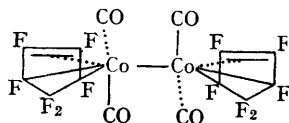


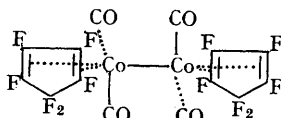
Perfluorocyclopentadiene-Transition Metal Complexes

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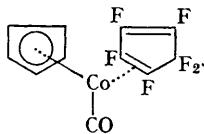
MANY cyclopentadiene-transition metal complexes are known; the first perfluorocyclopentadiene-transition metal complexes are now reported.



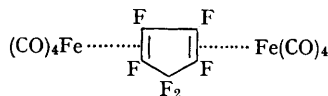
(I)



(II)



(III)



(IV)

Perfluorocyclopentadiene¹ combines readily with cobalt carbonyl in light petroleum at room temperature to give a 65% yield of an air-stable, weakly paramagnetic ($\mu \sim 0.5$ BM), crystalline, orange-yellow solid, m.p. 58–59°, which has been shown by elemental analysis, molecular weight measurement, and spectroscopic analysis [i.r. (no absorption in the bridging carbonyl or uncomplexed C=C regions of the spectrum), ¹⁹F. n.m.r., and mass spectroscopy]

to be dimeric perfluorocyclopentadienecobalt dicarbonyl. By ¹⁹F n.m.r. spectroscopy, this complex was shown to contain one pair of equivalent fluorine nuclei and two non-equivalent fluorine nuclei, in addition to a CF₂ group with non-equivalent fluorines; these data are accommodated by structure (I), a model of which shows that one of the pair of apparently equivalent vinylic fluorine substituents in (I) may approach the Co-Co bond more closely than the other and thereby become magnetically non-equivalent with its partner. The alternative structure (II), involving attachment of the diene to cobalt *via* two π -bonds, seems inconsistent with the n.m.r. data. In the absence of X-ray structural data the exact nature of the bonding in dimeric perfluorocyclopentadiene cobalt dicarbonyl cannot be decided finally, although it is pertinent to note that recent X-ray analyses of the structures of tricarbonyloctafluorocyclohexa-1,3-dieneiron² and the tetrakis(trifluoromethyl)cyclopentadienone complexes (CF₃)₄C₅O·Fe(CO)₃³ and (CF₃)₄C₅O·Co(π -C₅H₅)⁴ have shown that the diene or dienone is attached to the metal atom by one π -bond and two σ -bonds.

Photochemical reaction of perfluorocyclopentadiene with π -cyclopentadienylcobalt dicarbonyl in benzene solution at room temperature gives a product from which perfluorocyclopentadiene- π -cyclopentadienylcobalt carbonyl (III) can be isolated in 8% yield by liquid-solid chromatography. The structure of this complex, an air-stable crystalline yellow solid, m.p. 83–84°, was confirmed by elemental analysis and infrared,

¹ R. E. Banks, R. N. Haszeldine, and J. B. Walton, *J.*, 1963, 5581.

² M. R. Churchill and R. Mason, *Proc. Chem. Soc.*, 1964, 226.

³ N. A. Bailey, M. Gerloch, and R. Mason, *Nature*, 1964, 201, 72.

⁴ M. Gerloch and R. Mason, *Proc. Roy. Soc.*, 1964, A, 279, 170.

^{19}F and ^1H n.m.r., and mass spectroscopic analyses. Its n.m.r. spectra contain satellite bands that reveal the presence of two isomers of closely related structure in the approximate ratio of 7:1; these isomers possibly differ in the relative orientation of the C_5F_8 ring to the carbonyl group or to the cyclopentadienyl entity. The infrared spectrum of (III) (Nujol mull) shows a strong carbonyl band at 2035 cm.^{-1} , a weak absorption at 1990 cm.^{-1} (possibly due to the carbonyl group in the least abundant isomer), and a strong $\text{C}=\text{C}$ absorption at 1713 cm.^{-1} (cf. $^1\text{perfluorocyclopentadiene vapour}$, $\text{C}=\text{C}$ absorption at 1770 cm.^{-1}).

Iron pentacarbonyl reacts with perfluorocyclopentadiene under the influence of u.v. radiation

to give yellow, crystalline μ -(perfluorocyclopentadiene)bis(tetracarbonyliron) (IV), m.p. 95.5° (8% yield after chromatographic isolation), the structure of which was determined by the methods used for (I) and (III). The ^{19}F n.m.r. spectrum of (IV) revealed that it contained three pairs of equivalent fluorine nuclei, while its infrared spectrum disclosed that bridging carbonyl groups were absent and that both olefinic bonds in the diene were co-ordinated.

Preliminary work has shown that reaction of perfluorocyclopentadiene with manganese pentacarbonyl hydride yields two 1:1 adducts.

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