# Crystal Structures of Two Organo-manganese Complexes Formed by Acetyl Migration to a Co-ordinated Double Bond

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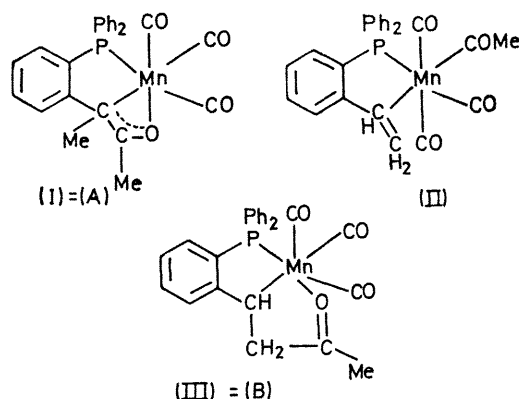(Research School of Chemistry, The Australian National University, P.O. Box 4, Canberra, A.C.T., 2600, Australia)

Summary The structures of a delocalised pseudo-$\pi$-allylic (three electron) $\pi$-oxopropyl manganese tricarbonyl complex (A) and a $\sigma$-bonded Mn–C oxobutyl tricarbonyl complex (B) have been determined by three-dimensional X-ray structural analysis.

INFRARED and n.m.r. data for the two isomeric products [(A) and (B); empirical formula $C_{25}H_{20}MnO_4P$] from the reaction of $MeMn(CO)_5$ with o-styryldiphenylphosphine ($o$-$CH_2$:$CH$·$C_6H_4$·$PPh_2$; sp) have led to their formulation as $\pi$-oxopropyl (I)† and acyl (II) derivatives respectively.[1] We now report single crystal X-ray studies of (A) and (B) which confirm that (A) is a $\pi$-oxopropyl complex and show that (B) is in fact a $\sigma$-bonded Mn–C and Mn–O complex containing a tridentate ($o$-3-oxobutylphenyl)diphenylphosphine ligand (III). The stereochemistries of (A) and (B) are shown in Figures 1 and 2 respectively.

Crystals of (A) are triclinic, space group $P\bar{1}$, $a = 9.30$, $b = 11.69$, $c = 10.65$ Å, $\alpha = 81.91°$, $\beta = 96.64°$, $\gamma = 83.72°$ $Z = 2$, while those of (B) are orthorhombic, space group $Pbca$, $a = 15.95$, $b = 17.18$, $c = 16.28$ Å, $Z = 8$. Reflexion data for both samples were collected on a PICKER FACS-I automatic diffractometer using crystal monochromated Cu-$K_\alpha$ radiation. Rejection of observations for which $F_0^2/\sigma(F_0^2) < 3.0$ yielded 2695(A) and 2130(B) unique reflexions. Least-squares analyses of positional and isotropic thermal parameters have converged to conventional

R-factors of 0.090(A) and 0.079(B). In both cases, the unsubstituted phenyl rings were constrained to $D_{6h}$ symmetry (C–C = 1.397 Å), and neither data set has been corrected for absorption and extinction effects.



In (A), the manganese atom is approximately octahedrally co-ordinated by three CO groups, a phosphorus, and the two terminal atoms of a pseudo-$\pi$-allylic oxopropyl group. Consistent with this formulation, C(107)–C(108) [1.44(1) Å] and C(108)–O(109) [1.30(1) Å] are each

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† The term oxopropenyl is preferable to "oxapropyl" used previously (ref. 1).

intermediate between their respective single- and double-bond distances.[2] The dihedral angle [117·2°] between the oxopropyl and the metal co-ordination plane [defined by Mn, C(1), and C(2)] is likewise typical of π-allyl–metal complexes.[3,4] The manganese-π-oxopropyl distances are 2·225(8), 2·137(9), and 2·070(6) Å to C(107), C(108), and O(109) respectively. Comparison of these distances with

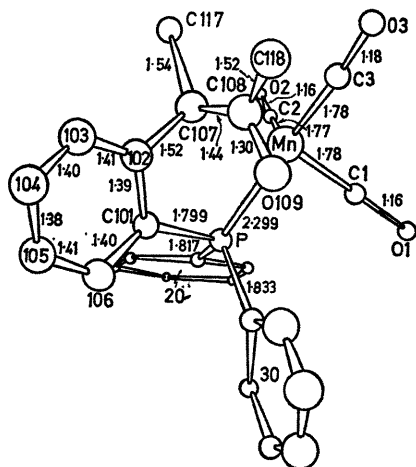The n.m.r. spectrum of (B) is in agreement with the revised formulation as a σ-bonded oxobutyl complex. The CHCH$_2$ protons comprise an ABX system ($\delta_A$, 2·46; $\delta_B$, 2·84; $\delta_X$, 3·85; $J_{gem}$, 20·1 Hz), with only the methine [C$H$–Mn] proton coupled to $^{31}$P ($J$ ca. 6·8 Hz). In contrast, the n.m.r. spectra of simple chelate complexes of type (II) show $^{31}$P coupling to both methine and methylene protons.[8]
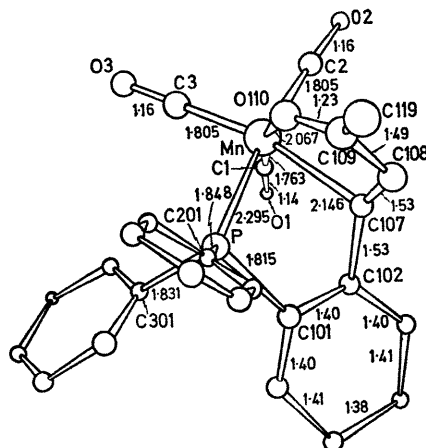


FIGURE 1. Stereochemistry of (A). E.s.d.s of bond-lengths are: Mn–P, 0·002; Mn–C, 0·01; Mn–O, 0·006; P–C, 0·006; C–O, 0·011; C–C, 0·014 Å.



FIGURE 2. Stereochemistry of (B). E.s.d.s of bond-lengths are: Mn–P, 0·003; Mn–C, 0·01; Mn–O, 0·007; P–C, 0·007; C–O, 0·013; C–C, 0·016 Å.

the covalent radii sums (Mn–C, 2·15; Mn–O, 2·04)[5,6] indicates that the metal–π-oxopropyl bonding is essentially "symmetric".[7] It seems likely, therefore, that the lengthening of C(107)–C(108) vis-à-vis the normal value for a symmetrically co-ordinated allyl [ca. 1·37 Å] reflects primarily the expected increase in π-electron localisation at C(108).

The manganese atom in (B) is also octahedrally co-ordinated, the bond distances to the oxobutyl substituent being as expected for Mn–C and Mn–O σ-bonds [Mn–C(107), 2·146(9); Mn–O(110), 2·067(7) Å: cf. foregoing covalent radii sums].[5,6] The remaining Mn–C distances [Mn–C(108), 2·991(9); Mn–C(109), 2·847(9) Å] indicate little, if any, interaction between these carbon atoms and the manganese. The C–C and C=O distances in the oxobutyl chelate ring are within experimental error of their expected values.

The Mn–P distances in (A) and (B) are virtually identical [Mn–P(A), 2·299(2); Mn–P(B), 2·295(3) Å], but are appreciably shorter than the calculated value for a simple σ-bond (covalent radii sum, 2·48 Å).[5,6]

The formation of (B) can be readily understood in terms of addition of an acetyl group (probably initially co-ordinated) at the β-carbon atom of the vinyl substituent of the co-ordinated (sp) ligand. Complex (A) obviously results from acetyl attack at the α-carbon atom of the vinyl group, accompanied by an hydride migration. Similar alternative modes of addition have been observed in the isomerisation of HMn(CO)$_4$(sp),[9] where the main product [(o-CH(Me)·C$_6$H$_4$·PPh$_2$)Mn(CO)$_4$] results from hydride attack at the α-carbon atom, while the minor product [(o-CH$_2$·CH$_2$·C$_6$H$_4$·PPh$_2$)Mn(CO)$_4$] results from addition at the β-carbon atom.

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