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New Mode of Coordination for the Dinitrogen Ligand: A Dinuclear Tantalum Complex with a Bridging N_2 Unit That Is Both Side-On and End-On

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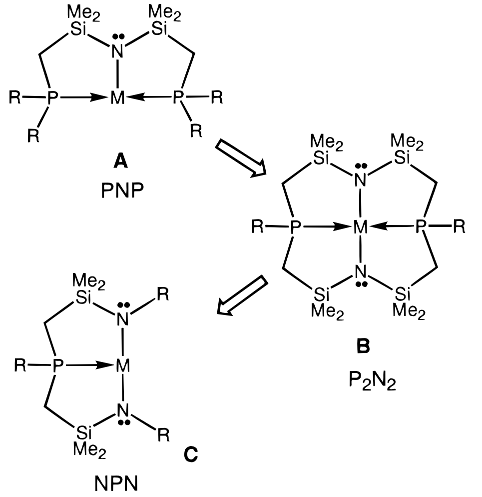
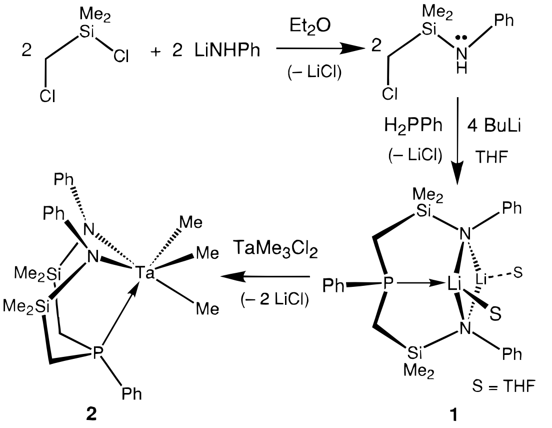
Interest in the coordination chemistry of the abundant yet inert nitrogen molecule is undergoing an apparent renaissance. Among the most notable recent achievements have been the splitting of the N_2 unit upon coordination[1−3] and its reactivity with H_2 and silanes to generate N−H and N−Si bonds, respectively.[4] While most dinuclear dinitrogen complexes have the N_2 bound in an end-on, bridging fashion,[5−7] the side-on mode of bonding is becoming more prevalent.[8−15] In this work, we detail a new coordination mode for the dinitrogen ligand when bound to two metals. In addition, the mode of formation of this early metal N_2 complex is unusual in that it entails the displacement of H_2 by N_2.

We have recently described the logical progression of ligand design from the PNP system (**A** in Scheme 1) to the P_2N_2 macrocycle (**B**).[16] It occurred to us that another combination within this group of donor types would be the NPN system (**C**) easily seen as the leftmost (or rightmost) quadrant of the macrocycle. One of the advantages of this system is the possible flexible coordination modes as well as the fact that there is the opportunity for coordinative unsaturation, at least as compared to the P_2N_2 system.

Scheme 1



Scheme 2



The synthesis of the NPN ligand is shown in Scheme 2; the reaction of 4 equiv of BuLi with a mixture of 2 equiv of $PhNHSiMe_2CH_2Cl$ and 1 equiv of $PhPH_2$ in diethyl ether followed by the addition of THF results in 85% yield of the ligand precursor $Li_2(THF)_2[NPN]$ (**1**) ([NPN] = $PhP(CH_2SiMe_2NPh)_2$). Coordination to tantalum(V) was achieved by the addition of **1** to $TaMe_3Cl_2$ to produce light-sensitive $[NPN]TaMe_3$ (**2**) as a pale yellow solid in 80% yield. The solid-state molecular structure of **2** demonstrates that the [NPN] ligand binds to Ta in a facial manner.[17]

A diethyl ether solution of **2** reacts cleanly with dihydrogen (1−4 atm) with elimination of methane to produce the diamagnetic purple dinuclear Ta(IV) hydride $\{[NPN]TaH_2\}_2$ (**3**). The ^{31}P and ^1H NMR spectra of **3** are consistent with a symmetrical complex with identical chemical environments at the two Ta centers. The hydride resonance at 10.6 ppm in the ^1H NMR spectrum shows no change upon cooling to −80 °C, which suggests that the hydrides are all bridging rather than a fluxional combination of bridging and terminal hydrides.[18−20] This conclusion is supported by the IR spectra of both **3** and **3**-D_4 for which no terminal Ta−H or Ta−D stretches could be identified;[21] assignment of the Ta(μ-H)Ta modes was not possible due to overlapping peaks.

Upon exposure of a solution of **3** to N_2 gas, the color of **3** changes from purple to brown, with the elimination of H_2 (1 equiv by stoichiometry). After less than 1 h under an atmosphere of N_2, **3** was converted to the dinitrogen compound $\{[NPN]TaH\}_2N_2$ (**4**) (Scheme 3). From the spectroscopic data, it is quite evident that the N_2 is bound unsymmetrically. The ^{31}P NMR spectrum shows two ^{31}P environments, a broad doublet and an apparent broad quartet with peaks in a 1:2:2:1 ratio, with an average coupling constant of 17.6 Hz, the result of near coincident

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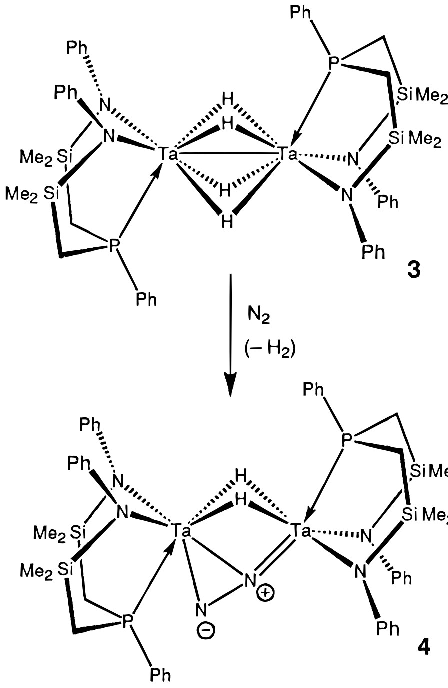
Scheme 3



coupling both to ^{31}P and quadrupolar ^{14}N. The ^{15}N NMR spectrum of ^{15}N-labeled **4** also shows two resonances at −20.4 and 163.6 ppm with $^{1}J_{\mathrm{NN}} = 21.5$ Hz. The two bridging hydrides are chemically equivalent in the room temperature ^{1}H NMR spectrum and appear as a doublet of doublets at 10.85 ppm.

The X-ray crystal structure of **4**, shown in Figure 1,[22] confirmed the unsymmetrical binding of N_2, but we were unable to locate the hydrides. The Ta_2N_2 core is approximately planar, and the Ta(2)−N(5)−N(6) angle is 151.9(4)°. The η^1 bound Ta(2)−N(5) distance of 1.888(5) Å is indicative of some double bond character, whereas the η^2 Ta(1)−N(6) and Ta(1)−N(5) distances of 1.975(5) Å and 2.141(4) Å are slightly longer. The N(5)−N(6) bond distance of 1.319(6) Å is typical for end-on bound N_2 units[7] and can be considered formally as the result of reduction of coordinated N_2 to N_2^{4-}.

The majority of dinuclear complexes bind dinitrogen in a bridging end-on manner, particularly derivatives of the group 5 metals.[9,23−32] The use of the less bulky tridentate NPN ligand has allowed for the characterization of a new (μ-η^2:η^1) binding mode for dinitrogen, the only example of a Ta dinitrogen complex not containing (μ-η^1:η^1) bound N_2. While this bonding mode for N_2 would appear to be unprecedented, there are examples of this kind of activation for the isoelectronic moieties CO, NO^+, and CN^- in dinuclear systems.[33−36] Related but distinctly different binding modes for N_2 have been found in heterobimetallic complexes of Ni with Li[37] and Co with K,[38] as well as an unusual titanocene derivative.[39]

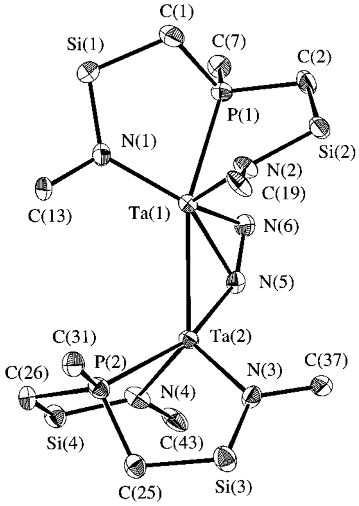


Figure 1. Molecular structure of {[(PhNSiMe$_2$CH$_2$)$_2$PPh]$_2$TaH}$_2$N$_2$ (**4**) with thermal ellipsoids at the 50% probability level. Silyl methyls have been omitted and only the ipso carbon atoms of the phenyl rings attached to phosphorus and nitrogen are shown. Selected distances (Å) and angles (deg): N(5)−N(6), 1.319(6); Ta(1)−N(5), 2.141(4); Ta(1)−N(6), 1.975(5); Ta(2)−N(5), 1.888(5); Ta(1)−N(1), 2.066(5); Ta(1)−N(2), 2.040(5); Ta(2)−N(3), 2.072(5); Ta(2)−N(4), 2.086(5); Ta(1)−Ta(2), 2.8311(3); Ta(2)−N(5)−N(6), 151.9(4); Ta(1)−N(5)−N(6), 64.6(3); Ta(1)−N(6)−N(5), 78.3(3); N(5)−Ta(1)−N(6); Ta(1)−N(5)−Ta(2), 89.0(2).

Also important is the manner in which this dinitrogen compound was formed. Although late transition metal hydrides are known to eliminate hydrogen and bind dinitrogen,[40,41] this usually occurs with minimal activation of the N−N bond. To our knowledge, no isolable early transition metal hydrides have previously been reported to bind N_2 by displacing coordinated hydride ligands. Such a transformation might be an important method of binding N_2 to a transition metal complex in a catalytic system. The second step in the proposed catalytic cycle would involve addition of reagents such as hydrogen or silanes to form N−H or N−Si bonds[4] and regenerate the original hydride. We are pursuing such goals.

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Supporting Information Available: Full experimental details for the preparation of all new compounds; details of the single-crystal X-ray analyses of **2** and **4** (30 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(22) Crystals of (μ-N$_2$)[(PhNSiMe$_2$CH$_2$)$_2$PPh)TaH]$_2$·2C$_6$H$_6$ (C$_{60}$H$_{74}$N$_6$P$_2$Si$_4$Ta$_2$) are orthorhombic, space group $P2_12_12_1$, a = 12.9290(7) Å, b = 15.11740(10) Å, c = 32.5768(4) Å, Z = 4, T = −93 °C, Rigaku AFC7/ADSC Quantum 1 CCD diffractometer. The structure was solved by the Patterson method and was refined by full-matrix least-squares procedures to R_w (F^2) = 0.065 for all 15996 reflections (including all available Friedel pairs) (R (F) = 0.037 for 12264 reflections with $I \geq 3\sigma(I)$). The absolute configuration was determined by Flack parameter refinement.

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