The Interaction of Perfluorobutadiene with Iron and Cobalt Carbonyls

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The interactions of perfluorobutadiene with pentacarbonyliron and octacarbonyldicobalt lead, respectively, to the complexes of stoicheiometry $C_4F_6Fe(CO)_4$ and $C_4F_6Co_2(CO)_6$. The infrared and ^{19}F nuclear magnetic resonance spectra and some chemical properties of the complexes are given. The cobalt complex reacts with triphenyl- and tri-n-butyl-phosphines and triphenylarsine to form paramagnetic adducts, *e.g.*, $C_4F_6Co_2(CO)_6(AsPh_3)_2$.

APART from a quotation [1] of unpublished work by Chatt and Guy to the effect that perfluorobutadiene forms an unstable complex with platinum, the only other studies involving transition metals is a recent mention [2] of its interaction with certain carbonylate anions.

Interaction with Pentacarbonyliron.—Perfluorobutadiene and pentacarbonyliron in petroleum solution interact under mercury-sensitised ultraviolet radiation to yield a yellow solid which, on vacuum sublimation, yields transparent colourless to greenish-yellow crystals. We have been unable to promote this reaction thermally, but dodecacarbonyltri-iron in petroleum reacts with perfluorobutadiene at *ca.* 120° for 12 hours to give, after sublimation, a similar product of somewhat lower melting

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[1] R. G. Guy and B. L. Shaw, *Adv. Inorg. Chem. Radiochem.*, 1962, **4**, 99.

[2] M. Green, N Mayne, and F. G. A. Stone, *Chem. Comm.*, 1966, 755.

point. This substance appears to be a mixture of the first complex with another (doubtless an isomer, as noted below) so similar to it that we have been unable to separate them by chromatography, the difficulty in part being due to decomposition on the columns.

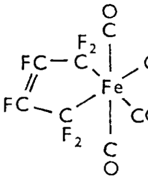
The first substance, which melts sharply at 61—61·5°, analyses as $C_4F_6Fe(CO)_4$ and has the correct molecular weight. The infrared spectrum shows four terminal carbon monoxide stretching frequencies, bands due to C–F groups and, in addition, a single sharp band at 1752 cm.$^{-1}$ which is assigned as a C=C stretching frequency.

The ^{19}F nuclear magnetic resonance (n.m.r.) spectrum has two peaks at $-4·0$ and $+71·9$ p.p.m. relative to benzotrifluoride as reference, the area ratios being, respectively, 2 : 1. The low-field peak is complex but compatible with an A_2X_4 system having a main doublet separation 6·8 c./sec. and is in a position typical for a $-CF_2-$ group σ-bonded to a metal.[3] The high-field line shows also complicated and incompletely resolved splittings but the line position is consistent for that for olefinic fluorine groups. The only structure accommodating these facts is (I), which is thus very similar to the first known complex of this type which had a saturated fluorocarbon ring.[3] *X*-Ray crystallographic studies [4] have confirmed the structure (I). The n.m.r. spectrum of the mixture referred to above suggests that the second component is an isomer with the double bond in the 2,3 position.

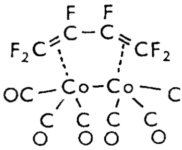
Interaction with Octacarbonyldicobalt.—The thermal interaction of octacarbonyldicobalt and perfluorobutadiene yields two products, one a non-volatile red substance which cannot be crystallised and which we have been unable to characterise, the other a material which can be readily purified by vacuum sublimation or crystallisation from solvents as large yellow crystals. The compound analyses as $C_4F_6Co_2(CO)_6$ and the molecular weight is also correct. The mass spectrum shows the highest mass at 448 although this value is somewhat unprecise, with peaks at 420, 392, 364, 335, 308, and 280. Although the successive loss of six carbon monoxide molecules is thus evident, there is no evidence for a species in which only the fluorocarbon has been lost; this is consistent with the strong binding of fluoro-olefins and with other similar data.[3] The complex is a non-conductor in nitrobenzene; it is unaffected by air in the solid state or in solution, by bromine at 85°, by iodine at 80°, strong acids, bases, or molten diphenylacetylene. With carbon monoxide at 150°/150 atm., partial conversion into octacarbonyldicobalt occurs.

The infrared spectrum in solution shows three terminal carbonyl frequencies, peaks assignable to C–F, but no band due to bridging carbonyl or to C=C groups.

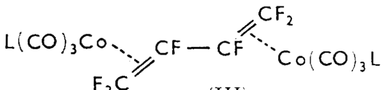
The ^{19}F n.m.r. spectrum has two peaks of relative area 1 : 2 at $+26·2$ and $+36·7$ p.p.m. relative to benzotrifluoride. The high-field line is a sharp doublet with separation 16·5 c./sec., but the low-field line is unusually poorly defined and broad (75 c./sec.). These resonance positions are not consistent with σ-bonding of a fluoroalkyl group and the structure best consistent with the evidence is one involving a co-ordinated bridging perfluorobutadiene and a cobalt–cobalt bond (II). The extremely large unit cell found for this complex [4] has made the *X*-ray structure determination very difficult, but the metal–metal distance does appear to be sufficiently short to satisfy the criterion for metal–metal bonding. This is in any case required by the observed diamagnetism of the complex.



(I)



(II)



(III)

Whilst attempts to substitute either the carbonyl or fluoro-olefin ligands have failed, the cobalt–cobalt bond can be opened by additional ligand co-ordination to yield paramagnetic complexes which evidently have the structure (III; L = Ph_3P, Ph_3As, $Bu^n{}_3P$). Thus on refluxing $C_4F_6Co_2(CO)_6$ with triphenylphosphine in petroleum, a very sparingly soluble adduct is obtained, which analyses as $C_4F_6Co_2(CO)_6(PPh_3)_2$. This complex is paramagnetic with μ_{eff} = 2·0 B.M. (1·4 B.M. per metal atom) at 298°K; over a temperature range, some deviation from the Curie–Weiss law is observed. The electron spin resonance spectra of the solid at 78° and 295°K are almost identical and show three, not too well resolved lines, g = 1·95, 2·67, and 2·95. The magnetic data are thus consistent with an unpaired electron on each cobalt atom but with some interaction probably due to the high magnetic concentration.

The comparable triphenylarsine complex is readily soluble in organic solvents such as chloroform, acetone, and benzene although sparingly soluble in petroleum. This complex is also paramagnetic, μ_{eff} = 2·6 B.M. at 282°; the e.s.r. spectrum shows only a broad band centred at g = 2·35.

EXPERIMENTAL

Microanalyses and molecular weights (Mechrolab osmometer, 37°) were by the Microanalytical Laboratory, Imperial College, and Dr. A. Bernhardt, Mülheim. Infrared spectra were recorded on a Grubb–Parsons Spectromaster grating instrument, n.m.r. spectra on a Varian V 4311 at 56·45 Mc./sec. (benzotrifluoride as internal reference), and e.s.r. spectra on a Varian V-4502–15. Mass spectra were taken on an MS-9 spectrometer. Melting points were taken on a Kofler hot-stage, and are uncorrected. Perfluorobutadiene was from the Peninsular Chemicals Company.

Interaction of Perfluorobutadiene and Pentacarbonyliron.—An excess of C_4F_6 (2 ml.) and $Fe(CO)_5$ (1·5 ml.) in a sealed

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[3] H. H. Hoehn, L. Pratt, K. F. Watterson, and G. Wilkinson, *J. Chem. Soc.*, 1961, 2738.

[4] R. Mason, Sheffield University, personal communication.

glass tube, containing a little mercury, was irradiated with ultraviolet light for 24 hr. After removal of liquid *in vacuo*, the residue was crystallised from petroleum (b. p. 30—40°) at −40°. The solid was then sublimed *in vacuo* from room temperature to a water-cooled probe to give the pure *complex*; yield, *ca.* 100 mg., m. p. 61—61·5° [Found: C, 29·0; F, 34·3; Fe, 17·0%; *M*, 325 (benzene) $C_8F_6FeO_4$ requires C, 29·1; F, 34·5; Fe, 16·9%; *M*, 330], $\nu_{max.}$ (cyclohexane): 2153s, 2097s, 2092s, 2076s, 1752s, 1344m, 1310s, 1287sh, 1122s, 1090m, 1059m, 977s, 928s, and 815m.

Interaction of Perfluorobutadiene and Octacarbonyldicobalt.—An excess of C_4F_6 (3·5 ml.) and $Co_2(CO)_8$ (4 g.) in a thick-walled glass tube were heated at 100° for 24 hr. After opening and removal of excess of C_4F_6, the residue was extracted with petroleum (b. p. 40—60°) to leave a red residue. The solution was evaporated and the residue sublimed *in vacuo* at 60° to a water-cooled probe. Two crystallisations from petroleum (b. p. 30—40°) produced yellow needles of the *complex*; yield *ca.* 4 g., m. p. 85—85·5° [Found: C, 27·1; Co, 26·3; F, 25·4%; *M*, 460 (benzene). $C_{10}Co_2F_6O_6$ requires C, 26·8; Co, 26·4; F, 25·4%; *M*, 448], $\nu_{max.}$ (cyclohexane): 2132s, 2096s, 2079s, 1284m, 1244m, 1199s, 1100s, 994s, 888m, 730s, and 665s.

Bis(triphenylphosphine)perfluorobutadienehexacarbonyldicobalt.—Perfluorobutadiene hexacarbonyldicobalt (0·2 g.; 1 equiv.) and triphenylphosphine (0·24 g.; 2 equiv.) in petroleum (20 ml., b. p. 60—80°) were refluxed 2 hr. and the yellow-orange precipitate of the *complex* then collected and washed with petroleum and acetone. The yield was quantitative; m. p. 146—150° (Found: C, 56·6; H, 3·4; F, 12·5. $C_{46}H_{30}Co_2F_6O_6P_2$ requires C, 56·8; H, 3·1; F, 11·7%), $\nu_{max.}$ (Nujol mull): 2073s, 2048s, 2024s, 2018s, 1277s, 1236s, 1186s, 1164m, 1098m, 1088m, 1070m, 1042m, 1000m, 977m, 969s, 880s, 746s, 715s, and 696s. The magnetic moment (from susceptibilities by the Gouy method, corrected for diamagnetism of ligands), μ_{eff} in B.M., °K: 2·0, 297°; 1·9, 254°; 1·8, 204°; 1·6, 155°; 1·4, 113°.

*Bis(tri-*n*-butylphosphine)perfluorobutadienehexacarbonyldicobalt.*—This was obtained in a similar way by use of stoicheiometric quantities with tri-n-butylphosphine as an orange tar after removal of petroleum. This was dissolved in methanol and cooled to −40° to give orange crystals of the *complex* which were collected and dried *in vacuo*; yield, *ca.* 70%, m. p. 77·5—78° (Found: C, 48·0; H, 6·6; Co, 14·0; F, 13·7. $C_{34}H_{54}Co_2F_6O_6P_2$ requires C, 47·9; H, 6·3; Co, 13·9; F, 13·4%), $\nu_{max.}$ (cyclohexane): 2058s, 2027s, 2008s, 1993m, 1381s, 1274s, 1230s, 1186s, 1092s, 1071s, 1053s, 977s, 882s, 775m, and 712s.

Bis(triphenylarsine)perfluorobutadienehexacarbonyldicobalt.—As for the Ph_3P complex, this yellow *complex* was obtained essentially quantitatively, m. p. 110° (decomp.) [Found: C, 52·2; H, 2·9; F, 10·8%; *M*, 1080 ($CHCl_3$). $C_{46}H_{30}As_2Co_2F_6O_6$ requires C, 52·1; H, 2·8; F, 10·8%; *M*, 1060], $\nu_{max.}$ (CH_2Cl_2) 2110m, 2045vs, 2018vs, 1931s, 1709w, 1597w, 1399m, 1220s, 1183s, 1157sh, 1073s, 1050ms, 977s, and 878s.

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