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Cycloaddition of Alkynes to the Complexed *cis*-Azo Group. Formation and Crystal Structure of the Diphenylacetylene Adduct of μ-1,2-[3,3-Bis(methoxycarbonyl)-4-phenyl-1-pyrazoline]-hexacarbonyldi-iron

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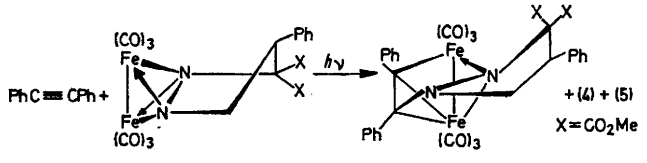
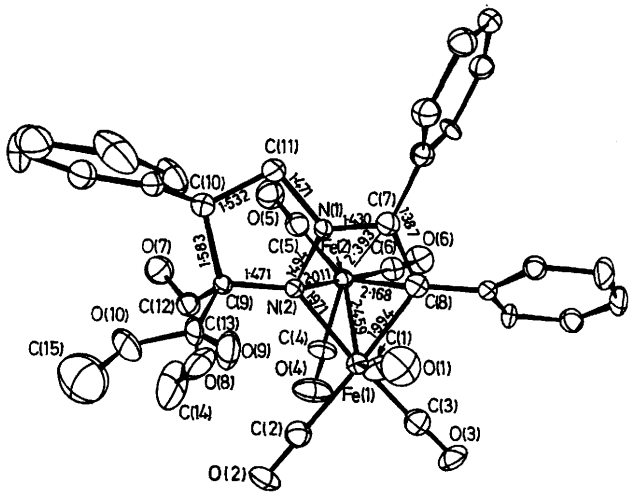
Summary The reaction of diphenylacetylene with μ-1,2-[3,3-bis(methoxycarbonyl)-4-phenyl-1-pyrazoline]-hexacarbonyldi-iron gives tetraphenylcyclobutadiene tricarbonyliron; possible intermediates have been isolated, and the structure of the initial cycloadduct has been determined by *X*-ray analysis.

Cyclic azo alkanes having a *cis*-azo link are known to react with iron carbonyls with the formation of mono,[1] bi-[2] and trinuclear[3] complexes in which the azo group serves as a two-, four- or six-electron donor. In an investigation of the reactivity of the complexed N=N double bond we have studied the reaction of diphenylacetylene with μ-1,2-[3,3-bis(methoxycarbonyl)-4-phenyl-1-pyrazoline]-hexacarbonyldi-iron (**1**).



(1) (3)

In the reaction of diphenylacetylene with (**1**) at 150° tetraphenylcyclobutadiene tricarbonyl iron (**2**) was formed besides small amounts of hexaphenylbenzene and known complexes of the alkyne.[4] In a search for possible intermediates the reaction was studied under milder conditions. Irradiation ($\lambda \geqslant 290$ nm) of a toluene solution of (**1**) in the presence of an excess of diphenylacetylene, followed by chromatography (silica gel, −20°) gave black crystals of a complex (**3**) analysing as $LFe_2(CO)_6PhC_2Ph$ [L = 3,3-bis-(methoxycarbonyl)-4-phenyl-1-pyrazoline], pink crystals of



Figure

composition $LFe(CO)_4PhC_2Ph$ (**4**), and deep red crystals of composition $LFe(CO)_3(PhC_2Ph)_2$ (**5**) as well as small amounts of (**2**). Complex (**3**), m.p. 132—134° decomp., is stable at room temperature only in the solid state and decomposes in solution into (**4**) and iron carbonyl fragments; (**4**) reacts with diphenylacetylene to give (**5**) which can be converted into the cyclobutadiene complex (**2**) by heating *in vacuo* to

150°. The ^1H n.m.r. spectrum of (**3**) at −70° ([$^2H_8$]-toluene) shows the ring protons of the pyrazoline at about the same chemical shift as in the starting compound (**1**) and the phenyl protons of the complexed PhC_2Ph at τ 3·1—3·4.

The structure of complex (**3**) was determined by single crystal *X*-ray crystallography. *Crystal data:* $C_{33}H_{24}Fe_2N_2O_{10}$, $M = 720{\cdot}27$, monoclinic, $a = 23{\cdot}406(3)$, $b = 8{\cdot}551(1)$, $c = 16{\cdot}157(2)$ Å, $\beta = 98{\cdot}73(1)°$, $V = 3196{\cdot}3$ Å^3, $Z = 4$, $D_c = 1{\cdot}497$ g cm^{-3}, space group $P2_1/c$; Mo-K_α radiation. 4212 reflections (2104 unobserved) were collected on a Nonius CAD-4 automatic diffractometer. After 10 cycles of block diagonal refinement, the *R*-value settled at $R = 0{\cdot}053$, $Rw = 0{\cdot}063$.

The molecule is shown in the Figure; it contains two $Fe(CO)_3$ groups connected by an Fe–Fe bond of typical length for a doubly bridged Fe-Fe system.[5] A nitrogen atom of the azo group and a carbon atom of the inserted acetylene molecule complete the nonplanar four-membered ring. The dihedral angle between the planes Fe(1)-X-Fe(2) [X = N(2), C(8)] is 100·3°. The distance Fe(2)–C(7) indicates a weaker interaction compared with Fe(2)–C(8). The C–C bond length of the inserted acetylenic group is increased characteristically upon co-ordination. This effect is paralleled by a bending of the phenyl groups towards sp^2-angles at atoms C(7) and C(8). Due to the asymmetric bonding situation, two different angles are found; whereas the Ph–C–C angle at the bridging carbon atom is found to be 120·4(7)°, at the nonbridging carbon atom it is 127·4(8)°. The Fe(1)–C(7)–C(8) fragment bears similarities to other ferra-π-allylic systems.[6] The second nitrogen N(1) does not bond to the iron atoms.

In the pyrazoline part the N–N distance indicates that the bond is single,[7] being much longer than the double bond values observed in the free ligand, 1·24 Å[8] and in a pyrazoline-$Fe(CO)_4$ complex in which one lone pair of the azo group donates to the Fe atom, 1·242 Å.[9] In complexes analogous to (**1**) this bond is found to be 1·39—1·404 Å.[10] Apart from the C–N–N–C fragment, the geometry of the pyrazoline remains unaltered.[9] Some changes in the ring bond angles occur which relieve strain in the five-membered heterocycle. Probably the compounds obtained previously in the reaction of μ-1,2-(3,6-diphenylpyridazine)-hexacarbonyldi-iron with dialkyl acetylenedicarboxylates are similar in structure.[11]

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