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Ligand-Enhanced Selectivity in the CH/CC Bond Activation of Ketones by Iron(I) Ions in the Gas Phase

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Fourier transform ion cyclotron resonance (FTICR) mass spectrometry has been used to study the mechanisms by which bare Fe^+ and ligated iron ions FeL^+ (L = ethene, propene, 1,3-butadiene) react with acyclic ketones in the gas phase. The rich chemistry observed for Fe^+ is, by and large, comparable with that reported earlier for metastable ion decompositions of $Fe(ketone)^+$ complexes in field-free regions of multisector instruments. The major effects of different ligands L on the reactivity of $Fe(ketone)^+$ ions, generated by ligand substitution of L by the ketone, can be categorized as follows: If the ligand substitution is thermochemically possible, the resulting $Fe(ketone)^+$ complexes have insufficient energy to fragment by CC bond cleavage or to induce multiple dehydrogenation. The only activation process observed corresponds to loss of molecular hydrogen. Labeling experiments demonstrate that the *site selectivity* of dehydrogenation ("remote functionalization") is dependent on the internal energy of the resulting $Fe(ketone)^+$ complexes and increases significantly with decreasing energy content. A unique situation is uncovered for the reaction of $Fe(C_4H_6)^+$ with 4-heptanone. Although the binding energy of 1,3-butadiene to Fe^+ is too high for direct substitution of C_4H_6 by a ketone, the encounter complex $[Fe(C_4H_6,ketone)^+]^*$, nevertheless, rearranges and eventually undergoes loss of C_4H_8. The mechanism and implications of the *interligand* transfer of two hydrogen atoms from the ketone via the metal ion to the butadiene ligand are discussed.

The rich gas-phase chemistry of transition-metal ions with aldehydes and ketones has been explored in several laboratories during the last decade.[1] Detailed studies[1h] revealed inter alia for Fe^+ complexes of several alkanones the operation of *consecutive, remote CH/CC bond activations of different alkyl chains of the ketones*, processes unprecedented in condensed-phase chemistry.[2] Here, we present an account of the reactions of bare Fe^+ and ligated iron ions FeL^+ (L = ethene, propene, and 1,3-butadiene) with some selected acyclic ketones by using the technique of Fourier transform ion cyclotron resonance (FTICR) mass spectrometry.

Experimental Section

The apparatus (a Spectrospin-CMS-47X equipped with an external ion source) and its operation have been described in detail previously.[3] Fe^+ is formed via laser desorption/ionization[4] in the external ion source[5] by focusing the beam of a Nd:YAG laser (Spectron Systems, fundamental frequency 1064 nm) onto a stainless steel target. The ions are extracted from the source and transferred into the analyzer cell by a system of electrostatic potentials applied to lenses. After deceleration, the ions are trapped in the field of the superconducting magnet (Oxford Instruments), which has a maximum field strength of 7.05 T. The $^{56}Fe^+$ isotope is isolated by double-resonance ejection pulses and allowed to react with the ketones of interest; the latter are present in the ICR cell at a constant pressure of $(1-5) \times 10^{-8}$ mbar. To quench possibly existing excited states of the metal ion, argon is also present at a constant "background" pressure of ca. 10^{-7} mbar. For collision-induced dissociation (CID) experiments,[6] argon is introduced via a pulsed valve.[7] The FeL^+ complexes ($L = C_2H_4, C_3H_6, C_4H_6$) are generated by reacting the isolated $^{56}Fe^+$ isotopes for ca. 1–3 s with pulsed-in C_2H_5Cl, i-C_4H_{10}, or 1-butene, respectively ($p_{max} \simeq 10^{-6}$ mbar); the FeL^+ complexes are isolated by double-resonance ejection and reacted with the ketones. All functions of the instrument are controlled by a Bruker-Aspect-3000 minicomputer.

The labeled compounds are synthesized by standard laboratory procedures, purified by gas chromatographic means, and characterized by spectroscopic methods.

Results and Discussion

In the reaction of Fe^+ with 2-hexanone (**1**), we observed, as primary products, the species given in Scheme I. The numbers in parenthesis refer to the results published by Freiser and co-workers[1b] for this system. The differences

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(1) (a) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *Anal. Chem.* **1980**, *52*, 1641. (b) Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360. (c) Halle, L. F.; Crowe, W. E.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1984**, *3*, 1694. (d) Grady, W. L.; Bursey, M. M. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *52*, 247. (e) Larsen, B. S.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 1912. (f) Jacobson, D. B.; Freiser, B. S. *Organometallics* **1984**, *3*, 513. (g) Schröder, D.; Schwarz, H. *Chimia* **1989**, *43*, 317. (h) Schröder, D.; Schwarz, H. *J. Am. Chem. Soc.* **1990**, *112*, 5947. (i) van Koppen, P. A. M.; Jacobson, D. B.; Illies, A.; Bowers, M. T.; Hanratty, M.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 1991. (j) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1978**, *100*, 163. (k) Tolbert, M. A.; Beauchamp, J. L. *J. Phys. Chem.* **1986**, *90*, 5015. (l) Lombarski, M.; Allison, J. *Int. J. Mass Spectrom. Ion Processes* **1985**, *65*, 31.

(2) For reviews on the concept of *remote functionalization*, both in solution (refs 2a–c) and in the gas phase (refs 2d–g), see: (a) Breslow, R. *Chem. Soc. Rev.* **1972**, *1*, 553. (b) Breslow, R. *Acc. Chem. Res.* **1980**, *13*, 170. (c) Breslow, R.; Adams, A.; Guo, T.; Hunger, J. *Lect. Heterocycl. Chem.* **1987**, *9*, 43. (d) Czekay, G.; Drewello, T.; Eller, K.; Lebrilla, C. B.; Prüsse, T.; Schulze, C.; Steinrück, N.; Sülzle, D.; Weiske, T.; Schwarz, H. In *Organometallics in Organic Synthesis 2*; Werner, H., Erker, G., Eds.; Springer Verlag: Heidelberg 1989; p 203. (e) Schwarz, H. *Acc. Chem. Res.* **1989**, *22*, 282. (f) Eller, K.; Schwarz, H. *Chimia* **1989**, *43*, 371. (g) Eller, K.; Karrass, S.; Schwarz, H. *Ber. Bunsen-Ges. Phys. Chem.* **1990**, *94*, 1201. For the CH/CC functionalization of *different* sites of flexible molecules by bare metal ions, see also: (h) Czekay, G.; Drewello, T.; Eller, K.; Zummack, W.; Schwarz, H. *Organometallics* **1989**, *8*, 2439. (i) Czekay, G.; Eller, K.; Schröder, D.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1277. (j) Prüsse, T.; Schwarz, H. *Helv. Chim. Acta* **1990**, *73*, 1163.

(3) (a) Eller, K.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1989**, *93*, 243. (b) Eller, K.; Zummack, W.; Schwarz, H. *J. Am. Chem. Soc.* **1990**, *112*, 621.

(4) (a) Freiser, B. S. *Talanta* **1985**, *32*, 697. (b) Freiser, B. S. *Anal. Chim. Acta* **1985**, *178*, 137.

(5) Kofel, P.; Allemann, M.; Kellerhans, Hp.; Wanczek, K. P. *Int. J. Mass Spectrom. Ion Processes* **1985**, *65*, 97.

(6) (a) Cody, R. B.; Freiser, B. S. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *41*, 199. (b) Cody, R. B.; Burnier, R. C.; Freiser, B. S. *Anal. Chem.* **1982**, *54*, 96. (c) Bricker, D. L.; Adams, T. A., Jr.; Russell, D. H. *Anal. Chem.* **1983**, *55*, 2417.

(7) Carlin, T. J.; Freiser, B. S. *Anal. Chem.* **1983**, *55*, 571.

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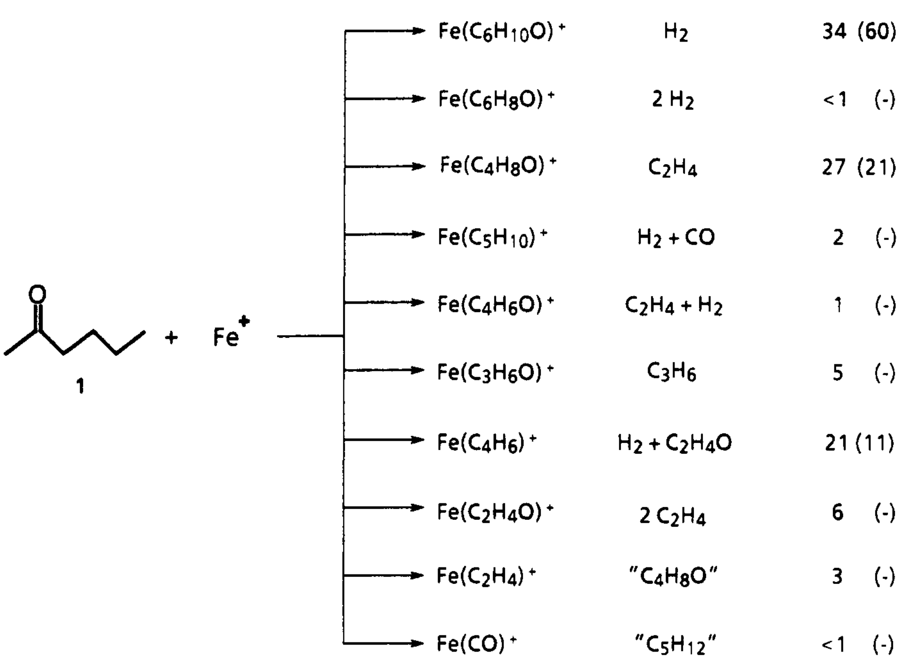
Table I. Losses of Hydrogen, Ethene, Propene, Hydrogen/Acetaldehyde, and Ethene/Ethene in the Reaction of Fe^+ with 2-Hexanone (1) and Its Isotopomers 1a,b

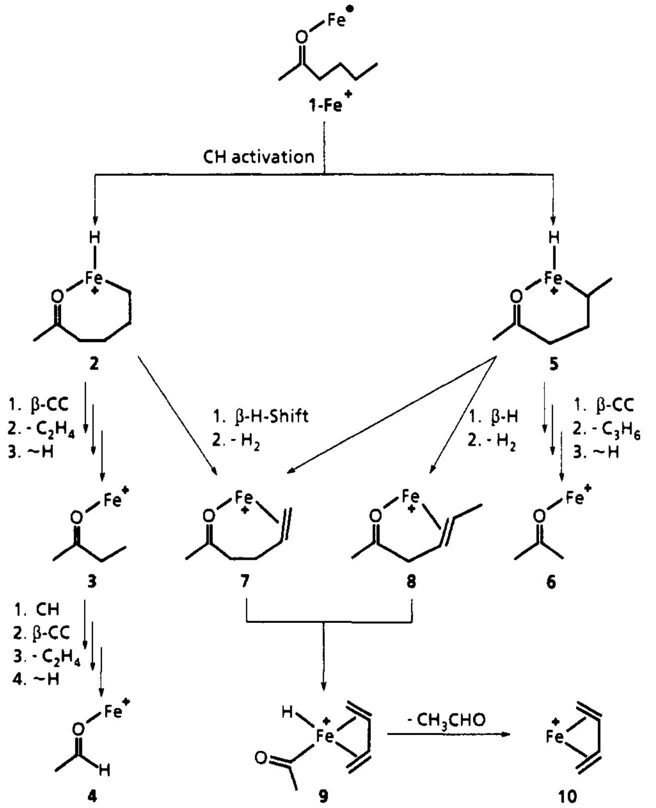
	Δm													
	hydrogen		ethene		propene		hydrogen/acetaldehyde					ethene/ethene		
ketone	2	3	28	30	42	45	46	47	48	49	50	56	58	59
$CH_3C(O)(CH_2)_3CH_3$ (**1**)	36		29		5		24					6		
$CH_3C(O)(CH_2)_3CD_3$ (**1a**)	7	25		34		6		15	6	2			1	4
$CD_3C(O)CD_2(CH_2)_2CH_3$ (**1b**)	36		29		3				<1	25	<1		5	

Scheme I



Ion	Neutral(s)	Relative Abundance [%]
$Fe(C_6H_{10}O)^+$	H_2	34 (60)
$Fe(C_6H_8O)^+$	$2 H_2$	<1 (-)
$Fe(C_4H_8O)^+$	C_2H_4	27 (21)
$Fe(C_5H_{10})^+$	$H_2 + CO$	2 (-)
$Fe(C_4H_6O)^+$	$C_2H_4 + H_2$	1 (-)
$Fe(C_3H_6O)^+$	C_3H_6	5 (-)
$Fe(C_4H_6)^+$	$H_2 + C_2H_4O$	21 (11)
$Fe(C_2H_4O)^+$	$2 C_2H_4$	6 (-)
$Fe(C_2H_4)^+$	"C_4H_8O"	3 (-)
$Fe(CO)^+$	"C_5H_{12}"	<1 (-)

Scheme II



in branching ratios in the two experiments are likely due to (i) inclusion secondary products in ref 1b and (ii) increased sensitivity of the Spectrospin-CMS-47X.

Insight into the mechanisms of product formation is provided by the study of the isotopomers **1a** and **1b** (Table I). In this table, only data for processes with >5% product abundance are included.

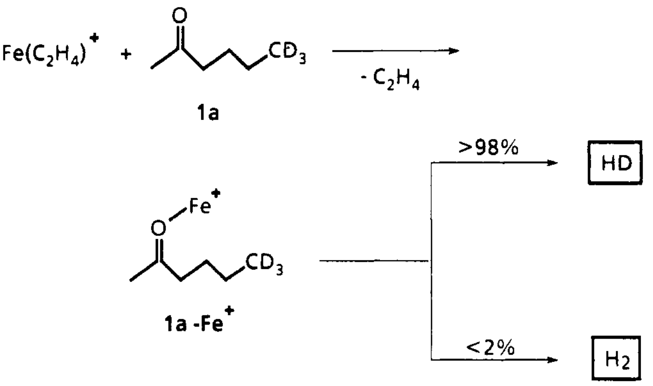
With regard to the genesis of the neutral molecules lost from **1**–Fe^+, the labeling data together with double-resonance and CID experiments provide an unequivocal answer as to the positions from which they originate and the sequence in which they are eliminated (Scheme II).

The consecutive loss of two ethene molecules is site-specific and involves the positions C(5)/C(6) (**1** → **3**) and C(3)/C(4) (**3** → **4**). Double-resonance experiments establish that **3** serves as a precursor for **4**. This conclusion is further supported by CID experiments upon **3**, which give rise to loss of C_2H_4 as well as formation of $Fe(C_2H_4)^+$ and Fe^+. Propene is also formed in a site-specific fashion involving C(4)/C(5)/C(6). As ethene loss commences with activation of C(6), we have to conclude that *two* processes are operative for the oxidative addition of the "anchored" Fe^+ to CH bonds: These involve activation of the ω-position (**1**–Fe^+ → **2**) and (ω - 1) as well (**1**–Fe^+ → **5**). The so-formed metallacycles serve two functions; they represent the intermediates en route to the above described losses of ethene and propene (CC bond activation) and to the reductive elimination of molecular hydrogen (CH bond activation). While at least the alkene losses are specific, competitive formation of **7** and **8** from **2** and **5** precludes

Table II. Losses of Hydrogen, Ethene/Hydrogen, Carbon Monoxide/Hydrogen, Ethene/Ethene, and Hydrogen/Carbon Monoxide/Propene in the Reaction of Fe^+ with 4-Heptanone (11) and Its Isotopomers (11a–e)

	m																
	hydrogen					ethene/H_2; CO/H_2				ethene/ethene			hydrogen/CO/propene				
ketone	2	3	4	5	6	30	31	32	33	56	58	60	72	73	74	75	76
$C_3H_7C(O)C_3H_7$ (**11**)	32		6			38				6			18				
$C_3H_7C(^{18}O)C_3H_7$ (**11a**)	28		5			21		24		5					17		
$C_3H_7C(O)CH_2CH_2CD_3$ (**11b**)	17	9		4		16	17	18			5		4	3	2	5	
$C_3H_7C(O)CH_2CD_2CH_3$ (**11c**)	17	8		5		16	15	17			6		1	10	5		
$C_2H_5CD_2C(O)CD_2C_2H_5$ (**11d**)	39		5			38				4				1	10	3	
$CD_3(CH_2)_2C(O)(CH_2)_2CD_3$ (**11e**)		23			3		22		28			7			7	6	4

Scheme III



any further information about reversibility, kinetic isotope effects, or eventual formation of **7** from **5**. However, it can be stated with certainty that the generation of a terminal double bond, i.e. **7**, is favored by a factor of 3.6:1 over that of an internal double bond, viz. **8**.

The last process to be discussed in this section concerns the formation of $Fe(C_4H_6)^+$, presumably a Fe(butadiene)$^+$ complex (**10**). Double-resonance analysis confirms that **10** originates from the primary dehydrogenation products, and the labeling data point to extensive hydrogen-exchange processes preceding the loss of "C_2H_4O". We note, however, that the hydrogen (deuterium) atoms of positions C(1)/C(3) are hardly involved (<1%) in this exchange. Although the nature of the neutral molecule "C_2H_4O" cannot be probed experimentally, the present labeling data together with previous studies[1] and thermochemical arguments make acetaldehyde a very likely candidate. Scheme II summarizes, in a simplified manner, the most important findings.

In preliminary experiments, we have explored the effects of alkene ligands L (L = C_2H_4, C_3H_6, C_4H_6) on the reactivity of FeL^+ with some ketones.[1h,8] As will be demonstrated, the effects are quite profound indeed, and three major observations were made.

(I) When [6,6,6-D_3]-2-hexanone (**1a**) is reacted with $Fe(C_2H_4)^+$, the major reaction of the so-formed ligand substitution product **1a**–Fe^+ corresponds to dehydrogenation, and HD and H_2 are formed in a ratio >49:1. It goes without saying that the **1a**–Fe^+ species generated in the course of a ligand substitution (Scheme III) have an energy content which is smaller than that of the complex generated directly from **1a** and Fe^+ by the amount of the metal–olefin binding energy $D°(Fe^+–C_2H_4)$. Consequently, higher selectivity can be expected to result. This is indeed observed, and the label distribution (Scheme III) demonstrates that for species with lower energy content the generation of a terminal double bond (**7**) is strongly favored (49:1) over that of an internal double bond (**8**).

Table III. Product Distribution (%) for the Reactions of FeL^+ with 4-Heptanone (11)

L	11-FeL^+	11-Fe^+	[(11-Fe) – H_2]$^+$
C_2H_4	6	35	59
$CH_3CH{=}CH_2$	12	36	52
$CH_2{=}CHCH{=}CH_2$			100

(II) When the complexes Fe(ketone)$^+$ are formed via ligand substitution, CC bond activation, which is prevalent in many Fe(ketone)$^+$ complexes,[1] is completely suppressed in favor of CH bond activation. This is evidenced, for example, by the Fe(4-heptanone)$^+$ system (**11**–Fe^+). If **11** is reacted directly with bare Fe^+, the product distribution given in Scheme IV is observed. The labeling data (Table II) point to processes that commence with CH bond activation of the ω-position of one alkyl chain. Except for the last step in Scheme V, i.e. the formation of $Fe(C_3H_6)^+$ from **15**, *all* reactions are specific as far as the labeling distribution is concerned and can be explained in terms of Scheme V.[9] As the mechanisms of these processes are identical with the ones reported earlier[1h] for metastable ion decomposition of Fe(ketone)$^+$ complexes, we refrain from further commenting upon them.

The pronounced ligand effect on the chemistry of **11**–Fe^+ becomes obvious when FeL^+ (L = C_2H_4, C_3H_6, C_4H_6) rather than bare Fe^+ is employed as a "reagent". Out of the many CH/CC bond activation processes described in Schemes IV and V, we only observe dehydrogenation, i.e. **11**–Fe^+ → **12** → **13**. Obviously, this reaction constitutes the least energy-demanding process. For the remaining reactions, the energy content of **11**–Fe^+, when formed via the ligand-substitution process FeL^+ + **11** → L + **11**–Fe^+, is too low to bring about any CC activation or multiple dehydrogenation.

(III) In addition to dehydrogenation, in the reaction of FeL^+ with **11**, we observe for L = C_2H_4 and C_3H_6 the formation of the addition complexes **11**–FeL^+ as well as the substitution product **11**–Fe^+ (Table III). These results imply that the binding energy of Fe^+ to 4-heptanone is larger than that of ethene and propene to Fe^+ (34 and 37 kcal/mol). Due to the absence of **11**–Fe^+ from the reaction of $Fe(C_4H_6)^+$ with **11**, the binding energy is probably smaller than 48 kcal/mol.[10] Obviously, an energy of <11 kcal/mol deposited in the resulting complex **11**–Fe^+ is

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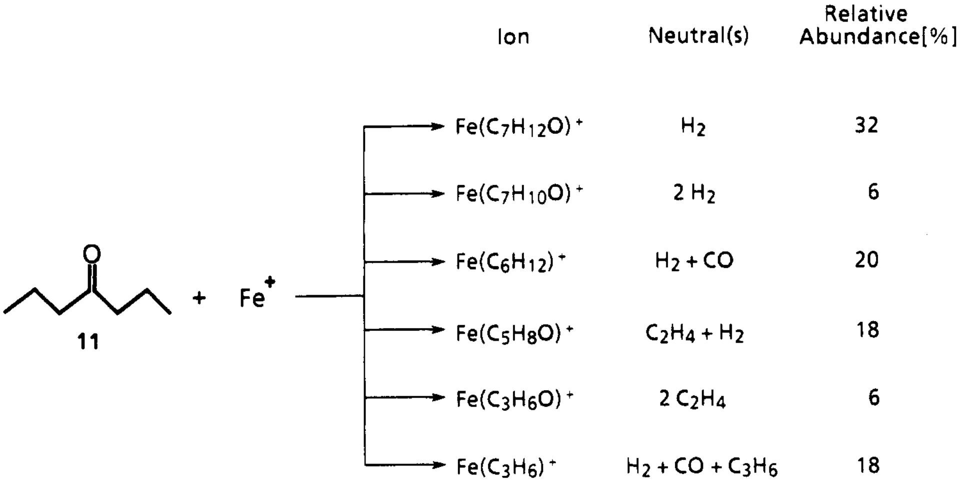
(8) For many references and the discussion of some selected examples of ligand effects, see: (a) Allison, J.; Mavridis, A.; Harrison, J. F. *Polyhedron* **1988**, *7*, 1559. (b) Hettich, R. L.; Freiser, B. S. *Organometallics* **1989**, *8*, 2447. (c) Buckner, S. W.; Freiser, B. S. *Polyhedron* **1988**, *7*, 1583.

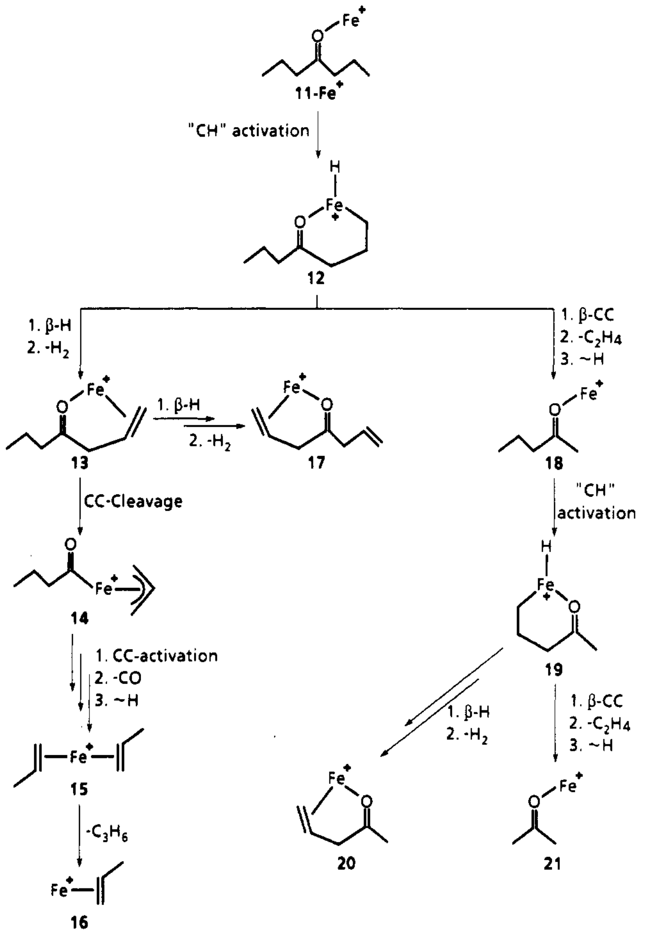
(9) We note that intermediate **18** in Scheme V has also been generated independently by reaction of Fe^+ with 2-pentanone. On the basis of extensive labeling data and double-resonance and CID experiments, its chemistry was probed and found to correspond to the reactions depicted in Scheme V with one notable difference: **20**, when formed from **11**–Fe^+, does not decompose further while decarbonylation is observed when the species is formed from 2-pentanone and Fe^+ (D. Schröder, H. Schwarz, unpublished results).

(10) Martinho Simões, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629.

Scheme IV



Scheme V

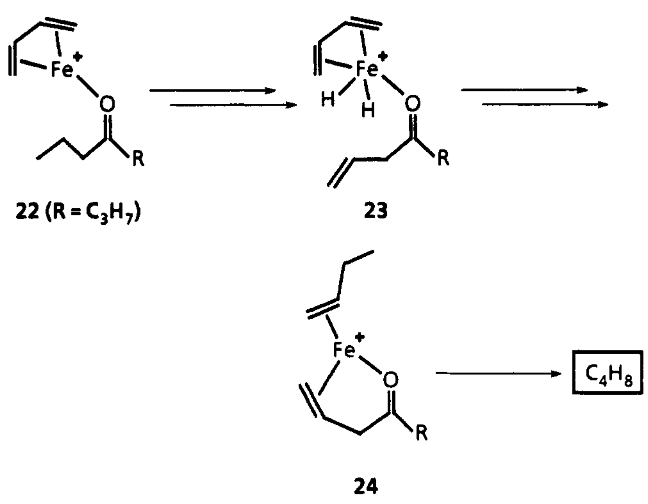


sufficient to bring about specific dehydrogenation of the $\omega/(\omega - 1)$ CH bonds of one alkyl chain.

Quite unexpected, and also puzzling at first sight, are the results obtained for the Fe(butadiene)$^+$/4-heptanone system. Ligand substitution (→**11**–Fe$^+$) or a detectable adduct (→**11**–FeL$^+$) are not observed—and yet we get a signal that corresponds to dehydrogenation of the Fe(ketone)$^+$ complex.

How to explain this finding? We favor the following mechanism (Scheme VI): In the chemically activated encounter complex **22**, hydrogen is transferred from the $\omega/(\omega - 1)$ positions of the ketone to the butadiene ligand (**22** → **24**). This Fe$^+$-induced transfer hydrogenation might proceed via **23**, although other intermediates are feasible.

Scheme VI



As the binding energy of butene to Fe$^+$ is smaller than that of the β,γ-unsaturated ketone (which acts as a bidentate ligand), detachment of 1-butene takes place; this reaction is experimentally revealed by a signal for the metal ion mediated dehydrogenation of 4-heptanone. Although the overall reaction $CH_2{=}CHCH{=}CH_2$ + *n*-butane → $2CH_2{=}CHC_2H_5$ is endothermic (3 kca/mol)[11] under *metal-free* conditions, the *double-hydrogen transfer within the ligand systems of **22** and **23** becomes thermochemically feasible because of the formation of a bidentate Fe$^+$ complex.*[12]

Acknowledgment. We gratefully acknowledge the financial support of our work by the Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, Volkswagen-Stiftung, and Graduiertenkolleg Chemie.

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(11) Thermochemical data for the relevant heats of formation of 1,3-butadiene, 1-butene, and butane were taken from: Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*; Chapman and Hall: London, 1986.

(12) We should like to recall that recently several remarkable examples for multiple interligand hydrogen migrations were reported. Common to these seemingly different processes is the fact that the hydrogen molecules are "stored" at ligands which themselves, like in the remarkable Crabtree–Felkin reaction,[13] serve as hydrogen acceptors: (a) Tsarbopoulos, A.; Allison, J. *Organometallics* **1984**, *3*, 86. (b) Steinrück, N.; Schwarz, H. *Organometallics* **1989**, *8*, 759. (c) Schulze, C.; Schwarz, H. *Organometallics* **1990**, *9*, 2164.

(13) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245.