684. *Transition-metal–Fluorocarbon Complexes. Part III.*[1] *Some Derivatives of Hexafluorobut-2-yne.*[2]

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Reaction of hexafluorobut-2-yne with iron and cobalt carbonyls and with carbonyl-π-cyclopentadienyl-cobalt and -nickel has given the very stable and unreactive complexes $C_9F_{12}OFe(CO)_3$, $C_4F_6Co_2(CO)_6$, π-$C_5H_5CoC_8F_{12}$, and $C_4F_6Ni_2(\pi\text{-}C_5H_5)_2$, respectively. Infrared and nuclear magnetic resonance spectra of these compounds and of π-$C_5H_5CoC_4(C_6H_5)_4$ are given and the structures of the compounds discussed.

A number of transition-metal complexes have been found to polymerise hexafluorobut-2-yne under mild conditions either to hexakistrifluoromethylbenzene or to a white infusible high polymer.

WE previously described[3] transition-metal complexes obtained from reaction of octafluorohexa-1,3-diene and of tetrafluoroethylene with metal carbonyls and π-cyclopentadienyl compounds; tricarbonyloctafluorohexa-1,3-dieneiron was further found[1] to react with cæsium fluoride to give a salt of the stable anion $[C_6F_9Fe(CO)_3]^-$.

It was not possible on the basis of infrared and nuclear magnetic resonance spectra to specify unequivocally the nature of the bonding in $C_6F_8Fe(CO)_3$, and models with two donor bonds or with one donor bond plus two Fe–C σ-bonds are consistent with the results. In either case, however, the existence of a donor bond of the type well known for hydrocarbons from the double bond of the fluoro-olefin to a transition-metal atom appears to be demonstrated for the first time. It thus seemed reasonable to expect that perfluorinated acetylenes would also give stable organometallic compounds, perhaps of a different nature to, or at least more stable than, the well-known hydrocarbon complexes.[4] This possibility has been realised,[2] and in one case discussed here the existence of a donor bond from a double bond to a metal atom has been confirmed. Since difluoroacetylene is not known and monofluoroacetylene trimerises spontaneously to 1,2,4-trifluorobenzene and is also highly explosive in the liquid state,[5] we have used hexafluorobut-2-yne, which can be prepared by dechlorination of 2,2,3,3-tetrachlorohexafluorobutane.[6] Reaction of this acetylene with metal complexes has so far given products in which it is incorporated as a recognisable entity or in which it is dimerised both with and without incorporation of a carbon monoxide group. There are notable differences from hydrocarbons in the nature of the reactions of carbonyl and π-cyclopentadienyl compounds with hexafluorobut-2-yne and in the properties of the products. In certain cases we have, in addition, observed polymerisation of the acetylene under mild conditions in the reactions with metal species.

Tricarbonyl tetrakis(trifluoromethyl)cyclopentadienoneiron.—Interaction of hexafluorobut-2-yne and pentacarbonyliron yields a single product at temperatures between 100° and 200° and autogenous pressure, in contrast to the multiplicity of products resulting from the use of acetylenic hydrocarbons.[7] This product forms orange-yellow crystals, $C_9F_{12}OFe(CO)_3$. It is volatile, subliming slowly in a vacuum at 60°, and is readily soluble in cold polar organic solvents although it is very sparingly soluble in light petroleum or other hydrocarbons. In the solid state it appears to be stable indefinitely in absence of air. Slight surface decomposition can be observed under the microscope within a day in air.

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[1] Part II, Parshall and Wilkinson, *J.*, 1962, 1132.

[2] Preliminary note, Boston, Sharp, and Wilkinson, *Chem. and Ind.*, 1960, 1358.

[3] Hoehn, Pratt, Watterson, and Wilkinson, *J.*, 1961, 2738.

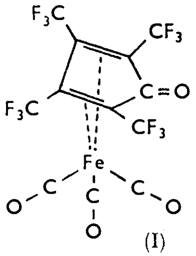
[4] For references see Coates, "Organometallic Compounds," 2nd edn., Methuen, London, 1960; *Ann. Reports*, 1957—1961.

[5] Middleton and Sharkey, *J. Amer. Chem. Soc.*, 1959, **81**, 803.

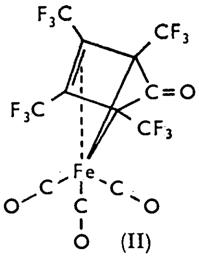
[6] Henne and Finnegan, *J. Amer. Chem. Soc.*, 1949, **71**, 298.

[7] Weiss and Hübel, *J. Inorg. Nuclear Chem.*, 1959, **9**, 204, and references cited in ref. 4.

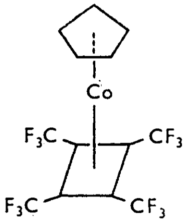
Solutions in air decompose slowly during 2—3 days. The compound is unaffected, and is not wetted, by water or aqueous acids but is readily soluble in concentrated sulphuric acid to form an orange solution from which is can be recovered by dilution. The compound is very sensitive to bases and is rapidly decomposed by sodium ethoxide in ethanol; if water is added to solutions of the compound in alcohol or acetone, rapid evolution of carbon monoxide occurs. The products of these reactions are complex and we have been unable to isolate a simple fluorocarbon from the solutions. The chemical and spectroscopic properties of the compound are consistent with its formulation as either a tetrakis(trifluoromethyl)cyclopentadienone complex (I) of iron(0) or a complex (II) involving a donor olefinic bond and two σ-bonds of iron(II). The infrared spectrum shows strong CF_3 group absorption in the region 1000—1300 cm.$^{-1}$,[8] and there are strong metal–carbonyl stretching frequencies at 2133, 2083, and 2040 cm.$^{-1}$ similar to those observed for tricarbonyltetraphenylcyclopentadienoneiron[9] but shifted by about 50 cm.$^{-1}$ to higher wave numbers. There are strong bands at 1742 and 1729 cm.$^{-1}$. In concentrated sulphuric acid, which protonates the keto-group, there is only a single band in the ketone stretching region. This band is assigned as a co-ordinated C=C stretching frequency. Since the position of this band is solvent-dependent it is impossible to decide which of the bands at 1742 and 1729 cm.$^{-1}$ is the ketone stretching frequency and which the co-ordinated C=C stretching frequency. The compound π-$C_5H_5CoC_8F_{12}$ discussed below also has a strong band in this region which must be due to the co-ordinated C=C.



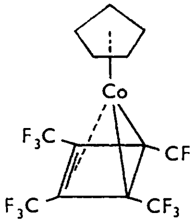
(I)



(II)



(III)



(IV)

The high-resolution ^{19}F resonance spectrum of $C_9F_{12}OFe(CO)_3$ shows two bands of equal intensity at 6·8 and 10·3 p.p.m. on the low-field side of the (internal) benzotrifluoride reference line, each of which is split into an approximate quadruplet. There thus appear to be two different types of CF_3 groups. In sulphuric acid solution the proton resonance spectrum shows only the broad sulphuric acid line, as would be expected from the rapid exchange of the hydrogen in the $>C^+$-OH group with solvent protons.

Despite the presence of the ketonic carbonyl group, the compound gives none of the usual reactions of ketones with, for example, 2,4-dinitrophenylhydrazine or semicarbazide, probably owing to the deactivating effect of the CF_3 groups; similar inactivity of the keto-group occurs in tricarbonyltetraphenylcyclopentadienoneiron.[10] Treatment of the iron compound with triphenylphosphine leads to smooth replacement of carbon monoxide, to give a complex $C_9F_{12}OFe(CO)_2PPh_3$. With pyridine, 2,2′-bipyridyl, or 1,10-phenanthroline in chloroform, red insoluble products are obtained; these give variable analyses and do not contain fluorine or carbon monoxide. The compound does not react when refluxed with norbornadiene, cyclo-octatetraene, or phenylacetylene, or with bromine in a sealed tube at 110°. On thermal decomposition of $C_9H_{12}OFe(CO)_3$ in a sealed tube at 200°, traces of a volatile liquid are occasionally obtained. The substance is very reactive and we have been unable to obtain sufficient material for satisfactory analysis. However, its ^{19}F resonance spectrum shows bands of equal intensity similar to those in the parent

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[8] (*a*) Bellamy, " The Infrared Spectra of Complex Molecules," 2nd edn., Methuen, London, 1958; see also (*b*) Haszeldine, *J.*, 1951, 2495; 1952, 2504.

[9] Hübel and Braye, *J. Inorg. Nuclear Chem.*, 1959, **10**, 250.

[10] Weiss and Hübel, *J. Inorg. Nuclear Chem.*, 1959, **11**, 42.

compound, suggesting that it is the unco-ordinated tetrakis(trifluoromethyl)cyclopentadienone.

Hexacarbonylhexafluorobut-2-ynedicobalt and Hexafluorobut-2-ynedi-(π-cyclopentadienylnickel).—Octacarbonyldicobalt and dicarbonyldi-π-cyclopentadienyldinickel react readily, the former even at room temperature, with perfluorobut-2-yne to give the crystalline compounds $C_4F_6Co_2(CO)_8$ and $(\pi\text{-}C_5H_5)_2Ni_2C_4F_6$, respectively. Both compounds are stable to air in the solid state and in solutions of common organic solvents; they are very volatile and the cobalt compound sublimes away if left exposed to the atmosphere. The cobalt compound is stable to dilute acids and bases and is only slowly attacked by hot concentrated sulphuric acid; unlike some other cobalt acetylene complexes [11] it does not react with carbon monoxide at 110°/150 atm.

The stoicheiometries and spectroscopic results suggest that in both compounds the acetylene has formed a bridge across the metal–metal bond as in the corresponding cobalt carbonyl [12] and π-cyclopentadienylnickel [13] complexes of diphenylacetylene. Thus the cobalt compound has strong carbonyl bands at 2131, 2101, and 2077 $cm.^{-1}$ which are displaced by 40—50 $cm.^{-1}$ to higher frequencies than in the corresponding diphenylacetylene complexes.[12a] In carbon tetrachloride solution, both compounds show only a single sharp ^{19}F resonance line at 10·0 and 11·5 p.p.m. on the low-field side of benzotrifluoride for the cobalt and the nickel compound, respectively.

π-Cyclopentadienyltetrakis(trifluoromethyl)cyclobutadienecobalt.—Interaction of hexafluorobut-2-yne and π-cyclopentadienylcobalt dicarbonyl gives high yields of a red crystalline compound, $\pi\text{-}C_5H_5CoC_8F_{12}$. This compound is also obtained though in very low yield, by the action of the acetylene on di-π-cyclopentadienylcobalt; the main product in the latter reaction is an adduct of stoicheiometry $C_{10}H_{10}CoC_8F_{12}$ which will be described in a later paper. The compound, $\pi\text{-}C_5H_5CoC_8F_{12}$, which sublimes in a vacuum above 100°, is moderately soluble in cold non-polar solvents, and in both the solid state and in solution is stable to air and extremely resistant to chemical attack. The $\pi\text{-}C_5H_5$ ring appears to be strongly deactivated by the fluorocarbon ligand, and the compound does not undergo Friedel–Crafts acylation, metallation with butyl-lithium, nitration with fuming nitric and concentrated sulphuric acid at 50°, sulphonation with boiling concentrated sulphuric acid or chlorosulphonic acid, or halogenation with bromine in a sealed tube at 110°, and it can be recovered unchanged from the mixtures. Boiling the fuming nitric–concentrated sulphuric acid solution causes decomposition, and a white insoluble fluorine-containing polymer is obtained which is incompletely attacked by either sodium or oxygen at 850°.

The infrared spectrum of the compound shows bands characteristic for $\pi\text{-}C_5H_5$ compounds and of CF_3 groups. There is also a strong band at 1697 $cm.^{-1}$ which we believe to be the C=C stretching frequency of a co-ordinated double bond. The proton nuclear magnetic resonance spectrum shows only one very sharp band (τ 4·4) corresponding to the π-cyclopentadienyl group. The ^{19}F resonance spectrum shows two bands of equal intensity on the low-field side of benzotrifluoride at 7·1 and 11·3 p.p.m.; each band shows complicated fine structure. On the basis of stoicheiometry, the diamagnetism and some of the spectroscopic data only two structures appear likely (III, IV). The structure (III) is similar to that found for the compounds $(C_6H_5)_4C_4Fe(CO)_3$ [14] and $[(CH_3)_4C_4NiCl_2]_2$ [15] in which four-membered rings are present and bound symmetrically to the metal atom. This type of structure has indeed been proposed for $\pi\text{-}C_5H_5CoC_4(C_6H_5)_4$.[16] This compound has also been prepared for comparison with the CF_3 derivative. Although the reaction

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[11] Sternberg, Shukys, Donne, Markby, Friedel, and Wender, *J. Amer. Chem. Soc.*, 1959, **81**, 2339.

[12] (*a*) Greenfield, Sternberg, Friedel, Wotiz, Markby, and Wender, *J. Amer. Chem. Soc.*, 1956, **78**, 120; (*b*) Sly, *ibid.*, 1959, **81**, 18.

[13] Tilney-Bassett and Mills, *J. Amer. Chem. Soc.*, 1959, **81**, 4757; Tilney-Bassett, *J.*, 1961, 577.

[14] Dodge and Schomaker, *Nature*, 1960, **186**, 798.

[15] Dunitz, Mez, and Shearer, 12th Internat. Congr. Pure Appl. Chem., 1959, Abs. A 164.

[16] Nakamura and Hagihara, *Bull. Chem. Soc. Japan*, 1951, **34**, 452.

of perfluorobut-2-yne with (π-$C_5H_5)_2Co$ yields only traces of π-$C_5H_5CoC_8F_{12}$, the corresponding reaction with diphenylacetylene gives high yields of the yellow-orange crystalline π-$C_5H_5CoC_4(C_6H_5)_4$. The infrared spectrum of this compound shows bands characteristic for π-C_5H_5 and C_6H_5 groups, and since the proton resonance spectrum has only one phenyl group resonance line (τ 2·6) it appears that the symmetrical structure (III) exists in this compound. It may be noted also that the nickel compound mentioned above shows only a single methyl group proton resonance line.[17] By contrast with these cases, π-$C_5H_5CoC_4(CF_3)_4$ clearly has two types of CF_3 groups present, each with complicated splitting. Despite the bulk of the CF_3 groups, it would be very difficult to account for the separation of the ^{19}F resonance lines on the basis of steric interaction in structure(III) and for this only one resonance line would be expected. Scale models of the four-membered ring, with C–C distances assumed to be *ca.* 1·5 Å,[14,15] show that there is no overlap between adjacent CF_3 groups even if these lie in the plane of the ring and are not bent away from it as the phenyl groups in $Ph_4C_4Fe(CO)_3$ are known to be.[14] Hence the only acceptable structure for the compound is (IV), in which there are two Co–C σ-bonds and the cobalt is formally in the +3 oxidation state. It is pertinent to recall that the proton resonance spectra of π-$C_5H_5CoC_5H_6$ and of related molecules [18] showed that the line positions of protons on terminal carbon atoms of conjugated diene systems when these are bound to a metal atom are shifted into the aliphatic region, while protons on central carbon atoms remain in the olefinic region. This observation led to the consideration of a structure similar to (IV) and involving two Co–C σ-bonds together with a donor olefinic bond for the five-membered ring bound to the metal (Fig. 1e of ref. 18). The infrared spectra did not give any clear support for the necessary rehybridisation at atoms C-2 and C-5. At the time this fact was given greater weight than the nuclear resonance spectra because of the unknown factors which could influence the latter. Thus the shift to the aliphatic region of certain proton lines could be a magnetic effect [19] rather than an electron-density effect, attributable to rehybridisation from sp^2 to approximately sp^3. *X*-Ray structural information on a co-ordinated cyclopentadiene compound is still not available. However, data for tricarbonylbutadieneiron,[20] which also shows the separation of the " olefinic " proton resonance lines,[21] indicate that no Fe–C σ-bonds are present and that the C–C bond distances are almost the same, implying complete delocalisation of π-electrons from the diene structure. These *X*-ray results and the explanation of the proton line separations as due to magnetic effects with a diene model [19] are, however, not necessarily incompatible.[22] *X*-Ray analysis [23] has confirmed that the product from the reaction of π-$C_5H_5Co(CO)_2$ and but-2-yne is cyclopentadienone-π-cyclopentadienyl cobalt where the C–C bonds are of equal length, implying extensive delocalisation of the double bonds as in the butadiene case, but nuclear resonance data are not reported. *X*-Ray crystallographic studies [24a] of π-$C_5H_5CoC_4(CF_3)_4$ suggest that the structure (IV) is correct. The molecule thus provides the first established case of a cyclic carbon system which is bound to a single metal atom by both σ-bonds and donor olefinic bonds. Since the cyclopentadienone complex $C_9F_{12}OFe(CO)_3$ has ^{19}F resonance lines in positions similar to those for the cobalt compound, the structure (II) may now well be correct; *X*-ray studies on this compound are in progress.[24b] Although the cobalt and the iron compound have two main ^{19}F resonance lines *ca.* 7 and *ca.* 10 p.p.m. on the low-field side of benzotrifluoride and the figure for the single band of the bridged nickel and cobalt compounds is *ca.* 10—11 p.p.m.,

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[17] Criegee and Schroder, *Annalen*, 1959, **623**, 1.

[18] Green, Pratt, and Wilkinson, *J.*, 1959, 3753.

[19] Bennett, Pratt, and Wilkinson, *J.*, 1961, 2037.

[20] Mills and Robinson, *Proc. Chem. Soc.*, 1960, 421.

[21] Burton, Pratt, and Wilkinson, *J.*, 1961, 594.

[22] Wilkinson, in Kirschner, " Advances in the Chemistry of the Coordination Compounds," Macmillan, New York, 1961, p. 50.

[23] Dahl and Smith, *J. Amer. Chem. Soc.*, 1961, **83**, 752.

[24] (*a*) Gerloch and Mason and (*b*) Bailey and Mason, Imperial College, personal communications.

it is still not clear which of these regions is associated with CF_3 groups bound to " *sp*^{3} " and which to " *sp*^{2} " carbon-atoms. If we take Sly's structure [12b] as model it seems that the bridged carbon atoms are closer to *sp*^{3}, which would then indicate the *ca.* 10 p.p.m. region for CF_3 groups bound to the carbon atoms involved in σ-bonding. Since *X*-ray structural information on molecules for which infrared and nuclear magnetic resonance data are available is so scanty, it is yet unwise to use the latter for structural predictions or correlations. However, if we accept the single phenyl group resonance line as indicating that π-$C_5H_5CoC_4(C_6H_5)_4$ has the same type of four-membered ring as $(C_6H_5)_4C_4Fe(CO)_3$, then we have two cases in which there is a choice for an R_4C_4 grouping of forming either π-bonds or a π-bond plus two σ-bonds to the cobalt atom. It seems that σ-bond formation will be favoured by highly electronegative R groups. This is in line with the stability of fluoralkyl carbonyl compounds with σ-bonds, such as $(CF_2)_4Fe(CO)_4$[3], or acyl compounds, such as the tetracarbonyl diacylirons.[25] The ease of formation of σ-bonds from the cyclic rings will also presumably depend on the stability of the resulting formal (higher) oxidation state of the metal, as well as on the energies involved in rehydridisation of carbon atoms and strengths of the different types of metal–carbon bonds.

Polymerisation of Hexafluorobut-2-yne.—It has been shown that, under pressure at 275° or in presence of iodine or CF_3I at 260°, hexafluorobut-2-yne is polymerised to hexakistrifluoromethylbenzene.[26] In the reactions of the acetylene with several metal complexes we have observed polymerisation of the acetylene at atmospheric pressure and temperature to give either the compound $C_{12}F_{18}$ or a high polymer $(C_4F_6)_n$. Thus bisacrylonitrilenickel gives both products while dicarbonyl bistriphenylphosphinenickel and dichlorobistri-n-propylphosphinenickel plus sodium borohydride in tetrahydrofuran, and the tetrahydrofuran solutions of triphenylchromium and diethylnickel, yield only the high polymer; although it is possible that metal-complex intermediates are present in these cases, no stable products could be isolated.

The high polymers are white solids which are almost completely insoluble in organic solvents. They do not melt at 850° and are unattacked by acids and bases. In mulls, they show poorly resolved but intense absorption in the C–F region.

EXPERIMENTAL

Microanalyses and molecular-weight determinations (ebullioscopic in benzene) were made by the Microanalytical Laboratory, Imperial College.

Hexafluorobut-2-yne, b. p. −24·6°, was prepared by dehalogenation of 2,2,3,3-tetrachlorohexafluorobutane with zinc in ethanol under reflux with vigorous stirring; the first rapid step in this reaction is the formation of a dichloro-compound which is then further dehalogenated as shown by Henne and Finnegan.[6] Higher yields of the acetylene can be obtained by using acetonitrile as solvent.[27]

Tricarbonyltetrakis(trifluoromethyl)cyclopentadienoneiron.—An excess of hexafluorobut-2-yne (15 g.) was condensed on to iron pentacarbonyl (5 g.) in a 25-ml. stainless-steel bomb, which was then heated at 110° for *ca.* 60 hr. After cooling, the excess of acetylene was removed, leaving yellow-brown crystals which on crystallisation from hot chloroform and vacuum-sublimation at 75° on to an ice-cooled probe gave orange-yellow crystals of the *compound*, m. p. 157—157·5° [*ca.* 7·5 g., *ca.* 60% based on $Fe(CO)_5$] (Found: C, 29·5; F, 46·4%; *M*, 486. $C_{12}F_{12}FeO_4$ requires C, 29·3; F, 46·7%; *M*, 492). The compound is insoluble in light petroleum and is soluble in benzene, chloroform, and carbon tetrachloride only when hot. It is extremely soluble in acetone, ethanol, and similar polar solvents. If these solvents contain water, or if water is added, some decomposition with gas evolution occurs immediately. Bases, or sodium ethoxide in ethanol, cause complete decomposition.

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[25] Case, Clarkson, Jones, and Whiting, *Proc. Chem. Soc.*, 1959, 150.

[26] Harris, Harder, and Sausen, *J. Org. Chem.*, 1960, **25**, 633; Brown, Gewanter, White, and Woods, *ibid.*, p. 634.

[27] Hoehn, personal communication.

Dicarbonyltetrakis(trifluoromethyl)cyclopentadienone triphenylphosphineiron.—To the tricarbonyl (1·5 g.) in refluxing benzene (20 ml.) was added triphenylphosphine (0·8 g.). After carbon monoxide evolution had ceased, yellow crystals were obtained on cooling. The product was chromatographed on alumina in benzene and crystallised, giving the *complex*, m. p. 156° (*ca.* 90%) (Found: C, 48·3; H, 2·7; F, 31·3%; *M*, 723. $C_{29}H_{15}F_{12}FeO_3P$ requires C, 48·0; H, 2·1; F, 31·4%; *M*, 726). The compound is only sparingly soluble in non-polar organic solvents but is very soluble in polar solvents; unlike the tricarbonyl the compound in acetone solution is unaffected by water. The solutions decompose within a few days in the presence of air but in absence of air both solutions and solid can be kept for long periods.

Hexacarbonylhexafluorobut-2-ynedicobalt.—An excess of hexafluorobutyne (*ca.* 10 g.) was condensed on to cobalt carbonyl (2 g.) in light petroleum (b. p. 30—40°; 10 ml.) in a thick-walled glass tube. After 15 hr. at 110°, the tube was cooled in liquid oxygen, then opened. The excess of acetylene was collected and the filtered petroleum solution cooled to −80°, giving crystals which were sublimed at room temperature on to a probe at −80°. The *compound* forms blood-red crystals, m. p. 114° [*ca.* 2 g., 75% based on $Co_2(CO)_8$] (Found: C, 26·8; F, 25·5%; *M*, 439. $C_{10}Co_2F_6O_6$ requires C, 26·8; F, 25·4%; *M*, 448).

Hexafluorobut-2-ynedi-(π-cyclopentadienylnickel).—In a similar way, dicarbonyldi-π-cyclopentadienyldinickel (1 g.) in benzene (5 ml.) with hexafluorobut-2-yne (*ca.* 5 g.) at 110° for 15 hr., during which the initial dark-red solution became green, gave from light petroleum at −80° crystals which were sublimed in a vacuum at 40°. The *compound* forms dark green-black crystals, m. p. 91—92° (*ca.* 0·7 g., 50% based on $[\pi\text{-}C_5H_5NiCO]_2$) (Found: C, 40·5; H, 2·6; F, 28·8; Ni, 28·3%; *M*, 421. $C_{14}H_{10}F_6Ni_2$ requires C, 41·0; H, 2·5; F, 27·8; Ni, 28·7%; *M*, 410). Solutions of the compound in most organic solvents are stable to air. It is attacked by concentrated acids and bases with complete breakdown.

π-Cyclopentadienyltetrakis(trifluoromethyl)cyclobutadienecobalt.—An excess of hexafluorobutyne (10 g.) was condensed on to $\pi\text{-}C_5H_5Co(CO)_2$ (*ca.* 2 g.) in light petroleum (b. p. 60—80°; 5 ml.) in a thick-walled glass tube. After about 60 hr. at 110° the tube was opened and the excess of acetylene and solvent were removed. The residue was extracted (Soxhlet) with light petroleum (b. p. 60—80°); on cooling, the solution gave orange-red plates of the *compound*, m. p. 166° [*ca.* 2·5 g., *ca.* 50% based on $\pi\text{-}C_5H_5Co(CO)_2$] (Found: C, 35·5; H, 2·0; F, 51·0%; *M*, 442. $C_{13}H_5CoF_{12}$ requires C, 34·9; H, 1·1; F, 50·9%; *M*, 448). The compound is sparingly soluble in cold light petroleum and carbon tetrachloride but is more soluble in the hot solvents. It is very soluble in acetone and other polar solvents. The solutions are stable indefinitely in air.

π-Cyclopentadienyltetraphenylcyclobutadienecobalt.—This compound has been made from $\pi\text{-}C_5H_5Co(CO)_2$ *via* $\pi\text{-}C_5H_5CoC_8H_8$.[16] We have prepared it as follows. Tetrahydrofuran (5 ml.) was condensed on to di-π-cyclopentadienylcobalt(II) (1·8 g.) and diphenylacetylene (3·4 g.) in a 25-ml. stainless steel bomb. The bomb was heated at 110° for *ca.* 60 hr. After cooling, volatile materials were removed under reduced pressure. The dark-brown residue was chromatographed on alumina with 1 : 5 benzene–light petroleum (b. p. 60—80°) as eluant, and crystallised from hot petroleum. The compound forms orange-yellow crystals, m. p. 264° (Nakamura and Hagihara [16] report m. p. 256°) [*ca.* 1·5 g., *ca.* 30% based on $(\pi\text{-}C_5H_5)_2Co$] (Found: C, 82·1; H, 5·5; Co, 12·9%; *M*, 462. Calc. for $C_{33}H_{25}Co$: C, 82·5; H, 5·2; Co, 12·3%; *M*, 480). It is sparingly soluble in cold light petroleum and carbon tetrachloride but is very soluble in the hot solvents.

Polymerisation of Hexafluorobut-2-yne.—(*a*) Triphenylchromium [28] in tetrahydrofuran (100 ml.) was prepared from chromic chloride (9·5 g.) and phenylmagnesium bromide (4·3 g. of magnesium) and was treated at −78° with hexafluorobutyne (10 g.). During 2 hr. the mixture (closed system) was allowed to warm to room temperature with stirring under reflux from a condenser at −78°. After 15 hr. unused acetylene was collected, the solvent removed, and the mixture hydrolysed with dilute hydrochloric acid (250 ml.) and filtered. The residue was extracted with ether but no fluorine-containing material was found in the extract. After washing and boiling with 4N-hydrochloric acid repeatedly, a grey-white residue (*ca.* 1 g.) remained [Found: C, 28·1; F, 71·6%. $(C_4F_6)_n$ requires: C, 29·6; F, 70·4%].

A similar procedure with diethylnickel [29] gave a similar product.

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[28] Zeiss and Herwig, *J. Amer. Chem. Soc.*, 1957, **79**, 6561; 1959, **81**, 4798.

[29] Zeiss and Tsutsui, *J. Amer. Chem. Soc.*, 1959, **81**, 6090.

(*b*) Dichlorobistripropylphosphinenickel (1 g.) and sodium borohydride (2 g.) in tetrahydrofuran (5 ml.) [30] were placed in a 25-ml. steel bomb, and hexafluorobutyne (10 g.) was condensed thereon at −190°. The bomb was kept for 15 hr. at room temperature during which virtually all of the butyne was absorbed. The solvent was removed and the residue washed with organic solvents and with dilute hydrochloric acid. The residue was pale pink, probably owing to traces of the highly coloured nickel species trapped in the polymer (Found: C, 29·6; F, 71·0%).

(*c*) Bisacrylonitrilenickel [31] (2 g.) and hexafluorobutyne (5 g.) were sealed in a steel bomb at 85° for 15 hr. After removal of unused butyne (1 g.) the residue was sublimed in a vacuum at 80°, to give hexakistrifluoromethylbenzene as needles (*ca.* 3 g.), identified by its m. p. (208°, lit., 209°) and infrared and ^{19}F resonance spectra (Found: C, 29·5; F, 70·8. Calc. for $C_{12}F_{18}$: C, 29·6; F, 70·4%). The residue was washed with dilute acids leaving a white insoluble powder (*ca.* 1 g.) (Found: C, 29·8; F, 70·6%).

Infrared and High-resolution Nuclear Magnetic Resonance Spectra.—Infrared spectra were taken on a Perkin–Elmer model 21 instrument with sodium chloride and calcium fluoride optics in the appropriate regions. Nuclear magnetic resonance spectra were taken on a Varian spectrometer V 4311 and 4310c at a frequency of 40 and 56·45 Mc./sec. Proton resonances are referred to tetramethylsilane and given as τ values and fluorine resonances to benzotrifluoride (all on the low field-side), both as internal references. The samples were measured in spinning Pyrex tubes 5 mm. in outside diameter, and line positions were measured by the conventional side-band technique. The following results were obtained:

$C_9F_{12}OFe(CO)_3$ ($CHCl_3$, CCl_4 solutions, Nujol mulls): 2133vs, 2083vs, 2040sh, (C–O str.); 1742s, 1729s, 1435m, 1357w; 1218s, 1191s, 1160m (C–F str.); 1043vw, 868w, 656w, 640m cm.$^{-1}$. ^{19}F 6·8, 10·3 p.p.m.

$C_9F_{12}OFe(CO)_2(C_{18}H_{15}P)$ ($CHCl_3$ solutions, Nujol mulls): 3060m (C–H str.); 2073vs, 2024vs, 1990sh (C–O str.); 1731w, 1660vs, 1626sh, 1588w, 1577w, 1485m, 1437vs, 1422vs, 1354m, 1310w; 1253s, 1230—1205vs (unres.), 1178vs, 1135s (C–F str.); 1089m, 1075sh, 1050m, 998m, 867s, 805m, 751s, 744s, 731m, 708s, 690s, 650w, 635m cm.$^{-1}$

π-$C_5H_5CoC_8F_{12}$ (CCl_4 solutions, Nujol mulls): 3095w (C–H str.); 1696s (1672 Nujol), 1411w, 1368w, 1346w, 1256sh, 1218vs, 1179vs (1159 Nujol), 1144w, (C–F str.); 1018w, 869m, 856m, 831w, 805m, 711s cm.$^{-1}$. ^1H, τ 4·4; ^{19}F 7·1, 11·3 p.p.m.

π-$C_5H_5CoC_{28}H_{20}$ (CCl_4 solutions, Nujol mulls): 3080w, 3030w (C–H str.); 1597m, 1501s, 1445w, 1262vw, 1176w, 1150vw, 1107w, 1071w, 1065w, 1025w, 1004w, 969vw, 914w, 851vw, 822vw, 813m, 784s, 775w, 747m, 744m, 705s, 699s, 687w cm.$^{-1}$, ^1H, τ 2·6 (Ph), 5·4 (cyclopentadienyl).

$C_4F_6Co(CO)_6$ (CCl_4 solutions, Nujol mulls): 2168w, 2131s, 2101vs, 2077vs (C–O str.); 1600m, 1283s, 1194vs, 1146vs, 1109m (C–F str,); 682m cm.$^{-1}$. ^{19}F 10·0 p.p.m.

(π-$C_5H_5)_2Ni_2C_4F_6$ (CCl_4 solutions, Nujol mulls). 3100vw (C–H str.); 1795w, 1710w, 1598s, 1416w, 1278s, 1196vs, 1143vs (C–F str.); 1050w, 1000w, 962m, 934w, 686m cm.$^{-1}$. ^{19}F 11·5 p.p.m.

We thank the Department of Scientific and Industrial Research for a studentship (J. L. B.), Messrs. S. D. Robinson and A. Davison for assistance in the polymerisation and nuclear magnetic studies, respectively, and Dr. E. L. Muetterties of E. I. du Pont de Nemours and Co. Wilmington, and Halocarbon Products Inc., Hackensack, N. J., for generous gifts of fluorocarbons.

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[*Received, March* 28*th*, 1962.]

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[30] Cf. acetylene polymerisation, Green, Nehmé, and Wilkinson, *Chem. and Ind.*, 1960, 1136; Luttringer, *ibid.*, 1960, 1135.

[31] Schrauzer, *J. Amer. Chem. Soc.*, 1959, **81**, 5310.