

Mn[⊕]-Induced Loss of Ethylene from Gaseous 4-Octyne**

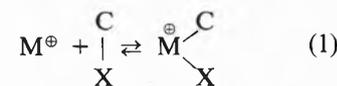
Christian Schulze and Helmut Schwarz*

Abstract: The mechanism established for the unimolecular loss of C₂H₄ from [Fe(4-octyne)][⊕], is somehow altered in the analogous Mn[⊕]-induced reaction in that some intramolecular hydrogen exchange (involving unprecedented manganese-carbene complexes) precedes the dissociation. Mechanistic variants are discussed, and brief mentioning is also made on the propene loss which is unique to the [Mn(4-octyne)][⊕] complex.

Gas-phase experiments with bare transition metal ions offer an unique opportunity 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 of these remarkable molecules in the initial stages of the activation of CH and CC bonds^[1]. While many transition metal ions

M[⊕] readily undergo oxidative insertion (Eq. (1)) in C-X bonds (X = hydrogen, carbon, nitrogen, oxygen, halogen, etc.)^[1], Mn[⊕] shows a distinctly lower reactivity towards these substrates^[2]. The decreased reactivity of Mn[⊕] in comparison with, for example, Fe[⊕] has been explained by using several qualitative concepts of MO theory. Allison and Ridge^[1d, 2d] ascribe the low reactivity of Mn[⊕] due to the quite high promotion energies to generate from the 3d⁵4s¹ ground state configuration of Mn[⊕] either a 3d⁴4s² or a 3d⁴4s¹4p¹ excited state, which may then be used to form two covalent bonds. Armentrout^[1c, 2b] and Weisshaar^[2f] explain the low reactivity of Mn[⊕] in terms of a frontier orbital MO concept, developed earlier by Saillard and Hoffmann^[3]. According to this, the metal insertion of a 3dⁿ4s⁰ configuration is favoured over that

with a 3dⁿ⁻¹4s¹ due to two favourable donor-acceptor interactions in the former. These are the interactions of (i) the doubly-occupied σ_{CX} orbital (donor) with the empty 4s_{M[⊕]} (acceptor) and (ii) of a doubly-occupied d_{xz}, say (donor) with the empty σ_{CX}^{*} (acceptor). Moreover, spin conservation also requires double occupancy of the d_{xz} orbital which can only occur for 3dⁿ metal ions with n ≥ 6, i.e. for Fe[⊕], Co[⊕], and Ni[⊕], but not for the ground state Mn[⊕] ion.



We recently reported^[4] that, in spite of these constraints, Mn[⊕] (presumably in excited electronic states) may well react with organic substrates like alkynes. Among the many reactions observed, a spectacular one corresponds to the Mn[⊕]-induced demethanation via an unprecedented 1,6-elimination mode across the triple bond, to generate metallacycloalkynes with Mn[⊕] in a high oxidation state. A mechanism which is in keeping with the labeling data and the chain-length effects is depicted in Scheme 1. Addition of either a CC (1→2) or a CH bond (1→3) to the π-complexed Mn[⊕] ion 1 generates intermediates which may further rearrange to the manganacycloheptyne cation 4; the latter may serve as direct precursor in the reductive elimination of methane to generate species 5.

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While metallacycles are often invoked or experimentally indicated to act as intermediates in gas-phase reactions of transition metal ions^[1b,d,f-1,5], in none of the previously reported cases CC multiple-bond containing metallacycles were involved. Apparently, the gas-phase chemistry of organometallic species containing Mn[⊕] is quite distinct.

The unusual behaviour of Mn[⊕] is also reflected in its overall reactivity^[6] as evidenced by a comparison of the metastable ion (MI) mass spectrum of [Fe(4-octyne)][⊕]

with that of [Mn(4-octyne)][⊕] (Fig. 1). While the [Fe(C₈H₁₄)][⊕] complex decomposes virtually via *one* reaction channel, i.e. loss of C₂H₄, the analogous [Mn(C₈H₁₄)][⊕] species gives rise to a multitude of processes. Moreover, the mechanism by which the major neutral fragment (i.e. C₂H₄) is eliminated, differs to some extent as shown by the study of ²H-labeled 4-octynes.

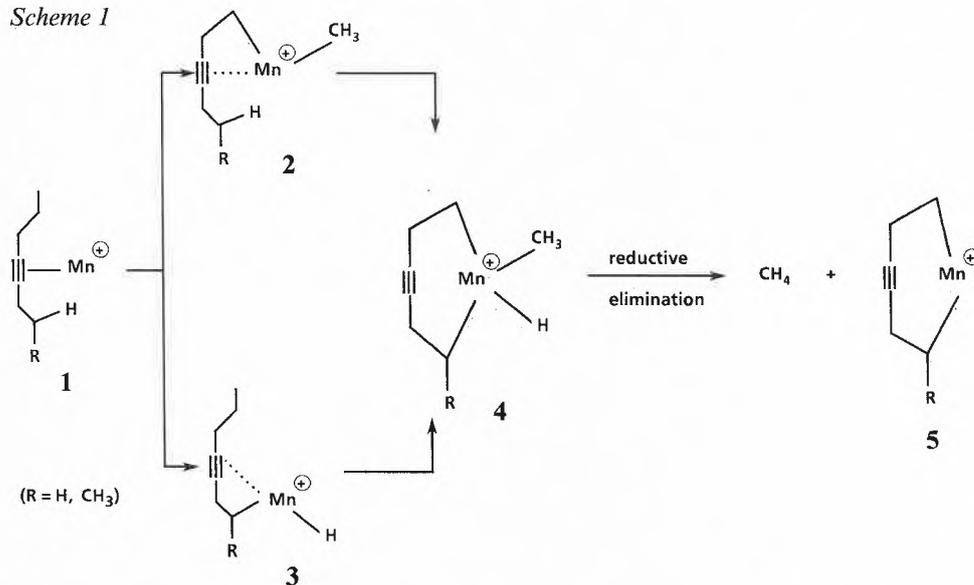
Detailed investigations of the [Fe(C₈H₁₄)][⊕] system^[11,7,9] support the mechanism depicted in Scheme 2 for C₂H₄ loss

from [Fe(4-octyne)][⊕]. The ethylene-hydrido complex **9** is, presumably, in competition generated via oxidative addition of the CC (6→7) or the CH bond (6→8) to the π-complexed Fe[⊕], followed by irreversible hydrogen migration (7→9) or cleavage of the propargylic CC bond (8→9). By probing the structure of the ethylene decomposition products, *Peake* and *Gross*^[9] were able to demonstrate that **12** and **13** are formed in an approximate ratio of 1.5:1. Another key feature of the overall reaction sequence 6→9 is that the β-hydrogen transfer (which involves specifically the methyl group) is neither reversible nor associated with a primary kinetic isotope effect; dissociation of **9** to generate C₂H₄ and [Fe(C₆H₁₀)][⊕] has, however, an isotope effect of *k_H/k_D* = 1.1 per deuterium atom in the ethylene eliminated^[7]. Hydrogen exchange processes do not precede the loss of C₂H₄.

The analysis of the labeling results (Table 1) suggests that a major part of the ethylene loss, induced by both Fe[⊕] and Mn[⊕], follows the same mechanism (Scheme 2). However, there is no doubt that the Mn[⊕]-induced process is to some extent distinct. This is clearly evidenced by the data of the isotopomers **14a**, **14b**, and **14d**, which demonstrate that prior to Mn[⊕]-induced ethylene loss partial exchange of the hydrogen atoms at C(2) and C(3) – but *not* C(1) – occur, which are not operative in the Fe[⊕] complex. A mechanistic variant which is in keeping with the hydrogen exchange processes is depicted in Scheme 3. Here, the central intermediate corresponds to the carbene complex **18** which via the reaction **18**→**19** brings about hydrogen exchange of C(2)/C(3). For the generation of **18** itself several routes are conceivable; those proceeding via **16** and **17** have precedences in the gas-phase chemistry involving other transition metal ions^[11]. Note, that **17** is also suggested^[4] to be involved in the Mn[⊕]-induced demethanation of alkynes (see species **3** in Scheme 1); ion **16** serves as branching point for both the hydrogen exchange reaction (via **18**⇌**19**) and the actual ethylene loss pathway analogous to 7→9 with Mn[⊕] substituted for Fe[⊕].

A further distinction between the Fe[⊕]- and Mn[⊕]-induced processes concerns the loss of C₃H₆ (presumably propene); this reaction is of minor importance for the [Fe(C₈H₁₄)][⊕] complex (< 3% rel. inten-

Scheme 1



Scheme 2

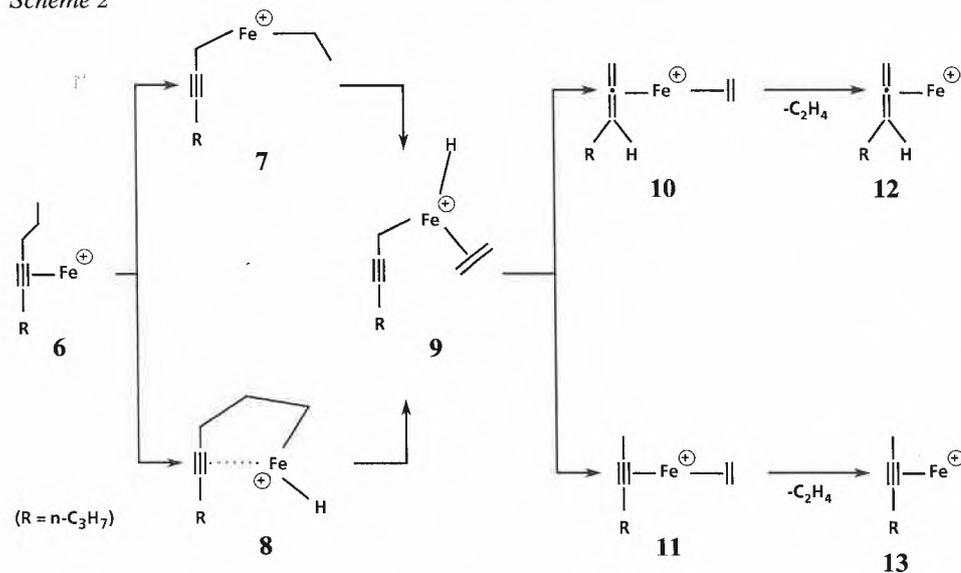


Table 1. Unimolecular ethylene loss from labeled [Mn(4-octyne)][⊕] complexes^{a)}.

Neutral Lost	4-Octyne Precursors				
C ₂ H _{4-x} D _x	CH ₃ (CH ₂) ₂ C≡CC ₃ H ₇ 14	CH ₃ CH ₂ CD ₂ C≡CC ₃ H ₇ 14a	CH ₃ CD ₂ CH ₂ C≡CC ₃ H ₇ 14b	CD ₃ (CH ₂) ₂ C≡CC ₃ H ₇ 14c	CD ₃ CD ₂ CH ₂ C≡CC ₃ H ₇ 14d
C ₂ H ₄	100 (100)	81.6 (100)	44.7 (54.5)	55.2 (54.8)	45.1 (59.1)
C ₂ H ₃ D		12.8	10.6		2.1
C ₂ H ₂ D ₂		5.6	44.7 (45.5)	44.8 (45.2)	1.8
C ₂ H ₁ D ₃					8.5
C ₂ D ₄					42.5 (40.9)

^{a)}Data are given in %, ΣC₂H_{4-x}D_x = 100%. Errors are ± 3% of reported data. For comparison the data of the analogous [Fe(4-octyne)][⊕] complexes are given in parentheses.

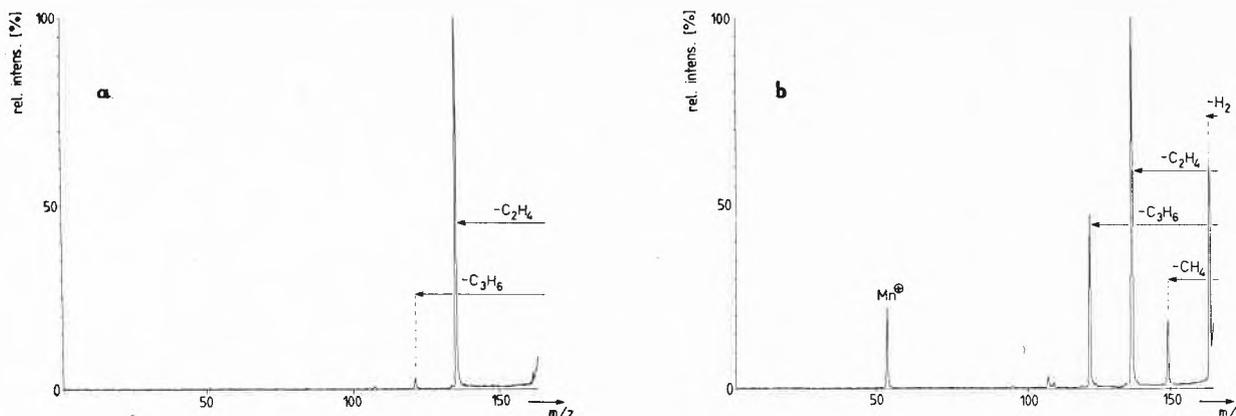


Fig. 1. Metastable ion (MI) mass spectra of (a) $[Fe(4\text{-octyne})]^{\oplus}$, generated from $Fe(CO)_5$ and 4-octyne according to Ref. ^[11,7], and (b) $[Mn(4\text{-octyne})]^{\oplus}$, generated from $Mn_2(CO)_{10}$ and 4-octyne. Briefly, in a typical experiment the metal carbonyl and the hydrocarbon (in a ratio 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) ^[8]. Experimental conditions were as follows: ionization energy 100 eV; emission current 0.5 mA; repeller voltage 0 V; acceleration voltage 8 kV; mass resolution 2000–5000 (10% valley definition); ion source pressure ca. 10^{-5} mbar; ion source block temperature 200°C. The metal-hydrocarbon complexes were formed by reaction of $M(CO)_x^{\oplus}$ ions and the appropriate hydrocarbon via displacement of the CO ligands. 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 spectra shown in Fig. 1 and the data reported in Table 1 correspond to the average of 10–100 spectra which were accumulated using the VG 11/250 data system.

sity) but amounts to 45% in the MI spectrum of $[Mn(C_8H_{14})]^{\oplus}$ (see Fig. 1). Although the interesting labeling results reported in Table 2 for the $[Mn(4\text{-octyne})]^{\oplus}$ isotopomers are very tempting to speculate on the mechanism(s) of this reaction, we refrain from doing so. Apparently, substantial rearrangements, presumably involving migration of the CC triple bond, must precede the loss of propene. This is, for example, indicated by the Mn[⊕]-induced loss of C₃H₅D from

CD₃CD₂CH₂≡CC₃H₇ (**14d**). In analogy to the ethylene elimination, the positions C(2)/C(3) seem to be involved in the hydrogen exchange reaction, while the methyl groups of 4-octyne are quantitatively transferred to the neutral propene formed. We note the inverse kinetic isotope effect ($k_H/k_D = 0.83$) favouring the loss of C₃H₅D₃ over C₃H₆. Again, a straightforward, unambiguous explanation is not at hand yet.

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Scheme 3

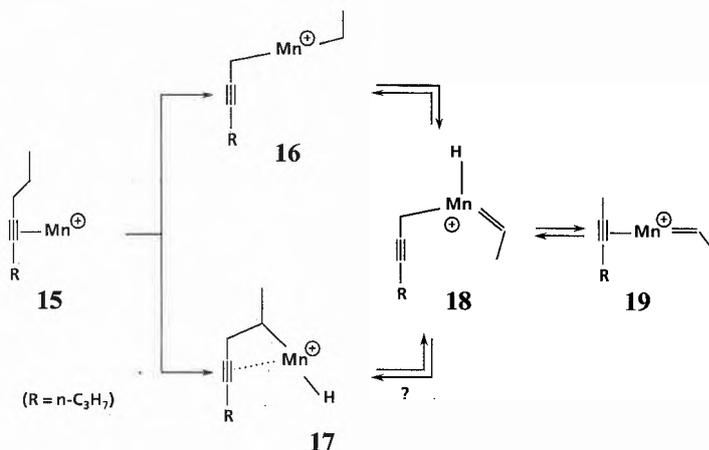


Table 2. Unimolecular propene loss from labeled $[Mn(4\text{-octyne})]^{\oplus}$ complexes^{a)}.

Neutral Lost	4-Octyne Precursors				
C ₃ H _{6-x} D _x	14	14a	14b	14c	14d
C ₃ H ₆	100	33.9	30.2	45.3	25.0
C ₃ H ₅ D		24.0	66.8		14.5
C ₃ H ₄ D ₂		42.1	3.0		2.9
C ₃ H ₃ D ₃				54.7	4.7
C ₃ H ₂ D ₄					52.9
C ₃ H ₁ D ₅					

^{a)}Data are given in %, $\Sigma C_3H_{6-x}D_x = 100\%$. Errors are $\pm 3\%$ of reported data.

- Selected references: a) J. Müller, *Angew. Chem. Int. Ed. Engl.* 11 (1972) 653; b) J. L. Beauchamp, A. E. Stevens, R. R. Corderman, *Pure Appl. Chem.* 51 (1979) 967; c) I. K. Gregor, M. Guilhaus, *Mass Spectrom. Rev.* 3 (1986) 39; d) J. Allison, *Prog. Inorg. Chem.* 34 (1984) 627; e) P. B. Armentrout, in P. Ausloos, S. G. Lias (Ed.): *Structure/Reactivity and Thermochemistry of Ions*, NATO ASI Series, Reidel, Dordrecht 193 (1987) 97; f) D. P. Ridge, *ibid.* 193 (1987) 165; g) J. A. Simoes, J. L. Beauchamp, *Chem. Rev.*, in press; h) J. L. Beauchamp, «High Energy Processes in Organometallic Chemistry», *ACS Symp. Ser.*, in press; i) more than 100 references concerning the reactions of bare transition metal ions with organic substrates, together with a detailed analysis of the reactions of gaseous octyne isomers with Fe[⊕], may be found in: C. Schulze, H. Schwarz, D. A. Peake, M. L. Gross, *J. Am. Chem. Soc.* 109 (1987) 2368.
- a) R. B. Freas, D. P. Ridge, *J. Am. Chem. Soc.* 102 (1980) 7129; b) P. B. Armentrout, L. F. Halle, J. L. Beauchamp, *ibid.* 103 (1981) 6501; c) L. F. Halle, P. B. Armentrout, J. L. Beauchamp, *Organometallics* 1 (1982) 963; d) S. J. Babinec, J. Allison, *J. Am. Chem. Soc.* 106 (1984) 7718; e) H. Mestdagh, N. Morin, C. Rolando, *Tetrahedron Lett.* 27 (1986) 33; f) L. Tonkyn, J. C. Weisshaar, *J. Phys. Chem.* 90 (1986) 2305; g) J. L. Elkind, P. B. Armentrout, *J. Chem. Phys.* 84 (1986) 4862; h) J. L. Elkind, P. B. Armentrout, *Inorg. Chem.* 25 (1986) 1080; i) D. A. Peake, M. L. Gross, *J. Am. Chem. Soc.* 109 (1987) 600.
- J.-Y. Saillard, R. Hoffmann, *J. Am. Chem. Soc.* 106 (1984) 2006.
- C. Schulze, H. Schwarz, *J. Am. Chem. Soc.*, in press.
- a) R. Houriet, L. F. Halle, J. L. Beauchamp, *Organometallics* 2 (1983) 1818; b) D. B. Jacobson, B. S. Freiser, *ibid.* 3 (1984) 513; c) C. B. Lebrilla, C. Schulze, H. Schwarz, *J. Am. Chem. Soc.* 109 (1987) 98; d) C. B. Lebrilla, T. Drewello, H. Schwarz, *ibid.* 109 (1987), in press.
- The term «reactivity» is used throughout in the sense suggested by Allison ^[2d], i. e. «the number of different products formed».
- C. Schulze, T. Weiske, H. Schwarz, *Chimia* 40 (1986) 362.
- For a description of the machine see: a) T. Weiske, Ph. D. Thesis, TU Berlin (1985); b) J. K. Terlouw, T. Weiske, H. Schwarz, J. L. Holmes, *Org. Mass Spectrom.* 21 (1986) 665.
- a) D. A. Peake, M. L. Gross, *Anal. Chem.* 57 (1985) 115; b) D. A. Peake, M. L. Gross, *Organometallics* 5 (1986) 1236.