

## Structural chemistry of titanium and aluminium bimetallic hydride complexes

### VII \*. Exchange reactions in the coordination sphere of aluminium atom. Crystal and molecular structure of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\mu_2\text{-H})_2]_2\text{Al}(\eta^2\text{-H}_2\text{BH}_2)$

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#### Abstract

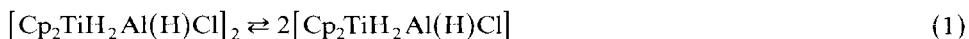
The interaction of  $\text{Cp}_2\text{TiH}_2\text{AlH}(\text{Cl})$ ,  $\text{Cp}_2\text{TiH}_2\text{AlCl}_2$ , and  $(\text{Cp}_2\text{Ti})\text{AlH}_4\text{Cl}$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) with  $\text{LiBH}_4$  in ether yields a four-nuclear complex  $\{\text{Cp}_2\text{Ti}(\mu_2\text{-H})_2\}_2\text{-Al}(\mu_2\text{-H})_2\text{BH}_2$  in 70–80% yields. The compound forms rhombic crystals:  $a$  9.515(3),  $b$  9.449(3),  $c$  22.051(4) Å, space group  $Pnab$ ,  $V$  1982 Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{calc}}$  1.35 g/cm<sup>3</sup>. The enlargement of the hydride complexes of aluminium and titanocene to three- and four-nuclear compounds is the result of the dissociation in solution of the bi-nuclear complexes to give the corresponding  $\text{AlXX}'_2$  alanes. This led us to revise the 17-component ESR spectrum of the complex  $\text{Cp}_2\text{TiH}_2\text{AlHCl}$ , and it was concluded that this spectrum is a superposition of the signals of  $\text{Cp}_2\text{TiH}_2\text{AlCl}_2$  and  $\text{Cp}_2\text{TiH}_2\text{AlHCl}$ , and perhaps of  $\text{Cp}_2\text{TiH}_2\text{AlH}_2$  (the singlet of  $(\text{Cp}_2\text{Ti})_2\text{AlH}_4\text{Cl}$ , which is also present in solution, does not affect the general picture of the spectrum). The specific rate of hydrogenation of hexene-1 on  $(\text{Cp}_2\text{Ti})\text{AlH}_4(\text{BH}_4)$  is 10 mol  $\text{H}_2$ /g-atom Ti min.

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\* For part VI, see ref. 4.

## Introduction

The bi-nuclear hydride complexes of the type  $(\eta^5\text{-C}_5\text{H}_5)_2\text{TiH}_2\text{M}$ , where  $\eta^5\text{-C}_5\text{H}_5 = \text{Cp}$ ,  $\text{M} = \text{AlH}_2$ ,  $\text{AlCl}_2$  [1,2],  $\text{MgX}$ ,  $\text{Li}$ ,  $\text{Na}$  [3], do not promote the reactions of olefin hydrogenation. The only exception is a mixed hydridochloride complex  $\text{Cp}_2\text{TiH}_2\text{Al}(\text{H})\text{Cl} \cdot \text{Et}_2\text{O}$  (I) [2]. This compound displays an activity, comparable to that of the three-centre complex  $[\text{Cp}_2\text{Ti}(\mu_2\text{-H})_2]_2\text{AlCl}$  (II), whose structure and the nature of catalytic action in the hydrogenation reaction have been discussed previously [1,4]. The hydrogenating properties of I, whose ether solution shows a characteristic 17-component ESR spectrum [5], are attributed to the



equilibrium, depicted in eq. 1, present in solution. This however, contradicts the conclusions arrived at previously [4,6]. It should also be noted that there is an alternative viewpoint [7] viz. the complex obtained described by Evdokimova [2] is not a single compound but a mixture of two substances,  $\text{Cp}_2\text{TiH}_2\text{Al}(\text{H})\text{Cl}$  and  $\text{Cp}_2\text{TiH}_2\text{AlCl}_2$  (III). Unfortunately, attempts to isolate I from solution in the form of single crystals were unsuccessful. However, it is known that replacement of the terminal hydrogens in the complexes,  $\text{Cp}_2\text{TiH}_2\text{AlH}_2 \cdot \text{L}$ , by more bulky acceptor (Hal) or donor (Alk) ligands in some cases increases the stability of the compounds [8]. It was suggested that the  $\text{BH}_4$  moiety, whose Van der Waals radius is close to that of chlorine atom but which unlike chlorine possesses donor properties, would serve as a stabilizing ligand for I.

Here we report on the results of a study of the exchanges which take place in the coordination sphere of the aluminium atom bound to the titanium atom via the Ti-H-Al bridges, on the results of the structural study of the heterometal complex  $\text{Cp}_2\text{TiH}_2\text{Al}(\text{BH}_4)\text{H}_2\text{TiCp}_2$ , and we illuminate some general aspects of catalysis by aluminium and titanium hydride complexes.

## Experimental

All reactions were carried out under air- and moisture-free conditions. Ether solutions of the titanium biscyclopentadienyl complexes  $\text{Cp}_2\text{TiBH}_4$  [9],  $\text{Cp}_2\text{TiAlH}_4 \cdot \text{L}$  [10],  $\text{Cp}_2\text{TiH}_2\text{Al}(\text{H})\text{Cl} \cdot \text{L}$  [5],  $\text{Cp}_2\text{TiH}_2\text{AlCl}_2 \cdot \text{L}$  [8], and  $(\text{Cp}_2\text{Ti})_2\text{AlH}_4\text{Cl}$  [4] were prepared by standard procedures.

Chemical analysis was carried out as described in Ref. 4. IR spectra (samples were suspensions in Nujol) in the region  $400\text{--}3000\text{ cm}^{-1}$  were recorded on an UR-20 spectrophotometer, and ESR spectra were recorded on a Varian E-3 instrument with  $\text{Mn}^{2+}$  in  $\text{MgO}$  as a standard. The catalytic activity of samples in the hydrogenation of hexene-1 was studied by use of a published procedure [1].

### *Synthesis of $(\text{Cp}_2\text{Ti})_2\text{AlH}_4\text{BH}_4$*

The complex  $(\text{Cp}_2\text{Ti})_2\text{AlH}_4\text{BH}_4$  was obtained in 70–80% yield on interaction of  $\text{Cp}_2\text{TiH}_2\text{Al}(\text{H})\text{Cl} \cdot \text{L}$ ,  $\text{Cp}_2\text{TiH}_2\text{AlCl}_2 \cdot \text{L}$ , and  $(\text{Cp}_2\text{Ti})_2\text{AlH}_4\text{Cl}$  with lithium borohydride ( $\text{Cl}/\text{LiBH}_4 = 1/1$ ), as well as on interaction of solutions of  $\text{Cp}_2\text{TiAlH}_4 \cdot \text{L}$  and  $\text{Cp}_2\text{TiBH}_4$  with  $\text{Cp}_2\text{TiBH}_4$  and  $\text{LiAlH}_4$ , respectively ( $\text{Ti}/\text{Al} = 2/1$ ). A typical synthesis was carried out as follows.

To a freshly prepared solution of 2 mmol of  $\text{Cp}_2\text{TiH}_2\text{Al}(\text{H})\text{Cl}$  in 25 ml of ether/benzene mixture (1/3) was added a cooled solution ( $-30^\circ\text{C}$ ) of 2 mmol of

Table 1

Atomic coordinates ( $\times 10^4$ ;  $\times 10^3$  for H) for the complex,  $(\text{Cp}_2\text{Ti})_2\text{AlH}_4(\text{BH}_4)$ 

Atom	x	y	z	$U_{\text{eq}}$
Ti	2808(3)	2620(3)	6147(1)	309(8)
Al	2500	3829(6)	5000	311(22)
C(1)	3245(16)	255(15)	6450(6)	481(67)
C(2)	3218(16)	298(15)	5830(9)	519(74)
C(3)	4291(29)	1100(24)	5607(8)	465(99)
C(4)	5030(13)	1595(13)	6128(7)	444(52)
C(5)	4399(23)	1072(20)	6640(9)	435(87)
C(6)	1948(29)	2786(24)	7148(8)	739(96)
C(7)	808(23)	2961(22)	6751(10)	551(89)
C(8)	986(26)	4188(25)	6423(8)	506(92)
C(9)	2241(28)	4821(18)	6607(9)	576(80)
C(10)	2836(19)	3970(20)	7040(6)	635(71)
B	2500	6227(28)	5000	621(135)
H(11)	159(9)	262(10)	5492(40)	
H(12)	165(10)	546(10)	520(4)	
H(13)	195(11)	670(11)	461(5)	
H(14)	343(10)	372(10)	567(5)	

$\text{LiBH}_4$  in 10 ml of  $\text{Et}_2\text{O}$  with stirring. The reaction mixture was allowed to warm to room temperature, the precipitate of  $\text{LiCl}$  was filtered off and the filtrate was kept overnight. The precipitate, dark-brown needles, was filtered, washed with ether, and dried in vacuo. The yield of  $(\text{Cp}_2\text{Ti})_2\text{AlH}_4\text{BH}_4$  was ca. 70%. Found: Ti, 24.5; Al, 7.0;  $\text{H}_{\text{act}}$ , 1.8.  $(\text{Cp}_2\text{Ti})_2\text{AlH}_4\text{BH}_4$  calc: Ti, 23.9; Al, 6.7;  $\text{H}_{\text{act}}$ , 2.0%.

#### Crystal structure determination for $(\text{Cp}_2\text{Ti})_2\text{AlH}_4\text{BH}_4$

The study was carried out on a single crystal of IV packed in a glass capillary, with an automatic Nicolet P3 diffractometer ( $\lambda(\text{Mo-K}_\alpha)$ , graphite monochromator,  $\theta/2\theta$  scanning to  $2\theta \leq 46^\circ$ ). The compound crystallized in a rhombic lattice with the unit cell parameters:  $a$  9.515(3),  $b$  9.449(3),  $c$  22.051(4) Å, space group  $Pnab$ ,  $Z = 4$ ,  $V$  1982(1) Å<sup>3</sup>,  $\rho_{\text{calc}}$  1.35 g/cm<sup>3</sup>. 387 reflections with  $I \geq 2\sigma(I)$  of a total of

Table 2

Main interatomic distances (Å) and bond angles ( $^\circ$ ) in molecule  $(\text{Cp}_2\text{Ti})_2\text{AlH}_4(\text{BH}_4)$ 

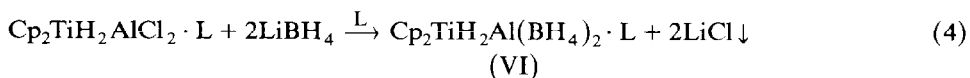
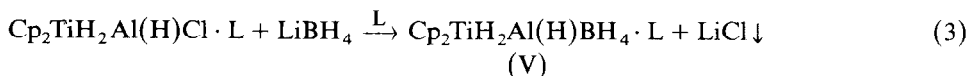
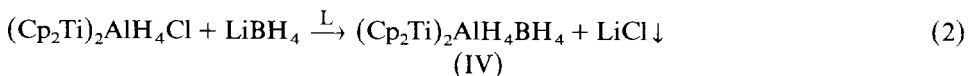
Ti...Al	2.790(4)	H(11)TiH(14)	73(4)
Ti-C(av)	2.35(3)	AlH(11)Ti	100(4)
Ti-Cp <sup>I</sup>	2.03	H(11)AlH(14)	72(4)
Ti-Cp <sup>II</sup>	2.04	AlH(14)Ti	115(6)
Al-B	2.27(3)	AlH(12)B	97(6)
Al-H(11)	1.8(1)	H(12)AlH(12A)	62(6)
Al-H(12)	1.8(1)	H(13)BH(13A)	132(6)
Al-H(14)	1.7(1)	H(12)BH(12A)	104(9)
B-H(12)	1.2(1)	H(12)BH(13)	102(7)
B-H(13)	1.1(1)	C-C-C (av)	108(2)
Ti-H(14)	1.6(1)	Cp <sup>I</sup> TiCp <sup>II</sup>	136.5
Ti-H(11)	1.9(1)	TiAlB	114
(C-C)(av)	1.39(3)		

456 were used in the calculations. The structure was solved by the direct method (absorption correction was neglected,  $\mu_{\text{Mo}} 8.8 \text{ cm}^{-1}$ ), and refined by the least-squares method in an anisotropic (isotropic for hydrogen atoms) approximation to  $R = 0.034$  ( $R_w = 0.032$ ).

The atomic coordinates are listed in Table 1; the main interatomic distances and angles are given in Table 2.

### Discussion and results

An interaction of  $\text{Cp}_2\text{TiH}_2\text{AlH}(\text{Cl}) \cdot \text{L}$ ,  $\text{Cp}_2\text{TiH}_2\text{AlCl}_2 \cdot \text{L}$ , and  $(\text{Cp}_2\text{Ti})_2\text{AlH}_4\text{Cl}$  with lithium borohydride in  $\text{Et}_2\text{O}$  or in  $\text{Et}_2\text{O}/\text{ArH}$  mixture was assumed to follow the reactions 2–4. However, quite unexpectedly it was found that the ESR signals of



the solutions of complexes IV–VI were identical, i.e. a singlet with  $g = 1.979$  and  $\Delta H = 12 \text{ G}$ . This value of  $g$  is close to that found for the titanium borohydride complexes  $\text{Cp}_2\text{TiBH}_4$  (1.982) and  $[(\text{Cp}_2\text{Ti}(\text{Cl})\text{BH}_4)_2]$  (1.979). It also coincides with the  $g$  factor for a solution of complex II and differs markedly from those values typical of the binuclear complexes  $\text{Cp}_2\text{TiH}_2\text{AlH}_n\text{Cl}_{2-n} \cdot \text{L}$  ( $1.991 \pm 0.002$ ) [11].

The IR spectra of the compounds and their crystallographic features were completely consistent with each other. These data show that reactions 2–4 yield exactly the same product, which, from chemical analysis, has been formulated as  $(\text{Cp}_2\text{Ti})_2\text{AlH}_4\text{BH}_4$  (IV). This compound was subjected to X-ray analysis.

The crystalline structure of complex IV is composed of four-nuclear monomeric molecules  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\mu_2\text{-H})\text{Al}(\mu_2\text{-H}_2\text{BH}_2)(\mu_2\text{-H})_2\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2$  (Fig. 1), whose  $\text{Cp}_2\text{Ti}$  moieties are linked to the aluminium atom by double hydrogen bridges. The structure of the wedge-like sandwiches  $(\text{C}_5\text{H}_5)_2\text{Ti}$  in molecule IV (Table 2) is close to that of the alumohydride complexes  $(\text{Cp}_2\text{TiH}_2\text{AlH}_2)_2 \cdot \text{TMEDA}$  [10],  $\text{Cp}_2\text{TiH}_2\text{AlCl}_2 \cdot \text{OEt}_2$  [8],  $[\text{Cp}_2\text{TiH}_2\text{Al}(\text{H})\text{OMe}]_2$  [12],  $[\text{Cp}_2\text{TiH}_2\text{AlH}(\text{C}_5\text{H}_4)\text{TiCpH}]_2$  [13], and  $(\text{Cp}_2\text{Ti})_2\text{AlH}_4\text{Cl}$  [4], i.e.  $r(\text{Ti}-\text{C}_{\text{Cp}}) = 2.32\text{--}2.36 \text{ \AA}$ ,  $\angle \text{CpTiCp} = 137\text{--}140^\circ$ .

The  $\text{Ti} \cdots \text{Al}$  distances in IV are identical ( $2.79 \text{ \AA}$ ) and are consistent with data published for compounds of this type ( $2.75\text{--}2.79 \text{ \AA}$ ) [4,8,10,12,13]. It should be noted that the  $\text{Ti}-\text{H}(11)$  and  $\text{Ti}-\text{H}(14)$  distances are noticeably different ( $1.59$  and  $1.85 \text{ \AA}$ ), whereas the  $\text{Al}-\text{H}(11)$  and  $\text{Al}-\text{H}(14)$  distances are almost the same (Table 2). Similar bonding between two transition metal atoms and an aluminium atom has been found in the complexes,  $[(\text{C}_5\text{Me}_5)_2\text{Ti}]_2\text{AlH}_5$  ( $r(\text{W} \cdots \text{Al}) = 2.77$  and  $2.83 \text{ \AA}$ ) [14],  $(\text{Cp}_2\text{Ti})_2\text{AlH}_4\text{Cl}$  ( $r(\text{Ti} \cdots \text{Al}) 2.77 \text{ \AA}$ ) [4], and  $(\text{Me}_3\text{P})_3\text{H}_3\text{W}_2\text{AlH}_5$  ( $r(\text{W} \cdots \text{Al}) 2.69 \text{ \AA}$ ) [15].

Replacement of the chlorine atom in II by the more bulky  $\text{BH}_4$  moiety in IV does not change the MAIM angle significantly ( $139.0^\circ$  in II and  $131.7^\circ$  in IV). As in the other derivatives of aluminium borohydride the borohydride moiety in complex IV shows bidentant properties. The  $\text{BH}_4$  moiety represents a distorted

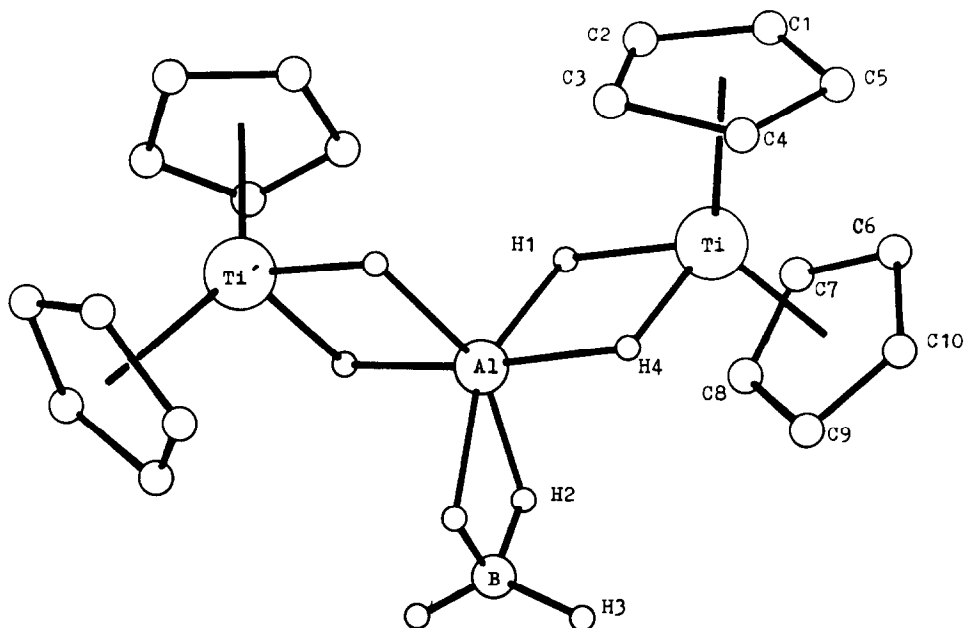
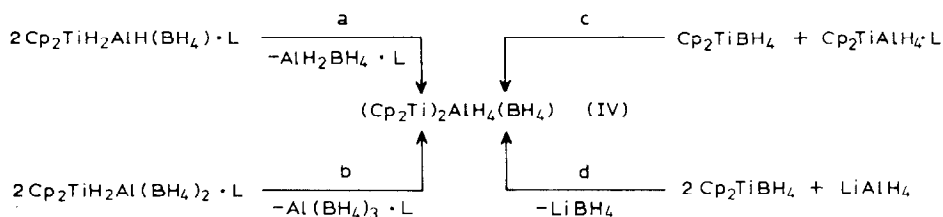


Fig. 1. Molecular structure of the complex  $[\text{Cp}_2\text{Ti}(\mu_2\text{-H})_2]_2\text{Al}(\eta^2\text{-H}_2\text{BH}_2)$ .

tetrahedron, with the  $\text{H}^b\text{BH}^b$  angle ( $132^\circ$ ) being essentially different from the others. The  $\text{Al}\cdots\text{B}$  distance in IV ( $2.27 \text{ \AA}$ ) is greater than the corresponding distance in  $\text{Al}(\text{BH}_4)_3$  ( $2.14 \text{ \AA}$ ) [16]. A noticeable bathochromic shift of the absorption band for  $(\text{Al}-\text{B})$  in the IR spectrum of IV ( $445 \text{ cm}^{-1}$ ), as compared with  $(\text{Al}-\text{B})$  in  $\text{Al}(\text{BH}_4)_3$  ( $616 \text{ cm}^{-1}$ ) [17], is consistent with the elongation of the  $\text{Al}\cdots\text{B}$  distance. At the same time, the absorption bands in the IR spectrum of IV, associated with the B-H bond vibrations in the bidentate borohydride moiety, viz. those at  $2450, 2400 \text{ cm}^{-1}$  for  $(\text{B}-\text{H}^a)$ ,  $2140, 1940 \text{ cm}^{-1}$  for  $(\text{B}-\text{H}^b)$ ,  $1355, 1280 \text{ cm}^{-1}$  for  $(\text{H}^a\text{BH}^a, \text{H}^a\text{BH}^b)$ , and  $1150 \text{ cm}^{-1}$  for  $(\text{H}^b\text{BH}^b)$ , differ little from those observed, e.g., in  $\text{Cp}_2\text{TiBH}_4$  ( $2470, 2405, 2105, 1950, 1350, 1240, 1150 \text{ cm}^{-1}$ ) [9], so that these vibrations are highly characteristic. A set of absorption bands in the range  $1100\text{--}1500 \text{ cm}^{-1}$  in the spectrum of IV is associated with Ti-H-Al bond vibrations.

The coordination polyhedron of the aluminium atom in molecule IV is a distorted octahedron ( $r(\text{Al}-\text{H}) = 1.7\text{--}1.8 \text{ \AA}$ ), which is unusual in that, they usually involve a trigonal-bipyramidal coordination [4,8,10,12-14]. It should be pointed out that the octahedral hydride environment of the aluminium atom is encountered only seldom and has been observed in  $\text{M}_3\text{AlH}_6$  ( $r(\text{Al}-\text{H}) = 1.60 \text{ \AA}$ ) [18], in polymeric aluminium hydride ( $r(\text{Al}-\text{H}) = 1.72 \text{ \AA}$ ) [19], and in the recently obtained complex  $(\text{Me}_3\text{P})_3\text{H}_2\text{WH}_3\text{AlCl}_2(\text{NMe}_3)$  ( $r(\text{Al}-\text{H}) = 1.68, 1.89, 1.91 \text{ \AA}$ ) [20].

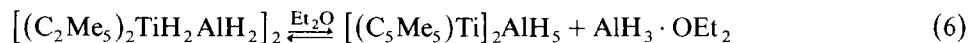
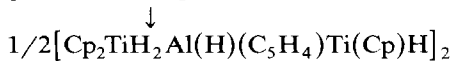
Thus, analysis of these data shows that complexes V and VI are unstable, and even if they are formed in reactions 3 and 4, they undergo rapid transformation which leads to splitting of the respective aluminium borohydride derivative to give stable complex IV (Scheme 1). This compound can also be obtained on interaction of  $\text{Cp}_2\text{TiBH}_4$  with the stoichiometric amounts of  $\text{Cp}_2\text{TiAlH}_4$  or  $\text{LiAlH}_4$ .



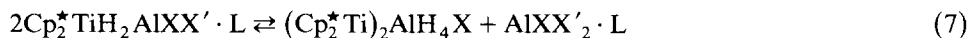
Scheme 1

A large number of reactions leading to complex IV shows that the migration of the covalently bonded borohydride moiety from Ti to Al (Scheme 1, c,d) and between the aluminium atoms (a,b) proceeds readily. A similar type of migration by halogen ligands was found in reactions of  $(\text{Cp}_2\text{TiX})_2$  with  $\text{AlH}_{3-n}\text{X}_n$  [11].

It should be pointed out that the rearrangement of complexes, similar to that observed for V and VI (Scheme 1, a,b), was also encountered in studies of titanocene alumohydride complexes. In fact, prolonged storage of  $\text{Cp}_2^*\text{TiH}_2\text{AlH}_2 \cdot \text{L}$  solutions leads to the formation of the tri-nuclear complexes  $(\text{Cp}_2^*\text{Ti})_2\text{AlH}_5$  (eqs. 5 [13] and 6 [14]):



It can easily be seen that these reactions are versions of the same process, i.e. the condensation (enlargement) of the binuclear complexes to trinuclear ones, as in eq. 7:



From the data presented in this work and in the literature it follows that the rate of reaction 7, and its conversion, increase for complexes with the ligands thus:  $\text{X}(\text{X}') = \text{Cl}(\text{H}) \ll \text{H}(\text{H},\text{Cl}) \ll \text{BH}_4(\text{H},\text{BH}_4)$ . So, reaction 7 in the case  $\text{X} = \text{X}' = \text{BH}_4$  or  $\text{X} = \text{H}, \text{X}' = \text{BH}_4$  in  $\text{Et}_2\text{O}$  proceeds at high rates with almost total conversion, which is evidenced by high yields of complex IV. For  $\text{X} = \text{X}' = \text{H}$  the reaction rate is much lower. Furthermore in order to shift the equilibrium towards the products the split  $\text{AlH}_3$  species should be fixed in a stable complex with TMEDA or 1,4-dioxane [13]. Since unsymmetric complexes are less stable as a rule, the equilibrium 7 is shifted towards  $\text{Cp}_2\text{TiH}_2\text{AlH}(\text{Cl}) \cdot \text{L}$  to a greater extent than in the case of  $\text{Cp}_2\text{TiH}_2\text{AlH}_2 \cdot \text{L}$ . The most stable compound with  $\text{L} = \text{Et}_2\text{O}$  in the series considered is the complex  $\text{Cp}_2\text{TiH}_2\text{AlCl}_2 \cdot \text{OEt}_2$  (VII) [8], for which the equilibrium 7 is shifted almost completely towards the reagents.

On the assumption that equilibrium 7 takes place, and taking into account the order of stabilities towards dissociation of the complexes with different X and X', we revised the 17-component ESR spectrum of the solution of complex  $\text{Cp}_2\text{TiH}_2\text{AlH}(\text{Cl})$  resulting from reaction 8 [5,11]. From the above considerations it



follows that the formation of I is accompanied by its partial dissociation (eq. 7). The

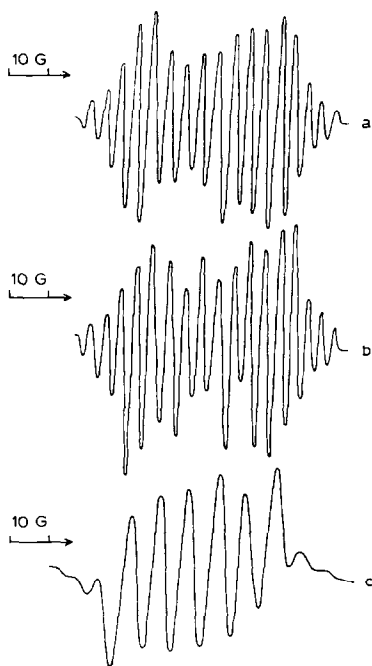


Fig. 2. ESR spectra: (a) Combined spectrum of  $\text{Cp}_2\text{TiH}_2\text{AlCl}_2$  and  $\text{Cp}_2\text{TiH}_2\text{AlH(X)}$  (3/1). (b) The spectrum of  $[\text{Cp}_2\text{TiH}_2\text{AlH(Cl)}]_2$  [5]. (c) The spectrum of  $\text{Cp}_2\text{TiD}_2\text{AlD(Cl)}$ .

monochloralane  $\text{AlH}_2\text{Cl}$  thus obtained enters a reaction in competition with that of  $(\text{Cp}_2\text{TiCl})_2$  by eq. 9 to give a stable dichloride III. From this it follows that the hyperfine structure of the ESR spectrum of the solution obtained by reaction 8 is probably determined, by a superposition of the signals for complexes I and III (the



signal for II, i. e. a broad singlet with  $g = 1.989$  and  $\Delta H = 45$  G [4], does not contribute to the hyperfine structure). The sum of the spectrum of I (similar to the 13-component spectrum of  $\text{Cp}_2\text{TiH}_2\text{AlHBr}$  with  $g = 1.941$ ,  $a_{\text{Al}} = 7.5$ ,  $a_{\text{H}} = 3.7$  G [10]), and that of III (a sextet of triplets with  $g = 1.990$ ,  $a_{\text{Al}} = 10.0$ ,  $a_{\text{H}} = 3.4$  G [11]), assuming that the weight ratio I/III = 3/1, gives a spectrum (Fig. 2a) close to that described elsewhere [5] (Fig. 2b). Table 3 shows that the intensity distribution in the combined spectrum 2a is more consistent with the observed than that the calculated, which assumes that there is spin splitting on three  $^1\text{H}$  and one  $^{27}\text{Al}$  nuclei ( $a_{\text{H}} = 7.0$ ,  $a_{\text{H}1} = 3.5$ ,  $a_{\text{Al}} = 3.0$  G [5]). The correctness of these considerations is supported by the ESR spectrum of the deuterio-substituted analogue of I, i. e.  $\text{Cp}_2\text{TiD}_2\text{AlD(Cl)}$  (Fig. 2c). Its spectrum is a sextet due to splitting on the  $^{27}\text{Al}$  nucleus ( $a_{\text{Al}} = 7.5$  G), with two weak satellites, which represent the components of the sextet associated with the complex  $\text{Cp}_2\text{TiD}_2\text{AlCl}_2$  ( $a_{\text{Al}} = 10.0$  G). This interpretation of the spectrum of I best explains the thermal dependence of its shape, which had been established previously [11]; when I is made at decreased temperature (eq. 8) the spectrum more closely resembles a 13-component multiplet, and at  $-60$ – $-70^\circ\text{C}$  the solution

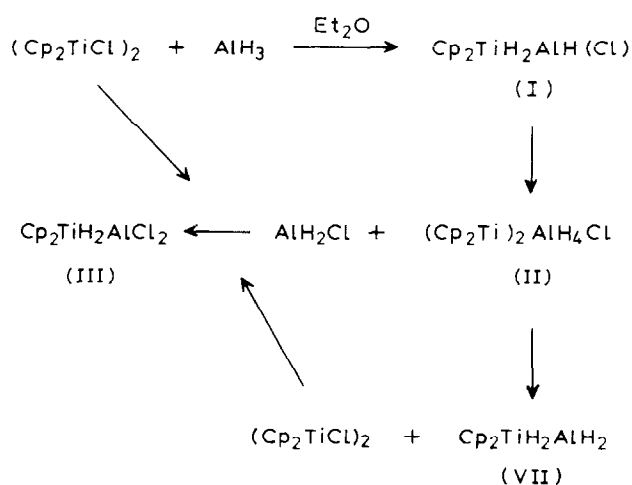
Table 3

Comparison of line intensities in the observed ESR spectrum of  $\text{Cp}_2\text{TiH}_2\text{AlH}(\text{Cl})$  solution with those calculated (B) [5] and with the sum of the spectra of complexes I and II (A)

Number of line	Observed	Calc	Calc	Number	Observed	Calc	Calc
Relative intensity		A	B	Relative intensity		A	B
1	1	1	1	10	6.5	7	4
2	2	2	1	11	3.5	6.5	3
3	4	4	3	12	6	7.5	4
4	7.5	7	3	13	9	8.5	4
5	8	8	4	14	8	7	3
6	6	5.5	4	15	3.5	3.5	3
7	3	4	3	16	2	2	1
8	4	4.5	4	17	1	1	1
9	4	5	2				

contains practically pure  $\text{Cp}_2\text{TiH}_2\text{AlH}(\text{Cl})$ . It is obvious that with an increase in temperature the dissociation of I (eq. 7) becomes more important and its spectrum becomes more complicated. Hence, the suggestion as to the nature of the spectrum of  $\text{Cp}_2\text{TiH}_2\text{AlH}(\text{Cl})$  [7], should be seen as being correct; however, taking into account published data [4], the actual situation in solution may well be still more complicated, as the 17-component multiplet could be the superposition of many as three spectra,  $\text{Cp}_2\text{TiH}_2\text{AlH}(\text{Cl})$ ,  $\text{Cp}_2\text{TiH}_2\text{AlCl}_2$ , and perhaps,  $\text{Cp}_2\text{TiH}_2\text{AlH}_2$  (VII) (Scheme 2).

The formation in solution of complex I of the trinuclear complex II accounts for the high catalytic activity of  $\text{Cp}_2\text{TiH}_2\text{AlH}(\text{Cl})$  in the reactions of olefin hydrogenation, and this eliminates the contrasting conclusions of the work refs. 4 and 6. That the introduction of an olefin and hydrogen into the system seems to shift the equilibrium 7 towards the products to an greater extent remains to be seen.



Scheme 2



Taking into account the similarity of structural features of the  $\text{BH}_4$  moiety and  $\text{Cl}^-$ , it was expected that complex IV, like II, would serve as an active catalyst in olefin hydrogenation. In fact, the specific rate of hydrogenation of hexene-1 on this catalyst is 10 mol  $\text{H}_2$ /g-atom Ti min. The reduced activity of IV, compared with that of II, can reasonably be accounted for by the structural differences of these compounds and by the greater stability of the trinuclear borohydride complex IV (compared with the chloride complex I), which hinders the generation of active species by a mechanism proposed previously [4].

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