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

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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. •Bu₃P (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)₃ was prepared according to literature procedures. H, 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 (values in Hz). Combustion analyses were performed in house employing a Perkin-Elmer CHN Analyzer.

¹⁷Bu₂PN₂OB(C₆H₄F)₃ (1). A 50 mL schlenk tube was charged with B(C₆H₄F)₃ (0.212 g, 0.716 mmol) and ²⁷Bu₂P (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 %). H NMR (400 MHz, CD₂Cl₂, 25 °C): δ 7.33 (m, 6H, α-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-P = 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 C₃₀H₄₀BF₃N₂OP: C, 66.43; H, 7.25; N, 5.16. Found: C, 66.25; H, 7.27; N, 5.17 %.

¹⁷Bu₂P¹⁵N₂OB(C₆H₄F)₃ (1-¹⁵N). A J. Young NMR tube containing a solution of B(C₆H₄F)₃ (0.025 g, 0.084 mmol) and ²⁷Bu₂P (0.017 g, 0.084 mmol) in C₆H₄Br (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. H and ¹⁹F NMR spectra were identical to 1. ¹⁵N NMR (40.6
MHz, CD$_2$Cl$_2$, 25 °C): δ 588.75 (dd, $^2J_{N,N} = 19$ Hz, $^1J_{N,P} = 18$ Hz, PNNO), 367.61 (dd, $^1J_{N,P} = 61$ Hz, $^1J_{N,N} = 18$ Hz, PNNO). $^3$P($^1$H) NMR (162 MHz, CD$_2$Cl$_2$, 25 °C): δ 64.27 (dd, $^1J_{P,N} = 61$ Hz, $^2J_{P,N} = 19$ Hz).

$[^{15}$Bu$_3$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, 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 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): δ 1.51 (d, 27H, $^3J_{C,P} = 14$ Hz). $^{13}$C($^1$H) NMR (101 MHz, CD$_2$Cl$_2$, 25 °C): δ 149.30 (br d, 1Br C, $^1J_{C,F} = 228$ Hz, o-C$_6$F$_5$), 140.46 (br d, $^1J_{C,F} = 244$ Hz, p-C$_6$F$_5$), 136.90 (br d, $^1J_{C,F} = 259$ Hz, m-C$_6$F$_5$), 120.71 (s, ipso-C$_6$F$_5$), 41.65 (d, $^1J_{C,F} = 31.65$, P(C(CH$_3$)$_3$)), 29.70 (s, P(C(CH$_3$)$_3$)). $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$, 25 °C): δ -117.44 (m, o-C$_6$F$_5$), -157.71 (t, $^3J_{F,F} = 19$ Hz, p-C$_6$F$_5$), -162.64 (m, m-C$_6$F$_5$). $^3$P($^1$H) NMR (162 MHz, CD$_2$Cl$_2$, 25 °C): δ 66.50 (s). Anal. Calcd. for C$_{36}$H$_{34}$F$_{30}$N$_2$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 %.

$[^{15}$Bu$_3$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): 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, PNNO). $^3$P($^1$H) NMR (162 MHz, CD$_2$Cl$_2$, 25 °C): δ 65.83 (dd, $^1J_{P,N} = 54$ Hz, $^2J_{P,N} = 9.3$ Hz).

$[^{15}$Bu$_3$N$_2$OZn(C$_6$F$_5$)$_2$]Zn(C$_6$F$_5$)$_2$ (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 CH$_2$Cl$_2$/pentane solution at -35 °C. $^1$H NMR (400MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ 1.46 (d, 27H, $^3$J$_{H-P}$ = 14 Hz). $^{13}$C($^1$H) NMR (101 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ 149.26 (br d, $^1$J$_{C-F}$ = 245 Hz, o-C$_6$F$_5$), 140.17 (br d, $^1$J$_{C-F}$ = 224 Hz, p-C$_6$F$_5$), 136.41 (br d, $^1$J$_{C-F}$ = 241 Hz, m-C$_6$F$_5$), 118.95 (s, ipso-C$_6$F$_5$), 41.86 (d, $^1$J$_{C-P}$ = 30 Hz, P(C(CH$_3$)$_3$)), 29.59 (s, P(C(CH$_3$)$_3$)). $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ -117.56 (m, o-C$_6$F$_5$), -156.73 (t, $^3$J$_{F-F}$ = 19 Hz, p-C$_6$F$_5$), -162.42 (m, m-C$_6$F$_5$). $^{31}$P($^1$H) NMR (162 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ 68.54 (s). Anal. Calcd. for C$_{20}$H$_4$F$_{10}$N$_2$O$_2$P$_2$Zn$_3$-CH$_2$Cl$_2$: C, 41.25; H, 3.18; N, 3.15. Found: C, 41.73; H, 3.39; N, 3.49 %.

($^5$Bu$_3$PN$_2$OZn(C$_6$F$_5$)$_2$)Zn(C$_6$F$_5$)$_2$ at -75 °C . A J. Young NMR tube was charged with 3 (0.006 g, 0.004 mmol) in CD$_2$Cl$_2$ (0.5 mL). The $^{19}$F NMR spectrum was recorded at -75 °C. $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$, -75 °C): $\delta$ -117.43 (br s, o-C$_6$F$_5$), -119.93 (br s, o-C$_6$F$_5$), -156.26 (t, $^3$J$_{F-F}$ = 19 Hz, p-C$_6$F$_5$), -157.65 (t, $^3$J$_{F-F}$ = 18 Hz, p-C$_6$F$_5$), -161.81 (br s, m-C$_6$F$_5$), -162.30 (br s, m-C$_6$F$_5$).

($^5$Bu$_3$N$_2$OZn(C$_6$F$_5$)$_2$)Zn(C$_6$F$_5$)$_2$ (3-$^{15}$N). A 10 mL scintillation vial was charged with 1-$^{15}$N (0.010 g, 0.018 mmol) and tol·Zn(C$_6$F$_5$)$_2$ (0.014 g, 0.028 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 solild 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. $^1$H and $^{19}$F NMR spectra are identical to 3. $^{15}$N NMR (40.6 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ 595.17 (dd, $^2$J$_{H-N}$ = 9.4 Hz, $^1$J$_{H-N}$ = 18 Hz, PNNO), 323.78 (dd, $^1$J$_{H-N}$ = 54 Hz, $^1$J$_{H-N}$ = 18 Hz, PANO). $^{31}$P($^1$H) NMR (162 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ 68.22 (dd, $^1$J$_{P-N}$ = 54 Hz, $^2$J$_{P-N}$ = 9.4 Hz).

$^5$Bu$_3$PN$_2$O(Zn(C$_6$F$_5$)$_2$ (4). Method I. A 20 mL scintillation vial was charged with 1 (0.064 g, 0.118 mmol) and tol·Zn(C$_6$F$_5$)$_2$ (0.116 g, 0.236 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 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(C$_6$F$_5$)$_2$ (0.046 g, 0.094 mmol) in CH$_2$Cl$_2$ (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 CH$_2$Cl$_2$/cyclohexane solution at 25 °C. $^1$H NMR (400MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ 1.143 (d, 27H, $^3$J$_{H-P}$ = 14 Hz). $^{13}$C($^1$H) NMR (101 MHz, CD$_2$Cl$_2$, 25 °C): $\delta$ 149.41 (br d, $^1$J$_{C-F}$ = 224 Hz, o-C$_6$F$_5$), 140.97 (br d, $^1$J$_{C-F}$ = 248 Hz, p-C$_6$F$_5$), 137.00 (br d, $^1$J$_{C-F}$ = 30 Hz, m-C$_6$F$_5$), 118.29 (s, ipso-C$_6$F$_5$), 42.04 (d, $^1$J$_{C-P}$ = 30 Hz, P(C(CH$_3$)$_3$)), 29.53 (s,
P(C(CH₃)₃)). ¹⁹F NMR (376 MHz, CD₂Cl₂, 25 °C): δ -117.62 (m, o-C₆F₅), -156.26 (t, 3J₆F = 20 Hz, p-C₆F₅), -162.18 (m, m-C₆F₅). ¹³¹P(¹H) NMR (162 MHz, CD₂Cl₂, 25 °C): δ 71.65 (s). Anal. Calcd. for C₃₆H₂₇F₂₀N₂OPZn₂·0.5CH₂Cl₂: C, 40.30; H, 2.59; N, 2.57. Found: C, 40.05; H, 2.80; N, 2.78 %.

ᵗBu₃P₂O(Zn(C₆F₅)₂)₂ 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, 3J₆F = 20 Hz, o-C₆F₅), -118.15 (d, 3J₆F = 20 Hz, o-C₆F₅), -154.85 (t, 3J₆F = 20 Hz, p-C₆F₅), -155.36 (t, 3J₆F = 21 Hz, p-C₆F₅), -161.10 (t, 3J₆F = 19 Hz, 2x m-C₆F₅).

ᵗBu₃P¹⁵N₂O(Zn(C₆F₅)₂)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, 2J₅P = 11 Hz, 1J₅N = 17 Hz, PNNO), 349.33 (dd, 1J₅P = 54 Hz, 1J₅N = 17 Hz, PNNO). ¹³¹P(¹H) NMR (162 MHz, CD₂Cl₂, 25 °C): δ 71.99 (dd, 1J₅P = 54 Hz, 2J₅P = 11 Hz).

References