

Structural chemistry of titanium and aluminium bimetallic hydride complexes

VI *. Molecular structure and physico-chemical properties of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\mu_2\text{-H})_2\text{Al}(\text{Cl})(\mu_2\text{-H})_2\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2$, a catalyst-precursor for hydrogenation in the $[(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}]_2\text{-LiAlH}_4$ system

A.I. Sizov, I.V. Molodnitskaya, B.M. Bulychev*, E.V. Evdokimova,

M.V. Lomonosov Moscow State University, Moscow 119899 (U.S.S.R.)

G.L. Soloveichik,

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

A.I. Gusev, E.B. Chuklanova,

Research Institute of Chemistry and Technology of Organo-Element Compounds, Moscow 111123 (U.S.S.R.)

and V.I. Andrianov

A.V. Shubnikov Institute of Crystallography, Academy of Sciences of the U.S.S.R., Moscow 117333 (U.S.S.R.)

(Received April 18th, 1987)

Abstract

The complex $(\text{Cp}_2\text{Ti})_2\text{AlH}_4\text{Cl}$ has been isolated from the catalytic system $(\text{Cp}_2\text{TiCl})_2\text{-LiAlH}_4$, which is a precursor of the catalyst for the hydrogenation and isomerization of olefins. This complex has been studied by X-ray diffraction. The complex forms rhomboidal crystals with unit cell dimensions $a = 10.414$, $b = 11.998$, $c = 16.008$ Å, space group $P2_12_12_1$, $Z = 4$, and density $\rho_{\text{calc}} = 1.40$ g/cm³. The Cp_2Ti moieties are linked to the Al atom via double hydrogen bridges; the Cl atom is bonded to the Al atom.

Analysis of the EPR spectral data and some chemical properties of $(\text{Cp}_2\text{Ti})_2\text{AlH}_4\text{Cl}$ solutions has led us to suggest a mechanism for the formation of the catalytically active species upon interaction of this compound with olefins and solvating solvents.

* For Part V see Ref. 24.

Introduction

The compounds formed in the system $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl-LiAlH}_4$ ($\text{C}_5\text{H}_5 = \text{Cp}$) are effective catalysts for the hydrogenation [1], isomerization [2–4], and hydrometallation [2] of olefins. Previously we established [1] that the complex $[\text{Cp}_2\text{Ti}]_2\text{AlH}_4\text{Cl}$, which was characterized by spectral and analytical methods [2], is most active in hydrogenation. This compound was also very effective in the isomerization of olefins [2], although its activity in this case was 6 times lower than that of $\text{Cp}_2\text{TiH}_2\text{AlH}_2$. Until recently the structure of this complex had not been established, and, hence, the nature of its catalytic activity was not clear. Moreover, conclusions [3], that only $\text{Cp}_2\text{TiH}_2\text{AlHX}$ complexes with terminal Al–H bonds are responsible for olefin isomerization, are contradicted by the catalytic activity shown in this reaction by $[\text{Cp}_2\text{Ti}]_2\text{AlH}_4\text{Cl}$, which, from its IR spectrum, contains no such bonds [2].

This work reports the results of a study on the structure and physico-chemical properties of the complex $[\text{Cp}_2\text{Ti}]_2\text{AlH}_4\text{Cl}$, which was isolated from the $(\text{Cp}_2\text{TiCl})_2\text{-LiAlH}_4$ system.

Discussion

The interaction of Cp_2TiCl and LiAlH_4 in 2 : 1 ratio, under air-free conditions, gives a violet solution, from which the complex $[\text{Cp}_2\text{Ti}]_2\text{AlH}_4\text{Cl}$ was crystallized after the LiCl precipitate had been removed (eq. 1).



From the X-ray data, it can be seen that the crystals of this complex are composed of individual three-nuclear molecules of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\mu_2\text{-H})_2\text{Al}(\text{Cl})(\mu_2\text{-H})_2\text{TiCp}_2$, in which two titanocene moieties are linked to an aluminium atom via double hydrogen bridges (Fig. 1). Bonds of a similar type, between transition metal atoms, were observed previously in two other structurally characterized alumohydride complexes with M : Al ratio of 2 : 1, viz. $[(\text{C}_5\text{Me}_5)_2\text{Ti}]_2\text{AlH}_5$ [5] and $[(\text{Me}_3\text{P})_3\text{H}_7\text{-W}]_2\text{AlH}_5$ [6].

The structure of the titanocene moieties in I is nearly identical with that of Cp_2Ti in the complexes $(\text{Cp}_2\text{TiH}_2\text{AlH}_2)_2 \cdot \text{TMEDA}$ [7], $\text{Cp}_2\text{TiH}_2\text{AlCl}_2 \cdot \text{OEt}_2$ [8], $[\text{Cp}_2\text{TiH}_2\text{Al}(\text{H})\text{OMe}]_2$ [9], and $[\text{Cp}_2\text{TiH}_2\text{AlH}(\text{C}_5\text{H}_4)\text{TiCp}(\text{H})]_2$ [10] ($r_{\text{Ti-Cp}} = 2.33\text{--}2.36$ Å, $\angle\text{Cp-Ti-Cp} = 137\text{--}140^\circ$). The Ti–C bonds in I vary in length from 2.30 to 2.37 Å (average values 2.33 and 2.34 Å), and the Cp–Ti–Cp angles are 138.6 and 137° for Ti(1) and Ti(2), respectively. The structural parameters of Cp_2Ti in I are nearest to the those of the complex $\text{Cp}_2\text{TiH}_2\text{AlCl}_2 \cdot \text{OEt}_2$, which also contains electronegative chlorine atoms in the coordination sphere of the aluminium atom.

As in the majority of other known alumohydride complexes of titanium, the titanium and aluminium atoms in I are linked by double hydrogen bridges. For both titanium atoms the interatomic distances $\text{Ti} \cdots \text{Al}$ in I are identical (within experimental error), being 2.772 and 2.770(3) Å. These are consistent with literature data for other compounds of this type (2.75–2.79 Å) [5,7–10].

The Ti–H distances in I are also only slightly different from $r_{\text{Ti-H}}$ in other hydride complexes of titanium and aluminium; however, the H–Ti–H bond angle is

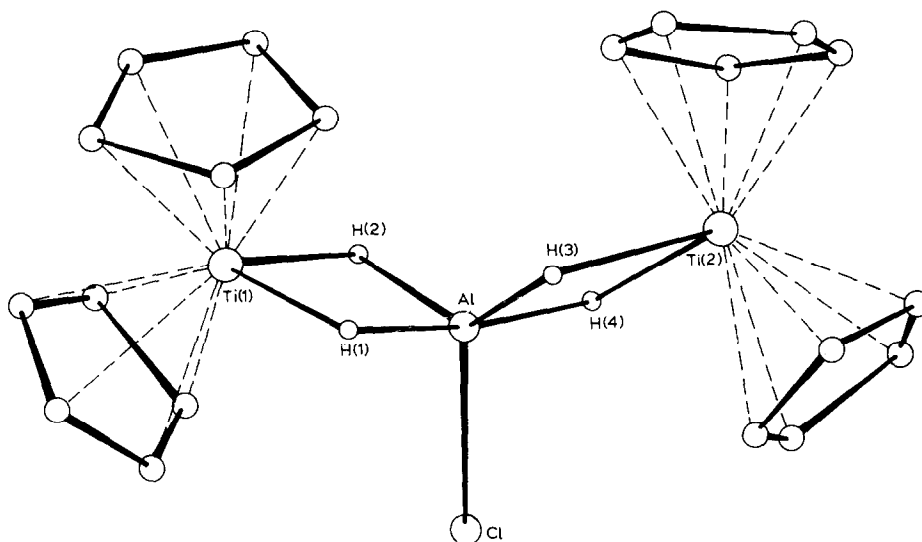


Fig. 1. Molecular structure of the complex $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\mu_2\text{-H})_2\text{Al}(\text{Cl})(\mu_2\text{-H})\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2$ (I).

smaller (63.5°), and this indicates a greater electron density at the titanium atom, compared to that in the complexes $\text{Cp}_2\text{TiH}_2\text{AlXX}' \cdot \text{L}$. At the same time, the Al–H distances differ noticeably from each other (Table 1). A similar effect is observed in the other alumohydride complexes of titanocene, and this seems to be related to some asymmetry of the coordination polyhedron of the aluminium atom. As in the majority of other alumohydride complexes of transition metals, the coordination polyhedron of the aluminium atom in I is a trigonal bipyramid, in which the

Table 1

Interatomic distances in $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}]_2\text{AlH}_4\text{Cl}$

Atoms	d (Å)	Atoms	d (Å)
Ti(1)–C(1)	2.36(1)	Ti(2)–C(16)	2.32(1)
Ti(1)–C(2)	2.35(1)	Ti(2)–C(17)	2.33(1)
Ti(1)–C(3)	2.33(1)	Ti(2)–C(18)	2.33(1)
Ti(1)–C(4)	2.34(1)	Ti(2)–C(19)	2.34(1)
Ti(1)–C(5)	2.33(1)	Ti(2)–C(20)	2.36(1)
Ti(1)–C(6)	2.30(1)	Ti(2)–C _{mean}	2.34 ± 0.01
Ti(1)–C(7)	2.32(1)	Ti(2)–Al	2.770(3)
Ti(1)–C(8)	2.34(1)	Al–Cl	2.176(3)
Ti(1)–C(9)	2.36(1)	C(1)–C(5) _{mean}	1.37(1)
Ti(1)–C(10)	2.31(1)	Al–H(1)	1.67
Ti(1)–C _{mean}	2.33 ± 0.02	Al–H(2)	1.43
Ti(1)–Al	2.772(3)	Al–H(3)	1.48
Ti(2)–C(11)	2.33(1)	Al–H(4)	1.61
Ti(2)–C(12)	2.35(1)	Ti(1)–H(1)	1.87
Ti(2)–C(13)	2.36(1)	Ti(1)–H(2)	1.85
Ti(2)–C(14)	2.34(1)	Ti(2)–H(3)	1.91
Ti(2)–C(15)	2.33(1)	Ti(2)–H(4)	1.75

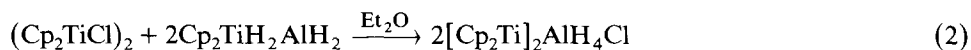
equatorial ligands, H(2), H(3), Cl, and Al, lie in a plane. It should be pointed out that although the bond angles in the bipyramid are markedly distorted (mainly due to small H–Al–H bond angles in metallocycles TiH_2Al), the value of the Ti–Al–Ti angle (139°) is practically the same as that calculated for this polyhedron (138°). The axial ligands in the bipyramid are H(1) and H(4), which form an angle of 166.3° . The Al–H(1) and Al–H(4) bond are naturally longer than those found for the equatorial Al–H bonds. In the IR spectrum of **1** the bond vibrations of the M–H–Al bridge bonds give rise to the absorption bands at 1160 and 1260 cm^{-1} .

The Al–Cl bond length in **1** (2.176(3) Å) is greater than that in complex $\text{Cp}_2\text{TiH}_2\text{AlCl}_2 \cdot \text{OEt}_2$ (2.156 Å) and is close to that found in $\text{AlCl}_3 \cdot 2\text{NHMe}_2$ (2.18 Å) [11]. An increase in the length of this bond in **1** causes a bathochromic shift of the absorption band for $\nu(\text{Al–Cl})$ to 420 cm^{-1} (in $\text{Cp}_2\text{TiH}_2\text{AlCl}_2 \cdot \text{Et}_2\text{O}$ $\nu(\text{Al–Cl}) = 437 \text{ cm}^{-1}$ [12]).

Thus, the most essential structural features of $[\text{Cp}_2\text{Ti}]_2\text{AlH}_4\text{Cl}$ are (a) coordination saturation of both metal atoms (taking into account the presence of a lone electron at the Ti atom, which occupies the b_2 orbital), and (b) the absence of terminal M–H bonds. From the ideas adopted on metallocomplex catalysis a compound having this structure should not show catalytic activity in olefin hydrogenation or isomerization, because the steps of coordination and introduction of a substrate would be hampered if no essential structural reorganization of the complex occurs. Nevertheless, benzene and ether/benzene solutions of $[\text{Cp}_2\text{Ti}]_2\text{AlH}_4\text{X}$ (X = Cl, Br) are effective homogeneous catalysts for both the hydrogenation and isomerization processes. It should be noted that freshly prepared, blue-violet ($\lambda = 600 \text{ nm}$) solutions of the complexes catalyze the isomerization reaction after an induction period of 10–20 min, whereas the solutions, “aged” for 30–40 min and brown-violet in colour ($\lambda = 457 \text{ nm}$), catalyse the reaction immediately after introduction of the substrate. These data suggest that the complexes $[\text{Cp}_2\text{Ti}]_2\text{AlH}_4\text{X}$, although not the catalyst as such, they are the precursor from which the catalytically active species derive on interaction with the solvent and/or substrate.

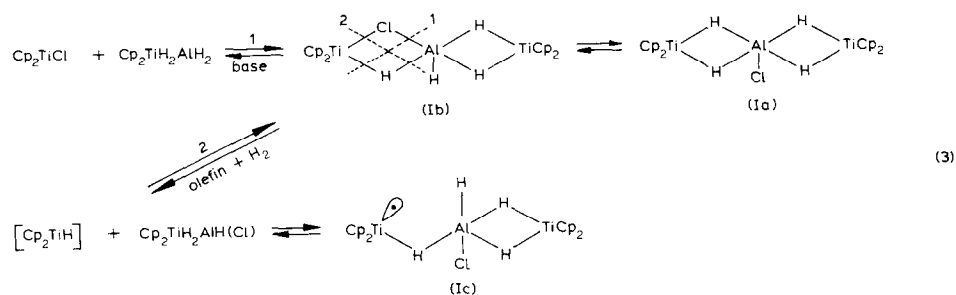
The molecular weight of **1**, determined by the isopiestic method, shows that **1** exists in benzene solutions as the monomer (measured molecular weight is 430 ± 10 dalton, the calculated value is 422.6 dalton). The EPR spectrum of this solution contains a broad unresolved singlet with a g -factor of 1.989 and $\Delta H = 45\text{--}50 \text{ G}$, as well as a signal of low intensity with $g = 1.977$. The lack of hyperfine structure, which is expected as a result of spin-decoupling by hydrogen ($I = 1/2$) and aluminium ($I = 5/2$) nuclei, could be explained by the spin-exchange process Ti–H–Al–H–Ti. However, the magnetic susceptibility measurements for crystals of $[\text{Cp}_2\text{Ti}]_2\text{AlH}_4\text{Cl}$ showed that μ_{eff} for this compound is 1.56 BM, which remains constant within a temperature range of 77–289 K (the low value of μ_{eff} is probably, due to the presence of impurities in the sample). Hence, broadening of the signals in the EPR spectrum is not due to the spin-exchange interaction, but results from the reorganization of the complex in solution. The following facts are consistent with this suggestion. Firstly, the existence of an induction period before catalysis occurs for freshly prepared solutions of the complexes and the associated colour changes. Secondly, the intensity of an additional signal with $g = 1.977$ (the value of which is close to that for individual $(\text{Cp}_2\text{TiCl})_2$ (1.978), increases somewhat during the storage of a solution of $[\text{Cp}_2\text{Ti}]_2\text{AlH}_4\text{Cl}$, made by dissolution of a crystalline sample the solution turning from violet into brown-violet. Thirdly, straightforward EPR

studies of the reaction mixture, eq. 1, showed that the additional signal (generally of essentially higher intensity) is observed immediately after reactants are mixed. A similar effect was observed when $(\text{Cp}_2\text{TiCl})_2$ solution was added to a solution of $\text{Cp}_2\text{TiH}_2\text{AlH}_2$ (eq. 2),



which has a peculiar EPR spectrum (octet, $g = 1.991$, $\Delta H = 36.0$ G, $a_{\text{Al}} = a_{\text{H}} = 4.8$ G). In this case the additional signal with $g = 1.997$ appears against a background of a gradually broadening octuplet signal which begins at a $\text{Cp}_2\text{TiCl}/\text{Cp}_2\text{TiH}_2\text{AlH}_2$ ratio of 1:10. When this ratio is 1:5 the EPR spectrum of the mixture is very similar to that of the solution, (made by dissolving crystalline $[\text{Cp}_2\text{Ti}]_2\text{AlH}_4\text{Cl}$). Further additions of $(\text{Cp}_2\text{TiCl})_2$ merely increases the intensity of the additional signal. It should also be noted that the catalytic properties of the solutions, obtained by the reactions 1 and 2, are identical.

All these facts allow the following hypothesis concerning the formation of catalytically active species in the system $(\text{Cp}_2\text{TiCl})_2\text{-LiAlH}_2$ ether/benzene with $\text{Ti}:\text{Al} = 2:1$ to be made. It is assumed that in the reaction mixtures (eqs. 1 or 2) there are a number of equilibrium reactions occurring between different forms of complex I, including those with homonuclear (violet-coloured form, Ia) and heteronuclear (brown-violet form, Ib) bridging bonds between Ti and Al, and perhaps, some fully dissociated forms. The possibility of an intramolecular rearrangement occurring with chlorine atom migration from Ti to Al, was observed previously in



the study of reactions between Cp_2TiCl and $\text{AlH}_{3-n}\text{Cl}_n \cdot \text{L}$ in ether [13]. The crystallization shifts the equilibrium 3 such that formation of individual complex Ia results. Judging from the increase in intensity of the additional signal with $g = 1.977$, and from molecular weight measurements, this equilibration proceeds slowly, this is to be expected taking into account the high stability of the metallohydride moiety $\text{Ti} \begin{smallmatrix} \text{H} \\ \diagup \quad \diagdown \end{smallmatrix} \text{Al}$, compared to the heteronuclear moiety $\text{Ti} \begin{smallmatrix} \text{Cl} \\ \diagup \quad \diagdown \end{smallmatrix} \text{Al}$.

The introduction into the system of bases (amines) or olefins that fix the $\text{Cp}_2\text{TiH}_2\text{AlH}_2$ moiety to the complex $\text{Cp}_2\text{TiH}_2\text{AlH}_2 \cdot \text{L}$, shifts equilibrium 1 to the left. Under the action of these reagents a dark-green compound crystallizes from the solution, which was identified as the α -modification of $(\text{Cp}_2\text{TiCl})_2$. Crystals of this compound are monoclinic with the unit cell parameters $a = 13.57$, $b = 8.17$, $c = 8.11$ Å, $\gamma = 90.04^\circ$, identical with those described in ref. 14. This accounts for the straightforward catalytic activity of I, observed in olefin isomerization, and for its

lower rate (with respect to a g-atom of Ti), as compared to individual $\text{Cp}_2\text{TiH}_2\text{AlH}_2$ [3]. Catalysts for isomerization are those alumohydrides $\text{Cp}_2\text{TiH}_2\text{AlH}_2$, which contain terminal Al-H bonds [3]. Exactly the same compound is formed when equilibrium 1 (eq. 3) is shifted to the left under the action of olefins. Thus the conclusions outlined in ref. [3] and the catalytic activity displayed by I in the isomerization reaction, are no longer contradictory.

The nature of the hydrogenating activity of I is less clear. Since neither $\text{Cp}_2\text{TiH}_2\text{AlH}_2$, nor Cp_2TiCl catalyses the hydrogenation reaction [3], there seems to be another possible mechanism for the dissociation of complex Ib in the presence of olefin and hydrogen, leading to the cleavage of the heterocycle $\text{Ti} \begin{smallmatrix} \text{H} \\ \text{Al} \end{smallmatrix}$, as in reaction 2 (eq. 3), to give complex Ic or even monomeric titanocene hydride, which are the actual catalysts of the hydrogenation process. The formation of titanocene hydrides of varying composition in the $(\text{Cp}_2\text{TiCl})_2\text{LiAlH}_4$ system, and a high catalytic activity of " Cp_2TiH " and its derivatives, have been reported [15-19]. In accord with the conclusions in ref. 3 and in agreement with the foregoing discussion, the second component of this equilibrium, $\text{Cp}_2\text{TiH}_2\text{AlH}(\text{Cl})$, should not catalyse the reaction of olefin hydrogenation. Nevertheless, this compound is a rather effective catalyst of this reaction, although the rate of hydrogenation of hexene-1 in its presence is several times lower than in the case of $[\text{Cp}_2\text{Ti}]_2\text{AlH}_4\text{Cl}$. The nature of this effect will be discussed in a later publication.

Thus, the nature of the catalytic sites of the catalysts of the isomerization and hydrogenation of olefins are thought to be different. However, if the bimetallic character of these sites for isomerization could be established with sufficient reliability, the bi- or monometallic nature of these sites for hydrogenation must be established all the more.

Experimental

All experiments were carried out under full exclusion of air. $(\text{Cp}_2\text{TiCl})_2$ was prepared by reduction of Cp_2TiCl_2 [20]. Solvents were dried by heating and distillation over LiAlH_4 . Hexene-1 was purified by fractional distillation over CaH_2 . IR spectra were recorded on a UR-20 spectrophotometer in the range $400\text{--}2500\text{ cm}^{-1}$; EPR spectra were run on a Varian E-3 radio spectrometer with a modulation frequency of 100 kHz with respect to the standard, Mn^{2+} in MgO ; static magnetic susceptibilities were measured by the Faraday method between $77\text{--}289\text{ K}$.

Catalytic activity of the complexes was studied in the reaction of hydrogenation of hexene-1. Hydrogenation was carried out in a two-chamber vessel, connected to a gas burette to measure the volume of absorbed gas at a hydrogen pressure of 1 atm at 20°C . Hydrogen was purified by sorption on LaNi_5 , followed by its desorption on heating.

Synthesis of $[\text{Cp}_2\text{Ti}]_2\text{AlH}_4\text{Cl}$ (I)

To a suspension of 1.2 g of $(\text{Cp}_2\text{TiCl})_2$ in 50 ml of $\text{Et}_2\text{O}/\text{C}_6\text{H}_6$ mixture (10:1) was added 30 ml of a solution of LiAlH_4 in Et_2O (3.53 g/L; $\text{Ti}:\text{Al} \approx 2:1$). The mixture was stirred for 30 min, then the precipitate of LiCl was filtered off, and the violet filtrate was kept overnight. The precipitated black crystals were separated from the mother liquor, washed with cold ether, and dried in vacuo. Found: Ti, 22.6; Al, 6.0; Cl, 8.5. $[(\text{C}_5\text{H}_5)_2\text{Ti}]_2\text{AlH}_4\text{Cl}$ Calc: Ti, 22.67; Al, 6.38; Cl, 8.39%.

Table 2

Bond angles in $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}]_2\text{AlH}_4\text{Cl}$

Angles	ω (°)	Angles	ω (°)
H(1)–Ti(1)–H(2)	63.5	Cl–Al–Ti(1)	110.3(3)
H(3)–Ti(2)–H(4)	63.5	Cl–Al–Ti(2)	110.7(3)
(C–C–C) _{mean}	107.9(9)	Cl–Al–H(1)	96.5
Ti(1)–Al–Ti(2)	139.0(1)	Cl–Al–H(2)	123.0
H(2)–Al–H(1)	77.7	Cl–Al–H(3)	121.5
H(3)–Al–H(2)	115.2	Cl–Al–H(4)	94.3
H(3)–Al–H(1)	89.9	Ti(1)–H(1)–Al	102.9
H(4)–Al–H(1)	166.3	Ti(1)–H(2)–Al	114.8
H(2)–Al–H(4)	103.3	Ti(2)–H(3)–Al	108.2
H(3)–Al–H(4)	77.3	Ti(2)–H(4)–Al	111.0

Single crystals of I were examined on an automatic CAD-4 “Enraf-Nonius” diffractometer ($\lambda\text{Mo-}K_\alpha$) graphite monochromator, $\theta/2\theta$ scanning ($2\theta \leq 50^\circ$), glass capillary). The unit cell parameters of rhomboidal crystals are $a = 10.414(1)$, $b = 11.998(2)$, $c = 16.008(1)$ Å, space group $P2_12_12_1$, $Z = 4$, $V = 2000$ Å³, $\rho_{\text{calc}} = 1.40$ g/cm³.

Table 3

Atomic coordinates ($\times 10^4$; $\times 10^3$ for H) in $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}]_2\text{AlH}_4\text{Cl}$

Atom	<i>x</i>	<i>y</i>	<i>z</i>
Ti(1)	4581(2)	2514(2)	8666(1)
Ti(2)	786(2)	3148(1)	6620(1)
C(1)	439(1)	376(1)	9799(7)
C(2)	487(1)	4357(8)	9117(8)
C(3)	607(1)	392(1)	8925(8)
C(4)	632(1)	307(1)	949(1)
C(5)	528(2)	296(1)	1,0006(8)
C(6)	396(1)	97(1)	791(1)
C(7)	511(2)	132(1)	758(1)
C(8)	602(1)	116(1)	818(1)
C(9)	544(1)	717(9)	8869(9)
C(10)	417(2)	62(1)	870(1)
C(11)	2696(9)	257(1)	6005(6)
C(12)	188(1)	164(1)	6006(7)
C(13)	84(1)	186(1)	5508(8)
C(14)	101(1)	290(1)	5181(7)
C(15)	211(1)	3320(9)	5459(7)
C(16)	132(1)	283(1)	703(1)
C(17)	137(1)	330(2)	626(1)
C(18)	91(1)	437(1)	634(1)
C(19)	58(1)	452(1)	715(1)
C(20)	–85(1)	356(2)	7584(7)
Cl	1626(3)	4732(2)	8809(2)
Al	2369(3)	3432(2)	7994(2)
H(1)	279	255	875
H(2)	371	328	784
H(3)	151	257	763
H(4)	186	401	715

The structure was solved by the direct method using an AREN-85 programme package [21]. 250 $|E|$ were selected, 1250 relationships were composed, and 128 phase versions were calculated. The second phase set gave the least value of R factor, according to the S estimate [22]. The structural motif was elucidated by automatic phase refinement, by use of cyclic inverse Fourier synthesis [23]. The hydrogen atoms in the Cp-rings were found from geometric calculations, the hydride hydrogens were located by difference synthesis. The structure was refined by the least-squares method in an anisotropic approximation for all non-hydrogen atoms to give $R = 0.025$. The interatomic distances and bond angles are given in Tables 1 and 2, and the coordinates of the atoms are listed in Table 3.

References

- 1 E.V. Evdokimova, B.M. Bulychev and G.L. Soloveichik, *Kinet. Katal.*, 22 (1981) 170.
- 2 E.V. Evdokimova, B.M. Bulychev and G.L. Soloveichik, *Kinet. Katal.*, 23 (1982) 1109.
- 3 B.M. Bulychev, E.V. Evdokimova, A.I. Sizov and G.L. Soloveichik, *J. Organomet. Chem.*, 239 (1982) 313.
- 4 K. Mach, H. Antropiusova, V. Hanuš, P. Tureček and P. Sedmeva, *J. Organomet. Chem.*, 269 (1984) 39.
- 5 V.K. Bel'sky, A.I. Sizov, B.M. Bulychev and G.L. Soloveichik, *J. Organomet. Chem.*, 280 (1985) 67.
- 6 A.R. Barron, M.B. Nursthouse, M. Motevalli and G. Wilkinson, *J. Chem. Soc., Chem. Comm.*, (1985) 664.
- 7 E.B. Lobkovskii, G.L. Soloveichik, A.I. Sizov, B.M. Bulychev, A.I. Gusev and N.I. Kirillova, *J. Organomet. Chem.*, 265 (1984) 167.
- 8 E.B. Lobkovskii, G.L. Soloveichik, B.M. Bulychev, R.G. Gerr and Yu T. Struchkov, *J. Organomet. Chem.*, 270 (1984) 45.
- 9 V.K. Bel'sky, A.I. Sizov, B.M. Bulychev and G.L. Soloveichik, *Koord. Khim.*, 11 (1985) 1003.
- 10 E.B. Lobkovskii, G.L. Soloveichik, A.I. Sizov and B.M. Bulychev, *J. Organomet. Chem.*, 280 (1985) 53.
- 11 K.N. Semenenko, E.B. Lobkovskii, V.B. Polyakova, I.I. Korobov and O.V. Kravchenko, *Koord. Khim.*, 4 (1978) 1649.
- 12 B.M. Bulychev, A.L. Kostenko, G.L. Soloveichik and V.B. Polyakova, *Trans. Met. Chem.*, 6 (1981) 240.
- 13 B.M. Bulychev, A.L. Kostenko, G.L. Soloveichik and N.A. Yakovleva, *Trans. Met. Chem.*, 6 (1981) 32.
- 14 V.K. Bel'sky, I.V. Sokolova, A.I. Sizov and B.M. Bulychev, *Zh. Strukt. Khim.*, in press.
- 15 H. Antropiusova, A. Dosedlova and V. Hanuš, K. Mach, *Trans. Met. Chem.*, 6 (1981) 90.
- 16 K. Mach, H. Antropiusova and V. Hanuš, *Trans. Met. Chem.*, 10 (1985) 302.
- 17 V.V. Saraev, F.K. Shmidt, N.M. Ryutina and V.A. Makarov, *Koord. Khim.*, 3 (1977), 1364.
- 18 E.E. Van Tamelen, W. Cretney, N. Klaentschi and J.S. Miller, *J. Chem. Soc., Chem. Comm.*, (1972), 481.
- 19 G.P. Pez and S.K. Kwan, *J. Am. Chem. Soc.*, 98 (1976), 8079.
- 20 A.I. Sizov, M.K. Alekseev, G.L. Soloveichik and B.M. Bulychev, *Koord. Khim.*, 9 (1983) 492.
- 21 V.I. Andrianov, *Zh. Kristallogr.*, 32 (1987) 228.
- 22 V.I. Andrianov, Z. Sh. Safina and B.L. Tarnopol'sky, *Zh. Strukt. Khim.*, 15 (1974) 911.
- 23 V.I. Andrianov, T.A. Shibanova and V.I. Simonov, *Zh. kristallogr.*, 32 (1987) 41.
- 24 E.B. Lobkovskii, A.I. Sizov, B.M. Bulychev, I.V. Sokolova and G.L. Soloveichik, *J. Organomet. Chem.*, 319 (1987) 69.