Ligand-Induced Selectivity Switch: The Gas-Phase Reactions of "Bare" and Ligated Iron(I) and Cobalt(I) Cations with *n*-Propyltrimethylsilane

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The unimolecular and bimolecular gas-phase reactivities of the model compound *n*-propyltrimethylsilane with "naked" transition-metal ions Fe^+ and Co^+ versus the one of the ligated complexes $Fe(L)^+$ and $Co(L)^+$ (L = HCN, CD_3CN, $(CD_3)_2CO$) have been investigated by tandem and Fourier transform ion cyclotron resonance mass spectrometry. The present study focuses on the changes in product selectivity upon coordination of the metal center to a spectator ligand L which serves to moderate the intrinsic reactivity of the metal. The bare metal cations Fe^+ and Co^+ suffer from a lack of selectivity, and C−H, C−C, and C−Si bond-activation processes compete with each other in the reactions of Fe^+ and Co^+ with *n*-propyltrimethylsilane. In marked contrast, the gas-phase chemistry of the ligated complexes of the two metal ions differs significantly in that $Fe(L)^+$ predominantly activates C−H and C−C bonds while $Co(L)^+$ favors C−H and C−Si bond activation.

Introduction

For now almost two decades, transition-metal mediated activation of C−H and C−C bonds of hydrocarbons has generated extensive research activity. The chemical inertness of alkanes that is due to their small polarizabilities, strong C−H and C−C bonds, and the absence of energetically low-lying unoccupied orbitals demands the use of highly reactive reagents. However, any reagent capable of activating alkanes is expected to activate almost any bond in a functionalized substrate. Hence, small selectivities are predictable and methodologies aimed at a more selective bond activation in "inert" organic molecules are of fundamental interest in several areas of contemporary chemistry.[1]

A promising approach to uncover the mechanistic details of bond activation by transition metals is provided by gas-phase experiments which probe reactions of mass-selected "naked" or partially ligated transition-metal ions.[2] Thus, mass spectrometers can serve as "chemical laboratories"[3] in which a particular reaction can be studied under well-defined conditions, without being obscured by counterions, solvents, aggregation, and other interfering effects.[4]

In the course of these studies, it was discovered that monofunctionalized alkanes, such as nitriles, react with bare transition-metal cations in a regioselective activation of C−H and C−C bonds far away from the functional group.[5] In analogy to Breslow's terminology,[6] these processes have been referred to as gas-phase examples of *remote functionalization*. Briefly, remote functionalization involves an initial coordination of the bare or ligated transition-metal cation to the functional group ("docking"). Due to internal solvation, the metal is then directed toward a particular region of the aliphatic backbone of the substrate in which bond activation occurs.[5,7] The selectivity of the metal-mediated bond-activation processes depends on the electronic structure of the transition metal,[5,8] the nature of the functional group,[5] the presence of additional ligands,[9] and the conformational flexibility as well as the presence of stereogenic centers in the backbone of the aliphatic chain.[10]

Multiply functionalized alkanes appear as promising model systems in order to achieve high selectivities in remote functionalization in the gas phase.[11] Due to multidentate coordination of the metal ion, an enhanced selectivity toward a particular bond activation channel

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[8] (a) Eller, K.; Zummack, W.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 803. (b) Eller, K.; Karrass, S.; Schwarz, H. *Ber. Bunsen-Ges. Phys. Chem.* **1990**, *94*, 1201. (c) Eller, K.; Karrass, S.; Schwarz, H. *Organometallics* **1992**, *11*, 1637. (d) For a complete transition-metal ion screening, see: Eller, K.; Schwarz, H. *Chem. Ber.* **1990**, *123*, 201.

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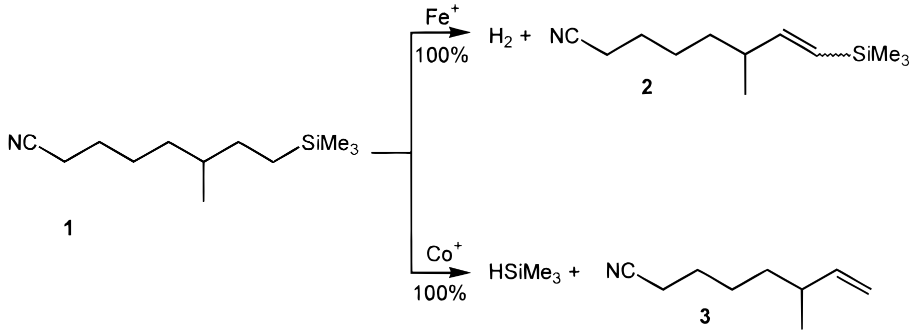
Scheme 1



can be expected. A most prominent example, which has also stimulated the present study, concerns the gas-phase reactivity of 6-methyl-8-trimethylsilyl-octanenitrile (**1**) with Fe^+ and Co^+ ions (Scheme 1).[10c] Two central aspects of this particular system shall be recalled: (i) The very interplay of the silyl and nitrile functional groups not only suppresses any side reactions but also induces some site-specificity in the bond-activation processes. (ii) The product selectivity is strictly controlled by the nature of the metal ion, i.e., reaction of **1** with bare Fe^+ leads to elimination of molecular hydrogen and formation of the Fe^+ complex of **2** whereas atomic Co^+ reacts via sole formation of neutral trimethylsilane and **3**$-Co^+$.[10c] Quite clearly, substrate **1** is unfortunately much too big for an adequate theoretical investigation aimed at understanding the interplay of the functional groups in the reactions of **1** with Fe^+ and Co^+. Therefore, the experimental study of smaller systems is indicated that contain the functional groups present in **1**, i.e., a CN and a $SiMe_3$ group.

In the present study, we have chosen the reactions of bare and ligated M^+ and $M(L)^+$ ions (M = Fe, Co) with *n*-propyltrimethylsilane **4** as the model system for the following reasons: (i) The role of a CN moiety in the Fe^+- and Co^+-mediated bond-activation processes of nitriles has already been elucidated in some detail by experimental[5] as well as theoretical means.[12] (ii) On the other hand, little work has been done concerning the effect of a silyl group toward the selectivity of transition-metal-mediated bond-activation processes.[10c,13] (iii) Finally, in the reactions of 6-methyl-8-trimethylsilyl-octanenitrile (**1**) with bare Fe^+ and Co^+, it has been shown by labeling experiments that only C−H bonds of the C(α) and C(β) positions (relative to the silyl group) are activated. Thus, the reaction of **4** with acetonitrile complexes of Fe^+ and Co^+ mimics the presence of these reactive sites and may still be "small" enough for forthcoming theoretical treatments at an adequate level of theory.

Table 1. Mass Differences (in amu) Observed in the Unimolecular Fragmentations of Isotopologous 4−M$^+$ Complexes[a,b]

	Δ*m*											
precursor	2	3	16	28	30	42	43	44	74	75	88	90
4$-Fe^+$	4		1	1		1		1	8		84	
4a$-Fe^+$	4	2	1	1	4			2	5		43	38
4b$-Fe^+$	3	1	1		1		1		1	2	90	
4$-Co^+$	45					28			25		2	
4a$-Co^+$	40	2						26	29		3	
4b$-Co^+$	4	39					24	2	2	27	2	

[a] Intensities are normalized to $\sum_{\text{reactions}} = 100\%$. [b] Reactions with intensities <1% are omitted.

For the ligated systems, we have used hydrogen cyanide, acetonitrile, and acetone as representative ligands (L) on the following grounds: (i) HCN and CH_3CN are the smallest nitriles that can be used to uncover the specific role of a cyano ligand in the cooperative interaction of a nitrile functionality and a trimethylsilyl group in the Fe^+- and Co^+-mediated bond activation of **1** (Scheme 1). Thus, the study of bis-ligated complexes of M^+ which contain silyl and cyano functionalities in separated ligands, e.g., **4**$-M(RCN)^+$ (M = Fe, Co; R = H, CH_3) may help to understand the chemistry of **1**$-M^+$, in which the two functional groups share a common hydrocarbon backbone. (ii) The comparison between the acetonitrile and acetone ligands has been included because both ligands have similar binding energies to Fe^+ and Co^+, respectively (Table 2). In a number of earlier studies on ligand effects, some correlations between the binding energy of the metal and the reactivity have been proposed.[9] Thus, the comparison of $M(CH_3CN)^+$ and $M(C_3H_6O)^+$ may elucidate as to whether in isoenergetic systems structural effects also matter in the bond activation.[14]

Experimental Section

Most experiments were performed with a modified VG ZAB/HF/AMD 604 four-sector mass spectrometer of BEBE config-

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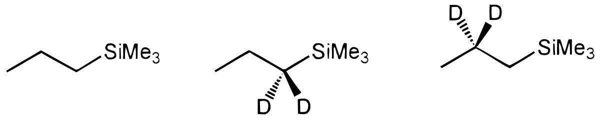
Table 2. Bond Dissociation Energies (BDE) of Metal−Ligand Complexes

M^+	ligand	BDE (kcal/mol)	ref
Fe^+	HCN	37.0 ± 0.8	23
	CH_3CN	41.3 ± 0.7	9e
	$C_3D_6O^a$	41.4 ± 0.7	9e
Co^+	HCN	45.4 ± 0.2	23
	CH_3CN	49.0 ± 1.5	23
	C_3H_6O	49.2 ± 1.4	23

[a] C_3D_6O was used instead of C_3H_6O in order to avoid isobaric interferences.

Chart 1



4 4a 4b

uration (B stands for magnetic and E for electric sectors), which has been previously described.[15] Briefly, the metal complexes were generated in a chemical ionization source (CI, repeller voltage ca. 0 V) by 100 eV electron bombardment of an approximately 5:1 mixture of the organic substrate of interest and $Fe(CO)_5$ or $Co(CO)_3(NO)$, respectively. The ions were accelerated to 8 keV of kinetic energy and mass-selected by means of B(1)/E(1) at a resolution of $m/\Delta m = 4000-5000$ to provide separation of isobaric ions. Unimolecular fragmentations of metastable ions (MI) occurring in the field-free region preceding B(2) were recorded by scanning this sector. All spectra were accumulated and on-line processed with the AMD-Intectra data system; 10−20 scans were averaged in order to improve the signal-to-noise-ratio.

Additional experiments were performed using a Spectrospin-CMS-47X Fourier transform ion cyclotron resonance mass spectrometer; the instrument and its operational details have been described elsewhere.[16] Fe^+ and Co^+ ions were generated by laser desorption/laser ionization in the external ion source by focusing the beam of a Nd:YAG laser (Spectron Systems; $\lambda_{max} = 1064$ nm) onto an appropriate metal target. Subsequently, the ions were extracted from the external ion source via a system of electrostatic potentials and lenses and transferred into the cylindrical analyzer cell, which is located in the field of a superconducting magnet (maximum field strength = 7.05 T). Then, the elements' most abundant isotopes were isolated using FERETS,[17] a computer-controlled ion ejection protocol which combines frequency sweeps and single-frequency pulses to optimize ejection of all undesired ions by resonant excitation. Prior to the examination of ion/molecule reactions, the metal ions were thermalized by allowing them to collide repeatedly with pulsed-in argon (maximum pressure = ca. 5×10^{-5} mbar, ca. 200 collisions per ion). All metal−ligand complexes $M(L)^+$ (M = Fe, Co; L = HCN, CD_3CN, CD_3COCD_3) investigated in this study were generated via consecutive ligand-exchange reactions of the corresponding neutrals with $M(C_2H_4)^+$. This complex was obtained by reacting the metal ion with propane. The reagents used for the generation of $M(L)^+$ were introduced via pulsed valves. For subsequent ion−molecule reactions, the $M(L)^+$ complexes were mass selected and thermalized as described above. Reactants were admitted to the cell via a leak valve at stationary pressures in the order of 1×10^{-8} mbar, as measured by a calibrated ion gauge (BALZERS IMG070). Branching ratios were calculated from the initial slopes of the primary product ion intensities and are reported with an estimated error of ±10%. Rate constants were determined from the pseudo-first-order decay of the reactant ions and are given as relative rate constants (k_{rel}), using the reactivity of the corresponding bare metal ion as a reference. Ion thermalization was monitored by the reproducibility of the reaction kinetics as well as the strict first-order behavior of the reactant ion decay. If necessary reaction products were identified using high-resolution mass spectra ($m/\Delta m > 100\,000$) in order to ensure the assigned elemental compositions of the product ions. All functions of the FTICR mass spectrometer were controlled by a Bruker ASPECT 3000 minicomputer.

Both unlabeled and labeled *n*-propyltrimethylsilanes were synthesized by standard laboratory procedures, i.e., reactions of (labeled) Grignard reagents with chlorotrimethylsilane or via copper-mediated cross couplings[18] with chloromethyltrimethylsilane. The Grignard reagents were obtained from alkyl bromides, which were made from the corresponding acids by reduction with lithium aluminum hydride (or deuteride) and subsequent, in situ reaction with aqueous HBr (48%). The final products were purified by distillation and preparative gas chromatography. The purity of the products as well as the location and degree of deuterium incorporation were confirmed by ^1H NMR and mass spectrometry. Gaseous hydrogen cyanide was generated on-line by mild heating of a 1:1 mixture of sodium cyanide and lauric acid. Acetonitrile, acetonitrile-d_3 (Aldrich Chemicals), and acetone-d_6 (Merck AG) were used as supplied.

Results and Discussion

Let us first address the unimolecular reactivity of the bare metal ions Fe^+ and Co^+ with *n*-propyltrimethylsilane (**4**) in order to elucidate the reaction mechanisms with the aid of isotopic labeling data. Next, we will discuss how precoordination of a ligand to the metal center affects the bimolecular reactivity under FTICR conditions. Finally, the effect of an acetonitrile ligand upon the reaction mechanisms will be discussed in depth based on the unimolecular fragmentation data combined with isotopic labeling.

Reactivity of Bare Fe^+ and Co^+ with *n*-Propyltrimethylsilane. The unimolecular fragmentation of metastable **4**−Fe^+ proceeds with moderate product selectivity, giving rise to loss of neutral tetramethylsilane ($\Delta m = 88$) as the major channel along with minor pathways leading to the elimination of molecular hydrogen, methane, ethene, propene, propane, and trimethylsilane (Table 1). Isotopic labeling reveals that the neutral tetramethylsilane is formed via two competing routes (Scheme 2). The reaction sequence commences either with an insertion of the metal into the C−Si bond (**4** → **5**) followed by β-methyl migration[19] (path a) or by an oxidative addition to the C(1)−C(2) bond and subsequent β-hydrogen transfer (path b); note that we do not specify whether further insertion intermediates are formed en route to the products[12] and rather focus on the initial site of bond activation. The mechanistic proposal depicted in Scheme 2 is in com-

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(14) Throughout the paper we denote acetone and acetone-d_6 by the formulas C_3H_6O and C_3D_6O, respectively; for the discussion of the complexity of possible $[M, C_3, H_6, O]^+$ isomers with M = Fe^+, see: Schwarz, J.; Wesendrup, R.; Schröder, D.; Schwarz, H. *Chem. Ber.* **1996**, *129*, 1463.

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(16) (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.

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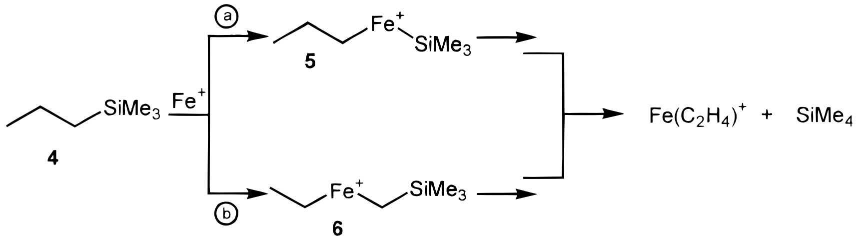
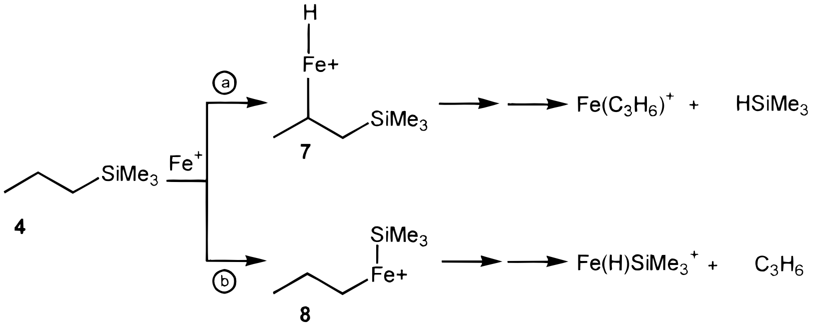
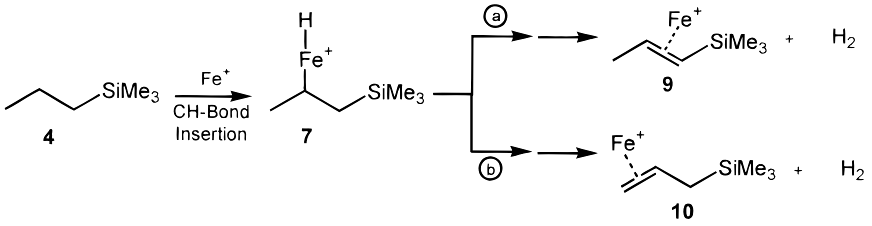
Scheme 2



Scheme 3



Scheme 4



plete accord with the experimental results. Metastable **4a**$-$Fe$^+$ undergoes unimolecular losses of CH_3SiMe_3 ($\Delta m = 88$) and CHD_2SiMe_3 ($\Delta m = 90$) in almost equal abundances, while from **4b**$-$Fe$^+$ unlabeled CH_3SiMe_3 ($\Delta m = 88$) is formed exclusively. Both routes, however, lead to the formation of $Fe(C_2H_4)^+$ as the ionic product and the elimination of neutral tetramethylsilane, suggesting that the bond dissociation energy (BDE) of $Fe^+-C_2H_4 = 34.5$ kcal/mol[20] exceeds the BDE of Fe^+-SiMe_4. The formation of neutral trimethylsilane ($\Delta m = 74$) can be explained in terms of an insertion into a C$-$H bond at C(2) (**4** → **7**) followed by β-SiMe$_3$ transfer (Scheme 3, path a) or by a primary C$-$Si bond activation completed by a β-H shift (path b). However, in addition to the expected loss of $DSiMe_3$ ($\Delta m = 75$) from metastable **4b**$-$Fe$^+$, a weak signal due to loss of neutral $HSiMe_3$ ($\Delta m = 74$) is also observed, suggesting the occurrence of some H/D exchange prior to dissociation. Similarly, dehydrogenation of the n-propyl side chain (Scheme 4)[21] exhibits only moderate selectivity because both H_2 ($\Delta m = 2$) and HD ($\Delta m = 3$) are lost from **4a**$-$Fe$^+$ as well as **4b**$-$Fe$^+$. We assume that only the n-propyl moiety of the substrate is activated; the methyl groups of the silyl functionality remain inert. This assumption is based on two experimental findings: (i) While dehydrogenation is prominent in the unimolecular fragmentation of $Fe(n\text{-}C_7H_{15}Si(CD_3)_3)^+$, no evidence for the occurrence of C$-$D bond activation of the methyl group was observed for the metastable ions.[13b] (ii) Unimolecular dehydrogenation of the complex $Fe(C_2D_5SiMe_3)^+$ exclusively involves loss of D_2 from the ethyl moiety.

The unimolecular chemistry of **1**$-$Co$^+$ differs in several respects compared to that of Fe$^+$ (Table 1). Thus, instead of the dominant loss of tetramethylsilane in the MI spectra of **4**$-$Fe$^+$, dehydrogenation and the competitive formations of trimethylsilane and propene dominate the unimolecular decomposition of **4**$-$Co$^+$. Further, these bond activations occur with quite some specificity, because the labeling experiments clearly demonstrate that H/D equilibration preceding fragmentation is much less pronounced. For example, dehydrogenation largely involves the C$-$H bonds at the C(2)/C(3) position as evidenced by the preferential loss of H_2 ($\Delta m = 2$) from **4a**$-$Co$^+$ and of HD ($\Delta m = 3$) from **4b**$-$Co$^+$. Loss of trimethylsilane preferentially involves (as indicated in Scheme 3 for the Fe$^+$ complex) a C$-$H bond at C(2), i.e., exclusive loss of Me_3SiH ($\Delta m = 74$) from **4a**$-$Co$^+$ and preferred elimination of Me_3SiD ($\Delta m = 75$) from **4b**$-$Co$^+$. Similarly, propene formation proceeds in a highly specific way, i.e., exclusive elimination of $\Delta m = 44$ from **4a** and preferred loss of $\Delta m = 43$ from **4b**.

Common, however, to the reactivity of the two "naked"

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(19) For other examples for genuine β-methyl shifts are dicussed, see: (a) Houriet, R.; Halle, L. F.; Beauchamp, J. L. *Organometallics* **1983**, *2*, 1818. (b) Karrass, S.; Schwarz, H. *Organometallics* **1990**, *9*, 2409. (c) Schalley, C. A.; Wesendrup, R.; Schröder, D.; Schroeter, K.; Schwarz, H. *J. Am. Chem. Soc.* **1995**, *117*, 12235.

(20) Armentrout, P. B.; Kickel, B. L. In *Organometallic Ion Chemistry*; Freiser, B. S., Ed.; Kluwer: Dordrecht, 1996; p 1.

(21) For the sake of clarity, only one oxidative insertion intermediate is shown; of course, the reaction can also commence with insertion of the metal ion into a C$-$H bond at C(1) or C(3). On the basis of the present data no distinction can be made between these possibilities.

Table 3. Neutral Reaction Products Generated in the Ion−Molecule Reactions of M^+ and $M(L)^+$ and *n*-Propyltrimethylsilane, 4, As Obtained with ICR[a]

products	Fe^+	$Fe(HCN)^+$	$Fe(CD_3CN)^+$	$Fe(C_3D_6O)^+$	Co^+	$Co(HCN)^+$	$Co(CD_3CN)^+$	$Co(C_3D_6O)^+$
H_2	4	10	25	40				
CH_4		35	55	30				5
C_2H_4	4							
C_3H_6					27			
$HSiMe_3$	20				57	45	100	95
$SiMe_4$	72	15	20	30	16			
HCN[b]		40				55		
k_{rel}[c]	1	0.5	0.5	0.4	1	0.2	0.4	0.5

[a] Intensities are normalized to $\sum_{reactions} = 100\%$; reactions with intensities <1% are omitted. [b] This entry corresponds to the formation of **4**−M^+ due to ligand-exchange reactions. [c] Relative rate constants defined as $k_{rel} = k(M(L)^+)/k(M^+)$.

Table 4. Mass Differences (in amu) Observed in the Unimolecular Fragmentations of Isotopologous 4−$M(L)^+$ Complexes[a]

	Δm														
precursor	2	3	16	17	28	30	41	42	43	44	74	75	88	90	118[b]
4−$Fe(CH_3CN)^+$	29		54		4		2			2			8		1
4−$Fe(CD_3CN)^+$	24		54		5					8			8		1
4a−$Fe(CD_3CN)^+$	5	18		58	3					3	1		1	10	1
4b−$Fe(CD_3CN)^+$		15	60			4			2	5	2	1	8		1
4−$Co(CH_3CN)^+$	6		9		4		4	8			54				15
4−$Co(CD_3CN)^+$	6		12		1			9		2	55				15
4a−$Co(CD_3CN)^+$		3		6						11	62		1		17
4b−$Co(CD_3CN)^+$		2	8						8	2		58	1		21

[a] Intensities are normalized to $\sum_{reactions} = 100\%$; reactions with intensities <1% are omitted. [b] This entry correspond to loss of the silane ligand **4**.

metal cations Fe^+ and Co^+ with *n*-propyltrimethylsilane (**4**) is the large manifold of products which result from activation of C−H, C−C, and C−Si bonds within the *n*-propyl side chain.

Reactivity of $Fe(L)^+$ and $Co(L)^+$ with *n*-Propyltrimethylsilane. For the sake of brevity, we shall restrict this comparison to the bimolecular reactivity of the metal−ligand complexes $M(L)^+$ (M = Co, Fe; L = HCN, CD_3CN, $(CD_3)_2CO$) with **4** as studied with the FTICR instrument (Table 3). Under FTICR conditions, the generation of metal−ligand complexes by ligand-exchange reactions is straightforward and not obscured by isobaric interferences, a problem which in unfortunate cases hampers the study of mixed, bis-ligated metal ion complexes in the sector mass spectrometer.[22] The bimolecular reactions of **4** with Fe^+ obtained under FTICR conditions are, except for some minor differences in the intensity ratios, in good agreement with the results from the metastable ion decay discussed in the previous section. All three ligands L exert a similar influence upon the reactivity of $Fe(L)^+$ toward *n*-propyltrimethylsilane (**4**), as indicated by the drop in k_{rel}. In addition, as compared to the bare metal, C−H bond activation is much more pronounced, and in particular, C−C bond activation of the propyl side chain appears as a new reaction channel, which was hardly detected for the bare metal ions. This switch of the reactivity toward losses of H_2 and CH_4, respectively, occurs at the expense of C−Si bond activation of **4**. The differences among the different ligands are minor, but it is apparent that the hydrogen cyanide and acetonitrile ligands favor C−C bond activation leading to enhanced loss of neutral methane rather than dehydrogenation; the latter prevails for the acetone-ligated complex. In addition to these processes, exchange of the ligand by the silane **4** is observed for the hydrogen cyanide complex, indicating that BDE(**4**−Fe^+) ≥ BDE(Fe^+−NCH) = 37 kcal/mol. Similarly, we conclude that BDE(**4**−Co^+) ≥ BDE(Co−NCH^+) = 45.4 kcal/mol.[23]

Due to the fact that acetonitrile best mimics the binding situation encountered in the 6-methyl-8-trimethylsilyl-octanenitrile system **1**−M^+, in addition to the FTICR experiments, the unimolecular reactivity of **4**−$Fe(CX_3CN)^+$ and **4**−$Co(CX_3CN)^+$ (X = H, D) has also been analyzed in detail using isotopic-labeling data obtained with the four-sector mass spectrometer. The unimolecular fragmentations of isotopologous **4**−$Fe(CH_3CN)^+$ are quite instructive (Table 4). First, the acetonitrile ligand itself is not involved at all in the bond activation as demonstrated by the close similarity of the MI spectra of **4**−$Fe(CH_3CN)^+$ and **4**−$Fe(CD_3CN)^+$. The generation of neutral hydrogen can be described in analogy to the mechanisms depicted in Scheme 4 for a bare Fe^+. Note, however, that in contrast to **4**−Fe^+, no complete H/D scrambling is involved in the course of dehydrogenation; this is demonstrated by the exclusive loss of HD (Δm = 3) from **4b**−$Fe(CD_3CN)^+$ and its preferred formation from **4a**−$Fe(CD_3CN)^+$. The formation of methane, a process which is hardly observed in the reactions of the naked metal cation, gains importance and can be rationalized according to the mechanism illustrated in Scheme 5. This process is characterized by a high degree of selectivity, in that the neutral methane originates exclusively from the methyl moiety of the propyl chain and one hydrogen atom from C(1).

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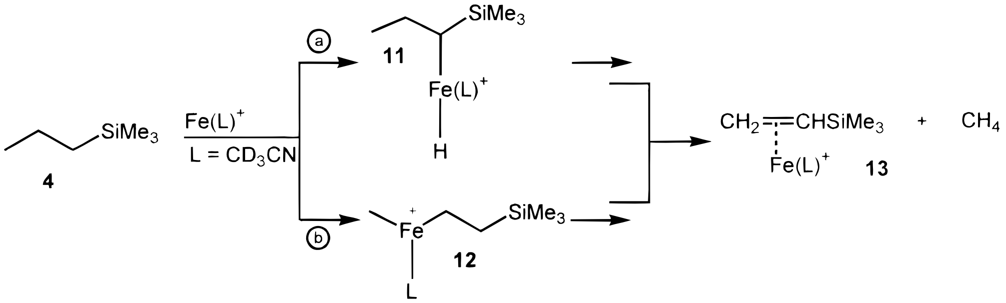
[22] In particular, the generation of weakly bound complexes, such as $M(HCN)(L)^+$, is often associated with isobaric interferences. To circumvent this problem high mass resolution is required with the consequence that the resulting low ion intensities make it impossible to acquire reproducible MI spectra.

[23] The metal−ligand bond dissociation energies reported in Table 2 have been determined by us according to the kinetic method of Cooks; for details, see: Cooks, R. J.; Patrick, J. S.; Kotiaho, T.; McLuckey, S. A. *Mass Spectrom. Rev.* **1994**, *13*, 287.

Scheme 5



The formation of neutral tetramethylsilane ($\Delta m = 88$) can be explained in terms of the same mechanistic picture as presented in Scheme 2 for the bare metal ion; however, in marked contrast to **4**$-$Fe$^+$, for the ligated system, only pathway b is involved. The almost exclusive formation of CHD_2SiMe_3 ($\Delta m = 90$) and CH_3SiMe_3 ($\Delta m = 88$) from **4a**$-$Fe(CD_3CN)$^+$ and **4b**$-$Fe(CD_3CN)$^+$, respectively, clearly indicates that Fe$^+$-induced formation of the double bond in position C(1)/C(2) is strongly favored by the presence of a CD_3CN ligand.

For the ligated Co$^+$ complexes, the interpretation of the results obtained in the tandem MS and FTICR experiments is not as straightforward as for the Fe$^+$ system. In particular, a comparison between the data obtained under unimolecular and bimolecular reaction conditions is rather difficult, especially because the metastable complexes **4**$-$Co$^+$ and **4**$-$Co(CH_3CN)$^+$ exhibit a much richer chemistry as compared to the ion$-$molecule complexes generated in the FTICR.[24] Nevertheless, some more general principles concerning the effect of ligation upon the reactivity of Co$^+$ cations with *n*-propyltrimethylsilane emerge from the FTICR data (Table 3). In analogy to Fe$^+$, all three ligands have a similar influence upon both the reactivity and chemoselectivity of Co$^+$ toward **4**. The hydrogen cyanide and the acetonitrile ligands lead both to the generation of neutral trimethylsilane as the only bond-activation product. For acetone, an additional weak signal due to formation of methane is observed. In comparison, the ion$-$molecule reactions of the "naked" Co$^+$ cation with **4** are much less product selective than those of the ligated Co(L)$^+$ complexes, but the behavior of the metastable bis-ligated complexes of the type **4**$-$Co(CX_3CN)$^+$ (X = H, D) is more subtle. For a more thorough mechanistic analysis, a closer look at the data of the unimolecular fragmentation of isotopologous **4**$-$Co(CX_3CN)$^+$ (X = H, D) is required (Table 4). The major reaction products, in good agreement with the FTICR results, observed in the unimolecular decay of the **4**$-$Co(CX_3CN)$^+$ complexes (X = H, D) are due to activation of the C$-$Si bond as depicted in Scheme 3 to yield $HSiMe_3$ or C_3H_6 as the complementary neutral product.[25] These findings are further supported by the MI data for the isotopologs in that only loss of $HSiMe_3$ ($\Delta m = 74$) is observed for **4a**$-$Co(CD_3CN)$^+$ while **4b**$-$Co(CD_3CN)$^+$ yields $DSiMe_3$ ($\Delta m = 75$). In addition, small amounts of molecular hydrogen and methane are formed; this is in marked contrast to the unimolecular reaction of bare Co$^+$ with *n*-propyltrimethylsilane for which the dominant fragmentation pathway was found to correspond to dehydrogenation. It is interesting to note that the labeling data reveal a high specificity for these two side reactions. Dehydrogenation occurs from C(1) and C(2), as evidenced by the exclusive elimination of HD from **4a**$-$Co(CD_3CN)$^+$ and **4b**$-$Co(CD_3CN)$^+$. Demethanation, as observed by the exclusive formation of CH_3D from **4a**$-$Co(CD_3CN)$^+$ and CH_4 from **4b**$-$Co(CD_3CN)$^+$, respectively, involves activation of the methyl moiety of the propyl chain and one hydrogen atom from C(1).

In the comparison of experimental results obtained with FTICR and sector mass spectrometry, respectively, the reader should keep in mind some general aspects: (i) In an FTICR experiment reaction, products arise from the bare M$^+$ ion; hence, signals due to ligand detachment, i.e., regeneration of the of M$^+$, cannot be detected. (ii) On the other hand, adduct formation cannot be monitored in the sector experiments as it is precisely the unimolecular decay of this complex which is investigated.[16] (iii) The amount of internal energy deposited in the rovibrationally excited encounter complex generated under bimolecular conditions in a FTICR can differ significantly from the one of metastable ions generated by chemical ionization.[9e] While the Fe$^+$ system (see above) as well as some previous studies[9] have demonstrated that metal ion's reactivities can exhibit close similarities under uni- and bimolecular conditions, the Co$^+$ system does not follow this pattern. Thus, while the bimolecular reactivity of Co(L)$^+$ with **4** shows an increase of selectivity, as compared to the bare metal ion, the unimolecular decay of the mixed **4**$-$Co(L)$^+$ complexes does not result in a change of selectivity except for the product distribution. This phenomenon may arise from the fundamental differences of the two experimental approaches, but for the time being, we attribute them to some limitations of chemical ionization to yield pure and internally cold ions of this type in the cobalt system.

Notwithstanding these restrictions, either approach permits one to draw some general conclusions about the influence of ligation upon the intrinsic reactivity of a transition-metal ion: (i) For both metal ions, Fe$^+$ and Co$^+$, the product selectivity is enhanced upon ligation. (ii) In addition, the ligands also seem to exert a considerable influence upon the reaction mechanisms that are operative. The ligated metal complexes, in general, give rise to neutral products in mechanistically more clean fashions, while the reactions of the bare metal cations with *n*-propyltrimethylsilane follow less

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[24] For a more detailed discussion concerning the differences between the two experimental approaches FTICR and tandem mass spectrometry, see ref 15.

[25] Note that for **4a**$-$Co(CD_3CN)$^+$ and **4b**$-$Co(CD_3CN)$^+$, the generation of propene-d_2 is obscured by the competitive loss of isobaric CD_3CN as evidenced by the loss of acetonitrile from **4**$-$Co(CH_3CN)$^+$.

specific pathways and are often associated with isotopic scrambling processes. In general, while the reactivity switch upon ligation is similar for the three different ligands L, the nature of the metal ion matters more. Ligation of Fe^+ strongly increases the amount of C−H and C−H bond activation at the expense of C−Si bond cleavage, and in the Co^+ system, the preferential C−Si bond activation is concentrated on the trimethylsilane channel for the ligated species. Despite these similarities, some specific effects of the ligands can also be deduced. Thus, the role of the acetonitrile ligand is closer to that of the lower homologue HCN than to the acetone ligand. Considering the similarity of the binding energies of acetonitrile and acetone to the metal ions under study, this result implies that other than energetic parameters are relevant for the outcome of the bond-activation processes; quite likely, the influence of the ligands upon the electronic structure of the metal center also affects the height of the activation barriers associated with the corresponding transition structures for bond activation.

Conclusions

The present study demonstrates that the interaction of two functional groups can substantially influence the product and site selectivity and the mechanism of the Fe^+- and Co^+-mediated activation for the model substrate *n*-propyltrimethylsilane. The naked metal cations react in quite an unselective fashion to generate a great variety of products due to activation of C−H, C−C, and C−Si bonds. In addition, several reactions are accompanied by isotope scrambling processes as uncovered by the labeling data. In contrast, the bis-ligated metal cations react more selectively, i.e., $Fe(L)^+$ favors generation of molecular hydrogen and methane whereas $Co(L)^+$ prefers to activate the C−Si bond to form trimethylsilane. The cooperative influence of the ligands on the reactivity of these two transition-metal cations with **4** nicely mimics the reactivity pattern of these metal ions with 6-methyl-8-trimethylsilyloctanenitrile (Scheme 1) in which the cyano and silyl moieties are attached to the same hydrocarbon backbone.

In conclusion, the interaction of the two separate ligands in **4**−$M(L)^+$ is such that the overall effects are comparable to the ones described in Scheme 1 for the much more complex system **1**−M^+ (M = Fe, Co). Consequently, we trust that the results described here will not only stimulate further experimental work on ligand effects but will also serve as a starting point for a theoretical description of metal-ion mediated bond activation of polyfunctionalized molecules.

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