METAL-LIGAND MULTIPLE BONDS IN ORGANOMETALLIC COMPLEXES CONTAINING TRIAMIDOAMINE LIGAND SYSTEMS

by

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To Mom, Dad, Peri, and Gram

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ABSTRACT

Chapter 1

The synthesis and reactivity of $[N_3N]Ta{=}E$ complexes is presented where E is a 1σ, 1π or 1σ, 2π donor and $[N_3N]^{3-} = [(Me_3SiNCH_2CH_2)_3N]^{3-}$. $[N_3N]Ta{=}PPh$ reacts with excess lithium metal in tetrahydrofuran to give "$[N_3N]Ta{=}PLi$" which reacts 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 two equivalents of LiN(H)R (R = H, CMe_3, Ph) to produce imido complexes, $[N_3N]Ta{=}NR$, and with two equivalents of benzylmagnesium chloride or trimethylsilylmethyllithium to afford the alkylidene complexes, $[N_3N]Ta{=}CHR$. The ethylene complex, $[N_3N]Ta(\eta^2\text{-}C_2H_4)$, is formed quantitatively upon adding two equivalents of ethylmagnesium chloride to $[N_3N]TaCl_2$. An X-ray structure of $[N_3N]Ta(Me)Et$, a precursor to $[N_3N]Ta(\eta^2\text{-}C_2H_4)$ in a first order reaction, shows it to be a six coordinate species with two alkyl ligands in crowded apical coordination sites. $[N_3N]Ta(\eta^2\text{-}C_2H_4)$ decomposes in a first order manner to afford a complex in which a C-N bond in the tren backbone has been cleaved. Alkylation of $[N_3N]TaCl_2$ with two equivalents 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 decomposition products. $[N_3N]TaCl_2$ reacts with two equivalents of vinylmagnesium bromide to afford $[N_3N]Ta(\eta^2\text{-}C_2H_2)$, which has been characterized by an X-ray study. An analogous benzyne complex can be prepared by refluxing $[N_3N]TaCl_2$ with two equivalents of phenyllithium in toluene for 1 day. $[N_3N]Ta(Me)Ph$ can be synthesized and shown to convert into $[N_3N]Ta(\eta^2\text{-}C_6H_4)$ in a first order reaction. $[N_3N]Ta(\eta^2\text{-}C_2H_4)$ 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, addition of an excess of Me_3SiAsH_2 to $[N_3N]Ta(\eta^2\text{-}C_2H_4)$ affords $[N_3N]Ta{=}CHMe$ immediately, and then over a period of days, what is proposed to be $[N_3N]Ta{=}AsSiMe_3$. $[N_3N]Ta(\eta^2\text{-}C_6H_4)$ reacts with $ArNH_2$ (Ar = Ph, C_6F_5) to give $[N_3N]Ta{=}NAr$ complexes and $PhAsH_2$ to afford $[N_3N]Ta{=}AsPh$.

Chapter 2

The synthesis and reactivity of $[N_3N^*]Ta{=}E$ complexes is described where E is a 1σ, 1π or 1σ, 2π donor and $[N_3N^*]^{3-} = [(Et_3SiNCH_2CH_2)_3N]^{3-}$. Tris(2-aminoethyl)amine (tren) reacts successively with three equivalents of *n*-butyllithium and three equivalents of triethylchlorosilane in tetrahydrofuran to form $H_3[N_3N^*]$ quantitatively. Deprotonation of $H_3[N_3N^*]$ with three equivalents of *n*-butyllithium generates $Li_3[N_3N^*]$ *in situ*, which is then treated with $TaCl_5$ to afford $[N_3N^*]TaCl_2$. $[N_3N^*]TaMe_2$ is formed quantitatively upon adding two equivalents of methylmagnesium chloride to $[N_3N^*]TaCl_2$. Alkylation of $[N_3N^*]TaCl_2$ with two equivalents of ethylmagnesium chloride yields $[N_3N^*]Ta(\eta^2\text{-}C_2H_4)$ along with ~10% $[N_3N^*]Ta{=}CHMe$, while addition of two equivalents of alkyllithium or Grignard reagent RCH_2M (R = CH_2CH_3, $CH_2CH_2CH_3$, $CH_2CH(CH_3)_2$, Ph, $SiMe_3$; M = Li, MgCl or MgBr) 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 $[N_3N^*]Ta(\eta^2\text{-}C_2H_4)$ decomposes in a first order manner (k = 4.23 (4) x 10^{-5} s^{-1} at 70 °C) to produce $EtTa[N(SiEt_3)(CH=CH_2)][N(CH_2CH_2NSiEt_3)_2]$. An X-ray structure of the latter demonstrates it to be a distorted trigonal bipyramid in which a C-N bond in the original tren backbone has been cleaved. An equimolar mixture of $[N_3N^*]Ta(\eta^2\text{-}C_2H_2)$ and $\{[N_3N^*]Ta=CHCH_2\}_2$ is formed upon treating $[N_3N^*]TaCl_2$ with two equivalents of vinylmagnesium bromide in refluxing toluene. An X-ray structure of $\{[N_3N^*]Ta=CHCH_2\}_2$ shows it to contain two distorted trigonal bipyramidal $[N_3N^*]Ta$ units bridged by a four carbon "dialkylidene" unit in which the alkylidenes are severely "distorted" (average $\angle$ Ta=C-C = 173°). These results are compared and contrasted with those obtained in analogous $[N(CH_2CH_2NSiMe_3)_3]^{3-}$ tantalum chemistry.

Chapter 3

The synthesis and reactivity of $[N_3N]NbX$ complexes is presented where X is a nitrogen- or oxygen-based donor and $[N_3N]^{3-} = [(Me_3SiNCH_2CH_2)_3N]^{3-}$. The reactions of $NbCl_5$, $NbCl_4(THF)_2$, and $NbCl_3(dme)$ with $Li_3[N_3N]$ in a variety of solvents do not produce an identifiable $[N_3N]NbCl_n$ (n = 0, 1, 2) species. $NbOCl_3(THF)_2$ and $Nb(NSiMe_3)Cl_3(py)_2$ react with one equivalent of $Li_3[N_3N]\bullet THF_2$ to afford $[N_3N]Nb=O$ and $[N_3N]Nb=NSiMe_3$, respectively, in good yields. $[N_3N]Nb=O$ reacts with triethylaluminum to form the base adduct $[N_3N]Nb=O\bullet AlEt_3$ as judged by ^1H, ^{13}C, and ^{27}Al NMR. The oxo species reacts quantitatively with Me_3SiX (X = OTf, I) to prepare $[N_3N]NbOSiMe_3^+X^-$ and MeOTf to afford $[N_3N]NbOMe^+OTf^-$. These d^0 salts are reduced in high yield by sodium amalgam to provide d^1 $[N_3N]NbOR$ (R = $SiMe_3$, Me). The reaction of $[N_3N]NbOSiMe_3$ with $SiCl_4$ provides $[N_3N]NbOSiCl_3$ in moderate yield.

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Abbreviations Used in Text

br	broad
C_α	carbon bound to metal
C_β, etc.	carbon bound to C_α, etc.
Cp	C_5H_5
Cp^*	C_5Me_5
Cy	cyclohexyl
d	doublet
dme	1,2-dimethoxyethane
Bu	butyl
eq	equation
Et	ethyl
h	hours
H_α	hydrogen (proton) bound to C_α
H_β, etc.	hydrogen (proton) bound to C_β, etc.
Hz	Hertz
IR	Infrared
J	coupling constant in Hertz
Lut	2,6-lutidine
Me	methyl
m	multiplet
$[N_3N]^{3-}$	$[(Me_3SiNCH_2CH_2)_3N]^{3-}$
$[N_3N^*]^{3-}$	$[(Et_3SiNCH_2CH_2)_3N]^{3-}$
$[N_3N']^{3-}$	$[(t\text{-}BuMe_2SiNCH_2CH_2)_3N]^{3-}$
NMR	nuclear magnetic resonance
OTf	O_3SCF_3, triflate, trifluoromethanesulfonate
Ph	phenyl
ppm	parts per million
Pr	propyl
py	pyridine
s	singlet
t	triplet
THF	tetrahydrofuran
tol	toluene
tren	tris(2-aminoethyl)amine, $N(CH_2CH_2NH_2)_3$

UV/Vis	ultraviolet/visible
δ	chemical shift downfield from tetramethylsilane
λ_{max}	wavelength of maximum optical absorption

CHAPTER 1

Synthetic and Mechanistic Investigations of Trimethylsilyl-Substituted Triamidoamine Complexes of Tantalum

Much of the material covered in this chapter has appeared in print:

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

Freundlich, J. S., Schrock, R. R., Davis, W. M. *J. Am. Chem. Soc.* **1996**, *118*, 3643.

Introduction

The use of tris(2-aminoethyl)amine (tren) as a tetradentate trianionic ligand was first realized by Verkade and co-workers for group 14 elements.[1] Workers in our laboratories and Verkade's anticipated that tren-based complexes of the early transition metals would be feasible synthetic targets because the ligands offer three amide nitrogen donors in addition to a tertiary amine to bind to the Lewis acidic metal center. Additionally, we believed the introduction of bulky amide nitrogen substituents such as silyl groups (usually $SiMe_3$ or $Si(t\text{-Bu})Me_2$) would confer kinetic stability to these species by producing a sterically-protected apical coordination site. With these design criteria in mind, we initiated a study of tren-based triamidoamine metal complexes utilizing the following ligands: $[N_3N]^{3-} = [(Me_3SiNCH_2CH_2)_3N]^{3-}$ and $[N_3N']^{3-} = [(t\text{-}BuMe_2SiNCH_2CH_2)_3N]^{3-}$.

Our initial efforts resulted in the preparation of some rarely observed types of complexes and encouraged us that these tren-based ligands conferred considerable stability to their early and middle transition metal centers.[2-4] The first early transition metal trigonal monopyramidal complexes $[N_3N']M$ were synthesized[3] in addition to a Ti(IV) hydride[2] and a vanadium parent imide.[4] The key features of these complexes included the sterically protected "pocket" formed by the bulky silyl groups and the presence of one σ-type and two orthogonal π metal orbitals directed toward the apical coordination site. This orbital arrangement is ideally suited for forming d^0 transition metal 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. In view of tantalum's ability to form double and triple bonds with main group elements,[5] we chose to explore the chemistry of $[N_3N]Ta$ complexes associated with multiple Ta-ligand bonds. We found that $[N_3N]TaCl_2$ reacts with two equivalents of a lithium phosphide LiP(H)R (R = Ph, Cy, *t*-Bu) to afford one equivalent of RPH_2 and the first d^0 terminal linear phosphinidenes $[N_3N]Ta{=}PR$, in moderate to high yields.[6] An X-ray crystal structure of $[N_3N]Ta{=}PCy$ revealed a Ta-P linkage of 2.145 Å, which is short in comparison to the sum of the atomic radii of Ta and P (2.44 Å).[7] Given the successful preparation of complexes featuring a pseudo-triple bond between Ta and P, we have since directed efforts to synthesize a wide variety of organometallic Ta complexes containing σ- and π-bonded ligands in the apical coordination site.

Results

Synthesis of Tantalum Phosphinidene Complexes.

The successful syntheses of $[N_3N]M{\equiv}P$ (M = Mo, W)[8] piqued our interest in preparing a compound containing an unsubstituted tantalum-phosphorus triple bond, namely $\{[N_3N]Ta{\equiv}P\}^-$. $[N_3N]Ta{=}PPh$ reacts with excess lithium metal in tetrahydrofuran to give a species whose room temperature ^{31}P NMR spectrum reveals a resonance at 575 ppm ($\Delta\nu_{1/2} \approx 600$ Hz) and the ^{1}H and ^{13}C NMR spectra are consistent with a pseudo-C_3 symmetric ligand-containing complex. The lithium-induced cleavage of a P-Ph bond in organophosphorus systems is well-precedented to afford P-Li species.[9-11] Since these lithium phosphides are reported to react with electrophiles to form P-C bonds, we were interested in exploring the reactivity of our proposed anionic phosphide. $\{[N_3N]Ta{\equiv}P\}^-$ 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**, according to ^{31}P NMR data (eq 1). The yields of the phosphinidene complexes, as determined by proton NMR integration versus an internal standard, are listed in Table 1.1. The 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. This Wittig-like reaction is known for several isolated tantalum phosphinidene complexes.[6] We have also prepared complex **1b** as shown in eq 2, although the isolated yield is again low (10%) due to its high solubility in common organic solvents.

$$[N_3N]Ta{=}PPh \xrightarrow[\text{2. 3 equiv RX, THF, -35 °C}]{\text{1. 5 equiv Li, THF}} [N_3N]Ta{=}PR + PhR + 2\,LiX \tag{1}$$

R = Me (**1a**), *n*-Bu (**1b**),
$SiMe_3$ (**1c**), $SiMe_2Ph$ (**1d**)

Table 1.1. ^{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 ^1H NMR integration versus 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).

$$[N_3N]TaCl_2 \xrightarrow[\text{Et}_2\text{O, -35 °C}]{\text{2 LiP(H)}n\text{-Bu}} \underset{\mathbf{1b}}{[N_3N]Ta{=}P\text{-}n\text{-}Bu} + n\text{-}BuPH_2 \tag{2}$$

It is puzzling that the phosphorus resonances for the tantalum phosphinidenes 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 **d** have widths of 300 - 400 Hz at -60 °C. We currently attribute the broadened phosphinidene resonances to ^{31}P-^{181}Ta coupling, but why coupling is more significant in the silyl-substituted phosphinidene complexes is unclear.

We propose that the intermediate whose ^{31}P NMR spectrum contains a resonance at 575 ppm ($\Delta\nu_{1/2} \approx 600$ Hz, T = 25 °C) is "$[N_3N]Ta{=}PLi$" 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, $[N_3N]Mo{\equiv}P$,[8] $[N_3N]W{\equiv}P$,[8] and $[(t\text{-}Bu)NAr]_3Mo{\equiv}P$[12] (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), is believed 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 $(t\text{-}Bu_3SiO)_3Ta{=}PPh$[13] and 600 - 800 ppm in $Cp_2M{=}PAr$ complexes (M = Mo, W, Zr)[14-16]), a chemical shift of 575 ppm might be more consistent with a "$[N_3N]Ta{=}PLi$" species in which the Ta-P-Li bond angle is considerably less than 180°. Unfortunately, "$[N_3N]Ta{=}PLi$" could not be separated from phenyllithium, the other product of the cleavage reaction, and, thus, could not be isolated and structurally characterized.

All attempts to prepare $[N_3N]Ta{=}PH$ so far have failed. For example, the reaction of $[N_3N]TaCl_2$ with two equivalents of $LiPH_2$ in 1,2-dimethoxyethane at -78 °C affords intractable products, while quenching "$[N_3N]Ta{=}PLi$" with proton sources such as $[HNMe_3]Cl$ or 2,6-lutidinium triflate leads to mixtures of unidentifiable species.

Synthesis of Tantalum Imide Complexes.

$[N_3N]TaCl_2$ reacts with two equivalents of LiN(H)R (R = H, CMe_3, Ph) to produce one equivalent of RNH_2 and imido complexes **2a - c** in 62 - 95% isolated yield (eq 3). Mixing $[N_3N]TaCl_2$ with only one equivalent of lithium amide results in an equimolar mixture of dichloride and imide. The synthesis of **2a** is noteworthy, as parent imido complexes are relatively rare.[4,17-20] NMR and IR spectra of **2a** are similar to those for $[N_3N]V{=}NH$, which has been structurally characterized.[4] 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 ^1H NMR spectrum of $[N_3N]V{=}NH$,[4] presumably as a consequence of additional coupling to ^{51}V ($I = 7/2$, 99.75%). Resolved coupling to ^{14}N has also been observed in $Cp^*MMe_3(NH)$ (M = Mo, W) complexes[18,19] and was attributed to a low electric field gradient about the imide nitrogen.[21] The white crystalline imide complexes are stable when heated as ~0.1 M solutions in toluene-d_8 in sealed NMR tubes to 110 °C for several days. **2a** - **c** do not react with benzaldehyde in benzene-d_6 (~0.1 M in Ta, 2 days) at ~25 °C.

$$[\mathrm{N_3N}]\mathrm{TaCl_2} \xrightarrow[\substack{\mathrm{Et_2O}\ (\mathrm{R} = \mathrm{CMe_3, Ph}) \\ \mathrm{THF}\ (\mathrm{R} = \mathrm{H}) \\ -35\ ^\circ\mathrm{C}}]{2\ \mathrm{LiN(H)R}} [\mathrm{N_3N}]\mathrm{Ta{=}NR} + \mathrm{RNH_2}$$

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

(3)

Synthesis and Reactivity of Tantalum Alkylidene Complexes.

$[N_3N]TaCl_2$ reacts with two equivalents of trimethylsilylmethyllithium or benzylmagnesium chloride to afford the alkylidene complexes, **3a** and **3b** (eq 4) in >90% isolated yield. We propose that dialkyl complexes are intermediates in these reactions for several reasons. First, if only one equivalent 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 equivalent of the appropriate metal alkyl. Second, reaction of $Li_3[N_3N]$ with $Ta(CH_2R)_2Cl_3$ (R= Ph,[22] CMe$_3$[23]) gives **3b** and **3c** in yields of 86% and 56%, respectively (eq 5).

$$[\mathrm{N_3N}]\mathrm{TaCl_2} \xrightarrow[\mathrm{Et_2O},\ -35\ ^\circ\mathrm{C}]{2\ \mathrm{RCH_2M}} [\mathrm{N_3N}]\mathrm{Ta{=}CHR} + \mathrm{RCH_3}$$

$$\mathrm{R} = \mathrm{SiMe_3}\ (\mathbf{3a};\ \mathrm{M} = \mathrm{Li})$$
$$\mathrm{R} = \mathrm{Ph}\ (\mathbf{3b};\ \mathrm{M} = \mathrm{MgCl})$$

(4)

$$\mathrm{Ta(CH_2R)_2Cl_3} \xrightarrow[\mathrm{Et_2O},\ -35\ ^\circ\mathrm{C}]{\mathrm{Li_3[N_3N]}} [\mathrm{N_3N}]\mathrm{Ta{=}CHR} + \mathrm{RCH_3}$$

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

(5)

Complexes **3a** - **c** all have ^{1}H and ^{13}C NMR spectra consistent with three-fold symmetry on the NMR time scale. H_α resonances are found near 0 ppm in ^{1}H NMR spectra, a region characteristic of alkylidenes that are highly "distorted" through an α-agostic[24] C-H interaction,[5,25] 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 $^1J_{CH\alpha}$ (~72 Hz), the lowest known for d^0 alkylidene complexes.[5] The alkylidene ligands are effectively pseudo-triply-bound to tantalum as σ, 2π ligands. In spite of the fact that the π interactions in the apical position are of two distinct types, all alkylidene complexes show three-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, as the Ta=C_α-C_β angle is likely to be relatively large. Although crystals of **3a** - **c** suitable for X-ray studies have not yet been obtained, an X-ray study of a related alkylidene complex of tantalum $\{[(Et_3SiNCH_2CH_2)_3N]Ta=CHCH_2\}_2$ has been conducted and will be discussed in detail in Chapter 2. The structure of this "dialkylidene" confirms that the Ta=C_α-C_β angle is indeed large (ca. 173°) and, therefore, that large Ta=C_α-C_β angles can be expected in alkylidene complexes with a tantalum triamidoamine core.

Alkylidenes **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, such as benzaldehyde and pivaldehyde, in a Wittig-like fashion[26] to afford a mixture of *cis*- and *trans*-isomers of the expected olefin and $[N_3N]Ta=O$. A variety of reported tantalum alkylidenes are known to react readily with aldehydes in this manner.[5] Alkylidenes **3a** - **c** (~0.05 M in diethyl ether) react with 1 atm of ethylene to produce complex mixtures containing unreacted alkylidene and products proposedly formed via the decomposition (*vide infra*) of tantalum olefin species. All attempts to isolate and fully characterize these decomposition products were unsuccessful. The reaction of tantalum alkylidenes with ethylene to produce olefin complexes via β-H elimination in the intermediate tantallacyclobutane is well-precedented.[5]

Synthesis and Decomposition of a Tantalum Ethylene Complex.

An η^2-ethylene complex (**4**) is produced quantitatively upon adding two equivalents of ethylmagnesium chloride to $[N_3N]TaCl_2$ (eq 6). An alternate route to **4** consists of alkylation of $[N_3N]Ta(Me)OTf$[27] with one equivalent of ethylmagnesium chloride. Proton and carbon NMR spectra of **4** are consistent with it being a three-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 gated ^{13}C NMR spectrum. We propose that **4** has a structure similar to that of $[N_3N]Ta(\eta^2\text{-}C_2H_2)$ (*vide infra*) in the solid state, i.e., one in which the C-C axis of the unsaturated organic moiety is lined up with one of the Ta-N bonds.

$$[N_3N]TaCl_2 \xrightarrow[Et_2O,\ -35\ ^\circ C]{2\ EtMgCl} \underset{\mathbf{4}}{[N_3N]Ta(\eta^2\text{-}C_2H_4)} + EtH \tag{6}$$

Reaction of $[N_3N]TaCl_2$ with only one equivalent of ethyl Grignard yields the yellow crystalline monoethyl derivative **5** in 72% isolated yield (eq 7). **5** reacts immediately with one equivalent of ethylmagnesium chloride to yield **4**, and with one equivalent of CD_3CD_2MgBr to afford a 5.7:1 mixture of $[N_3N]Ta(\eta^2\text{-}C_2H_4)$ and $[N_3N]Ta(\eta^2\text{-}C_2D_4)$. The labeling study suggests that the intramolecular isotope effect for β abstraction is 5.7.

$$[N_3N]TaCl_2 \xrightarrow[Et_2O,\ -35\ ^\circ C]{EtMgCl} \underset{\mathbf{5}}{[N_3N]Ta(Et)Cl} \tag{7}$$

Although **4** is formed upon treating $[N_3N]Ta(Me)OTf$ with one equivalent of ethylmagnesium chloride, $[N_3N]Ta(Me)Cl$ reacts with one equivalent of ethyl Grignard over the same time period (ca. 1 day) 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 three-fold symmetry on the NMR time scale from 25 to -80 °C. Over a period of one day at ~25 °C, **6** decomposes to yield **4** and methane. At 52 °C in toluene-d_8, the decomposition of **6** was followed by ^{1}H NMR and shown to obey first order kinetics with $k = 2.4\ (1) \times 10^{-4}\ s^{-1}$. $[N_3N]Ta(Me)Et$ is also formed in the reaction between **5** and one equivalent of methylmagnesium chloride.

$$[N_3N]Ta(Me)Cl \xrightarrow[Et_2O,\ -35\ ^\circ C]{EtMgCl} \underset{\mathbf{4}}{[N_3N]Ta(\eta^2\text{-}C_2H_4)} + \underset{\mathbf{6}}{[N_3N]Ta(Me)Et} \quad (8)$$

An X-ray structure of **6** (Table 1.2; Figure 1.1) 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 1.3.) 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° in crystallographically characterized $[N_3N]M$ species.[2-4,6,8,28] The ethyl ligand points away from the methyl group. Consequently 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, and in any case there is no readily available orbital with which the β C-H bond can interact when the ethyl group is oriented in the observed fashion. 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 Ta-N(4) distance (2.444 Å) is comparable to that found in $[N_3N]Ta{=}Te$ (2.487 Å),[29] but is somewhat longer than found in $[N_3N]Ta(\eta^2\text{-}C_2H_2)$ (2.30 Å; *vide infra*).

Table 1.2. Crystallographic Data, Collection Parameters, and Refinement Parameters for [N_3N]Ta(Me)Et (**6**).

Empirical Formula	$C_{18}H_{47}N_4Si_3Ta$
Formula Weight	584.80
Crystal Color, Habit	yellow, plate
Crystal Dimensions (mm)	0.150 x 0.150 x 0.05
Crystal System	monoclinic
No. Reflections Used for Unit Cell Determination (2θ range)	25 (14.0 - 22.0°)
a	10.0504 (8) Å
b	15.010 (1) Å
c	17.937 (1) Å
β	95.79 (1)°
V	2692.1 (6) $Å^3$
Space Group	$P2_1/n$
Z	4
D_{calc}	1.443 g/cm^3
F_{000}	1192
$\mu(MoK_\alpha)$	41.75 cm^{-1}
Scan Type	ω-2θ
Temperature	187 K
Total No. Unique Reflections	3679
No. Observations with $I > 3.00\sigma(I)$	2270
No. Variables	235
R	0.041
R_w	0.035
GoF	1.25

Figure 1.1. X-ray Crystal Structure of [N_3N]Ta(Me)Et (**6**).

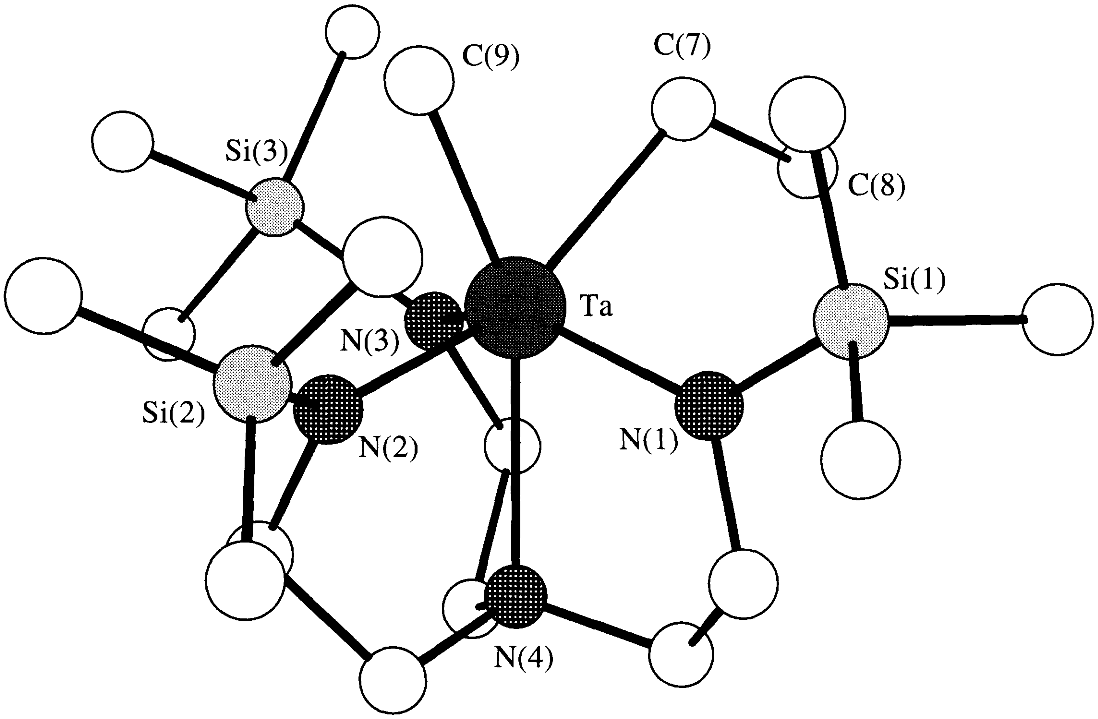


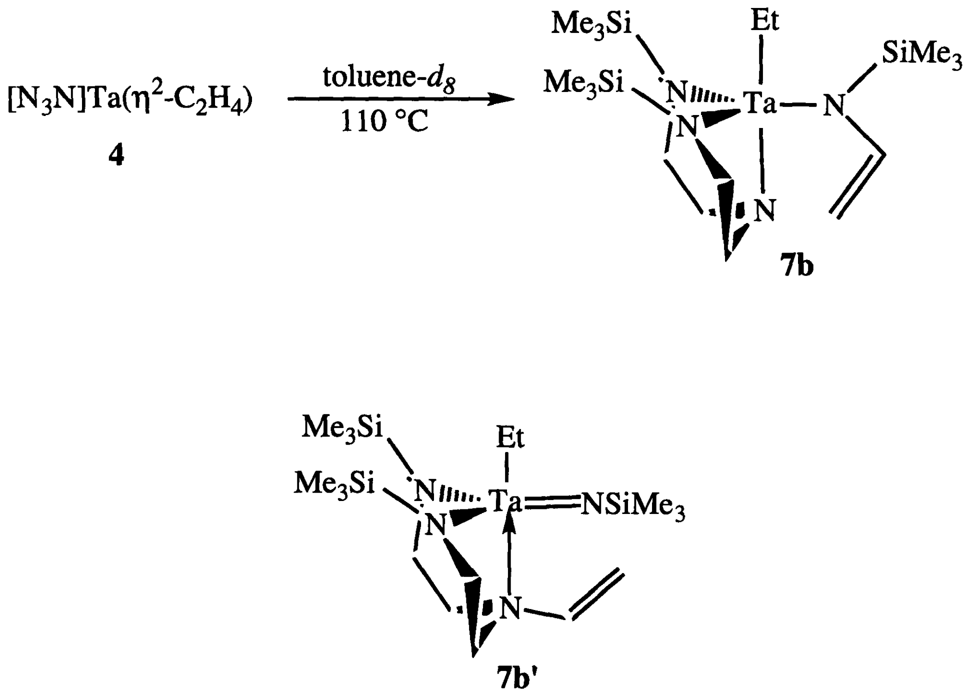
Table 1.3. Selected Intramolecular Distances (Å) and Angles (deg) for the Non-Hydrogen Atoms of $[N_3N]Ta(Me)Et$ (**6**).

Bond	**Lengths**
Ta-N(1)	2.00 (1)
Ta-N(2)	2.071 (9)
Ta-N(3)	1.956 (9)
Ta-N(4)	2.444 (8)
Ta-C(7)	2.21 (1)
Ta-C(9)	2.21 (1)
C(7)-C(8)	1.55 (2)

Bond	**Angles**
Ta-N(1)-Si(1)	131.6 (5)
Ta-N(2)-Si(2)	136.1 (5)
Ta-N(3)-Si(3)	128.8 (5)
N(1)-Ta-N(2)	99.6 (4)
N(1)-Ta-N(3)	133.1 (4)
N(2)-Ta-N(3)	103.7 (4)
Ta-C(7)-C(8)	112.0 (9)

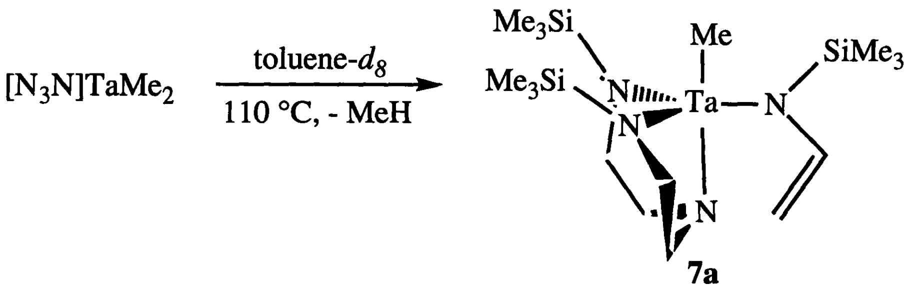
$[N_3N]Ta(Et)Cl$ reacts with one equivalent of benzylmagnesium chloride to yield **4**. If only 0.5 equivalent of Grignard is used, the proton NMR spectrum shows no evidence for $[N_3N]Ta(CH_2Ph)Cl$ formed by alkyl exchange. $[N_3N]Ta(CH_2Ph)Cl$ similarly reacts with one equivalent of ethylmagnesium 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.

$[N_3N]Ta(\eta^2\text{-}C_2H_4)$ is not stable in solution. After a period of days at ~25 °C, solutions of **4** show signs of decomposition; the red color lightens and NMR spectra are consistent with formation of the yellow ethyl complex **7b** (eq 9). The decomposition of a toluene solution of **4** ([**4**] = 0.0059, 0.0089, 0.010, 0.012 M) was followed at $\lambda_{max} \approx 494$ 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 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. Proton and carbon NMR spectral data are similar to those for the product resulting from the thermolysis of $[(Et_3SiNCH_2CH_2)_3N]Ta(\eta^2\text{-}C_2H_4)$, whose structure has been determined in an X-ray study and will be discussed in Chapter 2. Heating a toluene-d_8 solution of $[N_3N]Ta(\eta^2\text{-}C_2D_4)$ at 110 °C in a sealed tube yields a product analogous to **7b** that contains a $TaCD_2CD_2H$ group. The decomposition of $[N_3N]Ta(\eta^2\text{-}C_2D_4)$ was determined to be a first order process with $k = 1.53\ (2) \times 10^{-4}\ s^{-1}$ at 70 °C. This measurement allowed the calculation of an inverse α-secondary kinetic isotope effect of 0.89 (2) at 70 °C, significant of a change in hybridization of the ethylene carbons from sp^2 to sp^3 in the rate-limiting step.[30] Thermolysis of $[N_3N]Ta(\eta^2\text{-}C_2D_4)$ (0.03 M in toluene-d_8) in the presence of 1 atm of ethylene only produces a $TaCD_2CD_2H$ species. All of these data are consistent with decomposition of **4** by irreversible 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 β C-H bond to the metal for proton removal and transfer to the ethylene ligand. Formation of **7b'** would constitute removal of a γ-proton if the apical donor nitrogen is not coordinated at the time. Evidently this process is less facile.



(9)

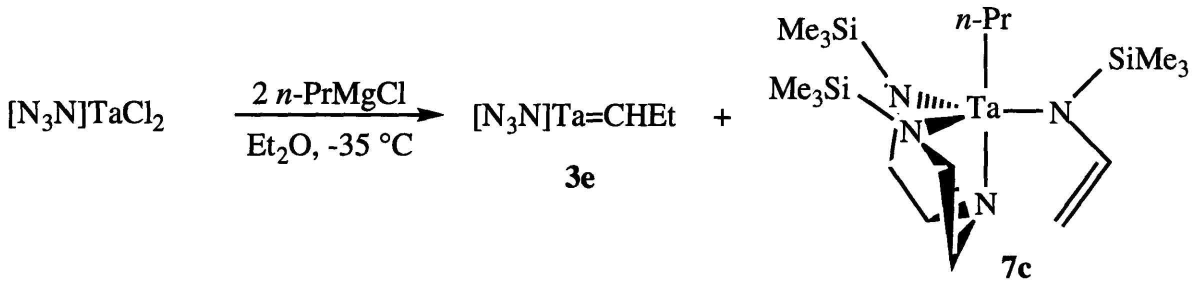
$[N_3N]TaMe_2$[27] decomposes when heated above 60 °C to produce **7a**, according to ^1H and ^{13}C NMR spectra (eq 10). Thermolysis of $[N_3N]Ta(CD_3)_2$ produces CD_3H and **7a** that contains a CD_3 ligand as evidenced by ^1H and ^2H NMR spectra. Therefore, we can rule out $[N_3N]Ta(CD_2)$ as an intermediate. ($[N_3N]Ta(CH_2)$ is still an unknown compound.) It is interesting to note that this decomposition, like that of **4**, takes place in a complex in which only two of the three orbitals in the apical position are used for bonding to apical ligands. Other $[N_3N]$Ta-based species in which all three orbitals are involved in binding to a ligand in the apical position do not decompose upon heating for days at 100 °C.



(10)

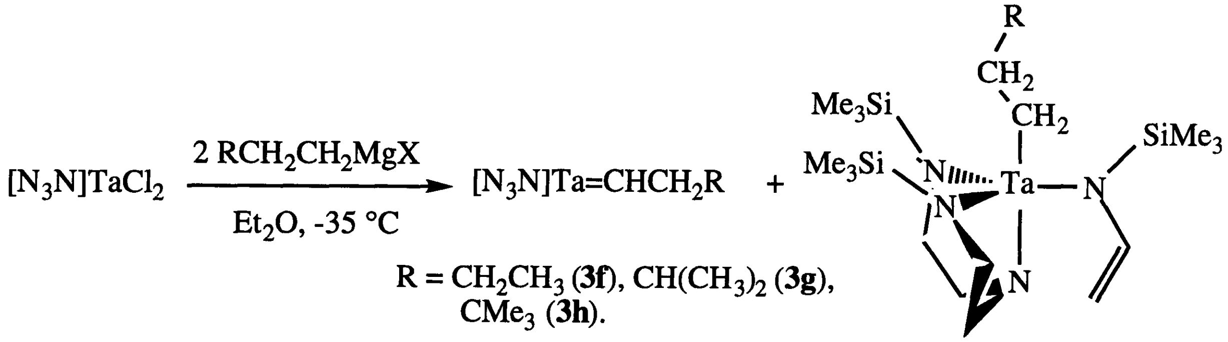
Alkylation of $[N_3N]TaCl_2$ with RCH_2CH_2MgX where R≠H: Competitive α- and β-H Abstraction Pathways.

Reactions between $[N_3N]TaCl_2$ and two equivalents of RCH_2CH_2MgX (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**. We propose that these latter products arise via facile decomposition of intermediate olefin complexes. For example, the reaction with *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 ^1H NMR integration versus an internal standard (eq 11). The spectra of **3e** are analogous to those of other alkylidenes described here; in this case H_α is a triplet at -0.28 ppm in the proton NMR spectrum. Most notable in the proton NMR spectrum of **7c** is a doublet of doublets at 6.61 ppm that can be assigned to a vinyl CH proton ($CH=CH_2$). We propose that **3e** and **7c** arise via competitive α and β abstraction in a dialkyl intermediate.



(11)

Increasing the size of the alkyl group in the alkylation reaction leads to formation of more of the expected alkylidene complex as a consequence of α-abstraction and less of the decomposition product that is proposed to arise from decomposition of an intermediate olefin complex formed by a β-abstraction process (eq 12). As shown in Table 1.4, the percent yield of alkylidene (by ^1H NMR) increases from 32% (for R = CH_3) to 84% (for R = $CHMe_2$) while the amount of decomposition product falls from 66% to 15%, respectively. The reaction between [N_3N]$TaCl_2$ and two equivalents of $Me_3CCH_2CH_2MgCl$, affords an 83% yield of **3h** and *no* observable decomposition product **7e** (< 1% via ^1H NMR). This last reaction contrasts markedly with that where R = H in which no alkylidene is formed and **4** is isolated in 96% yield.



(**7d**, **7e**, and **7f**, respectively)

(12)

Table 1.4. Percent Yields of Alkylidene and Decomposition Products Resulting from the Reaction Between [N_3N]$TaCl_2$ and 2 RCH_2CH_2MgX.

R	% Alkylidene	% Olefin or Decomp
H	0	96[b]
Me	32	66
CH_2Me	42	54
$CHMe_2$	84 (76[b])	15
CMe_3	83(77[b])	<1

[a] Determined by ^1H NMR integration versus an internal standard of $(Me_3Si)_2O$, unless otherwise noted.

[b] Isolated yield.

Synthesis of Tantalum Alkyne Complexes.

$[N_3N]TaCl_2$ reacts with two equivalents of vinylmagnesium bromide to afford white crystalline **8** in 80% yield (eq 13). **8** also can be prepared in 61% yield by treating $[N_3N]Ta(Me)OTf$ with one equivalent 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 $(t\text{-}Bu_3SiO)_3Ta(\eta^2\text{-}C_2H_2)$[31]). ^1H NMR spectra show that **8** is C_3 symmetric on the NMR time scale from 25 to -90 °C, consistent with rapid "rotation" of the acetylene about the pseudo-C_3 axis of the complex. The IR spectrum of **8** shows an acetylenic C≡C stretch at 1725 cm^{-1}. $[N_3N]Ta(\eta^2\text{-}C_2H_2)$ 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.

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

An X-ray crystal study of **8** revealed two independent molecules in the unit cell. (See Table 1.5 for crystallographic details and Table 1.6 for selected intramolecular distances and angles.) A drawing of one of them is shown in Figure 1.2. In the other molecule, the acetylene ligand is disordered - a site disorder not imposed by any space group symmetry. Bond distances and angles in the two molecules are not statistically different. **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 $[N_3N]Ta{=}PCy$[6] and $[N_3N]Ta{=}Se$ (2.349 Å).[29] 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 ° and we can say, therefore, that **8** is relatively uncrowded compared to **6**.

Table 1.5. Crystallographic Data, Collection Parameters, and Refinement Parameters for $[N_3N]Ta(\eta^2\text{-}C_2H_2)$ (**8**).

Empirical Formula	$C_{17}H_{41}N_4Si_3Ta$
Formula Weight	566.74
Crystal Color, Habit	colorless, needle
Crystal Dimensions (mm)	0.280 x 0.120 x 0.120
Crystal System	orthorhombic
No. Reflections Used for Unit Cell Determination (2θ range)	25 (15.0 - 25.0°)
a	17.154 (1) Å
b	16.756 (1) Å
c	34.365 (3) Å
β	90.0°
V	9878 (2) $Å^3$
Space Group	Pbca
Z	8
D_{calc}	1.525 g/cm^3
F_{000}	4528
$\mu(MoK_\alpha)$	45.47 cm^{-1}
Scan Type	ω-2θ
Temperature	201 K
Total No. Unique Reflections	9483
No. Observations with $I > 3.00\sigma(I)$	5137
No. Variables	439
R	0.048
R_w	0.053
GoF	3.42

Figure 1.2. X-ray Crystal Structure of $[N_3N]Ta(\eta^2\text{-}C_2H_2)$ (**8**).

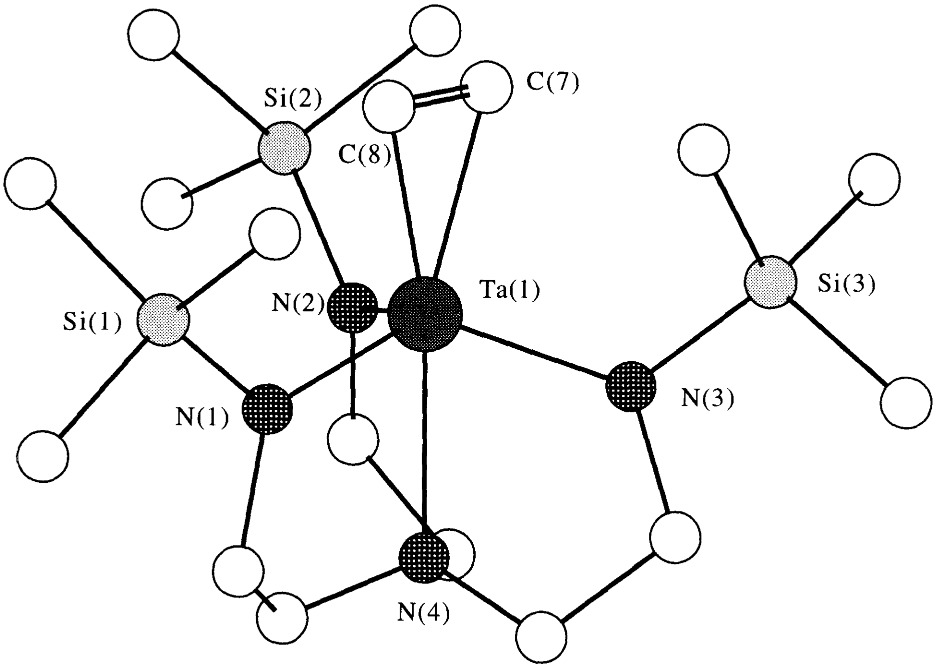


Table 1.6. Selected Intramolecular Distances (Å) and Angles (deg) for the Non-Hydrogen Atoms of $[N_3N]Ta(\eta^2\text{-}C_2H_2)$ (**8**).

Bond Lengths	
Ta-N(1)	2.07 (1)
Ta-N(2)	2.02 (1)
Ta-N(3)	2.04 (1)
Ta-N(4)	2.30 (1)
Ta-C(7)	2.09 (1)
Ta-C(8)	2.10 (1)
C(7)-C(8)	1.26 (2)

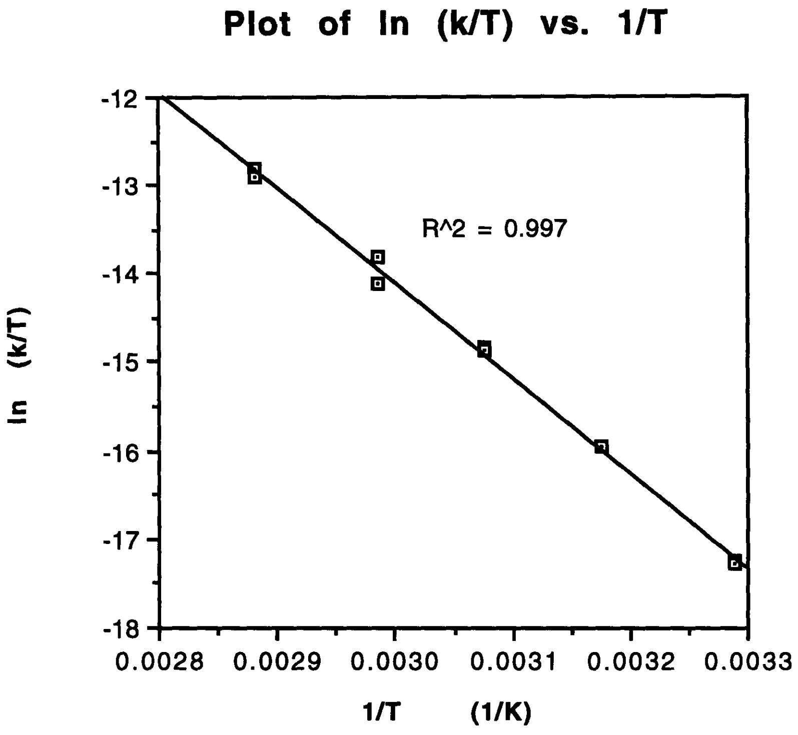
Bond Angles	
Ta-N(1)-Si(1)	126.1 (6)
Ta-N(2)-Si(2)	125.7 (6)
Ta-N(3)-Si(3)	126.4 (6)
N(1)-Ta-N(2)	110.5 (5)
N(1)-Ta-N(3)	110.6 (4)
N(2)-Ta-N(3)	122.5 (5)

A white crystalline η^2-benzyne complex (**9**) can be prepared in 70% yield by refluxing $[N_3N]TaCl_2$ with two equivalents of phenyllithium in toluene for 1 day (eq 14). $[N_3N]Ta(Ph)Cl$ can be observed as an intermediate in the reaction, and can be generated by treating **9** with a stoichiometric amount of ethereal hydrogen chloride. 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 significantly broaden the aromatic proton or carbon resonances, and the compound maintains its C_3 symmetry on the NMR time scale. Similar to **4** and **8**, benzyne complex **9** contains an unsaturated organic moiety that is proposed to be rotating rapidly about the molecule's pseudo-C_3 axis.

$$[N_3N]TaCl_2 \xrightarrow[\text{toluene, 80 °C, 1 d}]{\text{2 PhLi}} \underset{\mathbf{9}}{[N_3N]Ta(\eta^2\text{-}C_6H_4)} + C_6H_6 \tag{14}$$

Addition of one equivalent of phenylmagnesium bromide in toluene to $[N_3N]Ta(Me)Cl$ followed by heating 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 hours mixtures containing primarily (~80%) **10** can be obtained. Following the disappearance of **10** in such mixtures in toluene-d_8 in a sealed tube (ferrocene standard) via ^1H NMR demonstrates that conversion of **10** to **9** is first order in **10** through several half-lives. Data were collected between 31 °C and 74 °C (Figure 1.3). The resulting activation parameters ($\Delta H^\ddagger$ = 21.3 (5) kcal mol^{-1} and $\Delta S^\ddagger$ = -11 (1) cal mol^{-1} K^{-1}) are comparable to those for thermolysis of $Cp^*{}_2Ti(Me)Ph$ to produce transient $Cp^*{}_2Ti(\eta^2\text{-}C_6H_4)$ ($\Delta H^\ddagger$ = 23.0 kcal mol^{-1}, $\Delta S^\ddagger$ = -9.8 cal mol^{-1} K^{-1} [32]). The negative activation entropy demonstrates an increased amount of order as one moves along the reaction coordinate from **10** to the transition state, most likely due to restricted rotation about the Ta-Me and Ta-Ph bonds. Labelling experiments conducted at 74 °C (see Experimental Section) suggest that the primary isotope effect is 3.6 (6). This value is significantly smaller than that measured for the 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[32]) but is still demonstrative of C-H(D) bond cleavage in the transition state.

Figure 1.3. Plot of ln(k/T) vs. 1/T for the Formation of $[N_3N]Ta(\eta^2\text{-}C_6H_4)$ (**9**) from $[N_3N]Ta(Me)Ph$ (**10**). (See Experimental Section for a list of individual values.)



Reactions of Ethylene, Acetylene, and Benzyne Complexes.

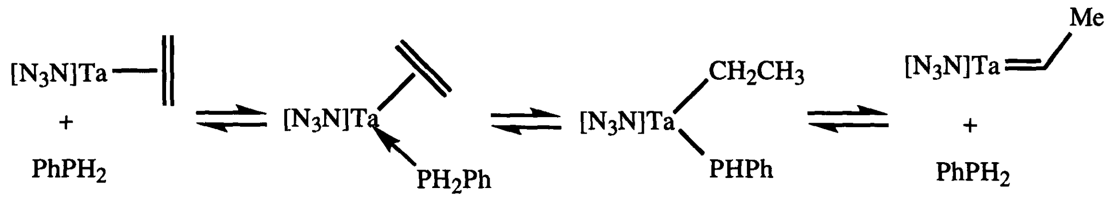
$[N_3N]Ta(\eta^2\text{-}C_2H_4)$ has proven to be relatively reactive, probably largely because one empty orbital is available to which nucleophiles can bind. Fortunately, decomposition of **4** to **7b** (eq 9) is rarely a competitive reaction, although it sometimes is a complication.

One unusual reaction is that between **4** and a catalytic amount of phenylphosphine (0.3 equivalents) 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. Alkylidene complexes of Ta(V) that contain β-protons are rare[5,33] because they usually rearrange to the olefin complex readily. 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_α 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.

$$\underset{\mathbf{4}}{[N_3N]Ta(\eta^2\text{-}C_2H_4)} \xrightarrow[Et_2O]{RPH_2} \underset{\mathbf{3d}}{[N_3N]Ta{=}CHMe}$$

$$R = H,\ n\text{-Bu},\ Ph,\ Cy \qquad (15)$$

Two equivalents of a 9:1 mixture of $PhPD_2$ and PhPHD in diethyl ether at ~25 °C convert **4** (0.04 M) to **3d** over a period of two days. In this sample of **3d** the percent deuterium at the alkylidene methyl and H_α positions is equal. Similarly, $[N_3N]Ta(\eta^2\text{-}C_2D_4)$ (0.02 M) reacts with one equivalent of $PhPH_2$ in diethyl ether for 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 $PhPH_2$ addition shows the initial build-up of a singlet resonance at 2.15 ppm, consistent with the presence of **4** with protons in the ethylene ligand. Finally, addition of one equivalent 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 postulated to be $[N_3N]Ta(Et)(PHPh)$, 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 equivalents of phenylphosphine in toluene-d_8 at 85 °C over 24 hours. (Both **3d** and $[N_3N]Ta{=}PPh$ are stable when heated to 100 °C in sealed NMR tubes in toluene-d_8.) Loss of ethane from $[N_3N]Ta(Et)(PHPh)$ simply must be slow, if we make the reasonable assumption that it would be irreversible.



(16)

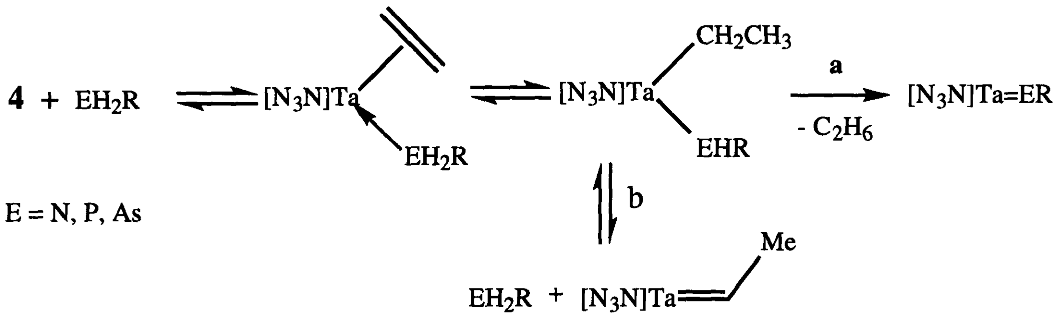
$[N_3N]Ta(\eta^2-C_2H_4)$ reacts differently with amines. Upon mixing **4** with ammonia, aniline, or pentafluoroaniline, the imido complexes **2a**, **c**, and **d** are formed in yields of 62 - 78% (eq 17). **4** does not react with *t*-butylamine under similar conditions. It is interesting to note that **2a** is also formed in 70% isolated yield by mixing **4** with one equivalent of hydrazine in tetrahydrofuran. **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 one equivalent of aniline in toluene-d_8 at ~25 °C is quite slow, being only 23% complete after 8 days, as determined via ^1H NMR integration versus an internal standard. These two observations argue against the formation of imido complexes via **3d** as an intermediate. Instead we propose that ethane is lost rapidly and irreversibly from $[N_3N]Ta(CH_2CH_3)(NHR)$ intermediates.

$$\underset{\textbf{4}}{[N_3N]Ta(\eta^2\text{-}C_2H_4)} \xrightarrow[Et_2O]{RNH_2} [N_3N]Ta{=}NR \tag{17}$$

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

Addition of 10 equivalents of Me_3SiAsH_2 to an NMR tube containing a toluene-d_8 solution of **4** (0.03 M) affords **3d** immediately, 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 ^{13}C NMR and its reaction with pivaldehyde to form $[N_3N]Ta{=}O$ and the unstable arsaalkene, $Me_3SiAs{=}C(H)CMe_3$. The reaction of **4** (0.02 M in toluene-d_8) with 5 equivalents of $PhAsH_2$ at ~25 °C affords **3d** immediately. Over the period of a week, the product mixture is observed to contain $H_3[N_3N]$, $[N_3N]Ta{=}AsPh$ (*vide infra*), and other unidentifiable ligand-containing species. If the mechanism of reaction of arsines with **4** is the same in principle as the reactions of **4** with amines and phosphines (Scheme 1.1), then we must conclude that only when E = P is path **a** unobservable, only when E = N is path **b** slow relative to **a**, and when E = As both paths can be observed with the rate of path **b** greater than that of path **a**.

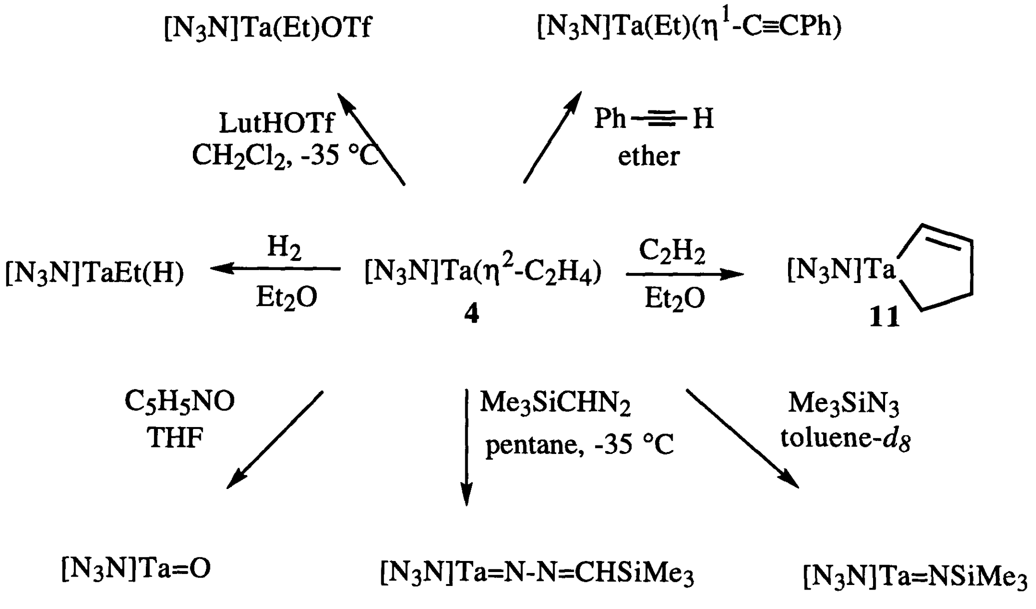
Scheme 1.1. Proposed Mechanism for Ethylene Complex **4** Reacting with EH_2R.

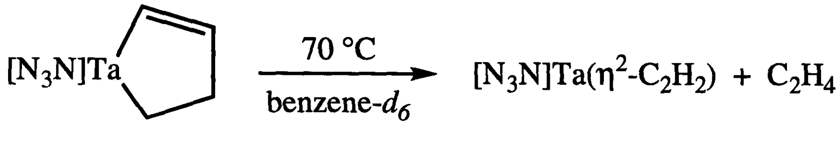


Three reactions in which ethylene is protonated to give an ethyl complex are shown in Scheme 1.2. $[N_3N]Ta(\eta^2-C_2H_4)$ reacts with 0.5 atm of hydrogen gas to afford $[N_3N]Ta(Et)H$. Exposure of a solution of the hydride complex to a dynamic vacuum results in loss of hydrogen gas and reformation (over a period of hours) of **4**. $[N_3N]Ta(Et)H$ is stable to loss of hydrogen gas in the solid state (~ 0.1 mm Hg dynamic vacuum at 25 °C for 8 hours). The reversibility of this protonation reaction is demonstrated via monitoring by ^1H or ^2H NMR the reactions of **4** with 0.25 atm D_2 and $[N_3N]Ta(\eta^2-C_2D_4)$ with 0.25 atm H_2 in toluene-d_8 (ca. 0.02 M in Ta). In all cases, the H and D labels are scrambled between the hydride and ethyl (on both C_α and C_β) ligands. $[N_3N]Ta(Et)H$ can be obtained as a white crystalline solid in 93% yield via fractional recrystallization from a diethyl ether solution of it and the ethylene complex. ^1H NMR shows the hydride as a singlet at 24.77 ppm that remains relatively sharp down to -80 °C. The Ta-H stretch is found in the IR at 1816 cm^{-1} (ν Ta-D = 1301 cm^{-1}). A 0.40 M solution of $[N_3N]Ta(Et)H$ in toluene-d_8 decomposes at 100 °C over a period of hours to provide Me_3SiH and a colorless oil that is proposed to $EtTa[N(CH_2CH_2NSiMe_3)_2(CH_2CH_2N)]$ on the basis of ^1H and ^{13}C NMR data. Unfortunately, we have been unable to obtain crystals of this decomposition product to further support this formulation. **4** is cleanly protonated by 2,6-lutidinium triflate (LutHOTf) to afford

$[N_3N]Ta(CH_2CH_3)(OTf)$ in 91% yield. When $[N_3N]Ta(\eta^2\text{-}C_2D_4)$ is employed the product is $[N_3N]Ta(CD_2CD_2H)(OTf)$, as judged by ^1H and ^2H NMR. Metathesis of the triflate ligand for a chloride or bromide is achieved in high yield by mixing $[N_3N]Ta(Et)OTf$ with $[NEt_4]X$ (X = Cl or Br) in dichloromethane. **4** is also protonated cleanly by phenylacetylene to afford yellow crystalline $[N_3N]Ta(CH_2CH_3)(\eta^1\text{-}C{\equiv}CPh)$ in 87% yield. When $[N_3N]Ta(\eta^2\text{-}C_2D_4)$ is employed in this reaction the product is $[N_3N]Ta(CD_2CD_2H)(\eta^1\text{-}C{\equiv}CPh)$, according to proton 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 tantallacyclopentene complex. Similar reactivity towards acetylenes has been reported for $Cp^*_2Ti(\eta^2\text{-}C_2H_4)$.[34,35] Upon heating 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 $[N_3N]Ta(\eta^2\text{-}C_2H_2)$ (**8**) quantitatively (eq 18).

Scheme 1.2. Some reactions of $[N_3N]Ta(\eta^2\text{-}C_2H_4)$ (**4**).





11 **8**

(18)

Several reactions of **4** resulted in displacement of ethylene (Scheme 1.2). Mixing two equivalents of pyridine-N-oxide with a 0.02 M toluene-d_8 solution of **4** at room temperature in a sealed tube for 2 days afforded $[N_3N]Ta{=}O$ in 90% yield plus ethylene and pyridine. $[N_3N]Ta(\eta^2\text{-}C_2H_4)$ reacts with trimethylsilyldiazomethane instantly to form yellow crystalline $[N_3N]Ta{=}N\text{-}N{=}CHSiMe_3$ in 91% yield. The doublet at 166.1 ppm ($^1J_{CH}$ = 138 Hz) in the ^{13}C NMR spectrum is characteristic of diazoalkane adducts,[4,36-38] most closely $[N_3N]V{=}N\text{-}N{=}CHSiMe_3$.[4] Heating a 0.02 M toluene-d_8 solution of $[N_3N]Ta{=}N\text{-}N{=}CHSiMe_3$ in a sealed tube at 110 °C for weeks fails 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 one equivalent of trimethylsilylazide over a period of three weeks in a sealed NMR tube at ~25 °C to afford $[N_3N]Ta{=}NSiMe_3$ (**2d**) quantitatively as determined via ^1H NMR integration versus an internal standard. A reaction intermediate has been observed by ^1H NMR which we presume to be the azide adduct $[N_3N]Ta{=}N\text{-}N{=}NSiMe_3$.[39] Two azide adducts have been crystallographically characterized and shown to decompose, albeit via different pathways, to the corresponding arylimido species.[40,41] 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 $[N_3N]Ta(\eta^2\text{-}C_2D_4)$ (0.03 M) under 1 atm of ethylene in a sealed tube at ~25 °C.

In contrast, **8** and **9** are relatively unreactive. For example, **8** does not react with ethylene, pyridine-N-oxide, phenylphosphine, or with $ArNH_2$ (Ar = Ph or C_6F_5) at 100 °C for weeks, while **9** does not react with PH_3 (1 atm) after one week in diethyl ether at ~25 °C or with 10 equivalents of phenylphosphine in toluene-d_8 at 110°C for 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-d_8 (0.02 - 0.03 M) do react with one equivalent 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 19). A toluene solution of $[N_3N]Ta(\eta^2\text{-}C_6H_4)$ also reacts with an excess of phenylarsine in the absence of light to afford $[N_3N]Ta{=}AsPh$ (**12**) in 53% yield (eq 20). The arsinidene is isolated as yellow crystals via recrystallization of the crude reaction product which is contaminated with by-products formed via protonation of the ligand to yield $H_3[N_3N]$ and decomposition of phenylarsine, presumedly to cyclic oligomers.[42] The ^1H NMR spectrum of **12** shows three distinct resonances in the 7.12 - 7.55 ppm window for the phenyl group and the corresponding ^{13}C NMR spectrum shows the phenyl ipso carbon as a singlet at 165.8 ppm. A 0.01 M toluene-d_8 solution of **12** shows no sign of decomposition by ^1H NMR after heating at 110 °C for 5 days. Adding two equivalents of pivaldehyde to a 0.02 M solution of **12** in CD_2Cl_2 affords within minutes, as judged by ^1H NMR, $[N_3N]Ta{=}O$ and unidentifiable resonances which may be due to the decomposition of $PhAs{=}C(H)CMe_3$. A 0.01 M solution of **12** in toluene-d_8 does not, however, react with one atm of ethylene upon heating in a sealed tube at 80 °C for five days. The preliminary results of an X-ray study of **12** show a linear Ta=As-C linkage, thus, demonstrating $[N_3N]Ta{=}AsPh$ to be the first linear mononuclear transition metal arsinidene complex. The first bent mononuclear transition metal arsinidene complex $(t\text{-}Bu_3SiO)_3Ta{=}AsPh$ was prepared by Wolczanski and co-workers and was shown to have a Ta=As-C bond angle of 107°.[13] Efforts in this laboratory have recently resulted in the synthesis and structural characterization of $[N_3N]W{=}AsMe^+OTf^-$ - a complex featuring a W-C-As bond angle of 173°.[43]

$$\underset{\mathbf{9}}{[N_3N]Ta(\eta^2\text{-}C_6H_4)} \xrightarrow[\text{toluene-}d_8]{RNH_2} \underset{R = Ph\ (\mathbf{2c}),\ C_6F_5\ (\mathbf{2d})}{[N_3N]Ta{=}NR} \qquad (19)$$

$$\underset{\mathbf{9}}{[N_3N]Ta(\eta^2\text{-}C_6H_4)} \xrightarrow[\text{toluene}]{PhAsH_2} \underset{\mathbf{12}}{[N_3N]Ta{=}AsPh} \qquad (20)$$

Discussion

One of the themes that runs through the chemistry reported here is the stability and relatively low reactivity of $[N_3N]Ta{=}E$ complexes that contain pseudo-triply bound E ligands (where E = CHR, O, NR, PR, or alkyne). For example, we are able to prepare phosphinidenes **1a** and **b** which feature small P-substituents (Me and *n*-Bu) whereas all other reported mononuclear phosphinidenes utilize large substituents such as Ph,[13] 2,4,6-$Me_3C_6H_2$,[14,15] and 2,4,6-*t*-$Bu_3C_6H_2$[14,15,44] to prohibit P-bridging interactions.[44,45] $[N_3N]Ta{=}E$ species where E is a σ, 2π donor attain an 18-electron count as long as the apical nitrogen remains bound to the metal, and are sterically protected against intermolecular decomposition reactions by the bulky $SiMe_3$ groups. (Only two π bonds can form between the three nitrogen p orbital combinations and the metal.) Intramolecular reactions such as C-H activation of a methyl group in a $SiMe_3$ substituent[2] 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, most likely for the same reason.

Another characteristic of the chemistry reported here is the "steric pressure" that the three $SiMe_3$ 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**, and also from the tendency to form alkylidene complexes by α-abstraction instead of olefin complexes by β-abstraction as the size of the alkyl group increases in the hypothetical intermediate $[N_3N]TaR_2$ species formed by alkylation of $[N_3N]TaCl_2$. However, the question is still open as to whether ligands (alkylidene and phosphinidene species, in particular) are linear, instead of bent, solely for electronic reasons, or whether steric factors also play a major role in stabilizing the linear form. At this stage we feel that the metal π orbitals involved in formation of a pseudo-triple bond to a ligand in the apical position are extraordinarily electrophilic, and therefore are likely to be the primary driving force in, for example, the formation of alkylidenes in which the $C\text{-}H_\alpha$ electron pair is strongly donated to the metal. Steric repulsion between the substituent on a "bent" apical ligand and the bulky $SiMe_3$ groups is almost certainly not an insignificant factor, although we have not been able to prepare a species in which we could test this supposition. A desirable species in this regard is $[N_3N]Ta{=}CH_2$. We suspect that should $[N_3N]Ta{=}CH_2$ be prepared, it will have a "T-shaped" methylene ligand in which the two protons are dramatically different, as observed in unstable $Cp^*Me_3W{=}CH_2$,[46] 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 will be interesting in this regard ultimately to compare the chemistry of $[N_3N]Ta$ complexes with that of $(silox)_3Ta$ complexes.

The demonstration that α-elimination or abstraction processes are preferred over analogous β-processes in a sterically crowded environment provides evidence that alkylidene ligands could be formed in classical olefin metathesis systems[47] from ethyl (or longer) alkyl ligands. 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.[48] The two tautomers interconvert by α- and β-H elimination processes of roughly equal rates. The decomposition of $Cp^*_2(H)Ta{=}C{=}CH_2$ occurs through the intermediacy of $Cp^*(\eta^5\text{-}C_5Me_4CH_2CH_2CH_2)Ta$ to afford an equilibrium mixture ($K_{eq} = 5.8(2)$ at 100 °C) of the kinetic product, $Cp^*(H)Ta{=}CHCH_2CH_2(\eta^5\text{-}C_5Me_4)$, and the thermodynamic product, $Cp^*(\eta^5\text{-}C_5Me_4CH_2CH{=}CH_2)TaH$.[49] There are other examples in the literature where α-H processes occur preferentially.[50-53] For example, $Ta(CHCMe_3)(H)(PMe_3)_3I_2$ reacts with n equivalents of ethylene to afford the α-H elimination product $Ta[CH(CH_2CH_2)_nCMe_3](H)(PMe_3)_3I_2$.[50,51] More recently,[28] α-elimination in $[N_3N]W$(cyclopentyl) to give $[N_3N]W$(cyclopentylidene)(H) has been shown by deuterium-labeling experiments to proceed more rapidly than β-elimination; the slowest step is loss of cyclopentene to give $[N_3N]W(H)$.

Conclusions

The synthesis and reactivity of a variety of complexes featuring the $[N_3N]Ta$ core have been examined with regard to preparing Ta-ligand multiple bonds. The $[N_3N]^{3-}$ ligand facilitates the formation of these multiple bonds by presenting three orbitals (σ, d_{xz}, d_{yz}) in the apical coordination site and offering a steric "pocket" to protect the reactive linkage. The bulky trimethylsilyl groups encircling the apical site, most interestingly, effect a preference for α- over β-H abstraction pathways in sterically crowded environments while not being directly involved in the decomposition of the dimethyl and ethylene complexes. A logical and interesting extension of the $[N_3N]Ta$-based chemistry would be to study how these abstraction and decomposition reactions are affected by an increase in size of the amide nitrogen silyl substituent. The synthesis and reactivity of $[N_3N^*]Ta$ complexes ($[N_3N^*] = [(Et_3SiNCH_2CH_2)_3N]^{3-}$) will be discussed in Chapter 2.

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. $Li_3[N_3N]$,[2,4] $[N_3N]TaCl_2$,[6] $Ta(CH_2CMe_3)_2Cl_3$[23] and $Ta(CH_2Ph)_2Cl_3$[22] 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 Hz. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer. Elemental analyses (C, H, N) were performed by Oneida Research Services, Whitesboro, New York or on-site using a Perkin-Elmer 2400 CHN analyzer. X-ray data were collected on an Enraf-Nonius CAD-4 diffractometer. NMR tube reactions were carried out in a Wilmad 512-7" or 512-9" 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 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$_3$N]Ta=PR via P-Ph Cleavage: Preparation of [N$_3$N]Ta=PSiMe$_3$ (1c). A yellow solution of [N$_3$N]Ta=PPh (0.500 g, 0.771 mmol) in 50 mL tetrahydrofuran was transfered via cannula to a 100 mL Schlenk flask containing clean Li ribbon (27 mg, 3.89 mmol) under an atmosphere of Ar. The reaction mixture was stirred at room temperature for 19 h and was then decanted from the remaining Li ribbon. Trimethylsilylchloride (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 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: ^{1}H NMR (C$_6$D$_6$) 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{^{1}H} NMR (C$_6$D$_6$) 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{^{1}H} NMR (toluene-*d_8*, -60°C) δ 212 ($\Delta\nu_{1/2}$ = 300).

"[N$_3$N]Ta=PLi" can be observed as an intermediate in reactions of this general type: ^{1}H NMR (C$_6$D$_6$) 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{^{1}H} NMR (C$_6$D$_6$) δ 68.5 (THF), 54.4 (CH$_2$), 51.3 (CH$_2$), 25.8 (THF), 6.5 (SiMe$_3$); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 575 ($\Delta\nu_{1/2} \approx 600$).

[N$_3$N]Ta=PMe (1a). ^{1}H NMR (C$_6$D$_6$) 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{^{1}H} NMR (C$_6$D$_6$) 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{^{1}H} NMR (C$_6$D$_6$) δ 157.

[N$_3$N]Ta=P*n*-Bu (1b). [N$_3$N]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 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: ^{1}H NMR (C_6D_6) δ 3.51 (t, 6, CH_2), 3.20 (m, 2, $\mathrm{PC}\mathit{H}_2\mathrm{CH_2CH_2CH_3}$), 2.14 (t, 6, CH_2), 1.86 (m, 2, $\mathrm{PCH_2C}\mathit{H}_2\mathrm{CH_2CH_3}$), 1.42 (m, 2, $\mathrm{PCH_2CH_2C}\mathit{H}_2\mathrm{CH_3}$), 0.88 (t, 3, $\mathrm{PCH_2CH_2CH_2C}\mathit{H}_3$), 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, $\mathrm{PCH_2}\mathit{C}\mathrm{H_2}$), 24.1 (s, $\mathrm{PCH_2CH_2}\mathit{C}\mathrm{H_2}$), 13.8 (s, $\mathrm{PCH_2CH_2CH_2}\mathit{C}\mathrm{H_3}$), 6.1 (s, $SiMe_3$); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 186.

[N_3N]Ta=PSiMe$_2$Ph (1d). ^{1}H 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$_3$CCHO. Observation of *trans*-Me$_3$C(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 C_6D_6. Within minutes the red-brown solution turned colorless: ^{1}H NMR (C_6D_6) δ 8.56 (dq, $^2J_{PH}$ = 25, 1, $\mathrm{P{=}C}\mathit{H}\mathrm{CMe_3}$), 1.34 (m, 3, MeP=C), 1.12 (d, $^4J_{PH}$ = 2, 9, $\mathrm{P{=}CHC}\mathit{Me_3}$); $^{31}P\{^1H\}$ (C_6D_6) δ 229.

***Trans*-Me$_3$C(H)C=P(*n*-Bu).** ^{1}H NMR (C_6D_6) δ 8.65 (m, $^2J_{PH}$ = 25, 1, $\mathrm{P{=}C}\mathit{H}\mathrm{CMe_3}$), 1.85 (m, 2, $\mathrm{PC}\mathit{H}_2\mathrm{CH_2CH_2CH_3}$), 1.59 (m, 2, $\mathrm{PCH_2C}\mathit{H}_2\mathrm{CH_2CH_3}$), 1.30 (m, 2, $\mathrm{PCH_2CH_2C}\mathit{H}_2\mathrm{CH_3}$), 1.16 (d, $^3J_{PH}$ = 2, 9, $\mathrm{P{=}CHC}\mathit{Me_3}$), 0.81 (t, 3, $\mathrm{PCH_2CH_2CH_2C}\mathit{H}_3$); $^{31}P\{^1H\}$ (C_6D_6) δ 243.

***Trans*-Me$_3$C(H)C=PSiMe$_3$.** ^{1}H NMR (C_6D_6) δ 9.52 (d, $^2J_{PH}$ = 24, 1, $\mathrm{P{=}C}\mathit{H}\mathrm{CMe_3}$), 1.18 (d, 9, $\mathrm{P{=}CHC}\mathit{Me_3}$), 0.21 (d, 9, $PSiMe_3$); $^{31}P\{^1H\}$ (C_6D_6) δ 244.

***Trans*-Me$_3$C(H)C=PSiMe$_2$Ph.** ^{1}H NMR (CD_2Cl_2) δ 9.44 (d, $^2J_{PH}$ = 24, 1, $\mathrm{P{=}C}\mathit{H}\mathrm{CMe_3}$), 7.56 (m, 2, Ph), 7.37 (m, 3, Ph), 1.16 (d, $^4J_{PH}$ = 2, 9, $\mathrm{P{=}CHC}\mathit{Me_3}$), 0.56 (d, $^4J_{PH}$ = 3, 6, $\mathrm{PSi}\mathit{Me_2}\mathrm{Ph}$); $^{31}P\{^1H\}$ (CD_2Cl_2) δ 238.

[N$_3$N]Ta=NH (2a). [N$_3$N]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 in vacuo and the residue was extracted with 50 mL 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: ^{1}H NMR (C_6D_6) δ 5.59 (br t (1:1:1), $^1J_{14NH}$ = 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) 3436 cm^{-1} (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$_3$N]Ta=NCMe$_3$ (2b). [N$_3$N]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: ^{1}H 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, *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$_3$N]Ta=NPh (2c). [N$_3$N]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 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: ^{1}H 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$_3$N]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 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 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 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 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: ^1H 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 methylene chloride, tetraethylammonium chloride (71 mg, 0.426 mmol) was added. After 23 h, the yellow solution was concentrated in vacuo, extracted with 30 mL 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. ^1H 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.

$[N_3N]Ta(Me)Cl$ may also be prepared by the adaptation of a synthetic route used to make $Cp_2Zr(Me)Cl$ from the corresponding dichloride and dimethyl complexes.[54,55] A solution of $[N_3N]TaMe_2$ (13 mg, 0.0213 mmol) and $[N_3N]TaCl_2$ (12 mg, 0.213 mmol) in 1 mL benzene-d_6 was heated in a sealed tube in an oil bath at 65 °C for four days. ^1H NMR spectroscopy demonstrated the product mixture to contain $[N_3N]Ta(Me)Cl$ contaminated by ca. 20% $MeTa[N(SiMe_3)(CH{=}CH_2)][N(CH_2CH_2NSiMe_3)_2]$ due to the decomposition of $[N_3N]TaMe_2$.

$[N_3N]Ta(Et)Cl$ (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 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: ^1H 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.

$[N_3N]Ta{=}CHSiMe_3$ (3a). Trimethylsilylmethyllithium (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: ^1H 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 one equivalent of trimethylsilylmethyllithium is added then **$[N_3N]Ta(CH_2SiMe_3)Cl$** can be isolated by fractional crystallization: ^1H NMR (C_6D_6) δ 3.63

(t, 6, CH_2), 2.12 (t, 6, CH_2), 1.29 (s, 2, C*H*$_2$SiMe$_3$), 0.50 (s, 9, CH_2Si*Me$_3$*), 0.36 (s, 27, NSiMe$_3$); ^{13}C NMR (C_6D_6) δ 76.8 (t, *C*H$_2$SiMe$_3$), 62.1 (t, $^1J_{CH}$ = 136, CH_2), 53.7 (t, $^1J_{CH}$ = 136, CH_2), 4.7 (q, $^1J_{CH}$ = 119, CH_2Si*Me$_3$*), 2.5 (q, $^1J_{CH}$ = 118, NSiMe$_3$).

[N$_3$N]Ta=CHPh (3b). (a) From [N$_3$N]TaCl$_2$. PhCH$_2$MgCl (642 µL, 1.0 M in diethyl ether, 0.642 mmol) was added via syringe to a -35 °C solution of [N$_3$N]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*H*Ph), 0.39 (s, 27, SiMe$_3$); ^{13}C NMR (C_6D_6) δ 201.4 (d, $^1J_{CH}$ = 72, *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 one equivalent of PhCH$_2$MgCl is added then **[N$_3$N]Ta(CH$_2$Ph)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*H*$_2$Ph), 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, Ph), 127.0 (dd, Ph), 121.7 (dt, $^1J_{CH}$ = 157, Ph), 91.4 (t, $^1J_{CH}$ = 129, *C*H$_2$Ph), 57.5 (t, $^1J_{CH}$ = 138, CH_2), 52.4 (t, $^1J_{CH}$ = 136, CH_2), 3.3 (q, $^1J_{CH}$ = 119, SiMe$_3$).

(b) From Ta(CH$_2$Ph)$_2$Cl$_3$. Ta(CH$_2$Ph)$_2$Cl$_3$ (250 mg, 0.532 mmol) was added to a -35 °C solution of Li$_3$[N$_3$N] (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$_3$N]Ta=CHCMe$_3$ (3c). A solution of Ta(CH$_2$CMe$_3$)$_2$Cl$_3$ (2.41 g, 5.61 mmol) in 40 mL diethyl ether was prepared as was a solution of Li$_3$[N$_3$N] (2.14 g, 5.61 mmol) in 40 mL 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*Me*$_3$), 0.93 (s, 1, C*H*CMe$_3$), 0.39 (s, 27, SiMe$_3$); ^{13}C NMR (C_6D_6) δ 213.3 (d, $^1J_{CH}$ = 72, *C*HCMe$_3$), 59.4 (t, CH_2), 48.7 (t, CH_2), 47.7 (s, *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$_3$N]Ta=CHCH$_2$CH$_3$ (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$_3$N]TaCl$_2$ (510 mg, 0.834 mmol) in 10 mL 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 integration versus a $(Me_3Si)_2O$ internal standard, the solid was determined to contain [N$_3$N]Ta=CHCH$_2$CH$_3$ (**3e**) and (*n*-Pr)Ta[N(CH$_2$CH$_2$NSiMe$_3$)$_2$][N(SiMe$_3$)(CH=CH$_2$)] (**7c**) in 32% and 66% yields, respectively. [N$_3$N]Ta=CHCH$_2$CH$_3$ (**3e**): ^{1}H NMR (C_6D_6) δ 3.43 (t, 6, CH_2), 3.29 (m, 2, TaCHC*H*$_2$), 2.21 (t, 6, CH_2), 1.19 (t, 3, TaCHCH$_2$C*H*$_3$), 0.38 (s, 27, SiMe$_3$), -0.28 (t, 1, TaC*H*); ^{13}C NMR (C_6D_6) δ 201.5 (d, $^1J_{CH}$ = 68, Ta*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*C*H$_2$), 18.1 (q, $^1J_{CH}$ = 121, TaCHCH$_2$*C*H$_3$), 4.5 (q, $^1J_{CH}$ = 117, SiMe$_3$). (*n*-Pr)Ta[N(CH$_2$CH$_2$NSiMe$_3$)$_2$][N(SiMe$_3$)(CH=CH$_2$)] (**7c**): ^{1}H NMR (C_6D_6) δ 6.61 (dd, 1, C*H*=CH$_2$), 4.20 (d, 1, CH=C*H*$_2$), 4.06 (m, 3, CH_2 and CH=C*H*$_2$), 3.87 (m, 4, CH_2), 3.65 (m, 2, CH_2), 2.21 (m, 2, TaCH$_2$C*H*$_2$CH$_3$), 1.45 (t, 2, TaC*H*$_2$CH$_2$CH$_3$), 1.04 (t, 3, TaCH$_2$CH$_2$C*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, *C*H=CH$_2$), 92.8 (t, $^1J_{CH}$ = 157, CH=*C*H$_2$), 73.1 (t, $^1J_{CH}$ = 116, Ta*C*H$_2$CH$_2$CH$_3$), 66.7 (t, $^1J_{CH}$ = 133, CH_2), 55.7 (t, $^1J_{CH}$ = 133, CH_2), 26.7 (t, $^1J_{CH}$ = 127, TaCH$_2$*C*H$_2$CH$_3$), 21.3 (q, $^1J_{CH}$ = 125, TaCH$_2$CH$_2$*C*H$_3$), 1.8 (q, $^1J_{CH}$ = 118, NSiMe$_3$), 0.06 (q, $^1J_{CH}$ = 119, NSiMe$_3$).

Observation of [N$_3$N]Ta=CHCH$_2$CH$_2$CH$_3$ (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$_3$N]TaCl$_2$ (504 mg, 0.834 mmol) in 10 mL 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, the solvents were removed from the yellow filtrate in vacuo to afford a yellow solid. Via ^{1}H NMR integration versus a (Me$_3$Si)$_2$O internal standard, the solid was determined to contain [N$_3$N]Ta=CHCH$_2$CH$_2$CH$_3$ (**3f**) and (*n*-Bu)Ta[N(CH$_2$CH$_2$NSiMe$_3$)$_2$][N(SiMe$_3$)(CH=CH$_2$)] (**7d**) in 42% and 54% yields, respectively. [N$_3$N]Ta=CHCH$_2$CH$_2$CH$_3$ (**3f**): ^{1}H NMR (C$_6$D$_6$) δ 3.42 (t, 6, CH$_2$), 3.26 (m, 2, TaCHC*H*$_2$), 2.20 (t, 6, CH$_2$), 1.71 (m, 2, TaCHCH$_2$C*H*$_2$), 0.95 (t, 3, TaCHCH$_2$CH$_2$C*H*$_3$), 0.41 (s, 27, SiMe$_3$), -0.20 (t, 1, TaC*H*); ^{13}C NMR (C$_6$D$_6$) δ 199.7 (d, $^1J_{CH}$ = 70, Ta*C*H), 53.5 (t, $^1J_{CH}$ = 136, CH$_2$), 50.3 (t, $^1J_{CH}$ = 135, CH$_2$), 48.4 (t, $^1J_{CH}$ = 126, TaCH*C*H$_2$), 27.1 (t, $^1J_{CH}$ = 126, TaCHCH$_2$*C*H$_2$), 14.8 (q, $^1J_{CH}$ = 125, TaCHCH$_2$CH$_2$*C*H$_3$), 4.4 (q, $^1J_{CH}$ = 117, SiMe$_3$). (*n*-Bu)Ta[N(CH$_2$CH$_2$NSiMe$_3$)$_2$][N(SiMe$_3$)(CH=CH$_2$)] (**7d**): ^{1}H NMR (C$_6$D$_6$) δ 6.64 (dd, 1, C*H*=CH$_2$), 4.21 (d, 1, CH=C*H*$_2$), 4.07 (m, 3, CH$_2$ and CH=C*H*$_2$), 3.87 (m, 4, CH$_2$), 3.66 (m, 2, CH$_2$), 2.21 (m, 2, TaCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.47 (t, 2, TaC*H*$_2$CH$_2$CH$_2$CH$_3$), 1.36 (m, 2, TaCH$_2$CH$_2$C*H*$_2$CH$_3$), 0.94 (t, 3, TaCH$_2$CH$_2$CH$_2$C*H*$_3$), 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, *C*H=CH$_2$), 92.8 (t, $^1J_{CH}$ = 156, CH=*C*H$_2$), 69.9 (t, $^1J_{CH}$ = 117, Ta*C*H$_2$CH$_2$CH$_2$CH$_3$), 66.7 (t, $^1J_{CH}$ = 134, CH$_2$), 55.7 (t, $^1J_{CH}$ = 134, CH$_2$), 35.7 (t, $^1J_{CH}$ = 125, TaCH$_2$*C*H$_2$CH$_2$CH$_3$), 29.6 (t, $^1J_{CH}$ = 124, TaCH$_2$CH$_2$*C*H$_2$CH$_3$), 14.1 (q, $^1J_{CH}$ = 124, TaCH$_2$CH$_2$CH$_2$*C*H$_3$), 1.8 (q, $^1J_{CH}$ = 118, NSiMe$_3$), 0.05 (q, $^1J_{CH}$ = 119, NSiMe$_3$).

[N$_3$N]Ta=CHCH$_2$CHMe$_2$ (3g). A -35 °C solution of [N$_3$N]TaCl$_2$ (318 mg, 0.520 mmol) in 10 mL diethyl ether was subjected to the addition of *i*-pentylmagnesium 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 pentane, and filtered through Celite. The filtrate was concentrated in vacuo to afford a yellow solid that was determined via ^{1}H NMR integration versus 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 obtain $[N_3N]Ta{=}CHCH_2CHMe_2$ (**3g**) free of the decomposition product. Yellow crystals of the alkylidene were collected to afford 242 mg (0.396 mmol, 76%) of product: ^1H NMR (C_6D_6) δ 3.41 (t, 6, CH_2), 3.37 (dd, 2, $TaCHC\mathit{H}_2CHMe_2$), 2.15 (t, 6, CH_2), 2.03 (m, 1, $C\mathit{H}Me_2$), 1.14 (d, 6, $CH\mathit{Me}_2$), 0.46 (s, 27, $NSiMe_3$), 0.10 (t, 1, $TaC\mathit{H}CH_2CHMe_2$); ^{13}C NMR (C_6D_6) δ 199.7 (d, $^1J_{CH}$ = 71, $Ta\mathit{C}HCH_2CHMe_2$), 54.9 (t, $^1J_{CH}$ = 122, $TaCH\mathit{C}H_2CHMe_2$), 54.8 (t, $^1J_{CH}$ = 136, CH_2), 50.1 (t, $^1J_{CH}$ = 135, CH_2), 31.3 (d, $^1J_{CH}$ = 129, $\mathit{C}HMe_2$), 23.7 (q, $^1J_{CH}$ = 125, $CH\mathit{Me}_2$), 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 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 pentane, and filtered through Celite. The filtrate was concentrated in vacuo to afford orange solid that 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 ^1H NMR spectroscopy. The crude reaction product was recrystallized to obtain **3h** free of the decomposition product. Orange crystals of the alkylidene were collected to afford 393 mg (0.629 mmol, 77%) of product: ^1H NMR (C_6D_6) δ 3.71 (d, 2, $TaCHC\mathit{H}_2CMe_3$), 3.34 (t, 6, CH_2), 2.13 (t, 6, CH_2), 1.21 (s, 9, $C\mathit{Me}_3$), 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, $Ta\mathit{C}HCH_2CMe_3$), 58.6 (t, $^1J_{CH}$ = 124, $TaCH\mathit{C}H_2CMe_3$), 57.5 (t, $^1J_{CH}$ = 135, CH_2), 49.3 (t, $^1J_{CH}$ = 135, CH_2), 34.3 (s, $\mathit{C}Me_3$), 30.5 (q, $^1J_{CH}$ = 124, $C\mathit{Me}_3$), 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.

$[N_3N]Ta(\eta^2\text{-}C_2H_4)$ (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 $[N_3N]TaCl_2$ (750mg, 1.23 mmol) in 30 mL 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: ^1H 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.

$[N_3N]Ta(Me)Et$ (6). A -35 °C solution of $[N_3N]Ta(Et)Cl$ (166 mg, 0.274 mmol) in 5 mL 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 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 that was shown to be an 8:1 mixture of $[N_3N]Ta(Me)Et$ (**6**) and $[N_3N]Ta(\eta^2\text{-}C_2H_4)$ (**4**) by ^1H NMR. Four recrystallizations from pentane at -35 °C afforded X-ray quality yellow plates of **6**: ^1H NMR (C_6D_6) δ 3.42 (t, 6, CH_2), 2.16 (t, 6, CH_2), 1.89 (t, 3, CH_2CH_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, CH_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_2CH_3), 2.6 (q, $^1J_{CH}$ = 118, $SiMe_3$).

$EtTa[N(SiMe_3)(CH{=}CH_2)][N(CH_2CH_2NSiMe_3)_2]$ (7b). A solution of $[N_3N]Ta(\eta^2\text{-}C_2H_4)$ (82 mg, 0.144 mmol) in ~1 mL 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. ^1H NMR demonstrated the sole reaction product to be **7b**: ^1H 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, *C*H$_2$CH$_3$), 55.7 (t, $^1J_{CH}$ = 135, CH$_2$), 18.0 (q, $^1J_{CH}$ = 125, CH$_2$*C*H$_3$), 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$_2$CH$_2$NSiMe$_3$)$_2$] (7a). A solution of [N$_3$N]TaMe$_2$ (277 mg, 0.485 mmol) in ~1 mL 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, C*H*=CH$_2$), 4.27 (d, 1, CH=C*H$_2$*), 4.10 (d, 1, CH=C*H$_2$*), 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 (toluene-*d$_8$*) δ 135.2 (d, $^1J_{CH}$ = 160, *C*H=CH$_2$), 93.7 (t, $^1J_{CH}$ = 157, CH=*C*H$_2$), 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$_3$N]Ta(η^2-C$_2$H$_2$) (8). Vinylmagnesium bromide (1.37 mL, 1.0 M in tetrahydrofuran, 1.37 mmol) was added to a -35 °C solution of [N$_3$N]TaCl$_2$ (400 mg, 0.654 mmol) in 25 mL diethyl ether. After 17 h, the pale gold mixture was concentracted in vacuo and the residue was extracted with 50 mL pentane. The extract was filtered through Celite and the pale gold filtrate was taken to dryness in vacuo to yield an off-white solid that was recrystallized from pentane at -35 °C to afford 298 mg (0.526 mmol, 80%) of colorless needles. X-ray quality crystals were obtained by recrystallization of the product from pentane at -35 °C. ^{1}H NMR (C$_6$D$_6$) δ 12.22 (s, 2, *H*CC*H*), 3.51 (t, 6, CH$_2$), 2.42 (t, 6, CH$_2$), 0.20 (s, 27, SiMe$_3$); ^{13}C NMR (C$_6$D$_6$) δ 219.9 (dd, $^1J_{CH}$ = 169, H*CC*H), 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) 1725 cm^{-1} (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$_3$N]Ta(η^2-C$_6$H$_4$) (9). (a) From [N$_3$N]TaCl$_2$. A mixture of [N$_3$N]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 hydrogen chloride: ^{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 that 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 ^{1}H NMR (see earlier description). The individual values for runs at a given temperature (K) are (k x 10^6 s^{-1}) 304 (9.58, 9.84), 315 (36.8, 36.8), 325 (110, 119), 335 (250, 337), 347 (858, 937).

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

To calculate the uncertainties in the reported rate constants, kinetic isotope effects, and activation parameters, similar methods were applied as previously described by Xue and co-workers.[56] We assumed a systematic uncertainty of 5% which 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 to calculate the uncertainties in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.[57]

Reactions of $[N_3N]Ta(\eta^2\text{-}C_2H_4)$. (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 $[N_3N]Ta(\eta^2\text{-}C_2H_4)$ (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: ^1H 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, $C\mathit{H}CH_3$); ^{13}C NMR (C_6D_6) δ 191.2 (d, $^1J_{CH}$ = 69, $\mathit{C}HCH_3$), 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 $[N_3N]Ta{=}AsSiMe_3$. ^1H 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 $[N_3N]Ta{=}AsSiMe_3$ at -35°C yields $Me_3SiAs{=}C(H)CMe_3$: ^1H NMR (C_6D_6) δ 11.46 (s, 1, $C\mathit{H}CMe_3$), 1.20 (s, 9, $CHC\mathit{Me_3}$), 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 $[N_3N]Ta(\eta^2\text{-}C_2H_4)$ (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 19h. 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 ^1H NMR spectroscopy to contain a 78% yield of $[N_3N]Ta{=}NH$ by use of $(Me_3Si)_2O$ as an internal standard.

(d) With hydrazine to give $[N_3N]Ta{=}NH$. A -35 °C solution of $[N_3N]Ta(\eta^2\text{-}C_2H_4)$ (100 mg, 0.176 mmol) in 3 mL tetrahydrofuran was subjected to addition of hydrazine (5.5 µL, 0.176 mmol) via syringe. The red solution immediately turned orange and was stirred for 24 h. The yellow solution was then concentrated in vacuo to afford a yellow solid that was extracted with 5 mL pentane and filtered through Celite. The yellow filtrate was concentrated in vacuo to provide a light yellow solid that was recrystallized from pentane at -35 °C. White crystals were collected to afford 69 mg (0.124 mmol, 70%) of product.

(e) 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 $[N_3N]Ta(\eta^2\text{-}C_2H_4)$ (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 pentane. The extract was filtered through Celite and the solvents 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: ^1H 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.

(f) With aniline to give $[N_3N]Ta{=}NPh$. $[N_3N]Ta(\eta^2\text{-}C_2H_4)$ (15 mg, 0.0264 mmol) and ferrocene (5 mg, 0.0269 mmol) were dissolved in ~1 mL 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 ^1H NMR to contain a 62% yield of $[N_3N]Ta{=}NPh$ (vs. ferrocene internal standard).

(g) With hydrogen gas to give $[N_3N]Ta(Et)H$. A 100 mL glass bomb fitted with a teflon stopcock was charged with a solution of $[N_3N]Ta(\eta^2\text{-}C_2H_4)$ (319 mg, 0.561 mmol) in 10 mL diethyl ether. The mixture was subjected to three freeze(-196 °C)-pump-thaw cycles and then 0.5 atm hydrogen gas was added. The magenta color of the solution bleached over a period of one hour to provide a colorless solution. After 2 h, the colorless 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 ^1H NMR demonstrated the presence of $[N_3N]Ta(Et)H$ along with a small amount (ca. 5%) of $[N_3N]Ta(\eta^2\text{-}C_2H_4)$. Recrystallization of the mixture from diethyl ether at -35 °C afforded $[N_3N]Ta(Et)H$ in the amount of 298 mg (0.522 mmol, 93%) as a white crystalline solid: ^1H NMR (C_6D_6) δ 24.77 (s, 1, TaH), 3.44 (t, 6, CH_2), 2.26 (t, 8, CH_2 and $C\mathit{H_2}CH_3$), 1.50 (t, 3, $CH_2C\mathit{H_3}$), 0.25 (s, 27, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 62.4 (t, $^1J_{CH}$ = 124 Hz, $Ta\mathit{C}H_2CH_3$), 56.3 (t, $^1J_{CH}$ = 137 Hz, CH_2), 51.1 (t, $^1J_{CH}$ = 134 Hz, CH_2), 11.2 (q, $^1J_{CH}$ = 123 Hz, $TaCH_2\mathit{C}H_3$), 2.3 (q, $^1J_{CH}$ = 119 Hz, $SiMe_3$). IR (nujol, background subtracted): 1816 cm^{-1} (s, ν Ta-H). Anal. Calcd for $TaSi_3N_4C_{17}H_{45}$: C, 35.77; H, 7.95; N, 9.82. Found: C, 36.13; H, 7.95; N, 9.86.

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 reaction mixture was determined by ^1H NMR to contain $EtTa[N(CH_2CH_2NSiMe_3)_2(CH_2CH_2N)]$ and Me_3SiH [δ 4.12 (m, 1, $Me_3Si\mathit{H}$), 0.02 (d, $^3J_{HH}$ = 4, 9, $\mathit{Me_3}SiH$)], contaminated by a small amount (< 5%) of $EtTa[N(SiMe_3)(CH{=}CH_2)][N(CH_2CH_2NSiMe_3)_2]$ resulting from initial dihydrogen loss from the hydride starting material followed by decomposition of the product ethylene complex. 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 the imido decomposition product 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, $CH_2C\mathit{H_3}$), 1.08 (q, 2, $C\mathit{H_2}CH_3$), 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, $\mathit{C}H_2CH_3$), 18.3 (q, $^1J_{CH}$ = 124, $CH_2\mathit{C}H_3$), 3.4 (q, $^1J_{CH}$ = 115, $SiMe_3$).

(h) 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(η^2-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, $\mathit{C}H_2CH_3$), 60.8 (t, $^1J_{CH}$ = 137, CH_2), 54.1 (t, $^1J_{CH}$ = 137, CH_2), 17.5 (q, $^1J_{CH}$ = 126, $CH_2\mathit{C}H_3$), 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.

[N_3N]Ta(Et)Cl may be prepared via addition of tetraethylammonium chloride (94 mg, 0.566 mmol) to a -35 °C solution of [N_3N]Ta(Et)OTf (407 mg, 0.566 mmol) in 8 mL methylene chloride. After 23 h, the yellow solution was concentrated in vacuo, extracted with 10 mL diethyl ether, and filtered through Celite. The yellow filtrate was concentrated in vacuo to provide a yellow solid that was recrystallized from diethyl ether at -35 °C. Yellow crystals were collected to afford 273 mg (0.451 mmol, 80%) of product.

[N_3N]Ta(Et)Br may be prepared via addition of tetraethylammonium bromide (88 mg, 0.417 mmol) to a -35 °C solution of [N_3N]Ta(Et)OTf (300 mg, 0.417 mmol) in 8 mL methylene chloride. After 24 h, the yellow solution was concentrated in vacuo, extracted with 50 mL diethyl ether, and filtered through Celite. The yellow filtrate was concentrated in vacuo to provide a yellow solid that was recrystallized from diethyl ether at -35 °C. Yellow crystals were collected to afford 227 mg (0.349 mmol, 84%) of product: ^{1}H NMR (C_6D_6) δ 3.66 (t, 6, CH_2), 2.60 (t, 3, $CH_2C\mathit{H_3}$), 2.16 (t, 6, CH_2), 1.76 (q, 2, $C\mathit{H_2}CH_3$), 0.39 (s, 27, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 80.5 (t, $^1J_{CH}$ = 112, $\mathit{C}H_2CH_3$), 61.7 (t, $^1J_{CH}$ = 137, CH_2), 54.5 (t, $^1J_{CH}$ = 136, CH_2), 22.7 (q, $^1J_{CH}$ = 127, $CH_2\mathit{C}H_3$), 2.3 (q, $^1J_{CH}$ = 118, $SiMe_3$). Anal. Calcd for $TaSi_3N_4BrC_{17}H_{44}$: C, 31.43; H, 6.83; N, 8.62. Found: C, 31.46; H, 6.75; N, 8.76.

(i) With phenylacetylene to give $[N_3N]Ta(CH_2CH_3)(\eta^1\text{-}C{\equiv}CPh)$. Phenylacetylene (24.3 μL, 0.211 mmol) was added via syringe to a solution of $[N_3N]Ta(\eta^2\text{-}C_2H_4)$ (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, $C\mathit{H_2}CH_3$), 1.66 (t, 3, $CH_2C\mathit{H_3}$), 0.24 (s, 27, $SiMe_3$); ^{13}C NMR (CD_2Cl_2) δ 172.0 (s, $\mathit{C}CPh$), 132.1 (s, Ph), 129.4 (m, Ph), 128.5 (m, Ph), 128.1 (s, $C\mathit{C}Ph$), 126.1 (m, Ph), 79.5 (t, $^1J_{CH}$ = 124, $\mathit{C}H_2CH_3$), 59.1 (t, $^1J_{CH}$ = 136, CH_2), 52.0 (t, $^1J_{CH}$ = 136, CH_2), 16.1 (q, $^1J_{CH}$ = 122, $CH_2\mathit{C}H_3$), 3.0 (q, $^1J_{CH}$ = 118, $SiMe_3$); IR (diethyl ether solution, KBr cells, background subtracted) 1963 cm^{-1} (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.

(j) With pyridine-N-oxide to give $[N_3N]Ta{=}O$. Pyridine-N-oxide (12 mg, 0.127 mmol) was added to a solution of $[N_3N]Ta(\eta^2\text{-}C_2H_4)$ (36 mg, 0.0633 mmol) in 3 mL tetrahydrofuran. After 2 d, the gold reaction mixture was stripped to afford a light yellow solid that by ^{1}H NMR using $(Me_3Si)_2O$ as an 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 previously reported.[6]

(k) With trimethylsilyldiazomethane to give $[N_3N]Ta{=}N\text{-}N{=}CHSiMe_3$. Trimethylsilyldiazomethane (500 μL, 2.0 M in hexanes, 1.00 mmol) was added via syringe to a -35 °C solution of $[N_3N]Ta(\eta^2\text{-}C_2H_4)$ (400 mg, 0.703 mmol) in 5 mL 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 that 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.

(l) With trimethylsilylazide to give [N$_3$N]Ta=NSiMe$_3$. [N$_3$N]Ta(η^2-C_2H_4) (30 mg, 0.0527 mmol) and ferrocene (10 mg, 0.0580 mmol) were dissolved in ~1 mL toluene-d_8 in an NMR tube. Trimethylsilylazide (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$_3$N]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$_3$).

(m) With acetylene to give [N$_3$N]Ta(CHCHCH$_2$CH$_2$) (11). A 100 mL glass bomb fitted with a Teflon stopcock was charged with a solution of [N$_3$N]Ta(η^2-C_2H_4) (381 mg, 0.670 mmol) in 10 mL 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 filtered through Celite in order to remove the polyacetylene and the solvents were removed from the resulting 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, 2, 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$_2$C*H*$_2$), 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, TaCHCH*C*H$_2$), 60.0 (t, $^1J_{CH}$ = 136, CH_2), 50.1 (t, $^1J_{CH}$ = 135, CH_2), 44.0 (t, $^1J_{CH}$ = 124, TaCHCHCH$_2$*C*H$_2$), 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.

Kinetics of decomposition of [N_3N]Ta(η^2-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(η^2-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. 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.

Reactions of [N_3N]Ta(η^2-C_6H_4). (a) With aniline to give [N_3N]Ta=NPh. An NMR tube was charged with a solution of [N_3N]Ta(η^2-C_6H_4) (20 mg, 0.0324 mmol) and ferrocene (3 mg, 0.0161 mmol) in ~1 mL 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 d. The reaction mixture was determined by ^{1}H NMR spectroscopy to contain a >99% yield of [N_3N]Ta=NPh via integration versus ferrocene as an internal standard.

(b) With pentafluoroaniline to give [N_3N]Ta=NC_6F_5. An NMR tube was charged with a solution of [N_3N]Ta(η^2-C_6H_4) (10 mg, 0.0162 mmol), pentafluoroaniline (3 mg, 0.0162 mmol), and ferrocene (2 mg, 0.0122 mmol) in ~1 mL 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 to contain a 98% yield of [N_3N]Ta=NC_6F_5 via integration versus ferrocene as an internal standard.

(c) With phenylarsine to give [N_3N]Ta=AsPh (12). A glass bomb fitted with a teflon stopcock was charged with a solution of [N_3N]Ta(η^2-C_6H_4) (550 mg, 0.892 mmol) in 3 mL toluene. A solution of phenylarsine (200 µL, 1.30 mmol) in 3 mL toluene was added to the bomb via a pipet containing a 2" column of activated alumina. The bomb was sealed and its contents were stirred magnetically in the dark over a period of four weeks. The brown-yellow mixture was concentrated in vacuo and extracted with 80 mL pentane. The brown extract was filtered through Celite to yield an orange filtrate. The orange filtrate was concentrated in vacuo to provide an orange solid that was shown via ^{1}H NMR to contain the arsinidene contaminated by small amounts of $N[CH_2CH_2N(H)SiMe_3]_3$ and an unknown product proposed to be a cyclic oligomer of phenylarsine. Recrystallizations of the product mixture from diethyl ether at -35 °C afforded 326 mg (0.471 mmol, 53%) of product as orange needles: ^{1}H NMR (CD_2Cl_2) δ 7.55 (d, 2, Ph), 7.34 (t, 2, Ph), 7.12 (t, 1, Ph), 3.86 (t, 6, CH_2), 2.94 (t, 6, CH_2), 0.32 (s, 27, $SiMe_3$); ^{13}C NMR (CD_2Cl_2) δ 165.8 (s, Ph), 134.9 (d, $^1J_{CH}$ = 163, Ph), 129.0 (d, $^1J_{CH}$ = 160, Ph), 127.4 (d, $^1J_{CH}$ = 162, Ph), 55.2 (t, $^1J_{CH}$ = 136, CH_2), 51.4 (t, $^1J_{CH}$ = 136, CH_2), 5.9 (q, $^1J_{CH}$ = 118, $SiMe_3$). Anal. Calcd for $TaAsSi_3N_4C_{21}H_{44}$: C, 36.41; H, 6.40; N, 8.09. Found: C, 36.02; H, 6.30; N, 7.80.

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CHAPTER 2

Alkyl and Alkylidene Complexes of Tantalum that Contain a Triethylsilyl-Substituted Triamidoamine Ligand

Much of the material covered in this chapter has appeared in print:

Freundlich, J. S., Schrock, R. R., Davis, W. M. *Organometallics* **1996**, *15*, 0000.

Introduction

Chapter 1 documented our implementation of the $[N_3N]Ta$ core ($[N_3N]^{3-}$ = $[(Me_3SiNCH_2CH_2)_3N]^{3-}$) to prepare monomeric complexes that contain a Ta-ligand multiple bond. The main features of the triamidoamine ligand system responsible for the stability of these species are the steric protection of the multiple bond afforded by the encircling trimethylsilyl groups and the presence of one σ-type and two orthogonal π orbitals used in forming the multiple bond. The majority of $[N_3N]Ta{=}E$ species prepared feature a pseudo-triple bond between tantalum and phosphorus,[1,2] nitrogen,[2,3] arsenic,[2] carbon,[2,3] oxygen,[1,3] selenium,[4] or tellurium.[4] The alkylidene ligands in $[N_3N]Ta{=}CHR$ may be viewed as σ, 2π ligands by virtue of an agostic interaction[5] of the $C_{alkylidene}$-H bond[6,7] with a d-orbital on Ta. Efforts to prepare alkylidenes with C_β substituents other than hydrogen led to the discovery that α- and β-H abstraction are competitive processes in this system. In the reaction of $[N_3N]TaCl_2$ with two equivalents 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 suggested that the larger C_β substituent forces the Ta-C_α-C_β angles in the proposed dialkyl intermediate to increase as a consequence of unfavorable steric interactions between R' and the encircling silylamide substituents, thereby activating the α-H's and leading to formation of the alkylidene. At the same time the required intermediate in which a β-hydrogen was activated toward abstraction became sterically more difficult to form.

On the basis of these results, it seemed possible that an increase in the steric bulk of the trialkylsilyl groups may lead to α-H abstraction processes being favored over β-H abstraction processes. Therefore, we turned to the synthesis of $[N_3N^*]Ta$ complexes where $[N_3N^*]^{3-}$ = $[(Et_3SiNCH_2CH_2)_3N]^{3-}$. The results of this endeavor are described in this chapter along with two X-ray crystallography 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

Synthesis and Alkylation of a Tantalum Dichloride Complex.

$Li_3[N_3N^*]$ ($[N_3N^*]^{3-} = [(Et_3SiNCH_2CH_2)_3N]^{3-}$) can be prepared by a method analogous to that used to synthesize $Li_3[N(CH_2CH_2NSiMe_3)_3]$,[8,9] i.e. treatment of $N(CH_2CH_2NH_2)_3$ successively with three equivalents of *n*-butyllithium, three equivalents of triethylchlorosilane, and three equivalents again of *n*-butyllithium.[10] However, unlike $Li_3[N(CH_2CH_2NSiMe_3)_3]$, which is isolated as white microcrystals from pentane at -35 °C, $Li_3[N_3N^*]$ has not yet been induced to crystallize. It is most convenient to isolate crude intermediate $N(CH_2CH_2NHSiEt_3)_3$ as an oil (eq 1), and 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 hindrance in developing the chemistry to be described here.

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

Tantalum pentachloride reacts with $Li_3[N_3N^*]$ at -78 °C to afford $[N_3N^*]TaCl_2$ (**1**) in 19% yield (eq 2),[11] which is less than half the yield of $[N_3N]TaCl_2$.[1] We have speculated that the low yield of $[N_3N]TaCl_2$ can be ascribed to reduction of tantalum(V) to intractable products. A decrease in yield upon increasing the bulk of the silyl substituent would be consistent with that proposal, as nucleophilic attack at the metal would be slower for steric reasons. Fortunately, $[N_3N^*]TaCl_2$ can be isolated in pure form as a solid. Proton and carbon NMR data suggest that it, like $[N_3N]TaCl_2$, is C_3-symmetric on the NMR time scale between 25 °C and -90 °C.

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

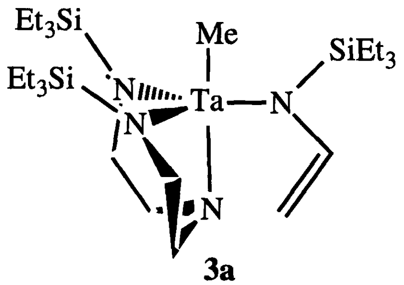
Alkylation of $[N_3N^*]TaCl_2$ with two equivalents of methylmagnesium chloride in diethyl ether affords $[N_3N^*]TaMe_2$ (**2**) quantitatively as a yellow-brown oil (eq 3). Samples of yellow crystalline $[N_3N^*]TaMe_2$ can be obtained upon standing concentrated pentane solutions of **2** at

-35 °C for weeks, although the crystallized yield is low. A resonance for the two methyl groups of $[N_3N^*]TaMe_2$ is found as a singlet at 1.31 ppm in the ^1H NMR spectrum between 25 °C 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 a solution-state structure analogous to that of $[N_3N]TaMe_2$.[3]

$$\underset{\mathbf{1}}{[N_3N^*]TaCl_2} \xrightarrow[Et_2O,\ -35\ °C]{2\ MeMgCl} \underset{\mathbf{2}}{[N_3N^*]TaMe_2} \qquad (3)$$

A toluene-d_8 solution (~0.01 M) of **2** in a sealed NMR tube is stable up to ~70 °C where it begins to evolve methane. At 110 °C decomposition is complete over the period of 1 day to afford a product that appears to be analogous to the thermolysis product of $[N_3N]TaMe_2$[2] and to the thermolysis product of $[N_3N^*]Ta(\eta^2\text{-}C_2H_4)$, whose X-ray structure is described later in this chapter. Most prominent in the ^1H NMR spectrum of **3a** are diastereotopic ligand methylene resonances and a singlet at 0.80 ppm for a methyl group. Thermolysis of $[N_3N^*]Ta(CD_3)_2$ affords CD_3H and product characterized by a singlet at 0.91 ppm in the ^2H NMR spectrum. Therefore formation of CD_4 and $[N_3N^*]Ta{=}CD_2$ can be ruled out. Details of the method of formation of methane are not known. As only two of the three orbitals in the apical coordination site are involved in bonding to the two methyl groups, we speculate that a C-H bond in a backbone methylene group is activated by the metal, possibly in a species where the apical nitrogen atom is dissociated from the metal. The activation of a ligand C-H bond then facilitates the abstraction of that proton by the methyl group. Most significant is the finding that an increase in the steric bulk in the silyl substituents does not alter the manner in which these tren-based complexes decompose.

$$\underset{\mathbf{2}}{[N_3N^*]TaMe_2} \xrightarrow[110\ °C,\ -\ CH_4]{toluene\text{-}d_8}$$



3a

(4)

Addition of two equivalents of ethylmagnesium chloride to $[N_3N^*]TaCl_2$ produces the ethylene complex **4** as red-purple crystals in 82% isolated yield (eq 5). As in the case of $[N_3N]Ta(\eta^2\text{-}C_2H_4)$, 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** makes up ~10% of the crude product mixture, judging from a quartet resonance at -0.52 ppm in the ^1H NMR, a position to be expected for an alkylidene H_α in complexes of this type (cf. -0.41 ppm for H_α in $[N_3N]Ta{=}CHMe$[3]). The low yield and high solubility of **5a** prevented its isolation in pure form. This result differs from that obtained in the N_3N system where only $[N_3N]Ta(\eta^2\text{-}C_2H_4)$ is formed upon adding two equivalents of ethyl Grignard to $[N_3N]TaCl_2$.

$$\underset{\mathbf{1}}{[N_3N^*]TaCl_2} \xrightarrow[\text{Et}_2\text{O, -35 °C}]{\text{2 EtMgCl}} \underset{\mathbf{4}}{[N_3N^*]Ta(\eta^2\text{-}C_2H_4)} + \underset{\mathbf{5a}}{[N_3N^*]Ta{=}CHMe} \qquad (5)$$

Reactions between $[N_3N^*]TaCl_2$ and two equivalents of RCH_2CH_2MgX (R = Me, Et, *i*-Pr; X = Cl or Br) 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 mixtures for species that arise from decomposition of the olefin complex by 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.[2] Unfortunately, only **5b** could be crystallized, and then only after storage of a concentrated pentane solution at -35 °C for several months. **5b** - **d** are stable at 110 °C for days as toluene-d_8 solutions (~0.1 M). Like complexes that contain the $[N_3N]Ta$ core, **5b** - **d** exhibit an upfield triplet resonance for H_α (-0.27 to 0.14 ppm) in the ^1H NMR spectrum and a very low value of $^1J_{CH}$ (~70 Hz) for the alkylidene carbon in the ^{13}C NMR spectrum, characteristic of "distorted" alkylidenes[6,7] in which there is an α-agostic[5] interaction of the C-H_α electron pair with the metal. The alkylidenes are effectively pseudo-triply bonded via σ, 2π interactions to the electrophilic tantalum center. The Ta=CHR functionality may be cleaved in a Wittig-like reaction[12] with benzaldehyde to give a mixture of *cis*- and *trans*- isomers of the expected olefin and $[N_3N^*]Ta{=}O$.[13]

$$\underset{\mathbf{1}}{[N_3N^*]TaCl_2} \xrightarrow[Et_2O,\ -35\ ^\circ C]{2\ RCH_2CH_2MgX} [N_3N]Ta{=}CHCH_2R \qquad (6)$$

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

$[N_3N^*]TaCl_2$ reacts with two equivalents of trimethylsilylmethyllithium or benzylmagnesium chloride to yield **5e** and **5f** (eq 7). $[N_3N^*]Ta{=}CHSiMe_3$ (**5e**) may be attained 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 as determined by ^1H NMR. Both complexes exhibit similar NMR spectra and reactivity to other alkylidenes prepared with the triamidoamine ligand framework.

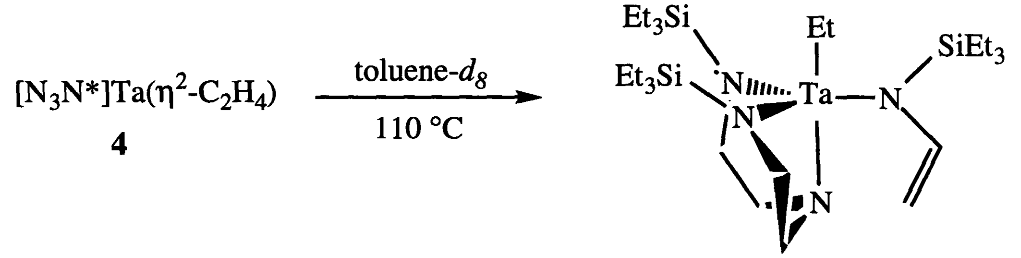
$$\underset{\mathbf{1}}{[N_3N^*]TaCl_2} \xrightarrow[Et_2O,\ -35\ ^\circ C]{2\ RCH_2M} [N_3N^*]Ta{=}CHR \qquad (7)$$

R = $SiMe_3$ (**5e**: M = Li)
R = Ph (**5f**: M = MgCl)

An X-ray Study of the Product of Decomposition of $[N_3N^*]Ta(\eta^2\text{-}C_2H_4)$.

Thermolysis of a 0.16 M toluene-d_8 solution of **4** affords ethyl species **3b** (eq 8). Decomposition of **4** in toluene at concentrations between 0.0061 and 0.015 M was followed by UV/Vis at $\lambda_{max} \approx 510$ nm and shown to be first order in tantalum with k = 4.23 (4) x 10^{-5} s^{-1} at 70 °C. This rate is approximately one-third of that for the trimethylsilyl-substituted analog (k = 1.37 (1) x 10^{-4} s^{-1}) under the same conditions.[2] 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). Heating a 0.22 M solution of $[N_3N^*]Ta(\eta^2\text{-}C_2D_4)$ in toluene-d_8 to ~100 °C in a sealed tube affords a product analogous to **3b** that contains a CD_2CD_2H group, according to ^1H and ^2H NMR. The decomposition of $[N_3N^*]Ta(\eta^2\text{-}C_2D_4)$ was determined to be a first order process with k = 4.72 (5) x 10^{-4} s^{-1} at 70 °C. This measurement allowed the calculation of an inverse α-secondary kinetic isotope effect of

0.90 (2) at 70 °C, signifying a change in hybridization of the ethylene carbons from sp^2 to sp^3 in the rate-limiting step.[14] This kinetic isotope effect is identical within experimental error to that measured in the related N_3N system: $k_H/k_D = 0.89$ (2) at 70 °C.[2] Thermolysis of $[N_3N^*]Ta(\eta^2\text{-}C_2D_4)$ (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 proton α to the equatorial nitrogen atom in the ligand methylene backbone. The data rigorously discount a mechanism involving initial loss of ethylene to generate a trigonal monopyramidal Ta(III) species, followed by β-H elimination from the ligand backbone to form a Ta(V) hydride complex that would insert free ethylene to form the decomposition product.



3b

(8)

An X-ray crystal study of **3b** (Table 2.1; Figure 2.1) showed it to be a "tetraamido" ethyl complex with a distorted trigonal bipyramidal geometry. (Relevant bond lengths and angles are listed in Table 2.2). A mirror plane bisects silylamide nitrogens N(1) and N(3) 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) = 1.97 Å). The Ta-N-Si bond angles for the two equivalent amide groups (133° and 135°) are comparable to those in $[N_3N]Ta(Me)Et$.[2] The ethyl group appears to be relatively undistorted with a Ta-C(1) bond length of 2.17 Å and a Ta-C(1)-C(2) bond angle of 118° and is similar to the Ta-Et linkage in $[N_3N]Ta(Me)Et$.[2]

Table 2.1. Crystallographic Data, Collection Parameters, and Refinement Parameters for $EtTa[N(SiEt_3)(CH{=}CH_2)][N(CH_2CH_2NSiEt_3)_2]$ (**3b**).

Empirical Formula	$C_{26}H_{61}N_4Si_3Ta$
Formula Weight	695.00
Diffractometer	Enraf-Nonius CAD-4
Crystal Color, Morphology	yellow, parallelepiped
Crystal Dimensions (mm)	0.260 x 0.320 x 0.340
Crystal System	Triclinic
a	9.9701 (8) Å
b	11.3064 (9) Å
c	15.586 (2) Å
α	82.34 (2) °
β	75.96 (1) °
γ	86.26 (2) °
V	1688.3 (7) $Å^3$
Space Group	$P\bar{1}$ (#2)
Z	2
D_{calc}	1.368 g/cm^3
F_{000}	718
$\mu(MoK_\alpha)$	33.40 cm^{-1}
Scan Type	ω-2θ
Temperature	187 K
Total No. Unique Reflections	4404
No. Observations with $I > 3.00\sigma(I)$	3811
No. Variables	308
R	0.041
R_w	0.053
GoF	1.93

Figure 2.1. X-ray Crystal Structure of $EtTa[N(SiEt_3)(CH=CH_2)][N(CH_2CH_2NSiEt_3)_2]$ (**3b**).

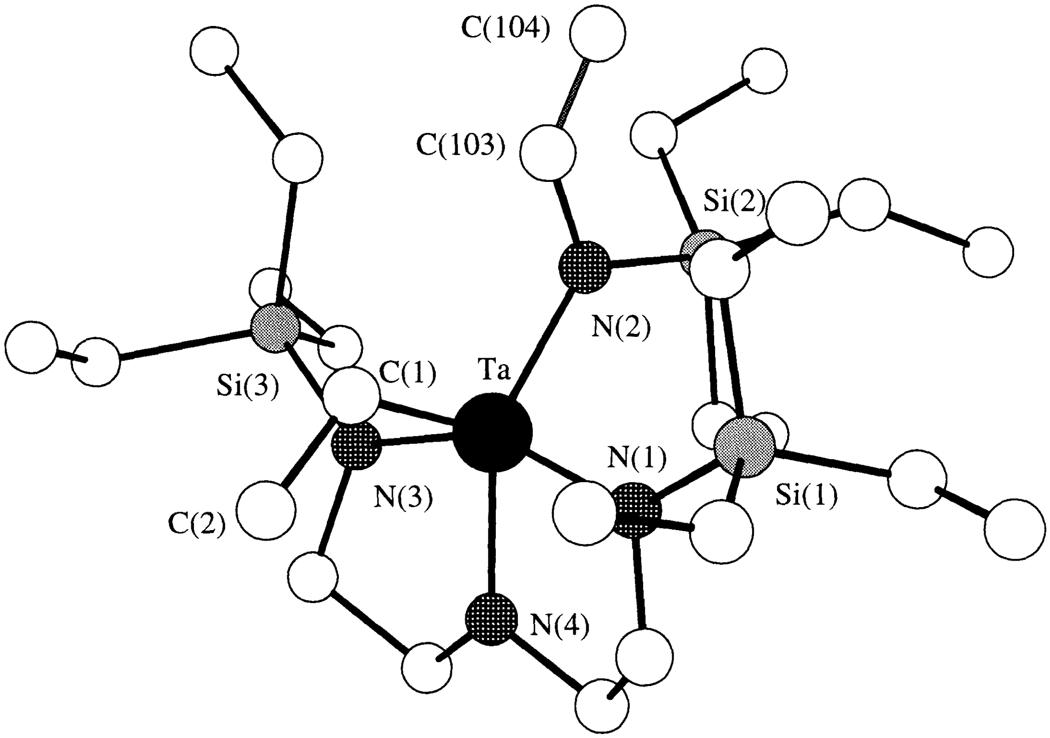


Table 2.2. Selected Intramolecular Distances (Å) and Angles (deg) for the Non-Hydrogen Atoms of $EtTa[N(SiEt_3)(CH{=}CH_2)][N(CH_2CH_2NSiEt_3)_2]$ (**3b**).

Bond Lengths

Ta-N(1)	2.025 (7)
Ta-N(2)	2.009 (7)
Ta-N(3)	2.035 (8)
Ta-N(4)	1.966 (8)
Ta-C(1)	2.17 (1)
C(1)-C(2)	1.53 (1)
C(103)-C(104)	1.32 (1)

Bond Angles

Ta-N(1)-Si(1)	134.7 (4)
Ta-N(2)-Si(2)	125.2 (4)
Ta-N(3)-Si(3)	133.5 (4)
N(1)-Ta-N(3)	152.2 (3)
N(1)-Ta-C(1)	97.2 (3)
N(3)-Ta-C(1)	94.6 (3)
Ta-C(1)-C(2)	117.6 (7)

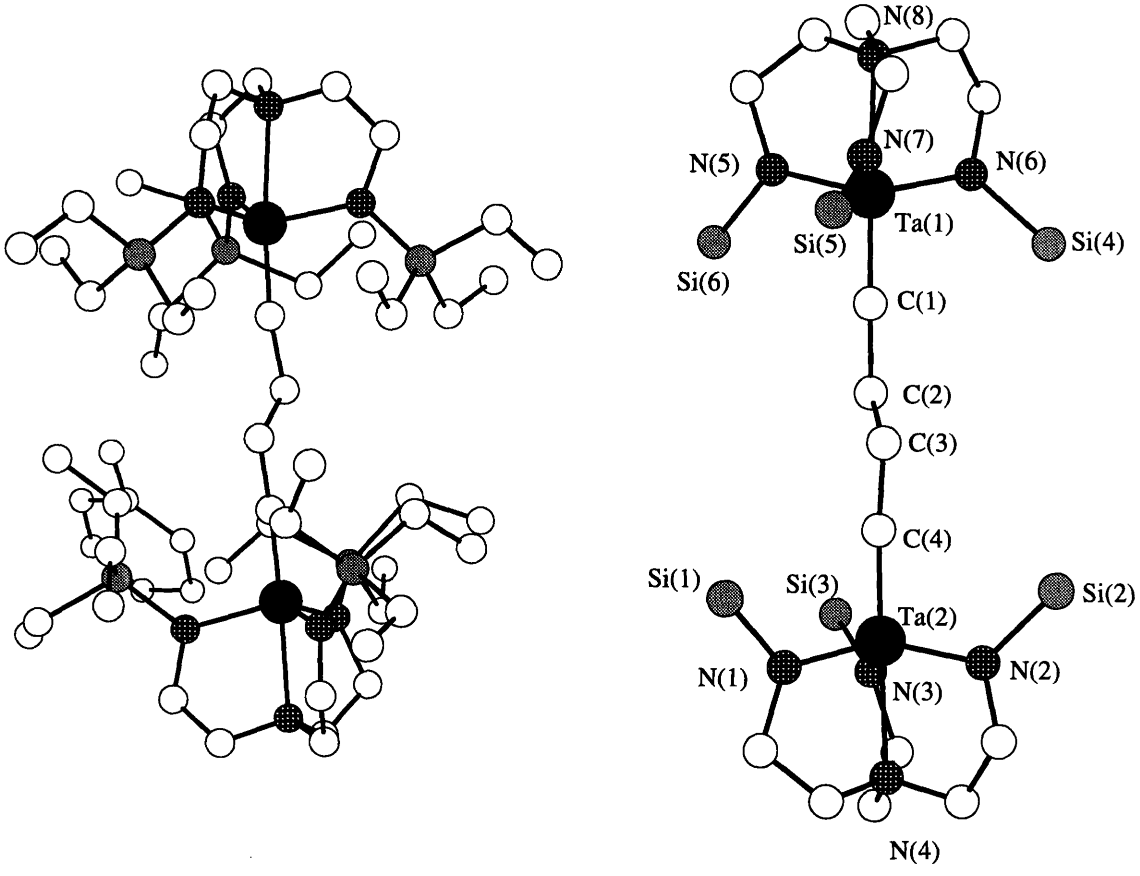
Synthesis and X-ray Study of a Dimeric Alkylidene Complex.

$[N_3N]TaCl_2$ is known to react with two equivalents of vinylmagnesium bromide to afford structurally characterized $[N_3N]Ta(\eta^2\text{-}C_2H_2)$ in high yield.[2] 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 $[N_3N]Ta{=}C{=}CH_2$ initially could not be ruled out. In contrast, $[N_3N^*]TaCl_2$ reacts with two equivalents of vinylmagnesium bromide in refluxing toluene to afford a mixture of two species, one of which is $[N_3N^*]Ta(\eta^2\text{-}C_2H_2)$ **6**, according to proton and carbon NMR spectra that are analogous to those of $[N_3N]Ta(\eta^2\text{-}C_2H_2)$ (eq 9). The other product **7** of the ~1:1 mixture is a yellow crystalline solid that could be isolated in 39% yield. 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 ($^1J_{CH} = 69$ Hz) and an H_α resonance at -0.27 ppm. A methylene group attached to C_α is the origin of a proton resonance at 3.51 ppm and a carbon resonance at 49.4 ($^1J_{CH} = 128$ Hz) as determined by ^1H-^{13}C HETCOR spectroscopy. Therefore, we postulated that **7** was a dimer $\{[N_3N^*]Ta{=}CHCH_2\}_2$, formed from two hypothetical d^1 $[N_3N^*]Ta(CH{=}CH_2)$ molecules in which the β-carbon atoms had coupled.

$$\underset{\mathbf{1}}{[N_3N^*]TaCl_2} \xrightarrow[\text{toluene, 80 °C}]{2\ H_2C=CHMgBr} \underset{\mathbf{6}}{[N_3N^*]Ta(\eta^2\text{-}C_2H_2)} + \underset{\mathbf{7}}{\{[N_3N^*]Ta{=}CHCH_2\}_2} \qquad (9)$$

An X-ray crystal study of **7** (Table 2.3; Figure 2.2) revealed that it is indeed a dimeric alkylidene complex, $\{[N_3N^*]Ta{=}CHCH_2\}_2$. (Relevant bond lengths and angles are listed in Table 2.4). 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-N_{eq} distances of 2.02 - 2.03 Å, average Ta-N_{ax} (2.36 Å), and N_{eq}-Ta-N_{eq} and Ta-N_{eq}-Si bond angles are similar to those found in $[N_3N]Ta(\eta^2\text{-}C_2H_2)$[2] and $[N_3N]Ta{=}PCy$.[1] The average Ta=C_α-C_β bond angle (173°) and Ta=C bond length (1.89 Å) are characteristic of a "distorted" alkylidene in which there is a significant interaction of the C-H_α bond with the metal. Among the early examples of "distorted" alkylidenes in the literature[6] are $[Ta(CHCMe_3)(PMe_3)Cl_3]_2$ (Ta=C = 1.898 Å, ∠ Ta=C-C = 161.2°)[7,15] and $Cp^*Ta(CHCMe_3)(C_2H_4)(PMe_3)$ (Ta=C = 1.946 Å, ∠ Ta=C-C = 170.0°).[15] Compound **7** is actually the first triamidoamine complex 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 that alkylidene ligands are more distorted in $SiEt_3$ derivatives than in $SiMe_3$ derivatives (at least according to the values for $^1J_{CH}$).

Figure 2.2. Two Views of the X-ray Crystal Structure of $\{[N_3N^*]Ta{=}CHCH_2\}_2$ (**7**). (a) View with hydrogen atoms omitted. (b) View with hydrogen atoms, triethylsilyl carbon atoms, and toluene solvent molecule omitted for greater clarity.



(a) (b)

Table 2.3. Crystallographic Data, Collection Parameters, and Refinement Parameters for $\{[N_3N^*]Ta{=}CHCH_2\}_2$ (**7**)[a].

Empirical Formula	$C_{59}H_{128}N_8Si_6Ta_2$
Formula Weight	1480.12
Diffractometer	Siemens SMART/CCD
Crystal Color, Morphology	yellow, prismatic
Crystal Dimensions (mm)	0.33 x 0.28 x 0.28
Crystal System	Monoclinic
a	19.3176 (11) Å
b	20.8010 (12) Å
c	18.6252 (11) Å
α	90 °
β	99.3130 (10) °
γ	90 °
V	7385.4 (7) $Å^3$
Space Group	$P2_1/c$
Z	4
D_{calc}	1.331 g/cm^3
F_{000}	3060
$\mu(MoK_\alpha)$	30.96 cm^{-1}
Scan Type	ω scans
Temperature (°C)	193 (2) K
Total No. Unique Reflections	10616
No. Variables	642
R	0.0719
R_w	0.2075
GoF	1.022

[a] Crystals of **7** contain one molecule of toluene per dimer.

Table 2.4. Selected Intramolecular Distances (Å) and Angles (deg) for the Non-Hydrogen Atoms of $\{[N_3N^*]Ta{=}CHCH_2\}_2$ (**7**).

Bond Lengths

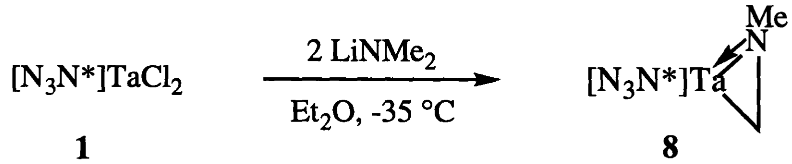
Ta(1)-N(5)	2.031 (11)
Ta(1)-N(6)	2.030 (10)
Ta(1)-N(7)	2.024 (10)
Ta(1)-N(8)	2.375 (10)
Ta(1)-C(1)	1.891 (11)
Ta(2)-C(4)	1.898 (10)
C(1)-C(2)	1.53 (2)
C(13)-C(20)	1.42 (2)

Bond Angles

Ta(1)-N(5)-Si(6)	128.3 (5)
Ta(1)-N(6)-Si(4)	124.9 (6)
Ta(1)-N(7)-Si(5)	125.4 (5)
N(5)-Ta-N(6)	113.1 (4)
N(5)-Ta-N(7)	116.6 (4)
N(6)-Ta-N(7)	115.8 (4)
Ta(1)-C(1)-C(2)	172.1 (12)
Ta(2)-C(4)-C(3)	173.1 (12)

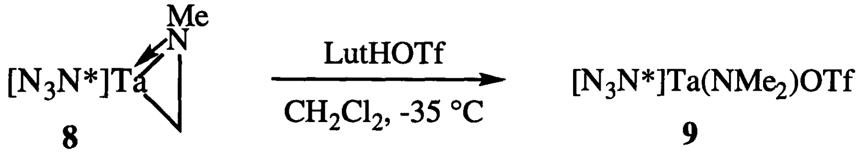
Synthesis and Reactivity of a Metallaaziridine Complex.

The reaction of dichloride **1** with two equivalents of lithium dimethylamide in diethyl ether affords $[N_3N^*]Ta(CH_2NMe)$ (**8**) as colorless crystals in 74% yield (eq 10). It is interesting to note that the analogous $[N_3N]$Ta-based complex cannot be prepared cleanly via a similar route. The reaction of $[N_3N]TaCl_2$ with two equivalents of lithium dimethylamide in diethyl ether at room temperature or in refluxing toluene affords metallaaziridine product contaminated by unidentifiable ligand-containing species. The 500 MHz ^1H NMR spectrum of **8** supports a metallaaziridine (vs. imine) description of the species based on the equivalence (25 to -90 °C) of the methylene protons (singlet at 2.23 ppm) in the metallacycle and the well-precedented electrophilicity of the tantalum triamidoamine core. These protons are inequivalent in the ^1H NMR spectra of uncoordinated methyleneimines.[16] The ^{13}C NMR of **8** locates the methylene carbon as a triplet ($^1J_{CH}$ = 151 Hz) at 61.3 ppm. The relatively low energy metallaaziridine N-C stretch is found at 1269 cm^{-1} and should be compared to those for organoimines (ca. 1450 - 1700 cm^{-1}) and organoamines (ca. 1000 - 1250 cm^{-1}).[17] A number of early transition metal imine/metallaaziridine complexes have been reported[18-25] and the NMR and IR data for $[N_3N^*]Ta(CH_2NMe)$ are quite similar to that for $Cp^*Ta(CH_2NMe)Me_2$ prepared by Bercaw and co-workers.[20] In both complexes, the metallaaziridine may be viewed as a $2\sigma, \pi$ donor.



(10)

Solutions of **8** in toluene-d_8 (~0.04 M) are stable upon thermolysis at 110 °C for days. $[N_3N^*]Ta(CH_2NMe)$ reacts cleanly with 2,6-lutidinium triflate (LutHOTf) in dichloromethane to afford white crystalline triflate **9** in 51% yield (eq 11). The dimethylamide ligand is seen as a singlet at 3.14 ppm in the ^{1}H NMR and as a quartet ($^1J_{CH}$ = 137 Hz) in the ^{13}C NMR. ^{19}F NMR and IR spectroscopy confirm the presence of the coordinated triflate. **9** is converted back to metallaaziridine **8** via reaction with one equivalent of methylmagnesium chloride. Other than its protonation, **8** has proven to be quite unreactive. An ~0.03 M toluene-d_8 solution of $[N_3N^*]Ta(CH_2NMe)$ does not react with one atmosphere of ethylene or acetylene at 80 °C over a period of days. Diethyl ether solutions (~0.03 M) of **8** do not react with one equivalent of trimethylsilyldiazomethane or pyridine-N-oxide after one day at room temperature.



(11)

Discussion

The synthesis of $[N_3N^*]Ta$ complexes was undertaken in order to probe the effect of changing the amide 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 two equivalents of RCH_2CH_2MgX where R is larger than hydrogen. This contrasts with the $[N_3N]Ta$-based system in which α- and β-H abstraction processes are competitive for R groups smaller than *t*-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; the Ta-C_α-C_β bond angles in the dialkyl intermediate are forced to increase, thereby inhibiting β-hydrogen abstraction and encouraging α-hydrogen abstraction.

The increase in sterics about the apical coordination site has also allowed the synthesis of complexes not obtainable by similar routes in the trimethylsilyl-based system. Metallaaziridine **8** may be prepared whereas the reaction of $[N_3N]TaCl_2$ with two equivalents of lithium dimethylamide at room temperature or 80 °C in toluene affords a product mixture containing a metallaaziridine along with intractable ligand-containing products. Presumably, the increased steric protection offered by the ligand "pocket" stabilizes an intermediate along the reaction coordinate with respect to decomposition. Compound **7** is also a compound for which no $[N_3N]Ta$-based relative is known, simply because treatment of $[N_3N]TaCl_2$ with two equivalents of vinylmagnesium bromide affords only $[N_3N]Ta(\eta^2\text{-}C_2H_2)$.[3] We speculate that $\{[N_3N^*]Ta{=}CH\text{-}CH_2\}_2$ forms via coupling of β-carbon atoms in d^1 $[N_3N^*]Ta(CH{=}CH_2)$ and that an analogous species is not formed when $[N_3N]TaCl_2$ reacts with vinyl Grignard because nucleophilic substitution is faster than reduction of the metal via electron transfer in this sterically more accessible coordination sphere. This result, therefore, is another consequence of the more crowded coordination sphere in $[N_3N^*]Ta$ complexes versus $[N_3N]Ta$ complexes. We suggest, in the absence of an in-depth mechanistic study, that two $[N_3N^*]Ta(CH{=}CH_2)$ may couple to form **7** in analogy to the reaction of $[N_3N]MoCl$ with sodium or lithium acetylide to afford $\{[N_3N]Mo{\equiv}C\text{-}CH{=}\}_2$.[26] Again, the increased sterics surrounding the apical coordination site are proposed to promote this coupling possibly by stabilizing a Ta(IV) intermediate and/or promoting its formation via reduction of a Ta(V) precursor.

The X-ray structure of $\{[N_3N^*]Ta{=}CHCH_2\}_2$ supports our proposal that alkylidene complexes with the tantalum triamidoamine core are "distorted" and provides a key example of the preference for these systems to form a pseudo-triple bond. Oxo, imido, phosphinidene, and arsinidene ligands are well-suited electronically to form a pseudo-triple bond with tantalum via utilization of lone-pair electrons. The alkylidene ligand, however, can only form a pseudo-triple bond with a metal center by interaction of its $C\text{-}H_\alpha$ bond. Structural and spectroscopic data have demonstrated that alkylidenes with the $[N_3N]Ta$ and $[N_3N^*]Ta$ cores are among the most "distorted" to be reported. These systems contrast sharply with those, ie. $Cp_2Ta(CH_2)CH_3$,[27] in which the metal center does not have an available orbital to form a pseudo-triple bond to the alkylidene.

The steric hindrance in triamidoamine complexes could be increased even further than found in [N_3N^*]Ta species by employing (*i*-Pr_3)Si amide nitrogen substituents. Although $Li_3\{N[CH_2CH_2NSi(i\text{-}Pr_3)]_3\}$ has been prepared by methods analogous to those used to synthesize $Li_3[N_3N^*]$,[28] attempts to isolate 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 tantalum is too slow relative to the rate of reduction of the metal, at least under the conditions employed so far. A greater propensity toward other side reactions (ie. loss of the silyl substituent to form a chlorosilane) as the silyl substituents become larger cannot be ruled out. The failure to prepare (*i*-Pr_3)Si-substituted TREN derivatives of tantalum is unfortunate, since it would be interesting to observe how further steric pressure in the apical coordination site would effect the chemistry of these complexes. Future efforts in this research group will forego the synthesis of these (*i*-Pr_3)Si-substituted TREN complexes of tantalum in deference to the preparation of novel triamidoamine ligands that should form complexes of tantalum that are stable to the decomposition pathways documented in this and the preceding chapter.

Conclusions

The synthesis of a variety of [N_3N^*]Ta-based complexes has been explored in order to determine the effect of changing the ligand amide nitrogen substituent from trimethyl- to triethylsilyl. The increase in steric bulk about the apical coordination site of these species favors α- over β-H abstraction reactions and facilitates the preparation of novel alkylidene dimer and metallaaziridine complexes unaccessible via similar routes with the [N_3N]Ta core. Expectedly, the bulkier coordination "pocket" does not alter the tantalum center's propensity to utilize the three orbitals (1σ and 2π) available in that protected site to form a pseudo-triple bond to a ligand. However, when all three of these orbitals are not utilized to bond to the ligand(s) in the apical coordination site, such complexes are prone to β-H abstraction in the ligand backbone. Thus, further explorations of triamidoamine complexes of tantalum will necessitate the design of new ligand systems which are not subject to this decomposition pathway.

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.

^{1}H 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 Hz. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer. Elemental analyses (C, H, N) were performed by Oneida Research Services, Whitesboro, New York or on-site using a Perkin-Elmer 2400 CHN analyzer. X-ray data were collected on an Enraf-Nonius CAD-4 diffractometer or a Siemens platform goniometer with a CCD detector. A complete description of data collection, structure solution, and structure refinement can be found in the supplementary material. NMR tube reactions were carried out in a Wilmad 512-7" or 512-9" 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.

$H_3[N_3N^*]$. A solution of tris(2-aminoethyl)amine (12.00 g, 0.0820 mol) in 200 mL tetrahydrofuran was chilled to -78 °C and was subjected to the addition of *n*-butyllithium (154 mL, 1.6 M in hexanes, 0.246 mol) via cannula. The milky-white mixture was allowed to warm slowly to room temperature and was then stirred for 8 h. The mixture was then chilled to -78 °C and subjected to the addition of triethylchlorosilane (37.10 g, 0.246 mol) via cannula. The cloudy white mixture was allowed to warm slowly to room temperature and was then stirred for 12 h. All volatiles were then removed in vacuo to yield a cloudy pink oil. The oil was extracted with 150 mL pentane and was filtered through Celite. The light pink filtrate was then concentrated in vacuo for 2 d. A light pink oil was collected to afford 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, $SiCH_2C\mathit{H_3}$), 0.77 (t, 3, NH), 0.59 (q, 18, $SiC\mathit{H_2}CH_3$); ^{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, $SiCH_2CH_3$), 5.25 (t, $^1J_{CH}$ = 116, $SiCH_2CH_3$).

$[N_3N^*]TaCl_2$ (1). A solution of $[N_3N^*]H_3$ (3.912 g, 8.00 mmol) in 100 mL diethyl ether was chilled to -35 °C and was subjected to the addition of *n*-butyllithium (15 mL, 1.6 M in hexanes, 24.0 mmol) via cannula. The pale yellow reaction mixture was stirred for 7 h and was then chilled to -78 °C. Tantalum(V) chloride (2.866 g, 8.00 mmol) was then added under Ar counterflow. The reaction mixture was allowed to warm slowly to room temperature and was then stirred for 14 h. All volatiles were removed in vacuo and the resulting brown solid was extracted with 70 mL diethyl ether. The extract was filtered through Celite and the brown-yellow filtrate was concentrated in vacuo to yield oily brown solid. The solid was recrystallized from pentane at -35 °C. Yellow-orange crystals were collected to afford 1.117 g (1.51 mmol, 19%) of product: ^1H NMR (C_6D_6) δ 4.00 (t, 6, CH_2), 2.56 (t, 6, CH_2), 1.13 (t, 27, $SiCH_2CH_3$), 1.06 (q, 18, $SiCH_2CH_3$); ^{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, $SiCH_2CH_3$), 7.0 (t, $^1J_{CH}$ = 119, $SiCH_2CH_3$). 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). A -35 °C solution of $[N_3N^*]TaCl_2$ (300 mg, 0.407 mmmol) in 8 mL diethyl ether was subjected to the addition of methylmagnesium chloride (298 μL, 3.0 M in tetrahydrofuran, 0.895 mmol) via syringe. A white precipitate was observed immediately and the mixture was stirred for 2 h. The mixture was concentrated in vacuo, extracted with 70 mL pentane, and was filtered through Celite. 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 as pale yellow crystals upon recrystallization from pentane at -35 °C over a period of weeks. ^1H 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, $SiCH_2CH_3$), 0.88 (q, 18, $SiCH_2CH_3$); ^{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, $SiCH_2CH_3$), 7.0 (t, $^1J_{CH}$ = 118, $SiCH_2CH_3$). 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 ca. 1 mL toluene-d_8 was added to an NMR tube which was then sealed. The tube was heated to 110 °C in an oil bath for 24 h. ^1H NMR demonstrated the sole reaction products to be methane (δ 0.17) and **3a**: ^1H NMR (toluene-d_8) δ 6.45 (dd, 1, $CH{=}CH_2$), 4.63 (d, 1, $CH{=}CH_2$), 4.18 (d, 1, $CH{=}CH_2$), 3.94 (m, 4, CH_2), 3.83 (m, 4, CH_2), 1.03 (t, 9, $NSiCH_2CH_3$), 1.00 (t, 18, $NSiCH_2CH_3$), 0.81 (q, 6, $NSiCH_2CH_3$), 0.80 (s, 3, CH_3), 0.66 (q, 12, $NSiCH_2CH_3$); ^{13}C NMR (toluene-d_8) δ 133.9 (d, $^1J_{CH}$ = 164, $CH{=}CH_2$), 97.8 (t, $^1J_{CH}$ = 161, $CH{=}CH_2$), 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, $NSiCH_2CH_3$), 7.8 (q, $^1J_{CH}$ = 121, $NSiCH_2CH_3$), 6.6 (t, $^1J_{CH}$ = 117, $NSiCH_2CH_3$), 5.6 (t, $^1J_{CH}$ = 115, $NSiCH_2CH_3$).

$[N_3N^*]Ta(\eta^2\text{-}C_2H_4)$ (4). A -35 °C solution of $[N_3N^*]TaCl_2$ (500 mg, 0.678 mmol) in 10 mL diethyl ether was subjected to the addition of ethylmagnesium chloride (627 μL, 2.3 M in diethyl ether, 1.44 mmol) via syringe. Within 5 minutes, the yellow solution turned red-purple with the formation of a white precipitate. After 2 h, the reaction mixture was concentrated in vacuo, extracted with 20 mL pentane, and was filtered through Celite. The red-purple filtrate was stripped to solid that was determined to be a 9:1 mixture of $[N_3N^*]Ta(\eta^2\text{-}C_2H_4)$ (**4**) and $[N_3N^*]Ta{=}CHMe$ (**5a**) via ^1H NMR spectroscopy. $[N_3N^*]Ta{=}CHMe$: ^1H NMR (C_6D_6) δ 3.43 (t, 6, CH_2), 2.83 (d, 3, $CHMe$), 2.20 (t, 6, CH_2), 1.10 (t, 27, $SiCH_2CH_3$), 0.92 (q, 18, $SiCH_2CH_3$), -0.52 (q, 1, $CHMe$). 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 product: ^1H NMR (C_6D_6) δ 3.46 (t, 6, CH_2), 2.37 (t, 6, CH_2), 2.10 (s, 4, $H_2C{=}CH_2$), 1.03 (t, 27, $SiCH_2CH_3$), 0.71 (q, 18, $SiCH_2CH_3$); ^{13}C NMR (C_6D_6) δ 62.7 (t, $^1J_{CH}$ = 141, $H_2C{=}CH_2$), 60.7 (t, $^1J_{CH}$ = 136, CH_2), 49.5 (t, $^1J_{CH}$ = 135, CH_2), 8.1 (q, $^1J_{CH}$ = 125, $SiCH_2CH_3$), 7.0 (t, $^1J_{CH}$ = 117, $SiCH_2CH_3$). 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 $[N_3N^*]Ta(\eta^2\text{-}C_2H_4)$ (76 mg, 0.109 mmol) in ca. 1 mL toluene-d_8 was added to an NMR tube which was then sealed. The tube was heated to 110 °C in an oil bath for 24 h. ^1H NMR demonstrated the sole reaction product to be **3b**: ^{1}H NMR (toluene-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, $\mathrm{CH_2}$ and $\mathrm{CH{=}C}H_2$), 3.87 (m, 6, $\mathrm{CH_2}$), 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 (toluene-$d_8$) δ 135.5 (d, $^1J_{\mathrm{CH}}$ = 161, $C\mathrm{H{=}CH_2}$), 95.5 (t, $^1J_{\mathrm{CH}}$ = 161, $\mathrm{CH{=}}C\mathrm{H_2}$), 67.6 (t, $^1J_{\mathrm{CH}}$ = 133, $\mathrm{CH_2}$), 55.7 (t, $^1J_{\mathrm{CH}}$ = 134, $\mathrm{CH_2}$), 54.8 (t, $^1J_{\mathrm{CH}}$ = 117, $C\mathrm{H_2CH_3}$), 18.1 (q, $^1J_{\mathrm{CH}}$ = 125, $\mathrm{CH_2}C\mathrm{H_3}$), 8.4 (q, $^1J_{\mathrm{CH}}$ = 125, $\mathrm{NSiCH_2}C\mathrm{H_3}$), 8.1 (q, $^1J_{\mathrm{CH}}$ = 123, $\mathrm{NSiCH_2}C\mathrm{H_3}$), 6.8 (t, $^1J_{\mathrm{CH}}$ = 116, $\mathrm{NSi}C\mathrm{H_2CH_3}$), 5.7 (t, $^1J_{\mathrm{CH}}$ = 118, $\mathrm{NSi}C\mathrm{H_2CH_3}$).

[N$_3$N*]Ta=CHEt (5b). A -35 °C solution of [N$_3$N*]TaCl$_2$ (340 mg, 0.461 mmol) in 8 mL diethyl ether was subjected to the addition of *n*-propylmagnesium chloride (387 µL, 2.5 M in diethyl ether, 0.968 mmol). The precipitation of a white solid was evident within 5 minutes and over a period of 1 h the mixture changed in color to yellow-brown. After 23 h, the reaction mixture was concentrated in vacuo, extracted with 30 mL pentane, and was filtered through Celite. The yellow filtrate was concentrated in vacuo to afford 285 mg (0.402 mmol, 87%) of a yellow oil. ^{1}H NMR ($\mathrm{C_6D_6}$) δ 3.43 (t, 6, $\mathrm{CH_2}$), 3.30 (m, 2, $\mathrm{C}H_2\mathrm{CH_3}$), 2.24 (t, 6, $\mathrm{CH_2}$), 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 ($\mathrm{C_6D_6}$) δ 202.8 (d, $^1J_{\mathrm{CH}}$ = 70, Ta=CH), 56.3 (t, $^1J_{\mathrm{CH}}$ = 135, $\mathrm{CH_2}$), 49.7 (t, $^1J_{\mathrm{CH}}$ = 134, $\mathrm{CH_2}$), 38.6 (t, $^1J_{\mathrm{CH}}$ = 126, $C\mathrm{H_2CH_3}$), 18.2 (q, $^1J_{\mathrm{CH}}$ = 125, $\mathrm{CH_2}C\mathrm{H_3}$), 8.2 (q, $^1J_{\mathrm{CH}}$ = 120, $\mathrm{SiCH_2}C\mathrm{H_3}$), 7.5 (t, $^1J_{\mathrm{CH}}$ = 120, $\mathrm{Si}C\mathrm{H_2CH_3}$).

[N$_3$N*]Ta=CHPr (5c). A -35 °C solution of *n*-butylmagnesium chloride (569 µL, 2.5 M in diethyl ether, 1.42 mmol) in 10 mL diethyl ether was subjected to the addition of [N$_3$N*]TaCl$_2$ (500 mg, 0.678 mmol). After 24 h, the yellow cloudy mixture was concentrated in vacuo to yield an oily yellow solid. The solid was extracted with 30 mL pentane and filtered through Celite. The yellow filtrate was concentrated to afford 348 mg (0.481 mmol, 71%) of product as a yellow oil. ^{1}H NMR ($\mathrm{C_6D_6}$) δ 3.43 (t, 6, $\mathrm{CH_2}$), 3.25 (m, 2, $\mathrm{TaCHC}H_2\mathrm{CH_2CH_3}$), 2.24 (t, 6, $\mathrm{CH_2}$), 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 ($\mathrm{C_6D_6}$) δ

201.3 (d, $^1J_{CH}$ = 69, Ta*C*HCH$_2$CH$_2$CH$_3$), 56.4 (t, $^1J_{CH}$ = 136, CH$_2$), 49.7 (t, $^1J_{CH}$ = 135, CH$_2$), 48.3 (t, $^1J_{CH}$ = 124, TaCH*C*H$_2$CH$_2$CH$_3$), 21.2 (t, $^1J_{CH}$ = 127, TaCHCH$_2$*C*H$_2$CH$_3$), 9.0 (q, $^1J_{CH}$ = 124, TaCHCH$_2$CH$_2$*C*H$_3$), 8.2 (q, $^1J_{CH}$ = 127, SiCH$_2$*C*H$_3$), 7.5 (t, $^1J_{CH}$ = 124, Si*C*H$_2$CH$_3$).

[N$_3$N*]Ta=CHCH$_2$CHMe$_2$ (5d). A -35 °C solution of *i*-pentylmagnesium bromide (502 µL, 1.7 M in diethyl ether, 0.854 mmol) in 8 mL diethyl ether was subjected to the addition of [N$_3$N*]TaCl$_2$ (300 mg, 0.406 mmol). After 24 h, the cloudy yellow-orange mixture was concentrated in vacuo, extracted with 30 mL pentane, and filtered through Celite. The filtrate was concentrated in vacuo to afford 244 mg (0.331 mmol, 81%) of product as a yellow oil. ^{1}H NMR (C$_6$D$_6$) δ 3.41 (t, 6, CH$_2$), 3.35 (dd, 2, TaCHC*H*$_2$CHMe$_2$), 2.19 (t, 6, CH$_2$), 1.95 (m, 1, C*H*Me$_2$), 1.11 (t, 27, SiCH$_2$C*H*$_3$), 1.10 (d, 6, CH*Me*$_2$), 0.95 (q, 18, SiC*H*$_2$CH$_3$), 0.14 (t, 1, TaC*H*CH$_2$CHMe$_2$); ^{13}C NMR (C$_6$D$_6$) δ 201.2 (d, $^1J_{CH}$ = 71, Ta*C*HCH$_2$CHMe$_2$), 57.1 (t, $^1J_{CH}$ = 136, CH$_2$), 54.9 (t, $^1J_{CH}$ = 123, TaCH*C*H$_2$CHMe$_2$), 49.5 (t, $^1J_{CH}$ = 135, CH$_2$), 31.6 (d, $^1J_{CH}$ = 126, *C*HMe$_2$), 23.6 (q, $^1J_{CH}$ = 125, CH*Me*$_2$), 8.2 (q, $^1J_{CH}$ = 125, SiCH$_2$*C*H$_3$), 7.4 (t, $^1J_{CH}$ = 116, Si*C*H$_2$CH$_3$).

[N$_3$N*]Ta=CHSiMe$_3$ (5e). A -35 °C solution of [N$_3$N*]TaCl$_2$ (300 mg, 0.407 mmol) in 8 mL diethyl ether was subjected to the addition of trimethylsilylmethyllithium (80 mg, 0.854 mmol). After 22 h, the cloudy orange solution was concentrated in vacuo, extracted with 10 mL pentane, and was filtered through Celite. The orange filtrate was concentrated in vacuo to afford an orange solid that was recrystallized from pentane at -35 °C. Yellow crystals were collected to provide 218 mg (0.289 mmol, 71%) of product: ^{1}H NMR (C$_6$D$_6$) δ 3.36 (t, 6, CH$_2$), 2.10 (t, 6, CH$_2$), 2.09 (s, 1, C*H*SiMe$_3$), 1.09 (t, 27, SiCH$_2$C*H*$_3$), 0.96 (q, 18, SiC*H*$_2$CH$_3$), 0.43 (s, 9, CHSi*Me*$_3$); ^{13}C NMR (C$_6$D$_6$) 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$_2$*C*H$_3$), 7.1 (t, $^1J_{CH}$ = 118, Si*C*H$_2$CH$_3$), 4.8 (q, $^1J_{CH}$ = 118, SiMe$_3$). Anal. Calcd for TaSi$_4$N$_4$C$_{28}$H$_{67}$: C, 44.65; H, 8.97; N, 7.44. Found: C, 44.53; H, 8.88; N, 7.29.

[N$_3$N*]Ta=CHPh (5f). A -35 °C solution of benzylmagnesium chloride (1.08 mL, 1.1 M in diethyl ether, 1.19 mmol) in 7 mL diethyl ether was subjected to the addition of $[N_3N^*]TaCl_2$ (419 mg, 0.568 mmol). 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, $SiCH_2C\mathit{H_3}$), 0.82 (q, 18, $SiC\mathit{H_2}CH_3$); ^{13}C NMR (C_6D_6) δ 200.9 (d, $^1J_{CH}$ = 71, Ta*C*H), 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, $SiCH_2\mathit{C}H_3$), 7.3 (t, $^1J_{CH}$ = 120, $Si\mathit{C}H_2CH_3$).

$\{[N_3N^*]Ta{=}CHCH_2\}_2$ (7). A solution of $[N_3N^*]TaCl_2$ (708 mg, 0.959 mmol) in 10 mL toluene was subjected to the addition of vinylmagnesium bromide (1.55 mL, 1.3 M in tetrahydrofuran, 2.01 mmol). The resulting brown-red mixture was then heated at ca. 80 °C for 1 d. The yellow-brown mixture was concentrated in vacuo and extracted with 60 mL pentane. The extract was filtered through Celite and the filtrate was concentrated to provide a yellow-brown solid. The product was determined to be a 1:1 mixture of alkylidene **7** and $[N_3N^*]Ta(\eta^2\text{-}C_2H_2)$ (**6**) via ^1H NMR. $[N_3N^*]Ta(\eta^2\text{-}C_2H_2)$: ^1H NMR (C_6D_6) δ 12.15 (s, 2, $\mathit{H}C{\equiv}C\mathit{H}$), 3.55 (t, 6, CH_2), 2.46 (t, 6, CH_2), 1.17 (t, 27, $SiCH_2C\mathit{H_3}$), 1.10 (q, 18, $SiC\mathit{H_2}CH_3$); ^{13}C NMR (C_6D_6) δ 219.4 (dd, $^1J_{CH}$ = 168, $H\mathit{C}{\equiv}\mathit{C}H$), 55.9 (t, $^1J_{CH}$ = 136, CH_2), 49.4 (t, $^1J_{CH}$ = 135, CH_2), 8.3 (q, $^1J_{CH}$ = 120, $SiCH_2\mathit{C}H_3$), 7.5 (t, $^1J_{CH}$ = 117, $Si\mathit{C}H_2CH_3$). Fractional recrystallization of the product mixture from pentane afforded the alkylidene free of the acetylene complex. Yellow crystals were collected to afford 261 mg (0.194 mmol, 39%) of product: ^1H NMR (C_6D_6) δ 3.51 (br s, 4, $TaCHC\mathit{H_2}$), 3.45 (t, 12, CH_2), 2.21 (t, 12, CH_2), 1.20 (t, 54, $SiCH_2C\mathit{H_3}$), 1.03 (q, 36, $SiC\mathit{H_2}CH_3$), -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, $TaCH\mathit{C}H_2$), 8.0 (q, $^1J_{CH}$ = 124, $SiCH_2\mathit{C}H_3$), 7.5 (t, $^1J_{CH}$ = 117, $Si\mathit{C}H_2CH_3$). 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.

[N$_3$N*]Ta(CH$_2$NMe) (8). A -35 °C solution of [N$_3$N*]TaCl$_2$ (150 mg, 0.203 mmol) in 8 mL diethyl ether was subjected to the addition of lithium dimethylamide (22 mg, 0.427 mmol). After 23 h, the cloudy yellow solution was concentrated in vacuo, extracted with 5 mL pentane, and was filtered through Celite. The yellow filtrate was concentrated to afford to a yellow-brown oil that was recrystallized from pentane at -35 °C. Colorless crystals were collected to provide 200 mg (0.282 mmol, 74%) of product: ^{1}H NMR (C$_6$D$_6$) δ 3.89 (s, 3, NMe), 3.43 (t, 6, CH$_2$), 2.38 (t, 6, CH$_2$), 2.23 (s, 2, MeNC*H*$_2$), 1.05 (t, 27, SiCH$_2$C*H*$_3$), 0.68 (q, 18, SiC*H*$_2$CH$_3$); ^{13}C NMR (C$_6$D$_6$) δ 61.3 (t, $^1J_{CH}$ = 151, MeNCH$_2$), 60.1 (t, $^1J_{CH}$ = 136, CH$_2$), 50.5 (q, $^1J_{CH}$ = 133, NMe), 48.8 (t, $^1J_{CH}$ = 135, CH$_2$), 8.2 (q, $^1J_{CH}$ = 124, SiCH$_2$*C*H$_3$), 6.8 (t, $^1J_{CH}$ = 116, Si*C*H$_2$CH$_3$). Anal. Calcd for TaSi$_3$N$_5$C$_{26}$H$_{62}$: C, 43.98; H, 8.80; N, 9.86. Found: C, 43.79; H, 9.13; N, 9.69. IR (nujol, background subtracted): 1269 cm^{-1} (ν Me*N*CH$_2$).

[N$_3$N*]Ta(NMe$_2$)OTf (9). A -35 °C solution of [N$_3$N*]Ta(CH$_2$NMe) (739 mg, 1.04 mmol) in 10 mL dichloromethane was subjected to the addition of 2,6-lutidinium triflate (268 mg, 1.04 mmol). After 22 h, the light yellow-brown solution was concentrated in vacuo, extracted with 20 mL diethyl ether, and filtered through Celite. The filtrate was concentrated in vacuo to provide a yellow-brown oily solid that was recrystallized from diethyl ether at -35 °C. White crystals were collected to afford 458 mg (0.532 mmol, 51%) of product: ^{1}H NMR (C$_6$D$_6$) δ 3.69 (t, 6, CH$_2$), 3.19 (t, 6, CH$_2$), 3.14 (s, 6, NMe$_2$), 0.94 (t, 27, SiCH$_2$C*H*$_3$), 0.58 (q, 18, SiC*H*$_2$CH$_3$); ^{13}C NMR (C$_6$D$_6$) δ 62.9 (t, $^1J_{CH}$ = 139, CH$_2$), 51.4 (t, $^1J_{CH}$ = 140, CH$_2$), 45.2 (q, $^1J_{CH}$ = 137, NMe$_2$), 7.7 (q, $^1J_{CH}$ = 126, SiCH$_2$*C*H$_3$), 6.6 (t, $^1J_{CH}$ = 117, Si*C*H$_2$CH$_3$); ^{19}F NMR (C$_6$D$_6$) δ -76.3 (s). Anal. Calcd for TaSi$_3$N$_5$SF$_3$O$_3$C$_{27}$H$_{63}$: C, 37.70; H, 7.38; N, 8.14. Found: C, 38.02; H, 7.44; N, 8.16. IR (nujol, background subtracted): 1276 cm^{-1} (ν OTf).

Kinetics of decomposition of [N$_3$N*]Ta(η^2-C$_2$H$_4$) (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$_3$N*]Ta(η^2-C$_2$H$_4$) (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 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.

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CHAPTER 3

Synthesis of Trimethylsilyl-Substituted Triamidoamine Complexes of Niobium

Introduction

Chapters 1 and 2 described the use of tren-based triamidoamine ligand systems to prepare complexes containing Ta=E multiple bonds where E = C, N, P, As, and O. The syntheses of these species are in part successful due to the presence of three metal-based orbitals (1σ and 2π) that can form a tantalum-ligand multiple bond in an apical coordination site sterically-protected by three encircling trialkylsilyl groups. Tren-based triamidoamine complexes of vanadium have also been prepared that exhibit a propensity for forming vanadium-ligand multiple bonds.[1] A logical extension of these studies of vanadium and tantalum is the synthesis of analogous triamidoamine complexes of niobium. In the literature, the number of niobium amides pales in comparison to the multitude of niobium complexes featuring one or more cyclopentadienyl ligands.[2,3] The relatively few reports of niobium amide complexes feature NR_2^- ligands where R is an alkyl,[4-6] aryl,[7] or silyl[7,8] group. Gambarotta and co-workers have examined the reactivity of complexes with the $Nb[NCy_2]_x$ (x = 2 or 3) core and have found a transient tris(amido) species binds dinitrogen in end-on fashion.[4] It is anticipated that these species and other low-valent niobium amides may have the potential for performing interesting and useful organic transformations such as the coupling of imines with aldehydes and ketones as has been demonstrated with $NbCl_3$(dme).[9,10] Thus, we have decided to pursue the synthesis of $[N_3N]$Nb-based complexes ($[N_3N]^{3-}$ = $(Me_3SiNCH_2CH_2)_3N]^{3-}$) with the goals of preparing a trigonal monopyramidal niobium(III) species and molecules featuring niobium-ligand multiple bonds.

Results

Synthesis of Niobium Oxo and Imido Complexes.

Given the successful use of $TaCl_5$ as a precursor to $[N_3N]TaCl_2$ and $[N_3N^*]TaCl_2$, our initial efforts to prepare tren-based complexes of niobium involved niobium halide starting materials. $NbCl_5$ reacts with $Li_3[N_3N]$ in a variety of solvents including pentane, diethyl ether, and toluene at -78 °C to afford intractable brown solids. ^1H NMR spectra of the product mixtures fail to demonstrate the presence of the triamidoamine ligand, most likely signifying the formation of reduced niobium species. In the hope that a stable dialkyl or alkylidene complex could be prepared by analogy with the tantalum chemistry, we mixed NbR_2Cl_3 (R = Me,[11] CH_2CMe_3[12]) with $Li_3[N_3N]$ in pentane or diethyl ether at -35 °C. The products were characterized by numerous resonances in the ligand regions of the ^1H NMR spectra. While apparently obviating the problem of reduction of the d^0 metal center, the introduction of niobium alkyl groups does not result in the formation of identifiable $[N_3N]Nb$-based species. Mixing $NbCl_4(THF)_2$ with $Li_3[N_3N]$ in tetrahydrofuran at -35 °C affords a brown-purple solid upon standard work-up. ^1H NMR demonstrates this solid to be a mixture of $[N_3N]Nb{=}O$ (*vide infra*) and an unknown species identified by broad resonances at ca. 3.3, 0.0, and -6.0 ppm. While this unknown has a ^1H NMR spectrum similar to that for complexes of the type $[N_3N]NbOR$ (*vide infra*), its isolation and complete characterization are hampered by its extreme solubility in common organic solvents. Tetrahydrofuran solvent appears to be the source of the oxo functionality in $[N_3N]Nb{=}O$ as the reaction of $NbCl_4(THF)_2$ with $Li_3[N_3N]$ in diethyl ether at -35 °C affords only the unidentifiable paramagnetic species. The niobium oxo complex may be formed via ring opening of tetrahydrofuran by a low valent niobium intermediate as has been purported to occur in the syntheses of $NbO[N(SiMe_3)_2]_3$[8] and $WOCl_3(THF)_2$[13] from their respective metal halide starting materials. We will later in this section present a logical and high-yielding synthetic route to prepare $[N_3N]Nb{=}O$. The final attempt to mix a niobium perhalide with $Li_3[N_3N]$ also failed, since $NbCl_3(dme)$[10] reacts with $Li_3[N_3N]$ in tetrahydrofuran or toluene at -35 °C to afford intractable products.

Successful placement of the triamidoamine ligand on niobium is achieved via mixing $NbOCl_3(THF)_2$[14] with $Li_3[N_3N]{\bullet}THF_2$[15] in diethyl ether at -35 °C to afford **1** as a white crystalline solid in 81% yield (eq 1). $NbOCl_3(CH_3CN)_2$[14] reacts with $Li_3[N_3N]{\bullet}THF_2$ in diethyl ether at -35 °C to afford **1** contaminated by $H_3[N_3N]$ which is formed most likely via deprotonation of three molecules of CH_3CN by the trilithium salt of the ligand. ^1H and ^{13}C NMR spectra demonstrate the presence of the tren framework bound to niobium and show that the complex has C_3 symmetry on the NMR timescale at room temperature. Unfortunately, the Nb-O stretch could not be located in the IR spectrum of **1** as it is most likely obscured by N-Si absorptions in the 800 - 1000 cm^{-1} region (cf. $NbOCl_3(THF)_2$ ν Nb-O = 960 cm^{-1} [14]).

$$\mathrm{NbOCl_3(THF)_2} \xrightarrow[\mathrm{Et_2O,\ -35\ ^\circ C}]{\mathrm{Li_3[N_3N]{\bullet}THF_2}} \underset{\mathbf{1}}{\mathrm{[N_3N]Nb{=}O}} \tag{1}$$

$Nb(NSiMe_3)Cl_3(py)_2$[16] reacts with $Li_3[N_3N]{\bullet}THF_2$ in diethyl ether at -35 °C to afford white crystalline **2** in 53% yield (eq 2). ^1H and ^{13}C NMR spectra verify the presence of the ligand bound to niobium in a complex with apparent C_3 symmetry on the NMR timescale at room temperature. The trimethylsilyl imide is found as a singlet at 0.52 ppm in the ^1H NMR spectrum.

$$\mathrm{Nb(NSiMe_3)Cl_3(py)_2} \xrightarrow[\mathrm{Et_2O,\ -35\ ^\circ C}]{\mathrm{Li_3[N_3N]{\bullet}THF_2}} \underset{\mathbf{2}}{\mathrm{[N_3N]Nb{=}NSiMe_3}} \tag{2}$$

Reactivity of Niobium Complexes Containing Imido, Oxo, Alkoxide, and Siloxide Donors.

Imide **2** exhibits a lack of reactivity similar to the tantalum imides described in Chapter 1. $[N_3N]Nb{=}NSiMe_3$ (0.01 M in diethyl ether) does not react with one equivalent of methyl triflate, aniline, or pivaldehyde over a period of days. Cleavage of the imide nitrogen-silicon bond is not realized upon mixing a 0.02 M solution of **2** in tetrahydrofuran with cesium fluoride for 6 hours at room temperature. Addition of iodomethane to the reaction mixture only affords $[N_3N]Nb{=}NSiMe_3$ upon standard work-up. Mixing a 0.02 M solution of **2** in dichloromethane with three equivalents of 2,6-lutidinium triflate for one day at room temperature does produce a reaction. However, the ^1H NMR spectrum of the product mixture does not contain any resonances attributable to ligand-containing species. Similar results are observed upon stirring one equivalent of pyridinium triflate with a 0.02 M solution of oxo **1** in dichloromethane for one day at room temperature. Curiously, **1** (0.02 M in diethyl ether) does not react with one equivalent of ethereal hydrogen chloride under similar conditions. $[N_3N]Nb{=}O$ reacts with excess triethylaluminum in pentane at -35 °C to afford $[N_3N]Nb{=}O{\bullet}AlEt_3$ (**3**) in 84% yield as white crystals (eq 3). The three equivalent ethyl groups on Al are characterized by triplet and quartet resonances at 1.67 and 0.44 ppm, respectively, in the ^1H NMR spectrum, and quartet ($^1J_{CH}$ = 123 Hz) and triplet ($^1J_{CH}$ = 108 Hz) resonances at 12.1 and 5.1 ppm, respectively, in the ^{13}C NMR spectrum. An ^{27}Al NMR spectrum of **3** shows a broad singlet at 180 ppm which should be compared to a resonance at 154 ppm for $AlEt_3$.

$$\underset{\mathbf{1}}{[N_3N]Nb{=}O} \xrightarrow[C_5,\ -35\ ^\circ C]{AlEt_3} \underset{\mathbf{3}}{[N_3N]Nb{=}O{\bullet}AlEt_3} \qquad (3)$$

Niobium siloxide complexes are prepared via reaction of **1** with Me_3SiX (X = OTf, I) in dichloromethane to afford **4a** and **4b** quantitatively (eq 4). Both siloxides are proposed to be salts, with non-coordinated triflates, on the basis of their insolubility in diethyl ether and solubility in tetrahydrofuran and dichloromethane. $[N_3N]Ta(Me)OTf$, a complex which has been demonstrated to contain a bound triflate ligand via an X-ray study, is soluble in diethyl ether.[17] The presence of the triflate ligand in **4a** is confirmed by a singlet resonance in the ^{19}F NMR spectrum at -78.9 ppm and a stretch at 1276 cm^{-1} in the IR spectrum. A 0.01 M solution of **1** in diethyl ether does not react with five equivalents of chlorotrimethylsilane after stirring the mixture for one day at room temperature. $[N_3N]Nb{=}O$ reacts with methyl triflate to afford $[N_3N]NbOMe^+OTf^-$ (**5**) in quantitative yield (eq 5). However, a 0.03 M solution of **1** in dichloromethane fails to react with one equivalent of iodomethane after one day at room temperature. Methoxide **5** exhibits similar NMR and IR spectra to **4a**. In the reactions described in eqs 5 and 6, it is interesting to note that Nb-O singly-bonded complexes are formed even in the presence of excess silylating or methylating reagent.

$$\underset{\mathbf{1}}{[N_3N]Nb{=}O} \xrightarrow[CH_2Cl_2,\ -35\ ^\circ C]{Me_3SiX} \underset{X = OTf\ (\mathbf{4a}),\ I\ (\mathbf{4b})}{[N_3N]NbOSiMe_3{}^+\,X^-} \tag{4}$$

$$\underset{\mathbf{1}}{[N_3N]Nb{=}O} \xrightarrow[CH_2Cl_2,\ -35\ ^\circ C]{MeOTf} \underset{\mathbf{5}}{[N_3N]NbOMe^+\,OTf^-} \tag{5}$$

Limited success has been realized while exploring the reactivity of these niobium alkoxide and siloxide complexes. Reactions of **4a**, **4b**, and **5** with methyl or ethyl Grignard reagents in tetrahydrofuran for one day afford intractable product mixtures. The salts (~0.02 M in dichloromethane) do not react with proton sources such as pyridinium triflate and ethereal hydrogen chloride over the period of one day at room temperature. Attempts to replace the iodide or triflate counterions in these species via reaction with one or more equivalents of $[Et_4N]Cl$ or $[Ph_4As]Cl$ in dichloromethane provide oxo **1**. These transformations most likely occur via attack of chloride ion on silicon to produce chlorotrimethylsilane and **1**. Reductions of **4a**, **4b**, and **5** with sodium amalgam in tetrahydrofuran are readily achieved to provide blue-purple $[N_3N]NbOSiMe_3$ (**6a**) and blue $[N_3N]NbOMe$ (**6b**) in 82 - 91% yields (eq 6). The ^1H NMR spectra of these highly-colored species feature broad singlets in the +3 to -3 ppm window for hydrogens associated with the amide trimethylsilyl groups, the trimethylsiloxide or methoxide moieties, and one of the two types of ligand methylene units. The resonance for the second set of ligand methylene hydrogens is most likely too broad to be observed due to paramagnetic line broadening associated with the d^1 niobium center. In comparison, the ^1H NMR spectrum of $[N_3N]V$-Cl does locate both ligand methylene resonances, but one of them is an extremely broad singlet ($\Delta\nu_{1/2}$ = 310 Hz) at -46.13 ppm.[18] Elemental analyses of **6a** and **6b** are consistent with their formulations.

$$[\mathrm{N_3N}]\mathrm{NbOR^+\,X^-} \xrightarrow[\text{THF, -35 °C}]{\text{Na/Hg}} [\mathrm{N_3N}]\mathrm{NbOR}$$

4a R = $SiMe_3$, X = OTf
4b R = $SiMe_3$, X = I
5 R= Me, X = OTf

R = $SiMe_3$ (**6a**), Me (**6b**)

(6)

As with the related d^0 siloxide and alkoxide complexes, **6a** and **6b** contain rather unreactive Nb-O bonds. These niobium(IV) species are not reduced by excess sodium amalgam in pentane at room temperature over a period of days and they do not react with one equivalent of methylmagnesium chloride under similar conditions. Subjection of solid **6a** or **6b** to dichloromethane affords oxo **1**, most likely via chloride abstraction followed by loss of chlorotrimethylsilane. **6a** reacts with one equivalent of $SiCl_4$ to provide $[N_3N]NbOSiCl_3$ (**7**) (eq 7). Siloxide **7**, isolated as a purple solid in 46% yield, exhibits a ^1H NMR spectrum similar to **6a** and **6b** and also has been characterized by elemental analysis. It is interesting to note that all of the other species containing a niobium-oxygen bond (**1**, **4a**, **4b**, **5**, and **6b**) do not react with $SiCl_4$, a reagent that has been demonstrated to cleave Ta(μ-O) bonds,[19] to afford tractable ligand-containing products.

$$\underset{\mathbf{6a}}{[\mathrm{N_3N}]\mathrm{NbOSiMe_3}} \xrightarrow[\mathrm{C_5},\ \text{-35 °C}]{\mathrm{SiCl_4}} \underset{\mathbf{7}}{[\mathrm{N_3N}]\mathrm{NbOSiCl_3}}$$

(7)

Discussion

One of the major goals of this work has been the preparation of triamidoamine species containing a niobium-ligand multiple bond. Our inability to make $[N_3N]NbCl_2$ necessitated the implementation of routes different from those used to prepare related tantalum complexes described in Chapters 1 and 2. The syntheses of **1** and **2** rely upon the use of oxo and imido functionalities to protect the niobium(V) center from reduction by the trilithium salt of the ligand. Imido groups, in particular, have been utilized to stabilize high oxidation state transition metal alkylidene complexes of molybdenum[20] and tungsten.[21,22] The inaccessibility of a dichloride species also prevents the exploration of routes to niobium alkylidene, phosphinidene, imide, and alkyne complexes that would be analogous to those described in the preceding chapters for tantalum. Such species should be stable with regard to decomposition pathways given the orbital arrangement and steric environment in the apical coordination site of the metal center that lends homage to the Nb=E (E = O, $NSiMe_3$) linkages in **1** and **2**.

$[N_3N]Nb{=}NSiMe_3$, similar to the tantalum imides described in Chapter 1, is observed to be relatively inert under the employed reaction conditions. The oxo complex is more reactive by virtue of the additional lone pair on oxygen. It is interesting to note that reaction of **1** with $AlEt_3$ produces a base adduct of the oxo moiety rather than $[N_3N]NbEt_2$ which should be unstable to β-H abstraction. An example of trialkylaluminum-facilitated metal-oxo bond cleavage is the reaction of $OsO(NAr)(CH_2CMe_3)_2$ with trimethylaluminum to afford $Os(NAr)Me_2(CH_2CMe_3)_2$ where Ar = 2,6-i-Pr_2-C_6H_3.[23] Reduction of the formal niobium-oxygen bond order may be achieved by mixing **1** with strongly electrophilic silylating or alkylating agents to form d^n (n = 0, 1) siloxides or alkoxides. However, complete removal of oxygen from the early transition metal's coordination sphere has not been realized. The metal-oxo bond may be cleaved by a silylating agent in cases where the metal is less oxophilic, e.g. $OsO(NAr)(CH_2CMe_3)_2$ reacts with two equivalents of Me_3SiI to afford $Os(NAr)(CH_2CMe_3)_2I_2$ where Ar = 2,6-i-Pr_2-C_6H_3.[23] All of these observations demonstrate the $[N_3N]Nb$ core to be well-suited to form robust covalent bonds to nitrogen and oxygen.

The successful synthesis of these $[N_3N]Nb$-based complexes contrasts with our inability to prepare a hypothetical niobium(III) trigonal monopyramidal species. The preference for forming a niobium-heteroatom covalent bond in the apical coordination site is demonstrated by the failure to completely remove the nitrogen or oxygen ligand from the niobium center in **1** and **2**. The reactions of niobium perhalides of various oxidation states with $Li_3[N_3N]$ also do not afford the trigonal monopyramidal complex. The reduction of $NbCl_5$ by lithium amides is well-known,[5] but we have been unable to harness this reduction chemistry to provide an identifiable ligand-containing complex. Equally fruitless are the reactions of $NbCl_4(THF)_2$ and $NbCl_3(dme)$ with $Li_3[N_3N]$. Although no reports exist in the literature to our knowledge concerning the reaction of $NbCl_3(dme)$ with lithium amides, the reaction of $NbCl_4(THF)_2$ with lithium amides is well known to form niobium(IV) amido species.[7,24] We are, thus, unable to prepare $[N_3N]Nb$ and observe its stability with regard to the ligand decomposition pathways documented for some tantalum triamidoamine complexes in Chapters 1 and 2. The successful preparation of a triamidoamine complex of niobium(III) may rest on the development of more robust ligands than $[N_3N]^{3-}$ and new methods for placing these ligands on niobium(V) while avoiding unproductive reduction of the metal.

Conclusions

The synthesis of $[N_3N]Nb$-based complexes has been explored in order to compare and contrast the chemistry to that with the related tantalum core. In contrast to the rather large number of tantalum complexes described in Chapter 1, only a few such niobium species have been prepared. $[N_3N]Nb$-based chemistry remains at this time limited by the dearth of methods for placing the tren-based ligand on the niobium center while tantalum chemistry is greatly aided by the facile, albeit low-yielding synthesis of $[N_3N]TaCl_2$. Similar to their tantalum analogs, the prepared niobium complexes take advantage of the presence of the proper frontier orbitals and steric environment in the apical coordination site to form metal-ligand multiple bonds. Robust niobium-oxygen covalent bonds are formed which unfortunately contribute to our inability to prepare the hypothetical $[N_3N]Nb$. Future work should allow us to harness the strengths of tren-based ligands to further explore the organometallic chemistry of niobium with a major goal remaining to be the preparation of a trigonal monopyramidal complex of niobium(III).

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. $NbOCl_3(THF)_2$,[14] $Nb(NSiMe_3)Cl_3(py)_2$,[16] and $Li_3[N_3N]\bullet THF_2$[15] were prepared according to literature 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) and ^{27}Al NMR data is listed in parts per million downfield from hexaaquoaluminum(III) (δ 0.00). Routine coupling constants are usually not reported; those listed are in units of Hz. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer. Elemental analyses (C, H, N) were performed by Oneida Research Services, Whitesboro, New York or on-site using a Perkin-Elmer 2400 CHN analyzer. NMR tube reactions were carried out in a Wilmad 512-7" or 512-9" 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.

$[N_3N]Nb{=}O$ (1). A -35 °C mixture of $NbOCl_3(THF)_2$ (2.341 g, 6.51 mmol) and $Li_3[N_3N]\bullet THF_2$ (3.417 g, 6.51 mmol) was subjected to addition of 100 mL diethyl ether at -35 °C. After stirring for 23 h at room temperature, the brown reaction mixture was filtered through Celite to yield a brown filtrate. The filtrate was concentrated in vacuo to afford solid that was recrystallized from pentane at -35 °C. White crystals were collected to provide 2.467 g (5.26 mmol, 81%) of product: ^1H NMR (C_6D_6) δ 3.20 (t, 6, CH_2), 2.23 (t, 6, CH_2), 0.45 (s, 27, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 54.2 (t, $^1J_{CH}$ = 136, CH_2), 49.4 (t, $^1J_{CH}$ = 134, CH_2), 2.1 (q, $^1J_{CH}$ = 118, $SiMe_3$). Anal. Calcd for $NbSi_3N_4C_{15}H_{39}O$: C, 38.44; H, 8.39; N, 11.95. Found C, 38.26; H, 8.32; N, 11.98.

$[N_3N]Nb{=}NSiMe_3$ (2). A -35 °C solution of $Nb(NSiMe_3)Cl_3(py)_2$ (366 mg, 0.823 mmol) in 20 mL diethyl ether was subjected to addition of $Li_3[N_3N]\bullet THF_2$ (432 mg, 0.823 mmol). The brown reaction mixture was stirred for 13 h and was then filtered through Celite. The brown filtrate was concentrated in vacuo to provide solid that was recrystallized from pentane at -35 °C. White crystals were collected to afford 555 mg (1.03 mmol, 53%) of product: ^1H NMR

(C_6D_6) δ 3.16 (t, 6, CH_2), 2.19 (t, 6, CH_2), 0.52 (s, 9, $SiMe_3$), 0.36 (s, 27, $SiMe_3$); ^{13}C NMR (C_6D_6) δ 58.7 (t, $^1J_{CH}$ = 139, CH_2), 49.3 (t, $^1J_{CH}$ = 136, CH_2), 4.7 (q, $^1J_{CH}$ = 118, $SiMe_3$), 2.7 (q, $^1J_{CH}$ = 120, $SiMe_3$). Anal. Calcd for $NbSi_4N_5C_{18}H_{48}$: C, 40.05; H, 8.96; N, 12.97. Found: C, 40.10; H, 8.83; N, 12.81.

[N_3N]Nb=O•$AlEt_3$ (3). A -35 °C solution of [N_3N]Nb=O (337 mg, 0.719 mmol) in 15 mL pentane was subjected to addition of triethylaluminum (197 μL, 1.44 mmol). A white precipitate formed immediately and the solution was stirred for 28 h. The cloudy white solution was concentrated in vacuo, extracted with 50 mL diethyl ether, and filtered through Celite. The off-white filtrate was concentrated in vacuo to afford an off-white solid that was recrystallized from diethyl ether at -35 °C. White crystals were collected to afford 354 mg (0.607mmol, 84 %) of product: ^1H NMR (toluene-d_8) δ 3.05 (t, 6, CH_2), 2.14 (t, 6, CH_2), 1.67 (t, 9, CH_3), 0.44 (q, 6, CH_2), 0.26 (s, 27, $SiMe_3$); ^{13}C NMR (toluene-d_8) δ 60.4 (t, $^1J_{CH}$ = 135, CH_2), 51.3 (t, $^1J_{CH}$ = 137, CH_2), 12.1 (q, $^1J_{CH}$ = 123, $CH_2\mathit{CH_3}$), 5.1 (t, $^1J_{CH}$ = 108, $\mathit{CH_2}CH_3$), 1.6 (q, $^1J_{CH}$ = 119, $SiMe_3$); ^{27}Al {^1H} NMR (C_6D_6) δ 180. Anal. Calcd for $NbSi_3N_4OAlC_{21}H_{54}$: C, 43.28; H, 9.34; N, 9.61. Found: C,. 42.80; H, 9.28; N, 9.76.

[N_3N]$NbOSiMe_3{}^+OTf^-$ (4a). A -35 °C solution of [N_3N]Nb=O (1.00 g, 2.13 mmol) in 40 mL dichloromethane was subjected to addition of -35 °C trimethylsilyltriflate (413 μL, 2.13 mmol). The colorless solution turned yellow and was stirred for 24 h. The yellow solution was concentrated in vacuo to provide a yellow solid that was washed with 10 mL of -35 °C diethyl ether and then dried in vacuo. Light yellow crystals were collected to afford 1.42 g (2.06 mmol, 97%) of product: ^1H NMR (CD_2Cl_2) δ 3.82 (t, 6, CH_2), 3.13 (t, 6, CH_2), 0.43 (s, 9, $OSiMe_3$), 0.30 (s, 27, $NSiMe_3$); ^{13}C NMR (CD_2Cl_2) δ 62.7 (t, $^1J_{CH}$ = 138, CH_2), 54.5 (t, $^1J_{CH}$ = 139, CH_2), 3.6 (q, $^1J_{CH}$ = 118, $OSiMe_3$), 1.2 (q, $^1J_{CH}$ = 120, $NSiMe_3$); ^{19}F {^1H} NMR (CD_2Cl_2) δ -78.9. Anal. Calcd for $NbSi_4N_4O_4F_3SC_{19}H_{48}$: C, 33.03 H, 7.00; N, 8.11. Found: C, 33.34; H, 7.30; N, 8.36. IR (nujol, background subtracted): 1276 cm^{-1} (s, ν OTf).

[N_3N]$NbOSiMe_3{}^+I^-$ (4b). A -35 °C solution of [N_3N]Nb=O (700 mg, 1.49 mmol) in 30 mL dichloromethane was subjected to addition of trimethylsilyliodide (425 μL, 2.99 mmol) via syringe. The color of the reaction mixture changed from colorless to orange-red immediately and was stirred for 24 h. The solution was concentrated in vacuo to yield solid that was recrystallized from pentane/dichloromethane (10:1) at -35 °C. Light-yellow crystals were collected to provide 957 mg (1.43 mmol, 96%) of product: ^{1}H NMR (CD_2Cl_2) δ 3.84 (t, 6, CH_2), 3.23 (t, 6, CH_2), 0.42 (s, 9, $OSiMe_3$), 0.30 (s, 27, $NSiMe_3$); ^{13}C NMR (CD_2Cl_2) δ 62.9 (t, $^1J_{CH}$ = 141, CH_2), 54.6 (t, $^1J_{CH}$ = 139, CH_2), 3.6 (q, $^1J_{CH}$ = 120, $OSiMe_3$), 1.3 (q, $^1J_{CH}$ = 120, $NSiMe_3$). Anal. Calcd for $NbSi_4N_4OC_{18}H_{48}I$: C, 32.33; H, 7.23; N, 8.38. Found: C, 32.52; H, 7.58; N, 8.22.

$[N_3N]NbOMe^+OTf^-$ (5). A -35 °C solution of $[N_3N]Nb{=}O$ (500 mg, 1.07 mmol) in 20 mL dichloromethane was subjected to addition of -35 °C methyl triflate (241 μL, 2.13 mmol). The colorless solution turned yellow and was stirred for 24 h. The yellow solution was then concentrated in vacuo to afford a yellow solid that was recrystallized from pentane/dichloromethane (10:1) at -35 °C. Lemon yellow crystals were collected to provide 651 mg (1.03 mmol, 96%) of product: ^{1}H NMR ($CDCl_3$) δ 4.43 (s, 3, OMe), 3.79 (t, 6, CH_2), 3.20 (t, 6, CH_2), 0.16 (s, 27, $SiMe_3$); ^{13}C {^{1}H} NMR ($CDCl_3$) δ 65.9 (OMe), 59.4 (CH_2), 53.4 (CH_2), 1.0 ($SiMe_3$); ^{19}F {^{1}H} NMR (CD_2Cl_2) δ -78.9. Anal. Calcd for $NbSi_3N_4O_4F_3SC_{17}H_{42}$: C, 32.27; H, 6.69; N, 8.85. Found: C, 31.97; H, 6.84; N, 8.58.. IR (nujol, background subtracted): 1276 cm^{-1} (s, ν OTf).

$[N_3N]NbOSiMe_3$ (6a). (a) From $[N_3N]NbOSiMe_3^+OTf^-$. A -35 °C solution of $[N_3N]NbOSiMe_3^+OTf^-$ (800 mg, 1.16 mmol) in 40 mL tetrahydrofuran was subjected to addition of freshly-prepared sodium amalgam (0.5 wt% Na, 2.32 mmol). The yellow-orange solution turned purple after approximately 2 minutes. After 6 h, the purple solution was decanted from remaining amalgam and was concentrated in vacuo. The purple solid was extracted with 25 mL pentane and was filtered through Celite. The blue-purple filtrate was concentrated in vacuo to provide solid that was recrystallized from pentane at -35 °C. Blue-purple crystals were collected to afford 571 mg (1.05 mmol, 91%) of product: ^{1}H NMR (C_6D_6) δ 3.23 (br s, 27, $NSiMe_3$), 1.28 (br s, 9, $OSiMe_3$), -3.23 (br s, 6, CH_2). Anal. Calcd for $NbSi_4N_4OC_{18}H_{48}$: C, 39.90; H, 8.93; N, 10.34. Found: C, 40.17; H, 9.22; N, 10.35.

(b) From $[N_3N]NbOSiMe_3^+I^-$. A -35 °C solution of $[N_3N]NbOSiMe_3^+I^-$ (590 mg, 0.882 mmol) in 20 mL tetrahydrofuran was subjected to addition of freshly-prepared sodium amalgam (0.5 wt% Na, 1.76 mmol). The yellow-orange solution turned purple after approximately 2 minutes. After 11 h, the purple solution was decanted from remaining amalgam and was concentrated in vacuo. The purple solid was extracted with 25 mL pentane and was filtered through Celite. The blue-purple filtrate was concentrated in vacuo to afford solid that was recrystallized from pentane at -35 °C. Blue-purple crystals were collected to provide 391 mg (0.726 mmol, 82%) of product.

[N$_3$N]NbOMe (6b). A -35 °C solution of [N$_3$N]NbOMe$^+$OTf$^-$ (394 mg, 0.623 mmol) in 20 mL tetrahydrofuran was subjected to addition of freshly-prepared sodium amalgam (0.5 wt% Na, 1.25 mmol). The yellow solution turned blue after 2 minutes and was then stirred for 8 h. The blue solution was decanted from remaining amalgam and was concentrated in vacuo. The resulting oily solid was extracted with 30 mL pentane and was filtered through Celite. The filtrate was concentrated in vacuo to 268 mg (0.554 mmol, 89%) of product as an oily blue solid. The complex may be isolated as blue crystals by recrystallization from pentane at -35 °C. ^{1}H NMR (C_6D_6) δ 3.37 (br s, 27, NSiMe$_3$), 1.25 (br s, 3, OMe), -0.43 (br s, 6, CH$_2$). Anal. Calcd for $NbSi_3N_4OC_{16}H_{42}$: C, 39.73; H, 8.75; N, 11.58. Found: C, 39.66; H, 8.37; N, 12.01.

[N$_3$N]NbOSiCl$_3$ (7). A -35 °C solution of [N$_3$N]NbOSiMe$_3$ (1.57 g, 2.90 mmol) in 18 mL pentane was subjected to addition of silicon tetrachloride (366 μL, 3.20 mmol). The blue-purple solution slowly turned purple over a period of hours and after 24 h, the reaction mixture was filtered through Celite. The purple filtrate was concentrated in vacuo to yield purple solid that was recrystallized from pentane at -35 °C. Purple crystals were collected to afford 802 mg (1.33 mmol, 46%) of product: ^{1}H NMR (C_6D_6) δ 3.30 (br s, 27, NSiMe$_3$), -6.04 (br s, 6, CH$_2$). Anal. Calcd for $NbSi_4N_4Cl_3OC_{15}H_{39}$: C, 29.87; H, 6.52; N, 9.28. Found: C, 30.27; H, 6.25; N, 9.10.

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APPENDIX A

Synthesis of Trimethylsilyl-Substituted Triamidoamine Complexes of Tungsten

Introduction

The three chapters of this thesis have described the successful use of tren-based triamidoamine moieties as ligands for tantalum and niobium. Previous efforts in these laboratories have also outlined the chemistry of triamidoamine complexes of vanadium.[1,2] These group 5 complexes all demonstrate a propensity for forming metal-ligand multiple bonds in a sterically-protected apical coordination site containing three metal-based orbitals (1σ and 2π). A logical extension of these studies is the examination of group 6 triamidoamine complexes where one would also anticipate the formation of metal-ligand multiple bonds. Initial studies began with the synthesis of $[N_3N']Cr$ where $[N_3N']^{3-} = [(t\text{-}BuMe_2SiNCH_2CH_2)_3N]^{3-}$.[3] The focus of research then turned toward molybdenum and tungsten given their involvement in systems participating in olefin[4-6] and acetylene[5-7] metathesis in addition to dinitrogen fixation.[8-10] The implementation of the $[(F_5C_6NCH_2CH_2)_3N]^{3-}$ ligand allowed the preparation of molybdenum and tungsten d^2 monochloride complexes.[11] A related $[(F_5C_6NCH_2CH_2)_3N]MoOTf$ species may be reduced to afford what is proposed to be the sodium salt of a molybdenum(II) complex of dinitrogen. The use of silylated tren-based ligands also met with some success in the early stages of this project as $[N_3N]MoCl$ could be prepared, albeit in low yield, where $[N_3N]^{3-} = [(Me_3SiNCH_2CH_2)_3N]^{3-}$.[12] Interesting reactions of these molybdenum triamidoamine species include dinitrogen fixation and acetylide coupling to form $\{[N_3N']Mo\}_2(\mu\text{-}N_2)$ and $\{[N_3N]Mo{\equiv}CCH\}_2$, respectively. Thus, the early success in preparing species with molybdenum-ligand multiple bonds to nitrogen and carbon encouraged efforts in the direction of synthesizing analogous tungsten complexes.

Results

Synthesis of a Tungsten Neopentylidyne Complex.

Initial efforts to react $Li_3[N_3N]$ with tungsten perhalides of various oxidation states were unsuccessful, affording unidentifiable product mixtures.[13] These results mirrored those in niobium chemistry and, thus, the idea arose of using a tungsten-ligand multiple bond to protect the tungsten starting material from reduction by $Li_3[N_3N]$. The ready availability of complexes of the general type $Me_3CC{\equiv}WCl_3L_x$[14] suggested that an alkylidyne moiety might be a useful protecting group for the d^0 metal center. $W(CCMe_3)Cl_3(dme)$[14] reacts with $Li_3[N_3N]$ in diethyl ether at -78 °C to afford yellow crystalline **1** in 54% isolated yield (eq 1). The ^1H NMR spectrum of **1** locates the characteristic tren-based ligand resonances in addition to a singlet at 1.63 ppm for the *t*-butyl hydrogens. Most prominent in the ^{13}C NMR spectrum of **1** is the alkylidyne carbon singlet at 295.2 ppm which may be compared to the analogous resonance for $W(CCMe_3)Cl_3(dme)$ at 335.1 ppm. Unfortunately, we were unable to observe satellites about this singlet due to coupling to ^{183}W ($S = 1/2$, 14% natural abundance); $^1J_{CW}$ is expected to be in the range of 200 - 300 Hz.[15]

$$W(CCMe_3)Cl_3(dme) \xrightarrow[Et_2O,\ -78\ ^\circ C]{Li_3[N_3N]} \underset{\mathbf{1}}{[N_3N]W{\equiv}CCMe_3} \qquad (1)$$

Reactivity of a Tungsten Neopentylidyne Complex with Terminal Acetylenes.

Given the well-documented ability of tungsten alkylidynes to engage in acetylene metathesis reactions,[15] we were interested in exploring the reactions of alkylidyne **1** with acetylenes in an effort to prepare other tungsten-carbon triply-bonded species. A 0.02 M solution of **1** in diethyl ether does not react with two equivalents of 2-butyne over the period of one day at room temperature. A 0.04 M solution of **1** in diethyl ether, however, does react with five equivalents of phenylacetylene in one day to afford benzylidyne **2** as orange needles in 60% yield (eq 2). Most prominent in the ^{13}C NMR spectrum of **2** is a singlet at 277.2 ppm for the alkylidyne carbon. As with the ^{13}C NMR spectrum of **1**, we were unable to observe satellites attributable to one-bond tungsten-carbon coupling. A red-orange solid by-product is formed that is insoluble in diethyl ether but is soluble in dichloromethane. This species is characterized by a ^1H NMR spectrum showing only resonances in the aromatic region. The olefinic region of the spectrum is absent of resonances, ruling out the formation of poly(phenylacetylene), while the lack of resonances associated with the tren-based ligand argues against a $[N_3N]W$-containing product.

$$\underset{\mathbf{1}}{[N_3N]W{\equiv}CCMe_3} \xrightarrow[Et_2O]{5\ PhC{\equiv}CH} \underset{\mathbf{2}}{[N_3N]W{\equiv}CPh} \tag{2}$$

$[N_3N]W{\equiv}CCMe_3$ (0.04 M in diethyl ether) reacts with five equivalents of trimethylsilylacetylene in one day at room temperature to afford a 2:1 mixture of **1** and $[N_3N]W{\equiv}CSiMe_3$ (**3**) along with a yellow insoluble material (eq 3). This insoluble product is proposedly formed via a similar reaction pathway that yields the red-orange by-product in the formation of **2** from **1**. Although the mixture of alkylidynes **1** and **3** could not be separated by fractional recrystallization, the ^1H NMR resonances atttributable to **3** are identical to those observed for a pure sample of $[N_3N]W{\equiv}CSiMe_3$ prepared via an independent route.[16,17] These referenced publications by co-workers contain a complete description of the characterization of **3** via NMR and elemental analysis.

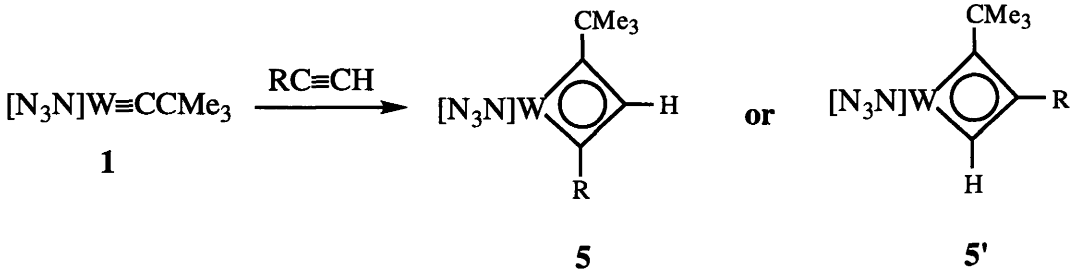
$$\underset{\mathbf{1}}{[N_3N]W{\equiv}CCMe_3} \xrightarrow[Et_2O]{5\ Me_3SiC{\equiv}CH} \underset{\mathbf{3}}{[N_3N]W{\equiv}CSiMe_3} \tag{3}$$

Mixing a 0.01 M solution of neopentylidyne **1** in diethyl ether with five equivalents of acetylene for three days produces an insoluble black-purple solid, presumed to be poly(acetylene), and methylidyne **4** in 48% isolated yield (eq 4). Most notably, the ^1H NMR spectrum of **4** shows the methylidyne hydrogen as a singlet at 7.08 ppm ($^2J_{HW}$ = 81 Hz). A more complete description of the characterization of **4** via ^1H and ^{13}C NMR and elemental analysis is published elsewhere via co-workers who prepared the methylidyne complex by a more direct route.[16,17]

$$\underset{\mathbf{1}}{[N_3N]W{\equiv}CCMe_3} \xrightarrow[Et_2O]{5\ HC{\equiv}CH} \underset{\mathbf{4}}{[N_3N]W{\equiv}CH} \qquad (4)$$

Discussion

The neopentylidyne moiety functions as a protecting group to allow placement of the triamidoamine ligand on the d^0 tungsten center. The resulting alkylidyne $[N_3N]W{\equiv}CCMe_3$ does not react with internal acetylenes such as 2-butyne, most likely for steric reasons due to the amide trimethylsilyl groups that encircle the tungsten-carbon triple bond. We, thus, chose to explore the reactivity of **1** with terminal acetylenes. Neopentylidyne **1** reacts with excess $RC{\equiv}CH$ (R = Ph, $SiMe_3$) to afford new alkylidynes **2** and **3**. Methylidyne **4** is not isolated as a product, although it may be prepared via mixing **1** with acetylene. These reactions of **1** all presumably proceed through the intermediacy of a metallacyclobutadiene[7] and, when considering the reaction of **1** with $RC{\equiv}CH$, two such metallacyclobutadienes are viable intermediates (eq 5). It is possible that the formation of the α,α'-disubstituted metallacyclobutadiene (**5**) is preferred over formation of the α,β-disubstituted metallacyclobutadiene (**5'**). Steric interactions between the α-*t*-butyl group and R may render the formation of **5'** thermodynamically unfavorable. It is interesting to note that the reaction of $W(CPh)(OCMe_3)_3$ with phenylacetylene in the presence of pyridine is proposed to involve an intermediate α,α'-disubstituted metallacycle.[18] However, the isolated product in this reaction is not an alkylidyne but rather a deprotonated metallacyclobutadiene $W(OCMe_3)_2(C_3Ph_2)(py)_2$. In some related tungsten systems, careful tuning of the size of the alkoxide ligand and the reaction conditions facilitates the isolation of small amounts of alkylidyne product.[19] Alterations in the nature of the alkoxide ligands in $Mo(CCMe_3)(OR)_3$ also effect a preference for deprotiometallacyclobutadiene vs. alkylidyne formation.[19] These examples from the literature all describe reactions that invoke the preferential formation of α,α'-disubstituted metallacyclobutadienes and, thus, lend credence to our proposal that the reaction of **1** with a terminal acetylene may occur via the intermediacy of **5** which then decomposes to afford the new alkylidyne product. However, further efforts in these laboratories are necessary to test this proposed mechanism and attain a better understanding of the reactivity of $[N_3N]W{\equiv}CR$ with terminal acetylenes.



(5)

Conclusions

The synthesis of tren-based triamidoamine complexes of tungsten containing a metal-carbon triple bond has been achieved. The triple bond is favorable due to the presence of three tungsten-centered orbitals (1σ and 2π) to form the multiple bond that is sterically protected by the three encircling trimethylsilyl groups of the ligand framework. The neopentylidyne complex is reactive with terminal acetylenes to produce benzylidyne, trimethylsilylmethylidyne, and methylidyne complexes. The successful preparation of these species with the $[N_3N]W$ core has spurred efforts in these laboratories to further explore group 6 triamidoamine chemistry. $[N_3N]WCl$ may be synthesized in moderate yield and its reactions with alkyllithium reagents afford transient tungsten(IV) alkyls that undergo α,α-dehydrogenation to provide alkylidynes,[16,17] some of which were first prepared as described herein. Other work has studied competitive α- and β-H elimination processes in these molybdenum and tungsten systems[20] and the synthesis of metal-ligand multiple bonds to phosphorus[21] and arsenic.[22] Future efforts should continue to uncover new and interesting chemistry of these group 6 tren-based triamidoamine complexes.

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. W(CCMe$_3$)Cl$_3$(dme) was prepared according to a published procedure.[14] ^{1}H and ^{13}C NMR data are listed in parts per million downfield from TMS. Routine coupling constants are usually not reported; those listed are in units of Hz.

[N$_3$N]W≡CCMe$_3$ (1). A -78 °C mixture of W(CCMe$_3$)Cl$_3$(dme) (310 mg, 0.690 mmol) and Li$_3$[N$_3$N] (263 mg, 0.690 mmol) was subjected to addition of 30 mL diethyl ether at -78 °C via cannula. After 19 h, the green-brown mixture was filtered through Celite to provide a brown-red filtrate. The filtrate was concentrated in vacuo to yield a brown-red solid that was recrystallized from pentane at -35 °C. Yellow crystals were collected to provide 228 mg (0.372 mmol, 54%) of product: ^{1}H NMR (C$_6$D$_6$) δ 3.35 (t, 6, CH$_2$), 2.06 (t, 6, CH$_2$), 1.63 (s, 9, CMe$_3$), 0.46 (s, 27, SiMe$_3$); ^{13}C NMR (C$_6$D$_6$) δ 295.2 (s, *C*CMe$_3$), 55.9 (t, CH$_2$), 51.5 (s, C*C*Me$_3$), 50.8 (t, CH$_2$), 35.5 (q, CC*Me$_3$*), 4.6 (q, SiMe$_3$). Elemental analysis results may be found elsewhere.[17]

[N$_3$N]W≡CPh (2). Phenylacetylene (94 μL, 0.816 mmol) was added via syringe to a room temperature solution of [N$_3$N]W≡CCMe$_3$ (100 mg, 0.163 mmol) in 4 mL diethyl ether. After 24 h, the red mixture was filtered through Celite to remove an insoluble red-orange solid. The resulting filtrate was concentrated in vacuo to afford a red-orange solid that was recrystallized from pentane at -35 °C. Orange needles were collected to provide 62 mg (0.0980 mmol, 60%) of product: ^{1}H NMR (CD$_2$Cl$_2$) δ 7.25 (m, 4, Ph), 6.89 (m, 1, Ph), 3.88 (t, 6, CH$_2$), 2.81 (t, 6, CH$_2$), 0.25 (s, 27, SiMe$_3$); ^{13}C NMR (CD$_2$Cl$_2$) δ 277.2 (s, *C*Ph), 152.0 (s, Ph), 134.5 (m, Ph), 126.8 (m, Ph), 125.1 (m, Ph), 52.6 (t, CH$_2$), 52.4 (t, CH$_2$), 5.1 (q, SiMe$_3$). Elemental analysis results may be found elsewhere.[17]

[N$_3$N]W≡CSiMe$_3$ (3). Trimethylsilylacetylene (81 μL, 0.571 mmol) was added via syringe to a room temperature solution of [N$_3$N]W≡CCMe$_3$ (70 mg, 0.114 mmol) in 3 mL diethyl ether. After 22 h, the yellow mixture was concentrated in vacuo and the resulting yellow solid was extracted with 20 mL diethyl ether. The extract was filtered through Celite to remove an insoluble yellow solid and the filtrate was concentrated in vacuo to afford 62 mg of yellow solid. A benzene-d_6 solution of the solid was demonstrated via ^{1}H NMR to contain a 2:1 mixture of neopentylidyne **1** and trimethylsilylmethylidyne **3**. $[N_3N]W{\equiv}CSiMe_3$: ^{1}H NMR (C_6D_6) δ 3.47 (t, 6, CH_2), 1.98 (t, 6, CH_2), 0.52 (s, 27, $NSiMe_3$), 0.51 (s, 9, $CSiMe_3$). ^{13}C NMR and elemental analysis data may be found elsewhere.[17]

$[N_3N]W{\equiv}CH$ (4). Acetylene (0.334 mmol) was condensed into a -196 °C glass bomb containing $[N_3N]W{\equiv}CCMe_3$ (41 mg, 0.0669 mmol) in 10 mL diethyl ether. Upon warming to room temperature, the reaction mixture changed in color from yellow to black-purple. After stirring at room temperature for 3 d, the reaction mixture was filtered through Celite to remove poly(acetylene). The removal of volatiles from the filtrate produced 18 mg (0.0323 mmol, 48%) of product as a yellow solid: ^{1}H NMR (C_6D_6) δ 7.08 (s, $^2J_{HW}$ = 81, WCH), 3.46 (t, 6, CH_2), 2.06 (t, 6, CH_2), 0.50 (s, 27, $NSiMe_3$). ^{13}C NMR and elemental analysis data may be found elsewhere.[17]

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