Cycloaddition to a Nitrogen-bridged Iron Complex. Preparation and Crystal Structure of the Maleic Anhydride Adduct of μ-(3,6-Diphenylpyridazine)-hexacarbonyldi-iron

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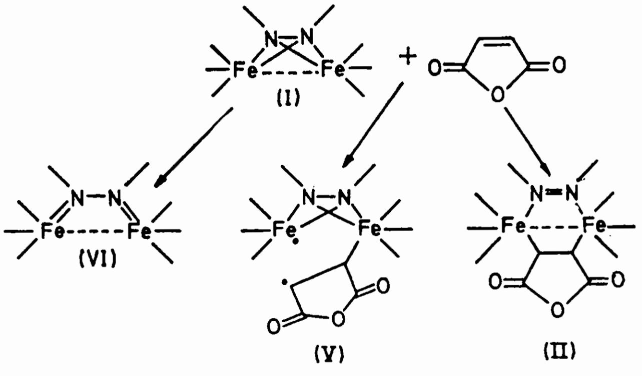
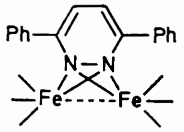
Summary Novel cycloadducts of μ-(3,6-diphenylpyridazine)-hexacarbonyldi-iron with maleic anhydride and acetylenes have been prepared; the molecular structure of the maleic anhydride cycloaddition product has been determined by *X*-ray structure analysis.

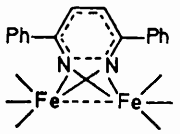
Although the Woodward–Hoffmann rules[1] have stimulated interest in organic cycloaddition reactions, the reactions involving co-ordinated ligands in organometallic compounds have not been extensively studied.[2,3] We have found an unprecedented type of cycloaddition reaction (see Scheme) whereby a doubly nitrogen-bridged complex (I) is converted into the cycloadduct (II) containing a μ-h^2 maleic anhydride ligand. The reaction involves a remarkable change in the pyridazine ligand† and resembles cycloadditions to strained carbocyclic systems.[4] Indeed, the occurrence of a number of strained M_2X_2 rings[5] analogous to (I) suggests that the present type of cycloaddition reaction may be of general significance.



Scheme



(III)



(IV)

The reaction of 3,6-diphenylpyridazine with $Fe_2(CO)_9$ in benzene, followed by chromatography (Al_2O_3) gave air-stable red needles of a complex (I) analysing as $C_{22}H_{12}N_2O_6Fe_2$. The n.m.r. spectrum shows a marked upfield shift of protons in the 4 and 5 positions of the pyridazine ring, consistent with a decrease in ring current following complexing. The i.r. spectrum is typical of an $Fe_2(CO)_6$ derivative and, together with a strong parent ion peak at m/e of 512 in the mass spectrum, confirms the formulation $(C_{16}H_{12}N_2)Fe_2(CO)_6$. Fragmentation of the parent ion proceeds *via* successive loss of the 6-CO groups, followed by loss of N_2, giving an ion $(C_{16}H_{12})Fe_2$ at m/e of 316. The latter process, together with the appearance of a peak at m/e of 232 due to $C_{16}H_{12}N_2^+$, implies retention of the N–N bond in the complex. The Mössbauer spectrum indicates two equivalent iron atoms ($\delta = 0{\cdot}35$ mm s^{-1}; $\Delta = 1{\cdot}05$ mm s^{-1} relative to $Na_2[Fe(CN)_5NO],2H_2O$) in contrast to the non-equivalence for the two iron nuclei in $(C_{23}H_{18}N_2)Fe_2(CO)_6$,[6] where the N–N

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† In (I) the nitrogen atoms of the ligand behave as 3 electron donors and in (II) as 2 electron donors if obedience to the 18 electron rule is assumed.

bond is cleaved. These data are consistent with a nitrogen-bridged structure although it is not clear whether (III) or (IV) best represents the bonding in the pyridazine ring.[7]

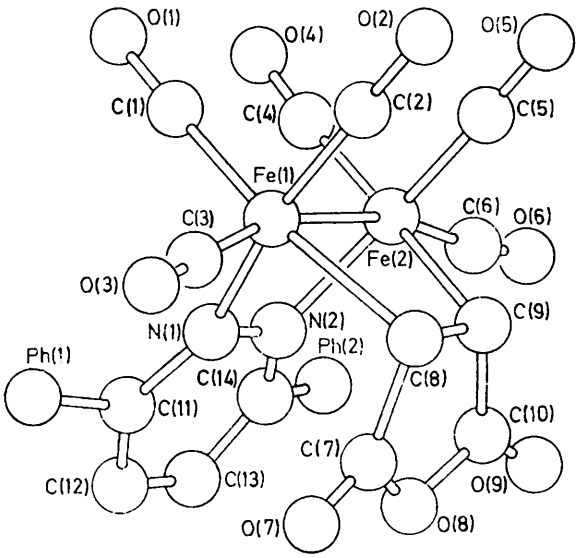

FIGURE. *A view of the maleic anhydride adduct of μ-(3,6-diphenylpyridazine)-hexacarbonyldi-iron showing the atomic numbering and configuration.*

The reaction of (I) with maleic anhydride in benzene yields red crystals of a 1 : 1 adduct (II). Physical measurements (i.r., Mössbauer, n.m.r.) indicated an $Fe_2(CO)_6$ derivative having two equivalent iron atoms, a delocalised pyridazine ring, and a symmetrically co-ordinated maleic anhydride ligand. Details of the bonding and structure were revealed by an X-ray crystal structure study.

Crystal data: $C_{26}H_{14}N_2O_9Fe_2$, $M = 608{\cdot}1$, monoclinic, $a = 14{\cdot}759$, $b = 13{\cdot}152$, $c = 13{\cdot}716$ Å, $\beta = 109{\cdot}59°$, D_m (flotation) $= 1{\cdot}60$, $D_c = 1{\cdot}610$ g cm^{-3}, $Z = 4$, $F(000) = 1224$, graphite monochromatized Mo-K_α radiation ($\lambda = 0{\cdot}71069$ Å). Systematic absences of $h0l$ if $l = 2n + 1$, $0k0$ if $k = 2n + 1$ indicate space group $P2_1/c$. At the present stage of refinement the R value is 0·080.

The binuclear molecule, as shown in the Figure, contains two $Fe(CO)_3$ groups linked by an Fe–Fe bond, a bridging maleic anhydride, and a bridging pyridazine ligand. The Fe–Fe bond distance of 2·597(3) Å is longer than in other compounds with bridging nitrogen atoms but intermediate in the values found for other organometallic compounds.[8] The Fe–N bond lengths [Fe(1)–N(1) of 2·00(1) and Fe(2)–N(2) of 2·01(1) Å] are comparable to the values in organonitrogen compounds where there is no N–N bond but are longer than the examples where the N–N bond is retained.[5] The Fe(1)–C(8) distance of 2·15(1) Å and Fe(2)–C(9) distance of 2·14(1) Å indicate that the Fe atoms are σ-bonded to the maleic anhydride portion.[9] The much shorter Fe–CO distances (av. 1·78 Å) support this hypothesis. The C–C and C–N bonds in the planar pyridazine ring are normal for a delocalized system. Therefore, the pyridazine has changed from a 6 electron donor in (I) to a 4 electron donor with complete ring delocalization in (II).[10] Since the plane containing the pyridazine ligand is expected to be normal to the Fe–Fe bond in (I),[5] the reaction of (I) to yield (II) must involve bringing Fe(1), Fe(2), N(1), and N(2) into a coplanar arrangement while delocalization is occurring in the pyridazine ring.

The addition of maleic anhydride to (I) can be compared to the cycloaddition to bicyclo[2,1,0]pentane.[4] Possible mechanisms for the formation of (II) may involve a diradical intermediate (V) formed by attack on the Fe–Fe bond of (I) or alternatively a Diels-Alder addition to a valence isomer (VI) of (I).

Diphenylacetylene reacted with (I) giving the free pyridazine and the complex $Fe_2(CO)_7(PhC_2Ph)_2$. Dimethyl acetylenedicarboxylate and diethyl acetylenedicarboxylate, however, afforded 1 : 1 adducts with (I) having i.r. and n.m.r. spectra similar to (II) but exhibiting two non-equivalent iron sites in the Mössbauer spectra.

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[1] R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Verlag Chemie, Gmbh, Weinheim, Germany, 1971.

[2] Several novel organometallic complexes have recently been synthesised in this way but there are as yet insufficient data to justify a unifying theory of predictive value. See for example: J. Ashley-Smith, M. Green, and D. C. Wood, *J. Chem. Soc.* (*A*), 1969, 1172; A. Bond and M. Green, *Chem. Comm.*, 1971, 12; P. Reeves, J. Henry, and R. Pettit, *J. Amer. Chem. Soc.*, 1969, **91**, 5888; M. Green, S. Tolson, J. Weaver, D. C. Wood, and P. Woodward, *Chem. Comm.*, 1971, 222; J. S. Ward and R. Pettit, *J. Amer. Chem. Soc.*, 1971, **93**, 262; W. P. Giering and M. Rosenblum, *ibid.*, p. 5299.

[3] The role of transition metals in catalysing symmetry-forbidden reactions has recently been reviewed. See F. D. Mango and J. H. Schachtschneider in 'Transition Metals in Homogeneous Catalysis,' ch. 6, ed. G. N. Schrauzer, Marcel Dekker, New York, 1971.

[4] P. G. Gassman, *Accounts Chem. Res.*, 1971, **4**, 128.

[5] For a summary of X-ray data for nitrogen-bridged complexes see R. J. Doedens, *Inorg. Chem.*, 1970, **9**, 429.

[6] A. J. Carty, D. P. Madden, M. Mathew, G. J. Palenik, and T. Birchall, *Chem. Comm.*, 1970, 1664.

[7] Since completion of this work Nesmeyanov and his co-workers have briefly described a complex $(C_{16}H_{12}N_2)Fe_2(CO)_6$. Although structural characterisation was incomplete these authors favoured structure (III) for this compound. A. N. Nesmeyanov, L. V. Rybin, M. I. Rybinskaya, A. V. Arutyangan, N. T. Gubenko, and P. V. Petrovskii, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1971, **7**, 1574.

[8] M. R. Churchill, *Inorg. Chem.*, 1967, **6**, 190 and references therein.

[9] See M. R. Churchill, 'Perspectives in Structural Chemistry,' vol. III, eds. J. D. Dunitz and J. A. Ibers, Wiley, New York, 1970, p. 91 for a review of the data on σ-bonded organometallic compounds.

[10] Structure (III) implies bond localisation in the pyridazine ring. R. E. Davis and R. Pettit, *J. Amer. Chem. Soc.*, 1970, **92**, 716, have found a similar type of bond localisation in aromatic iron tricarbonyl complexes.