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Synthetic and Mechanistic Investigations of Trimethylsilyl-Substituted Triamidoamine Complexes of Tantalum That Contain Metal−Ligand Multiple Bonds

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Abstract: $[N_3N]Ta{=}PPh$ ($[N_3N]^{3-} = [(Me_3SiNCH_2CH_2)_3N]^{3-}$) reacts with excess lithium metal in tetrahydrofuran to give "$[N_3N]Ta{=}PLi$", as judged by NMR studies and by reactions with RX at −35 °C to afford the phosphinidene complexes $[N_3N]Ta{=}PR$ (R = Me, *n*-Bu, $SiMe_3$, $SiMe_2Ph$). $[N_3N]TaCl_2$ reacts with 2 equiv of LiN(H)R (R = H, CMe_3, Ph) to produce 1 equiv of RNH_2 and imido complexes $[N_3N]Ta{=}NR$ and with 2 equiv of benzylmagnesium chloride or ((trimethylsilyl)methyl)lithium to afford the alkylidene complexes $[N_3N]Ta{=}CHR$ (R = Ph or $SiMe_3$). The ethylene complex $[N_3N]Ta(C_2H_4)$ is formed quantitatively upon addition of 2 equiv of ethylmagnesium chloride to $[N_3N]TaCl_2$. $[N_3N]Ta(C_2H_4)$ decomposes in a first-order manner in solution over a period of days at room temperature to give a complex in which a C−N bond in the TREN backbone has been cleaved. Alkylation of $[N_3N]TaCl_2$ with 2 equiv of RCH_2CH_2MgX (R = CH_3, CH_2CH_3, $CH(CH_3)_2$, $C(CH_3)_3$; X = Cl or Br) produces a mixture of alkylidene and products derived from decomposition of the incipient olefin complex. When R = *t*-Bu, only an alkylidene complex is formed as a consequence of a sterically disfavored β abstraction process. $[N_3N]TaCl_2$ reacts with 2 equiv of vinylmagnesium bromide to afford white crystalline $[N_3N]Ta(C_2H_2)$. An analogous benzyne complex can be prepared by refluxing $[N_3N]TaCl_2$ with 2 equiv of phenyllithium in toluene. $[N_3N]Ta(C_2H_4)$ reacts with a catalytic amount of phenylphosphine to afford $[N_3N]Ta{=}CHMe$, while reactions with ammonia, aniline, or pentafluoroaniline yield $[N_3N]Ta{=}NR$ complexes. In contrast, excess Me_3SiAsH_2 reacts with $[N_3N]Ta(C_2H_4)$ to afford $[N_3N]Ta{=}CHMe$ first, and then what is proposed to be $[N_3N]Ta{=}AsSiMe_3$. $[N_3N]Ta(C_2H_4)$ reacts with dihydrogen to give $[N_3N]Ta(H)(C_2H_5)$ reversibly. $[N_3N]Ta(C_6H_4)$ reacts with $ArNH_2$ (Ar = Ph, C_6F_5) to give $[N_3N]Ta{=}NAr$ complexes, but $[N_3N]Ta(C_2H_2)$ is relatively unreactive. X-ray structures of $[N_3N]Ta(Me)Et$ and $[N_3N]Ta(C_2H_2)$ are included.

Introduction

Recent efforts in these laboratories[1−10] and others[11−19] have focused on the preparation of complexes of metals in groups 4, 5, and 6 that contain tetradentate triamidoamine ligands, $[(RNCH_2CH_2)_3N]^{3-}$. When R is a bulky silyl group (usually $SiMe_3$), rare types of complexes can be prepared, e.g., a tantalum(V) phosphinidene,[3] a V=NH species,[6] and molybdenum and tungsten terminal phosphido complexes.[10] Key features of complexes that contain a $[(RNCH_2CH_2)_3N]^{3-}$ ligand include the sterically protected "pocket" formed by the bulky R groups and the presence of one σ-type and two orthogonal π metal orbitals directed toward the remaining (fifth) coordination site. This orbital arrangement is ideally suited for forming d^0 complexes that contain a triple bond or pseudo triple bond between the metal and the ligand in the apical coordination site, a double and a single bond, or (sterically least feasibly) three single bonds. (The $[(RNCH_2CH_2)_3N]^{3-}$ ligand itself is only a 12-electron donor ($4\sigma,2\pi$) since one of the three linear combinations of atomic orbitals constructed from the p orbitals on the three amido nitrogens is a ligand-centered nonbonding orbital.) In view of tantalum's ability to form multiple bonds to C, N, or O,[20] and because many starting materials are readily available, we chose to explore the chemistry of $[(Me_3SiNCH_2CH_2)_3N]Ta(X)$ complexes that contain a multiple Ta−X bond. We first reported that $[N_3N]TaCl_2$ ($[N_3N]^{3-} = [(Me_3SiNCH_2CH_2)_3N]^{3-}$) reacts with 2 equiv of a lithium phosphide LiP(H)R (R = Ph, Cy, *t*-Bu) to afford 1 equiv of RPH_2 and gold crystalline d^0 phosphinidene complexes, $[N_3N]Ta{=}PR$, in moderate to high yields.[3] An X-ray crystal structure of $[N_3N]Ta{=}PCy$ revealed

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Table 1. ^{31}P NMR Data and Yields for Phosphinidene Complexes

RX	product	^{31}P δ	yield^{a} (%)
MeI	**1a**	157	33
n-BuBr	**1b**	186	68
Me_3SiCl	**1c**	212^{b}	58
$PhMe_2SiCl$	**1d**	203^{c}	77

[a] Determined via ^{1}H NMR with a $(Me_3Si)_2O$ internal standard. [b] $\Delta\nu_{1/2} \approx$ 3600 Hz (23 °C), 400 Hz (−30 °C), 300 Hz (−60 °C). [c] $\Delta\nu_{1/2} \approx$ 3600 Hz (23 °C), 800 Hz (−30 °C), 400 Hz (−60 °C).

an essentially linear Ta−P−C angle and a Ta−P bond length (2.145 Å) consistent with a pseudo triple bond between Ta and P. We subsequently turned to the synthesis and reactions of alkylidene, olefin, and acetylene complexes.[5] Full details and additional results in both areas are reported here.

Results

Synthesis of Tantalum Phosphinidene and Imido Complexes. We became interested in the possibility of preparing the parent phosphinidene complex, $[N_3N]Ta{=}PH$, or the terminal phosphido complex, $\{[N_3N]Ta{\equiv}P\}^-$. We found that $[N_3N]Ta{=}PPh$ reacts with excess lithium metal in tetrahydrofuran to give a species whose ^{31}P NMR spectrum reveals a resonance at 575 ppm ($\Delta\nu_{1/2} \approx$ 600 Hz). This species reacts at −35 °C with alkyl and silyl halides to yield the phosphinidene complexes $[N_3N]Ta{=}PR$ (R = Me, *n*-Bu, $SiMe_3$, $SiMe_2Ph$), **1a−d** (eq 1), according to ^{31}P NMR data. The yields of the phosphinidene complexes, as judged by proton NMR versus an internal standard, are listed in Table 1. The NMR yields are modest, and isolated yields are poor (10−20%) as a consequence of the extreme solubility of the phosphinidene complexes in common organic solvents. The formulations of **1a−d** are confirmed by reactions with pivaldehyde to yield $[N_3N]Ta{=}O$ and the corresponding *trans*-phosphaalkenes, which were identified by ^{1}H and ^{31}P NMR, a reaction that is known for several isolated tantalum phosphinidene complexes.[3] We have also prepared complex **1b** as shown in eq 2, although the isolated yield is again low (10%) as a consequence of the high solubility of **1b** in common organic solvents.

$$[N_3N]Ta{=}PPh \xrightarrow[\text{2. 3 equiv of RX, THF, }-35\ ^\circ\text{C}]{\text{1. 5 equiv of Li, THF}} \underset{\textbf{1a−d}}{[N_3N]Ta{=}PR} + PhR + 2LiX \quad (1)$$

$$R = Me\ (\textbf{1a}),\ n\text{-Bu}\ (\textbf{1b}),\ SiMe_3\ (\textbf{1c}),\ SiMe_2Ph\ (\textbf{1d})$$

$$[N_3N]TaCl_2 \xrightarrow[Et_2O,\ -35\ ^\circ C]{2LiP(H)\text{-}n\text{-Bu}} \underset{\textbf{1b}}{[N_3N]Ta{=}P\text{-}n\text{-Bu}} + n\text{-}BuPH_2 \quad (2)$$

A puzzling fact is that the phosphorus resonances in compounds **1** are broad, especially those in **1c** and **1d**. Alkyl- and arylphosphinidenes exhibit a ^{31}P resonance with a half-height width of 100−200 Hz at 25 °C, while the analogous resonances in **1c** and **1d** have widths of 300−400 Hz at −60 °C. We currently attribute the broadened phosphinidene phosphorus resonances to coupling to ^{181}Ta, but why coupling is greater in the silyl-substituted phosphinidene complexes is unclear. Broadened resonances are not found in proton NMR spectra.

The intermediate whose ^{31}P NMR spectrum contains a resonance at 575 ppm ($\Delta\nu_{1/2} \approx$ 600 Hz) we propose to be "$[N_3N]Ta{=}PLi$", rather than $\{[N_3N]Ta{\equiv}P\}^-$. The primary reason is that the chemical shifts of the terminal phosphido ligands in related neutral d^0 complexes, $[N_3N]Mo{\equiv}P$,[10] $[N_3N]W{\equiv}P$,[10] and $[(t\text{-Bu})NAr]_3Mo{\equiv}P$[21] (Ar = 3,5-$Me_2C_6H_3$), range from 1080 to 1346 ppm. Therefore a chemical shift of 575 ppm, even though it is ∼400 ppm larger than that in a typical Ta=PR species (∼200 ppm), we believe to be too small to ascribe to a "$\{[N_3N]Ta{\equiv}P\}^-$" species, i.e., one in which lithium is not bound to the phosphorus. Since bent phosphinidenes are characterized by a more downfield resonance (335 ppm in $(t\text{-}Bu_3SiO)_3Ta{=}PPh$[22] and 600−800 ppm in $Cp_2M{=}PR$ complexes (M = Mo, W, Zr)[23−25]), a chemical shift of 575 ppm would be more consistent with a "$[N_3N]Ta{=}PLi$" species in which the Ta−P−Li bond angle is less than 180°. Unfortunately, we could find no way to separate the "$[N_3N]Ta{=}PLi$" species from phenyllithium, the other product of the cleavage reaction, and so could not isolate and structurally characterize it.

All attempts to prepare $[N_3N]Ta{=}PH$ so far have failed. For example, the reaction of $[N_3N]TaCl_2$ with 2 equiv of $LiPH_2$ in 1,2-dimethoxyethane at −78 °C afforded intractable products, while quenching "$[N_3N]Ta{=}PLi$" with proton sources such as $HNMe_3Cl$ or 2,6-lutidinium triflate led to complex mixtures in which no species could be identified.

$[N_3N]TaCl_2$ reacts with 2 equiv of LiN(H)R (R = H, CMe_3, Ph) to produce 1 equiv of RNH_2 and imido complexes **2a−c** in 62−95% yield (eq 3). The synthesis of **2a** is noteworthy, as parent imido complexes are relatively rare.[6,26−29] NMR and IR spectra of **2a** are similar to those for $[N_3N]V{=}NH$, which has been structurally characterized.[6] A notable difference is that the imido proton resonance is observed as a broad 1:1:1 triplet ($^1J_{^{14}NH}$ = 50 Hz) in **2a** whereas it is not seen in the ^{1}H NMR spectrum of $[N_3N]V{=}NH$, presumably as a consequence of additional coupling to ^{51}V ($I = {}^7/_2$, 99.75%). Resolved coupling between the imido proton and ^{14}N has also been observed in $Cp^*MMe_3(NH)$ (M = Mo, W) complexes[27,28] and was attributed to a low electric field gradient about the imido nitrogen.[30] The white crystalline imido complexes are stable when heated as ∼0.1 M solutions in toluene-d_8 in sealed NMR tubes to 110 °C for several days. They do not react with benzaldehyde in benzene-d_6 (∼0.1 M in Ta, 2 days) at ∼25 °C to yield known $[N_3N]Ta{=}O$.[3]

$$[N_3N]TaCl_2 \xrightarrow[\substack{Et_2O\ (R\,=\,CMe_3,\ Ph)\\ THF\ (R\,=\,H)\\ -35\ ^\circ C}]{2LiN(H)R} \underset{\textbf{2a−c}}{[N_3N]Ta{=}NR} + RNH_2 \quad (3)$$

$$R = H\ (\textbf{2a}),\ CMe_3\ (\textbf{2b}),\ Ph\ (\textbf{2c})$$

Synthesis and Reactivity of Tantalum Alkylidene Complexes. $[N_3N]TaCl_2$ reacts with 2 equiv of ((trimethylsilyl)-

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methyl)lithium or benzylmagnesium chloride to afford the alkylidene complexes **3a** and **3b** (eq 4) in >90% yield. We propose that dialkyl complexes are intermediates in these reactions for several reasons. First, if only 1 equiv of alkylating agent is employed, $[N_3N]Ta(CH_2Ph)Cl$ and $[N_3N]Ta(CH_2SiMe_3)Cl$ can be isolated by fractional crystallization, and each is converted into the expected alkylidene upon reaction with an additional 1 equiv of the appropriate metal alkyl. Second, reaction of $Li_3[N_3N]$ with $Ta(CH_2R)_2Cl_3$ (R = Ph,[31] CMe_3[32]) gives **3b** and **3c** (eq 5) in yields of 86% and 56%, respectively. Complexes **3a**−**c** show no signs of decomposition in toluene-d_8 (∼0.1 M) after being heated for days in sealed tubes at 110 °C. They react rapidly with aldehydes to afford a mixture of $[N_3N]Ta{=}O$ and *cis*- and *trans*-isomers of the expected olefin. A variety of tantalum alkylidene complexes are known to react readily with aldehydes in this manner.[20,33]

$$[N_3N]TaCl_2 \xrightarrow[\text{Et}_2\text{O},\ -35\ ^\circ\text{C}]{\text{dialkylation}} \underset{\textbf{3a,b}}{[N_3N]Ta{=}CHR} + RCH_3 \qquad (4)$$

$$R = SiMe_3\ (\textbf{3a};\ LiCH_2SiMe_3),\ Ph\ (\textbf{3b};\ PhCH_2MgCl)$$

$$Ta(CH_2R)_2Cl_3 \xrightarrow[\text{Et}_2\text{O},\ -35\ ^\circ\text{C}]{Li_3[N_3N]} \underset{\textbf{3b,c}}{[N_3N]Ta{=}CHR} + RCH_3 \qquad (5)$$

$$R = Ph\ (\textbf{3b}),\ CMe_3\ (\textbf{3c})$$

Complexes **3a**−**c** all have NMR spectra consistent with 3-fold symmetry on the NMR time scale. H_α resonances are found near 0 ppm in ^1H NMR spectra, a region characteristic of alkylidenes that are highly "distorted" through an α-agostic[34] CH interaction,[20,35] and ^{13}C NMR spectra show an alkylidene carbon resonance in the range 200−215 ppm. We were surprised by the unusually low values for $^1J_{CH_\alpha}$ (∼70 Hz), the lowest known for d^0 alkylidene complexes.[20] The alkylidene ligands are effectively pseudo triply bound to tantalum as $1\sigma,2\pi$ ligands. In spite of the fact that the π interactions in the apical position are of two distinct types, all alkylidene complexes show 3-fold symmetry on the NMR time scale down to −90 °C. Apparently only steric constraints would lead to a breaking of the d_{xz}/d_{yz} degeneracy and slowing of "rotation" of the alkylidene about the Ta−C bond. Such steric constraints would seem to be minimal, if the $Ta{=}C_\alpha{-}C_\beta$ angle is relatively large. No crystals suitable for X-ray studies have yet been obtained, although an X-ray study of a related $Et_3SiTREN$ alkylidene complex of tantalum has recently confirmed that the $Ta{=}C_\alpha{-}C_\beta$ angle is indeed large (>170°)[36] and, therefore, that a large $Ta{=}C_\alpha{-}C_\beta$ angle should be expected for any alkylidene complex in this category.

Synthesis of a Tantalum Ethylene Complex. α versus β Abstraction Processes. An ethylene complex (**4**) is formed quantitatively upon addition of 2 equiv of ethylmagnesium chloride to $[N_3N]TaCl_2$ (eq 6). An alternate route to **4** consists of alkylation of $[N_3N]Ta(Me)OTf$[5] with 1 equiv of ethylmagnesium chloride. Proton and carbon NMR spectra of **4** are consistent with it being a 3-fold-symmetric complex on the NMR time scale, even at −90 °C. The ethylene ligand is observed as a singlet at 2.15 ppm in the proton NMR spectrum and a triplet ($^1J_{CH}$ = 144 Hz) at 62.6 ppm in the ^{13}C NMR spectrum. We propose that **4** has a structure similar to that of $[N_3N]Ta(C_2H_2)$ (vide infra) in the solid state, i.e., one in which the C−C axis of the ethylene is lined up with one of the Ta−N bonds, but that the ethylene rotates readily in solution to give a C_3-symmetric species on the NMR time scale as a consequence of the degeneracy of the d_{xz} and d_{yz} orbitals.

$$[N_3N]TaCl_2 \xrightarrow[\text{Et}_2\text{O},\ -35\ ^\circ\text{C}]{2EtMgCl} \underset{\textbf{4}}{[N_3N]Ta(C_2H_4)} \qquad (6)$$

Reaction of $[N_3N]TaCl_2$ with only 1 equiv of ethyl Grignard reagent yields the yellow crystalline monoethyl derivative **5** in 72% yield (eq 7). **5** reacts immediately with 1 equiv of ethylmagnesium chloride to yield **4**, and with 1 equiv of CD_3CD_2MgBr to afford a 5.7:1 mixture of $[N_3N]Ta(C_2H_4)$ and $[N_3N]Ta(C_2D_4)$. The labeling experiment suggests that the intramolecular isotope effect for β abstraction in the diethyl intermediate is 5.7.

$$[N_3N]TaCl_2 \xrightarrow[\text{Et}_2\text{O},\ -35\ ^\circ\text{C}]{EtMgCl} \underset{\textbf{5}}{[N_3N]Ta(Et)Cl} \qquad (7)$$

Although **4** is formed upon treatment of $[N_3N]Ta(Me)OTf$ with 1 equiv of ethylmagnesium chloride over a period of 1 day, $[N_3N]Ta(Me)Cl$ reacts with 1 equiv of ethyl Grignard under the same conditions to afford a 2:1 mixture of **4** and $[N_3N]Ta(Me)Et$ (**6**, eq 8). $[N_3N]Ta(Me)Et$ can be isolated as a yellow crystalline solid via fractional recrystallization. It shows 3-fold symmetry on the NMR time scale. Over a period of 1 day at ∼25 °C, **6** decomposes to yield **4** and methane. At 52 °C in toluene-d_8, decomposition of **6** was shown to follow first-order kinetics with $k = 2.4(1) \times 10^{-4}\ s^{-1}$ (two runs). $[N_3N]Ta(Me)Et$ is also formed in the reaction between $[N_3N]Ta(Et)Cl$ and 1 equiv of methylmagnesium chloride.

$$[N_3N]Ta(Me)Cl \xrightarrow[\text{Et}_2\text{O},\ -35\ ^\circ\text{C}]{EtMgCl} \underset{\textbf{4}}{[N_3N]Ta(C_2H_4)} + \underset{\textbf{6}}{[N_3N]Ta(Me)Et} \qquad (8)$$

An X-ray structure of **6** (Table 2; Figure 1) shows it to be a six-coordinate species with methyl and ethyl ligands in apical coordination sites that lie approximately in the N(2)−Ta−N(4) plane. (Relevant bond lengths and angles are listed in Table 3.) The smaller methyl group is pointed toward N(2). Consequently, the Ta−N(2)−Si(2) angle (136°) is somewhat larger than the other two Ta−N−Si angles (129° and 132°), but all are larger than the usual values of 125−126 °C in crystallographically characterized $M[N_3N]$ species.[1−3,6,9,10,19] Since the ethyl ligand points away from the methyl group and between N(1) and N(3), the N(1)−Ta−N(3) angle opens to 133°, compared to 104° and 100° for the other two N−Ta−N angles. The distance between C_β of the ethyl group and Ta is 3.14 Å, too far for any β agostic interaction; in any case there is no readily available orbital with which the methyl CH bond can interact when the ethyl group is oriented in the observed manner. Therefore we propose that β abstraction first involves rotation of the ethyl group past one $SiMe_3$ group, possibly with concomitant "dissociation" of the amine nitrogen donor from the metal, followed by activation of H_β through an agostic interaction with the remaining π orbital that lies in a plane approximately 90° to that containing Ta, C(9), and C(7). The

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Table 2. Crystallographic Data, Collection Parameters, and Refinement Parameters for $[N_3N]Ta(Me)Et$ (**6**) and $[N_3N]Ta(C_2H_2)$ (**8**)

	$[N_3N]Ta(Me)Et$	$[N_3N]Ta(C_2H_2)$
empirical formula	$C_{18}H_{47}N_4Si_3Ta$	$C_{17}H_{41}N_4Si_3Ta$
formula wt	584.80	566.74
cryst color, habit	yellow, plate	colorless, needle
cryst dimens (mm)	0.150 × 0.150 × 0.05	0.280 × 0.120 × 0.120
cryst syst	monoclinic	orthorhombic
no. reflns used for unit cell determination (2θ range, deg)	25 (14.0− 22.0)	25 (15.0− 25.0)
a (Å)	10.0504(8)	17.154(1)
b (Å)	15.010(1)	16.756(1)
c (Å)	17.937(1)	34.365(3)
β (deg)	95.79(1)	90.0
V (Å^3)	2692.1(6)	9878(2)
space group	$P2_1/n$	$Pbca$
Z	4	8
D_{calc} (g/cm^3)	1.443	1.525
F_{000}	1192	4528
μ(Mo Kα) (cm^{-1})	41.75	45.47
scan type	$\omega-2\theta$	$\omega-2\theta$
temp (°C)	−86	−72
total no. of unique reflns	3679	9483
no. of observations with $I > 3.00\sigma(I)$	2270	5137
no. of variables	235	439
R	0.041	0.048
R_w	0.035	0.053
GOF	1.25	3.42

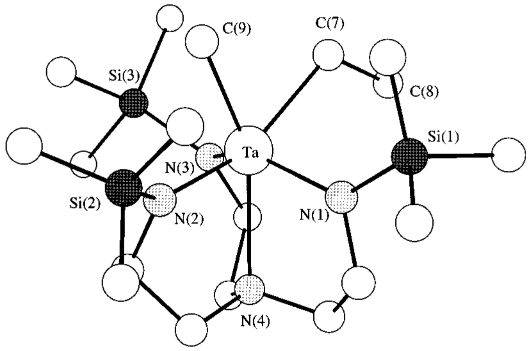


Figure 1. X-ray crystal structure of $[N_3N]Ta(Me)Et$ (**6**).

Ta−N(4) distance (2.444 Å) is comparable to that found in $[N_3N]Ta{=}Te$ (2.487 Å),[11] but is somewhat longer than found in $[N_3N]Ta(HC{\equiv}CH)$ (2.30 Å; see later).

$[N_3N]Ta(Et)Cl$ reacts with 1 equiv of benzylmagnesium chloride to yield **4**. If only 0.5 equiv of Grignard is used, the proton NMR spectrum shows no evidence for $[N_3N]Ta(CH_2Ph)Cl$ formed by alkyl exchange. $[N_3N]Ta(CH_2Ph)Cl$ similarly reacts with 1 equiv of ethylmagnesium chloride to afford **4**. We propose that $[N_3N]Ta(Et)(CH_2Ph)$ is the intermediate in each of these reactions. The benzylidene complex (**3b**) is not formed in either reaction.

$[N_3N]Ta(C_2H_4)$ is not stable in solution. After a period of several days at ~25 °C, solutions of **4** show signs of decomposition; the red color lightens, and NMR spectra consistent with formation of the yellow ethyl complex **7b** (eq 9) are observed. Decomposition of a toluene solution of **4** ([**4**] = 0.0059, 0.0089, 0.010, 0.012 M) was followed by UV/vis at 494 nm and shown to be first order in tantalum with $k = 1.37(1) \times 10^{-4}$ s^{-1} at 70 °C. Most prominent in the ^1H NMR spectrum of **7b** are the vinyl resonances, a doublet of doublets at 6.49 ppm and a doublet at 4.25 ppm. (The latter is obscured by the 4.07 ppm resonance for the diastereotopic ligand methylene protons.) The triplet and quartet resonances for the ethyl ligand are found at 1.93 and 1.46 ppm, respectively. Heating of a toluene-d_8 solution of $[N_3N]Ta(C_2D_4)$ at 110 °C in a sealed tube yields a product analogous to **7b** that contains a $TaCD_2CD_2H$ group. At 70 °C $k_D = 1.53(2) \times 10^{-4}$ s^{-1} for a k_H/k_D of 0.89(2), consistent with a change in hybridization of the ethylene carbon atoms from sp^2 to sp^3 in the rate-limiting step.[37] Proton and carbon NMR spectral data are similar to those for the product resulting from the thermolysis of $[(Et_3SiNCH_2CH_2)_3N]Ta(C_2H_4)$, whose structure has been determined in an X-ray study.[36] Thermolysis of $[N_3N]Ta(C_2D_4)$ (0.03 M in toluene-d_8) in the presence of 1 atm of ethylene produces only a $TaCD_2CD_2H$ species. All of these data are consistent with decomposition of **4** by intramolecular β abstraction of a proton from the side chain of the amido ligand. The TREN backbone must turn and flex to a considerable degree, possibly after dissociation of the apical nitrogen donor atom, in order to present the C−H$_\beta$ bond to the metal for removal of H$_\beta$ and transfer to the ethylene ligand. Formation of **7b′** would constitute removal of a γ proton if the apical donor nitrogen were not coordinated at the time.

Table 3. Selected Intramolecular Distances[a] and Angles[b] for the Non-Hydrogen Atoms of $[N_3N]Ta(Me)Et$ and $[N_3N]Ta(C_2H_2)$

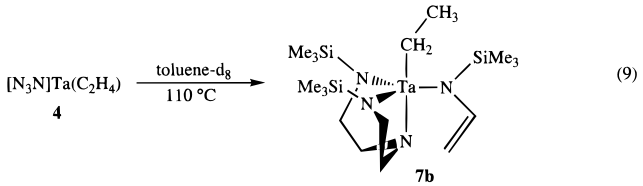
Bond Lengths

$[N_3N]Ta(Me)Et$		$[N_3N]Ta(C_2H_2)$	
Ta−N(1)	2.00(1)	Ta−N(1)	2.07(1)
Ta−N(2)	2.071(9)	Ta−N(2)	2.02(1)
Ta−N(3)	1.956(9)	Ta−N(3)	2.04(1)
Ta−N(4)	2.444(8)	Ta−N(4)	2.30(1)
Ta−C(7)	2.21(1)	Ta−C(7)	2.09(1)
Ta−C(9)	2.21(1)	Ta−C(8)	2.10(1)
C(7)−C(8)	1.55(2)	C(7)−C(8)	1.26(2)

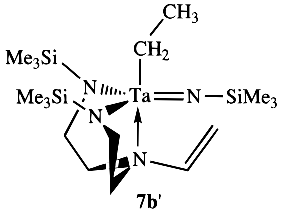
Bond Angles

$[N_3N]Ta(Me)Et$		$[N_3N]Ta(C_2H_2)$	
Ta−N(1)−Si(1)	131.6(5)	Ta−N(1)−Si(1)	126.1(6)
Ta−N(2)−Si(2)	136.1(5)	Ta−N(2)−Si(2)	125.7(6)
Ta−N(3)−Si(3)	128.8(5)	Ta−N(3)−Si(3)	126.4(6)
N(1)−Ta−N(2)	99.6(4)	N(1)−Ta−N(2)	110.5(5)
N(1)−Ta−N(3)	133.1(4)	N(1)−Ta−N(3)	110.6(4)
N(2)−Ta−N(3)	103.7(4)	N(2)−Ta−N(3)	122.5(5)
Ta−C(7)−C(8)	112.0(9)		

[a] In angstroms. [b] In degrees.



4 **7b** (9)



7b′

$[N_3N]TaMe_2$[5] decomposes when heated above 60 °C to produce **7a**, according to ^1H and ^{13}C NMR spectra (eq 10). Thermolysis of $[N_3N]Ta(CD_3)_2$ produces CD_3H and **7a** that contains a CD_3 ligand, according to ^1H and ^2H NMR spectra. Therefore we can rule out $[N_3N]Ta(CD_2)$ as an intermediate.

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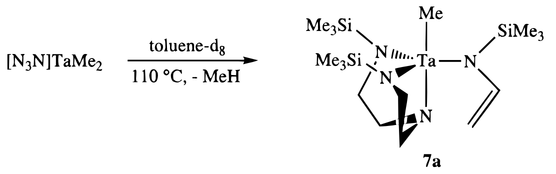
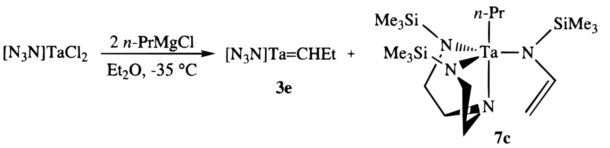
(37) Carpenter, B. K. *Organic Reaction Mechanisms*; John Wiley & Sons: New York, 1984.



(10)

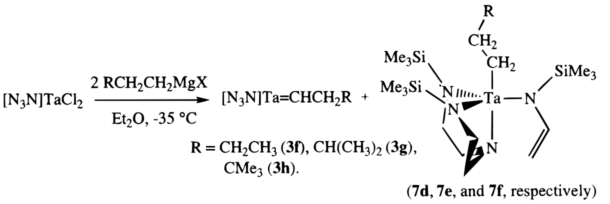
([N$_3$N]Ta(CH$_2$) is still an unknown compound.) It is interesting to note that in [N$_3$N]TaMe$_2$, as in **4**, only two of the three orbitals in the apical position are used for bonding to apical ligands, i.e., one orbital is empty. Other species discussed in this paper in which all three orbitals are involved in bonding to a ligand in the apical position do not decompose upon heating for days at 100 °C.

Reactions between [N$_3$N]TaCl$_2$ and 2 equiv of RCH$_2$CH$_2$MgX (X = Cl or Br) in which R is not a proton do not yield olefin complexes analogous to **4**, but alkylidene complexes in yields that correlate with the bulk of the R group, and products whose NMR spectra are analogous to those of **7a** and **7b**. We propose that the latter products arise via facile decomposition of intermediate olefin complexes. For example, *n*-propylmagnesium chloride affords a mixture of a propylidene complex (**3e**) in 32% yield and a decomposition product (**7c**) in 66% yield, as determined by ^{1}H NMR versus an internal standard (eq 11). The spectra of **3e** are analogous to those of other alkylidenes described here; in this case H$_\alpha$ is a triplet at −0.28 ppm in the proton NMR spectrum. We propose that **3e** and **7c** arise via competitive α and *β* abstraction, respectively, in a dipropyl intermediate.



(11)

Increasing the size of the alkyl group in the alkylation reaction affords the expected alkylidene complex formed via α abstraction and less of the decomposition product that ultimately is formed as a consequence of a *β* abstraction process (eq 12). As shown in Table 4 the percent yield of alkylidene (by NMR) increases from 32% (for R = CH$_3$) to 84% (for R = CHMe$_2$), while the amount of decomposition product falls to 66% and 15%, respectively. The reaction between [N$_3$N]TaCl$_2$ and 2 equiv of Me$_3$CCH$_2$CH$_2$MgCl affords an 83% yield of **3h** and *no* observable decomposition product **7e** (<1% via ^{1}H NMR). This last reaction contrasts markedly with that in which R = H, in which no alkylidene is formed and **4** is isolated in 96% yield.



(12)

Synthesis of a Tantalum Acetylene and a Benzyne Complex. [N$_3$N]TaCl$_2$ reacts with 2 equiv of vinylmagnesium bromide to afford white crystalline **8** in 80% yield (eq 13). **8** also can be prepared in 61% yield by treating [N$_3$N]Ta(Me)OTf with 1 equiv of vinyl Grignard. The acetylene protons are observed as a singlet at 12.22 ppm and the acetylenic carbon atoms as a doublet ($^1J_{CH}$ = 169 Hz) at 219.9 ppm (cf. δ C$_{acet}$ at 217 ppm with $^1J_{CH}$ = 169 Hz in (t-Bu$_3$SiO)$_3$Ta(C$_2$H$_2$)[38]). ^{1}H NMR spectra show that **8** is C_3 symmetric on the NMR time scale at −90 °C, consistent with rapid “rotation” of the acetylene about the acetylene−tantalum bond relative to the TREN ligand. The IR spectrum of **8** shows an acetylenic C≡C stretch at 1725 cm^{-1}. [N$_3$N]Ta(C$_2$H$_2$) can be heated to 100 °C for weeks as a 0.01 M toluene-d_8 solution in a sealed NMR tube with no sign of decomposition.

Table 4. Percent Yields of Alkylidene and Decomposition Products Resulting from the Reaction between [N$_3$N]TaCl$_2$ and 2RCH$_2$CH$_2$MgX

R	% alkylidene	% olefin or dec prod.
H	0	96[b]
CH$_3$	32	66
CH$_2$Me	42	54
CHMe$_2$	84 (76[b])	15
CMe$_3$	83 (77[b])	<1

[a] Determined by ^{1}H NMR versus an internal standard of (Me$_3$Si)$_2$O, unless otherwise noted. [b] Isolated yield.

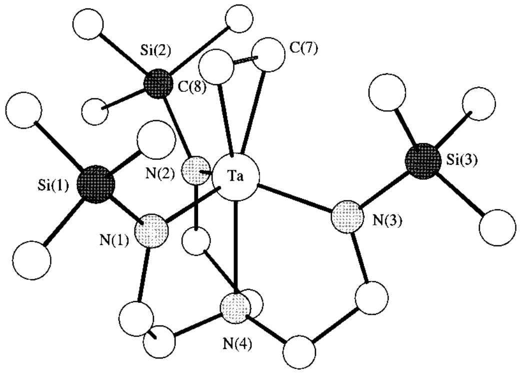


Figure 2. X-ray crystal structure of [N$_3$N]Ta(C$_2$H$_2$) (**8**).

$$[N_3N]TaCl_2 \xrightarrow[Et_2O,\ -35\ ^\circ C]{2H_2C{=}CHMgBr} \underset{\mathbf{8}}{[N_3N]Ta(C_2H_2)} + H_2C{=}CH_2 \qquad (13)$$

An X-ray crystal study of **8** revealed two independent molecules in the unit cell. (See Table 2 for crystallographic details and Table 3 for selected intramolecular distances and angles.) A drawing of one of the two molecules is shown in Figure 2. In the other, the acetylene ligand is disordered; the site disorder is not imposed by any space group symmetry. Bond distances and angles in the two molecules are not statistically different. (For further information, see supporting information.) **8** is best described as a distorted trigonal bipyramid in which the two axial sites are occupied by the acetylene and the amine nitrogen donor. The tantalum−N$_{eq}$ distances of 2.02−2.07 Å and the Ta−N$_{ax}$ bond length of 2.30 Å are similar to those found in [N$_3$N]Ta=PCy^3 and [N$_3$N]Ta=Se (2.349 Å).[11] The C−C bond length in the acetylene ligand (1.26 Å) is consistent with a bond order of ∼2.5. The acetylene C−C bond axis lines up with the Ta(1)−N(1) bond, therefore opening the N(2)−Ta−N(3) angle to 123° for steric reasons. The remaining two N−Ta−N angles are 111°. However, all three Ta−N−Si bond angles are 126°. Therefore we can say that steric crowding in the trigonal pocket in **8** is not as severe as it is in **6**.

A white crystalline benzyne complex (**9**) can be prepared in 70% yield by refluxing [N$_3$N]TaCl$_2$ with 2 equiv of phenyllithium in toluene for 1 day (eq 14). [N$_3$N]Ta(Ph)Cl can be observed as an intermediate in the reaction and can be generated by treating **9** with a stoichiometric amount of hydrochloric acid.

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[38] Covert, K. J.; Neithamer, D. R.; Zonnevylle, M. C.; LaPointe, R. E.; Schaller, C. P.; Wolczanski, P. T. *Inorg. Chem.* **1991**, *30*, 2494.

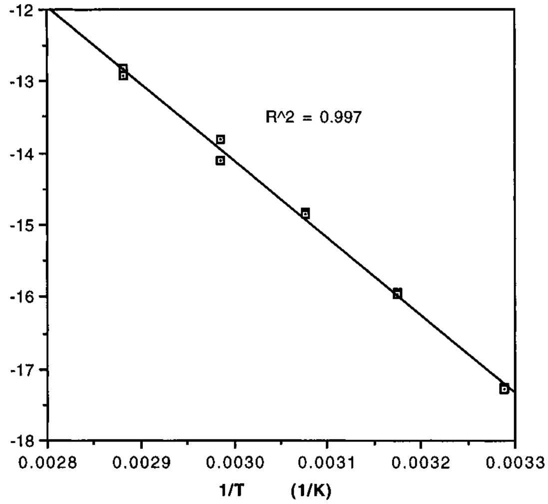


Figure 3. Plot of ln(k/T) vs $1/T$ for the formation of $[N_3N]Ta(C_6H_4)$ (**9**) from $[N_3N]Ta(Me)Ph$ (**10**) (ten runs; see Experimental Section for a list of individual values).

The proton NMR spectrum of **9** exhibits the expected downfield resonances for the benzyne ligand at 7.52 and 8.45 ppm, and the ipso carbon resonances are found in the ^{13}C NMR spectrum at 215.1 ppm. Cooling a toluene-d_8 solution of the benzyne complex in the NMR probe to −90 °C does not lead to significant broadening of the aromatic proton or carbon resonances, and the compound maintains its C_3 symmetry on the NMR time scale.

$$\underset{}{[N_3N]TaCl_2} \xrightarrow[\text{toluene, 80 °C, 1 day}]{\text{2LiPh}} \underset{\mathbf{9}}{[N_3N]Ta(C_6H_4)} + C_6H_6 \quad (14)$$

Addition of 1 equiv of phenylmagnesium bromide in toluene to $[N_3N]Ta(Me)Cl$ followed by heating of the mixture to 55 °C also affords **9** in 77% yield. In this case $[N_3N]Ta(Me)Ph$ (**10**) can be observed as an intermediate. If the reaction is conducted at room temperature for ~8 h, mixtures containing ~80% **10** can be obtained. Following the disappearance of **10** in such mixtures in toluene-d_8 in a sealed tube (ferrocene standard) demonstrates that conversion of **10** to **9** is first order in **10** through several half-lives. Data were collected between 31 and 74 °C (Figure 3). The resulting activation parameters ($\Delta H^‡ = 21.3(5)$ kcal/mol and $\Delta S^‡ = -11(1)$ cal/(mol K)) are comparable to those for thermolysis of $Cp^*_2Ti(Me)Ph$ to produce transient $Cp^*_2Ti(C_6H_4)$ ($\Delta H^‡ = 23.0$ kcal/mol, $\Delta S^‡ = -9.8$ cal/(mol K)[39]). Labeling experiments conducted at 74 °C (see Experimental Section) suggest that the primary isotope effect is 3.6(6), a value that is significantly smaller than that measured for decomposition of $Cp^*_2Ti(Me)(C_6R_5)$ (R = H or D; $k_H/k_D = 5.1$ at 80 °C in benzene-d_6[39]). A comparison of the rates of decomposition of $[N_3N]Ta(CH_3)(C_6H_5)$ and $[N_3N]Ta(CD_3)(C_6H_5)$ suggests that the secondary isotope effect is negligible (1.1(1)).

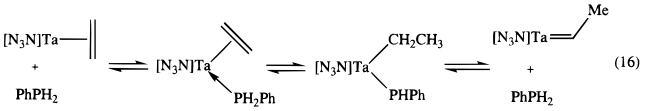
Reactions of Ethylene, Acetylene, and Benzyne Complexes. $[N_3N]Ta(C_2H_4)$ has proven to be relatively reactive, probably largely because one empty orbital is available to which nucleophiles can bind. Fortunately, decomposition of **4** to **7b** (eq 9) is rarely a competitive reaction, although it sometimes is a complication.

One unusual reaction is that between **4** and a catalytic amount of phenylphosphine (0.3 equiv) to afford the ethylidene complex (**3d**) in 88% yield (eq 15). Less acidic phosphines RPH_2 (R = H, *n*-Bu, Cy) require longer reaction times. NMR studies suggest that **3d** is entirely analogous to **3a**−**c**; the alkylidene H_α resonance is a quartet at −0.41 ppm, and the C_α resonance is a doublet at 191.2 ppm with $^1J_{CH} = 69$ Hz. We speculate that the lower energy of **3d** relative to **4** in this case is achieved via the strong interaction between the ethylidene's $C-H_\alpha$ bond and the metal. Like other alkylidene complexes in this class, **3d** reacts with benzaldehyde to afford $[N_3N]Ta{=}O$ and (in this case) a mixture of the *cis*- and *trans*-isomers of β-methylstyrene.

$$\underset{\mathbf{4}}{[N_3N]Ta(C_2H_4)} \xrightarrow[\text{Et}_2\text{O}]{RPH_2} \underset{\mathbf{3d}}{[N_3N]Ta{=}CHMe} \quad (15)$$

$$R = H,\ n\text{-Bu},\ Ph,\ Cy$$

Two equivalents of a 9:1 mixture of $PhPD_2$ and PhPHD in diethyl ether at ~25 °C converts **4** (0.04 M) to **3d** over a period of 2 days. In this sample of **3d** the percent deuterium at the alkylidene methyl and H_α positions is equal. Similarly, $[N_3N]Ta(C_2D_4)$ (0.02 M) reacts with 1 equiv of $PhPH_2$ in diethyl ether over a period of 1 day at ~25 °C to provide **3d** with the H label washed into both alkylidene positions equally. Monitoring the same reaction in benzene-d_6 via ^1H NMR immediately after $PhPH_2$ has been added shows the initial buildup of **4** that has protons in the ethylene ligand. Finally, addition of 1 equiv of the 9:1 $PhPD_2$/PhPHD mixture to $[N_3N]Ta{=}CHMe$ (0.04 M) in diethyl ether for 2 days at ~25 °C leads to incorporation of the deuterium label into the alkylidene H_α and methyl locations in roughly the same percentage. These results are consistent with a mechanism in which all steps are reversible. We propose the essential features to be those shown in eq 16. The key intermediate is $[N_3N]Ta(Et)(PHPh)$, in which an α hydrogen migrates from the ethyl group back to the phosphide. In theory, ethane could be lost to yield the known phenylphosphinidene complex. However, **3d** (0.02 M) does not react with 10 equiv of phenylphosphine in toluene-d_8 at 85 °C over 24 h. (Both **3d** and $[N_3N]Ta{=}PPh$ are stable in toluene-d_8 when solutions are heated to 100 °C in sealed NMR tubes.) Loss of ethane from $[N_3N]Ta(Et)(PHPh)$ evidently is simply too slow.



(16)

$[N_3N]Ta(C_2H_4)$ reacts differently with amines. Upon mixing **4** with ammonia, aniline, or pentafluoroaniline, **2a**, **2c**, and **2d** (eq 17) are formed in yields of 62−78%. **4** does not react with *tert*-butylamine under similar conditions. **3d** is not observed by ^1H NMR during the reaction of **4** with $ArNH_2$ (Ar = C_6H_5, C_6F_5). The reaction of **3d** (0.05 M) with 1 equiv of aniline in toluene-d_8 at ~25 °C is slow; it is only 23% complete after 8 days, as determined via ^1H NMR (internal standard). These two observations argue against the formation of imido complexes via **3d** as an intermediate. We propose that ethane is lost rapidly and irreversibly from $[N_3N]Ta(CH_2CH_3)(NHR)$ intermediates.

$$\underset{\mathbf{4}}{[N_3N]Ta(C_2H_4)} \xrightarrow[\text{Et}_2\text{O}]{RNH_2} \underset{\mathbf{2a,c,d}}{[N_3N]Ta{=}NR} \quad (17)$$

$$R = H\ (\mathbf{2a}),\ Ph\ (\mathbf{2c}),\ C_6F_5\ (\mathbf{2d})$$

Addition of 10 equiv of Me_3SiAsH_2 to an NMR tube containing a toluene-d_8 solution of **4** (0.03 M) affords **3d** rapidly, according to proton NMR. However, over a period of days at ~25 °C, **3d** is converted into what we propose to be the arsinidene complex, $[N_3N]Ta{=}AsSiMe_3$, according to ^1H and

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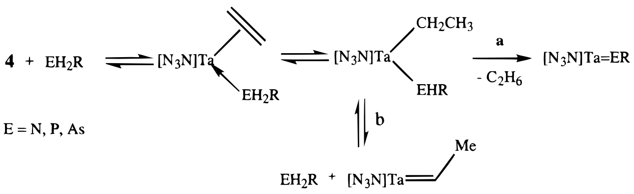
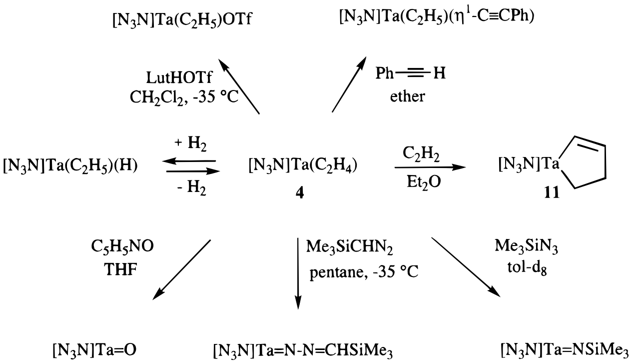
[39] Luinstra, G. A.; Teuben, J. H. *Organometallics* **1992**, *11*, 1793.

Scheme 1. Proposed Mechanism for Ethylene Complex **4** Reacting with EH_2R

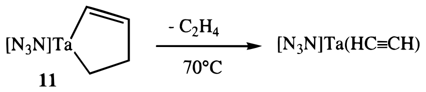


Scheme 2. Some Reactions of $[N_3N]Ta(C_2H_4)$ (**4**)



^{13}C NMR and its reaction with pivaldehyde to form the unstable arsaalkene $Me_3SiAs{=}C(H)CMe_3$. If the mechanism of reaction of Me_3SiAsH_2 with **4** is the same in principle as the reactions of **4** with amines and phosphines (Scheme 1), then we must conclude that path a is unobservable when E = P, path b is slow relative to path a when E = N, and both paths can be observed (with the rate of path b being greater than that of path a) when E = As. These results should be compared with those obtained by Wolczanski for a series of $Ta(silox)_3(ER)$ complexes prepared by loss of hydrogen from $Ta(silox)_3(EHR)(H)$ complexes.[22,40]

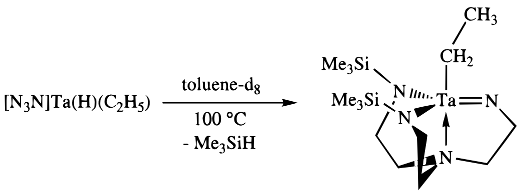
Two reactions in which ethylene is protonated to give an ethyl complex are shown in Scheme 2. **4** is cleanly protonated by 2,6-lutidinium triflate (LutHOTf) to afford $[N_3N]Ta(CH_2CH_3)(OTf)$ in 91% yield. When $[N_3N]Ta(C_2D_4)$ is employed, the product is $[N_3N]Ta(CD_2CD_2H)(OTf)$, as judged by ^1H and ^2H NMR. **4** also is protonated cleanly by phenylacetylene to afford yellow crystalline $[N_3N]Ta(CH_2CH_3)(\eta^1\text{-}C{\equiv}CPh)$ in 87% yield. When $[N_3N]Ta(C_2D_4)$ is employed in this reaction, the product is $[N_3N]Ta(CD_2CD_2H)(\eta^1\text{-}C{\equiv}CPh)$, according to ^1H and ^2H NMR. In contrast, acetylene itself adds to **4** to form the metallacyclopentene complex **11** in 91% yield. We assume that phenylacetylene is sterically prohibited from adding to the ethylene complex to form a similar tantalacyclopentene complex. Similar reactivity toward acetylenes has been reported for $Cp^*_2Ti(C_2H_4)$.[41,42] Upon heating of a 0.03 M benzene-d_6 solution of **11** to 70 °C in a sealed tube for 1 day, ethylene is extruded to yield $[N_3N]Ta(C_2H_2)$ quantitatively (eq18).



(18)

Several reactions of **4** resulted in displacement of ethylene (Scheme 2). Mixing of 2 equiv of pyridine *N*-oxide with a 0.02 M toluene-d_8 solution at room temperature in a sealed tube of **4** for 2 days afforded $[N_3N]Ta{=}O$ in 90% yield plus ethylene and pyridine. $[N_3N]Ta(C_2H_4)$ reacts with (trimethylsilyl)diazomethane instantly to form yellow crystalline $[N_3N]Ta{=}NN{=}CHSiMe_3$ in 91% yield. The doublet at 166.1 ppm ($^1J_{CH}$ = 138 Hz) in the ^{13}C NMR spectrum is characteristic of diazoalkane adducts[6,43−45] (cf. $[N_3N]V{=}NN{=}CHSiMe_3$[6]). Heating a 0.02 M toluene-d_8 solution of $[N_3N]Ta{=}NN{=}CHSiMe_3$ in a sealed tube at 110 °C for weeks failed to induce loss of dinitrogen and formation of $[N_3N]Ta{=}CHSiMe_3$. In contrast, **4** (0.07 M in toluene-d_8) reacts with 1 equiv of trimethylsilyl azide over a period of 3 weeks in a sealed NMR tube at ∼25 °C to afford $[N_3N]Ta{=}NSiMe_3$ (**2d**) quantitatively as determined via ^1H NMR versus an internal standard. We presume that the azide adduct $[N_3N]Ta{=}NN{=}NSiMe_3$ is an intermediate, as such species have now been observed,[46,47] although we have not yet observed an azide adduct in this case. The ethylene ligand in **4** does not exchange readily with free ethylene as determined by monitoring via ^1H NMR a toluene-d_8 solution of $[N_3N]Ta(C_2D_4)$ (0.03 M) under 1 atm of ethylene in a sealed tube at ∼25 °C.

$[N_3N]Ta(C_2H_4)$ reacts with 0.5 atm of hydrogen gas to afford white $[N_3N]Ta(H)(Et)$. The reversibility of addition of dihydrogen to $[N_3N]Ta(C_2H_4)$ is demonstrated by monitoring the reactions of **4** with 0.25 atm of D_2 and $[N_3N]Ta(C_2D_4)$ with 0.25 atm of H_2 in toluene-d_8 (∼0.02 M in Ta) by ^1H or ^2H NMR. In all cases, H and D are scrambled between the metal, C_α, and C_β sites. $[N_3N]Ta(H)(Et)$ can be obtained as a white crystalline solid in 93% yield via fractional recrystallization from diethyl ether. The hydride resonance at 24.77 ppm remains sharp down to −80 °C. The Ta−H stretch is found in the IR spectrum at 1816 cm^{-1} (ν_{TaD} = 1301 cm^{-1}). A 0.40 M solution of $[N_3N]Ta(H)(Et)$ in toluene-d_8 decomposes at 100 °C over a period of hours to yield Me_3SiH and a colorless oil whose proton and carbon NMR are consistent with it being "$EtTa[(NCH_2CH_2)N(CH_2CH_2NSiMe_3)_2]$". Unfortunately, we have been unable to obtain crystals of "$EtTa[(NCH_2CH_2)N(CH_2CH_2NSiMe_3)_2]$" in order to provide further support for its formulation. On the basis of its solubility and an X-ray structure of a related monomeric complex of tungsten,[48] we assume at this point that "$EtTa[(NCH_2CH_2)N(CH_2CH_2NSiMe_3)_2]$" is a monomer (eq 19). Loss of trimethylsilane is one example of what is likely to be a general tendency to lose the silyl group in some manner in silylated TREN complexes.



(19)

In contrast, **8** and **9** are relatively unreactive. For example, **8** does not react with ethylene, pyridine *N*-oxide, phenylphosphine, or $ArNH_2$ (Ar = Ph or C_6F_5) at 100 °C for weeks, while **9** does not react with PH_3 (1 atm; 1 week in diethyl ether at ∼25 °C) or 10 equiv of phenylphosphine (toluene-d_8 at 110 °C for 3 weeks). Solutions of **9** in toluene-d_8 (0.01 M) also do not react with 1 atm of ethylene or acetylene at 100 °C for 3 days in sealed NMR tubes. However, solutions of **9** in toluene-

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d_8 (0.02−0.03 M) do react with 1 equiv of $ArNH_2$ (Ar = Ph, C_6F_5) in sealed NMR tubes over a period of days at 110 °C to give **2c** and **2d**, respectively, in quantitative yields (eq 20).

$$\underset{\mathbf{9}}{[N_3N]Ta(C_6H_4)} \xrightarrow[\text{toluene-}d_8]{RNH_2} \underset{\mathbf{2c,d}}{[N_3N]Ta{=}NR} \qquad (20)$$

$$R = Ph\ (\mathbf{2c}),\ C_6F_5\ (\mathbf{2d})$$

Discussion

One of the themes that runs through the chemistry reported here is the stability and relatively low reactivity of $[N_3N]Ta(X)$ complexes that contain pseudo triply bound X ligands (where X = CHR, O, NR, PR, or alkyne). Such compounds attain an 18-electron count as long as the apical nitrogen remains bound to the metal, and they are sterically protected against intermolecular decomposition reactions by the bulky TMS groups. (Only two π bonds can form between the three nitrogen p orbital combinations and the metal; the third is a ligand-based nonbonding orbital.) Intramolecular reactions, such as CH activation of a methyl group in a TMS substituent,[1] are also slow in such species. Conversely, 16-electron $[N_3N]$Ta(olefin) complexes decompose relatively easily by abstraction of a β proton in the TREN backbone to give species in which the cage structure of the TREN ligand is disrupted and a vinyl amido ligand is formed. Attempts to reduce $[N_3N]TaCl_2$ to $[N_3N]Ta$, or to prepare species such as $[N_3N]TaH_2$ so far have been unsuccessful, possibly for the same reason. It should also be noted that $[N_3N]Ta(H)(C_2H_5)$ does not lose ethane to give "$[N_3N]Ta$." Ultimate decomposition of $[N_3N]Ta(H)(C_2H_5)$ via loss of trimethylsilane points out a pervasive and not entirely unexpected problem with the Me_3Si-substituted TREN system that also will limit the utility of this ligand system, at least for preparing complexes in which the metal is aggressively reactive.

Another characteristic of the chemistry reported here is the "steric pressure" that the three TMS substituents exert on ligands bound in the apical position. The degree of steric hindrance in the apical "pocket" is evident from the structure of **6** (Figure 1) and also from the tendency to form alkylidene complexes by α abstraction instead of olefin complexes by β abstraction as the size of the R group increases in the hypothetical intermediate $[N_3N]Ta(CH_2CH_2R)_2$ species formed by alkylation of $[N_3N]TaCl_2$. The question is still open as to whether ligands that could be bent instead of linear (alkylidene and phosphinidene species, in particular) are linear *solely* for electronic reasons, or whether steric factors also play a major role in stabilizing the linear form. At this stage we believe that the metal π orbitals involved in formation of a pseudo triple bond to a ligand in the apical position are extraordinarily electrophilic, and that π donation to give a pseudo triple bond is an important stabilizing feature of such compounds. For example, alkylidene complexes of Ta(V) that contain β-protons are rare[20,49] because they usually rearrange to the olefin complex readily. They are stable in $[N_3N]Ta{=}CHR$ complexes because the $C-H_\alpha$ electron pair is strongly donated to the metal. Steric repulsion between the substituent on a "bent" apical ligand and the bulky TMS groups is believed simply to reinforce linearity, although we have not been able to prepare a species such as $[N_3N]Ta{=}CH_2$ that would allow us to test this supposition. We suspect that the methylene ligand in $[N_3N]Ta{=}CH_2$ would be "T-shaped", as observed in unstable $Cp^*Me_3W{=}CH_2$,[50] a result that would confirm that electronic factors alone can account for formation of a pseudo triple bond between the metal and the apical ligand. It is interesting to note that π bonding to an apical ligand in $Ta(silox)_3$ complexes[40] is considerably weaker than in $[N_3N]Ta$ complexes, judging from the fact that the phosphinidene ligand in $(silox)_3Ta{=}PR$ complexes is bent rather than linear. Another way to increase "steric pressure" in the pocket, by increasing the size of the amide nitrogen silyl substituent, will be described in a forthcoming publication.[36]

The demonstration that α elimination or abstraction processes are preferred over analogous β processes in a sterically crowded environment can be taken as evidence that alkylidene ligands could be formed in classical olefin metathesis systems[51] from alkyls that have β protons. There is other evidence in the literature that α and β processes in Ta complexes can be competitive. An equilibrium between $Ta(CHCMe_3)(Et)Cl_2(PMe_3)_2$ and $Ta(CH_2CMe_3)(C_2H_4)Cl_2(PMe_3)_2$ has been demonstrated via magnetization transfer experiments.[52] Decomposition of $Cp^*_2(H)Ta{=}C{=}CH_2$ is believed to involve $Cp^*(\eta^5\text{-}C_5Me_4CH_2CH_2CH_2)Ta$ as an intermediate, from which the kinetic product is $Cp^*(H)Ta{=}CHCH_2CH_2(\eta^5\text{-}C_5Me_4)$ and the thermodynamic product is $Cp^*(\eta^5\text{-}C_5Me_4CH_2CH{=}CH_2)TaH$.[53] Finally, $Ta(CHCMe_3)(H)(PMe_3)_3I_2$ is known to react with *n* equiv of ethylene to afford the α-H elimination product $Ta[CH(CH_2CH_2)_nCMe_3](H)(PMe_3)_3I_2$.[54,55] There are other examples in the literature where α-H processes are proposed to occur preferentially.[54−57] Most recently and convincingly,[9] deuterium-labeling experiments have shown that α-elimination in $[N_3N]W$(cyclopentyl) to give $[N_3N]W$(cyclopentylidene)(H) proceeds more rapidly than β elimination, the slowest step being loss of cyclopentene from intermediate $[N_3N]W$(cyclopentene)(H) to give $[N_3N]W(H)$.

Several extensions of the work reported here currently are being pursued. For example, we would like to isolate and determine the structure of an arsinidene complex in order to compare it with the *bent* arsinidene (107°) in $(silox)_3Ta{=}AsPh$;[22,40] we expect the Ta=AsR linkage in $[N_3N]Ta{=}AsR$ to be linear, as is the Ta=P−R linkage in $[N_3N]Ta{=}PCy$.[3] We also hope to find a way to generate "$[N_3N]Ta{=}PLi$" cleanly and isolate it in high yield. However, the main focus will be on new TREN-like ligands. On the basis of the decomposition reactions described here, it seems likely that complexes that contain aggressively reactive metal centers, e.g., "trigonal monopyramidal" $[N_3N]Ta$, are likely to be short-lived and to decompose readily in an intramolecular fashion. Therefore it is imperative to design TREN-like ligands that are more resistant to cage decomposition reactions, metalation reactions involving the substituents on the amido nitrogen atoms,[1] or loss of amido substituents than is $[N_3N]^{3-}$.

Experimental Section

General Procedures. All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques, unless otherwise mentioned. Reagent grade solvents were purified by standard methods. $Li_3[N_3N]$,[1,6] $[N_3N]TaCl_2$,[3]

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$Ta(CH_2CMe_3)_2Cl_3$,[32] and $Ta(CH_2Ph)_2Cl_3$[31] were prepared according to literature methods.

^1H and ^{13}C NMR data are listed in parts per million downfield from TMS while ^{31}P NMR data are listed in parts per million downfield from triphenylphosphine (δ −4.51), and ^{19}F NMR data are listed in parts per million downfield from trifluoroacetic acid (δ −76.53). Routine coupling constants are usually not reported; those listed are in units of hertz. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer. Elemental analyses (C, H, N) were performed by Oneida Research Services, Whitesboro, NY, or in our laboratory using a Perkin-Elmer 2400 CHN analyzer. X-ray data were collected on an Enraf-Nonius CAD-4 diffractometer. A complete description of data collection, structure solution, and structure refinement can be found in the supporting information. NMR tube reactions were carried out in a Wilmad 512-7 in. or 512-9 in. NMR tube sealed to a 14/20 outer joint. This joint was connected to a gas adapter outfitted with a 28/15 ball joint and a Teflon stopcock. The contents of the tube were degassed on a high-vacuum line using three freeze(−196 °C)−pump−thaw cycles before flame-sealing under a static vacuum.

Kinetic Studies via ^1H NMR Spectroscopy. An NMR tube sealed to a 14/20 outer joint was charged with a solution of the reactant and ferrocene (internal standard) in 1 mL of toluene-d_8 and then fitted with a gas adapter. The tube was sealed according to the above procedure and placed in the preshimmed NMR probe for monitoring. Probe temperature was calibrated prior to the run utilizing neat ethylene glycol and was maintained to within ±0.1 °C of the set point.

Sample Procedure for Synthesis of $[N_3N]Ta=PR$ via P−Ph Cleavage: Preparation of $[N_3N]Ta=PSiMe_3$ (1c). A yellow solution of $[N_3N]Ta=PPh$ (0.500 g, 0.771 mmol) in 50 of mL tetrahydrofuran was transfered via cannula to a 100 mL Schlenk flask containing clean Li ribbon (27 mg, 3.89 mmol). The reaction mixture was stirred at room temperature for 19 h and was then decanted from the remaining Li ribbon. Trimethylsilyl chloride (0.250 g, 2.31 mmol) was added to the red-brown liquid at −35 °C, and the mixture was allowed to warm to 25 °C. After 45 min, the reaction mixture was taken to dryness in vacuo and the residue was extracted with 30 mL of pentane. The extract was filtered through a bed of Celite to remove LiCl, and the filtrate was concentrated in vacuo to yield a red-brown solid. The solid was recrystallized from pentane at −35 °C to yield 37 mg (0.060 mmol, 8%) of a gold powder: ^1H NMR (C_6D_6) δ 3.51 (t, 6, CH_2), 2.05 (t, 6, CH_2), 0.63 (s, 27, $NSiMe_3$), 0.55 (d, $^3J_{PH} = 5$, 9, $PSiMe_3$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 53.7 (s, CH_2), 51.7 (d, $^3J_{PC} = 6$, CH_2), 6.0 (d, $^4J_{PC} = 4$, $NSiMe_3$), 5.3 (d, $^2J_{PC} = 6$, $PSiMe_3$); $^{31}P\{^1H\}$ NMR (toluene-d_8, −60 °C) δ 212 ($\Delta\nu_{1/2} = 300$).

“$[N_3N]Ta=PLi$” can be observed as an intermediate in reactions of this general type: ^1H NMR (C_6D_6) δ 3.75 (t, 6, CH_2), 3.60 (br t, 4, THF), 2.13 (t, 6, CH_2), 1.42 (br t, 4, THF), 0.91 (s, 27, $SiMe_3$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 68.5 (THF), 54.4 (CH_2), 51.3 (CH_2), 25.8 (THF), 6.5 ($SiMe_3$); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 575 ($\Delta\nu_{1/2} \approx 600$).

$[N_3N]Ta=PMe$ (1a): ^1H NMR (C_6D_6) δ 3.49 (t, 6, CH_2), 2.56 (d, $^2J_{PH} = 20$, 3, CH_3), 2.18 (t, 6, CH_2), 0.56 (s, 27, $SiMe_3$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 54.1 (s, CH_2), 51.0 (d, $^3J_{PC} = 9$, CH_2), 30.8 (d, $^1J_{PC} = 33$, CH_3), 5.8 (s, $SiMe_3$); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 157.

$[N_3N]Ta=P$-*n*-Bu (1b). $[N_3N]TaCl_2$ (1.500 g, 2.45 mmol) was added to a suspension of LiP(H)-*n*-Bu (0.500 g, 5.15 mmol) in 100 mL of diethyl ether at −35 °C. The reaction mixture turned dark red immediately. After 19 h the mixture was filtered through a bed of Celite, and the filtrate was taken to dryness in vacuo. The red solid was recrystallized from pentane at −35 °C to yield 150 mg (0.239 mmol, 10%) of a gold powder: ^1H NMR (C_6D_6) δ 3.51 (t, 6, CH_2), 3.20 (m, 2, $PC\mathit{H_2}CH_2CH_2CH_3$), 2.14 (t, 6, CH_2), 1.86 (m, 2, $PCH_2C\mathit{H_2}CH_2CH_3$), 1.42 (m, 2, $PCH_2CH_2C\mathit{H_2}CH_3$), 0.88 (t, 3, $PCH_2CH_2CH_2C\mathit{H_3}$), 0.61 (s, 27, $SiMe_3$); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 53.8 (s, CH_2), 51.1 (s, CH_2), 48.0 (d, $^1J_{PC} = 29$, PCH_2), 33.4 (s, $PCH_2\mathit{C}H_2$), 24.1 (s, $PCH_2CH_2\mathit{C}H_2$), 13.8 (s, $PCH_2CH_2CH_2\mathit{C}H_3$), 6.1 (s, $SiMe_3$); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 186.

$[N_3N]Ta=PSiMe_2Ph$ (1d): ^1H NMR (CD_2Cl_2) δ 7.65 (m, 2, Ph), 7.33 (m, 3, Ph), 3.80 (t, 6, CH_2), 2.76 (t, 6, CH_2), 0.66 (d, $^3J_{PH} = 4$, $SiMe_2Ph$), 0.27 (s, 27, $SiMe_3$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 140.3 (d, $^2J_{PC} = 12$, Ph), 134.5 (s, Ph), 129.0 (s, Ph), 127.9 (s, Ph), 54.9 (s, CH_2), 51.8 (s, CH_2), 5.25 (s, $SiMe_3$), 3.76 (d, $^2J_{PC} = 7$, $SiMe_2Ph$); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −60 °C) δ 203 ($\Delta\nu_{1/2} = 400$).

Sample Procedure for Reaction of a Phosphinidene $[N_3N]Ta=PR$ with Me_3CCHO. Observation of *trans*-$Me_3C(H)C=PMe$ by NMR. Pivaldehyde (21 μL, 0.194 mmol) was added via syringe to an NMR tube containing $[N_3N]Ta=PMe$ (57 mg, 0.0971 mmol) in 700 μL of C_6D_6. Within minutes the red-brown solution turned colorless: ^1H NMR (C_6D_6) δ 8.56 (dq, $^2J_{PH} = 25$, 1, $P=C\mathit{H}CMe_3$), 1.34 (m, 3, $MeP=C$), 1.12 (d, $^4J_{PH} = 2$, 9, $P=CHC\mathit{Me_3}$); $^{31}P\{^1H\}$ (C_6D_6) δ 229.

***trans*-$Me_3C(H)C=P(n\text{-}Bu)$:** ^1H NMR (C_6D_6) δ 8.65 (m, $^2J_{PH} = 25$, 1, $P=C\mathit{H}CMe_3$), 1.85 (m, 2, $PC\mathit{H_2}CH_2CH_2CH_3$), 1.59 (m, 2, $PCH_2C\mathit{H_2}CH_2CH_3$), 1.30 (m, 2, $PCH_2CH_2C\mathit{H_2}CH_3$), 1.16 (d, $^3J_{PH} = 2$, 9, $P=CHC\mathit{Me_3}$), 0.81 (t, 3, $PCH_2CH_2CH_2C\mathit{H_3}$); $^{31}P\{^1H\}$ (C_6D_6) δ 243.

***trans*-$Me_3C(H)C=PSiMe_3$:** ^1H NMR (C_6D_6) δ 9.52 (d, $^2J_{PH} = 24$, 1, $P=C\mathit{H}CMe_3$), 1.18 (d, 9, $P=CHC\mathit{Me_3}$), 0.21 (d, 9, $PSiMe_3$); $^{31}P\{^1H\}$ (C_6D_6) δ 244.

***trans*-$Me_3C(H)C=PSiMe_2Ph$:** ^1H NMR (CD_2Cl_2) δ 9.44 (d, $^2J_{PH} = 24$, 1, $P=C\mathit{H}CMe_3$), 7.56 (m, 2, Ph), 7.37 (m, 3, Ph), 1.16 (d, $^4J_{PH} = 2$, 9, $P=CHC\mathit{Me_3}$), 0.56 (d, $^4J_{PH} = 3$, 6, $PSi\mathit{Me_2}Ph$); $^{31}P\{^1H\}$ (CD_2Cl_2) δ 238.

$[N_3N]Ta=NH$ (2a). $[N_3N]TaCl_2$ (200 mg, 0.327 mmol) was added to a −35 °C slurry of lithium amide (16 mg, 0.687 mmol) in 12 mL of tetrahydrofuran. After 23 h, the solvents were removed from the reaction mixture in vacuo and the residue was extracted with 50 mL of pentane. The extract was filtered through Celite, and the pale yellow filtrate was taken to dryness in vacuo to yield a pale yellow solid. Recrystallization of the solid from pentane at −35 °C gave 112 mg (0.201 mmol, 62%) of white crystalline product: ^1H NMR (C_6D_6) δ 5.59 (br t (1:1:1), $^1J_{^{14}NH} = 50$, NH), 3.39 (t, 6, CH_2), 2.22 (t, 6, CH_2), 0.40 (s, 27, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 53.9 (t, CH_2), 49.2 (t, CH_2), 3.3 (q, $SiMe_3$); IR (diethyl ether solution, KBr cells, background subtracted) cm^{-1} 3436 (s, ν NH). Anal. Calcd for $TaSi_3N_5C_{15}H_{40}$: C, 32.42; H, 7.25; N, 12.60. Found: C, 32.35; H, 7.36; N, 12.37.

$[N_3N]Ta=NCMe_3$ (2b). $[N_3N]TaCl_2$ (1.00 g, 1.64 mmol) was added to a −35 °C solution of $LiN(H)CMe_3$ (271 mg, 3.43 mmol) in 60 mL of diethyl ether. After 15 h, the pale yellow-orange mixture was filtered through Celite. The pale yellow filtrate was taken to dryness in vacuo to yield a pale yellow solid. Recrystallization of the yellow solid from pentane at −35 °C gave 727 mg (1.19 mmol, 73%) of off-white crystalline product: ^1H NMR (C_6D_6) δ 3.22 (t, 6, CH_2), 2.18 (t, 6, CH_2), 1.66 (s, 9, CMe_3), 0.37 (s, 27, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 64.8 (s, $\mathit{C}Me_3$), 60.1 (t, CH_2), 47.6 (t, CH_2), 35.4 (q, CMe_3), 2.9 (q, $SiMe_3$). Anal. Calcd for $TaSi_3N_5C_{19}H_{48}$: C, 37.30; H, 7.91; N, 11.45. Found: C, 37.55; H, 7.87; N, 11.37.

$[N_3N]Ta=NPh$ (2c). $[N_3N]TaCl_2$ (250 mg, 0.409 mmol) was added to a −35 °C solution of LiN(H)Ph (85 mg, 0.858 mmol) in 12 mL of diethyl ether. After 22 h, the cloudy white mixture was passed through Celite. The solvents were removed from the filtrate in vacuo to provide an off-white solid. Recrystallization of this solid from diethyl ether at −35 °C gave 246 mg (0.389 mmol, 95%) of white crystalline product: ^1H NMR (C_6D_6) δ 7.42 (m, 2, Ph), 7.34 (m, 3, Ph), 3.42 (t, 6, CH_2), 2.23 (t, 6, CH_2), 0.40 (s, 27, $SiMe_3$); ^{13}C NMR (CD_2Cl_2) δ 159.5 (s, Ph), 128.7 (dt, Ph), 127.6 (dd, Ph), 56.0 (t, CH_2), 49.8 (t, CH_2), 3.2 (q, $SiMe_3$). Anal. Calcd for $TaSi_3N_5C_{21}H_{44}$: C, 39.92; H, 7.02; N, 11.08. Found: C, 39.91; H, 7.03; N, 10.95.

$[N_3N]TaMe_2$. Methyllithium (2.34 mL, 1.4 M in diethyl ether, 3.28 mmol) was added via syringe to a −35 °C solution of $[N_3N]TaCl_2$ (910 mg, 1.49 mmol) in 50 mL of diethyl ether. A white LiCl precipitate was observed in a few minutes. After 3 h, the reaction mixture was taken to dryness in vacuo. The off-white solid was extracted with 40 mL of pentane, the extract was filtered through Celite, and the pentane was removed from the filtrate in vacuo to provide 840 mg (1.47 mmol, 99%) of a waxy, beige solid. The complex may be isolated as colorless crystals by recrystallization from pentane at −35 °C: ^1H NMR (C_6D_6) δ 3.34 (t, 6, CH_2), 2.09 (t, 6, CH_2), 1.27 (s, 6, $TaMe_2$), 0.29 (s, 27, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 64.6 (q, $^1J_{CH} = 117$, $TaMe_2$), 60.3 (t, $^1J_{CH} = 138$, CH_2), 50.3 (t, $^1J_{CH} = 136$, CH_2), 2.3 (q, $^1J_{CH} = 118$, $SiMe_3$). Anal. Calcd for $TaSi_3N_4C_{17}H_{45}$: C, 35.77; H, 7.95; N, 9.82. Found: C, 35.40; H, 8.40; N, 9.68.

$[N_3N]Ta(Me)OTf$. $[FeCp_2][O_3SCF_3]$ (373 mg, 1.11 mmol) was added to a −35 °C solution of $[N_3N]TaMe_2$ (607 mg, 1.11 mmol) in 50 mL of tetrahydrofuran. The color of the stirred reaction mixture changed to gold as the blue $[FeCp_2][O_3SCF_3]$ dissolved. After 1 h, the reaction mixture was concentrated in vacuo. The residue was washed with 40 mL of pentane, collected on a frit, and dried to afford 585 mg (0.83 mmol, 75%) of a tan powder. The complex may be isolated as colorless crystals by recrystallization from diethyl ether at −35 °C: ^{1}H NMR (C_6D_6) δ 3.53 (t, 6, CH_2), 2.04 (t, 6, CH_2), 1.42 (s, 3, Me), 0.27 (s, 27, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 67.0 (q, TaMe), 60.4 (t, CH_2), 53.0 (t, CH_2), 1.8 (q, $SiMe_3$). Anal. Calcd for $TaSi_3N_4O_3SF_3C_{17}H_{42}$: C, 28.97; H, 6.01; N, 7.95. Found: C, 28.93; H, 6.14; N, 7.67.

$[N_3N]Ta(Me)Cl$. To a −35 °C solution of $[N_3N]Ta(Me)OTf$ (300 mg, 0.426 mmol) in 8 mL of methylene chloride was added tetraethylammonium chloride (71 mg, 0.426 mmol). After 23 h, the yellow solution was concentrated in vacuo, extracted with 30 mL of diethyl ether, and filtered through Celite. The yellow filtrate was concentrated in vacuo to provide 175 mg (0.296 mmol, 69%) of yellow powder. The complex may be isolated as yellow crystals by recrystallization from diethyl ether at −35 °C: ^{1}H NMR (C_6D_6) δ 3.56 (t, 6, CH_2), 2.04 (t, 6, CH_2), 1.49 (s, 3, Me), 0.35 (s, 27, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 64.4 (q, $^1J_{CH} = 118$, TaMe), 61.7 (t, $^1J_{CH} = 136$, CH_2), 53.6 (t, $^1J_{CH} = 136$, CH_2), 2.0 (q, $^1J_{CH} = 119$, $SiMe_3$). Anal. Calcd for $TaSi_3N_4ClC_{16}H_{42}$: C, 32.51; H, 7.16; N, 9.48. Found: C, 32.55; H, 7.21; N, 9.54.

$[N_3N]Ta(Et)Cl$ (5). Ethylmagnesium chloride (164 μL, 2.27 M in diethyl ether, 0.373 mmol) was added via syringe to a solution of $[N_3N]TaCl_2$ (228 mg, 0.373 mmol) in 30 mL of diethyl ether at −35 °C. After 45 h, the light orange reaction mixture was taken to dryness in vacuo and the residue was extracted with 30 mL of pentane. The extract was filtered through Celite, and the filtrate was concentrated in vacuo to give a yellow-orange solid that was recrystallized from pentane at −35 °C to afford 163 mg (0.269 mmol, 72%) of yellow-orange crystals: ^{1}H NMR (C_6D_6) δ 3.58 (t, 6, CH_2), 2.60 (t, 3, CH_3), 2.07 (t, 6, CH_2), 1.86 (q, 2, CH_2), 0.37 (s, 27, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 76.8 (t, $^1J_{CH} = 114$, $\mathit{C}H_2CH_3$), 61.8 (t, $^1J_{CH} = 136$, CH_2), 53.6 (t, $^1J_{CH} = 136$, CH_2), 21.2 (q, $^1J_{CH} = 125$, $CH_2\mathit{C}H_3$), 2.1 (q, $^1J_{CH} = 119$, $SiMe_3$). Anal. Calcd for $TaSi_3N_4ClC_{17}H_{44}$: C, 33.74; H, 7.33; N, 9.26. Found: C, 33.51; H, 7.49; N, 8.82.

$[N_3N]Ta(Me)Et$ (6). A −35 °C solution of $[N_3N]Ta(Et)Cl$ (166 mg, 0.274 mmol) in 5 mL of diethyl ether was subjected to the addition of methylmagnesium chloride (100 μL, 0.302 mmol, 3.0 M in tetrahydrofuran) via syringe. The orange mixture was stirred for 3.5 h and was then taken to dryness in vacuo. The resulting orange solid was extracted with 5 mL of diethyl ether and filtered through Celite to afford an orange solution. The filtrate was concentrated in vacuo to afford 151 mg of an orange solid, which was shown to be an 8:1 mixture of $[N_3N]Ta(Me)Et$ (**6**) and $[N_3N]Ta(C_2H_4)$ (**4**) by ^{1}H NMR. Four recrystallizations from pentane at −35 °C afforded X-ray quality yellow plates of **6**: ^{1}H NMR (C_6D_6) δ 3.42 (t, 6, CH_2), 2.16 (t, 6, CH_2), 1.89 (t, 3, $CH_2C\mathit{H}_3$), 1.69 (q, 2, CH_2CH_3), 1.35 (s, 3, CH_3), 0.28 (s, 27, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 78.7 (t, $^1J_{CH} = 117$, $\mathit{C}H_2CH_3$), 65.6 (q, $^1J_{CH} = 117$, CH_3), 59.7 (t, $^1J_{CH} = 136$, CH_2), 51.1 (t, $^1J_{CH} = 135$, CH_2), 17.0 (q, $^1J_{CH} = 123$, $CH_2\mathit{C}H_3$), 2.6 (q, $^1J_{CH} = 118$, $SiMe_3$).

$[N_3N]Ta{=}CHSiMe_3$ (3a). ((Trimethylsilyl)methyl)lithium (96 mg, 1.02 mmol) was added to a solution of $[N_3N]TaCl_2$ (250 mg, 0.409 mmol) in 8 mL of diethyl ether at −35 °C. After 24 h, the cloudy yellow solution was filtered through Celite and the yellow filtrate concentrated in vacuo to provide a yellow solid. The solid was recrystallized from diethyl ether at −35 °C to afford 234 mg (0.373 mmol, 91%) of yellow crystalline product: ^{1}H NMR (C_6D_6) δ 3.29 (t, 6, CH_2), 2.55 (s, 1, $C\mathit{H}SiMe_3$), 2.03 (t, 6, CH_2), 0.47 (s, 9, $CHSi\mathit{Me}_3$), 0.41 (s, 27, $NSiMe_3$); ^{13}C NMR (C_6D_6) δ 206.5 (d, $^1J_{CH} = 72$, $\mathit{C}HSiMe_3$), 57.9 (t, $^1J_{CH} = 135$, CH_2), 49.6 (t, $^1J_{CH} = 136$, CH_2), 5.2 (q, $^1J_{CH} = 118$, $CHSi\mathit{Me}_3$), 3.4 (q, $^1J_{CH} = 118$, $NSiMe_3$). Anal. Calcd for $TaSi_3N_4C_{22}H_{45}$: C, 36.40; H, 7.88; N, 8.94. Found: C, 36.18; H, 7.53; N, 8.92.

If only 1 equiv of (trimethylsilyl)methyl)lithium is added, then **$[N_3N]Ta(CH_2SiMe_3)Cl$** can be isolated by fractional crystallization: ^{1}H NMR (C_6D_6) δ 3.63 (t, 6, CH_2), 2.12 (t, 6, CH_2), 1.29 (s, 2, $C\mathit{H}_2SiMe_3$), 0.50 (s, 9, $CH_2Si\mathit{Me}_3$), 0.36 (s, 27, $NSiMe_3$); ^{13}C NMR (C_6D_6) δ 76.8 (t, $\mathit{C}H_2SiMe_3$), 62.1 (t, $^1J_{CH} = 136$ Hz, CH_2), 53.7 (t, $^1J_{CH} = 136$ Hz, CH_2), 4.7 (q, $^1J_{CH} = 119$ Hz, $CH_2Si\mathit{Me}_3$), 2.5 (q, $^1J_{CH} = 118$ Hz, $NSiMe_3$).

$[N_3N]Ta{=}CHPh$ (3b). (a) From $[N_3N]TaCl_2$. $PhCH_2MgCl$ (642 μL, 1.0 M in diethyl ether, 0.642 mmol) was added via syringe to a −35 °C solution of $[N_3N]TaCl_2$ (187 mg, 0.306 mmol) in 8 mL of diethyl ether. After 17 h, the cloudy orange mixture was filtered through Celite and the orange filtrate concentrated in vacuo to yield an orange solid. The solid was recrystallized from diethyl ether at −35 °C, and two crops of orange needles were collected to yield 175 mg (0.277 mmol, 91%) of product: ^{1}H NMR (C_6D_6) δ 7.34 (m, 3, Ph), 6.80 (m, 2, Ph), 3.39 (t, 6, CH_2), 2.16 (t, 6, CH_2), 2.01 (s, 1, $C\mathit{H}Ph$), 0.39 (s, 27, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 201.4 (d, $^1J_{CH} = 72$, $\mathit{C}HPh$), 152.6 (s, Ph), 129.5 (d, Ph), 127.4 (d, Ph), 122.4 (m, Ph), 56.4 (t, CH_2), 49.8 (t, CH_2), 3.7 (q, $SiMe_3$). Anal. Calcd for $TaSi_3N_4C_{22}H_{45}$: C, 41.89; H, 7.19; N, 8.88. Found: C, 41.68; H, 7.09; N, 8.81.

If only 1 equiv of $PhCH_2MgCl$ is added to $[N_3N]TaCl_2$, then **$[N_3N]Ta(CH_2Ph)Cl$** can be isolated by fractional crystallization: ^{1}H NMR (C_6D_6) δ 7.21 (t, 2, Ph), 6.98 (d, 2, Ph), 6.74 (t, 1, Ph), 3.45 (t, 6, CH_2), 3.13 (s, 2, $C\mathit{H}_2Ph$), 2.10 (t, 6, CH_2), 0.42 (s, 27, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 149.0 (s, Ph), 131.9 (dd, $^1J_{CH} = 156$ Hz, Ph), 127.0 (dd, Ph), 121.7 (dt, $^1J_{CH} = 157$ Hz, Ph), 91.4 (t, $^1J_{CH} = 129$ Hz, $\mathit{C}H_2Ph$), 57.5 (t, $^1J_{CH} = 138$ Hz, CH_2), 52.4 (t, $^1J_{CH} = 136$ Hz, CH_2), 3.3 (q, $^1J_{CH} = 119$ Hz, $SiMe_3$).

(b) From $Ta(CH_2Ph)_2Cl_3$. $Ta(CH_2Ph)_2Cl_3$ (250 mg, 0.532 mmol) was added to a −35 °C solution of $Li_3[N_3N]$ (203 mg, 0.532 mmol) in 10 mL of diethyl ether. After 20 h, the reaction mixture was filtered through Celite and the solvents were removed from the red-orange filtrate in vacuo to afford a red-brown solid. Recrystallization of the red-brown solid from diethyl ether at −35 °C gave several crops of orange needles; yield 288 mg (0.456 mmol, 86%).

$[N_3N]Ta{=}CHCMe_3$ (3c). A solution of $Ta(CH_2CMe_3)_2Cl_3$ (2.41 g, 5.61 mmol) in 40 mL of diethyl ether was prepared, as was a solution of $Li_3[N_3N]$ (2.14 g, 5.61 mmol) in 40 mL of diethyl ether. Both solutions were chilled to −35 °C and then combined. After 2.5 h, the yellow reaction mixture was filtered through a bed of Celite and the filtrate was concentrated in vacuo to yield an orange solid. Recrystallization of the orange solid from pentane at −35 °C yielded several crops of crystals; yield 1.92 g (3.14 mmol, 56%): ^{1}H NMR (C_6D_6) δ 3.25 (t, 6, CH_2), 2.12 (t, 6, CH_2), 1.54 (s, 9, $CHC\mathit{Me}_3$), 0.93 (s, 1, $C\mathit{H}CMe_3$), 0.39 (s, 27, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 213.3 (d, $^1J_{CH} = 72$, $\mathit{C}HCMe_3$), 59.4 (t, CH_2), 48.7 (t, CH_2), 47.7 (s, $\mathit{C}Me_3$), 35.7 (q, $CHMe_3$), 3.0 (q, $SiMe_3$). Anal. Calcd for $TaSi_3N_4C_{20}H_{49}$: C, 39.33; H, 8.09; N, 9.17. Found: C, 39.05; H, 7.95; N, 9.02.

Observation of $[N_3N]Ta{=}CHCH_2CH_3$ (3e). *n*-Propylmagnesium chloride (700 μL, 2.5 M in diethyl ether, 1.75 mmol) was added via syringe to a −35 °C solution of $[N_3N]TaCl_2$ (510 mg, 0.834 mmol) in 10 mL of diethyl ether. After 23 h, the mixture was taken to dryness in vacuo and the residue was extracted with 40 mL of pentane. The extract was filtered through Celite, and the solvent was removed from the yellow filtrate in vacuo to afford a yellow solid. Via ^{1}H NMR with a $(Me_3Si)_2O$ internal standard, the solid was determined to contain $[N_3N]Ta{=}CHCH_2CH_3$ (**3e**) and (*n*-Pr)$Ta[N(CH_2CH_2NSiMe_3)_2][N(SiMe_3)(CH{=}CH_2)]$ (**7c**) in 32% and 66% yields, respectively. $[N_3N]Ta{=}CHCH_2CH_3$ (**3e**): ^{1}H NMR (C_6D_6) δ 3.43 (t, 6, CH_2), 3.29 (m, 2, $TaCHC\mathit{H}_2$), 2.21 (t, 6, CH_2), 1.19 (t, 3, $TaCHCH_2C\mathit{H}_3$), 0.38 (s, 27, $SiMe_3$), −0.28 (t, 1, $TaC\mathit{H}$); ^{13}C NMR (C_6D_6) δ 201.5 (d, $^1J_{CH} = 68$, $Ta\mathit{C}H$), 54.2 (t, $^1J_{CH} = 136$, CH_2), 50.3 (t, $^1J_{CH} = 135$, CH_2), 38.5 (t, $^1J_{CH} = 125$, $TaCH\mathit{C}H_2$), 18.1 (q, $^1J_{CH} = 121$, $TaCHCH_2\mathit{C}H_3$), 4.5 (q, $^1J_{CH} = 117$, $SiMe_3$). (*n*-Pr)$Ta[N(CH_2CH_2NSiMe_3)_2][N(SiMe_3)(CH{=}CH_2)]$ (**7c**): ^{1}H NMR (C_6D_6) δ 6.61 (dd, 1, $C\mathit{H}{=}CH_2$), 4.20 (d, 1, $CH{=}C\mathit{H}_2$), 4.06 (m, 3, CH_2 and $CH{=}C\mathit{H}_2$), 3.87 (m, 4, CH_2), 3.65 (m, 2, CH_2), 2.21 (m, 2, $TaCH_2C\mathit{H}_2CH_3$), 1.45 (t, 2, $TaC\mathit{H}_2CH_2CH_3$), 1.04 (t, 3, $TaCH_2CH_2C\mathit{H}_3$), 0.22 (s, 18, $NSiMe_3$), 0.20 (s, 9, $NSiMe_3$); ^{13}C NMR (toluene-d_8) δ 137.9 (d, $^1J_{CH} = 159$, $\mathit{C}H{=}CH_2$), 92.8 (t, $^1J_{CH} = 157$, $CH{=}\mathit{C}H_2$), 73.1 (t, $^1J_{CH} = 116$, $Ta\mathit{C}H_2CH_2CH_3$), 66.7 (t, $^1J_{CH} = 133$, CH_2), 55.7 (t, $^1J_{CH} = 133$, CH_2), 26.7 (t, $^1J_{CH} = 127$, $TaCH_2\mathit{C}H_2CH_3$), 21.3 (q, $^1J_{CH} = 125$, $TaCH_2CH_2\mathit{C}H_3$), 1.8 (q, $^1J_{CH} = 118$, $NSiMe_3$), 0.06 (q, $^1J_{CH} = 119$, $NSiMe_3$).

Observation of $[N_3N]Ta{=}CHCH_2CH_2CH_3$ (3f). *n*-Butylmagnesium chloride (692 μL, 2.5 M in diethyl ether, 1.73 mmol) was added via syringe to a −35 °C solution of $[N_3N]TaCl_2$ (504 mg, 0.834 mmol) in 10 mL of diethyl ether. After 23 h, the mixture was taken to dryness in vacuo and the residue was extracted with 40 mL of pentane. The extract was filtered through Celite, and the solvents were removed from the yellow filtrate in vacuo to afford a yellow solid. Via ^{1}H NMR with a $(Me_3Si)_2O$ internal standard, the solid was determined to contain

$[N_3N]Ta{=}CHCH_2CH_2CH_3$ (**3f**) and (n-Bu)$Ta[N(CH_2CH_2NSiMe_3)_2][N(SiMe_3)(CH{=}CH_2)]$ (**7d**) in 42% and 54% yields, respectively. $[N_3N]Ta{=}CHCH_2CH_2CH_3$ (**3f**): ^{1}H NMR (C_6D_6) δ 3.42 (t, 6, CH_2), 3.26 (m, 2, $TaCHCH_2$), 2.20 (t, 6, CH_2), 1.71 (m, 2, $TaCHCH_2CH_2$), 0.95 (t, 3, $TaCHCH_2CH_2CH_3$), 0.41 (s, 27, $SiMe_3$), −0.20 (t, 1, $TaCH$); ^{13}C NMR (C_6D_6) δ 199.7 (d, $^1J_{CH} = 70$, $TaCH$), 53.5 (t, $^1J_{CH} = 136$, CH_2), 50.3 (t, $^1J_{CH} = 135$, CH_2), 48.4 (t, $^1J_{CH} = 126$, $TaCHCH_2$), 27.1 (t, $^1J_{CH} = 126$, $TaCHCH_2CH_2$), 14.8 (q, $^1J_{CH} = 125$, $TaCHCH_2CH_2CH_3$), 4.4 (q, $^1J_{CH} = 117$, $SiMe_3$). (n-Bu)$Ta[N(CH_2CH_2NSiMe_3)_2][N(SiMe_3)(CH{=}CH_2)]$ (**7d**): ^{1}H NMR (C_6D_6) δ 6.64 (dd, 1, $CH{=}CH_2$), 4.21 (d, 1, $CH{=}CH_2$), 4.07 (m, 3, CH_2 and $CH{=}CH_2$), 3.87 (m, 4, CH_2), 3.66 (m, 2, CH_2), 2.21 (m, 2, $TaCH_2CH_2CH_2CH_3$), 1.47 (t, 2, $TaCH_2CH_2CH_2CH_3$), 1.36 (m, 2, $TaCH_2CH_2CH_2CH_3$), 0.94 (t, 3, $TaCH_2CH_2CH_2CH_3$), 0.23 (s, 18, $NSiMe_3$), 0.20 (s, 9, $NSiMe_3$); ^{13}C NMR (toluene-d_8) δ 137.8 (d, $^1J_{CH} = 160$, $CH{=}CH_2$), 92.8 (t, $^1J_{CH} = 156$, $CH{=}CH_2$), 69.9 (t, $^1J_{CH} = 117$, $TaCH_2CH_2CH_2CH_3$), 66.7 (t, $^1J_{CH} = 134$, CH_2), 55.7 (t, $^1J_{CH} = 134$, CH_2), 35.7 (t, $^1J_{CH} = 125$, $TaCH_2CH_2CH_2CH_3$), 29.6 (t, $^1J_{CH} = 124$, $TaCH_2CH_2CH_2CH_3$), 14.1 (q, $^1J_{CH} = 124$, $TaCH_2CH_2CH_2CH_3$), 1.8 (q, $^1J_{CH} = 118$, $NSiMe_3$), 0.05 (q, $^1J_{CH} = 119$, $NSiMe_3$).

$[N_3N]Ta{=}CHCH_2CHMe_2$ (3g). A −35 °C solution of $[N_3N]TaCl_2$ (318 mg, 0.520 mmol) in 10 mL of diethyl ether was subjected to the addition of isopentylmagnesium bromide (642 μL, 1.7 M in diethyl ether, 1.09 mmol) via syringe. After 23 h, the cloudy yellow mixture was concentrated in vacuo, extracted with 30 mL of pentane, and filtered through Celite. The filtrate was concentrated in vacuo to afford a yellow solid, which was determined via ^{1}H NMR spectroscopy with a $(Me_3Si)_2O$ internal standard to contain $[N_3N]Ta{=}CHCH_2CH(CH_3)_2$ (**3g**) and $(Me_2CHCH_2CH_2)Ta[N(CH_2CH_2NSiMe_3)_2][N(SiMe_3)(CH{=}CH_2)]$ (**7e**) in 84% and 15% yields, respectively. The crude reaction product was recrystallized to provide $[N_3N]Ta{=}CHCH_2CHMe_2$ (**3g**) free of the decomposition product. Yellow crystals of the alkylidene were collected to afford 242 mg (0.396 mmol, 76%) of product: ^{1}H NMR (C_6D_6) δ 3.41 (t, 6, CH_2), 3.37 (dd, 2, $TaCHCH_2CHMe_2$), 2.15 (t, 6, CH_2), 2.03 (m, 1, $CHMe_2$), 1.14 (d, 6, $CHMe_2$), 0.46 (s, 27, $NSiMe_3$), 0.10 (t, 1, $TaCHCH_2CHMe_2$); ^{13}C NMR (C_6D_6) δ 199.7 (d, $^1J_{CH} = 71$, $TaCHCH_2CHMe_2$), 54.9 (t, $^1J_{CH} = 122$, $TaCHCH_2CHMe_2$), 54.8 (t, $^1J_{CH} = 136$, CH_2), 50.1 (t, $^1J_{CH} = 135$, CH_2), 31.3 (d, $^1J_{CH} = 129$, $CHMe_2$), 23.7 (q, $^1J_{CH} = 125$, $CHMe_2$), 4.3 (q, $^1J_{CH} = 118$, $NSiMe_3$). Anal. Calcd for $TaSi_3N_4C_{20}H_{49}$: C, 39.33; H, 8.09; N, 9.17. Found: C, 39.18; H, 8.25; N, 9.03.

$[N_3N]Ta{=}CHCH_2CMe_3$ (3h). A −35 °C solution of $[N_3N]TaCl_2$ (500 mg, 0.818 mmol) in 8 mL of diethyl ether was subjected to the addition of neohexylmagnesium chloride (818 μL, 2.1 M in diethyl ether, 1.72 mmol) via syringe. After 23 h, the cloudy yellow-orange mixture was concentrated in vacuo, extracted with 30 mL of pentane, and filtered through Celite. The filtrate was concentrated in vacuo to afford an orange solid, which was determined to be $[N_3N]Ta{=}CHCH_2CMe_3$ (**3h**) contaminated by a trace (<1%) amount of $(Me_3CCH_2CH_2)Ta[N(SiMe_3)(CH{=}CH_2)][N(CH_2CH_2NSiMe_3)_2]$ **(7f)** via ^{1}H NMR spectroscopy. The crude reaction product was recrystallized to provide **3h** free of the decomposition product. Orange crystals of the alkylidene were collected to afford 393 mg (0.629 mmol, 77%) of product: ^{1}H NMR (C_6D_6) δ 3.71 (d, 2, $TaCHCH_2CMe_3$), 3.34 (t, 6, CH_2), 2.13 (t, 6, CH_2), 1.21 (s, 9, CMe_3), 0.75 (t, 1, $TaCHCH_2CMe_3$), 0.41 (s, 27, $NSiMe_3$); ^{13}C NMR (C_6D_6) δ 200.6 (d, $^1J_{CH} = 75$, $TaCHCH_2CMe_3$), 58.6 (t, $^1J_{CH} = 124$, $TaCHCH_2CMe_3$), 57.5 (t, $^1J_{CH} = 135$, CH_2), 49.3 (t, $^1J_{CH} = 135$, CH_2), 34.3 (s, CMe_3), 30.5 (q, $^1J_{CH} = 124$, CMe_3), 3.9 (q, $^1J_{CH} = 118$, $NSiMe_3$). Anal. Calcd for $TaSi_3N_4C_{21}H_{51}$: C, 40.37; H, 8.23; N, 8.97. Found: C, 40.43; H, 8.25; N, 8.62.

$[N_3N]Ta(C_2H_4)$ (4). Ethylmagnesium chloride (1.17 mL, 2.2 M in diethyl ether, 2.58 mmol) was added via syringe to a −35 °C solution of $[N_3N]TaCl_2$ (750 mg, 1.23 mmol) in 30 mL of diethyl ether. After 1 h, the mixture was taken to dryness in vacuo and the residue was extracted with 60 mL of pentane. The extract was filtered through Celite, the solvents were removed from the red filtrate in vacuo, and the red solid was recrystallized from pentane at −35 °C to provide 673 mg (1.18 mmol, 96%) of magenta crystals: ^{1}H NMR (C_6D_6) δ 3.38 (t, 6, CH_2), 2.29 (t, 6, CH_2), 2.15 (s, 4, $H_2C{=}CH_2$), 0.20 (s, 27, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 62.6 (t, $^1J_{CH} = 144$, $H_2C{=}CH_2$), 59.7 (t, $^1J_{CH} = 135$, CH_2), 49.7 (t, $^1J_{CH} = 135$, CH_2), 3.2 (q, $^1J_{CH} = 118$, $SiMe_3$). Anal. Calcd for $TaSi_3N_4C_{17}H_{43}$: C, 35.90; H, 7.62; N, 9.85. Found: C, 35.94; H, 7.41; N, 9.61.

$EtTa[N(SiMe_3)(CH{=}CH_2)][N(CH_2CH_2NSiMe_3)_2]$ (7b). A solution of $[N_3N]Ta(C_2H_4)$ (82 mg, 0.144 mmol) in ~1 mL of toluene-d_8 was added to an NMR tube, which was then sealed. The tube was then heated to 50 °C in an oil bath for 24 h. ^{1}H NMR demonstrated the sole reaction product to be **7b**: ^{1}H NMR (toluene-d_8) δ 6.59 (dd, 1, $CH{=}CH_2$), 4.25 (d, 1, $CH{=}CH_2$), 4.07 (m, 3, CH_2 and $CH{=}CH_2$), 3.87 (m, 4, CH_2), 3.67 (m, 2, CH_2), 1.99 (t, 3, CH_2CH_3), 1.46 (q, 2, CH_2CH_3), 0.23 (s, 18, $NSiMe_3$), 0.21 (s, 9, $NSiMe_3$); ^{13}C NMR (toluene-d_8) δ 137.1 (d, $^1J_{CH} = 160$, $CH{=}CH_2$), 92.9 (t, $^1J_{CH} = 158$, $CH{=}CH_2$), 66.7 (t, $^1J_{CH} = 133$, CH_2), 60.4 (t, $^1J_{CH} = 118$, CH_2CH_3), 55.7 (t, $^1J_{CH} = 135$, CH_2), 18.0 (q, $^1J_{CH} = 125$, CH_2CH_3), 1.7 (q, $^1J_{CH} = 118$, $NSiMe_3$), 0.08 (q, $^1J_{CH} = 118$, $NSiMe_3$).

$MeTa[N(SiMe_3)(CH{=}CH_2)][N(CH_2CH_2NSiMe_3)_2]$ (7a). A solution of $[N_3N]TaMe_2$ (277 mg, 0.485 mmol) in ~1 mL of toluene-d_8 was added to an NMR tube, which was then sealed. The tube was then heated to 110 °C in an oil bath for 24 h. ^{1}H NMR demonstrated the sole reaction products to be methane (δ 0.17) and **7a**: ^{1}H NMR (toluene-d_8) δ 6.55 (dd, 1, $CH{=}CH_2$), 4.27 (d, 1, $CH{=}CH_2$), 4.10 (d, 1, $CH{=}CH_2$), 3.97 (m, 2, CH_2), 3.83 (m, 4, CH_2), 3.68 (m, 2, CH_2), 0.75 (s, 3, CH_3), 0.19 (s, 9, $NSiMe_3$), 0.16 (s, 18, $NSiMe_3$); ^{13}C NMR (tol-d_8) δ 135.2 (d, $^1J_{CH} = 160$, $CH{=}CH_2$), 93.7 (t, $^1J_{CH} = 157$, $CH{=}CH_2$), 67.0 (t, $^1J_{CH} = 132$, CH_2), 55.4 (t, $^1J_{CH} = 136$, CH_2), 40.5 (q, $^1J_{CH} = 120$, CH_3), 1.6 (q, $^1J_{CH} = 119$, $NSiMe_3$), −0.1 (q, $^1J_{CH} = 120$, $NSiMe_3$). Anal. Calcd for $TaSi_3N_4C_{16}H_{41}$: C, 34.64; H, 7.45; N, 10.10. Found: C, 34.38; H, 6.90; N, 9.94.

$[N_3N]Ta(C_2H_2)$ (8). Vinylmagnesium bromide (1.37 mL, 1.0 M in tetrahydrofuran, 1.37 mmol) was added to a −35 °C solution of $[N_3N]TaCl_2$ (400 mg, 0.654 mmol) in 25 mL of diethyl ether. After 17 h, the pale gold mixture was concentracted in vacuo and the residue was extracted with 50 mL of pentane. The extract was filtered through Celite, and the pale gold filtrate was taken to dryness in vacuo to yield an off-white solid, which was recrystallized from pentane at −35 °C to afford 298 mg (0.526 mmol, 80%) of colorless needles. X-ray quality needle crystals were obtained by recrystallization of the product from pentane at −35 °C: ^{1}H NMR (C_6D_6) δ 12.22 (s, 2, $HCCH$), 3.51 (t, 6, CH_2), 2.42 (t, 6, CH_2), 0.20 (s, 27, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 219.9 (dd, $^1J_{CH} = 169$, $HCCH$), 54.2 (t, $^1J_{CH} = 136$, CH_2), 51.0 (t, $^1J_{CH} = 134$, CH_2), 4.3 (q, $^1J_{CH} = 118$, $SiMe_3$); IR (Nujol, background subtracted) cm^{-1} 1725 (s, $\nu_{C\equiv C}$). Anal. Calcd for $TaSi_3N_4C_{17}H_{41}$: C, 36.03; H, 7.29; N, 9.89. Found: C, 35.97; H, 7.19; N, 10.01.

$[N_3N]Ta(C_6H_4)$ (9). (a) From $[N_3N]TaCl_2$. A mixture of $[N_3N]TaCl_2$ (257 mg, 0.420 mmol) and phenyllithium (81 mg, 92 mol % solid, 0.882 mmol) in 10 mL of toluene was heated at ~80 °C for 24 h. The reaction mixture was taken to dryness in vacuo, and the residue was extracted with 10 mL of pentane. The extract was filtered through Celite, and the solvents were removed in vacuo from the yellow-orange filtrate to give a solid. Recrystallization of this solid from pentane at −35 °C provided 166 mg (0.269 mmol, 64%) of white crystals: ^{1}H NMR (C_6D_6) δ 8.45 (m, 2, Ph), 7.52 (m, 2, Ph), 3.59 (t, 6, CH_2), 2.49 (t, 6, CH_2), 0.06 (s, 27, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 215.1 (d, $^2J_{CH} = 6$, C_6H_4), 136.5 (d, $^1J_{CH} = 158$, C_6H_4), 132.6 (d, $^1J_{CH} = 156$, C_6H_4), 55.7 (t, $^1J_{CH} = 136$, CH_2), 51.2 (t, $^1J_{CH} = 136$, CH_2), 3.2 (q, $^1J_{CH} = 118$, $SiMe_3$). Anal. Calcd for $TaSi_3N_4C_{21}H_{43}$: C, 40.89; H, 7.03; N, 9.08. Found: C, 40.89; H, 7.02; N, 8.84.

$[N_3N]Ta(Ph)Cl$ can be observed as an intermediate in the reaction to form **9**. It can be generated by treating **9** in toluene or benzene with a stoichiometric amount of ethereal hydrochloric acid: ^{1}H NMR (C_6D_6) δ 7.37 (t, 3, Ph), 7.15 (m, 2, Ph), 3.68 (t, 6, CH_2), 2.32 (t, 6, CH_2), 0.21 (s, 27, $SiMe_3$).

(b) From $[N_3N]Ta(Me)Cl$. Phenylmagnesium bromide (209 μL, 3.5 M in tetrahydrofuran, 0.731 mmol) was added to a solution of $[N_3N]Ta(Me)Cl$ (393 mg, 0.665 mmol) in 10 mL of toluene. The mixture was heated at 55 °C for 2 days. The cloudy yellow-orange solution was subsequently concentrated in vacuo, and the residue was extracted with 20 mL of diethyl ether. The orange extract was filtered through Celite, and the filtrate was concentrated in vacuo to yield a light orange solid, which was recrystallized from pentane at −35 °C to produce 316 mg (0.512 mmol, 77%) of product as white crystals.

$[N_3N]Ta(Me)Ph$ (**10**) can be observed as an intermediate in this reaction. If the reaction is conducted at room temperature for ~8 h, mixtures containing ~80% **10** can be obtained: ^{1}H NMR (C_6D_6) δ 8.11 (dd, 2, Ph), 7.44 (t, 2, Ph), 7.24 (t, 1, Ph), 3.43 (t, 6, CH_2), 2.24 (t, 6, CH_2), 1.81 (s, 3, CH_3), 0.11 (s, 27, $SiMe_3$).

Kinetics of Decomposition of $[N_3N]Ta(CH_3)(C_6H_5)$. Decomposition reactions were followed by NMR (see earlier description). The individual values for runs at a given temperature (K) are ($k \times 10^6$ s^{-1}) 304 (9.58, 9.84), 315 (36.8, 36.8), 325 (110, 119), 335 (250, 337), 347 (858, 937). The resulting activation parameters are $\Delta H^{\ddagger} = 21.3(5)$ kcal/mol and $\Delta S^{\ddagger} = -11$ (1) cal/(mol K).

The rate of decomposition of $[N_3N]Ta(CH_3)(C_6H_5)$ was found to be 1.4 times faster than that of $[N_3N]Ta(CD_3)(C_6H_5)$ for a secondary isotope effect (per D) of $\{1.4(2)\}^{1/3}$ or 1.1(1), while comparison of the rates of decomposition of $[N_3N]Ta(CH_3)(C_6H_5)$ and $[N_3N]Ta(CH_3)(C_6D_5)$ yielded a primary isotope effect of 3.6(6).

In order to calculate the uncertainties in the reported rate constants, kinetic isotope effects, and activation parameters, methods similar to those described in a recent paper by Xue[58] were employed. A systematic uncertainty of 5% was averaged with the calculated random uncertainty in root-mean-square fashion to determine the total uncertainty in k. This value was utilized in error propagation formulas derived by Girolami and co-workers[59] to calculate the uncertainties in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

Reactions of $[N_3N]Ta(C_2H_4)$. (a) With $PPhH_2$ To Give $[N_3N]Ta{=}CHCH_3$ (3d). Phenylphosphine (17 μL, 0.158 mmol) was added via syringe to a solution of $[N_3N]Ta(C_2H_4)$ (300 mg, 0.527 mmol) in 2 mL of diethyl ether. After 24 h, the gold solution was filtered through Celite and the gold filtrate was concentrated in vacuo to yield an oily yellow solid. The oily solid was recrystallized from pentane at −35 °C to afford 264 mg (0.464 mmol, 88%) of product as yellow crystals: ^{1}H NMR (C_6D_6) δ 3.42 (t, 6, CH_2), 2.84 (d, 3, CH_3), 2.16 (t, 6, CH_2), 0.44 (s, 27, $SiMe_3$), −0.41 (q, 1, C*H*CH_3); ^{13}C NMR (C_6D_6) δ 191.2 (d, $^1J_{CH} = 69$, *C*HCH_3), 53.9 (t, CH_2), 50.1 (t, CH_2), 30.5 (dq, $^1J_{CH} =$ 126, CH_3), 4.1 (q, $SiMe_3$). Anal. Calcd for $TaSi_3N_4C_{17}H_{43}$: C, 35.90; H, 7.62; N, 9.85. Found: C, 36.08; H, 7.75; N, 9.73.

(b) With $AsSiMe_3H_2$ to give $[N_3N]Ta{=}AsSiMe_3$: ^{1}H NMR (C_6D_6) δ 3.52 (t, 6, CH_2), 2.05 (t, 6, CH_2), 0.65 (s, 27, $NSiMe_3$), 0.63 (s, 9, $AsSiMe^3$); ^{13}C NMR (C_6D_6) δ 53.6 (t, $^1J_{CH} = 136$, CH_2), 51.3 (t, $^1J_{CH}$ = 136, CH_2), 6.4 (q, $^1J_{CH} = 118$, $NSiMe_3$), 6.3 (q, $^1J_{CH} = 118$, $AsSiMe_3$).

Addition of pivaldehyde to $[N_3N]Ta{=}AsTMS$ at −35 °C yields $Me_3SiAs{=}C(H)CMe_3$: ^{1}H NMR (C_6D_6) δ 11.46 (s, 1, C*H*CMe_3), 1.20 (s, 9, CHC*Me*$_3$), 0.29 (s, 9, $AsSiMe_3$).

(c) With Ammonia To Give $[N_3N]Ta{=}NH$. A 100 mL glass bomb fitted with a Teflon stopcock was charged with a solution of $[N_3N]Ta(C_2H_4)$ (42 mg, 0.0738 mmol) in 5 mL of diethyl ether. The mixture was subjected to three freeze(−196 °C)−pump−thaw cycles. Ammonia (0.148 mmol) was condensed into the bomb at −196 °C. The reaction mixture was allowed to warm to room temperature and stirred for 19 h. The resulting light orange solution was filtered through Celite and concentrated in vacuo to afford a light yellow solid. The reaction product was determined by ^{1}H NMR spectroscopy with a $(Me_3Si)_2O$ internal standard to contain a 78% yield of $[N_3N]Ta{=}NH$.

(d) With Pentafluoroaniline To Give $[N_3N]Ta{=}NC_6F_5$ (2d). Pentafluoroaniline (66 mg, 0.362 mmol) was added to a −35 °C solution of $[N_3N]Ta(C_2H_4)$ (206 mg, 0.362 mmol) in 5 mL of diethyl ether. Over a period of 3 days the red solution turned light yellow. The solvents were removed in vacuo, and the resulting solid was extracted with 5 mL of pentane. The extract was filtered through Celite, and the solvents were removed from the filtrate to provide a light yellow solid. The solid was recrystallized from pentane at −35 °C to afford 191 mg (0.264 mmol, 73%) of product: ^{1}H NMR (C_6D_6) δ 3.36 (t, 6, CH_2), 2.25 (t, 6, CH_2), 0.22 (s, 27, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 56.9 (t, $^1J_{CH} = 136$, CH_2), 49.3 (t, $^1J_{CH} = 136$, CH_2), 2.3 (q, $^1J_{CH} = 119$, $SiMe_3$); ^{19}F NMR (C_6D_6) δ −146.6 (d, $^3J_{FF} = 24$, C_6F_5), −165.2 (dt, $^3J_{FF} = 24$, C_6F_5), −168.2 (dt, $^3J_{FF} = 23$, C_6F_5). Anal. Calcd for $TaSi_3F_5N_5C_{21}H_{39}$: C, 34.95; H, 5.45; N, 9.70. Found: C, 35.15; H, 5.62; N, 9.64.

(e) With Aniline To Give $[N_3N]Ta{=}NPh$. $[N_3N]Ta(C_2H_4)$ (15 mg, 0.0264 mmol) and ferrocene (5 mg, 0.0269 mmol) were dissolved in ~1 mL of toluene-d_8 in an NMR tube. Aniline (2.4 μL, 0.0264 mmol) was then added via syringe, and the tube was sealed. After 24 h at ~25 °C, the mixture was found by ^{1}H NMR to contain a 62% yield of $[N_3N]Ta{=}NPh$ (vs ferrocene internal standard).

(f) With 2,6-Lutidinium Triflate To Give $[N_3N]Ta(Et)OTf$. 2,6-Lutidinium triflate (226 mg, 0.879 mmol) was added to a −35 °C solution of $[N_3N]Ta(C_2H_4)$ (500 mg, 0.879 mmol) in 20 mL of dichloromethane. The red solution immediately turned orange. After 8 h the solvents were removed in vacuo, and the resulting solid was extracted with 40 mL of diethyl ether. The extract was filtered through Celite, and the filtrate was taken to dryness in vacuo to yield a yellow solid. Recrystallization of the yellow solid from diethyl ether at −35 °C gave 578 mg (0.804 mmol, 91%) of yellow crystalline product: ^{1}H NMR (C_6D_6) δ 3.62 (t, 6, CH_2), 2.26 (t, 6, CH_2), 2.11 (t, 3, CH_3), 1.78 (q, 2, CH_2), 0.30 (s, 27, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 80.0 (t, $^1J_{CH} =$ 112, *C*H$_2$CH$_3$), 60.8 (t, $^1J_{CH} = 137$, CH_2), 54.1 (t, $^1J_{CH} = 137$, CH_2), 17.5 (q, $^1J_{CH} = 126$, CH$_2$*C*H$_3$), 2.0 (q, $^1J_{CH} = 119$, $SiMe_3$). Anal. Calcd for $TaSi_3N_4O_3SF_3C_{18}H_{44}$: C, 30.08; H, 6.17; N, 7.79. Found: C, 29.77; H, 6.50; N, 7.75.

(g) With Phenylacetylene To Give $[N_3N]Ta(CH_2CH_3)(C{\equiv}CPh)$. Phenylacetylene (24.3 μL, 0.211 mmol) was added via syringe to a solution of $[N_3N]Ta(C_2H_4)$ (100 mg, 0.176 mmol) in 4 mL of diethyl ether. After 45 h, the gold solution was filtered through Celite and the filtrate was stripped to yield a yellow oily solid. Recrystallization of the solid from pentane at −35 °C afforded 103 mg (0.153 mmol, 87%) of yellow crystalline product: ^{1}H NMR (CD_2Cl_2) δ 7.38 (m, 2, Ph), 7.27 (m, 2, Ph), 7.20 (m, 1, Ph), 3.86 (t, 6, CH_2), 2.95 (t, 6, CH_2), 1.85 (q, 2, C*H*$_2$CH$_3$), 1.66 (t, 3, CH$_2$C*H*$_3$), 0.24 (s, 27, $SiMe_3$); ^{13}C NMR (CD_2Cl_2) δ 172.0 (s, *C*CPh), 132.1 (s, Ph), 129.4 (m, Ph), 128.5 (m, Ph), 128.1 (s, C*C*Ph), 126.1 (m, Ph), 79.5 (t, $^1J_{CH} = 124$, *C*H$_2$CH$_3$), 59.1 (t, $^1J_{CH} = 136$, CH_2), 52.0 (t, $^1J_{CH} = 136$, CH_2), 16.1 (q, $^1J_{CH} = 122$, CH$_2$*C*H$_3$), 3.0 (q, $^1J_{CH} = 118$, $SiMe_3$); IR (diethyl ether solution, KBr cells, background subtracted) cm^{-1} 1963 (s, $\nu_{C\equiv C}$). Anal. Calcd for $TaSi_3N_4C_{25}H_{49}$: C, 44.76; H, 7.36; N, 8.35. Found: C, 44.26; H, 7.26; N, 8.35.

(h) With Pyridine *N*-Oxide To Give $[N_3N]Ta{=}O$. Pyridine *N*-oxide (12 mg, 0.127 mmol) was added to a solution of $[N_3N]Ta(C_2H_4)$ (36 mg, 0.0633 mmol) in 3 mL of tetrahydrofuran. After 2 days, the gold reaction mixture was stripped, to afford a light yellow solid, which by ^{1}H NMR spectroscopy with a $(Me_3Si)_2O$ internal standard was determined to contain a 90% yield of $[N_3N]Ta{=}O$. The ^{1}H and ^{13}C NMR spectra for $[N_3N]Ta{=}O$ have been reported previously.[3]

(i) With (Trimethylsilyl)diazomethane To Give $[N_3N]Ta{=}NN{=}CHSiMe_3$. (Trimethylsilyl)diazomethane (500 μL, 2.0 M in hexanes, 1.00 mmol) was added via syringe to a −35 °C solution of $[N_3N]Ta(C_2H_4)$ (400 mg, 0.703 mmol) in 5 mL of pentane. The red solution immediately turned bright yellow and was stirred for 45 min. The yellow solution was filtered through Celite, and the filtrate was concentrated in vacuo to provide a yellow solid, which was recrystallized from pentane at −35 °C. Yellow crystals were collected to afford 422 mg (0.644 mmol, 91%) of product: ^{1}H NMR (C_6D_6) δ 8.39 (s, 1, C*H*SiMe$_3$), 3.44 (t, 6, CH_2), 2.27 (t, 6, CH_2), 0.43 (s, 27, $NSiMe_3$), 0.32 (s, 9, $CHSiMe_3$); ^{13}C NMR (C_6D_6) δ 166.1 (d, $^1J_{CH} = 138$, *C*HSiMe$_3$), 54.2 (t, $^1J_{CH} = 135$, CH_2), 49.7 (t, $^1J_{CH} = 135$, CH_2), 3.5 (q, $^1J_{CH} = 118$, $NSiMe_3$), −1.8 (q, $^1J_{CH} = 120$, $CHSiMe_3$). Anal. Calcd for $TaSi_4N_6C_{19}H_{49}$: C, 34.84; H, 7.54; N, 12.83. Found: C, 34.99; H, 7.48; N, 12.86.

(j) With Trimethylsilyl Azide To Give $[N_3N]Ta{=}NSiMe_3$. $[N_3N]Ta(C_2H_4)$ (30 mg, 0.0527 mmol) and ferrocene (10 mg, 0.0580 mmol) were dissolved in ~1 mL of toluene-d_8 in an NMR tube. Trimethylsilyl azide (8.0 μL, 0.0580 mmol) was then added via syringe, and the tube was sealed. After 3 weeks at ~25 °C, the mixture was found by ^{1}H NMR to contain a >99% yield of $[N_3N]Ta{=}NSiMe_3$ (vs ferrocene internal standard): ^{1}H NMR (C_6D_6) δ 3.26 (t, 6, CH_2), 2.17 (t, 6, CH_2), 0.45 (s, 9, $=NSiMe_3$), 0.34 (s, 27, $NSiMe_3$); ^{13}C{^{1}H} NMR (C_6D_6) δ 58.7 (CH_2), 48.6 (CH_2), 5.7 ($=NSiMe_3$), 2.8 ($NSiMe_3$).

(k) With Acetylene To Give $[N_3N]Ta(CHCHCH_2CH_2)$ (11). A 100 mL glass bomb fitted with a Teflon stopcock was charged with a solution of $[N_3N]Ta(C_2H_4)$ (381 mg, 0.670 mmol) in 10 mL of diethyl ether. The mixture was subjected to three freeze(−196 °C)−pump−thaw cycles. Acetylene (1.61 mmol) was condensed into the bomb at −196 °C. The reaction vessel was allowed to warm to room temperature and was stirred for 19 h. The purple reaction mixture was

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filtered through Celite in order to remove the polyacetylene, and the solvents were removed from the yellow-orange filtrate. The resulting solid was recrystallized from pentane at −35 °C to give yellow crystals (364 mg, 0.612 mmol, 91%): ^{1}H NMR (C_6D_6) δ 8.62 (dd, $J = 9$, 1.6, 1, TaCH), 8.12 (dd, $J = 9$, 2, 1, TaCHC*H*), 3.64 (m, 2, $TaCHCHCH_2$), 3.35 (t, 6, CH_2), 2.17 (t, 6, CH_2), 2.14 (t, 2, $TaCHCHCH_2CH_2$), 0.25 (s, 27, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 208.4 (dt, $^1J_{CH} = 126$, TaCH), 159.2 (d, $^1J_{CH} = 145$, TaCH*C*H), 80.3 (t, $^1J_{CH} = 116$, $TaCHCHCH_2$), 60.0 (t, $^1J_{CH} = 136$, CH_2), 50.1 (t, $^1J_{CH} = 135$, CH_2), 44.0 (t, $^1J_{CH} = 124$, $TaCHCHCH_2CH_2$), 2.5 (q, $^1J_{CH} = 118$, $SiMe_3$). Anal. Calcd for $TaSi_3N_4C_{19}H_{45}$: C, 38.37; H, 7.62; N, 9.42. Found: C, 38.50; H, 7.60; N, 9.35.

(l) With Dihydrogen To Give $[N_3N]Ta(H)(C_2H_5)$. A 100 mL glass bomb fitted with a Teflon stopcock was charged with a solution of $[N_3N]Ta(C_2H_4)$ (319 mg, 0.561 mmol) in 10 mL of diethyl ether. The mixture was subjected to three freeze(−196 °C)−pump−thaw cycles, and 0.5 atm of hydrogen gas was then added. The magenta color of the solution bleached over a period of 1 h to yield a colorless solution. After 2 h, the solution was filtered through Celite and the filtrate was concentrated in vacuo to provide a white solid containing small amounts of red solid. Examination of the product mixture via ^{1}H NMR revealed that the white $[N_3N]Ta(H)(Et)$ was contaminated with ~5% $[N_3N]Ta(C_2H_4)$. Recrystallization of the mixture from diethyl ether at −35 °C afforded $[N_3N]Ta(H)(Et)$ as a white crystalline solid; yield 298 mg (0.522 mmol, 93%): ^{1}H NMR (C_6D_6) δ 24.77 (s, 1, TaH), 3.44 (t, 6, CH_2), 2.26 (t, 8, CH_2 and CH_2CH_3), 1.50 (t, 3, CH_2CH_3), 0.25 (s, 27, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 62.4 (t, $^1J_{CH} = 124$, $TaCH_2CH_3$), 56.3 (t, $^1J_{CH} = 137$, CH_2), 51.1 (t, $^1J_{CH} = 134$, CH_2), 11.2 (q, $^1J_{CH} = 123$, $TaCH_2CH_3$), 2.3 (q, $^1J_{CH} = 119$, $SiMe_3$); IR (Nujol) cm^{-1} 1816 (s, ν_{TaH}). Under a dynamic vacuum $[N_3N]Ta(Et)H$ loses hydrogen gas slowly in solution at 25 °C to regenerate $[N_3N]Ta(C_2H_4)$ quantitatively.

A 0.40 M toluene-d_8 solution of $[N_3N]Ta(Et)H$ in a sealed NMR tube decomposed upon heating in an oil bath at 100 °C for 5 h. The ^{1}H NMR was consistent with formation of $EtTa[N(CH_2CH_2NSiMe_3)_2(CH_2CH_2N)]$ and Me_3SiH [δ 4.12 (m, 1, Me_3SiH), 0.02 (d, $^3J_{HH} = 4$, 9, Me_3SiH)], contaminated by a small amount (<5%) of $EtTa[N(SiMe_3)(CH{=}CH_2)][N(CH_2CH_2NSiMe_3)_2]$ resulting from dihydrogen loss to give $[N_3N]Ta(C_2H_4)$ followed by decomposition of $[N_3N]Ta(C_2H_4)$. The light yellow reaction mixture was concentrated in vacuo to provide a yellow oil. Recrystallization of the yellow oil from diethyl ether at −35 °C afforded $EtTa[N(SiMe_3)(CH{=}CH_2)][N(CH_2CH_2NSiMe_3)_2]$ as yellow crystals. The mother liquor was concentrated in vacuo to afford "$EtTa[N(CH_2CH_2NSiMe_3)_2(CH_2CH_2N)]$" as a colorless oil: ^{1}H NMR (C_6D_6) δ 4.40 (br m, 2, CH_2), 3.74 (br m, 2, CH_2), 3.58 (br m, 2, CH_2), 3.37 (br m, 2, CH_2), 2.58 (br s, 4, CH_2), 2.07 (t, 3, CH_2CH_3), 1.08 (q, 2, CH_2CH_3), 0.46 (s, 18, $NSiMe_3$); ^{13}C NMR (C_6D_6) δ 54.6 (t, $^1J_{CH} = 141$, $=NCH_2$), 52.6 (t, $^1J_{CH} = 134$, CH_2), 51.7 (t, $^1J_{CH} = 135$, CH_2), 49.5 (t, $^1J_{CH} = 135$, CH_2), 46.2 (t, $^1J_{CH} = 115$, CH_2CH_3), 18.3 (q, $^1J_{CH} = 124$, CH_2CH_3), 3.4 (q, $^1J_{CH} = 115$, $SiMe_3$). "$EtTa[N(CH_2CH_2NSiMe_3)_2(CH_2CH_2N)]$" could not be induced to crystallize.

Kinetics of Decomposition of $[N_3N]Ta(C_2H_4)$. Decomposition reactions were followed by UV/vis spectroscopy. In UV/vis runs a Hellma 221-QS quartz cell (path length = 10 mm) sealed to a gas adapter fitted with a Teflon stopcock was charged with 2 mL of a stock solution of $[N_3N]Ta(C_2H_4)$ (**4**) via syringe. The cell was placed in the HP 8452 diode array spectrophotometer, and the temperature was then set utilizing a HP 89090A Peltier temperature control accessory. Upon reaching the desired temperature, the reaction was monitored by observing the decrease in the absorbance of the solution at 494 nm at fixed time intervals via an interface to a HP 9000 Series 300 computer. The reaction temperature was maintained to within ±0.2 °C of the set point. Decomposition of a toluene solution of **4** ([**4**] = 0.0059, 0.0089, 0.010, 0.012 M) was shown to be first order in tantalum with $k = 1.37(1) \times 10^{-4}$ s^{-1} at 70 °C. At 70 °C $k_D = 1.53(2) \times 10^{-4}$ s^{-1}, for a k_H/k_D of 0.89(2). The fractional uncertainty in the measured rate constants was assumed to be 1% on the basis of inspection of the sensitivity of the fits to the absorbance versus time plots.

Reactions of $[N_3N]Ta(C_6H_4)$. (a) With Aniline To Give $[N_3N]Ta{=}NPh$. An NMR tube was charged with a solution of $[N_3N]Ta(C_6H_4)$ (20 mg, 0.0324 mmol) and ferrocene (3 mg, 0.0161 mmol) in ~1 mL of toluene-d_8. Aniline (2.9 μL, 0.0324 mmol) was then added via syringe, and the tube was sealed and placed in an oil bath at 90 °C for 4 days. The reaction mixture was determined by ^{1}H NMR spectroscopy with a ferrocene internal standard to contain a >99% yield of $[N_3N]Ta{=}NPh$.

(b) With Pentafluoroaniline To Give $[N_3N]Ta{=}NC_6F_5$. An NMR tube was charged with a solution of $[N_3N]Ta(C_6H_4)$ (10 mg, 0.0162 mmol), pentafluoroaniline (3 mg, 0.0162 mmol), and ferrocene (2 mg, 0.0122 mmol) in ~1 mL of toluene-d_8. The tube was then sealed and placed in an oil bath at 110 °C for 7 days. The reaction mixture was shown by ^{1}H NMR spectroscopy with a ferrocene internal standard to contain a 98% yield of $[N_3N]Ta{=}NC_6F_5$.

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Supporting Information Available: A detailed description of X-ray data collection, structure solution, and refinement, labeled ORTEP diagrams, and tables of fractional coordinates, isotropic and anisotropic thermal parameters, intramolecular distances, intramolecular angles, and torsional angles for $[N_3N]Ta(Me)Et$ and $[N_3N]Ta(C_2H_2)$ (26 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm edition of this journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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