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ELECTRON PARAMAGNETIC RESONANCE ON TRANSITION METAL COMPLEXES
IX*. ELECTRON RESONANCE EVIDENCE FOR AN INTRAMOLECULAR DYNAMIC PROCESS IN A Ti-Al HYDRO COMPLEX

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SUMMARY

The EPR signal of $Cp_2Ti^{III}H_2AlCl_2$ in tetrahydrofuran shows an alternating line-width effect involving the $M_I = \pm 1$ and $M_I = 0$ spin states of the two bridge hydrogens, and indicating the existence of a dynamic molecular process in which the involved coupling constant undergoes an out-of-phase modulation. Evaluation of the temperature dependence of the line-width effect leads to an activation energy of 4 kcal/mol, which implies that complete breaking of a chemical bond is not involved. It is proposed that one hydrogen is more tightly bonded to the Al, the other to the Ti, and that the molecular motion concerns the flopping to the reverse conformation.

When di-π-cyclopentadienyltitanium dichloride (Cp_2TiCl_2) in tetrahydrofuran is reduced with metallic sodium in the presence of freshly sublimed $AlCl_3$, a paramagnetic species is formed after several hours stirring at room temperature. The reaction solution gives a strong electron resonance signal. Double integration of the first derivative spectrum indicates some 60% of the initial amount of titanium ($[Ti] = 10 \times 10^{-3}$ mol/l) is present in the signal-producing form. The essential feature of the spectrum is the interaction of the unpaired electron of a Ti^{III} species with one nucleus of Al ($I = \frac{5}{2}$), giving rise to six equivalent hyperfine lines.

On extreme dilution further hyperfine structure is resolved (Fig. 1). Each of the six lines is split into a 1/2/1 triplet by two equivalent hydrogen nuclei, and furthermore a splitting of each component into an uneven number of very narrow lines is

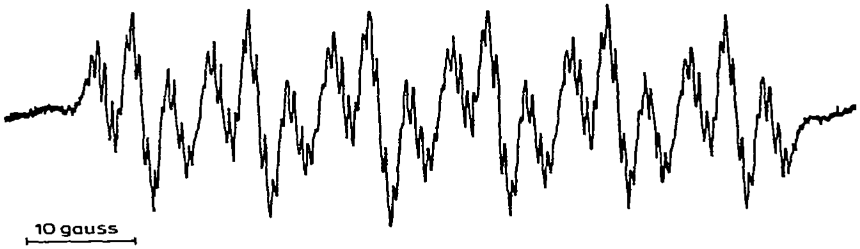

Fig. 1. EPR signal of $Cp_2TiH_2AlCl_2$ (II) in THF at room temperature.

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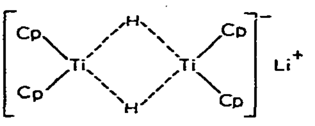
* For Part VIII see ref. 1.

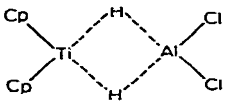
observed, presumably due to the interaction with the ten aromatic hydrogen atoms of the two cyclopentadienyl rings. By analogy to the recently[2] investigated complex (I), structure (II) is ascribed to the new Ti^{III} species:

(I)



$g = 1.9938$
$a_H = 26.5$ MHz
$a_{H(Cp)} = 0.75$ MHz

(II)



$g = 1.993$
$a_{Al} = 30.2$ MHz
$a_H = 8.6$ MHz
$a_{H(Cp)} = 1.6$ MHz

On cooling the reaction solution, a remarkable alternating line width effect involving the $M_I = \pm 1$ and $M_I = 0$ spin states of the two "equivalent" bridge hydrogen atoms can be observed (see Fig. 2). According to present theories[3] such an effect is the result of a dynamic molecular process in which the coupling constant concerned undergoes an out-of-phase modulation. Analysis of the temperature dependence of the line width changes permits an estimate of the activation energy for this molecular motion, and this may indicate the mechanism involved.

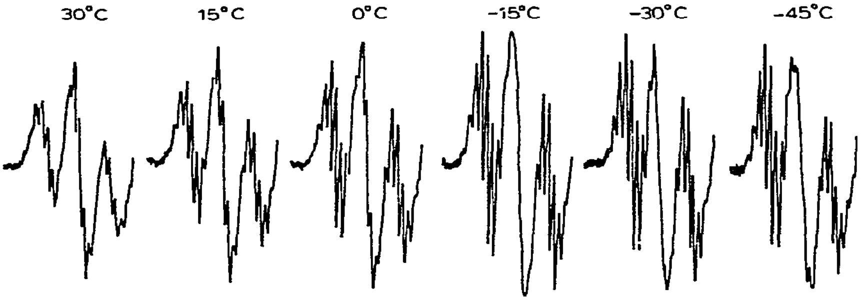


Fig. 2. Alternating line width effect at lower temperatures (first low field triplet of the spectrum).

If the modulation is the result of rapid exchange between only two conformations of the complex then the line width is given by eqn. (1), where τ is the life time

$$T_2^{-1} = \pi \cdot (a_{H,1} - a_{H,2})^2 \cdot (m_1 - m_2)^2 \cdot \tau/4 \qquad (1)$$

of a particular conformation and m_1 and m_2 are the individual nuclear spin quantum numbers of hydrogens 1 and 2, respectively[3]. In a given conformation the coupling constants of the bridge hydrogens 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 will be exchanged. From eqn. (1) it follows that hyperfine components with $m_1 = m_2$ ($M_I = \pm 1$) are not broadened whereas the components due to $M_I = 0$ (central lines of the 1/2/1 triplets) are broadened by an amount:

$$T_2^{-1} = (\pi/4) \cdot (a_{H,1} - a_{H,2})^2 \cdot \tau \simeq \text{const} \cdot \tau \qquad (2)$$

Assuming that the difference between the two coupling constants $a_{H,1}$ and $a_{H,2}$ is independent of temperature in the observed range, it is customary to estimate the activation energy directly from the temperature dependence of T_2^{-1}.

Before doing so, it should be noted that a second type of line-width effect is operative in the spectrum under investigation, for the $M_I = \pm 1$ lines sharpen at lower temperatures (see Fig. 2). This kind of line width change has also been observed with complex (I)[2], for which all the components of the spectrum sharpen on lowering the temperature, and only at $T \leqslant -40°$ is a completely resolved signal obtained. The reason for this sharpening, which appears to be typical of the kind of complex under investigation, is not yet clear. It seems, however, safe to assume that this effect is also present in the $M_I = 0$ components of the spectra in Fig. 2.

For the evaluation of the temperature dependence of T_2^{-1} we must thus modify eqn. (2). Assuming that the $M_I = \pm 1$ lines are unaffected by exchange we write:

$$T_2^{-1}(\pm 1) = A$$

The width of the $M_I = 0$ line is the sum of two contributions, one is A and the other results from exchange, *i.e.*:

$$T_2^{-1}(0) = T_2^{-1}\,(\text{exch.}) + A \qquad (3)$$

This treatment at the same time takes account of all other relaxation processes which affect the $M_I = \pm 1$ and $M_I = 0$ components equally.

In order to obtain numerical values for the relevant line-width data, we used the method of comparison with computer simulated spectra. Fig. 3 shows a selection of 4 simulated signals. Each refers to just one line of the triplets. The lines are split by the field of 10 equivalent protons, corresponding to the influence of the two cyclopentadienyl groups. The hyperfine splitting parameter $a_{\text{H,Cp}}$ is maintained constant, and the line width is varied. Satisfactory agreement with the experimental spectra could be obtained only by using Gaussian line shape in the computer reconstruction.

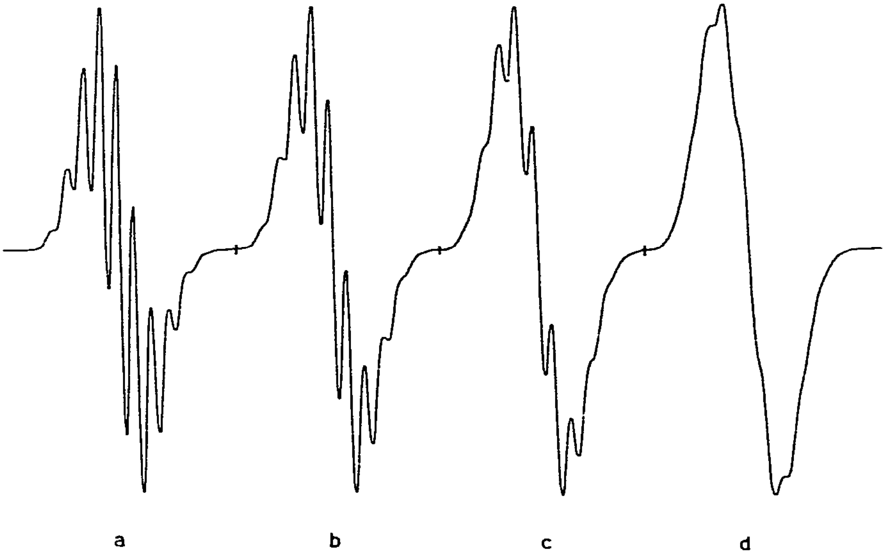


Fig. 3. Simulated spectra for the evaluation of line-width. T_2^{-1} in arbitrary units: 1.2(a); 1.3(b); 1.4(c) and 1.6(d).

Assigning line widths (in arbitrary units) to the $M_I = \pm 1$ and $M_I = 0$ lines of Fig. 2 by comparison with the simulated spectra, and making use of eqn. (3), T_2^{-1} (exch.) may be calculated as a function of the temperature. The activation energy of the dynamic process under consideration follows then from an Arrhenius plot of these data (see Fig. 4). The slope of the straight lines gives $E_A \simeq 4$ kcal/mol.

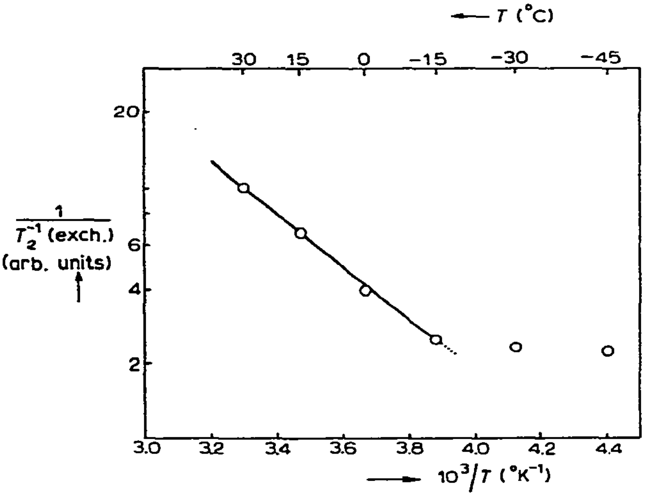
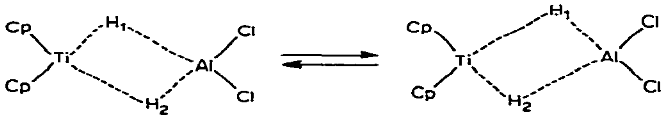


Fig. 4. Arrhenius plot of reciprocal line width of the $M_I = 0$ lines (exchange contribution).

At $T < -15°$ the straight line in Fig. 4 starts to level off. Simultaneously the $M_I = 0$ line begins to sharpen again. Presumably the exchange rate at these lower temperatures is already sufficiently reduced as to approach the slow exchange limit (see *e.g.* ref. 4). (At this limit two sets of doublets, all of equal intensity, would be expected instead of the 1/2/1 triplet.) Similar size of the $M_I = \pm 1$ and the $M_I = 0$ lines, as well as a somewhat different line shape (compare the $M_I = 0$ lines at $-45°$ and $30°$) seem to support this assumption.

The relatively low value of the activation energy obtained from Fig. 4 indicates that complete breaking of a chemical bond cannot be involved in the molecular motion responsible for the alternating line-width effect.

Compound (II) may be regarded as an electron-donor–acceptor complex of the one-electron-donor Cp_2TiH and the acceptor $HAlCl_2$ (compare similar complexes[5]). From this picture it seems feasible that the two three-center bonds are not completely symmetrical at any instant, but that one hydrogen is somewhat more tightly bonded to the Al, and the other to the Ti. It is suggested that the observed molecular motion involves the simultaneous tightening of the bonds $Ti–H_1$ and $Al–H_2$ and loosening of the bonds $Ti–H_2$ and $Al–H_1$, and *vice versa*. This may be depicted as follows:



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