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Metallaaziridine Complexes of Tantalum Derived from 1,8-Bis(isopropylamino)naphthalene via β-H Activation

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Summary: The isolation of the novel metallaaziridine complex $[\eta^3\text{-}(Me_2CN)(Me_2CHN)C_{10}H_6]TaCl_2]_2$ *(**1**) is presented. Complex **1** can be cleaved with 2-methylpyrroline to yield the structurally characterized mononuclear complex* $[\eta^3\text{-}(Me_2CN)({}^iPrN)C_{10}H_6]TaCl_2(NC_5H_9)$*, in which the metallaaziridine remains intact despite the presence of enolizable protons on the pyrroline. Metathesis reactions of **1** with* LiC_5Me_5 *or* $C_6H_5CH_2MgCl$ *provided excellent yields of* $[\eta^3\text{-}(Me_2CN)({}^iPrN)C_{10}H_6]Ta(\eta^5\text{-}C_5Me_5)Cl$ *and* $[\eta^3\text{-}(Me_2CN)({}^iPrN)C_{10}H_6]Ta(CH_2C_6H_5)_2$*, respectively.*

Much of the attention aimed at the preparation and characterization of d^0 transition-metal complexes arises from the implication of these species in a host of small-molecule transformations.[1] While the effects of a particular ligand on the course of these reactions remain somewhat obscure, the influence of the ligand environment on these transformations provides a compelling motivation for the design and exploration of new ligands and novel coordination environments. One of our general interests, the design and implementation of rigid chelating ligands with delocalized π-electrons, led us to investigate the utilization of a new family of diamido ligands, $1,8\text{-}(RN)_2C_{10}H_6$, in transition-metal complexes. We now report the formation of an unusual metallaaziridine complex, $\{[\eta^3\text{-}(Me_2CN)({}^iPrN)C_{10}H_6]TaCl_2\}_2$ (**1**), derived from one such ligand as well as some of the initial reactivity of this complex.

The reaction of an equimolar ratio of $TaMe_3Cl_2$ and $[1,8\text{-}({}^iPrNH)_2C_{10}H_6]$ was carried out with the expectation of preparing $[\eta^2\text{-}C_{10}H_6({}^iPrN)_2]TaMeCl_2$. This reaction proceeded smoothly but produced complex **1** as a red solid in 75% yield (Scheme 1). The identity of compound **1** as a cyclometalated species was first indicated by the NMR spectra obtained for this complex. In particular, the absence of a Ta−Me signal, the appearance of a singlet for the methyl groups of the metallaziridine moiety, and a ^{13}C NMR resonance at δ 65.8 ppm consistent with the tertiary carbon of the metallacycle supported this structure.

Metallaaziridines or η^2-imine complexes have been prepared by similar C−H activation reactions from zirconocene methyl amido complexes,[2] from an *N*-isopropylanilido ligand on a Mo(III) center,[3] from an *N*-methylanilido ligand bonded to Ta(V),[4] and from a Nb(IV) dicyclohexylamido complex.[5] The route to **1** appears to follow a σ-bond metathesis mechanism

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[1] For selected reviews see: (a) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428 and references therein. (b) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154 and references therein. (c) Berresford, D. J.; Bolm, C.; Sharpless, K. B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1059 and references therein. (d) Negishi, E.; Takahashi, T. *Acc. Chem. Res.* **1994**, *27*, 124 and references therein. (e) Tilley, T. D. *Acc. Chem. Res.* **1993**, *26*, 22 and references therein.

[2] (a) Buchwald, S. L.; Watson, B. T.; Wannamaker, M. W.; Dewan, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 4486. (b) Gately, D. A.; Norton, J. R.; Goodson, P. A. *J. Am. Chem. Soc.* **1995**, *117*, 986. (c) Tunge, A.; Gately, D. A.; Norton, J. R. *J. Am. Chem. Soc.* **1999**, *121*, 4520.

[3] Tsai, Y.; Johnson, M. J.; Mindiola, D. J.; Cummins, C. C.; Klooster, W. T.; Koetzle, T. F. *J. Am. Chem. Soc.* **1999**, *121*, 10426.

[4] Boncella, J. M.; Cajigal, M. L.; Abboud, K. A. *Organometallics* **1996**, *15*, 1905.

[5] Berno, P.; Gambarotta, S. *Organometallics* **1995**, *14*, 2159.

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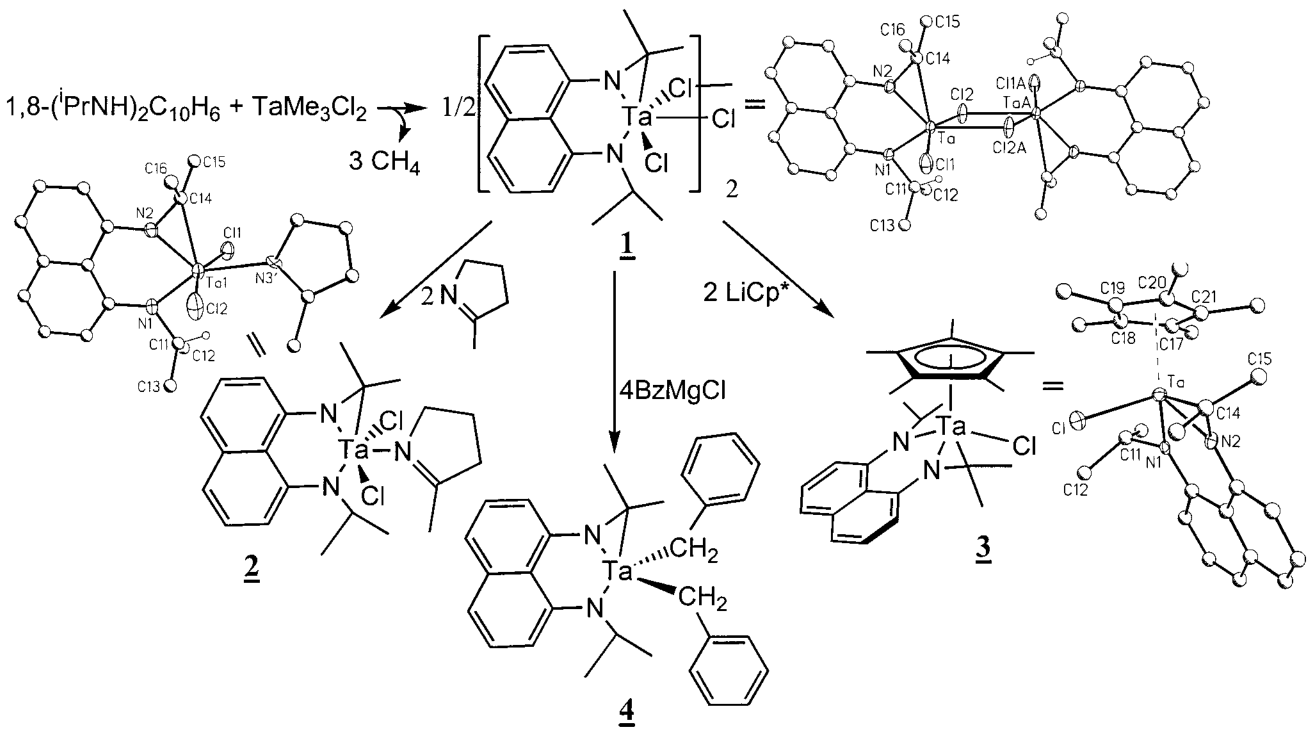
Scheme 1



involving an isopropyl C−H and a Ta−Me group with methane elimination.

Details for the connectivity and level of aggregation for **1** were revealed through X-ray crystallography.[6] The distinguishing features of **1** include the trianionic tridentate ligand [η^3-$C_{10}H_6(Me_2CN)(Me_2CHN)]^{3-}$, derived from the diaminonaphthalene starting material and the dinuclear nature of this species. The trianionic ligand is bonded to Ta to produce a planar bicyclic system. The N(1) and N(2) centers are planar, with their lone pairs of electrons aligned for π overlap with their adjacent atoms. Except for the N(1)−Ta−N(2) angle of 81.6°, the internal angles within the six-membered ring approach the ideal angles of 120°.

The coordination geometry of each Ta(V) center can be described as distorted trigonal bipyramidal by considering the midpoint of the C(14)−N(3) bond as one coordination site. Thus, N(1), N(2), C(14), Ta, and Cl(2A) define the equatorial plane (0.03 Å deviation from the mean plane), while the Cl(1)−Ta−Cl(2) vector (151.9(4)°) defines the axis. Two of these units share an axial/equatorial edge to generate the molecular structure. The Ta−N bond lengths in **1** (average 1.915 Å) and the angles within the three-membered heterocycle compare well with the few related metallaaziridine complexes of Ta(V).[4,7,8] The N(2)−C(14) distance of 1.413(7) Å is consistent with a single-bond azametallacycle formulation.[9]

The related rigid chelating aromatic diamido ligands *N*,*N'*-bis(trialkylsilyl)-*o*-phenylenediamide (pda) have been employed in the preparation of high-valent group 4,[10] Ta,[11,12] Mo,[13] and W[14] species. A common structural feature of all but one of these pda complexes is a distortion of the ligand from planarity. The folding of the ligand about the N−N vector has been attributed to the presence of an additional π-type bonding interaction of an empty metal d orbital with the lone electron pairs of the amido N centers (i.e., a 3c−4e interaction).[13a,14c,15] This should quench the electrophilicity of the metal. These observations contrast with the structural details for the diaminonaphthalene-based system reported here. We attribute this difference to a combination of the geometric constraints of the metallaaziridine moiety and the naphthalene frame of the ligand.

Complex **1** can be cleaved to yield mononuclear species using nitrogen donor ligands. For example, reaction of **1** with 2-methylpyrroline generated compound **2** (Scheme 1). This complex displayed NMR spectroscopic signatures similar to those of complex **1**, with the addition of signals for coordinated pyrroline, thus indicating that the essential bonding framework remained intact after this transformation. Interestingly, even though the pyrroline possesses both enolizable protons and a CN double bond, moieties that could

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[6] Crystal data: empirical formula $C_{44}H_{50}Cl_4N_4Ta_2$, $T = 203(2)$ K, $\lambda = 0.710\,73$ Å, space group $P\bar{1}$, $a = 9.085(1)$ Å, $\alpha = 110.555(2)°$, $b = 9.529(1)$ Å, $\beta = 95.041(2)°$, $c = 13.481(2)$ Å, $\gamma = 95.855(2)°$, $V = 1077.4(2)$ Å^3, $Z = 1$, R indices ($I > 2\sigma(I)$) R1 = 0.0355 and wR2 = 0.0650.

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reasonably be anticipated to react with the metallaaziridine, no further transformation of **2** was observed.

Structural characterization confirmed the geometric features of **2** (Scheme 1).[16] These include the presence of an intact [η^3-$C_{10}H_6(Me_2CN)(Me_2CHN)]^{3-}$ ligand and the coordination of the pyrroline nitrogen. As in **1**, the Ta(V) coordination geometry is distorted trigonal bipyramidal with N(1), N(2), C(14), Ta, and N(3) defining the equatorial plane (0.03 Å deviation from the mean plane) and Cl(1)−Ta−Cl(2) defines the pseudoaxial vector (157.56(9)°). Essentially, N(3) now inhabits the site formerly occupied by the bridging chloro ligand of **1**. The bonding parameters within the [η^3-$C_{10}H_6$(Me_2CN)(^{i}Pr)N)]Ta frame are similar to those observed in **1**.

Metathesis reactions of the Ta−Cl groups of **1** are also possible. Pentamethylcyclopentadienyl can be introduced through reaction of **1** with 2 equiv of LiCp* to generate **3** as a purple solid in 65% isolated yield (Scheme 1). Complex **3** displayed new ^{1}H and ^{13}C NMR signals consistent with the Cp* methyl groups at 1.831 and 12.1 ppm, respectively. The remaining NMR signals were consistent with the intact η^3-diaminonaphthalene-derived ligand.

A structural determination for **3** confirmed our postulated structure (Scheme 1).[17] The bond lengths and the internal angles for the tridentate trianionic ligand are similar to those observed in **1** and **2** and include the fact that N(1), N(2), and C(14) remain coplanar with the naphthalene backbone. Taking the Cp* centroid and the midpoint of the N(2)−C(14) bond as single coordination sites gives a distorted-tetrahedral coordination geometry for **3** with average angles of 108.7° (range 98.5−123.6°).

Two related cyclopentadienyl tantalum complexes possessing rigid pda ligands have been reported, [1,3-$(Me_3Si)_2C_5H_3$]Ta[o-[$(Me_3Si)N]_2C_6H_4]Cl_2$[11] and Cp*Ta(1,2-(^{i}$Pr_3SiN)_2C_6H_4)Cl_2$.[12] In both of these cases the metal-bonded nitrogen atoms are trigonal planar but the interaction of the metal center with the phenylene ring π system leads to folding of the five-membered chelate ring along the N−N vector and a nonplanar ligand.

Both chloro ligands in **1** can be replaced in a metathetical reaction with 4 equiv of benzyl Grignard reagent to produce **4** (Scheme 1). Again, the ^{1}H and ^{13}C NMR spectra of **4** suggest an intact trianionic ligand and the incorporation of two benzyl groups. The diastereotopic methylene protons of the benzyl groups appear as doublets at δ 1.25 and 1.19 ppm in C_6D_6, and the methylene carbon appears as a singlet at δ 72.8 ppm. These features support a formula for this complex of [η^3-$C_{10}H_6(Me_2CN)$(^{i}PrN)]Ta$(CH_2Ph)_2$ and do not suggest a static η^2-benzyl interaction for the electron-deficient complex **4**.

A family of Ta(V) complexes has been isolated as stable crystalline solids possessing a novel tridentate trianionic ligand, [η^3- $(Me_2CN)(Me_2CHN)C_{10}H_6]^{3-}$, derived from 1,8-bis(isopropylamino)naphthalene. This species was formed from an unanticipated σ-bond metathesis/C−H activation and is coordinated to Ta in a planar mode to generate a bicyclic [6.3.0] system. This bonding arrangement is apparently quite robust and remains intact through transformations of the Ta coordination sphere. Our ongoing investigations are directed at understanding the effects produced by variation of the N-alkyl substituents and the potential of compounds **1**−**4** as a building blocks to new Ta compounds as well as the capability of this ligand to provide support for other transition-metal complexes.

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Supporting Information Available: Text giving experimental details for compounds **1**−**4** and tables of crystal data and structure solution and refinement details, atomic coordinates, bond lengths and angles, and anisoptropic thermal parameters for compounds **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Crystal data: empirical formula $C_{30}H_{37}Cl_2N_3Ta$, $T = 203(2)$ K, $\lambda = 0.710\,73$ Å, space group $P\bar{1}$, $a = 10.093(2)$ Å, $\alpha = 70.143(2)°$, $b = 16.240(2)$ Å, $\beta = 81.021(3)°$, $c = 19.669(3)$ Å, $\gamma = 80.977(3)°$, $V = 2976.4(8)$ Å^3, $Z = 4$, R indices ($I > 2\sigma(I)$) R1 = 0.0442 and wR2 = 0.0807.

(17) Crystal data: empirical formula $C_{26}H_{34}ClN_2Ta$, $T = 203(2)$ K, $\lambda = 0.710\,73$ Å, space group $Pbcn$, $a = 23.328(2)$ Å, $\alpha = 90°$, $b = 10.1925(9)$ Å, $\beta = 90°$, $c = 19.3464(17)$ Å, $\gamma = 90°$, $V = 4599.9(7)$ Å^3, $Z = 8$, R indices ($I > 2\sigma(I)$) R1 = 0.0498 and wR2 = 0.1090.