112. Dichotomy of Fe^+-Mediated Sequential Activation of C–H/C–C Bonds of Aldimines: A Case of Efficient Reaction Control by Chain-Length Effects

Preliminary Communication

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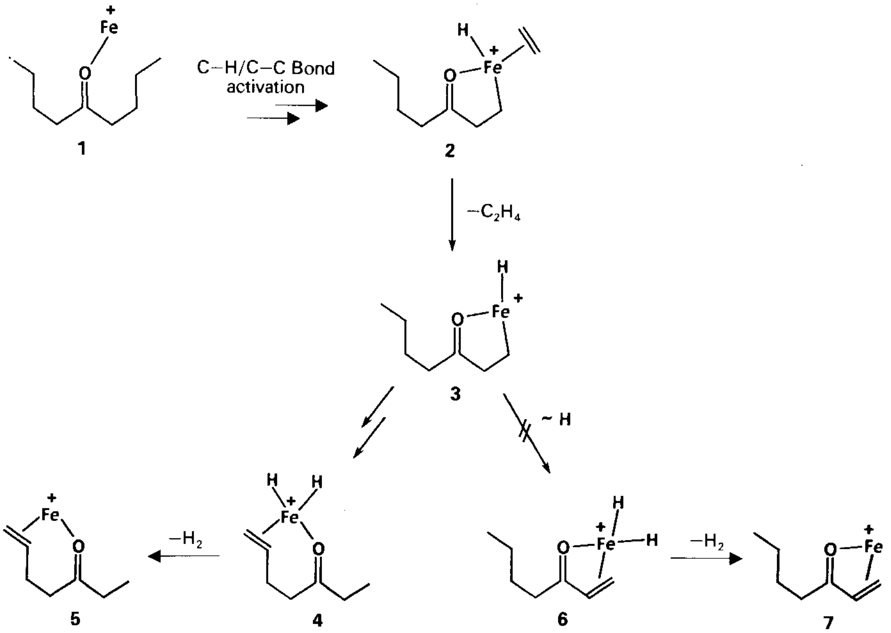
The metastable ions of Fe^+ complexes of aldimines $R^1N{=}CHR^2$ exhibit a unique behaviour in that sequential loss of olefin/H_2 follows two distinct pathways: one corresponds to the familiar pattern of double remote functionalization, involving either alkyl chain R^1 and R^2. In addition, based on labeling studies, evidence is presented demonstrating that the consecutive elimination of C_2H_4/H_2 from the Fe^+ complex of $C_6H_{13}N{=}CHC_3H_7$ involves exclusively the C_6H_{13} part of the substrate. These and other Fe^+-mediated C–H/C–C bond activations of aldimines are controlled by chain-length effects, reflecting the preferential formation of metallacyclic intermediates of particular ring sizes.

In recent studies [1], we demonstrated the operation of transition-metal-ion-mediated successive *C–H/C–C bond activation*[1]) *of different sites of flexible molecules,* a reaction

Scheme 1



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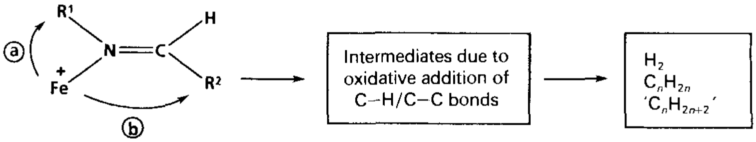
[1]) For leading references on the topic of C–H/C–C bond activation by bare and ligated transition-metal ions, see [2].

having no precedent in traditional organic chemistry. Evidence was presented that, for example, bare Fe^+ 'anchored' to a C=O function of ketones is capable to generate olefins (C_2H_4, C_3H_6) from the terminal part of one alkyl chain ('remote functionalization'); subsequently, H_2 is formed from the [*M* – alkene]$^+$ intermediate by regiospecific C–H bond activation of the *other* alkyl chain (*Scheme 1* for undecan-5-one/Fe^+ [1a,c]). A similar principle of double remote functionalization was also found to be operative in Fe^+ complexes of α-branched aliphatic nitriles [1a,b]. Processes, in which the consecutive losses of C_nH_{2n}/H_2[2]) take place within the same alkyl chain (*Scheme 1*: **3**→**6**→**7**) have never been encountered yet.

In the course of a detailed study of the gas-phase chemistry of Fe^+ complexes of aliphatic aldimines **8**[3]), we did not only observe activation of both the geminal R^1 chain and, across the C=N bond, C–H/C–C bonds of R^2 (*Scheme 2*); more interestingly, an initial study of several deuterated isotopomers of $C_4H_9N{=}CHC_3H_7$ (**8a**) and $C_6H_{13}N{=}CHC_3H_9$ (**8b**) revealed that, depending upon the chain lengths of R^1 and R^2, sequential activation of different sites of R^1/R^2 as well as within one alkyl chain (R^1) is operative.

Scheme 2



8-Fe^+ (R^1,R^2 = alkyl)

The metastable-ion (MI) mass spectrum of **8a**-Fe^+ contains signals due to losses of H_2 (89%), C_2H_4 (4%), 'C_2H_6' (3%), and C_4H_8 (4%). In the analogous spectrum of **8b**-Fe^+ we observe H_2 (33%), C_2H_4 (22%), 'C_2H_6' (10%), C_3H_6 (25%), 'C_3H_8' (8%), and C_4H_8 (2%). With regard to the actual nature of the mass differences $\Delta m = 30$ and 44 ('C_2H_6' and 'C_3H_8'), it should be mentioned that these do *not* correspond to the generation of authentic alkane molecules. Rather, these mass differences are due to consecutive losses of C_nH_{2n}/H_2. As noted earlier for the Fe^+ complexes of ketones and α-branched nitriles [1], the reverse sequence, *i.e.* elimination of H_2 followed by loss of C_nH_{2n}, is not observed. This conclusion is inferred from the fact that only mass-selected (*M* – alkene]$^+$ ions decompose further *via* H_2 loss; in contrast, in the MI mass spectra of mass-selected (*M* – H_2]$^+$ species, no signal is observed corresponding to further losses of alkenes. Presumably, the [*M* – H_2]$^+$ fragment ion is stabilized due to the formation of a bidentate structure.

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[2] The reverse sequence, *i.e.* loss of H_2 followed by elimination of C_nH_{2n}, was not observed.

[3] The experimental set-up has been described repeatedly in earlier papers. Briefly, Fe^+ ions are generated by 100-eV electron impact ionisation of $Fe(CO)_5$. The ions were then reacted with the organic substrates in the ion source of our modified ZAB mass spectrometer, which is of BEBE configuration (B stands for magnetic and E for electric sector). The resulting complexes **8** are accelerated to 8-keV kinetic energy and mass selected by using B(1) E(1); the unimolecular reactions (MI spectra) occurring in the field-free region between E(2) and B(1) were recorded by scanning B(2). Signal averaging techniques were used to increase the signal-to-noise-ratio. All compounds studied were synthesized and purified by standard laboratory procedures and characterized by established spectroscopic techniques. In line with previous studies [3], we assume an (*E*)-configuration for the C=N bond of the aliphatic aldimines.

Table. *Isotopomer Distributions for the Losses of Molecular Hydrogen, Ethylene, and Propene from Fe^+ Complexes of Labeled Aldimines* **8f**, **8j**, *and* **8r**[a])

Precursor		Δm									
		2	3	28	30	31	32	42	43	44	45
$C_4H_9N{=}CHC_3H_7$	**8a**	100		61	39[b])						
$C_4H_9N{=}CHCH_2CH_2CD_3$	**8a′**	96	4	23	28[c])	7[e])	42[d])				
$CD_3(CH_2)_3N{=}CHC_3H_7$	**8a″**	14	86	36	15[c])	43[e])	6[d])				
$C_6H_{13}N{=}CHC_3H_7$	**8b**	100		68	32[b])			77		23[f])	
$C_6H_{13}N{=}CHCH_2CD_2CH_3$	**8b′**	100		64	36[b])			80			20[g])
$CH_3CD_2(CH_2)_4N{=}CHC_3H_7$	**8b″**	15	85	3	67[c])		30[d])		75		25[h])

[a]) Data are expressed in $\Sigma\Delta m = 100\%$ for each class of neutrals separately.
[b]) $\Delta m = 30$ corresponds to C_2H_4/H_2.
[c]) $\Delta m = 30$ corresponds to $C_2H_2D_2$.
[d]) $\Delta m = 32$ corresponds to $C_2H_2D_2/H_2$.
[e]) $\Delta m = 31$ corresponds to C_2H_4/HD.
[f]) $\Delta m = 44$ corresponds to C_3H_6/H_2.
[g]) $\Delta m = 45$ corresponds to C_3H_6/HD.
[h]) $\Delta m = 45$ corresponds to C_3H_5D/H_2.

Quite unexpected are the results *(Table)* obtained for the isotopomers of $C_4H_9N{=}CHC_3H_7$ (**8a**). Here, H_2 preferentially originates from the $\omega/(\omega - 1)$ positions of R^1 (86%). This finding clearly points to a preferential interaction of the metal ion with the geminal substituent (*Scheme 2*: trajectory ⓐ), provided R^1 contains at least a C_4 chain. In contrast, ethylene is provided to roughly the same amount by the terminal positions of either R^1 and R^2. The sequential ethylene/hydrogen reactions uncover a further mechanistic subtlety: while in the first step ethylene originates from either alkyl chain, the subsequent molecular hydrogen loss involves mainly R^1 (presumably the $\omega/\omega - 1$ positions). This follows directly from the fact that the Fe^+ complex of **8a′** splits off preferentially $\Delta m = 32$ ($C_2H_2D_2/H_2$) and only little of $\Delta m 31$ (C_2H_4/HD) in a relative ratio of 42:7; in constrast, **8a″**-Fe^+ undergoes loss of Δm 31 with 42% and Δm 32 with 6%. This again, points to a preferential C–H bond activation of the geminal, saturated alkyl chain R^1. From the data of the isomeric isotopomers **8a′** and **8a″**, we are forced to conclude that a degenerate, Fe^+-mediated isomerization of the aldimines, *via* double-bond migration, does not take place.

If the chain length of R^1 is increased to $C_6H_{13}N{=}CHC_3H_7$ (**8b**), molecular hydrogen remains to originate from R^1, involving the $(\omega - 1)$ position (> 85%) together with an H-atom from either the ω or the $(\omega - 2)$ positions. R^2 does not serve as a source for molecular hydrogen as evidenced by the exclusive formation of H_2 from $C_6H_{13}N{=}CHCH_2CD_2CH_3$. In comparison with **8a**, a strikingly dissimilar behaviour is encountered for the consecutive formations of C_2H_4/H_2 *vs.* C_3H_8/H_2. The latter sequence follows the familiar pattern already described in *Scheme 1* for ketone/Fe^+ complexes, *i.e.* propene originates from the terminal part of R^1 and H_2 from the other alkyl chain R^2. A novel pattern is found for the combined elimination of C_2H_4/H_2. The labeling data clearly suggest that *both* neutral molecules are formed from the *same* side chain, *i.e.* from R^1. These findings permit the following generalizations to be made for aldimines: whenever permitted by the chain length of R^1, it is the geminal alkyl group whose C–H/C–C bonds are preferentially activated by Fe^+. If the alkyl chain R^1 contains less than four C-atoms, as is the case after loss of C_3H_8 from $C_6H_{13}N{=}CHC_3H_7$ (**8b**), the reactivity is 'transferred' to the *alkenyl* group R^2; as a consequence, the consecutive generation of H_2 involves the $\omega/(\omega - 1)$ positions of R^2. In contrast, loss of C_2H_4 from the terminal part of the C_6H_{13} chain generates, in a formal sense, $C_4H_9N{=}CHC_3H_7$ (**8a**); as already demonstrated for **8a**-Fe^+, this species undergoes with high selectivity C–H bond activation of the C_4H_9 chain. Obviously, the dichotomy of Fe^+-mediated C–H/C–C bond activation of different sites of aldimines is a direct consequence of chain-length effects of R^1 and R^2 reflecting the particular role of the ring sizes of metallacycles generated as intermediates.

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