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PROTON MAGNETIC RESONANCE SPECTRA AND STRUCTURE OF IRON π-ALLYL COMPLEXES

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SUMMARY

1. The proton magnetic resonance spectra of a series of π-allylirontricarbonyl compounds have been studied. π-allylirontricarbonyl halides have been shown to exist in the form of two rotation isomers and their structure has been discussed.

2. Temperature-dependence of the di(π-allyl)irondicarbonyl NMR spectrum has been investigated and the energy barriers for hindered internal rotation of the allyl groups have been estimated to be 4.6±0.8 kcal/mole.

Six-coordinated iron complexes with bi-dentate π-allyl ligands are a challenging problem because in these compounds rotational isomers may exist due to the hindered internal rotation around the metal–π-allyl group bond. Isomerism of this kind has recently been discovered for the π-allyl complexes[1] of rhodium and metals of the platinum series[2]. In some earlier papers we have described the preparation and properties of a variety of π-allylirontricarbonyl halides and nitrate. Our preliminary investigation of the PMR spectra[3] as well as the results of Plowman and Stone[4] indicate a more complex pattern of their spectra than would be expected of complexes with a symmetrical π-allyl ligand.

According to X-ray investigations[5], π-allylirontricarbonyl iodide has the

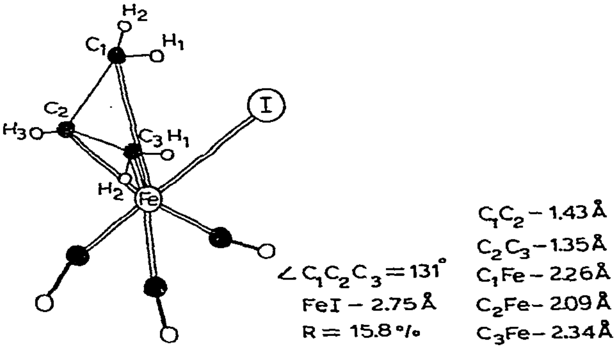

Fig. 1. Structure of π-allylirontricarbonyl iodide[5].

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structure shown in Fig. 1. The C_1–C_2 and C_2–C_3 bond lengths as well as those of the C_1–Fe and C_3–Fe bonds are somewhat unequivalent. A shorter C–Fe distance corresponds to a longer C–C bond in the allyl ligand. However, the differences observed only slightly exceed experimental error.

A distortion in symmetry of the π-allyl ligand has been shown earlier for π-(2-$CH_3C_3H_4$)PdClP(C_6H_5)$_3$[6] and [(π-C_3H_5)$_2$RhCl]$_2$[7], where the ligands in positions *trans* to the allyl group vary sharply. In π-allylirontricarbonyl iodide these ligands are equivalent (two CO groups). There may be no other alternative than to suggest that this slight symmetry distortion in the π-allyl group is a result of the *inter*molecular crystal lattice interactions.

In the present paper we have studied in detail high-resolution PMR spectra of 5–7% solutions of π-allylirontricarbonyl chloride, bromide, iodide and nitrate,

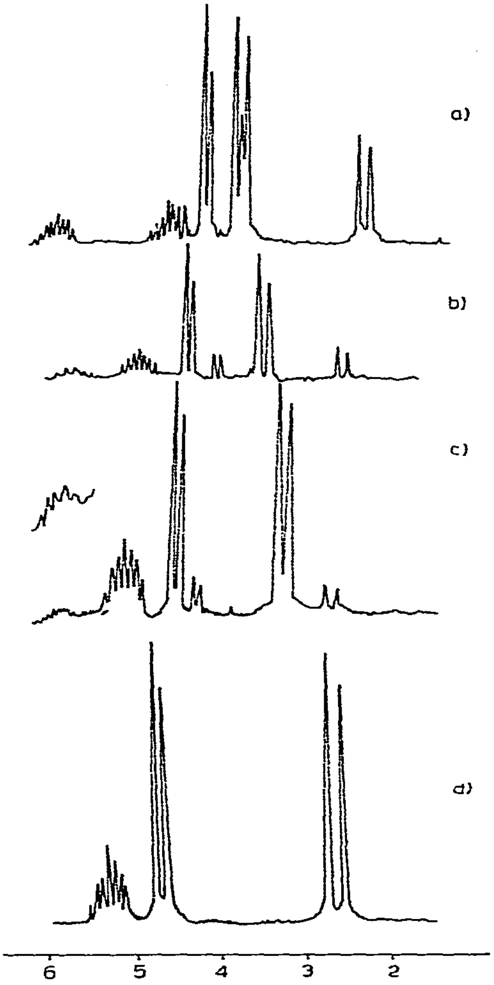

Fig. 2. PMR spectra of π-allylirontricarbonyl nitrate and halides at 100 Mc. (a), π-allylirontricarbonyl iodide; (b), π-allylirontricarbonyl bromide; (c), π-allylirontricarbonyl chloride; (d), π-allylirontricarbonyl nitrate.

π-(2-bromoallyl)irontricarbonyl bromide, π-(2-methylallyl)irontricarbonyl chloride and di(π-allyl)irondicarbonyl* in $CDCl_3$, CCl_4 and CS_2. JNM-4H-100 and JNM-C-60H JEOL Model instruments with 100 and 60 Mc operational frequencies gave rise to relatively simple spectra and their first-order interpretation. The iron–π-allyl complexes investigated are rather unstable in solution and the preparation of all the samples has, therefore, been carried out under a dry pure argon atmosphere, just before the measurements. Hexamethyldisiloxane has been used as internal reference.

The PMR spectra of the chloride, bromide and iodide of π-allylirontricarbonyl (Fig. 2) show that in all cases there is actually a mixture of two isomers, each having the A_2M_2X spectrum characteristic of a symmetrical π-allyl group. The spectra parameters (Table 1) enable the structure of each isomer to be assigned.

TABLE 1

CHEMICAL SHIFTS AND SPIN–SPIN COUPLING CONSTANTS OF $C_3H_5Fe(CO)_3X$ DERIVATIVES (in ppm, with hexamethyldisiloxane reference)

X	Solvent	H_1 chemical shifts		H_2 chemical shifts		H_3 chemical shifts		$J(H_1–H_3)$ (cps)	$J(H_2–H_3)$ (cps)	Isomer ratio I:II
		isomer I	isomer II	isomer I	isomer II	isomer I	isomer II			
NO_3	$CDCl_3$	2.63		4.70		5.31		15	7.5	
Cl	$CDCl_3$	3.21	2.63	4.48	4.22	5.11	5.80	14.7	7.7	7.7:1
Br	CS_2	3.41	2.58	4.28	3.94	4.85	5.7	13.4	7.7	4:1
I	CS_2	3.67	2.21	4.03	3.57	4.67	5.83	13	8.7	2:1
	CCl_4	3.77	2.24	4.13	3.75	4.55	5.90	13	7.5	2.2:1
π-C_3H_5	HMDSO[a]	1.85	0.96	3.08	1.99	4.11	4.11	12.3	6.5	1:1

[a] The spectrum was taken in hexamethyldisiloxane solution at −67°.

Isomer I having the same structure as that of a solid compound (see Fig. 1) predominates in all three halides. The intensive doublets with chemical shifts of 3.77, 3.41 and 3.21 ppm, respectively, for iodide, bromide and chloride have a spin–spin coupling constant of 13–14.7 cps and should be thus assigned to the H_1 protons in isomer I. The H_1 shift values in the halide series vary in reverse pattern from what would be expected from the known electronegativities of halogens. Since the H_1 protons in isomer I are the nearest neighbours to the halogen, its magnetic anisotropy should substantially contribute to their shielding. Indeed, as can seen from Fig. 3, very good linear correlation is observed between the H_1 and methyl proton chemical shifts in the relevant ethyl halides where the deciding function is that of the magnetic anisotropy contribution to the shielding^9. On the other hand, the H_2 chemical shifts (doublets with spin–spin coupling constants of 8.7–7.7 cps) as well as the shifts of the H_3 protons, which are far away from the halogen in this isomer, are in good correlation with the electronegativities (Fig. 4). The chemical shift [$\delta(H_3–H_2)$] difference is almost the same for all three compounds (about 0.6 ppm).

The H_1 and H_2 resonance signals in the second isomer are at a higher field value than the corresponding proton signals in isomer I. Chemical shifts of the H_1 and H_2 nuclei in the second isomer are in a fair correlation with the halogen electro-

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* The synthesis and the properties of the compound are described in ref. 8.

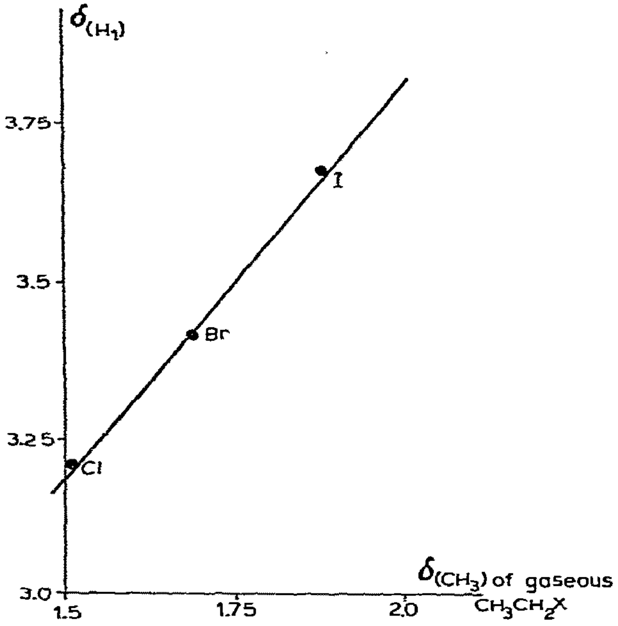

Fig. 3. Correlation between the H_1 shifts for $C_3H_5Fe(CO)_3$ halides and the CH_3 shifts of ethyl halides.

negativities (Fig. 4). The $\delta(H_1{}^{I}-H_1{}^{II})$ difference is always much larger than the $\delta(H_2{}^{I}-H_2{}^{II})$ value, both quantities regularly decreasing with the halogen magnetic anisotropy contribution, from iodide to chloride. Both these facts testify unambiguously to the almost insignificant halogen magnetic anisotropic effect upon the shielding of the H_1 and H_2 protons in the second isomer. Thus these protons in isomer II should be the farthest removed from the halogen atom.

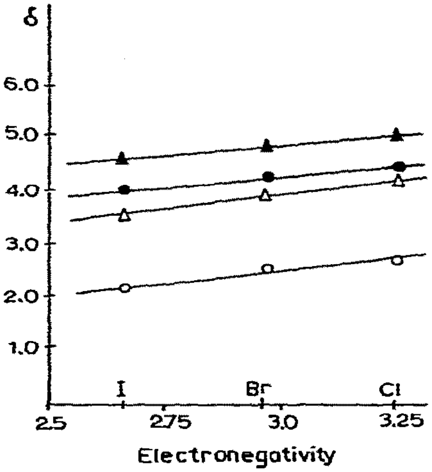

Fig. 4. The allyl group proton shifts of $C_3H_5Fe(CO)_3X$ derivatives *vs.* electronegativities of the halogens. (●), H_2 protons of isomer I; (▲), H_3 protons of isomer I; (○), H_1 protons of isomer II; (△), H_2 protons of isomer II.

The H_3 chemical shifts in the second isomer are practically the same for all three halides. Their resonance signals appear at a lower field value than those of the H_3 protons in isomer I, while an absolute value of $\delta(H_3{}^{I}-H_3{}^{II})$ difference increases from the chloride to the iodide. Thus, the halogen magnetic anisotropy contribution to the H_3 shielding in isomer II is quite essential. Therefore, the H_3 protons in isomer II should reside in the vicinity of the halogen atom. The above data indicate that isomers I and II differ only in the orientation of the allyl group with respect to the halogen atom. Most probably, isomer II has the structure shown in Fig. 5. The constancy of the H_3 chemical shift for such a rotational isomer may be readily explained by the increasing halogen electronegativity deshielding effect in passing from iodide to chloride, while the same sign contribution from magnetic anisotropy becomes smaller.

No second isomer was signalled in the π-allylirontricarbonyl nitrate spectrum (see Fig. 2d). The H_2 and H_3 resonance signals are in this case shifted by 0.2 ppm downfield with respect to those from the same protons in isomer I of the chloride. The nitrate evidently either completely dissociates in the solution or exists as ion pairs with a very weak bond between the $[C_3H_5Fe(CO)_3]^+$ cation and the nitrate anion. An IR spectrum analysis leads to the same conclusions[3].

The ratio of rotational isomers I and II for the halides of π-allylirontricarbonyl, found by integration of the spectra, decreases regularly from 7.7 : 1 to 4 : 1 to 2 : 1 for chloride, bromide and iodide, respectively. This is not, undoubtedly, mere coincidence. Qualitative investigation into the nature of the metal–π-allyl ligand bond may assist in appropriate deductions on the nature of the phenomenon.

A major contribution to the iron–π-allyl ligand bond formation is associated with an interaction of the $3d_{yz}$- and $4p_z$-metal orbitals, with the a_2 and b_2 Hückel MO's of allyl. The latter may be written as:

$$\psi_{a_2} = \frac{1}{\sqrt{2}}(\varphi_1 - \varphi_3)$$

$$\psi_{b_2} = \frac{1}{\sqrt{2}}\varphi_2 + \tfrac{1}{2}(\varphi_1 + \varphi_3)$$

Then the group overlap integrals will have the form:

$$< a_2|3d_{yz} > = \frac{1}{\sqrt{2}} \sin 2\omega \sin 2\varepsilon < 3d\pi|2p\pi > ;$$

$$< b_2|4p_z > = \cos^2\omega < 4p\pi|2p\sigma > - \sin^2\omega \cos 2\varepsilon \times < 4p\pi|2p\pi > +$$
$$+ \frac{1}{\sqrt{2}}\left[\cos^2\omega < 4p\sigma|2p\sigma > - \sin^2\omega < 4p\pi|2p\pi >\right].$$

A choice of both the coordinate axes and the ε and ω angles is shown in Fig. 6.

The interaction of the first type provides a covalent bonding, the second is the metal–ligand donor–acceptor interaction, the ligand being a donor. The covalent bonding is defined by ψ_{a_2}, involving no φ_2 orbital but only the AO's of the terminal carbon atoms in the allyl ligand (φ_1 and φ_3). The atomic orbital of the C_2 atom is involved only in the expression for ψ_{b_2} describing the donor-acceptor interaction. The stability of the donor–acceptor bond will depend on the C_2–Fe distance, as well

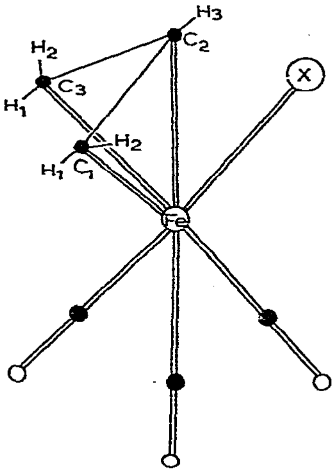

Fig. 5. Structure of isomer II for π-allylirontricarbonyl halides.

as on the ability of other ligands of the internal coordination sphere of the complex to release electrons. Bearing in mind the coplanarity of the π-allyl group, the C_2–Fe distance in the rotation isomer I will be by about 0.2 Å less than in isomer II according to an X-ray investigation[5]. Therefore, the contribution from the donor–acceptor interaction is larger for isomer I; thus the latter should gain in energy. However, with an increase in the donor ability of the halogen from Cl to I, a contribution from the donor–acceptor interaction $< b_2|4p_z >$ decreases. Hence, for the series, π-allylirontricarbonyl iodide, bromide and chloride, a regular increase in the difference between the two rotation isomer total energies should be expected. At the same temperature, isomer II (less favourable in terms of energy) would be represented by a greater statistical weight for the iodide than for the bromide and chloride; which was actually observed. These concepts lead us to expect that the magnitude of the rotational barrier will regularly increase from iodide to chloride and should be lowest for di(π-allyl)irondicarbonyl.

We have been unable to investigate the temperature-dependence of the PMR spectra for the halides of π-allylironcarbonyl because the compounds rapidly decompose in solution when the sample is heated above 25°. However, this dependency has been studied for the hexamethyldisiloxane solution of di(π-allyl)irondicarbonyl.

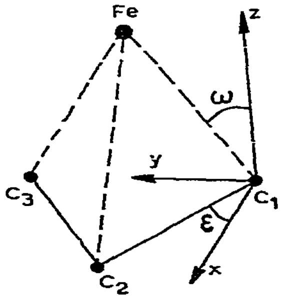

Fig. 6. Coordinate system for the metal–π-allyl group fragment.

As seen from the spectra (Fig. 7) both allyl groups in the compound are equivalent. The A_2M_2 part of the spectrum gradually widens with temperature decrease and at $-67°$ each allyl group has its own A_2M_2X spectrum with the H_3 chemical shifts (X-parts of the spectra) superimposed.

An examination of the spectrum of di(π-allyl)irondicarbonyl at $-67°$ and the spectra of the nitrate and halides (Fig. 2) shows that this complex has the structure shown in the upper part of Fig. 7. The doublets with chemical shifts of 1.85 and 0.96 ppm ($J = 12.3$ cps) should be assigned to the H_1 and H_4 protons, and those with chemical shifts of 3.08 and 1.99 ppm belong to the H_2 and H_5 protons, while the H_3 and H_6 protons give rise to a multiplet at 4.11 ppm. This is the only possible assignment because any other one should provide the A_2B_2X spectra with an impossible first-order interpretation.

A calculation of the hindered rotation activation energy gives a value of 4.6 ± 0.8 kcal/mole. The differences in chemical shifts [$\delta(H_1 - H_4)$ and $\delta(H_2 - H_5)$] are similar in magnitude to those observed for the similar protons in the halide isomers. Since in their spectrum, the two isomers are unequivalent at 20°, one may with certainty say that the rotation barriers for π-allylirontricarbonyl halides will exceed those for $(\pi\text{-}C_3H_5)_2Fe(CO)_2$ as deduced from the qualitative theoretical analysis.

We have also studied the ^{1}H NMR spectra of π-(2-methylallyl)irontricarbo-

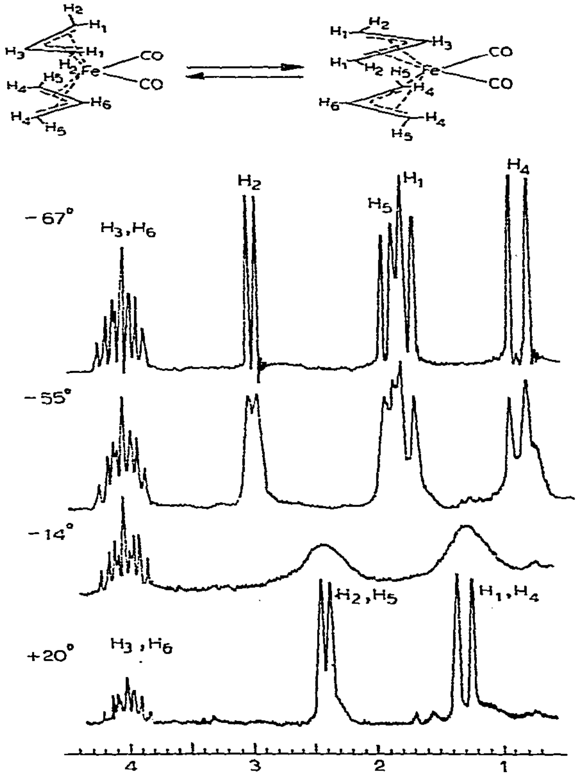

Fig. 7. PMR spectra of $(\pi\text{-}C_3H_5)_2Fe(CO)_2$. (a), $-67°$; (b), $-55°$; (c), $-14°$; (d), 20°.

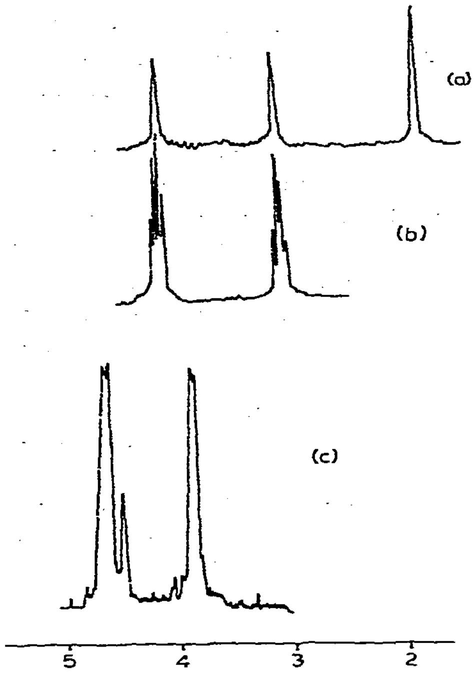

Fig. 8. PMR spectra of the 2-substituted allylirontricarbonyl halides. π-(2-methylallyl)irontricarbonyl chloride: (a), at 100 Mc; (b), at 60 Mc; (c), π-(2-bromoallyl)-irontricarbonyl at 100 Mc.

nyl chloride and π-(2-bromoallyl)irontricarbonyl bromide. Rotation isomers corresponding to structure II are less likely to exist since the steric hindrance due to the vicinity of a substituent in position 2 to the halogen atom will be too high to overcome. Indeed, as seen from the spectra (Fig. 8) both compounds exist in the form of the most favourable isomer (see Fig. 9). Introduction of the electron-releasing methyl fragment shifts the resonance signals of the H_1 and H_2 protons somewhat upfield with respect

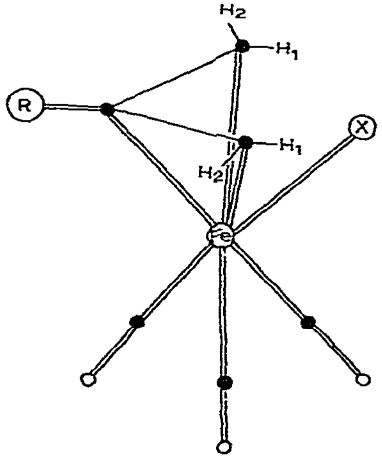

Fig. 9. Structure of the 2-substituted π-allylirontricarbonyl halides.

to their position in the π-allylirontricarbonyl chloride spectrum; the effect of electron-withdrawing bromide is directly opposite. The signal at 4.5 ppm in the bromide spectrum is due to an impurity of unknown structure. The signals of the H_1 and H_2 protons in the spectra of the two latter compounds have a fine structure almost unresolved at 100 Mc, but more pronounced in the π-(2-methylallyl)irontricarbonyl chloride spectrum at 60 Mc (see Fig. 8b). The observed spectrum can probably be assigned to an AA'XX' pattern. Further communications will deal with a complete analysis of the spectra of this and other 2-substituted iron π-allylcomplexes as well as the magnitudes of the geminal spin–spin coupling constants. It would also be of interest to investigate the gradual increase of the $J(H_1–H_3)$ spin–spin coupling constants for $C_3H_5Fe(CO)_3X$ in the series: $X=\pi\text{-}C_3H_5$, I, Br, Cl, NO_3. It is likely that this phenomenon is due to a gradual reduction of the $C_1C_2C_3$ angle in the allyl group for such a series. The results presented above show that a study of the rotational isomerism in the π-allyl organometallic compounds yields new valuable information either on the origin of the metal–ligand bond or on the nature of the electronic and steric interactions in a molecule.

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