Heptafulveneiron Tricarbonyl, a Cyclic Trimethylenemethane-type Complex

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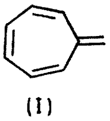
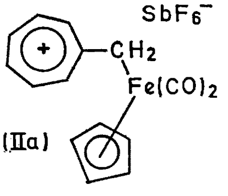
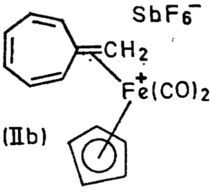
Summary The preparation and characterization of heptafulveneiron tricarbonyl and its reaction to give a heptafulvene–dimethyl acetylenedicarboxylate adduct are described.

UNSTABLE organic species such as cyclobutadiene[1] and trimethylenemethane[2] have been isolated as iron tricarbonyl complexes, and subsequently freed from these complexes by various means.[3,4] We report a similar complex of the extremely reactive unsaturated molecule, heptafulvene,[5] (I). The only known complex of (I) is a salt,[6] (II), but it has proved difficult to isolate any free heptafulvene derivative from the decomposition of this species.†


(I)

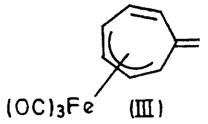


(IIa)

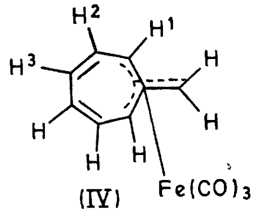


(IIb)

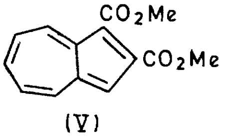
Reaction of 7-hydroxymethylcycloheptatriene[6] in diethyl ether with a large excess of di-iron nonacarbonyl [$Fe_2(CO)_9$] afforded, upon attempted distillation of the product, a 25% yield of heptafulveneiron tricarbonyl, which was further purified by sublimation (40°/0·1 mm), m.p. 37—41°. The i.r. spectrum of this compound displayed iron carbonyl absorptions at 1980 and 2050 cm^{-1} (CH_2Cl_2); its n.m.r. spectrum (unchanged from $-60°$ to $+140°$) consisted of a centrosymmetric multiplet at τ 4·13, a doublet of doublets at τ 6·30 ($J_{1,2}$ 6; $J_{1,3}$ 1 Hz), and a singlet at τ 8·60, in the ratio 4 : 2 : 2 (CS_2). A mass spectrum of the complex showed peaks corresponding to $C_8H_8Fe(CO)^{+}_{0-3}$, and a fragmentation pattern at and below *m/e* 104 presumably characteristic of free heptafulvene (large peaks at *m/e* 103, 91, 78, 77, 52, 51, 50, 40, and 39). Although heptafulveneiron tricarbonyl could have adopted a dieneiron tricarbonyl configuration such as (III), the n.m.r. spectrum can best be explained by complexation of heptafulvene as a trimethylenemethane-type ligand, as in (IV).



(III)



(IV)



(V)

The heptafulvene complex (IV) does not react with tetracyanoethylene on stirring at room temperature in

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† This material possesses the σ-complex structure (IIa) in the crystal.[7]

benzene for one day.‡ An attempted Diels–Alder reaction of (IV) with dimethyl acetylenedicarboxylate in refluxing xylene led to the decomposition of the heptafulvene complex and the isolation, after dehydrogenation with air in the presence of Pd/C, of a 16% yield of 1,2-di(methoxycarbonyl)azulene (V), identified by comparison of its u.v. spectrum with that of the heptafulvene–dimethyl acetylenedicarboxylate adduct originally reported by Doering.[5]

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‡ (IV) readily reacts further with $Fe_2(CO)_9$ to give a complex which has not yet been fully characterized.

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