A Novel Stereochemistry for Azulene–Metal Carbonyl Complexes: the Structure of *trans*-Azulenedimanganese Hexacarbonyl

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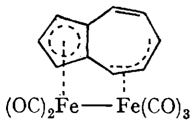
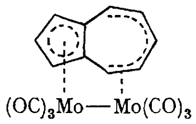
RECENT studies on azulene–metal carbonyl complexes have confirmed a suggestion[1] that the five-membered ring of the azulene bonds to the metal as a substituted π-cyclopentadienyl ligand. In the 1 : 2 azulene-to-metal complexes azulenedi-iron pentacarbonyl[2] (I) and azulenedi-molybdenum hexacarbonyl[3] (II), the metal atoms take up a *cis*-stereochemistry in order to achieve the appropriate inert-gas configuration *via* metal–metal bond formation. Although no definitive structural information is available for simple azulene–metal carbonyls having a 1 : 1 azulene-to-metal ratio, the closely related azulenetricarbonylmethylmolybdenum dimerizes *via* a 4-*exo*,4′-*exo* carbon–carbon bond.[4]

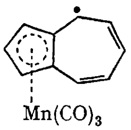
In the course of preparing $[C_{10}H_8Mn(CO)_3]_2$ (following the procedure of Burton *et al.*[5]) we have isolated a new air-stable complex, azulenedimanganese hexacarbonyl. This new molecule exhibits four carbonyl stretching frequencies (2031, 2016, 1966, 1943 cm.$^{-1}$); a mass-spectral analysis shows the parent peak $[C_{10}H_8Mn_2(CO)_6]^+$ along with species consistent with the step-wise loss of CO, *viz.*, $[C_{10}H_8Mn_2(CO)_{6-n}]^+$ (n = 1—6). The complex, $C_{10}H_8Mn_2(CO)_6$, crystallizes in the triclinic space group $P\bar{1}$ (no. 2) with $a = 12{\cdot}90$, $b = 9{\cdot}64$, $c = 6{\cdot}95$ Å, $\alpha = 106{\cdot}5°$, $\beta = 106{\cdot}5°$, $\gamma = 70{\cdot}5°$, $Z = 2$. The crystal structure was solved by conventional Patterson, Fourier, and least-squares refinement procedures. The present discrepancy



(I)

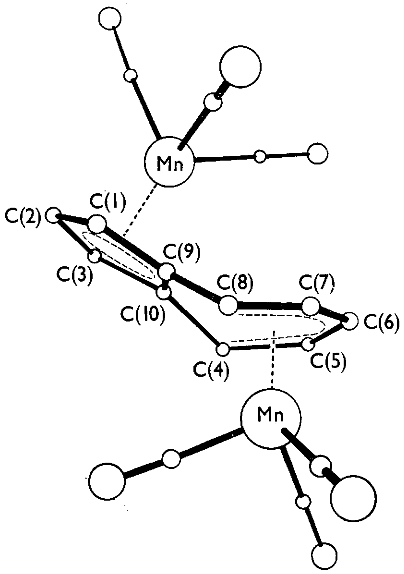


(II)



(III)

index is $R = 8{\cdot}1\%$ for 1683 independent non-zero reflections collected with a Buerger Automated Diffractometer. Estimated standard deviations are ~0·01Å for metal–carbon, and ~0·015Å for carbon–carbon, bond lengths. The molecule contains two $Mn(CO)_3$ groups which are bonded to opposite sides of the azulene ligand, *i.e.*, the molecule has an overall *trans*-configuration (see Figure). One $Mn(CO)_3$ group lies 1·79Å above the planar (r.m.s. deviation = 0·005 Å) five-membered ring, individual Mn–C distances varying from 2·15—2·19 Å [*cf.*, 2·13—2·18 Å in π-$C_5H_5Mn(CO)_3$[6]]. Carbon–carbon distances around the π-cyclopentadienyl system are in the range 1·42—1·45 Å. The second $Mn(CO)_3$ group lies 1·59 Å below the remaining five atoms of the azulene ligand and participates in a non-cyclic π-pentadienylmanganese linkage. Individual distances are Mn–C(4) = 2·28, Mn–C(5) = 2·13, Mn–C(6) = 2·12, Mn – C(7) = 2·14, and Mn–C(8) = 2·28 Å. The five atoms constituting the π-pentadienyl system are approximately co-planar (r.m.s. deviation = 0·021 Å). Carbon–carbon bond lengths within the π-pentadienyl group range from 1·40 to 1·43 Å, whereas the bonds linking π-cyclopentadienyl and π-pentadienyl systems [C(4)–C(10) = 1·48, C(8)–C(9) = 1·48 Å] are in agreement with the expected sp^2–sp^2 single-bond distance. Although the azulene ligand maintains its chemical identity it is badly distorted from planarity, the dihedral angle between π-cyclopentadienyl and π-pentadienyl systems being 34°.



FIGURE

The relationship of $C_{10}H_8Mn_2(CO)_6$ to the dimeric species $[C_{10}H_8Mn(CO)_3]_2$ may be clarified by postulating an intermediate (III) which may either react with a further manganese carbonyl residue giving a *trans*-product (for steric reasons) or dimerize (presumably *via* 4-*exo*, 4′-*exo* carbon–carbon bond-formation).

Further studies on azulene–metal carbonyl species are in progress. This work has been generously supported by the Advanced Research Projects Agency.

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