88657-66-3; **3a**, 112682-00-5; **3b**, 112682-02-7; **3c**, 112712-03-5; $[PPn]_2[Fe_3(CO)_9(CCO)]$, 87710-96-1; $Co_2(CO)_8$, 15226-74-1; Fe, 7439-89-6; Co, 7440-48-4.

Supplementary Material Available: Listings of positional parameters and bond angles and distances for the PPN cation of 1 and a complete listing of anisotropic thermal parameters for 1 and a numbering scheme for PPN (8 pages); a listing of observed and calculated structure factors for 1 (44 pages). Ordering information is given on any current masthead page.

Activation of C–H and C–C Bonds of 4-Octyne in the Gas Phase by Bare Transition-Metal Ions, M^+ (M = Cr, Mn, Fe)[†]

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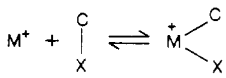
Organometallic complexes of 4-octyne with bare Cr^+ were generated in the gas phase and the unimolecular dissociations studied by means of tandem mass spectrometry. A detailed comparison is made with the previously reported M^+/4-octyne systems (M = Mn, Fe). All transition-metal ions (presumably in excited states) were found to activate C–H and C–C bonds, though the nature and amounts of neutrals eliminated differ for the various metal ions. While Fe^+ nearly exclusively generates C_2H_4, both Cr^+ and Mn^+ form, in addition to C_2H_4, molecular hydrogen, and methane. Moreover, Mn^+ causes loss of C_3H_6. The study of labeled isotopomers provides a relatively detailed insight into the mechanistic variants of the various activation steps, and it is demonstrated that all metal ions behave distinctly, with the chemistry of the Fe^+/4-octyne complex as the least complicated one. An unprecedented 1,6-elimination process across the C–C triple bond is reported for the Mn^+-induced demethanation of 4-octyne. This mechanism is not operative for the analogous elimination of CH_4 from the Cr^+/4-octyne complex; the latter reaction follows a straightforward 1,2-elimination mode, which is associated with some remarkable kinetic isotope effects. Distinct mechanisms are also operative for the metal ion induced dehydrogenation of 4-octyne, which for M = Mn^+ follows a formal 1,2-elimination (involving the terminal methyl and the adjacent CH_2 group). In contrast, for M = Cr^+ this process contributes to only a minor extent (ca. 22%); the major part (ca. 78%) of H_2 originates from C(2)/C(3). The kinetic isotope effects associated with $H_{2-x}D_x$ (x = 0, 1) losses are practically identical for the two routes (i.e. C(1)/C(2) versus C(2)/C(3)); this may indicate that the reductive elimination step is rate-determining. The analysis further suggests that Cr^+-induced reductive elimination of hydrogen proceeds through a symmetric transition structure with respect to the metal–hydrogen bonds to be cleaved. Ethylene loss from M^+/4-octyne, while being similar for M = Cr^+ or Fe^+, must have some metal-specific features that are also reflected in the isotope effects associated with the elimination of C_2H_4.

Introduction

Gas-phase experiments with bare transition-metal ions offer an unique possibility to probe, in the absence of any solvation and ion-pairing effects, the inherent properties of reactive organometallic species and to evaluate the potential role these remarkable transients may well play in the initial stages of the activation of C–H and C–C bonds. This topic is, not surprisingly, of fundamental interest in catalysis and has attracted considerable attention in the last decade.[1,2] While many transition-metal ions M^+ readily undergo oxidative insertion (eq 1) in C–X bonds (X = hydrogen, carbon, halogen, nitrogen, oxygen, etc.[1]), some metals like Mn^+ and Cr^+ show a distinctly lower reactivity toward these substrates.[3,4]



$$\mathrm{M}^+ + \begin{matrix}\mathrm{C}\\ | \\ \mathrm{X}\end{matrix} \rightleftharpoons \overset{+}{\mathrm{M}}\begin{matrix}\diagup\mathrm{C}\\ \diagdown\mathrm{X}\end{matrix} \qquad (1)$$

The decreased reactivity[5] has been explained by the particular ground-state electronic configurations of Cr^+ ($3d^5$) and Mn^+ ($3d^54s^1$), which are not favorable for the formation of M–X bonds. It has been suggested that in those cases in which reactions of Cr^+ and Mn^+ with organic substrates are observed, the insertion processes may be

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[†] Dedicated to Professor Emanuel Vogel, Köln, on the occasion of the 60th birthday.

(1) Selected references: (a) Müller, J. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 653. (b) Parshall, G. W. *Catalysis* **1977**, *1*, 335. (c) Beauchamp, J. L.; Stevens, A. E.; Corderman, R. R. *Pure Appl. Chem.* **1979**, *51*, 976. (d) Collman, J. P.; Hegedus, L. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980. (e) Haggin, J. *Chem. Eng. News* **1982**, *60*, 13. (f) Gregor, I. K.; Guilhaus, M. *Mass Spectrom. Rev.* **1984**, *3*, 39. (g) Allison, J. *Prog. Inorg. Chem.* **1986**, *34*, 627. (h) Shilov, A. E. *Activation of Saturated Hydrocarbons by Transition Metal Complexes*; D. Reidel: Dordrecht, 1984. (i) Green, M. L.; O'Hare, D. *Pure Appl. Chem.* **1985**, *57*, 1897. (j) Bandry, D.; Ephritikine, M.; Felkin, H.; Fillebeen-Khan, T.; Gault, Y.; Holmes-Smith, R.; Yingrui, L.; Zakrzewski, J. In *Organic Synthesis*; Streith, J., Prinzbach, H., Schill, G., Eds.; Blackwell Scientific Publications: Oxford, 1985; p 25. (k) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7332. (l) Armentrout, P. B. In *Structure/Reactivity and Thermochemistry of Ions*; Ausloos, P., Lias, S. G., Eds.; D. Reidel: Dordrecht, 1987; No. 193, p 97. (m) Ridge, D. P. *Ibid* **1987**; No. 193, p 165. (n) Simoes, J. A.; Beauchamp, J. L. *Chem. Rev.*, in preparation. (o) Beauchamp, J. L. *ACS Symp. Ser.*, in press. (p) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (q) Freiser, B. S. *Talanta*, **1985**, *32*, 697.

(2) More than 100 references on the reactions of bare transition-metal ions with organic substrates, together with a detailed description 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.

0276-7333/88/2307-0898$01.50/0

caused by electronically excited metal ions. For Cr^+ species, for example, there is indeed ample evidence[3b,c,f,g,4b] that electron-impact ionization of $Cr(CO)_6$ generates both ground-state and ca. 70%, long-lived excited-state metal ions, and it has been suggested[3e,k] that the former are nonreactive while the latter account for the sometimes remarkably highly selective processes.[3d,o] In spite of the knowledge accumulated on the gas-phase reactions of transition-metal ions, a thorough understanding of the mechanistic details is often seriously hampered, if not precluded, by the fact that in most studies no labeled substrates were employed. As a consequence, the actual C–H or C–C bond oxidatively added to the metal ion is inferred from quite indirect observations. Recently, it was demonstrated[6] that the time-honored "labeling approach" is indeed a powerful technique for the study of bare metal ions with organic substrates in particular if combined with appropriate mass spectrometric methodologies like tandem mass spectrometry (MSMS).

In the following we will give a detailed report on the unexpectedly rich gas-phase chemistry of 4-octyne (1) with Cr^+, and a comparison will be made with the previously described reactions of 1 with Fe^+ and Mn^+.[2,4d,e,6c] As will be shown the reactivity of these three transition-metal ions is quite distinct. Moreover, the unimolecular losses of neutrals from the $(MC_8H_{14})^+$ complexes, as, for example, H_2, CH_4, and C_2H_4, follow quite different mechanisms, some of which seem to have no precedence in organometallic chemistry.

Experimental Section

The experimental setup has been described in earlier papers.[2,6a] Briefly, transition-metal ions M^+ are generated by electron-impact ionization of appropriate organometallic precursors, i.e., $Cr(CH_3COCH_2COCH_3)_3$, $Mn_2(CO)_{10}$, and $Fe(CO)_5$. In a typical experiment the organometallic compound and 4-octyne (in a ratio of 1:5–10) were introduced simultaneously via the gas inlet system in the chemical ionization source of a Vacuum Generator ZAB-HF-3F triple sector mass spectrometer of BEB configuration (B denotes magnetic and E electric sector).[7] Experimental conditions were as follows: ionization energy, 100 eV; emission current, 0.5 mA; repeller voltage, 0 V; acceleration voltage, 8 kV; mass reso-

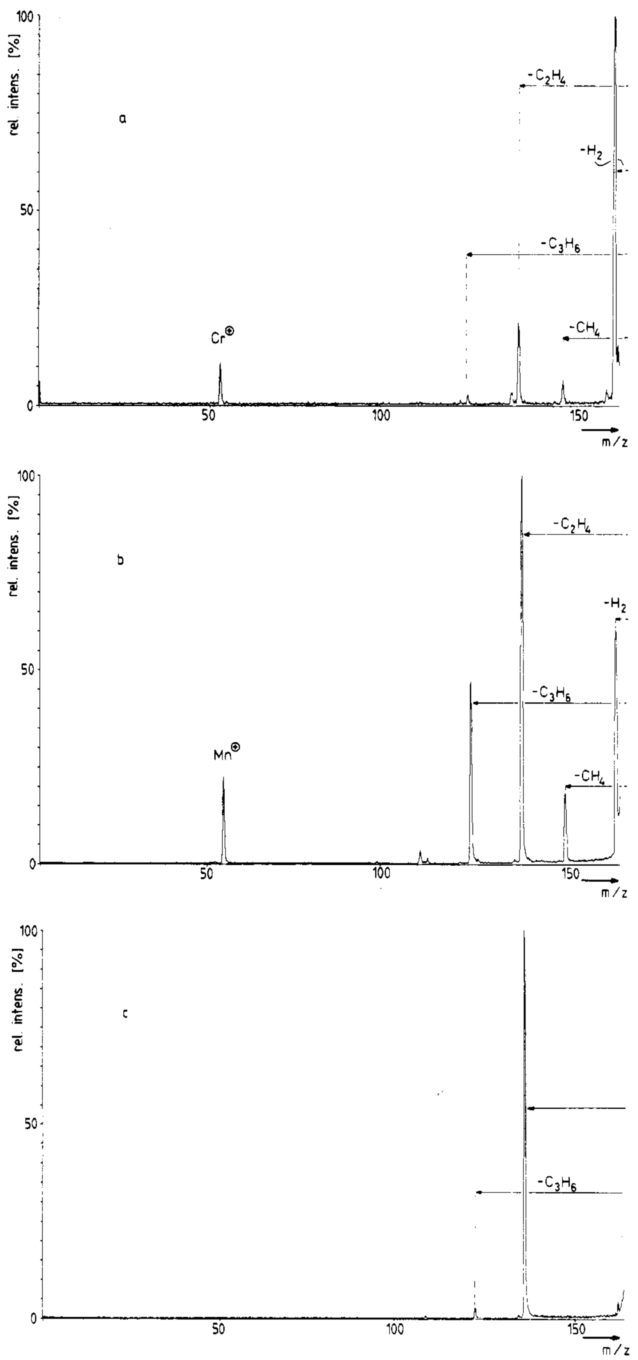
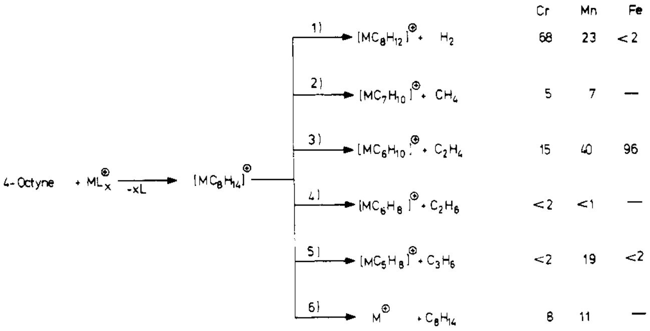


Figure 1. Metastable ion mass spectra of M^+/4-octyne complexes: (a) M = Cr; (b) M = Mn; (c) M = Fe.

Scheme I



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(3) For references on the gas-phase chemistry of Cr^+ see: (a) ref. 1g,l–o. (b) Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 962. (c) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6501. (d) Huang, S. K.; Allison, J. *Organometallics* **1983**, *2*, 883. (e) Babinec, S. J.; Allison, J. *J. Am. Chem. Soc.* **1984**, *106*, 7718. (f) Huang, S. K.; Gross, M. L. *J. Phys. Chem.* **1985**, *89*, 4422. (g) Reents, W. D., Jr.; Strobel, F.; Freas, R. B., III; Wronka, J.; Ridge, D. P. *J. Phys. Chem.* **1985**, *89*, 5666. (h) Schilling, J. B.; Goddard, W. A., III; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 582. (i) Elkind, J. L.; Armentrout, P. B. *Inorg. Chem.* **1986**, *25*, 1078. (j) Hanratty, M. A.; Carter, E. A.; Beauchamp, J. L.; Goddard, W. A., III; Illies, A. J.; Bowers, M. T. *Chem. Phys. Lett.* **1986**, *123*, 239. (k) Sonnenfroh, D. M.; Farrar, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 3521. (l) Kang, H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 7502. (m) Tonkyn, R.; Weisshaar, J. C. *J. Phys. Chem.* **1986**, *90*, 2305. (n) Mestdagh, H.; Morin, N.; Rolando, C. *Tetrahedron Lett.* **1986**, *27*, 33. (o) Huang, S.; Holman, R. W.; Gross, M. L. *Organometallics* **1986**, *5*, 1857. (p) Peake, D. A.; Gross, M. L. *J. Am. Chem. Soc.* **1987**, *109*, 600.

(4) Reactions of bare Mn^+ with organic substrates in the gas phase are described in: (a) ref 1n,o and 2b,c,e,h,i,m. (b) Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1980**, *102*, 7129. (c) Elkind, J. L.; Armentrout, P. B. *J. Chem. Phys.* **1986**, *84*, 4862. (d) Schulze, C.; Schwarz, H. *J. Am. Chem. Soc.* **1988**, *110*, 57. (e) Schulze, C.; Schwarz, H. *Chimia* **1987**, *41*, 245.

(5) The term "reactivity" is used throughout as suggested earlier by Allison,[3e] i.e., "the number of different products formed".

(6) (a) See references 1n,o, 2, and 4d,c. (b) Lebrilla, C. B.; Schulze, C.; Schwarz, H. *J. Am. Chem. Soc.* **1987**, *109*, 98. (c) Schulze, C.; Weiske, T.; Schwarz, H. *Chimia* **1986**, *40*, 362. (d) Schulze, C.; Schwarz, H. *Chimia* **1987**, *41*, 29. (e) Lebrilla, C. B.; Drewello, T.; Schwarz, H. *J. Am. Chem. Soc.* **1987**, *109*, 5639. (f) Lebrilla, C. B.; Drewello, T.; Schwarz, H. *Organometallics* **1987** *6*, 2268. (g) Hanratty, M. A.; Beauchamp, J. L.; Illies, A. J.; Koppen, P. v.; Bowers, M. T. *J. Am. Chem. Soc.* **1988**, *110*, 1 and many references on the work from Beauchamp's laboratory cited therein.

(7) For a description of the machine see: (a) Weiske, T. Ph. D. Thesis, Technical University, Berlin, 1985. (b) Terlouw, J. K.; Weiske, T.; Schwarz, H.; Holmes, J. L. *Org. Mass Spectrom.* **1986**, *21*, 665.

lution, 2000–5000 (10% valley definition); ion source pressure, 10^{-5} mbar; ion source temperature, 200 °C. The metal ion/alkyne complexes were formed by substitution reactions of ML_x^+ species with 4-octyne.[8] The so-formed organometallic complexes, having 8 keV kinetic energy, were mass-selected and focussed with B(1)E, and the unimolecular dissociations occurring in the field-free region between E and B(2) were monitored by scanning B(2). The data reported correspond to the average of 10–100 spectra that were on-line accumulated by using the VG 11/250 data system.[9]

4-Octyne (1) and its deuteriated isotopomers **1a**–**1d** were synthesized[11] by standard laboratory procedures, purified by preparative gas chromatography, and fully characterized by NMR spectroscopy and mass spectrometry.

$CH_3(CH_2)_2C{\equiv}C(CH_2)_2CH_3$ **1**

$CD_3(CH_2)_2C{\equiv}C(CH_2)_2CH_3$ **1a**

$CH_3CD_2CH_2C{\equiv}C(CH_2)_2CH_3$ **1b**

$CH_3CH_2CD_2C{\equiv}C(CH_2)_2CH_3$ **1c**

$CD_3CD_2CH_2C{\equiv}C(CH_2)_2CH_3$ **1d**

Results and Discussion

While Fe^+ readily activates alkenes,[12] Mn^+ and Cr^+ do not insert in either C–H or C–C bonds of olefins but condense slowly to form adducts, the structure(s)[13] of which are unknown. Keeping this in mind the results of the reactions of M^+ (M = Cr, Mn, Fe) with 4-octyne (Figure 1) are quite unexpected, as all metal ions activate C–H and C–C bonds of the alkyne. The relative cross sections (expressed in % fragment ions generated in the unimolecular dissociations of mass-selected $(MC_8H_{14})^+$ complexes) are given in Scheme I. Obviously, the richest chemistry in terms of different products formed is exhibited by Cr^+ and Mn^+ metal ions, which in the light of the results reported by Peake and Gross[3p] were expected to be least reactive. Both metal ions, obviously, activate CH as well as CC bonds, which eventually leads to the losses of H_2 as well as alkanes (CH_4, C_2H_6) and alkenes (C_2H_4 and C_3H_6). In contrast, Fe^+ mainly activates 4-octyne such that C_2H_4 is eliminated. For all three metal ions M^+, the sum of the daughter ion intensities relative to that of the M^+/4-octyne complexes is ca. 10%.

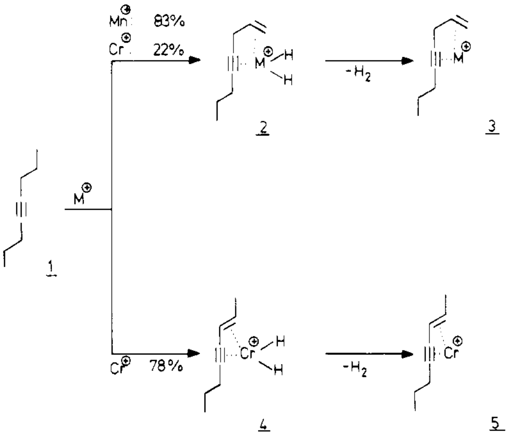
The organization of the following discussion is such that we will describe in detail most of the reactions of the Cr^+-induced activation of 4-octyne and compare these with the "analogous" reactions caused by Mn^+ and Fe^+, which were reported in detail previously.[14]

Table I. Unimolecular Loss of H_2, HD, and D_2 from Labeled M^+/4-Octyne Complexes (M = Cr, Mn)[a,b]

	4-octyne			
neutral	**1a**	**1b**	**1c**	**1d**
H_2	92 (68)	62 (64)	72 (95)	63 (72)
HD	8 (32)	38 (36)	28 (5)	30 (7)
D_2				7 (21)

[a] Data are given in % $\sum H_{2'}$, HD, D_2 = 100%. Errors are ±2% of reported data. [b] Data in parentheses refer to M = Mn and are given for comparison.

Scheme II



(1) Metal Ion Induced Dehydrogenation. While H_2 loss is a very minor reaction for the Fe^+/4-octyne system (<2%), it is the second most important process for the Mn^+/4-octyne complex and accounts for 68% of the fragments generated from Cr^+/4-octyne. With regard to the origin of the hydrogens eliminated as neutrals, there is a distinctly different behavior of Cr^+ and Mn^+. The latter metal ion activates to 83% the nonactivated C-(1)/C(2) positions and to 17% the C(2)/C(3) positions of 4-octyne,[4d] and the hydrogen molecule is eliminated in a formal 1,2-fashion generating presumably the unsaturated hydrocarbon/Mn^+ complex **3** (M = Mn). The manganese(I)-mediated dehydrogenation is associated with an average kinetic isotope effect $k_{H_2}/k_{HD} = 1.7$.[15] This process amounts, however, to only 22% for the Cr^+/4-octyne system; an algebraic analysis of the data, reported in Table I, reveals that 78% of the hydrogen originates from C-(2)/C(3). There is also an overall kinetic isotope effect, k_{H_2}/k_{HD}, operative. Most interestingly, we obtain for the losses of H_2 versus HD from the three isotopomers **1b**, **1c**, and **1d**, an *identical* value of $k_{H_2}/k_{HD} = 1.6$, *irrespective of the position of the deuterium in the 4-octyne precursor.*

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[8] For the generation of $(FeC_8H_{14})^+$ complexes it has been shown by FTICR ((a) Reference 2. (b) Peake, D. A.; Gross, M. L. *Organometallics*, **1986**, *5*, 1236) that $FeCO^+$ and $Fe(CO)_2^+$ serve as major precursor ions. This was also found for the generation of Fe^+/RCN complexes (Lebrilla, C. B.; Drewello, T.; Nibbering, N. M. M.; Schwarz, H., in preparation). It should, however, be emphasized that double-resonance experiments performed at 10^{-7} Torr give results that may not strictly apply at the high pressure used under chemical ionization conditions.

[9] In view of the fact that electron-impact ionization of $Mn_2(CO)_{10}$ generates electronically excited Mn^+ ions[4c] (as is also the case for $Fe(CO)_5$), we have generated a Mn^+ species also by fast atom bombardment (FAB) of solid $Mn(NO_3)_2{\cdot}4H_2O$ with 8-kV xenon atoms. This method is believed[10] to generate ground-state metal ions. However, as described elsewhere,[4d] the $(MnC_8H_{14})^+$ species generated by this procedure were found to have *practically identical properties* with those formed by reaction of 4-octyne with $Mn(CO)_x^+$ species. It should be mentioned that the gas-phase chemistry of RCN/Fe^+ and RCN/Co^+ complexes is also unaffected by the mode of complex generation (Drewello, T.; Eckart, K.; Lebrilla, C. B.; Schwarz, H. *Int. J. Mass Spectrom. Ion Proc.* **1987**, *76*, R1).

[10] Rabrenovic, M.; Ast, T.; Beynon, J. H. *Int. J. Mass Spectrom. Ion Proc.* **1984**, *61*, 31.

[11] Schulze, C. Diploma Thesis, Technical University, Berlin, 1985.

[12] Peake, D. A.; Gross, M. L.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 4307.

[13] Suggested structures are hypothetical and speculative in nearly all cases studied in mass spectrometry. They are based on plausibility arguments using as much direct and indirect evidence as available from experiments and model considerations. Strictly speaking, none of the structures are proven. Nevertheless, the heuristic values of such structural representations are undeniable as long as speculations remain within acceptable limits.

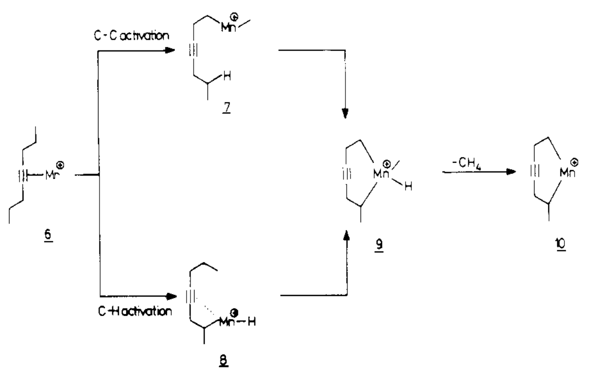
[14] For a detailed analysis see ref 2 and 6c (for Fe^+) and ref 4d,e (for Mn^+) and also for Fe^+: Peake, D. A.; Gross, M. L. *Anal. Chem.* **1985**, *57*, 115.

[15] Both the average kinetic isotope effect and the sites from which the hydrogen atoms originate were calculated by using a straightforward algebraic procedure, which is briefly outlined for the formation of hydrogen from, let us say, $CH_3{}^aCH_2{}^bCH_2{}^cX$. If one assumes that no 1,1-eliminations occur and that the elimination is not preceded by scrambling processes, the probabilities, *w*, of a given C–H bond to contribute to the formation of $[H_2]$ is given by the equation

$$[H_2] = 6w_aw_b + 6w_aw_c + 4w_bw_c$$

Similar equations can be formulated for the losses of [HD] and $[D_2]$ from labeled precursors, and the probabilities are then obtained from a matrix calculation. In the second step, the average isotope effects are evaluated by matching the experimental data for H_2, HD, and D_2 losses, respectively, against the calculated ones.

Scheme III



This result already points to the fact that it is not the insertion of the metal ion into a C–H (or C–D) bond which constitutes the rate-determining step. If this would be the case, one should obtain different k_{H_2}/k_{HD} values for compounds **1b** and **1c**. Rather, in line with previous findings,[16] we believe that the reductive elimination constitutes the rate-determining step. For the loss of H_2 versus HD from **1d** we obtain a slightly smaller value of $k_{H_2}/k_{HD} = 1.4$ which, we believe, is to some extent due to a larger experimental error. (Note, that for this particular compound loss of HD, in comparison to H_2, gives rise to a relatively weak signal). As an average isotope effect for loss of H_2 versus HD, we suggest a value of $k_{H_2}/k_{HD} = 1.6$.

In the context of concerted versus stepwise elimination processes of hydrogen, Thornton and Thornton[17] have developed a simple formula which with use of k_{H_2}/k_{HD} values enables one to distinguish between these two extremes. For a symmetric reaction, in which both hydrogen (deuterium) bonds to a given atom are stretched synchronously k_{HD} follows the simple equation (2); in contrast, for the asynchronous process (which in its extreme would correspond to a two-step reaction) the k_{HD} value is described by eq 3.

$$k_{HD} = (k_{H_2}k_{D_2})^{1/2} \qquad (2)$$

$$k_{HD} = {}^{1}/_{2}(k_{H_2} + k_{D_2}) \qquad (3)$$

In fact, there are many reports[18] in which this simple criterion has been successfully applied for gas-phase dehydrogenation processes. If we apply this analysis to the Cr^+-induced hydrogen loss from labeled 4-octynes, we calculate, by using the above-mentioned average value of $k_{H_2}/k_{HD} = 1.6$, a value of $k_{H_2}/k_{D_2} = 2.6$ for the symmetic cleavage of the metal–hydrogen (deuterium) bonds and of $k_{H_2}/k_{D_2} = 4.0$ for the unsymmetric case. The experimentally determined value of $k_{H_2}/k_{D_2} = 2.2$ for **1d** is much closer to the former, and we are inclined to conclude that the Cr^+-induced reductive elimination of hydrogen proceeds via a symmetric transition structure with respect to the Cr–H bonds to be cleaved. We also note from the data in Table I that dehydrogenation is not preceded by any H/D scrambling.

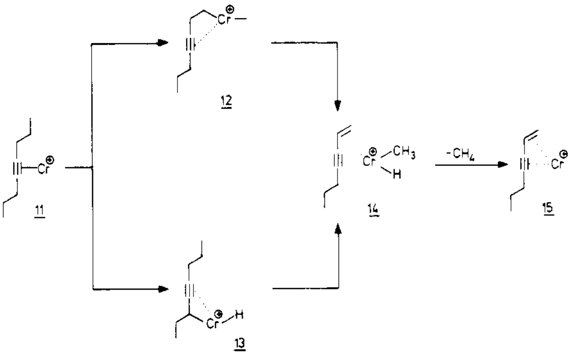
(2) Metal Ion Induced Demethanation of 4-Octyne. While this reaction is, for both Cr^+ and Mn^+, of moderate importance (5 and 7%, respectively) and completely absent in the metastable ion (MI) spectrum of Fe^+/4-octyne complexes, the mechanism by which the metal ions generate a CH_4 unit from 4-octyne is highly remarkable and, again, different for Cr^+ and Mn^+. The labeling data[4d] suggest for Mn^+ a mechanism that is described in Scheme III. Intramolecular addition of either a C–C (**6** → **7**) or a C–H bond (**6** → **8**) to the π-complexed manganese ion **6** generates intermediates that may further rearrange to the manganese–cycloheptyne cation **9**; from the latter, reductive elimination of CH_4 generates **10**. The labeling data reveal[4d] that >82% of CH_4 is generated by this unprecedented 1,6-elimination mode across the C–C triple bond to generate as an intermediate an unsaturated metallacycle, **9**, with manganese in a high oxidation state. From thermochemical data, **9** and **10** are estimated to have ring strain energies of <18 kcal/mol.[4d] The remaining 18% of CH_4 are formed in a formal 1,2-elimination involving the terminal CH_3 group and a hydrogen atom from C(3).

Table II. Unimolecular Loss of $CH_{4-x}D_x$ (x = 0–4) from Labeled M^+/4-Octyne Complexes (M = Cr, Mn)[a,b]

	4-octyne			
neutral	**1a**	**1b**	**1c**	**1d**
CH_4	58 (59)	100 (61)	71 (85)	45 (10)
CH_3D		(39)	29 (15)	(41)
CH_2D_2				
CHD_3	42 (41)			55 (49)
CD_4				

[a] Data are given in $\% \sum CH_{4-x}D_x = 100\%$. Errors are ±2% of reported data. [b] Data in parentheses refer to M = Mn and are given for comparison. They were taken from ref 4d.

Scheme IV



As demonstrated by the data in Table II, Cr^+-induced methane loss from 4-octyne follows a different pathway in that the reaction typical for Mn^+ (Scheme III) is completely absent. Methane is exclusively generated in a formal 1,2-elimination mode involving the intact terminal CH_3 group and a hydrogen atom from the propargylically activated C(3) position (Scheme IV). Again, the labeling results rule out any hydrogen scrambling preceding the reductive elimination; moreover, kinetic isotope effects seem to be operative at various stages of the multistep sequence. For example, the preferred loss of CH_4 over CHD_3 from **1a** indicates that an isotope effect is operative in the reductive elimination step (**14** → **15**). Similarly, the diminished losses of CH_3D from **1c** can be interpreted in terms of a combined isotope effect for both the insertion step (**11** → **13**) and the terminating loss of methane. Quite unexpected and not yet understood is the *inverse* isotope effect observed for **1d** (loss of CHD_3 is favored (!) over the elimination of CH_4). Obviously, the CD_2 group of C(2) does not act as an indifferent "spectator" in the overall reaction but seems to affect crucial stages of the overall reactions. Clearly, this result demands further studies including

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(16) Reductive elimination of RH (R = H, alkyl) from complexes of the type ML_x(R)H were shown to be associated with kinetic isotope effects, k_H/k_D = 1.5–3.3. (a) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915. (b) Brown, J. M.; Parker, D. *Organometallics* **1982**, *1*, 950. (c) See also ref 6g.

(17) Thornton, E. K.; Thornton, E. R. *Isotope Effects in Chemical Reactions*; Collings, C. J., Bowman, N. S., Eds.; Van Nostrand-Reinhold: New York 1973.

(18) For references see: Schwarz, H.; Franke, W.; Chandrasekhar, J.; Schleyer, P. v. R. *Tetrahedron* **1979**, *35*, 1969.

Scheme V

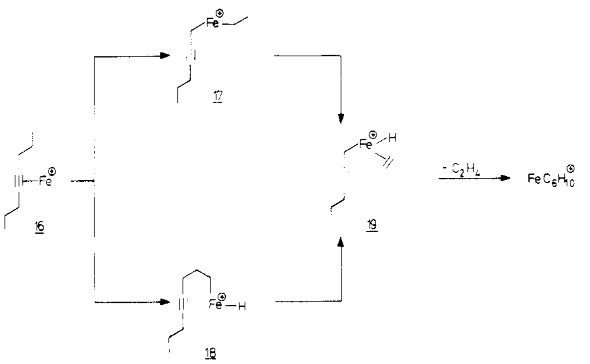


Table III. Unimolecular Loss of $C_2H_{4-x}D_x$ (x = 0–4) from Labeled M^+/4-Octyne Complexes (M = Cr, Mn, Fe)[a,b]

	4-octyne			
neutral	1a	1b	1c	1d
C_2H_4	58 (55) [55]	50 (45) [55]	100 (82) [100]	57 (45) [59]
C_2H_3D		50 (11)	(13)	(2)
$C_2H_2D_2$	42 (45) [45]	(45) [45]	(5)	(2)
C_2HD_3				(8)
C_2D_4				43 (43) [41]

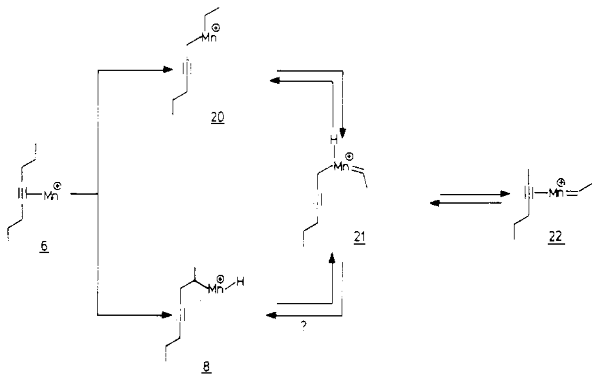
[a] Data are given in % $\sum C_2H_{4-x}D_x$ = 100%. Errors are ±2% of reported data. [b] Data in parentheses refer to M = Mn and in square brackets to M = Fe. They are given for comparison and were taken from ref 2, 4d, e, and 6c.

double-labeling experiments with $^{13}C/^{2}H$-labeled isotopomers.

(3) Metal Ion Induced Loss of Ethylene from 4-Octyne. This process is common to all three transition-metal ions used in the present study. The investigation of the unlabeled precursor already indicates that this process is of prime importance for Fe^+ (>96%) and drops to 40% for Mn^+ and 15% for Cr^+, respectively. Some insight in the mechanistic features is provided by the study of the 4-octyne isotopomers, and the results leave no doubt on the crucial importance of labeling studies as a necessary (though by no means sufficient) tool for the complete elucidation of metal ion induced activation of organic substrates.

As reported earlier[2,6c,8b,14a] loss of C_2H_4 from Fe^+/4-octyne can be explained by the mechanism shown in Scheme V. The ethylene–hydrido complex **19**, which serves as intermediate for the elimination of C_2H_4, is generated, presumably in competition, via oxidative addition of the C–C bond (**16** → **17**) or the C–H bond (**16** → **18**) to the π-complexed Fe^+, followed by irreversible rearrangement of both **17** and/or **18** to **19**. While the insertion reactions are *not* associated with a kinetic isotope effect, a value k_H/k_D = 1.1 per deuterium atom was observed for the loss of $C_2H_{4-x}D_x$. Hydrogen exchange reactions do not precede the elimination of ethylene (see data in Table III).

Scheme VI



For the Mn^+-induced loss of C_2H_4 from 4-octyne it was observed[4e] that a major part follows a mechanism similar to the one described for Fe^+ in Scheme V. However, the labeling data (Table III) prove that partial exchange of the hydrogens of C(2)/C(3)—but *not* C(1)—occurs, and the experimental findings are in keeping with Scheme VI. Here, the central intermediate corresponds to the carbene complex **21** which via the reaction **21** → **22** brings about the hydrogen exchange of C(2)/C(3). For the generation of **21** itself several mechanistic variants are conceivable; the one proceeding via **20** and **8** have precedences in the gas-phase chemistry involving many transition-metal ions.[1] Note that **8** is also suggested to be involved in the Mn^+-induced demethanation of 4-octyne (see Scheme III); species **20** serves as branching point for both the hydrogen exchange (via **20** → **21** → **22**) and the actual ethylene loss analogous to **17** → **19** with Mn^+ substituted for Fe^+ (Scheme V).

The behavior of Cr^+ is quite unique in that, on the one hand, it has in common with Fe^+ the high site specificity of the reaction (no hydrogen scrambling); however, in contrast to Fe^+, the formation of **19** (Fe^+ replaced by Cr^+) is associated with a kinetic isotope effect, k_H/k_D = 1.30 (Table III), while no isotope effect is operative for the loss of ethylene (Note that the *reverse* holds for Fe^+). Obviously, for the Cr^+ system the oxidative addition of the terminal CH bond to Cr^+ constitutes the rate-determining step.

In conclusion, the present comparative study of M^+/4-octyne complexes (M = Cr, Mn, Fe) reveals an unexpectedly rich chemistry of these species. The metal ions are distinct with regard to the generation of smaller fragments like H_2, CH_4, and C_2H_4, for Cr, Mn, and Fe, respectively, but more important is the finding that for analogous reactions the mechanisms seem to be quite different for the individual metal ions. Some insight in the intriguing, sometimes unprecedented elementary steps was provided by employing labeled substrates. A further refinement of the mechanistic conclusions may be achieved by studying the chemistry of state-selected metal ions with these substrates.

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