# Organometallic Chemistry in the Gas Phase[‡]

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> 'Naked'—and in a postcript here he says 'Alone'. Can you advise me?
>
> *Hamlet*, Act 4, Scene 7

## I. Introduction

The gas-phase chemistry of organometallic systems is not only a very interesting field in its own right, but it has also undergone rapid progress over the last decade. Certainly part of the interest arises from the fact that now, more than ever, it is being realized that knowledge about the *intrinsic* properties of bare or

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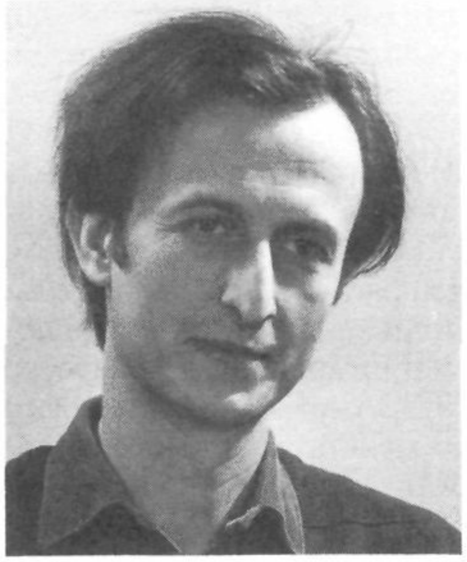

Helmut Schwarz was born in Nickenich (Rheinland-Pfalz) in 1943. He spent four years as a technician in chemical industry before studying chemistry at the Technische Universität Berlin (1966–1971). He received his Ph.D. with Professor Ferdinand Bohlman in 1972, and since 1978 he has been Professor of Chemistry at the TU Berlin. He received several awards, the most recent ones being the 1989 Otto Bayer Award for Chemistry and a Leibniz Research Award by the Deutsche Forschungsgemeinschaft. His research interests include gas-phase organometallic chemistry, mechanistic studies in organic mass spectrometry, computational chemistry, as well as peptide sequencing and the generation of elusive neutrals using MS techniques.

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[‡] Dedicated to Professor Dr. K.-H. Büchel, BAYER AG Leverkusen, on the occasion of his 60th birthday.

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ligated transition-metal ions, or the respective neutrals, can give valuable hints on mechanisms operative in the condensed phase and efficiencies of stoichiometric or catalytic processes in general. Especially the activation of C–H or C–C bonds in alkanes, processes that are not that easily achieved in homogeneous or heterogeneous catalysis,[1,2] is an important area of research. A better understanding of the crucial steps[3] and a complete characterization of possible intermediates[4] would be desirable in order to improve catalysts and to make use of the huge potential that lies in the (chemical) exploitation of natural gases and fuel feedstocks. No wonder that many of the first organometallic reactions studied in the gas phase were concerned with alkane functionalization. But even today, as the activation of numerous X–Y bonds in many model compounds is being studied, e.g., the cleavage of *nonactivated* C–H and/or C–C bonds in functionalized alkane derivatives *anchored* with their functional group to the metal center, there still is a major challenge as the details of these processes are not yet fully understood. Thus, interest in gas-phase organometallic chemistry is continuing, and the fascination about these mechanistic studies has not decreased at all.

Gas-phase studies are particularly well-suited for the elucidation of basic properties of isolated molecules and for probing elementary reactions under well-defined conditions since they are not hampered by the various disturbing factors that prevail in solution which include, e.g., associations by ion pairing, solvent-shell interactions, intra- and intermolecular processes which lead to destruction and/or modification of the catalytically active species (e.g. cyclometalation[5]). The advantages of gas-phase studies arise, of course, from the spatial dispersion of the organometallic species under the high-vacuum conditions employed. To maintain control over the particles of interest and to identify eventually formed reaction products, a charge on them is of great help, and for that reason most of the research has been performed with ionic compounds. This review will therefore be restricted to the gas-phase *ion* chemistry of transition-metal containing species while studies on neutrals[6] will be excluded. We will also exclude negatively charged particles from the discussion since a fairly recent, comprehensive review is available already,[7] and only a few additional papers have appeared in the meantime which deal with anion/molecule reactions.[8–28] The related field of gas-phase cluster chemistry, i.e., reactions of transition-metal clusters $M_x$[29,30] or cluster ions $M_x^+$,[30a,31–33] $M_xM'_y{}^+$,[34] or $M_xL_y^+$ [33x,z,35–40] (M, M′ = transition metal, L = ligand) with neutral substrates, will also be excluded, and only few references will be given where appropriate.

What will be described in great depth is the chemistry of bare ("naked") or ligated transition-metal ions with the ensemble of substrates that has arisen interest in the various groups active in this field. An earlier review on the topic is available,[41] but for the sake of better understanding, and since nowadays slightly modified views about several of the mechanisms proposed earlier have to be adapted, part of this material is included as well. Besides, several more specialized reviews exist which are concerned with the work of individual groups, namely those of Freiser,[42] Armentrout,[43] Beauchamp,[43b,44,45] Bowers,[45] Allison,[46] and ours.[47] In addition, a recent review focuses on MS/MS techniques for elucidation of metal ion/molecule reactions.[48] We refrain from a further compilation of all the thermochemical data, that has been determined so far, since this information can already be found tabulated in refs 41–45. In the present article, the literature is covered up to early 1991.

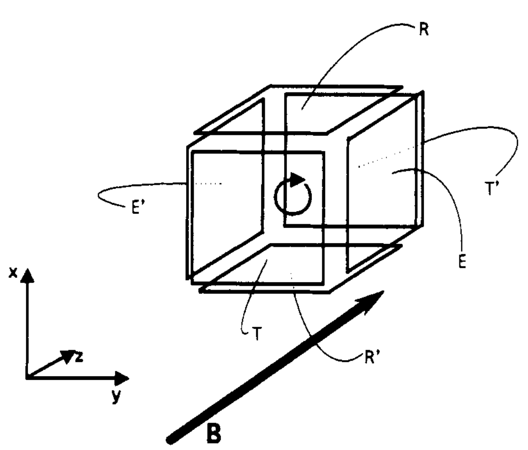


**Figure 1.** Schematic drawing of a cubic FTIR cell, located in a magnetic field of the strength *B* (1 – 7 T in modern instruments) in the positive *z* direction. T and T′ are the trapping, E and E′ the excitation, and R and R′ the receiver plates.

## II. Instrumentation

For the vast majority of the studies to be described, three different instrumental techniques have been employed, viz. ion/molecule reactions in ion cyclotron resonance spectrometers, ion-beam experiments in the appropriate apparatuses, and metastable or collision-induced decompositions of organometallic complexes in tandem mass spectrometers of the sector or quadrupole type.

Ion cyclotron resonance (ICR)[49] and in particular Fourier transform ion cyclotron resonance (FTICR)[50] mass spectrometers are ideally suited for the study of ion/molecule reactions, and the potential of ICR studies for gas-phase organometallic chemistry has been realized early.[51] The technique will be depicted only briefly for the modern FTICR instruments. Ions, generated by one of the many ionization methods, can be stored in crossed magnetic and electric fields, by using for example the cubic cell shown in Figure 1. The magnetic field restricts the ion motion to circular paths in the *xy* dimension while small potentials on the trapping plates T and T′ limit the *z*-axial motion. Transition-metal ions, stored in the FTICR cell, can undergo reactions with simultaneously present neutral compounds, and, after a variable reaction delay, products can be detected by the image current that is induced in the receiver plates R and R′. The angular, or cyclotron frequency, i.e., the frequency by which the ions are circling in the *xy* plane, is dependent on the mass-to-charge ratio, and the superposition of all frequencies is subjected to a Fourier transformation to obtain the mass spectrum. Double resonance techniques[52] allow the identification of the precursor ions that give rise to the individual reaction products, and therefore primary, secondary, tertiary, etc. reactions can be determined unambiguously. To obtain structural information, low-energy collisional activation (CA), or collision-in-

**Figure 2.** Schematic drawing of a guided ion-beam instrument, consisting of ion source (IS), acceleration (AS) and deceleration (DS) stage, magnetic sector (B), octopole ion guide (O), collision chamber (CC), quadrupole mass filter (Q), and detector (D).

duced dissociation (CID)[53] which is the more common term in the FTICR literature, can be brought about by accelerating a specific ion into a stationary target gas with subsequent detection of the resulting fragment ions. The kinetic energy is hereby enlarged by applying a pulse with the ion's cyclotron frequency to the excitation plates E and E′. Alternatively, shining light onto stored ions may result in photodissociation which gives a characteristic PD spectrum as well as an upper limit for bond dissociation energies.[54] The most convenient way to generate transition-metal ions is by laser desorption/ionization (LD/I) from a pure metal target; this not only affords abundant metal ion currents but also ideally matches the pulsed nature of the FTICR experiment.[55]

Ion-beam experiments are performed in guided ion-beam mass spectrometers designed to measure the energy dependencies of reactions of mass selected ions with stationary target gases at ambient temperature. Application of the technique to organometallic chemistry has been pioneered by Armentrout and Beauchamp. Early studies employed a simple instrument which, basically, consisted of an ionization source, energy selection device, collision chamber, and a quadrupole mass filter with detector.[56-59] All ions that were provided by the surface-ionization source were accelerated to a defined energy and collided in the chamber with the reagent gases, and reaction products were determined with the quadrupole. Shortly after, improvement was gained by the introduction of a magnetic sector for mass selection of the primary ions which were decelerated after the magnet before entering the collision chamber.[60,61] The method has been brought to near perfection by Armentrout, mainly by the use of an octopole ion guide, which provided efficient product collection and precise energy determinations, and by the use of drift cells for collisional relaxation of excited states in the primary ion beam.[62,63] A schematic representation of such an ion-beam instrument is given in Figure 2; a detailed description of one of the latest versions used in the Armentrout group may be found in ref 64a and the technique is reviewed in ref 64b.

Similar to the ion-beam instruments is the use of triple-quadrupole mass spectrometers for ion/molecule reactions, where $Q_1$ is used for selection of e.g. a metal ion, $Q_2$ is operated in the "RF only" mode and filled with the neutral reagent gas while $Q_3$ is used for product ion identification.[65]

Metastable or collision-induced decompositions represent the third major variant in gas-phase organometallic studies; the first application was by Freas and Ridge in 1980. Multisector instruments have been employed, although in principle every kind of tandem mass spectrometer[66,67] could be used. The major difference to the other techniques is that organometallic *complexes* are studied, whose decomposition pathways are investigated. These complexes are formed in the ion source of the instrument, and most conveniently, a high-pressure chemical ionization (CI) source is employed in which a ca. 1:5 mixture of an appropriately volatile organometallic compound (e.g. $Fe(CO)_5$ or $Co(CO)_3NO$) and the substrate is ionized with 100-eV electrons. Various ion/molecule reactions inside the source may give rise to 1:1 complexes of the metal ion with the substrate. Alternatively, such complexes can also be generated by the "FAB method",[68] where a target of an inorganic salt is bombarded with fast Xe atoms, and liberated metal ions and/or clusters react with the simultaneously present substrate. Complexes formed by either ionization method are then extracted from the source and mass selected with a magnetic or an electric sector. In a field-free region of the instrument their unimolecular decompositions (metastable ions, MI[69]) or high-energy collision-induced dissociations (CID or CA, collisional activation[70]) are studied by scanning of a further sector. Multisector instruments such as the one schematically given in Figure 3 also allow structural characterization of unimolecularly generated daughter ions by further collisional activation in a collision cell in front of a final sector. To achieve high parent ion resolution, the complex is usually selected in a double-focusing mode employing the first two sectors (MS I + II), while products are detected by scanning of MS III.

**Figure 3.** Schematic drawing of a multisector mass spectrometer, consisting of an ion source (IS), three sectors (MS I–III), which can be either magnetic or electrostatic analysers, several collision cells (CC), and a detector (D).

It is not self-evident that, e.g., ion/molecule reactions of bare transition-metal ions $M^+$ with a neutral substrate S is an FTICR instrument and metastable-ion studies on $M(S)^+$ adduct complexes yield similar results, but comparisons have shown that if several restrictions are kept in mind, agreement in product distribution is fair, and good, if not excellent, agreement is found for label distributions of individual reactions.[71-75] Similar comparisons have been drawn between low-energy ion-beam investigations and MI and CID spectra of transition-metal ion/alkane complexes.[76]

## *III. Reactions of Bare Metal Ions with Diatomics and Triatomics*

### A. Dihydrogen

Probably the simplest reaction involving transition-metal ions is the one given in eq 1. In view of its

$$M^+ + H_2 \rightarrow MH^+ + H \qquad (1)$$

fundamental nature, this reaction has been studied most carefully with ion-beam instruments by reacting different metal ions of a well-defined energy with $H_2$ and its isotopomers HD and $D_2$. The absolute reaction cross section, $\sigma(E_T)$, is studied as a function of the metal ion's kinetic energy, and one obtains curves such as the one given in Figure 4. To account for kinetic energy distributions of the reactants, this experimental curve is fitted to a parameterized equation in order to obtain the true threshold of the reaction, from this the bond dissociation energy $D°(M^+–H)$ can be calculated. Data is now available for the complete first row of the d-

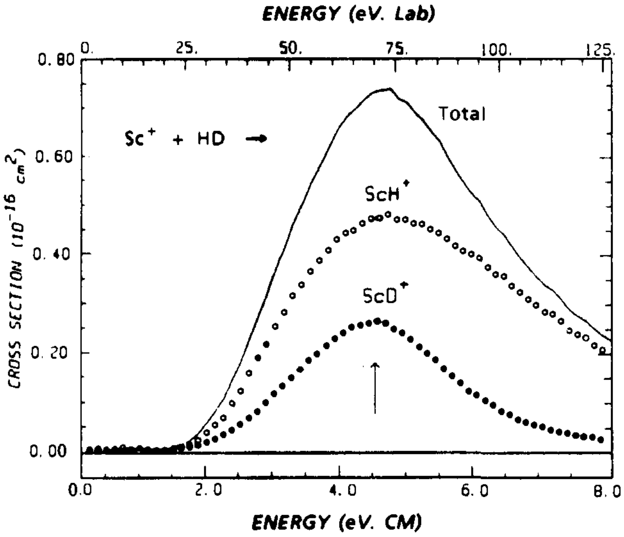


**Figure 4.** Cross sections for the reaction of Sc$^+$ with HD as a function of kinetic energy in the center of mass frame (lower scale) and laboratory frame (upper scale). Open and closed circles show the results for production of ScH$^+$ and ScD$^+$, respectively. The line shows the total cross section. The arrow indicates the bond dissociation energy of HD at 4.52 eV (reprinted from ref 78; copyright 1989 American Chemical Society).

block, Ca$^+$–Zn$^+$,[63,77-88] the second row, Y$^+$–Ag$^+$,[78,89,90] except for Tc$^+$, of course, Ba$^+$,[59] La$^+$, and Lu$^+$ as the only lanthanides,[78] and U$^+$ as the only actinide ion.[56,57] Thermochemical data, especially those derived from elder works, suffered from the problem of excited states of the metal ion that may be present in the primary ion beam. The use of different ion sources, each generating a specific population of electronic states, combined with data subtraction techniques has allowed the determination of *state-specific* cross sections and ground-state bond dissociation energies.

From comparison of the various metal ions, several periodic trends in reactivity emerged, and simple MO arguments were used to classify the metal ions into three categories.[43] Reaction 1 can proceed in two different ways: A $C_{\infty v}$ approach of $H_2$ results in hydrogen abstraction and avoids insertion into the H–H bond, but requires a low-spin configuration of the metal ion. Alternatively, a $C_{2v}$ approach with subsequent insertion gives a dihydride intermediate, $MH_2^+$, which then splits off a hydrogen atom. A prerequisite for this mechanism is an unoccupied s or d$\sigma$ orbital. The three categories are therefore: (1) metal ions with unoccupied s or d$\sigma$ orbitals, which can react efficiently via a $MH_2^+$ intermediate (reaction with HD leads to near statistical behavior for these ions), (2) low-spin ions with occupied s/d$\sigma$ orbitals, which also react efficiently, but via direct abstraction, favoring by ca. 4:1 the MH$^+$ product over MD$^+$ in the reaction with HD, (3) high-spin ions with occupied s/d$\sigma$ orbitals, which react inefficiently via pairwise interaction, substantially favoring MD$^+$. Exceptions from these simple rules may occur if crossings of potential-energy surfaces are possible.

A correlation has been found for metal-hydride dissociation energies $D°(M^+–H)$ and promotion energies ($E_p$) to s$^1$d$^n$ spin-decoupled configurations, which works well for first-row ions and shows deviations for the second row, where exceptions from the concept of exclusive s or d$\sigma$ bonding seem to exist.[43,89,91,92] An *intrinsic* M$^+$–H bond dissociation energy of 56 kcal mol$^{-1}$ for first-row metal ions and of 58 kcal mol$^{-1}$ for second-row metal ions has been derived from the resulting linear graphs, taking the maximum values for $E_p = 0$ as references.[43g]

Many MH$^+$ systems have also been studied theoretically due to their relative simplicity so that a comparison with the experimentally determined data is possible. Agreement between experimental and theoretical values is usually good, with the first row giving a smaller discrepancy than the second. It is indeed calculated that bonding results from overlap of s and d$\sigma$ orbitals, thus justifying the assumptions used to derive the rules described above.[93-96] The assumptions are also supported by calculations on some of the dihydride intermediates $MH_2^+$.[93e,h,o,v,97]

## B. Others

Similar to the determination of $D°(M^+–H)$ energies, other diatomics and simple polyatomic molecules R–X can be employed to determine $D°(M^+–X)$ energies. Dioxygen has been used to measure the $D°(M^+–O)$ bond dissociation energies of Ca$^+$–Zn$^+$,[32g,i,98-100] Nb$^+$,[32g] and U$^+$[101] in ion-beam instruments. Exothermic reactions with several oxygen donors in an ICR instrument were used to bracket some $D°(M^+–O)$ energies,[102-104] and photodissociation[105] as well as variable-energy CID[60,106] on MO$^+$ ions was also employed to determine the dissociation energies. The technique is also applicable to small clusters, as evidenced for example with $Mn_2^+$[32c,i] or $Co_2^+$.[43c]

Other gases have been occasionally employed as well; dinitrogen, carbon monoxide, carbon oxysulfide, and others gave several $D°(M^+–N)$, $D°(M^+–C)$, and $D°(M^+–S)$,[32i,56,101,107] while lower limits for $D°(M^+–I)$ and $D°(M^+–Cl)$ were determined with ICl.[108] Only few theoretical[46b,95,109] or other experimental[110] data exists for these diatomics so that reliable comparisons are difficult.

## IV. Reactions of Bare Metal Ions with Alkanes

### A. Methane and Ethane

### 1. Methane

The reactions of bare metal ions with methane have been studied with a variety of techniques. Most transition-metal ions do not react with $CH_4$ in FTICR experiments since only exothermic ion/molecule reactions can be observed by using this method.[11,42g,103,104,111-114]

Under the multicollision conditions of a flowing afterglow instrument,[115] all first-row ions, except for Mn$^+$, were observed to undergo clustering reactions, forming $M(CH_4)_n^+$ ions, without any indication of C–H activations.[116] Mn$^+$ was apparently unreactive, or the rate constant for the third-body collisional stabilization of the reactive intermediate $(MnCH_4^+)^*$ was too slow to be observed. A high-pressure drift cell was also employed to study the $CoCH_4^+$ adduct formation.[117] Since the drift cell is able to separate ground and excited states of Co$^+$ by their different mobilities,[118] the rate constant could be specifically determined for the ground state. Low-energy Ru$^+$ and Rh$^+$ ions were also found to be unreactive toward methane.[119]

Exothermic dehydrogenation of $CH_4$ by Cr$^+$ (eq 2) was found to arise from the formation of long-lived excited states of $Cr^+$ under the 70-eV electron-impact conditions employed.[33v,73,120-123] The electronic states of the $CrCH_2^+$ ion have been investigated by using high-resolution translational energy loss spectroscopy.[122]

$$(Cr^+)^* + CH_4 \rightarrow CrCH_2^+ + H_2 \qquad (2)$$

Two (ground-state) metal ions are known to react *exothermically* with methane analogous to eq 2, viz. $Os^+$[124] and $Ta^+$.[114,125] The *endothermic* reactions of many transition-metal ions with $CH_4$ to afford $D°(M^+–H)$, $D°(M^+–CH_3)$, $D°(M^+–CH_2)$, and $D°(M^+–CH)$ from eqs 3–6, respectively, have been studied in ion-beam experiments.[43,56,57,86,126-130]

$$M^+ + CH_4 \rightarrow MH^+ + CH_3 \qquad (3)$$

$$\rightarrow MCH_3^+ + H \qquad (4)$$

$$\rightarrow MCH_2^+ + H_2 \qquad (5)$$

$$\rightarrow MCH^+ + H_2 + H \qquad (6)$$

Bond dissociation energies derived from eq 3 can be compared to those from eq 1 as a check for consistency. The formation of $MH^+$ in eq 3 has been described as a result of a competition between direct abstraction and insertion into a C–H bond. The metal ion–methyl bond dissociation energies $D°(M^+–CH_3)$ were found to be slightly larger than the metal–hydrogen values. This finding is in strong contrast to the condensed-phase data which indicate a large difference between M–H and M–C bond dissociation energies in *neutral* organometallic complexes, at least for the late transition elements.[131-134] The significantly weaker M–C bonds are believed to result from steric crowding in the multiligated complexes, factors which are absent for the bare metal ions. It has also been suggested that agostic interactions,[135] electronegativity differences,[136] or exchange repulsions between occupied metal orbitals and the fully occupied $\sigma$-orbital on $CH_3$[93r,137] might be responsible for the discrepancy.

The $M^+—CH_3$ bond has been discussed in terms of a single bond while $M^+{=}CH_2$ and $M^+{\equiv}CH$ are regarded as double and triple bonds; correlations of $D°(M^+—CH_x)$ versus $D°(H_xC—CH_x)$ of the neutral organic hydrocarbons are found to be linear.[138] From correlations of bond dissociation energies versus promotion energies to $sd^{n-1}$ spin-decoupled states, similar to the correlation for $M^+—H$ mentioned above,[43,91,139] *intrinsic* single, double, and triple bond dissociation energies were derived from the graphs for $D°(M^+—CH_3)$, $D°(M^+{=}CH_2)$, and $D°(M^+{\equiv}CH)$ and given as 60, 101, and 135 kcal $mol^{-1}$, respectively.[43g]

The bond dissociation energies obtained in the ion-beam studies have been compared with the results from photodissociation and bracketing experiments in FTICR instruments and were found to correlate well.[105,140-142] A lot of theoretical data is also available for the transition-metal methyl, methylidene, and methylidyne cations,[93d,f,r,94c,96,109g,143-146] and a prescription has been published that converts the experimental data for ligand-deficient complexes into those for saturated organometallic complexes.[147]

Three studies have been reported that deal with the chemistry of *dipositive* metal ions with $CH_4$. The reactions of $Ti^{2+}$[148] and $Nb^{2+}$[149,150] are very similar and give rise to three products, (eqs 7–9) except for clustering reactions to $Ti(CH_4)_n^{2+}$ that were observed under the higher pressures possible in the flowing afterglow.

$$M^{2+} + CH_4 \rightarrow MCH_2^{2+} + H_2 \qquad (7)$$

$$\rightarrow MH^+ + CH_3^+ \qquad (8)$$

$$\rightarrow M^+ + CH_4^+ \qquad (9)$$

### 2. *Ethane*

In the gas-phase chemistry of transition-metal ions with ethane, several reactions are observed, eqs 10–16, that can be rationalized in terms of the general mechanism depicted in Figure 5. For a given metal ion only some of the reactions may be observed, and they are endothermic in most cases. A multitude of bond dissociation energies was once again derived from eqs 10–16, and the occurrence or nonoccurrence of certain reactions for the different metal ions was discussed in terms of spin-allowed or spin-forbidden C–H/C–C oxidative additions,[43] or impulsive, pairwise interactions.[151]

$$M^+ + C_2H_6 \rightarrow MCH_3^+ + CH_3 \qquad (10)$$

$$\rightarrow MCH_2^+ + CH_4 \qquad (11)$$

$$\rightarrow MC_2H_4^+ + H_2 \qquad (12)$$

$$\rightarrow MC_2H_2^+ + 2H_2 \qquad (13)$$

$$\rightarrow MH_2^+ + C_2H_4 \qquad (14)$$

$$\rightarrow MH^+ + C_2H_5 \qquad (15)$$

$$\rightarrow MH + C_2H_5^+ \qquad (16)$$

The only exothermic reactions that are observed are the single and double dehydrogenation, eqs 12 and 13. For ground-state metal ions, the only members of the first row to exothermically dehydrogenate $C_2H_6$ are $Sc^+$ and $Ti^+$.[42g,79,116,126,152-156] On the contrary, most of the second- and third-row transition-metal ions were observed to react exothermically with $C_2H_6$, thus the C–H activation is much more facile for 4d and 5d ions.[11,103,111,113,114,119,124-126,157] Very inefficient exothermic dehydrogenation of ethane for ground-state $Fe^+$ ($^6D$) has been reported,[130] but more recent work indicates that this is due to a small amount of highly excited states.[43e] Observing the reactions in eqs 12 and 13 to proceed with exothermicity implies $D°(M^+–C_2H_4) \geq 32.7$ kcal $mol^{-1}$ and $D°(M^+–C_2H_2) \geq 74.5$ kcal $mol^{-1}$, which can be compared to calculated data for $MC_2H_4^+$[96,97e,158a,159] and $MC_2H_2^+$;[96,97e,158] however, the agreement with the experimental data is not too good.

The dehydrogenation of ethane for the early transition metal ion $V^+$ has been found to be due to excited states;[160] although the overall reaction is exothermic, a barrier arising from spin conservation prevents ground-state $V^+$ from forming the $H–V^+–C_2H_5$ insertion intermediate. Using a very elegant technique,[161a] Weisshaar and co-workers were able to show that the $H_2$ loss was due to the second excited $a^3F$ term (1.1 eV above ground state) and that the spin–orbit levels $J$ = 2, 3, and 4 react with *indistinguishable cross sections*.[161b,162,163]

An interesting correlation has been found for the rate of adduct formation between the first-row ions $Sc^+$ through $Zn^+$ and ethane under multicollision conditions

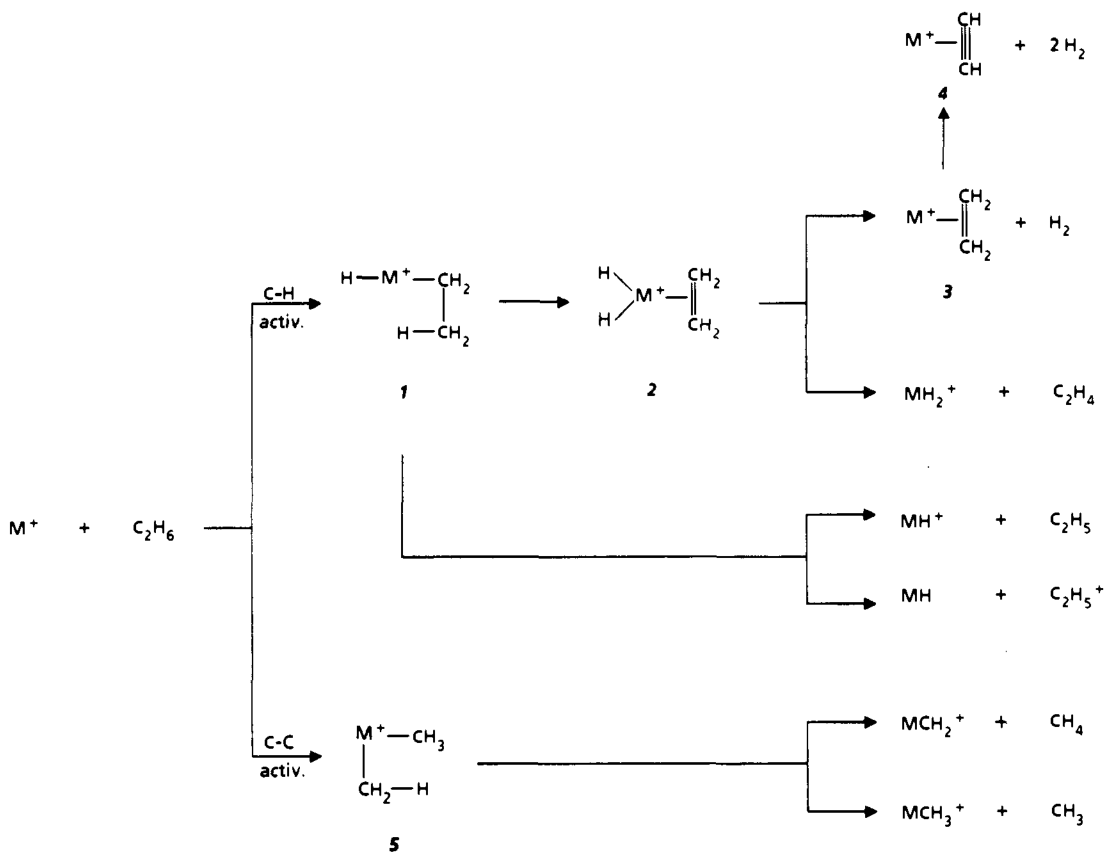


**Figure 5.** Generalized mechanism for the exothermic and endothermic reactions of transition-metal ions $M^+$ with ethane.

(eq 17) and the energies of the $3d^n$ configurations.[153] Notably is an extremely low rate for $Mn^+$ which, as is shown below, is generally reacting quite slowly with various substrates.

$$M^+ + C_2H_6 + He \rightarrow MC_2H_6^+ + He \qquad (17)$$

The doubly charged $Ti^{2+}$ is reported to react with $C_2H_6$ to ≥90% via $H^-$ transfer and to a smaller extent (≤10%) via charge transfer, affording $TiH^+$ and $Ti^+$, respectively.[148] The same types of reactions take place with propane. In contrast, $Nb^{2+}$ affords $NbC_2H_2^{2+}$, $NbH^+$, and $Nb^+$ with ethane, but almost exclusively $Nb^+$ with propane and butane.[150]

## B. Linear Alkanes

The reaction of a transition-metal ion with propane is distinct from the one with ethane. In the former case it is (a) now possible to exothermically activate a C-C bond, and (b) two types of C-H bonds are present in the substrate. As a result, exothermic reactions that further reveal preferences for either C-H or C-C activation are observed for most of the metal ions. Exceptions are $Cr^+$, $Mn^+$, $Cu^+$, and $Zn^+$ in the first row, and the lanthanides $Eu^+$ and $Pr^+$; all those metal ions are generally unreactive with alkanes in the sense that no exothermic reactions are found. Three reactions are noted frequently, C-H activation gives rise to loss of $H_2$ and $2H_2$ (eqs 18 and 19), while C-C activation affords loss of $CH_4$ (eq 20).

$$M^+ + C_3H_8 \rightarrow MC_3H_6^+ + H_2 \qquad (18)$$

$$\rightarrow MC_3H_4^+ + 2H_2 \qquad (19)$$

$$\rightarrow MC_2H_4^+ + CH_4 \qquad (20)$$

Furthermore, triple dehydrogenation has been observed for $Nb^+$ and $Ta^+$,[114,125] $Os^+$ shows the unusual losses of $H_2/CH_4$ and, formally, $[C_2H_6]$,[124] and finally, for $Au^+$, loss of AuH was also observed.[11] In general, the second- and third-row transition-metal ions reveal an increased tendency for C-H activations with the losses of $H_2$ and $2H_2$ clearly dominating. For the first-row ions the double dehydrogenation is only observed for $Sc^+$,[79] but this reaction is probably endothermic.[164] The now commonly accepted mechanism for the losses of $H_2$ and $CH_4$ is given in Figure 6.

Insertion of the metal ion into the weaker secondary C-H bond generates intermediate **6** that rearranges by β-hydrogen shift[165] to **9**, from which reductive elimination[166] of $H_2$ can occur.[167] Insertion into a C-C bond followed by β-hydrogen shift produces **10**, from which the reductive methane elimination[188] is possible. The intermediacy of **7** is uncertain since it needs not to be introduced to explain the formation of the products; especially the β-methyl shift **7** → **10** is subject of controversies which have yet to be settled. Recently, angular momentum constraints have been put forward as an argument in favor of *initial and rate-limiting* C-H activation in the demethanation of propane by $Co^+$.[169] Kinetic energy release distributions (KERD's[170]) for the unimolecular dissociations of $Co(C_3H_8)^+$ complexes and several $^2H$-labeled isotopomers thereof, together with the determination of absolute cross sections for the individual isotopomers and the energy dependences for the loss of $H_2$ versus $CH_4$ were interpreted as follows:[171] At low kinetic energies, initial C-H insertion exclusively prevails, and both **6** and **7** are produced; **6** in a multicenter elimination and bypassing **9** undergoes loss of $H_2$, while **7** rearranges by β-H shift to **9** or by β-$CH_3$

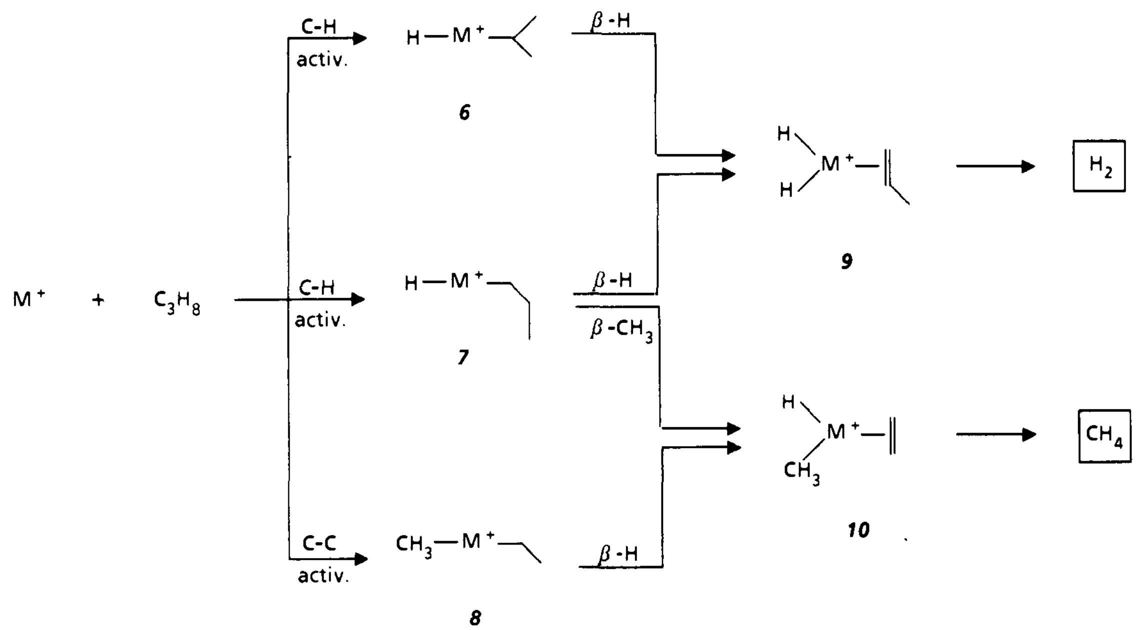


**Figure 6.** Generalized mechanism for the reactions of transition-metal ions $M^+$ with propane.

shift to **10**, from which via reductive elimination $H_2$ and $CH_4$ are lost. At slightly elevated energies C–C activation to generate **8** is also observed, and the $CH_4$-loss channel becomes relatively enhanced. Quite similarly, the energy dependence for the loss of $H_2$ versus $CH_4$ from the $Fe(C_3H_8)^+$ ion/(induced) dipole complex compared to that of the direct reaction of $Fe^+$ with propane indicated that starting from the adduct complex, the C–H insertion has the lowest activation barrier ($\sim$11 kcal mol$^{-1}$) and may lead to loss of $H_2$ *as well as of* $CH_4$. Loss of $CH_4$ by C–C insertion has a higher barrier, albeit still less than the $\sim$20 kcal mol$^{-1}$ ion/(induced) dipole well; hence, bare $Fe^+$ may easily surmount this activation barrier.[172]

A deviation from the generally operative 1.2 elimination mode in Figure 6 is reported for $Sc^+$, where in addition 1.3 elimination has been postulated.[79,164] For $Ti^+$, a small amount of 1.3 elimination (7%) besides 1.2 elimination has been proposed, even though this could not be distinguished from possible scrambling processes.[155]

An important observation has been made, concerning the reactivity of ground and first excited state of $Fe^+$ ($^6D$, $^4F$) with $C_3H_8$.[130,173] In contrast to the endothermic reactions of $Fe^+$ with $H_2$, $CH_4$, or $C_2H_6$, the $^6D$ ground state is *more reactive* in exothermic processes below 0.4 eV while above that energy the $^4F$ state is reacting slightly more effective. This behavior is explained with *adiabatic* potential energy surfaces with an avoided crossing due to spin–orbit coupling at low energies. As the kinetic energy increases, the coupling becomes less efficient and the crossing becomes permitted, giving rise to *diabatic* potential energy surfaces. This result is significant beyond the particular $Fe^+/C_3H_8$ system; it demonstrates that the question of electronic excitation, which is of vital importance for small systems, in which even small amounts of excited states can influence the results dramatically, is less crucial for larger systems, for which surface crossings are frequent and occur at even lower energies because of deeper polarization wells. Yet, more recent results cast some doubt on this explanation; the spin–orbit quantum number $J$ affects the $Fe^+ + C_3H_8$ cross section by as much as a factor of 2 while the branching for $CH_4$ versus $H_2$ loss is independent of $J$.[174] In particular, the 400-cm$^{-1}$ increase in total energy from $J = {}^7/_2$ to $J = {}^5/_2$ may be important in overcoming a small barrier along the reaction path, so that different $J$ distributions may seriously complicate the interpretation of experimental results that do not allow a distinction among the $J$'s. Little change in reactivity with electronic state has also been found for $Ti^+$[152] and $V^+$,[161b] but for the latter ion the cross section was again independent of $J$, contrary to the $Fe^+/C_3H_8$ system but identical with $V^+/C_2H_6$.[161b]

A similar pattern of the rate constants for adduct formation has been noted for the methane and propane analogues of eq 17.[116]

The majority of the gas-phase studies of *n*-alkanes, and especially *n*-butane, with bare metal ions has been concerned with the group 8–10 metal ions $Fe^+$, $Co^+$, and $Ni^+$. Early studies already revealed the occurrence of several reactions which proceeded exothermically and quite facile (eqs 21–24).[73,120,175]

$$M^+ + n\text{-}C_4H_{10} \rightarrow MC_4H_8^+ + H_2 \qquad (21)$$

$$\rightarrow MC_4H_6^+ + 2H_2 \qquad (22)$$

$$\rightarrow MC_3H_6^+ + CH_4 \qquad (23)$$

$$\rightarrow MC_2H_4^+ + C_2H_6 \qquad (24)$$

By employing $CD_3CH_2CH_2CD_3$, the mechanisms that led to the products could be determined. Using an ion-beam instrument, Armentrout and Beauchamp were able to show that the reaction of $Co^+$ with *n*-butane to afford $CoC_2H_4^+$ is due to an initial insertion into the weak internal $C_{(2)}$–$C_{(3)}$ bond followed by β-hydrogen shift and reductive elimination of ethane (**14** → **15** → **3**, Figure 7). Scrambling processes at low energies precluded exact determinations for the dehydrogenations, but loss of methane could be shown to proceed analogous to the propane system (**11** → **12** → **13**).[86] Later it was shown for $Ni^+$ that eq 21 is a highly specific 1.4 dehydrogenation.[176] The intermediate **15** still has the possibility for a second β-H shift to produce **16**, from which reductive elimination of $H_2$ and formation of the bis(olefin) complex **17** can occur. 1.4 dehydro-

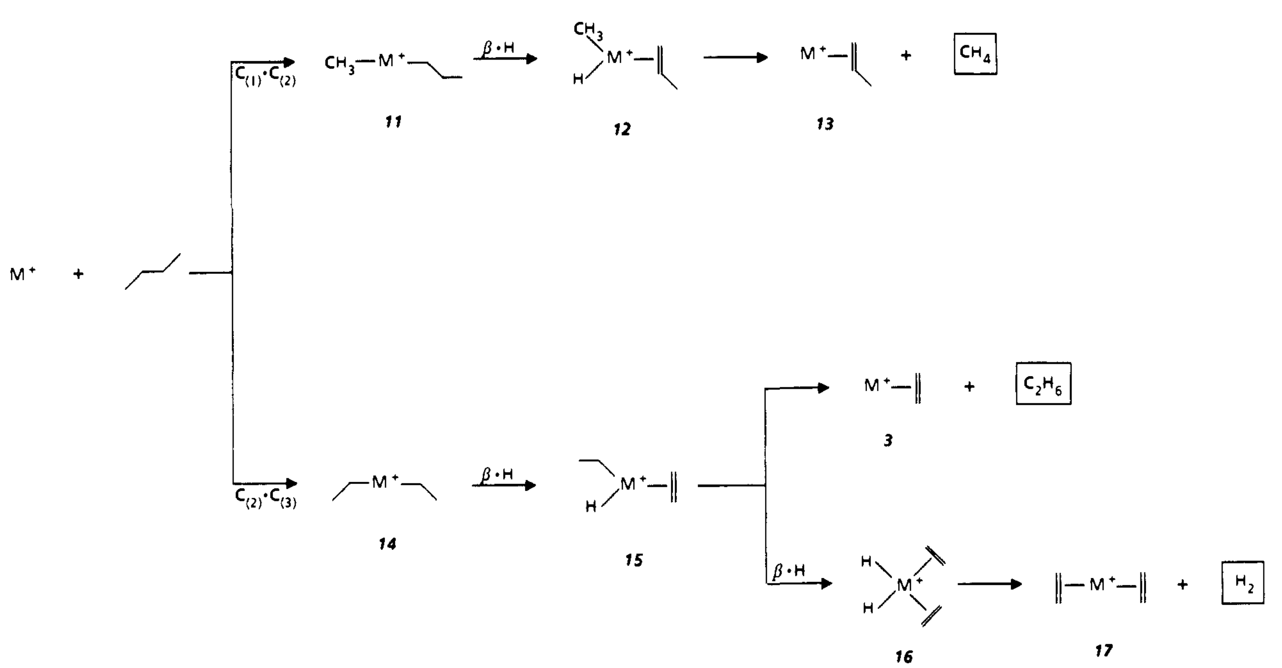


**Figure 7.** Generalized mechanism for the reactions of group 8–10 transition-metal ions $M^+$ with $n$-butane, which arise from initial C–C insertions.

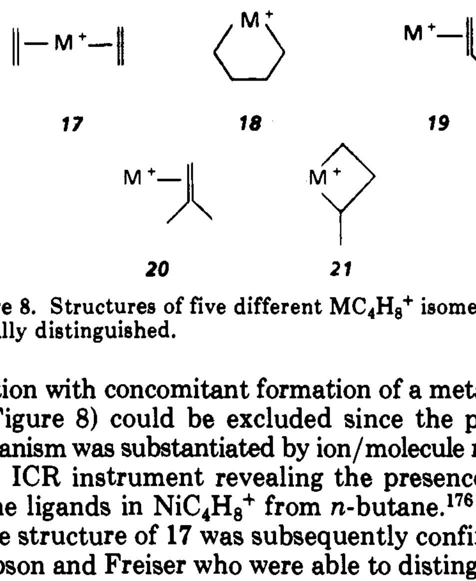


**Figure 8.** Structures of five different $MC_4H_8^+$ isomers experimentally distinguished.

genation with concomitant formation of a metallacycle 18 (Figure 8) could be excluded since the proposed mechanism was substantiated by ion/molecule reactions in an ICR instrument revealing the presence of two ethene ligands in $NiC_4H_8^+$ from $n$-butane.[176]

The structure of 17 was subsequently confirmed by Jacobson and Freiser who were able to distinguish the four $MC_4H_8^+$ (M = Fe, Co, Ni) isomers **17–20** (Figure 8) by an elegant combination of CID experiments and ion/molecule reactions.[177,178] **17**, formed from $n$-$C_4H_{10}$ and $Ni^+$, upon CID exclusively loses $C_2H_4$ and, formally, $C_4H_8$; reaction with $CH_3CN$ gives sequential exchange of the two ethene ligands. If $NiC_4H_8^+$ is formed from alkanes larger than butane, CID affords loss of $H_2$ and $C_4H_8$, consistent with structure **19**. Isomer **20** is formed from branched alkanes (see below) and shows only loss of $C_4H_8$. **18** is believed to be formed by decarbonylation of cyclopentanone and fragments upon CID by loss of $H_2$, $C_2H_4$, and $C_4H_8$. A fifth $FeC_4H_8^+$ isomer has been characterized and distinguished from **17–20** in high-energy CID experiments; the reaction of methyl cyclopropane with $Fe(CO)_x^+$ in a high-pressure chemical ionization (CI) source generates **21**.[179] **17–20** (M = Ni) may also be distinguished by photodissociation as **17** affords losses of $C_2H_4$ and $C_4H_8$, **18** in addition $H_2$, **19** $H_2$, $C_2H_4$, $C_4H_8$, and $CH_3$, forming $Ni(\eta^3\text{-}C_3H_5)^+$, and **20** in addition to $C_4H_8$ loses $CH_4$.[105] While the reaction of $Ni^+$ with $n$-butane was found to be highly specific,[176,177] the analogous reactions of $Fe^+$ and $Co^+$ were not. Both ions dehydrogenate this alkane by a combination of 1.2 and 1.4 elimination. For $Co^+$, it has been estimated from the CID results that ca. 10% 1.2 dehydrogenation is active, while for $Fe^+$ this is the even more important process, being responsible for ca. 70% of the dehydrogenation products.[178] The same percentages for $Fe^+$ were later obtained from high-energy collisional-activation experiments.[74]

Another possibility to distinguish 1.2 and 1.4 eliminations has been introduced by Beauchamp, Bowers, and co-workers.[75,76] Kinetic energy release distributions[170] for the unimolecular dissociations of M(alkane)$^+$ complexes showed characteristic differences for the loss of HD from $Co(CD(CH_3)_3)^+$ (eq 25), which is believed to be a typical example for a 1.2 elimination (see below), and for loss of $D_2$ from $Ni(CD_3CH_2CH_2CD_3)^+$ (eq 26), i.e., the 1.4 elimination. It could thus be shown that

$$Co(CD(CH_3)_3)^+ \rightarrow Co(CH_2C(CH_3)_2)^+ + HD \qquad (25)$$

$$Ni(CD_3CH_2CH_2CD_3)^+ \rightarrow Ni(CH_2CD_2)_2^+ + D_2 \qquad (26)$$

the observation of $H_2$, HD, and $D_2$ loss from $Co(CD_3CH_2CH_2CD_3)^+$ was not due to the simultaneous operation of 1.2 and 1.4 eliminations; instead, the dehydrogenation of $n$-butane by $Co^+$ proceeds predominantly by a 1.4 mechanism, and scrambling processes are responsible for the observed label distribution.[75,76] Further information which could be derived from the kinetic energy release distributions were a greater exothermicity for the 1.4 elimination as compared to the 1.2 process, and the data was also suggestive of significant barriers for the reverse reactions, i.e., oxidative addition of $H_2$ to the M(olefin)$^+$ and, even more so, to the M(olefin)$_2^+$ complexes. This seems to be a general phenomenon for alkane dehydrogenation by $Fe^+$–$Ni^+$.[45] On the contrary, for alkane losses, e.g., loss of $CH_4$ from $M(C_4H_{10})^+$, the data could best be interpreted in terms of a loose transition state in which the C–H bond has already been formed and intact alkane molecules are detached.[45,76] In favorable cases, metal–ligand bond dissociation energies could be estimated by a comparison of experimental and theoretical data.[76]

The reactions of $Fe^+$, $Co^+$, and $Ni^+$ with linear alkanes larger than butane are merely an extension of the chemistry discussed so far. All the results can be explained with oxidative additions to C–H or C–C bonds followed by $\beta$-H shifts and reductive eliminations of neutral molecules to afford metal(olefin)$^+$ or metal bis(olefin)$^+$ complexes. If sufficient energy is available, subsequent reactions may lead to alkadiene complexes. The following generalizations emerged:

The dehydrogenation of linear alkanes with more than three carbon atoms by $Ni^+$ proceeds exclusively by 1.4 eliminations as evidenced by deuterium labeling[176] and CID as well as ion/molecule reaction studies, which substantiated the resulting bis(olefin) structures of the dehydrogenation products.[177,178] For $Fe^+$ and $Co^+$, in addition, 1.2 eliminations are operative.[178,180] This is explained by the higher $M^+$–H bond dissociation energies of the resulting R–$M^+$–H insertion products in case of $Fe^+$ and $Co^+$, which make this C–H activation competitive with the C–C insertion that finally leads to the 1.4 dehydrogenation; the significantly weaker $Ni^+$–H bond renders C–H insertion unattractive as compared to C–C activation.

The elimination of smaller alkanes in the reactions of $Fe^+$ through $Ni^+$ with linear alkanes are with one notable exception[180] always explained in terms of mechanisms analogous to those in Figures 6 and 7. $Ni^+$ is found to exclusively activate C–C bonds to afford monoolefin complexes for larger alkanes than butane.[177] For $Fe^+$ and $Co^+$, C–H activation is also observed but insertion into C–C bonds is always favored and similarly gives rise to monoolefin complexes.[177,178]

Selectivity is also observed for alkanes possessing different kinds of C–C bonds. Insertion into the terminal C–$CH_3$ bond is the least preferred which is explained by the slightly higher strength of this bond. This is in line with the selectivities found for the internal C–C bonds; the weakest bond is preferentially cleaved. *Selectivity increases* in the row $Fe^+ < Co^+ \ll Ni^+$,[86,156,177,178,181] and is explained *with the decreasing exothermicity of the insertion reaction.* Models have been developed to predict the site of insertion in larger alkanes. If the bond dissociation energies of the resulting insertion intermediates R–$M^+$–R′ are taken as the most significant factor and differences in $D°$(R–R′) are neglected, and if one assumes that the $D°(M^+–C_2H_{2n+1})$ values increase with increasing polarizability of the $C_nH_{2n+1}$ fragments, and if, as such polarizabilities are not available, one furthermore assumes that the ionization potentials of the alkyl radicals, $C_nH_{2n+1}^\bullet$, reflect, in part, their polarizabilities, one may correlate the site of insertion with the sum of the ionization energies of R and R′.[182] It has also been argued that initial electrostatic interactions in complexes of the intact substrate and the metal ion might control the final product distributions.[183]

Once the insertion has been accomplished, $\beta$-H shifts from different positions are optional. $\beta$-Hydrogen shifts from a secondary carbon are clearly more facile than those from a primary one for $Co^+$ and $Ni^+$.[86,177,178,181] $Co^+$ even shows preference for $\beta$-H shifts from a butyl over a propyl group.[184] $Fe^+$ has been reported to be less selective, once again because of the greater exothermicities of its reactions,[181] and even a reversal in selectivity has been proposed,[178] although this is in conflict with the other study[181] and results for other substrates discussed below.[185] In general, $\beta$-H shifts are more facile for $Co^+$ than for $Ni^+$,[178] a result that may also account for the observation that deuterium scrambling in the reactions with alkanes is frequent for $Co^+$, rarely observed for $Fe^+$, and absent for $Ni^+$.[180]

Using an extensive set of labeled compounds, Houriet et al. concluded that while $Ni^+$ reacts "normal" in the sense of the just mentioned processes, for $Fe^+$, and to a lesser extent also for $Co^+$, *$\beta$-methyl shifts* are responsible for part of the products formed.[180]

In the reactions of gas-phase $Sc^+$ with alkanes a unique reactivity is exhibited which is clearly distinct from the behavior of the other first-row ions. Labeling studies revealed that dehydrogenations predominantly proceeded as 1.3 eliminations and that scandium–dialkyl ions were formed via loss of alkenes.[79] Figure 9 shows the proposed mechanisms for the reactions of $Sc^+$ with butane. C–H insertion generates intermediate **22** from which, by a concerted mechanism to conserve the oxidation state, $H_2$ elimination forms the metallacycle **23**. Thermodynamic and possibly kinetic reasons were proposed to explain this unusual behavior. C–C insertion affords **24**, and is followed by $\beta$-methyl transfer[186] and subsequent loss of ethene or, less favored, reductive elimination of ethane.

The products that are formed by $Ti^+$ and $V^+$ are very much alike. Both ions predominantly activate C–H bonds, giving rise to losses of $H_2$, multiples of $H_2$, or of $H_2$ together with small alkanes.[42g,112,156,175] The use of labeled compounds showed that while $V^+$ clearly dehydrogenates alkanes via the 1.2 mechanism and with a preference for internal positions, for $Ti^+$ small amounts of product were formed that could either arise from 1.3 eliminations or scrambling processes.[155] No distinction was possible, and as for $V^+$, from butane, 2-butene was formed in the single dehydrogenation. However, the observation of $Ti(CD_3)_2^+$ by loss of $C_2H_4$ from $CD_3CH_2CH_2CD_3$ is also reported so that 1.3 dehydrogenation in analogy to the neighboring $Sc^+$, which also formed this dimethyl complex, is not altogether unlikely.

The reactivity of second- and third-row transition-metal ions has not been exploited in the same depth as that of the first row; the overall picture that emerges is, however, relatively straightforward. The activation of C–H bonds in the alkanes clearly dominates with only slight differences between the individual ions. This is completely in line with the results for $C_2H_6$.

$Y^+$ and $La^+$ are found to singly and doubly dehydrogenate *n*-alkanes, with carbon-chain cleavages and multiple-loss products also observed. Metal-dialkyl ions,[96] such as $CH_3$–$M^+$–$CH_3$, are postulated on the basis of deuterium labeling and CID experiments.[113] $Nb^+$ and $Ta^+$ show mainly dehydrogenations with only small amounts of C–C cleavages.[114,125] The unusual loss of a hydrogen *radical* has to be involved in the formation of $NbCp^+$ (Cp = $\eta^5$-c-$C_5H_5$) from *n*-pentane.[114] In marked contrast to $Cr^+$, which is unreactive with alkanes, $Mo^+$ is seen to undergo facile multiple dehydrogenations. This has been explained by the greater $M^+$–H and H–$M^+$–R bond dissociation energies for M = Mo. The weak $\sigma$-bonds formed by $Cr^+$ make the

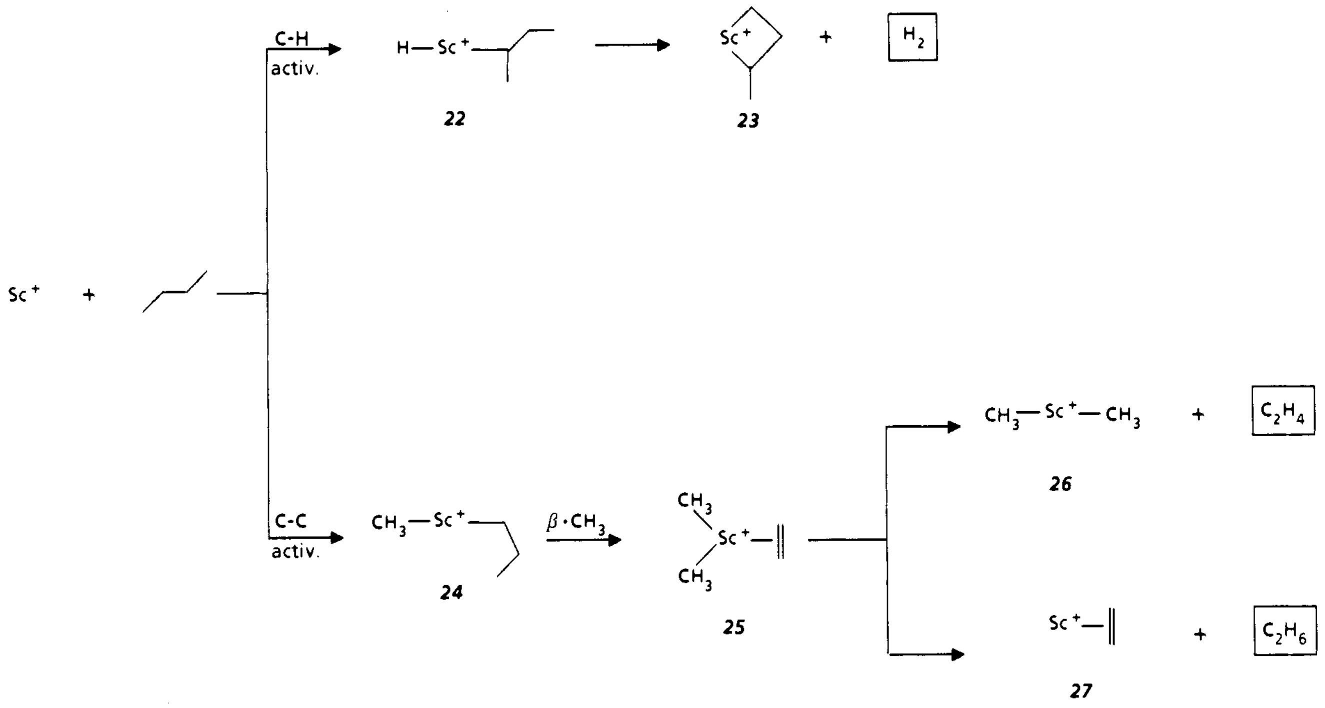


**Figure 9.** Mechanism for the reaction of Sc$^+$ with *n*-butane, which affords 1.3 dehydrogenation and formation of Sc$^+$–dialkyl ions.

insertion in a C–H bond considerably more endothermic than for Mo$^+$, where the larger size of the d orbitals is responsible for strong $\sigma$-bonds.[157] This picture seems to be supported by the results of ab initio calculations on CrH$_2^+$ and MoH$_2^+$.[97a,d] In contrast to their first-row congeners, Ru$^+$ and Rh$^+$ are observed to dehydrogenate alkanes predominantly by 1.2 eliminations. The exclusive activation of C–H bonds, in contrast to Fe$^+$ and Co$^+$, is explained by differences in size and shape of the bonding orbitals and is believed not to be due to bond-strength differences.[119] In the reactions with alkanes larger than C$_4$H$_{10}$, Rh$^+$ also forms small amounts of C–C cleavages besides multiple dehydrogenations, and dehydrocyclization is observed for *n*-C$_5$H$_{12}$ and *n*-C$_6$H$_{14}$.[111] Pd$^+$, which forms H$_2$ and small alkanes from propane and butane, also exclusively dehydrogenates in a 1.2 elimination mode; from C$_4$H$_{10}$, 2-butene is selectively formed. Hydride abstraction due to the uniquely high Lewis acidity of Pd$^+$ is postulated as the first step in the mechanism of C–H bond activation, leaving behind the hydrocarbon fragment with an appreciable amount of carbenium ion character in the reaction intermediate.[119] Os$^+$ has only been studied with propane and butane, where once again multiple dehydrogenation occurs and small alkanes are formed.[124] Au$^+$ shows an exceptional behavior which is completely different from the other metal ions studied. Mainly H$^-$ abstraction with concomitant AuH formation is encountered (93% for C$_3$H$_8$ and 99% for C$_5$H$_{12}$ and larger *n*-alkanes), with only very small amounts of H$_2$ loss in addition.[11] From the three lanthanide ions studied so far, only Gd$^+$ reacts with alkanes; dehydrogenations and small amounts of alkane and alkene losses are observed. Gd$^+$–dialkyl species are assigned on the basis of labeling experiments, and dehydrocyclization of C$_6$H$_{14}$ to benzene is noted. The reactivity of Gd$^+$ in contrast to Pr$^+$ and Eu$^+$ is explained by the necessity of f-electron involvement in bonding for the latter ions.[103]

## C. Branched Alkanes

Compared to the linear alkanes, the reactions of bare metal ions with branched alkanes have been much less exploited. The majority of the studies employed two prototypical compounds, 2-methylpropane (isobutane) and 2,2-dimethylpropane (neopentane). The former is the very first representative of a branched alkane while the latter is unique in that no $\beta$-hydrogen atoms are available following C–H insertion.

Once again the interest has focused on the group 8–10 metal ions Fe$^+$, Co$^+$, and Ni$^+$. Upon reaction with isobutane two products are formed, molecular hydrogen and methane,[61,65,73-76,86,156,175,180,181,187] with the commonly accepted mechanism given in Figure 10 (R = H). Initial C–H or C–C insertion is followed by reductive elimination of H$_2$ or CH$_4$. This mechanism is supported by high-energy CID results, which verify the structure of **20**,[74] and labeling results for (CH$_3$)$_3$CD. Exclusive loss of HD and CH$_4$ is observed for this compound,[175,180] and the HD loss (eq 25) has therefore been used to serve as a reference spectrum for 1.2 eliminations in kinetic energy release distributions (see above).[75,76]

With neopentane only methane loss is observed in the reactions with Fe$^+$–Ni$^+$.[86,156,177,178,180,181,188] The same mechanism (Figure 10, R = CH$_3$) is assumed to be operative, in line with low-energy CID studies in an FTICR instrument which support the structure of **32**, viz. isobutene complexes.[177,178] As already mentioned above, C–H insertion would afford an intermediate lacking $\beta$-hydrogens, and hence, the absence of H$_2$ loss may be taken as an indication for the unfavorableness of $\alpha$- or $\gamma$-hydrogen shifts for these metal ions. For the other branched alkanes studied, similar mechanisms as the one in Figure 10 were sufficient to explain the observed products.[86,156,180] Exceptions were only observed for highly branched alkanes, e.g. 2,2,3,3-tetramethylbutane. Loss of H$_2$ from this alkane was formulated as a 1.4 elimination, furnishing a cobaltacyclopentane.[86,181]

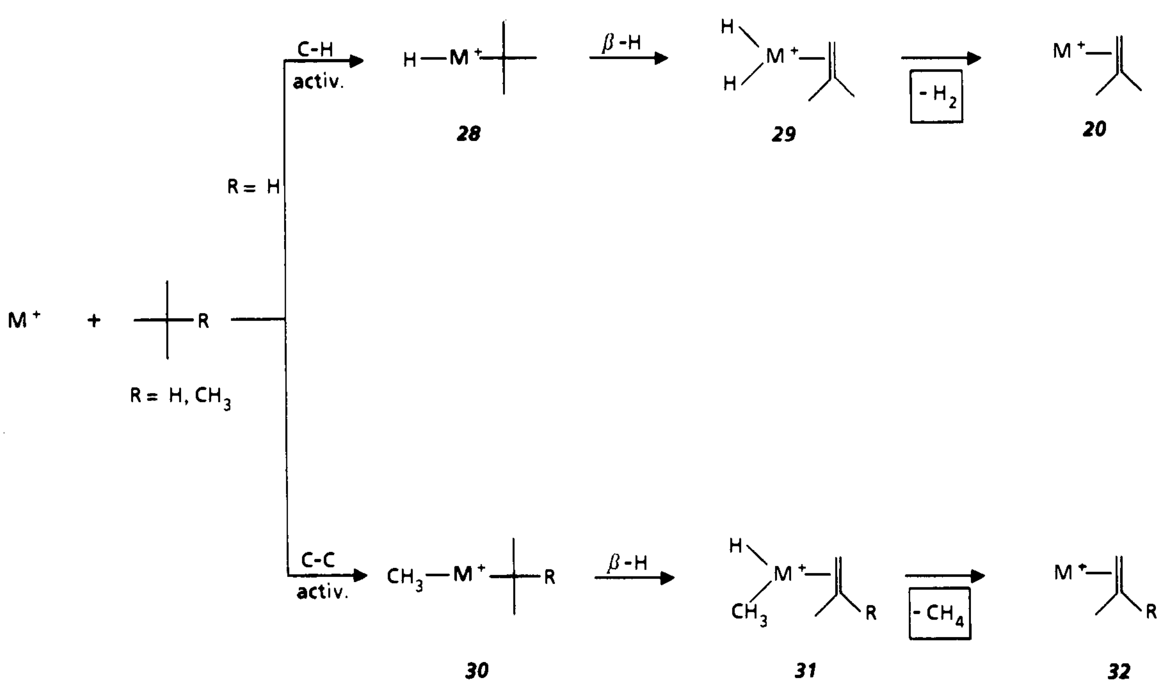


**Figure 10.** Mechanism for the reactions of the group 8–10 metal ions $Fe^+$–$Ni^+$ with 2-methylpropane (R = H) and 2,2-dimethylpropane ($R = CH_3$).

Deuterium and $^{13}C$ labeling was employed to get further information, and it could be shown that $Ni^+$ selectively inserts into the weakest C–C bond present in the alkane.[180] β-Methyl shifts were invoked for $Fe^+$ in a few cases while none were observed for $Co^+$ or $Ni^+$.[180]

The already noted tendency of the early transition metal ions for C–H activation is also found with branched alkanes. However, the reactions of $Sc^+$ with $(CH_3)_3CD$ in an ion-beam instrument and with a kinetic energy of 0.5 eV are unspecific as losses of $H_2$ and HD, $2H_2$, and $H_2$/HD, and $C_2H_3D$ besides $C_2H_4$ are observed.[79] This result has been interpreted again with the combined operation of 1.2 and 1.3 eliminations as well as β-methyl shifts. 0.5-eV-$Sc^+$ reacts with neopentane by loss of $H_2$, presumably in a 1.3 elimination.[79] $Ti^+$ mainly gives rise to multiple dehydrogenations with only small amounts of C–C cleavage products observed, and rearrangements of the carbon skeleton were most likely involved.[65,155,156] Eliminations mainly proceeded as 1.2, but some 1.3 losses were also proposed, yet, could not be distinguished from scrambling processes.[155] $V^+$, while still favoring C–H activation, does not give rise to *multiple* dehydrogenations as extensively as $Ti^+$, and it is also more selective;[112,155] upon reaction of $V^+$ with $(CH_3)_3CD$ only HD is lost.[155] Although β-methyl shifts were proposed to explain the observed reactivity with neopentane,[112] the cross sections for the reported losses were extremely small so that the possibility of excited states being responsible for the products was made highly likely.[155]

As with other alkanes, $Cr^+$, $Mn^+$, $Cu^+$, and $Zn^+$ are unreactive with the branched compounds, i.e., they do not *exothermically* react to form any other products besides adduct complexes in (probably mostly) termolecular reactions.[65,68a,73,181,187,188–190] *Endothermic* reactions have been studied, however, for $Mn^+$, $Cu^+$, and $Zn^+$. High-energy CID upon $Cu(i\text{-}C_4H_{10})^+$ complexes, formed by the "FAB method"[88] (see section II), resulted in the losses of $H_2$, $CH_4$, as well as of neutral CuH, forming the $t\text{-}C_4H_9^+$ cation.[68a] Ion-beam experiments of $Cu^+$ with isobutane and neopentane produced organic products, see eqs 27 and 28 for the case of $C_4H_{10}$, but also led to the formation of the adduct complexes (eq 29).[188]

$$Cu^+ + i\text{-}C_4H_{10} \rightarrow C_4H_9^+ + CuH \tag{27}$$

$$\rightarrow C_3H_7^+ + CuCH_3 \tag{28}$$

$$\rightarrow CuC_4H_{10}^+ \tag{29}$$

Low-energy CID upon the $Cu(i\text{-}C_4H_{10})_n^+$ complexes ($n = 1$; 2) afforded exclusively loss of the intact isobutane moieties, thus demonstrating that these are indeed van der Waals adducts.[187] Surprisingly, the adduct formation was found to proceed *bimolecularly*.[188] Equations 27 and 28 and also analogous reactions with $Co^+$,[188] $Ni^+$,[188] and $Mn^+$[189] were used to determine the $D°(M\text{-}H)$, $D°(M\text{-}CH_3)$ and, using eq 32 below, $D°(M^+\text{-}CH_3)$ bond dissociation energies. Ion-beam studies of $Zn^+$ with several alkanes $CH_3R$, including R = $i\text{-}C_3H_7$ and $t\text{-}C_4H_9$, have similarly been used to determine $D°(Zn^+\text{-}CH_3)$ and $D°(Zn\text{-}CH_3)$ data.[190] Estimated stabilities of intermediates were used to show that the reactions of $Cu^+$ do not proceed via insertion but most plausibly via *heterolytic cleavage*.[188] On the contrary, the reactions of $Co^+$ and $Ni^+$,[188] as well as of $Mn^+$,[189] with $i\text{-}C_4H_{10}$ and $neo\text{-}C_5H_{12}$ are believed to proceed via the insertion intermediates **28** and **30** (Figure 10). For $Co^+$ and $Ni^+$, the exothermic pathways to **20** and **32** are open, so that the endothermic decompositions of the C–H or C–C insertion products via eqs 30–33 are not competitive at low energies and are only observed at higher energies. $Mn^+$ exclusively reacts by cleavage of the M–R bond (eqs 30–33).

$$H\text{-}M^+\text{-}R \rightarrow H\text{-}M^+ + R \tag{30}$$

$$\rightarrow H\text{-}M + R^+ \tag{31}$$

$$CH_3\text{-}M^+\text{-}R \rightarrow CH_3\text{-}M^+ + R \tag{32}$$

$$\rightarrow CH_3\text{-}M + R^+ \tag{33}$$

The branching ratio between eqs 30 and 31 and eqs 32 and 33, respectively, reflects the different ionization energies (IE's) of the two cleavage products MH ($MCH_3$) and R. The bond dissociation energies (BDE's) and the IE's of the particles involved are related to each other by eq 34. For example, $MnCH_3$ has a relatively

$$\mathrm{IE}\ (\mathrm{MR}) + D°(\mathrm{M^+{-}R}) = \mathrm{IE}\ (\mathrm{M}) + D°(\mathrm{M{-}R}) \qquad (34)$$

low BDE, $D°(\mathrm{Mn{-}CH_3})$ = 0.4–1.3 eV,[189] while $D°(\mathrm{Co{-}CH_3})$ = 1.99 eV.[188] As the IE's of Mn and Co and the $D°(\mathrm{M^+{-}CH_3})$ bond dissociation energies are comparable, it follows from eq 34 that $MnCH_3$ has a lower IE (5.6 eV[189]) and $CoCH_3$ a higher IE (7.7 eV[188]) than the $t$-$C_4H_9$ radical (6.70 eV). Hence, $Mn^+$ reacts with neopentane mainly to $MnCH_3^+$,[189] while the endothermic reactions of $Co^+$ mainly give $t$-$C_4H_9^+$.[188] Numerous theoretical studies concerning $D°(\mathrm{M{-}H})$[93g,j,l–n,p–r,w,94b,c,96,167q,r,v,ae,an,ao,191,192] and $D°(\mathrm{M{-}CH_3})$[93r,94c,96,146,193,194] have also been reported; the agreement to thus or otherwise[195–197] experimentally derived data varies, however, depending upon the level of calculation. The *intrinsic* $D°(\mathrm{M{-}H})$ and $D°(\mathrm{M{-}CH_3})$ BDE's have been determined to 54 and 49 kcal $mol^{-1}$, thus the charge is not influential for the hydrogen bonding, but is important for the methyl bonding (c.f. intrinsic $D°(\mathrm{M^+{-}H})$ = 56 kcal $mol^{-1}$ and $D°(\mathrm{M^+{-}CH_3})$ = 60 kcal $mol^{-1}$).[43g]

The behavior of the second- and third-row ions toward branched alkanes is very similar to the chemistry already described for the linear representatives. $Y^+$ and $La^+$ upon reaction with isobutane and neopentane once again demonstrate their preference for C–H activation as two molecules of $H_2$ are lost, respectively.[113] The products generated are assigned to trimethylenemethane complexes on the basis of CID experiments. In addition, $Y(CH_3)_2^+$ and $La(CH_3)_2^+$ are formed in minor amounts from both compounds. 2,2- and 2,3-dimethylbutane with both of the group 3 ions lose mainly $CH_4/H_2$.[113] The products have not been characterized further but isoprene complexes are not unlikely in view of the structures of the precursors. Quite similar, $Nb^+$ and $Ta^+$,[114,125] as well as $Mo^+$,[157] also mainly form multiple dehydrogenation products from $i$-$C_4H_{10}$ and *neo*-$C_5H_{12}$, and the CID spectra of the $NbC_4H_8^+$ complex formed from $i$-$C_4H_{10}$ are different from those of Nb(butadiene)$^+$, just as in the case of $Y^+$ and $La^+$.[114] The only significant C–C cleavage product is due to loss of $CH_4/2H_2$ observed in the reaction of $Ta^+$ with neopentane.[114,125] In an ion-beam experiment, the reactions of $Ru^+$, $Rh^+$, and $Pd^+$, each possessing 0.5 eV of kinetic energy, with several branched alkanes have been studied.[119] While $Ru^+$ and $Rh^+$ behave quite similar, $Pd^+$ is slightly different. With $i$-$C_4H_{10}$, the former two ions generate mainly $H_2$ and $2H_2$, and by deuterium labeling the single dehydrogenation has been shown to be mainly a 1.2 elimination, albeit with ca. 20% scrambled products observed. $Pd^+$ in a specific 1.2 elimination exclusively forms the single dehydrogenation product. With *neo*-$C_5H_{12}$, $Pd^+$ generates exclusively methane while with the other two ions, in addition, multiples of $H_2$ as well as $CH_4/H_2$ are observed.[119] The $RhC_4H_8^+$ ion formed from $i$-$C_4H_{10}$ has been formulated as a hydrido–metal–2-methylallyl complex according to H/D exchange experiments with $D_2$ in an FTICR instrument.[111] While branched alkanes such as 2-methylbutane and 2,3-dimethylbutane are only doubly dehydrogenated by $Rh^+$ and no C–C cleavage products arise, alkanes which lack $\beta$-hydrogen atoms after insertion of $Rh^+$ into certain C–H bonds, e.g., neopentane and neohexane, do indeed also produce methane and methane combined with $H_2$. This has been explained with carbon skeleton rearrangements in cases where $\beta$-H shifts are impossible.[111] As with linear alkanes, $Au^+$ reveals an unique behavior that is completely different from the other transition-metal ions studies so far.[11] Hydride abstraction is observed for $i$-$C_4H_{10}$ and, quite unusual, methanide abstraction leading to $AuCH_3$ and $C_4H_9^+$ is the exclusive reaction with *neo*-$C_5H_{12}$.

In the case of the lanthanide ions, $Pr^+$ and $Eu^+$, just as with the linear alkanes, only form adduct complexes with branched alkanes while $Gd^+$ induces (multiple) dehydrogenations as well as $CH_4$ loss in combination with dehydrogenations.[103] The dehydrogenation and the also observed $Gd(CH_3)_2^+$ formation from $(CH_3)_3CD$ are unspecific, so unfortunately no further mechanistic conclusions could be gained.[103]

## D. Cycloalkanes

Cycloalkanes have been studied relatively thoroughly as insertions of the metal ions into C–C bonds will give rise to metallacycles[198] for these substrates. Especially cyclopropane is of particular interest in that respect as the inherent ring strain weakens the C–C bonds and should favor insertions to form metallacyclobutanes. Metallacyclobutanes are proposed as intermediates for olefin metathesis,[199] for the cyclopropanation of alkenes,[200] in transition-metal-catalyzed rearrangements of strained carbocyclic rings,[201] for the polymerization of alkenes by Ziegler–Natta catalysts,[202] and in Fischer–Tropsch synthesis.[203] Therefore they have formed the object of many theoretical[96,97e,204] and experimental studies in traditional organometallic chemistry. An ever-increasing number of metallacyclobutanes has been isolated and characterized since the discovery of the first platinacyclobutanes,[205] and today examples are known for several different metals.[206]

Yet, $Fe^+$, $Co^+$, as well as $Ni^+$ are unreactive with cyclopropane; under ICR conditions no exothermic products are observed.[156,207] The *endothermic* reaction to metal alkylidenes (metal carbenes) and ethene (eq 35) has been studied, however, for several metal ions in ion-beam instruments, i.e., for $Cr^+$,[208] $Mn^+$,[189] $Co^+$,[209–211] $Ni^+$,[211,212] and $Cu^+$,[211] and $Co^+$ in an FTICR instrument as well.[341,213] The reaction in eq 35 has been

$$\mathrm{M^+ + c\text{-}C_3H_6 \rightarrow M^+{=}CH_2 + C_2H_4} \qquad (35)$$

used to derive $D°(\mathrm{M^+{-}CH_2})$ data, which can be compared to those from other reactions, e.g., from eqs 5 or 11, to ensure that no activation barriers in excess of the endothermicity are present. Formation of the metal alkylidenes is explained by the mechanism in Figure 11. The so far generally accepted mechanism assumes C–C insertion to form the metallacyclobutane **33**, which, in analogy to conventional organometallic chemistry,[198,199,206a] cleaves to afford **34** that decomposes to the alkylidene **35**[93d,f,94c,109g,144] and ethene. Recently, this mechanism has been questioned by Armentrout and co-workers who argue that the conversion of **33** to **34** is a symmetry-forbidden [2 + 2] reaction; rather, these authors favor the alternative pathway via the radical

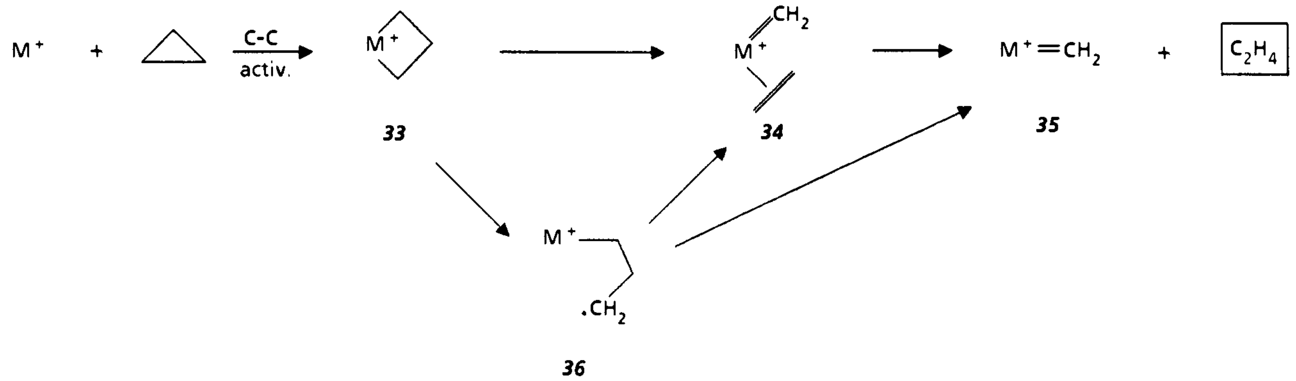


**Figure 11.** Generalized mechanism for the formation of alkylidene ions from the reaction of transition-metal ions $M^+$ with cyclopropane.

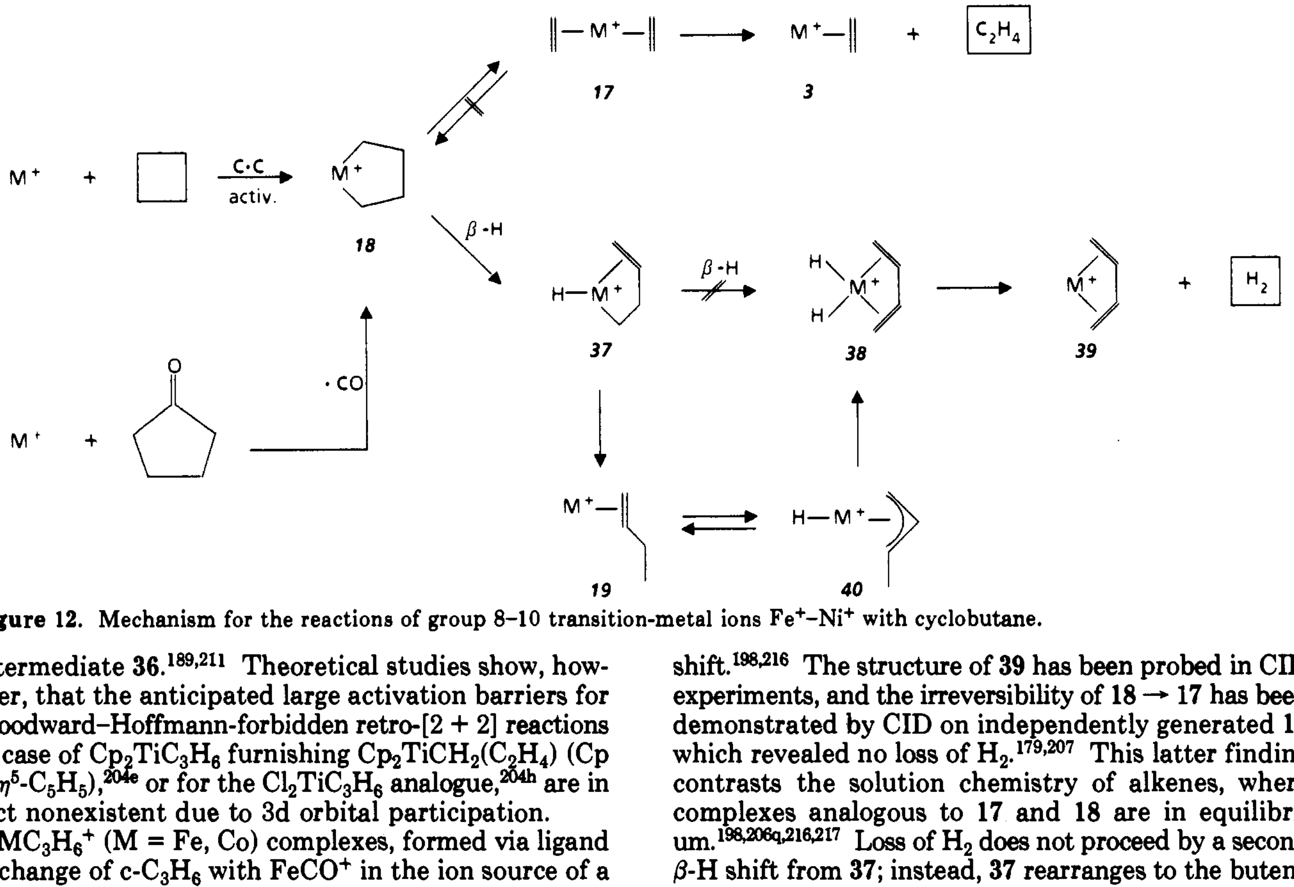


**Figure 12.** Mechanism for the reactions of group 8–10 transition-metal ions $Fe^+$–$Ni^+$ with cyclobutane.

intermediate 36.[189,211] Theoretical studies show, however, that the anticipated large activation barriers for Woodward–Hoffmann-forbidden retro-[2 + 2] reactions in case of $Cp_2TiC_3H_6$ furnishing $Cp_2TiCH_2(C_2H_4)$ (Cp = $\eta^5$-$C_5H_5$),[204e] or for the $Cl_2TiC_3H_6$ analogue,[204h] are in fact nonexistent due to 3d orbital participation.

$MC_3H_6^+$ (M = Fe, Co) complexes, formed via ligand exchange of c-$C_3H_6$ with $FeCO^+$ in the ion source of a sector-field instrument, apparently behave differently. While $FeC_3H_6^+$ possesses the stable ferracyclobutane structure **33**, the analogous cobaltacyclobutane at least partly rearranges to the more stable cobalt–propene structure **13**.[214] The same result is obtained for the $MC_3H_6^+$ ions (M = Fe–Ni) formed by decarbonylation of cyclobutanone; here as well the cobalta- and nickelacyclobutane ions rearrange (see section VII.C).

In contrast to their behavior toward c-$C_3H_6$, $Fe^+$, $Co^+$, and $Ni^+$ do undergo exothermic reactions with c-$C_4H_8$.[180,207,209] The losses of $H_2$ and $C_2H_4$ proceed via initial C–C insertion furnishing **18** (Figure 12), which decomposes either by symmetric ring cleavage and loss of ethene from **17**, or by a β-hydrogen shift which eventually leads to the butadiene complex **39** and molecular hydrogen. Decompositions of metallacyclopentanes by symmetric cleavage are well-precedented in conventional organometallic chemistry;[215] similarly, the transformation **18** → **37** → **19** finds its parallel in the reductive elimination of alkenes from metallacyclopentanes, which also proceed by initial β-H shift.[198,216] The structure of **39** has been probed in CID experiments, and the irreversibility of **18** → **17** has been demonstrated by CID on independently generated **17** which revealed no loss of $H_2$.[179,207] This latter finding contrasts the solution chemistry of alkenes, where complexes analogous to **17** and **18** are in equilibrium.[198,206q,216,217] Loss of $H_2$ does not proceed by a second β-H shift from **37**; instead, **37** rearranges to the butene complex **19**. In **19**, an allylic C–H bond is activated, and the resulting intermediate **40** is not only the precursor to **38**, but also serves to equilibrate the hydrogen atoms of the $C_4H_8$ moiety. Evidence for this comes from deuterium-labeling studies, employing cyclopentanone-α,α′-$d_4$, which, via decarbonylation, also yields **18** (see above and below). CID on the thus generated $d_4$-labeled **18** shows complete equilibration of all hydrogen atoms, but exclusive loss of $C_2H_2D_2$.[207,218]

The gas-phase chemistry of cyclopentane with $Fe^+$–$Ni^+$ parallels that of its lower homologue; while $Fe^+$ mainly dehydrogenates c-$C_5H_{10}$, $Co^+$ and $Ni^+$ additionally produce significant amounts of $C_2H_4$ and $C_3H_6$.[76,156,179,180,207,209,218,219] For $Co^+$, methane is also a minor product.[207,209,218] The presumed mechanism, presented in Figure 13, has been substantiated with several mass spectrometric techniques. Kinetic energy release distributions (KERD's) have been employed to show that the dehydrogenation (not shown in the figure) for $Fe^+$[219b] and $Co^+$[76] proceeds as a simple 1.2 elimination, i.e., without preceding C–C cleavage, and

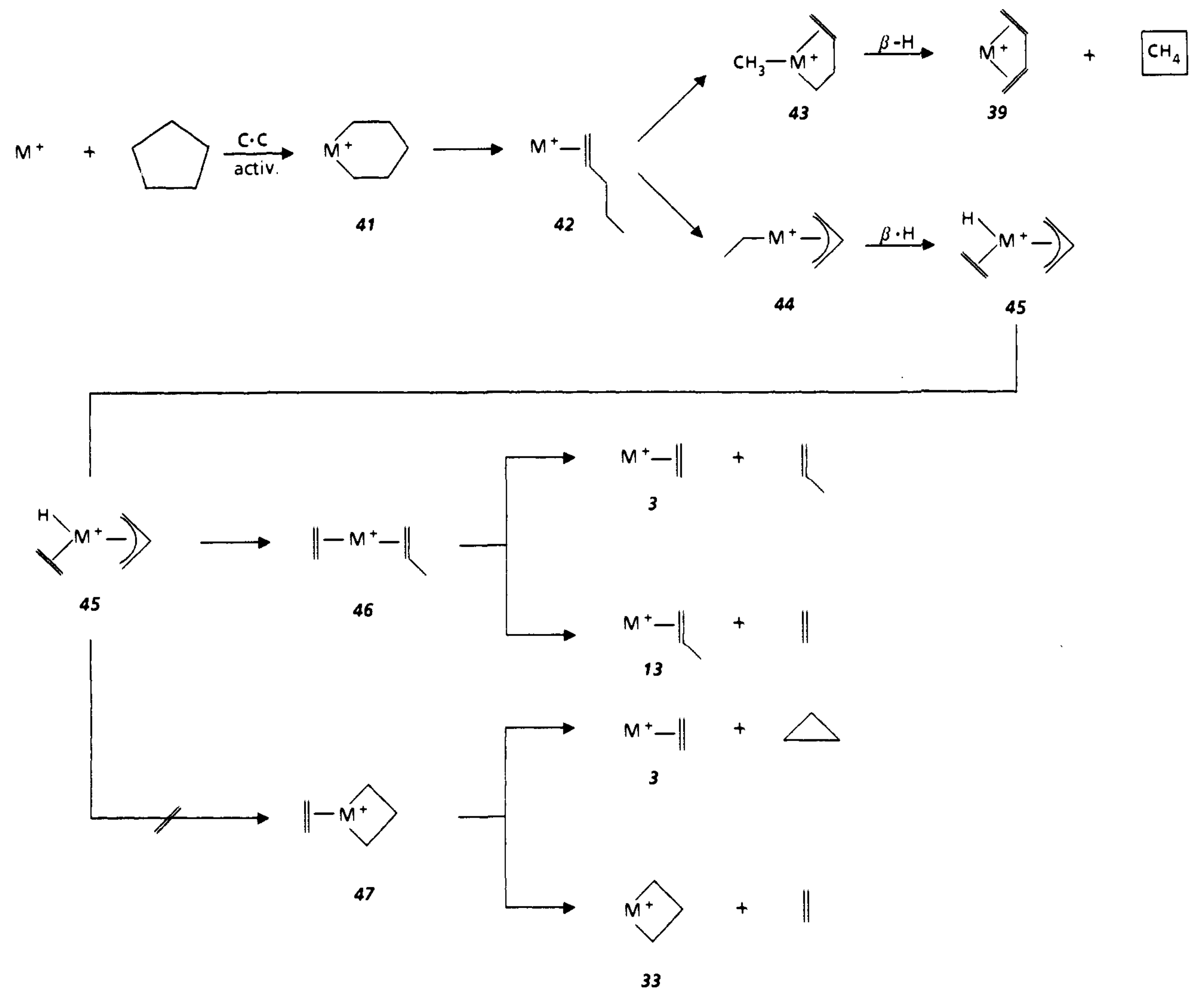


**Figure 13.** Mechanism for the reactions of group 8–10 transition-metal ions Fe$^+$–Ni$^+$ with cyclopentane.

for Fe$^+$ the same could be demonstrated by comparison with reference CID spectra.[179] The remainder of the products arises from initial rearrangement to an acyclic pentene complex, most likely via initial C–C insertion. The isomerization of the metallacyclohexane **41** to **42** might well be achieved analogous to **18** → **19** in Figure 12. 1-Pentene[207,218,219a] as well as 2-pentene[76] have been suggested for the acyclic intermediate en route to $CH_4$, $C_2H_4$, and $C_3H_6$, based on KERD[76,219a] and CID experiments.[207,218]

The identity of the $C_3H_6$ neutral which is lost, as well as the structure of the $CoC_3H_6^+$ ion left behind after the loss of $C_2H_4$, have been elucidated further. The metal-bound hydrogen atom in **45**, which is produced after allylic C–C insertion and β-H shift from **42**, could be transferred to one of the outer, or to the central, carbon atom(s) of the allyl ligand; the latter opens up the possibility of cyclopropane elimination and cobaltacyclobutane formation. While on energetic grounds, by using estimated binding energies of the intermediates, the elimination of c-$C_3H_6$ can already be discarded,[209] the KERD data in addition convincingly demonstrates that exclusively propene is lost and also retained in the $CoC_3H_6^+$ complex.[76,219a] Thus, **46** is an intermediate and hence, phase-space theory could be used to derive $D°(Co^+\text{–propene})$ and $D°(Co^+–C_2H_4)$ dissociation energies.[76,219a] Interestingly, $Co(C_5H_{10})^+$ complexes, formed directly from Co$^+$ and 1-pentene, and therefore containing more internal energy, show a composite curve for the $C_3H_6$ elimination, demonstrating that propene *and* cyclopropane are lost.[214,219a]

Cyclohexane is dehydrogenated up to three times by Fe$^+$,[42g,156,179,207,218,219b] Co$^+$,[33z,76,207,209,218] and Ni$^+$,[180,207,218] the final products being benzene complexes. Small amounts of C–C cleavage products are also observed for Co$^+$ and Ni$^+$.[33z,180,207,209,218] Methylcyclopentane and -hexane have also been studied with Fe$^+$–Ni$^+$, but this resulted only in loss of methane combined with dehydrogenations.[156,180,207] $^2$H and $^{13}$C labeling showed that the demethanation is a 1.2 process and exclusively involves the methyl groups while single dehydrogenation produces mainly endocyclic double bonds for both substrates reacting with 0.5-eV-Ni$^+$.[180] Fitting the KERD data according to phase-space theory suggests a barrier for the reverse of the single dehydrogenation of cyclopentane and -hexane, i.e., addition of $H_2$ to the cycloalkene complexes.[219b]

The amount of C–H activation by Fe$^+$ in cycloalkanes decreases once again; cyclooctane and cyclononane exclusively form C–C cleavage products.[35i] This has been rationalized by assuming linear C–Fe$^+$–C intermediates; smaller cycloalkanes are unable to accomodate the hereby induced ring strain and hence only produce C–H activation products.

$Sc^+$,[42g,113] $Ti^+$,[156] and $V^+$ [105,112] mainly give rise to (multiple) dehydrogenations in their reactions with several cycloalkanes and show exothermic reactions even with cyclopropane, producing mainly $H_2$ and smaller amounts of $CH_4$. All of the second- and third-row metal ions studied also react with c-$C_3H_6$; here as well, dehydrogenation is the dominant reaction observed for $Y^+$,[113] $Nb^+$,[114] $Ta^+$,[114] $Mo^+$,[157] $Rh^+$,[111,140] and the lanthanide ion $Gd^+$.[103] The $MC_3H_4^+$ ions that arise have been formulated as allene complexes, hence ring-opened species that arise from metallacyclobutane decompositions. A different behavior was noted for $La^+$, that mainly produced $LaCH_2^+$ ions with c-$C_3H_6$,[113] and $Au^+$, that formed the hydride-abstraction product and an $AuC_3H_6^+$ adduct complex proposed to have the metallacyclobutane structure.[11]

In reactions with other cycloalkanes, most of the heavier ions once again demonstrated their preference for C–H activation; multiple dehydrogenations and losses of small alkanes and alkenes together with $H_2$ were the only processes observed.[103,111,113,114,157] Notable is an obvious inability of $La^+$, in contrast to its congener $Y^+$, to insert into C–C bonds; e.g., double dehydrogenation of c-$C_4H_8$ produces the cyclobutadiene complex, which in part decomposes into acetylene units (eq 36).[113] The same mechanism has been postulated for $Sc^+$,[341,220] while $Y^+$ is believed to initially insert into a C–C bond.[113] $NbCp^+$ ions are formed from the reactions of

$$Nb(c\text{-}C_4H_4)^+ \rightarrow NbC_2H_2^+ + C_2H_2 \qquad (36)$$

$Nb^+$ with c-$C_5H_{10}$, one of the rare cases where a *radical is lost* in an exothermic gas-phase organometallic reaction.[114] Highly unsaturated hydrocarbons are produced by $Nb^+$ and $Ta^+$ (eqs 37 and 38), but unfortunately no further information concerning their structure is available.[114]

$$M^+ + c\text{-}C_3H_6 \rightarrow MC_3H_2^+ + 2H_2 \qquad (37)$$

$$M = Nb,\ 65\%;\ M = Ta,\ 81\%$$

$$M^+ + c\text{-}C_4H_8 \rightarrow MC_4H_2^+ + 3H_2 \qquad (38)$$

$$M = Nb,\ 9\%;\ M = Ta,\ 14\%$$

As with most other alkanes, $Au^+$ only forms neutral AuH from c-$C_5H_{10}$ and c-$C_6H_{12}$.[11]

## *V. Reactions of Bare Metal Ions with Unsaturated Hydrocarbons*

### A. Alkenes

Ethene and propene are unreactive with late transition metal ions. $Cr^+$,[208] $Fe^+$,[221] $Co^+$,[341,210,213,222,223] and $Ni^+$ [33m,r,222] only form adduct complexes under ICR conditions and show no exothermic reactions in ion-beam experiments. High-energy CID upon $FeC_2H_4^+$ or $FeC_3H_6^+$, formed in the ion source of sector-field instruments from the reaction of $Fe(CO)_x^+$ with the alkenes, reveals that the ligands are present as intact molecules, with $Fe^+$ being the by far dominant product ion in the spectra.[74,179] As shown for other substrates, high abundances of ligand-detachment signals, i.e., loss of the complete ligand to form $M^+$, in CID or metastable-ion spectra generally reveal the inability of the metal ion $M^+$ to activate the substrate.[224] The endothermic reactions in eqs 39 and 40 have been studied in ion-beam instruments to derive BDE's for $V^+$,[160] $Cr^+$,[208] $Co^+$,[210,223] and $Ni^+$.[212] The threshold for $CoCH_2^+$ formation has also been determined with an FTICR instrument.[341,213] The metal–alkylidene product ion is

$$M^+ + C_2H_4 \rightarrow MCH_2^+ + CH_2 \qquad (39)$$

$$\rightarrow MH^+ + C_2H_3 \qquad (40)$$

believed to be formed via a direct abstraction mechanism since the intermediacy of a bis(alkylidene) ion, $M(CH_2)_2^+$, seems quite unlikely.[208] Interestingly, fluorine substitution substantially weakens the metal–alkylidene bond energy.[212]

Exothermic reactions of ethene and propene are, however, observed for early first row and heavier transition metal ions as well as for lanthanides. The dehydrogenation of ethene by $Sc^+$ generates an acetylene complex as evidenced by CID and by the exclusive loss of HD in the reaction with $CH_2CD_2$.[341,220] $V^+$ is also observed to exothermically dehydrogenate ethene.[160,161b] The $ScC_3H_4^+$ ion formed in the reaction with propene exchanges up to four hydrogen atoms with $C_3D_6$ and has therefore been formulated as an allene complex;[341,220] yet, thermochemical arguments are in favor of a propyne complex.[164] Although the reactions of $Ti^+$ with $C_2H_4$ and $C_3H_6$ have not been studied directly, there is indirect evidence available from ion-beam experiments with *ethane* and *propane* that at least ethene can be exothermically dehydrogenated.[152]

Exothermic dehydrogenations of ethene and propene have further been observed for $Nb^+$,[114] $Ta^+$,[225] $Os^+$,[124] $Pr^+$,[103] which was unreactive with alkanes, and $Gd^+$.[103] Interestingly, the $Nb(C_2H_2)^+$ complex generated from $C_2H_4$ is observed to react five more times with $C_2H_4$, and, by ligand coupling,[226] finally $Nb(benzene)_2^+$ is formed;[114] $Ta^+$ even reacts sequentially with 10 $C_2H_4$ molecules.[225] $Au^+$ forms only the adduct complex with $C_2H_4$, and with propene, besides $AuC_3H_6^+$, AuH is once again formed.[11]

For the three linear butene isomers, loss of $H_2$ is the exclusive or by far dominating reaction with $Fe^+$–$Ni^+$ and leads to butadiene complexes.[74,179,221-223] This contrasts the behavior of 2-methylpropene (isobutene), which is insofar unreactive with $Fe^+$ as it forms exclusively the adduct complex,[74,179,221] but which is exothermically dehydrogenated by $Co^+$ and $Ni^+$.[222,223] Loss of $H_2$ accounts for 96% of the products for both metal ions; in addition $C_2H_4$ and, for $Ni^+$ only, $CH_4$ are also observed. The nature of the $MC_4H_6^+$ ions (M = Co, Ni) generated from isobutene has been further probed by CID and H/D exchange experiments.[222] CID affords exclusively $M^+$, while four fast and two slow H/D exchanges were observed with $C_3D_6$. An identical behavior was found for the $MC_4H_6^+$ ions generated from 1-butene so that it was concluded that in this case, *too*, butadiene complexes were formed; the mechanism for this rearrangement still remains to be established. $FeC_4H_6^+$ from 1-butene could be distinguished from $FeC_4H_6^+$ formed by 30-eV electron impact on (trimethylenemethane)$Fe(CO)_3$ by means of CID, photodissociation, and ligand–exchange experiments.[105]

In an 1981 ion-beam study on the reactions of $Co^+$ with several alkenes, Beauchamp and co-workers were able to present evidence that the insertions of the metal ions into the various bonds do not proceed at random; rather, the double bond directs this addition to the

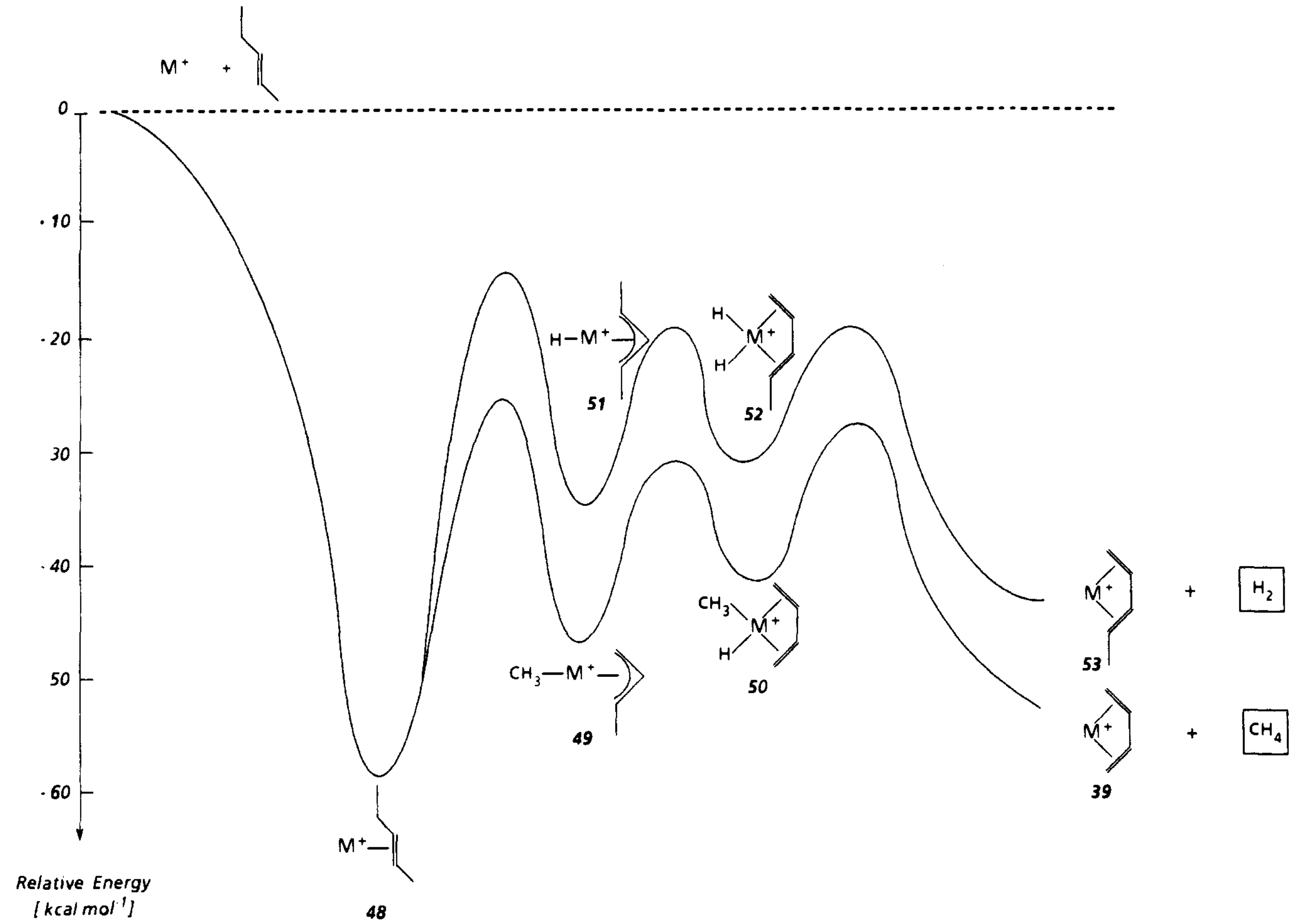


**Figure 14.** Potential energy surface for the reaction of transition-metal ions $M^+$ with 2-pentane (adapted from ref 228).

allylic C–C bond.[223] This proposal was largely based on the study of the six pentene isomers which all generate $H_2$, $CH_4$, $C_2H_4$, and $C_3H_6$ upon reaction with $Co^+$. The formation of alkadiene complexes by loss of $H_2$ and $CH_4$ is favored for all pentenes, except for 1-pentene which is preferentially cleaved to $C_2H_4$ and $C_3H_6$. The dominant loss of ethene from 1-pentene was explained by initial allylic C–C insertion, **42** → **44** (see Figure 13), β-hydrogen transfer, **44** → **45**, and rearrangement to the diligated complex **46**, which mainly loses the smaller alkene, furnishing **13**. The loss of ethene and propene from the other pentenes is explained by initial isomerization to the 1-pentene complex **42**. $H_2$ and $CH_4$ may be formed by allylic C–H or C–C insertion followed by β-hydrogen shift and reductive elimination from all isomeric pentenes, either directly or after isomerization by double-bond migration.[223]

Subsequently, the chemistry of small alkenes has been studied in more detail by several groups with $Fe^+$,[179,219b,221,227] $Co^+$,[214,219a,222,227,228] and $Ni^+$,[222,227] and in particular the reactions of 1-pentene have been studied in great depth. In general, the three metal ions once again showed similar reactivity although it could still be noted that the abundance of dehydrogenated products decreased in the row $Co^+ > Fe^+ > Ni^+$.[222] The preferential insertion of $Co^+$ into allylic C–C bonds over allylic C–H bonds, which was already deduced from the early ion-beam experiments, could be convincingly demonstrated and shown to be even highly selective when infrared multiphoton dissociation (IRMPD) is employed as a means to activate stable $Co(C_5H_{10})^+$ adducts, formed by ligand-exchange processes in an ICR instrument.[228] Thus, while the pentene isomers gave rise to rather similar product distributions in the ion-beam experiment, IRMPD gives exclusively $C_2H_4$ from $Co(1\text{-pentene})^+$ and exclusively $CH_4$ from the other isomers. Yet, these pentenes could still easily be distinguished as the photodissociation spectra were found to be different. Known thermochemical data combined with the results of the IRMPD experiments were then used to derive the potential-energy surfaces for the reactions. An example is given in Figure 14 for 2-pentene, demonstrating that the production of $CH_4$ is the lowest energy pathway for this system.[228]

As already mentioned above (section IV.D), the *direct* reaction of $Co^+$ with 1-pentene gives rise to a *bimodal* kinetic energy release distribution for the loss of $C_3H_6$, with a high-energy component for loss of cyclopropane and a low-energy component for loss of propene.[214,219a] $Fe(1\text{-pentene})^+$ gave a similar result with a broadened KERD curve.[214] Fitting the kinetic energy release distributions for the loss of $C_2H_4$ to the experimental data allowed the determination of the branching ratio between **46** and **47**, respectively **13** and **33** (Figure 13). Good fits were obtained if it was assumed that 67% cobaltacyclobutane and 50% ferracyclobutane ions were formed, corresponding to 33% and 50% propene complexes, respectively. Reductive elimination of c-$C_3H_6$ from metallacyclobutanes is a common decomposition mode in the condensed phase, too.[199,206a,229] KERD data for the dehydrogenation of cyclopentene and -hexene was used to derive bond dissociation energies for cy-

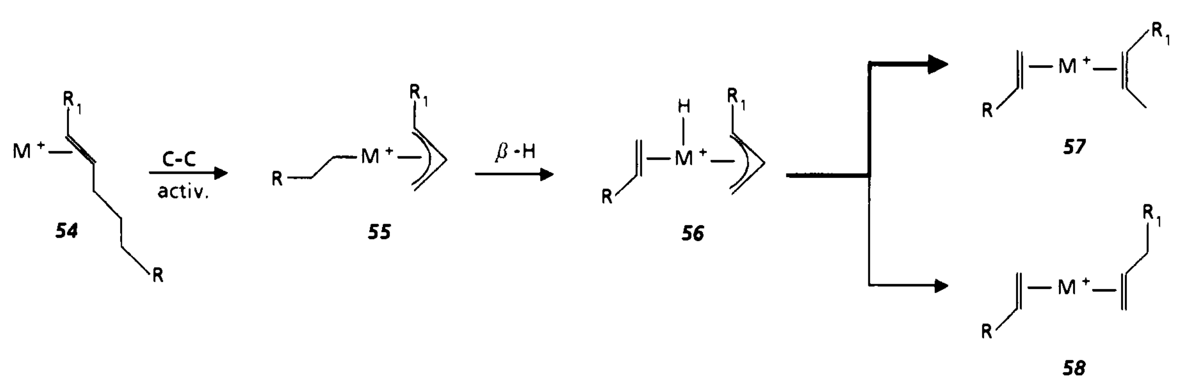


**Figure 15.** Generalized mechanism for the allylic cleavage of alkenes by transition-metal ions $M^+$.

clopentadiene and 1,3-cyclohexadiene.[219b] No barrier for the reverse process was observed for the two 1,3-dienes, contrary to the alkene complexes,[45,75,76] but in line with the observation of H/D exchange in $FeC_5H_6^+$ using $D_2$.[207]

Gross and co-workers observed that the products of the allylic C-C insertions were dominating over the products of double-bond isomerizations via reversible allylic C-H insertion in the high-energy CID spectra of $Fe(alkene)^+$ complexes.[179] After isomerization to the bis(alkene) complexes **57** and **58**, according to the general mechanism in Figure 15, the stronger bound alkene, i.e., the *larger* one, is preferentially retained so that loss of the smaller alkene corresponds to the base peak in the CID spectra.[179] The analytical utility of this finding was recognized and applied to locate the positions of the double bonds in several decenes, fatty acid esters and alkenyl acetates,[230] as well as for mixture analysis.[231] That indeed **57** *and* **58** were formed could be shown by high-energy CID, which revealed that 1-alkene as well as 2-alkene complexes were produced upon loss of $RCH{=}CH_2$; **57** prevails, however.[232]

Only few studies are available which deal with the reactions of other metal ions toward alkenes. As with alkanes, $Cr^+$ and $Mn^+$ were found to be unreactive,[157,227] and $Zn^+$ is also not observed to activate any bonds, but it is seen to undergo charge transfer to 1-pentene instead.[227] In light of the latter findings, it is surprising that $Cu^+$, also unreactive with alkanes, was observed to react similar to $Fe^+$–$Ni^+$, with $C_2H_4$ being the dominant product in the reaction with 1-pentene besides $H_2$, $CH_4$, and $C_3H_6$.[227] With some other alkenes, $Cu^+$ also activates predominantly the allylic C-C bond. $Ti^+$,[152,227,233] $V^+$,[105,227] $Nb^+$,[114] $Mo^+$,[157] as well as $Gd^+$ and $Pr^+$[103] mainly give rise to (multiple) dehydrogenations and combined losses of $H_2$ with $CH_4$ or $C_2H_4$ in their reactions with several alkenes, whereas $Eu^+$ is unreactive.[103] The structure of the multiple dehydrogenation products is mostly unknown, formation of en-yne systems, dehydrocyclizations, and C-C cleavages to afford bis(alkyne) complexes have been proposed.

Some more detailed information is available for $Sc^+$, which has been studied with several linear, branched, and cyclic alkenes.[341,164,220] As with the other early and higher row transition-metal ions, $Sc^+$ mainly dehydrogenates alkenes, but small amounts of C-C cleavages are also observed.[341,220] The relative importance of the C-C cleavage products increases with branching and with increased chain lengths. $H_2$ can be produced either by insertion into an allylic C-H bond followed by β-H shift from a homoallylic position or vice versa; allylic C-H activation precedes, as is indicated by the predominant loss of $CH_4$ from 2,2-dimethylbutene, which lacks allylic C-H bonds. $ScC_4H_6^+$ ions are produced from linear butenes as well as from isobutene; the former ions are butadiene complexes ($ScBD^+$), while in the latter reaction the trimethylene methane complex ($ScTMM^+$) is formed. This is evident from CID experiments, where $ScTMM^+$ shows slightly less loss of $H_2$ as does $ScBD^+$, from ion/molecule reactions with $C_6H_6$ and $CH_3CN$, where $ScBD^+$ yields exclusively condensation and $ScTMM^+$ 50% condensation and 50% dehydrogenation, and finally from H/D exchange experiments with $C_3D_6$, where $ScBD^+$ undergoes four rapid and two slow and $ScTMM^+$ six slow exchanges. It is interesting to compare this result to the analogous experiments with $Co^+$ and $Ni^+$, where exclusively $MBD^+$ complexes were formed from all the butenes (see above). Unfortunately, scrambling is observed in the dehydrogenation of isobutene-$d_3$, so that no mechanistic conclusions could be gained. Cyclic alkenes undergo exclusive dehydrogenation, but the CID spectra of the products are different from those of the same formula produced from acyclic precursors. Different H/D exchange results are also obtained which both reveals that dehydrocyclization can be excluded for the multiple $H_2$ losses from acyclic alkenes.[341,220] In contrast, thermochemical data was used to propose a metallacyclopentadiene structure for the $ScC_4H_4^+$ ion from dehydrogenation of *cis*- and *trans*-butene.[164]

## B. Alkynes

The gas-phase chemistry of alkynes with transition-metal ions resembles that of the alkenes; in analogy to the *allylic* C-C cleavage that is observed in the high-energy CID spectra of $Fe(alkene)^+$ complexes, for the $Fe(alkyne)^+$ ions cleavage of the *propargylic* C-C bond is the dominant fragmentation pathway. This was used to distinguish the isomeric octynes.[230,231] CID studies revealed the identity of the two cleavage products by comparison with reference spectra from complexes that were formed by ion/molecule reactions in the ion source.[230,232] While exclusively 1-alkenes were produced by the β-hydrogen shift from the insertion product **60** (Figure 16), the termination of this very hydrogen atom can be either the C(1) or the C(3) position of the propargylic fragment, forming 2-alkynes or 1,2-alkadienes, respectively; formation of allenes, i.e., intermediate **62**, is favored, though.

Deviations from the generalized mechanism in Figure 16 seem to occur in cases when the chain length of the

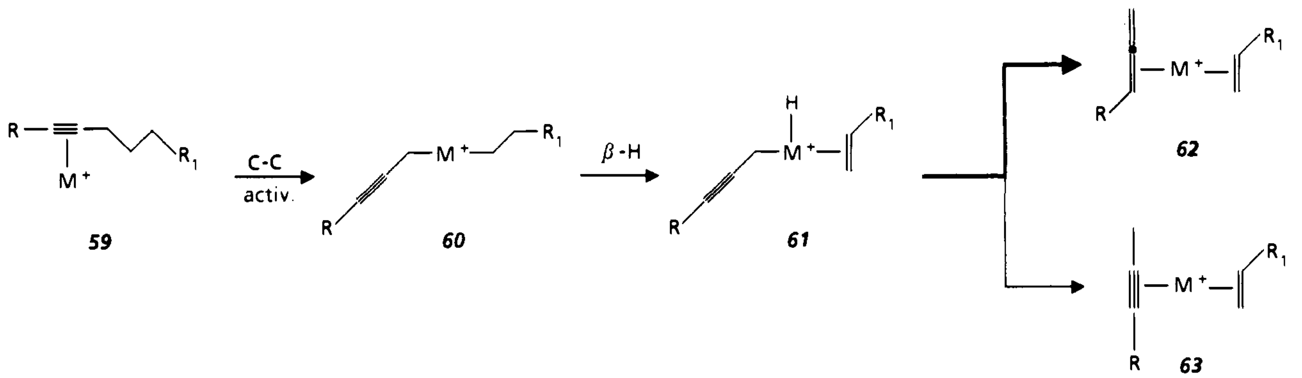


**Figure 16.** Generalized mechanism for the propargylic cleavage of alkynes by transition-metal ions $M^+$.

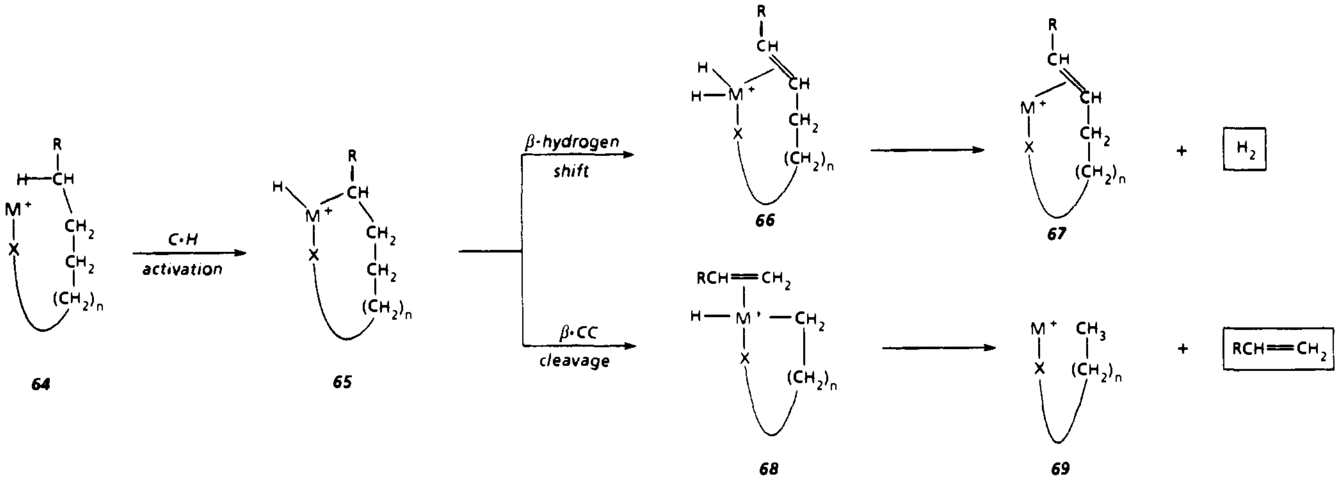


**Figure 17.** Generalized scheme for the remote functionalization of distant methyl or methylene groups by bare transition-metal ions $M^+$, complexed to the functional group X of the organic substrate.

alkyne is not sufficient to permit the insertion of $Fe^+$, or if the alkyl fragment in **60** lacks β-hydrogen atoms. So, although $Fe(propyne)^+$ can be distinguished from $Fe(allene)^+$, both complexes undergo mainly ligand detachment, i.e., reformation of $Fe^+$, upon high-energy CID;[232] hence, the ligands are not activated.[224] The same applies to several $Fe(C_4H_6)^+$ complexes, which are, however, believed to be partly in equilibrium with each other.[232] In line with Figure 16, $Fe^+$ forms ethene and $C_3H_4$, probably allene, from 1-pentyne, but for 2-pentyne no β-hydrogen atoms are available after propargylic insertion, so that $Fe(2\text{-pentyne})^+$ therefore first isomerizes to pentadiene complexes, which subsequently can decompose to $FeC_2H_2^+$ and $FeC_3H_6^+$. Similarly, 3-hexyne first isomerizes to 2-hexyne, for which loss of $C_2H_4$ is possible.[232]

Much more detailed insight about alkyne activation by late transition metal ions was gained by employing $^2H$-labeled compounds. In doing so, it was possible to confirm the general mechanism (Figure 16) for the reactions of $Fe^+$ with 3-octyne; in the case of 2-octyne, reversible processes that led to H/D scrambling prevented any mechanistic conclusions with regard to Figure 16.[234] Yet, for the loss of $H_2$ and $C_2H_4$ in the $Fe^+$/2-octyne system, the mechanism could be determined, and it became evident that another, much more general mechanism applies, viz. remote functionalization.[234,235]

*Remote functionalization* was first discovered for nitriles in 1987,[236] but since then the generality of this mechanism has been amply demonstrated for a variety of different substrates,[47] inter alia alkynes. The name was chosen following Breslow's concept of biomimetic synthesis;[237] Figure 17 presents the generalized mechanism for an unspecified functional group X. Complexation of the metal ion $M^+$ to that functional group will effectively prevent (on geometric grounds) any insertion into bonds within the proximity of X. Instead, only remote bonds can be reached, e.g., by folding back of the alkyl chain. For substrates with a not-too-long alkyl chain it is exclusively a C–H bond of the terminal $CH_3$ group that is activated (R = H), and the so-formed intermediate **65** will then undergo competitively either β-hydrogen shift or β-CC cleavage. Reductive elimination of $H_2$ from **66** furnishes the ω-unsaturated complex **67**, while loss of $C_2H_4$ (R = H) from **68** yields the shortened (by two methylene groups) ligand in **69**.

For 2-octyne ($X = CH_3C{\equiv}C{-}$), and maybe also for 3-octyne, $H_2$ and $C_2H_4$ are formed by remote functionalization,[234,235] as evidenced by the labeling results and by CID, which was used to reveal the identity of the dehydrogenation product **67** with the $Fe^+$ complex of 1-octen-6-yne, formed independently in the ion source.[235] The formation of $C_2H_4$ from $Fe(4\text{-octyne})^+$, which is the almost exclusive mode of decomposition for this complex, might be described by both mechanisms, via the traditional propargylic insertion in Figure 16,[230,232] or by remote functionalization (Figure 17). The two possibilities differ in their order of C–H/C–C activation steps. The observed isotope effects—no primary kinetic isotope effect for the C–H breaking step and a secondary kinetic isotope effect of $k_H/k_D = 1.1$ per deuterium for the loss of ethene—together with the absence of scrambled products unambiguously shows that C–H insertion must precede the C–C cleavage. As no isotope effect is observed, any β-H shift in the C–C insertion product should require less energy than the loss of the alkene ligand and should therefore be reversible, which it is not. Hence, it can be concluded that $C_2H_4$ is formed via remote functionalization for 4-octyne as well.[234,238]

It is informative to compare this result with those for the other late first row ions, which all give rise to loss of ethene upon reaction with 4-octyne. $^2H$ labeling reveals that except for $Mn^+$, where H/D exchange processes prevail,[239–241] $Cr^+$ through $Cu^+$ produce $C_2H_4$ exclusively from the $\omega$ and $(\omega - 1)$ positions.[240] Thus, kinetic isotope effects (KIE's) could be determined and three types of metal-ion-dependent reactivity emerged. $Fe^+$ is the only example where it is not the C–H activation that is rate-determining, but the ethene loss, for which an isotope effect is observed.[234,238,240,241] For $Cr^+$ [240,241] and $Cu^+$ [240] the reversed situation is encountered; the activation of the C–H bond is rate-determining as a primary KIE is observed, but on the other hand no secondary KIE is found for the loss of ethene. The third category is formed by $Co^+$ and $Ni^+$, for which *both* processes, C–H activation *and* ethene loss are rate-determining.[240] An interesting inverse relationship between the magnitude of the primary KIE for C–H activation and the $D°(M^+–H)$ bond dissociation energies could be noted in the course of this study: weak $M^+$–H bonds give rise to large isotope effects and vice versa.[240]

The reactions of $Cr^+$ [240,241] and $Mn^+$ [239–243] with 4-octyne have been studied quite thoroughly by using $^2H$ labeling; the observed reactivity in the metastable-ion studies is remarkable in view of the unreactivity of both metal ions with alkanes (see section IV). It was therefore carefully ensured by means of charge stripping[244] and high-resolution translational energy loss spectroscopy[122] experiments that indeed ground-state $Cr^+$ is formed under the high-pressure chemical ionization conditions employed;[245] furthermore, under FTICR[71] and ion-beam[43i,246] conditions, similar reactivity could be noted. In addition to the already mentioned loss of $C_2H_4$, Mn(4-octyne)$^+$ shows in its metastable-ion spectrum signals due to several other losses (eqs 41–45). The hydrogen stems to 83% from

$$\mathrm{Mn(4\text{-}octyne)^+ \rightarrow MnC_8H_{12}^+ + H_2\ (23\%)} \quad (41)$$

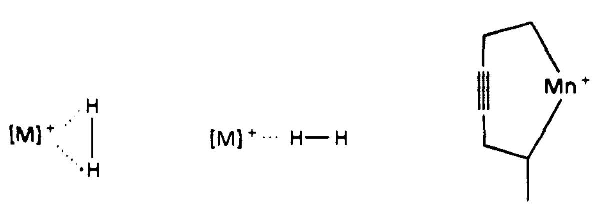
$$\mathrm{\rightarrow MnC_7H_{10}^+ + CH_4\ (7\%)} \quad (42)$$

$$\mathrm{\rightarrow MnC_6H_{10}^+ + C_2H_4\ (40\%)} \quad (43)$$

$$\mathrm{\rightarrow MnC_5H_8^+ + C_3H_6\ (19\%)} \quad (44)$$

$$\mathrm{\rightarrow Mn^+ + C_8H_{14}\ (11\%)} \quad (45)$$

dehydrogenation across the C(1)–C(2) bond and to 17% from across the C(2)–C(3) bond.[241–243] An *average* isotope effect of $k_{H_2}/k_{HD} = 1.7$[241,242] or 1.6,[243] respectively, for both processes has been derived from the labeling data. On the contrary, the reaction of $Cr^+$, which also dehydrogenates 4-octyne (68%), results in 22% 1.2 and 78% 2.3 elimination, but with nearly the same isotope effect observed, viz. 1.6 for both processes.[241] From the theory of kinetic isotope effects, the relation of $k_{H_2}/k_{HD}/k_{D_2}$ shows that this has to be due to a symmetric cleavage, where both $M^+$–H bonds are broken at the same time.[241] An interesting corollary of this finding is that the reverse process, oxidative addition of $H_2$ to the metal centers, has to proceed in a "side-on", or parallel fashion, via $[M]^+–\eta^2–H_2$ (**70**), and not "end-on", or perpendicular, via $[M]^+$–H–H (**71**), in line with the theoretical expectations[2a] (Figure 18). Kinetic energy release distributions for the dehydrogenations induced by $Mn^+$ have been used to derive lower binding energies for the resulting complexes.[243] While the demethanation of 4-octyne by $Cr^+$ (5%) proceeds exclusively as a simple 1.2 process,[241] for $Mn^+$ (7%, eq 42) this is only true for 18% of the $CH_4$ formed. 82% are produced in a formal 1.6 elimination, generating the manganese cycloalkyne **72**.[239,241,242]



**70** **71** **72**

**Figure 18.** Parallel or perpendicular approach of $H_2$ to a metal center and structure of the manganese cycloalkyne produced by 1.6 demethanation of 4-octyne.

Rather unusual results have also been reported for the reactions of $Fe^+$ with 1-heptyne. Seventy-eight percent of the unimolecularly generated products are due to loss of $C_3H_6$. MS/MS and collision-induced dissociative ionization (CIDI) experiments[247] are compatible with the generation of a mixture of propene and cyclopropane for the neutrals that are lost.[248] $^2H$ and $^{13}C$ labeling shows that 91% of the $C_3H_6$ *include* the acetylenic carbon atoms, hence three hydrogen atoms were transferred from the butyl chain to the $C_3H_3$ moiety which arises from propargylic insertion of $Fe^+$.[248] This has been discussed as an intramolecular gas-phase variant of the Crabtree–Felkin mechanism[1e,g,u,249,250] for transfer hydrogenations. Ten percent dehydrogenation is also observed in this system and is mainly due to remote functionalization.[251]

C–H activation processes for 2-octyne by several metal ions have also been reported, but H/D scrambling often precluded mechanistic information. Notable are 19% loss of a hydrogen *radical*, H•, for $Ni^+$ and loss of neutral CuH for $Cu^+$, which accounts for 50% of the metastable-ion yield.[251]

The reaction of 3,3-dimethylbutyne (*t*-BuC≡CH, **73**) and its homologue 3,3-dimethylpentyne with $Fe^+$ are the only reported examples for branched alkynes[71,185] (Figure 19). For the latter, the expected behavior, insertions into the propargylic C–$CH_3$ and C–$C_2H_5$ bonds followed by β-H shifts and loss of $CH_4$ and $C_2H_4$ was found, with insertion into the bond to the ethyl group greatly favored. The reaction of $Fe^+$ with *t*-BuC≡CH was different, though. The predicted loss of $CH_4$ was an abundant process in MI, high-energy CID, and FTICR spectra, yet, the main product arose by loss of $C_3H_6$. MS/MS experiments revealed that this did not correspond to loss of an intact molecule, but to the consecutive losses of $CH_4$ and $C_2H_2$. After loss of $CH_4$ according to the usual mechanism, the complex of $Fe^+$ with 2-methyl-1-buten-3-yne (**74**) is formed, still possessing an allylic C–H bond. Insertion into this bond followed by cleavage of the acetylenic C–C bond and rearrangement yields **77**, which then loses ethyne. This

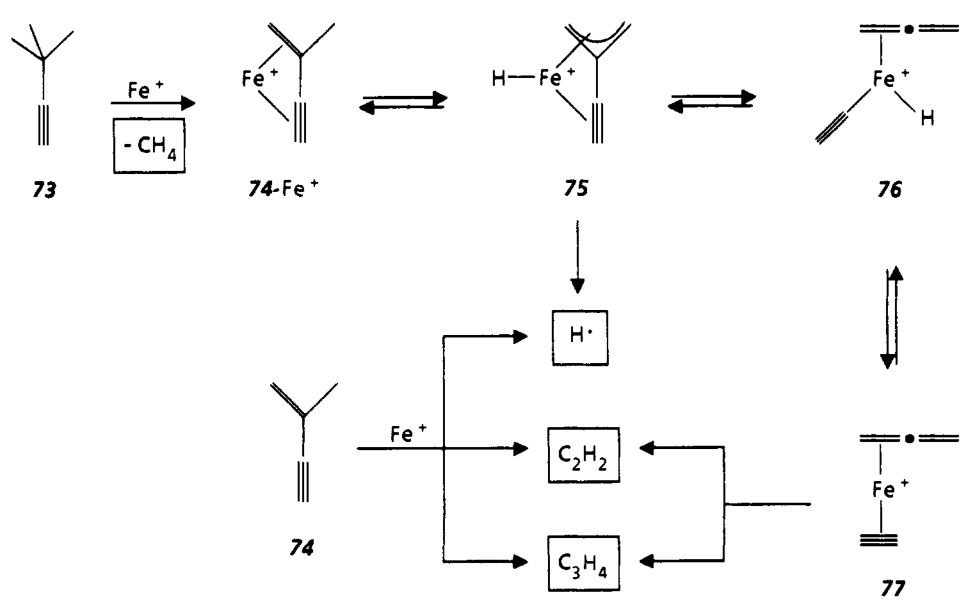


**Figure 19.** Reaction of Fe$^+$ with 3,3-dimethylbutyne (73) and 2-methyl-1-buten-3-yne (74).

mechanism was further substantiated by the direct reaction of 74 with Fe$^+$ which not only afforded $C_2H_2$ as the dominant product, but in addition led to loss of a hydrogen atom and $C_3H_4$, thus demonstrating the lability of the allylic C–H bond and the existence of the mixed complex 77. An identical spectrum was obtained in the MS/MS experiments, and the consecutive losses of $CH_4/H^•$ and $CH_4/C_3H_4$ were also detected in the FTICR study.[71,185] $^2$H labeling revealed the reversibility of the transformation 74-Fe$^+$ $\rightleftharpoons$ 77.[252]

### C. Alkadienes

Most of the studies with alkadienes have been performed in sector-field instruments as either metastable-ion or high-energy CID studies, and the majority of the data has been collected for Fe$^+$, which is unreactive with allene, 1,3-butadiene, and 1,2-butadiene, but induces isomerization of the latter to the 1,3-butadiene complex 39.[232] Loss of $C_2H_4$ from Fe(1,2-pentadiene)$^+$ generates a mixture of propyne and allene complexes; 2,3-pentadiene isomerizes to 1,3- or 1,4-pentadiene, and all of these form $FeC_2H_2^+$ and $FeC_3H_6^+$ by vinylic insertion.[232] Vinylic insertion is also observed for 1,2-hexadiene, albeit in competition with allylic insertion. It was argued that observation of vinylic insertion for allenes is due to the fact that this bond is simultaneously allylic to the other double bond.[232] Various other noncumulated hexadienes fragmented via a common bis(allyl) structure, forming propene and $FeC_3H_4^+$, for which a vinyl carbene structure has been proposed.[232]

The spectra of several octadienes containing conjugated or isolated double bonds were compatible with the conventional allylic insertion, $\beta$-H shift, alkene loss mechanism, except for 2,4-octadiene, which rearranges to 1,3-octadiene before fragmentation.[230,232] Extensive $^2$H and $^{13}$C labeling for several allenes, 4,5-nonadiene and the three isomeric octadienes, showed that the most favored reaction for Fe$^+$ is always the expected allylic C–C cleavage.[253,254] Fe(4,5-nonadiene)$^+$ produces unimolecularly 66% $C_2H_4$ by allylic and 30% $C_3H_6$ by vinylic cleavage; both processes show negligible H scrambling.[253,254] This contrasts the behavior of the octadienes, for which extensive H/D scrambling was observed, due to isomerization processes that did, however, not result in the formation of octynes, but instead afforded other dienes. This tendency for isomerization is much more pronounced for these allenes than for the isomeric alkynes. In addition to the analogous mechanism to Figure 16, remote functionalization is operative, as evidenced by the dehydrogenation of 3,4-octadiene, which affects mainly the $\omega/(\omega - 1)$ pairs.[254]

Ethene loss from 1,7-octadiene complexes of Fe$^+$, Ni$^+$, and Cr$^+$ has also been reported; while Ni$^+$ and Cr$^+$ give rise to H/D exchange processes, the $C_2H_4$ formation for Fe$^+$ (8% of the MI fragments) is to 90% specific.[255] *Double* allylic insertion generates $Fe(C_2H_4)(\eta^3\text{-}C_3H_5)_2^+$, which loses $C_2H_4$ to yield $Fe(\eta^3\text{-}C_3H_5)_2^+$. CID spectra on an isotopomer of this ion reveal that H/D exchange between the two allyl ligands occurs, a process that can be explained by invoking reversible coupling to 1,5-hexadiene.[255] Propene loss from 1,7-octadiene proceeds for Cr$^+$ (15%) slightly more specific than for Fe$^+$ (50%) and Ni$^+$ (69%), which produce $C_3H_6$ according to Figure 15, but with extensive H/D scrambling. Cr$^+$ produces about 60% of the propene by allylic insertion followed by transfer of an *allylic* hydrogen from $C_{(6)}$ and only about 40% by the traditional mechanism.[256]

The reaction of norbornadiene with Co$^+$ and Rh$^+$ has been investigated with an FTICR instrument. Co$^+$ mainly gives rise to the retro-Diels–Alder reaction, affording $C_2H_2$ and $C_5H_6$; Rh$^+$, in addition, yields loss of $H_2$, $C_6H_6$, and $H_2/C_6H_6$.[257]

## *VI. Reactions of Bare Metal Ions with Nitriles and Isonitriles*

### A. Linear Nitriles and Related Compounds

As already described above (section V.B), investigations on the reaction of Fe$^+$ with linear nitriles led to the discovery of the remote functionalization mechanism (Figure 17, M = Fe, X = CN, R = H).[236] In the row of *n*-alkanenitriles, beginning with *n*-PrCN, losses of $H_2$ and $C_2H_4$ were observed, and a dramatic increase with the chain length could be noted.[88b,236] $^2$H and $^{13}$C labeling for some of the nitriles substantiated the

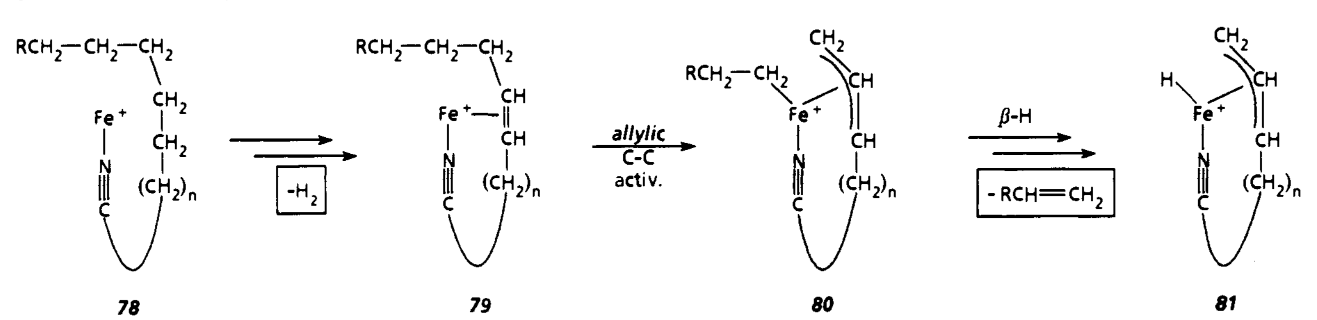


**Figure 20.** Consecutive loss of $H_2$ and alkenes from $Fe^+$ complexes of longer alkanenitriles.

mechanism as both neutrals stemmed from the $\omega/(\omega - 1)$ positions. For longer chain nitriles the activation of internal C–H bonds was also observed (R = $CH_3$, $C_2H_5$, etc.); this leads to the production of higher alkenes and molecular hydrogen from internal methylene groups.[258] The preferred ring size of the intermediates formed (**65**) differs slightly for $Fe^+$ versus $Co^+$ [258,259] and $Ni^+$,[260] which also react with nitriles by remote functionalization. $Fe^+$ preferentially inserts into a $C_{(8)}$–H and $Co^+$ and $Ni^+$ into a $C_{(7)}$–H bond. The amount of d → $\pi^*$ back-bonding of the metal ions, which in turn induces deviations of the C–C–N angle from linearity, has been suggested as a possible explanation for the differences. Upon collisional activation, formal loss of "alkanes" is observed for the $Fe^+$ and $Co^+$ complexes.[258] This reaction is either absent or of negligible intensity in metastable-ion spectra.[261] While for $Co^+$, $^2H$ labeling and MS/MS experiments show that indeed alkanes are formed by a conventional C–C insertion, β-H shift, reductive elimination mechanism, for $Fe^+$ this applies only to the loss of methane. Other products due to loss of "$C_nH_{2n+2}$" arise by the mechanism shown in Figure 20 in a consecutive reaction; dehydrogenation (**78** → **79**) is followed by allylic C–C insertion (**79** → **80**), β-H shift, and loss of an alkene.[258] Starting directly from alkenenitriles the loss of an alkene is even observed in metastable-ion spectra.[262] The reaction of $Fe^+$ with several nitriles of the type $CH_3(CH_2)_nCH{=}CH(CH_2)_mCN$ demonstrates that for $m = 2$–$4$ exclusively insertion into that allylic C–C bond which is further away from the cyanide group, occurs; partial isomerization of the double bond "away" from CN is a competing process. For $m = 0$ or 1, no bidentate complexation of the metal ion seems to be possible as exclusively remote functionalization according to Figure 17 is observed in this case.[262]

The preference of $Fe^+$ to insert into remote C–H bonds, particularly at $C_{(7)}$ or $C_{(8)}$, was used to test the ability of the metal ion for insertion into C–C bonds and for β-$CH_3$ shifts.[263] Insertion into the remote $C_{(7)}$–H bond of 8,8-dimethylnonanenitrile might have led to a situation, where a β-$CH_3$ transfer from $C_{(8)}$ would have been feasible. Actually,$^2H$ labeling revealed no indication for such a β-$CH_3$ shift, but showed instead that insertion into the $C_{(7)}$–$C_{(8)}$ (15%) and the $C_{(8)}$–$C_{(9)}$ bond (76%) occurred with high specifity. In the latter case, β-H shift from $C_{(9)}$ (90%) or $C_{(7)}$ (10%) and reductive elimination of $CH_4$ resulted, while in the former case exclusively a β-hydrogen from $C_{(9)}$ was transferred. Loss of isobutene and rearrangement according to Figure 17 (**68** → **69**, $(CH_3)_2C{=}CH_2$ in place of RCH = $CH_2$) finally afforded $CH_3(CH_2)_5CN$–$Fe^+$, whose structure was evidenced in an MS/MS experiment by comparison with the authentic complex.[263]

As a β-$CH_3$ shift from a silicon atom might be accomplished more easily, the Si analogue of 8,8-dimethylnonanenitrile, i.e. 7-(trimethylsilyl)heptanenitrile, was studied with $Fe^+$.[264] Indeed, exclusive insertion into the $C_{(7)}$–H bond was observed, but instead of a β-$CH_3$ shift from the trimethylsilyl group, a β-H shift from $C_{(6)}$ and loss of $H_2$ occurred. The high specifity of the insertion was ascribed to the well-known β-effect of silicon.[265]

It is not unreasonable to expect deviations from the remote functionalization mechanism in Figure 17 if the number of methylene groups *n* becomes so small that the ring strain in the intermediate **68** gets prohibitively high. In line with this assumption, the reaction of $Fe^+$, $Co^+$, and $Ni^+$ with *n*-pentanenitrile (**82**) illustrates that, depending on the mode of complexation, ethene formation by remote functionalization can be completely suppressed.[266,267] It is already known from the longer nitriles that $Fe^+$ prefers insertions into positions that are more remote than for $Co^+$ and $Ni^+$;[258,260] thus for $Co^+$ and $Ni^+$ greater deviations from a linear $CH_2CNM^+$ arrangement are possible and can help to minimize any strain. This might explain why $Ni^+$, but not $Fe^+$, generates $C_2H_4$ by remote functionalization via the strained intermediate **87**.[266,267] For $Fe^+$, ethene is produced from *internal* positions by the direct activation of a C–C bond that is not preceded by C–H activation. Insertion into the C–$CH_3$ bond and subsequent β-CC cleavage affords the intermediate **86** (Figure 21), which loses $C_2H_4$ to form **88**. This complex can be distinguished from the isomeric propanenitrile complex **89**, which would arise from remote functionalization, by its characteristic CID spectrum. $Co^+$ reacts with **82** to produce $C_2H_4$ by *both* mechanisms, hence, the isomeric complexes **88** and **89** are formed in competition, a finding that was derived by combining $^2H$ labeling with CID spectrometry.[267]

Several reversible processes were revealed by the $^2H$ labeling, e.g., between **85** and **87**. The most interesting concerns the collision complex **83** between $Fe^+$ and **82** which is in equilibrium with the ferracyclobutane complex **90**. This ion, owing to its symmetry, upon reopening equilibrates the α- and the γ-positions of the substrate. This indirect demonstration for the viability of bare $Fe^+$ to form ferracyclobutane structures may be interesting with regard to the discussion on the mechanism of alkene cyclopropanation, where, for example, the existence of positively charged ferracyclobutane intermediates has not unambiguously been determined or ruled out.[200] The absence of analogous cobalta- or nickelacyclobutane ions is reminiscent of the stabilities of the unsubstituted metallacyclobutane ions (see section IV.D) and could indicate that the stability of these complexes is not only relatively independent upon

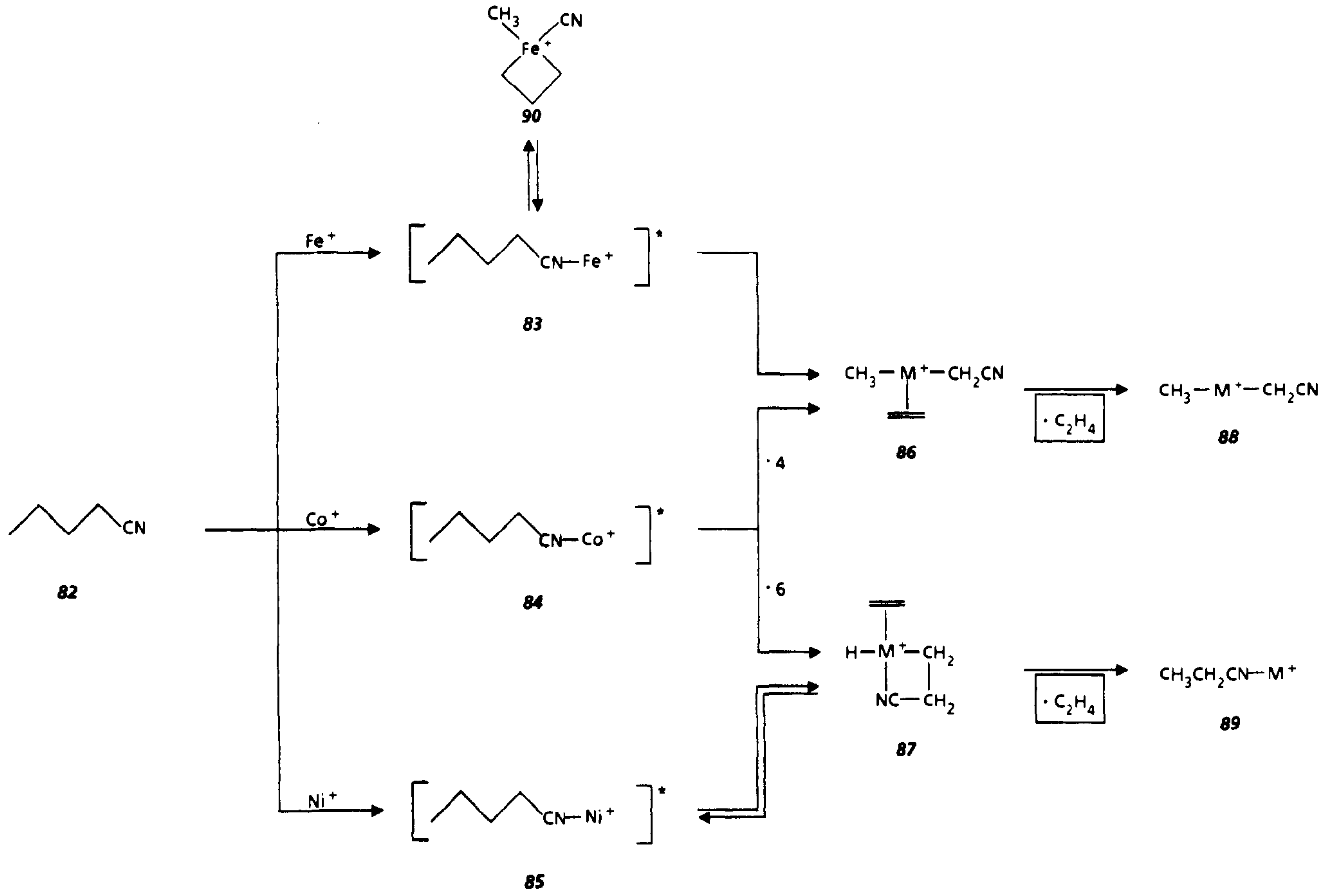


**Figure 21.** Reaction of pentanenitrile (**82**) with Fe$^+$, Co$^+$, and Ni$^+$, generating two distinguishable MC$_3$H$_5$N$^+$ isomers.

substitution, but might even reflect inherent properties of these intermediates.

All three metal ions dehydrogenate **82** as well; probably because the strain in **66** is smaller than in **68**, this reaction is specific and proceeds by remote functionalization. The product that arises, an $\gamma,\delta$-unsaturated nitrile, however, undergoes further reversible processes that could only be revealed by CID spectra of the dehydrogenation products. All three ions activate the allylic C$_{(\beta)}$–H bond to form a hydrido–allyl complex. Similar to other allylic systems,[44a,111,268–270] the terminal, but not the central, hydrogens exchange rapidly.[266,267]

Other metal ions have not been studied in the same depth as Fe$^+$–Ni$^+$ with linear nitriles. Mn$^+$ is reported to exclusively dehydrogenate heptanenitrile[259] while Cr$^+$ [259] and Cu$^+$ [71] only form adduct complexes with nitriles under FTICR conditions. Cu(RCN)$^+$ complexes show no unimolecular cleavages, except for ligand detachment, but upon collisional activation other products are observed.[71,271] The formation of Cu(H,C,N)$^+$, Cu$^+$—CH$_2$CN, and Cu(CH$_2$=CH—CN)$^+$ has been interpreted in terms of a "side-on" coordination.[271]

## B. Isonitriles and Branched Nitriles

A markedly different chemistry is encountered in the reaction of Fe$^+$ with 2,2-dimethylpropanenitrile (*t*-BuCN) as two completely "new" products are formed.[272] These are a complex of Fe$^+$ with [H,C,N] and Fe(C$_4$H$_8$)$^+$ by loss of [H,CN]; both obviously arise from a common intermediate of the general structure Fe(H,CN)(C$_4$H$_8$)$^+$. The latter is, however, not formed by the insertion/$\beta$-hydrogen shift mechanism, formulated by Allison and Ridge for other functionalized alkanes,[273,274] as this mechanism is expected to afford **94**, which in turn should decompose to **95** (Figure 22), i.e. Fe(HNC)$^+$, and to **20** by loss of HNC. This mechanism can be discarded by comparison with the reaction of 2-isocyano-2-methylpropane (*t*-BuNC), which also affords Fe(H,C,N)$^+$ and loss of (H,CN).[272] High-energy CID reveals that Fe(HCN)$^+$ is formed from *t*-BuCN and Fe(HNC)$^+$ from *t*-BuNC, thus complexes **98** are formed in lieu of **95**. This has been explained by invoking an ion/dipole mechanism.[272,275] Complexation of the metal ion to the functional group XY (XY = NC, CN) induces cleavage of the C–X bond and gives rise to the ion/dipole complex **96**. The incipient carbenium ion therein now serves as an intramolecular protonating reagent for the XYM dipole;[276] this leads to the diligated complex **97**, which eventually dissociates, reflecting the relative binding energies of its two ligands. This mechanism not only explains why complexes **98** are formed, but also why **97**, generated from *t*-BuCN, preferentially *loses* HCN while **97**, generated from *t*-BuNC, preferentially *retains* HNC as the stronger bound ligand. This observation indirectly proves that indeed the thermodynamically at least 10 kcal mol$^{-1}$ more unfavorable HNC[277] is produced; the appropriate CIDI experiment[247,278] to demonstrate this directly was impossible due to intensity reasons. Ion/dipole complexes are known to be quite long lived,[279a–c] being trapped on the reaction coordinate by a potential-energy barrier on one side and an entropic bottleneck on the other side. On the contrary, hydrogen rearrangements in carbenium ions are fast processes,[279d] and H/D scrambling in **96** has therefore to be expected, but cannot be observed,

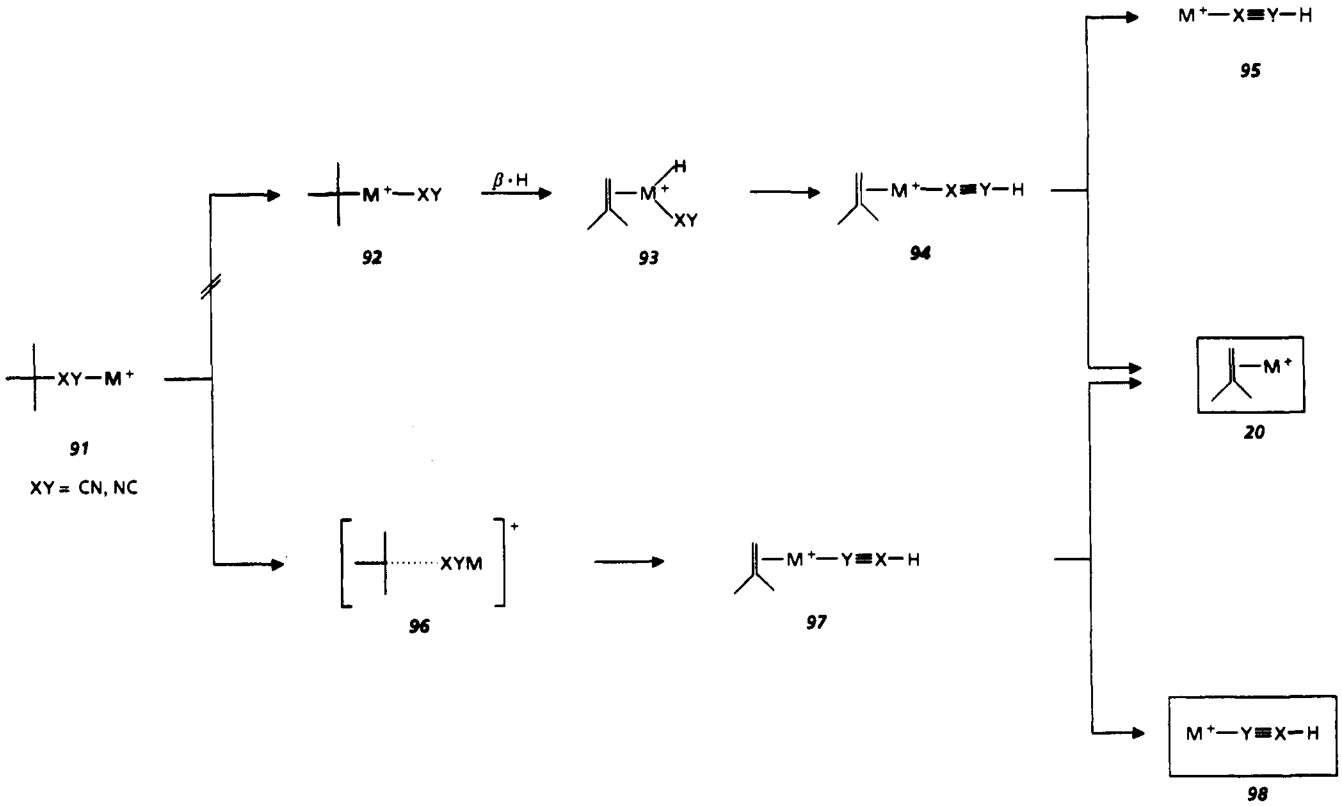


**Figure 22.** Reaction of transition-metal ions $M^+$ with *t*-BuCN and *t*-BuNC via the ion/dipole mechanism.

owing to the equivalency of all hydrogen atoms. However, the reactions of $Co^+$, $Ni^+$, and $Cu^+$ with 2-methylbutanenitrile (see below) as well as the reaction of $Fe^+$ with 2,2-dimethylbutanenitrile also afford $M(HCN)^+$ ions and loss of HCN. As in these substrates the hydrogens are no longer equivalent, $^2H$ labeling indeed proves that not only the β-hydrogen atoms, but in fact all positions contribute to the hydrogen-transfer step.[72,261]

The $Cu(HCN)^+$ and $Cu(HNC)^+$ complexes retain their structure even upon neutralization to Cu(HCN) and Cu(HNC) as was shown in a neutralization reionization (NRMS[280]) study.[281]

The different behavior of *t*-BuNC and *t*-BuCN already indicates that a metal ion induced isomerization of the isonitriles[282] to the thermodynamically more stable nitriles[283] is absent, although this long-known reaction[284] occurs in solution,[285] at metal surfacs,[286] or in the gas phase at elevated temperatures.[287] The same result was obtained in a more detailed study on the reaction of $Fe^+$ with several *n*-alkyl isocyanides.[288] Comparison with the analogous nitriles revealed rather large differences; for short isocyanides, $Fe(HNC)^+$ formation via the ion/dipole mechanism (Figure 22) was observed while with increasing chain length dehydrogenation by remote functionalization effectively began to compete and was the most favored pathway already for $n\text{-}C_5H_{11}NC$. While for the ion/dipole mechanism H/D scrambling in the primary carbenium ions is observed, dehydrogenation involves the $\omega/(\omega - 1)$ positions. In a screening study with *nearly all d-block transition-metal ions*, isonitriles were used to reveal trends across the periodic table.[224] It resulted that dehydrogenation in general increased in importance with increasing chain length, and was most prominent in the "left part" of the transition-metal series for the group 4 metal ions, and then rapidly drops, with $Mn^+$ from group 7 being found as totally unable for dehydrogenation of isonitriles. In the "right part" of the series a steady decrease from group 8, which is highest, to group 11 and 12, which show no $H_2$ loss at all, is observed. Second- and third-row metal ions give rise to significantly higher amounts of $H_2$ and $2H_2$. This evidences that the general properties of the different metal ions found in their reactions toward alkanes (see section IV) are conserved also for other substrates.

The ion/dipole mechanism is operative for all transition-metal ions.[224] It is reduced in importance for those metal ions that effectively dehydrogenate and is most important for groups 6 and 11, i.e., those ions that are often unable to insert into C–H or C–C bonds. As any insertion is avoided in Figure 22, the ion/dipole mechanism may be the only alternative left for those ions and thus, *the extent by which the mechanism is operative depends on the need for it.*

Ligand-detachment signals, that is, loss of the intact isonitrile from the $M(RNC)^+$ complexes, are most pronounced in cases where no other reactions are possible. Thus they decrease with increasing chain length and are highest for relatively unreactive metal ions, such as $Mn^+$. The intensity of the ligand-detachment signals can therefore be taken as a measure for lacking reactivity.[224]

Additional support for this hypothesis comes from a comparison of the relative amounts of ligand-detachment signals versus other processes in the reactions of $Fe^+$ with secondary nitriles $R^1R^2CHCN$.[261] For these nitriles only two other mechanisms are operative, remote functionalization and loss of $CH_4$ by initial C–CN insertion (see below). As can be seen from Figure 23, ligand detachment rapidly diminishes as soon as the alkyl chains are long enough to permit the operation

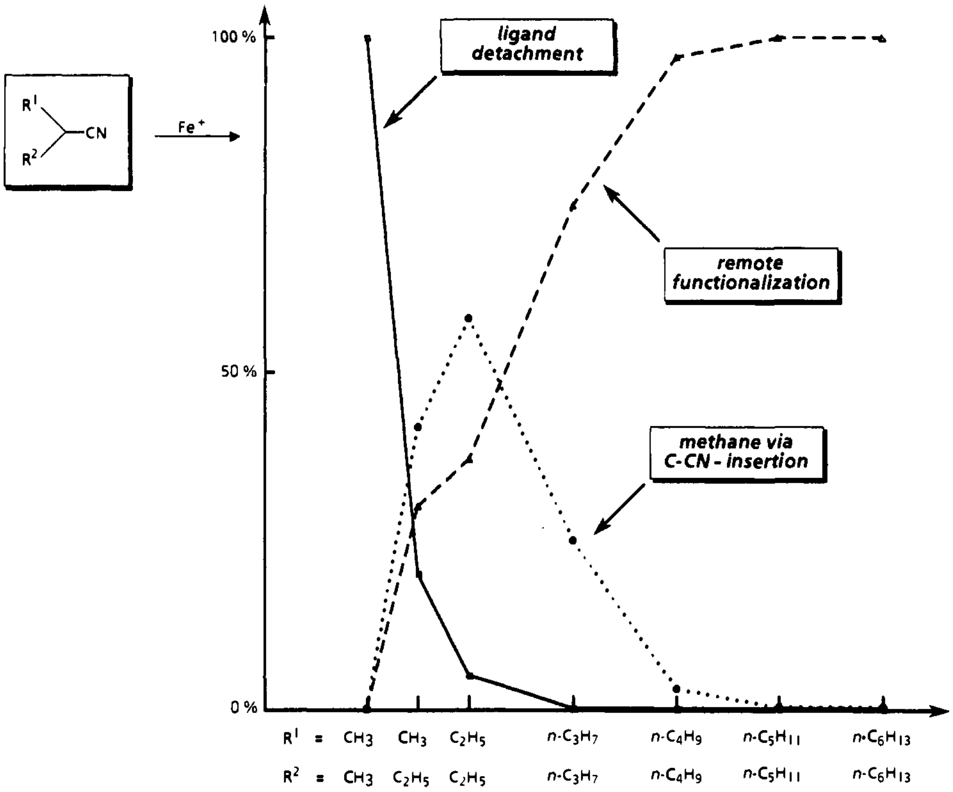


**Figure 23.** Effect of alkyl chain length variation on the three types of reactions of secondary nitriles $R^1R^2CHCN$ with $Fe^+$.

of the other two mechanisms.

With regard to remote functionalization, the secondary nitriles behave strictly analogous to linear nitriles; therefore the determination of intramolecular kinetic isotope effects for symmetric substrates allowed more insight about the kinetics of the individual steps in Figure 17. Extensive labeling on 2-butylhexanenitrile ($(n\text{-}C_4H_9)_2CHCN$) demonstrated that C–H activation is not rate determining, that a secondary kinetic isotope effect is present for the ethene loss, and that both, the $\beta$-hydrogen shift *and* the reductive elimination of $H_2$, are associated with a primary KIE.[261,289]

Formal unimolecular loss of alkanes ($C_2H_6$, $C_3H_8$), which is observed for nitriles with two long chains, actually is the product of a successive *double remote functionalization* of both alkyl chains, viz. combined losses of alkenes and $H_2$.[261,290] $^2H$ labeling and MS/MS experiments revealed that unlike the linear nitriles in Figure 20, which only lost $H_2/C_nH_{2n}$ in CID experiments, here the loss of the alkene from the one chain ($C_2H_4$, $C_3H_6$) precedes the loss of $H_2$ from the other chain, and not vice versa. Only recently an example for double remote functionalization of a *rigid* molecule in the condensed phase has been reported.[291]

The methane loss in Figure 23 is also unique to branched nitriles as it commences with insertion of $Fe^+$ into the C–CN bond of the substrate followed by $\beta$-hydrogen shift. Reductive elimination of HCN from the resulting intermediate is obviously thermodynamically unfavorable or kinetically hindered as activation of a C–$CH_3$ bond and subsequent reductive elimination of $CH_4$ is observed instead.[261] The C–C bond to be broken can even be a remote C–$CH_3$ bond, as for example in 2-butylhexanenitrile, but then the loss of $CH_4$ is only a minor process. Examination of the various $R^1R^2CHCN$–$Fe^+$ complexes showed that loss of methane is most pronounced for systems where it is an *allylic* C–$CH_3$ bond that is activated. Figure 24 depicts the mechanism for 2-methylbutanenitrile and also includes a degenerate isomerization which is observed for this particular system. Small signals due to loss of $CH_3^{\bullet}$ *radicals* are observed in the metastable-ion and FTICR spectra and may arise from intermediates **102**/**102′**.[71,72,261] For $(CH_3)_2CHCN$, the mechanism in Figure 24 is impossible, and, on the other hand, methane generation is suppressed as soon as one chain is long enough to allow competition by the more favorable remote functionalization (Figure 17) and thus has an intermediate maximum for $(C_2H_5)_2CHCN$ (Figure 23).[261]

The reaction of $Fe^+$ with 2,2-dimethylbutanenitrile is interesting because of this substrate being an intermediate between the secondary 2-methylbutanenitrile, where remote functionalization and the allylic mechanism in Figure 24 applied, and the tertiary nitrile *t*-BuCN, where the ion/dipole mechanism was the exclusive decomposition mode. Indeed, products due to all three mechanisms were noted, with the latter two prevailing.[71,261]

Looking at the behavior of the other first-row metal ions $Ti^+$ through $Zn^+$ with small secondary nitriles $R^1R^2CHCN$ is informative; again some intrinsic properties of the metal ions and general trends across the first row are revealed. The reaction of $Fe^+$ with 2-methylbutanenitrile has already been described to proceed by the two mechanisms in Figures 17 and 24.[261] $Cu^+$, on the other hand, with the same substrate exclusively forms $Cu(HCN)^+$ and $Cu(C_4H_8)^+$ by loss of HCN according to the ion/dipole mechanism in Figure 22.[72] Study of $Co^+$ and $Ni^+$ as the two elemental ions in between shows that a gradual switching between the three mechanisms is operative. For $Co^+$, products due to all three mechanisms were present, and for $Ni^+$ remote functionalization and ion/dipole mechanism ap-

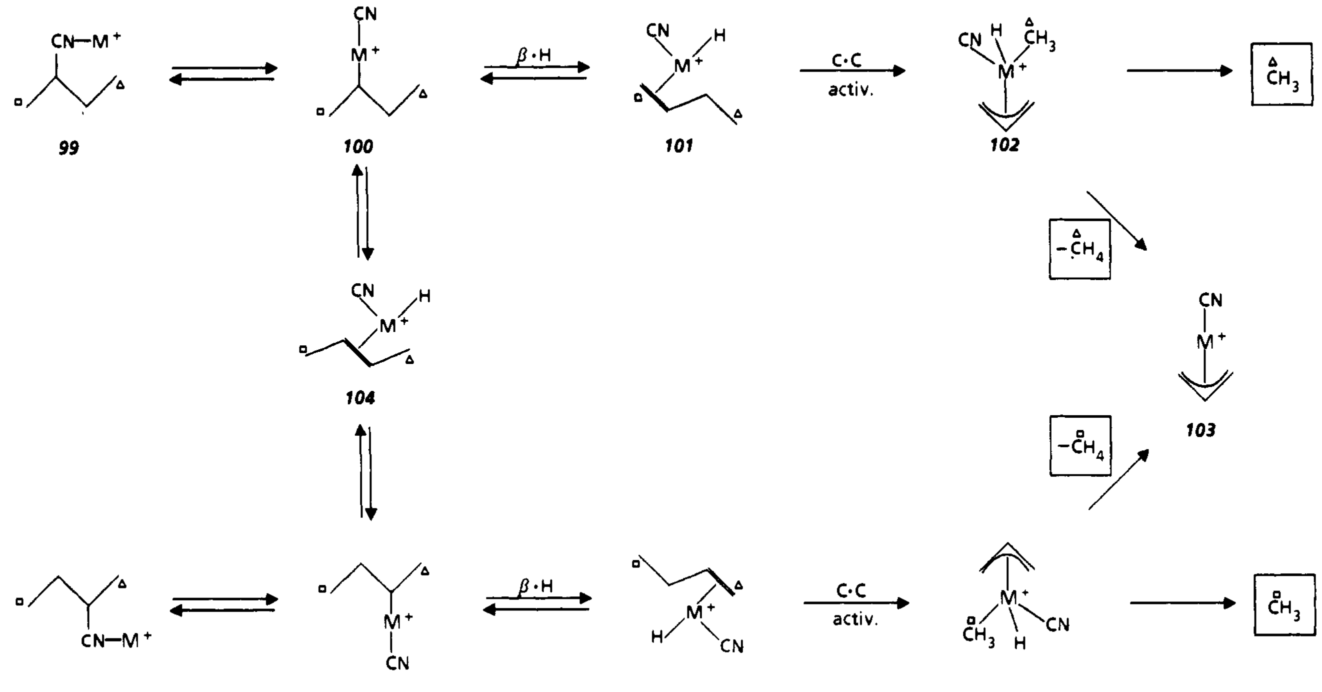


**Figure 24.** Generalized mechanism for the generation of $CH_4$ and $CH_3^•$ by allylic insertion of group 8–10 transition-metal ions $M^+$ with 2-methylbutanenitrile.

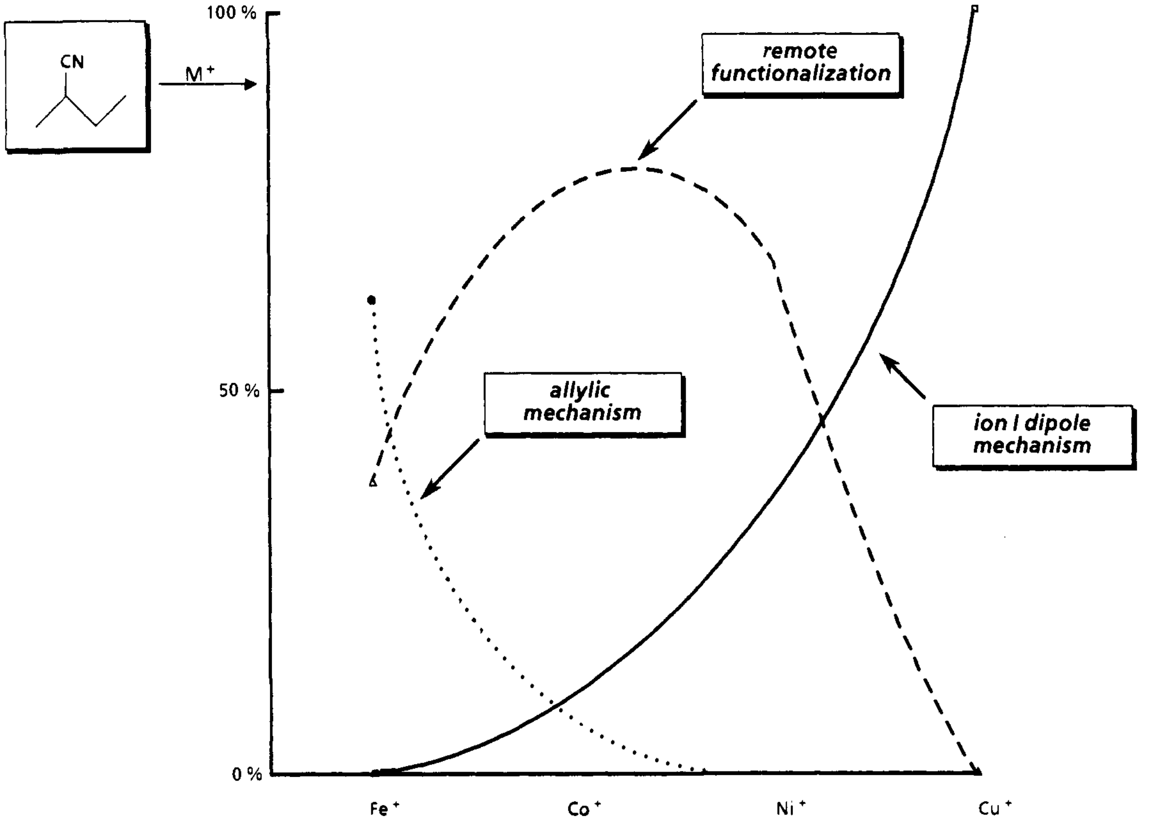


**Figure 25.** Effect of different transition-metal ions on the relative contributions of the three mechanisms operative in the reaction with 2-methylbutanenitrile.

plied (Figure 25).[72] The same result has been obtained for 2-ethylbutanenitrile.[292] The steadily increasing amount of the ion/dipole mechanism reveals the increasing tendency to avoid insertion reactions, again by the principle that the extent by which it is operative depends on the need for it.[224] It is therefore highly likely that formation of $Co(HCN)^+$ and $CoC_3H_6^+$ by loss of HCN in the reaction of $Co^+$ with 2-methylpropanenitrile, which has been ascribed to the insertion/β-hydrogen-shift mechanism,[259] is also accomplished via the ion/dipole mechanism.

Early transition metal ions like $Ti^+$ and $V^+$ mainly give rise to dehydrogenation with losses of $H_2$, $2H_2$, and $H_2$ together with other neutrals being observed.[72,292] $Cr^+$, $Mn^+$, and $Zn^+$ are unreactive with 2-methyl- and 2-ethylbutanenitrile; under FTICR conditions adduct formation is observed and exclusively ligand detachment in metastable-ion spectra. $Zn^+$ in addition undergoes charge-transfer reactions with the nitriles. Collision-induced dissociation on the adduct complexes leads to ligand detachment and sometimes to low-intense products from the ion/dipole mechanism and from radical losses.[72,292] However, $Cr^+$ reacts with $t$-$C_4H_9CN$[47c] and $t$-$C_5H_{11}CN$,[252] and the two products of the ion/dipole mechanism (Figure 22) are observed. Thus, similar reactivity of the first-row ions as toward alkanes is found in the reactions with the nitriles.

## *VII. Reactions of Bare Metal Ions with Other Substrates*

### A. Alkyl Halides and Alcohols

In their chemistry with bare metal ions, alkyl halides and alcohols have very much in common, and that is why they will be discussed together. The first studies with these substrates employed alkali-metal ions and were designed to determine heterolytic bond dissociation energies, $D°(M^+–X^-)$ and $D°(R^+–X^-)$. But instead of showing only the expected chloride abstraction (eq 46, M = Li, X = Cl) $Li^+$ was observed to cleave branched alkyl chlorides into HCl and alkanes (eqs 47 and 48) while $Na^+$ and $K^+$ were more or less unreactive with the substrates employed.[293-295] Use of 2-chloropropane-$d_6$ revealed that DCl was formed by 1.2 elimination, and a mechanism was proposed that was later termed "*dissociative attachment*" or simply referred to as Lewis acid chemistry and which may be regarded as precursor of the ion/dipole mechanism in Figure 22. The intermediacy of ion/dipole complexes was, however, not yet recognized, and it was only proposed that association of the metal ion to the substrate leads to a chemically activated species which may either dissociate to metal halide and a carbenium ion, or which may rearrange to a diligated complex of $M^+$ with HX and the alkene, i.e., analogous to **97**, followed by competitive ligand loss.[293] The barrier for the production of the $Li(H_2O)(i\text{-}C_4H_8)^+$ complex from *tert*-butyl alcohol has been estimated to be *larger* than the activation energy for dissociation of the $Li(t\text{-}C_4H_9OH)^+$ collision complex by 1.6 ± 0.7 kcal $mol^{-1}$.[296a,b] This contrasts the results for $i$-$C_3H_7Cl$, $i$-$C_3H_7Br$, and $n$-$C_3H_7Cl$ reacting with $Li^+$; the isomerization barriers to $Li(HX)(C_3H_6)^+$ increase in the order of citation and are lower than the activation energy for the redissociation back to $Li^+$ and RX.[296c]

$$M^+ + C_nH_{2n+1}X \rightarrow C_nH_{2n+1}^+ + MX \qquad (46)$$

$$\rightarrow M(HX)^+ + C_nH_{2n} \qquad (47)$$

$$\rightarrow M(C_nH_{2n})^+ + HX \qquad (48)$$

Soon afterward, Allison and Ridge extended the work with halides and alcohols to transition-metal ions.[273,274,297] Reaction of $Fe^+$, $Co^+$, $Ni^+$, and $Hg^+$ with the methyl halides allowed to derive limits for $D°(M^+–CH_3)$ and $D°(M^+–X)$. Observation of the processes depicted in eqs 49 and 50 in some cases indicated insertion of the metal ions into the $CH_3–X$ bond, although mostly $MX^+$ was the sole product. Convincing evidence for this assumption was obtained using the reaction sequence in eqs 51 and 52. Exclusive loss of $CH_3$ in eq 52 excludes a symmetrical collision complex of the type $[Fe(CH_3I)(CD_3I)^+]^*$, thus $CH_3–Fe^+–I$ is formed in eq 51. Analogous behavior could be demonstrated for $CH_3OH$.[273,274] Many other halides or alcohols reacted with $Fe^+$–$Ni^+$ exclusively according to eqs 46–48 (X = Cl, Br, I, OH), as did $Li^+$ and $Na^+$, the latter formed $Na(alkene)^+$ and HCl from *tertiary* chlorides, while $K^+$ was still unreactive. Yet, despite this similarity, based on the following observations, Allison and Ridge concluded that the alkali-metal ions reacted only superficially like transition-metal ions:[273,274] Similar to $CH_3I$ and $CH_3OH$, they could show that $Ni^+$ inserted into the $C_2H_5–I$ bond (eqs 53 and 54), i.e., $Ni(C_2D_4)(DI)^+$ is actually formed in eq 53. $Li^+$ reacts with $t$-$C_4H_9Cl$ according to eqs 55–58. Double-resonance experiments with a mixture of $t$-$C_4H_9Cl$ and $t$-$C_4D_9Cl$ inter alia identified the reactions in eqs 59 and 60, which point to a symmetrical intermediate $[Li(C_4H_9{}^{35}Cl)(C_4D_9{}^{37}Cl)^+]^*$. It was proposed that alkali-metal ions reacted via dissociative attachment and transition-metal ions via an insertion/β-hydrogen shift mechanism. Statistical loss of HI and DI from $CD_3CH_2I/Fe^+$ indicated that the β-hydrogen shift was reversible.[273,274]

$$M^+ + CH_3X \rightarrow MX^+ + CH_3 \qquad (49)$$

$$\rightarrow MCH_3^+ + X \qquad (50)$$

$$Fe(CO)^+ + CH_3I \rightarrow FeCH_3I^+ + CO \qquad (51)$$

$$FeCH_3I^+ + CD_3I \rightarrow FeCD_3I_2^+ + CH_3 \qquad (52)$$

$$Ni(CO)^+ + C_2D_5I \rightarrow NiC_2D_5I^+ + CO \qquad (53)$$

$$NiC_2D_5I^+ + C_2H_5I \rightarrow Ni(C_2D_4)(C_2H_5I)^+ + DI \qquad (54)$$

$$Li^+ + t\text{-}C_4H_9Cl \rightarrow LiC_4H_8^+ + HCl \qquad (55)$$

$$LiC_4H_8^+ + t\text{-}C_4H_9Cl \rightarrow LiC_4H_9Cl^+ + C_4H_8 \qquad (56)$$

$$\rightarrow Li(C_4H_8)_2^+ + HCl \qquad (57)$$

$$LiC_4H_9Cl^+ + t\text{-}C_4H_9Cl \rightarrow Li(C_4H_8)C_4H_9Cl^+ + HCl \qquad (58)$$

$$LiC_4H_9{}^{35}Cl^+ + t\text{-}C_4D_9{}^{37}Cl \rightarrow Li(C_4H_8)(C_4D_9{}^{37}Cl)^+ + H^{35}Cl \qquad (50\%) \quad (59)$$

$$\rightarrow Li(C_4H_9{}^{35}Cl)(C_4D_8)^+ + D^{37}Cl \qquad (50\%) \quad (60)$$

It has already been shown in the discussion on the ion/dipole mechanism that transition-metal ions may very well react by abstraction instead of insertion, hence, the distinction between alkali- and transition-metal ions must not be generalized. Furthermore, it may be argued that loss of CO in eq 53 is more exothermic than loss of $i$-$C_4H_8$ in eq 56 so that only in the former case sufficient energy for an insertion remains in the product. In addition, in a recent ion-beam study, Armentrout and co-workers were able to demonstrate from features of the cross section that *two mechanisms* apply in the reactions of $Fe^+$–$Ni^+$ with $CH_3X$ (X = Cl, Br, I). At low energies indeed insertion into the $CH_3–X$ bond with subsequent cleavage into $MCH_3^+$ and $MX^+$ is observed, but at higher energies direct abstraction of X, but not $CH_3$, is possible as well.[298,299]

The reactions of $Mg^+$,[300] $Al^+$,[58,300,301] $Ga^+$,[301] $In^+$,[301] $Ti^+$,[302,303] $Mn^+$,[304] $Cu^+$,[55,305,306] $Ag^+$,[55,305-307] and $Au^+$[11,306]

with several alkyl halides and alcohols proceed almost exclusively via eqs 46–48 and 61 furthermore. Notable

$$M^+ + C_nH_{2n+1}X \rightarrow MX^+ + C_nH_{2n+1} \qquad (61)$$

exceptions are the formation of $AlCl_2^+$ ions and $MgX_2$ neutrals from 1,2-dihaloalkanes and tetrahalomethanes.[58,300] For the former substrates a concerted mechanism has been suggested.[58] $Ti^+$ forms, among other products, $TiF_2$ from $CF_2Cl_2$ and $TiCl_2^+$ from di-, tri-, and tetrachloroethene.[302] The group 11 ions $Cu^+$–$Au^+$ are reported to dehydrogenate alcohols, and it has been suggested that $H_2$ arises from initial O–H insertion followed by β-H shift and reductive elimination, furnishing aldehydes or ketones.[305,306] The main product for $Au^+$ reacting with alcohols is AuH, similarly to the alkanes, but methanide and hydroxide abstraction are also observed; on the contrary, CuH, $CuCH_3$, and CuOH are only minor products for $Cu^+$, and $Ag^+$ does not form the analogous neutrals at all, but mainly furnishes the adduct complexes.[306] With $CH_3Cl$ and $CH_3Br$, $AuCH_2^+$ is the main product besides the $AuCH_3X^+$ adduct complexes, which are shown by CID and ligand-exchange experiments to actually have the $Au(CH_3X)^+$ structure.[11] $Rh^+$ generates inter alia $RhCO^+$ and $RhC_2H_4^+$ from $C_2H_5OH$ as shown by high-resolution spectra;[42a,308] $Pd^+$ dehydrogenates $C_2H_5OH$,[196] and $Ta^+$ forms $TaOH^+$ and $TaO^+$ from $CH_3OH$.[125]

A generalization that emerges from these studies is a more pronounced tendency to form $C_nH_{2n+1}^+$ with increasing $n$,[300,307] a consequence of the decreasing ionization energies of the $C_nH_{2n+1}^{\bullet}$ radicals, which makes the carbenium ion formation more and more exothermic.[184] Various limits for $D°(M^+–X^-)$ and $D°(M^+–X)$ can be derived from these studies, but there are few theoretical values to compare with.[109a,b]

More quantitative thermochemical data has been collected for $MgOH^+$ and MgOH by performing variable-energy CID and photodissociation experiments on $Mg(ROH)^+$ complexes ($R = i\text{-}C_3H_7$, $s\text{-}C_4H_9$, $t\text{-}C_4H_9$).[309] $Mg^+$, $MgH_2O^+$, $MgOH^+$, and MgOH are the products observed, and the data obtained inter alia allowed the derivation of $D°(Mg^+–ROH)$, $D°(Mg^+–OH)$, and $D°(Mg–OH)$ bond dissociation energies. $D°(Mg^+–OH)$ was also directly determined by photodissociation upon $MgOH^+$.[309]

Some of the reactions of $Co^+$ with alkyl chlorides and alcohols can be described with eqs 46–48 and 61,[33v] but as the chain length increases, a more "alkane-like" chemistry is observed, with C–C insertions prevailing.[184,310] An important process for substrates with linear chains of at least four carbon atoms is diene-complex formation by loss of $HX/H_2$. To explain the preferred product distributions 5- or 6-membered ring intermediates *preceding* C–C insertions have been postulated,[184,311a] yet, no labeling to substantiate this proposal was done. Unfortunately, several assumptions with regard to the mechanisms operative were therefore necessary to derive an order of preference for metal insertion into certain bonds.[184] In a theoretical approach, part of the potential-energy surface of $Cr^+$ with $n\text{-}C_4H_9Cl$ has been calculated and electrostatic interactions in the initial ion/molecule adduct complex were proposed to account for the final product distribution; the most stable point indeed corresponded to a 6-membered ring intermediate.[312]

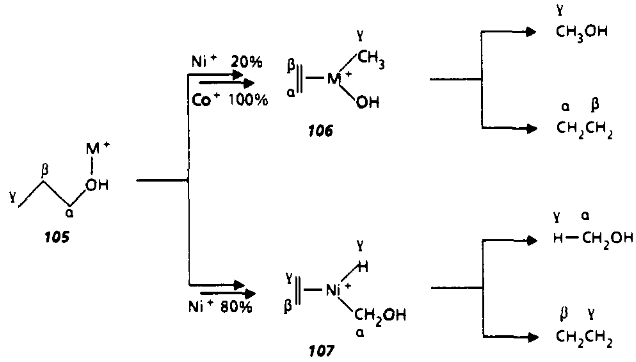


**Figure 26.** Mechanism for the reactions of $Co^+$ and $Ni^+$ with propanol to afford methanol and ethene.

In a comparison of the overall reactivity of $Fe^+$, $Cr^+$, and $Mo^+$, various alcohols were employed; while for the first-row ions reactivity increased with chain length, for $Mo^+$ a decrease was observed.[313] Three classes of reactions emerged, dehydration by insertion/β-hydrogen shift, dehydrogenation by supposedly C–H *or* O–H insertion, and finally C–C insertions. $Cr^+$ was unreactive with methanol and ethanol, dehydrogenated propanol, and predominantly inserted into C–C bonds of longer *n*-alkanols. Branched alcohols mainly underwent loss of $H_2O$ upon reaction with $Cr^+$.[313,314] Similar to other substrates $Mo^+$ afforded multiple dehydrogenations except for $t\text{-}C_4H_9OH$ where loss of $H_2O/H_2$ was favored.[313] C–C insertions were only observed in smaller amounts for longer alcohols. $Fe^+$ yielded mainly dehydration for smaller and mainly C–C insertion products for longer alcohols.[313] This finding contrasts results from metastable-ion decompositions of $Fe(alcohol)^+$ complexes. Here, loss of $H_2$ was predominant for butanol through octanol.[311a] Multiple losses under the FTICR conditions employed in ref 313 might be responsible for this discrepancy, in this case the "alkane" products would have to be reformulated as $H_2$/alkene products. $Co^+$ complexes showed such multiple losses already in the MI spectra, where many different products were observed.[311a] Indeed, for the $Co(n\text{-hexanol})^+$ system, loss of 30 amu does not correspond to the elimination of intact $C_2H_6$, but rather to the combined losses of $C_2H_4/H_2$.[311b]

Results from $^2H$ labeling are only available for 1-propanol[315] and 1-pentanol.[311a] Loss of $H_2O$ from propanol reacting with $Fe^+$, $Co^+$, and $Ni^+$ showed contributions from all positions. The origin of the $C_2H_4/CH_3OH$ neutrals, that are observed for $Co^+$ and $Ni^+$ in addition to $H_2O$, differs substantially for the two ions (Figure 26). For $Co^+$, all of the ethene stems from the α/β-position and methanol from $C_{(\gamma)}$; for $Ni^+$ this accounts only for 20% of the products, the remainder is produced by cleavage of the $C_{(\alpha)}$–$C_{(\beta)}$ bond (**105** → **107**).[315] $H_2$ and $C_2H_4$ are the main products in the reactions of $Fe^+$ and $Co^+$ with 1-pentanol, their formation is mainly accomplished by remote functionalization; besides, $H_2O$ loss is observed, which is unspecific for $Fe^+$ and in case of $Co^+$ mainly affects the γ-position.[311a]

The chemistry of $Co^+$ with bifunctional substrates has also been studied in order to determine the favored site of attack. Thus, dominant loss of CoBr besides CoCl and HCl/HBr from 4-chloro-1-bromobutane points to a preferred attack at the bromide end of the molecule.[310]

The 4-halo-1-butanols, however, gave rise to products that were unique to these particular substrates. $Co^+$–butadiene complexes by loss of $HX/H_2O$ were the main products; observation of $CoC_2H_2O^+$ was explained with insertion into the central C–C bond, β-hydrogen shift followed by loss of $C_2H_5X$ and subsequently $H_2$. Yet, production of HX in each case, but not of $H_2O$, might indicate some preference for halogen attack.[310] Besides HCl, $CoClOH^+$ is formed by loss of $C_2H_2$ in the reactions of $Co^+$ with 2-chloroethanol, probably in a concerted fashion.[316] α,ω-Dihaloalkanes and α,ω-haloalkanols react with $Li^+$ by intermediate formation of LiX complexes of cyclic halonium ions or protonated cyclic ethers. Owing to the stability of the cyclic halonium ions, LiX is lost from the former complexes, while proton transfer occurs for the latter, resulting in HX loss.[317] Allyl chloride, allyl bromide, and allyl alcohol all afford loss of HX (X = Cl, Br, OH) upon reaction with $Co^+$, thus vinylic C–H bonds are activated as well. Allyl bromide in addition gives the simple cleavage products of the allylic C–Br insertion, i.e., $CoC_3H_5^+$ and $CoBr^+$.[316] On the contrary, $Fe^+$ reacting with allyl chloride exclusively affords $FeC_3H_5^+$ and minor amounts of $FeCl^+$.[318] Many different products arise from the reaction of $Co^+$ with 3-chloro-2-butanone; however, no interaction of the functional groups is observed, but simultaneously products of "ketone and chloride chemistry" are noted.[316]

## B. Ammonia and Amines

Ammonia is unreactive with $Cr^+$–$Cu^+$, and $Ag^+$,[55,319–321] but is exothermically dehydrogenated by $Sc^+$, $Ti^+$, $V^+$, $Y^+$, $Zr^+$, $La^+$, $Ta^+$, and $Os^+$ (eq 62) indicating $D°(M^+–NH) > 96$ kcal mol$^{-1}$.[107,124,319,322] $D°$(Sc$^+$–NH) has also been studied theoretically.[46b] In an ion-beam study two isomeric $CoNH_3^+$ ions were distinguished. At the lowest energies accessible $Co(NH_3)^+$ is formed exothermically with an approximate lifetime of ~0.2 μs at ~0.05 eV; above ~0.8 eV, H–$Co^+$–$NH_2$, which has a lifetime of >60 μs at 1.4 eV, is formed in an endothermic reaction.[323a] In contrast, for $Ni^+$ and $Cu^+$, only the exothermic adduct formation was observed.[323b]

$$M^+ + NH_3 \rightarrow MNH^+ + H_2 \qquad (62)$$

Plotting $D°(M^+–NH_x)$ versus $D°(H_{x+1}C–NH_x)$ gives linear correlations which are displaced from the $D°(M^+–CH_x)/D°(H_xC–CH_x)$ lines by the amount of the nitrogen lone-pair contribution. The magnitude of this extra stabilization depends upon the electronic unsaturation of the metal ions and reaches ~28 kcal mol$^{-1}$ for early transition-metal ions, such as $Sc^+$, $Ti^+$, and $V^+$.[43g]

The rates of hydride abstraction from mono-, di-, and trimethylamine by $Cu^+$ and $Ag^+$ have been determined, formation of the metal hydride is the only process observed; it is fast and exothermic in all cases, except for the reaction of $Ag^+$ with $CH_3NH_2$, which is endothermic and affords only the adduct complex.[324] The same amines have been studied with the group 8–10 metal ions $Fe^+$, $Co^+$, $Ni^+$, $Ru^+$, and $Rh^+$.[196] Hydride abstraction is seen in competition with dehydrogenation and demethanation. As expected the second-row ions afford significantly more loss of $H_2$ than the first-row ions. MH is the sole product in the reaction of $Ag^+$ with 2-butylamine[33g] and of $Cu^+$ with propylamine.[292]

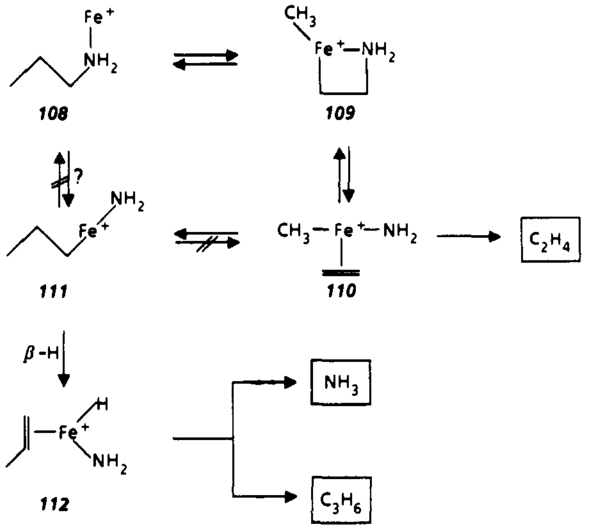


**Figure 27.** Mechanism for the reactions of $Fe^+$ with propylamine involving complete equilibration of the α- and β-position.

In case of $Co^+$ hydride abstraction is a major reaction with various primary amines, and the exclusive or predominant reaction with secondary and tertiary amines. The reaction is absent for t-$C_4H_9NH_2$, which affords only $CH_4$ with $Co^+$, and has therefore been interpreted as α-hydride abstraction, which yields the stable immonium ions.[325] This result is fully supported by $^2$H-labeling studies with several amines, many of which afford metal hydrides with $Co^+$ and $Ni^+$.[315,326,327] Loss of $H_2$, $CH_4$, $C_2H_4$, $C_2H_6$, and others was observed in an ICR study of $Co^+$ with several primary amines. It was concluded that $Co^+$ does not insert into the C–N bond of primary and secondary amines but does so in case of tertiary amines. The products were proposed to derive from C–C insertions, and thus the chemistry of amines was thought to parallel that of alkanes.[325] Support for this conclusion was drawn from a study of propylamine with $Cr^+$–$Zn^+$; similar to alkanes, $Mn^+$ and $Zn^+$ were unreactive, $Cr^+$, $Cu^+$, and $Ni^+$ formed only one product, respectively, and $Co^+$ and $Fe^+$ were able to react in several different ways to afford various products. The observed reactivity was explained in terms of promotion energies to a configuration capable of forming two σ-bonds.[328] Loss of $H_2$ from nearly all amines studied with $Co^+$, in particular $CH_3NH_2$, but not from t-$C_4H_9NH_2$ or $(C_2H_5)_3N$, as well as loss of HD with $C_2H_5ND_2$, led Radecki and Allison into thinking that $H_2$ in *all* cases arose by N–H insertion, which is followed by β-H shift and formation of imines.[325] And yet, $^2$H labeling results (see below) are not in support of this generalization.

Propylamine has been studied with $Fe^+$, $Co^+$, and $Ni^+$ by employing $^2$H labeling.[315,326] All three metal ions afford loss of $H_2$, but while for $Ni^+$ all positions are affected, $Fe^+$ and $Co^+$ generate $H_2$ specifically from the $\omega/(\omega - 1)$ position by remote functionalization (Figure 17). The production of $C_2H_4$ by $Co^+$ and $Ni^+$ is also due to remote functionalization, albeit with scrambling of the ethyl hydrogens in case of $Co^+$, yet, the situation is completely different for $Fe^+$. Contrary to earlier conclusions,[325,328] $C_2H_4$ stems from the α/β-position of the substrate.[315,326] The α- and β-methylene groups are completely equilibrated via intermediate **110** (Figure 27) before $NH_3$ and $C_3H_6$ are formed; **111**, once formed,

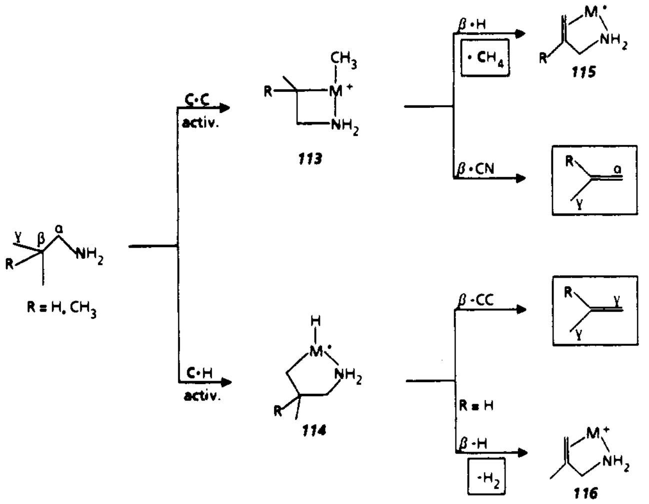


**Figure 28.** Generalized mechanism for the reactions of group 8–10 transition-metal ions $Fe^+$–$Ni^+$ with $i$-$C_4H_9NH_2$ (R = H) and *neo*-$C_5H_{11}NH_2$ (R = $CH_3$).

rapidly decomposes by β-H shift.

Dehydrogenation of butylamine by $Fe^+$, which accounts for 93% of the products, is also due to remote functionalization, but the remaining 7% $C_2H_4$ originate from several positions.[329] 2-Methyl-1-propylamine ($i$-$C_4H_9NH_2$) and 2,2-dimethyl-1-propylamine (*neo*-$C_5H_{11}NH_2$) have been studied with $Fe^+$, $Co^+$, and $Ni^+$.[327] In analogy to propylamine, $H_2$ production for $Ni^+$ is combined with extensive scrambling processes while $Fe^+$ and $Co^+$ dehydrogenate $i$-$C_4H_9NH_2$ specifically by remote functionalization. $CH_4$ for all metal ions and both substrates arises from insertion into a $C_{(2)}$–$C_{(3)}$ bond followed by β-hydrogen shift from another γ-$CH_3$ group and reductive elimination of methane. Production of $C_3H_6$ from isobutylamine and of $C_4H_8$ from neopentylamine is, depending on the metal ion, due to different mechanisms so that even a "tuning" between C–H or C–C activation processes is possible. Figure 28 depicts a generalized view of both mechanisms and also includes the $CH_4$ and $H_2$ losses. Initial C–C or C–H activation generates the intermediates **113** and **114** which may decompose by β-CC or β-CN cleavage, or by β-H shift. $Co^+$ and $Ni^+$ exclusively produce $C_3H_6$ or $C_4H_8$ by the C–H insertion sequence but $Fe^+$ is able to react in *both* ways.[327]

The isomeric substrates 2,2-dimethyl-1-butylamine and 2-ethyl-1-butylamine have been investigated upon their reactivity with $Fe^+$ and $Co^+$.[329,330] $Fe^+$ only affords $H_2$ and $C_4H_8$ from both amines while $Co^+$, in addition, loses $CH_4$, $C_2H_4$, and $C_2H_6$. $^2H$ labeling revealed that $H_2$ and $C_2H_4$ are once again due to remote functionalization and that methane and ethane are formed in a mechanism analogous to Figure 28 by C–C insertion/β-H shift. The production of $C_4H_8$ from both substrates is noteworthy as this represents another case of *C–C activation without preceding C–H activation*. Insertion of the metal ion into a terminal C–$CH_3$ bond is followed by β-cleavage of the C–$CH_2NH_2$ bond; by loss of $n$- or $i$-$C_4H_8$ in both cases $CH_3$–$M^+$–$CH_2NH_2$ ions arise as final products.[329,330] Similarly, $t$-$C_5H_{11}NH_2$ affords $C_4H_8$ loss with $Fe^+$ by insertion into the terminal C–$CH_3$ bond and β-CN cleavage to generate $CH_3$–$Fe^+$–$NH_2$, whose structure has been characterized in CID experiments.[331]

Allylamine has been studied with $Co^+$; $NH_3$, $NH_2$, $C_2H_2$, and $H_2$ are formed.[316] Methanide abstraction from $NH(Si(CH_3)_3)_2$ by $Fe^+$ and $Co^+$ has been reported and attributed to the stability of the resulting organic fragment.[332a] The main product of $Fe^+$ interacting with this substrate is methane which incorporates the unique hydrogen, as revealed from study of the ND analogue.[332b] Interestingly, $CH_3N(Si(CH_3)_3)_2$ produces mainly $C_2H_6$ with $Fe^+$ so that, regardless if N–C or Si–C insertion precedes, the second step of the mechanism requires a β-$CH_3$ shift, either from Si[333] or from N. This unusual step is even reversible, as shown by $^2H$ labeling.[332b]

A report on the reactions of $Ti^+$–$Ni^+$ and $Nb^+$ with mono-, di-, and triethylamine once again showed the preference of the early transition metal ions for C–H activation.[334] $Ti^+$, $V^+$, and $Nb^+$ gave rise to extensive dehydrogenations or losses of hydrogen molecules together with ethane while for $Fe^+$–$Ni^+$ loss of $CH_4$ and $C_2H_4$ was observed, too. $Cr^+$ and $Mn^+$ formed adduct complexes but unspecified amounts of single dehydrogenation were also present. Radical losses were often encountered and may point to the production of excited states in the laser ablation/pulsed molecular beam technique.

## C. Carbonyl Compounds

### 1. Aldehydes and Acyclic Ketones

Already the first representatives, i.e., formaldehyde, acetaldehyde, and acetone, are reactive with several metal ions. $Fe^+$–$Ni^+$ afford decarbonylation according to Figure 29 (R, R′ = H, $CH_3$).[74,76,196,335–338] **120**, which is only observed for acetone (R = R′ = $CH_3$), has been shown by high-energy CID to possess the metal–dimethyl structure indeed.[74] For the decarbonylation of acetaldehyde by $Cr^+$ an excited state is responsible;[337] $Cr^+$ is also unreactive with propanal and acetone.[339] KERD experiments for $Co^+/CH_3COCH_3$ demonstrate the absence of an activation barrier for **118** → **119**, hence, no barrier exists for the reaction of $CH_3$–$CH_3$ with $CoCO^+$.[76]

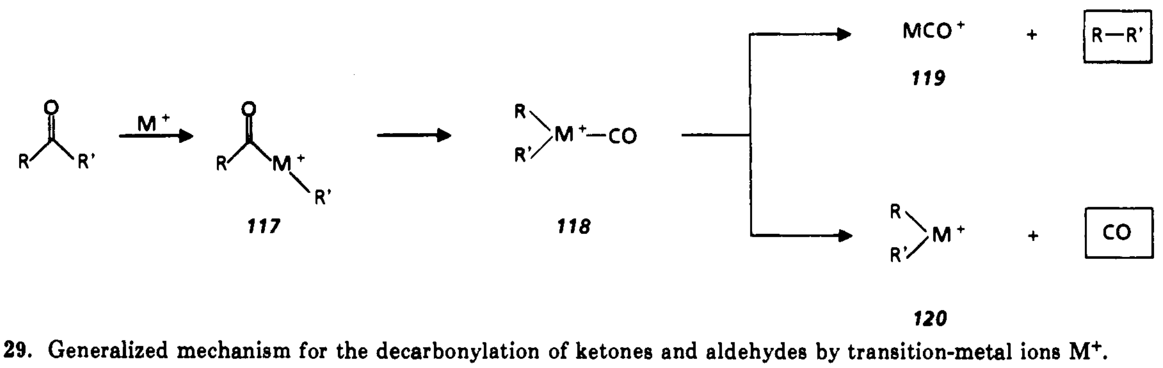


**Figure 29.** Generalized mechanism for the decarbonylation of ketones and aldehydes by transition-metal ions $M^+$.

The second-row group 8–10 ions show a somewhat different behavior than their lighter congeners. Toward acetone, $Pd^+$ behaves analogously to $Ni^+$, but $Ru^+$ and $Rh^+$ in addition to loss of CO and $C_2H_6$ afford mainly loss of $CH_4$ and further $CO/H_2$.[119] With acetaldehyde, besides loss of $CH_4$, which is the only product in case of $Co^+$ and $Ni^+$, $Rh^+$ produces $H_2$ while $Pd^+$ forms PdH.[196] While for propanal the same products are formed by $Fe^+$ and $Ru^+$, and $Co^+$ and $Rh^+$ also give a very similar product distribution, $Ni^+$ and $Pd^+$ show a pronouncedly different reactivity. Dehydrogenation, which accounts for 43% of the $Ni^+$ products, is absent for $Pd^+$, which mainly forms PdH.[196] $Rh^+$ and $Pd^+$ both dehydrogenate formaldehyde.[338] $Mn^+$ is unreactive with acetone, but endothermic formation of $MnCH_3^+$ and $MnCH_3$ has been reported in an ion-beam study.[189] Hydride or methanide abstraction by $Cu^+$ for propanal[340] or acetone,[335] respectively, is not believed to involve an insertion mechanism; with $CH_2O$ only adduct formation is observed.[338]

Transition-metal ions with high oxygen affinities often form predominantly $MO^+$ ions in their reactions with acetaldehyde and acetone, e.g., $Sc^+$,[79] $Ti^+$,[341] or $Gd^+$ and $Pr^+$.[103] This is however not necessarily true for formaldehyde, which often gives rise to $MH_2^+$ ions, e.g., with $Sc^+$ [79] and $Gd^+$;[103] thus the strength of two $M^+$–H bonds may in combination with CO even outweigh that of a $M^+$–O bond with $H_2$. Quite similarly, $Os^+$ forms 75% $OsCO^+$ and 25% $OsH_2^+$ with $CH_2O$; however, with $CH_3CHO$, $OsCH_2^+$ is the sole product.[124] A 1:1 formation of $OsCH_2^+$ and $OsCHD^+$ from $CH_3CDO$ indicates that this reaction proceeds via decarbonylation and involves fast and reversible $\alpha$-hydrogen shifts in the hydrido–methyl intermediate.[124]

The difference in the ionization energies is held responsible for contrasting UV-photodissociation results for $Ag(CH_3COCH_3)^+$ versus $Al(CH_3COCH_3)^+$. The latter complex undergoes simple ligand detachment, while for $Ag^+$ photoinduced charge transfer is possible and affords acetone ions and by dissociative charge transfer acetyl ions.[342] This latter reaction also gives an upper limit for $D°(Ag^+$–acetone).[342b]

The chemistry of medium-sized ketones with $Fe^+$ [42g,74,335] and $Co^+$ [42g,336,343] is also dominated by C–CO insertions. Yet, the migratory deinsertion[344] **117** → **118** is now in competition with $\beta$-hydrogen shifts from R or R′ which finally yield alkanes, alkenes, or aldehydes by reductive elimination; loss of CO is generally absent. Dehydrogenation is observed as well, and for 2-pentanone/$Fe^+$ it has been shown by $^2H$ labeling that remote functionalization is operative and is also responsible for the $C_2H_4$ loss.[335] Methyl-branched ketones are observed to react via C–C insertions, $\beta$-H shifts, and reductive elimination of $CH_4$.[74,335,336] Allyl complexes are postulated as important intermediates in the reactions of $Fe^+$, e.g., after dehydrogenation allylic C–C insertion precedes decarbonylation.[335] $Cu^+$ is reported to react with linear ketones by either loss of $H_2O$ and diene-complex formation, or by cleavage of the substrate into an alkene and an enol and competitive ligand loss. Mechanisms devoid of metal-ion insertions are suggested and in analogy to the reactions of alkali-metal ions in section VII.A termed "dissociative attachment".[340] For branched ketones, $CuCH_3$ formation effectively competes with these reactions.[335,340] The group 13 ions $Al^+$, $Ga^+$, and $In^+$ only form adduct complexes with ketones.[42g,301]

For several linear ketones, ranging from heptanone to undecanone, extensive $^2H$- and $^{18}O$-labeling studies permitted detailed mechanistic insights about the reactions with $Fe^+$. For these substrates C–CO insertions are completely absent and remote functionalization is the only mechanism still being operative. The symmetric 4-heptanone served to determine kinetic isotope effects; all steps in Figure 17 ($X = C_3H_7CO$, $R = H$) were found to be rate determining, except for the C–H insertion.[345,346] Exactly paralleling the behavior of nitriles, for longer-chain ketones the C–H insertion not only affects the $\omega$-$CH_3$ but also the $(\omega - 1)$-$CH_2$ group, affording propene and $H_2$ from the $(\omega - 1)/(\omega - 2)$ position. $Fe^+$ generates $H_2$ from 4-octanone and 4-nonanone exclusively from the longer chain and with preferential formation of 8-membered metallacycles.[346]

Another analogy to nitriles is the *double remote functionalization* of ketones reacting with $Fe^+$. By use of $^2H$ and MS/MS techniques it could be shown that $C_2H_6$ loss from 5-nonanone is actually due to consecutive loss of first $C_2H_4$ from one chain followed by dehydrogenation of the other chain.[290,346] Just as for the nitriles the reversed sequence could be excluded. Loss of 30 and 44 amu from 6-undecanone similarily arises from loss of first $C_2H_4$ or $C_3H_6$ followed by dehydrogenation of the $(\omega - 1)/(\omega - 2)$ position of the alternate chain. For the asymmetrical 4-nonanone $C_2H_4$ exclusively stems from the shorter chain but $H_2$ is provided from both, now identical chains, demonstrating that the hydrogen rearrangement in the course of **68** → **69** is fast compared to the subsequent second C–H insertion.[346]

2-Hexanone and 4-heptanone reacting with $Fe^+$ under FTICR conditions give rise to products which are all due to initial remote functionalization; yet, multiple losses are observed by subsequent decomposition of the primary products.[347] Some of the final products arise by double remote functionalization. Multiple losses and C–C cleavage products are completely suppressed by forming "colder" $Fe(ketone)^+$ collision complexes by means of ligand substitution (see section VIII.E).[347]

The analytical utility of the reactions of bare metal ions with aldehydes, ketones, esters, and ethers has been evaluated in several studies. As a test for simple cationization the group 11 ions $Cu^+$–$Au^+$ were reacted in a spark source with several compounds, but owing to the presence of excited states under the experimental conditions many products were formed which further differed from ICR results.[348] By employing pattern recognition techniques to distinguish ketones, aldehydes and ethers, several metal ions were evaluated for use as chemical ionization reagents. The results reflect several inherent properties of the individual ions, e.g., while $Cr^+$ mainly gives rise to adduct complexes, $Cu^+$ does only so with ketones and mainly forms CuH with aldehydes, and the oxygen affinity of $Sc^+$, $Y^+$, and $La^+$ leads to abundant $MO^+$ ions.[349–351] $MO^+$ ions are also the exclusive products for several aldehydes and ketones studied with $Ti^+$ [42g,341] and $V^+$.[42g]

### 2. Cyclic Ketones

Cyclic ketones are of special interest as decarbonylation might give rise to metallacycle formation, therefore they have been studied in more detail with quite a variety of mass-spectrometric techniques. $Fe^+$, $Co^+$, and $Ni^+$ are the only metal ions that have been investigated. All three of them react with cyclobutanone as shown in eqs 63 and 64; $Fe^+$ in addition produces a small amount of $FeC_2H_4^+$.[207,214,218,268]

$$M^+ + c\text{-}C_4H_6O \rightarrow MC_3H_6^+ + CO \qquad (63)$$

$$\rightarrow MCO^+ + C_3H_6 \qquad (64)$$

With regard to the structure of the $MC_3H_6^+$ ions, there is agreement that $Fe^+$ forms *stable ferracyclobutane* ions **33**, while the initially formed metallacycles of $Co^+$ and $Ni^+$ at least partly isomerize to the thermodynamically more favorable propene complexes **13**. This has been demonstrated with H/D exchange experiments, employing $C_2D_4$,[268] in ligand-exchange[207,218] and CID studies,[207,214,218] as well as from kinetic energy release distributions.[214] The identity of the $C_3H_6$ neutral eliminated in eq 64 differs, depending on the history of the precursor ions. Metastable loss of cyclopropane, $c\text{-}C_3H_6$, from $M(c\text{-}C_4H_6O)^+$ complexes (M = Fe, Co) is associated with a large kinetic energy release, indicating a substantial barrier for the reverse reaction. On the other hand, $MC_3H_6^+$ ions, formed in the *ion source* from $M^+$ and cyclobutanone, unimolecularly exclusively lose the thermodynamically more stable propene as indicated by the small average kinetic energy release.[214]

Decarbonylation of cyclopentanone by $Fe^+$–$Ni^+$ produces stable metallacyclopentanes **18**, as was shown by CID and ligand-exchange experiments (see above).[33v,74,105,177,178,207,218,335,336] Further products are $H_2$, $CO/H_2$, and $CO/C_2H_4$; the mechanism which applies for the consecutive losses has already been presented in Figure 12 and discussed in section IV.D.

Cyclohexanone-$\alpha,\alpha'$-$d_4$ with $Fe^+$ produces mainly $H_2$ and $H_2/CD_2CO$.[33v,335] Initial C–CO insertion, $\beta$-H shift and allylic C–H activation generates $H_2$; this product partly decomposes further by $\beta$-CC cleavage to afford Fe(butadiene)$^+$ by loss of ketene. An alternative mechanism involving electrocyclic processes has also been suggested.[33v] Decarbonylation is only a minor process in this system (3%).

Norbornanone upon reaction with $Fe^+$ shows loss of $CH_2CO/H_2$ as well as decarbonylation combined with dehydrogenation.[33v]

### *3. Carboxylic Acids and Their Derivatives*

Carboxylic acids have only been studied with $Co^+$[343] and $Cu^+$;[340] loss of $H_2O$ and $MH_2O^+$ formation are the major processes for $Co^+$ and the exclusive reactions of $Cu^+$. With increasing chain length, again, a chemistry which is more "alkane-like" is observed, C–C insertions being operative.[343] Functionalized acids show a mixture of the individual group reactivities and the preferential site of $Co^+$ attack decreases in the row COOH > Br > Cl > SH > OH > CO > H.[343]

$Cu^+$ induces cleavage of esters $RCO_2R'$ into alcohol/ketene and acid/alkene pairs, with all four possible complexes observed. Absence of aldehyde losses has been interpreted as an absence of C–CO insertion, and thus mechanisms avoiding $Cu^+$ insertions have been suggested and referred to as dissociative attachment. Besides, $RCO_2^-$ abstraction with concomitant $R'^+$ formation is noted and increases with the stability of $R'^+$.[340] $Al^+$ similarly produces $Al(R'OH)^+$ by loss of ketenes and very small amounts of $RCO^+$ by alkoxide abstraction,[300,301] while $Ga^+$ and $In^+$ only form the adduct complexes.[301] $Ti^+$ is unreactive with esters.[341]

Carboxylic acid halides react with $Li^+$,[274,293,294,297] $Fe^+$,[297] or $Co^+$[297] either by loss of HX or by formation of LiX and are inert with $Na^+$.[274]

## D. Ethers

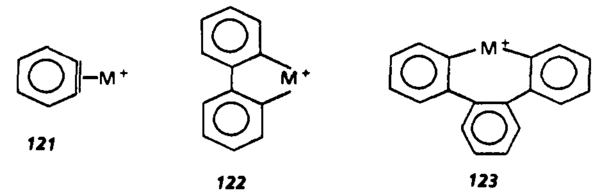
The chemistry of ethers is dominated by C–O insertions for most transition-metal ions studied so far; subsequent $\beta$-hydrogen shifts from both sides are assumed to explain the losses of alkenes, alcohols, and alkanes from acyclic ethers. For instance, besides a small amount of dehydrogenation only $C_2H_4$, $C_2H_6O$, and $C_2H_6$ are generated from $Fe^+$ reacting with $Et_2O$.[196,335,352] All of them may be explained by the outlined mechanisms. The same products are formed by $Co^+$ and $Ni^+$, but in addition, hydride abstraction is noted.[196,325] Interestingly, $Co^+$ produces about 30% CoH with $Et_2O$, $Ni^+$ already 81% NiH, and for $Cu^+$, CuH is the exclusive product with all ethers besides the adduct complex.[335,350] In the second row, MH formation rises similarly from $Ru^+$ (1%) over $Rh^+$ (17%) to $Pd^+$ (100%).[196] Even $Al^+$ affords loss of $C_2H_4$ from $Et_2O$ but is otherwise unreactive with $Me_2O$, *t*-BuOMe, and $MeOC_2H_3$.[300]

Exceptions from the general mechanism are noted for $Sc^+$ which yields again mainly $ScO^+$, but also $ScOH^+$ and $ScCH_2O^+$, from ethers.[350] $Ti^+$, if it reacts at all, with ethers also exclusively forms $TiO^+$.[341] In a study of $Fe^+$ and $Cr^+$ reacting with two polyethers, the products formed from triethylene glycol dimethyl ether could still be described by C–O insertion/$\beta$-H shift sequences, yet, for the cyclic 12-crown-4 "double metal insertion/double $\beta$-H shift processes" were proposed.[352] $Fe^+$[335] and $Co^+$[325] were studied with tetrahydrofuran; both ions afford loss of $H_2O$ and of $CH_2O$; $Co^+$ in addition forms CoH. Two mechanisms have been suggested, both with initial C–O insertion.

Ethylene oxide has been used frequently to derive $D°(M^+–CH_2)$ and $D°(M^+–O)$ bond dissociation energies in ion-beam instruments (M = $Cr^+$,[208,339] $Mn^+$,[189] $Co^+$,[210,211] $Ni^+$,[211,212] $Cu^+$[211]), or to produce $MCH_2^+$ alkylidene ions for further investigations in ICR instruments (M = $Mn^+$,[353] $Fe^+$,[105,354–356] $Co^+$,[105,354–356] $Rh^+$[140]). Usually, the two possible metallacycles which arise from C–O or C–C insertion are invoked as reaction intermediates; retro-[2 + 2] reaction affords $C_2H_4$ or $CH_2O$ loss, respectively. Interestingly, iron atoms in a matrix were also found to spontaneously insert into the C–O bond of ethylene oxide to yield ferraoxetane[357a] which upon UV photolysis rearranged to $FeO(C_2H_4)$.[357b,c] For $Co^+$ and $Ni^+$, loss of $CH_4$, i.e., $MCO^+$ formation, is an important exothermic process, too.[210–212] Metal ion induced isomerization of ethylene oxide to acetaldehyde has been suggested to explain this product. The only exothermic reaction for $Cu^+$ is hydride abstraction which, however, must afford acetyl ions for thermodynamic reasons.[211]

## E. Aromatic Compounds

Only a few aromatic compounds have been studied so far, all of them are benzene derivatives, and already the first study in 1978 dealt with the most intensely employed class, viz. halobenzenes. Ridge and coworkers observed the formation of a benzyne complex



121 122 123

**Figure 30.** Proposed structures of the products that arise from the consecutive reaction of phenyl halides with transition-metal ions $M^+$.

upon reaction of $Fe^+$ with fluoro-, chloro-, and bromobenzene (eq 65, $n = 1$).[358] The $Fe^+$–benzyne complex

$$M(C_6H_4)_{n-1}^+ + C_6H_5X \rightarrow M(C_6H_4)_n^+ + HX \qquad (65)$$

was found to react similarly ($n = 2$). Instrumental limitations precluded the observation of further reactions, but in more recent FTICR instruments the reaction could be followed up to $n = 7$ for X = Cl, Br, but it stops at $n = 2$ for X = F.[359–361] Coupling of the $C_6H_4$ units may be inferred from the observation of oligophenylene ions $C_{6n}H_{4n}^+$, arising from secondary reactions,[359–361] or as CID products. CID upon $FeC_{6n}H_{4n}^+$ affords only $Fe^+$ for $n = 1$, but exclusively $C_{6n}H_{4n}^+$ for $n = 2$–4.[361] Structures **121–123** (Figure 30) have been suggested for $n = 1$–3 and analogous ones may be drawn for larger values of $n$. Iodobenzene behaves differently, $FeC_6H_5^+$ being the sole product.[358–360] $FeI^+$, reported earlier as a primary product, is probably a secondary product, arising from $FeC_6H_5^+$ reacting with iodobenzene to yield $FeI^+$ and biphenyl.[359] Equation 65 was also noted for $Ti^+$ (X = Cl; $n = 1$–3)[302] and $Ni^+$ (X = Br, I; $n = 1$),[362] while $Ni^+$ [362] and $Cu^+$ [307] only form the chlorobenzene adduct-complexes. Phenol also loses $H_2O$ in the reaction with $Fe^+$ (X = OH; $n = 1, 2$),[360] but all other phenyl derivatives studied so far do not form any benzyne complexes.

Benzene itself is unreactive with $Ti^+$,[363a] $V^+$,[363a] $Cr^+$,[363a] $Mn^+$,[363a] $Fe^+$,[360,363a] $Co^+$,[363a] $Ni^+$,[33w,362,363a] $Cu^+$,[307,363a] $Mo^+$,[363a] $Ag^+$,[33w] and $W^+$ [363a] but is dehydrogenated by $Sc^+$,[42e] $Nb^+$,[114,363a] and $Ta^+$;[125] the latter ion affords loss of $C_2H_2$ and $C_2H_4$ as well. Surprisingly, the thus formed $Sc^+$–benzyne ion can be *hydrogenated* by $H_2$ to form presumably $Sc^+$–benzene.[42e] UV photodissociation of $Al(C_6H_6)^+$ gives ligand detachment only, while several transition-metal complexes $M(C_6H_6)^+$ (M = Ag, Cu, Fe), owing to the lower ionization energy of M, undergo photoinduced charge transfer (CT) to $C_6H_6^+$.[342] $Au^+$, in the reaction with benzene, even forms small amounts of the CT product directly, aside from the adduct.[11,364] Benzene clusters $(C_6H_6)_n$ have been reacted with several metal ions, and mainly $M(C_6H_6)_m^+$ ions resulted; however, $Y^+$, $Nb^+$, and $Ta^+$ also formed fragment ions $M(C_6H_6)(C_xH_y)^+$.[363b] Several benzene bond dissociation energies, $D°(M^+–C_6H_6)$ and $D°(M(C_6H_6)^+–C_6H_6)$, have been determined by photodissociation.[341,105,342b]

Toluene is inert with $V^+$,[363a] $Fe^+$–$Ni^+$,[257,360,362] $Cu^+$,[363a] and $Nb^+$ [363a] but is dehydrogenated by $Rh^+$;[257] from CID experiments, which afforded exclusively $RhC^+$, a $RhC(C_6H_6)^+$ structure was inferred for the product. Yet, in another study by the same authors the latter structure could be excluded and now a phenyl–alkylidene structure was considered to be more likely.[365] Similar to $ScC_6H_4^+$ the $RhC_7H_6^+$ complex may be hydrogenated by $H_2$ or $C_2H_6$ to furnish $RhC_7H_8^+$, probably the toluene complex.[365] $Au^+$, besides the predominant charge-transfer reaction, affords $C_7H_7^+$ by hydride abstraction; from the study of secondary reactions 90% benzyl and 10% tropylium structure were suggested for this ion.[11] Ethylbenzene, which is dehydrogenated by $Fe^+$,[360] similarly affords hydride and methanide abstraction with $Au^+$ but cleavage to $C_2H_4$ and $C_6H_6$ is also observed.[11] Photodissociation of $Ag(toluene)^+$ yields only $C_7H_8^+$, from which $D°(Ag^+–C_7H_8)$ was obtained as an upper limit.[342b]

Several phenyl compounds have been studied with $Fe^+$ [360] and $Ni^+$.[362] Both ions readily insert into benzylic bonds; products are formed by subsequent $\beta$-H shifts producing, e.g., $CH_2O$ from $C_6H_5OCH_3$, $CH_4$ from $C_6H_5CD(CH_3)_2$, or $C_3H_6$ from $n$-$C_4H_9$-$C_6H_5$. Benzoyl compounds are decarbonylated, and benzylic substrates often yield $C_6H_5CH_2^+$ ions. The integrity of the phenyl group is only affected in case of nitrobenzene which forms $MC_5H_5^+$ via loss of NO/CO.[360,362] Pentafluorophenyl compounds behave differently, they often give rise to the formation of $FeF_2$ *neutrals*.[360]

Differentiation of disubstituted benzene derivatives could be accomplished with $Fe^+$; three classes of substrates emerged.[366] For some compounds all three isomers could be identified by either their primary or their secondary reactions, for others only the ortho isomer could be distinguished from meta and para, and the xylylenes could not be distinguished at all. The unique position of the ortho isomer results most likely from cooperative effects, furnishing chelated products. The para isomers showed the individual reactivities of their substituents, and the meta compounds revealed a mixed behavior.[366]

## F. Others

### 1. Silicon Compounds

Only silanes have been studied so far with bare metal ions. Silane itself is dehydrogenated by $Ti^+$,[367] $Co^+$,[367] $Ni^+$,[367] and $Y^+$.[368] $Os^+$ even double dehydrogenates $SiH_4$, forming the osmium silicide $OsSi^+$.[124] $V^+$ and $Fe^+$ do not react with $SiH_4$, and $Cr^+$ is even unreactive with all silanes, similar as toward alkanes.[367] CID upon $CoSiH_2^+$ reveals its silylene structure, $Co^+{=}SiH_2$, which has been described in terms of a $\sigma$-donor/$\pi$-acceptor bonding.[367] The facility of this 1.1 elimination is probably due to the fact that loss of $H_2$ from $SiH_4$ requires only 61 kcal mol$^{-1}$, compared to 112 kcal mol$^{-1}$ in the case of $CH_4$.

Methylsilanes $SiH_n(CH_3)_{4-n}$ give rise to losses of $H_2$ and $CH_4$ upon reaction with $Ti^+$, $V^+$, $Fe^+$, $Co^+$, $Ni^+$, and $Rh^+$.[196,367] $^2H$ labeling proves the silylene-complex formation through 1.1 eliminations.[367] $Co^+$ and $Ni^+$ with $SiH(CH_3)_3$ mainly react by hydride abstraction and with $Si(CH_3)_4$ exclusively by methanide abstraction.[196,367] Methanide abstraction is also a minor process which is observed for $CH_2(Si(CH_3)_3)_2$ with $Fe^+$ and $Co^+$.[332a] $Os^+$ affords losses of $CH_4/H_2$ and $2H_2$ with $SiH_3CH_3$.[124] While for $Fe^+$–$Ni^+$ reacting with $Si_2(CH_3)_6$ only the Si–Si cleavage products $SiH(CH_3)_3$ and $Si(CH_3)_4$ are observed, for $Ti^+$ and $V^+$ in most of the various products this bond remains unaffected, despite of its weakness.[367] $Si(CH_3)_4$ from the reaction of $Fe^+$ with $CH_2(Si(CH_3)_3)_2$ does not arise from $CH_2$–Si insertion/$\beta$-H shift since for the $CD_2$ analogue no deuterium incorporation is observed.[332b] Thus, either a $\beta$-$CH_3$ or a $\beta$-$Si(CH_3)_3$ shift is operative.

Several products arise from the metastable decays of $Fe^+$/*n*-heptyltrimethylsilane complexes.[369] Insertion of $Fe^+$ into the $C_{(\alpha)}$–$C_{(\beta)}$ bond is favored, probably due to the $\beta$-silicon effect.[265] $\beta$-H shift affords $Si(CH_3)_4$; the reaction is specific, as shown by $^2H$ labeling. Insertion into the $C_{(\beta)}$–$C_{(\gamma)}$ bond and subsequent $\beta$-H shifts from both sides yield $Si(CH_3)_3C_2H_5$, $C_3H_8$, and $C_5H_{12}$; $H_2$ and $SiH(CH_3)_3$ specifically originate from $C_{(\alpha)}/C_{(\beta)}$. $C_2H_4$ is provided equally from $C_{(\alpha)}/C_{(\beta)}$ and $C_{(\gamma)}/C_{(\delta)}$; a ferracyclopentane intermediate is suggested to account for this rapid equilibration of the $CH_2CH_2$ units.

### 2. *Nitrogen and Phosphorus Compounds*

Except for the nitrogen compounds discussed earlier, nitroalkanes, alkyl nitrites, isocyanates, and aldimines have been studied.

Several products arise from the reactions of $Fe^+$–$Ni^+$ with methyl nitrite.[338,370] $Fe^+$ and $Co^+$ react almost identically, with loss of NO and concomitant $MOCH_3^+$ formation predominating. For $Ni^+$ this ion is also formed, yet, a major part undergoes further loss of $H_2$ to $NiCHO^+$. CID upon $MOCH_3^+$ affords $MH^+$, which is also observed as an important primary product, and three H/D exchanges are observed with $C_2D_4$, indicating either a $H$–$M^+$–$(OCH_2)$ structure or a rapid equilibrium with $M^+$–$OCH_3$. Cleavage of the weak O–NO bond is also important in the reactions with 1-butyl nitrite, where losses of NO, $NO/H_2$, or $NO/2H_2$ are major processes for $Fe^+$–$Ni^+$.[370,371] Abundant $MCH_2NO_2^+$ products are found for $Co^+$ and $Ni^+$, indicating that radical losses may be favored over $\beta$-H shifts for C–C insertion intermediates in some cases.

$Ni^+$ is unreactive with nitromethane, $Fe^+$ and $Co^+$ mainly produce $MOCH_3^+$, besides $MO^+$ and $MOH^+$.[338,370] A metal-assisted nitro-to-nitrite isomerization has been suggested to account for the main product while $CH_3N$–$MO_2^+$ is believed to be an intermediate for the other ions. Several other nitroalkanes have been studied with $Fe^+$–$Ni^+$, and it could be concluded that isomerization becomes less favorable with increasing chain length.[370,371] Insertions into C–H, C–C, C–N, and N–O bonds are proposed to explain the multitude of products which are formed. For example, $MCH_2NO_2^+$ ions are assumed to arise from C–C insertions with subsequent radical losses, indicating, similar to the 1-butyl nitrite case above, that $\beta$-H shifts are disfavored. In general, $Ni^+$ seems to prefer C–N insertion and $Fe^+$ C–C and N–O insertion, with $Co^+$ being intermediate. Alkyl ions that arise from loss of $MNO_2$ are frequently observed and drastically gain in importance for branched nitroalkanes; $Ni^+$ yields the highest amount of these ions and is also observed to form abundant $NiHNO_2^+$ ions. While those were explained by invoking a C–N insertion/$\beta$-hydrogen shift mechanism,[370,371] the simultaneous formation of alkyl ions could indicate that in fact the ion/dipole mechanism (analogous to Figure 22) might be operative.

Some other metal ions have been studied with methyl nitrite and nitromethane.[338] In line with the increased tendency of second-row ions for dehydrogenations, the reactions of $Rh^+$ and $Pd^+$ with methyl nitrite produce higher amounts of $MOCH^+$ ions by loss of $NO/H_2$ than those of their first-row congeners $Co^+$ and $Ni^+$. But while for the first-row ions less than 10% NO retention obtained, for $Rh^+$ and $Pd^+$ more than 50% of the products retain NO as $MNO^+$ or $MHNO^+$ ions; CID upon the latter affords $MH^+$. $Cu^+$ yields mainly and $Ag^+$ exclusively $MOCH_2^+$ with methyl nitrite. $CuOCH_3^+$, which is the other product for $Cu^+$, does not exchange its hydrogens with $D_2$ or $C_2D_4$, possibly indicative of a $Cu^+$–$OCH_3$ structure. $Cu^+$ does not react with nitromethane and $Rh^+$ and $Pd^+$ afford $MNO^+$ ions as sole products.[338]

Isopropyl isocyanate has been studied in particular depth[372,373] as some data was available for its catalyzed and uncatalyzed decomposition. Bock and Breuer reported that the uncatalyzed pyrolysis of *i*-$C_3H_7NCO$ begins at 920 K and yields propene and isocyanic acid (eq 66).[374] In contrast, $Ni_x$ clusters on carbon as support ($Ni_x/C_\infty$) are able to catalyze at 500 K the decomposition of the substrate to carbon monoxide, methane, and acetonitrile (eq 67); most likely this reaction proceeds via surface-bound nitrenes.[374]

$$i\text{-}C_3H_7NCO \rightarrow CH_3CH = CH_2 + HNCO \quad (66)$$

$$\begin{aligned} &i\text{-}C_3H_7NCO + Ni_x/C_\infty \rightarrow \\ &\qquad CH_3CN + CH_4 + CO + Ni_x/C_\infty \quad (67) \end{aligned}$$

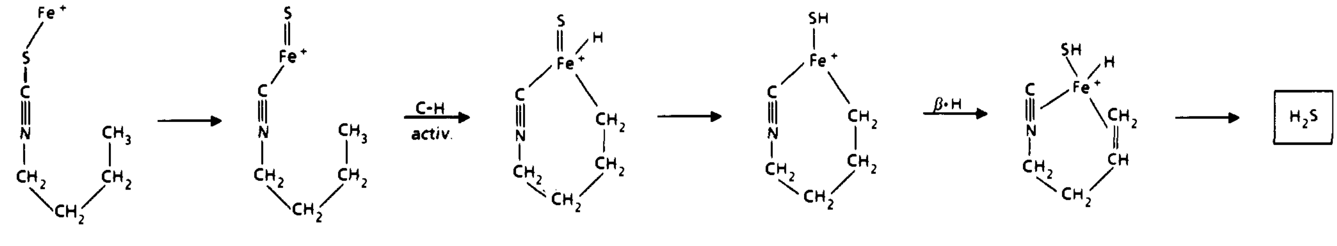
Yet, $Ni^+$ treated with *i*-$C_3H_7NCO$ did not afford a similar cleavage but instead gave propene and HNCO (eqs 68 and 69).[372,373] $Cr^+$, $Mn^+$, $Fe^+$, $Co^+$, $Cu^+$, and $Zn^+$

$$\begin{aligned} &Ni^+ + i\text{-}C_3H_7NCO \\ &\qquad \rightarrow Ni(HNCO)^+ + C_3H_6 \quad (95\%) \quad (68) \\ &\qquad \rightarrow Ni(C_3H_6)^+ + HNCO \quad (5\%) \quad (69) \end{aligned}$$

showed strictly analogous behavior with at least 80% propene loss. $^2H$ labeling revealed that a specific 1.2 elimination was operative and that the kinetic isotope effects for both pathways were identical, respectively, and all in the range between 1.2 ± 0.1 and 1.6 ± 0.1. The reactions of $Ti^+$ and $V^+$ with *i*-$C_3H_7NCO$ substantially differed from those of $Cr^+$–$Zn^+$, with 57% (Ti) and 74% (V) of the products being formed according to eq 70. CID and $^2H$-labeling studies were in support

$$M^+ + i\text{-}C_3H_7NCO \rightarrow M(CH_3CN)^+ + CH_4 + CO \quad (70)$$

of acetonitrile complexes, formally generated in a specific 1.1 elimination. The first step of the mechanism is believed to be loss of CO and nitrene-complex formation, in analogy to the surface-catalyzed process[374] and general knowledge about condensed-phase chemistry of isocyanates with transition-metal complexes.[375,376] The question of if C–H or C–C activation precedes could not be resolved, despite the labeling. The different outcome of the reaction for early versus late first row transition-metal ions is explained by the nitrene binding energies which are quite high for $Ti^+$ ($D°(Ti^+$–$NH) = 111 \pm 3$ kcal $mol^{-1}$ [322]) and $V^+$ ($D°(V^+$–$NH) = 99 \pm 4$ kcal $mol^{-1}$ [107]), but significantly lower for the other metal ions. $D°(Fe^+$–$NH) = 54 \pm 14$ kcal $mol^{-1}$,[319] and the absence of $NH_3$ dehydrogenation for $Cr^+$–$Cu^+$ [55,319,320,321a,b] could furthermore indicate that $D°(M^+$–$NH) < 96$ kcal $mol^{-1}$, respectively, if no barriers are present. It was thus concluded that initial nitrene formation was the crucial factor. Transcribing this into the condensed phase would imply that catalysts with high binding energies for surface nitrenes[377] should work best for the production of acetonitrile.



124 125 126 127 128

**Figure 31.** Mechanism for the dehydrosulfurization reaction of butyl isothiocyanate with $Fe^+$.

$^2H$ labeling on two aldimines $R^1N{=}CHR^2$ showed that $Fe^+$ exclusively reacted via remote functionalization to produce hydrogen and alkenes and via double remote functionalization to afford $C_2H_{2n}/H_2$.[378] Activation of $R^1$ is favored as long as it is longer than $R^2$; for $R^1 = R^2$, $R^2$ is preferentially attacked.

Reactions of phosphaalkynes[379] with bare $Fe^+$ have been investigated[185] in order to compare the gas-phase behavior of phosphaalkynes $RC{\equiv}P$ with that of nitriles $RC{\equiv}N$ and alkynes $RC{\equiv}CH$. In view of the closer analogies of $RC{\equiv}P$ with $RC{\equiv}CH$ rather than $RC{\equiv}N$ in the condensed phase, in e.g., addition reactions,[380] cycloadditions,[381] transition metal mediated cyclotrimerizations,[382a,b] reactions with carbene complexes,[382c,d] and last but not least in coordination chemistry,[383] it is not surprising that in their reactivity toward $Fe^+$ phosphaalkynes resembles more the corresponding alkynes than the nitriles. While for $t\text{-}C_4H_9CN$ and $t\text{-}C_5H_{11}CN$ loss of HCN and $Fe(HCN)^+$ formation are the most important processes (c.f. section VI.B), from $t\text{-}C_4H_9CP$ $CH_4$, and from $t\text{-}C_5H_{11}CP$ $CH_4$, $C_2H_4$, and $C_2H_4/CH_4$ are produced. As discussed in section V.B, from $t\text{-}C_4H_9CCH$ $CH_4$ and $CH_4/C_2H_2$ are generated, and $t\text{-}C_5H_{11}CCH$ affords $CH_4$ and $C_2H_4$. Both *tert*-pentyl "alkynes" afford 6% methane and around 80% ethene, thus insertion into $C\text{-}C_2H_5$ is clearly favored over that into $C\text{-}CH_3$, in line with the results of Radecki and Allison.[182] The absence of the consecutive elimination (Figure 19) for $t\text{-}C_4H_9CP$ is most likely due to the fact that this would imply loss of the elusive HCP molecule. $^2H$ labeling revealed that all losses are specific for $t\text{-}C_5H_{11}CP$. Methane arises from insertion into the "phosphapropargylic" $C\text{-}CH_3$ bond, followed by β-H shift exclusively from the methylene group, indicating a preference of hydrogen transfer from $\beta\text{-}CH_2$ over $\beta\text{-}CH_3$. $C_2H_4$ is specifically provided by the ethyl group and the arising product partly decomposes further by loss of $CH_4$.

### 3. Sulfur Compounds

Sequential sulfur abstraction is noted for $Ti^+$,[384] $V^+$,[384] $Fe^+$,[105,308,384-386] $Co^+$,[105,384,386] and $Ta^+$,[125] if treated with ethylene sulfide (eq 71). $Fe^+$ attaches up to six, $Ta^+$

$$MS_{n-1}^+ + c\text{-}C_2H_4S \rightarrow MS_n^+ + C_2H_4 \qquad (71)$$

eight, and $V^+$ at least eight sulfur atoms. $Al^+$ and $Cu^+$, however, only form the ethylene sulfide adduct complexes, albeit at higher pressures.[384] Metal sulfide ions can also be formed by reaction of $Ni^+$ with methanethiol $CH_3SH$,[105,386] or of $Ti^+$ or $V^+$ with ethanethiol,[42g] and $FeS^+$ is even the sole product in the reaction of $Fe^+$ with thiophenol.[360] Elemental sulfur $S_8$, introduced in the FTICR via a heated direct-insertion probe, produces with $Fe^+$ in primary and secondary reactions $FeS_n^+$ ions with $n$ = 1–10.[308,385]

CID and photodissociation of $MS^+$ (M = Fe–Ni) affords the bare metal ions so that $D°(M^+\text{-}S)$ data could be determined.[105,385,386] Quite surprisingly, the most prominent CID and photodissociation process for $FeS_n^+$ ($n$ = 2–10) is loss of $S_2$. This applies, regardless if $FeS_n^+$ is formed from ethylene sulfide, from $S_8$, or even by sequential CID from $FeS_{10}^+$ in an impressive $MS^7$ experiment.[308,385] Unfortunately, $S_2$ loss may not be very diagnostic of the structure; for example, $FeS_{10}^+$ containing only coordinated $S_2$ units, i.e. $Fe(S_2)_5^+$, would result in the unreasonable oxidation state of Fe(XI); ring structures are therefore more likely.

The majority of the products which arise from $Co^+$ reacting with alkanethiols stems from C–S cleavage.[343] Loss of $H_2S$ together with $CoH_2S^+$ formation accounts for the majority of the products formed; retention of the olefin is slightly favored for the studied ethane-, propane-, and butanethiols. $SH^-$ abstraction also occurs in some cases, but C–C insertions are always of minor importance, except for 2-methyl-1-propanethiol, where 24% $C_3H_6$, arising from $C_{(1)}\text{-}C_{(2)}$ insertion, is observed. The two main products are explained by C–S insertion/β-H shift, but again, their formation could equally well be described by the ion/dipole mechanism (c.f. Figure 22); indeed, carbenium ion formation seems to indicate its operation.

The ion/dipole mechanism has also been noted to apply in the reactions of isothiocyanates with bare $Fe^+$.[387] For ethyl isothiocyanate ($C_2H_5NCS$) and propyl isothiocyanate ($n\text{-}C_3H_7NCS$) loss of HNCS and $Fe(HNCS)^+$ formation are the most important processes. For $n\text{-}C_4H_9NCS$, however, their combined intensity drastically drops to 21% as other processes come into competition. $^2H$ labeling proves that all positions participate to their formation, indicative of the intermediate carbenium ions. HNCS is preferentially retained, but the ratio of HNCS versus alkene loss increases for larger alkenes, demonstrating their higher binding energies. In case of butyl isothiocyanate, remote functionalization may compete; $H_2$ is exclusively provided by the $\omega/(\omega - 1)$ positions according to the mechanism in Figure 17 and $C_2H_4$ probably as well, although this could not be tested due to unresolved isobaric losses for the labeled substrates. The most important process, accounting for 35% of the products, is loss of $H_2S$, whose hydrogen atoms originate by more than 90% from the $\omega/(\omega - 1)$ positions. The first step of the mechanism (Figure 31) is believed to be sulfur abstraction; this is well-precedented for isothiocyanates[388] and other substrates[389] in homogeneous or heterogeneous catalysis. The next steps proceed analogous to the usual remote functionalization mechanism, except for a *ligated* metal ion being involved; as will be shown below, the same mechanism can indeed be operative for a ligated metal ion. Interestingly, *n*-$C_4H_9NC$ is also the first isocyanide to show loss of $H_2$ by remote functionalization with $Fe^+$.[288] $HS^-$ attack at coordinated isocyanides may also give rise to isothiocyanate complexes;[390] thus, the reverse reaction is also feasible.

This *dehydro*sulfurization may be viewed as an intramolecular variant of the important catalytic *hydrodesulfurization* (HDS),[391] only that the hydrogen is provided internally from the remote positions in this system. The absence of $H_2O$ loss from *n*-$C_4H_9NCO$ is explained by the different bond dissociation energies involved, the stronger RNC=O bond seems to prevent the formation of the intermediate analogous to **125** although the overall reaction to generate $H_2O$ is estimated to be 14 kcal mol$^{-1}$ *more exothermic* than loss of $H_2S$.

## VIII. Reactions of Ligated Metal Ions

Much less is known about the reactions of *ligated* metal ions with organic substrates in the gas phase than about *bare* metal ions. Thus, the gap between gas-phase studies and condensed-phase chemistry of transition-metal complexes with several ligands has yet to be closed. We will discuss several ligands in turn that have already been studied in more detail, but will refrain from reporting the various secondary reactions observed in the course of ICR studies as this data is neither systematic nor is the structure of the primary reaction products always unambiguous.

### A. $MH^+$ and $L_nMH^+$ Ions

$FeH^+$, generated by electron impact upon 1,1′-dimethylferrocene, does not react with $D_2$ in an ion-beam experiment, indicating a significant barrier for formation of an Fe(IV) intermediate.[85] This is completely in line with FTICR results which show that the roughly thermoneutral exchange of $FeD^+$ with $H_2$ to $FeH^+$ does not occur, in contrast to $CoD^+$ and $NiD^+$ which undergo this reaction.[392] In the latter study $MD^+$ ions were generated from CID upon $MOCD_3^+$ which itself is formed in the reaction of $M^+$ with $CD_3ONO$ (see VII.G.2). H/D exchange of $FeH^+$ with $C_2D_4$, however, proceeds without any barrier which is explained by facile alkene insertion/β-H elimination.[85,392] These results are significant with regard to H/D exchange experiments in FTICR instruments, where $D_2$ is often not observed to exchange while $C_2D_4$ or $C_3D_6$ are more effective reagents.

In their reaction with alkanes the metal hydrides either afford metal–alkyl ions by loss of $H_2$, or allyl complexes by further loss of a second molecule $H_2$ or $CH_4$.[85,392] Alkenes also predominantly produce the allyl complexes by loss of $H_2$, while benzene mainly displaces the hydrogen atom.[392] With aldehydes, alcohols, or ethers, $FeH^+$ showed complex reactivity involving considerable bond rearrangements so that no mechanisms could be determined.[85] $MnH^+$ is reported to react with acetaldehyde to afford $MnCH_3^+$ by loss of $H_2$ and CO.[393]

Deprotonation of $FeH^+$ [85] and $MnH^+$ [393] was used to determine the proton affinities of the metal atoms and, with the help of the ionization energies, $D°(M^+–H)$ data. Similarly, protonation of several organometallic compounds B, which occurred mostly on the metal center, and subsequent proton-affinity measurements of the resulting $BH^+$ ions allowed to derive $D°(B^+–H)$ data.[394] An average $D°(B^+–H)$ of 68 kcal mol$^{-1}$ resulted, albeit with a rather large range of individual bond strengths. A maximum for $D°(Fe(CO)_5{}^+–H)$ was noted in the first row, and the bond dissociation energy generally increased by going from a first-row compound to its second-row homologue. On the other hand, hydride abstraction by $FeH^+$ from neutral acids gave the hydride affinity of this ion.[85]

Strictly analogous to $MH^+$, the more ligated $Cp_2ZrD^+$ produces exclusively $Cp_2ZrH^+$ with ethene and nearly statistical loss of $H_2$ and HD with propene.[395,396] $CpRhD^+$, generated by deuteronation of $CpRh(CO)_2$ by $D_3^+$, produces the unlabeled $Cp_2Rh^+$ and $CpRh(\eta^3\text{-}C_3H_5)^+$ complexes upon reaction with cyclopentane and propane, respectively.[44a] $CpRh(CO)H^+$ exchanges its hydrogen with $D_2$.[44a]

### B. $MCH_3^+$ and $L_nMCH_3^+$ Ions

$FeCH_3^+$ and $CoCH_3^+$ ions have been studied quite thoroughly with alkanes,[397] cycloalkanes and -alkenes,[398] alkenes and alkynes,[269] and some nitrogen bases.[399] While $FeCH_3^+$ is completely unreactive with acyclic alkanes, $CoCH_3^+$ reacts with alkanes larger than ethane by initial insertion into a C–H bond, resulting in $CH_4$ loss which is followed by dehydrogenation or alkane elimination yielding Co(allyl)$^+$ products. With $CoCD_3^+$ complete loss of the label was observed. In addition, $CoCH_3^+$ undergoes hydride abstraction with all alkanes except for 2,2-dimethylpropane, and the resulting product is described as $Co(CH_4)$.[397]

$FeCH_3^+$ reacts with cyclopropane and -butane but does not so with cyclopentane or -hexane.[398] Insertion of $FeCH_3^+$ into a C–C bond of cyclopropane produces the metallacyclobutane complex **129**, which undergoes ring opening to the alkylidene–alkene intermediate **130**; rearrangement to the ethyl–ethene complex **131**, which is in rapid equilibrium with **132**, precedes ethene detachment (Figure 32).

Besides $C_2H_4$, $CoCH_3^+$ reacting with cyclopropane produces $CH_4$ and $H_2$ in low intensity while $C_2H_4$ is the sole product from the reaction of $FeCH_3^+$ with cyclobutane. The suggested mechanism is analogous to that of the bare metal ions (Figure 12). C–C insertion followed by ring opening to $FeCH_3(C_2H_4)_2^+$ and subsequent loss of $C_2H_4$ produces $FeCH_3(C_2H_4)^+$, whose structure was probed by $^2H$ labeling, CID and ligand-exchange experiments.[398] For $CoCH_3^+$ $C_2H_4$ is also the main product but the resulting $CoC_3H_7^+$ ion partly decomposes further via $H_2$ loss to $CoC_3H_5^+$; $CH_4$ and $2H_2$ are observed as well. With cyclopentane Co(cyclopentenyl)$^+$ and $CoCp^+$ complexes were formed by loss of $CH_4/H_2$ and $CH_4/2H_2$, respectively; $MCp^+$ ions (M = Fe, Co) may also be generated starting from cyclopentene. Cyclohexane affords loss of $CH_4/2H_2$ with $CoCH_3^+$, and the same product ion results from cyclohexene. Both, $FeCH_3^+$ and $CoCH_3^+$ form $HM(C_6H_6)^+$ ions with the latter substrate as evidenced by H/D exchange and CID experiments.[398]

The reaction of $MCH_3^+$ ions with alkenes is particularly important with regard to the mechanism of the Ziegler–Natta polymerization, where migratory insertion of alkenes into metal–alkyl bonds is regarded as

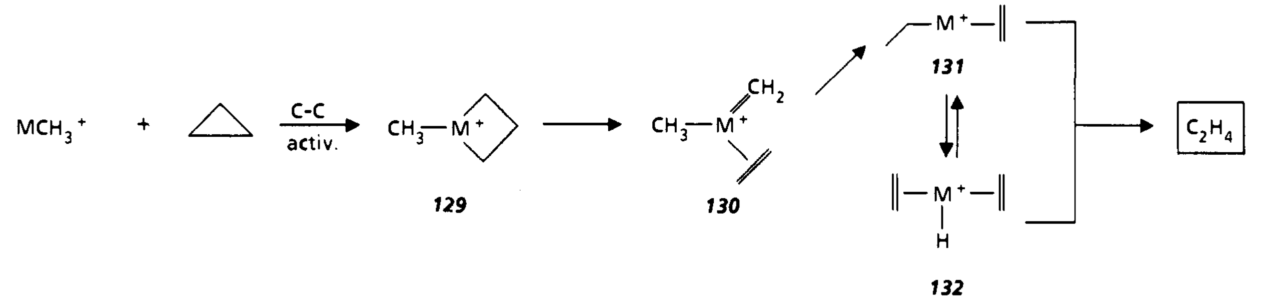


**Figure 32.** Generalized mechanism for the production of ethene from cyclopropane and $FeCH_3^+$ or $CoCH_3^+$.

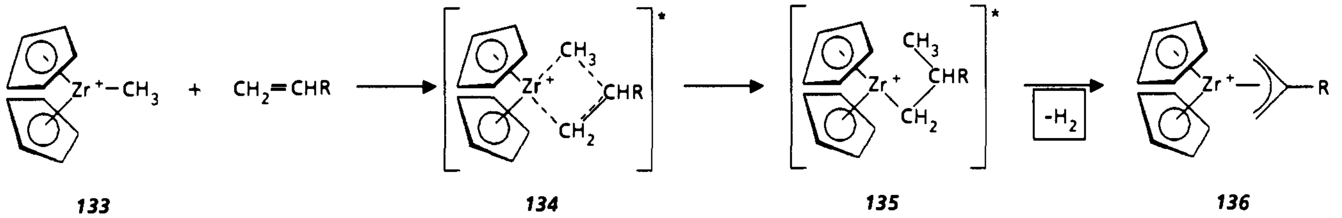


**Figure 33.** Generalized mechanism for the Markovnikov-type addition of 1-alkenes to $Cp_2ZrCH_3^+$ (**133**) leading to allyl complexes.

a key step of the traditional Cossee–Arlman mechanism.[400] $FeCH_3^+$, however, is unreactive with ethene, and although insertion is observed for $CoCH_3^+$, the product decomposes via loss of $H_2$ to the stable $CoC_3H_5^+$.[269] Allyl complexes are also formed by $FeCH_3^+$ and $CoCH_3^+$ from other alkenes via loss of $CH_4$; subsequent $H_2$ or alkene elimination may follow if enough energy is retained after the demethanation. With butadiene $CH_3$ is added to the substrate, and the resulting pentenyl ion decomposes via loss of $C_2H_4$ or by dehydrocyclization to cyclopentenyl and cyclopentadienyl complexes. For 2,2-dimethyl-1-butene, which lacks allylic hydrogen atoms, allylic C–C insertion with loss of $C_2H_6$ is observed; the reaction of labeled $FeCD_3^+$ exclusively produces $CD_3CH_3$.[269] Ethyne inserts into the $M^+$–$CH_3$ bond (M = Fe, Co) to afford vinyl complexes by loss of $H_2$; for propyne, eliminations of $C_2H_4$, $CH_4$, and $H_2$ are observed.[269]

The proton affinity of $MCH_2$ (M = Fe, Co) was determined by proton abstraction from $FeCH_3^+$ and $CoCH_3^+$ with several nitrogen bases;[399] with knowledge of $D°(M^+\text{–}CH_3)$ this allowed estimations for $D°(M\text{–}CH_2)$ of the neutral alkylidenes.[401]

Similar to $FeCH_3^+$ and $CoCH_3^+$, $Cl_2TiCH_3^+$ formed allyl complexes with ethene and propene via loss of $H_2$,[402,403] but $HgCH_3^+$ was insofar unreactive with ethene,[404] allene,[405] or other alkenes,[406] that only the mercurinium adduct ions were formed; the propensity for adduct formation increased with increasing methyl substitution of the double bond.

$[Cp_2ZrCH_3(THF)]^+$[407a–d,f] is an ethene-polymerization catalyst in solution,[407f,408] and $Cp_2ZrCH_3^+$ is thought to be the reactive complex; thus it is not uninteresting to look at the reactions of $Cp_2ZrCH_3^+$ (**133**) in the gase phase.[409] However, similar to other methyl ions, only allyl complexes are formed with ethene and propene via loss of $H_2$.[395,398] Statistical loss of $H_xD_{2-x}$ was found for $C_2D_4$, in contrast to $Cl_2TiCH_3^+$, which afforded mainly HD.[402] In the reaction with $D_2$, via a four-membered transition state and in analogy to the solution chemistry of $[Cp_2ZrR(THF)]^+$,[407c,408b] $Cp_2ZrD^+$ and $CH_3D$ were formed, indicating $D°(Cp_2Zr^+\text{–}CH_3) < D°(Cp_2Zr^+\text{–}H)$.[395,396,410] Thus, *the addition of ligands leads to a gas-phase bond order typical for condensed-phase complexes* (c.f. section IV.A). Quite similarly, $CpRh(CO)CH_3^+$ yields exclusively $CpRh(CO)D^+$ with $D_2$,[44a] although $D°(Rh^+\text{–}H) < D°(Rh^+\text{–}CH_3)$.[43]

With various 1-alkenes $Cp_2ZrCH_3^+$ mainly lost $H_2$, and scrambling was noted for the labeled $Cp_2ZrCD_3^+$.[396] A four-membered transition state (**134**) leads to the Markovnikov-type addition product (**135**), which decomposes subsequently to the allyl complex **136** (Figure 33).

Allene showed exceptional behavior since mainly adduct formation was observed. 1,1-disubstituted alkenes produced only $CH_4$ via σ-bond metathesis[411] with the allylic C–H bond.[396] Here as well, a four-membered transition state is involved, and complete loss of label is found in the case of $Cp_2ZrCD_3^+$. One of the products of $Cp_2ZrCD_3^+$ reacting with isobutene is $Cp_2ZrCH_3^+$, which is best explained by reversible insertion of $i\text{-}C_4H_8$ to the Markovnikov product, $\beta$-$CH_3$ shift, and elimination of $d_3$-labeled isobutene.[396] Termination of alkene polymerization via $\beta$-$CH_3$ transfer was also found for $Cp^*{}_2ZrCH_3^+$ ($Cp^* = \eta^5\text{-}C_5(CH_3)_5$) in solution.[186e] Stereospecific behavior was observed for cis and trans alkenes as the cis compounds reacted more slowly than their trans isomers ($k_{cis} \approx {}^1/_3k_{trans}$) and produced mainly $H_2$, in contrast to trans alkenes which nearly exclusively underwent $CH_4$ loss by σ-bond metathesis.[396] Vinyl fluoride and $CH_2{=}CHCF_3$ exclusively formed $Cp_2ZrF^+$, and from alkynes $H_2$ and/or $CH_4$ were produced by insertion or σ-bond metathesis. Observation of the reactions in eqs 72 and 73 shows that the insertion even is reversible;[396] in solution, too, $[Cp_2ZrCH_3(THF)]^+$ reacts rapidly with 2-butyne to yield the insertion product.[407e]

$$Cp_2ZrCD_3^+ + HC{\equiv}C{-}CH_3 \rightarrow Cp_2ZrCH_3^+ + HC{\equiv}C{-}CD_3 \quad (72)$$

$$Cp_2ZrCH_3^+ + HC{\equiv}C{-}Ph \rightarrow Cp_2ZrPh^+ + HC{\equiv}C{-}CH_3 \quad (73)$$

Related to these latter reactions is eq 74 which was observed in a study of $Cp_2ZrCH_3^+$ with nitiriles.[412] In

$$Cp_2ZrCH_3^+ + N{\equiv}C{-}CD_3 \rightarrow Cp_2ZrCD_3^+ + N{\equiv}C{-}CH_3 \quad (74)$$

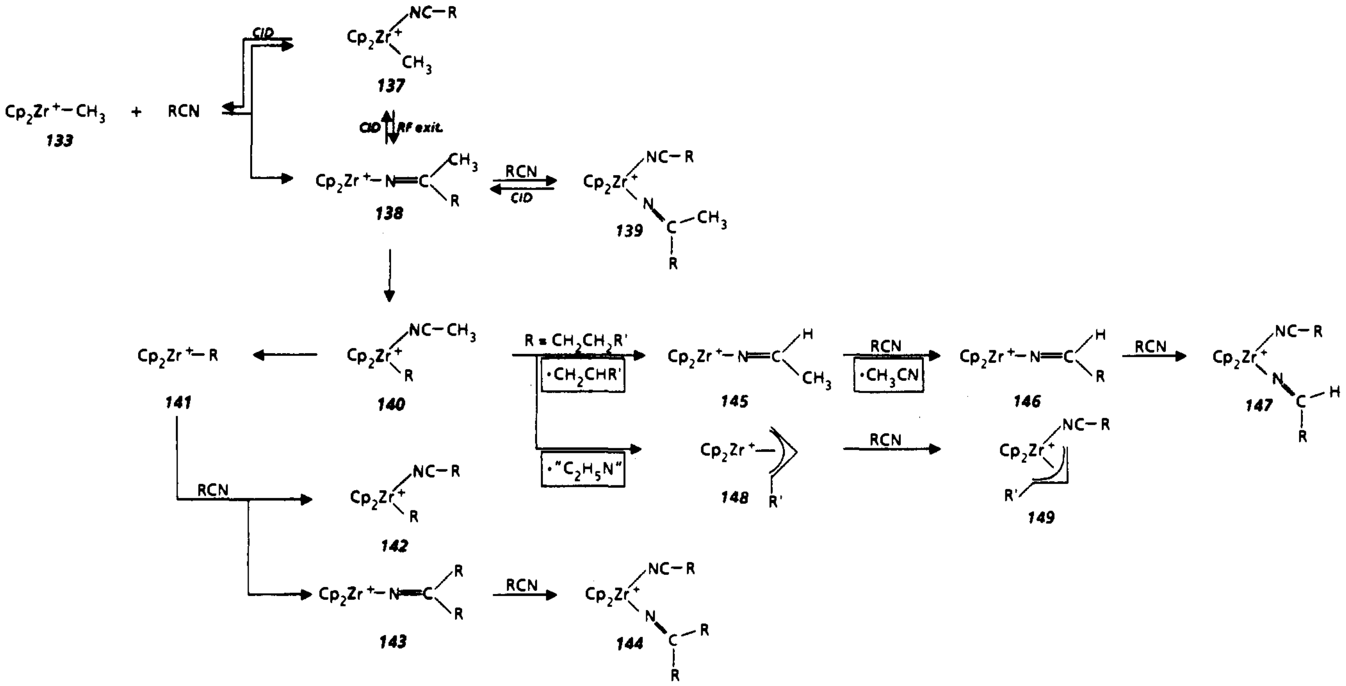


**Figure 34.** Generalized mechanism for reactions of nitriles with $Cp_2ZrCH_3^+$ (133).

analogy to solution studies[407c,408b,c,413] a generalized mechanism shown in Figure 34 was suggested, accounting for all observed products. Reaction of **133** with nitriles may either lead to the addition complex **137** or to the insertion product **138**. The relative amount of **138** decreases in the row $CH_3CN > C_2H_5CN > n\text{-}C_3H_7CN > n\text{-}C_4H_9CN > t\text{-}C_4H_9CN$. **138** may add another nitrile (**138** → **139**) or may rearrange to **140**; the latter may lose acetonitrile to afford **141**, which behaves similarly to **133**, or, in the case of longer nitriles, lose an alkene or [$C_2H_5N$]. The resulting products are still able to add further nitriles.[412] Very recently, Jordan and co-workers reinspected the nitrile insertion in solution and modified the mechanism.[207f] In contrast to the gas phase (eq 74), in solution the insertion is irreversible and **137** (R = $CD_3$) does not rearrange to **138**. Insertion to yield **139** proceeds via $[Cp_2ZrCH_3(CD_3CN)_2]^+$ instead. For $Cp_2TiCH_3^+$, however, the kinetic results could rule out this pathway and were best explained analogous to Figure 34, i.e., **137** → **138** → **139**.[413d] The rate of the insertion step increased in the order $CH_3CN \ll t\text{-}C_4H_9CN < n\text{-}C_3H_7CN$, though.

## C. $MX_n^+$ Ions (X = F, Cl, OR, $NH_2$)

### 1. Metal Halide Ions

The majority of studies about metal halide ions deals with $TiX_n^+$ (X = F, Cl). With organic halides three general reactions are observed, halogen or halide abstraction (eqs 75 and 76, X, Y = F, Cl) and halogen exchange (eq 77).[302,303,402] Rarely noted is charge

$$TiX_n^+\ (n = 1;\ 2) + RY \rightarrow TiX_nY^+ + R \qquad (75)$$

$$TiX_x^+\ (n = 1\text{-}3) + RY \rightarrow TiX_nY + R^+ \qquad (76)$$

$$TiCl_{n-x}F_x^+\ (n = 1\text{-}3) + RF \rightarrow TiCl_{n-x-1}F_{x+1}^+ + RCl \qquad (77)$$

transfer or simultaneous abstraction of $XY^-$ (X, Y = F, Cl) from dihalides.[302] Chloride abstraction was also reported for $AlCl_2^+$,[300] $MgCl^+$,[300] and $MnCl^+$,[304] furnishing the stable neutral di- or trichlorides.

$TiCl^+$ reacts with small alkenes via (multiple) dehydrogenation, while $TiCl_2^+$ and $TiCl_3^+$ mainly afford loss of HCl or $HCl/H_2$.[233,402] For longer alkenes all three chlorotitanium ions in addition give rise to C–C cleavages with losses of smaller alkenes observed.[233] $TiCl_4^+$ does not react with alkenes.[233]

$TiCl^+$ mainly forms $TiClO^+$ from aldehydes, ketones, and ethers; with $CH_3COOC_2H_5$, $Ti(CH_3COO)^+$ is formed.[341] With small aldehydes or ketones, $TiCl_2^+$ and $TiCl_3^+$ lose HCl to generate enolate ions. With larger representatives, $TiCl_x(RCHO)^+$ ions are formed by alkene loss. Mechanistically, both losses are assumed to proceed not via insertions but via rearrangements of the O-complexed ligands.[341] Toward ethers and esters both ions display high reactivity forming various products, viz. alkyl radicals and chlorides, HCl, and alkenes; again, no insertion was assumed.[341] All of the oxygen-containing substrates studied,[341] as well as $CH_3F$,[303] only displace a chlorine radical from $TiCl_4^+$.

The reactions of $CrCl^+$, $MnCl^+$, and $FeCl^+$ with small alkanes have been studied.[414] $FeCl^+$ was completely unreactive, and $MnCl^+$ only produced $Mn(alkane)^+$ adducts by Cl$^{\bullet}$ displacement. $CrCl^+$ was inert with propane, but dehydrogenated n-butane and isobutane and afforded $CH_4$ from neopentane. This, as compared to the unligated metal ions, unusual behavior was explained by the bonding situation of the reacting species. For $FeCl^+$ and $MnCl^+$ an empty p orbital on chlorine overlaps with a filled metal s orbital to form a covalent σ-bond, therefore the two ions have no energetically available electrons left for oxidative additions. $CrCl^+$ has a π-bond at its disposal which is close in energy to the σ-bond; this gives the ion some diradical character and enables addition of $CrCl^+$ across a C–H bond to form $R\text{-}Cr(ClH)^+$ intermediates which rearrange further.[414] A similar explanation was also put forward in a theoretical study on $CrCl^+$.[109b] $FeCl^+$ undergoes a metathetical reaction to $FeBr^+$ with $CH_3Br$.[415]

$FeI^+$ and $FeI_2^+$, generated by electron impact on $Fe(CO)_4I_2$, do not react with pentane; with 1-pentene $FeI^+$ induces loss of $H_2$ and of $C_2H_4$ while $FeI_2^+$ still does not react. Both ions afford cleavage of 2-propanol into $C_3H_6$ and $H_2O$ whereby loss of the alkene is favored, respectively.[416]

### 2. Metal Hydroxide and Alkoxide Ions

So far ion/molecule reactions have only been studied for $FeOH^+$ and $CoOH^+$; both ions can be generated from nitromethane (eq 78). Their bond dissociation energies $D°(M^+–OH)$ have been determined by deprotonation with several bases yielding the proton affinity (PA) of MO. With the help of a thermodynamic cycle $D°$ is available from PA(MO).[417] Furthermore, photodissociation of $MOH^+$, affording $M^+$ as the sole product, also allowed an independent determination of $D°$ from the threshold energy.[417] Both methods were in good agreement with each other and in line with other experimental data.[418,419]

$$M^+ + CH_3NO_2 \rightarrow MOH^+ + CH_2NO \qquad (78)$$

With alkanes both ions formed products still containing the OH ligand as well as others, where it was lost to form $H_2O$.[420] The former were shown by CID and ligand-exchange experiments to possess a still intact OH group; no H/D scrambling was observed when $MOD^+$ were employed. OH loss was noted more often for $FeOH^+$ than for $CoOH^+$. $FeOH^+$ was unreactive with linear alkanes, except for hexane where rapid adduct formation, besides $H_2O$ and $H_2O/H_2$ loss, was observed. $CoOH^+$, while unreactive with methane and ethane, formed several products with other linear alkanes; C–H and C–C insertions were noted, but loss of $H_2O$ combined with dehydrogenation, forming allyl complexes, was predominating.[420] With branched alkanes products of C–H and C–C insertions were found for both ions. $FeOH^+$ mainly gave rise to loss of $H_2O$, but the analogous products for $CoOH^+$ retained enough energy to decompose further so that losses of $H_2O$ together with $H_2$ or small alkanes were the most important processes in this case.

Similar to $MCH_3^+$, $FeOH^+$ was only able to activate cyclopropane and -butane but was unreactive with cyclopentane and -hexane, while $CoOH^+$ reacted with all cycloalkanes.[420] Cyclopropane afforded loss of water with both ions, probably by C–C insertion, $\beta$-H shift, and reductive elimination. Analogous to $MCH_3^+$, $MOH^+$ exclusively gave rise to loss of $C_2H_4$ with cyclobutane, obviously by the same mechanism as $MCH_3^+$ and $M^+$ (Figure 12). The structure of the resulting $MOH(C_2H_4)^+$ ion was probed by CID and ligand-exchange experiments, and no H/D exchange could be observed with $D_2$. With larger cycloalkanes, only (multiple) dehydrogenation and mainly loss of $H_2O$ together with $H_2$ or $2H_2$ was found for $CoOH^+$. $FeOH^+$, unreactive with cyclohexane, reacted with methylcyclohexane, therefore the C–H bond of the tertiary carbon must be susceptible to an attack. Apart from the adduct complex loss of $H_2O$ and of $H_2O$ together with one or two hydrogen molecules was observed.[420]

$MgOH^+$ has been studied by photodissociation to yield $D°(Mg^+–OH)$, and its proton affinity, i.e. $D°(MgO–H^+)$, has been determined by reaction with several bases.[309]

Iron–alkoxide ions have been studied with ketones and aldehydes,[421] and processes were discovered which were strictly analogous to the well-known Meerwein–Ponndorf–Verley–Oppenauer reaction. $Fe^+–OCH_3$ ions transferred a hydride to the carbonyl carbon of acetone to form $Fe^+–O–i–C_3H_7$ via loss of $CH_2O$. The isopropoxide ion reacted further with another molecule of acetone to transfer $H^-$ as well as $CH_3^-$ to the carbonyl carbon atom, whereby the latter actually dominates. $^2H$ labeling revealed that even a rapid, consecutive hydride/methanide shift occurred within the collision complex. Interestingly, $Fe^+–O–t–C_4H_9$ reacted by a $\beta$-$CH_3$ with acetone-$d_6$ to generate $CH_3–Fe(CD_3COCD_3)^+$ and not $Fe^+–O–C(CD_3)_2(CH_3)$ as shown by CID. Similarly, $H^-$ and $CH_3^-$ shifts could be observed for $Fe^+–OC_2H_5$ reacting with acetaldehyde.[421]

### 3. Transition-Metal Amide Ions

$FeNH_2^+$ and $CoNH_2^+$ may be formed from $MOH^+$ and ammonia (eq 79).[270,422] $FeNH_2^+$ is also obtained from $FeH^+$ and $NH_3$.[270] By using ion/molecule reaction bracketing techniques the bond dissociation energies $D°(M^+–NH_2)$ were derived.[422] Both metal–amide complexes react with propene and cyclopropane to the allyl complexes and $NH_3$. Labeled propene-$d_6$ exclusively forms $NH_2D$.[422]

$$MOH^+ + NH_3 \rightarrow MNH_2^+ + H_2O \qquad (79)$$

$D°(M^+–NH_2)$ data has also been gained from ion-beam studies with ammonia for M = Sc,[322] Ti,[322] V,[107] Co,[323a] $Ni^+$,[323b] and $Cu^+$,[323b] and there is also theoretical data available.[46b]

## D. $M = X^+$ and $L_nL'_mM = X^+$ Ions ($X = CH_2$, O, S, NH)

### 1. Transition-Metal Alkylidene Ions

Several alkylidene or carbene ions have been studied. The reactions with alkenes in particular have found great interest in view of the potential intermediacy of alkylidene–alkene complexes in olefin metathesis,[199] and in the cyclopropanation[200] or Ziegler–Natta polymerization[202] of alkenes.[423] $MCH_2^+$ ions may be generated in reactions of $M^+$ with ethylene oxide, cyclopropane, or cycloheptatriene, as well as from $MO^+$ and $C_2H_4$.

The chemistry of $FeCH_2^+$ and $CoCH_2^+$ has been studied most detailed with acyclic alkanes,[356] cycloalkanes,[354] alkenes,[355] and alkynes.[255] By also employing the labeled analogues it became evident that $FeCD_2^+$ reacted specifically while for $CoCD_2^+$ some scrambling was noted. $FeCH_2^+$ reacted with alkanes larger than ethane and $CoCH_2^+$ with alkanes larger than methane.[356] In contrast to the bare metal ions, predominantly C–H activation was observed for the alkylidenes but C–C cleavages occurred, too. Loss of $CH_4$ by sequential C–H activation, $\beta$-H shift generated activated alkene complexes which decomposed further. Facile alkylidene–alkyl coupling was postulated for C–C insertion intermediates.[356] The products which arose from the reactions with cyclopropane and -butane seemed exclusively due to initial C–C insertions.[354] Three decomposition pathways were assumed for the alkylidene–metallacycle complexes formed this way. Incorporation of $CH_2$ into the metallacycle leads to the next higher ring, i.e., metallacyclopentane or -hexane,

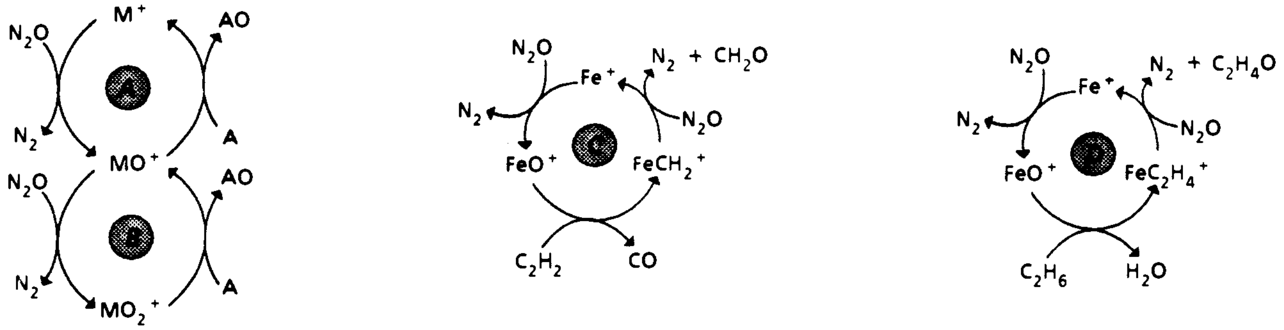


**Figure 35.** Four types of catalytic cycles achieved in the gas phase for transition-metal oxo ions $MO^+$.

which may then decompose. Alternatively, the initially formed metallacycle may open, or a $\beta$-hydrogen atom may be abstracted from it; coupling of these fragments with the $CH_2$ ligand followed. On the contrary, for cyclopentane and -hexane integrity of the rings is mainly preserved. C–H insertion leads to loss of methane which is followed by further dehydrogenation(s) of the activated cycloalkene complexes.[354]

$FeCH_2^+$ and $CoCH_2^+$ are converted to bare metal ions by ethene, the identity of the resulting $C_3H_6$ neutral could, however, not be determined; therefore it is unclear if cyclopropanation actually occurred.[355] Employing $MCD_2^+$, it could be seen that 20% (Fe) respectively 2% (Co) of the olefin-metathesis products $MCH_2^+$ were also formed. With propene or isobutene the expected olefin-metathesis products $MC_2H_4^+$ and $MC_3H_6^+$ were indeed observed, but surprisingly *no* $MCH_2^+$ resulted from the reaction of $MCD_2^+$. CID and ligand-exchange experiments further revealed that the initially formed alkylidene complexes had rearranged to the corresponding alkene complexes.[355] Such rearrangements are well-precedented in solution chemistry.[424] A variety of products is formed from higher alkenes; olefin metathesis with subsequent alkylidene–alkene rearrangement competes with other processes such as dehydrogenation, loss of $CH_4$ by C–H activation, and others.

Butadiene, apart from the metathesis products, reacted with both $MCH_2^+$ ions to $M(c\text{-}C_5H_6)^+$ and $MCp^+$, as shown by CID and H/D exchange experiments. With ethyne and propyne the bare metal ions were exclusively formed.[355]

$MnCH_2^+$ behaved strictly analogous to $FeCH_2^+$ and $CoCH_2^+$ in its reactions with alkenes.[353] $Mn^+$ and $MnCD_2^+$ were formed with $C_2D_4$ and $MnC_2H_4^+$ and $MnC_3H_6^+$ from propene and isobutene, respectively. With isobutene-$d_8$, correspondingly, no $MnCD_2^+$ was observed. The metathesis products were formulated as alkylidenes, but rearrangements to alkene complexes were also considered.

$RhCH_2^+$ showed a somewhat different chemistry as encountered for the other three $MCH_2^+$ (M = Mn, Fe, Co) alkylidene ions.[140,142] Upon CID a small amount of $RhC^+$ was observed indicating a relative facility of $\alpha$-hydrogen shifts;[140] photodissociation produces $Rh^+$, $RhC^+$, and $RhCH^+$.[142] In addition, unlike the other ions, $RhCH_2^+$ reacted with $H_2$ to $Rh^+$ and with $CH_4$ to $Rh^+$ and $RhC_2H_4^+$, the latter ion being the ethene complex. Scrambling was observed for $RhCD_2^+$ but also rapid formation of $RhCH_2^+$ and $RhCHD^+$. These ions most likely arise by reversible formation of $Rh(CH_3)_2^+$ which undergoes rapid $\alpha$-elimination back to $CH_4$ and $RhCH_2^+$. Ethane forms only $RhC_2H_4^+$ with $RhCD_2^+$, besides a small amount of $Rh^+$. From $C_2H_4$, $Rh^+$ and $RhC_3H_4^+$ were generated, the latter most likely by rearrangement of the initially formed rhodacyclobutane ion to the propene complex with subsequent dehydrogenation. Only 3% of the $RhCH_2^+$ metathesis product was formed with $RhCD_2^+$. The reaction with propene and cyclopropane resembled those of its cobalt congener, including the ethylidene–ethene rearrangement of the metathesis products, yet, higher amounts of dehydrogenation products were present.[140]

$NbCH_2^+$ has analogous properties to $RhCH_2^+$ with regard to CID, photodissociation, and the reaction with $H_2$ which affords $Nb^+$. With $CH_4$, $NbC_2H_4^+$ is the sole product.[142] $LaCH_2^+$, which upon CID only decomposes to $La^+$, photodissociates to $La^+$, $LaC^+$, and $LaCH^+$ as well.[142]

Three ligated alkylidene ions have been studied, $(CO)_nMnCH_2^+$ ($n$ = 4; 5)[353] and $CpFe(CO)_2CH_2^+$,[425] which were obtained by protonation of $(CO)_5MnCH_2F$ and $CpFe(CO)_2CH_2OCH_3$. Only $(CO)_5Mn^+$ was produced from $(CO)_5MnCH_2^+$ and alkenes, and only CO displacement occurred for $(CO)_4MnCH_2^+$.[353] Similarly, $CpFe(CO)_2CH_2^+$ reacted with cyclohexene by $CH_2$ transfer; adduct formation was noted for $NH_3$, $CH_3CN$, and $CD_3CDO$. An $CpFeCOCH_2^+$ ion was formed by the deprotonation as well, but its reactions pointed to a ketene structure, i.e. $CpFe(CH_2CO)^+$.[425]

### 2. Metal Oxo Ions

For the production of diatomic transition-metal oxo ions $MO^+$,[32g,i,98–104] $N_2O$ is the most widely employed reagent (eq 80). $FeO^+$ may also be generated from $O_3$,

$$M^+ + N_2O \rightarrow MO^+ + N_2 \qquad (80)$$

and for highly oxophilic metal ions, such as $Ti^+$, $V^+$, $Zr^+$, or $Nb^+$, many other oxygen donors are also suitable, even $O_2$ or $CO_2$.[102,112,426] Metal dioxides $MO_2^+$ are formed by $N_2O$ with $Ti^+$, $V^+$, $Zr^+$, and $Nb^+$; $Cr^+$ even forms the trioxide, $CrO_3^+$.[102b,426] Electron-impact or surface ionization of oxygen-containing, volatile organometallic compounds was also used to obtain $MO_x^+$ or $L_mMO_x^+$ cations.[110a,124,314,339,427]

Interest in the chemistry of the oxo ions arises from the possibility to gain information about intermediates in conventional oxidation reactions and from the wish to devise catalytic cycles for the oxidation of simple hydrocarbons or other substrates. In particular $FeO^+$ has been used quite often for the latter motive. The first example reported is the catalytic oxidation of CO to $CO_2$ with $FeO^+$ according to cycle A in Figure 35 (M = Fe, A = CO).[102b,426] Other substrates that served as

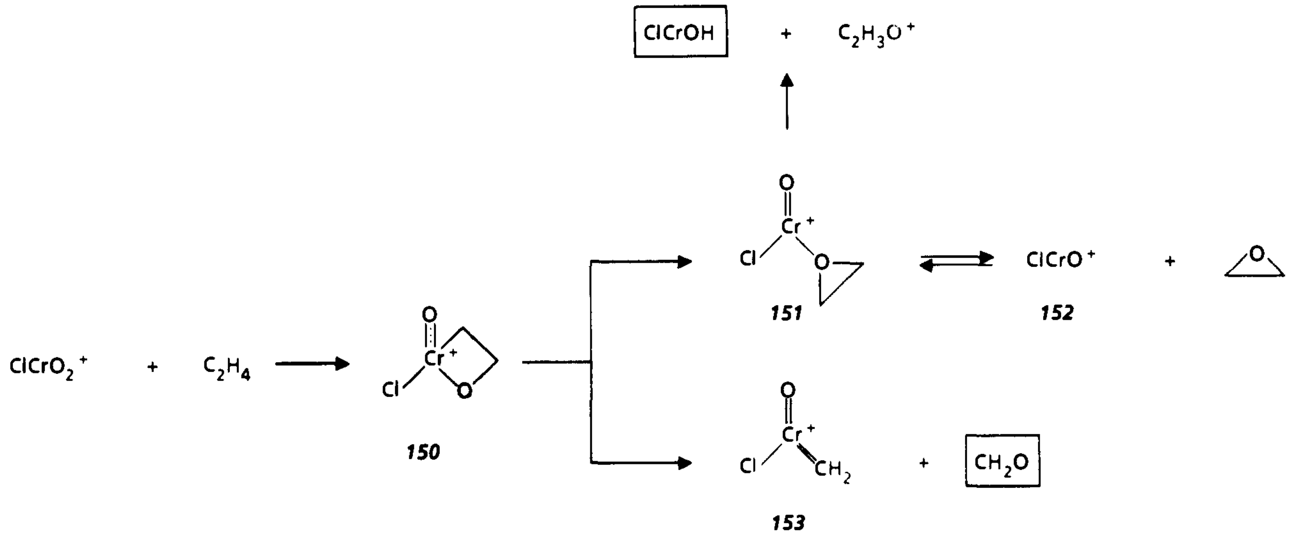


**Figure 36.** Mechanism for the reaction of $ClCrO_2^+$ with ethene.

oxygen acceptor A in **A** were ethene, propene, allene, ethane, and propane.[102b,426] With $TiO^+$, $VO^+$, $CrO^+$, $ZrO^+$, or $NbO^+$, cycle **B** via the dioxides could also be accomplished.[102b,426] For ethyne cycle **A** accounts only for roughly half of the oxidative decomposition, the three-step cycle C is operative as well.[102b,426]

The catalytic oxidation of $C_2H_6$ with $FeO^+$ was recently rediscovered and studied in more detail.[428] $FeO^+$ reacts with ethane by 67% to $FeC_2H_4^+$, while 12% is directly reduced to $Fe^+$ again. Since $Fe(C_2H_4)^+$ may be oxidized by $N_2O$ to $Fe^+$ with 72% yield, cycle **D** is accomplished (Figure 35); most likely, $CH_3CHO$ is the product of this oxidation. From the determination of the individual rate constants for all steps, it was calculated that one $Fe^+$ ion is able to oxidize about 2.5 ethane molecules; this low turn-over number results from the occurrence of side products that function as sinks.[428]

In 1981 it was reported that the reaction of $FeO^+$ with either $H_2$ or $CH_4$ afforded $FeOH^+$;[102a] apparently, this initial report was overlooked, and in 1984 Freiser and co-workers claimed that $FeO^+$ was unreactive with methane.[429] Recent results show, however, that methane may well be oxidized by $FeO^+$; $CH_3OH$ and $Fe^+$ account for 41% of the products and are formed via cycle **A**; the main product, however, is $FeOH^+$.[430] The reactions of $FeO^+$ with other alkanes are characterized by initial C–H activation.[429] Subsequent $\beta$-H shifts and loss of $H_2O$ leave activated alkene complexes, which may decompose further. The observation of radical losses points to C–C activations as well, mainly in cases in which C–H activation leads to intermediates bare of $\beta$-hydrogens; the radical-loss products have $Fe(OH)(alkene)^+$ structures, as shown in ligand-exchange experiments, but upon CID may rearrange to $Fe(H_2O)(allyl)^+$. $FeO^+$ is generally more reactive than $Fe^+$ owing to the greater exothermicity of the water loss.[429]

Loss of $H_2O$ and $H_2O$ with alkenes is also observed upon reaction of $FeO^+$ with 4-heptanone and 5-nonanone.[431] $^{18}O$ and $^2H$ labeling proved that the oxygen of the water molecule lost was exclusively provided by the ionic reagent while the hydrogen atoms derived from the $\omega/(\omega - 1)$ position in the case of the smaller ketone and from the $\omega/(\omega - 1)/(\omega - 2)$ position in the case of the larger substrate. Thus, a mechanism analogous to Figure 31 is operative, with the one difference that the reaction already begins by complexation of a ligated metal ion. The consecutive elimination of $H_2O$ and $C_2H_4$, respectively $C_3H_6$, also starts by the activation of a remote C–H bond and is followed by $\beta$-CC cleavage and loss of the alkene. The second hydrogen for the water is then provided by the $\omega/(\omega - 1)$ position of the *other* alkyl chain.[431]

The reactivity of $Cr^+$ is greatly enhanced by an additional oxo ligand; $CrO^+$, although unreactive with $H_2$ and $CH_4$, is reduced to $Cr^+$ by $C_2H_6$.[314] For other alkanes several other products are also formed, and $^2H$ labeling revealed intriguing mechanistic details.[314] $H_2$, for instance, is formed by multicenter addition of a primary or secondary C–H bond across the $Cr^+$–O bond. $\beta$-Hydrogen shifts in the resulting $Cr(OH)(alkyl)^+$ intermediates are, however, not followed by reductive elimination of $H_2O$ from the resulting $Cr(OH)(H)(alkene)^+$ ions; instead, allylic C–H activation seems to be kinetically favored, and reductive elimination of $H_2$ produces $Cr(OH)(allyl)^+$ complexes. Quite similarly, loss of methane is explained by assuming a $\beta$-$CH_3$ shift in the primary insertion product followed by allylic C–H activation. Loss of $C_2H_4$ from cyclopropane and -butane is explained by assuming that a C–C bond adds across the $Cr^+$–O bond and oxametallacyclopentane or -hexane ions are initially formed; on the contrary, for cyclopentane and -hexane only C–H activation is observed.[314]

With ethene, $CrO^+$ reacts exothermically to $Cr^+$ and, on thermodynamic grounds, acetaldehyde; the formation of $CrCH_2^+$ is endothermic and most likely proceeds via a four-membered metallacyclic intermediate.[339] An analogous intermediate has been postulated for the exothermic metathesis reaction of $MnO^+$ with $C_2H_4$ to $MnCH_2^+$ and $CH_2O$.[353] For other alkenes reduction of $CrO^+$ to $Cr^+$ is always a major process;[339] besides, allylic C–H activation leads to $CrOH^+$, and the resulting $Cr(OH)(allyl)^+$ complex partly rearranges to afford loss of $H_2O$. For 1-alkenes $Cr(CH_2O)^+$ is observed and points to the formation of oxametallacyclobutane ions.[339] Such an intermediate has also been invoked for the reaction of $ClCrO_2^+$ with ethene which yields $C_2H_3O^+$, $ClCrO^+$, and $ClCrOCH_2^+$.[427] In line with a proposal by Sharpless et al.[432] theoretical studies predict the formation of **150** (Figure 36) owing to the energy gained upon formation of the CrO triple bond, which consists of two $\pi$-bonds and a donor/acceptor $\sigma$-bond.[204b,d,i,401c] The retro-[2 + 2] process to $CH_2O$ competes with rearrangement to **151**. The reaction of ethylene oxide with $ClCrO^+$, which exclusively affords $C_2H_3O^+$, shows that formation of **152** from **151** is reversible.[427] Furthermore, hydrogen- and hydride-abstraction reactions of $CrO^+$ with several saturated and unsaturated hydrocarbons have been used to determine $D°(CrO^+–H)$ and $D°(CrO^+–H^-)$ data.[314]

In contrast to $Cr^+$, addition of an oxo ligand to $V^+$ does not change the character of the metal very much. $VO^+$ gives rise to similar products with alkanes as does $V^+$, although reacting slower and showing slightly less multiple losses which is probably due to coordinative saturation.[112] The oxygen does not participate as loss of $H_2O$ is endothermic owing to the high $D°(V^+–O)$ bond dissociation energy. On the other hand, $Ti^+$ and $V^+$ react completely different from their oxides with 2-butanone,[42g] whereas $OsO^+$ often forms the same products with several substrates as $Os^+$.[124] Yet, additional oxygen atoms lead to different behavior as it was evidenced in an investigation on the chemistry of the $OsO_x^+$ ions ($x$ = 1–4).[124] $OsO_x^+$ ($x$ = 1–3) are reduced by molecular hydrogen while $OsO_4^+$ exclusively abstracts a hydrogen atom. Formation of $OsO_4H^+$ as the sole product is observed for several other hydrogen-containing substrates and underlines the oxygen centered radical character of $OsO_4^+$. Reduction of $OsO_x^+$ with several oxygen acceptors or hydrogen donors was used to bracket various metal–ligand bond dissociation energies. The mechanism of the different reactions could often be estimated based upon a relative unreactivity of $OsO_3^+$, for which oxidative additions are impossible, as this would formally generate Os(IX); four-centered additions were also frequently observed.[124]

Photodissociation of $MgO^+$ afforded the bond dissociation energy $D°(Mg^+–O)$, while the ionization energy of MgO has been bracketed by reaction of $MgO^+$ with several charge-transfer reagents.[309]

### *3. Transition-Metal Sulfide Ions*

The reactivity of $MS^+$ (M = Fe–Ni) with alkanes has been studied and compared with the corresponding $MO^+$ ions.[386] All three sulfide ions react with alkanes larger than methane, primarily by $H_2S$ loss, thus demonstrating a similar preference for C–H activation as other metal–ligand ions. The resulting metal–alkene complex may then decompose further. Less multiple losses as for $FeO^+$ are observed for $FeS^+$, however, owing to the fact that $H_2S$ loss is less exothermic than $H_2O$ loss. While for $FeS^+$ and $CoS^+$ the intermediate $M(H_2S)(alkene)^+$ complexes exclusively lose $H_2S$, for $NiS^+$, $H_2S$ retainment is also observed but decreases with increasing size of the alkane. For branched alkanes C–H and C–C activation is observed, whereby $CH_4S$ loss by C–C activation predominates in cases where no dehydrogenation is possible.

Similar to other reagent ions, cyclopropane and -butane are activated by initial C–C insertion while for cyclopentane, cyclohexane, and methylcyclohexane the integrity of the carbocyclic ring is maintained in the products.[386] Ethene is dehydrogenated by $FeS^+$ to form $FeC_2H_2^+$ under loss of $H_2S$, while $FeS_2^+$ is unreactive with $C_2H_4$.[385] On the other hand benzene forms the adduct complex with $FeS^+$ but displaces $S_2$ from $FeS_2^+$.[385]

### *4. Transition-Metal Nitrene Ions*

$MNH^+$ ions may be formed by dehydrogenation of $NH_3$ (eq 62) or by reaction of $MO^+$ with $NH_3$ by loss of $H_2O$.[124,319] For the oxophilic $V^+$, this reaction proceeds in the other direction (eq 81).[319] $VNH^+$ and

$$VNH^+ + H_2O \rightarrow VO^+ + NH_3 \qquad (81)$$

$FeNH^+$ react with $O_2$ to produce $MO^+$ ions.[319] $VNH^+$ is unreactive with ethene but reacts with propene mainly to afford dehydrogenation; deprotonation with several bases yielded the proton affinity of VN.[319] $FeNH^+$ forms a variety of products with $C_2H_4$, all of which are explained by initial formation of a four-membered metallacycle; upon reaction with benzene, $[C_6H_7N]^+$ is produced by loss of an iron *atom*.[319] The structure of $VNH^+$ has been described as a double-bonded nitrene complex with an electron-deficient nitrogen atom, while $FeNH^+$ supposedly is a single-bonded imido complex with an electron-rich N.[319] $OsNH^+$ even dehydrogenates $NH_3$ to form the dinitrene $Os(NH)_2^+$.[124]

## E. $MC_xH_y^+$ Ions

### *1. Alkene Complexes*

Alkene complexes of the group 8–10 metal ions $Fe^+$,[221] $Co^+$,[222] and $Ni^+$ [222] have been compared in their reactivity with other alkenes. Aside from simple ligand-displacement and condensation reactions, new products, which were absent for the bare metal ions, were also observed, e.g., dehydrogenation by double allylic C–H activation and concomitant formation of bis(allyl) complexes. These allylic C–H activations are most facile for $Co^+$, intermediate for $Fe^+$, and the least facile for $Ni^+$. Ligand coupling, such as metal-assisted Diels–Alder reactions, was most pronounced for $Co(alkene)^+$, very limited for $Fe(alkene)^+$, and virtually absent for the $Ni^+$ complexes, which were often unreactive with alkenes.

$Fe(alkene)^+$ complexes have been studied with chlorobenzene and afford loss of HCl, or HCl together with hydrogen.[433] This reaction does, however, not proceed via an ethene–benzyne intermediate; $^2H$ labeling proves that the hydrogen for the HCl is exclusively provided by the alkene. Ligand coupling to styrene derivatives occurs, as shown by CID. The reaction commences with C–Cl insertion of $Fe^+$ followed by migratory insertion of the alkene into the newly formed Fe–C bond, $\beta$-H shift, and finally reductive elimination of HCl. CID and $^2H$-labeling experiments show that a remarkable selectivity is observed by coupling of the least-substituted carbon with the phenyl ring.

Extraordinary selectivity is also observed for $FeL^+$ (L = $C_2H_4$, $C_3H_6$, and $C_4H_6$) reacting with ketones.[347] While bare $Fe^+$ forms several products (see section VII.C), the ligated $FeL^+$ ions selectively undergo loss of L and $H_2$, the latter specifically by remote functionalization of the $\omega/(\omega - 1)$ bonds. The higher selectivity is due to the fact that the $Fe(ketone)^+$ collision complex, when generated from $FeL^+$, is "colder" by the amount of $D°(Fe^+–L)$ compared to the directly formed collision complex. While the ethene and propene complexes, besides dehydrogenation and adduct formation, react via simple ligand substitution, butadiene is not directly displaced by the ketones. Nevertheless, a signal for the loss of $C_4H_8$ is observed; transfer hydrogenation within the $Fe(C_4H_6)(ketone)^+$ collision complex takes place and produces butene which eventually is lost. The transferred hydrogens are specifically provided by the $\omega/(\omega - 1)$ positions, thus the situation is completely analogous to $FeO^+$ (section VIII.D.2).[431]

Cyclopentadiene complexes are different from those of other 1,3-dienes since they may be in equilibrium with hydrido–cyclopentadienyl complexes. The existence of this equilibrium for $Fe(c\text{-}C_5H_6)^+$ and $Co(c\text{-}C_5H_6)^+$ is evidenced in their reaction with $NH_3$ where displacement of a hydrogen atom and loss of $H_2$ with concomitant $CpM(NH_2)^+$ formation is observed.[270,422] This contrasts the behavior of $Rh(c\text{-}C_5H_6)^+$ and $Ni(c\text{-}C_5H_6)^+$ where only ligand-displacement and condensation reactions are observed, ruling out $CpMH^+$ structures.[270] $Rh(propene)^+$, which, as five H/D exchanges with $D_2$ demonstrate, is in equilibrium with $H\text{-}Rh(\eta^3\text{-}C_3H_5)^+$, rapidly loses $H_2$ to generate $Rh(NH_2)(\eta^3\text{-}C_3H_5)^+$, thus indicating that a $Rh(L)H^+$ ion is likely to form $Rh(L)NH_2^+$.[270] The different character of $Fe(c\text{-}C_5H_6)^+$ and $Rh(c\text{-}C_5H_6)^+$ is further underlined by their reactions with other substrates, though both complexes will lose $H^\bullet$ upon photodissociation. $Fe(c\text{-}C_5H_6)^+$ reacts with alkanes to form $CpFe(allyl)^+$ complexes, as shown by CID and $^2H$-labeling experiments.[434] $Rh(c\text{-}C_5H_6)^+$, although it double dehydrogenates cyclopentane to $Rh(c\text{-}C_5H_6)_2^+$, will only form $RhCp_2^+$ in a rare *photoinduced* reaction or upon photodissociation of the $Rh(c\text{-}C_5H_6)_2^+$ product.[435]

$In(C_3H_6)^+$ has been suggested and applied as a chemical ionization reagent for mixture analysis since it affords cationized sample molecules via ligand exchange.[436]

### 2. Benzyne Complexes

Except for the hydrogenation of $ScC_6H_4^+$ (section VII.E),[42e] only the $FeC_6H_4^+$ benzyne complex has been studied so far; reactions with alkanes[361] and alkenes[437] have been reported. The reagent ion was formed from chlorobenzene (c.f. section VII.E); it does not react with methane and singly dehydrogenates ethane. Other alkanes form a variety of products, which can all be explained by initial C–H or C–C insertion followed by alkyl or hydrogen migration onto the benzyne ligand. For instance, most of the alkanes form $FeC_6H_6^+$ and $FeC_7H_8^+$, presumably the benzene and toluene complexes of $Fe^+$. Absence of the $FeC_6H_6^+$ hydrogenation product from *neo*-$C_5H_{12}$ indicates 1.2 dehydrogenation but $^2H$ labeling reveals reversible steps. $FeC_7H_8^+$ is explained by either C–H insertion followed by $\beta$-$CH_3$ shift from the resulting phenyl–alkyl complex and further migration to the phenyl ligand, or, alternatively, by initial C–C insertion, $\beta$-H shift from the resulting alkyl *o*-tolyl complex and migration of the hydrogen to the tolyl ligand.[361] From the alkenes studied so far, different products were formed in each case.[437] $FeC_6H_4^+$ reacts with ethene mainly to the benzocyclobutene complex which partly decomposes to $Fe^+$. Both propene and isobutene afford exclusively $Fe(toluene)^+$ while from the three linear butenes quite a variety of products are formed among which $C_3H_4$, $H_2$, and $2H_2$ are dominant. Cyclopentene and -hexene mainly give rise to the $FeC_6H_6^+$ hydrogenation product.

### 3. Allyl Complexes

Iron and cobalt allyl complexes have been studied so far, and once again the chemistry with alkanes and alkenes has been explored. They are generated either by reacting $MX^+$ (M = Fe, Co; X = $CH_3$, OH) with alkanes to afford $M(allyl)^+$, $H_2$, and HX,[397,398,420] or directly from $MCH_3^+$ and alkenes by loss of $CH_4$.[289] In general, $Co(allyl)^+$ is more reactive than $Fe(allyl)^+$, and both $M(allyl)^+$ react rapidly with alkanes (except $CH_4$) by C–H activation to produce predominantly $H_2$ or $2H_2$. The structure of the resulting $M(allyl)(alkene)^+$ complexes has been probed by CID and ligand-exchange experiments.[397,420] With cyclopropane and -butane insertion into the C–C bond is assumed and $C_2H_4$ is lost in both cases, analogous to other $M^+$ or $ML^+$ systems.[398,420]

$Fe(allyl)^+$ and $Co(allyl)^+$ are unreactive with ethene but react with propene and isobutene to produce mainly or exclusively $H_2$.[269]

### 4. Cyclopentadienyl Complexes

Reactions of $M(\eta^5\text{-}C_5H_5)^+$ ions have been observed as early as 1973, when Müller and Goll reported ion/molecule reactions of $CpNi(NO)^+$ and $CpNi^+$ with several substrates in the ion source of their mass spectrometer. While many neutrals L, such as $H_2O$, $NH_3$, acetone, $C_2H_4$, or $C_2H_2$, only formed the $CpNiL^+$ complexes, for other substrates, including alkanes, dehydrogenation and C–C cleavage reactions were observed as well.[438]

A more recent investigation on $CpCo^+$ showed that all aliphatic alkanes larger than methane (with the exception of neopentane) are mainly dehydrogenated with only small amounts of products due to C–C cleavages or occasional skeletal rearrangements observed besides.[439] As frequently observed in other systems, cyclopropane and -butane react by initial C–C insertion, and cyclopentane and -hexane undergo exclusive C–H activation. $CpNi^+$ in a similar manner dehydrogenates $c\text{-}C_5H_{10}$ up to two times.[44a] $CpCo^+$ does not react with ethene and slowly dehydrogenates propene and isobutene. Higher alkenes mainly produce $H_2$, but in competition to the simple dehydrogenation, skeletal isomerizations followed by dehydrocyclization to cobaltocene ($Cp_2Co^+$) is observed for $C_5$ and $C_6$ alkenes and alkadienes. CID upon $CpCo(alkene)^+$ derived from $C_5$ and $C_6$ alkanes gives similar results.[439] $CpFe^+$, formed from $FeCH_3^+$ and cyclopentene, dehydrogenates cyclopentene, but only 31% $Cp_2Fe^+$ is formed;[398] the analogous reaction for cobalt afforded exclusively $Cp_2Co^+$.

Decarbonylation of aldehydes by $CpNi^+$ according to eqs 82 and 83 has been reported for a variety of different RCHO; the reaction is absent for $CH_2O$ and $CF_3CHO$.[362,440] With aromatic compounds, $CpNi^+$ often was found to be unreactive or formed only the adduct complexes; however, with chloro-, bromo-, and iodobenzene $CpNiC_6H_4^+$ was formed, benzylamine was

$$CpNi^+ + RCHO \rightarrow CpNiCO^+ + RH \qquad (82)$$

$$\rightarrow CpNiRH^+ + CO \qquad (83)$$

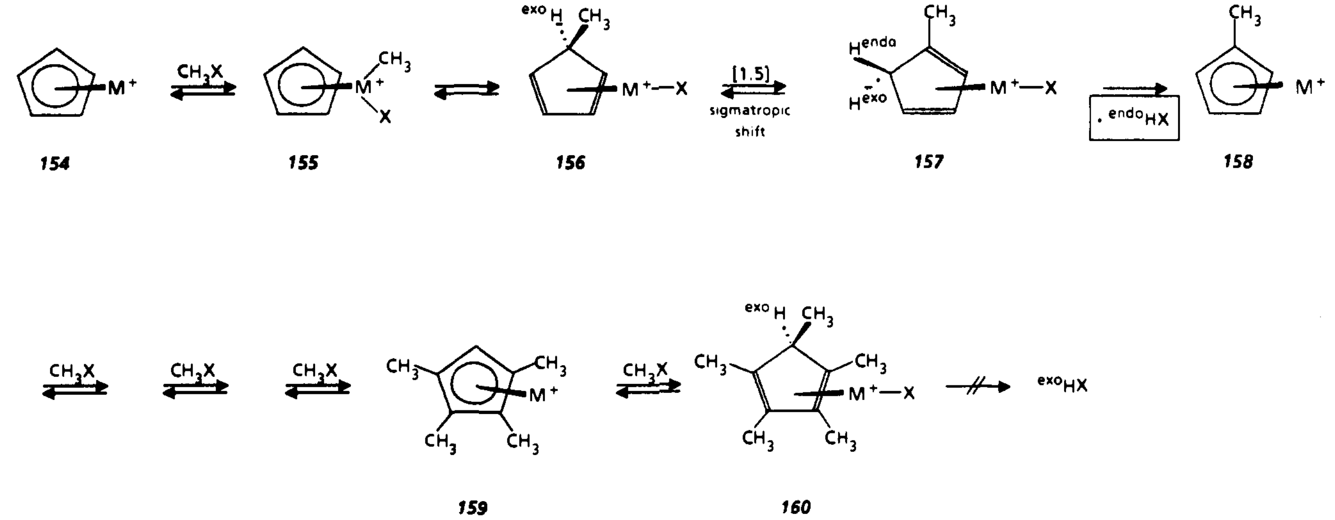


**Figure 37.** Mechanism for the 4-fold alkylation of cyclopentadienyl complexes $CpM^+$ (M = Fe, Ni) with halomethanes $CH_3X$.

one and two times dehydrogenated, and $H_2O$ was lost from $PhCH(OH)CH_3^+$.[362]

$Cp_2Zr^+$ was found to abstract Cl from $CCl_4$, $CCl_2F_2$, and $CHCl_3$, forming $Cp_2ZrCl^+$ and thereby placing a lower limit of 81 kcal mol$^{-1}$ for $D°(Cp_2Zr^+–Cl)$.[410]

A remarkable alkylation of the cyclopentadienyl ligand has been reported for $CpNi^+$ and $CpFe^+$ (eq 84, $n$ = 0–3).[441] For unknown reasons, the reaction is much

$$(CH_3)_nC_5H_{5-n}M^+ + CH_3X \rightarrow (CH_3)_{n+1}C_5H_{4-n}M^+ + HX \quad (84)$$

more efficient for X = Br than for X = F, Cl, or I and stops after $n$ = 3, i.e., the fifth alkylation is not observed. This latter finding is explained by the mechanism in Figure 37 assuming that exclusively the endocyclic hydrogens can be transferred.

A metal-switching reaction (eq 85) for metal ions reacting with metallocenes was discovered by Freiser and co-workers; besides, the charge-exchange product in eq 86 formed (M = Ti, Rh, Nb; M′ = Fe, Ni).[114,442] $Fe^+$ afforded exclusively charge exchange with $NiCp_2$.[442]

$$M^+ + Cp_2M' \rightarrow Cp_2M^+ + M' \quad (85)$$

$$\rightarrow Cp_2M'^+ + M \quad (86)$$

In order to obtain information about the barrier in electron-transfer processes, charge-transfer reactions of $Pd(CH_3NC)_3^+$ with $FeCp'_2$ ($Cp' = \eta^5\text{-}C_5(CH_3)_5$)[308] and of $MCp_2^+$ with $M'Cp_2^+$ [443a] and the self-exchange reactions of $MCp_2^+$ with $MCp_2$ (M = Mn, Fe, Co, Ru; Cp = $\eta^5\text{-}C_5H_5$, $\eta^5\text{-}C_5(CH_3)_5$, $\eta^5\text{-}C_5H_4R$ (R = $OCH_3$, $COCH_3$))[443] have been studied.[444] This latter studies employed double-resonance techniques using naturally occurring isotopes; it was found that ferrocene, cobaltocene, and ruthenocene reacted with 10–40% of the Langevin collision rate, while for manganocene the efficiency was significantly lower (0.6%). Different spin multiplicities or Mn–C bond lengths in the cation and the neutral could be responsible for this finding.[443a,b] Methyl substitution significantly enhances the efficiency of the manganocene reactions as does increased exothermicity in mixed CT systems.[443a] The rate constants in the gas phase showed the same ordering as in solution.[443c]

Binding energies to $CpNi^+$ have been determined for NO by photodissociation[445] and appearance-potential measurements,[438] and for 30 further neutrals, including alcohols, ethers, aldehydes, amines, phosphines, etc., in an ICR equilibrium study.[446] A linear correlation to the proton affinities of the neutrals was observed for most of the compounds studied; exceptions arose from π-bonding abilities. Further, binding energy generally increased with increasing substitution and was greater for second-row than for first-row compounds (e.g., $(CH_3)_3P > (CH_3)_3N$; $(CH_3)_2S > (CH_3)_2O$).

### *5. Transition-Metal Carbide Ions*

Tantalum carbide cluster ions $TaC_x^+$ ($x$ = 1–14) produced by laser desorption of a tantalum powder/carbon mixture have been studied upon their reactivity.[225] With $D_2$ three different types of products were formed; D abstraction is noted for $x$ = 1 and 3, $TaC_{x-2}^+$ by loss of $C_2D_2$ is formed for $x$ = 2 and 5–7, and $TaC_xD_2^+$ adducts for $x$ = 8–14. Methane formed two products, $TaC_{x+1}H_2^+$ by loss of $H_2$ and $TaC_{x-1}H_2^+$ by loss of $C_2H_2$; $TaC^+$ in addition is converted to $Ta^+$. $^{13}CH_4$ gives rise to a completely statistical label distribution, indicative of $CH_4$ incorporation before ethyne elimination. Loss of $H_2$ and $C_2H_2$ is also observed in the reaction with $C_2H_4$, and here as well, extensive, but not completely statistical carbon scrambling is noted. Ethane loses mainly $2H_2$ and $C_2H_4$, thus the same ionic products are formed as for ethene. CO is produced in the reaction with water. From the rate constants it became obvious that $TaC_x^+$ with $x$ = 7–9 existed as a mixture of at least two isomeric structures, respectively.

## F. $M(CO)_n^+$ Ions

We will discuss only transition-metal carbonyl ions in this final section about ligated metal ions since here the most data has been reported, and the results can easily be transcribed for other ligands, such as NO or $PR_3$. Carbonyl ions have been studied quite extensively owing to the fact that they are readily available upon electron impact on volatile organometallic compounds, e.g., $Fe(CO)_5$ or $Co(NO)(CO)_3$.[447] There are copious cases in the literature, where $M(CO)_n^+$ ions react by a simple ligand-substitution reaction (eq 87).[46a,51,73,274,310,316,325,352,362,370,448–451] The number $m$ of

$$M(CO)_n^+ + L \rightarrow M(CO)_{n-m}L^+ + mCO \quad (87)$$

displaced CO molecules depends upon the relative binding energy of L to the metal center; strong ligands are able to displace more CO's than the weakly bonding ones.[452] However, as already discussed in section VII.A, what looks like a simple ligand-substitution reaction may not necessarily be one. $CH_3I$, $CH_3OH$, $C_2H_5NH_2$, or $C_2H_5I$ react with $MCO^+$ by loss of CO; yet, the resulting product ions possess "inserted" structures, i.e., $CH_3{-}Fe^+{-}X$, or consist of multiligand complexes $M(C_2H_4)(HX)^+$.[273,274,325] Often the available energy in the collision complex $[M(CO)_nL^+]^*$ is not only sufficient to cleave L but also to lose some of its fragments $F^i$ (eq 88).[46a,73,274,310,316,318,325,352,362,370,449,450] The amount of

$$M(CO)_n^+ + L \rightarrow [M(CO)_nL^+]^* \rightarrow M(CO)_{n-m}F^{1+} + mCO + F^2 \quad (88)$$

simple ligand substitution increases with the number $n$ of ligands on the reactant ion. For relatively small substrates two or three CO's are already sufficient to suppress fragmentation upon complexation.[46a,274,316,325,352,362,370] However, when L, and hence its binding energy, increases fragmentation becomes more abundant.[370] The fragmentation products observed for $MCO^+$ are often the same as for $M^+$. This has been explained theoretically by examining the $M^+{-}CO$ bonding. It has been proposed that the bonding situation cannot be described by the usual Dewar–Chatt–Duncanson formalism[453] but is mainly due to the electrostatic attraction.[46,95,454–457] Thus, M is in the same electronic configuration and spin state in $M^+$ as in $MCO^+$ and hence reacts similarly.[46a]

And yet, in many cases new products have been observed for $M(CO)_n^+$, which were absent for $M^+$, so CO can be more than a spectator ligand.[46a,310,316,325,352,362,370] $MCO^+$ insertion has been postulated to account for some of the findings; the resulting acyl complexes subsequently decompose to form new products. Coupling of other ligands has been described as well; for instance, the reaction of $Fe(CO)_4^+$ with two molecules of allyl chloride furnishes $FeC_6H_{10}Cl_2^+$, which, according to CID and ligand-exchange experiments, consists to 60% as a hexadiene–dichloro complex in which the two allyl units have been coupled.[318]

The reaction of the acetyl ion $CH_3CO^+$ with $CpRh(CO)_2$ produces $CpRh(CO)COCH_3^+$ and $CpRh(CO)CH_3^+$; $^{18}O$ labeling of the reagent ion showed that the label was retained completely in the former and exactly to one half in the latter product, revealing the irreversible formation of a $CpRh(CO)_2CH_3^+$ intermediate.[44a] Methylation of $CpRh(CO)_2$ with $(CH_3)_2F^+$ produces initially the same complex which then loses CO to generate $CpRh(CO)CH_3^+$.[44a]

## IX. Bond Dissociation Energies

Out of the various means to determine bond dissociation energies,[42e,133,458] we will restrict ourselves to ion/molecule equilibrium reactions in ICR spectrometers and dissociations of adduct complexes in sector-field mass spectrometers, results of KERD, ion-beam, and photodissociation experiments already being included in the previous chapters. We will also refrain from discussing the numerous examples for bracketing experiments in ICR spectrometers where the occurrence or nonoccurrence of a reaction is relevant; these kind of BDE determinations are beyond the scope of this review, just like most of the high-pressure mass spectrometry (HPMS) experiments with bare metal ions.[459]

Similar to the binding energies for $CpNi^+$ mentioned above,[446] relative binding energies for various substrates L have been determined by measuring the equilibrium constants for eq 89 for M = Li,[460] Mg,[461] Al,[462] and Mn.[304] Accordingly, the equilibrium in eq 90 was used

$$ML_1^+ + L_2 \rightleftharpoons ML_2^+ + L_1 \quad (89)$$

to derive relative $D°(M^+{-}2L)$ two-ligand bond dissociation energies for M = Co,[463] Ni,[464] Cu,[465] and FeBr;[415] most of the results have been summarized.[102b] The

$$M(L_1)_2^+ + 2L_2 \rightleftharpoons M(L_2)_2^+ + 2L_1 \quad (90)$$

equilibrium constants can be used to derive relative bond dissociation energies if (a) $\Delta H$ for the ligand exchange does not exceed 2 kcal $mol^{-1}$, otherwise the reverse reaction is too slow to be followed, (b) entropy changes are negligible, (c) occasional symmetry corrections are applied, and (d) no further reactions of the $M(L)^+$ or $M(L)_2^+$ complexes interfere. If at least one of the bond dissociation energies is known absolutely, the relative scales can be tied to this value and converted into absolute scales. In the case of $Li^+$ [480] this has been done on the basis of $D°(Li^+{-}H_2O)$, and for $Mg^+$ $D°(Mg^+{-}CH_3OH)$ and $D°(Mg^+{-}CH_3COCH_3)$ have been determined with the help of photodissociation experiments.[461]

For all Lewis acids studied, the BDE's increased upon substitution, e.g., $H_2O < CH_3OH < (CH_3)_2O$, or $C_2H_4 < C_3H_6 < C_4H_8$. By comparing $D°(M_1^+{-}L)$ versus $D°(M_2^+{-}L)$ it was observed that linear correlations resulted for similar molecules, e.g., oxygen bases fell on one line and sulfur bases on another. The offsets and the slopes of these lines gave indications about the nature of the bonding interactions. In particular, the relative hardness or softness of the Lewis acids could be evaluated. Softness increases in the row $H^+ < Al^+ \ll Mn^+ \leq FeBr^+ < Co^+ \leq CpNi^+ < Ni^+ < Cu^+$, which has also been discussed in terms of increasing metal–ligand bond distance. There is a discrepancy for $Mg^+$ with regard to its softness, which does not fit in with the remaining correlations, but the ion is certainly softer than the hard acids $H^+$ and $Al^+$.[461]

Synergistic effects have been evaluated for $Co^+$, $Ni^+$, and $Cu^+$ by examining mixed complexes $MAB^+$ in relation to $MA_2^+$ and $MB_2^+$.[466] From five combinations of different types of bases studied ($\sigma$-, $\pi$-, S-, and N-bases), a significant synergistic effect was only noted for $\sigma$-base/$\pi$-base combinations, which was explained by the trans influence of the ligands. The filled $\sigma$-orbital of the one ligand ($\sigma$-donor) overlaps with an empty $\sigma$-orbital of the metal, so that a filled d orbital can give maximum electron density to the empty $\pi$-orbital of the other ligand ($\pi$-acceptor).

*Relative* metal ion affinities may also be determined by studying competitive ligand loss in MI or CID spectra of mixed adduct complexes $MAB^+$, a method developed by Cooks and co-workers for proton-bound dimers.[467] It allows estimation of relative bond dissociation energies from the intensities of $MA^+$ versus $MB^+$ if (a) the reverse activation energies for the ligand losses are negligible or equal for both ligands and (b) similar frequency factors (entropy changes) obtain. The method has been applied to compare the binding energies of $(C_2H_5)_2NH$ and $i$-$C_3H_7NH_2$ to $Al^+$,[468] of several alcohols to $Ag^+$,[468] and of $CH_3CN$ and $CH_3NC$ to $Fe^+$.[272] As expected, increased substitution results in higher binding energies,[468] and the isocyanide is more strongly bound than the nitrile.[272] Synergistic effects were noted for $ML_1L_2^+$ and $ML_1L_2L_3^+$ complexes ($M = Mn, Fe, Co$; $L_i = CO, NO, H_2O, CH_3OH$).[469] In the $Fe(CO)_n(H_2O)^+$ series, additional CO's weakened the M–CO interaction and addition of CO to $Co(H_2O)(NO)^+$ reverses the relative order of the $H_2O$ and NO binding energies. Both effects arise from a competition of $\pi$-acceptors, i.e., mutually destabilizing effects of two or more $\pi$-bases are noted.

*Absolute* bond dissociation energies can be obtained by determining the threshold for ligand loss in CID complexes. These experiments have been performed in triple-quadrupole instruments where either the absolute energy zero is precisely known[470] or differences are measured.[419,471] The first and second water binding energies $D°(M^+–H_2O)$ and $D°(M(H_2O)^+–H_2O)$ have been determined for the first-row transition-metal ions $Sc^+$–$Zn^+$ [419,470,471] and several ammonia binding energies $D°(M(NH_3)_n{}^+–NH_3)$ for M = V–Ni.[470] Quite surprisingly, *several metal ions bind the second solvent molecule more strongly than the first.* This could be confirmed in theoretical studies on $M(H_2O)_n{}^+$ [454,472–474] and $M(NH_3)^+$ [46b,472b] which showed that the bonding is mainly electrostatic for the monohydrates as well as the dihydrates.[454,473] The larger binding energy of the second water molecule can arise from changes in the mixing of the metal–ion asymptotes as a result of the differences in the metal–water repulsion between one and two $H_2O$.[473] Clustering of $H_2O$ and $NH_3$ to $Cu^+$ and $Ag^+$ has also been studied by using HPMS,[321] and $D°(V^+–H_2O)$ was determined by photodissociation.[475] Quite similarly, $D°(M^+–OH)$ has been determined by CID for M = Sc–Ni and Zn,[471] and this data can be compared to other experimental[314,417–419] or theoretical[109h] values.

Protonation of $(CO)_5MnCH_3$ by organic acids $BH^+$ gives some interesting estimates for dissociation and elimination processes.[476] With increasing acidity of $BH^+$, the reactions in eqs 91–93 are subsequently observed to happen. Equation 91, observed for weak

$$(CO)_5MnCH_3 + BH^+ \rightarrow (CO)_5Mn^+ + CH_4 + B \tag{91}$$

$$\rightarrow (CO)_5Mn(CH_3)H^+ + B \tag{92}$$

$$\rightarrow (CO)_4Mn(CH_3)H^+ + CO + B \tag{93}$$

acids, is due to protonation of the Mn–C bond, which needs little or no activation barrier. Stronger acids are also able to protonate the manganese atom (eq 92), and if there is still sufficient energy, one carbonyl may be lost in addition (eq 93). Loss of CO from $(CO)_5Mn(CH_3)H^+$ may also be induced by CID. From comparison of the gas-phase acidities of $BH^+$ it follows that $D°[(CO)_4Mn(CH_3)H^+–CO] = 7 \pm 2$ kcal mol$^{-1}$; evidently the activation energy for reductive elimination of $CH_4$ from $(CO)_5Mn(CH_3)H^+$ must exceed this value. The homologous $(CO)_5ReCH_3$ shows analogous behavior upon protonation.[476]

An isomeric $(CO)_5Mn(CH_4)^+$ ion is formed in a high-pressure CI source from $Mn_2(CO)_{10}$ and $CH_4$.[477] Upon CID methane is lost before any CO elimination is observed; the bond dissociation energy $D°((CO)_5Mn^+–CH_4) < 7.2$ kcal mol$^{-1}$ is in accordance with a weakly bound methane complex. In a similar way complexes of $Mn(CO)_5^+$ with $H_2$ and $H_2O$ could be characterized by CID as dihydrogen[478] and water complexes.[477]

## X. Addendum

In the period following completion of the manuscript several new papers came to our knowledge which are reported below.

Several third-row ions were examined upon their reactivity, in particular toward methane.[479–481] $Os^+$,[124] $Ta^+$,[114,125] $W^+$, $Ir^+$, and $Pt^+$ are able to form $MCH_2^+$ ions while $Hf^+$, $Re^+$, and $Au^+$ [11] did not react with $CH_4$.[479,480] Upon translational excitation $Hf^+$ and $Re^+$ are, however, seen to react; with $H_2$ the thus formed $MCH_2^+$ ions are reduced to $M^+$ again. Sequential reactions with methane to $MC_xH_{2x}^+$ complexes are observed for M = Ta–Pt, with $WC_8H_{16}^+$ being the highest order product.[479,480] With ethane dehydrogenation to $MC_2H_4^+$ or $MC_2H_2^+$ is observed for $Hf^+$, $W^+$, $Ir^+$, and $Au^+$ [11] while ground-state $Re^+$ did not react with $C_2H_6$, in contrast to translationally excited $Re^+$.[480] $Re^+$ does react with cyclopropane, however, and $ReCH_2^+$, $ReC_3H_4^+$, and $ReC_3H_2^+$ are formed; $Hf^+$ in addition produces $HfC_2H_2^+$.[480] $Hf^+$ and $W^+$ but not $Re^+$ yield the metal oxide ions $MO^+$ upon reaction with $O_2$, $H_2O$, or $CO_2$; with formaldehyde $Hf^+$ not only affords $HfO^+$ but also $HfH_2^+$, similar to e.g. $Sc^+$,[79] $Gd^+$,[103] or $Os^+$.[124] $Re^+$ forms $ReO^+$ and $ReCH_2^+$ with ethylene oxide, $Ir^+$ produces $IrCO^+$, $IrCH_2O^+$, and $IrH_2^+$ from methanol, and $W^+$ forms $WC_3H_2O^+$ and $WCH_2O^+$ from acetone. Reactions of metal oxide ions were also studied.[480] $WO^+$ is oxidized to $WO_2^+$ by $O_2$ or $CO_2$ and $ReO^+$ to $ReO_2^+$ and $ReO_3^+$ by $O_2$; methane dehydrogenation is observed for $ReO^+$ and $ReO_2^+$, and, similarly to $OsO_2^+$,[124] $ReO_2^+$ undergoes sequential metathesis with $NH_3$ to $ReN_2H_2^+$.[480]

Alkanedinitriles have been studied with $Fe^+$, and a chemistry completely different from alkanenitriles was encountered.[482] Several processes were operative and included insertions into C–CN, other C–C, as well as C–H bonds, and losses of HCN, saturated and unsaturated nitriles, ethene, hydrogen, and even radicals resulted. $Fe^+$ was also used to study chain-length effects with unsaturated halides of the general formula $CH_3(CH_2)_mC{\equiv}C(CH_2)_nX$ or $CH_3(CH_2)_mCH{=}CH(CH_2)_nX$ ($m, n = 2$–$4$; X = Cl, Br).[483] For $n = 3$ exclusively $C_2H_4$ was produced, originating to >93% (alkynes) or 100% (alkenes) from $C_{(1)}$ and $C_{(2)}$. For $n = 4$, alkynes were mainly dehydrogenated, indicating triple-bond coordination, while alkenes mainly afforded HX loss, indicative of halide coordination. For $n = 2$ many products were observed, presumably from both coordination modes.

In a combined experimental/theoretical approach $Sc^{2+}$, $Y^{2+}$, and $Cu^+$ binding energies to small alkanes and alkenes were evaluated.[484] While $Sc^{2+}$ initiated charge-splitting reactions only, $Y^{2+}$–L ions (L = ligand) could be formed in condensation, dehydrogenation, and ligand-exchange reactions. In a series of ligand-displacement reactions the following order in $Y^{2+}$ binding energies could be obtained: $CH_4, C_2H_6 < C_2H_2, C_2H_4 < C_3H_8 < C_3H_6 < C_4H_{10} < C_4H_6$. Thus, $C_n$ alkanes are bound more strongly than are $C_{n-1}$ alkenes. In contrast, for $Cu^+$, $C_3H_8 < C_2H_4 < C_3H_6$ was found. These findings were supported by calculations which show that binding for dications is mainly electrostatic in origin; $\pi^*$-back-bonding is reduced and polarization is much more important than for monocations.[97e,484]

The reaction of $Y^{2+}$ with *n*-butane affords $YCH_3^+$ as one of the products; since $Y^+$ with $CH_3I$ yielded $YI^+$ only, this allowed to study the $YCH_3^+$ chemistry.[485] $YCH_3^+$ did not react with $H_2$, small alkanes, or benzene, but activated allylic or benzylic C–H bonds via $\sigma$-bond metathesis. $CH_4$ loss was the main or exclusive reaction with small alkenes and was accompanied by subsequent dehydrogenation for larger alkenes. Ethene exclusively afforded the Y(allyl)$^+$ ion by insertion/dehydrogenation, but the reaction of $YCD_3^+$, which resulted in 50% $YCH_3^+$, indicated also reversible formation of Y(*i*-Pr)$^+$ via ethene insertion and rapid, reversible $\beta$-hydrogen and $\beta$-methyl shifts.

Metalloporphyrin ions M(P)$^+$ were synthesized by reaction of bare or ligated metal ions ($M^+ = Cr^+$–$Ni^+$) with porphine; labeling showed that exclusively N,N′-dehydrogenation occurred. Fe(P)$^+$ could not be oxidized to Fe(P)O$^+$ although several oxidants were attempted.[486]

The reaction of $Cp_2ZrCH_3^+$ with $E(CH_3)_3$ (E = Al, Ga) affords loss of two methane molecules and is believed to yield $Cp_2Zr(\mu\text{-}CH_2)_2E^+$ metallacycles.[487] Both carbon atoms arise from the neutral reagents, as indicated by labeling as well as by the reaction with $Zn(CH_3)_2$ which produces only one molecule of methane and, presumably, $Cp_2Zr(\mu\text{-}CH_2)(\mu\text{-}CH_3)Zn^+$.

Completing earlier studies,[302,307,358-362] the reactions of $Sc^+$–$Zn^+$ with the four halobenzenes have been studied.[488] $Sc^+$, $Ti^+$, and $V^+$ reacted with all of them according to eq 65 and with *n* up to 6. $Fe^+$ has already been described in section VII.E; $Co^+$ and $Ni^+$ only formed adduct complexes with fluoro- and chlorobenzene and $MC_6H_5^+$ ions with iodobenzene, but eq 65 could still be noted for $Co^+$ and X = Br (*n* = 6) and for $Ni^+$ and X = Br (*n* = 6) or I (*n* = 5). $Cr^+$, $Mn^+$, $Cu^+$, and $Zn^+$ were either completely unreactive or only adduct-complex formation, halide abstraction, or charge transfer could be noted.

As described in section VII.F.2, the primary reactions of $Cr^+$–$Cu^+$ with isopropyl isocyanate led to M(HNCO)$^+$ and $M(C_3H_6)^+$ ions with comparable branching ratios.[372,373] The secondary reactions were metal-ion dependent, though; both products afforded $MC_4H_7NO^+$ ions but while for $Cr^+$, $Mn^+$, and $Zn^+$ these correspond to adduct complexes $M(i\text{-}C_3H_7NCO)^+$, for $Fe^+$–$Cu^+$, at least partly, isomeric $M(HNCO)(C_3H_6)^+$ complexes are formed.[489] This finding, albeit obtained in an FTICR instrument, should make researchers using sector instruments more precautious as they are mass-selecting adduct complexes, or better what they *believe* to be adduct complexes.

The relative abundances of nitrile adduct-complexes, formed in an ion source by the "FAB method",[88] compared to the bare metal ions were interpreted as giving the following order of bond energies: $D°(Mn^+\text{–}NCR) < D°(Fe^+\text{–}NCR) < D°(Co^+\text{–}NCR) < D°(Ni^+\text{–}NCR)$.[490] Very small losses of $CH_3^\bullet$, $C_2H_4$, and $C_2H_5^\bullet$ in CID spectra of these RCN–M$^+$ complexes (R = $CH_3$, $C_2H_5$) were assigned to a small amount of side-on coordinated metal ions. However, the authors were assuming that a metal-ion insertion precedes the radical losses, neglecting direct C–C cleavages in the course of the collision process.

The bonding strength of ethene in $Ag(C_2H_4)^+$ and $Ag(C_2H_4)_2^+$ has been determined by using HPMS and was found to be much higher than expected on the basis of simple electrostatic attraction.[491] The latter bonding mode was suggested in theoretical studies on $AgC_2H_4^+$.[159a,c,e] Clustering of He with state-selected transition-metal ions has been studied, too.[492] While $Ti^+$, $Mn^+$, and $Zn^+$ did not form $MHe^+$ adducts, ground-state $V^+$, $Cr^+$, $Co^+$, and $Ni^+$ ions did; $FeHe^+$ was also observed but was probably due to the reaction of an excited state. The measured binding energies were low, 1–3.5 kcal mol$^{-1}$, thus only electrostatic bonding obtains.

The interaction of a methane chemical-ionization plasma with $Cr(CO)_6$ and $Mn_2(CO)_{10}$ results in $[Cr(CO)_6]C_2H_5^+$, $[Mn_2(CO)_{10}]C_2H_5^+$, and $[Mn_2(CO)_{10}]C_3H_7^+$ ions. CID of these ions reveals alkene loss ($C_2H_4$ or $C_3H_6$, respectively) with rather low thresholds, and proton-bridged structures, e.g. $(CO)_5CrCO\text{-}\,\text{-}H^+\text{-}\,\text{-}(C_2H_4)$, have been proposed.[493]

The thresholds for endothermic hydride abstraction of $Fe^+$ with propane,[130] cyclopropane, *n*-butane, cyclopentane, and acetaldehyde were determined to derive $D°$(Fe–H).[494] Similarly, $D°$(Ti–H) was obtained from the reaction of $Ti^+$ with mono-, di-, and trimethylamine.[495] For all three systems many products were observed in addition to TiH, with loss of $H_2$ dominating, respectively.

The barrier for loss of CO from $V(CO_2)^+$ has been estimated by RRK modeling of the wave length dependent $VO^+/V^+$ branching ratio upon photodissociation.[496] Last, but not least, the reader is referred to an impressively comprehensive review by Tsipis about calculations on transition-metal compounds which covers many of the systems discussed here.[497]

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