

## Unusual Fluorocarbon-ligand Geometries

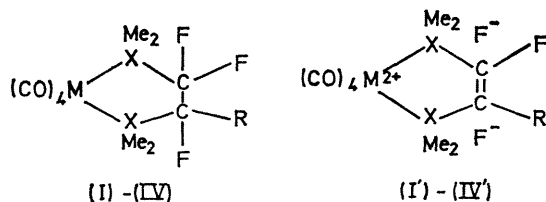
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**Summary** X-Ray crystal analyses of four compounds of the type  $\text{Me}_2\text{X}\cdot\text{CFR}\cdot\text{CF}_2\cdot\text{XMe}_2\cdot\text{M}(\text{CO})_4$  ( $\text{M} = \text{Cr}$  or  $\text{Mo}$ ;  $\text{X} = \text{P}$  or  $\text{As}$ ;  $\text{R} = \text{H}$  or  $\text{CF}_3$ ) have revealed unusual ligand geometries.

STUDIES of the n.m.r. spectra of some fluorocarbon bridged ditertiary arsine complexes of chromium hexacarbonyl have revealed an unusual tendency of fluorine atoms to occupy axial positions in the puckered chelate ring.<sup>1</sup> X-Ray analyses of crystals of four complexes of this type,  $\text{Me}_2\text{X}\cdot\text{CFR}\cdot\text{CF}_2\cdot\text{XMe}_2\cdot\text{M}(\text{CO})_4$  ( $\text{M} = \text{Cr}$  or  $\text{Mo}$ ;  $\text{X} = \text{P}$  or  $\text{As}$ ;  $\text{R} = \text{H}$  or  $\text{CF}_3$ ) (Table) have now provided details of the molecular structures, and revealed novel geometrical features.

Crystals of (I) have space group  $C2/c$ ,  $Z = 8$ ,  $a = 25.06$ ,  $b = 13.27$ ,  $c = 11.56$  Å,  $\beta = 102.8^\circ$ . Crystals of (II), (III), and (IV) are isomorphous, space group  $Pbca$ ,  $Z = 8$ ,  $a = 18.26$ ,  $17.51$ ,  $17.85$ ,  $b = 14.87$ ,  $14.77$ ,  $14.70$ ,  $c = 12.52$ ,  $12.63$ ,  $12.58$  Å. The structures were determined with Mo- $K_\alpha$  diffractometer data by Patterson, electron-density, and full-matrix least-squares methods, the final  $R$  values being 0.073, 0.052, 0.089, and 0.078 for 1510, 1759, 1593, and 1670 observed reflexions for (I), (II), (III), and (IV) respectively.



The molecular structures can be derived from the metal hexacarbonyls by replacement of two carbonyl groups by the arsenic or phosphorus atoms of the chelating ligands. The five-membered chelate rings are non-planar, the C-C bonds of the rings being twisted out of the XMX planes by the angle  $\alpha = 23$ , 11, 3, and  $3^\circ$  in (I), (II), (III), and (IV) respectively (Figure and Table). The substituent fluorine atoms and group R may be classified as axial or equatorial with respect to the chelate ring. The R group, whether it

be the bulky trifluoromethyl group or the smaller hydrogen atom, occupies an equatorial position in all four compounds.

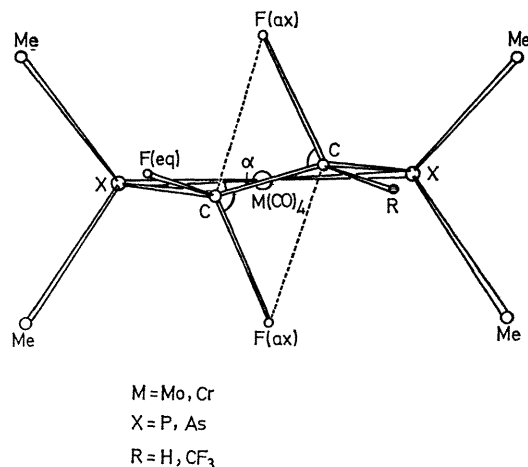


FIGURE. View showing the chelate ring, and the positions of the axial fluorine atoms (see Table for dimensions).

TABLE

|               |       | Molecular dimensions (see Figure) |         |         |                    |
|---------------|-------|-----------------------------------|---------|---------|--------------------|
|               |       | (I)                               | (II)    | (III)   | (IV)               |
| M             | .. .. | Mo                                | Mo      | Mo      | Cr                 |
| X             | .. .. | As                                | As      | P       | As                 |
| R             | .. .. | CF <sub>3</sub>                   | H       | H       | H                  |
| C-C           | .. .. | 1.40(4)                           | 1.30(2) | 1.42(3) | 1.30(4) Å          |
| C-F(axial)    | .. .. | 1.51(4)                           | 1.73(2) | 1.79(3) | 1.82(4)            |
| C...F(axial)  | .. .. | 2.19(4)                           | 2.00(2) | 1.87(3) | 1.87(4)            |
| C-F(eq.)      | .. .. | 1.37(4)                           | 1.38(2) | 1.37(2) | 1.36(3)            |
| C-C-F(axial)  | .. .. | 98(3)                             | 84(2)   | 71(2)   | 69(3) <sup>o</sup> |
| $\alpha$      | .. .. | 23                                | 11      | 3       | 3                  |
| X(1)-C-R      | .. .. | 113(2)                            |         |         |                    |
| X(1)-C-C      | .. .. | 118(2)                            | 116(1)  | 107(2)  | 117(2)             |
| R-C-C         | .. .. | 112(3)                            |         |         |                    |
| X(2)-C-F(eq.) | .. .. | 113(2)                            | 112(1)  | 114(2)  | 113(2)             |
| X(2)-C-C      | .. .. | 111(2)                            | 125(1)  | 131(2)  | 123(2)             |
| F(eq.)-C-C    | .. .. | 121(3)                            | 119(2)  | 115(2)  | 124(3)             |

The bond distances and valency angles in the fluorocarbon groupings (Figure and Table) show some unusual and

interesting features, the deviations from normal values becoming more extreme as the chelate ring tends towards planarity. The formally single C-C bond is as short as 1.30 Å, in comparison with normal single- and double-bond distances of 1.54 and 1.34 Å respectively. All the C-F (axial) bond lengths are very significantly longer than a normal C-F bond (1.33 Å), with distances as long as 1.8 Å. The C-F (equatorial) and C-F(CF<sub>3</sub>) bond distances are close to normal values. The valency angles at the carbon atoms which do not involve axial fluorine atoms are greater than the regular tetrahedral value, the three bonds around each carbon atom approaching a planar arrangement. The angles involving axial fluorine atoms are correspondingly less than the tetrahedral value, with C-C-F angles as small as 69° being found in (IV), where the fluorines are in fact situated above and below the centre of the C-C bond.

All these exceptional features can be explained in terms of a bonding system, which, in valence bond language, contains a contribution not only from the normal structures (I)–(IV), but also from the canonical forms (I')–(IV'). The normal structures are believed to have a certain

amount of  $d\pi-d\pi$  back-bonding, involving filled metal and empty phosphorus or arsenic  $d$ -orbitals, this back-bonding being enhanced by electronegative bridging groups. The other canonical forms involve an extension of this back-bonding into orbitals of the fluorocarbon group. In molecular orbital terminology, the chelate ring contains a delocalized  $\pi$ -bond system, which includes a filled metal  $d$  orbital, empty arsenic or phosphorus  $d$  orbitals, and an orbital on each carbon atom which approximates a  $p$  orbital, normal to an approximately  $sp^2$   $\sigma$ -bonding system. The bonding in this bridging-fluorine region could be described in terms of a four-centre (two carbon and two fluorine atoms) six-electron system.

In this model the deviations of C-F bond lengths from normal values result from interaction of the axial fluorine atoms with the  $\pi$ -bond system, in the extreme case the fluorine atoms interacting equally with the two carbon atoms. The  $\pi$ -system accounts for the short C-C bonds and the tendency towards a planar chelate ring.

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<sup>1</sup> W. R. Cullen, L. D. Hall, and J. E. H. Ward, *Chem. Comm.*, 1970, 625.