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Preliminary communication

The structure of $[\{(\pi\text{-}C_6H_5)P(C_6H_5)_2\}Cr(CO)_2]_2$; a complex with a π-bonded bridging triphenylphosphine group

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SUMMARY

The structure of $[\{(\pi\text{-}C_6H_5)P(C_6H_5)_2\}Cr(CO)_2]_2$ has been determined by X-ray methods; each dimer consists of two Cr atoms bridged by two triphenylphosphine groups while each triphenylphosphine group is P-bonded to one Cr-atom, and is involved in π-arene bonding to the second Cr atom.

The reaction of $Cr(CO)_6$ with triphenylphosphine, tri-*m*-tolylphosphine, and tri-*p*-tolylphosphine in refluxing decalin, produces two series of complexes of empirical formula $[Cr(CO)_3L]$ and $[Cr(CO)_2L]_2$ [1]. The tricarbonyl derivatives, which cannot be isolated in the pure state, are thought to be structurally analogous to simple $[(\pi\text{-arene})Cr(CO)_3]$ complexes; the phosphine is bonded to the Cr atom via Cr—π-arene bonds alone, and there is no Cr—P interaction[2]. In contrast, pure samples of the dimeric species are readily isolated, and the structure of $[Cr(CO)_2\{P(C_6H_5)_3\}]_2$ has now been established by single-crystal three-dimensional X-ray structural analysis.

Crystals of $[\{(\pi\text{-}C_6H_5)P(C_6H_5)_2\}Cr(CO)_2]_2$ are triclinic, space group $P\bar{1}$, with $a = 16.58$, $b = 9.56$, $c = 13.10$ Å, α 109.92, β 68.14, γ 121.15°, $Z = 2$. Solution and refinement of the structure is based on 4956 unique reflections, with $I/\Delta I \geqslant 3.0$, recorded on a Picker FACS-I fully automatic four-circle diffractometer using graphite-crystal monochromated Mo-K_α radiation. Data have yet to be corrected for absorption effects, and hydrogen atom contributions have not been included in the scattering model. Allowing for anisotropic thermal motion for all non-hydrogen atoms, block-diagonal least-squares refinement has converged to the present conventional R-factor of 0.050.

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The two dimeric molecules which comprise the unit cell are crystallographically independent, but each has exact $\bar{1}$ (C_i) symmetry. Except for small angular differences (largely at the phosphorus atoms), the dimensions of both molecules are in excellent agreement. The stereochemical arrangement of one of the two independent dimeric molecules is shown in Fig. 1. Each dimeric unit results from bridging of two equivalent (inversion related) chromium atoms by a pair of equivalent triphenylphosphine groups. The Cr—Cr distances average 4.657Å, and preclude any significant contribution from metal—metal bonding.

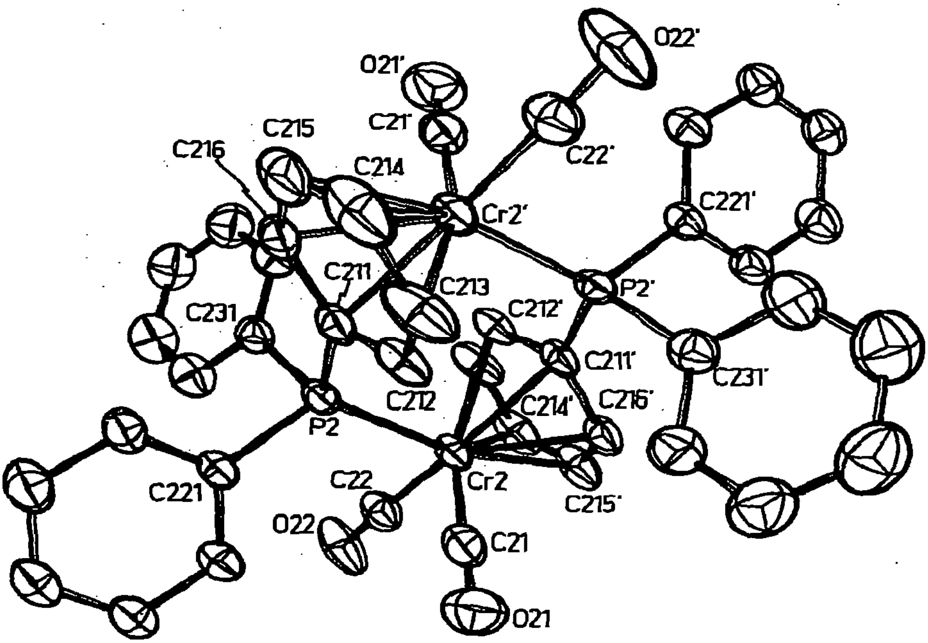

Fig. 1. The overall stereochemistry of $[\{(\pi\text{-}C_6H_5)P(C_6H_5)_2\}Cr(CO)_2]_2$.

The carbon atoms of the π-arene ring [C(211)—C(216)] are planar within experimental error, and the ligand arrangement about the metal atoms bears a close resemblance to that observed for the bis(diphenylarsino)methane derivative $[\{(\pi\text{-}C_6H_5)(C_6H_5)AsCH_2As(C_6H_5)_2\}Cr(CO)_2]$ [3]. The major difference is reflected by a ca. 12° variation in the relative orientations of the π-arene and carbonyl ligands. The present complex exhibits a near eclipsed configuration characteristic of $[(h^6\text{-monosubstituted-arene})Cr(CO)_3]$ complexes[4]; the average torsion angle [defined as the angle between the two three atom planes {CO(or P), Cr, CofG} and {Cr, CofG, π-arene carbon atom} (where CofG is the centre of gravity of the π-arene ring)] is 3.5°, compared with an average value of 15.9° for $[\{(\pi\text{-}C_6H_5)(C_6H_5)AsCH_2As(C_6H_5)_2\}Cr(CO)_2]$ [3]. Despite this configurational difference, both $[\{(\pi\text{-}C_6H_5)P(C_6H_5)_2\}Cr(CO)_2]_2$ and $[\{(\pi\text{-}C_6H_5)(C_6H_5)AsCH_2As(C_6H_5)_2\}Cr(CO)_2]$ exhibit almost identical metal—ligand distances. For the dimer, the Cr–C(arene) and Cr–C(carbonyl) distances average 2.19 and 1.83Å respectively, *cf.* 2.18 and 1.83Å for the corresponding distances in the bis-(diphenylarsino)methanechromium dicarbonyl derivative[3]. In contrast, the metal–arene distances in $[(\pi\text{-}C_6H_6)Cr(CO)_3]$ average some 0.04–0.05Å longer[5], while those in $[(\pi\text{-}C_6H_6)_2Cr]$ average some 0.05Å less than the present values[6]. These data suggest, unequivocally, that the Cr–arene bond strength is inversely related to the π-acid strength of those ligands *trans* to the arene group. As expected, the decreased π-acidity of the phosphine (or arsine) ligand (compared with a carbonyl group), also results in some strengthening of the remaining chromium–carbonyl bonds. Thus, the Cr–C(carbonyl) distances in both $[\{(\pi\text{-}C_6H_5)P(C_6H_5)_2\}Cr(CO)_2]_2$ and $[\{(\pi\text{-}C_6H_5)(C_6H_5)AsCH_2As(C_6H_5)_2\}Cr(CO)_2]$ [3] average 1.83Å, while the average Cr–C(carbonyl) distance is 1.841Å [5], for $[(\pi\text{-}C_6H_6)Cr(CO)_3]$.

Inspection of the interbond angles suggests that there is very little accumulated steric strain in the dimeric units. Both the Cr–P–C angles (greater than the tetrahedral angle) and the C–P–C angles (less than tetrahedral) are entirely characteristic of the values observed for numerous coordinated tertiary phosphine derivatives. The Cr–C–O angles show small deviations from linearity (average 176.6°). This effect has been attributed to π-bonding rather than crystal packing forces[7].

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