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EPR INVESTIGATION OF TRANSITION METAL COMPLEXES
XIII. EPR DETECTION OF THE COMPLEX $(C_5H_5)_2TiH_2AlH_2$

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SUMMARY

The complex $(C_5H_5)_2TiH_2AlH_2$ has been detected and its EPR spectrum interpreted. Use of $LiAlD_4$ has allowed the study of the corresponding deuterated compound. Comparison with computer-simulated spectra strongly supports the suggested structure.

INTRODUCTION

The complex $Cp_2TiH_2AlH_2$ ($Cp = \pi$-cyclopentadienyl) has been obtained in solution by reacting $(Cp_2TiCl)_2$ with $LiAlH_4$in THF, presumably according to:

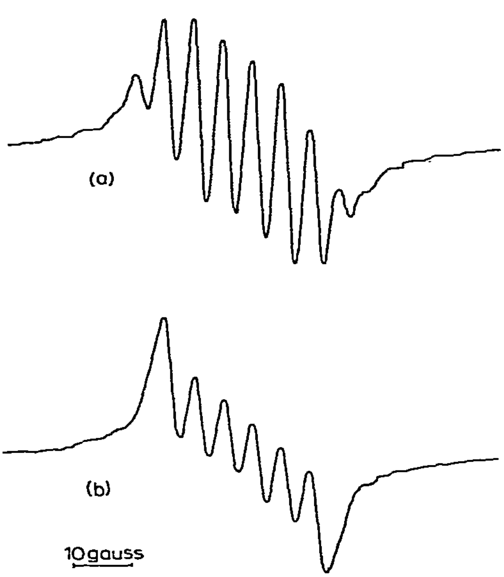
$$(Cp_2TiCl)_2 + 2\ LiAlH_4 \rightarrow 2\ Cp_2TiH_2AlH_2 + 2\ LiCl \qquad (1)$$

The dimeric $(Cp_2TiCl)_2$ was prepared beforehand by reduction of Cp_2TiCl_2 with lithium naphthalide (Li/Ti 1/1), and identified by its EPR signal (one narrow line, $g = 1.979$, peak-to-peak line-width 9.2 MHz). The synthesis according to eqn. (1) is similar to that adopted by Nöth[1] for the preparation of $Cp_2TiH_2BH_2$ from Cp_2TiCl_2 and $NaBH_4$, except for the intermediate preparation of the dimeric Ti^{III} species.

RESULTS AND DISCUSSION

The EPR spectrum of $Cp_2TiH_2AlH_2$ is shown in Fig. 1a. It is composed of six equivalent, equidistant lines, due to the interaction of the unpaired electron of the Ti^{III} with the nucleus of the Al ($I = 5/2$). Each line is further split into a 1/2/1 triplet. Since, however, the hyperfine splitting constants a_{Al} and a_H are practically the same, only the outer lines of the first and the last triplets can be discerned. This assignment was confirmed by the use of $LiAlD_4$ (Fig. 1b), and the subsequent computer simulation of the two experimental spectra (Fig. 2a and b). The signal 2a was obtained by varying a_{Al}, a_H and the line width T_2^{-1} (Lorentzian line shape) until best fit with the experimental spectrum 1a. For 2b, a_{Al} and T_2^{-1} were maintained, and a_H was replaced by $a_D = (g_D/g_H) \cdot a_H = 0.153\ a_H$.

Although the general aspect of the computed spectra is a satisfactory confirmation of the line assignment, there is some additional line broadening in the experi-



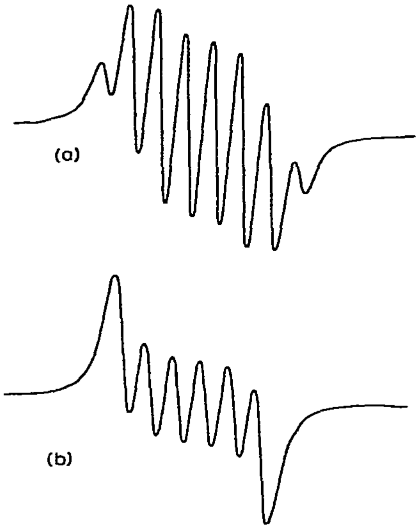


Fig. 1. EPR signal a, of $Cp_2TiH_2AlH_2$ and b, of $Cp_2TiD_2AlD_2$. $T=20°$.

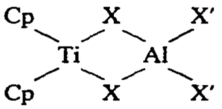
Fig. 2. Computer simulated spectra.

mental 1b. This is ascribed temptatively to an isotope effect, affecting an intramolecular dynamic process. For the very similar complex $Cp_2TiH_2AlCl_2$, an alternating line-width effect could be interpreted in terms of such a process[2]. A rapid exchange between two conformations takes place. In a given conformation the coupling constants of the bridge hydrogen atoms are no longer the same but take the values $a_{H(1)}$ and $a_{H(2)}$. On passing to the other conformation these coupling constants are exchanged. Such a process would obviously be slowed down by the replacement of hydrogen by deuterium, and a broadening of the $m_I = \pm 1$ lines of the 1/2/3/2/1 quintet of the two bridge deuterium atoms would be the consequence. Unfortunately the present spectra are not resolved well enough to check this hypothesis.

The EPR data of the complex $Cp_2TiH_2AlH_2$ are summarized in Table 1, and compared there with the data of similar complexes investigated recently.

TABLE 1

EPR DATA OF BRIDGED COMPLEXES



Compound	X	X'	g-factor	a_{Al} (MHz)	a_H (MHz)	T_2^{-1} (MHz)	Ref.
(I)	H	H	1.991	14.0	14.0	8.3	
(II)	H	Cl	1.993	30.2	8.6	1.4	2
(III)	Cl	Cl	1.975	18.7		10.3	3

The structure of complex (III) has been investigated by Natta *et al.*[4]: Ti as well as Al are in approximately tetrahedral environment, and linked together by chlorine bridges (three-center-bonds). The same structure has been proposed by Nöth for the complex $Cp_2TiH_2BH_2$[1], and by us for complex (II) in Table 1[2]. The data in Table 1 are consistent with such a structure also for the new complex (I). Both hydrogen bridged compounds have very similar g-factors near the free electron value, suggesting tetrahedral environment of the Ti^{III}. The difference between $g = 1.975$ for the chlorine bridged complex and $g = 1.99$ for the hydrogen bridged complexes reflects the known fact that the crystal field of hydrogen is by far stronger than that of chlorine[5] (the lowering from $g = 2$ being inversely proportional to the crystal field splitting Δ[6]). The difference of the hyperfine splitting constants a_{Al} and a_H in compounds (I) and (II) are due to the different electron donor ability of the exocyclic ligands X'. The stronger donor H 'pushes' unpaired spin density away from the Al nucleus and onto the bridge hydrogen atoms. Analogous effects have been reported for the chlorine bridged complexes, comparing $X' = Cl$, C_2H_5 and CH_3[7]. The broad lines of complexes (I) and (III) reflect unresolved hyperfine structure from the cyclopentadienyl hydrogens [in case of (III) perhaps also of the chlorine bridges], which in complex (II) has been completely resolved [a_H(Cp) 1.6 MHz[2]]. The reasons for this difference in line width for such similar compounds are at present speculative. One possible explanation would be that the unsymmetric environment of the Al in (II) may slightly change the bond angles in the bridge, leading to increased spin-lattice relaxation time.

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