Structure of a Non-fluxional π-Arene Chromium Dicarbonyl Complex

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Summary A non-fluxional π-arene chromium(0) dicarbonyl complex, [Ph(π-Ph)As·CH$_2$·AsPh$_2$Cr(CO)$_2$], which has approximately octahedral symmetry about the central chromium atom, has been prepared, and its structure has been determined by three-dimensional X-ray crystallographic analysis.

WHEN Cr(CO)$_5$(dam) [dam = Ph$_2$AsCH$_2$AsPh$_2$] or stoicheiometric amounts of Cr(CO)$_6$ and (dam) are heated in decane under nitrogen, an orange diamagnetic molecular complex of empirical formula [Cr(CO)$_2$(dam)] is obtained: m.p. 182—184°; n.m.r. [(CD$_3$)$_2$CO)] δ 7·4 (15H, free phenyls), 5·0 (5H, π-arene), and 3·4 p.p.m. (2H, CH$_2$); i.r. (KBr disc) 1880 and 1830 cm^{-1} [ν(C≡O)]. The corresponding [Mo(CO)$_2$(dam)] has also been prepared, but all attempts to isolate the tungsten analogue have been unsuccessful.

Crystals of [Ph(π-Ph)As·CH$_2$·AsPh$_2$Cr(CO)$_2$] suitable for X-ray work, were recrystallised from hexane–CH$_2$Cl$_2$ solution, and the structure has been determined by three-dimensional single-crystal X-ray analysis. The crystals are triclinic, space group P1̄, a = 7·61, b = 8·56, c = 18·68 Å, α = 83·16°, β = 82·52°, γ = 81·66°, Z = 2. The 3213 independent reflexions, for which $F_0^2/\sigma(F_0^2) \geqslant 3\cdot0$, were measured on a PICKER FACS-I automatic diffractometer (crystal monochromated Cu-K_α radiation). With all atoms isotropic, the π-arene carbon atoms unrestrained, and the remaining three unco-ordinated phenyl groups restricted to D_{6h} symmetry (C–C, 1·397 Å), the refinement has converged to a conventional R-factor of 0·090. Average e.s.d.s for the more important bond distances shown in Figures 1 and 2 are: Cr–As, 0·002; Cr–C, 0·015; As–C, 0·01; C–O, 0·02; and C–C, 0·02 Å. The data have yet to be corrected for absorption and extinction effects.

The molecule consists of a central chromium atom with two carbonyl groups and one arsenic of the (dam) ligand occupying three mutually cis octahedral co-ordination sites. One phenyl group attached to the second arsenic of the (dam) ligand occupies the three remaining co-ordination sites on the other "side" of the central chromium atom (Figures 1 and 2).
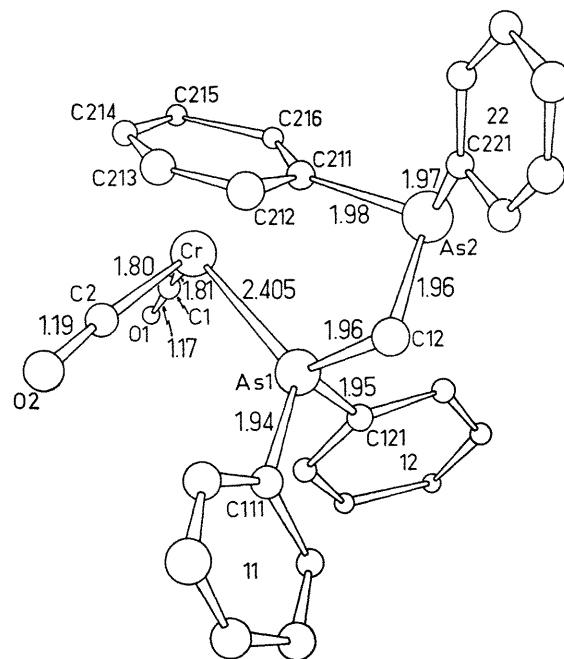

FIGURE 1. The overall stereochemistry of the molecule.

The carbon atoms of the π-arene ring are coplanar, within experimental error, and the chromium atom is located directly below the ring centre of gravity. The Cr–ring separation is 1·68 Å, cf., 1·60 Å in dibenzenechromium,[1] 1·73 Å in hexamethylbenzenechromiumtricarbonyl,[2] and 1·72 Å in benzenechromiumtricarbonyl.[3] Similar values have also been observed for a number of mono-, di-, and tri-substituted π-arene chromium tricarbonyl

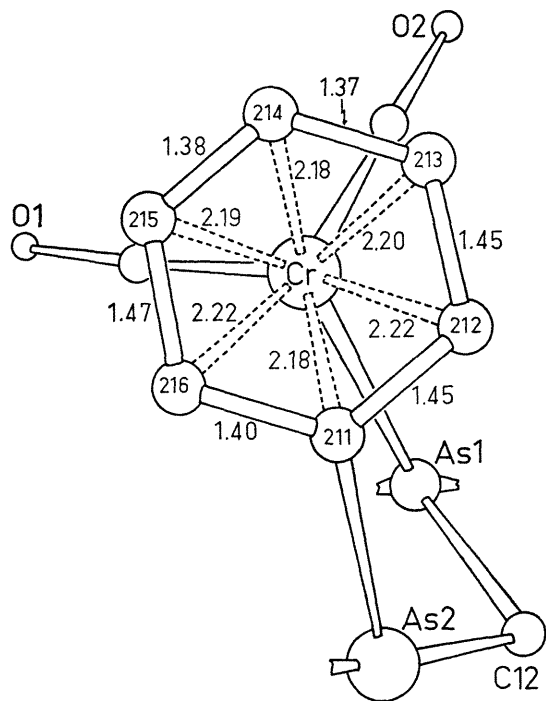derivatives.[4-7] The carbon atoms of the CO ligands are

FIGURE 2. *Part of the molecule projected on to the π-arene plane.*

both 2·75 Å below the π-arene plane, a value similar to those previously observed.[2-7] Unlike hexamethylbenzene-chromiumtricarbonyl[2] and benzenechromiumtricarbonyl,[3] where the CO groups are *trans* to the mid-points of alternate π-arene C–C bonds (*i.e.*, a staggered arrangement), the configuration of [Cr(CO)₂(dam)] is partially eclipsed; the average (ligand–Cr:CG–"eclipsed"-arene-carbon) torsion angle is 17° (CG is the centre of gravity of the π-arene ring). Deviations of the Cr–C(arene) and C–C(arene) distances from their mean values [2·20(1) and 1·42(1) Å respectively] are not statistically significant.

The fact that As(2) lies 0·24 Å out of the π-arene plane, together with the small deformation of the As(1)–C(12)–As(2) angle [106·5(5)°] from the regular tetrahedral value, is indicative of a small degree of steric strain. The angles Cr–As(1)–C(12) and C(12)–As(2)–C(211) [109·4° and 94·8° respectively] are presumably strain affected to a similar (energetic) degree.

The Cr–C(carbonyl) distances are equal within experimental error [1·80(1) and 1·81(1) Å], and are in good agreement with the previously observed average values of 1·81(1) and 1·84(1) Å for hexamethylbenzenechromiumtricarbonyl[2] and benzenechromiumtricarbonyl,[3] respectively. The average C–O distance (1·18 ± 0·015 Å) is normal.

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