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Study of the Gas-Phase Chemistry of YCH_3^+: σ-Bond Metathesis and Migratory Insertion of C=C Bonds into the Y^+–Methyl Bond

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Abstract: The gas-phase chemistry of YCH_3^+ is studied, with particular emphasis on C–H activation via a multicentered intermediate. This activation pathway is observed for the benzyl–hydrogen bond and allylic C–H bonds but not for the H–H bond, C–H bonds in simple alkanes, vinylic C–H bonds, and phenyl–H bonds. The reaction of YCH_3^+ with toluene generates (benzyl)yttrium ion and methane, exclusively. The reaction of YCH_3^+ with ethylene occurs by migratory insertion of the C=C double bond into Y^+–CH_3, followed by H_2 elimination to give Y^+–allyl. Labeling experiments indicate facile reversible steps in the reaction mechanism, resulting in rapid isomerization of the Y^+–propyl intermediate to Y^+–isopropyl, which occurs prior to H_2 loss. In contrast, for propene, such C=C bond migratory insertion accounts for only a minor amount of the reaction and leads to the formation of $YC_4H_7^+$ consisting of about 80% (2-methylallyl)yttrium ion and 20% (1-methylallyl)yttrium ion. The majority of the reaction proceeds by methane elimination involving an allylic hydrogen and the methyl group originally attached to the yttrium center, leading to the formation of (allyl)yttrium ion. (1-Methylallyl)yttrium ion and (2-methylallyl)yttrium ion are formed from the linear butenes and isobutene, respectively, and they yield distinctive CID patterns and reactivities. (η^5-Cyclopentadienyl)yttrium ion, (η^5-cyclohexadienyl)yttrium ion, (η^7-cycloheptatrienyl)yttrium ion, and (η^7-cyclooctatrienyl)yttrium ion are formed from 5-, 6-, 7-, and 8-membered cyclic alkenes, respectively.

Introduction

Intense interest in gas-phase transition-metal ions over the past 10 years has yielded a substantial body of data concerning various aspects of their chemistry.[1] One of our ongoing efforts is to extend such study to systems with one or more ligands attached to the metal center, enabling the detailed examination of the intrinsic effect of the ligand on the reactivity of the metal center and the interaction between the metal center and the ligands. A wide variety of ML^+ (L = ligand) ions have been studied.[2] Gas-phase transition-metal ions often exhibit different reactivities, and a certain ligand can also exert different effects on different metal ions. Thus, the study of the chemistry of ionic systems with different metal–ligand combinations is not only interesting but also necessary to reveal the delicate interaction between the ligand and the metal center. An earlier study examined the chemistry of MCH_3^+ (M = Co, Fe) with unsaturated hydrocarbons and suggested that the dominant reaction pathway is by metal center insertion into an allylic C–H bond, followed by reductive elimination of CH_4 from the metal center to give an M^+–allyl product ion.[3] C=C bond insertion into the M^+–CH_3 bond was found to be less favorable and was observed only for the reaction between ethylene and $CoCH_3^+$ and not for $FeCH_3^+$.

As an extension of this work, the chemistry of YCH_3^+ is examined in this study. Group 3 transition-metal ions are interesting because of their unique two valence electron structure.[4,5] Bonding of a methyl group to Y^+ leaves only one unpaired electron on the metal center. This should effectively block the pathway of oxidative addition of the yttrium center and provide an opportunity to examine alternative pathways such as migratory insertion and C–H bond activation via the σ-bond metathesis mechanism involving a multicentered transition state.[6] C=C bond insertion into metal–ligand bonds is particularly interesting because of its relevance to the catalysis of alkene polymerization.[7]

Experimental Section

All experiments were performed on a prototype Nicolet FTMS-1000 Fourier transform mass spectrometer previously described in detail.[8] The instrument is equipped with a 5.2-cm cubic trapping cell situated between the poles of a Varian 15-in. electromagnet maintained at 0.9 T. The cell utilizes two 80% transmittance stainless steel screens as the transmitting plates, permitting the irradiation of the interior with various light sources. Y^{2+} was generated by focusing the beam of a Quanta Ray Nd:YAG laser (operated at 1.064 μm) onto a thin high-purity target of yttrium and then isolated by ejecting Y^+. Details of the laser desorption experiment are described elsewhere.[9] Compared to singly charged metal ions, generation of doubly charged metal ions usually requires finer tuning and our experience shows that the favorable spot for generating more abundant doubly charged ions seems to be at the edge of the metal target.

All chemicals were obtained in high purity from commercial sources and used as supplied except for multiple freeze–pump–thaw cycles to remove noncondensible gases. Sample pressures were measured with an uncalibrated Bayard-Alpert ionization gauge and were usually $\sim 6 \times 10^{-6}$ Torr for samples and $\sim 4 \times 10^{-5}$ Torr for background argon used for collision-induced dissociation.

Details of the collision-induced dissociation (CID) experiment have been described previously.[10] The laboratory collision energy can be varied typically in the range 0–100 eV. The spread in kinetic energy depends on the average kinetic energy and is typically about 35% at 1 eV, 10% at 10 eV, and 5% at 30 eV.[11]

While MCH_3^+ (M = Fe, Co) is conveniently generated from CH_3I, reaction of this agent with Y^+ yields YI^+ exclusively. In a separate study on the reactions of Y^{2+} with small hydrocarbons, it was found that YCH_3^+ could be made in high abundance from the reaction of Y^{2+} with *n*-butane.[12] Like its iron and cobalt counterparts, CID on YCH_3^+ yields Y^+ exclusively over the energy range studied (24–75 eV), strongly supporting the Y^+–methyl structure. *n*-Butane was introduced into the vacuum chamber through a General Valve Corp. Series 9 pulsed solenoid valve.[13] The pulsed reagent gas fills the chamber to a maximum pressure of about 10^{-5} Torr with about a 150-ms rise time and is pumped away by a high-speed 5-in. diffusion pump in about 300 ms. The reactant ion

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(1) For a review on gas-phase transition-metal ion chemistry, see: Allison, J. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley-Interscience: New York, 1986; Vol. 34, p 628 and references therein.

(2) Some examples are: Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 3891; **1985**, *107*, 67. Cassady, C. J.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 6176. Jackson, T. C.; Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 1252. Huang, Y.; Freiser, B. S. *J. Am. Chem. Soc.* **1989**, *111*, 2387. Buckner, S. W.; Freiser, B. S. *Polyhedron* **1988**, *7*, 1583.

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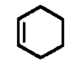
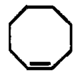
Table I. Product Ion Distributions from the Reactions of YCH_3^+ with Alkenes

ion													
$YC_3H_5^+$	100	94											
$YC_4H_7^+$		6	89	89	85	100							
$YC_4H_8^+$							20						
$YC_5H_5^+$										100			
$YC_5H_7^+$			7	6	10		53	52	45				6
$YC_5H_8^+$									13				
$YC_5H_9^+$			4	5	5		16	48					
$YC_6H_7^+$											100		1
$YC_6H_8^+$													1
$YC_6H_9^+$							7		18				3
$YC_6H_{10}^+$													4
$YC_6H_{11}^+$							4		24				
$YC_7H_7^+$												92	5
$YC_7H_9^+$												8	
$YC_7H_{11}^+$													3
$YC_8H_8^+$													14
$YC_8H_9^+$													50
$YC_8H_{11}^+$													9
$YC_9H_{13}^+$													4

was then isolated by a swept double resonance pulse and trapped in the background pressure of another reagent to study its chemistry. *n*-Butane-*1,1,1,4,4,4-d*$_6$ was used to prepare YCD_3^+ for the deuterium-labeling experiments. The product ion distributions are reproducible to ±10% absolute for primary product ions and ±15% for CID fragmentation ions.

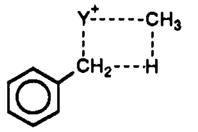
Results and Discussion

C–H Bond Activation via σ-Bond Metathesis. The activation of a C–H bond by a transition-metal center in solution generally falls into one of two different mechanisms. The first mechanism involves oxidative addition by a coordinatively unsaturated metal center. The second mechanism is sometimes referred to as σ-bond metathesis and generally occurs on a highly-electron-deficient transition-metal center, typically a d^0 system, and involves a multicentered transition state as the key intermediate.[6] The chemistry of gas-phase transition-metal ions with hydrocarbons is dominated by studies on the metal ions of groups 8–10 which proceed by the first mechanism involving oxidative insertion into both C–H and C–C bonds and ensuing reductive elimination. The other reaction pathway could also be possible, especially when the first pathway is not plausible. Richardson and co-workers recently reported the gas-phase reaction between $ZrCp_2CH_3^+$ and D_2 to give $ZrCp_2D^+$ and CH_3D.[14] Because of the d^0 electronic structure of the Zr center, this reaction could only be explained by a mechanism based on a four-centered transition-state pathway. A recent study in our group demonstrated that La^{2+}, a d^1 metal ion, can activate C–H bonds in propane to form $LaC_3H_6^{2+}$, for example. It is less clear, however, how this activation occurs.[15]

YCH_3^+ provides another opportunity to examine the possibility of C–H activation by the less common reaction pathway involving a multicentered transition state in the gas phase, because the d^1 electronic structure of the Y^+ center prevents it from oxidatively adding into chemical bonds. No reaction was observed for YCH_3^+ with H_2, D_2, propane, and *n*-butane. Absence of reaction with H_2 is not inconsistent with the recently determined values of $D°(Y^+{-}H) = 62 \pm 2$ kcal/mol and $D°(Y^+{-}CH_3) = 59 \pm 1$ kcal/mol.[16] However, when toluene is reacted with YCH_3^+, a product corresponding to $YC_7H_7^+$ is observed, exclusively (reaction 1). The primary product ion reacts further by condensing with

$$YCH_3^+ + \text{toluene} \rightarrow YC_7H_7^+ + CH_4 \qquad 100\% \qquad (1)$$

toluene to form $YC_{14}H_{15}^+$, the CID of which gives back $YC_7H_7^+$, confirming that it is a condensation process. Reaction 1 is analogous to the formation of Cp_2ZrD^+ from the reaction of $Cp_2ZrCH_3^+$ with D_2 and is also postulated to proceed via a multicentered intermediate. One peculiar feature of solution-phase C–H activation is that sp^2-hybridized C–H bonds are more susceptible to activation than sp^3-hybridized C–H bonds, despite the lower bond strength of the latter.[6] For example, the reaction of Cp_2ScCH_3 with toluene gives 86% of the Cp_2Sc–(methylphenyl) and only 14% of the Cp_2Sc–(benzyl) product.[6] This raised the possibility that both phenyl–hydrogen and benzyl–hydrogen bond activations may be present in reaction 1. In order to probe the possibility of phenyl–H activation, the reaction of YCH_3^+ with benzene was studied. Only the condensation product ion $YCH_3(C_6H_6)^+$ is observed. This is confirmed by CID of the product ion, which yields YCH_3^+ upon CID at 14 eV. The absence of a methane loss product ion both in the reaction of YCH_3^+ with benzene and in the CID of $YCH_3(C_6H_6)^+$ indicates that both thermal and collisionally activated phenyl–H bond activations do not occur. Thus, reaction 1 most likely proceeds by activation of only the benzyl–hydrogen bond, yielding (benzyl)yttrium ion. The enhanced reactivity of toluene, as compared to hydrogen, benzene, and simple alkanes, can be attributed to at least two factors: the lower bond strength of benzyl–hydrogen (~89 kcal/mol[17]) compared to those of H–H (~104 kcal/mol[17]), D–D, phenyl–H (~109 kcal/mol[17]), and C–H bonds in simple alkanes (~100 kcal/mol in ethane[17]), and the increased ion-induced dipole interaction between YCH_3^+ and toluene. The presence of the phenyl group should also lower the energy of the four-centered intermediate (structure I). A multicentered intermediate is also possible in this case in which the Y^+ can bond to the π-orbitals of the aromatic ring resulting in an η^3-bonding mode for the benzyl species.[18] CID on the product ion $YC_7H_7^+$ at 54 eV gives reactions 2–6. Reactions 3 and 4 involve the fragmentation of the ring system. Finally, the reversed order of reactivities with respect



I

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[19] Scheme I suggests that H/D scrambling should result in the formation of $YCH_xD_{3-x}^+$ in reaction 13. Due to noise in this region of the spectrum, we estimate that the unscrambled product, YCH_3^+, accounts for at least 85% of the $YCH_xD_{3-x}^+$ product ion while YCD_2H^+ and $YCHD_2^+$ may be present at 15% or less. Absence of substantial H/D scrambling suggests that either interconversion of the intermediates in Scheme I is slow compared to methyl abstraction or a different mechanism is operative.

$$\begin{array}{llrr} YC_7H_7^+ \xrightarrow{\text{CID}} & Y^+ + C_7H_7 & 7\% & (2) \\ \longrightarrow & YC_5H_2^+ + (C_2H_4 + H^\cdot) & 6\% & (3) \\ \longrightarrow & YC_5H_5^+ + C_2H_2 & 9\% & (4) \\ \longrightarrow & YC_7H_4^+ + H_2 + H^\cdot & 20\% & (5) \\ \longrightarrow & YC_7H_5^+ + H_2 & 58\% & (6) \end{array}$$

to C–H activation, i.e., benzyl-H bond over phenyl-H bond, from that observed in solution could arise due to different electronic structures and degree of coordinative saturation or possibly due to solvent effects.

Reactions with Alkenes. YCH_3^+ is reactive with all of the alkenes studied (Table I). The reaction of YCH_3^+ with ethylene forms $YC_3H_5^+$, exclusively (reaction 7). The lack of the product

$$YCH_3^+ + C_2H_4 \rightarrow YC_3H_5^+ + H_2 \quad 100\% \quad (7)$$

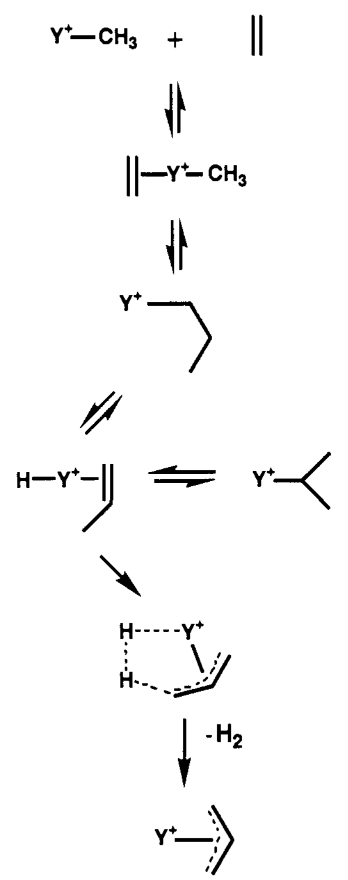
ion, $YC_2H_3^+$, indicates that vinyl-H bond activation does not occur for ethylene. The most likely structure for the product ion is (allyl)yttrium ion. CID on the product ion gives reactions 8–12 at 60 eV, which, with the exception of reaction 9, argue against

$$\begin{array}{llrr} YC_3H_5^+ \xrightarrow{\text{CID}} & Y^+ + C_3H_5 & 40\% & (8) \\ \longrightarrow & YH^+ + C_3H_4 & 16\% & (9) \\ \longrightarrow & YCH_3^+ + C_2H_2 & 13\% & (10) \\ \longrightarrow & YC_3H^+ + 2H_2 & 7\% & (11) \\ \longrightarrow & YC_3H_3^+ + H_2 & 24\% & (12) \end{array}$$

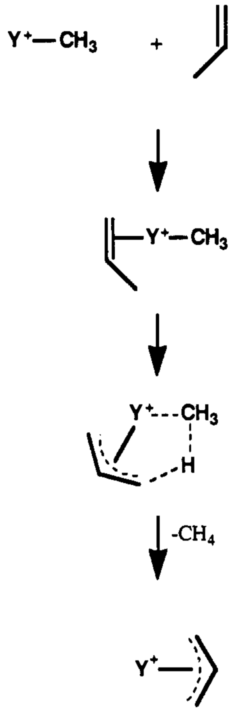
the less likely structure of (hydrido)(allene)yttrium ion. The reaction of benzene with $YC_3H_5^+$ yields the condensation product $Y(C_3H_5)(C_6H_6)^+$, exclusively, whose CID at 12 eV gives back $YC_3H_5^+$ only. The lack of allene displacement by benzene from $YC_3H_5^+$ and the lack of competitive elimination of allene with benzene upon CID of $Y(C_3H_5)(C_6H_6)^+$ all support the (allyl)yttrium ion structure. Reactions 13–16 are observed for the reaction of YCD_3^+ with ethylene. $YC_3H_5^+$ is also observed, but it arises from the secondary reaction of YCH_3^+, as confirmed by a double resonance experiment. Reactions 13 and 14 are particularly surprising. In contrast, for the reactions of $CoCD_3^+$ with ethylene and $Cp_2ZrCH_3^+$ with C_2D_4, only metal–allyl product ions with close to statistical H/D scrambling were observed.[3,14] Scheme I is proposed to explain the above results for YCH_3^+. In this mechanism, the reaction occurs by initial ethylene insertion into Y^+–CH_3 to form Y^+–propyl. Its rearrangement to Y^+–isopropyl through the (hydrido)(propene)yttrium ion intermediate, coupled with the various reversible steps, explains the emergence of YCH_3^+ in reaction 13. The predominance of YCH_3^+ in reaction 13 indicates that such processes are facile.[19] As shown in Scheme I, it is necessary to incur a multicentered mechanism for H_2 elimination from the (hydrido)(propene)yttrium intermediate to give (allyl)yttrium ion, except in this case, one member of the multicentered transition state is a partially formed allyl ligand bonded to the metal center, contributing to the lowering of the energy of the transition state.

$$\begin{array}{lllrr} YCD_3^+ + C_2H_4 & \rightarrow & YCH_3^+ + C_2HD_3 & 49\% & (13) \\ & \rightarrow & YCH_nD_{3-n}^+ + C_2H_{4-n}D_n & 6\% & (14) \\ & & (n = 1, 2) & & \\ & \rightarrow & YC_3H_3D_2^+ + HD & 41\% & (15) \\ & \rightarrow & YC_3H_2D_3^+ + H_2 & 4\% & (16) \end{array}$$

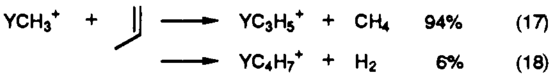
Scheme I



Scheme II



Reactions 17 and 18 were observed between YCH_3^+ and propene. CID on $YC_3H_5^+$ from reaction 17 gives fragmentations



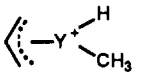
$$\begin{array}{lrr} YCH_3^+ + C_3H_6 \longrightarrow YC_3H_5^+ + CH_4 & 94\% & (17) \\ \longrightarrow YC_4H_7^+ + H_2 & 6\% & (18) \end{array}$$

identical with that from reaction 7 of YCH_3^+ with ethylene, supporting the (allyl)yttrium ion structure in reaction 7. Reactions 19–24 were observed for the reaction of YCD_3^+ with propene. The

$$\begin{array}{lllrr} YCD_3^+ + C_3H_6 & \rightarrow & YCH_3^+ + C_3H_3D_3 & 6\% & (19) \\ & \rightarrow & YCH_2D^+ + C_3H_4D_2 & 3\% & (20) \\ & \rightarrow & YC_3H_5^+ + CD_3H & 83\% & (21) \\ & \rightarrow & YC_3H_3D_2^+ + CH_3D & 2\% & (22) \\ & \rightarrow & YC_4H_5D_2^+ + HD & 3\% & (23) \\ & \rightarrow & YC_4H_4D_3^+ + H_2 & 3\% & (24) \end{array}$$

product ions in reactions 21 and 22 are particularly interesting and cannot be explained solely by the migratory insertion of the C=C double bond into the Y^+—CH_3 bond, followed by CH_4 elimination. The initial intermediates generated by migratory insertion, (2-methylpropyl)yttrium ion and (*sec*-butyl)yttrium ion, would yield equal amounts of CH_4 and CD_3H, respectively. Instead, this result can be explained by a σ-bond metathesis mechanism involving a multicentered mechanism with a partially formed allyl ligand as one center during the transition state (Scheme II). This mechanism involves the activation of an allylic C–H bond, indicating the contribution of the allyl group when compared to the inability to activate C–H bonds of ethylene and saturated alkanes. Reactions 19, 20, 23, and 24, however, can still be explained by a mechanism involving migratory insertion in analogy to Scheme I and will be discussed in more detail later.

Although the σ-metathesis mechanism is appealing, alternative mechanisms can also be proposed to explain the elimination of CH_4 in these reactions. While oxidative addition of YCH_3^+ into the allylic C–H bond of propene to form the intermediate structure II is not possible since 2 electrons are required on the metal center



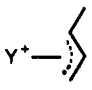
II

and only 1 electron is available, structure II can still be formed by an alternative route. Specifically, the energy available in the ion-induced dipole complex formed between YCH_3^+ and propene is sufficient to permit simple hydrogen abstraction by YCH_3^+ to form structure II followed by CH_4 elimination. To test for this mechanism, YCH_3^+ was reacted with CD_3CHCH_2 (reactions 25–32). While σ-metathesis would yield CH_3D as the exclusive

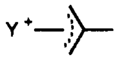
$YCH_3^+ + CD_3CHCH_2 \rightarrow YCD_3^+ + C_3H_6$ 11% (25)
$\rightarrow YCHD_2^+ + C_3H_5D$ 4% (26)
$\rightarrow YC_3H_5^+ + CHD_3$ 11% (27)
$\rightarrow YC_3H_4D^+ + CH_2D_2$ 6% (28)
$\rightarrow YC_3H_3D_2^+ + CH_3D$ 43% (29)
$\rightarrow YC_3H_2D_3^+ + CH_4$ 6% (30)
$\rightarrow YC_4H_5D_2^+ + HD$ 6% (31)
$\rightarrow YC_4H_4D_3^+ + H_2$ 13% (32)

methane loss product, the hydrogen-abstraction mechanism would permit scrambling of the allylic hydrogens on propene resulting in both CH_3D and CH_4 loss. The predominance of CH_3D loss in reaction 29 strongly supports the presence of σ-metathesis, while H/D scrambling in reactions 27, 28, and 30 indicates the presence of at least two other mechanisms of which hydrogen abstraction and migratory insertion are reasonable candidates. These results indicate that the hydrogen abstraction mechanism may indeed be operative in all of the reactions in this study. However, it will not be further emphasized here.

$YC_4H_7^+$ is the sole product ion formed from the reaction of YCH_3^+ with isobutene and is predominant in the reaction with *trans*-2-butene. The reactions of YCD_3^+ with these two compounds yield CD_3H loss, exclusively, again indicating the functioning of Scheme II. Y^+–(1-methylallyl), structure III, and Y^+–(2-methylallyl), structure IV, are expected from such a mechanism for *trans*-2-butene and isobutene, respectively. CID



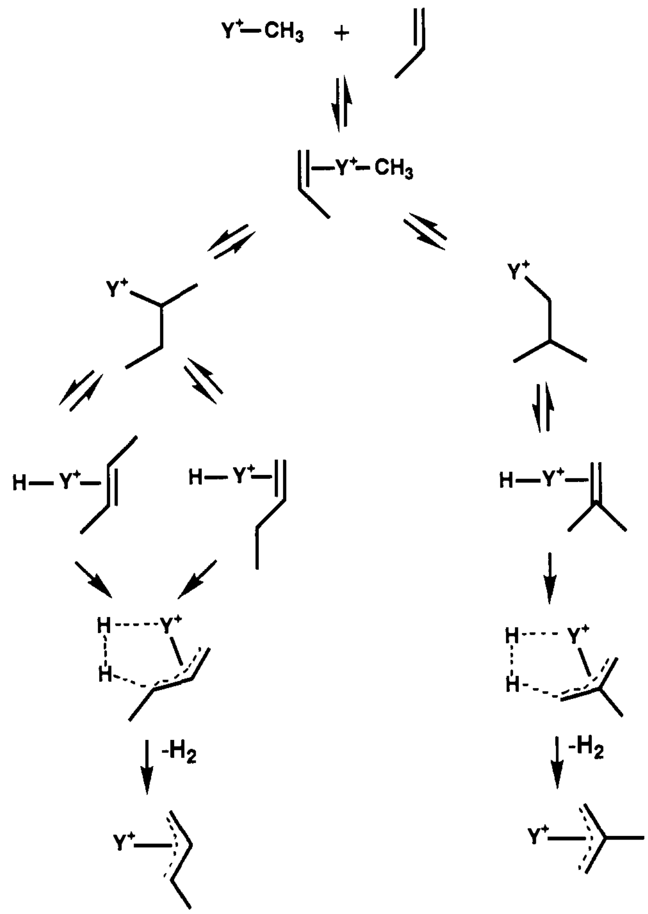
III



IV

on the product ions indeed reveals different structures, with the CID at 34 eV shown in reactions 33–40 (Table II) for the ion from both butenes, as well as for the product ion from propene in reaction 18. It can be seen that the $YC_4H_7^+$ from propene consists mainly of structure IV. This is also indicated by the appearance of a minor amount of YCH_3^+ from reaction 19. Unlike the ethylene case, the migratory insertion of the C═C bond into $Y^+–CH_3$ by the unsymmetrical propene ligand can lead to the formation of (*sec*-butyl)yttrium ion and (2-methylpropyl)-yttrium ion (Scheme III).

Scheme III



Specific ion–molecule reactions of structures III and IV were studied in order to determine their relative contributions in reaction 18. The product ion from isobutene reacts with benzene to form $Y(C_4H_7)(C_6H_6)^+$, exclusively, whose CID gives back only $YC_4H_7^+$ over the energy range studied (7–22 eV), confirming that it is a simple condensation process. In contrast, the reaction of the product ion from *trans*-2-butene with C_6H_6 gives ~63% $YC_8H_9^+$ and ~37% $YC_{10}H_{11}^+$. CID of the former at 25 eV yields 11% YC_2H^+, 48% $YC_2H_3^+$, and 41% $YC_8H_7^+$, and CID of the latter at 22 eV yields $YC_4H_5^+$ only, both suggesting the cleavage of the allyl structure upon reacting with benzene. In the reaction of C_6H_6 with $YC_4H_7^+$ from reaction 18, $Y(C_4H_7)(C_6H_6)^+$ accounts for ~80% and $YC_8H_9^+$ and $YC_{10}H_{11}^+$ account for ~20% of the product ions, indicating the presence of roughly 20% of structure III and 80% of structure IV, respectively. It should be noted that these ratios may not necessarily reflect the relative preference for CH_3 migration onto propene, i.e., the 1- vs 2-position, but rather the "equilibrium" proportions of (*sec*-butyl)yttrium ion and (2-

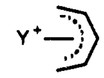
Table II. Product Ion Distributions from the Collision-Induced Dissociation of $YC_4H_7^+$ from Various Sources

reaction	2-butene	isobutene	propene	predicted (see text)	reaction no.
$YC_4H_7^+ \xrightarrow{\text{CID}} Y^+ + C_4H_7$	3	9	12	8	(33)
$\rightarrow YH^+ + C_4H_6$	18	2	7	5	(34)
$\rightarrow YCH_3^+ + C_3H_4$		38	34	30	(35)
$\rightarrow YC_2H^+ + C_2H_6$	21	6	7	9	(36)
$\rightarrow YC_2H_3^+ + C_2H_4$	14	4	6	6	(37)
$\rightarrow YC_3H_3^+ + CH_4$		32	19	26	(38)
$\rightarrow YC_4H_3^+ + 2H_2$	6	2	3	3	(39)
$\rightarrow YC_4H_5^+ + H_2$	38	7	12	13	(40)

methylpropyl)yttrium ion achieved by their easy interconversion. However, this could not be achieved by a (hydrido)(butene)yttrium intermediate, but rather requires a (methyl)(propene)yttrium ion intermediate from a facile β-methyl abstraction, as shown in Scheme III. Finally, the predicted relative intensities for the CID of $YC_4H_7^+$ from propene in reactions 33–40, assuming 20% structure III and 80% structure IV, agree well within our experimental uncertainty.

The chemistry of the other two linear butene isomers, 1-butene and *cis*-2-butene, with YCH_3^+ is identical with that of *trans*-2-butene discussed above, with the major product ion $YC_4H_7^+$ also having the same structure and reactivity with benzene. Finally, it is also interesting that facile reactions are observed for the ion of structure III with linear butenes to give mostly $YC_8H_{13}^+$, along with some $YC_5H_9^+$, $YC_5H_{11}^+$, and $YC_7H_{12}^+$. No reaction was observed for structure IV with isobutene. The lack of further reaction for structure IV with small alkenes seems to be somewhat general. For example, C_2H_4 reacts with III, but not with IV.

The reaction of YCH_3^+ with 1-pentene gives a predominant peak of $YC_5H_7^+$. The formation of this ion may be explained by the elimination of an allylic hydrogen, along with the methyl originally attached to the metal center in the form of CH_4, followed by another dehydrogenation to give (pentadienyl)yttrium ion, structure V, the linear counterpart of a cyclopentadienyl structure.

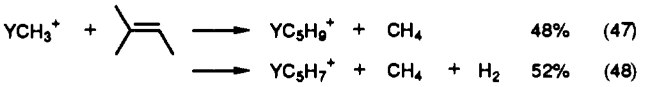


V

Reactions 41–46 are observed upon its CID at 50 eV. As discussed below, subsequent CID on $YC_5H_5^+$ generated from reaction 45 suggests that cyclization accompanied by dehydrogenation is a facile process. The two minor product ions from the reaction of YCH_3^+ with 1-pentene, $YC_6H_9^+$ and $YC_6H_{11}^+$, are formed from the migratory insertion mechanism, again indicating that such a process is not as favored as the allylic hydrogen elimination. The observation of $YC_4H_8^+$ ion is somewhat unusual and surprising, indicating that as the alkene gets larger, other alternative reaction pathways also occur.

$$\begin{array}{lllrr}
YC_5H_7^+ & \xrightarrow{\text{CID}} & Y^+ + C_5H_7 & 4\% & (41)\\
 & \longrightarrow & YC_3H_3^+ + C_2H_4 & 11\% & (42)\\
 & \longrightarrow & YC_3H_5^+ + C_2H_2 & 6\% & (43)\\
 & \longrightarrow & YC_4H_6^+ + CH & 7\% & (44)\\
 & \longrightarrow & YC_5H_5^+ + H_2 & 66\% & (45)\\
 & \longrightarrow & YC_5H_6^+ + H^{\bullet} & 6\% & (46)
\end{array}$$

Reactions 47 and 48 were observed for the reaction of YCH_3^+ with 2-methyl-2-butene. Corresponding reaction of YCD_3^+ leaves no deuterium labeling on the product ions. Either (1,1-dimethylallyl)yttrium ion (structure VI) or (1,2-dimethylallyl)yttrium ion (structure VII) is expected for the product ion in reaction 47 from the activation of an allylic C–H bond by the σ-bond metathesis mechanism. CID on $YC_5H_9^+$ from reaction 47 at 16 eV gives mostly single and double dehydrogenation product ions, 72% $YC_5H_7^+$, 24% $YC_5H_5^+$, and 4% $YC_3H_4^+$. Further dehydrogenation of both structures VI and VII is expected to give structure VIII for the product ion in reaction 48. CID on the product ion $YC_5H_7^+$ at 31 eV gives reactions 49 and 50, indicating that it is indeed a different structure from (pentadienyl)yttrium ion, structure V. Surprisingly, CID on $YC_5H_5^+$ from reaction 51 is strikingly similar to that of $YC_5H_5^+$ from reaction 45 and from $YC_5H_5^+$ generated in the reaction of YCH_3^+ and cyclopentene, as discussed below.



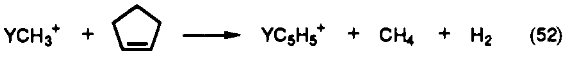
VI

VII

VIII

$$\begin{array}{lllrr}
YC_5H_7^+ & \xrightarrow{\text{CID}} & YC_3H_2^+ + C_2H_4 + H^{\bullet} & 8\% & (49)\\
 & \longrightarrow & YC_3H_3^+ + C_2H_4 & 14\% & (50)\\
 & \longrightarrow & YC_5H_5^+ + H_2 & 78\% & (51)
\end{array}$$

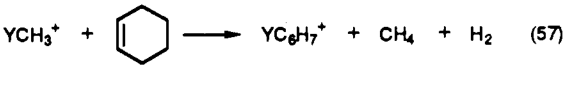
The reaction of YCH_3^+ with cyclopentene leads to the formation of $YC_5H_5^+$ exclusively (reaction 52). Again, the reaction proceeds by the activation of an allylic C–H bond. Subsequent dehydrogenation presumably leads to the formation of (cyclopentadienyl)yttrium ion. CID on the product ion at 70 eV leads to ring cleavage as well as ring elimination (reactions 53–56). For comparison, the CID results of $YC_5H_5^+$ species generated in reactions 45 and 51, under otherwise identical conditions, are also given. The variations of these product distributions fall well within the experimental error of ±15% absolute and suggest, although not conclusively, that they may all have the same structure, presumably that of the stable Y^+–cyclopentadienyl species. For the ion in reaction 51, this would require a fairly complex rearrangement.

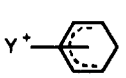


$$\begin{array}{lllrrrr}
 & & & \text{rxn. } 52 & \text{rxn. } 45 & \text{rxn. } 51 & \\
YC_5H_5^+ & \xrightarrow{\text{CID}} & Y^+ + C_5H_5 & 41\% & 33\% & 39\% & (53)\\
 & \longrightarrow & YC_3H^+ + C_2H_4 & 20\% & 25\% & 18\% & (54)\\
 & \longrightarrow & YC_3H_2^+ + C_2H_2 + H^{\bullet} & 10\% & 17\% & 19\% & (55)\\
 & \longrightarrow & YC_3H_3^+ + C_2H_2 & 29\% & 25\% & 24\% & (56)
\end{array}$$

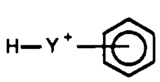
The secondary reaction of the product ion in reaction 52 with cyclopentene leads to the formation of yttrocene cation exclusively. Its CID at low energy (22–36 eV) eliminates one cyclopentadienyl fragment to give $YC_5H_5^+$. However, the ring cleavage product ion, $YC_8H_8^+$, was also observed at higher energy (55 eV). The observation of a facile secondary reaction for (cyclopentadienyl)yttrium ion is interesting because it is also formally a d^1 system incapable of undergoing oxidative addition by the metal center. This suggests that the cyclopentadienyl ligand actively participates in the reaction.

The reaction of YCH_3^+ and YCD_3^+ with cyclohexene yields $YC_6H_7^+$ exclusively (reaction 57). Its similarity to reaction 52 suggests that the product ion is the (η^5-cyclohexadienyl)yttrium ion (structure IX). However, its rearrangement to the (hydrido)(benzene)yttrium ion (structure X) is also possible. CID on $YC_6H_7^+$ at 29 eV gives reactions 58–62. As discussed below, the fragmentation pattern observed suggests the presence of at least a finite amount of the (η^5-cyclohexadienyl)yttrium ion structure. To further probe this structure, the $YC_6H_7^+$ was reacted with deuterated benzene (reactions 63–65). The dehydrogenation product ion in reaction 64 strongly argues against a (hydrido)(benzene)yttrium structure. CID on the product ion $YHC_6D_6^+$ from reaction 63 at 45 eV gives 60% YH^+ and 40% $YC_6D_6^+$, suggesting a (hydrido)(benzene)yttrium structure in this case. This result is consistent with $D°(Y^+–H) = 62 \pm 2$ kcal/mol >





IX



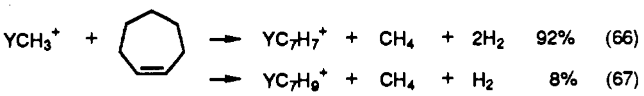
X

$$\begin{array}{lllrr}
YC_6H_7^+ & \xrightarrow{\text{CID}} & Y^+ + C_6H_7 & 2\% & (58)\\
 & \longrightarrow & YH^+ + C_6H_6 & 53\% & (59)\\
 & \longrightarrow & YC_6H_4^+ + H_2 + H^{\bullet} & 7\% & (60)\\
 & \longrightarrow & YC_6H_5^+ + H_2 & 17\% & (61)\\
 & \longrightarrow & YC_6H_6^+ + H^{\bullet} & 21\% & (62)
\end{array}$$

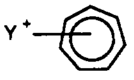
$$\begin{array}{lllrr}
YC_6H_7^+ + C_6D_6 & \rightarrow & YHC_6D_6^+ + C_6H_6 & 63\% & (63)\\
 & \rightarrow & YC_6H_5C_6D_6^+ + H_2 & 6\% & (64)\\
 & \rightarrow & YC_6H_7C_6D_6^+ & 31\% & (65)
\end{array}$$

$D°(Y^+-C_6H_6) = 50 \pm 3$ kcal/mol.[16,20] In addition, the further reaction of $YHC_6D_6^+$ with C_6D_6 gives only the condensation product ion $YH(C_6D_6)_2^+$. These results support the presence of the (η^5-cyclohexadienyl)yttrium ion structure in reaction 57. Finally, the observation of reaction 62 suggests that either the conversion from structure IX to structure X is a facile process or reaction 57 gives a mixture of structures IX and X.

Reactions 66 and 67 were observed for the reaction of YCH_3^+ with cycloheptene. The most likely structure for the product ion



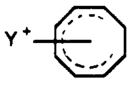
from reaction 66 is (cycloheptatrienyl)yttrium ion (structure XI). This is supported by CID, which gives only the ring-reduction



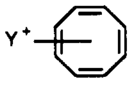
XI

product ion, $YC_5H_5^+$, over the energy range studied (14–67 eV). This is in obvious contrast to that of (benzyl)yttrium ion discussed earlier.

Finally, the reaction with cyclooctene gives 50% $YC_8H_9^+$ and 14% $YC_8H_8^+$, along with a wide variety of other ring-cleavage product ions. The likely structures for these two product ions are (η^7-cyclooctatrienyl)yttrium ion (structure XII) and (cyclooctatetrene)yttrium ion (structure XIII), respectively. CID of the former at 62 eV gives reactions 68–72. The observation of



XII



XIII

$$\begin{array}{llll} YC_8H_9^+ \xrightarrow{CID} & YC_5H_5^+ + C_3H_4 & 6\% & (68) \\ \longrightarrow & YC_6H_5^+ + C_2H_4 & 19\% & (69) \\ \longrightarrow & YC_7H_7^+ + CH_2 & 10\% & (70) \\ \longrightarrow & YC_8H_7^+ + H_2 & 14\% & (71) \\ \longrightarrow & YC_8H_8^+ + H^\bullet & 51\% & (72) \end{array}$$

$YC_8H_8^+$ as both a product ion and a significant CID fragment suggests the likelihood of the rearrangement of structure XIII into (hydrido)(cyclooctatetrene)yttrium ion. This is supported by the fact that upon reacting $YC_8H_9^+$ with perdeuterated benzene, both $Y(C_8H_8)(C_6D_6)^+$ and $Y(C_8H_9)(C_6D_6)^+$ are observed in about equal intensities.

Conclusion

This study shows interesting chemistry between YCH_3^+ and a wide variety of small olefins in the gas phase. The lone valence electron on the yttrium center in YCH_3^+ prevents it from undergoing oxidative addition into C–H or C–C bonds. This provides an opportunity to explore alternative pathways of C–H or C–C bond activation.

The reaction of YCH_3^+ with toluene to form Y^+–benzyl provides conclusive evidence that C–H bond activation is achieved by a multicentered intermediate. However, such a reaction pathway is unfavorable for H–H, D–D, and C–H bonds in simple alkanes and phenyl–hydrogen bonds. The latter is in contrast to solution-phase results.

Such C–H bond activation via a multicentered mechanism is also the predominant pathway for the reaction of YCH_3^+ with alkenes. An allylic hydrogen atom is activated and eliminated with the methyl group on YCH_3^+. This leads to the formation of a series of (allyl)yttrium product ions, such as Y^+–allyl, Y^+–(1-methylallyl), and Y^+–(2-methylallyl) from propene, butene, and isobutene, respectively. The two $YC_4H_7^+$ isomers show distinctive CID fragmentation patterns and further ion–molecule reactivities. With cyclic alkenes, such an allyl structure undergoes further dehydrogenation to give the ring structures (η^5-cyclopentadienyl)yttrium ion, (η^5-cyclohexadienyl)yttrium ion, (η^7-cycloheptatrienyl)yttrium ion, and (η^7-cyclooctatrienyl)yttrium ion from 5-, 6-, 7-, and 8-membered cyclic alkenes, respectively.

It is interesting that allylic C–H activation of alkenes is a favored pathway over the alternative reaction pathway of C=C double bond insertion into Y^+-CH_3. Migratory insertion is the exclusive reaction initiation pathway for ethylene because of the lack of allylic C–H bonds. A labeling study using YCD_3^+ indicated facile rearrangement of Y^+–propyl to Y^+–isopropyl and facile reversible steps for the migratory insertion and the β-methyl abstraction processes. In the case of propene, however, migratory insertion only accounts for a minor amount of the total reaction.

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[20] Lech, Leo M. Ph.D. Thesis, Purdue University, 1988.