Metal Perfluoro-alkyl- and -aryl-thiolates. Part II.[1] Molybdenum, Tungsten, Manganese, Iron, and Nickel Derivatives †

By **J. L. Davidson** and **D. W. A. Sharp,*** Department of Chemistry, University of Glasgow, Glasgow G12 8QQ

Photolytic reactions between disulphides and carbonyl derivatives produce unstable $Mn(CO)_5SR$ and $(\pi\text{-}C_5H_5)Ni(CO)SR$ ($R = CF_3$ or C_6F_5) which dimerise through decarbonylation. $(\pi\text{-}C_5F_5)Fe(CO)_2SCF_3$ undergoes decarbonylation to isomers of $[(\pi\text{-}C_5H_5)Fe(CO)SCF_3]_2$ on photolysis. The structures of the isomers and factors affecting tendencies to dimerisation are discussed. $[M(CO)_4SCF_3]_2$ (M = Mo and W) are formed by photolysis of $M(CO)_6$ and CF_3SSCF_3 using filtered radiation. Substitution of $[Fe(CO)_3SCF_3]_2$ by triphenylphosphine to produce $Fe_2(CO)_5(PPh_3)(SCF_3)_2$ and $[Fe(CO)_2(PPh_3)SCF_3]_2$ and by nitric oxide to produce $[Fe(NO)_2SCF_3]_2$ is described.

WE have recently[1] described the preparation of some transition metal trifluoromethylthio-derivatives by irradiating metal carbonyl compounds in the presence of bis(trifluoromethyl) disulphide. We now describe some new examples of this type of complex formed by the same method.

Bis(trifluoromethyl) disulphide has been previously shown[1,2] to react with dimanganese decacarbonyl to form the thio-bridged species $[Mn(CO)_4SCF_3]_2$. In a closed system trifluoromethylthiomanganese pentacarbonyl, $CF_3SMn(CO)_5$, is first formed but is unstable on standing without an atmosphere of carbon monoxide and decomposes to the bridged species with loss of carbon monoxide.

Although $CF_3SMn(CO)_5$ cannot be isolated pure, identification can be made by comparison of its i.r. and n.m.r. spectra with data for $CF_3SRe(CO)_5$ and $C_6F_5SMn(CO)_5$.[3,4] As for other compounds containing terminal CF_3S-groups,[4] there are only two bands in the C–F stretching region of the i.r. spectrum. Bis(pentafluorophenyl)disulphide reacts similarly to give the previously described[3] $C_6F_5SMn(CO)_5$ which also undergoes decarbonylation to $[Mn(CO)_4SC_6F_5]_2$; the irradiation method gives much higher yields of metal pentafluorophenylthiolate than were reported[3] for the reaction of pentafluorobenzenethiol and dimanganese decacarbonyl.

The monomeric carbonyl(π-cyclopentadienyl)nickel thiolates, $(\pi\text{-}C_5H_5)Ni(CO)SR$ ($R = CF_3$ or C_6F_5), are formed similarly when (π-cyclopentadienyl)nickel carbonyl dimer is irradiated with the appropriate disulphide in a closed system. In an open system carbon monoxide is lost and $[(\pi\text{-}C_5H_5)NiSR]_n$ formed (the formation of $[(\pi\text{-}C_5H_5NiSCF_3]_2$ from $[(\pi\text{-}C_5H_5)NiCO]_2$ proceeds in much greater yield than from bis(π-cyclopentadienyl)nickel).[1] It is, again, not possible to isolate the

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† No reprints available.

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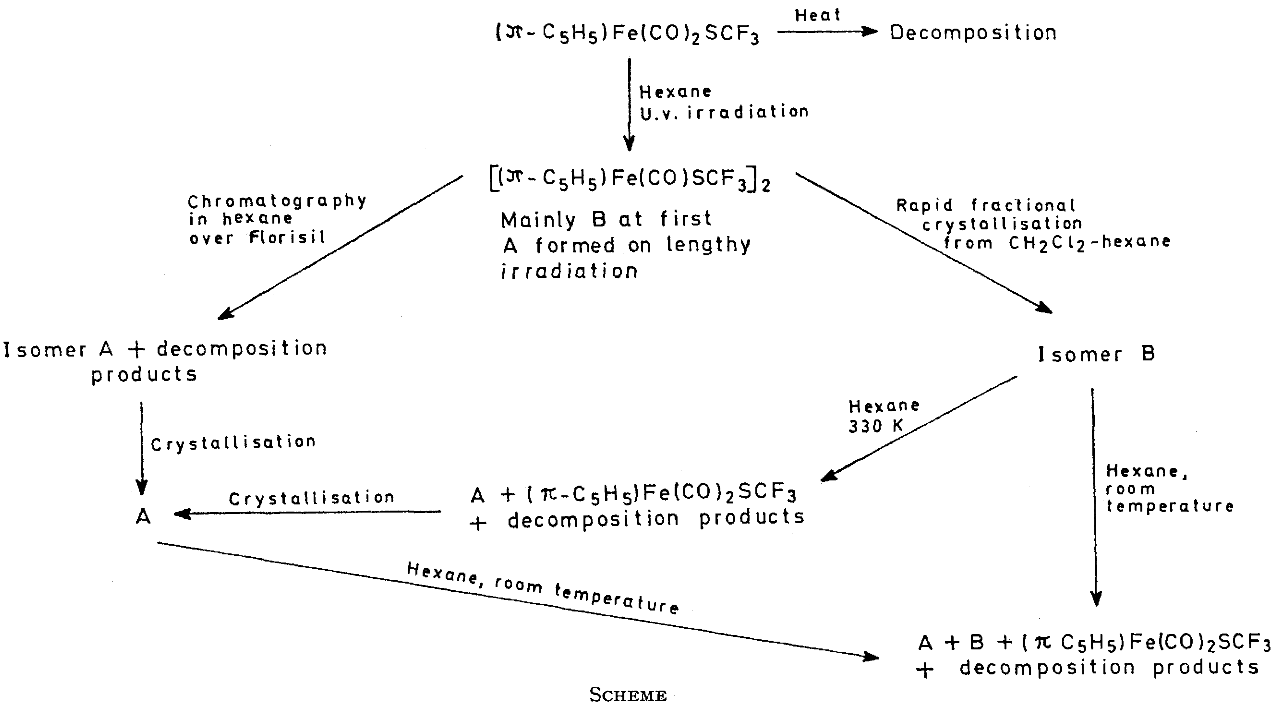
monomeric (π-C_5H_5)Ni(CO)SR species but identification was made by i.r. spectroscopy, the C–O stretching modes occurring at the frequencies expected by analogy with other (π-cyclopentadienyl)nickel carbonyl derivatives.[5] Monomeric (π-C_5H_5)Ni(CO)SR derivatives have not been reported previously although the (π-C_5H_5)Ni(CO)SeC_6F_5 derivative has been briefly mentioned.[6]

	I.r. spectral data/cm^{-1}		N.m.r. spectral data	
	Carbonyl region	C–F region	^{19}F *	^1H (τ)
$Mn(CO)_5SCF_3$	2134wm, 2052vs(br), 2012s	1129m, 1085s	+25·3	
(π-C_5H_5)Ni(CO)SCF_3	2047vs, 2012vw			
(π-C_5H_5)Ni(CO)SC_6F_5	2040vs			
[(π-C_5H_5)Fe(CO)SCF_3]$_2$ A	2000vs	1133mw, 1121m 1101wsh, 1089s	+37·4	5·39
B	1991vs, 1972s	1130wm(sh), 1119m 1994m(sh), 1087(vs)	+34·0	5·39
$[Mo(CO)_4SCF_3]_2$	2059s, 2019s, 1999vs	1155m, 1151sh 1091sh, 1055m	+40·5	
$[W(CO)_4SCF_3]_2$	2049s, 2004s, 1995vs	1162m, 1157sh 1092sh, 1083m	+43·1	
$Fe_2(CO)_5(PPh_3)(SCF_3)_2$	2064vs, 2016vs, 2000ms, 1968m	1121m, 1090sh, 1084m	*anti* +26·3 +36·3 *syn* +32·9	
$[Fe(NO)_2SCF_3]_2$	ν(NO) 1823vs, 1720vs	1157s, 1123vw, 1100w 1091m, 1081s	+23·0	

* *Chemical shift with respect to* CCl_3F *in p.p.m.*



SCHEME

Previous attempts[1] to decarbonylate bis(carbonyl)-(π-cyclopentadienyl)iron trifluoromethylthiolate, (π-C_5H_5)Fe$(CO)_2SCF_3$, by thermal methods as used for the analogous molybdenum and tungsten derivatives were unsuccessful.[1] However, it is now found that irradiation of the monomer in hexane with unfiltered u.v. light in an open system under nitrogen gives the sulphur-bridged species [(π-C_5H_5)Fe(CO)SCF_3]$_2$ as a mixture of two isomers (A) and (B). Separation of these two isomers may be effected by accidental methods (Scheme) depending upon their different reactivities. The species (A) and (B) are characterised as dimers by their i.r. and n.m.r. spectra (Table) and by other physical properties, particularly their mass spectra which show the molecular ion. Derivatives (π-C_5H_5)Fe$(CO)_2$SR (R = *e.g.* Me, Et, or Ph) readily undergo thermal and photolytic decarbonylation to give various isomers of sulphur-bridged dimers.[7,8] The Scheme demonstrates the ready reversible interconversion of isomers and also the ready

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carbonyl transfer with formation of monomers from dimers. It is also clear that dimers could never have been isolated (when R = CF_3) by thermal decarbonylation of the monomer.

It is not possible to make positive identification of the isomers (A) and (B). Both isomers show only one ^{19}F n.m.r. signal indicating either an equivalence of the CF_3 groups or an achievement of equivalence through fluxional behaviour. However, fluxional behaviour leading to equivalence of R groups in $[(\pi\text{-}C_5H_5)Fe(CO)SR]_2$ and $[Fe(CO)_3SR]_2$ derivatives has not yet been observed so that this possibility is excluded from the present argument. The ^1H n.m.r. spectra of isomers (A) and (B) show only one signal for the C_5H_5 groups. Isomer (A) shows a single CO stretching frequency in the i.r. spectrum whilst isomer (B) shows two such frequencies.

From the spectroscopic properties isomers (A) and (B) seem to be similar to those considered previously in other thio-[7,8] and seleno[9]-bridged systems. The various isomers possible in this type of system have been considered in some detail by Knox.[7,8] The $[(\pi\text{-}C_5H_5)Fe(CO)SMe]_2^+$ cation in the fluoroborate salt has *cis*-cyclopentadienyl groups with *cis*-carbonyls '*trans*' to the bridging sulphur atoms.[10] The i.r. spectrum of the hexafluoroantimonate contains two CO stretches in agreement with this geometry.[11] One isomer of $[(\pi\text{-}C_5H_5)Fe(CO)SPh]_2$ also has this conformation[12] but only one CO stretch is observed which is more compatible with an all *trans* conformation[8,9] in solution. Spectroscopic data for isomer (A) of $[(\pi\text{-}C_5H_5)Fe(CO)SCF_3]_2$ is compatible with structure (e) of Knox, the Fe_2S_2 ring probably being planar since this is an all *trans*-structure.[13] Spectroscopic data for isomer (B) are compatible with isomers (a) or (c) of Knox.

The tendencies of alkyl- or aryl-thiometal carbonyls to dimerise by decarbonylation reactions have been correlated with the electronegativity of the substituents on the sulphur and with the metal and its other substituents.[14] The (π-cyclopentadienyl)nickel monocarbonyl derivatives show greater tendencies to dimerise than the pentacarbonyl manganese compounds. However, in both the $Mn(CO)_5SR$ and $(\pi\text{-}C_5H_5)Ni(CO)SR$ series the pentafluorophenyl derivatives are more stable with respect to dimerisation than the trifluoromethyl derivatives. The relative electronegativities of the CF_3 and C_6F_5 groups would have suggested an opposite order and it must be concluded that steric effects, which would be greatest in the thio-bridged dimers, must also play an important part in stability as also in inhibiting nucleophilic attack of one monomer on another.[15] In agreement with this, neither thermal nor photolytic decarbonylation has yet been shown for $(\pi\text{-}C_5H_5)Fe(CO)_2SC_6F_5$[16,17] or $(\pi\text{-}C_5H_5)M(CO)_3SC_6F_5$ (M = Mo or W).[18]

Although thio-derivatives are known for π-cyclopentadienyl carbonyl derivatives of Group VI the corresponding metal carbonyl derivatives do not appear to have been described [heteronuclear derivatives, *e.g.* $(\pi\text{-}C_5H_5)_2Ti(SR)_2M(CO)_4$ have been prepared (M = Cr, Mo, or W)[19] and phosphido-bridged species are well known[20]].

Irradiation of Group VI hexacarbonyls with CF_3SSCF_3 in hexane using unfiltered radiation produced insoluble polymeric materials which were not characterised. In the case of chromium hexacarbonyl a transient purple colour was produced after four to five minutes but this disappeared on further irradiation. By using a filtered u.v. source the complexes $[M(CO)_4SCF_3]_2$ (M = Mo or W) were obtained but it proved impossible to obtain $[Cr(CO)_4SCF_3]_2$ either photolytically or by an attempted thermal reaction at 370 K. The species $[M(CO)_4SCF_3]_2$ must be formulated with a metal–metal bond.

It was of interest to examine the reactions of transition metal trifluoromethylthiolates with other ligands to investigate the stability of the metal–sulphur bond systems. Substitution,[1,21] bridge-cleavage,[1,21] and complete expulsion[22] of the thio-group can occur. Triphenylphosphine reacts with $[Fe(CO)_3SCF_3]_2$ to give $Fe_2(CO)_5(PPh_3)(SCF_3)_2$ in a *syn* : *anti* isomer ratio of 1 : 4 as an intractable red oil that can only be characterised by spectroscopic methods. As mentioned previously,[1] further substitution gives $[Fe(CO)_2(PPh_3)SCF_3]_2$ in a *syn* : *anti* ratio of 1 : 1. Further substitution was not observed under the conditions used. The i.r. spectra of these derivatives indicate[23] that the carbonyl groups *trans* to the metal–metal bond have been replaced. The *syn*-isomer in these species is likely to be *equatorial–equatorial*[24] so that bulky triphenylphosphine ligands in the positions indicated should favour the isomer with no *axial* substituents as is found.

Nitric oxide effects complete substitution of CO in $[Fe(CO)_3SCF_3]_2$ and $[Fe(NO)_2SCF_3]_2$ is formed without detection of intermediates. A similar reaction has been observed for $[Fe(CO)_3NH_2]_2$[25] but this does not appear to be a general route to such nitrosyl derivatives since

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there is no reaction between nitric oxide and $[Fe(CO)_3PMe_2]_2$.[26]

EXPERIMENTAL

Manipulation of materials was carried out under dry oxygen-free nitrogen in a Lintott inert atmosphere box. Hydrocarbon solvents were dried over sodium and deaerated before use. Unless stated otherwise, photolytic reactions were carried out in a Pyrex reaction flask irradiated by a Hanovia medium pressure mercury lamp, the reaction mixtures being stirred magnetically. Analyses are by Bernhardt. ^1H and ^{19}F N.m.r. spectra were taken at 60 and 56·4 MHz respectively on a Perkin-Elmer R10 spectrometer in $CDCl_3$ and CH_2Cl_2 solution with Me_4Si and CCl_3F as internal standards. I.r. spectra were recorded in hexane solution on a Perkin-Elmer 457 spectrophotometer calibrated against water vapour. Mass spectra were recorded on an A.E.I. MS 12 mass spectrometer at 70 eV with probe inlet (temperature *ca.* 370 K). M.p.s are uncorrected.

$[Mn(CO)_5]_2$, $Cr(CO)_6$, $Mo(CO)_6$, and $[(\pi\text{-}C_5H_5)NiCO]_2$ were obtained commercially (Strem Chemicals Inc.) as was CF_3SSCF_3 (Peninsular Chem. Research Inc.). $(\pi\text{-}C_5H_5)Fe(CO)_2SCF_3$ and $[Fe(CO)_3SCF_3]_2$ were prepared as described previously.[1]

Trifluoromethylthiomanganese Pentacarbonyl.—$[Mn(CO)_5]_2$ (1 g) and CF_3SSCF_3 (1 g) in pentane (*ca.* 50 ml) were irradiated for 24 h. The flask and contents were cooled to 263 K when, from the i.r. spectrum, the sample contained pure $Mn(CO)_5SCF_3$. Volatile materials were removed under vacuum at 263 K. The residue was dissolved in cold CH_2Cl_2, centrifuged and cold hexane added to the solution. Crystallisation was effected at 263 K by removing solvent with a stream of nitrogen to give a mixture of $[Mn(CO)_4SCF_2]_2$ and $Mn(CO)_5SCF_3$. The monomer is more soluble than the dimer. The monomer appears to be a pale yellow solid. It decomposed slowly in the solid state (rapidly in solution) to the dimer with carbon monoxide evolution. Total yield, $Mn(CO)_5SCF_3$ plus $[Mn(CO)_4SCF_3]_2$ *ca.* 90%.

Pentafluorophenylthiomanganese Pentacarbonyl.—Obtained in 92% yield by the same method as used for the trifluoromethyl derivative.

Cyclopentadienyl(carbonyl)nickel Trifluoromethylthiolate and Pentafluorophenylthiolate.—Dark red solutions were obtained on irradiation of $[(\pi\text{-}C_5H_5)NiCO]_2$ (*ca.* 1 g) in the presence of excess of disulphide in pentane for 25 h, but all attempts to isolate the solid monomers were unsuccessful, and only $[(\pi\text{-}C_5H_5)NiSR]_n$ were obtained in *ca.* 90% yield. The solution contained small amounts of a further species giving rise to carbonyl absorption near 2100 cm^{-1} but these species could not be isolated or identified.

Cyclopentadienyl(carbonyl)iron Trifluoromethylthiolate Dimer.—$(\pi\text{-}C_5H_5)Fe(CO)_2SCF_3$ (0·35 g) in hexane (*ca.* 100 ml) was irradiated with unfiltered u.v. light in an open stirred system under nitrogen for 30 h. The solution was centrifuged and solvent removed in a stream of nitrogen to give olive-green crystals of $[(\pi\text{-}C_5H_5)Fe(CO)SCF_3]_2$ yield *ca.* 72%. The product contained mainly isomer B with a small amount of A and pure B was obtained by fractional crystallisation from hexane. Pure A was obtained as shown in the Scheme and also different relative yields of (A) and (B) were found depending upon the time of irradiation {Found for *isomer* (*A*) of *cyclopentadienyl*(*carbonyl*)*iron trifluoromethylthiolate dimer*: C, 33·6; H, 2·0; F, 22·8; Fe, 22·4; S, 12·8; *M*, 500 (mass spec.), m.p. >386 K (with decomposition). $[C_7H_5F_3FeOS]_2$ requires C, 32·9; H, 1·7; F, 23·5; Fe, 21·9; S, 12·6%; *M*, 500. Found for *isomer* (*B*): C, 33·1; H, 2·1; F, 23·4; Fe, 22·8; S, 12·5%; *M*, 500, m.p. 377 K (decomp.)}.

Tetracarbonylmetal Trifluoromethylthiolate Dimers (*Molybdenum and Tungsten*).—Metal hexacarbonyl (0·3 g) and CF_3SSCF_3 (0·5 g) in pentane (50 ml) were irradiated with filtered u.v. light (Chance–Pilkington Colour Filter O X 9A) for 40 h to give dark blue solutions. Volatile materials were removed and the residue dissolved in hexane and chromatographed over silica gel with hexane as eluant. In each case unreacted hexacarbonyl was eluted first followed by a single green band which on crystallisation from hexane gave dark blue $[M(CO)_4SCF_3]_2$. Yield: $M = Mo$, 5·5%; $M = W$, 8·0% {Found for *tetracarbonylmolybdenum trifluoromethylthiolate dimer* (decomposition temperature 363 K): C, 19·1; F, 17·8; Mo, 30·6; S, 10·2; *M*, 618 (mass spec.). $[C_5F_3MoO_4S]_2$ requires C, 19·4; F, 18·4; Mo, 31·1; S, 10·4%; *M*, 618. Found for *tetracarbonyltungsten trifluoromethylthiolate dimer* (decomposition temperature 381 K): C, 15·6; F, 14·0; S, 7·8; W, 45·5; *M*, 794 (mass spec.). $[C_5F_3O_4SW]_2$ requires C, 15·1; F, 14·4; S, 8·1; W, 46·3%; *M*, 794}.

Pentacarbonyltriphenylphosphinedi-iron Bis(*trifluoromethylthiolate*).—$[Fe(CO)_3SCF_3]_2$ (0·25 g) was dissolved in pentane (10 ml) and an equimolar quantity of PPh_3 in pentane (20 ml) added under nitrogen. Immediate carbon monoxide evolution was observed and, after shaking the solution for *ca.* 30 min in a sealed flask, i.r. and ^{19}F n.m.r. spectra indicated the complete formation of $Fe_2(CO)_5PPh_3(SCF_3)_2$. Solvent removal gave a red oil, identified spectroscopically, which could not be crystallised.

Dinitrosyliron Trifluoromethylthiolate Dimer.—$[Fe(CO)_3SCF_3]_2$ (0·3 g) was dissolved in pentane cooled to 77 K and nitric oxide condensed in and the flask allowed to stand at room temperature for 12 h with shaking, during which time carbon monoxide was evolved. After removal of volatile materials *dinitrosyliron trifluoromethylthiolate dimer* was sublimed in a 72% yield, m.p. 324 K [Found: C, 5·2; F, 26·9; Fe, 25·4; S, 14·4; *M*, 434 (mass spec.). $CF_3FeN_2O_2S$ requires C, 5·5; F, 26·3; Fe, 25·8; S, 14·7%; *M*, 434].

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