Journal of Organometallic Chemistry, 99 (1975) C15—C18
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Preliminary communication

CYCLOOCTATETRAENEHEXACARBONYLDIMANGANESE, $(C_8H_8)Mn_2(CO)_6$. A CORRECTED STRUCTURAL FORMULATION, BASED ON AN X-RAY CRYSTALLOGRAPHIC STUDY

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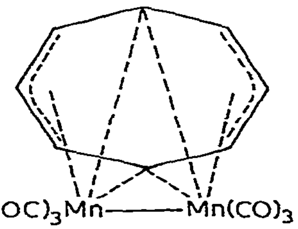
(Received July 17th, 1975)

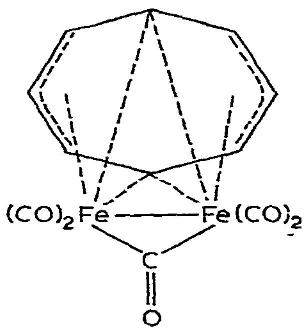
Summary

The structure of $(C_8H_8)Mn_2(CO)_6$ has been determined by a single crystal X-ray diffraction study. The molecule may be regarded as a derivative of $Mn_2(CO)_{10}$ in which 2 carbon monoxide ligands have been replaced by diene units from the C_8H_8 ligand, with concomitant lengthening of the Mn—Mn bond.

The reaction of $H_3Mn_3(CO)_{12}$ with cyclooctatetraene has recently been shown [1] to give rise to the species $(C_8H_9)Mn(CO)_3$ and $(C_8H_8)Mn_2(CO)_6$. The ^1H NMR spectrum of $(C_8H_8)Mn_2(CO)_6$ consists of a sharp singlet, thus indicating that the molecule is "fluxional". Structure I was



(I)



(II)

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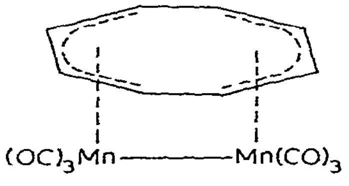
therefore proposed for $(C_8H_8)Mn_2(CO)_6$ by analogy with the known iron derivative $(C_8H_8)Fe_2(CO)_5$ II [2].

We have now completed a single-crystal X-ray diffraction study of $(C_8H_8)Mn_2(CO)_6$ and show that its true structure is different from that originally suggested.

The complex crystallizes in the centrosymmetric orthorhombic space group *Pbca* (D_{2h}^{15}; No. 61), unit cell parameters (at 22.6 °C) being a = 10.096(3), b = 23.825(8), c = 11.472(4) Å, V = 2759(3) Å^3, ρ_{obsd} = 1.842(5), ρ_{calcd} = 1.839 g cm^{-3} for M = 382.1 and Z = 8.

Intensity data to 2θ = 45° (Mo-K_α radiation) were collected with a Picker FACS-1 automated diffractometer using a coupled θ(crystal)—2θ(counter) scan and were corrected for absorption (μ = 19.51 cm^{-1}). The structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques, the final R value being 8.64% for the 1252 independent nonzero (i.e., $I > 3\sigma(I)$) reflections.

The molecule has approximate C_2 symmetry; the possible C_{2v} symmetry is broken by the zig-zag configuration of the (*trans*) OC—Mn—Mn—CO system (see Figs. 1 and 2) with concomitant torsion of the *cis*-Mn—CO linkages. The eight π-electrons of the cyclooctatetraene ligand are factored into two *cis*-diene systems and the molecule is correctly represented by structure III.



(III)

Each of the d^7 Mn^0 atoms achieves the noble gas configuration by the donation of two electrons from each of three carbonyl groups, four electrons from a *cis*-diene system, and one electron from the other manganese atom. The Mn(1)—Mn(2) distance of 3.045(2) Å is considerably longer than the Mn—Mn distance of 2.923 Å in $Mn_2(CO)_{10}$ [3] and is almost as long as the μ_2-hydrido-bridged Mn· · ·Mn vector of 3.111(2) Å in $H_3Mn_3(CO)_{12}$ [4].

The Mn—C(diene) distances, taken cyclically, are: Mn(1)—C(1) = 2.294(11), Mn(1)—C(2) = 2.106(11), Mn(1)—C(3) = 2.102(11), Mn(1)—C(4) = 2.243(12); Mn(2)—C(5) = 2.321(11), Mn(2)—C(6) = 2.141(10), Mn(2)—C(7) = 2.129(12), and Mn(2)—C(8) = 2.230(13) Å. Distances within the diene systems are: C(1)—C(2) = 1.385(17), C(2)—C(3) = 1.359(17), C(3)—C(4) = 1.366(17), C(5)—C(6) = 1.402(16), C(6)—(7) = 1.425(18), C(7)—C(8) = 1.378(19) Å.

Mn—CO bond lengths range from 1.779(14) to 1.800(13) Å and C—O distances from 1.130(12) to 1.183(13) Å. The angles Mn(1)—Mn(2)—C(22) and Mn(2)—Mn(1)—C(13) are 173.5(4) and 165.4(4)°, respectively. The torsion of the CO ligands is illustrated by the inequivalencies Mn(1)—Mn(2)—C(23) = 82.0(3) $\neq$ Mn(1)—Mn(2)—C(21) = 94.3(3) °, and Mn(2)—Mn(1)—C(11) = 80.9(3) ° $\neq$ Mn(2)—Mn(1)—C(12) = 96.8(3) °.

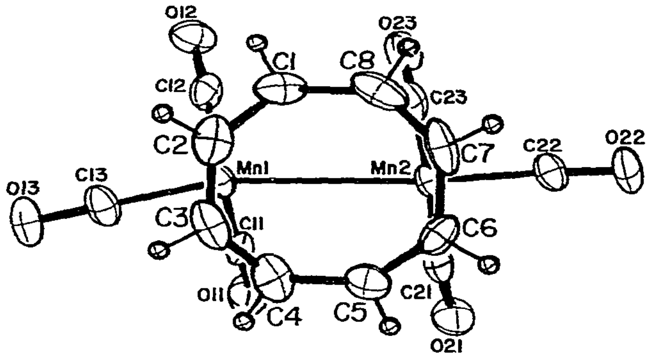


Fig.1. The $(C_8H_8)Mn_2(CO)_6$ molecule projected onto the C(8)—C(1)· · ·C(4)—C(5) plane, showing the torsion in the O(13)—C(13)—Mn(1)—Mn(2)—C(22)—O(22) system.

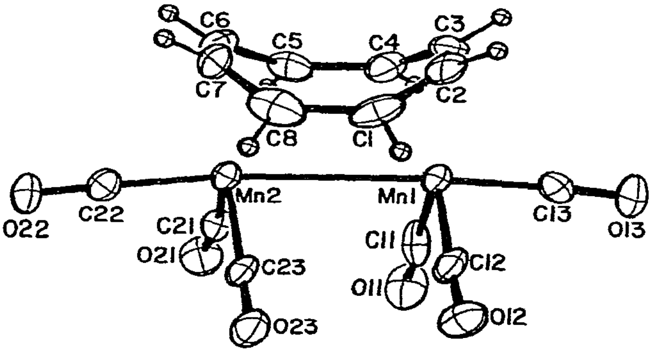


Fig.2. A side view of the $(C_8H_8)Mn_2(CO)_6$ molecule, showing the "tub" conformation of the C_8H_8 ligand.

The differences in the structures of $(C_8H_8)Mn_2(CO)_6$ (III) and $(C_8H_8)Fe_2(CO)_5$ (II) bear a striking similarity to the differences between the corresponding parent bimetallic carbonyls, $Mn_2(CO)_{10}$ and $Fe_2(CO)_9$. Thus, structure III may be thought of as resulting from the replacement of two terminal carbonyl ligands on each manganese atom in $Mn_2(CO)_{10}$ with diene units from the C_8H_8 ligand, along with a lengthening of the Mn—Mn distance to allow for the distance between these two diene units. Structure II may be regarded as derived from $Fe_2(CO)_9$ by replacing two of the bridging carbonyl ligands with single carbon atoms (in relative 1,5 positions) and substitution of one terminal carbonyl ligand on each iron atom with a *trihapto*-allylic unit.

The gross differences between III and II (and between $Mn_2(CO)_{10}$ and $Fe_2(CO)_9$) probably result from the difference in covalent radii of the two metals rather than from any subtle electronic phenomena.

Acknowledgments

This work was generously supported by the National Science Foundation (Grants GP-42724X to M.R.C. and GP-31347X to R.B.K.). M.N.A. is indebted to Oberlin College for a research status appointment during his sabbatical at the University of Georgia.

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