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Tricarbonyl(η^6-chlorobenzene)-chromium

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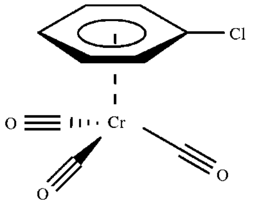
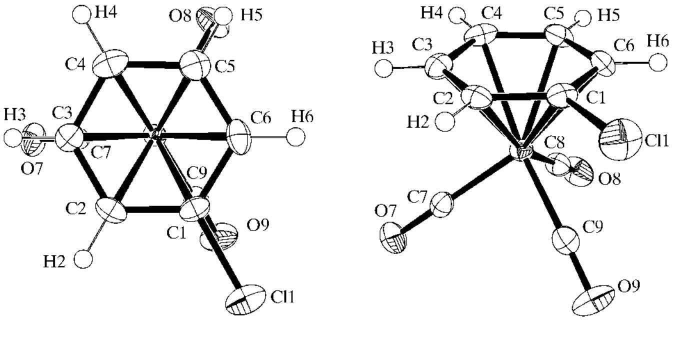
The title compound, [$Cr(C_6H_5Cl)(CO)_3$], is the first group 6 tricarbonyl η^6-monohaloarene compound to be structurally characterized. It adopts a classic piano-stool structure, with the $Cr(CO)_3$ tripod assuming a *syn*-eclipsed conformation relative to the arene ring ($\varphi = 2.0°$). The extended structure is dominated by intermolecular $\pi\cdots H$ interactions (H⋯ring centroid = 2.94 Å) and non-classical hydrogen bonds between carbonyl and arene moieties (O⋯H = 2.50–2.58 Å).

Comment

Metal–arene π-complexes continue to be the subject of extensive study because of their utility as intermediaries for key synthetic transformations. In particular, the tricarbonylchromium moiety has long been employed as a means of activating aromatic hydrocarbons towards nucleophilic reaction pathways, because of its strongly electrophilic nature. Consequently, complexes containing this moiety continue to be investigated, and numerous examples have been structurally characterized. However, while the structural facets of η^6-benzene–chromium–tricarbonyl (Rees & Coppens, 1973) and a range of polysubstituted analogues are well documented, no such investigation of the monohalo derivatives has previously been undertaken. We report here the first structural study of [$Cr(\eta^6-C_6H_5Cl)(CO)_3$], (I).



(I)



(*a*) (*b*)

Figure 1
(*a*) The ring-plane projection and (*b*) a molecular view of (I), showing the atomic numbering scheme and displacement ellipsoids at the 30% probability level.

The asymmetric unit (Fig. 1) of (I) comprises a single molecule that exhibits the classic 'piano-stool' structure, with the $Cr(CO)_3$ tripod adopting a *syn*-eclipsed conformation relative to the aromatic ring ($\varphi = 2.0°$). This conformation is typical of the presence of a π-donor substituent (Muetterties *et al.* (1982). The σ-acceptor character of chlorine is manifest in a relatively short [1.707 (2) Å] Cr⋯*Cg* distance (*Cg* is the ring centroid), which is characteristic of an electron-poor complex which is confirmed by high carbonyl stretching frequencies (ν_{max} = 1988 and 1923 cm^{-1}), similar to those reported previously (Gassman & Deck, 1994). The metal–centroid distance agrees with that of 1.7 Å reported for [$Cr(\eta^6-C_6H_5Cl)(CO)_2PPh_3$] (Eglin & Smith, 2001) and 1.680 (5) Å observed in the fully substituted [$Cr(\eta^6-C_6Cl_6)(CO)_3$] (Gassman & Deck, 1994). The latter is the current limiting case for halosubstituted [$Cr(\eta^6$-arene$)(CO)_3$] complexes. It is, however, interesting to note that the distance found here for the monochloroarene is comparable to that determined in [$Cr(\eta^6-p-C_6H_4F_2)(CO)_3$] (Cr⋯*Cg* = 1.719 Å), which is counterintuitive. Further internal distances are largely as expected,

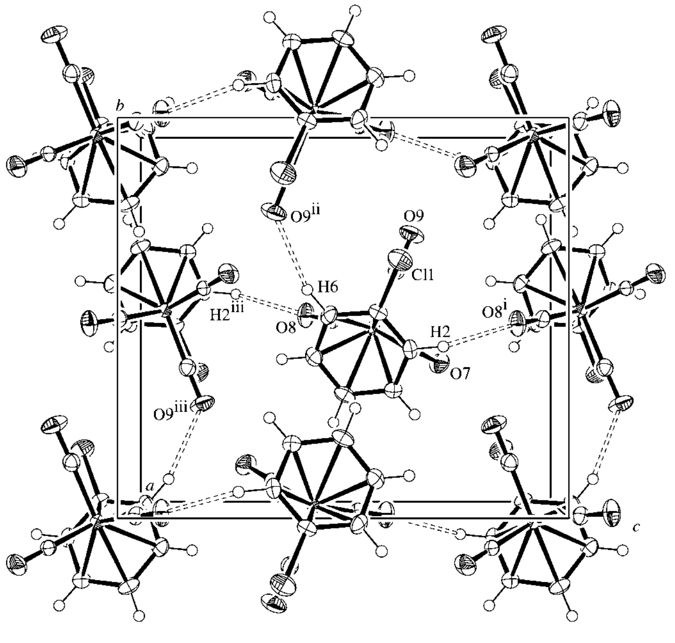


Figure 2
A view of the intermolecular non-classical hydrogen bonds in the crystal structure of (I). The cell origin is at the lower front left corner. [Symmetry codes: (i) $\frac{3}{2} - x, 1 - y, \frac{1}{2} + z$; (ii) $-\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$; (iii) $\frac{3}{2} - x, 1 - y, -\frac{1}{2} + z$.]

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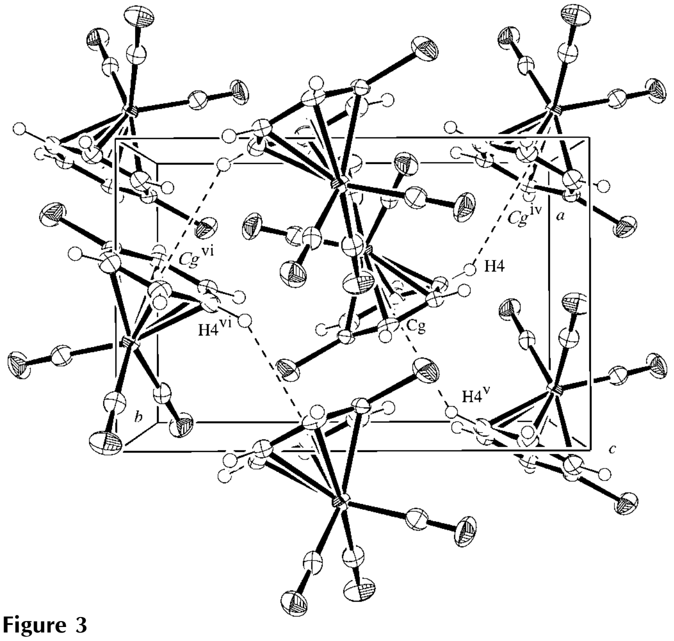

Figure 3
A view of the H$\cdots\pi$ interactions in the crystal structure of (I) (*Cg* is the ring centroid). The cell origin is at the lower rear right corner. [Symmetry codes: (iv) $\frac{1}{2}+x$, $\frac{1}{2}-y$, $1-z$; (v) $-\frac{1}{2}+x$, $\frac{1}{2}-y$, $1-z$; (vi) $1-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$.]

with Cr—CO, C—O and ring C—C distances (Table 1) falling in the typical ranges for related materials.

The extended structure is dominated by an extensive network of non-classical hydrogen bonds involving the arene H atoms and carbonyl fragments of adjacent molecules. The two *ortho*-H atoms (H2 and H4) of each arene interact with the O atom of one of the carbonyl groups from each of two different neighbouring molecules (Fig. 2), thus generating an extended three-dimensional network. A search of the Cambridge Structural Database (Allen, 2002) shows that the C—H$\cdots$O bond distances (Table 2) are unexceptional. Indeed, analogous bonding is observed in [Cr(η^6-C_6H_5Cl)$(CO)_2PPh_3$], with an H$\cdots$O bond distance of 2.50 Å. The interaction angles observed in the present case (134 and 160°) are also similar. In addition, a significant H$\cdots\pi$ interaction is apparent (Fig. 3) between the *para*-H atom (H4) and the arene ring of an adjacent molecule at ($\frac{1}{2}+x$, $\frac{1}{2}-y$, $1-z$) (H$\cdots$*Cg* = 2.94 Å). The H$\cdots$*Cg* vector lies at 10° to the ring normal, while the C4—H4$\cdots$*Cg* angle at the H atom is 143°. These interactions result in stacks of molecules through the crystal, with molecules alternately aligned by 54° with respect to one another in each stack.

Experimental

The title compound was prepared according to the method of Alemagna *et al.* (1983). A mixture of hexacarbonylchromium (1.77 g, 8.04 mmol), chlorobenzene (2.5 ml, 24.56 mmol) and catalytic THF (10 ml) were refluxed in di-*n*-butyl ether (80 ml) for 20 h. The mixture was subsequently cooled to 253 K and filtered through a No. 4 frit, in order to effect separation of residual $Cr(CO)_6$. Concentration of the filtrate *in vacuo* led to the formation of a bright-yellow solid, which was purified by sublimation (2 mm Hg, 333 K), yielding single crystals suitable for X-ray diffraction analysis.

Crystal data

$[Cr(C_6H_5Cl)(CO)_3]$
$M_r = 248.58$
Orthorhombic, $P2_12_12_1$
$a = 7.1159\ (6)$ Å
$b = 10.7627\ (11)$ Å
$c = 12.1055\ (10)$ Å
$V = 927.12\ (14)$ Å^3
$Z = 4$
$D_x = 1.781$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5505 reflections
$\theta = 1.0$–27.5°
$\mu = 1.49$ mm^{-1}
$T = 150\ (2)$ K
Prism, yellow
0.20 × 0.15 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer
ω and φ scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.754$, $T_{max} = 0.807$
6363 measured reflections
2071 independent reflections
1208 reflections with $I > 2\sigma(I)$
$R_{int} = 0.123$
$\theta_{max} = 27.4°$
$h = -9 \rightarrow 7$
$k = -13 \rightarrow 13$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R(F) = 0.056$
$wR(F^2) = 0.097$
$S = 0.99$
2071 reflections
127 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.031P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.50$ e Å^{-3}
$\Delta\rho_{min} = -0.52$ e Å^{-3}
Absolute structure: Flack (1983), 837 Friedel reflections
Flack parameter = −0.06 (4)

Table 1
Selected geometric parameters (Å, °).

Cr1—C1	2.206 (5)	Cr1—C8	1.833 (6)
Cr1—C2	2.214 (5)	Cr1—C9	1.834 (6)
Cr1—C3	2.195 (5)	Cl1—C1	1.745 (5)
Cr1—C4	2.226 (6)	O7—C7	1.161 (6)
Cr1—C5	2.189 (5)	O8—C8	1.157 (6)
Cr1—C6	2.226 (5)	O9—C9	1.163 (6)
Cr1—C7	1.830 (6)		
C7—Cr1—C8	89.0 (2)	O7—C7—Cr1	179.5 (5)
C7—Cr1—C9	87.0 (2)	O8—C8—Cr1	178.6 (5)
C8—Cr1—C9	88.7 (2)	O9—C9—Cr1	178.4 (5)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
C2—H2$\cdots$O8^{i}	0.96	2.58	3.306 (6)	134
C6—H6$\cdots$O9^{ii}	0.96	2.50	3.409 (6)	160

Symmetry codes: (i) $\frac{3}{2}-x$, $1-y$, $\frac{1}{2}+z$; (ii) $-\frac{1}{2}+x$, $\frac{3}{2}-y$, $1-z$.

Compound (I) crystallized in the orthorhombic system, and space group $P2_12_12_1$ was determined uniquely from the systematic absences. H atoms were visible in difference maps and were treated as riding atoms, with C—H distances of 0.95 Å. The value of the Flack (1983) parameter shows that the absolute structure has been determined correctly.

Data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1692). Services for accessing these data are described at the back of the journal.

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