Bridging Binding Modes of Phosphine-Stabilized Nitrous Oxide to Zn(C₆F₅)₂

Rebecca C. Neu, Edwin Otten, and Douglas W. Stephan*
General Considerations. All manipulations were carried out under an atmosphere of dry, O₂-free N₂ employing standard Schlenk-line and glovebox techniques. Solvents (pentane, hexanes, CH₂Cl₂) were dried by employing a Grubbs-type column system (Innovative Technology), degassed and stored under N₂. Cyclohexane was distilled under N₂ from Na/benzophenone while bromobenzene was distilled under N₂ from CaH₂. CD₂Cl₂ was vacuum transferred from CaH₂, degassed and stored under N₂. ¹⁵N₂O (Cambridge Isotope Laboratories; 99.9%, 98.8% ¹⁵N enriched) were used as received. Zn(C₆F₅)₂ (Sigma-Aldrich; 97%) was recrystallized from toluene at -35 °C, yielding the toluene adduct, tol·Zn(C₆F₅)₂. The reagent B(C₆H₄F)₃¹ was prepared according to literature procedures.

¹H, ¹¹B, ¹³C, ¹⁵N, ¹⁹F and ³¹P NMR spectra were recorded at 25 °C, unless otherwise stated, on a Varian NMR System 400 MHz or Bruker Avance III 400 MHz spectrometer and were referenced using (residual) solvent resonances relative to SiMe₄ (¹H, ¹³C), or relative to an external standard (¹¹B: (Et₂O)BF₃, ¹⁹F: CFCl₃, ³¹P: 85% H₃PO₄). 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.

¹Bu₂PN₂OB(C₆H₄F)₃ (1). A 50 mL schlenk tube was charged with B(C₆H₄F)₃ (0.212 g, 0.716 mmol) and ¹Bu₂P (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 N₂O 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 %). ¹H NMR (400 MHz, CD₂Cl₂, 25 °C): δ 7.33 (m, 6H, α-C₆H₄F), 6.87 (s, 6H, m-C₆H₄F), 4.38 (m, 27H, J₆₋₇ = 14 Hz). ¹¹B(¹H) NMR (128 MHz, CD₂Cl₂, 25 °C): δ 6.69 (s). ¹³C(¹H) NMR (101 MHz, CD₂Cl₂, 25 °C) partial: δ 161.25 (br d, J₀₋₁ = 247 Hz, p-C₆H₄F), 135.54 (br s, m-C₆H₄F), 113.50 (br s, α-C₆H₄F), 41.31 (d, Jₗ₋₆ = 31 Hz, P(C(CH₃)₃)), 29.85 (s, P(C(CH₃)₃)). ¹⁹F NMR (376 MHz, CD₂Cl₂, 25 °C): δ -120.87 (s). ³¹P(¹H) NMR (162 MHz, CD₂Cl₂, 25 °C): δ 65.38 (s). Anal. Calcd. for C₃₀H₃₀BF₃N₂O:P: C, 66.43; H, 7.25; N, 5.16. Found: C, 66.25; H, 7.27; N, 5.17 %.

¹Bu₂P¹⁵N₂OB(C₆H₄F)₃ (1-¹⁵N). A J. Young NMR tube containing a solution of B(C₆H₄F)₃ (0.025 g, 0.084 mmol) and ¹Bu₂P (0.017 g, 0.084 mmol) in C₆H₆Br (0.5 mL) was subjected to 3 freeze-pump-thaw cycles using liquid nitrogen to degas the solution and backfilled with ¹⁵N₂O. After standing overnight, the product was precipitated by addition of hexanes (5 mL). The product was allowed to settle and the solvent was decanted followed by washing with hexanes (2 x 1 mL). The solid was dried in vacuo for 1 hour. ¹H and ¹⁹F NMR spectra were identical to 1. ¹⁵N NMR (40.6
MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ 588.75 (dd, $^2$$J_{N\cdot P} = 19$ Hz, $^1$$J_{N\cdot N} = 18$ Hz, PNNO), 367.61 (dd, $^1$$J_{N\cdot P} = 61$ Hz, $^1$$J_{N\cdot N} = 18$ Hz, PNNO).$^{31}$P($^1$H) NMR (162 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ 64.27 (dd, $^1$$J_{P\cdot N} = 61$ Hz, $^2$$J_{P\cdot N} = 19$ Hz).

$[^{18}$Bu$_2$PN$_2$OZn(C$_6$F$_5$)$_2$]$_2$(2). A 20 mL scintillation vial was charged with 1 (0.100 g, 0.184 mmol) and tol-Zn(C$_6$F$_5$)$_2$ (0.091 g, 0.185 mmol) in CH$_2$Cl$_2$ (5 mL). The solution was initially opaque but cleared after a few seconds of stirring. The reaction was left stirring for 1 hour at room temperature. At this time, hexanes (10 mL) was added precipitating a fine white solid. The solid was isolated by filtration, washed with hexanes (3 x 5 mL) and dried in vacuo for 2 hours. Crystals suitable for X-ray diffraction were grown from a layered CH$_2$Cl$_2$/pentane solution at -35 °C. Yield: 0.118 g (99 %). $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ 1.51 (d, 27H, $^3$$J_{C\cdot F} = 14$ Hz). $^{13}$C($^1$H) NMR (101 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ 149.30 (br d, $^1$$J_{C\cdot F} = 228$ Hz, $\alpha$-C$_6$F$_5$), 140.46 (br d, $^1$$J_{C\cdot F} = 244$ Hz, $\rho$-C$_6$F$_5$), 136.90 (br d, $^1$$J_{C\cdot F} = 259$ Hz, $m$-C$_6$F$_5$), 120.71 (s, ipso-C$_6$F$_5$), 41.65 (d, $^1$$J_{C\cdot P} = 31.65$, P(C(CH$_3$)$_2$)), 29.70 (s, P(C(CH$_3$)$_3$)). $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ -117.44 (m, $\alpha$-C$_6$F$_5$), -157.71 (t, $^3$$J_{F\cdot F} = 19$ Hz, $p$-C$_6$F$_5$), -162.64 (m, $m$-C$_6$F$_5$). $^{31}$P($^1$H) NMR (162 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ 66.50 (s). Anal. Calcd. for C$_{58}$H$_{50}$F$_{30}$N$_3$O$_3$P$_2$Zn$_2$: C: 44.63, H: 4.21, N: 4.34. Found: C: 44.32, H: 4.14, N: 4.66 %.

$[^{18}$Bu$_2$P$^{15}$N$_2$OZn(C$_6$F$_5$)$_2$]$_2$ (2-$^{15}$N). A 10 mL scintillation vial was charged with 1-$^{15}$N (0.023 g, 0.042 mmol) and tol-Zn(C$_6$F$_5$)$_2$ (0.021 g, 0.043 mmol) in CH$_2$Cl$_2$ (3 mL). The clear solution was left stirring for 1 hour at room temperature. At this time, hexanes (5 mL) was added precipitating a fine white solid. The solid was allowed to settle and the solvent was decanted followed by washing of the solid with hexanes (2 x 1 mL). The product was dried in vacuo for 1 hour. $^1$H and $^{19}$F NMR spectra are identical to 2. $^{15}$N NMR (40.6 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ 599.07 (dd, $^2$$J_{N\cdot P} = 9.3$ Hz, $^1$$J_{N\cdot N} = 18$ Hz, PNNO), 317.97 (dd, $^1$$J_{N\cdot P} = 54$ Hz, $^1$$J_{N\cdot N} = 18$ Hz, PNNO). $^{31}$P($^1$H) NMR (162 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ 65.83 (dd, $^1$$J_{P\cdot N} = 54$ Hz, $^2$$J_{P\cdot N} = 9.3$ Hz).

$[^{18}$Bu$_3$N$_2$OZn(C$_6$F$_5$)$_2$Zn(C$_6$F$_5$)$_2$]$_2$ (3). Method I. A 20 mL scintillation vial was charged with 1 (0.060 g, 0.111 mmol) and tol-Zn(C$_6$F$_5$)$_2$ (0.082 g, 0.167 mmol) in CH$_2$Cl$_2$ (10 mL). The clear solution was left stirring for 1 hour at room temperature. At this time, pentane (10 mL) was added precipitating a fine white solid. The product was allowed to settle and the solvent was decanted followed by washing of the solid with pentane (3 x 5 mL). The product was dried in vacuo for 1 hour. Yield: 0.076 g (81 %). Method II. A 20 mL scintillation vial was charged with 2 (0.037 g, 0.029 mmol) and tol-Zn(C$_6$F$_5$)$_2$ (0.014 g, 0.028 mmol) in CH$_2$Cl$_2$ (10 mL). The clear solution was left stirring for 1 hour at room temperature. At this time, pentane (10 mL) was added precipitating a fine white solid. The product was allowed to settle and the solvent was decanted followed by washing of the solid with pentane (3 x 5 mL). The product was dried in vacuo for 1 hour. Yield:
0.037 g (77 %). Crystals suitable for X-ray diffraction were grown from a layered CH2Cl2/pentane solution at -35 °C. 1H NMR (400MHz, CD2Cl2, 25 °C): δ 1.46 (d, 27H, 3J_{H-P} = 14 Hz). 13C{1H} NMR (101 MHz, CD2Cl2, 25 °C): δ 149.26 (br d, 1J_{C-F} = 245 Hz, o-C6F5), 140.17 (br d, 1J_{C-F} = 224 Hz, p-C6F5), 136.41 (br d, 1J_{C-F} = 241 Hz, m-C6F5), 118.95 (s, ipso-C6F5), 41.86 (d, 1J_{C-P} = 30 Hz, P(C(CH3)3)), 29.59 (s, P(C(CH3)3)). 19F NMR (376 MHz, CD2Cl2, 25 °C): δ -117.56 (m, o-C6F5), -156.73 (t, 3J_{F-F} = 19 Hz, p-C6F5), -162.42 (m, m-C6F5). 31P{1H} NMR (162 MHz, CD2Cl2, 25 °C): δ 68.54 (s). Anal. Calcd. for C41H42F6N3O2P2: C, 41.73; H, 3.39; N, 3.49 %.

0.004 mmol) in CD2Cl2 (3 mL). The cloudy, faintly yellow solution was left stirring for 1 hour at room temperature. At this time, hexanes (10 mL) was added precipitating a fine white solid. The product was allowed to settle and the solvent was decanted followed by washing with hexanes (3 x 5 mL). The clear solution was left stirring for 1 hour. Yield: 0.068 g (70 %). Crystals suitable for X-ray diffraction were grown from a layered CH2Cl2/cyclohexane solution at 25 °C. 1H NMR (400MHz, CD2Cl2, 25 °C): δ 1.43 (d, 27H, 3J_{H-P} = 14 Hz). 13C{1H} NMR (101 MHz, CD2Cl2, 25 °C): δ 149.41 (br d, 1J_{C-F} = 224 Hz, o-C6F5), 140.97 (br d, 1J_{C-F} = 248 Hz, p-C6F5), 137.00 (br d, 262 Hz, m-C6F5), 118.29 (s, ipso-C6F5), 42.04 (d, 1J_{C-P} = 30 Hz, P(C(CH3)3)), 29.53 (s, P(C(CH3)3)).
P(C(CH₃)₃)₃. ¹⁹F NMR (376 MHz, CD₂Cl₂, 25 °C): δ -117.62 (m, o-C₆F₅), -156.26 (t, ³JF-F = 20 Hz, p-C₆F₅), -162.18 (m, m-C₆F₅). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂, 25 °C): δ 71.65 (s). Anal. Calcd. for C₃₆H₂₇F₂₀N₂OPZn₂·0.5CD₂Cl₂: C, 40.30; H, 2.59; N, 2.57. Found: C, 40.05; H, 2.80; N, 2.78 %.

¹Bu₃PN₂O(Zn(C₆F₅)₂)(4) at -75 °C. A J. Young NMR tube was charged with 4 (0.006 g, 0.006 mmol) in CD₂Cl₂ (0.5 mL). The ¹⁹F NMR spectrum was recorded at -75 °C. ¹⁹F NMR (376 MHz, CD₂Cl₂, -75 °C): δ -117.61 (d, ³JF-F = 20 Hz, o-C₆F₅), -118.15 (d, ³JF-F = 20 Hz, o-C₆F₅), -154.85 (t, ³JF-F = 20 Hz, p-C₆F₅), -155.36 (t, ³JF-F = 21 Hz, p-C₆F₅), -161.10 (t, ³JF-F = 19 Hz, 2 x m-C₆F₅).

¹Bu₃P¹⁵N₂O(Zn(C₆F₅)₂)(4-¹⁵N). A 10 mL scintillation vial was charged with 2-¹⁵N (0.014 g, 0.011 mmol) and (C₆F₅)₂Zn-toluene (0.010 g, 0.020 mmol) in dichloromethane (3 mL). The clear solution was left stirring for 1 hour at room temperature. At this time, hexanes (5 mL) was added precipitating a fine white solid. The solid was allowed to settle and the solvent was decanted followed by washing with hexanes (2 x 1 mL). The product was dried in vacuo for 1 hour. ¹H and ¹⁹F NMR spectra are identical to 4. ¹⁵N NMR (40.6 MHz, CD₂Cl₂, 25 °C): δ 582.52 (dd, ²J_N,P = 11 Hz, ¹J_N,N = 17 Hz, PNNO), 349.33 (dd, ¹J_N,P = 54 Hz, ¹J_N,N = 17 Hz, PNNO). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂, 25 °C): δ 71.99 (dd, ¹J_P,N = 54 Hz, ²J_P,N = 11 Hz).

References