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Supporting Information

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**Bridging Binding Modes of Phosphine-Stabilized Nitrous Oxide to
 $\text{Zn}(\text{C}_6\text{F}_5)_2^{**}$**

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

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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. ^tBu₃P (Strem Chemicals), N₂O (Sigma-Aldrich; 99%) and 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: CFCI₃, ³¹P: 85% H₃PO₄, ¹⁵N: NH₃(l) via the ¹⁵N resonance of 90% formamide in DMSO-*d*₆ at 112 ppm).² 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.

^tBu₃PN₂OB(C₆H₄F)₃ (1). A 50 mL schlenk tube was charged with B(C₆H₄F)₃ (0.212 g, 0.716 mmol) and ^tBu₃P (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, *o*-C₆H₄F), 6.87 (m, 6H, *m*-C₆H₄F), 1.38 (d, 27H, ³J_{H-P} = 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, ¹J_{C-F} = 247 Hz, *p*-C₆H₄F), 135.54 (br s, *m*-C₆H₄F), 113.50 (br s, *o*-C₆H₄F), 41.31 (d, ¹J_{C-P} = 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 C₃₀H₃₉BF₃N₂OP: C, 66.43; H, 7.25; N, 5.16. Found: C, 66.25; H, 7.27; N, 5.17 %.

^tBu₃P¹⁵N₂OB(C₆H₄F)₃ (1-¹⁵N). A J. Young NMR tube containing a solution of B(C₆H₄F)₃ (0.025 g, 0.084 mmol) and ^tBu₃P (0.017 g, 0.084 mmol) in C₆H₅Br (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, CD₂Cl₂, 25 °C): δ 588.75 (dd, ²J_{N-P} = 19 Hz, ¹J_{N-N} = 18 Hz, PNNO), 367.61 (dd, ¹J_{N-P} = 61 Hz, ¹J_{N-N} = 18 Hz, PMNO). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂, 25 °C): δ 64.27 (dd, ¹J_{P-N} = 61 Hz, ²J_{P-N} = 19 Hz).

[^tBu₃PN₂OZn(C₆F₅)₂]₂ (2). A 20 mL scintillation vial was charged with **1** (0.100 g, 0.184 mmol) and tol-Zn(C₆F₅)₂ (0.091 g, 0.185 mmol) in CH₂Cl₂ (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, the solution was cloudy. 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 CH₂Cl₂/pentane solution at -35 °C. Yield: 0.118 g (99 %). ¹H NMR (400 MHz, CD₂Cl₂, 25 °C): δ 1.51 (d, 27H, ³J_{H-P} = 14 Hz). ¹³C{¹H} NMR (101 MHz, CD₂Cl₂, 25 °C): δ 149.30 (br d, ¹J_{C-F} = 228 Hz, *o*-C₆F₅), 140.46 (br d, ¹J_{C-F} = 244 Hz, *p*-C₆F₅), 136.90 (br d, ¹J_{C-F} = 259 Hz, *m*-C₆F₅), 120.71 (s, *ipso*-C₆F₅), 41.65 (d, ¹J_{C-P} = 31.65, P{C(CH₃)₃}), 29.70 (s, P{C(CH₃)₃}). ¹⁹F NMR (376 MHz, CD₂Cl₂, 25 °C): δ -117.44 (m, *o*-C₆F₅), -157.71 (t, ³J_{F-F} = 19 Hz, *p*-C₆F₅), -162.64 (m, *m*-C₆F₅). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂, 25 °C): δ 66.50 (s). Anal. Calcd. for C₄₈H₅₄F₂₀N₄O₂P₂Zn₂: C, 44.63; H, 4.21; N, 4.34. Found: C, 44.32; H, 4.14; N, 4.66 %.

[^tBu₃P¹⁵N₂OZn(C₆F₅)₂]₂ (2-¹⁵N). A 10 mL scintillation vial was charged with **1-¹⁵N** (0.023 g, 0.042 mmol) and tol-Zn(C₆F₅)₂ (0.021 g, 0.043 mmol) in CH₂Cl₂ (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. ¹H and ¹⁹F NMR spectra are identical to **2**. ¹⁵N NMR (40.6 MHz, CD₂Cl₂, 25 °C): δ 599.07 (dd, ²J_{N-P} = 9.3 Hz, ¹J_{N-N} = 18 Hz, PNNO), 317.97 (dd, ¹J_{N-P} = 54 Hz, ¹J_{N-N} = 18 Hz, PMNO). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂, 25 °C): δ 65.83 (dd, ¹J_{P-N} = 54 Hz, ²J_{P-N} = 9.3 Hz).

(^tBu₃N₂OZn(C₆F₅)₂)₂Zn(C₆F₅)₂ (3). Method I. A 20 mL scintillation vial was charged with **1** (0.060 g, 0.111 mmol) and tol-Zn(C₆F₅)₂ (0.082 g, 0.167 mmol) in CH₂Cl₂ (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(C₆F₅)₂ (0.014 g, 0.028 mmol) in CH₂Cl₂ (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 C₆₀H₅₄F₃₀N₄O₂P₂Zn₃·CH₂Cl₂: C, 41.25; H, 3.18; N, 3.15. Found: C, 41.73; H, 3.39; N, 3.49 %.

(¹Bu₃PN₂OZn(C₆F₅)₂)₂Zn(C₆F₅)₂ at -75 °C. A J. Young NMR tube was charged with **3** (0.006 g, 0.004 mmol) in CD₂Cl₂ (0.5 mL). The ¹⁹F NMR spectrum was recorded at -75 °C. ¹⁹F NMR (376 MHz, CD₂Cl₂, -75 °C): δ -117.43 (br s, *o*-C₆F₅), -117.93 (br s, *o*-C₆F₅), -156.26 (t, ³J_{F-F} = 19 Hz, *p*-C₆F₅), -157.65 (t, ³J_{F-F} = 18 Hz, *p*-C₆F₅), -161.81 (br s, *m*-C₆F₅), -162.30 (br s, *m*-C₆F₅).

(¹Bu₃N₂OZn(C₆F₅)₂)₂Zn(C₆F₅)₂ (3-¹⁵N). A 10 mL scintillation vial was charged with **1-¹⁵N** (0.010 g, 0.018 mmol) and tol·Zn(C₆F₅)₂ (0.014 g, 0.028 mmol) in CH₂Cl₂ (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 solid was then dried *in vacuo* for 1 hour. ¹H and ¹⁹F NMR spectra are identical to **3**. ¹⁵N NMR (40.6 MHz, CD₂Cl₂, 25 °C): δ 595.17 (dd, ²J_{N-P} = 9.4 Hz, ¹J_{N-N} = 18 Hz, PNNO), 323.78 (dd, ¹J_{N-P} = 54 Hz, ¹J_{N-N} = 18 Hz, PMNO). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂, 25 °C): δ 68.22 (dd, ¹J_{P-N} = 54 Hz, ²J_{P-N} = 9.4 Hz).

¹Bu₃PN₂O(Zn(C₆F₅)₂)₂ (4). Method I. A 20 mL scintillation vial was charged with **1** (0.064 g, 0.118 mmol) and tol·Zn(C₆F₅)₂ (0.116 g, 0.236 mmol) in CH₂Cl₂ (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 with pentane (3 x 5 mL). The solid was dried *in vacuo* for 1 hour. Yield: 0.099 g, (80 %). **Method II.** A 20 mL scintillation vial was charged with **2** (0.060 g, 0.046 mmol) and tol·Zn(C₆F₅)₂ (0.046 g, 0.094 mmol) in CH₂Cl₂ (8 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 powder. The solid was allowed to settle and the solvent was decanted followed by washing with hexanes (3 x 5 mL). The solid was dried *in vacuo* 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,

$P\{C(CH_3)_3\}$. ^{19}F NMR (376 MHz, CD_2Cl_2 , 25 °C): δ -117.62 (m, *o*- C_6F_5), -156.26 (t, $^3J_{F-F}$ = 20 Hz, *p*- C_6F_5), -162.18 (m, *m*- C_6F_5). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2 , 25 °C): δ 71.65 (s). Anal. Calcd. for $C_{36}H_{27}F_{20}N_2OPZn_2 \cdot 0.5CH_2Cl_2$: C, 40.30; H, 2.59; N, 2.57. Found: C, 40.05; H, 2.80; N, 2.78 %.

$^tBu_3PN_2O(Zn(C_6F_5)_2)_2$ at -75 °C . A J. Young NMR tube was charged with **4** (0.006 g, 0.006 mmol) in CD_2Cl_2 (0.5 mL). The ^{19}F NMR spectrum was recorded at -75 °C. ^{19}F NMR (376 MHz, CD_2Cl_2 , -75 °C): δ -117.61 (d, $^3J_{F-F}$ = 20 Hz, *o*- C_6F_5), -118.15 (d, $^3J_{F-F}$ = 20 Hz, *o*- C_6F_5), -154.85 (t, $^3J_{F-F}$ = 20 Hz, *p*- C_6F_5), -155.36 (t, $^3J_{F-F}$ = 21 Hz, *p*- C_6F_5), -161.10 (t, $^3J_{F-F}$ = 19 Hz, 2 x *m*- C_6F_5).

$^tBu_3P^{15}N_2O(Zn(C_6F_5)_2)_2$ (4**- ^{15}N)**. A 10 mL scintillation vial was charged with **2**- ^{15}N (0.014 g, 0.011 mmol) and $(C_6F_5)_2Zn$ -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 ^{19}F NMR spectra are identical to **4**. ^{15}N NMR (40.6 MHz, CD_2Cl_2 , 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, $PMNO$). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2 , 25 °C): δ 71.99 (dd, $^1J_{P-N}$ = 54 Hz, $^2J_{P-N}$ = 11 Hz).

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