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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

Received June 4, 2009; E-mail: dstephan@chem.utoronto.ca

Anthropogenic disturbance of Earth's atmospheric composition is a source of great environmental concern due to its contribution to global warming. Of the trace gases that have increased steadily relative to preindustrial levels, carbon dioxide has attracted the most attention because of its established relationship to human activity. Although nitrous oxide (N_2O) is only a minor constituent of the atmosphere (319 ppb), it is ~300 times more potent as a greenhouse gas than CO_2.[1] N_2O is also a potentially strong and yet environmentally benign oxidant; however its high kinetic stability has hampered its use.[2] Nonetheless, Nature uses a Cu_4S cluster in nitrous oxide reductase (NOR) to convert N_2O to dinitrogen and water, a process that is part of microbial denitrification.[3] A synthetic NOR analogue has recently been shown to reduce N_2O.[4] Transition metal mediated reactivity of N_2O includes O-transfer reactions to low-valent metal centers,[5] insertion of the oxygen atom into M−R (R = alkyl, hydride) bonds,[6] N−N bond cleavage,[7] and hydrogenation to give N_2 and H_2O.[8] In addition, (catalytic) oxidation of organic substrates using N_2O has received renewed attention.[9] A possible reason for its generally sluggish reactivity is the fact that N_2O is a very poor ligand. Despite being comprised of N_2 and NO fragments, both of which are well-established as ligands in transition metal chemistry, only a few N_2O complexes are described in the literature.[10] None of these species have been structurally characterized although computational studies have probed the interactions of N_2O with various metal systems. Perhaps the most well-studied N_2O complex is $[Ru(NH_3)_5(N_2O)]^{2+}$ reported by Armor and Taube in 1969, which is thought to contain a linear Ru−NNO fragment based on spectroscopic[10a,11] and computational studies.[11c,12]

We have recently developed the concept of "frustrated Lewis pairs" (FLPs) in which steric congestion precludes formation of classical Lewis adducts so that the unquenched acidity/basicity can be exploited for further reactivity.[13] This has led to unique main-group systems capable of (reversible) H_2 activation,[14] hydrogenation,[15] and unprecedented small-molecule reactivity.[16] In this report, we demonstrate FLP binding of N_2O and describe the first crystallographic characterizations of bound N_2O species.

The reaction of an equimolar mixture of tBu$_3$P and $B(C_6F_5)_3$ with N_2O (1 bar) in bromobenzene results in the precipitation of a white solid **1**, which was isolated in 76% yield after recrystallization from CH_2Cl_2/hexane (Figure 1). NMR spectroscopic analysis in CD_2Cl_2 showed a single ^{31}P resonance at 68.5 ppm. The observed ^{11}B (0.4 ppm) and ^{19}F ($\Delta\delta(p,m\text{-F}) = 5.7$ ppm) resonances are indicative of a four-coordinate boron center. The ^{15}N isotopomer **1-^{15}N** was synthesized from ^{15}N^{15}NO. The observation of ^{15}N NMR signals at 566.6 and 381.7 ppm which exhibit N−P coupling of 58.7 and 19.6 Hz, respectively, and $^1J_{NN} = 15.6$ Hz establishes the presence of two inequivalent nitrogen atoms. Taken together, these spectroscopic data are consistent with the formulation of **1** as tBu$_3$P(NNO)-$B(C_6F_5)_3$. Comparing the ^{15}N NMR parameters for **1-^{15}N** to those for free N_2O (218 and 135 ppm, $^1J_{NN} = 8.1$ Hz)[17] or the N_2O complex *cis*-RuCl$_2$(η^1-^{15}N^{14}NO)(P−N)(PPh$_3$) (P−N = 1-Ph$_2$P-2-Me$_2$NC$_6$H$_4$; N$_t$ 125.8 ppm)[10b] suggests substantial perturbations within the N_2O fragment. The infrared spectrum of **1** showed no bands that could be unambiguously assigned to N−N or N−O vibrations. However, comparison with **1-^{15}N** reveals an additional band isotopically shifted to 1410 cm^{-1} which was attributed to the N−N stretch. The corresponding absorption in **1** is obscured by a broad peak due to aromatic C−C vibrations. A crystal structure determination confirmed the proposed formulation, with a N_2O molecule bridging the P and B fragments in a 1,3 mode (Figure 1).[18] The N−N and N−O bonds in the N_2O fragment (1.2570(17) and 1.3361(15) Å, respectively) are significantly elongated in comparison to free N_2O (1.127 and 1.186 Å).[19] For related phosphazides $R_3P(N_\alpha N_\beta N_\gamma)R'$ the N_α−N_β bond lengths (~1.34 Å) are generally longer than those observed for **1**.[20] The P−N bond in **1** (1.7088(12) Å) is also significantly longer than the corresponding P−N bond lengths in phosphazides.[21] Collectively, these metrical data indicate the bonding in **1** to be best described as P−N=N−O−B (*vide infra*) in which the tBu$_3$P and $OB(C_6F_5)_3$ fragments adopt a *transoid* disposition with respect to the N=N double bond.

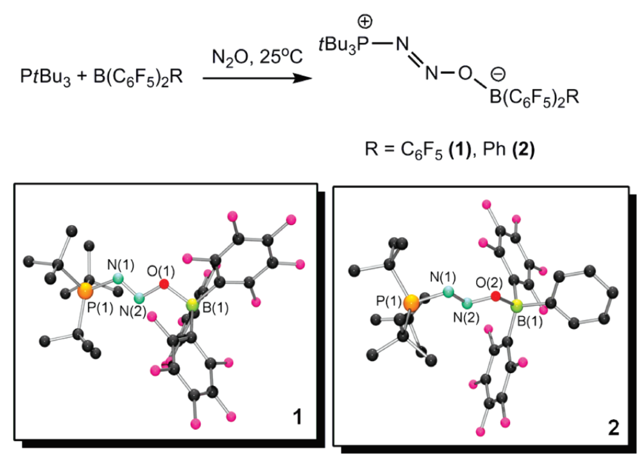

Figure 1. Synthesis and POV-ray depictions of the molecular structures of **1** and **2**. Selected bond distances (Å) and angles (deg): (1): P−N 1.7087(12); N−N 1.2573(17); N−O 1.3362(15); O−B 1.5428(18); P−N−N 117.04(10); N−N−O 109.11(11); N−O−B 114.43(10); (2): P−N 1.7107(6); N−N 1.2602(8); N−O 1.3270(8); O−B 1.5475(9); P−N−N 112.85(5); N−N−O 111.68(6); N−O−B 111.61(5).

A dependence on the combined Lewis acidity and basicity has been previously noted in the interaction of small molecules with FLPs.[13] Attempts to generate N_2O complexes with less basic phosphines have so far not been successful. For example, the frustrated Lewis pair (o-tolyl)$_3$P/$B(C_6F_5)_3$ does not react with N_2O. On the other hand, variation of the Lewis acid shows that N_2O binding using FLPs is not restricted to the very acidic borane $B(C_6F_5)_3$. Treatment of tBu$_3$P and $B(C_6F_5)_2$Ph, a substantially weaker Lewis acid than $B(C_6F_5)_3$,[22] with N_2O (1 bar) gave the product **2** in 76% yield (Figure 1). This species exhibited ^{31}P and

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^{11}B NMR resonances at 67.3 and 3.3 ppm respectively, suggesting a formulation similar to that of **1**. This was confirmed crystallographically (Figure 1).[18] While the general structural features of **2** are similar to those of **1**, the P−N and N−N bonds are slightly longer at 1.7107(6) and 1.2602(8) Å, respectively, while the N−O bond distance is slightly shorter at 1.3270(8) Å. The O−B distance in **2** is similar to that in **1**. These perturbations demonstrate that the Lewis acidity at B has a greater impact on the remote N−N and P−N interactions without a dramatic effect on the B−O bond.

Additional insight into the bonding in **1** was obtained from DFT calculations at the B3LYP/6-31G(d) level of theory. The optimized geometry $\mathbf{1}_{\mathbf{calc}}$ is in good agreement with the crystallographically determined structure, with a somewhat longer N−N (1.273 Å) and shorter N−O bond (1.298 Å). A frequency analysis for $\mathbf{1}_{\mathbf{calc}}$ revealed N−N and N−O infrared frequencies in the fingerprint region at 1483 and 1257 cm^{-1}, respectively, corroborating the experimental observation that NNO vibrations are obscured in the IR spectrum of **1**. Natural Bond Orbital analysis shows the bonding within the NNO fragment to consist of a N═N double bond and a N−O single bond (Figure 2), consistent with the crystallographic data.

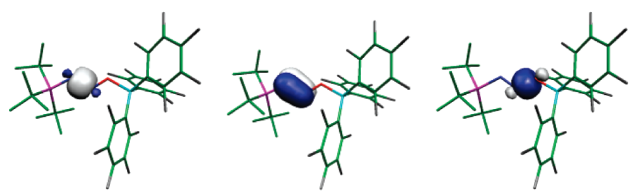

Figure 2. NBO orbitals for the N═N σ- and π-bond (left, middle) and N−O σ-bond (right).

The formation of $\mathbf{1}_{\mathbf{calc}}$ is exothermic by 17.4 kcal/mol. However, $\mathbf{1}_{\mathbf{calc}}$ is shown to be a kinetic product as extrusion of N_2 and formation of tBu$_3$P═O and $B(C_6F_5)_3$ is thermodynamically favorable by 60.4 kcal/mol relative to **1**. This notion was confirmed experimentally. Heating an NMR sample of **1** in C_6D_5Br at 135 °C for 44 h resulted in the liberation of N_2 and formation of the Lewis acid−base adduct (tBu$_3$P═O)$B(C_6F_5)_3$ **3** as the main product (∼80% at 95% conversion) as evidenced by spectroscopic data and independent synthesis (Figure 3). In addition, photolysis of **1** readily afforded **3** (5 min of irradiation gives ∼75% at 90% conversion), but prolonged photolysis resulted in decomposition to unidentified species. These observations suggest that isomerization of **1** placing P and O *cis* to one another prompts loss of N_2. This notion is reminiscent of proposed transition states in Staudinger oxidations of phosphines.[23]

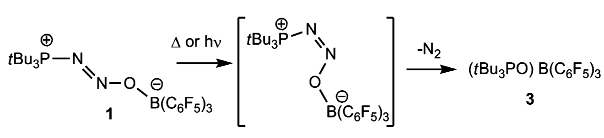

Figure 3. Proposed mechanism of thermolysis or photolysis of **1** to **3**.

In summary, frustrated Lewis pairs of a basic yet sterically encumbered phosphine with Lewis acids bind nitrous oxide to give intact PNNOB linkages. The reactivity of these new N_2O species and the utility of FLPs in the activation of small molecules continue to be the focus of efforts in our laboratory.

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Supporting Information Available: Experimental and computational details, NMR spectra of **1-^{15}N** and X-ray crystallographic details of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) X-ray data: **1**: $P\bar{1}$, a = 9.5265(4) Å, b = 11.6603(5) Å, c = 14.3458(7) Å, α = 76.6040(10)°, β = 89.0710(10)°, γ = 87.1940(10)°, V = 1548.32(12) $Å^3$, data (>3σ) = 5446, var 451, R = 0.0286, R_w = 0.0778, GOF 1.013. **2**: $P\bar{1}$, a = 10.3832(8) Å, b = 11.9066(9) Å, c = 14.5601(12) Å, α = 70.621(4)°, β = 76.818(4)°, γ = 65.912(4)°, V = 1541.2(2) $Å^3$, data (>3σ) = 16452, var 415, R = 0.0377, R_w = 0.1043, GOF 1.021.
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