X-Ray Molecular Structure of Tricarbonyl-(1—5,α-η-diphenylfulvene)chromium, [(η-$C_5H_4CPh_2$)$Cr(CO)_3$]

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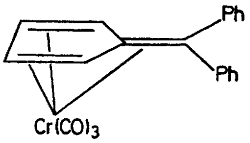
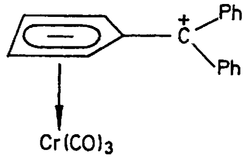
Summary In the title complex, the $Cr(CO_3)$ fragment is bonded to the six carbon atoms of the fulvene system, causing a significant distortion in planarity of the fulvene system, and a loss of C_{3v} symmetry of the $Cr(CO)_3$ fragment.

THE tricarbonylchromium complex of diphenylfulvene, [($C_5H_4CPh_2$)$Cr(CO)_3$], (I) was first obtained by Fischer *et al*[1] and we have studied its reactivity by isotopic exchange of hydrogen. The ^1H n.m.r. spectra of (I) show that the cyclopentadiene and not the phenyl ring is co-ordinated to the metal as Fischer supposed. Since the $Cr(CO)_3$ group is well known to form stable complexes with 6-electron donor ligands, it seemed probable that in (I) the Cr atom is co-ordinated to the double bonds of the five-membered ring and also to the exocyclic double bond (A), or that fulvene is co-ordinated in its ylide form with stabilization of the α-carbonium centre by interaction with the Cr atom (B).

We have established the molecular geometry of (I) by *X*-ray crystallography.



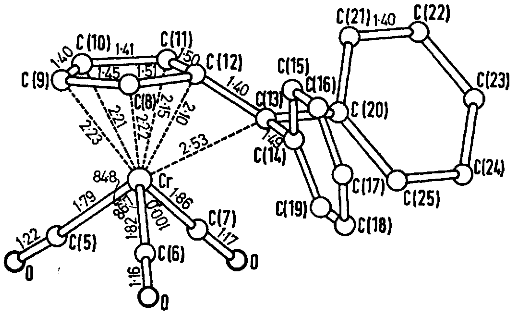
(A)



(B)

Crystal data: $C_{21}H_{14}CrO_3$, monoclinic, space group $P2_1/a$, $a = 20{\cdot}008(6)$, $b = 6{\cdot}504(2)$, $c = 13{\cdot}064(4)$ Å, $\beta = 94{\cdot}36(2)°$, $U = 1695$ Å^3, $D_m = 1{\cdot}44$, $D_c = 1{\cdot}44$ g cm^{-3} for $Z = 4$. Intensities of 1019 independent reflections with $|F|^2 > 3\sigma(|F|^2)$ were measured on an automatic Hilger-Watts diffractometer (Cu-K_α radiation, graphite monochromator, ω-scan, no absorption correction). The structure was solved by direct methods and refined by isotropic least-squares to a current *R*-value of 0·096. Standard deviations in bond lengths and angles are: Cr–C 0·01, C–O 0·02, C–C 0·02 Å, ∠ Cr–C–O 1·0, C–Cr–C 1·0, C–C–C 1·3°.

In the molecule of (I) the Cr atom has a distorted octahedral co-ordination and is bonded to six C atoms of the fulvene ligand and three CO groups (Figure). The distortion present is shown by the inequality of the Cr–C(fulvene) distances (2·10—2·53 Å) and the loss of the C_{3v} symmetry of the Cr(CO)$_3$ fragment. The OC–Cr–CO bond angles (86·7, 84·8, and 100·0°) and Cr–CO bond lengths (1·79, 1·82, and 1·86 Å) are unequal. An analogous effect which is not characteristic for arene–tricarbonylchromium complexes is observed in all LCr(CO)$_3$ complexes, where L is not arene. In tricarbonylcyclo-octa-1,3,5-trienylchromium[2] the OC–Cr–CO bond angles are 91·0, 95·4, and 78·8° and the Cr–CO bond lengths are 1·78, 1·83, and 1·87 Å, which reflects some inequality in the octahedral chromium orbitals. Also, steric effects cannot be neglected since interaction between Cr and the exocyclic C(13) with conservation of the C_{3v} symmetry of the Cr(CO)$_3$ fragment would cause very short non-bonded distances C(13) ··· C(7) and C(13) ··· C(6). This steric repulsion may also contribute to a significant lengthening of the Cr–C(13) bonding distance (2·53 Å). Interaction of the Cr atom with the fulvene system leads to a significant distortion of the ligand geometry in comparison to the planar non-co-ordinated dimethylfulvene molecule[3] where a pronounced alternation of double and single bonds is observed. In complex (I) the fulvene ligand is not planar: the C(12)–C(13) double bond is inclined by 31° to the planar five-membered ring and by 23° to the C(13)C(14)C(20) triangle, leading to loss of conjugation. Co-ordination causes the length of this bond (1·40 Å) to increase markedly from the standard value of 1·337 Å.



FIGURE

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