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Iron(I) Mediated Activation of C−C and C−H Bonds of *cis*- and *trans*-1-Acetyl-2-methylcyclopropanes in the Gas Phase: Competition between Ring Cleavage and α-CC-Bond Insertion Reactions‡

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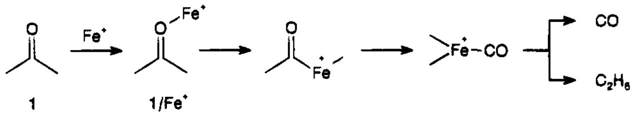
Abstract: Unimolecular and collision induced fragmentations of *cis*- and *trans*-1-acetyl-2-methylcyclopropanes, complexed to bare Fe$^+$ cations, were examined by means of tandem mass spectrometry. Stereoselective isotopic labeling data as well as comparative studies with acylic isomers reveal that two reaction pathways are in competition with each other. On the one hand, dehydrogenation, loss of ethene, and loss of acetaldehyde proceed via a common intermediate which is formed via ring cleavage of 1-acetyl-2-methylcyclopropane/Fe$^+$ to yield the corresponding 3-hexen-2-one/Fe$^+$ complexes; these undergo subsequently CH- and CC-bond activation via the remote functionalization mechanism. These ring cleavages are associated with a complete loss of stereochemical features for the *cis* and *trans* isomers. In contrast, unimolecular decarbonylation occurs stereoselectively and is favored for the *trans* isomers; this is rationalized via a stereoselective formation of *cis*- and *trans*-η^3-allyl complexes in the course of the electrocyclic ring-opening process. Furthermore, interconversion reactions, thermodynamic and kinetic aspects, and isotope effects of the CH- and CC-bond activation processes are discussed.

Introduction

In the last two decades the study of mechanistic aspects of the gas-phase chemistry of bare transition-metal cations has attracted considerable interest,[1] and the reactions of aliphatic ketones with Fe$^+$ may serve as an illustrative example:[2] Ketones with short side chains, e.g. acetone **1** (Scheme 1), react via α-CC-bond insertion and subsequent transfer of the second alkyl group to the metal center to yield an intermediate from which carbon monoxide and alkanes are eliminated as neutral products.[2a,3] In contrast, ketones containing side chains with at least three carbon atoms follow the energetically more favorable[2e] mechanism of "remote functionalization"[4] (Scheme 2) resulting in the losses of molecular hydrogen and alkenes from the terminal part of the alkyl chain.

Hitherto, only a few articles deal with the topic of *stereoselective* gas-phase reactions of transition-metal ions.[5] Here, we report the results of the unimolecular decomposition reactions of the Fe$^+$ complexes of *cis*-1-acetyl-2-methylcyclopropane (**2**) and its *trans* isomer **3** which serve as models for rigidly fixed side chains. The cyclopropyl backbone seems to be particularly interesting due to its unique properties: The high strain energy weakens the C−C bonds, while the C−H bonds of cyclopropanes possess bond dissociation energies as high as 106 kcal/mol.[6] These features indicate that **2** and **3** are crucial systems to further probe the concept of remote functionalization of C−H bonds, and two aspects will form the focus of interest: (i) Will the cyclopropyl backbone remain intact, thus resulting in a different chemistry for the *cis* and *trans* isomers? (ii) Is the Fe$^+$-mediated fragmentation preceded by a ring-opening which may reflect the stereochemical features of the reactants and eventually give rise to Fe$^+$ complexes of acyclic, unsaturated ketones? It is the latter aspect which led us to include the acyclic ketones **4**−**6** in the present study (Chart 1).

Scheme 1



By combining mass spectrometric methods with isotopic labeling techniques we will provide evidence for the operation of two competing reaction channels in the unimolecular decomposition reactions of **2**/Fe$^+$ and **3**/Fe$^+$. One of them corresponds to the Fe$^+$-mediated stereounselective ring opening leading to the 3-hexen-2-one/Fe$^+$ complex **4**/Fe$^+$; this species serves as a central intermediate for the losses of molecular hydrogen, ethene, and acetaldehyde in the metastable ion (MI) mass spectra of **2**/Fe$^+$ and **3**/Fe$^+$. On the other hand, in competition with this process α-CC-bond insertion of the metal ion occurs in analogy to **1**/Fe$^+$ (Scheme 1); this path is accompanied by a stereoselective, electrocyclic cleavage of the

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‡ Dedicated to Professor H.-G. Viehe on the occasion of his 65th birthday.

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Scheme 2

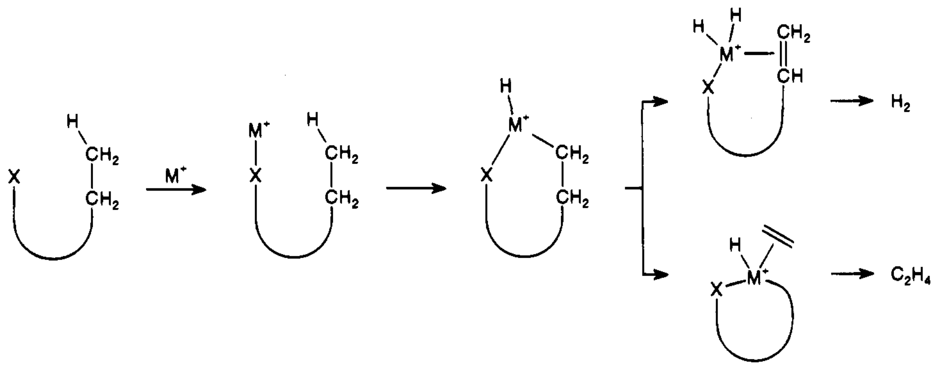
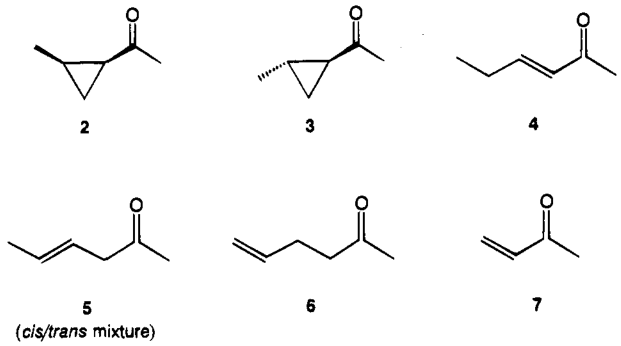


Chart 1


2
3
4
5
(*cis/trans* mixture)
6
7

cyclopropyl ring resulting in the formation of an η^3-allyl/Fe$^+$ complex which subsequently undergoes decarbonylation.

Experimental Section

The experiments were performed with a modified VG ZAB/HF/AMD four-sector mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sectors), which has been described previously.[7] Briefly, a mixture of $Fe(CO)_5$ and ketone was introduced *via* the heated (70 °C) septum inlet system into a chemical ionization source (CI, repeller voltage ca. 0 V) and subsequently ionized by a beam of electrons having 50−100 eV kinetic energy. The ions were accelerated to 8 keV translational energy and mass-selected by means of B(1)/E(1) at a resolution of $m/\Delta m$ 2−5000 sufficient to separate the ion of interest from isobaric impurities. Unimolecular fragmentations of metastable ions (MI) occurring in the field-free region preceding B(2) were recorded by scanning this sector. For collisional activation (CA) experiments, ions were collided with helium (80% transmission). The values reported here were independently measured at least three times. The error of the averaged relative intensities in MS/MS experiments does not exceed ±10%.[8] Branching ratios for H_2, HD, and D_2 losses were determined by scanning the mass region of the isotopomeric fragment ions separately in a linked-scan mode with B(2)/E(2) = constant, thus providing a higher resolution of the product ions and a more accurate determination of the quite weak D_2 losses. MS/MS/MS experiments[9] were performed by selecting the primary fragment ions by means of B(2), and the unimolecular or collision-induced fragmentations occurring in the subsequent field-free region were recorded by scanning E(2); these experiments will be referred to as MI/MI or MI/CA spectra, respectively. On principal grounds the MS/MS/MS experiments are less sensitive as compared to the MS/MS experiments and the error is estimated not to exceed ±20%. All spectra were accumulated and on-line processed with the AMD-Intectra data system; 5 to 30 scans were averaged to improve the signal-to-noise ratio.

In this study chemical ionization was used for the production of the metal ions. In contrast to electron impact conditions, the relatively high pressure that prevails in the ion source allows efficient cooling of the complexes generated. Excited states[10] of Fe$^+$ ions most likely do not participate in the reactions observed. This is supported by comparative ion cyclotron resonance and ion beam studies,[2f,10e] which revealed similar product distributions for ion/molecule reactions of organic substrates with thermalized metal cations under ICR conditions as compared to the fragmentations of metastable metal−substrate complexes generated under CI conditions. Nevertheless, the complexes must contain a certain amount of excess internal energy in order to undergo time-delayed unimolecular fragmentations.

Commercially available **6** was used as purchased (Fluka). Most of the unlabeled and some of the deuterium labeled compounds (in general >98 atom % D incorporation) were prepared by standard laboratory procedures,[8] e.g. reaction of the corresponding carboxylic acids with methyllithium[11] (2.5 equiv) and methyl-d_3 lithium (99.5 atom % D), respectively, or base catalyzed exchange of the α-hydrogen atoms; hydrogen exchange involving the α-position within the cyclopropyl ring was not observed. All products were purified by vacuum distillation or preparative gas chromatography and fully characterized by spectroscopic means.[8] **2** and **2b−e** were synthesized according to Scheme 3 by (i) chain elongation of 3-butyn-2-ol with 2 equiv of butyl lithium and 1 equiv of methyl iodide[12] (methyl-d_3 iodide; 99.5 atom % D), (ii) hydrogenation[13] (deuteration; 99.95 atom % D) of the 3-pentyn-2-ol triple bond with Lindlar catalyst, followed by (iii) Simmons−Smith cyclopropanation using CH_2I_2 (CD_2I_2; 95 atom % D) and (iv) Swern oxidation.[14] The Simmons−Smith reactions were carried out with the zinc−copper couple as described by Rawson and Harrison,[15] using dimethoxyethane[16] for the precipitation of ZnI_2. **3** and **3b−e** were made as outlined in Scheme 4 by (i) reduction of 3-pentyn-2-ol[17] with $LiAlH_4$ ($LiAlD_4$; 98 atom % D) in tetrahydrofurane and quenching with H_2O (D_2O; 99.9 atom % D) yielding stereospecifically the *trans*-configurated 3-penten-2-ols, (ii) Swern oxidation to the corresponding α,β-unsaturated ketones, and (iii) application of Corey's cyclopropanation method with NaH and trimethyloxosulfonium iodide[18] (or its d_9 analogue; >97 atom % D). The ^{18}O-isotope was incorporated (as demonstrated in Scheme 5 for **3a**) by mildly acidic hydrolysis of the

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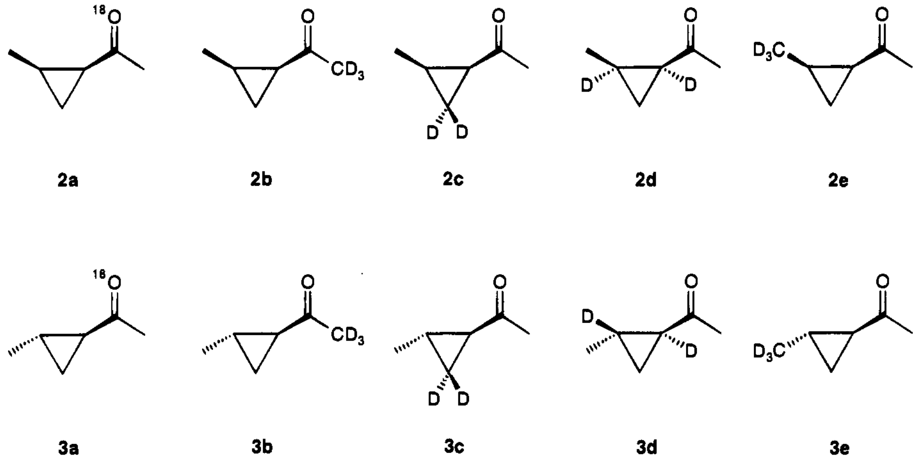
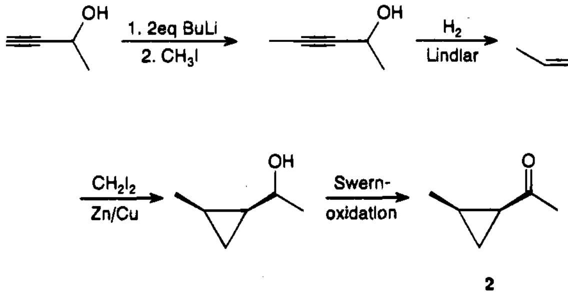
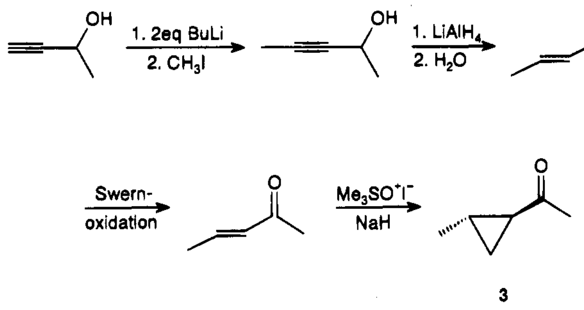
Chart 2



Scheme 3



Scheme 4



corresponding cyclohexylimines[19] (synthesized from ketone, cyclohexylamine, and $TiCl_4$) with $H_2{}^{18}O$ (96.5 atom % ^{18}O).

Table 1. Mass Differences (Δm in amu) Observed in the Unimolecular Decomposition (MI) of $2/Fe^+$–$6/Fe^+$, $2a/Fe^+$, and $3a/Fe^+$ [a]

	Δm						
	−2	−18	−20[b]	−28	−30[b]	−44	−46[b]
$2/Fe^+$	100	2		43		27	
$3/Fe^+$	100	1		76		34	
$4/Fe^+$	100	<1		22		16	
$5/Fe^+$	42	<1		35		100	
$6/Fe^+$	33	<1		35		100	
$2a/Fe^+$	100	1	2	17	19		25
$3a/Fe^+$	100	<1	1	22	46		32

[a] Intensities are given relative to the base peak (100%). [b] Neutral losses containing the ^{18}O-label of $2a/Fe^+$ and $3a/Fe^+$.

Table 2. Mass Differences (Δm in amu) Observed in the Collisional Activation (CA) Mass Spectra of $2/Fe^+$–$6/Fe^+$ [a]

	Δm								
	−2	−15[b]	−18	−28	−30[b]	−31[b]	−44	$Fe(CH_3)^+$	Fe^+
$2/Fe^+$	100	2	2	66	3	<1	66	1	3
$3/Fe^+$	97	4	1	100	7	<1	77	2	4
$4/Fe^+$	100	5	<1	28	1	<1	25	2	2
$5/Fe^+$	28	3	<1	32	5	4	100	4	5
$6/Fe^+$	25	2	2	29	3	4	100	4	4

[a] Intensities are given relative to the base peak (100%). For the sake of clarity, some fragmentations of low intensities are omitted. [b] Neutral products not mentioned in the text correspond to the following: loss of $CH_3^•$ ($\Delta m = 15$) and consecutive losses of CO/C_2H_4 and H_2 ($\Delta m = 30$); the neutral(s) corresponding to $\Delta m = 31$ cannot be specified.

Results and Discussion

The Fe^+ complexes of both stereoisomers **2** and **3** exhibit four major unimolecular fragmentation processes which are also observed for the Fe^+ complexes of the isomeric, acyclic hexenones **4**–**6** (Table 1): (i) dehydrogenation ($\Delta m = 2$), (ii) loss of ethene and isobaric carbon monoxide ($\Delta m = 28$), and (iii) expulsion of acetaldehyde ($\Delta m = 44$). The formation of water ($\Delta m = 18$) is a side reaction of low intensity and will not be pursued further in the discussion. For the sake of clarity the CA data are given for the unlabeled ketones only (Table 2). The CA spectra[8] of the labeled compounds are in line with the findings reported below, and the complete set of data is available upon request from the authors.

Identification of the Ionic Products. The mass difference of $\Delta m = 2$ corresponds to the loss of molecular hydrogen. The MI/CA spectra of the corresponding dehydrogenation product ions from all five unlabeled ketone/Fe^+ complexes $2/Fe^+$–$6/Fe^+$ are identical within experimental error; this indicates a common structure of the product ions, most likely stereoisomers of 3,5-hexadien-2-one/Fe^+ complexes.

The signals due to the losses of $\Delta m = 28$ and 30 in the MI spectra of the ^{18}O-labeled ketones **2a** and **3a** establish the expulsion of ethene as well as carbon monoxide. The MI/CA spectra and even the MI/MI spectra[8] of the [$2a/Fe^+$–$C^{18}O$] and [$3a/Fe^+$–$C^{18}O$] are dominated by the expulsions of molecular hydrogen, methane, and ethene from the resulting C_5H_{10}/Fe^+ fragments; this is in line with previous data for the Fe^+ complexes of pentene isomers.[20] Similarly, the products of the ethene losses from $2a/Fe^+$ and $3a/Fe^+$ can be identified as the Fe^+ complex of the ^{18}O-labeled methyl vinyl ketone $7/Fe^+$: The CA spectrum of the authentic methyl vinyl ketone complex, $7/Fe^+$, is close to the MI/CA spectra of the $C_4H_6{}^{18}O/Fe^+$ fragments generated via ethene losses from $2a/Fe^+$ and $3a/Fe^+$ (except for mass shifts arising from the presence of the ^{18}O label).[21] The similarity of the MI/CA spectra (Table 3) of

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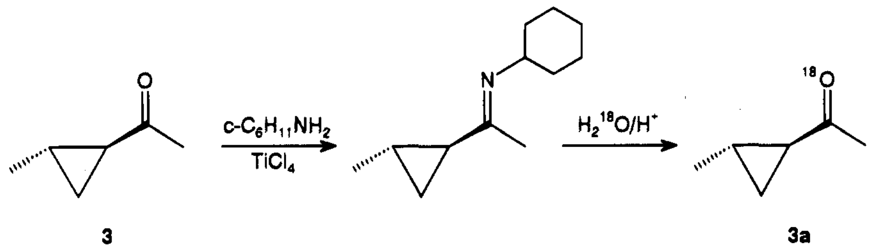
Table 3. Partial MI/CA Spectra of Mass Selected Fragment Ions Generated from Different $C_6H_{10}O/Fe^+$ Precursors[a]

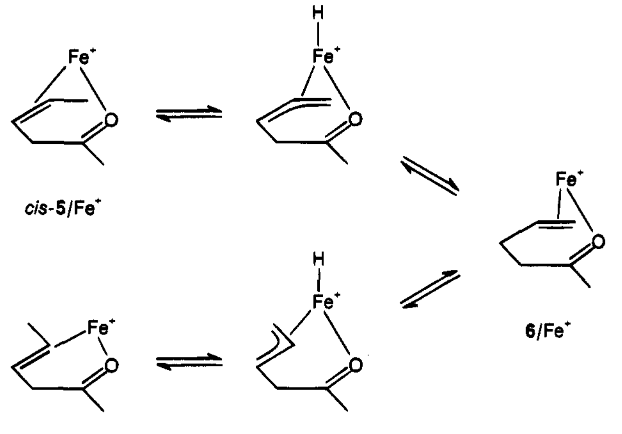
	Δm										
	-2^b	-16^b	-27	-28^b	-30	-42	-43	-44	-45	-46	Fe^+
[**2**/Fe^+-CO/C_2H_4]	45	65	2	100		11	12	15	7		20
[**3**/Fe^+-CO/C_2H_4]	40	85	3	100		15	7	9	6		18
[**4**/Fe^+-CO/C_2H_4]	25	70	4	100		18	11	7	9		19
[**5**/Fe^+-CO/C_2H_4]	45	85	2	100		14	8	8	7		20
[**6**/Fe^+-CO/C_2H_4]	40	75	3	100		11	9	5	6		12
[**3a**/$Fe^+-C^{18}O$]	45	95		100		13	8	5	4		15
[**3a**/$Fe^+-C_2H_4$]^c		100	45		70				55	50	80
[**7**/Fe^+]^d		100	25	65			30	40			65

[a] Intensities are given relative to the base peak (100%). For the sake of clarity, some fragmentations of low intensities are omitted. [b] These processes are also observed in the MI/MI spectra of **2**/Fe^+–**6**/Fe^+. [c] Mass shifts resulting from ^{18}O-label. [d] See ref 21.

Scheme 5



Scheme 6



fragment ions corresponding to the losses of $\Delta m = 28$ from **2**/Fe^+–**6**/Fe^+ implies that both CO and C_2H_4 losses are also operative in the ring-opened isomers. Although an exact value for the ratio of ethene and carbon monoxide losses in the MI spectra of **4**/Fe^+ to **6**/Fe^+ cannot be given, the loss of carbon monoxide most probably corresponds to a minor reaction channel (see below).

Further, a comparative MI/CA analysis demonstrates that the loss of acetaldehyde from the Fe^+ complexes of all $C_6H_{10}O$ isomers **2**–**6** leads to the same C_4H_6/Fe^+ product ion; this iron complex very likely is that of butadiene/Fe^+, since the MI/CA spectrum is dominated by the loss of the complete C_4H_6 unit as base peak and a strong loss of $\Delta m = 27$ corresponding to the symmetrical cleavage of the ligand.[8]

Reactions of the Iron(I) Complexes of the Hexen-2-ones. The MI spectra of **5**/Fe^+ and **6**/Fe^+ are similar to each other, indicating a rapid interconversion between both isomers. We assume that these isomerization processes occur *via* allylic intermediates (Scheme 6) in analogy to the double bond migration in the Fe^+ complexes of 1- and 2-pentene as reported previously.[20,22] Since the intensities of the four product channels are clearly different for **4**/Fe^+ as compared to **5**/Fe^+ and **6**/Fe^+, a higher activation barrier probably renders the migration of the conjugated α,β-double bond in **4**/Fe^+ more difficult.[23] A partial double-bond migration in **4**/Fe^+ is, however, indicated by the acetaldehyde loss from **4**/Fe^+, since only **5**/Fe^+ and **6**/Fe^+ can easily lead to acetaldehyde formation *via* 1,4- or 1,2-eliminations, respectively (see below).

Deconvolution of Ethene and Carbon Monoxide Losses. For an analysis of the data for the isotopologues of **2** and **3** (Tables 4 and 5) it is necessary to deconvolute the isobaric ethene and carbon monoxide losses ($\Delta m = 28$). **2a**/Fe^+ and **3a**/Fe^+ allow this separation[24] and, since heavy atom isotope effects of ^{18}O are expected to be negligible, the study of these isotopologues reflects the ratio of C_2H_4 to CO losses for the unlabeled **2**/Fe^+ and **3**/Fe^+. It is evident that, far beyond the error limit, the $C^{18}O$ loss ($\Delta m = 30$) from **3a**/Fe^+ is favored as compared to **2a**/Fe^+, while the intensity for ethene elimination is practically identical for both stereoisomers.

An intuitively plausible analysis would assume as a first approximation a constant intensity for the CO losses, e.g. 11% from **2**/Fe^+ and 23% from **3**/Fe^+. However, this is not consistent with the experimental findings as demonstrated by inspecting a few cases: For example, CO loss from **2a**/Fe^+ amounts to 11% (Table 4). Consequently, for **2e**/Fe^+ a constant intensity of CO loss would imply the formation of 12% ethene-d_0; however, formation of ethene-d_0 from **2e**/Fe^+ is rather improbable, since this would require that *all* hydrogen atoms of the cyclopropyl ring are "consumed" in the ethene formation. This is not only unlikely on mechanistic grounds, it is also in conflict with the experimental results: For example, *no* losses of ethene-d_2 from the cyclopropane-ring-labeled complexes **2c**/

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[21] The CA spectrum of **7**/Fe^+ was recorded at a reduced acceleration voltage of 6564 V, in order to ensure that this ion has the same kinetic energy as those produced by unimolecular ethene losses from **2a**/Fe^+ and **3a**/Fe^+.

[22] For a recent example demonstrating very extensive H/D exchanges within an organometallic gas-phase system, see: Schwarz, J.; Schwarz, H. *Chem. Ber.* **1993**, *126*, 1257.

[23] All attempts toward the synthesis of pure *cis*-3-hexen-2-one failed. Rapid *cis*/*trans* isomerization took place during either the catalytic hydrogenation of 3-hexyn-2-one or the oxidation of *cis*-3-hexen-2-ol employing numerous procedures. The possibility as to whether *cis*/*trans* isomerization of the Fe^+ complexes of **4** is facile remains unexplored. For the sake of simplicity, in the text 3-hexen-2-one is represented by its *trans* isomer only.

[24] This separation could be done for the deuterated isotopologues as well by introducing an additional ^{18}O-label; however, this seems to be out of proportion in view of the high expenditure of experimental work and the additional insight one might possibly gain from this experiment.

Table 4. Mass Differences (Δm in amu) Observed in the Unimolecular Decomposition of the 2/Fe$^+$ Isotopologues[a]

	dehydrogenation			CO/ethene losses				acetaldehyde loss			
	−2	−3	−4	−28	−29	−30	−31	−44	−45	−46	−47
2/Fe$^+$	59			25				16			
2a/Fe$^+$	62			11		11				16	
2b/Fe$^+$	57			25							18
2c/Fe$^+$	33	17	0.1	23	6			15	6		
2d/Fe$^+$	35	17		13	13			21	1		
2e/Fe$^+$	4	34	<0.1	23		12	1	10	16		

[a] Intensities are normalized to the sum of fragmentations considered equal to 100%. Intensities less than 1% are omitted (except for the losses of D_2). In addition, minor losses of water are observed, see Table 1 (Δm = 18).

Table 5. Mass Differences (Δm in amu) Observed in the Unimolecular Decomposition Reactions of the 3/Fe$^+$ Isotopologues[a]

	dehydrogenation			CO/ethene losses				acetaldehyde losses			
	−2	−3	−4	−28	−29	−30	−31	−44	−45	−46	−47
3/Fe$^+$	49			35				16			
3a/Fe$^+$	50			11		23				16	
3b/Fe$^+$	61			22							17
3c/Fe$^+$	34	17	0.1	23	7			14	5		
3d/Fe$^+$	34	17		20	11			17	1		
3e/Fe$^+$	5	41	<0.1	18		12	1	10	13		

[a] Intensities are normalized to the sum of fragmentations considered equal to 100%. Intensities less than 1% are omitted (except for the losses of D_2). In addition, minor losses of water are observed; see Table 1 (Δm = 18).

Table 6. Calculated Fractional Abundances of the Carbon Monoxide Losses (See Text)[a]

neutral	**2**/Fe$^+$	**2a**/Fe$^+$	**2b**/Fe$^+$	**2c**/Fe$^+$	**2d**/Fe$^+$	**2e**/Fe$^+$
CO	13		13	17	13	23
$C^{18}O$		11				
neutral	**3**/Fe$^+$	**3a**/Fe$^+$	**3b**/Fe$^+$	**3c**/Fe$^+$	**3d**/Fe$^+$	**3e**/Fe$^+$
CO	24		10	18	19	18
$C^{18}O$		23				

[a] CO abundances are calculated assuming the ethene losses to be constant for all isotopomers at a value of 12% of the sum of all fragmentations.

Fe$^+$ and **2d**/Fe$^+$ are observed. Furthermore, the hypothesis of facile H/D exchange processes cannot resolve the contradictory results for the ethene loss from **2e**/Fe$^+$, since no ethene-d_1 (Δm = 29) is formed.[25] For similar reasons, a model assuming any constant ratios of ethene and carbon monoxide formation can be excluded. Rather, we postulate that it is the ethene elimination that, to a first approximation, is constant for all isotopologues. As a working hypothesis for the deconvolution of the data for the deuterium-labeled complexes we assume that the ethene loss occurs with a constant intensity of ca. 12% for all isotopologues in agreement with the values measured for **2a**/Fe$^+$ (11%), **2e**/Fe$^+$ (13%), **3a**/Fe$^+$ (11%), and **3e**/Fe$^+$ (13%). Although this assumption is probably not perfectly correct for **2c**/Fe$^+$ and **3c**/Fe$^+$, it turned out to be essential for achieving internal consistency in the data analysis. As will be discussed below, the mechanism for the ethene expulsion will lead to the conclusion that for **2c**/Fe$^+$ and **3c**/Fe$^+$ a kinetic isotope effect is indeed operative. If, for the time being, this effect is ignored, the CO losses from all complexes are as given in Table 6. While one may argue about the quantitative reliability of this assumption, the essential qualitative conclusions (see below) will not alter when the amount of ethene loss is varied.

Substraction of the so-obtained data for CO elimination from the abundances given in Tables 4 and 5, followed by renormalization of the intensities of the remaining fragments (i.e., hydrogen, ethene, and acetaldehyde formation), results in two data sets for the *cis* and the *trans* isomers of 1-acetyl-2-methylcyclopropane/Fe$^+$ complexes that exhibit only very minor differences within experimental error limits. This finding already indicates that in the course of these Fe$^+$-mediated product formations of **2** and **3**, the stereochemical information is lost. Consequently, the *cis*/*trans* differences reported in Table 1 (and in Tables 4 and 5 for the isotopologues) are mainly due to different intensities for the CO losses from **2**/Fe$^+$ and **3**/Fe$^+$. From that we conclude that two competing mechanistic pathways are operative: (i) Ring cleavage eventually yields **4**/Fe$^+$ from which hydrogen, ethene, and acetaldehyde are formed. In the course of this reaction channel the stereochemical information is not preserved. (ii) The second reaction channel leads to decarbonylation[26] *via* α-CC-bond insertion without initial cyclopropane ring opening. This pathway is responsible for the differences observed for the ease with which CO is eliminated from **2**/Fe$^+$ and **3**/Fe$^+$. We will first discuss those reactions which commence with the cleavage of the three-membered ring.

Ring Cleavage. The observation of identical unimolecular fragmentation products arising from all five ketone/Fe$^+$ complexes **2**/Fe$^+$–**6**/Fe$^+$ strongly indicates that the cyclopropyl rings in **2**/Fe$^+$ and **3**/Fe$^+$ are not preserved. Based on the similarity of the MI spectra of **2**/Fe$^+$ and **3**/Fe$^+$ with that of **4**/Fe$^+$ as well as the apparent intensity differences as compared to **5**/Fe$^+$ and **6**/Fe$^+$, we suppose that **4**/Fe$^+$ is initially formed in the ring cleavages and that this acyclic unsaturated ketone/Fe$^+$ complex serves as an intermediate for dehydrogenation and the losses of ethene and acetaldehyde. The higher intensities of the acetaldehyde and combined ethene/carbon monoxide losses from **2**/Fe$^+$ and **3**/Fe$^+$ (as compared with **4**/Fe$^+$) can be explained by a higher internal energy content of the corresponding ions resulting from the release of ring-strain energy upon cleavage. As a consequence, processes with a larger activation barrier are favored at the expense of those with a lower barrier. According to earlier experiences,[2e,27] the loss of molecular hydrogen *via* remote functionalization of aliphatic ketones exhibits the lowest

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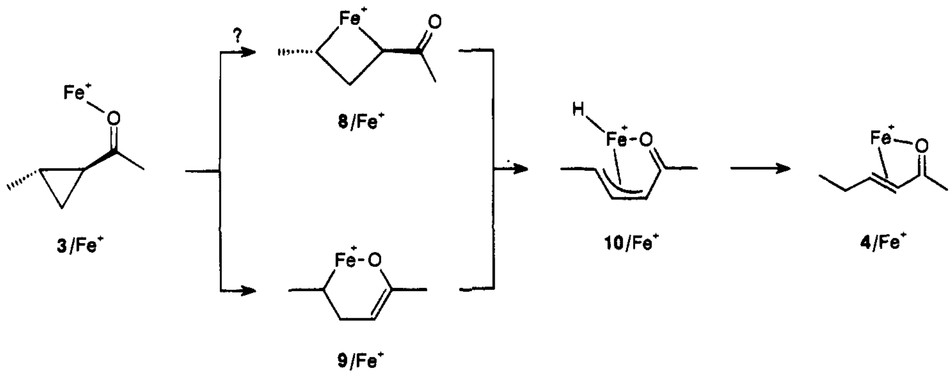
[25] Similar arguments can be applied for the *trans* complexes; for example, for **3b**/Fe$^+$ the assumption of a constant CO intensity leads to the conclusion that no ethene is formed at all from this complex, whereas the other isotopologues clearly reveal the occurrence of ethene loss.

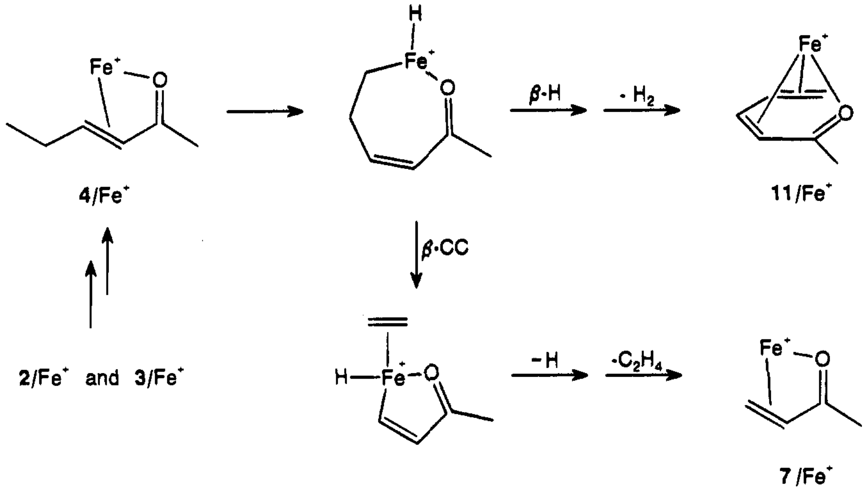
[26] As shown by a comparison of the MI/CA spectra, carbon monoxide is also formed to a minor extent by decarbonylation of **4**/Fe$^+$. But, since this is a negligible channel for CO formation, the discussion will focus on the decarbonylation *via* α-CC-bond insertion of the metal ion.

[27] Stöckigt, D.; Sen, S.; Schwarz, H. *Chem. Ber.* **1993**, *126*, 2553.

Scheme 7



Scheme 8



activation barrier. In line with this reasoning, collisional activation leads to enlarged losses of ethene/carbon monoxide and acetaldehyde (Table 2) relative to dehydrogenation.

Ring cleavages induced by naked or ligated metal cations are well-known for cyclopropane itself, and metallacyclobutanes have been suggested as intermediates.[28] However, in the present case the formation of such a species is not likely on the grounds that in the formation of the metallacyclobutane derivative **8**/Fe^+ from **2**/Fe^+ and **3**/Fe^+ the initial bonding between the iron atom and the carbonyl group had to be weakened substantially; in fact, we believe that a pathway involving **8**/Fe^+ is probably energetically too demanding. Therefore, we propose an alternative mechanism (Scheme 7), which describes ring cleavage in terms of first generating the enolic intermediate **9**/Fe^+ in which the metal coordination to the oxygen atom is even strengthened. In addition, **9**/Fe^+ enjoys the advantage of a less strained six-membered metallacycle. Subsequently, **9**/Fe^+ may isomerize *via* a β-H shift to give rise to an allylic complex **10**/Fe^+, from which **4**/Fe^+ is formed eventually. These qualitative arguments for the preference of **9**/Fe^+ as compared to **8**/Fe^+ are supported by a thermochemical estimate[29] for both species assuming a simple additivity scheme:[30] If ring strain is neglected, the heats of formation of **8**/Fe^+ and **9**/Fe^+ differ by only ca. 1 kcal/mol. Thus, it is the strain of the four-membered metallacycle in **8**/Fe^+ which makes this intermediate thermochemically less favorable.

Losses of Molecular Hydrogen and of Ethene. The analysis of the MI spectra (Tables 4 and 5) of the deuterium-labeled isotopologues of **2** and **3** (Chart 2) provides quite a detailed insight into the mechanistic aspects underlying these C−H/C−C bond activation processes. Both the loss of molecular hydrogen and the explusion of ethene can be explained by the concept of remote functionalization proceeding via **4**/Fe^+ as depicted in Scheme 8. After Fe^+-mediated activation of an ω-C−H bond a β-H-shift from the (ω − 1)-position leads to the formation of molecular hydrogen, while cleavage of the β-C−C bond gives rise to the loss of ethene. This scenario is in accord with the formation of **11**/Fe^+ and **7**/Fe^+ as ionic products (see above).

In line with earlier studies of α-labeled ketone/Fe^+ complexes,[2a,d-f,5f] the labeling data for **2b**/Fe^+ and **3b**/Fe^+ show that the α-methyl group is not involved in dihydrogen or ethene losses. However, the losses of HD ($\Delta m = 3$) from **2c**/Fe^+, **2d**/Fe^+, and **2e**/Fe^+ as well as from the stereoisomeric *trans* isotopologues demonstrate that hydrogen elimination must involve positions C(2), C(3) of the ring as well as the 2-methyl group.

The striking similarity of H_2 and HD losses for **2c**/Fe^+ and **2d**/Fe^+, which is also observed for the corresponding *trans* isomers, can be rationalized in terms of the intermediates **4c**/

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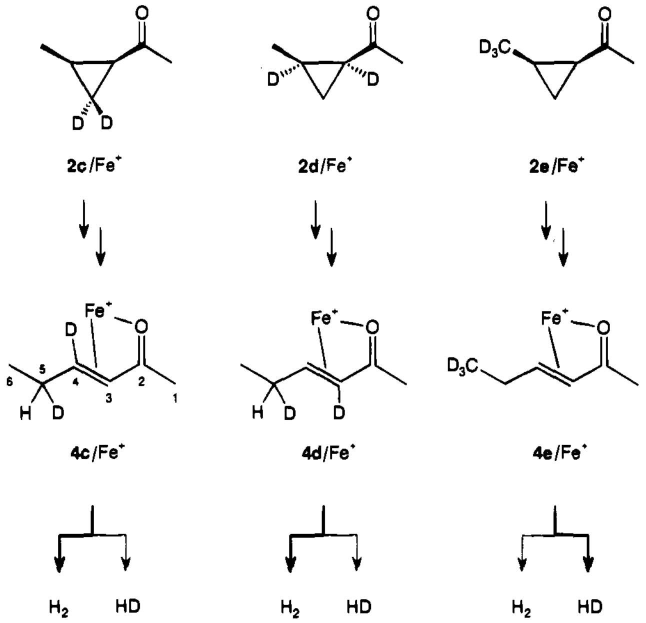
[28] (a) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 3900. (b) Jacobson, D. B.; Freiser, B. S. *Organometallics* **1984**, *3*, 513. (c) Cassady, C. J.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 5690. (d) van Koppen, P. A. M.; Jacobson, D. B.; Illies, A.; Bowers, M. T.; Hanratty, M.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 1991. (e) Fisher, E. R.; Armentrout, P. B. *J. Phys. Chem.* **1990**, *94*, 1674. (f) Schultz, R. H.; Armentrout, P. B. *Organometallics* **1992**, *11*, 828.

[29] Neglecting ring strain, ΔH_f is derived as (ref 30): $\Delta H_f(\mathbf{8}/Fe^+) = \Delta H_f(CH_3CH_2CH_2CH_2COCH_3) + \Delta H_f(Fe^+) - 2\cdot BDE(Fe^+{-}CH_3) + 2\cdot BDE(C{-}H) - 2\cdot\Delta H_f(H^\bullet)$. $\Delta H_f(\mathbf{9}/Fe^+) = \Delta H_f(CH_3CH_2CH_2CH{=}C(OH)CH_3) + \Delta H_f(Fe^+) - BDE(Fe^+{-}CH_3) - BDE(Fe^+{-}OH) + BDE(C{-}H) + BDE(O{-}H) - 2\cdot\Delta H_f(H^\bullet)$. Additional thermochemical data were taken from ref 31.

[30] Benson, S. W. *Thermochemical Kinetics: Methods for the Estimation of Thermochemical Data and Rate Parameters*, 2nd ed.; Wiley: New York, 1976.

[31] Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. Gas Phase Ion and Neutral Thermochemistry. *J. Phys. Chem. Ref. Data, Suppl. 1* **1988**, *17*.

Scheme 9



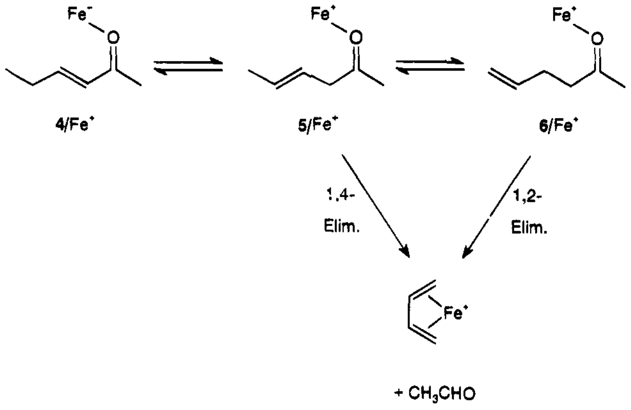
Fe$^+$ and **4d**/Fe$^+$. Both bear one deuterium atom in the (ω − 1)-position (Scheme 9). From the ratio of 34% versus 17% for H_2/HD losses, an intramolecular kinetic isotope effect (KIE) of ca. 2 can be estimated; similar KIEs have been measured for the Fe$^+$-mediated dehydrogenation of other carbonyl compounds.[2e,5f] For several Fe$^+$-mediated dehydrogenations it has been demonstrated that this isotope effect is almost exclusively associated with the last step, i.e. the reductive elimination of molecular hydrogen.[2d,32]

Although the remote functionalization mechanism[4] predicts exclusive HD loss from intermediate **4e**/Fe$^+$, explulsion of H_2 is also observed though with low intensity. As noted above, it has to be assumed that **4**/Fe$^+$ partially isomerizes to **5**/Fe$^+$ and **6**/Fe$^+$, and if this process is reversible it will result in H/D exchanges between C(4) and C(6), thus leading to H_2 formation. However, the barriers associated with the interconversion of **4**/Fe$^+$ to **5**/Fe$^+$ and **6**/Fe$^+$, respectively, have to be high enough to prevent complete equilibration while not rendering partial isomerization impossible.

This mechanistic picture is supported by the extremely weak losses of D_2 ($\Delta m = 4$) observed for all isotopologues studied, and this finding also rules out statistical H/D equilibration prior to dissociation. Since an allylic isomerization mechanism demands that H/D exchange occurs specifically between C(4)/C(6) and/or C(3)/C(5) of **4**/Fe$^+$, respectively, loss of D_2 should be observed only for **2c**/Fe$^+$, while **2d**/Fe$^+$ and **2e**/Fe$^+$ should not give rise to the expulsion of D_2 at all. This is indeed the case: For **2c**/Fe$^+$ we observe loss of D_2 with ca. 0.1% intensity; D_2 loss is absent for **2d**/Fe$^+$ and hardly exceeds the signal-to-noise ratio for **2e**/Fe$^+$.

It is quite clear that—based on this mechanism—ethene losses from intermediates **4c**/Fe$^+$ and **4d**/Fe$^+$ *via* remote functionalization should give rise to ethene-d_1 ($\Delta m = 29$) as the major product. This is found for both the *cis* and the *trans* isomers. **2c**/Fe$^+$ exhibits a somewhat lower intensity of ethene-d_1 than **2d**/Fe$^+$ that cannot be satisfactorily explained on the basis of these mechanisms, and thus we conclude that an isotope effect has to be operative in the deuterium transfer associated with the isomerization **2c**/Fe$^+$ → **4c**/Fe$^+$. As mentioned above, the existence of an H/D kinetic isotope effect associated with the ethene losses weakens our assumption of constant ethene losses from all isotopomeric **2**/Fe$^+$ complexes. Thus, for the time being, we cannot decide to what extent the KIE affects the ethene losses from **2c**/Fe$^+$ and **3c**/Fe$^+$. However, as demonstrated above, an internally consistent deconvolution of the isobaric ethene/carbon monoxide losses is not possible without making this assumption.

Scheme 10



In the literature, cleavage of *two* C−C bonds of the cyclopropane ring system by various cationic metals has been reported,[28a−c,e,33] and ethene-ligated metal carbene complexes have been proposed as intermediates. The operation of a similar mechanism in the present system involving ethylidene intermediates, which after rearrangement give rise to ethene formation, can be excluded, since the expected losses of ethene-d_3 from **2e**/Fe$^+$ as well as from **3e**/F$^+$ are hardly observed and can be accounted for in terms of H/D exchange processes as outlined above for unimolecular dehydrogenation.

Loss of Acetaldehyde. According to the MI spectra of **2a**/Fe$^+$ and **2b**/Fe$^+$, for the formation of acetaldehyde the intact acetyl moiety is combined with one hydrogen atom originating from the C_4H_7 backbone of the cyclopropyl ketones. We assume that expulsion of acetaldehyde from **2**/Fe$^+$ and **3**/Fe$^+$ proceeds *via* ring cleavage as discussed above, followed by an isomerization of the intermediate **4**/Fe$^+$ to **5**/Fe$^+$ and/or **6**/Fe$^+$, respectively. Acetaldehyde loss from the directly generated, genuine complexes **5**/Fe$^+$ and **6**/Fe$^+$ is facile and gives rise to the base peak in the MI spectra of these precursors (Table 1),[2a] thus indicating that 1,4- and/or 1,2-elimination modes are favored (Scheme 10). In contrast, **4**/Fe$^+$ has to undergo isomerization prior to dissociation to acetaldehyde and C_4H_6/Fe$^+$. These considerations lead to the prediction that the hydrogen abstraction from the backbone should predominantly involve C(4) and C(6) of **5**/Fe$^+$ and **6**/Fe$^+$ in agreement with the observed losses of acetaldehyde-d_1 from **2c**/Fe$^+$ and **2e**/Fe$^+$. Similarly, the small amount of deuterium incorporation in the neutral fragment measured for **2d**/Fe$^+$ is in line with the corresponding acyclic intermediate **4d**/Fe$^+$ (Scheme 9), which bears deuterium atoms at C(3) and C(5) and is unlabeled at C(4) and C(6). Not surprisingly, similar considerations apply to the isotopologues of the *trans* compounds of **3**/Fe$^+$.

Decarbonylation. As outlined above, the differences in the MI spectra of the stereoisomeric pairs **2**/Fe$^+$ and **3**/Fe$^+$ arise from the losses of carbon monoxide, while ring cleavage and the consecutive formation of H_2, C_2H_4, and CH_3CHO result in similar intensities for either stereoisomer. Therefore, we conclude that a second reaction channel exists besides the ring cleavage/remote functionalization mechanism, and it is this additional path which is responsible for the major part of the carbon monoxide losses (Scheme 11).

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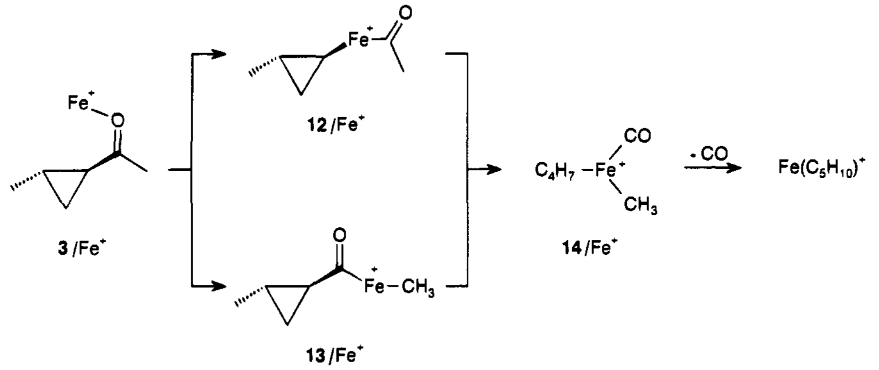
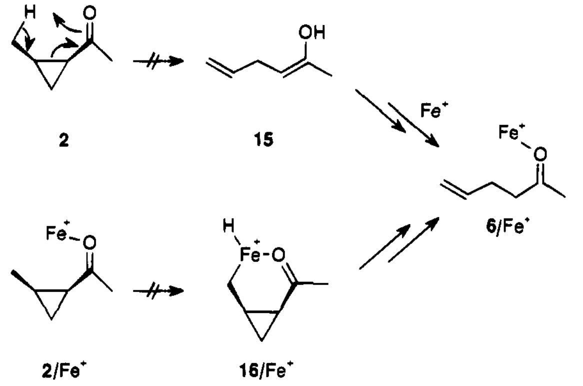
(32) Schröder, D.; Schwarz, H. *Chimia* **1989**, *43*, 317.

(33) (a) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 67. (b) Jackson, T. C.; Carlin, T. J.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 1120.

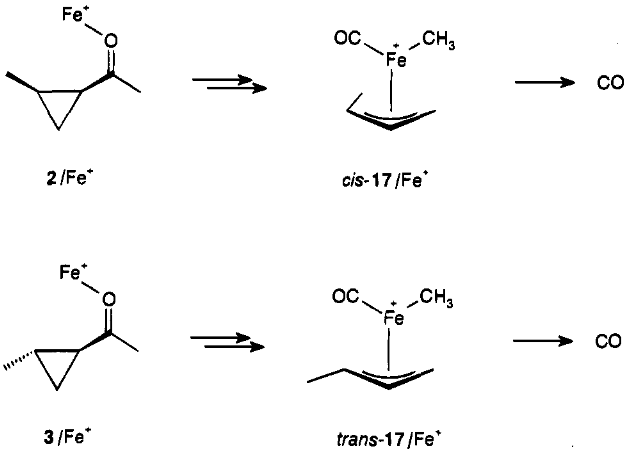
Scheme 11



Scheme 12



Scheme 13



We propose that the explusion of carbon monoxide from 3/Fe$^+$ (and also 2/Fe$^+$; see below) follows the mechanism depicted in Scheme 11 for the *trans* complex 3/Fe$^+$. This sequence is analogous to the decarbonylation of 1/Fe$^+$ (Scheme 1): Insertion of the metal ion in an α-C–C bond leads to either **12**/Fe$^+$ or **13**/Fe$^+$ as primary intermediates. On the basis of our data as well as thermochemical considerations[31] we cannot distinguish between these two modes of insertion processes, i.e. whether **12**/Fe$^+$ or **13**/Fe$^+$ is formed preferentially. However, in either event transfer of the other side chain to the metal center leads to **14**/Fe$^+$, from which expulsion of carbon monoxide results in the formation of C_5H_{10}/Fe$^+$. Furthermore, the MI/MI and MI/CA spectra of C_5H_{10}/Fe$^+$ generated from **2**/Fe$^+$ and **3**/Fe$^+$ are in accordance with the data of pentene/Fe$^+$ complexes (see above).[20] In conclusion, decarbonylation is also associated with ring opening of the cyclopropyl backbone; however, a principally different mechanism must be operative in order to account for the stereochemical effect.

Energetic and Stereochemical Effects. The similarity of the spectra of **2**/Fe$^+$ and **3**/Fe$^+$ implies that the thermal, metal-free rearrangement[34] of **2** (Scheme 12), which *via* enolization would lead to 5-hexen-2-one **6**, does not take place. This is based on the fact that an analogous reaction is not feasible on steric grounds for the *trans* isomer **3**. In addition, direct metal-mediated C–H bond activation of the terminal methyl group in intact **2**/Fe$^+$ can be ruled out for the following reasons: If we assume that the Fe$^+$ insertion into a ω-C–H bond involves the sextet surface only, we expect a highly radicaloid character[35] of the terminal methylene group in **16**/Fe$^+$ (Scheme 12); as a consequence, ring cleavage of the so-formed metallacycle via a cyclopropyl carbinyl rearrangement is expected to be facile[36] to generate an enolate/Fe$^+$ complex which is expected to isomerize rapidly[2e] to **6**/Fe$^+$. Both pathways depicted in Scheme 12 should lead to MI spectra of **2**/Fe$^+$ similar to that of **6**/Fe$^+$, whereas for the *trans* compound **3**/Fe$^+$ these processes are, on stereochemical grounds, much less feasible if not impossible. Consequently, the MI spectra of **2**/Fe$^+$ and **6**/Fe$^+$ should be similar and distinct from the spectrum of **3**/Fe$^+$. However, this is not born out experimentally (see Table 1), and we conclude that none of the reactions depicted in Scheme 12 play a dominant role.

Table 6 summarizes the data for the CO losses from the isotopologues of **2**/Fe$^+$ and **3**/Fe$^+$, calculated on the assumption that the intensity for the loss of ethene is constant (see above). As evidenced by the ^{18}O-labeled complexes **2a**/Fe$^+$ and **3a**/Fe$^+$, the higher intensity of the combined ethene/carbon monoxide losses from the unlabeled **3**/Fe$^+$ is due to an increase of decarbonylation for the *trans* compound as compared to the *cis* isomer **2**/Fe$^+$. This change in the product distribution can be rationalized in terms of a *stereoselective* formation of the allyl complexes *cis*-**17**/Fe$^+$ (from **2**/Fe$^+$) and *trans*-**17**/Fe$^+$ from **3**/Fe$^+$ (Scheme 13). According to the DePuy rule,[37] we suggest that stereoselective ring opening of the *cis* precursor **2**/Fe$^+$ will lead to a stereochemically congested *cis*-allyl complex *cis*-**17**/Fe$^+$; in contrast, starting from **3**/Fe$^+$ one obtains in an energetically less demanding process the complex *trans*-**17**/Fe$^+$. As a consequence, decarbonylation of **3**/Fe$^+$ is expected to be favored as compared to **2**/Fe$^+$, which is indeed observed experimentally.

Moreover, Table 6 reveals that the differences in the CO loss intensities are not confined to the stereoisomeric pair of unlabeled complexes **2**/Fe$^+$ and **3**/Fe$^+$. Upon deuteration kinetic isotope effects are found to be operative, which also points to distinct differences between the *cis* and *trans* isomers. While

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(34) (a) Roberts, R. M.; Landolt, R. G. *J. Am. Chem. Soc.* **1965**, *87*, 2281. (b) Roberts, R. M.; Landolt, R. G.; Greene, R. N.; Heyer, E. W. *J. Am. Chem. Soc.* **1967**, *89*, 1404.

(35) Schröder, D.; Fiedler, A.; Hrušák, J.; Schwarz, H. *J. Am. Chem. Soc.* **1992**, *114*, 1215.

(36) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.

(37) DePuy, C. H. *Acc. Chem. Res.* **1968**, *1*, 33.

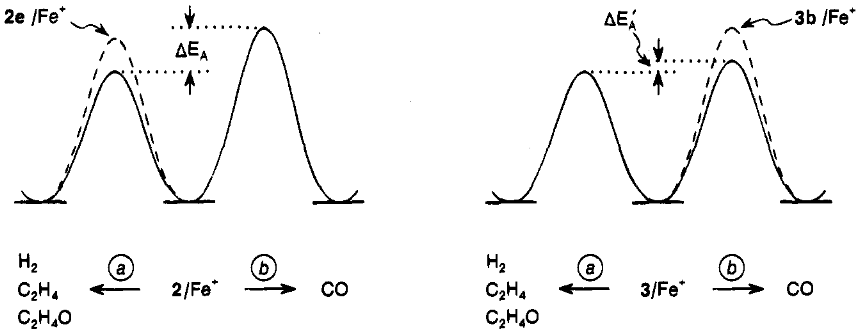

Figure 1. Schematic potential energy diagram for the competing reaction channels a and b for the *cis* and *trans* isomers **2**/Fe$^+$ and **3**/Fe$^+$, respectively. Note that the presentation is only qualitative and is exaggerated for the sake of clarity.

the *cis* isotopologues **2c**/Fe$^+$ and, in particular, **2e**/Fe$^+$ show enlarged intensities of carbon monoxide formation, the *trans* isotopologue **3b**/Fe$^+$ exhibits a drastic decrease and the complexes **3c**/Fe$^+$–**3e**/Fe$^+$ a slight decrease for the CO loss channel. This observation supports the proposal that at least two reaction channels compete with each other. A kinetic isotope effect, which affects one of these channels, leads to a retardation of this pathway and brings about a simultaneous increase of the other. Figure 1 illustrates this idea schematically: Stereounspecific ring cleavage (channel a) followed by hydrogen, ethene, and acetaldehyde formation results in the loss of stereochemical information. Thus, we may assume that the activation barriers associated with channel a are similar for **2**/Fe$^+$ and **3**/Fe$^+$. On the other hand, the increase of the CO loss from **3**/Fe$^+$ as compared to **2**/Fe$^+$ indicates a higher activation barrier associated with decarbonylation of the latter complex (channel b; Figure 1, left diagram), and this difference can be rationalized by the formation of *cis*- and *trans*-**17**/Fe$^+$, respectively. As a consequence, the difference in the activation barriers associated with channels a and b is larger for the *cis* isomer **2**/Fe$^+$ (ΔE_A) than for the *trans* isomer **3**/Fe$^+$ ($\Delta E_A'$). Hence, since both pathways are in direct competition, decarbonylation is more abundant for **3**/Fe$^+$. Moreover, this scenario accounts for the H/D kinetic isotope effects associted with decarbonylation that are observed in the experiment, in particular for **2e**/Fe$^+$ and **3b**/Fe$^+$: A primary deuterium isotope effect on dehydrogenation and ethene formation from **2e**/Fe$^+$ increases the activation barrier associated with channel a; consequently, ΔE_A is reduced and channel b gains in importance as compared to unlabeled **2**/Fe$^+$. In contrast, the α,α,α-d_3 labeled complex **3b**/Fe$^+$ gives rise to a secondary deuterium kinetic isotope effect for methyl migration en route to **17**/Fe$^+$ which increases $\Delta E_A'$ and thus decreases the decarbonylation channel b in favor of channel a. According to this scenario, the sum of the intensities of H_2 and HD losses from **2e**/Fe$^+$ is expected to be lower than the intensity of the H_2 loss from **2**/Fe$^+$. Likewise, the secondary isotope effect being operative for **3b**/Fe$^+$ should favor dehydrogenation. This is indeed observed in the experiment (Tables 4 and 5), pointing to another example for the existence of isotopically sensitive branching[5b,c] in gas-phase organometallic chemistry. As far as the other isotopologues are concerned, similar arguments are applicable; however, the isotope effects on the branching ratios of channels a and b vanish with decreasing deuterium incorporation. Finally, the finding that the α,α,α-d_3 labeled *cis* complex **2b**/Fe$^+$ does not exhibit a secondary deuterium isotope effect for the CO loss indicates that the rate-determining step associated with decarbonylation of **2**/Fe$^+$ differs from that for **3**/Fe$^+$, which is also in line with the proposed mechanism involving the sterically congested *cis*-allyl complex for **2**/Fe$^+$ (Scheme 13).

Conclusions

The *cis*- and *trans*-1-acetyl-2-methylcyclopropanes (**2** and **3**, respectively) represent interesting systems for probing subtle details of the concept of Fe$^+$-mediated remote functionalization of CH/CC bonds in hydrocarbon derivatives. Direct dehydrogenation of the intact three-membered-ring systems is not operative; rather, ring cleavages occur, resulting in the loss of the stereochemical differences between **2**/Fe$^+$ and **3**/Fe$^+$. After formation of acyclic isomers remote functionalization is again the dominant reaction channel. In contrast, decarbonylation of **2**/Fe$^+$ and **3**/Fe$^+$ exhibits a distinct stereochemical effect favoring CO loss from the *trans* complex **3**/Fe$^+$.

The detailed analysis of the isotopic fragmentation pattern of the isotopologues not only reveals the competition of ring cleavage and decarbonylation but also points to the operation of kinetic isotope effects which affect the intensity distribution in terms of isotopically sensitive branching.

Although the Fe$^+$ complexes of **2** and **3** do not seem to be too complicated systems, their unimolecular chemistry follows quite complex reaction mechanisms. Insight would not have been gained without application of extensive deuterium and ^{18}O labeling techniques, and even the present set of isotopologues is not sufficient for a complete quantitative analysis of isotope and steric effects. Therefore, the results described here may also serve as a warning toward inferring mechanisms based on the investigation of unlabeled compounds only.

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