169. Refined Insight in Stereochemical and Directional Features of the Fe^I-Mediated Dehydrogenation of Tetralin

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Dedicated to Professor *Wolfgang Steglich* on the occasion of his 60th birthday

(22. VII. 93)

Experimental results demonstrate that, in the course of gas-phase Fe$^+$-mediated dehydrogenation of tetralin, the metal ion sticks to the same plane of the hydrocarbon surface. The study of 5-substituted, labeled tetralin analogues reveal the operation of an interesting substituent effect: Steric hindrance imposed by a CH$_3$ group at C(5) deflects the metal to the more easily accessible region of C(1)/C(2); in contrast, a CH$_3$O substituent at C(5) directs the metal ion to the more congested C(3)/C(4) region which clearly points to a coordination of Fe$^+$ to the MeO group in the course of the haptotropic migration.

In a recent communication [1], evidence was provided that the transition-metal-ion-mediated [2] consecutive losses of H$_2$ and 2 H$_2$ from tetralin (**1**) in the gas phase to generate the [M(naphthalene)]$^+$ complexes **3** (M = Fe, Co) are highly specific in that both reactions follow a *syn*-1,2-elimination involving C(1)/C(2) and C(3)/C(4), respectively (*Scheme 1*).

Scheme 1
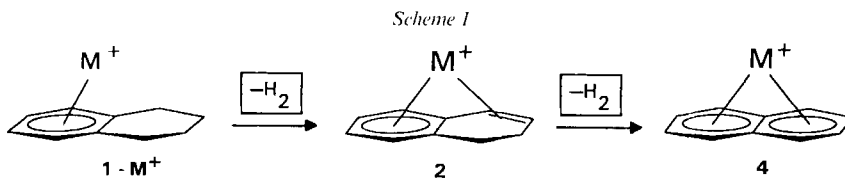
In addition to the as yet incomplete understanding of the actual bonding situation of **3**, a problem which cannot be solved by using mass-spectrometry-based methodologies, there remain two further questions related to the mechanism of tetralin dehydrogenation: *i*) Is there a preferred directionality with regard to the metal-ion migration from one ring to the other? For bicyclic [ML$_n$(polyene)] complexes, where ML$_n$ = M(CO)$_3$ and MCp, a theoretical analysis [3] of these haptotropic rearrangements [4] has been conducted in great detail. Although this analysis does not pertain – in a strict sense – to the present study, for the ring slippage of the 'bare' metal ion from the π-surface towards the C–H bonds of the saturated ring of tetralin, three pathways have to be considered: In path ⓐ (*Scheme 2*) the metal ion crosses in a symmetrical fashion the central C(9)/C(10) C–C bond. This path is not expected to be significantly affected by substituents attached to C(5), with the consequence that in the elimination of the *first* molecule of H$_2$, the

Scheme 2
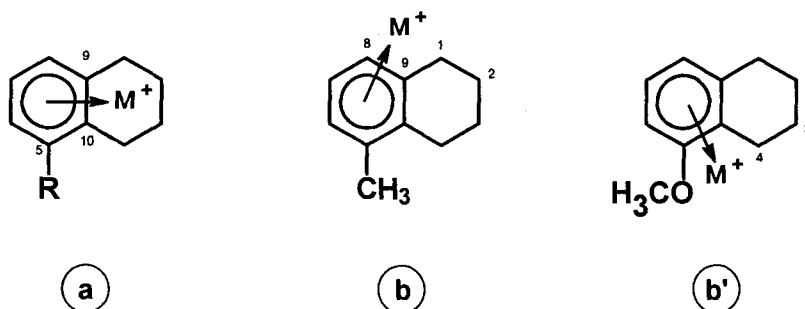
positions C(1)/C(2) and C(3)/C(4) should participate equally. In contrast, if the metal ion prefers to travel *via* path ⓑ, the nature of the substituent at C(5) will matter. For non-complexing substituents (*e.g.*, R = CH₃) one can expect that M⁺ will be directed *away* from R to the region C(8)/C(9); consequently, the loss of the first H₂ molecule is expected to preferentially involve C(1)/C(2). However, substituents which are capable to compensate for the loss of π-electron complexation energy by coordinating the migratory metal ion M⁺ to the substituent, *e.g.* for R = CH₃O, are predicted to direct the metal ion's migration *towards* C(5)/C(10), thus favouring activation of the C(3)/C(4) C−H bonds (*Scheme 2*; path ©).

ii) The second hitherto not properly solved problem concerns the (admittedly hypothetical) question as to whether a metal ion in an *electrostatically* bound complex may switch from one surface to the other (*Scheme 3*). This feature is of general interest for the understanding of the role of ion-dipole complexes in unimolecular dissociations of ions.

In the present communication, we will report experimental results[1]) which will provide unambiguous answers to these two questions.

In the *Table*, the MI data for the Fe⁺ complexes of tetralin (**1**), its isotopomers **1a** and **1b** and its 5-substituted analogues **4, 4a, 4b**, and **5, 5a, 5b** are given. The analysis of the data is straightforward. With regard to the possibility that – in the course of the C−H bond activation – the metal ion may switch from one π-surface to the other, the results of

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¹)　As the experimental set-up has been described repeatedly [5], a brief description may suffice: A 1:1 mixture of Fe(CO)₅ and tetralin is bombarded with 100-eV electrons in the chemical-ionization source (repeller voltage 0 V) of a modified four-sector tandem mass spectrometer of *BEBE* configuration (*B* stands for magnetic and *E* for electric sector), in which MS-I is the original *ZAB-2F* part and MS-II is an *MD 604* mass spectrometer [6]. Although the actual mechanisms by which the complexes are formed is yet unknown, the pressure in the ion source is high enough to permit collisional cooling, thus, increasing the lifetime such that time-delayed decomposition reactions after *ca.* 1 μs take place (metastable-ion (MI) dissociations). To this end, the organometallic complexes of Fe⁺ and tetralin (and its isotopomers) having 8-keV translational energy are mass-selected by means of *B*(1)*E*(1). Unimolecular reactions occurring in the field-free region between *E*(1) and *B*(2) were recorded by scanning *B*(2). In these experiments, the fourth sector *E*(2) is not used. Spectra were recorded on-line and averaged by using signal-averaging techniques employing the *AMD Intectra* data system. In typical experiments, 10–15 spectra were recorded. All compounds were synthesized by standard laboratory procedures, purified by chromatographic means, and fully characterized by spectroscopic methods.
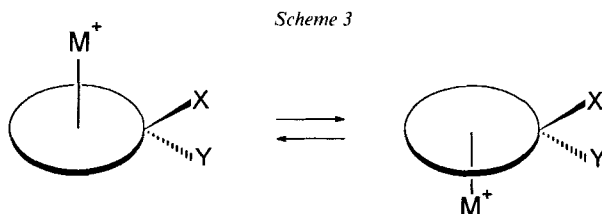
Scheme 3

Table. *Unimolecular Single and Double Dehydrogenation of Fe$^+$ Complexes of Tetralin* (**1**), *Its Isotopomers* **1a** *and* **1b**, *and 5-Substituted Analogues* **4, 4a, 4b**, *and* **5, 5a, 5b^2)^a)

		H$_2$	HD	2 H$_2$	H$_2$/HD	2 HD
	1	35	–	65	–	–
	1a	29	12	–	59	–
	1b	29	8	44	–	19
	4	26	–	74	–	–
	4a	28	5	–	67	–
	4b	18	14	–	68	–
	5	22	–	78	–	–
	5a	29	2	1^b)	68	–
	5b	20	–	79	1	–

^{a}) Data are given in % of Σ fragment intensities = 100%.

^{b}) The quite minor loss of 2 H$_2$ (1%) from **5a**-Fe$^+$, which is not expected to take place if only the positions C(1)/C(2) and C(3)/C(4) serve as H$_2$ sources [1], originates from a new channel in which the CH$_3$O substituent participates. This follows from the combined elimination of H$_2$/HD (1%) from the CD$_3$O-labeled isotopomer **5b**.

^{2}) For a comprehensive analysis of the kinetic isotope effects associated with the metal-ion mediated dehydrogenation of tetralin isotopomers, see [1].

complex **1b** are unambiguous: If the Fe^+ cation changes the surface, one must observe combined loss of H_2/HD, irrespective from which site of the complex the first molecule of molecular H_2 originates. This is *not* observed. Rather, the isotope distribution demands that the metal ion sticks to the same plane of the hydrocarbon surface throughout the whole sequence, *i.e.* migration from the π-surface to the saturated ring, *syn*-elimination of the first molecule of H_2 from $C(1)/C(2)$ followed by a further *syn*-elimination involving $C(3)/C(4)$.

An answer to the *directionality* of the metal-ion migration (*Scheme 2*) can also be extracted from the study of the 5-substituted tetralins **4** and **5** and their isotopomers. For the CH_3-substituted tetraline **4**, a comparison of the isotopomers **4a** and **4b** clearly demonstrates that the CH_3 group directs the metal ion *away* from its region. This is clearly indicated by the increased ratio of H_2/HD losses from **4a** (5.6); in contrast, for the isotopomer **4b** this ratio drops to 1.3. If one assumes that the kinetic isotope effects[2]) associated with the metal-ion-mediated dehydrogenation are approximately the same for the isotopomers of tetralin (**1**) and 5-methyltetralin (**4**), from a simple algebraic analysis, it follows that the steric hindrance imposed by the CH_3 group amounts to a factor of *ca.* 2, preferring oxidative insertion of the metal ion at the sterically easier accessible $C(1)/C(2)$ C–H bonds (*Scheme 2*, path ⓑ). On the other hand, a CH_3O substituent at $C(5)$, *i.e.* **5**, clearly directs the metal ion *towards* the sterically more congested $C(3)/C(4)$ region. This follows immediately from the large H_2/HD ratio of 14.5 for the complex **5a**-Fe^+. Obviously, the loss of complexation energy associated with the migration of the metal ion from the π-surface[3]) is partially compensated for by chelating the migrating Fe^+ to the lone-pair electrons of the CH_3O substituent.

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[3])　Typical bond-dissociation energies of Fe^+ to some ligands, pertinent to the problem of metal-ion migration in **4**-Fe^+, are: benzene (55 kcal/mol [7]), and H_2O (28.8–32.8 kcal/mol [8]).