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SPIN LATTICE RELAXATION TIME STUDIES OF RING ROTATION IN CYCLOPENTADIENYLMETAL COMPLEXES

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Summary

Proton spin lattice relaxation time measurements have been used to determine the barriers to rotation of the cyclopentadienyl ring in the complexes (η^5-2,4-cyclopentadien-1-yl)trichlorotitanium(IV), $CpTiCl_3$ (9.6 kJ mol^{-1}); di-η^5-cyclopentadien-1-ylhexacarbonyldimolybdenum(I), $[CpMo(CO)_3]_2$ (13.9 kJ mol^{-1}); and di-η^5-2,4-cyclopentadien-1-yltitanium(IV) pentasulphide, Cp_2TiS_5, for which two T_1 processes were observed, with barriers of 8.9 and 7.7 kJ mol^{-1} assigned to the axial and equatorial rings, respectively.

Introduction

The nature of the bonding of the cyclopentadienyl ligand in transition metal π-complexes has long been a subject of interest [1]. Since many of the arguments involved depend upon precise structural information obtained from X-ray crystal structure determinations, it is rather surprising that so little attention has been paid to the solid state dynamics of cyclopentadienyl ring motions in complexes containing this ligand. Studies on various metallocenes by NMR methods have been reported at intervals for some years [2–5] and ferrocene and ruthenocene were re-examined recently in conjunction with atom–atom potential energy calculations of the barriers to rotation [6]. In general the barriers in the solid state tend to be rather low so that wide line NMR measurements of line widths and second moments produce motionally narrowed lines at 77 K and only an upper limit to the barrier height can be estimated, usually in the range of 10–12 kJ mol^{-1}. Recent studies of the ^{13}C resonance of several cyclopentadienyl complexes in the solid state show that the chemical shift anisotropy is averaged by ring rotation at 77 K [7], while for the heavily substituted decamethylferrocene the barrier to rotation is 13.5 kJ mol^{-1} [8].

The use of pulsed NMR methods to obtain the temperature dependence of the

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spin lattice relaxation time is a more useful technique and we have reported the results of such a study on the "slipped sandwich" complex di-η^5-2,4-cyclopentadien-1-yldichloromolybdenum(IV), Cp_2MoCl_2 [9]. In this compound the T_1 behaviour as a function of temperature is quite complex as four crystallographically unique cyclopentadienyl rings occur in the unit cell [10], each with a different barrier to rotation. In order to examine further the range of activation energies for ring rotation we have studied three quite different π-bonded complexes: (η^5-2,4-cyclopentadien-1-yl)trichlorotitanium(IV), $CpTiCl_3$; di-η^5-2,4-cyclopentadien-1-ylhexacarbonyldimolybdenum(I), $[CpMo(CO)_3]_2$ and di-η^5-2,4-cyclopentadien-1-yltitanium(IV) pentasulphide, Cp_2TiS_5. The first compound possesses "cylindrical" symmetry and thus the intramolecular contribution to the rotational barrier should be small, while the second complex is highly substituted and should have a substantial intramolecular barrier to rotation. The compound Cp_2TiS_5 has a very interesting molecular structure in which the titanium and five sulphur atoms form a six-membered ring with a chair conformation in the solid state [11,12]. The two cyclopentadienyl rings occupy axial and equatorial positions at the titanium atom and are, therefore, inequivalent and should have different barriers to rotation. All three compounds have room temperature crystal structures in which the molecules occupy equivalent positions in the unit cell and thus only one T_1 process should occur for the first two compounds and two processes for the titanium pentasulphide complex. We therefore avoid the difficulties encountered with resolving the multiple T_1 versus temperature behaviour in the case of Cp_2MoCl_2.

Experimental

Samples of $CpTiCl_3$ and $[CpMo(CO)_3]_2$ were obtained from Strem Chemical Co. The sample of Cp_2TiS_5 was prepared by the method of McCall and Shaver [13] using the sulphur transfer agent Li_2S_2. This complex can adopt three different crystal forms [11,12]. An X-ray powder diffraction photograph confirmed that our sample had the structure reported by Bernal et al. [11] which, in fact, is the one most suitable for our purposes since the four molecules in the unit cell are symmetry related and thus only two unique cyclopentadienyl rings occur.

Spin lattice relaxation time measurements were made using a Spin-Lock CPS-2 coherent pulsed NMR spectrometer at 33 MHz with a 180°-τ-90° pulse sequence. The free induction decays were captured on a Biomation 805 transient recorder and plotted on a strip chart recorder. The sample temperature was controlled by a flow of cold nitrogen gas and measured (± 1°C) with a copper-constantan thermocouple and digital thermometer. Non-linear least squares fits to the T_1 plots were performed on an Amdahl V7 computer using programs written in this laboratory.

Results and discussion

For a single spin lattice relaxation process, the relaxation rate is given by eq. 1,

$$1/T_1 = \tfrac{2}{3}C\left(\frac{\tau}{1+\omega^2\tau^2} + \frac{4\tau}{1+4\omega^2\tau^2}\right) \tag{1}$$

where C is a constant related to the change in the second moment of the resonance absorption line, ω is the resonance frequency, and $\tau = \tau_0 \exp(E/RT)$ is the correlation time for the motion responsible for relaxation. This function has a minimum value when $\omega\tau = 0.62$ and thus plots of ln T_1 versus reciprocal temperature exhibit V-shaped curves with high and low temperature slopes of $-E/R$ and $+E/R$. If the critical value of $\omega\tau$ is not met over the temperature range of the experiment then the limiting forms, eq. 2a and 2b, must be used and the pre-exponential factor and the constant C cannot be evaluated.

$$1/T_1 = 10C\tau/3 \tag{2a}$$

$$1/T_1 = 4C/3\omega^2\tau \tag{2b}$$

If more than one T_1 spin lattice relaxation process occurs than it is assumed that spin exchange between the two (or more) systems is rapid and that a single free induction decay results with the value of T_1 now given by eq. 3.

$$1/T_1 = (1/T_1)_a + (1/T_1)_b \tag{3}$$

Cyclopentadienyltrichlorotitanium(IV)

The crystal structure of this complex was examined some years ago but the details are sparse [14]. The titanium atom, one of the chlorine atoms and the centre of the ring lie on a crystallographic mirror plane. The carbon atoms of the ring were described as poorly resolved and the orientation of the ring is in doubt. This could arise from either a static disorder in ring atom positions or from a low barrier to rotation i.e., from dynamic effects. The T_1 data (Fig. 1) showed that a minimum in T_1 occurs just below the lowest temperature reached, and application of eq. 1 gave a

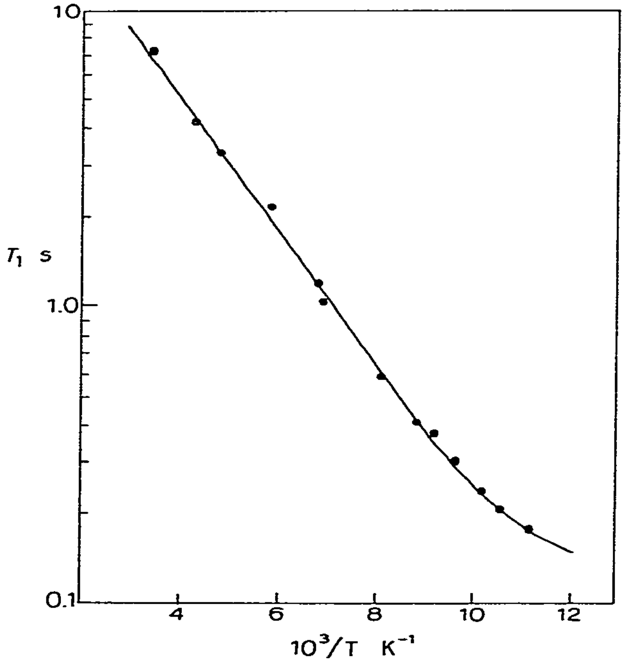

Fig. 1. Dependence of spin lattice relaxation times, T_1, on reciprocal temperature for $CpTiCl_3$. The solid line was calculated using eq. 1.

barrier of 8.8 kJ mol^{-1}. This value is similar to that found for ferrocene [6] where it is now known [15–17] that the apparent molecular centre of symmetry, as seen in the X-ray crystal structure of the high temperature monoclinic phase, is due to statistical disorder and a transition occurs at 164 K to an ordered triclinic phase in which the molecules have an eclipsed conformation. It is possible that in $CpTiCl_3$ the lack of resolution in the X-ray study is attributable to disorder and perhaps a transition to an ordered phase occurs below room temperature. No evidence of such a transition was observed over the temperature range of the present study but a re-investigation of the crystal structure might be worthwhile. In a Raman spectroscopic study of $CpTiCl_3$ a much lower barrier to rotation of 3.8 kJ mol^{-1} was calculated from a peak of 105 cm^{-1} assigned to the ring torsional mode [18].

Dicyclopentadienylhexacarbonyldimolybdenum(I)

The T_1 behaviour of this compound as a function of temperature is shown in Fig. 2. A single minimum in T_1 at 200 K was observed which allowed the full curve to be fitted using eq. 1. The barrier to rotation of 13.5 kJ mol^{-1} is one of the highest observed for cyclopentadienyl ring rotation *.

The crystal structure has been reported by Adams, Collins and Cotton [19]. There

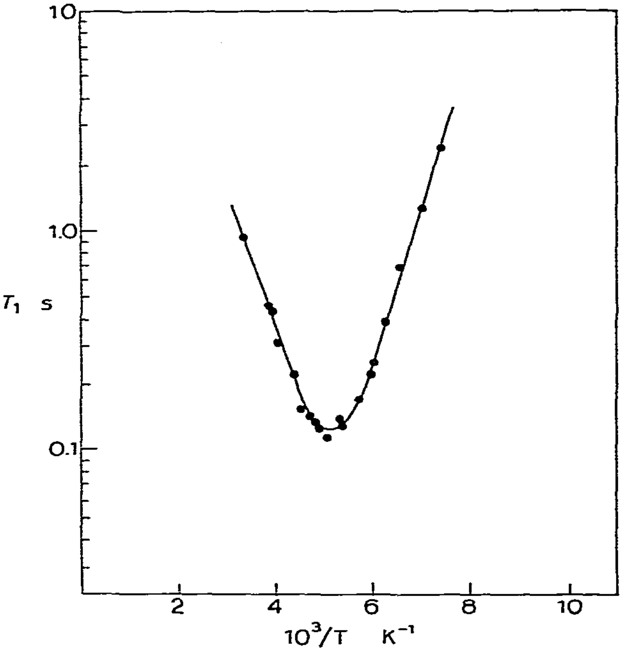

Fig. 2. Dependence of spin lattice relaxation times, T_1, on reciprocal temperature for $[CpMo(CO)_3]_2$. The solid line was calculated using eq. 1.

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* This barrier is high enough that line narrowing occurs above 77 K. The second moment (measured using CW methods) was 5.8 ± 0.5 gauss^2 at 77 K compared with 0.80 ± 0.08 gauss^2 at room temperature.

are no unusually short intermolecular contact distances but there are very close intramolecular contacts between the ring atoms and the carbonyl groups atoms in the other half of the dimeric molecule. In the solid state the molecule adopts a *trans* conformation and an internal rotation about the Mo–Mo bond could be an alternative motion. However, the barrier has been measured in solution as 64 kJ mol^{-1} which is too high to be a likely process in the solid. The carbon atoms of the cyclopentadienyl ring are well-defined in the crystal structure with only a small spread in the C–C distances. These observations are consistent with a high barrier to rotation arising primarily from intramolecular, rather than intermolecular, interactions.

Dicyclopentadienyltitanium pentasulphide

A more complicated behaviour is observed for the T_1 dependence in this compound. A minimum occurs at 131 K and a second decrease in T_1 at lower temperatures shows that another minimum would occur but is below the lowest temperature attainable with our apparatus (Fig. 3). This behaviour is easily explained if the two cyclopentadienyl rings are rotating at different rates due to different hindering potentials. The experimental results were analysed using eq. 3 with eq. 1 and 2. The computer fit gave acceptable values for the higher temperature process but only an approximate value for the barrier could be derived for the other, Table 1.

This complex has three different crystalline modifications. In addition to the monoclinic form described by Bernal and co-workers [11], and examined in this study, a second monoclinic and also an orthorhombic structure have been reported by Muller, Peterson and Dahl [12], although the orthorhombic structure was not

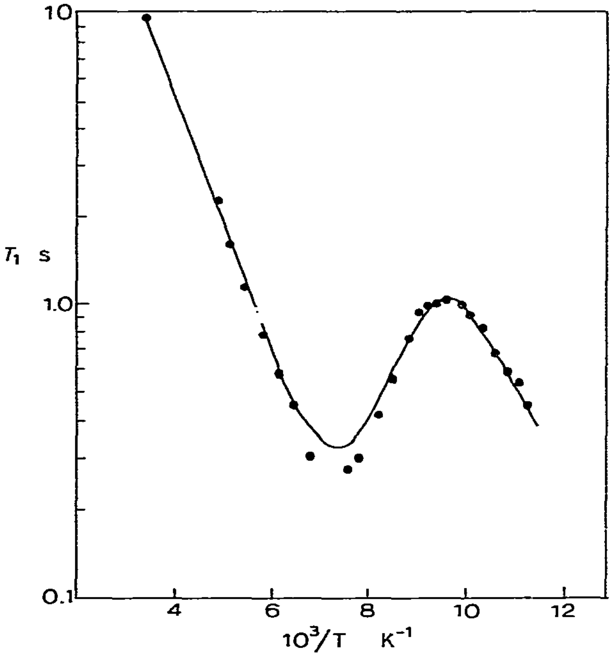

Fig. 3. Dependence of spin lattice relaxation times, T_1, on reciprocal temperature for Cp_2TiS_5. The solid line was calculated using eq. 3 with eq. 1 and 2.

TABLE I
ACTIVATION ENERGIES FOR RING ROTATION

Compound	C (s^{-2})	τ_0 (s)	E (kJ mol^{-1})
$CpTiCl_3$	1.4×10^9 [a]	2.5×10^{-14} [a]	8.8 ± 0.8
$[CpMo(CO)_3]_2$	$1.77 \pm 0.26 \times 10^9$	$8.20 \pm 0.36 \times 10^{-13}$	13.6 ± 0.7
Cp_2TiS_5 axial	$6.1 \pm 0.4 \times 10^8$	$1.3 \pm 0.6 \times 10^{-12}$	9.0 ± 1.0
equatorial	– [b]	– [b]	7.7 ± 1.2

[a] Approximate values. The actual T_1 minimum was not reached. [b] T_1 minimum not observed. $C\tau_0 = 5.8 \times 10^{-5}\ s^{-1}$.

analysed. Both investigations gave essentially the same molecular structure. The axial ring has very close contact distances to the two sulphur atoms S(3) and S(5) (Ti = 1) and to relieve the strain the Cp_2Ti fragment is twisted by about 7.5° with respect to a symmetrical arrangement about the S(2)–Ti–S(6) plane. In spite of this, the measured barriers are low. Based on the anisotropic temperature factors, Bernal et al., have calculated that the axial ring undergoes librational oscillations of amplitude ±5° compared with ±20° for the equatorial ring. Thus it seems reasonable to assign the lower barrier at 7.7 kJ mol^{-1} to the latter, and the higher barrier at 9.0 kJ mol^{-1} to the axial ring. The similarity in the magnitudes of the two barriers is, however, rather surprising in view of the difference in the amplitudes of libration and the details of the molecular structure. Since the barriers are quite low, large thermal parameters are to be expected and it is possible that the finer details of the crystal structure are obscured. A plausible explanation of the extremely high calculated amplitude for the equatorial ring is that some disorder exists and this, and not librational motion, is responsible for the anisotropy of the thermal parameters. Some support of this argument is obtained from the results of non-bonded atom-atom potential calculations [20] which show that both the inter- and intra-molecular contributions to the angular dependence of the lattice energy have a minimum in the potential which is displaced from zero angle, i.e. from the crystallographic atomic coordinates used as input to the computations.

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