Ligand-Induced Directionality Shift in the Fe^+-Mediated Dehydrogenation of 1,8-Diphenyloctane

Norbert Raabe, Sigurd Karraß and Helmut Schwarz*

Institut für Organische Chemie der Technischen Universität Berlin,
Straße des 17. Juni 135, D-10623 Berlin, Germany

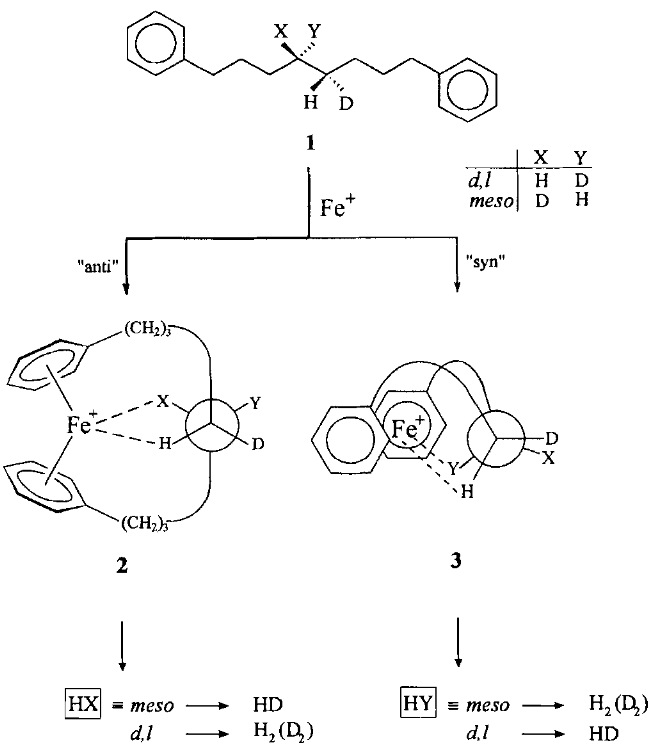
Received February 27, 1995

Key Words: C–H bond activation / Ligand effects / Iron chemistry / Reaction mechanisms

The presence of a cyclopentadienyl ligand brings about a complete shift of regioselectivity in the Fe^+-mediated dehydrogenation of 1,8-diphenyloctane (**1**). While "bare" Fe^+, due to the formation of an intramolecular sandwich-like complex, activates the internal C-4/C-5 positions of the alkyl chain, this chelate effect is no longer operative in the gas-phase chemistry of $Fe(C_5H_5)^+$ with **1**. Labeling experiments demonstrate that the C-1/C-2 and (to a minor extent) the C-2/C-3 methylene groups are activated, and a possible origin of this remarkable ligand effect is discussed.

In a previous study[1] we demonstrated that the gas-phase $Fe^{(I)}$-mediated dehydrogenation of 1,8-diphenyloctane (**1**) involves to > 92% the internal methylene groups C-4/C-5. For the Fe^+ complex of **1** the results clearly evidence the existence of a chelate effect such that the "bare" Fe^+ does not randomly attack various C–H bonds of the methylene chain. Rather, the metal ion most likely forms an intramolecular sandwich complex (Scheme 1) with the arene rings[2], thus preventing most of the alkane C–H bonds to interact with the metal ion. Model considerations indicate, however, that at least two conformations (**2** and **3**) are conceivable in which the central C-4/C-5 region is brought in the vicinity (< 2.2 Å) of the metal ion, thus permitting the oxidative insertion of Fe^+ in these *unactivated* C–H bonds. This interpretation gained further support by the study of stereospecifically deuterated *d,l* and *meso* precursors of [4,5-D_2]-**1** which provided evidence for the operation of isotopically sensitive branching ("metabolic switching"); this concept is well-known to exist in enzymatic reactions[3] and also to control the $Fe^{(I)}$-mediated dehydrogenation of α,ω-alkanediols[4]. For the *d,l* form of [4,5-D_2]-**1** the path involving the *"anti"* conformer **2** is favored by a factor of 3.8 as compared with **3**. Due to the operation of a kinetic isotope effect, for the *meso* form of [4,5-D_2]-**1** the branching ratio of the *"anti"* versus *"syn"* route is reduced to 1.4.

Scheme 1



In this paper we describe a further, independent test for the importance of a cooperative effect in the chemistry of "bare" Fe^+ with α,ω-diphenylalkanes[5]. It is well-established that Fe^+ forms a much stronger bond to the C_5H_5 ligand than to C_6H_6 (87 versus 49 kcal mol^{-1}[6]). Consequently, on energetic grounds the formation of an intramolecular sandwich-like structure (i.e. **4**) is no longer favored in the reactions of $Fe(C_5H_5)^+$ with **1**. Rather, the $Fe(C_5H_5)^+$ fragment may interact intermolecularly with **1** by generating, for example **5** (Scheme 2). In the latter complex, the transition metal is not capable of interacting with the internal positions of the flexible methylene chain, i.e. C-4/C-5. Instead, C–H bond activation is expected to include positions closer to the benzene ring. As demonstrated by the data listed in Table 1, this expectation is precisely born out experimentally: While for the reations with "bare" Fe^+ the chemistry is confined to the internal part (C-4/C-5) of **1**[1], for the $Fe(C_5H_5)^+$ fragment this region is not accessible as evidenced by the absence of HD and D_2 losses from the metastable ion mass spectra of $Fe(C_5H_5)^+$ with **1a**. Rather, chemistry is shifted to the C-1, -2, -3 region. The data are in keeping with two competing 1,2-elimination processes; the major part involves activation of the methylene groups of C-1/C-2 (> 80%), and a minor path proceeds by activation of the C-2/C-3 region. Interestingly, as evidenced by the absence of HD loss from the $Fe(C_5H_5)^+$/**1b** complex, activation of the C–H bond of C-3 is subject to a huge kinetic isotope effect, thus resulting in a complete suppression of this path when deuterium is attached to C-3. In conclusion, the present study reveals the existence of an extraordinary pronounced ligand effect[7] in

Scheme 2

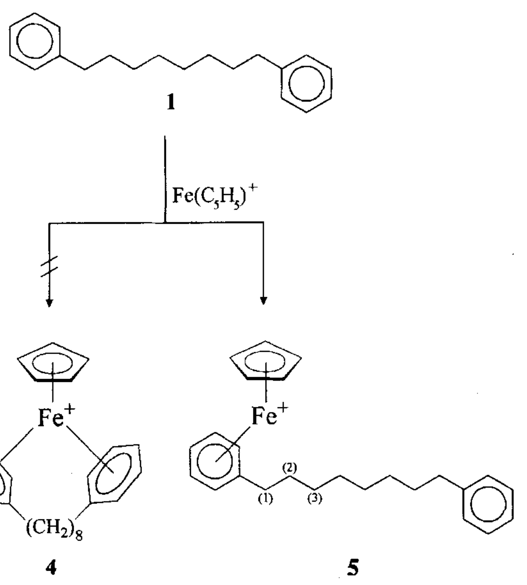


Table 1. Dehydrogenation products in the metastable ion mass spectra of Fe^+ and $Fe(C_5H_5)^+$ complexes of 1,8-diphenyloctane isotopologues **1a–d**[a]

	Reaction with Fe+[b]			Fe(C5H5)+		
	H_2	HD	D_2	H_2	HD	D_2
$Ph[CH_2]_3[CD_2]_2[CH_2]_3Ph$ (**1a**)	8	8	84	100	–	–
$Ph[CH_2]_2CD_2[CH_2]_2CD_2$-$[CH_2]_2Ph$ (**1b**)	97	3	–	100	–	–
$PhCH_2CD_2[CH_2]_4CD_2$-CH_2Ph (**1c**)	100	–	–	–	100	–
$PhCD_2[CH_2]_6CD_2Ph$ (**1d**)	100	–	–	20	80	–

[a] Data are normalized to $\Sigma H_{2-x}D_x$ = 100%. – [b] Data are taken from ref.[1].

transition-metal-mediated dehydrogenation processes, and further work is indicated to probe the potential of these reactions.

Financial support of our work by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* is acknowledged.

Experimental

The experimental setup has been described in earlier papers[1,8]. Briefly, the organic substrates and ferrocene are introduced separately by means of the heated direct-inlet system of a modified four-sector ZAB mass spectrometer with *BEBE* geometry (*B* stands for electric and *E* for electrostatic analyzer). In the chemical ionization source the mixture is bombarded with 100-eV electrons (repeller voltage ca. 0 V). The organometallic complexes were accelerated to 8 keV kinetic energy, mass and energy were selected by means of *B*(1)/*E*(1) at a resolution of 3000–4000 (10% valley definition). Unimolecular reactions occurring in the field-free region between *E*(1) and *B*(2) were recorded by sanning *B*(2). Spectra were recorded on-line and 10–20 spectra were accumulated by using signal-averaging techniques employing the ADM Intectra data system. The synthesis of the labeled compounds has been described previously[1].

[1] N. Raabe, S. Karraß, H. Schwarz, *Chem. Ber.* **1994**, *127*, 261.

[2] The gas-phase chemistry of Fe^+ complexes of 1-phenylalkanes does not exhibit the remarkable site selectivity observed for **1**-Fe^+: O. Blum, P. O'Bannon, H. Schwarz, unpublished results.

[3] [3a] D. B. Northop, *Biochemistry* **1975**, *14*, 2644. – [3b] G. T. Miwa, J. S. Walsh, A. Y. H. Lu, *J. Biol. Chem.* **1984**, *259*, 3000. – [3c] N. Harada, G. T. Miwa, J. S. Walsh, A. Y. H. Lu, *J. Biol. Chem.* **1984**, *259*, 3005. – [3d] K. S. Eble, J. H. Dawson, *J. Biol. Chem.* **1984**, *259*, 14389. – [3e] R. E. White, J. P. Miller, L. V. Favreau, A. Bhattacharyya, *J. Am. Chem. Soc.* **1986**, *108*, 6024. – [3f] J. P. Jones, K. R. Korukua, A. E. Rettie, W. F. Trager, *J. Am. Chem. Soc.* **1986**, *108*, 7074. – [3g] F. P. Guengerich, L. A. Peterson, R. H. Böcker, *J. Biol. Chem.* **1988**, *263*, 8176. – [3h] For an excellent review on this topic with regard to the elucidation of reaction mechanisms, see: A. Thibblin, P. Ahlberg, *Chem. Soc. Rev.* **1989**, *18*, 209.

[4] [4a] T. Prüsse, A. Fiedler, H. Schwarz, *Helv. Chim. Acta* **1991**, *74*, 1127. – [4b] K. Seemeyer, T. Prüsse, H. Schwarz, *Helv. Chim. Acta* **1993**, *76*, 1632.

[5] For other examples of cooperative effects in gas-phase reactions, see: [5a] T. Prüsse, C. B. Lebrilla, T. Drewello, H. Schwarz, *J. Am. Chem. Soc.* **1988**, *110*, 5986. – [5b] T. Prüsse, T. Drewello, C. B. Lebrilla, H. Schwarz, *J. Am. Chem. Soc.* **1989**, *111*, 2857. – [5c] N. Steinrück, O. Dange, D. Stöckigt, H. Schwarz, *Angew. Chem.* **1990**, *102*, 429; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 402. – [5d] A. Hässelbarth, T. Prüsse, H. Schwarz, *Chem. Ber.* **1990**, *123*, 209. – [5e] T. Prüsse, H. Schwarz, *Int. J. Mass Spectrom. Ion Processes* **1991**, *197*, 135. – [5f] T. Prüsse, G. Czekay, H. Schwarz, *Chem. Ber.* **1991**, *124*, 141.

[6] [6a] J. A. M. Simoes, J. L. Beauchamp, *Chem. Rev.* **1990**, *90*, 629. – [6b] D. Schröder, H. Schwarz, *J. Organomet. Chem.*, in press.

[7] For examples of a significant ligand effect in the gas-phase chemistry of "bare" FeO^+, see: [7a] D. Stöckigt, H. Schwarz, *Chem. Ber.* **1994**, *127*, 2499. – [7b] D. Stöckigt, H. Schwarz, *Liebigs Ann.* **1995**, 429.

[8] [8a] R. Srinivas, D. Sülzle, T. Weiske, H. Schwarz, *Int. Mass Spectrom. Ion Processes* **1991**, *107*, 369. – [8b] R. Srinivas, D. Sülzle, W. Koch, C. H. DePuy, H. Schwarz, *J. Am. Chem. Soc.* **1991**, *113*, 5970.

[95029]