Supporting Information to:

Complexation of Nitrous Oxide by Frustrated Lewis Pairs

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

Department of Chemistry, University of Toronto, 80 St. George Street,
Toronto, Ontario, Canada, M5S 3H6

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)2 and tBu3P=O 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: CFCl3; 31P: 85% H3PO4; 15N: NH3(l) via the 15N resonance of 90% formamide in DMSO-d6 at 112 ppm). 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, JPH = 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, 1JFF = 23.9, 2JFF = 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, JFC = 240, o-C6F5), 139.9 (d, JFC = 246, p-C6F5), 137.5 (d, JCF = 248, m-CF), 121.2 (br, ipso-C6F5), 41.8 (d, JPC = 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.
\textsuperscript{1}Bu\textsubscript{3}P(\textsuperscript{15}N\textsubscript{2}O)B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} (1-\textsuperscript{15}N). An NMR tube containing a solution of B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} (25 mg, 0.049 mmol) and \textsuperscript{1}BuP (10 mg, 0.049 mmol) in 0.5 mL C\textsubscript{6}D\textsubscript{5}Br was degassed and backfilled with \textasciitilde 0.9 bar of \textsuperscript{15}N\textsubscript{2}O. After standing overnight, the product was precipitated by addition of hexanes. The white precipitate was dried \textit{in vacuo} and dissolved in 0.5 mL of C\textsubscript{6}D\textsubscript{5}Cl. NMR analysis was consistent with formation of 1-\textsuperscript{15}N. \textsuperscript{1}H/\textsuperscript{19}F NMR spectra are identical to 1. \textsuperscript{31}P(\textsuperscript{1}H) NMR (162 MHz, C\textsubscript{6}D\textsubscript{5}Cl, 25 °C) δ 68.5 (dd, \textsuperscript{1}J\textsubscript{PN} = 58.7, \textsuperscript{2}J\textsubscript{PN} = 19.6). \textsuperscript{15}N NMR (40.6 MHz, C\textsubscript{6}D\textsubscript{5}Cl, 25 °C) δ 566.6 (dd, \textsuperscript{2}J\textsubscript{NN} = 19.6, \textsuperscript{1}J\textsubscript{NN} = 15.6, NNO), 381.7 (dd, \textsuperscript{1}J\textsubscript{PN} = 58.7, \textsuperscript{2}J\textsubscript{PN} = 15.6, ANO).

\textsuperscript{1}Bu\textsubscript{3}P(N\textsubscript{2}O)B(C\textsubscript{6}F\textsubscript{5})\textsubscript{2}Ph (2). A 50 mL schlenk tube was charged with PhB(C\textsubscript{6}F\textsubscript{5})\textsubscript{2} (0.119 g, 0.282 mmol) and \textsuperscript{1}BuP (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\textsubscript{2}O for a period of 1 minute. The solution was stirred at room temperature for 12 hours. At this time, the solution was clear and colourless. Pentane (10 mL) was added precipitating a white solid. The solid was isolated by filtration, washed with pentane (3 x 5 mL) and dried \textit{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. \textsuperscript{1}H NMR (400 MHz, C\textsubscript{6}D\textsubscript{5}Cl, 25 °C) δ 7.40 (d, 2H, \textsuperscript{3}J\textsubscript{HH} = 7 Hz, o-C\textsubscript{6}H\textsubscript{5}), 7.17 (t, 2H, \textsuperscript{3}J\textsubscript{HH} = 8 Hz, m-C\textsubscript{6}H\textsubscript{4}), 7.09 (t, 1H, \textsuperscript{3}J\textsubscript{HH} = 8 Hz, p-C\textsubscript{6}H\textsubscript{4}), 1.44 (d, 27H, \textsuperscript{3}J\textsubscript{HP} = 14Hz, P(C(H\textsubscript{3})\textsubscript{3})). \textsuperscript{11}B(\textsuperscript{1}H) NMR (CD\textsubscript{2}Cl\textsubscript{2}) δ 3.27 (s). \textsuperscript{13}C(\textsuperscript{1}H) NMR (CD\textsubscript{2}Cl\textsubscript{2}) δ 148.25 (br d, \textsuperscript{1}J\textsubscript{CF} = 240 Hz, o-C\textsubscript{6}F\textsubscript{5}), 139.68 (br d, \textsuperscript{1}J\textsubscript{CF} = 218 Hz, p-C\textsubscript{6}F\textsubscript{5}), 137.23 (br d, \textsuperscript{1}J\textsubscript{CF} = 226 Hz, m-C\textsubscript{6}F\textsubscript{5}), 132.31 (s, p-C\textsubscript{6}F\textsubscript{5}), 127.35 (s, o-C\textsubscript{6}F\textsubscript{5}), 125.77 (s, m-C\textsubscript{6}F\textsubscript{5}), 41.64 (d, \textsuperscript{1}J\textsubscript{CP} = 30 Hz, P(C(CH\textsubscript{3})\textsubscript{3})), 29.71 (s, CH\textsubscript{3}). \textsuperscript{19}F NMR (CD\textsubscript{2}Cl\textsubscript{2}) δ -131.87 (dd, 4F, \textsuperscript{3}J\textsubscript{FF} = 25 Hz, \textsuperscript{4}J\textsubscript{FF} = 9 Hz, o-C\textsubscript{6}F\textsubscript{5}), -161.71 (t, 2F, \textsuperscript{3}J\textsubscript{FF} = 20 Hz, m-C\textsubscript{6}F\textsubscript{5}), -166.45 (td, 4F, \textsuperscript{3}J\textsubscript{FF} = 23 Hz, \textsuperscript{4}J\textsubscript{FF} = 8 Hz m-C\textsubscript{6}F\textsubscript{5}). \textsuperscript{31}P(\textsuperscript{1}H) NMR (CD\textsubscript{2}Cl\textsubscript{2}): δ 67.26 (s). Anal. Calcd for C\textsubscript{30}H\textsubscript{30}BF\textsubscript{10}N\textsubscript{2}OP: C, 53.83; H, 4.97; N, 4.18. Found: C, 54.06; H, 4.94; N, 4.27 %.

Thermolysis of \textsuperscript{1}Bu\textsubscript{3}P(N\textsubscript{2}O)B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} (1) to give (\textsuperscript{1}Bu\textsubscript{3}P=O)B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} (3). A solution of 1 (9 mg, 12 µmol; 0.5 mL of C\textsubscript{6}D\textsubscript{5}Br) was heated in a J. Young NMR tube to 135 °C for 44h. NMR spectroscopy showed 95% conversion to one major product (~ 80% pure based on \textsuperscript{31}P NMR integration) which was identified as 3 (the minor products have not been identified). Thermolysis using 1-\textsuperscript{15}N results in an identical product that shows no \textsuperscript{15}N NMR resonances or \textsuperscript{31}P,\textsuperscript{15}N coupling, consistent with \textsuperscript{15}N\textsubscript{2} loss. The spectral data are identical to those obtained from an equimolar mixture of \textsuperscript{1}BuP=O and B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} in C\textsubscript{6}D\textsubscript{5}Br. \textsuperscript{1}H NMR (400 MHz, C\textsubscript{6}D\textsubscript{5}Br, 25 °C) δ 0.99 (d, \textsuperscript{1}J\textsubscript{PH} = 14.4). \textsuperscript{31}P(\textsuperscript{1}H) NMR (162 MHz, C\textsubscript{6}D\textsubscript{5}Br, 25 °C) δ 93.5 (br s). \textsuperscript{19}F NMR (377 MHz, C\textsubscript{6}D\textsubscript{5}Cl, 25 °C) δ -127.2 (br, 2F, o-F), -155.5 (br, 1F, p-F), -163.4 (2F, m-F). \textsuperscript{11}B NMR (128 MHz, C\textsubscript{6}D\textsubscript{5}Br, 25 °C) δ 4.5.

Photolysis of \textsuperscript{1}Bu\textsubscript{3}P(N\textsubscript{2}O)B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} (1) to give (\textsuperscript{1}Bu\textsubscript{3}P=O)B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} (3). A solution of 1 (9 mg, 12 µmol; 0.5 mL of C\textsubscript{6}D\textsubscript{5}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 (~ 75% pure based on \textsuperscript{31}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 \(\text{1, } ^1\text{Bu}_3\text{P, } ^1\text{Bu}_3\text{P} = \text{O, } \text{B} \left( \text{C}_6\text{F}_{5} \right)_3\) and \(\text{N}_2\text{O}\) were optimized (for \(\text{1:}\) 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.

\[ \begin{align*}
\downarrow & \quad \downarrow \\
\uparrow & \quad \uparrow \\
U_{\text{mp}} & = 58.7 \text{ Hz} \\
U_{\text{mr}} & = 19.6 \text{ Hz}
\end{align*} \]

**Figure S1.** \(^{31}\text{P} \left( ^1\text{H} \right) \text{NMR spectrum of } \text{1-}^{15}\text{N}.\)

\[ \begin{align*}
\downarrow & \quad \downarrow \\
\uparrow & \quad \uparrow \\
U_{\text{mp}} & = 58.7 \text{ Hz} \\
U_{\text{mr}} & = 19.6 \text{ Hz} \\
U_{\text{mn}} & = 15.6 \text{ Hz}
\end{align*} \]

**Figure S2.** \(^{15}\text{N} \text{NMR spectrum of } \text{1-}^{15}\text{N}.\)
References