Organosulphur–Transition-metal Chemistry. Part 1. Reactions of Carbon Disulphide with Metal Carbonyl Anions

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The trithiocarbonato-complex $[N(PPh_3)_2][Mn(CO)_4(S_2CS)]$ is formed in high yield on treatment of $[N(PPh_3)_2]$-$[Mn(CO)_5]$ with CS_2 in tetrahydrofuran (thf) over 4 d. Reactions also occur between CS_2 and the iminium salts of $[Re(CO)_5]^-$ and $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ but no products have been isolated. Methylation of $[N(PPh_3)_2]$-$[Mn(CO)_4(S_2CS)]$ with either MeI or $SFO_2(OMe)$ gives $[Mn(CO)_4(S_2CSMe)]$ in *ca.* 40% yield, but $GeBrMe_3$ or $[PhN_2][BF_4]$ provide $[Mn(CO)_4(S_2CSMe)]$ and $[Mn(CO)_4(S_2CSPh)]$, respectively, in only small amounts. Low (<10%) yields of trithiocarbonato-complexes are produced when thf solutions of sodium salts of $[M(CO)_5]^-$ (M = Mn or Re), $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$, $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$, and $[M(CO)_4]^{2-}$ (M = Fe, Ru, or Os) are treated with CS_2 and MeI consecutively. Very small amounts of dimetal complexes $[(OC)_4M(\mu\text{-}S_2CS)M(CO)_5]$ (M = Mn or Re) have also been isolated from reactions of $[M(CO)_5]^-$ with CS_2 and MeI, with $\overline{C(SMe)SC(S)SC}(SMe)$ as an additional product from $Na[Mn(CO)_5]$. The complex $[(OC)_4Re(\mu\text{-}S_2CS)Re(CO)_5]$ is better obtained (45% yield) when $Na[Re(CO)_5]$ is treated successively with CS_2 and $[ReBr(CO)_5]$. Analogous complexes $[(OC)_4Mn$-$(\mu\text{-}S_2CS)Re(CO)_5]$ and $[(OC)_4Re(\mu\text{-}S_2CS)Mn(CO)_5]$ are similarly prepared. The effect of added sulphur on various reactions is described. Addition to $[N(PPh_3)_2][Mn(CO)_5]$ causes an immediate colour change from yellow to red, i.r. spectroscopic evidence for the formation of $[N(PPh_3)_2][MnS_n(CO)_5]$ being obtained. With CS_2 this species generates $[N(PPh_3)_2][Mn(CO)_4(S_2CS)]$ slowly, while MeI gives $[N(PPh_3)_2][MnI_2(CO)_4]$. Possible mechanisms of trithiocarbonato-complex formation from CS_2 are discussed.

THE activation of carbon disulphide by transition-metal complexes[1] has been widely studied, but prior to the work described here, and to contemporary work by Ellis *et al.*,[2] there have been only isolated reports of attempts to directly exploit the electrophilic reactivity of carbon in the molecule, a reactivity well established in reactions with common nucleophiles (*e.g.* $[CN]^-$, $[OMe]^-$, $[N_3]^-$, and $[SR]^-$). Reaction of CS_2 with $[Co(CN)_5]^{3-}$ has been shown[3] to provide a complex $[Co_2(CN)_{10}(CS_2)]^{6-}$, whose structure is open to question,[3,4] while Angelici has described the formation of $[M(CS_2)(CO)_2(\pi\text{-}C_5H_5)]^-$ (M = Fe[5] or Ru[6]) on treating CS_2 with $Na[M(CO)_2$-

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[1] I. S. Butler and A. E. Fenster, *J. Organometallic Chem.*, 1974, **66**, 161.

[2] J. E. Ellis, R. W. Fennel, and E. A. Flom, *Inorg. Chem.*, 1976, **15**, 2031.

[3] M. C. Baird, G. Hartwell, and G. Wilkinson, *J. Chem. Soc.* (*A*), 1967, 2037.

[4] T. Mizuta, T. Susuki, and T. Kwan, *Nippon Kagaku Zasshi*, 1967, **88**, 573.

[5] L. Busetto and R. J. Angelici, *J. Organometallic Chem.*, 1969, **18**, 213.

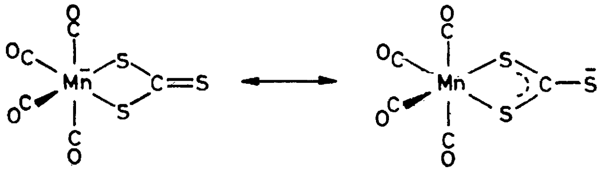
[6] T. A. Wnuck and R. J. Angelici, *Inorg. Chem.*, 1977, **16**, 1173.

(η-C_5H_5)]. Similar observation of metallodithiocarboxylates has been made by Ellis for [Fe(CO)$_2$(η-dienyl)]$^-$ and [{Mn(CO)$_4${P(C_6H_{11})$_3$}]$^-$.[2] We describe here a parallel study of the reactions of CS_2 with various metal carbonyl anions under somewhat different conditions, which lead to the formation of trithiocarbonato-complexes. Some aspects of the work have appeared as a preliminary communication.[7]

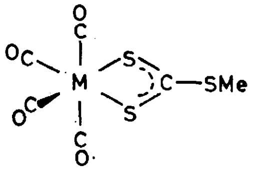
Spectroscopic and other data for the new complexes

Complex	Colour	M.p. (θ_c/°C)	Carbonyl-stretching bands (cm^{-1}) [a]	^{1}H N.m.r. (τ) [b]
[N(PPh$_3$)$_2$][Mn(CO)$_4$(S_2CS)] (1)	Buff	132 (decomp.)	2 067m, 1 987s, 1 967s, 1 923ms [c]	
[Mn(CO)$_4$(S_2CSMe)] (2a)	Yellow	78	2 093m, 2 017vs, 2 005s, 1 967s	7.32(s)
[Re(CO)$_4$(S_2CSMe)] (2b)	Yellow	94	2 109m, 2 014vs, 1 999s, 1 963s	7.42(s)
[Re(CO)$_5${SC(S)SMe}] (3)	Yellow	83	2 140w, 2 038vs, 1 991s	7.27(s)
[(OC)$_4$Re(μ-S_2CS)Re(CO)$_5$] (4a)	Yellow	135—140 (decomp.)	2 147w, 2 103m, 2 046s, 2 005vs, 1 992s, 1 965s	
[(OC)$_4$Mn(μ-S_2CS)Mn(CO)$_5$] (4b)	Yellow		2 126w, 2 084m, 2 040vs, 2 019m, 2 007s, 2 001s, 1 965s	
[(OC)$_4$Mn(μ-S_2CS)Re(CO)$_5$] (4c)	Yellow	135—138 (decomp.)	2 146w, 2 086m, 2 046vs, 2 011s, 2 004m, 1 998s, 1 962s	
[(OC)$_4$Re(μ-S_2CS)Mn(CO)$_5$] (4d)	Yellow		2 126w, 2 099m, 2 039s, 2 019s, 2 005s, 1 994s, 1 957s	
[(OC)$_5$Re{μ-SC(S)S}Re(CO)$_5$] (8)	Yellow	71—75 (decomp.)	2 139w, 2 075w, 2 038vs, 1 986s	
[Mo(CO)$_2$(S_2CSMe)(η-C_5H_5)]	Red	118	1 976s, 1 907m	4.48(s, 5 H), 7.37 (s, 3 H)
[Fe(CO)$_2$(S_2CSMe)$_2$]	Orange	91—92	2 041s, 1 995s	7.27(s)
[Ru(CO)$_2$(S_2CSMe)$_2$]	Yellow	98—99	2 051s, 1 995s	7.31(s)

[a] In hexane. [b] In $CDCl_3$. [c] In CH_2Cl_2.



(1a) (1b)



(2a) M = Mn

(2b) M = Re

RESULTS

The bis(triphenylphosphine)iminium salt of the pentacarbonylmanganate(1−) anion [N(PPh$_3$)$_2$][Mn(CO)$_5$] reacts slowly with carbon disulphide in tetrahydrofuran (thf), but to completion after *ca.* 4 d. The product, isolated in good yield as air-stable buff crystals, was identified as the trithiocarbonato-complex [N(PPh$_3$)$_2$][Mn(CO)$_4$(S_2CS)] (1) on the basis of analytical and i.r. data (Table) and its ready conversion into [Mn(CO)$_4$(S_2CSMe)] (2a), described below.

The i.r. spectrum of (1) shows four carbonyl-stretching bands of the relative frequencies and intensities to be expected [8] of a C_{2v} structure, but the band pattern as a whole is of interest in being at rather high energy for an anionic complex. Thus, for [Mn(CO)$_5$]$^-$ carbonyl bands at 1 898 and 1 858 cm^{-1} are observed while for (1) these are at 2 067, 1 987, 1 967, and 1 923 cm^{-1}. The values indicate relatively low back bonding to CO in (1), compatible with a high inductive withdrawal of electron density from manganese by the two co-ordinated sulphur atoms, but also perhaps as a consequence of a relatively high contribution of resonance form (1b) to the overall structure of the anion. Bands attributable to CS stretching frequencies were observed in the solid-state spectrum of (1) at 1 024, 993, and 870 cm^{-1}, and can be compared with corresponding bands at 1 010, 1 000, and 843 cm^{-1} recorded for [Ni(S_2CS)$_2$]$^{2-}$.[9]

The bis(triphenylphosphine)iminium salt of [Mo(CO)$_3$(η-C_5H_5)]$^-$ also reacts slowly with CS_2 in thf, the carbonyl bands of the reactant (1 895s and 1 767s cm^{-1}) being replaced over several days by two at 2 032s and 1 936s cm^{-1}. In the light of the shift to higher frequency observed for trithiocarbonato-complex formation with manganese, production of [Mo(CO)$_2$(S_2CS)(η-C_5H_5)]$^-$ appears likely, but attempts at isolation were unsuccessful. No reaction was observed between CS_2 and [N(PPh$_3$)$_2$][Co(CO)$_4$], and although reaction did occur between [N(PPh$_3$)$_2$][Re(CO)$_5$] and CS_2 no products were identified.

Treatment of anion (1) with MeI or SFO$_2$(OMe) generates the neutral methylated complex [Mn(CO)$_4$(S_2CSMe)] (2a) in *ca.* 40% yield, the ethyl analogue of which has been previously prepared.[10] Surprisingly, the same product was obtained in small amounts on addition of trimethylgermanium bromide to the anion, with no detection of the expected [Mn(CO)$_4$($S_2CSGeMe_3$)]. Attempted phenylation of the anion with benzenediazonium tetrafluoroborate was also inefficient, yielding only enough [Mn(CO)$_4$(S_2CSPh)] to allow identification by i.r. and mass spectroscopy.

Addition of CS_2 to thf solutions of the sodium salts of various metal carbonyl anions also led to trithiocarbonato-complexes. Yields of less than 10% were general when neutralisation was effected with methyl iodide, but neutralisation with metal carbonyl halides can produce more substantial quantities (30—50%). Thus, reaction of Na[M(CO)$_5$]

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[7] J. Hunt, S. A. R. Knox, and V. Oliphant, *J. Organometallic Chem.*, 1974, **80**, C50.

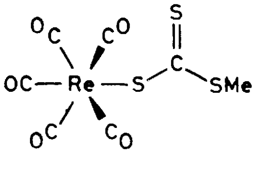
[8] L. E. Orgel, *Inorg. Chem.*, 1962, **1**, 25.

[9] J. P. Fackler and D. Coucouvanis, *J. Amer. Chem. Soc.*, 1966, **88**, 3913.

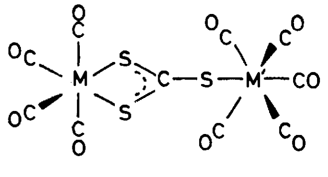
[10] R. Bruce, unpublished work.

(M = Mn or Re) with CS_2 for 1—24 h at room temperature, followed by addition of MeI, gave the trithiocarbonates (2) in 5—10% yield. Analogous reactions with thf solutions of $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$, $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$, and $Na_2[M(CO)_4]$ (M = Fe or Ru) gave $[Fe(CO)(S_2CSMe)(\eta\text{-}C_5H_5)]$ (1%),[11] $[Mo(CO)_2(S_2CSMe)(\eta\text{-}C_5H_5)]$ (2%),[12] and $[M(CO)_2(S_2CSMe)_2]$ (*ca.* 1%), respectively.

Confirmation of the nature of these products as trithiocarbonato-complexes was obtained through the synthesis of $[Re(CO)_5\{SC(S)SMe\}]$ (3) from $[ReBr(CO)_5]$ and $Na[CS_2(SMe)]$, and the observation of its ready decarbonylation on warming in hexane to yield a complex with properties identical to those of (2b).

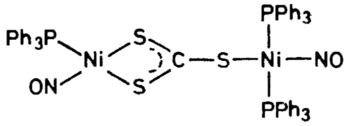


(3)

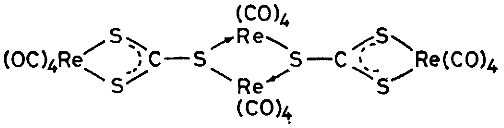


(4a) M = M′ = Re
(4b) M = M′ = Mn
(4c) M = Mn, M′ = Re
(4d) M = Re, M′ = Mn

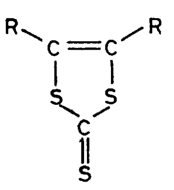
The reaction of $Na[Re(CO)_5]$ with CS_2–MeI also gave small amounts of a yellow crystalline complex identified as $[(OC)_4Re(\mu\text{-}S_2CS)Re(CO)_5]$ (4a). The trithiocarbonate-bridged structure is strongly indicated by the carbonyl i.r. spectrum, which is composed of bands typical of both the C_{2v} symmetry $[(OC)_4ReS_2C]$ (2 103m, 2 005s, 1 992s, and 1 955s cm^{-1}) and C_{4v} symmetry $[SRe(CO)_5]$ (2 147w, 2 046s, and 1 992s cm^{-1}) structural units. Comparison with the spectra of $[Re(CO)_4(S_2CSMe)]$ (2b) (2 109m, 2 014s, 1 999s, and 1 963s cm^{-1}) and $[Re(CO)_5\{SC(S)SMe\}]$ (3) (2 140w, 2 038vs, and 1 991s cm^{-1}) is striking. The mass spectrum of (4a) shows the series of ions $[M - nCO]^+$ (n = 0—9) and $[M - CS_2 - nCO]^+$ (n = 0—7), with distinctive dirhenium isotope distribution, and other significant ions corresponding to $[Re_2(CS_2)]^+$, $[Re_2S_2]^+$, $[Re_2(CS)]^+$, and $[Re_2S]^+$. The base peak of the spectrum is $[CS_2]^+$.



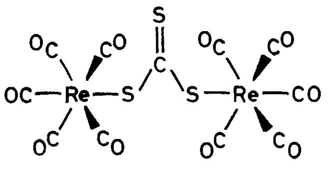
(5)



(6)



(7a) R = SMe
(7b) R = H



(8)

The likely intermediacy of anionic trithiocarbonato-complexes such as (1) in the syntheses described above suggested that $Na[Re(CO)_5]$ be treated with CS_2 and $[ReBr(CO)_5]$ successively in the expectation of producing (4a). The ready formation (45% yield) of the dirhenium complex by this route is further support both for the formation of species like (1) and for the structural assignment (4a). Only very small amounts of the analogous dimanganese complex (4b) were isolated from reactions of $Na[Mn(CO)_5]$ with CS_2 and MeI or $[MnBr(CO)_5]$, identified by its i.r. spectrum. Mixed-metal analogues were obtained, however, although in low yield, from treatment of $Na[Mn(CO)_5]$ or $Na[Re(CO)_5]$ with CS_2, followed by neutralisation with $[ReBr(CO)_5]$ or $[MnBr(CO)_5]$ respectively. From each reaction both complexes (4c) and (4d) were isolated, with (4c) predominant. Distinction between the isomeric (4c) and (4d) is clearly drawn when the carbonyl i.r. spectra are ' factored ' as for (4a) above.

Attempts to synthesise trithiocarbonate-bridged complexes related to (4) were unsuccessful. Thus treatment of $Na[Re(CO)_5]$ with CS_2 and $[MI(CO)_2(\eta\text{-}C_5H_5)]$ (M = Fe or Ru) afforded only a low yield of (4a) in addition to $[Re_2(CO)_{10}]$, while $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$ with CS_2 and then $[MoBr(CO)_3(\eta\text{-}C_5H_5)]$ gave only $[\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$. A complex $[(ON)(Ph_3P)Ni(\mu\text{-}S_2CS)Ni(PPh_3)_2(NO)]$ has been reported, however, as the product of treating $[CS_3]^{2-}$ with $[NiI(PPh_3)_2(NO)]$, and probably has structure (5).[13] Reaction of $[CS_3]^{2-}$ with $[ReBr(CO)_5]$ did not yield (4a).

Another example of the tendency of CS_2 towards trithiocarbonato-complex formation exists in the formation from $[Re(CF_3)(CO)_5]$ and CS_2 of $[\{(OC)_4Re(S_2CS)Re(CO)_4\}_2]$ (6), whose structure has been determined by *X*-ray diffraction.[14] This complex can be envisaged as arising from dimerisation of (4a), with sulphur-bridge formation and CO elimination, but heating (4a) at 150 °C, although effecting decomposition, did not yield (6).

Each of the reactions of sodium salts of metal carbonyl anions with CS_2–MeI gave several apparently organosulphur compounds as co-products. However, only one reaction, that of $Na[Mn(CO)_5]$ with CS_2 and MeI, gave such a product in quantities which encouraged its further investigation. The orange crystalline material, whose yield increased as reaction times were extended, was shown by elemental analyses and mass spectroscopy to be of composition $C_5H_6S_5$.

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[11] R. Bruce and G. R. Knox, *J. Organometallic Chem.*, 1966, **6**, 67.

[12] R. Havlin and G. R. Knox, *Z. Naturforsch.*, 1966, **B21**, 1108.

[13] H. Brunner, *Z. Naturforsch*, 1969, **B24**, 275.

[14] G. Thiele, G. Liehr, and E. Lindner, *J. Organometallic Chem.* 1974, **70**, 427.

The ^{1}H n.m.r. spectrum showed a singlet at τ 7.51, typical of SMe, and the i.r. spectrum a medium-intensity band at 1 058 cm^{-1} characteristic of ν(C=S), suggesting the structure (7a). Compounds of this type are well known, the parent 1,3-dithiole-2-thione (7b)[15] having ν(C=S) at 1 047 cm^{-1} by comparison.[16]

The observed transformation of CS_2 to an η^2-S_2CS ligand in the above reactions invited an investigation of the effect of adding elemental sulphur. Although an increase in the often low yields of products might be expected, a surprising re-direction of the reaction was achieved, in favour of σ-SCS_2 complexes.

Addition of a mixture of sulphur and CS_2 to Na[Re(CO)$_5$] in thf followed, after a 2 h reaction period, by MeI gave (2b) (5%) and (3) (9%). None of the latter had been obtained in the absence of sulphur. Moreover, when Na[Re(CO)$_5$] was treated with sulphur, MeI, and CS_2 successively, at 1 h intervals, only (3) (5%) was formed. A similar effect arises when sulphur, CS_2, and [ReBr(CO)$_5$] are added stepwise to Na[Re(CO)$_5$]. A reaction which in the absence of sulphur provided (4a) in 45% yield now gave only trace amounts of this complex, but with [(OC)$_5$Re{μ-SC(S)S}Re(CO)$_5$] (8) as the major product (35%). This new complex was identified by analysis and mass and i.r. spectra (Table), the spectra being nearly identical to that of (3). A complex of formulation (8) might have been expected to decarbonylate in favour of (4a) on heating, but no such change could be induced in hexane at reflux. Under the extreme conditions employed in mass spectroscopy, however, CO loss was evident in the observation of a weak molecular ion for (8) and a dominant $[M - \mathrm{CO}]^+$ ion.

Formation of σ-SCS_2 complexes in the presence of sulphur could arise as a result of initial generation of a species such as $[\mathrm{ReS(CO)_5}]^-$ which subsequently suffers CS_2 insertion into the Re–S bond. Insertions of this type are a characteristic feature of CS_2–transition-metal chemistry. In order to test this proposal the reaction of [N(PPh$_3$)$_2$][Mn(CO)$_5$] with sulphur in dichloromethane solution was studied, since this is a system readily amenable to i.r. monitoring. An immediate colour change from yellow-orange to dark red occurred on addition of sulphur to the anion solution, and three new carbonyl bands replaced the two of $[\mathrm{Mn(CO)_5}]^-$. These bands, at 2 121w, 2 040vs, and 2 005s cm^{-1}, are in a pattern typical of a C_{4v} symmetry [MnX(CO)$_5$] molecule and we propose that a species $[\mathrm{MnS}_n\mathrm{(CO)_5}]^-$ is formed. Such formation is reminiscent of the manner in which sulphur (S_8) is progressively cleaved by cyanide to yield thiocyanate ion, a reaction which proceeds *via* intermediate $[\mathrm{S}_n\mathrm{CN}]^-$ ions (n = 2—8).[17] We cannot therefore rule out the possibility that a series of ions $[\mathrm{MnS}_n\mathrm{(CO)_5}]^-$ (n = 1—8) is present, since each member should have an almost identical carbonyl spectrum. The relatively high frequencies of the bands of the uninegative anion(s) may, as discussed earlier for (1), be attributed to a localisation of negative charge on sulphur rather than manganese. Attempts to isolate a salt of $[\mathrm{MnS}_n\mathrm{(CO)_5}]^-$ were unsuccessful.

The dark red colour generated on addition of sulphur to $[\mathrm{Mn(CO)_5}]^-$ fades within 5 min to leave a clear yellow solution with a substantially unchanged i.r. spectrum. New carbonyl bands increase in relative intensity over a period of hours, but over 3 d a general decay occurs to leave a colourless carbonyl-free solution. Evidently the dark red colouration is not associated with a carbonyl complex.

In accord with the proposal that trithiocarbonato-complexes could be formed through a CS_2 insertion into a metal–sulphur bond, addition of CS_2 immediately after adding sulphur to $[\mathrm{Mn(CO)_5}]^-$ yields (1) in good yield after 3 d. Addition of excess of MeI to $[\mathrm{MnS}_n\mathrm{(CO)_5}]^-$ in an attempt to isolate a neutralised derivative, induced the slow formation of a new complex. After 4 h a four-band carbonyl spectrum very similar to that of (1) developed, when crystallisation yielded the known [N(PPh$_3$)$_2$][*cis*-MnI$_2$(CO)$_4$][18] as the species responsible. A plausible path for formation involves methylation and displacement of sulphur as SMe_2 [equations (1)—(4)].

$$[\mathrm{MnS(CO)_5}]^- + \mathrm{MeI} \longrightarrow [\mathrm{Mn(SMe)(CO)_5}] + \mathrm{I}^- \quad (1)$$

$$[\mathrm{Mn(SMe)(CO)_5}] + \mathrm{MeI} \longrightarrow [\mathrm{Mn(SMe_2)(CO)_5}]^+ + \mathrm{I}^- \quad (2)$$

$$[\mathrm{Mn(SMe_2)(CO)_5}]^+ + \mathrm{I}^- \longrightarrow [\mathrm{MnI(CO)_5}] + \mathrm{SMe_2} \quad (3)$$

$$[\mathrm{MnI(CO)_5}] + \mathrm{I}^- \longrightarrow [\mathrm{MnI_2(CO)_4}]^- + \mathrm{CO} \quad (4)$$

DISCUSSION

The first reaction of CS_2 with a transition-metal carbonyl anion was reported by Busetto and Angelici,[5] as the initial step of a route to [Fe(CO)$_2$(CS)(η-C$_5$H$_5$)][BPh$_4$]. Addition of a large excess of CS_2 to Na[Fe(CO)$_2$(η-C$_5$H$_5$)] followed, after 5 h, by MeI provided spectroscopically identified [Fe{C(S)SMe}(CO)$_2$(η-C$_5$H$_5$)], which was converted into the cationic thiocarbonyl complex *via* HCl addition and precipitation with Na[BPh$_4$]. The rather low yield of the thiocarbonyl so obtained has subsequently been much improved by shortening of reaction times.[19] Recently Wnuck and Angelici[6] described the analogous [Ru(CO)$_2$(CS)(η-C$_5$H$_5$)][S(CF$_3$)O$_3$] which was similarly prepared. In neither case was the presumed first-formed anion $[\mathrm{M(CS_2)(CO)_2}(\eta\text{-}\mathrm{C_5H_5})]^-$ (M = Fe or Ru) or the subsequently formed dithioester [M{C(S)SMe}(CO)$_2$(η-C$_5$H$_5$)] isolated, although there is little doubt of their involvement.

Further studies by Ellis *et al.*[2] of the reactions of K[Fe(CO)$_2$(η-dienyl)] (dienyl = C$_5$H$_5$, C$_5$H$_4$Me, or C$_5$Me$_5$) and K[Mn(CO)$_4${P(C$_6$H$_{11}$)$_3$}] or [NBu$_4$][Mn(CO)$_4${P(C$_6$H$_{11}$)$_3$}] with CS_2 in thf at −20 °C have provided substantial evidence for the generation of metallodithiocarboxylate anions whose thermal instability again precluded isolation, although neutralised derivatives of varying stability were obtained.

This work describes a general formation of trithiocarbonates on reaction of CS_2 with, predominantly, the sodium salts of various metal carbonyl anions, also in thf, and at room temperature. For Na[Fe(CO)$_2$(η-C$_5$H$_5$)], Na[Mo(CO)$_3$(η-C$_5$H$_5$)], and Na$_2$[M(CO)$_4$] (M = Fe or Ru) this observation is not necessarily incompatible with the work of Angelici and Ellis. The instability of $[\mathrm{Fe(CS_2)(CO)_2}(\eta\text{-}\mathrm{C_5H_5})]^-$ and [Fe{C(S)SMe}(CO)$_2$(η-C$_5$H$_5$)] has been mentioned, and taken with the low yields

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[15] R. Mayer and B. Gebhardt, *Chem. Ber.*, 1964, **97**, 1298.

[16] R. Mecke, R. Mecke, and A. Luttringhaus, *Z. Naturforsch.*, 1955, **B10**, 367.

[17] See R. E. Davis in ' Inorganic Sulphur Chemistry,' Elsevier, Amsterdam, 1968.

[18] E. W. Abel and I. S. Butler, *J. Chem. Soc.*, 1964, 434.

[19] B. D. Dombek and R. J. Angelici, *Inorg. Synth.*, in the press.

of $[\mathrm{Fe(CO)(S_2CSMe)(\eta\text{-}C_5H_5)}]$, $[\mathrm{Mo(CO)_2(S_2CSMe)(\eta\text{-}C_5H_5)}]$, and $[\mathrm{M(CO)_2(S_2CSMe)_2}]$ (M = Fe or Ru), it seems probable that the latter are products of decomposition of dithioester complexes or their precursors. The establishment of their existence in reaction mixtures prior to chromatography rules out this technique as a factor in their evolution.

For the reactions of $[\mathrm{M(CO)_5}]^-$ (M = Mn or Re) with CS_2 it is not so easy to rationalise our observations with those of the other workers. Although, following methylation, yields of $[\mathrm{M(CO)_4(S_2CSMe)}]$ are low (5—10%) and the decomposition interpretation could again be invoked, when $\mathrm{Na[Re(CO)_4]}$ is treated with CS_2 and $[\mathrm{ReBr(CO)_5}]$ a 45% yield of $[\mathrm{(OC)_4Re(\mu\text{-}S_2CS)Re(CO)_5}]$ (4a) is obtained. This suggests rather strongly that an anion $[\mathrm{Re(CO)_4(S_2CS)}]^-$ is present in appreciable quantities following addition of CS_2 to $\mathrm{Na[Re(CO)_5]}$. Further support for this conclusion is our study of the reaction of $[\mathrm{Mn(CO)_5}]^-$ with CS_2 and with sulphur. It has been reported[2] that although $\mathrm{[Na(thf)_{\mathit{x}}][Mn(CO)_5]}$ dissolves partially in CS_2 to give a strongly coloured solution, no reaction occurs within 1 h as disclosed by i.r. spectroscopy. Reaction with the more basic $[\mathrm{Mn(CO)_4\{P(C_6H_{11})_3\}}]^-$ was observed, however, generating metallodithiocarboxylate complexes. We have found that $[\mathrm{Mn(CO)_5}]^-$, as the bis(triphenylphosphine)iminium salt, *does* react with CS_2 in thf at room temperature, very slowly but to give $[\mathrm{Mn(CO)_4(S_2CS)}]^-$ (1) exclusively and in high yield. The anion is readily isolated and represents a convenient source of $[\mathrm{Mn(CO)_4(S_2CSMe)}]$ (2a) on methylation. It appears that the reactivity of $[\mathrm{Mn(CO)_5}]^-$ is to a degree modified by the nature of the counter ion; both we and Ellis note little significant reaction of $\mathrm{Na[Mn(CO)_5]}$ or $\mathrm{Na[Mo(CO)_3(\eta\text{-}C_5H_5)]}$ with CS_2, whereas the bis(triphenylphosphine)iminium salts are clearly more reactive. A similar control of reactivity by the cation has recently been noted in the very different behaviour of $\mathrm{K[Fe(CO)_3(NO)]}$ and $\mathrm{[N(PPh_3)_2][Fe(CO)_3(NO)]}$ towards iodine.[20]

Monitoring of the reaction of $\mathrm{[N(PPh_3)][Mn(CO)_5]}$ with CS_2 revealed direct replacement of the carbonyl bands of the pentacarbonyl anion by those of $[\mathrm{Mn(CO)_4(S_2CS)}]^-$. No intermediate complex was detected. Should there be initial formation of a metallodithiocarboxylate $[\mathrm{Mn(CS_2)(CO)_5}]^-$ there must therefore follow a rapid abstraction of sulphur from some source and CO loss. On this basis it is attractive to envisage the substitution of CO in $[\mathrm{Mn(CS_2)(CO)_5}]^-$ by an additional molecule of CS_2 acting as a two-electron ligand through sulphur, yielding $[\mathrm{Mn(CS_2)(SCS)(CO)_4}]^-$. Precedent for such a species exists in $[\mathrm{RhCl(CS_2)(SCS)(PPh_3)_2}]$.[21] Rearrangement with ejection of CS could then give (1). Support for this path is provided by a study[22] of the reaction of MeNCS with $[\mathrm{Mn(CO)_5}]^-$.

In view of the established high affinity of $[\mathrm{Mn(CO)_5}]^-$ for sulphur, a viable alternative path involves $[\mathrm{MnS(CO)_5}]^-$ as an intermediate which undergoes CS_2 insertion to afford $[\mathrm{Mn(CO)_5(\sigma\text{-}SCS_2)^-}]$ and subsequently $[\mathrm{Mn(CO)_4(\eta^2\text{-}S_2CS)}]^-$. Formation of $[\mathrm{MnS(CO)_5}]^-$ could come about either by direct abstraction of sulphur from CS_2 or by attack of $[\mathrm{Mn(CO)_5}]^-$ on elemental sulphur released in some manner from CS_2 in the reaction mixture. Rapid reaction of $[\mathrm{Mn(CO)_5}]^-$ with sulphur was observed to occur, to give a species believed to be $[\mathrm{MnS_{\mathit{n}}(CO)_5}]^-$ (n = 1—8) (see earlier), and slow reaction of this with CS_2 was established to indeed yield (1). Although i.r. identification of $[\mathrm{MnS_{\mathit{n}}(CO)_5}]^-$, if an intermediate in the reaction of CS_2 with $[\mathrm{Mn(CO)_5}]^-$, was therefore to be expected, we do not rule out this path totally.

The tendency of CS_2 towards formation of a CS_3 unit is best known in the treatment of the disulphide with base, which affords the trithiocarbonate ion $[CS_3]^{2-}$. The formation of trithiocarbonato-complexes on reaction of CS_2 with metal carbonyl anions is not therefore surprising. The isolation of the complex (6) from reaction of $[\mathrm{Re(CF_3)(CO)_5}]$ with CS_2, previously mentioned,[14] is further evidence of this tendency, as is the identification of (7a). It is noteworthy that similar behaviour has been observed for carbon dioxide in its reactions with transition-metal complexes, the most vivid examples being provided by the complex $[\mathrm{Mo(CO)_2(PMe_2Ph)_4}]$, which spontaneously changes in solution to the carbonate-bridged $[\mathrm{(PhMe_2P)_2(OC)Mo(\mu\text{-}OCO_2)_2Mo(CO)(PMe_2Ph)_2}]$,[23] and by $[\mathrm{(Ph_3P)_3Rh\{\mu\text{-}OCO_2\}Rh(PPh_3)_2}]$,[24] formed from $[\mathrm{RhH(PPh_3)_4}]$ and CO_2.

EXPERIMENTAL

Infrared spectra were recorded using a Perkin-Elmer 257 instrument, mass spectra with an A.E.I. MS902 instrument, and n.m.r. spectra with Varian Associates T60 or HA100 spectrometers. All the reactions were performed at room temperature in a nitrogen atmosphere, using deaerated solvents dried by distillation from lithium tetrahydridoaluminate or calcium hydride. Carbon disulphide of spectroscopic grade quality (Hopkin and Williams Ltd.) was purified prior to use by standing over bromine for several hours, then shaking with aqueous KOH and subsequently copper turnings, before final drying over calcium chloride. Sodium salts of metal carbonyl anions were prepared by sodium amalgam reduction of thf solutions of the appropriate carbonyl. Excess of amalgam was removed *via* a stopcock attached to the bottom of the reaction flask, and the remaining solution briefly stirred with clean mercury before being employed as a reactant.

Reactions of $\mathrm{Na[Re(CO)_5]}$–CS_2.—(*a*) *With* MeI. The complex $[\mathrm{Re_2(CO)_{10}}]$ (0.9 g, 1.38 mmol) in thf (50 cm³) was treated with sodium amalgam (1 g Na, 10 cm³ Hg) for 1.25 h. To the yellow-green solution of the anion, CS_2 (1.5 g, 19.7 mmol) in thf (20 cm³) was added dropwise over *ca.* 10 min, then the whole mixture was stirred for 1 h. Over this period the solution became initially mustard yellow and finally red. Methyl iodide (1.0 g, 7.0 mmol) in thf

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(20 cm^3) was then added dropwise over *ca.* 10 min, and the solution again stirred for 1 h, when an orange-red colour had developed. Removal of solvent left a red residue which was extracted with 100 cm^3 of hexane–dichloromethane (1 : 1). Concentration and chromatography on silica gel eluting with hexane–dichloromethane (2 : 1) gave two pale yellow bands. The first yielded 0.09 g (8%) of yellow crystalline $[\mathrm{Re(CO)_4(S_2CSMe)}]$ (2b) (Found: C, 17.7; H, 0.8; S, 23.0%; *M* 422. $\mathrm{C_6H_3O_4ReS_3}$ requires C, 17.1; H, 0.7; S, 22.7%; *M* 422), and the second *ca.* 50 mg of $[\mathrm{ReMe(CO)_5}]$, identified by its i.r. and n.m.r. spectra.

(*b*) *With* $[\mathrm{ReBr(CO)_5}]$. To an anion solution prepared as above from $[\mathrm{Re_2(CO)_{10}}]$ (0.5 g, 0.77 mmol), a solution of $\mathrm{CS_2}$ (0.76 g, 10.0 mmol) in thf (20 cm^3) was added dropwise and the mixture stirred for 2 h. A solution of $[\mathrm{ReBr(CO)_5}]$ (0.73 g, 1.8 mmol) in thf (20 cm^3) was then added similarly, and after stirring for 1 h solvent was evaporated and the residue extracted with dichloromethane–hexane (1 : 1). Chromatography, eluting with hexane, yielded a small amount of $[\mathrm{Re_2(CO)_{10}}]$, while dichloromethane–hexane (2 : 3) developed a broad yellow band which yielded 0.25 g (45%) of yellow powdery $[\mathrm{(OC)_4Re(\mu\text{-}S_2CS)Re(CO)_5}]$ (4a), purified by recrystallisation from benzene (Found: C, 16.8; H, 0.0%; *M* 732. $\mathrm{C_{10}O_9Re_2S_3}$ requires C, 16.4; H, 0.0%; *M* 732).

(*c*) *With* $[\mathrm{MnBr(CO)_5}]$. A reaction performed as in (*b*) employing the anion derived from $[\mathrm{Re_2(CO)_{10}}]$ (0.25 g, 0.39 mmol), with $\mathrm{CS_2}$ (0.5 g, 6.7 mmol), and $[\mathrm{MnBr(CO)_5}]$ (0.3 g, 1.0 mmol), yielded in turn on chromatography *ca.* 50 mg of $[\mathrm{Re_2(CO)_{10}}]$, eluted with hexane, *ca.* 10 mg of yellow $[\mathrm{(OC)_4Re(\mu\text{-}S_2CS)Mn(CO)_5}]$ (4d), eluted with dichloromethane–hexane (1 : 4) and identified by mass (Found: *M* 602. $\mathrm{C_{10}MnO_9ReS_3}$ requires *M* 602) and i.r. spectra, and finally *ca.* 25 mg of yellow $[\mathrm{(OC)_4Mn(\mu\text{-}S_2CS)Re(CO)_5}]$ (4c), eluted with dichloromethane–hexane (2 : 3) (Found: C, 20.4; H, 0.0%; *M* 602. $\mathrm{C_{10}MnO_9ReS_3}$ requires C, 20.0; H, 0.0%; *M* 602).

Reactions of $\mathrm{Na[Re(CO)_5]}$–$\mathrm{CS_2}$–$\mathrm{S_8}$.—(*a*) *With* MeI. A thf (100 cm^3) solution of anion prepared from $[\mathrm{Re_2(CO)_{10}}]$ (1.0 g, 1.53 mmol) was treated with a mixture of sulphur (0.32 g) and $\mathrm{CS_2}$ (0.76 g, 10.0 mmol) for 2 h, then to this was added 0.57 g (4.0 mmol) of MeI with stirring for 1 h. Removal of solvent and chromatography of the residue on silica gel afforded with hexane *ca.* 0.3 g of $[\mathrm{Re_2(CO)_{10}}]$, with dichloromethane–hexane (1 : 9) yellow crystalline $[\mathrm{Re(CO)_4(S_2CSMe)}]$ (2b) (67 mg, 5%) identified by its i.r. spectrum, and with dichloromethane–hexane (2 : 3) yellow crystalline $[\mathrm{Re(CO)_5\{SC(S)SMe\}}]$ (3) (110 mg, 9%) (Found: C, 18.8; H, 0.7%; *M* 450. $\mathrm{C_7H_3O_5ReS_3}$ requires C, 18.7; H, 0.7%; *M* 450). Repetition of this reaction, in which the anion derived from 0.5 g (0.77 mmol) of $[\mathrm{Re_2(CO)_{10}}]$ was stirred for 1 h with sulphur (0.32 g), another hour with MeI (0.57 g, 4.0 mmol), and another hour with $\mathrm{CS_2}$ (0.76 g, 10.0 mmol) yielded only (3) (30 mg, 5%) on chromatography in addition to recovered $[\mathrm{Re_2(CO)_{10}}]$ (*ca.* 200 mg).

(*b*) *With* $[\mathrm{ReBr(CO)_5}]$. The anion prepared from $[\mathrm{Re_2(CO)_{10}}]$ (0.5 g, 0.77 mmol) in thf (50 cm^3) was treated with sulphur (0.32 g) for 0.5 h and then $\mathrm{CS_2}$ (0.76 g, 10.0 mmol) for 1.5 h, followed by addition of $[\mathrm{ReBr(CO)_5}]$ (0.73 g, 1.8 mmol) and stirring for another hour. Chromatography as above gave 10 mg of (4a) identified by i.r., on elution with dichloromethane–hexane (1 : 1), and 0.41 g (35%) of yellow powdery $[\mathrm{(OC)_5Re\{\mu\text{-}SC(S)S\}Re(CO)_5}]$ (8) (Found: C, 15.9; H, 0.3%; *M* 760. $\mathrm{C_{11}O_{10}Re_2S_3}$ requires C, 17.4; H, 0.0%; *M* 760), on elution with neat dichloromethane.

Reactions of $\mathrm{Na[Mn(CO)_5]}$–$\mathrm{CS_2}$.—(*a*) *With* MeI. To a solution of $\mathrm{Na[Mn(CO)_5]}$ prepared by treating $[\mathrm{Mn_2(CO)_{10}}]$ (1.95 g, 5.0 mmol) in thf (100 cm^3) with sodium amalgam (1 g Na, 10 cm^3 Hg) for 24 h, excess of $\mathrm{CS_2}$ (12.6 g, 1.66 mmol) was added and the whole stirred for a further 24 h. A deep red solution was formed, to which was added MeI (11.4 g, 80.3 mmol). After stirring for 4 h the solution had become yellow, and solvent was removed to leave a red residue. Extraction with boiling hexane gave a dark red solution which was concentrated and placed on a 100-cm alumina column. Elution with hexane removed a yellow band which provided 0.12 g (4%) of yellow crystalline $[\mathrm{Mn(CO)_4(S_2CSMe)}]$ (2a) (Found: C, 25.9; H, 1.4; S, 33.1%; *M* 290. $\mathrm{C_6H_3MnO_4S_3}$ requires C, 24.8; H, 1.0; S, 33.1%; *M* 290), purified by sublimation (60 °C, 10^{-2} Torr) * onto a water-cooled probe. Further elution with dichloromethane developed a red band, yielding a red solution which on concentration afforded orange crystals. Filtration and washing in ice-cold hexane gave 0.45 g of 4,5-bis(methylthio)-1,3-dithiole-2-thione (7a) (Found: C, 26.7; H, 2.8; S, 71.1%; *M* 226. $\mathrm{C_5H_6S_5}$ requires C, 26.5; H, 2.7; S, 70.7%; *M* 226).

A similar reaction performed using $[\mathrm{Mn_2(CO)_{10}}]$ (1.0 g), $\mathrm{CS_2}$ (3.0 g), and MeI (3.0 g) with successive reaction periods of 1 h gave large quantities of $[\mathrm{MnMe(CO)_5}]$, a similar yield of (2a) to that above, and small amounts of (7a) and (4b), identified by i.r. spectroscopy.

(*b*) *With* $[\mathrm{ReBr(CO)_5}]$. The anion prepared from $[\mathrm{Mn_2(CO)_{10}}]$ (0.6 g, 1.5 mmol) in thf (100 cm^3) was treated with $\mathrm{CS_2}$ (1.5 g, 20.0 mmol) for 2 h, then with $[\mathrm{ReBr(CO)_5}]$ (1.27 g, 3.15 mmol) for 1 h. Chromatography afforded $[\mathrm{(OC)_4Re(\mu\text{-}S_2CS)Mn(CO)_5}]$ (4d) (15 mg, 2%) on elution with dichloromethane–hexane (1 : 4), $[\mathrm{(OC)_4Mn(\mu\text{-}S_2CS)Re(CO)_5}]$ (4c) (40 mg, 5%) with dichloromethane–hexane (2 : 3), and $[\mathrm{(OC)_4Re(\mu\text{-}S_2CS)Re(CO)_5}]$ (4a) (10 mg) with dichloromethane–hexane (3 : 2), each identified by their i.r. spectra.

Reaction of $\mathrm{Na[Fe(CO)_2(\eta\text{-}C_5H_5)]}$ *with* $\mathrm{CS_2}$ *and* MeI.—Treatment of the anion derived from $[\mathrm{\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2}]$ (2.0 g, 5.65 mmol) with $\mathrm{CS_2}$ (4.0 g, 51.2 mmol) and MeI (3.0 g, 21.1 mmol), exactly as for $\mathrm{Na[Mn(CO)_5]}$ above, gave a deep orange solution which was evaporated and the residue subjected to chromatography on silica gel. Elution with hexane gave, in turn, yellow $[\mathrm{FeMe(CO)_2(\eta\text{-}C_5H_5)}]$ (*ca.* 60 mg), identified by i.r. and n.m.r. spectroscopy, a foul-smelling yellow liquid, and dark red crystalline $[\mathrm{Fe(CO)(S_2CSMe)(\eta\text{-}C_5H_5)}]$ (27 mg, 1%), identified by i.r. [ν(CO) at 1 962 cm^{-1} in hexane; lit.,[11] 1 964 cm^{-1} in $\mathrm{CCl_4}$], ^{1}H n.m.r. [τ 5.31(s, 5 H) and 7.42(s, 3 H) in $\mathrm{CDCl_3}$; lit.,[11] τ 5.40(s, 5 H) and 7.45 (s, 3 H) in $\mathrm{CS_2}$], and mass spectra (Found: *M* 272. $\mathrm{C_8H_8FeOS_3}$ requires *M* 272).

Reaction of $\mathrm{Na[Mo(CO)_3(\eta\text{-}C_5H_5)]}$ *with* $\mathrm{CS_2}$ *and* MeI.—Treatment of $[\mathrm{\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2}]$ (2.0 g, 4.1 mmol) in thf (100 cm^3) with sodium amalgam for 1 h, and then $\mathrm{CS_2}$ (6.0 g, 79 mmol) for 24 h, generated a dark yellow solution, which became orange on addition of MeI (3.0 g, 21.1 mmol) and stirring for another hour. Evaporation of solvent, extraction of the residue with hexane, and chromatography on silica gel gave on elution with hexane–dichloromethane (4 : 1) an intense yellow band and a red band. The former gave rise to 1.67 g (79%) of yellow $[\mathrm{MoMe(CO)_3(\eta\text{-}C_5H_5)}]$, identified by i.r. and n.m.r. spectroscopy, and the latter to 55 mg (2%) of red needle-like $[\mathrm{Mo(CO)_2(S_2CSMe)(\eta\text{-}C_5H_5)}]$

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* Throughout this paper: 1 Torr = 101 325/760 Nm^{-2}.

(Found: C, 31.7; H, 2.3%; *M* 342. $C_9H_8MoO_2S_3$ requires C, 31.8; H, 2.4%; *M* 342).

Reaction of $Na_2[Fe(CO)_4]$ *with* CS_2 *and* MeI.—Excess of CS_2 (2.50 g, 32.9 mmol) was added to a solution of $Na_2[Fe(CO)_4]$ (1.0 g, 3.0 mmol) in thf (50 cm^3). An immediate dark brown colour developed, and the solution was stirred for 48 h. Methyl iodide (2.0 g, 14.1 mmol) was then added and the mixture stirred for another 24 h. Evaporation of solvent, extraction of the residue with hexane–dichloromethane (2 : 1), and chromatography on alumina yielded an orange band with hexane. This provided 10 mg (1%) of orange crystalline $[Fe(CO)_2(S_2CSMe)_2]$ (Found: C, 20.4; H, 1.8%; *M* 358. $C_6H_6FeO_2S_6$ requires C, 20.1; H, 1.7%; *M* 358).

Reaction of $Na_2[Ru(CO)_4]$ *with* CS_2 *and* MeI.—A thf (80 cm^3) solution of $Na_2[Ru(CO)_4]$ was generated from $[Ru_3(CO)_{12}]$ (0.32 g, 0.5 mmol) as described in the literature,[25] and to this was added CS_2 (2.5 g, 32.9 mmol). An immediate dark brown colour developed, and after stirring for 70 h MeI (2.0 g, 14.1 mmol) was added and the mixture was again stirred (3 h). Treatment of the reaction mixture as above yielded 6 mg (1%) of yellow crystalline $[Ru(CO)_2(S_2CSMe)_2]$ (Found: C, 18.2; H, 1.7%; *M* 404. $C_6H_6O_2RuS_6$ requires C, 17.9; H, 1.5%; *M* 404).

Reaction of $[N(PPh_3)_2][Mn(CO)_5]$ *with* CS_2.—Excess of CS_2 (10 cm^3) was added to a stirred thf (100 cm^3) solution of $[N(PPh_3)_2][Mn(CO)_5]$ (3.66 g, 5.0 mmol) and the reaction monitored by i.r. scanning of the carbonyl-stretching region. Over a period of 4 d the solution changed in colour from orange to brown, while the i.r. spectrum revealed the replacement of the original two carbonyl bands of $[Mn(CO)_5]^-$ by four new bands. After filtration and evaporation of solvent at reduced pressure the residue was dissolved in dichloromethane (50 cm^3). On adding this solution to 200 cm^3 of diethyl ether, 2.45 g (60%) of buff crystalline $[N(PPh_3)_2][Mn(CO)_4(S_2CS)]$ (1) were precipitated (Found: C, 60.8; H, 4.2; N, 1.8; S, 11.4. $C_{41}H_{30}MnO_4P_2S_3$ requires C, 60.5; H, 3.7; N, 1.7; S, 11.8%) and washed with ether.

Reactions of $[N(PPh_3)_2][Mn(CO)_4(S_2CS)]$ (1).—(*a*) *With* MeI. The complex (0.5 g, 0.62 mmol) was dissolved in dichloromethane (20 cm^3) and excess of MeI (0.70 g, 4.93 mmol) added. After stirring for 5 min, solvent and residual MeI were evaporated and hexane-soluble material was chromatographed on alumina. Elution with hexane gave a single yellow band which yielded 68 mg (38%) of yellow crystalline $[Mn(CO)_4(S_2CSMe)]$ (2a), purified by sublimation (50—60 °C, 10^{-2} Torr) onto a water-cooled probe, and identified by i.r. and mass spectra.

(*b*) *With* $SFO_2(OMe)$. Treatment of a solution of the complex as in (*a*) with excess of $SFO_2(OMe)$ (2 cm^3), stirring for 1 h, and subsequent similar work-up yielded (2a) in 44% yield.

(*c*) *With* $GeBrMe_3$. The complex (0.5 g, 0.62 mmol) in dichloromethane (25 cm^3) was treated with $GeBrMe_3$ (2 g, 10 mmol) over 24 h. Work-up as in (*a*) then gave *ca.* 10 mg of yellow crystalline (2a), identified by i.r., n.m.r., and mass spectra.

(*d*) *With* $[PhN_2][BF_4]$. The complex (0.5 g, 0.62 mmol) in dichloromethane (25 cm^3) was treated with excess of $[PhN_2][BF_4]$ over 30 min. Work-up as in (*a*) above gave a trace amount of yellow oil with mass (Found: *M* 352. $C_{11}H_5O_4MnS_3$ requires *M* 352) and i.r. spectra [ν(CO) in hexane at 2 088m, 2 013vs, 2 002s, and 1 964s cm^{-1}] characteristic of $[Mn(CO)_4(S_2CSPh)]$.

Reactions of $[N(PPh_3)_2][Mn(CO)_5]$–S_8.—(*a*) *With* CS_2. Sulphur (*ca.* 0.5 g) was added to a stirred dichloromethane (25 cm^3) solution of the anion (1.0 g, 1.24 mmol), inducing an immediate yellow-orange to dark red colour change and the generation of new carbonyl bands in the i.r. at 2 121w, 2 040vs, and 2 005s cm^{-1}. Addition of CS_2 (5.0 g, 66 mmol) reversed the colour change at once and over a period of 4 d i.r. monitoring revealed the slow replacement of the above bands exclusively by those characteristic of (1). Addition of the reaction solution to diethyl ether precipitated the salt as an orange powder (0.37 g, 42%).

(*b*) *With* MeI. Sulphur was added to a solution of $[N(PPh_3)_2][Mn(CO)_5]$ exactly as in (*a*) and to this was then added excess of MeI (2.0 g, 14.1 mmol), again regenerating an orange solution. After stirring for 24 h, solvent was removed and the residue leached of a little hexane-soluble material, which was discarded. Residual sulphur present was sublimed *in vacuo* and the remaining material recrystallised from diethyl ether–dichloromethane to yield 79 mg (7%) of orange crystalline $[N(PPh_3)_2][cis\text{-}MnI_2(CO)_4]$, m.p. 175 °C (decomp.) (Found: C, 50.1; H, 3.3; I, 23.8; N, 1.5. $C_{40}H_{30}I_2MnNO_4P_2$ requires C, 50.1; H, 3.1; I, 26.5; N, 1.5%), further identified by its i.r. spectrum [ν(CO) in CH_2Cl_2 at 2 071m, 1 999vs, 1 975s, and 1 930s cm^{-1}; lit.,[18] 2 075w, 2 001s, 1 982m, and 1 940m cm^{-1} in $CHCl_3$].

Preparation and Thermal Decomposition of $[Re(CO)_5\{SC(S)SMe\}]$ (3).—Excess of methanethiol was bubbled through a stirred suspension of sodium hydride (0.1 g, 4.2 mmol) in thf (25 cm^3) at 0 °C for 1 min. Excess of CS_2 in thf (25 cm^3) was then added to provide a yellow solution of $Na[CS_2(SMe)]$. To this was added 1.0 g (2.5 mmol) of $[ReBr(CO)_5]$ in thf (25 cm^3) and the whole stirred at 0 °C for 1 h. After this time, solvent and other volatiles were evaporated and the remaining hexane-soluble material chromatographed on a silica-gel column. Elution with hexane developed a yellow band, which provided *ca.* 20 mg of yellow crystalline (2b), identified by its i.r. and mass spectra. A second yellow band, eluted with dichloromethane–hexane (2 : 3), gave yellow crystals of $[Re(CO)_5\{SC(S)SMe\}]$ (3) (Found: C, 18.8; H, 0.7%; *M* 450. $C_7H_3O_5ReS_3$ requires C, 18.7; H, 0.7%; *M* 450).

Heating a hexane solution of (3) under reflux in hexane provoked conversion into (2b) within 30 min, as shown by periodic i.r. monitoring.

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