Gas-Phase Chemistry of the Yttrium−Imido Cation YNH^+ with Alkenes: β-Hydrogen Activation by a d^0 System via a Multicentered Transition State

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The gas-phase chemistry of the yttrium−imido cation with alkenes was studied by using Fourier transform mass spectrometry to explore the chemistry of transition metal ion complexes with low-valence metal centers. The YNH^+ species was synthesized by reacting Y^+, generated by laser desorption, with ammonia. The dehydrogenation reaction is exothermic, yielding a lower limit for the imido bond energy of $D°(Y^+−NH) > 101$ kcal/mol. Due to the electron deficiency of the metal center upon binding to NH, the further reactivity of YNH^+ can only be explained by a reaction mechanism involving a multicentered transition state. YNH^+ reacts with ethene predominantly by dehydrogenation to produce $YC_2H_3N^+$. Thus, instead of the metathesis reaction involving the cleavage of the 2-aza-1-metallacyclobutane intermediate, a β-hydrogen transfers to the metal center and is then eliminated with a hydrogen from the remaining CH_2 group to complete the reaction. $YC_2H_3N^+$ is proposed to be 2-aza-1-metallacyclobut-3-ene. The subsequent reaction of $YC_2H_3N^+$ with C_2H_4 again proceeds by dehydrogenation, forming the metallabenzene $YC_4H_5N^+$, with a CH replaced by NH. Dehydrogenation is also facile in the reaction with propene, and the structure of the product, $YC_3H_5N^+$, is proposed to be either 2-azametallacyclobut-3-ene or bent 2-aza-1-metallacyclopentene complex ions. The product from loss of CH_4 in the reaction of YNH^+ with propene, $YC_2H_3N^+$, has the same structure as the dehydrogenation product from the reaction between YNH^+ and C_2H_4. $YC_3H_5N^+$, formed as the predominant product ion by loss of CH_4 in the reaction of YNH^+ with isobutene, is proposed to be the 2-aza-1-metallacyclobut-3-ene complex isomer, again consistent with the suggested multicentered transition state mechanism. All three linear butenes, 1-butene, *cis*-2-butene, and *trans*-2-butene, react very similarly with YNH^+, yielding a variety of product ions with the predominant loss of NH_3 resulting in the formation of $YC_4H_6^+$. Structural studies on this ion suggest that it is bent metallacyclopent-3-ene, not the butadiene isomer.

Introduction

The gas-phase chemistry of transition-metal ions has developed into an active and interesting area of research which provides a great deal of information on reaction mechanisms, kinetics, and thermochemistry.[1,2] One important aspect of our ongoing research is the detailed study of the chemistry of transition-metal complex ions with a limited number of ligands attached to the metal center. Such studies not only examine the intrinsic effect of the ligand on the reactivity of the metal center but also provide important mechanistic information and models for analogous coordination complexes proposed to exist as intermediates in homogeneous and heterogeneous catalytic transformations. To this extent, a wide variety of ionic metal−ligand species have been studied in the gas phase by several groups.[3] In addition, potentially important types of hydrocarbon activation by d-block elements have been rapidly developed over the past several years in the solution phase.[4] Generally, in these processes C−H activation is initiated by electron-rich metal centers via an oxidative insertion pathway which is predominant. In contrast, low-valence d^0 systems preclude the oxidative insertion of the metal center into the C−H bond as the initiation step[5] and, hence, must undergo different mechanisms such as σ-bond metathesis which involves a multicentered transition state as the key intermediate.[6]

One of our current focuses, therefore, has been on species with low-valence electron metal centers to probe

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alternative mechanisms of C—C and C—H activation in the gas phase besides oxidative insertion. For example, we recently reported the chemistries of YCH_3^+ and $Sc(CH_3)_2^+$, having d^1 and d^0 electronic configurations, respectively.[5a,b] Both of these low-valence metal centers react with ethene, exclusively, by migratory insertion of the C═C bond into the M^+—CH_3 bond, followed by the elimination of H_2. However, the activation of the allylic C—H bond via a multicentered σ-bond metathesis mechanism is observed to be the favored pathway over the migratory insertion pathway for higher alkenes.

An earlier study from our group reported the gas-phase chemistry of MNH^+ (M = V, Fe) in detail and suggested that $FeNH^+$ transfers the NH group to the olefin molecule through a metathesis reaction involving a four-centered metallacyclic intermediate.[7a] In contrast, VNH^+ is unreactive with ethene and, while it reacts with propene, it is not observed to transfer the NH group in part due to the higher bond strength of $D°(V^+{-}NH) = 101 \pm 7$ kcal/mol compared to $D°(Fe^+{-}NH) = 54 \pm 14$ kcal/mol.[7a]

In this paper we report the interesting chemistry of YNH^+ with simple alkenes and compare the results to those from previous studies on $FeNH^+$ and VNH^+.[7a] Due to the deficiency of electrons on the metal center, YNH^+ also precludes reaction pathways involving oxidative addition of the metal center into C—C or C—H bonds and provides an opportunity to probe other reaction mechanisms involving multicentered transition states.

Experimental Section

All experiments were performed on a prototype Extrel FTMS-1000 Fourier transform ion cyclotron resonance mass spectrometer (FTICRMS).[8] The instrument is equipped with a 5.2 cm cubic trapping cell situated between the poles of a Walker Scientific 15 in. electromagnet maintained at 1.0 T. Y^+ was produced by focusing the fundamental output (1064 nm) of a pulsed Quanta Ray Nd:YAG laser onto a thin high-purity target of yttrium.[9,10]

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. The reagents were introduced into the cell either through Varian leak valves, producing a constant background pressure, or via General Valve Corp. Series 9 pulsed solenoid valves.[11] Pressures were measured with an uncalibrated Bayard-Alpert ionization gauge and were usually 1×10^{-6} Torr for samples and 2×10^{-5} Torr total with added background argon serving as collision gas for collision-induced dissociation (CID) experiments[12,13] and for cooling ions before ion—molecule reactions.

CID experiments were performed on product ions of structural importance. CID in the FTICRMS is known to be a multiple-collision process.[12] Thus, the collision energy, given in the laboratory frame throughout the paper, corresponds to the maximum translational energy achievable and was varied typically in the range of 0—100 eV. The spread in kinetic energy depends on the average kinetic energy and is less than 5% at the energies used in this study.[14]

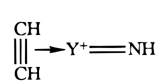
YNH^+ and YND^+ were generated by the reaction of Y^+ with pulsed-in NH_3 and ND_3, respectively.[7a] Observation of this reaction implies $D°(Y^+{-}NH) > 101$ kcal/mol.[15] The reactant ions were allowed to collide with background argon for at least 1 s to produce thermalized ions and were then carefully isolated by swept double-resonance experiments.[16] Alkene neutrals were introduced into the cell by a second pulsed valve after the isolation of YNH^+ or YND^+ to avoid any complications due to reactions of Y^+ with alkene neutrals. The reproducibility of the results obtained under different background pressures and cooling times suggests that the results are representative of the thermalized species. However, a contribution due to unthermalized ions cannot be completely ruled out. The relative percentage ratios reported are the average of at least three runs and are reproducible with a ±5% absolute uncertainty.

Results and Discussion

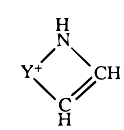
Reaction with Ethene. YNH^+ reacts with ethene by dehydrogenation to form $YC_2H_3N^+$ (reaction 1). At higher pressures (about 10^{-5} Torr), a trace amount of $YC_2H_2^+$ was also observed. Formation of $YC_2H_2DN^+$ from the reaction of YND^+ with ethene (reaction 3) indicates that the two hydrogens lost are from ethene. Observation of exothermic dehydrogenation of ethene by YNH^+ in reaction 1 suggests a lower limit for $D°(YNH^+{-}C_2H_2) > 42$ kcal/mol.[15]

YNH^+	+	C_2H_4	⟶	$YC_2H_3N^+$	+	H_2	> 99%	(1)
			⟶	$YC_2H_2^+$	+	NH_3	trace	(2)
YND^+	+	C_2H_4	⟶	$YC_2H_2DN^+$	+	H_2	> 99%	(3)
			⟶	$YC_2H_2^+$	+	NH_2D	trace	(4)

There are two reasonable structures for $YC_2H_3N^+$ in reaction 1, **1** and **2**. CID on $YC_2H_3N^+$ from reaction 1



1



2

at 50 eV yields YNH^+, exclusively, while CID on $YC_2H_2DN^+$ from reaction 3 at 50 eV gives 16% YNH^+ and 84% YND^+. The H/D scrambling probably occurs during the CID activation process. Unfortunately, the CID results

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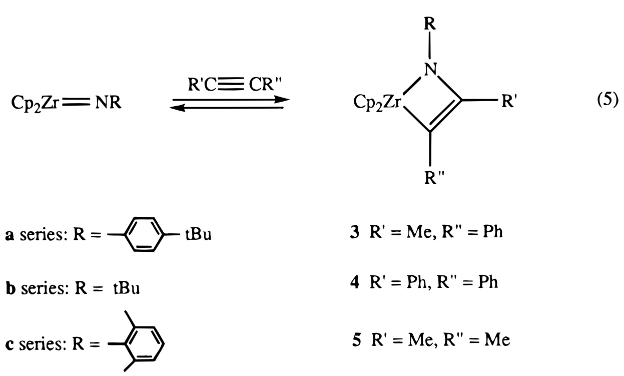
are insufficient to distinguish the two structures, since both would be expected to fragment by C_2H_2 loss.

Thus, the structure of $YC_2H_3N^+$ was probed further by reacting it with benzene, which resulted in the condensation product, $YC_2H_3N(C_6H_6)^+$, exclusively. The lack of displacement of C_2H_2 by benzene favors structure **2**, since such a displacement is expected with structure **1**, given $D°(Y^+{-}C_6H_6) = 54 \pm 5$ kcal/mol[17] $\approx D°(Y^+{-}C_2H_2) = 52 \pm 3$ kcal/mol.[18] Furthermore, CID of this condensation product at 10 eV gives back $YC_2H_3N^+$, exclusively, again implying that the C_2H_3N is intact. It is possible that the imido group in structure **1** would alter the relative bond energies of benzene and acetylene to Y^+, yielding misleading results. The absence of the thermoneutral exchange of C_2D_2 with $YC_2H_3N^+$, however, provides additional support that structure **2**, 2-aza-1-metallacyclobut-3-ene, is most likely to be the structure for the dehydrogenation product, $YC_2H_3N^+$.

In solution, the chemistry of cyclometalation in the reactions of alkylidene, oxo, sulfido, and imido complexes with unsaturated hydrocarbons has been well established.[19] Particularly relevant to this study are the bond-coupling reactions of two-membered group 4 metallacyclic complexes which are supported by cyclopentadiene or aryloxide ligands.[20] The alkyne cycloaddition of zirconium−imido, for example, was observed to give azametallacyclobutene complexes (reaction 5).[21]



Later, the zirconium−imido analogues $Cp^*_2Zr{=}O$ and $Cp^*_2Zr{=}S$ (Cp^* = pentamethylcyclopentadienyl ligand) were also generated and alkyne cycloaddition of these complexes was successfully demonstrated by the same group.[22] The possibility that compounds **3**−**5** exist as imidoalkyne adducts was ruled out by an X-ray diffraction study of **4c**, which confirmed its azametallacyclobutene structure.[21]

The proposed mechanism for reaction 1 is shown in Scheme 1 and involves a multicentered transition state generated by opening the double bonds of both YNH^+ and ethene. β-Hydrogen transfer onto the yttrium metal center, followed by the elimination of hydrogen, completes the reaction. Reaction 2 apparently involves the transfer of hydrogens from C_2H_4 to the yttrium metal center and then to NH, followed by elimination of NH_3 to form Y^+−acetylene. Assuming that reaction 2 is thermoneutral or somewhat endothermic (one explanation for it being observed only in trace amounts) and given that $D°(Y^+{-}C_2H_2) = 52 \pm 3$ kcal/mol[18] and that the process $C_2H_4 + NH \rightarrow C_2H_2 + NH_3$ is 59 kcal/mol exothermic,[15] the limit $D°(Y^+{-}NH) \geq 111 \pm 3$ kcal/mol is suggested. If the absence of reaction 2 is due to kinetic rather than thermochemical reasons, however, a limit cannot be derived. Otherwise, this limit is consistent with $D°(Y^+{-}NH) > 101$ kcal/mol, mentioned above, and can be compared to theoretical[23] and experimental[24] values of $D°(Sc^+{-}NH) = 106$ and 119 kcal/mol, respectively.

Interestingly, in an earlier study, VNH^+ was found to be unreactive with ethene, even though $V^+{-}NH$ is considered to have a double bond like $Y^+{-}NH$, while $FeNH^+$ with a single bond[7b] was observed to react with ethene to produce a wide variety of products (reactions 6−10).[7a] Reaction 7 involves olefin metathesis to form

$FeNH^+ + C_2H_4$	⟶	$Fe^+ + C_2H_4NH$	38%	(6)
	⟶	$FeCH_2^+ + CH_2NH$	19%	(7)
	⟶	$Fe(NH_3)^+ + C_2H_2$	16%	(8)
	⟶	$Fe(HCN)^+ + CH_4$	15%	(9)
	⟶	$FeNH(C_2H_2)^+ + H_2$	12%	(10)

$FeCH_2^+$, a process which does not occur in the reaction of YNH^+ with ethene. Reaction 8 is analogous to reaction 2, except that NH_3 is apparently more strongly bound to Fe^+ than is C_2H_2 while for Y^+ the opposite is apparently true. The observation of reactions 6 and 7, and the lower percentage of dehydrogenation (reaction 10), can be attributed to the bond energy $D°(Fe^+{-}NH) = 54 \pm 14$ kcal/mol[7a] being weaker than $D°(Y^+{-}NH) > 101$ kcal/mol.[15]

$YC_2H_3N^+$ from reaction 1 also reacts readily with ethene by dehydrogenation to form $YC_4H_5N^+$ (reaction 11), and $YC_2H_2DN^+$ from reaction 3 reacts to give $YC_4H_4DN^+$ (reaction 12). CID on $YC_4H_5N^+$ from reac-

$$YC_2H_3N^+ + C_2H_4 \longrightarrow YC_4H_5N^+ + H_2 \quad (11)$$

$$YC_2H_2DN^+ + C_2H_4 \longrightarrow YC_4H_4DN^+ + H_2 \quad (12)$$

tion 11 at 52 eV shows extensive cleavage (reactions 13−16). The loss of HCN from nitrogen-containing heteroaromatic compounds upon CID is not uncommon in gas-phase chemistry.[25]

$YC_4H_5N^+$	$\xrightarrow{CID}$	$YC_3H_4^+ + HCN$	58%	(13)
	⟶	$YC_3H_2^+ + HCN + H_2$	16%	(14)
	⟶	$YNH^+ + C_4H_4$	15%	(15)
	⟶	$Y^+ + C_4H_5N$	11%	(16)

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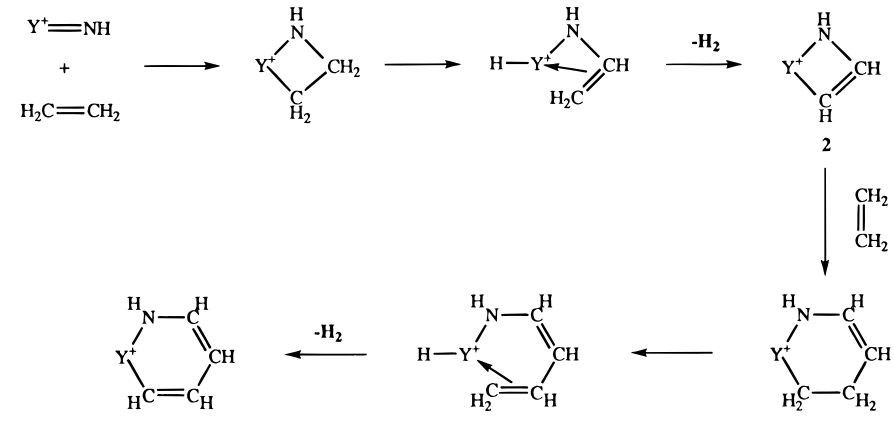
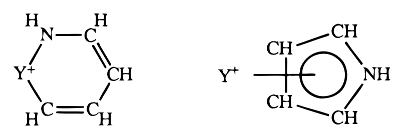
Scheme 1



Reaction of $YC_4H_5N^+$ from reaction 11 with benzene yields the condensation product, $YC_4H_5N(C_6H_6)^+$, exclusively, which upon CID at 11 eV gives back $YC_4H_5N^+$. In addition, no exchange with C_2D_2 is observed. These experiments indicate an intact ligand in the product ion, $YC_4H_5N^+$. Thus, two reasonable structures, **6** and **7**, can be suggested for $YC_4H_5N^+$ in reaction 11. The C_4H_5N ligand in structure **7** is the stable heteroaromatic compound pyrrole.



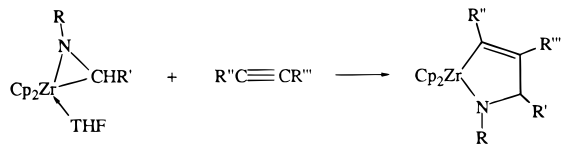
6 **7**

Further information on the structure of $YC_4H_5N^+$ was obtained by generating $YC_4H_5N^+$ via an alternative route. The reaction of Y^+ with pyrrolidine yields a $YC_4H_5N^+$ species by dehydrogenation which would be expected to be Y^+–pyrrole. CID of this $YC_4H_5N^+$ (Y^+–pyrrole) yields different product ions (reactions 17 and 18) from the CID results of $YC_4H_5N^+$ from reaction 11 (reactions 13–16). Thus, structure **6** is most likely to be the structure for $YC_4H_5N^+$ from reaction 11.

$$YC_4H_5N^+ \xrightarrow{\text{CID}} YC_4H_3N^+ + H_2 \quad 72\% \quad (17)$$

$$\longrightarrow YC_3H_3^+ + HCN + H \quad 28\% \quad (18)$$

As shown in Scheme 1, we propose that this reaction proceeds by the insertion of ethene into the Y–C bond to form a 2-aza-1-metallacyclohexene intermediate. Next, a β-hydrogen transfers to the metal center and elimination of H_2 yields 2-aza-1-metallacyclohex-3,5-diene (structure **6**). Note that while the CID results cannot distinguish between the ortho structure **6** and its para isomer, it is reasonable to expect insertion of ethene into the weaker Y–C bond. Furthermore, the insertion of alkynes into the Zr–C bond to form metallacyclic complexes in solution (reaction 19) serves as the model for our mechanism and illustrates the consequence of the strong bonding between an electron-deficient metal center and nitrogen due to the greater electron-donating ability of nitrogen compared to carbon.[26]



(19)

R = $SiMe_3$

R'	R''	R'''
Ph	Ph	H
H	Ph	Ph
n-C_5H_{11}	Et	Et

The six-membered metallacyclic structure **6** proposed for $YC_4H_5N^+$ can also be considered to be a metallabenzene with a CH replaced by NH. Metallabenzene chemistry has been an active area of research for more than 10 years, especially with the recent development of the synthesis and characterization of new metallabenzene compounds.[27] The quasi-aromatic nature of metallabenzene has been proven by X-ray crystal structure studies of these compounds on the basis of a planar six-membered ring with C–C bond lengths resembling an aromatic system.[27a,e–g] Furthermore, the theoretical investigation of electron delocalization in a metallabenzene has been considered by using extended Hückel molecular orbital calculations.[28] It is also known that aromaticity is retained if the CH in benzene is replaced with an isoelectronic nitrogen, phosphorus, arsenic, or antimony atom.[29]

Reactions with Propene. In the reaction of YNH^+ with propene, dehydrogenation is again the predominant process, resulting in the formation of $YC_3H_5N^+$ (reaction 20). Demethanation to form $YC_2H_3N^+$ is also observed as a minor product (reaction 21). YND^+ reacts with propene to form $YC_3H_4DN^+$ and $YC_2H_2DN^+$ (reactions 22 and 23), again indicating the retention of deuterium on the product ions.

The reaction of YNH^+ with 3,3,3-trideuterio propene, however, resulted in the loss of H_2, HD, and D_2 for the

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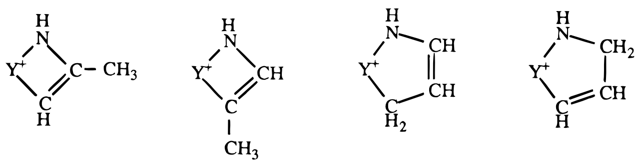
YNH^+	+	C_3H_6	⟶	$YC_3H_5N^+$	+ H_2	92%	(20)
			⟶	$YC_2H_3N^+$	+ CH_4	8%	(21)
YND^+	+	C_3H_6	⟶	$YC_3H_4DN^+$	+ H_2	94%	(22)
			⟶	$YC_2H_2DN^+$	+ CH_4	6%	(23)

dehydrogenation process (reactions 24−26) and the exclusive loss of CD_3H for the demethanation process (reaction 27). If H_2, HD, and D_2 are eliminated due to

YNH^+	+	CD_3CHCH_2	⟶	$YC_3H_2D_3N^+$	+ H_2	48%	(24)
			⟶	$YC_3H_3D_2N^+$	+ HD	33%	(25)
			⟶	$YC_3H_4DN^+$	+ D_2	14%	(26)
			⟶	$YC_2H_3N^+$	+ CD_3H	5%	(27)

complete scrambling (note that reaction 22 indicates that the H in YNH^+ is not involved in scrambling), the predicted relative reaction product intensities[30a] for reactions 24−26 are 20%, 60%, and 20%, respectively, which are different from the respective experimental results[30b] of 50%, 35%, and 15%.

As suggested in Scheme 2, there are two possible ways of adding propene to YNH^+. In pathway <u>**1**</u>, a β-hydrogen transfer to the metal center followed by the loss of H_2 yields 2-aza-1-metallacyclobut-3-ene complex ion **8**. In



8 **9** **10** **11**

pathway <u>**2**</u>, it is possible to transfer β-hydrogens from two different positions to the metal center to form two different intermediates, I and II. Subsequent dehydrogenation from intermediate I can yield either 2-aza-1-metallacyclobut-3-ene **9**, an isomer of **8**, and 2-aza-1-metallacyclopent-3-ene **10**, an enamine, as indicated by the labeling experiment with respective losses of H_2 and HD, whereas the intermediate II can undergo elimination of H_2 to yield the 2-aza-1-metallacyclopent-4-ene complex ion **11**. Elimination of D_2 in the labeling experiment (see Scheme 3) occurs through intermediate III (analogous to intermediate II in Scheme 2) obtained via β-D transfer to the metal center. As shown in Scheme 3, its rearrangement to intermediate IV through H/D scrambling can also be postulated as an alternative pathway for the elimination of HD in reaction 25. The product ions resulting from these two processes are isotopologs of **11**. Finally, demethanation from intermediate I (Scheme 2) can take place to yield a small percentage of 2-aza-1-metallacyclobut-3-ene ion $YC_2H_3N^+$, which according to Scheme 2 is also predicted to have structure **2**. Demethanation may also arise in pathway <u>**1**</u> from initial β-CH_3 transfer (not shown), but β-CH_3 transfers are less likely in general than β-H transfers.

$YC_3H_5N^+$ can also be considered to be an yttrium butadiene with a CH_2 group substituted by the isoelectronic NH group. There are several probable modes of interaction between transition metals and 1,3-dienes. However, for the early transition metals, bent metallacyclopent-3-ene structure **10** has been shown by ^1H NMR to be a preferred structure in the solution phase.[20] Interestingly, **11** can undergo metal-mediated isomerization via β-H transfer onto the metal center from the methylene group followed by α-H transfer to the adjacent CH group to yield **10**. This mechanism is analogous to that observed for 2-aza-1-metallacyclopent-2-ene ring systems with early transition metals in the solution phase.[31] Recently, Hill and co-workers reported another example of such an isomerization for a 2,5-diaza-1-titanacyclopent-2-ene ring system supported by aryloxide ligation.[32] In this study, the 2,5-diaza-1-titanacyclopent-2-ene complex was observed to isomerize to the 3-ene complex and the latter product was isolated as its pyridine adduct.

CID on $YC_3H_5N^+$ from reaction 20 yields 100% YNH^+ at low energies (17 eV), and 90% YNH^+ and 10% $YC_2H_2^+$ at intermediate energies(28−42 eV), with Y^+ appearing at about 67 eV (reactions 28−30). The ob-

$YC_3H_5N^+$	⟶ CID (67 eV)	$YC_2H_2^+$	+ HCN	+ H_2	8%	(28)
	⟶	YNH^+	+ C_3H_4		86%	(29)
	⟶	Y^+	+ C_3H_5N		6%	(30)

servation of $YC_2H_2^+$ supports the presence of 2-aza-1-metallacyclopentene structures. CID of $YC_3H_4DN^+$, formed in reaction 22, gives fragmentation patterns identical with that of $YC_3H_5N^+$ within experimental variations (reactions 31−34). Formation of both YND^+ and YNH^+ in reaction 29 probably occurs through H/D scrambling during the CID activation process.

$YC_3H_4DN^+$	⟶ CID (67 eV)	$YC_2H_2^+$	+ HCN	+ HD	7%	(31)
	⟶	YND^+	+ C_3H_4		73%	(32)
	⟶	YNH^+	+ C_3H_3D		13%	(33)
	⟶	Y^+	+ C_3H_4DN		7%	(34)

The reaction of $YC_3H_5N^+$ with benzene results in the condensation product, $YC_3H_5N(C_6H_6)^+$, exclusively. CID on $YC_3H_5N(C_6H_6)^+$ shows predominant loss of C_6H_6 at low energies (0−23 eV) and yields 95% $YC_3H_5N^+$ and 5% YNH^+ at higher energies, consistent with a simple condensation complex. While these results do not provide strong evidence to support any of the structures **8**−**11** for $YC_3H_5N^+$, they suggest an intact ligand since smaller ligands might be displaced.

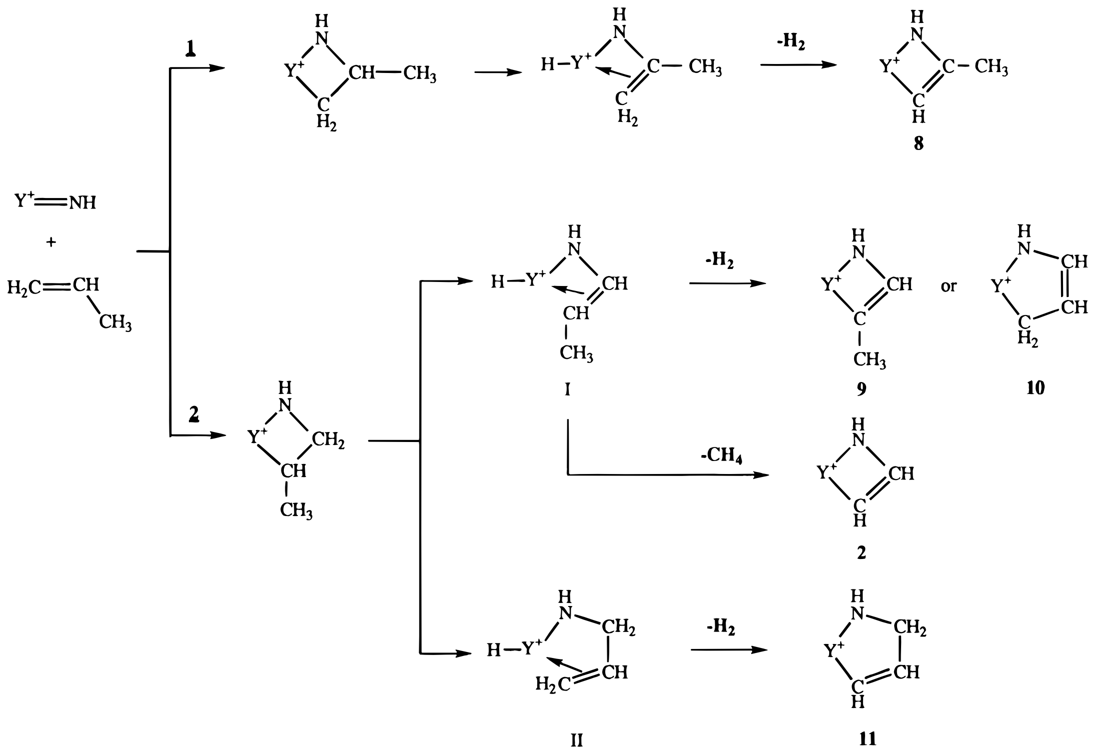
The reaction of VNH^+ with propene was observed to give a higher percentage of dehydrogenation and two other processes[7a] (reactions 35−37), which do not occur in the reaction of YNH^+ with propene. Absence of NH transfer to the olefin or olefin metathesis to form VCH_2^+, as in the case of YNH^+, is again consistent with the high bond strengths of $D°(V^+{-}NH) = 101 \pm 7$ kcal/mol and $D°(Y^+{-}NH) > 101$ kcal/mol.

VNH^+	+	C_3H_6	⟶	$VNH(C_3H_4)^+$	+ H_2	62%	(35)
			⟶	$VC_2NH_6^+$	+ CH	5%	(36)
			⟶	VCH_2NH^+	+ C_2H_4	33%	(37)

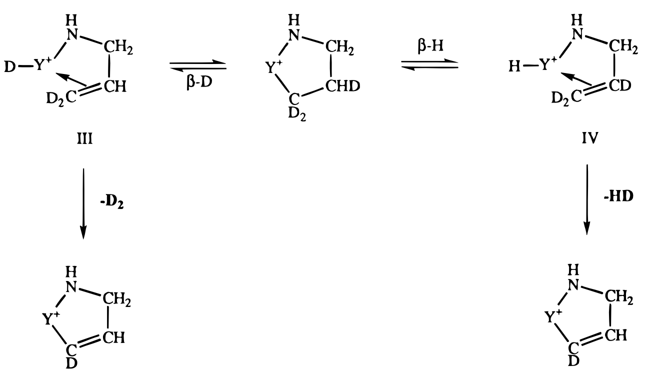
The dehydrogenation product from reaction 20, $YC_3H_5N^+$, reacts further with propene to give the

(30) (a) The number of combinations of n different things taken r at a time, denoted ^nC_r, is given by the equation of $^nC_r = n!/[r!\,(n-r)!]$. Assuming complete scrambling, the ratio of the products in reactions would be $^3C_2{:}^3C_1{\times}^3C_1{:}^3C_2$ or 1:3:1, which gives the percentages reported. (b) Values normalized for dehydrogenation processes (reactions 24−26).

Scheme 2



Scheme 3



secondary products $YC_6H_9N^+$ and $YC_5H_7N^+$ due to loss of H_2 and CH_4, respectively (reactions 38 and 39). Since

$YC_3H_5N^+$ + C_3H_6	——>	$YC_6H_9N^+$	+	H_2	84%	(38)
	——>	$YC_5H_7N^+$	+	CH_4	16%	(39)

there is no conclusive structure determination on $YC_3H_5N^+$, these reactions can proceed by reaction of any one of structures **8**–**11** with propene, increasing the number of possible structures for the product ions. These processes likely result in the enlargement of the metallacycle basically by following the same reaction mechanism proposed in Scheme 2 for the primary reaction of YNH^+ with propene: insertion of the C=C bond into the Y^+–C bond followed by a β-hydrogen transfer onto the metal center and elimination of H_2 or CH_4 to complete the reaction. Reactions 40 and 41 were observed when $YC_3H_4DN^+$ from reaction 22 reacts further with propene. The deuterium atom on the nitrogen is retained during the dehydrogenation and demethanation processes in reactions 40 and 41, as observed in the primary reactions of YND^+ with propene (reactions 22 and 23).

$YC_3H_4DN^+$ + C_3H_6	——>	$YC_6H_8DN^+$	+	H_2	81%	(40)
	——>	$YC_5H_6DN^+$	+	CH_4	19%	(41)

Reactions with Isobutene. Reactions 42–44 were observed between YNH^+ and isobutene. $YC_3H_5N^+$ resulting from demethanation is observed as the predominant product, in contrast to the reaction with propene, where it is seen only as a minor product. This is an interesting result, considering that loss of methane from isobutene or propene both require approximately 31 kcal/mol,[15] but is as yet unexplained.

YNH^+ + i-C_4H_8	——>	$YC_4H_9N^+$			7%	(42)
	——>	$YC_4H_7N^+$	+	H_2	15%	(43)
	——>	$YC_3H_5N^+$	+	CH_4	78%	(44)

The corresponding reaction of YND^+ yields the loss of H_2 in reaction 43 and CH_4 in reaction 44, indicating the neutrals lost are from the alkene. A reaction mechanism involving the formation of a 2-aza-1-metallacyclic intermediate with the opening of the double bonds of both YNH^+ and the alkene is again plausible and can be used to explain these primary products (Scheme 4). As suggested in Scheme 4, the demethanation product, $YC_3H_5N^+$, has the same structures **8** and **9**, obtained from the dehydrogenation reaction of YNH^+ with propene. CID on $YC_3H_5N^+$ ion arising from reaction 44 resulted in YNH^+, exclusively, over a wide range of energies (0–54 eV) with 90% YNH^+, 4% $YC_2H_2^+$, and 6% Y^+ at 67 eV. This result is in agreement with 2-aza-1-metallacyclobutene complexes, **8** and **9**, and indicates the absence of metallacyclopentene structures **10** and **11** for the product ion in reaction 44.

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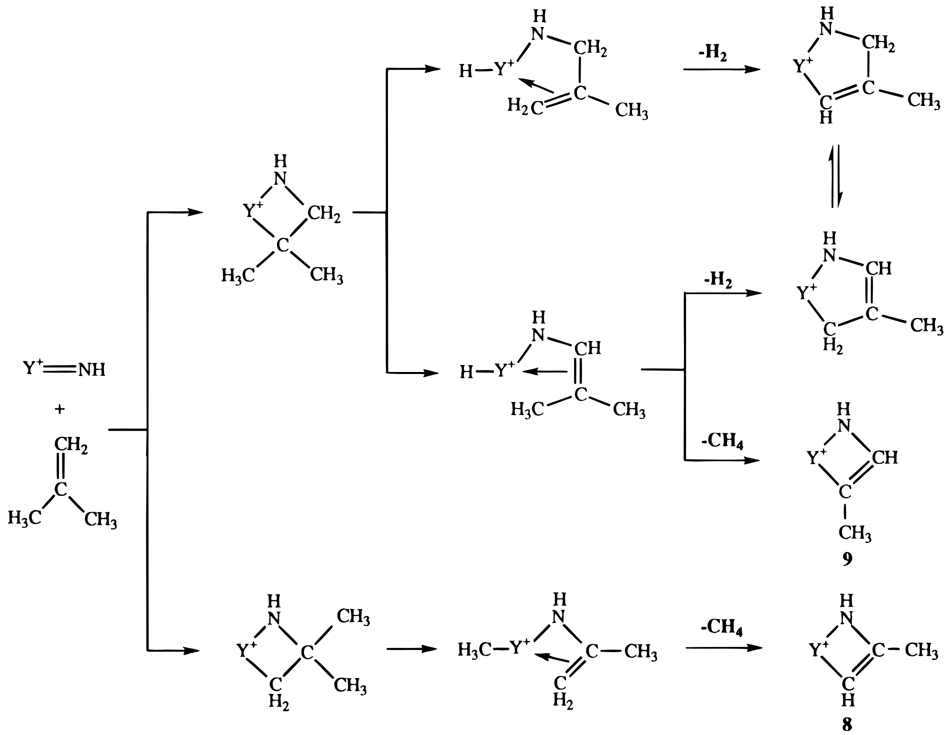
Scheme 4



This conclusion arises due to the absence of $YC_2H_2^+$ as a CID product at 0–54 eV, as opposed to the observed CID results from $YC_3H_5N^+$ generated in reaction 20. The possible rearrangement of structure **9** to **10** during the CID activation process may be the reason for the formation of a minor amount of $YC_2H_2^+$ at higher energies. The demethanation product from reaction 44 reacts further with isobutene to yield reactions 45–47,

$YC_3H_5N^+ + C_4H_8$	⟶	$YC_7H_{13}N^+$	16%	(45)
	⟶	$YC_7H_{11}N^+ + H_2$	48%	(46)
	⟶	$YC_6H_9N^+ + CH_4$	36%	(47)

presumably via a similar reaction mechanism previously discussed for the secondary reactions between YNH^+ and propene, resulting in the enlargement of the metallacycles. Due to the presence of two possible structures **8** and **9** for $YC_3H_5N^+$, several structures can be suggested for $YC_7H_{11}N^+$ and $YC_6H_9N^+$ arising from reactions 46 and 47.

Reactions with Linear Butenes. YNH^+ reacts with 1-butene, *cis*-2-butene, and *trans*-2-butene to give a wide variety of product ions (reactions 48–53). All

YNH^+ + butene	1-butene	cis-2-butene	trans-2-butene	
⟶ $YC_4H_9N^+$	6%	11%	12%	(48)
⟶ $YC_4H_7N^+ + H_2$	15%	2%	2%	(49)
⟶ $YC_4H_5N^+ + 2H_2$	5%	--	—	(50)
⟶ $YC_3H_5N^+ + CH_4$	5%	2%	4%	(51)
⟶ $YC_4H_6^+ + NH_3$	64%	83%	78%	(52)
⟶ $YC_2H_5N^+ + C_2H_4$	5%	2%	4%	(53)

three linear butenes react similarly, with *cis*-2-butene and *trans*-2-butene being identical within our experimental uncertainty. $YC_4H_6^+$ is observed as the predominant product with loss of NH_3 for all three linear butenes, as exemplified for *cis*-2-butene in Figure 1b, in contrast to demethanation in the reaction with

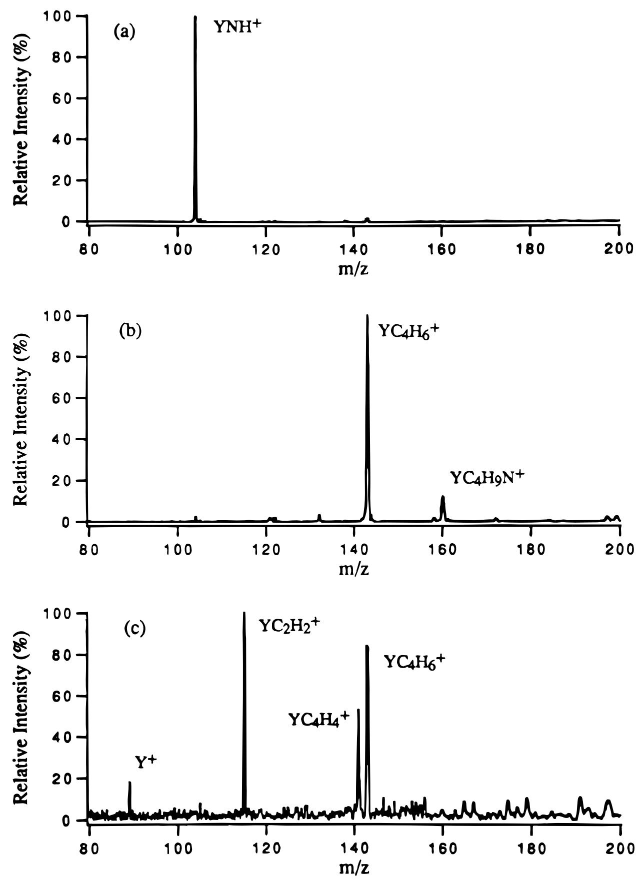
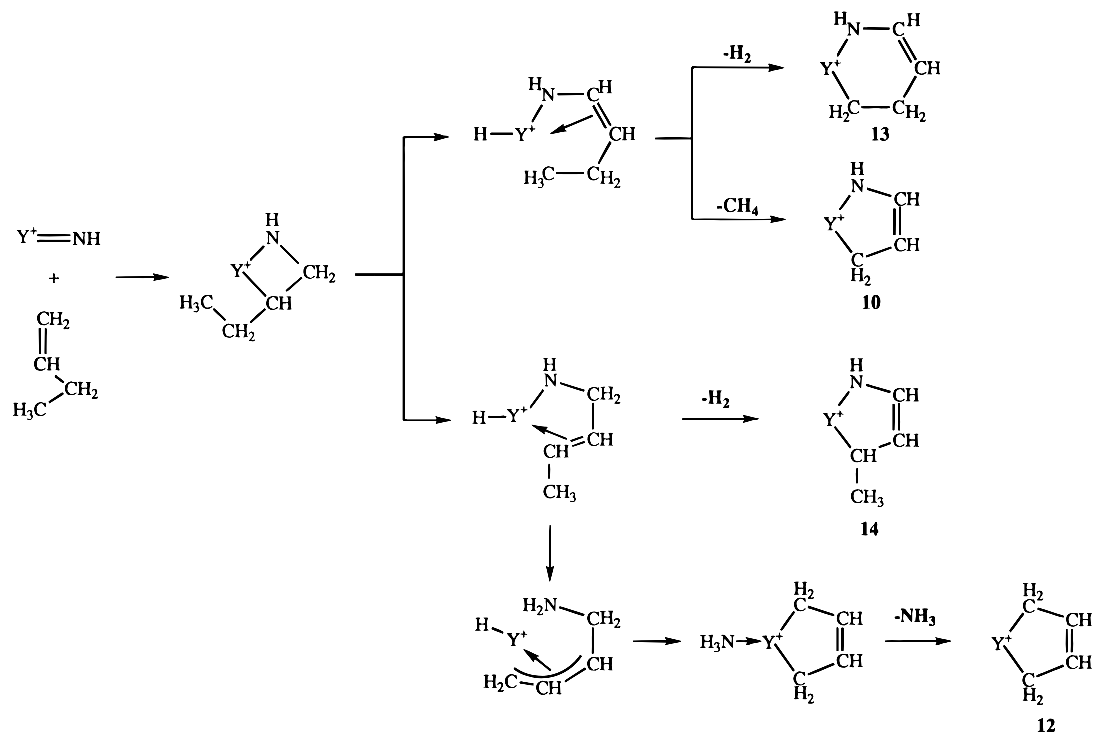


Figure 1. Mass spectra: (a) isolation of YNH^+ from the reaction of Y^+ with ammonia; (b) reaction of isolated YNH^+ with *cis*-2-butene; (c) CID of $YC_4H_6^+$ isolated from the reaction of YNH^+ with *cis*-2-butene.

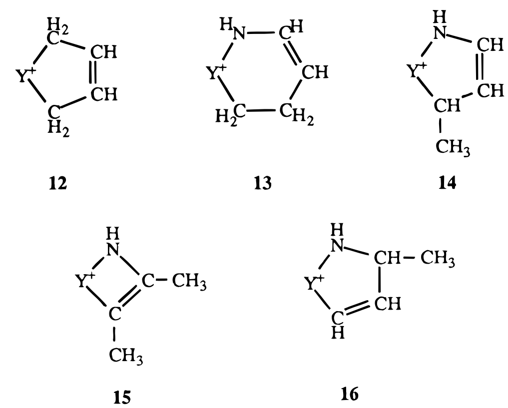
Scheme 5



isobutene. Perhaps the $Y^+-C_4H_6$ bond strength of the product ion with the loss of NH_3 plays an important role in the reactions with linear butenes. The corresponding reaction of YND^+ yields the loss of NH_2D in reaction 52, indicating the transfer of two hydrogens from the butene molecule onto the −NH group prior to elimination of NH_3 and suggesting the proposed reaction mechanism shown in Scheme 5. After the formation of the azametallacyclic intermediate, two β-hydrogens transfer to the metal center and then onto NH, to give an ammonia−metallacyclopentene complex. Finally, the metallacyclopent-3-ene **12** can be easily generated by losing NH_3, indicating $D°(Y^+-C_4H_6) > D°(Y^+-NH_3)$.

CID of $YC_4H_6^+$ from reaction 52 for all three linear butenes resulted in 30% $YC_4H_4^+$, 60% $YC_2H_2^+$, and 10% Y^+ at 30 eV. These results are considerably different from those observed in the CID of $YC_4H_6^+$ produced in the reaction of Y^+ with *n*-butane, which correspond to the loss of C_2H_4 and the entire ligand with nearly equal abundances at 30 eV, and which presumably arise from the yttrium−butadiene structure for $YC_4H_6^+$.[33] The observation of the dehydrogenation product $YC_4H_4^+$ supports the proposed metallacyclopent-3-ene **12** for $YC_4H_6^+$ obtained in reaction 52. Previous CID studies on group 8 metallacyclopentane ions have similarly shown these ions to yield fragmentation due to loss of H_2, C_2H_4, and the entire ligand.[34]

The amount of dehydrogenation product observed in the reactions of YNH^+ with linear butenes is much lower than observed with ethene and propene. Only with 1-butene was a considerable amount of H_2 loss product observed, and structures **13** and **14** are proposed for the product ion as described in Scheme 5. Following the same mechanistic steps, structures **15** and **16** can be



suggested for the dehydrogenation products for reactions with *cis*-2-butene and *trans*-2-butene. Interestingly, only structures **13** and **14** can undergo further dehydrogenation via β-hydrogen activation, resulting in metallabenzene **6**. Formation of this stable quasi-aromatic metallabenzene product ion is probably the reason for the observation of the double-dehydrogenation process only with 1-butene.

Conclusions

As an extension of our studies of low-valence electron species, YNH^+ has shown interesting chemistry with a variety of small alkenes. This provides an opportunity to explore the reaction mechanisms other than conventional pathways involving oxidative addition due to the presence of the d^0 metal center. Even though the chemistry of cyclometalation has been well developed in the solution phase, study of this subject in the gas phase allows a better understanding of the chemistry without the effects of solvents. In comparison with $FeNH^+$ and VNH^+, YNH^+ also has its unique chemistry, even though the direct cleavage of a multicentered intermediate was not observed. The formation of the

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(34) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 736.

2-aza-1-metallacyclic intermediate followed by a β-hydrogen transfer to the metal center is proposed as the general scheme for the reactions observed with the alkenes studied. A higher percentage of dehydrogenation was observed in the reactions with ethene and propene, and 2-aza-1-metallacyclobut-3-ene and 2-aza-1-metallacyclopentene structures are suggested for the product ions in light of supportive examples from the solution phase studies. Demethanation was facile in the reaction between isobutene and YNH^+. Expansion of the metallacycles through the insertion of another C=C bond into the Y^+—C bond is observed for the secondary reactions with ethene, propene, and isobutene, including the formation of a stable metallabenzene structure for ethene. In the reactions with linear butenes, loss of NH_3 becomes the predominant reaction pathway and the stability of the product ion, $YC_4H_6^+$, seems to explain this observation. Finally, we note here that YO^+, which is isoelectronic with YNH^+, is considerably less reactive than YNH^+. YO^+ is unreactive with ethene and only forms condensation products with propene and butene.

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