

REACTIONS OF COORDINATED POLYOLEFINS *. SIGMAHAPTOTROPIC REARRANGEMENTS INVOLVING NITROGEN MIGRATION

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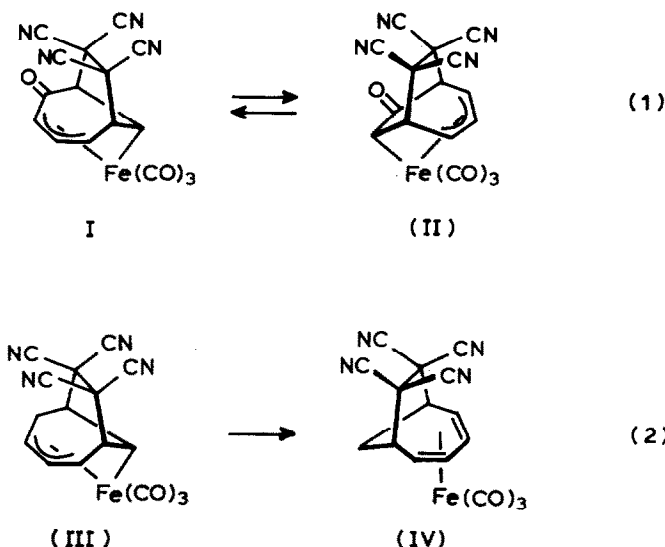
Summary

(η^4 -Tropone)Fe(CO)₃ reacts with 4-phenyl-triazoline-3,5-dione (NPTD) to give the [3 + 2]- and [4 + 2]-cycloadducts as the initial kinetic products, in a ratio of 3/1. The second order rate constant (at 24°C, in acetone) for the [3 + 2] reaction is $1.56 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ and that for the [4 + 2] reaction $5.10 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ with free activation energies of $\Delta G_1^\ddagger$ 21.20 kcal mol⁻¹ and $\Delta G_2^\ddagger$ 21.86 kcal mol⁻¹, respectively. Under thermodynamic conditions an equilibrium mixture is reached containing, in addition to the [3 + 2]- and [4 + 2]-adducts, the [5 + 2]-isomer, with the three products in a ratio of 2/1/39. The kinetic data are consistent with a mechanism in which the [3 + 2]- and the [4 + 2]-adducts equilibrate, with first order constants $k_{34} = 9.8 \times 10^{-6} \text{ s}^{-1}$ and $k_{43} = 2.0 \times 10^{-5} \text{ s}^{-1}$, respectively, via a [2,2]-sigmahaptotropic rearrangement, while equilibration of the [3 + 2]- and [5 + 2]-isomers takes place with rate constants $k_{35} = 2.9 \times 10^{-5} \text{ s}^{-1}$ and $k_{53} = 1.5 \times 10^{-6} \text{ s}^{-1}$, respectively, via the [3,3]-sigmahaptotropic rearrangement pathway.

Introduction

The term sigmahaptotropic rearrangements is used to describe the class of pericyclic reactions in which a σ -bonded group and a coordinated metal fragment exchange bonding sites antarafacially across a conjugated chain [1,2]. Of the number of reactions noted in the literature [1–3] only rearrangements of the type [3,3] (eq. 1) and [4,4] (eq. 2) have been studied by kinetic methods [1,2], and these were shown to proceed by a thermally allowed $\sigma 2a + (\pi 2s + \sigma 2a)$ pathway. So far, all the rearrangements have involved a carbon sigmatropic migration, although, in principle, other σ -bonded groups might equally well migrate. The present paper focuses on the ability of a nitrogen-bonded group to participate in sigmahaptotropic rearrangements.

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



Results

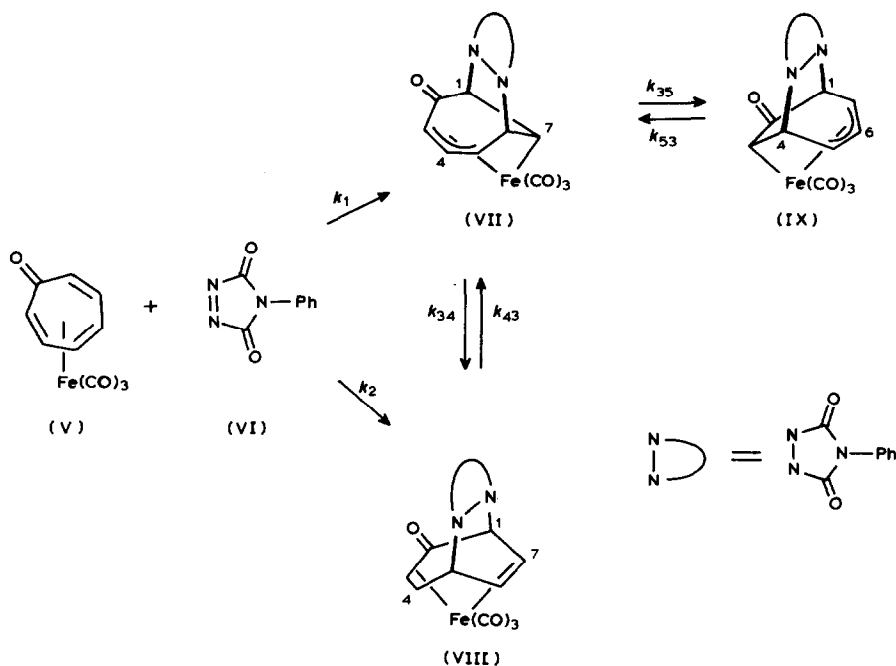
The choice of a σ -bonded nitrogen fragment as the migrating group stems from the observation that triazoline-3,5-diones react with (tropone) $\text{Fe}(\text{CO})_3$ (V) to give a single isolable product, identified as the [5 + 2]-adduct [4,5]. The analogous reaction of V with tetracyanoethylene (TCNE) gave initially, under kinetic conditions, the [3 + 2]-adduct I, which subsequently rearranged to the [5 + 2]-isomer II (eq. 1). It was therefore reasonable to suspect that the cycloaddition with a triazolinodione would show similar behavior. Indeed, when equimolar amounts of (tropone) $\text{Fe}(\text{CO})_3$

TABLE 1

¹H NMR SPECTROSCOPIC DATA FOR (TROPONE) $\text{Fe}(\text{CO})_3$ -NPTD ADDUCTS ^a

Compound	Solvent	H(1)	H(3)	H(4)	H(5)	H(6)	H(7)
VII	(CD ₃) ₂ CO	4.21	4.69	5.40	5.30	5.03	2.20
	CDCl ₃	4.25	4.60		4.93–5.03		1.93
		$J_{13} = 1.9$, $J_{16} = 0.2$, $J_{17} = 8.6$, $J_{34} = 9.3$, $J_{35} = 0.9$, $J_{45} = 8.0$, $J_{46} = 1.0$, $J_{56} = 6.2$, $J_{57} = 1.4$, $J_{67} = 8.7$					
VIII	(CD ₃) ₂ CO	4.92	3.25	4.13	5.75	4.37	3.89
	CDCl ₃	4.93–5.03	3.15	3.79	5.62	3.38	3.92
		$J_{13} = 1.9$, $J_{16} = 1.3$, $J_{17} = 7.8$, $J_{34} = 8.1$, $J_{35} = 0.6$, $J_{45} = 8.1$, $J_{46} = 0.3$, $J_{47} = 0.4$, $J_{56} = 7.7$, $J_{57} = 1.5$, $J_{67} = 6.6$					
IX	(CD ₃) ₂ CO	4.92	2.53	5.02	4.64	5.53	5.50
	CDCl ₃	5.04	2.57	4.90	4.33	5.11	5.18
		$J_{13} = 2.4$, $J_{16} = 0.8$, $J_{17} = 7.3$, $J_{34} = 9.6$, $J_{35} = 0.6$, $J_{45} = 6.7$, $J_{46} = 0.9$, $J_{56} = 6.0$, $J_{57} = 2.0$, $J_{67} = 7.4$					

^a δ (ppm) from TMS; J in Hz; numbering as in Scheme 1; coupling constants were measured in (CD₃)₂CO except for IX which were taken in CDCl₃.



SCHEME 1

(V) and 4-phenyltriazoline-3,5-dione (NPTD) (VI) were mixed in acetone- d_6 at room temperature and the reaction monitored by ^1H NMR spectroscopy, the initial formation of two products in a ratio of 3/1 was observed. These were identified by NMR spectroscopy (Table 1) as the [3 + 2]- (VII) and [4 + 2]- (VIII) -cycloadducts, respectively. For VII we note in particular the high-field resonance of H(7) at δ 2.20, and the three low-field signals of the allylic protons at 4.69, 5.30 and 5.40 ppm. Adduct VIII shows characteristic signals at a relatively high field from the four protons of the coordinated olefins at 3.25, 3.89, 4.13 and 4.37 ppm. The initial formation of VII and VIII is followed by the appearance of a third product, whose resonances correspond to the [5 + 2]-isomer (IX), which we previously isolated [4]. After 48 h an equilibrium mixture is approached containing > 80% of IX, which was isolated by recrystallization.

Kinetic studies

The reaction of V with an equimolar amount of NPTD was carried out in 0.1 M acetone- d_6 solutions at 24°C and monitored by ^1H NMR spectroscopy. The general reaction scheme is outlined in Scheme 1. The relative concentrations of V and the three products VII, VIII and IX, were derived by integration of the relevant proton signals, and progress with time of the reaction is shown in Fig. 1. The kinetic data are listed in Tables 2 and 3.

The six rate constants were evaluated by means of a computer simulation, for which eqs. 3–6 were used.

$$d[\text{V}]/dt = -(k_1 + k_2)[\text{V}]^2 \quad (3)$$

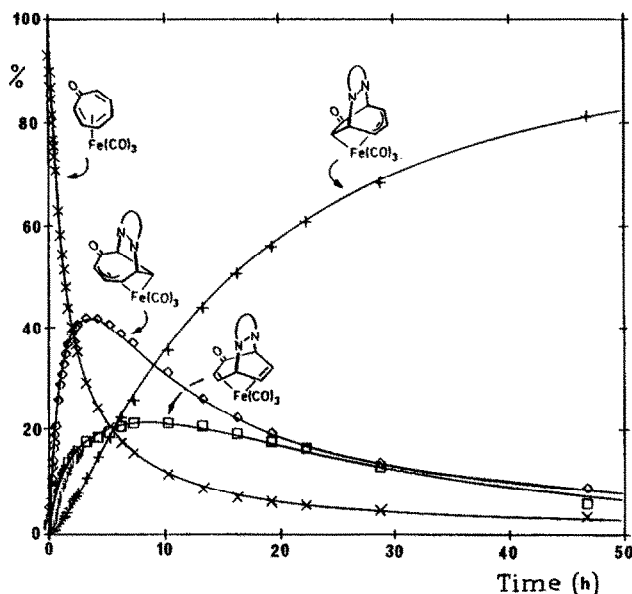


Fig. 1. Progress with time of the 1:1 reaction of (tropone)Fe(CO)₃ and NPTD in acetone-*d*₆ at 24°C.

TABLE 2

KINETIC DATA FOR THE CYCLOADDITION OF NPTD TO (TROPONE)Fe(CO)₃ (acetone-*d*₆, 24°C)

Reaction	k (M ⁻¹ s ⁻¹)	$\Delta G^\ddagger$ (kcal mol ⁻¹)	$t_{1/2}^a$ (h)	Ref.
V + VI → VII	1.56×10^{-3}	21.20	1.8	This work
V + VI → VIII	5.10×10^{-4}	21.86	5.5	This work
V + TCNE → I	4.41×10^{-2}	19.21	0.1	[2]

^a $t_{1/2} = 1/kc_0$ ($c_0 = 9.83 \times 10^{-2}$ M).

TABLE 3

KINETIC DATA FOR THE SIGMAHAPTOTROPIC REARRANGEMENTS (acetone-*d*₆, 24°C)

Reaction	k (s ⁻¹)	$\Delta G^\ddagger$ (kcal mol ⁻¹)	$t_{1/2}^a$ (h)	Ref.
VII → VIII	9.8×10^{-6}	24.19	19.6	This work
VIII → VII	2.0×10^{-5}	23.77	9.6	This work
VII → IX	2.9×10^{-5}	23.55	6.6	This work
IX → VII	1.5×10^{-6}	25.30	128.3	This work
I → II	3.3×10^{-4}	22.08	0.58	[2]
II → I	5.0×10^{-5}	23.23	3.9	[2]

$\Delta G_{34}^\circ = 0.42$ kcal mol⁻¹

$\Delta G_{35}^\circ = 1.75$ kcal mol⁻¹

$\Delta\Delta G^\ddagger = 0.64$ kcal mol⁻¹

^a $t_{1/2} = \ln 2/k$.

$$d[\text{VII}]/dt = k_1[\text{V}]^2 + k_{43}[\text{VIII}] + k_{53}[\text{IX}] - (k_{34} + k_{35})[\text{VII}] \quad (4)$$

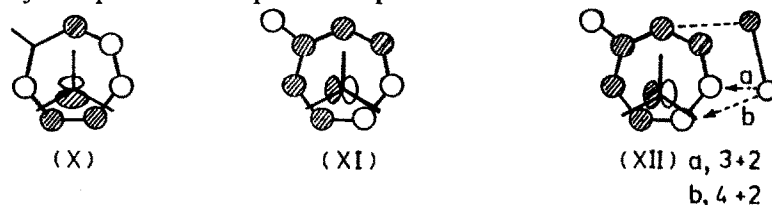
$$d[\text{VIII}]/dt = k_2[\text{V}]^2 + k_{34}[\text{VII}] - k_{43}[\text{VIII}] \quad (5)$$

$$d[\text{IX}]/dt = k_{35}[\text{VII}] - k_{53}[\text{IX}] \quad (6)$$

The values of the specific rate constants were derived by modification of estimated values until a best fit to the experimental points was obtained. The good correlation is illustrated in Fig. 1, where the points represent the experimental values and the lines are those obtained by computer simulation.

Discussion

The main feature to be noted is the marked resemblance between the reactions of NPTD and TCNE with (tropone)Fe(CO)₃ (V) in both cycloadditions and rearrangements of their adducts. We note in particular that only two cycloadducts are initially formed, namely the [3 + 2]- (VII) and the [4 + 2]- (VIII) -isomers. On the assumption that the cycloadditions are subject to frontier orbital control, the controlling interaction appears to involve the subjacent molecular orbital (NHOMO) [2,6] of the complex and the LUMO of NPTD, as illustrated in XII. The occurrence of this unusual interaction may be associated with the stereospecific requirement for the addend (NPTD) to approach the organic ligand from the side opposite to the metal bonding face. Since the complex HOMO (X) (backbonding orbital) is essentially a metal orbital, whereas the NHOMO (XI) is mainly an organic ligand orbital, it is to be expected that the dominant frontier orbital interaction at the face *anti* to metal will indeed occur between the subjacent metal-perturbed tropone orbital and the LUMO of NPTD. This view is strongly supported by previous studies on the (cycloheptatriene)Fe(CO)₃ series [1,7,8] and on the tropone complex [2]; in those cases, also, the [3 + 2]- and [4 + 2]-adducts are the only kinetic products observed, even though rearrangements between all the formal $n + 2$ ($n = 1-6$) adducts of cycloheptatriene complexes are possible.



Another interesting observation is the high rate of cycloaddition of TCNE compared to that of NPTD, $k(\text{TCNE})/k(\text{NPTD}) = 17.2$. This ratio is usually inverted in most Diels-Alder reactions [9]. However, it has been noted [10] that hindered dienes such as anthracene react with NPTD more slowly than with TCNE. Therefore, it is expected that the congested complex V, being shielded on one side by the Fe(CO)₃ group and folded on the side of attack, will react with the bulky NPTD less readily than with TCNE. On the other hand, NPTD shows higher selectivity than TCNE toward [4 + 2]-cycloaddition [2]. This may be attributed to secondary orbital interactions [11] between NPTD and V, which are better in the [4 + 2] than in the [3 + 2] reaction mode, and negligible with TCNE. The important role of secondary orbital interactions has also been observed in the reaction between (cycloheptatriene)Fe(CO)₃ and (carbomethoxy)maleic anhydride, where the selectivity toward the [4 + 2]-cycloaddition was found to be even higher [8].

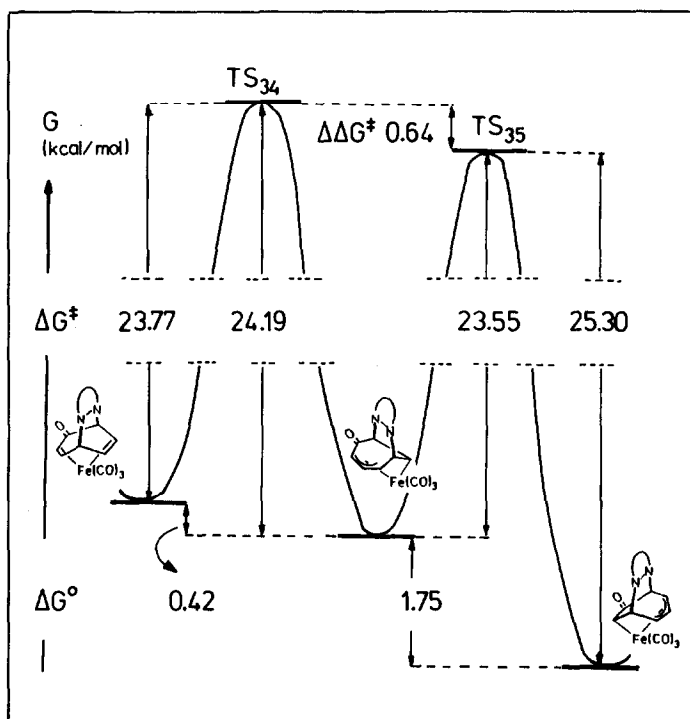
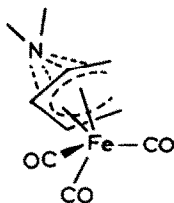


Fig. 2. Free energy profile for the sigmahaptotropic rearrangements (TS = transition state).

We turn now to the subsequent rearrangements, and note that two sigmahaptotropic reactions are observed. One is of the type [2,2], involving interconversion of the two primary cycloaddition products VII and VIII [7], and the other is of the type [3,3], involving interconversion of VII and the thermodynamically more stable [5 + 2]-adduct IX [2]. Interestingly, we see here the first clear example of a [2,2]-sigmahaptotropic rearrangement which leads to equilibration of a η^2, η^2 -diene complex and a η^1, η^3 - σ, π -allylic complex. The previously reported rearrangements of type [2,2] transformed η^4 -butadiene complexes into their η^1, η^3 - σ, π -allylic counterparts [7]. In this context, we recall the earlier observation that the cycloaddition of V and TCNE similarly gave the corresponding [3 + 2]- and [4 + 2]-adducts, which subsequently rearranged to the [5 + 2]-adduct. In this case, however, the rearrangement of the [4 + 2]-adduct could not be monitored owing to its low concentration in the reaction mixture [2]. In light of the present results, it is reasonable to believe that the [4 + 2] TCNE adduct also rearranges to the [5 + 2]-isomer via the [3 + 2]-adduct, but this could only be verified by independent experiments using the labile [4 + 2]-adduct, which was not isolated.

The kinetic data clearly show that the three isomers do not differ much in their relative stability. This is perhaps best illustrated by the free energy reaction profile depicted in Fig. 2, which shows that the [5 + 2]-isomer IX is by 1.75 kcal mol⁻¹ more stable than the [3 + 2]-isomer VII, which in turn is more stable than the [4 + 2]-isomer VIII by only 0.42 kcal mol⁻¹. It is thus not surprising that the ratio between the various isomers can readily be changed by varying either the migrating

group [2] or the substitution on the central seven-membered ring [1,7,8], or alternatively the metal fragment [12]. Particularly noteworthy is the thermodynamic stability of the [5 + 2]-adducts of tropone complex [2] as opposed to the cycloheptatriene counterparts [1,7,8], for which no [5 + 2]-adducts could be detected. Possibly it is the carbonyl adjacent to the Fe–C σ bond which preferentially stabilizes the [5 + 2]-isomer over the other products.



(XIII)

We conclude with a comment on the mechanism of the rearrangements. The kinetic results clearly show that the rearrangements are first order reactions. Attempts to trap the starting complex V, which might be formed through cycloreversion, by adding TCNE to the equilibrium mixture were unsuccessful. The rearrangements are therefore likely to be concerted. Like their carbon counterparts, they are thermally allowed pericyclic reactions of the type $\sigma 2a + (\pi 2s + \sigma 2a)$ which involve one carbon–nitrogen σ bond and two bonds between the metal and the organic ligand. The two inversions of configuration occur at the exchanging sites of the iron and the nitrogen. The transition state (XIII) is reached along a reaction coordinate involving pseudorotation about the pentacoordinated metal. During this pseudorotation the metal orbitals of one isomer are transformed symmetrically into those of the other [1,2]. Interestingly, there is no direct interconversion between the [4 + 2]- and the [5 + 2]-isomers. They do equilibrate, however, via the [3 + 2]-intermediate. The transition states for both rearrangements are seen (Fig. 2) to be very close in energy, $\Delta\Delta G^\ddagger = 0.64 \text{ kcal mol}^{-1}$. They probably both resemble structure XIII in having a central pentadienyl system flanked by the metal fragment on one face and by the migrating nitrogen group on the other.

Experimental

(Tropone)Fe(CO)₃ (V) was prepared from tropone and Fe₂(CO)₉ as described by Eisenstadt and Hunt [13], and was sublimed (40–50 °C/0.1 mmHg) shortly before use. 4-Phenyl-triazoline-3,5-dione (VI) was prepared as described by Cookson [9] and was sublimed before use. All the kinetic experiments were performed in NMR tubes. Equimolar amounts of the reactants were mixed in (CD₃)₂CO or CDCl₃ to give ca. 0.1 M solutions, which were purged with nitrogen and were sufficiently stable for the period of the experiment.

NMR spectra were recorded on a Bruker AM300 spectrometer equipped with an ASPECT 3000 data system.

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References

- 1 Z. Goldschmidt, H.E. Gottlieb, E. Genizi, D. Cohen and I. Goldberg, *J. Organomet. Chem.*, 301 (1986) 337.
- 2 Z. Goldschmidt, H.E. Gottlieb and D. Cohen, *J. Organomet. Chem.*, 294 (1985) 219.
- 3 e.g. (a) R. Aumann, *Chem. Ber.*, 108 (1975) 1974; (b) L.A. Paquette, R.P. Micheli and J.M. Photis, *J. Am. Chem. Soc.*, 99 (1977) 7911; (c) M. Green, S.M. Heathcock, T.W. Turney and D.M.P. Mingos, *J. Chem. Soc., Dalton Trans.*, (1977) 204; (d) Z. Goldschmidt and S. Antebi, *Tetrahedron Lett.*, (1978) 271; (e) S.K. Chopra, G. Moran and P. McArdle, *J. Organomet. Chem.*, 214 (1981) C36; (f) H.R. Beer, P. Bigler, W. von Philipsborn and A. Salzer, *Inorg. Chim. Acta*, 52 (1981) L49.
- 4 Z. Goldschmidt and Y. Bakal, *Tetrahedron Lett.*, (1976) 955.
- 5 G.D. Andreetti, G. Bocelli and P. Sgarabotto, *J. Organomet. Chem.*, 150 (1978) 85.
- 6 V. Gold, *Pure and Appl. Chem.*, 55 (1983) 1281.
- 7 Z. Goldschmidt, S. Antebi, D. Cohen and I. Goldberg, *J. Organomet. Chem.*, 273 (1984) 347.
- 8 Z. Goldschmidt, S. Antebi, H.E. Gottlieb, D. Cohen, U. Shmueli and Z. Stein, *J. Organomet. Chem.*, 282 (1985) 369.
- 9 R.C. Cookson, S.S.H. Gilani and I.D.R. Stevens, *J. Chem. Soc. (C)*, (1967) 1905.
- 10 J. Sauer and B. Schröder, *Chem. Ber.*, 100 (1967) 678.
- 11 R. Gleiter and L.A. Paquette, *Acc. Chem. Res.*, 16 (1983) 328.
- 12 Unpublished results.
- 13 A. Eisenstadt, *J. Organomet. Chem.*, 97 (1975) 443; D.F. Hunt, G.C. Farant and R.T. Rodheaver, *J. Organomet. Chem.*, 38 (1972) 349.