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ON THE INTERACTION OF CYCLOPENTADIENYLTITANIUM(IV) CHLORIDES WITH LITHIUM ALUMINIUM HYDRIDE

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Summary

The interactions in the systems $Cp_2TiCl_2/LiAlH_4$ and $CpTiCl_3/LiAlH_4$ have been studied by calorimetric titration and EPR techniques. There are four steps to each of these reactions corresponding to the following Cp_2TiCl_2 ($CpTiCl_3$) to $LiAlH_4$ ratios: 2/1 (reduction of titanium(IV) to titanium(III) and formation of trinuclear complexes $Cp_2TiH_2AlCl_2 \cdot Cp_2TiCl$ or $Cp(Cl)TiH_2AlCl_2 \cdot CpTiCl_2$), 1/1 (formation of dimers $[Cp_2TiH_2AlH(Cl)]_2$ or $[Cp(Cl)TiH_2AlH(Cl)]_2$), 1/1.5 (replacement of a terminal chloro atom in the dimers and formation of $(Cp_2TiH_2)_2Al_2H_3Cl$ or $(Cp(Cl)TiH_2)_2Al_2H_3Cl$), and 1/2 (replacement of the remaining terminal chloro atom, dissociation of dimers and formation of unstable triple complexes $Cp_2TiH_2AlH_2 \cdot AlH_3$ or $Cp(Cl)TiH_2AlH_2 \cdot AlH_3$). The catalytic properties of the system $Cp_2TiCl/LiAlH_4$ in the hydrogenation of cyclohexene and hex-1-ene are described.

Introduction

The systems $Cp_2TiCl_2/LiAlH_4$ and $CpTiCl_3/LiAlH_4$ have been used as catalysts for hydrogenation, isomerization and hydrometallation of olefins [1—4]. The intermediate and final products occurring in the interaction of titanium(IV) compounds with lithium aluminium hydride have, however, been thus far undetermined. We have studied these reactions in ether and ether/benzene (1/1) solutions by calorimetric titration (CT) and EPR techniques at 20°C. Some of the products have been tested as catalysts for the hydrogenation of olefins.

Experimental

Materials

Cp_2TiCl_2, $CpTiCl_3$ and Cp_2TiCl were synthesized by literature methods [5—7]. Recrystallized lithium aluminium hydride was of 98.5—99.0% or higher purity. The solvents were thoroughly dried and distilled over $LiAlH_4$. All the operations were carried out under spectroscopically pure argon or under vacuum. The solutions were prepared immediately before use. Hydrogen was purified by adsorption onto and desorption from the intermetallic compound, $LaNi_5$. Hex-1-ene and cyclohexene were sublimed into calibrated vessels under vacuum.

Apparatus

Calorimetric titration [8] was performed in an airtight cell made as a Dewar vessel. Temperature changes were registered with a thermistor of 40000 Ω resistivity. The calorimeter heat capacity was determined by electrical technique. The EPR spectra were recorded on a "Varian" E-3 3 cm band radiospectrometer under a 100 kHz high-frequency modulation. The *g*-factor values were calculated from the EPR spectra of the complex and the signal from Mn^{2+} in magnesium oxide recorded simultaneously.

Experimental technique

Titanium compounds were titrated in ether and ether/benzene (1/1 v/v) solutions. The mixed solvent has certain advantages because of the higher solubility of titanium compounds and lower residual water content after distillation over $LiAlH_4$ (0.006 and 0.004 weight % in Et_2O and Et_2O/C_6H_6, respectively). The presence of trace amounts of water manifest itself by the appearance of features corresponding to hydrolysis of lithium aluminium hydride on CT curves (segments "oa" and "o′a′" in Figs. 1 and 3). The hydrolysis reaction did not affect the major process; it should, however, be taken into account in calculations of thermal effects and reagent ratios corresponding to the equivalence points.

Solutions of Cp_2TiCl_2 and $CpTiCl_3$ were made by dissolving weighed amounts of the compounds in fixed quantities of the solvents. The titer of the $LiAlH_4$ solution was determined by measuring Li and Al contents. The reaction between $CpTiCl_3$ and $LiAlH_4$ was studied by direct ($LiAlH_4$ as titrant) and reverse (a titanium(IV) compound as titrant) titration. The reaction involving Cp_2TiCl_2 was studied by direct titration only because of the low solubility of the dichloro derivative. For EPR and visible absorption spectrum measurements the solutions were sampled at the equivalence points corresponding to the formation of definite complexes. The samples were then transferred to airtight ampoules, and sealed under vacuum. The spectra from $CpTiCl_3/LiAlH_4$ and $Cp_2Ti\ Cl_2/LiAlH_4$ solutions containing the components in the same ratio were identical. Reproducibility of the spectra obtained with the former system was, however, rather poor because of the low stability of the complexes formed. We will therefore concentrate on the spectra of $Cp_2TiCl_2/LiAlH_4$ mixtures.

Hydrogenation of olefins was carried out following the standard procedure (a two-chamber reaction vessel, $p(H_2)$ 1 atm, t 20 ± 1°C.). The course of the reaction was followed both chromatographically and by measuring the hydrogen uptake.

Results and discussion

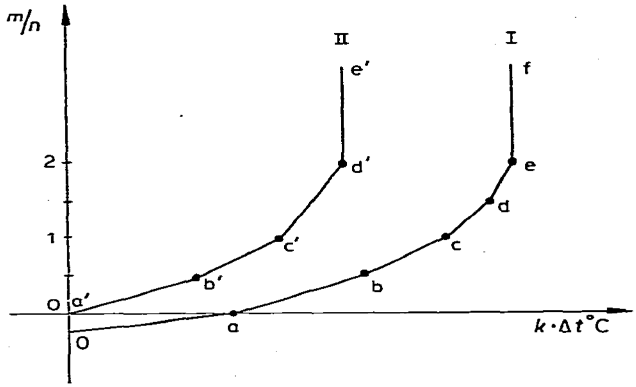
The results for the $CpTiCl_3/LiAlH_4$ system obtained by direct and reverse CT in ether/benzene (1/1) are given in Table 1. The CT curves are depicted in Fig. 1. The interaction between the components proceeds in 4 steps, the overall heat

TABLE 1

DIRECT (No. 1—6) AND REVERSE (No. 7—13) CT RESULTS FOR THE $CPTiCl_3/LiAlH_4$ SYSTEM IN ETHER/BENZENE AT 20°C

No.	C_{solid} (mol/l)	$C_{titrant}$ (mol/l)	Q_x (cal/degree)	I (e.p.)[a] $CpTiCl_3/LiAlH_4$	$-H_1$	II (e.p.) $CpTiCl_3/LiAlH_4$	$-H_2$	III (e.p.) $CpTiCl_3/LiAlH_4$	$-H_3$	IV (e.p.) $CpTiCl_3/LiAlH_4$	$-H_4$	$-H_{total}$ (kcal/mol)
1	0.0017	0.29	117.62	2.1/1	48.11	1.0/1	26.46	1/1.4	15.64	1/2.0	6.82	97.03
2	0.0020	0.34	94.25	2.0/1	46.58	1.0/1	27.36	1/1.4	14.79	1/2.0	6.65	95.38
3	0.0027	0.29	230.75	1.9/1	48.71	1.0/1	25.03	1/1.5	16.91	1/2.0	8.12	98.77
4	0.0029	0.45	244.96	2.0/1	50.66	1.0/1	25.96	1/1.5	14.94	—	—	—
5	0.0031	0.36	99.90	2.0/1	48.96	1.0/1	25.80	1/1.5	15.53	1/2.0	6.32	96.61
6	0.0037	0.40	280.23	2.0/1	48.73	1.0/1	27.29	1/1.5	12.67	1/2.0	7.80	96.51
	average			2.0/1	48.63	1.0/1	26.32	1/1.5	15.08	1/2.0	7.14	96.86
					±1.08		±0.54		±1.14		±0.70	±1.10
7	0.0004	0.14	107.15	2.0/1	50.20	1.0/1	26.19	1/2.0	19.86			96.22
8	0.0016	0.09	92.64	2.1/1	53.91	1.0/1	24.81	1/2.0	17.11			95.83
9	0.0017	0.14	109.15	2.0/1	50.94	1.0/1	24.93	1/2.0	20.59			96.46
10	0.0026	0.13	103.22	2.0/1	54.49	1.0/1	21.84	1/1.7	16.54			92.97
11	0.0027	0.10	114.52	2.0/1	48.84	1.0/1	22.01	1/2.0	19.95			90.80
12	0.0035	0.13	120.76	2.0/1	48.82	1.0/1	26.15	1/2.1	22.66			97.63
13	0.0038	0.26	82.52	2.0/1	47.86	1.0/1	22.48	—	—			—
	average			2.0/1	50.73	1.0/1	24.06	1/2.0	19.45			94.99
					±1.97		±1.44		±1.86			±2.10

[a] e.p. = equivalence point.



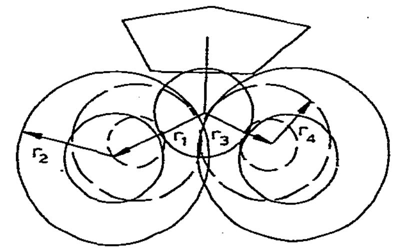


Fig. 1. Direct (II) and reverse CT of $CpTiCl_3$ with $LiAlH_4$ in ether/benzene solution n = number of mols of the compound undergoing titration, m = number of mols of the titrant, k = scale factor for conversion of instrument readings (mm) into degrees centigrade.

Fig. 2. Molecular model of $CpTi(MH_4)_2$ (M = Al, B). ($r_1 = r(Al—Ti)$; $r_2 = vdWr(AlH_4)$; $r_3 = r(B—Ti)$; $r_4 = vdWr(BH_4)$).

being equal to —96.86 ± 1.10 kcal/mol. (All heat values are given per mol of the titrated compound). The process terminates at the formation of a 1/2 $CpTiCl_3/LiAlH_4$ complex. The overall equation for the reaction may be written in the form:

$$CpTiCl_3 + 2\ LiAlH_4 \rightarrow \{Cp(Cl)TiH_2AlH_2 + AlH_3\} + 2LiCl + \tfrac{1}{2} H_2 \qquad (1)$$

The first step corresponds to the "ab" segment of curve 1 (Fig. 1). The heat of reaction is equal to —48.63 ± 1.08 kcal/mol; it terminates at a $CpTiCl_3$ to $LiAlH_4$ ratio of 2/1. Judging by the evolution of hydrogen and the appearence of an EPR signal, the first step involves reduction of titanium(IV) to titanium(III) and follows eq. 2.

$$2\ CpTiCl_3 + LiAlH_4 \rightarrow \{2\ CpTiCl_2 \cdot AlH_2Cl\} + LiCl + H_2 \qquad (2)$$

The EPR data show that the monochloroalane formed in reaction 2 is bound to a complex with $CpTiCl_2$ via two hydrogen bridges: $\mathrm{CpClTi}\begin{matrix}\mathrm{H}\\ \\ \mathrm{H}\end{matrix}\mathrm{Al}\begin{matrix}\mathrm{Cl}\\ \\ \mathrm{Cl}\end{matrix}$. One more $CpTiCl_2$ molecule remains in solution although it has been reported in the literature [7] that the compound is practically insoluble. It therefore seems probable that the trinuclear complex $[Cp(Cl)TiH_2AlCl_2 \cdot CpTiCl_2]$ occurs in the solution.

The second step (segment "bc") contributes —26.32 ± 0.54 kcal/mol and terminates at a $CpTiCl_3/LiAlH_4$ ratio of 1/1. The process is likely to involve the replacement of chlorine in $CpTiCl_2$ with AlH_4^- and may follow eq. 3 and/or 3a:

$$\{Cp(Cl)TiH_2AlCl_2 \cdot CpTiCl_2\} + LiAlH_4 \rightarrow \{Cp(Cl)TiH_2AlCl_2 + Cp(Cl)TiH_2AlH_2\} + LiCl \qquad (3)$$

$$\{Cp(Cl)TiH_2AlCl_2 \cdot CpTiCl_2\} + LiAlH_4 \rightarrow 2\{Cp(Cl)TiH_2AlHCl\} + LiCl \qquad (3a)$$

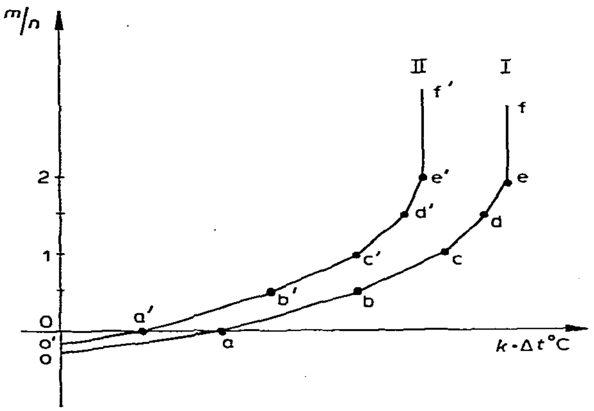


Fig. 3. CT curves for Cp_2TiCl_2 in ether(I) and ether/benzene(II). n = number of mols of the compound undergoing titration, m = number of mols of the titrant, k = scale factor for conversion of instrument readings (mm) to degrees centigrade.

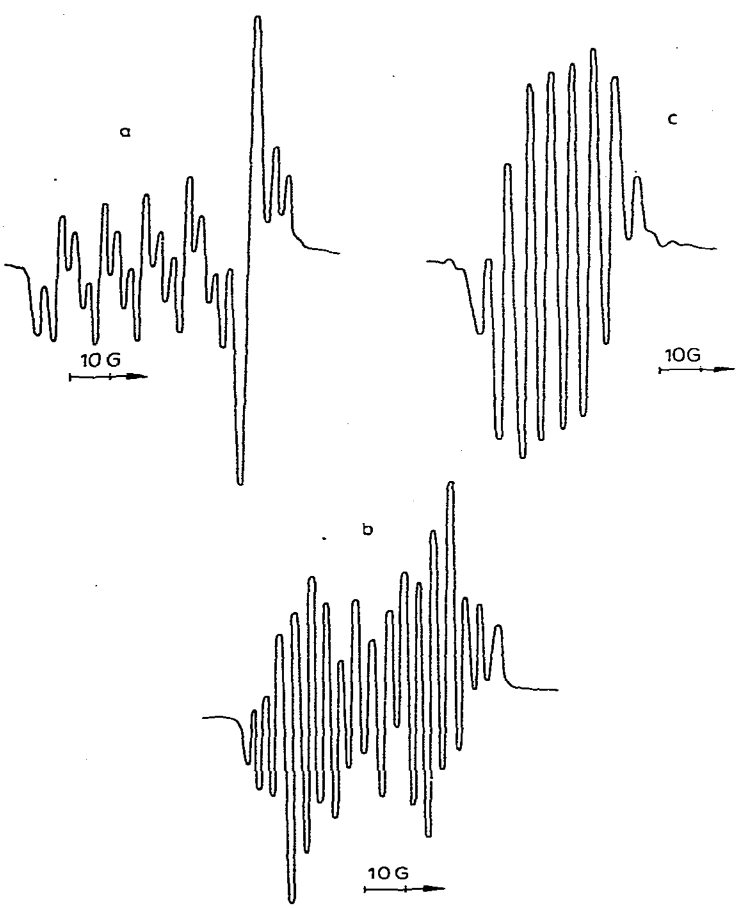


Fig. 4. EPR spectra of the complexes obtained by mixing Cp_2TiCl_2 and $LiAlH_4$ in the ratios 2/1 (a), 1/1 (b), 1/2 (c).

TABLE 2

CT OF Cp_2TiCl_2 WITH $LiAlH_4$ IN DIETHYL ETHER OR ETHER/BENZENE SOLUTIONS (No. 9–13) AT 20°C

No.	C_{solid} (mol/l)	$C_{titrant}$ (mol/l)	Q_x (cal/degree)	I (e.p.)[a] Cp_2TiCl_2/$LiAlH_4$	$-H_1$	II (e.p.) Cp_2TiCl_2/$LiAlH_4$	$-H_2$	III (e.p.) Cp_2TiCl_2/$LiAlH_4$	$-H_3$	IV (e.p.) Cp_2TiCl_2/$LiAlH_4$	$-H_4$	$-H_{total}$ (kcal/mol)
1	0.0004	0.27	81.18	—	—	—	—	—	—	—	—	90.07
2	0.0005	0.25	78.00	—	—	—	—	—	—	—	—	91.12
3	0.005	0.23	107.56	2.0/1	48.39	1.0/1	26.40	1/2.0	19.80			94.59
4	0.0007	0.20	113.93	1.7/1	47.56	0.9/1	25.61	1/2.1	18.29			91.46
5	0.0007	0.19	99.33	2.0/1	45.27	0.9/1	27.86	1/2.1	22.64			95.77
6	0.0008	0.23	99.86	2.1/1	43.59	1.0/1	26.72	1/2.0	22.50			92.81
7	0.0008	0.19	76.86	—	—	—	—	—	—			91.53
8	0.0009	0.23	113.10	2.1/1	46.85	1.0/1	23.43	1/2.0	19.29	—	—	89.57
	average			2.0/1	46.33	1.0/1	26.00	1/2.0	20.50			92.12
					±1.72		±1.48		±1.76			±2.54
9	0.0018	0.21	95.70	2.1/1	44.68	1.0/1	24.13	1/1.5	14.48	1/1.9	6.82	90.11
10	0.0018	0.15	102.79	2.0/1	45.97	1.0/1	24.05	1/1.5	13.13	1/2.0	10.22	93.37
11	0.0021	0.15	90.89	2.1/1	46.98	1.1/1	27.64	1/1.5	13.47	1/2.0	8.29	96.38
12	0.0021	0.15	238.81	2.0/1	43.90	1.0/1	20.26					
13	0.0024	0.44	110.10	2.1/1	44.18	1.1/1	23.79	1/1.5	12.93	1/1.9	6.47	88.34
	average			2.1/1	45.14	1.0/1	23.97	1/1.5	13.50	1/2.0	7.95	92.06
					±1.16		±2.34		±0.68		±1.70	±3.50

[a] e.p. = equivalence point.

As the EPR signal observed at "c" corresponds to an individual compound rather than to a mixture (Fig. 4b), the preferred equation is 3a. On the other hand, two points of equivalence occur in the further titration, at $CpTiCl_3/LiAlH_4$ ratios of 1/1.5 and 1/2, and all the steps proceed with precipitation of LiCl. This requires that the $Cp(Cl)TiH_2AlHCl$ molecule contains two chlorine atoms at two aluminium atoms which suggests an at least dimeric structure. Steps III and IV may then be written as follows

$$\{Cp(Cl)TiH_2AlHCl\}_2 + LiAlH_4 \rightarrow \{[Cp(Cl)TiH_2]_2Al_2H_3Cl + AlH_3\} + LiCl \quad (4)$$

$$\{[Cp(Cl)TiH_2]_2Al_2H_3Cl + AlH_3\} + LiAlH_4 \rightarrow 2\{Cp(Cl)TiH_2AlH_2 + AlH_3\} + LiCl \quad (5)$$

The analytical data and the X-ray powder photograph of the products from eq. 5 show that aluminium hydride decomposes in solution almost completely after 2 to 5 h (eq. 6):

$$AlH_3 \rightarrow Al + 1\tfrac{1}{2}H_2 \quad (6)$$

For this reason the amount of hydrogen evolved significantly exceeds the expected value (see eq. 1).

The addition of the third mol of $LiAlH_4$ results in replacement of one more chlorine atom. No detectable heat release occurs. The reaction supposedly follows eq. 7.

$$\{Cp(Cl)TiH_2AlH_2 + AlH_3\} + LiAlH_4 \rightarrow \{CpTi(AlH_4)_2 + AlH_3\} + LiCl \quad (7)$$

The mixture formed is exceedingly unstable and decomposes vigorously within 20—30 min of the addition of $LiAlH_4$ to give 4.5—5.0 mol of hydrogen and aluminium metal (when gas evolution ceases, the Ti/Al ratio in solution becomes 1/1). It is not clear, however, whether the reason for decomposition is the instability of the $CpTi(AlH_4)_2$ complex or the catalytic action by decomposition products from AlH_3. It is possible that both factors contribute. In fact, $CpTi(AlH_4)_2$ may be thought to have a similar structure to $CpTi(BH_4)_2$ (a monomeric molecule of C_{2v} symmetry [9]). In such a unit with the angle AlTiAl of 120°, r(Al—Ti) of 2.79 Å [1] and the AlH_4^- Van der Waals radius of 2.6 Å, a considerable spatial overlap between the two AlH_4^- moieties should occur (Fig. 2). As the Al—Ti distance in a doubly-bridged species should be shorter than 2.79 Å (this value being observed in singly-bridged $[Cp(C_5H_4)TiHAlEt_2]_2$ [10]), the overlap may be still larger, to the extent that makes the complex unstable.

The results of the reverse CT of $CpTiCl_3$ (Table 1, Fig. 1, II) agree on the whole with the results of the direct CT. The first step of the process corresponds to the summarized eq. 1, the second and third steps may be described by eq. 8 and 9, respectively;

$$\{Cp(Cl)TiH_2AlH_2 + AlH_3\} + CpTiCl_3 \rightarrow \{Cp(Cl)TiH_2AlHCl\}_2 + \tfrac{1}{2}H_2 \quad (8)$$

$$\{Cp(Cl)TiH_2AlHCl\}_2 + 2\ CpTiCl_3 \rightarrow 2\{Cp(Cl)TiH_2AlCl_2 \cdot CpTiCl_2\} + \tfrac{1}{2}H_2 \quad (9)$$

The overall heat of the reverse process, ca. 95 kcal/mol $LiAlH_4$, approaches the value found for the first step of the direct CT (ca. 97 kcal/mol $LiAlH_4$). It should, however, be noted that the formation of $\{Cp(Cl)TiH_2AlHCl\}_2$ from $\{Cp(Cl)TiH_2AlH_2 + AlH_3\}$ is a one-step reaction unlike the reverse reaction occurring in the direct CT which involves two steps. This may be due to the fact that in the reverse CT, $CpTiCl_3$ reacts with aluminium hydride bound to a complex with $Cp(Cl)TiH_2AlH_2$ rather than with free AlH_3.

The direct CT results for the $Cp_2TiCl_2/LiAlH_4$ system in diethyl ether and ether/benzene (1/1) solutions are given in Fig. 3 and Table 2.

It can be readily seen that the reactions in both solvents follow the same pathway. The low solubility of Cp_2TiCl_2 in ether, ca. 0.2 g/l, hinders the detection of the point of equivalence "d" (curve 1, Fig. 3). To overcome this difficulty, an additional experiment was performed. A heterogeneous reaction between the components in the ratio corresponding to "c" was carried out to obtain a solution of higher concentration. As the solubility of the reaction products at that point considerably exceeds the solubility of the initial Cp_2TiCl_2, the results obtained with the solution thus prepared prove more instructive. It has been shown that an arched segment "cde" represents two steps with an intermediate point of equivalence at "d". The results obtained in the mixed solvent where the solubility of Cp_2TiCl_2 was sufficiently high fully confirm this conclusion.

According to the CT data, the interaction of lithium aluminium hydride with both $CpTiCl_3$ and Cp_2TiCl_2 proceeds in four steps with reagent ratios at the equivalence points of 2/1, 1/1, 1/1.5 and 1/2. The reaction heats are also similar. From this information it may be concluded that both reactions follow the same scheme. The interaction between Cp_2TiCl_2 and $LiAlH_4$ may therefore be described by eq. 10—14 similar to eq. 1—5:

$$2\,Cp_2TiCl_2 + LiAlH_4 \rightarrow \{Cp_2TiH_2AlCl_2 \cdot Cp_2TiCl\} + LiCl + H_2 \qquad (10)$$

$$\{Cp_2TiH_2AlCl_2 \cdot Cp_2TiCl\} + LiAlH_4 \rightarrow \{Cp_2TiH_2AlHCl\}_2 + LiCl \qquad (11)$$

$$\{Cp_2TiH_2AlHCl\}_2 + LiAlH_4 \rightarrow \{[Cp_2TiH_2]_2Al_2H_3Cl + AlH_3\} + LiCl \qquad (12)$$

$$\{[Cp_2TiH_2]_2Al_2H_3Cl + AlH_3\} + LiAlH_4 \rightarrow 2\{Cp_2TiH_2AlH_2 + AlH_3\} + LiCl \qquad (13)$$

$$Cp_2TiCl_2 + 2\,LiAlH_4 \rightarrow \{Cp_2TiH_2AlH_2 + AlH_3\} + 2\,LiCl + \tfrac{1}{2}H_2 \qquad (14)$$

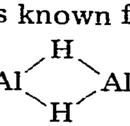
Though the reaction mixture at the equivalence point "e" (Fig. 3) is more stable than with $CpTiCl_3$, it also evolves hydrogen and aluminium metal on standing (until a Ti/Al ratio of 1/1 is achieved). With the Cp_2TiCl_2 system, the formation of an AlH_3 complex with $Cp_2TiH_2AlH_2$ has been proved directly: the interaction of $Cp_2TiH_2AlH_2$ made from Cp_2TiCl and $LiAlH_4$ with a solution of aluminium hydride is accompanied by heat release. Similar complexes known for alkali metal aluminium hydrides [11,12] are supposed to involve  hydrogen bridges. In both cases, changes in the electronic state of the aluminium hydride molecule have a destabilizing effect which explains the rapid decomposition of the molecules.

TABLE 3

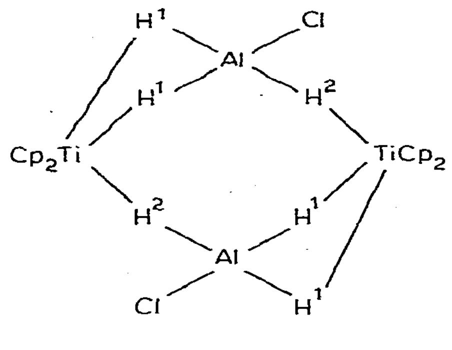
EPR PARAMETERS FOR THE COMPLEXES OBTAINED IN THE $Cp_2TiCl_2/LiAlH_4$ SYSTEM

Compound	g-factor	a(Al)	$a(H^1)$	$a(H^2)$	References
$Cp_2TiH_2AlCl_2$ + Cp_2TiCl	1.989	10.5 G	3.4 G	—	This work
	1.977, H 3.7 G				
$Cp_2TiH_2AlCl_2$	1.993	10.5 G	3.0 G		14
	1.992	30.2 MHz	8.6 MHz	15	15
Cp_2TiCl	1.979, H 9.2 MHz				14
$Cp_2TiH_2AlH_2$	1.989	5.0 G	5.0 G	0	This work
$Cp_2TiH_2AlH_2$	1.991	14.0 MHz	14.0 MHz	0	14
	1.991	5.5 G	5.5 G	0	15
Cp_2TiAlH_3Cl	1.981	3.5 G	6.5 G	25.5 G	This work

The conclusions on the reaction paths and product structures made from the CT data agree well with what may be inferred from the EPR spectra of mixtures containing a titanium(IV) compound and $LiAlH_4$ in the ratios of 2/1, 1/1, 1/2 (Fig. 4). The principal EPR parameters of the bimetallic complexes occurring in the $Cp_2TiCl_2/LiAlH_4$ system are summarized in Table 3.

The EPR spectrum of a 2/1 ($Cp_2TiCl_2/LiAlH_4$) solution (Fig. 4a) represents a superposition of two signals. The eighteen-component signal (sextet of triplets) is characterized by parameters similar to those reported for $Cp_2TiH_2AlCl_2$ (I). The other signal is a sharp singlet resembling the signal observed in a THF solution of Cp_2TiCl (g = 1.979, ΔH 3.3 G) [13,14]. It should be noted that the EPR parameter values for Cp_2TiCl and its chloro-bridged complexes of the type Cp_2TiCl_2Li, Cp_2TiCl_2Na fall rather close together [15]. Therefore the formation of a trinuclear complex incorporating Cp_2TiCl (or $CpTiCl_2$) and $Cp_2TiH_2AlCl_2$ (or $Cp(Cl)TiH_2AlCl_2$) suggested on the basis of the CT data cannot be ruled out. The octet signal with a 1/3/4/4/4/4/3/1 peak area ratio (Fig. 4c) observed in the final product of the reaction between $LiAlH_4$ and Cp_2TiCl_2 practically coincides with that reported for $Cp_2TiH_2AlH_2$ (II). It is worthwhile mentioning that the g-factor values for $Cp_2TiH_2AlCl_2$ and $Cp_2TiH_2AlH_2$ obtained in this work are by ca. 0.002 smaller than those reported in the literature [13,14]. This may be due to the lower solvation power of Et_2O employed as reaction medium as compared with THF used in the earlier studies.

The EPR spectrum of the complex obtained by mixing equimolar amounts of Cp_2TiCl_2 and $LiAlH_4$ (eq. 11) contains 17 components (Fig. 4b). No corresponding literature data exist. The observed pattern cannot be described as a superposition of the signals from compounds I and II. It may readily be interpreted on the assumption of coupling of the titanium(III) unpaired electron with three protons ($J = \frac{1}{2}$) two of which are equivalent and with the aluminium nucleus (J = 5/2). The following relations should then hold: ($2a(Al) = a(H^1)$, $a(H^1) < a(H^2)$ (Table 3). The high HFC constant value for the third proton attracts attention. This is significantly larger than those reported for titanium(III) complexes with double hydrogen bridges of the type $Cp_2TiH_2MX_n$. It seems unlikely that the replacement of $AlCl_2$ in I or AlH_2 in II with AlHCl in Cp_2TiH_2AlHCl (III) will have a strong effect on the EPR parameters. The g-factor and a(Al) values do in fact vary only insignificantly in the series $Cp_2TiCl_2AlCl_2$, $Cp_2TiCl_2AlEtCl$, $Cp_2TiCl_2AlEt_2$, and the HFC constant value for the terminal H atoms in II is equal to zero [16]. It thus seems likely that the corresponding H atom in the 1/1 complex, H^2, forms one more bridge. Taking into consideration this and the CT data, structure IV that does not contain terminal hydrogens may be suggested.

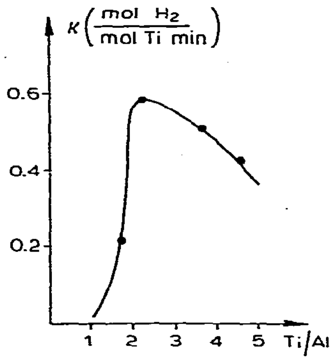


(IV)

It appears that complex IV is an inorganic biradical where two spins do not interact. The fact that the titanium(III) unpaired electron does not interact with the second Al atom via the H^2 bridge may be explained by a significantly larger Ti—Al distance between the singly-bridged atoms compared with the distance in the doubly-bridged fragment $\mathrm{Ti}\overset{H^1}{\underset{H^1}{\lessgtr}}\mathrm{Al}$. This suggestion seems more probable since structural data on $Cp_2TiH_2BH_2$ [17] and $Cp(Cl)TiH_3BH$ [18] show these molecules to contain bi- and tri-dentate borohydride groups, with r(Ti—B) distances of 2.37 and 2.17 Å, respectively. It should also be noted that the Ti—Ti distances in the complexes $Cp_2TiH_2AlEt_2 \cdot (C_{10}H_8)$ and $[Cp(C_5H_4)TiHAlEt_2]_2$ [10] are too large for direct Ti—Ti bonding (2.8—3.1 Å). The formation of the dimeric or ($2n$) meric structure $[Cp_2TiAlH_3Cl]_{2n}$ is also confirmed by the IR spectrum of the product obtained directly from Cp_2TiCl and aluminium hydride and of its deuterated counterpart. The spectrum of crystalline Cp_2TiAlH_3Cl does not contain bands that can be assigned to terminal Al—H stretches (1600—1850 cm^{-1}). On the other hand, a number of bands observed in the range 1300—1500 cm^{-1} may correspond to the Ti—H—Al bridge-stretching vibrations.

It is generally accepted at present that the active centres of the Ziegler—Natta catalysts for homogeneous hydrogenation are transition metal hydride derivatives, in particular, titanium compounds. As the compounds obtained in this work contain Ti—H bonds, one might expect them to catalyze homogeneous hydrogenation of olefins. The reduction of Cp_2TiCl_2 with $LiAlH_4$ yields solutions containing aluminium hydride which decomposes with time. For this reason, the catalytic activity of the complexes obtained in a simpler system, $Cp_2TiCl/LiAlH_4$, has been studied.

Blue solutions of Cp_2TiAlH_4 (λ_{max} 660 nm) obtained by treatment of Cp_2TiCl with a stoichiometric amount of $LiAlH_4$ lack catalytic activity in the hydrogenation of cyclohexene and hex-1-ene. The catalytic activity increases rapidly with the relative content of the titanium component and reaches a maximum at the Ti to Al ratio of 2/1. Further increase of that ratio weakens the catalytic activity.



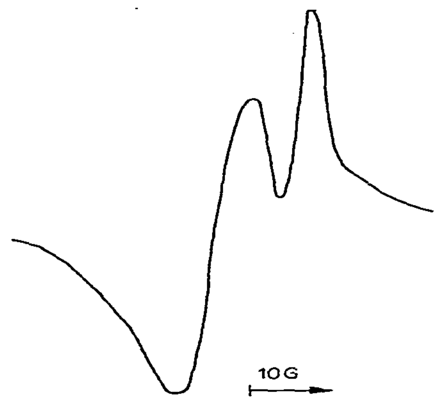


Fig. 5. Cyclohexene hydrogenation rate as a function of the Ti/Al ratio in solution.

Fig. 6. EPR spectrum of catalytically active complexes (Ti/Al of 2 to 3).

The rate constant for cyclohexene hydrogenation K (mol H_2/mol Ti min) is shown in Fig. 5 as a function of the Ti/Al ratio in solution. A similar dependence is observed in hydrogenation of hex-1-ene the K value in the latter case increases by a factor of 10 to 15.

A typical EPR spectrum of a catalytically active solution containing Ti and Al in a 2—3 ratio is shown in Fig. 6. The spectral pattern (a poorly resolved doublet) may be explained by the presence of two sorts of paramagnetic particles characterized by g-factor values of $g_1 = 1.978$, $g_2 = 1.989$, respectively.

The results obtained show that homogeneous hydrogenation of olefins in the presence of titanium aluminium hydride derivatives is catalyzed by intermediate dinuclear complexes rather than by the relatively stable final products such as Cp_2TiAlH_4.

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