X-Ray Molecular Structure of Dicarbonyl-η^5-cyclopentadienyl-(η^2-tetramethylallenyl)iron Tetrafluoroborate. A Sterically Crowded Allene Complex

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Summary Steric interactions in $[(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_7H_{12})Fe(CO)_2]BF_4$ cause large distortions in the tetramethylallene ligand and are important in determining the ligand conformation.

Temperature-dependent ^1H n.m.r. studies of the dicarbonyl-η^5-cyclopentadienyliron(tetramethylallene) cation indicate that all four methyl groups become equivalent through a combination of metal–olefin rotation and an orthogonal 1,2-shift of the organometallic radical.[1] The rotational barrier has been attributed largely to steric interactions between the methyl substituents and the cyclopentadienyl and carbonyl ligands.[1] We have studied the magnitude of such interactions by *X*-ray crystal structure analysis of the tetramethylallene complex.

Crystals of $[(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_7H_{12})Fe(CO)_2]BF_4$ are monoclinic, space group $P2_1/c$, $a = 9{\cdot}299$, $b = 13{\cdot}686$, $c = 12{\cdot}746$ Å; $\beta = 94{\cdot}03°$, $Z = 4$. The 1984 independent reflexions for which $I/\sigma(I) \geqslant 3{\cdot}0$ were measured on a Syntex $P2_1$ automatic diffractometer (crystal-monochromated MoK_α radiation). Block-diagonal least-squares refinement of positional and anisotropic thermal parameters for all non-hydrogen atoms has converged to a conventional *R*-factor of 0·068. E.s.d.s of the bond lengths at the present stage of refinement are: Fe–C, 0·007; C–C, 0·010; C–O, 0·008 Å.

The molecular structure of the iron cation (Figure) may be considered to be formally derived from the $[(\eta^5\text{-}C_5H_5)Fe(CO)_3]^+$ cation[2] by replacement of a carbon monoxide ligand with a η^2-tetramethylallene ligand. Although the co-ordination geometries of the dicarbonylcyclopentadienyliron part of the two complexes are similar, they are not isostructural. Thus, Fe–C(carbonyl) distances (1·782, 1·765 Å) are shorter by *ca.* 0·04 Å, and C–O distances (1·127, 1·150 Å) longer by *ca.* 0·03 Å, than the analogous distances in the tricarbonyl cation. These trends are consistent with the expected smaller intrinsic back-accepting ability of an olefin, compared to carbon monoxide. Further, back-bonding effects may depend upon olefin conformation;[3] here the angle between the normal to the plane of the C_5H_5 ring and the C(3)–C(4) vector is 74·0°.

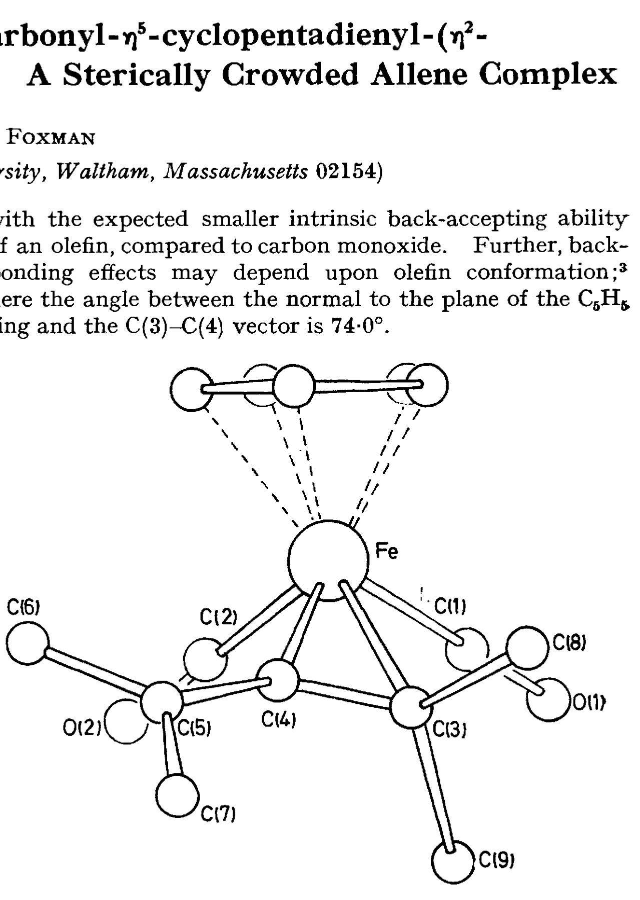

Figure. The structure of the complex cation in $[(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_7H_{12})Fe(CO)_2]BF_4$.

The most interesting features of this structure are those associated with the tetramethylallene fragment. The variations in C–C bond length are similar to those observed for d^8-metal–allene complexes;[4] thus, bond lengths are 1·367 Å for C(3)–C(4) and 1·335 Å for C(4)–C(5). However, the C(3)–C(4)–C(5) angle is 145·7(7)°, one of the smallest angles observed for other than d^{10}-metal–allene complexes.

A study of two square-planar tetramethylallene complexes indicated that the C=C=C angle was likely to be sensitive to non-bonded interactions.[5] Intramolecular non-bonded contacts from C(1) to C(8) and C(9) are 3·345 and 2·803 Å, respectively, and from C(2) to C(5) and C(6) are 3·156 and 3·332 Å, respectively. This is reflected in the dihedral angles between the Fe–C(3)–C(4) plane and (a) the C(3)–C(4)–C(8) plane (100·8°); (b) the C(3)–C(4)–C(9) plane (107·1°). The expected angle is 90° for planar olefin geometry, and 112·6° for tetrahedral geometry.[6] Such an asymmetric distortion has not been observed in other tetramethylallene complexes,[5] nor are distortions evident in the uncomplexed part of the ligand here. It is unlikely that the distortions are caused by packing effects, as all intermolecular contacts appear to be normal.

Finally, there is considerable asymmetry in the Fe–C (allene) distances: Fe–C(3), 2·237; Fe–C(4), 2·063; Fe-bond centre, 2·04 Å. This asymmetry is among the largest observed for transition-metal–allene complexes;[4] however, comparison is difficult owing to the lack of structural information on first-row transition-metal–allene complexes. A complete interpretation of bonding effects awaits the determination of additional cationic iron-olefin structures.

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