Journal of Organometallic Chemistry, 346 (1988) 385–395
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Metal-carbonyl complexes of dodecahydrotriphenylene; a comparison of the structures of iso-electronic $[(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3]^+$ and $(\eta^6\text{-}C_{18}H_{24})Cr(CO)_3$

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(Received November 30th, 1987)

Abstract

The structures of $(\eta^6\text{-}C_{18}H_{24})Cr(CO)_3$ (**1**) and of a trigonal form of $[(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3]BF_4$ (**2**) are reported. For **1** the CO ligands project on to the unbridged C–C bonds of the substituted benzene ring with Cr–C(aryl) 2.230(5) Å (average). Crystals of **2** are intimately twinned, but this was successfully modelled in the refinement. There are two independent cations in the structure, one with the same conformation found for **1** and the other with the CO ligands rotated so they project over the peripheral rings of the arene ligands. The Mn–C(aryl) bonds average 2.224(2) Å. Together with the previously reported orthorhombic form of **2**, the structures discussed provide the first comparisons of an iso-electronic pair of $(arene)Cr(CO)_3$ and $[(arene)Mn(CO)_3]^+$ species.

Introduction

Interest in the structures of $(\eta^6\text{-arene})M(CO)_3$ complexes [1] relates partly to assessing the factors which determine the orientation of the $M(CO)_3$ group relative to the arene, especially for substituted arenes. This work is of importance since the orientation of this tripod can direct regioselective electrophilic and nucleophilic attack at the arene [2]. Experimental and theoretical analyses confirm two ideal cases [1–3]. The first has the $M(CO)_3$ group orientated so that the CO ligands lie across the mid-points of C–C bonds, and is observed for unsubstituted or hexa-sub-

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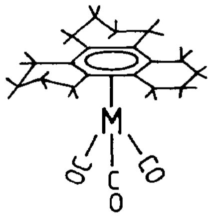
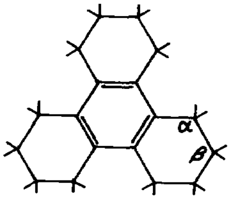


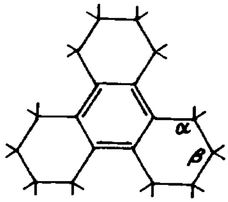
(1) M = Cr
(2) M = Mn$^+$

stituted benzenes. The second has the CO ligands projected on to carbon atoms of the ring, and is adopted by mono- or 1,3,5-tri-substituted species with electron-releasing substituents.

We are interested in complexes of the arene dodecahydrotriphenylene, $C_{18}H_{24}$ (**3**). This is a hexa-substituted benzene ring with each carbon atom electronically equivalent, but the overall symmetry is only three-fold. There is long-standing interest in molecules with saturated rings fused to an arene ring [4*], with some unresolved debate as to whether there is partial double-bond localisation, i.e. whether there is a predominance of either of the Kékulé forms **3a** or **3b**. For a $M(CO)_3$ fragment there are three vacant orbital *trans* to each carbonyl which are directed towards the regions of a coordinated ring where the π electron density is



3a



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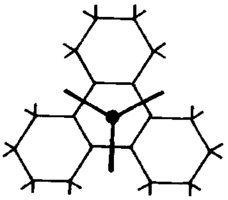
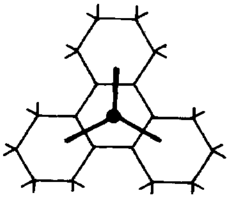


4a



4b

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* A reference number with an asterisk indicates a note in the list of references.

greatest [2,3], so that any bond localisation in the arene ring should be reflected in orientational preferences of coordinated $M(CO)_3$. Thus a dominance of form **3a** in the free ligand could be expected to lead to conformation **4a** in the complex, and similarly for **3b** and **4b**. An earlier report of the structure of an orthorhombic modification of **2** as the BF_4^- salt, showed the cation adopted the configuration **4a**, although it was not clear whether the observed structure was dictated by electronic or crystal-packing forces [5]. To probe this further we have structurally characterised the neutral $(\eta^6\text{-}C_{18}H_{24})Cr(CO)_3$ (**1**) and a trigonal modification of $[(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3]BF_4$ (**2**). As an additional interest, **1** and **2** represent the first directly comparable isoelectronic pair of (arene)$M(CO)_3$ complexes, $M = Cr, Mn^+$, for which structural data is available.

Experimental

The ligand $C_{18}H_{24}$ [6] and $Cr(NH_3)_3(CO)_3$ [7] were prepared by published methods. General procedures have been described earlier, as have the preparation and spectra of the two forms of $[(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3]BF_4$ [5].

Preparation of $[(\eta^6\text{-}C_{18}H_{24})Cr(CO)_3]$ (1). A solution of $Cr(NH_3)_3(CO)_3$ (0.20 g, 1.07 mmol) and $C_{18}H_{24}$ (0.25 g, 1.04 mmol) in dioxane (15 ml) was refluxed under a flow of nitrogen for 4 h. The solution was cooled in ice, then filtered through a glass frit, and the dioxane was removed under vacuum. The yellow residue was dissolved in CH_2Cl_2 and chromatographed on a silica column with hexane/CH_2Cl_2 (4/1) as eluant. The yellow band on evaporation yielded **1** as yellow flakes (0.23 g, 59%). Well-developed crystals were obtained from hexane at $-20\,°C$, m.p. 175–178 °C. Infrared spectrum: $\nu(CO)$ (CH_2Cl_2) 1942, 1857 cm^{-1}; (Nujol) 1950, 1932, 1874, 1850 cm^{-1} (all strong). NMR spectrum; ^1H ($CDCl_3$) δ 2.57m (H_α), 1.76m (H_β) ppm; ^{13}C δ 235.21 (CO), 107.25 (C_{aryl}), 26.05 (C_α), 22.02 (C_β) ppm.

X-ray structure of $[(\eta^6\text{-}C_{18}H_{24})Cr(CO)_3]$ (1)

A yellow block-shaped crystal 0.18 × 0.19 × 0.20 mm was obtained from hexane. Preliminary precession photography defined the space group as $P2_1/a$. Intensity data were obtained on a Nicolet XRD P3 diffractometer using monochromated Mo-K_α X-rays.

Crystal data. $C_{21}H_{24}CrO_3$, $M = 376.42$, monoclinic, space group $P2_1/a$, a 19.484(2), b 9.855(1), c 20.951(5) Å, β 113.44(2)°, U 3630 Å^3. D_c 1.375 g cm^{-1} for $Z = 8$. $F(000)$ 1584, μ(Mo-K_α) 5.9 cm^{-1}, T 23 °C. Intensity data in the range $3° < 2\theta < 43°$ C were collected using a θ–2θ scan technique. Absorption corrections were applied (max, min transmission factors 0.87, 0.80 respectively). A total of 3717 unique reflexions were collected and those 3135 for which $I > 2\sigma(I)$ were used in all calculations.

The positions of the two unique chromium atoms were located by Patterson methods, and all other non-hydrogen atoms were found routinely in subsequent difference maps. In the final cycles of full-matrix least-squares refinement the chromium and methylene carbon atoms were assigned anisotropic temperature factors, other atoms were treated isotropically, and hydrogen atoms were included in their calculated positions with a common isotropic temperature factor. The refinement converged at $R = 0.0531$, $R_w = 0.0610$ where $w = [\sigma^2(F) + 0.0008F^2]^{-1}$, with no parameter shifting more than 0.1 times its e.s.d. in the final cycle. The

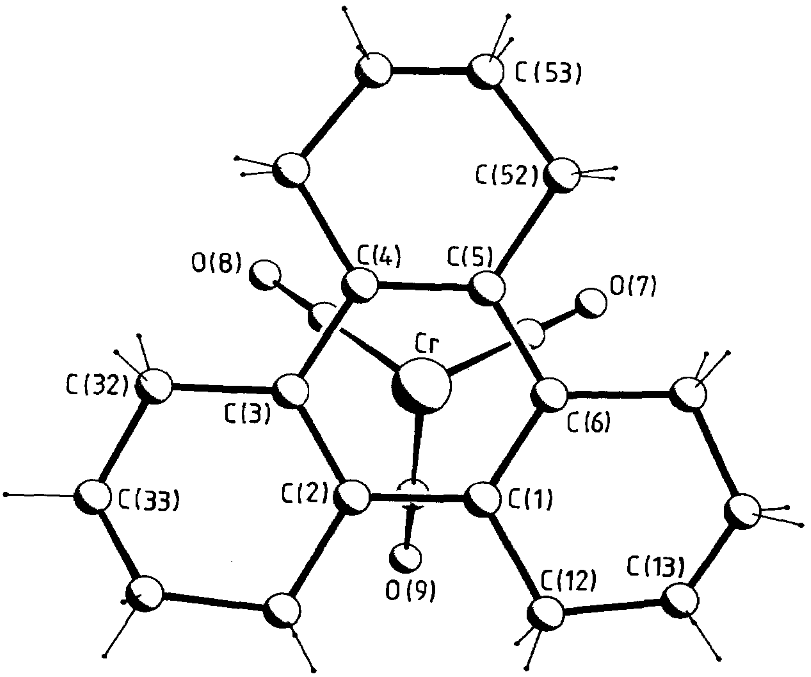


Fig. 1. One of the independent molecules of $(\eta^6\text{-}C_{18}H_{24})Cr(CO)_3$ viewed perpendicular to the arene plane.

Table 1

Final positional parameters for $[(\eta^6\text{-}C_{18}H_{24})Cr(CO)_3]$

Atom	Molecule 1			Molecule 2		
	x	*y*	*z*	*x*	*y*	*z*
Cr	0.1590(1)	0.7191(1)	0.1243(1)	0.0910(1)	0.1496(1)	0.3762(1)
C(1)	0.1668(3)	0.8912(5)	0.0573(2)	0.2106(3)	0.1913(5)	0.4446(3)
C(2)	0.1377(3)	0.7753(5)	0.0126(2)	0.1682(3)	0.1956(5)	0.4873(2)
C(3)	0.1765(3)	0.6517(5)	0.0286(2)	0.1056(3)	0.2817(5)	0.4686(2)
C(4)	0.2465(3)	0.6428(5)	0.0894(2)	0.0862(3)	0.3643(5)	0.4067(2)
C(5)	0.2742(3)	0.7557(5)	0.1325(2)	0.1275(3)	0.3614(5)	0.3664(2)
C(6)	0.2352(3)	0.8816(5)	0.1167(2)	0.1898(3)	0.2714(5)	0.3834(2)
C(12)	0.1234(3)	1.0230(6)	0.0388(3)	0.2809(3)	0.1013(7)	0.4686(3)
C(13)	0.1604(6)	1.1317(8)	0.0904(6)	0.3302(4)	0.1300(8)	0.4282(4)
C(14)	0.2221(5)	1.1282(8)	0.1419(5)	0.2852(3)	0.1450(7)	0.3521(3)
C(15)	0.2679(3)	1.0029(6)	0.1647(3)	0.2327(3)	0.2651(6)	0.3369(3)
C(32)	0.1477(3)	0.5291(6)	−0.0176(3)	0.0605(3)	0.2872(6)	0.5135(3)
C(33)	0.0731(4)	0.5434(9)	−0.0747(4)	0.0986(5)	0.221(1)	0.5843(4)
C(34)	0.0527(5)	0.6674(9)	−0.0999(5)	0.1357(5)	0.1004(9)	0.5854(4)
C(35)	0.0655(3)	0.7900(6)	−0.0524(3)	0.1922(3)	0.1093(6)	0.5538(3)
C(52)	0.3502(3)	0.7492(6)	0.1961(3)	0.1098(3)	0.4528(6)	0.3021(3)
C(53)	0.3836(5)	0.6120(9)	0.2079(6)	0.0525(4)	0.5595(8)	0.2948(4)
C(54)	0.3566(6)	0.511(1)	0.1715(5)	−0.0084(4)	0.5118(8)	0.3134(4)
C(55)	0.2885(3)	0.5071(6)	0.1057(3)	0.0184(3)	0.4583(6)	0.3877(3)
C(7)	0.1849(3)	0.7587(6)	0.2175(3)	0.0745(3)	0.1039(7)	0.2855(3)
C(8)	0.1422(3)	0.5450(6)	0.1422(3)	0.1002(4)	−0.0296(7)	0.3991(3)
C(9)	0.0626(3)	0.7626(6)	0.1085(3)	−0.0102(4)	0.1406(7)	0.3520(3)
O(7)	0.2017(3)	0.7833(5)	0.2766(2)	0.0633(3)	0.0784(6)	0.2271(2)
O(8)	0.1333(3)	0.4316(4)	0.1523(3)	0.1070(4)	−0.1415(5)	0.4146(3)
O(9)	0.0014(3)	0.7894(6)	0.0969(3)	−0.0733(3)	0.1430(6)	0.3371(3)

Table 2

Final positional parameters for $[(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3][BF_4]$

Atom	Molecule 1			Molecule 2		
	x	*y*	*z*	*x*	*y*	*z*
Mn	0.6667	0.3333	0.31828(2)	0.6667	0.3333	0.81751(2)
C(1)	0.5222(2)	0.2171(2)	0.4014(1)	0.6967(2)	0.2190(2)	0.9004(1)
C(2)	0.5503(2)	0.3605(2)	0.4000(1)	0.8106(2)	0.3628(2)	0.9005(1)
C(3)	0.4293(2)	0.3934(3)	0.4008(1)	0.9650(2)	0.3966(3)	0.9022(1)
C(4)	0.2835(3)	0.2643(3)	0.3855(1)	0.9849(3)	0.2700(3)	0.8879(1)
C(5)	0.2617(3)	0.1373(3)	0.4245(1)	0.8768(3)	0.1378(3)	0.9260(1)
C(6)	0.3709(2)	0.0925(2)	0.4044(1)	0.7243(3)	0.0935(2)	0.9050(1)
C(7)	0.5631(4)	0.1773(4)	0.2691(1)	0.7469(4)	0.4908(3)	0.7664(1)
O(7)	0.4944(4)	0.0741(3)	0.2397(1)	0.7984(4)	0.5915(3)	0.7346(1)
B(1)	0.6667	0.3333	0.5690(2)	0.6667	0.3333	0.0698(2)
F(1)	0.6667	0.3333	0.6364(1)	0.6667	0.3333	0.1372(1)
F(2)	0.7106(2)	0.2393(2)	0.5464(1)	0.5290(2)	0.2398(2)	0.0471(1)

highest peak in a final difference map was < 0.4 e Å^{-3}. The final positional parameters are give in Table 1, while selected bond length and angle data are given in Table 3. Calculations were performed using SHELX76 [8].

*X-ray structure of trigonal $[(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3]BF_4$ (**2**)*

Yellow triangular plates were obtained on recrystallisation from acetone/ether 4/1 (together with needles of the previously reported modification [5]). Preliminary precession photography indicated trigonal symmetry, with no systematic absences.

Crystal data: $C_{21}H_{24}BF_4MnO_3$, $M = 466.17$, trigonal, space group $P\bar{3}$ (twinned), a 10.762(2), c 20.679(5) Å, U 2074 Å^3, D_c 1.47 g cm^{-1} for $Z = 4$. $F(000) = 960$, μ(Mo-K_α) 6.34 cm^{-1}, T -130 °C. A total of 7072 reflections in the segment $h \geqslant 0$, $k \geqslant 0$, l, or the Friedel equivalent, were collected in the range $0 < 2\theta < 70°$ using a θ–2θ scan technique. An analysis of the data showed $P\bar{3}m1$ symmetry with no systematic absences. Merging the data to create observations $Y(hkl) = 0.5[|F(h,k,l)|^2 + |F(k,h,-l)|^2]$ showed no statistically significant indication of lower diffraction symmetry.

Table 3

Average bond lengths in $[(\eta^6\text{-}C_{18}H_{24})M(CO)_3]$

Bond	M = Cr^0		M = Mn^I		
	Molecule 1	Molecule 2	Orthorhombic [a]	Trigonal 1	Trigonal 2
M–C(arene)	2.230(5)	2.229(5)	2.212(7)	2.221(3)	2.228(3)
C(arene)–C(arene)					
bridged	1.399(8)	1.395(8)	1.393(10)	1.416(4)	1.416(4)
unbridged	1.434(8)	1.430(8)	1.437(10)	1.433(4)	1.427(4)
M–CO	1.821(6)	1.822(6)	1.80(1)	1.796(3)	1.808(3)
C–O	1.157(7)	1.153(7)	1.15(1)	1.152(4)	1.146(3)
C(arene)–C_α	1.520(6)	1.522(7)	1.52(1)	1.509(4)	1.519(4)
C_α–C_β	1.48(1)	1.50(1)	1.51(1)	1.527(5)	1.512(4)
C_β–C_β	1.26(1) [b]	1.44(1)	1.43(1)	1.501(50	1.509(4)

[a] From ref. 5. [b] Shortened by excessive thermal motion.

The Mn atoms were readily located at positions separated by $1/2c$, and a Fourier map based on only $l = 2n$ data produced a recognisable disordered structure of $P\bar{3}m1$ symmetry in a cell with a halved c axial length. This disordered structure contains cations and anions in a column along $\frac{1}{3},\frac{2}{3},z$ and an inverted column along $\frac{2}{3}$, $\frac{1}{3},-z$. Whereas the remaining atoms could be described as fragments disordered across a mirror plane, the C–O ligands occur as two non-equivalent groups lying on the mirror planes and related by a 180° rotation about $\frac{1}{3},\frac{2}{3},z$. This structure may be ordered to account for the $l = 2n + 1$ data using a space group with four formula units per unit cell. However, in $P\bar{3}c1$ it is impossible to order the C–O ligands, and the lack of c-glide absences suggests the C–O ligands are ordered in one of the lower symmetry space group $P\bar{3}$ or $P321$. Twinning is necessary to account for the diffraction symmetry in the $P\bar{3}$ instance, where the two columns are related by a centre of inversion. For $P321$ the two columns would be related by a 2-fold rotation. $P3$ is a common subgroup of these two options and the refinement possibilities can be considered in this spacegroup.

The electron density of the untwinned $P3$ structure can be separated into eight components, so that $\rho(r) = \Sigma_n \rho_n(r)$ where components

$$\rho_1(r) = [\rho_A(r) + \rho_A(r + 1/2c)]/2$$
$$\rho_2(r) = [\rho_B(r) + \rho_B(r + 1/2c)]/2$$
$$\rho_3(r) = [\rho_C(r) + \rho_C(r + 1/2c)]/2$$
$$\rho_4(r) = [\rho_D(r) + \rho_D(r + 1/2c)]/2$$
$$\rho_5(r) = [\rho_A(r) - \rho_A(r + 1/2c)]/2$$
$$\rho_6(r) = [\rho_B(r) - \rho_B(r + 1/2c)]/2$$
$$\rho_7(r) = [\rho_C(r) - \rho_C(r + 1/2c)]/2$$
$$\rho_8(r) = [\rho_D(r) - \rho_D(r + 1/2c)]/2$$

and

$$\rho_A(r) = [\rho(r) + \rho(mr) + \rho(2r) + \rho(-r)]/4$$
$$\rho_B(r) = [\rho(r) - \rho(mr) - \rho(2r) + \rho(-r)]/4$$
$$\rho_C(r) = [\rho(r) + \rho(mr) - \rho(2r) - \rho(-r)]/4$$
$$\rho_D(r) = [\rho(r) - \rho(mr) + \rho(2r) - \rho(-r)]/4$$

are generated as irreducible representations of a pseudosymmetry group formed by three generators, one corresponding to a c-glide of $P\bar{3}c1$, the second to a $1/2c$ translation and a third to an inversion at the origin. Consequently $F(h) = \Sigma_n F_n(h)$ where $F_n(h)$ is the Fourier transform of $\rho_n(r)$. It may be shown [9] that if twinning creates observations

$$|Y(h)|^2 = |F(h)|^2 + |F(mh)|^2 + |F2h|^2 + |F(-h)|^2]/4$$

of $P\bar{3}m1$ diffraction symmetry then

$$|Y(h)|^2 = |F_1(h)|^2 + |F_2(h)|^2 + |F_3(h)|^2 + |F_4(h)|^2 \text{ for } l = 2n \text{ data,}$$

$$|Y(h)|^2 = |F_5(h)|^2 + |F_6(h)|^2 + |F_7(h)|^2 + |F_8(h)|^2 \text{ for } l = 2n + 1 \text{ data.}$$

Each component $\rho_n(r)$ has its associated space group (antisymmetry operations are excluded) viz., $P\bar{3}m1$, $P\bar{3}$, $P3m1$, $P321$ (for a cell of halved c axis) for $n = 1$ to 4, and $P\bar{3}m1$, $P\bar{3}c1$, $P\bar{3}m1$, $P\bar{3}c1$ (for the correct cell) for $n = 5$ to 8. The centre of inversion is at the origin for $n = 5$, 6 while it is at $1/4c$ for $n = 7$, 8. All eight components are possible if the true spacegroup is $P3$ but for higher symmetries certain components $\rho_n(r)$ are identically zero, as are their corresponding $F_n(h)$. If the true space group is $P321$ then $\rho_2(r) = \rho_3(r) = 0$ and either $\rho_5(r) = \rho_8(r) = 0$ or $\rho_6(r) = \rho_7(r) = 0$ depending on the origin (0 or $1/4c$) chosen for $\rho_1(r)$. Likewise, if the true spacegroup is $P\bar{3}$ then $\rho_3(r) = \rho_4(r) = 0$ and either $\rho_5(r) = \rho_6(r) = 0$ or $\rho_7(r) = \rho_8(r) = 0$. If the true spacegroup is $P\bar{3}c1$ then only $\rho_1(r)$ and either $\rho_6(r)$ or $\rho_8(r)$ are non zero. If the true spacegroup is $P\bar{3}m1$ then only $\rho_1(r)$ and either $\rho_5(r)$ or $\rho_7(r)$ are non zero.

A reasonably successful refinement can be obtained using the spacegroup $P\bar{3}c1$ for which $\rho(r) = \rho_1(r) + \rho_6(r)$, having made the distinction between origins for the asymmetric unit which are $1/4c$ apart. ($R_1 = 0.06$ for data with $I > 3\sigma(I)$ excluding $h,0,l$ $l = 2n + 1$ data). This indicates the dominance of $|F_1(h)|^2$ as a contributor to $l = 2n$ data and $|F_6(h)|^2$ as a contributor to $l = 2n + 1$ data. Only for $h,0,l$ $l = 2n + 1$ is $|Y(h)|^2$ observed without these dominant contributions. The model for $\rho_1(r) + \rho_6(r)$ is ordered for all but the CO ligands. These make a zero contribution to $\rho_6(r)$ should they lie exactly on the glide planes. The Mn, B, and F(1) atoms lie on the three-fold axis and thus only contribute to $l = 2n$ data which is consequently of stronger intensity. The observation of non zero intensities for $h,0,l$ $l = 2n + 1$ data suggests that these reflections result from an ordering of the CO ligands.

Should the CO ligands in isolation have $P\bar{3}m1$ symmetry while the remainder of the structure in isolation has $P\bar{3}c1$ symmetry then the true symmetry is either $P\bar{3}$ or $P321$ depending on whether or not the centres of inversion of the component structures coincide. The extra contribution to $\rho(r)$ obtained by ordering the CO ligands is thus either $\rho_5(r)$ if the true spacegroup is $P\bar{3}$ or $\rho_7(r)$ if it is $P321$.

It would appear at first sight that the phases of the $\rho_n(r)$ components can change without altering the observed intensities, presenting the possibility of homometric solutions. However if $\rho_2(r) = 0$ for $P\bar{3}$ and if $\rho_4(r) = 0$ for $P321$ then the different signed combinations of the non zero $\rho_n(r)$ replace $\rho(r)$ by $\rho(r + 1/2c)$ or $\rho(mr)$ or $\rho(mr + 1/2c)$. These choices constitute a selection of origin and a selection between twin related reflections as the reference orientation. This is the case should the structure be composed of two parts of $P\bar{3}c1$ and $P\bar{3}m1$ symmetry respectively. Allowing the CO ligands to move away from their pseudo special positions creates contributions to $\rho_6(r)$ and either $\rho_2(r)$ or $\rho_4(r)$ depending on the true spacegroup. The coherence of the restricted form of atom parameterisation causes the $\rho_2(r)$ or $\rho_4(r)$ component to have a unique final form determined by the well defined contribution to $\rho_6(r)$. There are two non-equivalent CO ligands in the $P\bar{3}c1$ model used for the initial refinement (see above) and an unconstrained refinement of these atoms is possible in this model.

Choice of $P\bar{3}$ over $P321$

The success of the twinned $P\bar{3}$ model is demonstrated by comparing data of different index condition. A final $R_1 = 0.046$ was obtained for the 2650 of 3623 data with $I > 3\sigma(I)$ considered to be observed. A final value of 0.098 was found for the

162 observed $h,0,l$ $l=2n+1$ reflections, 0.037 for the 323 observed $h,0,l$ $l=2n$ reflections, 0.049 for the $h,k,0$ reflections, 0.035 for the remaining h,k,l $l=2n$ data and 0.055 for the remaining h,k,l $l=2n+1$ observed reflections. A good fit of the relatively weak $h,0,l$ $l=2n+1$ reflections is not possible using the space group $P321$.

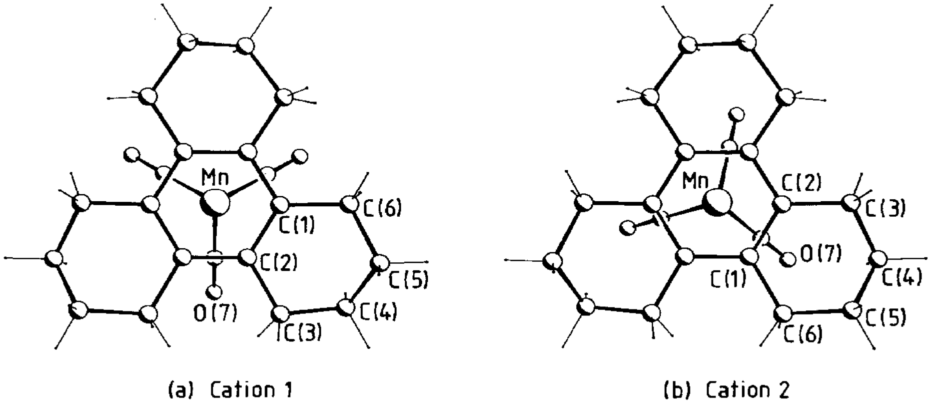
Initial refinement cycles in the twinned $P\bar{3}$ model imposed an exact c-glide relationship between the two non-equivalent units in the structure. The C–O ligands were not included in this constraint and instead were constrained to lie on the pseudo glide planes with a 2_1 screw relationship between the non-equivalent ligands. The sensitivity of the $l=2n+1$ data to the refinement of the C–O ligands rapidly showed that an unconstrained model for these atoms was meaningful and necessary. Constrained refinement is necessary for any atom which makes little contribution to more than half of the non zero $\rho_n(r)$ components.

The symmetry restrictions of the pseudo $P\bar{3}c1$ space group were applied to couple anisotropic thermal parameters of one non-equivalent unit to the other. The C–O ligand anisotropic thermal parameters were unrestricted. Restraints to make the differences in pseudoequivalent distances between the two formula units approach zero were also applied, as were constraints to make the BF_4^- ions approach tetrahedral symmetry and the C–H distances to approach equality while maintaining sensible geometry. H atoms were given the same thermal parameters as the atoms to which they were attached.

The constrained least-squares refinement program RAELS87 [9] was used to carry out the refinement using standard options of the program. In a final cycle restraints on all non-hydrogen distances were removed with minimal effect on the refinement.

Rationale behind constrained refinement

The structure consists of a $P\bar{3}c1$ component describable as $\rho_1(r)+\rho_6(r)$ and a $P\bar{3}m1$ component describable as $\rho_1(r)+\rho_5(r)$. Distortion away from these pseudo symmetries creates components $\rho_2(r)+\rho_5(r)$ and $\rho_2(r)+\rho_6(r)$ respectively. Twinning creates observations $|F_1(h)|^2+|F_2(h)|^2$ for $l=2n$ and $|F_5(h)|^2+|F_6(h)|^2$



(a) Cation 1

(b) Cation 2

Fig. 2. The structure of the two independent cations $[(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3]^+$ viewed down the three-fold axis.

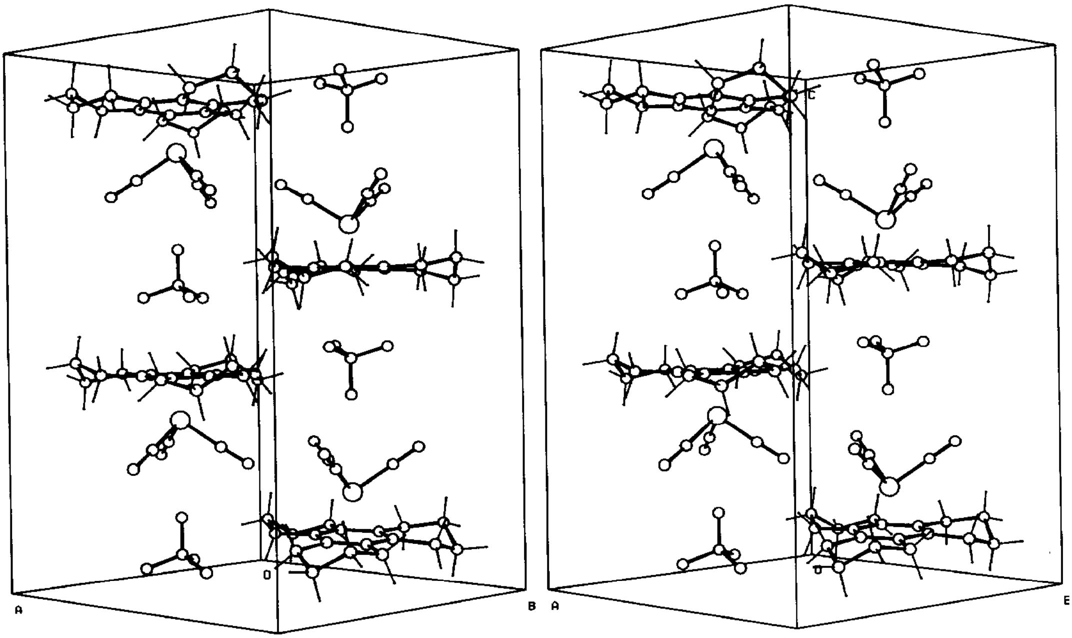


Fig. 3. The packing of the ions in the twinned unit cell found for $[(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3]BF_4$.

for $l = 2n + 1$ which are dominated by the $|F_1(h)|^2$ and $|F_6(h)|^2$ components. Thus the distortion away from $P\bar{3}m1$ for the second component is well defined by the $|F_6(h)|^2$ contribution but distortion away from $P\bar{3}c1$ for the first component is only well defined by the relatively weak $h0l$ $l = 2n + 1$ data that contains only $|F_5(h)|^2$. However this data only sees the structure in projection. Constraints that restrict the form of distortion away from $P\bar{3}c1$ of the first component of the structure were therefore thought necessary for the initial refinement cycles. Equivalence of thermal parameters and distances (but not positions) were maintained until refinement converged. Only then were restraints on non-hydrogen distances removed for a final refinement cycle. The distances C(1)–C(2) for both cations remained marginally smaller than the distances C(1)–C(2)′. These results do not preclude a larger difference between independent ions; rather it suggests that a small difference is undetectable.

Table 2 contains the final parameters from the twinned $P\bar{3}$ refinement, while bond data are included in Table 3. The structures of the two independent cations are shown in Fig. 2, while the unit cell packing is given in Fig. 3.

For both structures full lists of bond parameters, thermal parameters, hydrogen atom positions and structure factors can be obtained from the authors (BKN).

Results and discussion

The complex $[(\eta^6\text{-}C_{18}H_{24})Cr(CO)_3]$ was readily synthesised by reaction of $Cr(NH_3)_3(CO)_3$ and the ligand $C_{18}H_{24}$ in refluxing dioxane [7]. The chemical and spectroscopic properties were as expected by comparison with other $(arene)Cr(CO)_3$ compounds [10].

The crystal structure of $[(\eta^6\text{-}C_{18}H_{24})Cr(CO)_3]$ consists of two independent, discrete molecules in the asymmetric unit which do not differ significantly. Figure 1 shows the overall geometry for both molecules. In each, the arene ring is symmetrically bonded to the $Cr(CO)_3$ group, with an average Cr–C(ring) distance of 2.230(2) Å and an average Cr–CO distance of 1.822(3) Å. Both independent cations adopt the staggered configuration **4a**. The outer cyclohexene rings have the expected 'half-boat' conformation, although some appear to be flattened. However the carbon atoms of the outer methylene groups show quite large anisotropy, indicative of partial disorder between the two equivalent 'half-boat' forms so that the reported geometry is that of an average structure, and the C_β–C_β bond lengths are artificially shortened.

The structure determination of the trigonal form of $[(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3]BF_4$ was complicated by twinning in the crystal, but this way successfully modelled (see experimental). The crystal contains columns of alternating $[(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3]^+$ and BF_4^- ions about inversely related three-fold axes (Fig. 3). There are two independent formula units in the asymmetric unit of the cell. The first cation, Fig. 2a, adopts the same conformation as that found for the chromium analogue (**1**) and for the orthorhombic form of (**2**), i.e. arrangement **4a**. The other cation, Fig. 2b, has the CO ligands best represented by the alternative orientation, **4b**, but are rotated by about 12° from the idealised position towards eclipsing an arene carbon atom.

Table 3 summarises some bond distances for all the $[(\eta^6\text{-}C_{18}H_{24})M(CO)_3]$ species determined. There is surprising little difference between the M–C(arene) distances going from the chromium molecule (2.230 Å) to the manganese cations (2.220 Å averaged over all forms). The M–CO distances change by slightly more, being 1.821 Å in **1** and 1.801 Å in **2**. This suggests a difference in the bonding radii of Cr^0 and Mn^I of only ca. 0.01–0.02 Å, which is less than that found for example, when comparing $Cr(CO)_3$(dien) [11] and $Mn(CO)_3(NH_3)_3^+$ [12] where a difference of 0.05–0.09 Å is found for the M–C and M–N bonds. It is interesting that the increased nuclear charge on going from the Cr complex **1** to the Mn complex **2** affects the M–C(ring) distance less than the M–CO distance, since the increased charge on the metal might have been expected to enhance the bonding to the π-donor arene ligand to a greater extent than to CO, where the π-acceptor interaction is more important.

The most interesting feature of all the structures is that the carbonyl groups are projected onto the unbridged C–C bonds of the planar arene ligand, corresponding to orientation **4a**, for both $[(\eta^6\text{-}C_{18}H_{24})Cr(CO)_3]$ molecules, for the $[(\eta^6\text{-}C_{18}H_{24})Mn(CO)_3]^+$ cation in the orthorhombic form, and for one of the trigonal form cations. This means that this orientation is observed for four out of the five different crystal environments with different crystal packing interactions. This suggests that there is a clear preference for **4a** over **4b**, but the observation of the alternative orientation **4b** co-existing in the trigonal form suggests that the energy difference between the two is not great. An examination of the bond localisation in the arene ring for each species shows that the bridged C–C bonds are 1.404 Å, while the unbridged ones average 1.432 Å. For the four species with conformation **4a** this is consistent with higher π-electron density in the C–C bonds towards which the acceptor orbitals of the $M(CO)_3$ groups are directed, and the difference between the short and long C–C arene bonds is close to that observed in other (arene)$Cr(CO)_3$ complexes [1–3,13]. For the unique example with structure **4b** however the bond alternation appears to be in the opposite sense to that expected. Unfortunately the uncertainties arising from the refinement problems associated with the twinning for this last structure preclude any definite conclusions but if the result is correct it would suggest that the dodecahydrotriphenylene ligand does prefer the Kékulé form **3a** which tends to direct the $M(CO)_3$ unit towards conformation **4a**, but that the alternative orientation can be formed without reversing the natural bond alternation. On the other hand it may be that intramolecular interactions between the peripheral rings and the CO groups favour the predominantly observed staggered arrangements, and that the bond alternation in the arene ring arises as a consequence, with the true data for the trigonal example obscured in the refinement. The fact that the magnitude of the difference between the long and short C(arene)–C(arene) bonds is similar to those in higher symmetry arene complexes [3] suggests that the latter explanation is probably favoured.

Acknowledgements

We wish to express our gratitude to the New Zealand Universities Grants Committee for financial support, and for the provision of a Postgraduate Scholarship (to LHPG). A referee is thanked for comments on an earlier version of this paper.

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