Reactions of Co-ordinated Ligands. Part 20.[1] Insertion and Ring-forming Reactions of Fluorinated Olefins with η^3-Allylcobalt Species; Molecular and Crystal Structure of Dicarbonyl[4—5-η-1,2-difluoro-1,2-bis(trifluoromethyl)pent-4-enyl](trimethyl phosphite)cobalt

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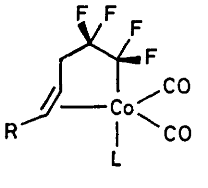
Thermal reaction of C_2F_4 with $[Co(CO)_2(PMe_2Ph)(\eta\text{-}C_3H_5)]$, $[Co(CO)_2\{P(OMe)_3\}(\eta\text{-}C_3H_5)]$, or $[Co(CO)_3(\eta^3\text{-}1\text{-}syn\text{-}PhC_3H_4)]$ affords respectively $[Co(CF_2CF_2CH_2CH{=}CH_2)(CO)_2(PMe_2Ph)]$, $[Co(CF_2CF_2CH_2CH{=}CH_2)(CO)_2\{P(OMe)_3\}]$, and $[Co(CF_2CF_2CH_2CH{=}CHPh)(CO)_3]$. Hexafluoropropene with $[Co(CO)_2\{P(OMe)_3\}(\eta^3\text{-}2\text{-}MeC_3H_4)]$ and octafluorobut-2-ene with $[Co(CO)_3(\eta\text{-}C_3H_5)]$, $[Co(CO)_2\{P(OMe)_3\}(\eta\text{-}C_3H_5)]$, or $[Co(CO)_2(PMe_2Ph)(\eta\text{-}C_3H_5)]$ give $[Co\{CF(CF_3)CF_2CH_2CMe{=}CH_2\}(CO)_2\{P(OMe)_3\}]$, $[Co\{CF(CF_3)CF(CF_3)CH_2CH{=}CH_2\}(CO)_3]$, $[Co\{CF(CF_3)CF(CF_3)CH_2CH{=}CH_2\}(CO)_2\{P(OMe)_3\}]$, and $[Co\{CF(CF_3)CF(CF_3)CH_2CH{=}CH_2\}(CO)_2(PMe_2Ph)]$ respectively. The penultimate compound is structurally identified by single-crystal *X*-ray diffraction. Crystals are triclinic, space group $P\bar{1}$, in a unit cell of dimensions $a = 9.544(9)$, $b = 11.682(9)$, $c = 12.421(12)$ Å, $\alpha = 122.27(6)$, $\beta = 119.78(6)$, and $\gamma = 96.04(7)°$ at 183 K. The structure is essentially trigonal bipyramidal with the fluoroalkyl group and the phosphite ligand occupying axial sites. Chlorotrifluoroethylene with $[Co(CO)_3(\eta\text{-}C_3H_5)]$, $[Co(CO)_3(\eta^3\text{-}2\text{-}MeC_3H_4)]$, and $[Co(CO)_3(\eta^3\text{-}1\text{-}MeC_3H_4)]$ leads to an unusual cyclisation reaction and the formation of $[Co\{\eta^3\text{-}CH{\cdots}CH{\cdots}CFCF_2CH_2\}(CO)_2]$, $[Co\{\eta^3\text{-}CMe{\cdots}CH{\cdots}CFCF_2CH_2\}(CO)_2]$, and $[Co\{\eta^3\text{-}CH{\cdots}CMe{\cdots}CFCF_2CH_2\}(CO)_3]$.

WE have previously studied[2] the reactions of the compounds $[Ir(CO)L_2(\eta^3\text{-allyl})]$ ($L = PPh_3$ or $AsPh_3$) with tetrafluoroethylene with a view to obtaining a better understanding of the related insertion reaction which $[Co(CO)_3(\eta\text{-}C_3H_5)]$ readily undergoes with C_2F_4.[3] Whilst leading to some interesting new reactions, the study of the iridium system did not provide the sought-for insights into the cobalt reactions. We have therefore further examined the cobalt system, and in this paper are described the effect of phosphorus ligands, the structural elucidation by *X*-ray crystallography of the insertion product obtained with octafluorobut-2-ene, and the observation of an unusual ring-closure reaction with chlorotrifluoroethylene.

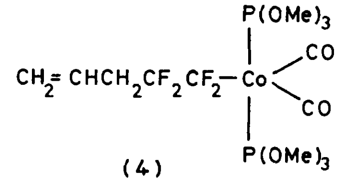
RESULTS AND DISCUSSION

Reaction of tetrafluoroethylene with $[Co(CO)_3(\eta\text{-}C_3H_5)]$ occurs readily at room temperature to form a 1 : 1 adduct, for which the structure $[Co(CF_2CF_2CH_2CH{=}CH_2)(CO)_3]$ was proposed on the basis of ^1H and ^{19}F n.m.r. data. The initial objective was to examine the effect of replacing one of three carbon monoxide ligands by a poorer π acceptor. It had previously[4] been shown that reaction of PPh_3 with $[Co(CO)_3(\eta\text{-}C_3H_5)]$ afforded $[Co(CO)_2(PPh_3)(\eta\text{-}C_3H_5)]$, the rate-determining step being independent of phosphine concentration. A simple extension of this reaction afforded the complexes $[Co(CO)_2(PMe_2Ph)(\eta\text{-}C_3H_5)]$, $[Co(CO)_2\{P(OMe)_3\}(\eta\text{-}C_3H_5)]$, $[Co(CO)_2\{P(OMe)_3\}(\eta^3\text{-}2\text{-}MeC_3H_4)]$, and $[Co(CO)_2\{P(OMe)_3\}(\eta^3\text{-}syn\text{-}1\text{-}PhC_3H_4)]$, which were characterised by i.r., n.m.r., and mass spectroscopy.

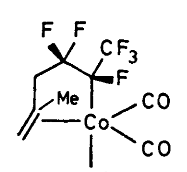
Reaction of fluoro-olefins with these phosphorus-ligand-substituted η^3-allylic complexes occurred less readily than with the tricarbonyl complexes; however, prolonged reaction times, and in some cases (see Experimental section) heating (80 °C), led to the formation of the expected 1 : 1 adducts. Tetrafluoroethylene with $[Co(CO)_2(PMe_2Ph)(\eta\text{-}C_3H_5)]$, $[Co(CO)_2\{P(OMe)_3\}(\eta\text{-}C_3H_5)]$, or $[Co(CO)_3(\eta^3\text{-}1\text{-}syn\text{-}PhC_3H_4)]$ afforded respectively the crystalline complexes (1), (2), and (3). Hexafluoropropene with $[Co(CO)_2\{P(OMe)_3\}(\eta^3\text{-}2\text{-}MeC_3H_4)]$, and octafluorobut-2-ene [*trans-cis* (3.4 : 1) mixture] with $[Co(CO)_3(\eta\text{-}C_3H_5)]$, $[Co(CO)_2\{P(OMe)_3\}(\eta\text{-}C_3H_5)]$, or $[Co(CO)_2(PMe_2Ph)(\eta\text{-}C_3H_5)]$ gave regioselectively the 1 : 1 adducts (5), (6), (7), and (8). Elemental analysis and i.r., ^1H, ^{19}F, ^{13}C n.m.r., and mass spectroscopy confirmed the identity of the complexes as 1 : 1 insertion products. In order to provide a firm



(1) R = H, L = PMe_2Ph
(2) R = H, L = $P(OMe)_3$
(3) R = Ph, L = CO



(4)



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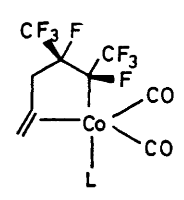

(6) L = CO
(7) L = $P(OMe)_3$
(8) L = PMe_2Ph

basis for a discussion of the molecular geometry of these complexes, a single-crystal *X*-ray diffraction study was carried out with compound (7).

The *X*-ray analysis (Tables 1—3, Figure 1) shows that one of the two central carbon atoms of the octafluorobut-2-ene molecule has become σ-bonded to the cobalt atom [Co–C 2.029(4) Å] while the other has become σ-bonded to the terminal carbon atom of the original η^3-allyl group. The pentenyl chain so produced retains only the two end carbon atoms bonded to cobalt in a π-ethenic manner [Co–C(5) 2.116(7), Co–C(4) 2.110(9) Å].

The configuration of the co-ordination sites around the cobalt atom is almost ideally trigonal bipyramidal with the Co–C σ bond and the Co–P bond occupying the axial positions. Bond distances and angles in the rest of the molecule call for no special comments although, as often occurs, the fluorine atoms of the CF_3 groups show high thermal activity and the C–F bond lengths are correspondingly short when uncorrected for vibration effects (Table 2).

The stereochemistry of the carbon chain in (7) invites immediate comparison with that of the iron compound formed[5] by the photochemical reaction of hexafluoropropene with tricarbonyl(isoprene)iron, the crystal structure of which has been reported. The conformation of the substituent groups is most easily seen by comparison of the torsion angles; comparable values are given side by side in Table 3, having been calculated where necessary from the data of ref. 5, but with signs reversed in order to conform with current convention.[6,*]

TABLE 1

Atomic positional (fractional co-ordinates) parameters, with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Co	0.214 39(8)	0.206 51(6)	0.449 35(7)
C(1)	0.494 1(6)	0.303 5(5)	0.626 5(5)
C(11)	0.622 0(6)	0.425 3(5)	0.652 8(6)
F(11)	0.625 3(5)	0.561 0(3)	0.732 4(4)
F(12)	0.799 5(4)	0.456 2(4)	0.742 2(4)
F(13)	0.566 9(4)	0.374 8(4)	0.505 4(4)
F(1)	0.545 5(4)	0.186 5(3)	0.578 6(4)
C(2)	0.535 3(6)	0.360 1(5)	0.790 0(5)
C(21)	0.737 1(7)	0.433 7(7)	0.946 8(6)
F(21)	0.738 9(5)	0.456 3(5)	1.066 1(4)
F(22)	0.850 7(5)	0.574 1(4)	1.017 4(4)
F(23)	0.808 6(5)	0.341 4(5)	0.911 2(5)
F(2)	0.494 4(4)	0.479 4(3)	0.847 7(3)
C(3)	0.402 6(7)	0.221 1(6)	0.739 3(6)
H(31)	0.462(8)	0.158(7)	0.742(7)
H(32)	0.405(9)	0.273(7)	0.840(8)
C(4)	0.208 9(7)	0.131 2(5)	0.569 1(6)
H(4)	0.114(11)	0.151(9)	0.586(10)
C(5)	0.162 6(7)	0.006 7(5)	0.419 5(6)
H(51)	0.247(10)	−0.028(8)	0.417(8)
H(52)	0.034(9)	−0.075(7)	0.313(8)
Phosphite ligand			
P	−0.086 2(2)	0.109 0(1)	0.274 0(1)
O(6)	−0.197 8(5)	0.085 7(4)	0.329 2(4)
C(6)	−0.172 6(11)	0.220 1(7)	0.464 6(8)
H(61)	−0.042(13)	0.299(10)	0.584(11)
H(62)	−0.216(10)	0.275(8)	0.437(9)
H(63)	−0.239(7)	0.192(6)	0.472(6)
O(7)	−0.192 1(5)	−0.063 5(4)	0.100 7(4)
C(7)	−0.394 0(8)	−0.149 1(6)	−0.031 9(7)
H(71)	−0.455(18)	−0.133(15)	0.015(17)
H(72)	−0.430(14)	−0.097(11)	−0.067(12)
H(73)	−0.424(16)	−0.253(14)	−0.072(15)
O(8)	−0.159 7(5)	0.205 9(4)	0.228 6(4)
C(8)	−0.088 2(9)	0.272 1(7)	0.184 0(7)
H(81)	−0.009(13)	0.253(9)	0.179(11)
H(82)	−0.176(18)	0.178(15)	0.048(16)
H(83)	−0.110(13)	0.355(11)	0.203(11)
Carbonyl groups			
C(01)	0.234 8(6)	0.393 6(5)	0.553 8(5)
O(01)	0.237 0(5)	0.510 9(4)	0.612 1(5)
C(02)	0.220 8(8)	0.122 9(6)	0.282 7(6)
O(02)	0.221 6(7)	0.064 9(6)	0.175 0(5)

TABLE 2

Bond lengths (Å) and angles (°)

(*a*) Distances			
Co–C(1)	2.029(4)	C(1)–F(1)	1.423(7)
Co–C(4)	2.110(9)	C(11)–F(11)	1.332(7)
Co–C(5)	2.116(7)	C(11)–F(12)	1.345(6)
C(1)–C(11)	1.537(10)	C(11)–F(13)	1.343(9)
C(1)–C(2)	1.560(10)	C(2)–F(2)	1.390(7)
C(2)–C(21)	1.542(7)	C(21)–F(21)	1.350(11)
C(2)–C(3)	1.524(10)	C(21)–F(22)	1.333(9)
C(3)–C(4)	1.526(6)	C(21)–F(23)	1.330(9)
C(4)–C(5)	1.388(8)	C(4)–H(4)	1.05(12)
C(3)–H(31)	0.98(8)	C(5)–H(51)	0.94(10)
C(3)–H(32)	1.05(10)	C(5)–H(52)	0.98(5)
Phosphite ligand			
Co–P	2.175(1)	O(6)–C(6)	1.432(9)
P–O(6)	1.594(6)	O(7)–C(7)	1.452(6)
P–O(7)	1.579(3)	O(8)–C(8)	1.445(13)
P–O(8)	1.597(5)	C(7)–H(71)	0.97(23)
C(6)–H(61)	1.03(7)	C(7)–H(72)	0.93(16)
C(6)–H(62)	0.92(11)	C(7)–C(73)	0.97(17)
C(6)–H(63)	0.76(8)	C(8)–H(82)	1.09(13)
C(8)–H(81)	0.83(13)	C(8)–H(83)	0.94(13)
Carbonyl groups			
Co–C(01)	1.769(5)	Co–C(02)	1.796(9)
C(01)–O(01)	1.149(7)	C(02)–O(02)	1.136(11)
(*b*) Angles			
C(1)–Co–C(01)	91.1(2)	C(1)–C(11)–F(11)	112.3(6)
C(1)–Co–C(02)	92.4(3)	C(1)–C(11)–F(12)	112.4(6)
C(1)–Co–P	175.8(2)	C(1)–C(11)–F(13)	111.7(3)
P–Co–C(01)	87.0(1)	F(11)–C(11)–F(12)	107.5(3)
P–Co–C(02)	91.8(2)	F(12)–C(11)–F(13)	105.4(6)
Co–C(1)–C(2)	106.7(4)	F(13)–C(11)–F(11)	107.1(6)
Co–C(1)–C(11)	116.8(4)	C(2)–C(21)–F(21)	109.7(6)
Co–C(1)–F(1)	110.2(2)	C(2)–C(21)–F(22)	112.3(7)
C(1)–C(2)–C(3)	106.8(4)	C(2)–C(21)–F(23)	112.1(4)
C(1)–C(2)–C(21)	119.1(6)	F(21)–C(21)–F(22)	106.4(4)
C(1)–C(2)–F(2)	108.3(5)	F(22)–C(21)–F(23)	109.0(6)
C(2)–C(3)–C(4)	110.8(7)	F(23)–C(21)–F(21)	107.1(7)
C(3)–C(4)–C(5)	120.9(6)	C(3)–C(4)–H(4)	110(4)
C(2)–C(3)–H(31)	107(5)	C(5)–C(4)–H(4)	126(3)
C(2)–C(3)–H(32)	103(4)	C(4)–C(5)–H(51)	123(4)
C(4)–C(3)–H(31)	114(2)	C(4)–C(5)–H(52)	124(6)
C(4)–C(3)–H(32)	114(4)	H(51)–C(5)–H(52)	111(6)
H(31)–C(3)–H(32)	107(8)	Co–C(5)–H(5, mean)	110(6)
Phosphite ligand			
Co–P–O(6)	117.3(2)	P–O(6)–C(6)	119.7(5)
Co–P–O(7)	113.0(2)	P–O(7)–C(7)	121.1(4)
Co–P–O(8)	117.8(1)	P–O(8)–C(8)	122.9(5)
O(6)–P–O(7)	100.9(2)	O(6)–C(6)–H(6, mean)	113(5)
O(7)–P–O(8)	106.7(2)	O(7)–C(7)–H(7, mean)	107(6)
O(8)–P–O(6)	99.0(3)	O(8)–C(8)–H(8, mean)	110(10)
Carbonyl groups			
C(01)–Co–C(02)	119.2(4)	C(01)–Co–C(5)	146.2(3)
Co–C(01)–O(01)	175.6(4)	C(02)–Co–C(4)	131.7(3)
Co–C(02)–O(02)	177.6(7)		

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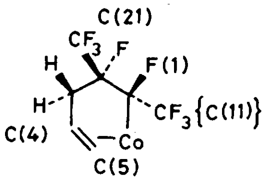
[*] In calculating the torsion angles from the atomic co-ordinates listed in ref. 5 it became apparent that, in the drawing of the structure, atoms F(4) and F(6) should have their labels reversed.

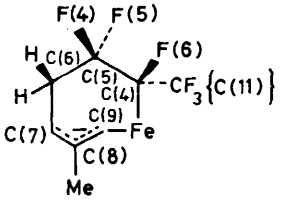
TABLE 3

Some torsion angles for [$Co\{CF(CF_3)CF(CF_3)CH_2CH{=}CH_2\}(CO)_2\{P(OMe)_3\}$] and for [$Fe\{CF(CF_3)CF_2CH_2CH{\cdots}CMe{\cdots}CH_2\}(CO)_3$]

Co–C(1)–C(2)–C(3)	+51.9	Fe–C(4)–C(5)–C(6)	+48.9
C(11)–C(1)–C(2)–F(2)	+66.1	C(11)–C(4)–C(5)–F(4)	+51.8
C(11)–C(1)–C(2)–C(3)	−176.9	C(11)–C(4)–C(5)–C(6)	+174.4
F(1)–C(1)–C(2)–C(21)	+60.5	F(6)–C(4)–C(5)–F(5)	+47.0
F(1)–C(1)–C(2)–F(2)	+177.9	F(6)–C(4)–C(5)–F(4)	+162.5
C(11)–C(1)–C(2)–C(21)	−51.3	C(11)–C(4)–C(5)–F(5)	−63.4
C(1)–C(2)–C(3)–C(4)	−40.2	C(4)–C(5)–C(6)–C(7)	−51.7
F(2)–C(2)–C(3)–C(4)	+76.5	F(4)–C(5)–C(6)–C(7)	+69.5
C(21)–C(2)–C(3)–C(4)	+171.0	F(5)–C(5)–C(6)–C(7)	−174.7
C(2)–C(3)–C(4)–C(5)	+89.1	C(5)–C(6)–C(7)–C(8)	+107.9

It is at once clear that an overall similarity of conformation exists. The torsion angles have comparable magnitudes in every case, and the same sign except where the conformation is antiperiplanar (in which case a change of sign implies only a small change in angle). In particular, the CF_3 group on the carbon atom which is σ-bonded to the metal is for both structures in an *exo* relationship to the metal ring π attachment.





As demonstrated by the structural determination, only the *trans* isomer of octafluorobut-2-ene had been incorporated in the insertion reaction. Examination of the ^{19}F spectrum of the octafluorobut-2-ene used in the reaction showed it to be a *trans–cis* mixture in the ratio of 3.4 : 1. When the reaction with [$Co(CO)_3(\eta\text{-}C_3H_5)$] was carried out using an excess of fluoro-olefin, then examination of the ^{19}F spectrum of the unchanged octafluorobut-2-ene showed it to be enriched in the *cis* isomer, suggesting that the *trans* isomer reacts preferentially, possibly for steric reasons.

Comparison of the n.m.r. spectrum for (7) with that observed for the other 1 : 1 adducts obtained with C_2F_4, $CF_2{=}CFCF_3$, and *trans*-octafluorobut-2-ene established that these complexes are essentially isostructural, the fluoroalkyl group and the phosphorus ligand when present occupying axial sites in the trigonal-bipyramidal structure. The reaction with hexafluoropropene is regiospecific producing only the *exo* isomer (relative position of the CF_3 group to the co-ordinated olefin) with the trifluoromethyl group attached to the carbon α to the cobalt atom. In the ^{19}F spectrum of (5) the CF_3 resonance at 67.5 p.p.m. showed coupling to F^2, F^3, and F^4 with additional coupling to the ^{31}P nucleus of the phosphite ligand of 5.0 Hz. The corresponding spectrum of (7) exhibited resonances due to CF_3 groups at 66.4 and 73.7 p.p.m., only the low-field resonance showing ^{31}P coupling (5.0 Hz). The ^{13}C spectrum of (5) showed the methylene carbon, to which H^4 and H^5 are attached as a triplet [$J(CF^3) = J(CF^4)$ 23 Hz] indicating again that the CF_2 group and the CH_2 group are bonded to each other in compound (5).

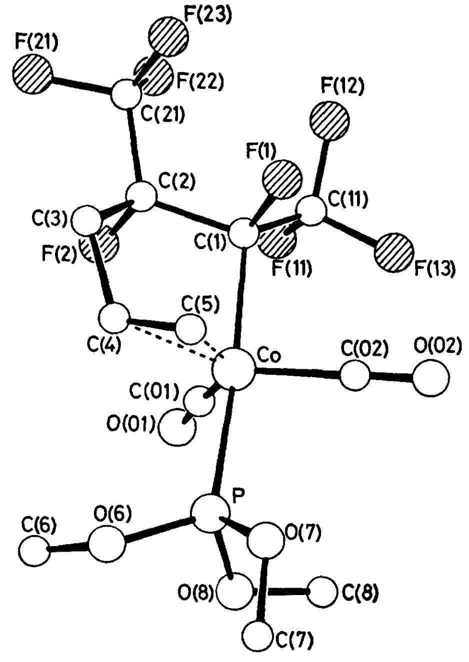


FIGURE 1 Molecular structure of [$Co\{CF(CF_3)CF(CF_3)CH_2CH{=}CH_2\}(CO)_2\{P(OMe)_3\}$]

An additional point of interest is the regioselectivity of the reaction of tetrafluoroethylene with [$Co(CO)_3(\eta^3\text{-}1\text{-}syn\text{-}PhC_3H_4)$] leading to the attachment of the fluoro-olefin at the unsubstituted end of the three-carbon allylic system, and the formation of complex (3).

Further confirmation of the structure of (2) was obtained by its reaction (refluxing hexane) with excess of trimethyl phosphite to give (4). The occurrence in the i.r. spectrum of two terminal carbonyl bands, and the appearance of the $POCH_3$ ^1H resonance as an apparent triplet, is consistent with either of the illustrated trigonal-bipyramidal structures, which could arise *via* reaction of a square-planar cobalt(I) species formed by dissociation of the co-ordinated olefin followed by a polytopal (BPR) rearrangement. The ^{19}F spectrum of (4) showed only

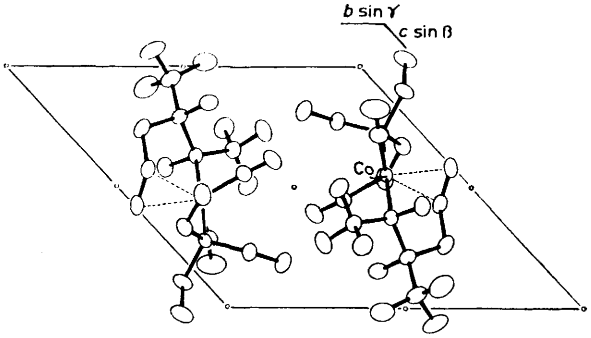
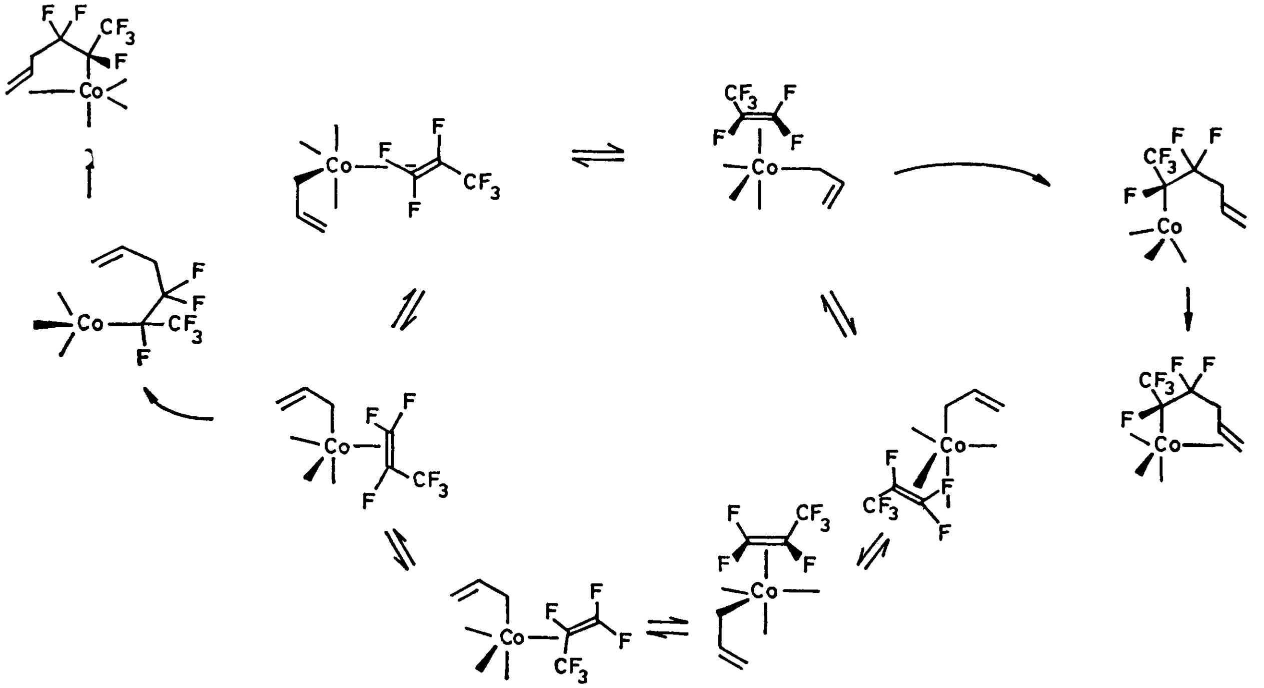


FIGURE 2 Contents of the triclinic unit cell seen in projection down *a* looking towards the origin

two ^{19}F environments due to free rotation about the C–C bond of the fluoroalkyl group.

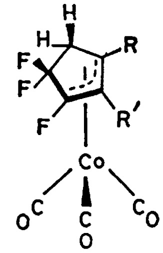
A reaction path for the insertion of fluoro-olefins into η^3-allylic cobalt bonds must account for the preferential attack at the unsubstituted end of the η^3-allyl system, the regiospecificity of the hexafluoropropene reaction including the preferred *exo* configuration for the CF_3 group, and the slower rates of reaction of the phosphine-substituted complexes. If the rate-determining step in these reactions involved electrophilic attack by the fluoro-olefin on a terminal carbon atom of the allylic system then it would be expected that replacement of carbon monoxide by a poorer π acceptor such as a phosphine or phosphite, leading to an increased electron density on the three carbons of the η^3-allyl system, would facilitate reaction. That a decrease in rate is actually observed argues against such a reaction path. If, however, a rate-determining step in the reaction with C_2F_4 involved an initial η^3- to σ-allyl conversion followed by capture of the resulting 16-electron species with the π-accepting fluoro-olefin, then replacement of CO by PR_3 would result in a decrease in rate of reaction as observed. Furthermore, in an η^3- to σ-allyl interconversion with an unsymmetrical allyl system, the formation of the isomer with the least substituted end σ-bonded to the cobalt would be favoured, thus explaining the formation of compound (3).



SCHEME 1 Carbon monoxide ligands are omitted for clarity

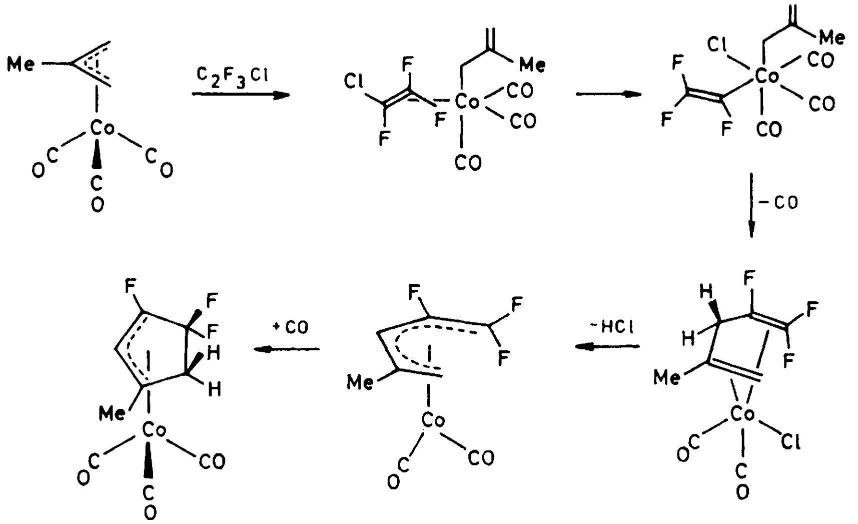
The capture of the 16-electron species with a fluoro-olefin results in the formation of a five-co-ordinate species, a member of the five-co-ordinate manifold of readily interconverting square-pyramidal and trigonal-bipyramidal geometries. Following Thorn and Hoffmann's analysis [7] of the analogous insertion reaction of ethylene with the Pt–H bond of the d^8 species *trans*-[PtH(Cl)(PR$_3$)$_2$], the only trigonal-bipyramidal geometries for the cobalt system from which insertion can be expected (Scheme 1) to occur are those with an axial σ-allyl group and an equatorial upright η^2-co-ordinated fluoro-olefin, or an axial fluoro-olefin and equatorial σ-allyl ligand. These geometries from which insertion can readily occur are of relatively high energy since backbonding is better in a planar orientation of an equatorial olefin, there being steric repulsion if an olefin occupies an axial site. In addition a σ-donating σ-allyl group would be expected to show a preference for an axial site. Thus energy must be expended to achieve the required geometry for ready insertion. As illustrated the regiospecificity observed with the hexafluoropropene reaction could originate from a steric effect.

Reaction (room temperature, 2 d) of chlorotrifluoroethylene with (η-allyl)tricarbonylcobalt in tetrahydrofuran as solvent afforded pink crystals of cobalt(II) chloride, and on column chromatography yellow crystals



(9) R = H, R′ = H
(10) R = Me, R′ = H
(11) R = H, R′ = Me

of a cobalt compound (9). Elemental analysis and mass spectroscopy indicated a molecular formula of $[Co(C_5H_4F_3)(CO)_3]$, there being no evidence for the presence of chlorine in the molecule. The i.r. spectrum showed terminal carbonyl bands at 2 088, 2 035, and 2 027 cm^{-1} typical of a $Co(CO)_3$ group, in agreement with the presence in the mass spectrum of peaks corresponding to the consecutive loss of three carbon monoxides. Examination of the ^1H and ^{19}F n.m.r. spectra suggested the illustrated cyclic structure. In particular the ^1H spectrum showed four proton environments; a complex AB spin system assigned to H^1 and H^2 centred at τ 7.6 and 7.9 [$J(H^1H^2)$ 16 Hz] with additional ^{19}F coupling [$J(H^1F^2)$ 4, $J(H^1F^3)$ 8, $J(H^2F^2)$ 8 Hz]. The chemical shifts of the resonances assigned to protons H^3 and H^4 at τ 6.4 and 4.6 are typical of the outer and central hydrogens of a cyclic η^3-allylic system, showing the expected ^1H–^1H couplings with additional splitting due to ^{19}F coupling. The ^{13}C spectrum detailed in the Experimental section fully supported the proposed structure. Additional confirmation of this structural assignment was provided by the spectroscopic properties of the methyl-substituted analogues (10) and (11), which were obtained on reaction under similar conditions of chlorotrifluoroethylene with tricarbonyl(η^3-2-methylallyl)cobalt and tricarbonyl(η^3-1-methylallyl)cobalt respectively. Aside from confirming the n.m.r. assignments, the formation of the compounds (10) and (11) is of interest in that it indicates that the three carbon atoms of the original η^3-allyl fragment remain intact in the cyclisation reaction. A reaction of this type is without precedent.



SCHEME 2

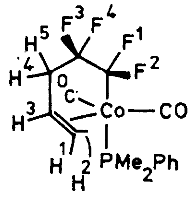
If it is assumed that as in the 'normal' insertion reactions the initial step involves capture by a fluoro-olefin molecule of a 16-electron σ-allyl species formed in a dissociative step, then it is possible to understand the formation of (9)—(11). There is substantial evidence to show[8-11] that chlorotrifluoroethylene η^2-bonded to platinum(0) readily undergoes a so-called 'vinyl-rearrangement' reaction, and it is likely that a similar reaction could occur with d^8 cobalt(I) species. Such a reaction sequence would lead to the generation of the illustrated (Scheme 2) cobalt(III) species containing adjacent σ-trifluorovinyl and σ-allyl groups. We have previously[12,13] shown that iron(II) complexes containing adjacent σ-bonded vinyl and σ-allyl groups readily undergo reductive [$Fe^{II} \longrightarrow Fe^0$] carbon–carbon bond formation, and it is reasonable to expect a similar reaction to occur in cobalt chemistry [$Co^{III} \longrightarrow Co^I$], leading to the formation of a substituted 1,4-diene complex. Elimination of HCl, which would be captured by the cobalt(I) complex to form cobalt(II) chloride, results in the formation of a dicarbonyl(η^5-pentadienyl)-cobalt complex. Ring closure could then occur to give the observed cyclopentenyl product. Pentadienyl cations[14] and anions[15] have been shown to undergo concerted ring-closure reactions *via* cyclic pentenyl systems. A disrotatory ring closure has been previously postulated[16] in the reaction of $[Co(C_8H_{12})(C_8H_{13})]$ with excess of 1,5-C_8H_{12} to form $[Co(1,5\text{-}C_8H_{12})(\eta^5\text{-}C_8H_9)]$ containing a bicyclo[3.3.0]octyl system. It would therefore appear that such reactions may be common within the co-ordination sphere. However, it is not possible to determine the stereochemistry of the reaction described here on the basis of the evidence so far available.

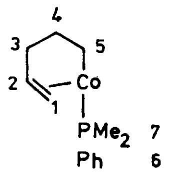
EXPERIMENTAL

Hydrogen-1 n.m.r. spectra were recorded on a Varian Associates HA 100 spectrometer at 100 MHz with $SiMe_4$ (τ 10.00) as internal reference; ^{19}F and ^{13}C spectra were obtained on a JEOL PFT-100 spectrometer at 94.1 and 25.1 MHz respectively, chemical shifts being measured relative to $CFCl_3$ (external) and $SiMe_4$. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer, mass spectra on an A.E.I. MS902 spectrometer operating at 70 eV (1 eV $\approx 1.60 \times 10^{-19}$ J). Reactions, except those in sealed tubes, were carried out in a dry oxygen-free nitrogen atmosphere.

The complexes [Co(CO)$_2$L(η^3-allyl)] used as starting materials were prepared straightforwardly by reaction (room temperature) of the tricarbonyl complex with an excess of the ligand L in tetrahydrofuran. Infrared and ^{1}H n.m.r. data for these complexes are as follows: [Co(CO)$_2$-{P(OMe)$_3$}(η-C$_3$H$_5$)], ν(CO) at 2 005s, 1 951s cm^{-1}, ^{1}H (C$_6$D$_6$), τ 5.4 [septet, H^3, J(H^{2}H^3) 6.0, J(H^{1}H^3) 10.0], 6.7 [d, POMe, J(PH) 12.0], 7.35 [dd, H^2(*syn*), J(H^{1}H^2) 2.0, J(H^{2}H^3) 6.0], and 8.15 [dd, H^1(*anti*), J(H^{1}H^2) 2.0, J(H^{1}H^3) 10.0 Hz]; [Co(CO)$_2$(PMe$_2$Ph)(η-C$_3$H$_5$)], ν(CO) at 1 990s and 1 937s cm^{-1}, ^{1}H (C$_6$D$_6$), τ 2.6—3.0 (brs, Ph), 5.6 [m, H^3, J(H^{1}H^3) 10.0, J(H^{2}H^3) 6.0], 7.7 [d, H^2, J(H^{2}H^3) 6.0], 8.1 [d, H^1, J(H^{1}H^3) 10.0], and 8.7 [d, PMe, J(PH) 8.0 Hz]; [Co(CO)$_2${P(OMe)$_3$}-(η^3-2-MeC$_3$H$_4$)], ν(CO) at 1 999s, and 1 945s cm^{-1}, ^{1}H (C$_6$D$_6$), τ 6.5 [d, POMe, J(PH) 12.0], 7.2 [d, H^2, J(H^{1}H^2) 3.0], 7.9 [d, H^1, J(H^{1}H^2) 3.0 Hz], and 8.2 (s, Me); [Co(CO)$_2$-{P(OMe)$_3$}(η^3-*syn*-1-PhC$_3$H$_4$)], ν(CO) at 2 003s and 1 953s cm^{-1}, ^{1}H (C$_6$D$_6$), τ 2.8 (m, Ph), 4.8 (m, H^3), 6.6 [d, POMe, J(PH) 11.0 Hz], 7.2 (m, H^1), and 8.1 (m, H^2 and H^4).

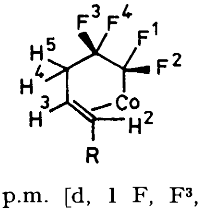
Reactions of Tetrafluoroethylene.—(*a*) *With* (η-*allyl*)*dicarbonyl*(*dimethylphenylphosphine*)*cobalt*. Tetrafluoroethylene (10 mmol) was condensed (−196 °C) into a Carius tube containing a solution of [Co(CO)$_2$(PMe$_2$Ph)(η-C$_3$H$_5$)] (1.0 g, 3.4 mmol) in hexane (20 cm^3). After 5 d at room temperature, volatile material was removed *in vacuo*, and the residue dissolved in diethyl ether (40 cm^3), the solution filtered, and the solvent removed. The resulting orange oil was recrystallised (−20 °C) from hexane–methylene chloride (4 : 1) giving yellow *crystals* of (1) (0.63 g, 47%), m.p. 79 °C (Found: C, 45.7; H, 4.3. C$_{15}$H$_{16}$CoF$_4$O$_2$ requires C, 45.7; H, 4.1%), ν(CO) (hexane) at 2 036s and 1 987s cm^{-1}. N.m.r.: ^{1}H (CDCl$_3$), τ 2.6 (m, 5 H, Ph), 6.4—7.1 (m, 3 H, H^1, H^2, and H^3), 7.4—7.9 (m, 2 H, H^4 and H^5), 8.4 [m, 6 H, PMe$_2$, J(PH) 8.0 Hz]; ^{19}F [(CD$_3$)$_2$CO], 77.9 [d, 2 F, F^1 and F^2, J(FP) 31], 107.7 [dm, 1 F, F^4, J(F^{3}F^4) 226], and 110.9 p.p.m. [d, 1 F, F^3, J(F^{3}F^4) 226 Hz]; ^{13}C (CDCl$_3$), −145.0 (s, C^4, ^{19}F-decoupled), −142.5 (s, C^5, ^{19}F-decoupled), −129.8 (m, Ph), −60.5 [d, C^2, J(CP) 9], −57.4 (s, C^1), −35.3 [t, C^3, J(CF) 24], −15.5 [dd, C^7, J(CP) 30 Hz, inequivalent methyl groups].

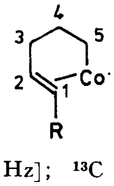




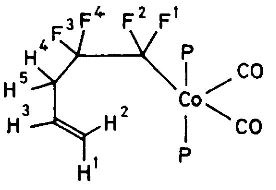
(*b*) *With* (η-*allyl*)*dicarbonyl*(*trimethyl phosphite*)*cobalt*. A similar reaction (7 d) of tetrafluoroethylene (10 mmol) with [Co(CO)$_2${P(OMe)$_3$}(η-C$_3$H$_5$)] (1.4 g, 5 mmol) in hexane (20 cm^2) gave an orange oil, which was chromatographed on an alumina-packed column. Elution with hexane gave unchanged [Co(CO)$_2${P(OMe)$_3$}(η-C$_3$H$_5$)]. Elution with hexane–methylene chloride (1 : 1) then gave a yellow band, which on removal of solvent, followed by crystallisation (−30 °C) from hexane–methylene chloride (4 : 1), gave yellow *crystals* of (2) (0.47 g, 25%), m.p. 63 °C (Found: C, 31.9; H, 3.8. C$_{10}$H$_{14}$CoF$_4$O$_5$P requires C, 31.6; H, 3.7%), ν(CO) (hexane) at 2 046s and 1 996s cm^{-1}. N.m.r.: ^{1}H (CDCl$_3$), τ 6.0 (m, 1 H, H^3), 6.4 [d, 9 H, POMe, J(PH) 12.0 Hz], 6.6—7.0 (m, 2 H, H^1 and H^2), and 7.8—8.2 (m, 2 H, H^4 and H^5); ^{19}F (CDCl$_3$), 78.4 [dt, 2 F, F^1 and F^2, J(FP) 46.8, J(FF^3) = J(FF^4) 9.0], 107.3 [dm, 1 F, F^4, J(F^{3}F^4) 2.9], 110.6 p.p.m. [dt, 1 F, F^3, J(F^{3}F^4) 2.9, J(F^{1}F^3) = J(F^{2}F^3) 9.0 Hz]; ^{13}C (CDCl$_3$), −127.6 (s, C^5), −61.9 [d, C^2, J(CP) 9.0], −58.6 [d, C^1, J(CP) 5.0], −52.5 [d, POC, J(CP) 6.0], and −35.2 p.p.m. [t, C^3, J(CF^3) 24 Hz]. The mass spectrum showed peaks at *m/e* 380 (*P*), 352 (*P* − CO), and 324 (*P* − 2CO).

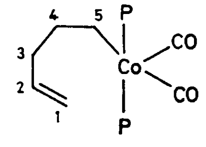
(*c*) *With tricarbonyl*(η^3-1-syn-*phenylallyl*)*cobalt*. A solution of tetrafluoroethylene (10 mmol) and [Co(CO)$_3$(η^3-1-*syn*-PhC$_3$H$_4$)] (1.2 g, 4.6 mmol) in tetrahydrofuran (20 cm^3) was allowed to stand at room temperature for 1 d. The solvent was removed *in vacuo*, and the residue crystallised (−78 °C) from hexane to give yellow *crystals* of (3) (1.1 g, 66%), m.p. 70 °C, ν(CO) (hexane) at 2 099s, 2 054s, and 2 041s cm^{-1}. N.m.r.: ^{1}H (CDCl$_3$), τ 2.7 (m, 5 H, Ph), 4.5—5.0 (m, 2 H, H^2 and H^3), and 7.8—8.0 (m, 2 H, H^4 and H^5); ^{19}F (CDCl$_3$), 71.9 (br s, 2 F, F^1 and F^2), 107.1 [d, 1 F, F^4, J(F^{3}F^4) 225], 111.1 p.p.m. [d, 1 F, F^3, J(F^{3}F^4) 225 Hz]; ^{13}C (CDCl$_3$), −139.8 (s, C^5, ^{19}F-decoupled), −129.2 to −126.3 (m, Ph), −85.1 (s, C^2), −58.7 (s, C^1), −34.0 p.p.m. [t, C^3, J(CF^3) = J(CF^4) 23 Hz]. The mass spectrum showed peaks at *m/e* 360 (*P*), 332 (*P* − CO), 304 (*P* − 2CO), and 276 (*P* − 3CO).



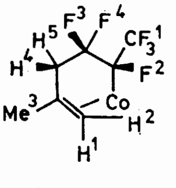


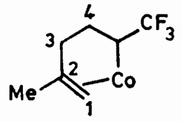
Reaction of Complex (2) *with Trimethyl Phosphite*.—A solution of (2) (0.6 g, 1.6 mmol) and trimethyl phosphite (0.5 g, 4 mmol) in hexane (30 cm^3) was heated (1 h) under reflux, when examination of the i.r. spectrum showed that reaction was complete. The solvent was removed *in vacuo* after filtration, and the residue recrystallised (−78 °C) from hexane to give yellow *crystals* of (4) (0.51 g, 65%), m.p. <20 °C (Found: C, 31.1; H, 4.8. C$_{13}$H$_{23}$CoF$_4$O$_8$P$_2$ requires C, 31.0; H, 4.6%), ν(CO) (hexane) at 2 021m and 1 964s cm^{-1}. N.m.r.: ^{1}H (CDCl$_3$), τ 4.1 [m, 1 H, H^3, J(H^{2}H^3) 15, J(H^{1}H^3) 12, J(H^{3}H^4) = J(H^{3}H^5) 7], 4.75 [d, 1 H, H^1, J(H^{1}H^3) 12], 4.8 [d, 1 H, H^2, J(H^{2}H^3) 15], 6.4 [apparent t, 18 H, POMe, J(POCH) 6], 7.2 [td, 2 H, H^4 and H^5, J(H^{4}H^3) or J(H^{4}F^4) = J(H^{5}F^3) or J(H^{5}F^4) 18, J(H^{3}H^4) = J(H^{3}H^5) 7 Hz]; ^{19}F (CDCl$_3$), 59.7 [t, 2 F, F^1 and F^2, J(F^{1}P) = J(F^{2}P) 52], 100.9 p.p.m. [t, 3 F, F^3 and F^4, J(H^{4}F^3) 18 Hz]; ^{13}C (CDCl$_3$), −120.8 (s, C^5), −129.8 (s, C^2), −119.6 (s, C^1), −51.8 (s, POMe), and −35.0 p.p.m. [t, C^3, J(CF) 26 Hz]. The mass spectrum showed peaks at *m/e* 504 (*P*), 476 (*P* − CO), and 448 (*P* − 2CO).



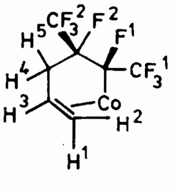


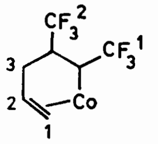
Reaction of Hexafluoropropene with Dicarbonyl(η^3-2-*methylallyl*)(*trimethyl phosphite*)*cobalt*.—An excess of hexafluoropropene (13 mmol) was condensed (−196 °C) into a tube containing [Co(CO)$_2${P(OMe)$_3$}(η^3-2-MeC$_3$H$_4$)] (1.9 g, 6.5 mmol) dissolved in hexane (20 cm^3). After 5 d at room temperature the volatile material was removed *in* *vacuo*, and the residue chromatographed on alumina. Elution with hexane gave starting material. Further elution with hexane–methylene chloride (1 : 1) gave an orange band. Recrystallisation (−30 °C) from hexane–methylene chloride (4 : 1) gave large orange *crystals* of (5) (1.19 g, 42%), m.p. 70 °C (Found: C, 32.4; H, 3.7. $C_{12}H_{16}CoF_6O_5P$ requires C, 32.4; H, 3.6%), ν(CO) (hexane) at 2 039s and 1 988s cm^{-1}. N.m.r.: ^1H ($CDCl_3$), τ 6.05 (6s, 1 H, H^1), 6.25 (br s, 1 H, H^2), 6.3 [d, 9 H, POMe, J(HP) 11 Hz], 7.0—7.6 (complex m, H^4 and H^5), and 8.05 (s, 3 H, Me^3); ^{19}F ($CDCl_3$), 67.5 [dq, 3 F, $CF_3{}^1$, $J(F^2CF_3{}^1)$ = $J(F^3CF_3{}^1)$ = $J(F^4CF_3{}^1)$ 11, $J(CF_3{}^1P)$ 5], 96.3 [d, 1 F, F^4, $J(F^3F^4)$ 230], 107.6 [dm, 1 F, F^3, $J(F^3F^4)$ 230 Hz], and 169.2 p.p.m. (br s, 1 F, F^2); ^{13}C ($CDCl_3$) −127.8 [s, CF_3 (^{19}F-decoupled)], −109.9 (m, C^4), −93.9 [d, C^2, J(CP) 7], −69.0 (s, C^1), −53.0 [d, POMe, J(CP) 8], −44.4 [t, C^3, J(CF) 23 Hz], and −28.0 (s, Me). The mass spectrum showed peaks at *m/e* 444 (*P*), 416 (*P* − CO), and 388 (*P* − 2CO).





Reactions of Octafluorobut-2-ene.—(*a*) *With* (*η-allyl*)*tricarbonylcobalt*. In a similar way [$Co(CO)_3(\eta\text{-}C_5H_5)$] (0.64 g, 3.5 mmol) and octafluorobut-2-ene (12 mmol) in tetrahydrofuran (20 cm^3) were allowed to react (2 d) at room temperature. Removal of the solvent and recrystallisation (−78 °C) of the residue from hexane gave yellow *crystals* of (6) (1.0 g, 86%), m.p. 41 °C (Found: C, 31.1; H, 1.4. $C_{10}H_5CoF_8O_3$ requires C, 31.3; H, 1.3%), ν(CO) (hexane) at 2 103s, 2 052s, and 2 042s cm^{-1}. N.m.r.: ^1H ($CDCl_3$), τ 4.9 [m, 1 H, H^3, $J(H^1H^3)$, 8, $J(H^2H^3)$ 13, $J(H^3H^4)$ = $J(H^3H^5)$ 5], 6.0 [d, 1 H, H^2, $J(H^2H^3)$ 13], 6.4 [dd, 1 H, H^1, $J(H^1H^3)$ 8, $J(H^1F^1)$ 3], 7.2 [t, 1 H, H^4, $J(H^3H^4)$ 5, $J(H^4F^2)$ 5], 7.6 [t, 1 H, H^5, $J(H^3H^5)$ = $J(H^5F^2)$ 5 Hz]; ^{19}F ($CDCl_3$), 66.6 [h, 3 F, $CF_3{}^1$, $J(CF_3{}^1CF_3{}^2)$ 10, $J(CF_3{}^1F^1)$ = $J(CF_3{}^1F^2)$ 10], 74.2 [m, 3 F, $CF_3{}^2$, $J(CF_3{}^1CF_3{}^2)$ 10, $J(CF_3{}^2F^2)$ 18 Hz], 155.2 (br m, 1 F, F^1), and 157.0 p.p.m. (br m, 1 F, F^2); ^{13}C ($CDCl_3$), −124.6 [s, $CF_3{}^1$ (^{19}F-decoupled)], 121.1 [s, $CF_3{}^2$ (^{19}F-decoupled)], −72.0 (s, C^2), −65.9 (s, C^1), and −35.9 p.p.m. [d, C^3, $J(CF^2)$ 20 Hz]. The mass spectrum showed peaks at *m/e* 384 (*P*), 356 (*P* − CO), 328 (*P* − 2CO), and 300 (*P* − 3CO).

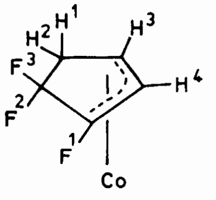


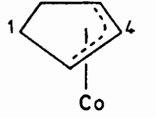


(*b*) *With* (*η-allyl*)*dicarbonyl*(*trimethyl phosphite*)*cobalt.* Octafluorobut-2-ene (13 mmol) and [$Co(CO)_2\{P(OMe)_3\}(\eta\text{-}C_3H_5)$] (1.1 g, 3.9 mmol) in hexane (20 cm^3) were allowed to react (80 °C, 16 h) in a sealed tube. Removal of solvent and chromatography gave a pale yellow band on elution with hexane–methylene chloride (1 : 1). Recrystallisation (−30 °C) from hexane–methylene chloride (4 : 1) gave pale yellow-green *crystals* of (7) (1.05 g, 56%), m.p. 61 °C (Found: C, 29.7; H, 3.0. $C_{12}H_{24}CoF_8O_5P$ requires C, 30.0; H, 2.9%), ν(CO) (hexane) at 2 048s and 1 997s cm^{-1}. N.m.r.: ^1H ($CDCl_3$), τ 5.6 (m, 1 H, H^3), 5.9—6.8 (m, 2 H, H^1 and H^2), 6.3 [d, 9 H, POMe, J(HP) 11 Hz], 7.2—7.8 (m, 2 H, H^4 and H^5); ^{19}F ($CDCl_3$), 66.4 [m, 3 F, $CF_3{}^1$, $J(CF_3{}^1CF_3{}^2)$ 10, $J(CF_3{}^1F^1)$ = $J(CF_3{}^1F^2)$ 10, $J(CF_3{}^1P)$ 5.0], 73.7 [m, 3 F, $CF_3{}^2$, $J(CF_3{}^1CF_3{}^2)$ 10, $J(CF_3{}^2F^2)$ 18 Hz], 156.1 (m, 1 F, F^1), and 166.0 p.p.m. (m, 1 F, F^2); ^{13}C ($CDCl_3$), −129.2 [s, $CF_3{}^1$ (^{19}F-decoupled)], −122.6 (m, $CF_3{}^2$), −68.6 (s, C^2), −63.2 [d, C^1, J(CP) 8], −53.2 [d, POMe, J(CP) 6], and −36.8 [d, C^3, J(CF) 20 Hz]. The mass spectrum showed peaks at *m/e* 480 (*P*), 452 (*P* − CO), and 424 (*P* − 2CO).

(*c*) *With* (*η-allyl*)*dicarbonyl*(*dimethylphenylphosphine*)-*cobalt*. A similar reaction (80 °C, 16 h) between [$Co(CO)_2(PMe_2Ph)(\eta\text{-}C_3H_5)$] (1.0 g, 3.5 mmol) and octafluorobut-2-ene (10 mmol) gave yellow *crystals* of (8) (0.65 g, 39%), m.p. 110 °C (Found: C, 41.5; H, 3.3. $C_{17}H_{16}CoF_8O_2P$ requires C, 41.3; H, 3.2%), ν(CO) (hexane) at 2 033s and 1 985s cm^{-1}. N.m.r.: ^1H ($CDCl_3$), τ 2.6 (br s, 5 H, C_6H_5), 6.2—6.7 (br m, 3 H, H^1, H^2, and H^3), 7.3—7.9 (br m, 2 H, H^4 and H^5), 8.4 [d, 6 H, PMe, J(HP) 9 Hz]; ^{19}F ($CDCl_3$), 66.4 [m, 3 F, $CF_3{}^1$, $J(CF_3{}^1CF_3{}^2)$ 10, $J(CF_3{}^1F^1)$ = $J(CF_3{}^1F^2)$ 10], 73.8 [m, 3 F, $CF_3{}^2$, $J(CF_3{}^1CF_3{}^2)$ 10, $J(CF_3{}^2F^2)$ 18 Hz], 156.0 (br s, 1 F, F^1), and 165.1 p.p.m. (br s, 1 F, F^2); ^{13}C ($CDCl_3$), −132.1 [s, $CF_3{}^1$ (^{19}F-decoupled)], −129.5 (m, C_6H_5), −121.7 [s, $CF_3{}^2$ (^{19}F-decoupled)], −67.4 (s, C^2), −61.1 [d, C^1, J(CP) 10], −36.9 [d, C^3, J(CF) 20], −16.4 p.p.m. [d, PMe, J(CP) 30 Hz]. The mass spectrum showed peaks at *m/e* 494 (*P*), 466 (*P* − CO), and 438 (*P* − 2CO).

Reactions of Chlorotrifluoroethylene.—(*a*) *With* (*η-allyl*)*tricarbonylcobalt*. An excess of chlorotrifluoroethylene (13 mmol) was condensed (−196 °C) into a tube containing [$Co(CO)_3(\eta\text{-}C_3H_5)$] (0.36 g, 2.1 mmol) in tetrahydrofuran (20 cm^3). After 2 d at room temperature the solution had changed colour from yellow to green and pink crystals of $CoCl_2$ were precipitated. The solvent was removed *in vacuo*, and the residue chromatographed. Elution with hexane gave first [$Co(CO)_3(\eta\text{-}C_3H_5)$] followed by a yellow band. Recrystallisation (−78 °C) from hexane gave yellow *crystals* of (9) (0.15 g, 28%), m.p. 31 °C (Found: C, 36.8; H, 2.0. $C_9H_4CoF_3O_3$ requires C, 36.4; H, 1.6%), ν(CO) (hexane) at 2 088s, 2 035s, and 2 027s cm^{-1}. N.m.r.: ^1H ($CDCl_3$), τ 4.6 [m, 1 H, H^4, $J(H^3H^4)$ 3, $J(H^4F^1)$ 5], 6.4 [m, 1 H, H^3, $J(H^3H^4)$ 3.0, $J(H^1H^3)$ = $J(H^2H^3)$ 2, $J(H^3F^3)$ = $J(H^3F^2)$ 4], 7.6 [m, 1 H, H^1, $J(H^1H^2)$ 16, $J(H^1H^3)$ 4, $J(H^1F^2)$ 4, $J(H^1F^3)$ 8], 7.9 [m, 1 H, H^2, $J(H^1H^2)$ 16, $J(H^2H^3)$ 4, $J(H^2F^2)$ 8 Hz]; ^{19}F ($CDCl_3$), 96.2 [dm, 1 F, F^2, $J(F^2F^3)$ 227], 100.4 (dm, 1 F, F^3, $J(F^2F^3)$ 227 Hz], 172.6 p.p.m. (br s, 1 F, F^1); ^{13}C ($CDCl_3$), −122.5 [s, C^4 (^{19}F-decoupled)], 65.8 [d, C^3, $J(C^3F^1)$ 8], −50.8 (br s, C^2), and −44.0 p.p.m. [t, C^1, $J(C^1F^2)$ = $J(C^1F^3)$ 24 Hz]. The mass spectrum showed peaks at *m/e* 264 (*P*), 236 (*P* − CO), 208 (*P* − 2CO), 188 (*P* − 2CO − HF), 180 (*P* − 3CO), and 160 (*P* − 3CO − HF).





(*b*) *With tricarbonyl*(*η*^{3}-*2-methylallyl*)*cobalt.* Similarly, reaction of [$Co(CO)_3(\eta^3\text{-}2\text{-}MeC_3H_4)$] (1.2 g, 6 mmol) and chlorotrifluoroethylene (13 mmol) in tetrahydrofuran (20 cm^3) gave yellow *crystals* of (10) (0.65 g, 33%), m.p. 36 °C (Found: C, 38.6; H, 2.4. $C_{10}C_6CoF_3O_3$ requires C, 38.8; H, 2.2%), ν(CO) (hexane) at 2 085s, 2 030s, and 2 021s cm^{-1}. N.m.r.: ^{1}H ($CDCl_3$), τ 4.6 [d, 1 H, H^4, $J(H^4F^1)$ 5], 7.6 [m, 1 H, H^1, $J(H^1H^2)$ 17, $J(H^1F^2)$ 4, $J(H^1F^3)$ 8], 7.8 [m, 1 H, H^2, $J(H^1H^2)$ 17 Hz], and 8.3 (s, 3 H, Me^3); ^{19}F ($CDCl_3$), 95.8 [d, 1 F, F^2, $J(F^2F^3)$ 217], 100.5 [d, 1 F, F^3, $J(F^2F^3)$ 217 Hz], 175.0 p.p.m. (br s, 1 F, F^1); ^{13}C ($CDCl_3$), −123.3 [br s, C^1 (^{19}F-decoupled)], −68.7 (br s, C^4), −49.7 [t, C^2, $J(C^2F^3)$ 24 Hz], and −21.7 p.p.m. (s, Me^3). The mass spectrum showed peaks at *m/e* 278 (*P*), 250 (*P* − CO), 222 (*P* − 2CO), 202 (*P* − 2CO − HF), 194 (*P* − 3CO), and 174 (*P* − 3CO − HF).

(*c*) *With tricarbonyl*(η^3-*1-methylallyl*)*cobalt*. By the same procedure reaction of [$Co(CO)_3(\eta^3\text{-}1\text{-}MeC_3H_4)$] (1.2 g, 6 mmol) and chlorotrifluoroethylene (13 mmol) in tetrahydrofuran (20 cm^3) gave pale yellow *crystals* of (11) (0.05 g, 3%), m.p. 40 °C (Found: C, 38.2; H, 2.4. $C_{10}H_6CoF_3O_3$ requires C, 38.8; H, 2.2%), ν(CO) (hexane) at 2 087s, 2 029s, and 2 020s cm^{-1}. N.m.r.: ^{1}H ($CDCl_3$), τ 6.3 [sextet, 1 H, H^3, $J(H^1H^3) = J(H^2H^3) = J(H^3F^1) = J(H^3F^2) = J(H^3F^3)$ 4], 7.6 [m, 1 H, H^1, $J(H^1H^2)$ 16, $J(H^1H^3)$ 4], 7.8 (s, 3 H, Me^4), 7.9 [m, 1 H, H^2, $J(H^2H^3)$ 4, $J(H^1H^2)$ 16 Hz]; ^{19}F ($CDCl_3$), 96.2 [d, 1 F, F^2, $J(F^2F^3)$ 227], 100.8 [d, 1 F, F^3, $J(F^2F^3)$ 227 Hz], 177.2 p.p.m. (br s, 1 F, F^1); ^{13}C ($CDCl_3$), −122.3 [s, C^1 (^{19}F-decoupled)], −55.9 (br s, C^3), −44.0 [C^2, $J(CF^2) = J(CF^3)$ 24 Hz], and −16.3 (s, Me^4). The mass spectrum showed peaks at *m/e* 278 (*P*), 250 (*P* − CO), 222 (*P* − 2CO), 202 (*P* − 2CO − HF), 194 (*P* − 3CO), and 174 (*P* − 3CO − HF).

Structure Determination of Dicarbonyl[4—5-η-*1,2-difluoro-1,2-bis*(*trifluoromethyl*)*pent-4-enyl*](*trimethyl phosphite*)*cobalt, Complex* (7), *by* X-*Ray Diffraction*.—The crystal chosen for intensity measurements, 0.027 × 0.025 × 0.023 cm, was mounted on a Syntex $P2_1$ four-circle diffractometer, and maintained at a low temperature (183 K) by a stream of cold dry N_2 gas (10 ft^3 h^{-1}) passing through an annular nozzle (diameter 0.7 cm) electrically heated to prevent serious icing. Nitrogen gas was conducted through a heat exchanger immersed in a Dewar tank of liquid N_2. The cooled gas was transferred through glass Dewar tubing swivel-jointed so that it was affixed to the χ circle, and the jet was directed along the ϕ axis throughout data collection. Scan rates varied from 0.033 to 0.488° s^{-1} according to the magnitude of a 2-s sample count. Check reflections for the planes $1\bar{5}3$, $0\bar{3}3$, and $22\bar{6}$ were remeasured every 40 reflections and showed no significant diminution during the 98 h of data collection. Of the total 5 666 independent reflections (complete for $3 < 2\theta < 65°$), 4 671 satisfied the criterion $I > 2.5\sigma(I)$, and only these were used in the solution and refinement of the structure.

Crystal data. $C_{12}H_{14}CoF_8O_5P$, $M = 480.2$, Triclinic, $a = 9.544(9)$, $b = 11.682(9)$, $c = 12.421(12)$ Å, $\alpha = 122.27(6)$, $\beta = 119.78(6)$, $\gamma = 96.04(7)°$ at 183 K, $U = 877.4(13)$ Å^3 $D_m = 1.81$, $Z = 2$, $D_c = 1.82$ g cm^{-3}, $F(000) = 480$, space group $P\bar{1}$, Mo-K_α *X*-radiation (graphite monochromator),' $\lambda = 0.710\,69$ Å; μ(Mo-K_α) = 12.2 cm^{-1}.

The structure was solved by conventional heavy-atom methods and refined by blocked-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms. Weights were applied according to the scheme $1/w = (1.50 - 0.05F + 0.015F^2)$, and this gave a satisfactory weight analysis. Hydrogen atoms were incorporated at positions estimated from the electron-density maps and were refined isotropically. The refinement converged to *R* 0.066 (*R′* 0.103) and a final electron-density difference synthesis (including unobserved data) showed no peaks > 1.3 or < -1.3 e Å^{-3}, with a general background level very much less than this. Positional parameters are in Table 1, interatomic distances and bond angles in Table 2, and some significant torsion angles in Table 3. No absorption correction was applied, and the atomic scattering factors were those of ref. 17 for Co, C, F, P, and O, and those of ref. 18 for H. All computational work was carried out at the University of London Computing Centre with the *X*-RAY system of programs.[19] Observed and calculated structure factors, together with all thermal parameters, are listed in Supplementary Publication No. SUP 22563 (22 pp.).*

[8/1928 *Received*, 6*th November*, 1978]

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

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