Catalytic Benzene Formation in the Gas-Phase Reactions of $MC_4H_4^+$ (M = Ru, Rh) with C_2H_2

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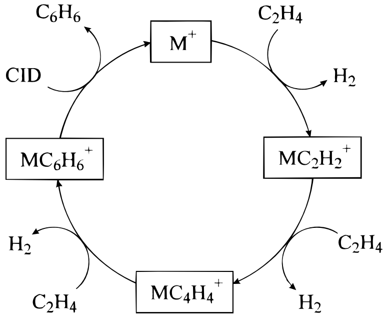
A catalytic cycle for the formation of benzene from butadiene and ethyne, mediated by Ru^+ and Rh^+ with a turnover number of 6 for the rhodium and 4 for the ruthenium system, has been realized in an FT-ICR mass spectrometry experiment. In the first step, dehydrogenation of butadiene by M^+ generates $MC_4H_4^+$ (M = Ru, Rh); this key intermediate reacts with ethyne to yield C_6H_6 and "bare" M^+. Structural investigations of the $MC_4H_4^+$ intermediate by CID and ion−molecule reactions suggest a metallacyclopentadiene for $RuC_4H_4^+$ and a rhodium-cyclobutadiene complex as the most probable structures. In addition, C_4H_4 complexes of all other group 8 transition metal cations have been generated and reacted with ethyne. While $FeC_4H_4^+$ and C_2H_2 also produce benzene and Fe^+, the analogous complexes of Co^+ and Ni^+ are unreactive toward ethyne. The C_4H_4 complexes of Os^+, Ir^+, and Pt^+ and ethyne give rise to $MC_6H_4^+$ which probably correspond to the benzyne complexes of these metal ions.

Introduction

Cycloaddition and cyclooligomerization of unsaturated hydrocarbons are versatile reactions for the synthesis of organic ring systems. Although these reactions are quite exothermic, they are usually hampered by large kinetic barriers as long as nonactivated hydrocarbons are concerned. Transition metals have been found to facilitate these reactions in the condensed phase,[1] and mass spectrometric studies revealed that certain "bare" transition-metal cations effect cyclization reactions of unsaturated hydrocarbons in the gas phase, too.[2] One major difference to the Lewis acid based cyclization catalysts which are used in condensed phase systems is the ability of many "bare" transition-metal cations to efficiently couple the cyclization with CH-bond activation. As a consequence, M^+-mediated cyclization reactions in the gas phase are often accompanied by one or several dehydrogenation steps to eventually form stable aromatic complexes. The most general example is the gas-phase trimerization of ethene by Fe_4^+, W^+, and U^+ which proceeds in a consecutive manner.[3] As depicted in Scheme 1, the sequence commences with the formation of a cationic metal−ethyne complex via dehydrogenation of ethene by M^+.

Scheme 1



In the next and often rate-determining step the ethyne complex undergoes dehydrogenation of a further ethene molecule to yield $MC_4H_4^+$; for some metal cations, e.g. U^+, there is experimental evidence that this complex already contains a C_4 hydrocarbon rather than two separate ethyne ligands.[3c] Upon the third addition of ethene, benzene complexes are formed via loss of molecular hydrogen.[4] Although the latter reaction step is very exothermic, the heat of reaction liberated is usually not sufficient to overcome the large bond dissociation energy (BDE) of M^+−(benzene);[5] as a consequence, regeneration of the "bare" metal ion with concomitant loss of the benzene ligand is not observed. This dehydrogenative cyclization of hydrocarbons may be driven in a catalytic manner by detaching the new benzene ligand from the metal center by collision-induced dissociation (CID), thus regenerating the "bare" cation to start a new catalytic cycle.[3] Of course, in an ideal catalytic system the catalytically active species should be regenerated in the reaction system without additional supply of energy. This is conveniently achieved in gas-phase experiments by employing "high-energy" reactants. For example, substituting ethene by

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(3) (a) Schnabel, P.; Irion, M. P.; Weil, K. G. *J. Phys. Chem.* **1991**, *95*, 9688. (b) Berg, C.; Kaiser, S.; Schindler, T.; Kronseder, C.; Niedner-Schatteburg, G.; Bondybey, V. E. *Chem. Phys. Lett.* **1994**, *231*, 139. (c) Heinemann, C.; Cornehl, H. H.; Schwarz, H. *J. Organomet. Chem.* **1995**, *501*, 201.

(4) In the case of Fe_4^+, this cyclization, however, occurs only partially: Gehret, O.; Irion, M. P. *Chem. Phys. Lett.* **1996**, *254*, 379.

(5) See for example: (a) Willney, K. F.; Yeh, C. S.; Robbins, D. L.; Duncan, M. A. *J. Phys.Chem.* **1992**, *96*, 9106. (b) Bauschlicher, C. W., Jr.; Patridge, H.; Langhoff, S. R. *J. Phys. Chem.* **1992**, *96*, 3273. (c) Meyer, F.; Khan, F. A.; Armentrout, P. B. *J. Am. Chem. Soc.* **1995**, *117*, 9740. (d) Schröder, D.; Schwarz, H. *J. Organomet. Chem.* **1995**, *504*, 123. (e) Dunbar, R. C.; Klippenstein, S. J.; Hrušak, J.; Stöckigt, D.; Schwarz, H. *J. Am. Chem. Soc.* **1996**, *118*, 5277.

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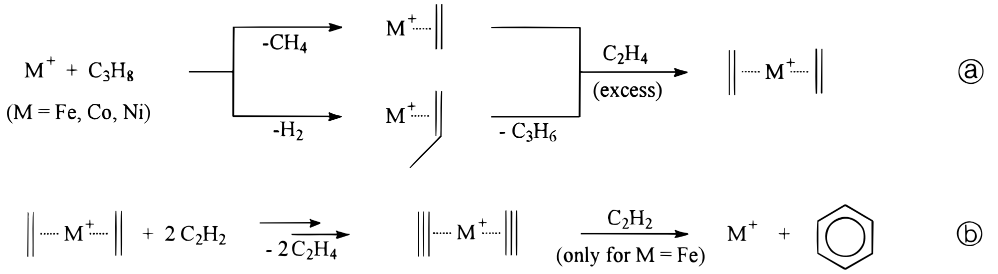
Scheme 2



ethyne as a reactant increases the exothermicity of the final step, i.e. the reaction $MC_4H_4^+ + C_2H_2 \rightarrow MC_6H_6^+$, approximately by the heat of dehydrogenation of ethene to ethyne, i.e. 42 kcal/mol.[6] This additional reaction energy is stored completely in the reactive complex. Consequently, detachment of the newly formed benzene ligand is eased and, thus, the catalyst M^+ becomes available to start a further catalytic cycle. To test this concept, we have generated $MC_4H_4^+$ complexes for all nine members of the transition-metal group 8 cations by ion−molecule reactions with different unsaturated hydrocarbons and studied their reactions with ethyne in a Fourier-transform ion cyclotron (FT-ICR) mass spectrometer.

Experimental Section

All experiments were performed with a Spectrospin CMS 47X FT-ICR machine equipped with an external ion source and a superconducting magnet (Oxford Instruments, 7.05 T). The instrument and its operation have been described in detail previously.[7] In brief, M^+ atomic ions were generated via laser desorption/laser ionization by focusing the beam of a Nd:YAG laser (1064 nm) onto a metal target.[8] The cations were extracted from the ion source and transferred to the analyzer cell by a system of electrostatic potentials and lenses. Isolation of the metal's most abundant isotope and all subsequent isolation steps were performed by using FERETS,[9] a computer-controlled ion-ejection protocol which combines single-frequency ion-ejection pulses with frequency sweeps to optimize ion isolation. $MC_4H_4^+$ complexes were prepared from M^+ via ion−molecule reactions, by pulsing-in appropriate reactant gases (see text). The ions were thermalized by pulsing-in argon for about 2 s at a pressure of 5×10^{-5} mbar (>1000 collisions). Thermalization of the bis(ethyne) complexes of Fe^+, Co^+, and Ni^+ was achieved by collisions with pulsed-in propane. In general, in the ion isolation procedure great care was taken to avoid any off-resonance excitation.[10] Ethyne and [D_2]ethyne were on-line synthesized by the reactions of calcium carbide with water or deuterium oxide, respectively, and directly admitted to the FT-ICR cell via a leak valve at a constant pressure. The pseudo-first-order rate constants were determined from the logarithmic decay of the precursor-ion intensity over time with an accuracy of ±30%; the corresponding branching ratios are reported within ±10% error bars. For collision-induced dissociation[11] argon was present at a pressure of ca. 10^{-7} mbar.

Results and Discussion

Generation and Reactivity of $MC_4H_4^+$ (M = Fe, Co, Ni). As amply demonstrated, the first-row transition metals Fe^+, Co^+, and Ni^+ exhibit a remarkably rich gas-phase chemistry, and their reactions form the subject of a large number of studies.[12] However, the ion−molecule reactions of their C_4H_4 complexes have not been investigated yet. A convenient way to produce these complexes is shown in Scheme 2. For all three metal ions ($M^+ = Fe^+, Co^+, Ni^+$) we first generated the bis(ethene) complexes by the reaction of the "bare" metal ions with pulsed-in propane, followed by a consecutive pulse of ethene (path a). The resulting $M(C_2H_4)_2^+$ complexes were isolated and served subsequently as precursors in ligand exchange with residual ethyne (p = ca. 3×10^{-8} mbar). For all three metals, we observe the stepwise displacement of C_2H_4 by C_2H_2. CID of the obtained $MC_4H_4^+$ products showed consecutive losses of two C_2H_2 units which suggests that the complexes retained their bis-ligated structure $M(C_2H_2)_2^+$ during the ligand exchange. Further evidence for a bis(ethyne) structure is also provided by the reversible ligand exchange reaction of $MC_4H_4^+$ with background water which results in $(H_2O)M(C_2H_2)^+$. Using as reference points the bond dissociation energies (BDEs) of the corresponding mono-ligated species $Fe^+{-}(C_2H_2)$ (38 ± 0.5 kcal/mol)[5d] and $Fe^+{-}(H_2O)$ (30.6 ± 1.1 kcal/mol),[13] one would not expect ethyne to be replaced by the more weakly bound water molecule from $Fe(C_2H_2)_2^+$. Either in the bis(ethyne) complex the second ligand is less strongly bound than the first one due to a mutual destabilizing effect of both ligands or the bond dissociation energy (BDE) of $(C_2H_2)Fe^+{-}(H_2O)$ is increased relative to BDE $Fe^+{-}(H_2O)$ due to synergistic interactions of the σ-donor water with the π-acceptor ethyne.[14] A similar effect has been observed in the metastable fragmentation of the tris-ligated mixed water carbonyl complex $(H_2O)Co(CO)_2^+$ where loss of the π-bounded ligand carbon monoxide dominates over the loss of water[15] in contrast to the relative BDEs of the mono-ligated complexes.[13,16]

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[12] For reviews, see: (a) Eller, K.; Schwarz, H. *Chem. Rev.* **1991**, *91*, 1121. (b) Eller, K. *Coord. Chem. Rev.* **1993**, *126*, 93. (c) Freiser, B. S. *Acc. Chem. Res.* **1994**, *27*, 353.

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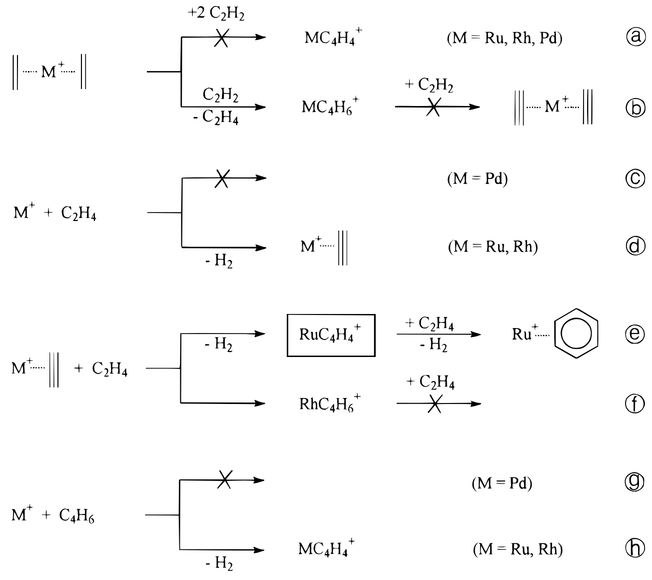
While the structural characterization by CID and the exchange reactions with background water demonstrate that the $MC_4H_4^+$ ions produced according to Scheme 2 correspond to bis(ethyne) complexes for all three metals Fe^+, Co^+, and Ni^+, these metals' reactivity toward ethyne differs remarkably: Only $Fe(C_2H_2)_2^+$ undergoes an efficient reaction to yield bare Fe^+ and neutral C_6H_6; according to thermochemical considerations the liberated C_6H_6 molecule must correspond to benzene, in agreement with a former ion-beam study of $Fe(C_6H_6)^+$, formed from Fe^+ and ethyne.[17] The reaction rate constant (k_r) for the cyclization process $Fe(C_2H_2)_2^+ + C_2H_2 \rightarrow Fe^+ + C_6H_6$ is 2.8×10^{-10} cm^3 molecule^{-1} s^{-1}; this corresponds to ca. 30% of the theoretical collision rate k_{ADO} (9.2×10^{-10} cm^3 molecule^{-1} s^{-1}).[18] As mentioned, in contrast to the iron complex, $Co(C_2H_2)_2^+$ and $Ni(C_2H_2)_2^+$ are totally unreactive toward ethyne and neither adduct formation nor generation of the "bare" metal cations is observed. Since the detailed mechanism of the Fe^+-mediated trimerization of ethyne is yet unknown, the question why its neighbors in the periodic table Co^+ and Ni^+ do not bring about this cyclization must await further experimental and theoretical investigations. In any case, the reaction of $Fe(C_2H_2)_2^+$ with C_2H_2 serves as yet another example for the exceptional reactivity of atomic Fe^+ among first-row transition metal cations.[19]

Scheme 3



Generation of $MC_4H_4^+$ (M = Ru, Rh, Pd). The gas-phase reactions of the 4d metal cations Ru^+, Rh^+, and Pd^+ have experienced much less attention as compared to their 3d congeners, and for unsaturated hydrocarbons only the reactions of ligated species are reported.[20] In contrast to their lighter homologs, these metals exhibit a more pronounced tendency to activate CH bonds, and bis(ethene) complexes can be generated in the reaction of the "bare" ions with an excess of ethane.[20c] Unfortunately, all attempts failed to use $M(C_2H_4)_2^+$ (M = Ru, Rh, Pd) as precursors in the exchange reaction with ethyne en route to $MC_4H_4^+$ (Scheme 3, path a). Although, in the primary reaction, all three complexes undergo a formal C_2H_4 exchange with ethyne to yield $MC_4H_6^+$ (path b), the consecutive reactions of $MC_4H_6^+$ with ethyne do not yield the required $MC_4H_4^+$ complexes. Instead, in a fast secondary step the ruthenium ion $RuC_4H_6^+$ gives rise to $RuC_6H_6^+$ and H_2 while the corresponding Rh^+ and Pd^+ species are unreactive. No experiments were performed aimed at the structural characterization of the $MC_4H_6^+$ species; however, the absence of ligand exchange with ethyne suggests that they correspond to butadiene rather than to bis-ligated complexes.

In an alternative approach to generate $MC_4H_4^+$, we studied the reactions of Ru^+, Rh^+, and Pd^+ with C_2H_4. While Pd^+ proved unreactive (path c), Ru^+ and Rh^+ react exothermically with ethene to yield the corresponding ethyne complexes $MC_2H_2^+$ (path d). In the consecutive reaction, $RuC_2H_2^+$ is able to dehydrogenate ethene to yield $RuC_4H_4^+$ which eventually forms $RuC_6H_6^+$ upon dehydrogenation of a further 1 equiv of ethene (path e). CID of the $RuC_6H_6^+$ product results in the exclusive formation of "bare" Ru^+; this indicates that an intact C_6H_6 moiety has been formed at the metal center either in the reaction of $RuC_4H_4^+$ with ethene or in the CID event. To exclude the latter possibility, $RuC_6H_6^+$ was reacted with [D$_6$]benzene, and besides some adduct formation to yield $(C_6H_6)Ru(C_6D_6)^+$, complete substitution of C_6H_6 by C_6D_6 was observed. Replacement of $C_6H_{6-x}D_x$ did not take place. These results clearly demonstrate that benzene has been formed at the metallic center via dehydrogenative trimerization of ethene. In contrast to the corresponding ruthenium species, $RhC_2H_2^+$ does not bring about dehydrogenation of C_2H_4; rather than $RhC_4H_4^+$ one obtains $RhC_4H_6^+$ (path f). This complex, probably either representing an adduct or a butadiene complex, is itself unreactive toward a third 1 equiv of ethene. As an alternative to the reaction with ethene, direct dehydrogenation of C_4H_6 by M^+ also represents a feasible entry to generate $MC_4H_4^+$. Consequently, we studied the reactions of Ru^+, Rh^+, and Pd^+ with butadiene (paths g and h). Indeed, Ru^+ and Rh^+ yield the desired C_4H_4 complex as the dominant product (>80% of overall products),[21] while Pd^+, like in the ethene case, is unreactive.

Reactivity and Structure of $MC_4H_4^+$ (M = Ru, Rh). With a convenient method at hand to generate $RuC_4H_4^+$ and $RhC_4H_4^+$ we next explored their potential use as cyclization catalysts in the reactions with ethyne. As expected, isolated and thermalized $RuC_4H_4^+$, generated from Ru^+ and butadiene or from 2 equiv of ethene, does indeed react with ethyne to regenerate mainly "bare" Ru^+ (95%) and neutral C_6H_6; on thermochemical grounds C_6H_6 must correspond to benzene as the only possible neutral product liberated from the reactive complex. The reaction occurs with 80% efficiency, and

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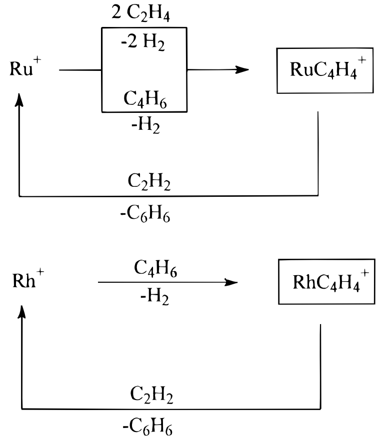
(21) As minor products the ethene complexes $M(C_2H_4)^+$ and the adducts $MC_4H_6^+$ are formed.

Scheme 4



some $RuC_6H_6^+$ (5%) is produced as cationic byproduct which probably corresponds to a benzene complex; due to its low intensity this product ion could not be further characterized. With regard to the major channel, the overall reaction constitutes an example of a Ru^+-mediated catalytic cycle for benzene generation from ethene (or butadiene) and ethyne. Similarly, isolated $RhC_4H_4^+$, generated via dehydrogenation of butadiene by Rh^+, undergoes cyclization with ethyne yielding Rh^+ and benzene as the exclusive neutral product; this reaction occurs with ca. 50 percent efficiency.

The catalytic behavior of Rh^+ in a mixture of butadiene and ethyne is shown in Figure 1. Figure 1a corresponds to the ion−molecule reaction of Rh^+ with butadiene only; the usual pseudo-first-order decay of the reactant intensity over time is depicted. The intermediate $RhC_4H_4^+$ is only observed for reaction times <1 min; as a transient, it undergoes consecutive reactions with butadiene to yield $RhC_8H_8^+$ (20%) and the adduct $RhC_8H_{10}^+$ (80%). Upon longer reaction times, C_{16} complexes evolve as final products. In contrast, the reaction of Rh^+ with a mixture of butadiene and ethyne (Figure 1b) reveals the typical features of catalytic behavior: We note a quasi-stationary intensity of $RhC_4H_4^+$, which itself represents the key intermediate in the catalytic cycle, and a remarkably much slower decay of the Rh^+ intensity as compared to the upper case concomitant with a slower increase of the consecutive products. The turnover number of the system $Rh^+/C_4H_6/C_2H_2$ corresponds to 6,[22] which is in the typical range of turnover numbers reported for other examples of gas-phase catalysis probed in FT-ICR experiments.[23] The corresponding catalytic system using ruthenium as reactant yields a lower turnover number of ca. 4, due to the formation of unreactive $RuC_6H_6^+$ in the reaction of $RuC_4H_4^+$ with ethyne. Obviously, the reaction of $MC_4H_4^+$ (M = Ru, Rh) with ethyne is sufficiently exothermic to release the newly formed benzene ligand from the metal center, thus recreating the "bare" metal cation, which is subsequently used to produce $MC_4H_4^+$. Considering a possible mechanism for the observed cyclization, we refer to the condensed phase. Here, the generally accepted mechanism for the cyclization of MC_4H_4 complexes with alkynes invokes a metallacyclic structure. This metallacyclopentadiene may either react by an alkyne insertion to form a metallacycloheptatriene or, alternatively, by a Diels−Alder type cycloaddition to yield a metallanorbonadiene. Eventually, both complexes may undergo reductive elimination to furnish the aromatic product.[1c]

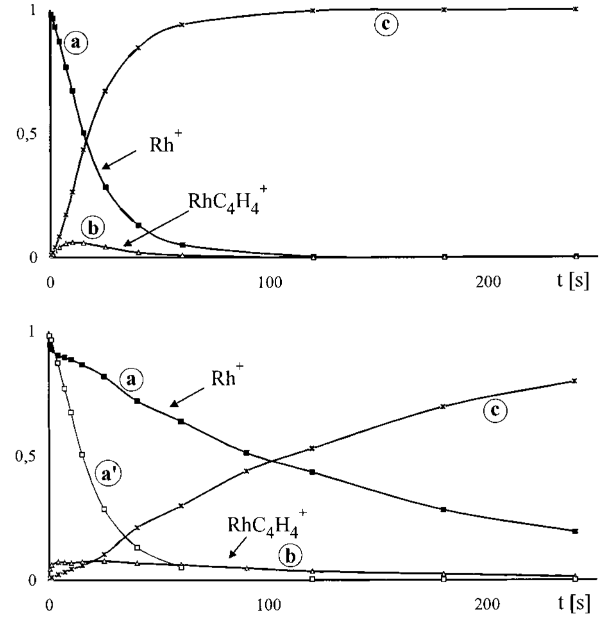
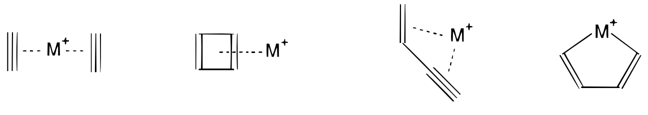


Figure 1. (a) Top: Temporal evolution of the ion intensities for the reaction of Rh^+ a with butadiene ($p = 5 \times 10^{-9}$ mbar) showing explicitly the reactant Rh^+ and the main primary product $RhC_4H_4^+$ (b). Intensities of the minor primary ($RhC_4H_6^+$ and $RhC_2H_4^+$) and all consecutive products are summarized and represented by (c). (b) Bottom: Temporal evolution of the intensities of Rh^+ (a), $RhC_4H_4^+$ (b), and all side or consecutive products (c) for the catalytic reaction of Rh^+ in a mixture of butadiene (5×10^{-9} mbar) and ethyne (5×10^{-8} mbar). For comparison, (a′) represents the Rh^+ intensity in the noncatalytic case (part a, top).

Chart 1



1 **2** **3** **4**

The comparable reactivity of $MC_4H_4^+$ (M = Ru, Rh) with C_2H_2 suggests that structurally related intermediates are involved; in principle four different structures are conceivable (Chart 1): The $MC_4H_4^+$ complex may correspond to a bis-ligated metal cation, i.e. the bis(ethyne) structure **1**, or it may contain an intact C_4 moiety, e.g. a cyclobutadiene ligand **2**, or a vinylethyne ligand **3**; finally, $MC_4H_4^+$ may correspond to a metallacyclopentadiene complex **4**. In order to distinguish between these isomers and to establish the structure of the complexes $MC_4H_4^+$ which actually serve as intermediates en route to benzene production a combination of CID and ion−molecule reactions was employed together with labeling experiments.[24] First, we studied the dehydrogenation of [1,1,4,4-D_4]butadiene by atomic Ru^+ and Rh^+ to investigate the generation of $MC_4H_4^+$.

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(22) This value corresponds to the average number of cycles each rhodium ion undergoes. It is obtained by (i) intergrating the temporal evolution of the Rh^+ intensities in the catalytic and the non-catalytic case and (ii) dividing the first by the second integral.

(23) For other recent examples of catalysis in FT-ICR, see: (a) Wesendrup, R.; Schröder, D.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 223. (b) Ryan, M. F.; Stöckigt, D.; Schwarz, H. *J. Am. Chem. Soc.* **1994**, *116*, 9565. (c) Stöckigt, D.; Schwarz, H. *Liebigs Ann.* **1995**, 429.

Table 1. Losses of Isotopomeric Molecular Hydrogen in the Reaction of M^+ (M = Ru, Rh) with [1,1,4,4-D_4]Butadiene and of $Ru(C_2H_2)^+$ with [D_4]Ethene[a]

reacn	H_2	HD	D_2
$Ru^+ + C_4H_2D_4$	13	50	37
$Rh^+ + C_4H_2D_4$	11	59	30
$Ru(C_2H_2)^+ + C_2D_4$	17	52	31
statistical H/D loss	7	53	40

[a] All data are normalized to $\Sigma = 100\%$.

Table 2. Neutrals Lost upon CID of $MC_4H_4^+$ (M = Ru, Rh) Normalized to $\Sigma = 100\%$[a]

	C_2H_2	C_4H_4
$RuC_4H_4^+$	55	45
$RhC_4H_4^+$	25	75

[a] $E_{lab} \approx 15$ eV; collision gas = argon.

The results of these reactions are listed in Table 1. In the case of Ru^+ the ratios of H_2:HD:D_2 losses correspond to an almost statistical H/D exchange with only a minor kinetic isotope effect (KIE) being operative. The deviation from statistic behavior is slightly more pronounced for the reaction of Rh^+ with [1,1,4,4-D_4]butadiene. After correcting for the number of hydrogen and deuterium atoms, one obtains the interesting correlation of KIE(H_2/HD) = KIE(HD/D_2) $\approx$ 1.5. As shown earlier,[25] this equivalency is indicative for a rate-determining reductive elimination of molecular hydrogen from a *symmetrical* transition structure. Such a symmetrical intermediate would be in keeping with all isomers except **3**. For both metal ions the occurrence of near-statistical H/D scrambling demonstrates that reversible hydrogen transfer steps precede the dehydrogenation of butadiene by Ru^+ and Rh^+; this finding also serves as an argument against the vinylethyne complex **3**. Further, while the generation of **3** would easily be rationalized by a 1,2-dehydrogenation, thus favoring loss of HD, this is not observed. Since $RuC_4H_4^+$ is also formed in the reaction of $Ru(C_2H_2)^+$ with ethene (see Scheme 3, path e), we also investigated the reaction of $Ru(C_2H_2)^+$ with [D_4]ethene. The ratios of hydrogen versus deuterium elimination nearly match the results obtained for the reaction of Ru^+ with [1,1,4,4-D_4]-butadiene. Again, all positions are involved in H/D-exchange processes preceding the liberation of molecular hydrogen which strongly suggests that the same isomer (or the same mixture of isomers) of $RuC_4H_4^+$ is formed both upon dehydrogenation of butadiene and of ethene.

This idea is further explored by CID of $RuC_4H_4^+$ which exhibits comparably intense losses of C_2H_2 and C_4H_4, regardless whether the complex was formed from butadiene or from ethene (Table 2). Even at a relatively low collision energy ($E_{lab} \approx 15$ eV, collision gas = argon),[26] where only ca. 10% of the ions undergo fragmentation, "bare" Ru^+ is formed upon CID to ca. 45% from $RuC_4H_4^+$. This result favors a structure containing a single ligand since for bis-ligated complexes, like the bis(ethyne) complex **1**, consecutive losses of both ligands should occur with loss of a single ligand prevailing in the low-energy range. For example, in the case of genuine $Co(C_2H_2)_2^+$, C_2H_2 loss amounts to 95% of the fragmentation products at comparable energies. The same argument holds true for $RhC_4H_4^+$ where loss of the complete ligand is even the dominant process in the low-energy CID, thus favoring structures **2**−**4**. Note that losses of the complete cyclobutadiene ligand and of ethyne are characteristic fragmentations in the mass spectra of transition metal cyclobutadiene complexes,[27] the latter process probably involving **4** as an intermediate *en route* from **2** to the fragment ion. Therefore, structures **2** and **4** are in good accord with the CID results. In addition, **3** which was already ruled out on the basis of the labeling experiment, is also expected to give rise to a different CID behavior: Loss of molecular hydrogen via 1,2-dehydrogenation to form a butadiyne complex $MC_4H_2^+$ would be a less endothermic process as compared to the detachment of ethyne.[6] In view of the well-established ability of Ru^+ and Rh^+ to activate CH bonds far more efficiently than CC bonds,[20] loss of molecular hydrogen from a vinylethyne ligand as in **3** should also be favored kinetically over the observed loss of ethyne. The complete absence of hydrogen loss in the CID of $MC_4H_4^+$ (M = Ru^+, Rh^+) serves as another indication that **3** is not likely to be formed as a $MC_4H_4^+$ complex in the present study.

Further information can be obtained from the reaction of $MC_4H_4^+$ with [D_2]ethyne. For the bis(ethyne) complex **1** in this experiment at least partial displacement of one unlabeled ligand from **1** should take place yielding $(C_2D_2)M(C_2H_2)^+$. However, in addition to some adduct formation of $RuC_6H_4D_2^+$, only regeneration of the "bare" metal cations is observed. Products of the composition $RuC_4H_{4-x}D_x^+$ are not detected at all. Thus, also the bis(ethyne) structure **1** can almost certainly be excluded for both metals.

In addition to the reaction with [D_2]ethyne we also reacted C_4H_4 complexes of both metal ions with [D_6]benzene, a method which has been previously shown to yield valuable structural information.[28] For $RuC_4H_4^+$ a mixture of $Ru(C_6D_6)^+$ (35%), $(C_6D_6)Ru(C_2H_2)^+$ (50%), and $(C_6D_6)RuC_4H_4^+$ (15%) is obtained, corresponding to displacement of C_4H_4, loss of ethyne, and presumably adduct formation. This product distribution agrees well with the CID results and indicates again that $RuC_4H_4^+$ contains an intact C_4 unit which is either displaced by the incoming benzene or undergoes ligand induced CC-bond cleavage to deliberate ethyne. Furthermore, the ligand is bound to the ruthenium cation strong enough to form a benzene adduct complex. The structure which best matches all these features is the metallapentadiene **4**. Addition of a benzene ligand may induce reductive elimination of cyclobutadiene or a rearrangement **4** → **1**, followed by the loss of one ethyne ligand. Since both processes involve a certain energetic barrier, it is reasonable to assume that **4** may also form a stable benzene adduct as alternative pathway. In contrast to the ruthenium complex, $RhC_4H_4^+$ exclusively undergoes ligand displacement to form $Rh(C_6D_6)^+$ upon reaction

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[24] We also tried to investigate the $MC_4H_4^+$ complexes in our sector-field mass spectrometer; however, all attempts failed to generate sufficient intensities of $RuC_4H_4^+$ and $RhC_4H_4^+$ in the chemical ionization source.

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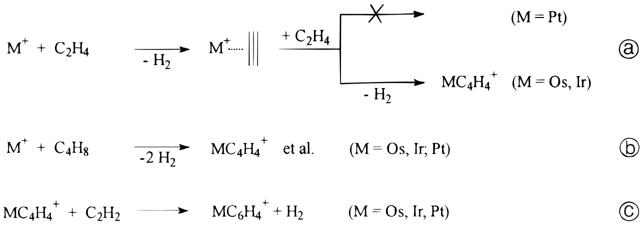
Scheme 5



with [D_6]benzene; formation of an adduct complex and loss of ethyne are not observed. It is tempting to suggest that this difference in reactivity corresponds to a different structure of $RhC_4H_4^+$, thus favoring the cyclobutadiene complex **2** as most appealing candidate. In summary, the structural investigations suggest that the key intermediates in the catalytic reaction of Ru^+ and Rh^+ in a mixture of butadiene and ethyne are quite likely a ruthenocyclopentadiene **4** and a rhodium−cyclobutadiene complex **2**. Nevertheless, it has to be stated that the experimental results may alternatively be explained by a mixture of equilibrating structures of $MC_4H_4^+$ or by isomerization of the complexes within the time scale of the corresponding experiments. Theoretical studies are indicated to help in solving this problem.

Generation and Reactivity of $MC_4H_4^+$ (M = Os, Ir, Pt). The most characteristic feature of the 5d cations Os^+, Ir^+, and Pt^+ is their ability to efficiently activate CH bonds which is most dramatically demonstrated by their reactions with methane to generate the corresponding carbene complexes MCH_2^+.[29] Accordingly, the "bare" metal ions also react with ethene to yield the complexes $MC_2H_2^+$ via loss of molecular hydrogen.[30] In the secondary reaction with ethene, $OsC_2H_2^+$ and $IrC_2H_2^+$ form $OsC_4H_4^+$ and $IrC_4H_4^+$, respectively, whereas $PtC_2H_2^+$ does not undergo further reactions (Scheme 5, path a). An alternative approach to $MC_4H_4^+$ complexes would involve the consecutive dehydrogenation of butene, and indeed, $MC_4H_4^+$ ions are the dominant products in the ion−molecule reactions of all three metals with 2-butene (path b). As minor products, the singly dehydrogenated complexes $MC_4H_6^+$ are found in amounts which slightly vary for the different metals. But regardless on their genesis the $MC_4H_4^+$ complexes of Os, Ir, and Pt exhibit the same behavior in their reactions with ethyne. The exclusive reaction products are the complexes $MC_6H_4^+$ (path c) which are formed via loss of molecular hydrogen and formally correspond to benzyne complexes. A possible explanation for this result is that, like in the corresponding reactions of $RuC_4H_4^+$ and $RhC_4H_4^+$, initially excited benzene complexes are formed. But unlike their lighter congeners, Os^+, Ir^+, and Pt^+ are capable to activate the CH bonds in the ligated aromatic ring, thus giving rise to the observed dehydrogenated products instead of detaching the intact benzene ring and to regenerate the "bare" metal ions. This scenario is supported by the ion−molecule reactions of thermalized Os^+, Ir^+, and Pt^+ with benzene which also proceeds via deliberation of molecular hydrogen and formation of $MC_6H_4^+$ complexes; stable, long-lived $MC_6H_6^+$ adducts are not observed. Obviously, the reactivity of these metal ions is too high for them to serve as catalysts in the formation of benzene.

Conclusions

We have generated C_4H_4 complexes for all nine atomic transition metal cations of the group 8 of the periodic table and studied their reactions with ethyne. Although the structures of the precursor complexes vary for the different metals, thus making a direct comparison more difficult, as a general trend the reactivity of the complexes increases from the first to the third transition row. The reactivity of $MC_4H_4^+$ (M = Os, Ir, Pt) is highest; all are reactive and form C_6H_4 complexes as the primary product. In contrast, only $RuC_4H_4^+$ and $RhC_4H_4^+$ react with ethyne to produce C_6H_6 and the "bare" M^+, while among the bis(ethyne) complexes of Fe^+, Co^+, and Ni^+ only the first one is reactive. Similar to condensed-phase reactions, certain $MC_4H_4^+$ complexes (M = Fe, Ru, Rh) undergo cyclization reactions with ethyne via formation of benzene. Using ethene or butadiene as reactants and Ru^+ or Rh^+ as the catalyst, this process may even be conducted in a catalytic manner. As expected, use of ethyne in the cyclization step proves indeed superior to ethene since the enhanced entrance energy facilitates the detachment of the benzene ligand from the metal ion, thus regenerating the atomic metal catalyst.

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