

Transformation of Coordinated Dinitrogen by Reaction with Dihydrogen and Primary Silanes

Michael D. Fryzuk,* Jason B. Love, Steven J. Rettig, Victor G. Young

The reaction of dihydrogen with a side-on bound dinitrogen complex of zirconium was investigated. Instead of a displacement of the dinitrogen moiety, which is the common mode of reactivity, a complex containing both a bridging hydride and a bridging hydrazido unit with a nitrogen-hydrogen bond was observed. This reaction was extended to primary silanes to produce a species that contained a nitrogen-silicon bond. In addition, an intermediate in the dihydrogen addition has been structurally characterized as having a bridging dihydrogen unit.

Molecular nitrogen, or dinitrogen (N_2), is so unreactive that it is used routinely as an inert gas in the food industry and in laboratories in academia and industry (1). Yet N_2 does undergo chemical transformations. Perhaps the most famous reaction is the energy-intensive Haber-Bosch process (2), which accounts for the production of millions of tons of NH_3 yearly. Although high pressures and temperatures are necessary for this reaction, N_2 can also be fixed at atmospheric pressure and ambient temperature by certain types of bacteria to produce NH_3 . The recent crystal structure of nitrogenase from *Azotobacter vinelandii* has provided insights into how these biological systems activate N_2 in an aqueous environment (3).

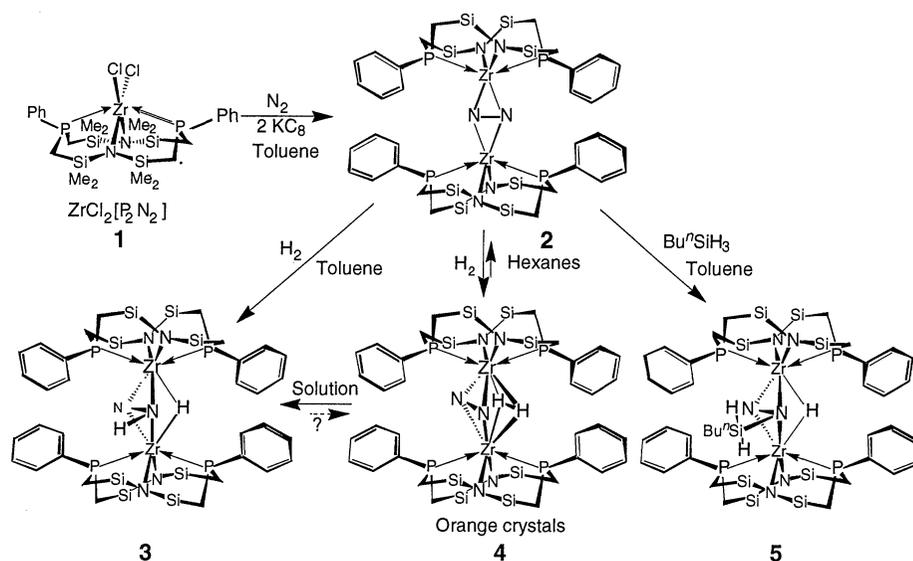
Attempts to duplicate the Haber process and the nitrogenase system in the laboratory have not met with success. However, much fundamental knowledge on the bonding modes and reactivity patterns of the N_2 molecule have accrued (4). For example, when coordinated to a metal, protonation reactions that stoichiometrically produce either NH_3 or H_2NNH_2 (5) and the synthesis of organonitrogen derivatives by reaction with carbon-based electrophiles (6) are well known. However, a common transformation of a coordinated N_2 unit is displacement of the N_2 by a better donor. For example, the addition of H_2 to $[(\eta^5-C_5Me_5)_2ZrN_2]_2(\mu-N_2)$ (Me = methyl) results in the dissociation of all of the coordinated N_2 moieties and the irreversible formation of the dihydride derivative $(\eta^5-C_5Me_5)_2ZrH_2$ (7). Similarly, N_2 complexes of molybdenum release N_2 when H_2 is added (8). To our knowledge, there are no reported examples that describe the addition of H_2 to a coordinated N_2 wherein the

N_2 unit undergoes a transformation. Given the importance of the Haber-Bosch process, wherein H_2 acts as both the reductant and the source of H in the formation of NH_3 from N_2 , such a reaction would be of fundamental interest. Here we detail the addition of H_2 and primary silanes to a coordinated N_2 unit in a dinuclear Zr-centered environment and report on our initial findings of an intermediate in the addition of H_2 to a dinuclear Zr N_2 complex.

We have previously reported the preparation of the dinuclear N_2 complex of Zr $\{[(^iPr)_2PCH_2SiMe_2]_2N\}ZrCl_2(\mu-\eta^2-N_2)$ (iPr = isopropyl) (9). In this derivative, the N_2 is coordinated in a side-on mode with the N–N bond elongated to 1.55 Å (as compared with that of free N_2 at 1.0976 Å). By changing the ancillary ligand set from a tridentate system to a macrocyclic variation, we have been able to prepare another complex with a side-on bound N_2 unit.

Addition of $syn-Li_2(THF)[P_2N_2]$ [$[P_2N_2] = PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh$, THF = tetrahydrofuran, and Ph = phenyl] (10) to $ZrCl_4(THT)_2$ (THT = tetrahydrothiophene) in diethyl ether produces the corresponding dichloride species $ZrCl_2[P_2N_2]$ (1). Upon reduction with 2 equivalents of potassium graphite (KC_8) under N_2 , the corresponding dark-blue N_2 complex $\{[P_2N_2]Zr\}_2(\mu-\eta^2-N_2)$ (2) is obtained in high yield (Fig. 1). The x-ray crystal structure of 2 (Fig. 2) confirms that the N_2 unit is bound side-on with a N–N bond length of 1.43(1) Å (the number in parentheses is the error in the last digit) (11). This bond length is comparable to the observed bond length of 1.47 Å in hydrazine, H_2NNH_2 (12), but shorter than that observed in the aforementioned other side-on N_2 complex. Formally, one can consider the oxidation state of each Zr to be Zr(IV) and the bridging N_2 as a N_2^{4-} unit.

Stirring a dark-blue toluene solution of the N_2 complex 2 under 1 to 4 atm of H_2 resulted in a slow color change to yellow over a period of 7 to 14 days. The 1H nuclear magnetic resonance (NMR) spectra indicated the formation of a species that displayed a broad N–H resonance at 5.53 parts per million (ppm) and a multiplet at 2.07 ppm for the bridging hydride; for the corresponding reaction with the ^{15}N -labeled complex $\{[P_2N_2]Zr\}_2(\mu-\eta^2-^{15}N_2)$ ($^{15}N_2$ -2), the N–H resonance was split into a doublet with a one-bond coupling constant ($^1J_{N-H}$) of 71.3 Hz (13). The hydride multiplet showed coupling to four equivalent ^{31}P nuclei and long-range coupling to the N–H moiety; these coupling patterns were confirmed by a series of



M. D. Fryzuk, J. B. Love, S. J. Rettig, Department of Chemistry, University of British Columbia, Vancouver, British Columbia V6T 1Z1, Canada.
V. G. Young, Chemistry Department, University of Minnesota, Minneapolis, MN 55455, USA.

*To whom correspondence should be addressed.

Fig. 1. Scheme for the preparation of the N_2 complex 2 and its reactions with H_2 and n -butyrsilane. In complexes 2 to 5, all of the methyls on the Si atoms have been omitted for clarity.

homonuclear and ^{31}P decoupling experiments. When D_2 was added to **2**, both of these resonances were absent, thus confirming that the protons in the H_2 reaction arise from the added H_2 . Therefore, we formulate the product of the H_2 reaction as a dinuclear system having the formula $\{[\text{P}_2\text{N}_2]\text{Zr}\}_2(\mu\text{-}\eta^2\text{-N}_2\text{H})(\mu\text{-H})$ (**3**) (Fig. 1). Such a structure is also consistent with the

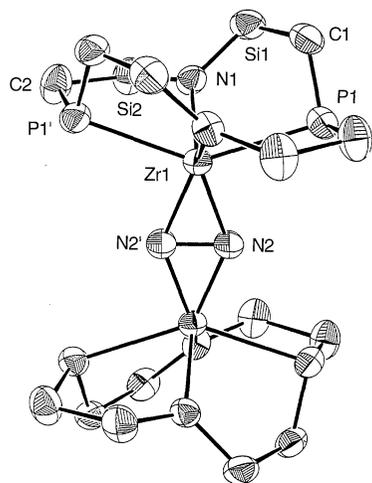


Fig. 2. The x-ray crystal structure of $\{[\text{P}_2\text{N}_2]\text{Zr}\}_2(\mu\text{-}\eta^2\text{-N}_2)$ (**2**); all of the methyls attached to silicon and the phenyls attached to phosphorous have been removed for clarity. Selected bond lengths (in angstroms) and angles (in degrees): N2-N2', 1.43(1); Zr1-N1, 2.203(4); Zr1-N2, 2.010(2); Zr1-P1, 2.734(2); N1-Zr1-N1', 108.4(2); P1-Zr1-P1', 140.90(7); Zr1-N2-N2', 69.1(2); and N2-Zr1-N2', 41.8(3).

$^{15}\text{N}\{^1\text{H}\}\text{NMR}$ spectrum of $(^{15}\text{N}_2\text{-3})$, which showed distinct resonances at 373 and 155 ppm, with the latter coupled to the directly attached hydrogen nucleus.

Attempts to confirm our solution spectroscopic assignment by a solid-state x-ray crystal structure gave unexpected results. When a saturated solution of the starting N_2 complex **2** in hexanes was allowed to stand under 1 atm of H_2 , air- and moisture-sensitive orange prisms were obtained over a period of 2 weeks. The low-temperature x-ray crystal structure of these crystals mounted under hydrogen is shown in Fig. 3 (11). The observed solid-state structure did not show the expected N-H and $\text{Zr}_2(\mu\text{-H})$ features proposed above from the solution data; instead, the crystalline material exhibited a side-on bridging H_2 unit and an intact N_2 moiety (Fig. 1). The core of the dinuclear complex **4**, a $\text{Zr}_2(\mu\text{-}\eta^2\text{-H}_2)(\mu\text{-}\eta^2\text{-N}_2)$ unit, represents a possible intermediate in the addition of H_2 to a coordinated N_2 . This side-on bridging H_2 moiety was located from the difference Fourier maps and was isotropically refined. The $\mu\text{-}\eta^2\text{-H}_2$ unit has a H-H bond distance of 1.21(5) Å, intermediate between those observed for H_2 complexes (0.8 to 1.0 Å) and dihydride complexes (>1.6 Å); in other words, **4** contains an elongated H_2 molecule (14, 15). Although the N-N bond distance of 1.443(5) Å observed in **4** is only slightly different from that of the starting N_2 complex **2**, 1.43(1) Å, the main difference is that the $\text{Zr}_2(\mu\text{-}\eta^2\text{-N}_2)$ unit is no longer planar but is now hinged, with an averaged 0.1 Å increase in Zr-N bond lengths. To our knowledge,

complex **4** is the first example of an isolated H_2 complex of Zr (15). Although bridging and terminal hydrides of Zr are well known (16), dihydrogen complexes of zirconium are unknown except as proposed intermediates (17). Moreover, examples of dinuclear compounds containing a bridging H_2 molecule are rare, and to our knowledge, none have been structurally characterized (18). Other dinuclear and heterobimetallic H_2 complexes are known, but in these complexes, the $\mu^2\text{-H}_2$ molecule is located at a single metal site (19).

When the crystals of **4** were dissolved in $d_8\text{-THF}$ (deuterated tetrahydrofuran), solution ^1H NMR spectroscopy showed the clean formation of **3** incorporating the $\mu\text{-}\eta^2\text{-N}_2\text{H}$ and $\text{Zr}_2(\mu\text{-H})$. This isomerization process appears to be reversible, because the infrared spectra of crystalline **4** and the material recovered from dissolution of **4** in $d_8\text{-THF}$ (to form **3**) are identical. The process by which isomerization of **4** to **3** proceeds is unknown; however, one possibility is by means of heterolytic cleavage of the coordinated H_2 molecule by interaction with a basic nitrogen of the N_2 unit and the electropositive Zr center, presumably by way of a four-center transition state. The apparent phase-dependent equilibrium between **3** and the H_2 complex **4** is intriguing and still under investigation.

The close analogy between H-H and Si-H bonds (20) prompted us to investigate the reaction between the starting N_2 complex **2** and primary silanes RSiH_3 . When *n*-butylsilane (Bu^nSiH_3) was added to the

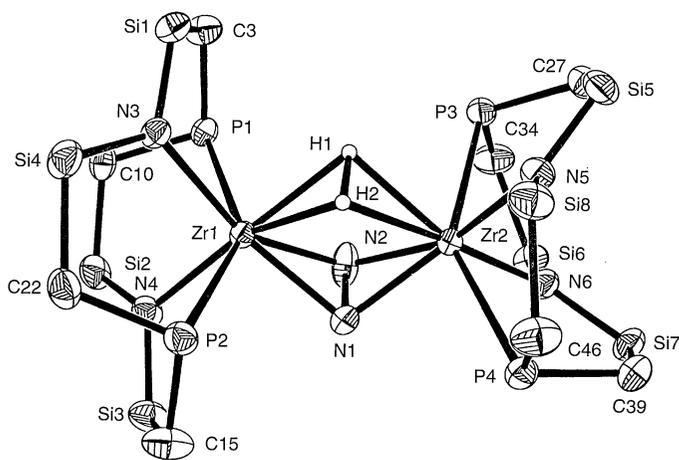


Fig. 3. The x-ray crystal structure of $\{[\text{P}_2\text{N}_2]\text{Zr}\}_2(\mu\text{-}\eta^2\text{-H}_2)(\mu\text{-}\eta^2\text{-N}_2)$ (**4**); all of the methyls attached to silicon and the phenyls attached to phosphorous have been removed for clarity. Selected bond lengths (in angstroms) and angles (in degrees): H1-H2, 1.21(5); N1-N2, 1.443(5); Zr1-H1, 2.17(3); Zr-H2, 2.12(5); Zr1-N1, 2.120(3); Zr-N2, 2.125(3); Zr-N3, 2.254(3); Zr-N4, 2.199(3); Zr-P1, 2.7193(9); Zr1-P2, 2.7554(10); P1-Zr1-P2, 146.82(3); N3-Zr1-N4, 99.25(11); N1-Zr1-H2, 70.3(8); N1-Zr1-N2, 39.75(13); and H1-Zr1-H2, 32.4(13).

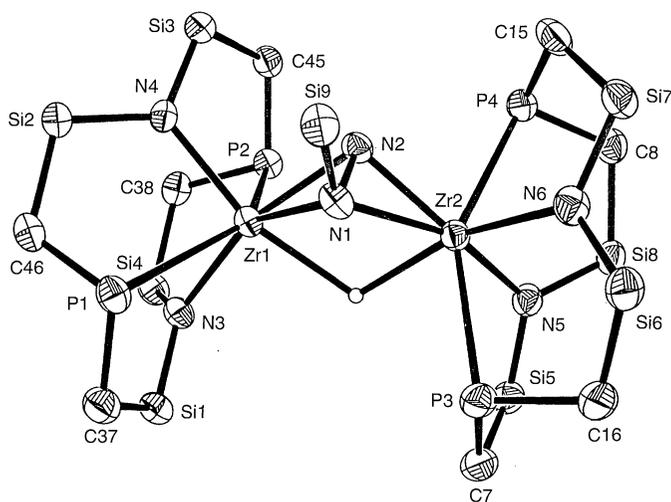


Fig. 4. The x-ray crystal structure of $\{[\text{P}_2\text{N}_2]\text{Zr}\}_2(\mu\text{-}\eta^2\text{-N}_2\text{SiH}_2\text{Bu}^n)(\mu\text{-}\eta)$ (**5**); all of the methyls attached to silicon and the phenyls attached to phosphorous have been removed for clarity. Selected bond lengths (in angstroms) and angles (in degrees): N1-N2, 1.530(4); N1-Si9, 1.735(4); Zr1-N1, 2.163(3); Zr1-N2, 2.129(3); Zr1-H1, 2.13(4); Zr2-H1, 2.03(4); Zr1-N3, 2.278(3); Zr1-N4, 2.176(3); Zr1-P1, 2.8644(11); Zr1-P2, 2.7301(11); P1-Zr1-P2, 142.51(3); N3-Zr1-N4, 100.56(12); N1-Zr1-H1, 71.9(11); N1-Zr1-N2, 41.76(12); and Zr1-N1-Si9, 125.9(2).

N_2 complex **2**, the butylsilyl derivative **5**, having the formula $\{[P_2N_2]Zr\}_2(\mu-\eta^2-N_2SiH_2Bu^t)(\mu-H)$, was isolated as yellow needles (Fig. 1). In the 1H NMR spectrum, there were observed two broad singlets at 5.07 and 4.80 ppm due to two inequivalent Si-H protons. There was also a broad quintet at 1.53 ppm that collapsed to a broad singlet upon ^{31}P decoupling; this resonance can be assigned to a $Zr_2(\mu-H)$ moiety on the basis of its similarity to the signal observed at 2.07 ppm for **3**, which was proposed to be a bridging hydride. This assignment suggests that, analogous to **3**, heterolytic cleavage of the Si-H bond has occurred, with the silyl fragment now bound to the N_2 unit. The solution characteristics of **5** are very similar to those observed for **3**, supporting the proposed solution structure for **3**. The proposition that both **3** and **5** contain a hydride bridging the two Zr centers is reinforced by the low-temperature, solid-state structure of **5** (**II**) (Fig. 4), in which the Bu^tSiH_2 fragment is bonded to the bridging N_2 unit, with the remaining silyl-derived H atom symmetrically bridging the two Zr atoms; the bridging hydride was located from the difference Fourier maps and isotropically refined and is at a similar Zr-H bond distance to those observed for the $\mu-\eta^2-H_2$ unit in **4**. The incorporation of the silyl group at N-1 has resulted in a lengthening of the N-N bond distance from 1.43(1) Å in **2** to 1.530(4) Å in **5**.

The fact that coordinated N_2 can be induced to react stoichiometrically with H_2 and silanes suggests that other transformations of the N_2 moiety are possible using complexes with the appropriate combination of ancillary ligands and central metal. Further studies are needed to determine if the reactions reported here can be incorporated into catalytic cycles.

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- Crystal data for **2**: formula, $C_{48}H_{64}N_6P_4Si_8Zr_2$; molecular weight $M = 1276.25$; lattice system, orthorhombic; space group $Ccca(\#68)$; temperature = $21.0^\circ C$; lattice parameters $a = 14.290(3)$ Å, $b = 19.213$ Å, and $c = 24.033(2)$ Å; unit cell volume $V = 6598(1)$ Å³; calculated density $D_{calc} = 1.285$ g cm⁻³; number of molecules in the unit cell $Z = 4$; linear absorption coefficient $\mu = 52.63$ cm⁻¹; empirical absorption correction; CuK α rays with graphite monochromator recorded on a Siemens SMART platform CCD diffractometer; 3499 measured reflections; 1649 reflections used with $I > 3\sigma(I)$; maximum diffraction angle $2\theta = 155^\circ$; 155 varied parameters; non-H atoms were refined anisotropically, H atoms were fixed in calculated positions with C-H = 0.98 Å; full least square matrix refinement; reliability factor $R = 0.042$; weighted reliability factor $R_w = 0.041$. Crystal data for **3**: formula $C_{48}H_{66}N_6P_4Si_8Zr_2$; $M = 1278.27$; lattice system, orthorhombic; space group $P2_12_12_1$; temperature = $173(2)$ K; lattice parameters $a = 12.2256(1)$ Å, $b = 21.0139(2)$ Å, and $c = 24.7043(3)$ Å; $V = 6346.72(11)$ Å³; $D_{calc} = 1.338$ g cm⁻³; $Z = 4$; $\mu = 0.617$ mm⁻¹; MoK α rays with graphite monochromator recorded on a Siemens SMART platform CCD diffractometer; 32,406 measured reflections; 11,145 reflections used with $I > 2\sigma(I)$; $\Theta_{max} = 25.03^\circ$; 721 varied parameters; non-H atoms were refined anisotropically, H1 and H2 were refined positionally and isotropically, and all other H atoms were placed in ideal positions and refined as riding atoms; full least square matrix refinement; $R = 0.0336$; $R_w = 0.0634$. Crystal data for **5**: formula $C_{52}H_{66}N_6P_4Si_8Zr_2$; $M = 1364.48$; lattice system, monoclinic; space group $C2/c$; temperature = $173(2)$ K; lattice parameters $a = 49.1499(2)$ Å, $b = 13.0446(2)$ Å, and $c = 24.0133(1)$ Å, $\beta = 116.579(1)^\circ$; $V = 13768.8(2)$ Å³; $D_{calc} = 1.316$ g cm⁻³; $Z = 8$; $\mu = 0.589$ mm⁻¹; MoK α rays with graphite monochromator recorded on a Siemens SMART platform CCD diffractometer; 34,508 measured reflections; 12,143 reflections used with $I > 2\sigma(I)$; $\Theta_{max} = 25.10^\circ$; 794 varied parameters; non-H atoms were refined anisotropically, the butyl chain refined as a split atom model with an occupancy of 0.74(2) to 0.26(2), the bridging hydride H1A was refined positionally and isotropically, and all other H atoms were placed in ideal positions and refined as riding atoms; full least-square matrix refinement; $R = 0.0491$; $R_w = 0.1223$.
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Soft-Landing of Polyatomic Ions at Fluorinated Self-Assembled Monolayer Surfaces

S. A. Miller, H. Luo, S. J. Pachuta, R. G. Cooks*

A method of preparing modified surfaces, referred to as soft-landing, is described in which intact polyatomic ions are deposited from the gas phase into a monolayer fluorocarbon surface at room temperature. The ions are trapped in the fluorocarbon matrix for many hours. They are released, intact, upon sputtering at low or high energy or by thermal desorption, and their molecular compositions are confirmed by isotopic labeling and high-resolution mass measurements. The method is demonstrated for various silyl and pyridinium cations. Capture at the surface is favored when the ions bear bulky substituents that facilitate steric trapping in the matrix.

Modification of surfaces to control their chemical and physical properties is of interest in many areas of science, including microelectronics, catalysis, optics, and electrochemistry (1). High-energy ion beams ($>10^3$ eV) have long been used for thin-film modification, especially in the technique of ion implanta-

S. A. Miller, H. Luo, R. G. Cooks, Department of Chemistry, Purdue University, West Lafayette, IN 47907, USA. S. J. Pachuta, 3M Corporate Research Labs, 3M Center, St. Paul, MN 55144, USA.

*To whom correspondence should be addressed.

tion (2), and collisions of hyperthermal energy (<100 eV) gas-phase ions are beginning to be used for surface modification. For example, metal carbides can be generated by exposing metals such as nickel, tungsten, and gold to beams of C^+ ions (20 to 200 eV) (3); CO can be absorbed molecularly on nickel(111) when delivered as the molecular ion (4); and methyl groups can be chemisorbed to a platinum surface when gaseous methyl ions are used as reagents (5). Complex ion-surface reactions also occur in this energy regime; for example,