Metal Carbonyl Chemistry. Part XX.[1] A Novel Method for the Synthesis of Nonacarbonyl(fluoroalkylcarbon)tricobalt Derivatives

By **Brian L. Booth, Robert N. Haszeldine,*** and **Tom Inglis**, Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD

The compounds $[RCCo_3(CO)_9]$ (R = F, CHF_2, CF_3, or C_2F_5) have been obtained in yields of 15—70% from reaction between the fluoroalkyltetracarbonylcobalt derivatives $[(RCF_2)Co(CO)_4]$ and either sodium tetracarbonylcobaltate(−1), or octacarbonyldicobalt in the presence of donor solvents, such as tetrahydrofuran or ether. Reaction of $Na[Co(CO)_4]$ with $[\{(CO)_4Co(CF_2)\}_2]$ similarly gives $[\{(CO)_9Co_3C\}_2]$ in *ca.* 16% yield. Evidence is presented that the reaction of $ClCO{\cdot}(CF_2)_2{\cdot}COCl$ or $ClCO{\cdot}(CF_2)_3{\cdot}COCl$ with an excess of $Na[Co(CO)_4]$ gives the compounds $[(CO)_9Co_3C(CF_2{\cdot}CO_2H)]$ and $[(CO)_9Co_3C(CF_2{\cdot}CF_2{\cdot}CO_2H)]$ respectively as major reaction products, in addition to the expected products $[(CO)_4Co(CF_2)_2Co(CO)_4]$ and $[(CO)_4Co(CF_2)_3Co(CO)_4]$. Attempts to extend the reactions of $[(CF_3)Co(CO)_4]$ or $[(n\text{-}C_3F_7)Co(CO)_4]$ to other carbonylmetal anions were unsuccessful, as was the attempted reaction of $[(CF_3Co(CO)_3(PPh_3)]$ with $Na[Co(CO)_4]$. The preparation of $[(CF_3)_2CF\text{-}Co(CO)_4]$ is described, and its reaction with $Na[Co(CO)_4]$ has been shown to give a low yield of a product tentatively identified as $[(CO)_3Co(CO)\{C(CF_3)_2\}Co(CO)_3]$. In the light of these findings possible mechanisms for the reaction are discussed.

THERE has been a great deal of interest in recent years in the preparation and reactions of cluster compounds of the type $[RCCo_3(CO)_9]$.[2] A wide variety of methods have been reported for their preparation, but one method that has been frequently employed is the reaction of 1,1,1-trihalogenoalkanes with $Na[Co(CO)_4]$,[3] and in particular $[Co_2(CO)_8]$[4-7] in donor solvents under conditions where the disproportionation reaction occurs. The mechanism

$$3[Co_2(CO)_8] + 12\ \text{Donor} \longrightarrow 2[Co(donor)_6][Co(CO)_4]_2$$

of formation of $[RCCo_3(CO)_9]$ compounds by this route is not well understood, but it seems reasonable to suppose that the first step is the formation of an intermediate $[(RCX_2)Co(CO)_4]$ (X = Cl, Br, or I), which undergoes further attack by the anion to give the isolated cluster compounds. Although compounds of the type $[(RCX_2)\text{-}Co(CO)_4]$ (X = Cl, Br, or I) have never been prepared, and are presumably extremely unstable, the stable fluoroalkyl analogues are well known, and we now report an investigation which indicates that these react in a similar manner with $Na[Co(CO)_4]$ to give cluster compounds.

Reactions of $[(RCF_2)Co(CO)_4]$ *Compounds*.—When tetracarbonyltrifluoromethylcobalt is treated with more than two equivalents of an ethereal solution of $Na[Co(CO)_4]$ at room temperature $[FCCo_3(CO)_9]$ is obtained in 70% yield. The same compound is also obtained in lower yield (44%) upon reaction of the sodium salt with $[(CF_3CO)Co(CO)_4]$ under similar conditions. This latter reaction almost certainly occurs *via* the trifluoromethyl complex formed by decarbonylation in solution. The compounds $[RCo(CO)_4]$ (R = C_2F_5, $CHF_2{\cdot}CF_2$, or n-C_3F_7) also react with $Na[Co(CO)_4]$ under these conditions to give the known compounds $[(CF_3)CCo_3(CO)_9]$ (68%) and $[(C_2F_5)\text{-}CCo_3(CO)_9]$ (15%),* and the new compound $[(CHF_2)\text{-}CCo_3(CO)_9]$ (42%) respectively. Thus, the method is of general applicability, although the yields appear to decrease with increasing fluoroalkyl chain-length. Some improvement in yield may be effected by carrying out the reaction at the reflux temperature of ether for a shorter time; in this way the yield of $[(C_2F_5)CCo_3(CO)_9]$ is almost doubled. Cluster formation may also be effected using $[Co_2(CO)_8]$ in a donor solvent although yields are generally lower and longer reaction times are necessary. So, for example, $[(CF_3)Co(CO)_4]$, $[(CHF_2{\cdot}CF_2)Co(CO)_4]$ or $[(n\text{-}C_3F_7)Co(CO)_4]$ react with $[Co_2(CO)_8]$ in tetrahydrofuran at room temperature to give $[FCCo_3(CO)_9]$, $[(CHF_2)CCo_3\text{-}(CO)_9]$, and $[(C_2F_5)CCo_3(CO)_9]$ in yields of 11, 15, and 14% respectively. In support of the conclusion that $[Co(CO)_4]^-$ is the attacking species in polar solvents no reaction takes place between $[(n\text{-}C_3F_7)Co(CO)_4]$ and $[Co_2(CO)_8]$ in n-pentane even after 48 h at 90—100 °C. In diethyl ether, which is a poorer donor solvent than tetrahydrofuran, no reaction occurs after 17 h at room temperature, but evidently some disproportionation occurs at higher temperatures in this solvent, since on heating the reactants at 40—50 °C $[(C_2F_5)CCo_3(CO)_9]$ is obtained in 25% yield.

It is not essential to use preformed alkyl- or acyltetracarbonylcobalt derivatives in this reaction, and some cluster formation occurs upon reaction of an acid halide with an excess of $Na[Co(CO)_4]$, although yields are much poorer. So, for example, reaction between n-C_3F_7COCl and $Na[Co(CO)_4]$ at room temperature gives $[(C_2F_5)CCo_3(CO)_9]$ in 8% yield. An attempt to use this route to prepare the previously unreported asymmetric cluster compound $[(CHFCl)CCo_3(CO)_9]$ from $CHFCl{\cdot}CF_2{\cdot}COCl$ was unsuccessful. A possible explanation for this failure is that the expected intermediate $[(CHFCl{\cdot}$

---

* The preparation of this compound from $CCl_3C_2F_5$ and $[Co(CO)_4]^-$ in THF has been reported in a recent note,[8] but few details were given.

[1] Part XIX, B. L. Booth, R. N. Haszeldine, and N. I. Tucker, *J.C.S. Dalton*, preceding paper.

[2] G. Palyi, F. Piacenti, and L. Marko, *Inorg. Chim. Acta Rev.*, 1970, **4**, 109; B. R. Penfold and B. H. Robinson, *Accounts Chem. Res.*, 1973, **6**, 73.

[3] R. B. King, unpublished results quoted in *Adv. Organometallic Chem.*, 1965, **2**, 157.

[4] G. Bor, L. Marko, and B. Marko, *Chem. Ber.*, 1962, **95**, 333.

[5] W. T. Dent, L. A. Duncanson, R. G. Guy, H. W. B. Reed, and B. L. Shaw, *Proc. Chem. Soc.*, 1961, 169.

[6] R. Ercoli, E. Santambrogio, and G. T. Casagrande, *Chimica e Industria*, 1962, **44**, 1344.

[7] G. Bor, B. Marko, and L. Marko, *Acta Chim. Acad. Sci. Hung.*, 1961, **27**, 395.

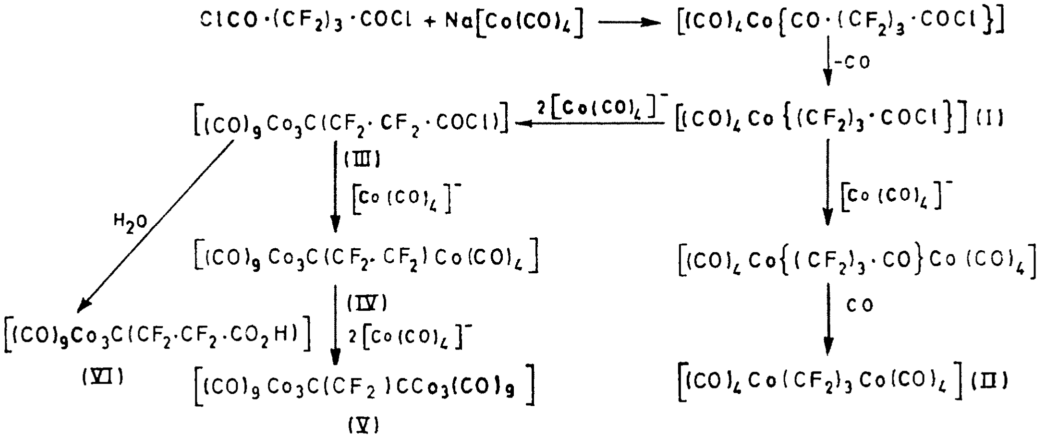
[8] G. Pályi, F. Baumgartner, and I. Czájlik, *J. Organometallic Chem.*, 1973, **49**, C85.

$CF_2)Co(CO)_4]$ is extremely unstable and decomposes before further attack by anion can occur. In support of this assumption, attempts to prepare $[(CFCl{\cdot}CF_2)Co(CO)_4]$ by the stoicheiometric reaction of $CHFCl{\cdot}CF_2{\cdot}COCl$ and $Na[Co(CO)_4]$ at 0 °C gave only a low yield of a volatile yellow oil which decomposes rapidly at room temperature. The inherent instability of $[(CHFCl{\cdot}CF_2)Co(CO)_4]$ could also account for the failure to detect this isomer among the products from the reaction of $[HCo(CO)_4]$ and $CF_2{:}CFCl$ which has been reported previously.[9]

In an effort to extend the scope of this reaction between fluoroalkylcobalt carbonyls and $Na[Co(CO)_4]$ the reactions between the anions $Na[Co(CO)_4]$ or $Na[Co(CO)_3(PPh_3)]$ and $[(CF_3)Co(CO)_3(PPh_3)]$ have been investigated under various conditions, but no evidence for cluster formation was obtained. Similarly no reaction occurs between $[(CF_3)Co(CO)_3(PPh_3)]$ and $[Co_2(CO)_8]$ in tetrahydrofuran at room temperature, but on heating these reactants at 90—100 °C for 48 h in n-hexane the phosphine-free cluster, $[FCCo_3(CO)_9]$ can be isolated in 13% yield, together with $[\{Co(CO)_3(PPh_3)\}_2]$ and $[Co_4(CO)_{12}]$. In view of the reaction conditions employed this reaction may occur by a different mechanism to that operating in the reactions with $Na[Co(CO)_4]$ or $[Co_2(CO)_8]$ in polar solvents.

The anions $[Co(CO)_3(PPh_3)]^-$, $[Co(CO)_3\{P(OPh)_3\}]^-$, $[Mn(CO)_5]^-$, $[Mn(CO)_4PPh_3]^-$, or $[Fe(CO)_2(\pi\text{-}C_5H_5)]^-$ fail to give cluster formation upon reaction with $[(n\text{-}C_3F_7)Co(CO)_4]$ at room temperature. Similarly no reaction occurs between $[(CF_3)Co(CO)_4]$ and $[Rh(CO)_4]^-$ under these conditions. The reactions involving phosphorus-ligand substituted anions are unusual in that the major reaction products are $[(n\text{-}C_3F_7)Co(CO)_3L]$ [L = PPh_3 or $P(OPh)_3$] and the carbonyl derivatives $[\{Co(CO)_3L\}_2]$ or $[\{Mn(CO)_4(PPh_3)\}_2]$ respectively, despite rigorous efforts to ensure that the anion precursors $[\{Co(CO)_3L\}_2]$ [L = Ph_3P or $P(OPh)_3$] and $[\{Mn(CO)_4(PPh_3)\}_2]$ contained no free ligand.

Reaction of the Compounds $[(CO)_4Co(CF_2)_nCo(CO)_4]$ (*n* = 2 *or* 3).—The compound $[(CO)_4Co(CF_2{\cdot}CF_2)Co(CO)_4]$ reacts with $Na[Co(CO)_4]$ in an analogous manner to give $[\{(CO)_9Co_3C\}_2]$ in *ca.* 16% yield, but the similar reaction of $[(CO)_4Co(CF_2)_3Co(CO)_4]$ failed to give an $[RCCo_3(CO)_9]$ derivative. This latter reaction was carried out on a relatively small scale, and there is some evidence, discussed later, to suggest that cluster formation may occur to a small extent in this reaction. These reactions were of interest as previous work in this Department has shown that the reaction of $Na[Co(CO)_4]$ with either tetrafluorosuccinyl chloride[10] or hexafluoroglutaryl chloride[11] gives moderate yields of purple solids, believed to be $[RCCo_3(CO)_9]$ derivatives, in addition to the expected products $[(CO)_4Co(CF_2)_2Co(CO)_4]$ and $[(CO)_4Co(CF_2)_3Co(CO)_4]$. The reaction of $ClCO{\cdot}(CF_2)_3{\cdot}COCl$ with $Na[Co(CO)_4]$ has now been re-investigated in the light of these more recent findings.



SCHEME 1 Reaction of $ClCO{\cdot}(CF_2)_3{\cdot}COCl$ and $Na[Co(CO)_4]$

Dropwise addition of $ClCO{\cdot}(CF_2)_3{\cdot}COCl$ to an excess of $Na[Co(CO)_4]$ in tetrahydrofuran at 0 °C gives as major products the yellow solid $[(CO)_4Co(CF_2)_3Co(CO)_4]$ [(II); Scheme 1] (25%), and a deep purple, involatile solid, which is almost completely insoluble in all common organic solvents, and could not be adequately purified. Its u.v. spectrum closely resembles those of other $[RCCo_3(CO)_9]$ derivatives, and its i.r. spectrum shows the characteristic pattern of four bands in the metal carbonyl region. A broad band in the spectrum at 3279 cm^{-1} [ν(OH)] and a band at 1715 cm^{-1} [ν(CO)] indicate the presence of a carboxylic acid group, and bands in the region of 1400—1000 cm^{-1} show that it is a fluorocarbon derivative. The ^{19}F n.m.r. spectrum in acetone shows two weak, broad bands of approximately equal intensity at −2·0 and +32·0 p.p.m. relative to external trifluoroacetic acid. On the basis of the spectroscopic data the structure $[(CO)_9Co_3C(CF_2{\cdot}CF_2{\cdot}CO_2H)]$ [(VI); Scheme 1] is proposed for this compound.

Another purple, crystalline solid, soluble in hexane, is also isolated in low yield (<1%) from this reaction. The i.r. spectrum is complex, and shows six bands in the metal carbonyl region, and no bands attributable to a

---

[9] B. L. Booth, R. N. Haszeldine, and P. R. Mitchell, *J. Organometallic Chem.*, 1970, **21**, 203.

[10] B. L. Booth, R. N. Haszeldine, P. R. Mitchell, and J. J. Cox, *J. Chem. Soc.* (*A*), 1969, 691.

[11] P. R. Mitchell, Ph.D. Thesis, Manchester, 1967.

carboxylic acid group. The ^{19}F n.m.r. spectrum is also complex, showing two triplets at $-1{\cdot}5$ and $-32{\cdot}0$ p.p.m. ($J = 21$ Hz) in the ratio of 1 : 1, and a sharp singlet at $+25{\cdot}0$ p.p.m., the intensity of which had no obvious relationship with those of the other two bands. The spectroscopic data is reasonably consistent with the product being a mixture of $[(CO)_9Co_3C(CF_2{\cdot}CF_2)Co(CO_4)]$ [(IV); Scheme 1], which gives rise to the two triplets, and $[(CO)_9Co_3C(CF_2)CCo_3(CO)_9]$ [(V); Scheme 1], accounting for the singlet absorption in the n.m.r. spectrum. A possible reaction sequence, which could account for the formation of these various products, is given in Scheme 1. As the intermediate (I) is formed in the presence of a large excess of the anion, subsequent attack on (I) can either occur at the acyl chloride moiety giving (II), or at the fluoroalkylcobalt carbonyl moiety to give (III), which on further reaction with the anion yields the minor products (IV) and (V), and on hydrolysis during work-up gives (VI). When this reaction is repeated under conditions where the anion is never present in large excess a greatly improved yield of [(II); 63%] is obtained and only traces of (IV), (V), and (VI) are detected. The reaction of tetrafluorosuccinyl chloride and $Na[Co(CO)_4]$ briefly reported previously[10] to give $[(CO)_4Co(CF_2)_2Co(CO)_4]$ and a purple solid now believed to be $[(CO)_9Co_3C(CF_2{\cdot}CO_2H)]$ [i.r. bands at 2333m (OH), 1764 (CO of a CO_2H group), and 2116s, 2072vs, 2052vs, 2024ssh (Co–CO) cm^{-1}] probably occurs by a similar reaction sequence.

Preparation and Reactions of $[\{(CF_3)_2CF\}Co(CO)_4]$.—Attempts to monitor the reaction of $[(CF_3)Co(CO)_4]$ and $Na[Co(CO)_4]$ by i.r. and ^{19}F n.m.r. spectroscopy in ether at 0 °C gave no evidence for the formation of any intermediates, indicating that these intermediates must react more quickly with the anion than does the fluoroalkyltetracarbonylcobalt complex. In an effort to block further anion attack, and hence facilitate the detection or isolation of an intermediate, the preparation of $[\{(CF_3)_2CF\}Co(CO)_4]$ has been undertaken and its reaction with $Na[Co(CO)_4]$ investigated. Reaction between $(CF_3)_2CF{\cdot}COCl$ and $Na[Co(CO)_4]$ at room temperature gives $[\{(CF_3)_2CF\}Co(CO)_4]$ in 71% yield as a slightly volatile, yellow oil which slowly decomposes *in vacuo* or in solution. Although satisfactory analytical data have not been obtained for this compound it has been adequately characterised by i.r. and ^{19}F n.m.r. spectroscopy and by isolation of its mono-triphenylphosphine derivative for which correct analytical data (C, H, and F) have been obtained. Upon reaction with $Na[Co(CO)_4]$ in ether $[\{(CF_3)_2CF\}Co(CO)_4]$ gives an immediate pale red solution, which does not change appreciably in intensity during 24 h. The volatile reaction products have been shown to consist mainly of starting material together with a small amount of a bright red product. This could not be separated from $[\{(CF_3)_2CF\}Co(CO)_4]$ owing to their similar volatilities, but the i.r. spectrum of the mixture shows, in addition to bands due to the starting material, several intense bands at 2120, 2086, and 2060(broad) cm^{-1} in the terminal metal carbonyl region and a band at 1868 cm^{-1} which is almost identical in position to that reported for the bridging CO band in $[(CO)_3Co(CO)\{C(CF_3)_2\}Co(CO)_3]$ (1867 cm^{-1}).[11] The ^{19}F n.m.r. spectrum shows an unresolved sharp singlet at $-25{\cdot}0$ p.p.m., which also corresponds approximately to the spectrum previously reported for $[Co_2(CO)_7\{C(CF_3)_2\}]$;[12] other bands in the spectrum are those of the starting material $[\{(CF_3)_2CF\}Co(CO)_4]$. The spectroscopic data is thus consistent with the bright red product being $[(CO)_3Co(CO)\{C(CF_3)_2\}Co(CO)_3]$. Although this compound could not be isolated in a pure state or in sufficiently high yield to enable its reactions to be studied the analogous compound $[(CO)_3Co(CO)(CF{\cdot}CF_3)Co(CO)_3]$ can be obtained in good yield on heating $[(CO)_4Co(CF_2{\cdot}CF_2)Co(CO)_4]$ *in vacuo*.[10] It has now been shown that $[(CO)_3Co(CO)(CF{\cdot}CF_3)Co(CO)_3]$ reacts with $Na[Co(CO)_4]$ at room temperature in ether to give $[(CF_3)CCo_3(CO)_9]$ in 68% yield after only 3 h. Under similar conditions the yield of $[(CF_3)CCo_3(CO)_9]$ from $[(C_2F_5)Co(CO)_4]$ and $Na[Co(CO)_4]$ is only 6%, supporting the conclusion that compounds of the type $[(CO)_4Co(CO)(CFR)Co(CO)_4]$ are intermediates in these reactions.

DISCUSSION

Although the evidence does not allow any firm conclusions to be made regarding the mechanism of cluster formation it is considered that attack of $[Co(CO)_4]^-$ on $[(RCF_2)Co(CO)_4]$ compounds can occur in one of two ways. Attack can either take place initially at the α-carbon atom with displacement of fluoride ion (Scheme 2), which, in the light of recent evidence, may occur by a radical mechanism.[13] The feasibility of this scheme rests on the lability of the α-fluorine atoms, and although spectroscopic[14] and *X*-ray crystallographic[15,16] evidence does indicate that the α-C–F bonds in fluoroalkyl transition-metal complexes are longer, and therefore weaker, than normal C–F bonds, chemical manifestation of bond weakening is restricted to detection of fluoride lability only under rather severe thermal conditions[17] or on reaction with strong nucleophiles.[16]

An alternative is attack of the $[Co(CO)_4]^-$ ion at the cobalt atom with displacement of carbon monoxide followed by loss of fluoride ion to give a carbene intermediate (Scheme 3). This mechanism has a certain analogy with the recently reported reactions of alkylmanganese carbonyls with $[Mn(CO)_5]^-$ which afford carbene complexes.[18,19] The essential difference between

---

[12] J. Cooke, W. R. Cullen, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1969, 1872.

[13] D. Seyferth and M. D. Millar, *J. Organometallic Chem.*, 1972, **38**, 373.

[14] F. A. Cotton and J. McCleverty, *J. Organometallic Chem.*, 1965, **4**, 490.

[15] M. R. Churchill and J. P. Fennessy, *Chem. Comm.*, 1966, 695.

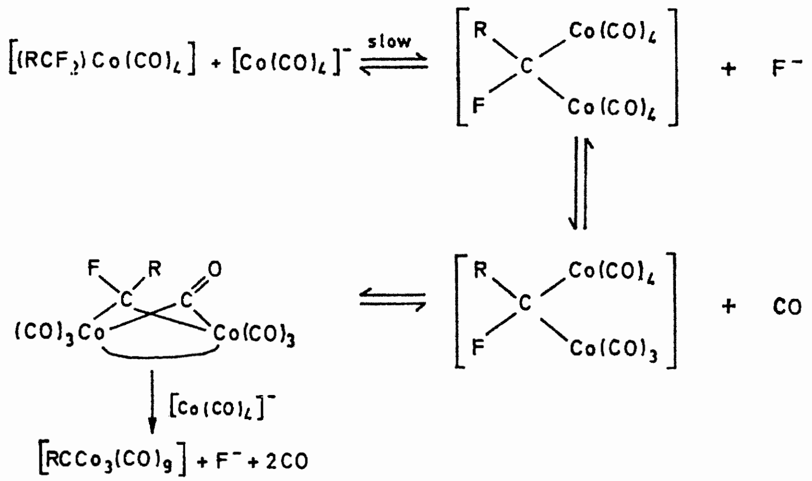
[16] M. I. Bruce, J. R. Knight, and F. G. A. Stone, unpublished results quoted in *Preparative Inorg. Reactions*, 1968, **4**, 177.

[17] F. G. A. Stone, *Endeavour*, 1966, **25**, 33.

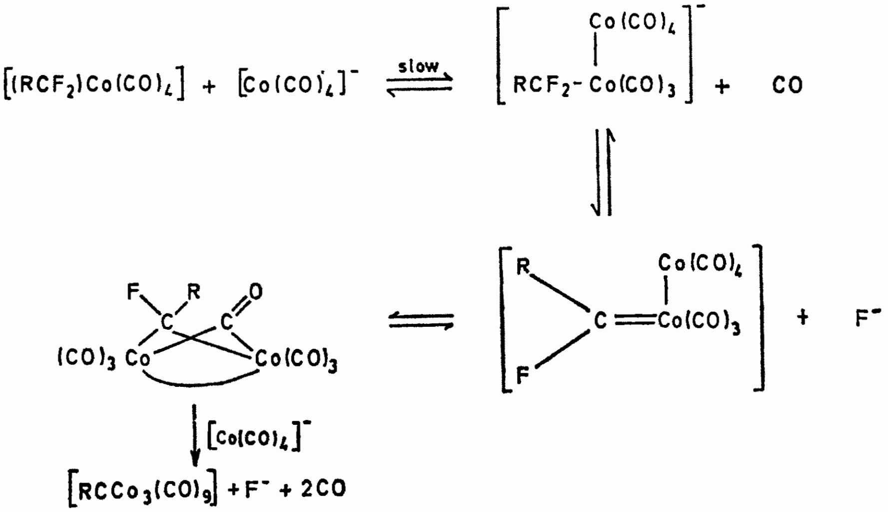
[18] M. Green, J. R. Moss, I. W. Nowell, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1972, 1339.

[19] C. P. Casey and R. L. Anderson, *J. Amer. Chem. Soc.*, 1971, **93**, 3554.

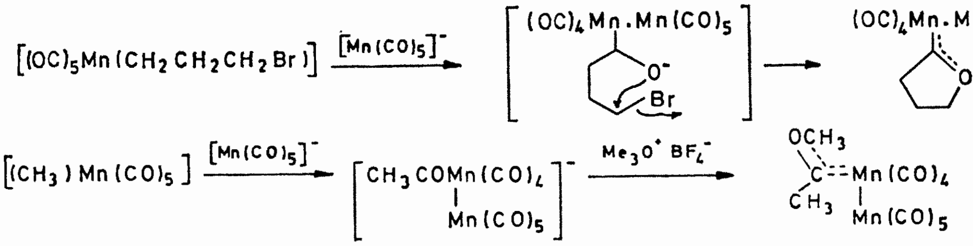
these reactions and that proposed in Scheme 3 being the poor migratory aptitude of fluoroalkyl groups attached to transition metal atoms preventing formation of an acyl complex and causing alternative breakdown by loss of F^-. A similar displacement of halide ion from a σ-bromocyclopropenyl metal anion may be involved in the formation of the carbene complexes isolated recently from reaction between 3,3-dibromo-1,2-diphenylcyclopropene and the anions $[Na_2M(CO)_5]$ (M = Cr or Mo).[20]



Scheme 2



Scheme 3



A third possibility that attack may occur at the carbon atom of a co-ordinated CO ligand seems unlikely in view of the mild conditions employed and the low nucleophilic strength of $[Co(CO)_4]^-$.[21]

The failure of $[(n\text{-}C_3F_7)Co(CO)_3(PPh_3)]$ to react in an analogous manner with $[Co(CO)_4]^-$ may be due to steric factors or to the fact that replacement of CO by the more basic ligand, PPh_3, lowers the susceptibility of either the cobalt atom or the C−F bond towards attack. The formation of $[(n\text{-}C_3F_7)Co(CO)_3L]$ [L = PPh_3 or $P(OPh)_3$] and

---

[20] K. Öfele and C. G. Kreiter, *Chem. Ber.*, 1972, **105**, 529.

[21] M. I. Bruce and F. G. A. Stone, *Angew. Chem. Internat. Edn.*, 1969, **7**, 747.

the corresponding dimers $[\{Co(CO)_3L\}_2]$ and $[\{Mn(CO)_4PPh_3\}_2]$ on reaction of the anions $[Co(CO)_3L]^-$ and $[Mn(CO)_4PPh_3]^-$ could be readily explained if radical intermediates are involved at some stage during the reaction, as recently proposed for the reactions of Ph_2CHBr and Ph_2CCl_2 with $Na[Co(CO)_3(PPh_3)]$.[13]

EXPERIMENTAL

^1H and ^{19}F N.m.r. spectra were recorded on a Hitachi–Perkin-Elmer R20 spectrometer at 60 and 56·46 MHz respectively. U.v. spectra were obtained on a Hilger and Watts Ultrascan spectrometer on dilute solutions in n-hexane, and i.r. spectra using a Perkin-Elmer model 257 spectrometer. Detailed spectral data for some compounds have been deposited as a Supplementary Publication * (SUP. No. 21249, 14 pp.). An asterisk attached to the experimental detail for a particular compound indicates the availability of such material. Accurate determination of metal carbonyl frequencies were carried out on dilute solution in either n-hexane or cyclohexane with maximum wavelength expansion. Except where stated, all reactions were in dry solvents under an atmosphere of dry nitrogen. Chromatographic separations were carried out on Florisil (B.D.H., 60—100 mesh).

Tetracarbonyltrifluoromethylcobalt,[22] tetracarbonylpentafluoroethylcobalt,[22] tetracarbonylheptafluoro-n-propylcobalt,[23] tetracarbonyl-1,1,2,2-tetrafluoroethylcobalt,[24] μ-tetrafluoroethylene-bis(tetracarbonylcobalt),[10] and μ-carbonyl-μ-tetrafluoroethylidene-bis(tricarbonylcobalt) [10] were prepared by previously reported procedures. Sodium tetracarbonylcobaltate(−1) was prepared by reaction of octacarbonyldicobalt with 1% sodium amalgam in diethyl ether or tetrahydrofuran [25] and was filtered through a sinter (porosity 3) before use.

Preparation of Nonacarbonyl(fluorocarbon)tricobalt.—(a) *From tetracarbonyltrifluoromethylcobalt*. (i) With sodium tetracarbonylcobaltate(−1). A solution of sodium tetracarbonylcobaltate(−1) (0·58 g, 3·0 mmol) in ether (45 ml) was added to tetracarbonyltrifluoromethylcobalt (0·20 g, 0·80 mmol) and the solution was stirred at room temperature for 16·5 h. Removal of the solvent under vacuum, followed by extraction of the residue with light petroleum, filtration, and evaporation of the solvent from the extract gave a black solid, which sublimed *in vacuo* to yield nonacarbonyl(fluorocarbon)tricobalt (0·27 g, 0·6 mmol, 70%), m.p. 74—75 °C, (reported [5,6] 75—76 °C) (Found: C, 25·8; H, 0·2. Calc. for $C_{10}Co_3FO_9$: C, 26·1; H, 0·0%); u.v.*; its i.r. spectrum agreed with that reported.[6]

(ii) With octacarbonyldicobalt. Tetracarbonyltrifluoromethylcobalt (1·0 g, 4·2 mmol) and octacarbonyldicobalt (0·85 g, 2·5 mmol) in tetrahydrofuran (25 ml) were stirred at room temperature for 3 days to give nonacarbonyl(fluorocarbon)tricobalt (0·21 g, 0·5 mmol, 11%).

(b) *From tetracarbonyltrifluoroacetylcobalt*. Tetracarbonyltrifluoroacetylcobalt (0·20 g, 0·80 mmol) and sodium tetracarbonylcobaltate(−1) (0·20 g, 1·0 mmol) in ether (15 ml) were stirred at room temperature for 17 h to yield nonacarbonyl(fluorocarbon)tricobalt (0·15 g, 0·3 mmol, 44%)

(c) *From tricarbonyltrifluoromethyl(triphenylphosphine)cobalt*. A solution of octacarbonyldicobalt (0·35 g, 1·02 mmol) and tricarbonyltrifluoromethyl(triphenylphosphine)cobalt (0·42 g, 0·89 mmol) in n-hexane (25 ml) heated *in vacuo* at 100 °C for 48 h in a sealed tube (100 ml) gave, on filtration of the solution, impure bis[tricarbonyl(triphenylphosphine)cobalt]. Chromatography of the solution (hexane eluant) gave nonacarbonyl(fluorocarbon)tricobalt (53 mg, 0·12 mmol, 13%), dodecacarbonyltetracobalt (0·12 g, 0·21 mmol), and tricarbonyltrifluoromethyl(triphenylphosphine)cobalt (25 mg, 0·05 mmol, 6% recovery). The products were identified by i.r. spectroscopy.

When this reaction was repeated using tricarbonyltrifluoromethyl(triphenylphosphine)cobalt (85 mg, 0·18 mmol) and octacarbonyldicobalt (2·27 g, 6·65 mmol) in tetrahydrofuran (25 ml) stirred at room temperature for 66 h, the starting materials were recovered unchanged in 59 and 88% yields respectively.

Preparation of Nonacarbonyl(trifluoromethylcarbon)tricobalt.—(a) *From tetracarbonylpentafluoroethylcobalt*. A solution of tetracarbonylpentafluoroethylcobalt (0·40 g, 1·4 mmol) and sodium tetracarbonylcobaltate(−1) (5·8 mmol) in ether (50 ml) was stirred at room temperature for 3 h. The solution was poured into hexane (50 ml) and put aside overnight before filtration and concentration of the filtrate. Chromatography of the solution (hexane eluant) followed by sublimation *in vacuo* at 40—50 °C gave deep purple crystals of nonacarbonyl(trifluoromethylcarbon)tricobalt (45 mg, 0·09 mmol, 6%) identified by i.r. spectroscopy.[10]

(b) *From μ-carbonyl-μ-tetrafluoroethylidene-bis(tricarbonylcobalt)*. Sodium tetracarbonylcobaltate(−1) (1·3 mmol) and the cobalt complex (79 mg, 0·2 mmol) in ether (50 ml), on stirring at room temperature for 3 h, gave nonacarbonyl(trifluoromethylcarbon)tricobalt (62 mg, 0·12 mmol, 68%).

Preparation of Nonacarbonyl(difluoromethylcarbon)tricobalt.—(a) *From tetracarbonyl*-1,1,2,2-*tetrafluoroethylcobalt and sodium tetracarbonylcobaltate*(−1). The sodium salt (5·3 mmol) and tetracarbonyl-1,1,2,2-tetrafluoroethylcobalt (0·38 g, 1·4 mmol) in ether (50 ml) at room temperature for 60 h gave, after chromatography (hexane eluant) and sublimation *in vacuo*, deep purple crystals of *nonacarbonyl(difluoromethylcarbon)tricobalt* (0·2 g, 0·59 mmol, 42%) [Found: C, 27·1; H, 0·5; F, 7·9%; *M*, 492 (mass spectroscopy). $C_{11}HCo_3F_2O_9$ requires C, 26·8; H, 0·2; F, 7·7%; *M*, 492]; i.r.*; u.v.*; ^1H n.m.r.*

(b) *From tetracarbonyl*-1,1,2,2-*tetrafluoroethylcobalt and octacarbonyldicobalt*. Octacarbonyldicobalt (1·01 g, 2·9 mmol) and tetracarbonyl-1,1,2,2-tetrafluoroethylcobalt (0·30 g, 1·1 mmol) stirred in tetrahydrofuran (30 ml) at room temperature for 21 h gave nonacarbonyl(difluoromethylcarbon)tricobalt (80 mg, 0·16 mmol, 15%).

Preparation of Nonacarbonyl(pentafluoroethylcarbon)tricobalt.—(a) *From tetracarbonylheptafluoro-n-propylcobalt*. (i) With sodium tetracarbonylcobaltate(−1). Tetracarbonylheptafluoro-n-propylcobalt (0·25 g, 0·7 mmol) and the sodium salt (5·8 mmol) in ether (60 ml) at room temperature for 16 h gave nonacarbonyl(pentafluoroethylcarbon)tricobalt (60 mg, 0·1 mmol, 15%), which was purified by chromatography and vacuum sublimation [Found: C, 25·7; H, 0·3; F, 17·3%; *M*, 560 (mass spectroscopy). $C_{12}Co_3F_5O_9$ requires C, 25·7; H, 0·0; F, 17·0%; *M*, 560]; i.r.*; u.v.*; ^{19}F n.m.r.*

---

* For details of the Supplementary publications scheme, see Notice to Authors No. 7, in *J.C.S. Dalton*, 1974, Index issue.

[22] W. Hieber, W. Beck, and E. Lindner, *Z. Naturforsch.*, 1961, **16b**, 229.

[23] W. R. McClellan, *J. Amer. Chem. Soc.*, 1961, **83**, 1598; R. B. King, *Organometallic Synth.*, 1965, **1**, 152.

[24] J. B. Wilford, A. Forster, and F. G. A. Stone, *J. Chem. Soc.*, 1965, 6519.

[25] R. B. King, *Organometallic Synth.*, 1965, **1**, 148.

When this reaction was repeated using tetracarbonylheptafluoro-n-propylcobalt (0·5 g, 1·3 mmol) and the sodium salt (5·8 mmol) in ether (80 ml), heated under reflux for 3 h, nonacarbonyl(pentafluoroethylcarbon)tricobalt (0·24 g, 0·4 mmol, 30%) was obtained.

(ii) With octacarbonyldicobalt. Tetracarbonylheptafluoro-n-propylcobalt (0·82 g, 2·4 mmol) and octacarbonyldicobalt (1·35 g, 3·9 mmol) in tetrahydrofuran at room temperature for 60 h gave nonacarbonyl(pentafluoroethylcarbon)tricobalt (0·20 g, 0·36 mmol, 14%).

A repeat of this reaction using octacarbonyldicobalt (3·0 g, 8·8 mmol) and the fluoroalkyl complex (0·75 g, 2·2 mmol) in ether (75 ml) at room temperature for 16 h gave only recovered starting materials. However, when the complex (0·25 g, 0·74 mmol) and octacarbonyldicobalt (0·30 g, 0·88 mmol) in ether (10 ml) were heated at 40—50 °C for 4 days in a sealed tube, nonacarbonyl(pentafluoroethylcarbon)tricobalt (95 mg, 0·17 mmol, 25%) was obtained.

A similar reaction carried out between the fluoroalkyl complex (0·47 g, 1·38 mmol) and the carbonyl (0·45 g, 1·32 mmol) in n-pentane (15 ml) at 90 °C for 48 h in a sealed tube gave only recovered tetracarbonylheptafluoro-n-propylcobalt (32%) and a residue consisting of octacarbonyldicobalt and dodecacarbonyltetracobalt.

(b) *From heptafluoro-n-butyryl chloride.* Sodium tetracarbonylcobaltate(−1) (14·6 mmol) and heptafluoro-n-butyryl chloride (1·0 g, 4·3 mmol) in ether (50 ml) at 25 °C for 21 h gave nonacarbonyl(pentafluoroethylcarbon)tricobalt (0·19 g, 0·34 mmol, 8%).

Attempted Reaction of 3-*Chloro*-2,2,3-*trifluoropropionyl chloride with sodium tetracarbonylcobaltate*(−1).—When 3-chloro-2,2,3-trifluoropropionyl chloride [26] (0·50 g, 2·8 mmol) was added dropwise to a solution of the sodium salt (8·8 mmol) in ether (50 ml) and the solution was maintained at 0 °C for 0·5 h and at room temperature for 48 h, concentration of the solution and chromatography yielded only octacarbonyldicobalt (93 mg) and no trace of any compound of type $[RCCo_3(CO)_9]$.

When this reaction was repeated using the acyl chloride (3·54 g, 19·8 mmol) and the sodium salt (19·9 mmol) in tetrahydrofuran (100 ml) at 0 °C for 16 h, fractionation of the volatile reaction products under high vacuum gave a trace of a yellow oil which condensed at −23 °C, and rapidly decomposed at room temperature.

Preparation of Bis[*nonacarbonyl*(*carbon*)*tricobalt*].—μ-Tetrafluoroethylene-bis(tetracarbonylcobalt) (0·40 g, 0·9 mmol) and sodium tetracarbonylcobaltate(−1) (3·9 mmol) in ether (30 ml) were stirred at room temperature for 21·5 h. Evaporation of the solvent, and extraction of the residue with n-pentane afforded black crystals of bis[nonacarbonyl(carbon)tricobalt] (0·13 g, 0·15 mmol, 16%) identified by i.r. spectroscopy.[4]

Preparation of Hexafluorotrimethylenebis(*tetracarbonylcobalt*).—(a) *Using an excess of sodium salt* (with P. R. Mitchell). Hexafluoroglutaryl chloride (10·0 g, 36·2 mmol) was added dropwise to a solution of sodium tetracarbonylcobaltate(−1) (66·5 mmol) in tetrahydrofuran (250 ml) at 0 °C, and the solution was then allowed to warm up to room temperature and put aside overnight. The solvent was then removed, and the residue was washed with water, dried *in vacuo*, and fractionally recrystallised to give an involatile, deep purple solid (7·79 g) believed to be impure *nonacarbonyl*(1-*carboxytetrafluoroethylcarbon*)*tricobalt* (Found: C, 29·0; H, 1·3; F, 17·6. $C_{13}HCo_3F_4O_{11}$ requires C, 26·6; H, 0·2; F, 13·0%); i.r.*; u.v.* Further recrystallisation gave *μ-hexafluorotrimethylene-bis*(*tetracarbonylcobalt*) (8·20 g, 16·6 mmol, 25%) as a yellow crystalline solid, m.p. 109—109·5 °C (Found: C, 27·0; H, 0·2; Co, 24·3. $C_{11}Co_2F_6O_8$ requires C, 26·8; H, 0·0; Co, 24·0%); i.r.*; ^{19}F n.m.r.*

Bis(tetracarbonylcobalt)mercury (25 mg) was also isolated by fractional recrystallisation.

When the mother liquor was put aside in air overnight, and the purple solution filtered, addition of hexane (15 ml), concentration of the solution, and chromatography (1 : 1 mixture of ether–hexane as eluant) gave black crystals (0·25 g) thought to be a mixture of $[(CO)_9Co_3C(CF_2CF_2)Co(CO)_4]$ and $[\{(CO)_4Co_3C\}_2CF_2]$ on the basis of ^{19}F n.m.r. spectroscopy (ether) *; i.r.*

(b) *In a sealed tube.* Hexafluoroglutaryl chloride (1·2 g, 4·3 mmol) was condensed *in vacuo* into a tube containing potassium tetracarbonylcobaltate(−1) (2·20 g, 10·5 mmol) and ether (25 ml). The tube was sealed, maintained at 0 °C for 2 h, then put aside overnight at room temperature to give hexafluorotrimethylenebis(tetracarbonylcobalt) (3·25 g, 6·60 mmol, 63%).

Attempted Reaction of Tricarbonyltrifluoromethyl(*triphenylphosphine*)*cobalt*.—(a) *With sodium tetracarbonylcobaltate*(−1). When a solution of tricarbonyltrifluoromethyl(triphenylphosphine)cobalt (0·40 g, 0·84 mmol) and the sodium salt (5·8 mmol) in tetrahydrofuran (40 ml) was stirred at room temperature for 15 h the starting materials were recovered unchanged (78% recovery).

When this reaction was repeated at 75—80 °C for 3·5 h only unchanged tricarbonyltrifluoromethyl(triphenylphosphine)cobalt (89% recovery) was obtained.

(b) *With sodium tricarbonyl*(*triphenylphosphine*)*cobaltate*(−1). A solution of tricarbonyltrifluoromethyl(triphenylphosphine)cobalt (50 mg, 0·11 mmol) and the anion (1·0 mmol) in tetrahydrofuran (30 ml) stirred at room temperature for 18 h gave bis[tricarbonyl(triphenylphosphine)-cobalt] (0·14 g, 0·17 mmol) and unchanged fluoroalkyl complex (25 mg, 0·05 mmol, 50% recovery).

Attempted Reactions of Tetracarbonylheptafluoro-n-propylcobalt with Anions.—(a) *Sodium dicarbonyl*(π-*cyclopentadienyl*)*ferrate*(−1). Only bis[dicarbonyl(π-cyclopentadienyl)iron] (0·60 g, 1·69 mmol) and a yellow solid (*ca.* 5 mg) thought to be bis[dicarbonyl(π-cyclopentadienyl)iron]mercury were isolated from reaction of the sodium salt (6·74 mmol) and tetracarbonylheptafluoro-n-propylcobalt (0·46 g, 1·35 mmol) in tetrahydrofuran (35 ml) at room temperature for 48 h.

(b) *Sodium pentacarbonylmanganate*(−1). A solution of tetracarbonylheptafluoro-n-propylcobalt (0·50 g, 1·47 mmol) and the salt (2·56 mmol) in tetrahydrofuran (20 ml) under similar conditions gave only decacarbonyldimanganese (*ca.* 0·15 g) and recovered fluoroalkyl complex.

(*c*) *Sodium tricarbonyl*(*triphenylphosphine*)*cobaltate*(−1). The sodium salt (3·56 mmol) and tetracarbonylheptafluoro-n-propylcobalt (0·60 g, 1·76 mmol) in tetrahydrofuran (30 ml) stirred at room temperature for 12 h gave pale yellow crystals of tricarbonylheptafluoro-n-propyl(triphenylphosphine)cobalt (0·21 g, 0·37 mmol, 21% based on fluoroalkyl complex taken) after recrystallisation from a mixture of ether–hexane. The compound was identified by i.r. and ^{19}F n.m.r. spectroscopy, and mixed m.p. (110—111 °C) with an authentic sample prepared by reaction of tetracarbonylheptafluoro-n-propylcobalt and triphenylphosphine. The

---

[26] D. C. England, R. V. Lindsay, and L. R. Melby, *J. Amer. Chem. Soc.*, 1958, **80**, 6442.

m.p. 210 °C reported previously [27] for this compound is presumably a misprint. Close examination of the hexane-insoluble residue from this reaction showed it to be a mixture of bis[tricarbonyl(triphenylphosphine)cobalt] and its mercury derivative.

(d) *Sodium tricarbonyl(triphenyl phosphite)cobaltate*(−1). A solution of tetracarbonylheptafluoro-n-propylcobalt (0·50 g, 1·47 mmol) and the salt (3·53 mmol) in tetrahydrofuran (30 ml) under similar conditions gave, after chromatography (hexane eluant), tricarbonylheptafluoro-n-propyl(triphenyl phosphite)cobalt (0·25 g, 0·40 mmol, 27%) identified by i.r. spectroscopy.[27]

(e) *With sodium tetracarbonyl(triphenylphosphine)manganate*(−1). Tetracarbonylheptafluoro-n-propylcobalt (0·80 g, 2·35 mmol) and the salt (3·22 mmol) in tetrahydrofuran (50 ml) stirred overnight at room temperature gave, after chromatography (1 : 1 mixture of ether–hexane as eluant), tricarbonylheptafluoro-n-propyl(triphenylphosphine)cobalt (185 mg, 0·32 mmol, 14%), and an insoluble residue containing bis[tetracarbonyl(triphenylphosphine)manganese].

Attempted Reaction of Tetracarbonyltrifluoromethylcobalt with Sodium Tetracarbonylrhodate(−1).—Tetracarbonyltrifluoromethylcobalt (0·50 g, 2·08 mmol) added to a solution of sodium tetracarbonylrhodate(−1) [28] [from bis(chlorodicarbonylrhodium) (1·05 g, 2·70 mmol)] in tetrahydrofuran (35 ml) gave an immediate gas evolution. The solution was stirred for 48 h at room temperature under an atmosphere of carbon monoxide, but the only product isolated was a small quantity (0·10 g, 0·13 mmol) of dodecacarbonyltetrarhodium.

Preparation of Tetracarbonylheptafluoroisopropylcobalt.—Heptafluoroisobutyric acid (78%), b.p. 35 °C/0·5 mmHg (reported [29] 54·4 °C/52 mmHg), was prepared from hexafluoropropene, carbon dioxide, and caesium fluoride in bis-(2-methoxyethyl) ether at 50—60 °C over several days as reported previously.[29] The product was identified by i.r. spectroscopy; [30] ^{19}F n.m.r.*

Reaction of the acid with phosphorus pentachloride at room temperature for 15 h gave the corresponding acid chloride in 81% yield; [31] i.r.*; ^{19}F n.m.r.*

Heptafluoroisobutyryl chloride (2·0 g, 8·6 mmol) and sodium tetracarbonylcobaltate(−1) (1·82 g, 9·3 mmol) in ether (20 ml) were stirred at 0 °C for 2 h, and for a further 1 h at room temperature. Distillation of the volatile products *in vacuo* gave *tetracarbonylheptafluoroisopropylcobalt* (2·26 g, 6·6 mmol, 71%) as a slightly volatile yellow liquid which condensed at −23 °C, and which could not be separated completely from a trace of heptafluoroisobutyric acid; a satisfactory microanalysis could not be obtained (Found: C, 26·8; H, 1·0; F, 37·9. $C_7CoF_7O_4$ requires C, 24·7; H, 0·0; F, 39·1%); i.r.*; ^{19}F n.m.r.*

When the yellow liquid (65 mg, 0·2 mmol) was condensed *in vacuo* into a tube containing triphenylphosphine (100 mg, 0·4 mmol) in hexane (5 ml), and the mixture put aside overnight at room temperature, *tricarbonylheptafluoroisopropyl(triphenylphosphine)cobalt* (65 mg, 0·1 mmol, 59%) precipitated as yellow needles, m.p. 115 °C (Found: C, 50·2; H, 2·6; F, 23·2. $C_{24}H_{15}CoF_7O_3P$ requires C, 50·2; H, 2·6; F, 22·7%); i.r.*.

Reaction of Tetracarbonylheptafluoroisopropylcobalt with Sodium Tetracarbonylcobaltate(−1).—Tetracarbonylheptafluoroisopropylcobalt (1·40 g, 4·12 mmol) was condensed *in vacuo* into a solution of the anion (11·6 mmol) in ether (100 ml), and the mixture was put aside at room temperature overnight. The volatile products were removed, and distilled *in vacuo* to give a volatile orange-red oil (0·98 g) shown by t.l.c. to contain unchanged starting material and a red compound. The ^{19}F n.m.r. spectrum showed a band at *ca.* −25 p.p.m. relative to external trifluoroacetic acid, in addition to bands due to the starting material.

Thanks are due to the S.R.C. for a studentship award to one of us (T. I.).

[4/1970 *Received*, 26*th September*, 1974]

---

[27] W. Hieber, J. Muschi, and H. Duchatsch, *Chem. Ber.*, 1965, **98**, 3924.

[28] P. Chini and S. Martinengo, *Inorg. Chim. Acta*, 1969, **3**, 21.

[29] D. P. Graham, U.S. Patent 3,311,657.

[30] J. H. Simons, ' Fluorine Chemistry,' Academic Press, New York, 1950, vol. 2, p. 488.

[31] I. L. Knunyants, V. V. Shokina, V. V. Tyuleneva, Y. A. Cheburkov, and Y. E. Aronov, *Izvest. Akad. Nauk. S.S.S.R., Ser. Khim.*, 1966, **10**, 1831 (*Chem. Abs.*, 1967, **66**, 94,675).