Organometallic Complexes of Tantalum That Contain the Triamidoamine Ligand, $[(\mathrm{Me_3SiNCH_2CH_2})_3\mathrm{N}]^{3-}$, Including an Ethylidene Complex Formed via a Phosphine-Catalyzed Rearrangement of an Ethylene Complex

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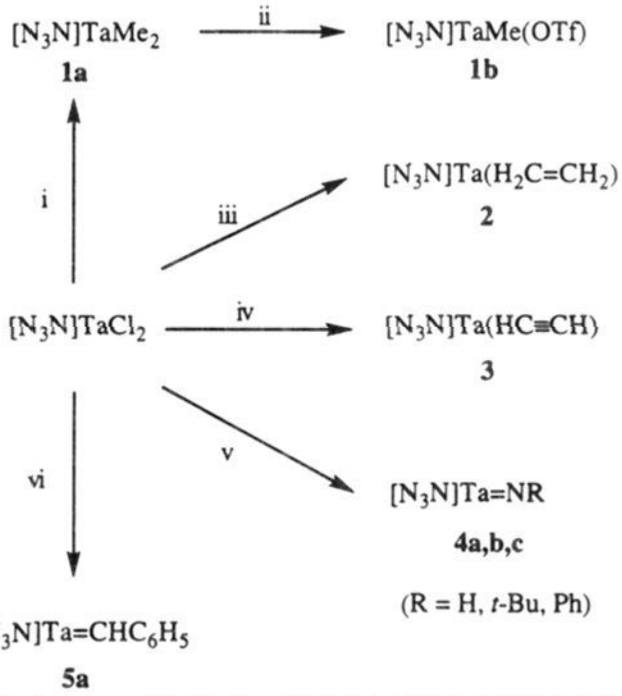
Examples of complexes that contain tetradentate triamidoamine ligands of the type $[(\mathrm{RNCH_2CH_2})_3\mathrm{N}]^{3-}$ are now known for metals Ti through Fe, Ta, and Mo.[1-10] When R is a sterically bulky group such as trimethylsilyl or *tert*-butyldimethylsilyl, rarely observed types of complexes can be prepared, e.g., a tantalum phosphinidene,[6] a titanium(IV) hydride,[3] a V=NH complex,[9] Ta=Se and Ta=Te complexes,[7] an Fe(IV) cyanide complex,[8] and trigonal monopyramidal first row metal (Ti through Fe) complexes that have no ligand in the apical site trans to the amine donor.[2] In view of the presence of two π-orbitals and one σ-type orbital within the "pocket" formed by the three trimethylsilyl groups, we were interested in exploring what types of organometallic Ta complexes could be prepared that contain σ- or π-bonded ligands in that position. We report here the synthesis of several such complexes.

A convenient starting material for Ta chemistry is $[\mathrm{N_3N}]\mathrm{TaCl_2}$ ($[\mathrm{N_3N}]^{3-} = [(\mathrm{Me_3SiNCH_2CH_2})_3\mathrm{N}]^{3-}$);[6,7] its structure is not known. As shown in Scheme 1, it reacts smoothly with methyllithium to give **1a** quantitatively. Oxidative cleavage[11-14] of a methyl group with ferrocenium triflate provides **1b** in 75% yield. **1a** and **1b** are trigonally symmetric on the NMR time scale at room temperature. Preliminary variable temperature ^{1}H NMR studies suggest that the methyl groups in **1a** remain equivalent on the NMR time scale at –80 °C, although there appears to be a slowing down of a conformational change in the ethylene bridge protons. An X-ray study of **1b** shows it to be a "weakly-capped" trigonal bipyramidal species having two equatorial amido nitrogens and an equatorial methyl group (Figure 1).[15] Apparently two ligands *can* be accommodated in the "pocket" when the triamidoamine complex adopts a structure in which the amine nitrogen is weakly bound. The amine N—Ta distance of 2.536 Å in **1b** is significantly longer than the corresponding bond length of 2.376 Å in $[\mathrm{N_3N}]$Ta=PCy,[6] 2.487 Å in $[\mathrm{N_3N}]$Ta=Te,[7] 2.349 Å in $[\mathrm{N_3N}]$Ta=Se,[7] and 2.29 Å in $[\mathrm{N_3N}]$Ta(HC≡CH) (see below). We expect that the ligand's somewhat "flexible" coordination ability may play a significant role in reactions of such species, perhaps as significant as its role in sterically protecting the apical position in pseudo-five-coordinate 3-fold-symmetric complexes. It should be noted that the element–N(amine) distance in trianionic tren derivatives of main group elements varies widely.[16]

Scheme 1. Reactions of $[\mathrm{N_3N}]\mathrm{TaCl_2}^a$



^{a} (i) 2LiMe in ether; (ii) $[\mathrm{FeCp_2}]^+\mathrm{OTf}^-$ in THF: (iii) $2\mathrm{C_2H_5MgCl}$ in ether; (iv) $2\mathrm{H_2C{=}CHMgBr}$ in ether; (v) $2\mathrm{LiNH_2}$ or $2\mathrm{NaNH_2}$ in THF or 2LiNHR in ether; (vi) $2\mathrm{C_6H_5CH_2MgCl}$ in ether.

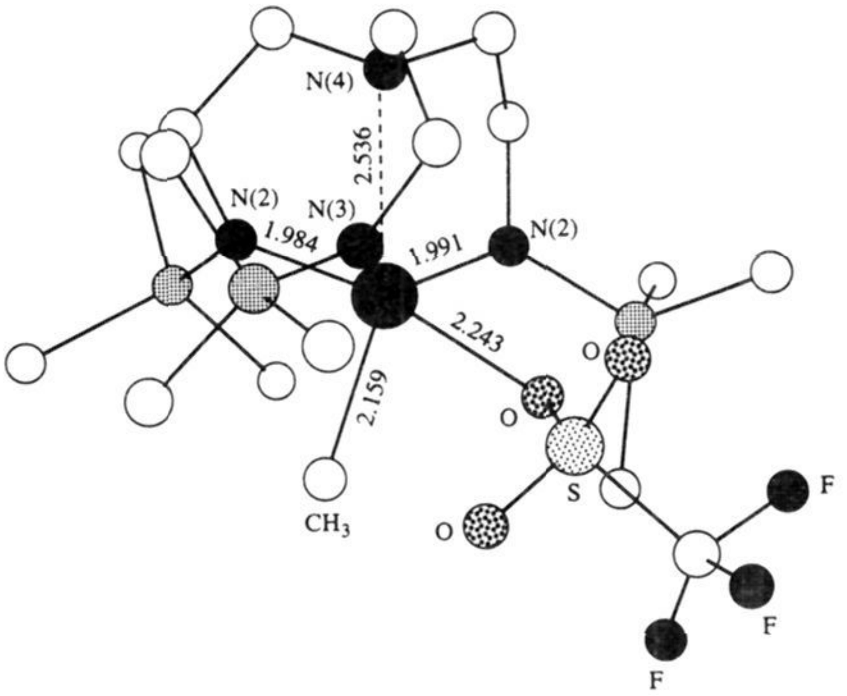


Figure 1. X-ray structure of $[\mathrm{N_3N}]$TaMe(OTf): O–Ta–N(2) = 167.3°; C–Ta–N(4) = 170.9°; N(2)–Ta–N(1) = 99.8°; N(2)–Ta–N(3) = 104.6°; N(2)–Ta–C = 89.3°; N(1)–Ta–N(3) = 129.4°.

Reactions between $[\mathrm{N_3N}]\mathrm{TaCl_2}$ and ethyl or vinyl Grignard reagents provide **2** and **3** in 96% and 80% yields, respectively. Formation of a parent acetylene complex via a hydrogen abstraction reaction is rare, although a Ta benzyne complex, $\mathrm{TaCp^*Me_2(C_6H_4)}$, was prepared via loss of methane from $\mathrm{TaCp^*Me_3(C_6H_5)}$,[17] and internal acetylene complexes of Zr are commonly prepared in a similar manner.[18,19] We have also found

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[11] Oxidative cleavage of alkyl groups has found much application in group 4 metal chemistry[12,13] although there is a relatively old example of what may be an analogous oxidative cleavage reaction between $\mathrm{TaCp_2Me_3}$ and $[\mathrm{CPh_3}]^+$ to give $[\mathrm{TaCp_2Me_2}]^+$.[14]

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[15] $a = 14.628(2)$ Å, $b = 9.874(1)$ Å, $c = 20.227(2)$ Å, $\beta = 92.91(2)°$, space group $P2_1/c$, $V = 2918(1)$ Å^3, $Z = 4$, $D_{\mathrm{calc}} = 1.604$ g/cm^3. Details can be found in the supplementary material.

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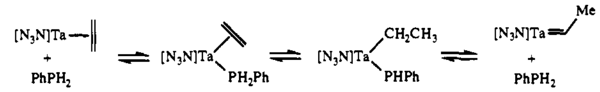
that **1b** reacts with EtMgCl and $CH_2{=}CHMgBr$ in ether at −35 °C to give **2** and **3**, respectively. An X-ray study of **3**[20] showed the structure to be unexceptional and, in particular, the amine nitrogen to be bound (Ta–N = 2.29 Å). Preliminary variable temperature ^1H NMR experiments for **2** and **3** (25 to −85 °C) show that the ethylene and acetylene singlet resonances do not broaden significantly. Evidently facile "rotation" of the π bound ligand gives such species apparent 3-fold symmetry, although we cannot exclude partial dissociation of the nitrogen donor in the N_3N ligand at some point as part of that fluxional process.

Reactions that give **4a–c** in 69%, 73%, and 95% yields, respectively, are analogous to those between $[N_3N]TaCl_2$ and 2 equiv of LiPHR (R = cyclohexyl, *tert*-butyl, phenyl) to give $[N_3N]Ta{=}PR$.[6] The synthesis of **4a** is noteworthy, as parent transition metal imido (M=NH) complexes are relatively rare.[21] NMR and IR spectra[22] of **4a** are similar to those of the analogous vanadium species, which has been structurally characterized.[9] The stability of **4a** is another example of what we believe to be steric protection against bimolecular reactions in this class of triamidoamine complexes when relatively small and/or especially reactive ligands are present in the "pocket".

Given the propensity for Ta neopentyl, (trimethylsilyl)methyl, and benzyl complexes to undergo α-hydrogen abstraction reactions,[23,24] it is not surprising that **5a** is formed in 91% yield upon adding benzylmagnesium chloride to $[N_3N]TaCl_2$. Addition of $Li_3[N_3N]$ to $Ta(CH_2C_6H_5)_2Cl_3$[25] also provides **5a** in 86% yield, while addition of $Li_3[N_3N]$ to $Ta(CH_2CMe_3)_2Cl_3$[26] affords $[N_3N]Ta(CHCMe_3)$ (**5b**) in 56% yield. Both **5a** and **5b** are trigonally symmetric molecules on the NMR time scale at room temperature. $^1J_{CH_\alpha}$ in the alkylidene ligands is unusually low (~70 Hz), a characteristic of "distorted alkylidene" ligands[23,27] in which there is an "α agostic" interaction of the CH_α bond with the metal.[28] Both **5a** and **5b** react readily with benzaldehyde in a Wittig-like manner to give a mixture of *cis* and *trans* isomers of the expected olefin.[29]

Complex **2** is proving to be a useful source of "$[N_3N]Ta^{2+}$". For example, **2** reacts readily with ammonia to give **4a** in 78% yield by ^1H NMR. However, an attempt to prepare $[N_3N]Ta{=}PPh$[6] by treating **2** in diethyl ether with phenylphosphine was unsuccessful. The product was shown to be the ethylidene complex, $[N_3N]Ta{=}CHCH_3$ (**5c**) (88% isolated yield; $^1J_{CH_\alpha} = 69$ Hz). Preliminary deuterium labeling and kinetic studies are consistent with the phosphine-catalyzed mechanism shown in eq 1. Alkylidene complexes of Ta(V) that contain alkylidene β protons are extremely rare;[23] they usually rearrange to the olefin readily. However, there is some evidence that tantalum alkylidenes can form from alkyls that contain β protons.[30,31] If the structure of the $[N_3N]Ta$ core is the same in **2** and **5c**, then **5c** must be favored primarily because of the α agostic interaction and other accompanying changes in the Ta=C bond. This would be the first example of rearrangement of an ethylene complex to give a *lower energy* ethylidene complex. The only other example of a reaction in which an ethylene ligand rearranges to an ethylidene ligand appears to be that between $[WCp_2(C_2H_4)H]^+$ and I_2 to give $[WCp_2(CHCH_3)I]^+$, which Cooper proposed involves formation of intermediate (higher energy) $[WCp_2(CHCH_3)H]^+$.[32] It is interesting to note that the reaction of $[N_3N]TaCl_2$ with ethyl Grignard gives **2**, not **5c**.



(1)

We conclude that the organometallic chemistry of $[(Me_3SiNCH_2CH_2)_3N]Ta$ complexes reported here is successful in part because of the steric protection provided by the three $SiMe_3$ groups, because the $[(Me_3SiNCH_2CH_2)_3N]^{3-}$ ligand is somewhat "flexible" in terms of the coordination geometries it can adopt in reaction intermediates or transition states, and because the metal appears to be more electrophilic than one might have predicted for a compound that contains four Ta–N bonds. With regard to the last point it should be noted that reactions typical of "electrophilic" metals (e.g., CH activation) are now known for not only silylamido or siloxide complexes of zirconium[33] and titanium[34] but also tantalum[35] and vanadium.[36]

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Supplementary Material Available: Experimental details, final positional parameters, and final thermal parameters for **1b** (12 pages); final observed and calculated structure factors for **1b** (47 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(20) Full details will be presented elsewhere in due course.

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(22) ^1H NMR (C_6D_6): δ 5.59 (br 1:1:1 t, $^1J_{^{14}NH} = 50$ Hz, 1, 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 (ether, KBr cells): 3436 cm^{-1} (NH).

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