

Supporting Information to:

Complexation of Nitrous Oxide by Frustrated Lewis Pairs

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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; bromobenzene was vacuum transferred from CaH₂ and stored under N₂. Deuterated solvents were vacuum transferred from CaH₂ (CD₂Cl₂; C₆D₅Br). ^tBu₃P (Strem Chemicals), N₂O (Sigma-Aldrich; 99%) and ¹⁵N₂O (Cambridge Isotope Laboratories; 99.9%, 98.8% ¹⁵N enriched) were used as received. The reagents PhB(C₆F₅)₂¹ and ^tBu₃P=O² were prepared according to literature procedures; ^tBu₃P=O was recrystallized from pentane at -30 °C. ¹H, ¹¹B, ¹³C, ¹⁹F, ³¹P and ¹⁵N 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 SiMe₄ (¹H, ¹³C), or relative to an external standard (¹¹B: (Et₂O)BF₃; ¹⁹F: CFCF₃; ³¹P: 85% H₃PO₄; ¹⁵N: NH₃(l) via the ¹⁵N resonance of 90% formamide in DMSO-*d*₆ at 112 ppm).³ Chemical shifts are reported in ppm and coupling constants as scalar values in Hz. Infrared spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer; samples were prepared as thin films on KBr plates by evaporation of a CH₂Cl₂ solution. Photolysis experiments were performed in conventional glass J. Young NMR tubes using a quartz mercury arc lamp (ACE Glass) equipped with water cooling. Combustion analyses were performed in house employing a Perkin-Elmer CHN Analyzer.

^tBu₃P(N₂O)B(C₆F₅)₃ (1). A solution of B(C₆F₅)₃ (200 mg, 0.391 mmol) and ^tBu₃P (79 mg, 0.391 mmol) in 5 mL of C₆H₅Br was allowed to sit under an atmosphere of N₂O for a day, resulting in the precipitation of a colorless product. Hexane (15 mL) was stirred in and the precipitate was allowed to settle. The supernatant was decanted and the white residue was recrystallized by diffusion of hexane into a CH₂Cl₂ solution to give 225 mg of **1** as white microcrystalline material (0.296 mmol, 76%). ¹H NMR (400 MHz, CD₂Cl₂, 25 °C) δ 1.46 (d, *J*_{PH} = 14.5). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂, 25 °C) δ 68.5 (s). ¹⁹F NMR (377 MHz, CD₂Cl₂, 25 °C) δ -133.8 (dd, ¹*J*_{FF} = 23.9, ²*J*_{FF} = 6.9, 2F, *o*-F), -160.3 (t, *J* = 20.2, 1F, *p*-F), -166.0 (m, 2F, *m*-F). ¹¹B NMR (128 MHz, CD₂Cl₂, 25 °C) δ 0.4. ¹³C NMR (101 MHz, CD₂Cl₂, 25 °C) δ 148.5 (d, *J*_{FC} = 240, *o*-C₆F₅), 139.9 (d, *J*_{FC} = 246, *p*-C₆F₅), 137.5 (d, *J*_{CF} = 248, *m*-CF), 121.2 (br, *ipso*-C₆F₅), 41.8 (d, *J*_{PC} = 29, PCMe₃), 29.7 (PCMe₃). Anal. Calcd for C₃₀H₂₇BF₁₅N₂OP: C, 47.52; H, 3.59; N, 3.69. Found: C, 47.78; H, 3.96; N, 3.47.

${}^t\text{Bu}_3\text{P}({}^{15}\text{N}_2\text{O})\text{B}(\text{C}_6\text{F}_5)_3$ (1- ${}^{15}\text{N}$**).** An NMR tube containing a solution of $\text{B}(\text{C}_6\text{F}_5)_3$ (25 mg, 0.049 mmol) and ${}^t\text{Bu}_3\text{P}$ (10mg, 0.049 mmol) in 0.5 mL $\text{C}_6\text{D}_5\text{Br}$ was degassed and backfilled with ~ 0.9 bar of ${}^{15}\text{N}_2\text{O}$. After standing overnight, the product was precipitated by addition of hexanes. The white precipitate was dried *in vacuo* and dissolved in 0.5 mL of CD_2Cl_2 . NMR analysis was consistent with formation of **1- ${}^{15}\text{N}$** . ${}^1\text{H}/{}^{19}\text{F}$ NMR spectra are identical to **1**. ${}^{31}\text{P}\{{}^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2 , 25 °C) δ 68.5 (dd, ${}^1J_{\text{PN}} = 58.7$, ${}^2J_{\text{PN}} = 19.6$). ${}^{15}\text{N}$ NMR (40.6 MHz, CD_2Cl_2 , 25 °C) δ 566.6 (dd, ${}^2J_{\text{PN}} = 19.6$, ${}^1J_{\text{NN}} = 15.6$, *NNO*), 381.7 (dd, ${}^1J_{\text{PN}} = 58.7$, ${}^1J_{\text{NN}} = 15.6$, *NNO*).

${}^t\text{Bu}_3\text{P}(\text{N}_2\text{O})\text{B}(\text{C}_6\text{F}_5)_2\text{Ph}$ (2**).** A 50 mL schlenk tube was charged with $\text{PhB}(\text{C}_6\text{F}_5)_2$ (0.119 g, 0.282 mmol) and ${}^t\text{Bu}_3\text{P}$ (0.057 g, 0.282 mmol) in bromobenzene (5 mL). The colourless solution was subjected to 3 freeze-pump-thaw cycles using liquid nitrogen to degas the solution. The sample was exposed to a continuous flow of N_2O for a period of 1 minute. The solution was stirred at room temperature for 12 hours. 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: 0.144 g (76%). Crystals suitable for X-ray diffraction were grown from a layered dichloromethane/cyclohexane solution at 25 °C. ${}^1\text{H}$ NMR (400 MHz, CD_2Cl_2 , 25 °C) δ 7.40 (d, 2H, ${}^3J_{\text{HH}} = 7$ Hz, *o*- C_6H_5), 7.17 (t, 2H, ${}^3J_{\text{HH}} = 8$ Hz, *m*- C_6H_5), 7.09 (t, 1H, ${}^3J_{\text{HH}} = 8$ Hz, *p*- C_6H_5), 1.44 (d, 27H, ${}^3J_{\text{HP}} = 14$ Hz, $\text{P}\{\text{C}(\text{CH}_3)_3\}$). ${}^{11}\text{B}\{{}^1\text{H}\}$ NMR (CD_2Cl_2) δ 3.27 (s). ${}^{13}\text{C}\{{}^1\text{H}\}$ NMR (CD_2Cl_2) δ 148.25 (br d, ${}^1J_{\text{CF}} = 240$ Hz, *o*- C_6F_5), 139.68 (br d, ${}^1J_{\text{CF}} = 218$ Hz, *p*- C_6F_5), 137.23 (br d, ${}^1J_{\text{CF}} = 226$ 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, ${}^1J_{\text{CP}} = 30$ Hz, $\text{P}\{\text{C}(\text{CH}_3)_3\}$), 29.71 (s, CH_3). ${}^{19}\text{F}$ NMR (CD_2Cl_2): δ -131.87 (dd, 4F, ${}^3J_{\text{FF}} = 25$ Hz, ${}^4J_{\text{FF}} = 9$ Hz, *o*- C_6F_5), -161.71 (t, 2F, ${}^3J_{\text{FF}} = 20$ Hz, *m*- C_6F_5), -166.45 (td, 4F, ${}^3J_{\text{FF}} = 23$ Hz, ${}^4J_{\text{FF}} = 8$ Hz *m*- C_6F_5). ${}^{31}\text{P}\{{}^1\text{H}\}$ NMR (CD_2Cl_2): δ 67.26 (s). Anal. Calcd for $\text{C}_{30}\text{H}_{32}\text{BF}_{10}\text{N}_2\text{OP}$: C, 53.83; H, 4.97; N, 4.18. Found: C, 54.06; H, 4.94; N, 4.27 %.

Thermolysis of ${}^t\text{Bu}_3\text{P}(\text{N}_2\text{O})\text{B}(\text{C}_6\text{F}_5)_3$ (1**) to give $({}^t\text{Bu}_3\text{P}=\text{O})\text{B}(\text{C}_6\text{F}_5)_3$ (**3**).** A solution of **1** (9 mg, 12 μmol ; 0.5 mL of $\text{C}_6\text{D}_5\text{Br}$) was heated in a J. Young NMR tube to 135 °C for 44h. NMR spectroscopy showed 95% conversion to one major product ($\sim 80\%$ pure based on ${}^{31}\text{P}$ NMR integration) which was identified as **3** (the minor products have not been identified). Thermolysis using **1- ${}^{15}\text{N}$** results in an identical product that shows no ${}^{15}\text{N}$ NMR resonances or ${}^{31}\text{P}$, ${}^{15}\text{N}$ coupling, consistent with ${}^{15}\text{N}_2$ loss. The spectral data are identical to those obtained from an equimolar mixture of ${}^t\text{Bu}_3\text{P}=\text{O}$ and $\text{B}(\text{C}_6\text{F}_5)_3$ in $\text{C}_6\text{D}_5\text{Br}$. ${}^1\text{H}$ NMR (400 MHz, $\text{C}_6\text{D}_5\text{Br}$, 25 °C) δ 0.99 (d, $J_{\text{PH}} = 14.4$). ${}^{31}\text{P}\{{}^1\text{H}\}$ NMR (162 MHz, $\text{C}_6\text{D}_5\text{Br}$, 25 °C) δ 93.5 (br s). ${}^{19}\text{F}$ NMR (377 MHz, CD_2Cl_2 , 25 °C) δ -127.2 (br, 2F, *o*-F), -155.5 (br, 1F, *p*-F), -163.4 (2F, *m*-F). ${}^{11}\text{B}$ NMR (128 MHz, $\text{C}_6\text{D}_5\text{Br}$, 25 °C) δ 4.5

Photolysis of ${}^t\text{Bu}_3\text{P}(\text{N}_2\text{O})\text{B}(\text{C}_6\text{F}_5)_3$ (1**) to give $({}^t\text{Bu}_3\text{P}=\text{O})\text{B}(\text{C}_6\text{F}_5)_3$ (**3**).** A solution of **1** (9 mg, 12 μmol ; 0.5 mL of $\text{C}_6\text{D}_5\text{Br}$) in a J. Young NMR tube was irradiated for 5 minutes at room temperature using a water-cooled quartz mercury arc lamp. NMR spectroscopy indicated 90% conversion to **3** ($\sim 75\%$ pure based on ${}^{31}\text{P}$ NMR integration). Prolonged photolysis (> 30 min) resulted in decomposition of **3** to unidentified species. NMR data: see above.

Computational Studies. Calculations were performed with the Gaussian03 program using density functional theory (DFT).⁴ The geometry of **1**, $t\text{Bu}_3\text{P}$, $t\text{Bu}_3\text{P}=\text{O}$, $\text{B}(\text{C}_6\text{F}_5)_3$ and N_2O were optimized (for **1**: starting from the X-ray structure) at the B3LYP/6-31G(d) level without (symmetry) constraints, and the resulting structures were confirmed to be minima on the potential energy surface by frequency calculations (number of imaginary frequencies = 0). The relative energies reported in the text are electronic energies.

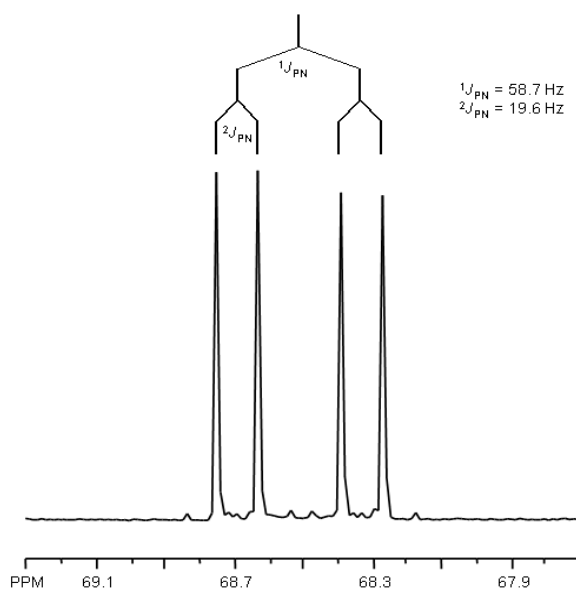


Figure S1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1**- ^{15}N .

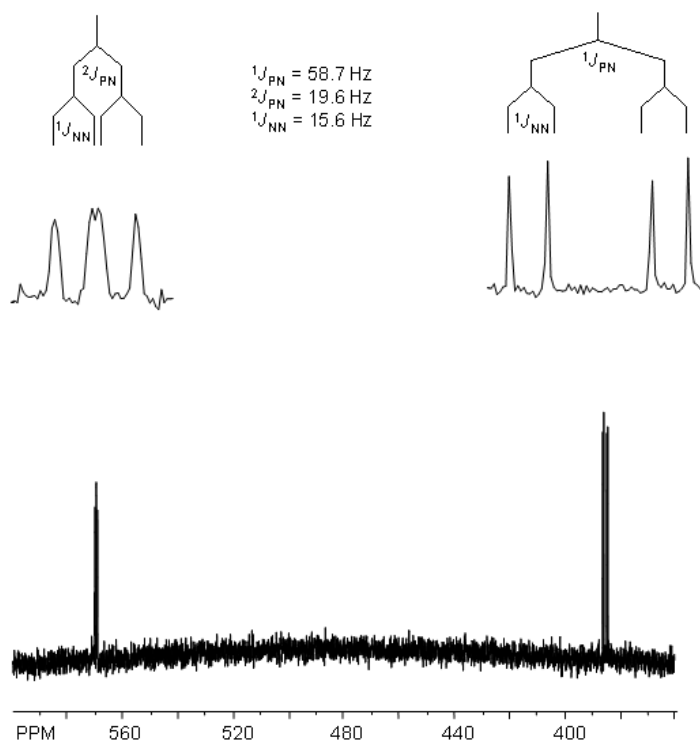


Figure S2. ^{15}N NMR spectrum of **1**- ^{15}N .

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