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Preliminary communication

Preparation and structure of tricarbonyl{bis(ethoxycarbonyl)methyl}cyclohexadienylmanganese(I)

ANNE MAWBY

Department of Inorganic and Structural Chemistry, University of Leeds (Great Britain)

P.J.C. WALKER* and R.J. MAWBY**

Department of Chemistry, University of York (Great Britain)

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SUMMARY

X-Ray diffraction analysis of tricarbonyl{bis(ethoxycarbonyl)methyl}cyclohexadienylmanganese(I) has provided the first detailed information about the bonding of an *exo*-substituent added by nucleophilic attack on a coordinated arene.

Reaction of the arene complex $[(C_6H_6)Mn(CO)_3]^+$ with the anion $(EtO_2C)_2CH^-$ at room temperature in ethanol yields the cyclohexadienyl complex *exo*-$\{C_6H_6CH(CO_2Et)_2\}$-$Mn(CO)_3$. The fact that the product is reconverted to $[(C_6H_6)Mn(CO)_3]^+$ by treatment with $[Ph_3C]BF_4$, which fails to remove the same substituent from the closely related *exo*-cyclohexadiene and *exo*-cycloheptatriene complexes $\{C_6H_7CH(CO_2Et)_2\}$ $Fe(CO)_3$ [1] and $\{C_7H_7CH(CO_2Et)_2\}$ $Cr(CO)_3$ [2] appears to indicate a marked weakness in the bonding between substituent and ring in $\{C_6H_6CH(CO_2Et)_2\}$ $Mn(CO)_3$. This is at odds with the only relevant crystallographic information, which is that the C–H bond between the ring and the added hydrogen atom in $(C_6H_7)Mn(CO)_3$ (obtained from $[(C_6H_6)Mn(CO)_3]^+$ and hydride ion) is unusually short[3]. We therefore decided to determine the structure of $\{C_6H_6CH(CO_2Et)_2\}$ $Mn(CO)_3$ by X-ray analysis, using a crystal grown from pentane solution.

Crystal data: $C_{16}H_{17}MnO_7$, orthorhombic, $a = 25.24(1)$, $b = 9.20(2)$, $c = 14.89(2)$ Å, $Z = 8$. Space group *Pbcn*. Cu-K_α radiation. 1094 independent reflections were recorded by Weissenberg photography and estimated visually. The structure was solved by Patterson and Fourier techniques and refined by block diagonal least squares to $R = 10.8\%$. Thermal parameters were anisotropic for the metal atom and isotropic otherwise: hydrogen atom positions were not determined. The structure of the complex is shown in Fig. 1.

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[*] Present address: Department of Chemistry, University of Exeter.

[**] Author to whom communications should be addressed.

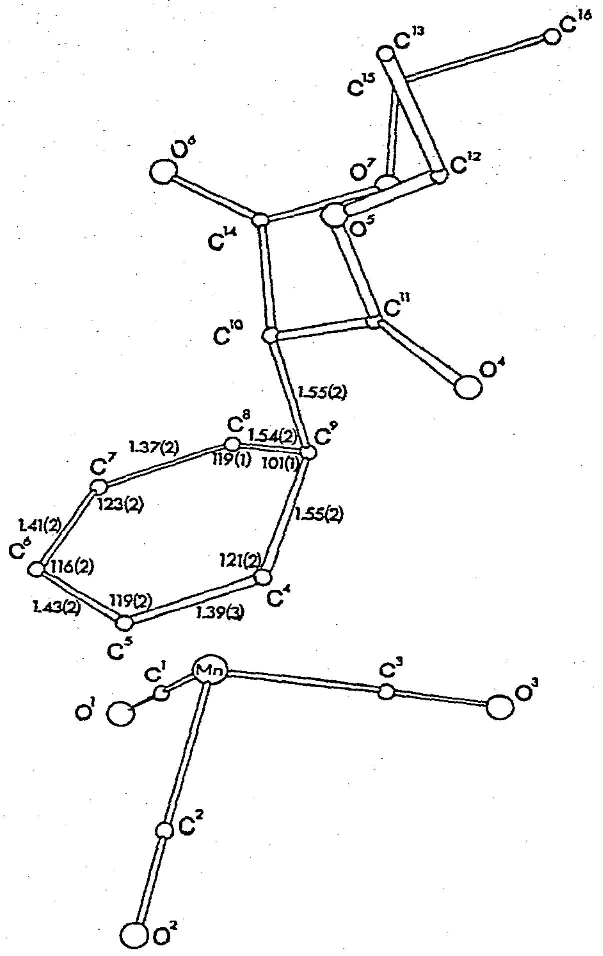

Fig. 1.

Although the NMR spectrum of the complex in solution indicates the presence of a plane of symmetry passing through C^6, C^9, C^{10} and the manganese atom, this is lost in the solid state, presumably as a result of the packing requirements of the $CH(CO_2Et)_2$ group in the crystal lattice. Five ring carbon atoms (C^4, C^5, C^6, C^7, C^8) are almost exactly co-planar, while the remaining atom, C^9, lies on the opposite side of this plane from the $Mn(CO)_3$ moiety. The plane makes an angle of 41° with that defined by C^8, C^9 and C^4. While the bonds and angles within the group of five co-planar atoms are those expected for sp^2 hybridization, the angle C^8—C^9—C^4 is less than the normal tetrahedral angle expected for sp^3 hybridization at C^9, and the bond lengths C^8—C^9 and C^9—C^4 are greater than the expected values for $C(sp^2)$—$C(sp^3)$ bonds (1.51 Å).

The bond between the *exo*-$CH(CO_2Et)_2$ substituent and the ring (C^9—C^{10}) is not significantly longer than a normal $C(sp^3)$—$C(sp^3)$ bond (1.54 Å) nor shorter, as might be expected[3] from the data for $(C_6H_7)Mn(CO)_3$. The ease with which the substituent is removed is presumably associated with the relief of the strain indicated by the bond lengths and angles in the C^8–C^9–C^4 section of the ring.

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