Photochemical Reaction of a Conjugated Diacetylene with Iron Pentacarbonyl; Preparation and Structure of Tetracarbonyl(2-methyl-3-prop-1-ynylmaleoyl)iron(O)

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Summary U.v. irradiation of $Fe(CO)_5$ and dimethyldiacetylene (DMDA) in tetrahydrofuran gave tetracarbonyl-(2-methyl-3-prop-1-ynylmaleoyl)iron(o), (**1**); its structure has been determined by *X*-ray crystallography.

The chemistry of the iron carbonyls with monoalkynes has been investigated,[1] but their reactions with diacetylenes have been less well-studied. Recent work has shown that macrocyclic alkadiynes can react to form complexes which are analagous to monoacetylene-type compounds produced under similar conditions.[2] Reaction of diphenylbutadiyne can lead to derivatives of the well-known[1] type (tricarbonylferrole)$Fe(CO)_3$;[3] reaction of DMDA with $Fe_3(CO)_{12}$ produces a novel trimetallic product in addition to a (tricarbonylferrole)$Fe(CO)_3$ type complex.[4] U.v. irradiation of $Fe(CO)_5$ in the presence of monoalkynes produces (cyclopentadienone)$Fe(CO)_3$[5] and (quinone)$Fe(CO)_3$[6] derivatives in addition to polynuclear species.[5] We now report that conjugation of two acetylenic groups changes the course of this photolytic reaction to produce (**1**), a type of iron carbonyl acetylene complex not previously prepared photochemically. We have characterised (**1**) by an *X*-ray structural study. Independent syntheses of this class of iron complex have also been reported.[7]

After u.v. irradiation of $Fe(CO)_5$ and DMDA in tetrahydrofuran for 20 min, the solvent was evaporated and the residue sublimed to give crude (**1**) which after recrystallization from acetonitrile gave red-orange crystals of pure (**1**). *Crystal data:* $FeC_{12}H_6O_6$, m.wt. 302·0, monoclinic, $P2_1/c$, $Z = 4$, a = 6·848(2), b = 32·396(8), c = 7·361(2) Å; β = 128·91(2)°; D_m = 1·57, D_c = 1·58 g cm^{-3}; R = 0·042 for 989 observed reflections (General Electric XRD-7 manual diffractometer). The molecular structure of (**1**) (Figure) shows an iron atom which is approximately octahedrally co-ordinated and joined to the DMDA group through two *cis*-ketonic carbonyl groups. The six Fe–C distances are 1·833, 1·857, 1·829, 1·808, 2·035, and 2·012 Å for C(1)—C(6) respectively. The axial terminal carbonyl groups are slightly bent towards the five-membered ring, with ∠C(1)–Fe–C(4) being 166°. Other significant bond distances are: C(5)–C(7), 1·494; C(7)–C(9), 1·485; C(7)–C(8), 1·341; C(6)–C(8), 1·502; C(8)–C(10), 1·414; C(10)–C(11), 1·195; C(11)–C(12), 1·457; C(5)–O(5), 1·206; C(6)–O(6), 1·201 Å. The structure is consistent with the ^1H n.m.r. spectrum in CCl_4 (resonances at δ 2·23 and 2·10 in a 1 : 1 intensity ratio) and the i.r. spectrum [ν_{max} (CCl_4) 2226w (C≡C); 2116m, 2058s, 2037s (C≡O); 1682sh, 1668s (C=O); 1614w (C=C) cm^{-1}].

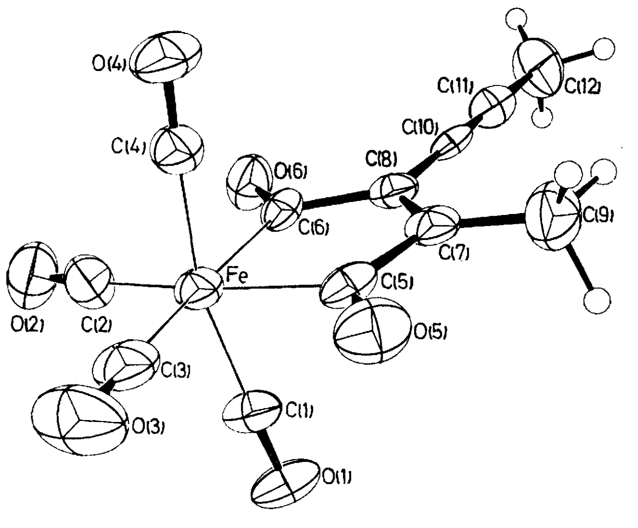

FIGURE. Structure of tetracarbonyl(2-methyl-3-prop-1-ynylmaleoyl)iron(o).

We find that the photochemical reaction of dimethylacetylene with $Fe(CO)_5$ in tetrahydrofuran does give the expected (duroquinone)$Fe(CO)_3$.[6] Also, the reaction of DMDA with $Fe(CO)_5$ in cyclohexane produces what has been identified as a (cyclopentadienone)$Fe(CO)_3$ derivative. No additional products have been identified using a variety of solvents. It is suggested that complexes with structures similar to that of (**1**) may be intermediates in the photolytic reaction of monoacetylenes with $Fe(CO)_5$ to form (quinone)$Fe(CO)_3$ species. The conjugation in DMDA may help to stabilize (**1**); we have not yet been able to add either DMDA or dimethylacetylene to (**1**) in the presence of u.v. irradiation.

We thank the Robert A. Welch Foundation for support, and Mary D. James for technical assistance.

(*Received*, 3*rd March* 1975; *Com.* 257.)

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