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Synthesis and properties of unsolvated bis(cyclopentadienyl)titanium alumohydride. Structure of $\{[(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}H)]_2[(\eta^5\text{-}C_5H_5)Ti(\mu\text{-}H_2]Al_3(\mu\text{-}H_4)(H)\}_2\cdot C_6H_6$ a 12-nuclear titanium aluminum hydride complex with a short Al–Al bond length, and refined structure of $LiAlEt_4$

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Abstract

Unsolvated bis(cyclopentadienyl)titanium alumohydride was synthesized by two methods: heterogeneous reaction between $(Cp_2TiCl)_2$ and $LiAlH_4$ in toluene and desolvation of $Cp_2TiAlH_4\cdot Et_2O$ in vacuum. In the presence of cyclohexene, Cp_2TiAlH_4 (**1**) synthesized by the first method transforms to the known complex $[Cp_2TiH_2Al(H)(C_5H_4)TiCp(H)]_2$ (**3**). The desolvation reaction apparently yields $(Cp_2TiAlH_4)_2$ (**7**). In toluene, **7** transforms to a 12-nuclear titanium aluminum hydride complex **8** with short Al–Al distances. Complex **1** catalyzes the hydrometallation of ethylene to $LiAlEt_4$ by $LiAlH_4$. Complex **7**, unsolvated $(Cp_2Ti)_2AlH_4Cl$, and $(Cp_2TiAlH_3OEt)_2$ were tested as catalysts in hexene-1 hydrogenation. Complexes $LiAlEt_4$ and **8** were characterized by X-ray structure analysis. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Metallocene; Titanium; Aluminium; Hydride; Crystal structure; Catalysts; Hydrometallation; Hydrogenation

1. Introduction

Bis(cyclopentadienyl)titanium alumohydride complexes have attracted considerable attention because of their diversified structures and ability to catalyze various reactions of unsaturated hydrocarbons. Earlier [1], we studied the structural and catalytic properties of ether- and amine-solvated bis(cyclopentadienyl)-titanium alumohydride complexes and transformations of these complexes in donor solvents.

Unsolvated complexes are also very interesting, particularly as catalysts, since many catalytic reactions are favored by a hydrocarbon medium. This paper concerns the chemical and catalytic properties of bis(cyclopentadienyl)titanium alumohydride in toluene and presents the structure of its condensation product (12-nuclear hydrido complex) as well as the refined structure of $LiAlEt_4$.

2. Results and discussion

2.1. Synthesis and transformations of bis(cyclopentadienyl)titanium alumohydride in toluene

It was found earlier [2–4] that unsolvated bis(cyclopentadienyl)titanium alumohydride, Cp_2TiAlH_4 (**1**) can be synthesized by the heterogeneous reaction of $(Cp_2TiCl)_2$ with excess $LiAlH_4$ in an aromatic solvent. Complex **1**, forming by reaction (1), is detected in solution by EPR. However, during aging or isolation from solution, it partially decomposes to give polynuclear complex **2** [2] by reaction (2).

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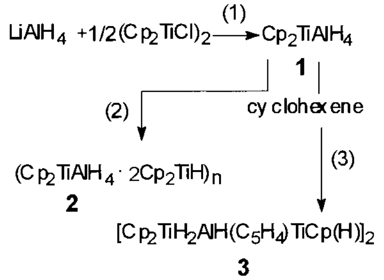
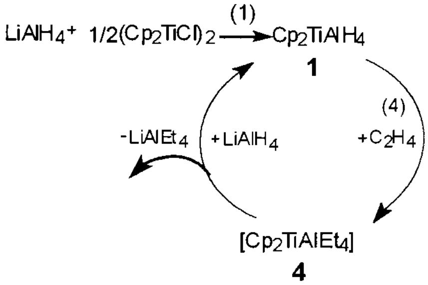


We found that, in the presence of cyclohexene, which is not hydrometalated [5–8] or is hydrometalated slowly [8,9] by $LiAlH_4$ during reactions catalyzed by titanium compounds, reaction (1) yields hexanuclear complex **3**, which is a well-known product of the transformation of $Cp_2TiAlH_4·L$ ($L = $ Lewis base) in solvating solvents [1]. The formation of **3** indicates that some transformations of bis(cyclopentadienyl)titanium alumohydride may occur similarly in a solvating and in an aromatic solvent. Apparently, the role of cyclohexene is that it forms a π-complex with **1** that is stable to migratory insertion. It is also not impossible that cyclohexene reacts with by-products of compound **1** decomposition, favoring the formation of **3**.

Unlike cyclohexene, ethylene undergoes fast hydroalumination [6–9]. As would be expected, reaction (1) conducted in toluene in the presence of ethylene does not yield polynuclear complexes **2** and **3**, because **1** apparently transforms to an alkyl derivative at the instant it forms (reaction (4)).



On completion of the process, there occurs crystallization of colorless needles of $LiAlEt_4$, which result from the catalyzed hydroalumination of ethylene with overstoichiometric excess of lithium aluminum hydride[1]. This reaction belongs to the same type as the known soft addition reactions between olefins and $LiAlH_4$ catalyzed by compounds of Ti(+4) (Cp_2TiCl_2, $TiCl_4$) and other transition metals [6–9]. Apparently, the catalytic effect of Cp_2TiCl_2 in these processes (including the heterogeneous reaction in benzene [8]) is also due to reaction (4), since Cp_2TiCl_2 is known [5] to reduce to $(Cp_2TiCl)_2$ in the first stage of its reaction with $LiAlH_4$ under our experimental conditions.

Pure complex **4** cannot be isolated from solution, because it is highly soluble and cannot be separated from $LiAlEt_4$, which is also highly soluble in the reaction mixture. It is possible that **4** is unstable and condenses gradually into the Natta–Tebbe complex $[Cp(\eta^1{:}\eta^5\text{-}C_5H_4)TiHAlEt_2]_2$ (**5**), since **5** is known [5] to form above 60°C in a related Cp_2TiCl_2–$LiAlH_4$–α-olefin system.

Synthesis of complex **1** by reaction (1), which is carried out in toluene, is somewhat inconvenient, as it is heterogeneous, requiring excess amounts of activated $LiAlH_4$ or elevated temperatures, and yields the Cp_2TiH_2AlHCl and $Cp_2TiH_2AlCl_2$ by-products [2–5]. These conditions are known [11] to be favorable for titanium reduction giving labile titanocene(+2) intermediates or even further titanium reduction. It is apparently due to these processes that reaction (1) is sometimes accompanied by the release of hydrogen and aluminum metal.

We found it more convenient to prepare unsolvated bis(cyclopentadienyl)titanium alumohydride by $Cp_2TiAlH_4·Et_2O$ (**6**) desolvation, which can be realized under milder conditions. Complex **6** is the single product of the homogeneous reaction between $(Cp_2TiCl)_2$ and $LiAlH_4$ (1:2) in an ether–toluene mixture [1,12], and it appeared to lose the ether molecule readily during solvent removal in vacuum at room temperature (r.t.). The resulting yellow–gray substance differs markedly in color from the product obtained by the first method. As judged from IR data (absorption bands at 1840 and 1600 cm^{-1}, which are due to the vibrations of terminal Al–H and bridging Ti–H–Al or Al–H–Al bonds, respectively [1,13]), it is the $(Cp_2TiAlH_4)_2$ dimer (**7**) with an $\{AlH_2Al\}$ bridging fragment, which is the same as in the complex $(Cp^*_2TiAlH_4)_2$ ($Cp^* = C_5Me_5$) [1,13].

Fairly reproducible results were obtained when **6** was desolvated in the presence of small amounts of a low-volatile hydrocarbon, which prevents the precipitate from both side reactions and surface and prevents the formation of large aggregates. For example, the yellow–green suspension of complex **7** remaining after evaporation of a solution of complex **6** in an ether–toluene–tetradecane mixture dissolves readily on addition of toluene to give an intensely green solution.

The EPR spectrum of a freshly prepared toluene solution of **7** is a partially resolved octet with $g = 1.991$, component intensity ratios close to 1:3:4:4:4:4:3:1, and $a\text{Al} = a\text{H} = 0.5$ mT. These parameters nearly coincide with the parameters of complex **1** or, more exactly, green solution of Cp_2TiAlH_4 resulting from heterogeneous reaction (1) [2]. This finding suggests that, in solutions complexes **7** and **1** are the same compound [2] and their toluene solutions differ only in the concentration of impurities, if at all.

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[1] The complex $LiAlEt_4$ was characterized by X-ray structure analysis (Table 1). Since our data differ only little from the data reported earlier [10] (e.g. our Li–C distance is 0.02 Å shorter), we do not discuss the structure of this compound in detail.

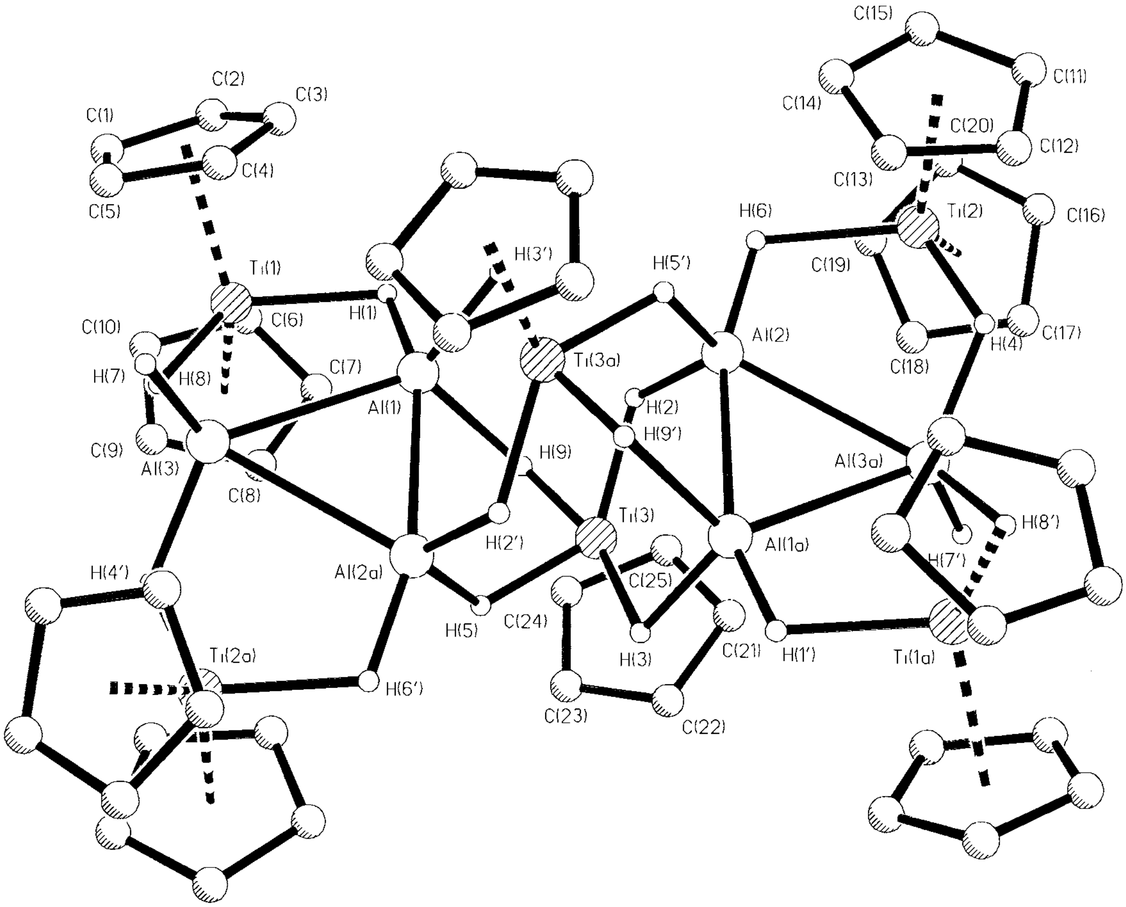

Fig. 1. Molecular structure of the complex {[(η^5-C_5H_5)$_2$Ti(μ-H)]$_2$[(η^5-C_5H_5)Ti(μ-H_2]Al_3(μ-H_4)(H)}.

The intense green color of toluene solutions of pale crystals of complex **7** can be accounted for by solvate formation. Note that AlH_3 forms unstable π-complexes with arenes [14], and bis(cyclopentadienyl)titanium alumohydrides can be considered to be its derivatives [1]. The existence of such complexes is confirmed by the fact that addition of a polycyclic arene (anthracene) to a solution of **7** causes further darkening of the solution, which becomes dark green or even almost black. This effect is likely explained by the lengthening of the conjugate chain as a result of the replacement of coordinated toluene with anthracene.

The properties of complex **7** dissolved in toluene are well predictable. Freshly prepared solutions of **7** react readily with ether to yield violet ether-solvated complex **6** characterized by a well-resolved EPR octet [12,15]. Complex **7** reacts with hexene-1 to form hydrometalation products giving rise to a multicomponent EPR signal similar to that observed upon the reaction between **6** and hexene-1 in an ether–toluene mixture [12,15]. Toluene solutions of **7** are much less stable than solutions of $Cp_2TiAlH_4 \cdot L$ [1,12] and $(Cp_2^*TiAlH_4)_2$ [1,13] in ether–toluene. When stored at 20°C for 24 h, they change their color from green to violet and release aluminum and hydrogen. Most of the substance remaining in solution is only isolable as an amorphous precipitate whose elemental analysis is similar to that of complex **2**, which is reported [2] to be a product of heterogeneous reaction (1). A smaller proportion of the substance was isolated as crystals (complex **8**) and characterized by X-ray structure analysis.

Compound **8** is the 12-nuclear complex {[(η^5-C_5H_5)$_2$Ti(μ - H)]$_2$[(η^5 - C_5H_5)Ti(μ - H_2]Al_3(μ - H_4)(H)}$_2$, which contains of six titanium and six aluminum atoms hydrogen-bridged in a complex fashion (Fig. 1, Table 2)[2]. As a whole, complex **8** differs markedly in structure from the previously reported hydrido complexes of bis(cyclopentadienyl)titanium and aluminum. Firstly, 16 of its 18 hydride hydrogens are bridging, and only two of its Al–H bonds are terminal. Secondly, its terminal fragments Cp_2Ti(1)H(01)H(08), having a distorted tetrahedral geometry typical for bis(cyclopentadienyl)titanium alumohydrides, form single bridges through the H(01) and H(08) atoms with the inequivalent atoms Al(1) and Al(3) rather than Ti–H_2–Al double bridges [1] typical for these compounds. Correspondingly, it is characterized by a very large

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[2] According to X-ray data, the structure of **8** contains a disordered benzene molecule.

H(01)–Ti(1)–H(08) angle of 116.6°, while Ti–H_2–Al bridges typically have an angle about 75°. The basic interatomic distances Ti(1)–Cp, Ti(1)–H(01), Ti(1)–H(08), Al(1)–H(01), and Al(3)–H(08) are 2.05, 1.90, 1.68, 1.59, and 1.55 Å, respectively, in agreement with the known values [1].

The most surprising and interesting structural feature of **8** is the geometry and surrounding of fragments containing three aluminum atoms. All of the Al(1)–Al(2), Al(1)–Al(3), and Al(2)–Al(3) distances (2.640, 2.709, and 2.728 Å, respectively) lie within the range of values reported [16–18] for binuclear aluminum compounds with a direct Al–Al bond. Allowing for direct Al–Al bonding and taking into account the composition of complex **8**, the oxidation number of the Ti atoms (+3), and the known coordinates of hydride hydrogen atoms, we arrive at the conclusion that the fragment in question is a trinuclear aluminum cluster stabilized by hydrogen bridges.

The Ti(3) atom, positioned in the central part of the structure of **8**, has a heavily distorted trigonal–bipyramidal environment of four hydrogen atoms and one Cp ring. The bis(cyclopentadienyl)titanium alumohydride condensation under report is the first process of its kind where the loss of one Cp ligand is confirmed by structure analysis. Such processes are typical of compounds with more ionic Cp–M bonds (e.g. lanthanidocene alumohydrides [1]), while in bis(cyclopentadienyl)titanium complexes, there usually occurs the activation of a C–H bond in a Cp ligand, resulting in η^1:η^5 bonding. These fragments are present in **3** [1], its alkoxyl analog [19], the above-mentioned Natta–Tebbe complexes [5], and labile titanocenes [11].

Another peculiarity of **8** is the empty space (about 2.5 Å in size) in the center of its structure; because of this, the system of metal–hydrogen bonds in the central fragment looks like a Chinese lantern.

Reactions yielding **8** are uncertain. It can only be stated that complexes **7** and **1** (mentioned above as being most likely the same compound) transform to complexes **2** and/or **8** in an aromatic solvent at r.t. and to these and complex **3** in the presence of cyclohexene. These transformations occur under identical or very similar conditions. The process as a whole is undirected and can apparently yield not only the products considered but also other, yet unknown compounds. Although the tendency to bis(cyclopentadienyl)titanium alumohydride condensation is more pronounced in aromatic hydrocarbons than in donor solvents — in the latter case, the only reliably identified condensation product is complex **3** (and its closely related analog [19]) — it is not impossible that the reactions occurring in donor solvents are more complex than they have so far been thought about [1].

2.2. Catalytic activity of unsolvated bis(cyclopentadienyl)titanium alumohydride complexes in hexene-1 hydrogenation

Binuclear solvates of composition $Cp_2TiAlH_4 \cdot L$ (L = Et_2O, THF, NR_3) in ether–toluene are known [1,12] to be absolutely inactive in hexene-1 hydrogenation. By contrast, a toluene solution of complex **7** was found to exert a strong catalytic effect on this process: the initial hydrogen uptake rate was 250 mol H_2/(g-at Ti min), comparable to those observed with the most effective trinuclear hydrido complexes of bis(cyclopentadienyl)titanium and aluminium in ether-containing solvents [1].

Encouraged by this finding, we studied the activity of $(Cp_2Ti)_2AlH_4Cl$ (**9**) [1,20] and $(Cp_2TiAlH_3OEt)_2$ (**10**) [1,19,20] in pure toluene, for these complexes have been known to actively catalyze hexene-1 hydrogenation in ether–toluene mixtures. Toluene solutions proved to be much more active. The initial hydrogen uptake rate with complex **9** was 320 mol H_2/(g-at Ti min) (against 125 mol H_2/(g-at Ti min) for an ether–toluene mixture [1,20]), and that with complex **10** was 280 mol H_2/(g-at Ti min) (against 150 mol H_2/(g-at Ti min [1,19]) for an ether–toluene mixture.

The deactivating effect of excess solvating solvent on Ziegler catalysts is well known, and so the observed gain in activity is quite predictable. However, the examples of the similar complexes **7** and **6** demonstrate that, in some cases, solvation can selectively hamper the catalytic activity. For example, complex **7** in toluene accelerates hexene-1 hydrogenation and likely isomerize the substrate[3]. Complex **6** in ether–toluene neither catalyzes hexene-1 hydrogenation nor affects the capability of hexene-1 for isomerization [1,12]. Thus, solvation with a weak base can serve as a means for varying the kind of activity and, possibly, the substrate selectivity of a catalyst.

3. Experimental

All manipulations were performed in an argon atmosphere or in vacuum. Solvents were purified by boiling and distillation over $LiAlH_4$ in an argon atmosphere. Ethylene was purified by double condensation into a 20% solution of $Al(i\text{-}Bu)_3$ in toluene with subsequent vaporization.

EPR spectra were recorded on a Varian E-3 spectrometer operated at 100 kHz with an Mn(+2) reference. IR spectra were taken on an UR-20 spectrophotometer as Nujol mulls.

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[3] Olefin hydrometallation with $LiAlH_4$ in the presence of Cp_2TiCl_2 may be accompanied by olefin isomerization [8]. Above 60°C, the Cp_2TiCl_2–$LiAlH_4$ systems actively isomerize olefins [5].

3.1. $\{(Cp_2TiH_2AlH(\eta_1{:}\eta_5\text{-}C_5H_4)TiCp(H)\}_2$ (**5**)

To activated [2] $LiAlH_4$ (0.06 g, 1.6 mmol) was added a solution of $(Cp_2TiCl)_2$ (0.1 g, 0.23 mmol) in a mixture of toluene (16 ml) and cyclohexene (2 ml). The resulting mixture was stirred for 5 h at 35°C and filtered. After the filtrate had been held at 20°C for 2 weeks, a crystalline precipitate (0.03 g) resulted, which was filtered off, washed with toluene, and dried in vacuum. Found (%): Ti, 22.8; Al, 6.5. Anal. Calc. for $C_{40}H_{46}Ti_4Al_2{\cdot}C_7H_8$ (%): Ti, 22.20; Al, 6.26. X-ray structure analysis was performed on a selected single crystal sealed in a glass capillary. The crystallographic parameters of the compound obtained were found to be identical to those reported previously [22].

3.2. *Catalyzed hydroalumination of ethylene with lithium aluminum hydride*

A solution of $(Cp_2TiCl)_2$ (0.12 g, 2 mmol) in toluene (15 ml) was added to activated [2] $LiAlH_4$ (0.08 g, 2 mmol) in an ethylene atmosphere ($p = 1$ atm). The reaction mixture was stirred at 35°C for 3 h and at 20°C for another 10 h and then filtered. Next, the mixture was cooled to 5°C, and the resulting colorless needle-like crystals (0.1 g, 50% yield in terms of $LiAlH_4$) were filtered off the mother liquor, washed with toluene, and dried in vacuum. Found (%): Li, 4.5; Al, 17.8. Anal. Calc. for $C_8H_{20}AlLi$ (%): Li, 4.67; Al, 18.0. One crystal was selected for X-ray structure determination (Table 1).

Table 1
Crystal data and structure refinement for $LiAlEt_4$ and $\{[(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}H)]_2[(\eta^5\text{-}C_5H_5)Ti(\mu\text{-}H_2]Al_3(\mu\text{-}H_4)(H)\}_2{\cdot}C_6H_6$ (**8**)

Compound	$LiAlEt_4$	**8**
Empirical formula	$C_8H_{20}AlLi$	$C_{50}H_{68}Al_6Ti_6{\cdot}C_6H_6$
Formula weight	150.16	1195.88
Color	Colorless	Dark-red
Crystal size (mm)	0.3 × 0.2 × 0.2	0.28 × 0.25 × 0.20
Unit cell dimensions		
a (Å)	9.999(1)	12.296(2)
b (Å)	9.999(1)	21.915(4)
c (Å)	5.400(1)	12.096(2)
β (°)	90	117.05(3)
Wavelength (Å)	0.71073	1.54179
Radiation type	Mo–K_α (β-filter)	Cu–K_α (β-filter)
Crystal system	Tetragonal	Monoclinc
Space group	$P4_2/nmc$	$P2_1/c$
Z	2	2
V (Å^3)	539.89(13)	2902.9(9)
D_{calc} (g cm^{-3})	0.924	1.364
Diffractometer	CAD-4	Syntex $P\bar{1}$
Collection method	$\theta/2\theta$	$\theta/2\theta$
θ range for data collection (°)	2.88–24.36	4.04–50.04
Absorption coefficient (mm^{-1})	0.124	7.840
Reflections collected	164	2108
Independent reflections	113	1996
Goodness-of-fit on F^2	1.133	1.097
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0292$ $wR_2 = 0.0733$	$R_1 = 0.0527$ $wR_2 = 0.1331$

3.3. $(Cp_2TiAlH_4)_2$ (**7**)

A solution of 2 mmol of complex **6** in 35 ml of an ether–toluene (1:5) mixture, prepared [12] by reacting $(Cp_2TiCl)_2$ (0.43 g, 1 mmol) with $LiAlH_4$ (0.068 g, 2 mmol), was evaporated in vacuum without heating. The resulting yellow–gray substance was dried in vacuum at 25°C. Found (%): Ti, 22.3; Al, 12.0. Anal. Calc. for $C_{20}H_{28}Ti_2Al_2$ (%): Ti, 22.93; Al, 12.92. A toluene solution of complex **7** was prepared similarly, with the only difference that tetradecane was added to a solution of **6** in ether–toluene (about 2 ml of alkane per mmol of **6**) prior to evaporation. The yellow–gray suspension obtained after solvent evaporation was stirred at 0.1 mmHg and 25°C for 0.5 h and then dissolved in toluene (60 ml per 0.5 mmol of **7**). The resulting green solution was reacted with excess anthracene, ether, and hexene-1 and used in other experiments.

3.4. $\{[(C_5H_5)_2TiH]_2[(C_5H_5)TiH_2]Al_3H_5\}_2$ (**8**)

A solution of complex **7** (0.5 mmol) in 60 ml of toluene–benzene (1:1) was prepared as described above and held at 20°C for 1 day. The resulting aluminum metal was filtered off, and the violet filtrate was reduced in volume and held at 20°C for 1 week to obtain a dark precipitate (0.05 g), which was washed with benzene and dried in vacuum. Found (%): Ti, 22.8; Al, 4.6. Anal. Calc. for complex **2** ($C_{30}H_{36}Ti_3Al$ [2]) (%): Ti, 25.36; Al, 4.7. Upon standing at 20°C for 3 weeks, the filtrate yielded dark crystals, which were separated, washed with toluene, and dried in vacuum and identified by X-ray structure determination as complex **8** (Tables 1 and 2).

3.5. *Evaluation of the catalytic activity of complexes in hexene-1 hydrogenation*

In hydrogenation, we tested a solution of complex **7** (0.5 mmol) in toluene (60 ml) prepared as described above, as well as complexes **9** [20] and **10** [19,21] prepared by standard procedures. The latter were separated from reaction mixtures by evaporating their solutions in the presence of tetradecane (as in the case of **7**) and dissolved in toluene up to a concentration of 0.02–0.05 (mg-at Ti)/ml.

Hydrogenation was performed at 20°C and 1 atm in a reactor attached to a set of burettes for measuring the volume of consumed gas as described elsewhere [12]. The hexene-1:titanium ratio was 120:150. Hydrogen,

Table 2
Selected bond lengths and bond angles for **8**

Bond	(Å)	Angle	(°)
Ti(1)–H(1)	1.90	H(8)–Ti(1)–H(1)	116.6
Ti(1)–H(8)	1.68	Cp(1)–Ti(1)–H(1)	99.6
Ti(1)–Cp(1)	2.04	Cp(1)–Ti(1)–H(8)	101.2
Ti(1)–Cp(2)	2.06	Cp(2)–Ti(1)–H(1)	101.1
		Cp(2)–Ti(1)–H(8)	101.9
		Cp(1)–Ti(1)–Cp(2)	137.5
Ti(2)–H(6)	1.94	H(4)–Ti(2)–H(6)	117.3
Ti(2)–H(4)	1.60	Cp(3)–Ti(2)–H(6)	102.3
Ti(2)–Cp(3)	2.05	Cp(3)–Ti(2)–H(4)	95.2
Ti(2)–Cp(4)	2.05	Cp(4)–Ti(2)–H(6)	98.9
		Cp(4)–Ti(2)–H(4)	107.3
		Cp(3)–Ti(2)–Cp(4)	137.2
Ti(3)–Cp(5)	2.04	H(5)–Ti(3)–Cp(5)	103.4
Ti(3)–H(5)	1.68	H(9)–Ti(3)–Cp(5)	97.2
Ti(3)–H(9)	1.43	H(9)–Ti(3)–H(5)	86.5
Ti(3)–H(2)	1.82	H(2)–Ti(3)–Cp(5)	103.3
Ti(3)–H(3)	1.77	H(2)–Ti(3)–H(5)	137.6
		H(2)–Ti(3)–H(9)	57.9
		H(3)–Ti(3)–Cp(5)	100.0
		H(3)–Ti(3)–H(5)	72.2
		H(3)–Ti(3)–H(9)	155.1
		H(3)–Ti(3)–H(2)	133.5
Al(1)–Al(3)	2.708	H(1)–Al(1)–Al(3)	103.9
Al(1)–H(1)	1.59	H(9)–Al(1)–Al(3)	126.2
Al(1)–H(9)	2.01	H(9)–Al(1)–H(1)	95.0
Al(1)–Al(2a)	2.640	Al(2a)–Al(1)–Al(3)	61.3
Al(1)–H(3′)	1.78	Al(2a)–Al(1)–H(1)	160.1
		Al(2a)–Al(1)–H(9)	85.1
		H(3′)–Al(1)–Al(3)	117.3
		H(3′)–Al(1)–H(1)	98.5
		H(3′)–Al(1)–H(9)	108.6
		H(3′)–Al(1)–Al(2a)	100.2
Al(2)–H(2)	1.66	H(2)–Al(2)–H(6)	95.5
Al(2)–H(6)	1.60	Al(3a)–Al(2)–H(2)	121.5
Al(2)–Al(3a)	2.727	Al(3a)–Al(2)–H(6)	104.3
Al(2)–Al(1a)	2.640	Al(1a)–Al(2)–H(2)	101.7
Al(2)–H(5′)	1.76	Al(1a)–Al(2)–H(6)	161.4
		Al(1a)–Al(2)–Al(3a)	60.6
		H(5′)–Al(2)–H(2)	117.5
		H(5′)–Al(2)–H(6)	101.0
		H(5′)–Al(2)–Al(3a)	111.8
		H(5′)–Al(2)–Al(1a)	77.2
Al(3)–Al(1)	2.708	Al(1)–Al(3)–H(7)	116.5
Al(3)–H(7)	1.58	Al(1)–Al(3)–H(8)	88.1
Al(3)–H(8)	1.55	H(7)–Al(3)–H(8)	100.2
Al(3)–Al(2a)	2.727	Al(2a)–Al(3)–Al(1)	58.1
Al(3)–H(4′)	1.73	Al(2a)–Al(3)–H(7)	114.3
		Al(2a)–Al(3)–H(8)	139.4
		H(4′)–Al(3)–Al(1)	127.3
		H(4′)–Al(3)–H(7)	111.6
		H(4′)–Al(3)–H(8)	103.6
		H(4′)–Al(3)–Al(2a)	83.8

was delivered from a cylinder filled with $LaNi_5H_x$. The initial rate of hydrogen uptake was considered a measure of catalyst activity.

3.6. X-ray structure determination

The structures of $LiAlEt_4$ and complex **8** were determined on single crystals sealed in glass capillaries. The data-collection conditions and basic crystallographic parameters of the complexes are presented in Table 1. The structures were solved by heavy-atom methods and refined by anisotropic full-matrix least-squares with the use of the SHELXTL-PLUS and SHELXL software packages. Hydride hydrogen atoms were located from difference syntheses, and their coordinates and isotropic thermal parameters were not refined. The other hydrogen atoms were placed geometrically, and their coordinates were introduced in the refinement with fixed displacement and thermal parameters.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC, no. 135237 for compound $LiAlEt_4$ and no. 135238 for compound **8**. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk.

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