Metal Perfluoro-alkane- and -arene-thiolates. Part IV.[1] The Reactions of some Manganese, Iron, and Cobalt Derivatives with Alkynes †

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The products of reactions between the thiolates $[\{Mn(CO)_4(SR)\}_2]$, $[(cp)Fe(CO)_2(SR)]$, $[\{Fe(CO)_3(SR)\}_2]$, $[\{(cp)Co(SCF_3)\}_2]$, $[(cp)Co(CO)(SC_6F_5)_2]$, and $[\{Co(CO)_3(SC_6F_5)\}_2]$ ($R = CF_3$ or C_6F_5) and the alkynes $C(CF_3){\vdots}C(CF_3)$ and $C(CF_3){\vdots}CH$ are described. The products include metallothiacyclobutenes $[Mn(CO)_4\{(alkyne)SR\}]$ and $[(cp)Fe(CO)\{(alkyne)SR\}]$, metallated vinyls $[(cp)Fe(CO)_2\{(alkyne)SR\}]$, dimetallated olefins $[\{Fe(CO)_3(SR)\}_2(alkyne)]$, η^4-C_4S complexes $[Mn(CO)_3\{(alkyne)_2SR\}]$ and $[(cp)Fe\{(alkyne)_2SR\}]$, the η^4 benzene complex $[(cp)CO\{(alkyne)_3\}]$, and the 'flyover' complex $[Co_2(CO)_4\{(alkyne)_2S\}]$ (cp = η-cyclopentadienyl).

IT has been shown[2] that alkynes and other unsaturated organic derivatives can react with the ligands of thio-complexes to give products with new sulphur-containing ligands. The ready availability[3,4] of metal perfluoro-alkane- and -arene-thiolates has permitted us to

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† No reprints available.

[1] Part III, J. L. Davidson and D. W. A. Sharp, *J.C.S. Dalton*, 1975, 813.

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[3] J. L. Davidson and D. W. A. Sharp, *J.C.S. Dalton*, **1973**, 1957.

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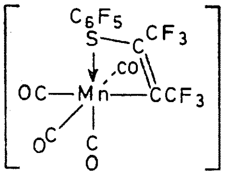
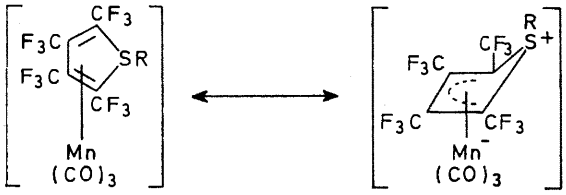
examine the reactions of these complexes with certain alkynes.

RESULTS

(a) *Reactions of* $[\{Mn(CO)_4(SR)\}_2](R = CF_3$ *or* $C_6F_5)$.—$[\{Mn(CO)_4(SC_6F_5)\}_2]$ reacted with hexafluorobut-2-yne in pentane at 293 K to give the pale-yellow adduct $[Mn(CO)_4\{C(CF_3)\!:\!C(CF_3)S(C_6F_5)\}]$ (I), whereas at higher temperatures



(I)



(II) $R = C_6F_5$
(III) $R = CF_3$

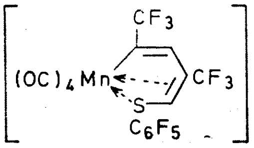
yellow $[Mn(CO)_3\{C_4(CF_3)_4S(C_6F_5)\}]$, (II; $R = C_6F_5$), was formed [(I) acting as an intermediate)]. Hexafluorobut-2-yne did not react with $[\{Mn(CO)_4(SCF_3)\}_2]$ at temperatures below 348 K but above this temperature oily yellow crystals of $[Mn(CO)_3\{C_4(CF_3)_4S(CF_3)\}]$, (III; $R = CF_3$), similar to (II), were formed.

Spectroscopic data on (I) are in accord with a structure in which the alkyne has inserted into the Mn–S bonds of $[\{Mn(CO)_4(SC_6F_5)\}_2]$ to give a three-electron donor. The mass spectrum showed a molecular ion M^+ and ions $[M - 2CO]^+$, $[M - 3CO]^+$, and $[M - 4CO]^+$ due to successive loss of carbonyl groups. Although no peak assignable to the complete ligand ion was observed, prominent ions were observed corresponding to loss of F and CF_3 groups from $C_2(CF_3)_2S(C_6F_5)$. The i.r. spectrum showed four terminal C–O stretching modes as would be expected[5] for an octahedral *cis*-$M(CO)_4XY$ species and the olefinic bond absorbed at 1 609 cm^{-1} which is too low in frequency for a co-ordinated alkyne.[6] The ^{19}F n.m.r. spectrum of (I) was in accord with the postulated structure.

From their spectroscopic properties the complexes (II) and (III) have similar structures and the structure of (II; $R = C_6F_5$) has been determined by *X*-ray crystallography[7] and shown to contain a η^4 five-membered C_4S ring in an envelope conformation with the sulphur atom displaced above the plane of the carbon atoms away from the manganese. The Mn–S distance of 2.793 Å is longer than any reasonable estimate of the sum of the covalent radii and since the complex is diamagnetic, but without any evidence for the presence of an extra hydrogen atom, it is considered that there must be an appreciable contribution from a zwitterionic structure with the ligand being formally a sulphonium derivative complexed to manganese(−I).

Spectroscopic data on these complexes are fully in accord with the established structure. The mass spectra showed parent ions and the parent ion less one fluorine. Weak peaks corresponding to the ligand ions $[C_4(CF_3)_4SR]^+$ and fragmentation processes from these ions were also observed. There was no ion at *m/e* 82 corresponding to CF_2S in the spectrum of (III; $R = CF_3$); this ion is characteristic of complexes containing $MSCF_3$ groups[8] and its absence is further evidence for the lack of a formal M–S linkage. The chemical shift of the CF_3 group attached to the heterocyclic sulphur in (III) at +68.2 p.p.m. is unusual since CF_3S groups normally give shifts well below 50 p.p.m.,[3,4,9] but there are no trifluoromethylsulphonium compounds with which adequate comparison can be made. CF_3S^{IV} Compounds have chemical shifts in the range +50 to +80 p.p.m.[10]

The complex $[\{Mn(CO)_4(SC_6F_5)\}_2]$ reacted with trifluoropropyne at temperatures below 293 K to give $[Mn(CO)_4\{(CF_3C_2H)_2S(C_6F_5)\}]$, (IV), as a pale-yellow crystalline material together with quantities of a white insoluble polymer which analysed as $(CF_3C_2H)_n$. The spectroscopic properties of (IV) are in accord with a σ-bonded ring structure with sulphur bonded to the metal although co-ordination of one of the olefinic bonds cannot be ruled out. The i.r. spectrum contained four CO stretching modes and is very similar to that observed for (I) but with two weak olefinic bands at 1 559 and 1 530 cm^{-1}. The mass spectrum showed a molecular ion with stepwise loss of carbonyl groups, but for this complex the ligand ion was observed together with peaks from the fragmentation of this species. There are clearly several different isomers possible depending on the mode of addition of the alkyne to the Mn–S bond but the n.m.r. spectra were simple and suggest the presence of only one isomer. The ^{19}F n.m.r. spectrum did not show strong F–F coupling suggesting that CF_3 groups are not present on adjacent carbons and the lack of strong H–H coupling {*cf.* the H–H coupling of 6 Hz in the ring system of $[Fe_2(CO)_6(C_2H_4Te)]^{11}$} suggests non-adjacent protons. The complex is therefore formulated as shown, although the isomer with a CH group adjacent to sulphur is not ruled out. At 353 K thermal decarbonylation of (IV) gave a very small yield of a yellow oil (V) which on spectroscopic evidence only is formulated as $[Mn(CO)_3\{C_4(CF_3)_2H_2S(C_6F_5)\}]$ being similar to (II) with a heterocyclic sulphur-containing ring η^4-bonded to a $Mn(CO)_3$ group. The i.r. spectrum contained three carbonyl peaks and is characteristic of a metal tricarbonyl



(IV)

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[7] M. J. Barrow, J. L. Davidson, W. Harrison, D. W. A. Sharp, G. A. Sim, and F. B. Wilson, *J.C.S. Chem. Comm.*, 1973, 583.

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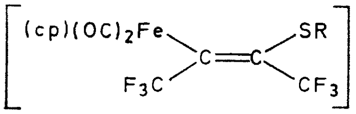
species. Olefinic modes were not observed in the i.r. spectrum, although bands characteristic of the C_6F_5 group [12] were present. The ion of highest mass observed in the mass spectrum corresponds to the parent ion of (V) and ions due to the fragmentation of the ligand (L) were observed with a particularly intense peak corresponding to $[L-2F]^+$. These observations are comparable with those for (II), but in contrast to the observed mass spectrum of (II) fragments corresponding to successive decarbonylation of the parent ion were observed.

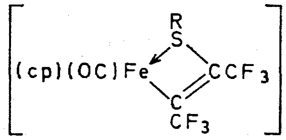
(b) *Reactions of* $[(cp)Fe(CO)_2(SR)]$ ($R = CF_3$ *or* C_6F_5; $cp = \eta$-*cyclopentadienyl*).—The complexes $[(cp)Fe(CO)_2(SR)]$ ($R = CF_3$ and C_6F_5) reacted with hexafluorobut-2-yne at *ca.* 350 K to give yellow air-stable crystals of $[(cp)Fe(CO)_2\{C(CF_3){:}C(CF_3)SR\}]$, (VI; $R = CF_3$ or C_6F_5), in which, from spectroscopic evidence, the alkyne has inserted into the FeS bond to give a *cis*-bis(trifluoromethyl)olefin.



(VI) $R = CF_3$ or C_6F_5

For (VI; $R = CF_3$) the ^{19}F n.m.r. signal of the CF_3S group was identified at 42.7 p.p.m. by comparison with the spectrum of the C_6F_5 derivative and from the generalisation that trifluoromethyl groups attached to bivalent sulphur have lower chemical shifts than those attached to carbon.[13] The coupling constants for the other two CF_3 groups, 15.8 Hz for $R = CF_3$ and 16.0 Hz for $R = C_6F_5$, are comparable with values of 11—15 Hz for other *cis*-bis(trifluoromethyl) derivatives rather than for *trans* derivatives (2 Hz).[14] The carbonyl regions of the i.r. spectra of complexes (VI) were more complicated than would be expected for simple dicarbonyl species and in particular the spectrum of (VI; $R = CF_3$) was strongly temperature dependent. These spectra are consistent with the presence of rotational isomers due to preferred conformations of the $C(CF_3){:}C(CF_3)SR$ ligands as has been established for $[(cp)Fe(CO)_2(SiCl_2Me)]$.[15]

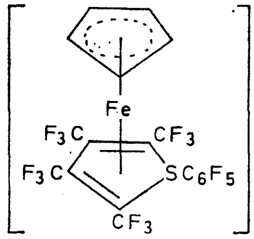
The dicarbonyl derivatives underwent photochemical decarbonylation in pentane. Complex (VI; $R = CF_3$) gave $[(cp)Fe(CO)\{C(CF_3){:}C(CF_3)SR\}]$, (VII; $R = CF_3$), together with some $[(cp)Fe(CO)_2(SCF_3)]$ and similar products were also formed by thermal decomposition in hexane at 333 K



(VII) $R = CF_3$ or C_6F_5

although the latter reaction is more complicated and other fluorocarbon derivatives were detected but not isolated. Photochemical irradiation of (VI; $R = C_6F_5$) gave only (VII; $R = C_6F_5$) as a brown oil. The spectroscopic data for these monocarbonyl derivatives are rather similar to those of the dicarbonyls (VI) although the F–F coupling constants between the *cis*-CF_3 groups (8.5 and 7.9 Hz respectively) are now comparable with those observed for (I) (8.9 Hz) and there was also a shift in the ^{19}F resonances to higher field. The i.r. spectra showed olefinic modes at *ca.* 1 600 cm^{-1}, and the spectroscopic data are thus completely consistent with the presence of a three-electron donor system similar to that in (I). In the carbonyl region the i.r. spectrum of (VII; $R = CF_3$) showed two carbonyl modes which would be consistent with the presence of two isomers due either to the relative positions of the sulphur lone pair and *S*-trifluoromethyl group with respect to the carbonyl, or to the relative positions of the cp and CO groups. Complex (VII; $R = C_6F_5$) did not show the presence of isomers.

Complex (VII; $R = C_6F_5$) reacted photochemically in pentane with hexafluorobut-2-yne to give yellow-brown crystals of $[(cp)Fe\{C_4(CF_3)_4S(C_6F_5)\}]$, (VIII), which is spectroscopically very similar to (II; $R = C_6F_5$) and which is also formulated as containing a co-ordinated heterocyclic ring and is formally a thiaferrocene. The mass spectrum showed an ion from the heterocyclic ring and also ions from similar fragmentation processes to those observed for (II; $R = C_6F_5$). The ^{19}F n.m.r. spectrum showed only one broad CF_3 resonance at 51.3 MHz suggesting that each set of CF_3 groups have almost identical magnetic environments; the signal showed asymmetry and splitting at 94.1 MHz.



(VIII)

The thermal reaction of (VII; $R = C_6F_5$) with $C(CF_3){:}C(CF_3)$ yielded only (VI; $R = C_6F_5$) as an identifiable product and no new complexes were isolated from the reaction between (VII; $R = CF_3$) and hexafluorobut-2-yne.

(c) *Reactions of* $[\{Fe(CO)_3(SR)\}_2]$ ($R = CF_3$ *or* C_6F_5).—Trifluoropropyne and hexafluorobut-2-yne gave 1 : 1 adducts $[\{Fe(CO)_3(SR)\}_2(alkyne)]$ [alkyne $= C(CF_3){:}C(CF_3)$ (IX) or $C(CF_3){:}CH$ (X)] with the iron thiolate dimers. The conditions for the reactions varied slightly but hexafluorobut-2-yne reacted at higher temperatures than those used to form the adducts to give the known tetrakis(trifluoromethyl)cyclopentadienone derivative [16] $[Fe(CO)_3\{C_4(CF_3)_4CO\}]$. Sulphur-containing species were not identified after formation of the cyclopentadienone derivatives and the fate of the thiolate residues is unknown. Cyclopentadienone derivatives were not isolated from the products of the reactions of trifluoropropyne.

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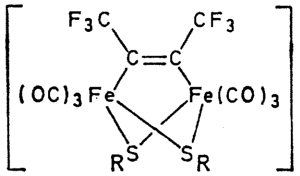
[16] J. L. Boston, D. W. A. Sharp, and G. Wilkinson, *J. Chem. Soc.*, 1962, 3488.

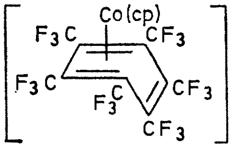
The structures of the 1 : 1 adducts have been established by an *X*-ray crystallographic study [17] on (IX; R = CF_3) which shows that the acetylene has inserted into the Fe–Fe bond of the original dithiolate. All the 1 : 1 adducts [except (X; R = CF_3)] have an i.r. band near 1 525 cm^{-1} which we assign to the C=C stretch of the dimetallated olefin, although it is somewhat surprising that this band has appreciable intensity in a relatively symmetrical molecule. The mass spectra of the CF_3 derivatives (spectra could not be obtained for the C_6F_5 derivatives because of decomposition in the spectrometer) showed stepwise loss of carbonyl groups and loss of the alkyne residue in complexes (IX). In solution the ^{19}F n.m.r. spectrum of (IX; R = CF_3) showed the presence of *syn* and *anti* isomers (ratio 3 : 1) originating from the relative orientations of the CF_3 groups with respect to the Fe_2S_2 cluster. In the solid state the configuration is *syn* (axial–axial) and it is probable that the *syn* form in solution also has this configuration. The axial–axial orientation is stable because of the opening of the Fe_2S_2 cluster on insertion of the alkyne, whereas in complexes containing metal–metal bonds this configuration is unstable because of the very close approach of the sulphur substituents.[18] The *syn* : *anti*-isomer ratio in (X; R = CF_3) is 2 : 1 and the *syn* isomer is likely to have an axial–axial configuration, but from the n.m.r. spectra only *syn* isomers are present in the C_6F_5 complexes although it is not established that these are in the axial–axial configuration.



(IX) R = CF_3 or C_6F_5

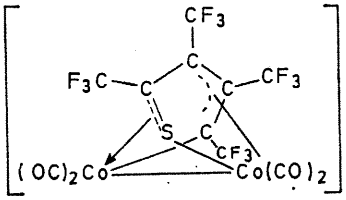
Substitution of the carbonyl groups in $[\{Fe(CO)_3(SCF_3)\}_2]$ by triphenylphosphine led to destabilisation of the axial positions.[17] Triphenylphosphine reacted with (IX; R = CF_3) to give the disubstituted derivative $[\{Fe(CO)_2(PPh_3)(SCF_3)\}_2\{C(CF_3)\text{:}C(CF_3)\}]$, (XI), without any trace of the monosubstituted derivative. From the i.r. spectrum the carbonyl ligands *trans* to the bridging olefin have been replaced but the solubility of the complex is too low in all solvents tried to allow the ^{19}F n.m.r. spectrum to be obtained and thus the isomer distribution investigated.

(d) *Reactions of* $[\{(cp)Co(SR)\}_2]$ (R = CF_3 *or* C_6F_5), $[(cp)Co(CO)(SC_6F_5)_2]$, *and* $[\{Co(CO)_3(SC_6F_5)\}_2]$.—The complexes $[\{(cp)Co(SR)\}_2]$[1] probably have very similar structures to the dimers $[\{Fe(CO)_3(SR)\}_2]$ but the reactions with hexafluorobut-2-yne are very different. There was no reaction, even with photolysis, at temperatures below 340 K but at 350 K a complicated mixture of products was obtained of which only $[(cp)Co\{C_6(CF_3)_6\}]$, (XII), [19,20] could be identified. This complex has recently been obtained [21] in low yield from the reaction between $[(cp)Co(CO)_2]$ and hexafluorobut-2-yne. The two products are spectroscopically identical although we found a rather higher m.p. than that described previously. Hexafluorobut-2-yne reacted with $[(cp)Co(CO)(SC_6F_5)_2]$ to give good yields of the known [22] cyclopentadienone complex $[(cp)Co\{C_4(CF_3)_4CO\}]$ and dipentafluorophenyl disulphide.



(XII)

Hexafluorobut-2-yne reacted with $[\{Co(CO)_3(SC_6F_5)\}_2]$ to give $[Co_2(CO)_4\{C_4(CF_3)_4S\}]$, (XII), and the known complexes $[\{Co(CO)_3\}_2\{C(CF_3)\text{:}C(CF_3)\}]$ [16] and $[Co_2(CO)_4\{C_6(CF_3)_6\}]$ [23] which have been previously prepared from dicobalt octacarbonyl and hexafluorobut-2-yne. *X*-Ray crystallography [24] has shown that (XIII) has a ' flyover ' structure with a SC_4 unit bridging between the cobalt atoms. The ' flyover ' consists of a η^3-allyl function bonded to one cobalt whilst the other cobalt atom is linked to a C–S moiety which apparently functions as a three-electron donor. Complex (XIII) gave a mass spectrum which contained weak ions with *m*/*e* values up to 650 suggesting that some recombination takes place in the spectrometer; the $[C_4(CF_3)_4S]^+$ ion was observed at *m*/*e* 356, but neither a molecular ion nor ions due to loss of CO from such an ion were observed.



(XIII)

DISCUSSION

The complexes described in the present study present several novel features from a structural viewpoint. Three-electron donor insertion products [(I), (VII), and probably (IV)] have not been specifically described previously although related complexes of the heteroligand CH_2SMe are known [25] and the ' flyover ' dicobalt complex (XIII) appears to contain a similar bond system.

The complexes containing η^4-C_4S units [(II), (III), (V), and (VIII)] are novel but these systems must be considered analogous to the cyclopentadienone complexes which are frequently formed during reactions of alkynes

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with metal carbonyl systems. We have recently reported[7] the formation of a similar η^4-C_4P system on reaction between an alkyne and a metal trifluorophosphine. Thiophen complexes, *e.g.* tricarbonyl(thiophene)chromium, have planar η^5 rings[26] rather than the envelope-shaped ligands of the complexes presented here. The formation of dimetallated olefins [(IX)—(XI)] from the interaction of alkynes and tricarbonyliron thiolate dimers has precedent in the formation of similar derivatives from reactions of $[MeAu(PPh_3)]$ and $[Ir(NO)(PPh_3)_3]$,[27] although the present complexes have additional thio-bridges. In the present study insertion of hexafluorobut-2-yne into a M–SR group gives only the *cis*-bis(trifluoromethyl)vinyl products (VI) although these reactions can give either *cis* or *trans* derivatives depending on the mechanism and the thermodynamic stability of the products.[14] The ' flyover ' complex (XIII) has analogies with $[Co_2(CO)_4\{C_6(CF_3)_3H_3\}]$[28] and ' flyover ' complexes containing sulphur or tellurium in the bridge are formed in reactions involving thiophen and tellurophen.[11,29]

The effect of reaction of the alkyne on the MSR_f group varies greatly throughout the series of metals studied. Insertion of the alkyne into the M–S group is clearly a favourable path for reaction although in the present series no initial η-alkyne complexes were identified. Group 6 thiolates, $[(cp)M(CO)_3(SR_f)]$, do form 16-electron alkyne complexes $[(cp)M(RC_2R')(CO)(SR_f)]$ with alkynes[30] and the dimetallated olefins (IX) and (X) undergo further reaction. A double insertion product of the type (IV) provides a ready path to the η^4-C_4S complexes although it is not clear whether the hetero η-allyl complexes, *e.g.* (I), are direct intermediates in the path to the heterocyclic ligands.

With all the elements studied there is a tendency to break the M–SR_f linkage and apart from insertion products there are also observed products containing no sulphur. Many of these result from reactions of alkynes with non-sulphur-containing carbonyl derivatives which have been formed by disproportionation of sulphur-containing species. The ultimate fate of the thio-group was not generally established although dipentafluorophenyl disulphide was isolated from the reactions of $[(cp)Co(CO)(SC_6F_5)_2]$. A sulphur atom was incorporated into the bridging system of a product from the reaction of $[\{Co(CO)_3(SC_6F_5)\}_2]$, implying ready cleavage of the S–C_6F_5 bond, but it is not clear at which stage of the reaction this cleavage occurred. The $[Co_2(CO)_4\{C_6(CF_3)_6\}]$ formed in this latter reaction is produced at a temperature some 50 °C below that at which it is obtained from $[Co_2(CO)_6\{C(CF_3){\vdots}C(CF_3)\}]$. The presence of the thiolate bridges clearly allow a facile path for the reaction of the alkyne.

EXPERIMENTAL

The preparations of the thiolate derivatives have been previously described;[1,3,4] $[\{Fe(CO)_3(SC_6F_5)\}_2]$[31] was prepared by irradiation of pentane solutions of $Fe_2(CO)_9$ and $F_5C_6SSC_6F_5$. The alkynes $C(CF_3){\vdots}C(CF_3)$ (P.C.R. Inc.) and $C(CF_3){\vdots}CH$ (Fluorochem Ltd.) were used as supplied.

I.r. spectra were recorded as solutions on Perkin-Elmer 225 or 457 spectrophotometers. Mass spectra were determined at 70 eV on an A.E.I. M.S.12 spectrometer.* N.m.r. spectra were recorded in CH_2Cl_2 (^{19}F) or $CDCl_3$ (^1H) solutions on Perkin-Elmer R10 (normal probe temperature, 307 K) or Jeol C60 (293 K) spectrometers; Me_4Si and CCl_3F were used as internal references. Analyses were by Bernhardt. Known derivatives were identified spectroscopically. All analytical and spectroscopic data for the complexes are in Supplementary Publication No. SUP 21457 (4 pp.).†

In a typical reaction *ca.* 0.4 g complex was transferred to a thick glass reaction vessel fitted with a Teflon stopcock. This was evacuated, cooled to 77 K, and pentane (*ca.* 15 cm^3) and the alkyne (*ca.* 2.5 g) condensed in. The reaction mixture was then allowed to warm slowly to room temperature and placed in an oven (or irradiated) at the temperature given in SUP 21457. The reaction was followed by i.r. spectroscopy in the $\nu(CO)$ and $\nu(CF)$ region until after several hours (see SUP 21457) the reaction stopped and the volatiles were removed *in vacuo*. The product was then extracted with methylene chloride, hexane added, and the solution centrifuged. Solvent was then removed slowly (under a stream of nitrogen) from the decanted solution to give the crystalline product. Repeated recrystallisation gave analytically pure samples. The complex $[Mn(CO)_3\{C_4(CF_3)_4S(CF_3)\}]$, (III), was chromatographed over Florisil eluted with pentane, and recrystallised from pentane at 249 K; $[(cp)Fe(CO)\{C(CF_3){\vdots}C(CF_3)SR\}]$, (VII), were chromatographed over Florisil and eluted with hexane–benzene (5 : 1). The product mixture from the reaction of $[\{Co(CO)_3(SC_6F_5)\}_2]$ and $C(CF_3){\vdots}C(CF_3)$ was chromatographed over Florisil and eluted with light petroleum to give three bands: (*a*) purple, $[Co_2(CO)_4\{C_6(CF_3)_6\}]$; (*b*) orange, $[Co_2(CO)_6\{C(CF_3){\vdots}C(CF_3)\}]$; (*c*) green, $[Co_2(CO)_4\{C_4(CF_3)_4S\}]$, (XIII). These were each collected and, following removal of solvent, products (*a*) and (*b*) sublimed at 313 K to give solids, identified by comparison of i.r. spectra with authentic samples;[16,23] (XIII) was recrystallised from pentane at 249 K.

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* 1 eV ≈ 1.60×10^{-19} J.

† For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1974, Index issue (items less than 10 pp. are supplied as full size copies).

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