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Alkyl and Alkylidene Complexes of Tantalum That Contain a Triethylsilyl-Substituted Triamido−Amine Ligand

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Addition of $Li_3[N_3N^*]$ ($[N_3N^*]^{3-} = [N(CH_2CH_2NSiEt_3)_3]^{3-}$) to $TaCl_5$ yields $[N_3N^*]TaCl_2$, from which $[N_3N^*]TaMe_2$ is formed quantitatively upon adding 2 equiv of methylmagnesium chloride. Alkylation of $[N_3N^*]TaCl_2$ with 2 equiv of ethylmagnesium chloride yields $[N_3N^*]Ta(C_2H_4)$ along with ~10% $[N_3N^*]Ta{=}CHMe$, while dialkylation with Grignard or lithium reagents (alkyl = RCH_2^-, in which R = CH_2CH_3, $CH_2CH_2CH_3$, $CH_2CH(CH_3)_2$, $SiMe_3$, or Ph) yields the alkylidene complexes $[N_3N^*]Ta{=}CHR$. $[N_3N^*]TaMe_2$ decomposes upon thermolysis to afford $MeTa[N(SiEt_3)(CH{=}CH_2)][N(CH_2CH_2NSiEt_3)_2]$, while $[N_3N^*]Ta(C_2H_4)$ decomposes in a first-order manner to afford $EtTa[N(SiEt_3)(CH{=}CH_2)][N(CH_2CH_2NSiEt_3)_2]$. An X-ray structure of the latter showed it to be a distorted trigonal bipyramid in which a $C{-}N_{ax}$ bond in the original TREN backbone has been cleaved. An approximately equimolar mixture of $[N_3N^*]Ta(C_2H_2)$ and $\{[N_3N^*]Ta{=}CHCH_2\}_2$ is formed upon treating $[N_3N^*]TaCl_2$ with 2 equiv of vinylmagnesium bromide in refluxing toluene. An X-ray structure of $\{[N_3N^*]Ta{=}CHCH_2\}_2$ showed it to contain two distorted trigonal bipyramidal $[N_3N^*]Ta$ units bridged by a four carbon "dialkylidene" unit in which each alkylidene is severely distorted (average $\angle Ta{-}C{-}C = 172°$).

Introduction

Recent efforts in these laboratories[1−3] and others[4] have focused on the synthesis and chemistry of monomeric $[N_3N]Ta$ ($[N_3N]^{3-} = [N(CH_2CH_2NSiMe_3)_3]^{3-}$) complexes that contain a Ta-ligand multiple bond. The triamido−amine ligand system stabilizes $[N_3N]Ta{=}E$ species by sterically preventing bimolecular decomposition reactions and by providing one σ orbital along the z axis and two orthogonal π orbitals (approximately d_{xz} and d_{yz}) to form a double or pseudotriple bond between Ta and E. The majority of $[N_3N]Ta{=}E$ species prepared feature a pseudotriple bond between tantalum and phosphorus,[1,3] nitrogen,[1,2] arsenic,[1] carbon,[1,2] oxygen,[2,3] selenium,[4] or tellurium.[4] The alkylidene ligands in $[N_3N]Ta{=}CHR$ complexes are best viewed as $1\sigma,2\pi$ ligands by virtue of an agostic interaction[5] of the alkylidene $C{-}H_\alpha$ bond[6,7] in addition to the formal double bond. Efforts to prepare alkylidene complexes with C_β substituents other than hydrogen led to the discovery that α- and β-H abstractions are competitive processes in this system.[1] In the reaction of $[N_3N]TaCl_2$ with 2 equiv of $R'CH_2CH_2MgX$ it was shown that as R′ increased in size (from Me to *i*-Pr to *t*-Bu) the preference for α-H abstraction increased to the point where no β abstraction took place at all. It was proposed that the larger C_β substituent forces the $Ta{-}C_\alpha{-}C_\beta$ angles in the dialkyl intermediate, $[N_3N]Ta(CH_2CH_2R')_2$, to increase as a consequence of unfavorable steric interactions between R′ and the encircling trimethylsilyl substituents, thereby activating the α-H's toward formation of the alkylidene and sterically blocking a β abstraction process.

On the basis of these results, it seemed appropriate to look for evidence that an increase in the steric bulk of the trialkylsilyl groups also leads to α-H abstraction processes being favored over β-H abstraction processes. Therefore we turned to the synthesis of $[N_3N^*]Ta$ complexes, where $[N_3N^*]^{3-} = [N(CH_2CH_2NSiEt_3)_3]^{3-}$. The results of these studies are reported here along with two X-ray studies, one that illustrates a significant limitation of trialkylsilyl-substituted TREN ligands in preparing reactive tantalum complexes and the other that confirms the dramatically distorted nature of alkylidene ligands in tantalum complexes of this general type.

Results

$Li_3[N_3N^*]$ ($[N_3N^*]^{3-} = [N(CH_2CH_2NSiEt_3)_3]^{3-}$) can be prepared by a method analogous to that used to prepare $Li_3[N(CH_2CH_2NSiMe_3)_3]$,[8,9] i.e., treatment of $N(CH_2CH_2NH_2)_3$ successively with 3 equiv of *n*-butyllithium, 3 equiv of triethylchlorosilane, and 3 equiv again of *n*-butyllithium (eq 1).[10,11] Since $Li_3[N_3N^*]$ has not yet

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[2] Freundlich, J. S.; Schrock, R. R.; Cummins, C. C.; Davis, W. M. *J. Am. Chem. Soc.* **1994**, *116*, 6476.

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[8] Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Organometallics* **1992**, *11*, 1452.

[9] Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Inorg. Chem.* **1994**, *33*, 1448.

$$N(CH_2CH_2NH_2)_3 \xrightarrow[\text{2. 3 Et}_3\text{SiCl, THF, -78 °C}]{\text{1. 3 }n\text{-BuLi, THF, -78 °C}} N(CH_2CH_2NHSiEt_3)_3 \quad (1)$$

been induced to crystallize, it is most convenient to isolate crude $N(CH_2CH_2NHSiEt_3)_3$ and to generate $Li_3[N_3N^*]$ from it for each reaction. The greater solubility of triethylsilyl derivatives versus trimethylsilyl derivatives is to be expected and is a persistent problem in the chemistry to be described here.

Tantalum pentachloride reacts with $Li_3[N_3N^*]$ at −78 °C to afford $[N_3N^*]TaCl_2$ (**1**) in ~20% yield (eq 2),[11]

$$H_3[N_3N^*] \xrightarrow[\text{2. TaCl}_5\text{, -78 °C}]{\text{1. 3 }n\text{-BuLi, Et}_2\text{O, -35 °C}} \underset{\mathbf{1}}{[N_3N^*]TaCl_2} \quad (2)$$

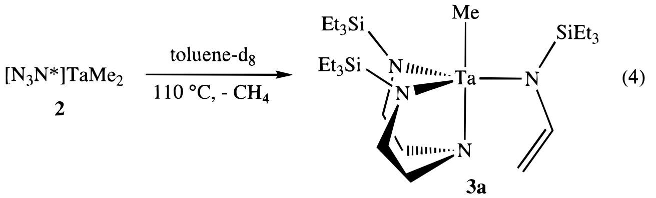
which is less than half the yield of $[N_3N]TaCl_2$ prepared under similar conditions. We presume that the decrease in yield upon increasing the bulk of the silyl substituent is a consequence of slower nucleophilic attack at the metal. We do not yet know what is the dominant reaction, although we have speculated that the low yield of $[N_3N]TaCl_2$ can be ascribed to reduction of tantalum(V) to intractable products.[1] Fortunately, $[N_3N^*]TaCl_2$ can be isolated readily as a pure solid in spite of its low yield. Proton and carbon NMR data suggest that it, like $[N_3N]TaCl_2$, is C_3-symmetric on the NMR time scale between 25 and −90 °C.

Alkylation of $[N_3N^*]TaCl_2$ with 2 equiv of methylmagnesium chloride in diethyl ether affords $[N_3N^*]TaMe_2$ (**2**) quantitatively as a yellow-brown oil (eq 3).

$$\underset{\mathbf{1}}{[N_3N^*]TaCl_2} \xrightarrow[\text{Et}_2\text{O, -35 °C}]{\text{2 MeMgCl}} \underset{\mathbf{2}}{[N_3N^*]TaMe_2} \quad (3)$$

Small samples of yellow crystalline $[N_3N^*]TaMe_2$ could be obtained by storing concentrated pentane solutions of **2** at −35 °C for several weeks. A resonance for the two methyl groups bound to tantalum in **2** is found as a singlet at 1.31 ppm in the ^1H NMR spectrum between 25 and −90 °C and as a quartet ($^1J_{CH} = 117$ Hz) at 64.9 ppm in the ^{13}C NMR spectrum. All NMR data are consistent with **2** having an average structure in solution in which the two methyl groups are equivalent.

Methane begins to evolve upon heating a toluene-d_8 solution (~10 mM) of **2** in a sealed NMR tube to ~70 °C. At 110 °C decomposition is complete after 1 day to afford a product (**3a**, eq 4) that appears to be analogous to the thermolysis product of $[N_3N]TaMe_2$[1] and to the thermolysis product of $[N_3N^*]Ta(C_2H_4)$, whose X-ray structure is described later here. Most prominent in the ^1H NMR spectrum of **3a** are diastereotopic methylene resonances in the ligand backbone and a singlet at 0.80 ppm for a methyl group bound to tantalum.



(4)

3a

Thermolysis of $[N_3N^*]Ta(CD_3)_2$ affords CD_3H and product characterized by a singlet for the $TaCD_3$ group at 0.91 ppm in the ^2H NMR spectrum. Therefore formation of CD_4 and intermediate $[N_3N^*]Ta{=}CD_2$ by α hydrogen abstraction can be ruled out. Evidently a "*β*" $TaN_{eq}CH_2$ proton is abstracted by the methyl group on Ta, possibly after being activated by coordination to the metal. (Only two of the three orbitals in the apical coordination site are involved in bonding to the two methyl groups.) No further details are known at this stage. These results suggest that an increase in the steric bulk in the silyl substituents does not alter the manner in which these tren-based complexes decompose, and that loss of methane to give hypothetical $[N_3N^*]Ta{=}CH_2$ must be a relatively slow reaction. Similar slow decomposition of tantalum methyl complexes by α hydrogen abstraction relative to the rate of α hydrogen abstraction in substituted dialkyl intermediates is relatively well-documented,[6] and is consistent with facile α hydrogen abstraction in other (presumed) dialkyl intermediates in this $[N_3N^*]$ system (see below).

Addition of 2 equiv of ethylmagnesium chloride to $[N_3N^*]TaCl_2$ produced the ethylene complex **4** (eq 5) as

$$\underset{\mathbf{2}}{[N_3N^*]TaCl_2} \xrightarrow[\text{Et}_2\text{O, -35 °C}]{\text{2 EtMgCl}} \underset{\mathbf{4}}{[N_3N^*]Ta(C_2H_4)} + \underset{\mathbf{5a}}{[N_3N^*]Ta{=}CHMe} \quad (5)$$

red-purple crystals in 82% isolated yield. Rotation of the ethylene ligand about the ligand−metal bond is fast on the NMR time scale. Therefore the complex has apparent C_3 symmetry at temperatures down to −90 °C. However, the ethylidene complex (**5a**; eq 5) makes up ~10% of the crude product, judging from a quartet resonance at -0.52 ppm, a chemical shift to be expected for an alkylidene H_α resonance in complexes of this type (cf. −0.41 ppm for $\delta(H_\alpha)$ in $[N_3N]Ta{=}CHMe$).[2] The low yield and high solubility of **5a** prevented its being isolated in pure form. This result differs significantly from that obtained in the N_3N system, where only $[N_3N]Ta(C_2H_4)$ is formed upon adding ethyl Grignard to $[N_3N]TaCl_2$.

Reactions between $[N_3N^*]TaCl_2$ and 2 equiv of RCH_2CH_2MgX (X = Cl, Br; R = Me, Et, *i*-Pr) afforded the alkylidene complexes **5b**−**d** in 87%, 71%, and 81% isolated yields, respectively (eq 6). There is no evidence in NMR spectra of the crude product mixture for products that would arise from decomposition of the unstable olefin complex formed via a *β* abstraction process. These results contrast markedly with those for analogous reactions involving $[N_3N]TaCl_2$, where products from both α- and *β*-H abstraction pathways are observed.[1] Unfortunately, only **5b** could be crystallized and then only after storage of a concentrated pentane solution at −35 °C for months. Complexes **5b**−**d** are stable at 110 °C for days in toluene-d_8 (~0.1 M). Similar reactions between $[N_3N^*]TaCl_2$ and 2 equiv of ((trimethylsilyl)methyl)lithium or benzylmagnesium chloride yield **5e** or **5f** (eq 7). $[N_3N^*]Ta{=}CHSiMe_3$ (**5e**) may be

$$[N_3N^*]TaCl_2 \xrightarrow[\text{Et}_2\text{O, -35 °C}]{\text{2 RCH}_2\text{CH}_2\text{MgX}} [N_3N^*]Ta{=}CHCH_2R \quad (6)$$

R = Me (**5b**), Et (**5c**), *i*-Pr (**5d**)

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[10] Schrock, R. R.; Cummins, C. C.; Wilhelm, T.; Lin, S.; Reid, S.; Kol, M.; Davis, W. M. *Organometallics* **1996**, *15*, 1470.

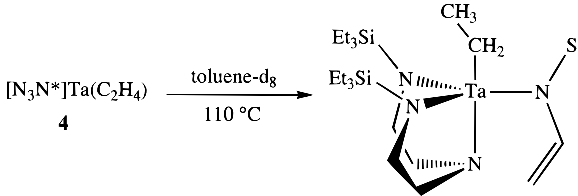
[11] Cummins, C. C. Ph.D. Thesis, Massachusetts Institute of Technology, 1993.

$$[N_3N^*]TaCl_2 \xrightarrow[Et_2O,\ -35\ °C]{dialkylation} [N_3N^*]Ta{=}CHR \qquad (7)$$

R = $SiMe_3$ (**5e**; employing Me_3SiCH_2Li)
R = Ph (**5f**; employing $PhCH_2MgCl$)

isolated as a yellow crystalline solid in 71% yield, whereas **5f** could be isolated only as a red-orange oil contaminated by small amounts of remaining Grignard reagent. Like complexes that contain the $[N_3N]Ta$ core, **5b**−**f** exhibit an upfield resonance for H_α (−0.27 to 0.14 ppm) in the ^1H NMR spectrum and a low value for $^1J_{CH_\alpha}$ (~70 Hz) in the alkylidene ligand, characteristic of a "distorted" alkylidene[6,7] in which there is an α agostic[5] interaction of the CH_α electron pair and the metal. The Ta=CHR functionality may be cleaved with benzaldehyde[12] to give a mixture of *cis*- and *trans*-isomers of the expected olefin and what we presume to be $[N_3N^*]Ta{=}O$, according to its proton NMR spectrum and by analogy with reactions that yield isolated $[N_3N]Ta{=}O$.[1]

Thermolysis of a 0.16 M toluene-d_8 solution of **4** produced the ethyl complex, **3b** (eq 8). Decomposition



3b (8)

of **4** in toluene at concentrations between 0.0061 and 0.015 M was followed by UV/vis at λ_{max} = 510 nm and shown to be first order in tantalum with k = 4.23(4) × 10^{-5} s^{-1} at 70 °C. This rate is approximately one-third that observed for decomposition of the trimethylsilyl-substituted analog (k = 1.37(1) × 10^{-4} s^{-1}) under the same conditions.[1] Most characteristic in the proton NMR spectrum of **3b** are the vinyl resonances at 6.55 ppm (dd), 4.54 ppm (d), and 4.11 ppm (d, obscured by diastereotopic ligand methylene resonances). $[N_3N^*]Ta(C_2D_4)$ decomposed slightly more readily (k = 4.72(1) × 10^{-5} s^{-1}; three runs) to afford an analogous complex containing a $TaCD_2CD_2H$ ligand (according to ^1H and ^2H NMR), consistent with a rate-limiting step that involves rehybridization from sp^2 to sp^3 in the ethylene ligand (k_H/k_D = 0.90(2) at 70 °C).[13] Thermolysis of $[N_3N^*]Ta(C_2D_4)$ (0.010 M in toluene-d_8) in the presence of 1 atm of ethylene also produces a $TaCD_2CD_2H$ species. All of these data are consistent with decomposition of **3b** by irreversible intramolecular abstraction of a methylene proton α to the equatorial nitrogen atom in the ligand backbone.

An X-ray crystal study of **3b** (Table 1; Figure 1) showed it to be a "tetramido" ethyl complex with a distorted trigonal bipyramidal geometry. (Relevant bond lengths and angles are listed in Table 2). A mirror plane bisects the two silylamido nitrogens that remain tethered to what was once the tertiary amine donor in **4** and is now an amide donor to the metal center (Ta−N(4) = 1.966(8) Å). N(1) and N(3) now occupy approximately axial positions in the distorted trigonal bipyramid (N(1)−Ta−N(3) = 152.2(3)°). The vinyl- and Et_3Si-substituted amido ligand has "rotated" approximately 180° from its position upon cleavage of the $C{-}N_{ax}$ bond, presumably in order to allow more room for the relatively bulky Et_3Si group. The Ta−N−Si bond angles for the two equivalent amido groups (133 and 135°) are comparable to those in $[N_3N]Ta(Me)Et$.[1] The ethyl group appears to be relatively undistorted with a Ta−C(1) bond length of 2.17(1) Å, a Ta−C(1)−C(2) angle of 117.6(7)°, and a C(1)−C(2) bond length of 1.53(1) Å.

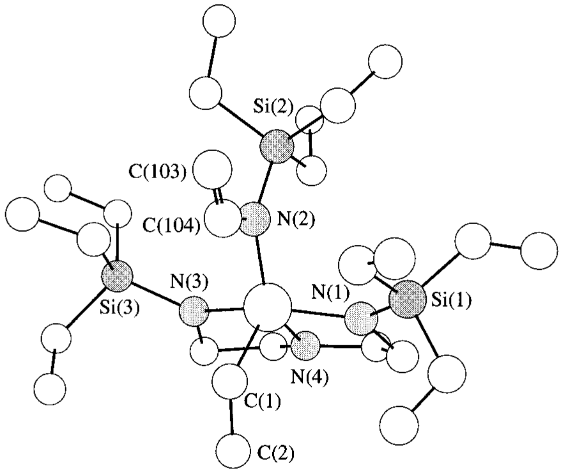


Figure 1. Chem 3D drawing of the structure of $EtTa[N(SiEt_3)(CH{=}CH2)[N(CH_2CH_2NSiEt_3)_2]$ (**3b**).

Table 1. Crystallographic Data, Collection Parameters, and Refinement Parameters for $EtTa[N(SiEt_3)(CH{=}CH_2)][N(CH_2CH_2NSiEt_3)_2]$ (3b) and $\{[N_3N^*]Ta{=}CHCH_2\}_2$ (7)

	3b	7
empirical formula	$C_{26}H_{61}N_4Si_3Ta$	$C_{59}H_{128}N_8Si_6Ta_2$
fw	695.00	1478.78
diffractometer	Enraf-Nonius CAD-4	Siemens SMART/ CCD
cryst color, morphology	yellow, parallelepiped	yellow, prism
cryst dimens (mm)	0.260 × 0.320 × 0.340	0.33 × 0.28 × 0.28
crystal system	triclinic	monoclinic
a (Å)	9.9701(8)	19.3176 (11)
b (Å)	11.3064(9)	20.8010(12)
c (Å)	15.586(2)	18.6252(11)
b (deg)	75.96(1)	99.3130(10)
V (Å^3)	1688.3(7)	7385.4 (7)
space group	$P(\bar{1})$(No. 2)	$P2_1/c$
Z	2	4
D_{calc} (g/cm^3)	1.368	1.331
F_{000}	718	3060
μ(Mo Kα) (cm^{-1})	33.40	30.96
scan type	$\omega{-}2\theta$	ω scans
temp (K)	187	193 (2)
tot. no. unique reflcns	4404	10616
no. observns with $I > 3.00\sigma(I)$	3811	n/a
no. variables	308	642
R	0.041	0.0719
R_w	0.053	0.2075
GoF	1.93	1.022

$[N_3N]TaCl_2$ is known to react with 2 equiv of vinylmagnesium bromide to afford structurally characterized $[N_3N]Ta(HC{\equiv}CH)$ in high yield.[1] The reaction is proposed to proceed via β hydrogen abstraction in intermediate $[N_3N]Ta(HC{=}CH_2)_2$, although α hydrogen abstraction to yield $[N_3N]Ta{=}C{=}CH_2$ as the first product could not be ruled out. In contrast, $[N_3N^*]TaCl_2$ reacts with 2 equiv of vinylmagnesium bromide in refluxing

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[12] Schrock, R. R. *J. Am. Chem. Soc.* **1976**, *98*, 5399.

[13] Carpenter, B. K. *Organic Reaction Mechanisms*; John Wiley & Sons: New York, 1984.

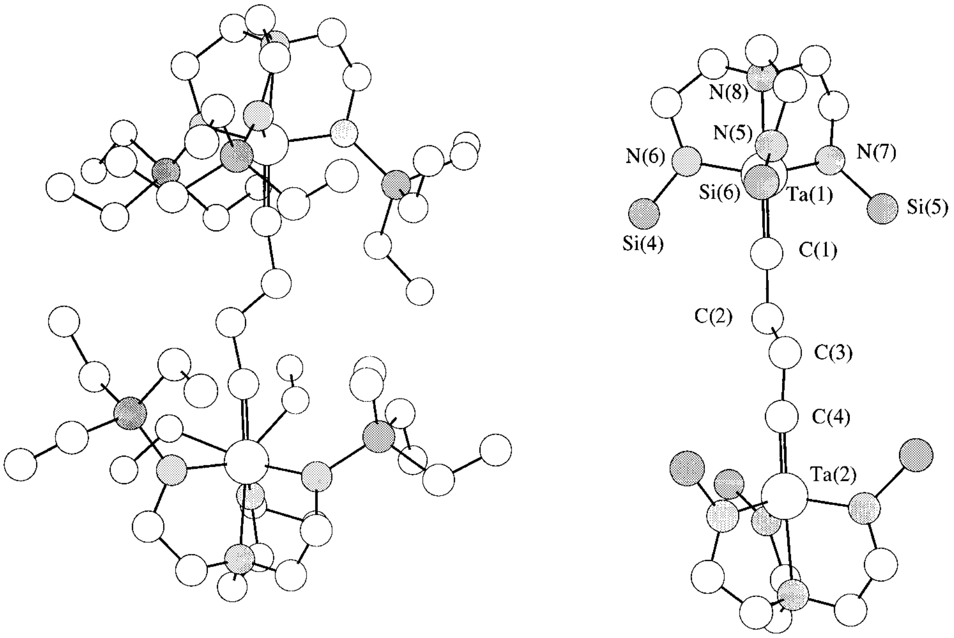

Figure 2. Two Chem 3D views of the structure of $\{[N_3N^*]Ta{=}CHCH_2\}_2$ (**7**). Ethyl groups are omitted in the view on the right.

Table 2. Selected Intramolecular Distances (Å) and Angles (deg) for the Non-Hydrogen Atoms of $EtTa[N(SiEt_3)(CH{=}CH_2)][N(CH_2CH_2NSiEt_3)_2]$ (3b) and $\{[N_3N^*]Ta{=}CHCH_2\}_2$ (7)

3b		**7**	
		Bond Lengths	
Ta−N(1)	2.025(7)	Ta(1)−N(5)	2.031(11)
Ta−N(2)	2.009(7)	Ta(1)−N(6)	2.030(10)
Ta−N(3)	2.035(8)	Ta(1)−N(7)	2.024(10)
Ta−N(4)	1.966(8)	Ta(1)−N(8)	2.375(10)
Ta-C(1)	2.17 (1)	Ta(1)−C(1)	1.891(11)
C(1)−C(2)	1.53 (1)	Ta(2)−C(4)	1.898(10)
C(103)−C(104)	1.32 (1)	C(1)−C(2)	1.53(2)
		C(2)−C(3)	1.42(2)
		Bond Angles	
Ta−N(1)−Si(1)	134.7(4)	Ta(1)−N(5)−Si(6)	128.3(5)
Ta−N(2)−Si(2)	125.2(4)	Ta(1)−N(6)−Si(4)	124.9(6)
Ta−N(3)−Si(3)	133.5(4)	Ta(1)−N(7)−Si(5)	125.4(5)
N(1)−Ta−N(3)	152.2(3)	N(5)−Ta−N(6)	113.1(4)
N(1)−Ta−C(1)	97.2(3)	N(5)−Ta−N(7)	116.6(4)
N(3)−Ta−C(1)	94.6(3)	N(6)−Ta−N(7)	115.8(4)
Ta−C(1)−C(2)	117.6(7)	Ta(1)−C(1)−C(2)	172.1(12)
		Ta(2)−C(4)−C(3)	173.1(12)
		C(1)−C(2)−C(3)	118(2)

toluene to afford a mixture of two species, one of which is $[N_3N^*]Ta(HC{\equiv}CH)$ (**6**, eq 9), according to proton and

$$[N_3N^*]TaCl_2 \xrightarrow[\text{tol, 80 °C}]{2\ H_2C{=}CHMgBr} \underset{\mathbf{6}}{[N_3N^*]Ta(HC{\equiv}CH)} + \underset{\mathbf{7}}{\{[N_3N^*]Ta{=}CHCH_2\}_2} \qquad (9)$$

carbon NMR spectra that are analogous to those of crystallographically characterized $[N_3N]Ta(HC{\equiv}CH)$. The other product of the ∼1:1 mixture is a yellow crystalline solid that could be isolated in 39% yield, owing to its significantly lower solubility versus that of **6**. Proton and carbon NMR established that this molecule is a C_3-symmetric "distorted" alkylidene complex with a C_α resonance at 201.3 ppm ($^1J_{CH_\alpha} = 69$ Hz) and an H_α resonance at −0.27 ppm. What is apparently a methylene group attached to C_α is the origin of a resonance at 3.51 ppm and a carbon resonance at 49.4 (J_{CH} = 128 Hz). Therefore we postulated that **7** is a dimer of hypothetical d^1 $[N_3N^*]Ta(CH{=}CH_2)$ in which the β carbon atoms have coupled, i.e., $\{[N_3N^*]Ta{=}CHCH_2\}_2$.

An X-ray crystal study of **7** (Table 1; Figure 2) revealed that the proposed dimeric formulation is correct. (Relevant bond lengths and angles are listed in Table 2.) The precision of the structure was lowered by the presence of a disordered toluene in the lattice. The two $[N_3N^*]Ta$ units are identical within statistical deviations. Each end may be described as a distorted trigonal bipyramid. The $Ta(1){-}N_{eq}$ distances (2.02−2.03 Å), $Ta(1){-}N_{ax}$ distance (2.375 (10) Å), and $N_{ax}{-}Ta{-}N_{ax}$ and $Ta{-}N_{ax}{-}Si$ bond angles are similar to those found in $[N_3N]Ta(C_2H_2)$[1] and $[N_3N]Ta{=}PCy$.[3] The $Ta{=}C_\alpha{-}C_\beta$ bond angle and Ta=C bond length are characteristic of a "distorted" alkylidene in which there is a significant interaction of the CH_α bond with the metal and a consequent shortening of the $Ta{=}C_\alpha$ bond. These data should be compared with those for the earliest example of a distorted d^0 species in the literature,[6] $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$ (Ta=C = 1.898 Å, ∠Ta=C−C = 161.2°).[7,14] Compound **7** actually is the first of the triamido−amine type in which the distorted nature of the alkylidene ligand has been confirmed. Although steric factors would certainly contribute to an increase in the Ta=C−C angle, it does not appear (according to the values for $^1J_{CH}$) that alkylidene ligands are *more* distorted in $SiEt_3$ derivatives than in $SiMe_3$ derivatives. We conclude that the agostic C−H interaction with the metal in alkylidene complexes is largely electronic in origin.

Discussion

The synthesis of $[N_3N^*]Ta$ complexes was undertaken in order to probe the effect of changing the amido

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[14] Schultz, A. J.; Brown, R. K.; Williams, J. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 169.

nitrogen substituent from trimethylsilyl to the more bulky triethylsilyl. The most pronounced effect is that α-H abstraction is the *sole* process observed upon alkylating $[N_3N^*]TaCl_2$ with 2 equiv of RCH_2CH_2MgX where R is larger than hydrogen. In the $[N_3N]$Ta-based system, both α-H and β-H abstraction processes are observed for R groups smaller than *tert*-butyl. These observations are consistent with α hydrogen abstraction from a dialkyl intermediate being much more favored in the more crowded coordination pocket created by $SiEt_3$ substituents. We presume that the larger $Ta-C_\alpha-C_\beta$ bond angles in the dialkyl intermediate inhibit β-hydrogen abstraction and at the same time encourage α-hydrogen abstraction. Evidence for a similar sterically induced preference for α abstraction in a tantalum alkyl was discovered several years ago;[15] decomposition of $Cp^*_2(H)Ta{=}C{=}CH_2$ was proposed 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 $Cp^*(\eta^5\text{-}C_5Me_4CH_2\text{-}CH{=}CH_2)TaH$. There are other examples in the literature where α-H processes are proposed to occur preferentially,[16-21] although in our opinion none demonstrates as clearly the trend toward α abstraction as a consequence of a more sterically crowded environment as the results presented for the $[N_3N]$Ta and $[N_3N^*]$Ta systems.

Compound **7** has no $[N_3N]$Ta-based relative, as treatment of $[N_3N]TaCl_2$ with 2 equiv of vinylmagnesium bromide affords only $[N_3N]Ta(C_2H_2)$.[1] We speculate that $\{[N_3N^*]Ta{=}CHCH_2\}_2$ forms via coupling of β carbon atoms in d^1 $[N_3N^*]Ta(CH{=}CH_2)$, a reaction that is related to coupling of alkynyl ligands in d^2 $[N_3N]W(C{\equiv}CH)$[22] or, perhaps most analogously, to coupling of imino ligands in d^1 niobium complexes to give d^0 bimetallic Nb imido complexes.[23] We propose that a species analogous to **7** is not formed when $[N_3N]TaCl_2$ reacts with vinyl Grignard because nucleophilic substitution to give $[N_3N]Ta(CH{=}CH_2)_2$ is complete before intermediate $[N_3N]Ta(CH{=}CH_2)Cl$ can be reduced by electron transfer from the Grignard reagent. We propose that the more crowded coordination sphere in $[N_3N^*]Ta(CH{=}CH_2)Cl$ leads to reduction to $[N_3N^*]Ta(CH{=}CH_2)$ by the Grignard reagent. Formation of $\{[N_3N^*]Ta{=}CHCH_2\}_2$ could be taken as another consequence of a more crowded coordination sphere in a $[N_3N^*]$Ta complex versus a $[N_3N]$Ta complex.

The X-ray structure of $\{[N_3N^*]Ta{=}CHCH_2\}_2$ supports our proposal that alkylidene complexes with the tantalum triamido−amine core are severely "distorted" through an α agostic interaction of the CH_α bond with the metal and that a pseudotriple tantalum−carbon bond is established. Structural and spectroscopic data suggest that d^0 alkylidene complexes with a $[N_3N]$Ta or $[N_3N^*]$Ta core are among the most "distorted" d^0 species to be reported to date. (An alkylidene in a reduced specie, e.g. $Cp^*Ta(CHCMe_3)(C_2H_4)(PMe_3)$ ($Ta{-}C = 1.946$ Å, $\angle Ta{=}C{-}C = 170.0°$),[14] has typically been the most distorted, and alkylidyne hydride complexes eventually can form.[6]) The reason why an alkylidene is so effectively pseudotriply bound to the metal in $[N_3N]$Ta and $[N_3N^*]$Ta complexes is still not clear, although the presence of two *degenerate* low-energy π orbitals directed along the *z* axis is certainly a feature of complexes of this type that dramatically favors the formation of metal−ligand triple bonds in general.

Steric hindrance in triamido−amine complexes could be increased even further than found in the $SiEt_3$ derivatives in this work by employing $Si(i\text{-}Pr)_3$ substituents. Although $Li_3\{N[CH_2CH_2NSi(i\text{-}Pr)_3]_3\}$ has been prepared by methods analogous to those used to prepare $Li_3[N(CH_2CH_2NSiEt_3)_3]$,[24] attempts to prepare a tantalum dichloride derivative so far have not been successful. We postulate that for steric reasons nucleophilic attack by $Li_3\{N[CH_2CH_2NSi(i\text{-}Pr)_3]_3\}$ on $TaCl_5$ simply is too slow relative to the rate of alternative (perhaps intermolecular) reactions, at least under the conditions that we have used so far. The failure to prepare *i*-Pr-substituted TREN derivatives of tantalum is unfortunate, since steric protection might be increased to the point of stabilizing a d^1 Ta(IV) vinyl complex, an analog of the proposed intermediate in the reaction that yields **7**.

Future work will be directed primarily toward synthesizing complexes that contain new TREN-like ligands that are more stable toward the type of N−C bond cleavage observed here. One of the ultimate goals is to access much more reactive heavy metal species, e.g., d^2 trigonal monopyramidal tantalum complexes analogous to those synthesized for the first row metals.[25]

Experimental Section

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques, unless otherwise noted. Reagent grade solvents were purified by standard methods.

^1H and ^{13}C NMR data are listed in parts per million downfield from TMS, while ^{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 or a Siemens SMART/CCD 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 or 512 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 (−196 °C) freeze−pump−thaw cycles before flame sealing under a static vacuum.

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$H_3[N_3N^*]$.[10] *n*-Butyllithium (154 mL, 1.6 M in hexanes, 0.246 mol) was added via cannula to a solution of tris(2-aminoethyl)amine (12.00 g, 82 mmol) in 200 mL of tetrahydrofuran that had been cooled to −78 °C. The milky-white mixture was allowed to warm slowly to room temperature and was then stirred for 8 h. The mixture was then cooled to −78 °C, and triethylchlorosilane (37.10 g, 246 mmol) was added via cannula. The mixture was allowed to warm to room temperature and was stirred for an additional 12 h at room temperature. All solvent was then removed in vacuo to yield a cloudy pink oil. The oil was dissolved in 150 mL of pentane, and the solution was filtered through Celite. The pentane was removed from the light pink filtrate, and the oil was kept in vacuo for 2 days to yield 39.16 g (0.0801 mol, 98%) of product: ^{1}H NMR (C_6D_6) δ 2.80 (q, 6, CH_2), 2.39 (t, 6, CH_2), 1.05 (t, 27, $\mathrm{SiCH_2C}H_3$), 0.77 (t, 3, NH), 0.59 (q, 18, $\mathrm{SiC}H_2\mathrm{CH_3}$); ^{13}C NMR ($C_6D_6$) 59.4 (t, $^1J_{CH} = 132$, CH_2), 40.5 (t, $^1J_{CH} = 133$, CH_2), 7.6 (q, $^1J_{CH} = 125$, $\mathrm{SiCH_2}C\mathrm{H_3}$), 5.25 (t, $^1J_{CH} = 116$, $\mathrm{Si}C\mathrm{H_2CH_3}$).

$[N_3N^*]TaCl_2$ (1). A solution of $H_3[N_3N^*]$ (3.91 g, 8.00 mmol) in 100 mL of diethyl ether was chilled to −35 °C, and *n*-butyllithium (15 mL, 1.6 M in hexanes, 24.0 mmol) was added via cannula. The pale yellow reaction mixture was stirred for 7 h and was then chilled to -78 °C. Solid $TaCl_5$ (2.87 g, 8.00 mmol) was then added under a counterflow of argon. The reaction mixture was allowed to warm slowly to room temperature and was stirred for 14 h. All solvents were removed in vacuo, and the resulting brown solid was extracted with 70 mL of diethyl ether. The extract was filtered through Celite, and the brown-yellow filtrate was concentrated in vacuo to yield an oily brown solid that was recrystallized from pentane at −35 °C to give yellow-orange crystals of product; yield 1.117 g (1.51 mmol, 19%): ^{1}H NMR (C_6D_6) δ 4.00 (t, 6, CH_2), 2.56 (t, 6, CH_2), 1.13 (t, 27, $\mathrm{SiCH_2C}H_3$), 1.06 (q, 18, $\mathrm{SiC}H_2\mathrm{CH_3}$); ^{13}C NMR ($C_6D_6$) δ 66.2 (t, $^1J_{CH} = 139$, CH_2), 55.7 (t, $^1J_{CH} = 137$, CH_2), 8.6 (q, $^1J_{CH} = 125$, $\mathrm{SiCH_2}C\mathrm{H_3}$), 7.0 (t, $^1J_{CH} = 119$, $\mathrm{Si}C\mathrm{H_2CH_3}$). Anal. Calcd for $TaSi_3N_4Cl_2C_{24}H_{57}$: C, 39.07; H, 7.79; N, 7.59. Found: C, 39.42; H, 7.62; N, 7.48.

$[N_3N^*]TaMe_2$ (2). Methylmagnesium chloride (298 μL, 3.0 M in tetrahydrofuran, 0.895 mmol) was added via syringe to a −35 °C solution of $[N_3N^*]TaCl_2$ (300 mg, 0.407 mmmol) in 8 mL of diethyl ether. A white precipitate was observed immediately. After 2 h the mixture was concentrated in vacuo and the residue was extracted with 70 mL of pentane. The solution was filtered through Celite, and the brown-yellow filtrate was concentrated in vacuo to afford 263 mg (0.377 mmol, 93%) of product as a brown-yellow oil. The complex may be isolated (irreproducibly) as pale yellow crystals upon recrystallization from pentane at −35 °C over a period of weeks: ^{1}H NMR (C_6D_6) δ 3.49 (t, 6, CH_2), 2.23 (t, 6, CH_2), 1.31 (s, 6, CH_3), 1.09 (t, 27, $\mathrm{SiCH_2C}H_3$), 0.88 (q, 18, $\mathrm{SiC}H_2\mathrm{CH_3}$); ^{13}C NMR ($C_6D_6$) δ 64.9 (q, $^1J_{CH} = 117$, CH_3), 61.1 (t, $^1J_{CH} = 135$, CH_2), 50.4 (t, $^1J_{CH} = 135$, CH_2), 8.5 (q, $^1J_{CH} = 123$, $\mathrm{SiCH_2}C\mathrm{H_3}$), 7.0 (t, $^1J_{CH} = 118$, $\mathrm{Si}C\mathrm{H_2CH_3}$). Anal. Calcd for $TaSi_3N_4C_{26}H_{63}$: C, 44.80; H, 9.11; N, 8.04. Found: C, 44.89; H, 8.96; N, 7.91.

$MeTa[N(SiEt_3)(CH{=}CH_2)][N(CH_2CH_2NSiEt_3)_2]$ (3a). A solution of $[N_3N^*]TaMe_2$ (175 mg, 0.251 mmol) in ~1 mL of toluene-d_8 was added to an NMR tube which was then sealed 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 **3a**: ^{1}H NMR (tol-d_8) δ 6.45 (dd, 1, $\mathrm{C}H{=}\mathrm{CH_2}$), 4.63 (d, 1, $\mathrm{CH{=}C}H_2$), 4.18 (d, 1, $\mathrm{CH{=}C}H_2$), 3.94 (m, 4, CH_2), 3.83 (m, 4, CH_2), 1.03 (t, 9, $\mathrm{NSiCH_2C}H_3$), 1.00 (t, 18, $\mathrm{NSiCH_2C}H_3$), 0.81 (q, 6, $\mathrm{NSiC}H_2\mathrm{CH_3}$), 0.80 (s, 3, CH_3), 0.66 (q, 12, $\mathrm{NSiC}H_2\mathrm{CH_3}$); ^{13}C NMR (tol-$d_8$) δ 133.9 (d, $^1J_{CH} = 164$, $C\mathrm{H{=}CH_2}$), 97.8 (t, $^1J_{CH} = 161$, $\mathrm{CH{=}}C\mathrm{H_2}$), 68.0 (t, $^1J_{CH} = 134$, CH_2), 55.2 (t, $^1J_{CH} = 136$, CH_2), 34.9 (q, $^1J_{CH} = 120$, CH_3), 8.3 (q, $^1J_{CH} = 125$, $\mathrm{NSiCH_2}C\mathrm{H_3}$), 7.8 (q, $^1J_{CH} = 121$, $\mathrm{NSiCH_2}C\mathrm{H_3}$), 6.6 (t, $^1J_{CH} = 117$, $\mathrm{NSi}C\mathrm{H_2CH_3}$), 5.6 (t, $^1J_{CH} = 115$, $\mathrm{NSi}C\mathrm{H_2CH_3}$).

$[N_3N^*]Ta(C_2H_4)$ (4). Ethylmagnesium chloride (627 μL, 2.3 M in diethyl ether, 1.44 mmol) was added via syringe to a −35 °C solution of $[N_3N^*]TaCl_2$ (500 mg, 0.678 mmol) in 10 mL of diethyl ether. Within 5 min, the yellow solution turned red-purple and a white precipitate formed. After 2 h, the reaction mixture was concentrated in vacuo and the residue was extracted with 20 mL of pentane. The extract was filtered through Celite, and the solvents were removed from the red-purple filtrate in vacuo to yield a solid that was determined to be a 9:1 mixture of $[N_3N^*]Ta(C_2H_4)$ (**4**) and $[N_3N^*]Ta{=}CHMe$ (**5a**) via ^{1}H NMR spectroscopy. $[N_3N^*]Ta{=}CHMe$: ^{1}H NMR (C_6D_6) δ 3.43 (t, 6, CH_2), 2.83 (d, 3, $\mathrm{CH}Me$), 2.20 (t, 6, CH_2), 1.10 (t, 27, $\mathrm{SiCH_2C}H_3$), 0.92 (q, 18, $\mathrm{SiC}H_2\mathrm{CH_3}$), −0.52 (q, 1, $\mathrm{C}H\mathrm{Me}$). The solid was recrystallized from pentane at −35 °C. Two crops of red-purple needles were collected to afford 386 mg (0.555 mmol, 82%) of **4**: ^{1}H NMR (C_6D_6) δ 3.46 (t, 6, CH_2), 2.37 (t, 6, CH_2), 2.10 (s, 4, $H_2\mathrm{C{=}C}H_2$), 1.03 (t, 27, $\mathrm{SiCH_2C}H_3$), 0.71 (q, 18, $\mathrm{SiC}H_2\mathrm{CH_3}$); ^{13}C NMR ($C_6D_6$) δ 62.7 (t, $^1J_{CH} = 141$, $\mathrm{H_2}C{=}C\mathrm{H_2}$), 60.7 (t, $^1J_{CH} = 136$, CH_2), 49.5 (t, $^1J_{CH} = 135$, CH_2), 8.1 (q, $^1J_{CH} = 125$, $\mathrm{SiCH_2}C\mathrm{H_3}$), 7.0 (t, $^1J_{CH} = 117$, $\mathrm{Si}C\mathrm{H_2CH_3}$). Anal. Calcd for $TaSi_3N_4C_{26}H_{61}$: C, 44.93; H, 8.85; N, 8.06. Found: C, 44.73; H, 8.61; N, 7.90.

$EtTa[N(SiEt_3)(CH{=}CH_2)][N(CH_2CH_2NSiEt_3)_2]$ (3b). A solution of $[N_3N^*]Ta(C_2H_4)$ (76 mg, 0.109 mmol) in ~1 mL of toluene-d_8 was added to an NMR tube which was then sealed and heated to 110 °C in an oil bath for 24 h. ^{1}H NMR demonstrated the sole reaction product to be **3b**: ^{1}H NMR (tol-d_8) δ 6.55 (dd, 1, $\mathrm{C}H{=}\mathrm{CH_2}$), 4.54 (d, 1, $\mathrm{CH{=}C}H_2$), 4.11 (m, 3, CH_2 and $\mathrm{CH{=}C}H_2$), 3.87 (m, 6, CH_2), 2.06 (t, 3, $\mathrm{CH_2C}H_3$), 1.56 (q, 2, $\mathrm{C}H_2\mathrm{CH_3}$), 1.06 (t, 18, $\mathrm{NSiCH_2C}H_3$), 1.05 (t, 9, $\mathrm{NSiCH_2C}H_3$), 0.85 (q, 6, $\mathrm{NSiC}H_2\mathrm{CH_3}$), 0.74 (q, 12, $\mathrm{NSiC}H_2\mathrm{CH_3}$); ^{13}C NMR (tol-$d_8$) δ 135.5 (d, $^1J_{CH} = 161$, $C\mathrm{H{=}CH_2}$), 95.5 (t, $^1J_{CH} = 161$, $\mathrm{CH{=}}C\mathrm{H_2}$), 67.6 (t, $^1J_{CH} = 133$, CH_2), 55.7 (t, $^1J_{CH} = 134$, CH_2), 54.8 (t, $^1J_{CH} = 117$, $C\mathrm{H_2CH_3}$), 18.1 (q, $^1J_{CH} = 125$, $\mathrm{CH_2}C\mathrm{H_3}$), 8.4 (q, $^1J_{CH} = 125$, $\mathrm{NSiCH_2}C\mathrm{H_3}$), 8.1 (q, $^1J_{CH} = 123$, $\mathrm{NSiCH_2}C\mathrm{H_3}$), 6.8 (t, $^1J_{CH} = 116$, $\mathrm{NSi}C\mathrm{H_2CH_3}$), 5.7 (t, $^1J_{CH} = 118$, $\mathrm{NSi}C\mathrm{H_2CH_3}$).

$[N_3N^*]Ta{=}CHEt$ (5b). *n*-Propylmagnesium chloride (387 μL, 2.5 M in diethyl ether, 0.968 mmol) was added to a −35 °C solution of $[N_3N^*]TaCl_2$ (340 mg, 0.461 mmol) in 8 mL of diethyl ether. A white precipitate appeared within 5 min, and over a period of 1 h the mixture changed in color to yellow-brown. After 24 h, the reaction mixture was concentrated in vacuo and the residue was extracted with 30 mL of pentane. The extract was filtered through Celite, and the yellow filtrate was concentrated in vacuo to afford 285 mg (0.402 mmol, 87%) of a yellow oil: ^{1}H NMR (C_6D_6) δ 3.43 (t, 6, CH_2), 3.30 (m, 2, $\mathrm{C}H_2\mathrm{CH_3}$), 2.24 (t, 6, CH_2), 1.19 (t, 3, $\mathrm{CH_2C}H_3$), 1.08 (t, 27, $\mathrm{SiCH_2C}H_3$), 0.90 (q, 18, $\mathrm{SiC}H_2\mathrm{CH_3}$), −0.27 (t, 1, $Ta{=}CH$); ^{13}C NMR (C_6D_6) δ 202.8 (d, $^1J_{CH} = 70$, $Ta{=}CH$), 56.3 (t, $^1J_{CH} = 135$, CH_2), 49.7 (t, $^1J_{CH} = 134$, CH_2), 38.6 (t, $^1J_{CH} = 126$, $C\mathrm{H_2CH_3}$), 18.2 (q, $^1J_{CH} = 125$, $\mathrm{CH_2}C\mathrm{H_3}$), 8.2 (q, $^1J_{CH} = 120$, $\mathrm{SiCH_2}C\mathrm{H_3}$), 7.5 (t, $^1J_{CH} = 120$, $\mathrm{Si}C\mathrm{H_2CH_3}$).

$[N_3N^*]Ta{=}CHPr$ (5c). **5c** was prepared in a manner analogous to **5b** from *n*-butylmagnesium chloride (569 μL, 2.5 M in diethyl ether, 1.42 mmol) in 10 mL of diethyl ether and $[N_3N^*]TaCl_2$ (500 mg, 0.678 mmol) to yield 348 mg (0.481 mmol, 71%) of **5c** as a yellow oil: ^{1}H NMR (C_6D_6) δ 3.43 (t, 6, CH_2), 3.25 (m, 2, $\mathrm{TaCHC}H_2\mathrm{CH_2CH_3}$), 2.24 (t, 6, CH_2), 1.64 (m, 2, $\mathrm{TaCHCH_2C}H_2\mathrm{CH_3}$), 1.23 (t, 3, $\mathrm{TaCHCH_2CH_2C}H_3$), 1.07 (t, 27, $\mathrm{SiCH_2C}H_3$), 0.95 (q, 18, $\mathrm{SiC}H_2\mathrm{CH_3}$), −0.19 (t, 1, $\mathrm{TaC}H\mathrm{CH_2CH_2CH_3}$); ^{13}C NMR ($C_6D_6$) δ 201.3 (d, $^1J_{CH} = 69$, $\mathrm{Ta}C\mathrm{HCH_2CH_2CH_3}$), 56.4 (t, $^1J_{CH} = 136$, CH_2), 49.7 (t, $^1J_{CH} = 135$, CH_2), 48.3 (t, $^1J_{CH} = 124$, $\mathrm{TaCH}C\mathrm{H_2CH_2CH_3}$), 21.2 (t, $^1J_{CH} = 127$, $\mathrm{TaCHCH_2}C\mathrm{H_2CH_3}$), 9.0 (q, $^1J_{CH} = 124$, $\mathrm{TaCHCH_2CH_2}C\mathrm{H_3}$), 8.2 (q, $^1J_{CH} = 127$, $\mathrm{SiCH_2}C\mathrm{H_3}$), 7.5 (t, $^1J_{CH} = 124$, $\mathrm{Si}C\mathrm{H_2CH_3}$).

$[N_3N^*]Ta{=}CHCH_2CHMe_2$ (5d). **5d** was prepared as described for **5b** from isopentylmagnesium bromide (502 μL, 1.7 M in diethyl ether, 0.854 mmol) in 8 mL of diethyl ether and $[N_3N^*]TaCl_2$ (300 mg, 0.406 mmol) to yield 244 mg (0.331 mmol, 81%) of **5d** as a yellow oil: ^{1}H NMR (C_6D_6) δ 3.41 (t, 6, CH_2), 3.35 (dd, 2, $\mathrm{TaCHC}H_2\mathrm{CHMe_2}$), 2.19 (t, 6, CH_2), 1.95 (m, 1, $\mathrm{C}H\mathrm{Me_2}$), 1.11 (t, 27, $\mathrm{SiCH_2C}H_3$), 1.10 (d, 6, $\mathrm{CH}Me_2$), 0.95 (q, 18, $\mathrm{SiC}H_2\mathrm{CH_3}$), 0.14 (t, 1, $\mathrm{TaC}H\mathrm{CH_2CHMe_2}$); ^{13}C NMR ($C_6D_6$) δ 201.2 (d, $^1J_{CH} = 71$, $\mathrm{Ta}C\mathrm{HCH_2CHMe_2}$), 57.1 (t, $^1J_{CH}$

= 136, CH_2), 54.9 (t, $^1J_{CH}$ = 123, $TaCHCH_2CHMe_2$), 49.5 (t, $^1J_{CH}$ = 135, CH_2), 31.6 (d, $^1J_{CH}$ = 126, $CHMe_2$), 23.6 (q, $^1J_{CH}$ = 125, $CHMe_2$), 8.2 (q, $^1J_{CH}$ = 125, $SiCH_2CH_3$), 7.4 (t, $^1J_{CH}$ = 116, $SiCH_2CH_3$).

$[N_3N^*]Ta{=}CHSiMe_3$ (5e). **5e** was prepared as described for **5b** from $[N_3N^*]TaCl_2$ (300 mg, 0.407 mmol) in 8 mL of diethyl ether and ((trimethylsilyl)methyl)lithium (80 mg, 0.854 mmol) to yield 218 mg (0.289 mmol, 71%) of **5e** as yellow crystals from pentane: ^1H NMR (C_6D_6) δ 3.36 (t, 6, CH_2), 2.10 (t, 6, CH_2), 2.09 (s, 1, $CHSiMe_3$), 1.09 (t, 27, $SiCH_2CH_3$), 0.96 (q, 18, $SiCH_2CH_3$), 0.43 (s, 9, $CHSiMe_3$); ^{13}C NMR (C_6D_6) δ 206.8 (d, $^1J_{CH}$ = 69, Ta=CH), 58.3 (t, $^1J_{CH}$ = 135, CH_2), 49.9 (t, $^1J_{CH}$ = 135, CH_2), 8.0 (q, $^1J_{CH}$ = 127, $SiCH_2CH_3$), 7.1 (t, $^1J_{CH}$ = 118, $SiCH_2CH_3$), 4.8 (q, $^1J_{CH}$ = 118, $SiMe_3$). Anal. Calcd for $TaSi_4N_4C_{28}H_{67}$: C, 44.65; H, 8.97; N, 7.44. Found: C, 44.53; H, 8.88; N, 7.29.

$[N_3N^*]Ta{=}CHPh$ (5f). $[N_3N^*]TaCl_2$ (419 mg, 0.568 mmol) was added to a −35 °C solution of benzylmagnesium chloride (1.08 mL, 1.1 M in diethyl ether, 1.19 mmol) in 7 mL of diethyl ether. After 23 h, the cloudy orange mixture was concentrated in vacuo and extracted with 20 mL pentane. The orange extract was concentrated in vacuo to provide a red-orange oil that was shown to contain $[N_3N^*]Ta{=}CHPh$ contaminated by small amounts of benzylmagnesium chloride. Numerous attempts to separate the benzylidene from remaining Grignard reagent via recrystallizations from diethyl ether and/or pentane at −35 °C failed: ^1H NMR (C_6D_6) δ 7.19 (t, 3, Ph), 6.67 (t, 2, Ph), 3.42 (t, 6, CH_2), 2.25 (t, 6, CH_2), 2.09 (s, 1, TaCH), 0.97 (t, 27, $SiCH_2CH_3$), 0.82 (q, 18, $SiCH_2CH_3$); ^{13}C NMR (C_6D_6) δ 200.9 (d, $^1J_{CH}$ = 71, TaCH), 152.6 (s, Ph), 129.1 (d, $^1J_{CH}$ = 148, Ph), 127.2 (d, $^1J_{CH}$ = 156, Ph), 122.4 (d, $^1J_{CH}$ = 158, Ph), 57.6 (t, $^1J_{CH}$ = 135, CH_2), 49.7 (t, $^1J_{CH}$ = 135, CH_2), 8.1 (q, $^1J_{CH}$ = 127, $SiCH_2CH_3$), 7.3 (t, $^1J_{CH}$ = 120, $SiCH_2CH_3$).

$\{[N_3N^*]Ta{=}CHCH_2\}_2$ (7). Vinylmagnesium bromide (1.55 mL, 1.3 M in tetrahydrofuran, 2.01 mmol) was added to a solution of $[N_3N^*]TaCl_2$ (708 mg, 0.959 mmol) in 10 mL of toluene. The resulting brown-red mixture was then heated at ~80 °C for 1 day. The yellow-brown mixture was concentrated in vacuo, and the residue was extracted with 60 mL of pentane. The extract was filtered through Celite, and the filtrate was concentrated in vacuo to yield a yellow-brown solid that was determined to be a 1:1 mixture of **7** and $[N_3N^*]Ta(C_2H_2)$ (**6**) via ^1H NMR. $[N_3N^*]Ta(C_2H_2)$: ^1H NMR (C_6D_6) δ 12.15 (s, 2, $HC{\equiv}CH$), 3.55 (t, 6, CH_2), 2.46 (t, 6, CH_2), 1.17 (t, 27, $SiCH_2CH_3$), 1.10 (q, 18, $SiCH_2CH_3$); ^{13}C NMR (C_6D_6) δ 219.4 (dd, $^1J_{CH}$ = 168, $HC{\equiv}CH$), 55.9 (t, $^1J_{CH}$ = 136, CH_2), 49.4 (t, $^1J_{CH}$ = 135, CH_2), 8.3 (q, $^1J_{CH}$ = 120, $SiCH_2CH_3$), 7.5 (t, $^1J_{CH}$ = 117, $SiCH_2CH_3$). Fractional recrystallization of the product mixture from pentane afforded pure **7** as yellow crystals, yield 261 mg (0.194 mmol, 39%): ^1H NMR (C_6D_6) δ 3.51 (br s, 4, $TaCHCH_2$), 3.45 (t, 12, CH_2), 2.21 (t, 12, CH_2), 1.20 (t, 54, $SiCH_2CH_3$), 1.03 (q, 36, $SiCH_2CH_3$), −0.27 (br s, 2, Ta=CH); ^{13}C NMR (C_6D_6) δ 201.3 (d, $^1J_{CH}$ = 69, Ta=CH), 56.6 (t, $^1J_{CH}$ = 136, CH_2), 49.6 (t, $^1J_{CH}$ = 135, CH_2), 49.4 (t, $^1J_{CH}$ = 128, $TaCHCH_2$), 8.0 (q, $^1J_{CH}$ = 124, $SiCH_2CH_3$), 7.5 (t, $^1J_{CH}$ = 117, $SiCH_2CH_3$). Anal. Calcd for $Ta_2Si_6N_8C_{52}H_{120}$: C, 45.00; H, 8.71; N, 8.07. Found: C, 45.10; H, 8.90; N, 8.16.

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 via syringe with 2 mL of a stock solution of $[N_3N^*]Ta(C_2H_4)$. The cell was placed in the HP 8452 diode array spectrophotometer, and the temperature was then controlled with a HP 89090A Peltier temperature control accessory. The decomposition reaction was monitored by observing the decrease in the absorbance of the solution at 510 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. The fractional uncertainty in the measured rate constants was assumed to be 1% on the basis of subjective inspection of the sensitivity of the fits to the absorbance vs time plots.

Reaction of Alkylidene Complexes with Benzaldehyde. Approximately 2 equiv of benzaldehyde was added to an NMR tube containing $[N_3N^*]Ta{=}CHR$ (~0.01 M in C_6D_6). The characteristic color of the alkylidene complexes disappeared within 30 s. After 10 min the mixture was found to contain $[N_3N^*]Ta{=}O$ and *cis*- and *trans*-Ph(H)C=CHR as the only products. ^1H NMR of $[N_3N^*]Ta{=}O$ (C_6D_6): δ 3.36 (t, 6, CH_2), 2.23 (t, 6, CH_2), 1.00 (t, 27, $SiCH_2CH_3$), 0.87 (q, 18, $NSiCH_2CH_3$).

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Supporting Information Available: Text providing detailed description of X-ray data collection, structure solution, and refinement, labeled ORTEP diagrams, and tables of fractional coordinates and isotropic and anisotropic thermal parameters for $EtTa[N(SiEt_3)(CH{=}CH_2)][N(CH_2CH_2NSiEt_3)_2]$ and $\{[N_3N^*]Ta{=}CHCH_2\}_2$ (22 pages). Ordering information is given on any current masthead page.

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