The mechanism of pericyclic organometallic reactions *. Competitive [4,4]-sigmahaptotropic rearrangement versus metal–hydride shift

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Abstract

The *anti*-2-^{2}H labeled 3 + 2 adduct of tricarbonyl(η^4-cycloheptatriene)iron and tetracyanoethylene undergoes a thermal rearrangement to the 6 + 2 isomeric complex, exclusively labeled at the *anti* position of the methylene group. Rate studies reveal no kinetic isotope effect. These observations exclude a hydrogen transfer mechanism, and suggest a pericyclic [4,4]-sigmahaptotropic ($\sigma\eta$) rearrangement.

Introduction

Consider the rearrangement of the 3 + 2 adduct I of (η^4-cycloheptatriene)Fe(CO)$_3$ and tetracyanoethylene (TCNE) to the corresponding 6 + 2 isomer II (eq. 1). Although both isomers have the same bicyclo[4.2.1]nonane framework, I is a η^1,η^3-σ,π-allylic complex having the methylene group within the four carbon chain, whereas II coordinates to the metal in a η^4-butadiene π-bonding mode with the methylene group at the one carbon bridge.

In principle, two intramolecular mechanistic pathways could account for this rearrangement. One involves a hydrogen transfer from the *syn*-2 to *syn*-7 position (eq. 1a), presumably via formation of a metal hydride intermediate. The alternative rearrangement pathway consists of a 1,4-C(8) migration to position 3 (eq. 1b). Both processes involve a concomitant metal shift. In process (a) the iron migrates from C(7) to C(2), whereas in (b) migration takes place from C(3) to C(6). There is ample precedent for both pathways. Isomerizations involving the hydrogen transfer reaction have been encountered for tricarbonyliron complexes [2] as well as for many other transition metal complexes [3]. These metal hydride-shift reactions are also the major pathway in numerous transition metal catalyzed isomerizations [4]. The

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* For the preceding paper in this series see Ref. 1.
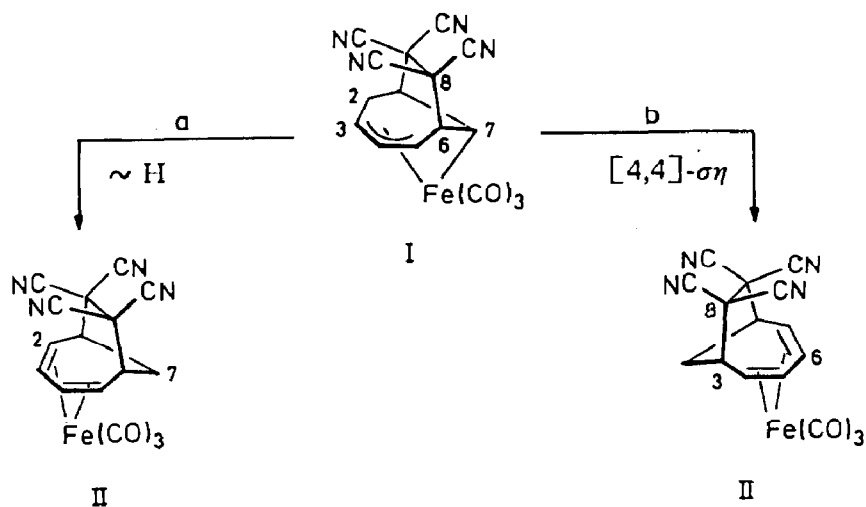
alternative coupled carbon–metal rearrangements of type (b), termed sigmahapto-tropic ($\sigma\eta$) reactions [5], occur most frequently in coordinated bicyclic olefins [6]. Structural and kinetic studies suggest that these reactions are concerted [5,7]. A detailed molecular orbital analysis of the pericyclic [4,4]-$\sigma\pi$ rearrangement specifically presented herein has been reported before [8].

In order to distinguish between the two mechanistic pathways, the ^{2}H-labeled σ,π-allylic complex I-d was prepared by cycloaddition of (2-$anti$-^{2}H-η^4-cycloheptatriene)Fe(CO)$_3$ (III-d) [9] with TCNE (eq. 2) [10], and was subjected to the thermal conditions used for the parent compound I [8].
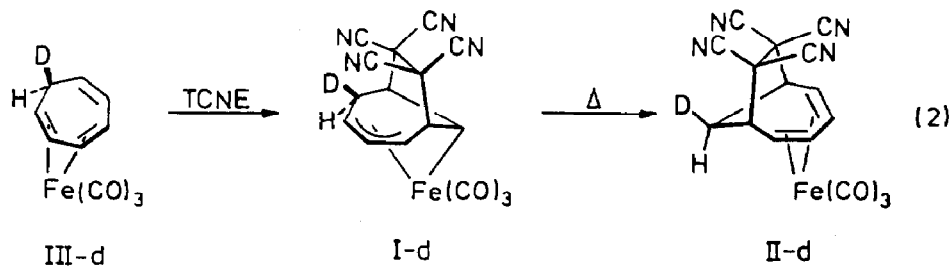
Results and Discussion

The ^{1}H NMR spectrum depicted in Fig. 1b shows that I-d is more than 95% labeled at the $anti$ (to metal) position. Especially notable is the absence of the $anti$-2 proton signal at δ 2.42 (cf. Fig. 1a). Heating of I-d in acetone at 50°C for several days resulted in a clean conversion into a single product, readily identified as the $anti$-^{2}H 6 + 2 adduct II-d (Fig. 1d) by the singlet at δ 1.53 of the methylene syn-H and absence of the $anti$-H signal at 2.07 (cf. Fig. 1c). No scrambling of the deuterium could be detected by NMR, clearly indicating that no hydrogen shift occurred.

Further evidence for the absence of a metal hydride shift was obtained from a study of the α-secondary kinetic isotope effect [11]. Thus, the rearrangement was followed by ^{1}H NMR in acetone-d_6 as described before [8]. The first order rate
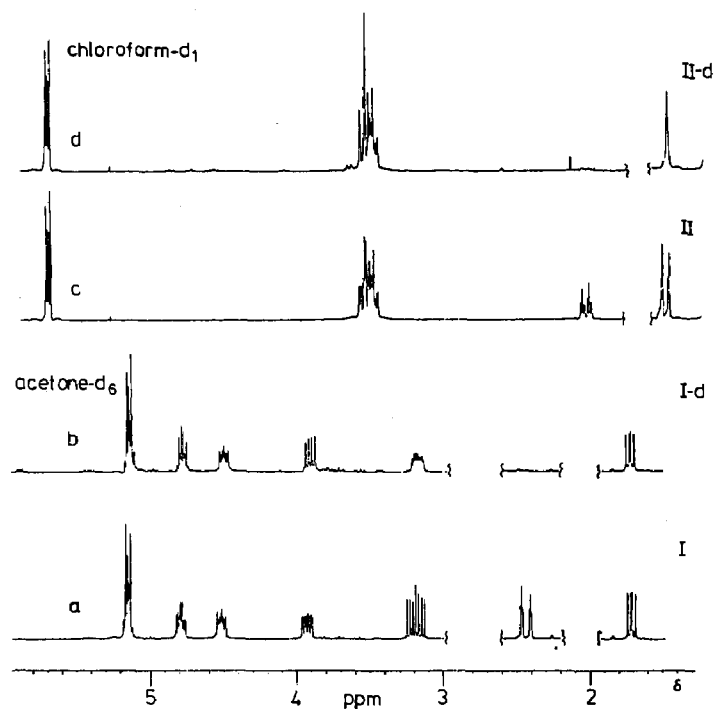
Fig. 1. ^1H NMR spectrum of (a) I, (b) I-d (acetone-d_6), (c) II, and (d) II-d (chloroform-d_1).

constants for the rearrangement at $42°C$ were $k_D = (1.29 \pm 0.01) \times 10^{-5}$ s^{-1} and $k_H = (1.23 \pm 0.02) \times 10^{-5}$ s^{-1} (Fig. 2). In addition, a run was carried out in which equimolar amounts of I and I-d were subject to the reaction conditions. The ^1H NMR spectrum of the initial mixture was compared with that taken after about 96% conversion; the ratio of the deuterated to non-deuterated residual starting material was estimated as 1.0 ± 0.2, which implies that $k_H/k_D = 1.00 \pm 0.06$. These experiments clearly reveal the absence of an α-secondary isotope effect for the rearrangement, which, together with the NMR analysis (Fig. 1) exclude a hydrogen transfer mechanism in favor of a carbon–metal [4,4]-sigmahaptotropic rearrangement.
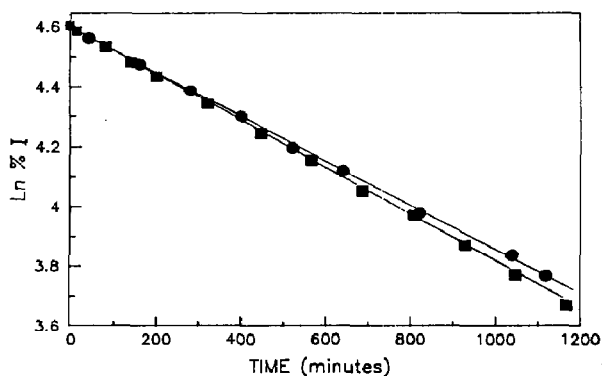

Fig. 2. Plots of ln % I (●) and ln % I-d (■) vs. time (min) (acetone-d_6, $42°C$).

A final point regarding the intramolecular mode of the reaction deserves comment. We have previously shown [8] that the presence of cyclohexadiene, or the powerful dienophile (carbomethoxy)maleic anhydride (CMA), in the reaction mixture did not affect the rearrangement course. This was taken as evidence for the absence of a cycloreversion–addition pathway. In order to pursue this argument further we carried the 1-d → II-d rearrangement to completion in the presence of an excess of the unlabeled cycloheptatriene complex. The sole 6 + 2 adduct isolated was the labeled isomer II-d.

It may thus be concluded that the mechanism of the I → II transformation is a true pericyclic [4,4]-$\sigma\eta$ rearrangement, a concerted reaction in which a σ-bonded group and a metal fragment exchange bonding sites antarafacially, in a single kinetic step [8].

Experimental

(2-anti-^{2}H-η^4-cycloheptatriene)Fe(CO)$_3$ (III-d) was prepared as described by Brookhart [9], from (cht)Fe(CO)$_3$ and NaOMe in MeOD. The deuterated complex was purified by column chromatography (Merck Kieselgel 60, hexane). The ^{1}H NMR (CDCl$_3$) spectrum at the methylene region shows a single broad signal at δ 2.39 of the syn proton.

The 3 + 2 adduct I-d was prepared as described by Green [10], by reactions of III-d with freshly sublimed TCNE, in CHCl$_3$. The crystalline product which separated from the reaction mixture was washed with CHCl$_3$ and used without further purification. The ^{1}H NMR spectrum in (CD$_3$)$_2$CO is shown in Fig. 1b.

Rearrangements were carried out in acetone solutions at 50°C. The product (II-d) was recrystallized from CH$_2$Cl$_2$/hexane [12]. The ^{1}H NMR spectrum in CDCl$_3$ is shown in Fig. 1d.

The kinetic experiments were performed in NMR tubes. Dilute solutions (10–20 mM) of I-d in (CD$_3$)$_2$CO were purged with nitrogen and were sufficiently stable during the experimental period.

NMR spectra were recorded on a Bruker AM300 spectrometer equipped with an ASPECT 3000 data system. The sample temperatures were measured with a Eurotherm 840/T digital thermometer, and are estimated to be correct within ±0.5°C.

References

1 Z. Goldschmidt and H.E. Gottlieb, J. Organomet. Chem., 361 (1989) 207.
2 D.V. Banthorpe, H. Fitton and J. Lewis, J. Chem. Soc. Perkin Trans. I, (1973) 2051; T.H. Whitesides and J.P. Neilan, J. Am. Chem. Soc., 98 (1976) 63; Z. Goldschmidt, Y. Bakal, D. Hoffer, A. Eisenstadt and P.F. Lindley, J. Organomet. Chem., 25 (1983) 53.
3 J.M. Brown I. Midgley and W.J. Albery, J. Chem. Soc. Perkin Trans. II, (1982) 767, and references cited therein.
4 G.W. Parshall, Homogeneous Catalysis, Wiley-Interscience New York, 1980; R.J. Cross, in F.R. Hartley and S. Patai (Eds.), The Chemistry of the Metal–Carbon Bond, Wiley, Chichester, 1985, Vol. 2, Chap. 8, p. 559.
5 Z. Goldschmidt, H.E. Gottlieb and D. Cohen, J. Organomet. Chem., 294 (1985) 219.
6 W. Grimme, Chem. Ber., 100 (1967) 113; R. Aumann, Chem. Ber., 108 (1975) 1974; ibid., 109 (1976) 168; A. Salzer, J. Organomet. Chem., 117, (1976) 245; L.A. Paquette, R.P. Micheli and J.M. Photis, J. Am. Chem. Soc., 99 (1977) 7911; M. Green, S.M. Heathcock, T.W. Turney and D.M.P. Mingos, J.

Chem. Soc., Dalton Trans., (1977) 204; Z. Goldschmidt and S. Antebi, Tetrahedron Lett., (1978) 271; S.K. Chopra, G. Moran and P. McArdle, J. Organomet. Chem., 214 (1981) C36; H.R. Beer, P. Bigler, W. von Philipsborn and A. Salzer, Inorg. Chim. Acta, 52 (1981) L49; J. Celebuski, G. Munro and M. Rosenblum, Organometallics, 5 (1986) 256; F.J. Liotta, Jr. G.V. Duyne and B.K. Carpenter, Organometallics, 6 (1987) 1010; D. Cunningham, N. Hallinane, G. Moran and P. McArdle, J. Organomet. Chem., 333 (1987) 85; S.K. Chopra, D. Cunningham, S. Kavanagh, P. McArdle, and G. Moran, J. Chem. Soc. Dalton Trans., (1987) 2927.

7 Z. Goldschmidt and H.E. Gottlieb, J. Organomet. Chem., 329 (1987) 391; Z. Goldschmidt, H.E. Gottlieb and A. Almadhoun, J. Organomet. Chem., 326 (1987) 405.

8 Z. Goldschmidt, H.E. Gottlieb, E. Genizi, D. Cohen and I. Goldberg, J. Organomet. Chem., 301 (1986) 337.

9 M. Brookhart, K. Karel and L.E. Nance, J. Organomet. Chem., 140 (1977) 203.

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

11 W.H. Saunders Jr. in C.F. Bernasconi, Investigation of Rates and Mechanisms of Reactions, Wiley, New York, 1986, Pt. 1, Chap. 8, p. 565; B.K. Carpenter, Determination of Organic Reaction Mechanisms, Wiley, New York, 1984, Chap. 5, p. 83.

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