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Structural chemistry of titanium and aluminium bimetallic hydride complexes

VIII *. Crystal and molecular structures of the complex $(\eta^5\text{-}C_5H_5)_2Ti(\mu_2\text{-}H)_2Al(CH_3)(\mu_2\text{-}H)_2Ti(\eta^5\text{-}C_5H_5)_2$, an effective catalyst for olefin hydrogenation, and its decomposition product, $[(\eta^5\text{-}C_5H_5)_2Ti(\mu_2\text{-}H)_2Al(\mu_2\text{-}H)(\eta^1:\eta^5\text{-}C_5H_4)Ti(\eta^5\text{-}C_5H_5)(\mu_2\text{-}H)]_2 \cdot C_6H_6$

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Abstract

Reactions of $(Cp_2Ti)_2AlH_4Cl$ and $(Cp_2Ti)_2AlH_4BH_4$ ($Cp = \eta^5\text{-}C_5H_5$) with $LiCH_3$ and $LiAl(CH_3)_4$ in ether or in an ether/benzene mixture yield a trinuclear complex $Cp_2Ti(\mu_2\text{-}H)_2Al(CH_3)(\mu_2\text{-}H)_2TiCp_2$, which crystallizes in a rhombic lattice with unit cell parameters *a* 8.405(1), *b* 21.349(3), *c* 22.337(3) Å, space group *F2dd*, $Z = 8$. The compound is unstable and decomposes in solution to give a new modification of a hexanuclear complex $[Cp_2Ti(\mu_2\text{-}H)_2Al(\mu_2\text{-}H)(\eta^1:\eta^5\text{-}C_5H_4)\text{-}TiCp(\mu_2\text{-}H)]_2$ with unit cell parameters *a* 11.354(2), *b* 23.360(3), *c* 16.062(3) Å, γ 94.07(3)°, space group $P2_1/n$, $Z = 4$. The instability of $(Cp_2Ti)_2AlH_4Me$ is accounted for by an increase in the electron density on metal atom nuclei on coordination of the methyl group. For the same reason elevated catalytic activity of this compound in the reactions of hexene-1, homogeneous hydrogenation (180 mol H_2/g-atom Ti min) and isomerization (11.8 mol C_6H_{12}/g-atom Ti min) is observed.

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* For part VII see ref. 5.

Introduction

We recently showed [1–3] that the trinuclear heterometallic hydride complex $(Cp_2Ti)_2AlH_4Cl$ (I) (Cp = η^5-C_5H_5) is an effective catalyst for homogeneous olefin hydrogenation and isomerization. Since catalytic activity of the binuclear complexes $Cp^\star_2TiH_2AlHX \cdot L$ ($Cp^\star = C_5H_5$, C_5H_4Me, C_5Me_5; X = Hal, H; L = Lewis base) during isomerization strongly depends on the number of donor substituents in the cyclopentadienyl rings and on the nature of the ligand X [4], changes in the ligand environment of the aluminium atom in I were expected to affect its catalytic activity in a similar way. In fact, replacement of the accepting chlorine atom in I by the dative bidentate BH_4 moiety results in a sharp drop in hydrogenating activity [5]. However, the coordination of the BH_4 moiety was shown [5] to alter the coordination number of the aluminium atom to 6 and to stabilize the complex. In this connection it seemed reasonable to attempt the synthesis of a trinuclear compound, in which the aluminium atom was linked with a donor moiety but retained five-coordination. In this work we report the results of the study of the structure and properties of one such compound, $(Cp_2Ti)_2AlH_4CH_3$ (II), and of a product of its decomposition, a hexanuclear titanocene alumohydride complex.

Results and discussion

The interaction of the complexes $(Cp_2Ti)_2AlH_4X$ (X = Cl or BH_4) with $LiCH_3$ in ether or in an ether/benzene mixture leads to the replacement of the X moiety by the methyl group at the aluminium atom (eq. 1, Fig. 1), accompanied by the appearance of an intense violet colour of the solution. When X = Cl lithium chloride is precipitated.

$$(Cp_2Ti)_2AlH_4X + LiMe \xrightarrow{Et_2O} (Cp_2Ti)_2AlH_4Me + LiX \qquad (1)$$

The ESR spectra of the resulting solutions, both for X = Cl and X = BH_4, are identical and represent the superposition of a poorly resolved, 11–13-component signal ($g = 1.989$) and an octet ($g = 1.977$, $a = 3.8$ G) with an intensity ratio of 1/3/4/4/4/4/3/1. Also, the rates of hydrogenation of hexene-1 (180 ± 10 mol H_2/g-atom Ti min) and its isomerization into hexene-2 (11.8 ± 1.3 mol C_6H_6/g-atom Ti min) were practically identical, regardless of the method employed for the synthesis of II.

The attempts undertaken to isolate individual compounds from solutions of complex II in the ether/benzene mixture rather unexpectedly led to a new modification of a crystallo-solvate, formulated thus (Fig. 2): $[Cp_2Ti(\mu_2\text{-}H)_2Al(\mu_2\text{-}H)(\eta^1:\eta^5\text{-}C_5H_4)TiCp(\mu_2\text{-}H)]_2 \cdot C_6H_6$ (IIIa), with gull-like metal framework in high yield. When the synthesis of II was carried out in an ether/toluene mixture, the reaction mixture yielded crystals of the known compound IIIb solvated with toluene [6]. Interatomic distances and bond angles for IIIa (Table 4) are practically identical with those found in complex IIIb [6], while the observed distinctions evidently result from packing requirements.

Although attempts to isolate complex II from the solutions obtained by reaction 1 were unsuccessful, it is possible to synthesize and isolate II by reaction 2. Such

$$(Cp_2Ti)_2AlH_4Cl + LiAlMe_4 \rightarrow (Cp_2Ti)_2AlH_4Me + AlMe_3 + LiCl \qquad (2)$$

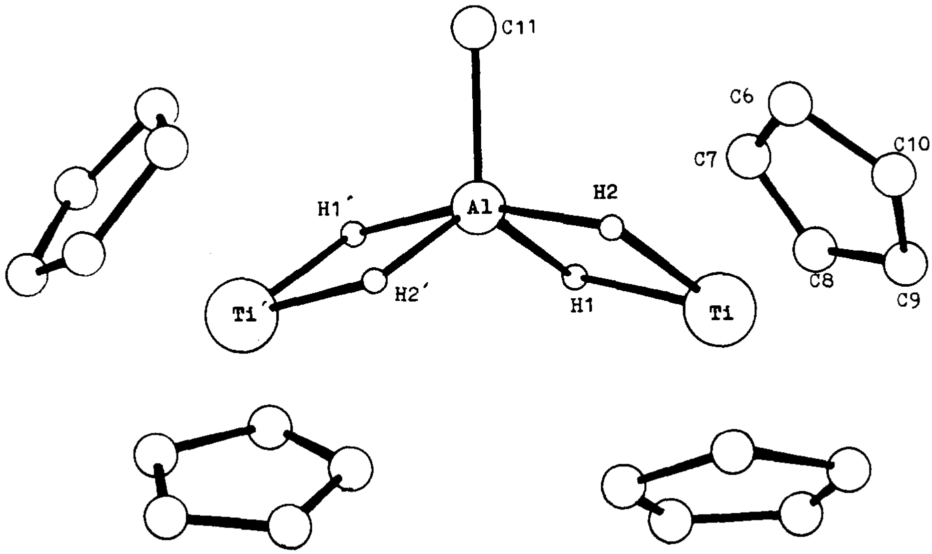


Fig. 1. Molecular structure of the complex $Cp_2Ti(\mu_2H)_2Al(CH_3)(\mu_2\text{-}H)_2TiCp_2$.

distinctions in the behaviour of this compound can be explained in terms of the formation of an intermediate complex $(Cp_2Ti)_2AlH_4(\mu_2\text{-}Me)_2AlMe_2$ (reaction 2), similar to the known complex $(Cp_2Ti)_2AlH_4(\mu_2\text{-}H)_2BH_2$ (IV) [5], followed by its

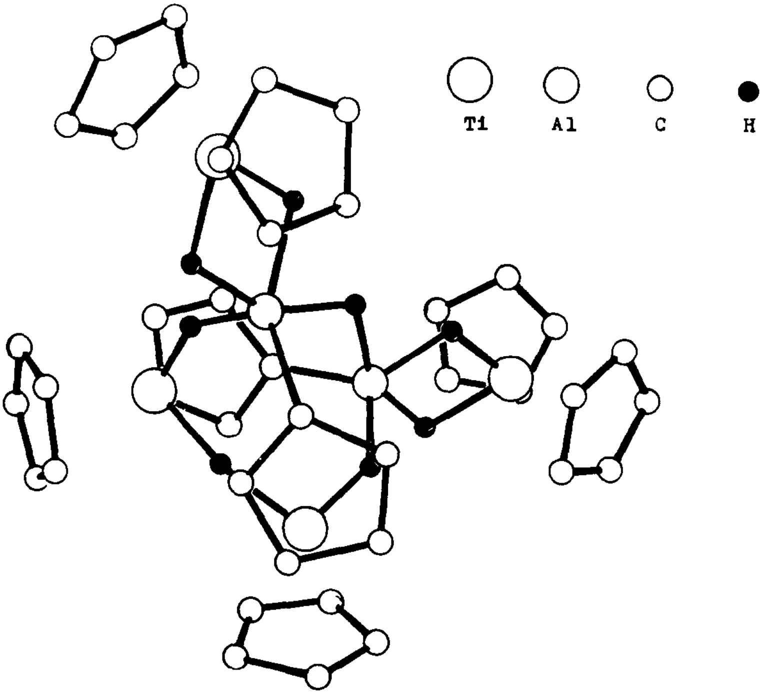


Fig. 2. Molecular structure of the complex $[Cp_2Ti(\mu_2\text{-}H)_2Al(\mu_2\text{-}H)(\eta^1-\eta^5\text{-}C_5H_4)TiCp_2(\mu_2\text{-}H)]_2 \cdot C_6H_6$.

relatively slow dissociation into II and $AlMe_3 \cdot OEt_2$. This permits complex II to be isolated as individual crystals. It is noteworthy that the catalytic activity of the solutions of complex II, obtained from reactions 1 and 2, is identical.

The X-ray data indicate that crystals of II are built up of trinuclear molecules $Cp_2Ti(\mu_2\text{-}H)_2Al(CH_3)(\mu_2\text{-}H)_2TiCp_2$, similar to the known complexes I [2] and IV [5]. The same bonding,  $\mathrm{M}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\langle\,\rangle}}\mathrm{Al}\overset{\mathrm{H}}{\underset{\mathrm{H}}{\langle\,\rangle}}\mathrm{M}$, is characteristic also of other transition metal alumohydride complexes with a M/Al ratio of 2/1, e.g., $[(CpMe_5)_2Ti]_2AlH_5$ [7] and $[(Me_3P)_3H_3W]_2AlH_5$ [8].

The geometric parameters of the wedge-like sandwiches Cp_2Ti in II are usual for the biscyclopentadienyl titanium alumohydride complexes, and, in particular, are closely coincident with those found in the complexes IV [5] and $Cp_2TiH_2AlCl_2 \cdot OEt_2$ [9] (Table 5). It should be noted that the Ti $\cdots$ Al distance in II (2.82 Å) is somewhat greater than the usual value in the other bi- and trinuclear complexes (2.75–2.79 Å). This is connected, evidently, with the alteration of the coordination polyhedron of the aluminium atom in II, and with an increase in electron density on the metal atoms. The coordination polyhedron of the aluminium atom (coordination number 5) in II is a tetragonal pyramid, whereas in practically all of the structurally studied transition metal alumohydride complexes, except for the octanuclear $\{[(C_5Me_5)Ti(C_5Me_4CH_2)H_2Al]_2O\}_2$ [10], the aluminium atom has a trigonal-bipyramidal environment. In contrast to I, such an environment in molecule II has a symmetry axis C_2 passing through the Al and C(11) atoms. The same symmetry axis passing through the Al and B atoms is present in the molecule of complex IV, involving the octahedral environment of the aluminium atom (coordination number 6) [5]. An increase in the electron density on the metal atoms seems to contribute to the increase in the Ti $\cdots$ Al distance to a greater or lesser extent. At any rate, the introduction of the dative methyl groups into the Cp-rings, such as in the complex $[(C_5Me_5)_2Ti]_2AlH_5$, also leads to an increase in the Ti $\cdots$ Al distance to 2.83 Å [9].

The Al–C bond length in molecule II (Table 2) is close to that in the molecules Al_2Me_6 (1.96 Å) [11], $(HAlMe_2)_2$ (1.95 Å) [12], IIIb (1.95 Å) [6], and IIIa (1.94 Å),

Table 1

Atomic coordinates ($\times 10^4$; $\times 10^3$ for H) for $[(C_5H_5)_2Ti]_2AlH_4CH_3$

Atom	x	y	z	U_{eq}
Ti	0	268(1)	1125(1)	328(4)
Al	1357(5)	0	0	412(13)
C(1)	2729(12)	173(6)	907(5)	606(47)
C(2)	2624(16)	382(7)	1493(5)	667(52)
C(3)	1929(15)	962(5)	1521(5)	636(49)
C(4)	1622(15)	1135(5)	920(5)	591(44)
C(5)	2122(14)	656(5)	547(4)	538(41)
C(6)	2647(14)	223(5)	1514(5)	663(41)
C(7)	2066(14)	380(6)	1488(5)	704(53)
C(8)	772(16)	442(6)	1866(5)	718(47)
C(9)	565(13)	133(6)	2135(4)	687(46)
C(10)	1690(16)	559(6)	1907(5)	652(47)
C(11)	3660(18)	0	0	977(69)
H(1)	43(11)	25(3)	53(3)	
H(2)	104(9)	52(3)	53(3)	

Table 2

Main interatomic distances (Å) and bond angles (°) for $[(C_5H_5)_2Ti]_2AlH_4CH_3$

Ti–C(av)(1)	2.36(1)	C–C–C(av)	108(2)
Ti–C(av)(2)	2.35(1)	TiAlTi(A)	132
Ti–Al	2.819(2)	H(1)TiH(2)	60(3)
Ti–H(1)	1.76(7)	H(1)AlH(2)	66(3)
Ti–H(2)	1.68(7)	H(1)AlH(2A)	104(4)
Al–C(11)	1.94(2)	H(2)AlH(2A)	162(5)
Al–H(1)	1.52(7)	H(1)AlH(1A)	104(4)
Al–H(2)	1.65(7)	H(2)AlH(1A)	118(6)
C(1)–C(5)	1.39(2)	TiH(1)Al	118(2)
Ti–Cp(1)	2.03	TiH(2)Al	116(2)
Ti–Cp(2)	2.03	Ti(A)H(1A)Al	119(2)
		Ti(A)H(2A)Al	117(2)
		C(11)AlH(1)	121(3)
		C(11)AlH(2)	99(3)
		C(11)AlTi	114
		Cp(1)TiCp(2)	136.7

Table 3

Atomic coordinates (×10^4; ×10^3 for H) for $[(\eta^5\text{-}C_5H_5)_2Ti(\mu_2\text{-}H)_2Al(\mu_2\text{-}H)(\eta^1:\eta^5\text{-}C_5H_4)Ti(\eta^5\text{-}C_5H_5)(\mu_2\text{-}H)]_2 \cdot C_6H_6$

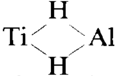
Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
Ti(1)	27(2)	3546(1)	8042(1)	38(1)	C(25)	1321(29)	340(8)	7398(18)	91(12)
Ti(2)	−1433(2)	3714(1)	4871(2)	45(1)	C(26)	3289(13)	749(6)	6246(9)	80(7)
Ti(3)	1983(2)	1257(1)	7021(1)	42(1)	C(27)	2632(14)	1060(6)	5684(9)	79(7)
Ti(4)	2954(2)	3547(1)	7066(1)	45(1)	C(28)	2934(16)	1604(7)	5822(11)	83(8)
Al(1)	1263(3)	2368(2)	7105(3)	41(2)	C(29)	3743(7)	1689(8)	645(15)	133(10)
Al(2)	191(4)	3387(2)	6065(3)	43(2)	C(30)	3937(14)	1129(8)	6698(11)	107(9)
C(1)	212(8)	2565(4)	7989(7)	37(4)	C(31)	1810(11)	3686(6)	5901(8)	49(6)
C(2)	558(11)	2760(5)	8807(10)	45(6)	C(32)	2291(14)	4229(6)	6175(9)	63(7)
C(3)	−420(10)	2968(4)	9207(7)	61(5)	C(33)	3541(14)	4284(7)	6099(10)	78(7)
C(4)	−1420(13)	2883(6)	8690(11)	54(7)	C(34)	3828(12)	3755(8)	5767(9)	70(7)
C(5)	−1026(12)	2640(5)	7966(10)	52(6)	C(35)	2811(14)	3400(6)	5642(9)	59(7)
C(6)	875(21)	4207(6)	8898(11)	67(8)	C(36)	4716(12)	3245(6)	7644(9)	61(6)
C(7)	316(20)	4363(6)	8880(13)	69(9)	C(37)	3803(13)	3097(6)	8227(10)	66(7)
C(8)	600(13)	4547(5)	8103(13)	58(7)	C(38)	3396(12)	3595(7)	8499(8)	71(7)
C(9)	−407(19)	4480(6)	7608(9)	58(7)	C(39)	4002(12)	4064(5)	8132(9)	72(6)
C(10)	−1324(13)	4273(6)	8130(14)	57(7)	C(40)	4819(12)	3834(6)	7604(9)	72(6)
C(11)	−3096(17)	3247(8)	5452(21)	90(11)	C(B1)	8441(22)	1670(7)	5530(15)	98(9)
C(12)	−2753(16)	3677(17)	5987(12)	100(11)	C(B2)	7569(21)	1420(11)	6024(12)	107(10)
C(13)	−2867(16)	4209(9)	5617(21)	101(11)	C(B3)	7323(15)	866(11)	6034(11)	96(9)
C(14)	−3295(15)	4056(10)	4825(13)	76(9)	C(B4)	7906(22)	506(7)	5569(15)	96(10)
C(15)	−3471(12)	3475(11)	4750(11)	64(8)	C(B5)	8813(19)	738(13)	5037(13)	115(10)
C(16)	155(17)	4121(7)	4120(9)	119(9)	C(B6)	9024(17)	1318(14)	5078(15)	129(11)
C(17)	151(16)	3583(10)	3957(12)	99(10)	H(01)	2493(74)	2827(34)	6960(59)	
C(18)	−863(31)	3411(14)	3580(15)	188(17)	H(02)	358(74)	3464(35)	7077(6)	
C(19)	−1449(23)	3906(19)	3465(16)	234(23)	H(03)	452(75)	2597(36)	6229(56)	
C(20)	−777(23)	4309(10)	3812(15)	174(14)	H(04)	2042(77)	1892(37)	7556(56)	
C(21)	1808(12)	549(6)	8044(9)	130(7)	H(05)	490(75)	3959(36)	5607(57)	
C(22)	1196(22)	986(9)	8329(11)	163(11)	H(06)	804(74)	3142(36)	5280(56)	
C(23)	284(11)	1021(5)	7803(10)	121(7)	H(07)	1510(76)	3594(36)	7570(55)	
C(24)	376(21)	610(12)	7204(13)	85(10)	H(08)	1107(76)	1741(36)	6599(57)	

Table 4

Main interatomic distances and bond angles for $[(\eta^5\text{-}C_5H_5)_2Ti(\mu_2\text{-}H)_2Al(\mu_2\text{-}H)(\eta^1-\eta^5\text{-}C_5H_4)Ti(\eta^5\text{-}C_5H_5)(\mu_2\text{-}H)]_2 \cdot C_6H_6$

Ti–H(av)	1.79(9)	Ti(4)H(7)Ti(1)	173(4)
Ti(1)–C(av)(1)	2.34(1)	H(5)Al(2)H(3)	154(4)
Ti(1)–C(av)(2)	2.36(2)	H(3)Al(1)H(4)	150(4)
Ti(2)–Al(2)	2.80(1)	H(1)Ti(4)H(7)	84(4)
Ti(2)–C(av)(3)	2.35(2)	H(4)Ti(3)H(8)	67(4)
Ti(2)–C(av)(4)	2.31(2)	H(1)Al(1)H(3)	97(4)
Ti(3)–Al(1)	2.78(0)	H(1)Al(1)H(4)	92(4)
Ti(3)–C(av)(5)	2.32(2)	H(1)Al(1)H(8)	121(4)
Ti(3)–C(av)(6)	2.33(2)	H(3)Al(1)H(4)	150(4)
Ti(4)–C(av)(7)	2.33(2)	H(3)Al(1)H(8)	82(4)
Ti(4)–C(av)(8)	2.32(2)	H(4)Al(1)H(8)	70(4)
Al(1)–C(1)	1.93(1)	H(2)Al(2)H(3)	93(4)
Al(1)–H(01)	1.72(8)	H(2)Al(2)H(5)	97(4)
Al(1)–H(03)	1.79(9)	H(2)Al(2)H(6)	118(4)
Al(1)–H(04)	1.64(9)	H(3)Al(2)H(5)	154(4)
Al(1)–H(08)	1.67(9)	H(3)Al(2)H(6)	86(4)
Al(2)–C(31)	1.94(1)	H(5)Al(2)H(6)	69(4)
Al(2)–H(02)	1.75(9)		
Al(2)–H(03)	1.91(8)		
Al(2)–H(05)	1.75(9)		
Al(2)–H(06)	1.76(9)		
C–C(av)	1.36(4)		

and is normal for the terminal Al–C bond. It should be pointed out that the positions of the hydrogen atoms of the methyl groups were not established owing to a statistical irregularity.

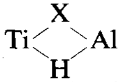
Taking into account the low accuracy with which the hydrogen atom coordinates were determined, there is no significant difference in the Al–H and Ti–H bond lengths in molecule II (Table 2) from those in the known Cp_2Ti alumohydride complexes ($r_{Ti-H} = 1.6–1.8$ Å, $r_{Al-H} = 1.6–1.8$ Å) [2,6–9]. This is consistent with the presence of an intensive absorption band at 1280 cm^{-1} (1260 cm^{-1} in the spectrum of I [2]) in the IR spectrum of II, associated with the bond vibrations of the  $\mathrm{Ti}\genfrac{}{}{0pt}{}{\mathrm{H}}{\mathrm{H}}\mathrm{Al}$ bridge. At the same time, the IR spectrum of II does not contain the absorption band at 1160 cm^{-1}, which was observed in the spectrum of I [2]. This seems to be related to the presence in molecule II of the symmetry axis within the TiH_2AlH_2Ti moiety. The TiH_2Al bridges in this case have a more symmetric form than the molecules with a trigonal-bipyramidal environment about the Al atom, in which the lengths of the axial and equatorial bonds differ markedly [2,7,9].

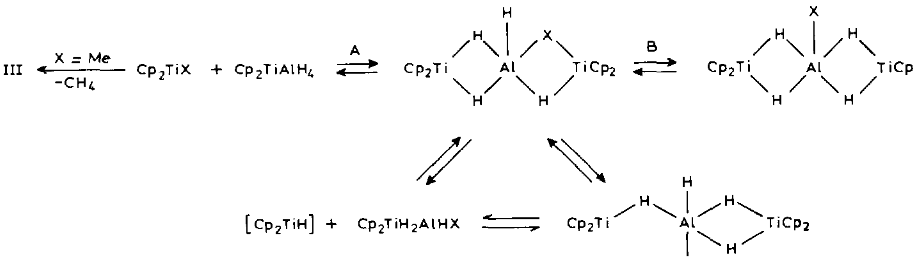
A characteristic structural feature of complex II is the small value of the HTiH angle (Table 5), which differs considerably from the values found in the complexes IIIa (74°), IV (73°) [5], $[(C_5Me_5)_2TiAlH_4]_2$ (73°) [7], $Cp_2TiH_2AlCl_2 \cdot OEt_2$ (75°) [9]. The small HTiH angle value characterizes an increased electron density on the titanium atom. Judging by the HTiH angle, the electron density on the Ti atom in the complexes $(Cp_2Ti)_2AlH_4X$ increases along the series $X = BH_4 < Cl < Me$ (Table 5). The activity of these complexes in the hydrogenation also increases in the same order. This supports the suggested mechanism [2] of formation of the catalyti-

Table 5

Structural and catalytic characteristics of the $(Cp_2Ti)_2AlH_4X$ complexes ($X = Cl$, CH_3 or BH_4)

	$(Cp_2Ti)_2AlH_4Cl$ [2]	$(Cp_2Ti)_2AlH_4CH_3$	$(Cp_2Ti)_2AlH_4BH_4$
Ti–Cp (Å)	2.02, 2.03	2.03, 2.04	2.03, 2.04
Ti–H (Å)	1.86(1); 1.83(8)	1.76(7); 1.68(7)	1.59(10); 1.85(9)
Al–H (Å)	1.46(2); 1.64(3)	1.52(7); 1.65(7)	1.72(10); 1.80(9)
Ti ··· Al (Å)	2.77	2.82	2.79
Cp–Ti–Cp (°)	138.6; 137.0	136.7	136.5
Ti–Al–Ti (°)	139	132	131.7
H–Ti–H (°)	63.5	60.0	73
Rate of hydrogenation (mol H_2/g-atom Ti min)	125	180	10
Rate of isomerization (mol C_6H_{12}/g-atom Ti min)	3.4	11.8	–

cally active species from $(Cp_2Ti)_2AlH_4Cl$ (Scheme 1), the mechanism is based on the hypothesis that the  $\mathrm{Ti}\langle\begin{smallmatrix}X\\ \\ H\end{smallmatrix}\rangle\mathrm{Al}$ dissociate (Scheme 1), since their strength depends directly on the electron density on the metal atoms.



Scheme 1

With X = Cl, the equilibria A and B are shifted towards the left only when base is added [2]. At the same time, the fact that the "metallogull" IIIa is formed readily indicates that the rate at which II dissociates in solution exceeds that at which it crystallizes into an individual state. A tentative explanation may be found in the low stability of Cp_2TiMe, which is unstable even at low temperatues [13]. Its decomposition leads to the formative of metastable Cp_2Ti, which can react with Cp_2TiAlH_4 to give an intermediate $Cp_2TiHAlH(H)_2TiCp_2$ and more III (eq. 3). The ease with which the "metallogull" III results from II and a higher stability of complexes I and IV, with regard to their participation in reaction 3, can be considered to be additional confirmation of the scheme of formation of III from $Cp_2TiH_2AlH_2$,

$$(Cp_2Ti)_2AlH_4R \rightleftarrows Cp_2TiAlH_4 + Cp_2TiR \xrightarrow{-R} Cp_2TiHAl(H)H_2TiCp_2 \rightarrow$$

$$[Cp_2TiHAl(\mu\text{-}H)H_2TiCp_2]_2 \xrightarrow{-H_2} \mathrm{III} \quad (3)$$

proposed previously [6]. This also shows that the "metallogull" III is thermodynamically the most stable compound in systems such as $Cp_2TiX_2/Cp_2TiX-LiAlH_4$.

Thus, the introduction of the dative monodentate alkyl group in the trinuclear complex leads to considerable enhancement of its catalytic activity both in olefin hydrogenation and olefin isomerization. This provides scope for the useful modification of hydride catalysts, based on titanocene and aluminium, with a view to refining their catalytic properties.

Experimental

All reactions were carried out under air-free conditions. Solvents were dried by heating over $LiAlH_4$, followed by distillation. Hexene-1 was purified by fractional distillation over CaH_2.

Reduction of Cp_2TiCl_2 by a published procedure [14] gave $(Cp_2TiCl)_2$; treatment of Cp_2TiCl_2 with $LiBH_4$ afforded Cp_2TiBH_4 [15]. Solutions of $LiCH_3$ were prepared by a standard procedure [16].

Catalytic activity of samples was studied as described previously [2]. IR spectra of samples (suspensions in Nujol) were recorded on an UR-20 spectrophotometer in the region 400–3500 cm^{-1}; ESR spectra were recorded on a Varian E-3 instrument (3 cm range, modulation frequency 100 kHz) with Mn^{2+} in MgO as a standard.

Synthesis of $(Cp_2Ti)_2AlH_4Me$ (II)

To a suspension of 1.1 g (5 mmol) of Cp_2TiCl in 20 ml of Et_2O was added 7.4 ml of a 0.34 *M* solution of $LiAlH_4$ (2.5 mmol) in ether. The mixture was stirred for 10 min, and to the resulting violet suspension was added 20 ml of a solution of 0.235 g (2.5 mmol) of $LiAlMe_4$ in 20 ml of ether. The reaction mixture turned dark red. The precipitate was filtered off, the filtrate was kept overnight, and the precipitated black crystals (0.65 g, 65%) were separated and dried in vacuo. Found: Al, 6.2; Ti, 24.6. $C_{21}H_{27}AlTi_2$ calc: Al, 6.72; Ti, 23.88%.

Synthesis of $[Cp_2TiH_2Al(H)(C_5H_4)TiCpH]_2 \cdot ArH$ (IIIa,b)

To a solution of 0.15 mmol of $(Cp_2Ti)_2AlH_4Cl$ or $(Cp_2Ti)_2AlH_4BH_4$, obtained in situ from 3 mmol of Cp_2TiCl or Cp_2TiBH_4 in toluene or benzene and 1.5 mmol of $LiAlH_4$ in ether, was added with stirring a solution of LiMe in Et_2O. The reaction mixture turned intense violet. After separation of the LiCl precipitate, black hexagonal crystals of complex IIIb (from the ether/toluene mixture) or complex IIIa (from the ether/benzene mixture) were precipitated from the solution in 87% yield. Found: Al, 6.5; Ti, 22.3. $C_{46}H_{52}Al_2Ti_4$ calc: Al, 6.99; Ti, 24.79%.

X-Ray crystallographic data

The X-ray study, on single crystals of complexes II and IIIa packed in glass capillaries was carried out on a Syntex P1 automatic diffractometer (λ (Mo-K_α), graphite monochromator, $\theta/2\theta$ scanning).

Compound II crystallized in a rhombic lattice with the unit cell parameters *a* 8.405(1), *b* 21.349(3), *c* 22.337(3) Å, space group *F2dd*, $Z = 8$, ρ_{calc} 1.32 g/cm^3, μ_{Mo} 9.1 cm^{-1}. Of the total 575 reflections 517 with $I \geqslant 3\sigma(I)$ were used in the calculations. The structure was solved by the Patterson method and refined by the least-squares method in a full-matrix anisotropic (isotropic for hydrogen atoms) approximation to $R = 0.030$ ($R_w = 0.029$). The atomic coordinates and thermal parameters are listed in Table 1; the main interatomic distances and bond angles are given in Table 2.

Compound IIIa crystallized in a monoclinic lattice with the unit cell parameters a 11.345(2), b 23.360(3), c 16.062(3) Å, γ 94.07(3)°, space group $P2_1/n$, $Z = 4$, V 4246 Å^3, μ_{Mo} 8.1 cm^{-1}. 1662 reflections with $I \geqslant 2\sigma(I)$ were used in the calculations. The structure was solved by the direct method and refined by the least-squares method in a full-matrix anisotropic (isotropic for hydrogen atoms) approximation to $R = 0.041$ ($R_w = 0.040$). The atomic coordinates are listed in Table 3; the main interatomic distances and bond angles are given in Table 4.

References

1 E.V. Evdokimova, B.M. Bulychev and G.L. Soloveichik, Kinet. katal., 22 (1981) 170.
2 A.I. Sizov, I.V. Molodnitskaya, B.M. Bulychev, G.L. Soloveichik, A.I. Gusev, E.B. Chuklanova and V.I. Andrianov, J. Organomet. Chem., 335 (1987) 323.
3 E.V. Evdokimova, G.L. Soloveichik and B.M. Bulychev, Kinet. katal., 23 (1982) 1109.
4 B.M. Bulychev, E.V. Evdokimova, A.I. Sizov and G.L. Soloveichik, J. Organomet. Chem., 239 (1982) 313.
5 A.I. Sizov, I.V. Molodnitskaya, B.M. Bulychev, G.L. Soloveichik and V.K. Belsky, J. Organomet. Chem. 344 (1988) 185.
6 E.B. Lobkovsky, G.L. Soloveichik, A.I. Sizov and B.M. Bulychev, J. Organomet. Chem., 280 (1985) 53.
7 V.K. Belsky, A.I. Sizov, B.M. Bulychev and G.L. Soloveichik, J. Organomet. Chem., 280 (1985) 67.
8 A.R. Barron, M.B. Hursthouse, M. Motevalli and G. Wilkinson, J. Chem. Soc., Chem. Commun., (1985) 664.
9 E.B. Lobkovskii, G.I. Soloveichik, N.M. Bulychev, R.G. Gerr and Yu.T. Struchkov, J. Organomet. Chem., 270 (1984) 75.
10 E.B. Lobkovskii, A.I. Sizov, B.M. Bulychev, G.L. Soloveichik and I.V. Sokolova, J. Organomet. Chem., 319 (1987) 69.
11 J.G. Huffman and E.W. Streib, J. Chem. Soc., Chem. Commun., (1971) 911.
12 A. Almennigen, G.A. Anderson, F.R. Forgaard and A. Haaland, Acta Chem. Scand., 26 (1972) 2315.
13 E. Klei and J.H. Teuben, J. Organomet. Chem., 188 (1980) 97.
14 G.L. Soloveichik, Candidate thesis, Moscow, 1982, 152 pp.
15 H. Nöth and R. Hartwimmer, Chem. Ber. Bd. 93, 10 (1960) 2238.
16 C. Tegner, Acta Chem. Scand., 6 (1952) 782.