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Preliminary communication

PHOTOREACTION OF *O*-QUINODIMETHANETRICARBONYLIRON WITH PENTACARBONYLIRON

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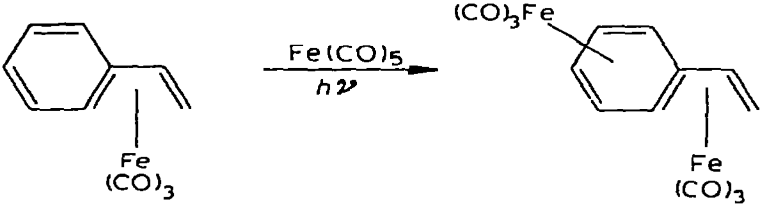
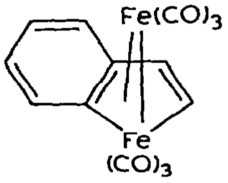
Summary

Irradiation of (*tetrahapto-o*-quinodimethane)tricarbonyliron in the presence of $Fe(CO)_5$ gives three isomeric $C_8H_8Fe_2(CO)_6$ complexes.

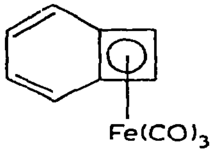
We recently described the first example of a photochemical reaction in which a *tetrahapto*-tricarbonyliron complex, I, of the 8 π-electron conjugated type gives the bis(*tetrahapto*) derivative, Ia on reaction with pentacarbonyliron [1]. Later we showed that similar reactions can be carried out with the related 8π-electron systems of ferraindentricarbonyliron, II [2], benzocyclobutadienetricarbonyliron, III [3], and ferra-2H-indenetricarbonyliron, IV [3], leading to the formation of the respective bis(*tetrahapto*) complexes IIa, IIIa and IVa.



(I) (Ia)



(II)



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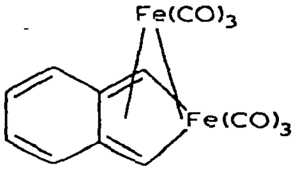
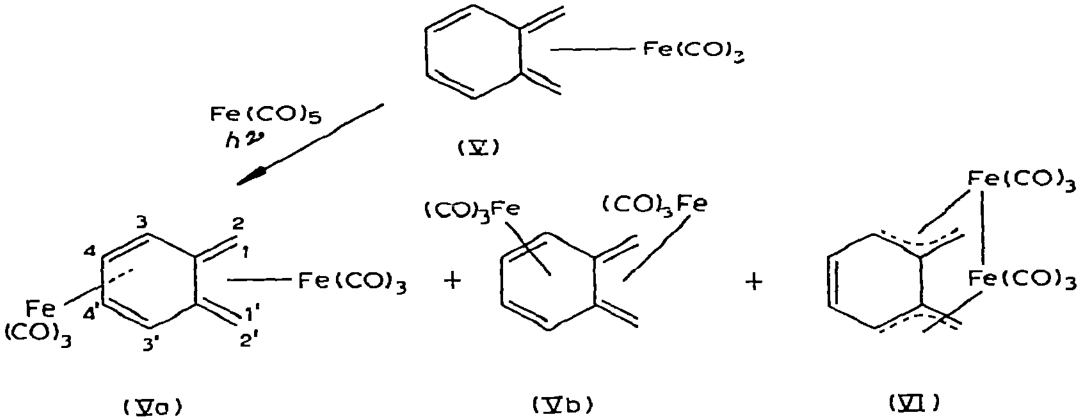


(IV)

These results, and in particular the formation of IVa from IV, suggested that *o*-quinodimethanecarbonyliron, V [4], should by analogy form the corresponding bis(*tetrahapto*) derivative under similar conditions.



The photochemical reaction [3] of V with $Fe(CO)_5$ has been found to give three isomeric $C_8H_8Fe_2(CO)_6$ complexes in comparable yields: Va, bis(*tetrahapto*)-*o*-quinodimethane-*trans*-bis(tricarbonyliron), red crystals, m.p. 94—96° (decomp.); Vb, bis(*tetrahapto*)-*o*-quinodimethane-*cis*-bis(tricarbonyliron), purple crystals, m.p. 95° (decomp.) and VI, bis(*trihapto*)-*o*-quinodimethane-hexacarbonyldiiron, red crystals, m.p. 126—127° (decomp.). Formation of Va and Vb from V involves the expected diene-type coordination of the residual four π-electron system, while that of VI involves a redistribution of the π-electron density in the 8π-electron-conjugated system.

The structures of Va, Vb and VI follow from their physical, analytical and spectroscopic properties[*].

Va: m/e 384 (M^+). IR: 1962, 1977, 1983, 2000, 2041, 2055 cm^{-1} (ν(Fe—CO)) NMR (τ): 3.26m (H-4), 6.61m (H-3), 8.29d (H-2), 9.80d (H-1), J_{12} ~3.0, J_{34} ~6.4, $J_{34'}$ ~1.6, $J_{44'}$ ~4.5 Hz.

Vb: m/e 356 [$(M - CO)^+$]. IR: 1930, 1982, 1990, 2044 cm^{-1} (ν(Fe—CO))[**] NMR (τ): 3.95m (H-4), 7.02m (H-3), 9.37d (H-2), 9.70d (H-1), J_{12} ~5.1, J_{34} + $J_{34'}$ ~7.2 Hz. The assignment of the *cis*-structure to Vb is supported by the following: (a) Vb is more polar and less stable than Va, (b) Vb is converted readily on standing in solution to complex VI, which by virtue of its iron—iron bond involves a *cis* Fe—Fe relationship.

VI: m/e 384 (M^+). IR (Nujol): 1958, 1964, 1980, 1998, 2020, 2061 cm^{-1} (ν(Fe—CO))[***] and 752 cm^{-1} (ν(C=C)). NMR (τ): 3.63m (H-4), 5.49m (H-3),

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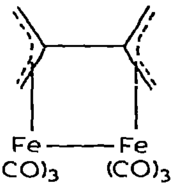
[*] On column chromatography (Florisil), p.e. 30—40, the products were eluted in the order: (a) unreacted V, (b) Va, (c) VI and (d) Vb. All the new compounds gave satisfactory elemental analysis. Unless otherwise indicated, IR spectra refer to hexane solutions, and NMR spectra to $CDCl_3$ solutions.

[**] The Fe—CO absorptions are analogous to those of styrenebis(tricarbonyliron), for which the *trans*-relationship has been established [5].

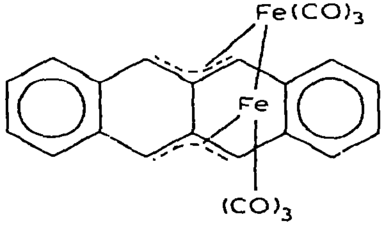
[***] The pattern of the ν(CO) absorptions is characteristic for a bis-π-allene structure, cf. refs. 6 and 7.

8.45d and 8.50d (H-2 and H-1), J_{12} ~3.1, J_{34} ~6.6, $J_{34'}$ ~1.0, $J_{44'}$ ~10.3 Hz[*]

Complex VI belongs to the family of bis-π-allylene iron complexes for which the parent complex VII [6] and the naphthacene derivative VIII [7] have been reported. It is also structurally related to the π-benzyl-π-cyclopentadienylcarbonyl complexes IX, of molybdenum [8] and tungsten [8c]. Its identification as the remaining $C_6H_8Fe_2(CO)_6$ isomer was based inter alia on (a) the presence of an uncoordinated double bond in the ligand (vide IR), (b) the presence of an Fe—Fe bond, as indicated by the mass spectrum (strong peak at *m/e* 112), (c) the *sp*^{2} character of the exocyclic carbon bonds, as shown by $^{13}C—^1H$ NMR $J(^{13}C—H)$ ~ 157 Hz), which excludes any structure involving C—Fe σ bonds, and (d) the formation of α,α'-dibromoxylene on bromine degradation, consistent with the formation of 2,3-bis(bromomethyl)-1,4-dibromobutene on similar bromination of VII [6a].



(VII)



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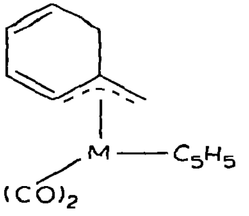

(IXa) M = Mo, R = H or CH_3

(IXb) M = W, R = CH_3

Acknowledgement

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[*] This value for the exocyclic geminal hydrogen coupling is in accord with that for a related *trihapto* complex, the π-benzyl complex IXa, R = H (J ~ 3.0 Hz) [8a].

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