

STRUCTURAL CHEMISTRY OF TITANIUM AND ALUMINIUM BIMETALLIC HYDRIDE COMPLEXES

II *. CRYSTAL AND MOLECULAR STRUCTURE OF $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\mu\text{-H})_2\text{AlCl}_2 \cdot \text{O}(\text{C}_2\text{H}_5)_2$

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Summary

A structural study of the complex $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\mu\text{-H})_2\text{AlCl}_2 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ (I) was carried out. The crystals are rhombic, a 12.322(2), b 15.090(3), c 37.941(7) Å; ρ_{calcd} 1.326 g/cm³, $Z = 16$, $R_1 = 0.071$, $R_2 = 0.050$. The unit cell of I involves two independent molecules of I. The immediate environment of the titanium atom involves two cyclopentadienyl moieties and two bridging hydrogen atoms occupying the vertices of a distorted tetrahedron. The coordination polyhedron at the aluminium atom is a distorted trigonal bipyramid, in which the axial positions are occupied by the bridging hydrogen atom and the oxygen atom ($\mu\text{-HALO}$ angle 158°).

Introduction

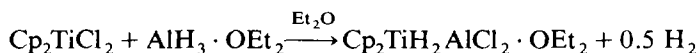
Interaction of the systems $\text{Cp}_2\text{TiHal}_n/\text{LiAlH}_4(\text{AlH}_{3-m}\text{Hal}_m)/\text{Et}_2\text{O}$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, $n = 1,2$) results in the formation of $\text{Cp}_2\text{TiH}_2\text{AlXX}'$ complexes (where $\text{X} = \text{H}$, Hal [1,2]) whose stability, as regards decomposition reactions with H_2 liberation, increases in the series $\text{Cp}_2\text{TiH}_2\text{AlH}_2 < \text{Cp}_2\text{TiH}_2\text{Al}(\text{H})\text{Cl} < \text{Cp}_2\text{TiH}_2\text{AlCl}_2$. The stability of these compounds is also increased upon the addition of stoichiometric amounts of stronger bases such as tertiary amines or diamines [3]. In the latter case,

* For part I see ref. 4.

the complex $[\text{Cp}_2\text{Ti}(\mu\text{-H})_2\text{AlH}_2]_2 \cdot \text{Me}_2\text{NC}_2\text{H}_4\text{NMe}_2$ was isolated and characterized by X-ray analysis [4]. However, the incorporation of strong bases leads simultaneously to the loss of catalytic properties for systems active in diethyl ether medium [1,5,6]. Although $\text{Cp}_2\text{TiH}_2\text{AlXX}'$ complexes can be isolated from Et_2O solutions as their solvates [7], the EPR spectral parameters of their solutions in Et_2O [1,2], THF [8,9] and non-solvating solvents [10] are practically coincident. Thus the question of the degree and character of solvation, and, respectively, of stereochemistry of the coordination environment of the titanium and aluminium atoms, which is of importance in elucidating the catalytic mechanism for Ziegler-type systems, is still open for discussion. In this connection we carried out an X-ray study of one of the titanium and aluminium hydride-haloid complexes synthesized in Et_2O medium, $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiH}_2\text{AlCl}_2 \cdot \text{O}(\text{C}_2\text{H}_5)$ (I). The results are presented in this paper.

Results and discussion

The titanium biscyclopentadienyl alumohydride complex $\text{Cp}_2\text{TiH}_2\text{AlCl}_2 \cdot \text{OEt}_2$ was obtained in the single-stage reaction between Cp_2TiCl_2 and an ether solution of aluminium hydride:



The crystalline structure of I was investigated by X-ray analysis. The atomic coordinates are presented in Table 1, while the main interatomic distances and bond angles are listed in Tables 2 and 3.

The crystals of I are built up of isolated molecules, the shortest contacts between which do not exceed the sum of the corresponding Van der Waals radii. The unit cell of complex I involves two independent molecules ("a" and "b") of the same structure (Fig. 1). The immediate environment of the titanium atom consists of two cyclopentadienyl moieties and two hydrogen atoms occupying the vertices of a distorted tetrahedron. Such a coordination polyhedron is typical of titanium dicyclopentadienyl d^1 -complexes. The planar Cp rings (deviations from the mean-squared planes do not exceed 0.02 Å) are connected to the titanium atom through a π -bond; the average Ti-C distance is equal to 2.33 Å and the variation range is 2.28–2.37 Å. The angle φ between the rings in the wedge-like sandwiches is equal to 137.2 and 137.0°. This angle is somewhat less than in the case of the similar moieties $\text{Cp}_2\text{TiH}_2\text{Al}$ within the molecules $(\text{Cp}_2\text{TiH}_2\text{AlH}_2)_2 \cdot \text{TMEDA}$ (II) (139.4° [4]) and $[\text{Cp}_2\text{TiH}_2\text{Al}(\mu\text{-H})(\eta^1 : \eta^5\text{-C}_5\text{H}_4)\text{TiCp}(\mu\text{-H})_2]$ (III) (138.4° [11]).

Two hydride hydrogen atoms are situated within the bisector plane of the wedge-like sandwich Cp_2Ti ; they connect the titanium and aluminium atoms to form the three-centre bridging hydrogen bonds. The H-Ti-H angle, which is equal to 70(2)° (a) and 80(2)° (b) for I, is close to the corresponding angles for II and III, namely, 71(3)° and 72(2)°, 76(2)°. The average Ti-H bond distance for molecule I, 1.80 Å, coincides with the analogous distance for III [11] but is somewhat greater than that for II (1.63 Å) [4]. However, whereas for complexes II and III the Ti-H bond lengths within the TiH_2Al metallocycle differ by 0.02–0.06 Å (within the measurement error range), in the case of I this difference is essentially greater (0.1–0.25 Å). A more noticeable difference, than that within complexes II and III, is also observed for the Al-H bond length values (by 0.2–0.3 Å). Thus, the geometry

TABLE 1

ATOMIC COORDINATES ($\times 10^4$ for non-hydrogen atoms; $\times 10^3$ for hydrogen atoms) AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS, $B_{eq} = 4/3\Sigma_i b_i^2 \bar{a}_i^2$ (\AA^2), OF COMPLEX I

Atom	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Ti(1)	1822(2)	8813(1)	4899(1)	4.7	H(1)	54(6)	889(5)	471(2)	7
Ti(2)	-1228(2)	3806(1)	3499(1)	5.2	H(2)	205(5)	819(4)	449(2)	3
Al(1)	922(3)	8452(2)	4253(1)	5.5	H(3)	-141(4)	879(3)	157(1)	2
Al(2)	286(3)	4445(2)	3029(1)	5.8	H(4)	88(5)	953(4)	190(1)	2
Cl(1)	-298(4)	7434(3)	4244(1)	8.5	H(5)	-37	795	509	7
Cl(2)	397(3)	9581(2)	3941(1)	8.7	H(6)	117	689	488	7
Cl(3)	1078(3)	3466(2)	2703(1)	8.8	H(7)	294	724	522	7
Cl(4)	1480(2)	5350(3)	3227(1)	8.8	H(8)	255	860	563	7
O(1)	1821(6)	7949(4)	3878(2)	5.8	H(9)	52	904	555	7
O(2)	-152(6)	5187(5)	2624(2)	8.3	H(10)	279	979	428	7
C(1)	453(9)	7968(7)	5179(3)	7	H(11)	132	65	461	7
C(2)	1260(9)	7382(7)	5071(3)	7	H(12)	182	51	529	7
C(3)	2210(9)	7589(7)	5252(3)	6	H(13)	360	964	534	7
C(4)	1988(10)	8291(7)	5474(3)	7	H(14)	419	905	472	7
C(5)	910(10)	8530(7)	5425(3)	7	H(15)	-97	578	362	7
C(6)	2751(11)	9835(8)	4548(2)	9	H(16)	41	476	395	7
C(7)	1988(11)	303(7)	4732(3)	9	H(17)	-68	351	425	7
C(8)	2260(12)	242(8)	5089(3)	10	H(18)	-271	375	412	7
C(9)	3191(10)	9745(8)	5106(3)	9	H(19)	-291	515	372	7
C(10)	3505(9)	9479(9)	4780(4)	9	H(20)	-116	199	378	7
C(11)	-1132(12)	5189(8)	3769(3)	9	H(21)	-17	215	317	7
C(12)	-413(10)	4650(9)	3952(3)	9	H(22)	-146	308	278	7
C(13)	-1023(11)	4012(8)	4099(3)	8	H(23)	-326	341	311	7
C(14)	-2089(11)	4125(8)	4023(3)	9	H(24)	-308	262	372	7
C(15)	-2180(9)	4872(9)	3813(3)	9					
C(16)	-1489(10)	2315(8)	3550(3)	8					
C(17)	-956(10)	2399(7)	3243(3)	8					
C(18)	-1635(11)	2890(7)	3028(3)	8					
C(19)	-2580(11)	3038(8)	3204(3)	9					
C(20)	-2501(11)	2652(9)	3541(3)	9					
C(21)	1924(12)	8236(9)	3492(3)	9					
C(22)	1051(14)	7858(9)	3290(4)	13					
C(23)	2347(10)	7057(7)	3950(3)	7					
C(24)	3535(9)	7192(10)	3972(4)	11					
C(25)	1417(18)	461(13)	2445(5)	21					
C(26)	-1235(21)	6240(7)	2709(4)	18					
C(27)	549(14)	5432(12)	2343(4)	14					
C(28)	235(16)	5106(10)	1993(3)	14					

of the TiH_2Al metallocycle within I is closer to that of a parallelogram than to the geometry of a rhombus. This evidence is in favour of the suggestion on the asymmetry of the TiH_2Al bridge in a tetrahydrofuran solution of the complex $\text{Cp}_2\text{TiH}_2\text{AlCl}_2$, which was put forward in [9] on the basis of EPR studies.

Besides the two bridging hydrogen atoms, the aluminium atom is connected to the two terminal chlorine atoms, and, through the donor-acceptor bonds, to the oxygen atom of the diethyl ether molecule, and thus has a coordination number of 5. The coordination polyhedron for the aluminium atom in I is a distorted trigonal bipyramid, as in the complexes $\text{AlCl}_3 \cdot 2\text{L}$ [12], $\text{AlH}_3 \cdot \text{TMEDA}$ [13], complexes II [4]

TABLE 2
BOND LENGTHS OF COMPLEX I

Bond	<i>r</i> (Å)	Bond	<i>r</i> (Å)	Bond	<i>r</i> (Å)
Ti(1)–C(1)	2.37(1)	Ti(2)–C(11)	2.33(1)	Ti(1)···Al(1)	2.747(4)
Ti(1)–C(2)	2.36(1)	Ti(2)–C(12)	2.36(1)	Ti(2)···Al(2)	2.755(4)
Ti(1)–C(3)	2.33(1)	Ti(2)–C(13)	2.31(1)	Ti(1)–H(1)	1.73(8)
Ti(1)–C(4)	2.33(1)	Ti(2)–C(14)	2.30(1)	Ti(1)–H(2)	1.84(6)
Ti(1)–C(5)	2.33(1)	Ti(2)–C(15)	2.32(1)	Ti(2)–H(3)	1.71(6)
Ti(1)–C(6)	2.34(1)	Ti(2)–C(16)	2.28(1)	Ti(2)–H(4)	1.91(6)
Ti(1)–C(7)	2.34(1)	Ti(2)–C(17)	2.36(1)	Al(1)–H(1)	1.93(7)
Ti(1)–C(8)	2.34(1)	Ti(2)–C(18)	2.32(1)	Al(1)–H(2)	1.70(6)
Ti(1)–C(9)	2.33(1)	Ti(2)–C(19)	2.32(1)	Al(2)–H(3)	1.82(5)
Ti(1)–C(10)	2.35(1)	Ti(1)–C(20)	2.35(1)	Al(2)–H(4)	1.47(6)
(Ti–C) _{av}	2.33	(Ti–H) _{av}	1.80	(Al–H) _{av}	1.73
Al(1)–Cl(1)	2.149(5)	Al(2)–Cl(3)	2.160(5)	Al(1)–O(1)	1.956(7)
Al(1)–Cl(2)	2.172(5)	Al(2)–Cl(4)	2.143(5)	Al(2)–O(2)	1.979(8)
O(1)–C(21)	1.53(1)	O(2)–C(25)	1.65(3)	C(21)–C(22)	1.44(2)
O(1)–C(23)	1.52(1)	O(2)–C(27)	1.42(2)	C(23)–C(24)	1.48(2)
		C(25)–C(26)	1.33(3)	C(27)–C(28)	1.47(2)

and III [11], (Cp₂YCl)₂AlH₃·OEt₂ (IV) [14], (Cp₂YH)₂(AlH₃·OEt₂)AlH₃ and (Cp₂YH)₂(AlH₃·THF)₂ (VI) [15]. The equatorial position is occupied by two chlorine atoms and by one of the bridging hydrogen atoms, while the second bridging hydrogen atom and the oxygen atom of the Et₂O molecule occupy the axial

TABLE 3
BOND ANGLES OF COMPLEX I

Angle	ω (°)	Angle	ω (°)	Angle	ω (°)
H(1)Ti(1)H(2)	80(3)	Cl(1)Al(1)Cl(2)	110.1(2)	Cl(3)Al(2)Cl(4)	109.1(2)
H(3)Ti(1)H(4)	70(2)	Ti(1)Al(1)Cl(1)	115.9(2)	Ti(2)Al(2)Cl(3)	115.9(2)
H(1)Al(1)H(2)	78(3)	Ti(1)Al(1)Cl(2)	116.8(2)	Ti(2)Al(2)Cl(4)	117.5(2)
H(3)Al(2)H(4)	78(3)	Ti(1)Al(1)O(1)	119.8(3)	Ti(2)Al(2)O(2)	121.1(3)
Ti(1)H(1)Al(1)	97(4)	H(1)Al(1)Cl(1)	95(2)	H(3)Al(2)Cl(3)	99(2)
Ti(1)H(2)Al(1)	101(3)	H(1)Al(1)Cl(2)	99(2)	H(3)Al(2)Cl(4)	97(2)
Ti(2)H(3)Al(2)	103(3)	H(1)Al(1)O(1)	158(2)	H(3)Al(2)O(2)	158(2)
Ti(2)H(4)Al(2)	108(3)	H(2)Al(1)Cl(1)	114(2)	H(4)Al(2)Cl(3)	128(2)
Al(1)O(1)Cl(21)	129.2(6)	H(2)Al(1)Cl(2)	136(2)	H(4)Al(2)Cl(4)	123(2)
Al(1)O(1)C(23)	117.1(6)	H(2)Al(1)O(1)	80(2)	H(4)Al(2)O(2)	80(2)
Al(2)O(2)C(27)	124.3(8)	Cl(1)Al(1)O(1)	96.2(3)	Cl(3)Al(2)O(2)	93.7(3)
Al(2)O(2)C(25)	121.9(9)	Cl(2)Al(1)O(1)	94.4(3)	Cl(4)Al(2)O(2)	95.7(3)
C(21)O(1)C(23)	112.7(8)	O(1)C(21)C(22)	110(1)	O(2)C(25)C(26)	90(1)
C(25)O(2)C(27)	113.3(9)	O(1)C(23)C(24)	108(1)	O(2)C(27)C(28)	115(1)
C(1)C(2)C(3)	108(1)	C(6)C(7)C(8)	107(1)	C(11)C(12)C(13)	106(1)
C(2)C(3)C(4)	108(1)	C(7)C(8)C(9)	106(1)	C(12)C(13)C(14)	111(1)
C(3)C(4)C(5)	108(1)	C(8)C(9)C(10)	111(1)	C(13)C(14)C(15)	108(1)
C(4)C(5)C(1)	109(1)	C(9)C(10)C(6)	106(1)	C(14)C(15)C(11)	106(1)
C(5)C(1)C(2)	107(1)	C(10)C(6)C(7)	109(1)	C(15)C(11)C(12)	109(1)
C(16)C(17)C(18)	105(1)	C(17)C(18)C(19)	108(1)	C(18)C(19)C(20)	109(1)
C(19)C(20)C(16)	104(1)	C(20)C(16)C(17)	113(1)	(C–C–C) _{av}	108

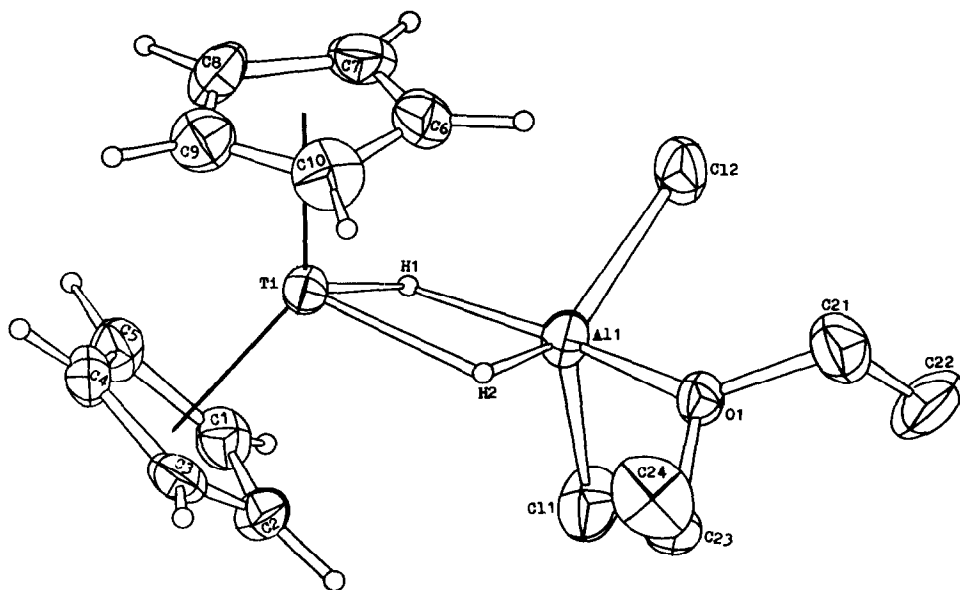


Fig. 1. Molecular structure of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\mu\text{-H})_2\text{AlCl}_2\cdot\text{O}(\text{C}_2\text{H}_5)_2$.

position. The angle between the axial ligands H(1)Al(1)O(1) and H(3)Al(2)O(2) for both independent molecules of complex I is equal to 158° , which is similar to the value of the angle H–Al–N in II (155° [4]), and of H–Al–H in III (160 and 162° [11]).

The Al–Cl bond length in I (2.156 \AA) is somewhat less than $r(\text{Al–Cl})$ for the complex $\text{AlCl}_3 \cdot 2\text{NMe}_2$ (2.18 \AA), in which the coordination number of the aluminium atom is also equal to 5, but is greater than that for the tetrahedral complexes $\text{AlCl}_3 \cdot \text{NR}_3$ (R = H, Me) (2.10 – 2.12 \AA) [16], as could be expected. The decrease in $r(\text{Al–Cl})$ for I against the value found for $\text{AlCl}_3 \cdot \text{NMe}_2$ seems to result from the poorer donor capability of Et_2O and the hydride ligand, which are situated in the axial positions of the bipyramid and play the role of Lewis bases, as compared with NMe_2 . In fact, substitution of amine in $\text{AlCl}_3 \cdot \text{L}$ for the weaker base (THF) results in a decrease in the Al–Cl distance to 2.159 \AA [17].

The Al–O bond length in I (1.96 \AA (a) and 1.98 \AA (b)) is practically coincident with $r(\text{Al–O})$ for the bimetallic hydride complexes involving the H_4O environment of the aluminium atom ($(\text{Cp}_2\text{YH})_2(\text{AlH}_3)(\text{AlH}_3 \cdot \text{OEt}_2)$ (1.95 \AA [15]) and $(\text{Cp}_2\text{YH})_2(\text{AlH}_3 \cdot \text{THF})_2$ (1.97 \AA [18]) and is close to $r(\text{Al–O})$ for the complex $\text{AlCl}_3 \cdot \text{THF}$ (1.99 \AA [17]). At the same time, for complex IV, in which one of the axial bonds in the trigonal bipyramid is a weak secondary bond, $\text{Al} \cdots \text{Cl}$ ($r(\text{Al–Cl})$ 3.01 \AA), and the coordination of the aluminium atom is intermediate between the 4- and 5-coordinated complexes, the Al–O distance is noticeably shorter (1.89 \AA) [14]. The geometry of the Et_2O molecule within complex I is practically unaffected, compared with the free molecule, as in complexes IV [14] and V [15]. The three atoms connected to the oxygen atom are situated within one plane. Thus, $\text{Cp}_2\text{TiH}_2\text{AlCl}_2 \cdot \text{OEt}_2$, as well as the complex $(\text{Cp}_2\text{TiH}_2\text{AlH}_2)_2 \cdot \text{TMEDA}$ [4], should be regarded not as the substituted alumohydride (for which a mixed hydride-haloid

environment of the aluminium atom is quite atypical), but rather as alane, i.e. the complex of the aluminium hydride (II) or haloidalane (I), in which one of the two usual Lewis n -bases is substituted for the organometallic ligand Cp_2TiH .

It should be noted that the $\text{Ti} \cdots \text{Al}$ distance in I (2.75 Å) is short enough, and is almost equal to the sum of the covalent radii (2.76 Å [19]). A short interatomic $\text{Ti} \cdots \text{Al}$ distance was also established in complexes II (2.79 Å [4]) and III (2.78 Å [11]). It is of interest to note that the $r(\text{Ti}-\text{Al})$ value is almost unaffected when one of the hydrogen atoms in the double bridge TiH_2Al is substituted for the considerably bulkier carbon atom. For instance, for the molecule of $[\text{CpTi}(\text{C}_5\text{H}_4)\text{HAlEt}_2]_2$ the distance $r(\text{Ti} \cdots \text{Al})$ 2.79 Å [20], while for $(\text{C}_{10}\text{H}_8)(\text{C}_5\text{H}_4\text{TiHAlEt}_2)_2$ the latter distance is equal to 2.82 Å [21]. Such a short contact can be suggested to result from the formation of a weak titanium–aluminium bond originating due to the transfer of d -electrons of the titanium atom to the vacant d -orbitals of the aluminium atom. The geometrical considerations alone cannot ascertain the presence of the metal–metal bond. However, there is no doubt that the formation of a metallocycle is extremely advantageous from an energy point of view. The latter is substantiated, in particular, by its stability against cleavage in the strongly solvating solvents, as well as by the results of calorimetric studies [1,2]. This suggestion is also consistent with the relatively high values of the HFI constant a_{Al} in the EPR spectra of the $\text{Cp}_2\text{TiH}_2\text{AlXX}'$ complexes, which characterizes the s -electron density of the unpaired electron at the Al nucleus. As should be expected, the shortening of the $\text{Ti} \cdots \text{Al}$ distance on passing from II (2.79 Å) to I (2.75 Å) is accompanied with an increase in a_{Al} from 5 [3] to 10.4 G [2]. At the same time, for the yttrium complexes V and VI, for which yttrium–aluminium bonding is precluded, the $\text{Y} \cdots \text{Al}$ distance (3.20–3.24 Å) [15,18] is considerably greater than the sum of the covalent radii (3.00 Å). We note, in conclusion, that the results of the X-ray study for complexes I and II completely confirmed the suggestion [2] about the solvation of $\text{Cp}_2\text{TiH}_2\text{AlXX}'$ complexes in solution at the aluminium atom even in the case where $\text{X} = \text{Cl}$, which is bulkier than H. This conclusion from our viewpoint is of principal importance for one of the possible catalytic mechanisms of Ziegler-type systems, which suppose a coordination of the olefin molecule displaying π -basal properties, at the aluminium atom.

Experimental

Synthesis of $\text{Cp}_2\text{TiH}_2\text{AlCl}_2 \cdot \text{OEt}_2$. 1.50 g (6 mmol) of freshly ground Cp_2TiCl_2 was quickly added to a solution of 0.18 g (6 mmol) of AlH_3 in 65 ml of diethyl ether. The mixture was shaken until termination of gas evolution, and then filtered. The violet-coloured filtrate was carefully added to a layer of pentane. Single crystals of I were obtained in the phase border of ether/pentane. The precipitated crystals were separated and dried in vacuo. Found: Ti, 13.9; Al, 7.7; Cl, 20.0; H_{act} 0.54. $(\text{C}_5\text{H}_5)_2\text{TiH}_2\text{AlCl}_2 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ calcd.: Ti, 13.60; Al, 7.66; Cl, 20.14; H_{act} 0.57%.

Crystalline structure determination. Due to the high sensitivity of I as regards oxidation and hydrolysis, the measurements were carried out in a capillary. The unit cell parameters and experimental reflections were recorded using a Hilger & Watts automatic X-ray diffractometer (Mo- K_α irradiation, graphite monochromator. $\theta/2\theta$ scanning, $2\theta \leq 50^\circ$). The main crystallographic data were as follows: rhombic crystals, space group P_{bca} , a 12.322(2), b 15.090(3), c 37.941(7) Å, V 7054 Å³,

$M = 352.1$, $\rho_{\text{calcd}} 1.326 \text{ g/cm}^3$, $Z = 16$, $\mu(\text{Mo-K}\alpha) 8.44 \text{ cm}^{-1}$.

1735 reflections with $I > 2\sigma(I)$ of a total of 3897 were used for calculations. The structure was solved by the direct method using the EXTL program complex. The hydride hydrogens were localized by difference Fourier synthesis, and the hydrogen atoms of the cyclopentadienyl groups were determined from geometrical considerations. The structure was refined by the least-squares method in the block-diagonal anisotropic (for non-hydrogen atoms) and isotropic (for the hydride hydrogen atoms) approximation. The resting H atoms were not refined. The final values for the R -factors were $R_1 = 0.071$ and $R_2 = 0.050$.

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