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Preliminary communication

X-RAY STRUCTURE OF (π-CYCLOPENTADIENYL)(BENZOYLPHENYLCARBENE)DICARBONYLMANGANESE

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Summary

The structure of (π-cyclopentadienyl)(benzoylphenylcarbene)dicarbonylmanganese, a transition metal carbene complex not containing hetero-atom substituents, has been determined by X-ray methods; the phenyl substituent and the carbene system are almost co-planar but the C(carbene)—C(phenyl) distance of 1.47(2) Å does not indicate any strong π-interaction between the two groups.

The structures of transition metal carbene complexes in which the carbene species has hetero-atom substituents are characterised by C(carbene)—X(hetero) bond lengths which are considerably shorter than single bond distances. This has been interpreted in terms of a strong π-interaction between the carbene and the hetero-atom, any metal—carbene π-interaction being of secondary importance in the stabilisation of the ligand [1].

(π-Cyclopentadienyl)(benzoylphenylcarbene)dicarbonylmanganese [2] is among the few stable carbene complexes without a hetero substituent and its structure was therefore determined in order to obtain information on the metal—carbene and intracarbene bond distances.

Crystal data: red monoclinic crystals, spacegroup $P2_1/n$ (No. 14), a = 7.11(2), b = 10.87(2), c = 21.94(2) Å, β = 93.5(2)°, density 1.41 g ml^{-3}, calculated for Z = 4, 1.45 g ml^{-3}. A total of 799 visually estimated non-zero reflections was used in the structure determination. Standard heavy atom procedures were followed, and the structure was refined using least-squares methods to a current conventional R value of 0.085.

The molecular structure is shown in the Fig. 1, together with some relevant bond lengths. The Mn—C(1) distance of 1.88(2) Å is shorter than any previous recorded manganese—carbene distance (e.g. 1.950(5) Å in $(CH_3OCC_6H_5)Mn_2(CO)_9$ [3], 1.96(2) Å in $[(\pi\text{-}C_5H_5)(OCC_6H_5)Mn(CO)_2]^-$ [4]), although the difference is only on the border of statistical significance. An estimated Mn—C(sp^2) single bond distance of 2.15 Å [4] indicates the considerable shortening of the metal—carbene bond.

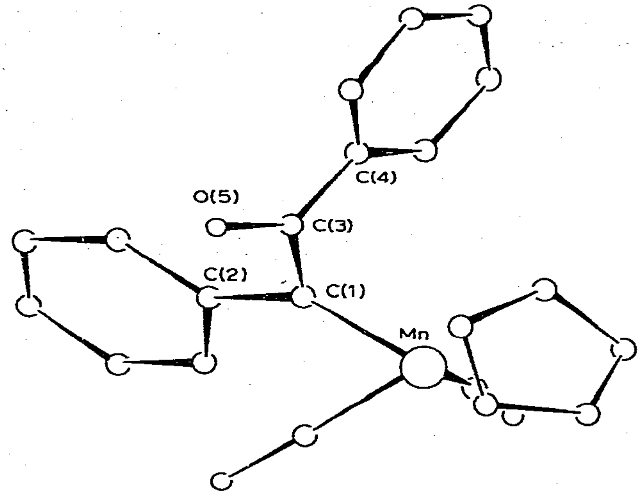

Fig. 1. Molecular structure of (π-cyclopentadienyl)(benzoylphenylcarbene)dicarbonylmanganese. Bond lengths (Å), e.s.d. in parentheses: Mn—C(1) 1.88(2), C(1)—C(2) 1.47(2), C(1)—C(3) 1.49(3). C(3)—C(4) 1.49(3), C(3)—O(5) 1.24(2).

The phenyl substituent is almost co-planar with the carbene system, defined by atoms C(1), C(2), C(3) and Mn, the dihedral angle being 4.7°. Although this arrangement is favourable for interaction between the ring π-system and the p_z orbital of the carbene carbon, the C(1)—C(2) bond length does not reflect such an interaction. Indeed there is no significant difference, at the present stage of refinement, between C(1)—C(2) 1.47(2) Å, C(1)—C(3) 1.49(3) Å and C(3)—C(4) 1.49(3) Å, all of which are close to the accepted value of 1.48 Å for a C(sp^2)—C(sp^2) single bond length.

The angle between the plane defined by C(1), C(2), C(3) and Mn and that defined by the atoms C(1), C(3), C(4) and O(5) is 86.8° which implies that there is no π-interaction between the benzoyl group and the carbene carbon atom.

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