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Preliminary communication

METAL CARBONYL COMPLEXES OF 3,5-DIMETHYLACEHEPTYLENE. SYNTHESIS AND MOLECULAR STRUCTURES OF $(C_{14}H_8Me_2)Mn_2(CO)_6$ AND $(C_{14}H_8Me_2)Fe_3(CO)_8$

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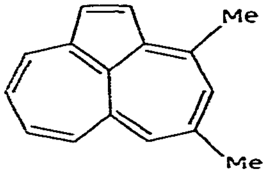
Summary

The reactions of the non-alternant polycyclic aromatic hydrocarbon 3,5-dimethylaceheptylene, $C_{14}H_8Me_2$, with various transition metal carbonyls and the molecular geometry of the compounds $(C_{14}H_8Me_2)Mn_2(CO)_6$ and $(C_{14}H_8Me_2)Fe_3(CO)_8$ is shown.

The reactions of the tricyclic hydrocarbon I (3,5-dimethylaceheptylene, $C_{14}H_8Me_2$) with various transition metal carbonyls have been investigated:



(I)

Reaction of $C_{14}H_8Me_2$ with $Mn_2(CO)_{10}$. 1.0 g (4.9 mmol) of $C_{14}H_8Me_2$ and 8.0 g (20.5 mmol) of $Mn_2(CO)_{10}$ were boiled under reflux in 2,2,5-trimethylhexane for 16 h. The solvent was removed at ~25°C/0.1 mm Hg, and the residue was chromatographed on alumina using pentane. The

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major red band was eluted with pentane. Recrystallization (9/1 heptane/dichloromethane) yielded 0.85 g (36% yield) of dark red crystalline $(C_{14}H_8Me_2)Mn_2(CO)_6$ (m.p. 162—164°C; ν(C—O) 2070s, 1970vs cm^{-1}).

Reaction of $C_{14}H_8Me_2$ with $Fe_3(CO)_{12}$. 1.0 g (4.9 mmol) of $C_{14}H_8Me_2$ and 8.0 g (16 mmol) of $Fe_3(CO)_{12}$ in hexane (100 ml) were heated under reflux for 44 h. Chromatography of the mixture on alumina with hexane and recrystallization from hexane/dichloromethane yielded 2.2 g of red-brown $(C_{14}H_8Me_2)Fe_3(CO)_8$ (ν(C—O) 2060s, 1990s, 1972s cm^{-1}).

The molecular structures of $(C_{14}H_8Me_2)Mn_2(CO)_6$ and $(C_{14}H_8Me_2)Fe_3(CO)_8$ have each been determined unambiguously via single-crystal X-ray diffraction studies. Diffraction data were, in each case, collected with a Syntex $P2_1$ diffractometer and the structures were solved using a locally-modified version of the Syntex XTL system. The experimental method has been described previously [2]. Pertinent data are as follows: $(C_{14}H_8Me_2)Mn_2(CO)_6$: orthorhombic, space group $P2_12_12_1$, a 9.678(1), b 13.100(2), c 15.639(3) Å; final R_F 6.7% for 1079 reflections with $5° < 2\theta < 40°$ [Mo-K_α]. $(C_{14}H_8Me_2)Fe_3(CO)_8$: monoclinic, space group $P2_1/c$, a 22.580(4), b 7.299(1), c 14.520(2) Å, β 104.62(1)°; final R_F 5.6% for 1930 reflections in the range $5° < 2\theta < 40°$ [Mo-K_α].

The molecular geometry of these species is illustrated in Fig. 1 and 2.

The $(C_{14}H_8Me_2)Mn_2(CO)_6$ molecule contains two $Mn(CO)_3$ groups, on opposite sides of the organic ligand; one $Mn(CO)_3$ group is bound symmetrically to

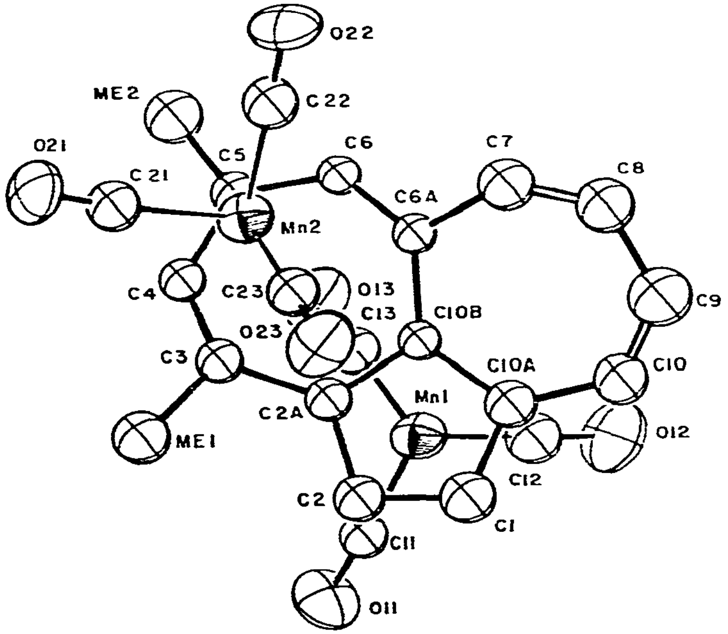

Fig. 1. Molecular geometry of $(C_{14}H_8Me_2)Mn_2(CO)_6$. Metal-to-ligand bond distances (in Å) are as follows: Mn(1)—C(1) 2.085(14), Mn(1)—C(2) 2.139(15), Mn(1)—C(2a) 2.203(14), Mn(1)—C(10a) 2.194(17), Mn(1)—C(10b) 2.177(14); Mn(2)—C(3) 2.256(15), Mn(2)—C(4) 2.119(14), Mn(2)—C(5) 2.149(13), Mn(2)—C(6) 2.151(13), and Mn(2)—C(6a) 2.404(14).

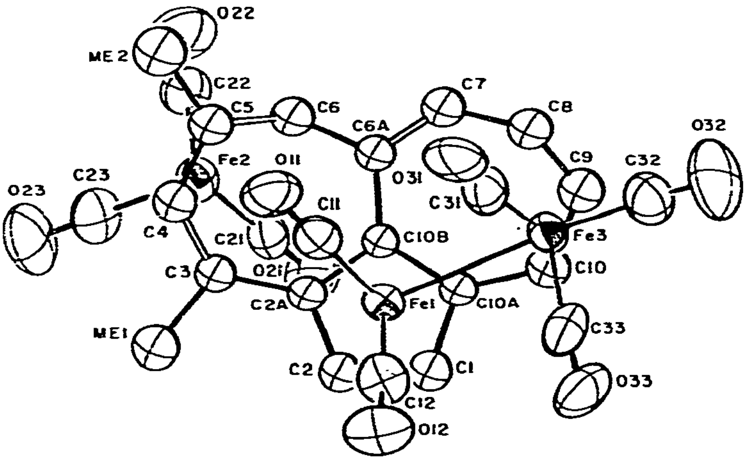

Fig. 2. Molecular geometry of $(C_{14}H_8Me_2)Fe_3(CO)_8$. Metal-to-ligand distances (Å) are as follows: Fe(1)—C(1) 2.098(8), Fe(1)—C(2) 2.098(8), Fe(1)—C(2a) 2.120(7), Fe(1)—C(10a) 2.116(7), Fe(1)—C(10b) 2.106(7); Fe(2) C(3) 2.188(7), Fe(2) C(4) 2.060(9), Fe(2)—C(5) 2.071(8), Fe(2)—C(6) 2.151(8); Fe(3)—C(8) 2.222(9), Fe(3)—C(9) 2.050(9), and Fe(3)—C(10) 2.140(8).

the five-membered ring, while the other $Mn(CO)_3$ group is linked somewhat asymmetrically to five carbon atoms of a seven-membered ring (i.e., C(3)—C(4)—C(5)—C(6)—C(6a)). The metal-to-ligand bonding is similar to that in (azulene) $Mn_2(CO)_6$ [3]. The system C(7)—C(8)—C(9)—C(10), in which C(7)—C(8) 1.294(21), C(8)—C(9) 1.488(23), and C(9)—C(10) 1.270(24) Å, remains a conjugated non-coordinated *cis*-diene system.

In the $(C_{14}H_8Me_2)Fe_3(CO)_8$ molecule, an $Fe(CO)_2$ group is linked symmetrically to the five-membered ring, and an $Fe(CO)_3$ group is bound via a π-allylic linkage to the C(8)—C(9)—C(10) system; the associated iron—iron bond length is 2.793(2) Å. This overall portion of the molecule resembles (azulene)$Fe_2(CO)_5$ [4]. However, there is an additional $Fe(CO)_3$ group linked via an η^4-*cis*-diene→metal linkage to the atoms C(3)—C(4)—C(5)—C(6).

It appears therefore that, as in azulene [5] and acenaphthylene [6] chemistry, the dominant feature in the reaction of aceheptylene with metal carbonyls is the utilization of its five-membered ring in an η^5-cyclopentadienyl→metal linkage.

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