Bridging Binding Modes of Phosphine-Stabilized Nitrous Oxide to Zn(C6F5)2
Neu, Rebecca C.; Otten, Edwin; Stephan, Douglas W.

Published in:
Angewandte Chemie International Edition

DOI:
10.1002/ange.200905650

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2009

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.
Zinc Complexes

Bridging Binding Modes of Phosphine-Stabilized Nitrous Oxide to Zn(C₆F₅)₂

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

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 complexation and hydrogenation yielding N₂ and H₂O. Applications to organic synthesis have recently exploited (transition metal catalyzed) N₂O oxidations of organic substrates. As a component of the global nitrogen cycle, N₂O is produced and consumed by anaerobic bacteria in denitrification processes that convert NO₃⁻ or NO₂⁻ 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 metal complexes 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 [Bu₃PN₂OB(C₆F₅)₂(Ar)] (Ar = C₆H₅, 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 Bu₃PN₂O fragment. These species exhibit two unique bridging modes of the phosphine-stabilized N₂O fragment with the transition metal atoms.

The reactions of [Bu₃PN₂OB(C₆F₅)₃] with the toluene adduct of Zn(C₆F₅)₂ and Zn(C₆F₅)₂ containing a relatively weakly Lewis acidic borane, was prepared in a fashion similar to that described for [Bu₃PN₂OB(C₆F₅)₂(Ar)] (Ar = C₆F₅, Ph). NMR spectral parameters for I were similar to those reported for the perfluoroarylborane derivatives. However, in contrast to the known compounds, I undergoes a clean and facile reaction with an equivalent of tolu-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 ¹³P resonance at 66.5 ppm. The fully ¹⁵N labeled isotope 2-¹⁵N was synthesized from [Bu₃P¹⁵N₂OB(C₆H₅)₂(Ar)]⁻. ¹⁵N NMR signals at δ = 318.0 and 599.1 ppm which exhibit N–P coupling of 9.3 and 14.3 kHz, respectively. The N and N–P coupling constant of 7.73 Å and 8.0 Å, respectively, and a coupling constant of 17.1 Å establishes 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 [Bu₃PN₂OZn(C₆F₅)₂]. A crystal structure determination established the centrosymmetric and dimeric nature of 2 (Figure 1) in which two Bu₃PN₂O fragments bridge two Zn centers forming a [Zn₂O₂] core. The Zn–O distances were found to be 2.088(2)Å and 2.144(2)Å, while the corresponding Zn–O–Zn and O–Zn–O angles are 107.15(10)° and 117.4°, respectively. The N–N and O–N distances in 2 are 1.266(4)Å 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 manner that minimizes the non-bonded interactions with Zn. The Zn(1) atoms are bridged to two N₅ pyrazolate struts. The structure of 2 is characterized by two interactions: (1) a Zn–N and (2) a N–O–Zn.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200905650.

[**] D.W.S. gratefully acknowledges the financial support of NSERC of Canada and the award of a Canada Research Chair and a Killam Research Fellowship. 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.

[1] R. C. Neu, Dr. E. Otten, Prof. Dr. D. W. Stephan Department of Chemistry, University of Toronto 80 St. George St., Toronto, Ontario, M5S3H6 (Canada) E-mail: dstephan@chem.utoronto.ca Homepage: http://www.chem.utoronto.ca/staff/dstephan

[14] D.W.S. gratefully acknowledges the financial support of NSERC of Canada and the award of a Canada Research Chair and a Killam Research Fellowship. 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.

[15] R. C. Neu, Dr. E. Otten, Prof. Dr. D. W. Stephan Department of Chemistry, University of Toronto 80 St. George St., Toronto, Ontario, M5S3H6 (Canada) E-mail: dstephan@chem.utoronto.ca Homepage: http://www.chem.utoronto.ca/staff/dstephan

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200905650.

DOI: 10.1002/anie.200905650

© 2009 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim
a trans position, as is observed in the main group species [Bu3PN2OBAr3].\[14\]

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)2N2OZn(C6F5)2] (Figure 2)[16] in which a single pseudo-tetrahedral Zn center bridges two [(Bu3P)2N2OZn(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 Zn(1)–O(1) distance in this case is 2.09(2) 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 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 [Bu3PN2O(Zn(C6F5)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 N2O fragment and two perfluoroaryl rings. The Zn(1)–O(1) distance in this case is 2.09(2) 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

---

**Scheme 1.** Synthesis of 2–4 starting from 1 (a, b, c = 2, 3, 4 equivalents [tol·Zn(C6F5)2], respectively, per 2 equivalents of 1) and conversion of 2–3–4.
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 19F NMR spectrum of 4 shows rapid exchange between the two [Zn(CF3)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(CF3)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 PN=O fragment. A marginal elongation of the N–N bond is observed upon coordination of a [Zn(CF3)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 interaction of Zn(2). It thus appears that coordination of a [Zn(CF3)2] group does not lead to a substantial perturbation of the PN=O fragment. The terminal, three-coordinate Zn(2) away from O(1) towards N(1). The formation of 2–4 from 1 is presumably driven by several factors, including the greater Lewis acidity of Zn(CF3)2 compared to B(C6H4F), and the basicity of the N and O atoms within the PN=O fragment that facilitates binding to additional Lewis acidic centers. In addition, the diminished steric congestion about [Zn(CF3)2] in comparison to triarylborenanes allows the interaction of the PN=O 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 N2O 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 N2O 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·Zn(C6F5)2] (0.091 g, 0.185 mmol) in CH2Cl2 (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 CH2Cl2/pentane solution at ~35 °C. Yield: 0.118 g (99%). 19F NMR (376 MHz, CD2Cl2, δ = -117.44 (m, o-CF3), -157.71 (t, JN-P = 19 Hz, p-CF3), -162.64 ppm (m, m-CF3); 31P{1H} NMR (162 MHz, CD2Cl2, δ = -117.56 (m, o-CF3), -156.73 (t, JN-P = 19 Hz, p-CF3), -162.42 ppm (m, m-CF3); 31P{1H} NMR (162 MHz, CD2Cl2, δ = -68.54 ppm (s)); 15N NMR (40.6 MHz, CD2Cl2, δ = 54.52 ppm (dd, JN-P = 54, JN-N = 18 Hz, PNNO), 317.97 ppm (dd, JN-P = 54, JN-N = 18 Hz, PNNO).

Synthesis of 3: A 20 mL scintillation vial was charged with 1 (0.060 g, 0.111 mmol) and [tol·Zn(C6F5)2] (0.082 g, 0.167 mmol) in CH2Cl2 (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 CH3Cl/pentane solution at ~35 °C. Yield: 0.08 g (92%). 19F NMR (376 MHz, CD2Cl2, δ = -117.56 (m, o-CF3), -156.73 (t, JN-P = 19 Hz, p-CF3), -162.42 ppm (m, m-CF3); 31P{1H} NMR (162 MHz, CD2Cl2, δ = -68.54 ppm (s)); 15N NMR (40.6 MHz, CD2Cl2, δ = 54.52 ppm (dd, JN-P = 54, JN-N = 18 Hz, PNNO), 317.97 ppm (dd, JN-P = 54, JN-N = 18 Hz, PNNO).

Synthesis of 4: A 20 mL scintillation vial was charged with 1 (0.064 g, 0.118 mmol) and [tol·Zn(C6F5)2] (0.116 g, 0.236 mmol) in CH2Cl2 (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 CH3Cl/cyclohexane solution at 25 °C. 19F NMR (376 MHz, CD2Cl2, δ = -117.62 (m, o-CF3), -156.26 (t, JN-P = 19 Hz, p-CF3), -162.18 ppm (m, m-CF3); 31P{1H} NMR (162 MHz, CD2Cl2, δ = 71.65 (s)); 15N NMR (40.6 MHz, CD2Cl2, δ = 582.52 ppm (dd, JN-P = 54, JN-N = 17 Hz, PNNO), 349.33 ppm (dd, JN-P = 54, JN-N = 17 Hz, PNNO).

Received: October 8, 2009
Published online: November 17, 2009

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

<table>
<thead>
<tr>
<th></th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(1)–N(1)</td>
<td>1.703(2)</td>
<td>1.703(3)</td>
<td>1.7103(11)</td>
</tr>
<tr>
<td>N(1)–N(2)</td>
<td>1.266(4)</td>
<td>1.287(4)</td>
<td>1.2793(15)</td>
</tr>
<tr>
<td>N(2)–O(1)</td>
<td>1.303(3)</td>
<td>1.303(3)</td>
<td>1.3057(15)</td>
</tr>
<tr>
<td>Zn(1)–N(1)</td>
<td>2.088(2)</td>
<td>2.118(2)</td>
<td>2.0912(9)</td>
</tr>
<tr>
<td>Zn(2)–N(1)</td>
<td>2.242(2)</td>
<td>2.3086(12)</td>
<td></td>
</tr>
<tr>
<td>Zn(2)–O(1)</td>
<td>2.184(2)</td>
<td>2.1435(10)</td>
<td></td>
</tr>
<tr>
<td>N(1)–N(2)–O(1)</td>
<td>117.2(2)</td>
<td>109.2(2)</td>
<td>109.29(10)</td>
</tr>
<tr>
<td>Zn(1)–O(1)–Zn(2)</td>
<td>107.15(10)</td>
<td>135.57(9)</td>
<td>139.95(5)</td>
</tr>
<tr>
<td>Zn(1)–N(1)–O(1)</td>
<td>56.91(9)</td>
<td>56.38(4)</td>
<td></td>
</tr>
</tbody>
</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)2] to 2 (Scheme 1).