1,3- and 1,6-Addition of Electronegatively Substituted Olefins to Co-ordinated Cycloheptatriene and *N*-Methoxycarbonylazepine: *X*-Ray Diffraction Study of the Tricarbonylcycloheptatrieneiron–Tetracyanoethylene Adduct

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Summary A single-crystal *X*-ray diffraction study establishes that tetracyanoethylene undergoes a 1,3-addition reaction to tricarbonylcycloheptatrieneiron, with formation of a novel 2,3,4,6-*tetrahapto*-bonded system: the corresponding reaction with tricarbonyl-*N*-methoxycarbonylazepine-ruthenium or -iron affords, respectively, a 1,3 adduct or a mixture of 1,6 and 1,3 adducts.

THERE is considerable interest in the way in which co-ordination modifies the chemistry of olefinic ligands. Tricarbonylcycloheptatrieneiron, which may be reversibly protonated to form a tricarbonylcycloheptadienyliron tetrafluoroborate,[1] has been shown to undergo electrophilic substitution in the 2-position on treatment with Me_2NCHO–$POCl_3$ or a typical Friedel–Crafts reagent.[2] Similarly, acylation of tricarbonyl-*N*-ethoxycarbonylazepineiron gives the 3-acyl substituted product;[3] electron release by the nitrogen lone pair presumably accounts for the difference in the orientation of the substituent. We have found that in the reaction of these seven-membered ring systems with electronegatively substituted molecules such as tetracyanoethylene or hexafluoroacetone, co-ordination to a tricarbonyl-iron or -ruthenium unit leads to different reactions from those observed with the free olefinic systems.

Reaction of tricarbonylcycloheptatrieneiron with hexafluoroacetone, 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene, *trans*-1,2-dicyano-1,2-bis(trifluoromethyl)ethylene, and tetracyanoethylene affords 1 : 1 adducts. For example, at room temperature tetracyanoethylene forms (0·5 h) the yellow crystalline complex (I) (90%), m.p. 160°, ν_{max} (CO) 2073s and 2011s,b, cm^{-1}. Examination of the ^{1}H n.m.r. spectrum, which showed resonances at τ 4·90 (H^3 and H^4†), 5·24 (H^2), 5·57 (H^5), 6·12 (H^7), 6·85 (H^1), 7·62 (H^1), and 8·32 (H^6), did not establish the structure, however, so a single-crystal *X*-ray diffraction study was undertaken.

Crystals of $C_{16}H_8N_4O_3Fe$ are triclinic, $a = 12·18$, $b = 9·05$, $c = 7·38$ Å, $\alpha = 107·2$, $\beta = 82·3$, $\gamma = 88·3°$; space group $P\bar{1}$ with $Z = 2$. The intensities of 1128 non-zero reflections were measured on a Supper–Pace 0·01° incrementing auto-diffractometer using equi-inclination geometry, ω-scan, and Mo-K_α radiation. The structure (Figure) was solved by conventional heavy-atom methods and has been refined using isotropic thermal parameters for all atoms to $R = 0·125$. The seven-membered ring C(1)—C(7) is bonded to the iron atom not only by a π-allyl linkage through C(2), C(3), and C(4) but also by a direct σ-bond between Fe and C(6). A second, five-membered, ring is formed by C(8) and C(9); these two carbon atoms each carry two cyano-groups and are attached to C(7) and C(5), respectively. This cyclopentane ring has an "envelope" conformation, with C(7), C(6), C(5), and C(9) approximately coplanar and C(8) out of the plane. There are three carbonyl groups on the iron atom, around which the configuration is approximately octahedral. This description of the bonding in (I) is supported by the bond lengths: Fe–C(6) = 2·09(3), Fe–C(2) = 2·13(4), Fe–C(3) = 2·11(2), Fe–C(4) = 2·09(2), C(2)—C(3) = 1·40(4), C(3)–C(4) = 1·49(4) Å; the angle at C(3) of the π-allyl group is 115(2)°. The average Fe–C and C–O distances for the three carbonyl groups are 1·74(3) and 1·19(4) Å, respectively.

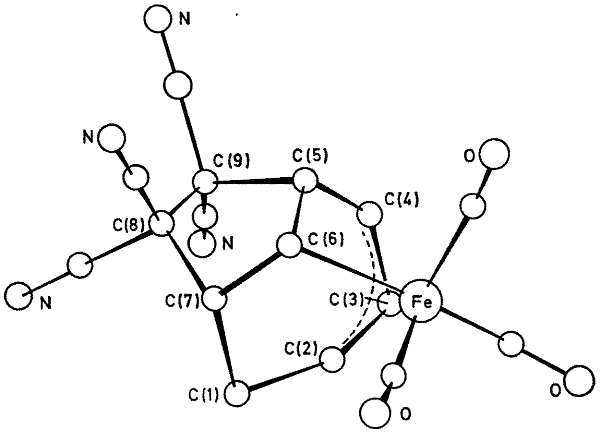
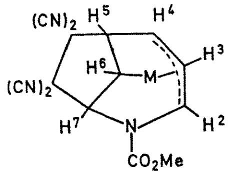


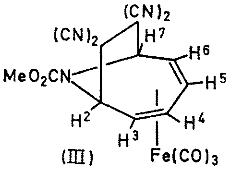
FIGURE. *Structure of the tricarbonylcycloheptatrieneiron–tetracyanoethylene adduct* (I).

Thus the reaction involves a 1,3-addition of tetracyanoethylene to co-ordinated cycloheptatriene; the $Fe(CO)_3$ group, which is bonded *via* a novel 4-electron donor system *exo* to the new 5-ring system, stabilises the resultant adduct. Comparison of ^{1}H n.m.r. data suggests that a similar 1,3-addition reaction occurs between $C_7H_8Fe(CO)_3$ and $(CF_3)_2C{=}O$, $(CF_3)_2C_2(CN)_2$, and $CF_3(CN)\text{-}C{=}C(CN)CF_3$. As might be expected for compounds containing a C–Fe σ-bond the adducts may be readily carbonylated to give organic ketones.[4]

The reaction of tricarbonyl-*N*-methoxycarbonylazepineruthenium[4] with tetracyanoethylene gives yellow crystals of (II), m.p. 164°, ν_{max} (CO) 2086s and 2026s,b, cm^{-1}, which by comparison of ^{1}H n.m.r. chemical shifts, coupling constants, and decoupling experiments is assigned structure (IIa) *i.e.*, 1,3-addition of $C_2(CN)_4$; it is assumed that the metal is bonded as in (I). In contrast, the corresponding reaction of tricarbonyl-*N*-methoxycarbonylazepineiron[5] with $C_2(CN)_4$ affords two 1 : 1 adducts; the minor product (14%) is the 1,3-addition product (IIb). The ^{1}H n.m.r. spectrum of the major product (III) showed only three resonances at τ 4·05 (A-multiplet, H^4 and H^5), 4·25 (P-multiplet, H^2 and H^7) and 6·00 (X-multiplet, H^3 and H^6) where $J_{23} = J_{67} = 8·8$, $J_{34} = J_{56} = 7·5$, $J_{45} = 4·5$, and $J_{35} = J_{46} = 1·6$ Hz;[6] decoupling experiments are consistent with the assignments. This suggests that (III) arises by a 1,6-addition of tetracyanoethylene to the co-ordinated azepine.



(IIa;) M = $Ru(CO)_3$
(IIb;) M = $Fe(CO)_3$



(III)

The formation of both 1,3- and 1,6-addition products suggests that these reactions are not concerted. Uncoordinated *N*-ethoxycarbonylazepine undergoes a 1,4-addition reaction with tetracyanoethylene;[7] the 1,6-concerted reaction is thermally forbidden.

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† Assignments are based on decoupling experiments and on the results of the crystal-structure analysis.

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