1220. *Transition-metal Fluorocarbon Complexes. Part VII.*[1] *Some Complexes of Cobalt and Rhodium with Tetrafluoroethylene, Chlorotrifluoroethylene, and Hexafluorobut-2-yne*

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The reactions of C_2F_4, C_2F_3Cl, and $CF_3{\cdot}C{\equiv}C{\cdot}CF_3$ with cyano- and cyano-hydrido-complexes of cobalt and with chlorotris(triphenylphosphine)rhodium(I) are described. The very stable complexes $K_6[(CN)_5CoC_2F_4Co(CN)_5]$, $K_3[Co(CN)_5C_2F_4H]$, $K_3[Co(CN)_5C_2F_4H]$, $RhCl(Ph_3P)_2C_2F_4$, $RhCl(Ph_3P)_2C_2F_3Cl$ and $RhCl(Ph_3P)_2C_4F_6$, have been isolated as crystalline compounds from these reactions. Infrared and nuclear magnetic resonance spectra of these complexes are given and their structures discussed. Some chemical properties of the rhodium complexes have also been investigated.

WE have previously described transition-metal complexes formed by the reaction of tetrafluoroethylene and hexafluorobut-2-yne with octacarbonyldicobalt.[2,3] Complexes are also formed by these fluorocarbons with dicarbonyl-π-cyclopentadienylcobalt.[3,4] Since the present work started two rhodium complexes containing tetrafluoroethylene, $Rh(AcAc)(C_2H_4)C_2F_4$ and $[RhCl(C_2H_4)C_2F_4]_2$, have been described briefly.[5] In this Paper we report new fluorocarbon complexes of cobalt and rhodium with C_2F_4, C_2F_3Cl, and $CF_3{\cdot}C{\equiv}C{\cdot}CF_3$, formed by addition across the metal–metal or metal–hydrogen bond in cobalt complexes containing cyanide ligands as stabilising groups, and by the displacement of π-acid ligands such as triphenylphosphine and ethylene from phosphine complexes of rhodium.

Cobalt and Rhodium Fluoroalkyl Complexes.—Acetylene reacts with an aqueous solution of the pentacyanocobaltate(II) ion to give a bridged complex in which each tervalent cobalt atom is bound to five cyanides and an ethylenic bridge. Ethylene itself does not form a complex.[6] However, tetrafluoroethylene is rapidly taken up (0·5 mole per mole of Co) at atmospheric pressure and a yellow crystalline air-stable salt of stoicheiometry $K_6[Co_2(CN)_{10}C_2F_4],2H_2O$ may be readily isolated from the solution. That this salt is a bridged dimeric species is shown by its diamagnetism and by the observation of a single fluorine resonance peak in the ^{19}F nuclear magnetic resonance (n.m.r.) spectrum of the compound (see Table 1). It may be regarded as a complex of cobalt(III), with the tetrafluoroethylene acting as a doubly negatively charged ligand. It has been suggested [7] that the reactive species in solutions of $[Co(CN)_5]^{3-}$ is the dimer, with a Co–Co bond, in which case the reaction may be regarded as a 2-carbon atom insertion into the metal–metal bond, analogous to the recently described insertion of C_2F_4 into a Mn–Sn bond.[8] The complex is stable up to 250° *in vacuo* but decomposes rapidly above this temperature with liberation of tetrafluoroethylene and deposition of cobalt metal. Hexafluorobut-2-yne does not react with the cobalt cyanide solution at atmospheric pressure, and chlorotrifluoroethylene does not give a stable fluorocarbon complex.

Solutions of $[Co(CN)_5]^{3-}$ may be reduced by potassium amalgam to give a species

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[1] Part VI, J. A. McCleverty and G. Wilkinson, *J.*, 1964, 4200.

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

[3] J. L. Boston, D. W. A. Sharp, and G. Wilkinson, *J.*, 1962, 3488.

[4] T. D. Coyle, R. B. King, E. Pitcher, S. L. Stafford, P. M. Treichel, and F. G. A. Stone, *J. Inorg. Nuclear Chem.*, 1961, **20**, 172.

[5] R. Cramer and G. W. Parshall, *J. Amer. Chem. Soc.*, 1965, **87**, 1392.

[6] W. P. Griffith and G. Wilkinson, *J.*, 1959, 1629.

[7] B. De Vries, *J. Catalysis*, 1962, **1**, 489.

[8] H. C. Clark and J. H. Tsai, *Chem. Comm.*, 1965, 111.

thought [9] to be $[Co(CN)_5H]^{3-}$. This reduced solution also reacts rapidly with tetrafluoroethylene at atmospheric pressure, twice as much gas (1 mole per mole of Co) being taken up as previously required for the unreduced solutions. Very pale yellow crystals of a compound of stoicheiometry $K_3[Co(CN)_5C_2F_4H]$ were isolated from solution. A 3-dimensional *X*-ray analysis on a single crystal has shown that the complex is octahedral, and that the metal–fluorocarbon bond distance is somewhat shorter than that expected from assumed single-bond covalent radii (0·06 Å).[10] However, such calculations are often misleading, and the shortening does not seem sufficient to provide any definite evidence for π-bonding to the fluorocarbon group.

The compound is stable in air and can be heated to 250° *in vacuo* and recovered substantially unchanged. Its infrared (i.r.) spectrum shows four strong bands in the 1200—900-cm.$^{-1}$ region which may be attributed to CF stretching modes, in addition to CN bands.

The ^{19}F n.m.r. spectrum of both the cobalt compounds so far described is interesting in that the α-CF_2 resonance consists of a single broad band with a line-width of approx. 60 c./sec. This may be contrasted with $(CO)_4CoC_2F_4Co(CO)_4$ where the line-width is <2 c./sec. and indeed with the width in all other cobalt–fluorocarbon complexes so far prepared.[11] The broadening must be due to incomplete averaging of the spin coupling with the ^{59}Co nucleus ($I = 7/2$) which is normally brought about by quadrupole relaxation of this nucleus. The electric-field gradient at the cobalt nucleus must be low in these two cases, presumably because of the quite high symmetry around the nucleus.

The n.m.r. data for the two cobalt compounds are summarised in Table 1 along with the results for $K_3[Rh(CN)_5C_2F_4H]$ and $HC_2F_4Mn(CO)_5$ for comparison. The rhodium complex results from an unusual reaction of tetrafluoroethylene with the new potassium hydridotetracyanoaquorhodate(III).[12] It will be seen that, in the case of rhodium, the α-CF_2 resonance is well resolved, and spin-coupling to ^{103}Rh ($I = \frac{1}{2}$, relative abundance 100%) is observed, there being no nuclear quadruple moment for ^{103}Rh to bring about relaxation. The β-CF_2 resonance for $K_3[Co(CN)_5C_2F_4H]$ is a double triplet, each component of which is further split into a doublet in the rhodium analogue ($J_{Rh-F_\beta} = 1{\cdot}9$ c./sec.). The triplet splitting ($J_{F_\alpha-F_\beta} = 6{\cdot}6$ for Co, 5·4 c./sec. for Rh) is unusually large for a transition-metal–fluorocarbon complex of this type.[13] The proton spectrum is the expected triple triplet in both cases, there being no observable coupling between ^{103}Rh and H.

TABLE 1

Proton and fluorine-19 nuclear magnetic resonance of σ-bonded perfluoralkyl complexes

		^{19}F Shifts [a]		^{1}H Shifts [b]	Coupling constants [c]				
Compound	Ref.	δ_α	δ_β	δ	$J_{F_\alpha-F_\beta}$	$J_{F_\alpha-H}$	$J_{F_\beta-H}$	J_{M-F_α}	J_{M-F_β}
$[(CN)_5CoCF_2]_2^{6-}$	[d]	11·2	—	—	—	—	—	[e]	—
$[(CN)_5(C_2F_4H)Co]^{3-}$	[d]	17·0	67·3	4·02	5·4	7·5	55·9	[e]	[e]
$[(CN)_5(C_2F_4H)Rh]^{3-}$	12	16·8	66·9	4·14	6·6	7·4	54·0	11·1	1·9
$(C_2F_4H)Mn(CO)_5$ ...	14	−3·7	75·0	4·68	<1	5·3	58·0	—	—

[a] In p.p.m. relative to benzotrifluoride as external reference, positive values indicating lines on the high field side of this reference. CCl_3F used as internal reference for manganese complex and value converted approx. [b] τ values measured relative to t-butyl alcohol as internal reference (τ 8·80). [c] Couplings in c./sec. [d] This work. [e] See text.

The monomeric cobalt and rhodium complexes have a microsymmetry of C_{4v} and a splitting of the $^1T_{1g} \longleftarrow {}^1A_{1g}$ transition in the ultraviolet for O_h into $^1E_g + {}^1A_g \longleftarrow {}^1A_{1g}$

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[9] W. P. Griffith and G. Wilkinson, *J.*, 1959, 2757.

[10] R. Mason and D. R. Russell, *Chem. Comm.*, 1965, 182.

[11] P. M. Treichel and F. G. A. Stone, *Adv. Organometallic Chem.*, 1964, **1**, 143.

[12] D. N. L. Lawson, M. J. Mays, and G. Wilkinson, *J.*, 1966, in the press.

[13] E. Pitcher, A. D. Buckingham, and F. G. A. Stone, *J. Chem. Phys.*, 1962, **36**, 124.

[14] P. M. Treichel, E. Pitcher, and F. G. A. Stone, *Inorg. Chem.*, 1962, **1**, 511.

is expected. Only a single *d–d* band is observed, at 311 mμ for the former and 225 mμ for the latter. These values are comparable to those for $[Co(CN)_6]^{3-}$ ($\lambda_{max.}$ 311 mμ) and $[Rh(CN)_6]^{3-}$ ($\lambda_{max.}$ 225 mμ), and suggests that the ligand-field strength of the fluoroalkyl ligand is at least as high as CN^- and somewhat higher than that of the methyl ligand in the recently prepared $[CH_3Co(CN)_5]^{3-}$ ($\lambda_{max.}$ 318 mμ).[15]

We have not been successful in isolating other analogous σ-bonded fluoroalkyl complexes with $CF_3{\cdot}C{\equiv}C{\cdot}CF_3$ or C_2F_3Cl. The former is not taken up at atmospheric pressure by aqueous solutions of $[Co(CN)_5]^{3-}$ or $[CoH(CN)_5]^{3-}$ and complexes of the latter olefin are unstable, presumably disproportionating with the formation of such species as $[Co(CN)_5Cl]^{3-}$. We could not isolate any fluorocarbon complex from the mixture.

Fluoro-olefin and Acetylene Complexes of Rhodium.—Chlorotris(triphenylphosphine)-rhodium(I) has been shown to be a particularly effective homogeneous hydrogenation catalyst for olefins.[16] In the presence of an excess of ethylene one triphenylphosphine molecule is displaced and a crystalline olefin complex, $RhCl(Ph_3P)_2(C_2H_4)$, precipitates from solution.[17] The co-ordinated ethylene is labile and the complex dissociates readily in solution when the excess of olefin is removed, although the solid is indefinitely air-stable. It was of interest to determine whether fluoro-olefins would similarly displace triphenylphosphine from the complex. An excess of tetrafluoroethylene was sealed in a thick-walled glass tube with a chloroform suspension of chlorotris(triphenylphosphine)-rhodium(I) and after 24 hr. the deep red crystals had been replaced by pale yellow crystals of $RhCl(Ph_3P)_2(C_2F_4)$. Unlike its ethylene or triphenylphosphine analogues this complex does not dissociate in benzene at 37°, molecular-weight measurements by Mechrolab Osmometer giving the value required for a monomeric complex. As expected from this, the C_2F_4 moeity in the complex is not displaced by an excess of triphenylphosphine or ethylene and is therefore more firmly bound to the rhodium than either of the other two ligands which it displaces. The complex can also be recovered unchanged from solution in boiling benzene or chloroform and the solutions are unaffected by hydrogen (100 atm.) during 3 days at room temperature. At 70°, however, the complex is destroyed by hydrogen; $C_2F_4H_2$ (identified by its characteristic ^{19}F n.m.r. spectrum) is recovered as a major product, although unchanged C_2F_4 and other unidentified fluorinated products are also obtained. The C_2F_4 is also displaced from solutions of the complex by carbon monoxide at room temperature, $RhCl(CO)(Ph_3P)_2$ (identified by its i.r. spectrum) being formed.

That the C_2F_4 occupies a position *trans* to the chloro-ligand in $RhCl(Ph_3P)_2(C_2F_4)$ is indicated by the ^{19}F n.m.r. spectrum of the complex in dichloromethane (see Table 2). This consists of a triplet ($J_{P-F} = 24{\cdot}3$ c./sec.) each component of which is further split into a doublet ($J_{Rh-F} = 9{\cdot}6$ c./sec.). The separations are the same at 56·45 and at 40 Mc./sec., showing that all four fluorines are equivalent and that there is no chemical-shift element included in the observed splittings. The most probable structure of the complex is therefore a planar one in which the fluorocarbon moiety occupies a similar position to that of π-bonded ethylene in, *e.g.*, planar platinum complexes.[18] The ^{19}F n.m.r. spectrum of a solution of the complex at −80° is identical with the spectrum at room temperature and there is neither broadening nor a change in position of the signal in the presence of a large excess of free C_2F_4 in solution, indicating that no exchange of co-ordinated and free C_2F_4 can take place on the n.m.r. time scale. This is in contrast to Cramer's results on ethylene complexes [19] and also to the rapid exchange found in the corresponding ethylene complex, $RhCl(Ph_3P)_2C_2H_4$. The nature of the bonding in the complex is not clear. No band attributable to a C=C stretching frequency is observed in the i.r. spectrum between 2000

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[15] J. Halpern and J. P. Maher, *J. Amer. Chem. Soc.*, 1964, **86**, 2311.
[16] J. F. Young, J. A. Osborn, F. H. Jardine, and G. Wilkinson, *Chem. Comm.*, 1965, 131.
[17] J. F. Young, J. A. Osborn, F. H. Jardine, and G. Wilkinson, unpublished results.
[18] J. Chatt and L. A. Duncanson, *J.*, 1953, 2939.
[19] R. Cramer, *J. Amer. Chem. Soc.*, 1964, **86**, 217; *Inorg. Chem.*, 1965, **4**, 445.

and 1500 cm.$^{-1}$, or in the spectrum of the analogous C_2F_3Cl complex, in which its intensity should be enhanced. In complexes containing co-ordinated ethylene such a band is observed [20] at frequencies 100—150 cm.$^{-1}$ below its position in ethylene itself although the bond is often very weak. On the other hand a 5-co-ordinate complex in which both carbon atoms are bound to rhodium by predominantly σ-bonds in a 3-membered ring is also not likely, as this would lead to a restriction of rotation and non-equivalence of the fluorine atoms.

TABLE 2

^{19}F N.m.r. spectra of rhodium phosphine complexes

Compound	Ref.	^{19}F Shifts [a] δ	Coupling constants [b] $J_{(M-F)}$	$J_{(P-F)}$
$RhCl(Ph_3P)_2C_2F_4$	This work	36·0	9·6 [c]	24·5 [c]
$RhCl(Ph_3P)_2C_2F_3Cl$	This work	26·6	[d]	[d]
$RhCl(Ph_3P)_2C_4F_6$	This work	$-9{\cdot}45$	1·6	<1
$Pt(Ph_3P)_2C_4F_6$	21	$-9{\cdot}0$	65·1	10·3

[a] In p.p.m. relative to benzotrifluoride, positive values indicating lines on the high field side of this reference. [b] Coupling in c./sec. [c] Measured at 40 Mc./sec. and 56·4 Mc./sec. [d] Complex multiplet ~300 c./sec., broad.

The complex formed by interaction of chlorotrifluoroethylene with chlorotris(triphenylphosphine)rhodium(I) in chloroform is analogous to the C_2F_4 complex. Its preparation by the same method, however, is slow, taking several weeks to reach completion. It is more readily prepared from the ethylene complex in benzene, replacement of ethylene being complete after 16 hr. Unlike the C_2F_4 complex, its formation is reversible and the ethylene complex is reformed on reacting the C_2F_3Cl complex with ethylene under pressure for 16 hr. It is also attacked by chlorinated solvents, and unchanged C_2F_3Cl is recovered when hydrogen (though not nitrogen) is bubbled through a benzene solution of the complex. The dimer, $[RhCl(Ph_3P)_2]_2$, precipitates from solution.

Hexafluorobut-2-yne reacts readily with a suspension of chlorotris(triphenylphosphine)-rhodium(I) in benzene to form a stable crystalline complex. The excess of the fluoro-alkyne used in the preparation is polymerised to a white solid which is insoluble in organic solvents and does not melt at 800°.[3] The i.r. spectrum of the complex shows a band of medium strength at 1917 cm.$^{-1}$ and molecular-weight measurements indicate that it is monomeric. The fluoro-alkyne must therefore act merely as a donor as in other acetylene–metal complexes, and as in dicarbonylhexafluorobut-2-yne-π-cyclopentadienylmanganese-(I),[21] in which complex the corresponding i.r. band occurs at 1919 cm.$^{-1}$. It was suggested for this compound that the CF_3 groups must be bent away from the C–C axis in order for this i.r. band to become active. Even if the carbon atom chain remains linear, however, the C≡C stretching mode in the complex is still associated with a change of dipole moment and therefore no rehybridisation of σ-bonds need occur. Two square transition-metal complexes of hexafluorobut-2-yne have been described previously, namely bis(triphenylphosphine)hexafluorobut-2-yneplatinum(II) and its arsine analogue.[21] In these, however, the fluoro-alkyne occupies two co-ordination positions in the plane and the corresponding i.r. bands occur at 1775 cm.$^{-1}$ indicating a substantial reduction in the C–C bond order. The ^{19}F n.m.r. spectrum of the rhodium complex consists of a doublet [$J_{Rh-F} = 1{\cdot}6$ c./sec.] 533 c./sec. below benzotrifluoride (internal reference). Any coupling with the phosphorus atoms (^{31}P, $I = \frac{1}{2}$, relative abundance 100%) is <1 c./sec. These values may be contrasted with those for the platinum complex where J_{Pt-F} is 65·1 and J_{P-F} is 10·3 c./sec. As with the tetrafluoroethylene complex, the spectrum is identical in the presence of a large excess of free fluoro-alkyne, indicating that no exchange takes place on the n.m.r. time scale.

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[20] D. B. Powell and N. Sheppard, *Spectrochim. Acta*, 1958, **13**, 69.

[21] J. L. Boston, S. O. Grim, and G. Wilkinson, *J.*, 1963, 3468.

The compound is considerably more soluble in most organic solvents than the fluoro-olefin complexes already described and, in particular, is soluble in diethyl ether, whereas the olefin complexes are only slightly soluble in this solvent. A benzene solution of the complex is not affected by ethylene under pressure at room temperature but is decomposed on boiling, or by triphenylphosphine at room temperature, and is therefore less stable than a corresponding solution of the tetrafluoroethylene complex. On bubbling hydrogen through a benzene solution at room temperature the dimer, $(Ph_3P)_4Rh_2Cl_2$, precipitates and 1,1,1,4,4,4-hexafluorobutane (identified by ^{19}F and ^1H n.m.r.) is recovered in *ca.*, 90% yield. A minor fluorinated product is probably either *cis-* or *trans-*$CF_3CH{=}CHCF_3$ but its ^{19}F n.m.r. spectrum is equivocal, and it was not present in sufficient concentration to identify it by its i.r. spectrum. Carbon monoxide displaces the fluoro-acetylene from a benzene solution of the complex to give $RhCl(CO)(Ph_3P)_2$. The order of stability of the rhodium complexes described appears, from the above chemical reactions, to be $C_2F_4 > C_4F_6 > C_2F_3Cl \gg C_2H_4$.

EXPERIMENTAL

Microanalyses were by the Microanalytical Laboratory, Imperial College. Potassium was determined gravimetrically as tetraphenylborate; cyanide by the potassium fusion method. Infrared spectra were recorded using a Grubb–Parsons Spectromaster grating instrument in Nujol mulls unless otherwise stated. Electronic spectra were taken using a Perkin-Elmer 350 spectrophotometer. N.m.r. spectra were taken on a Varian V4311 spectrometer at 56·45 Mc./sec. Proton resonances are referred to t-butyl alcohol (internal) and expressed as τ values (τ for Bu^tOH 8·80). ^{19}F Resonances are referred to benzotrifluoride as external reference for aqueous solutions, and as internal reference for non-aqueous solutions. All petroleum used had b. p. 40—60°. Melting points were taken on a Kofler hot-stage apparatus and are uncorrected. Molecular weights (benzene) by Mechrolab Osmometer at 37°.

Hexapotassium μ-Tetrafluoroethylenebis(pentacyano)dicobaltate(III) *Dihydrate*.—An aqueous air-free solution (100 ml.) of $CoCl_2,6H_2O$ (2·38 g.) and potassium cyanide (3·3 g.) was shaken with tetrafluoroethylene (1 atm.) (external ice-cooling). Gas uptake took place for ½ hr. and the solution gradually changed from deep green to straw-yellow. Addition of ethanol precipitated the *complex* as pale yellow crystals which were washed with ethanol, (yield, 3·4 g., 90%) (Found: C, 19·3; H, 0·9; F, 9·7; K, 31·4; N, 18·7; loss in weight for $2H_2O$, 4·8. $C_{12}H_4Co_2F_4K_6N_{10}O_2$ requires C, 19·3; H, 0·5; F, 10·2; K, 31·4; N, 18·7; loss in weight for $2H_2O$, 4·8%), $\nu_{max.}$ 4320w, 4232w, 3581w, 3483w, 2724w, 2677w; 2139m, 2129m, 2119s, 2116s, 2085w, 2077w (CN str); 1608m; 1304w, 1165w, 1152w, 992s, 955s (CF str); 769w, 683s, 556m, 548m, 532m cm.$^{-1}$; $\lambda_{max.}$ (in H_2O): 320, 276 mμ (log ε 3·32, 4·18).

*Tripotassium Pentacyano-*1,1,2,2-*tetrafluoroethylcobaltate*(III).—To an air-free solution (150 ml.) of $CoCl_2,6H_2O$ (2·38 g.) and potassium cyanide (3·3 g.) (external ice-cooling) was added 3% potassium amalgam (50 g.). The solution was shaken until pale yellow, and decanted under nitrogen into a round-bottomed flask (250 ml.) and then shaken with tetrafluoroethylene (1 atm.) until no more gas was taken up (½ hr.). Addition of ethanol (150 ml.) precipitated a small quantity of hexapotassium μ-tetrafluoroethylenebis(pentacyano)dicobaltate(III). This was filtered off and addition of more ethanol (300 ml.) precipitated the *salt* as a yellow oil which slowly crystallised at ice temperature. The crystals were washed with ethanol and dried *in vacuo* (yield, *ca.*, 50%) (Found: C, 20·8; Co, 14·2; F, 18·0; K, 29·1; N, 17·4. $C_7HCoF_4K_3N_5$ requires C, 20·6; Co, 14·5; F, 18·7; K, 28·8; N, 17·2%), $\nu_{max.}$ 4324w, 4250w, 3046m, 2767w, 2618w; 2145m, 2130s, 2121s, 2089m, 2082m (CN str); 1349m; 1160s, 1066sh, 1057s, 1041m, 969s, 927s (CF str); 784s, 595m, 562m, 550m, 533m cm.$^{-1}$; $\lambda_{max.}$ (in H_2O) 311 mμ (log ε 2·40). For the rhodium analogue $\lambda_{max.}$ 225 mμ (log ε 2·94).

Chlorobis(triphenylphosphine)tetrafluoroethylenerhodium(I).—An excess of tetrafluoroethylene (2·5 g.) was condensed on to chlorotris(triphenylphosphine)rhodium(I) (0·75 g.) in chloroform (10 ml.) in a thick-walled glass tube. After 24 hr. at room temperature the tube was opened and the excess of tetrafluoroethylene removed. The yellow microcrystals were filtered off from the brown solution and washed with a little chloroform and ether. The *complex*, m. p. 156° (decomp.), was recrystallised from dichloromethane at −80° (yield, *ca.* 70%) [Found: C, 59·9;

H, 4·2; Cl, 4·8; F, 9·9; P, 8·1%; *M* (benzene), 743. $C_{38}H_{30}ClF_4RhP_2$ requires C, 59·8; H, 3·9; Cl, 4·8; F, 10·7; P, 8·1%; *M*, 762], $\nu_{max.}$ 3058m, 1477m, 1432s, 1161m (CF str), 1125s, 1116s (CF str), 1096s, 1091sh, 1040s (CF str), 999m, 797s (CF str), 752sh, 746sh, 742s, 704sh, 692s, 622s, 617s, 522s, 509s, 498m, 459m cm.$^{-1}$. The compound is soluble in dichloromethane and chloroform and sparingly soluble in benzene. Solutions are stable in air for several days.

Chlorobis(triphenylphosphine)hexafluorobut-2-ynerhodium(I).—An excess of hexafluorobut-2-yne (*ca.* 3 g.) was condensed on to chlorotris(triphenylphosphine)rhodium (0·75 g.) in benzene (10 ml.) in a thick-walled glass tube. After 2—3 min. the tube became hot and the contents set to a gelatinous yellow solid. After ½ hr. the tube was opened but none of the excess of hexafluorobut-2-yne was recoverable. The benzene was removed and the residue extracted with diethyl ether (3 × 10 ml.). On addition of light petroleum to the ether extract orange crystals of the *complex* m. p. 141° (decomp.), precipitated slowly (yield, *ca.* 50%) [Found: C, 58·3; H, 4·1; F, 13·8%; *M* (benzene), 818. $C_{40}H_{30}ClF_6P_2Rh$ requires C, 58·3; H, 4·1; F, 13·8%; *M*, 824], $\nu_{max.}$ 3062m, 1917m (C≡C str), 1481m, 1430s, 1250s (CF str), 1221s (CF str), 1139s, (CF str), 1127s, 1095s, 1000m, 899m, 744s, 714sh, 692s, 517s, 497m cm.$^{-1}$. The residue which had been extracted with ether could not be sublimed at temperatures up to 200°, did not melt up to 800°, and no hexakistrifluoromethylbenzene was present in the ether extract.

Chlorobis(triphenylphosphine)chlorotrifluoroethylenerhodium(I).—The ethylene complex was first prepared by condensing an excess of ethylene (0·5 g.) on to chlorotris(triphenylphosphine)-rhodium(I) (1 g.) in chloroform (10 ml.) in a thick-walled glass tube. After 10 min. the tube was opened, the contents quickly filtered and the precipitate washed with diethyl ether. The yellow microcrystals were transferred to another tube and suspended in benzene (10 ml.). An excess of chlorotrifluoroethylene (3 g.) was condensed into the tube which was then shaken at room temperature for 24 hr. The yellow crystals of the *compound*, m. p. 148°, were filtered off, washed with diethyl ether and dried *in vacuo* (yield, *ca.* 90%) (Found: C, 58·1: H, 3·8; Cl, 9·1; F, 7·2. $C_{38}H_{30}Cl_2F_3P_2Rh$ requires C, 58·5; H, 3·9; Cl, 9·1; F, 7·3%), $\nu_{max.}$ 3053m, 1477m, 1433m, 1112s (CF str), 1045s (CF str), 1034s (CF str), 922s (CF str), 754m, 742s, 718m, 703sh, 692s, 529sh, 522s, 511s, 497m cm.$^{-1}$.

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