Hydrosilylation of a Dinuclear Tantalum Dinitrogen Complex: Cleavage of N₂ and Functionalization of Both Nitrogen Atoms

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Research into the activation of molecular nitrogen by metal complexes has reached a high level of sophistication.[1] While early work concentrated on the discovery of new examples of N_2 coordinated to metals in a variety of bonding modes,[2] it is clear that further advancement in this area will require systems that show enhanced reactivity patterns. In particular, discovery of metal dinitrogen complexes that undergo transformations resulting in the cleavage and/or functionalization[3] of the coordinated N_2 unit is of interest especially if the conditions are mild and potentially applicable to catalytic deployment.[4]

We recently reported the hydroboration of the tantalum dinitrogen complex ([NPN]Ta)$_2$(μ-H)$_2$(μ-η^1:η^2-N$_2$), **1** (where [NPN] = (PhNSiMe$_2$CH$_2$)$_2$PPh), in which addition of the B−H bond of 9-BBN across a metal−dinitrogen π bond gave a new N−B bond and a terminal tantalum hydride.[5] A key finding was that this reaction triggered a cascade of events including N−N bond cleavage. Unfortunately, an ancillary [NPN] ligand was irreversibly rearranged via silyl migration to a metal nitrido ligand, limiting the usefulness of this process. However, the success of this reaction provided the incentive to examine other simple hydride reagents that might add E−H bonds to **1** without the unattractive features of the hydroboration chemistry. We have previously reported hydrosilylation of dinitrogen complexes of zirconium,[6] and thus exploring addition reactions with primary silanes seemed attractive. Herein we report preliminary results that extend this reactivity pattern for the N_2 ligand and establish new possibilities for cleavage and complete functionalization of coordinated dinitrogen without the involvement of the ancillary ligands.

The reaction between 2 equiv of butylsilane (BuSiH$_3$) and the ditantalum dinitrogen complex **1** proceeds cleanly over 36 h to produce **2** in 63% yield (eq 1). The NMR spectral data of **2**, particularly the presence of a single [NPN] silyl resonance and a single butylsilyl resonance in the ^{29}Si{^{1}H} NMR spectrum, are consistent with C_{2h} symmetry in solution.[7] No ^{1}H NMR resonances typical of hydrides, either bridging or terminal, are observed.

$$\text{1} \xrightarrow[\text{- 2 H}_2]{\text{2 BuSiH}_3} \text{2} \qquad (1)$$
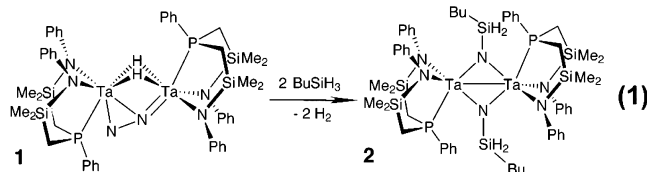
The solid-state molecular structure of **2**, determined from a twinned crystal, is shown in Figure 1.[8] It is evident that the dinitrogen fragment has been cleaved and that both dinitrogen-derived N atoms have been functionalized in the same manner despite their asymmetric activation in parent complex **1**. These bridging units can be considered as bridging silylimides bracketing a Ta(IV)−Ta(IV) metal−metal bond, thus accounting for the observed diamagnetism. Labeling studies using the enriched dini-
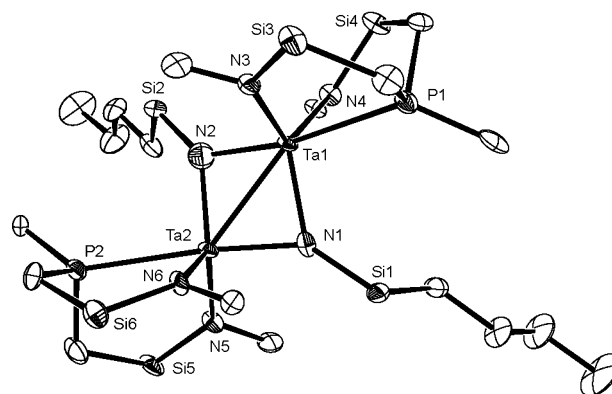
Figure 1. ORTEP drawing of **2** (ellipsoids at 50% probability, silyl methyl and phenyl carbons other than *ipso* omitted for clarity). Selected bond lengths (Å) and angles (deg): Ta1−N1 1.997(9), Ta1−N2 2.007(9), Ta2−N1 2.038(10), Ta2−N2 1.990(9), N1···N2 2.935(4), N1−Si1 1.729(10), N2−Si2 1.739(10), Ta1−Ta2 2.6677(6), Ta1−P1 2.735(3), Ta2−P2 2.687(3), Ta2−N5 2.077(9), Ta2−N6 2.069(8), Ta1−N3 2.070(9), Ta1−N4 2.045(9), Ta1−N1−Ta2 82.8(4), N1−Ta2−N2 93.5(4), Ta2−N2−Ta1 83.7(3), N2−Ta1−N1 94.3(4), Ta1−N1−Si1 143.2(6), Ta2−N2−Si2 134.8(5), Ta1−N2−Ta2−N1 155.8(5).

trogen complex $^{15}N_2$-**1** clearly indicate that the coordinated dinitrogen is the source of the N-atoms of the bridging silylimide units of **2**.

Other silanes such as PhSiH$_3$ and Ph$_2$SiH$_2$ also add across the Ta$_2$N$_2$ moiety with similar outcomes as will be reported in due course.

Insight into the intervening processes in this reaction was obtained by periodically observing the ^{31}P{^{1}H} NMR spectra of the reaction of butylsilane and **1**. The first step is an addition reaction analogous to the hydroboration sequence[5] that gives a new N−Si bond and new terminal hydride; the characteristic ^{31}P resonances of **1** convert cleanly to those of complex **3** within 8 h at room temperature. This species has been isolated in excellent yield as crystals from a cooled solution of pentane; its solid-state molecular structure is shown in Figure 2.[9] Complex **3** maps closely onto the N-boryl congener, but the butylsilyl group is clearly not coplanar with the Ta$_2$N$_2$ core. The Ta−N−Si angle is 133.6(5)° versus 163.1(10)° in the N-boryl analogue, and this may indicate a lack of N−Si π overlap and thus a change in hybridization at N1 between the two otherwise very similar complexes. The hydride ligands shown in Figure 2 were not located in the diffraction experiment but were successfully modeled using XHYDEX[10] and are strongly implied by the ^{1}H NMR spectrum of **3**.

Complex **3** is thermally unstable and undergoes spontaneous elimination of H$_2$, cleanly converting to **4** over 8 h at room temperature; this process occurs both in solution and in the solid state. This new species exhibits C_s symmetry in solution in its ^{1}H NMR spectrum; a resonance typical of a terminal tantalum hydride is observed at δ 17.4 ppm, but no resonances suggestive of bridging
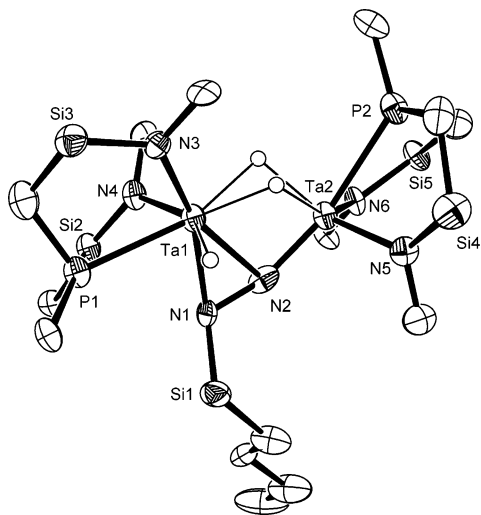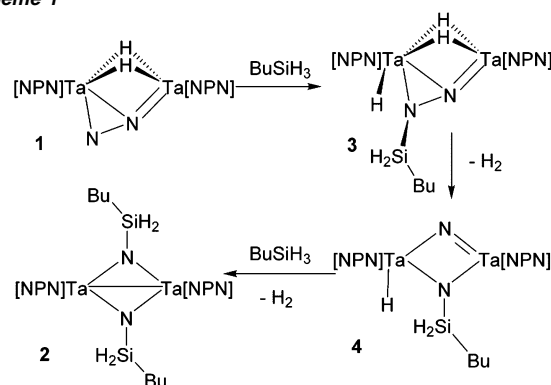
Scheme 1

Figure 2. ORTEP drawing of **3** (ellipsoids at 50% probability, silyl methyl and phenyl carbons other than *ipso* omitted for clarity). Hydrides were placed using XHYDEX. Selected bond lengths (Å) and angles (deg): N1−N2 1.363(13), Ta1−N1 2.181(10), Ta1−N2 2.179(10), Ta2−N2 1.835(10), N1−Si1 1.732(11), Ta1···Ta2 2.8430(9), Ta1−P1 2.583(3), Ta1−N3 2.028-(10), Ta1−N4 1.236(11), Ta2−P2 2.632(3), Ta2−N5 2.044(8), Ta2−N6 2.075(7), Ta1−N1−Si1 133.6(5), Ta1−N1−N2 71.7(6), Ta1−N2−Ta2 89.7(4), N1−Ta1−P1 79.3(3), N1−Ta1−N3 159.5(4), N1−Ta1−N4 87.0-(4), N2−Ta2−P2 166.6(3), N2−Ta2−N5 108.4(4), N2−Ta2−N6 105.8-(4), N1−Ta1−Ta2−N2 1.0(5), Ta2−Ta1−N1−Si1 105.7(8), P1−Ta1−Ta2−P2 −170.6(2).

Supporting Information Available: X-ray and complete experimental details for **2**, **3**, **4**, and isotopomers (PDF). Structural information for **2** and **4** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

hydrides or N−H species are present. We have previously proposed that loss of the bridging hydride ligands via reductive elimination as H$_2$ provides the final two electrons required for overall reductive cleavage of the N−N bond. Evidence for this cleavage event comes from ^{15}N{^{1}H} NMR spectra of the isotopomers $^{15}N_2$-**3** and $^{15}N_2$-**4** prepared using enriched dinitrogen complex $^{15}N_2$-**1**. Scalar coupling of $^1J_{NN}$ = 16.6 Hz between the two resonances in $^{15}N_2$-**3** presumably results from the intact N−N bond. However, the spectrum of $^{15}N_2$-**4** shows no N−N scalar coupling and therefore indicates that N−N bond scission has occurred.[11]

Disilylimide **2** therefore appears to derive from intermediate **4** via a second addition of BuSiH$_3$ across the Ta−N≡Ta unit,[12] a dinuclear reductive elimination of the hydride ligands as H$_2$ completes the process (Scheme 1).[13]

These results suggest three general conclusions regarding the addition of E−H bonds across the dinitrogen unit of **1**. First, the initial reaction involves a common intermediate formed by the addition of 1 equiv of E−H across the π-bond of the ditantalum dinitrogen moiety. Second, this addition triggers loss of the bridging hydride ligands as H$_2$, which provides the two electrons necessary to completely cleave the N−N bond. Third, the reducing power of this system is "built-in" via the reductive elimination of H$_2$, which can occur repeatedly. As **1** is itself derived from a tantalum(IV) hydride dimer that forms via reductive elimination,[14] this finding may bear strongly on the development of catalytic processes for the incorporation of dinitrogen-derived N atoms into other substrates. Such studies are in progress as are investigations into reactions of other organometallic E−H reagents with **1**.

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(7) ^{29}Si NMR spectral data for **2**: (C$_6$D$_6$, 30 °C, 79.5 MHz) δ 8.70, (d, $^2J_{PSi}$ = 7.0 Hz, NSiMe$_2$), −1.74 (dd, $^2J_{PSi}$ = 4.1 Hz, dd, $^2J_{PSi}$ = 3.9 Hz, BuSiμN).
(8) Crystallographic data for **2**: C$_{56}$H$_{84}$N$_6$P$_2$Si$_6$Ta$_2$, triclinic, space group *P*-1, *a* = 11.843(1) Å, *b* = 11.853(1) Å, *c* = 23.382(2) Å, α = 86.68(1)°, β = 76.24(1)°, γ = 79.36(1)°, *Z* = 4, two-component twin, related by 44° rotation normal to (−0.1, −1.0, −1.2), R1, 0.097 (*I* > 2.00σ(*I*)), wR2 0.211.
(9) Crystallographic data for **3**: C$_{52}$H$_{76}$N$_6$P$_2$Si$_5$Ta$_2$, orthorhombic, space group *Pna*21, *a* = 27.600(6) Å, *b* = 17.262(4) Å, *c* = 14.701(3) Å, *Z* = 4, R1, 0.0566 (*I* > 2.00σ(*I*)), wR2 0.1353.
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(11) ^{15}N NMR spectral data for $^{15}N_2$-**3**: (C$_7$D$_8$, −60 °C, 40 MHz) δ −163.5 (d, $^1J_{NN}$ = 16.6 Hz), −52.5 (dd, $^2J_{PN}$ = 26.4 Hz, $^1J_{NN}$ = 16.6 Hz). ^{15}N NMR spectral data for $^{15}N_2$-**4**: (C$_6$D$_6$, 30 °C, 40 MHz) δ 284.4 (b), −44.8 (d, $^2J_{PN}$ = 18.7 Hz).
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