

Preliminary communication

The structure of a chelated σ -bonded Mn–C complex formed by hydro-metallation of an olefinic tertiary phosphine

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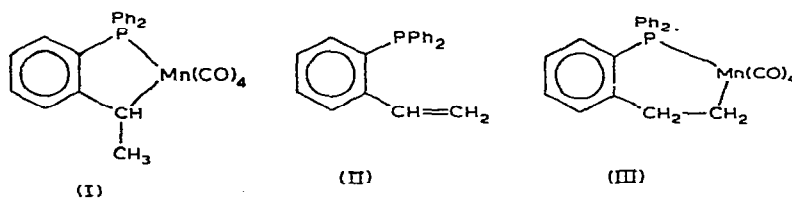
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SUMMARY

The structure of a σ -bonded Mn–C complex, $[(\text{MeCHC}_6\text{H}_4\text{PPh}_2)\text{Mn}(\text{CO})_4]$ has been determined from three-dimensional X-ray data collected by counter methods.

There is very little structural information regarding the Mn–C σ -bond in simple manganese–alkyl complexes¹. We have previously described the structure of a σ -oxobutyl complex $[\{\text{O}=\text{C}(\text{Me})\text{CH}_2\text{CHC}_6\text{H}_4\text{PPh}_2\}\text{Mn}(\text{CO})_3]$ which contains a Mn–C σ -bond². We now report the structure of a second σ -bonded complex $[(\text{MeCHC}_6\text{H}_4\text{PPh}_2)\text{Mn}(\text{CO})_4]$ (I), one of two isomers formed from $\text{HMn}(\text{CO})_4(\text{sp})$ ($\text{sp} = 2$ -vinylphenyldiphenylphosphine, II) by rapid intramolecular hydride addition at the free vinyl group of the coordinated ligand³.



Crystals of $[(\text{MeCHC}_6\text{H}_4\text{PPh}_2)\text{Mn}(\text{CO})_4]$ are monoclinic, space group $P2_1/n$, $a = 9.83$, $b = 22.43$, $c = 10.01$ Å, $\beta = 98.58^\circ$, $Z = 4$. Preliminary Weissenberg and precession photographs showed about 20 symmetry disallowed reflections ($h0l$ data; $h+l = 2n+1$), albeit of low intensity. No Bijvoet differences (indicative of space group $P2_1$) could be observed. The symmetry disallowed reflections do not show the “sharpness” characteristic of double reflection. Most probably, they result from the presence of a second isomer (III) in very low concentration in the crystal lattice (*vide infra*). The 2251 independent

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reflections, with $I/\sigma(I) \geq 3.0$, were collected on a Picker FACS-I automatic diffractometer using crystal-monochromated $\text{Cu-K}\alpha$ radiation. With all atoms isotropic, the block-diagonal least-squares refinement has converged to the present conventional R -factor of 0.090. The corresponding bond distance e.s.d.'s are: Mn-P , 0.003; Mn-C , 0.01; P-C , 0.009; C-C , 0.015 Å. The stereochemistry of the molecule, which is essentially octahedral about the central manganese atom, is shown in Fig. 1, while bond distances and inter-bond angles within the five-atom chelate ring are shown in Fig. 2.

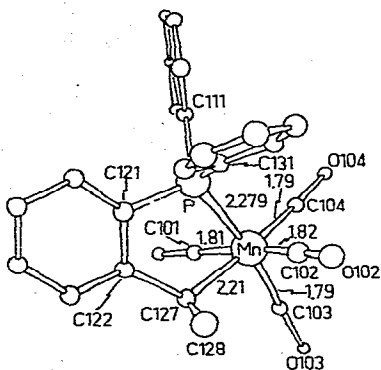


Fig. 1. The overall stereochemistry of the molecule.

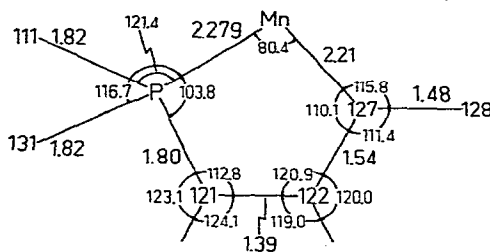


Fig. 2. Bond distances and inter-bond angles within the five-membered chelate ring about the manganese atom.

At 2.21(1) Å, the Mn-C σ -bond distance ($\text{Mn-C}(127)$) is significantly longer than that found in the σ -oxobutyl derivative (2.146(9) Å)². The present structural analysis implies an octahedral radius of 1.44 Å for Mn^{I} . This value is close to that of 1.46 Å inferred by Doedens and Dahl⁴, and, in view of the chelate character of the ligand, probably represents a realistic lower limit of the σ -orbital radius. The origin of the substantially smaller value (1.38 Å) derived from the σ -oxobutyl Mn-C distance is not clear, particularly as the Mn-O distance in the oxobutyl complex yields a value of ca. 1.44 Å. Given this anomaly in the σ -oxobutyl complex, we feel that the longer value derived from the present less strained complex is to be preferred. We also note that this longer value (1.44 Å) agrees well with the upper limit of ca. 1.43–1.46 Å proposed by Cotton and Richardson⁵.

The individual Mn-C (carbonyl) distances (av. 1.80(1) Å), equal within experimental error, are in good agreement with the average value of 1.79 Å found for the pseudo- π -allylic π -oxopropenyl complex [π -{O...C(Me)...C(Me)} $\text{C}_6\text{H}_4\text{PPh}_2\text{Mn}(\text{CO})_3$]², and with the two longer distances in the σ -oxobutyl derivative [av. 1.805 Å *trans* to P and σ -bonded C]. The Mn-C-O angles show the expected deviation from linearity⁶, and average 177.9°.

The Mn-P distance (2.279(3) Å) is shorter than those observed for either the σ -oxobutyl or π -oxopropenyl complex (2.295(3) and 2.299(2) Å, respectively)². In each case, however, the Mn-P distance is very much shorter than the value of ca. 2.50 Å calculated from covalent radii sums, and is indicative of considerable π -bond character in the Mn-P bond.

The P-C and C-C bond lengths within the five-membered chelate ring (defined by Mn, P, C(121), C(122), and C(127)) are within experimental error of their expected values (Fig. 2). In contrast, substantial angular deformations, particularly those defined by P-Mn-C(127), Mn-P-C(121), and P-C(121)-C(122), are indicative of some steric strain within this chelate ring.

Since this structure was commenced, further analysis of the proton NMR spectrum of a supposedly pure sample of I has shown that in solution, at least, the sample consists of the two isomers I and III, in the ratio of ca. 10/1 respectively⁷. This isomerism results from Markownikoff and anti-Markownikoff hydride addition at the free vinyl group of the coordinated (sp) ligand. To date, we have been unable to substantiate the presence of III as an impurity in the lattice of I, although a Fourier difference map at the present stage of refinement does show some residual electron density in the vicinity of C(127). Nevertheless, it seems that lattice inclusion of a small amount of III is the most probable source of the symmetry forbidden reflections discussed above.

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