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Structural chemistry of titanium and aluminium bimetallic hydride complexes

X*. Reactions of titanocene aluminium hydride with alcohols, amines and ethers. The structures of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\mu_2\text{-H})_2\text{Al}(\text{H})(\mu_2\text{-OC}_2\text{H}_5)]_2$ and $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\mu_2\text{-H})_2\text{Al}(\text{H})\{\mu_2\text{-N}(\text{C}_2\text{H}_5)_2\}]_2$

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Abstract

Reactions of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\mu_2\text{-H})_2\text{AlH}_2$ ($\eta^5\text{-C}_5\text{H}_5 = \text{Cp}$) in ether with the vapours of alcohols, diethylamine and ethyl acetate produced dimer binuclear complexes of compound $[\text{Cp}_2\text{Ti}(\mu_2\text{-H})_2\text{AlH}(\mu_2\text{-X})]_2$, where $\text{X} = \text{OR}, \text{NEt}_2$.

The structures of $[\text{Cp}_2\text{Ti}(\mu_2\text{-H})_2\text{AlH}(\mu_2\text{-OEt})]_2$ (I) and $[\text{Cp}_2\text{Ti}(\mu_2\text{-H})_2\text{AlH}(\mu_2\text{-NEt}_2)]_2$ (II) were determined by X-ray crystallography. I crystallizes in a monoclinic unit cell with a 8.402(2), b 10.228(2), c 15.868 Å, γ 106.92(2)°, space group $P2_1/n$, $Z = 2$. The crystals of II are also monoclinic with a 11.093(2), b 16.947(4), c 8.078(1) Å, γ 91.99(2)°, space group $P2_1/b$, $Z = 2$. Dimerization in molecules of I and II is effected by two bridge atoms of oxygen or nitrogen. The coordination polyhedron of the aluminium atom in both compounds is a trigonal bipyramid.

Introduction

The chemistry of the aluminiumhydrides of non-transition metals has been studied in detail which is reflected in the numerous reviews and monographs that

* For part IX see ref. 1.

have appeared. However, the chemistry of the aluminiumhydrides of transition metals, particularly their reactions with compounds containing an acidic H atom or multiple element-carbon bonds has been studied to a much lesser extent, and reports in the literature are only sporadic. From these works it follows that the chemical properties of the compounds of both types have principal differences. Thus, soft hydrolysis of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\mu_2\text{-H})_2\text{AlH}_2$ or $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}]_2\text{AlH}_4\text{Cl}$ ($\eta^5\text{-C}_5\text{H}_5 = \text{Cp}$) results not in the production of unexpected hydroxoaluminiumhydride, but mainly in formation of a hexa-nuclear polycyclic complex of $[\text{Cp}_2\text{Ti}(\mu_2\text{-H})_2\text{-Al}(\mu_2\text{-H})(\eta^1 : \eta^5\text{-C}_5\text{H}_4)\text{TiCp}(\mu_2\text{-H})]_2$ [1]. Hydrolysis of $[(\text{C}_5\text{Me}_5)_2\text{Ti}(\mu_2\text{-H})_2\text{-AlH}_2]_2$ produces the octo-nuclear cluster $\{[\text{Cp}^*(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2)\text{Ti}(\mu_2\text{-H})_2\text{Al}]_2(\mu_3\text{-O})\}_2$ [2], whereas hydrolysis of the aluminiumhydrides of metals of groups V-VI gives the respective mononuclear hydrides [3,4]. Only one example is known of the reaction of aluminiumhydrides of transition metals with participation of the $\text{N}\equiv\text{C}$ multiple bond viz., reaction of nitriles with $[(\text{Me}_3\text{P})_3\text{H}_3\text{W}(\mu_2\text{-H})_2\text{AlH}(\mu_2\text{-H})_2]_2$ which results in the substitution of the tetranuclear cycle, $\text{Al}(\mu_2\text{-H})_2\text{Al}$, for the cycle, $\text{Al}(\mu_2\text{-N}=\text{CHR})_2\text{Al}$, in the dimer [5].

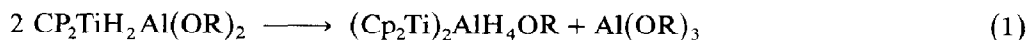
Here we describe the reactions of titanocene alumohydride $\text{Cp}_2\text{Ti}(\mu_2\text{-H})_2\text{AlH}_2$ with alcohols, amines acetonitrile and ethyl acetate, and the structures of two of the products of these reactions viz., $[\text{Cp}_2\text{Ti}(\mu_2\text{-H})_2\text{Al}(\text{H})(\mu_2\text{-OEt})]_2$ (I) and $[\text{Cp}_2\text{Ti}(\mu_2\text{-H})_2\text{Al}(\text{H})(\mu_2\text{-NEt}_2)]_2$ (II).

Results and discussion

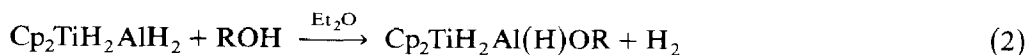
Soft hydrolysis, alcoholysis and ammonolysis of the aluminiumhydrides of non-transition metals in all cases gives the compounds $\text{MAIH}_{4-n}\text{ER}_n$ ($n = 1-3$; $\text{E} = \text{O}, \text{N}$; $\text{R} = \text{H}, \text{Alk}$). Alcoholysis of $\text{Cp}_2\text{Ti}(\mu_2\text{-H})_2\text{AlH}_2$ by alcohols in ether or toluene solutions permits the separation from the mother liquor of the complex $[\text{Cp}_2\text{Ti}(\mu_2\text{-H})_2\text{Al}(\mu_2\text{-H})(\eta^1 : \eta^5\text{-C}_5\text{H}_4)\text{TiCp}(\mu_2\text{-H})]_2$ (III), as crystals in about 60% yield, which is structurally similar to the compound obtained by the soft hydrolysis [1] or the decomposition [6] of titanocene aluminium hydride.

Only for cyclohexyl alcohol, which has a relatively low reactivity, was it possible to obtain a complex formulated as $\text{Cp}_2\text{TiAlH}_3\text{OC}_6\text{H}_{11}$ (IV), as deduced from the elemental analysis. However, this synthesis is poorly reproducible and usually results in the formation of III or a trinuclear complex $(\text{Cp}_2\text{Ti})_2\text{AlH}_4\text{OC}_6\text{H}_{11}$.

As has been described previously [1], $(\text{Cp}_2\text{Ti})_2\text{AlH}_4\text{OC}_6\text{H}_{11}$ is readily formed by heterogeneous reaction of $\text{Cp}_2\text{Ti}(\mu_2\text{-H})_2\text{Al}(\text{H})\text{Cl}$ with MX ($\text{X} = \text{OR}, \text{NR}_2$; $\text{M} = \text{Li}, \text{Na}$) or by the decomposition of the binuclear complexes $\text{Cp}_2\text{Ti}(\mu_2\text{-H})_2\text{AlX}_2$. Thus the reaction of $\text{Cp}_2\text{Ti}(\mu_2\text{-H})_2\text{AlH}_2$ with alcohols probably proceeds under conditions of local supersaturation, and the obtained products of further alcoholysis catalyse the decomposition of titanocene alumohydride to III and/or lead to disproportionation, such as in reaction 1.



To prevent the supersaturation phenomenon, we have developed a special method to carry out reaction 2. It involves the slow evaporation of alcohols which have a sufficiently high vapour pressure, from a solution of $\text{Cp}_2\text{TiH}_2\text{AlH}_2$ in Et_2O .

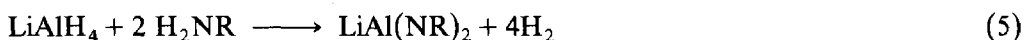
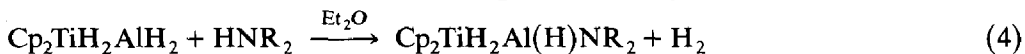


By this method we have obtained compounds formulated as $\text{Cp}_2\text{TiH}_2\text{Al(H)OR}$ where $\text{R} = \text{Me}$ (V), Et (I), Bu^i (VI).

Complex I is also formed under restoration of ethyl acetate (equation 3) by titanocene alumohydride. It is noteworthy that other products in reaction 3 are not formed in a large excess of ethyl acetate.



The reaction of $\text{Cp}_2\text{TiH}_2\text{AlH}_2$ in Et_2O with secondary amines (equation 4) in Et_2O proceeds as in reaction 2, to give complex II. The same reaction with participation of the primary amine (H_2NBU^i) produces an elastic polymer film with an unusual $\text{Ti}:\text{Al}$ of ratio 1:2. The formation of polymers in the reaction with secondary amines is well known from alane chemistry [7], while tetrahydroaluminates of alkali metals react with H_2NR according to reaction 5 [7].



The IR spectra of all complexes synthesized, $\text{Cp}_2\text{TiH}_2\text{Al(H)X}$ where $\text{X} = \text{OR}$, NEt_2 , are alike (Fig. 1) and comprise three groups of metal-hydrogen bond absorption bands that are shifted on deuteration: (i) at $1750\text{--}1850 \text{ cm}^{-1}$, attributable to the valence vibrations of the Al-H terminal bond, (ii) at $1100\text{--}1500 \text{ cm}^{-1}$,

attributable to the valence vibrations of the $\text{Al} \begin{array}{c} \text{H} \\ \diagdown \quad \diagup \\ \text{Ti} \end{array}$ metalocycle [9], and (iii)

at $550\text{--}800 \text{ cm}^{-1}$, attributable to the deformation vibrations with participation of metal-hydrogen bonds. In this case the IR spectrum of complex V completely coincides with that of the dimer $[\text{Cp}_2\text{Ti}(\mu_2\text{-H})_2\text{Al(H)OMe}]_2$ obtained as by reaction of $\text{Cp}_2\text{Ti}(\mu_2\text{-H})_2\text{AlH}_2$ with dimethoxyethane [10]. The X-ray (H atoms were not located) [10], and IR data for complex V, strongly suggest that the complexes I, II and IV, V have the same structure; a dimer, in which the Ti and Al atoms are linked

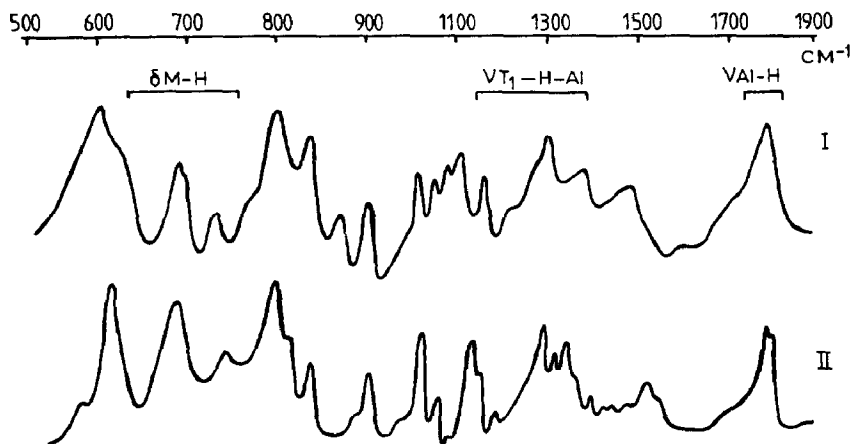


Fig. 1. IR spectra of $[\text{Cp}_2\text{TiH}_2\text{AlHOEt}]_2$ (I) and $[\text{CpTiH}_2\text{AlHNEt}_2]_2$ (II)

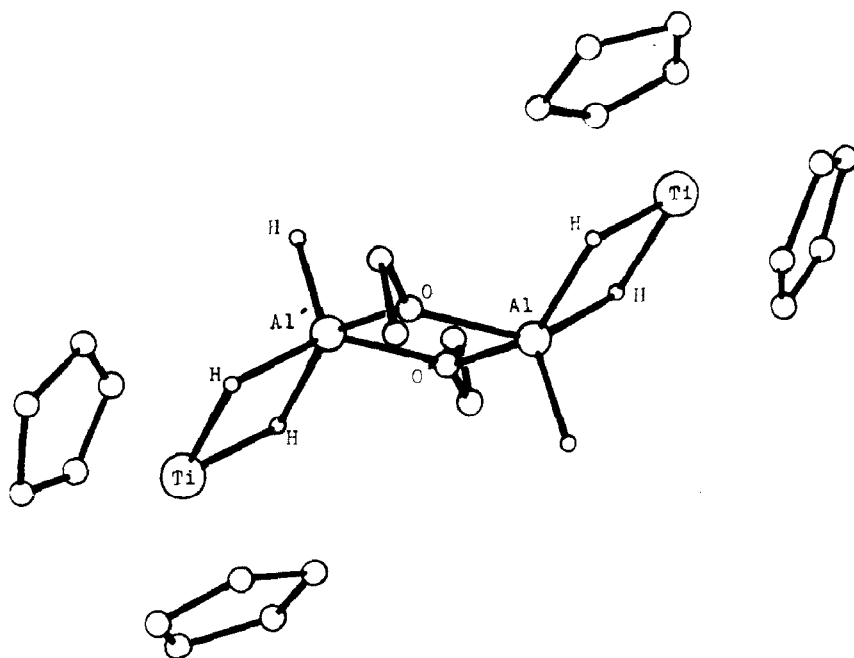


Fig. 2. Structure of $[\text{Cp}_2\text{TiH}_2\text{AlHOEt}]_2$ (I)

by a double hydride bridge, while the aluminium atoms are linked by OR or NR_2 groups. This suggestion has been confirmed by an X-ray diffraction study of complexes I and II.

Both compounds are centrosymmetrical dimers, in which the bonds between monomeric fragments $\text{Cp}_2\text{Ti}(\mu_2\text{-H})_2\text{Al}(\text{H})\text{X}$ are $\text{Al}\leftarrow\text{O}$ and $\text{Al}\leftarrow\text{N}$ coordinate

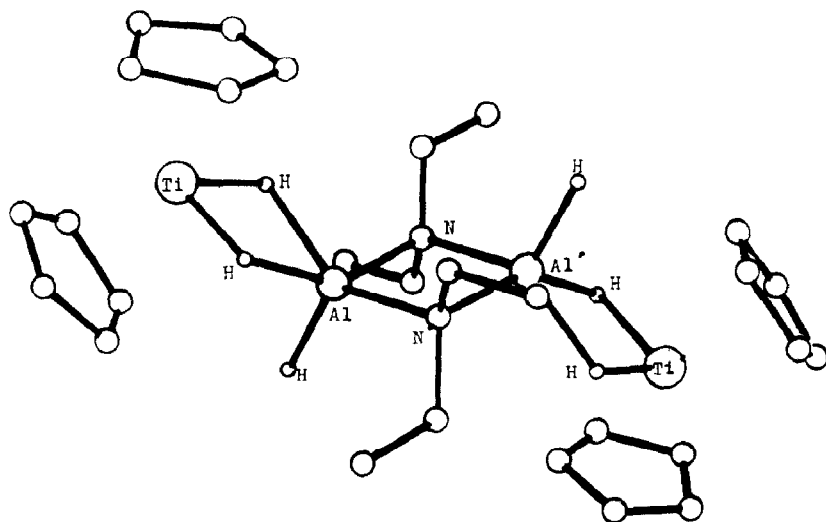


Fig. 3. Structure of $[\text{Cp}_2\text{TiH}_2\text{AlHNEt}_2]_2$ (II)

bonds, forming metallocycle $\text{Al} \begin{array}{c} \diagup \text{OEt} \\ \diagdown \text{OEt} \end{array} \text{Al}$ or $\text{Al} \begin{array}{c} \diagup \text{NEt}_2 \\ \diagdown \text{NEt}_2 \end{array} \text{Al}$ (Figs. 2, 3). Similar metallocycles have been observed in the molecules of $[\text{Cp}_2\text{Ti}(\mu_2\text{-H})_2\text{AlH}(\mu_2\text{-OMe})_2]$ [10] and $[(\text{Me}_3\text{P})_3\text{H}_3\text{W}(\mu_2\text{-H})_2\text{AlH}(\mu_2\text{-OBU}^n)]_2$ [11], obtained from the cleavage of dimethoxyethane and THF, and in the molecule of $[(\text{dmpe})_2\text{Ta}(\mu_2\text{-H})_2\text{Al}(\text{OC}_2\text{H}_4\text{OMe})(\mu_2\text{-OC}_2\text{H}_4\text{OMe})_2]$, obtained from the reaction of $(\text{dmpe})_2\text{TaCl}_2$ with two equivalents of $\text{NaAlH}_2(\text{OC}_2\text{H}_4\text{OMe})_2$ in Et_2O [12].

The metallocycle, $\text{Al} \begin{array}{c} \diagup \text{N} \\ \diagdown \text{N} \end{array} \text{Al}$, but with sp^2 -hybridized atoms of nitrogen, is found in $[(\text{Me}_3\text{P})_2\text{H}_3\text{W}(\mu_2\text{-H})_2\text{AlCl}(\mu_2\text{-N}=\text{CHEt})_2]$ [5].

The geometric parameters of the wedge-like Cp_2Ti sandwich in complexes I and II (Table 1) are similar to those found for complex V [7] and other alumohydride complexes of titanocene, such as $[\text{Cp}_2\text{Ti}(\mu_2\text{-H})_2\text{AlH}_2]_2 \cdot \text{Me}_2\text{NC}_2\text{H}_4\text{NMe}_2$ [13], $\text{Cp}_2\text{Ti}(\mu_2\text{-H})_2\text{AlCl}_2 \cdot \text{OEt}_2$ [14], $(\text{Cp}_2\text{Ti})_2\text{AlH}_4\text{CH}_3$ [15]. The parameters of the metallocycle $\text{Ti}(\mu_2\text{-H})_2\text{Al}$ (distances Ti-H, Al-H, Ti...Al) are also alike, and for complexes I and V the Ti...Al separations are practically the same (Table 2). The only marked difference in the structure of complexes I and V is shown by the geometry of the metallocycle $\text{Al} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{O} \end{array} \text{Al}$: although the average values of distances Al-O and angles TiAlO in both compounds are almost equal (Table 2), the metallocycle $\text{Al}(\mu_2\text{-O})_2\text{Al}$ in molecule of I is almost a planar rhomb (Table 1),

Table 1

Main interatomic distances $d(\text{\AA})$ and valence angles $\omega(^{\circ})$ in I and II

Bond	$d(\text{I})$	$d(\text{II})$	Bond	$d(\text{I})$	$d(\text{II})$
Ti-CpI	2.03	2.00	Al-H3	1.60(4)	1.64(9)
Ti-CpII	2.03	2.01	Al-X ^a	1.850(3)	1.99(1)
Ti-C _{av}	2.34(1)	2.33(2)	Al-X' ^a	1.853(3)	2.00(1)
Ti-H1	1.75(3)	1.74(9)	X-C ^a	1.431(5)	1.45(2)
					1.46(2)
Ti-H2	1.75(3)	1.60(9)	Ti...Al	2.782(2)	2.824(5)
Al-H1	1.75(3)	1.85(9)	Al...Al'	2.887(3)	2.911(8)
Al-H2	1.77(3)	1.90(8)			
Angle	$\omega(\text{I})$	$\omega(\text{II})$	Angle	$\omega(\text{I})$	$\omega(\text{II})$
CpITiCpII	138.6	137.5	H1AlH3	107.3(1)	108(4)
H1TiH2	75.6(1)	79(4)	H2AlH3	113.2(2)	100(4)
H1AlH2	74.8(1)	69(5)	XAlX' ^a	77.5(1)	86.2(4)
TiH1Al	105.2(1)	104(5)	AlXAl' ^a	102.5(1)	93.8(4)
TiH2Al	104.3(1)	107(4)	TiAlAl'	130.6(1)	140.3(3)
H1AlX ^a	142.5(1)	88(3)	AlXC ^a	126.8(3)	117.2(9)
					111.2(9)
H2AlX ^a	91.4(1)	148(3)	TiAlX ^a	121.1(1)	123.9(4)
H3AlX ^a	110.2(1)	107(3)	TiAlX' ^a	120.0(1)	124.5(3)
H3AlX' ^a	106.0(1)	112(3)			

^a X = O or N.

Table 2

Comparison of the interatomic distances (Å) and valence angles (°) in $[\text{Cp}_2\text{TiH}_2\text{AlH}(\mu\text{-X})_2]_2$ for various X groups

Bond/ Angle	$[\text{Cp}_2\text{TiH}_2\text{-Al(H)OMe}]_2$ [10]	$[\text{Cp}_2\text{TiH}_2\text{-Al(H)OEt}]_2$	$[\text{Cp}_2\text{TiH}_2\text{-Al(H)NEt}_2]_2$	$[(\text{C}_5\text{Me}_5)_2\text{TiH}_2\text{-Al(H)H}]_2$
Ti-Cp	2.03	2.03	2.01	2.07
Ti...Al	2.78	2.78	2.82	2.75
Al...Al	2.88	2.89	2.91	2.80
Al-X	1.86 ^a	1.85	2.00	1.94, 1.56
CpTiCp	138.0	138.6	137.5	142.2
TiAlAl'	130.0	130.6	140.3	134.0
TiAlX	119.8 ^a	120.6 ^a	124.2 ^a	122.7

^a Average value

whereas in V it is markedly asymmetric [10]. The coordination polyhedron of the aluminium atom in I is a tetragonal pyramid with an axial terminal atom hydrogen. Such coordination polyhedra have previously been observed in $\{[(\text{C}_5\text{Me}_5)(\eta^5\text{-C}_5\text{Me}_4\text{-CH}_2)\text{Ti}(\mu_2\text{-H})_2\text{Al}]_2(\mu_3\text{-O})\}_2$ [2] and $(\text{Cp}_2\text{Ti})_2\text{AlH}_4\text{Me}$ [15].

The asymmetry of the $\text{Al}(\mu_2\text{-O})_2\text{Al}$ fragment in V obviously shows that the coordination polyhedron of the aluminium atom in this compound, such as those in $[(\text{C}_5\text{Me}_5)_2\text{Ti}(\mu_2\text{-H})_2\text{AlH}(\mu_2\text{-H})_2]$ [9] and $[(\text{dmpe})_2\text{Mn}(\mu_2\text{-H})_2\text{AlH}(\mu_2\text{-H})_2]$ [16], is a trigonal bipyramid.

The causes of such a difference in the coordination about the aluminium atom in I and V are unclear. Interestingly, $[(\text{Me}_3\text{P})_3\text{H}_3\text{W}(\mu_2\text{-H})_2\text{AlH}(\mu_2\text{-OBu}^n)]_2$, has bridge butoxy-groups, and transition metal atom are *cis* [11] with respect to the symmetrical rhomb

$\text{Al} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{Al}$, whereas the other complexes of a similar type show the *trans* conformation. The authors [11] explain this difference in terms of the presence of the bulky butyl groups on the oxygen atoms.

Complex II also shows the trigonal-bipyramidal surrounding about the aluminium atom with an almost planar rhomb $\text{Al} \begin{array}{c} \diagup \text{N} \diagdown \\ \diagdown \text{N} \diagup \end{array} \text{Al}$.

Distance Al-N in II (1.99 Å), as expected, has a value (Table 1) that is intermediate between the respective values for the Al-N→Al bond in the trimer $[\text{H}_2\text{Al}(\mu_2\text{-NMe}_2)]_3$ (1.93 Å) [17] with a tetracoordinated aluminium atom, and for Al←N bond in complex $[\text{Cp}_2\text{Ti}(\mu_2\text{-H})_2\text{AlH}_2]_2 \cdot \text{TMEDA}$ (2.11 Å) [13] with penta-coordinated aluminium atom in a trigonal-bipyramidal surrounding.

The increase of electron-donor properties of the ligands both in the aluminium and titanium atoms (on going to C_5Me_5 -ligands) results in higher yields of products in which the Al atom deviates from the plane of equatorial ligands; angle TiAlAl' increases along the series $\text{V} < \text{I} < [(\text{C}_5\text{Me}_5)_2\text{Ti}(\mu_2\text{-H})_2\text{Al}(\mu_2\text{-H})_2]_2 < \text{II}$ (Table 2).

In all cases coordination of the undivided electron pair of the substitute of an Al atom occurs at another atom of aluminium, and never at a titanium atom, and is obviously a result of the high strength of the twin $\text{Ti}(\mu_2\text{-H})_2\text{Al}$ bridges and of the hardness of the Lewis bases, OR or NR_2 groups, which prefer to coordinate towards hard acid.

Experimental

Preparation of $[Cp_2Ti(\mu_2-H)_2AlH(\mu_2-X)]_2$. The complexes were prepared by a standard procedure (except for $X = OC_6H_{11}$).

A boat containing equimolar amounts of the reactants (alcohol, amine, ethyl acetate) was placed in flask containing 2 to 5 mmol of $Cp_2Ti(\mu_2-H)_2AlH_2$, obtained from the reaction of Cp_2TiCl with $LiAlH_4$ in 20–40 ml of ether [13], and was upset over the solution surface. The solution was slowly stirred until the reactant had completely evaporated off.

The precipitated crystals were separated from the mother liquor, washed with cold ether and dried in vacuo.

$[Cp_2Ti(\mu_2-H)_2AlH(\mu_2-OEt)]_2$ (I). A. Obtained from C_2H_5OH as violet crystals in 70% yield. Found: Ti, 18.8; Al, 9.9. $C_{12}H_{18}TiAlO$ calcd: Ti, 18.87, Al, 10.67. B. Obtained from CH_3COOEt , in 58% yield. Found: Ti, 18.1; Al, 10.1%.

$[Cp_2Ti(\mu_2-H)_2AlH(\mu_2-NEt_2)]_2$ (II). Obtained from Et_2NH as dark-violet crystals in 60% yield. Found: Ti, 17.4; Al, 9.7%. $C_{14}H_{23}TiAlN$ calcd: Ti, 17.14; Al, 9.64%.

$[Cp_2Ti(\mu_2-H)_2AlH(\mu_2-OMe)]_2$ (IV). Obtained from CH_3OH as fine, grey crystals in 70% yield. Found: Ti, 19.9; Al, 11.5. $C_{11}H_{16}TiAlO$ calcd: Ti, 20.08; Al, 11.30%.

$[Cp_2Ti(\mu_2-H)_2AlH(\mu_2-OBu^i)]_2$ (VI). Obtained from Bu^iOH as small dark-grey crystals in 65% yield. Found: Ti, 16.2; Al, 9.6. $C_{14}H_{22}TiAlO$ calcd: Ti, 16.93; Al, 9.64%.

$[Cp_2Ti(\mu_2-H)_2AlH(\mu_2-OC_6H_{11})]_2$ (IV). To a 1.98 mmol solution of $Cp_2TiH_2-AlH_2$ in 25 ml of Et_2O was added 1.96 mmol of cyclohexanol in 50 ml of ether with vigorous stirring. The mixture was stirred for 3 h and left overnight at $0^\circ C$. The fine

Table 3

Atomic coordinates ($\times 10^4$, $\times 10^3$ for H) and equivalent thermal factors ($\text{\AA}^2 \times 10^4$) of $[Cp_2TiH_2Al(H)OEt]_2$ (I)

Atom	x	y	z	U_{eq}
Ti	2945(1)	6183(1)	3070(1)	39
Al	4914(2)	5081(1)	4094(1)	48(1)
O	6034(4)	6037(3)	5010(2)	48(1)
C1	488(9)	6770(10)	3230(5)	125(5)
C2	566(8)	5899(7)	3878(6)	111(4)
C3	1925(9)	6570(8)	4385(4)	91(4)
C4	2560(9)	7803(7)	4040(5)	100(4)
C5	1761(9)	7936(7)	3356(5)	107(3)
C6	4770(9)	5905(9)	2019(4)	89(3)
C7	4339(7)	7033(5)	1830(3)	82(2)
C8	2669(10)	6667(8)	1652(4)	92(3)
C9	2119(9)	5218(7)	1751(3)	95(3)
C10	3425(9)	4806(7)	1965(3)	91(3)
C11	7422(7)	7244(5)	4990(3)	62(2)
C12	7000(7)	8407(5)	5370(4)	87(2)
H1	300(4)	467(3)	356(2)	52(9)
H2	486(4)	662(3)	359(2)	46(8)
H3	606(4)	432(4)	362(3)	67(10)

Table 4

Atomic coordinates ($\times 10^4$, $\times 10^3$ for H) and equivalent thermal factors ($\text{\AA}^2 \times 10^4$) of $[\text{Cp}_2\text{TiH}_2\text{Al(H)NEt}_2]_2$ (II)

Atom	x	y	z	U_{eq}
Ti	3143(2)	1052(1)	1524(3)	45(1)
Al	1096(3)	484(2)	-245(6)	58(2)
C1	2338(20)	296(13)	3709(24)	90(9)
C2	2475(21)	1025(14)	4290(20)	108(10)
C3	3642(24)	1279(12)	4293(23)	128(11)
C4	4350(16)	669(15)	3643(25)	167(12)
C5	3453(19)	22(10)	3378(23)	107(9)
C6	3151(16)	1942(16)	-691(29)	94(9)
C7	3859(22)	1347(12)	-1160(22)	83(8)
C8	4856(16)	1329(12)	-68(30)	96(9)
C9	4781(19)	1920(15)	1025(25)	92(9)
C10	3748(24)	2306(9)	679(31)	91(10)
N	-592(8)	658(6)	451(14)	43(4)
C11	-781(15)	908(8)	2138(22)	79(7)
C12	-2044(16)	999(9)	2769(24)	110(9)
C13	-1177(14)	1207(9)	-662(23)	94(8)
C14	-820(16)	2055(10)	-575(24)	110(8)
H1	160(8)	119(6)	138(12)	59(32)
H2	272(8)	33(5)	35(12)	43(30)
H3	130(7)	91(5)	-205(12)	45(29)

crystalline sediment was separated off by filtration. Yield, 55%. Found: Ti, 15.3; Al, 8.5. $\text{C}_{16}\text{H}_{24}\text{TiAlO}$ calcd: Ti, 15.64; Al, 8.79%.

Reaction of $\text{Cp}_2\text{TiH}_2\text{AlH}_2$ with Bu^1NH_2 was carried out under evaporation of amine from a solution of $\text{Cp}_2\text{TiH}_2\text{AlH}_2$ in ether. Overnight an elastic film, insoluble in organic solvents, had formed on the flask walls. Found: Ti, 13.0; Al, 17.8%.

The crystal structure. Single crystals of complexes I and II, packed in glass capillaries, were examined on an automatic diffractometer "Syntex P1" (graphite monochromator, Mo- K_α -irradiation $\theta/2\theta$ scanning).

Crystals of I are monoclinic, a 8.402(2) b 10.228(2) c 15.868(4) \AA , γ 106.92(2)°, V 1304,60(6) \AA^3 , space group $P2_1/n$, $Z = 2$. 1386 reflections with $I \geq 3\sigma(I)$ were used for the calculations. The structure was solved by direct methods (extinction correction was neglected, μ_{Mo} 7.3 cm^{-1}) and anisotropically (isotropically for H atoms) refined by full-matrix least squares to $R = 0.042$ ($R_w = 0.049$).

Crystals of II are monoclinic, a 11.093(2) b 16.947(4) c 8.078(1) \AA , γ 91.99(2)°, V 1517.69(9) \AA^3 , space group $P2_1/b$, $Z = 2$. 815 reflections with $I \geq 2\sigma(I)$ were used for the calculations. The structure was solved by the direct methods (extinction correction was neglected, μ_{Mo} 6.2 cm^{-1}) and anisotropically (isotropic for H atoms) refined by full-matrix least squares to $R = 0.074$ ($R_w = 0.082$).

The main interatomic distances and valence angles in molecules I and II are given in Table 1, and the atomic coordinates and thermal corrections in Tables 3 and 4.

References

- 1 A.I. Sizov, I.V. Molodnitskaya, B.M. Bulychev, V.K. Belsky, E.V. Evdokimova, G.L. Soloveichik, *Metalloorgan. Chimya*, in press.

- 2 E.B. Lobkovskii, A.I. Sizov, B.M. Bulychev, I.V. Sokolova, G.L. Soloveichik, *J. Organomet. Chem.*, 319 (1987) 69.
- 3 A.R. Barron, G. Wilkinson, *Polyhedron*, 5 (1986) 1897.
- 4 J.E. Salt, G.S. Giolami, G. Wilkinson, M. Motevalli, M. Thornton-Pett, M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1985) 685.
- 5 A.R. Barron, G. Wilkinson, M. Motevalli, M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1987) 837.
- 6 E.B. Lobkovskii, G.L. Soloveichik, A.I. Sizov, B.M. Bulychev, *J. Organomet. Chem.*, 280 (1985) 53.
- 7 H. Noth, E. Wiberg, *Forsch. und Forsch.*, 8 (1967) 321.
- 8 J.A. Krynitsky, J.E. Johnson, H.W. Carhart, *J. Am. Chem. Soc.*, 70 (1948) 486.
- 9 V.K. Belsky, A.I. Sizov, B.M. Bulychev, G.L. Soloveichik, *J. Organomet. Chem.*, 280 (1985) 67.
- 10 V.K. Belsky, A.I. Sizov, B.M. Bulychev, G.L. Soloveichik, *Koord. Chimija*, 11 (1985) 1003.
- 11 A.R. Barron, D. Lyons, G. Wilkinson, M. Motevalli, A.J. Howes, M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1986) 279.
- 12 T.J. McNeese, S.S. Wreford, B.M. Foxman, *J. Chem. Soc., Chem. Comm.*, (1978) 500.
- 13 E.B. Lobkovskii, G.L. Soloveichik, B.M. Bulychev, A.I. Sizov, A.I. Gusev, N.I. Kirillova, *J. Organomet. Chem.*, 265 (1984) 167.
- 14 E.B. Lobkovskii, G.L. Soloveichik, B.M. Bulychev, R.G. Gerr, Yu.T. Struchkov, *J. Organomet. Chem.*, 270 (1984) 45.
- 15 A.I. Sizov, I.V. Molodnitskaya, B.M. Bulychev, E.V. Evdokimova, V.K. Belsky, G.L. Soloveichik, *J. Organomet. Chem.*, 344 (1988) 293.
- 16 C.G. Howard, G.S. Girolami, G. Wilkinson, M. Thornton-Pett, M.B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1985) 921.
- 17 K.N. Semenenko, E.B. Lobkovskii, A.L. Dorosinskii, *Zh. Struktur. Chimii*, 13 (1972) 743.