Zinc Complexes

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Bridging Binding Modes of Phosphine-Stabilized Nitrous Oxide to $Zn(C_6F_5)_2$**

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In 1969, Armor and Taube formulated $[Ru(NH_3)_5(N_2O)]^{2+}$ as the first example of a metal complex of nitrous oxide.[1] Subsequent studies have supported this formulation with spectroscopic and computational data.[2] 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 N_2O with transition metal species have been shown to result in oxidation of low-valent metal centers,[3] insertion of O into metal–carbon or metal–hydride bonds,[4] and very recently, O-atom transfer to a Ni–carbene complex.[5] In addition, reactions of N_2O have led to metal mediated N–N bond cleavage[6] and hydrogenation yielding N_2 and H_2O.[7] Applications to organic synthesis have recently exploited (transition metal catalyzed) N_2O oxidations of organic substrates.[8] As a component of the global nitrogen cycle, N_2O is produced and consumed by anaerobic bacteria in denitrification processes that convert NO_3^- or NO_2^- to gaseous products.[9] 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 N_2O reduction.[9a] In these nitrous oxide reductases, an unusual Cu_4S cluster is responsible for the conversion of N_2O to N_2 and H_2O,[10] and functional synthetic analogues have recently been prepared.[11] In the field of heterogeneous catalysis, various systems containing transition metals have been developed that decompose N_2O, but these invariably require high temperatures.[12]

Investigations into the conversion of N_2O to less harmful chemicals have been fueled recently by the realization that N_2O contributes to global warming and stratospheric ozone destruction.[13] In all the cases mentioned above, the inference of metal–N_2O interactions is clear. Nevertheless, the nature of that interaction remains unknown.

We have recently reported the synthesis of the N_2O complexes $[t\mathrm{Bu}_3PN_2OB(C_6F_5)_2(Ar)]$ ($Ar = C_6F_5$, Ph),[14] derived from the reaction of the corresponding "frustrated Lewis pairs" and N_2O. Herein, we describe the exploitation of the reactivity of related main group species to prepare Zn complexes incorporating the $t\mathrm{Bu}_3PN_2O$ fragment.[15] These species exhibit two unique bridging modes of the phosphine-stabilized N_2O fragment with the transition metal atoms.

The reactions of $[t\mathrm{Bu}_3PN_2OB(C_6F_5)_3]$[14] with the toluene adduct of $Zn(C_6F_5)_2$ ($tol{\cdot}Zn(C_6F_5)_2$) were explored. NMR data for reaction mixtures containing up to 5 equivalents of $tol{\cdot}Zn(C_6F_5)_2$ showed no discernible reaction, although resonances for the components were slightly broadened. Diffusion of pentane into a CH_2Cl_2 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 $[t\mathrm{Bu}_3PN_2OB(C_6F_5)_3]$ and a new $\{Zn(C_6F_5)_2\}$-containing compound, **4**, that is silent in the ^{11}B 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 $[t\mathrm{Bu}_3PN_2OB(C_6H_4F)_3]$ (**1**), containing a relatively weakly Lewis acidic borane, was prepared in a fashion similar to that described for $[t\mathrm{Bu}_3PN_2OB(C_6F_5)_2(Ar)]$ ($Ar = C_6F_5$, Ph).[14] NMR spectral parameters for **1** were similar to those reported for the perfluoroarylborane derivatives. However, in contrast to the known compounds, **1** undergoes a clean and facile reaction with an equivalent of $tol{\cdot}Zn(C_6F_5)_2$ resulting in the precipitation of a white solid **2**, which was isolated in essentially quantitative yield. NMR spectroscopic analysis in CD_2Cl_2 showed a new single ^{31}P resonance at 66.5 ppm. The fully ^{15}N labeled isotologue **2-^{15}N** was synthesized from $[t\mathrm{Bu}_3P^{15}N_2OB(C_6H_4F)_3]$ (**1-^{15}N**). ^{15}N NMR signals at $\delta = 318.0$ and 599.1 ppm which exhibit N–P coupling of 9.3 and 54 Hz, respectively, and a coupling constant of $^1J_{NN} = 18$ Hz establish that the PN_2O fragment remains intact upon formation of **2**. ^{11}B and ^{19}F NMR spectra of the reaction mixture support the quantitative liberation of $B(C_6H_4F)_3$. In addition, the ^{19}F NMR spectrum shows resonances at $\delta = -117.4$, -157.7, and -162.6 ppm attributable to a $\{Zn(C_6F_5)_2\}$-containing product. These data suggest the empirical formula of **2** is $[t\mathrm{Bu}_3PN_2OZn(C_6F_5)_2]$. A crystal structure determination established the centrosymmetric and dimeric nature of **2** (Figure 1)[16] in which two $t\mathrm{Bu}_3PN_2O$ fragments bridge two Zn centers forming a $\{Zn_2O_2\}$ 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 N_2O (1.127 and 1.186 Å).[17]

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

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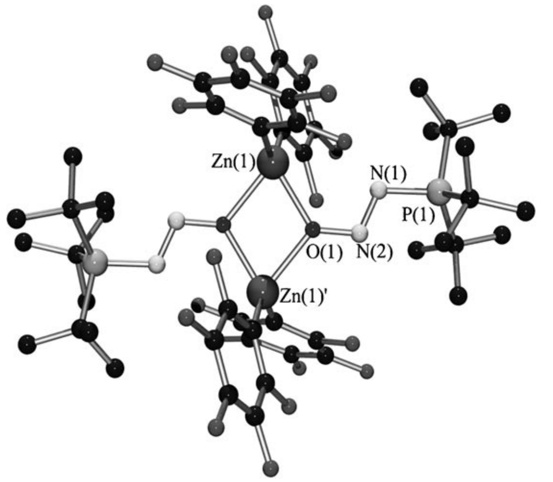
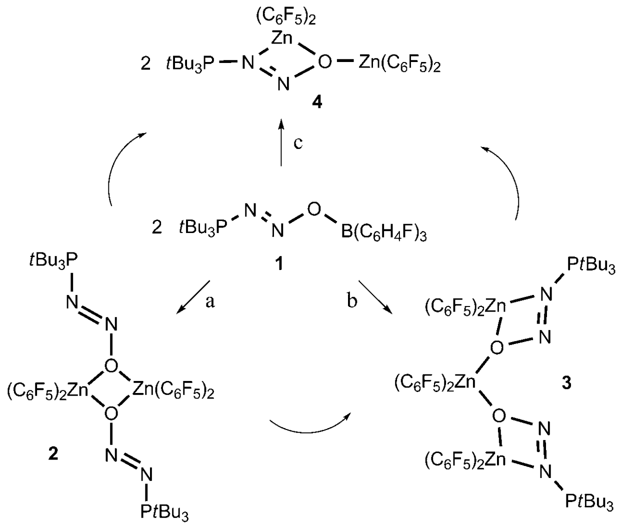


Figure 1. POV-ray depiction of the molecular structure of **2**.

a *trans* position, as is observed in the main group species [$tBu_3PN_2OBAr_3$].[14]



Scheme 1. Synthesis of **2**–**4** starting from **1** (a, b, c = 2, 3, 4 equivalents [tol·Zn(C_6F_5)$_2$], respectively, per 2 equivalents of **1**) and conversion of **2**→**3**→**4**.

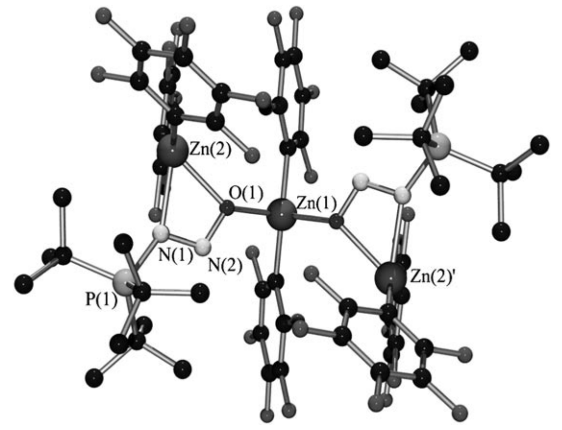


Figure 2. POV-ray depiction of the molecular structure of **3**.

Reaction of **1** with 1.5 equivalents of [tol·$Zn(C_6F_5)_2$] 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 C_2 symmetric compound [$(tBu_3N_2OZn(C_6F_5)_2)_2Zn(C_6F_5)_2$] (Figure 2)[16] in which a single pseudo-tetrahedral Zn center bridges two {$tBu_3PN_2OZn(C_6F_5)_2$} 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 N_2O fragment at distances of 2.184(2) and 2.242(2) Å, respectively. This yields a chelating four-membered {ZnN_2O} ring and results in a N(1)-Zn(2)-O(1) angle of 56.91(9)°. The ^{31}P NMR resonance of **3** is shifted slightly downfield ($\delta = 68.5$ ppm) compared to **2**. The room temperature ^{19}F NMR spectrum shows only one set of resonances for the C_6F_5 rings, suggesting that exchange between the two different {$Zn(C_6F_5)_2$} environments is facile. Measuring the spectrum at −75 °C reveals two distinct {$Zn(C_6F_5)_2$} fragments in a 2:1 ratio, which is consistent with the solid state structure of **3**. ^{15}N NMR signals for the isotopologue **3-^{15}N** are observed at $\delta = 323.8$ 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·$Zn(C_6F_5)_2$] affording a new species **4** in 80 % isolated yield. Compound **4** gave rise to a ^{31}P resonance at $\delta = 71.7$ ppm, and ^{15}N NMR signals for the isotopologue **4-^{15}N** are observed at $\delta = 349.3$ 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 [$tBu_3PN_2O(Zn(C_6F_5)_2)_2$].[16] This molecule contains two Zn atoms, one of which has a rare[18] three-coordinate geometry being bound to the O atom of the N_2O 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 comprised of two perfluoroaryl

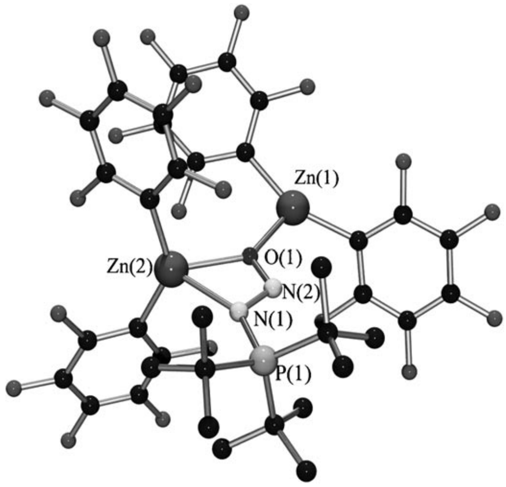
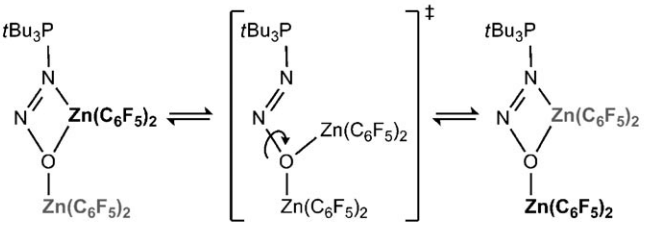


Figure 3. POV-ray depiction of the molecular structure of **4**.

rings, an O, and the P-bound N of N_2O, creating a ZnN_2O 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 ^{19}F NMR spectrum of **4** shows rapid exchange between the two $\{Zn(C_6F_5)_2\}$ moieties. Decoalescence of the *o*-F resonances is observed at −34.6 °C, corresponding to $\Delta G^{\neq} = 10.9\ \text{kcal mol}^{-1}$ for the process exchanging the $\{Zn(C_6F_5)_2\}$ 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).



Scheme 2. Proposed mechanism of $\{Zn(C_6F_5)_2\}$ exchange in **4**.

A comparison of the metrical parameters of **2**–**4** (Table 1) shows that there is little variation in the bond lengths of the PN_2O fragment. A marginal elongation of the N=N bond is observed upon coordination of a $\{Zn(C_6F_5)_2\}$ group to the N_2O moiety (cf. **2** vs. **3** or **4**). At the same time, the N-N-O bond angle becomes slightly more acute in order to accommodate binding of Zn(2). It thus appears that coordination of a $\{Zn(C_6F_5)_2\}$ group does not lead to a substantial perturbation of the PN_2O fragment. The terminal, three-coordinate Zn(1) center in **4** is more tightly bound to O(1) than the bridging Zn(1) in **3**, as expected based on its coordinative unsaturation. In addition, the greater steric congestion around the central Zn(1) in **3** forces the $\{Zn(C_6F_5)_2\}$ fragment to be almost perpendicular to the PN_2O plane (C-Zn(1)-C/N-N-O interplanar angle **3**: 67.1(3)°; **4**: 23.84(16)°). This results in a close approach of two C_6F_5 rings in **3**, with concomitant displacement of Zn(2) away from O(1) towards N(1).

Table 1: Comparison of pertinent metrical parameters in **2**–**4**.[a]

	2	**3**	**4**
P(1)–N(1)	1.703(2)	1.702(3)	1.7103(11)
N(1)–N(2)	1.266(4)	1.287(4)	1.2793(15)
N(2)–O(1)	1.308(3)	1.301(3)	1.3057(15)
Zn(1)–O(1)	2.088(2)	2.118(2)	2.0912(9)
Zn(2)–N(1)		2.242(2)	2.3086(12)
Zn(2)–O(1)		2.184(2)	2.1435(10)
N(1)-N(2)-O(1)	111.7(2)	109.2(2)	109.29(10)
Zn(1)-O(1)-Zn(2)[b]	107.15(10)	135.57(9)	139.95(5)
N(1)-Zn(2)-O(1)		56.91(9)	56.38(4)

[a] Distances in Å, angles in °. [b] Zn(1)′ in case of **2**.

The formation of **2**–**4** from **1**[19] is presumably driven by several factors, including the greater Lewis acidity of $Zn(C_6F_5)_2$ compared to $B(C_6H_4F)_3$ and the basicity of the N and O atoms within the PN_2O fragment that facilitates binding to additional Lewis acidic centers. In addition, the diminished steric congestion about $\{Zn(C_6F_5)_2\}$ in comparison to triarylboranes allows the interaction of the PN_2O fragment with multiple Zn centers.

The chemistry described herein demonstrates that frustrated Lewis pairs can be employed to generate unusual species such as phosphine-stabilized N_2O fragments that can undergo exchange with other Lewis acids offering a unique route to Zn complexes containing the PNNO moiety. Moreover, the characterization of **2**, **3**, and **4** illustrates multiple binding modes for the interaction of an N_2O fragment with a metal. We continue to actively examine the further chemistry of frustrated Lewis pairs and in particular the potential for small-molecule complexation and activation.

Experimental Section

Synthesis of **2**: A 20 mL scintillation vial was charged with **1** (0.100 g, 0.184 mmol) and $[tol{\cdot}Zn(C_6F_5)_2]$ (0.091 g, 0.185 mmol) in CH_2Cl_2 (5 mL). The solution was initially opaque but cleared after a few seconds of stirring. The reaction was left stirring for 1 h at room temperature. At this time, the solution was cloudy. Hexanes (10 mL) was added precipitating a fine white solid. The solid was isolated by filtration, washed with hexanes (3 × 5 mL), and dried in vacuo for 2 h. Crystals suitable for X-ray diffraction were grown from a layered CH_2Cl_2/pentane solution at −35 °C. Yield: 0.118 g (99 %). ^{19}F NMR (376 MHz, CD_2Cl_2, 25 °C): $\delta = -117.44$ (m, *o*-C_6F_5), −157.71 (t, $^3J_{F\text{-}F} = 19$ Hz, *p*-C_6F_5), −162.64 ppm (m, *m*-C_6F_5); $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 25 °C): $\delta = 66.50$ ppm (s); ^{15}N NMR (40.6 MHz, CD_2Cl_2, 25 °C): $\delta = 599.07$ (dd, $^2J_{N\text{-}P} = 9.3$, $^1J_{N\text{-}N} = 18$ Hz, PN*N*O), 317.97 ppm (dd, $^1J_{N\text{-}P} = 54$, $^1J_{N\text{-}N} = 18$ Hz, P*N*NO).

Synthesis of **3**: A 20 mL scintillation vial was charged with **1** (0.060 g, 0.111 mmol) and $[tol{\cdot}Zn(C_6F_5)_2]$ (0.082 g, 0.167 mmol) in CH_2Cl_2 (10 mL). The clear solution was left stirring for 1 h at room temperature. At this time, pentane (10 mL) was added precipitating a fine white solid. The product was allowed to settle and the solvent was decanted followed by washing of the solid with pentane (3 × 5 mL). The product was dried in vacuo for 1 h. Yield: 0.076 g (81 %). Crystals suitable for X-ray diffraction were grown from a layered CH_2Cl_2/pentane solution at −35 °C. ^{19}F NMR (376 MHz, CD_2Cl_2, 25 °C): $\delta = -117.56$ (m, *o*-C_6F_5), −156.73 (t, $^3J_{F\text{-}F} = 19$ Hz, *p*-C_6F_5), −162.42 ppm (m, *m*-C_6F_5); $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 25 °C): $\delta = 68.54$ ppm (s); ^{15}N NMR (40.6 MHz, CD_2Cl_2, 25 °C): $\delta = 595.17$ (dd, $^2J_{N\text{-}P} = 9.4$, $^1J_{N\text{-}N} = 18$ Hz, PN*N*O), 323.78 ppm (dd, $^1J_{N\text{-}P} = 54$, $^1J_{N\text{-}N} = 18$ Hz, P*N*NO).

Synthesis of **4**: A 20 mL scintillation vial was charged with **1** (0.064 g, 0.118 mmol) and $[tol{\cdot}Zn(C_6F_5)_2]$ (0.116 g, 0.236 mmol) in CH_2Cl_2 (10 mL). The clear solution was left stirring for 1 h at room temperature. At this time, pentane (10 mL) was added precipitating a fine white solid. The product was allowed to settle and the solvent was decanted followed by washing with pentane (3 × 5 mL). The solid was dried in vacuo for 1 h. Yield: 0.099 g, (80 %). Crystals suitable for X-ray diffraction were grown from a layered CH_2Cl_2/cyclohexane solution at 25 °C. ^{19}F NMR (376 MHz, CD_2Cl_2, 25 °C): $\delta = -117.62$ (m, *o*-C_6F_5), −156.26 (t, $^3J_{F\text{-}F} = 20$ Hz, *p*-C_6F_5), −162.18 ppm (m, *m*-C_6F_5); $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 25 °C): $\delta = 71.65$ (s); ^{15}N NMR (40.6 MHz, CD_2Cl_2, 25 °C): $\delta = 582.52$ (dd, $^2J_{N\text{-}P} = 11$, $^1J_{N\text{-}N} = 17$ Hz, PN*N*O), 349.33 ppm (dd, $^1J_{N\text{-}P} = 54$, $^1J_{N\text{-}N} = 17$ Hz, P*N*NO).

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[19] Compounds **3** and **4** are also cleanly obtained by consecutive addition of [tol·Zn(C_6F_5)] to **2** (Scheme 1).