

Ferraindene-iron Tricarbonyl Complexes by a Novel Dehydrobromination of *o*-Bromostyrene on Photolysis with $\text{Fe}(\text{CO})_5$

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Summary Irradiation of *o*-bromostyrene in the presence of $\text{Fe}(\text{CO})_5$ leads to the formation of ferraindenetricarbonyliron $[\text{C}_8\text{H}_6\text{Fe}_2(\text{CO})_6]$ and ferraindenebistricarbonyliron $[\text{C}_8\text{H}_6\text{Fe}_3(\text{CO})_9]$ *via* dehydrobromination, in addition to complexes derived from direct co-ordination of the original substrate.

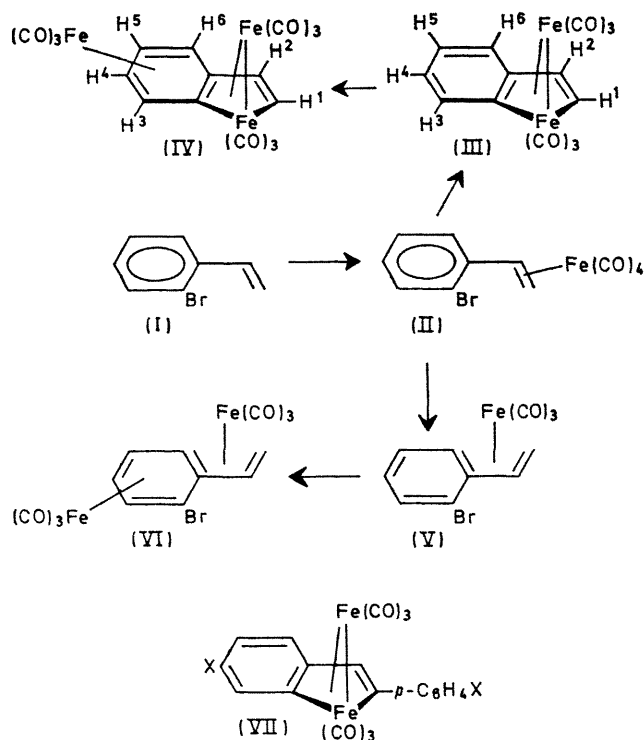
In previous reports we have described the formation of complexes derived from iron carbonyl co-ordination of two, four, and eight π -electrons of styrenes on their irradiation with $\text{Fe}(\text{CO})_5$.¹ We report now that on similar irradiation (r.t., Pyrex vessel), *o*-bromostyrene (I) yielded in addition to such complexes of direct co-ordination [(II), (V), and (VI)],[†] complexes derived from a novel 1,4-dehydrobromina-

tion of (I) coupled with σ -co-ordination to iron: 1,1,1-tricarbonylferraindene- π -tricarbonyliron (III), red-purple crystals, m.p. 120°; and 1,1,1-tricarbonylferraindene- π -bis-tricarbonyliron (IV), purple-brown crystals, m.p. 126°. In separate experiments, (I), (III), and (VI)[†] were isolated from the photolysis of (II) in hexane solution, and complex (IV) was the major product from the irradiation of (III) with an excess of $\text{Fe}(\text{CO})_5$ in hexane. Complexes (III) and (IV) were not detected in similar reactions of *o*-fluoro- and *o*-chloro-styrenes.

Analogues (VII) of compound (III) have been reported by Hübel and Braye to result from reactions of diphenylacetylenes with $\text{Fe}_3(\text{CO})_{12}$ ^{2,3} but their attempts aimed at introducing the additional tricarbonyliron moiety in the

[†] (II), m.p. 67° (decomp.), and (VI), m.p. 95° (decomp.), were isolated and analysed by mass spectroscopy, n.m.r., and i.r. Complex (V) was monitored by i.r. during the reactions from (I) and (II), but was unstable to work-up conditions; its appearance preceded that of (VI) (ref. 1b).

production of a complex analogous to (IV) were unsuccessful.³ These authors suggested that the aromatic nature of



the fused benzene ring is not appreciably disturbed, since the two unco-ordinated double bonds exhibited no diene-

like reactivity.† By contrast, we observed ready conversion of (III) into (IV) in the presence of Fe(CO)₅. The evidence strongly indicates that the six π -electrons of the fused benzene ring of complexes (III) and (IV) are part of two different diene units, two electrons in one unit and four electrons in the second. The ligands of both complexes are therefore nonaromatic in character.

The elemental analyses (C, H, Fe) and mass spectra of (III) and (IV) were in good agreement with their assigned formulae. Complex (III) gave i.r. bands ν_{CO} (hexane) 2070, 2036, 2000, and 1993 (sh) cm^{-1} ; and $\nu_{\text{C}=\text{C}}$ (KBr) ca. 1600 (w) and 755 (s) cm^{-1} . Its 100 MHz n.m.r. spectrum (CDCl_3) showed six nonequivalent protons at low field (τ): 1-H, 2-H: 3.36 (d), 2.90 (d) (J_{12} 5.8 Hz); 3-H, 6-H: 2.34 (d), 2.20 (d); 4-H, 5-H: 3.03 (m), 2.71 (m) ($J_{34} \sim J_{56}$ ca. 8.5 Hz). The magnitudes of the coupling constants are consistent with structure (III) in which 1-H and 2-H are involved in a complexed system, and 3-, 4-, 5-, and 6-H are part of an unsaturated cyclic system.

Complex (IV) exhibited i.r. bands, ν_{CO} (hexane), at 2075, 2055, 2030, 2008, 1998, and 1988 cm^{-1} and no absorption characteristic of free carbon-carbon double bonds. The 100 MHz n.m.r. spectrum (CDCl_3) gave chemical shifts: 1-H, 2-H: 4.29 (d), 3.27 (d) (J_{12} 5.2 Hz); 3-H, 6-H: 6.53 (dd), 6.17 (dd); 4-H, 5-H: 3.57 (m), 3.33 (m) ($J_{34} \sim J_{56}$ ca. 6.1 Hz; J_{45} ca. 4.4 Hz; $J_{35} \sim J_{46}$ ca. 1.5 Hz). The observed separation of chemical shifts between the inner protons (4-H, 5-H) and the outer protons (3-H, 6-H) of the diene unit, and values of coupling between protons of this unit concur with those of classical diene-tricarbonyliron complexes.^{6§}

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† X-Ray data are more in line with, though do not sharply define, a diene-like arrangement of the four unco-ordinated carbons in the benzene ring.⁴ The n.m.r. spectrum showing low-field chemical shifts of all protons was used in support of retention of aromatic character in complexes (VII), yet protons of ferracyclopentadiene itself [$\text{C}_4\text{H}_4\text{Fe}_2(\text{CO})_6$] appear at quite low field [τ ca. 3.2(2H), ca. 3.8(2H)],⁵ and such a strong anisotropic effect should also lead to partial deshielding on the diene residue of the fused ring (see also following footnote).

§ The absolute chemical shifts of 3-6-H of complex (IV) appear at markedly lower fields than the corresponding protons in cyclohexadienetricarbonyliron.^{6b}

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