The Reaction of Tropone with Manganese Carbonyl. The X-Ray Crystal Structure of Tricarbonyl-1-*syn*-(1′,2′-dihydro-2′-oxo-1′-oxa-azulen-3′-yl)-*h*^{5}-pentadienylmanganese

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Summary The structure of the title compound has been determined and shows that its formation involves cleavage of one molecule of tropone, condensation with a second molecule, and formation of a tricarbonylmanganese complex with the open-chain dienyl system so generated.

IN extension of our studies of tropone complexes of iron and chromium[1] carbonyls, and cycloheptatriene complexes of manganese,[2] we have examined the reaction of tropone with decacarbonyldimanganese. The main product of this reaction is a purple crystalline solid giving orange solutions, of composition $C_{17}H_{11}MnO_5$ for which we have determined the structure shown in the Figure.

Crystal data: $C_{17}H_{11}MnO_5$, $M = 350{\cdot}2$, monoclinic, $a = 13{\cdot}249$, $b = 7{\cdot}178$, $c = 15{\cdot}662$ Å, $\beta = 96{\cdot}66°$, $U = 1479{\cdot}5$ Å^3, $Z = 4$, space group $P2_1/c$ by systematic absences, 1045 reflexions with intensities $>3\sigma$ (counting statistics), four-circle diffractometer[3] data, Fourier methods, $R = 6{\cdot}6\%$ (refinement complete).

The structure represents the first recognised example of an open-chain π-pentadienyl complex of manganese. Structural features of interest in this system include the equality of the four carbon–carbon distances of the dienyl group (mean bond length 1·40 Å) and the twisting of the terminal CH_2 group out of the plane of the five carbon atoms by approximately 48°.

The $Mn(CO)_3$ group takes up the same orientation with respect to the five carbon atoms of the pentadienyl group in this open chain structure as it does in the reported cyclic pentadienyl complexes tricarbonyl-π-cyclohexadienylmanganese[4] and hexacarbonyl-*trans*-azulenedimanganese.[5]

The entire carbon skeleton is nearly planar and the Figure shows the molecule projected on that plane. The

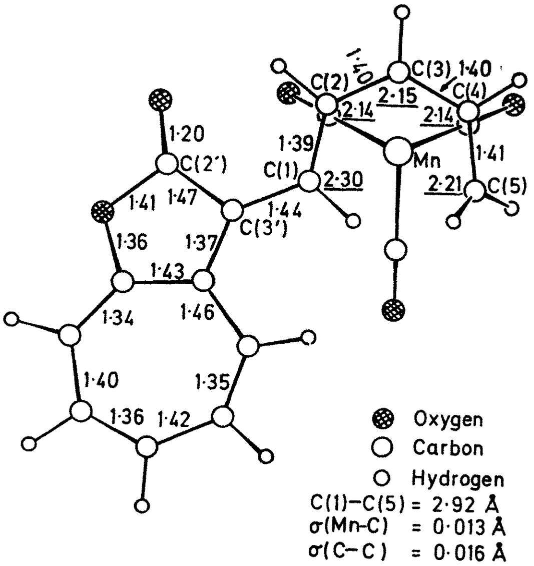

FIGURE *Projected view of molecule. The underlined figures refer to manganese–carbon distances.*

alternation of bond lengths clearly shows the location of single and double bonds in the oxa-azulenone portion. The latter must have arisen through cleavage of one tropone molecule, possibly to a keten intermediate, with addition of a further molecule of tropone. Further changes necessary in the formation of the compound include the migration of a hydrogen atom to C(5), loss of a second hydrogen and rotations about C(1)–C(2) and C(2′)–C(3′).

Mass spectrometric measurements are in accord with the structure. Parent peaks occur at 349·9988 ($C_{17}H_{11}MnO_5$ requires 349·9987) and 351·0017 ($C_{16}{}^{13}CH_{11}MnO_5$ requires 351·0021) and the base peak at *m/e* 266·0123 ($C_{14}H_{11}MnO_2$ requires 266·0140) represents loss of the three carbonyl groups. The next strong peak at *m/e* 263·9961 ($C_{14}H_9MnO_2$ requires 263·9983) represents loss of two hydrogen atoms, probably associated with cyclisation of the five-carbon chain to a cyclopentadienyl group.

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