$_4$] (13). A 20 mL scintillation vial was charged with Cp*$_2$Zr(OMe)Me (0.060 g, 0. 147 mmol) in C_6H_5Br (5 mL). A second 10 mL vial was charged with

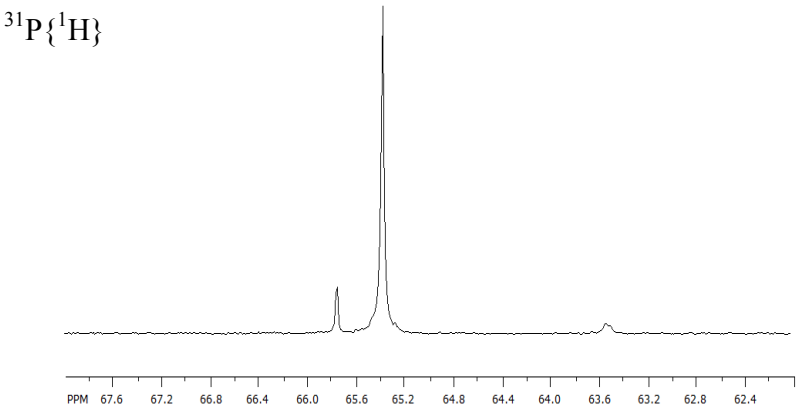
$[Ph_3C][B(C_6F_5)_4]$ (0.136 g, 0.147 mmol) in C_6H_5Br (2 mL). The trityl borate solution was added in a dropwise fashion to the solution of $Cp^*_2Zr(OMe)Me$ and was stirred at room temperature for 5 minutes. At this time, $^tBu_3P$ (0.030 g, 0.148 mmol) in bromobenzene (1 mL) was added resulting in a deep yellow solution. The solution was then transferred to a 100 mL bomb and was degassed and backfilled with N_2O (1 atmosphere). The reaction was allowed to stir at room temperature for 12 hours. Pentane (10 mL) was then added precipitating a yellow oil which was subsequently taken up in CH_2Cl_2 (2 mL), filtered through a plug of celite and triturated with pentane (15 mL). The solvents were decanted from the pale yellow solid. The product was washed with pentane (3 x 5 mL) and dried *in vacuo* for 2 hours. Crystals suitable for X-ray diffraction were grown from a layered CH_2Cl_2/pentane solution at -35 °C. Yield: 0.142 g (74 %). ^{1}H NMR (400MHz, CD_2Cl_2, 25 °C): δ 3.98 (s, 3H, OCH_3), 1.91 (s, 30H, $C_5(CH_3)_5$), 1.63 (d, 27H, $^3J_{H\text{-}P}$ = 14 Hz, $P\{C(CH_3)_3\}_3$). ^{11}B NMR (128 MHz, CD_2Cl_2, 25 °C): δ -16.66 (s). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 25 °C): δ 148.77 (br d, $^1J_{C\text{-}F}$ = 242 Hz, *o*-C_6F_5), 138.85 (br d, $^1J_{C\text{-}F}$ = 244 Hz, *p*-C_6F_5), 136.90 (br d, $^1J_{C\text{-}F}$ = 244 Hz, *m*-C_6F_5), 124.36 (br s, *ipso*-C_6F_5), 122.70 (s, $C_5(CH_3)_5$), 58.92 (s, OCH_3), 41.95 (d, $^1J_{C\text{-}P}$ = 31 Hz, $P\{C(CH_3)_3\}$), 30.04 (s, $P\{C(CH_3)_3\}$), 11.27 (s, $C_5(CH_3)_5$). ^{15}N NMR (40.6 MHz, CD_2Cl_2, 25 °C): δ 591.01 (dd, $^2J_{N\text{-}P}$ = 16 Hz, $^1J_{N\text{-}N}$ = 17 Hz, PN*N*O), 386.28 (dd, $^1J_{N\text{-}P}$ = 62 Hz, $^1J_{N\text{-}N}$ = 17 Hz, P*N*NO). ^{19}F NMR (376 MHz, CD_2Cl_2, 25 °C): δ -133.07 (d, 8F, $^3J_{F\text{-}F}$ = 20 Hz, *o*-C_6F_5), -163.73 (t, 4F, $^3J_{F\text{-}F}$ = 20 Hz, *p*-C_6F_5), -167.54 (m, 8F, *m*-C_6F_5). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 25 °C): δ 64.33 (dd, $^1J_{P\text{-}N}$ = 62 Hz, $^2J_{P\text{-}N}$ = 16 Hz).. Anal. Calcd. for $C_{57}H_{60}BF_{20}N_2O_2PZr$: C, 51.91; H, 4.59; N, 2.13. Found: C, 51.24; H, 4.75; N, 2.28 %.

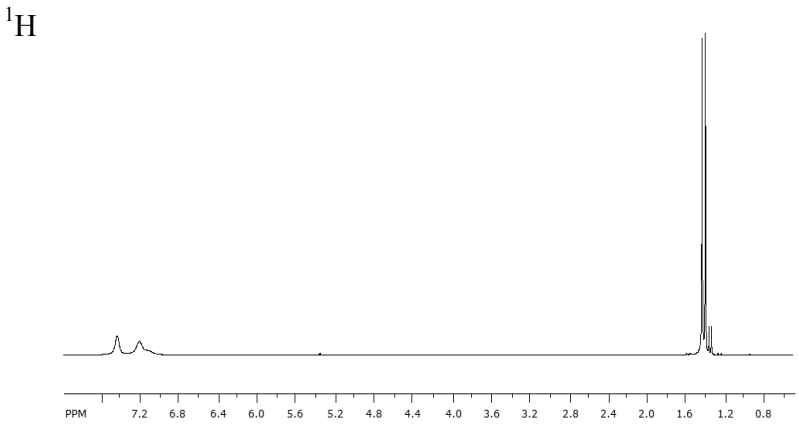
Crystallographic Data Tables

	1	**2**	**5**	**7**
formula	$C_{30}H_{27}BF_{15}N_2OP$	$C_{30}H_{32}BF_{10}N_2OP$	$C_{30}H_{30}BF_{12}N_2OP$	$C_{60}H_{66}B_2F_{24}N_4O_2P_2$
M_r	758.32	668.36	704.34	1414.73
cryst syst	Triclinic	triclinic	Orthorhombic	Triclinic
color, habit	Colourless, block	Colourless, block	Colourless, needles	Colourless, plates
size (mm)	0.22 x 0.18 x 0.17	0.25 x 0.22 x 0.29	0.60 x 0.40 x 0.40	0.40 x 0.40 x 0.10
space group	*P*-1	*P*-1	$P2_12_12_1$	*P*-1
a (Å)	9.5265(4)	10.3832(8)	11.6507(6)	11.6910(5)
b (Å)	11.6603(5)	11.9066(9)	13.7877(6)	12.8326(5)
c (Å)	14.3458(7)	14.5601(12)	19.5448(8)	13.5442(6)
α (º)	76.6040(10)	70.621(4)	90	63.637(2)
β (º)	89.0710(10)	76.818(4)	90	88.082(2)
γ (º)	87.1940(10)	65.912(4)	90	72.341(2)
V ($Å^3$)	1548.32(12)	1541.2(2)	3139.6(2)	1722.62(13)
Z	2	2	4	1
ρ_{calc}, $g.cm^{-3}$	1.627	1.440	1.490	1.364
$\mu(MoK_\alpha)$, cm^{-1}	0.210	0.178	0.187	0.171
F(000)	768	688	1440	726
temp (K)	150(2)	150(2)	150(2)	150(2)
θ range (º)	1.80–25.04	2.11–37.83	1.81-27.49	1.69-27.53
data collected (h,k,l)	-11:11, -11:13, -16:17	-17:17, -20:20, -25:25	-15:15, -17:17, -25:25	-14:15, -16:16, -17:16
min and max transm	0.6888, 0.7452	0.6920, 0.7474	0.6472, 0.7456	0.9348, 0.9831
no. of rflns collected	19946	60932	28943	27807
no. of indpndt reflns	5446	16452	7187	7846
reflns $F_o \geq 2.0\ \sigma(F_o)$	4919	12630	6151	5627
R(F) (%)	2.86	3.77	3.67	4.77
$wR(F^2)$ (%)	7.78	11.51	8.56	13.37
GooF	1.013	1.021	1.029	1.061
weighting a,b	0.0396, 0.7977	0.0590, 0.2143	0.0404, 0.5434	0.0780, 0.0529
params refined	451	415	445	433
min, max resid dens	-0.281, 0.306	-0.259, 0.543	-0.273, 0.307	-0.279, 0.385

	8	**9**	**10**	**11**	**13**
chem formula	$C_{36}H_{36}BF_{12}N_2OP$	$C_{37}H_{47}BClF_3OP_2$	$C_{55}H_{42}BF_{20}N_2OP$	$C_{42}H_{42}BF_{15}N_2OPZr$	$C_{57}H_{60}BF_{20}N_2O_2PZr$
M_r	782.45	672.95	1168.69	1009.78	1318.07
cryst syst	Orthorhombic	Monoclinic	$C_{55}H_{42}BF_{20}N_2OP$	Monoclinic	Monoclinic
color, habit	Colourless, blocks	Colourless, blocks	Yellow, plates	Colourless, blocks	Yellow, blocks
size (mm)	0.55 x 0.35 x 0.10	0.65 x 0.50 x 0.45	0.80 x 0.60 x 0.40	0.65 x 0.50 x 0.45	0.25 x 0.22 x 0.20
space group	Pbca	$P2_1/c$	P-1	$P2_1/n$	C2/c
a (Å)	19.5019(10)	9.5346(5)	12.3838(3)	15.6655(7)	36.218(7)
b (Å)	16.3963(7)	21.1476(9)	12.5415(3)	12.5681(6)	12.304(3)
c (Å)	21.7273(11)	17.6877(8)	18.4914(5)	21.5094(10)	31.224(10)
α (º)	90	90	94.7030(10)	90	90.00
β (º)	90	102.6040(10)	103.5460(10)	93.812(2)	122.397(5)
γ (º)	90	90	101.7340(10)	90	90.00
V ($Å^3$)	6947.5(6)	3480.5(3)	2708.21(12)	4225.5(3)	11749(5)
Z	8	4	2	8	8
ρ_{calc}, $g.cm^{-3}$	1.496	1.284	1.433	1.587	1.490
μ(Mo K_α), cm^{-1}	0.178	0.247	0.161	0.401	0.321
F(000)	3216	1424	1188	2048	5376
temp (K)	150(2)	150(2)	150(2)	150(2)	150(2)
θ range (º)	1.87-27.57	1.52-30.95	1.67-28.50	1.56-27.42	1.78-27.61
data collected (h,k,l)	-21:25, -21:21, -25:28	-13:13, -30:30, -25:25	-15:16, -16:16, -24:24	-20:12, -16:14, -21:27	-46:39, 0:16, 0:40
Min/max transm	0.9086, 0.9825	0.8562, 0.8971	0.6711, 0.7457	0.6714, 0.7461	0.6741, 0.7456
rflns collected	60514	44879	51443	35224	13566
indpndt reflns	7992	11037	13665	9538	13566
reflns $F_o \geq 2.0\,\sigma(F_o)$	5435	8728	9659	6004	7588
R(F) (%)	4.21	4.37	4.24	5.76	5.87
wR(F^2) (%)	10.42	11.65	10.77	14.90	14.25
GooF	1.010	1.035	1.047	1.037	0.997
weighting a,b	0.0394, 3.3204	0.0540, 1.1971	0.0529, 0.0857	0.0661, 3.7172	0.0638, 0.0000
params refined	478	432	730	568	760
min, max resid	-0.338, 0.395	-0.334, 0.747	-0.266, 0.351	-0.877, 1.599	-0.688, 0.826

Figure S1. NMR (CD_2Cl_2) of solid product precipitated by addition of hexane to the reaction of $^tBu_3P$ and BPh_3 in bromobenzene under an N_2O atmosphere (1 bar).





^{19}F EXSY NMR details.

EXSY spectra were acquired on a Bruker AVANCE III spectrometer operating at 376.7 MHz (^{19}F) in phase-sensitive mode, using the standard Bruker pulse sequence (noesyph). In the indirectly detected dimension 64 complex points were collected with 8 scans and 1024 points per increment. EXSY spectra were recorded with appropriate mixing times at each temperature (see Figure S2). Sample temperatures were calibrated with a 4% CH_3OH in CD_3OD sample using the standard method implemented in Bruker Topspin 2.1.

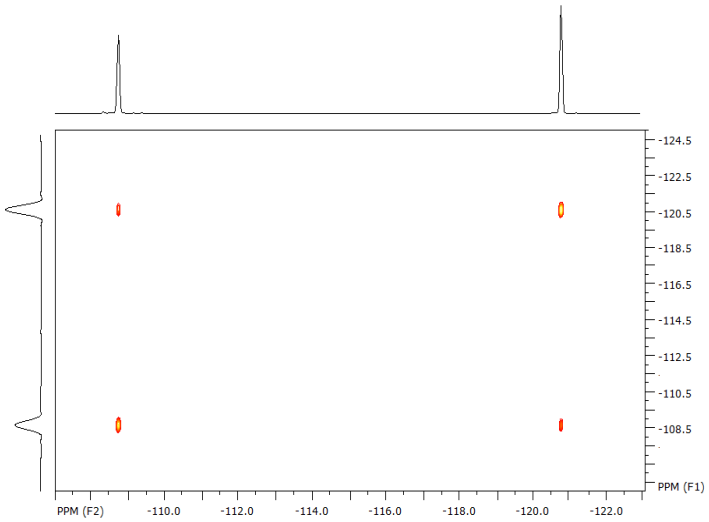


Figure S2. Example of an ^{19}F EXSY NMR spectrum

Integration of diagonal- and cross-peak volumes of the ^{19}F resonances was performed using the Gaussian fit integration method implemented in Sparky.[11] Using Mathematica 5.0,[12] cross-peak volumes of all spectra were normalized (I_x/I_d) and plotted against mixing time. The data points were all at once fitted against equation (1)[13] by non-linear regression (black lines, figure S3).

$$\frac{I_x}{I_d} = \frac{1 - e^{-2k\tau_{mix}}}{1 + e^{-2k\tau_{mix}}} \quad \text{with} \quad k = \frac{k_B T}{h} e^{-\frac{\Delta H^{\ddagger} - T\Delta S^{\ddagger}}{RT}} \qquad (1)$$

The error in determining the activation parameters from the EXSY data is related to the error in the normalized peak volumes ($0 \le I_x/I_d \le 1$) introduced in the integration routine. An estimate of the errors in the activation parameters was obtained by generating peak volumes (I_x/I_d + R), in which R was randomly chosen from a normal distribution with mean μ = 0 and standard deviation σ = 0.025 (corresponding to ca. 5% of the average I_x/I_d). Non-linear regression (equation (1)) was performed on the simulated peak data (I_x/I_d + R), and the procedure independently repeated 1000 times. This gave 1000 simulated values for the activation parameters, for which the mean and standard deviation are reported in the text as $\Delta H^{\ddagger} = \mu(\Delta H^{\ddagger}_{sim}) \pm \sigma(\Delta H^{\ddagger}_{sim})$ and $\Delta S^{\ddagger} = \mu(\Delta S^{\ddagger}_{sim}) \pm \sigma(\Delta S^{\ddagger}_{sim})$.

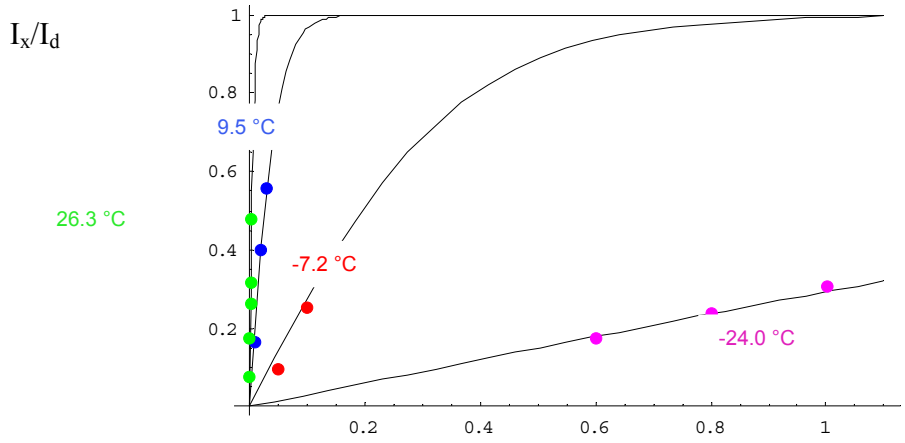


Figure S3. Plot of experimental I_x/I_d values, and fitted curve (black line)

1. P. A. Deck, C. L. Beswick and T. J. Marks, *Journal of the American Chemical Society*, 1998, **120**, 1772-1784.
2. S. A. Cummings, M. Iimura, C. J. Harlan, R. J. Kwaan, I. V. Trieu, J. R. Norton, B. M. Bridgewater, F. Jäkle, A. Sundararaman and M. Tilset, *Organometallics*, 2006, **25**, 1565-1568.
3. G. J. P. Britovsek, J. Ugolotti and A. J. P. White, *Organometallics*, 2005, **24**, 1685-1691.
4. M. Ullrich, A. J. Lough and D. W. Stephan, *Journal of the American Chemical Society*, 2009, **131**, 52-53.
5. D. Naumann, H. Butler and R. Gnann, *Zeitschrift fur Anorganische und Allgemeine Chemie*, 1992, **618**, 74-76.
6. H. Li, L. Li, D. J. Schwartz, M. V. Metz, T. J. Marks, L. Liable-Sands and A. L. Rheingold, *Journal of the American Chemical Society*, 2005, **127**, 14756-14768.

7. D. D. Devore, F. J. Timmers and D. R. Neithamer, WO: 9736937 A1, 1997.
8. E. Samuel and M. D. Rausch, *Journal of the American Chemical Society*, 1973, **95**, 6263-6267.
9. G. J. Erskine, D. A. Wilson and J. D. McCowan, *Journal of Organometallic Chemistry*, 1976, **114**, 119-125.
10. G. E. Martin and C. E. Hadden, *Journal of Natural Products*, 2000, **63**, 543-585.
11. T. D. Goddard and D. G. Kneller, *SPARKY 3*, University of California, San Francisco.
12. Mathematica 5.2, *Wolfram Research Inc.*
13. R. R. Ernst, G. Bodenhausen and A. Wokaun, in *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*, Clarendon Press, Oxford, 1987, p. p. 490.