Complexation of Nitrous Oxide by Frustrated Lewis Pairs

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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\(_{2}\)O) 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\(_{2}\)O 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\(_4\)S cluster in metal chemistry, only a few N\(_{2}\)O complexes are described in the literature.\(^{10}\) None of these species have been structurally characterized although computational studies have probed the interactions of N\(_{2}\)O with various metal systems. Perhaps the most well-studied N\(_{2}\)O complex is [Ru(NH\(_3\))\(_5\)(N\(_{2}\)O)]\(^{2-}\) 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 small-molecule 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\(_{2}\)O and describe the first crystallographic characterizations of bound N\(_{2}\)O species.

The reaction of an equimolar mixture of tBu\(_3\)P and B(C\(_6\)F\(_5\))\(_3\) with N\(_{2}\)O (1 bar) in bromobenzene results in the precipitation of a white solid 1, which was isolated in 76% yield after recrystallization from CH\(_2\)Cl\(_2\)/hexane (Figure 1). NMR spectroscopic analysis in CD\(_2\)Cl\(_2\) showed a single \(^{31}\)P resonance at 68.5 ppm. The observed \(^{11}\)B (0.4 ppm) and \(^{19}\)F (\(\Delta\delta\),p,m,F) = 5.7 ppm) resonances are indicative of a four-coordinate boron center. The \(^{15}\)N isotopomer 1-\(^{15}\)N was synthesized from \(\text{tBu}_3\)P(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 \(J_{NN} = 15.6\) Hz establishes the presence of two inequivalent nitrogen atoms. Taken together, these spectroscopic data are consistent with the formulation of 1 as \(\text{tBu}_3\)P(N\(^{15}\)NO)-B(C\(_6\)F\(_5\))\(_3\). Comparing the \(^{15}\)N NMR parameters for 1-\(^{15}\)N to those for free N\(_{2}\)O (218 and 135 ppm, \(J_{NN} = 8.1\) Hz)\(^{17}\) or the N\(_{2}\)O complex cis-Ru\(_2\)Cl\(_2\)(\(\eta^2\)-N\(_{2}\)O)(P=NN=PPh\(_3\)) (P=N = 1-Ph-P=2-Me\(_3\)N\(_2\)C\(_6\)H\(_4\); N, 125.8 ppm)\(^{10b}\) suggests substantial perturbations within the N\(_2\)O 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 isopropositively shifted to 1410 cm\(^{-1}\), which was attributed to the N=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\(_2\)O molecule bridging the P and B fragments in a 1,3 mode (Figure 1).\(^{18}\) The N–N and N–O bands in the N\(_2\)O fragment (1.2570(17) and 1.3361(15) Å, respectively) are significantly elongated in comparison to free N\(_2\)O (1.127 and 1.186 Å).\(^{19}\) For related phosphazides R\(_3\)P(N\(_x\)N\(_y\)N\(_z\))R’ the N–N 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=NN=N–O–B (\(\text{vide infra}\)) in which the \(\text{tBu}_3\)P and OB(C\(_6\)F\(_5\))\(_3\) fragments adopt a transoid disposition with respect to the N=NNN 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 1.1170(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 1.1185(5); N–N–O 111.68(6); N–O–B 111.61(5).

A dependence on the combined Lewis acidity/basicity has been previously noted in the interaction of small molecules with FLPs.\(^{13}\) Attempts to generate N\(_{2}\)O complexes with less basic Lewis acids were not successful. For example, the frustrated Lewis pair (o-tolyli)P(B(C\(_6\)F\(_5\))\(_3\)) does not react with N\(_{2}\)O. On the other hand, variation of the Lewis acid shows that N\(_2\)O binding using FLPs is not restricted to the very acidic borane B(C\(_6\)F\(_5\))\(_3\). Treatment of \(\text{tBu}_3\)P and B(C\(_6\)F\(_5\))\(_3\)Ph, a substantially weaker Lewis acid than B(C\(_6\)F\(_5\))\(_3\),\(^{22}\) with N\(_{2}\)O (1 bar) gave the product 2 in 76% yield (Figure 1).
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 species. These observations suggest that isomerization of bond distance is slightly shorter at 1.3270(8) Å. The O1 infrared frequencies in the fingerprint region at 1483 and 1257 cm−1, respectively, corroborating the experimental observation that NO 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–O single bond (Figure 2), consistent with the crystallographic data.

The formation of 1calc is exothermic by 17.4 kcal/mol. However, 1calc is shown to be a kinetic product as extrusion of N2 and formation of Bu3P=O and B(C6F5)3 is thermodynamically favorable by 60.4 kcal/mol relative to 1. This notion was confirmed experimentally. Heating an NMR sample of 1 in C6D5Br at 135 °C for 44 h resulted in the liberation of N2 and formation of Lewis acid–base adduct (Bu3P=O)B(C6F5)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 one to another prompts loss of N2. This notion is reminiscent of proposed transition states in Staudinger oxidations of phosphines.23

In summary, frustrated Lewis pairs of a basic yet sterically encumbered phosphine with Lewis acids bind nitrous oxide to give intact PNNo linkages. The reactivity of these new N2O species and the utility of FLPs in the activation of small molecules continue to be the focus of efforts in our laboratory.

Acknowledgment. D.W.S. gratefully acknowledges the financial support of NSERC of Canada and the award of a Canada Research Chair. E.O. is grateful for the support of a Rubicon postdoctoral fellowship from The Netherlands Organisation for Scientific Research (NWO). R.C.N. is grateful for the award of an NSERC of Canada scholarship.

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

References