prove interesting. A previous example of unusual thermochemistry in the hydration of an ion is that of t-$C_4H_9^+$ where the unusual behavior is ascribed to the transfer of charge to water to produce a protonated *tert*-butyl alcohol.[26]

Conclusions

The thermodynamic results of the present study support the conclusion of Henchman et al.[10] concerning the unreactive nature of PO_3^- in the gas phase. Our results suggest that the reaction of PO_3^- with water in the gas phase produces the simple adduct $PO_3^- \cdot H_2O$. However, hydration of PO_3^- by three water molecules leads to a chemical transformation, presumably to the dihydrogen orthophosphate anion. The thermochemical data on $\Delta H_f°(PO_3^-)$ from Rudnyi and co-workers[3] are consistent with the present interpretation.

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Registry No. PO_3^-, 15389-19-2.

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Revised and Modified Mechanisms for the Reactions of Bare Transition-Metal Ions M^+ (M = Fe, Co, Ni) with n-C_3H_7X (X = NH_2, OH) in the Gas Phase

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Abstract: The metastable ion (MI) decompositions of n-C_3H_7X/M^+ complexes (X = OH, NH_2; M = Fe, Co, Ni) in the gas phase have been studied by tandem mass spectrometry. The analysis of the MI spectra of a large set of isotopomers uncovers processes which require a revision and modification of the previously suggested mechanisms for the activation of CH and CC bonds in these particular systems. Highlights of the novel findings are inter alia the observation that Fe^+-mediated ethylene loss from n-$C_3H_7NH_2$ involves the α- and β-methylene units. "Scrambling" of these two intact CH_2 groups precedes the β-hydrogen transfer which eventually leads to NH_3 and C_3H_6 from $C_3H_7NH_2/Fe^+$. For the Co^+ and Ni^+ complexes this exchange process is not observed, and ethylene loss can be described in terms of the "remote functionalization" concept. In the n-C_3H_7OH/M^+ system, the most unexpected findings concern the mechanism of the competitive formations of CH_3OH and C_2H_4. For M^+ = Co^+, methanol contains the intact methyl and OH groups of the precursor propanol, and C_2H_4 originates from the internal part of the alkyl chain ($C(\alpha)/(C(\beta))$. This reaction sequence is to approximately 20% also operative for the Ni^+ system. In addition, the "anchored" Ni^+ induces cleavage of the $C(\alpha)/C(\beta)$ bond to eventually generate C_2H_4 (containing $C(\beta)$ and $C(\gamma)$) and CH_3OH. The methyl group of the latter contains the original α-CH_2 unit and one hydrogen from the CH_3 group of propanol. The results underline the necessity of employing labeled presursors in mechanistic studies of organometallic systems in the gas phase.

Gas-phase experiments with "naked" transition-metal ions offer a unique possibility to probe, in the absence of any solvation, ion-pairing and/or ligand effects, the intrinsic properties of reactive organometallic species and to evaluate the potential role these remarkable transients play in the initial steps of the activation of C–H and C–C bonds.[1] Not surprisingly, this topic is of fundamental interest in catalysis and has attracted considerable attention in the last decade.[1,2]

Quite a few reactions of transition-metal ions M^+ with organic substrates can be described by a mechanism (Scheme I), suggested for the first time by Allison and Ridge.[3a] Oxidative addition of the C–X bond (X = functional group) of the organic substrate **1** to M^+ produces **2** which generates via β-hydrogen transfer the olefin–hydrido complex **3**. Depending on the binding energies, **3** undergoes either alkene detachment (**3** → $RCH{=}CH_2$) or reductive elimination of HX.

The selective functionalization of *remote* C–H or C–C bonds, i.e., several carbon atoms away from the activating group X,

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(1) Selected references: (a) Müller, J. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 653. (b) Müller, J. *The Organic Chemistry of Iron*; Academic Press: New York, 1978; Vol. 1, p 145. (c) Beauchamp, J. L.; Stevens, A. E.; Corderman, R. R. *Pure Appl. Chem.* **1979**, *51*, 967. (d) Gregor, I. K.; Guilhaus, M. *Mass Spectrom. Rev.* **1984**, *3*, 39. (e) Freiser, B. S. *Talanta* **1985**, *32*, 697. (f) Allison, J. *Prog. Inorg. Chem.* **1986**, *34*, 627. (g) Armentrout, P. B. In *Structure/Reactivity and Thermochemistry of Ions*; Ausloos, P., Lias, S. G., Eds.; D. Reidel: Dordrecht, 1987; No. 193, p 97. (h) Ridge, D. P. *Ibid.* 1987; No. 193, p 165. (i) Squires, R. R. *Chem. Rev.* **1987**, *87*, 623. (j) Armentrout, P. B. In *Gas Phase Inorganic Chemistry*; Russell, D. H., Ed.; Plenum: New York, 1989. (k) Czekay, G.; Drewello, T.; Eller, K.; Lebrilla, C. B.; Prüsse, T.; Schulze, C.; Steinrück, N.; Sülzle, D.; Weiske, T.; Schwarz, H. In *Organometallics in Organic Synthesis 2*; Werner, H., Erker, G., Eds.; Springer Verlag: Heidelberg, 1989; p 203. (l) Schwarz, H. *Acc. Chem. Res.* **1989**, *22*, 282. (m) More than 100 references on the reactions of bare transition-metal ions with organic substrates, together with a detailed discussion of the reactions of gaseous octyne isomers with Fe^+, may be found in: Schulze, C.; Schwarz, H.; Peake, D. A.; Gross, M. L. *J. Am. Chem. Soc.* **1987**, *109*, 2368. (n) Buckner, S. W.; Freiser, B. S. *Polyhedron* **1988**, *7*, 1583. (o) Eller, K.; Schwarz, H. *Chimia*, in press.

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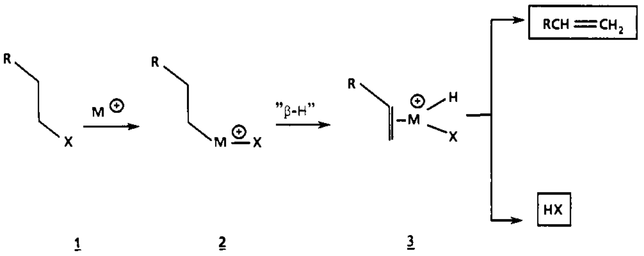
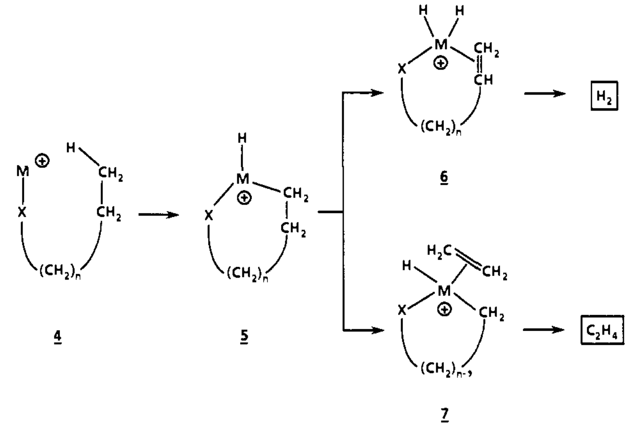
(3) (a) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 4998. (b) Babinec, S. J.; Allison, J. *Ibid.* **1984**, *106*, 7718.

Scheme I



Scheme II



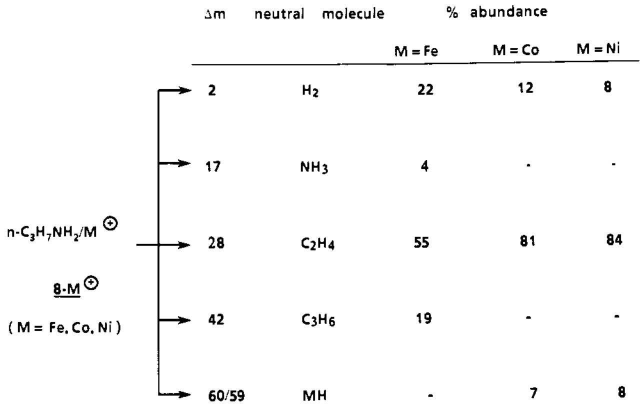
represents a great challenge. Such processes are common to enzymes (for example, enzymatic conversion of stearic to oleic acid and/or microbiological hydroxylation of C–H bonds) which "anchor" a functional group and *geometrically* select a specific segment of the substrate; however, in solution chemistry only a few cases are reported[4] where a similar principle seems to be operative. Breslow[4] has coined the term "*remote functionalization*" for the coordination to a functional group followed by selective reactions at sites separated spatially from the complexing group X. We,[1k,l,o,5] and later others,[6] have recently demonstrated that remote functionalization can be achieved in the gas phase for quite a variety of aliphatic substrates including nitriles,[5,6] isonitriles,[7] alcohols,[8] ketones,[9] alkynes,[1m,10] and allenes,[11] respectively. Specifically, we have shown that the C–H bond of a terminal methyl group of a flexible alkyl chain can be oxidatively added to the "anchored" transition-metal ion M^+ (Scheme II). The insertion is followed by a β-hydrogen shift (**5** → **6**) or β-cleavage of the C–C bond (**5** → **7**) to generate intermediates which eventually undergo reductive elimination of H_2 or ligand detachment. This behavior contrasts sharply with that depicted in Scheme I, and it demonstrates that selective C–H activation can indeed be achieved at positions remote from the functional group X.

Table I. Neutral Products Formed from Fe^+ Complexes of *n*-Propylamine Isotopomers **8a–d**

	CH_3CH_2-CH_2ND_2/Fe^+ **8a**-Fe^+	CH_3CH_2-CD_2NH_2/Fe^+ **8b**-Fe^+	CH_3CD_2-CH_2NH_2/Fe^+ **8c**-Fe^+	CD_3CH_2-CH_2NH_2/Fe^+ **8d**-Fe^+
H_2	100	100		
HD			100	100
NH_3		50	50	100
NH_2D		50	50	
NHD_2	100			
C_2H_4	100			100
$C_2H_2D_2$		100	100	
C_3H_6	100			
C_3H_5D		50	50	
$C_3H_4D_2$		50	50	
$C_3H_3D_3$				100

[a] Data are given in %Σneutral products, for each neutral normalized to 100%.

Scheme III



Δm	neutral molecule	% abundance M = Fe	M = Co	M = Ni
2	H_2	22	12	8
17	NH_3	4	-	-
28	C_2H_4	55	81	84
42	C_3H_6	19	-	-
60/59	MH	-	7	8

Here, we shall present data which warrant a revision and substantial modification of the mechanism (Scheme I) previously suggested[3,12] for *n*-propyl alcohol and *n*-propylamine (C_3H_7OH and $C_3H_7NH_2$) with transition metal ions M^+ (M = Fe, Co, Ni). By studying a large set of labeled isotopomers of *n*-C_3H_7X,[13] not only a detailed insight into the activation of C–H and C–C bonds is achieved, but, in addition, several fundamental aspects of many unimolecular reactions of organometallic species in the gas phase are unravelled.

For didactic purposes the organization of the paper is as follows. First, we describe the metastable ion (MI) decompositions of *n*-$C_3H_7NH_2/M^+$ complexes (M = Fe, Co, Ni), and then discuss the C_3H_7OH/M^+ systems. A comparison of the two systems will be made, together with an evaluation of the data reported in the literature.[3,12,14]

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(5) (a) Lebrilla, C. B.; Schulze, C.; Schwarz, H. *J. Am. Chem. Soc.* **1987**, *109*, 98. (b) Drewello, T.; Eckart, K.; Lebrilla, C. B.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1987**, *76*, R1. (c) Lebrilla, C. B.; Drewello, T.; Schwarz, H. *Ibid.* **1987**, *79*, 287. (d) Lebrilla, C. B.; Drewello, T.; Schwarz, H. *J. Am. Chem. Soc.* **1987**, *109*, 5639. (e) Prüsse, T.; Lebrilla, C. B.; Drewello, T.; Schwarz, H. *Ibid.* **1988**, *110*, 5986. (f) Prüsse, T.; Drewello, T.; Lebrilla, C. B.; Schwarz, H. *Ibid.* **1989**, *111*, 2857. (g) Czekay, G.; Drewello, T.; Schwarz, H. *Ibid.* **1989**, *111*, 4561. (h) Czekay, G.; Drewello, T.; Eller, K.; Zummack, W.; Schwarz, H. *Organometallics*, in press.

(6) Stepnowski, R. M.; Allison, J. *Organometallics* **1988**, *7*, 2097.

(7) (a) Eller, K.; Lebrilla, C. B.; Drewello, T.; Schwarz, H. *J. Am. Chem. Soc.* **1988**, *110*, 3068. (b) Eller, K.; Schwarz, H. *Chem. Ber.*, in press.

(8) Prüsse, T.; Schwarz, H. *Organometallics*, in press.

(9) Czekay, G.; Eller, K.; Schröder, D.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.*, in press.

(10) (a) Schulze, C.; Schwarz, H. *Chimia* **1987**, *41*, 29. (b) Schulze, C.; Schwarz, H. *J. Am. Chem. Soc.* **1988**, *110*, 67. (c) Schulze, C.; Weiske, T.; Schwarz, H. *Organometallics* **1988**, *7*, 898.

(11) Steinrück, N.; Schwarz, H. *Organometallics* **1989**, *8*, 759.

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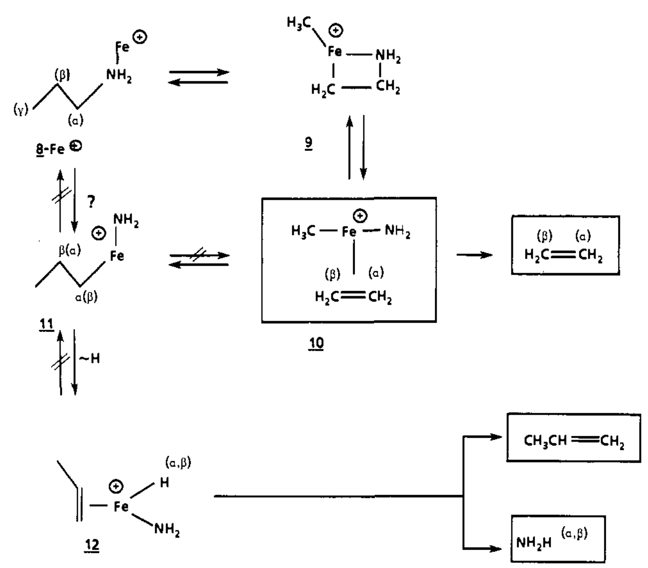
(13) Preliminary results for the system $C_3H_7NH_2/M^+$ (M = Fe, Co) were reported as a short communication: Karrass, S.; Eller, K.; Schulze, C.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 607.

(14) It has been argued by a referee that it might be unjustified to compare the results of metastable ion dissociation (as reported in the present study) with data obtained from ion/molecule reactions using ion cyclotron resonance mass spectrometry (as described in ref 3 and 12). It might suffice to state that in two recent comparative studies evidence was presented that a comparison between MI and FTICR data is indeed meaningful after consideration of a few minor points; beyond that, very good if not excellent agreement is found with regard to the *isotope distribution* of neutral molecules generated in the reactions of many transition-metal ions with quite a variety of organic substrates. These findings support our view that the data presented in the present contribution for the C_3H_7X/M^+ systems reflect *intrinsic* properties of the organometallic complexes rather than special features of the mass spectrometric methodology used. This is also supported by preliminary results (Eller, K.; Schwarz, H., unpublished) on $C_3H_7NH_2/M^+$ systems under FTICR conditions. For leading references, see: (a) Eller, K.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1989**, *93*, 243. (b) Eller, K.; Zummack, W.; Schwarz, H. *J. Am. Chem. Soc.*, in press.

Scheme IV



Results and Discussion

1. n-$C_3H_7NH_2/M^+$ Systems. The product distribution of metastable ions of the $C_3H_7NH_2/Fe^+$ complex is given in Scheme III. Although the *actual* structures of both the ions and the neutrals[15] are unknown, the study of the isotopomers of n-propylamine (Table I) provides a detailed insight with regard to the genesis of the species formed.

The labeling data prove that molecular hydrogen originates exclusively from the β and γ positions of the propyl chain. This 1,2-elimination is not preceded by hydrogen scrambling, and the process can be described in terms of Scheme II (X = NH_2: **4** → **5** → **6** → H_2). We note the absence of oxidative addition of Fe^+ to the N–H bond, followed by β-hydrogen transfer and reductive elimination of H_2 to eventually generate an Fe^+/imine complex, as previously suggested[16] for the Co^+-induced dehydrogenation of amines (see, however, below).

The remaining processes of the n-$C_3H_7NH_2/Fe^+$ system, i.e., formation of NH_3, C_3H_6, and C_2H_4, will be discussed together as all three reactions proceed via the same intermediate. While NH_3 and C_3H_6 could in principle be formed according to the traditional mechanism (Scheme I), this scheme cannot explain the generation of C_2H_4. The presumption that C_2H_4 may result from a "remote functionalization" process (Scheme II) is, however, also not supported by the labeling data. The latter leave no doubt that C_2H_4 exclusively contains the α- and β-methylene units of the propyl chain. The γ position, which would be incorporated in the neutral, if Scheme II pertains to the formation of C_2H_4, is not involved. In addition, ammonia and propene whose formation is linked with each other via intermediate **3** (R = CH_3; X = NH_2; M = Fe) are not formed in a straightforward manner from n-$C_3H_7NH_2/Fe^+$. If this were the case, the hydrogen transferred from the propyl chain should originate specifically from the β position; as a consequence, the Fe^+ complex of $CH_3CD_2CH_2NH_2$ should decompose exclusively to NH_2D and $CH_3CD{=}CH_2$ while from $CH_3CH_2CD_2NH_2/Fe^+$ only NH_3 and $CH_3CH{=}CD_2$ are expected to be formed. These expectations are not met by the labeling data. Both the α- *and* β-methylene groups participate to exactly the same amount in the products formation. As a degenerate hydrogen exchange within the alkyl chain via, for example, dyotropic rearrangements[17] can be ruled out,[18] we have to conclude that the "intact" α- and β-methylene groups become chemically equivalent prior to the generation of ammonia and propene. We propose the olefin complex **10** (Scheme IV) as the central species in the eventual production of C_2H_4, NH_3, and C_3H_6. This complex, which can be formed by oxidative addition of the C(β)–C(γ) bond to the "anchored" Fe^+ followed by cycloreversion (Scheme IV: **8**-Fe^+ → **9** → **10**), serves two functions: (i) **10** can be viewed as the immediate precursor for the detachment of C_2H_4 containing specifically the α- and β-methylene groups; (ii) complex **10** also accounts for the "equilibration" of the α- and β-CH_2 groups. Although the geometric and electronic details of this equilibration are unknown and no thermochemical data seem to exist for the $C_3H_7NH_2/Fe^+$ system, it is not unreasonable to assume that rotation around the Fe–C_2H_4 bond is energetically less demanding than alkene detachment.[19] Insertion of the ethylene unit in the Fe^+–CH_3 bond (a gas-phase analogue of the Ziegler–Natta type C–C bond formation[20,21]) generates **11**, rendering the original α- and β-methylene groups indistinguishable. Rapid, irreversible hydrogen transfer leads to the olefin complex **12**; the latter decomposes to ammonia and propene.

Although it remains open to question whether the reactions connecting **8**-Fe^+, **9**, **10**, and **11** are reversible or not, decisions can be made at least for some of the steps depicted in Scheme IV. For example, we do not think that the β-methyl transfer **11** → **10** is of any importance in the $C_3H_7NH_2/Fe^+$ system; this presumption is based on the following grounds. If this reaction would indeed occur, its rate must be significantly faster than the "β"-hydrogen transfer **11** → **12** in order to account for the required equilibration of the α- and β-methylene groups from a directly formed insertion product **8**-Fe^+ → **11**. As a β-hydrogen transfer to a metal center is known as an extremely fast process in organometallic systems[1,2] and no clear-cut proof for the operation of an authentic β-methyl migration seems to exist,[21,22] we discard the reaction path **11** → **10**. Similarly, we rule out the possibility that **11** undergoes a metal extrusion reaction **11** → **8**-Fe^+. On the other hand, the direct insertion step **8**-Fe^+ → **11** is feasible; however, in view of the conflicting[3b,23] thermochemical data for insertion of M^+ into a C–N bond of amines, no definitive decision can be made. It is important to note that if this reaction occurs, its rate must be significantly smaller than that of the multistep reaction **8**-Fe^+ $\rightleftarrows$ **9** $\rightleftarrows$ **10**. With regard to the reversibility of the process **9** $\rightleftarrows$ **10** as well as reductive ring-opening of metallacycles, there exist many precedents in literature.[24,25]

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(15) Owing to sensitivity limitations, we were unable to apply the otherwise powerful method of collisionally induced dissociative ionization (CIDI), a variant of neutralization–reionization mass spectrometry (NRMS), for the characterization of the neutrals generated from the organometallic complexes. For pertinent reviews, see: (a) Wesdemiotis, C.; McLafferty, F. W. *Chem. Rev.* **1987**, *87*, 485. (b) Terlouw, J. K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 805. (c) Terlouw, J. K. *Adv. Mass Spectrom.* **1989**, *11*, 984. (d) Holmes, J. L. *Ibid.* **1989**, *11*, 53. (e) Schwarz, H. *Pure Appl. Chem.* **1989**, *61*, 685. (f) McLafferty, F. W. *Science*, in press.

(16) Radecki, B. D.; Allison, J. *J. Am. Chem. Soc.* **1984**, *106*, 946.

(17) Definition: Reetz, M. T. *Tetrahedron* **1973**, *29*, 2189.

(18) This conclusion follows directly from the observation that the α-methylene group is *not* involved in the generation of molecular hydrogen from $C_3H_7NH_2/Fe^+$.

(19) The (M^+–olefin) bond dissociation energies are, for many systems, of the order of 40–60 kcal/mol (see: Hanratty, M. A.; Beauchamp, J. L.; Illies, A. J.; v. Koppen, P.; Bowers, M. T. *J. Am. Chem. Soc.* **1988**, *110*, 1, and references cited therein). In contrast, the barrier for olefin rotations in complexes of the general structure $(CO)_4$Fe–olefin is significantly smaller (10–15 kcal/mol): (a) Kruczynski, L.; Li Sing, L. K. K.; Takats, M. J. *J. Am. Chem. Soc.* **1974**, *96*, 4006. (b) Wilson, S. T.; Coville, N. J.; Shapley, J. R.; Osborn, J. A. *Ibid.* **1974**, *96*, 4038. (c) Segal, J. A.; Johnson, B. F. G. *J. Chem. Soc., Dalton Trans.* **1975**, 677, 1990.

(20) Watson, P. L. *J. Am. Chem. Soc.* **1982**, *104*, 337.

(21) Migratory insertion of an alkyl group to an alkylidene fragment (CH_3–M=CH_2 $\rightleftarrows$ M–CH_2CH_3) is well known for many cationic alkylidene/alkyl transition-metal complexes. See, for example: (a) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98. (b) Threlkel, R. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1981**, *103*, 2650. (c) Hajes, J. C.; Pearson, G. D. N.; Cooper, N. J. *Ibid.* **1981**, *103*, 4648. (d) Thorn, D. L. *Organometallics* **1982**, *1*, 879. (e) Kletrin, H.; Werner, H.; Serhadli, P.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 46.

(22) In none of the systems studied so far in our group were we able to obtain evidence for the operation of a β-methyl shift: (a) Prüsse, T.; Lebrilla, C. B.; Drewello, T.; Schwarz, H. *J. Am. Chem. Soc.* **1988**, *110*, 5986. (b) Eller, K.; Drewello, T.; Zummack, W.; Allspach, T.; Annen, U.; Regitz, M.; Schwarz, H. *Ibid.* **1989**, *111*, 4228. For a counter example, see: (c) Houriet, R.; Halle, L. F.; Beauchamp, J. L. *Organometallics* **1983**, *2*, 1818.

(23) Buckner, S. W.; Freiser, B. S. *J. Am. Chem. Soc.* **1987**, *109*, 4715.

Table II. Neutral Products Formed from Co^+ and Ni^+ Complexes of *n*-Propylamine Isotopomers[a]

	$CH_3CH_2CH_2ND_2$		$CH_3CH_2CD_2NH_2$		$CH_3CD_2CH_2NH_2$		$CD_3CH_2CH_2NH_2$	
	8a-Co^+	**8a**-Ni^+	**8b**-Co^+	**8b**-Ni^+	**8c**-Co^+	**8c**-Ni^+	**8d**-Co^+	**8d**-Ni^+
H_2	100	45	100	70		67		43
HD		55		30	100	33	100	43
D_2								14
C_2H_4	100	100	100	>99		3		
C_2H_3D					23			
$C_2H_2D_2$				<1	77	97	75	100
C_2HD_3							25	
MH	100	100			100	100	100	100
MD			100	100				

[a] See footnote in Table I.

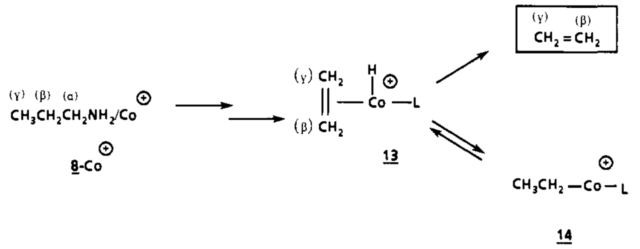
We have considered several alternatives to Scheme IV without success. One example concerns the possibility that Fe^+ may mediate an isomerization $n\text{-}C_3H_7NH_2 \rightarrow i\text{-}C_3H_7NH_2$. However, both the labeling data in Table I as well as the observation that the independently generated complex $i\text{-}C_3H_7NH_2/Fe^+$ forms only H_2 (95%) and CH_4 (5%) rule out this possibility.

For the $n\text{-}C_3H_7NH_2/Co^+$ system, the metastable ion spectrum is quite distinct from that of the analogous Fe^+ complex (see Scheme III and Table II). Common to both transition metal ions is the production of H_2 and C_2H_4. For the Co^+ system, we observe in addition transfer of a hydride ion from the α-methylene group (specific loss of neutral CoD from **8b**-Co^+ and of CoH from the remaining isotopomeric complexes). Both C_3H_6 and NH_3 are not generated from the $C_3H_7NH_2/Co^+$ complex. Molecular hydrogen, liberated from $C_3H_7NH_2/Co^+$, originates from the β and γ positions; H-scrambling is not observed, and the reaction may well proceed analogous to Scheme II: **4** $\rightarrow$ **5** $\rightarrow$ **6** ($X = NH_2$; M = Co). In view of Allison's conjecture[16] it is important to stress that there exists *no* evidence for activation of N–H bonds by Co^+ (see also above for Fe^+).

With regard to the Co^+-mediated formation of C_2H_4 from $n\text{-}C_3H_7NH_2$, the labeling data prove that the olefin originates from the β and γ positions of the propyl chain (loss of C_2H_4 and not of $C_2H_2D_2$ from $CH_3CH_2CD_2NH_2/Co^+$). This indicates that a reaction analogous to Scheme II is operative (**4** $\rightarrow$ **5** $\rightarrow$ **7**). However, the study of $CH_3CD_2CH_2NH_2$ (**8c**) and of $CD_3CH_2CH_2NH_2$ (**8d**) reveals that ethylene detachment is preceded by a partial exchange of the hydrogens originally attached to the β and γ positions of the propyl chain. From **8c**-Co^+ the neutrals $C_2H_2D_2$ and C_2H_3D are formed in a ratio 2.8:1, and from **8d**-Co^+ the isotopomers $C_2H_2D_2$ and C_2HD_3 are generated in a ratio 2.7:1. For a complete equilibration of an A_3B_2 system (A, B = H, D), from the precursors **8c** and **8d** the isotopomers $C_2A_2B_2$ and C_2A_3B should be formed in a ratio 1.5:1. We suppose, that the direct ethylene detachment is in competition with an exchange process, as depicted in Scheme V (with $L = CH_2NH_2$). It is interesting to note that Co^+-mediated generation of C_2H_4 involving the α position of the propyl chain, which is completely absent in the MI mass spectrum of $C_3H_7NH_2/Co^+$, is observed upon collisional activation. Under this condition roughly 20% of the total ethylene originates from $C(\alpha)/C(\beta)$, and an intermediate analogous to **10** (Fe^+ replaced by Co^+) may account for this observation.

The $C_3H_7NH_2/M^+$ systems are only deceptively similar for M = Co, Ni in that the same neutral products are formed. The labeling data for M = Ni (Table II) demonstrate a more complex reaction pattern. The hydride abstraction by both transition-metal ions Co^+ and Ni^+ is a specific process which involves only the α-methylene group ($C_3H_7NH_2/M^+ \rightarrow MH + CH_3CH_2CH{=}NH_2^+$). The generation of molecular hydrogen is no longer a reaction which results from activation of the β and γ positions for M = Ni. In contrast to M = Co, where hydrogen is specifically generated from these positions, *all* hydrogens of the $C_3H_7NH_2/Ni^+$ complex contribute to the production of molecular hydrogen. Obviously, extensive hydrogen exchange must precede the actual reductive elimination step. This is also indicated by the data for the formation of $C_2H_{4-x}D_x$. While the major part of the neutral originates from $C(\beta)$ and $C(\gamma)$, in addition an unprecedented "coupling" of $C(\alpha)/C(\gamma)$ must occur as demonstrated by the 3% loss of C_2H_4 from $CH_3CD_2CH_2NH_2/Ni^+$.

Scheme V



In their detailed ICR study of the $n\text{-}C_3H_7NH_2/M^+$ system (M = Cr, Mn, Fe, Co, Ni, Cu, and Zn), Babinec and Allison[3b] note that Fe^+ is the only metal ion that inserts into the C–N bond of this particular amine. This result is not borne out by our experiments (Scheme III, Table I), which point to an activation of the $C(\beta)/C(\gamma)$ bond of $C_3H_7NH_2$. In addition, for the major reaction (loss of C_2H_4) a mechanism was put forward[1f] which involves insertion of the metal ions into the $C(\alpha)$–$C(\beta)$ bond. Again, our labeling data (Table I) do not support this generalized proposal; rather, the results given in Table I point to a highly specific interaction of the "anchored" Fe^+ with the $C(\beta)$–$C(\gamma)$ bond, thus giving rise to isotopomeric products which had to go unnoticed in the earlier studies as no adequately labeled substrates were employed. However, for M = Co^+ and Ni^+ it is the central C–C bond which is eventually cleaved. The mechanism of this reaction may, however, commence with the remote functionalization of a C–H bond of the methyl group, followed by C–C cleavage, rather than direct C–C bond addition.[26]

2. $n\text{-}C_3H_7OH/M^+$ Systems. Several studies are already known in the literature for the gas-phase chemistry of transition-metal ions with *n*-propyl alcohol.[3a,12] With regard to the various bonds of C_3H_7OH to be oxidatively added to M^+, the existing data were reported to favor insertion into the C–O bond followed by β-hydrogen transfer to generate complex **3** (Scheme I: $R = CH_3$; X = OH). In fact, for M = Fe^+ and Co^+ the major process (loss of H_2O) can be accounted for in terms of Scheme I. Unfortunately, no pertinent labeling experiments were included in the previous studies. As will be demonstrated, the study of a large set of isotopomers of *n*-propyl alcohol (**15**), i.e., $n\text{-}C_3H_7OD$ (**15a**), $CH_3CH_2CD_2OH$ (**15b**), $CH_3CD_2CH_2OH$ (**15c**), and $CD_3CH_2CH_2OH$ (**15d**), permits a more refined description of the various

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(24) For bimolecular metathesis reactions of transition-metal ions in the gas phase, see: (a) Stevens, A. E.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 6449. (b) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Ibid.* **1983**, *105*, 1829. (c) Jacobson, D. B.; Freiser, B. S. *Ibid.* **1985**, *107*, 2605. (d) Kang, H.; Beauchamp, J. L. *Ibid.* **1986**, *108*, 5663. (e) Buckner, S. W.; Gord, J. R.; Freiser, B. S. *Ibid.* **1988**, *110*, 6606. (f) Reference 1n.

(25) (a) Reference 1c. (b) Reference 1f.

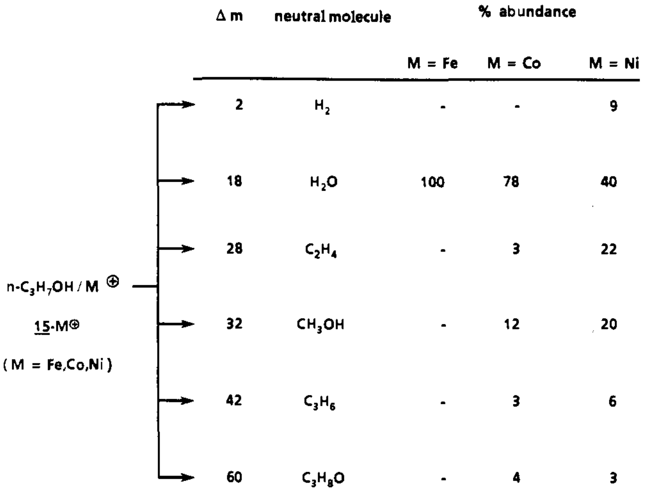
(26) A clear-cut case for metal-ion induced activation of C–C bonds, without any C–H activation steps involved, was recently described for the C_4H_8 loss from $(C_2H_5)_2CHCH_2NH_2/Fe^+$: Karrass, S.; Schwarz, H. *Helv. Chim. Acta* **1989**, *72*, 633.

Table III. Hydrogen and Water Losses from n-C_3H_7OH/M^+ Isotopomers (MI Spectra)[a]

	$CH_3CH_2CH_2OD$ (**15a**)			$CH_3CH_2CD_2OH$ (**15b**)			$CH_3CD_2CH_2OH$ (**15c**)			$CD_3CH_2CH_2OH$ (**15d**)		
	Fe^+	Co^+	Ni^+	Fe^+	Co^+	Ni^+	Fe^+	Co^+	Ni^+	Fe^+	Co^+	Ni^+
H_2			24			25			83			50
HD			76			76			17			50
H_2O	13	18	14	80	56	86	81	57	29	80	91	94
HDO	87	82	86	20	44	14	19	43	71	20	9	6

[a] See footnote in Table I.

Scheme VI



Δm	neutral molecule	% abundance M = Fe	M = Co	M = Ni
2	H_2	-	-	9
18	H_2O	100	78	40
28	C_2H_4	-	3	22
32	CH_3OH	-	12	20
42	C_3H_6	-	3	6
60	C_3H_8O	-	4	3

Table IV. Co^+- and Ni^+-Mediated Formation of Ethylene from n-Propyl Alcohol Isotopomers[a,b]

	CH_3CH_2-CD_2OH (**15b**)		CH_3CD_2-CH_2OH (**15c**)		CD_3CH_2-CH_2OH (**15d**)	
	Co^+	Ni^+	Co^+	Ni^+	Co^+	Ni^+
C_2H_4		83		6	100	25
$C_2H_2D_2$	100	17	100	94		75

[a] See footnote in Table I. [b] In the MI spectrum of $CH_3CH_2CH_2OD/Ni^+$ in addition to C_2H_4 (97%), there is also a signal due to the elimination of C_2H_3D (3%).

Table V. Co^+- and Ni^+-Mediated Formation of Methanol from n-Propyl Alcohol Isotopomers[a,b]

	CH_3CH_2-CD_2OH (**15b**)		CH_3CD_2-CH_2OH (**15c**)		CD_3CH_2-CH_2OH (**15d**)	
	Co^+	Ni^+	Co^+	Ni^+	Co^+	Ni^+
CH_3OH	100	20	100	100		
CH_2DOH						81
CD_2HOH		80				
CD_3OH					100	19

[a] See footnote in Table I. [b] In the MI spectrum of $CH_3CH_2CH_2OD/M^+$ (M = Co, Ni) in addition to signals for CH_3OD, there appear weak signals (<3%) due to CH_3OH.

reactions, which are observed in addition to the dehydration process in the MI spectra (Scheme VI) of n-C_3H_7OH/M^+ (**15**-M^+). For the sake of clarity each process will be discussed separately for the various metal ions M^+.

The loss of molecular hydrogen is only observed for the C_3H_7OH/Ni^+ complex. While a significant portion originates from the β position, from the data in Table III it has to be concluded that all C–H bonds as well as the O–H bond are involved in the dehydrogenation. It remains open to question whether this reflects extensive reversible processes or, as suggested by Gross et al.,[12b] is due to unspecific direct insertion of the metal ion into the various X–H bonds, followed by β-hydrogen migration and reductive elimination.

Dehydration of n-C_3H_7OH is mediated by all three metal ions Fe^+, Co^+, and Ni^+. The labeling data (Table III) reveal significant differences with regard to the sites which participate in the formation of the neutral molecule. For n-C_3H_7OH/Fe^+, all CH bonds serve as a hydrogen source. Interestingly, loss of H_2O from C_3H_7OD/M^+ is observed for all three metal ions to some extent (13–18%). Obviously, the hydroxyl group is capable of exchanging its hydrogen atom with the alkyl chain. For the Co^+ system the data clearly reveal the near-equivalence of the α- and β-methylene group, which serve as major source in the hydrogen-transfer step. This situation is reminiscent of the Fe^+-mediated NH_3 loss from $C_3H_7NH_2$ and may suggest that a mechanism similar to the one depicted in Scheme IV is operative for the Co^+-induced dehydration of n-C_3H_7OH. In the C_3H_7OH/Ni^+ system, this "equilibration" is less pronounced compared to the Co^+ complex. Most of the hydrogen is provided by the "intact" β-methylene unit. Common to Co^+ and Ni^+ is the relatively minor involvement of the methyl group in the production of H_2O (9 and 6%, respectively); for the C_3H_7OH/Fe^+ system this position is involved to a larger extent (20%), supporting Gross's view[12b] that Fe^+ is the

Scheme VII

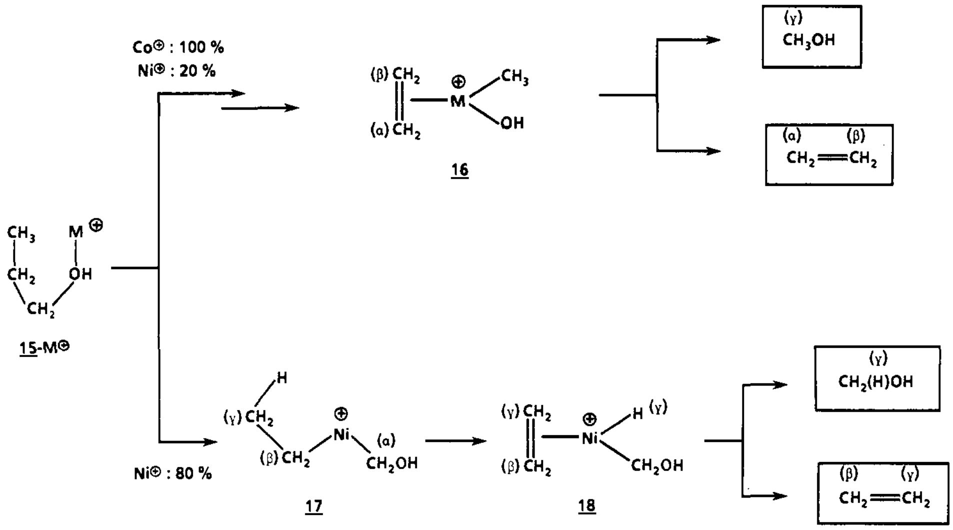


Table VI. Co^+- and Ni^+-Mediated Formation of Propene from *n*-Propyl Alcohol Isotopomers[a]

	$CH_3CH_2CH_2OD$ (**15a**)		$CH_3CH_2CD_2OH$ (**15b**)		$CH_3CD_2CH_2OH$ (**15c**)		$CD_3CH_2CH_2OH$ (**15d**)	
	Co^+	Ni^+	Co^+	Ni^+	Co^+	Ni^+	Co^+	Ni^+
C_3H_6	100	95						
C_3H_5D		5	44	43	40	25		
$C_3H_4D_2$			56	57	60	75	25	24
$C_3H_3D_3$							75	76

[a] See footnote in Table I.

least selective metal ion for this particular substrate.

Though formed with different abundance (Scheme VI), C_2H_4 is generated from *n*-C_3H_7OH by both Co^+ and Ni^+. However, the mechanism of this reaction must be completely different for either metal ion as demonstrated by the study of the isotopomers of **15**. For the Co^+ system, ethylene consists exclusively of the α- and β-methylene units. This result is in line with the data reported above for the Co^+-mediated dehydration of C_3H_7OH and supports the mechanism analogous to Scheme IV. In distinct contrast, Ni^+ generates ethylene in a more complex manner (see Table IV). While the major fraction (ca. 75%) contains the β/γ positions (Scheme II) and to ca. 17% the α/β-methylene groups (analogous to Scheme IV), there has to exist an additional path which "couples" the α/γ units (see loss of C_2H_4 (6%) from $CH_3CD_2CH_2OH/Ni^+$). It is interesting to recall (see above) that in the analogous *n*-$C_3H_7NH_2/M^+$ complexes, both metal ions generate C_2H_4 from the β/γ positions, however, with a significant amount of scrambling for $M = Co^+$. Obviously, for the time being it is by no means justified to describe the gas-phase metal-ion chemistry of systems structurally as similar as $C_3H_7NH_2/M^+$ and C_3H_7OH/M^+ in terms of a "generalized" mechanism!

The distinct role of the transition-metal ions is also evidenced by the mechanisms operative in the formation of methanol from *n*-propyl alcohol. For the Co^+ system the labeling data (Table V) prove a highly specific path (Scheme VII); methanol is built up from the intact OH and CH_3 groups of the educt. In contrast, for the Ni^+ complex, this mode constitutes a minor route (ca. 19%); the major path (81%) is due to a cleavage of the C(α)/C(β) bond of CH_3CH_2–CH_2OH, followed by β-hydrogen transfer from the methyl group (Scheme VII: **15**-$Ni^+ \rightarrow$ **17** $\rightarrow$ **18**). The alternative path, commencing with CH activation, cannot be ruled out with certainty. We note that these results are in full accord with our interpretation for the formation of ethylene and water from C_3H_7OH/M^+ (M = Co, Ni) (see above).

The metal-ion mediated formation of C_3H_6 (presumably propene) from C_3H_7OH/M^+ (M = Co, Ni) is for either complex accompanied or preceded by quite extensive hydrogen exchange processes, the actual amount of which, again, differs for Co^+ and Ni^+ (see Table VI). Although the data for the Co^+ complexes indicate an "equilibration" of the α- and β-methylene groups prior to propene loss (see also Co^+-mediated H_2O elimination which constitutes the counterpart to the propene formation), further studies are indicated before a definitive mechanism should be put forward.

Experimental Section

The experimental set-up has been described in earlier papers.[5,7,10,11,13,22a,b] Metal ions are either generated by 100-eV electron impact ionization of $Fe(CO)_5$ or by bombarding $CoCl_2$ or $NiCl_2$ with 8-keV xenon atoms, using a procedure originally developed by Freas and Campana.[27] The sputtered metal ions (or organometallic species of unknown composition) were then reacted in the ion source of a VG instruments ZAB-HF-3F mass spectrometer[28] with the organic substrates *n*-C_3H_7X (X = NH_2, OH) and their isotopomers.[29] The resulting complexes are accelerated to 8-keV kinetic energy and mass selected by using BE; the unimolecular reactions (MI spectra) occurring in the field-free region between E and B(2) were recorded by scanning B(2). Signal-averaging techniques were used to increase the signal-to-noise ratio. All compounds were synthesized and purified by standard laboratory procedures and characterized by established spectroscopic techniques.

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(27) Freas, R. B.; Campana, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 6202.

(28) This instrument is of BEB configuration (B stands for magnetic and E for electric sector). For a description of the machine, see: (a) Weiske, T. Ph.D. Thesis, Technische Universität Berlin, D 83, 1985. (b) Terlouw, J. K.; Weiske; T.; Schwarz, H.; Holmes, J. L. *Org. Mass Spectrom.* **1986**, *21*, 665.

(29) It should be mentioned that the detailed mechanism by which the C_3H_7X/M^+ complexes are formed to open to speculation. The pressure in the ion source is, however, high enough to collisionally stabilize the complexes by multiple collisions.