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STRUCTURAL CHEMISTRY OF TITANIUM AND ALUMINIUM BIMETALLIC HYDRIDE COMPLEXES

IV *. MOLECULAR STRUCTURES AND CATALYTIC PROPERTIES OF $\{[\eta^5\text{-}C_5(CH_3)_5]_2Ti(\mu_2\text{-}H)_2Al(H)(\mu_2\text{-}H)\}_2$ AND $[\eta^5\text{-}C_5(CH_3)_5]_2Ti(\mu_2\text{-}H)_2Al(H)(\mu_2\text{-}H)_2Ti[\eta^5\text{-}C_5(CH_3)_5]_2$

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Summary

Interaction between $(\eta^5\text{-}C_5Me_5)_2TiH_2BH_2$ and $LiAlH_4$ in ether produced the complex $[(\eta^5\text{-}C_5Me_5)_2TiH_2AlH_2]_2$. The compound crystallized in a monoclinic unit cell with the parameters *a* 11.196(4), *b* 8.915(3), *c* 20.777(7) Å, γ 101.74(3)°, space group $P2_1/n$, $Z = 4$. The linkage between the Ti and Al atoms is accomplished via the double hydrogen bridge TiH_2Al, whereas dimerization occurs via the AlH_2Al bridges. The coordination polyhedron for the Al atom is a distorted trigonal-bipyramid with five hydride ligands at its apices. Decomposition of $[(\eta^5\text{-}C_5Me_5)_2TiH_2AlH_2]_2$ in solution produced the complex $[(\eta^5\text{-}C_5Me_5)_2Ti]_2AlH_5$, crystallizing in a triclinic unit cell with the parameters *a* 11.881(4), *b* 18.951(8), *c* 8.868(3) Å, α 93.04(3), β 104.33(3), γ 79.26(3)°, space group $P\bar{1}$, $Z = 2$. The Al atom in this compound is assumed to have coordination number 5 and to be surrounded by hydride hydrogens only. The isomerization rate for 1-hexene in the presence of $[(\eta^5\text{-}C_5Me_5)_2TiH_2AlH_2]_2$ was 0.3 mol olef/g-atom Ti · min, while the hydrogenation rate of the complex $[(\eta^5\text{-}C_5Me_5)_2Ti]_2AlH_4Cl$ was 38 mol H_2/g-atom Ti · min.

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* For part III see ref. 6.

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Introduction

In contrast to the stable and well-studied transition metal borohydrides $L_nM(BH_4)_m$ [1], the transition metal alumohydrides $L_nM(AlH_4)_m$, which prove to be even more interesting from the practical standpoint, have been studied far less extensively, mainly by indirect methods (IR, NMR, EPR spectroscopy) [2]. This is accounted for, apparently, by the greater experimental difficulties when dealing with thermodynamically and kinetically unstable compounds. Thus titanocene alumohydrides $Cp'_2TiH_2AlH_2$ (I), where $Cp'_2 = (\eta^5\text{-}C_5H_5)$, $C_2H_4(C_5H_4)$, $(t\text{-}BuC_5H_4)_2$, $C_3H_6(C_5H_4)_2$, were established [3,4] to be unstable in ether solutions, and attempts to isolate the individual compounds resulted in decomposition with partial evolution of hydrogen to give the compounds with σ-π bonded Cp′ rings. The stability of complexes of type I is essentially increased on their solvation with strong bases. The solvate $[Cp'_2TiH_2AlH_2]_2 \cdot (CH_3)_2NCH_2CH_2N(CH_3)_2$ (II) [5] has been obtained in this way and studied by X-ray analysis. However, even this compound on storage in toluene solution undergoes rather fast decomposition with recombination of basic hydride hydrogens and acidic protons of the Cp rings to give a polycyclic complex, $[Cp_2Ti(\mu_2\text{-}H)_2Al(\mu_2\text{-}H)(\eta^1:\eta^5\text{-}C_5H_4)TiCp(\mu_2\text{-}H)]_2$ (III) [6].

Taking into account the results of our previous papers [3,4,6], there appears to be an alternative method for stabilizing the molecules of I, namely by replacing the acidic protons of the Cp rings by methyl groups. This paper presents the results of the study of the structures and certain physico-chemical properties of the permethylated complex $[C_5(CH_3)_5]_2TiAlH_4$ (IV) and the product of its decomposition, $\{[C_5(CH_3)_5]_2Ti\}_2AlH_5$ (V).

Results and discussion

Titanium bis(permethylcyclopentadienyl) alumohydride $(C_5Me_5)_2TiAlH_4$ was prepared as green crystals via the exchange reaction of the corresponding borohydride with $LiAlH_4$ (eq. 1).

$$(C_5Me_5)_2TiBH_4 + LiAlH_4 \xrightarrow{Et_2O} (C_5Me_5)_2TiAlH_4 + LiBH_4 \qquad (1)$$

The borohydride required was obtained via reaction 2. Its spectroscopic features (IR, EPR) proved to be practically the same as those established for $(C_5H_5)_2TiBH_4$. Reaction 2, however, proceeds at extremely low rates, as compared with the reaction

$$(C_5Me_5)_2TiCl_2 + 2LiBH_4 \xrightarrow{Et_2O} (C_5Me_5)_2TiBH_4 + 1/2H_2 + 1/2B_2H_6 + 2LiCl \qquad (2)$$

of Cp_2TiBH_4 synthesis. The "direct" methods to prepare $(C_5Me_5)_2TiAlH_4$, e.g. along reactions 3 and 4, proved to be of low efficiency because of difficulties in the preparation of $(C_5Me_5)_2TiCl$ and purification of the product required from the by-products.

$$(C_5Me_5)_2TiCl_2 + 2LiAlH_4 \xrightarrow{Et_2O} (C_5Me_5)_2TiAlH_4 + 1/2H_2 + AlH_3 + 2LiCl \qquad (3)$$

$$(C_5Me_5)_2TiCl + LiAlH_4 \xrightarrow{Et_2O} (C_5Me_5)_2TiAlH_4 + LiCl \qquad (4)$$

In contrast to ordinary biscyclopentadienyltitanium alumohydride, its permethylated analogue crystallized in an unsolvated state, even in the presence of such a strong base as $(CH_3)_2NCH_2CH_2N(CH_3)_2$ (TMEDA). The compound is moderately soluble in diethyl ether and toluene, giving green solutions that are extremely sensitive to oxidation. On prolonged storage, the solution turns violet, and the evolution of hydrogen and the formation of an aluminium mirror are observed. In this case, minute quantities of violet crystals of the composition $[(C_5Me_5)_2Ti]_2AlH_5$ (V) are precipitated from the solution. It should be noted that the ratio Ti/Al = 2/1 in V is exactly the same as that for complex III [6]. Unfortunately, the amount of isolated crystals of V was far too small to allow its IR spectrum to be recorded. The IR spectrum of IV is different from that of the solvate II and from that of the unsolvated complex $CH_2(C_5H_4)_2TiAlH_4$ (VI) [7], in which spectra, in the region of the Al–H bond vibrations, there is a doublet of absorption bands at 1730, 1745 cm^{-1} and 1810, 1825 cm^{-1}, respectively, associated with the vibrations involving the terminal hydride atoms (Fig. 1). The IR spectrum of complex IV shows in this region two absorption bands, a narrow one at 1835 cm^{-1} and a broad one at 1600 cm^{-1}, which can be confidently assigned to the terminal Al–H and bridging Al–H–Al bond vibrations (ν(Al–H–Al) in a polymeric etherate of aluminium hydride $AlH_3 \cdot$

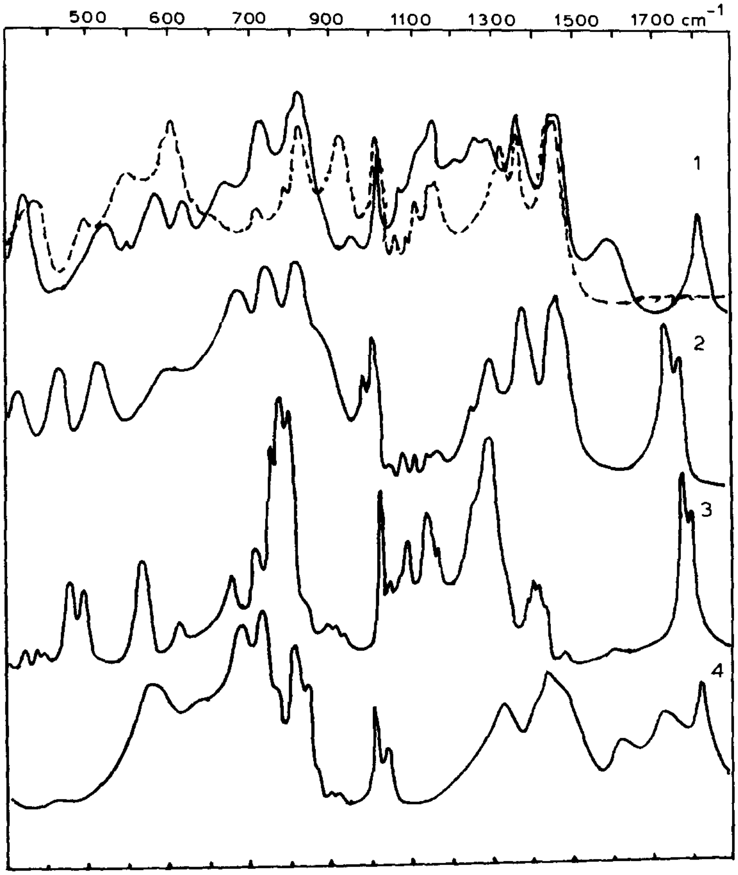

Fig. 1. IR spectra of $[(C_5Me_5)_2TiH_2AlH_2]_2$ (1) (dashed line - deutero-analogue), $[(C_5H_5)_2TiH_2$-$AlH_2]_2$.TMEDA (2), $CH_2(C_5H_4)_2TiH_2\ AlH_2$ (3) and $[(C_5H_5)_2Zr(H)AlH_4]_x$ (4).

$0.3R_2O$ is 1610 cm^{-1} [8]). Taking into account the EPR data for complex IV, according to which the oxidation number of the Ti atom is +3 ($g = 1.989$), and the occurrence of absorption bands in the region of the bridging Ti–H–Al bond vibrations (1160 and 1280 cm^{-1}), we can suppose that the titanium and aluminium atoms in IV are bonded via the bridging hydrogen linkages and that the molecule $(C_5Me_5)_2TiAlH_4$ is in an associated state in the crystal.

This suggestion was confirmed by X-ray study of a single crystal of IV. The crystals of complex IV are built-up of the centrosymmetric dimeric molecules $(C_5Me_5)_2Ti(\mu_2\text{-}H)_2Al(H)(\mu_2\text{-}H)_2Al(H)(\mu_2\text{-}H)_2Ti(C_5Me_5)_2$, in which the monomeric moieties $(C_5Me_5)_2TiH_2AlH_2$ are linked to each other via two three-centre bridging bonds, Al–H–Al (Fig. 2).

The structure of wedge-like $(C_5Me_5)_2Ti$ sandwiches is common for dicyclopentadienyltitanium compounds. Within the 0.02 Å limits, the pentamethylcyclopentadienyl rings may be considered as planar. The methyl carbons are somewhat off the ring plane (by 0.1-0.4 Å) in the direction of the titanium atom (as in $(C_5Me_5)_2TiCl_2$ [9]). The Ti–C distance for the ring in IV (2.39 Å) (Table 1) is practically the same as that in $[(C_5Me_5)_2Ti]_2N_2$ (2.39 Å) [10] and $(C_5Me_5)_2Ti(C_5Me_4CH_2)O_2Ti(C_5Me_5)$ (2.40 Å) [11], and slightly less than that in $(C_5Me_5)_2TiCl_2$ (2.44 Å) [9]. The CpTiCp angle in IV (142.2°) falls between the corresponding values for the complexes of tetravalent (137.4° for $(C_5Me_5)_2TiCl_2$ [9]) and bivalent (147.8° for $(C_5Me_5)_2Ti(CO)_2$ [12], and 145.7° for $[C_5Me_5)_2Ti]_2N_2$ [10]) titanium.

Besides two pentamethylcyclopentadienyl groups, the coordination sphere of the titanium atom involves two hydrogen atoms (pseudo-tetrahedral configuration with C_{2v} symmetry), which link the titanium and aluminium atoms via the three-centre bonds. The aluminium atom is located on the C_2 symmetry axis of the wedge-like sandwich. The parameters of the TiH_2Al metallocycle within complex IV, compared with those for other alumohydride complexes of titanocene, are listed in Table 2. The asymmetry of the bridging bonds in TiH_2Al, which is rather appreciable in the complex $Cp_2TiH_2AlCl_2 \cdot OEt_2$ (VII) [13] and, particularly, in complexes of the

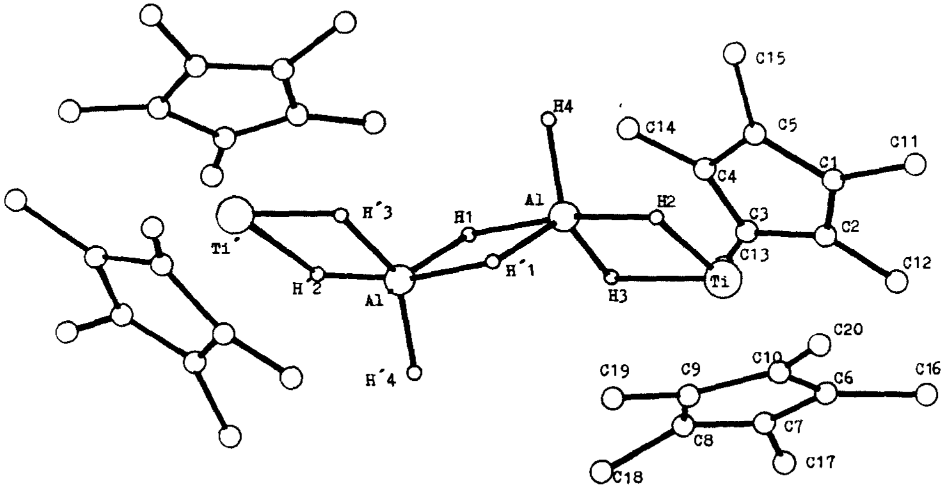

Fig. 2. Molecular structure of $[(C_5Me_5)_2TiH_2AlH_2]_2$.

TABLE 1

MAIN INTERATOMIC DISTANCES, *d*(Å), AND BOND ANGLES, ω(°), IN THE COMPLEXES $[(C_5Me_5)_2TiH_2AlH_2]_2$ (IV) AND $[(C_5Me_5)_2Ti]_2AlH_5$ (V)

Distance *d*	(Å)	Angle ω	(°)
Complex IV			
Ti–C_{av}	2.392(19)	Cp[a]TiCp[a]	142.2(2)
C–C (in rings)$_{av}$	1.398(14)	H(2)TiH(3)	72.6(1)
C–C(ring-CH_3)$_{av}$	1.512(18)	H(2)AlH(3)	84.5(1)
Ti–H(2)	1.92(1)	TiH(2)Al	101.1(1)
Ti–H(3)	1.86(1)	TiH(3)Al	101.3(1)
Al–H(1)	1.56(1)	H(1)AlH(4)	111.6(1)
Al–H(2)	1.63(1)	H(2)AlH(4)	100.5(1)
Al–H(3)	1.70(1)	H(2)AlH(1)	107.2(1)
Al–H(4)	1.51(1)	H(2)AlH′(1)	166.9(1)
Al–H(1)	1.94(1)	C–C–C(in rings)$_{av}$	108.0(8)
Ti...Al	2.750(3)	C–C–$C_{Me,av}$	125.6(14)
Ti–Cp_{av} [a]	2.075	TiAlH′(1)	122.7(1)
Al...Al	2.800(4)	H(2)AlH(3)	84.5(1)
		H(3)AlH′(1)	83.1(1)
		H(4)AlH′(1)	90.6(1)
Complex V			
Ti–C_{av}	2.376(27)	C[a]Ti(1)Cp[a]	146.8
Ti–Cp_{av} [a]	2.070	Cp[a]Ti(2)Cp[a]	144.2
C–C(in rings,$_{av}$)	1.370(59)	C–C–C(in rings,av)	107.5(3)
C–C(ring-CH_3)	1.519(50)	C–C–$C_{Me,av}$	125.6(4)
Ti(1)...Al	2.833(7)	Ti(1)AlTi(2)	151.0(3)
Ti(1)...Al[b]	2.769(7)	Ti(1)Al[b]Ti(2)	158.2(3)
Ti(2)...Al	2.836(7)	Cp′Cp′Ti(1)/Cp′Cp′Ti(2)	87
Ti(2)...Al[b]	2.811(7)		
Ti(1)...Ti(2)	5.479(3)		

[a] Centre of the cyclopentadienyl ring. [b] The aluminium atom of smaller statistical weight.

$Cp_2MoH_2MX_2$ type (M = Cu, Fe; X = Hal) [2], in the case of complex IV, falls within the measurement error limits. The short Ti...Al distance in IV (2.75 Å), as in complex VII, is also noteworthy. However, if in the case of VII such a shortening is accounted for by the presence in the coordination sphere of aluminium-accepting chlorine atoms, then for IV an additional transfer of electron density seems to result from the enhancement of the donor character of the C_5Me_5 rings as compared with that of the C_5H_5 rings.

The coordination polyhedron of the aluminium atom in IV is a distorted trigonal-bipyramid, as for other structurally characterized alumohydride complexes of titanocene, II [5], III [6], VII [13], $[Cp_2TiH_2Al(H)OMe]_2$ (VIII) [14], and of yttriecene $Cp_2YAlH_4 \cdot L$, where L = NEt_3 [15], THF [16]. However, as distinguished from the known analogies, the compound with aluminium coordination number 5, with all the ligands being hydrogens, has been obtained for the first time *. Four-

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* At the time of manuscript preparation, the paper by Girolami et al. [26] became available, describing the structure $[(dmpe)_2MnH_2AlH_2]_2$ which involves a five-coordinated Al atom with a likewise purely hydride environment.

TABLE 2

CERTAIN STRUCTURAL PARAMETERS FOR COMPLEXES INVOLVING THE $Cp_2TiH_2AlXX' \cdot L$ MOIETY

Compound	X,X′	L	Ti...Al (Å)	Ti–H^M (Å)	Al–H^M (Å)	Al–H^I (Å)	HTiH(°)	$M^M AlH^M$(°)	XAlX′(°)	HAlL(°)	TiAlL(°)	Ref.
$(Cp_2TiH_2AlH_2)_2 \cdot TMEDA$	H	N	2,79	1.6	1.75	1,55	71	66	118	155	122	5
$Cp_2TiH_2AlCl_2 \cdot Et_2O$	Cl	O	2,75	1.8	1.7	–	75	78	110	158	120	13
$[Cp_2TiH_2Al(H)(C_5H_4)Ti(H)Cp]_2$	H,C	H	2,78	1.8	1.7	–	74	76	119,116	161	–	6
$[Cp_2TiH_2Al(H)(OMe)]_2$	H,O	H	2.76 2.79	–	–	–	–	–	–	–	118.7;123.6 120.5;116.6	14
$[(C_5Me_5)_2TiH_2AlH(H)]_2$	H	H	2.75	1.9	1.7	1.5	73	84	112	167	124	this paper
$[(C_5Me_5)_2Ti]_2AlH_5$	H	H	2.77 2.83	–	–	–	–	–	–	–	–	this paper

and six-coordinated complexes of aluminium with a purely hydride environment are now well-known, e.g. the tetrahedral AlH_4^- anions in alkaline and alkaline-earth metal alumohydrides, and the M_3AlH_6 and AlH_6 octahedrons in a polymeric aluminium hydride [17]. That is why the stereochemistry of a formerly unknown five-coordinated hydride environment of the aluminium atom (Fig. 3) is of particular interest. Besides the two hydrogen atoms involved in the metallocycle TiH_2Al and a terminal hydrogen, the aluminium atom is bonded to two hydrogens forming the double hydrogen bridge AlH_2Al. This fact conforms to the IR data and substantiates the correctness of the assignments in the IR spectra of IV. The AlH_2Al bridge is sharply asymmetric (r(Al–H) 1.6 and 1.9 Å), although the average Al–H distance in the bridge (1.75 Å) is close to that in the polymeric aluminium hydride (1.72 Å) [17]. The asymmetry of the AlH_2Al bridge seems to result from steric hindrance in the coordination of the fifth ligand due to repulsion from the C_5Me_5 rings. This fact, together with the increased electron density on the aluminium atom, can be suggested to be the reason for the lack of interaction between $(C_5Me_5)_2TiH_2AlH_2$ and TMEDA. The H′(1) atom, occupying an axial position in the bipyramid, "belongs" to the other monomeric moiety, situated practically in the TiH(2)H(3)Al plane. The donor atoms of the solvating ligands in the molecules II and VII are also situated in the bisecting plane of the wedge-like sandwich $(C_5H_5)_2Ti$, with the TiAlL angles being nearly coincident for all compounds (Table 2). It should be noted that although the angle between the axial ligands of the bipyramid in IV is closer to 180° than in the other compounds, the polyhedron itself is distorted to a greater extent because of the repulsion of the H(1) and H(4) atoms from the C_5Me_5 moieties.

The dimeric molecule IV is a close analogue of the molecule VIII involving a bridging methoxy group [14], which is manifested in the similarity of such structural parameters as the TiAlX angles (134.0 and 130.0°, respectively), the Ti–Al–X^{ax} angles (122.7 and 120.8°, respectively), and the Al...Al distances (2.80 and 2.88 Å).

Thus, the structural data obtained in the investigation of titanium and aluminium [5,6,13], in this paper, and for yttrium and aluminium [15,16] dicyclopentadienyl

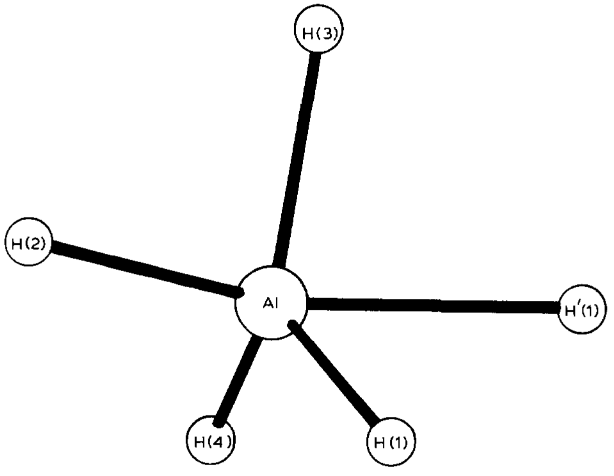

Fig. 3. Geometry of the hydride environment of the aluminium atom in the molecule of $[(C_5Me_5)_2TiH_2AlH_2]_2$.

alumohydride complexes show that it is necessary to discard the description of these compounds as alumohydrides with a tetrahedral environment of the aluminium atom (as was considered, for example, in ref. 18 for the complex labelled IV therein, the more so, since with such an interpretation of the structure of this compound, one of the metal atoms must possess an oxidation number of +2). As a matter of fact, all these compounds are derivatives of alane, $AlH_3 \cdot L \cdot L'$, in which one or both coordination positions are occupied by hydride ligands connected with an organometal moiety. The only questionable compound is, in fact, the complex of titanocene hydride and aluminium hydride, $CH_2(C_5H_4)_2TiH_2AlH_2$ [7]. However, this compound is undoubtedly the alane derivative with the aluminium coordination polyhedron as either a distorted tetrahedron or a distorted trigonal pyramid.

Evidently, this conclusion can be extended to the alumohydride complexes of other transition metals (cf. [26]). In fact, analysis of the IR spectrum for the complex $[Cp_2Zr(H)AlH_4]_x$ (IX) (Fig. 1), for which a polymeric structure with a bidentate or ionic AlH_4 group and bridging Zr–H–Zr bonds is assumed [19], shows that its appearance is quite atypical for complexes with two terminal hydrogen atoms. The occurrence of a narrow absorption band at 1794 cm^{-1} indicates the presence of a single terminal Al–H bond, whereas a broad band at 1610 cm^{-1} indicates the formation of an Al–H–Al bond (as in IV). Evidently, the absorption band at 1709 cm^{-1} ought to be assigned to $(Zr–H^{term})$ (1945 cm^{-1} for $Cp_2Zr(H)BH_4$ [20], and 1565 cm^{-1} for $[(C_5H_4Me)_2Zr(H)H]_2$ [21]). On the basis of these data, complex IX can be suggested to be a dimer with terminal Zr–H bonds and ZrH_2Al bridges, the monomeric moieties of which are linked via bridging $Al(\mu\text{-}H)_2Al$ linkages as in IV. This suggestion is confirmed, apart from the IR data, by the fact that complex IX (like IV) is not solvated by TMEDA (i.e. all the coordination positions at the aluminium atom are already occupied).

Although the hydride hydrogens in molecule V were not localized, reliable evidence on the nature of the nearest environment of the metal atoms in this compound can be obtained on the basis of the structural data for complex IV and other titanium alumohydride complexes. The molecular structure of V is built up of two mutually perpendicular wedge-like $(C_5Me_5)_2Ti$ sandwiches, connected with the aluminium atom (Fig. 4). The structures of the wedge-like sandwiches within V and IV are practically identical. However, closer contact between the C_5Me_5 rings results in essentially greater distortions of the latter, which is reflected by the greater root-mean-square errors of their geometric parameters. We also point out the somewhat larger value of the CpTiCp bond angle in V as compared with that in IV (144, 146 and 142°, respectively (Table 1)), which indicates greater electron density on the Ti atom in V. This is in agreement with the increase in the Ti...Al distance in V up to 2.81 Å (mean value). The value of this distance certainly shows that the titanium and aluminium atoms in V are bonded via the double hydrogen bridges since r(Ti–Al) for an ordinary TiHAl bridge is essentially larger (3.22 Å for complex III) [6].

In the structure of complex V the aluminium atoms occupy (statistically) two pseudo-equivalent (with respect to the Ti(1)–Ti(2) axis) positions with weights of 0.67 and 0.33 for the atoms Al and Al*, respectively. (It is this feature of structure V that precluded the determination of hydride hydrogens.) The absence of non-hydrogen atoms at the Al atom within a sphere of 2.5 Å radius indicates a purely hydride environment, as in complex IV. In this case, the coordination number of the

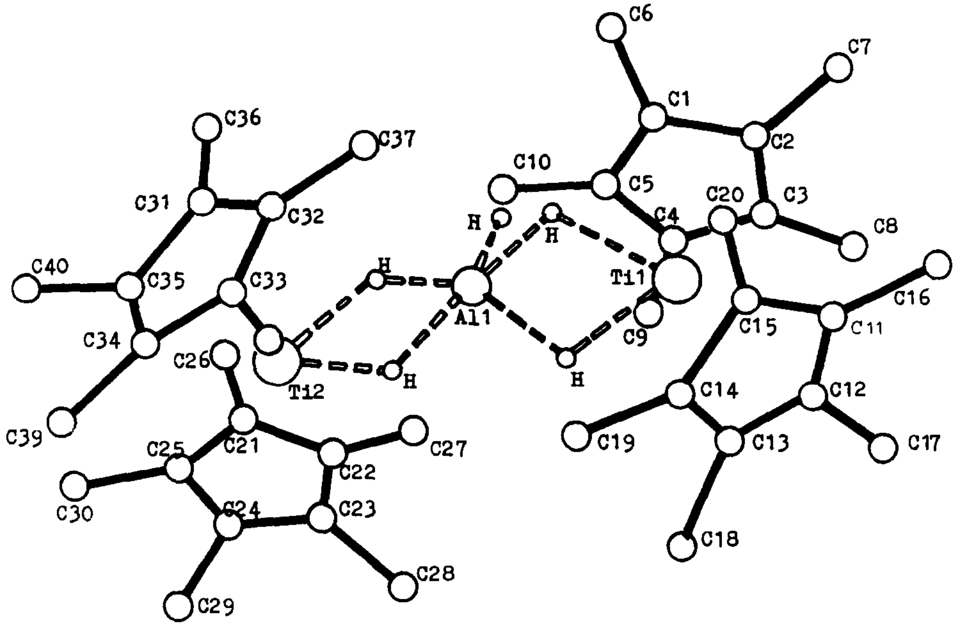

Fig. 4. Molecular structure of $[(C_5Me_5)_2Ti]_2AlH_5$ (dashed lines indicate feasible positions of the hydride hydrogen atoms).

aluminium atom can be 4, 5 or 6. The tetrahedral and octahedral environments require the TiAlTi angle to be 180 and 120°, respectively, whereas for the regular trigonal-bipyramid this angle must be equal to 138°. However, taking into account the features of structure IV, the $Al-H^{bridge}$ distances found in complexes II, III, IV and VI (Table 2), and the fact that the angle between the axial ligands within the distorted trigonal-bipyramids of these complexes differs from 180° but varies within the range 155–165° [5,6,13], one can arrive at a feasible value of the TiAlTi angle of 150–155° for the trigonal-bipyramidal environment of the Al atom in complex V. This value is in good agreement with the observed values 151 and 158° (Table 1). In contrast to molecule IV, in which the Al atom belongs to the plane passing through the Ti atom and the centres of the cyclopentadienyl rings (CpTiCp), both aluminium atoms, Al(1) and Al(2), in molecule V are somewhat off the corresponding planes (CpTi(1)Cp and CpTi(2)Cp), by 0.20 and 0.65 Å, and 0.25 and 0.38 Å, respectively. This appears to result from differences in the conformation of the hydride framework of the molecule. It can be suggested that for different positions of the Al atoms, the axial Al–H–Ti bond of the bipyramid will be localized at the different Ti atoms. In the case of the Al(2) atom, the distortions of the HTiH bond angles should have smaller values, but this fact seems to result in a greater distortion of the bipyramidal environment of the Al atom (the Ti...Al distances differ by 0.4 Å), and specifies a smaller statistical weight of the structure $[(C_5Me_5)_2Ti]_2Al(2)H_5$.

As can be seen from Fig. 4 and Table 1, the planes CpCpTi(1) and CpCpTi(2) are practically perpendicular with respect to one another and, thus, the bisecting planes of the wedge-like sandwiches, to which the TiH_2Al metallocycles should belong, are also perpendicular. Thus, it can be concluded that one of the axial ligands is the terminal hydrogen, and, as a consequence, the metallocycles Ti(1)H_2Al and Ti(2)H_2Al prove to be inequivalent.

Thus, the data considered indicate with great certainty that the Al atom in complex V is surrounded by five hydrogens, i.e. the composition of the complex is described by the formula $[(C_5Me_5)_2Ti]_2AlH_5$, with the oxidation number of the Ti atom being +3. Judging from the composition, the decomposition of $(C_5Me_5)_2TiH_2AlH_2$ can be described by eq. 5. Complex II seems to decompose

$$2(C_5Me_5)_2TiH_2AlH_2 \rightarrow \left[(C_5Me_5)_2Ti\right]_2AlH_5 + Al + 1\tfrac{1}{2}H_2 \qquad (5)$$

along the same pathway, with formation of the intermediate complex $[(C_5H_5)_2Ti]_2AlH_5$ [6]. However, if in the case of the permethyl derivative the decomposition reaction finishes at the stage of complex V, then in the case of the (η^5-C_5H_5) derivative the reaction proceeds further to give the polycyclic complex III. This is facilitated by both a greater readiness of $(\eta^5\text{-}C_5H_5)_2Ti^{III}$ for reduction, as compared with $(\eta^5\text{-}C_5Me_5)_2Ti^{III}$ [22], and a greater mobility of the protons of the cyclopentadienyl rings as compared with the protons of the methyl groups.

The complexes of type I between alane and titanocene hydride were shown [23,24] to be the effective catalysts for the reactions of olefin isomerization. The catalytic activity of these compounds decreases on replacement of terminal hydrogens by acceptor halogen atoms, on solvation of the Al atom with a strong Lewis base, and on rigid bonding of the cyclopentadienyl rings. On these grounds, the first stage of the process of homogeneous isomerization is assumed to be connected with the coordination of olefin at the Al atom, followed by formation of the alkyl complex and conversion at the Ti atom [24]. The results obtained in the study of the catalytic activity of $[(\eta^5\text{-}C_5Me_5)_2TiH_2AlH_2]_2$ in the isomerization of 1-hexene confirm, on the whole, the proposed mechanism: displacement of the electron density from the Ti atom to the Al atom (occurring on replacement of the protons of the Cp rings by donor methyl groups), a feasible dimeric character of the complex in solution (lack of the interaction with TMEDA), and steric overcrowding at the Ti atom result in the decrease of the isomerization rate down to 0.3 mol olef./g-atom Ti · min, as compared with 20 mol olef./g-atom Ti · min for $(\eta^5\text{-}C_5H_5)_2TiH_2AlH_2$ and 6 mol olef./g-atom Ti · min for $(\eta^5\text{-}C_5H_5)_2TiH_2Al(H)Cl$ [23,24]. The main factor leading to such a sharp drop in the catalytic activity of IV seems to be its dimeric character in the ether solution. The formation of the rather strong bridging AlH_2Al bond, which is unaffected even under the effect of TMEDA, is essentially similar to the formation of solvates of I with the strong Lewis bases, and, hence, should produce exactly the same effect. Two other factors affecting the catalytic activity of IV in the isomerization reaction should not, however, be underestimated. This can be seen, in particular, from the fact that the incorporation of only one methyl group into the Cp ring (to give the complex $(\eta^5\text{-}MeC_5H_4)_2TiH_2AlH_2$), while retaining a monomeric character of the compound in solution, produces a decrease in the isomerization rate to 14 mol olef./g-atom Ti · min.

Hydrogenation of olefins in the presence of titanium alumohydride complexes, as distinguished from the isomerization reaction, proceeds most likely at the titanium atoms, which form the polynuclear catalytic centres [25] (the maximal rate of the homogeneous hydrogenation of 1-hexene, 20 mol H_2/g-atom Ti · min, was observed in the $(\eta^5\text{-}C_5H_5)_2TiCl\text{-}LiAlH_4$ system with the reagents' ratio being 2/1 [25]). As a result of redistribution of the electron density at the Ti and Al atoms in the permethylated complex, the rate of the hydrogenation reaction of this compound is expected to be increased when the Ti/Al ratio is 2/1. In fact, the hydrogenation rate of $[(\eta^5\text{-}C_5Me_5)_2Ti]_2AlH_4Cl$ increases to 38 mol H_2/g-atom Ti · min, while that of the complex $[(\eta^5\text{-}MeC_5H_4)_2Ti]_2AlH_4Cl$ increases to 68 mol H_2/g-atom Ti · min. The data obtained demonstrate clearly the significance of structural and electronic factors in the catalysis on bimetallic hydride complexes of the Ziegler type, and show ways to increase the activity of these catalysts further in reactions of homogeneous hydrogenation and isomerization.

Experimental

Pentamethylcyclopentadiene, $(C_5Me_5)_2TiCl_2$ and $(C_5Me_5)_2TiCl$ were prepared according to refs. 27, 28 and 29, respectively.

$(C_5Me_5)_2TiBH_4$. A suspension of 0.47 g (1.2 mmol) of $(C_5Me_5)_2TiCl_2$ in 20 ml of Et_2O under argon was added to a solution of $LiBH_4$ (2.5 mmol) in 15 ml of Et_2O. The mixture was stirred for 48 h, during which the crystals of $(C_5Me_5)_2TiCl_2$ gradually vanished, while the solution turned violet. LiCl was filtered off, the solvent was removed in vacuo, and the residue was sublimated at 100°C under a vacuum of

TABLE 3

COORDINATES OF ATOMS IN THE MOLECULE OF $[(C_5Me_5)_2TiH_2AlH_2]_2$ ($\times 10^4$ for Ti, Al, C; $\times 10^3$ for H)

Atom	x	y	z
Ti	6928(1)	2885(1)	6077(1)
Al	5165(2)	3637(3)	5289(1)
C(1)	6336(6)	586(8)	6694(3)
C(2)	6868(6)	1775(8)	7120(3)
C(3)	6147(7)	2883(8)	7136(3)
C(4)	5124(6)	2352(8)	6745(3)
C(5)	5241(6)	950(8)	6469(3)
C(6)	9053(5)	2748(8)	6048(4)
C(7)	8973(5)	4255(10)	6227(3)
C(8)	8508(6)	4918(7)	5704(4)
C(9)	8281(5)	3832(8)	5213(3)
C(10)	5883(5)	2503(7)	5430(3)
C(11)	6731(8)	−890(9)	6577(4)
C(12)	7870(7)	1665(10)	7604(3)
C(13)	6309(7)	4242(10)	7568(4)
C(14)	4010(7)	3068(10)	4741(4)
C(15)	4307(7)	−112(8)	6071(4)
C(16)	9766(7)	1705(11)	6389(4)
C(17)	9474(8)	5115(12)	6821(4)
C(18)	8391(8)	6559(8)	5643(5)
C(19)	7990(7)	4121(10)	4510(3)
C(20)	8526(7)	1013(9)	5038(4)
H(1)	547(5)	450(6)	464(3)
H(2)	596(5)	229(6)	532(2)
H(3)	606(4)	441(5)	591(2)
H(4)	389(6)	269(7)	529(3)

10^{-2} Torr 0.26 g (65%) of the dark-blue crystals was obtained. Found: Ti, 13.9; H_{act}, 1.0. $C_{20}H_{30}TiBH_4$ calcd.: Ti, 14.4; H_{act}, 1.2%.

$(C_5Me_5)_2TiH_2AlH_2$. A solution of 0.38 g (1.1 mmol) of $(C_5Me_5)_2TiBH_4$ in 8 ml of Et_2O was added on stirring and cooling to −10°C to a solution of $LiAlH_4$ (1.2 mmol) in 1.5 ml of Et_2O. Green crystals precipitated from the solution, after

TABLE 4

COORDINATES OF ATOMS IN THE MOLECULE OF $[(C_5Me_5)_2Ti]_2AlH_5$ ($\times 10^4$)

Atom	*x*	*y*	*z*
Ti(1)	7035(2)	6554(1)	1994(3)
Ti(2)	3108(2)	8388(1)	3076(3)
Al(1)	4885(6)	7569(3)	1738(9)
Al(2)	5357(28)	7578(17)	3006(41)
C(1)	7199(12)	7230(6)	−122(14)
C(2)	8025(10)	6577(7)	−98(14)
C(3)	7405(13)	6014(7)	−417(15)
C(4)	6193(11)	6316(7)	−655(13)
C(5)	6045(10)	7066(7)	−484(12)
C(6)	7514(15)	7954(8)	34(18)
C(7)	9329(13)	6534(10)	0(19)
C(8)	7930(15)	5247(8)	−776(18)
C(9)	5139(14)	5922(9)	−1163(18)
C(10)	4902(14)	7596(9)	−667(20)
C(11)	8805(11)	5838(11)	3518(17)
C(12)	8023(17)	5466(10)	3391(20)
C(13)	7219(14)	5771(10)	4064(18)
C(14)	7406(14)	6418(8)	4703(15)
C(15)	8476(15)	6535(9)	4320(17)
C(16)	9946(21)	5541(21)	3097(26)
C(17)	8010(26)	4670(11)	2734(26)
C(18)	6105(21)	5468(12)	4380(23)
C(19)	6657(22)	6883(11)	5670(22)
C(20)	9012(36)	7144(20)	4847(31)
C(21)	1352(13)	8059(9)	1577(15)
C(22)	2174(14)	7421(8)	1948(24)
C(23)	2383(16)	7356(13)	3475(35)
C(24)	1790(21)	7912(16)	4097(22)
C(25)	1079(12)	8330(8)	2944(24)
C(26)	782(19)	8339(13)	−60(22)
C(27)	2514(21)	6896(13)	730(39)
C(28)	3171(19)	6704(15)	4491(48)
C(29)	1688(32)	7984(25)	5813(25)
C(30)	58(16)	8942(12)	3033(42)
C(31)	3323(18)	9516(7)	2292(16)
C(32)	4430(15)	9200(8)	3229(27)
C(33)	4220(14)	9141(7)	4722(19)
C(34)	3133(22)	9436(10)	4658(24)
C(35)	2570(14)	9659(7)	3183(26)
C(36)	3127(28)	9731(12)	683(22)
C(37)	5575(26)	8995(14)	2859(51)
C(38)	5056(27)	8916(11)	6257(32)
C(39)	2605(28)	9608(15)	6088(35)
C(40)	1316(22)	176(11)	2777(44)

standing for some time. The crystals were filtered, washed with ether, and dried in vacuo (yield 40%). Found: Ti, 13.03; Al, 7.4; H_{act}, 0.9. $C_{20}H_{30}TiAlH_4$ calcd.: Ti, 13.73; Al, 7.74; H_{act} 1.15%.

$(C_5Me_5)_2TiH_2Al(H)H_2Ti(C_5Me_5)_2$. The mother liquor obtained after isolation of the $(C_5Me_5)_2TiH_2AlH_2$ crystals was kept under argon for 3 weeks. During this time, the green solution turned violet, the flask's walls became covered with an aluminium mirror, and a small amount of violet crystals precipitated. The crystals were separated from the mother liquor and dried in vacuo.

Singe crystals of complexes IV and V, packed in glass capillaries, were run on a Syntex-P$\bar{1}$ diffractometer (Mo-K_α inrradiation, graphite monochromator, $\theta/2\theta$ scanning, $2\theta < 50°$).

The monoclinic unit cell parameters for the complex $[(C_5Me_5)_2TiH_2AlH_2]_2$ are as follows: a 11.196(4), b 8.915(3), c 20.777(7) Å, γ 101.74(3)°, V 2030 Å^3, space group $P2_1/n$, $Z = 4$, $\rho = 1.14$ g/cm^3. An extinction correction was neglected (μ 4.8 cm^{-1}). 1186 reflections with $I > 2\sigma(I)$ were used for the calculations. The structure was solved using the Patterson method (the hydrogen atoms were localized by a difference synthesis) and refined by the full-matrix least-squares method in the anisotropic (isotropic for hydrogen atoms) approximation to $R = 0.037$. The atomic coordinates for complex IV are listed in Table 3.

The triclinic unit cell parameters for the complex $[(C_5Me_5)_2Ti]_2AlH_5$ are as follows: a 11.881(4), b 18.951(8), c 8.868(3) Å, α 93.04 (3)°, β 104.33(3)°, γ 79.26(3)°, V 1894 Å^3, space group $P\bar{1}$, $Z = 2$, ρ 1.17 g/cm^3. An extinction correction was neglected (μ 4.9 cm^{-1}). 2773 reflections with $I > 2\sigma(I)$ were used for the calculations. The structure was solved by a combination of the direct and the heavy atom methods, and refined by the full-matrix least-squares method in the anisotropic (Ti and C atoms) and isotropic (Al atoms) approximations to $R = 0.088$. The atomic coordinates for complex V are listed in Table 4.

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