Organosulphur–Transition-metal Chemistry. Part 2.[1] Reactions of Isothiocyanates with Metal Carbonyl Anions: Crystal and Molecular Structure of Di-μ-*N*-methylimino(methylthio)methanethiolato-bis(tricarbonylmanganese)

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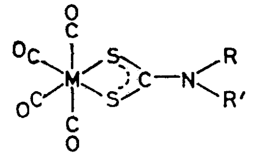
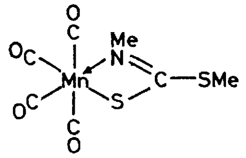
Treatment of $Na[Mn(CO)_5]$ with RNCS (R = Me or Ph) provides dithiocarbamato-complexes $[Mn(CO)_4\{S_2CN(H)R\}]$ and $[Mn(CO)_3(CNR)\{S_2CN(H)R\}]$ as a result of sulphur incorporation, the former complex being readily converted into the latter with RNC. Addition of MeI subsequent to MeNCS diverts the reaction to yield the title complex $[Mn_2(CO)_6\{\mu\text{-}SC(SMe)(NMe)\}_2]$ predominantly, with small amounts of $[Mn(CO)_4(S_2CSMe)]$ and $[Mn(CO)_4\{S_2CN(H)Me\}]$. Reaction of $[N(PPh_3)_2][Mn(CO)_5]$ with MeNCS produces the same monomanganese complexes as the sodium salt, but also a trimer $(MeNCS)_3$ when MeI is added. This trimer is formed in the reaction of $[N(PPh_3)_2][Mo(CO)_3(\eta\text{-}C_5H_5)]$ with MeNCS, co-products being $[Mo(CO)_2(S_2CSMe)(\eta\text{-}C_5H_5)]$ and $[Mo(CO)_2\{S_2CN(H)Me\}(\eta\text{-}C_5H_5)]$, while $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$ yields only the trithiocarbonate. The sodium salt of $[Re(CO)_5]^-$ treated with MeNCS and then MeI behaves similarly to manganese, affording low yields of $[Re(CO)_4\{S_2CN(H)Me\}]$, $[Re(CO)_3(NCMe)\{S_2CN(H)Me\}]$, and $[ReI(CO)_4(CNMe)]$. A scheme is proposed to account for the various products of the $[Mn(CO)_5]^-$–MeNCS–MeI system, features of which are applicable to other anions. Crystals of $[Mn_2(CO)_6\{\mu\text{-}SC(SMe)(NMe)\}_2]$ are monoclinic, space group $P2_1/n$ with $Z = 4$ in a unit cell of dimensions $a = 9.845(2)$, $b = 13.791(4)$, $c = 14.972(5)$ Å, and $\beta = 98.23(4)°$. Atoms have been located by a combination of direct methods (Mn) and successive difference-Fourier syntheses (S, O, N, C, and H) from diffractometer data, and refined to R 0.029 for 3 239 independent reflections. There are two octahedrally co-ordinated manganese atoms joined by sulphur bridges; the four-atom ring so produced carries, on opposite edges, two further four-membered $\overline{\text{MnSC(SMe)NMe}}$ rings in a *cis* orientation to one another. Each of the three rings is planar and the molecule as a whole has C_2 symmetry (not required crystallographically). Within the bridge system, Mn–S is 2.41—2.43 Å and the Mn · · · Mn distance (3.23 Å) is non-bonding.

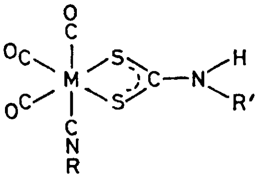
In the first paper of this series we described reactions of carbon disulphide with various metal carbonyl anions, which gave rise to trithiocarbonato-complexes as the result of a sulphur incorporation.[1] Like CS_2, structurally related organic isothiocyanates RNCS contain an electrophilic carbon atom and this prompted an investigation into the possibility of a similar transformation occurring with these reagents. That this is indeed the case is described here; some aspects of the work have appeared as a preliminary communication.[2]



(1a) M = Mn, R = R' = Me
(1b) M = Mn, R = H, R' = Me
(1c) M = Mn, R = H, R' = Ph
(1d) M = Re, R = H, R' = Me



(2)



(3a) M = Mn, R = R' = Me
(3b) M = Mn, R = R' = Ph
(3c) M = Re, R = R' = Me

RESULTS AND DISCUSSION

The anion $[Mn(CO)_5]^-$, which played a central role in the study of the reactions of CS_2 with metal carbonyl anions,[1] occupies a similar position with isothiocyanates. Also, as for the previous study, it was found that the nature of the counter ion, whether Na^+ or $[N(PPh_3)_2]^+$, has an effect on the reactions of $[Mn(CO)_5]^-$.

Unlike CS_2, which provides only a low yield of $[Mn(CO)_4(S_2CSMe)]$ on treatment with $Na[Mn(CO)_5]$ and then MeI, moderate to good yields of products arising from sulphur incorporation are obtained from $Na[Mn(CO)_5]$ and RNCS (R = Me or Ph). The products are not, however, those which might have been anticipated. For example, should a sulphur incorporation occur in the reaction of $[Mn(CO)_5]^-$ with MeNCS, in concert with methylation by either MeNCS itself or added MeI, then the expected product would be the dithiocarbamate $[Mn(CO)_4(S_2CNMe_2)]$ (1a)[3] and/or the unknown $[Mn(CO)_4\{SC(SMe)NMe\}]$ (2). In reality, reaction of an excess of MeNCS with $Na[Mn(CO)_5]$ in tetrahydrofuran (thf) at room temperature for 2—3 h provides the dithiocarbamato-complex $[Mn(CO)_4\{S_2CN(H)Me\}]$ (1b) and a methyl isocyanide derivative thereof $[Mn(CO)_3(CNMe)\{S_2CN(H)Me\}]$ (3a), each in *ca.* 15% yield. Allowing the reaction to proceed for 24 h reduced the yields of (1b) and (3a) to *ca.* 5% each, but now gave the trithiocarbonate $[Mn(CO)_4(S_2CSMe)]$ [1] in 7% yield.

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[1] Part 1, preceding paper.

[2] S. R. Finnimore, R. Goddard, S. D. Killops, S. A. R. Knox, and P. Woodward, *J.C.S. Chem. Comm.*, 1975, 391.

[3] E. W. Abel and M. O. Dunster, *J.C.S. Dalton*, 1973, 98.

Characterisation of (1b) and (3a) was readily achieved on the basis of analysis and i.r., n.m.r., and mass spectra (Table 1). Thus the ^1H n.m.r. spectra show a signal for an NMe group at τ 6.9, split into a doublet (J 5 Hz) as a consequence of coupling with the N*H* atom, which appears for each complex as a resonance at *ca.* τ 3.0, significantly broadened by the nitrogen quadrupole. The presence of MeNC as a ligand in (3a) is clearly revealed both by an Me signal in the ^1H n.m.r. spectrum at τ 6.35, and by the observation of $\nu(C\equiv N)$ in the i.r. spectrum at 2 190 cm^{-1}. The three strong carbonyl bands of (3a) are consistent with a *fac*-$Mn(CO)_3$ arrangement, *i.e.* substitution of MeNC *cis* to the dithiocarbamate ligand. The i.r. spectrum of (1b) is as expected virtually identical to that of $[Mn(CO)_4(S_2CNMe_2)]$,[3] prepared by us from $[MnBr(CO)_5]$ and $Na[SC(S)NMe_2]$.

TABLE 1

Physical and spectroscopic data for the new compounds

Compounds	Colour	M.p.(θ_c/°C)	I.r. bands (cm^{-1}) [a] $\nu(C\equiv N)$	I.r. bands (cm^{-1}) [a] $\nu(C\equiv O)$	^1H N.m.r. (τ) [b]
$[Mn(CO)_4\{S_2CN(H)Me\}]$ (1b)	Yellow	80 (decomp.)		2 088m, 2 012vs, 1 997s, 1 959vs	3.0(br, 1 H), 6.9(d, J 5 Hz, 3 H)
$[Mn(CO)_4\{S_2CN(H)Ph\}]$ (1c)	Orange	146 (decomp.)		2 085m, 2 010vs, 1 997s, 1 966vs	2.60(br)
$[Mn(CO)_3(CNMe)\{S_2CN(H)Me\}]$ (3a)	Yellow	123—125	2 190m,br	2 029s, 1 964vs, 1 931vs	3.0(br, 1 H), 6.35(s, 3 H), 6.9(d, J 5 Hz, 3 H)
$[Mn(CO)_3(CNPh)\{S_2CN(H)Ph\}]$ (3b)	Brown	142 (decomp.)	2 140m,br	2 025vs, 1 971s, 1 937s	2.60(br)
$[Mn_2(CO)_6\{\mu\text{-}SC(SMe)(NMe)\}_2]$ (4a)	Orange	165 (decomp.)		2 039m, 2 020vs, 1 954m, 1 942vs, 1 930(sh), 1 926s	6.73(s, 6 H), 7.45(s, 6 H)
$[Mn_2(CO)_6\{\mu\text{-}S_2CN(H)Me\}_2]$	Orange	125 (decomp.)		2 033m, 2 015vs, 1 930s,br [c]	7.07(br) [d]
$[Re(CO)_4\{S_2CN(H)Me\}]$ (1d)	Yellow	162 (decomp.)		2 103w, 2 003vs, 1 988s, 1 951s	
$[Re(CO)_3(CNMe)\{S_2CN(H)Me\}]$ (3c)	Yellow	107 (decomp.)	2 220w,br	2 028s, 1 952vs, 1 923s	
$[ReI(CO)_4(CNMe)]$	Yellow	124—126	2 220w, br	2 103m, 2 027s, 2 018vs, 1 961s	6.35
$[Mo(CO)_2\{S_2CN(H)Me\}(\eta\text{-}C_5H_5)]$	Orange	146—150		1 962s, 1 883m	4.4(s, 5 H), 6.9(d, J 5 Hz, 3 H)
$(MeNCS)_3$	Yellow	159—160			5.6(s)

[a] In hexane. [b] In $CDCl_3$. [c] In CH_2Cl_2. [d] In $(D_3C)_2CO$.

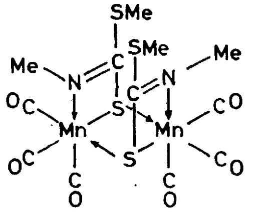
Phenyl isothiocyanate behaves in the same way as MeNCS with $Na[Mn(CO)_5]$ under similar conditions, the products being $[Mn(CO)_4\{S_2CN(H)Ph\}]$ (1c; 11%) and $[Mn(CO)_3(CNPh)\{S_2CN(H)Ph\}]$ (3b; 2%).

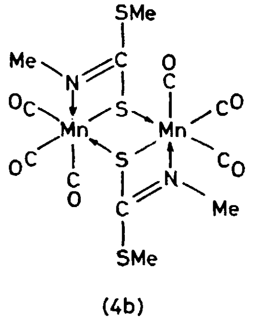
Unequivocal confirmation of the relation between (1b) and (3a), and between (1c) and (3b), was provided by treating (1b) and (1c) with MeNC and PhNC respectively in hexane at room temperature, when (3a) and (3b) were formed within 1 h.

The reaction of $[Mn(CO)_5]^-$ with CS_2 yielded an anion $[Mn(CO)_4(S_2CS)]^-$, which in the presence of a methylating agent readily generated $[Mn(CO)_4(S_2CSMe)]$.[1] In this light the products of the reaction of RNCS with $Na[Mn(CO)_5]$ are best explained in terms of an intermediate anion $[Mn(CO)_4(S_2CNR)]^-$ (which could not be isolated) which abstracts a proton from some source to give (1b) or (1c). The incorporation of sulphur required by such an ion arises plausibly by abstraction from RNCS, and the consequent evolution of an isocyanide RNC then accounts for the isolation of complexes (3a) and (3b) *via* attack on (1b) or (1c).

Should an anion $[Mn(CO)_4(S_2CNMe)]^-$ be produced in the reaction of MeNCS with $Na[Mn(CO)_5]$ it is evidently not readily methylated by the excess of MeNCS, protonation occurring preferentially. In an effort to divert the reaction in favour of $[Mn(CO)_4(S_2CNMe_2)]$ (1a), MeNCS and the methylating agent MeI were added consecutively to $Na[Mn(CO)_5]$, when substantially different reaction products were indeed obtained. Complex (1a) was not one of these, however. Only a trace amount of (1b) was now formed and a low yield (3%) of the trithiocarbonate $[Mn(CO)_4(S_2CSMe)]$,[1] the major product (31%) being the binuclear complex $[Mn_2(CO)_6\{\mu\text{-}SC(SMe)(NMe)\}_2]$ (4).

Although the ^1H n.m.r. spectrum of (4) indicates the presence of both NMe (τ 6.7, 6 H, s) and SMe (τ 7.5, 6 H, s) groups, it does not distinguish between the possible *cis*- and *trans*-bridged structures (4a) and (4b). The six carbonyl-stretching bands (Table 1) observed in the i.r. spectrum, however, are as expected ($3A + 3B$) for the C_2 structure (4a) rather than the more symmetric C_i structure (4b), for which three bands ($3A_u$) are predicted. Several complexes related to (4) are known, and have been assigned *cis*- or *trans*-bridged structures on this i.r. criterion; thus $[Mn_2(CO)_6\{\mu\text{-}OC(NMe_2)S\}_2]$ [3] is apparently *cis* while $[Mn_2(CO)_6\{\mu\text{-}XC(NMe_2)(NPh)\}_2]$ (X = O


(4a)


(4b)

or S)[3] and $[Mn_2(CO)_6\{\mu\text{-}SCMe(NPh)\}_2]$[4] are *trans*. The configuration of the last three complexes has been attributed to the steric strain which the phenyl groups would bring to a *cis*-bridged structure; however, the complexes $[Mn_2(CO)_6(\mu\text{-}XYCNMe_2)_2]$ (XY = SS, SSe, or SeSe)[5] appear also to be *trans*, and there are no grounds for attributing this to steric effects. In order to establish unequivocally the structure of (4) and to place the i.r. criterion for assigning structures to such complexes on a firm basis, an *X*-ray diffraction study was undertaken.

The *X*-ray analysis (Tables 2—4) establishes that the molecule has the overall configuration shown in Figure 1 and represented as (4a). Two octahedrally co-ordinated manganese atoms are joined by sulphur bridges, and the planar four-membered ring so produced carries, on opposite edges, two further planar four-membered [MnSC(SMe)NMe] rings in a *cis* orientation to one another. The molecule as a whole has C_2 symmetry which is not required crystallographically. Within the Mn_2S_2 ring the Mn–S distances alternate, those carrying

TABLE 2

Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Mn(1)	1.026 29(5)	0.342 81(4)	0.217 80(4)
Mn(2)	0.748 41(5)	0.243 68(4)	0.319 08(3)
S(1)	0.793 45(9)	0.387 18(6)	0.233 06(6)
S(2)	0.965 00(9)	0.188 06(7)	0.280 53(6)
S(11)	0.632 05(11)	0.356 54(8)	0.041 18(7)
S(21)	0.883 78(12)	0.054 07(8)	0.113 97(7)
N(1)	0.897 2(3)	0.321 5(2)	0.101 6(2)
N(2)	0.721 9(3)	0.159 5(2)	0.206 3(2)
C(10)	0.781 7(4)	0.350 2(3)	0.119 4(2)
C(11)	0.515 1(4)	0.416 8(4)	0.103 0(3)
C(12)	0.918 9(5)	0.292 4(4)	0.009 9(3)
C(20)	0.844 3(4)	0.134 6(2)	0.196 9(2)
C(21)	1.066 6(5)	0.046 0(4)	0.136 5(4)
C(22)	0.601 7(4)	0.121 2(3)	0.147 9(3)
Carbonyl groups			
C(1)	1.111 0(4)	0.369 6(3)	0.330 6(3)
O(1)	1.165 4(3)	0.388 4(2)	0.400 4(2)
C(2)	0.807 8(4)	0.315 7(3)	0.418 6(2)
O(2)	0.842 9(4)	0.359 9(2)	0.481 6(2)
C(3)	1.075 7(5)	0.461 9(4)	0.184 1(3)
O(3)	1.111 0(4)	0.537 3(3)	0.166 0(3)
C(4)	1.178 1(4)	0.292 9(4)	0.181 8(3)
O(4)	1.272 1(4)	0.261 0(3)	0.157 0(3)
C(5)	0.573 8(4)	0.281 1(3)	0.322 9(2)
O(5)	0.465 1(3)	0.306 1(3)	0.327 5(2)
C(6)	0.725 0(4)	0.141 9(3)	0.391 2(2)
O(6)	0.708 4(3)	0.080 6(2)	0.438 9(2)
Hydrogen atoms			
H(111)	0.493(5)	0.382(4)	0.148(3)
H(112)	0.436(5)	0.424(4)	0.058(3)
H(113)	0.548(5)	0.481(4)	0.111(3)
H(121)	0.955(5)	0.345(4)	−0.016(3)
H(122)	0.849(5)	0.311(4)	−0.032(3)
H(123)	0.905(5)	0.227(4)	−0.005(3)
H(211)	0.096(5)	0.018(4)	0.207(4)
H(212)	0.090(5)	1.001(4)	0.102(4)
H(213)	0.115(5)	0.104(4)	0.115(4)
H(221)	0.585(4)	0.052(3)	0.154(3)
H(222)	0.615(4)	0.111(3)	0.089(3)
H(223)	0.522(4)	0.135(3)	0.174(3)

TABLE 3

Bond lengths (Å) and angles (°)

(*a*) Distances			
Mn(1) · · · Mn(2)	3.233(1)		
S(1) · · · S(2)	3.251(1)		
Mn(1)–S(1)	2.416(1)	Mn(2)–S(2)	2.414(1)
Mn(1)–S(2)	2.441(1)	Mn(2)–S(1)	2.435(1)
Mn(1)–N(1)	2.023(2)	Mn(2)–N(2)	2.035(3)
N(1)–C(10)	1.269(5)	N(2)–C(20)	1 280(5)
C(10)–S(11)	1.747(3)	C(20)–S(21)	1.751(4)
S(11)–C(11)	1.784(5)	S(21)–C(21)	1.786(5)
N(1)–C(12)	1.476(5)	N(2)–C(22)	1.464(5)
C(10)–S(1)	1.765(3)	C(20)–S(2)	1.759(3)
C(10) · · · N(2)	3.028(5)	C(20) · · · N(1)	3.026(5)
Carbonyl groups			
Mn(1)–C(1)	1.811(4)	Mn(2)–C(2)	1.817(4)
C(1)–O(1)	1.135(5)	C(2)–O(2)	1.134(5)
Mn(1)–C(3)	1.804(5)	Mn(2)–C(6)	1.804(4)
C(3)–O(3)	1.140(6)	C(6)–O(6)	1.134(5)
Mn(1)–C(4)	1.797(5)	Mn(2)–C(5)	1.804(4)
C(4)–O(4)	1.140(6)	C(5)–O(5)	1.136(5)
C(11)–H(mean)	0.93(4)	C(21)–H(mean)	0.99(5)
C(12)–H(mean)	0.92(4)	C(22)–H(mean)	0.94(4)
(*b*) Angles			
S(1)–Mn(1)–S(2)	84.03(3)	S(2)–Mn(2)–S(1)	84.20(4)
Mn(1)–S(1)–Mn(2)	95.17(4)	Mn(2)–S(2)–Mn(1)	95.07(4)
S(1)–Mn(1)–N(1)	68.3(1)	S(2)–Mn(2)–N(2)	68.4(1)
S(2)–Mn(1)–N(1)	92.6(1)	S(1)–Mn(2)–N(2)	92.1(1)
Mn(1)–N(1)–C(10)	104.3(2)	Mn(2)–N(2)–C(20)	103.5(2)
Mn(1)–N(1)–C(12)	133.1(3)	Mn(2)–N(2)–C(22)	134.2(2)
C(10)–N(1)–C(12)	122.2(3)	C(20)–N(2)–C(22)	122.0(3)
Mn(1)–S(1)–C(10)	76.5(1)	Mn(2)–S(2)–C(20)	76.9(1)
S(1)–C(10)–N(1)	110.8(2)	S(2)–C(20)–N(2)	111.1(3)
S(1)–C(10)–S(11)	124.3(2)	S(2)–C(20)–S(21)	125.0(2)
N(1)–C(10)–S(11)	124.8(3)	N(2)–C(20)–S(21)	123.9(3)
C(10)–S(11)–C(11)	102.8(2)	C(20)–S(21)–C(21)	103.1(2)
Mn(2)–S(1)–C(10)	106.4(1)	Mn(1)–S(2)–C(20)	105.7(1)
S(1)–Mn(1)–C(1)	100.2(1)	S(2)–Mn(2)–C(2)	100.3(1)
S(1)–Mn(1)–C(4)	165.3(1)	S(2)–Mn(2)–C(5)	167.8(1)
S(1)–Mn(1)–C(3)	95.3(2)	S(2)–Mn(2)–C(6)	95.0(1)
S(2)–Mn(1)–C(1)	85.7(1)	S(1)–Mn(2)–C(2)	85.9(1)
S(2)–Mn(1)–C(4)	92.4(2)	S(1)–Mn(2)–C(5)	91.7(1)
S(2)–Mn(1)–C(3)	173.7(1)	S(1)–Mn(2)–C(6)	174.9(1)
N(1)–Mn(1)–C(1)	168.5(2)	N(2)–Mn(2)–C(2)	168.7(2)
N(1)–Mn(1)–C(4)	97.7(2)	N(2)–Mn(2)–C(5)	100.4(2)
N(1)–Mn(1)–C(3)	93.0(2)	N(2)–Mn(2)–C(6)	92.3(1)
C(3)–Mn(1)–C(4)	89.8(2)	C(6)–Mn(2)–C(5)	90.0(2)
C(1)–Mn(1)–C(3)	88.2(2)	C(2)–Mn(2)–C(6)	89.3(2)
C(1)–Mn(1)–C(4)	93.8(2)	C(2)–Mn(2)–C(5)	90.8(2)
Mn(1)–C(1)–O(1)	178.3(4)	Mn(2)–C(2)–O(2)	178.6(4)
Mn(1)–C(3)–O(3)	177.1(4)	Mn(2)–C(6)–O(6)	177.2(4)
Mn(1)–C(4)–O(4)	178.2(4)	Mn(2;–C(5)–O(5)	178.0(3)

TABLE 4

Equations of some least-squares planes: distances (Å) of relevant atoms from these planes are given in square brackets

Plane (1): Mn(1), S(1), Mn(2), S(2)

$$2.6714x + 5.2803y + 12.5004z = 7.1759$$

[Mn(1) 0.098, S(1) −0.099, Mn(2) 0.099, S(2) −0.098]

Plane (2): Mn(1), S(1), C(10), N(1)

$$2.2164x + 12.8628y - 4.6320z = 5.6680$$

[Mn(1) 0.007, S(1) −0.009, C(10) 0.016, N(1) −0.015, S(11) 0.128, C(11) 0.357, C(12) 0.084]

Plane (3): Mn(2), S(2), C(20), N(2)

$$1.\ 3589x + 11.1220y - 8.8047z = 0.9246$$

[Mn(2) −0.007, S(2) 0.008, C(20) −0.015, N(2) 0.013, S(21) −0.126, C(21) −0.164, C(22) −0.062]

Angles (°) between least-squares planes: (1)–(2) 80.1; (1)–(3) 80.8; (2)–(3) 19.1

The angles between the normals to planes (2) and (3) and the axis of two-fold molecular symmetry are 80.4°

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[4] E. W. Abel and I. D. H. Towle, *J. Organometallic Chem.*, 1976, **122**, 253.

[5] K. Tanaka, Y. Miya-Uchi, and T. Tanaka, *Inorg. Chem.*, 1975, **14**, 1545.

the chelate rings being longer; the mean values are 2.415(1) and 2.438(1) Å. The bond angles likewise alternate, S–Mn–S being 84.1 and Mn–S–Mn 95.1°.

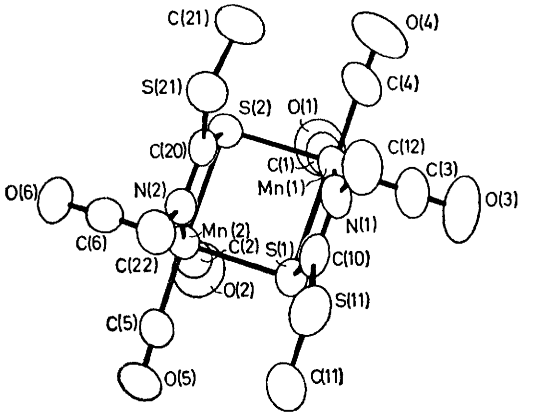


FIGURE 1 Molecular configuration of $[Mn_2(CO)_6\{\mu\text{-}SC(SMe)(NMe)\}_2]$ viewed perpendicular to the mean plane through Mn(1)–S(1)–Mn(2)–S(2), showing idealised C_2 molecular symmetry

The metal–metal distance [3.233(1) Å] must be non-bonding. The four ring atoms of the bridging chelate are closely planar (Table 4), and the carbon atom of the methyl group on the nitrogen atom deviates from the plane by less than 0.1 Å, giving an effectively trigonal-planar nitrogen atom. The N=C bond length (mean 1.275 Å) evidences its description as a localised double bond, and indicates electron-pair donation from nitrogen to manganese as shown in (4a). The configuration of the SMe group on the carbon atom of the chelate ring also supports the description of N=C double bonding, since again the deviation from planarity is relatively slight. This is, however, the only feature to contravene slightly the two-fold symmetry, in that C(11) deviates from the plane of the chelate significantly more than does the symmetry-related atom C(21). In both cases the deviation is away from the molecular centre. The mean Mn–C and C–O distances are 1.806(3) and 1.136(4) Å respectively, and there are no significant differences according to whether a carbonyl group is *trans* to S or N. There are no significantly short intermolecular contacts. The packing of the molecules in the monoclinic unit cell is illustrated in Figure 2.

The localisation of π bonding to the N=C bond of the bridging chelate is necessary if the sulphur atom is to bridge effectively, since increased sp^2 character in this atom would involve a direction of lone-pair electron density away from manganese.

The probable precursor of (4a) is the complex $[Mn(CO)_4\{SC(SMe)(NMe)\}]$ (2) which readily dimerises with CO loss and sulphur-bridge formation. Such dimerisations have been observed[5] for $[Mn(CO)_4(XYCNMe_2)]$ (XY = SS, SSe, or SeSe) and $[Mn(CO)_4\{XOC(NMe_2)\}]$ (X = S or Se); moreover, we have established that (1b) on heating in heptane for 1 h is quantitatively converted into $[Mn_2(CO)_6\{\mu\text{-}S_2CN(H)Me\}_2]$. The three carbonyl bands of the latter indicate a *trans*-bridged structure related to (4b), and in accord with the structure proposed[5] for $[Mn_2(CO)_6(\mu\text{-}S_2CNMe_2)_2]$.

In an attempt to establish the intermediacy of (2) in the formation of (4a), $[MnBr(CO)_5]$ was treated with a mixture of MeNCS and Na[SMe]. The last two reagents were intended to provide Na[SC(SMe)(NMe)] which with the halide would yield (2) and thence hopefully (4a). The latter was indeed a product, but in only 1% yield; however, the fact that it was formed at all is significant. Other products were (1b), $[Mn(CO)_4(S_2CSMe)]$, and $[\{Mn(CO)_4(\mu_2\text{-}SMe)\}_2]$, each in similarly low yield.

Intermediacy of (2) in the formation of (4a) suggests the presence, prior to methylation by MeI, of the anion (5) (see Scheme), which appears in conflict with the previous conclusion that an anion $[Mn(CO)_4(S_2CNMe)]^-$ (6) precedes the formation of the dithiocarbamates (1b) and (3a). These views may, however, be reconciled by supposing that the reaction of MeNCS with $Na[Mn(CO)_5]$ yields a mixture of the anions (5) and (6), which could perhaps be in equilibrium *via* an *S*-bonded unidentate intermediate. It is then postulated that, in the absence of MeI, the exocyclic negatively charged nitrogen of (6) abstracts a proton (from thf or contaminant water) to yield the observed (1b) and thence (3a). When MeI is added, however, methylation of unprotonated (5) at exocyclic sulphur occurs to give (2) and subsequently (4a). Ready protonation of (6) is to be expected, while it is significant that the postulated preference of (5) for methylation rather than protonation is exactly mirrored by the established behaviour of $[Mn(CO)_4(S_2CS)]^-$.[1] Should either (5) or (6) be formed exclusively from Na-

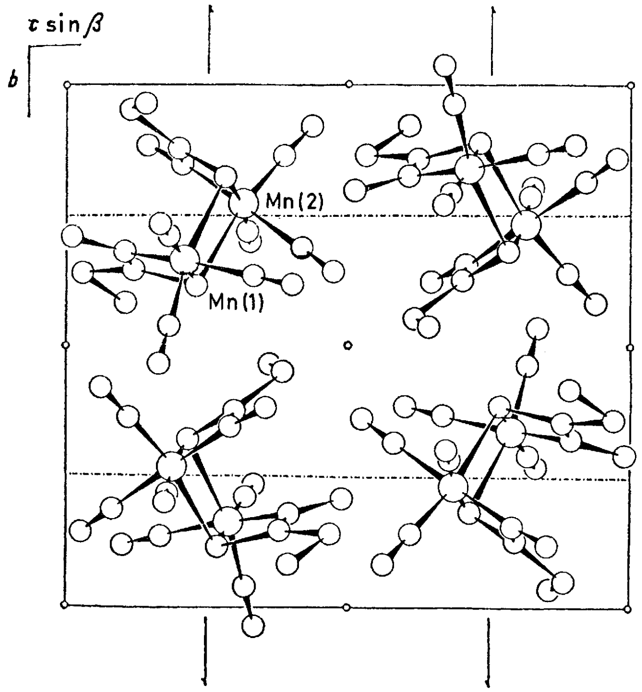
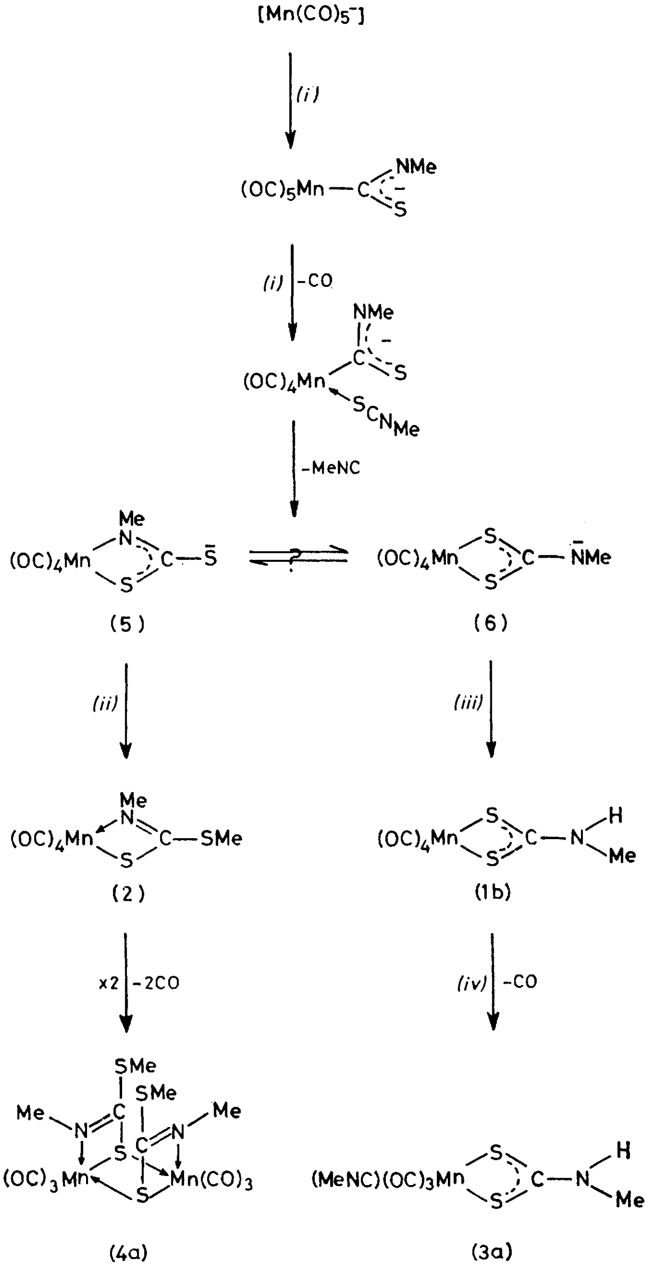


FIGURE 2 Contents of the monoclinic unit cell of $[Mn_2(CO)_6\{\mu\text{-}SC(SMe)(NMe)\}_2]$ viewed down *a* looking towards the origin

$[Mn(CO)_5]$ and MeNCS, then, in the absence of MeI, protonation at nitrogen of either must be favoured, and in its presence methylation at sulphur, with rearrangement where necessary.

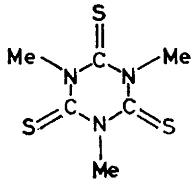


SCHEME Proposed path of the reaction between $Na[Mn(CO)_5]$ and MeNCS. (*i*) MeNCS; (*ii*) MeI, (*iii*) H^+; (*iv*) MeNC

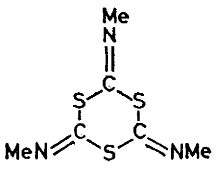
An overall picture of the reaction of $[Mn(CO)_5]^-$ with MeNCS therefore emerges as presented in the Scheme. The first step parallels the behaviour of CS_2 with metal carbonyl anions, while the abstraction of sulphur from an isothiocyanate and evolution of an isocyanide has ample precedent. The first such report concerned the reactions of PhNCS with $[Fe_3(CO)_{12}]$ and $[Mo(CO)_6]$, which provided $[Fe(CO)_4(CNPh)]$ and $[Mo(CO)_3(CNPh)_3]$ respectively,[6] while we have observed that MeNCS displaces MeCN from $[Cr(CO)_5(NCMe)]$, but only to form $[Cr(CO)_5(CNMe)]$.[7] Even more significant, in terms of the work described here, is the report by Bowden *et al.*[8] of iminomethanedithiolato-complex formation upon treating $[Pt(PPh_3)_2(allene)]$ or $[Pt(PPh_3)_4]$ with RNCS (R = Me or Ph). The isolation of an isocyanide complex $[Pt(PPh_3)(CNPh)(S_2C{:}NPh)]$ speaks for striking similarities in reaction path.

It is difficult to account for the virtual disappearance of (1b) and (3a) as products when MeI is added following reaction of $Na[Mn(CO)_5]$ with MeNCS. The reaction of the latter reagents was allowed to proceed for the usual time, so that (1b) and (3a) must have been present when MeI was added, and it has been established independently that MeI does not react with these complexes. Interestingly, addition of MeI following reaction of PhNCS with $Na[Mn(CO)_5]$ has no effect, the products being (1c) and (3b), as when MeI was absent. This suggests that for PhNCS an anion structurally analogous to (6) is formed exclusively, perhaps on steric grounds.

Reaction of MeNCS with $[N(PPh_3)_2][Mn(CO)_5]$ was slow, but shown to be complete after 2 d by i.r. monitoring, and yielded (1b; 24%) and (3a; 4%). When MeI was added after 2 d, destruction of these complexes occurred, the isolated products being $[Mn(CO)_4(S_2CSMe)]$ and a trimer of methyl isothiocyanate, yellow crystalline $(MeNCS)_3$. Of the two most likely structures (7a) and (7b) for the trimer, that with exocyclic sulphur



(7a)



(7b)

(7a) is favoured in view of the observation of ν(C=S) in the i.r. spectrum at 1 080 cm^{-1}, whereas ν(C=N) would be expected for (7b) in the 1 600—1 700 cm^{-1} region. An n.m.r. signal at τ 5.6 is typical of NMe.

The effect of adding sulphur to reactions of metal carbonyl anions with CS_2 has been investigated and found significant.[1] Sulphur was therefore added to $[N(PPh_3)_2][Mn(CO)_5]$, a procedure believed[1] to yield $[MnS_n(CO)_5]^-$, followed immediately by MeNCS. The only product isolated under these conditions was (1b) in 23% yield. The non-production of the MeNC derivative (3a) argues strongly that the provided elemental sulphur is incorporated into (1b). This then makes a sulphur abstraction from MeNCS unnecessary, so that consequently there is no free MeNC in the system to afford (3a). Addition of sulphur to $[N(PPh_3)_2][Mn(CO)_5]$

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[6] T. A. Manuel, *Inorg. Chem.*, 1964, **3**, 1703.

[7] R. Goddard, S. D. Killops, S. A. R. Knox, and P. Woodward, *J.C.S. Dalton*, following paper.

[8] F. L. Bowden, R. Giles, and R. N. Haszeldine, *J.C.S. Chem. Comm.*, 1974, 578.

followed by RNCS (R = Me or Ph) and then $SFO_2(OMe)$ gives only (1b) or (1c), respectively, in low yield.

The reaction of $Na[Re(CO)_5]$ with CS_2 and then $[ReBr(CO)_5]$ provided a good yield of the trithiocarbonate-bridged complex $[(OC)_4Re(\mu\text{-}S_2CS)Re(CO)_5]$,[1] prompting the treatment of $Na[Mn(CO)_5]$ successively with MeNCS and $[MnBr(CO)_5]$. No related dimanganese complex was obtained, however, the products including $[Mn(CO)_4(S_2CSMe)]$ in surprisingly high yield (*ca.* 20%), a trace amount of (1b), and (3a) (5%). The major product was a mixture of the known $[\{Mn(CO)_4(\mu_2\text{-}SMe)\}_2]$ and $[\{Mn(CO)_3(\mu_3\text{-}SMe)\}_4]$. No simple mechanism for the formation of these complexes is apparent.

A variety of other metal carbonyl anions was treated with MeNCS, but with less success than for $[Mn(CO)_5]^-$. The sodium salt of $[Re(CO)_5]^-$, treated with MeNCS and then MeI, gave four low-yield products, two of which were identified as $[Re(CO)_4\{S_2CN(H)Me\}]$ (1d) and $[Re(CO)_3(CNMe)\{S_2CN(H)Me\}]$ (3c) and another as $[ReI(CO)_4(CNMe)]$. The latter, isolated as fine yellow needle-like crystals, has ν(C≡N) at 2 220 cm^{-1} and four carbonyl bands (Table 1) typical of a *cis*-octahedral geometry. Clearly, a complicated reaction has occurred with degradation of MeNCS to MeNC again prevalent, but with parallels to the behaviour of $[Mn(CO)_5]^-$.

Reaction of $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$ with MeNCS and MeI successively gave the trithiocarbonate $[Mo(CO)_2(S_2CSMe)(\eta\text{-}C_5H_5)]$, strangely in higher yield than when the anion is treated with CS_2 and MeI (14 against 2%).[1] Only a trace amount of this complex and of $[Mo(CO)_2\{S_2CN(H)Me\}(\eta\text{-}C_5H_5)]$ were formed when MeNCS and MeI were added to $[N(PPh_3)_2][Mo(CO)_3(\eta\text{-}C_5H_5)]$, but now the trimer $(MeNCS)_3$ was obtained as a major product. It is noteworthy that $(MeNCS)_3$ is only formed from the $[N(PPh_3)_2]^+$ salts of $[Mn(CO)_5]^-$ and $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ and not from the sodium salts. Complexes $[Mo(CO)_2\{S_2CN(H)R\}(\eta\text{-}C_5H_5)]$ [R = Pr^i or CH(Me)Ph] have been described,[9] prepared from $[MoCl(CO)_3(\eta\text{-}C_5H_5)]$ and $Na[S_2CN(H)R]$.

Reactions of $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$ and $Na_2[Ru(CO)_3\{P(OMe)_3\}]$ [10] with MeNCS, followed by addition of MeI, gave no identifiable products. A similar sequence performed with $Na[Ru(SiMe_3)(CO)_4]$,[11] however, gave a small amount of yellow oil showing weak ν(N≡C) at 2 205 cm^{-1}, two carbonyl bands (2 025s and 1 955vs cm^{-1}), and in the ^1H n.m.r. spectrum three singlets of relative intensity 1 : 1 : 3 at τ 6.85, 7.60, and 9.80, characteristic of NMe, SMe, and $SiMe_3$. These data are in accord with a complex $[Ru(SiMe_3)(CO)_2(CNMe)(S_2CSMe)]$, having *cis* carbonyl groups.

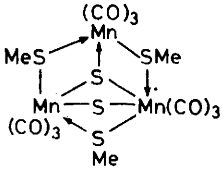
Attempts were made to activate bis(cyclohexyl)-carbodi-imide, $C_6H_{11}N{:}C{:}NC_6H_{11}$, by $[Mn(CO)_5]^-$. The products of treating the di-imides RN:C:NR (R = Pr^i or C_6H_{11}) with $[Fe(CO)_5]$, *viz.* $[Fe_2(CO)_6\{C(NR)_3\}]$ and $[Fe(CO)_4(CNR)]$, provide striking evidence of a capacity for di-imides to rearrange in a similar manner to isothiocyanates with transition-metal complexes.[12] However, addition of $C_6H_{11}N{:}C{:}NC_6H_{11}$ then MeI to $Na[Mn(CO)_5]$ yielded only the urea $C_6H_{11}N(H)C(O)N(H)C_6H_{11}$, as a result of hydration. This was likewise the only product of a similar reaction employing the more nucleophilic $Na[Mn(CO)_4(PMe_2Ph)]$. Addition of sulphur to $[N(PPh_3)_2][Mn(CO)_5]$, followed by the di-imide and then $SFO_2(OMe)$ also failed to activate the C=N bond.

Alkyl isocyanates have been activated by metal carbonyl anions such as $Na[W(CO)_3(\eta\text{-}C_5H_5)]$ [13] and $Na[Re(CO)_5]$,[14] a typical reaction being (1). In an

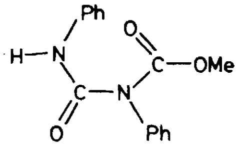
$$[Re(CO)_5]^- + MeNCO + [NHEt_3]^+ \longrightarrow [Re\{CO(NHMe)\}(CO)_5] + NEt_3 \quad (1)$$

attempt to activate phenyl isocyanate, this was added to $Na[Mn(CO)_5]$ followed by $SFO_2(OMe)$; only $[MnMe(CO)_5]$ was obtained, however, indicating negligible reaction. Consecutive addition of sulphur, PhNCO, and $SFO_2(OMe)$ to $[N(PPh_3)_2][Mn(CO)_5]$ was more successful, yielding a carbonylmanganese product, but again no involvement of PhNCO occurred. The orange crystalline, rather insoluble, complex exhibited several carbonyl bands (2 026vs, 2 017vs, 1 968ms, 1 949s, br, and 1 934m cm^{-1}) and three equal-intensity n.m.r. signals at τ 7.10, 7.20, and 7.23 typical of SMe groups. The involatility of the complex did not permit the recording of a satisfactory mass spectrum; that recorded became indistinct above *m/e* 300, but an ion at *ca. m/e* 620 was visible. Osmometric determination of the molecular weight in chloroform gave a value of 734. Clearly, a polynuclear manganese complex was formed. Elemental analyses reveal the absence of nitrogen and best fit a formulation $C_{12}H_9Mn_3O_9S_5$, for which structure (8) is tentatively proposed.

Also formed in this last reaction was a white organic compound whose mass spectrum and analyses conformed to the formulation $C_{15}H_{14}N_2O_3$. The structure (9) is proposed on the basis of i.r. and n.m.r. spectra. There are resonances at τ 2.95 (*ca.* 10 H) and 6.30 (3 H) due to phenyl and methoxy-protons. Although the NH signal was not discerned it might be expected at τ 3.0, as for complexes (1b) and (1c) and would therefore be obscured by the phenyl proton resonance. The i.r. spectrum showed ν(NH) at 3 240 cm^{-1}, ν(CO) at 1 725



(8)



(9)

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[9] H. Brunner, T. Burgemeister, and J. Wachter, *Chem. Ber.*, 1975, **108**, 3349.

[10] S. D. Killops and S. A. R. Knox, unpublished work.

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[14] R. W. Brink and R. J. Angelici, *Inorg. Chem.*, 1973, **12**, 1062.

cm^{-1}, and tertiary and secondary amine ν(CN) at 1 320 and 1 270 cm^{-1} respectively.

EXPERIMENTAL

Instrumentation and experimental techniques were as described in Part 1.[1] Methyl isothiocyanate was freshly distilled prior to use.

Reactions of Na[Mn(CO)$_5$].—(*a*) *With* MeNCS. Methyl isothiocyanate (4.15 g, 57 mmol) in thf (75 cm^3) was added to a thf (75 cm^3) solution of Na[Mn(CO)$_5$] prepared from [Mn$_2$(CO)$_{10}$] (1.11 g, 2.85 mmol) and sodium amalgam (1.5 g Na,13 cm^3 Hg) and the mixture stirred for 2.5 h. The resulting solution was filtered and solvent removed under reduced pressure to leave an orange oil. Chromatography on an alumina column (30 × 2 cm), eluting with dichloromethane–hexane (1 : 2), developed two yellow bands. The first provided 196 mg (15%) of yellow crystalline [Mn(CO)$_4${S$_2$CN(H)Me}] (1b) (Found: C, 26.9; H, 1.6; N, 5.2; S, 26.7%; *M* 273. $C_6H_4MnNO_4S_2$ requires C, 26.4; H, 1.5; N, 5.1; S, 23.5%; *M* 273) and the second 194 mg (14%) of yellow crystalline [Mn(CO)$_3$(CNMe)-{S$_2$CN(H)Me}] (3a) (Found: C, 29.8; H, 2.6; N, 9.9; S, 21.2%; *M* 286. $C_7H_7MnN_2O_3S_2$ requires C, 29.4; H, 2.1; N, 9.8; S, 22.4%; *M* 286).

(*b*) *With* MeNCS *and* MeI. Methyl isothiocyanate was added to Na[Mn(CO)$_5$] exactly as in (*a*), but after stirring for 2 h MeI (2.17 g, 15.3 mmol) in thf (25 cm^3) was added and the whole stirred for another 17.5 h. After treatment of the resulting solution as in (*a*), chromatography on a silica-gel column (30 × 2 cm) yielded, with hexane, 37 mg (3%) of yellow crystalline [Mn(CO)$_4$(S$_2$CSMe)], identified by i.r., mass, and n.m.r. spectra.[1] Further elution with dichloromethane–hexane (1 : 4) provided a trace amount of i.r.-identified (1b), while dichloromethane–hexane (1 : 2) removed a yellow-orange band from which 414 mg (31%) of yellow crystalline [Mn$_2$(CO)$_6${μ-SC(SMe)(NMe)}$_2$] (4a) (Found: C, 27.4; H, 2.3; N, 5.3%; *M* 518. $C_{12}H_{12}Mn_2N_2O_6S_4$ requires C, 27.8; H, 2.3; N, 5.4%; *M* 518) was obtained on crystallisation.

(*c*) *With* PhNCS. Similar treatment of Na[Mn(CO)$_5$] with a solution of PhNCS (4.4 g, 32.6 mmol) in thf (30 cm^3) for 1.5 h gave a red oil after removal of solvent. Chromatography as above with dichloromethane–hexane (1 : 4) gave 197 mg (11%) of orange crystalline [Mn(CO)$_4${S$_2$CN(H)Ph}] (1c) (Found: C, 38.1; H, 2.2; N, 3.8; S, 17.9%; *M* 335. $C_{11}H_6MnNO_4S_2$ requires C, 39.4; H, 1.8; N, 4.2; S, 19.1%; *M* 335), and with dichloromethane–hexane (1 : 2) 41 mg (2%) of yellow crystalline [Mn(CO)$_3$(CNPh){S$_2$CN(H)Ph}] (3b), identified by comparison of its i.r. spectrum with (3a).

Addition of MeI following reaction of Na[Mn(CO)$_5$] with PhNCS affected neither the nature of the products nor their yields.

(*d*) *With* MeNCS *and* [MnBr(CO)$_5$]. To a thf solution of Na[Mn(CO)$_5$] obtained as in (*a*) was added MeNCS (3.75 g, 51 mmol) in thf (30 cm^3) and the mixture stirred for 1 h. The complex [MnBr(CO)$_5$] (2.51 g, 8 mmol) in thf (50 cm^3) was then added and the whole stirred for another 17 h. Filtration and evaporation left a dark brown oil which was introduced onto a 30 × 2 cm silica-gel column. Elution with dichloromethane–hexane (1 : 20) provided a yellow band from which 0.32 g (20%) of [Mn(CO)$_4$(S$_2$CSMe)] was obtained, identified by i.r. and mass spectra.[1] Dichloromethane–hexane (1 : 9) eluted a trace amount of (1b), and a 1 : 7 solvent mixture gave a broad yellow band which yielded a substantial quantity of yellow powder, indicated by i.r. spectroscopy to be a mixture of [{Mn(CO)$_4$(μ$_2$-SMe)}$_2$][15] and [{Mn(CO)$_3$(μ$_3$-SMe)}$_4$].[16] Finally, elution with a dichloromethane–hexane (1 : 2) mixture developed a yellow-orange band which provided 106 mg (5%) of (4a) on crystallisation.

Subsequent heating of the [{Mn(CO)$_4$(μ$_2$-SMe)}$_2$]–[{Mn(CO)$_3$(μ$_3$-SMe)}$_4$] mixture in hexane (100 cm^3) under reflux for 10 min effected conversion into the tetramer. Cooling, concentration, and crystallisation yielded 845 mg (88% based on Na[Mn(CO)$_5$]) of [{Mn(CO)$_3$(μ$_3$-SMe)}$_4$],[16] identified by i.r. and mass spectra, and analysis (Found: C, 25.8; H, 1.7; S, 17.8%; *M* 744. $C_{16}H_{12}Mn_4O_{12}S_4$ requires C, 25.8; H, 1.6; S, 17.2%; *M* 744).

(*e*) *With* $C_6H_{11}N{:}C{:}NC_6H_{11}$ *and* MeI. To a thf solution of Na[Mn(CO)$_5$] obtained as in (*a*) was added $C_6H_{11}N{:}C{:}NC_6H_{11}$ (8.49 g, 41 mmol) in thf (75 cm^3) and the mixture stirred for 20 h. Methyl iodide (2.22 g, 18 mmol) was then added and the whole stirred for another 6 h. Evaporation of the mixture and extraction and filtration of the residue with dichloromethane yielded a dark orange solution. The solvent was removed under reduced pressure and the residue chromatographed on a 30 × 2 cm alumina column. Elution with hexane provided [MnMe(CO)$_5$], while dichloromethane–hexane (1 : 4) afforded white crystalline C_6H_{11}-N(H)C(O)N(H)C_6H_{11} (Found: C, 68.7; H, 10.8; N, 12.6%; *M* 224. $C_{13}H_{24}N_2O$ requires C, 69.6; H, 10.8; N, 12.5%; *M* 224), m.p. 224—225 °C (lit.,[17] 229—230 °C), ν(NH) at 3 320 cm^{-1}, ν(CO) at 1 630 and 1 580 cm^{-1}. Near quantitative conversion of di-imide into the urea occurred.

Reactions of [N(PPh$_3$)$_2$][Mn(CO)$_5$].—(*a*) *With* MeNCS. Infrared monitoring showed that reaction of [N(PPh$_3$)$_2$]-[Mn(CO)$_5$] (1.0 g, 1.37 mmol) with MeNCS (1.04 g, 10.4 mmol) in thf (150 cm^3) was complete after 2 d. Removal of solvent and chromatography of the residue as in (*a*) above gave 90 mg (24%) of (1b) and 14 mg (4%) of (3a).

(*b*) *With* MeNCS *and* MeI. After 2 d reaction of MeNCS with [N(PPh$_3$)$_2$][Mn(CO)$_5$] as immediately above, the solvent was removed and the orange residue dissolved in dichloromethane (50 cm^3). Methyl iodide (2 g, 14.1 mmol) was then added and the solution stirred for 17 h. Evaporation of solvent gave an orange oil which, on chromatography, yielded with hexane 5 mg (1%) of [Mn(CO)$_4$(S$_2$-CSMe)][1] and with dichloromethane–hexane (1 : 9) a yellow band from which 28 mg of yellow crystalline (MeNCS)$_3$ (7a) (Found: C, 33.1; H, 4.2; N, 19.4; S, 43.3%; *M* 219. $C_6H_9N_3S_3$ requires C, 32.9; H, 4.1; N, 19.2; S, 43.9%; *M* 219) was obtained.

(*c*) *With sulphur and* MeNCS. To 2.1 g (2.87 mmol) of [N(PPh$_3$)$_2$][Mn(CO)$_5$] in CH$_2$Cl$_2$ (50 cm^3) was added sulphur (0.5 g, 0.016 g atoms), effecting an immediate colour change from yellow to red. Methyl isothiocyanate (1.33 g, 18.3 mmol) in CH$_2$Cl$_2$ (30 cm^3) was then quickly added, causing the mixture to become yellow then orange. The mixture darkened on stirring overnight, and gave an orange oil on evaporation of solvent. Chromatography on silica gel with dichloromethane–hexane (1 : 2) then gave 165 mg (23%) of (1b).

Addition of SFO$_2$(OMe) (1 cm^3) after stirring [N(PPh$_3$)$_2$]-[Mn(CO)$_5$], sulphur, and MeNCS together overnight served only to reduce the yield of (1b) (53 mg, 7%).

(*d*) *With sulphur*, PhNCS, *and* SFO$_2$(OMe). As above,

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$[N(PPh_3)_2][Mn(CO)_5]$ was treated successively with sulphur, PhNCS (4.4 g, 32.6 mmol), and $SFO_2(OMe)$ (1 cm^3) over similar reaction periods. Identical work-up then gave (1c) (14 mg, 2%).

(*e*) *With sulphur,* PhNCO, *and* $SFO_2(OMe)$. As above, $[N(PPh_3)_2][Mn(CO)_5]$ (7.0 g, 9.5 mmol) was treated successively with sulphur (1.0 g, 0.031 g atoms), PhNCO (4.0 g, 34 mmol), and $SFO_2(OMe)$ (1 cm^3). Removal of solvent and chromatography of the residue on an alumina column gave, with dichloromethane–hexane (1 : 9), a yellow band which yielded *ca.* 100 mg of orange crystalline $[Mn_3S_2(CO)_9(SMe)_3]$ (8) (Found: C, 23.1; H, 1.6; N, 0.0; S, 23.7%; *M ca.* 620. $C_{12}H_9Mn_3O_9S_5$ requires C, 23.2; H, 1.4; N, 0.0; S, 25.7%; *M* 622). Further elution with dichloromethane–hexane (1 : 4) afforded 180 mg of white crystalline PhN(H)C(O)N(Ph)CO(OMe) (9) (Found: C, 67.1; H, 5.5; N, 10.1%; *M* 270. $C_{15}H_{14}N_2O_3$ requires C, 66.7; H, 5.2; N, 10.4%; *M* 270).

Reactions of MeNCS *with other Anions*.—(*a*) *With* $Na[Re(CO)_5]$. To a thf (50 cm^3) solution of $Na[Re(CO)_5]$, prepared from $[Re_2(CO)_{10}]$ (1.0 g, 1.52 mmol) and sodium amalgam (1.5 g Na, 13 cm^3 Hg) for 1 h, was added MeNCS (2.36 g, 32.3 mmol) in thf (25 cm^3) and the whole stirred for another hour. Methyl iodide (1.37 g, 9.6 mmol) in thf (25 cm^3) was then added and after 24 h the solvent was removed from the clear yellow-brown solution giving a brown oil which was extracted with CH_2Cl_2, filtered, and evaporated to yield an orange oil. Chromatography on alumina with dichloromethane–hexane (1 : 4) yielded 75 mg (5%) of pale yellow needle-like $[ReI(CO)_4(CNMe)]$ (Found: C, 16.9; H, 1.0; N, 2.8%; *M* 467. $C_6H_3INO_4Re$ requires C, 15.5; H, 0.6; N, 3.0%; *M* 467) and with dichloromethane–hexane (3 : 2) three pale yellow bands giving in turn *ca.* 1 mg of a yellow powder identified from its i.r. spectrum (Table 1) as $[Re(CO)_4\{S_2CN(H)Me\}]$ (1d), 45 mg (4%) of pale yellow $[Re(CO)_3(CNMe)\{S_2CN(H)Me\}]$ (3c) (Found: C, 20.5; H, 1.9; N, 6.2%; *M* 418. $C_7H_7N_2O_3ReS_2$ requires C, 20.1; H, 1.7; N, 6.7%; *M* 418), and 24 mg of a bright yellow powder [ν(CO) at 2 024s,br and 1 977m cm^{-1}; m.p. 96—102 °C] which was not identified.

(*b*) *With* $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$. To a thf (100 cm^3) solution of $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$ prepared from $[\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ (0.69 g, 1.42 mmol) and sodium amalgam as above was added MeNCS (2.02 g, 27.6 mmol) in thf (50 cm^3) and the mixture stirred for 18 h. Methyl iodide (4.5 g, 32 mmol) was then added and after stirring for 4.5 h the mixture was filtered, the orange-red filtrate being evaporated to yield a dark orange oil. Chromatography on silica gel, eluting with hexane, developed two orange bands, the first providing 5 mg (1%) of $[MoMe(CO)_3(\eta\text{-}C_5H_5)]$ and the second 140 mg (14%) of red crystalline $[Mo(CO)_2(S_2CSMe)(\eta\text{-}C_5H_5)]$, each identified by i.r. and mass spectra.[1]

(*c*) *With* $[N(PPh_3)_2][Mo(CO)_3(\eta\text{-}C_5H_5)]$. A mixture of $[N(PPh_3)_2][Mo(CO)_3(\eta\text{-}C_5H_5)]$ (0.62 g, 0.87 mmol) and MeNCS (2.12 g, 29.0 mmol) in dichloromethane (100 cm^3) was stirred for 3 d at room temperature. After this time MeI (1.0 g, 7.0 mmol) was added and the whole stirred for another 17 h; evaporation of solvent then left a dark red-brown oil which was subjected to chromatography. Elution with dichloromethane–hexane (1 : 2) gave two yellow bands, the first providing 117 mg of $(MeNCS)_3$ and the second a trace amount of $[Mo(CO)_2(S_2CSMe)(\eta\text{-}C_5H_5)]$,[1] each identified by i.r. and n.m.r. spectra. Finally, neat dichloromethane eluted 5 mg (2%) of $[Mo(CO)_2\{S_2CN(H)Me\}(\eta\text{-}C_5H_5)]$, identified by i.r. (Table 1) and mass spectra (Found: *M* 325. $C_9H_9MoNO_2S_2$ requires *M* 325).

Similar reactions performed with $Na_2[Ru(CO)_3\{P(OMe)_3\}]$, $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$, and $[N(PPh_3)_2][Co(CO)_4]$ provided neither identifiable nor significant quantities of products. That of MeNCS and MeI with $Na[Ru(SiMe_3)(CO)_4]$ did yield a very small amount of yellow oil following chromatography, which exhibited ν(C≡N) at 2 025s and 1 955vs cm^{-1}, and ^1H n.m.r. signals at τ 6.85 (1 H), 7.60 (1 H), and 9.80 (3 H).

Reactions of $[Mn(CO)_4\{S_2CN(H)R\}]$ *with* RNC.—About 10 mg of the complexes $[Mn(CO)_4\{S_2CN(H)R\}]$ (1b) and (1c) was stirred in hexane (50 cm^3) at room temperature with excess (1 cm^3) of the appropriate isocyanide RNC. Infrared monitoring witnessed complete conversion into $[Mn(CO)_3(CNR)\{S_2CN(H)R\}]$ (3a) and (3b) within 1 h.

Thermolysis of $[Mn(CO)_4\{S_2CN(H)Me\}]$ (1b).—A heptane (50 cm^3) solution of (1b) (50 mg, 0.17 mmol) was heated under reflux for 1 h. During this time a precipitate formed which increased in quantity as the reaction mixture cooled to room temperature. Solvent was decanted to leave an orange powder which was washed with dichloromethane and vacuum-dried to provide 40 mg (89%) of $[Mn_2(CO)_6\{S_2CN(H)Me\}_2]$ (Found: C, 24.5; H, 1.8; N, 5.3; S, 26.0. $C_{10}H_8Mn_2N_2O_6S_4$ requires C, 24.5; H, 1.6; N, 5.7; S, 26.1%).

Reaction of $[MnBr(CO)_5]$ *with* Na[SMe] *and* MeNCS.—A solution of Na[SMe] was prepared by bubbling MeSH through a stirred suspension of NaH (0.103 g, 2.14 mmol) in thf (25 cm^3) at 0 °C for 2 min. To this was added MeNCS (1.2 g, 16.4 mmol) in thf (25 cm^3), giving a pale yellow solution. Further addition of $[MnBr(CO)_5]$ (0.7 g, 2.54 mmol) in thf (25 cm^3) was made, the mixture slowly becoming green over 2 h as it was allowed to warm to room temperature. The solvent was then evaporated and the residue extracted with dichloromethane, re-evaporation giving a brown oil. Chromatography on silica gel with hexane provided two pale yellow bands containing in turn 72 mg (14%) of $[Mn_2(CO)_{10}]$ and 7 mg (1%) of $[Mn(CO)_4(S_2CSMe)]$.[1] With dichloromethane–hexane (1 : 9), (1 : 4), and (1 : 2) solvent mixtures, 21 mg (3%) of (1b), 22 mg (2%) of $[\{Mn(CO)_4(\mu_2\text{-}SMe)\}_2]$, and 11 mg (1%) of (4a), each identified by i.r. spectroscopy, were successively eluted.

X-Ray Data Collection and Structure Determination.—Crystals of $[Mn_2(CO)_6\{\mu\text{-}SC(SMe)(NMe)\}_2]$ (4a) grow as orange-red plates. Diffracted intensities were collected from a crystal of dimensions 0.26 × 0.70 × 0.10 mm mounted on a Syntex $P2_1$ four-circle diffractometer according to methods described earlier.[18] Of the total (3 239) reflections for $2.9 < 2\theta < 50°$, 2 525 were deemed 'observed' according to the criterion $I > 2.5\sigma(I)$, where $\sigma(I)$ is the estimated standard deviation based on counting statistics, and only these were used in the solution and refinement of the structure. The intensities were corrected for the effects of *X*-ray absorption.[19]

Crystal data. $C_{12}H_{12}Mn_2N_2O_6S_4$, $M = 518$, Monoclinic, $a = 9.845(2)$, $b = 13.791(4)$, $c = 14.972(5)$ Å, $\beta = 98.23(4)°$, $U = 2\,012(2)$ Å^3, $D_m = 1.68$ g cm^{-3}, $Z = 4$, $D_c = 1.71$ g cm^{-3}, $F(000) = 1\,040$, space group $P2_1/n$, Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 17.5$ cm^{-1}.

The two manganese atoms were located by direct

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methods,[20] the rest of the atoms (including hydrogen) by successive electron-density difference syntheses. The structure was refined by blocked-matrix least squares, with anisotropic thermal parameters for all the non-hydrogen atoms. For the hydrogen atoms the positional parameters were allowed to refine, but the isotropic thermal parameters were kept invariant at 110% of the value of the isotropic thermal parameter of the carbon atom to which they are bonded. The refinement converged at R 0.029 (R' 0.038) with a mean shift-to-error ratio in the last cycle of 0.06. A weighting scheme of the form $1/w = 2.0 - 0.01|F| + 0.002\,5|F|^2 - 0.000\,01|F|^3$ gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks >0.2 or < -0.1 e Å^{-3}. Scattering factors were from ref. 21 for C, N, O, S, and Mn, and from ref. 22 for H. Atomic positional parameters are in Table 2, interatomic distances and angles in Table 3, and some least-squares planes in Table 4. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22259 (14 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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