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Reversible Intramolecular Hydride Transfer between Tantalum and an Aromatic Ring: An η^5-Cyclohexadienyl Complex as a Masked Hydride

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Tantalum hydrides are known to mediate a number of interesting catalytic transformations including olefin polymerization,[1] alkane hydrogenolysis,[2] and arene hydrogenation.[3] In these processes, a somewhat limited range of ancillary ligands have been employed in tuning the chemical properties of the tantalum complexes.[4] Although considerable recent research has focused on development of the tantalum chemistry of imido ligands,[5] only a few imido-hydride complexes have been reported.[6−8] The few such species that are known exhibit high reactivities and have been found to mediate interesting C−H and Si−H bond activations.[6] In the exploration of imido-tantalum complexes in potentially useful transformations involving hydride transfers, we have employed sterically demanding aryl-imido ligands in attempts to stabilize monomeric, highly reactive tantalum hydrides. In this communication, we report use of the $[2,6\text{-}Mes_2C_6H_3N{=}]^{2-}$ ($[Ar^*N{=}]^{2-}$, Mes = $2,4,6\text{-}Me_3C_6H_2$) ligand in generation of the tantalum hydride $[(Ar^*N{=})(Ar^*NH)Ta(H)OTf]$ (**4**, OTf = OSO_2CF_3), which rapidly rearranges to an η^5-cyclohexadienyl tantalum imido complex $(Ar^*N{=})[2\text{-}(\eta^5\text{-}2,4,6\text{-}Me_3C_6H_3)\text{-}6\text{-}MesC_6H_3NH]Ta(OTf)$ (**3**). The latter species exists in equilibrium with **4**, such that it behaves as a “masked hydride” in its reaction chemistry. This reaction is therefore relevant to the mechanism of Rothwell’s tantalum-catalyzed arene hydrogenations,[3b] which appear to involve an analogous, initial migration of hydrogen from tantalum to an arene ring.[9]

The imido-amido complex $(Ar^*N{=})(Ar^*NH)TaMe_2$ (**1**) was prepared in 71% yield by the treatment of $TaMe_3Cl_2$ with 2 equiv of LiNHAr* (prepared via modification of a literature procedure[10]). Attempts to convert **1** to a hydride complex by the reaction with H_2 (e.g., at 1 atm in benzene-d_6) resulted in complex reaction mixtures containing the free amine Ar^*NH_2. We therefore attempted to obtain a tantalum complex with a more reactive Ta−Me bond, by conversion of **1** to the triflate derivative $(Ar^*N{=})(Ar^*NH)Ta(Me)OTf$ (**2**) via reaction with 1 equiv of AgOTf.[11,12] Heating a bromobenzene solution of complex **2** to 95 °C over 2 d in the presence of H_2 (1 atm) provided a red-orange crystalline solid (**3**) which was purified by recrystallization from toluene at −35 °C (Scheme 1). The ^1H NMR spectrum of **3** contains two coupled doublets at 3.53 and 4.54 ppm (J = 16 Hz), consistent with the presence of a methylene group with diastereotopic protons. However, this spectrum appears to be devoid of a resonance attributable to a Ta hydride ligand.[13]

The identity of **3** was established by X-ray crystallography, which revealed a structure containing an η^5-cyclohexadienyl ligand (Figure 1). This complex contains a normal imido ligand, as indicated by the Ta(1)−N(2)−C(25) bond angle of 175.6(5)° and the Ta═N bond length of 1.788(5) Å.[5] The amido ligand in **3** is metalated via the transfer of a hydrogen atom to one mesityl group, to give rise to an η^5-cyclohexadienyl ligand. The reduced mesityl ring is puckered at C(1), such that the Ta(1)···C(1) distance is 3.141(7) Å, while the bond lengths from Ta(1) to C(2)−C(6) range from 2.349(6) to 2.830(6) Å. The internal angles of the cyclohexadienyl ligand involving C(2)−C(6) range from 116.2(6) to 121.0(6)°, suggesting sp^2 hybridization, whereas the C(6)−C(1)−C(2) angle (109.6(6)°) is consistent with sp^3 hybridization.

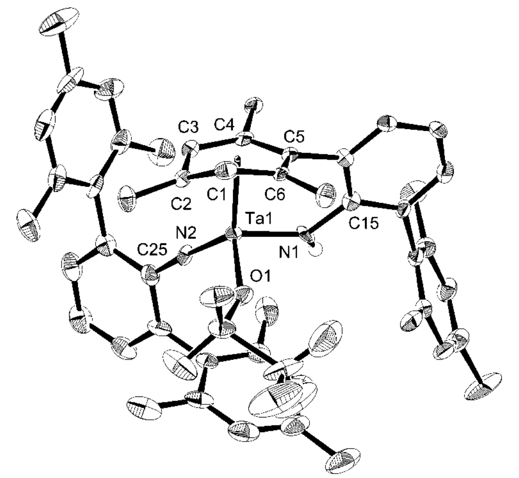
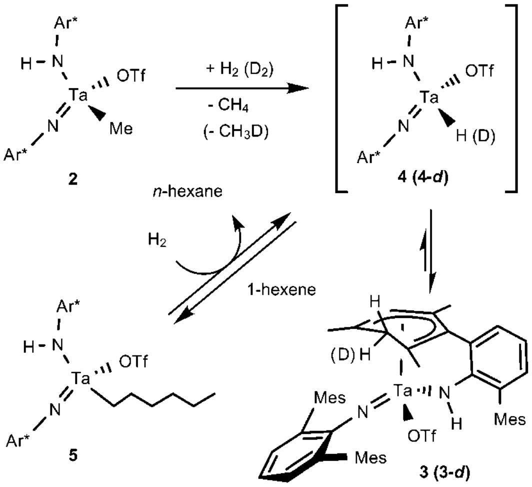


Figure 1. ORTEP diagram of $(Ar^*N{=})[2\text{-}(\eta^5\text{-}2,4,6\text{-}Me_3C_6H_3)\text{-}6\text{-}MesC_6H_3NH]Ta(OTf)$ (**3**).

Scheme 1



Complex **3** presumably forms via the tantalum hydride intermediate $[(Ar^*N{=})(Ar^*NH)Ta(H)OTf]$ species (**4**, Scheme 1), and evidence for the existence of this species was obtained by trapping experiments. When a bromobenzene-d_5 solution of **2** was treated with H_2 in the presence of 1-hexene (1 equiv), methane was produced along with quantitative amounts of *n*-hexane and complex **3**. This observation suggests that **4** reacted with 1-hexene to give a hexyl triflate complex (**5**), which then reacted with H_2 to give *n*-hexane and complex **3** (Scheme 1). In fact, the reaction of **2** with

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H_2 (1 atm) in the presence of 10 equiv of 1-hexene (in bromobenzene, 95 °C, over 2 d) produced the *n*-hexyl derivative (Ar*N═)(Ar*NH)Ta(Hex)OTf (**5**) as yellow crystals in 66% yield. The diastereotopic $TaCH_2$ hydrogens are clearly identified by two triplets of doublets appearing at 0.58 and 1.00 ppm. The ^{13}C NMR signal for this methylene group occurs at 66.9 ppm, in approximately the same region as those for the related carbon atoms in **1** and **2**.

Experimental data suggest that in solution, complexes **3** and **4** exist in equilibrium. Thus, **3** reacts with 1-hexene (1 equiv, in the absence of H_2) in bromobenzene-d_5 at 95 °C to form the *n*-hexyl derivative **5** (Scheme 1). However, attempts to observe **4** by monitoring the reaction of complex **2** with H_2 (1 atm) by ^1H NMR spectroscopy in bromobenzene-d_5 at 95 °C were unsuccessful; only resonances due to complexes **2** and **3** were observed. Thus, **3** is highly favored in its equilibrium with **4**.

Further insight into the mechanism of formation of **3** was gained by a deuterium-labeling experiment. Treatment of **2** with D_2 (1 atm) in bromobenzene at 95 °C over 3 d provided **3-*d*** as red-orange crystals from toluene (Scheme 1). The ^1H NMR spectrum of **3-*d*** has no signal at ∼3.5 ppm (unlike **3**), but contains a broad singlet at 4.52 ppm integrating to 1 H. The ^2H NMR spectrum, as expected, contains a single, broad resonance at 3.48 ppm, consistent with deuterium incorporation into only one position of the molecule. The $^{13}C\{^1H\}$ NMR spectrum contains a 1:1:1 triplet at 34.5 ppm due to C−D coupling ($^1J_{CD} = 20$ Hz). No further deuterium incorporation was observed after heating a bromobenzene-d_5 solution of complex **3-*d*** with D_2 (1 atm) to 95 °C for 3 d. Furthermore, complex **3-*d*** was found to undergo H/D exchange to yield **3** upon exposure to H_2 (1 atm) in bromobenzene-d_5 at 95 °C (24 h). This is believed to proceed via a σ-bond metathesis pathway involving the postulated intermediate **4** (or **4-*d***).

To determine the fate of the hydrogen atom that is introduced in the formation of **3**, the through-space couplings involving the reduced mesityl ring in **3** were determined. A ^1H ROESY NMR experiment (mixing time = 1 s) was used to observe an ROE (rotating frame Overhauser effect) between the singlet at 4.26 ppm (H_{Mes} = H bonded to C(3), Figure 1) and the doublet at 4.54 ppm (H_{exo} bonded to C(1), Figure 1). However, no ROE was observed between H_{Mes} and H_{endo} (bonded to C(1), Figure 1). In the structure of complex **3**, the puckered η^5-cyclohexadienyl ring places H_{Mes} closer to H_{exo} than H_{endo} (3.53 Å vs 4.06 Å). Therefore, the doublet at 4.54 ppm is due to H_{exo}, and the doublet at 3.53 ppm is due to H_{endo}. Furthermore, since the deuterium-labeling experiment incorporates deuterium into only one position of the molecule (the H_{endo} position), the hydride transfer proceeds in an *endo* fashion.

Complex **3** results from the insertion of an arene ring into a M−H bond, to give a stable η^5-cyclohexadienyl complex. Complexes of this type have been postulated by Rothwell and co-workers as intermediates in the intramolecular hydrogenation of aryl oxide phenyl substituents to cyclohexyl groups.[9] In previous work aimed at the characterization of potential arene hydrogenation intermediates, intramolecular transfers of two and four hydrides to aryl oxide phenyl substituents were observed.[14]

The observed stoichiometric hydrogenation of 1-hexene with **3** suggested the use of this complex as a hydrogenation catalyst. Treatment of bromobenzene-d_5 solutions of 1-hexene (10 equiv) and cyclohexene (5 equiv) with catalyst precursor **2** and H_2 at 95 °C (7 and 12 d, respectively) gave high conversions to *n*-hexane and cyclohexane, respectively. This system was also found to effect the catalytic reductive cyclization of 1,5-hexadiene (14 equiv) to methylcyclopentane (9 d, quantitative conversion, 50% yield).[15] The slow rates of these hydrogenations probably reflect the sterically encumbered nature of the catalyst.

The results described here provide further evidence that imido-hydride complexes are accessible, potentially reactive species that can give rise to novel chemistry. Complex **3**, with an imido-amido ligand set featuring the sterically demanding 2,6-$Mes_2C_6H_3$ aryl group, represents an arene hydrogenation intermediate resulting from the transfer of hydride from tantalum to one of the mesityl rings. This complex reacts with small molecules via its more reactive isomer **4**, with which it is in equilibrium. Continuing studies focus on the development of imido-hydrides that are highly reactive in σ-bond metathesis processes.

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Supporting Information Available: Procedures for the synthesis and characterization of **1**−**5** and ^1H ROESY NMR spectra (PDF). X-ray crystallographic information for **3** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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