In 1969, Armor and Taube formulated [Ru(NH₃)₅(N₂O)]⁺ as the first example of a metal complex of nitrous oxide. Subsequent studies have supported this formulation with spectroscopic and computational data. Since then, the interactions of nitrous oxide with transition metals have been shown to play important roles across the discipline. For example, in inorganic synthetic chemistry, reactions of N₂O with transition metal species have been shown to result in oxidation of low-valent metal centers, insertion of O into metal–carbon or metal–hydride bonds, and very recently, O-atom transfer to a Ni-carbene complex. In addition, reactions of N₂O have led to metal mediated N₂O oxidation of metal–N₂O interactions is clear. Nevertheless, the nature of the reaction of the corresponding “frustrated Lewis pairs” and N₂O. Herein, we describe the exploitation of synthetic analogues have recently been prepared. In the context of the global nitrogen cycle, N₂O is produced and consumed by anaerobic bacteria in denitrification processes that convert NO₂⁻ or NO₃⁻ to gaseous products. The four enzymes that are sequentially involved contain Mo, Fe, and Cu centers in their active sites, of which the latter is required for the last step of N₂O reduction. In these nitrous oxide reductases, an unusual Cu₄S cluster is responsible for the conversion of N₂O to N₂ and H₂O, and functional synthetic analogues have recently been prepared. In the field of heterogeneous catalysis, various systems containing transition metals have been developed that decompose N₂O, but these invariably require high temperatures.

Investigations into the conversion of N₂O to less harmful chemicals have been fueled recently by the realization that N₂O contributes to global warming and stratospheric ozone destruction. In all the cases mentioned above, the inference of metal–N₂O interactions is clear. Nevertheless, the nature of that interaction remains unknown.

We have recently reported the synthesis of the N₂O complexes [Bu₃PN₂O[Bu(CF₃)₂]₂(Ar)] (Ar = C₆F₅, Ph). Derived from the reaction of the corresponding “frustrated Lewis pairs” and N₂O. Herein, we describe the exploitation of the reactivity of related main group species to prepare Zn complexes incorporating the tBu₃PN-O fragment. These species exhibit two unique bridging modes of the phosphine-stabilized N₂O fragment with the transition metal atoms.

The reactions of [Bu₃PN₂O[Bu(CF₃)₂]]⁺ with the toluene adduct of Zn(C₆F₅)₂ (tol-Zn(C₆F₅)₂) were explored. NMR data for reaction mixtures containing up to 5 equivalents of tol-Zn(C₆F₅)₂ showed no discernible reaction, although resonances for the components were slightly broadened. Diffusion of pentane into a CH₂Cl₂ solution resulted in the precipitation of a mixture of two different types of crystals. Manual separation and subsequent NMR analysis showed these to be the starting material [Bu₃PN₂O[Bu(CF₃)₂]] and a new [Zn(C₆F₅)₂]-containing compound, 4, that is silent in the ¹¹B NMR spectrum, suggesting the possibility of a Zn/B exchange process. Seeking a clean synthesis of this new product, we engineered a scheme to facilitate such an exchange. The species [Bu₃PN₂O[Bu(C₆H₄F)₃]] (Ar) containing a relatively weakly Lewis acidic borane, was prepared in a fashion similar to that described for [Bu₃PN₂O[Bu(CF₃)₂]] with the toluene derivative. However, in contrast to the known compounds, 1 undergoes a clean and facile reaction with an equivalent of tol-Zn(C₆F₅)₂ resulting in the precipitation of a white solid 2, which was isolated in essentially quantitative yield. NMR spectroscopic analysis in CDCl₃ showed a new single ³¹P resonance at 66.5 ppm. The fully ¹⁵N labeled isotope 2-¹⁵N was synthesized from [Bu₃P⁺⁵N-OB(C₆H₄F)₃](Ar) and N₂O. ¹⁵N NMR signals at δ = 318.0 and 599.1 ppm which exhibit N-P coupling of 9.3 and 18 Hz establish that the PN₂O fragment remains intact upon formation of 2. ¹¹B and ¹⁹F NMR spectra of the reaction mixture support the quantitative liberation of B(C₆H₄F)₃. In addition, the ¹⁹F NMR spectrum shows resonances at δ = −117.4, −157.7, and −162.6 ppm attributable to a [Zn(C₆F₅)₂]-containing product. These data suggest the empirical formula of 2 is [tBu₃P[N₂OZn(C₆F₅)₂]]. A crystal structure determination established the centrosymmetric and dimeric nature of 2 (Figure 1) in which two tBu₃P[N₂O] fragments bridge two Zn centers forming a [Zn₂O₂] core. The Zn–O distances were found to be 2.088(2) and 2.144(2) Å, while the corresponding Zn–O–Zn and O-Zn-O' angles are 107.15(10) and 72.85(8)°, respectively. The N–N and N–O distances in 2 are 1.266(4) and 1.308(3) Å, and are significantly elongated in comparison to free N₂O (1.127 and 1.186 Å). The dimeric nature of the complex positions Zn(1) proximal to N(1) at a non-bonded distance of 3.035(2) Å. The substituents around the N=N double bond are disposed in...
a trans position, as is observed in the main group species [Bu3PN3OBAr3].14

Reaction of 1 with 1.5 equivalents of [tol·Zn(C6F5)2] resulted in the clean formation of a new species 3, which was isolated in 81% yield after crystallization (Scheme 1). A
crystallographic study established the structure of 3 as the C2 symmetric compound [(Bu3P)3N·OZn(C6F5)2]2Zn(C6F5)2] (Figure 2)16 in which a single pseudo-tetrahedral Zn center bridges two [Bu3PN3OZn(C6F5)2] units with Zn(1)–O(1) distances of 2.118(2) Å. The Zn(2) atoms in the latter units are coordinated to O(1) and N(1) of the N2O fragment at distances of 2.184(2) and 2.242(2) Å, respectively. This yields a chelating four-membered {ZnN2O} ring and results in a N(1)–Zn(2)–O(1) angle of 56.91(9)°. The 31P NMR resonance of 3 is shifted slightly downfield (δ = 68.5 ppm) compared to 2. The room temperature 19F NMR spectrum shows only one set of resonances for the C6F5 rings, suggesting that exchange between the two different [Zn(C6F5)2] environments is facile. Measuring the spectrum at −75 °C reveals two distinct [Zn(C6F5)2] fragments in a 2:1 ratio, which is consistent with the solid state structure of 3. 15N NMR signals for the isotopologue 3-15N are observed at δ = 323.8 and 595.2 ppm with N–P and N–N couplings of 9.4, 54, and 18 Hz, respectively.

In an analogous reaction, 1 was treated with two equivalents of [tol·Zn(C6F5)2] affording a new species 4 in 80% isolated yield. Compound 4 gave rise to a 31P resonance at δ = 71.7 ppm, and 15N NMR signals for the isotopologue 4-15N are observed at δ = 349.3 and 582.5 ppm with N–P and N–N couplings of 11, 54, and 17 Hz, respectively. The precise structural details of 4 were confirmed crystallographically (Figure 3), unambiguously establishing the formula as [Bu3PN3O(Zn(C6F5)2)2].16 This molecule contains two Zn atoms, one of which has a rare three-coordinate geometry being bound to the O atom of the N2O fragment and two perfluoroaryl rings. The Zn(1)–O(1) distance in this case is 2.0912(9) Å while the C–Zn(1)–C angle is 153.23(6)°. A second Zn atom, Zn(2), has a pseudo-tetrahedral coordination sphere comprising of two perfluoroaryl
rings, an O, and the P-bound N of N₂O, creating a ZnN₂O four-membered chelate ring similar to that seen in 3. The resulting Zn(2)–O(1) and Zn(2)–N(1) distances in this case are 2.1435(10) and 2.3086(12) Å, respectively, while the chelate bite-angle at Zn(2) is 56.38(4)°.

As in 3, the room temperature ³¹P NMR spectrum of 4 shows rapid exchange between the two [Zn(C₅F₇)₂] moieties. Decoalescence of the o-F resonances is observed at −34.6 °C, corresponding to ΔG° = 10.9 kcal mol⁻¹ for the process exchanging the [Zn(C₆F₅)₂] environments. This low barrier suggests a mechanism involving the dissociation of the weak Zn–N interaction, followed by rotation about the N–O bond (Scheme 2).

A comparison of the metrical parameters of 2–4 (Table 1) shows that there is little variation in the bond lengths of the PN₂O fragment. A marginal elongation of the N–N bond is observed upon coordination of a [Zn(C₅F₇)₂] group to the N₂O moiety (cf. 2 vs. 3 or 4). At the same time, the N–N bond angle becomes slightly more acute in order to accommodate binding of Zn(2). It thus appears that coordination of bond angle becomes slightly more acute in order to accommodate binding of Zn(2) to the PN₂O fragment. A marginal elongation of the N to be almost perpendicular to the PN₂O plane (C–Zn(1)–C/N–O angle of 10.9 kcal mol⁻¹ for the process exchanging the [Zn(C₆F₅)₂] environments. This low barrier suggests a mechanism involving the dissociation of the weak Zn–N interaction, followed by rotation about the N–O bond (Scheme 2).

Table 1: Comparison of pertinent metrical parameters in 2–4.

<table>
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<td>P(1)–N(1)</td>
<td>1.703(2)</td>
<td>1.702(3)</td>
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<td>N(1)–N(2)</td>
<td>1.266(4)</td>
<td>1.287(4)</td>
<td>1.2793(15)</td>
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<td>1.303(3)</td>
<td>1.303(3)</td>
<td>1.3075(15)</td>
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<td>Zn(1)–O(1)</td>
<td>2.088(2)</td>
<td>2.118(2)</td>
<td>2.0912(9)</td>
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<td>109.2(2)</td>
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<tr>
<td>N(1)–Zn(2)–O(1)</td>
<td>56.91(9)</td>
<td>56.38(4)</td>
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</table>

[a] Distances in Å, angles in °. [b] Zn(1)° in case of 2.
Keywords: frustrated Lewis pairs - nitrous oxide - zinc

[16] See Supporting Information.
[19] Compounds 3 and 4 are also cleanly obtained by consecutive addition of [tol·Zn(C6F5)] to 2 (Scheme 1).