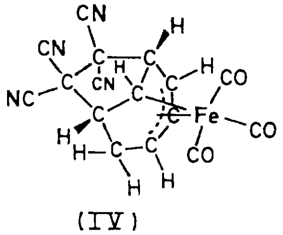
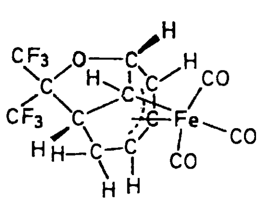
Reactions of Co-ordinated Ligands. Part II.[1] The Reaction of Tricarbonylcycloheptatrieneiron and Tricarbonyl(methyl-, bromo-, and phenyl-cyclo-octatetraene)iron with Hexafluoroacetone, Dicyanobis(trifluoromethyl)ethylene, and Tetracyanoethylene

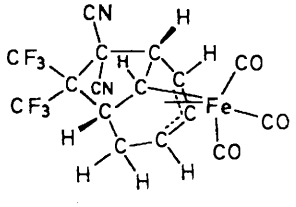
By **Michael Green,* Susan Heathcock, and Dennis C. Wood,** Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS

Tetracyanoethylene, hexafluoroacetone, 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene, and 1,2-dicyano-1,2-bis-(trifluoromethyl)ethylene add *exo*-1,3- to tricarbonylcycloheptatrieneiron; the Fe(CO)$_3$ group is bonded in the 1,2,3,5-h^4 mode in the resultant adducts. A similar reaction occurs with tetracyanoethylene and tricarbonyl-(methyl-, bromo-, and phenyl-cyclo-octatetraene)iron. The cycloheptatriene iron adducts undergo an unusual transannular carbonylation reaction.

RECENT synthetic studies have shown that co-ordination of olefinic molecules such as tetramethylallene,[2] buta-1,3-dienes,[3] cyclobutadiene,[4] cycloheptatriene,[5] tropone,[6] *N*-alkoxycarbonylazepine [7] and cyclo-octatetraene [8] to a tricarbonyliron unit can lead to significant changes in the reactivity and reaction patterns towards electrophilic reagents. These investigations have, however, been largely restricted to reactions of protons and acylium cations. In the previous paper [1] in this series it was shown that electrophilic molecules like tetrafluoroethylene and hexafluoropropene react on u.v. irradiation with tricarbonyl-tetramethylcyclobutadiene and -cyclobutadieneiron to form π-cyclobutenyl systems, in which the fluoro-olefin links the iron and the C_4 ring. Preliminary studies [9] suggest that reactions of this type are quite general. In principle, molecules like tetracyanoethylene and 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene, which are more electrophilic than C_2F_4, might be expected to undergo analogous reactions, but experiments described in this paper show that such electrophiles alternatively attack the π-system of co-ordinated cycloheptatriene and cyclo-octatetraene *exo* to the metal.


(IV)


(I)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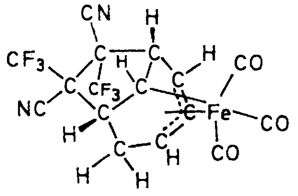
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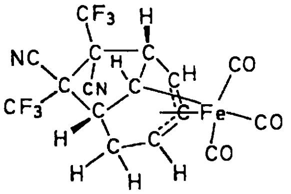
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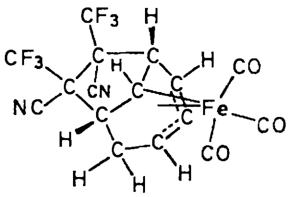
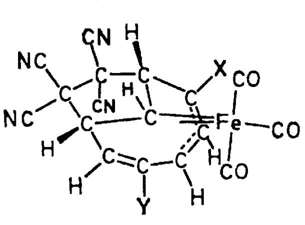
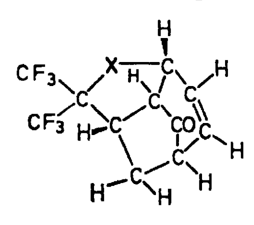

(IIIc)


(V; X = Y = H)
(VI; X = Me, Y = H)
(VII; X = H, Y = Br)
(VIII; X = H, Y = Ph)


(XII; X = O)
[XIII; X = C(CN)$_2$]

Tricarbonylcycloheptatrieneiron rapidly reacts at room temperature with hexafluoroacetone, 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene, *trans*-1,2-dicyano-1,2-bis(trifluoromethyl)ethylene, and tetracyanoethylene to

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[1] A. Bond and M. Green, *J.C.S. Dalton*, 1972, 763.

[2] D. H. Gibson, R. L. Vonnahme, and J. E. McKiernan, *Chem. Comm.*, 1971, 720.

[3] E. O. Greaves, G. R. Knox, and P. L. Pauson, *Chem. Comm.*, 1969, 1124.

[4] J. D. Fitzpatrick, L. Watts, G. F. Emerson, and R. Pettit, *J. Amer. Chem. Soc.*, 1965, **87**, 3254.

[5] B. F. G. Johnson, J. Lewis, P. McArdle, and G. L. P. Randall, *J.C.S. Dalton*, 1972, 456.

[6] D. F. Hunt, G. C. Farrant, and G. T. Rodeheaver, *J. Organometallic Chem.*, 1972, **38**, 349.

[7] G. B. Gill, N. Gourlay, A. W. Johnson, and M. Mahendran, *Chem. Comm.*, 1969, 631.

[8] B. F. G. Johnson, J. Lewis, and G. L. P. Randall, *J. Chem. Soc.* (*A*), 1971, 422.

[9] A. Bond, M. Green, B. Lewis, and S. F. W. Lowrie, *Chem. Comm.*, 1971, 1230.

form respectively the crystalline compounds (I)—(IV).* Elemental analysis and mass spectroscopy showed that the complexes are 1 : 1 adducts and in agreement the i.r. spectra showed bands at 2066s and 2001s,br cm^{-1} indicating the presence of an $Fe(CO)_3$ group; the mass spectrum showed peaks corresponding to the consecutive loss of three carbon monoxides in agreement with this structural feature.

The ^1H n.m.r. spectra (Table) of the adducts (I)—(IV) show multiplets with relative intensities corresponding to eight protons. Proton decoupling experiments suggested the presence of the cyclic arrangement $\overline{CH_fH_gCH_eCH_hCH_aCH_bCH_cCH_d}$, and allowed the assignment of the coupling constants listed in the Table. However, the chemical shift and coupling constant data did not allow the unequivocal establishment of a structure for these adducts, and there seemed even less hope of establishing the stereochemistry and hence the mechanism of formation. An *X*-ray crystallographic study of complex (IV) was therefore undertaken, which resulted in the establishment of the illustrated structure.[10] This allowed the firmer assignment of chemical shifts to the various proton environment. The low field shifts are typical of protons attached to a π-allylic system, and the resonance at highest field (τ 8·32) may be assigned to the hydrogen attached to the carbon σ-bonded to iron. The resonances at τ 6·85 and 7·62 are assigned respectively to the *endo* (H_f) and *exo* (H_g) methylene protons; J_{fg} being 16·0 Hz. This assignment is supported by examination of a molecular model of (IV), which showed dihedral angles for H_e–H_{endo} *ca.* 20° and H_e–H_{exo} *ca.* 80° in agreement with the observation of a small (2·0 Hz) coupling constant for J_{eg} and a larger (12·0 Hz) coupling for J_{ef}.[11] Comparison of the ^1H n.m.r. data for (IV) with that found for (I)—(III) suggests similar structures for these adducts.

The ^{19}F n.m.r. spectra are consistent with such a formulation. The spectra of the hexafluoroacetone (I) and 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (II) adducts both show two quartet resonances with a small additional ^1H–^{19}F coupling, in the case of (I) to the high field resonance.

The adduct (III) showed (Table) in the ^{19}F spectrum two sets of two quartets with ^{19}F–^{19}F coupling constants of 6·2 and 4·1 Hz from which it can be inferred that the reaction with *trans*-1,2-dicyano-1,2-bis(trifluoromethyl)-ethylene forms two isomers in the ratio of 1 : 1·5 (IIIa) and (IIIb). This contrasts with the stereospecific formation of only one isomer (II) in the reaction with $(CF_3)_2C=C(CN)_2$. However, as illustrated (IIIa) and (IIIb) probably only differ in that a cyano-group can be either *cis* or *trans* to the methylene group.

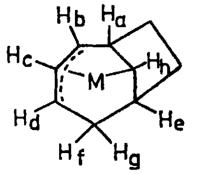
The reaction of a mixture of *cis*- and *trans*-1,2-dicyano-1,2-bis(trifluoromethyl)ethylene (*cis* : *trans*, 1 : 3) gave a product with a ^{19}F n.m.r. spectrum showing three sets of quartets; two sets corresponding to (IIIa) and (IIIb) and a third set with J_{FF} 13·0 Hz assigned to the adduct (IIIc) with trifluoromethyl groups in a relative *cis*-configuration.

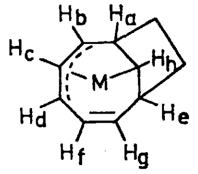
It is interesting that the ratio (3 : 1) of the isomers (IIIa) and (IIIb) to (IIIc) implies that in the formation of the adducts there is no change in the stereochemistry of the reacting olefin.

Thus these reactions involve a 1,3-addition of the electrophilic olefin to co-ordinated cycloheptatriene; the $Fe(CO)_3$ group, which becomes bonded *via* a novel four-electron donor system (1,2,3,5-*h*^{4}) *exo* to the new five-membered ring formed by the reacting olefin, stabilises the resultant adduct.

These observations led us to reconsider the related problem of the reaction of tetracyanoethylene with

^{19}F and ^1H N.m.r. data* for cycloheptatriene (I)—(IV) and cyclo-octatetraene (V)—(VIII) adducts





Complex	$\delta_{(1)}$	$\delta_{(2)}$	J_{FF}	J_{HF1}	J_{HF2}	τ_a	τ_b	τ_c	τ_d	τ_e	τ_f	τ_g	τ_h	J_{ab}	J_{ah}	J_{bc}	J_{ef}	J_{eg}	J_{eh}	J_{fc}	J_{fg}	J_{cd}
(I)	70·9	77·1	10·7	0	1·7	5·16	5·34	5·58	5·58	7·08	7·32	7·32	8·34	7·0	8·0	4·0	8·0	4·0	8·0			
(II)	60·1	63·8	12·8	0		5·98	5·40	5·28	5·44	6·74	7·11	7·11	8·35	8·0	9·0	4·0	6·0	3·0	6·0			
(IIIa)	61·7	68·4	4·1	1·5	0	6·23	5·46	5·21	5·46	6·75	7·25	7·25	8·45	8·0					6·0			
(IIIb)	62·0	67·1	6·2	0	0·8	6·32	5·46	5·21	5·46	6·75	7·25	7·25	8·45	8·0	8·0				6·0			
(IIIc)	61·1	66·9	13·0	0		6·23	5·46	5·21	5·46	6·75	7·25	7·25	8·45	8·0	8·0				6·0			
(IV) †						5·57	4·9	4·9	5·24	6·12	6·85	7·62	8·32		10·0		12·0	2·0	6·0	6·0	16·0	
(V) †						5·4	4·9	4·9	5·4	6·12	3·37	4·16	8·0		12·0		2·0	5·0	7·0		12·0	
(VI) †						5·32		4·9	5·58	6·0	3·34	4·12	8·1		12·0			5·0	6·0		9·0	
(VII) †						5·48	4·74	4·74	5·30	5·90		4·10	8·24	6·0	10·0			5·0	7·0			11·0
(VIII) †						5·44	4·80	4·86	5·23	6·0		3·82	8·20	8·0	10·0			4·0	8·0			10·0

* Measured in $CDCl_3$, chemical shifts are in p.p.m. (internal $CFCl_3$) and τ values (Me_4Si); coupling constants in Hz. † Measured in [$^2H_6$]acetone.

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* The hydrogen atom on the central carbon atom of the allyl group in structures (I)—(IV) has been omitted for clarity.

[10] M. Green, S. Tolson, J. Weaver, D. C. Wood, and P. Woodward, *Chem. Comm.*, 1971, 222; J. Weaver and P. Woodward, *J. Chem. Soc.* (*A*), 1971, 3521.

[11] H. S. Gutowsky, M. Karplus, and D. M. Grant, *J. Chem. Phys.*, 1959, **31**, 1278.

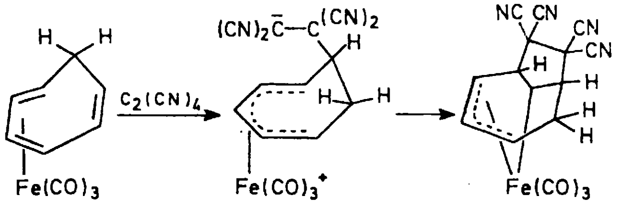
tricarbonyl(cyclo-octatetraene)iron.[12,13] We had previously suggested [14] that these reactions involved a 1,2-addition of the electrophilic olefin to co-ordinated cyclo-octatetraene; the formation of a 1,2,3,5-h^4 adduct as in the cycloheptatriene reaction not being considered.

Reaction of tetracyanoethylene with tricarbonyl-cyclo-octatraene, -methylcyclo-octatetraene, -phenyl-cyclo-octatetraene, -bromocyclo-octatetraene, and -triphenylmethylcyclo-octatetraeneiron afforded respectively the crystalline 1 : 1 adducts (V)—(IX); the adduct (V) has been previously described. The ^{1}H n.m.r. spectrum of (V) measured (50 accumulations) in deuterioacetone and nitrobenzene showed (Table) chemical shifts and coupling constants very similar to those found for (IV); with the exception that the methylene resonances were replaced by two resonances with shifts typical of an unco-ordinated olefin. The spectrum (50 accumulations) of the methyl substituted adduct (IV) was again very similar except that a resonance centred at τ 4·88 (assigned to H_b) was absent, this being replaced by a methyl singlet resonance at τ 8·20. In addition the resonances assigned to H_a and H_c appeared as doublets. The spectra of the adducts (VII) and (VIII) showed the same chemical shifts and coupling constant pattern except that both the bromine and phenyl substituents occupied the position H_f. The resonance H_g in the spectrum of both (VII) and (VIII) appeared as a doublet; double irradiation of the resonance H_e collapsed the H_g signal to a singlet.

These comparisons strongly indicated that in all the cyclo-octatetraene adducts the Fe(CO)$_3$ group is bonded *via* a 1,2,3,5-h^4 system, *i.e.* σ–π, to the C_8 ring; the tetracyanoethylene having added *exo*-1,3. This has been confirmed by an *X*-ray single cystal structural determination of the methyl substituted adduct (VI), which has established the illustrated structure (current *R* factor 12%).[15] In agreement with the ^{1}H n.m.r. measurements the methyl group in the adduct occupies the position H_b, *i.e.* adjacent to the ring juncture of the new *exo*-C_5 ring.

In the original report on the reaction of tetracyanoethylene with tricarbonylcyclo-octatetraeneiron it was suggested [12,13] that the formation of a 1 : 1 adduct was diagnostic of the presence of an unco-ordinated 1,3-diene system, and that the adduct was a simple Diels–Alder $(2_\pi + 4_\pi)$cyclo-addition product. This is clearly not the case, moreover, on this basis tricarbonylcycloheptatrieneiron would not have been expected to react with tetracyanoethylene or related systems. Since, the ionic character of numerous tetracyanoethylene cyclo-additions to a variety of alkenes,[16] strained unsaturated hydrocarbons,[17] and cyclic polyolefins [18] is well recognised, we suggest that the reactions described in this paper proceed *via* the initial formation of transient dipolar species. In the particular case of the reaction of tetracyanoethylene with tricarbonylcycloheptatrieneiron the development of a metal stabilised pentadienyl cation would provide a significant driving force for the ionic pathway.

Reaction of co-ordinated cycloheptatriene, which as a consequence of being bonded to the Fe(CO)$_3$ group by only four of the carbon atoms of the C_7 ring adopts a folded structure, with tetracyanoethylene (Scheme 1) can occur at either a co-ordinated or unco-ordinated double bond; *exo*-attack in both cases being preferred at a carbon atom adjacent to the methylene group as has also been observed with both protonation and acylation of tricarbonylcycloheptatrieneiron.[5]



SCHEME 1

In the former case the Fe(CO)$_3$ group must migrate to the free double bond during the course of the reaction, whereas, attack at an unco-ordinated double bond leads directly to a co-ordinated pentadienyl cation; five of the ring carbon atoms becoming coplanar. At the present time it is not possible to distinguish between these two alternative modes of attack. Nevertheless, it is interesting to note that in the protonation of tricarbonyltroponeiron it has been shown [6] that the proton attacks a co-ordinated double bond *exo* to the iron. In the case of the corresponding reaction of tricarbonylcycloheptatrieneiron it has not been possible to distinguish between attack on the co-ordinated or unco-ordinated double bond, although an *exo*-approach has been demonstrated for the proton.[5] Interestingly, it is suggested [5] that acylation involves an alternative *endo*-approach.

As noted previously the stereochemistry around the central C–C bond of 1,2-dicyano-1,2-bis(trifluoromethyl)-ethylene is preserved on reaction with $C_7H_8Fe(CO)_3$, implying that collapse of the postulated dipolar intermediate occurs more rapidly than rotation about the C–C bond of the reacting olefin. It is possible that conformational rigidity results from internal stabilisation of the dipolar intermediate by a charge-transfer interaction.[19]

Heteronuclear (^{1}H–^{19}F) decoupling experiments on the hexafluoroacetone adduct (I) demonstrated the

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[12] A. Davidson, W. McFarlane, and G. Wilkinson, *Chem. and Ind.*, 1962, 820.

[13] G. N. Schrauzer and S. Eichler, *Angew. Chem. Internat. Edn.*, 1962, **1**, 454.

[14] M. Green and D. C. Wood, *J. Chem. Soc.* (*A*), 1969, 1172.

[15] J. Weaver and P. Woodward, private communication.

[16] P. D. Bartlett, *Quart. Rev.*, 1970, **24**, 473.

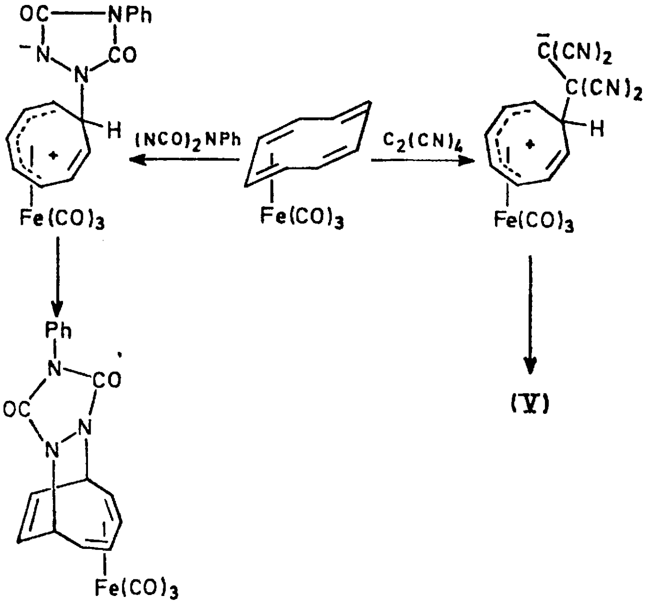
[17] S. Nishida, I. Moritani, and T. Teraji, *Chem. Comm.*, 1971, 36; J. E. Baldwin and R. E. Peavy, *J. Org. Chem.*, 1971, **36**, 1441; R. Noyori, N. Hayashi, and M. Katô, *J. Amer. Chem. Soc.*, 1971, **93**, 4948.

[18] H. P. Löffler, T. Martini, H. Muso, and G. Schröder, *Chem. Ber.*, 1970, **103**, 2109.

[19] R. Gommper, *Angew. Chem. Internat. Edn.*, 1969, **8**, 312.

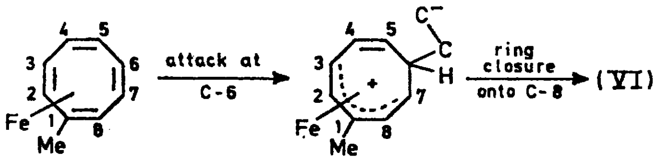
presence of coupling between the proton H_e and the fluorines of the $C(CF_3)_2$ group as required by the illustrated structure for this adduct. The stereoselective formation of this one isomer, and the formation of the one adduct (II) in the reaction with 1,1-dicyano-2,2-tris-(trifluoromethyl)ethylene is fully consistent with the postulated ionic reaction pathway.

Both the previously reported[14] 1,4-addition of 4-phenyl-1,2,4-triazoline-3,5-dione to $C_8H_8Fe(CO)_3$ and the *exo*-1,3-addition of tetracyanoethylene to methyl-, phenyl-, bromo-, triphenylmethyl-, and unsubstituted tricarbonylcyclo-octatetraeneiron complexes can be accommodated by a similar two-stage reaction pathway. In the case of the triazoline the dipolar intermediate must collapse preferentially to form the 1,4-adduct in contrast with the 1,3-collapse observed with tetracyanoethylene (Scheme 2).



SCHEME 2

Anet has shown[20] that tricarbonylmethylcyclo-octatetraeneiron exists exclusively (>95%) as the isomer with the methyl group bonded to one of the internal carbon atoms of the co-ordinated 1,3-diene (Scheme 3), and therefore initial attack by tetracyanoethylene at the co-ordinated double bond carbon atoms C-2 or C-8 or at the un-co-ordinated carbon atoms C-6 or C-4 could lead to the observed *exo*-1,3-adduct with the methyl substituent adjacent to the tetracyanoethane bridge. Although attack at C-6 might be expected to lead to a more stable pentadienyl cation, it is not certain that this is the preferred mode of attack; however, it is interesting to note that protonation of tricarbonylmethylcyclo-octatetraeneiron is considered to occur *exo* at C-5 and C-6.[21]

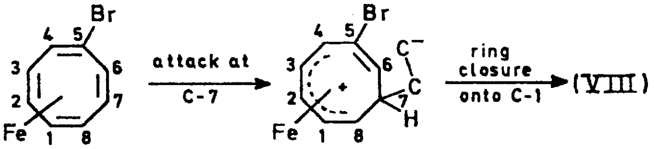


SCHEME 3

A simple extension of this concept can be used to explain the formation of different isomers in the corresponding reactions of $C_8H_7BrFe(CO)_3$ and $C_8H_7PhFe(CO)_3$. For example, it is likely that tricarbonylbromocyclo-octatetraeneiron exists as the isomer with the bromine bonded to one of the carbon atoms of the unco-ordinated 1,3-diene. Since electrophilic attack would be expected to occur preferentially at a non-halogen substituted double, initial reaction of $C_2(CN)_4$ at C-1 or C-7 could afford the observed product (Scheme 4).

In describing the *exo* attack by $C_2(CN)_4$ on $C_8H_8Fe(CO)_3$ the intermediate dipolar species has been written as a 1—5-h^5 bonded cation, *i.e.* pentadienyl system, as has been inferred[22] for the cation $C_8H_9Fe(CO)_3^+$ observed in the low temperature protonation of $C_8H_8Fe(CO)_3$. However, other modes of bonding[23] may be preferred, and this could perhaps provide an explanation for the different products obtained from $C_2(CN)_4$ and 4-phenyl-1,2,4-triazoline-3,5-diene. It is interesting that in contrast with the protonated $C_8H_9Fe(CO)_3^+$ species,[21,22] there was no evidence for products arising from the disrotatory ring closure of an open system to afford bicyclo[5,1,0] adducts.

The adducts (I) and (II) undergo a novel transannular carbonylation reaction on treatment with carbon monoxide to give respectively the white crystalline organic compounds (XII) and (XIII). The i.r. spectra of both compounds showed a ketonic carbonyl band at 1778 and 1769 cm^{-1} respectively, which when considered together with elemental analyses and mass spectra suggested the illustrated structures. The ^1H and ^{19}F n.m.r. spectra are consistent with such a formulation, and suggested that the carbonylation reactions did not involve skeletal rearrangement.



SCHEME 4

The formation of (XII) and (XIII) probably involves an initial alkyl migration or ' carbonyl insertion ', which would not involve a stereochemical inversion at the migrating carbon, followed by a transannular reaction of the resultant iron acyl group with the π-allyl system;

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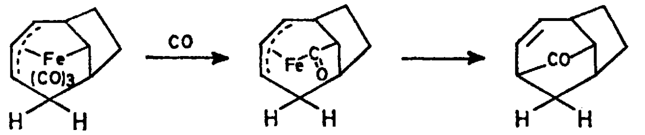
[20] F. A. L. Anet, *J. Amer. Chem. Soc.*, 1967, **89**, 2491.

[21] M. Brookhart and E. R. Davis, *Tetrahedron Letters*, 1971, **46**, 4349.

[22] M. Brookhart and E. R. Davis, *J. Amer. Chem. Soc.*, 1970, **92**, 7622.

[23] M. Cooke, P. T. Draggett, M. Green, B. F. G. Johnson, J. Lewis, and D. J. Yarrow, *Chem. Comm.*, 1971, 621.

a reaction which would involve a formal reduction in the oxidation state of the iron from Fe^{II} to Fe^{0} (Scheme 5).



SCHEME 5

Migration of an acyl group onto a co-ordinated diene has been previously observed in manganese chemistry.[24] Recently, in a preliminary communication [25] a possibly related transannular carbonylation has been briefly described. The conversion of (I) ⟶ (XII) is also promoted by nitric oxide, which is compatible with the previous observation of a nitric oxide promoted ' carbonyl insertion reaction '.

EXPERIMENTAL

^1H and ^{19}F N.m.r. spectra were recorded on a Varian HA 100 spectrometer. The 220 MHz ^1H spectra were measured on a Varian spectrometer (I.C.I. Runcorn). Chemical shifts are relative to Me_4Si (τ 10·00) and CCl_3F (0·00 p.p.m.). I.r. spectra were recorded with a Perkin-Elmer 257 spectrometer using Nujol and hexafluorobutadiene mulls. Mass spectra were observed on an MS 9 spectrometer using an ionising voltage of 70 eV. Tricarbonylcycloheptatrieneiron and tricarbonylmethylcyclo-octatetraeneiron were prepared by the published methods.

Reactions of Tricarbonylcycloheptatrieneiron.—(a) *With hexafluoroacetone*. An excess of hexafluoroacetone (1·12 g, 6·75 mmol) was condensed (−196°) into a Carius tube (50 ml) containing tricarbonylcycloheptatrieneiron (1·0 g, 4·31 mmol) in hexane (10 ml). After 2 days at room temperature the solvent was removed *in vacuo* and the residue recrystallised (−78°) from hexane to give pale yellow *crystals* of (I) (1·20 g, 69%), m.p. 75—76° (Found: C, 39·7; H, 2·1; F, 28·7; Fe, 13·7. $C_{13}H_8F_6O_4Fe$ requires C, 39·2; H, 2·0; F, 28·6; Fe, 14·0%), $\nu_{max.}$ (hexane) 2066s and 2001s cm^{-1}. The mass spectrum showed peaks at *m/e* 398 (1·5%, *P*), 3·70 (3·5%, *P* − CO), 342 (7·4%, *P* − 2CO), and 314 (7·2%, *P* − 3CO).

(b) *With* 1,1-*dicyano*-2,2-*bis*(*trifluoromethyl*)*ethylene*. A solution of tricarbonylcycloheptatrieneiron (0·13 g, 0·56 mmol) and 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (0·12 g, 0·56 mmol) in hexane (5 ml) was stirred (½ h) at room temperature. The precipitate was collected and recrystallised from methylene chloride–hexane to afford pale yellow crystals of (II) (0·18 g, 79%), m.p. 120° dec. (Found: C, 43·1; H, 2·0; F, 25·9; N, 6·1; Fe, 12·5. $C_{16}H_8F_6N_2O_3Fe$ requires C, 43·1; H, 1·8; F, 25·6; N, 6·3; Fe, 12·5%), $\nu_{max.}$(cyclohexane) 2067s and 2005s(broad) cm^{-1}. The mass spectrum showed peaks at *m/e* 446 (8%, *P*), 418 (3%, *P* − CO), 390 (5%, *P* − 2CO), and 362 (30%, *P* − 3CO).

(c) *With* trans-1,2-*dicyano*-1,2-*bis*(*trifluoromethyl*)*ethylene*. A solution of *trans*-1,2-dicyano-1,2-bis(trifluoromethyl)-ethylene (0·25 g, 1·17 mmol) and tricarbonylcycloheptatrieneiron (0·23 g, 0·99 mmol) in methylene chloride (15 ml) was stirred (4 h) at room temperature. The solvent was removed *in vacuo* and the residue recrystallised from methylene chloride–hexane to give pale yellow crystals of (IIIa) and (IIIb) (0·23 g, 52%), m.p. 138—139° (Found: C, 43·1; H, 2·0; F, 25·7; N, 6·2; Fe, 12·7. $C_{16}H_8F_6N_2O_3Fe$ requires C, 43·1; H, 1·8; F, 25·6; N, 6·3; Fe, 12·5%), $\nu_{max.}$ (cyclohexane) 2065s and 2003s(broad) cm^{-1}. The mass spectrum showed peaks at *m/e* 446 (3%, *P*), 418 (5%, *P* − CO), 390 (13%, *P* − 2CO), and 362 (67%, *P* − 3CO).

(d) *With tetracyanoethylene*. A solution of tetracyanoethylene (0·46 g, 3·6 mmol) and tricarbonylcycloheptatrieneiron (0·83 g, 3·58 mmol) in methylene chloride (10 ml) was stirred (½ h) at room temperature. The resultant crystalline precipitate was collected and recrystallised from methylene chloride–hexane to give pale yellow *crystals* of (IV) (1·08 g, 84%), m.p. 160° dec. (Found: C, 53·3; H, 2·0; N, 15·9. $C_{16}H_8N_4O_3Fe$ requires C, 53·4; H, 2·2; N, 15·6%), $\nu_{max.}$ ($CHCl_3$) 2073s and 2011s(broad) cm^{-1}. The mass spectrum showed peaks at *m/e* 360 (1%, *P*), 332 (22%, *P* − CO), 304 (13%, *P* − 2CO), and 276 (35%, *P* − 3CO).

Reactions of Tetracyanoethylene.—(a) *With tricarbonylmethylcyclo-octatetraeneiron*. A solution of tetracyanoethylene (0·064 g, 0·50 mmol) and tricarbonylmethylcyclo-octatetraeneiron (0·20 g, 0·52 mmol) in methylene chloride (15 ml) was stirred (1 h) at room temperature. The precipitated product was collected and recrystallised from methylene chloride–hexane to give yellow *crystals* of (VI) (0·18 g, 60%), m.p. 162° dec. (Found: C, 55·8; H, 2·5; N, 14·3. $C_{18}H_{10}N_4O_3Fe$ requires C, 55·9; H, 2·6; N, 14·5%), $\nu_{max.}$ (CH_2Cl_2) 2070s and 2008s,br cm^{-1}. The mass spectrum showed peaks at *m/e* 358 (1%, *P* − CO), 331 (1%, *P* − 2CO), 303 (4%, *P* − 3CO), and 175 (100%, *P* − 3CO − C_6N_4).

(b) *With tricarbonylphenylcyclo-octatetraeneiron*. A solution of tetracyanoethylene (0·12 g, 0·90 mmol) and tricarbonylphenylcyclo-octatetraeneiron (0·28 g, 0·88 mmol) in methylene chloride (15 ml) was stirred (2 h) at room temperature. The product slowly precipitated and was recrystallised from methylene chloride–hexane to give yellow *crystals* of (VII) (0·30 g, 76%), m.p. 120° dec. (Found: C, 61·3; H, 2·6; N, 12·3. $C_{23}H_{12}N_4O_3Fe$ requires C, 61·6; H, 2·7; N, 12·5%), $\nu_{max.}$ (cyclohexane) 2070s, 2016s, and 2009s cm^{-1}. The mass spectrum showed peaks at *m/e* 320 (1%, *P* − C_6N_4), 292 (21%, *P* − C_6N_4 − CO), 264 (69%, *P* − C_6N_4 − 2CO), and 236 (83%, *P* − C_6N_4 − 3CO).

(c) *With tricarbonylbromocyclo-octatetraeneiron*. A solution of tetracyanoethylene (0·07 g, 0·93 mmol) and tricarbonylbromocyclo-octatetraeneiron (0·30 g, 0·93 mmol) in methylene chloride (25 ml) was stirred (½ h) at room temperature. The solvent was removed *in vacuo* and the residue recrystallised from methylene chloride–hexane to give yellow *crystals* of (VIII) (0·34 g, 81%) (Found: C, 45·9; H, 1·8; N, 12·3. $C_{17}H_7N_4O_3BrFe$ requires C, 46·0; H, 1·6; N, 12·4%, $\nu_{max.}$ (CH_2Cl_2) 2089s and 2028s,br cm^{-1}. The mass spectrum only showed peaks corresponding to the fragmentation of C_8H_7Br.

(d) *With tricarbonyl*(*triphenylmethyl*)*cyclo-octatetraeneiron*. A solution of tetracyanoethylene (0·03 g, 0·25 mmol) and tricarbonyl(triphenylmethyl)cyclo-octatetraeneiron (0·125 g, 0·26 mmol) in methylene chloride (15 ml) reacted similarly to give pale yellow *crystals* of (IX) (0·12 g, 75%), m.p. 170° dec. (Found: C, 69·9; H, 3·7; N, 9·2. $C_{36}H_{22}N_4O_3Fe$ requires C, 70·0; H, 3·6; N, 9·3%), $\nu_{max.}$ (CH_2Cl_2) 2076s and 2016s,br. The mass spectrum showed peaks at *m/e* 432 (0·8%, *P* − C_6N_4 − CO), 404 (19%, *P* − C_6N_4 −

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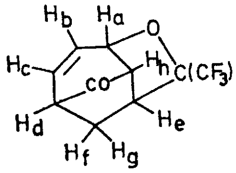
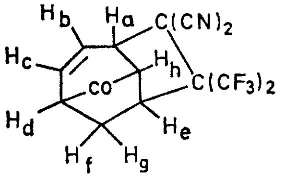
2CO), and 376 (3%, $P - C_6N_4 - 3CO$). The low solubility precluded n.m.r. measurements.

Reaction of 1,1-*Dicyano*-2,2-*bis*(*trifluoromethyl*)*ethylene with Tricarbonyl*(*triphenylmethyl*)*cyclo-octatetraeneiron*.— Reaction (24 h, room temperature) of 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (0·20 g, 0·93 mmol) and tricarbonyl(triphenylmethyl)cyclo-octatetraeneiron (0·20 g, 0·86 mmol) in hexane (15 ml) gave from methylene chloride–hexane pale yellow *crystals* of (XI) (0·15 g, 25%), m.p. 210° dec. (Found: C, 61·7; H, 3·6; N, 3·7; Fe, 7·7. $C_{36}H_{22}F_6N_2O_3Fe$ requires C, 61·7; H, 3·2; N, 3·7; Fe, 8·0%), $\nu_{max.}$ (cyclohexane) 2068s, 2013s, and 2003s cm^{-1}. The mass spectrum showed peaks at *m/e* 700 (1%, *P*), 672 (1%, *P* — CO), 644 (4%, *P* — 2CO), and 616 (100%, *P* — 3CO). The low solubility precluded ^{1}H n.m.r. measurements.

Reaction of Carbon Monoxide with Complex (I).—A solution of (I) (0·05 g, 0·13 mmol) in methylene chloride (20 ml) contained in a stainless-steel autoclave (100 ml, glass liner) under a pressure (100 atm) of carbon monoxide was heated (60°) for 24 h. The reaction mixture was filtered and the solvent removed *in vacuo*. The residue was recrystallised (−78°) from hexane to give white *crystals* of (XII) (0·03 g, 84%), m.p. 87° (Found: C, 46·4; H, 3·0; F, 39·6. $C_{11}H_8F_6O_2$ requires C, 46·7; H, 2·8; F, 39·9%), $\nu_{max.}$ (Nujol) 1778s (CO) cm^{-1}. The ^{1}H n.m.r. spectrum (CDCl$_3$) showed resonances at 3·76 (apparent t, 1H, H_c, J_{cb} 4·0 Hz, J_{cd} 3·8 Hz); 4·14 (d of d, 1H, H_b, J_{bc} 4·0 Hz, J_{ba} 2·0 Hz), 4·66 (m, 1H, H_a, J_{ah} 3·0 Hz), 6·72 (complex m, 2H, H_e and H_h), 7·16 (m, 1H, H_d, J_{dc} 3·8 Hz), and 7·62 (m, 2H, H_f, and H_g). These assignments were supported by double irradiation experiments. The ^{19}F n.m.r. spectrum (CDCl$_3$) showed resonances at 68·7 p.p.m. (q, J_{FF} 10·0 Hz) and 77·5 p.p.m. (q, J_{FF} 10 Hz). The mass spectrum showed peaks at *m/e* 286 (28·4%, *P*) and 258 (36·6%, *P* — CO).

Reaction of Carbon Monoxide with Complex (II).—Similarly reaction of (II) (0·30 g, 0·67 mmol) in methylene chloride (20 ml) with carbon monoxide (100 atm/60°) gave after recrystallisation (−78°) from hexane white *crystals* of (XIII) (0·15 g, 67%), m.p. 115—116° (Found: C, 50·3; H, 3·1; N, 9·0. $C_{14}H_8F_6N_2O$ requires C, 50·1; H, 2·4; N, 8·5%), $\nu_{max.}$ (Nujol) 3050w, 2964w, 2931w, 2860w, 1769m(CO), 1452w, 1420w, 1388w, 1359m, 1349m, 1275s, 1250s, 1219s, 1145s, 1116s, 1090s, 1057s, 1027s, 1014s, 983s, 937m, 925m, 915m, 892m, 881m, 863m, 857sh, 819m, 810sh, 790m, 758, 751s, 738s, and 714s cm^{-1}. The ^{1}H n.m.r. spectrum (CDCl$_3$) showed resonances at 3·64 (apparent t, 1H, H_c, J_{cb} 4·5 Hz, J_{cd} 3·5 Hz), 4·18 (d of d, 1H, H_b, J_{bc} 4·5 Hz. J_{ba} 2·0 Hz), 5·78 (m, 1H, H_a), 6·72 (m, 2H, H_c and H_h), 7·24 (m, 1H, H_d), and 7·48 (m, 2H, H_f, and H_g).





Double irradiation experiments support these assignments. The ^{19}F n.m.r. spectrum (CDCl$_3$) showed resonances at 61·1 p.p.m. (q, J_{FF} 13·0 Hz) and 66·9 p.p.m. (q, 13·0 Hz). The mass spectrum showed peaks at *m/e* 334 (100%, *P*) and 306 (85%, *P* — CO).

Reaction of Nitric Oxide with Complex (I).—An excess of nitric oxide (0·5 mmol) was condensed (−196°) into a Carius tube containing a solution of (I) (0·10 g, 0·55 mmol) in hexane (10 ml). After 4 h at room temperature the volatile products were removed *in vacuo*. Chromatography of the residue on a Florisil-packed column gave on elution with methylene chloride white *crystals* of (XII) (0·03 g, 42%).

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