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Communication

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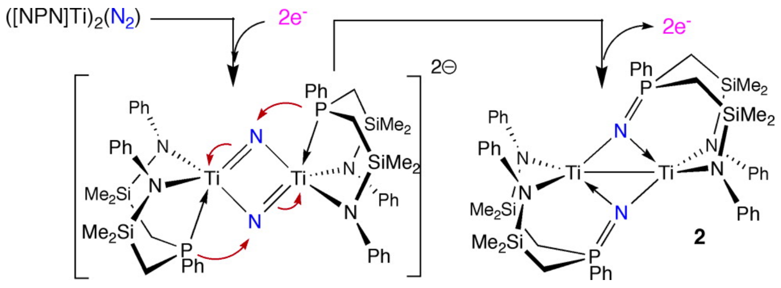

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Formation of Phosphorus−Nitrogen Bonds by Reduction of a Titanium Phosphine Complex under Molecular Nitrogen

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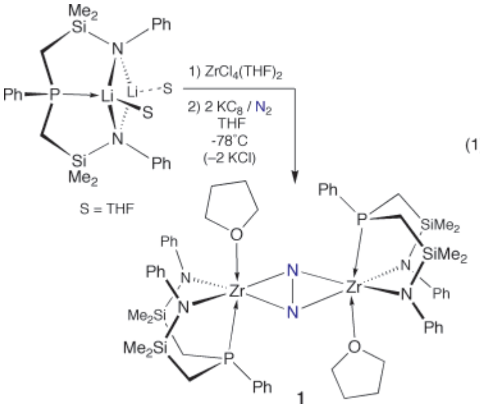
A very common synthetic method to generate dinitrogen metal complexes is via reduction, wherein addition of some alkali or alkaline earth metal (e.g., Li, Na/Hg, KC_8, Mg) to a high oxidation state, precursor metal complex in the presence of N_2 can result in dinitrogen binding.[1] Only in a few cases have lower oxidation state complexes been isolated or detected and shown to react independently with dinitrogen.[2] In most instances, little is known about intermediates and how the N_2 interacts with the metal. As a result, these reduction protocols are not easily controlled because the combination of strong reducing agents and poor binding ability of molecular nitrogen can result in unpredictable outcomes.[3] In this work, we detail the effect of a change of the metal center within a particular ligand during such a reduction process; what results is an unanticipated process that involves intramolecular phosphorus−nitrogen bond formation, where the nitrogen originates from added N_2.

Our recent efforts have been directed at the synthesis and reactivity of well-defined dinitrogen complexes. Within group 4, we have previously reported[4] the synthesis of dinuclear dinitrogen complexes with side-on bridging N_2 units stabilized by ancillary ligands that contain phosphine and amido donors. In the case of the reduction of $[P_2N_2]ZrCl_2$ (where $[P_2N_2] = PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh$) with KC_8 under N_2, $([P_2N_2]Zr)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ is generated in good yields if the N_2 pressure is maintained at 4 atm; lower pressures of N_2 can result in contamination by a P-phenyl bridged dimer.[5]

Reduction of the related Zr(IV) precursor complex $[NPN]ZrCl_2(THF)$ (where $[NPN] = PhP(CH_2SiMe_2NPh)_2$) with KC_8 in THF under N_2 generates $([NPN]Zr(THF))_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ (**1**) in very good yields (eq 1).



(1)

1

This complex was characterized[6] by solution NMR spectroscopy and solid-state X-ray crystallography. The overall high symmetry of **1** in solution is evident by the observation of a singlet in the ^{31}P NMR spectrum at δ −5.6 along with resonances in the ^1H NMR spectrum consistent with one kind of coordinated THF environment along with appropriate signals for the remaining protons of the ancillary ligand backbone. The solid-state structure is shown in Figure 1. The dinuclear complex displays a side-on bound N_2 ligand with a long N−N bond of 1.503(3) Å consistent with an N−N single bond and a N_2^{4-} unit. There are a number of side-on bridged dizirconium dinitrogen complexes that display similar levels of activation as evidenced by long N−N bond lengths.[4,7]

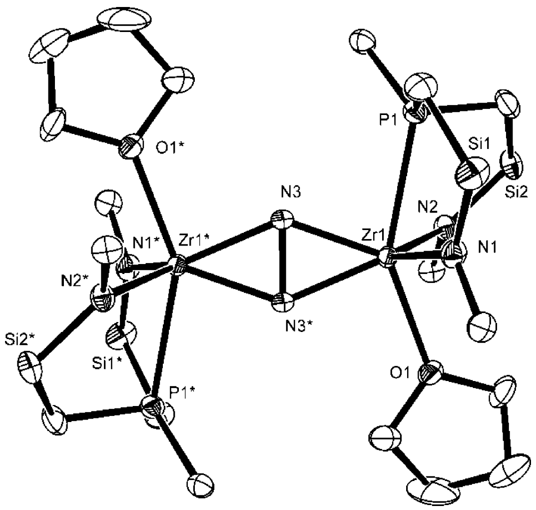


Figure 1. ORTEP diagram of complex **1**. The ellipsoids are drawn at the 50% level. Selected bond distances (Å) are: N3−N3*, 1.503(3); Zr1−N3, 2.026(2); Zr1−N3*, 2.069(2); Zr1−N1, 2.175(2); Zr1−N2, 2.228(2); Zr1−O1, 2.305(1); Zr1−P1, 2.6685(5). Silylmethyl groups are omitted for clarity; only ipso carbons of the phenyl groups are shown.

Reduction of the Ti(IV) precursor $[P_2N_2]TiCl_2$ with activated KC_8 generates $([P_2N_2]Ti)_2(\mu\text{-}N_2)$;[6] the bridging N_2 unit is end-on bound to each Ti center, and the N−N bond length is 1.255(7) Å. However, when the corresponding diamidophosphine precursor, $[NPN]TiCl_2$, is utilized, a different outcome is obtained.

The reaction of $[NPN]TiCl_2$ with 2 equiv of KC_8 under dinitrogen in THF results in a series of color changes from the initial orange of the starting material to generate an olive green solution from which emerald green crystals could be obtained. The elemental analysis and mass spectral data are consistent[6] with a molecular formula that involves incorporation of 1 equiv of N_2, that is, $([NPN]Ti)_2(N_2)$ **2** (eq 2). The complex is diamagnetic and displays a singlet in the $^{31}P\{^1H\}$ NMR spectrum at δ 39.9, considerably downfield of the starting dichloride (δ 3.7); the resonances in the ^1H NMR spectrum are consistent with a molecule of high symmetry as only two silylmethyl peaks are observed, and the methylene protons appear as an ABX-type pattern. With the assumption that this was a bona fide dinitrogen complex, all that remained was to determine the bonding mode of the N_2 unit, either end-on bridging in analogy to $([P_2N_2]Ti)_2(\mu\text{-}N_2)$ described above, or side-on bridging similar to that found for the zirconium derivative **1**.

The structure of **2** as determined by X-ray crystallography is shown in Figure 2. What is clearly evident is that there is no intact

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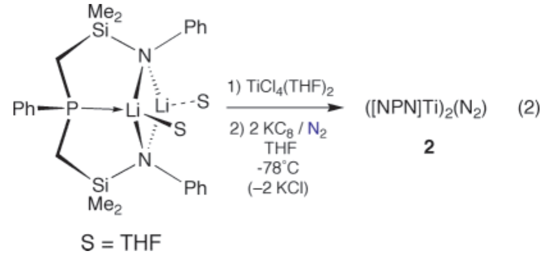


dinitrogen moiety coordinated to the dititanium core. In fact, the dinuclear metal complex has only the [NPN] bound but with one important change: the phosphine donor has been transformed into a phosphinimide unit.[8] Formally, the [N(PN)N] ligand set (where [N(PN)N] = (PhNSiMe$_2$CH$_2$)$_2$P(═N)Ph) is a trianion, and thus the formal oxidation state of each titanium center in ([N(PN)N]Ti)$_2$ (**2**) is Ti(III). The Ti−Ti bond distance is 2.6710(6) Å and is bridged by the imido unit of the phosphinimide portion of the ancillary ligand; the remaining sites are occupied by the phenylamido units of the original ligand set. The P−N bond distance of 1.591(2) Å is not unusual, being well in the range of reported bond lengths for this unit.[9]

The origin of the nitrogen atoms that have been inserted between the phosphine and the titanium centers was investigated by reduction under ^{15}N$_2$, which produced ([N(P^{15}N)N]Ti)$_2$ (^{15}N-**2**) as evidenced by mass spectrometry and confirmed by ^{31}P NMR spectroscopy (δ 39.9, d, $^1J_{15N}$ = 22 Hz). This clearly indicates that the source of the nitrogen of the phosphinimide unit is added N$_2$.

Shown in Scheme 1 is a possible mechanism for the cleavage of coordinated N$_2$ and insertion into the Ti−P bond. There is no precedent for direct attack of a phosphine on a coordinated N$_2$ moiety. However, it is presumed that some dinuclear N$_2$ complex initially forms, which is subsequently reduced further to generate the dianionic bridging dinitride species **B**. The transformation of **B** to **C** involves nucleophilic attack of a phosphine to the bridging nitride, a process that has precedent in nitride coupling reactions and in the reaction of PPh$_3$ with Os(VI) nitrides[10] to generate Os−NPPh$_3$ species in which reduction to Os(IV) has taken place. The transformation of the dianion **C** to product **2** requires release of two electrons, making the over reduction of **A** electrocatalytic.

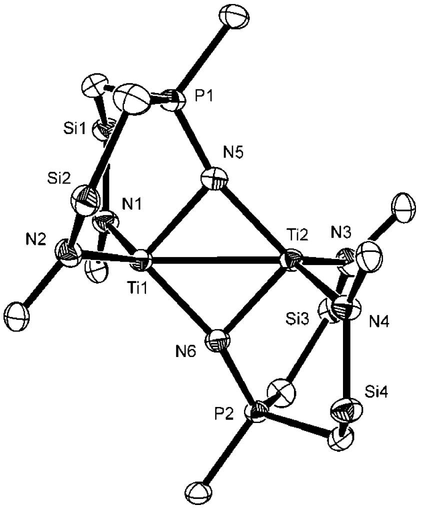
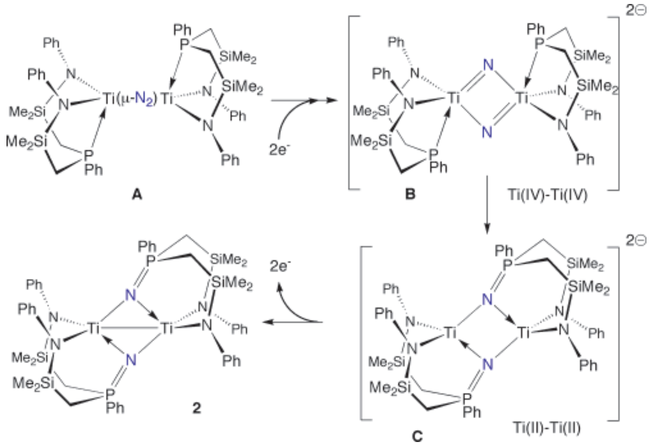


Figure 2. ORTEP diagram of complex **2**. The ellipsoids are drawn at the 50% probability level. Selected bond distances (Å) are: Ti1−Ti2, 2.6710(6); Ti1−N5, 1.997(2); Ti1−N6, 1.980(2); Ti2−N5, 1.978(2); Ti2−N6, 1.993(2); Ti1−N1, 2.042(2); Ti1−N2, 2.008(2); Ti2−N3, 1.992(2); Ti2−N4, 2.046(2); P1−N5, 1.591(2); P2−N6, 1.590(2). Silylmethyl groups are omitted for clarity; only ipso carbons of the phenyl groups are shown.

Scheme 1



The zirconium congener **1** does not undergo this reaction under any conditions that we have tried. It is likely the ease of reduction of Ti(IV) in **2** versus Zr(IV) in **1** that facilitates this new transformation.

This study reinforces the notion of the lack of control that is possible in using strong reducing agents as a method to incorporate molecular N$_2$ into the coordination sphere of metal complexes. Cleavage of the N−N bond in N$_2$ complexes to form metal nitrides is well documented in the literature[11] as is the reaction of nucleophiles with high oxidation state nitrides;[10] the combination of these two processes leads to ancillary ligand modification by the formation of a phosphinimide functionality facilitated by the over reduction of the initially formed N$_2$ complex.

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Supporting Information Available: Experimental details for all of the compounds reported. Details on the solution and refinement of X-ray crystal structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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