

observed in spectra (not shown) obtained for complexes containing peptides labeled selectively with ^{15}N at I84 or G86. It is clear from Figure 2 that deuteration greatly improved the sensitivity, due to a reduction in line width as previously noted,^{2–5} but more significantly to an increase in the NOE via elimination of some competing relaxation pathways. In addition, the results from the deuterated peptide verify that the observed NH–NH NOEs do not arise from spin diffusion through the intervening $\text{C}^{\alpha}\text{H}$ proton.

In this communication we demonstrate the use of a specific deuteration strategy to enhance NOEs observed in high molecular weight systems. Random fractional deuteration will not adequately eliminate troublesome spin-diffusion pathways and also results in poor sensitivity compared to specific deuteration (except for NH–NH interactions). Extensive deuteration of a particular molecular fragment can be expensive and is usually unnecessary to achieve the desired goals. While the example provided here focused on amide–amide NOEs, the specific deuteration strategy is completely general and can be used to enhance NOEs between any pair of protons. The specific deuteration strategy is ideally suited for studies of synthetic peptides or other small molecules bound to protein receptors and should also be applicable to studies of proteins that are biosynthetically deuterated. The specificity of α and β deuteration will depend upon amino acid type, however, while specific deuteration at other side-chain positions will usually be independent of this factor and much less susceptible to problems of label scrambling.¹⁷

Through the use of a model structure for the system of interest, specific deuteration patterns may be designed to facilitate the observation of direct NOEs; experimental results subsequently obtained may then either lend support for the proposed model or indicate that modifications in it are required. Application of this strategy should render many high molecular weight systems more amenable to solution NMR studies.

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Reduction of Dinitrogen by a Zirconium Phosphine Complex To Form a Side-On-Bridging N_2 Ligand. Crystal Structure of $\{(\text{Pr}^i_2\text{PCH}_2\text{SiMe}_2)_2\text{N}\}\text{ZrCl}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)$

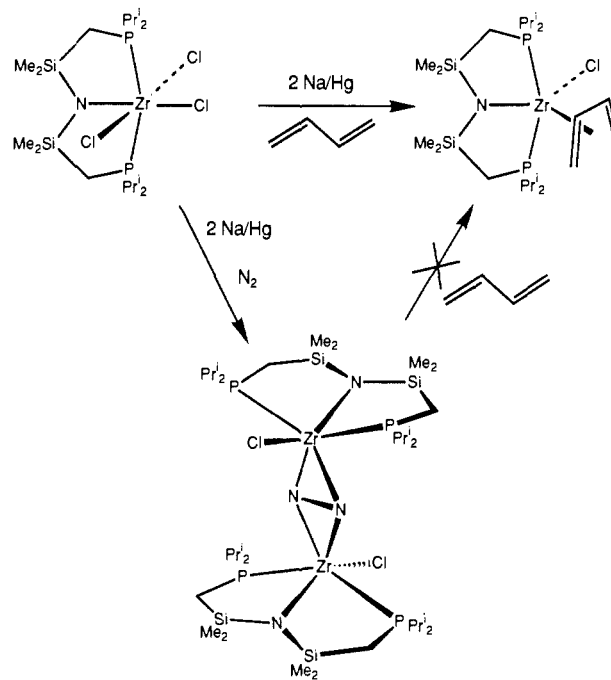
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One of the milestones of modern inorganic chemistry was the discovery that dinitrogen ($\text{N}\equiv\text{N}$) could act as a ligand. Since the original report¹ by Allen and Senoff in 1965 on the preparation of $[\text{Ru}(\text{NH}_3)_5\text{N}_2]^{2+}$, numerous N_2 complexes have been synthesized and structurally characterized.² By far the most prevalent

Scheme 1



mode of coordination to a metal is end-on to one metal or end-on bridging to two metals. Activation of the coordinated N_2 is indicated by a lengthening of the N–N bond distance of 1.0975 Å for free N_2 .³ Typical N–N bond lengths are 1.03–1.16 Å for mononuclear complexes and 1.12–1.33 Å for binuclear compounds. The side-on mode of N_2 coordination is extremely rare, and only a few polynuclear complexes displaying this mode of coordination have been crystallographically characterized.⁴ Herein we report the synthesis and structure of only the second binuclear complex containing a *planar* side-on-bound bridging N_2 ligand, wherein dinitrogen has been irreversibly reduced to a $(\text{N–N})^{4-}$ hydrazido ligand.⁵

Previous work from our laboratory has shown that phosphine complexes of zirconium(IV) can bind 1,3-butadiene under reducing conditions. Thus, reaction of $\text{ZrCl}_2[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPr}^i_2)_2]$ (1) with Na/Hg and 1,3-butadiene generates red $\text{ZrCl}(\eta^4\text{-C}_4\text{H}_6)[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPr}^i_2)_2]$ (2), which can also be prepared⁶ from magnesium butadiene ($\text{Mg}\cdot\text{C}_4\text{H}_6\cdot 2\text{THF}$) and 1. However, if reduction of 1 by Na/Hg is carried out just under N_2 , a deep blue solution is obtained from which dark blue crystals of the formula $\{[(\text{Pr}^i_2\text{PCH}_2\text{SiMe}_2)_2\text{N}]\text{ZrCl}_2(\text{N}_2)\}$ (3), can be isolated in moderate yield.⁷ Addition of 1,3-butadiene to the N_2 complex 1 does not

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(7) Compound 3 was synthesized by stirring a toluene solution of $\text{ZrCl}_2[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPr}^i_2)_2]$ (0.680 g, 1.15 mmol) with a 0.1% Na/Hg amalgam (0.106 g, 4.60 mmol) under 4 atm of N_2 for 2 days to give, after recrystallization from toluene, 0.270 g of product (44% yield). Satisfactory microanalysis and NMR spectral parameters were obtained for the dinitrogen complex 3 as detailed in the supplementary material.

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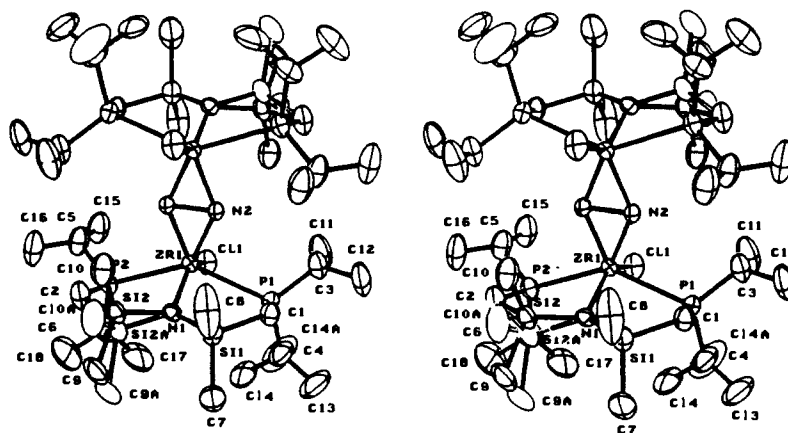
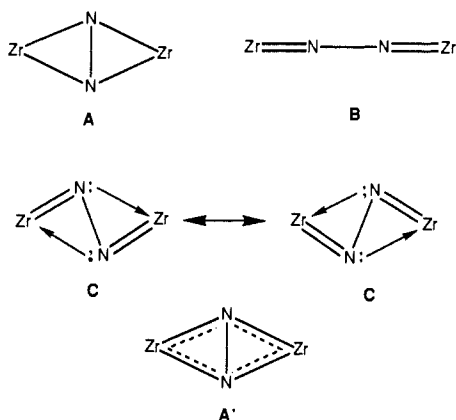


Figure 1. Stereoview of **3** with thermal ellipsoids at 25% probability. Bond lengths (Å): N2–N2', 1.548 (7); Zr–N2, 2.024 (4); Zr–N2', 2.027 (4); Zr–N1, 2.175 (3); Zr–Cl, 2.493 (1); Zr–P1, 2.764 (1); Zr–P2, 2.772 (1). Bond angles (deg): N2–Zr–N2', 44.9 (2); Zr–N2–Zr', 135.1 (2); Zr–N2–N2', 67.6 (2); Cl–Zr–N1, 139.3 (1); P1–Zr–P2, 141.00 (5); Cl–Zr–N2, 112.3 (1); Cl–Zr–N2', 111.9 (1); N1–Zr–N2, 105.2 (1); N1–Zr–N2', 105.5 (2).

Scheme II



generate the butadiene complex **2** (Scheme I).

The X-ray crystal structure⁸ of $\{[(\text{Pr}^i_2\text{PCH}_2\text{SiMe}_2)_2\text{N}]\text{ZrCl}_2(\text{N}_2)\}$ (**3**) is shown in Figure 1. The most important feature is the bridging side-on-bound N_2 ligand that generates a completely planar, symmetric Zr_2N_2 unit in which the zirconium–nitrogen bond lengths are essentially identical at 2.024 (4) Å, significantly shorter than the zirconium–amide bond length (Zr–N1) of 2.175 (3) found in the ancillary ligand. By comparison, a very short Zr–N bond length of 1.826 (4) Å has been reported⁹ for the imide derivative $\text{Cp}_2\text{Zr}(\text{NBu}^t)(\text{THF})$. The N–N bond distance of the bridging N_2 ligand is 1.548 (7) Å, which is longer than that found in hydrazine (1.47 Å), the prototypical N–N single bond. In fact, this is the longest N–N bond length ever measured for a transition-metal dinitrogen complex. The only other planar side-on-bridging dimer,^{4a} $(\text{Cp}^*\text{Sm})_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-N}_2)$, has a very short N–N bond of 1.088 (12) Å and readily loses N_2 in solution or under vacuum. There is one structure of a tetranuclear titanium N_2 complex,^{4b} $(\text{C}_{10}\text{H}_8)(\text{C}_5\text{H}_5)_5(\text{C}_5\text{H}_4)\text{Ti}_4(\mu_3\text{-N}_2)$, where the N_2 is terminally bound to two titaniums and side-on bound to one

titanium. It has a long N–N bond distance of 1.301 Å, somewhat longer than a N–N double bond (cf. azomethane at 1.24 Å). There are two reported^{4c,d} nickel clusters, $[(\text{PhLi})_6\text{Ni}_2\text{N}_2(\text{OEt}_2)_2]$ and $[\text{Ph}_5\text{Ni}_2\text{N}_2\text{Na}_3\text{Li}_6(\text{OEt})_4(\text{OEt}_2)_3]$, which display nonplanar side-on N_2 bonding. These clusters have tetrahedral Ni_2N_2 cores with additional bonding interactions to four lithium atoms; the N–N bond lengths are 1.35 and 1.36 (2) Å, respectively.

The structure of the binuclear zirconium dinitrogen complex **3** is somewhat surprising. Other dinitrogen complexes of zirconium,¹⁰ cf. $[\text{Cp}^*\text{ZrN}_2]_2(\mu\text{-N}_2)$, show linear end-on N_2 coordination. However, there are some theoretical predictions¹¹ that a side-on structure should be more stable than a linear end-on structure particularly for the early transition elements. Given the long N–N bond length, it is reasonable to suggest that this complex consists of two Zr^{4+} centers and a bridging N_2^{4-} unit. Even with this formalism, it is difficult to reconcile the planar, symmetric structure **A** particularly since this same formalism should also hold for a linear diimide structure of the type **B** (Scheme II), a common occurrence particularly for N_2 complexes of groups 5 and 6.¹² Although an oversimplification, valence bond arguments suggest that unsymmetrical resonance structures similar to **C** might be possible if the metal is sterically and electronically unsaturated as is the case in complex **3**. That these resonance structures result in a symmetrical, planar structure **A'** (Scheme II) having delocalized bonds is consistent with the relatively short Zr–N bond lengths found for the Zr_2N_2 core of **3** and theoretical considerations of related bridging imide systems.¹³

The dinitrogen complex **3** reacts with excess acid to generate 1 equiv of H_2NNH_2 ,¹⁴ as expected. Additional studies on the transformations of this hydrazido(4–) ligand are in progress.

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Supplementary Material Available: Experimental details for the preparation of **3** and for the X-ray analysis, tables of crystallographic data, final atomic coordinates and equivalent isotropic thermal parameters, calculated hydrogen atom parameters, anisotropic thermal parameters bond lengths, bond angles, torsion angles, intermolecular distances, and least-squares planes (36 pages); tables of measured and calculated structure factor amplitudes (45 pages). Ordering information is given on any current masthead page.

(8) Crystals of $\{[(\text{Pr}^i_2\text{PCH}_2\text{SiMe}_2)_2\text{N}]\text{ZrCl}_2(\text{N}_2)\}$ ($\text{C}_{36}\text{H}_{88}\text{Cl}_2\text{N}_4\text{P}_4\text{Si}_4\text{Zr}_2\text{C}_7\text{H}_8$, fw = 1158.84) are monoclinic, space group $P2_1/c$, $a = 14.103$ (3) Å, $b = 16.233$ (3) Å, $c = 14.678$ (3) Å, $\beta = 114.24$ (1)°, $Z = 2$, $\rho_{\text{calcd}} = 1.256 \text{ g}^{-3}$. Data were collected at 21 °C on a Rigaku AFC6S diffractometer with graphite-monochromated $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178$ Å). The structure was solved by heavy-atom methods and was refined by full-matrix least-squares methods to $R = 0.0040$ and $R_w = 0.049$ for 4158 reflections with $I \geq 3\sigma(I)$. Data (collected to $2\theta = 155^\circ$) were corrected for absorption. Twofold orientational disorder of one isopropyl group and 2-fold conformational disorder of one of the two crystallographically unique ZrPCSiN chelate rings were modeled by split-atom refinement. Peripheral atoms of this molecule all exhibit a high degree of thermal motion at room temperature, but the molecular core (the Zr atoms and all atoms directly bonded to the metals) is well-determined.

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