STRUCTURAL CHEMISTRY OF TITANIUM AND ALUMINIUM BIMETALLIC HYDRIDE COMPLEXES

III *. SYNTHESIS, MOLECULAR STRUCTURE AND CATALYTIC PROPERTIES OF $[(\eta^5\text{-}C_5H_5)_2Ti(\mu_2\text{-}H)_2Al(\mu_2\text{-}H)(\eta^1:\eta^5\text{-}C_5H_4)Ti(\eta^5\text{-}C_5H_5)(\mu_2\text{-}H)]_2 \cdot C_6H_5CH_3$

EMIL B. LOBKOVSKII, GRIGORII L. SOLOVEICHIK,

Institute of New Chemical Problems, Academy of Sciences of the U.S.S.R., Chernogolovka 142432 (U.S.S.R.)

ALEKSANDR I. SIZOV and BORIS M. BULYCHEV *,

M.V. Lomonosov Moscow State University, Chemical Faculty, Moscow 117234 (U.S.S.R.)

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Summary

By decomposition of the complex $[(\eta^5\text{-}C_5H_5)_2TiH_2AlH_2]_2 \cdot$ TMEDA in toluene, the complex $[(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}H)_2Al(\mu\text{-}H)(\eta^1:\eta^5\text{-}C_5H_4)Ti(\eta^5\text{-}C_5H_5)(\mu\text{-}H)]_2 \cdot C_6H_5CH_3$ was obtained. It crystallized in a monoclinic lattice with the unit cell parameters a 11.753(5); b 15.701(7); c 23.95(1) Å, β 99.24(4)°, space group $P2_1/c$, V 4363 Å^3, $Z = 4$, ρ_{calcd} 1.32 g/cm^3. The compound proved to be polycyclic. Two four-membered $\mathrm{Ti}\underset{H}{\overset{H}{\diamond}}\mathrm{Al}$, two six-membered $\overline{\mathrm{Ti}(\mu\text{-}C_3H_4)Al(\mu\text{-}H)Ti(\mu\text{-}H)}$ and one eight-membered $\overline{\mathrm{Ti}(\mu\text{-}H)Ti(\mu\text{-}H)Al(\mu\text{-}H)Al(\mu\text{-}H)}$ cycles can be distinguished in its structure. All hydride hydrogens are the bridging atoms. The titanium atom framework represents two almost regular isosceles triangles, while taking into account the aluminium atoms produces a gull-like figure with the "gull wings" being linked with the bridging hydrogen atom. Feasible pathways for the formation of this compound are discussed. The complex was shown not to promote the hydrogenation reaction of 1-hexene in a hydrocarbon medium, whereas in THF medium the hydrogenation rate amounted to 8 mol H$_2$/g-atom Ti · min after a certain induction period.
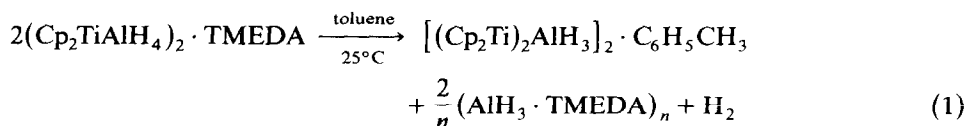
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* For part II see ref. 17.

Introduction

The well-known catalytic system Cp_2TiCl_2/Cp_2TiCl-$LiAlH_4$ ($Cp = \eta^5$-C_5H_5) displays a higher activity in the hydrogenation [1,2], isomerization [3–5] and hydrometallation [4,6] reactions of olefins. In this connection, it is of particular practical and theoretical interest to study the nature and type of the interaction between Cp_2TiCl_{2-n} and $LiAlH_4$ thoroughly, to isolate the individual compounds from the system, to establish their structure, and, finally, to study the catalytic properties of the compounds obtained in the reactions involving hydrogen transfer.

The main products of the reactions between $LiAlH_4$ and Cp_2TiCl_{2-n} were shown [2,4,7–10] to be heterometallic hydride complexes of the composition Cp_2TiH_2-$AlH_2 \cdot L$ (where L is a Lewis base). In solution these compounds are unstable and decompose with evolution of part of the hydrogen, with the latter process proceeding the faster, the less the basicity of L. Only in the case of L = $(CH_3)_2NCH_2CH_2N(CH_2)_3$ (TMEDA) were sufficiently stable solvates of composition $(Cp_2'TiH_2AlH_2)_2 \cdot TMEDA$ (where $Cp_2' = (C_5H_5)_2$, $(C_5H_4CH_3)_2$, $(C_5H_4)_2C_2H_4$, or $(C_5H_4)_2C_3H_6$) isolated in a crystalline state [11]. Unfortunately, increasing the stability of the titanium alumohydride complexes via incorporation of a strong base into the coordination sphere results in the deterioration of their catalytic properties. In fact, the decomposition products of $Cp_2'TiH_2AlH_2$, obtained in the medium of the weakest base, diethyl ether, were shown [12] to be the most active species in olefin hydrogenation reactions. That is why the decomposition products of the titanium alumohydride complexes prove to be of great interest as the objects of investigation in catalytic hydrogenating systems.

The present paper reports the results of the structural and physico-chemical investigation of one of the complexes formed on decomposition of $(Cp_2TiH_2$-$AlH_2)_2 \cdot TMEDA$ in solution.

Results and discussion

Prolonged storage of the toluene solutions of $(Cp_2TiH_2AlH_2)_2 \cdot TMEDA$ (I) complexes results in the precipitation of black crystals with the overall composition $(C_5H_5)_4Ti_2AlH_3 \cdot 0.5C_6H_5CH_3$ (II). Since the precipitate lacks the metallic aluminium phase, the formation of the latter compound can be described by eq. 1. The ratio between the number of hydride (active) hydrogens entering the hydrolysis reaction and the number of metallic atoms in II is $Ti/Al/H_{act} = 2/1/4$, thus indicating that its synthesis is accompanied with rearrangements involving the cyclopentadienyl rings. The formation of II according to eq. 1 appears to be typical of aluminium and

$$2(Cp_2TiAlH_4)_2 \cdot TMEDA \xrightarrow[25^\circ C]{toluene} \left[(Cp_2Ti)_2AlH_3 \right]_2 \cdot C_6H_5CH_3$$
$$+ \frac{2}{n}(AlH_3 \cdot TMEDA)_n + H_2 \qquad (1)$$

titanocene hydride complexes with Lewis bases, since a similar compound was also obtained upon decomposition of $Cp_2TiH_2AlH_2$ in toluene in the presence of equimolar amounts of dioxane, although the process of formation and crystallization of II took more than 2 months in this case.

The IR spectrum of the compound obtained is presented in Fig. 1. All attempts to

obtain the deutero-substituted derivative of II by decomposing $[Cp_2TiD_2AlD_2]_2 \cdot$ TMEDA in $C_6H_5CH_3$ failed. In this case, reaction 1 proceeds at essentially lower rates and results in the crystallization of a compound whose IR spectrum and diffractogram are identical to those of II. Since the IR spectrum of the latter compound lacks absorption bands in the region of 2250–2300 cm^{-1}, which are typical of $\nu(C-D)$ in the Cp rings [13], deutero-hydrogen exchange of the hydride deuterons with the solvent's protons may be concluded to take place in this case. In other words, the titanium alumohydride complexes formed upon decomposition of I (most likely, the intermediate complexes) are capable of activating the C–H bonds in toluene (the decomposition of $[Cp_2TiD_2AlD_2]_2 \cdot$ TMEDA in $C_6D_5CD_3$ seems to proceed at extremely low rates if at all).

The IR spectrum of II is quite complicated and resembles, on the one hand, the spectrum of the $Cp_2TiH_2Al(H)Cl \cdot 0.5$ Et$_2$O complex [14], whose structure is supposed to involve two types of bridging linkages, AlH$_2$Ti and AlHTi, while, on the other hand, it resembles the spectra of the complexes $Cp_2TiH_2AlCl(H) \cdot 0.5Et_2O$ [14] and $[Cp_2Ti]_2AlH_4Cl \cdot 0.5Et_2O$ [4], which lack the absorption bands typical of the $\nu(Al-H)$ term. Among the most important features of the spectrum of II, one can distinguish the broad absorption band in the region 1600–1900 cm^{-1} with maxima at 1600 and 1720 cm^{-1}, which are characteristic of the Al–H bridging bond vibrations [15], and an intensive absorption band at 950 cm^{-1}, the frequency of which is considerably greater as compared with that generally observed for the deformation vibrations involving the hydride hydrogens (600–800 cm^{-1}) [11,14]. Thus, the data of the spectroscopic investigation show that the structure of II lacks
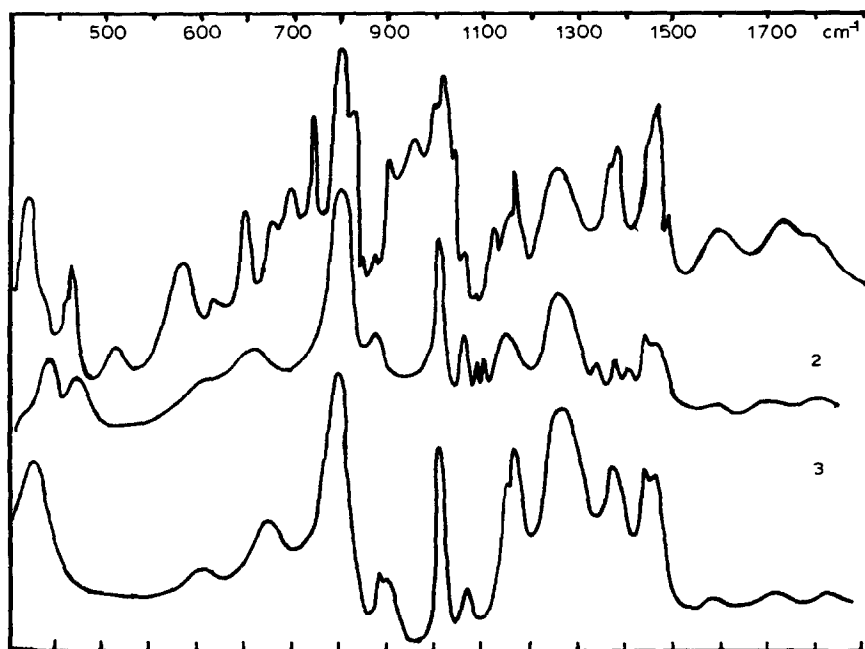
Fig. 1. IR spectra of $[CpTi(H)_2Al(H)(\eta^1 : \eta^5\text{-}C_5H_4)TiCp(H)]_2 \cdot C_6H_5CH_3$ (1), $Cp_2TiH_2AlCl(H) \cdot 0.5Et_2O$ [14] (2), and $[Cp_2Ti]_2AlH_4Cl \cdot 0.5Et_2O$ [4] (3).
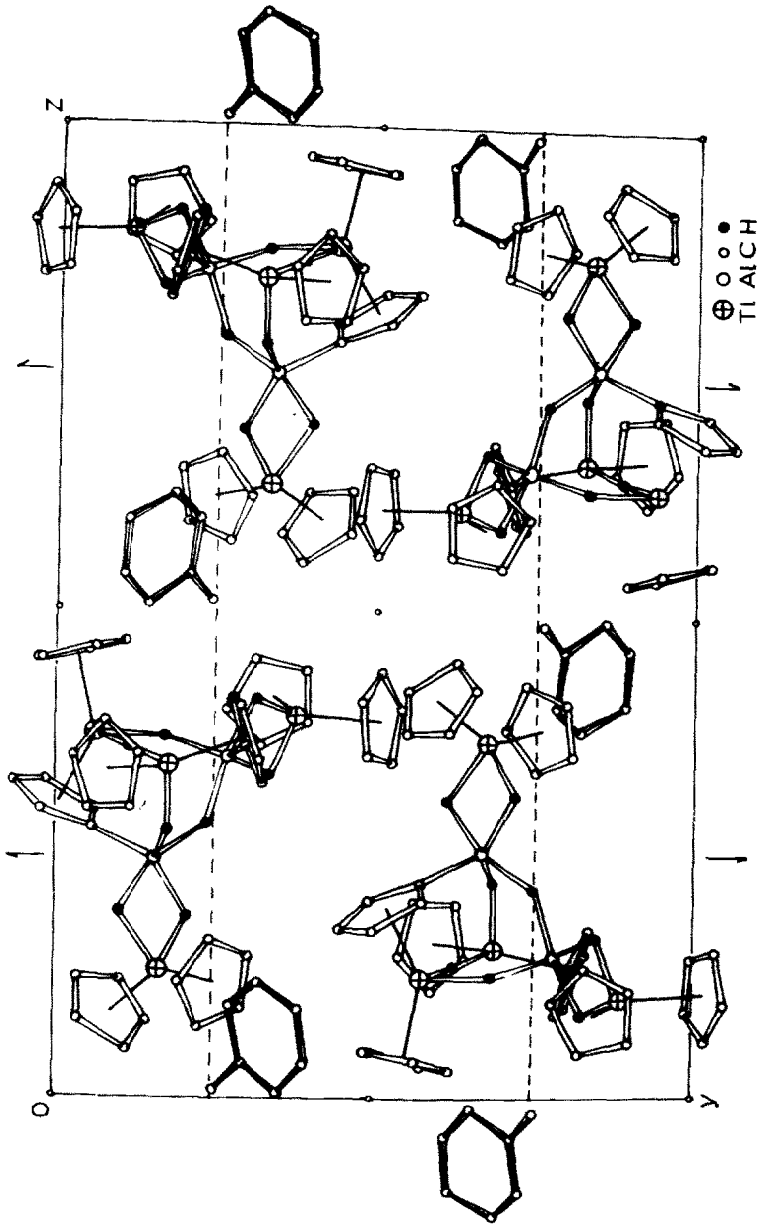
Fig. 2. Crystal packing of the $[Cp_2Ti(H)_2Al(H)(\eta^1 : \eta^5\text{-}C_5H_4)TiCp(H)]_2C_6H_5CH_3$ molecules.

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Ti Al C H

the terminal Al–H bonds, while the linkage between the metal heteroatoms is accomplished via the bridging hydrogen atoms. This conclusion was substantiated by the direct X-ray investigation of II.

The crystal structure of $(C_5H_5)_4Ti_2AlH_3 \cdot 0.5C_6H_5CH_3$ represents a joint packing of the six-nuclear molecules of $[(\eta^5\text{-}C_5H_5)_2Ti(\mu_2\text{-}H)_2Al(\mu_2\text{-}H)(\eta^1 : \eta^5\text{-}C_5H_4)Ti(\eta^5\text{-}C_5H_5)(\mu_2\text{-}H)]_2$ and of molecules of crystallization toluene (Fig. 2). All the intermolecular distances are not less than the Van der Waals contacts.

Because of the complexity of the architectonics molecule II, we provide two different projections of the molecule, along the Ti(2)–Ti(3) direction (Fig. 3), and along the direction perpendicular to the former (Fig. 4). Four wedge-like sandwiches, two of composition $(C_5H_5)(\eta^1 : \eta^5\text{-}C_5H_4)TiH_2$ and two of composition $(\eta^5\text{-}C_5H_5)_2TiH_2$, interconnected with a complex system of bridging linkages, form the basic framework of the structure of II. The cyclopentadienyl groups within both types of wedge-like sandwiches are planar. The deviation of the carbon atoms within the Cp rings from the mean-squared planes does not surpass 0.02 Å. The wedge-like sandwiches possess the usual staggered conformation with the dihedral angles between the Cp planes being 41.7, 41.3, 43.2 and 41.5° at the Ti(1), Ti(2), Ti(3) and Ti(4) atoms, respectively. Within similar wedge-like sandwiches, the former angle is equal to 40.5° in the case of complex I [16], and to 42.8, 43.1° in the case of $Cp_2TiH_2AlCl_2 \cdot OEt_2$ (III) [17]. The Ti–C bond lengths vary between 2.22 and 2.40 Å (the average bond length being 2.34 Å) and are common for the titanium $\eta^5\text{-}C_5H_5$ complexes (2.33 Å for III [17], 2.35 Å for $Cp_2TiH_2BH_2$ [18], and 2.36 Å for I [16]). In this case, the distance from the titanium atoms and the corresponding planes of the Cp rings falls within the region of 2.01–2.04 Å.

The framework of titanium atoms within molecule II forms two almost regular isosceles triangles, Ti(1)Ti(2)Ti(3) and Ti(4)Ti(2)Ti(3), with a common base Ti(2)Ti(3) and a dihedral angle of ~ 90° (a "metallobutterfly" configuration). With the aluminium atoms taken into consideration, the metallic framework forms a gull-like figure (Fig. 5). In this case, the dihedral angle between the Ti(2)Al(1)Ti(3) and Ti(2)Al(2)Ti(3) planes amounts to 78°, while that between the Al(1)Ti(4) and Al(2)Ti(1) directions is ~ 110°.

For convenience, we divide molecule II into the following parts: the central part (Ti(2)...Ti(3)), the "chelatic" part (Ti(2)$\overset{\text{Al}}{\cdots\cdots}$Ti(3)), and the peripheral one (Ti(1)...Al(2) and Ti(4)...Al(1)).

The central part of the molecule may be regarded as the two moieties of titanium dicyclopentadienyl hydride, $(\eta^5\text{-}C_5H_5)(\eta^1 : \eta^5\text{-}C_5H_4)TiH$, bonded through an ordinary hydrogen bridge, Ti–H–Ti, in which H(5) is arranged in the intersection of the bisecting planes of the wedge-like sandwiches at the Ti(2) and Ti(3) atoms. The Ti–H bond length within the Ti–H–Ti moiety (1.8 Å) resembles that for the similar bridge observed in $(C_{10}H_8)[CpTi(\mu_2\text{-}H)(H_2AlEt_2)TiCp](IV)$ [19], the Ti(2)H(5)Ti(3) bond angle (171°) and the corresponding Ti(2)...Ti(3) distance (3.72 Å) in II, however, being essentially greater than those in IV, which involves a bridging fulvalene ligand, $\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4$ (138° and 3.37 Å, respectively [19]).

The structure of the "metallochelates" TiC_5H_4AlHTi is conventionally similar to that of the same cycles in the complexes $(C_{10}H_8)[(C_5H_4)TiHAlEt_2]_2$ (V) [19] and $[CpTi(C_5H_4)HAlEt_2]_2$ (VI) [20]. Thus, the Ti–H and Al–H bond distances within the bridge in II and in complexes V and VI are very similar to each other and fall

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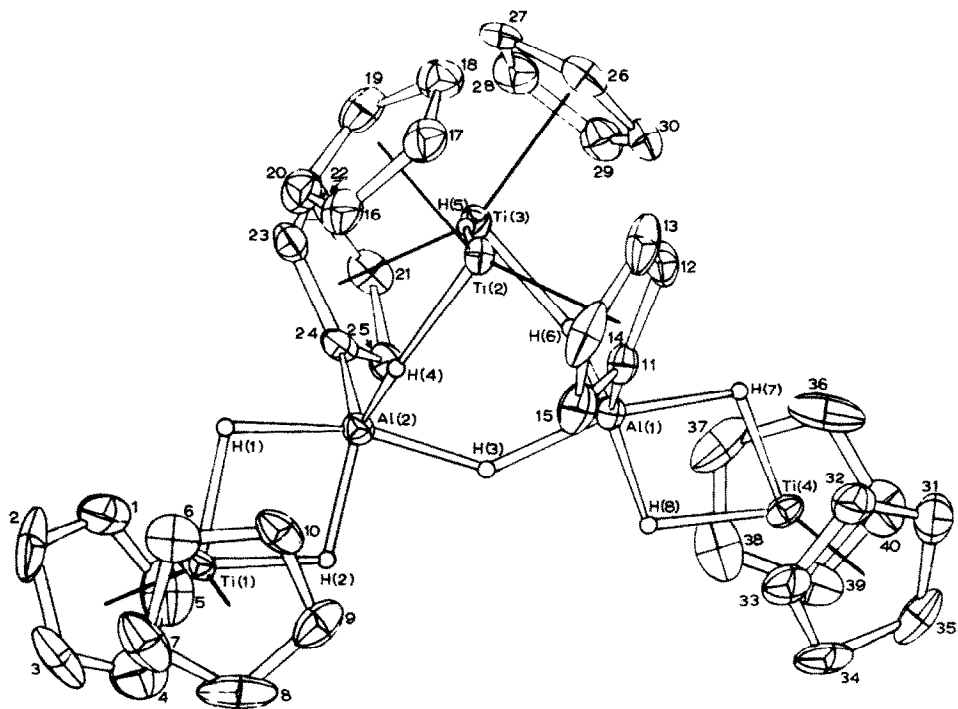
Fig. 3. Molecular structure of $[Cp_2Ti(H)_2Al(H)(\eta^1 : \eta^5\text{-}C_5H_4)TiCp(H)]_2$ (projection along the Ti(2)–Ti(3) direction).
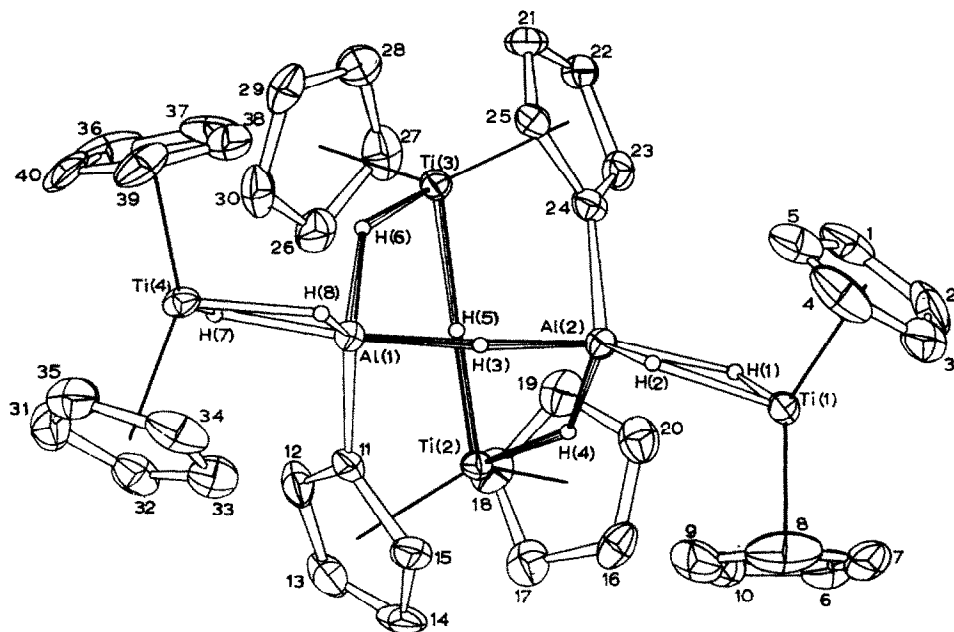
Fig. 4. Molecular structure of $[Cp_2Ti(H)_2Al(H)(\eta^1 : \eta^5\text{-}C_5H_4)TiCp(H)]_2$ (projection along the direction perpendicular to the Ti(2)–Ti(3) one).

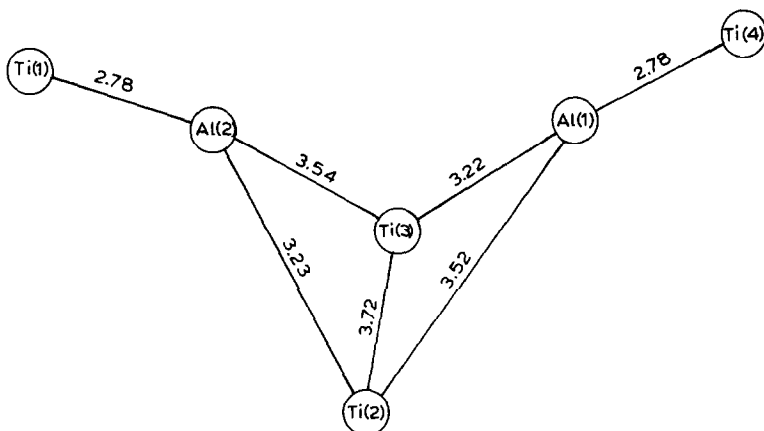Fig. 5. Framework of the metal atoms in the molecule $[Cp_2Ti(H)_2Al(H)(\eta^1 : \eta^5-C_5H_4)TiCp(H)]_2$.

within the 1.7–1.8 and 1.6–1.7 Å limits, respectively [19,20]. The principal distinction between "metallochelates" within the "metallogull" and complexes V and VI is the occurrence of the Ti–H–Al bridge within II. In other words, the second coordination position at the Ti(2) and Ti(3) atoms is occupied by hydrogen atoms (coordination number (c.n.) of Ti = 8, assuming the Cp groups as tridentate ligands), while the c.n. of the titanium atoms in complexes V and VI increases up to 8 due to the formation of the Ti–C_{ring} bond (r(Ti–$C^{\star}$) 2.24 Å for V [19], and 2.25 Å for VI [20]). Similar coordination character is also observed in the complexes $[CpMo(C_5H_4)H]_2Al_3Me_5$ and $[(C_5H_4)_2MoAl_2Me_3]_2$ [21], and in "ferrocenyl-alanes", e.g. $CpFe(C_5H_4)Al_2Me_4Cl$ [22]. Since in the "metallogull" the C_5H_4 groups are σ-bonded to only one metal atom, the Al–C bond length (1.95 Å) is notably shorter than that in structures with the C_5H_4 group σ-bonded to two metal atoms (2.06–2.35 Å) [19,20]. In addition, the aluminium atoms in II, in contrast to those in V and VI, are just slightly off the plane formed by the C_5H_4 groups bonded to the former (the angle beteween the C_5H_4 plane and the Al–C direction amounts to 7°), and the bond angles Ti(2)H(4)Al(2) (144°) and Ti(3)H(6)Al(1) (136°) and the distances Ti(2)...Al(2) and Ti(3)...Al(1) (3.22 Å) in II are essentially greater than similar parameters in complexes V (102° and 2.82 Å) and VI (2.79 Å) [19,20] due to the lack of Ti(2)–C(24) and Ti(3)–C(11) bondings. Therefore, the linear dimensions of "metallochelates" in V and VI are appreciably less, which is apparently the reason for the shortening of the Ti...Ti distance down to 2.91 Å in V [19] and 3.11 Å in VI [20], as compared with II (3.72 Å).

Both aluminium atoms in the "metallogull" are linked with the peripheral Ti(1) and Ti(4) atoms via the double hydrogen bridges. The geometrical parameters of these metallocycles, namely the HTiH angle (71–75°), the distances Al–H (1.7–1.8 Å) and Ti...Al (2.78 Å), are practically coincident for complexes I and II. The TiHAl angle within the TiH_2Al moiety (105°) is obviously less than that within the TiHAl moiety. Some difference in the Ti–H bond lengths for complexes II and I (1.8 and 1.6 Å, respectively) is apparently stipulated by the different ligand environment of the aluminium atom in these compounds and, in particular, by the presence of such a strong electron donor as TMEDA in I. At the same time, the occurrence of

electron-accepting substituents at the aluminium atom in complex III results in elongation of the Ti–H bond length (1.8–1.9 Å) and contraction of the Ti...Al distance (2.75 Å) [17].

A distorted trigonal bipyramid, [H$_4$C], proves to be the coordination polyhedron for the aluminium atoms within the "metallogull", as in complexes I and III, as well as in "alumohydrides" of biscyclopentadienylyttrium (Cp$_2$YH)$_2$(AlH$_3$ · L)$_n$, with L = NEt$_3$ [23], THF [24]. The axial positions in the former are occupied by bridging hydrogen atoms. The average bond length for Al–H is 1.70(8) Å. The differences in the Al–H bond lengths, relevant to the different types of hydrogen bridges, failed to be detected on account of a large standard error.
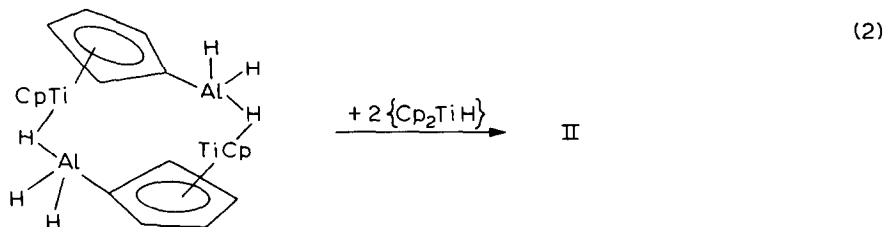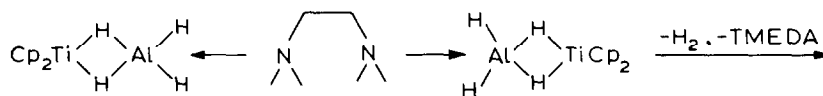
The angle between the axial bonds in the bipyramids (160, 162°) is close to that for alumohydride complexes involving a trigonal-bipyramidal environment of the aluminium atom [H$_4$L]-II (155°) [17] and (Cp$_2$YH)$_2$(AlH$_3$ · THF)$_2$ (164°) [24]. The axial ligand common to both bipyramids, i.e. the H(3) atom, is a member of the Al–H–Al bridge, which ensures a folded conformation of the "gull wings". It is worth noting that the geometrical parameters of the Al–H–Al bridge (i.e. the Al–H–Al angle and the Al...Al distance) for molecule II and hexagonal modification of (AlH$_3$)$_n$ [25], involving a six-coordinated aluminium atom, are essentially close to each other (138 and 141°, 3.22 and 3.23 Å, respectively).

The number of hydride hydrogen atoms observed upon X-ray study of II indicates that the formal oxidation number for all the titanium atoms is +3, which is in agreement with the type of coordination environment of these atoms and the occurrence of the corresponding signal in the EPR spectrum (solvent: toluene, THF; doublet with g = 1.991 and g = 1.978).

The results obtained prove that molecule II is polycyclic. Two four-membered TiH$_2$Al, two six-membered Ti-(μ-C$_5$H$_4$)μ-HTi-μ-H and one eight-membered Ti(2)H(5)Ti(3)H(6)Al(1)H(3)Al(2)H(4) cycles can be distinguished in its structure. The eight-membered cycle has a saddle conformation. Conformational calculations prove a saddle conformation for eight-membered cycles to be unstable because of a rather strong repulsion of non-bonded atoms [26]. In the present case, however, the saddle conformation is stabilized owing to tightening by the six-membered cycles.

It is the polycyclic character, together with the formation of strong Al–C$_5$H$_4$ σ-bonds, that can be suggested to provide the greater thermodynamic stability of complex II as compared with Cp$_2$TiH$_2$AlH$_2$, even in the case when the latter is solvated with such strong bases as TMEDA and dioxane. It should also be noted that the conversion I → II, which is accompanied with desolvation involving Al ← N and Al ← O bond breaking while at the same time preserving the Al–H bonds, has no similarities in alane chemistry [15].

On the basis of stoichiometry and structural evidence for complexes I [16] and II, one can suggest certain pathways for the conversion of I into II. Conventionally, the "metallogull" can be considered as an adduct of the hydride analogue of the Tebbe complex VI [20] [CpTi(C$_5$H$_4$)HAlH$_2$]$_2$, formed, for example, when eliminating H$_2$ and splitting off TMEDA (dioxane) (eq. 2), followed by addition of hydride of titanium dicyclopentadienyl (III). However, as can be seen, this scheme assumes both Al ← N (Al ← O) bond breaking and additional generation of titanocene hydride Cp$_2$TiH, e.g. via splitting off of an extremely strong bridge Ti $\diagdown$ $\diagup$ Al (eq. 3).

$$Cp_2Ti\begin{smallmatrix}H\\ \diagdown\diagup\end{smallmatrix}Al\begin{smallmatrix}H\\ \diagup\\ \diagup\end{smallmatrix} \longleftarrow \quad N\diagup\diagdown \quad N\diagup\diagdown \longrightarrow \begin{smallmatrix}H\\ \diagdown\end{smallmatrix}Al\begin{smallmatrix}H\\ \diagup\\ \diagdown\end{smallmatrix}TiCp_2 \xrightarrow{-H_2,\,-TMEDA}$$

(2)

$$\xrightarrow{\;+\,2\{Cp_2TiH\}\;} \quad \text{II}$$

Since reaction 3 failed to be observed even under the action of excess amounts of TMEDA on $Cp_2TiH_2AlH_2$ [11], eq. 2 seems to be hardly possible. From our viewpoint, an alternative scheme whereby the splitting off of the aluminium hydride adduct with TMEDA results in complex VII with a Ti/Al ratio = 2/1 (eq. 4) seems to be more reasonable for the formation of II.

$$[Cp_2TiH_2AlH_2]_2\cdot TMEDA \xrightarrow{TMEDA} 2\{Cp_2TiH\} + \tfrac{2}{n}\,(AlH_3\cdot TMEDA)_n \quad (3)$$

$$\text{I} \longrightarrow Cp_2Ti\begin{smallmatrix}H\\ \diagdown\diagup\end{smallmatrix}Al\begin{smallmatrix}H\\ \diagup\\ \diagdown\end{smallmatrix}TiCp_2 + \tfrac{1}{n}\left[\rightarrow AlH_3\leftarrow N\diagup\diagdown \quad N\diagup\diagdown \rightarrow\right]_n \quad (4)$$

(VII)
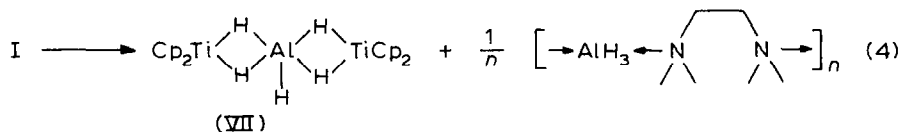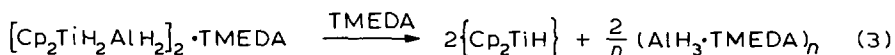
The formation of the analogous compound was exemplified by us with the decomposition of the complex $(C_5Me_5)_2TiH_2AlH_2$ [27]. The subsequent formation of the Al–C σ-bond can proceed along two pathways: via the recombination of the basic hydrogen atom of the Cp-ring (pathway A), or via the reduction of Ti^{III} by hydride hydrogen, followed by oxidative addition of the C–H bond of the Cp group to the latter (pathway B). In both cases Al–H bond breaking should play the determining role; this suggestion conforms to a noticeable deviation in the reaction kinetics for the decomposition of aluminium and titanocene hydride complexes for the different hydrogen isotopes. Pathway A is apparently realized in the synthesis of the Tebbe complexes IV and VI [19,20]. However, the intramolecular elimination
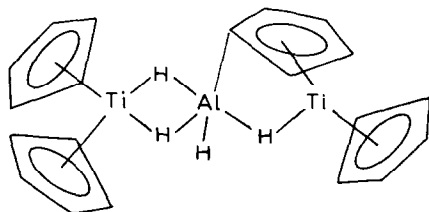
reaction in complex VII must produce a monomeric, sterically strained structure for which dimerization into the "metallogull" appears to be questionable. On the other hand, the intramolecular reduction of titanium in VII must produce the coordinatively unsaturated complex VIII capable of dimerizing (into VIIIa) due to the

formation of bridging Al–H–Al bonds (eq. 5). The atom of titanium(II) in VIII

(5)
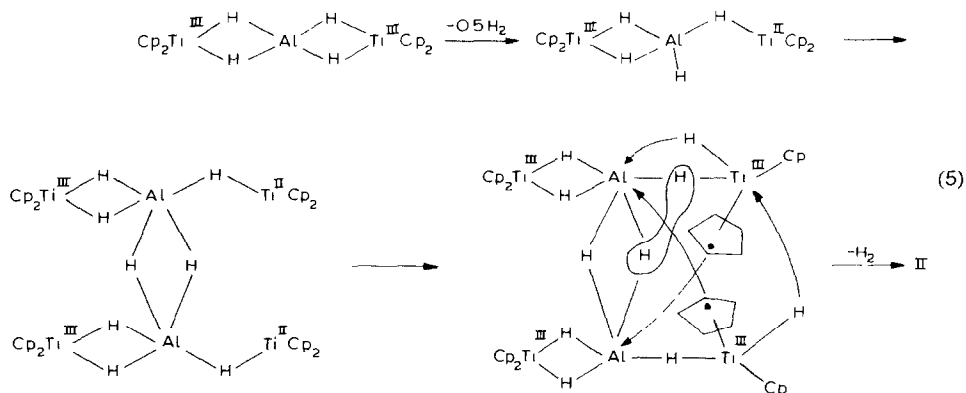
involves a vacant orbital providing the opportunity for oxidative addition of the C–H bond. Activation of the aromatic C–H bonds was also observed for other metallocenes involving a metal atom with a vacant orbital, e.g. for Cp_2Ti [28], Cp_2V [29] and Cp_2Re^+ [30]. The competition between toluene and C_5H_5 groups for a space at the titanium(II) atom appears to be the reason for the deutero–hydrogen exchange of hydride protons with a solvent on decomposition of the complex $[Cp_2TiD_2AlD_2]_2 \cdot$ TMEDA. Oxidative addition of the C–H bond should result in the formation of the Ti^{III}–H bond and the $[C_5H_4^-]$ anion-radical, the latter replacing the hydrogen atom nucleophilically at the aluminium atom to produce the Al–C σ-bond. Thus, pathway B explains the features of the conversion I → II adequately, in particular, the dimeric character of molecule II, the occurrence of deutero-exchange with a solvent, the presence of the Ti–H–Ti bridge and $\overline{TiC_5H_4AlHTiH}$ cycles, and, hence, appears to be the more feasible pathway, taking into account the polarographic results for Cp'_2TiCl_2 substituted at a ring [31] and the data on the synthesis and stability of substituted $Cp'_2TiH_2AlH_2$ [11]. The reduction of the Ti atoms in the peripheral metallocycles of molecule II may prove to be hampered due to the origination of a stable polycyclic structure or because of steric hindrance.

As expected, the high stability of complex II results in the suppression of catalytic activity of this compound in the olefin hydrogenation reaction in toluene medium, whereas lack of terminal Al–H bonds causes disappearance of an activity in the isomerization reactions. The latter fact is obviously related both to the difficulty in breaking the bridging hydrogen bonds in II and to the low solubility of the compound in non-polar solvents. In fact, solutions of II in the strong donor solvent THF display (after a 30 min induction period) fairly high catalytic activity in the hydrogenation of 1-hexene, comparable to that of the complex $(Cp_2Ti)_2AlH_4Cl$ (the reaction rates are 8 and 20 [2] mol H_2/g-atom Ti · min, respectively). THF can be supposed to affect the Ti–H–Al and/or Ti–H–Ti bridge breaking with the induction period being stipulated either by this reaction or by the competition between the THF and olefin molecules for the coordination position at the titanium atom. One of the possible products of cleavage of the polycyclic structure II by THF may prove to be the complex $[CpTiH(L)(\eta^1 : \eta^5-C_5H_4)Al(\mu-H)(\mu-H)_2TiCp_2]_2$.

In conclusion, it should be noted that since complex II is the product of the far-reaching conversion of $Cp_2TiH_2AlH_2 \cdot$ L, the nature of the reactions proceeding

TABLE 1

ATOMIC COORDINATES ($\times 10^4$ for Ti, Al, C; $\times 10^3$ for H) AND THERMAL FACTORS FOR ATOMS IN COMPLEX II

Atom	x	y	z	B_{ISO}^{eq}	Atom	x	y	z	B_{ISO}^{eq}
Ti(1)	4105(1)	1681(1)	6253(1)	3.5	H(1)	447(6)	106(5)	688(3)	4
Ti(2)	5579(1)	1801(1)	8486(1)	3.3	H(2)	321(5)	212(4)	673(3)	2
Ti(3)	2829(1)	684(1)	8582(1)	3.0	H(3)	300(5)	240(4)	767(3)	4
Ti(4)	1210(1)	3883(1)	8608(1)	3.5	H(4)	484(8)	180(7)	775(4)	1
Al(1)	2806(1)	2701(1)	8345(1)	3.2	H(5)	433(4)	121(3)	857(2)	3
Al(2)	3677(1)	1601(1)	7360(1)	3.2	H(6)	229(6)	176(5)	852(3)	0
C(1)	2997(11)	451(6)	6084(3)	6.7	H(7)	223(5)	314(4)	890(2)	1
C(2)	3754(9)	464(8)	5708(7)	10.0	H(8)	173(4)	333(3)	805(2)	2
C(3)	3324(15)	1205(12)	5369(3)	11.8	H(9)	304	5	634	7
C(4)	2448(15)	1509(7)	5593(7)	10.7	H(10)	425	44	545	7
C(5)	2293(9)	1103(10	6010(6)	9.8	H(11)	346	141	510	7
C(6)	6072(6)	1985(5)	6277(4)	6.7	H(12)	216	196	548	7
C(7)	5455(10)	2294(8)	5764(4)	8.4	H(13)	170	111	626	7
C(8)	4730(9)	2935(8)	5904(6)	10.1	H(14)	684	157	625	7
C(9)	4943(7)	3035(5)	6469(5)	7.4	H(15)	585	220	541	7
C(10)	5734(7)	2454(5)	6693(3)	5.8	H(16)	440	318	566	7
C(11)	4423(5)	2970(3)	8595(2)	3.7	H(17)	443	350	670	7
C(12)	5075(6)	2774(4)	9133(3)	5.3	H(18)	595	241	701	7
C(13)	6229(6)	2897(5)	9143(4)	7.0	H(19)	480	251	936	7
C(14)	6365(5)	3186(5)	8590(5)	7.4	H(20)	700	300	923	7
C(15)	5248(6)	3255(4)	8264(3)	5.5	H(21)	702	335	846	7
C(16)	7183(6)	1221(5)	8163(3)	5.7	H(22)	517	340	791	7
C(17)	7498(5)	1355(5)	8746(3)	5.5	H(23)	770	160	800	7
C(18)	6834(6)	841(5)	9027(3)	5.7	H(24)	801	171	886	7
C(19)	6110(6)	350(4)	8615(4)	6.0	H(25)	697	67	940	7
C(20)	6322(6)	582(5)	8084(3)	6.0	H(26)	561	5	871	7
C(21)	1378(6)	−64(4)	7982(2)	5.0	H(27)	603	48	759	7
C(22)	2348(6)	−578(4)	8050(2)	4.8	H(28)	72	−23	808	7
C(23)	3197(5)	−142(4)	7819(2)	4.5	H(29)	240	−105	825	7
C(24)	2776(5)	666(4)	7601(2)	3.7	H(30)	391	−34	783	7
C(25)	1612(5)	685(4)	7703(2)	5.6	H(31)	113	110	762	7
C(26)	3785(6)	703(5)	9544(2)	5.9	H(32)	439	89	963	7
C(27)	3506(8)	−135(5)	9387(3)	5.9	H(33)	399	−55	935	7
C(28)	2306(8)	−188(5)	9289(3)	6.3	H(34)	196	−66	921	7
C(29)	1844(7)	599(6)	9349(3)	6.3	H(35)	115	79	932	7
C(30)	2767(8)	1149(5)	9518(3)	5.9	H(36)	273	166	962	7
C(31)	1945(9)	5059(5)	9148(4)	6.8	H(37)	202	510	955	7
C(32)	2831(7)	4757(5)	8911(3)	6.0	H(38)	345	458	906	7
C(33)	2594(8)	4827(5)	8343(4)	6.5	H(39)	295	471	813	7
C(34)	1526(9)	5207(5)	8191(4)	7.1	H(40)	111	534	783	7
C(35)	1098(7)	5354(5)	8706(5)	7.9	H(41)	44	555	878	7
C(36)	49(7)	3119(10)	9130(5)	9.3	H(42)	40	286	949	7
C(37)	27(7)	2686(5)	8610(7)	8.7	H(43)	28	218	851	7
C(38)	−489(8)	3197(9)	8206(4)	8.5	H(44)	−68	314	782	7
C(39)	−808(6)	3906(7)	8419(4)	7.1	H(45)	−105	437	816	7
C(40)	−519(7)	3897(7)	8968(4)	7.4	H(46)	−73	425	927	7
C(41)	197(12)	1469(8)	494(7)	12.0	C(44)	668(18)	1863(13)	1655(7)	16
C(42)	9526(11)	2106(8)	744(6)	11.0	C(45)	1422(18)	1163(14)	1452(10)	16
C(43)	9772(13)	2249(8)	1342(5)	11.0	C(46)	1030(18)	1094(14)	853(11)	17
					C(47)	8657(11)	2445(9)	410(6)	13

in the conversion of I → II, as well as the structures of the compounds formed, will possibly have many features in common with the other compounds, including the catalytically active ones, which are generated in Cp_2TiCl_2/Cp_2TiCl-$LiAlH_4$ systems. It is also noteworthy that the formation of the six-nuclear complex II per se with a rather complicated geometry indicates extensive stereochemical opportunities originating in the course of the decomposition of $Cp'_2TiH_2AlH_2$, which seems to specify a unique catalytic activity of the Cp_2TiCl_2/Cp_2TiCl-$LiAlH_4$ systems [1–6]. The results of the X-ray study of II confirm, in an indirect way, the suggestion made in our previous papers that the origination of hydrogenating activity in these systems

TABLE 2

MAIN BOND LENGTHS, d (Å) IN MOLECULE II

Bond	d	Bond	d	Bond	d
Ti(1)–H(1)	1.79(7)	Al(1)–H(3)	1.72(6)	Al(1)–C(11)	1.95(1)
Ti(1)–H(2)	1.81(7)	Al(1)–H(6)	1.68(8)	Al(2)–C(24)	1 95(1)
Ti(2)–H(4)	1.84(9)	Al(1)–H(7)	1.74(6)	Ti(1)–Al(2)	2.781(2)
Ti(2)–H(5)	1.78(5)	Al(1)–H(8)	1.67(5)	Ti(4)–Al(1)	2.782(2)
Ti(3)–H(5)	1.95(5)	Al(2)–H(1)	1.79(7)	Al(1)–Al(2)	3.222(2)
Ti(3)–H(6)	1.79(7)	Al(2)–H(2)	1.72(6)	Al(2)–Ti(2)	3.230(2)
Ti(4)–H(7)	1.73(8)	Al(2)–H(3)	1.73(6)	Ti(3)–Al(1)	3 217(2)
Ti(4)–H(8)	1.79(5)	Al(2)–H(4)	1.56(9)	Ti(2)–Ti(3)	3.717
(Ti–H)av.	1.80(8)	(Al–H)av.	1.70( )	(Ti–C)av.	2.34(2)
Ti(1)–C(1)	2.33(1)	Ti(2)–C(11)	2.32(1)	Ti(3)–C(21)	2.36(1)
Ti(1)–C(2)	2.31(1)	Ti(2)–C(12)	2.32(1)	Ti(3)–C(22)	2.37(1)
Ti(1)–C(3)	2.29(1)	Ti(2)–C(13)	2.37(1)	Ti(3)–C(23)	2 34(1)
Ti(1)–C(4)	2.32(1)	Ti(2)–C(14)	2.36(1)	Ti(3)–C(24)	2.34(1)
Ti(1)–C(5)	2.30(1)	Ti(2)–C(15)	2.36(1)	Ti(3)–C(25)	2.35(1)
Ti(1)–C(6)	2.35(1)	Ti(2)–C(16)	2.33(1)	Ti(3)–C(26)	2.40(1)
Ti(1)–C(7)	2.32(1)	Ti(2)–C(17)	2.35(1)	Ti(3)–C(27)	2.35(1)
Ti(1)–C(8)	2.30(1)	Ti(2)–C(18)	2.35(1)	Ti(3)–C(28)	2 34(1)
Ti(1)–C(9)	2.36(1)	Ti(2)–C(19)	2.37(1)	Ti(3)–C(29)	2.33(1)
Ti(1)–C(10)	2.37(1)	Ti(2)–C(20)	2.37(1)	Ti(3)–C(30)	2 37(1)
Ti(4)–C(31)	2.34(1)	C(1)–C(2)	1.37(2)	C(11)–C(12)	1.42(1)
Ti(4)–C(32)	2.37(1)	C(2)–C(3)	1.46(2)	C(12)–C(13)	1.37(1)
Ti(4)–C(33)	2.36(1)	C(3)–C(4)	1.32(2)	C(13)–C(14)	1.43(1)
Ti(4)–C(34)	2.36(1)	C(4)–C(5)	1.22(2)	C(14)–C(15)	1.42(1)
Ti(4)–C(35)	2.33(1)	C(5)–C(1)	1.31(2)	C(15)–C(11)	1.42(1)
Ti(4)–C(36)	2.33(1)	C(6)–C(7)	1.41(1)	C(16)–C(17)	1.40(1)
Ti(4)–C(37)	2.34(1)	C(7)–C(8)	1.39(2)	C(17)–C(18)	1.37(1)
Ti(4)–C(38)	2.34(1)	C(8)–C(9)	1.35(2)	C(18)–C(19)	1.42(1)
Ti(4)–C(39)	2.34(1)	C(9)–C(10)	1.35(1)	C(19)–C(20)	1.38(1)
Ti(4)–C(40)	2.33(1)	C(10)–C(6)	1.35(1)	C(20)–C(16)	1.42(1)
C(21)–C(22)	1.39(1)	C(31)–C(32)	1.35(1)	(C–C)av.	1.38(4)
C(22)–C(23)	1.40(1)	C(32)–C(33)	1 35(1)	C(41)–C(42)	1.46(2)
C(23)–C(24)	1.43(1)	C(33)–C(34)	1.39(1)	C(42)–C(43)	1.43(2)
C(24)–C(25)	1.43(1)	C(34)–C(35)	1.43(2)	C(43)–C(44)	1.34(2)
C(25)–C(21)	1.40(1)	C(35)–C(31)	1.41(1)	C(44)–C(45)	1.54(3)
C(26)–C(27)	1.39(1)	C(36)–C(37)	1.42(2)	C(45)–C(46)	1.44(3)
C(27)–C(28)	1.40(1)	C(37)–C(38)	1.33(2)	C(46)–C(41)	1.33(3)
C(28)–C(29)	1.37(1)	C(38)–C(39)	1.30(2)	C(42)–C(47)	1.31(2)
C(29)–C(30)	1.39(1)	C(39)–C(40)	1.30(2)		
C(30)–C(26)	1.38(1)	C(40)–C(36)	1.42(2)		

is related to the formation of associates involving not less than two titanium atoms, which are connected with aluminium atoms via an ordinary bridging Ti–H–Al bond.

Experimental

Synthesis of [Cp$_2$TiH$_2$Al(H)(η^1 : η^5-C$_5$H$_4$)TiCp]$_2$ · C$_6$H$_5$CH$_3$

A weighed quantity of [Cp$_2$TiH$_2$AlH$_2$]$_2$ · TMEDA (~ 0.8 g) prepared by the procedure described in ref. 11 was dissolved in toluene. The mixture was stirred for 4 h, filtered, and the filtrate was evaporated by concentration in vacuo to 15–20 ml and kept overnight. The precipitated black crystals were separated from the mother liquor, washed with toluene, and dried in vacuo. Found: Ti 22.8; Al 6.96; H$_{act}$ 0.93. C$_{40}$H$_{46}$Ti$_4$Al$_2$ · C$_6$H$_5$CH$_3$ calcd.: Ti 22.20; Al 6.26; H$_{act}$ 0.93%.

Single crystals of [Cp$_2$TiH$_2$Al(H)(C$_5$H$_4$)TiCpH]$_2$ · C$_6$H$_5$CH$_3$ were run, in a glass capillary, on an automatic Syntex 2P$_1$ diffractometer (λ(Mo-K_α), $\theta/2\theta$ scanning, graphite monochromator). The compound crystallized in a monoclinic lattice with

TABLE 3

MAIN BOND ANGLES, ω(°), IN MOLECULE II

Angle	ω	Angle	ω	Angle	ω
H(1)Ti(1)H(2)	76(3)	H(4)Ti(2)H(5)	88(3)	Ti(1)H(1)Al(2)	102(3)
H(7)Ti(4)H(8)	72(2)	H(5)Ti(3)H(6)	84(3)	Ti(1)H(2)Al(2)	104(3)
C(11)Al(1)H(3)	94(2)	C(24)Al(2)H(1)	101(2)	Ti(4)H(7)Al(1)	106(3)
C(11)Al(1)H(6)	119(2)	C(24)Al(2)H(2)	120(2)	Ti(4)H(8)Al(1)	107(3)
C(11)Al(1)H(7)	99(2)	C(24)Al(2)H(3)	96(2)	Ti(2)H(4)Al(2)	144(7)
C(11)Al(1)H(8)	130(2)	C(24)Al(2)H(4)	116(4)	Ti(3)H(6)Al(1)	136(5)
H(3)Al(1)H(6)	95(3)	H(1)Al(2)H(2)	78(3)	Ti(2)H(5)Ti(3)	171(3)
H(3)Al(1)H(7)	162(3)	H(1)Al(2)H(3)	160(3)	Al(1)H(3)Al(2)	138(4)
H(3)Al(1)H(8)	88(3)	H(1)Al(2)H(4)	89(4)	CpI CpII ^{a}	41.7
H(6)Al(1)H(7)	88(3)	H(2)Al(2)H(3)	86(3)	CpIII CpIV ^{a}	41.3
H(6)Al(1)H(8)	111(3)	H(2)Al(2)H(4)	124(4)	CpV CpVI ^{a}	43.2
H(7)Al(1)H(8)	74(2)	H(3)Al(2)H(4)	91(4)	CpVII CpVIII ^{a}	41.5
C(1)C(2)C(3) ^{a}	100	C(11)C(12)C(13)	112	C(21)C(22)C(23)	107
C(2)C(3)C(4)	107	C(12)C(13)C(14)	107	C(22)C(23)C(24)	111
C(3)C(4)C(5)	112	C(13)C(14)C(15)	108	C(23)C(24)C(25)	104
C(4)C(5)C(1)	110	C(14)C(15)C(11)	109	C(24)C(25)C(21)	109
C(5)C(1)C(2)	111	C(15)C(11)C(12)	105	C(25)C(21)C(22)	109
C(6)C(7)C(8)	107	C(16)C(17)C(18)	108	C(26)C(27)C(28)	107
C(7)C(8)C(9)	107	C(17)C(18)C(19)	108	C(27)C(28)C(29)	110
C(8)C(9)C(10)	109	C(18)C(19)C(20)	109	C(28)C(29)C(30)	107
C(9)C(10)C(6)	110	C(19)C(20)C(16)	107	C(29)C(30)C(26)	109
C(10)C(6)C(7)	107	C(20)C(16)C(17)	108	C(30)C(26)C(27)	108
C(31)C(32)C(33)	110	C(36)C(37)C(38)	107	C(41)C(42)C(43)	119
C(32)C(33)C(34)	109	C(37)C(38)C(39)	111	C(42)C(43)C(44)	120
C(33)C(34)C(35)	106	C(38)C(39)C(40)	110	C(43)C(44)C(45)	126
C(34)C(35)C(31)	107	C(39)C(40)C(36)	109	C(44)C(45)C(46)	105
C(35)C(31)C(32)	107	C(40)C(36)C(37)	103	C(45)C(46)C(41)	134
(CCC)$_{ave}$	108	C(47)C(42)C(41)	117	C(46)C(41)C(42)	115
		C(47)C(42)C(43)	124		

^{a} The angle between the corresponding root-mean-square planes. ^{b} Standard measurement error of the C-C-C angle is 1°.

the unit cell parameters a 11.753(5), b 15.701(7), c 23.95(1) Å, β 99.22(4)°, V 5353 Å^3, space group $P2_1/c$, $Z = 4$, $\rho_{calcd} = 1.32$ g/cm^3, μ(Mo) 8.1 cm^{-1}. 3475 reflections of a total of 4740 were used in the calculations. The structure was solved by the direct method. The hydrogen atoms were localized by a difference synthesis, the coordinates of the Cp-group hydrogens were calculated, and the toluene hydrogens were neglected. The structure was refined by the least-squares method in a full-matrix anisotropic (isotropic for hydrogen atoms) approximation to $R = 0.060$. The coordinates of the atoms and the thermal parameters are listed in Table 1; the main interatomic distances and bond angles are given in Tables 2 and 3, respectively.

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