The Constitution of Tricarbonylmanganese Sulphide Complexes

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THE current interest in metal atom clusters[1] is reflected in the most recent publications from the groups of Abel[2] and Stone,[3] concerning trinuclear carbonylmanganese sulphide complexes. We present here evidence which leads us to believe that these complexes should in fact be formulated as tetramers and not as trimers.

Thiols react with halogenometal carbonyls,[4,5] and nitrosyls,[6] in the presence of base, to yield mononuclear sulphides which in many cases may be isolated. Bromopentacarbonylmanganese is a typical substrate under such mild reaction conditions, but the initial mononuclear derivatives $RSMn(CO)_5$ are unstable with respect to dimer $[RSMn(CO)_4]_2$ formation, and to further reaction with sulphide anion. The exact course of the latter reaction, which yields intermediate paramagnetic products, is complicated and not known. However the final products are tetrameric materials, $[RSMn(CO)_3]_4$ (R = Me, Ph) or under slightly different conditions, $(RS)_3Br[Mn(CO)_3]_4$ (R = Ph). The dimers $[RSMn(CO)_4]_2$, which may be easily isolated are, however, also thermodynamically unstable with respect to tetramer formation.

Identification of the dimers, by comparison with the published data[7,8] is further substantiated by mass spectroscopy for R = Me. Stepwise losses of eight CO groups from the appropriate parent ions are accompanied by the appearance of the necessary metastable ions. The spectra of $[MeSMn(CO)_4]_2$ always reveal traces of tetramer, but no intermediate species. Similarly crude and purified samples of each tetramer show the characteristic stepwise loss of twelve CO groups from the parent, but no trace of trimer; the subsequent fragmentation of charged $[MnSR]_4$ species is to $[MnSR]_2$ and eventually $[Mn]_2$ units, and not trinuclear manganese species. $(PhS)_3Br[Mn(CO)_3]_4$ was identified mass spectrometrically by an accurate mass measurement of the $[P-12CO]^+$ ion.

Data (i.r. and ^1H n.m.r. spectra) concerning the supposed trimeric species $[Mn(CO)_3SR]_3$ which have been published recently,* coincide with those of the above tetramers. Repetition of two of these described preparations (Abel; R = Me, and Stone; R = Ph) has yielded products which are identical in every respect with the appropriate tetramers.

This identity was established in the solid phase by comparison of i.r. spectra and X-ray powder photographs, in the vapour phase by mass spectra, and in solution by i.r. and ^1H n.m.r. spectroscopy and osmometric molecular-weight measurements. In benzene solution the molecular weights are:

$[MeSMn(CO)_3]_4$ requires 744; found 785.

$[PhSMn(CO)_3]_4$ requires 992; found 982.

Clearly the nuclear aggregation of the corresponding rhenium analogues now requires re-investigation.

Although the i.r. spectra are consistent with other structures, the tetrahedral formulation shown (Figure) is suggested for $[RSMn(CO)_3]_4$. This depicts two of the possible tautomeric forms and infers localised bonding. There exists however, the possibility of valence tautomerism between these various forms. An alternative formulation, in which all four manganese atoms are equivalent and the four SR groups are symmetrically located above each face of the tetrahedron by three-centre bonds, is not supported by the mass-spectral data.

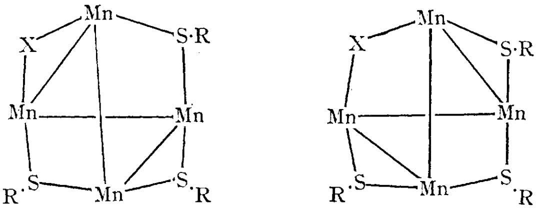

FIGURE. *Two possible bonding arrangements in complexes of type* $[Mn(CO)_3]_4$ $[RS]_3X$. (X = Br; SR.) (*Carbonyl groups omitted for clarity.*)

(*Received, November* 11*th*, 1966; *Com.* 879.)

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* We are pleased to acknowledge complete exchange of information with Dr. Abel prior to publication.