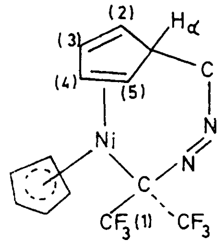
Reactions of Low-valent Metal Complexes with Fluorocarbons. Part XXVIII.[1] Nickelocene and Tricarbonyl(π-allylic)cobalt Complexes with Bis(trifluoromethyl)diazomethane

By **John Clemens, Michael Green,** and **F. Gordon A. Stone,*** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

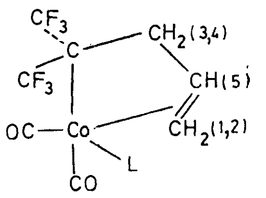
Reaction of nickelocene with bis(trifluoromethyl)diazomethane affords a complex which is formulated as a 1 : 2 adduct. A possible structure is discussed. Tricarbonyl(π-allyl, π-2-methylallyl, or π-1-methylallyl)cobalt react at room temperature with $(CF_3)_2CN_2$ to form 1 : 1 adducts $[\overline{Co{\cdot}C(CF_3)_2{\cdot}CH_2CH{:}CH_2}(CO)_3]$, $[\overline{Co{\cdot}C(CF_3)_2{\cdot}CH_2C(Me){:}CH_2}(CO)_3]$, $[\overline{Co{\cdot}C(CF_3)_2{\cdot}CH_2CH{:}CHMe}(CO)_3]$, and $[\overline{Co{\cdot}C(CF_3)_2{\cdot}CHMeCH{:}CH_2}(CO)_3]$; the latter is formed as a minor product. Reaction of these species with Ph_3P or Ph_3As leads to displacement of carbon monoxide.

PREVIOUSLY[1] it was shown that bis(trifluoromethyl)diazomethane reacts with zerovalent Ni, Pd, and Pt complexes to form species containing co-ordinated perfluoroacetone azine, *viz.* $[\overline{M{\cdot}C(CF_3)_2{\cdot}N}N{:}C(CF_3)_2]$. The corresponding reaction with *trans*-$[IrCl(N_2)(PPh_3)_2]$ afforded $[\overline{IrN{:}N}C(CF_3)_2(Cl)(PPh_3)_2]$. In this paper we describe results obtained with nickelocene and with tricarbonyl (π-allyl)cobalt complexes.

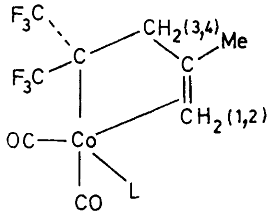
In hexane solution, nickelocene reacted (−5 °C) over a period of days with bis(trifluoromethyl)diazomethane[2] to form purple crystals of the air-stable complex (I). Elemental analysis and mass-spectrometry indicated a molecular formula $[Ni(C_5H_5)_2C_6F_{12}N_2]$. The i.r. spectrum showed a large number of medium intensity bands in the range 650—1100 cm^{-1}, and a strong band at 1445 cm^{-1}, which was assigned to a N=N stretching mode. There were no bands at higher frequency thus excluding possible structures containing the group $N{:}C(CF_3)_2$, either σ-bonded to the nickel or to some organic group.



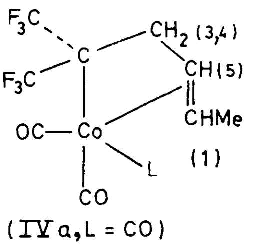
(I)



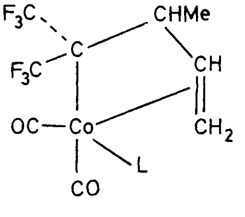
(II, L = CO)
(V, L = PPh$_3$)
(VI, L = AsPh$_3$)



(III, L = CO)
(VII, L = PPh$_3$)
(VIII, L = AsPh$_3$)



(IVa, L = CO)
(IX, L = PPh$_3$)
(X, L = AsPh$_3$)



(IVb, L = CO)

The ^{19}F n.m.r. spectrum showed four multiplets of equal intensity; resonances at 54·4 and 58·7 p.p.m. (relative to CCl_3F) were assigned to inequivalent CF_3 groups α to the metal in the azine chain. The shifts are similar to those of the group $Ni{\cdot}C(CF_3)_2$ present in the complex $[\overline{NiC(CF_3)_2N}{\cdot}N{:}C(CF_3)_2L_2]$.[1] The two resonances were split into two quartets [J(FF) 10·0 Hz], the low-field signal being further coupled to the protons in the C_5H_5 ring to give a multiplet. The two higher field resonances occurred at 66·9 and 70·1 p.p.m. as doublets of quartets [J(FF) 10·0, $J(FH_\alpha)$ 3·0 and 1·5 Hz, respectively]. That four CF_3 resonances are observed suggests that the molecule does not have a plane of

---

[1] Part XXVII, J. Clemens, M. Green, and F. G. A. Stone, *J.C.S. Dalton*, 1973, 1620.

[2] D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Amer. Chem. Soc.*, 1966, **88**, 3617.

symmetry through the nickel and the C_5-rings, in agreement with a structure in which the nickel is bonded to only one of the double bonds of the cyclopentadiene ring, as illustrated.

The ^1H n.m.r. spectrum supports this formulation showing a single resonance at τ 4·6 assignable to a *pentahapto*-bonded C_5 ring, and four multiplets of a fifth of the intensity at τ 4·1, 5·1, 6·5, and 7·2 assignable to the protons H_2, H_3, H_4, and H_5 of the unsymmetrically bonded C_5 ring. The signal due to H_α could not be located with certainty. It is suggested that the fluorocarbon ligand is bonded *endo* to the C_5H_5 ring. Although with this stereochemistry a band might have been expected[3,4] in the 2740 cm^{-1} region of the i.r. spectrum due to an *exo*-CH, the presence of the bridging $(CF_3)_2\overset{|}{C}{\cdot}N{=}N{\cdot}\overset{|}{C}(CF_3)_2$ could alter the geometry of the C_5 ring such that overlap of the *exo*-hydrogen orbitals with the C_5H_5 π-orbitals is reduced. Thus, the absence of such an i.r. band is not necessarily incompatible with the proposed structure.

Nickelocene can be considered as a potential π-allylic system, and in view of the ready reaction of tetrafluoroethylene with both this sandwich compound[5] and with tricarbonyl (π-allyl)cobalt complexes,[6a] the reactions of bis(trifluoromethyl)diazomethane with tricarbonyl-(π-allyl, π-2-methylallyl, and π-1-methylallyl)cobalt was investigated.

An excess of bis(trifluoromethyl)diazomethane reacted with a light petroleum solution of tricarbonyl-(π-allyl)cobalt to afford a bright orange air-sensitive distillable liquid (II), which is assigned the illustrated structure. Consistent elemental analyses could not unfortunately be obtained, however, a mass spectrum was in agreement with this formulation; that the double bond of a hydrocarbon ligand remained co-ordinated to the metal was indicated by the ^{19}F n.m.r. spectrum, which showed two resonances at 66·8 and 67·8 p.p.m.; the magnetic inequivalence of the trifluoromethyl groups implying hindered rotation about the $Co-C(CF_3)_2$ bond. The ^1H n.m.r. spectrum showed multiplets at τ 5·4, 7·4, and 8·2 with relative intensities of 1 : 2 : 2 due respectively to the protons H_5, $H_3 + H_4$, and $H_1 + H_2$; the signal of H_3 and H_4 was complex due to ^{19}F coupling (7·0 Hz) while that of H_5 appeared as a triplet. The i.r. spectrum showed terminal carbonyl bands at 2095vs and 2036br,vs cm^{-1} consistent with the presence of a $Co(CO)_3$ group; this also being indicated by the appearance in the mass spectrum of peaks corresponding to the consecutive loss of three carbon monoxide ligands.

Triphenylphosphine and triphenylarsine both reacted with (II) to form analytically pure crystalline derivatives (V) and (VI). A reaction involving displacement of carbon monoxide rather than the co-ordinated allyl group as observed previously[6a] with the complex $[\overline{CoCF_2{\cdot}CF_2CH_2{\cdot}CH}{:}CH_2(CO)_3]$. This was established by the ^{19}F n.m.r. spectra of (V) and (VI), which again showed two multiplets due to the inequivalent CF_3 groups at 65·9 and 66·8 p.p.m. and at 65·8 and 66·9 p.p.m. respectively. As with the parent complex (II), the ^1H n.m.r. spectra were too complex for a full analysis.

More stable products with less complex spectra were obtained from the reaction of bis(trifluoromethyl)diazomethane with tricarbonyl(π-2-methylallyl)cobalt to form (III), from which triphenylphosphine (VII) and triphenylarsine (VIII) derivatives were obtained. The ^{19}F n.m.r. spectrum of (III) showed resonances at 65·8 and 69·1 p.p.m.; the latter appearing as a doublet of quartets due to $^{19}F^{19}F$ coupling (10·0 Hz) and a coupling (7·0 Hz) to one proton only of the adjacent CH_2 group. A similar pattern was observed for the ^{19}F n.m.r. spectrum of the triphenylarsine derivative showing resonances at 65·5 (m) and 68·6 (doublet of quartets) p.p.m.

The ^1H n.m.r. spectrum of (VIII) was studied in detail by homo- and hetero-nuclear decoupling techniques. Resonances assignable to H_1 and H_2 appeared at τ 7·55 and 7·90; a small coupling (1·0 Hz) was observed between H_1 and H_2, the former also showed a coupling to H_4 (1·0 Hz). The protons H_3 and H_4 gave resonances at τ 7·80 and 6·70 respectively; the latter resonance appearing as a doublet of doublets. Interestingly, only the resonance at τ 7·80 (H_3) showed coupling to both of the inequivalent CF_3 groups $[J(H_{(3)}CF_3) = J(H_{(3)}CF_3'),$ 6·5 Hz] as well as to H_4 (11·0 Hz), and appeared as a very broad multiplet prior to decoupling experiments. The proton H_4 showed no evidence of ^{19}F coupling. The methyl resonance appeared at τ 8·55.

The ^{19}F n.m.r. spectrum of the triphenylphosphine complex (VII) showed resonances at 65·5 and 68·6 p.p.m., both appearing as doublets of quartets due to $^{19}F^{19}F$ coupling (10·0 Hz) and coupling (7·0 Hz) of each CF_3 to one proton. There was no evidence of $^{19}F^{31}P$ coupling suggesting that the phosphine ligand occupies a relative *cis*-configuration to the $-C(CF_3)_2-CH_2$ group. Comparison of the i.r. spectra suggests a similar stereochemistry for the other substitution products. Assuming a trigonal bipyramidal structure for these complexes, in which the electronegatively substituted $-C(CF_3)_2CH_2-$ group would be expected[7] to occupy preferentially an axial position, then the most labile carbon monoxide ligands in a substitution reaction of (II) or (III) would be expected to be the equatorial carbon monoxides, suggesting that the isolated complexes (V)—(VIII) are the kinetically controlled products.

---

[3] M. R. Churchill and R. Mason, *Proc. Roy. Soc.*, 1964, *A*, **279**, 191; M. R. Churchill and P. H. Bird, *Chem. Comm.*, 1967, 777.

[4] I. U. Khand, P. L. Pauson, and W. E. Watts, *J. Chem. Soc.* (*C*), 1969, 2024.

[5] D. W. McBride, R. L. Pruett, E. Pitcher, and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1962, **84**, 497.

[6] (*a*) A. Greco, M. Green, and F. G. A. Stone, *J. Chem. Soc.* (*A*), 1971, 3476; (*b*) J. Clemens, Ph.D. Thesis, Bristol University, 1972.

[7] E. L. Muetterties and R. A. Schunn, *Quart. Rev.*, 1966, **20**, 345, and references cited therein.

Bis(trifluoromethyl)diazomethane reacted with tricarbonyl(π-1-methylallyl)cobalt to give an orange distillable liquid (IV), from which the crystalline triphenylphosphine (IX) and triphenylarsine (X) substitution products were obtained.

The ^{19}F n.m.r. spectrum of (IV) suggested that two isomers (IVa) and (IVb) were present. One, comprising over 80% of the combined product, showed resonances at 67·0 and 67·9 p.p.m. of equal intensity, which appeared as doublets of quartets [*J*(FF) 9·0, *J*(FH) 7·0 and 8·5 Hz, respectively], a pattern similar to that observed with (III), (VII), and (VIII). The other isomer showed a quartet resonance at 65·3 p.p.m. [*J*(FF) 10·0 Hz], its associated resonance being partially co-incident with the resonance at 67·0 p.p.m. due to the other isomer. The resonances at 67·0 and 67·9 p.p.m. (major product) are assigned to the isomer (IVa) with each of the inequivalent CF_3 groups coupled to one proton of the adjacent CH_2 group. The minor product, which shows a presumed two quartet resonance pattern, is assigned structure (IVb); the stereochemistry being such that the C*H*Me proton does not couple to the two CF_3 groups.

Examination of models of these systems shows that the dihedral angles between the methylene hydrogens and the adjacent trifluoromethyl groups is almost the same, suggesting that the preferential $^{19}F^1H$ coupling observed is not due to a conformational effect.

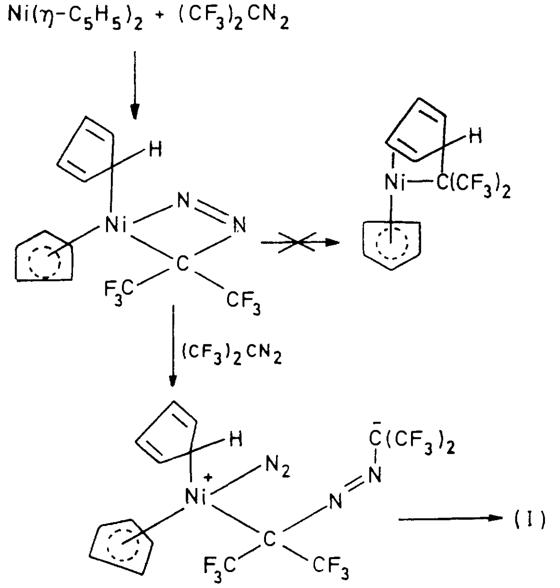
The ^{1}H n.m.r. spectrum of (IV) also showed that two isomers were present, one (IVa) predominating in a ratio of 4 : 1.

It is interesting that stereospecific insertion of tetrafluoroethylene into tricarbonyl(π-1-methylallyl)cobalt takes place at the less substituted carbon,[6] and similar stereospecific insertion at CH_2 rather than CHMe has been reported[8] in the reaction between hexafluorobut-2-yne and chloro(π-1-methylallyl)triphenylphosphinepalladium; and between norbornadiene and hexafluoroacetylacetonato(π-1-methylallyl)palladium.[9]

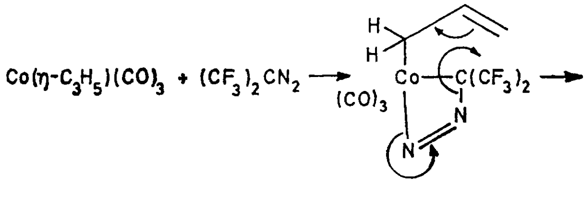
Using a sample of (IV) consisting almost entirely of isomer (IVa), triphenylphosphine (IX) and triphenylarsine (X) derivatives were prepared as orange crystals. Their n.m.r. spectra were in accord with the illustrated structures.

DISCUSSION

The formation of the nickelocene adduct (I) and the cobalt–allyl adducts (II)—(IV) can be understood in terms of the initial formation of a 1 : 1 adduct, which would be viewed as involving a change in the formal oxidation state of the metal (d^8 to d^6) or where there is no effective change in oxidation state.[10] In the absence of a crystal structure determination on a suitable 1 : 1 adduct it is not possible to decide on this point. In the reaction leading to (I), N–C bond cleavage could occur with capture of a further molecule of $(CF_3)_2CN_2$:



Whereas, in the cobalt reaction, possibly because of a more flexible system, the unco-ordinated double bond of the σ-allyl group could be attacked intramolecularly with displacement of dinitrogen:



EXPERIMENTAL

^{1}H and ^{19}F N.m.r. spectra were recorded on a Varian HA 100 spectrometer at 100 and 94·1 MHz respectively. Chemical shifts are relative to Me_4Si (τ 10·00) and CCl_3F (0·00 p.p.m., external standard). I.r. spectra were recorded with a Perkin-Elmer 257 spectrophotometer using Nujol and hexachlorobutadiene mulls. All operations were carried out under dry oxygen-free nitrogen or *in vacuo*. Light petroleum refers to the fraction b.p. 30—40°. Tricarbonyl(π-allyl)cobalt complexes were prepared from the appropriate propene halide and $[NaCo(CO)_4]$. Bis(trifluoromethyl)diazomethane was prepared by the lead tetra-acetate oxidation of the hydrazone $(CF_3)_2C{:}N{\cdot}NH_2$.[2]

Reaction of Bis(trifluoromethyl)diazomethane with (a) *Bis(cyclopentadienyl)nickel*. Bis(trifluoromethyl)diazomethane (0·45 g, 3·00 mmol) was condensed (−196°) into a Carius tube containing bis(cyclopentadienyl)nickel (0·20 g, 1·00 mmol) suspended in hexane (10 ml). After 6 days at −5 °C the purple material, which had been deposited was collected and recrystallised from methylene chloride to give purple *crystals* of (I) (0·08 g, 14%), m.p. 189—191° (dec.) (Found: C, 37·3; H, 2·1; F, 43·9; N, 5·4; Ni, 11·2. $C_{16}H_{10}F_{12}N_2Ni$ requires C, 37·2; H, 2·0; F, 44·2;

---

[8] T. G. Appleton, H. C. Clark, R. C. Potter, and R. J. Puddephatt, *J. Organometallic Chem.*, 1972, **39**, C13.

[9] R. P. Hughes and J. Powell, *J. Organometallic Chem.*, 1971, **30**, C45.

[10] S. Otsuka, A. Nakamura, T. Koyama, and Y. Tatsuno, *Chem. Comm.*, 1972, 1105.

N, 5·4; Ni, 11·4%), $\nu_{\text{max.}}$ 1445s, 1400w, 1315m, 1295m, 1280w, 1245s, 1230s, 1210s, 1190m, 1170w, 1150m, 1105s, 1080m, 1060w, 1040m, 1000w, 990m, 965w, 955w, 940m, 905w, 890w, 855m, 810s, 790w, 755w, 745m, 730m, 720m, and 700m cm^{-1}. The ^{1}H n.m.r. spectrum ($CDCl_3$) showed resonances at τ 4·1 [m, 1H, H_3 or H_4], 4·6 [s, 5H, π-C_5H_5], 5·1 [m, 1H, H_3 or H_4], 6·5 [m, 1H, H_2 or H_5] and 7·2 [m, 1H, H_2 or H_5]. The ^{19}F n.m.r. spectrum (CH_2Cl_2) showed resonances at 54·4 p.p.m. [m, 3F, $CF_3{}^{(1)}$], 58·7 [q, 3F, $CF_3{}^{(2)}$, $J(F_1F_2)$ 10·0 Hz; irradiation of this signal sharpened the resonance at 54·4 p.p.m.], 66·9 [d of q, 3F, $CF_3{}^{(3)}$, $J(F_3F_4)$ 10·0 Hz, $J(F_3H_\alpha)$ 3·0 Hz] and 70·1 [d of q, 3F, $CF_3{}^{(4)}$, $J(F_4F_3)$ 10·0 Hz, $J(F_4H_\alpha)$ 1·5 Hz]. The mass spectrum showed a peak at *m/e* 517 (*P*).

(b) *Tricarbonyl*(π-*allyl*)*cobalt*. Bis(trifluoromethyl)diazomethane (0·30 g, 2·00 mmol) was condensed (−196°) into a tube containing tricarbonyl(π-allyl)cobalt (0·37 g, 2·00 mmol) dissolved in light petroleum (10 ml). After 12 h (25 °C) the solvent was removed *in vacuo* at 0°; on warming (50°) an orange liquid distilled and was collected to give yellow *crystals* of (II) (0·15 g, 23%), m.p. <20°; $\nu_{\text{max.}}$ 2095vs, 2036b,vs, 2030b,vs, 1420w, 1350s, 1320s, 1265s, 1220s, 1155s, 1115s, 1095s, 1050m, 980w, 905w, 850m, 825w, 735s, 700m, and 670m cm^{-1}. The ^{1}H n.m.r. spectrum (C_6D_6) showed resonances at τ 5·4 [apparent t, 1H, H_5, $J(H_5H_1) = J(H_5H_2)$ 10·0 Hz], 7·4 [m, 2H, H_3 and H_4, J(HF) 7·0 Hz] and 8·2 [apparent t, 2H, H_1 and H_2, $J(H_1H_5) = J(H_2H_5)$ 10·0 Hz]. The ^{19}F n.m.r. spectrum (C_6H_6) showed resonances at 66·8 p.p.m. [m, 3F, CF_3] and 67·8 [m, 3F, CF_3]. The mass spectrum showed peaks at *m/e* 334 (*P*), 306 (*P* − CO), 278 (*P* − 2CO), and 250 (*P* − 3CO).

(c) *Tricarbonyl*(π-2-*methylallyl*)*cobalt*. Similarly, bis(trifluoromethyl)diazomethane (0·45 g, 3·00 mmol) was treated with tricarbonyl(π-2-methylallyl)cobalt (0·42 g, 2·10 mmol) to give yellow *crystals* of (III) (0·42 g, 57%), m.p. <20°; $\nu_{\text{max.}}$ 2080vs, 2020b,vs, 1440w, 1385w, 1350s, 1300s, 1278s, 1266s, 1240s, 1220s, 1151s, 1090s, 1038w, 1018w, 1000w, 893w, 870w, 845w, 730s, and 700s cm^{-1}. The ^{1}H n.m.r. spectrum (C_6D_6) showed resonances at τ 6·7—7·0 [m, 2H, H_3 and H_4] and 8·0 [m, 2H, H_1 and H_2]. The ^{19}F n.m.r. spectrum (C_6H_6) showed resonances at 65·8 p.p.m. [m, 3F, CF_3, J(FF) 10·0 Hz] and 69·1 [d of q, 3F, CF_3, J(FF) 10·0 Hz, J(FH) 7·0 Hz]. The mass spectrum showed peaks at *m/e* 348 (*P*), 320 (*P* − CO), 292 (*P* − 2CO), and 264 (*P* − 3CO).

(d) *Tricarbonyl*(π-1-*methylallyl*)*cobalt*. Similarly, bis(trifluoromethyl)diazomethane (0·75 g, 5·00 mmol) was reacted with tricarbonyl(π-1-methylallyl)cobalt (1·00 g, 5·00 mmol) in diethyl ether (30 ml) to give yellow *crystals* of (IV) (0·84 g, 50%), m.p. <20°, $\nu_{\text{max.}}$ 2060vs, 1995b,vs, 1406w, 1350s, 1307s, 1272s, 1250b,s, 1218s, 1145s, 1120s, 1091s, 1050w, 1027w, 950w, 912w, 845w, 830w, 742w, 730m, and 695s cm^{-1}. The ^{1}H n.m.r. spectrum (C_6D_6) showed overlapping resonances due to two similar isomers at τ 5·4—5·7 [m, 1H, H_5], 6·9—7·4 [m, 2H], 8·0—8·3 [m, 1H], and 8·6—8·7 [two d, 3H, CH_3; doublets centred at τ 8·65 and 8·70 with relative intensity approximately 4 : 1 respectively, J (CH_3–H) 6·0 Hz]. The ^{19}F spectrum (C_6H_6) showed resonances at 65·3 p.p.m. [q, 3F, CF_3, J(FF) 10·0 Hz] and 66·8 (m) due to one isomer; and at 67·0 p.p.m. [d of q, 3F, CF_3, J(FF) 9·0 Hz., J ($FH^{(1)}$) 7·0 Hz] and 67·9 [d of q, 3F, CF_3, J(FF) 9·0 Hz, $J(FH^{(1)})$ 8·5 Hz]. The mass spectrum showed peaks at *m/e* 348 (*P*), 320 (*P* − CO), 292 (*P* − 2CO), and 264 (*P* − 3CO).

Reaction of Complex (II) *with* (*a*) *Triphenylphosphine*. A solution of complex (II) (0·50 g, 1·50 mmol) in light petroleum (20 ml) was treated with triphenylphosphine (0·52 g, 2·00 mmol) and warmed (30°) for 20 min. The resultant precipitate was collected and recrystallised from light petroleum to give orange *crystals* of (V) (0·30 g, 33%), m.p. 136—138° (dec.) (Found: C, 54·7; H, 3·9; F, 18·6; P, 5·2. $C_{26}H_{20}F_6PO_2Co$ requires C, 55·0; H, 3·6; F, 20·0; P, 5·4%), $\nu_{\text{max.}}$ 3060w, 1993vs, 1938vs, 1910m, 1590w, 1575w, 1480m, 1436s, 1364m, 1335m, 1310w, 1290s, 1254s, 1228m, 1213m, 1190w, 1139s, 1118m, 1094s, 1030w, 1000w, 958w, 922w, 900w, 840w, 750m, 730w, and 696s cm^{-1}. The ^{1}H n.m.r. spectrum (C_6D_6) showed resonances at τ 2·4—3·2 [m, 15H, C_6H_5P], 5·5 [m, 1H, H_5], 7·1 [m, 1H, H_3 or H_4], 7·6—8·0 [m, 2H] and 8·2 [m, 1H, H_1 or H_2]. The ^{19}F n.m.r. spectrum (C_6H_6) showed resonances at 65·9 p.p.m. [m, 3F, CF_3] and 66·8 [m, 3F, CF_3].

(b) *Triphenylarsine*. A solution of complex (II) (1·20 g, 3·5 mmol) and triphenylarsine (1·07 g, 3·50 mmol) in light petroleum (30 ml) was heated (30°) for 45 min. Slow evaporation of the solvent gave orange *crystals* of (VI) (0·84 g, 40%), m.p. 114—115° (dec.) (Found: C, 51·3; H, 3·5. $C_{26}H_{20}F_6AsO_2Co$ requires C, 51·1; 3·3%), $\nu_{\text{max.}}$ 3060w, 1991vs, 1938vs, 1910m, 1580w, 1480m, 1426s, 1362m, 1332m, 1308w, 1287s, 1250s, 1220m, 1190w, 1135s, 1115m, 1094s, 1080m, 1025w, 1000w, 955w, 920w, 895w, 840w, 750m, 740m, and 698s cm^{-1}. The ^{1}H n.m.r. spectrum (C_6D_6) showed resonances at τ 2·3—3·2 [m, 15H, C_6H_5As], 5·3 [m, 1H, H_5], 7·2 [m, 1H, H_3 or H_4], 7·6 [d, 1H, H_1 or H_2, $J(HH^{(5)})$ 6·0 Hz], 8·0 [apparent t, 1H, H_3 or H_4, $J(HH^{(5)})$ 10·0 Hz] and 8·4 [d, 1H, H_1 or H_2, $J(HH^{(5)})$ 10·0 Hz]. The ^{19}F n.m.r. spectrum (C_6H_6) showed resonances at 65·8 p.p.m. [m, 3F, CF_3] and 66·9 [m, 3F, CF_3].

Reaction of Complex (III) *with* (*a*) *Triphenylphosphine*. A solution of complex (III) (0·42 g, 1·20 mmol) in diethyl ether (30 ml) was treated with triphenylphosphine (0·30 g, 1·20 mmol) and warmed (30 °C) for 20 min. The solvent was removed *in vacuo* and the residue recrystallised (−78°) from light petroleum to give orange *crystals* of (VII) (0·25 g, 38%), m.p. 167—168° (dec.) (Found: C, 55·9; H, 3·9; F, 18·2; P, 5·2. $C_{27}H_{22}F_6PO_2Co$ requires C, 55·7; H, 3·8; F, 19·6; P, 5·3%), $\nu_{\text{max.}}$ 3060w, 1995vs, 1935vs, 1902m, 1590w, 1575w, 1480m, 1438s, 1348m, 1310w, 1290s, 1274s, 1250s, 1240s, 1221s, 1184w, 1137s, 1091s, 1030w, 1000w, 952w, 915w, 893w, 865w, 840w, 750m, 736m, 724m, and 692s cm^{-1}. The ^{1}H n.m.r. spectrum (C_6D_6) showed resonances at τ 2·4—3·2 (m, 15H, C_6H_5P), 6·8 (d, 1H), 7·4—7·6 (m, 2H), 8·5 (m, 1H), and 8·6 (s, 3H, CH_3). The ^{19}F n.m.r. spectrum (C_6H_6) showed resonances at 65·5 p.p.m. [d of q, 3F, CF_3, J(FF) 10·0, J(FH) 7·0 Hz] and 68·6 [d of q, 3F, CF_3, J(FF) 10·0, J(FH) 7·0 Hz].

(b) *Triphenylarsine*. A solution of complex (III) (0·50 g, 1·50 mmol) in light petroleum (30 ml) was reacted with triphenylarsine (0·46 g, 1·50 mmol) for 45 min (30°). The volume of the solvent was reduced *in vacuo*, and cooling (−78°) gave orange *crystals* of (VIII) (0·25 g, 30%), m.p. 143—145° (dec.) (Found: C, 52·0; H, 3·7; F, 18·5; As, 12·1. $C_{27}H_{22}F_6AsO_2Co$ requires C, 51·8; H, 3·5; F, 18·2; As, 12·0%), $\nu_{\text{max.}}$ 3060w, 2000vs, 1940vs, 1903m, 1580w, 1440s, 1380m, 1345m, 1291s, 1274s, 1250s, 1242s, 1220s, 1183w, 1140s, 1090s, 1076m, 1030m, 1010w, 1000w, 987w, 950w, 917w, 892w, 864w, 840w, 740m, 730m, and 690s cm^{-1}. The ^{1}H n.m.r. spectrum (C_6D_6) showed resonances at τ 2·4—3·2 [m, 15H, C_6H_5As], 6·70 [d of d, 1H, H_4, $J(H_3H_4)$ 11·0, $J(H_1H_4)$ 1·0 Hz], 7·55 [t, 1H, H_1, $J(H_1H_2)$

1·0 Hz], 7·80 [d of q of q, 1H, $\mathrm{H_3}$, $J(\mathrm{H_3H_4})$ 11·0, $J(\mathrm{H_3CF_3}) = J(\mathrm{H_3CF_3'})$ 6·5 Hz], 7·90 [d, 1H, $\mathrm{H_2}$, $J(\mathrm{H_2H_1})$ 1·0 Hz] and 8·55 (s, 3H, $\mathrm{CH_3}$). The ^{19}F n.m.r. spectrum ($\mathrm{C_6H_6}$) showed resonances at 65·5 p.p.m. [m, 3F, $\mathrm{CF_3}$, $J(\mathrm{FF})$ 10·0 Hz] and 68·6 [d of q, 3F, $\mathrm{CF_3}$, $J(\mathrm{FF})$ 10·0; $J(\mathrm{H_3F})$ 6·5 Hz].

Reaction of Complex (IV) *with* (*a*) *Triphenylphosphine*. A solution of complex (IV) (0·61 g, 2·0 mmol) in ether (20 ml) was treated (30°, 20 min) with triphenylphosphine (0·52 g, 2·00 mmol); the solvent was removed *in vacuo* and light petroleum added to give orange *crystals* of (IX) (0·82 g, 67%), m.p. 133—134° (dec.) (Found: C, 56·2; H, 3·9. $\mathrm{C_{27}H_{22}F_6PO_2Co}$ requires C, 55·7; H, 3·8%), $\nu_{max.}$ 3060w, 1990vs, 1935vs, 1902m, 1590w, 1575w, 1480m, 1434s, 1407w, 1350s, 1300s, 1270s, 1244s, 1220s, 1195m, 1147s, 1120s, 1093s, 1050w, 1026w, 1000w, 950w, 918w, 888w, 840w, 820w, 750m, 740m, 720m, 704s, and 296s cm^{-1}. The ^{1}H n.m.r. spectrum ($\mathrm{C_6D_6}$) showed resonances at τ 2·4—3·2 [m, 15H, $\mathrm{C_6H_5P}$], 5·4 [apparent t, 1H, $\mathrm{H_5}$, $J(\mathrm{HH})$ 10·0 Hz], 7·0 [br m, 1H, $\mathrm{H_4}$], 7·6 [m, 1H, $\mathrm{H_1}$, $J(\mathrm{H_1H_5})$ 10·0, $J(\mathrm{H_1CH_3})$ 5·0 Hz], 8·2 [apparent t, 1H, $\mathrm{H_3}$, $J(\mathrm{H_3H_5}) = J(\mathrm{H_3H_4})$ 10·0 Hz] and 9·2 [d, 3H, $\mathrm{CH_3}$, $J(\mathrm{H_1CH_3})$ 5·0 Hz]; peaks due to a second isomer were also observed in a separate experiment at τ 5·7(1H), 6·7(1H), 7·9(1H), 8·5(1H), and 9·15 (d, 3H, $\mathrm{CH_3}$). The ^{19}F n.m.r. spectrum ($\mathrm{C_6H_6}$) showed resonances at 65·8 p.p.m. [d of q, 3F, $\mathrm{CF_3}$, $J(\mathrm{FF})$ 10·0, $J(\mathrm{FH})$ 7·0 Hz] and 67·8 [d of q, 3F, $\mathrm{CF_3}$, $J(\mathrm{FF})$ 10·0, $J(\mathrm{FH})$ 6·5 Hz].

(*b*) *Triphenylarsine*. Similarly, complex (IV) (0·76 g, 2·50 mmol) was reacted (30°, 30 min) with triphenylarsine (0·77 g, 2·50 mmol) to give orange *crystals* of (X) (0·65 g, 45%, m.p. 105—107° (dec.) (Found: C, 51·6; H, 3·3; F, 18·1; Co, 9·4. $\mathrm{C_{27}H_{22}F_6AsO_2Co}$ requires C, 51·8; H, 3·5; F, 18·2; Co, 9·9%), $\nu_{max.}$ 3060w, 2000vs, 1964vs, 1953vs, 1580w, 1482m, 1435s, 1400w, 1351s, 1300s, 1275s, 1245s, 1219s, 1190m, 1141s, 1116s, 1092s, 1050w, 1020w, 998w, 910w, 880w, 815w, 745s, 730s, 690s, and 644m cm^{-1}. The ^{1}H n.m.r. spectrum ($\mathrm{C_6D_6}$) showed the presence of one isomer with resonances at τ 5·3 [apparent t, 1H, $\mathrm{H_5}$, $J(\mathrm{H_3H_5})$ 10·0 Hz], 7·1 [br m, 1H, $\mathrm{H_4}$], 7·8 [m, 1H, $\mathrm{H_1}$], 8·5 [apparent t, 1H, $\mathrm{H_3}$, $J(\mathrm{H_3H_4}) = J(\mathrm{H_3H_5})$ 10·0 Hz] and 8·7 [d, 3H, $\mathrm{CH_3}$, $J(\mathrm{H_1CH_3})$ 6·0 Hz]. The ^{19}F n.m.r. spectrum ($\mathrm{C_6H_6}$) showed resonances at 65·9 p.p.m. [d of q, $J(\mathrm{FF})$ 10·0, $J(\mathrm{FH_4})$ 7·0 Hz] and 67·8 [apparent quintet, $J(\mathrm{FF}) = J(\mathrm{FH_4})$ 10·0 Hz].

We thank the S.R.C. for a research studentship (to J. C.) and the U.S.A.F. Office of Scientific Research for support.

[3/383 *Received*, 19*th February*, 1973]