Notiz / Note

Ligand-Induced Hydrogen Scrambling and Interligand Carbon–Carbon Bond Formation in the Gas-Phase Reactions of MCH_3^+ (M = Fe, Co) with 1-Octyne and 1-Octene☆

Josef Schwarz and Helmut Schwarz*

Institut für Organische Chemie der Technischen Universität Berlin,
Straße des 17. Juni 135, W-1000 Berlin 12, F.R.G.

Received January 18, 1993

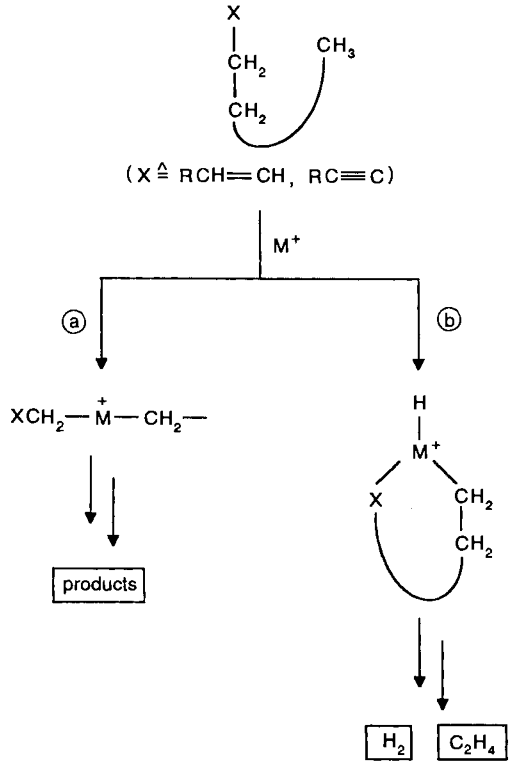
Key Words: Transition-metal chemistry / Bond activation; C–H and C–C bonds / Fourier-transform ion-cyclotron resonance

---

Evidence is presented that the encounter complexes of MCX_3^+ (M = Fe, Co; X = H, D) with 1-octyne, prior to C–H- and C–C bond activation, undergo *inter*ligand C–C bond coupling as well as extensive hydrogen exchange. In distinct contrast, in the related complexes formed by gas-phase reaction of MCX_3^+ (M = Fe, Co; X = H, D) with 1-octene, the metal-methyl group retains its identity while the alkene ligand is subject to extensive hydrogen scrambling presumably by β-hydrogen shift to and from the metal centers.

Hallmarks of the reactions of "bare" transition-metal ions M^+ (M = Fe, Co) with alkenes and alkynes in the gas phase are not only the oxidative insertions of M^+ into the allylic and propargylic C–C bonds (Scheme 1: path ⓐ)[1], recently it has become evident that also another, much more general mechanism applies, viz. *remote functionalization*[2]. Here, complexation of the metal ion M^+ with the functional group X will effectively prevent (on geometric grounds) insertion into bonds within the proximity of X. Instead, only remote bonds can be reached, e.g. by folding back of the alkyl chain. For substrates with not a too long alkyl chain it is exlusively a C–H bond of the *terminal* CH_3 group that is activated (path ⓑ), and the intermediate metallacycle will then undergo competitively either β-hydrogen shift or β-C–C cleavage. Reductive elimination of H_2 furnishes an ω-unsaturated complex, while loss of an olefin molecule yields a ligand shortened by two methylene groups[3].

Scheme 1



In spite of an increasing number of publications, in comparison with *bare* metal ions much less is know about (and even much more less understood are) the reactions of *ligated* metal ions with organic substrates in the gas phase[4]. The chemistry of $FeCH_3^+$ and $CoCH_3^+$ has been studied quite thoroughly with alkanes[5], cycloalkanes and -alkenes[6], simple alkenes and alkynes[7], and some nitrogen[8] and oxygen bases[9]. As compared with the "bare" metal ions Fe^+ and Co^+, MCH_3^+ has generally been found to be much less reactive. The reaction of MCH_3^+ ions with alkanes is not only of interest in the present context but also particularly important with regard to the mechanism of the Ziegler-Natta polymerization, where migratory insertion of alkenes into metal–alkyl bonds is regarded as a key step of the traditional Cossee-Arlman mechanism[10]. $FeCH_3^+$, however, is unreactive towards ethene[7] [in contrast to $Fe(NH_2)CH_3^+$ [11]], and although insertion is observed for $Co(CH_3)^+$, the product decomposes by loss of H_2 to the stable $Co(C_3H_5)^+$ [7]. Metal-allyl complexes are also formed by $FeCH_3^+$ and $CoCH_3^+$ from lower homologues of alkenes by loss of CH_4, and it is suggested that activation of an allylic C–H group takes place. The reaction of MCH_3^+ (M = Fe, Co) with ethylene and propyne commences with an insertion of the C–C triple bond into the metal–carbon bond[7]. We have wondered if this simple reactivity pattern also prevails for alkenes and alkynes bearing longer alkyl chains or if reactions, more analogous to a remote-type functionalization, will be operative. In this paper we describe the gas-phase reactions of MCX_3^+ (M = Fe, Co; X = H, D) with 1-octyne (**1**), its isotopomers [3,3-D_2]-**1**, [7,7-D_2]-**1** and [8,8,8-D_3]-**1**, and 1-octene (**2**), [3,3-D_2]-**2**, [7,7-D_2]-**2** and [8,8,8-D_3]-**2**, respectively. Further mechanistic insight has been obtained by employing $Co^{13}CH_3^+$.

Results and Discussion

The gas-phase chemistry of the reaction of $FeCH_3^+$ and $CoCH_3^+$ with 1-octyne (**1**) is quite rich and, as evidenced by the product distribution given in Scheme 2, many products are common to either metal ion. Some insight into the mechanism is given by studying the labeled substrates of **1**, and for some of the most prominent products the isotope distributions (obtained under high-resolution conditions) are given in Tables 1, 2.

Scheme 2

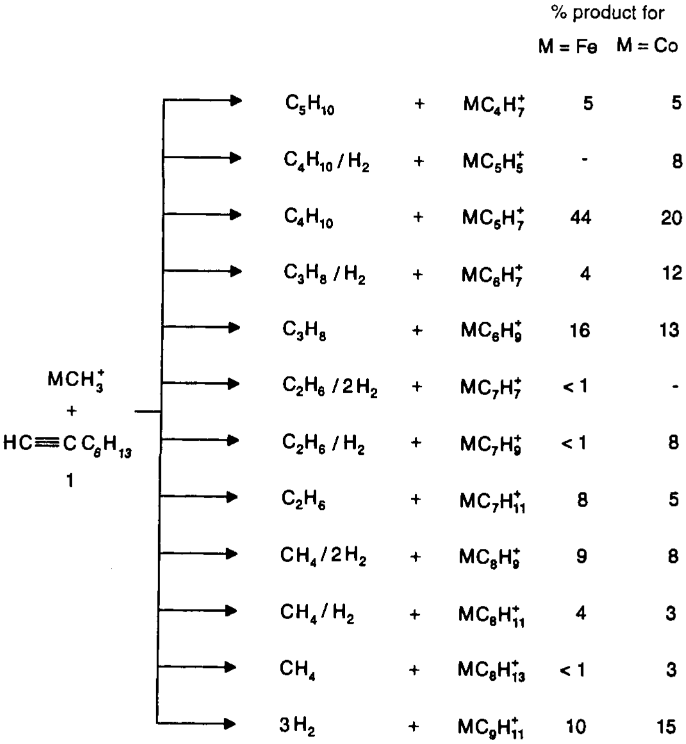


Table 1. Labeling distributions for the products $FeC_5H_{7-n}D_n^+$ and $FeC_6H_{9-n}D_n^+$ generated in the reactions of $FeCH_3^+$ with 1-octynes and of $FeCD_3^+$ with **1**[a,b]

Product Ions	[3,3-D_2]-**1**	[7,7-D_2]-**1**	[8,8,8-D_3]-**1**	$FeCD_3^+$-**1**
$FeC_5H_7^+$	30 (33)	39 (33)	24 (18)	24 (18)
$FeC_5H_6D^+$	54 (52)	47 (52)	37 (46)	43 (46)
$FeC_5H_5D_2^+$	16 (15)	8 (15)	31 (31)	27 (31)
$FeC_5H_4D_3^+$	-	-	8 (5)	6 (5)
$FeC_6H_9^+$	20 (21)	30 (21)	12 (8)	19 (8)
$FeC_6H_8D^+$	43 (53)	54 (53)	27 (37)	33 (37)
$FeC_6H_7D_2^+$	37 (26)	16 (26)	37 (42)	34 (42)
$FeC_6H_6D_3^+$	-	-	24 (13)	14 (13)

[a] The intensities are given in Σ(products) = 100% for each reaction. — [b] Numbers given in parentheses refer to labeling distributions calculated for a complete equivalency of all hydrogen/deuterium atoms in the respective encounter complexes assuming no kinetic isotope effects.

The labeling results are very surprising indeed for either metal system. For the reaction of $FeCH_3^+$ with 1-octyne we note, for example, that labeling of the substrate in the internal C-3 and C-7 positions gives rise to quite similar isotope distributions for both the formations of $FeC_5H_{7-n}D_n^+$ and $FeC_6H_{9-n}D_n^+$. Even more surprising is the observation that also for the systems **1**-$FeCD_3^+$ and [8,8,8-D_3]-**1**-$FeCH_3^+$ we obtain extraordinarily similar labeling distributions for the two ionic products. In addition, a comparison of the experimentally determined distributions with those calculated for a complete equivalence of *all* hydrogen/deuterium atoms in the encounter complexes clearly points to a situation in which hydrogen/deuterium scrambling must have preceded the dissociation step. More direct processes in which, for example, the intact methyl group of $FeCX_3^+$ (X = H, D) together with an intact alkyl rest from **1** are reductively eliminated as an alkane can be ruled out. Similarly, consecutive losses of CH_4 (generated from the metal-methyl group and a hydrogen atom from, for example, the allylic methylene group) and of alkanes/alkenes are not in keeping with the experimental findings. By and large the same observations and conclusions pertain also to the reactions of $CoCX_3^+$ (X = H, D) with 1-octyne and its isotopomers.

Table 2. Labeling distributions for the products $CoC_5H_{5-n}D_n^+$ and $CoC_5H_{7-n}D_n^+$ generated in the reactions of $CoCH_3^+$ with 1-octynes and of $CoCD_3^+$ with **1**[a,b]

Product Ions	[3,3-D_2]-**1**	[7,7-D_2]-**1**	[8,8,8-D_3]-**1**	$CoCD_3^+$-**1**
$CoC_5H_5^+$	45 (49)	49 (49)	38 (32)	46 (32)
$CoC_5H_4D^+$	44 (44)	43 (44)	36 (49)	42 (49)
$CoC_5H_3D_2^+$	11 (7)	8 (7)	15 (18)	12 (18)
$CoC_5H_2D_3^+$	-	-	11 (1)	<1 (1)
$CoC_5H_7^+$	41 (33)	42 (33)	25 (18)	29 (18)
$CoC_5H_6D^+$	44 (52)	43 (52)	31 (46)	37 (46)
$CoC_5H_5D_2^+$	15 (15)	15 (15)	34 (31)	28 (31)
$CoC_5H_4D_3^+$	-	-	10 (5)	6 (5)

[a,b] See footnotes to Table 1.

A possible mechanism which would account for the extensive hydrogen/deuterium exchange is depicted in Scheme 3. Here, the reaction commences with an insertion of the C–C triple bond into the M–C bond, followed by a set of sequential, reversible β-hydrogen transfers. As a consequence, not only the hydrogen atoms of the octyne become equilibrated, more interesting is the unexpected finding that *carbon–carbon bond formation between the two ligands attached to the metal centers must have taken place.* This suggestion is strongly supported by a further labeling experiment in which $Co^{13}CH_3^+$ is allowed to react with 1-octyne. As demonstrated by the data given in Table 3, except for the CH_4 loss channel, all products due to carbon–carbon bond activation of the alkyne ligand are formed such that the cobalt–methyl group has a nearly 50% probability of being incorporated in the product formation. This behavior is precisely expected for a system as described in Scheme 3. In addition, the presence of an intermediate having an exchangeable metal-hydrogen atom is experimentally probed by allowing MCH_3^+ to react with 1-octyne in the presence of C_2D_4. We observe the incorporation of a deuterium atom in the ionic products, as one would indeed expect for a metal hydride intermediate[12]. Further characterization of the ionic products by, for example, ligand exchange or collision processes have not been possible on sensitivity grounds.

Scheme 3

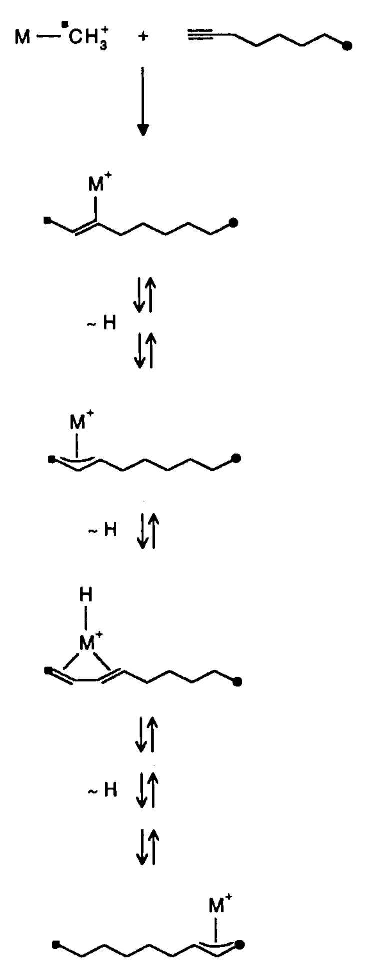


Table 3. Labeling distributions for the ionic products formed in the reaction of Co^{13}CH$_3^+$ with **1**

Product Ions	rel. intensity[a]
Co^{12}C$_4$H$_7^+$	57
Co^{12}C$_3$^{13}CH$_7^+$	43
Co^{12}C$_5$H$_5^+$	58
Co^{12}C$_4$^{13}CH$_5^+$	42
Co^{12}C$_5$H$_7^+$	51
Co^{12}C$_4$^{13}CH$_7^+$	49
Co^{12}C$_6$H$_7^+$	51
Co^{12}C$_5$^{13}CH$_7^+$	49
Co^{12}C$_6$H$_9^+$	44
Co^{12}C$_5$^{13}CH$_9^+$	56
Co^{12}C$_8$H$_{11}^+$	33
Co^{12}C$_7$^{13}CH$_{11}^+$	67

[a] See footnote[a] to Table 1.

The product distribution formed in the reactions of FeCH$_3^+$ and CoCH$_3^+$ with 1-octene (**2**) is given in Scheme 4. Among the numerous products, the combined losses of CH$_4$/H$_2$ dominate the ICR spectra. In a preliminary experiment, for this prominent process we have determined the isotope distribution (Table 4), and the data are quite revealing. We first note that, in distinct contrast to the MCX$_3^+$/1-octyne system, the metal-methyl group is eliminated as an intact unit. Further, the hydrogen atoms, however, which are used to complete the formation of methane and molecular hydrogen are provided, to a first approximation, from *all* positions of the olefin. This is clearly supported by a comparison of the experimental and computed data (Table 4). Obviously, while the M—CX$_3$ bond remains intact in the encounter complex, facile hydrogen transfer to and from the metal center precedes the reductive elimination step with the consequence that hydrogen atom equilibration takes place. A plausible mechanistic scenario is depicted in Scheme 5. We note that coupling of the metal-methyl group with the olefin does not take place, in contrast to the MCX$_3^+$/1-octyne system. Obviously, further experiments are indicated in order to arrive at an

Scheme 4

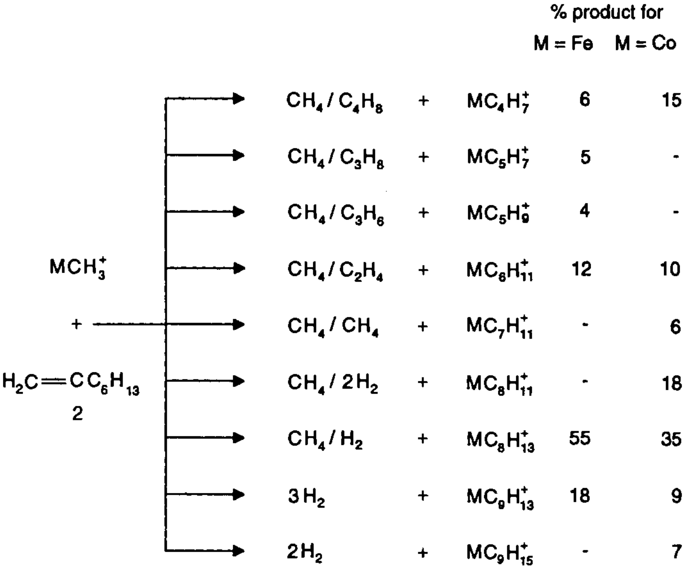


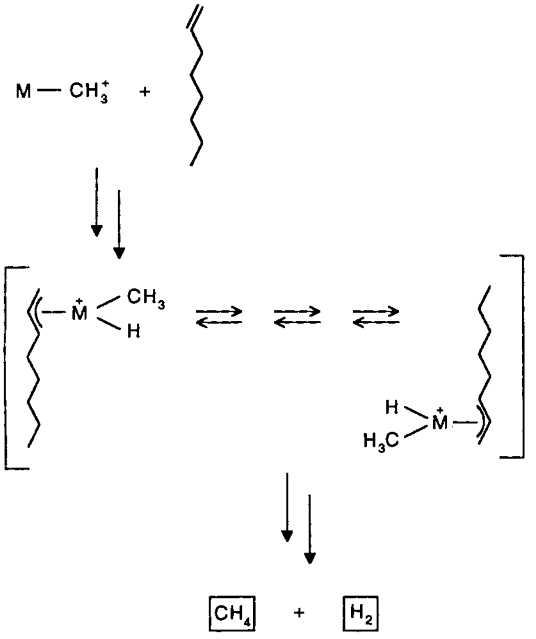
Table 4. Labeling distributions for the products MC$_8$H$_{13-n}$D$_n^+$ (M = Fe, Co) generated in the reaction of MCH$_3^+$ with **2** and its isotopomers[a,b,c]

Product Ions	[3,3-D$_2$]-2	[7,7-D$_2$]-2	[8,8,8-D$_3$]-2	MCD$_3^+$-2
FeC$_8$H$_{13}^+$	5 (3)	8 (3)	4 (1)	100
FeC$_8$H$_{12}$D$^+$	45 (42)	31 (42)	5 (7)	-
FeC$_8$H$_{11}$D$_2^+$	50 (65)	61 (65)	46 (46)	-
FeC$_8$H$_{10}$D$_3^+$	-	-	45 (50)	-
CoC$_8$H$_{13}^+$	16	17	15	100
CoC$_8$H$_{12}$D$^+$	36	34	41	-
CoC$_8$H$_{11}$D$_2^+$	48	49	38	-
CoC$_8$H$_{10}$D$_3^+$	-	-	6	-

[a] See footnote[a] to Table 1. — [b] Numbers given in parentheses refer to labeling distributions for a complete equilibration of H$_{16-n}$D$_n$ (n = 2 or 3) atoms assuming no kinetic isotope effects. — [c] On sensitivity grounds, the data in Table 4 are not obtained under the conditions of high resolution; consequently, the signals for CoC$_8$H$_{13}^+$ and CoC$_8$H$_{12}$D$^+$ are isobaric with CoC$_8$H$_9$D$_2^+$ and CoC$_8$H$_8$D$_3^+$, respectively, and the intensities given for the former are perhaps too high.

understanding of this remarkably different behavior of not too different ligands.

Scheme 5



Financial support of our work by the *Deutsche Forschungsgemeinschaft*, the *Fonds der Chemischen Industrie*, and the *Volkswagen-Stiftung* is appreciated. We are indebted to Dr. *Detlef Schröder* and Dipl.-Chem. *Detelef Stöckigt* for technical assistance and helpful discussions.

Experimental

The labeled compounds were synthesized according to well-established procedures and characterized by spectroscopic means[13]. The gas-phase experiments were performed by using a Spectrospin CMS 47X Fourier-transform ion-cyclotron resonance mass spectrometer (FTICR), which was equipped with an external ion source[14]; the instrument and further details of its operation were previously described[15]. Briefly, metal ions were generated by laser desorption/ionization[16] by focussing the beam of an Nd:YAG laser (Spectron System; $\lambda = 1064$ nm) onto a stainless-steel target (for Fe^+) or a cobalt rod, which were affixed in the external ion source. The metal ions were extracted from the source and transferred to the analyzer cell by a system of electrostatic potentials and lenses. The ion source, transfer system and ICR cell were differentially pumped by three turbo-molecular pumps. After deceleration, the ions were trapped in the field of a superconducting magnet (Oxford Instruments, maximum field strength of 7.05 T). The most abundant isotope of the metals was isolated by using FERETS[17], and allowed to react with pulsed-in methyl iodides (CH_3I, CD_3I or $^{13}CH_3I$), diluted with 90% argon to generate $M\text{–}CX_3^+$ (X = H, D)[7]. The metal–methyl$^+$ species were isolated again and allowed to react with 1-octyne and 1-octene, which were present at a stationary pressure of $3-5 \times 10^{-9}$ mbar (as measured with an uncalibrated ion gauge). All functions of the instrument were controlled by a Bruker Aspect-3000 minicomputer.

---

* Dedicated to Professor *Jochanan Blum* on the occasion of his 60th birthday.

[1] [1a] P. B. Armentrout, L. F. Halle, J. L. Beauchamp, *J. Am. Chem. Soc.* **1981**, *103*, 6624. – [1b] D. B. Jacobson, B. S. Freiser, *J. Am. Chem. Soc.* **1983**, *105*, 7484. – [1c] D. A. Peake, M. L. Gross, D. P. Ridge, *J. Am. Chem. Soc.* **1984**, *106*, 4307. – [1d] M. A. Hanratty, C. M. Paulsen, J. L. Beauchamp, *J. Am. Chem. Soc.* **1985**, *107*, 5074. – [1e] D. A. Peake, M. L. Gross, *Anal. Chem.* **1985**, *57*, 115. – [1f] D. A. Peake, M. L. Gross, *Organometallics* **1986**, *5*, 1236. – [1g] D. A. Peake, S.-K. Huang, M. L. Gross, *Anal. Chem.* **1987**, *59*, 1557. – [1h] D. A. Peake, S.-K. Huang, M. L. Gross, *Anal. Chem.* **1987**, *109*, 600. – [1i] P. A. M. van Koppen, D. B. Jacobson, A. Illies, M. T. Bowers, M. A. Hanratty, J. L. Beauchamp, *J. Am. Chem. Soc.* **1989**, *111*, 1991. – [1j] R. L. Hettich, B. S. Freiser, *Organometallics* **1989**, *8*, 2447. – [1k] P. A. M. van Koppen, M. T. Bowers, J. L. Beauchamp, *Organometallics* **1990**, *9*, 625. – [1l] D. V. Dearden, J. L. Beauchamp, P. A. M. van Koppen, M. T. Bowers, *J. Am. Chem. Soc.* **1990**, *112*, 9372.

[2] [2a] C. Schulze, H. Schwarz, *Chimia* **1987**, *41*, 29. – [2b] C. Schulze, H. Schwarz, D. A. Peake, M. L. Gross, *J. Am. Chem. Soc.* **1987**, *109*, 2368.

[3] For reviews on this topic, see: [3a] G. Czekay, T. Drewello, K. Eller, C. B. Lebrilla, T. Prüsse, C. Schulze, N. Steinrück, D. Sülzle, T. Weiske, H. Schwarz, in *Organometallics in Organic Synthesis* (Eds.: H. Werner, G. Erker), Springer-Verlag, Heidelberg, **1989**, vol. 2, p. 203. – [3b] H. Schwarz, *Acc. Chem. Res.* **1989**, *22*, 282. – [3c] K. Eller, H. Schwarz, *Chimia* **1989**, *43*, 371. – [3d] K. Eller, S. Karraß, H. Schwarz, *Ber. Bunsenges. Phys. Chem.* **1990**, *94*, 1201.

[4] Review: K. Eller, H. Schwarz, *Chem. Rev.* **1991**, *91*, 1121, and references therein.

[5] D. B. Jacobson, B. S. Freiser, *J. Am. Chem. Soc.* **1984**, *106*, 3891.

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

[7] D. B. Jacobson, B. S. Freiser, *J. Am. Chem. Soc.* **1985**, *107*, 5876.

[8] D. B. Jacobson, J. R. Gord, B. S. Freiser, *Organometallics* **1989**, *8*, 2957.

[9] O. Blum, D. Stöckigt, D. Schröder, H. Schwarz, *Angew. Chem.* **1992**, *104*, 637; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 603.

[10] E. J. Arlman, P. Cossee, *J. Catal.* **1964**, *3*, 99.

[11] S. Karraß, D. Stöckigt, D. Schröder, H. Schwarz, *Organometallics*, in press.

[12] [12a] T. J. Carlin, L. Sallans, C. J. Cassady, D. B. Jacobson, B. S. Freiser, *J. Am. Chem. Soc.* **1983**, *105*, 6320. – [12b] L. F. Halle, F. S. Klein, J. L. Beauchamp, *J. Am. Chem.Soc.* **1984**, *106*, 2543.

[13] J. Schwarz, Diploma Thesis, Technische Universität Berlin, **1992**.

[14] P. Kofel, M. Allemann, H. Kellerhals, K. P. Wanczek, *Int. J. Mass Spectrom. Ion Processes* **1985**, *65*, 97.

[15] [15a] K. Eller, H. Schwarz, *Int. J. Mass Spectrom. Ion Processes* **1989**, *93*, 243. – [15b] K. Eller, W. Zummack, H. Schwarz, *J. Am. Chem. Soc.* **1990**, *112*, 621. – [15c] K. Eller, Ph. D. Thesis, Technische Universität Berlin, **1991**, D83.

[16] R. B. Cody, R. C. Burnier, W. D. Reents, Jr., T. J. Carlin, D. A. McCrery, R. K. Lengel, B. S. Freiser, *Int. J. Mass Spectrom. Ion Processes* **1980**, *33*, 37.

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

[14/93]