Hydroalumination of a Dinuclear Tantalum Dinitrogen Complex: N−N Bond Cleavage and Ancillary Ligand Rearrangement

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The addition of diisobutylaluminum hydride (DIBAL) to the side-on end-on dinitrogen complex ([NPN]Ta)$_2$(μ-η^1:η^2-N$_2$)(μ-H)$_2$, **1** (where [NPN] = (PhNSiMe$_2$CH$_2$)$_2$PPh), is described. The two end products are diastereomeric rotational isomers in which N−N bond cleavage has occurred with an Al(^{i}Bu)H group attached to one of the nitride atoms. The reaction proceeds through addition of DIBAL to **1** to generate a thermally sensitive intermediate that has been characterized in solution as the result of Al−H addition across the TaN$_2$ moiety, namely, ([NPN]TaH)(μ-η^1:η^2-NNAl^{i}Bu$_2$)(μ-H)$_2$(Ta[NPN), **2**. This material subsequently rearranges via a second thermally labile intermediate to ultimately generate two diastereomeric end products that show N−N bond cleavage, loss of H$_2$, loss of an aluminum isobutyl group, and NPN ligand migration from tantalum to aluminum. Both of these complexes have been isolated in crystalline form and analyzed by single-crystal X-ray diffraction. The second thermally sensitive intermediate has been characterized on the basis of multinuclear NMR spectroscopy as ([NPN]TaH)(μ-η^1:η^2-NNAl^{i}Bu(μ-H))(μ-H)$_2$(Ta[NPN), **3**.

Introduction

In the 40 years since the first report that dinitrogen can bind to metal complexes,[1] considerable sophistication has been attained in the activation of N$_2$ by transition and lanthanide elements.[2−5] Fundamental advances in different synthetic methodologies, structural types, and levels of activation are now well described, as are reactions between activated N$_2$ and electrophiles.[6−8] The most recent fruits of this knowledge include homogeneous systems that produce ammonia stoichiometrically[9] and catalytically,[10] and synthetic methods that use titanium reagents to incorporate dinitrogen-derived N atoms into natural products.[11−17] With respect to the formation of higher value nitrogen-containing materials directly from dinitrogen, new reaction types for coordinated N$_2$ are especially important since they offer other avenues for use of this abundant, yet fundamentally unreactive molecule.[18]

Previous work from our laboratory[19,20] has explored addition reactions of simple hydride reagents (E−H) to the dinuclear tantalum dinitrogen complex, ([NPN]Ta)$_2$(μ-η^1:η^2-N$_2$)(μ-H)$_2$, **1** (where [NPN] = (PhNSiMe$_2$CH$_2$)$_2$PPh). Both hydroboration and hydrosilylation initially result in addition of HBR$_2$ and H$_3$SiR across the coordinated N$_2$ unit to generate a terminal Ta−H and a functionalized dinitrogen moiety with newly formed N−B and N−Si bonds, respectively. These initial addition products are thermally unstable and rearrange by processes that involve N−N bond cleavage and functionalization and, in the case of boron, ancillary ligand degradation. Both of these processes are summarized in Scheme 1. It is proposed that a common intermediate **A** forms via reductive elimination of H$_2$ to generate a species wherein the N−N bond has been cleaved. In the E = B manifold, loss of the N−Ph substituent as benzene and silyl-group migration generate the observed product. In the E = Si manifold, addition of another equivalent of silane, followed by H$_2$ elimination, results in the formation of the bis(silylimide) product. Given the remarkably different outcomes for boron-hydride versus silicon-hydride reagents, we examined other readily available sources of E−H. Herein we report the hydroalumination of **1** with diisobutylalumi-

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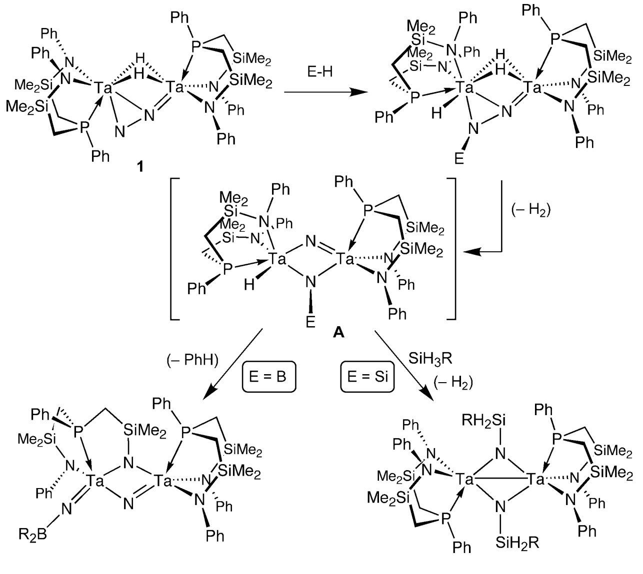
Scheme 1



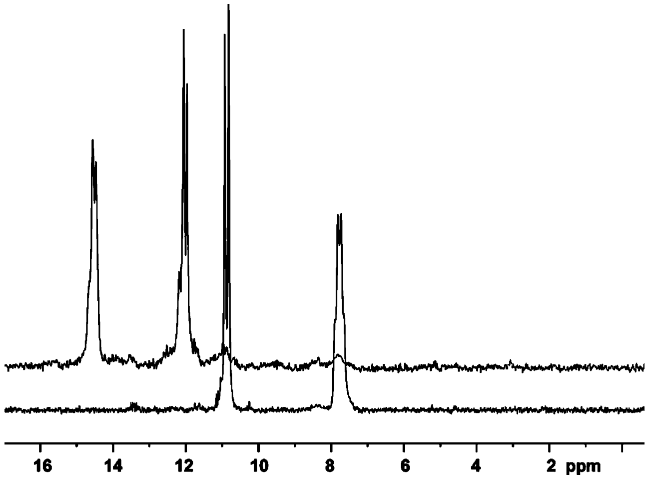


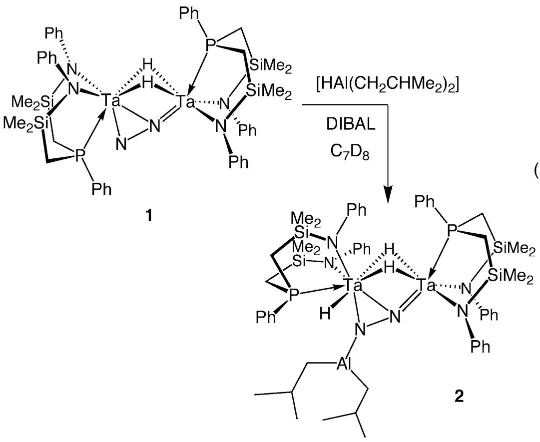
Figure 1. $^{31}P\{^1H\}$ NMR spectra (C_6D_6, 300 K) of **1** before (lower) and of **2** (upper) immediately after addition of 1 equiv of DIBAL. Almost complete conversion to **2** is observed and only a minor amount of **1** remains. The pseudoquartet at δ 7.8 for **1** (lower) and at δ 14.5 for intermediate **2** (upper) is due to additional coupling from the ^{14}N nucleus of the bridging, trans dinitrogen moiety.[21]

num hydride (DIBAL), in which N−N bond cleavage is again observed along with another type of ancillary ligand rearrangement.

Results and Discussion

The reaction between DIBAL (either neat or as a commercially prepared solution) and toluene or benzene solutions of **1** is immediate, as gauged by the rapid color change from red-brown to yellow-brown upon mixing. Monitoring this mixture by ^{31}P NMR spectroscopy shows that an intermediate, **2**, forms quantitatively but persists for only a few hours at room temperature before it converts into other products. Because of the thermal lability of **2**, only solution NMR spectroscopic characterization has been possible. The $^{31}P\{^1H\}$ NMR spectrum of **2** comprises two resonances, δ 12.1 and 14.5, coupled at J_{PP} = 18.3 Hz. The spectrum of **2** as shown in Figure 1 (upper) was obtained immediately after injection of 1 equiv of neat DIBAL into an NMR sample of **1** (lower), showing that the reaction to give **2** is complete in the time taken to reinsert the sample into the probe. This is a marked contrast to the hydroboration and hydrosilylation reactions shown in Scheme 1, each of which requires several hours under normal synthetic conditions (0.02−0.05 M, ambient temperature, aromatic solvent) for the dinitrogen starting complex **1** to be consumed.

The ^1H NMR spectra of **2** obtained at room temperature and at 213 K each show eight discrete silyl methyl resonances, two one-proton resonances at δ 10.1 and 10.8 indicative of chemically inequivalent bridging hydrido ligands, and a new resonance at δ 19.2 that is suggestive of a terminal hydride based on comparison to the boryl and silyl congeners. These findings suggest that the Al−H bond of DIBAL has added across the Ta−N π bond of **1** to give C_1 molecular symmetry, a new N−Al bond, and a new terminal tantalum hydride (eq 1). In terms of chemical shift, the ^{31}P NMR spectrum of **2** is intermediate between that of **1** and the hydroborated or hydrosilylated derivatives of **1**, several of which have been characterized in the solid state.[19,20]



(1)

Intermediate **2** was also characterized by ^{15}N NMR spectroscopy. The $^{15}N\{^1H\}$ NMR spectrum of *$^{15}N_2$*-**2** (prepared by addition of 1 equiv of DIBAL to a sample of *$^{15}N_2$*-**1** in C_7D_8 at −60 °C) is similar to the hydroborated and hydrosilylated derivatives of **1**, in that it features two resonances coupled to each other by 18.7 Hz, diagnostic of an intact N−N bond. The resonance at δ −26.23 shows couplings of J_{NN} = 18.7 Hz and J_{PN} = 26.0 Hz, and the resonance at δ −32.88 shows couplings of J_{PN} = 6.5 Hz and J_{NN} = 18.7 Hz. These resonances can be assigned as the bridging N and the terminal (Al-bound) N of the dinitrogen moiety, respectively, by comparison with the spectra of *$^{15}N_2$*-**1** and a trimethylaluminum adduct of **1** (in which no addition reaction has taken place).[22]

The instability of **2** toward further rearrangement was examined by ^{31}P NMR spectroscopy by following its concentration as a function of time relative to an internal standard. Three new species are observed in solution over the 24 h duration of the experiment, and each one is of sufficiently low symmetry that the phosphines are chemically inequivalent and thus appear

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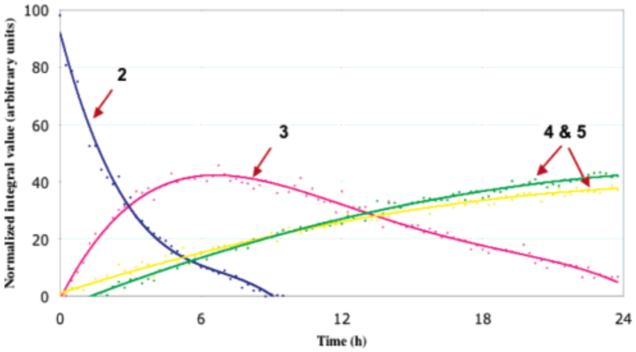

Figure 2. Relative concentrations of species **2**, **3**, **4**, and **5** in solution over time. Concentrations are measured by integration of ^{31}P NMR resonances versus an internal standard.

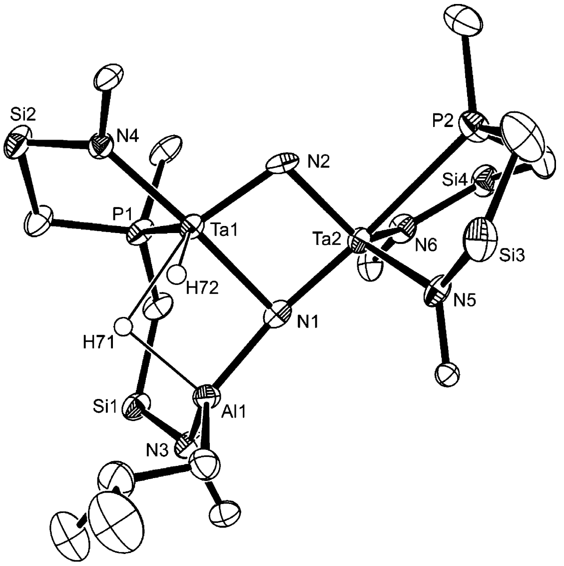

Figure 3. ORTEP drawing of the solid-state molecular structure of **4** as determined by X-ray crystallography (ellipsoids at 50% probability). Silyl methyls and phenyl ring carbons other than ipso are omitted for clarity. H71 was modeled using X-HYDEX,[23] and H72 was located in the difference map; both were refined isotropically. Selected bond distances and angles are presented in Table 1.

as discrete coupled resonances that can be correlated to a particular species. A plot of the integral values of the major species present versus time is shown in Figure 2.

As intermediate **2** decays, a new intermediate **3** is observed that builds up to a maximum concentration after 6 h and then eventually decreases in concentration. Two additional species, **4** and **5**, form in roughly equimolar amounts as the end products of the reaction. Before we discuss our attempts to determine the solution structure of the second intermediate **3**, the solid-state and solution structures of **4** and **5** will be discussed.

The solid-state molecular structure of **4** has been obtained by X-ray crystallography; an ORTEP drawing of **4** is shown in Figure 3. The N1$\cdots$N2 distance is 2.657(3) Å, clearly indicating that N−N bond cleavage has occurred. Metric parameters for the Ta_2N_2 square in **4** are similar to others reported previously in the hydroboration and hydrosilylation of **1**.[19,20] The [NPN] ligand attached to Ta2 is unchanged; however, the [NPN] ligand on Ta1 shows that one amido donor, N3, has migrated to Al1. This aluminum center is attached to N1 and contains only one isobutyl group and bridges to hydride H71. The bridging hydride ligand H71 was modeled using X-HYDEX,[23] while the terminal hydride, H72, was located in the difference map and refined isotropically. In solution, the terminal tantalum hydride is indicated by the presence of a doublet at δ 17.36 (J_{HH} = 11.3 Hz) in the $^1H\{^{31}P\}$ NMR spectrum of **4**. The source of the coupling was not initially obvious. The $^1H/^1H$ COSY spectrum of **4** shows a cross-peak between the terminal hydride and a one-proton resonance at δ 1.23 (doublet, J_{HH} = 11.3 Hz), which is partially occluded by overlap with [NPN] and isobutyl methylene resonances. This latter resonance is assigned to the bridging hydride, Ta(μ-H)Al. The Ta1$\cdots$Al1 distance is 2.9275(15) Å, which is substantially longer than in a previously reported complex featuring a dative Ta−Al bond, a bridging hydride, and a terminal aluminum hydride.[24]

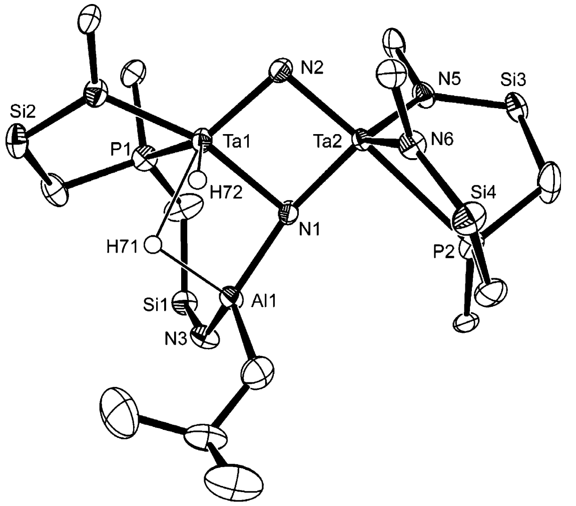

Figure 4. ORTEP drawing of the solid-state molecular structure of **5** as determined by X-ray crystallography (ellipsoids at 50% probability). Silyl methyls and phenyl ring carbons other than ipso are omitted for clarity. H71 and H72 were located in the difference map and refined isotropically. Selected bond distances and angles are presented in Table 1.

Crystals of end product **5** were manually separated from those of **4**. Despite the differences in the $^{31}P\{^1H\}$ NMR spectra of **4** and **5**, the two complexes have identical connectivities in the solid state (the ORTEP drawing of **5** is shown in Figure 4). It is clear that the difference between **4** and **5** is the rotational orientation of the intact [NPN] ligand bound to Ta2. In **4**, the P−Ta−Ta−P dihedral angle is −115.32(5)°, whereas the same angle in **5** is 79.94(4)°. The other significant structural attributes already listed for **4** are all present in **5**. Important metric parameters for the two complexes are compared in Table 1, and details of the diffraction experiments are summarized in Table 2.

Isomers **4** and **5** are consistently obtained in roughly equimolar amounts in approximately 88% combined yield as end products of the reaction given in Scheme 2, which summarizes the chemistry starting from intermediate **2**. These complexes are diastereomeric

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Table 1. Selected Bond Lengths (Å), Angles (deg), and Dihedral Angles (deg) for 4 and 5

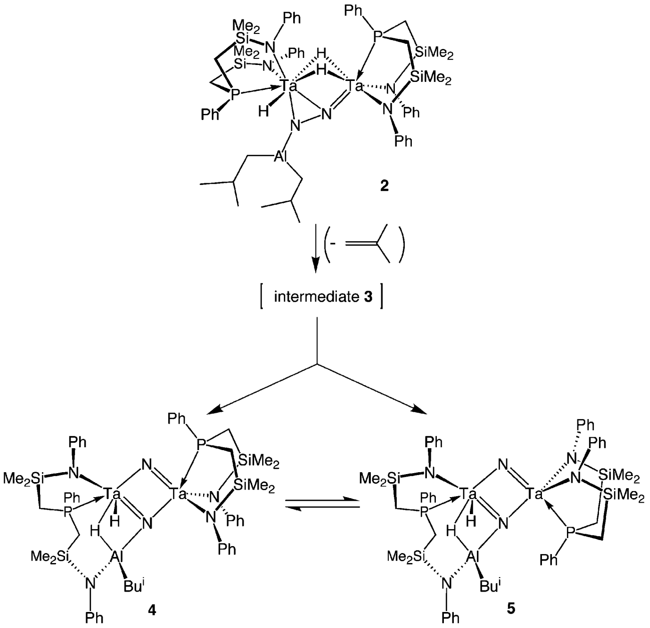
atoms involved:				**4**	**5**
Ta1	N1			2.158(4)	2.098(3)
Ta1	N2			1.861(4)	1.875(3)
Ta2	N1			1.892(4)	1.918(3)
Ta2	N2			1.917(4)	1.907(3)
N1	N2			2.657(3)	2.606(4)
Ta1	Ta2			2.8737(3)	2.84043(19)
Ta1	P1			2.6275(13)	2.6316(9)
Ta1	N4			2.037(4)	2.054(3)
Ta1	Al1			2.9275(15)	2.9105(10)
Ta2	P2			2.7423(13)	2.7273(9)
Ta2	N5			2.053(4)	2.039(3)
Ta2	N6			2.049(4)	2.046(3)
N1	Al1			1.856(4)	1.856(3)
Al1	N3			1.855(4)	1.845(3)
Ta1	N1	Ta2		90.15(16)	89.92(11)
Ta1	N2	Ta2		99.03(17)	97.34(13)
N1	Ta1	N2		82.38(16)	83.56(11)
N2	Ta2	N1		88.43(17)	87.80(12)
Ta1	N1	Al1		93.34(17)	94.60(12)
Ta2	N1	Al1		165.0(2)	156.79(17)
N4	Ta1	P1		77.07(11)	74.22(8)
N1	All	N3		115.25(19)	117.97(14)
P1	Ta1	N1		88.66(10)	90.24(8)
N1	Ta1	N4		165.73(14)	161.03(11)
N5	Ta2	N6		116.10(17)	116.00(12)
P2	Ta2	N1		173.48(12)	90.33(8)
P2	Ta2	N5		73.76(12)	79.69(9)
P2	Ta2	N6		81.21(12)	74.77(9)
Ta1	N1	Ta2	N2	179.7(2)	166.99(17)
P1	Ta1	Ta2	P2	−115.32(5)	79.94(4)
Al1	N1	Ta1	N2	165.64(18)	165.90(14)

Table 2. Crystallographic Data and Structure Refinement for *anti*-[NPN-Al(H)C_4H_9]Ta(μ-N)(μ-N)Ta[NPN] (4) and *syn*-[NPN-Al(H)C_4H_9]Ta(μ-N)(μ-N)Ta[NPN] (5)

	4	**5**
formula	$C_{52}H_{72}N_6Ta_2P_2Si_4Al$	$C_{52}H_{72}N_6Ta_2P_2Si_4Al$
fw	1344.34	1344.34
color, habit	yellow, chip	orange, prism
cryst size, mm	0.20 × 0.15 × 0.10	0.30 × 0.15 × 0.0
cryst syst	orthorhombic	monoclinic
space group	*Pbca*	$P2_1/c$
a, Å	20.4244(5)	19.7152(5)
b, Å	19.9666(5)	13.3919(3)
c, Å	29.2898(8)	22.6221(6)
α, deg	90	90
β, deg	90	101.282(2)
γ, deg	90	90
V, Å^3	11944.6(5)	5857.4(2)
Z	8	4
ρ_{calc}, g/cm^3	1.495	1.52
$F(000)$	5368.00	2680.00
μ(Mo Kα), mm^{-1}	3.848	3.923
transmn factors	0.7124−1.0000	0.69784−1.0000
$2\theta_{max}$, deg	58.24	55.8
total no. of reflns	14 991	46 802
no. of unique reflns	9395	13 747
R_{merge}	0.099	0.045
no. of reflns with $I \geq 2\sigma(I)$	8192	2480
no. of variables	910	729
R (F^2, all data)[a]	0.077	0.040
R_w (F^2, all data)[a]	0.086	0.067
R (F, $I > 2\sigma(I)$)[a]	0.034	0.026
R_w (F, $I > 2\sigma(I)$)[a]	0.079	0.061
gof	0.828	0.87

[a] Rigaku/ADSC CCD diffractometer, $R = \sum||F_o^2| - |F_c^2||/\sum|F_o^2|$; $R_w = (\sum w(|F_o^2| - |F_c^2|)^2$.

Scheme 2



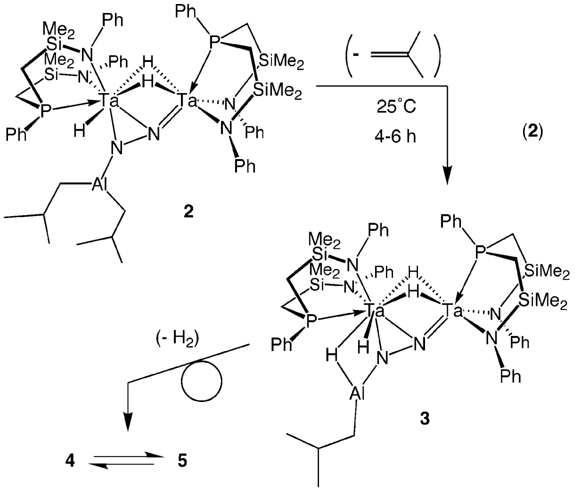
rotational isomers, and traces of one isomer become visible in C_6D_6 solutions of the other if left for several days. To demonstrate that **4** and **5** interconvert, an NMR sample of **4** and **5** (2:1 ratio) with an internal ^{31}P reference standard was subjected to heating; after 3 days at 50 °C, a 1:1 mixture was observed without a decrease in the overall integration of ^{31}P NMR active products versus the internal standard. Higher temperatures led to degradation of the complexes. The process that interconverts **4** and **5** effectively results from rotation of one [NPN] ligand with respect to the Ta_2N_2 core; however, how this occurs has not been investigated.

The formation of **4** and **5** from intermediates **2** and **3** was further investigated by adding DIBAL to the deuterated isotopomer of the starting dinitrogen complex, ([NPN]Ta)$_2$(μ-η^1:η^2-N_2)(μ-D)$_2$, d_2-**1**. In this case, end products **4** and **5** form with concomitant production of D_2 (no HD) as detected by GC-MS; therefore, the hydrides in **4** and **5** originate from the added DIBAL and are not the bridging hydrides in **1** and **2**. It is important to note that loss of H_2 (or D_2) from intermediate **2** is necessary for N−N bond cleavage, as it provides the additional two electrons required for this process, as discussed previously (see Scheme 1).[19,20]

Not including [NPN] ligand amide migration from Ta to Al, the significant differences between the proposed structure for **2** and that of **4** (or **5**) are cleavage of the N−N bond, the presence of only two hydride ligands, and the presence of only one isobutyl substituent on Al. The characteristic cross-peak that correlates the two hydride ligands in the ^{1}H/^{1}H COSY experiment is still present in spectra of complexes **4** and **5** derived from d_2-**1**. The loss of the isobutyl group during this process can be correlated with the detection of isobutene by ^{1}H NMR spectroscopy. In addition, the use of D-Al^{i}Bu$_2$, d_1-DIBAL, in the reaction with **1** results in the isolation of both end products **4** and **5** with the downfield resonance at δ 17.44 missing, clearly indicating that this terminal Ta−H originates from the initial addition of DIBAL and is the same terminal hydride as found in the first intermediate **2**. By process of elimination the bridging hydride in **4** and **5** results from β-elimination of the isobutyl group to aluminum. The cleaved N−N bond of both **4** and **5** was confirmed by ^{15}N NMR spectroscopy using ([NPN]Ta)$_2$(μ-η^1:η^2-$^{15}N_2$)(μ-H)$_2$, $^{15}N_2$-**1**, in the reaction with DIBAL. The resulting ^{15}N-labeled materials both showed resonances that did not display

N−N coupling as observed in the starting material and the first intermediate **2**.

The second intermediate **3** can be inferred to contain an intact N−N bond from its ^{15}N NMR spectrum (acquired at low temperature), which shows $J_{NN} = 19.1$ Hz. Although ^{1}H NMR spectroscopy of $^{15}N_2$-**3** in the absence of **2**, **4**, and **5** has been impossible, mutually coupled hydride resonances at δ 19.0 (terminal), 10.5, and 12.4 (bridging) unique to **3** were identified. Thus, **3** forms when the first intermediate **2** loses isobutene by β-elimination[25,26] and has only one isobutyl group at the Al center (eq 2). Migration of a ligand amide from Ta to Al, reductive elimination of H_2, and N−N bond cleavage complete the overall scheme. We cannot conclusively rule out a [NPN] ligand amide migration to Al from Ta at or prior to this point.



Aluminum has previously been shown to facilitate intramolecular rearrangements in transition metal hydride[27] and amide complexes.[28] It is worth noting that in survey reactions with alkenes and alkynes neither **4** nor **5** react via insertion at the Al−H moiety but rather at the terminal tantalum hydride, as shown by the disappearance of the downfield resonance in clean formation of what we believe are new tantalum alkyls. Although these reactions are relatively clean as observed by ^{31}P NMR spectroscopy, they proceed over several days and, unfortunately, no pure products have been isolated. Simple ^{13}C NMR experiments comparing reactions of **4** and $^{15}N_2$-**4** with ethylene, propylene, and acetylene showed no evidence for formation of N−C bonds, a process of interest to us. Cyclohexene and phenylacetylene did not react with **4** at all. This may indicate that the isobutene elimination is driven partially by steric congestion at Al.

Conclusions

This study extends our understanding of the 1,2-addition of E−H bonds across the side-on Ta−N_2 π bond of dinitrogen complex **1** and provides another example in which the functionalized dinitrogen complex spontaneously and rapidly undergoes N−N bond cleavage triggered by the reductive elimination of H_2. Set in the context of the hydroboration reaction[19] and hydrosilylation,[20] it is clear that the addition of E−H and the resulting cascade of chemical events are strongly influenced by the nature of E. In our previous reports, the initial addition reaction took place on a time scale of hours, whereas hydroalumination with DIBAL takes place in seconds under equivalent reaction conditions. Whereas the hydroborated complex [NPN]Ta(H)(μ-H)$_2$(μ-η^1:η^2-NNB(C_8H_{14}))Ta[NPN] undergoes N−N bond cleavage over several days, both the hydrosilylated and hydroaluminated congeners take only a few hours. The irreversible and obviously undesirable [NPN] ligand degradation found in the hydroboration sequence is not observed here with hydroalumination. Instead, amide ligand migration from tantalum to aluminum occurs. Ligand rearrangments have been reported previously especially when aluminum reagents are added to transition metal complexes.[29,30] The fact that the N−N bond cleavage is preserved across this "family" of reactions indicates that the latent reducing power of the system is a property of **1**. Although the ability to undergo E−H addition is also a property that is (so far) unique to **1**, it is worth noting that Lewis acid−base adducts of **1** are stable complexes that exhibit no tendency toward N−N bond cleavage.[22] We are continuing to examine this system and related derivatives. An obvious tactic is to make the ancillary ligand system more rigid and remove N−Si type linkers in the backbone to try to prevent the kinds of undesirable rearrangements seen here in hydroalumination and, previously, in hydroboration. This is currently underway in our laboratory.[31]

Experimental Section

General considerations for these experiments are published elsewhere,[19] as are the syntheses of **1** and its isotopomers.[21] DIBAL was purchased as a hexanes solution from Aldrich and used either as received or after evaporation of hydrocarbon solvent to a neat liquid. Diisobutylaluminum deuteride was prepared by literature methods.[26] Ethylene, propylene (Praxair), and acetylene (Matheson) were used as obtained from commercial gas suppliers. Phenylacetylene was distilled prior to preparation of a toluene solution of known concentration, which was used in synthesis.

Synthesis and NMR Characterization of [NPN]Ta(H)(μ-η^1:η^2-NNAl(C_4H_9)$_2$)(μ-H)$_2$Ta[NPN], 2. A solution of 40 mg of **1** in roughly 1 mL of d_8-toluene was added to 4.5 mg (0.32 mmol, 1 equiv) of neat DIBAL, and the two reagents were mixed using a Pasteur pipet prior to transfer into a 9 in. Wilmad NMR tube fitted with a Kontes valve. The sample was frozen in liquid nitrogen and flame-sealed before being thawed in an ethanol−liquid nitrogen slurry and inserted into the probe of a Bruker AVA-400 NMR spectrometer that had been cooled to −60 °C. ^{1}H NMR (400 MHz, C_7D_8, 213 K): δ −0.61, −0.55, −0.38, 0.17, −0.05, 0.48, 0.80, 0.83 (s, 3H each, 24H total), SiCH_3; 0.95 (b, 2H) $(CH_3)_2CHCH_2Al$; 0.31, 0.41 (s, 3H each) $(CH_3)_2CHCH_2Al$); 0.66, 1.22, 1.34, 1.46, 1.53, 1.71, 1.79, 1.84 (AMX, 8H total), PCH_2; 1.52 (s, ^{1}H), Al−H; 6.32, 6.50, 6.64, 6.70, 6.83, 6.90, 6.94, 7.20, 7.32, 7.34 (phenyl protons,

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various multiplicities, total 19 H; some resonances obscured by solvent), 7.66 (AMX, 2H, $J_{\mathrm{HH}} = 7.1$ Hz, $J_{\mathrm{PH}} = 1.7$ Hz, PPh *o-H*) 7.77 (AMX, 2H, $J_{\mathrm{HH}} = 7.2$ Hz, $J_{\mathrm{PH}} = 1.3$ Hz, PPh *o-H*), 10.11 (dd, 1H, $^2J_{\mathrm{HH}} = 11.2$ Hz, $^2J_{\mathrm{HP}} = 12.8$ Hz), 10.75 (vq, 1H, $^2J_{\mathrm{HH}} = 11.2$ Hz, $^2J_{\mathrm{HH}} = 11.1$ Hz $^2J_{\mathrm{HP}} = 15.8$ Hz), Ta*H*Ta; 19.20 (dd, 1H, $^2J_{\mathrm{HH}} = 11.1$ Hz, $^2J_{\mathrm{HP}} = 48.2$ Hz), Ta*H*. ^{31}P{^{1}H}NMR (161.9 MHz, C_7D_8, 213 K): δ 12.1 (d, $J_{\mathrm{PP}} = 18.31$ Hz), 14.5 (d, $J_{\mathrm{PP}} = 18.31$ Hz); [NPN] ligand. The product was not isolable and therefore no elemental analysis was obtained.

Synthesis of *$^{15}N_2$*-2. An 80 mg sample of *$^{15}N_2$*-**1** was treated with 9 mg of neat DIBAL in a manner analogous to that reported above for **2**. ^{31}P{^{1}H}NMR (161.9 MHz, C_7D_8, 213 K): δ 12.1 (ddd, $J_{\mathrm{PP}} = 18.31$ Hz, $J_{\mathrm{PN}} = 26.0$ and 6.5 Hz), 14.5 (d, (d, $J_{\mathrm{PP}} = 18.31$ Hz); [NPN] ligand. ^{15}N{^{1}H} NMR (40.6 MHz, C_7D_8, 213 K): δ −26.23 (dd, $J_{\mathrm{PN}} = 26.0$ Hz, $J_{\mathrm{NN}} = 18.7$ Hz), N_b; −32.88 (dd, $J_{\mathrm{PN}} = 6.5$ Hz, $J_{\mathrm{NN}} = 18.7$ Hz), N_t.

Spectroscopic Data for *$^{15}N_2$*-3, ([NPN]TaH)(μ-η^1:η^2-NNAl^{i}Bu(μ-H))(μ-H)$_2$(Ta[NPN). The sample of **2** described above was allowed to stand at room temperature for 8 h before being reinserted into the spectrometer. New resonances present: ^{1}H NMR: 10.50 (dd, 1H, $^2J_{\mathrm{HH}} = 11.1$ Hz, $^2J_{\mathrm{HP}} = 15.0$ Hz), 12.4 (vq, 1H, $^2J_{\mathrm{HH}} = 11.2$ Hz, $^2J_{\mathrm{HH}} = 10.6$ Hz $^2J_{\mathrm{HP}} = 13.6$ Hz), Ta*H*Ta; 19.0 (d, 1H, $^2J_{\mathrm{HH}} = 10.6$ Hz), Ta*H*. ^{31}P{^{1}H} NMR (161.9 MHz, C_7D_8, 213 K): δ −10.9 (d, $J_{\mathrm{PN}} = 4.06$ Hz), 11.2 (s); [NPN] ligand. ^{15}N{^{1}H} NMR (40.6 MHz, C_7D_8, 213 K): δ −25.56 (dd, $J_{\mathrm{PN}} = 4.1$ Hz, $J_{\mathrm{NN}} = 17.9$ Hz), N_b; 31.40 (d, $J_{\mathrm{NN}} = 17.9$ Hz), N_t.

Synthesis of [NPN−$\overline{\text{Al(H)C}_4\text{H}_9\text{]Ta(H)(}\mu\text{-N}}$)($\mu$-N)Ta[NPN], 4 and 5. To a stirred 20 mL toluene solution of **1** (0.5862 g, 0.465 mmol) was added dropwise 0.47 mL of a commercially prepared 1.0 M hexanes solution of diisobutylaluminum hydride in a glovebox. A color change from reddish-brown to yellowish-brown was immediate. The solution was stirred for 24 h, and the solvents were removed under vacuum. The resulting dark yellow-brown solid was taken up in hexanes. The solution was allowed to rest for 16 h undisturbed, and an initial crop of yellow chip crystals was recovered (281.9 mg, 45.1%, of **4**). The remaining brown hexanes solution was then refrigerated at −60 °C for 2 days, allowing recovery of a crop of orange prismatic crystals (270.0 mg, 43.2%, of **5**, overall yield 88.3%). The crystals were used for elemental, X-ray crystallographic, and NMR spectroscopic analyses.

Characterization of *anti*-[NPN−$\overline{\text{Al(H)C}_4\text{H}_9\text{]Ta(}\mu\text{-N}}$)($\mu$-N)Ta[NPN], 4. ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ −0.62, −0.27, −0.15, −0.12, 0.03, 0.15, 0.19, 0.59 (s, 3 H each, 24H total, Si*CH_3*), 1.06, 1.24 (d, 3H each, $^3J_{\mathrm{HH}} = 7$ Hz, (C*H*$_3$)$_2$CHCH$_2$Al), 1.05 (m, 1H (CH$_3$)$_2$C*H*CH$_2$Al), 0.57, 0.68 (AMX, ^{1}H each, (CH$_3$)$_2$CHC*H*$_2$Al), 0.62, 0.65, 1.19, 1.36, 1.42, 1.58, 1.76, 1.82 (AMX, 8H total, PC*H*$_2$), 1.23 (d, 1H, $J_{\mathrm{HH}} = 11.3$ Hz, Al−H), 6.38, 6.52, 6.60, 6.84, 6.90, 6.95, 7.08, 7.12, 7.26, 7.32, 7.41 (phenyl protons, various multiplicities, total 22 H), 8.09 (AMX, 2H, $J_{\mathrm{HH}} = 6.95$ Hz, $J_{\mathrm{PH}} = 1.70$ Hz, PPh *o-H*) 8.21 (AMX, 2H, $J_{\mathrm{HH}} = 6.95$ Hz, $J_{\mathrm{PH}} = 1.28$ Hz, PPh *o-H*), 17.36 (dd, 1H, $^2J_{\mathrm{HH}} = 11.3$ Hz, $^2J_{\mathrm{HP}} = 16.6$ Hz, Ta*H*). ^{13}C{^{1}H} NMR (100.6 MHz, C_6H_6, 300 K): δ −1.52, 0.56, 2.62, 3.36, 3.63, 4.33,5.12, 5.94 (s, Si*C*H$_3$), 0.53, 1.02, 1.50, 2.60, 14.08, 15.44, 18.40 (d, P*C*H$_2$), 24.61 (b, Al−CH$_2$), 21.17, 26.73, 28.53 (Al-^{i}Bu), 136.71, 134.91 (ipso P−C$_6$H$_5$), 130.56, 133.00 (ortho P−C$_6$H$_5$), 119.25, 121.52, 122.70, 123.74, 124.04, 126.30, 128.33, 128.54, 128.91, 129.56 (phenyl ring carbons). Note some proton and carbon resonances were eclipsed by solvent. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6, 300 K): δ −22.9 (s, [NPN] ligand), 19.8 (s [NPN] ligand). ^{29}Si-DEPT NMR (79.5 MHz, C_6D_6, 300 K): δ 7.52 (d, $^2J_{\mathrm{PSi}} = 5.9$ Hz), 8.77 (d, $^2J_{\mathrm{PSi}} = 15.1$ Hz), 9.24 (d, $^2J_{\mathrm{PSi}} = 14.2$ Hz), 11.32 (d, $^2J_{\mathrm{PSi}} = 12.9$ Hz); [NPN] ligand. Anal. Calcd for $C_{52}H_{73}N_6P_2Si_4Ta_2Al$: C, 47.42; H, 5.47; N, 6.25. Found: C, 47.47; H, 5.56; N, 6.29.

Characterization of *syn*-[NPN−$\overline{\text{Al(H)C}_4\text{H}_9\text{]Ta(}\mu\text{-N}}$)($\mu$-N)Ta[NPN], 5. ^{1}H NMR (400 MHz, C_6D_6, 300 K): δ −0.58-(3H), −0.22 (3H), −0.10 (6H), 0.16 (3H), 0.24 (3H), 0.36 (3H), 0.47 (3H) (s, 24H total, SiC*H*$_3$), 1.33, 1.87 (d, 3H each, $^3J_{\mathrm{HH}} = 7$ Hz, (C*H*$_3$)$_2$CHCH$_2$Al), 1.91 (m, 1H (CH$_3$)$_2$C*H*CH$_2$Al), 0.95, 1.16 (AMX, ^{1}H each, (CH$_3$)$_2$CHC*H*$_2$Al), 0.87, 1.21, 1.32, 1.41, 1.69, 1.83 (AMX, 5H total, PC*H*$_2$), 1.54 (d, 1H, $J_{\mathrm{HH}} = 12.4$ Hz, Al−H), 6.49, 6.77, 6.82, 6.89, 7.22, 7.34, 7.40, 7.95 (phenyl protons, various multiplicities, total 19 H), 8.15 (AMX, 2H, $J_{\mathrm{HH}} = 6.90$ Hz, $J_{\mathrm{PH}} = 1.58$ Hz, PPh *o-H*) 8.26 (AMX, 2H, $J_{\mathrm{HH}} = 7.15$ Hz, $J_{\mathrm{PH}} = 1.21$ Hz, PPh *o-H*), 15.96 (dd, 1H, $^2J_{\mathrm{HH}} = 12.4$ Hz, $^2J_{\mathrm{HP}} = 17.8$ Hz, Ta*H*). Note some proton resonances were eclipsed by solvent and silylmethyl resonances. ^{31}P{^{1}H}NMR (C_6H_6, 300 K): δ −5.8 (s, [NPN] ligand), 12.4 (s [NPN] ligand). Anal. Calcd for $C_{52}H_{73}N_6P_2Si_4Ta_2Al$: C, 47.42; H, 5.47; N, 6.25. Found: C, 47.49; H, 5.49; N, 6.23.

Synthesis of *$^{15}N_2$*-4. A solution of *$^{15}N_2$*-**1** was treated in a manner similar to the preparation of **4** and **5**. No changes to the ^{1}H NMR spectrum were observed compared to that of **4**. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6, 300 K): δ −22.9 (dd, $^2J_{\mathrm{NP}} = 16.7$ and 8.8 Hz), 19.8 (s), [NPN] ligand. ^{15}N{^{1}H} NMR (C_6D_6 300 K, 40 MHz): δ 57.9 (d, $^2J_{\mathrm{NP}} = 16.7$ Hz), 291.8 (d, $^2J_{\mathrm{NP}} = 8.8$ Hz).

Synthesis of *$^{15}N_2$*-5. A solution of *$^{15}N_2$*-**1** was treated in a manner similar to the preparation of **4** and **5**. No changes to the ^{1}H NMR spectrum were observed compared to that of **3** and **4**. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6, 300 K): δ −5.8 (d, $^2J_{\mathrm{NP}} = 10.1$ Hz), 12.4 (s), [NPN] ligand. ^{15}N{^{1}H} NMR (C_6D_6 300 K, 40 MHz): δ 54.8 (s), 313.9 (d, $^2J_{\mathrm{NP}} = 10.1$ Hz).

^{31}P NMR Spectroscopic Investigation of the Reaction of 1 with DIBAL. A 9 in. Wilmad NMR tube was charged with 40.2 mg of **1** in roughly 1 mL of C_6D_6 and a sealed glass capillary tube containing neat P(OMe)$_3$ as an internal reference. The tube was sealed with a 5 mm rubber septum and wrapped with ParaFilm laboratory film and inserted into the probe of a Bruker AVA-400 NMR spectrometer. The spectrometer was programmed to observe consecutive sets of ^{1}H{^{31}P} and ^{31}P{^{1}H} spectra every 15 min for 25 h. After initial spectrometer calibration was performed, the sample was ejected and 4.5 mg of neat DIBAL (0.32 mmol, 1 equiv) in roughly 0.25 mL of C_6D_6 was added as a bolus through the septum using a 20-gauge hypodermic needle. The reagents were mixed by brief inversion of the tube before the sample was returned to the probe and automated acquisition was begun. Individual resonances were integrated with respect to the internal standard. Similar experiments using *d_2*-**1** and *$^{15}N_2$*-**1** were also conducted.

Synthesis of *d_2*-2 and Its Decomposition. A toluene solution of *d_2*-**1** in a sealed flask was treated in a manner similar to the preparation of **2**, giving *d_2*-**2**. The solution was frozen in liquid nitrogen and sealed under vacuum, after which it was allowed to stir overnight. The headspace gas was analyzed by GC/MS, showing D_2 gas and no HD gas.

Interconversion of 4 and 5. In a glovebox, 2:1 and 1:2 mixtures of **4** and **5** were dissolved in C_7D_8 and transferred to an 8 in. Wilmad NMR tube, which was capped with a plastic stopper and sealed with ParaFilm laboratory film. Samples were observed initially and again after 24 h, after which no change in integration values was observed. In both cases heating overnight at 60 °C led to 1:1 mixtures with minimal loss of ^{31}P-active species.

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Supporting Information Available: X-ray crystallographic data for **4** and **5** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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