The Formation of Some Transition Metal Trifluoromethylthio-derivatives

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Bis(trifluoromethyl) disulphide under photolysis with some organometallic compounds in low oxidation states gives trifluoromethylthio-derivatives. On reaction with further ligands the trifluoromethylthio-group remains co-ordinated. The new compounds (cp)Mo$(CO)_3SCF_3$, (cp)W$(CO)_3SCF_3$, $[Fe(CO)_3SCF_3]_2$, $[Fe_2(CO)_6SCF_3]_2S$, $[(cp)NiSCF_3]_2$, $[(cp)Mo(CO)_2SCF_3]_2$, $[Fe(CO)_2PPh_3SCF_3]_2$, and (cp)$NiPPh_3SCF_3$ are reported.

On photolysis in Pyrex apparatus bis(trifluoromethyl) disulphide gives adducts and telomers with olefins in reactions which may be explained in terms of the presence of trifluoromethylthio, $CF_3S\cdot$, radicals.[1] We now report the synthesis of trifluoromethylthio–metal derivatives by the photoinduced reaction between bis(trifluoromethyl) disulphide and complexes of metals in low oxidation states. The compounds prepared in the present work are listed in Table 1 which contains analytical data and references to previous preparations of the particular trifluoromethylthio-derivatives. In each case there appeared to be little or no reaction in the absence of photochemical initiation (see also ref. 2). Previous preparations of metal trifluoromethanethiolates have involved metathetical reactions between silver trifluoromethanethiolate, $AgSCF_3$, and an appropriate halide[3] and thermal cleavage of trifluoromethylthio derivatives, CF_3SX [X = SCF_3, SCH_3, Cl, $P(CF_3)_2$] in the presence of metal carbonyls.[4] It is probable that all these reactions proceed through intermediate trifluoromethylthio radicals, although in the present case the formation of active organometallic species by photochemical decarbonylation is clearly a further possible route. Once formed, the metal trifluoromethanethiolates are stable and other groups are substituted in preference to the trifluoromethylthio-group.

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[1] G. Haran and D. W. A. Sharp, *J.C.S. Perkin I*, in the press.

[2] R. B. King, *J. Amer. Chem. Soc.*, 1963, **85**, 1584.

[3] R. B. King and N. Welcman, *Inorg. Chem.*, 1969, **8**, 2540; R. B. King and A. Efraty, *ibid.*, 1971, **10**, 1376.

[4] J. Grobe and F. Kober, *J. Organometallic Chem.*, 1970, **24**, 191.

The simple trifluoromethylthio-derivatives are the major products of the reactions but the formation of other derivatives suggests that further reaction of the CF_3S radicals or alternative modes of breakdown of the bis(trifluoromethyl) disulphide are also possible. Sulphide derivatives are formed indicating C–S cleavage; irradiation of bis(trifluoromethyl) disulphide in quartz yields bis(trifluoromethyl) sulphide and sulphur.[5] The formation of a non-sulphur-containing species from the reaction between octacarbonyldicobalt and bis(trifluoromethyl) disulphide is unexpected and would seem to indicate SF_2 elimination from a CF_3S radical. Bis(pentafluorophenylthio) disulphide reacts with cobalt carbonyl (without heating or irradiation) to give a product in which the S–S bond has been retained.[6]

TABLE 1

Material irradiated in the presence of CF_3SSCF_3	Products	Yield (%) based on organometallic	Colour	M.p. (K)	Analyses (Calculated figures in parentheses)					
					C	H	F	S	Metal	M [a]
$[(cp)Mo(CO)_3]_2$	$(cp)Mo(CO)_3SCF_3$	28	Yellow	343—347 (dec.)	31·6	1·5	16·8	9·2	27·9	346 (346)
					(31·2)	(1·4)	(16·5)	(9·2)	(27·8)	
$(cp)Mo(CO)_3I$	$(cp)Mo(CO)_3SCF_3$	28								
$[(cp)W(CO)_3]_2$	$(cp)W(CO)_3SCF_3$	31	Yellow	378—381	25·2	1·0	13·4	7·5	42·7	434 (434)
					(24·9)	(1·2)	(13·1)	(7·4)	(42·4)	
$Mn_2(CO)_{10}$	$[Mn(CO)_4SCF_3]_2$ [b]	51								
$Fe_2(CO)_9$	$[Fe(CO)_3SCF_3]_2$	30	Red	350	20·1		24·0	13·2	22·9	482 (482)
					(19·9)		(23·6)	(13·3)	(23·2)	
	$Fe_4(CO)_{12}S(SCF_3)_2$	0·5	Red	407—408	Insufficient sample available					792 (792)
	$[Fe(CO)_3S]_2$ [c]	0·3								
	$[Fe(CO)_3]_3S_2$ [c]	0·1								
$Fe(CO)_5$	$[Fe(CO)_3SCF_3]_2$	26								
	$Fe_4(CO)_{12}S(SCF_2)_2$	0·5								
$[(cp)Fe(CO)_2]_2$	$(cp)Fe(CO)_2SCF_3$ [d]	55								
$(cp)Fe(CO)_2Cl$	$(cp)Fe(CO)_2SCF_3$ [d]	37								
$Co_2(CO)_8$	$Co_3(CO)_9CF$ [e]	23								
	$[Co_2(CO)_5S]_n$ [c]	Trace								
$(cp)_2Ni$	$[(cp)NiSCF_3]_2$	47	Purple-black	390—396 (dec.)	32·4	2·1	25·1	14·2	26·4	448 (448)
					(32·1)	(2·2)	(25·4)	(14·3)	(26·1)	
	$[(cp)Mo(CO)_2SCF_3]_2$	46	Brown	436—440 (dec.)	31·0	1·8	16·8	9·8		
					(30·2)	(1·6)	(17·9)	(10·1)		
	$[Fe(CO)_2PPh_3SCF_3]_2$ [g]	89	Red-black	450—452	53·5	3·2	11·2	11·6	6·0	
					(53·1)	(3·2)	(11·8)	(12·0)	(6·5) [i]	
	$(cp)NiPPh_3SCF_3$ [h]	85	Orange-yellow	415 (dec.)	57·5	4·1	11·2	6·2	6·8	
					(58·0)	(4·1)	(11·7)	(6·4)	(6·4) [i]	

[a] Molecular weight from peak with highest m/e in mass spectrum. [b] Previously prepared, refs. 4 and 10. [c] Ref. 7. [d] Ref. 3. [e] Previously prepared by W. T. Dent, L. A. Duncanson, R. G. Guy, H. W. B. Reed, and B. L. Shaw, *Proc. Chem. Soc.*, 1961, 169; and R. Ercoli, E. Santambrogio, and G. T. Casagrande, *Chim. Ind.* (*Milan*), 1962, **44**, 1344. [f] Prepared by decarbonylation of $(cp)Mo(CO)_3SCF_3$ at 360 K. [g] Prepared by the action of triphenylphosphine on $[Fe(CO)_3SCF_3]_2$. [h] Prepared by the action of triphenylphosphine on $[(cp)NiSCF_3]_2$. [i] Phosphorus analysis.

TABLE 2

Compound	I.r. spectrum (cm^{-1})		^{19}F N.m.r. spectrum (chemical shift with respect to CCl_3F) p.p.m.
	Carbonyl region	C–F region	
$(cp)Mo(CO)_3SCF_3$	2048vs, 1981vs, 1966vs	1111m, 1087s, 1059w	+26·2
$(cp)W(CO)_3SCF_3$	2041vs, 1981vs, 1966vs	1113m, 1079s, 1960w	+27·0
$[Fe(CO)_3SCF_3]_2$	2099m, 2062vs, 2027s, 2020s	1153m, 1100msh, 1095m, 1081s	+22·7, +34·3 (*anti*-isomer)
$[Fe_2(CO)_6SCF_3]_2S$	2099m, 2072s, 2057vs, 2023s, 2014s	1159m, 1152m, 1091s, 1064w	+32·4 (*syn*-isomer)
$[(cp)NiSCF_3]_2$		1129m, 1122m, 1090msh, 1083s	+27·7 (*syn*-isomer)
$[(cp)Mo(CO)_2SCF_3]_2$	1958s, 1896s	1142m, 1131m, 1098m, 1087s	+40·6 (*syn*-isomer)
$[(cp)W(CO)_2SCF_3]_2$ [a]	1941s, 1891s	1147m, 1133m, 1093msh, 1085s	
$[Fe(CO)_2PPh_3SCF_3]_2$	2067vw, 2017vs, 1979m, 1962s	1140msh, 1133m, 1098m, 1080s	+21·9, +31·9 (*anti*-isomer); +28·9 (*syn*-isomer) (isomer ratio *ca.* 1 : 1)
$(cp)NiPPh_3SCF_3$		1095s, 1083s, 1075ssh	

[a] The species has not been isolated (see text).

Decarbonylation of $(cp)Mo(CO)_3SCF_3$ proceeds readily to form the dimer but isolation of the corresponding dimeric tungsten compound was not achieved although the i.r. spectrum of a sample of $(cp)W(CO)_3SCF_3$ which had been heated at 350 K for 4 h showed, in addition to unchanged starting material, the presence of a small amount of a compound with an i.r. spectrum almost identical to that of the dimeric molybdenum complex. Attempts to decarbonylate $(cp)Fe(CO)_2SCF_3$ were unsuccessful.

Spectroscopic studies indicate that the structures of

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[5] G. A. R. Brandt, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 1952, 2198.

[6] G. Bor and G. Natile, *J. Organometallic Chem.*, 1971, **26**, C33.

the trifluoromethylthio-derivatives prepared in this work are clearly analogous to the structures of corresponding alkylthio- and arylthio-derivatives.[7] Where two bridging trifluoromethylthio-groups are present there is the possibility of *syn*- and *anti*-isomers. N.m.r. spectroscopy (Table 2) is helpful in assigning structures which are probably as indicated in Table 2 although the observation of one ^{19}F signal only could be consistent with flexing of the molecule rather than presence of the *syn*-form.[8] Only in the case of $[Fe(CO)_2SCF_3PPh_3]_2$ are two isomeric forms identified in the product mixture. $[Fe_2(CO)_6SCF_3]_2S$, which is one of the products from the reaction between iron carbonyls and bis(trifluoromethyl) disulphide, has a very similar i.r. spectrum to $[Fe_2(CO)_6SCH_3]_2S$ (which has a structure with two $Fe_2(CO)_6SCH_3$ fragments bridged by a sulphur atom) [9] and is formulated, therefore, with a similar structure. The presence of only one ^{19}F n.m.r. resonance suggests that the bridging SCF_3 groups have the *syn*-configuration. It was surprising that $Fe_2(CO)_6S_3(CF_3)_2$, which has been previously claimed [10] to result from the thermal reaction between pentacarbonyliron and CF_3SX compounds under a pressure of carbon monoxide was not found as one of the products of the present photo-induced reactions. The C–F stretching region of the i.r. spectra show clear differences [3] between those complexes which would be formulated with bridging SCF_3 groups and those which clearly have terminal groups.

EXPERIMENTAL

All materials and reactions were handled under a dry nitrogen atmosphere, hydrocarbon solvents were dried over sodium and deaerated before use. Reactions were carried out in Pyrex flasks fitted with Teflon stopcocks; the contents of the flasks were stirred magnetically and were irradiated by a Hanovia medium-pressure mercury arc lamp. Analyses are by Bernhardt. ^{19}F N.m.r. spectra of dichloromethane solutions were measured on a Perkin-Elmer R10 spectrometer at 56·4 MHz using CCl_3F as internal reference. I.r. spectra were measured in hexane and carbon disulphide on a Perkin-Elmer 457 spectrometer; mass spectra on an A.E.I. MS12 spectrometer at 70 eV. Previously known products were identified by comparison of the i.r. and n.m.r. spectra with those previously reported.

CF_3SSCF_3, $Mn_2(CO)_{10}$, $Fe(CO)_5$, $Fe_3(CO)_9$, $[(cp)Fe(CO)_2]_2$, and $Co_2(CO)_8$ were commercial samples (Strem Chemicals). $[(cp)Mo(CO)_3]_2$,[11] $(cp)Mo(CO)_3I$,[12] $[(cp)W(CO)_3]_2$, $(cp)Fe(CO)_2Cl$,[13] and $(cp)_2Ni$ [14] were prepared by standard methods.

In a typical reaction metal complex (2 g) and an excess of bis(trifluoromethyl) disulphide were irradiated and stirred in hexane (50 ml) at room temperature for several hours. Solvent and unchanged disulphide were removed at 300 K under reduced pressure and the product was sublimed from the residue *in vacuo* onto a probe at 77 K. In the case of the reactions with iron carbonyls, $[Fe(CO)_3SCF)_3]_2$ was separated by sublimation at 303 K (0·01 mmHg) and the remaining products were separated by chromatography on an activated alumina column.

We thank the S.R.C. for a maintenance award.

[1/1608 *Received, September 6th*, 1971]

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[8] M. Ahmad, R. Bruce, and G. Knox, *Z. Naturforsch.*, 1966, **21***b*, 289.

[9] J. M. Coleman, A. Wojcicki, P. J. Pollick, and L. F. Dahl, *Inorg. Chem.*, 1967, **6**, 1236; J. A. DeBeer and R. J. Haines, *J. Organometallic Chem.*, 1970, **24**, 757.

[10] J. Grobe and F. Kober, *Z. Naturforsch.*, 1969, **24***b*, 1346.

[11] *Inorg. Synth.*, VII, 99.

[12] E. W. Abel, Apar Singh, and G. Wilkinson, *J. Chem. Soc.*, 1960, 1321.

[13] F. A. Cotton, A. D. Liehr, and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1955, **1**, 175.

[14] J. F. Cordes, *Chem. Ber.*, 1962, **95**, 3084.