Non-cyclopentadienyl Titanium(III)−Magnesium Hydride Formation by Reduction of an Amidotitanium(IV) Complex

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Summary: The reduction of an arylamido-based titanium(IV) chloride by magnesium has resulted in the formation of a unique, non-cyclopentadienyl titanium-(III)−magnesium hydride with the concomitant intramolecular metalation of the arylamido ligands.

Cyclopentadienyl titanium(III) hydrides are implicated in a variety of catalytic processes, including the hydrogenation of alkenes and ketimines, the hydrosilylation of C=X species (X = C, N, O), and perhaps most importantly the dehydrocoupling of silanes to form polysilanes.[1,2] Furthermore, related scandium(III) hydrides are involved in the remarkable catalytic dehydrosilylation of methane.[3] This rich vein of reactivity, coupled with the vast array of new amido ligand based titanium complexes that have been reported,[4] should mean that non-cyclopentadienyl titanium(III) hydrides are prominent in stoichiometric or catalytic transformations. In fact, non-Cp Ti(III) hydrides are extremely rare, with the dimeric hydride $[Ti(\mu\text{-H})(L)]_2$ (L = $(Me_3Si)N\{CH_2CH_2N(SiMe_3)\}_2$) being the sole isolated and fully characterized example.[5] We have been investigating the synthesis and reactivity of Ti-based mixed-metal complexes with a view to promoting controlled, dual-site catalytic chemistry[6] and so began to scrutinize the reactivity patterns of the monometallic, amido-based metallo ligand $TiCl_2[N(CHBu^t_2)(C_6H_4PPh_2\text{-}3)]_2$ (**1a**). We report here the outcome of the reduction of **1a** by magnesium, which leads to the formation of the unusual Ti^{III}−Mg hydride complex **2a**, a product more reminiscent of cyclopentadienyl−titanium than amido−titanium chemistry.

The di-*tert*-butylmethyl-substituted anilides are synthesized directly as the lithium salts Li[**L¹**] and Li[**L²**] via Schiff-base condensation of trimethylacetaldehyde with the respective anilines followed by Bu^{t}Li addition across the resultant imine C=N double bond.[7] The salt elimination reactions between Li[**L**] and $TiCl_4(THF)_2$ (2:1) in toluene generate the Ti(IV) halides **1a** and **1b** as dark red crystalline solids in high yield (Scheme 1).

Scheme 1. Synthetic Route to the Ti(III) Hydrides 2a and 2b

L¹ E = PPh₂
L² E= H

1a (E = PPh₂), 68 %
1b (E = H), 74 %

2.5 Mg, THF
− 0.5 MgCl₂

2a (E = PPh₂), R = Bu$^t_2$CH, 78 %
2b (E = H), R = Bu$^t_2$CH, 45 %

The X-ray crystal structure of **1b** was determined (Figure 1) and reveals a unique example of a structurally characterized, monomeric Ti(IV) dihalide supported solely by nonchelating amido ligands. The geometry at Ti1 is tetrahedral, although Cl1−Ti1−Cl2 is compressed (100.55(2)°) and N1−Ti1−N2 enlarged (117.74(6)°) and standard Ti−N and Ti−Cl bond lengths are observed. Two interactions appear to enforce the observed C_2 symmetry; thus, the π-stacking of the two aryl rings (C1⋯C16 = 3.27 Å) is reinforced by hydrogen-bonding interactions between the methine H's and opposing chlorides (H⋯Cl = 3.02 and 3.65 Å). This hydrogen-bonding interaction is conserved in solution. In the ¹H NMR spectrum of **1b**, the methine H resonates at 5.70 ppm and represents a downfield shift of 2.80 ppm as compared to that seen in Li[**L²**] (2.90 ppm).

The reaction between the Ti(IV) halides **1a** and **1b** and magnesium dust in THF results in the slow formation of dark brown solutions from which **2a** and **2b** were isolated as dark brown solids. ¹H NMR spectroscopy indicates that these compounds are paramagnetic and shows only broad resonances at ca. 3.5 and 1.7 ppm that are consistent with THF molecules undergoing dynamic exchange with the paramagnetic center. Furthermore, the solution susceptibility measurement of **2a** by the Evans method at 298 K results in μ_{eff} = 2.11 μ_B, which is consistent with a d¹ Ti(III) species. This value is higher than the expected spin-only moment (μ_{calcd} = 1.73 μ_B), which may be due to an orbital contribution and/or the loss of nonstoichiometric amounts of THF from **2a** prior to weighing. To establish the identity of **2a**, the solid-state structure was determined (Figure 2). It is

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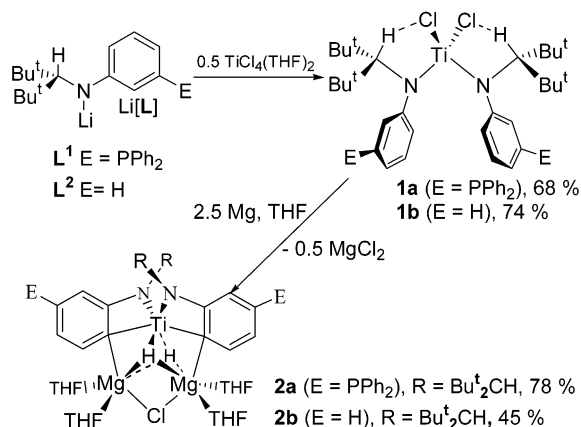(3) Sadow, A.; Tilley, T. D. *Angew. Chem., Int. Ed.* **2003**, *42*, 803.
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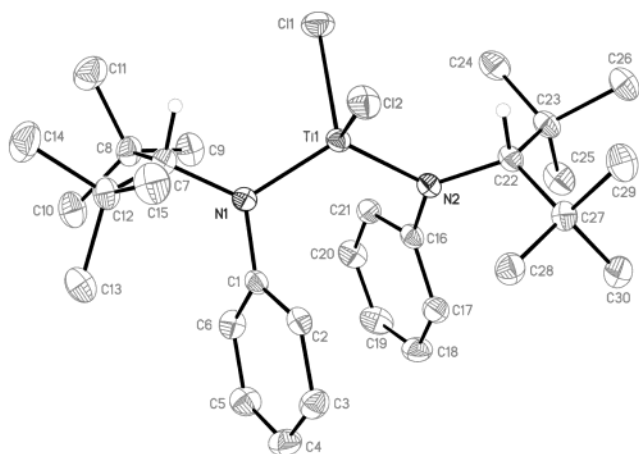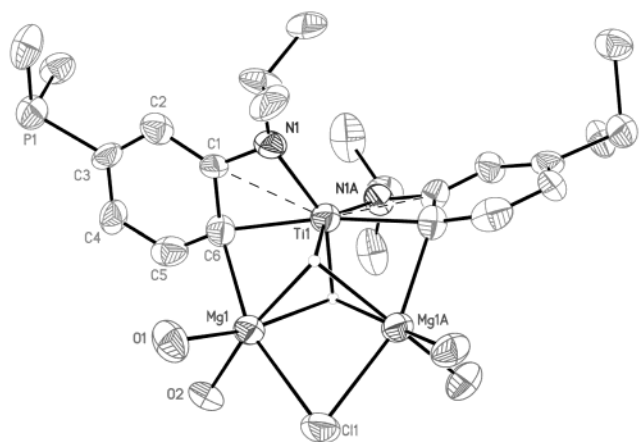(7) Mokuolu, Q. F.; Duckmanton, P. A.; Hitchcock, P. B.; Love, J. B. Submitted for publication.

Figure 1. Solid-state structure of **1b** (R = H).

Figure 2. Solid-state structure of **2a** (50% ellipsoids). For clarity, P-aryl, N–Bu^t, and THF carbons and all hydrogens except the metal hydrides are omitted.

apparent that the reduction product is not a straight-forward Ti(III) complex but instead features cyclometalated μ_2-aryl rings bridging Ti and Mg, incorporation of a MgClMg bonding motif, and, most importantly, μ_3-hydrides bridging the Ti and the two Mg metals.

No counterions were observed crystallographically; therefore, **2a** is charge neutral. This formulation was also confirmed by combustion analysis. The coordination of the ligand to the metal is unusual and warrants closer inspection. The Ti1–N1 (2.051(4) Å) and Ti1–C6 bond distances (2.249(6) Å) are longer than other known Ti^{III}–N (1.94–1.98 Å) and Ti^{III}–C (2.14–2.21 Å) bond distances[8] and are indicative of an η^3 interaction. This is further corroborated by the short Ti$\cdots$C1 interaction (2.535 Å) and the shortened N1–C1 bond distance (1.395(6) Å) and by comparison to the structure of Ti-[N(Bu^t)(C$_6$H$_3$Me$_2$-3,5)]$_3$; in this case, two of the anilide ligands adopt similar η^3 bonding modes with analogous bond length distortions.[9] Unlike the above Ti(anilide)$_3$, the aryl ring has been substituted by Mg in the ortho position, thus resulting in a Ti(μ_2-aryl)Mg bonding motif. The Mg1–C6 bond distance (2.314(5) Å) is similar to that found in the cluster complex Cu$_4$MgPh$_6$ (Mg–C = 2.35(1) Å), which contains a μ_2-aryl group between Mg

and Cu.[10] Structurally characterized Ti–μ_2-aryls are rare and are known only for [Cp$_2$Ti(μ_2-CH$_2$)(μ_2-C$_6$H$_4$X)-Rh(COD)] (X = H, 4-NMe$_2$, 2-OMe) and complexes of the type [Cp$_2$TiCl(μ_2-η^1:η^6-C$_6$H$_5$)Cr(CO)$_3$][11–13] Furthermore, while metalation of an activated arene by transition metals is commonplace, metalation of usually robust transition-metal arylamido ligands is rare. A titanium alkyl complex supported by the tridentate diamido ligand, [(Pr^{i}N-o-C$_6$H$_4$)$_2$O]$^{2-}$, was found to undergo C–O bond cleavage and aryl metalation in the presence of DMPE, significantly via a putative Ti(II) intermediate (see later).[14] The Mg1–Cl1 bond length (2.517(2) Å) and Mg1–Cl1–Mg1A angle (73.10(10)°) are similar to those reported for chloride-bridged dimagnesium motifs.[15]

The most intriguing aspect of the structure of **2a** is the presence of two μ_3-hydrides that symmetrically bridge the three metals. The hydrides were located in the difference Fourier map, and evidence for their presence is reinforced by the distorted-octahedral geometries thus observed at Ti1 (C6–Ti1–C6A = 169.6-(3)°, N1–Ti–N1A = 121.1(2)°) and Mg1 (C6–Mg1–Cl1 = 161.91(16)°, O1–Mg1–O2 = 92.71(16)°). However, further corroboration of the presence of hydrides was sought. Infrared spectroscopy proved inadequate, as the region in which Ti(μ-H)Mg absorptions would appear (ca. 1500–900 cm^{-1}) is masked by ligand absorptions; unfortunately, no deuterated version of the ligand is available at present. Preliminary solution EPR spectra were obtained for both **2a** and **2b** and show similar hyperfine patterns that superficially appear consistent with the presence of two hydrides and two amido nitrogens. Unfortunately, neither spectrum could be adequately simulated. Concrete evidence for the presence of hydrides came from D$_2$O quenching experiments, in which D$_2$O was vacuum-transferred to degassed solutions of **2a** or **2b**, the volatiles were vacuum-transferred into an NMR tube, and the ^{1}H NMR spectra were recorded. The volatiles sampled, albeit inefficiently, by this method clearly show the presence of HD (4.54 ppm, J_{HD} = 42.6 Hz), which can only arise from the reaction of a metal hydride with D$_2$O. At present, the structure of **2b** remains ambiguous, as no crystals suitable for X-ray diffraction are available and combustion analyses have been repeatedly unsatisfactory. However, the similarity of the EPR spectra of **2a** and **2b**, along with the generation of HD by quenching with D$_2$O, strongly suggests that **2a** and **2b** have similar structures.

The formation of the Ti(III) hydrides **2a** and **2b** by magnesium reduction is replicated in cyclopentadienyl-based titanium chemistry; thus, the reaction between titanocene dihalides and magnesium results in the formation of a variety of Cp$_2$Ti^{III}–Mg hydrides.[16,17] However, none of these compounds exhibit the same

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triply bridging hydride and $TiMg_2Cl$ motifs as **2a**. These systems also show a propensity for intramolecular C−H activation reactions,[18] which implies that Ti(II) species are mechanistic intermediates. By using bulky, silylated cyclopentadienyls, $C_5Me_4SiMe_2R$ (Cp′), the isolation of the parent titanocene $Cp′_2Ti$ was recently realized;[19] reduction of $Cp′_2TiCl_2$ by equimolar amounts of magnesium also resulted in titanocene synthesis.[20] It is therefore possible that **2a** is formed via a highly reactive Ti(II) intermediate. To assess this supposition, cyclic voltametry (CV) was carried out in CH_2Cl_2 and reveals a single reversible wave at $E° = -0.81$ V (0.1 V s^{-1}, $^{n}Bu_4$-NBF$_4$, SCE) with no further reductions to -2.0 V. By comparison to the CV of Cp_2TiCl_2, this is consistent with the formation of the monohalo species $\{TiCl(L^1)\}_n$ via one-electron uptake and halide loss.[21−23] Additionally, controlled-potential electrolysis at -0.86 V revealed that a multielectron process (number of electrons 2.44) leading to decomposition is operating. This may be a reaction of the electrochemically generated species with solvent or a mechanistic step in the formation of **2a**. Whatever the mechanism of formation of **2a**, it is apparent that reduction processes comparable to those of titanocene dihalides are in effect, thus reinforcing the similarity of this particular amido-based titanium complex to cyclopentadienyl analogues. We are at present investigating further the mechanism of formation of **2a**, in particular the source of hydride, and are exploring the reaction chemistry of these systems. Preliminary results show that **2a** is inert toward CO and also that, unlike Cp_2TiCl_2 reduction chemistry, reaction of **1a** with magnesium under an atmosphere of CO does not result in the formation of a Ti(II) carbonyl but instead forms **2a** as the sole product.

Supporting Information Available: Text giving full synthetic details and characterization data for all new compounds and tables giving X-ray crystallographic data for compounds **1b** and **2a**; crystallographic data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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