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THE STRUCTURE OF AN ARENEMANGANESE TRICARBONYL CATION; SYNTHESIS AND X-RAY ANALYSIS OF DODECAHYDROTRIPHENYLENE(TRICARBONYL)MANGANESE(I)* TETRAFLUOROBORATE

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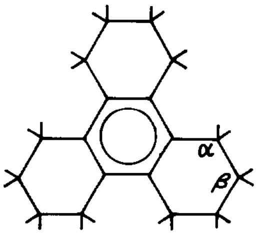
Summary

The synthesis, spectroscopic properties, and X-ray structure of dodecahydrotriphenylene(tricarbonyl)manganese(I) tetrafluoroborate, $[(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3][BF_4]$ are reported. The cation has approximate C_3 symmetry with the Mn–CO vectors projected across the unbridged C–C bonds of the arene ligand.

Introduction

There is a very extensive literature on the preparation, structures, spectroscopic properties, and use in syntheses of (arene)$Cr(CO)_3$ complexes, and to a lesser extent, on the analogous Mo and W analogues [1–7]. Surprisingly, the iso-electronic (arene)$Mn(CO)_3{}^+$ species have been relatively neglected, even although they are readily prepared and handled, and should exhibit enhanced susceptibility to nucleophilic attack [8–11]. As far as we are aware, there is no previous report of a structural characterisation of an (arene)$Mn(CO)_3{}^+$ derivative, although a recent



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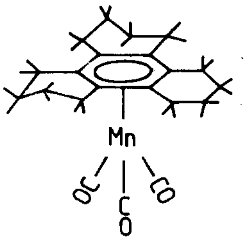

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* Systematically the ligand is named 1,2,3,4,5,6,7,8,9,10,11,12-dodecahydrotriphenylene.

X-ray study on a rhenium analogue, $(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)Re(CO)_3^+$, is available [12].

We are currently investigating the complexes formed by the substituted benzene derivative dodecahydrotriphenylene, (**1**), which has only C_3 symmetry in its most stable conformation, although each carbon of the aromatic ring is electronically equivalent. The hydrocarbon can be regarded as a benzene ring sharing a side with each of three cyclohexene rings. In this paper we report the coordination of arene (**1**) to a $Mn(CO)_3^+$ fragment, and the crystal structure of the complex cation as the BF_4^- salt.

Experimental

All reactions were performed under an atmosphere of dry nitrogen using standard Schlenk techniques. The ligand dodecahydrotriphenylene, (**1**), was prepared from cyclohexanone by a literature procedure [13]. Manganese carbonyl (Pressure Chemical Co.) and aluminium chloride (B.D.H.) were used as received. Infrared spectra were recorded on a Perkin–Elmer Model 180 spectrometer and are accurate to ±1 cm^{-1}. NMR spectra were obtained using a JEOL FX 90Q machine.

*Preparation of (dodecahydrotriphenylene)(tricarbonyl)manganese(I) tetrafluoroborate (**2**)*

This was prepared by the method of Munro and Pauson [9]. Bromopentacarbonylmanganese (1.0 g, 3.6 mmol) and dodecahydrotriphenylene (1.0 g, 4.2 mmol) were heated with finely-crushed aluminium trichloride (1.0 g, 7.5 mmol) in 1,3-dichlorobenzene (20 ml) for 4 h at 100°C. The solution was cooled in ice and extracted with ice-water (3 × 6 ml). The aqueous extract was shaken vigorously with carbon tetrachloride (10 ml) which was then separated and discarded. An excess of aqueous HBF_4 (40%) was added dropwise to the stirred aqueous solution. Filtration gave the pale yellow product, (0.87 g, 52% based on $BrMn(CO)_5$). Recrystallisation from acetone/diethyl ether (4/1) gave two crystal forms; orthorhombic needles and trigonal thick plates. Infrared spectra; $\nu(CO)$ (CH_2Cl_2) 2050vs, 1988vs; $\nu(CO)$ (Nujol, needles) 2047vs, 1986sh, 1972s; $\nu(CO)$ (Nujol, plates) 2050vs, 1980s. NMR spectra; ^1H $(CDCl_3)$ δ 2.73 m (H_α), 1.87 m (H_β); ^{13}C (acetone-d_6) δ 218.6 (CO), 114.6 (C_{aryl}), 26.5 (C_α), 21.5 (C_β). The needle-shaped crystals were further characterised by a full X-ray crystal structure determination.

*X-ray crystal structure of **2***

Yellow, needle-shaped crystals were obtained from acetone/diethyl ether solution. Preliminary precession photography indicated orthorhombic symmetry with systematic absences appropriate for space group $P2_12_12_1$. Intensity data were obtained on a Nicolet XRD P3 four-circle diffractometer with monochromated Mo-K_α radiation, using a crystal of dimensions 0.26 × 0.18 × 0.16 mm.

Crystal data. $C_{21}H_{24}BF_4MnO_3$, $M = 466.17$, orthorhombic, space group $P2_12_12_1$ (No. 19), a 9.950(2), b 10.398(2), c 20.412(3) Å, U 2112 Å^3. D_c 1.47 g cm^{-3} for $Z = 4$. $F(000) = 960$, μ(Mo-K_α) 6.2 cm^{-1}.

Intensity data were collected in the range $3° < 2\theta < 43°$ using a θ–2θ scan technique. A total of 1925 unique data were collected, and after correction for Lorentz, polarisation and absorption effects, the 1516 data for which $F > 3\sigma(F)$ were used in all calculations.

Solution and refinement. The structure was solved by Patterson methods and all

TABLE 1

FINAL POSITIONAL PARAMETERS FOR (η^6-$C_{18}H_{24}$)Mn(CO)$_3$ (**2**)

Atom	x	y	z	Atom	x	y	z
Mn	0.3003(1)	0.5096(1)	0.5642(1)	C(152)	0.570(1)	0.363(1)	0.6364(6)
C(1)	0.3470(8)	0.6654(7)	0.6340(4)	C(153)	0.690(2)	0.428(2)	0.605(1)
C(2)	0.2227(7)	0.6136(7)	0.6509(3)	C(154)	0.711(2)	0.550(2)	0.619(1)
C(3)	0.2071(7)	0.4779(7)	0.6605(3)	C(155)	0.597(1)	0.643(1)	0.6132(6)
C(4)	0.3187(8)	0.3986(7)	0.6572(4)	C(31)	0.345(1)	0.370(1)	0.5178(5)
C(5)	0.4502(8)	0.4507(7)	0.6397(4)	C(32)	0.1324(8)	0.511(1)	0.5302(4)
C(6)	0.4603(9)	0.5833(7)	0.6280(4)	C(33)	0.357(1)	0.613(1)	0.5001(5)
C(112)	0.362(1)	0.8096(8)	0.6213(5)	O(31)	0.379(1)	0.2794(8)	0.4901(5)
C(113)	0.230(1)	0.8748(9)	0.6097(5)	O(32)	0.0232(6)	0.508(1)	0.5119(3)
C(114)	0.131(1)	0.840(1)	0.6626(5)	O(33)	0.391(1)	0.6841(9)	0.4603(4)
C(115)	0.1003(9)	0.7022(9)	0.6616(5)	B	0.200(2)	0.470(1)	0.3335(6)
C(132)	0.0693(8)	0.4246(9)	0.6773(5)	F(1)	0.234(2)	0.5870(9)	0.3183(5)
C(133)	0.064(1)	0.280(1)	0.6660(6)	F(2)	0.074(1)	0.479(2)	0.2991(6)
C(134)	0.174(1)	0.217(1)	0.6999(6)	F(3)	0.255(1)	0.3783(9)	0.2981(4)
C(135)	0.313(1)	0.2555(8)	0.6716(5)	F(4)	0.168(1)	0.4445(8)	0.3915(3)

non-hydrogen atoms were located by standard difference map techniques. In the final cycles of full-matrix, least-squares refinement, all non-hydrogen atoms, except the arene carbon atoms, were assigned anisotropic temperature factors and hydrogen atoms were included in calculated positions (d(C–H) 0.98 Å) with a common isotropic temperature factor. The refinement converged at $R = 0.0551$, $R_w = 0.0580$ where $w = [\sigma^2(F_0) + 0.0008F_0^2]^{-1}$, with no parameter shifting by more than 0.1σ in the final cycle. The high values for the thermal parameters of the fluorine atoms, and some residual electron density (ca. 0.7 e Å^{-3}) indicated a partially disordered BF_4^- ion, but no attempts were made to compensate for this in the refinement. All calculations were performed using SHELX 76 [14].

Final atomic positions are given in Table 1, and selected bond parameters in Table 2. A view of the cation normal to the arene plane is given in Fig. 1, which also shows atom labelling, while the stereoview in Fig. 2 is chosen to illustrate the conformations of the peripheral cyclohexene rings.

Results and discussion

The preparation of the complex **2** was straightforward, good yields being obtained according to eq. 1:

$$C_{18}H_{24} + (CO)_5MnBr + AlCl_3 \rightarrow \left[(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3\right]^+ + AlCl_3Br^- + 2CO \quad (1)$$

The complex was isolated as air-stable yellow crystals with BF_4^- as counter-ion. Two distinct forms co-crystallised from acetone/diethyl ether; orthorhombic needles and trigonal plates. These were identical on redissolution, but showed significantly different carbonyl-stretching spectra in the solid state (see Experimental).

In solution the complex **2** exhibited the expected [8] two ν(CO) bands in the infrared spectrum. The ^1H NMR showed two poorly resolved multiplets corresponding to the CH_2 groups α and β to the aromatic ring.

Crystals of [(η^6-$C_{18}H_{24}$)Mn(CO)$_3$][BF_4] contain discrete cations and anions. The cations have essentially C_3 symmetry with the planar arene ring sitting above the $Mn(CO)_3$ fragment (Fig. 1). The Mn–C(ring) bond lengths range from 2.195–2.230 Å, average 2.211(4) Å, which is barely significantly shorter than the equivalent

TABLE 2

BOND LENGTHS (Å) AND ANGLES (°) FOR $(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3$ (**2**)

Bond lengths			
Mn---C(1)	2.206(7)	C(5)---C(152)	1.504(13)
Mn---C(2)	2.212(7)	C(6)---C(155)	1.530(13)
Mn---C(3)	2.198(7)	C(112)---C(113)	1.500(15)
Mn---C(4)	2.229(8)	C(113)---C(114)	1.503(15)
Mn---C(5)	2.230(8)	C(114)---C(115)	1.461(14)
Mn---C(6)	2.195(8)	C(132)---C(133)	1.528(16)
Mn---C(31)	1.791(12)	C(133)---C(134)	1.450(18)
Mn---C(32)	1.809(8)	C(134)---C(135)	1.554(17)
Mn---C(33)	1.786(11)	C(152)---C(153)	1.520(20)
C(1)---C(2)	1.393(10)	C(153)---C(154)	1.322(24)
C(1)---C(6)	1.420(11)	C(154)---C(155)	1.495(19)
C(1)---C(112)	1.528(11)	C(31)---O(31)	1.149(16)
C(2)---C(3)	1.432(10)	C(32)---O(32)	1.149(10)
C(2)---C(115)	1.542(12)	C(33)---O(33)	1.148(14)
C(3)---C(4)	1.385(11)	B---F(1)	1.303(16)
C(3)---C(132)	1.518(11)	B---F(2)	1.440(18)
C(4)---C(5)	1.460(11)	B---F(3)	1.312(15)
C(4)---C(135)	1.518(12)	B---F(4)	1.253(13)
C(5)---C(6)	1.403(11)	Mn---Ring centroid	1.70
Bond angles			
C(1)–Mn–C(2)	36.70(3)	C(4)–C(3)–C(132)	121.20(7)
C(1)–Mn–C(3)	67.80(3)	C(3)–C(4)–C(5)	120.60(7)
C(1)–Mn–C(4)	79.30(3)	C(3)–C(4)–C(135)	122.90(8)
C(1)–Mn–C(5)	67.40(3)	C(5)–C(4)–C(135)	116.50(7)
C(1)–Mn–C(6)	37.60(3)	C(4)–C(5)–C(6)	118.10(7)
C(2)–Mn–C(3)	37.90(3)	C(4)–C(5)–C(152)	119.70(7)
C(2)–Mn–C(4)	66.50(3)	C(6)–C(5)–C(152)	122.30(8)
C(2)–Mn–C(5)	79.40(3)	C(1)–C(6)–C(5)	121.30(7)
C(2)–Mn–C(6)	66.90(3)	C(1)–C(6)–C(155)	118.60(7)
C(3)–Mn–C(4)	36.50(3)	C(5)–C(6)–C(155)	120.00(8)
C(3)–Mn–C(5)	67.90(3)	C(1)–C(112)–C(113)	112.70(8)
C(3)–Mn–C(6)	80.10(3)	C(112)–C(113)–C(114)	110.30(8)
C(4)–Mn–C(5)	38.20(3)	C(113)–C(114)–C(115)	111.40(9)
C(4)–Mn–C(6)	67.40(3)	C(2)–C(115)–C(114)	114.80(8)
C(5)–Mn–C(6)	37.00(3)	C(3)–C(132)–C(133)	111.10(8)
C(31)–Mn–C(32)	91.80(5)	C(132)–C(133)–C(134)	110.10(10)
C(31)–Mn–C(33)	91.20(5)	C(133)–C(134)–C(135)	112.20(10)
C(32)–Mn–C(33)	90.40(4)	C(4)–C(135)–C(134)	111.10(8)
C(2)–C(1)–C(6)	119.60(7)	C(5)–C(152)–C(153)	111.90(10)
C(2)–C(1)–C(11)	120.50(7)	C(152)–C(153)–C(154)	117.40(15)
C(6)–C(1)–C(11)	119.90(7)	C(153)–C(154)–C(155)	119.20(14)
C(1)–C(2)–C(3)	120.70(6)	C(6)–C(155)–C(154)	113.20(10)
C(1)–C(2)–C(11)	120.30(7)	Mn–C(31)–O(31)	176.60(11)
C(3)–C(2)–C(11)	118.90(6)	Mn–C(32)–O(32)	176.10(8)
C(2)–C(3)–C(4)	119.50(6)	Mn–C(33)–O(33)	177.00(10)
C(2)–C(3)–C(132)	119.20(6)		

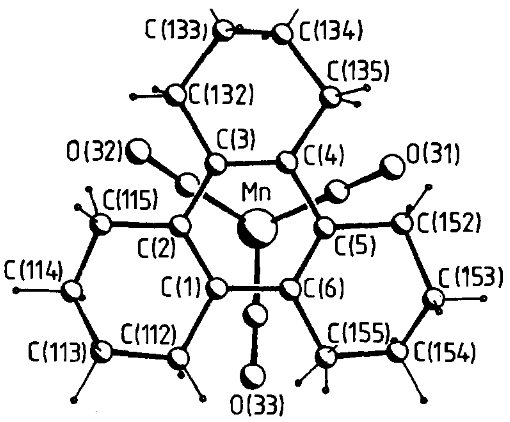
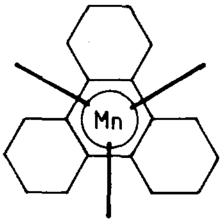


Fig. 1. A view of the cation (η^6-$C_{18}H_{24}$)Mn(CO)$^+$ normal to the arene ring, showing the relative orientation of the CO ligands.

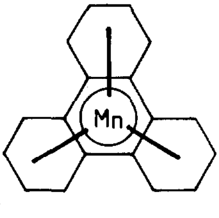
distances in related iso-electronic, but neutral, (arene)Cr(CO)$_3$ complexes (typically 2.23 Å [1]); the positive charge on the manganese atom results in surprisingly little contraction in the metal–ring distance. There is a more definite shortening of the Mn–CO bond distance (average 1.795(6) Å) in **2** compared with the analogous Cr–CO bonds (e.g. 1.823(5) Å in (η^6-Et_6C_6)Cr(CO)$_3$ [15,16]).

The peripheral cyclohexene rings adopt the expected half-chair conformation (Fig. 2). The C(ring)–C_α and C_α–C_β distances average 1.52(1) and 1.51(1) Å and are thus normal. The C_β–C_β lengths are 1.425(11) Å and appear to be shorter than normal for C–C bonds; however this is probably an artifact arising from the high thermal motion of these outer carbon atoms.

The main feature of interest in the structure of (η^6-$C_{18}H_{24}$)Mn(CO)$_3{}^+$ is the orientation of the Mn(CO)$_3$ fragment with respect to the arene ligand. Three



(3a)



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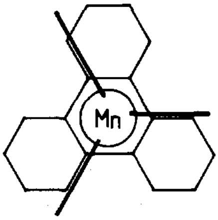

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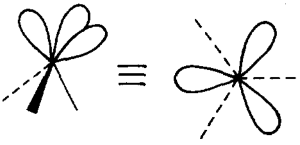

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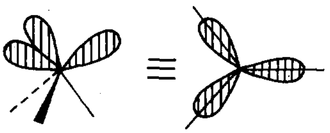

(4b)

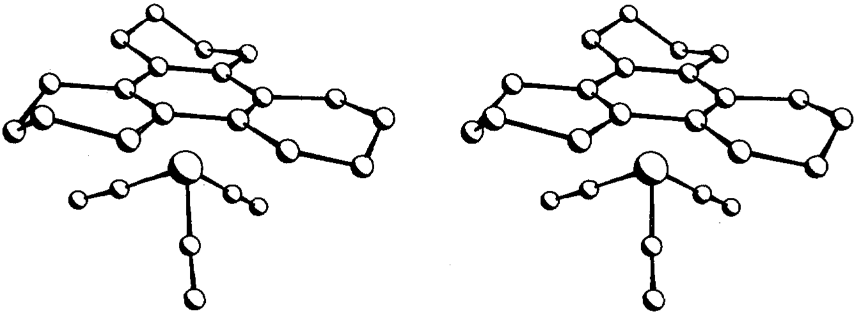

Fig. 2. Stereoview of $(\eta^6\text{-}C_{18}H_{24})Mn(CO)^+$ illustrating the half-chair conformation of the peripheral cyclohexene rings.

idealised structures can be proposed; the first has the Mn–CO vectors projected onto unbridged aromatic ring C–C bonds, (**3a**), the second has the carbonyls lying across the bridged C–C bonds, (**3b**), and the third has the carbonyls eclipsing three of the carbon atoms of the aromatic ring, (**3c**). Although the energy differences between staggered (**3a** or **3b**) and eclipsed (**3c**) forms would be small, the adoption of a particular orientation can usually be predicted [1,3,6,17]. Thus, unsubstituted or hexa-substituted arenes adopt one of the two equivalent staggered forms (except where there are strong steric interactions between ring substituents and the CO ligands, as in $(\eta^6\text{-}Et_6C_6)Cr(CO)_3$ [15,16]), while mono- or 1,3,5-tri-substituted arenes adopt a conformation in which the CO ligands eclipse the ring carbon atoms carrying the substituents if they are electron-releasing [1]. These differences relate to the bonding requirements of a $M(CO)_3$ fragment which presents three vacant orbitals *trans* to CO ligands (**4a**) which are directed towards regions of high π-electron density on the ring, and three filled orbitals (**4b**) which seek regions of low π-electron density [1,3,6,17].

In $(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3{}^+$, the $Mn(CO)_3$ fragment is orientated such that the CO ligands lie above the unbridged C–C bonds of the aromatic ring, (**3a**), which implies that the vacant orbitals are directed towards the bridged C–C bonds. These latter bonds are therefore assumed to have the higher π-electron density, as is consistent with the observation that they are significantly shorter (average 1.393(7) Å) than the unbridged bonds (average 1.437(7) Å). What is less clear is why orientation **3a** is preferred over **3b**. Two possibilities exist; firstly, that within the arene ligand the fused cyclohexene rings partially localise π-electron density in the bridged bonds, and this directs the orientation of the $Mn(CO)_3$ group. Alternatively, steric interaction between the CO ligands and the cyclohexene rings favours orientation (**3a**) and the bonding requirements of the $Mn(CO)_3$ group induce the bond alternation. At present we are unable to distinguish between these possibilities, but current structural studies on the neutral chromium analogue of **2** and the second crystalline modification of **2** should allow more definite conclusions.

Acknowledgments

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