Monocyclopentadienyltitanium(III) Complexes with Hydridoborato Ligands

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Graphic for Table of Contents and Abstract:
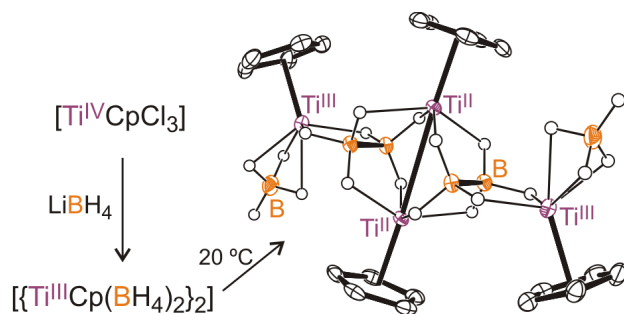
Abstract:

The synthesis, properties and reactivity of monocyclopentadienyltitanium(III) complexes stabilized by hydridoborato $(BH_3R)^-$ ligands are reported. The reactions of the titanium(IV) trichlorides $[Ti(\eta^5-C_5H_{5-n}Me_n)Cl_3]$ with excess $LiBH_3R$ (R = H, Me) afford dimeric $[\{Ti(\eta^5-C_5H_{5-n}Me_n)(BH_4)(\mu-BH_4)\}_2]$ (n = 5 (**1**), 4 (**2**), 0 (**3**)) or monomeric $[Ti(\eta^5-C_5Me_5)(BH_3Me)_2]$ (**4**) titanium(III) derivatives. Compound **3** is a thermally unstable oil and decomposes at room temperature forming a mixed-valence Ti^{II}/Ti^{III} tetrametallic species $[\{Ti(\eta^5-C_5H_5)(BH_4)\}_2\{(\mu_3-B_2H_6)Ti(\eta^5-C_5H_5)\}_2]$ (**5**) with dianionic diborane(6) ligands in a rare $\mu_3-\kappa^2:\kappa^2:\kappa^2-B_2H_6$ coordination mode. DFT calculations for **5** agree with a triplet ground state with two inner titanium(II) atoms bonded by a single bond and two outer titanium(III) centers. In contrast to **3**, the monomeric tetrahydrofuran adduct derivative $[Ti(\eta^5-C_5H_5)(BH_4)_2(thf)]$ (**6**) is a stable solid. Dimeric **1-3** react with 2,6-lutidinium salts (LutH)X (X = BPh_4, OSO_2CF_3) to afford ion pairs, $[Ti(\eta^5-C_5H_{5-n}Me_n)(BH_4)L_2](BPh_4)$ (L = thf, n = 5 (**7**), 4 (**8**), 0 (**9**); L = py, n = 5 (**10**)), or molecular aggregates, $[\{Ti(\eta^5-C_5Me_5)(BH_4)(\mu-O_2SOCF_3)\}_2]$ (**11**) and $[\{Ti(\eta^5-C_5H_{5-n}Me_n)(\mu-O_2SOCF_3)_2\}_x]$ (n = 5, x = 3 (**12**); n = 4, x = 4 (**13**)), via formation of H_2 and (Lut)BH_3. Diamagnetic titanium(II) derivatives $[\{Ti(\eta^5-C_5Me_5)(\mu-H)\}_2\{(\mu-H)_2Al(BH_3R)(thf)\}_2]$ (R = H (**14**), Me (**15**)) were isolated in reactions of complexes **1** and **4** with $LiAlH_4$ in tetrahydrofuran.

Introduction

Low-valent titanium complexes are highly reducing species with important applications as reagents and catalysts for many organic transformations and small-molecule activation processes.[1,2] In particular, titanium(III) complexes, and especially the bis(cyclopentadienyl)titanium(III) chloride [Ti(η^5-C$_5$H$_5$)$_2$Cl] (Nugent-RajanBabu reagent), are widely used in single-electron transfer reactions for the synthesis of organic compounds.[2,3] Titanium(II) species are also versatile reagents for two-electron redox chemistry with implications in a variety of C–X (X = C, O, B, N) bond-forming reactions.[1,4,5,6]

Owing to the stability of the high-valent titanium(IV) state, low-valent systems are usually prepared by treatment of titanium(IV) halide or alkoxide precursors with reducing metals or metal alkyls such as an alkyllithium or Grignard reagent having β-hydrogens.[2,7] The formation of titanium(II) species requires the use of strong reductants (alkali and alkaline-earth metals, NaC$_{10}$H$_8$, KC$_8$, LiAlH$_4$, etc.),[8] while weaker reducing metals (e.g., Zn, Mn) or organic reagents (e.g., organosilane reductants,[9] benzylamine[10]) are more appropriated for preparing titanium(III) compounds. In particular, the synthesis of titanium(III) tetrahydridoborato complexes by treatment of titanium(IV) halides with the mild reductant LiBH$_4$ has been known for decades.[11] The versatile tetrahydridoborato ligand stabilizes the titanium atoms through bridging hydrogen atoms, being the κ^2- and κ^3-coordination modes of the BH$_4^-$ group the most common for this element.[12] The titanium(III) tetrahydridoborato complexes exhibit variable thermal stability depending on the presence of other accompanying ligands in the coordination sphere of the metal. For instance, the homoleptic tetrahydridoborato complex [Ti(BH$_4$)$_3$] is an unstable volatile material that decomposes spontaneously at room temperature with hydrogen and diborane release.[13] The

thermal stability is enhanced in Lewis acid–base adducts $[Ti(BH_4)_3L_n]$ (n = 1, 2),[14] or by replacement of BH_4 units by strong stabilizing cyclopentadienyl ligands. Thus, the bis(cyclopentadienyl)titanium(III) tetrahydridoborato complex $[Ti(\eta^5-C_5H_5)_2(BH_4)]$ can be purified by sublimation at 120 ºC.[15] The synthesis of the monocyclopentadienyltitanium(III) bis(tetrahydridoborato) derivative $[Ti(\eta^5-C_5H_5)(BH_4)_2]$ was presented in 1968 by James and co-workers at the 155th ACS National Meeting.[16] This compound was described as a volatile green solid which melted below 25 ºC and displayed a thermal stability between $[Ti(BH_4)_3]$ and $[Ti(\eta^5-C_5H_5)_2(BH_4)]$, but further data have not been published later in the literature.[11] In contrast, monocyclopentadienyltitanium(III) chloride-tetrahydridoborato derivatives have been isolated as stable solids with dimeric structures $[\{Ti(\eta^5-C_5R_5)(BH_4)(\mu-Cl)\}_2]$ (R = H,[17] Me[18]) according to X-ray crystal structure determinations. Girolami and co-workers have reported the reduction of the latter pentamethylcyclopentadienyl derivative by treating with $[Li(nBu)]$ in the presence of chelating bisphosphanes to obtain mononuclear paramagnetic titanium(II) complexes $[Ti(\eta^5-C_5Me_5)(BH_4)(PP)]$ (PP = 1,2-bis(dimethylphosphino)ethane or (tert-butyl)tris(dimethylphosphinomethyl)silane) which are catalysts for the oligomerization of alkenes.[19]

Monocyclopentadienyl hydridoborato complexes are also implicated as key intermediates in the synthesis of metallaboranes by reaction of metal halides with monoborane precursors $(LiBH_4$ or $BH_3(thf))$.[20] This synthetic route has been intensively investigated by the groups of Fehlner and Ghosh to develop a variety of diborane and other borane moieties supported by cyclopentadienyl transition metal complexes.[21,22]

As part of a project devoted to the development of new structures and reactivity patterns of low-valent titanium complexes, we recently reported a detailed study on monopentamethylcyclopentadienyltitanium(III) dihalides.[23,24] Several $[Ti(\eta^5-C_5Me_5)Cl_2]$

derivatives were prepared by thermal homolysis or hydrogenolysis of the Ti–C(methyl) bond of [Ti(η^5-C$_5$Me$_5$)Cl$_2$Me] or by reaction of [Ti(η^5-C$_5$Me$_5$)Cl$_3$] with stoichiometric amounts of conventional reducing agents (Mg, LiAlH$_4$, Li$_3$N). Reduction of the latter titanium(IV) trichloride precursor with an excess of magnesium led to a mixed-valence Ti^{II}/Ti^{III} trinuclear complex [{Ti(η^5-C$_5$Me$_5$)(μ-Cl)}$_3$(μ_3-Cl)] capable of activating dinitrogen under ambient conditions.[25] Analogous treatment of [Ti(η^5-C$_5$Me$_5$)X$_3$] with excess LiAlH$_4$ in ethereal solvents (L) produced titanium(II) species [{Ti(η^5-C$_5$Me$_5$)(μ-H)}$_2${(μ-H)$_2$AlXL}$_2$] (L = thf, X = Cl, Br; L = OEt$_2$, X = Cl), while the reactions with the milder reductant LiBH$_4$ gave titanium(III) tetrahydridoborato complexes.[26] In particular, the X-ray crystal structure of the bis(tetrahydridoborato) derivative showed a dimer [{Ti(η^5-C$_5$Me$_5$)(BH$_4$)(μ-BH$_4$)}$_2$] with two bridging BH$_4$ ligands between the metal centers (Scheme 1).

Herein, we report the synthesis of several monocyclopentadienyltitanium(III) bis(hydridoborato) [Ti(η^5-C$_5$H$_{5-n}$Me$_n$)(BH$_3$R)$_2$] derivatives by reduction of titanium(IV) trichloride complexes with excess LiBH$_4$. This route provides the bis(hydridoborato) complexes in high purity, enabling us to undertake a detailed study of the properties of these poorly-characterized titanium(III) species. The novel complexes have been evaluated as precursors in the synthesis of other titanium(III) derivatives by their reactions with lutidinium salts (LutH)X or in the preparation of titanium(II) complexes through further reduction with LiAlH$_4$.

Results and Discussion

Synthesis and properties of titanium(III) complexes with hydridoborato ligands. The treatment of $[Ti(\eta^5\text{-}C_5H_{5-n}Me_n)Cl_3]$ (n = 5, 4, 0) with finely powdered $LiBH_4$ ($\geq$ 3 equiv) in toluene at room temperature afforded the titanium(III) derivatives $[\{Ti(\eta^5\text{-}C_5H_{5-n}Me_n)(BH_4)(\mu\text{-}BH_4)\}_2]$ (n = 5 (**1**), 4 (**2**), 0 (**3**)) (Scheme 1). We have previously reported the synthesis of **1** in 80% yield as a dark-blue pyrophoric solid which melts at 67-68 °C.[26] Complex **1** was also obtained in the attempted sublimation of $[Ti(\eta^5\text{-}C_5Me_5)(BH_4)_2(thf)]$ (75 °C, 0.1 Torr), and was stable in benzene-d_6 solutions up to 65 °C.[26] In contrast, the analogous complexes **2** and **3** were isolated as greenish-brown oils in lower yields (58 and 49%, respectively) presumably due to their higher volatility under dynamic vacuum. While complex **2** appears to be stable at room temperature for some weeks under argon, $[\{Ti(\eta^5\text{-}C_5H_5)(BH_4)(\mu\text{-}BH_4)\}_2]$ (**3**) decomposed in a few hours at 20 °C, or in several days at –35 °C, to form a brown crystalline solid (vide infra).
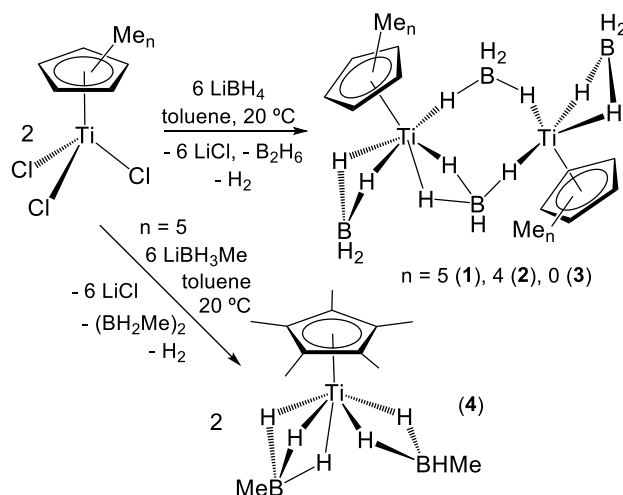

Scheme 1. Synthesis of bis(hydridoborato)titanium(III) complexes **1-4**.

The analogous reaction of $[Ti(\eta^5\text{-}C_5Me_5)Cl_3]$ with excess $LiBH_3Me$ led to the monomeric derivative $[Ti(\eta^5\text{-}C_5Me_5)(BH_3Me)_2]$ (**4**) in 93% yield. Complex **4** was isolated as a black solid which melts at 66-69 °C and sublimes at 65-68 °C under dynamic vacuum (0.1

Torr) to give dark-blue crystals. While the methyltrihydridoborato complex **4** was readily obtained in a pure form because the LiCl, H_2 and $(BH_2Me)_2$ byproducts are easily removed, the isolation of the analogous phenyltrihydridoborato derivative $[Ti(\eta^5-C_5Me_5)(BH_3Ph)_2]$ was challenging. Treatments of $[Ti(\eta^5-C_5Me_5)Cl_3]$ with $LiBH_3Ph$ in toluene repeatedly gave a mixture of $[Ti(\eta^5-C_5Me_5)(BH_3Ph)_2]$ and triphenylborane. The formation of the BPh_3 byproduct is most likely due to substituent redistribution of generated $(BH_2Ph)_2$ in the reaction.[27] Complex $[Ti(\eta^5-C_5Me_5)(BH_3Ph)_2]$ and BPh_3 exhibit a similar volatility and solubility in common solvents precluding the isolation of pure samples of the titanium(III) complex. Nevertheless, crystallization in hexane at $-35\ ^{\circ}C$ gave a mixture of white crystals of BPh_3 and dark-green crystals of $[Ti(\eta^5-C_5Me_5)(BH_3Ph)_2]$ suitable for an X-ray crystal structure determination (Figure S1 of the Supporting Information).

IR spectra (KBr) of complexes **1-3** show multiple absorptions in the range 2550-1920 cm^{-1} for the B–H stretching vibrations of the diverse terminal and bridging BH_4^- ligands of the molecules.[11,12] The ^1H NMR spectra of compounds **1-4** in benzene-d_6 are silent according to their paramagnetic nature. The magnetic moment measurements for complexes **1-3** in benzene-d_6 solution at room temperature by the Evans Method gave μ_{eff} values of 2.36, 1.97 and 2.39 μ_B per dimer. These effective magnetic moments in solution at 295 K are slightly lower than that expected for the theoretical spin-only value (2.45 μ_B) for two non-interacting spins S = 1/2 in a dinuclear titanium(III) complex. On the other hand, the magnetic moment measurement of **4** in benzene-d_6 at room temperature gave a $\mu_{eff} = 1.77\ \mu_B$ in good agreement with that estimated (1.73 μ_B) for the spin-only magnetic moment of a mononuclear species with an unpaired electron.

X-ray diffraction on a single crystal of **4** revealed a mononuclear structure with the titanium center bonded to one $\eta^5-C_5Me_5$ group and five μ-H bridging hydrides of two BH_3Me

ligands (Figure 1). If the centroid of the η^5-C_5Me_5 ring is considered, the coordination geometry about the titanium atom can be described as distorted octahedral. The κ^3-coordinated BH_3Me group exhibits a Ti(1)$\cdots$B(1) distance of 2.157(2) Å, which is shorter than that found for the κ^2-BH_3Me ligand, Ti(1)$\cdots$B(2) 2.377(2) Å. While the former Ti$\cdots$B length is similar to those determined for the κ^3-BH_3Me ligands in [{Ti(η^5-C_5Me_5)(BH_3Me)}$_2$(μ-B_2H_6)] (2.162(3) and 2.170(3) Å),[26] the latter Ti$\cdots$B distance compares well with that found for the κ^2-coordinated BH_3Me ligand in [Ti(η^5-C_5H_5)$_2$(BH_3Me)] (2.402(12) Å).[28] The analogous phenyltrihydridoborato derivative [Ti(η^5-C_5Me_5)(BH_3Ph)$_2$] crystallized with two independent molecules in the asymmetric unit (Figure S1). There are no substantial differences between the two molecules, and both exhibit κ^2-BH_3Ph and κ^3-BH_3Ph ligands bonded to each titanium center in a fashion similar to complex **4**.
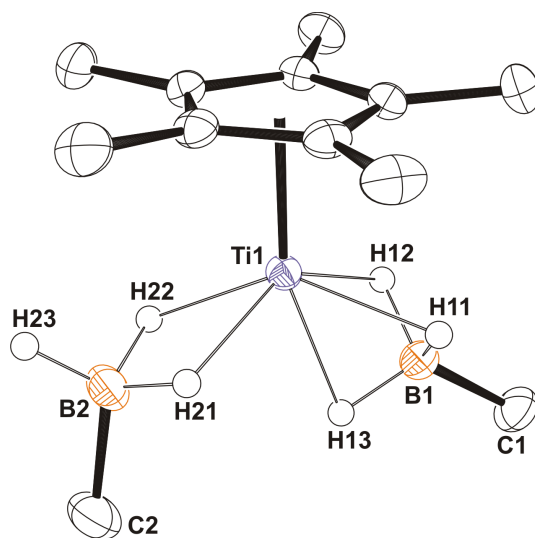
Figure 1. Perspective view of **4** with thermal ellipsoids at the 50% probability level. Hydrogen atoms of the methyl groups are omitted for clarity. Selected lengths (Å): Ti(1)–H 1.83(2)-1.97(2), Ti(1)$\cdots$B(1) 2.157(2), Ti(1)$\cdots$B(2) 2.377(2), B(1)–C(1) 1.575(2), B(2)–C(2) 1.599(3).

As mentioned above, complex **3** was isolated as a thermally unstable and volatile greenish-brown oil in good agreement with properties observed by James and co-workers.[11,16] The thermal decomposition of pure **3** under an argon atmosphere was examined (Scheme 2). A weighted sample of **3** at room temperature for 48 h underwent a mass loss of 18%, while a dark-brown crystalline solid formed at the bottom of the Schlenk tube. The IR spectrum and elemental analysis of this solid are different from those of complex **3**, and its structure was determined to be $[\{Ti(\eta^5\text{-}C_5H_5)(BH_4)\}_2\{(\mu_3\text{-}B_2H_6)Ti(\eta^5\text{-}C_5H_5)\}_2]$ (**5**) by an X-ray diffraction experiment on brown crystals grown from a hexane solution at –35 °C. Thus, complex **5** was isolated in 87% yield assuming the formation of volatile H_2 and B_2H_6 byproducts. The ^1H NMR spectrum of **5** in benzene-d_6 is silent and the magnetic moment measurement of this solution afforded a value of 2.27 μ_B which is slightly lower than that of complex **3** (2.39 μ_B).
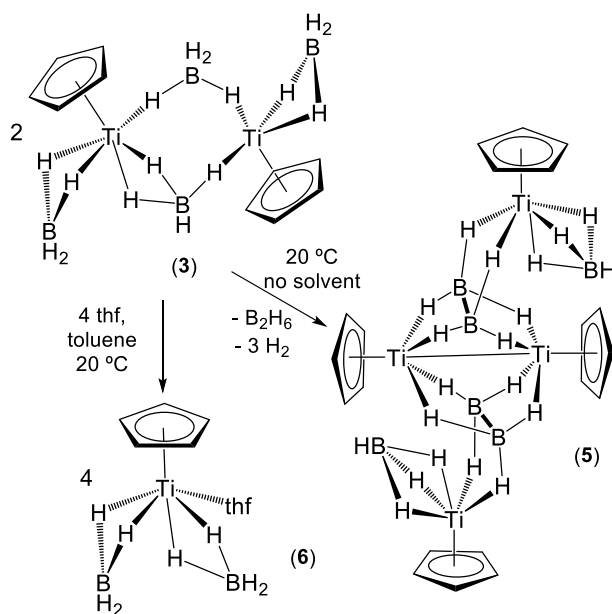

Scheme 2. Properties of complex **3**.

Complex **3** seems to be more thermally stable in solution since the ^1H NMR spectra of a highly concentrated solution of **3** in benzene-d_6 only showed the resonance signal for H_2 (δ

= 4.46) after 10 days at room temperature. The treatment of a freshly prepared toluene solution of **3** with an excess (ca. 7 equiv) of tetrahydrofuran at room temperature led to the precipitation of the monomeric adduct [Ti(η^5-C$_5$H$_5$)(BH$_4$)$_2$(thf)] (**6**) (Scheme 2). Complex **6** was isolated in 58% yield as a blue solid which is very soluble in tetrahydrofuran and somewhat soluble in toluene and benzene. In contrast to **3**, a solid sample of **6** under argon atmosphere maintained the original blue color and exhibited identical IR spectrum after three weeks at room temperature. Nevertheless, a small fraction of blue crystals of **6** sublimed at the top of the flask within a few days at room temperature. The poor quality of the crystals precluded an accurate X-ray crystal structure determination, but a mononuclear structure similar to that found in the analogous complex [Ti(η^5-C$_5$Me$_5$)(BH$_4$)$_2$(thf)] could be unambiguously established.[26] The ^{1}H NMR spectrum of complex **6** in benzene-d$_6$ shows only two broad resonances in a 1:1 ratio at δ = 4.09 and 3.35 which could be assigned to the tetrahydrofuran ligand. The magnetic moment measurement for a solution of **6** in benzene-d$_6$ at room temperature gave a μ_{eff} = 1.80 μ_B in good agreement with a mononuclear species with one unpaired electron.

The X-ray crystal structure of **5** shows two {Ti(η^5-C$_5$H$_5$)(BH$_4$)} units connected by one dimetallic {(μ_3-B$_2$H$_6$)Ti(η^5-C$_5$H$_5$)}$_2$ fragment (Figure 2). Molecules of **5** lie on an inversion center in the midpoint of the Ti(1)-Ti(1)^i segment. The Ti(2) atoms of the terminal {Ti(η^5-C$_5$H$_5$)(BH$_4$)} units exhibit a distorted octahedral geometry if the centroid of the η^5-C$_5$H$_5$ ligand is considered. Thus, each Ti(2) atom is bonded to one η^5-C$_5$H$_5$ ligand, three hydrogen atoms of a κ^3-BH$_4$ group, and two non-geminal hydrogen atoms of one μ_3-B$_2$H$_6$ ligand. The Ti(2)$\cdots$B(3) distance of 2.165(3) Å is typical for κ^3-BH$_4$ groups bonded to titanium(III) centers,[12,18] and it is clearly shorter than the Ti(2)$\cdots$B(1) and Ti(2)$\cdots$B(2) lengths associated to the B$_2$H$_6$ ligands of 2.454(2) and 2.473(2) Å, respectively. The remaining four hydrogens

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of each B_2H_6 ligand are bridging the Ti(1) and Ti(1)^i atoms which exhibit classical four-legged piano stool geometries with four hydrides at the legs. While the coordination mode μ-κ^2:κ^2 is well-documented for $(B_2H_6)^{2-}$ ligands,[21] examples of structurally characterized μ_3-κ^2:κ^2:κ^2-B_2H_6 groups are limited to a few trinuclear manganese or rhenium carbonyl complexes.[29] The B–B bond length of 1.746(3) Å in **5** is slightly longer than those found in the mentioned group 7 complexes (1.681(6)-1.706(7) Å). The central $\{(\mu_3$-$B_2H_6)Ti(\eta^5$-$C_5H_5)\}_2$ fragment of **5** strongly resembles the dinuclear titanium(III) complex $[\{Ti(\eta^5$-$C_5Me_5)(\mu$-$B_2H_6)\}_2]$ with two bridging μ-κ^2:κ^2-B_2H_6 diborane(6) ligands.[26] Despite the short Ti$\cdots$Ti separation in the crystal structure of that complex (2.936(1) and 2.948(1) Å in the two independent molecules), theoretical calculations revealed the absence of metal–metal bond and a triplet structure on the ground state was calculated in accord with the experimental μ_{eff} value of 2.33 μ_B. By comparison, the Ti(1)–Ti(1)^i distance is longer in complex **5**, 3.071(1) Å, while a similar magnetic moment of 2.27 μ_B was determined.
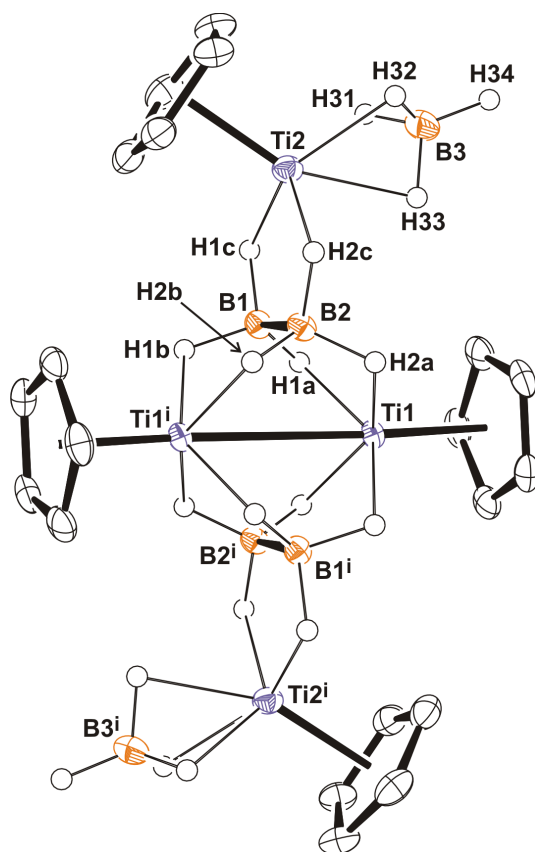
Figure 2. Perspective view of **5** with thermal ellipsoids at the 50% probability level. Hydrogen atoms of the cyclopentadienyl rings have been omitted for clarity. Selected lengths (Å): Ti–H 1.83(3)-2.00(3), Ti(1)···B(1) 2.376(2), Ti(1)···B(2) 2.412(2), Ti(1)···B(1)^i 2.410(2), Ti(1)···B(2)^i 2.402(2), Ti(2)···B(1) 2.454(2), Ti(2)···B(2) 2.473(2), Ti(2)···B(3) 2.165(3), B(1)–B(2) 1.746(3), Ti(1)–Ti(1)^i 3.071(1), Ti(1)···Ti(2) 4.169(1), Ti(1)···Ti(2)^i 4.263(1). Symmetry code: (i) $1 - x$, $1 - y$, $1 - z$.

Density functional theory (DFT) calculations have been carried out to understand the electronic structure of the tetrametallic complex **5** and to explain its magnetic data (B3LYP/TZVP + NBO analysis, see the Computational details section below). Given the total negative charges (10–) of the η^5-C_5H_5, BH_4 and B_2H_6 ligands a mixed-valence Ti^{II}/Ti^{III} species can be anticipated. For this reason, various electronic spin distributions, containing two Ti^{II} and two Ti^{III} centers, were computed with different overall spin states. These include one septet, a couple of different quintets, and several triplet and singlet structures. Among all

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the computed structures, the best one in terms of energy seems to display an open-shell singlet spin state distribution. This calculation suggests that the central Ti atoms (Ti1 and Ti2) may have a +2 oxidation state while the the outer Ti atoms (Ti3 and Ti4) should adopt a +3 oxidation state (Figure 3a). However, this singlet spin distribution showcases a relatively high spin contamination, indicating that it may contain several contributions of higher multiplicity, which end up producing an erroneous –too low– final energy. In addition, the magnetic measurement experiments show that complex **5** has a higher spin ground state (2.33 μ_B). This prompted us to explore the calculations of higher multiplicity electronic distributions. Neither of the triplets, the quintets nor the septet show large spin contamination issues and thus the best one of them was chosen as representative of the electronic structure of complex **5**. The best triplet state solution is only slightly higher in energy than the spin contaminated singlet (*ca.* +4 kcal mol^{-1}), and should have an expected magnetic moment (2.27 μ_B for two unpaired electrons) similar to that observed experimentally. This triplet spin distribution showcases the electronic structure shown in Figure 3b, in which again the inner Ti atoms should have an oxidation state close to +2 while the outer Ti atoms seem to be in a *ca.* +3 oxidation state. The geometry optimization of this electronic arrangement proceeds with minimal distortion of the initial crystal structure of the complex, indicating that the spin distribution should be close to that adopted by the tetranuclear species.

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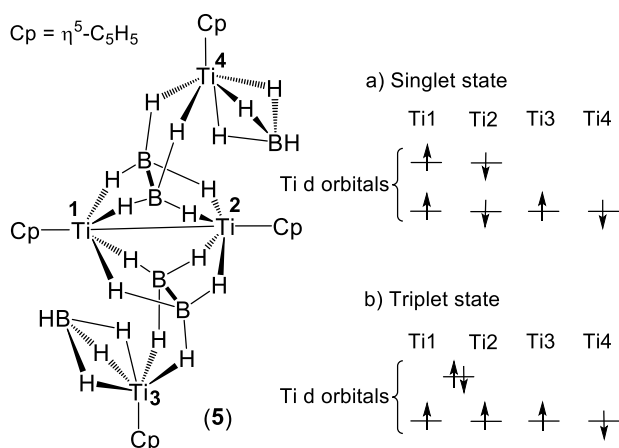
Figure 3. Computed best a) singlet and b) triplet electronic structures for compound **5**.

The computed Natural Bond Orbital (NBO) analysis for this triplet indicates that there is a single bond between both Ti1 and Ti2 (Figure 4a), while the other unpaired electrons remain in semioccupied d orbitals: alpha for Ti1, Ti2 and Ti3, and beta for Ti4 (Figure S5). The overall spin density (Figure 4b) for compound **5** results in two unpaired electrons pointing in the same orientation (α), so this compound should be expected to be paramagnetic, as observed in the experimental magnetic measurements. The most remarkable donor/acceptor interactions in complex **5** correspond to electron density donation from the B–H units, present both in the BH_4 and in the B_2H_6 ligands, to empty d orbitals of the titanium centers (Figure S6). The delocalization energies, computed by NBO7, range from 5 to 20 kcal mol^{-1}, suggesting that the non-covalent interactions have a reasonable impact on the stabilization of the complex.
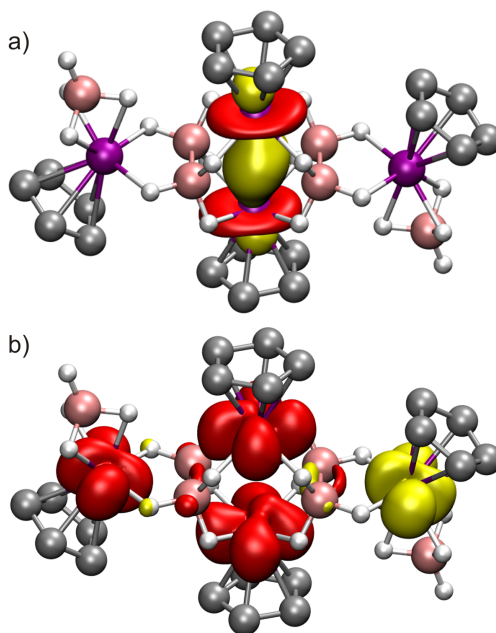

Figure 4. Computed a) doubly occupied Ti–Ti bond NBO orbital and b) spin density for compound **5**.

As mentioned above, the selected triplet structure has negligible spin contamination. Obviously, this is not the only triplet structure that may be found, and the inverted triplet spin distribution may be equally probable. The DFT calculations seems to indicate that there are other similar triplet structures close in energy to the one shown in Figure 3b; for instance, the triplet with two alpha electrons in Ti1, two beta electrons in Ti2, and one alpha electron in both Ti3 and Ti4 has a similar energy but a slightly higher spin contamination. In summary, there seems to be close spin distributions (both spin contaminated singlets and triplets) that may contribute to the overall configuration of the complex and this complicates the electronic structure analysis. Nevertheless, the agreement of the experimental data with the selected triplet electronic distribution suggests that the latter provides a proper description of the bonding situation.

Reactivity of Titanium(III) Hydridoborato Complexes.

The reactivity of the bis(tetrahydridoborato) complexes [{Ti(η^5-C$_5$H$_{5-n}$Me$_n$)(BH$_4$)(μ-BH$_4$)}$_2$] (n = 5 (**1**), 4 (**2**), 0 (**3**)) with 2,6-lutidinium salts (LutH)X (Lut = 2,6-Me$_2$C$_5$H$_3$N; X = BPh$_4$, OSO$_2$CF$_3$) was examined (Scheme 3). The reaction of dimeric complexes **1-3** with 2 equiv of 2,6-lutidinium tetraphenylborate (LutH)(BPh$_4$) in a 4:1 toluene–tetrahydrofuran mixture at room temperature led to the immediate precipitation of the ionic compounds [Ti(η^5-C$_5$H$_{5-n}$Me$_n$)(BH$_4$)(thf)$_2$](BPh$_4$) (n = 5 (**7**), 4 (**8**), 0 (**9**)) with vigorous gas evolution. No reaction between complexes **1-3** and (LutH)(BPh$_4$) was observed in absence of tetrahydrofuran presumably due to the insolubility of the lutidinium salts in toluene. The reactions most likely involve formation of H$_2$ by interaction of protonic [LutH]$^+$ ion with the hydridic BH$_4^-$ ligand and subsequent abstraction of the BH$_3$ by the Lewis base lutidine to form the soluble acid-base adduct (Lut)BH$_3$. Compounds **7-9** were isolated in 79-90% yield

as blue powders which are only slightly soluble in tetrahydrofuran. The analogous reaction of **1** with (LutH)(BPh$_4$) (2 equiv) in a 4:1 toluene–pyridine mixture afforded [Ti(η^5-C$_5$Me$_5$)(BH$_4$)(py)$_2$](BPh$_4$) (**10**) in 84% yield as a green solid which is only poorly soluble in pyridine. According to their paramagnetic nature, the ^{1}H NMR spectra of complexes **7-10** in tetrahydrofuran-d$_8$ or pyridine-d$_5$ are silent and their low solubility in those solvents precluded the determination of the magnetic moments in solution. The IR spectra (KBr) of complexes **7-10** show two absorptions between 2539 and 2059 cm^{-1} for the B–H bonds of the κ^3-BH$_4$ ligands,[11,12] and three bands between 1580 and 1427 cm^{-1} which are characteristic of the tetraphenylborate anion.[30]
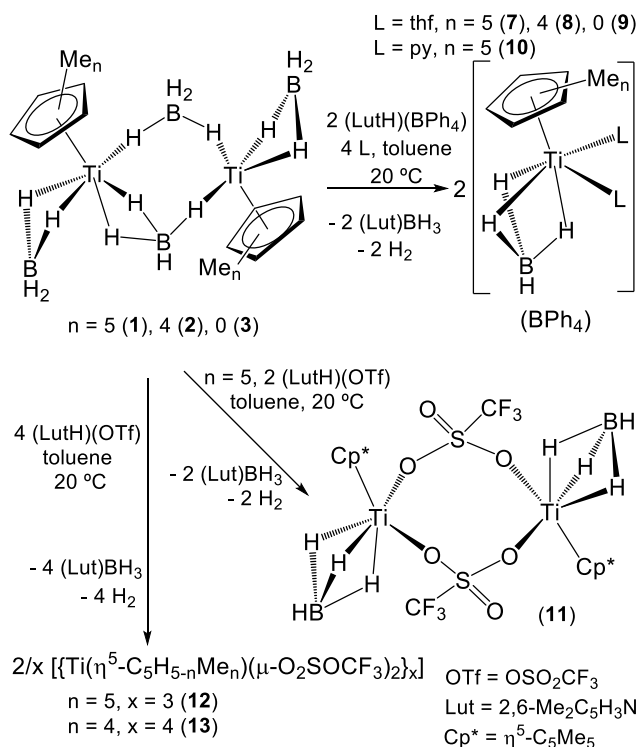
Scheme 3. Reactivity of complexes **1-3** with lutidinium salts (LutH)X.

The X-ray crystal structures of compounds **7** and **8** show two independent ion pairs of [Ti(η^5-C$_5$H$_{5-n}$Me$_n$)(BH$_4$)(thf)$_2$]$^+$ cations and (BPh$_4$)$^-$ anions in the asymmetric unit. There are no substantial differences between the ion pairs of each compound, and the structure of one of the cations of **7** is shown as example in Figure 5 whereas the second cation of **7** and those

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of **8** are presented in Figures S2 and S3 of the Supporting Information. The titanium atoms of the cations exhibit a distorted octahedral geometry with the vertexes occupied by three hydrogens of one κ^3-BH$_4$ ligand, the oxygen atoms of two tetrahydrofuran molecules, and one η^5-C$_5$H$_{5-n}$Me$_n$ ring. The Ti$\cdots$B distances range between 2.178(6) and 2.196(2) Å and are similar to those found in other titanium(III) complexes with κ^3-coordinated BH$_4$ groups such as **5** and [{Ti(η^5-C$_5$Me$_5$)(BH$_4$)(μ-Cl)}$_2$] (2.220(9) Å).[18] The Ti–O bond lengths (2.089(3)-2.126(3) Å) compare well with those determined in the titanium(III) derivatives with tetrahydrofuran ligands [Ti(η^5-C$_5$Me$_5$)Cl$_2$(thf)] (2.083(2) Å)[23,31] and [Ti(η^5-C$_5$Me$_5$)(BH$_4$)$_2$(thf)] (2.111(2) Å).[26]
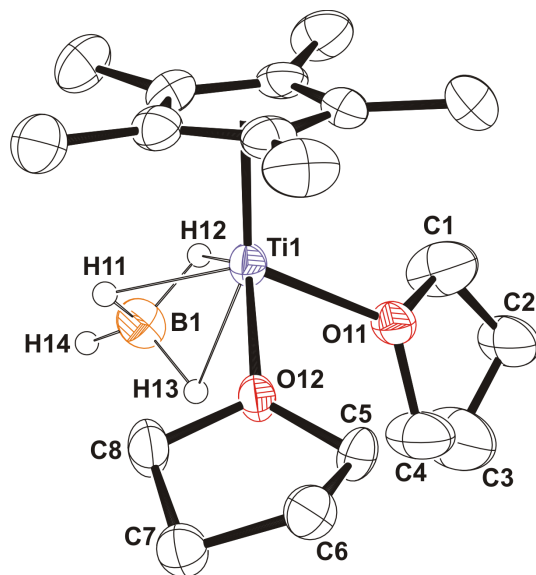
Figure 5. Perspective view of the cation in one independent ion pair of **7** with thermal ellipsoids at the 50% probability level. Hydrogen atoms of the pentamethylcyclopentadienyl and tetrahydrofuran ligands are omitted for clarity. Selected lengths (Å) and angles (deg): Ti(1)–H 1.85(6)-2.14(5), Ti(1)$\cdots$B(1) 2.178(6), Ti(1)–O(11) 2.123(3), Ti(1)–O(12) 2.107(3), O(11)–Ti(1)–O(12) 86.7(1).

The treatment of [{Ti(η^5-C$_5$Me$_5$)(BH$_4$)(μ-BH$_4$)}$_2$] (**1**) with 2 and 4 equiv of 2,6-lutidinium trifluoromethanesulfonate (LutH)(OTf) (OTf = OSO$_2$CF$_3$) in toluene at room

temperature led to the formation of H_2, the acid-base adduct (Lut)BH_3, and the triflato-bridged complexes [{Ti(η^5-C_5Me_5)(BH_4)(μ-O_2SOCF_3)}$_2$] (**11**) and [{Ti(η^5-C_5Me_5)(μ-O_2SOCF_3)$_2$}$_3$] (**12**), respectively (Scheme 3). While green crystals of the trimer **12** precipitated in 55% yield from the reaction mixture, the separation of the dimer **11** from the lutidine-borane adduct was complicated since both compounds exhibit similar solubility in hydrocarbon solvents. Nevertheless, complex **11** was isolated in 62% yield as a dark-green solid after sublimation of the (Lut)BH_3 byproduct under dynamic vacuum (120 ºC, 0.1 Torr).

IR spectra (KBr) of compounds **11** and **12** show several strong absorptions between 1338 and 1021 cm^{-1} for the coordinated trifluoromethanesulfonato groups.[32] In addition, the IR spectrum of **11** displays two bands at 2533 and 2065 cm^{-1} for the terminal and bridging B–H bonds of the κ^3-BH_4 ligands.[11,12] The ^{1}H NMR spectrum of **11** in benzene-d_6 is silent and the magnetic moment measurement in solution gave a value of 2.52 μ_B per dimer. In contrast, the negligible solubility of **12** in aromatic hydrocarbon or donor solvents (tetrahydrofuran-d_8 or pyridine-d_5) precluded the determination of its magnetic moment by NMR spectroscopy.

The crystal structure of **11** shows two {Ti(η^5-C_5Me_5)(BH_4)} units connected by two μ-O_2SOCF_3 bridging triflato ligands to form an eight-membered [$O_4S_2Ti_2$] ring (Figure 6). Molecules of **11** lie on an inversion center in the midpoint between the titanium atoms, which are separated by a long Ti$\cdots$Ti distance of 5.269(1) Å. Each titanium atom exhibits a distorted octahedral geometry with three hydrogens of one κ^3-BH_4 ligand (Ti$\cdots$B distance of 2.175(6) Å), two oxygen atoms of the μ-O_2SOCF_3 groups, and the η^5-C_5Me_5 ligand at the vertexes. The Ti–O bond lengths of 2.082(3) and 2.123(3) Å compare well with those determined in other dimeric titanium complexes with bridging triflato ligands.[33,34]
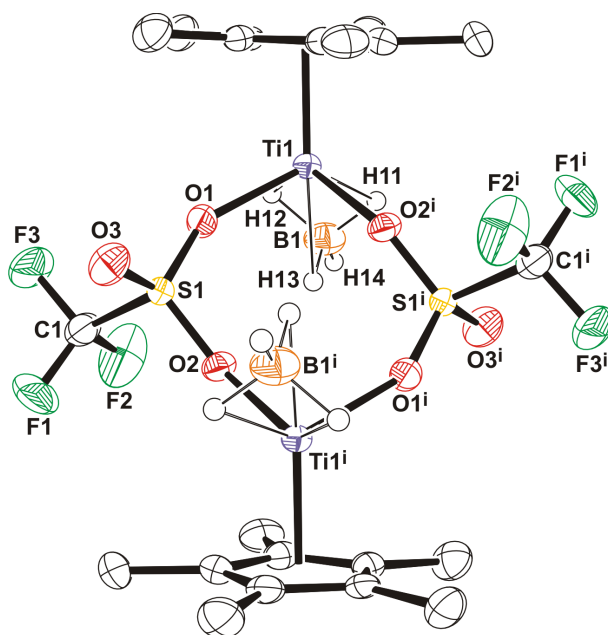
Figure 6. Perspective view of **11** with thermal ellipsoids at the 50% probability level. Hydrogen atoms of methyl groups are omitted for clarity. Selected lengths (Å) and angles (deg): Ti(1)–H 1.90(4)-2.06(4), Ti(1)···B(1) 2.175(6), Ti(1)–O(1) 2.082(3), Ti(1)–O(2)^i 2.123(3), Ti(1)···Ti(1)^i 5.269(1), O(1)–Ti(1)–O(2)^i 84.8(1). Symmetry code: (i) $1 - x$, $1 - y$, $1 - z$.

Crystals of **12**·C$_6$H$_6$ suitable for an X-ray crystal structure determination were obtained by slow cooling to room temperature of a heated suspension of **12** in benzene at 80 ºC. The crystal structure of **12** shows three titanium atoms forming an equilateral triangle (Ti···Ti averaged of 5.22(1) Å), wherein each edge of the triangle is bridged by two μ-O$_2$SOCF$_3$ bridging triflato ligands (Figure 7). Thus, there are three eight-membered [O$_4$S$_2$Ti$_2$] rings connected through the titanium centers. The titanium atoms have classical four-legged piano-stool arrangements, where the legs are occupied by oxygen atoms of four triflato groups. The titanium–oxygen bond lengths of averaged 2.12(1) Å are similar to those found in complex **11** and other half-sandwich titanium complexes with bridging triflato ligands.[33,34]
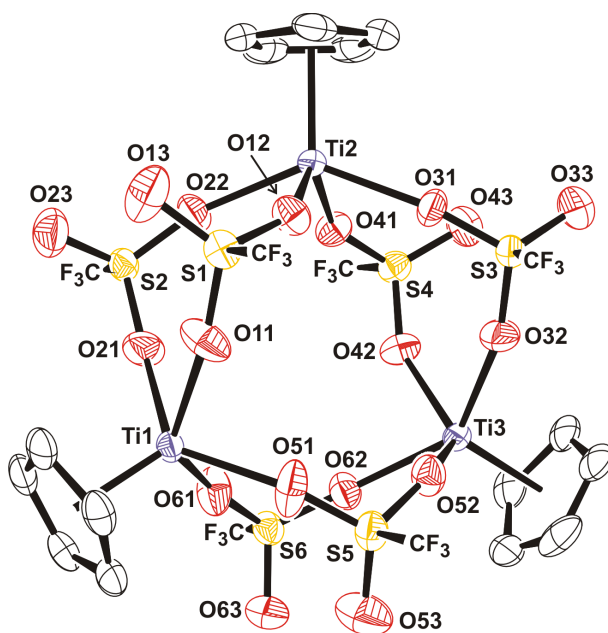
Figure 7. Perspective view of **12**·C_6H_6 with thermal ellipsoids at the 50% probability level. Methyl groups of the η^5-C_5Me_5 ligands, CF_3 groups and benzene molecules are omitted for clarity. Selected lengths (Å) and angles (deg): Ti–O (av) 2.12(1), Ti$\cdots$Ti (av) 5.22(1), O_{trans}–Ti–O_{trans} 125.9(1)-137.6(1), O_{cis}–Ti–O_{cis} 78.1(1)-83.0(1).

The analogous reaction of a freshly prepared toluene solution of [{Ti(η^5-C_5HMe_4)(BH_4)(μ-BH_4)}$_2$] (**2**) with 4 equiv of (LutH)(OTf) led to the molecular triflato-bridged complex [{Ti(η^5-C_5HMe_4)(μ-O_2SOCF_3)$_2$}$_4$] (**13**) along with H_2 and the adduct (Lut)BH_3 (Scheme 3). The solubility of **13** in common organic solvents is similar to that of the (Lut)BH_3 byproduct and crystallization of the reaction mixture at –35 ºC gave green crystals of **13** and white crystals of (Lut)BH_3. The poor quality of crystals of **13** precluded an accurate determination of the solid-state structure by crystallographic methods, but a cyclic tetrameric titanium aggregate with triflato groups bridging the titanium atoms in a manner similar to **12** was unambiguously established. The isolation of **13** in a pure form and good yield (80%) required the sublimation of the (Lut)BH_3 byproduct under dynamic vacuum. The

^{1}H NMR spectrum of **13** in benzene-d_6 is silent and the low solubility of the complex in that solvent precluded an accurate determination of its magnetic moment in solution.

Similarly, the reaction of toluene solutions of [{Ti(η^5-C$_5$H$_5$)(BH$_4$)(μ-BH$_4$)}$_2$] (**3**) with 4 equiv of (LutH)(OTf) at room temperature led to precipitation of blue or green crystalline fractions of aggregates [{Ti(η^5-C$_5$H$_5$)(μ-O$_2$SOCF$_3$)$_2$}$_x$]. The green crystals were suitable for an X-ray diffraction study which revealed a cyclic hexameric complex [{Ti(η^5-C$_5$H$_5$)(μ-O$_2$SOCF$_3$)$_2$}$_6$] (Figure S4). The molecular structure shows each titanium atom linked to other two metal centers through four μ-O$_2$SOCF$_3$ bridging triflato ligands in a fashion similar to that of complex **11**. Thus, the molecules exhibit six eight-membered [O$_4$S$_2$Ti$_2$] rings connected through the titanium atoms. Accurate and reliable elemental analyses could not be obtained for these crystalline fractions probably due to a variable number of toluene/lutidine molecules included in the crystal lattice.

We have also explored the possibility of further reduction of the titanium(III) bis(hydridoborato) complexes using the stronger reducing agent lithium tetrahydridoaluminate (Scheme 4).[8,35] Treatment of blue solutions of complexes [{Ti(η^5-C$_5$Me$_5$)(BH$_4$)(μ-BH$_4$)}$_2$] (**1**) and [Ti(η^5-C$_5$Me$_5$)(BH$_3$Me)$_2$] (**4**) in tetrahydrofuran with 2 equiv of LiAlH$_4$ at room temperature led to dark-blue solutions with vigorous gas evolution. Upon workup of the reaction mixtures, diamagnetic hydride-bridged heterobimetallic Ti–Al derivatives [{Ti(η^5-C$_5$Me$_5$)(μ-H)}$_2$\{(μ-H)$_2$Al(BH$_3$R)(thf)}$_2$] (R = H (**14**), Me (**15**)) were obtained. The reaction appears to occur by metathesis of one hydridoborato unit of the adducts [Ti(η^5-C$_5$Me$_5$)(BH$_3$R)$_2$(thf)] by a tetrahydridoaluminato ligand and subsequent reduction of the titanium(III) center to titanium(II), presumably by H$_2$ formation, and the remaining BH$_3$R group was transferred to the aluminum center. We have recently proposed an analogous mechanism for the formation of derivatives [{Ti(η^5-C$_5$Me$_5$)(μ-H)}$_2$\{(μ-

H)$_2$AlXL}$_2$] (L = thf, X = Cl, Br; L = OEt$_2$, X = Cl) by reaction of halide complexes [Ti(η^5-C$_5$Me$_5$)X$_3$] and [Ti(η^5-C$_5$Me$_5$)Cl$_2$(thf)] with LiAlH$_4$ in ethereal solvents.[26]
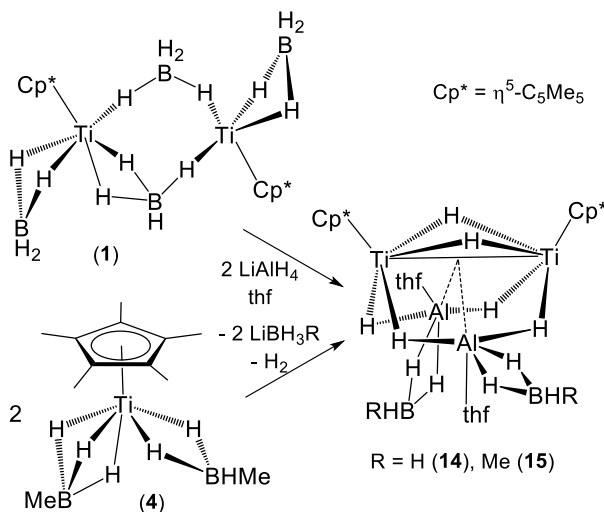
Scheme 4. Reactivity of complexes **1** and **4** with LiAlH$_4$.

Compounds **14**·0.5C$_7$H$_8$ and **15**·0.5C$_7$H$_8$ were isolated in good yields (84-88%) as dark-green solids which are very soluble in hydrocarbon solvents. Crystallization of **14** in toluene at –35 ºC gave a small fraction of dark-green crystals of **14**·0.5C$_7$H$_8$ suitable for an X-ray crystal structure determination. The molecular structure of **14** shows two {Ti(η^5-C$_5$Me$_5$)} units connected through two μ-H hydride ligands to form a butterfly structure for the [Ti$_2$(μ-H)$_2$] fragment (Figure 8). The Ti–Ti distance of 2.796(1) Å is shorter than that found in titanium metal (2.896 Å).[36] The titanium atoms are also bridged by two {(μ-H)$_2$Al(BH$_4$)(thf)} groups with five-coordinate aluminum centers. Thus, both Al atoms are bonded to the oxygen of a tetrahydrofuran ligand, two hydrogen atoms of a κ^2-BH$_4$ group and two hydrides bound to the titanium centers. However, the Al atoms exhibit different geometries, while Al(2) adopts an almost perfect square pyramidal environment (τ_5 = 0.07) with the tetrahydrofuran ligand at the apical position, the geometry for the Al(1) atom is approximately halfway (τ_5 = 0.47) between square pyramidal (τ_5 = 0) and trigonal

bipyramidal ($\tau_5 = 1$).[37] Both BH_4 groups are bidentate as in many other aluminum complexes with tetrahydridoborato ligands. However, the Al$\cdots$B distances of 2.303(3) Å in **14** are slightly longer than the observed in those aluminum complexes with κ^2-coordinated BH_4 units (2.10(1)-2.27(8) Å).[12,38]
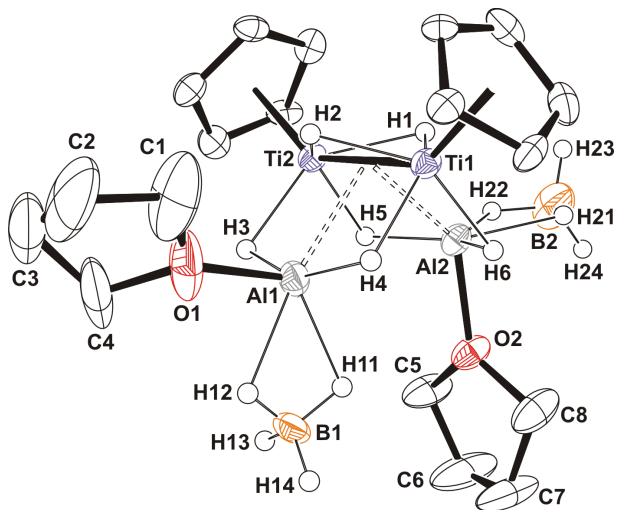
Figure 8. Perspective view of **14**·0.5C_7H_8 with thermal ellipsoids at the 50% probability level. Methyl groups of the η^5-C_5Me_5 ligands, hydrogen atoms of the tetrahydrofuran ligands, and toluene molecule are omitted for clarity. Selected averaged lengths (Å) and angles (deg): Ti(1)–Ti(2) 2.796(1), Ti–Al 2.630(1)-2.684(1), Ti–H(Ti) 1.86(3), Ti–H(Al) 1.84(2), Al–H(Ti) 1.67(1), Al–H(B) 1.87(1), Al$\cdots$B 2.303(1), Al(1)–O(1) 1.933(2), Al(2)–O(2) 1.890(2), H(1)–Ti–H(2) 76(1), Ti(1)–H–Ti(2) 98(2).

Overall, the molecular structure of **14** is similar to those determined in the solid-state of derivatives [{Ti(η^5-C_5Me_5)(μ-H)}$_2${(μ-H)$_2$AlX(thf)}$_2$] (X = Cl, Br) for which the electronic structure was studied by means of DFT calculations.[26] The theoretical studies revealed an open-shell singlet ground state with an additional Ti–Ti bond and therefore the compounds can be considered titanium(II) species. NBO analysis showed the existence of a strong electron density donation from the Ti–Ti bond to the empty s orbitals of the Al atoms. The Ti–Ti and Ti–Al distances found in the crystal structure of **14** are essentially identical to

those determined in the previously reported complexes and an analogous electronic structure can be proposed.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of complex **14** in benzene-d_6 at room temperature reveal sharp resonance signals for two equivalents η^5-C_5Me_5 ligands in accord with the nearly C_s symmetric structure in the solid-state. Remarkably, the spectra show a single set of broad resonances for the tetrahydrofuran ligands in contrast to the two expected for the non-equivalent tetrahydrofuran molecules in the X-ray structure and those observed in the ^1H and $^{13}C\{^1H\}$ NMR spectra of the analogous $[\{Ti(\eta^5$-$C_5Me_5)(\mu$-$H)\}_2\{(\mu$-$H)_2AlX(thf)\}_2].[26]$ While resonances for the hydride groups could not be assigned in the ^1H NMR spectra, the ^{11}B NMR spectrum of **14** at room temperature shows one slightly broad quintet at $\delta = -34.4$ ($^1J(^{11}B,^1H)$ = 77 Hz) for the BH_4 groups indicating the equivalence of the two tetrahydridoborato groups. These NMR data suggest a dynamic exchange process in solution, and we have recorded a variable-temperature ^1H NMR spectra of **14** in a toluene-d_8 solution in a 500 MHz spectrometer (Figure S13). Indeed, the spectrum at −50 °C revealed resonance signals for two non-equivalent tetrahydrofuran ligands in accord with the X-ray structure. Upon warming the solution, these resonances became broad and coalesced at about 0 °C to give one set of signals at higher temperatures. The dynamic behavior may be the result of an exchange of ligand sites at the five-coordinate aluminum centers, which is rapid enough at higher temperatures for the signals from the different environments to be averaged into a single set of resonances at the mean position.

The ^1H and $^{13}C\{^1H\}$ NMR spectra of complex **15** in benzene-d_6 at room temperature are very similar to those of **14** showing resonance signals for two equivalents η^5-C_5Me_5 ligands and a single set of broad resonances for the tetrahydrofuran ligands. In addition, the ^1H NMR spectrum reveals a broad singlet at $\delta = 0.44$ for the methyl group of the BH_3Me

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ligands. The ^{11}B NMR spectrum of **15** at room temperature displays a broad signal at $\delta = -25.5$ assignable to the BH$_3$Me units. Therefore, an analogous dynamic behavior appears to be occurring in complex **15** although with a slightly higher energy barrier than in **14**.

Conclusions

Monocyclopentadienyltitanium(IV) trichloride compounds undergo reduction when treated with excess lithium hydridoborate reagents LiBH$_3$R (R = H, Me, Ph) to yield dimeric or monomeric bis(hydridoborato)titanium(III) derivatives as oils or volatile solids of variable stability. The complex with the non-methylated C$_5$H$_5$ rings, [{Ti(η^5-C$_5$H$_5$)(BH$_4$)(μ-BH$_4$)}$_2$], cleanly decomposes at room temperature to form a mixed-valence tetrametallic species [{Ti(η^5-C$_5$H$_5$)(BH$_4$)}$_2${(μ_3-B$_2$H$_6$)Ti(η^5-C$_5$H$_5$)}$_2$] with rare bridging μ_3-κ^2:κ^2:κ^2-B$_2$H$_6^{2-}$ diborane(6) ligands. Theoretical calculations and magnetic measurements are in accord with a triplet ground state for this compound with two inner titanium(II) atoms bonded via a single bond and the two outer titanium atoms in the +3 oxidation state. The decomposition of [{Ti(η^5-C$_5$H$_5$)(BH$_4$)(μ-BH$_4$)}$_2$] is slower in solution or negligible in the tetrahydrofuran adduct derivative [Ti(η^5-C$_5$H$_5$)(BH$_4$)$_2$(thf)]. The half-sandwich bis(tetrahydridoborato)titanium(III) complexes react with lutidinium salts (LutH)X (X = BPh$_4$, OSO$_2$CF$_3$) to give H$_2$, the acid-base adduct (Lut)BH$_3$, and ion pairs [Ti(η^5-C$_5$H$_{5-n}$Me$_n$)(BH$_4$)L$_2$](BPh$_4$) or molecular aggregates with bridging μ-O$_2$SOCF$_3$ triflato ligands depending on the coordinating ability of the X$^-$ anions. The bis(hydridoborato)titanium(III) complexes can be further reduced with LiAlH$_4$ in tetrahydrofuran to afford hydride-bridged heterometallic derivatives [{Ti(η^5-C$_5$Me$_5$)(μ-H)}$_2${(μ-H)$_2$Al(BH$_3$R)(thf)}$_2$] with diamagnetic titanium(II) centers.

Experimental Section

General Comments. All manipulations were carried out under argon atmosphere using Schlenk line or glovebox techniques. Toluene and hexane were distilled from Na/K alloy just before use. Tetrahydrofuran was distilled from purple solutions of sodium benzophenone just prior to use. NMR solvents were dried with Na/K alloy (C_6D_6, C_7D_8, C_4D_8O) or calcium hydride (C_5D_5N) and vacuum-distilled. Oven-dried glassware was repeatedly evacuated with a pumping system (ca. 1×10^{-3} Torr) and subsequently filled with inert gas. Lithium tetrahydridoaluminate ($LiAlH_4$, 95%) was purchased from Aldrich and used as received. Lithium tetrahydridoborate ($LiBH_4$, ≥95%, Aldrich) was ground with a mortar and pestle until a very fine powder was obtained. Pyridine (Aldrich) was distilled from CaH_2. [$Ti(\eta^5$-$C_5H_{5-n}Me_n)Cl_3$] (n = 5,[39] 4,[40] 0[41]), lithium methyltrihydridoborate ($LiBH_3Me$),[42] and lithium phenyltrihydridoborate ($LiBH_3Ph$)[42] were prepared according to published procedures. 2,6-Lutidinium tetraphenylborate (LutH)(BPh_4) was prepared according to a published procedure.[43] 2,6-Lutidinium trifluoromethanesulfonate (LutH)(OTf)[44] was prepared by treating a toluene solution of 2,6-lutidine with a toluene solution of triflic acid (HOTf). The synthesis and characterization of complex [$\{Ti(\eta^5$-$C_5Me_5)(BH_4)(\mu$-$BH_4)\}_2$] (**1**) have been reported previously (CAUTION: compound **1** and analogous derivatives **2-4** are pyrophoric and special care should be taken when handling these substances and their residues).[26]

Samples for infrared spectroscopy were prepared as KBr pellets, and the spectra were obtained using a Perkin-Elmer FT-IR-Frontier or Bruker FT-IR-ALPHA II spectrophotometers. ^1H, $^{13}C\{^1H\}$ and ^{11}B NMR spectra were recorded on a Varian Mercury-300, Varian Unity-500, or Bruker Avance Neo 400 spectrometers. Chemical shifts (δ) in the ^1H and $^{13}C\{^1H\}$ NMR spectra are given relative to residual protons or to carbon of the solvent, C_6D_6 (^1H: δ = 7.15; ^{13}C: δ = 128.0) or C_7H_8 (^1H: δ = 2.08; ^{13}C: δ = 20.4). Chemical

shifts (δ) in the ^{11}B NMR spectra are given relative to BF$_3$(OEt$_2$) as external reference. The effective magnetic moments in solution were determined by the Evans NMR method at 295 K (using a 300 MHz instrument with a field strength of 7.05 Tesla).[45] Melting points were determined in sealed capillary tubes under argon and are uncorrected. Microanalyses (C, H, N, S) were performed in a Perkin Elmer CHNS/O 2400 or Leco CHNS-932 microanalyzers.

Synthesis of [{Ti(η^5-C$_5$HMe$_4$)(BH$_4$)(μ-BH$_4$)}$_2$] (2). A 100 mL Schlenk tube was charged with [Ti(η^5-C$_5$HMe$_4$)Cl$_3$] (0.50 g, 1.82 mmol), finely powdered LiBH$_4$ (0.21 g, 9.08 mmol), and toluene (30 mL). The reaction mixture was stirred at room temperature for 24 h to give a brown solution and a gray solid. After filtration, the volatile components of the solution were removed under reduced pressure to give **2** (0.21 g, 58%) as a greenish-brown oil. Cooling to –35 ºC afforded **2** as a brown solid. IR (KBr, cm^{-1}): 3082 (w), 2980 (m), 2960 (m), 2917 (s), 2865 (m), 2546 (s), 2465 (vs), 2420 (vs), 2288 (m), 2218 (m), 2133 (m), 2047 (s), 1925 (s), 1502 (w), 1401 (s), 1239 (s), 1130 (vs), 1027 (m), 980 (w), 839 (m), 695 (w). Anal. Calcd for C$_{18}$H$_{42}$B$_4$Ti$_2$ (M_w = 397.51): C 54.39, H 10.65. Found: C 54.52, H 10.62. The effective magnetic moment of **2** was determined to be 1.97 μ_B (based on a unit formula of C$_{18}$H$_{42}$B$_4$Ti$_2$) on a C$_6$D$_6$ solution.

Synthesis of [{Ti(η^5-C$_5$H$_5$)(BH$_4$)(μ-BH$_4$)}$_2$] (3). In a fashion similar to the preparation of **2**, [Ti(η^5-C$_5$H$_5$)Cl$_3$] (0.38 g, 1.73 mmol) and LiBH$_4$ (0.22 g, 10.40 mmol) were reacted in toluene (30 mL) for 24 h to give **3** (0.12 g, 49%) as a greenish-brown oil. Complex **3** decomposed even at –35 ºC, and analytical and spectral data were obtained using a freshly prepared sample. IR (KBr, cm^{-1}): 3108 (w), 2530 (m), 2451 (m), 2428 (w), 2288 (m), 2221 (m), 2120 (m), 2058 (m), 1915 (w), 1435 (m), 1405 (m), 1309 (s), 1125 (m), 1015 (s), 911 (w), 813 (vs), 528 (m). Anal. Calcd for C$_{10}$H$_{26}$B$_4$Ti$_2$ (M_w = 285.29): C 42.10, H 9.19. Found:

C 42.25, H 8.81. The effective magnetic moment of **3** was determined to be 2.39 μ_B (based on a unit formula of $C_{10}H_{26}B_4Ti_2$) on a C_6D_6 solution.

Synthesis of [Ti(η^5-C$_5$Me$_5$)(BH$_3$Me)$_2$] (4). A suspension of LiBH$_3$Me (0.43 g, 1.21 mmol) in toluene (20 mL) was gently added to a solution of [Ti(η^5-C$_5$Me$_5$)Cl$_3$] (1.00 g, 3.45 mmol) in toluene (30 mL). The reaction mixture was stirred at room temperature for 16 h to give a brown solution and a gray solid. After filtration, the volatile components of the solution were removed under reduced pressure to give **4** (0.77 g, 93%) as a black solid (mp 66-69 ºC). IR (KBr, cm^{-1}): 2925 (s), 2834 (m), 2729 (w), 2400 (s), 2253 (w), 2230 (m), 2192 (s), 2111 (s), 1869 (vs), 1826 (s), 1620 (m), 1438 (s), 1414 (s), 1361 (vs), 1288 (m), 1213 (m), 1134 (m), 1122 (s), 1093 (m), 1068 (w), 1026 (m), 1000 (m), 895 (w), 855 (w), 801 (w), 685 (w), 464 (s), 420 (m). Anal. Calcd for $C_{12}H_{27}B_2Ti$ (M_w = 240.83): C 59.85, H 11.30. Found: C 60.29, H 11.46. The effective magnetic moment of **4** was determined to be 1.77 μ_B (based on a unit formula of $C_{12}H_{27}B_2Ti$) on a C_6D_6 solution.

Synthesis of [{Ti(η^5-C$_5$H$_5$)(BH$_4$)}$_2${(μ_3-B$_2$H$_6$)Ti(η^5-C$_5$H$_5$)}$_2$] (5). A 25 mL Schlenk tube with 0.11 g (0.39 mmol) of **3** was allowed to stay at room temperature for 48 h under an argon atmosphere. After that time, the initial brown oil turned to a brown crystalline solid which was characterized as **5** (0.09 g, 87%). IR (KBr, cm^{-1}): 3103 (w), 2428 (w), 2391 (m), 2290 (w), 2039 (w), 1940 (m), 1432 (m), 1432 (w), 1369 (s), 1261 (m), 1150 (m), 1121 (w), 1040 (s), 803 (vs), 694 (w), 449 (w), 420 (w). Anal. Calcd for $C_{20}H_{40}B_6Ti_4$ (M_w = 536.87): C 44.74, H 7.51. Found: C 44.55, H 6.98. The effective magnetic moment of **5** was determined to be 2.27 μ_B (based on a unit formula of $C_{20}H_{40}B_6Ti_4$) on a C_6D_6 solution.

Synthesis of [Ti(η^5-C$_5$H$_5$)(BH$_4$)$_2$(thf)] (6). Tetrahydrofuran (1 mL, ρ = 0.888 g/mL, 12.3 mmol) was slowly added to a toluene solution of **3** prepared by treatment of [Ti(η^5-C$_5$H$_5$)Cl$_3$] (0.37 g, 1.69 mmol) with LiBH$_4$ (0.18 g, 8.26 mmol) in toluene (30 mL) and subsequent

filtration. Immediately, a fine blue solid was formed which was isolated by filtration onto a glass frit. The solid was vacuum-dried to afford **6** as a blue powder (0.21 g, 58%). IR (KBr, cm^{-1}): 3103 (m), 2982 (m), 2899 (m), 2394 (vs), 2233 (m), 2135 (s), 2085 (s), 1980 (s), 1753 (m), 1472 (s), 1349 (vs), 1176 (m), 1121 (vs), 1010 (s), 920 (m), 858 (s), 821 (vs), 682 (m), 439 (s). ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 ºC, δ): 4.09 (m br., 4H; OCH_2CH$_2$), 3.35 (m br., 4H; OCH$_2$CH_2), the μ-H and η^5-C$_5$H$_5$ resonance signals were not observed. Anal. Calcd for C$_9$H$_{21}$B$_2$OTi (M_w = 214.75): C 50.34, H 9.86. Found: C 50.59, H 9.59. The effective magnetic moment of **6** was determined to be 1.80 μ$_B$ (based on a unit formula of C$_9$H$_{21}$B$_2$OTi) on a C$_6$D$_6$ solution.

Synthesis of [Ti(η^5-C$_5$Me$_5$)(BH$_4$)(thf)$_2$](BPh$_4$) (7). A 150 mL Schlenk tube was charged with **1** (0.30 g, 0.70 mmol), (LutH)(BPh$_4$) (0.60 g, 1.41 mmol), toluene (20 mL) and tetrahydrofuran (5 mL). The reaction mixture was stirred at room temperature for 3 days to give a blue solid and a blue solution. The solid was isolated by filtration onto a glass frit and was washed with hexane (10 mL) to afford **7** as a blue powder (0.82 g, 89%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 3053 (m), 2998 (m), 2984 (m), 2905 (m), 2520 (m), 2076 (m), 1579 (m), 1479 (m), 1453 (m), 1427 (m), 1379 (w), 1307 (m), 1262 (m), 1183 (m), 1151 (w), 1110 (w), 1066 (w), 1032 (w), 999 (m), 845 (s), 745 (s), 735 (vs), 706 (vs), 624 (m), 612 (m), 534 (w). Anal. Calcd for C$_{42}$H$_{55}$B$_2$O$_2$Ti (M_w = 661.38): C 76.27, H 8.38. Found: C 76.16, H 8.44.

Synthesis of [Ti(η^5-C$_5$HMe$_4$)(BH$_4$)(thf)$_2$](BPh$_4$) (8). (LutH)(BPh$_4$) (0.62 g, 1.45 mmol) and tetrahydrofuran (5 mL) were added to a solution of **2** prepared by reaction of [Ti(η^5-C$_5$HMe$_4$)Cl$_3$] (0.50 g, 1.82 mmol) with LiBH$_4$ (0.21 g, 9.08 mmol) in toluene (30 mL) and subsequent filtration. Gas evolution was immediately observed and the initial brown suspension turned to a blue color. The reaction mixture was stirred at room temperature for 16 h to give a blue solid and a blue solution. The solid was isolated by filtration onto a glass

frit and was vacuum-dried to afford **8** as a blue powder (0.74 g, 79%). IR (KBr, cm^{-1}): $\tilde{v}$ 3055 (m), 2998 (m), 2522 (m), 2075 (m), 1579 (m), 1479 (m), 1427 (m), 1302 (w), 1192 (m), 1000 (m), 844 (s), 736 (s), 707 (s), 612 (m), 539 (w), 479 (w), 466 (w). Anal. Calcd for $C_{41}H_{53}B_2O_2Ti$ (M_w = 647.36): C 76.07, H 8.25. Found: C 76.38, H 8.34.

Synthesis of [Ti(η^5-C$_5$H$_5$)(BH$_4$)(thf)$_2$](BPh$_4$) (9). (LutH)(BPh$_4$) (0.65 g, 1.52 mmol) and tetrahydrofuran (5 mL) were added to a solution of **3** prepared by treatment of [Ti(η^5-C$_5$H$_5$)Cl$_3$] (0.35 g, 1.60 mmol) with LiBH$_4$ (0.18 g, 8.26 mmol) in toluene (30 mL) and subsequent filtration. The reaction mixture was stirred at room temperature for 20 h and the resultant blue solid was isolated by filtration onto a glass frit. This solid was vacuum-dried to afford **9** as a blue powder (0.81 g, 90%). IR (KBr, cm^{-1}): $\tilde{v}$ 3104 (m), 3052 (s), 2998 (s), 2897 (m), 2539 (s), 2059 (s), 1580 (s), 1478 (s), 1455 (s), 1427 (s), 1384 (w), 1365 (m), 1346 (m), 1312 (s), 1267 (m), 1197 (s), 1148 (s), 1093 (m), 1030 (s), 1004 (vs), 917 (m), 828 (vs), 740 (vs), 706 (vs), 626 (m), 604 (s), 557 (m), 480 (m), 462 (m). Anal. Calcd for $C_{37}H_{45}B_2O_2Ti$ (M_w = 591.25): C 75.16, H 7.67. Found: C 74.93, H 7.52.

Synthesis of [Ti(η^5-C$_5$Me$_5$)(BH$_4$)(py)$_2$](BPh$_4$) (10). A 150 mL Schlenk tube was charged with **1** (0.15 g, 0.35 mmol), (LutH)(BPh$_4$) (0.30 g, 0.70 mmol), toluene (20 mL) and pyridine (5 mL). The resultant green suspension was stirred at room temperature for 1 h. The solid was isolated by filtration onto a glass frit and was washed with hexane (10 mL) to afford **10** as a green powder (0.40 g, 85%). IR (KBr, cm^{-1}): $\tilde{v}$ 3054 (w), 2984 (m), 2955 (m), 2908 (m), 2532 (m), 2078 (m), 1604 (m), 1579 (m), 1484 (m), 1459 (w), 1442 (m), 1426 (m), 1381 (w), 1289 (m), 1216 (m), 1180 (w), 1153 (w), 1066 (m), 1030 (w), 1010 (w), 845 (w), 752 (m), 734 (s), 704 (vs), 613 (m), 538 (w). Anal. Calcd for $C_{44}H_{49}B_2N_2Ti$ (M_w = 675.37): C 78.25, H 7.31, N 4.15 Found: C 78.73, H 7.53, N 4.57.

Synthesis of [{Ti(η^5-C$_5$Me$_5$)(BH$_4$)(μ-O$_2$SOCF$_3$)}$_2$] (11). A 150 mL Schlenk tube was charged with **1** (0.30 g, 0.70 mmol), (LutH)(OTf) (0.36 g, 1.41 mmol), and toluene (30 mL). The resultant dark-blue solution was stirred at room temperature for 16 h. After filtration, the volatile components of the solution were removed under reduced pressure. The resultant blue solid was washed with hexane (10 mL) and this solid was loaded into a sublimation tube. The solid was slowly heated in a horizontal sublimation apparatus to 120 ºC under dynamic vacuum (0.1 Torr) for 3 h to give colorless crystals of (Lut)BH$_3$ at the cold end of the tube while a dark-green solid of **11** remained at the hot end (0.30 g, 62%).

Spectroscopic and analytic data for **11**: IR (KBr, cm^{-1}): $\tilde{\nu}$ 2960 (w), 2919 (w), 2863 (w), 2533 (m), 2065 (m), 1384 (w), 1327 (vs), 1239 (vs), 1210 (s), 1196 (s), 1040 (vs), 802 (w), 631 (s), 551 (w), 513 (w), 481 (w). Anal. Calcd for C$_{22}$H$_{38}$B$_2$F$_6$O$_6$S$_2$Ti$_2$ (M_w = 694.01): C 38.07, H 5.52, S 9.24. Found: C 38.07, H 5.75, S 9.32. The effective magnetic moment of **11** was determined to be 2.52 μ_B (based on a unit formula of C$_{22}$H$_{38}$B$_2$F$_6$O$_6$S$_2$Ti$_2$) on a C$_6$D$_6$ solution.

Spectroscopic data for (Lut)BH$_3$: IR (KBr, cm^{-1}): $\tilde{\nu}$ 3059 (w), 3044 (m), 2981 (m), 2926 (m), 2406 (vs), 2333 (vs), 1977 (m), 1895 (m), 1834 (w), 1813 (m), 1687 (m), 1618 (s), 1574 (s), 1478 (s), 1385 (s), 1256 (m), 1176 (vs), 1131 (s), 1048 (s), 920 (m), 786 (vs), 717 (w), 457 (m). ^{1}H NMR (500 MHz, C$_6$D$_6$, 20 ºC, δ): 6.61 (t, ^3J(H,H) = 13 Hz, 1H; NC$_5$*H*$_3$Me$_2$), 6.28 (d, ^3J(H,H) = 13 Hz, 2H; NC$_5$*H*$_3$Me$_2$), 3.10 (q, ^1J(^{1}H,^{11}B) = 100 Hz, 3H; BH$_3$), 2.55 (s, 6H; NC$_5$H$_3$*Me*$_2$). ^{11}B NMR (160 MHz, C$_6$D$_6$, 20 ºC, δ): 16.9 (q, ^1J(^{11}B,^{1}H) = 99 Hz; BH$_3$).

Synthesis of [{Ti(η^5-C$_5$Me$_5$)(O$_2$SOCF$_3$)$_2$}$_3$] (12). A 150 mL Schlenk tube was charged with **1** (0.30 g, 0.70 mmol), (LutH)(OTf) (0.72 g, 2.82 mmol), and toluene (25 mL). The reaction mixture was stirred at room temperature for 15 min and the resultant green solution was filtered and left without any stirring at room temperature for 3 days to afford green crystals. The crystals were isolated by filtration onto a glass frit and were washed with hexane (5 mL)

to afford **12** as green crystals (0.37 g, 55%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 2989 (w), 2968 (w), 2931 (w), 1491 (w), 1459 (w), 1388 (m), 1338 (vs), 1228 (vs), 1221 (vs), 1199 (s), 1150 (w), 1109 (w), 1021 (vs), 802 (w), 634 (s), 593 (w), 573 (w), 516 (m), 438 (m). Anal. Calcd for $C_{36}H_{45}F_{18}O_{18}S_6Ti_3$ (M_w = 1443.69): C 29.95, H 3.14, S 13.33. Found: C 30.19, H 3.26, S 13.02.

Synthesis of [{Ti(η^5-C$_5$HMe$_4$)(μ-O$_2$SOCF$_3$)$_2$}$_4$] (13). Over a solution of **2**, prepared by the reaction of [Ti(η^5-C$_5$HMe$_4$)Cl$_3$] (0.50 g, 1.82 mmol) with LiBH$_4$ (0.21 g, 9.08 mmol) in toluene (30 mL) and subsequent filtration, (LutH)(OTf) (0.93 g, 3.63 mmol) was added in small fractions while vigorous gas evolution ensued. The reaction mixture was stirred at room temperature for 30 min. The resultant blue solution was filtered and the volatile components were removed under reduced pressure to give a green powder. This solid was loaded into a sublimation tube and was heated at 120 ºC under dynamic vacuum (0.1 Torr) for 3 h to give colorless crystals of the (Lut)BH$_3$ adduct at the cold end of the tube. Complex **13** remained at the hot end and was isolated as a green powder (0.68 g, 80%). IR (KBr, cm^{-1}): $\tilde{\nu}$ 2965 (w), 2921 (w), 1508 (w), 1387 (s), 1374 (s), 1339 (m), 1254 (vs), 1234 (vs), 1208 (vs), 1168 (m), 1111 (w), 1037 (vs), 853 (w), 798 (w), 772 (w), 626 (s), 582 (w), 519 (m), 428 (m). Anal. Calcd for $C_{44}H_{52}F_{24}O_{24}S_8Ti_4$ (M_w = 1868.81): C 28.28, H 2.80, S 13.73. Found: C 28.00, H 3.02, S 13.50.

Synthesis of [{Ti(η^5-C$_5$Me$_5$)(μ-H)}$_2$ {(μ-H)$_2$Al(BH$_4$)(thf)}$_2$] (14). A suspension of LiAlH$_4$ (0.092 g, 2.35 mmol) in tetrahydrofuran (20 mL) was gently added to a stirred solution of **1** (0.50 g, 1.18 mmol) in tetrahydrofuran (20 mL) at room temperature. Vigorous gas evolution ensued. The reaction mixture was stirred for 20 h to give a dark-blue suspension. The volatile components were removed under reduced pressure and the resultant solid was extracted with toluene (15 mL). After filtration, the volatile components of the filtrate were removed under

reduced pressure to afford **14**·0.5C$_7$H$_8$ as a dark-green powder (0.64 g, 84%). IR (KBr, cm^{-1}): ṽ 2969 (s), 2948 (s), 2905 (vs), 2435 (s), 2375 (s), 2217 (m), 2183 (m), 1495 (m), 1452 (m), 1432 (s), 1376 (s), 1344 (s), 1246 (m), 1111 (s), 1039 (m), 1026 (m), 1006 (s), 860 (vs), 738 (m), 697 (m), 659 (m), 467 (w), 439 (w), 411 (m). ^{1}H NMR (500 MHz, C$_6$D$_6$, 20 °C, δ): 4.03 (m br., 8H; OCH_2CH$_2$), 2.30 (s, 30H; C$_5$Me$_5$), 1.31 (m br., 8H; OCH$_2$CH_2), the μ-H resonance signals were not observed. ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$, 20 °C, δ): 114.3 (*C*$_5$Me$_5$), 71.5 (br.; O*C*H$_2$CH$_2$), 25.1 (br.; OCH$_2$*C*H$_2$), 14.1 (C$_5$*Me*$_5$). ^{11}B NMR (128 MHz, C$_6$D$_6$, 20 °C, δ): –34.4 (quintet, $^1J(^{11}$B,^{1}H) = 77 Hz; BH$_4$). Anal. Calcd for C$_{31.5}$H$_{64}$Al$_2$B$_2$O$_2$Ti$_2$ (*M*$_w$ = 646.17): C 58.55, H 9.98. Found: C 56.60, H 9.48. Attempts to obtain satisfactory elemental analysis failed possibly due to incomplete combustion of the samples.

Synthesis of [{Ti(η^5-C$_5$Me$_5$)(μ-H)}$_2${(μ-H)$_2$Al(BH$_3$Me)(thf)}$_2$] (15). In a fashion similar to the preparation of **14**, **4** (0.50 g, 2.08 mmol) and LiAlH$_4$ (0.081 g, 2.08 mmol) were reacted in tetrahydrofuran (25 mL) for 16 h to give **15**·0.5C$_7$H$_8$ as a dark-green powder (0.62 g, 88%). IR (KBr, cm^{-1}): ṽ 2932 (s), 2901 (s), 2878 (s), 2832 (m), 2228 (vs), 2189 (vs), 2158 (vs), 1456 (m), 1432 (m), 1376 (m), 1343 (m), 1308 (s), 1293 (s), 1236 (m), 1200 (vs), 1110 (w), 1040 (s), 893 (m), 862 (s), 730 (m), 695 (m), 464 (w), 439 (w), 427 (w). ^{1}H NMR (400 MHz, C$_6$D$_6$, 20 °C, δ): 3.83 (m br., 8H; OCH_2CH$_2$), 2.27 (s, 30H; C$_5$Me$_5$), 1.28 (m br., 8H; OCH$_2$CH_2), 0.44 (s br., 6H; BCH$_3$), the μ-H resonance signals were not observed. ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$, 20 °C, δ): 114.3 (*C*$_5$Me$_5$), 70.5 (br.; O*C*H$_2$CH$_2$), 25.0 (br.; OCH$_2$*C*H$_2$), 14.1 (C$_5$*Me*$_5$), the B*C*H$_3$ resonance signal was not observed. ^{11}B NMR (128 MHz, C$_6$D$_6$, 20 °C, δ): –25.5 (s br.; BH$_3$Me). Anal. Calcd for C$_{33.5}$H$_{68}$Al$_2$B$_2$O$_2$Ti$_2$ (*M*$_w$ = 674.22): C 59.68, H 10.17. Found: C 54.80, H 10.03. Attempts to obtain satisfactory elemental analysis failed possibly due to incomplete combustion of the samples.

X-ray crystal structure determinations. Dark-blue crystals of complex **4** were obtained by sublimation of the compound under vacuum. Dark-green crystals of [Ti(η^5-C$_5$Me$_5$)(BH$_3$Ph)$_2$] and brown crystals of **5** were obtained from hexane solutions at –35 ºC. Dark-blue crystals of **7** were grown from a tetrahydrofuran solution at room temperature. Blue crystals of **8** were obtained after slow diffusion of hexane into a tetrahydrofuran solution of this compound. Blue crystals of **11** were obtained by slow diffusion of hexane into a toluene solution of this compound. Green crystals of **12**·C$_6$H$_6$ were grown by slow cooling at room temperature of a benzene suspension heated at 80 ºC in an NMR tube. Green crystals of [{Ti(η^5-C$_5$H$_5$)(μ-O$_2$SOCF$_3$)$_2$}$_6$]·3C$_7$H$_8$·C$_7$H$_9$N were obtained from the preparative reaction in toluene at room temperature as described in the Results and Discussion Section. Dark-green crystals of **14**·0.5C$_7$H$_8$ were obtained from a toluene solution at –35 ºC. The crystals were removed from the Schlenk tubes or the NMR tube and covered with a layer of a viscous perfluoropolyether (FomblinY). A suitable crystal was selected with the aid of a microscope, mounted on a cryoloop, and immediately placed in the low temperature nitrogen stream of the diffractometer. The intensity data sets were collected at 200 K on a Bruker-Nonius KappaCCD diffractometer (**12**), at 150 K on a Bruker Kappa Apex-II diffractometer (**11**) or at 150 K on a Bruker AXS D8 Venture diffractometer (the rest of crystals). All the diffractometers were equipped with an Oxford Cryostream 700 unit. Crystallographic data for all the complexes are presented in Tables S1 and S2 of the Supporting Information.

The structures were solved, using the WINGX package,[46] by intrinsic phasing methods (SHELXT),[47] and refined by least-squares against F^2 (SHELXL-2014/7).[48] Crystals of [Ti(η^5-C$_5$Me$_5$)(BH$_3$Ph)$_2$] contained two independent molecules in the asymmetric unit, whereas the asymmetric unit of **7** and **8** was formed by two independent ion pairs. In the crystallographic studies of **4**, **5**, **7**, **8**, **11** and [Ti(η^5-C$_5$Me$_5$)(BH$_3$Ph)$_2$], all non-hydrogen

atoms were anisotropically refined. Hydrogen atoms linked to carbon atoms were included, positioned geometrically, and refined employing a riding model. Whereas the rest of the hydrogen atoms were located in the difference Fourier map and refined isotropically.

On the other hand, **12** crystallized with a benzene molecule, which was found as a half of two independent molecules of the solvent in the difference Fourier map. Moreover, crystals of **12** showed disorder for the carbon atoms C(31)-C(40) of the pentamethylcyclopentadienyl ligand linked to Ti(3). This disorder was conventionally treated by using the PART tool and allowing free refinement of the occupancy factors with the FVAR command of the SHELXL program. The final values were 84.1 and 15.9%. All non-hydrogen atoms were anisotropically refined, except the carbon atoms corresponding to the minor position of the disordered C_5Me_5 ligand (C(31)'-C(40)'). All the hydrogen atoms were positioned geometrically and refined using a riding model. Moreover, the minor position for the disordered C_5Me_5 ring was constrained to retain a regular geometry, while carbon atoms C(31)-C(40) were restrained with DELU and SIMU commands. DFIX constraints were also employed for carbon–carbon lengths in benzene molecules.

The hexameric complex [{Ti(η^5-C_5H_5)(μ-O_2SOCF_3)$_2$}$_6$] crystallized with three toluene molecules and one more molecule, which could be lutidine according to the elemental analysis data and the IR spectrum of the crystals. All these additional molecules were found in the difference Fourier map, however it was only possible to obtain a chemically sensible model for two of the toluene molecules. Then Squeeze[49] procedure was used to remove the contribution of the lutidine and the third toluene molecule to the structure factors. Moreover, this crystal presented disorder for the carbon atoms C(11)-C(15) of the C_5H_5 ring connected to Ti(1). This disorder was also treated by using the PART tool with final values of 82 and 18%. All non-hydrogen atoms were anisotropically refined, except the carbon atoms related to the minor position of the disordered cyclopentadienyl ligand (C(11)'-C(15)'), which were

isotropically refined. All the hydrogen atoms were positioned geometrically and refined using a riding model. Furthermore, the carbon atoms corresponding to the main position for the disordered C_5H_5 ring (C(11)-C(15)) were constrained to form a regular pentagon and restrained with DELU and SIMU instructions.

Finally, compound **15** crystallized with a half molecule of toluene. This crystal showed disorder for both C_5Me_5 ligands (C(11)-C(20) and C(21)-C(30)) and one coordinated tetrahydrofuran molecule (C(5)-C(8)). This disorder was also treated by using the PART tool, giving final values of 51.2 and 48.8% for the carbon atoms C(11)-C(20) corresponding to the C_5Me_5 group linked to Ti(1), 50.8 and 49.2% for the carbon atoms C(21)-C(30) related to the pentamethylcyclopentadienyl ring connected to Ti(2), and 57 and 43% for the carbon atoms C(5)-C(8) associated to the tetrahydrofuran ligand. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms bound to carbon atoms were positioned geometrically and refined by using a riding model, whereas the rest of the hydrogen atoms were located in the difference Fourier map and isotropically refined. The atoms O(1), C(1), C(2), C(3) and C(4), which constituted the non-disordered tetrahydrofuran ligand, were restrained with DELU instructions, while SIMU command was employed for the carbon atoms C(5) and C(6). Additionally, SADI restraints were applied to the disordered tetrahydrofuran moieties and the tetrahydridoborato ligands.

Computational Details. All the structures have been fully optimized in gas phase employing the Gaussian09 suite of programs[50] and using the unrestricted formalism of the B3LYP functional.[51] All the Al, B, C, H and Ti atoms are described with the triple-ζ all electron basis set of Ahlrichs and co-workers.[52] The NBO analysis has been carried out at the same level of theory as above with the NBO 7.0 program.[53]

Associated Content:

Supporting Information.

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.xxxxxx.

Experimental crystallographic data of complexes; perspective views and selected lengths and angles of the crystal structure of additional complexes; table for experimental vs. calculated lengths and angles for complex **5**; SOMOs and donor/acceptor interactions for complex **5**; selected NMR spectra of compounds **14** and **15**; variable temperature (VT) ^{1}H NMR spectra of complex **14**; Cartesian coordinates (XYZ) of the optimized compound **5** (PDF).

Accession Codes:

CCDC 221507-2221515 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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