Reactivity of a Tantalum−Lithium Alkylidene Supported by an Anionic Triazacyclononane Ligand

Joseph A. R. Schmidt and John Arnold*

Department of Chemistry, University of California, Berkeley and Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720-1460

The development of new ancillary ligands to support stoichiometric and catalytic reactivity at transition metal and lanthanide centers is currently an intensively studied area of chemistry. We,[1] and others,[2] recently described the synthesis and some coordination chemistry of an unusual anionic triazacyclononane ligand, $^iPr_2$-tacn$^-$. Our interest in this general class of new ligands stems partially from their formal relationship to the ubiquitous Cp moiety, i.e., R_2tacn$^-$ may function as a tridentate, six-electron donor. In addition, partial ligand dissociation can potentially free coordination sites for further reactivity, and the ease of introducing alternate substituents at the amino nitrogens allows for tuning of steric properties.

We recently showed that alkylation of ($^iPr_2$-tacn)Ta(=NAr)-Cl_2 (Ar = 2,6-$^iPr_2C_6H_3$) with Me_3SiCH_2Li leads to a unique tantalum−lithium bridging alkyl, $(Me_3SiCH_2)_2(ArN=)Ta(\mu$-$^iPr_2$-tacn)($\mu$-$CH_2SiMe_3$)Li, that yields the corresponding bridging alkylidene on thermolysis.[3] The unusual nature of the heterobimetallic bridge in this latter compound, coupled with the postulated involvement of heterobimetallic alkylidenes[4] in a number of important catalytic reactions, led us to study some of its reaction chemistry. We probed two classes of reactivity: first, alkylidene-like transformations[5] at the tantalum center in an effort to gauge the effect of the lithium ion; second, use of these complexes as precursors to a new class of transition metal heterobimetallic species. As detailed below, we describe two examples for each reactivity mode.

The alkylidene, $(Me_3SiCH_2)(ArN=)Ta(\mu$-$CHSiMe_3)(\mu$-η_1:η_3-$^iPr_2$-tacn)Li (**1**), reacted cleanly with 1 equiv of benzophenone (see Scheme 1), liberating $Me_3SiCH=CPh_2$ and forming the oxo compound, $[(Me_3SiCH_2)(ArN=)Ta(\mu$-O)($\mu$-$\eta_1$:$\eta_3$-$^iPr_2$-tacn)Li]_2$ (**2**). NMR spectra of **2** were qualitatively similar to **1** (with the notable absence of alkylidene resonances), the elemental analysis was consistent with an oxo formulation, and ^7Li NMR data, along with a simple flame test, indicated retention of the lithium ion. To unambiguously determine the solid-state structure, we turned to X-ray crystallography and grew crystals of **2** by slow evaporation of a concentrated benzene solution.[6] As shown in Scheme 1, the compound is dimeric, with each oxo ligand spanning one Li and two Ta atoms. The dimer is held together by the commonly observed Ta_2O_2 metallocycle, with normal Ta−O bond lengths (1.97 and 2.06 Å).[7] The Ta−N(imido) bond length (1.81 Å), though longer than in **1**, is otherwise unremark-

able.[8] The remaining metal−ligand bond lengths are changed only slightly from those observed in **1**.

To further investigate its alkylidene-like reactivity, we exposed **1** to carbon monoxide (1 atm) at ambient temperature in toluene. The solution immediately changed from yellow to orange and, based on NMR data, a quantitative conversion to a new compound, **3**, was achieved (Scheme 1). The pale orange product was isolated as an orange oil that solidifies readily upon drying under vacuum. NMR spectra of this product are qualitatively very similar to that of **1**, except that the CH(alkylidene) resonance shifts significantly on formation of the new product (from 4.205 ppm (^1H) and 57.4 ppm (^{13}C) in **1** to 5.517 ppm (^1H) and 93.5 ppm (^{13}C) in **3**). Additionally, the ^7Li NMR resonance shows a noteworthy change (from 2.986 ppm (**1**) to 1.874 ppm (**3**)). Based on these data, we postulated an insertion of CO at the alkylidene functionality to form a ketene complex.[9] X-ray quality crystals of **3** were obtained by slowly cooling a saturated octane solution, and the resultant structure (Scheme 1) confirms the connectivity in this complex.[10] Indeed, the CO has inserted into the Ta−alkylidene bond to form a ketene ligand, which is coordinated η_2-(C,O) to Ta and η_1-O to Li. The Ta−C (2.13 Å) and Ta−O (2.07 Å) bond distances for **3** parallel a related η_2-Zr ketene (Zr−C = 2.17 Å, Zr−O = 2.03 Å) and a related η_2-Ta acyl complex (Ta−C = 2.07 Å, Ta−O = 2.11 Å),[11] while the Li−O interaction (1.82 Å) is similar to that observed in carboxylates and related ligands.[12] Again, the bridging structure of the $^iPr_2$-tacn$^-$ is retained, with virtually no change in the remaining metal−ligand bond lengths.

Our second goal in these studies has been the formation of novel heterobimetallic transition metal species, and the alkylidene **1** appeared to be an ideal precursor: we envisioned exchange of lithium for a transition metal, leading to a bimetallic species with two metals in close proximity and linked by single-atom bridges. Accordingly, reaction of **1** with an excess of $[RhCl(COD)]_2$ (COD = 1,5-cyclooctadiene) in toluene effected the salt metathesis. After removal of LiCl, the product (**4**) crystallized from Et_2O at low temperatures. The ^1H NMR spectrum of this compound is broad and quite complex at all temperatures between −80 and 100 °C. Nevertheless, a combination of elemental analysis and 2-D NMR techniques at 90 °C suggests formulation of the product as $(Me_3SiCH_2)(^iPr_2$-tacn)$(Me_3SiCH=)Ta(=NAr)Rh$−(COD).

Recrystallization of **4** from Et_2O yielded high-quality crystals, the X-ray structure of which shows a Ta−Rh bimetallic compound in which the alkylidene and *imido* groups bridge the metal

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(6) Crystal data for **2**: $C_{34}H_{60}N_4OLiSiTa$, M = 756.85, triclinic, space group P1̄ (no. 2), a = 11.5447(2) Å, b = 13.0903(1) Å, c = 13.6676(2) Å, α = 63.756(1)°, β = 84.930(1)°, γ = 77.214(1)°, V = 1806.54(5) Å^3, Z = 2, D_{calc} = 1.391 g cm^{-3}, μ(Mo Kα) = 31.01 cm^{-1}, $F(000)$ = 780.00, T = 168 K; 5159 independent reflections; R = 0.021, R_w = 0.070, R_{all} = 0.026.

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(10) Crystal data for **3**: $C_{33}H_{64}N_4Si_2TaLiO$, M = 776.95, orthorhombic, space group *Pbca* (no. 61), a = 17.1859(3) Å, b = 19.2859(3) Å, c = 24.3778(4) Å, V = 8079.9(2) Å^3, Z = 8, D_{calc} = 1.277 g cm^{-3}, μ(Mo Kα) = 28.03 cm^{-1}, $F(000)$ = 3216.00, T = 166 K; 3179 independent reflections; R = 0.025, R_w = 0.028, R_{all} = 0.060.

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Scheme 1
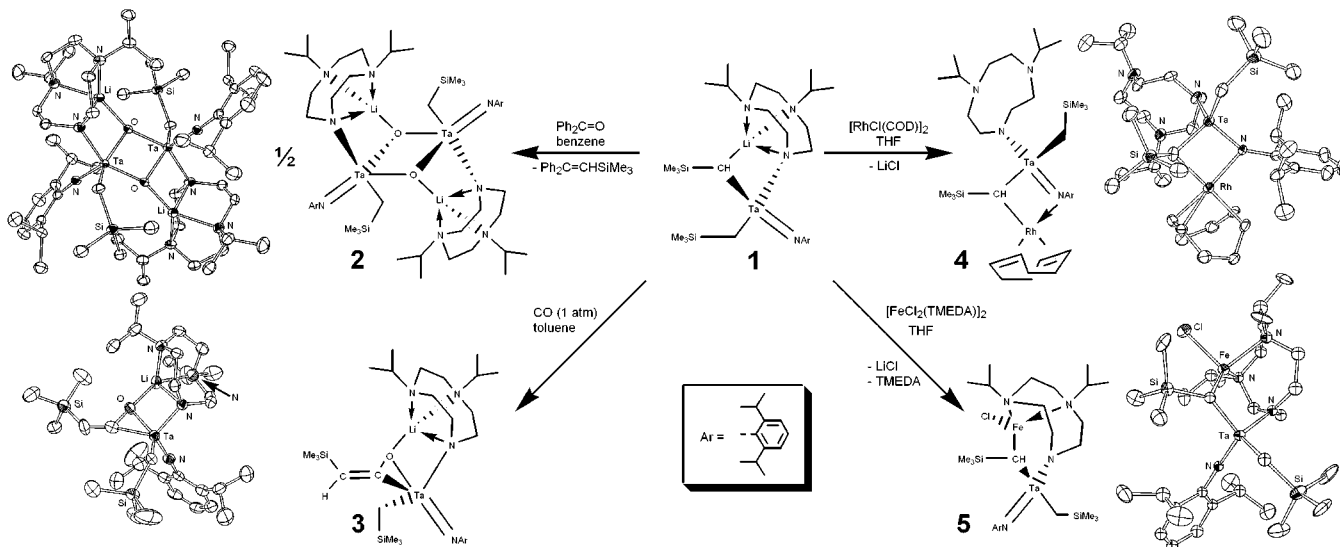
centers.[13] The pseudotetrahedral coordination of the tantalum is completed by a monodentate tacn⁻ ligand and the remaining alkyl group, while the Rh(I), still bound to COD, resides in its preferred square-planar environment.[14] Although somewhat unexpected, this species represents an additional structural motif by which we can form bimetallic complexes from the alkylidene **1**. In **4**, the Ta–N(imido) bond distance has lengthened to 1.87 Å, a value indicative of double-bond character. The Rh–N(imido) bond length (2.12 Å) is within the range of values observed for dative rhodium–nitrogen bonds.[15] This is the first example of a monodentate coordination of tacn⁻ to a transition metal and the bond length (Ta–N = 1.95 Å) is well within the established range for tantalum amides.[8] As the tantalum remains electronically unsaturated in **4**, the monodentate coordination is likely due to steric interactions within the molecule.

A different type of new heterobimetallic complex was synthesized by reaction of **1** with [FeCl₂(TMEDA)]₂ in tetrahydrofuran at room temperature (Scheme 1). The ¹H NMR spectrum of this complex (**5**) suggested strong paramagnetism with broad resonances ranging from +40 to −30 ppm; using Evans' NMR method,[16] the compound was found to have a solution magnetic susceptibility of $\mu_{eff} = 4.2$ μ_B, consistent with a high-spin d_6 Fe-(II). The compound was recrystallized from diethyl ether and its empirical formula, [(Me₃SiCH₂)(ArN=)Ta(=CHSiMe₃)(ⁱPr₂-tacn)FeCl]·Et₂O, was confirmed by elemental analysis.

The X-ray crystal structure of **5** showed the connectivity of this bimetallic species.[17] The iron atom is in a pseudotetrahedral environment with the bridging tacn⁻ ligand coordinated in a *bidentate* fashion (through the two amino nitrogens). The tantalum remains in a coordination environment quite similar to **1**. Surprisingly, the anionic nitrogen of the tacn⁻ does not appear to interact with the iron appreciably and exhibits a nearly trigonal planar environment (sum of angles = 359(2)°), even though the Ta–N(amido) bond length (1.99 Å) is typical of a Ta–N single bond. The Ta–C$_{br}$ bond length (2.02 Å) is much shorter than the Fe–C$_{br}$ distance (2.18 Å) and is most likely due to a greater Ta–C bond order.

In summary, we have shown two novel reactivity pathways derived from the tantalum–lithium alkylidene species **1**. The compound reacts with small organic molecules in a manner reminiscent of traditional alkylidenes, although the structural connectivity of the products is clearly dictated by the presence of the lithium ion. In addition, **1** reacts with metal chlorides to form new heterobimetallic compounds containing metals linked by one-atom bridges. On the basis of electronic requirements of the metals employed, two motifs are observed: (1) coordination of the *alkylidene* and the *tacn⁻* ligands and (2) coordination of the *alkylidene* and *imido* ligands. Our future investigations will include synthesis of further heterobimetallic complexes, as well as investigation of their cooperative reactivity with an eye for catalytic reactions. Additionally, we plan to further pursue the reactivity of **1** with other small organic molecules.

Supporting Information Available: Experimental procedures, characterization, and tables of coordinates, anisotropic displacement parameters, bond lengths, and angles for **2**−**5** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

(13) Crystal data for **4**: C₄₄H₈₆N₄OSi₂RhTa, $M = 1027.21$, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.0050(2)$ Å, $b = 13.5425(3)$ Å, $c = 17.5754(4)$ Å, $\alpha = 108.303(1)°$, $\beta = 93.722(1)°$, $\gamma = 95.154(1)°$, $V = 2464.74(9)$ Å³, $Z = 2$, $D_{calc} = 1.384$ g cm⁻³, μ(Mo Kα) = 26.32 cm⁻¹, $F(000) = 1064.00$, $T = 149$ K; 5984 independent reflections; $R = 0.040$, $R_w = 0.044$, $R_{all} = 0.056$.
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(17) Crystal data for **5**: C₃₆H₇₄N₄ClOSi₂TaFe, $M = 907.43$, orthorhombic, space group *Pbca* (no. 61), $a = 21.2081(2)$ Å, $b = 14.7430(2)$ Å, $c = 29.3458(6)$ Å, $V = 9175.6(2)$ Å³, $Z = 8$, $D_{calc} = 1.314$ g cm⁻³, μ(Mo Kα) = 28.35 cm⁻¹, $F(000) = 3760.00$, $T = 153$ K; 2652 independent reflections; $R = 0.033$, $R_w = 0.037$, $R_{all} = 0.107$.

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