Photoreaction of Benzocyclobutadienetricarbonyliron with Pentacarbonyliron

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Summary Irradiation of 1—2a(6a)-η-benzocyclobutadienetricarbonyliron (**5**) in the presence of Fe(CO)$_5$ gives a mixture of 1—2a(6a)-η : 3-6-η-benzocyclobutadienebistricarbonyliron (**6**), 1—3a(7a)-η-ferraindenetricarbonyliron (**3**), 1—3a(7a)-η : 4—7-η-ferraindenebistricarbonyliron (**4**), 1—3a(7a)-η-ferra-2*H*-indenetricarbonyliron (**7**), and 1—3(7a)-η : 4—7-η-ferra-2*H*-indenebistricarbonyliron (**8**); complex (**6**) is formed *via* diene-type co-ordination of the four ring π-electrons in (**5**), while complexes (**3**), (**4**) and (**7**), (**8**) result from cyclobutadiene ring opening and insertion of an Fe(CO)$_3$ unit.

Recently we showed that treatment of the styrenetricarbonyliron system (**1**)[1] and of the ferraindenetricarbonyliron system (**3**)[2] with Fe(CO)$_5$ under mild photolytic conditions led to the corresponding bis-tetra-*hapto*-complexes (**2**) and (**4**) *via* diene-type co-ordination of the four ring π-electrons. These results suggested that related tetra-*hapto*-complexes such as (**5**)[3] should be able to accommodate co-ordination of an additional tricarbonyliron unit at their residual four π-electrons.†

We report here the photoreaction of complex (5) with Fe(CO)$_5$,‡ showing that the major product is indeed the expected complex (**6**),§ dark purple crystals, m.p. 125°,

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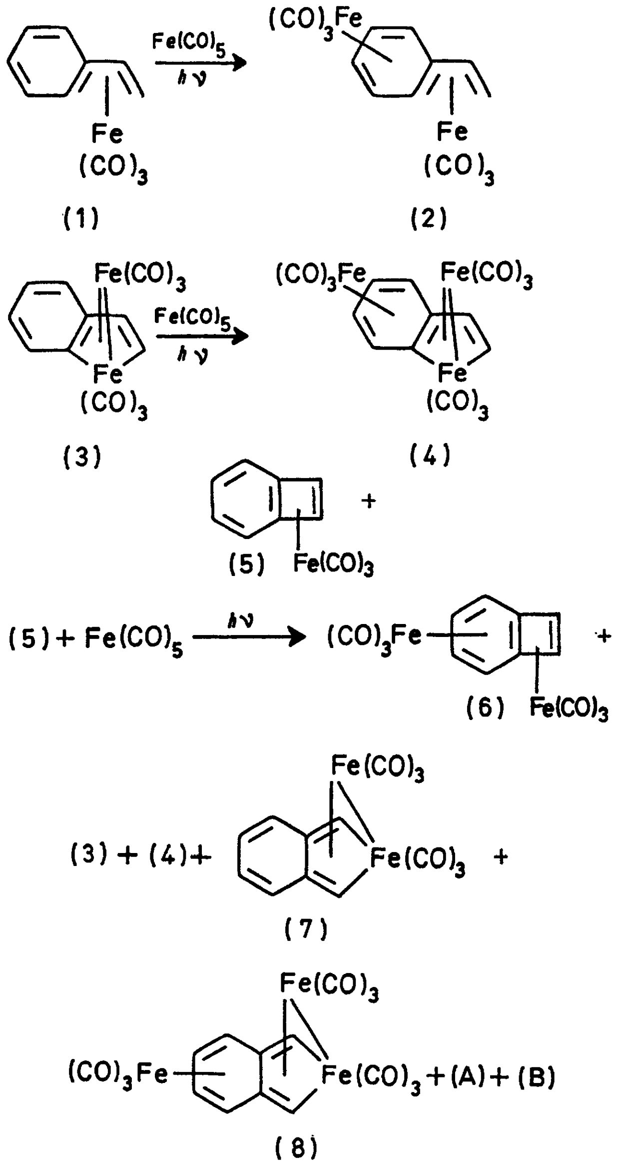
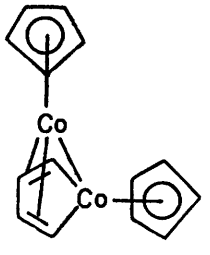
† However, no bis-tetra-*hapto*-iron carbonyl complex was detected under the conditions in which (5) has been obtained.[3,4]

‡ Irradiation of (5) and Fe(CO)$_5$ was carried out under N$_2$ in hexane solution using a 450 W mercury-arc lamp in a water-cooled quartz immersion vessel.

§ All new compounds gave satisfactory elemental analyses.

(decomp.), τ 3·64 (dd), 5·69 (s), and 6·53 (dd); ν(C=O) 2044, 2028, 1982, 1972, and 1964 cm^{-1}. In addition, six other iron-carbonyl complexes could be isolated, four of which were fully characterized. On the basis of i.r. and n.m.r. analysis, two of these were identified as the ferraindene complexes (**3**), m.p. 120—121°, and (**4**), m.p. 124—125°, reported previously.[2a] The other two complexes were assigned structures (**7**), yellow-orange crystals, m.p. 79·5—80·5°, δ2·70 (s), 2·62 (m), and 2·76 (m); ν(C=O) 2060, 2030, 1998, and 1983 cm^{-1}; ν(C=C) 750 cm^{-1}, and (**8**), orange-red crystals, m.p. 135—137°, (decomp.), τ 3·32 (dd), 3·90 (s), and 6·49 (dd); ν(C=O) 2064, 2045, 2023, 1995, 1986, and 1980 cm^{-1}, which are isomeric with the respective ferraindenes (**3**) and (**4**)¶ by inference from their physical** and spectroscopic properties. The characterization of the remaining two complexes (A) and (B), each obtained in minute quantities, requires further study.





(**9**)

The formation of complex (**6**) from (**5**) provides an additional example of diene-type reactivity shown towards iron carbonyl groups by originally 'aromatic' electrons, where initial co-ordination of the first pair of ring π-electrons to another iron atom has already taken place [as in (**5**)].†† In contrast, the formation of the ferraindene complexes (**3**) and (**4**) and the isomeric complexes (**7**) and (**8**) results *via* an unusual opening of the cyclobutadiene ring in complex (**5**). Though an analogous ring-opening takes place in the formation of complex (**9**) by photochemical reaction of cyclobutadiene(cyclopentadienyl)cobalt with dicarbonylcyclopentadienylcobalt,[6] no ferra-carbonyliron complex has ever been reported from reaction of the cyclobutadienetricarbonyliron system (**10**) either on photolysis of (**10**)[7,8] or under the photolytic conditions in which it was formed from photo-α-pyrone and pentacarbonyliron.[9] The question as to whether complexes (**3**), (**4**), (**7**), and (**8**) are derived directly from the tetra-*hapto*-complex (**5**) or from the bis-tetra-*hapto*-derivative (**6**) is of considerable interest, but no unequivocal answer can be given here, since there exists a photochemcial equilibrium between complexes (**5**) and (**6**).

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¶ It could be shown further that irradiation of (**7**) and Fe(CO)$_5$ gives complex (**8**), which is in line with the conversion of (**3**) into (**4**) under similar conditions.[2a]

** From column chromatography (silica) homogeneous mixtures of (**3**) and (**7**) and of (**4**) and (**8**) were obtained.

†† A major reduction in the π-electron delocalization of the benzene ring of (**5**) has been inferred both from bond length[5] and n.m.r.[4] studies.

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