

**808.** *Transition-metal Fluorocarbon Complexes. Part VI.<sup>1</sup> Nuclear Magnetic Resonance Studies of Perfluoroalkyl Compounds of Cobalt and Rhodium.*

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The proton and fluorine-19 nuclear magnetic resonance spectra of  $\pi\text{-C}_5\text{H}_5\text{M}(\text{CO})\text{RI}$  ( $\text{M} = \text{Co}$  or  $\text{Rh}$ ;  $\text{R} = \text{CF}_3$ ,  $\text{C}_2\text{F}_5$ , or  $\text{C}_3\text{F}_7$ ) have been measured. The spectra for  $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{CO})\text{C}_2\text{F}_5\text{I}$  and  $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{CO})\text{C}_3\text{F}_7\text{I}$  show that the metal atom is the asymmetric centre of a tetrahedral-type molecule in solution.

PERFLUOROALKYL derivatives of the type  $\pi\text{-C}_5\text{H}_5\text{Co}(\text{CO})\text{RI}$  ( $\text{R} = \text{CF}_3$ ,  $\text{C}_2\text{F}_5$ , or  $\text{C}_3\text{F}_7$ ) have been prepared<sup>2</sup> and similar compounds are obtained when the perfluoroalkyl iodide reacts with  $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{CO})_2$ . The products, which are the first reported perfluoroalkyl derivatives of rhodium, form red needles whose infrared spectra are similar to those of their cobalt analogues.

The fluorine-19 n.m.r. spectra of perfluoroalkyl compounds of transition metals have well-known characteristics;<sup>3</sup> while the chemical shifts of the  $\alpha\text{-CF}_2$ ,  $\beta\text{-CF}_2$ , and  $\alpha\text{-CF}_3$  group resonances of the rhodium compounds occur in the expected regions, their mutual couplings present some unusual features. The data for the rhodium compounds are summarised in the Table, together with data for the similar cobalt compounds whose spectra were not reported previously.<sup>2,3</sup>

The doublet in the fluorine-19 n.m.r. spectrum of  $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{CO})\text{CF}_3\text{I}$  arises from electron coupled spin-spin interaction between the fluorine-19 nuclei of the trifluoromethyl group and the rhodium-103 nucleus (spin  $\frac{1}{2}$ , relative abundance 100%). Multiplet structure observed on the doublets (6 components, splitting 0.5 c./sec.) is probably due to coupling between the fluorine nuclei and the protons of the cyclopentadienyl ring. The corresponding splitting of the cyclopentadienyl-ring proton resonance line was not seen and neither was the expected  $^{103}\text{Rh}\text{-H}$  coupling although the line-width at half-height was 2.0 c./sec. However, it is possible that the rotation of the cyclopentadienyl ring about the Rh-ring bond is considerably slower than the rotation of the trifluoromethyl group about the Rh-C bond and the nuclear relaxation time of the fluorine-19 nuclei will be

<sup>1</sup> Part V, Dickson and Wilkinson, *J.*, 1964, 2699.

<sup>2</sup> King, Treichel, and Stone, *J. Amer. Chem. Soc.*, 1961, **83**, 3593.

<sup>3</sup> Pitcher, Buckingham, and Stone, *J. Chem. Phys.*, 1962, **36**, 124.

longer than that of the protons; the proton line will then be broader and less well resolved than the fluorine-19 lines.

In the pentafluoroethyl-rhodium compound, the  $\alpha$ -CF<sub>2</sub> group resonance (Fig. 1) is a typical AB pair, each resonance line showing additional splittings into a doublet and again into a quartet. The notable feature of these additional splittings is that they are different

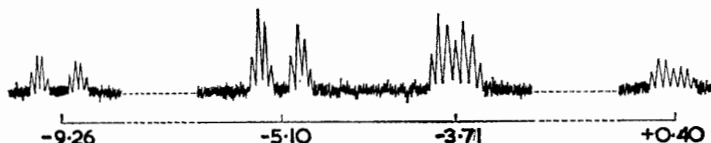


FIG. 1. The  $\alpha$ -CF<sub>2</sub> resonance in the fluorine-19 n.m.r. spectrum of  $\pi$ -C<sub>5</sub>H<sub>5</sub>Rh(CO)C<sub>2</sub>F<sub>5</sub>I (values in p.p.m. relative to benzotrifluoride, corrected for dichloromethane).

for F<sub>A</sub> and F<sub>B</sub>. The doublet splittings are 6.10 c./sec. for F<sub>B</sub> and 9.70 c./sec. for F<sub>A</sub>, and the separations between the quartet components are 2.30 c./sec. (F<sub>B</sub>) and 1.70 c./sec. (F<sub>A</sub>). In a first-order analysis the  $\gamma$ -CF<sub>3</sub> line might be expected to be a double doublet but a single broad line (line-width at half-height, 5.20 c./sec.) is found under even very high resolution. In an ABX<sub>3</sub> system,<sup>4</sup> however, the resonances due to the X nuclei and their coupling with the A and B nuclei would give rise to 6 or more lines whose separations are small and so a single broad line could result.  $\pi$ -C<sub>5</sub>H<sub>5</sub>Co(CO)C<sub>2</sub>F<sub>5</sub>I has a similar ABX<sub>3</sub> spectrum.

The fluorine-19 n.m.r. spectrum (Fig. 2) of  $\pi$ -C<sub>5</sub>H<sub>5</sub>Rh(CO)C<sub>3</sub>F<sub>7</sub>I is very complex and

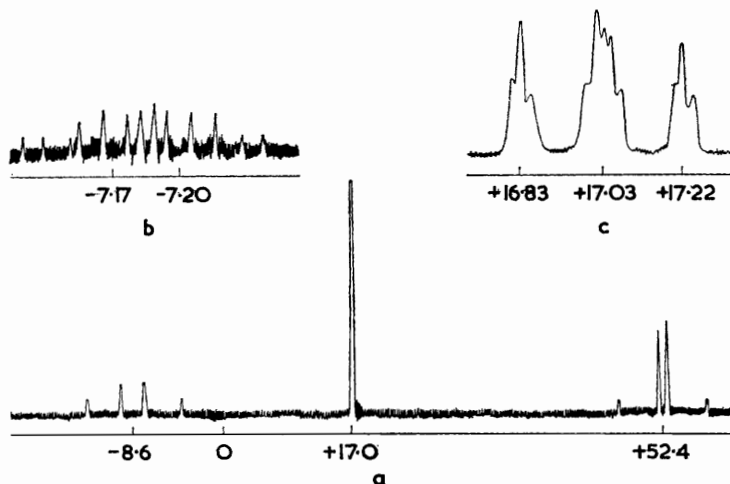


FIG. 2. The fluorine-19 n.m.r. spectrum of  $\pi$ -C<sub>5</sub>H<sub>5</sub>Rh(CO)C<sub>3</sub>F<sub>7</sub>I: (a) the total spectrum; (b) the well-resolved high-field lines of the  $\alpha$ -CF<sub>2</sub> group; (c) the  $\gamma$ -CF<sub>3</sub> group (values in p.p.m. relative to benzotrifluoride, corrected for dichloromethane).

may be regarded as an AA'BB'X<sub>3</sub> system.<sup>4</sup> The  $\gamma$ -CF<sub>3</sub> group is a double doublet, due to coupling with the non-equivalent  $\alpha$ -fluorine nuclei but owing to the difficulty in resolving one of the two components of the  $\alpha$ -CF<sub>2</sub> multiplet only the 11.5 c./sec. coupling could be confirmed. The outer lines of this double doublet show clearly a further splitting into triplets (splitting 1.2 c./sec.). The quintet structure (splitting 1.1 c./sec.) on the inner line of the double doublet can be explained by the overlapping of two triplets. The  $\beta$ -CF<sub>2</sub> group gives rise to an AB pair and there are additional splittings which are observed most clearly on the central components. The high-field line is a poorly resolved quartet (splitting

<sup>4</sup> Fessenden and Waugh, *J. Chem. Phys.*, 1959, **30**, 944.

*ca.* 1.5 c./sec.) and the low-field line a doublet (splitting 2.0 c./sec.). The lines due to the  $\alpha$ -CF<sub>2</sub> group constitute an AB pair with very complex splittings on each component. The high-field group is well resolved into sixteen lines, being a doublet doublet quartet. The quartet splitting is presumably due to  $J_{\alpha\gamma}$  (11.5 c./sec.) and one of the doublet splittings presumably the <sup>19</sup>F-<sup>103</sup>Rh coupling. The low-field set of lines could not be resolved although the group, as a whole, was more than 20 c./sec. wide.

The fluorine-19 n.m.r. of  $\pi$ -C<sub>5</sub>H<sub>5</sub>Co(CO)C<sub>3</sub>F<sub>7</sub>I is unusual because it displays the features expected of "normal" perfluoropropyl derivatives [*e.g.*, C<sub>3</sub>F<sub>7</sub>Fe(CO)<sub>4</sub>I or C<sub>3</sub>F<sub>7</sub>Mn(CO)<sub>5</sub>]. The  $\alpha$ -fluorine nuclei resonance is a quartet, the  $\beta$ -fluorine nuclei apparently a doublet, and the  $\gamma$ -CF<sub>3</sub> resonance a triplet. However, under very high radiofrequency power low-intensity satellite bands are observed on either side of the two strong  $\beta$ -fluorine lines, the group thus being an AB pair and not a simple doublet.

The most important feature emerging from the data is that indicated by the presence of  $\alpha$ -AB pairs. These show that the rhodium atom is the asymmetric centre of a molecule which in solution must have an overall tetrahedral or "piano-stool" configuration. The structure of the molecule would be similar to  $\pi$ -C<sub>5</sub>H<sub>5</sub>Mn(CO)<sub>3</sub> with two of the carbonyl groups replaced by iodine and the perfluoroalkyl group. Although the molecules should have optical isomers, we have not been able to separate these neutral species.

The values of  $\delta_{AB}$  decrease with increasing distance of the AB nuclei from the asymmetric rhodium atom. The values of  $J_{AB}$  are of the expected order for perfluoroalkyl compounds<sup>5</sup> and it is notable that in the perfluoro-ethyl and -propyl complexes the couplings between the fluorine nuclei on the  $\alpha$ -carbon are nearly constant for both cobalt and rhodium; this is also true of the cobalt and rhodium perfluoropropyl  $\beta$ -fluorine couplings.

As the perfluoro-ethyl and -propyl resonances are described as ABX<sub>3</sub> and AA'BB'X<sub>3</sub>, definite assignment of  $J_{\alpha\beta}$  and  $J_{\alpha\gamma}$  is not possible in a first-order analysis; the values indicated in the Table are tentative suggestions. However, in perfluoropropyl derivatives of transition metals,  $J_{\alpha\gamma}$  is of the order of 10–11 c./sec. and values in this region

Proton and fluorine-19 nuclear magnetic resonance spectra of the perfluoroalkyl derivatives of cobalt and rhodium.

CpM(CO)RI			<sup>19</sup> F shifts <sup>b</sup>			AB shifts <sup>c</sup>		AB couplings <sup>c</sup>		Coupling constants <sup>c</sup>		
R	M	$\tau^a$	$\delta\alpha$	$\delta\beta$	$\delta\gamma$	$\alpha$	$\beta$	$\alpha$	$\beta$	$J_{\alpha\beta}$	$J_{\alpha\gamma}$	$J_{Rh-F}$
						$\delta_{AB}$	$\delta_{AB}$	$J_{AB}$	$J_{AB}$			
CF <sub>3</sub> ...	Co	4.29	-73.42									
	Rh	4.01	-74.76									11.7
C <sub>2</sub> F <sub>5</sub> ...	Co	4.30	-1.70	18.48		164		233		2.0		
	Rh	4.03	-4.40	20.05		208		234		1.8		
C <sub>3</sub> F <sub>7</sub> ...	Co	4.28	-5.87	50.44	17.29		164		283		10.7	
	Rh	4.03	-8.60	52.40	17.03	318	136	239	284	1.9	11.5	4.3
										1.7	10.6	

<sup>a</sup> Measured in chloroform solution. <sup>b</sup> In p.p.m. relative to benzotrifluoride, positive values indicating lines on the high-field side of this reference, measured in methylene chloride solution corrected for this solvent (+1.2 p.p.m., see Evans, *J.*, 1960, 877). <sup>c</sup> Couplings in c./sec.

are observed in the complexes described here. The smaller splittings in the perfluoro-ethyl and -propyl compounds presumably include  $J_{Rh-F}$  but this, without spin decoupling, cannot be determined with certainty. It is tempting to suggest that the values of  $J_{Rh-F}$  decrease as the length of the alkyl chain increases [*e.g.*, 11.7 c./sec. for Rh-CF<sub>3</sub>; 6–9 c./sec. for Rh-C<sub>2</sub>F<sub>5</sub> ( $\alpha$  resonance) and *ca.* 4 c./sec. for Rh-C<sub>3</sub>F<sub>7</sub> ( $\alpha$  resonance)].

<sup>5</sup> Pople, Schneider, and Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, 1959, pp. 332, 379.

## EXPERIMENTAL

Microanalyses were by the Microanalytical Laboratories of this College. High-resolution n.m.r. spectra were recorded using a Varian Associates model 4311 spectrometer at 56.45 Mc./sec. and  $22 \pm 2^\circ$ . The compounds were studied in degassed dichloromethane solution, the fluorine resonance lines being given relative to benzotrifluoride (as internal reference), positive values representing lines on the high-field side of this reference. Tetramethylsilane was used as internal reference in the proton magnetic resonance spectra, measured in chloroform solution. Line positions were determined by conventional side-band techniques. The spectra were analysed, where feasible, using the standard procedures.<sup>5</sup>

*Iodocarbonyl- $\pi$ -cyclopentadienyltrifluoromethylrhodium.*—Dicarbonyl- $\pi$ -cyclopentadienylrhodium (0.5 g.) was dissolved in benzene (5 ml.), sealed in an evacuated Carius tube with trifluoromethyl iodide (3 ml.), and maintained at  $30\text{--}40^\circ$  for 30 hr. Large dark red crystals were formed. The tube was opened (carbon monoxide pressure), and the volatile materials removed ( $30^\circ/0.1$  mm.). The red residue was extracted with dichloromethane and the *complex* precipitated by addition of light petroleum (b. p.  $30\text{--}40^\circ$ ) as dark red needles, m. p.  $168\text{--}169^\circ$  (yield ca. 60%) (Found: C, 22.1; H, 1.4; F, 14.6; I, 32.9.  $C_7H_5F_3OIRh$  requires C, 21.4; H, 1.3; F, 14.6; I, 32.4%). The compound was purified by sublimation ( $100^\circ/0.1$  mm.) on to a probe cooled by acetone–solid carbon dioxide, and is soluble in most common organic solvents, but sparingly so in carbon tetrachloride and carbon disulphide.

*Iodocarbonyl- $\pi$ -cyclopentadienylpentafluoroethylrhodium.* The compound was prepared in the same way as its trifluoromethyl analogue, using pentafluoroethyl iodide. The *complex*, m. p.  $145\text{--}147^\circ$ , was purified by extracting the residue from the Carius tube in a Soxhlet apparatus with light petroleum (b. p.  $40\text{--}60^\circ$ ) (yield ca. 80–85%) (Found: C, 21.9; H, 1.3; F, 21.4; I, 28.6.  $C_8H_5F_5OIRh$  requires C, 21.7; H, 1.1; F, 21.5; I, 28.7%). The red compound is air-stable, and soluble in most organic solvents, except light petroleum (b. p.  $60\text{--}120^\circ$ ).

*Iodocarbonyl- $\pi$ -cyclopentadienylheptafluoropropylrhodium.* The compound was prepared by using heptafluoropropyl iodide and purified in the same way as the pentafluoroethyl derivative, to which it is very similar. It forms red crystals, m. p.  $118\text{--}119^\circ$  [yield ca. 80–85% based on  $\pi\text{-C}_6\text{H}_5\text{Rh}(\text{CO})_2$ ] (Found: C, 17.1; H, 1.6; F, 27.4; I, 26.2.  $C_9H_5F_7IORh$  requires C, 16.5; H, 1.2; F, 27.0; I, 25.8%).

The *perfluoroalkylcobalt* compounds were prepared in the same way as their rhodium analogues. The dark green-brown crystals are similar to those reported previously.<sup>3</sup> While the perfluoromethyl and perfluoroethyl compounds were best purified by sublimation, the perfluoropropyl derivative was easily recrystallised from light petroleum (b. p.  $40\text{--}60^\circ$ ) to form dark green-brown needles.

*Infrared Spectra.*—Measurements were made in carbon disulphide solution using a Grubb-Parsons grating spectrometer.

$\pi\text{-C}_5\text{H}_5\text{Rh}(\text{CO})\text{CF}_3\text{I}$ : 3000w, 2098vs, 2052w, 1982w, 1865vww, 1787vw, 1672vw, 1351w, 1073vs, 1040vs, 989w,sh, 846vw,sh, 832m, 818m.

$\pi\text{-C}_5\text{H}_5\text{Rh}(\text{CO})\text{C}_2\text{F}_5\text{I}$ : 3005w, 2098s, 2048vw, 1299m, 1272w, 1263sh, 1191s, 1070s, 1063sh, 1023w, 1017sh, 998vw, 990vw, 908s, 831w, 818m, 732m, 657w (broad).

$\pi\text{-C}_5\text{H}_5\text{Rh}(\text{CO})\text{C}_3\text{F}_7\text{I}$ : 2988w, 2099s, 2046vw, 1408w, 1322s, 1242sh, 1230s, 1197s, 1172sh, 1163m, 1091s, 1061sh, 1053m, 1022sh, 1013w, 990vw, 932vw, 846sh, 833m, 819s, 800s, 728s, 662w.

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