Covalent Assistance in Metal-Mediated [4 + 2] Cycloadditions of Butadiene and Acetylene in the Gas Phase

Katrin Schroeter, Christoph A. Schalley, Ralf Wesendrup, Detlef Schröder, and Helmut Schwarz*

Institut für Organische Chemie, Technische Universität Berlin, Strasse des 17. Juni 135, D-10623 Berlin, Germany

Received November 4, 1996[⊗]

The reactions of butadiene and acetylene, both complexed to atomic metal cations M^+ (M = Cr, Mn, Fe, Co, Cu), have been investigated using ion-beam four-sector and Fourier transform ion cyclotron resonance mass spectrometry. For all metal ions studied, with the exception of Cu^+, the reaction proceeds as a formal [4 + 2] cycloaddition involving 1,4-cyclohexadiene/M^+ as an intermediate. This subsequently eliminates molecular hydrogen to generate the corresponding benzene/M^+ complexes or bare M^+ and C_6H_6. The Fe^+-mediated reaction has been analyzed in detail, and isotopic labeling reveals that the cyclization step is rate-determining and that dehydrogenation of the six-membered ring occurs specifically from the C(1)/C(4)-positions of the butadiene building block. In conjunction with literature thermochemistry, qualitative potential-energy surfaces for the [4 + 2] cycloaddition are derived for M = Cr, Mn, Fe, and Co. The reactions are very efficient for Fe^+ and Co^+, while Cr^+ and Mn^+ are less capable of inducing C−C bond formation. Finally, Cu^+ with its closed-shell s^0d^{10} electronic ground state does not mediate the [4 + 2] cycloaddition at all. These differences are explained in terms of a model which invokes the active participation of the transition metal's d orbitals (covalent assistance), rather than mere Lewis-acid catalysis, which is known to catalyze many Diels−Alder reactions in the condensed phase.

Introduction

Notwithstanding the fact that Diels and Alder[1] discovered the [4 + 2] cycloaddition as early as 1928, this textbook reaction of organic chemistry is still of remarkable interest in current research[2] and the influence of transition metals on this process has been examined at great length.[3,4] Frequently, transition-metal catalysis of Diels-Alder type reactions can be ascribed to the Lewis acidity of the metal center:[5] the metal coordinates to a polar group of the reactant(s) and influences the relative energies of frontier orbitals, which results in enhanced reaction rates. In addition, the metal center can serve as a template by complexing the diene and the dienophile via π bonds, thus providing favorable orientations of the reactants. Furthermore, transition-metal ions may also mediate formal [4 + 2] cycloadditions in a stepwise manner involving metallacyclic intermediates.[3]

While it is difficult to distinguish between these (and other) mechanistic alternatives in the condensed phase, more detailed insight can be expected from the investigation of metal-mediated cyclization reactions in the gas phase because disturbing effects originating from solvation, aggregation, or counterions can be excluded under high-vacuum conditions. In fact, mass spectrometry has proved useful for the investigation of reaction mechanisms of many metal-mediated processes within the last two decades.[6]

Recently, Bakhtiar et al.[7] investigated the Fe^+-mediated [4 + 2] cycloaddition of 1,3-butadiene and acetylene in the gas phase, which is accompanied by rapid dehydrogenation to yield benzene/Fe^+. The present study is intended to give a more profound insight into the energetics and the mechanisms of these cyclization and dehydrogenation reactions.[8] In particular, a comparison of different transition metals will answer the question if, in addition to their Lewis acidity, the metals' electronic structures influence their catalytic activity in Diels−Alder reactions. To this end, two different mass spectrometric methods have been applied in order to study the M^+-mediated [4 + 2] cycloaddition of acetylene and butadiene: the unimolecular fragmentation reac-

---

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1997.

[1] Diels, O.; Alder, K. *Justus Liebigs Ann. Chem.* **1928**, *460*, 98.

[2] Fürstner, A. *Nachr. Chem., Tech. Lab.* **1996**, *44*, 150.

[3] Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49.

[4] For a striking example of metal-controlled regiocomplementarity in Diels−Alder reactions, see: Wender, P. A.; Jenkins, T. E.; Suzuki, S. *J. Am. Chem. Soc.* **1995**, *117*, 1843.

[5] (a) Yates, P.; Eaton, P. *J. Am. Chem. Soc.* **1960**, *82*, 4436. (b) Inukai, T.; Kasai, M. *J. Org. Chem.* **1965**, *30*, 3567. (c) Inukai, T.; Kojima, T. *J. Org. Chem.* **1967**, *32*, 872. (d) Fringuelli, F.; Pizzo, F.; Taticchi, A.; Wenkert, E. *J. Org. Chem.* **1983**, *48*, 2802. (e) Brown, F. K.; Houk, K. N.; Burnell, D. J.; Valenta, Z. *J. Org. Chem.* **1987**, *52*, 3050. (f) Otto, S.; Bertonicin, F.; Engberts, J. B. F. N. *J. Am. Chem. Soc.* **1996**, *118*, 7702.

[6] (a) Armentrout, P. B. *Annu. Rev. Phys. Chem.* **1990**, *41*, 313. (b) Eller, K.; Schwarz, H. *Chem. Rev.* **1991**, *91*, 1121. (c) Weisshaar, J. C. *Acc. Chem. Res.* **1993**, *26*, 213. (d) Eller, K. *Coord. Chem. Rev.* **1993**, *126*, 93. (e) Freiser, B. S. *Acc. Chem. Res.* **1994**, *27*, 353.

[7] Bakhtiar, R.; Drader, J. J.; Jacobson, D. B. *J. Am. Chem. Soc.* **1992**, *114*, 8304.

[8] For previous reports of M^+-mediated cyclizations in the gas phase, see: (a) Hettich, R. L.; Freiser, B. S. *Organometallics* **1989**, *8*, 2447. (b) Buckner, S. W.; MacMahon, T. J.; Byrd, G. D.; Freiser, B. S. *Inorg. Chem.* **1989**, *28*, 3511. (c) Schröder, D.; Sülzle, D.; Hrušák, J.; Böhme, D. K.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1991**, *110*, 145. (d) Heinemann, C.; Cornehl, H. H.; Schwarz, H. *J. Organomet. Chem.* **1995**, *501*, 201. (e) Bakhtiar, R.; Drader, J. J.; Arneson, R. K.; Jacobson, D. B. *Rapid Commun. Mass Spectrom.* **1996**, *10*, 1405.

S0276-7333(96)00937-5 CCC: $14.00

tions of butadiene/acetylene/M^+ complexes have been monitored by ion-beam mass spectrometry, and the bimolecular ion/molecule reactions of butadiene/M^+ with acetylene have been examined with a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer. With few exceptions,[9] it has been shown earlier that these two techniques are complementary and lead to consistent results for most chemical systems.[10]

Experimental Section

The experiments were performed with a modified VG ZAB/HF/AMD 604 four-sector mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sectors), which has been described elsewhere.[11] Organometallic cations were generated by chemical ionization (CI) of appropriate precursor mixtures by electrons of 50−100 eV kinetic energy; note that the generation of mixed-metal complexes of the type $M(L)(L')^+$ requires a careful optimization of the individual pressures of the components, because otherwise the homoligated complexes $M(L)_2^+$ or $M(L')_2^+$ prevail. After acceleration to 8 keV kinetic energy, the ions of interest were mass-selected using B(1)E(1) at a resolution of $m/\Delta m \geq 4000$, which is sufficient to resolve most isobaric ions. Formation of isobaric impurities is hardly avoidable in the generation of M^+ complexes from the corresponding organic substrates and volatile metal carbonyls, i.e. $Cr(CO)_6$, $Mn_2(CO)_{10}$, $Fe(CO)_5$, and $Co(NO)(CO)_3$; for example, the butadiene complex $^{56}Fe(C_4H_6)^+$ is isobaric with $^{54}Fe(CO)_2^+$. In some cases the intensities of the ions of interest were too low to completely resolve overlapping isobaric peaks, and small contributions (<5%) of interfering carbonyl complexes were unavoidable. These interferences are monitored by loss of CO ($\Delta m = 28$) in the MS/MS experiments. They disappear upon enhancing the resolution and do not display mass shifts upon deuterium labeling. For the sake of clarity, contributions of these CO losses are not included in the tables given below. Unimolecular dissociations of metastable ions (MI) in the field-free region preceding B(2) were monitored by scanning this sector; similarly, collisional activation (CA) was brought about by using helium as a target gas (80% transmission, T) in the field-free region preceding B(2). The resulting fragment ions were monitored by scanning B(2). For a comparison to MI/CA experiments (see below), some CA experiments were also performed by using B(1)E(1)B(2) to select the parent ion. Here, fragmentations induced by collisional activation in the field-free region between B(2) and E(2) were monitored by means of E(2). MS/MS/MS experiments[12] were performed by selecting the organometallic ions of interest by use of B(1) only. The fragment ions resulting from unimolecular decompositions in the field-free region preceding E(1) were selected using E(1)B(2) in order to avoid the appearance of artifacts[13] and subsequently collided with helium (He, 80% T). The CA spectra were recorded by scanning E(2); these experiments will be referred to as MI/CA spectra. All spectra were accumulated and on-line-processed with the AMD/Intectra data system; 5−30 scans were averaged to improve the signal-to-noise ratio. For a variation of the ionization conditions, the ion-source pressure was changed, as measured indirectly by determining the pressure in the ion source housing.

The ICR experiments were performed with a Spectrospin CMS 47X FT-ICR mass spectrometer equipped with an external ion source and a superconducting magnet (Oxford Instruments, 7.05 T).[14] In brief, M^+ ions were generated via laser desorption/laser ionization by focusing the beam of a Nd:YAG laser (1064 nm) onto a pure metal target.[15] The cations were extracted from the ion source and transferred to the analyzer cell by a system of electric potentials and lenses. The isolation of the most abundant metal isotope and all subsequent isolation steps were performed by using FERETS,[16] a computer-controlled ion-ejection protocol which combines single-frequency ion-ejection pulses with frequency sweeps to optimize ion isolation. Subsequently, the ions were thermalized by collisions with pulsed-in argon gas[17] and carefully reisolated to avoid off-resonance excitation.[18] Thermalization was assumed to be complete if no further changes in reactivity occurred upon increasing the number of collisions with argon.[19] Acetylene and 1,4-cyclohexadiene were admitted to the FT-ICR cell via a leak valve at a constant pressure of ca. 10^{-8} mbar. Butadiene/M^+ complexes were generated by the following routes:[6] (i) reaction of the bare metal ions with pulsed-in propene, affording a mixture of C_2H_4/M^+ and C_3H_6/M^+, which was then converted to C_4H_6/M^+ by pulsing in butadiene ($M = Fe$, Co), (ii) M^+-induced dehydrochlorination of chlorobut-2-ene ($M = Cr$, Mn), and (iii) association of M^+ with pulsed-in cyclohexane[20] followed by replacement of the cycloalkane ligand with pulsed-in butadiene ($M = Cu$). All functions of the instrument were controlled by a Bruker Aspect 3000 minicomputer.

Chemicals for the experiments were used as obtained commercially; butadiene-1,1,4,4-d_4 (98 atom % D) was purchased from Cambridge Isotope. Acetylene-d_2 was prepared from calcium carbide and D_2O and introduced into the ion source without further purification.

For the construction of qualitative potential-energy surfaces (PESs) the relative energies of the complexes were derived

---

[9] Schalley, C. A.; Wesendrup, R.; Schröder, D.; Weiske, T.; Schwarz, H. *J. Am. Chem. Soc.* **1995**, *117*, 7711 and references cited therein.

[10] (a) Eller, K.; Zummack, W.; Schwarz, H.; Roth, L. M.; Freiser, B. S. *J. Am. Chem. Soc.* **1991**, *113*, 833. (b) Schröder, D.; Eller, K.; Prüsse, T.; Schwarz, H. *Organometallics* **1991**, *10*, 2052. (c) Eller, K.; Karrass, S.; Schwarz, H. *Organometallics* **1992**, *11*, 1637. (d) Schröder, D. Ph.D. Thesis, Technische Universität Berlin, D83, 1992.

[11] (a) Srinivas, R.; Sülzle, D.; Weiske, T.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1991**, *107*, 368. (b) Srinivas, R.; Sülzle, D.; Koch, W.; dePuy, C. H.; Schwarz, H. *J. Am. Chem. Soc.* **1991**, *113*, 5970. (c) Schalley, C. A.; Schröder, D.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1996**, *153*, 173.

[12] Busch, K. L.; Glish, G. L.; McLuckey, S. A. *Mass Spectrometry/Mass Spectrometry: Techniques and Applications of Tandem Mass Spectrometry*; VCH: Weinheim, Germany, 1988.

[13] Schröder, D.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1995**, *146/147*, 183.

[14] (a) Eller, K.; Schwarz, H. *Int. J. Mass Spectrom. Ion Processes* **1989**, *93*, 243. (b) Eller, K.; Zummack, W.; Schwarz, H. *J. Am. Chem. Soc.* **1990**, *112*, 621.

[15] (a) Freiser, B. S. *Talanta* **1985**, *32*, 697. (b) Freiser, B. S. *Anal. Chim. Acta* **1985**, *178*, 137.

[16] Forbes, R. A.; Laukien, F. H.; Wronka, J. *Int. J. Mass Spectrom. Ion Processes* **1988**, *83*, 23.

[17] Carlin, T. J.; Freiser, B. S. *Anal. Chem.* **1983**, *55*, 574.

[18] Heck, A. J. R.; de Koning, L. J.; Pinske, F. A.; Nibbering, N. M. M. *Rapid Commun. Mass Spectrom.* **1991**, *5*, 406.

[19] (a) Schröder, D.; Fiedler, A.; Ryan, M. F.; Schwarz, H. *J. Phys. Chem.* **1994**, *98*, 68. Also, see: (b) Clemmer, D. E.; Chen, Y.-M.; Khan, F. A.; Armentrout, P. B. *J. Phys. Chem.* **1994**, *98*, 6522. (c) Baranov, V. I.; Javahery, G.; Hopkinson, A. C.; Böhme, D. K. *J. Am. Chem. Soc.* **1995**, *117*, 12801. (d) Schröder, D.; Schwarz, H.; Clemmer, D. E.; Chen, Y.; Armentrout, P. B.; Baranov, V. I.; Böhme, D. K. *Int. J. Mass Spectrom. Ion Processes*, in press.

[20] Dahrouch, A.; Mestdagh, H.; Rolando, C. *J. Chim. Phys. Phys.-Chim. Biol.* **1994**, *91*, 443.

[21] Meyer, F.; Khan, F. A.; Armentrout, P. B. *J. Am. Chem. Soc.* **1995**, *117*, 9740.

[22] Georgiadis, R.; Armentrout, P. B. *Int. J. Mass Spectrom. Ion. Processes* **1989**, *89*, 227.

[23] Dalleska, N. F.; Honma, K.; Sunderlin, L. S.; Armentrout, P. B. *J. Am. Chem. Soc.* **1994**, *116*, 3519.

[24] Sodupe, M.; Bauschlicher, C. W., Jr. *J. Phys. Chem.* **1991**, *95*, 8640.

[25] Sodupe, M.; Bauschlicher, C. W., Jr.; Langhoff, S. R.; Partridge, H. *J. Phys. Chem.* **1992**, *96*, 2118.

[26] Schröder, D.; Schwarz, H. *J. Organomet. Chem.* **1995**, *504*, 123.

[27] Schultz, R. H.; Armentrout, P. B., private communication.

[28] Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 3900.

[29] Haynes, C. L.; Fisher, E. R.; Armentrout, P. B. *J. Am. Chem. Soc.* **1996**, *118*, 3269.

[30] Goebel, S.; Haynes, L. C.; Khan, F. A.; Armentrout, P. B. *J. Am. Chem. Soc.* **1995**, *117*, 6994.

[31] Hertwig, R. H.; Koch, W.; Schröder, D.; Schwarz, H.; Hrušák, J.; Schwerdtfeger, P. *J. Phys. Chem.* **1996**, *100*, 12253.

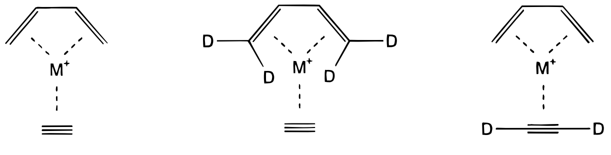
Table 1. Metal−Ligand Bond Dissociation Energies (BDEs) Used in This Study for the Construction of the Potential-Energy Surfaces

M^+	ligand	BDE (kcal/mol)	ref	M^+	ligand	BDE (kcal/mol)	ref
Cr^+	acetylene	29.4 ± 2.2	*a*	Fe^+	acetylene	38.0 ± 0.5	26
	butadiene	35.0 ± 2.9	*a*		butadiene	43.4 ± 1.0	26
	benzene	40.6 ± 2.3	21		benzene	49.6 ± 2.3	21
	ethene	30 ± 5	22		ethene	34.7 ± 1.4	27
	H_2O	30.9 ± 2.1	23		1,4-cyclohexadiene	60 ± 12	*a*
	1,4-cyclohexadiene	50 ± 16	*a*	Co^+	acetylene	43.0 ± 2	*a*
Mn^+	acetylene	19[b]	24		butadiene	52 ± 4	28
	butadiene	28.6 ± 1.4	*a*		benzene	61.1 ± 2.5	21
	benzene	31.8 ± 2.0	21		ethene	42.9 ± 1.6	29
	ethene	20[b]	25		carbon monoxide	41.5 ± 1.6	30
	H_2O	28.4 ± 1.4	23		H_2O	38.5 ± 1.4	23
	1,4-cyclohexadiene	36 ± 5	*a*		1,4-cyclohexadiene	73 ± 15	*a*
				Cu^+	benzene	52.1 ± 2.3	21
					ethene	47 ± 3	31
					1,4-cyclohexadiene	73 ± 25	*a*

[a] This work. [b] Calculated BDE.

from the enthalpies of formation[32] of the components and the corresponding bond-dissociation energies (BDEs).[33] As for most ligands no information on multiple bonding to M^+ is available, the BDEs of $M(L)(L')^+$ complexes (L, L′ = ligands) are approximated by assuming additivity,[34] despite the fact that additivity of BDEs in bis-ligand complexes does not always hold true.[35] Some unknown M^+−ligand BDEs were estimated using Cooks' kinetic method.[36] To this end, bis-ligated complexes of the type $M(L)(L')^+$ were generated by chemical ionization, and the fragments $M(L)^+$ and $M(L')^+$ formed upon unimolecular decomposition were monitored. The ratios $M(L)^+/M(L')^+$ were converted to ΔBDEs by assuming an effective temperature of 473 K.[26] Within the context of this paper, the qualitative ordering of the BDEs is sufficient, and a detailed description of the results including a discussion of the experimental uncertainties will be published elsewhere.[37] Using the BDEs of H_2O−M^+ (M = Cr, Mn, Co), benzene−Cr^+, OC−Co^+, and C_2H_4−Co^+ as absolute references,[21,23,30] BDE(butadiene−Mn^+), BDE(butadiene−Cr^+), BDE(acetylene−Cr^+) and BDE(acetylene−Co^+) values were determined (Table 1). Note that our result of BDE(acetylene−Cr^+) = 29 kcal/mol obtained in this manner contradicts the much larger value of earlier ion-beam measurements (44 kcal/mol)[38] but is in reasonable agreement with a recent theoretical estimate (25 kcal/mol)[24] and plausibility considerations with regard to the other BDEs given in Table 1. Unfortunately, it was not possible to derive BDE(1,4-cyclohexadiene−M^+) using the same method for M = Cr−Co, because in these systems unimolecular dehydrogenation of the corresponding $M(L)(L')^+$ dominates and ligand losses hardly take place. To obtain a qualitative value, the inert metal Cu^+ was subjected to ligand exchange reactions in the FTICR which lead to a lower limit of BDE(1,4-cyclohexadiene−Cu^+) > BDE(benzene−Cu^+) = 52 kcal/mol.[21] An upper limit could not be determined because appropriate BDEs for Cu^+ ligand complexes are not yet available. As a rough estimate, we use 2[BDE(ethene−M^+)] as the upper limit. This assumption is justified by (i) the same number of complexed π-bonds in $Cu(C_6H_8)^+$ and $Cu(C_2H_4)_2^+$ and (ii) the experimental observation that $Cu(C_2H_4)_2^+$ does only undergo sequential exchange of the olefin ligands when reacted with 1,4-cyclohexadiene, while displacement of both ethene ligands in a single event does not occur. Thus, we regard 2[BDE(ethene−M^+)] as an upper limit and BDE(benzene−M^+) as an lower limit for BDE(1,4-cyclohexadiene−M^+) and use the average of these figures throughout in the constructions of the qualitative PESs (see below).

Chart 1



1/M+ **1a/M+** **1b/M+**

Table 2. Mass Differences (Δ*m* in amu) Observed in the Unimolecular Decomposition (MI) and in the Collisional Activation (CA) Mass Spectra of Butadiene/Acetylene/Fe^+ and 1,4-Cyclohexadiene/Fe^+ [a]

		Δ*m*					
spectra	complex	2	4	26	54	55	M^+
MI[a]	**1**/Fe^+	>99		<1			
	1a/Fe^+		>99	<1			
	1b/Fe^+	>99					
	2/Fe^+	100					
CA[b]	**1**/Fe^+	100		11	2	1	3
	2/Fe^+	100				<1	<1

[a] Intensities are normalized to Σ =100. [b] Intensities are given relative to the base peak.

Results and Discussion

When a mixture of butadiene, acetylene, and $Fe(CO)_5$ is subjected to chemical ionization, considerable amounts of the mixed bis-ligand complex **1**/Fe^+ (Chart 1; M = Fe) are formed. Mass-selected **1**/Fe^+ reacts almost exclusively by unimolecular loss of molecular hydrogen (Table 2). This observation is in agreement with earlier experiments,[7] in which the dehydrogenation of **1**/Fe^+ was attributed to a formal [4 + 2] cycloaddition and subsequent dehydrogenation to yield benzene/Fe^+.

---

(32) (a) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. Gas Phase Ion and Neutral Thermochemistry. *J. Phys. Chem. Ref. Data, Suppl.* **1988**, *17*. (b) Lias, S. G.; Liebman, J. F.; Levin, R. D.; Kafafi, S. A. NIST Standard Reference Database, Positive Ion Energetics, Version 2.01; NIST, Gaithersburg, MD, January 1994.

(33) Freiser, B. S., Ed. *Organometallic Ion Chemistry*; Kluwer: Dordrecht, The Netherlands, 1995.

(34) Benson, S. W. *Thermodynamical Kinetics: Methods for the Estimation of Thermochemical Data and Rate Parameters*, 2nd ed.; Wiley: New York, 1976. For example: $\Delta H_f(\mathbf{1}/Fe^+) \cong \Delta H_f(Fe^+) + \Delta H_f$(acetylene) + ΔH_f(butadiene) − BDE(Fe^+−acetylene) − BDE(Fe^+−butadiene).

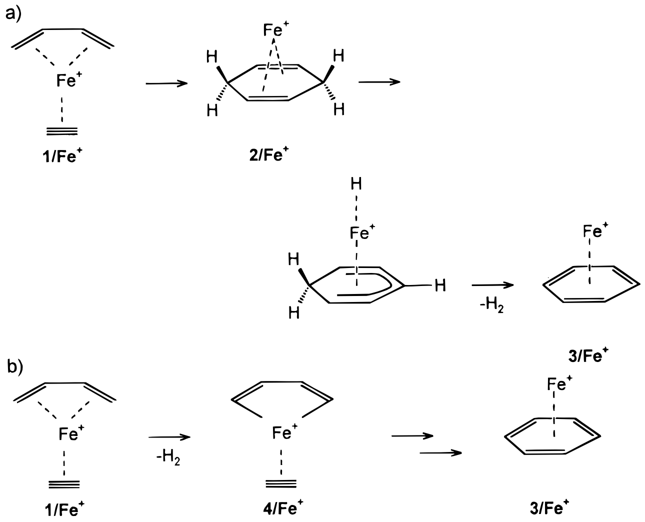
(35) (a) Rosi, M.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1990**, *92*, 1876. (b) Tjelta, B. L.; Armentrout, P. B. *J. Am. Chem. Soc.* **1995**, *117*, 5531. (c) Schultz, R. H.; Crellin, K.; Armentrout, P. B. *J. Am. Chem. Soc.* **1991**, *113*, 8590.

(36) Cooks, R. G.; Patrick, J. S.; Kotiqaho, T.; McLuckey, S. A. *Mass. Spectrom. Rev.* **1994**, *13*, 287.

(37) Schroeter, K.; Hornung, G.; Wesendrup, R.; Schröder, D.; Schwarz, H., unpublished results.

(38) Georgiadis, R.; Armentrout, P. B. *J. Phys. Chem. Soc.* **1988**, *92*, 7067.

Scheme 1



In general, two different mechanistic pathways are conceivable for the dehydrogenation of **1**/Fe$^+$. (i) In a formal [4 + 2] cycloaddition the 1,4-cyclohexadiene/Fe$^+$ complex **2**/Fe$^+$ is generated which subsequently eliminates H_2 to form the benzene/Fe$^+$ complex **3**/Fe$^+$ (Scheme 1a). The loss of molecular hydrogen from **2**/Fe$^+$ can easily be rationalized by a two-step process. In the first step, a hydrogen atom from one of the methylene groups is transferred to the metal, yielding a cationic cyclohexadienyl complex of iron hydride as an intermediate. Then, activation of a second C-H bond occurs, most likely coupled with direct formation of the dihydrogen complex **3**/Fe(H$_2$)$^+$ and subsequent loss of H_2, without involving an iron dihydrido species as intermediate.[39] (ii) Alternatively, a 1,4-hydrogen elimination from the butadiene moiety may occur as the first step, giving rise to the metallacyclic intermediate **4**/Fe$^+$ (Scheme 1b),[3] which may eventually undergo coupling of its ligands to yield **3**/Fe$^+$. However, this second pathway is unlikely to play a dominant role, because the energetic barrier associated with activation of the vinylic C−H bonds in butadiene by Fe$^+$ is significant and probably higher than BDE(C_4H_6−Fe$^+$) = 43.4 kcal/mol.[26] This assumption is based on the unimolecular decay of butadiene/Fe$^+$ complexes, where loss of the complete butadiene ligand is much more prevalent than loss of H_2.[40] Adding an acetylene ligand to butadiene/Fe$^+$ should not significantly reduce the barrier for C−H bond activation. Thus, in **1**/Fe$^+$ ligand detachment from the bis-ligand complex should also be favored over dehydrogenation of butadiene. Actually, loss of acetylene, which represents the more weakly bound ligand in **1**/Fe$^+$, is only observed to a negligible extent (<1%), in support of the first mechanistic scenario. The complete absence of acetylene loss in the MI/CA mass spectrum of [**1**/Fe$^+$ − H_2] suggests the exclusive formation of the genuine benzene complex **3**/Fe$^+$ (see below). In contrast, **4**/Fe$^+$, which represents the intermediary [Fe,C_6,H_6]$^+$ isomer in the second mechanism, is expected to lose C_2H_2 upon collisional activation. As this is not the case, we will not further pursue the mechanism depicted in Scheme 1b.

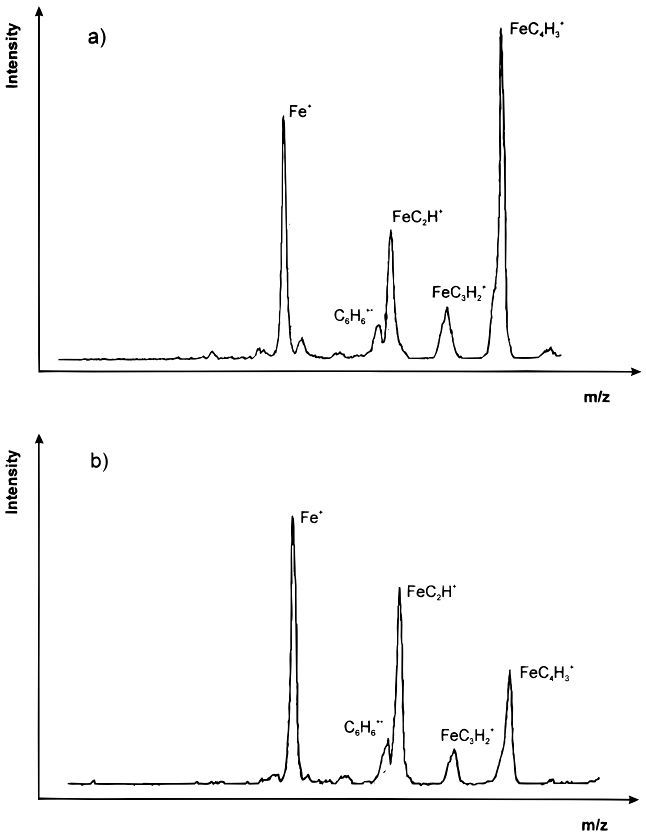


Figure 1. (a) MI/CA spectrum (helium, 80% transmission) of E(1)/B(2) mass-selected [**1**/Fe$^+$ − H_2] generated by unimolecular dehydrogenation of B(1) mass-selected **1**/Fe$^+$ in the field-free region preceding E(1). (b) CA spectrum (helium, 80% transmission) of B(1)/E(1)/B(2) mass-selected **3**/Fe$^+$.

In order to confirm the formation of **3**/Fe$^+$, the dehydrogenation product [**1**/Fe$^+$ − H_2] was characterized by collisional activation. A comparison of the corresponding MI/CA mass spectrum (Figure 1a) with the CA mass spectrum of genuine benzene/Fe$^+$ (Figure 1b) reveals a generally good agreement and supports the notion that **3**/Fe$^+$ is formed by dehydrogenation of **1**/Fe$^+$. Only the relative intensities of the fragment ions deviate. However, these differences can be attributed to different internal energy contents,[41] depending on the genesis of **3**/Fe$^+$. To further investigate the correlation of the internal energy of benzene/Fe$^+$ and its fragmentation pattern, CA mass spectra were recorded at different collision-gas and ion-source pressures (Table 3).

By application of higher collision-gas pressures the average number of collisions rises, thereby increasing the mean internal energy of the benzene/Fe$^+$ ions. The opposite effect is achieved by increasing the pressure in the ion source. Here, the enhanced number of collisions leads to a more effective cooling of the ions during their generation, thus lowering their average internal energy. Experimentally, enhancement of collision-gas pressure leads to a significant change of the spectra (rows 1−4 of Table 3) in that the intensity of Fe(C_4H_3)$^+$ decreases relative to the signal of Fe$^+$; the

---

(39) (a) Holthausen, M. C.; Fiedler, A.; Koch, W.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2282; *J. Phys. Chem.* **1996**, *100*, 6236. (b) Hendrickx, M.; Ceulemanns, M.; Vanquickenborne, L. *Chem. Phys. Lett.* **1996**, *257*, 8. (c) Holthausen, M. C.; Koch, W. *J. Am. Chem. Soc.* **1996**, *118*, 9932.

(40) Karrass, S. Ph.D. Thesis, Technische Universität Berlin, D83, 1994.

(41) Levsen, K.; Schwarz, H. *Mass Spectrom. Rev.* **1983**, *2*, 77.

Table 3. Dominant Fragments in the MI/CA Spectra of [acetylene/butadiene/Fe$^+$ − H$_2$] = [1/Fe$^+$ −H$_2$] and [1,4-cyclohexadiene/Fe$^+$ − H$_2$] = [2/Fe$^+$] in Comparison to the CA Spectrum of Benzene/Fe$^+$ (3/Fe$^+$) for Different Collision-Gas Pressures (p_{He}) and Ion-Source-Housing Pressures (p_s)[a]

					fragment					
	spectra	complex	$10^5 p_{He}$ (mbar)	p_S (mbar)	$FeC_4H_3^+$	$FeC_3H_4^+$	FeC_2H^+	$C_6H_6^{\bullet +}$	Fe^+	$FeC_4H_3^+/Fe^+$
1	CA	**3**/Fe$^+$	1.0	10^{-4}	100	15	39	7	74	1.35
2		**3**/Fe$^+$	1.4	10^{-4}	73	12	46	7	100	0.73
3		**3**/Fe$^+$	2.0	10^{-4}	55	11	41	7	100	0.55
4		**3**/Fe$^+$	3.0	10^{-4}	28	5	33	6	100	0.28
5		**3**/Fe$^+$	1.0	10^{-5}	75	25	76	13	100	0.75
6	MI/CA	[**1**/Fe$^+$ − H$_2$]	1.0	10^{-4}	43	13	74	11	100	0.43
7		[**2**/Fe$^+$ − H$_2$]	1.0	10^{-4}	38	11	49	13	100	0.38

[a] Intensities are given relative to the base peak.

ratio drops from ca. 1.3 to 0.3. Obviously, at higher internal energy, loss of the benzene ligand from **3**/Fe$^+$ is favored over the structural rearrangement leading to Fe(C$_4$H$_3$)$^+$. The same trend is observed upon changing the ion-source pressures (row 1 versus 5), where the intensity ratio Fe(C$_4$H$_3$)$^+$:Fe$^+$ increases with increasing pressure. Thus, to a good approximation this ratio correlates with the internal energy of **3**/Fe$^+$. Due to the experimental observation that the Fe(C$_4$H$_3$)$^+$:Fe$^+$ ratio is low (ca. 0.4) for the benzene/Fe$^+$ ion formed by cyclization and dehydrogenation of **1**/Fe$^+$, we conclude that **3**/Fe$^+$ formed via this route contains a relatively high amount of internal energy.

For comparison, we also investigated the unimolecular decomposition of the suggested intermediate, namely 1,4-cyclohexadiene/Fe$^+$ (**2**/Fe$^+$), which leads exclusively to the loss of molecular hydrogen (Table 2). The similarity of the MI/CA spectrum of the corresponding dehydrogenation product [**2**/Fe$^+$ − H$_2$] (Table 3, row 7) with that of [**1**/Fe$^+$ − H$_2$] indicates that **3**/Fe$^+$ is formed from both precursors, supporting the role of **2**/Fe$^+$ as a plausible intermediate in the course of the dehydrogenation of **1**/Fe$^+$. Further, in the MI/CA spectrum of the dehydrogenation product of authentic **2**/Fe$^+$, the ratio of Fe(C$_4$H$_3$)$^+$:Fe$^+$ amounts to ca. 0.4, which almost matches the value obtained in the MI/CA spectrum of the ions formed from **1**/Fe$^+$. This congruence implies that the **3**/Fe$^+$ ions generated by dehydrogenation of **1**/Fe$^+$ and **2**/Fe$^+$ contain comparable amounts of internal energy. The conclusion is further supported by the fact that the kinetic energy releases associated with dehydrogenation of **1**/Fe$^+$ and **2**/Fe$^+$ are identical within experimental error: they amount to ca. 50 meV for each precursor system.

These results lead to an interesting conclusion with respect to the activation barriers associated with the cyclization (**1**/Fe$^+$ → **2**/Fe$^+$) and the subsequent dehydrogenation step (**2**/Fe$^+$ → **3**/Fe$^+$). If cyclization was hindered by a significantly larger barrier than the dehydrogenation, the internal energy of resulting **3**/Fe$^+$ and also the kinetic energy release associated with the preceding loss of hydrogen would exceed those of the ions stemming from metastable 1,4-cyclohexadiene/Fe$^+$. The experimentally observed overall similarity of these features for both ions indicates that cyclization and dehydrogenation have comparable or even identical thresholds. In this respect, the unimolecular loss of acetylene from metastable **1**/Fe$^+$, though very low in intensity, adds further mechanistic implications. The exclusive elimination of C$_2$D$_2$ from metastable **1b**/Fe$^+$ (even upon collisional activation) demonstrates that the cyclization to the pseudo-symmetric intermediate **2b**/Fe$^+$ is irreversible within the time scale of the experiment. Otherwise, **2b**/Fe$^+$ would be expected to give rise to labeled *and* unlabeled acetylene. The same argument holds true for a comparison of the CA mass spectra of **1**/Fe$^+$ and genuine **2**/Fe$^+$ (Table 2): the spectrum of **1**/Fe$^+$ shows distinct signals due to losses of butadiene and acetylene ($\Delta m = 26$ and 54, respectively), while these fragmentations do not occur for **2**/Fe$^+$. Thus, we conclude that for the net reaction sequence **1**/Fe$^+$ → **3**/Fe$^+$, the formal [4 + 2] cyclization (**1**/Fe$^+$ → **2**/Fe$^+$) represents the rate-determining step (RDS), even though the activation barrier associated with the subsequent dehydrogenation is in a similar energy regime (see above).

It is not *a priori* evident whether the cyclization step **1**/Fe$^+$ → **2**/Fe$^+$ proceeds in a concerted or a stepwise manner.[42] Valuable hints on the actual mechanism of the metal-mediated reaction can sometimes be obtained by applying deuterium labeling. In general, stepwise bond formation involving long-lived intermediates is more likely to be associated with H/D equilibration[43] than is a concerted mechanism, because in the latter case dehydrogenation occurs rapidly after the rate-determining cyclization step. However, the nonoccurrence of H/D exchange processes by no means rules out a stepwise scenario via short-lived intermediates. As shown in Table 2, the deuterium-labeled complex **1a**/Fe$^+$ undergoes exclusively loss of D$_2$ ($\Delta m = 4$); expulsion of H$_2$ or HD is not observed at all. Further, the complex containing deuterium-labeled acetylene, **1b**/Fe$^+$, eliminates only H$_2$. Loss of HD is not observed, in contradiction to Bakhtiar et al.,[7] who reported a small amount of HD formation (3%) in the reaction of butadiene/Fe$^+$ with C$_2$D$_2$, perhaps due to imperfect deconvolution of the isotope patterns (^{12}C/^{13}C and H/D). Our results confirm, however, that dehydrogenation occurs specifically from the 1,4-positions of butadiene, which is fully in line with a concerted metal-mediated [4 + 2] cycloaddition reaction, as depicted in Scheme 2 (pathway a).

Let us briefly resume the experimental results with respect to the mechanistic discussion. (i) The cyclization is irreversible, i.e. rate determining, and HD equilibration is not observed. (ii) The activation barrier for dehydrogenation is located at a energy level close to that of the rate-determining TS associated with the cyclization step. These findings point to the presence of a

---

[42] For a very recent, superb discussion of this fundamental problem in the context of the retro-Diels−Alder femtosecond dynamics, see: Horn, B. A.; Herek, I. L.; Zewail, A. H. *J. Am. Chem. Soc.* **1996**, *118*, 8755 and references therein.

[43] (a) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7492. (b) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 72.

Scheme 2

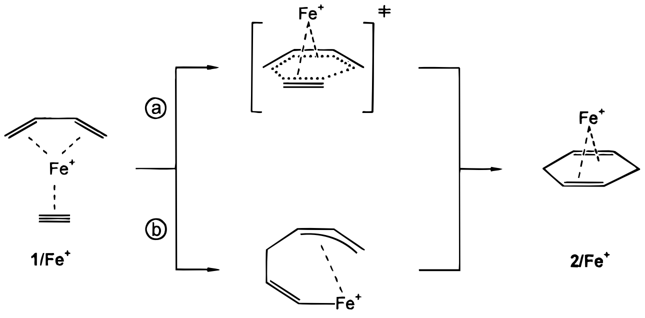


Table 4. Reactions of Butadiene/M$^+$ with Acetylene and of M$^+$ with Cyclohexadiene

M$^+$	k_{rel} (%)[a]	ionic product
Reaction of Butadiene/M$^+$ with Acetylene		
Cr$^+$	5	Cr$^+$
Mn$^+$	25	Mn$^+$
Fe$^+$	100	Fe$^+$ (12%); C_6H_6/Fe$^+$ (88%)
Co$^+$	45	C_6H_6/Co$^+$
Cu$^+$		only adduct formation[b]
Reaction of M$^+$ with Cyclohexadiene		
Cr$^+$	20	C_6H_6/Cr$^+$
Mn$^+$	20	C_6H_6/Mn$^+$
Fe$^+$	90	C_6H_6/Fe$^+$
Co$^+$	100	C_6H_6/Co$^+$
Cu$^+$	30	C_6H_6/Cu$^+$ [c]

[a] Rate of reaction k_{exp} relative to theoretical collision rate k_{ADO}.[45] [b] The adduct corresponds to intact **1**/Cu$^+$ rather than a cyclization product: (see text). No rate constant is given, because adduct formation involves collisional as well as radiative stabilization, and these components were not deconvoluted. [c] In addition, small amounts (ca. 5%) of the adduct C_6H_8/Cu$^+$ and $C_6H_7{}^+$ concomitant with neutral CuH are formed.

significant entropic bottleneck[44] for the reverse reaction **2**/Fe$^+$ → **1**/Fe$^+$, proposing that it proceeds via a tight transition structure, as expected for a concerted mechanism. In contrast, entropic constraints should not be severe for a stepwise bond formation such as the one suggested by Bakhtiar et al.[7] (Scheme 2, pathway b). However, in principle, a stepwise mechanism involving intermediates with lifetimes slower than the time scale of the experimental probe employed cannot be ruled out.

For comparison, the bimolecular reaction of thermalized butadiene/Fe$^+$ with acetylene has also been studied under FT-ICR conditions. In agreement with the results reported in ref 7, this process proceeds at collision rate[45] and yields benzene/Fe$^+$ and Fe$^+$ as products (Table 4). Thus, the energy requirements of the associated transition structures (TSs) are below the entrance channel of the reactants (C_4H_6)Fe$^+$ + C_2H_2. From a combination of these results with literature data, a qualitative potential-energy surface can be derived (Figure 2a). As discussed above, the barrier for dehydrogenation must have a height similar to that of the cyclization step; however, the latter represents the RDS due to entropic restrictions.

In a more general context, probing the actual role of the metal ion in [4 + 2] cycloadditions deserves particular attention. On the one hand, there is ample evidence that the Lewis acidity of M$^+$ helps to promote the cyclization.[5] This is achieved by narrowing the HOMO/LUMO energy gap of the relevant orbitals involved in the [4 + 2] cycloaddition. On the other hand, it is conceivable that specific electronic properties of the transition metals may determine the reactivity. Therefore, it is necessary to examine these effects by using other metal cations in [4 + 2] cycloaddition reactions. As representatives we have chosen the first-row transition-metal cations Cr$^+$, Mn$^+$, Fe$^+$, Co$^+$, and Cu$^+$, which classify three different types of metal ions:[6,46] (i) Fe$^+$ and Co$^+$ belong to a class of metal ions which are highly reactive in C−H and C−C bond activation of various hydrocarbons, due to the facile formation of insertion intermediates via oxidative addition.[39] (ii) In contrast, Cr$^+$ and Mn$^+$ are much less reactive toward hydrocarbons, which can be attributed to their spherical $4s^03d^5$ and $4s^13d^5$ ground-state configurations, respectively.[47] (iii) Finally, in the ground state of Cu$^+$ ($4s^03d^{10}$) the d shell is completely filled, and virtually no bond activations of saturated hydrocarbons have been observed for this metal cation under thermal conditions;[20,48] at elevated energies hydride and alkanide anion transfers from alkanes to Cu$^+$ prevail to yield neutral CuR (R = H, alkyl) concomitant with formation of carbocations.[49]

Similar to the **1**/Fe$^+$ complex, **1**/Co$^+$ undergoes unimolecular dehydrogenation and only loss of D_2 is observed for **1a**/Co$^+$ (Table 5). Thus, dehydrogenation of **1**/Co$^+$ can be explained by the same mechanism as proposed in Scheme 1a. Losses of acetylene or butadiene are not observed for metastable **1**/Co$^+$, which can qualitatively be attributed to the higher BDEs of Co$^+$ to organic ligands (Table 1). In the FT-ICR experiment (Table 4), the ion/molecule reaction of butadiene/Co$^+$ and acetylene takes place at 45% of collision rate. This reduced efficiency, as compared to Fe$^+$, implies that either the barrier of the RDS is closer to the energy level of the entrance channel of the reactants (C_4H_6)Co$^+$ + C_2H_2 or more severe entropic constraints pertain (Figure 2b). In analogy to Fe$^+$, the RDS is suggested to correspond to the cyclization step (**1**/Co$^+$ → **2**/Co$^+$), because Co$^+$-mediated dehydrogenation of 1,4-cyclohexadiene proceeds at collision rate.

Loss of H_2 is also the most prominent peak in the MI mass spectrum of **1**/Mn$^+$, which leads to the assumption that **1**/Mn$^+$ reacts to give **3**/Mn$^+$ as suggested in Scheme 1a for the Fe$^+$ system. However, loss of acetylene and particularly generation of Mn$^+$ compete efficiently with the elimination of molecular hydrogen (Table 5). Formation of Mn$^+$ is accomplished either by evaporation of the C_6H_8 ligand from **2**/Mn$^+$ or the combined expulsion of H_2 and benzene via **3**/Mn$^+$; consecutive losses of butadiene and acetylene from **1**/Mn$^+$ are very unlikely, because liberation of butadiene (Δm = 54) is not observed in the MI mass spectrum. The ion/molecule reaction of butadiene/Mn$^+$ with acetylene to produce bare Mn$^+$ proceeds at only 25% of the collision rate, suggesting that the RDS is much closer to the entrance channel compared to the reactions of Fe$^+$ and Co$^+$.

---

(44) Lorquet, J. C. *Mass Spectrom. Rev.* **1994**, *13*, 233.

(45) Su, T.; Bowers, M. T. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *12*, 347.

(46) Seemeyer, K.; Schröder, D.; Kempf, M.; Lettau, O.; Müller, J.; Schwarz, H. *Organometallics* **1995**, *14*, 4465.

(47) (a) Schilling, J. B.; Beauchamp, J. L. *Organometallics* **1988**, *7*, 194. (b) Georgiadis, R.; Armentrout, P. B. *Int. J. Mass Spectrom. Ion Processes* **1989**, *91*, 123. (c) Fisher, E. R.; Armentrout, P. B. *J. Am. Chem. Soc.* **1992**, *114*, 2039, 2049.

(48) For the reactions of Cu$^+$ with unsaturated hydrocarbons, see: Macmillan, D. K.; Gross, M. L.; Schulze, C.; Schwarz, H. *Organometallics* **1992**, *11*, 2079.

(49) (a) Georgiadis, R.; Fisher, E. R. Armentrout, P. B. *J. Am. Chem. Soc.* **1989**, *111*, 4251. (b) Fisher, E. R.; Armentrout, P. B. *J. Phys. Chem.* **1990**, *94*, 1674.

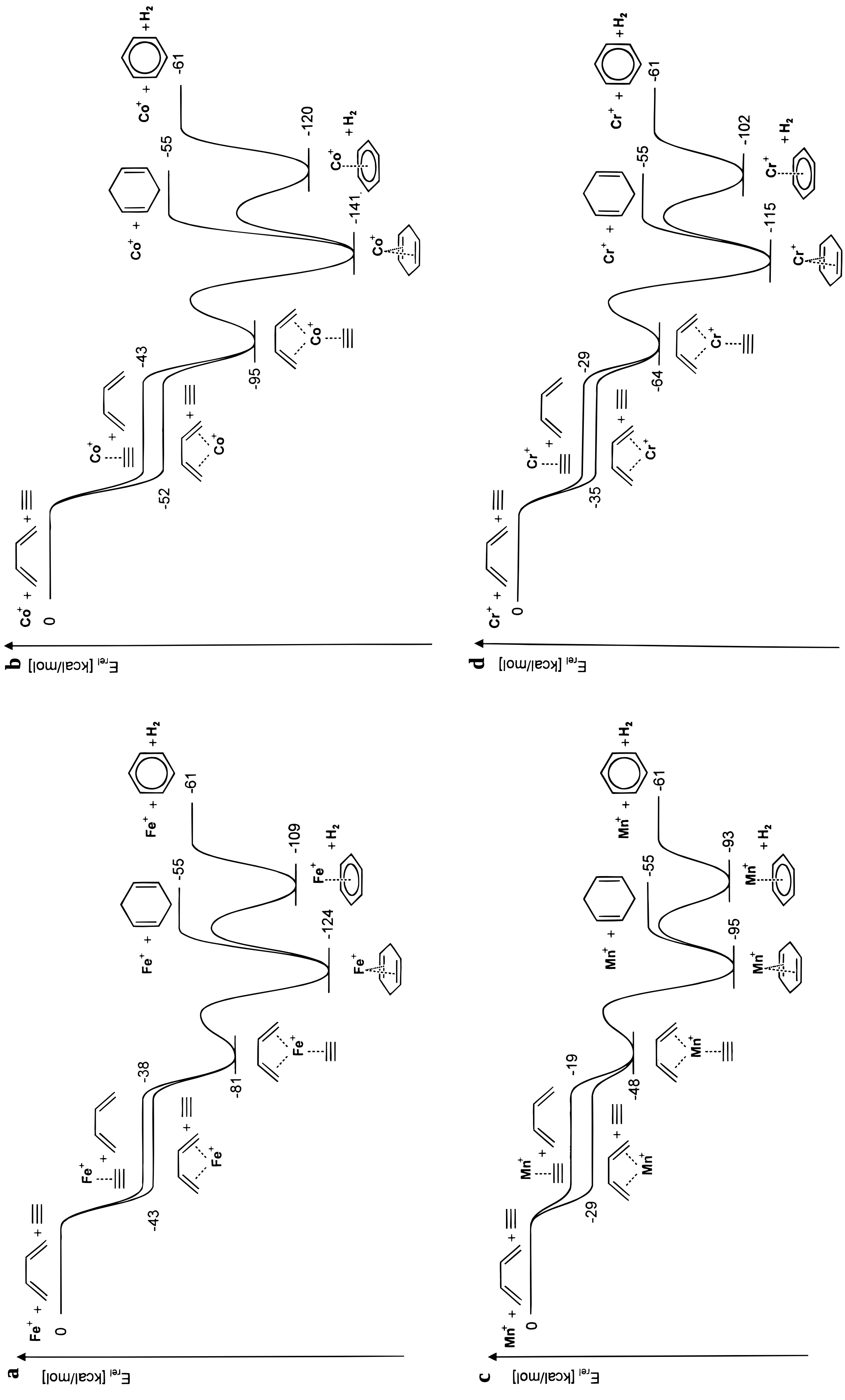


Figure 2. Qualitative potential-energy surfaces for the M$^+$-mediated [4 + 2] cycloaddition reactions for (a) M = Fe$^+$, (b) M = Co$^+$, (c) M = Mn$^+$, and (d) M = Cr$^+$.

Table 5. Mass Differences (Δm in amu) Observed in the Unimolecular Fragmentation of Metastable Butadiene/Acetylene/M$^+$ [a]

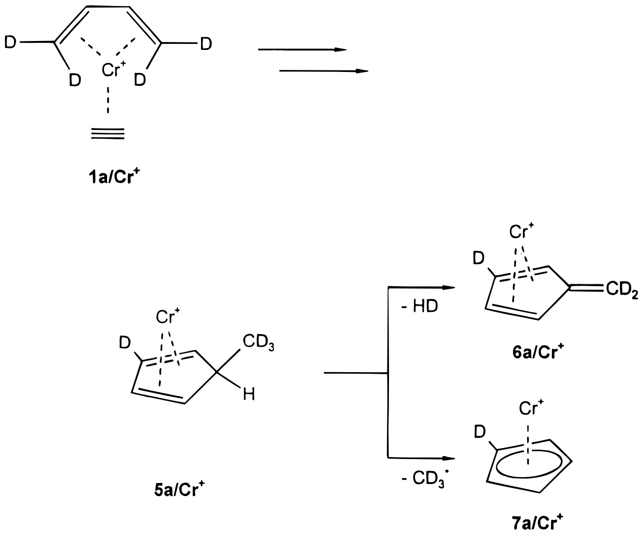
	Δm						
	2	3	4	15	18	26	M$^+$
1/Fe$^+$	>99					<1	
1a/Fe$^+$			>99			<1	
1b/Fe$^+$	>99						
1/Co$^+$	100						
1a/Co$^+$			100				
1/Mn$^+$	64					2	34
1a/Mn$^+$	<1	8	63			2	26
1/Cr$^+$	49			26		16	9
1a/Cr$^+$		28	14		22	26	10

[a] Intensities are normalized to $\Sigma = 100$.

Although the Mn$^+$-mediated dehydrogenation of 1,4-cyclohexadiene is also not very efficient (20% of the collision rate), a comparison of the entrance channels (Figure 2c) reveals that the cycloaddition step is rate-determining in the overall process **1**/Mn$^+$ → **3**/Mn$^+$. Further, the MI mass spectrum of **1a**/Mn$^+$ reveals minor losses of H_2 and HD besides the expected loss of D_2. This finding can be explained by H/D exchange via [1,5]-sigmatropic hydrogen migrations which have been similarly proposed for cyclopentadiene/MH$^+$ and cyclohexadiene/M$^+$ complexes.[7,43,46]

Metastable **1**/Cr$^+$ does also undergo unimolecular dehydrogenation, along with loss of acetylene and formation of Cr$^+$; in addition, a loss of $\Delta m = 15$ is observed (Table 5). The reduced tendency of Cr$^+$ to mediate bond activation is reflected by the small efficiencies of the ion/molecule reactions under ICR conditions (Table 4). With regard to the energetics of the Cr$^+$-promoted [4 + 2] cycloaddition of butadiene and acetylene, we arrive at conclusions similar to the ones outlined above for Mn$^+$ (Figure 2c,d). In contrast to the Fe$^+$ and Co$^+$ cases, dehydrogenation of **1a**/Cr$^+$ is not nearly as selective as predicted according to Scheme 1a. Because H/D equilibration can be ruled out by the absence of loss of H_2 from **1a**/Cr$^+$, a substantial fraction of the butadiene/acetylene/Cr$^+$ population probably reacts via multistep sequences which allow for specific H/D exchange processes. **5a**/Cr$^+$, for example, can be formed by different pathways involving C−C and C−H bond activation steps, and it represents a conceivable intermediate en route to HD loss (Scheme 3). Subsequently, **5a**/Cr$^+$ may undergo dehydrogenation to yield the fulvene complex **6a**/Cr$^+$. At first glance, the expulsion of a methyl radical from **1**/Cr$^+$ ($\Delta m = 15$) is surprising, and the observation of $\Delta m = 18$ for **1a**/Cr$^+$ indicates that all hydrogen atoms of the methyl group originate from the terminal positions of butadiene. Again, this process can consistently be explained by assuming the intermediate **5a**/Cr$^+$ which, upon C−C bond cleavage gives rise to a methyl radical and the cyclopentadienylchromium cation **7a**/Cr$^+$.

Scheme 3



Finally, let us examine Lewis-acid effects in the gas phase by means of a singly charged metal cation without the additional complications due to d electrons. As the number of metals available for chemical ionization is quite limited, we applied the more versatile FTICR technique. As representative metal cations we chose the alkali-metal cations Na$^+$ and K$^+$; however, the intensities of the butadiene/M$^+$ or acetylene/M$^+$ adducts with these alkali metals were not sufficient for further experiments. Therefore, we switched to Cu$^+$ which, due to the closed 3d shell in the Cu$^+$ (^{1}S) ground state, may serve as a representative Lewis acid. Reaction of acetylene/Cu$^+$ with butadiene leads to the exchange product butadiene/Cu$^+$ exclusively, implying that BDE(C_4H_6−Cu$^+$) > BDE(C_2H_2−Cu$^+$) = 37 kcal/mol.[24] Butadiene/Cu$^+$ and acetylene form a [Cu,C_6,H_8]$^+$ product, but neither dehydrogenation to yield Cu(C_6H_6)$^+$ nor loss of C_6H_8 concomitant with Cu$^+$ formation is observed. Further, at longer reaction time the [Cu,C_6,H_8]$^+$ ions disappear and [Cu,C_8,H_{12}]$^+$, most likely Cu(C_4H_6)$_2^+$, is formed instead. This observation indicates that the [Cu,C_6,H_8]$^+$ ion corresponds to the genuine bis-ligand complex **1**/Cu$^+$, in which at longer reaction times a second C_4H_6 molecule replaces the C_2H_2 ligand. However, bare Cu$^+$ is able to dehydrogenate genuine 1,4-cyclohexadiene to the corresponding benzene complex **3**/Cu$^+$ at a reasonable rate (Table 4). Accordingly, dehydrogenation as the second reaction step in the sequence **1**/Cu$^+$ → **3**/Cu$^+$ + H_2 should not be severely hindered, which leads to the conclusion that it is the coupling step in the anticipated [4 + 2] cycloaddition that cannot be mediated by Cu$^+$ cation.

Most significantly, with regard to the considerable BDEs of Cu$^+$ to hydrocarbon ligands (Table 1), the latter result indicates that the Lewis acidity of a metal cation is not sufficient to mediate the [4 + 2] cycloaddition in the gas phase.[50] Obviously, only transition-metal ions which possess unoccupied d shells mediate the reaction **1**/M$^+$ → **3**/M$^+$ + H_2. As bond insertion via oxidative activation is quite unfavorable in the case of chromium and manganese cations,[46,47] the metals must play another role in the formal [4 + 2] cycloaddition. We therefore propose that the cyclization proceeds in a concerted manner (pathway a in Scheme 2), like a classical Diels−Alder reaction, while the associated barriers are lowered by participation of covalent inter-

---

(50) If catalysis of the cyclization would be due to the Lewis acidity of the metal cations, the reactivities should somehow correlate with either the first or the second ionization energies of the metal atoms (Cr, 6.5 and 16.5 eV; Mn, 7.4 and 15.6 eV; Fe, 7.9 and 16.2 eV; Co, 7.9 and 17.1 eV; Cu, 7.7 and 20.3 eV). Experimentally, such a correlation is not observed at all.

actions with the transition-metal cation;[51] that is, the butadiene/M^+ subunit assumes some metallacyclopentene character. This phenomenon is denoted as covalent assistance and may effectively reduce the electron density of the diene, thus facilitating the cycloaddition with the precomplexed acetylene. This explanation also provides a rationale for the different reaction efficiencies, i.e. $Cu^+ << Cr^+ < Mn^+ < Co^+ < Fe^+$, which approximately parallel the trend of these metal ions to activate C−H and C−C bonds.[6,20,46,47]

Conclusions

The transition-metal cations Cr^+, Mn^+, Fe^+, and Co^+ mediate the formal [4 + 2] cycloaddition of butadiene and acetylene to yield 1,4-cyclohexadiene/M^+, which subsequently dehydrogenates to yield benzene/M^+ as the major product.[52] The highly exothermic cyclization step is rate-determining for all these metals and also provides the thermochemical requirements to overcome the energetic barrier of the final dehydrogenation step. The efficiency and the selectivity toward cycloaddition decrease from Fe^+ and Co^+ to Mn^+ and Cr^+; atomic Cu^+ is not able to mediate [4 + 2] cycloaddition at all. This behavior points to the operation of a covalent assistance by the metal cations in this gas-phase analog of a Diels−Alder reaction, rather than mere Lewis acid catalysis. However, some experimental evidence points toward the existence of an entropic bottleneck associated with the concerted nature of the [4 + 2] cycloaddition. Concise theoretical studies are necessary to unravel the underlying electronic features, and studies in these directions are underway.

Acknowledgment. We are indebted to the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Gesellschaft von Freunden der Technischen Universität Berlin for continuous support.

OM9609372

---

[51] Steigerwald, M. L.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1984**, *106*, 308.

[52] For a detailed experimental study on catalytic formation of benzene in the gas-phase reactions of $M(C_4H_4)^+$ (M = Ru, Rh) with C_2H_2, see: Wesendrup, R.; Schwarz, H. *Organometallics*, in press.