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Carbon–Carbon Bond Formation Promoted by "Bare" Lanthanide Cations: The Reactions of Ce^+ and La^+ with Propene in the Gas Phase

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The cationic butadiene and benzene complexes $CeC_4H_6^+$ and $CeC_6H_6^+$ are the main products in the reaction of thermalized Ce^+ ions with propene in the gas phase, as shown by FT MS. Following the formation of the primary products, i.e. $CeCH_2^+$ and $CeC_3H_4^+$, selective C–C coupling processes at the lanthanide cation occur as secondary reactions with high efficiency. Ligand-exchange reactions and comparative collision-induced dissociation experiments are applied to probe the structures of the final reaction products of this first example of Ce^+ gas-phase chemistry. The reaction of Ce^+ with cyclopropane yields a product distribution very similar to the propene reaction; however, it reacts significantly slower. Furthermore, La^+ reacts in nearly the same manner with propene as Ce^+ which indicates that the single f electron in the latter ion is chemically inert.

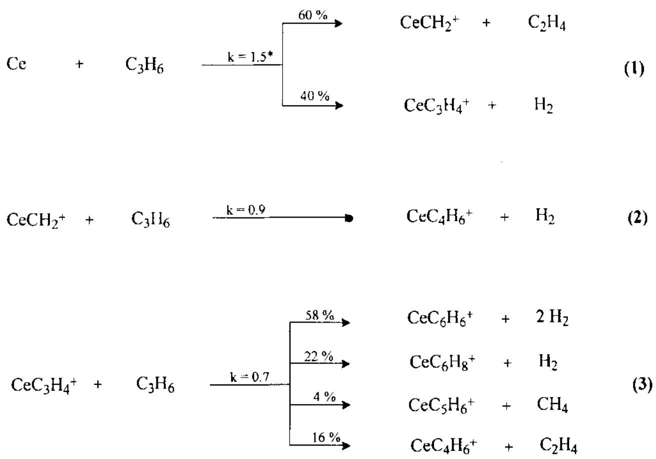
The growing importance of the long-neglected lanthanide elements in various catalytic processes of both homogeneous and heterogeneous nature[1] as well as promising perspectives for volatile organolanthanide precursors in chemical vapor deposition (CVD)[2] constitute a challenge to gas-phase organometallic chemistry. Studying the reactivity of "bare" and ligated lanthanide cations is likely to lead to an understanding of the intrinsic reactivities of these elements at a molecular level[3]. In this context, studies directed towards models for economically relevant processes such as polymerization of ethylene[1a] or propylene and activation of methane[1c,4] merit particular attention.

In this paper, we report on the reaction of the Ce^+ cation with propene as monitored by Fourier-transform ion-cyclotron resonance (FT-ICR) mass spectrometry. The study is part of a more general project aimed at investigating general trends in the gas-phase chemistry of lanthanide cations with hydrocarbons and various other substrates. Surprisingly, only a few studies of gas-phase ion-molecule reactions of the rare earth elements have been reported so far[5]. In particular, this first example of Ce^+ gas-phase chemistry can be compared to the interesting chemical behavior of the group-3 metal cations (Sc^+, Y^+, La^+), which have been studied in some detail over the last years[6].

Results and Discussion

An overview of the primary and secondary reactions in the Ce^+/propene system is given in Scheme 1. Figure 1 shows the concentrations of the observed ions over the monitored time, and Figure 2 displays a typical mass spectrum after a reaction period of 2 s. As evident from these figures, oxidation of the Ce^+ cation and all cationic complexes CeL^+ ($L = CH_2^+, C_3H_4^+, C_4H_6^+, C_5H_6^+, C_6H_6^+$) by residual water and oxygen present in the background ($p < 2 \times 10^{-9}$ mbar) represents an undesired side reaction resulting in the continuous rise of CeO^+ and $CeOH^+$ concentrations (ratio $CeO^+ : CeOH^+ \approx 10:1$) during the course of the reaction. However, due to the high oxophilicity of cerium [e.g. $BDE(Ce^+–O) = 197$ kcal/mol[9]], these complexes are totally unreactive towards propene, and thus the product analysis is not obscured by these species.

Scheme 1



* All rate constants in 10^{-9} cm^3 s^{-1} molecule^{-1}.

The primary reaction (1) of Ce^+ with propene yields two products, $CeCH_2^+$ (60%) and $CeC_3H_4^+$ (40%). As compared to the theoretical collision rate[10], $k_c = 1.1 \times 10^{-9}$ cm^3 s^{-1} molecule^{-1}, the measured rate constant, $k_{exp} = 1.5 \times 10^{-9}$ cm^3 s^{-1} molecule^{-1}, indicates that this process is rather efficient. While dehydrogenation of propene has been reported for many other metal cations M^+[3] (including M = Sc[6b]), formation of the cationic carbene complex $CeCH_2^+$, which is expected to be thermodynamically much more stable than the isomeric carbynehydrido and carbidodihydrido complexes $HCeCH^+$ and H_2CeC^+[11], as a major product of the

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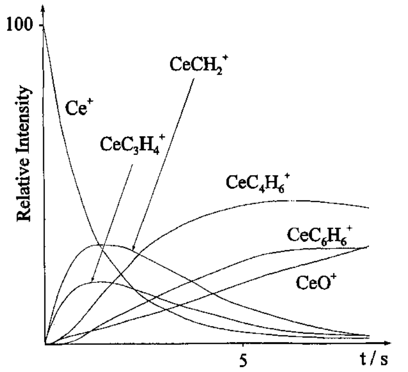


Figure 1. Relative intensities of starting compound and product ions in the Ce^+/propene reaction ($p_{Propene} = 5 \times 10^{-8}$ mbar)

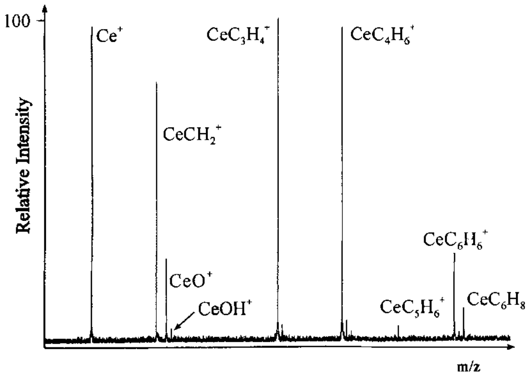
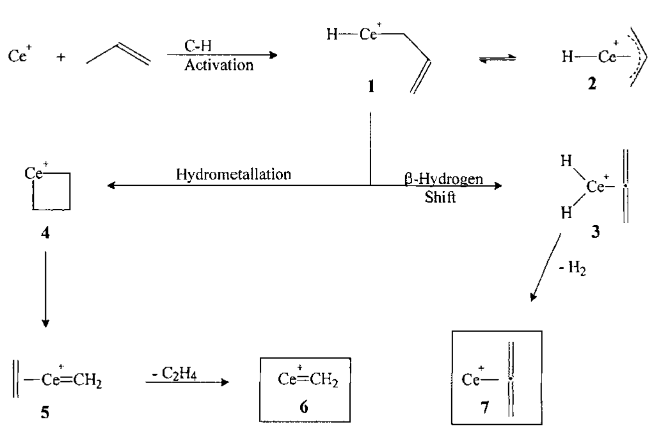


Figure 2. Fourier-transform ICR mass spectrum of the Ce^+/propene reaction obtained after a reaction period of 2 s

reaction of a transition-metal cation with propene is unprecedented. A possible mechanistic rationalization of the observed products in terms of elementary reaction steps well-known in organometallic chemistry is shown in Scheme 2. Upon insertion of the Ce^+ cation into the weakest bond of propene, i.e. the allylic C−H bond (*BDE* = 86.3 kcal/mol[9]), the allylhydrido complex **1** is formed. This may undergo a β-hydrogen shift to form the allene-dihydrido complex **3**, which can eliminate H_2 to form $CeC_3H_4^+$. According to earlier reports on $ScC_3H_4^+$[6b], we formulate this ion as an allene complex; however, it has to be stressed that allene-propyne rearrangements may easily occur at a metal center[12]. Alternatively, the primary insertion product **1** may rearrange by an *intra*molecular insertion of the C−C double bond into the Ce−H bond in the sense of a hydrometalation to form the ceracyclobutane cation **4** as an intermediate. Subsequent cycloreversion to the mixed carbene/ethylene complex **5** and loss of C_2H_4 then lead to the cationic carbene complex $CeCH_2^+$ (**6**). We note in passing that the simplest *inter*molecular insertion into a C−C double bond, the hydrometalation of ethylene by CeH^+ is not observed at thermal energies.

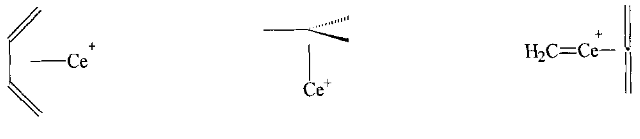
Since the cationic carbene complexes MCH_2^+ of third-row transition-metal cations constitute important intermediates in the gas-phase activation of methane[4,13,14] they have recently been investigated in some detail[11,15]. In contrast to the corresponding Ta, W, Os, Ir and Pt species[13], $CeCH_2^+$ does *not* react with methane. From its formation in the exothermic reaction of Ce^+ with propene we derive a lower limit of 101 kcal/mol for the bond dissociation energy (*BDE*) of $CeCH_2^+$ relative to Ce^+ and CH_2[9]. For comparison, the bond dissociation energy of the cationic carbene complex $LaCH_2^+$ is in the same range: $BDE(La^+{-}CH_2) = 98 \pm 1.5$ kcal/mol (ion-beam study[16l]), 106 ± 5 kcal/mol (photodissociation experiment[6h]). In accord with this, we find that the La^+ cation reacts with propene in almost the same manner as Ce^+, giving rise to the initial formation of $LaCH_2^+$ and $LaC_3H_4^+$ followed by secondary C−C coupling reactions to afford $LaC_4H_6^+$ and $LaC_6H_6^+$. This similarity in the reactivity of the first element of the 4f block and its congener from group 3 of the periodic table supports the generally accepted view[17] that the additional f electron of Ce^+ (electronic ground states[18]: La^+: $5d^2$; Ce^+: $5d^24f^1$) is chemically mainly inactive. However, further gas-phase experiments, in particular aimed at investigating higher oxidation states of the rare-earth elements, are in progress to test the general validity of this paradigm. We would like to point out that especially the cationic carbene complexes $LaCH_2^+$ and $CeCH_2^+$ constitute a challenge to theoretical investigations, since the influence of a single f electron on chemical bonding and reactivity as well as the role of relativistic effects in heavy-transition-metal complexes can be probed.

Scheme 2



In the secondary reaction (2) (see Scheme 1) the cationic carbene complex $CeCH_2^+$ reacts with propene to form exclusively $CeC_4H_6^+$. The rate constant for this process ($k_{exp} = 0.9 \times 10^{-9}$ cm^3 s^{-1} $molecule^{-1}$) is naturally somewhat smaller than that for the reaction of the unligated Ce^+ cation; still, the reaction has about 80% efficiency. Several structural isomers, such as a butadiene (**8**), a trimethylenemethane (**9**) or a mixed carbene/allene complex (**10**) (see Scheme 3) are conceivable for $CeC_4H_6^+$. To allow a discrimination between these isomers, collision-induced dissociation (CID) experiments of $CeC_4H_6^+$, generated from five different precursors, have been performed. The results (see Table 1) give strong evidence that in fact a cationic Ce^+−butadiene complex is formed in the present case: First, the CID spectra of $CeC_4H_6^+$ from $CeCH_2^+$/propene and from Ce^+/*n*-butane are very similar. At a center-of-mass collision energy (E_{COM}) of 35 eV, mainly C_2H_4 and H_2 are lost from the corresponding $CeC_4H_6^+$ complexes. At E_{COM} = 70 eV, loss of the entire C_4H_6 ligand constitutes an additional channel. As the double dehydrogenation of *n*-butane by transition-metal cations is known to proceed without rearrangement of the carbon skeleton[3], the $CeC_4H_6^+$ complex from $CeCH_2^+$/propene is most likely a Ce^+/butadiene complex **8**. A different $CeC_4H_6^+$ isomer is generated in the reactions of Ce^+ with isobutane as well as isobutene. Here, loss of C_3H_4, which is not observed in the case discussed above, constitutes the major CID process at E_{COM} = 70 eV while loss of C_2H_4 is less important. According to earlier experiments[6b] on structural isomers of $ScC_3H_4^+$, we suppose that this species is a Ce^+/trimethylenemethane complex **9**. Finally, the CID-fragmentation pattern of $CeC_4H_6^+$ formed from 1-butene is distinctly different from the first two cases with loss of the entire ligand as the most prominent process at both center-of-mass energies and only a small percentage of H_2 loss. However, we would like to stress that due to differences in internal energies of the $CeC_4H_6^+$ complexes generated from different precursors and possible rearrangement processes that may occur upon collision of the kinetically excited ions with the target gas the interpretation of the CID spectra is not without ambiguities. From the data presented here, the existence of at least two different $CeC_4H_6^+$ isomers can be inferred, the one from propene and *n*-butane most probably being a butadiene complex **8**.

Scheme 3. Possible isomers of the $CeC_4H_6^+$ complex



8 **9** **10**

Table 1. Fragmentation of $CeC_4H_6^+$ generated from different precursors in collision-induced dissociation (CID) experiments[a]

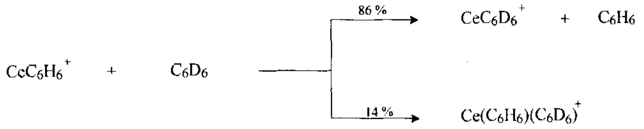
Precursor	Propene	*n*-Butane	Isobutane	Isobutene	1-Butene
(a) E_{COM} = 35 eV					
Ce^+	–	–	13	–	48
CeH^+	–	–	–	–	–
$CeCH_2^+$	–	–	39	41	–
$CeC_2H_2^+$	61	67	26	–	45
$CeC_4H_4^+$	39	33	22	59	7
(b) E_{COM} = 70 eV					
Ce^+	27	35	25	14	53
CeH^+	–	–	–	–	8
$CeCH_2^+$	9	–	40	37	–
$CeC_2H_2^+$	44	46	22	25	35
$CeC_4H_4^+$	20	19	13	24	4

[a] Intensities are normalized to Σ(fragment ions) = 100.

In earlier investigations of cationic transition-metal carbene complexes, similar $C_1 + C_3$ (where C_3 was either cyclopropane or a propene) coupling reactions at a "bare" transition metal cation to afford $MC_4H_6^+$ species have been reported for M = Fe[19], Co[19], Ta[20] and La[6g]. While in these examples additional $MC_2H_x^+$ and $MC_3H_y^+$ (x, y = 4, 6) products have been observed, it is the high selectivity towards the C–C coupling product butadiene that makes the reported cerium case noteworthy.

The secondary reaction starting from $CeC_3H_4^+$ [Reaction (3), Scheme 1] is, however, more complicated. Since a larger ligand is already attached to the metal cation the reaction is somewhat slower ($k_{exp} = 0.7 \times 10^{-9}$ s^{-1} molecule^{-1}) than the secondary process starting from $CeCH_2^+$. The "$C_3 + C_3$" coupling products, i.e. $CeC_6H_6^+$ and $CeC_6H_8^+$, constitute the most important product ions (80%) in this process. In addition, $CeC_4H_6^+$ (16%) and a small amount of $CeC_5H_6^+$ (4%) are formed. For the latter ion a subsequent tertiary reaction with C_3H_6 to form $CeC_7H_{10}^+$ is observed in the case of long reaction times. To investigate the nature of the $CeC_6H_6^+$ species, this ion is isolated from the reaction mixture and allowed to react with C_6D_6 (see Scheme 4). As expected for a thermoneutral ligand-exchange reaction, $CeC_6D_6^+$ is formed as the major product at ca. 50% of the theoretical collision rate ($k_{exp} = 0.4 \times 10^{-9}$ cm^3 s^{-1} molecule^{-1}; $k_C = 0.9 \times 10^{-9}$ cm^3 s^{-1} molecule^{-1}). This result gives strong evidence that in fact a cationic benzene complex is formed from two C_3 units. In addition to the ligand-exchange reaction, formation of the cationic bis(benzene) complexes $Ce(C_6H_6)(C_6D_6)^+$ and, subsequently $Ce(C_6D_6)_2^+$ may serve as further proof that the benzene ligand is π-bonded to the transition-metal ion. Accordingly, the $CeC_6H_8^+$ species is best considered as a hexadiene complex, in which the final dehydrogenation to the benzene complex has not yet occurred.

Scheme 4



Freiser and Lech have reported[6b] that $ScC_3H_4^+$ reacts with propene to give the same secondary products as reported here for the cerium case. However, similar to the $C_1 + C_3$ coupling discussed above, the selectivity towards the $MC_6H_x^+$ complexes is lower than in the present case. The formation of $MC_6H_6^+$ has also been mentioned to occur upon the reaction of $YC_3H_4^+$ and $LaC_3H_4^+$ with cyclopropane[6e], but further ligand-exchange experiments to prove a π-bonded benzene complex have, unfortunately, not been reported. The formation of a benzene molecule from small C_n fragments promoted by "bare" transition-metal cations and clusters has so far been established for n = 2 ($Fe^+ + 3\ C_2H_2$[21]; $Fe_4^+ + 3\ C_2H_4$[22]; $Nb^+ + 3\ C_2H_4$[20]) and n = 4[23]. The present example of a $C_3 + C_3$ route to benzene shows a new and interesting reaction pathway in gas-phase organometallic chemistry, which seems to be quite general for metals of the 4f block[24] and, supposing that the $MC_6H_6^+$ species (M = Y, La[6e]) reported by Freiser and co-workers are in fact genuine benzene complexes, for the related group-3 elements.

For comparison, we have also briefly investigated the reaction of Ce^+ with cyclopropane. Again, $CeCH_2^+$ and $CeC_3H_4^+$ are formed in almost equal amounts (branching ratio $CeCH_2^+$:$CeC_3H_4^+$ = 45:55) in the primary reaction. However, the measured rate constant ($k_{exp} = 0.3 \times 10^{-9}$ cm^3 s^{-1} molecule^{-1}) is only 30% of the theoretical collision rate k_c. The secondary products ($CeC_4H_6^+$ and $CeC_6H_6^+$) are identical with those of the Ce^+/propene system. Since it is generally accepted[3] that the activation of cyclopropane by a transition-metal cation involves a primary insertion into the C–C bond, we conclude that the cationic ceracyclobutane cation **4** constitutes the first reaction intermediate in the present case. The fact that the product distribution found in the Ce^+/cyclopropane reaction is almost identical with that in the Ce^+/propene reaction suggests that intermediates **1**–**5** (see Scheme 2) can easily interconvert. Thus, the significantly lower rate of the primary reaction found in the cyclopropane case is most likely due to a substantial activation barrier for insertion into the C–C bond of the cycloalkane[25].

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Experimental

The experiments were performed with a Spectrospin-CMS-47X Fourier-transform ion-cyclotron resonance mass spectrometer which was equipped with an external ion source (for details of the instrument and its operation see ref.[7]). Briefly, Ce^+ ions were generated by laser desorption/laser ionization by focussing the beam of an Nd:YAG laser (Spectron Systems; λ = 1064 nm) onto either a flint stone of a conventional lighter (Ce content: ca. 70%) or a pure cerium metal piece (Heraeus, 99.9%). Although undesired Fe, La, Pr, Nd, and Gd isotopes had to be ejected from the cell, the former procedure proved to be more convenient since a pure cerium target suffered from fast oxidative degradation upon exposure to air. 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 the ICR cell were differentially pumped by the three turbomolecular pumps. After deceleration, the ions were trapped in the field of a superconductive magnet (Oxford Instruments, maximum field strength 7.05 T). The $^{140}\mathrm{Ce}^+$ isotope was isolated by using FERETS[8], a computer-controlled ion-ejection protocol which combines frequency sweeps and single frequency pulses to optimize ion isolation. Thermalization of the ions and removal of excess energy were effected by collisions with pulsed-in argon (maximum pressure ca. 5×10^{-5} mbar). Reactants were admitted to the cell through a leak valve at a stationary pressure of $(1-5) \times 10^{-8}$ mbar (as measured by a calibrated ion gauge, BALZERS IMG 070). Reaction products were unambiguously identified by high-resolution spectra, and their reaction pathways were investigated by MS/MS and double-resonance techniques. Rate constants were determined from the pseudo first-order decay of the ion of the starting reactant and are reported with an estimated accuracy of ±30%. Collision-induced dissociation (CID) experiments were carried out by (i) isolation of the desired ion using FERETS, (ii) kinetic excitation of this ion by a radio-frequency pulse, and (iii) trapping it for 1 s in argon at a static pressure of 2×10^{-8} mbar. All functions of the mass spectrometer were controlled by a Bruker Aspect 3000 minicomputer.

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