Organometallic Chemistry

Activation of biscyclopentadienyl hydride complexes of titanium and aluminum by NH- and OH-acids in the reactions of hydrogenation of olefins. Crystal and molecular structures of $\{(\eta^5\text{-Cp})_2\text{Ti}(\mu\text{-H})_2\text{AlH}[\mu\text{-N}(\text{C}_2\text{H}_4)_2\text{O}]\}_2$ and $[(\eta^5\text{-Cp})_2\text{Ti}(\mu\text{-H})_2\text{Al}]_2(\mu\text{-OC}_2\text{H}_4\text{OMe})[(\eta^1{:}\eta^5\text{-C}_5\text{H}_4)\text{Ti}(\eta^5\text{-Cp})(\mu\text{-H})]_2$*

A. I. Sizov,[a]* *T. M. Zvukova,*[a] *V. K. Bel'sky,*[b] *and B. M. Bulychev*[a]

[a]*Department of Chemistry, M. V. Lomonosov Moscow State University,*
Leninskie Gory, 119899 Moscow, Russian Federation.
Fax: +7 (095) 932 9846. E-mail: highp@mch.chem.msu.su
[b]*State Research Center of the Russian Federation "L. Ya. Karpov Scientific-Research Physicochemical Institute,"*
10 ul. Vorontsovo Pole, 117120 Moscow, Russian Federation.
Fax: +7 (095) 975 2450. E-mail: belsky@cc.nifhi.ac.ru

The reactions of $\text{Cp}_2\text{TiH}_2\text{AlH}_2 \cdot \text{Et}_2\text{O}$ (**1**) with $\text{HN}(\text{C}_2\text{H}_4)_2\text{O}$, $\text{HOC}_2\text{H}_4\text{OMe}$, and water afforded the complexes $\{\text{Cp}_2\text{TiH}_2\text{AlH}[\mu\text{-N}(\text{C}_2\text{H}_4)_2\text{O}]\}_2$ (**5**), $[\text{Cp}_2\text{TiH}_2\text{AlH}(\mu\text{-OC}_2\text{H}_4\text{OMe})]_2$ (**6**) and $(\text{Cp}_2\text{TiH}_2\text{AlH})_2\text{O}$ (**4**), respectively. Compounds **5** and **6** are dimers containing bridging Al—E_2—Al fragments (E = N or O). Complex **6** in solution converted to the hexanuclear compound $[(\eta^5\text{-Cp})_2\text{Ti}(\mu\text{-H})_2\text{Al}]_2(\mu\text{-OC}_2\text{H}_4\text{OMe})[(\eta^1{:}\eta^5\text{-C}_5\text{H}_4)\text{Ti}(\eta^5\text{-Cp})(\mu\text{-H})]_2$ (**8**). The structures of complexes **5** and **8** were established by X-ray diffraction analysis. The rates of hydrogenation of hex-1-ene were determined using compounds **4**—**6** and the complexes $[\text{Cp}_2\text{TiH}_2\text{AlH}(\text{NEt}_2)]_2$ and $[\text{Cp}_2\text{TiH}_2\text{AlH}(\text{OEt})]_2$ as catalysts. The probable mechanism of hydrogenation with the participation of bimetallic hydride complexes of aluminum and titanocene is discussed.

Key words: titanium, aluminum, metallocenes, hydrides; olefins, hydrogenation, catalysis.

Previously, we have demonstrated that the reactions of $\text{Cp}'_2\text{TiHal}$ (Cp′ = $\eta^5\text{-C}_5\text{H}_5$ or C_5Me_5; Hal = Cl or Br) with MAlH_4, aluminum hydride, or its derivatives afforded bimetallic hydride complexes of two major types, namely, the binuclear $\text{Cp}'_2\text{Ti}(\mu\text{-H})_2\text{AlH(X)L}$ and the trinuclear $[\text{Cp}'_2\text{Ti}(\mu\text{-H})]_2\text{Al}(\mu\text{-H})_2\text{X}$ complexes (X = H, Hal, Alk, BH_4, OR, or NR_2; L is a Lewis base).[1]

The trinuclear complexes are weak catalysts for isomerization of olefins and efficient catalysts for their hydrogenation.[2] When the terminal chlorine atom (X = Cl) is replaced by the amide (X = NR_2) or alkoxy (X =

---

* Dedicated to the memory of Academician M. E. Vol'pin timed to his 75th birthday.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 6, pp. 1216—1222, June, 1998.

1066-5285/98/4706-1186 $20.00

OR) group, the activity of these compounds increases substantially.

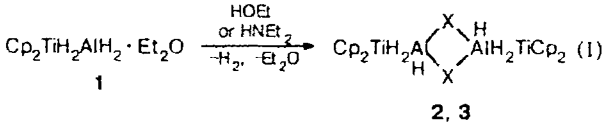
Binuclear and tetranuclear complexes with a purely hydride environment about the Al atom, such as monomeric aluminohydride $Cp_2Ti(\mu-H)_2AlH_2 \cdot Et_2O$ or the dimeric complex $[(C_5Me_5)_2Ti(\mu-H)_2Al(\mu-H)H]_2$, do not exhibit catalytic activity in hydrogenation of alkenes.[1,3] The first of these compounds is active only in the reactions of isomerization of olefins[1,4,5] and polymerization of acetylene.[6] At the same time, replacement of one terminal H atom in this complex by the Cl atom resulted in an increase in its activity in hydrogenation of olefins.[7]

Previously, products of replacement of hydrogen atoms in the binuclear complex by amide or alkoxy groups were obtained,[8] but their catalytic properties in the reactions of hydrogenation of olefins have not been studies. However, it is well known that treatment of Ziegler—Natta metallocene catalysts containing Group IV transition metals with OH-acids, in particular, with water, results in a radical change in their catalytic activity in polymerization of unsaturated hydrocarbons.[9] Previously,[1] it has been suggested that active centers have similar compositions and structures, and hydrogenation and polymerization proceed according to analogous mechanisms. Therefore, we attempted to use an analogous approach to the activation of hydride complexes of bis(cyclopentadienyl)titanium(III) and bis(cyclopentadienyl)aluminum by treating them with NH- and OH-acids.

In this work, we report the principal results of these studies. The catalytic properties of the resulting compounds were studied in the reactions of homogeneous hydrogenation of hex-1-ene. The structures of two new complexes isolated from these systems were established.

Results and Discussion

It is known[8] that the reactions of the complex $Cp_2TiH_2AlH_2 \cdot Et_2O$ (**1**) with an equimolar amount of alcohol or secondary amine proceed in a similar fashion (reaction (1)) to form dimers **2** or **3**, respectively. The structures of **2** and **3** have been established by X-ray diffraction analysis.



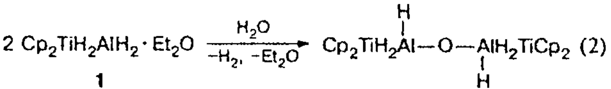
(1)

X = OEt (**2**), NEt_2 (**3**)

Unlike monomeric complex **1** and the dimeric complex $[(C_5Me_5)_2TiH_2AlH_2]_2$, compounds **2** and **3** catalyze hydrogenation of olefins. The rates of hydrogenation of hex-1-ene in the presence of these compounds (150 and 165 mol H_2 (g-at. Ti)$^{-1}$ min^{-1} for **2** and **3**, respectively) are lower that the rates of hydrogenation of the trinuclear complexes $[Cp_2TiH]_2AlH_2X$ (X = OR or NEt_2)[2] and are almost twice as large as the value determined for $Cp_2TiH_2AlH(Cl)$ (80 mol H_2 (g-at. Ti)$^{-1}$ min^{-1}).[7] Treatment of complex **1** with an excess of diethylamine did not lead to complete and rapid suppression of the hydrogenating activity of the compound. The rate of hydrogenation decreased smoothly from 165 mol H_2 (g-at. Ti)$^{-1}$ min^{-1} (observed at the ratio **1** : $HNEt_2$ = 1 : 1, which corresponded to the formation of complex **3**) to 102, 78, and 54 mol $H_2 \cdot$ (g-at. Ti)$^{-1}$ min^{-1} at **1** : $HNEt_2$ = 1 : 2, 1 : 3, and 1 : 4, respectively (at these ratios, all metal—hydride bonds in the catalyst should be converted into amide bonds). Even at the reagent ratio of 1 : 10, the activity of the catalyst remained rather high (46 mol H_2 (g-at. Ti)$^{-1}$ min^{-1}) over several days.

The observed regularity is most easily attributable to the low rate of interaction of the diethylamine with metal—hydride bonds. This rate should decrease noticeably due to an increase in the steric hindrance as the number of introduced diethylamide groups increases. This fact is rather well known for aluminum hydride. For example, an attempt to replace all hydride hydrogen atoms by amide groups by treating AlH_3 etherate with ammonia or monoalkylamines at ~20 °C was unsuccessful.[10]

In this respect, water is a more active modifier. Previously,[11] we have demonstrated that hydrolysis of the complex $[(C_5Me_5)_2TiH_2AlH_2]_2$ under mild conditions afforded a polynuclear compound, whose central fragment contains Al—O—Al bridges. By analogy, we carried out hydrolysis of complex **1** at the ratio **1** : H_2O = 2 : 1. We suggested that in this case, reaction (2) proceeded to form a compound with the primary structure of type **4**.



$$\underset{\mathbf{1}}{2\,Cp_2TiH_2AlH_2 \cdot Et_2O} \xrightarrow[-H_2,\ -Et_2O]{H_2O} \underset{\mathbf{4}}{Cp_2TiH_2\overset{H}{\overset{|}{Al}}—O—\underset{H}{\underset{|}{Al}}H_2TiCp_2} \quad (2)$$

The IR spectrum of a solid sample of complex **4** has bands at 1235 and 1260 cm^{-1}, which correspond to $M—H_{bridge}$ vibrations, and a band at 1810 cm^{-1} assigned to $Al—H_{term}$ stretching vibrations. On the whole, the spectrum is typical of aluminohydrides of bis(cyclopentadienyl)titanium[12,13] and does not contradict the suggested structure. Compound **4** exhibits catalytic activity in hydrogenation of hex-1-ene (120 mol H_2 (g-at. Ti)$^{-1}$ min^{-1}).

To explain the catalytic properties of the compounds under study, it is very important to elucidate the question of how the above-mentioned fact is associated with the existence of the Al—E_2—Al (E = O or N) fragments in complexes **2** and **3** or the Al—O—Al fragment in complex **4**. It is unlikely that these compounds are in themselves catalysts for hydrogenation because the Ti^{III} atom in these compounds is coordinatively saturated, while the five-coordinate Al atom, according to popular

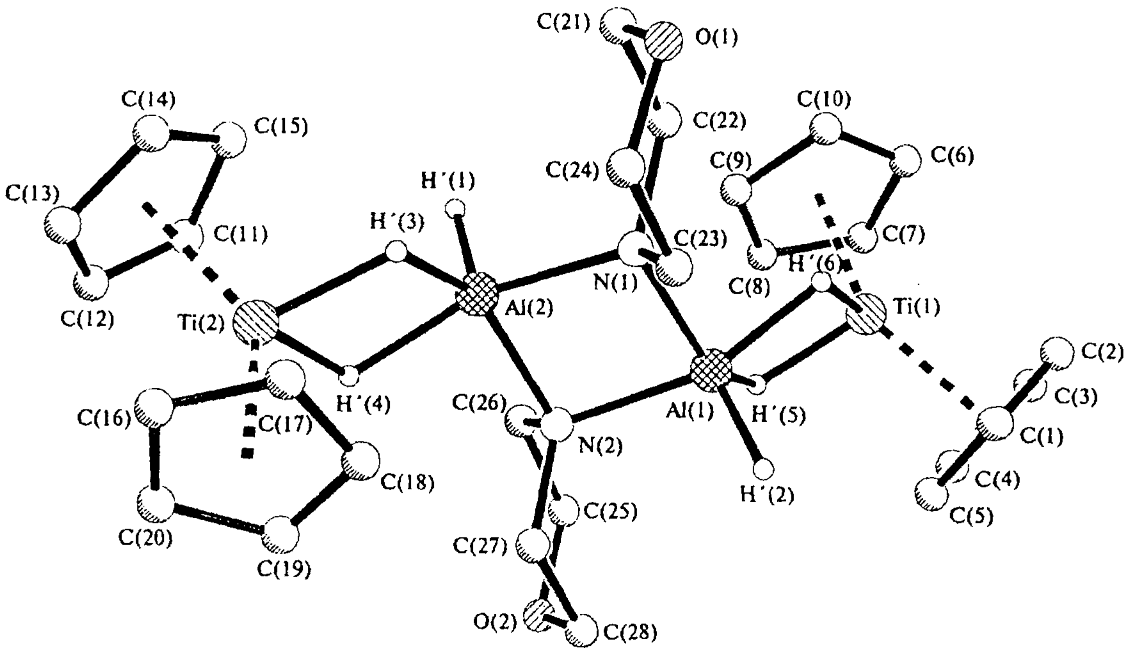


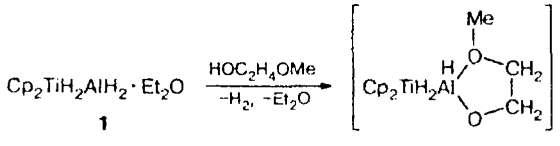
Fig. 1. Molecular structure of complex 5.

opinion, cannot act as a metal that forms a catalytically active center. Conceivably, dimers 2 and 3 in solutions exist in the equilibrium with the monomeric form (equilibrium (3)), and therefore, solvated monomeric molecules with an asymmetrical environment about the Al atom rather than dimeric molecules serve as a source of catalytically active particles.

$$[Cp_2TiH_2AlH(X)]_2 \underset{-Et_2O}{\overset{+Et_2O}{\rightleftharpoons}} 2\ Cp_2TiH_2AlH(X)\cdot Et_2O \quad (3)$$

Owing to the high strength of the Al—E$_2$—Al or Al—O—Al fragment, the concentration of this monomer can be very low. However, it can convert rapidly to the trinuclear complex, which is active in hydrogenation as exemplified by the compounds $Cp_2TiH_2AlH(X)\cdot Et_2O$ (X = Cl, Alk, or BH_4).[2,14–16]

Based on this assumption, we attempted to carry out the target synthesis of the monomeric compounds. For this purpose, we studied the reactions of complex **1** with morpholine ($HN(C_2H_4)_2O$) and methylcellosolve (HOC_2H_4OMe), *i.e.*, with bifunctional ligands, which exhibit chelating properties and which, in principle, can stabilize the monomeric state with the five-coordinate Al atom (reaction (4)).



(4)

However, it appeared that in the crystalline state, the product of the reaction of complex **1** with morpholine, namely, $\{(\eta^5\text{-}Cp)_2Ti(\mu\text{-}H)_2Al(H)[\mu\text{-}N(C_2H_4)_2O]\}_2$ (**5**), exists also as a dimer and has the structure (Fig. 1, Tables 1—3) similar to that of compound **3**. Dimerization occurs due to the formation of the Al—N—Al

Table 1. Details of X-ray diffraction study and crystallographic characteristics of complexes **5** and **8**

Parameter	5	8
Molecular formula	$C_{28}H_{42}Al_2N_2O_2Ti_2$	$C_{43}H_{52}Al_2O_2Ti_4$
a/Å	10.230(2)	21.200(4)
b/Å	20.655(4)	11.817(2)
c/Å	13.801(3)	16.401(3)
β/deg	98.61(3)	90.45(3)
V/Å^3	2883.3(10)	4108.7(13)
Z	4	4
Space group	*P*2(1)/*n*	*P*2(1)/*c*
M	588.4	846.4
d_{calc}/g cm^{-3}	1.355	1.368
Diffractometer	Syntex P$\bar{1}$	
Radiation	Mo-Kα (Ni-filter)	
$2\theta_{max}$/deg	40	50
Absorption coefficient/mm^{-1}	0.642	0.827
Crystal size/mm	0.30×0.24×0.21	0.40×0.35×0.18
Number of reflections	2018	2476
σ(*I*)	2	2
R	0.0353	0.0395
R_w	0.0817	0.0879

Table 2. Atomic coordinates ($\times 10^4$) and isotropic temperature factors ($U_{\text{iso}} \times 10^3$) for complex 5

Atom	*x*	*y*	*z*	U_{iso}/Å^2	Atom	*x*	*y*	*z*	U_{iso}/Å^2
Ti(1)	6937(1)	8037(1)	2019(1)	38(1)	C(14)	1135(9)	4560(5)	901(6)	66(2)
Ti(2)	2788(1)	4753(1)	2228(1)	36(1)	C(15)	2134(12)	4878(6)	524(6)	76(3)
Al(1)	5627(2)	7001(1)	2754(1)	33(1)	C(16)	1722(10)	4243(5)	3405(6)	78(3)
Al(2)	4147(2)	5891(1)	1892(1)	33(1)	C(17)	1714(10)	4904(6)	3588(6)	74(3)
O(1)	994(4)	7231(2)	2011(4)	63(1)	C(18)	3009(10)	5090(4)	3863(5)	56(2)
O(2)	8654(4)	5586(2)	3162(4)	69(1)	C(19)	3786(8)	4548(4)	3866(5)	48(2)
N(1)	3746(4)	6795(2)	2263(3)	28(1)	C(20)	3009(9)	4028(4)	3569(5)	61(2)
N(2)	5973(4)	6067(2)	2551(3)	29(1)	C(21)	1619(7)	7077(4)	1198(6)	51(2)
C(1)	6997(9)	8430(4)	3639(5)	58(2)	C(22)	3077(7)	7174(4)	1405(6)	45(2)
C(2)	7179(9)	8947(4)	3041(6)	64(2)	C(23)	2973(7)	6926(4)	3075(5)	46(2)
C(3)	8395(9)	8842(4)	2683(7)	75(2)	C(24)	1518(7)	6833(4)	2813(7)	56(2)
C(4)	8879(9)	8259(5)	3040(8)	76(3)	C(25)	8326(7)	5923(4)	2279(7)	58(2)
C(5)	8033(11)	8012(5)	3649(6)	69(2)	C(26)	6889(6)	5866(3)	1861(5)	40(2)
C(6)	6659(15)	8634(5)	562(6)	92(3)	C(27)	6416(7)	5719(3)	3485(5)	43(2)
C(7)	7830(13)	8286(7)	604(6)	87(3)	C(28)	7866(8)	5813(4)	3843(6)	60(2)
C(8)	7536(10)	7639(5)	550(5)	67(2)	H′(6)	5375(46)	7764(22)	2362(34)	61(15)
C(9)	6195(9)	7573(4)	477(5)	55(2)	H′(5)	7060(38)	7266(19)	2307(28)	33(12)
C(10)	5649(10)	8187(5)	471(5)	67(2)	H′(4)	4365(39)	5070(19)	2154(29)	36(13)
C(11)	3242(11)	4446(7)	672(7)	89(4)	H′(3)	2619(44)	5575(22)	2102(32)	54(15)
C(12)	2846(12)	3916(5)	1106(8)	84(3)	H′(2)	5757(40)	7073(19)	3886(29)	38(13)
C(13)	1580(10)	3962(5)	1252(6)	73(2)	H′(1)	4239(42)	5918(21)	774(31)	49(14)

Table 3. Principal bonds lengths (*d*) and bond angles (ω) in molecule 5

Bond	*d*/Å	Angle	ω/deg	Bond	*d*/Å	Angle	ω/deg
Al(1)—N(2)	1.988(4)	N(2)—Al(1)—N(1)	85.9(2)	Ti(1)—H′(5)	1.64(5)	H′(5)—Al(1)—N(2)	94
Al(1)—N(1)	1.988(4)	Al(2)—N(1)—Al(1)	93.6(2)	Ti(2)—H′(4)	1.76(5)	H′(5)—Al(1)—H′(6)	72
Al(2)—N(2)	1.985(4)	Al(2)—N(2)—Al(1)	93.8(2)	Ti(2)—H′(3)	1.71(5)	H′(2)—Al(1)—N(1)	107
Al(2)—N(1)	1.994(4)	N(2)—Al(2)—N(1)	85.8(2)	Al(1)—H′(6)	1.67(5)	H′(2)—Al(1)—N(2)	104
N(1)—C(23)	1.489(7)	H′(6)—Ti(1)—H′(5)	71	Al(1)—H′(5)	1.76(5)	H′(2)—Al(1)—H′(6)	103
N(1)—C(22)	1.498(7)	H′(4)—Ti(2)—H′(3)	73	Al(1)—H′(2)	1.56(5)	H′(2)—Al(1)—H′(5)	112
N(2)—C(27)	1.486(7)	H′(6)—Al(1)—N(1)	90	Al(2)—H′(4)	1.74(5)	Cp(1)—Ti(1)—Cp(2)	139.8
N(2)—C(26)	1.491(7)	H′(6)—Al(1)—N(2)	153	Al(2)—H′(3)	1.76(5)	Cp(3)—Ti(2)—Cp(4)	138.1
Ti(1)—H′(6)	1.82(5)	H′(5)—Al(1)—N(1)	137	Al(2)—H′(1)	1.56(5)		

amide bridge, whereas the O atoms are not involved in coordination to the Al atom. On the whole, the geometric parameters of this complex (see Table 3) differ only slightly from the corresponding parameters in complex 3 (in molecule 3, the interatomic Al—N, $\text{Al—H}_{\text{bridge}}$, $\text{Al—H}_{\text{term}}$, and Ti—Cp distances are 2.00, 1.75, 1.64, and 2.00 Å, respectively; the Cp—Ti—Cp, N—Al—N, and Al—N—Al angles are 137.5°, 86.2°, and 93.8°, respectively[8]).

We failed to isolate the product of the reaction of complex **1** with methylcellosolve as crystals suitable for X-ray diffraction study. However, the data of IR spectroscopy of a solid sample (absorption bands at 1220, 1250, and 1360 cm^{-1}, which belong to stretching vibrations of the bridging Al—H—Ti fragments,[13] and a symmetric band at 1800 cm^{-1}, which corresponds to stretching vibrations of the terminal Al—H bond[13]) suggest that in this case, too, the dimer $\{(\eta^5\text{-Cp})_2\text{Ti}(\mu\text{-H})_2\text{AlH}[\mu\text{-O(CH}_2)_2\text{OMe}]\}_2$ (**6**), whose structure is similar to that of complex **2**, was formed.

Both compounds catalyze hydrogenation of hex-1-ene. Morpholine derivative **5**, in spite of the fact that its structural parameters are similar to those of **3**, exhibits lower catalytic activity (20 mol H_2 $(\text{g-at.Ti})^{-1}$ min^{-1}) compared to that of complex **3**. Apparently, this fact is associated with the properties of the coordinated molecule of the cyclic ambidentate ligand. At the same time, the rate of hydrogenation with the participation of methylcellosolve derivative **6** (145 mol H_2 $(\text{g-at.Ti})^{-1}$ min^{-1}) is virtually equal to that observed in the case of complexes **2**, **3**, and **4**.

Therefore, the available data suggest that the formation of dimeric molecules of rather stable complexes containing bridging Al—O—Al or Al—N—Al fragments is a characteristic feature of compounds of this type. On the whole, this fact is not surprising because dimeric structures were observed for various amide and alkoxy derivatives of alane and alkylalanes.[17–19] This property distinguishes noticeably these compounds from the less stable complexes $\text{Cp}_2\text{TiH}_2\text{AlH(X)L}$ (X = Hal, BH_4, or Alk),

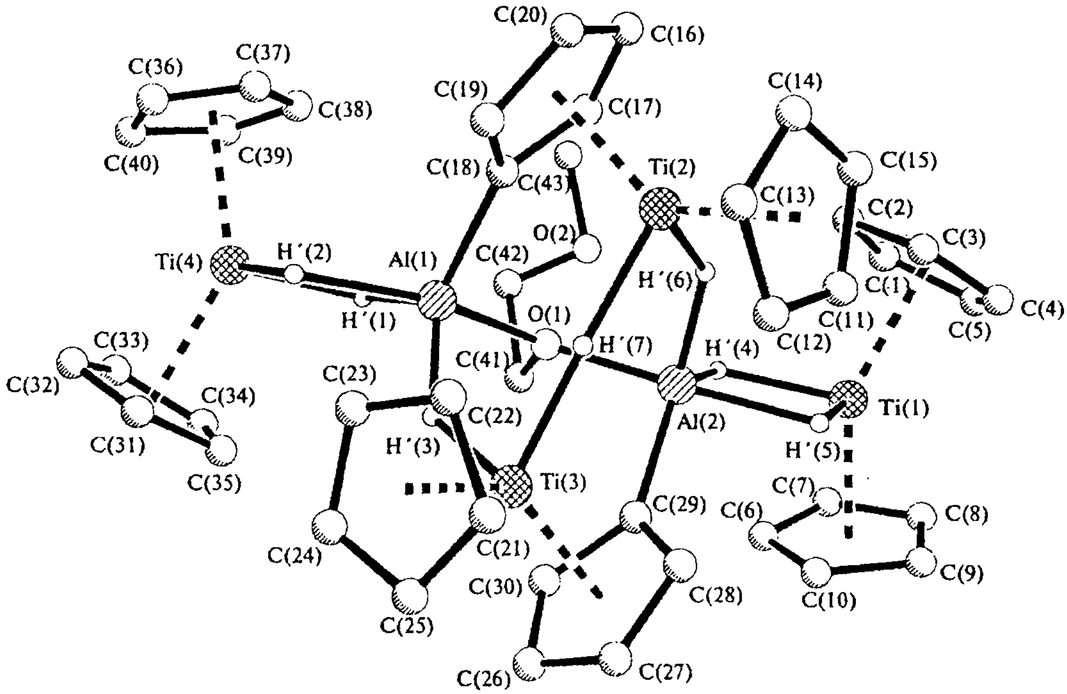


Fig. 2. Molecular structure of complex **8**.

which we have studied previously.[2,7,14–16] Apparently, the last-mentioned compounds do not form stable dimers and tend to convert rapidly to the trinuclear complexes $(Cp_2Ti)_2AlH_4X$,[2,14–16] which are catalytically active in hydrogenation. Upon prolonged storage in solution, the latter convert to the inactive hexanuclear complexes $[Cp_2Ti(\mu\text{-}H)_2Al(\mu\text{-}H')(\eta^1:\eta^5\text{-}C_5H_4)TiCp(\mu\text{-}H)]_2$ (**7**), which were isolated in three crystal modifications depending on the nature of the substituent X.[1,16,21]

The surprising thing is that, in spite of the substantially higher stability of compounds **2**—**6**, their behavior in solutions remains, apparently, analogous to the behavior of the complexes $Cp_2TiH_2AlH(X)L$ (X = Hal, BH_4, or Alk). This is evidenced by the fact that the hexanuclear complex $[(\eta^5\text{-}Cp)_2Ti(\mu\text{-}H)_2Al[\mu\text{-}OC_2H_4OMe](\eta^1:\eta^5\text{-}C_5H_4)Ti(\eta^5\text{-}Cp)(\mu\text{-}H)]_2$ (**8**) (Fig. 2, Table 4), whose structure is similar to that of compound **7**, was isolated from a solution of compound **6** upon prolonged storage (2 months). Unlike complex **7** that contains the Al—H′—Al hydride bridging fragment, molecule **8** contains the Al—O—Al bridge in which the O atom bonded to the C_2H_4OMe group plays a role identical to that of the hydride H′ atom in molecule **7**. Although these compounds are not isostructural, their principal structural characteristics and geometric parameters (the Al—H, Ti—H, and Ti—Cp distances, the bond angles) differ only slightly from each other (Table 5, see the published data[16,21]). This is indicative of the fact that the mechanisms of formation of these compounds, which involve generation of Cp_2TiH and, apparently, the mononuclear titanocene Cp_2Ti^{II}, are identical or, at least, very similar.[20] However, unlike decomposition of $Cp_2TiH_2AlH(X)L$ (X = Hal, BH_4, or Alk), decomposition of complex **6** afforded a compound in which the X substituent at the Al atom is retained. In our opinion, this is additional evidence for a higher strength of the Al—O or Al—O—Al bonds compared to the hydride fragments.

To summarize, at least two fundamental conclusions can be made based on the data on the catalytic activity of complexes **2**—**6** and taking into account the formation of complex **8**.

1. The nature and properties, including the catalytic properties, of binuclear hydride complexes of titanocene and aluminum are of the same type and are determined to a large extent by the environment about the Al atom. Complexes with the symmetrical environment, for example, $Cp_2TiH_2AlH_2$ or $Cp_2TiH_2AlCl_2$ (without considering coordinated Lewis bases), are rather stable in the reactions of decomposition and do not exhibit catalytic properties in hydrogenation of olefins. Binuclear monomeric and dimeric molecules with an asymmetrical environment about the Al atom are more or less unstable and, depending on the conditions, decompose according to different schemes. The principal scheme involves the dimer → monomer → trinuclear complex (the precursor of a catalytically active particle) conversions followed by formation of the most stable hexanuclear complex.

2. Decomposition of monomeric and dimeric binuclear molecules to form hexanuclear complex **8** can occur only if 15-electron mononuclear hydride $Cp_2Ti^{III}H$ is generated. In our opinion, this is a strong argument in favor of the previously suggested mechanism of catalytic hydrogenation of olefins[1] according to which it is the

Table 4. Atomic coordinates ($\times 10^4$) and isotropic temperature factors ($U_{iso} \times 10^3$) for complex **8**

Atom	*x*	*y*	*z*	U_{iso}/Å^2
Ti(1)	621(1)	774(1)	2762(1)	46(1)
Ti(2)	1938(1)	−819(1)	246(1)	45(1)
Ti(3)	3199(1)	−1280(1)	1789(1)	51(1)
Ti(4)	4050(1)	2660(1)	605(1)	66(1)
Al(1)	3040(1)	1208(2)	989(1)	47(1)
Al(2)	1798(1)	375(2)	2018(1)	44(1)
O(1)	2379(2)	1519(4)	1715(3)	46(1)
O(2)	1640(6)	3524(8)	1635(8)	210(5)
C(1)	−67(10)	1994(12)	2055(12)	132(6)
C(2)	284(6)	1400(26)	1460(9)	151(10)
C(3)	116(8)	282(17)	1537(9)	117(5)
C(4)	−310(6)	206(12)	2124(10)	89(3)
C(5)	−424(5)	1191(19)	2414(6)	91(5)
C(6)	1227(5)	1291(17)	3908(5)	89(4)
C(7)	645(9)	1767(8)	3995(5)	79(3)
C(8)	228(4)	929(16)	4072(5)	70(3)
C(9)	533(8)	−90(11)	4038(5)	79(3)
C(10)	1163(7)	157(14)	3921(5)	77(3)
C(11)	1263(5)	−2149(8)	838(5)	69(3)
C(12)	1807(5)	−2718(7)	671(6)	72(3)
C(13)	1884(4)	−2734(7)	−177(6)	69(3)
C(14)	1371(5)	−2168(8)	−512(5)	66(3)
C(15)	984(4)	−1801(7)	112(7)	69(3)
C(16)	1690(4)	470(8)	−816(5)	59(2)
C(17)	1913(4)	1080(6)	−151(4)	51(2)
C(18)	2548(3)	782(6)	37(4)	41(2)
C(19)	2704(3)	−26(7)	−573(4)	52(2)
C(20)	2175(4)	−213(7)	−1085(4)	60(2)
C(21)	3607(5)	−3020(8)	1303(8)	88(3)
C(22)	3578(5)	−2312(12)	642(6)	85(3)
C(23)	3984(5)	−1434(10)	779(6)	84(3)
C(24)	4272(4)	−1572(11)	1523(7)	88(3)
C(25)	4047(6)	−2569(12)	1856(6)	89(4)
C(26)	3310(4)	−1244(11)	3222(4)	74(3)
C(27)	2951(4)	−2195(9)	3022(5)	67(3)
C(28)	2394(3)	−1779(9)	2653(4)	54(2)
C(29)	2389(3)	−594(8)	2619(4)	42(2)
C(30)	2973(4)	−293(7)	2989(4)	48(2)
C(31)	4876(9)	1739(14)	1265(13)	141(6)
C(32)	5109(5)	2686(22)	995(7)	123(6)
C(33)	4823(7)	3545(11)	1404(9)	99(4)
C(34)	4426(7)	3041(21)	1928(8)	142(7)
C(35)	4450(8)	1875(24)	1826(11)	171(11)
C(36)	4221(9)	3054(17)	−761(7)	122(5)
C(37)	3642(11)	2702(14)	−715(8)	120(6)
C(38)	3334(7)	3463(23)	−304(9)	139(10)
C(39)	3724(16)	4232(10)	−102(9)	188(12)
C(40)	4318(9)	4012(28)	−358(14)	252(17)
C(41)	2441(4)	2493(10)	2228(5)	72(3)
C(42)	2217(5)	3593(12)	1739(10)	168(8)
C(43)	1513(10)	4278(13)	984(10)	227(9)
H′(7)	2583(21)	−1048(40)	997(27)	32
H′(1)	3315(20)	2565(40)	1165(26)	28
H′(2)	3831(23)	1290(45)	458(29)	46
H′(3)	3354(21)	225(40)	1571(26)	29
H′(4)	1318(25)	1378(48)	2361(31)	57
H′(5)	1099(22)	−374(43)	2456(28)	42
H′(6)	1580(27)	−46(52)	1063(35)	75

formation of this compound that is responsible for the catalytic properties of trinuclear hydride complexes of titanocene and aluminum.

Table 5. Principal bonds lengths (*d*) and bond angles (ω) in molecule **8**

Bond	*d*/Å	Angle	ω/deg
Al(1)—O(1)	1.883(5)	O(1)—Al(1)—C(18)	99.3(3)
Al(1)—C(18)	1.938(7)	O(1)—Al(2)—C(29)	97.8(3)
Al(2)—O(1)	1.898(5)	Al(1)—O(1)—Al(2)	121.0(3)
Al(2)—C(29)	1.957(8)	H′(4)—Ti(1)—H′(5)	74
Ti(1)—H′(4)	1.76(5)	H′(1)—Ti(4)—H′(2)	78
Ti(1)—H′(5)	1.74(5)	H′(6)—Ti(2)—H′(7)	84
Ti(2)—H′(7)	1.86(5)	H′(3)—Ti(3)—H′(7)	80
Ti(2)—H′(6)	1.82(5)	Ti(3)—H′(7)—Ti(2)	176
Ti(3)—H′(7)	1.85(5)	H′(5)—Al(2)—C(29)	102
Ti(3)—H′(3)	1.84(5)	H′(5)—Al(2)—O(1)	162
Ti(4)—H′(1)	1.82(5)	H′(4)—Al(2)—H′(5)	72
Ti(4)—H′(2)	1.68(5)	H′(6)—Al(2)—H′(4)	111
Al(1)—H′(1)	1.74(5)	H′(6)—Al(2)—H′(5)	91
Al(1)—H′(2)	1.90(5)	H′(4)—Al(2)—O(1)	89
Al(1)—H′(3)	1.63(5)	Cp(1)—Ti(1)—Cp(2)	140.2
Al(2)—H′(4)	1.66(5)	Cp(3)—Ti(2)—Cp(4)	138.0
Al(2)—H′(5)	1.89(5)	Cp(5)—Ti(3)—Cp(6)	137.7
Al(2)—H′(6)	1.68(5)	Cp(7)—Ti(4)—Cp(8)	139.13

Experimental

All operations associated with the synthesis, isolation, and purification of the samples were carried out under an atmosphere of argon or *in vacuo*. The solvents were purified by refluxing and distilling over $LiAlH_4$ under an atmosphere of argon. Diethylamine, morpholine, and methylcellosolve were dried over 3-Å molecular sieves and distilled over $LiAlH_4$. The IR spectra were recorded on a UR-20 instrument as KBr pellets.

Complex $[Cp_2TiH_2AlHN(C_2H_4)_2O]_2$ (5). A solution of morpholine (0.17 g, 1.95 mmol) in ether (8 mL) was slowly added with stirring and cooling to −78 °C to a solution of complex **1** (2 mmol), which was prepared[6,7] by the reaction of $(Cp_2TiCl)_2$ (0.43 g, 1 mmol) and $LiAlH_4$ (0.08 g, ~2 mmol) in a 1 : 5 ether—toluene mixture (35 mL). The reaction mixture was stirred at −78 °C for 10 min. Then the temperature was slowly raised to 20 °C, and the mixture was stirred for 1 h. Then the mixture was concentrated to 1/2 of the initial volume *in vacuo* and kept overnight. The precipitate that formed was filtered off, washed with a small amount of cold ether, and dried *in vacuo*. Dark-violet crystals were obtained in a yield of 0.3 g (25%). Found (%): Ti, 16.3; Al, 9.2; N, 4.9. $C_{28}H_{42}Al_2N_2O_2Ti_2$. Calculated (%): Ti, 16.24; Al, 9.16; N, 4.75.

Reaction of complex 1 with methylcellosolve was carried out as described above by adding a solution of methylcellosolve (0.15 g, 1.95 mmol) in ether (10 mL) to a solution of complex **1** (2 mmol) in a 1 : 5 ether—toluene mixture (35 mL). The mixture was concentrated to 1/3 of the initial volume. Hexane

(30 mL) was added, and the mixture was kept at −20 °C overnight. The precipitate that formed (~0.2 g, ~20%) as filtered off, washed with cold ether, and dried *in vacuo*. Found (%): Ti, 16.2; Al, 8.8. $C_{26}H_{40}Al_2O_4Ti_2$. Calculated (%): Ti, 16.93; Al, 9.54.

Upon prolonged storage (2 months) at ~20 °C, the mother liquor yielded a crystalline precipitate (0.1 g, 12%), which was filtered off, washed with a small amount of cold ether, and dried *in vacuo*. Found (%): Ti, 22.5; Al, 6.3. $C_{43}H_{54}Al_2O_2Ti_4$. Calculated (%): Ti, 22.61; Al, 6.37.

Reaction of complex 1 with water was carried out as described above by adding a solution of water (17 mg, 0.95 mmol) in ether (6 mL) to a solution of complex **1** (2 mmol) in a 1 : 5 ether—toluene mixture (30 mL). The reaction mixture was concentrated to 1/3 of the initial volume and kept overnight. The precipitate that formed (0.17 g, 20%) was filtered off, washed with a small amount of cold ether, and dried *in vacuo*. Found (%): Ti, 22.0; Al, 12.1. $C_{20}H_{26}Al_2OTi_2$. Calculated (%): Ti, 22.19; Al, 12.51.

Study of the catalytic activity of the complexes in the reactions of hydrogenation of hex-1-ene. Solutions of the catalysts, which were prepared as described above and diluted with toluene (the concentration of titanium in solutions was varied in the range of 0.05—0.10 mg-at mL^{-1}), were used in hydrogenation. Mixtures $Cp_2TiH_2AlH_2 \cdot Et_2O—HNEt_2$ were prepared by slow addition of the corresponding amounts of a solution of $HNEt_2$ in Et_2O to a solution of complex **1** at −78 °C. Hydrogenation was carried out at 20 °C and at a pressure of 1 atm in a reaction vessel joined to a system of burettes for measuring the volume of the absorbed gas according to a standard procedure.[7] The hex-1-ene/titanium ratio was 100—120. A vessel filled with a hydride phase $LaNi_5H_x$ served as the source of hydrogen. The initial rate of absorption of hydrogen was a measure of the activity of the catalyst.

X-ray diffraction study of complexes 5 and 8. The details of X-ray diffraction study of single crystals of complexes **5** and **8** sealed in glass tubes and their principal crystal-chemical parameters are given in Table 1. The structures of both complexes were solved by the heavy-atom method and refined anisotropically by the full-matrix least-squares method with the use of the SHELXTL-81 [21] and SHELXL-93 [22] program packages. The positions of the hydride hydrogen atoms were revealed from difference electron density syntheses. Their coordinates and isotropic temperature factors were refined. The coordinates of the remaining hydrogen atoms were calculated geometrically and included in the refinement with fixed thermal and positional parameters. Absorption was ignored. The atomic coordinates and isotropic temperature factors are given in Tables 2 and 4.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 95-03-09539 and 98-03-32704).

References

1. B. M. Bulychev, G. L. Soloveichik, V. K. Bel'sky, and A. I. Sizov, *Metalloorg. Khim.*, 1989, **2**, 82 [*Organomet. Chem. USSR*, 1989, **2**, 40 (Engl. Transl.)].
2. A. I. Sizov, I. V. Molodnitskaya, B. M. Bulychev, V. K. Bel'sky, E. V. Evdokimova, and G. L. Soloveichik, *Metalloorg. Khim.*, 1990, **3**, 430 [*Organomet. Chem. USSR*, 1990, **3**, 212 (Engl. Transl.)].
3. V. K. Belsky, A. I. Sizov, B. M. Bulychev, and G. L. Soloveichick, *J. Organomet. Chem.*, 1985, **280**, 67.
4. B. M. Bulychev, E. V. Evdokimova, A. I. Sizov, and G. L. Soloveichik, *J. Organomet. Chem.*, 1982, **239**, 313.
5. E. V. Evdokimova, G. L. Soloveichik, and B. M. Bulychev, *Kinet. Katal.*, 1982, **23**, 1109 [*Kinet. Catal.*, 1982, **23**, 943 (Engl. Transl.)].
6. E. A. Rozova, A. B. Erofeev, A. I. Sizov, and B. M. Bulychev, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 405 [*Russ. Chem. Bull.*, 1994, **43**, 364 (Engl. Transl.)].
7. E. V. Evdokimova, B. M. Bulychev, and G. L. Soloveichik, *Kinet. Katal.*, 1981, **22**, 170 [*Kinet. Catal.*, 1981, **22** (Engl. Transl.)].
8. T. Yu. Sokolova, A. I. Sizov, B. M. Bulychev, E. A. Rozova, V. K. Belsky, and G. L. Soloveichick, *J. Organomet. Chem.*, 1990, **288**, 11.
9. H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, and R. Waymouth, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1143.
10. E. Wiberg and A. May, *Z. Naturforsch.*, 1955, **10B**, 229.
11. E. B. Lobkovskii, A. I. Sizov, B. M. Bulychev, G. L. Soloveichik, and I. V. Sokolova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 956 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 874 (Engl. Transl.)].
12. A. I. Sizov, G. L. Soloveichik, and B. M. Bulychev, *Koord. Khim.*, 1985, **11**, 339 [*Sov. J. Coord. Chem.*, 1985, **11**, 183 (Engl. Transl.)].
13. V. K. Bel'sky, A. I. Sizov, B. M. Bulychev, and G. L. Soloveichik, *Koord. Khim.*, 1985, **11**, 1003 [*Sov. J. Coord. Chem.*, 1985, **11** (Engl. Transl.)].
14. A. I. Sizov, I. V. Molodnitskaya, B. M. Bulychev, E. V. Evdokimova, G. L. Soloveichick, A. I. Gusev, E. B. Chuklanova, and V. I. Andrianov, *J. Organomet. Chem.*, 1987, **335**, 323.
15. A. I. Sizov, I. V. Molodnitskaya, B. M. Bulychev, V. K. Belsky, and G. L. Soloveichick, *J. Organomet. Chem.*, 1988, **344**, 185.
16. A. I. Sizov, I. V. Molodnitskaya, B. M. Bulychev, E. V. Evdokimova, V. K. Belsky, and G. L. Soloveichick, *J. Organomet. Chem.*, 1988, **344**, 293.
17. H. Nöth and E. Wiberg, *Forschr. Chem. Forsch.*, 1966, **8/3**, 321.
18. C. E. Holloway and M. Melnik, *J. Organomet. Chem.*, 1997, **543**, 1.
19. A. R. Barron, *Macromol. Symp.*, 1995, **97**, 15.
20. E. B. Lobkovsky, G. L. Soloveichik, A. I. Sizov, and B. M. Bulychev, *J. Organomet. Chem.*, 1985, **280**, 53.
21. G. M. Sheldrick, *SHELXTL User Manual*, Nicolet XRD Corp. (USA), 1981.
22. G. M. Sheldrick, *SHELXL-93. Program for Crystal Structure Refinement*, Univ. of Göttingen, Göttingen (Germany), 1993.

Received November 25, 1997;
in revised form February 26, 1998