An Unusual Sulphur Incorporation: Formation and Crystal Structure of $[\mathrm{Mn(CO)_3\{\mu\text{-}SC(SMe)NMe\}}]_2$

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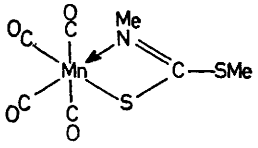
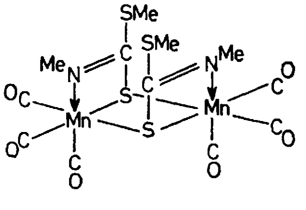
Summary Consecutive treatment of $[\mathrm{Mn(CO)_5}]^-$ with methyl isothiocyanate and methyl iodide yields $[\mathrm{Mn(CO)_3\{\mu\text{-}SC(SMe)NMe\}}]_2$; the molecular structure has been determined by X-ray diffraction, and shown to contain a previously unreported bridging chelate ligand.

We have recently described[1] the formation of trithiocarbonate complexes $\mathrm{M(CO)_4(S_2CSMe)}$ (M = Mn, Re) upon successive treatment of the anions $[\mathrm{M(CO)_5}]^-$ with carbon disulphide and methyl iodide. Like carbon disulphide, methyl isothiocyanate contains an electrophilic carbon atom, and we were prompted to investigate whether a similar sulphur incorporation would occur with this reagent. If reaction occurs with $[\mathrm{Mn(CO)_5}]^-$, formation of a dithiocarbamate complex $\mathrm{Mn(CO)_4(S_2CNMe_2)}$ or of $\mathrm{Mn(CO)_4\{SC(SMe)NMe\}}$ (I) containing a new three electron ligand, or of both, could be postulated.

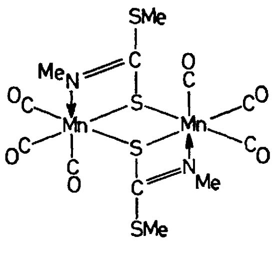
We now report that consecutive addition of excess methyl isothiocyanate and methyl iodide to a tetrahydrofuran solution of $\mathrm{NaMn(CO)_5}$ does result in incorporation of sulphur, but that orange crystalline $[\mathrm{Mn(CO)_3\{\mu\text{-}SC(SMe)NMe\}}]_2$ (II) is the major product (31%). Although the ^{1}H n.m.r. spectrum of (II) indicates the presence of both N*Me* {τ 6·7, 6H, s} and S*Me* {τ 7·5, 6H, s} groups, it does not distinguish between the possible *cis*- and *trans*-bridged structures (IIa) and (IIb). The six carbonyl stretching bands (2039m, 2020s, 1954m, 1942s, 1930sh, and 1926s cm^{-1}) observed in the i.r. spectrum, however, are compatible with structure (IIa) rather than with the more symmetric



(I)

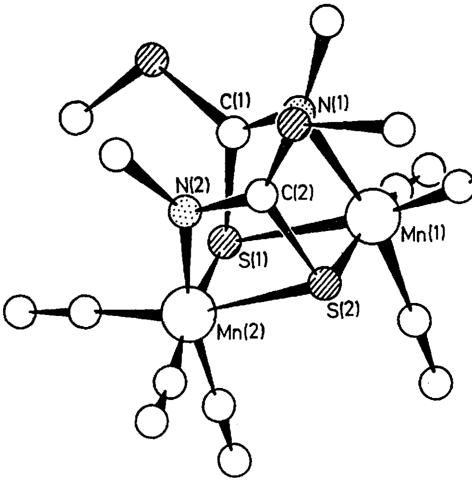


(IIa)



(IIb)

(IIb), for which three bands are predicted. On this same basis it has been suggested[2] that the complexes $[\overline{\mathrm{Mn(CO)_3\{\mu\text{-}SC(NMe_2)O}}\}]_2$ and $[\overline{\mathrm{Mn(CO)_3\{\mu\text{-}SC(NMe_2)NPh}}\}]_2$ are *cis*- and *trans*-bridged respectively. A single crystal *X*-ray diffraction study on (II) has confirmed the *cis*-bridged structure (IIa).



Crystal data: $C_{12}H_{12}N_2O_6S_4Mn_2$, $M = 518$, monoclinic, space group $P2_1/n$, $a = 9{\cdot}872(4)$, $b = 13{\cdot}784(3)$, $c = 15{\cdot}006(8)$ Å, $\beta = 98{\cdot}20(4)°$ at 23° C, $\mu = 2021(1)$ Å^3, $D_m = 1{\cdot}68$ g cm^{-3}, $Z = 4$, $D_c = 1{\cdot}70$ g cm^{-3}, $F(000) = 1040{\cdot}0$, Mo–K_α *X*-radiation (graphite monochromator), $\lambda = 0{\cdot}71069$ Å; μ (Mo–K_α) = 17·3 cm^{-1}. Atoms were located by a combination of direct methods (Mn) and successive difference Fourier syntheses (S, O, N, C and H) from data collected (to $2\theta = 50°$) on a Syntex P2_1 four-circle diffractometer. For the 2525 independent reflections, $R = 0{\cdot}056$.

The molecular geometry is as shown in the Figure. The molecule is a tricyclic sulphur-bridged dimer with each of the three 4-membered rings planar. There is no crystallographically imposed symmetry, but the molecular symmetry in fact approximates (less than 2σ of the atomic co-ordinates) to $C_2(2)$. Within the Mn_2S_2 ring, the Mn–S distances fall in the range 2·41—2·43 Å with ∠Mn–S–Mn = (mean 95°), and ∠S–Mn–S = (mean 84°). The Mn .... Mn distance of 3·233(2) Å is non-bonding. The N–C distances (mean 1·28 Å) are compatible with N=C double bonding, and indicate electron pair donation to manganese from an essentially trigonal nitrogen (mean Mn–N = 2·04 Å). Consistent with this the S(1)–C(1) and S(2)–C(2) distances, (mean 1·77 Å) are of single bond length.

The localisation of π-bonding to the N=C bond of the bridging chelate is evidently necessary if the sulphur atom is to bridge effectively. Increased sp^2 character in this atom would involve a direction of lone pair electron density away from manganese. It thus becomes apparent that (I), the probable precursor of (II), has localised π-bonding as shown, allowing tetrahedral sulphur to effect dimerisation *via* bridging. The related $Mn(CO)_4(S_2CSMe)$, which has two essentially sp^2 sulphur atoms co-ordinated to manganese, is not prone to dimerisation.

Formation of the probable intermediate (I) may occur *via* nucleophilic attack of $[Mn(CO)_5]^-$ upon MeNCS to yield $[Mn(CO)_5\{C(NMe)S\}]^-$ which, following CO substitution by MeNCS, ejects a molecule of MeNC to afford $[Mn(CO)_4\{SC(S)NMe\}]^-$, the source of (I) on methylation. Abstraction of sulphur from isothiocyanates by transition-metal complexes, with formation of isocyanides, has been observed.[3]

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