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PHOTOINDUCED REACTIONS OF $(CF_3S)_3N$ AND $CF_3SeSeCF_3$ WITH $Mn_2(CO)_{10}$ AND $Fe(CO)_5$

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Summary

Tris(trifluoromethylmercapto)amine, $N(SCF_3)_3$, and bis(trifluoromethyl)diselenide, $(SeCF_3)_2$, produce $\cdot ECF_3$ radicals (E = S, Se) under UV irradiation, and these react with metal carbonyl radicals $\cdot M(CO)_n$ (M = Mn, $n = 5$; M = Fe, $n = 4$) to give ultimately $[M(CO)_{n-1}(ESF_3)]_2$. The compounds have been characterised by elemental analysis, IR, NMR and mass spectral studies. The mass spectra of the trifluoromethylselenium derivatives are discussed.

Introduction

On photolysis in Pyrex apparatus tris(trifluoromethylmercapto)amine produces $\cdot N(SCF_3)_2$ and $\cdot SCF_3$ radicals [1] and bis(trifluoromethyl)disulfide produces $\cdot SCF_3$ radicals [2,3]. It was thought to be of interest to try to trap $\cdot N(SCF_3)_2$ with metal carbonyl radicals viz., $\cdot M(CO)_n$ (M = Mn, $n = 5$; M = Fe, $n = 4$), and also to see whether bis(trifluoromethyl)diselenide gives rise to compounds which could be explained in terms of the presence of $\cdot SeCF_3$ radicals. We describe below our studies of the reaction of $N(SCF_3)_3$ and $(SeCF_3)_2$ with $Mn_2(CO)_{10}$ and $Fe(CO)_5$.

Experimental

All manipulations were carried out under nitrogen or argon. Solvents were distilled before use. Analyses were performed by the Analytical Laboratories of this institute. IR spectra were recorded on a Perkin—Elmer 125 spectrometer in n-hexane solution. ^{19}F NMR spectra in n-pentane or CH_2Cl_2 were recorded on a Bruker HX-60/5 spectrometer at 60 MHz using CCl_3F as an internal standard. Mass spectrometric measurements were made on a CH-5 Varian MAT mass spectrometer at 70 eV electron energies.

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TABLE 1

YIELD ANALYTICAL AND SPECTRAL DATA

Product	Yield (%)	Analysis found (calcd.) (%)				^{19}F NMR (ppm)	ν(CO) (cm^{-1})	ν(CF) (cm^{-1})	Mol. wt. (by mass spectry.)
		X	S	F	Metal				
$[Mn(CO)_4(SCF_3)]_2$	78	22.51 (22.40)	12.08 (11.96)	21.87 (21.26)	20.91 (20.50)	34.2	2098m, 2040s, 2027vs, 1996s	1145s, 1130m, 1085s	536
$[Fe(CO)_3(SCF_3)]_2$	59	20.12 (19.94)	13.85 (13.31)	23.85 (23.66)	23.51 (23.17)	*anti* 35.1 23.3 *syn* 31.1	2097m, 2059vs, 2024s, 2020s	1152m, 1098s, 1079vs	482
$[Mn(CO)_4(SeCF_3)]_2$	67	19.61 (19.06)			17.82 (17.45)	28.9	2098s, 2057vs, 2022vs, 1970vs	1138vs, 1089vs 1050s	362
$[Fe(CO)_3(SeCF_3)]_2$	73	16.79 (16.69)			19.62 (19.40)	27.8	2093vs, 2051vs, 2010vs	1142s, 1078vs, 1052s	578

A typical photoinduced reaction

Metal carbonyl and $N(SCF_3)_3$ or $(SeCF_3)_2$ in 1 : 2 mole proportions were irradiated in a Pyrex glass bomb for 12—15 h at room temperature in presence of a minimum amount of CH_2Cl_2-n-hexane (1 : 1) solution. The Pyrex tube was then cooled at —196° C and the generated CO was pumped off through a vacuum line. The tube was warmed to 0° C. The crystalline compound obtained was filtered and purified by recrystallisation from CH_2Cl_2/n-hexane or by sublimation. The analytical data, yield, IR data for ν(CO) and ν(CF) regions, and ^{19}F NMR data are set out in Table 1.

Results and discussion

On photolysis $N(SCF_3)_3$ decomposes to $\cdot N(SCF_3)_2$ and $\cdot SCF_3$ radicals; information on this decomposition has already been reported [1,4]. With a view to trapping $\cdot N(SCF_3)_2$ radicals, photoinduced reactions of $N(SCF_3)_3$ with $Mn_2(CO)_{10}$ or $Fe(CO)_5$ have been carried out, but in both cases only SCF_3 derivatives of metal carbonyls were obtained. Changing the conditions, (solvent, time of irradiation etc.) did not bring about any significant trapping of $\cdot N(SCF_3)_2$. Failure to obtain $N(SCF_3)_2$ derivatives of metal carbonyls, however, does not rule out the possibility of the existence of $\cdot N(SCF_3)_2$ radicals, since it is possible that because of the presence of highly electronegative SCF_3 groups, the nitrogen of $N(SCF_3)_2$ acts as a very poor donor towards metal atoms. Moreover the nitrogen does not possess any acceptor properties making it difficult to function as a ligand. In view of the products a tentative mechanism of the reactions can be formulated as follows:

$$2\,N(SCF_3)_3 \rightarrow 2[\cdot N(SCF_3)_2] + 2(\cdot SCF_3)$$
$$2\,[\cdot N(SCF_3)_2] \rightarrow 4\cdot SCF_3 + N_2 \ [1]$$
$$2\cdot M(CO)_n + 2\cdot SCF_3 \rightarrow 2\,[(CO)_nM\cdot SCF_3]$$
$$2\,[(CO)_nMSCF_3] \rightarrow [M(CO)_{n-1}SCF_3]_2 + 2\,CO$$

(M = Mn, n = 5; M = Fe, n = 4)

UV irradiation of bis(trifluoromethyl)diselenide gives rise to the formation of $SeCF_3$ derivatives of metal carbonyls, which can be explained in terms of the formation of $\cdot SeCF_3$ radicals. Like its thioanalogue $SeCF_3$ reacts with $\cdot M(CO)_n$ radicals (M = Mn, n = 5; M = Fe, n = 4), and produces $[M(CO)_n(SeCF_3)]$, which because of its instability, dimerises to $[M(CO)_{n-1}(SeCF_3)]_2$ with the expulsion of CO groups.

The IR spectra of $[M(CO)_{n-1}ECF_3]_2$ (E = S, Se) in the ν(C—F) region show frequencies characteristic of bridging ECF_3 groups [5]. Since there is no absorption in the bridging CO region it is safe to assume that only terminal CO groups are present. From the typical pattern of the ν(CO) bands it appears that the manganese complexes structures similar to those of the analogous halides $[Mn(CO)_4X]_2$ [6] and the iron complexes structures similar to that of $[Fe_2(CO)_6S_2]$ [7].

Appearance of a sharp singlet in the ^{19}F NMR spectra of $[Mn(CO)_4ECF_3]_2$ and $[Fe(CO)_4SeCF_3]_2$ suggests that the SCF_3 and $SeCF_3$ groups are equivalent in the respective complexes and the complexes are diamagnetic. For $[Fe(CO)_3$-$(SCF_3)]_2$ the sharp signals at 35.1 and 23.3 ppm are assumed to be due to its *anti*-isomer and that at 31.1 ppm can been ascribed to the presence of *syn*-isomer. This feature of this compound has been noted by others [2].

The mass spectra of $[Mn(CO)_4SeCF_3]_2$ and $[Fe(CO)_3SeCF_3]_2$ are of interest and characteristic features of the mass spectra of $SeCF_3$ derivatives have been noted. The spectrum of $[Fe(CO)_3SeCF_3]_2$ is taken as a typical example. Its mass spectrum shows molecular ion at *m/e* 578, which undergoes successive loss of six carbonyl groups to give the series of ions $(CF_3Se)_2Fe_2(CO)_n^+$ (n = 6, 5, 4, 3, 2, 1 and 0). A peak due to the ion $CF_3SeFe_2F^+$ at *m/e* 300 indicates the ease of a fluorine shift from carbon to the metal atom somewhat similar to the formation of Cp_2TiF_2 from Cp_2TiCl_2 and $AgSCF_3$ [5]. In going from $Fe_2(SeCF_3)_2^+$ to $CF_3SeFe_2F^+$ a loss of $SeCF_2$ fragment is involved, and ionization of this fragment would lead to $SeCF_2^+$, which appears as one of the strongest ions (*m/e* = 130) in the mass spectra of $[Mn(CO)_4SeCF_3]_2$ and $[Fe(CO)_3SeCF_3]_2$. Moreover, very recently the simple molecule $SeCF_2$ has been isolated from pyrolysis of $B(SeCF_3)_3$ [8,9], which is consistent with the present mass spectral observations.

The presence of the ions $Fe_2(CO)_nSe_2^+$ (n = 6, 5, 4 and 1) at *m/e* 440, 412, 384 and 300 and the ions $Fe_2(CO)_nSe^+$ (n = 3 and 2) at *m/e* 276 and 248 indicates that cleavage of the F_3C—Se bond can compete with loss of CO groups. The observation of the ions $Fe_2(CO)_n^+$ (n = 6, 3, 2, 1 and 0) at *m/e* 280, 196, 168, 140 and 112 suggests that complete rupture of the metal—selenium bond can also compete with loss of the carbonyl groups and relatively strong iron—iron bonding must also be present in the molecule, which is consistent with the structure assumed.

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