Journal of Organometallic Chemistry, 301 (1986) 337–348
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

REACTIONS OF COORDINATED CYCLIC POLYOLEFINS *. THE MECHANISM OF THE PERICYCLIC [4,4]-SIGMAHAPTOTROPIC REARRANGEMENT; A KINETIC STUDY. CRYSTAL STRUCTURE OF TRICARBONYL[(2,3,4,5-η)BICYCLO[4.2.1]NONA-2,4-DIENE-7,7,8,8-TETRACARBONITRILE]IRON

ZEEV GOLDSCHMIDT*, HUGO E. GOTTLIEB, ELISHEVA GENIZI, DRORA COHEN,
Department of Chemistry, Bar-Ilan University, Ramat-Gan 52100 (Israel)

and ISRAEL GOLDBERG
Department of Chemistry, Tel-Aviv University, Ramat-Aviv 69978 (Israel)

(Received August 27th, 1985)

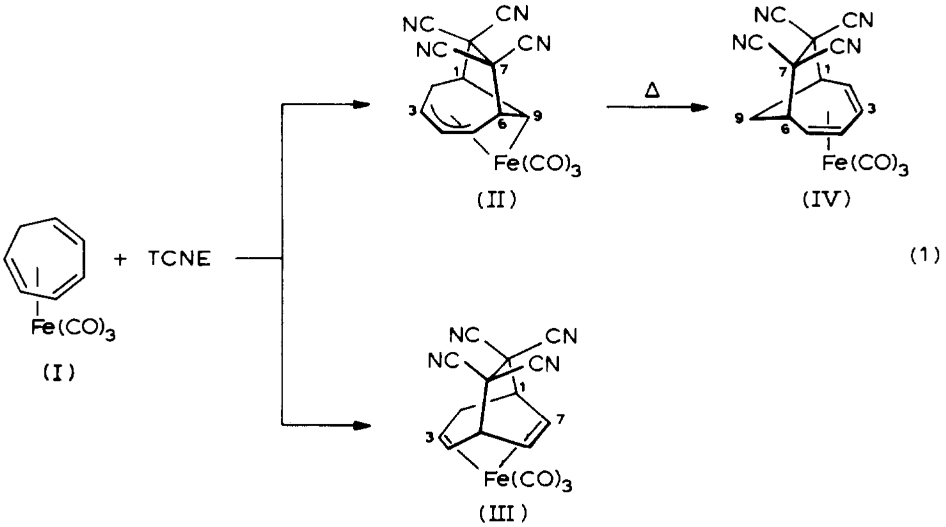
Summary

The novel [4,4]-sigmahaptotropic rearrangement II → IV, in which a σ-bonded group and a $Fe(CO)_3$ unit exchange bonding sites antarafacially across a four carbon skeleton, has been shown by kinetic data to involve a concerted, non-synchronous, one step process. First order rate constants for the rearrangement at 23°C are k 1.25×10^{-6} s^{-1} (acetone) and k 2.2×10^{-5} s^{-1} (methanol), with activation parameters $\Delta H^{\#}$ 21 kcal mol^{-1} and $\Delta S^{\#}$ -15 e.u. (acetone). The moderate value of the ratio of k in methanol to that in acetone, viz. 18, indicates that although a minor charge separation develops upon activation, no intermediate is formed. The least motion pathway mechanism is shown to involve a Berry pseudorotation about the metal, which maintains the bonding interaction between the metal and the organic fragment orbitals during the rearrangement. Topologically this rearrangement corresponds to a $[\sigma 2a + (\sigma 2s + \pi 2a)]$ thermally allowed pericyclic reaction. The structure of the rearranged complex IV was determined by single-crystal X-ray diffraction.

Of the three possible cycloadducts (II–IV) of (cycloheptatriene)$Fe(CO)_3$ (I) with tetracyanoethylene (TCNE) only the 3 + 2 adduct II has been reported to be formed by a direct cycloaddition reaction [2]. The 4 + 2 cycloaddition, to give III, which was previously predicted to be symmetry-forbidden, and the 6 + 2 cycloaddition to IV, claimed to be allowed, were not observed [3] (eq. 1).

---

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



(1)

We now report that all three cycloadducts are accessible from the reaction of I with TCNE. However, only II and III are primary cycloaddition products, IV being formed by a novel pericyclic rearrangement of II, which we term a [4,4]-sigmahaptotropic rearrangement [1].

Results and discussion

The reaction of I with TCNE in solvents of medium polarity, e.g. chloroform ($E_T(30) = 39.1$ kcal mol^{-1} [4]), is instantaneous [5], affording a mixture of II and III in a ratio of 96/4. The structure of III was deduced from the 300 MHz ^{1}H NMR spectrum, and shown to resemble that of the 4 + 2 adduct of I with (carbomethoxy)maleic anhydride, which was recently prepared [6]. It displayed four characteristic high field signals of the vinyl protons at δ (acetone-d_6) 3.2 (H(7), m, obscured by H(2)), 3.46 (H(3), bdd, J 8.2 and 4.5 Hz), 3.58 (H(6), ddd, J 7.5, 6.5 and 1.8 Hz) and 3.73 (H(4), td J 8.2 and 1.2 Hz). Additional signals were observed at 2.64 (H(2), bd, J 17.5 Hz), 3.2 (H(2'), m), 3.83 (H(1)) bdd, J 9.5 and 8.5 Hz) and 5.02 (H(5), dddd, J 8.2, 7.5, 1.3 and 0.8 Hz). When the reaction is conducted in polar solvents such as acetone ($E_T(30)$ 42.2 kcal mol^{-1}) or methanol ($E_T(30)$ 55.5 kcal mol^{-1}) II and III are again obtained in a similar ratio. However, upon standing at room temperature or heating, isomer II smoothly rearranges to the formal 6 + 2 adduct IV, in 75% isolated yield. Notably, this rearrangement was best effected in trifluoroethanol solutions at 50°C [7]. The ^{1}H NMR spectrum of IV, which has a plane of symmetry, is unequivocal. The five expected signals appear at δ ($CDCl_3$) 1.52 (H(9), dt, J 14 and 1.3 Hz), 2.07 (H(9'), dt, J 14 and 4.0 Hz), 3.52 (H(2) and H(5), m), 3.59 (H(1) and H(6), ddd, J 9.5, 4.0 and 1.0 Hz) and 5.72 (H(3) and H(4), m). The structure of IV was finally confirmed by a single-crystal X-ray analysis (see Experimental section). The ORTEP drawing of IV is shown in Fig. 1.

During the rearrangement of II the amount of adduct III also decreases, but because of the low concentration of III in the reaction mixture, we could not tell whether this is due to its rearrangement or slow decomposition.

The rearrangement was not affected by the addition of an excess of the powerful dienophile (carbomethoxy)maleic anhydride, which is known to react with I [6]. Nor

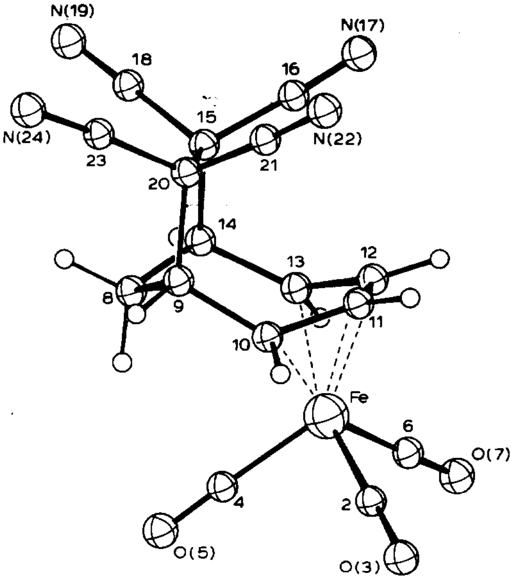


Fig. 1. ORTEP drawing of rearranged complex IV.

was TCNE trapped by cyclohexadiene added to the reaction solution [8]. Therefore, it is clear that the rearrangement must proceed by an intramolecular mechanism, and not via a cycloreversion-addition process.

We have recently termed such thermal reorganizations sigmahaptotropic rearrangements [1], to denote those pericyclic reactions in which both a sigmatropic [9] and a haptotropic shift [10] occur concurrently. Since the two migrating groups, C(7) and the metal, exchange bonding sites across a four carbon skeleton, this sigmahaptotropic rearrangement is of the order [4,4].

In order to determine whether this unique rearrangement proceeds concertedly, in a single kinetic step [11], or in two steps, via an intermediate, a kinetic study was undertaken. The progress of the reaction was monitored by ^{1}H NMR spectroscopy in acetone-d_6 and methanol-d_4 solutions. The relative concentrations of the reactants and products were determined from the integrations of the relevant proton signals. The first order rate constants and the thermodynamic parameters are listed in Table 1.

Our evidence that the present [4,4]-sigmahaptotropic rearrangement is indeed concerted rests upon the observations of (i) a low activation enthalpy, $\Delta H^{\#}$ 21 kcal mol^{-1}; (ii) a significant negative entropy of activation, $\Delta S^{\#}$ -15 e.u. and (iii) a relatively small solvent effect, $k_{\text{rel}} = k(\text{methanol})/k(\text{acetone}) = 17.6$ [4,12a]. Exclusion of a two step diradical mechanism is based on thermodynamic kinetics [13]. Since, however, thermodynamic data for the energy of metal–carbon radicals are scarce [14], it is possible to make a rough estimate of the homolytic bond dissociation energy of the pertinent C(6)–C(7) σ bond only by inference from data for uncomplexed compounds. From the difference between the C–H bond energy of a primary carbon (98 kcal mol^{-1}) [15] and the C–H bond energy of malononitrile (70 kcal mol^{-1}) [16], we calculate the resonance stabilization of malononitrile radical ($\cdot$CH(CN)$_2$)to be 28 kcal mol^{-1}. The pentadienyl radical has an estimated reso-

TABLE 1

KINETIC DATA FOR THE [4,4]-SIGMAHAPTOTROPIC REARRANGEMENT

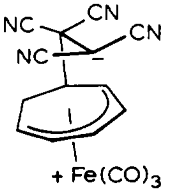
Solvent	T (K)	k ($\times 10^5$) (s^{-1})	$\Delta G^{\#}$ (kcal mol^{-1})	$t_{\frac{1}{2}}$ (h)
acetone-d_6 ^{a}	296	0.125 ± 0.002	25.32 ± 0.05	154
	316	1.23 ± 0.02	25.62 ± 0.05	15.7
methanol-d_4 ^{b}	296	2.2 ± 0.4	23.63 ± 0.11	8.8

$\Delta H^{\#}$ 21 ± 1 kcal mol^{-1}; $\Delta S^{\#}$ -15 ± 4 e.u. (in acetone-d_6)

^{a} Ca. 30 mM solutions, ^{b} Ca. 2 mM (saturated) solutions $k_{rel} = k(\text{methanol})/k(\text{acetone}) = 17.5$ (at 23°C).

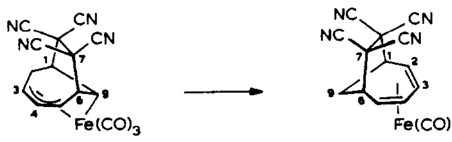
nance energy of ca. 15 kcal mol^{-1} [17]. Subtracting these values, plus an additional 6 kcal mol^{-1} for the cyclopentane ring strain [13], from the energy of a normal C–C bond (84 kcal mol^{-1}) [15], leaves 34 kcal mol^{-1} as a reasonable estimate of the C(6)–C(7) bond strength. This is 14 kcal mol^{-1} higher than the experimental value we observed. A two step diradical mechanism may thus be excluded. This conclusion is further supported by the negative entropy value, $\Delta S^{\#}$ -15 e.u., which indicates that the transition state is more constrained than the reactant.

The moderate rate increase which accompanies the change in solvent from acetone to methanol ($k_{rel} = 18$), points toward a somewhat polar transition state. However, it excludes a fully developed zwitterion intermediate such as V, which would presumably give rise to a rate increase of several orders of magnitude [4]. Furthermore, the acidity of malononitrile, pK_a 12 [16], is close to that of trifluoroethanol (TFE), pK_a 12.4 [18], suggesting that a zwitterion intermediate such as V would readily react with TFE, but no such reaction was observed; TFE was, in fact, found to be an excellent solvent for the rearrangement [7]. We thus arrive at the conclusion that the [4,4]-sigmahaptotropic rearrangement is a concerted, though non-synchronous [11], one-step reaction, involving a slightly polar transition state.



(V)

Having analyzed the reaction kinetics, we proceed to demonstrate the principle of the conservation of orbital symmetry [9]. For this it is important to find an appropriate reaction coordinate along which orbital overlap is retained during the rearrangement. We thus consider the structural modifications which take place in the reaction. First, the coordination geometry which is essentially that of a trigonal bipyramid (tbp) in II [19] becomes square pyramidal (sp) in IV (Fig. 1). This conformation change represents a partial Berry pseudorotation [20], known to be a symmetry allowed pathway for the interconversion of pentacoordinated compounds, inter alia d^8 transition metal complexes [21]. Secondly, two configuration inversions



(II) (IV)

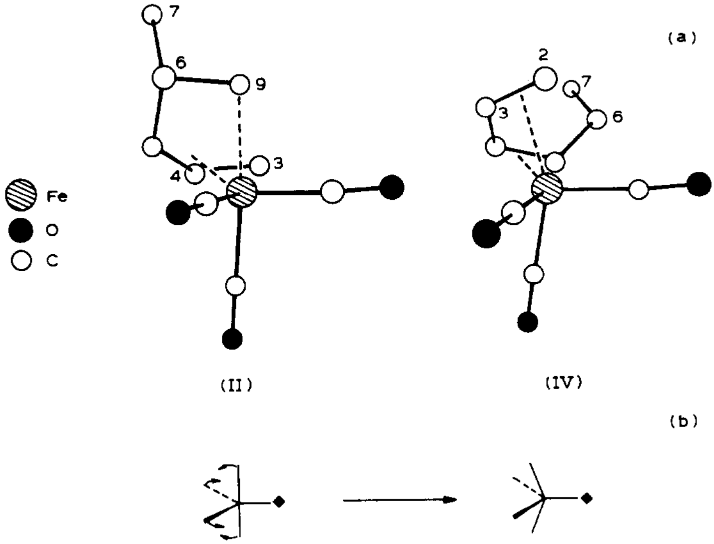
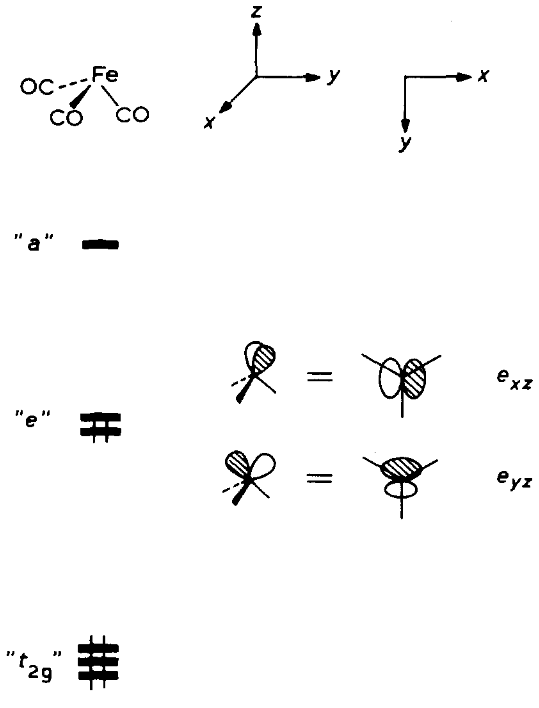


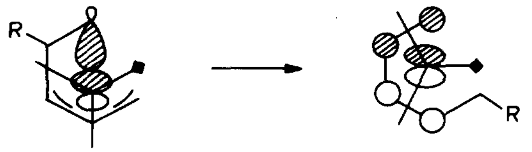
Fig. 2. (a) ORTEP drawing of tbp-II and sp-IV, (showing only the $Fe(CO)_3$ fragment and the organic carbons which participate in the rearrangement). Pseudorotation pivot = Fe–C(4)O(5) (Fig. 1). (b) Berry pseudorotation (pivot marked ◆).

take place at the carbon–metal sites of exchange. The iron-bonded allylic C(3) of II inverts to bind with migrating C(7), while C(6) inverts to become iron-bonded in IV (eq. 1). These structural variations are perhaps best illustrated in Fig. 2, by the ORTEP plots of II and IV, which show only the metal fragment and the organic ligand atoms which participate in the rearrangement, drawn with the pivot carbonyl–metal axis placed in the plane of the paper. Thus, as C(7) of the trigonal bipyramidal II migrates along the allylic moiety in a formal 1,4-sigmatropic shift, the metal undergoes a simultaneous haptotropic shift, to the tetragonal pyramid IV, along a pseudorotation coordinate. It is along this pathway that we look for the retention of orbital overlap.

There are three bonds which take part in the rearrangement process of II, the σ(C(6)–C(7)), the σ(Fe–C(9)), and the π(Fe–allyl) bonds. These bonds transform into the corresponding σ(C(6)–C(7)) and the pair of butadiene–$Fe(CO)_3$ π-bonds of IV (eq. 1). The molecular orbitals of both η^1,η^3-σ,π-allylic and η^4-butadiene complexes have been previously analyzed in detail by extended Hückel methods [22,1]. The two relevant metal-organic bonding orbitals, VII and VIII, of complex II, are those obtained by interaction of the frontier orbital pair e_{yz}, e_{xz} of the $Fe(CO)_3$ fragment (VI) [23] with the corresponding p_c and π_n (nonbonding) orbitals of the organic σ,π-allylic group [1]. The pertinent metal-organic orbitals, IX and X, of complex IV, result from interaction of the metal e pair with butadiene π_2(HOMO) and $\pi_3^{\star}$(LUMO), respectively [22], (pivot CO marked ◆; R = migrating carbon group). Note that e_{yz} and e_{xz} are hybridized metal d orbitals which are symmetric and antisymmetric with respect to the yz plane in the coordination system shown in VI. This is obviously not the pseudorotation plane (of the paper) described in Fig. 2.

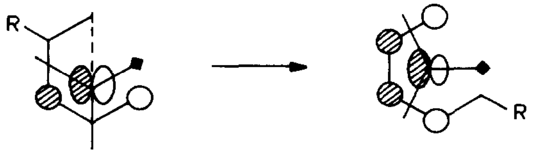


(VI)



(2)

(VII) (IX)

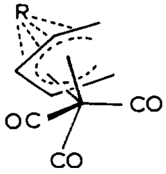


(3)

(VIII) (X)

Fig. 3. Topology of the thermally allowed $\sigma 2a + (\sigma 2s + \pi 2a)$ [4,4]-sigmahaptotropic rearrangement.

At every point along the pseudorotation coordinate, the general "t_{2g}", "$2e$", "a" pattern of the $Fe(CO)_3$ fragment orbitals remains essentially as shown in VI. That is, during the rearrangement the frontier e orbitals remain directed toward a pentadienyl-like organic ligand, along the z axis. The transition state (XI) would then consist of a central pentadienyl moiety, attached, on opposite sides, to the migrating carbon (R) and the metal fragment. Orbital overlap is thus maintained by a continuous interaction of the frontier orbitals of a pentadienyl-like group, with both the e orbitals of the metal fragment and the p orbital of the migrating carbon [23a].



(XI)

The orbital correlation is now straightforward. Orbital $\sigma(p_c + e_{yz})$ (VII) of II evolves into the $\pi(\pi_2 + e_{xz})$ orbital (IX) of IV (eq. 2), whereas $\pi(e_{xz} + \pi_n)$ (VIII) of II transforms into the backbonding orbital $\pi(e_{yz} + \pi_3^\star)$ (X) of IV (eq. 3). Evidently, the two σ(C(6)–C(7)) molecular orbitals correlate with each other.

A convenient formal alternative of viewing the [4,4]-sigmahaptotropic rearrangement is to apply the modified Woodward–Hoffmann topological rules for organometallic reactions, which utilize a valence bond presentation of the metal-organic bonding modes [3]. Thus, being a 3 bond-6 electron process, involving two inversions (Hückel system [12b]), this rearrangement is best described as a $[\sigma 2a + (\sigma 2s + \pi 2a)]$ thermally allowed reaction (Fig. 3).

Finally, it is important to notice that an immediate consequence of the topological analysis is that the 1,4-carbon migration occurs with retention of configuration. This is also consistent with our expectation that concerted reactions proceed via a least motion mechanism [24]. Experimentally, however, we have not yet been able to verify this stereochemical question.

Conclusions

The preceding analysis has shown that the [4,4]-sigmahaptotropic rearrangement is one member of a new class of organometallic pericyclic reactions, in which a carbon and a metal exchange bonding sites in concert [1,25]. The mechanistic details are very similar to those for the [3,3]-sigmahaptotropic counterparts [1]. Preliminary kinetic results indicate that the rearrangements of the order [2,2] (previously termed

TABLE 2

POSITIONAL AND ISOTROPIC THERMAL PARAMETERS FOR COMPOUND IV

Atom	x	y	z	U_{eq}/U (Å^2) [a]
Fe(1)	0.2147(1)	0.0271(3)	0.7465	0.0394
C(2)	0.1514(8)	−0.1704(22)	0.7475(7)	0.0548
O(3)	0.1123(6)	−0.2968(20)	0.7489(7)	0.0976
C(4)	0.1898(7)	0.1485(25)	0.6818(6)	0.0547
O(5)	0.1736(6)	0.2244(23)	0.6425(4)	0.0908
C(6)	0.1593(6)	0.1767(26)	0.7889(6)	0.0585
O(7)	0.1226(5)	0.2741(19)	0.8162(4)	0.0767
C(8)	0.3499(6)	0.1270(19)	0.6665(5)	0.0304
C(9)	0.3537(6)	−0.0897(19)	0.6816(5)	0.0330
C(10)	0.2941(7)	−0.1717(22)	0.7171(6)	0.0402
C(11)	0.2905(8)	−0.1520(22)	0.7779(7)	0.0490
C(12)	0.2948(6)	0.0320(21)	0.8016(5)	0.0377
C(13)	0.3020(6)	0.1975(19)	0.7677(5)	0.0346
C(14)	0.3601(6)	0.2210(17)	0.7240(5)	0.0296
C(15)	0.4323(6)	0.1272(18)	0.7419(6)	0.0348
C(16)	0.4443(6)	0.1140(20)	0.8029(5)	0.0376
N(17)	0.4559(6)	0.1002(17)	0.8489(5)	0.0466
C(18)	0.4893(7)	0.2418(20)	0.7162(5)	0.0374
N(19)	0.5301(6)	0.3398(21)	0.6954(5)	0.0565
C(20)	0.4268(6)	−0.0915(18)	0.7122(5)	0.0299
C(21)	0.4349(7)	−0.2460(19)	0.7539(6)	0.0395
N(22)	0.4428(6)	−0.3744(19)	0.7836(5)	0.0494
C(23)	0.4826(7)	−0.1161(18)	0.6701(6)	0.0369
N(24)	0.5238(7)	−0.1335(21)	0.6365(5)	0.0555
Fe(1)*	0.1207(1)	0.0586(3)	0.4981(1)	0.0390
C(2)*	0.1881(7)	0.2374(25)	0.5091(6)	0.0571
O(3)*	0.2323(7)	0.3432(20)	0.5134(5)	0.0981
C(4)*	0.1494(7)	−0.0198(27)	0.4273(6)	0.0569
O(5)*	0.1690(5)	−0.0545(21)	0.3851(5)	0.0840
C(6)*	0.1729(8)	−0.1170(28)	0.5388(6)	0.0608
O(7)*	0.2013(8)	−0.2284(23)	0.5647(6)	0.1134
C(8)*	−0.0116(6)	−0.0011(19)	0.4121(5)	0.0387
C(9)*	−0.0142(6)	0.2129(19)	0.4328(5)	0.0344
C(10)*	0.0445(7)	0.2768(21)	0.4728(5)	0.0338
C(11)*	0.0462(7)	0.2310(23)	0.5325(5)	0.0364
C(12)*	0.0386(7)	0.0386(19)	0.5509(5)	0.0385
C(13)*	0.0304(7)	−0.1128(19)	0.5110(5)	0.0379
C(14)*	−0.0271(7)	−0.1161(21)	0.4646(6)	0.0407
C(15)*	−0.0967(6)	−0.0143(19)	0.4860(5)	0.0371
C(16)*	−0.1105(7)	−0.0169(17)	0.5468(5)	0.0355
N(17)*	−0.1212(6)	−0.0230(15)	0.5930(4)	0.0459
C(18)*	−0.1580(7)	−0.1095(21)	0.4572(5)	0.0417
N(19)*	−0.2005(7)	−0.1977(22)	0.4354(6)	0.0715
C(20)*	−0.0893(7)	0.2142(18)	0.4610(5)	0.0367
C(21)*	−0.0973(6)	0.3646(17)	0.5054(6)	0.0311
N(22)*	−0.1054(6)	0.4865(17)	0.5367(5)	0.0511
C(23)*	−0.1416(7)	0.2552(22)	0.4172(5)	0.0431
N(24)*	−0.1813(7)	0.2837(23)	0.3826(5)	0.0698
H(8A)	0.301	0.164	0.649	0.050
H(8B)	0.389	0.168	0.638	0.050
H(9)	0.349	−0.185	0.647	0.050
H(10)	0.257	−0.271	0.703	0.050
H(11)	0.283	−0.277	0.803	0.050

TABLE 2 (continued)

Atom	x	y	z	U_{eq}/U (Å^2) [a]
H(12)	0.293	0.049	0.845	0.050
H(13)	0.284	0.316	0.792	0.050
H(14)	0.359	0.375	0.721	0.050
H(8A)*	0.038	−0.036	0.397	0.050
H(8B)*	−0.049	−0.026	0.381	0.050
H(9)*	−0.006	0.314	0.400	0.050
H(10)*	0.072	0.401	0.459	0.050
H(11)*	0.053	0.345	0.562	0.050
H(12)*	0.039	0.006	0.594	0.050
H(13)*	0.039	−0.255	0.528	0.050
H(14)*	−0.031	−0.267	0.455	0.050

[a] For non-hydrogen atoms U_{eq} represents the equivalent value of the anisotropic Debey-Waller factor.

dyotropic reactions) [25] are also one stage concerted reactions. We emphasize that all these reactions involve an intramolecular three-bond alteration process, which include a σ carbon–carbon and two metal–organic bonds. We also stress the point that metal translocation in these pentacoordinated complexes occurs by way of a symmetry-allowed pseudorotation.

The interesting question of whether the stereochemistry of the migrating carbon is indeed retained, as predicted, remains to be answered by future studies.

Experimental section

The 3 + 2 adduct II was prepared as described by Green [2], by reaction of tricarbonyl(cycloheptatriene)iron(I) [26] with freshly sublimed TCNE, in CH_2Cl_2. It crystallized out from the reaction mixture in > 90% yield, and was washed with $CHCl_3$ and then used without further purification.

All the kinetic experiments were performed in NMR tubes. Dilute solutions (2–30 mM) were purged with nitrogen, and were sufficiently stable for the period of the experiment.

Variable temperature NMR spectra were recorded on a Bruker AM300 spectrometer equipped with an ASPECT 3000 data system. Chemical shifts (δ) are in ppm downfield from internal TMS. Sample temperature were measured with an Omega 870 digital thermometer, before and after each experiment; readings were within 0.5°C.

X-ray structure determination of $(C_{13}H_8N_4)Fe(CO)_3$ *(IV)* *

Tricarbonyl[(2,3,4,5-η)-bicyclo[4.2.1]nona-2,4-diene-7,7,8,8-tetracarbonitrile]iron (IV) [7], was recrystallized from CH_2Cl_2/hexane.

X-ray diffraction data were recorded on an Enraf–Nonius CAD4 diffractometer equipped with a graphite monochromator, employing Mo-K_α radiation (λ 0.71069 Å). Intensity data were collected in the ω–2θ mode with a scan width of $1.0 + 0.3\tan\theta$ out to $2\theta = 54°$. The scan rate varied according to the detected intensity between 1 and 4° min^{-1}. The data were corrected for background counts, variable measuring

---

* The atom numbers in Tables 2 and 3 of this section are as shown in Fig. 1.

TABLE 3

BOND DISTANCES (Å) AND ANGLES (°) IN COMPOUND IV

Fe(1)-C(2)	1.799(15)	Fe(1)*-C(2)*	1.782(15)
Fe(1)-C(4)	1.803(14)	Fe(1)*-C(4)*	1.843(14)
Fe(1)-C(6)	1.774(14)	Fe(1)*-C(6)*	1.824(16)
Fe(1)-C(10)	2.140(14)	Fe(1)*-C(10)*	2.154(13)
Fe(1)-C(11)	2.026(15)	Fe(1)*-C(11)*	2.009(14)
Fe(1)-C(12)	2.010(11)	Fe(1)*-C(12)*	2.008(13)
Fe(1)-C(13)	2.085(12)	Fe(1)*-C(13)*	2.097(13)
C(2)-O(3)	1.134(19)	C(2)*-O(3)*	1.109(20)
C(4)-O(5)	1.107(18)	C(4)*-O(5)*	1.093(18)
C(6)-O(7)	1.158(18)	C(6)*-O(7)*	1.112(22)
C(8)-C(9)	1.509(18)	C(8)*-C(9)*	1.527(18)
C(8)-C(14)	1.516(16)	C(8)*-C(14)*	1.497(18)
C(9)-C(10)	1.518(18)	C(9)*-C(10)*	1.529(17)
C(9)-C(20)	1.571(16)	C(9)*-C(20)*	1.580(17)
C(10)-C(11)	1.449(21)	C(10)*-C(11)*	1.449(17)
C(11)-C(12)	1.366(20)	C(11)*-C(12)*	1.379(19)
C(12)-C(13)	1.384(18)	C(12)*-C(13)*	1.402(17)
C(13)-C(14)	1.525(16)	C(13)*-C(14)*	1.553(18)
C(14)-C(15)	1.573(16)	C(14)*-C(15)*	1.578(18)
C(15)-C(16)	1.467(18)	C(15)*-C(16)*	1.465(16)
C(15)-C(18)	1.467(17)	C(15)*-C(18)*	1.498(17)
C(15)-C(20)	1.640(17)	C(15)*-C(20)*	1.659(17)
C(16)-N(17)	1.117(16)	C(16)*-N(17)*	1.115(15)
C(18)-N(19)	1.134(18)	C(18)*-N(19)*	1.131(19)
C(20)-C(21)	1.446(18)	C(20)*-C(21)*	1.471(17)
C(20)-C(23)	1.468(18)	C(20)*-C(23)*	1.466(17)
C(21)-N(22)	1.127(18)	C(21)*-N(22)*	1.119(17)
C(23)-N(24)	1.125(18)	C(23)*-N(24)*	1.132(17)

C(2)-Fe(1)-C(4)	99.9(7)	C(2)*-Fe(1)*-C(4)*	96.6(6)
C(2)-Fe(1)-C(6)	90.9(6)	C(2)*-Fe(1)*-C(6)*	88.3(7)
C(4)-Fe(1)-C(6)	93.8(7)	C(4)*-Fe(1)*-C(6)*	97.6(7)
C(2)-Fe(1)-C(12)	120.9(6)	C(2)*-Fe(1)*-C(12)*	121.1(6)
C(2)-Fe(1)-C(11)	91.7(7)	C(2)*-Fe(1)*-C(11)*	93.3(6)
C(4)-Fe(1)-C(12)	138.2(6)	C(4)*-Fe(1)*-C(12)*	141.2(6)
C(4)-Fe(1)-C(11)	140.5(6)	C(4)*-Fe(1)*-C(11)*	138.2(6)
C(6)-Fe(1)-C(12)	94.3(5)	C(6)*-Fe(1)*-C(12)*	92.9(6)
C(6)-Fe(1)-C(11)	123.8(6)	C(6)*-Fe(1)*-C(11)*	123.2(6)
Fe(1)-C(2)-O(3)	178.6(15)	Fe(1)*-C(2)*-O(3)*	175.7(14)
Fe(1)-C(4)-O(5)	178.9(13)	Fe(1)*-C(4)*-O(5)*	175.1(15)
Fe(1)-C(6)-O(7)	179.3(11)	Fe(1)*-C(6)*-O(7)*	176.1(15)
C(9)-C(8)-C(14)	100.8(10)	C(9)*-C(8)*-C(14)*	102.6(10)
C(8)-C(9)-C(20)	99.2(10)	C(8)*-C(9)*-C(20)*	99.8(10)
C(8)-C(9)-C(10)	116.7(11)	C(8)*-C(9)*-C(10)*	116.3(10)
C(10)-C(9)-C(20)	113.9(10)	C(10)*-C(9)*-C(20)*	113.5(10)
Fe(1)-C(10)-C(9)	118.7(9)	Fe(1)*-C(10)*-C(9)*	118.2(9)
C(9)-C(10)-C(11)	123.6(12)	C(9)*-C(10)*-C(11)*	124.2(12)
Fe(1)-C(10)-C(11)	65.5(8)	Fe(1)*-C(10)*-C(11)*	64.3(7)
Fe(1)-C(11)-C(10)	73.9(8)	Fe(1)*-C(11)*-C(10)*	75.1(8)
C(10)-C(11)-C(12)	119.3(14)	C(10)*-C(11)*-C(12)*	120.5(11)
Fe(1)-C(11)-C(12)	69.6(8)	Fe(1)*-C(11)*-C(12)*	69.9(8)
Fe(1)-C(12)-C(11)	70.9(8)	Fe(1)*-C(12)*-C(11)*	70.0(8)
C(11)-C(12)-C(13)	120.1(12)	C(11)*-C(12)*-C(13)*	119.1(11)
Fe(1)-C(12)-C(13)	73.2(7)	Fe(1)*-C(12)*-C(13)*	73.5(8)
Fe(1)-C(13)-C(12)	67.3(7)	Fe(1)*-C(13)*-C(12)*	66.7(7)

TABLE 3 (continued)

C(12)-C(13)-C(14)	123.4(11)	C(12)*-C(13)*-C(14)*	124.6(11)
Fe(1)-C(13)-C(14)	118.2(8)	Fe(1)*-C(13)*-C(14)*	118.9(9)
C(8)-C(14)-C(13)	118.3(10)	C(8)*-C(14)*-C(13)*	116.3(11)
C(13)-C(14)-C(15)	114.2(10)	C(13)*-C(14)*-C(15)*	111.0(11)
C(8)-C(14)-C(15)	100.7(9)	C(8)*-C(14)*-C(15)*	102.0(10)
C(14)-C(15)-C(20)	101.0(9)	C(14)*-C(15)*-C(20)*	102.7(9)
C(14)-C(15)-C(18)	108.9(10)	C(14)*-C(15)*-C(18)*	108.8(10)
C(14)-C(15)-C(16)	115.3(10)	C(14)*-C(15)*-C(16)*	117.5(10)
C(18)-C(15)-C(20)	110.1(10)	C(18)*-C(15)*-C(20)*	107.6(10)
C(16)-C(15)-C(20)	112.2(11)	C(16)*-C(15)*-C(20)*	112.2(10)
C(16)-C(15)-C(18)	109.0(11)	C(16)*-C(15)*-C(18)*	107.7(10)
C(15)-C(16)-N(17)	177.2(13)	C(15)*-C(16)*-N(17)*	178.6(13)
C(15)-C(18)-N(19)	175.4(14)	C(15)*-C(18)*-N(19)*	173.3(15)
C(9)-C(20)-C(15)	104.4(9)	C(9)*-C(20)*-C(15)*	102.9(10)
C(15)-C(20)-C(23)	110.3(10)	C(15)*-C(20)*-C(23)*	111.8(10)
C(15)-C(20)-C(21)	110.5(10)	C(15)*-C(20)*-C(21)*	112.2(10)
C(9)-C(20)-C(23)	109.2(10)	C(9)*-C(20)*-C(23)*	108.5(10)
C(9)-C(20)-C(21)	114.6(10)	C(9)*-C(20)*-C(21)*	113.6(10)
C(21)-C(20)-C(23)	107.8(11)	C(21)*-C(20)*-C(23)*	107.8(11)
C(20)-C(21)-N(22)	175.4(15)	C(20)*-C(21)*-N(22)*	175.6(14)
C(20)-C(23)-N(24)	177.7(15)	C(20)*-C(23)*-N(24)*	178.4(15)

time and the Lorentz-polarization factor, but not for absorption or secondary extinction.

Crystal data. $C_{16}H_8FeN_4O_3$, $M_r = 360.1$, orthorhombic, *a* 19.058(3), *b* 6.755(3), *c* 23.709(2) Å, *V* 3052.3 Å^3, $Z = 8$, D_c 1.567 g cm^{-3} $F(000) = 1456$, space group $Pna2_1$.

The structure was solved by a combination of direct methods and Fourier techniques (MULTAN 80). There are two molecular entities in the asymmetric unit which are related to each other by a pseudo two-fold axis. Their refinement was carried out by block-diagonal least-squares including the atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms. All hydrogens were located directly from electron density difference maps, and were assigned isotropic temperature factors. No attempt was made however to refine their atomic parameters. The final discrepancy index at the end of the refinement was $R = 0.049$ for 1599 unique observations $> 3\sigma$. The final difference Fourier maps showed no indications of incorrectly placed or missing atoms. The refined atomic parameters are listed in Table 2 (atoms marked by an asterisk belong to the second molecule of the asymmetric unit). Bond lengths and bond angles are given in Table 3. Figure 1 shows a perspective view of the molecular structure, which is very similar for the two molecules.

Acknowledgement

We thank Mrs. Sima Alfi for technical assistance. Support by the Planning and Grant Committee of the Council for Higher Education for the purchase of the Bruker AM300 NMR Spectrometer is gratefully acknowledged.

References

1 Z. Goldschmidt, H.E. Gottlieb and D. Cohen, J. Organomet. Chem., 294 (1985) 219.

2 M. Green, S.M. Heathcock and D.C. Wood, J. Chem. Soc., Dalton Trans., (1973) 1564.

3 M. Green, S.M. Heathcock, T.W. Turney and D.M.P. Mingos, J. Chem. Soc., Dalton Trans., (1977) 204.

4 C. Reichardt, Solvent Effects in Organic Chemistry, Verlag Chemie, Weinheim, New York, 1978.

5 S.K. Chopra, M.J. Hynes and P. McArdle, J. Chem. Soc., Dalton Trans., (1981) 586.

6 Z. Goldschmidt, S. Antebi, H.E. Gottlieb, D. Cohen, U. Shmueli and Z. Stein, J. Organomet. Chem., 282 (1985) 369.

7 Z. Goldschmidt and E. Genizi, Synthesis, (1985) 949.

8 W.J. Middleton, R.E. Heckert, E.L. Little and C.G. Krespan, J. Am. Chem. Soc., 80 (1958) 2783.

9 R.B. Woodward and R. Hoffmann, The Conservation of Orbital Symmetry, Verlag Chemie, Weinheim, 1970.

10 N.T. Anh, M. Elian and R. Hoffmann, J. Am. Chem. Soc., 100 (1978) 110; T.A. Albright, P. Hofmann, R. Hoffmann, C.P. Lillya and P.A. Dobosh, J. Am. Chem. Soc., 105 (1983) 3396.

11 M.J.S. Dewar, Angew. Chem., Int. Ed. Engl., 10 (1971) 761; M.J.S. Dewar and A.B. Pierini, J. Am. Chem. Soc., 106 (1984) 203.

12 (a) R.E. Lehr, A.P. Marchand (Eds.), Pericyclic Reactions, Academic Press, New York, 1977, Vol. 1, p. 1; (b) H.E. Zimmerman, ibid., p. 53.

13 S.W. Benson, F.R. Cruickshank, D.M. Golden, G.R. Hangen, H.E. O'Neal, A.S. Rodgers, R. Show and R. Walsh, Chem. Rev., 69 (1969) 279.

14 H.A. Skinner, J.A. Connor, Pure and Appl. Chem., 57 (1985) 79 and references cited therein.

15 H.E. O'Neal and S.W. Benson in J.K. Kochi (Ed.), Free Radicals, Wiley, New York, 1973, Vol. 2, p. 275.

16 T.B. McMahon and P. Kebarle, J. Am. Chem. Soc., 98 (1976) 3399.

17 R.D. Ernst, Structure and Bonding, 57 (1984) 1, and references therein.

18 P. Ballinger and F.A. Long, J. Am. Chem. Soc., 81 (1959) 1050; 82 (1960) 795; S. Takahashi, L.A. Cohen, H.K. Miller and E.G. Peaks, J. Org. Chem., 36 (1971) 1205.

19 J. Weaver and P. Woodward, J. Chem. Soc. (A), (1971) 3521.

20 R.S. Berry, J. Chem. Phys., 32 (1960) 933.

21 A. Rossi and R. Hoffmann, Inorg. Chem., 14 (1975) 365; D.E. Eaton, J. Am. Chem. Soc., 90 (1968) 4272.

22 T.A. Albright, R. Hoffmann and P. Hofmann, Chem. Ber., 111 (1978) 1591.

23 (a) T.A. Albright, P. Hofmann and R. Hoffmann, J. Am. Chem. Soc., 99 (1977) 7546; (b) T.A. Albright, Tetrahedron, 38 (1982) 1339.

24 S.I. Miller, Ad. Phys. Org. Chem., 6 (1968) 185; O.S. Tee, J. Am. Chem. Soc., 91 (1969) 7144.

25 Z. Goldschmidt and S. Antebi, Tetrahedron Lett., (1978) 271.

26 H.A. Bockmuelen, A.W. Parkins, J. Chem. Soc., Dalton Trans., (1981) 262; M. Brookhart, K. Karel and L.E. Nance, J. Organomet. Chem., 140 (1977) 203.