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# Alkyl and Alkylidene Tantalum−Lithium Complexes Supported by an Anionic Triazacyclononane Ligand

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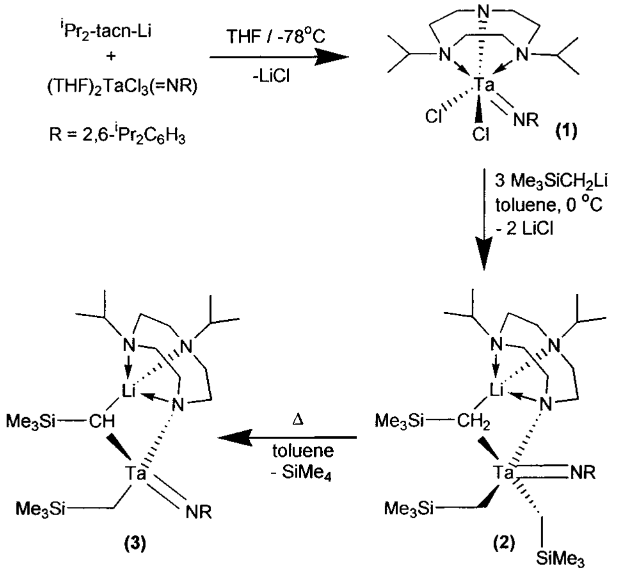
*Summary: A new* $^{i}Pr_2$*-tacn*$^{-}$*-supported alkyl tantalum species,* $(Me_3SiCH_2)_2(RN{=})Ta(\mu\text{-}CH_2SiMe_3)(\mu\text{-}\eta^1{:}\eta^3\text{-}^{i}Pr_2\text{-}tacn)Li$ *(R = 2,6-*$^{i}Pr_2C_6H_3$*;* ***2****), was synthesized and found to undergo α-H abstraction under gentle heating to form the alkylidene* $(Me_3SiCH_2)(RN{=})Ta(\mu\text{-}CHSiMe_3)(\mu\text{-}\eta^1{:}\eta^3\text{-}^{i}Pr_2\text{-}tacn)Li$ *(****3****). The syntheses and crystal structures of* ***2*** *and* ***3*** *and their precursor ((*$^{i}Pr_2$*-tacn)*$TaCl_2(=NR)$ *(****1****)) are described, as well as kinetic data for the first-order thermolysis reaction producing* ***3****.*

As part of a program aimed at developing new ancillary ligands to support reactive metal centers, we recently described the first examples of transition-metal complexes employing an anionic triazacyclononane ($^{i}Pr_2$-tacn$^{-}$) ligand.[1,2] Ligands of this general type are of interest to us due to their formal relationship to the ubiquitous Cp moiety; i.e., $R_2$tacn$^{-}$ ligands may function as tridentate, six-electron $\sigma$-donors.[3] We envisioned the prospects for steric and electronic control using these ligands via two main pathways: first, a variety of substituents can easily be introduced at the amino nitrogens, and second, the potential for partial ligand dissociation of the amino nitrogens would open up coordination sites for further reactivity. For our initial studies, we chose to investigate early transition metals and recently described some zirconium complexes with the $^{i}Pr_2$-tacn$^{-}$ ligand, showing that this bulky ligand forms stable monomeric ($^{i}Pr_2$-tacn)$ZrX_3$ species (X = Cl, $CH_2SiMe_3$).[2]

Drawing on the isolobal analogy between imido ligands and $Cp^{-}$ (i.e., both are $1\sigma$, $2\pi$ donors), we chose to examine the combination of $^{i}Pr_2$-tacn$^{-}$ and imido ligands on tantalum to provide a system for study, yielding compounds electronically similar to the metallocene dichloride species of group 4.[4] We found no previous reports of tantalum species containing either the neutral tacn or the recently described $R_2$-tacn$^{-}$ ligands.[5]

**Scheme 1**



Li−($^{i}Pr_2$-tacn) reacted with 1 equiv of $(THF)_2TaCl_3(=NR)$ (R = 2,6-$^{i}Pr_2C_6H_3$)[6] (Scheme 1) to provide the desired ($^{i}Pr_2$-tacn)$TaCl_2(=NR)$ (**1**). After removal of the liberated LiCl, the product was isolated as yellow crystals in moderate yield. The $^{1}H$ NMR spectrum indicates a highly asymmetric compound, with 6 sets of isopropyl doublets with relative integrations of 2:2:1:1:1:1. Additionally, there are 12 inequivalent $CH_2$ resonances due to the 3 ethylene bridges of the $^{i}Pr_2$-tacn backbone. On the basis of these data, the compound was assigned a pseudooctahedral coordination sphere with the tridentate $^{i}Pr_2$-tacn ligand coordinated facially and the imido ligand oriented trans to an amino donor from the $^{i}Pr_2$-tacn. This geometry agrees with that predicted by electronic considerations (i.e., due to the trans effect of the $\pi$-donor imido ligand, one would expect the relatively weakly $\sigma$-donor amino ligand to be oriented trans to the imido moiety).[7] On the basis of the integration of the isopropyl peaks, one can assign a static coordination geometry at the metal, with rapid rotation about the N−R bond to equilibrate the two sides of the aryl group. The $^{13}C$ NMR spectrum shows only 16 of the 19 expected carbon resonances, whereas a $^{13}C$-DEPT experiment divided the 16 observed signals into 2 quaternary, 4 methine, 6 methylene, and 4 methyl carbons, indicating a lack of 1 methine and 2 methyl carbons, likely an isopropyl group. A $^{13}C-^{1}H$ HMQC spectrum showed that cross-peak resonances for one $^{i}Pr$

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(1) Giesbrecht, G. R.; Gebauer, A.; Shafir, A.; Arnold, J. *J. Chem. Soc., Dalton Trans.* **2000**, 4018.

(2) Giesbrecht, G. R.; Shafir, A.; Arnold, J. *Chem. Commun.* **2000**, 2135.

(3) Qian, B.; Henling, L. M.; Peters, J. C. *Organometallics* **2000**, *19*, 2805.

(4) Gibson, V. C.; Poole, A. D.; Siemeling, U.; Williams, D. N.; Clegg, W.; Hockless, D. C. R. *J. Organomet. Chem.* **1993**, *462*, C12.

(5) While this paper was in preparation, the synthesis of a related alkylimido species was reported: Fletcher, J. S.; Male, N. A. H.; Wilson, P. J.; Rees, L. H.; Mountford, P.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **2000**, 4130.

(6) Chao, Y.-W.; Wexler, P. A.; Wigley, D. E. *Inorg. Chem.* **1989**, *28*, 3860.

(7) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988.

10.1021/om0010621 CCC: $20.00 © 2001 American Chemical Society
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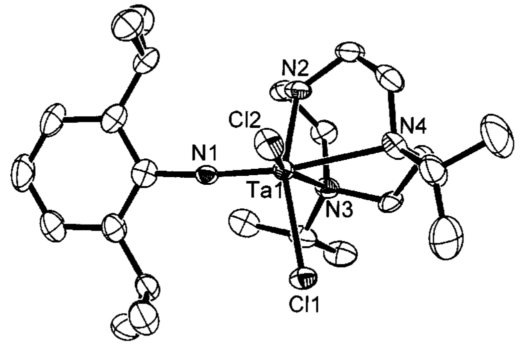

**Figure 1.** ORTEP diagram (50% probability) of ($^{i}$Pr$_2$-tacn)-TaCl$_2$═NR (**1**). Selected bond lengths (in Å): Ta1−N1 = 1.783(3), Tal−N2 = 2.006(4), Ta1−N3 = 2.403(3), Ta1−N4 = 2.512(4), Ta1−Cl1 = 2.441(1), Ta1−Cl2 = 2.373(1). Crystal data: $C_{24}H_{43}N_4TaCl_2$, orthorthombic, *Pna*2$_1$, *a* = 18.5236(3) Å, *b* = 11.1383(2) Å, *c* = 13.2433(1) Å, *T* = −113 °C, R1 = 0.016, wR2 = 0.022 (all data).

in the $^1$H spectrum have no corresponding peaks in the $^{13}$C NMR spectrum. On the basis of these data, we attribute the latter resonances to the isopropyls bound to the imido phenyl unit.

X-ray-quality crystals of **1** were obtained from a saturated diethyl ether solution, and the solid-state structure determined (Figure 1) confirms the coordination geometry deduced from spectroscopic data. At 1.78 Å, the Ta−N(imido) bond length falls well within the range observed previously for terminal Ar−N═Ta species (1.765−1.833 Å).[6,8−14] Notably, the Ta−N(amino) bond trans to the imido group (2.51 Å) is elongated in comparison to the cis amino bond (2.40 Å). The Ta−Cl bonds (2.37 and 2.44 Å) and the Ta−N(amido) bond (2.01 Å) are similar to the metrical parameters seen in related species.[6,9−16]

Alkylation of **1** with 3 equiv of Me$_3$SiCH$_2$Li leads to the replacement of both chlorides with alkyl groups. Unlike the simple alkylation observed with cyclopentadienyl ligands,[9] in our system a third equivalent of Me$_3$SiCH$_2$Li is consumed, forming (Me$_3$SiCH$_2$)$_2$(RN═)-Ta($\mu$-CH$_2$SiMe$_3$)($\mu$-$\eta^1$:$\eta^3$-$^{i}$Pr$_2$-tacn)Li (**2**). Interestingly, **2** is formed regardless of the stoichiometric ratios employed; i.e., reaction of **1** with only 2 equiv of Me$_3$SiCH$_2$-Li leads to a mixture of **2** and unreacted **1** (2:1 ratio).[17] Analytically pure samples of **2** were isolated as small yellow crystals from diethyl ether in good yields. The compound is fluxional in solution at room temperature, giving a $^1$H NMR spectrum consistent with a time-averaged mirror plane in the $^{i}$Pr$_2$-tacn ligand. This is indicated by the presence of only one CH, six CH$_2$, and two CH$_3$ resonances arising from the $^{i}$Pr$_2$-tacn ligand. Additionally, the three different SiMe$_3$ units are chemically equivalent, suggesting a rapid interconversion of these groups in solution.[18] The signals for the methylene groups bound to tantalum were not observed at room temperature, presumably due to broadening by both the fluxionality and their close proximity to the quadrupolar tantalum. Cooling to as low as −84 °C led only to broad peaks for the methyl groups, rather than resolution of the chemically inequivalent protons.

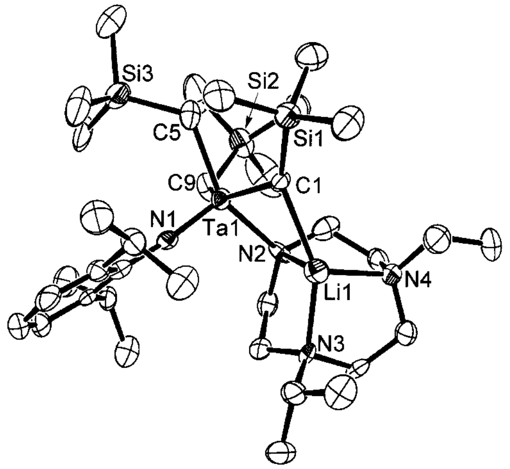

**Figure 2.** ORTEP diagram (50% probability) of (Me$_3$-SiCH$_2$)$_2$(RN═)Ta($\mu$-CH$_2$SiMe$_3$)($\mu$-$\eta^1$:$\eta^3$-$^{i}$Pr$_2$-tacn)Li (**2**). Bond lengths (in Å): Ta1−N1 = 1.723(7), Tal−N2 = 1.956(7), Ta1−C1 = 2.320(7), Ta1−C5 = 2.15(1), Ta1−C9 = 2.237(9), Li1−N2 = 2.04(2), Li1−C1 = 2.29(2). Crystal data: $C_{36}H_{76}N_4Si_3TaLi$, monoclinic, *P*2$_1$/*c*, *a* = 17.476(3) Å, *b* = 11.198(2) Å, *c* = 21.840(4) Å, $\beta$ = 99.506(4)°, *T* = −119 °C, R1 = 0.033, wR2 = 0.099 (all data).

Compound **2** crystallized from concentrated diethyl ether as small yellow plates. An X-ray crystal structure determination elucidated the structure of this compound (Figure 2), showing a $^{i}$Pr$_2$-tacn ligand bound in a monodentate fashion to the tantalum via the anionic nitrogen atom and tridentate to the lithium ion. Additionally, a carbon atom from a Me$_3$SiCH$_2$ anion bridges between the lithium and tantalum ions, a rare bonding mode in tantalum chemistry.[19,20] Finishing out the coordination sphere of the tantalum are two Me$_3$SiCH$_2^-$ ligands and the aryl imido group. The tantalum is in a square-pyramidal environment with the imido group occupying the axial coordination site and the tantalum atom located above the basal square plane (0.6 Å above the mean plane). Compound **2** shows shorter Ta−N(imido) (1.72 Å) and Ta−N(amido) (1.96 Å) bond lengths in comparison to those of **1**, which likely arises from the reduced tantalum coordination number, as well as reduced steric interaction between these ligands. The Ta═NR bond length is the shortest observed crystallographically for a tantalum-bound arylimido ligand, though some alkylimido ligands exhibit even shorter bonds.[15,16] The Ta−C$_{br}$ distance (2.32 Å) is substantially longer than those observed for Me$_3$SiCH$_2^-$

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[8] Royo, P.; Sanchez-Nieves, J.; Pellinghelli, M. A.; Tiripicchio, A. *J. Organomet. Chem.* **1998**, *563*, 15.

[9] Castro, A.; Galakhov, M. V.; Gomez, M.; Gomez-Sal, P.; Martin, A.; Royo, P. *J. Organomet. Chem.* **1998**, *554*, 185.

[10] Chamberlain, L. R.; Steffey, B. D.; Rothwell, I. P.; Huffman, J. C. *Polyhedron* **1989**, *8*, 341.

[11] Boncella, J. M.; Cajigal, M. L.; Gamble, A. S.; Abboud, K. A. *Polyhedron* **1996**, *15*, 2071.

[12] Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1982**, *21*, 223.

[13] Chao, Y.-W.; Wexler, P. A.; Wigley, D. E. *Inorg. Chem.* **1990**, *29*, 4592.

[14] Williams, D. N.; Mitchell, J. P.; Poole, A. D.; Siemeling, U.; Clegg, W.; Hockless, D. C. R.; O'Nei, P. A. *J. Chem. Soc., Dalton Trans.* **1992**, 739.

[15] Bates, P. A.; Nielson, A. J.; Waters, J. M. *Polyhedron* **1985**, *4*, 1391.

[16] Jones, T. C.; Nielson, A. J.; Rickard, C. E. F. *Chem. Commun.* **1984**, 205.

[17] In contrast, attempts to generate the dialkyl species from the corresponding Grignard reagent, Me$_3$SiCH$_2$MgCl, afforded an intractable mixture.

[18] Equivalent resonances have also been observed in a similar compound, [(Me$_3$CCH$_2$)$_3$Ta($\mu$-CCMe$_3$)][Li(dme)].[19]

[19] Gal, A. W.; van der Heijden, H. *Chem. Commun.* **1983**, 420.

[20] Guggenberger, L. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 2935.

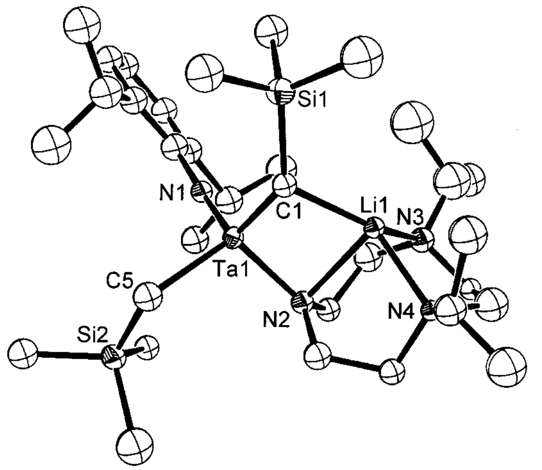

**Figure 3.** ORTEP diagram (50% probability) of (Me$_3$SiCH$_2$)$_2$(RN=)Ta($\mu$-CH$_2$SiMe$_3$)($\mu$-$\eta^1$:$\eta^3$-$^i$Pr$_2$-tacn)Li (**3**). Bond lengths (in Å): Ta1−N1 = 1.73(2), Tal−N2 = 2.05(3), Ta1−C1 = 1.93(3), Ta1−C5 = 2.24(3), Li1−N2 = 2.29(6), Li1−C1 = 2.23(6). Crystal data: C$_{32}$H$_{64}$N$_4$Si$_2$TaLi, monoclinic, $P2_1/c$, $a$ = 10.572(1) Å, $b$ = 18.131(2) Å, $c$ = 20.524(2) Å, $\beta$ = 103.789(2)°, $T$ = −119 °C, R1 = 0.061, wR2 = 0.169 (all data).

groups that bridge two tantalum centers (1.94−2.02 Å)[21,22] but is comparable to a Me$_3$CCH$_2^-$ bridging distance (2.26 Å) observed previously.[20] The Ta−C$_{term}$ bonds (2.15 and 2.24 Å) are well within the usual range of bond lengths (2.03−2.29 Å).[21−24]

The alkyl species **2** was found to undergo α-hydrogen abstraction upon gentle heating (50−100 °C), resulting in the clean formation of the alkylidene **3** with concomitant elimination of 1 equiv of SiMe$_4$ (Scheme 1). The resulting compound was isolated as pale yellow plates from a mixture of pentane and diethyl ether. The $^1$H NMR spectrum showed a slightly broadened signal for the alkylidene CH (4.205 ppm) and a pair of diastereotopic doublets (0.755 and 0.352 ppm) for the alkyl CH$_2$ fragment. The remaining $^1$H and $^{13}$C resonances are typical and indicate an asymmetric compound, with $^i$Pr$_2$-tacn no longer showing the pseudo-mirror plane observed in the fluxional **2**. The $^7$Li NMR spectrum showed only a broad singlet at 2.986 ppm. From these spectroscopic data, we were unable to differentiate between two possible products in this reaction: (Me$_3$SiCH$_2$)(RN=)Ta($\mu$-CHSiMe$_3$)($\mu$-$\eta^1$:$\eta^3$-$^i$Pr$_2$-tacn)Li and (Me$_3$SiCH=)(RN=)Ta($\mu$-CH$_2$SiMe$_3$)($\mu$-$\eta^1$:$\eta^3$-$^i$Pr$_2$-tacn)Li. This reactivity may be contrasted with our earlier finding that alkane elimination via thermolysis of ($^i$Pr$_2$-tacn)Zr(CH$_2$Ph)$_3$ leads not to alkylidene formation but, rather, to tacn ring opening and the generation of [CH$_2$=CHNCH$_2$CH$_2$N($^i$Pr)CH$_2$CH$_2$N$^i$Pr]Zr(CH$_2$Ph)$_2$.[2]

X-ray-quality crystals were obtained from saturated pentane, and the crystal structure was determined (Figure 3). The geometry is very similar to that of **2**, with a pseudotetrahedral tantalum coordinated by the anionic nitrogen from $^i$Pr$_2$-tacn, one imido ligand, one alkyl group, and the carbon from a bridging alkylidene moiety. The Ta−N(imido) and Ta−C$_{term}$ bond lengths are essentially unchanged, whereas the Ta−N(amido) bond (2.05 Å) has lengthened slightly. The Ta−C$_{br}$ bond (1.93 Å) is significantly shorter, in agreement with the stronger bonding expected for an alkylidene compared to an alkyl group. The Li−C$_{br}$ bond (2.23 Å) remains nearly the same in length as observed in **2**, while the Li−N(amido) distance has lengthened slightly (0.2 Å).

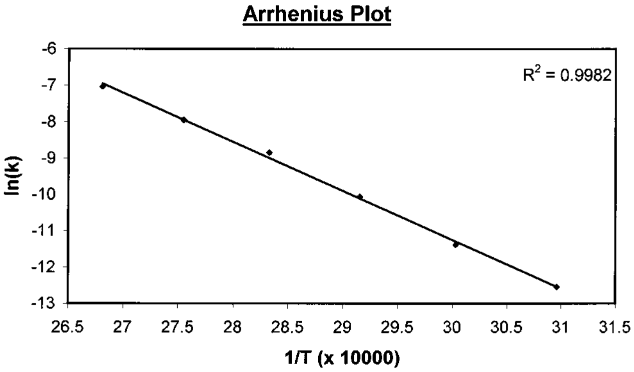

**Figure 4.** Arrhenius plot for thermolysis kinetics.

Using $^1$H NMR spectroscopy, we determined the kinetics of this thermolysis reaction from 50 to 100 °C. The resulting data gave first-order plots with excellent correlation coefficients ($R^2$ > 0.98). An Arrhenius plot (Figure 4) yielded values of $\Delta G^{\ddagger}$ = 113(2) kJ/mol, $\Delta H^{\ddagger}$ = 109(2) kJ/mol, and $\Delta S^{\ddagger}$ = −11.9(1) J/(mol K).[25] The magnitude of the observed transition state entropy is lower than that observed in similar systems.[26] From these data, we conclude that a simple first-order intramolecular decomposition reaction mechanism operates in this system, possibly assisted electronically by the lithium ion. The negative activation entropy, indicative of ordering in the transition state, is consistent with the intramolecular organization necessary to undergo α-hydrogen abstraction.

In summary, we have demonstrated the viability of anionic tacn ligands to support a series of reactive bimetallic tantalum imido alkyl and alkylidene complexes. The role played by intramolecular coordination of the lithium ion is under active scrutiny at present, and this aspect of the chemistry, along with reactivity of these materials toward various organic substrates, will be the subject of further publications.

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**Supporting Information Available:** Text giving experimental procedures and characterization data and tables of atomic coordinates, anisotropic displacement parameters, bond lengths, and bond angles for **1**−**3**, as well as kinetics data for the thermolysis reaction. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) Fanwick, P. E.; Ogilvy, A. E.; Rothwell, I. P. *Organometallics* **1987**, *6*, 73.

(22) Liu, X.; Li, L.; Diminnie, J. B.; Yap, G. P. A.; Rheingold, A. L.; Xue, Z. *Organometallics* **1998**, *17*, 4597.

(23) Diminnie, J. B.; Xue, Z. *J. Am. Chem. Soc.* **1997**, *119*, 12657.

(24) Li, L.; Diminnie, J. B.; Liu, X.; Pollitte, J. L.; Xue, Z. *Organometallics* **1996**, *15*, 3520.

(25) Kinetics experiments were performed over a temperature range from 323 to 373 K, and quoted values are those corresponding to the midpoint of this range, 348 K.

(26) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879 and references therein.