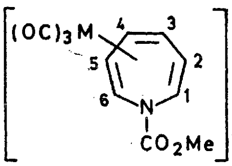
Reactions of Co-ordinated Ligands. Part 15.[1] The Cycloaddition of Electronegatively Substituted Unsaturated Systems to Tricarbonyl(η-*N*-methoxycarbonyl-1*H*-azepine)-iron and -ruthenium and Tricarbonyl(η-cyclohepta-2,4,6-trien-1-one)iron

By **Michael Green,* Susan M. Heathcock,** and **Terence W. Turney,** Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS
D. Michael P. Mingos, Department of Chemistry, Queen Mary College, University of London, London E1 4NS

Hexafluoroacetone, tetracyanoethylene, and 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene form *exo*-1,3 adducts with tricarbonyl(η-cyclohepta-2,4,6-trien-1-one)iron and tricarbonyl(η-*N*-methoxycarbonyl-1*H*-azepine)-iron and -ruthenium. A 1,6 adduct is also obtained with the azepineiron system. Deuteriation experiments show that the unco-ordinated double bond is the initial site of electrophilic attack. The 1,3-tetracyanoethylene adduct of the cycloheptatrienoneiron complex readily isomerises to a 1,5 adduct in solution. The generally accepted dipolar mechanism for these cycloaddition reactions is critically assessed and an alternative concerted reaction path is presented.

THERE is now a substantial body of experimental evidence showing that cycloaddition reactions of co-ordinated olefins give rise to different products to those derived from the free olefin. In general, unco-ordinated 1,3-dienes react with electrophiles to afford the $[\pi^4s + \pi^2s]$ cycloadducts. However, these are not the major products in the corresponding reactions of co-ordinated polyolefins, although they may be present in minor amounts.



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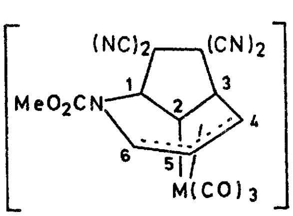
(1b) M = Fe



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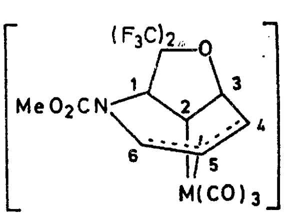

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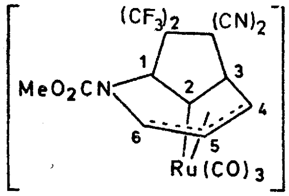

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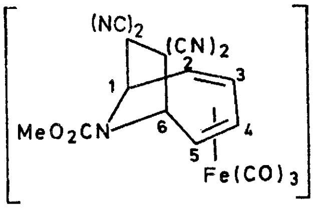

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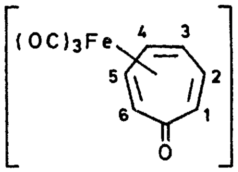

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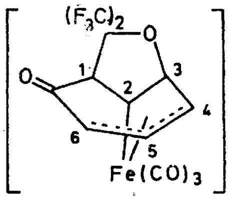

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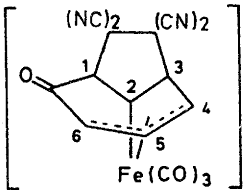

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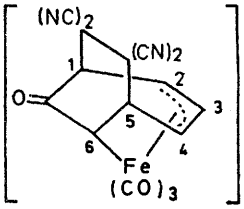

(9)

In the case of the reactions of cycloheptatriene and various cyclo-octatetraenes co-ordinated to an $Fe(CO)_3$ unit with, for example, tetracyanoethylene, the major product is usually the *exo*-1,3-adduct, with the metal bonding *via* a 1,2,3,5-η unit.[2] Previously, it has been assumed that the mechanism of these cycloaddition reactions is not concerted, but involves a dipolar intermediate.

In order to obtain a better insight into the stereospeci-

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[1] Part 14, M. Green, and R. P. Hughes, *J.C.S. Dalton*, 1976, 1907.

[2] M. Green, S. M. Heathcock, and D. C. Wood, *J.C.S. Dalton*, 1973, 1564.

ficity and regioselectivity of these reactions, the reactions of tricarbonyl(η-*N*-methoxycarbonyl-1*H*-azepine)-ruthenium and -iron, (1a) and (1b), and of tricarbonyl(η-cyclohepta-2,4,6-trien-1-one)iron, (VI), with a variety of electrophiles were examined. The initial goals were to establish the generality of these cycloaddition reactions, to obtain evidence for the initial site of attack of the electrophile, and to attempt to trap the dipolar intermediate (if formed). From these facts a more detailed mechanism would be at hand.

RESULTS

Tricarbonyl(η-*N*-methoxycarbonyl-1*H*-azepine)ruthenium, (1a), prepared from $[Ru_3(CO)_{12}]$ and the corresponding azepine, reacted rapidly with tetracyanoethylene (0.5 h, room temperature) to afford pale yellow crystals of (2a). More extreme conditions were required for the reaction of (1a) with hexafluoroacetone (5 d, 80 °C) and 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (24 h, 80 °C), from which (3a) and (4), respectively, were obtained as white crystals. The composition of these products as 1 : 1 adducts was established by elemental analysis as well as by mass spectrometry in the case of (3a) and (4). [The mass spectrum of (2a) was like (1a).] The presence of an Ru(CO) moiety was suggested by the i.r. spectrum which exhibited ν(CO) bands at *ca.* 2 085 and 2 020br cm^{-1} and was confirmed by the sequential loss of three CO ligands in the mass-spectral fragmentation patterns of (3a) and (4).

Hydrogen-1 n.m.r. data [a]

Complex	OCH_3	δ 1	2	3	4	5	6	*J* 1, 2	1, 3	1,6	2, 3	2, 4	3, 4	3, 5	4, 5	4, 6	5, 6	Solvent
(1a)	3.74	6.34	5.04	3.52	5.26	4.76	5.88	9.0			9.0		8.0	1.2	4.0	1.2	7.0	$CDCl_3$
(1b)	3.76	6.45	5.02	3.5	5.02	4.44	5.98	9.0			8.0		8.0	1.0	4.0		6.0	$CDCl_3$ (−10 °C)
(2a)	3.80	5.23	2.0	4.64	5.17	4.89	7.05	6.5			9.5		6.5	2.0	6.5	2.0	7.5	$(CD_3)_2CO$
(2b)	3.71	5.26	2.02	4.51	5.10	4.53	7.12	6.0			9.5		6.5		6.5		7.5	$(CD_3)_2CO$
(3a)	3.80	4.94	1.90	4.96	4.76	4.02	7.1	8.0			8.0	2.0	6.0		6.0	1.0	8.0	$CDCl_3$
(3b)	3.80	4.96	1.8	4.96	4.7	3.78	7.12	8.0			8.0	2.0	6.0	2.0	6.5	1.0	8.0	$CDCl_3$
(4)	3.74	5.12	2.0	4.50	5.02	4.76	7.32	7.0			9.5	1.5	6.5		7.0	1.0	8.0	$(CD_3)_2CO$
(5)	3.71	5.75	4.00	5.95	5.95	4.00	5.75		8.8		7.5	1.6	4.5	1.6	7.5	8.8		$(CD_3)_2CO$
(7)		3.04	1.7	4.98	4.9	4.84	4.42	8.0			7.0	1.0	*b*		*b*	4.0	7.0	$CDCl_3$
(8)		4.00	2.18	4.85	5.43	5.75	4.76	5.9					10.7		7.5		9.1	$(CD_3)_2CO$ (−20 °C)
(9)		3.99	5.31	5.67	4.58	4.24	2.30	8.5		2.2	8.0	2.0	7.3		7.6		9.0	$(CD_3)_2CO$

[a] Chemical shifts are in p.p.m. relative to $SiMe_4$. Coupling constants are in Hz. [b] Second-order spectrum.

The ^1H n.m.r. spectra (see Table) of (2a), (3a), and (4) could be interpreted only in terms of the formation of *exo*-1,3-addition products of the co-ordinated azepine. In each case six resonances of equal intensity were observed in addition to the resonance at 3.74—3.80 (3H) p.p.m. characteristic of the N–CO–OC*H*$_3$ group. A detailed assignment of the resonances and the various coupling constants was facilitated by proton decoupling. The magnitudes of the parameters correlate well with those found for the 1,3-addition products of $[Fe(\eta^4\text{-}C_7H_8)(CO)_3]$ and $[Fe(\eta^4\text{-}C_8H_8)(CO)_3]$.[2] Although only the proton H^2 shows evidence of fluorine coupling in (3a) and (4), the orientation of the added hexafluoroacetone and 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene appear to be the same as that found in previous work [2] from comparison of the chemical shifts in these systems. The ^{19}F n.m.r. spectrum of (3a) showed two quartets of equal intensity in which the low-field resonance was considerably broadened, as expected for the two inequivalent CF_3 environments. Only one well defined peak occurred in the ^{19}F n.m.r. spectrum of (4), as a quartet split further by ^1H–^{19}F coupling to H^2. The second CF_3 resonance could not be allocated in this case.

The reaction of tricarbonyl(η-*N*-methoxycarbonyl-1*H*-azepine)iron, (1b), with tetracyanoethylene occurred more readily (0.5 h, room temperature) than with hexafluoroacetone (24 h, 80 °C) as was the case with the analogous ruthenium complex. In contrast to (1a), 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene failed to react with (1b) under a variety of conditions. The adduct (3b) was readily assigned as being a 1,3-addition product. The ^1H n.m.r. spectrum of (3b) was almost identical to that of (3a), but all the assignments were confirmed by double-resonance experiments. The ^{19}F n.m.r. was also similar in showing two quartets, one of which was broadened.

The reaction of (1b) with tetracyanoethylene was complicated. The pale yellow product formed was characterised as a 1 : 1 adduct by elemental analysis. However, the ^1H n.m.r. spectrum showed the presence of two isomers in the ratio of 1 : 6. From decoupling experiments and by comparison with the ruthenium analogue (2a), the minor component was formulated as the *exo*-1,3-addition product (2b). The major isomer, the 1,6 adduct (5), exhibited a much simpler spectrum, having only three resonances in addition to to the characteristic signal at 3.71 (3H) p.p.m., (N–CO–OC*H*$_3$). The parameters, calculated by standard methods, for an AA′XX′ system,[3] are given in the Table, the assignments being confirmed by decoupling. When the reaction of (1b) with tetracyanoethylene was carried out in benzonitrile solution rather than methylene chloride, the same product ratio of 1 : 6 was found, thus indicating that the reaction is not dependent on the dielectric constant of the medium.

Tricarbonyl(η-cyclohepta-2,4,6-trien-1-one)iron, (6), was much less reactive than either $[Fe(\eta^4\text{-}C_7H_8)(CO)_3]$ [2] or (1b). Slow reactions of (6) with tetracyanoethylene (12 h, room temperature) or hexafluoroacetone (36 h, 80 °C) afforded 1 : 1 adducts. The hexafluoroacetone adduct (7) exhibited a ^1H n.m.r. spectrum very similar to the 1,3-addition product of $[Fe(\eta^4\text{-}C_7H_8)(CO)_3]$.[2] The ^1H n.m.r. spectral assignments shown in the Table were supported by proton decoupling. By comparison of the chemical shifts of the bridgehead protons, H^1 and H^3, the *exo*-1,3-addition of

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[3] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon Press, Oxford, 1966, vol. 1, p. 392.

hexafluoroacetone occurs stereospecifically to give a product in which the orientation of the $(CF_3)_2C{\cdot}O$ bridge is the same as found previously. The values of the chemical shifts indicate that the C=O group in these tropone complexes exerts very little electron-withdrawing influence on the neighbouring atoms, a fact also borne out by the similarity of the ^1H n.m.r. spectra of (6) with $[Fe(\eta^4-C_7H_8)(CO)_3]$.[4,5] The ^{19}F n.m.r. spectrum of (7) was compatible with the other *exo*-1,3-hexafluoroacetone adducts mentioned above.

The structure elucidation of the tetracyanoethylene adduct (8) was complicated by the readiness with which this material underwent isomerisation, rapidly in acetone, nitromethane, and methanol, but more slowly in methylene chloride and benzene to afford (9). The use of acetone by Goldsmidt and Bakal [6] to isolate the tetracyanoethylene adduct of (6) was unfortunate as the initial product (8) was overlooked, thus resulting in an incorrect conclusion about the mode of cycloaddition. The ^1H n.m.r. spectrum of (8) was that expected for a 1,3 adduct. This was confirmed by proton decoupling, the ^{13}C n.m.r. spectrum (-60 °C), and by partial-deuteriation experiments. It is interesting to note that this is the only system among these 1,3-cycloaddition products in which coupling between H^2 and H^3 is not detectable (usually it is of the order of 7—10 Hz). The ^{13}C n.m.r. spectrum (-60 °C) of (8) shows among other features a resonance at high field (5.2 p.p.m.) due to a σ-Fe-*C* unit, and the inner carbon of an η^3-allylic unit at low field (99.7 p.p.m.) conclusively demonstrating that the co-ordination of the $Fe(CO)_3$ moiety is *via* a 1,2,3,5-η^4 system. The product (8) reacts with NR_2H, MeOH–$Na_2[CO_3]$, or refluxing MeOH to afford intractable brown species [containing $Fe(CO)_3$ units]. The isomerised material (9) also exhibited ^1H and ^{13}C n.m.r. spectra characteristic of a 1,2,3,5-η^4-bonded $Fe(CO)_3$ complex. From the proton-coupling sequence and chemical shifts, this product can be readily assigned as an *exo*-1,5-cycloadduct.

Both the reaction between (6) and tetracyanoethylene, and the isomerisation of (8) and (9), were followed in the cavity of an e.s.r. spectrometer. No evidence of appreciable free-radical formation was detected in either case.

In order to confirm the structural assignments of the tetracyanoethylene adducts (8) and (9) and to gain information as to the initial site of electrophilic attack, H^1 of (6) was partially deuteriated (41% ^2H by n.m.r.) by the method of Eisenstadt.[7] This resulted in a reduction in intensity and a broadening of the resonances at 4.00 (^1H) and 61.95 (^{13}C) p.p.m. in (8) and those of 3.99 (^1H) and 47.69 (^{13}C) p.p.m. in (9). This confirmed the previous assignments for H^1 in (8) and (9) and indicated that the initial site of attack was at the unco-ordinated double bond (1,2) rather than at the co-ordinated double bond (5,6) in (6).

DISCUSSION

From the present study, (1a), (1b), and (2) exhibit a high stereospecificity to form mainly *exo*-1,3-cycloaddition products with the electrophiles hexafluoroacetone, tetracyanoethylene, and 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene. This is consistent with previous work on the reactions of $[Fe(\eta^4-C_7H_8)(CO)_3]$ and $[Fe(\eta^4-C_8H_7R)(CO)_3]$ (R = H, Me, Br, or Ph).[2] In all the systems so far examined the structure of the adduct is such as to indicate that the electrophile only attacks the ring *exo* to the metal moiety. Such an *exo* approach is also found in the protonation of (6) with trifluoroacetic acid.[4] Thus, it seems highly probable that initial attack of the electrophile is at a ring carbon rather than the metal. Evidence for attack of tetracyanoethylene at a metal centre, *via* a one-electron transfer and a radical intermediate, has recently been presented.[8] However, in view of the *exo* attack, and the fact that we have not been able to detect a radical process in the reaction of (6) with tetracyanoethylene, we discount this possibility.

The stereospecificity of these cycloaddition reactions extends not only to the sites of attack on the ring, but also to the correlation of the attacking electrophile. For example, the reaction of hexafluoroacetone with (1a), (1b), (6), or $[Fe(\eta^4-C_7H_8)(CO)_3]$ occurs in a stereoselective manner such that the $(CF_3)_2C$ unit is always found in a position α, and the O in a position γ, to the NCO_2Me, C=O, or CH_2 groups. It has been observed that stereospecificity is not always retained in the reactions of certain co-ordinated cyclo-octatetraene ligands (*e.g.* C_8H_7Me and and C_8H_7Ph) with tetracyanoethylene.[9] However, these reactions are still regiospecific as the position of the substituent does not grossly alter the bonding characteristics of the resulting 1,3 adduct. Nevertheless, there are a few reactions with a different regioselectivity, in that 1,6 adducts are produced. Thus, the reaction of (1b) with tetracyanoethylene affords a mixture of the 1,6 and 1,3 adducts (6 : 1 ratio which is independent of the medium). It is interesting to note that uncomplexed *N*-ethoxycarbonyl-1*H*-azepine also undergoes 1,6 addition with nitrosobenzene and *trans*-diethylazidocarbonylate (in which zwitterionic intermediates are proposed).[10,11] Other examples are the highly reactive electrophiles *N*-phenyl-1,2,4-triazoline-3,5-dione and chlorosulphonyl isocyanate which add to $[Fe(\eta^4-C_8H_8)(CO)_3]$ in a 1,6 manner.[2,12] The latter two examples may alternatively be considered as 1,4-addition products to the unco-ordinated diene. The metal also has a profound effect on the regiospecificity of the reaction. This can be seen in the case of the reaction of (1a) with tetracyanoethylene where only the 1,3 cycloadduct is found. The recent report of the direct formation of the 1,5 adduct (9) from the reaction of tetracyanoethylene with (6) is incorrect (see above).[6]

The position of electrophilic attack has been established by labelling the unco-ordinated double bond in (6) with deuterium. As the reaction of labelled (6) results in the

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

[5] R. Burton, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1961, 594.

[6] Z. Goldsmidt and Y. Bakal, *Tetrahedron Letters*, 1976, 1229.

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[8] A. L. Balch, *J. Amer. Chem. Soc.*, 1976, **98**, 285.

[9] L. A. Paquette, S. V. Ley, S. Maiorara, D. F. Schneider, M. J. Broadhurst, and R. A. Boggs, *J. Amer. Chem. Soc.*, 1975, **97**, 4658.

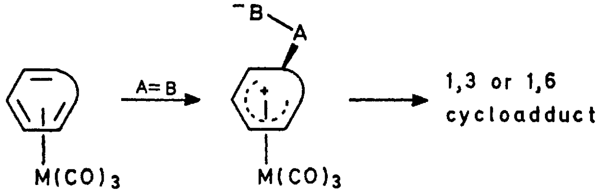
[10] W. S. Murphy and J. P. McCarthy, *Chem. Comm.*, 1968, 1155.

[11] W. S. Murphy and J. P. McCarthy, *Chem. Comm.*, 1970, 1129.

[12] L. A. Paquette, S. V. Ley, M. J. Broadhurst, D. Truesdell, J. Fayos, and J. Clardy, *Tetrahedron Letters*, 1973, 2943.

formation of (8) with the bridgehead position 1 labelled, the initial attack must occur directly at the unco-ordinated double bond rather than at a co-ordinated site with concurrent migration of the $Fe(CO)_3$ group to the free double bond during the reaction.

In view of the information now available about these cycloaddition reactions, any proposed mechanism must satisfactorily encompass the following points: (*i*) the reaction occurs on the *exo* surface of the ring,(*ii*) radical intermediates are not involved, (*iii*) the regiospecificity of the reaction is towards 1,3, and to a lesser extent 1,6 cycloaddition, and (*iv*) the initial attack is on an unco-ordinated double bond.

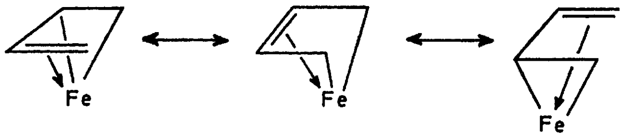


SCHEME 1

In a previous paper we proposed a mechanism to account for the cycloaddition of electrophiles to co-ordinated olefinic ligands. It was consistent with the above points and involved the initial formation of a transient dipolar intermediate (see Scheme 1). Here the intramolecular attack of the intermediate pentadienyl cation by the carbanion could account for the formation of either the *exo*-1,2, 1,3, 1,4, 1,5, or 1,6 cycloadducts. However, only the 1,3 and 1,6 adducts have been observed. There have been other reports where the cycloaddition of tetracyanoethylene to co-ordinated ligands was assumed to proceed through the intermediacy of dipolar species.[13,14] Such a mechanism is supported by the observation that cationic intermediates are often stabilised by complexation.[15,16] Dipolar mechanisms have been established for the electrophilic attack of tetracyanoethylene on several uncomplexed olefinic systems and there is a recent report of the interception with ethanol of a dipolar species derived from the cycloadduct of tetracyanoethylene with an activated olefin.[17,18]

However, there are problems associated with the assumption that a zwitterionic mechanism is the route to these cycloadducts, at least in some cases. For instance, it is known that the acetylation of the azepine ligand in $[Fe(\eta^4\text{-}C_6H_6NCO_2Et)(CO)_3]$ occurs at the 2 or 5 position [see (1b) for the numbering scheme].[19,20] Why then does the reaction of the electrophiles studies here proceed with attack exclusively at the 1 position? It is noted that the ratio of the tetracyanoethylene adducts (2b) and (5) is independent of the nature of the solvent. This is unexpected if the intermediate involves polar species. If a transient ion pair is formed then it must be very ' tight ' as repeated attempts to trap an intermediate zwitterion failed. It was shown previously that a mixture of *cis* and *trans* isomers (1 : 3) of 1,2-dicyano-1,2-bis(trifluoromethyl)ethylene reacts with $[Fe(\eta^4\text{-}C_7H_8)(CO)_3]$ such that the relative orientations of the CN and CF_3 groups about the central C–C bond of the electrophile are preserved in the adduct.[2] This was rationalized by assuming that the ring closure of the zwitterion occurred more rapidly than rotation about the central C–C bond of the reacting olefin.

Although all the experimental evidence presented so far can be used to support a non-concerted dipolar mechanism for cycloaddition, it may be more persuasive to argue that the mechanism of these reactions is a concerted cycloaddition. A concerted mechanism for the cycloaddition reactions described above immediately raises the problem of how to classify pericyclic reactions of organometallic complexes which involve both carbon–carbon and metal–carbon bond-making and -breaking processes. The ability of transition-metal complexes to alter the stereochemical course of organic pericyclic reactions has been recognised for several years; [21] however, theoretical discussions of this phenomenon have generally focused attention on the transformation of an orbitally ' forbidden ' process into an ' allowed ' one by the intervention of metal orbitals with the appropriate symmetry properties in the pericyclic transition state.[22-26] These approaches have relevance to a discussion of metal-catalysed processes but not to reaction paths of organometallic complexes, where the olefin remains strongly bonded to the metal throughout the course of the reaction.



(10)

We have found that the pericyclic transition states for cycloaddition reactions of metal–olefin complexes can be conveniently analysed using Woodward and Hoffmann's general topological rule [27] if the conventional bond

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[13] W. P. Giering and M. Rosenblum, *J. Amer. Chem. Soc.*, 1971, **93**, 5299.

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[22] F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, 1967, **89**, 2484.

[23] F. D. Mango, *Co-ordination Chem. Rev.*, 1975, **15**, 109.

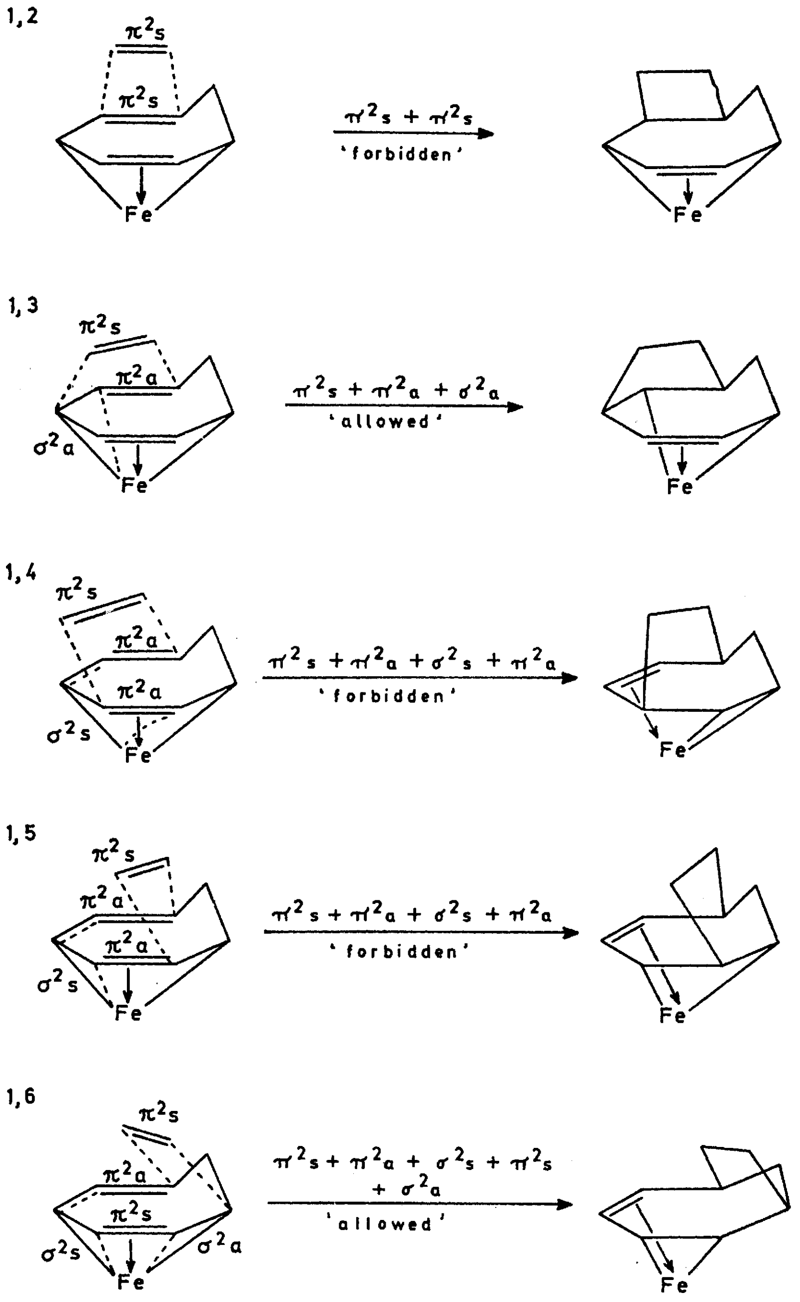
[24] R. G. Pearson, *J. Amer. Chem. Soc.*, 1972, **94**, 8387.

[25] M. J. S. Dewar, *Angew. Chem. Internat. Edn.*, 1971, **10**, 1761.

[26] W. Th. A. M. van der Lugt, *Tetrahedron Letters*, 1970, 2281.

[27] R. B. Woodward and R. Hoffmann, ' The Conservation of Orbital Symmetry,' Verlag Chemie–Academic Press, New York, 1969.

representations shown in (10) are used to describe the bonding in the metal–butadiene moiety. A perturbation molecular-orbital-theory analysis has suggested that the above resonance canonical forms may accurately represent the bonding in metal–butadiene complexes because of the even-alternant properties of the bonding networks generated by the butadiene *p*-orbitals and the metal d_π orbitals.[28]



Scheme 2

Scheme 2 illustrates how the canonical forms (10) may be used to describe the pericyclic transition states for 1,*n* (*n* = 2—6) cycloaddition paths of tricarbonyl(hexatriene)-iron in terms of Woodward and Hoffmann's topological notation. It is significant that only the 1,3- and 1,6-addition reactions are symmetry ' allowed ' according to the generalised Woodward–Hoffmann rule, *i.e.* have an odd number of total $(4q + 2)_s$ and $(4r)_a$ components.[27] This analysis therefore rationalises the observations that only 1,3- and 1,6-cycloaddition products are formed with cycloheptatriene, cyclo-octatetraene, azepine, and cyclohepta-2,4,6-trien-1-one metal tricarbonyl complexes but cannot predict the relative activation energies for the two allowed processes.

The topological analysis also cannot discriminate

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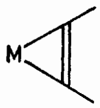
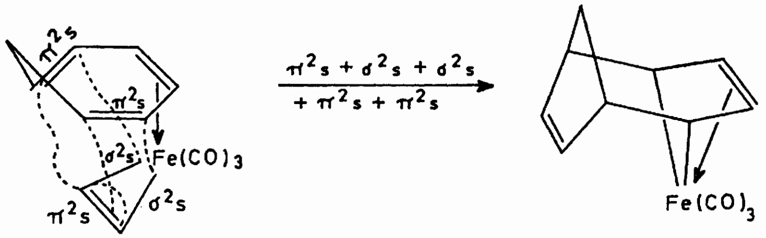
[28] D. M. P. Mingos, *J.C.S. Dalton*, 1977, 20, 26, 31.

between alternative *exo*- and *endo*-transition states. Differences in activation energy for these two possibilities probably arise from steric and secondary-orbital interactions.[27] Pettit and his co-workers [29] have elegantly



(11)

demonstrated that acetylenes will undergo an *endo*-1,6-cycloaddition reaction with tricarbonyl(η-cycloheptatriene)iron if they are first co-ordinated to the metal. This reaction may also be analysed in terms of the generalised Woodward–Hoffmann rule (see Scheme 3) if the conventional bond formula (11) is used to describe the co-ordinated acetylene moiety. The odd number of $(4q + 2)_s$ components clearly makes it an ' allowed process '.



SCHEME 3

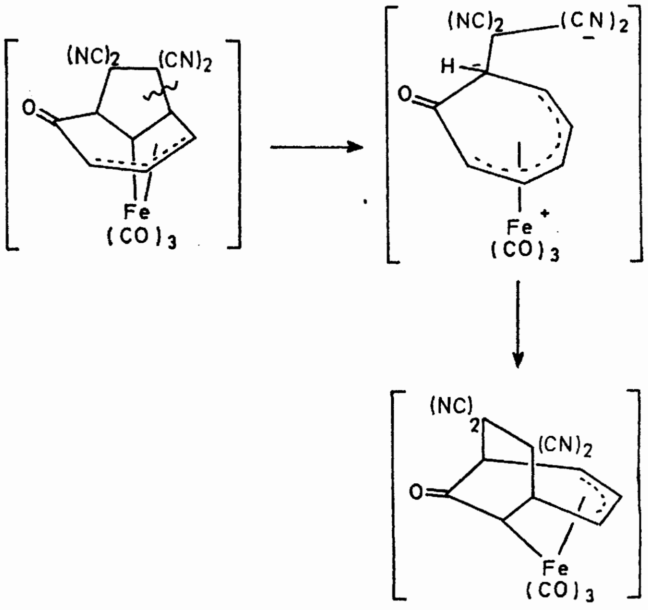
The pre-co-ordination of acetylene is achieved photochemically and under the conditions used for the cycloaddition reactions described in this paper an analogous process would not be accessible to the olefin dienophiles. In the absence of a pre-co-ordination step *exo* attack by the olefins on the metal–hexatriene complex is presumably more favourable on steric grounds.

The isomerisation of (8) to (9) is also of mechanistic interest. The sole reason that (8) can be isolated is that it is only sparingly soluble in the reaction medium and is thus an example of the kinetic stabilisation of a thermodynamically unstable product. In those more polar solvents in which (8) is soluble (acetone, nitromethane, and methanol), isomerisation occurs to afford the stable 1,5 adduct (9). No similar isomerisations of the 1,3 cycloadducts of tetracyanoethylene with $[Fe(\eta^4\text{-}C_8H_8)(CO)_3]$ or $[Fe(\eta^4\text{-}C_7H_8)(CO)_3]$ were detectable. The formation of a mixture of 1,3 and 1,6 adducts (2b) and (5) in the reaction of (1b) with tetracyanoethylene is not solvent dependent, and hence cannot be interpreted as a simple equilibrium mixture of the two isomers. Thus the isomerisation of (8) to (9) is presently unique.

One possible mechanism for the isomerisation reaction would involve carbon–carbon heterolysis and the formation of a pentadienyl zwitterionic intermediate of the kind considered in the 1,3- and 1,6-addition reactions (Scheme 4). Subsequent ring closure would afford the thermodynamically controlled product (9). However, if the ionic mechanism for the original 1,3-cycloaddition reaction is correct, there is no ready explanation as to why the 1,5 adduct is not formed in the first place. This might imply that there are no dipolar intermediates in the cycloaddition reaction. An alternative explanation in line with the ideas developed above is that the isomerisation reaction is a concerted $\sigma^2s + \sigma^2a + \pi^2a$ ' allowed process ' (Scheme 5).

EXPERIMENTAL

Hydrogen-1 and ^{19}F n.m.r. spectra were recorded on a Varian HA100 spectrometer, proton-decoupled ^{13}C n.m.r. spectra on a JEOL JNM-PFT-100 spectrometer. Chemical shifts are quoted in p.p.m. downfield relative to $SiMe_4$ or $CFCl_3$. I.r. spectra were recorded on Perkin-Elmer 257 and 457 spectrometers. All the mass spectra were obtained at 70 eV on an MS 9 spectrometer.[*] *N*-Methoxycarbonyl-1*H*-azepine and tricarbonyl(η-cyclohepta-2,4,6-trien-1-one)iron were prepared by published methods.[3,30]



SCHEME 4

Synthesis of Tricarbonyl(η-N-*methoxycarbonyl*-1H-*azepine*)-*ruthenium*, (1a).—*N*-Methoxycarbonyl-1*H*-azepine (1.0 g,

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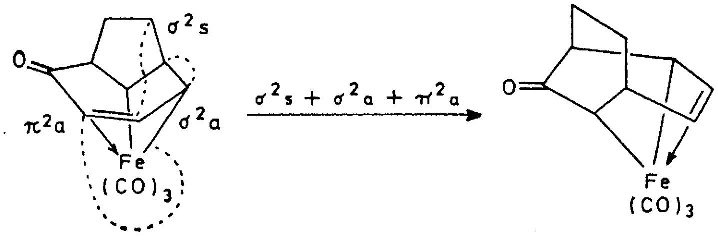
[*] Throughout this paper: 1 eV ≈ 1.60×10^{-19} J.

[29] R. E. Davis, T. A. Dodds, T.-H. Hseu, J. C. Wagnon, T. Devon, J. S. McKennis, and R. Pettit, *J. Amer. Chem. Soc.*, 1974, **96**, 7562.

[30] R. Cotton and W. Beach, *J. Org. Chem.*, 1964, **29**, 751.

6.63 mmol) and [$Ru_3(CO)_{12}$] (0.14 g, 0.22 mmol) were heated under reflux in cyclohexane (50 cm^3) under nitrogen for 18 h. After cooling and filtering to remove any unchanged [$Ru_3(CO)_{12}$], the solvent was removed *in vacuo*. Recrystallisation of the residue from hexane at 0 °C gave yellow crystals of (1a) (1.43 g, 64%), m.p. 109—110 °C (Found: C, 40.0; H, 3.1; N, 4.6. $C_{11}H_9FeNO_9$ requires C, 39.2; H, 2.7, N, 4.2%), ν(CO) (in hexane) at 2 068s, 2 006s, and 1 726m cm^{-1}. The mass spectrum showed peaks at *m/e* 337 (*P*, 15%), 309 (*P*—CO, 20%), 281 (*P*—2CO, 21%), and 253 (*P*—3CO, 30%).



SCHEME 5

Reactions of Complex (1a).—(a) *With hexafluoroacetone.* An excess of hexafluoroacetone (0.238 g, 1.43 mmol) was condensed into a Carius tube containing (1a) (0.10 g, 0.29 mmol) dissolved in hexane (10 cm^3). After 5 d at 80 °C the volatiles were removed *in vacuo* and the residue was recrystallised from acetone–water to give white *crystals* of (3a) (0.046 g, 29.8%), m.p. 170 °C (decomp.) (Found: C, 32.0; H, 1.8; F, 21.6; N, 2.9. $C_{14}H_9F_6NO_6Ru$ requires C, 32.4; H, 1.7; F, 22.0; N, 2.7%), ν(CO) (in hexane) at 2 082s, 2 081s, and 1 731 cm^{-1}. The mass spectrum showed peaks at *m/e* 502 (*P*, 3%), 474 (*P*—CO, 11%), 446 (*P*—2CO, 18%), and 418 (*P*—3CO, 31%). Fluorine-19 n.m.r. resonances occurred at 71.70 [q, 3F, ^4J(FF) 10 Hz] and 76.76 p.p.m. (q, 3F).

(b) *With* 1,1-*dicyano*-2,2-*bis*(*trifluoromethyl*)*ethylene*. Equimolar quantities of (1a) (0.10 g, 0.29 mmol) and 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene (0.06 g, 0.28 mmol) were heated under reflux in benzene (20 cm^3) for 24 h. After removal of the solvent *in vacuo* the residue was extracted with light petroleum (b.p. 40—60 °C). On recrystallising from light petroleum white *crystals* of (4) were obtained in 55% (0.09 g) yield, m.p. 140° C (decomp.) (Found: C, 38.0; H, 1.6; F, 22.0; N, 7.7. $C_{17}H_9F_6N_3O_5Ru$ requires C, 38.9; H, 1.7; F, 22.9; N, 8.0%), ν(CO) at 2 088s, 2 027s, br, and 1 739 cm^{-1} (in light petroleum). The mass spectrum showed peaks at *m/e* 550 (*P*, 1%), 522 (*P*—CO, 7%), 494 (*P*—2CO, 17%), and 466 (*P*—3CO, 12%). Only one ^{19}F n.m.r. resonance occurred at 59.0 p.p.m. [q, ^4J(FF) 12 Hz].

(c) *With tetracyanoethylene.* A solution of equimolar quantities of (1a) (0.05 g, 0.15 mmol) and tetracyanoethylene (0.019 g, 0.15 mmol) in methylene chloride (10 cm^3) was stirred at room temperature for 0.5 h. The product slowly precipitated and was recrystallised from methylene chloride–hexane at 0 °C to afford pale yellow *needles* of (2a) (0.018 g, 26%), m.p. 164 °C (decomp.) (Found: C, 43.2; H, 2.0; N, 16.0. $C_{17}H_{19}N_5O_5Ru$ requires C, 44.0; H, 1.9; N, 15.1%), ν(CO) at 2 081s, 2 026s, br, and 1 735m cm^{-1} (in CH_2Cl_2). The mass spectrum corresponded to that of (1a).

Synthesis of Tricarbonyl(η-N-*methoxycarbonyl*-1H-*azepine*)*iron*, (1b).—*N*-Methoxycarbonyl-1*H*-azepine (2.05 g, 13.6 mmol) was stirred for 12 h with an excess of [$Fe_2(CO)_9$] (6.0 g, 16.5 mmol) in hexane (20 cm^3). The solution changed from orange to red during the course of the reaction. After filtering off any unchanged [$Fe_2(CO)_9$], the solvent was removed *in vacuo* and the residue was recrystallised from hexane at 0 °C to afford bright yellow *crystals* of (1b) (2.09 g, 53%), m.p. 90—92 °C (Found: C, 41.9; H, 3.2; N, 4.7. $C_{11}H_9FeNO_5$ requires C, 41.6; H, 3.1; N, 4.1%), ν(CO) at 2 053s, 1 993s, 1 980s, and 1 735m cm^{-1} (in hexane). The mass spectrum showed peaks at *m/e* 263 (*P*—CO, 24%), 235 (*P*—2CO, 32%), and 207 (*P*—3CO, 28%).

Reactions of Complex (1b).—(a) *With hexafluoroacetone.* An excess of hexafluoroacetone (0.56 g, 3.37 mmol) was condensed into a Carius tube containing a solution of (1b) (0.2 g, 0.68 mmol) in benzene (10 cm^3). After 24 h at 80 °C the volatiles were removed *in vacuo* and the residue was recrystallised from methylene chloride–hexane to afford pale yellow *crystals* of (3b) (0.12 g, 38%), m.p. 111 °C (Found: C, 37.0; H, 2.1; F, 26.3. $C_{14}H_9F_6FeNO_6$ requires C, 36.8; H, 2.1; F, 26.4%), ν(CO) at 2 007s, 2 069s, and 1 737m cm^{-1} (in CS_2). The mass spectrum showed peaks at *m/e* 457 (*P*, 10%), 429 (*P*—CO, 11%), 401 (*P*—2CO, 71%), and 373 (*P*—3CO, 51%). Fluorine-19 n.m.r. resonances occurred at 71.65 [q, 3F, ^4J(FF) 10 Hz] and 76.80 p.p.m. (q, 3F).

(*b*) *With Tetracyanoethylene.* A solution of equimolar quantities of (1b) (0.049 g, 0.017 mmol) and tetracyanoethylene (0.021 6 g) in methylene chloride (10 cm^3) was stirred at room temperature for 0.5 h. The product slowly precipitated and was recrystallised from methylene chloride–hexane at 0 °C to afford pale yellow *crystals*, a mixture of (2b) and (5) (0.02 g, 28%) (Found: C, 48.6; H, 2.1; N, 16.9. $C_{17}H_9FeN_5O_5$ requires C, 48.7; H, 2.2; N, 16.7%), ν(CO) at 2 078s, 2 019m (sh), 2 015s, br, and 1 727m cm^{-1} (in CH_2Cl_2). The mass spectrum displayed a fragmentation pattern identical to that of (1b).

Reactions of Tricarbonyl(η-*cyclohepta*-2,4,6-*trien*-1-*one*)-*iron*, (6).—(*a*) *With hexafluoroacetone.* An excess of hexafluoroacetone (0.46 g, 2.88 mmol) was condensed into a Carius tube containing a solution of (6) (0.1 g, 0.43 mmol) in a hexane-benzene solution (10 cm^3). After 36 h at 80 °C the volatiles were removed *in vacuo* and the residue was recrystallised from hexane at —78 °C to afford white *crystals* of (7) (0.06 g, 35.8%), m.p. 119 °C (decomp.) (Found: C, 37.9; H, 1.8; F, 27.5. $C_{13}H_6F_6FeO_5$ requires C, 37.9; H, 1.5; F, 27.7%), ν(CO) at 2 081s, 2 026s, 2 017s, and 1 715m cm^{-1} (in hexane). The mass spectrum showed peaks at *m/e* 412 (*P*, 1%), 384 (*P*—CO, 11%), 356 (*P*—2CO, 50%), and 328 (*P*—3CO, 23%). Fluorine-19 n.m.r. resonances occurred at 69.0 (q, 3F) and 76.0 p.p.m. [dq, 3F, ^4J(FF) 10.0 Hz].

(*b*) *With tetracyanoethylene.* A solution of tetracyanoethylene (0.043 g, 0.34 mmol) in methylene chloride (10 cm^3) was added to a solution of (6) (0.084 g, 0.34 mmol) in methylene chloride (5 cm^3) and the mixture was stirred at room temperature for 12 h. The product which slowly precipitated was collected and recrystallised from methylene chloride–hexane at 0 °C to afford pale yellow crystals of (8) (0.053 g, 42%), m.p. 110 °C (decomp.) (Found: C, 51.6; H, 1.6. $C_{14}H_6FeN_4O_4$ requires C, 51.3; H, 1.6%), ν(CO) at 2 090s, 2 034m,br, and 1 692w cm^{-1} (in CH_2Cl_2). The mass spectrum only showed peaks similar to (6). Carbon-13 n.m.r. resonances (−60 °C, [$^2H_6$]acetone) appeared at 5.16, (C^2), 61.95, (C^1), 65.10, 57.15, 73.17, (C^3, C^4, and C^6), and 99.74 p.p.m. (C^5).

Isomerisation of Complex (8) *to* (9).—A slurry of (8) (0.25 g) in acetone (10 cm^3) was stirred at 30 °C for 2 d, whereupon the solid had completely dissolved. Addition of hexane (50 cm^3) resulted in the precipitation of (9) as a yellow powder, m.p. 144—146 °C (Found: C, 51.7; H, 1.8; N, 14.7. $C_{16}H_6FeN_4O_4$ requires C, 51.3; H, 1.6; N, 15.0%), ν(CO) at 2 090s, 2 030m,br, and 1 683w cm^{-1} (in CH_2Cl_2). Carbon-13 n.m.r. resonances (20 °C, [$^2H_6$]acetone) occurred at 17.11 (C^6), 47.69 (C^1), 45.93, 52.60, 57.09 (C^2, C^4, and C^5), and 96.29 p.p.m. (C^3).

Reaction of Tricarbonyl(η-2-*deuteriocyclohepta*-2,4,6-*trien*-1-*one*)*iron with Tetracyanoethylene.*—Using the method of Eisenstadt *et al.*,[7] (6) was monodeuteriated predominantly at position 1 (see diagrams) (41%) and to a much lesser extent (*ca.* 4%, by ^{1}H n.m.r.) at position 6. The deuteriated (6) was treated with an equimolar amount of tetracyanoethylene as above to afford monodeuteriated (8). The ^{1}H n.m.r. resonance (−20 °C, [$^2H_6$]acetone) at 4.00 p.p.m. decreased in intensity and the resonance at 2.18 p.p.m. collapsed to a broad singlet, while the ^{13}C n.m.r. resonance (−60 °C) at 61.95 p.p.m. became very broad and less intense. After standing for 2 d at room temperature, the ^{1}H n.m.r. resonance at 3.99 p.p.m. had decreased in intensity with the resonances at 2.30 and 5.31 p.p.m. broadening relative to an undeuteriated sample. The ^{13}C n.m.r. resonance at 47.69 p.p.m. disappeared.

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[6/1401 *Received*, 16*th July*, 1976]