Aminomethylenetetracarbonyls of Manganese: *X*-Ray Crystal Structure of Aziridinylmethyltetracarbonylmanganese

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Summary The reactions of dialkylaminomethyltrialkyltins and bromopentacarbonylmanganese provide dialkylaminomethylenetetracarbonyls of manganese(0); the molecular structure of aziridinylmethyltetracarbonylmanganese has been determined crystallographically.

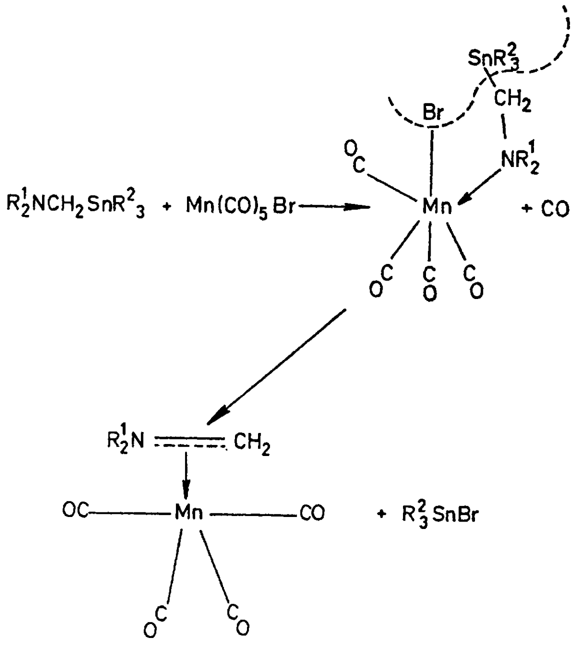
THE fission reactions of many organotin bases, such as amines[1] and sulphides[2] have previously been shown to be useful routes for the formation of inorganic complexes.

We have found that the dialkylaminomethyltrialkyltins react with bromopentacarbonylmanganese to produce the aminomethylenetetracarbonyls of manganese [equation (1)].

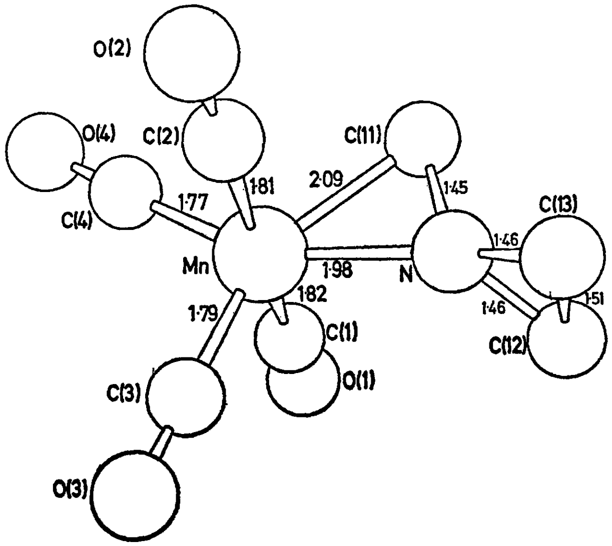
$$R^1_2NCH_2Sn^2R_3 + Mn(CO)_5Br \rightarrow [R^1_2NCH_2]Mn(CO)_4 + R^2_3SnBr + CO \qquad (1)$$

It is likely that the reaction proceeds by the initial displacement of carbon monoxide to form an amine complex, followed by an intramolecular elimination of organotin bromide (see Scheme). This is analogous to the suggested formation of π-allyl systems by a similar co-ordination–elimination sequence.[3]

For R^1 = Me, Et, Pr^n, Bu^n, Bu^i these novel complexes have been isolated as orange liquids at room temperature in 40—60% yields, and characterised by elemental analysis, n.m.r. and i.r. spectra, and mass spectrometry.



SCHEME



FIGURE

The methyleneaziridine complex forms yellow monoclinic crystals, m.p. 64—66°, with a = 10·803(1), b = 13·812(1), c = 6·347(1) Å; β = 93·99(1)°; $D_c = D_m$ = 1·56 g cm^{-3}; Z = 4; space group $P2_1/n$. Independent reflexions (1314) with $F_0^2 > 3\sigma(F_0^2)$ and having $4° < 2\theta < 50°$ were observed by four-circle diffractometry (Mo-K_α, graphite monochromator, ω–2θ scan routine). The structure analysis was straightforward and refinement by full-matrix least-squares techniques of positional parameters, of anisotropic temperature parameters for the manganese atom and of isotropic Debye factors for the other atoms, has converged to an unweighted discrepancy index R_1 of 0·078. The stereochemistry of the complex and important bond lengths are shown in the Figure. The average e.s.d's in the bond lengths are 0·009 Å for the metal–ligand and 0·015 Å for intra-ligand bonds, respectively.

The observation of essentially symmetric π-bonding of the aminomethylene ligand, rather than the alternative metal–nitrogen σ-bonded arrangement is obviously of interest in connection with the suggestions of Mason and Rucci[4] regarding the structures of copper(I) complexes synthesised directly from the dimethylmethyleneammonium cation. We feel that the difference between the Mn–C(11) and Mn–N bond lengths largely reflects enhanced π-bonding to the nitrogen from the metal in the (−1) oxidation state. The high π-acidity of the aminomethylene ligand is adequately reflected in the N–C(11) bond length of 1·45 Å which corresponds, within experimental error, to unit bond order.

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