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Triple-Hydrogen-Bridged Dititanium(III) and Dizirconium(IV) Aryloxide Complexes

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Summary: The triple-hydrogen-bridged dititanium(III) complex was prepared by the reaction of the titanium(IV) aryloxide complex with $LiBHEt_3$, while a similar reaction using the zirconium aryloxide complex gave the triple-hydrogen-bridged dizirconium(IV) complex. The titanium(III) dimer was found to be diamagnetic, and its dynamic behavior in solution was revealed by NMR studies.

Group 4 metal hydrides have attracted great attention for the wide range of insertion reactions into the metal–hydride bond,[1] silane polymerization,[2] and nitrogen fixation.[3] This rich chemistry is dominated by group 4 metal complexes based on cyclopentadienyl ligands.[4] In contrast, relatively little is known about the synthesis and chemistry of non-cyclopentadienyl group 4 metal hydride complexes, especially Ti(III) hydride complexes. Recently, Cloke reported the synthesis and structure of $[Ti_2\{(Me_3SiNCH_2CH_2)_2NSiMe_3\}_2(\mu\text{-}H)_2]$, which is only one example of a non-cyclopentadienyl Ti(III) hydride complex.[5]

The tridentate aryloxide ligand $[^t\text{Bu-L}]^{3-}$ ($H_3[^t\text{Bu-L}]$ = 2,6-bis(4-*tert*-butyl-6-methylsalicyl)-4-*tert*-butylphenol) has been employed by us to prepare a series of group 5 complexes.[6] For example, the reaction of $[\{Nb(^t\text{Bu-L})Cl_2\}_2]$ with $LiBHEt_3$ under N_2 afforded the nitride complex $[\{Nb(^t\text{Bu-L})(\mu\text{-}N)Li(thf)\}_2]$ along with the cleavage of dinitrogen.[6a] In this context, we were interested in extending this chemistry to titanium and zirconium.[7] In this paper we report that treatment of ^{t}Bu–L complexes of titanium and zirconium with $LiBHEt_3$ afforded the triple-hydride-bridged Ti(III) and Zr(IV) dimers $[Li_3(thf)_3\{Ti(^t\text{Bu-L})\}_2(\mu\text{-}H)_3]$ (**2**) and $[\{Li_2(thf)_4Cl\}\{Zr(^t\text{Bu-L})\}_2(\mu\text{-}H)_3]$ (**4**), respectively.

Addition of 5 equiv of $LiBHEt_3$ in THF to a toluene solution of $[\{Ti(^t\text{Bu-L})Cl\}_2]$ (**1**) at −98 °C led to the formation of a dark greenish brown solution, from which **2** was obtained as brown crystals in 50% isolated yield (Scheme 1).[8] During the course of the reaction, $LiBHEt_3$ is a hydride transfer reagent as well as a reductant, and the metal center is reduced from Ti(IV) to Ti(III). While **2** is stable in the solid state under an inert atmosphere and in solution for extended periods at low temperatures, it is unstable in solution at room temperature, slowly undergoing degradation into uncharacterized products. A measurement of the solution magnetic

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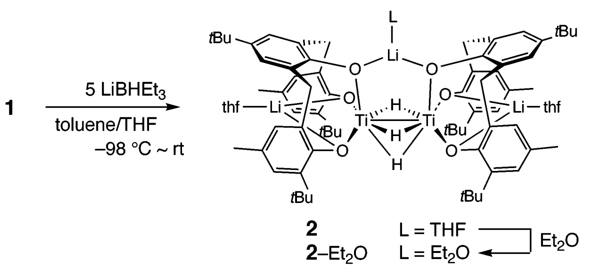
Scheme 1



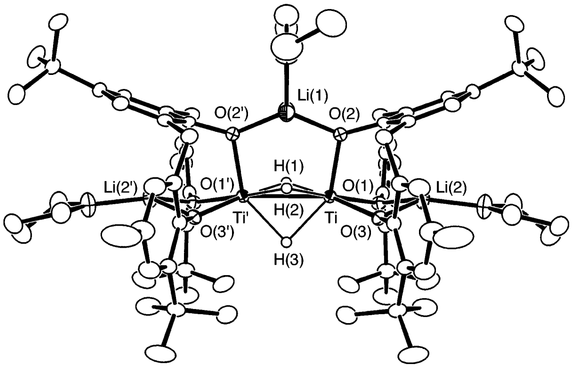


Figure 1. Structure of **2**. Selected interatomic distances (Å): Ti−Ti′ = 2.6210(10), Ti−H(1) = 1.94(3), Ti−H(2) = 1.92(3), Ti−H(3) = 1.94(3), Ti−O(1) = 2.010(2), Ti−O(2) = 1.954(2), Ti−O(3) = 2.044(2).

susceptibility (Evans method, 233−298 K) indicates that **2** is diamagnetic. Additionally, the hydride signals in the ^{1}H NMR spectra of **2** did not show any significant shift as a function of temperature (vide infra), thus excluding the presence of a small underlying paramagnetism again.[5] For a structural study, $[Li_3(thf)_2(Et_2O)\{Ti(^tBu\text{-}L)\}_2(\mu\text{-}H)_3]$ (**2-Et$_2$O**), in which one of the THF molecules was replaced by an Et$_2$O molecule (Figure 1), was prepared by addition of Et$_2$O to a toluene solution of **2**.[9,10]

A single-crystal X-ray structural determination confirmed the dimeric nature of **2**, and the molecule lies on a crystallographic mirror plane passing through the atoms Li(1), H(1), H(2), and H(3). The opposing ^{t}Bu-L ligands on the titanium centers are thus required to be eclipsed. A striking feature of the structure is the presence of the novel $[\{Ti(^tBu\text{-}L)\}_2(\mu\text{-}H)_3]^{3-}$ dimer, which adopts a face-sharing bioctahedral geometry. To our knowledge, there is no precedent for a titanium dimer bridged by three hydrides. Deviation from ideal octahedral geometry around Ti is indicated by the H(3)−Ti−O(2) angle of 146.4(8)°. The three lithiums are not innocent countercations but are bound strongly to the aryloxides. One Li(1) atom bridges the two central aryloxides (O(2) and O(2′)), while the remaining two Li atoms are accommodated inside the cavity of the ^{t}Bu-L ligand, binding two outer aryloxides of the ligand. The trigonal-planar coordination around each lithium is completed by THF or Et$_2$O. The Ti−Ti distance of 2.621(1) Å is comparable to the sum of titanium covalent radii (2.64 Å) but longer than in $[\{(^tBu_3SiNH)Ti\}_2(\mu\text{-}NSi^tBu)_2]$ (2.442(1) Å)[11] and $[(1,4\text{-}(Me_3Si)_2\text{-}cot)_2Ti_2]$ (2.326(2) Å).[12] Longer Ti−Ti interactions ranging from 2.73 to 3.46 Å have been observed in the hydride-bridged titanium dimers.[5,13] When the diamagnetism of this complex is taken into account, the short Ti−Ti distance might be explained by the formation of a metal−metal σ bond. Although the metal−metal distance alone is not a good criterion, a qualitative picture of the electronic structure of the face-sharing bioctahedral complexes[14] indicates that there is a σ-bonding interaction between two Ti centers in **2**. The acute Ti−H−Ti angles ranging from 84.8(15) to 86.3(16)° are in keeping with the idea of a Ti−Ti bonding interaction. The Ti−H bond distances (1.92(3)−1.94(3) Å) are at the upper part of the range of those previously reported in bridging hydrides (1.71−2.08 Å).[5,13]

The structure of **2** observed in the solid state is persistent in solution. In the variable-temperature ^{1}H NMR spectra of **2** in toluene-d_8 between 213 and 298 K, the resonances from the ^{t}Bu-L ligand are essentially invariant. The methylene protons of the ligand are observed as two doublets. At low temperature (233 K), the hydride resonances appears as a doublet and a triplet with 2:1 integration at 16.6 and −1.33 ppm, coupled with each other with a 12.0 Hz coupling constant. When the sample is warmed to room temperature, the two hydride resonances broaden and shift slightly (16.7 and −1.12 ppm, 298 K). Unfortunately, the thermal instability of **2** prevents us from acquiring the high-temperature NMR spectra. The breadth of the hydride signals suggests that a slow exchange process is operative at room temperature. Thus, we have studied the dynamic behavior of **2** by variable-temperature ^{1}H NMR line shape analysis (243−298 K) of the two hydride resonances, which gave the following activation parameters: $\Delta H^{\ddagger} = 6.00\ (\pm 0.24)$ kcal mol^{-1}; $\Delta S^{\ddagger} = 28.4\ (\pm 0.9)$ cal mol^{-1} K^{-1}. The positive entropy of activation

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(8) A THF (1.0 M) solution of LiBHEt$_3$ (12.5 mL, 12.5 mmol) was added to **1** (2.91 g, 2.50 mmol) in toluene (60 mL) at −98 °C. The reaction mixture turned from dark red to dark greenish brown along with the evolution of H$_2$. The mixture was warmed to room temperature and was stirred for 12 h. The resulting greenish brown suspension was centrifuged, and the precipitate was extracted with toluene (60 mL). The combined supernatant was concentrated and stored at −30 °C to give **2** as brown needles (1.67 g, 50%). ^{1}H NMR (toluene-d_8, 298 K): δ 16.7 (s, 2 H, μ-H), 7.18 (s, 4 H, Ar H), 7.12 (s, 4 H, Ar H), 6.89 (s, 4 H, Ar H), 5.30 (d, J = 13.5 Hz, 4 H, CH$_2$), 3.41 (d, J = 13.5 Hz, 4 H, CH$_2$), 3.02 (br s. THF), 2.22 (s, 12 H, Me), 1.57 (s, 36 H, ^{t}Bu), 1.10 (br s. THF), 1.08 (s, 18 H, ^{t}Bu), −1.12 (s, 1 H, μ-H). ^{7}Li NMR (toluene-d_8, 298 K): δ 0.42 (s, 1 Li), −2.65 (s, 2 Li). Anal. Calcd for $C_{80}H_{113}Li_3O_9Ti_2$: C, 71.96; H, 8.53. Found: C, 71.08; H, 7.86.

(9) The structure of **2** is analogous to that of **2-Et$_2$O**.

(10) Data for **2** (173 K): space group $C2/m$; a = 19.516(8) Å, b = 30.102(13) Å, c = 15.339(6) Å, β = 96.149(8) °; V = 8959.3(65) Å^3; Z = 4; 35 838 measured reflections ($2\theta_{max}$ = 55°), 10 453 unique reflections; R1 = 0.093 ($I > 2\sigma(I)$); wR2 = 0.220 (all data). Data for **2-Et$_2$O** (173 K): space group $C2/m$; a = 19.453(6) Å, b = 29.861(8) Å, c = 15.260(5) Å, β = 95.550(4)°; V = 8822.7(44)Å^3; Z = 4; 34 881 measured reflections ($2\theta_{max}$ = 55°), 10 258 unique reflections; R1 = 0.078 ($I > 2\sigma(I)$); wR2 = 0.184 (all data). The hydrides were located from the different Fourier map, and their positions were refined, although the thermal parameters remained fixed.

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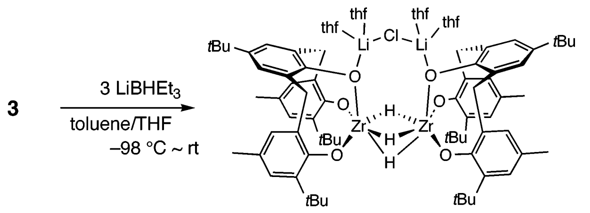
Scheme 2



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may be interpreted in terms of the dissociation of the bridging Li(1) cation in the transition state for hydride exchange. The characteristic hydride resonances are absent in the ^{1}H NMR spectrum of the trideuteride complex (**2-*d*$_3$**) prepared in the reaction of **1** and LiBDEt$_3$. In addition, the ^{1}H NMR spectrum of a mixture of **2** and **2-*d*$_3$** shows no evidence of any H/D exchange. The ^{7}Li NMR spectrum in toluene-d_8 consists of two singlets at 0.42 and −2.65 ppm in a 1:2 ratio. The upfield resonance is due to shielding anisotropy effects induced by the close proximity of Li(2) and Li(2′) to the center of the phenyl rings of the ligand.

In parallel studies, we are examining ^{t}Bu-L complexes of zirconium. A similar reaction of [Zr(^{t}Bu-L)Cl(thf)$_2$] (**3**) with LiBHEt$_3$ afforded **4** as colorless crystals in 59% yield (Scheme 2),[15] in which the Zr(IV) oxidation state is retained. The ^{1}H NMR spectrum of **4** in toluene-d_8 is consistent with a species of high symmetry. In contrast to **2**, the three hydrides are equivalent on the NMR time scale and appear as a singlet at 5.91 ppm. The ^{7}Li NMR spectrum displays a single resonance at −0.18 ppm.

The structure of **4** was clarified by a single-crystal X-ray analysis (Figure 2).[16] The molecule contains the [{Zr(^{t}Bu-L)}$_2$(μ-H)$_3$]$^-$ dimeric unit, which is analogous to that found in **2**. For **4**, one [Li−Cl−Li]$^+$ moiety spans the two central aryloxides (O(2) and O(5)) of the ligands. The accommodation of the [Li−Cl−Li]$^+$ moiety requires two (^{t}Bu-L)Zr fragments to be staggered at the O(2)−Zr(1)−Zr(2)−O(5) torsion angle of 53.1(2)°. Furthermore, each Zr center adopts a more trigonal-prismatic structure. The Zr−Zr separation of 3.163(1) Å is similar to those of [Cp*$_2$Zr$_2$(μ-H)$_3$Cl$_3$(PMe$_3$)] (3.126(1) Å)[17] and [Zr$_2$(μ-H)$_3$(BH$_4$)$_5$(PMe$_3$)$_2$] (3.124(1) Å).[18] In comparison with **2**, the angles at the hydride ligands are ca. 20° larger in **4**. The Zr−H distances fall in the ranges of those of other Zr bridging hydrides.[17−21]

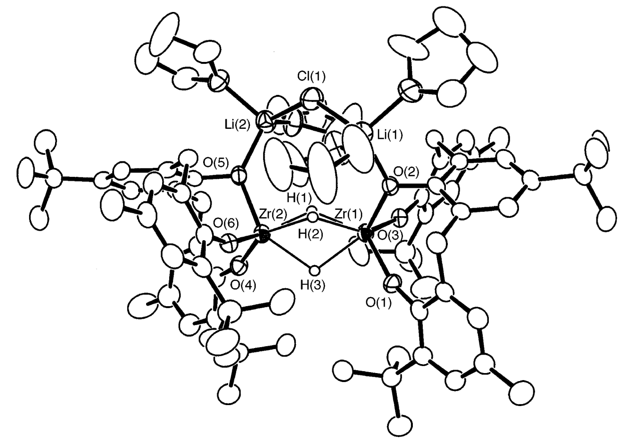

Figure 2. Structure of **4**. Selected interatomic distances (Å): Zr(1)−Zr(2) = 3.1630(10), Zr(1)−H(1) = 2.10(3), Zr(1)−H(2) = 1.95(4), Zr(1)−H(3) = 1.97(3), Zr(2)−H(1) = 1.92(3), Zr(2)−H(2) = 2.03(4), Zr(2)−H(3) = 1.98(3), Zr(1)−O(1) = 1.967(3), Zr(1)−O(2) = 1.967(3), Zr(1)−O(3) = 1.967(3), Zr(2)−O(4) = 1.958(3), Zr(2)−O(5) = 2.045(3), Zr(2)−O(6) = 1.973(3).

In conclusion, we have demonstrated that the tridentate aryloxide ligand can stabilize the Ti(III) and Zr(IV) dimers, which are rare examples of triple-hydride-bridging early transition metals. The facile synthesis of **2** and **4** provides us with a good opportunity to examine differences in the reactivity between d^1−d^1 and d^0−d^0 metal systems and to compare this reactivity with that of complexes bearing cyclopentadienyl ligands. The reactivity of these complexes is an ongoing study.

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Supporting Information Available: Text, tables, and figures giving experimental details, analytical data, spectroscopic data, and preliminary calculation results for **2-Et$_2$O**, **2**, and **4**; X-ray crystallographic data are available in electronic format as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] A THF (1.0 M) solution of LiBHEt$_3$ (1.50 mL, 1.50 mmol) was added to **3** (0.43 g, 0.55 mmol) in THF (20 mL). The mixture was warmed to room temperature and was stirred for 12 h. After evaporation of the solvent, the residue was extracted with toluene (20 mL). The solution was centrifuged, and then the supernatant was concentrated and stored at −30 °C to give colorless crystals of **4** (0.25 g, 59%). ^{1}H NMR (toluene-d_8, 298 K): δ 7.27 (s, 4 H, Ar H), 7.06 (s, 8 H, Ar H × 2), 5.91 (s, 3 H, μ-H), 4.98 (d, J = 13.5 Hz, 4 H, CH$_2$), 3.55 (br s. THF), 3.54 (d, J = 13.5 Hz, 4 H, CH$_2$), 2.30 (s, 12 H, Me), 1.48 (s, 36 H, ^{t}Bu), 1.38 (br s. THF), 0.96 (s, 18 H, ^{t}Bu). ^{7}Li NMR (toluene-d_8, 298 K): δ −0.18 (s). Anal. Calcd for $C_{84}H_{121}Li_2O_{10}ClZr_2 \cdot C_7H_8$: C, 67.69; H, 8.05. Found: C, 67.64; H, 8.04.

[16] Data for **4** (173 K): space group $P\bar{1}$; $a = 15.271(6)$ Å, $b = 17.876(6)$ Å, $c = 20.872(7)$ Å, $\alpha = 94.392(4)°$, $\beta = 106.356(3)°$, $\gamma = 108.872(4)°$; $V = 5084.1(31)$ Å^3; $Z = 2$; 39 248 measured reflections ($2\theta_{max} = 55°$), 21 602 unique reflections; R1 = 0.065 ($I > 2\sigma(I)$); wR2 = 0.130 (all data). The hydrides were located from the different Fourier map and refined isotropically.

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