Proton ENDOR and TRIPLE Resonance Spectra of a Frozen Solution of (1—8-η-Cyclo-octatetraene)(1—5-η-cyclopentadienyl)titanium

By **Gérard Labauze** and **J. Barrie Raynor,*** Department of Chemistry, University of Leicester, Leicester LE1 7RH
Edmond Samuel, Laboratoire de Chimie Organique Industrielle, E.N.S.C.P., 11 rue P. et M. Curie, 75231 Paris, France

ENDOR and TRIPLE resonance spectra for $[Ti(\eta\text{-}C_8H_8)(\eta\text{-}C_5H_5)]$ in frozen toluene solution have been recorded. The proton hyperfine couplings have been satisfactorily interpreted in terms of contact and dipolar contributions of the unpaired electron which is localised mainly on the Ti atom in a d_{z^2} orbital.

THE e.s.r. spectrum of $[Ti(\eta\text{-}C_8H_8)(\eta\text{-}C_5H_5)]$ in toluene at −130 °C has been reported by Samuel *et al.*[1] They found that the spectrum exhibited marked axial symmetry and there was some evidence for super-hyperfine coupling to the ring protons in the frozen-solution spectrum. In fluid solution at −30 °C, well resolved proton super-hyperfine coupling to the protons in each ring system was observed in addition to hyperfine coupling to the titanium isotopes. In this paper we report on a ^1H ENDOR and TRIPLE resonance study of a frozen solution of this complex which we believe is the first in which ligand super-hyperfine coupling is observed by ENDOR on *each* of the g features in a *frozen* solution.

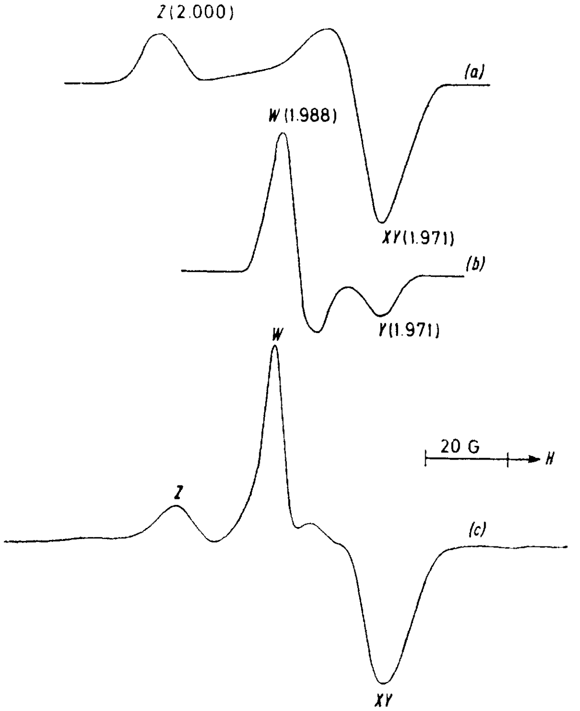

FIGURE 1 E.s.r. spectrum of (*a*) a rapidly frozen solution of $[Ti(\eta\text{-}C_8H_8)(\eta\text{-}C_5H_5)]$ in toluene or 2-methyltetrahydrofuran at 150 K, (*b*) complex in rapidly frozen dichloromethane or tetrahydrofuran, and (*c*) a slowly frozen solution of the complex in toluene at 150 K. ENDOR spectra were measured on (*a*) (toluene) and (*c*). The numbers in brackets are g values at the peaks indicated

EXPERIMENTAL

The compound was prepared according to known procedures, all manipulations being carried out under argon and using rigorously dried solvents.[2] Proton ENDOR spectra were recorded on a Bruker ER220 e.s.r. spectrometer with an EN200 S/E/T ENDOR–TRIPLE accessory.

RESULTS AND DISCUSSION

E.S.R. Spectra.—A feature of the e.s.r. spectrum was that the profile was very dependent upon the rate of freezing and the nature of the solvent. Rapid freezing of solutions in 2-methyltetrahydrofuran or toluene yielded spectra [Figure 1(*a*)] with $g_\parallel \approx 2 > g_\perp$. On the other hand, rapid freezing in dichloromethane or tetrahydrofuran (thf) yielded spectra [Figure 1(*b*)] with $g_\parallel < g_\perp < 2$. If, however, toluene, thf, or dichloromethane solutions were slowly cooled, a complicated spectrum [Figure 1(*c*)] was obtained, which we call the 'mixed' spectrum.

These ambivalent results were rationalised as follows. The true e.s.r. g factors are $g_z = 2.000$, $g_x = g_y = 1.971$ [Figure 1(*a*)] and are typical for a d^1 system with the unpaired electron in d_{z^2}. The Ti hyperfine tensor reported earlier supports this interpretation. We postulate that rapid freezing of the toluene or 2-methyltetrahydrofuran yields a glass with the complex trapped in a random manner. Conversely, in rapidly frozen thf or dichloromethane [Figure 1(*b*)] there are various types of cavity or cage in the frozen solvent which allow rotation of the molecule about the y axis (Figure 2) such that the g_z (2.000) and g_x (1.971) features average to an apparently perpendicular g feature at W (1.988); g_y is now an apparently parallel feature. In slowly cooled toluene or thf, a 'mixed' spectrum [Figure 1(*c*)] is obtained, comprising approximately equal amounts of

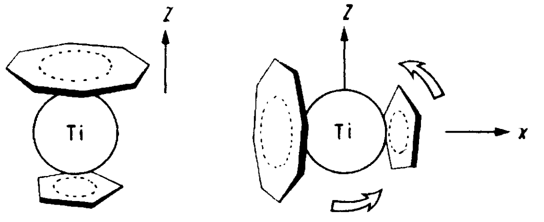

FIGURE 2 A representation of $[Ti(\eta\text{-}C_8H_8)(\eta\text{-}C_5H_5)]$ showing rotation of the molecule about the y axis which is perpendicular to the plane of the paper

1(*a*) and 1(*b*). This must arise from a solvent structure where there are two types of cavity, one which allows rotation and another which randomly freezes the molecule.

Examples of this behaviour are well known. For example, the stereochemically related complex bis(cyclopentadienyl)iron(II) in frozen thiourea is rigidly frozen at temperatures <144 K with its molecular axes either parallel or perpendicular to the clathrate channel axes.[3] As the temperature is raised, a phase transition takes place over the temperature range 144—153 K. Above this region, the perpendicular bis(cyclopentadienyl)iron molecules rotate rapidly whilst the parallel ones remain frozen. The rapidly rotating molecules have a symmetry axis oriented at 90° to that of the stationary molecules.

ENDOR Spectra.—The ENDOR spectra were recorded on both rapidly and slowly cooled frozen toluene solutions at 150 K. We were thus making measurements upon the randomly frozen [1(*a*)] and the 'mixed' [1(*c*)] systems. ENDOR spectra were recorded at magnetic fields corresponding to the peaks *Z* and *XY* in the e.s.r. spectrum 1(*a*) and at *Z*, *W*, and *XY* in the e.s.r. spectrum of Figure 1(*c*). A typical ENDOR spectrum is shown in Figure 3(*a*). This spectrum, recorded at point *Z* of Figure 1(*a*), is easily interpreted in terms of two pairs of resonances separated by 7.70 and 4.95 MHz, with numerous centrosymmetric lines at about the free proton frequency, 14.9 MHz, which arise from protons in the toluene solvent shell. The ENDOR spectra on e.s.r. peaks *XY*, *W*, and *Y* have similar profiles. The experimental results are recorded in the Table, where the hyperfine couplings have been converted to megahertz.

Proton hyperfine coupling parameters deduced from ENDOR measurements (MHz). *W*, *XY*, *Y*, *Z* refer to hyperfine couplings measured at these points in Figure 1. Deduced spin densities are derived from parameters of Figure 1(*a*)

		$C_8H_8^{2-}$	$C_5H_5^-$
Spectrum 1(*a*)	A at Z	7.70	4.95
	A at XY	9.52	3.76
	$A_{iso.}$ $(Z + 2XY)/3$	8.91	4.15
Spectrum 1(*c*) (mixed spectrum)	A at Z	7.32	5.00
	A at XY	9.31	3.74
	$A_{iso.}$ $(Z + 2XY)/3$	8.65	4.16
	A at W	8.35	4.35
	A $(X + Z)/2$	8.35	4.33
	s character	0.62%	0.29%
	$A_{aniso.}$ $(A_z - A_{iso.})$	−1.21	0.80
	$A_{dipolar}$ (calc.)	−1.04	0.42

General TRIPLE and Special TRIPLE Resonance Spectra.—Further resolution enhancement was achieved with a special TRIPLE resonance experiment whereby both possible n.m.r. transitions were driven simultaneously by mixing the frequency of a fixed oscillator set at the free proton frequency with the frequency of a swept oscillator. The spectrum so produced [Figure 3(*c*)] shows the signal from two different protons, their intensities closely approximating to their relative abundance (8 : 5). In addition, intense peaks due to the solvent protons are observed to the left (low-frequency end) of the spectrum. We thus confirm the earlier observation [1] that the larger hyperfine coupling arises from the C_8H_8 ring.

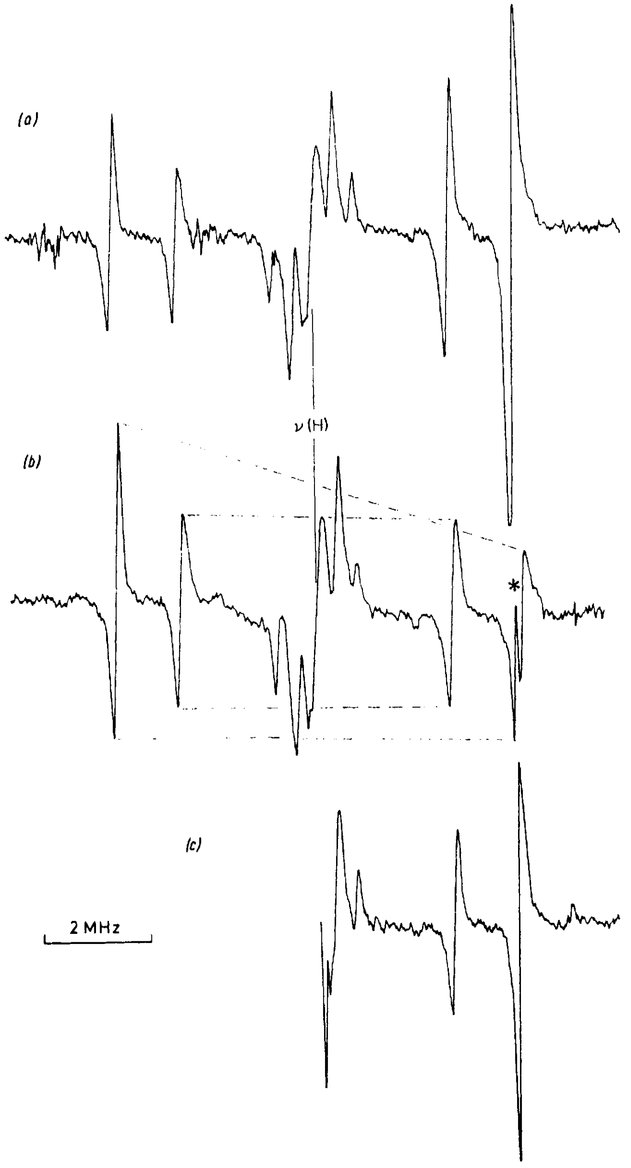

FIGURE 3 (*a*) ^1H ENDOR spectrum of $[Ti(\eta-C_8H_8)(\eta-C_5H_5)]$ in frozen toluene measured at point *Z* in Figure 1(*a*). (*b*) The general TRIPLE resonance spectrum of (*a*) where the resonance line (marked by an asterisk) has been saturated. The dashed lines show the changes in relative intensity compared with the corresponding lines in (*a*). (*c*) The special TRIPLE resonance spectrum. The free proton frequency ν(H) = 14.9 MHz

The general TRIPLE resonance experiment allows determination of the relative signs of the hyperfine couplings. In this experiment, the intensity change of the ENDOR signals from one of the protons was recorded whilst the n.m.r. transition of the other proton was saturated (*i.e.* the line at highest frequency). The spectrum so produced [Figure 3(*b*)] shows that the intensity of the two higher frequency ENDOR lines has been reduced, whilst the intensity of the two lower frequency ENDOR lines has been increased. Since pairs of lines from each type of proton have changed their relative intensity synchronously, then the signs of the hyperfine couplings associated with each type of proton are the same. The TRIPLE resonance spectra at Z, W, Y, and XY behaved similarly.

Interpretation of Proton Hyperfine Coupling Constants.—Analysis of the proton hyperfine couplings of the frozen-solution spectra provided further evidence that the signal at W arose from an averaging of the signals from X and Z. The experimental hyperfine splitting (h.f.s.) at W in the mixed spectrum 1(*c*) was identical to the average hyperfine coupling of Z and XY for the C_8H_8 and almost identical to that for the C_5H_5 protons (see Table), and in close agreement with those determined from spectrum 1(*a*) and earlier.[1]

In our analysis of the proton hyperfine couplings we refer to the molecular structure of the complex. The crystal-structure determination[4] gives Ti–C and C–C bond distances. The position of the hydrogen atoms may be deduced from neutron diffraction studies of related molecules. The C–H bond length is taken as 1.08 Å and the position of the H atoms is presumed to be *ca.* 0.05 Å out of the planes of the C_5H_5 and C_8H_8 rings towards the side of the metal as is found for $[Cr(C_6H_6)(CO)_3]$[5] and $[Fe(C_5H_5)_2]$.[6] The calculated Ti–H (C_5H_5) distances are 3.20 Å and that for Ti–H (C_8H_8), 3.19 Å. The bond angles between the z axis and the Ti–H vectors are 51.3 and 64.0° for C_5H_5 and C_8H_8 respectively.

We may now refer to ^1H h.f.s. on g_z as $A_{\parallel}$ and on g_{xy} as $A_{\perp}$. The average gives $A_{\text{iso.}}$ which is a measure of the ^1H *s* character of the unpaired electron. Although the Ti–H distances are almost identical for both rings, the hyperfine coupling to C_8H_8 protons is about twice that to the C_5H_5 protons. The reason is that the C_5H_5 protons are closer to the nodal cone of the d_{z^2} orbital and so the spin density will be less, the maxima in spin density occurring on the z axis ($\theta = 0°$) and at $\theta = 90°$. The signs of spin density are both the same and presumed positive, the evidence being that the TRIPLE resonance experiment shows that $A_{\parallel}$ for the C_5H_5 and C_8H_8 protons each have the same sign. It follows that $A_{\text{iso.}}$ for C_5H_5 and C_8H_8 protons both have the same sign and likewise $A_{\perp}$. Furthermore, $A_{\parallel}$ and $A_{\perp}$ must have the same sign so as to average to $A_{\text{iso.}}$ as deduced from the e.s.r. experiment.[1] We presume the spin density is positive because of the direct delocalisation of the unpaired electron from the $(a3d_{z^2} + b4s)$ hybrid orbital (where $a \gg b$), although there is probably a small contribution of negative spin density arising from spin polarisation of the C–H σ bonds. We believe our new $A_{\text{iso.}}$ values are better than those deduced from solution e.s.r. in ref. 1 (3.24 G for C_8H_8, 1.62 G for C_5H_5), in which there was considerable overlap of lines.

The anisotropic contribution to the ^1H hyperfine coupling must arise from a dipolar mechanism and this may be calculated from expression (1) where r is the

$$A_{\parallel} = (3\cos^2\theta - 1)g_N\beta_N g_e\beta_e/10^6hr^3 \text{ MHz} \qquad (1)$$

Ti–H distance and 0 the angle between the z axis and the Ti–H vector (Figure 4). The calculated values are −1.04 and 0.42 MHz for the protons of C_8H_8 and C_5H_5 respectively. It is gratifying that these are within 0.4 MHz of the experimental values and that the correct signs are predicted. The small discrepancy may be accounted for by second-order effects and inaccuracies in the structural dimensions used.

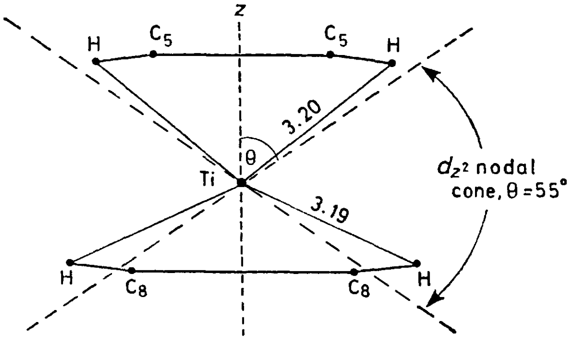

FIGURE 4 The structure of $[Ti(\eta\text{-}C_8H_8)(\eta\text{-}C_5H_5)]$ showing the relationship between the proton positions and the d_z nodal cone (dashed line)

We are indebted to Drs. D. Schmalbein and R. Biehl of Bruker Analytische Messtechnik GMBH for recording these spectra and for helpful discussions.

[0/411 *Received*, 13*th March*, 1980]

REFERENCES

[1] E. Samuel, G. Labauze, and D. Vivien, *J.C.S. Dalton*, 1979, 956.

[2] H. O. Van Oven and H. J. De Liefde Meijer, *J. Organometallic Chem.*, 1969, **19**, 373.

[3] T. C. Gibb, *J. Phys.* (*C*), 1976, **9**, 2627.

[4] P. A. Kroon and R. B. Helmholdt, *J. Organometallic Chem.*, 1970, **25**, 451.

[5] B. Rees and P. Coppens, *Acta Cryst.*, 1973, **B29**, 2516.

[6] R. K. Bohn and A. Haaland, *J. Organometallic Chem.*, 1966, **5**, 470.