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Preliminary communication

THE UNUSUAL IRON COMPLEX WITH A TRIMETHYLENEMETHANE TYPE LIGAND, (η^5-CYCLOPENTADIENYLDICARBONYLMANGANESE)-(PHENYLMETHYLENE)CARBOMETHANEIRON TRICARBONYL [$Cp(CO)_2MnC(CO)CHPh]Fe(CO)_3$

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Summary

The binuclear complex with composition $[Cp(CO)_2MnC(CO)CHPh]Fe(CO)_3$ is obtained by interaction of $CpMn(C{=}CHPh)(CO)_2$ with $Fe_2CO)_9$. An X-ray study of this complex has shown that besides three carbonyl groups the iron atom is covalently bonded to four atoms, viz. the carbon of a phenylmethylene group, the carbon of a bridging C=O group, the manganese atom and the central carbon of the organomanganese ligand lying just above iron. It seems to be the first example of a heteroatomic analogue of trimethylenemethane complexes.

The reaction of π-cyclopentadienylphenylvinylidenemanganese dicarbonyl (I) [1] with nonacarbonyldiiron in hexane at 20°C leads to a stable binuclear complex II with a yield of 40%:

$$\underset{\text{(I)}}{CpMn(C{=}CHPh)(CO)_2} + Fe_2(CO)_9 \rightarrow \underset{\text{(II)}}{[Cp(CO)_2MnC(CO)CHPh]Fe(CO)_3}$$

Compound II is a brown crystalline solid with m.p. 105—106°C. Its infrared spectrum showed the terminal carbonyl bands at 2086, 2055, 2029 (sh), 2000, 1970 and 1918 cm^{-1} (in CH_2Cl_2) and the ν(C=O) frequency at 1844 cm^{-1} (in KBr). The mass spectrum of II contains a molecular ion peak with m/e 446 as well as peaks of $[M - n(CO)]^+$ ions (n = 1—6) formed by successive splitting off of six CO groups.

The structure of II has been established by an X-ray study. Crystals of II are monoclinic, a 10.344(1), b 7.9855(3), c 21.796(2) Å, β 102.924(9)°, V 1754.9(5) Å^3; M 446.1, D_m 1.67, D_c 1.70 g cm^{-3} for $Z = 4$, space group $P2_1/c$. Intensities of 1966 independent reflections were measured with a four-circle automatic diffractometer Syntex P2$_1$, (λMo-K_α, graphite monochromator, $\vartheta/2\vartheta$ scan). In calculations 1165 reflections with $F^2 \geqslant 1.96\,\sigma(F^2)$ were used, neglecting absorbtion corrections. The structure was solved

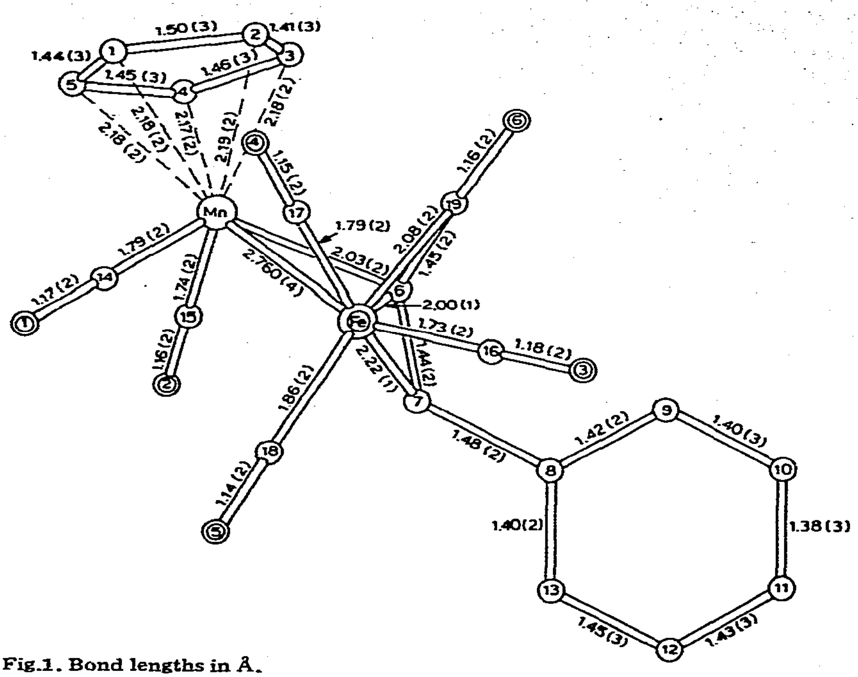
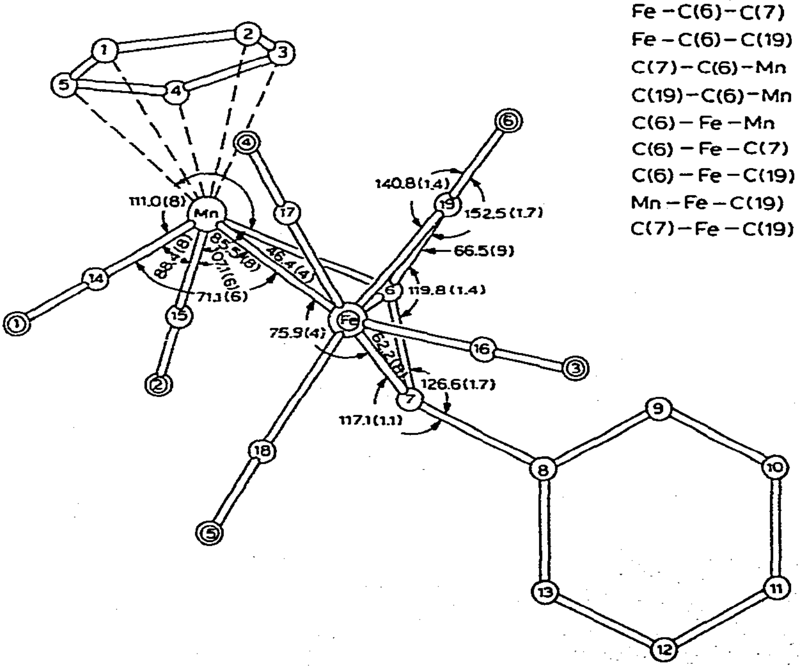


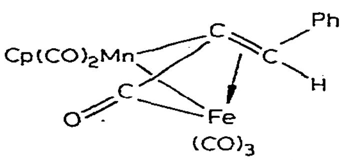
Fig.1. Bond lengths in Å.



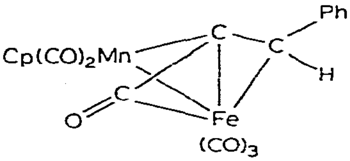
Fe – C(6) – Mn	86.3(6)
Fe – C(6) – C(7)	78.3(9)
Fe – C(6) – C(19)	72.1 (1.0)
C(7) – C(6) – Mn	124.8(1.1)
C(19) – C(6) – Mn	104.4(1.1)
C(6) – Fe – Mn	47.2(5)
C(6) – Fe – C(7)	39.6(6)
C(6) – Fe – C(19)	41.4(7)
Mn – Fe – C(19)	68.2(5)
C(7) – Fe – C(19)	71.1 (6)

by the heavy atom technique and refined by the full-matrix anisotropic least squares procedure to $R = 0.070$, $R_w = 0.053$.

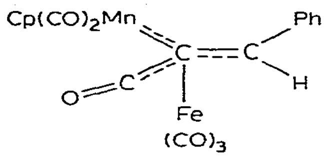
Molecular geometry with important bond lengths and angles is shown in Fig. 1 and 2. The rather unexpected structure of II shows that the reaction mentioned consists not only of coordination of a metalallene fragment of the original complex $Cp(OC)_2Mn{=}C{=}CHPh$ (I) to an iron atom but also involves addition of one of the CO groups, formerly bonded to iron, to the α-carbon of the vinylidene ligand in I. The structure of II can be represented by several resonance forms and the following three seem to be main contributors:



(A)



(B)



(C)

The Mn atom is coordinated by a Cp ligand and two CO groups and participates in σ-bonds with Fe and C(6). The Fe atom coordination can be considered either as a distorted octahedral with a π-ethylenic fragment occupying one coordination site (form A) or as involving a trimethylenemethane type ligand (form C) or finally with sevenfold coordination, i.e. octahedral monocapped with C(6) (form B). In any case the manganese—organic ligand $[Cp(CO)_2MnC(CO)CHPh]$ is a four electron donor with respect to the Fe atom and both metal atoms acquire a noble gas electronic configuration.

Comparison of the complex II with the original compound, I, shows considerable distortions of the vinylidene ligand due to its coordination with an iron atom. These distortions are revealed mainly by a bending of the formerly linear group Mn—C(6)—C(7) (now this angle is 124.8(1.6)°) and also in a change of bond lengths within this fragment. However, the dihedral angle MnC(6)C(7)/C(8). . .C(13) is only 3.1°, i.e. the "vinylidene" system remains coplanar with the phenyl ring and this seems to be evidence of conjugation involving the whole MnC(6)[C(19)O(6)] [C(7)HPh] system. Indeed the Mn—C(6) bond length, 2.03(2)Å, although greatly increased in comparison with the double Mn=C bond of 1.68 Å in I is still shorter than the sum, 2.15 Å of the covalent radii of single bonded Mn (1.38 Å) [2] and C(sp^3) (0.77 Å) [3]. The same refers to the distances C(6)—C(7) 1.44(2), C(6)—C(19) 1.45(2) and C(7)—C(8) 1.48(2) Å which according to form B formally correspond to single bonds.

The axis of the $Fe(CO)_3$ fragment with symmetry close to C_{3v} almost coincides with the Fe—C(6) bond. The $Fe(CO)_3$ and C(6)MnC(7)C(19) fragments are mutually staggered and the C(6) atom is displaced out of the MnC(7)C(19) plane by 0.10 Å opposite to the Fe atom.

All these features allow us to consider compound II as an analogue of a trimethylenemethane complex of iron (form C) and this conclusion is confirmed by the distance to the central carbon atom Fe—C(6) 2.00(1) Å which is considerably shorter than those to peripheral atoms C(7) 2.22(1) Å and C(19) 2.08(2) Å. It is to be noted that this "trimethylenemethane" system is formed by involvement of Mn and C(13) of an unusual carbonyl group in conjugation with the central atom C(6).

One more argument in favour of electron delocalisation over the whole five-centered central part of the molecule is the metal—metal distance, 2.760(4) Å, which is shortened compared to that found in other complexes with Fe—Mn bonds: 2.80 and 2.83 Å in $(OC)_5MnFe(CO)_4Mn(CO)_5$ [4], 2.84 Å in $CpFe(CO)_2Mn(CO)_5$ [5], 2.825 Å in $(OC)_4Fe[PPh_2]Mn(CO)_4$ [6] and 2.848 Å in $(OC)_4Fe[AsMe_2]Mn(CO)_4$ [7].

One of the metal—carbonyl units of the complex studied is clearly non-linear. The bond angle MnC(14)O(1) is contracted to 169.4(1.6)° which is due to a short intramolecular contact Fe. . .C(14) 2.76(2) Å. A similar effect is found in many structures including those of manganese complexes, e.g. in $CpMn(CO)_2[AsMe_2]Mn(CO)_4$ [8], where one of the MnCO band angles is equal to 160.0° with a corresponding Mn. . .C distance of 2.57 Å.

The rest of the geometry of molecule II is usual. However a non-equivalence of the Fe—CO bonds seems essential. Evidently this effect is caused by a *trans*-influence: the shortest bond, Fe—C(16) 1.73(2) Å is *trans* to the Fe—Mn bond and the longest bond Fe—C(18) 1.86(2) Å, is *trans* to the carbon atom C(19) of a CO group.

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