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Reactions of coordinated cyclic polyolefins *. The kinetics and stereochemistry of the pericyclic [2,2]-sigmahaptotropic rearrangement

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Abstract

The [2,2]-sigmahaptotropic rearrangement of the [2 + 2] adducts of (cycloheptatriene)Fe(CO)$_3$ with aryl ketenes to the corresponding σ,π-allylic [3 + 2] adducts, in which a σ-bonded carbon and a Fe(CO)$_3$ fragment exchange bonding sites antarafacially across a σ carbon–carbon bond, has been shown to proceed in a single kinetic step. The first order rate constants for the rearrangement are k 6.3×10^{-6} s^{-1} (methanol, 23°C) and k 3.4×10^{-6} s^{-1} (acetone, 51°C), with activation parameters $\Delta H^{\#}$ 21 kcal mol^{-1} and $\Delta S^{\#}$ -12 e.u. (methanol). Rearrangement without ring opening occurred also in trifluoroethanol. The ratio between the rate constants in methanol and acetone at 51°C is moderate, k_{rel} 40, indicating a partial charge separation in the transition state without formation of a fully developed zwitterionic intermediate. When the migrating carbon is unsymmetrically substituted, rearrangement occurs stereospecifically with retention of configuration. On the basis of these results a mechanism for the [2,2]-sigmahaptotropic rearrangement which involves a $2a + (2s + 2a)_{\text{mo}}$ (mo = metal–organic) thermally allowed pericyclic reaction is proposed.

Introduction

Sigmahaptotropic ($\sigma\eta$) rearrangements of the order $[j, j]$ are defined as pericyclic reactions in which a σ-bonded group and a ML$_n$ metal fragment exchange bonding sites antarafacially across a chain of j conjugated atoms [2]. Kinetic analysis of rearrangements of order [3,3] (eqs. 1 and 2) and [4,4] (eq. 3) provided evidence that these are thermally allowed pericyclic reactions [1–3]. Other formal sigmahaptotropic rearrangements have also been previously reported [4], but only in a few have mechanistic details been given.

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

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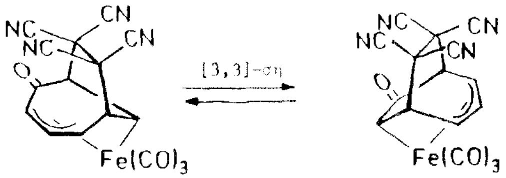

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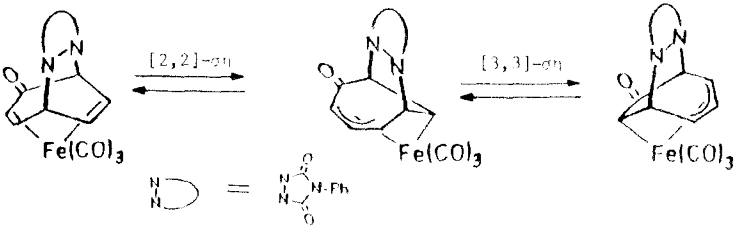

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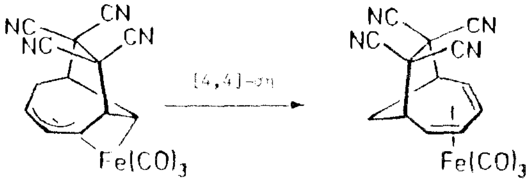

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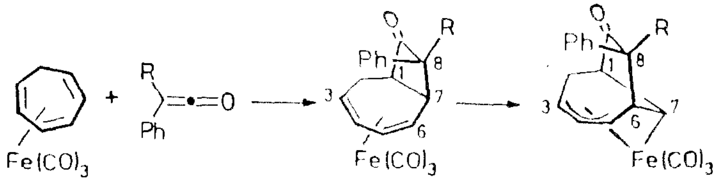
In an early publication we reported the regio- and stereospecific [2 + 2] cycloadditions of (cycloheptatriene)Fe(CO)$_3$ (I) with aryl ketenes (II) to give the cyclobutanone complexes (III) [5]. The diaryl adducts rearrange in a formal [2,2]-$\sigma\eta$ reaction to the corresponding σ,π-allylic [3 + 2] adducts (IV) (eq. 4). The methylphenyl adduct (IIIb) could not hitherto be rearranged in common solvents.

Herein we report the kinetic results for this rearrangement and provide the first clear evidence that as predicted [2], the migrating group retains its configuration during the rearrangement. We also discuss here in detail the mechanism of thermal pericyclic [2,2]-$\sigma\eta$ rearrangements of pentacoordinated complexes.



(I) (II) a = Ph b = CH$_3$ (III) (IV)

(4)

Results

The reaction of I with diphenylketene (IIa) and methylphenylketene (IIb) to give the corresponding cyclobutanones III was carried out as described before [5]. IIIa rearranges to IVa very sluggishly in benzene or toluene below 80 °C. At higher temperatures the rearrangement is accompanied by extensive decomposition. Under these conditions no rearrangement was observed with IIIb. However, in more polar solvents, such as acetone, methanol, or, best, trifluoroethanol (TFE), the rearrangement of IIIa takes place at lower temperatures without considerable decomposition. Cyclobutanone IIIb is stable in acetone and methanol at 70 °C, but readily rearranges at this temperature in TFE to a single [3 + 2] σ,π-allylic adduct identified (vide infra) as IVb, in which the phenyl group remains in the *endo* position. Details of the ^{1}H NMR spectra of both the [2 + 2] and [3 + 2] isomers are given in Table 1. The *endo* stereochemistry of the phenyl group in IIIb was previously determined by X-ray crystallography [5]. This configuration is retained after the rearrangement, as shown by NOE experiments. Thus, when the methyl signal of

Table 1

^{1}H NMR spectroscopic data for (cycloheptatriene)Fe(CO)$_3$-ketene adducts [a]

Compound	Solvent	H(1)	H(2*n*)	H(2*n*)	H(3)	H(4)	H(5)	H(6)	H(7)
IIIa	$(CD_3)_2CO$	3.39	2.07	2.43	3.15	5.31	4.82	2.94	4.01
		aromatic: 7.55, 7.53 (*o*); 7.34, 7.31 (*m*); 7.22, 7.20 (*p*)							
	CD_3OD	3.39	2.04	2.43	3.08	5.22	4.76	2.81	3.92
		aromatic: 7.46 (*o*); 7.32 (*m*), 7.20 (*p*)							
		$^{b}J_{12x}$ 8.3, J_{12n} 1.5, J_{16} 0.9, J_{17} 10.4, J_{22} 17.8, J_{2x3} 2.8, J_{2n3} 5.1, J_{2n4} 1.3, J_{2n7} ~ 0.3, J_{34} 8.1, J_{35} 1.5, J_{45} 5.3, J_{46} 0.9, J_{56} 7.8, J_{67} 4.3							
IIIb	$CDCl_3$	3.60	2.06	2.50	2.99	5.00	4.52	2.67	2.99
		Me: 1.70, aromatic: 7.42 (*o*), 7.36 (*m*), 7.25 (*p*)							
		J_{12x} 8.7, J_{12n} 1.3, J_{16} 0.7, J_{17} 10.2, J_{22} 17.3, J_{2x3} 2.8, J_{2n3} 4.9, J_{2n4} 1.3, J_{2n7} ~ 0.3, J_{34} 8.0, J_{35} 1.1 J_{45} 5.2, J_{46} 1.1, J_{56} 7.8, J_{57} 0.3, J_{67} 4.4							
IVa	C_6D_6	2.52	2.84	2.86	4.60	4.20	4.01	4.07	1.99
		aromatic: 6.98 (*o*), 7.16–7.35 (*m,p*)							
	$(CD_3)_2CO$	2.53	2.90	2.82	4.77	4.41	4.19	4.24	2.04
		aromatic: 7.08 (*o*), 7.19–7.39 (*m,p*)							
		$^{c}J_{12x}$ 9.0, J_{12n} 3.0, J_{13} ~ 0.5, J_{16} 1.0, J_{17} 9.0, J_{22} 16.0, J_{2x3} 3.0, J_{2n3} 3.0, J_{2n4} 0.5, J_{34} 9.3, J_{45} 7.8 J_{56} 6.5, J_{57} 2.1, J_{67} 7.0							
IVb	$CDCl_3$	2.74	2.95	2.74	4.57	4.14	4.08	3.27	1.88
		Me: 1.31, aromatic: 7.19 (*o*), 7.34 (*m*), 7.24 (*p*)							
		J_{12x} 11.8, J_{13} ~ 0.7, J_{16} 0.8, J_{17} 8.5, J_{22} 16.5, J_{2x3} 4.0 J_{2n3} 2.5, J_{2n4} 1.0, J_{34} 9.2, J_{35} 0.7, J_{45} 8.0, J_{56} 6.2, J_{57} 1.8, J_{67} 7.7							

[a] δ (ppm) from TMS; J in Hz, x = *exo*, n = *endo*; numbering as in eq. 4. [b] In $(CD_3)_2CO$. [c] In C_6D_6.

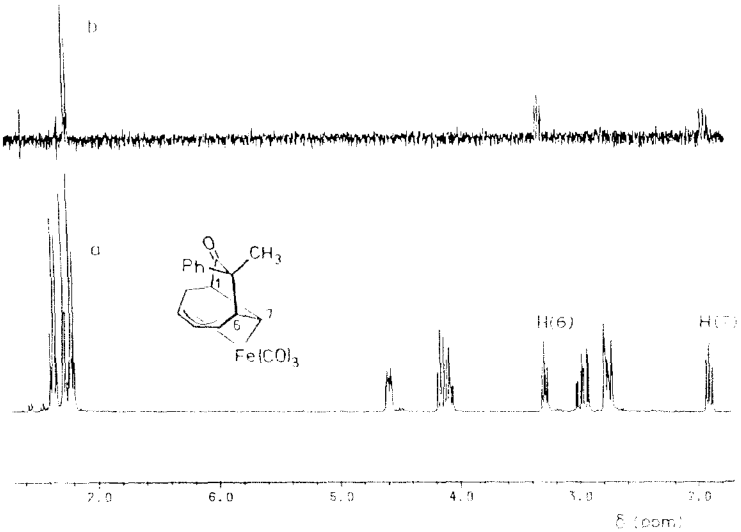


Fig. 1. Determination of the stereochemistry of IVb by NOE experiments. (a) ^{1}H NMR spectrum ($CDCl_3$) of IVb. (b) Difference spectrum of IVb irradiated at δ 1.31 ppm (methyl-8).

IVb, at δ 1.31, was irradiated, enhancement of the signal intensities of the aromatic *ortho* protons, the bridgehead H(6), and H(7) was observed (Fig. 1). Conversely, irradiation of the *ortho* protons at δ 7.19 caused enhancement of the signal intensities of the methyl protons, the allylic H(4) (at δ 4.14), and again the bridgehead H(6). The enhancements were determined by use of difference spectroscopy [6], and were of the order of 1–3%.

Kinetic studies

The progress of the [2,2]-$\sigma\eta$ rearrangement IIIa → IVa was monitored by ^{1}H NMR spectroscopy in acetone-d_6 and methanol-d_4 solutions. The relative concentrations of the reactant and the product were determined from the integrals of the relevant proton signals. First order rate constants were derived from the slopes of the plots of ln(% IVa) against time. The rate constants and other activation parameters are listed in Table 2.

Table 2

Kinetic data for the [2,2]-sigmahaptotropic rearrangement of IVa

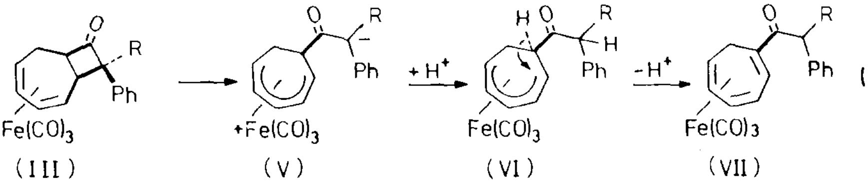
Solvent	T (K)	k (s^{-1})	$\Delta G^{\neq}$ (kcal mol^{-1})	$t_{1/2}$ [a] (h)
CD_3OD [b]	296	$6.3 \pm 0.7 \times 10^{-6}$	24.37 ± 0.04	13
	316	$5.5 \pm 0.3 \times 10^{-5}$	24.68 ± 0.04	3.5
	334	$4.1 \pm 0.2 \times 10^{-4}$	24.81 ± 0.09	0.5
$(CD_3)_2CO$	324	$3.4 \pm 0.4 \times 10^{-6}$	27.08 ± 0.04	56

$\Delta H^{\neq}$ 21 ± 1 kcal mol^{-1}; $\Delta S^{\neq}$ −12 ± 4 e.u. (in CD_3OD)

[a] $t_{1/2} = \ln 2/k$. [b] $k_{rel} = k(\text{methanol})/k(\text{acetone}) = 40$ (at 51 °C).

Discussion

The fact that the rearrangement of IIIa is a first order reaction, which can be successfully performed in protic solvents such as methanol and TFE without interception of diphenylketene (as its diphenylacetic acid ester derivative), clearly indicates that the reaction does not proceed by a two step cycloreversion-addition process, but is rather intramolecular. Furthermore, the formation of a fully developed zwitterionic intermediate enolate V may also be excluded, since this benzyl ketone enolate (pK_a 16.6 [7]) would be readily protonated in TFE (pK_a 12.4 [8]) to give VI, which in turn, would be expected to undergo a rapid deprotonation to the ring-opened ketone VII (eq. 5) [5,9]. However, although it is clear that no intermediate is formed during the rearrangement, the transition state is apparently somewhat polar, since a moderate solvent effect [10] is observed, $k_{rel} = k(\text{methanol})/k(\text{acetone}) = 40$ (at 51° C).



(5)

These results, together with the observations of a rather low enthalpy of activation ($\Delta H^{\#}$ 21 kcal mol^{-1}) and the negative entropy of activation ($\Delta S^{\#}$ −12 e.u.) all point to the conclusion that the [2,2]-sigmahaptotropic rearrangement is a thermal pericyclic reaction. The stereospecific rearrangement of IIIb in TFE further confirms the concerted nature of this reaction, and explicitly leads to the significant conclusion that during the [2,2]-$\sigma\eta$ rearrangements the σ-bonded carbon migrates with retention of configuration.

We proceed now to the analysis of the conservation of orbital symmetry in [2,2]-$\sigma\eta$ rearrangements. As for previous analyses of rearrangements of this series [2,3], it is important first to consider the structural changes which occur within the metal coordination sphere. Figure 2 presents ORTEP drawings of the pentacoordinated complexes III and IV, each showing only the Fe(CO)$_3$ fragment and the six carbon atoms directly involved in the reaction. The square pyramidal complex III [5] has three of its ligands placed in the plane of the paper: the apical carbonyl, one of the basal carbonyls, and one olefinic ligand. Similarly, the trigonal bipyramidal complex IV [11] has its two axial ligands (the carbonyl and the σ-bonded carbon), and one basal carbonyl ligand in the plane of the paper. It can be clearly seen that during the formal 1,2-sigmatropic shift of C(8), the metal is subjected to a conformational change from a square pyramid (sp) to a trigonal bipyramid (tbp). This corresponds to a partial Berry pseudorotation which symmetrically transforms the metal orbitals between sp and tbp pentacoordinated complexes about a C_s symmetry plane (Fig. 2b) [12]. It is thus reasonable to suggest that the concerted symmetry-allowed sigmahaptotropic rearrangements proceed along a reaction coordinate in which the metal undergoes a Berry pseudorotation about the plane containing the apical carbonyl ligand as its pivot (the plane of the paper in Fig. 2a).

Our next step is to identify the bonds which are directly associated with the sigmahaptotropic rearrangement, in order to construct the pertinent molecular

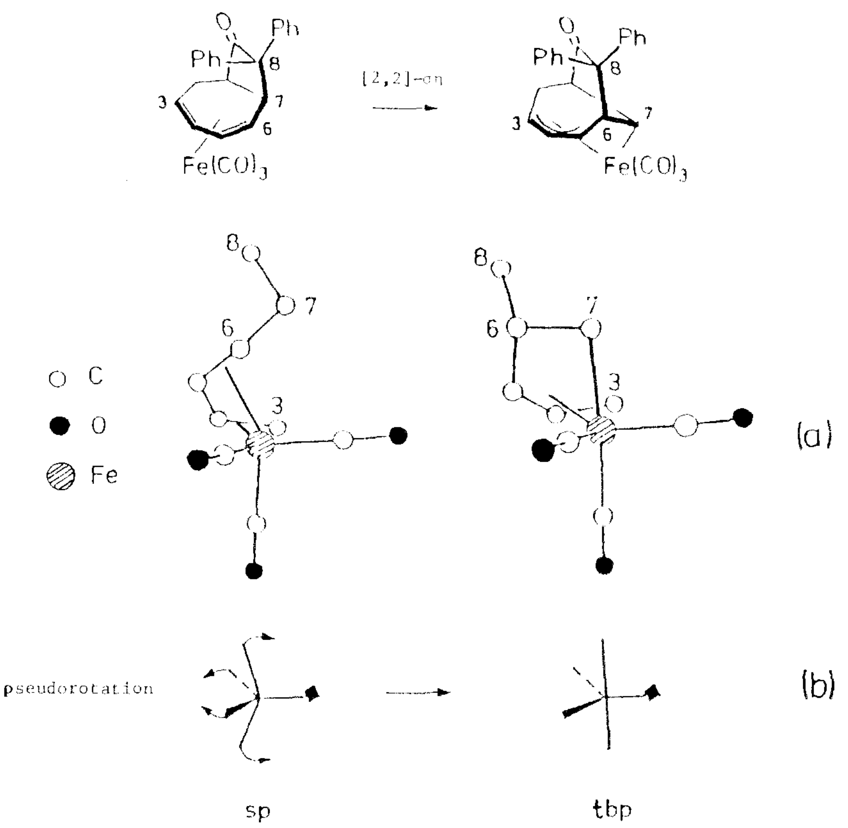


Fig. 2. Stereochemistry of the [2.2]-$\sigma\eta$ rearrangement of III → IV. (a) ORTEP drawing of sp IIIb and tbp IVb in the pseudorotation plane (of the paper). (b) sp → tbp Berry pseudorotation (pivot ligand marked (◆).

orbitals of the reactants and the products. These will then be correlated along a pseudorotation reaction pathway. From Fig. 2 it can be easily verified that three bonds are involved in the rearrangement, one σ C–C bond and two metal–organic ligand bonds. The σ(C(7)–C(8)) bond of III obviously correlates with its counterpart σ(C(6)–C(8)) of IV. On the other hand the two π(Fe–olefin) bonds of III transform into the corresponding σ(Fe–C(7)) and π(Fe–allyl) metal–organic ligand bonds of IV. Thus, the molecular orbitals which concern us here are the pair of the bonding orbitals of complex III, obtained by interaction of $Fe(CO)_3$ with the butadiene, and the corresponding two orbitals of complex IV, derived by interaction of the metal fragment with the saturated carbon and the allylic group.

The construction of an interaction diagram for butadiene and σ,π-allylic complexes with $Fe(CO)_3$ has been previously described in detail [2,13,14] and will therefore be dealt here only briefly and qualitatively. At the two far sides of Fig. 3 appear the familiar frontier orbitals of the d^8 $Fe(CO)_3$ fragment, characterized by its two high lying e_{xz} and e_{yz} orbitals [13]. They are the main contributors to the bonding between the metal and the organic ligand. On the left are the butadiene

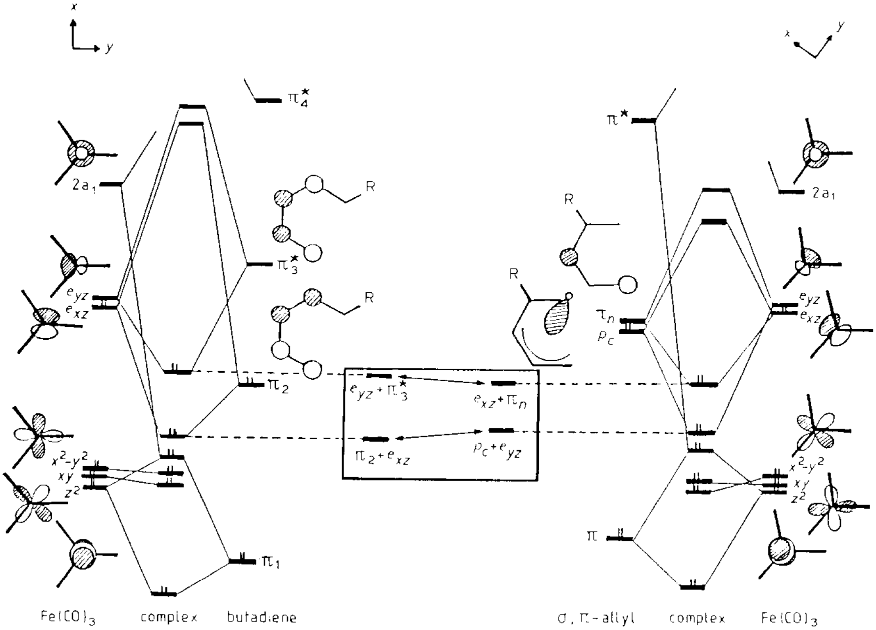
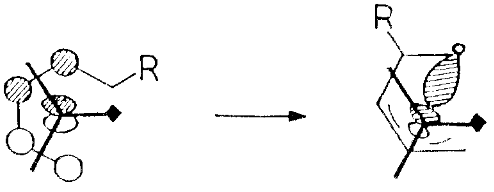


Fig. 3. Orbital interaction diagram of $Fe(CO)_3$ fragment with butadiene (left) and with a σ,π-allylic system (right). Top view.

π-orbitals, with π_2 and $\pi_3^\star$ as the HOMO–LUMO pair. On the right is the σ,π-allylic group, having the saturated carbon and the π_n (nonbonding) frontier orbitals. The two bonding interactions of complex III with $Fe(CO)_3$ are thus the $(\pi_2 + e_{xz})$ (VIII) and $(e_{yz} + \pi_3^\star)$ (IX) orbitals, whereas the $(p_c + e_{yz})$ (X) and $(e_{xz} + \pi_n)$ (XI) are the two corresponding bonding orbitals of complex IV. The correlation between the two pairs of bonding orbitals along the pseudorotation reaction coordinate may now readily be evaluated. The metal-stabilized HOMO of butadiene (VIII) evolves into the σ metal–carbon orbital (X) (eq. 6), while the backbonding metal–butadiene orbital (IX) transforms into the metal–allyl(nonbonding) orbital (XI) (eq. 7).

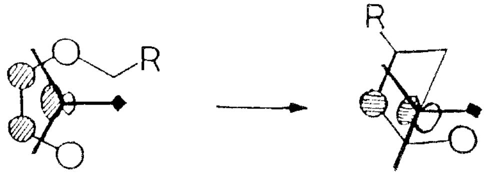
There remains the question of the stereochemistry of the migrating group. Inspection of Fig. 2 reveals that two inversions occur during the rearrangement at the two sites of interchange between the migrating carbon and the metal (C(6) and C(7)). The overall pericyclic process involves a three-bond six-electron alteration. Therefore, it is anticipated by the Woodward-Hoffmann topological rules [15], that these [2 + 2 + 2] thermally allowed reactions will take place with an even number of inversions. Since two inversions obviously occurred here, we are led to the conclusion that no inversion took place on the migrating carbon, as indeed was observed experimentally.

To complete the analysis it is appropriate to point out that along the whole pseudorotation pathway there is only a small overall change in the geometry of the tripodal $Fe(CO)_3$. Therefore, the energy and the shape of the frontier e orbitals of the metal fragment remain essentially the same. Moreover, these orbitals continuously overlap with the frontier orbitals of the pentadienyl-like system (C(3)–C(7)) [13b], made up of the butadiene group and the originally σ-bonded C(7). The



VIII $\pi(\pi_2 + e_{xz})$ X $\sigma(p_c + e_{yz})$

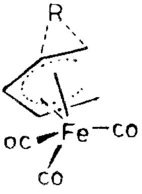
(6)



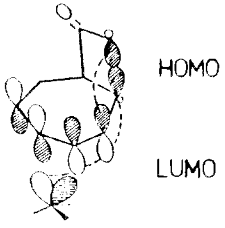
IX $\pi(e_{yz} + \pi_3^*)$ XI $\pi(e_{xz} + \pi_n)$

(7)

transition state (XII) is then likely to consist of a central pentadienyl chain, flanked on one face by a metal fragment having a square pyramidal coordination geometry, and on the other face by a carbon (R) group, apparently suspended between the two migration sites (C(6) and C(7)).

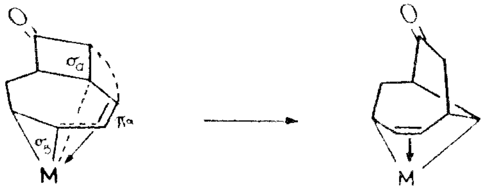


(XII)



(XIII)

Realizing the important role of metal pseudorotation in the reaction mechanism we may view the [2,2]-$\sigma\eta$ rearrangement by two alternative approaches which are less sensitive to the conformational changes (rehybridization) taking place during the reaction. First, utilizing the qualitative frontier-electron theory of Fukui [16], the rearrangement can be represented as an intramolecular HOMO–LUMO interaction between the bonding σ(C–C) and the antibonding π(Fe–butadiene) orbitals, as shown in XIII. The second alternative is based on the theoretical model by Mingos [4e,17], which uses a valence bond representation of the metal–organic bonding. This is illustrated in eq. 8 as a 6-electron process of the type $\sigma 2a + (\sigma 2s + \pi 2a)_{mo}$ (mo = metal–organic), and as expected is consistent with our present analysis



(8)

Conclusion

It will be seen that our analysis of the [2,2]-sigmahaptotropic rearrangements follows exactly that of the analogous pericyclic rearrangements of order [3,3] [2] and [4,4] [3]. Like the latter, they occur in a single kinetic step of low activation, with a negative entropy and moderate solvent effect. [2,2]-$\sigma\eta$ rearrangements thus belong to the novel class of thermal pericyclic reactions in which a σ-bonded group and a metal fragment exchange bonding sites concertedly [2]. Moreover, we have demonstrated for the first time that the [2,2]-$\sigma\eta$ rearrangements take place stereoselectively with retention of configuration at the migrating carbon. This supports our previous prediction that the configuration is indeed retained in all the $\sigma\eta$-rearrangements hitherto observed [2,3]. Mechanistically, these reactions, like their [3,3]- and [4,4]-$\sigma\eta$ counterparts, proceed via a transition state which consists of a 6-electron cyclic array, with two inversions. Topologically, they can thus be described as thermally allowed $2a + (2s + 2a)_{\text{mo}}$ reactions.

Finally, it is important to notice that this formal analysis, though very useful, fails to reveal how the principle of conservation of orbital symmetry [15] is obeyed around the metal center. Obviously, since all these reactions involve *d*-orbital bonding combinations, it is essential to show that they are indeed transformed symmetrically from reactants to products. This is done by correlating the corresponding coordination geometries in a symmetrical bending mode. In pentacoordinated compounds this symmetrical operation is likely to be a Berry pseudorotation [12]. Indeed, as has been demonstrated here and in previous work [2,3], the pentacoordinated complexes all undergo the pericyclic $\sigma\eta$-rearrangements along the pseudorotation pathway in which an apical auxiliary ligand (CO) occupies the pivot position (Fig. 2).

Experimental

The [2 + 2] adducts of (cycloheptatriene)Fe(CO)$_3$ (I) with diphenyl- and phenylmethyl-ketene were prepared as described previously [5], and were recrystallized before use from CH_2Cl_2/hexane.

All the kinetic experiments were performed in NMR tubes. Dilute solutions (20–30 m*M*) were purged with nitrogen, and were sufficiently stable during the experimental period.

Variable temperature NMR spectra were recorded on a Bruker AM300 spectrometer equipped with an ASPECT 3000 data system. The sample temperatures were measured with an Omega 870 digital thermometer, before and after each experiment; readings were within ±0.5 °C.

IR spectra were determined in KBr on a Nicolet 60 SXB FT-IR spectrometer. Mass spectra were recorded with a Finnigan Model 4000 spectrometer.

Tricarbonyl(η-2,3,4,9)-endo-8-phenyl-8-methyl-bicyclo[4.2.1]non-3-ene-7-one-2,9-diyl]-iron (IVb)

A solution of cyclobutanone complex IIIb [5b] (50 mg, 0.14 mmol) in TFE solution (1 ml) was kept at 70 °C under nitrogen for 4 h. The solvent was removed under reduced pressure. A sample of the residue was dissolved in $CDCl_3$ and was shown by ^{1}H NMR to contain a single isomer, identified as IVb (indicated by a single Me resonance at δ 1.31 ppm), together with $<5\%$ of the starting material. The crude product was chromatographed on a short silica gel 60 column, with 1% ethylacetate/hexane as eluent, to give 30 mg (60% yield) of IVb, mp. 91–92°C (from hexane). IR: 2052, 1978, 1963 (ligand CO) and 1733 (organic carbonyl) cm^{-1}. MS (EI, 20 eV): *m/e* 364 (M^+), 336, 308, 280 and 252 (base peak). ^{1}H NMR see Table 1.

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