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REACTIONS OF COORDINATED CYCLIC POLYOLEFINS *. A KINETIC STUDY OF THE PERICYCLIC [3,3]-SIGMAHAPTOTROPIC REARRANGEMENT

ZEEV GOLDSCHMIDT*, HUGO E. GOTTLIEB and DRORA COHEN

Department of Chemistry, Bar-Ilan University, Ramat-Gan 52100 (Israel)

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Summary

The reaction of tricarbonyl(tropone)iron with tetracyanoethylene (TCNE) was reinvestigated. Two primary cycloadducts, the 3 + 2 and 4 + 2 isomers are formed in a 96/4 ratio. The second order rate constant for the reaction is k 4.4×10^{-2} M^{-1} s^{-1} (at 24°C, in acetone) with a free activation energy of $\Delta G^{\#}$ 19.2 kcal mol^{-1}. The 3 + 2 cycloadduct undergoes a facile sigmahaptotropic rearrangement to the formal 5 + 2 adduct with rate constants of k 3.8×10^{-4} s^{-1} (24°C, acetone) and k 5.1×10^{-4} s^{-1} (24°C, methanol), and with activation parameters $\Delta H^{\#}$ 20 kcal mol^{-1} and $\Delta S^{\#}$ -7 e.u. (acetone). The kinetic results suggest that both the cycloaddition and the rearrangment are concerted, nonsynchronous, one-step reactions, involving a slightly polar transition state. Frontier molecular orbital considerations imply that the 3 + 2 and 4 + 2 cycloadditions are symmetry allowed reactions. The structural reorganization which takes place in the [3,3]-sigmahaptotropic rearrangement suggests that the metal migration proceeds by way of a Berry pseudorotation, and the simultaneous 1,3-sigmatropic shift occurs with configuration retention at the migrating carbon. A detailed molecular orbital analysis of the rearrangement is given.

Introduction

In 1976, we reported the isolation and characterization of the first 5 + 2 adduct of (tropone)$Fe(CO)_3$ (I) with tetracyanoethylene (TCNE) [2] (eq. 1). This was followed by a similar preparation of the 5 + 2 adducts of I with *N*-phenyl- [3] and *N*-methyltriazolinedione [4] (eq. 1). Concurrently, Green et al. [5] made the important observation that the primary product of the TCNE reaction is actually the kinetically labile 3 + 2 cycloadduct which rearranges rapidly in polar solutions to the stable 5 + 2 complex. The mechanism of this unprecedented rearrangement has not been elucidated, although both two-step dipolar and concerted pathways were

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* For previous paper in this series see ref. 1.

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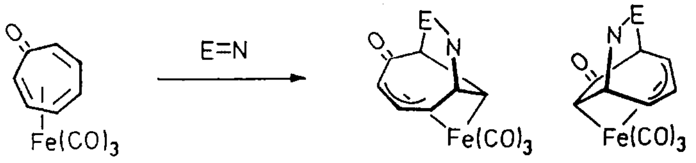
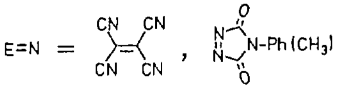
tentatively suggested [5].

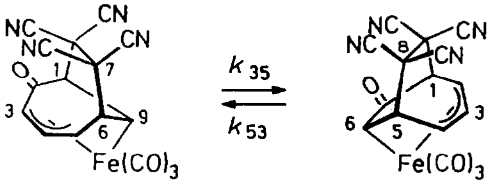


(I) '3+2' '5+2'

(1)

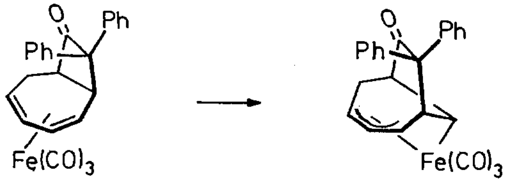


Our renewed interest in this unique isomerization, which leads to an equilibrium mixture in solution (vide infra) (eq. 2), stems from our recent discovery of two similar reactions: (a) The rearrangement of the cyclobutanone η^4-diene complex IV to the η^1,η^3-σ,π-allylic isomer V [6] (eq. 3), and (b) the rearrangement of the 3 + 2 adduct of (cycloheptatriene)Fe(CO)$_3$ with TCNE (VI) [7] to the formal 6 + 2 adduct



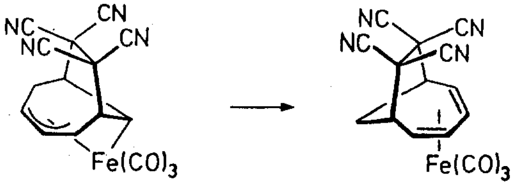
(II) (III)

(2)



(IV) (V)

(3)



(VI) (VII)

(4)

VII [8] (eq. 4). As may readily be seen, all three rearrangements involve both a carbon sigmatropic shift [9] and a metal haptotropic shift [10] across carbon skeletons of various lenghts. Thus, in eq. 2 the migrating carbon and the metal exchange bonding sites over a three carbon chain, in eq. 3 carbon–metal exchange takes place across a two carbon chain, whereas in eq. 4 a four carbon chain is implicated.

We term this new class of reactions sigmahaptotropic rearrangements, and define a sigmahaptotropic rearrangement of order $[j, j]$ as a pericyclic reaction whereby a σ bonded group and a coordinated ML_n unit exchange bonding sites antarafacially, across a chain of j atoms of a polyene complex.

In the present paper we present a detailed kinetic study of the reversible [3,3]-sigmahaptotropic rearrangement, II $\rightleftarrows$ III (eq. 2), which reveals that this process is concerted. We also reexamine the (tropone)$Fe(CO)_3$–TCNE cycloaddition reaction, and discuss the mechanistic features of the cycloaddition and the rearrangement in terms of orbital symmetry control.

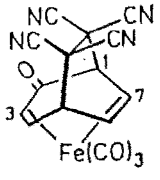
Results

Synthetic and structural considerations

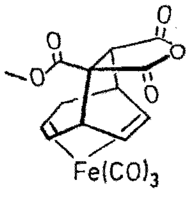
Since our kinetic studies were based upon ^1H NMR analysis it was important to have the full assignment of the resonances and the coupling constants of the various products. This has been difficult to achieve before [2,5] because of the low solubility of the adducts and the kinetic lability of the 3 + 2 complex II. In the present study use was made of high resolution 300 MHz FT NMR spectroscopy, which enabled the continuous monitoring of the reaction progress in dilute solutions.

The reaction of equimolar amounts of I and TCNE in $CHCl_3$ or CH_2Cl_2 is fast, as indicated by the almost immediate precipitation of the product. The reaction is essentially complete after 2 h when 0.1 *M* solutions of reactants are used. The ^1H NMR spectrum taken shortly after the product was dissolved in acetone-d_6 (ca. 4 min) revealed the presence of only two isomeric adducts II and VIII in a ratio of 96/4 respectively. The ^1H NMR spectrum of II (Table 1) is typical of 3 + 2 σ,π-allylic adducts [5–7], including the expected coupling constant (J 9.3 Hz) between the adjacent H(6) and H(9) protons which was overlooked before [5]. The specific proton assignments were confirmed by extensive decoupling experiments and by correlation with the corresponding carbon resonances (Table 2), using the off-resonance decoupling technique (Birdsall plots) [11].

Structural assignment of VIII, which could not be isolated, is based upon the ^1H NMR spectral data (Table 1). All four olefinic protons appear at relatively high field. This is characteristic of coordinated 1,4-diene systems, and has been observed in a similar 4 + 2 adduct IX whose structure was recently studied by us in detail [1]. Careful decoupling experiments confirmed the specific proton assignment.



(VIII)



(IX)

TABLE 1

^{1}H NMR DATA FOR TRICARBONYL(TROPONE)IRON-TCNE ADDUCTS ^{a}

Complex	Solvent	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	H(9)	J(CH) ^{b} (Hz)
II	$(CD_3)_2CO$	3.86	–	4.73	5.66	5.36	4.76	–	2.13	$J_{13}=J_{16}=1.5$, J_{19} 7.0,
	CD_3OD	3.70	–	4.60	5.46	5.04	4.47	–	1.94	J_{34} 9.5, J_{35} 1.0,
	$CDCl_3$	3.35	–	4.66	5.26	4.87	4.23	–	1.87	J_{45} 7.0, J_{46} 0.7,
										J_{56} 7.5, J_{59} 1.3
										J_{69} 9.3
III	$(CD_3)_2CO$	4.01	5.34	5.69	4.59	4.27	2.31	–	–	J_{12} 8.8, J_{13} 0.6,
	CD_3OD	3.82	5.07	5.52	4.37	4.04	2.22	–	–	J_{16} 2.2, J_{23} 7.3,
	$CDCl_3$	3.57	4.93	5.28	4.21	3.62	2.32	–	–	J_{24} 2.1, J_{34} 6.0,
										J_{35} 0.8, J_{45} 7.3,
										J_{46} 0.5, J_{56} 9.4
VIII	$(CD_3)_2CO$	4.12	–	3.23	3.86	5.17	4.55	3.73		$J_{13}=J_{16}=J_{57}=1.5$,
										J_{17} 7.7, J_{34} 7.8,
										J_{35} 0.7, J_{45} 8.7,
										J_{56} 7.6, J_{67} 6.3

^{a} δ ppm from TMS; numbering as in text. ^{b} Coupling constants were measured in $(CD_3)_2CO$.

TABLE 2

^{13}C NMR DATA FOR TRICARBONYL(TROPONE)IRON-TCNE ADDUCTS ^{a}

Complex		C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)
II	δ (ppm)	62.5	^{b}	73.5	100.3	65.2	58,0	^{b}	^{b}	5.8
	J(CH) (Hz)	140	–	165	170	175	150	–	–	160
III ^{c}	δ (ppm)	47.9	57.2	96.4	52.8	46.1	17.2	185.5	45.0 ^{d}	48.6 ^{d}
	J(CH) (Hz)	153	175	173	175	145	163	–	–	–

^{a} In acetone-d_6, δ ppm from TMS. ^{b} Not observed. ^{c} δ 110.5, 110.8, 112.0, 112.2 (4×CN), 203.2, 207.5, 210.5 (3×CO). ^{d} These assignments may be interchanged.

After 3 h at room temperature, an equilibrium mixture between II and III is established consisting of ca. 86% of III, which can be isolated by recrystallization [2]. During this time the amount of VIII decreases slowly, but because of its low concentration in the mixture we could not determine whether this is due to its rearrangement or slow decomposition. The ^{1}H and ^{13}C NMR spectra of III are essentially those reported previously [2,5]. The full assignment of the chemical shifts and coupling constants are given in Tables 1 and 2. We finally note that when the cycloaddition is conducted in $CDCl_3$ and the supernatant solution is examined after 17 h, both II and III are observed in a ratio of ca. 2/1 respectively, apparently indicating that III is less soluble than II in $CDCl_3$.

Kinetic studies

The reaction of (tropone)$Fe(CO)_3$ (I) with an equimolar amount of TCNE was conducted in acetone-d_6 at 24°C (ca. 60 mM solution) and followed by ^{1}H NMR spectroscopy (Fig. 1). The relative concentrations of I and the corresponding TCNE

TABLE 3

KINETIC DATA FOR THE CYCLOADDITION OF TRICARBONYL(TROPONE)IRON WITH TCNE

Solvent	T (K)	$10^3\,k$ ($M^{-1}\,s^{-1}$)	$\Delta G^{\#}$ (kcal mol^{-1})	$t_{1/2}$ [c] (min)
$(CD_3)_2CO$ [a]	297	44.1 ±2	19.21±0.04	6.3
CH_2Cl_2 [b]	298	6.44±0.24	20.43±0.02	

$\Delta H^{\#}$ 8.65±0.75 kcal mol^{-1}; $\Delta S^{\#}$ −39.5±3.0 e.u. (in CH_2Cl_2) [b]

[a] This work. [b] Taken from ref. 14. [c] $t_{1/2} = 1/kc_0$ (c_0 60 mM).

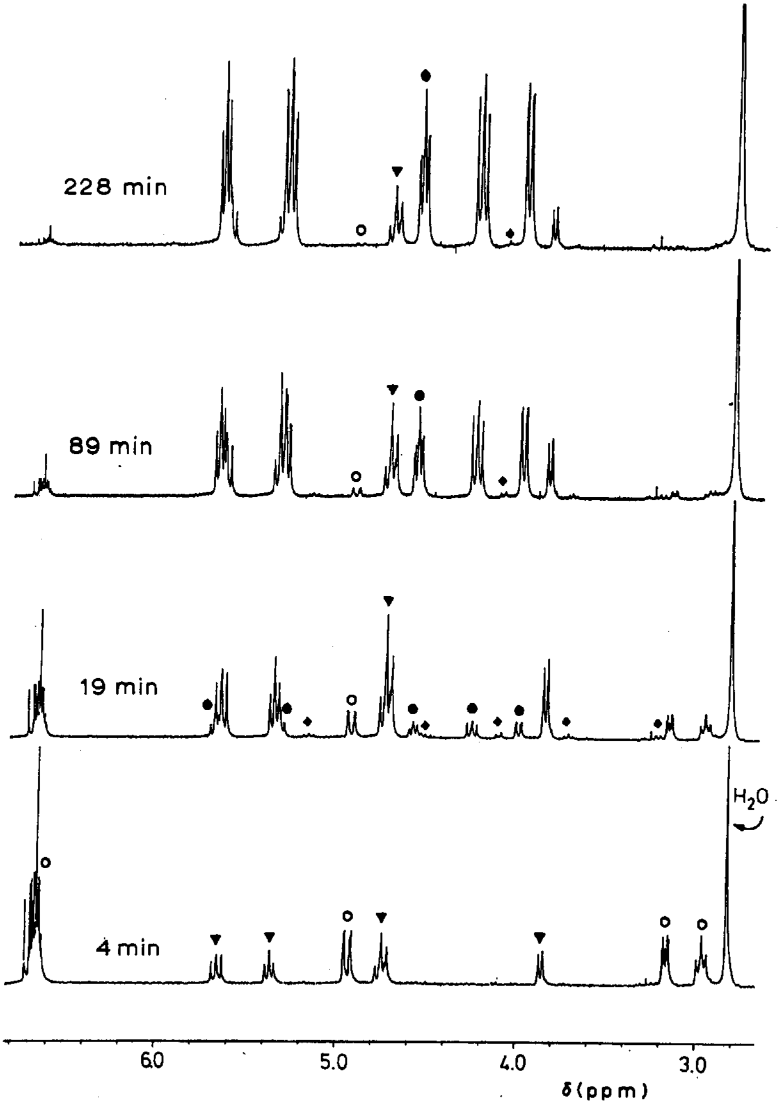


Fig. 1. Time-resolved ^1H NMR spectrum of tricarbonyl(tropone)iron–TCNE cycloaddition (in acetone-d_6). Signals of I (○), II (▼), III (●) and VIII (◆) between δ 2.8–6.8 ppm are shown. See Table 1 for the full signal assignment.

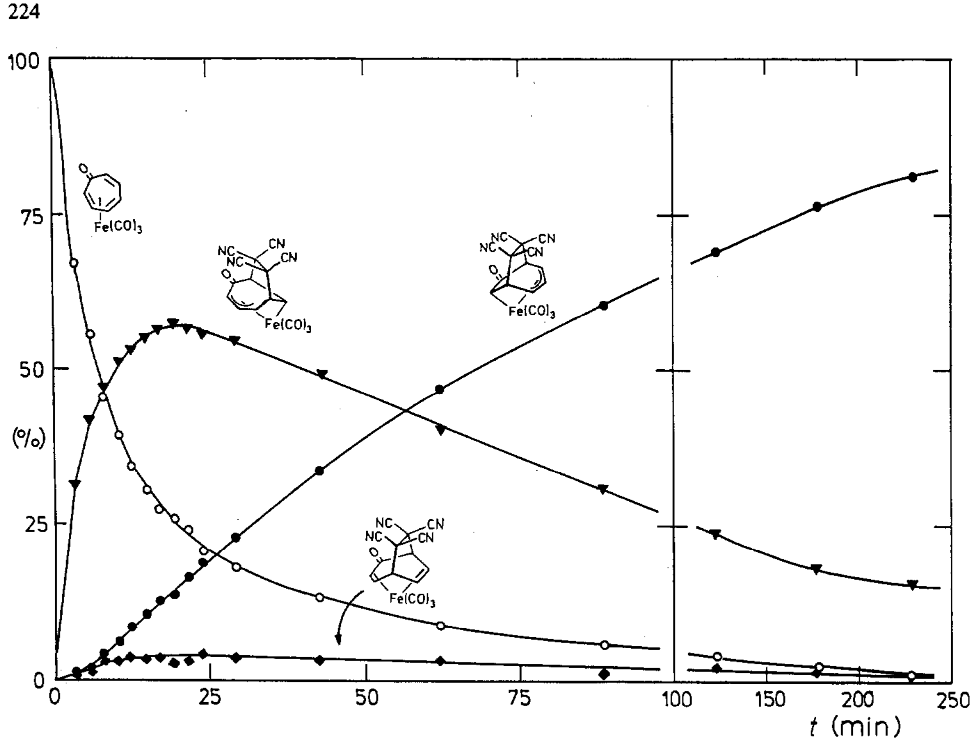


Fig. 2. Time-resolved progress of the 1:1 reaction of tricarbonyl(tropone)iron (I) with TCNE in acetone-d_6 (24°C). Plots of I (○), II (▼), III (●) and VIII (◆).

adducts II, III and VIII were determined from the integration of the appropriate proton signals. The time-resolved progress of the reaction is shown in Fig. 2. The second order rate constant for the reaction of I with TCNE, obtained from the slope of the plot of $1/c$ (c = concentration of I) vs. time [12a], and the activation parameters [13] are compared with kinetic data obtained previously by McArdle [14], in CH_2Cl_2 solutions by UV spectroscopy (Table 3).

The [3,3]-sigmahaptotropic rearrangement II ⇄ III (eq. 2) was studied in acetone-d_6 and methanol-d_4. Equilibrium can be reached by starting either from II or from recrystallized III; the kinetic data, however, were obtained starting from II. From

TABLE 4

KINETIC DATA FOR THE [3,3]-SIGMAHAPTOTROPIC REARRANGEMENT (II ⇄ III)

Solvent	T (K)	K [a]	$10^4\,k_{obs}$ [b] (s^{-1})	$10^4\,k_{35}$ [c] (s^{-1})	$\Delta G^{\#}$ (kcal mol^{-1})	$t_{1/2}$ [d] (min)
$(CD_3)_2CO$	283	7.0±0.5	0.66±0.03	0.58±0.03	22.03±0.04	199
	297	6.3±0.5	3.8 ±0.2	3.3 ±0.2	22.08±0.04	35
	305	5.9±0.5	9.4 ±0.5	8.0 ±0.5	22.19±0.04	14
CD_3OD	297	9.0±1.0	5.1 ±0.5	4.6 ±0.5	21.90±0.08	25

$\Delta H^{\#}$ 20±1 kcal mol^{-1}; $\Delta S^{\#}$ −7±3 e.u. (in aceton-d_6)

[a] $K = k_{35}/k_{53}$. [b] $k_{obs} = (k_{35} + k_{53})$. [c] $k_{35} = k_{obs}/(1 + 1/K)$. [d] $t_{1/2} = \ln 2/k_{35}$.

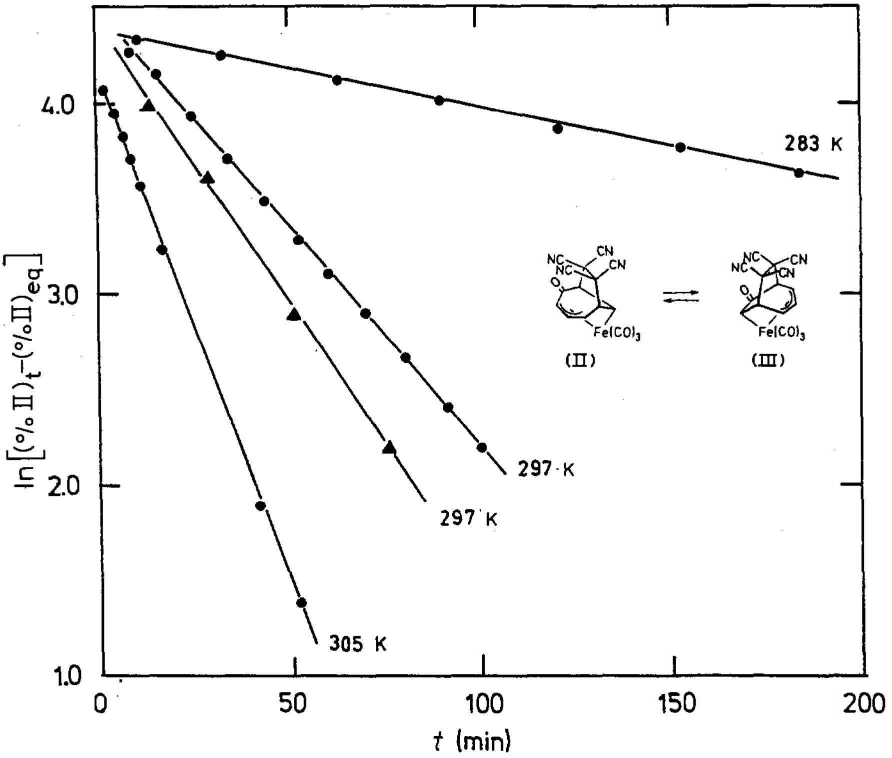


Fig. 3. Plot of ln[% II)$_t$ −(% II)$_{eq}$] vs. time at various temperatures in acetone-d_6 (●) and methanol-d_4 (▲).

the equilibrium constants $K = k_{35}/k_{53}$ between the two isomers II and III it is found that III is more stable than II by ΔG^0 1.1 in acetone, and by 1.3 kcal mol^{-1} in methanol (Table 4).

Addition of the powerful dienophile (carbomethoxy)maleic anhydride [1,15] to the isomeric mixture did not affect the rearrangement and no tropone complex (I) could be trapped. Therefore, a cycloreversion-addition mechanism can be excluded. The approach to equilibrium is thus a first order process with observed rate constant (k_{obs}) the sum of the constants for the forward and reverse direction, $k_{obs} = (k_{35} + k_{53})$ [12b]. The first order rate constants (k_{obs}) collected in Table 4 were derived from the slopes of the plots of ln[(% II)$_t$ − (% II)$_{eq}$] against time (Fig. 3), and the calculated rearrangement rate constants, $k_{35} = k_{obs}/(1 + 1/K)$, were then inserted in the Eyring equation to obtain the activation parameters [13].

Discussion

Cycloadditions

Of the five formally possible $n + 2$ ($n = 2$–6) cycloaddition reactions of (cycloheptatriene)Fe(CO)$_3$with uniparticulate electrophiles [16], the 3 + 2 reactions almost invariably predominate [3,5,7,14,17]. There are, however, two notable exceptions to this kinetic periselectivity: (cycloheptatriene)Fe(CO)$_3$ reacts with arylketenes to give cyclobutanones (e.g. IV) [6,17b], and with (carbomethoxy)maleic anhydride to give the 4 + 2 complex IX [1]. Both reactions are presumably concerted. Kinetic studies by McArdle [14] revealed that 3 + 2 cycloadditions with TCNE are also concerted, although the reaction rates of (cycloheptatriene)Fe(CO)$_3$ with TCNE increase slightly with solvent polarity. As we see from Table 3 this is also true for the reaction of I with TCNE, where $k_{\text{rel}} = k(\text{Me}_2\text{CO})/k(\text{CH}_2\text{Cl}_2) \simeq 6$ but the activation entropy ($\Delta S^{\#}$ -40 e.u.) is strongly negative [14].

The presence of adduct VIII in the initial reaction mixture suggests that the 4 + 2, like the 3 + 2 cycloaddition, is a symmetry-allowed [5] reaction. On the other hand, the absence of direct 5 + 2 and 6 + 2 adducts [5,8,17c] apparently indicates that these reactions are forbidden. The predominance of II is consistent with our previous prediction [1] that in the absence of secondary orbital interactions the 3 + 2 cycloadditions are expected to be preferred over the 4 + 2 reactions.

One way to explain these results is by invoking frontier molecular orbital theory. The major bonding between the organic ligand and the metal moiety is derived by interaction of the highest occupied (π_4) and lowest unoccupied (π_5) molecular orbitals of tropone [19] with the corresponding HOMO-LUMO $2e$ pair of the d^8

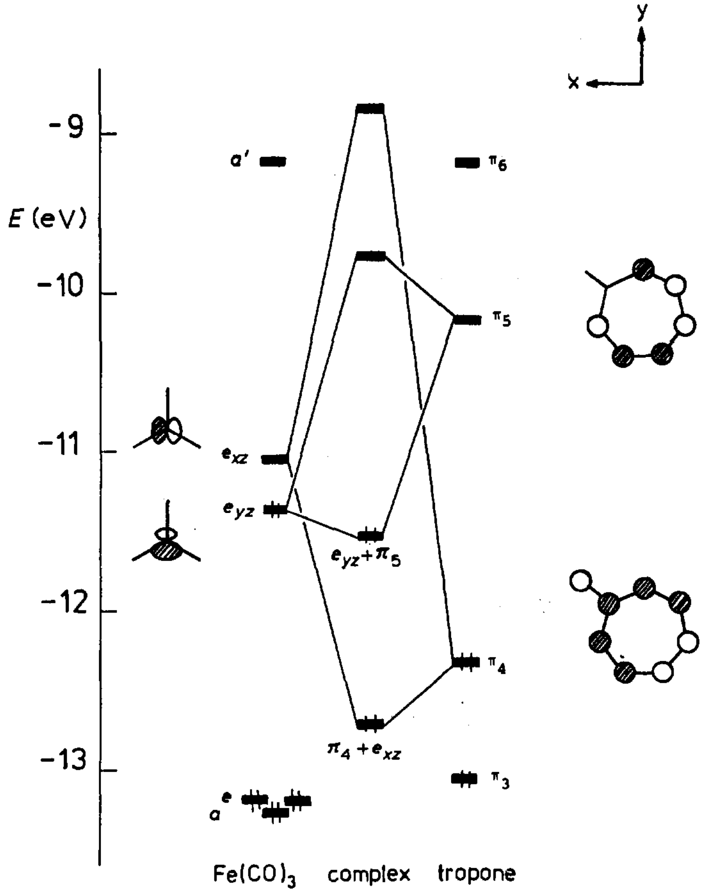


Fig. 4. Orbital interaction diagram for tricarbonyl(tropone)iron (I).

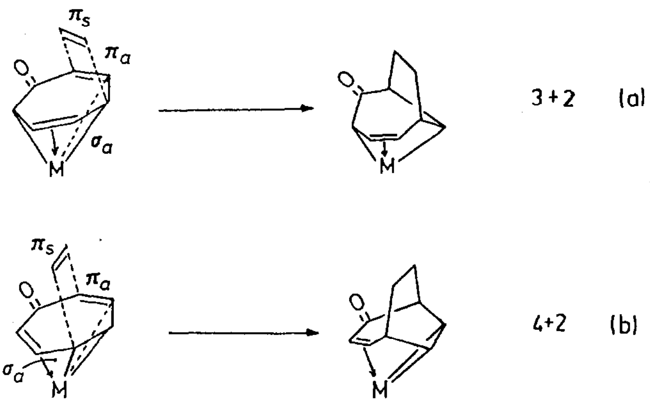
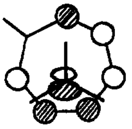


Fig. 5. Cycloadditions of tricarbonyl(tropone)iron (I) with uniparticulate electrophiles. Allowed [$(\pi 2a + \pi 2a) + \pi 2s$] (a) 3+2 and (b) 4+2 cycloadditions.

$Fe(CO)_3$ fragment [20]. Figure 4 shows the orbital interaction diagram of $Fe(CO)_3$ fragment with tropone, viewed along the z axis. The energy levels were computed by extended Hückel methods [21] (see Experimental section). Of the two bonding orbitals thus obtained, the higher $e_{yz} + \pi_5$ orbital X is mainly of metal character (backbonding orbital) while the lower $\pi_4 + e_{xz}$ orbital XI is essentially of organic ligand character. Therefore, orbital controlled cycloaddition reactions which occur at the organic site of the complex, opposite to the metal, are expected to be dominated by the subjacent orbital XI. It is thus the interaction of XI with the LUMO of uniparticulate electrophiles, shown in XII, which controls the observed periselectivity of the 3 + 2 and 4 + 2 cycloadditions.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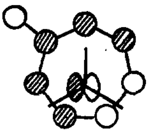
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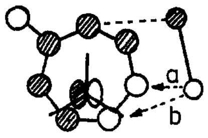


(XII) a, 3+2
b, 4+2

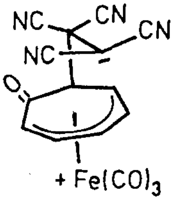
Alternatively, the extended Woodward–Hoffmann topological rules for organometallic pericyclic reactions [5] may be utilized to describe the allowed 3 + 2 and 4 + 2 reactions. This is shown in Fig. 5 where both cycloadditions appear as symmetry-allowed $(\pi 2a + \sigma 2a) + \pi 2s$ reactions [1].

The [3,3]-sigmahaptotropic rearrangement

Before we turn to the analysis of the pericyclic [3,3]-sigmahaptotropic rearrangement (eq. 2), a reaction in which an antarafacial carbon–metal exchange takes place across a three carbon skeleton, it is worthwhile to recall that the addition of (carbomethoxy)maleic anhydride [1,15] to the equilibrium mixture of II and III does not interfere with the rearrangement. The fact that no (tropone)$Fe(CO)_3$ (I) was intercepted by addition of this powerful dienophile clearly demonstrates that the rearrangement proceeds intramolecularly and not via a consecutive cycloreversion–addition mechanism.

Having established the intramolecular nature of the sigmahaptotropic rearrangement, we turn our attention to the intriguing question of whether the carbon and metal migrations occur in concert, and if so, by what mechanism orbital symmetry is conserved during the rearrangement.

The kinetic data gathered in Fig. 3 and Table 4 are consistent with a concerted mechanism. The rearrangement is a first order reaction with a relatively low activation energy ($\Delta H^{\#}$ 20 kcal mol^{-1}) and most importantly, a negative activation entropy ($\Delta S^{\#}$ -7 e.u.), which implies a highly ordered transition state for the reaction [22]. Furthermore, we find only a minor solvent effect on the rearrangement rate. The difference in rate upon changing the solvent from the moderately polar acetone to the highly polar methanol ($\Delta E_T(30)$ 13.3 kcal mol^{-1}) [18] is only $k_{rel} = k(MeOH)/k(Me_2CO) = 1.3$. Therefore, only a negligible charge separation is developed upon activation, even though a zwitterionic intermediate such as XIII could easily be stabilized by the pentadienyl-$Fe(CO)_3$ [23,20a,30] and the dicyanocarbinyl groups. Further supporting evidence for the isopolar nature [18] of the transition state comes from the inability to trap the intermediate with methanol. This would be expected had it been a zwitterionic species [24]. Since a diradical intermediate is probably not involved in the reactions [5,14] we are left with the conclusion that the pericyclic [3,3]-sigmahaptotropic rearrangement (II ⇄ III) is a concerted, nearly synchronous [25], one step reaction.



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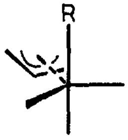


(XIV)

Let us now consider the rearrangement control by orbital symmetry. That is, we seek a least-motion pathway in which overlap between the orbitals of the migrating groups (carbon and metal) and the organic framework is retained during the rearrangement [10b]. Inspection of eq. 2 reveals that the structural changes that occur in the interconversion of II and III involve not only a 1,3-shift of the σ(C–C) bond but also a formal interchange between the two bonding modes of the metal to the organic ligand, σ(Fe–C) and π(Fe–allyl), and two configuration inversions at C(4) and C(6) of II, or equivalently at C(3) and C(5) of III. In addition, it is important to notice that the local symmetry of the pentacoordinated metal in II (and III) is trigonal bipyramidal (tbp) with the σ(Fe–C) carbon atom at an axial position and the allylic fragment in equatorial position, as shown in XIV. This structure is typical of 3 + 2 [26] and 5 + 2 [4] adducts of cycloheptatriene and tropone iron tricarbonyl complexes as well as of other pentacoordinated σ,π-allylic complexes [27]. Rearrangement of II to III (and vice versa) transforms II-tbp into the new III-tbp which has exactly the same relative positions between the carbon and allyl groups, but is differently oriented in the molecule. This spacial difference is illustrated in Fig. 6a by two ORTEP drawings representing II and III which, for clarity, show only the metal carbonyl fragment and the six carbon atoms which comprise the active sites of the organic ligand.

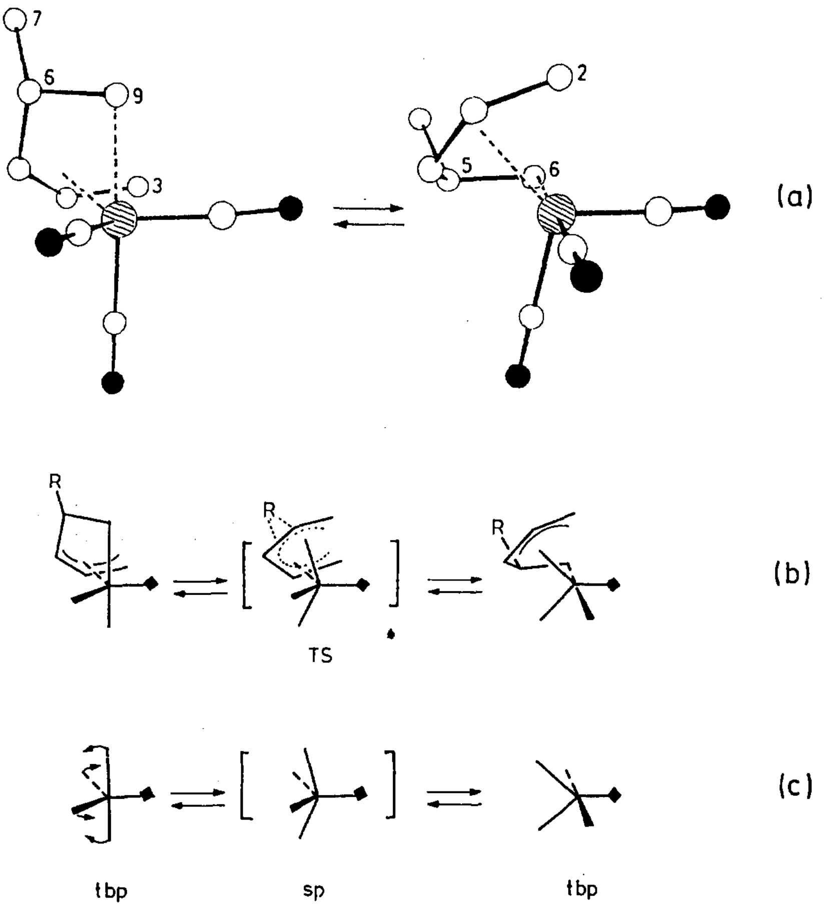


Fig. 6. Mechanism of the [3,3]-sigmahaptotropic rearrangement (II ⇄ III). (a) ORTEP plots: Fe, ▨; O, ●, C, ○; (b) View of the rearrangement pathway along the pseudorotation coordinate (pivot carbonyl marked ◆). (c) Berry pseudorotation.

Now, a least-motion pathway between the two isomers requires that the 1,3-sigmatropic carbon migration [9] be accompanied by a haptotropic shift [10b] which maintains a continuous bonding interaction between the metal fragment and the carbon chain backbone. This is precisely what happens when a Berry pseudorotation [28] is followed about the plane with the equatorial 'inner' carbonyl ligand (marked ◆) as pivot (Fig. 6b, c). Two crucial aspects of this conformational bending process should be realized. Firstly, the pseudorotation is a symmetry-allowed transformation in d^8 pentacoordinated complexes [28b,c]. Hence, metal orbital symmetry along this pathway is conserved. Secondly, the transition state (TS) for the rearrangement along the pseudorotation coordinate (Fig. 6b), which closely resembles that of the square pyramidal pentadienyl-Fe(CO)$_3$ complex [20a], is symmetric. It has a C_s symmetry plane (the *yz* plane) bisecting the complex and the migrating carbon group (R) which, in the transition state, resides midway between its two bonding sites. Thus, in the sigmahaptotropic rearrangement, like in sigmatropic reactions [9], only the transition state possesses a symmetry element. Our orbital analysis must therefore be followed along this pseudorotation pathway.

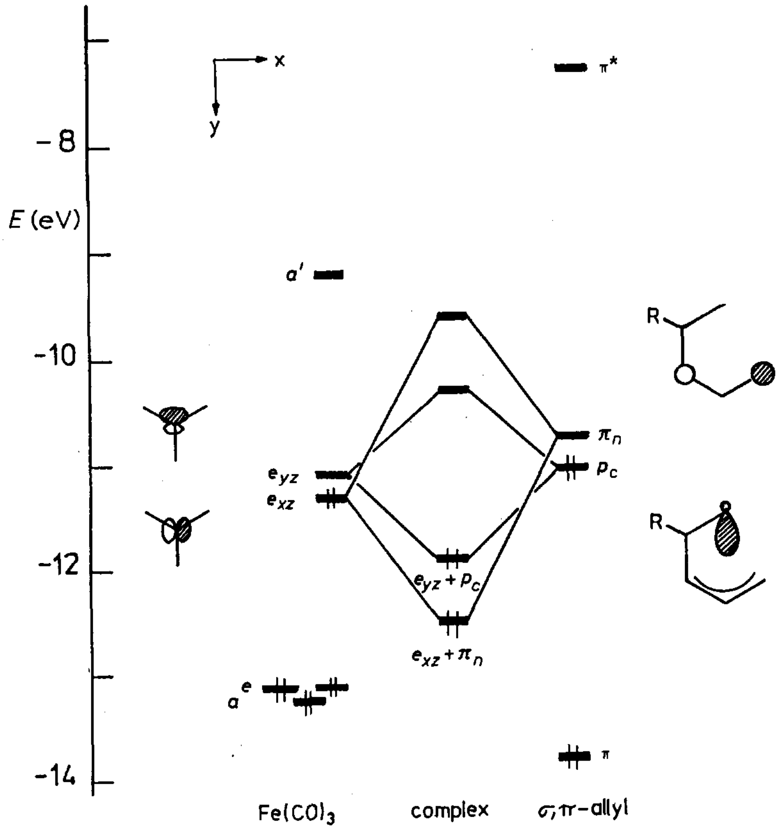


Fig. 7. Orbital interaction diagram for (σ,π-allyl)Fe(CO)$_3$ (II and III).

We start the molecular orbital analysis by focusing on the metal–organic bonds of σ,π-allylic complexes. The interaction diagram for the tricarbonyliron [20] (cf. Fig. 5) and the organic σ,π-allyl fragments in Fig. 7 shows the two major interactions between the frontier pair e_{yz}, p_c and e_{xz}, π_n fragment orbitals, symmetric and antisymmetric to the yz plane, respectively. The resulting bonding orbitals $\sigma(e_{yz}+p_c)$ and $\pi(e_{xz}+\pi_n)$ in Fig. 8 are the two bonding molecular orbitals which concern us, since they play the key role in the haptotropic part of the rearrangement. The orbitals are drawn as viewed along the z axis of the coordinate system [20]. The metal fragment is projected upon the allylic plane of the organic framework, which itself is parallel to the xy plane. If we now carry out the pseudorotation halfway to the transition state (cf. Fig. 6) and again view the resulting pentadienyl complex along the z axis, this time with the tripodal metal fragment projected on the pentadienyl xy-plane, we may see from Fig. 8 that the $\sigma(e_{yz}+p_c)$ and $\pi(e_{xz}+\pi_n)$ bonding orbitals of the σ,π-allylic complex evolve into the $\pi(e_{xz}+\pi_2)$ bonding and $\pi(e_{yz}+\pi_n)$ backbonding orbitals of the pentadienyl complex system [20a], respectively. This then represents the orbital correlation diagram for the haptotropic part of the rearrangement.

To complete the analysis there remains to follow the 1,3-migration of the σ(C–C) bond along the pseudorotation coordinate. Viewing along the z axis in Fig. 8, the

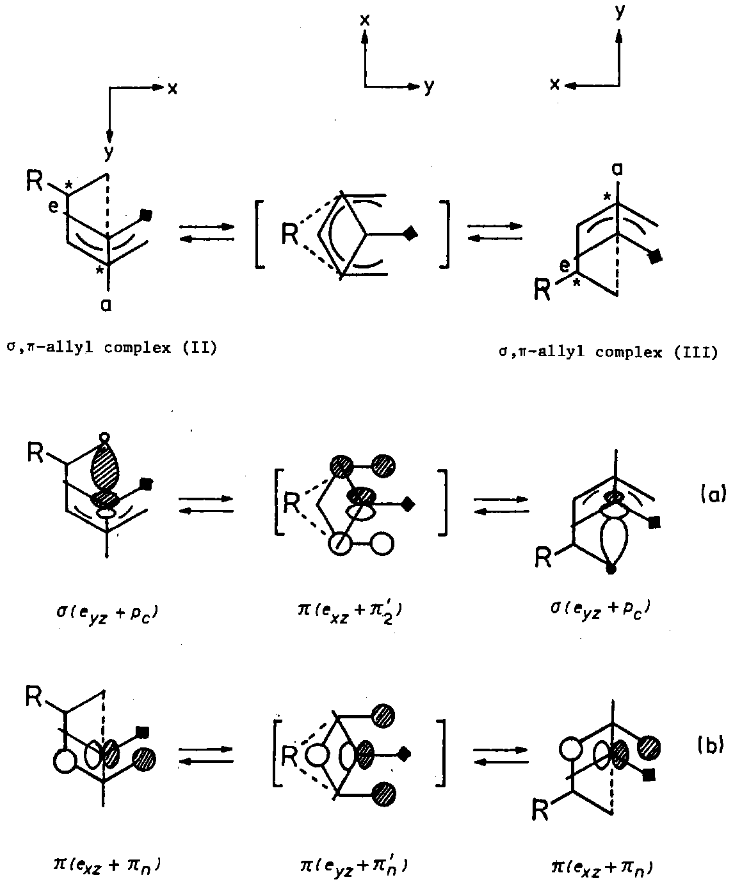
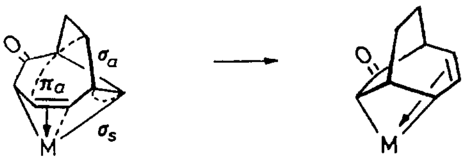


Fig. 8. Orbital correlation diagram for the metal-organic molecular orbitals (a) σ(Fe–C) and (b) π(Fe-allyl) in the [3,3]-sigmahaptotropic rearrangement, viewed along the z axis of the metal fragment coordinate system.

migrating carbon (R) appears to rotate in the xy plane away from the pentadienyl fragment, crossing the yz symmetry plane in the transition state. The question arises, however, whether this 1,3-sigmatropic shift proceeds with or without a configuration inversion at the migrating carbon [9]. This is perhaps best answered by invoking the Woodward–Hoffmann topological rules for pericyclic reactions [9]. The [3,3]-sigmahaptotropic rearrangement, being a 6 electron-3 bond process with two inversions, should, according to these rules, be described as a $[\sigma 2a + (\sigma 2s + \pi 2a)]$



(II) (III)

Fig. 9. The thermally allowed $\sigma 2a + (\sigma 2s + \pi 2a)$ [3,3]-sigmahaptotropic rearrangement.

thermally allowed reaction. Since both inversions must, for steric reasons, occur on pentadienyl carbons (starred positions in Fig. 8), we may conclude that in the sigmahaptotropic rearrangement, in contrast with the thermally allowed 1,3-sigmatropic reaction [9], carbon migration occurs with retention of configuration.

Finally, the alternative, but equivalent, valence bond presentation of the rearrangement may be advanced by utilizing Mingos' topological approach [5]. Realizing the stereochemical consequences of the rearrangement, the corrected (cf. [5]) form of the overall $[\sigma s + \sigma a + \pi a]$ process should be that illustrated in Fig. 9, namely, inversion at the two exchanging bonding sites and retention at both migrating atoms.

Conclusions

The principal objective of this paper was to gain insight into the mechanistic details of a new group of pericyclic organometallic reactions, which we term sigmahaptotropic reactions. The results provide evidence for the concertedness of thermal [3,3]-sigmahaptotropic rearrangements, and point out the importance of pseudorotation as a route for metal translocation in pentacoordinated complexes. The significance of this model for the analysis of other reactions which involve haptotropic shifts remains to be determined by further study. We are currently exploring the extent of sigmahaptotropic rearrangements in related systems [1,8].

Experimental section

Tricarbonyl(tropone)iron (I) was synthesized by the reaction of tropone [31] and $Fe_2(CO)_9$ according to Eisenstadt [32]. The complex was sublimed (40–50°C/0.1 mmHg) shortly before use. Commercial TCNE was twice sublimed before use.

The 3 + 2 adduct II [5] was prepared by mixing dilute solution (ca. 0.1 M) of the reactants in chloroform or methylene chloride. It crystallized out from the reaction mixture in > 90% yield, washed with chloroform, and was used without further purification. The 5 + 2 adduct III [2,5] was recrystallized from CH_2Cl_2/hexane.

All kinetic experiments were performed in NMR tubes. Dilute solutions (10–40 mM) were stable enough during experimental periods to be used without special precautions.

Variable temperature NMR spectra were recorded on a Bruker AM300 Spectrometer equipped with an ASPECT 3000 data system. All chemical shifts are in ppm downfield from internal TMS.

Sample temperatures were measured with a Omega 870 digital thermometer, before and after each experiment; readings were within 0.5°C.

The molecular orbital calculations were carried out using the extended Hückel method [21]. The parameters (H_{ij}) were taken from published data [20]. Bond lengths and angles were derived from the structures of tricarbonyl(tropone)iron [33], and from X-ray data of the 3 + 2 [26] and 5 + 2 [4] σ,π-allylic complexes of cycloheptatriene and tropone, respectively.

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