Reaction of Allene With Di-iron Enneacarbonyl

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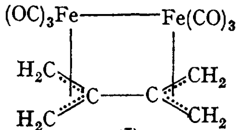
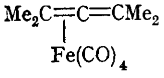
THE reactions of allenes with metal compounds have been little studied and the range of organometallic compounds which can be formed upon such interactions remains to be determined. With palladium(II) halides, allene reacts to produce π-allylpalladium complexes[1,2] while with $Fe_3(CO)_{12}$ a compound reported to have the bis-π-allyl formulation (I) is formed.[3] On the other hand, tetramethylallene and $Fe_2(CO)_9$ react to give the π-olefin type comples (II).[4] We report a novel type of complex produced by reaction of allene with $Fe_2(CO)_9$.

Treatment of allene with $Fe_2(CO)_9$ in an autoclave at 50° for 6 hr. produced two organometallic products having the molecular formulae $C_6H_8Fe_2(CO)_6$ and $C_3H_4Fe_2(CO)_7$, respectively. The first of these is identical with the compound previously reported for which structure (I) has been suggested.[3] The second compound, which is the predominant product when an excess of $Fe_2(CO)_9$ is used in the reaction, is a stable orange oil and, for reasons given below, this compound is assigned the 2-σ-tetracarbonyliron-π-allyltricarbonyliron formulation (III).†

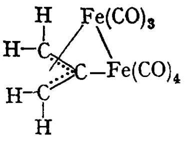


(I)



$Me_2C{=}\underset{\displaystyle Fe(CO)_4}{C}{=}CMe_2$

(II)



(III)

The structural formula (III) is suggested from the following chemical and spectroscopic evidence: (a) the mass-spectral cracking pattern shows a parent molecular ion at *m/e* 348 and peaks corresponding to the successive loss of seven carbonyl

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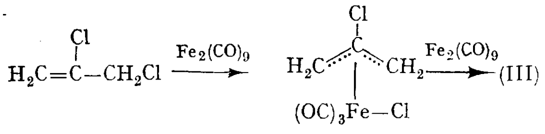
† Satisfactory elemental analyses have been obtained on all new compounds.

groups plus an intense peak at *m/e* 112 suggesting the presence of an iron–iron bond; (b) the i.r. spectrum indicates the presence of only terminal type carbonyl ligands;‡ (c) the n.m.r. spectrum is temperature independent in the range −67° to +70° and consists of two singlets of equal intensity at τ 6·23 and 7·60; (d) the Mössbauer spectrum (kindly determined by Prof. R. Collins) indicates the presence of two nonequivalent iron atoms in the molecule; and (e) oxidative degradation with ceric salts yields allene.

Further indirect support for the formulation (III) is afforded by an independent synthesis of the compound. Reaction of 2,3-dichloropropene with $Fe_2(CO)_9$ affords the expected 2-chloro-π-allyltricarbonyliron chloride (IV)§ which, upon further reaction with $Fe_2(CO)_9$, gives compound (III).



(IV)

Reaction of compound (IV) with zinc dust gives (I), traces of (III) and other unidentified compounds.

Treatment of compound (III) with triphenylphosphine produces two crystalline phosphine derivatives $C_3H_4Fe_2(CO)_6PPh_3$ and $C_3H_4Fe_2(CO)_5(PPh_3)_2$.¶ The i.r. spectrum of the monophosphine complex again indicates the absence of bridging carbonyl ligands and the n.m.r. spectrum of the C_3H_4 ligand remains very similar to the starting complex (III) (two absorptions of equal area at τ 6·52 and 7·78). The reaction therefore involves simple displacement of CO by PPh_3 and the basic nature of the attachment of the C_3H_4 ligand to the two iron atoms appears to be unaltered. The *X*-ray structural data for the monophosphine complex[5] indicates a σ-iron–π-iron type formulation as given by (III) with one of the CO groups on the σ-bonded iron replaced by PPh_3; this latter data then provides strong evidence for the formulation (III).

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‡ Intense absorptions at 1987, 1992, 2020, 2026, 2046, and 2101 cm.$^{-1}$ (in cyclohexane solution) are observed.

§ Yellow-gold crystals, m.p. 82—84°; i.r. spectrum, 2040, 2068, 2115 cm.$^{-1}$; n.m.r. spectrum, two broad peaks at τ 5·18 and 6·38 with relative intensities 1 : 1. The i.r. spectrum of the reported bromo-analogue of (IV) exhibits strong bands at 2025, 2058, and 2100 cm.$^{-1}$ (H. D. Murdoch and E. Weiss, *Helv. Chim. Acta*, 1962, **45**, 1927).

¶ The monophosphine complex, m.p. 99—100°, shows four bands in the carbonyl region at 1982, 1993, 2033, and 2076 cm.$^{-1}$. The bisphosphine derivative, m.p. 160—162°, shows three principal absorption bands in the carbonyl region and its n.m.r. spectrum consists of three bands at τ 6·45, 8·73 and 8·87 having areas 2 : 1 : 1 respectively.

[1] R. G. Schultz, *Tetrahedron*, 1964, **20**, 2809.
[2] M. S. Lupin, J. Powell, and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 1687.
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[5] R. Davis, following Communication.