

Preliminary Note

Polyfluoroaromatic derivatives of metal carbonyls

VIII*. Asymmetric pentafluorophenyl groups in some iridium complexes

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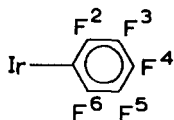
Treatment of $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ with LiC_6F_5 or AgC_6F_5 affords bright yellow $\text{Ir}(\text{C}_6\text{F}_5)(\text{CO})(\text{PPh}_3)_2$ (I), m.p. 208–210°(dec.), with $\nu(\text{CO})$ 1965 cm^{-1} . In the ^{19}F NMR spectrum, two resonances occur at 114.8 (multiplet, intensity 2, *ortho*-F) and 165.1 p.p.m. (multiplet, intensity 3, overlapping *para*- and *meta*-F)².

Oxidative-addition reactions proceed less readily with (I) than with Vaska's complex, as expected. Addition of hydrogen halide or of halogen occurs to give the white complexes $\text{Ir}(\text{C}_6\text{F}_5)(\text{CO})(\text{PPh}_3)_2\text{XY}$ ($\text{XY} = \text{Cl}_2, \text{Br}_2, \text{HCl}, \text{HBr}, \text{etc.}$). The ^{19}F NMR spectra of these complexes are unusual in showing five resonances, all of equal intensity, with chemical shifts listed in Table 1. The spectra of analogous complexes containing PMePh_2 in place of PPh_3 show only the usual three resonances with a 2:1:2 intensity pattern.

We have ruled out the possibility that a fortuitous equimolar mixture of isomers gives rise to the observed spectra by a detailed analysis (including appropriate decoupling experiments) of the spectrum of $\text{Ir}(\text{C}_6\text{F}_5)(\text{CO})(\text{PPh}_3)_2\text{HCl}$ (II) (see Fig. 1). The derived coupling constants are listed in Table 1. The proton

TABLE 1

^{19}F CHEMICAL SHIFTS (p.p.m. upfield from CFCl_3)



Complex	F ²	F ⁶	F ³	F ⁵	F ⁴
$\text{Ir}(\text{C}_6\text{F}_5)(\text{CO})(\text{PPh}_3)_2\text{Cl}_2$	103.3	108.6	163.5	164.5	162.0
$\text{Ir}(\text{C}_6\text{F}_5)(\text{CO})(\text{PPh}_3)_2\text{Br}_2$	101.8	104.0	163.2	164.1	161.4
$\text{Ir}(\text{C}_6\text{F}_5)(\text{CO})(\text{PPh}_3)_2\text{I}_2$	95.8	100.1	162.9	164.3	161.1
$\text{Ir}(\text{C}_6\text{F}_5)(\text{CO})(\text{PPh}_3)_2\text{HCl}^a$	100.1	112.2	164.5	166.0	163.2
$\text{Ir}(\text{C}_6\text{F}_5)(\text{CO})(\text{PPh}_3)_2\text{HBr}$	99.5	108.8	164.4	165.5	163.1
$\text{Ir}(\text{C}_6\text{F}_5)(\text{CO})(\text{PPh}_3)_2$		114.8		165.1	
$\text{Ir}(\text{C}_6\text{F}_5)(\text{CO})(\text{PMePh}_2)_2\text{Cl}_2$		110.0	166.0	162.0	

^a Coupling constants: $J(2,3)$, 28.5; $J(2,4)$, 0; $J(2,5)$, 7.0; $J(2,6)$, 0; $J(3,4)$, 20.0; $J(3,5)$, 3.5; $J(3,6)$, 9.0; $J(4,5)$, 20.0; $J(4,6)$, 0; $J(5,6)$, 26.0 Hz.

* For Part VII, see Ref. 1.

NMR spectrum contains a high-field signal at τ 26.15, assigned to the metal-bonded proton (triplet of doublets, $J(\text{HP})$, 12; $J(\text{HF})$, 6 Hz).

This is the first example of a compound containing a pentafluorophenyl group in which all five fluorine atoms are inequivalent. This feature results from restricted rotation of the C_6F_5 group, probably caused by its being positioned between two mutually-*trans* PPh_3 groups. Although the stereochemistry of (II) cannot be unequivocally determined, the proton NMR spectrum of the analogous PMePh_2 complex exhibits an apparent triplet for the PMe groups, suggesting that the two phosphorus ligands are mutually *trans* in this complex. The coupling of the IrH to only one fluorine suggests that it is *cis* to the C_6F_5 group; it has not yet been possible to determine the relative positions of the Cl and CO groups.

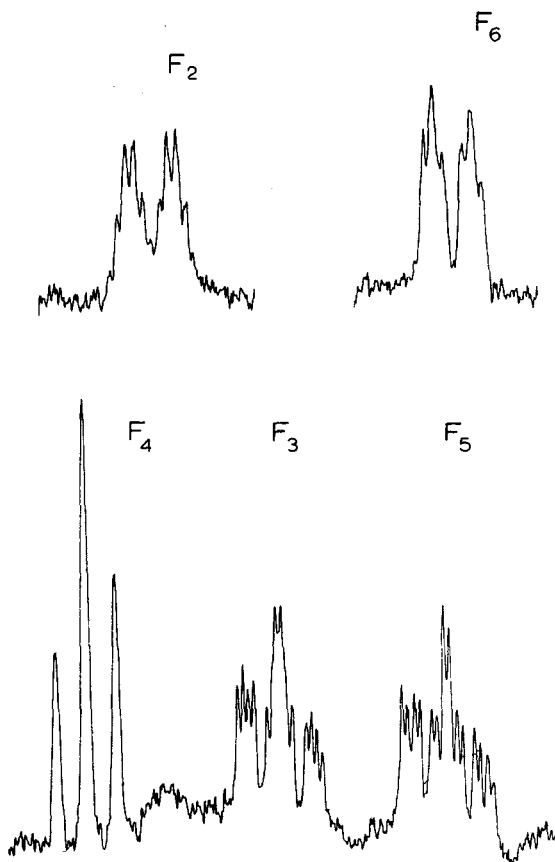


Fig. 1. ^{19}F NMR spectrum of $\text{Ir}(\text{C}_6\text{H}_5)(\text{CO})(\text{PPh}_3)_2\text{HCl}$.

REFERENCES

- 1 M. I. BRUCE AND A. D. REDHOUSE, *J. Organometallic Chem.*, 30 (1971) C78.
- 2 M. I. BRUCE, *J. Chem. Soc. (A)*, (1968) 1459; F. J. HOPTON, A. J. REST, D. T. ROSEVEAR AND F. G. A. STONE, *J. Chem. Soc. (A)*, (1966) 1326.