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Gas-Phase Reactions of $\mathrm{Nb^+}$ and $\mathrm{Ta^+}$ with Alkanes and Alkenes. C–H Bond Activation and Ligand-Coupling Mechanisms

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The gas-phase reactions of $\mathrm{Nb^+}$ with small alkanes and alkenes are reported. $\mathrm{Nb^+}$ sequentially activates C–H bonds in ethene six times to produce $\mathrm{NbC_{2\mathit{n}}H_{2\mathit{n}}^+}$ (n = 1–6). The $\mathrm{C_2H_2}$ ligands in this reaction couple via migratory insertion of the acetylene units. Ethane sequentially reacts with $\mathrm{Nb^+}$ five times. Ligand coupling is proposed for these reactions as well. Comparison of $\mathrm{NbC_4H_6^+}$ produced from isobutane, *n*-butane, and ethane indicates the presence of at least two isomeric forms. $\mathrm{NbC_4H_4^+}$ ions produced from ethene, cyclobutane, and 1-butene produce similar CID spectra, supporting the presence of one structure. Excited $\mathrm{Nb^+}$ produced by direct laser desorption reacts with methane to produce $\mathrm{NbCH_2^+}$ and $\mathrm{NbCH_3^+}$, but collisional cooling with argon quenches the reaction. Primary reactions indicate a strong preference for C–H insertion, and reaction products indicate 1,3-hydrogen migration when β-hydrogens are not present. The reactions with alkanes are compared to those with $\mathrm{Ta^+}$, which reacts with $\mathrm{CH_4}$ four times to produce $\mathrm{TaC_4H_8^+}$. $\mathrm{Ta^+}$ and $\mathrm{Nb^+}$, which react similarly, are by far the most reactive metal ions toward C–H bond activation reported to date. CID spectra of the products from the $\mathrm{Nb^+}$ reactions indicate that the extensive dehydrogenation reactions occur via ligand coupling and, for larger alkanes ($\mathrm{C_5}$ and $\mathrm{C_6}$), dehydrocyclization. For example, $\mathrm{Nb^+}$ undergoes a novel dehydrocyclization reaction with pentane to generate $\mathrm{Nb(Cp)^+}$ (Cp = cyclopentadienyl). $\mathrm{Nb^+}$ reacts with cyclopentane to generate $\mathrm{Nb(Cp)_2^+}$ as a secondary product. This represents the first mononuclear niobocene structure that has been synthesized.

Introduction

The reactivity of transition-metal ions and unsaturated organometallic ions with small organic molecules in the gas phase has been a topic of intense investigation in recent years.[1] These studies have yielded information on the energetics of these systems,[2-4] as well as structural information on reaction products, which has led to proposals of numerous reaction mechanisms.[5] To date, the focus has mainly been on the first row[6-8] and groups 8–10 metal ions[9-11] with and without ligands. These studies have shown first-row groups 8–10 metal ions to be more active toward C–C bond cleavage processes, whereas metal ions early in the transition series, as well as second- and third-row-metal ions, preferentially activate C–H bonds. The first-row-metal ion–alkyl bonds primarily involve s orbitals on the metal center, whereas second-row metals bind primarily by using orbitals with d character.[12] It has been proposed that if C–H bond insertion is the initial step for transition-metal ion reactions, then elimination of $\mathrm{H_2}$ as opposed to an alkane is controlled by β-H migration or β-alkyl migration. The highly directional d orbitals used by second-row-metal ions would then favor a β-H migration with its nondirectional s orbitals, whereas the first-row-metal ions with nondirectional s bonding could transfer the alkyl group with its more directional p orbitals.[13]

There have been a growing number of studies on the effects of ligands on the reactivity of metal ions toward alkanes in the gas phase.[14,15] The majority of these studies have again involved the groups 8–10 metal ions and have shown that, upon attachment of a ligand, there is an increased preference for C–H insertion over C–C insertion. In contrast, the present study shows that in certain cases, attachment of an alkene ligand to $\mathrm{Nb^+}$ or $\mathrm{Ta^+}$ increases the preference for C–C insertion.

$\mathrm{V^+}$ has been shown to react with alkanes via C–H insertion.[8] The early-transition-metal ions of the second and third rows that have been investigated are $\mathrm{Y^+}$,[16] $\mathrm{Mo^+}$,[13] and $\mathrm{La^+}$.[16] These metal ions predominantly activate C–H bonds in alkanes. In the present work, $\mathrm{Nb^+}$ and $\mathrm{Ta^+}$ are observed to be among the most reactive metal ions toward C–H bond activation studied to date, forming products including $\mathrm{MC_\mathit{n}H_\mathit{n}^+}$. These findings are in accordance with the high reactivity of early transition metals in general and with the observed reactivity of Nb clusters.[17] In addition, a recent study on $\mathrm{Os^+}$ [18] indicates a similar reactivity and provides an interesting comparison.

Experimental Section

All experiments were performed on a prototype Nicolet FTMS-1000 Fourier transform mass spectrometer.[19] The instrument is equipped with a 5.2-cm cubic trapping cell in a 0.9-T magnetic field. Metal ions were

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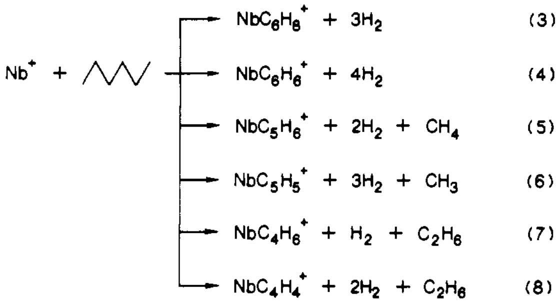
produced by laser desorption/ionization using the fundamental output (1064 nm) of a Quanta Ray Nd:YAG laser.[20] This technique has been shown to produce kinetically and electronically excited metal ions.[21] In the present study, the metal ions were collisionally cooled by addition of an excess static pressure (~1 × 10^{-5} Torr) of argon. A minimum cooling time of 250 ms was used permitting >50 thermalizing collisions with the Ar. The effect of cooling with argon can be illustrated by using two cases. First, directly laser desorbed Nb^+ undergoes reactions 1 and 2 with CH_4. After collisional cooling and reisolation of the remaining metal ion signal, no reaction is observed. Hexane reacts with directly laser desorbed Nb^+ by reactions 3–8. After collisional cooling, reactions 5–8 are not observed. This method appears to quench the majority of endothermic processes and to give branching ratios that are generally in agreement with those obtained by other methods. The presence of a small population of nonthermal ions, however, which could slightly alter the branching ratios reported in this study, cannot be completely ruled out.

$$Nb^+ + CH_4 \rightarrow NbCH_3^+ + H^\bullet \qquad (1)$$

$$ \rightarrow NbCH_2^+ + H_2 \qquad (2)$$



Results and Discussion

Tables I and II list the product distributions for the primary and secondary reactions of Nb^+ with alkanes together with the corresponding data on Ta^+[22] for comparison. Both metal ions are observed to dehydrogenate alkanes multiple times, often forming species with molecular formula $MC_nH_n^+$. The preference for C–H insertion over C–C insertion has also been observed in reactions of other early-transition-metal ions, including Ti^+,[7] Sc^+,[6] Y^+,[16] La^+,[16] V^+,[8] and W^+.[13] The extent of dehydrogenation of alkanes, however, is much greater for Nb^+ and Ta^+ than for any other metal ions reported to date with the possible exception of Os^+.[18] Nb^+ and Ta^+ even dehydrogenate 2,2-dimethylpropane, which has no β-hydrogens. However, the secondary reactions of Nb^+ and Ta^+ with *n*-hexane and 2,2-dimethylpropane show an increased preference for C–C insertion. This is in contrast to Fe^+, Co^+, and Ni^+,[14] where attachment of ligands tends to increase attack of C–H bonds relative to C–C bonds.

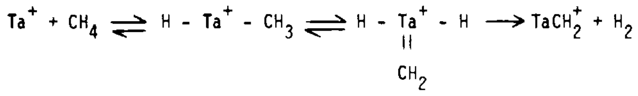
Reference ions were prepared where possible for structural identification by CID. Due to the high reactivities of Nb^+ and Ta^+, however, it was often difficult to generate reference ions for structural comparison by ligand displacement. These metal ions dehydrogenate NH_3, benzene, pyridine, and other molecules that are typically used for ligand-displacement reactions. This made structural identification difficult. Another difficulty in generating reference ions was brought about by the extent of dehydrogenation. For example, cyclopropane is dehydrogenated to produce $MC_3H_2^+$. This type of ligand is unusual, and structures for these ions can only be speculated on. Another problem is that low-energy multicollision CID often results in structural rearrangement prior to dissociation.[23] This difficulty arises in situations where low-energy barriers separate structural isomers, as is often the case in metal–ligand ion systems. Thus, even when reference ions are generated, CID as used presently is only suggestive of likely structures and is not conclusive for structure identification.

Table I. Primary and Secondary Reactions of Nb^+

reactant	primary prod	rel %	secondary prod	rel %
CH_4	no reaction			
C_2H_6	$NbC_2H_4^+$	58	$NbC_4H_6^+$	100
	$NbC_2H_2^+$	42	$NbC_4H_6^+$	100
C_3H_8	$NbC_3H_4^+$	85	$NbC_6H_8^+$	100
	$NbC_3H_2^+$	15	$NbC_6H_8^+$	100
C_4H_{10}	$NbC_4H_6^+$	68	$NbC_8H_{12}^+$	80
			$NbC_8H_8^+$	20
	$NbC_4H_4^+$	32	$NbC_8H_{10}^+$	17
			$NbC_8H_8^+$	83
C_5H_{12}	$NbC_5H_8^+$	6	*a*	
	$NbC_5H_6^+$	71	$NbC_{10}H_{11}^+$	100
	$NbC_5H_5^+$	14	*a*	
	$NbC_4H_4^+$	9	*a*	
C_6H_{14}	$NbC_6H_8^+$	36	*a*	
	$NbC_6H_6^+$	64	$NbC_{12}H_{14}^+$	42
			$NbC_{12}H_{12}^+$	58
c-C_3H_6	$NbC_3H_2^+$	65	$NbC_6H_4^+$	100
	$NbC_2H_2^+$	11	$NbC_5H_5^+$	34
			$NbC_3H_4^+$	66
	$NbCH_2^+$	24	$NbC_4H_4^+$	100
c-C_4H_8	$NbC_4H_4^+$	67	$NbC_8H_8^+$	67
			$NbC_6H_6^+$	33
	$NbC_4H_2^+$	9	*a*	
	$NbC_2H_2^+$	24	$NbC_6H_6^+$	100
c-C_5H_{10}	$NbC_5H_6^+$	81	$NbC_{10}H_{10}^+$	100
	$NbC_5H_5^+$	19	$NbC_{10}H_{11}^+$	100
c-C_6H_{12}	$NbC_6H_6^+$	100	$NbC_{12}H_{12}^+$	100
methyl-cyclohexane	$NbC_7H_8^+$	52	$NbC_{14}H_{16}^+$	70
			$NbC_{13}H_{14}^+$	26
			$NbC_{12}H_{12}^+$	4
	$NbC_7H_6^+$	17	$NbC_{14}H_{16}^+$	65
			$NbC_{13}H_{14}^+$	22
			$NbC_{12}H_{12}^+$	13
	$NbC_6H_6^+$	31	$NbC_{13}H_{14}^+$	66
			$NbC_{12}H_{16}^+$	34
isobutane	$NbC_4H_6^+$	90	$NbC_8H_{12}^+$	100
	$NbC_4H_4^+$	4	*a*	
	$NbC_3H_2^+$	6	*a*	
2,2-dimethyl-propane	$NbC_5H_8^+$	69	$NbC_{10}H_{12}^+$	9
			$NbC_9H_{14}^+$	65
			$NbC_9H_{12}^+$	13
			$NbC_8H_{12}^+$	13
	$NbC_5H_6^+$	17	$NbC_9H_{12}^+$	50
			$NbC_9H_{10}^+$	50
	$NbC_4H_6^+$	5	*a*	
	$NbC_4H_4^+$	9	*a*	

[a] Reaction product(s) not determined due to low signal intensity.

Scheme I



$$Ta^+ + CH_4 \rightleftharpoons H-Ta^+-CH_3 \rightleftharpoons H-\underset{\underset{CH_2}{\|}}{Ta^+}-H \longrightarrow TaCH_2^+ + H_2$$

Further discussion of alkanes will focus on some of the interesting reactions in Tables I and II, along with possible product ion structures and reaction mechanisms.

Methane. Prior to this work, the only ground-state thermal metal ion observed to dehydrogenate CH_4 was Os^+.[18] This is because the energy requirement for dehydrogenation is high, 111 kcal/mol, making the reaction endothermic.[24] As seen in Table I, thermalized Ta^+ also reacts with CH_4 to form $TaCH_2^+$, indicating $D(Ta^+–CH_2) > 111$ kcal/mol. Recently, photochemically induced α-hydrogen migrations have been observed in a solution Ta complex (reaction 9).[25] A mechanism for the reaction of Ta^+

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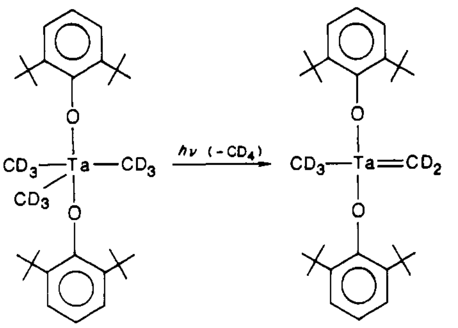
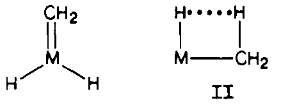


(9)

with CH_4 in the gas phase, which includes an α-hydrogen migration, is shown in Scheme I.

Armentrout and co-workers have recently studied the endothermic reactions of Sc^+, Ti^+, and V^+ with CH_4 in an ion-beam apparatus.[3d,f] Interestingly, all three metal ions can dehydrogenate CH_4. Both Sc^+ and Ti^+ do not have enough valence electrons to proceed through structure I as invoked in Scheme I and, although V^+ (the first-row analogue of Nb^+ and Ta^+) has enough valence electrons, the threshold observed for dehydrogenation is too low in energy to proceed through structure I. Thus, the authors propose an intermediate such as structure II for these metals, which can eliminate H_2 via a four-centered process. Because there is no way to probe the intermediate $TaCH_4^+$ structure by using our present methodology, structure II is equally possible in this case.



I II

Nb^+ that is not collisionally cooled reacts with CH_4 via reactions 1 and 2. Cooled Nb^+ is unreactive with CH_4, while $NbCH_2^+$ reacts with H_2 to regenerate Nb^+ (reaction 10). These results

$$NbCH_2^+ + H_2 \rightarrow Nb^+ + CH_4 \tag{10}$$

indicate $D(Nb^+\text{–}CH_2) < 111$ kcal/mol, in agreement with $D(Nb^+\text{–}CH_2) = 109 \pm 3$ kcal/mol recently obtained in a photodissociation threshold experiment.[26] In a process analogous to reaction 10, $RhCH_2^+$ has also been observed to react with H_2 to regenerate Rh^+.[27] On the basis of bond energy arguments, this latter reaction was proposed to proceed through a four-centered intermediate like structure II.

MCH_2^+ (M = Nb, Ta) undergo collisional activation as in reactions 11–15. These results contrast with the low-energy CID results for $LaCH_2^+$,[16] which loses H_2 and CH_2, and MCH_2^+ (M = Fe, Co, Rh),[14,27] which only lose CH_2 upon collisional activation.

$$NbCH_2^+ \xrightarrow{Ar} NbCH^+ + H^\bullet \tag{11}$$
$$NbCH_2^+ \xrightarrow{Ar} NbC^+ + H_2 \tag{12}$$
$$NbCH_2^+ \xrightarrow{Ar} Nb^+ \bullet CH_2 \tag{13}$$
$$TaCH_2^+ \xrightarrow{Ar} TaCH^+ + H^\bullet \tag{14}$$
$$TaCH_2^+ \xrightarrow{Ar} Ta^+ + CH_2 \tag{15}$$

$TaCH_2^+$ reacts sequentially with CH_4 three times (reaction 16). Interestingly, Os^+ has been observed to react sequentially with CH_4 twice to generate $OsC_2H_4^+$.[18] The product ions from reaction 16 undergo collisional activation via reactions 17–30. $TaC_2H_4^+$ from reaction 16 could have a metal–ethylene or a metal–bis(carbene) structure. Unfortunately, since Ta^+ forms insufficient amounts of $TaC_2H_4^+$ from reaction with C_2H_6 to perform CID, no reference ion could be prepared. Loss of H_2 in reaction 17 and the absence of loss of $H^\bullet$ in the CID of $TaC_2H_4^+$ from CH_4, however, are suggestive of either a metal–ethylene structure or rearrangement to this structure upon collisional activation. Since $TaCH_2^+$ loses $H^\bullet$ upon collisional activation, one might expect loss of $H^\bullet$ from a stable, nonisomerizing bis(carbene) structure. However, loss of CH_2 (reaction 18) is supportive of a bis(carbene) structure. There is also the possibility of a mixture of structures. The CID results for $TaC_3H_6^+$ and $TaC_4H_8^+$ could not be compared to ions generated by other methods due to difficulties in generating sufficient intensities.

$$TaC_nH_{2n}^+ + CH_4 \rightarrow TaC_{n+1}H_{2n+2}^+ + H_2 \tag{16}$$
$$n = 1\text{–}3$$

$$TaC_2H_4^+ \xrightarrow{Ar} TaC_2H_2^+ + H_2 \tag{17}$$
$$TaC_2H_4^+ \xrightarrow{Ar} TaCH_2^+ + CH_2 \tag{18}$$
$$TaC_2H_4^+ \xrightarrow{Ar} Ta^+ + C_2H_4 \tag{19}$$
$$TaC_3H_6^+ \xrightarrow{Ar} TaC_3H_4^+ + H_2 \tag{20}$$
$$TaC_3H_6^+ \xrightarrow{Ar} TaC_3H_2^+ + 2H_2 \tag{21}$$
$$TaC_3H_6^+ \xrightarrow{Ar} TaC_2H_2^+ + CH_4 \tag{22}$$
$$TaC_3H_6^+ \xrightarrow{Ar} TaCH_2^+ + C_2H_4 \tag{23}$$
$$TaC_3H_6^+ \xrightarrow{Ar} Ta^+ + C_3H_6 \tag{24}$$
$$TaC_4H_8^+ \xrightarrow{Ar} TaC_4H_6^+ + H_2 \tag{25}$$
$$TaC_4H_8^+ \xrightarrow{Ar} TaC_4H_4^+ + 2H_2 \tag{26}$$
$$TaC_4H_8^+ \xrightarrow{Ar} TaC_4H_2^+ + 3H_2 \tag{27}$$
$$TaC_4H_8^+ \xrightarrow{Ar} TaC_3H_4^+ + CH_4 \tag{28}$$
$$TaC_4H_8^+ \xrightarrow{Ar} TaC_3H_2^+ + CH_4 + H_2 \tag{29}$$
$$TaC_4H_8^+ \xrightarrow{Ar} TaC_2H_2^+ + C_2H_6 \tag{30}$$

C_2 and C_3 Alkanes. $NbC_2H_4^+$ and $NbC_2H_2^+$ formed from ethane undergo CID via reactions 31–33. These ions have, presumably, metal–ethylene and metal–acetylene structures.

$$NbC_2H_4^+ \xrightarrow{Ar} NbC_2H_2^+ + H_2 \tag{31}$$
$$NbC_2H_4^+ \xrightarrow{Ar} Nb^+ + C_2H_4 \tag{32}$$
$$NbC_2H_2^+ \xrightarrow{Ar} Nb^+ + C_2H_2 \tag{33}$$

$NbC_2H_4^+$ and $NbC_2H_2^+$ react with C_2H_6 to produce $NbC_4H_6^+$, solely. The structure of this ion will be compared to that of the other $NbC_4H_6^+$ isomers (vide infra). $NbC_4H_6^+$ reacts with C_2H_6 via reactions 34–36. These product ions also react with C_2H_6, reactions 37–39.

$$NbC_4H_6^+ + C_2H_6 \rightarrow NbC_5H_8^+ + CH_4 \tag{34}$$
$$NbC_4H_6^+ + C_2H_6 \rightarrow NbC_6H_{10}^+ + H_2 \tag{35}$$
$$NbC_4H_6^+ + C_2H_6 \rightarrow NbC_6H_6^+ + 2H_2 \tag{36}$$
$$NbC_5H_8^+ + C_2H_6 \rightarrow NbC_7H_{10}^+ + 2H_2$$
$$\xrightarrow{C_2H_6} NbC_9H_{10}^+ + 3H_2 \tag{37}$$
$$NbC_6H_{10}^+ + C_2H_6 \rightarrow NbC_8H_{10}^+ + 3H_2 \tag{38}$$
$$NbC_6H_{10}^+ + C_2H_6 \rightarrow NbC_8H_{14}^+ + H_2 \tag{39}$$

C_4 Alkanes. $NbC_4H_6^+$ is formed in the secondary reaction of Nb^+ with C_2H_6 (reactions 40 and 41) and in the primary reactions

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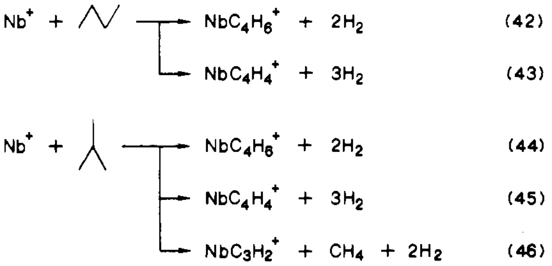
$$\mathrm{NbC_2H_4^+ + C_2H_6 \rightarrow NbC_4H_6^+ + 2H_2} \quad (40)$$

$$\mathrm{NbC_2H_2^+ + C_2H_6 \rightarrow NbC_4H_6^+ + H_2} \quad (41)$$

of $\mathrm{Nb^+}$ with *n*-butane and isobutane (reactions 42 and 44).



$\mathrm{NbC_4H_6^+}$ generated in reactions 42 and 44 produce ions with different CID fragmentation pathways. Figures 1 and 2 show energy-resolved mass spectra for these ions. The large differences in the CID spectra for these two ions are indicative of two distinct isomeric structures. $\mathrm{NbC_4H_6^+}$ generated from reactions 40 and 41 produce the same fragments (reactions 47–53), with roughly

$$\mathrm{NbC_4H_6^+} \xrightarrow{\mathrm{Ar}} \mathrm{NbC_4H_4^+ + H_2} \quad (47)$$

$$\rightarrow \mathrm{NbC_4H_2^+ + 2H_2} \quad (48)$$

$$\rightarrow \mathrm{NbC_4^+ + 3H_2} \quad (49)$$

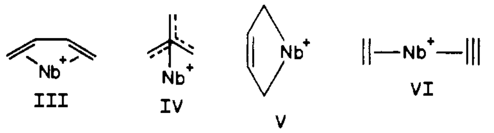
$$\rightarrow \mathrm{NbC_3H_3^+ + CH_3} \quad (50)$$

$$\rightarrow \mathrm{NbC_3H_2^+ + CH_4} \quad (51)$$

$$\rightarrow \mathrm{NbC_2H_2^+ + C_2H_4} \quad (52)$$

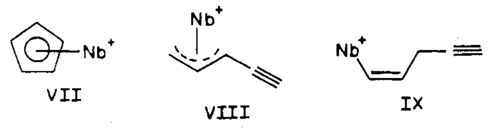
$$\rightarrow \mathrm{Nb^+ + C_4H_8} \quad (53)$$

the same CID energy dependencies as those produced by CID of $\mathrm{NbC_4H_6^+}$ from *n*-butane, suggesting that these ions have the same structure. Structures III–VI are possibilities for $\mathrm{NbC_4H_6^+}$. If



the initial carbon skeleton remains intact, structures III and/or V and structure IV would be expected from *n*-butane and isobutane, respectively. Since $\mathrm{Nb^+}$ is very active toward C–H bonds, while C–C cleavage products are much less prevalent in the primary reactions, these structures are the most reasonable. If $\mathrm{NbC_4H_6^+}$ formed from 1-butane is indeed a metal–butadiene structure, then coupling of the ligands is required in reactions 40 and 41 of $\mathrm{Nb^+}$ with $\mathrm{C_2H_6}$. This is consistent with the results for the reaction of $\mathrm{Nb^+}$ with ethene (vide infra). A mechanism for the reaction of $\mathrm{Nb^+}$ with $\mathrm{C_2H_6}$ to form $\mathrm{NbC_4H_6^+}$ is shown in Scheme II. After initial formation of $\mathrm{NbC_2H_4^+}$ or $\mathrm{NbC_2H_2^+}$, the ion oxidatively adds to a C–H bond in ethane, followed by migration of the ethene or acetylene into the Nb–C bond. Subsequent elimination of $\mathrm{H_2}$ from the activated complex leads to the final product.

C_5 and C_6 Alkanes. $\mathrm{Nb^+}$ dehydrogenates *n*-pentane and cyclopentane to form $\mathrm{NbC_5H_5^+}$. Loss of H• from an alkane is a high-energy process and is not generally observed in thermal ion–molecule reactions of metal ions. Loss of H• is only observed in the reaction of $\mathrm{Nb^+}$ with *n*-pentane and cyclopentane, indicating $\mathrm{NbC_5H_5^+}$ may be a cyclopentadienyl ring bound to $\mathrm{Nb^+}$ (structure VII). The only other reasonable structures that could result from



loss of H• would be metal–allyl or metal–alkenyl ions (structure VIII or IX). However, if these types of structures were formed, loss of H• would also be expected from other alkanes. Observation of $\mathrm{Nb(c\text{-}C_5H_5)^+}$ from pentane indicates $D(\mathrm{Nb^+\text{–}(c\text{-}C_5H_5)}) > 150$ kcal/mol.[24]

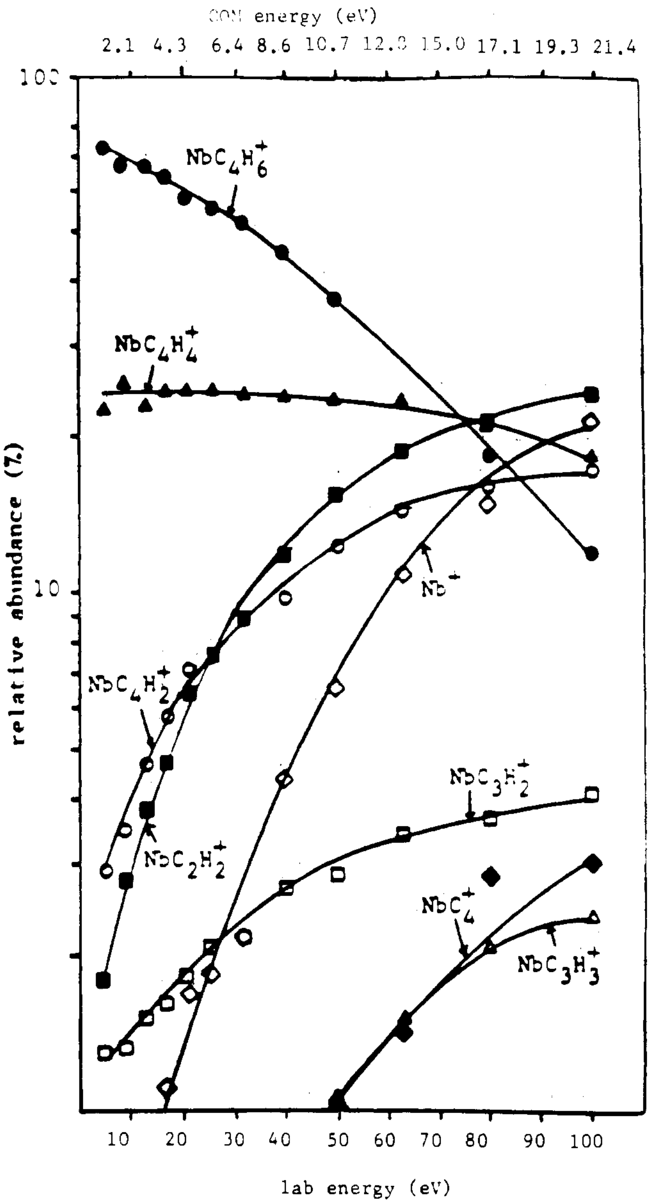
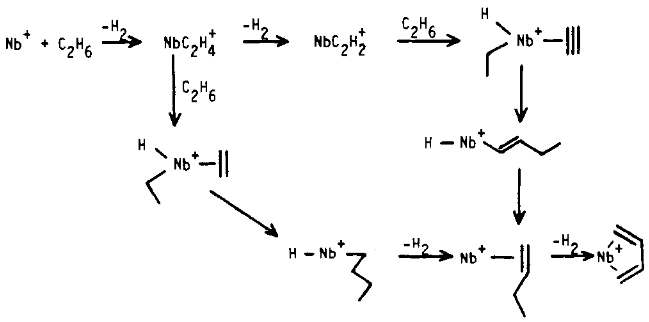


Figure 1. CID breakdown curve for $\mathrm{NbC_4H_6^+}$ generated in reaction 42.

Scheme II



Interestingly, $\mathrm{NbC_5H_5^+}$ reacts with cyclopentane to produce $\mathrm{NbC_{10}H_{11}^+}$ (reaction 54), whereas $\mathrm{NbC_5H_6^+}$ reacts with cyclopentane to produce $\mathrm{NbC_{10}H_{10}^+}$ (reaction 55). $\mathrm{NbC_{10}H_{10}^+}$ gen-

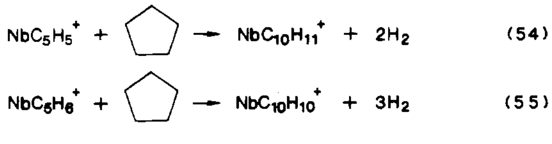


Table II. Primary and Secondary Reactions of Ta^+

reactant	primary prod	rel %	secondary prod	rel %
CH_4	$TaCH_2^+$	100	$TaC_2H_4^+$	100
C_2H_6	$TaC_2H_4^+$	10	$TaC_4H_8^+$	7
			$TaC_4H_6^+$	77
			$TaC_4H_4^+$	16
	$TaC_2H_2^+$	90	$TaC_4H_6^+$	45
			$TaC_4H_4^+$	55
C_3H_8	$TaC_3H_4^+$	78	$TaC_6H_8^+$	82
			$TaC_6H_6^+$	10
			$TaC_5H_6^+$	8
	$TaC_3H_2^+$	22	*a*	
C_4H_{10}	$TaC_4H_6^+$	12	$TaC_8H_{12}^+$	21
			$TaC_8H_{10}^+$	27
			$TaC_8H_8^+$	28
			$TaC_7H_{12}^+$	24
	$TaC_4H_4^+$	88	$TaC_8H_{12}^+$	12
			$TaC_8H_{10}^+$	23
			$TaC_8H_8^+$	65
C_5H_{12}	$TaC_5H_6^+$	71	$TaC_{10}H_{12}^+$	54
			$TaC_{10}H_{10}^+$	39
			$TaC_9H_{10}^+$	7
	$TaC_5H_4^+$	5	*a*	
	$TaC_4H_4^+$	16	$TaC_9H_{12}^+$	17
			$TaC_9H_{10}^+$	61
			$TaC_9H_8^+$	22
	$TaC_3H_4^+$	8	*a*	
C_6H_{14}	$TaC_6H_8^+$	21	$TaC_{12}H_{12}^+$	11
			$TaC_{11}H_{14}^+$	15
			$TaC_{11}H_{12}^+$	49
			$TaC_{11}H_{10}^+$	11
			$TaC_{10}H_{10}^+$	14
	$TaC_6H_6^+$	53	$TaC_{12}H_{12}^+$	38
			$TaC_{12}H_{10}^+$	26
			$TaC_{11}H_{12}^+$	36
	$TaC_6H_4^+$	5	*a*	
	$TaC_5H_6^+$	7	*a*	
	$TaC_5H_4^+$	5	*a*	
	$TaC_4H_6^+$	9	$TaC_{10}H_{10}^+$	100
c-C_3H_6	$TaC_3H_2^+$	81	$TaC_6H_6^+$	6
			$TaC_6H_4^+$	82
			$TaC_4H_4^+$	12
	$TaC_2H_2^+$	5	$TaC_5H_4^+$	54
			$TaC_3H_4^+$	46
c-C_3H_6	$TaCH_2^+$	14	$TaC_4H_6^+$	5
			$TaC_4H_4^+$	63
			$TaC_3H_4^+$	6
			$TaC_3H_2^+$	9
			$TaC_2H_2^+$	17
c-C_4H_8	$TaC_4H_4^+$	43	$TaC_8H_8^+$	30
			$TaC_8H_6^+$	18
			$TaC_6H_6^+$	52
	$TaC_4H_2^+$	14	*a*	
	$TaC_2H_2^+$	43	$TaC_6H_6^+$	47
			$TaC_6H_4^+$	24
			$TaC_4H_4^+$	29
c-C_5H_{10}	$TaC_5H_6^+$	70	$TaC_{10}H_{12}^+$	100
	$TaC_5H_4^+$	20	*a*	
	$TaC_3H_4^+$	10	*a*	
c-C_6H_{12}	$TaC_6H_8^+$	10	*a*	
	$TaC_6H_6^+$	84	$TaC_{12}H_{12}^+$	100
	$TaC_6H_4^+$	6	*a*	
methylcyclohexane	$TaC_7H_{10}^+$	5	*a*	
	$TaC_7H_8^+$	14	*a*	
	$TaC_7H_6^+$	46	$TaC_{14}H_{18}^+$	18
			$TaC_{14}H_{16}^+$	31
			$TaC_{14}H_{12}^+$	33
			$TaC_{14}H_{10}^+$	18
	$TaC_6H_6^+$	35	$TaC_{13}H_{16}^+$	31
			$TaC_{12}H_{12}^+$	69
isobutane	$TaC_4H_6^+$	32	$TaC_8H_{12}^+$	48
			$TaC_8H_{10}^+$	18
			$TaC_7H_{10}^+$	34
	$TaC_4H_4^+$	68	$TaC_8H_{10}^+$	74
			$TaC_8H_8^+$	26
2,2-dimethylpropane	$TaC_5H_8^+$	23	*a*	
	$TaC_5H_6^+$	37	$TaC_9H_{12}^+$	30
			$TaC_9H_{10}^+$	36
			$TaC_8H_{10}^+$	10
			$TaC_8H_8^+$	24
	$TaC_5H_6^+$	7	*a*	
	$TaC_4H_4^+$	28	$TaC_9H_{10}^+$	22
			$TaC_8H_{10}^+$	47
			$TaC_8H_8^+$	31
	$TaC_3H_4^+$	5	*a*	

[a] Reaction product(s) not determined due to low signal intensity.

erated from reaction 55 fragments upon CID with a very low cross section via reactions 56–65. While other metallocene cations have

86-eV laboratory energy

$$NbC_{10}H_{10}^+ \rightarrow NbC_{10}H_8^+ + H_2 \qquad 6\% \qquad (56)$$

$$\rightarrow NbC_{10}H_7^+ + H_2 + H^\bullet \qquad 6\% \qquad (57)$$

$$\rightarrow NbC_{10}H_6^+ + 2H_2 \qquad 19\% \qquad (58)$$

$$\rightarrow NbC_8H_6^+ + C_2H_4 \qquad 14\% \qquad (59)$$

$$\rightarrow NbC_7H_9^+ + C_3H \qquad 7\% \qquad (60)$$

$$\rightarrow NbC_6H_8^+ + C_4H_4 \qquad 12\% \qquad (61)$$

$$\rightarrow NbC_6H_4^+ + C_4H_6 \qquad 16\% \qquad (62)$$

$$\rightarrow NbC_5H_5^+ \quad C_5H_5 \qquad 9\% \qquad (63)$$

$$\rightarrow NbC_5H_3^+ + C_5H_5 + H_2 \qquad 3\% \qquad (64)$$

$$\rightarrow NbC_4H_2^+ + C_6H_8 \qquad 8\% \qquad (65)$$

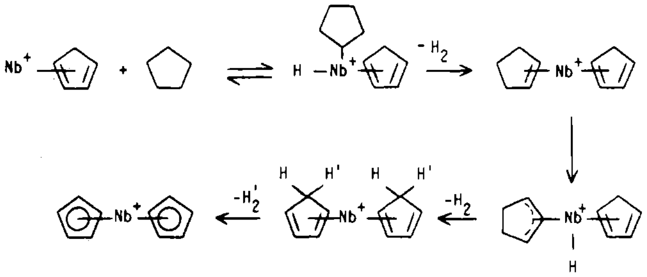
also been observed to have low cross sections for CID,[28] in contrast to $NbC_{10}H_{10}^+$, they characteristically fragment predominantly by loss of one and two C_5H_5 units. $NbC_{10}H_{10}^+$ can also be generated by reaction 66. Reaction 66 is representative of a

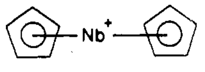
$$Nb^+ + Fe(Cp)_2 \rightarrow Nb(Cp)_2^+ + Fe \qquad (66)$$

Cp = cyclopentadienyl

general reaction developed for generating mononuclear metallocenes.[29] $NbC_{10}H_{10}^+$ generated in reaction 66 exhibits the same CID behavior as $NbC_{10}H_{10}^+$ generated in reaction 55, indicating $NbC_{10}H_{10}^+$ generated in reaction 55 is indeed a niobocene ion (structure X). To date, a mononuclear niobocene complex has

Scheme III





X

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(28) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 7399.

(29) Jacobson, D. B.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 2320.

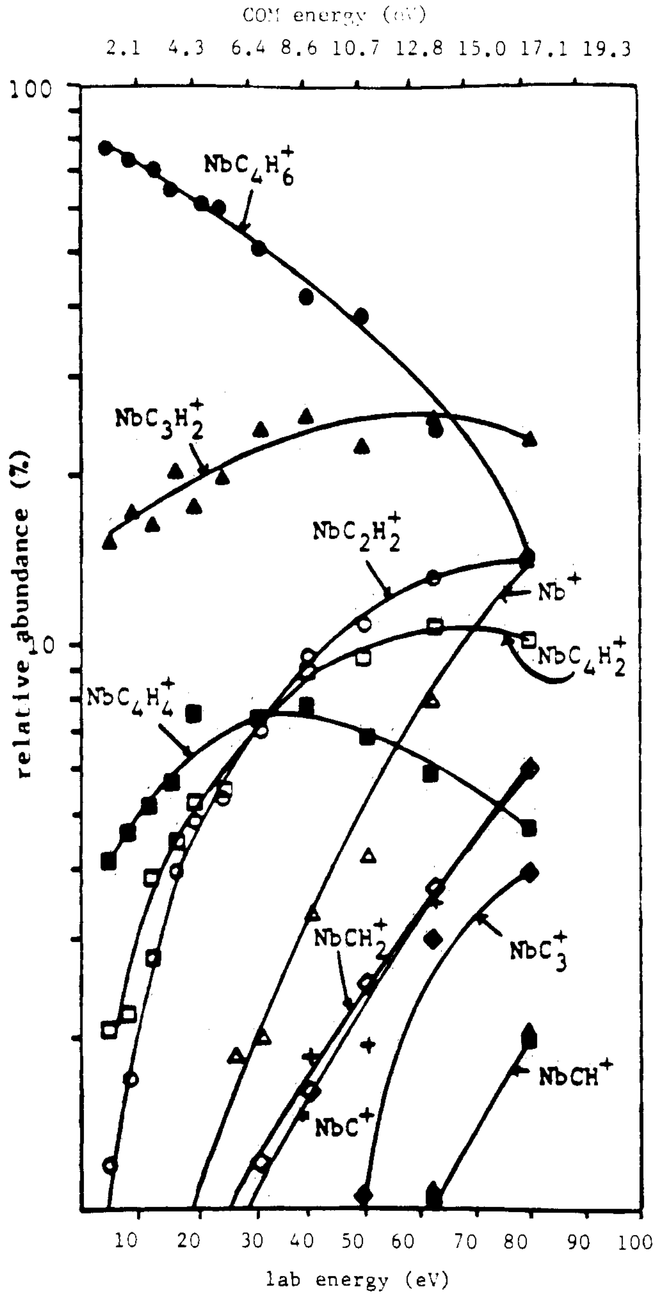
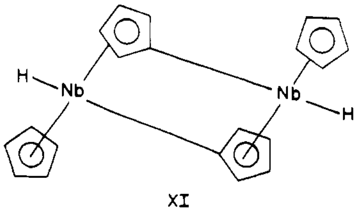


Figure 2. CID breakdown curve for $NbC_4H_6^+$ generated in reaction 44.

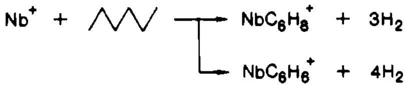
not been synthesized. A dinuclear "niobocene" has been prepared, (structure XI).[30] Since $Nb(Cp)_2^+$ is only formed from $NbC_5H_6^+$,



XI

we postulate concerted loss of H_2 from the intermediate bis(cyclopentadiene) complex involving an H• atom from each ring, as shown in Scheme III.

A dehydrocyclization mechanism, which occurs in the reaction of *n*-pentane with Nb^+ to form $NbCp^+$ and $Nb(c\text{-}C_5H_6)^+$, is also postulated in the reaction of Nb^+ with *n*-hexane (reactions 67 and 68). Dehydrocyclization has been observed in the reactions of Rh^+ with alkanes[31] and $CoCp^+$ with alkenes.[28]



$$Nb^+ + n\text{-}C_6H_{14} \rightarrow NbC_6H_8^+ + 3H_2 \quad (67)$$

$$\rightarrow NbC_6H_6^+ + 4H_2 \quad (68)$$

Alkenes. Nb^+ sequentially dehydrogenates C_2H_4 six times (reaction 69). This extensive reactivity with C_2H_4 is unprecedented in gas-phase metal ion chemistry. Most metal ions reported to date are unreactive with ethene. However, Sc^+ and Os^+ dehydrogenate two molecules of C_2H_4 (reaction 70).[18,32] In a recent ion-beam study, Mo^+ was also observed to exothermically dehydrogenate ethene.[13] Dehydrogenation of ethene presumably requires initial oxidative addition of a strong vinylic C–H bond to the metal center.

$$NbC_{2n}H_{2n}^+ + C_2H_4 \rightarrow NbC_{2(n+1)}H_{2(n+1)}^+ + H_2 \quad (69)$$

$$n = 0\text{–}5$$

$$M(C_2H_2)_n^+ + C_2H_4 \rightarrow M(C_2H_2)_{n+1}^+ + H_2 \quad (70)$$

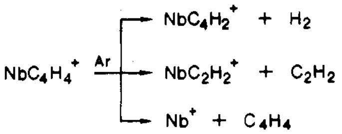
$$M = Sc, Os;\ n = 0, 1$$

Collision-induced dissociation of $NbC_{2n}H_{2n}^+$ (n = 1–6) from reaction 69 provides some insight to account for the large number of C_2H_2 units that can be incorporated onto the Nb^+ center.

$NbC_2H_2^+$ undergoes CID to form Nb^+ exclusively (reaction 71) at all energies studied (0–100-eV laboratory energy), indicating that this ion is, presumably, Nb^+–acetylene.

$$NbC_2H_2^+ \xrightarrow{Ar} Nb^+ + C_2H_2 \text{ (0–100 eV)} \quad (71)$$

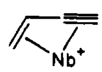
$NbC_4H_4^+$ produced in reaction 69 undergoes CID via loss of H_2, C_2H_2, and C_4H_4 (reactions 72–74). $NbC_4H_4^+$ can also be produced from cyclobutane and 1-butene. These ions undergo collisional activation to produce the same fragments as $NbC_4H_4^+$ produced from ethene with roughly the same energy dependencies, suggesting the three precursor molecules produce the same ion. An energy-resolved mass spectrum for $NbC_4H_4^+$ produced from 1-butene is shown in Figure 3. This ion could have a variety of structures. Structures XII–XIV represent the most reasonable structures. Structures XII and XIII require coupling of the ligands from ethene, whereas structure XIV requires cleavage of the carbon skeleton from 1-butene. Considering the CID results from the larger $NbC_{2n}H_{2n}^+$ produced from ethene (vide infra), the structures involving coupling of the C2 ligands appear most likely.



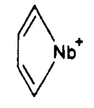
$$NbC_4H_4^+ \xrightarrow{Ar} NbC_4H_2^+ + H_2 \quad (72)$$

$$\rightarrow NbC_2H_2^+ + C_2H_2 \quad (73)$$

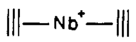
$$\rightarrow Nb^+ + C_4H_4 \quad (74)$$



XII

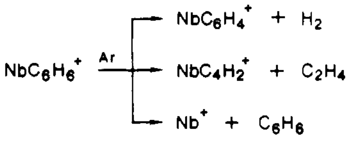


XIII



XIV

$NbC_6H_6^+$ produced in reaction 69 undergoes CID via loss of H_2, C_2H_4, and C_6H_6 (reactions 75–77). $NbC_6H_6^+$ produced from cyclohexane is presumably Nb^+–benzene and undergoes CID to produce the same fragments with approximately the same intensities. Thus, $NbC_6H_6^+$ produced from ethene apparently involves coupling of the ethene ligands to produce Nb^+–benzene.



40-eV laboratory energy

$$NbC_6H_6^+ \xrightarrow{Ar} NbC_6H_4^+ + H_2 \quad 67\% \quad (75)$$

$$\rightarrow NbC_4H_2^+ + C_2H_4 \quad 25\% \quad (76)$$

$$\rightarrow Nb^+ + C_6H_6 \quad 8\% \quad (77)$$

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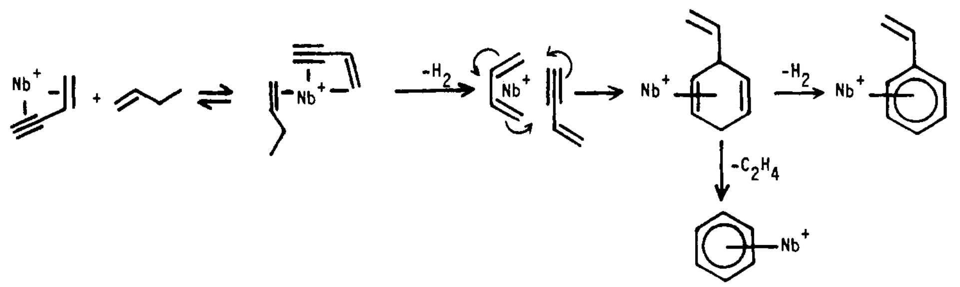
[30] Lemenovskii, D. A.; Urazowski, I. F.; Nifant'ev, I. E.; Perevalova, E. G. *J. Organomet. Chem.* **1982**, *292*, 217.

[31] Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 5944.

[32] Lech, L. M.; Freiser, B. S. *Organometallics* **1988**, *7*, 1949.

Scheme IV



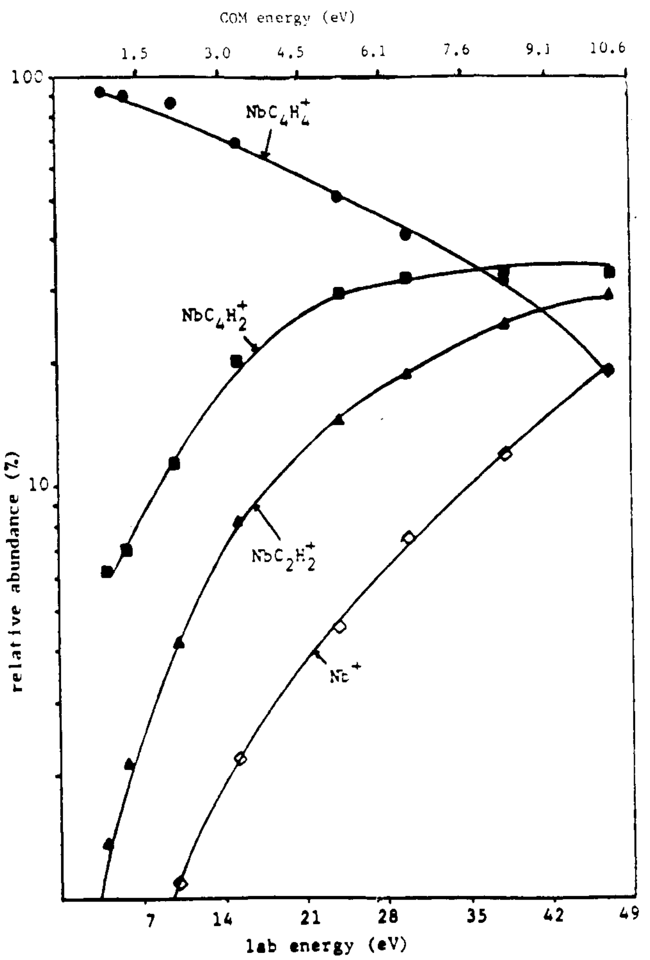


Figure 3. CID breakdown curve for $NbC_4H_4^+$ generated from 1-butene.

As is often the case, the ion–molecule reaction between Nb^+ and benzene (reaction 78) does not produce all of the same ions as

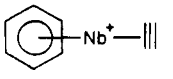
$$Nb^+ + c\text{-}C_6H_6 \rightarrow NbC_6H_4^+ + H_2 \qquad (78)$$

are produced from collisional activation of the ion–molecule complex. Observation of reaction 78 implies $D(Nb^+\text{–benzyne}) > 79$ kcal/mol.[33]

$NbC_8H_8^+$ produced in reaction 69 undergoes loss of C_2H_2 as the major product at all CID energies investigated (0–20-eV laboratory energy) with a small amount of H_2 loss observed at lower energies (reactions 79 and 80). These results are consistent with a Nb^+–benzene–acetylene structure (XV).

$$NbC_8H_8^+ \xrightarrow{Ar} NbC_6H_6^+ + C_2H_2 \quad 85\% \qquad (79)$$

$$NbC_8H_8^+ \xrightarrow{Ar} NbC_8H_6^+ + H_2 \quad 15\% \qquad (80)$$



XV

$NbC_4H_4^+$ produced from reaction of Nb^+ with 1-butene reacts with 1-butene as in reactions 81–84. $NbC_8H_8^+$ produced in

$$NbC_4H_4^+ + \text{1-butene} \rightarrow NbC_6H_4^+ + C_2H_6 + H_2 \qquad (81)$$

$$\rightarrow NbC_6H_6^+ + C_2H_6 \qquad (82)$$

$$\rightarrow NbC_8H_6^+ + 3H_2 \qquad (83)$$

$$\rightarrow NbC_8H_8^+ + 2H_2 \qquad (84)$$

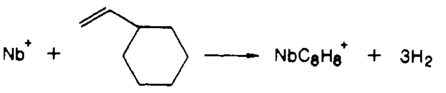
reaction 84 undergoes CID with loss of H_2 as the main dissociation pathway and loss of C_2H_2 and C_2H_4 at higher energies (reactions 85–87), indicating that it has a different structure than $NbC_8H_8^+$ produced from ethene.

$$NbC_8H_8^+ \xrightarrow{Ar} NbC_8H_6^+ + H_2 \quad 80\% \qquad (85)$$

$$\rightarrow NbC_6H_6^+ + C_2H_2 \quad 13\% \qquad (86)$$

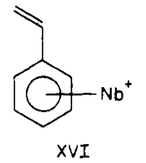
$$\rightarrow NbC_6H_4^+ + C_2H_4 \quad 7\% \qquad (87)$$

$NbC_8H_8^+$ was generated from reaction of Nb^+ with vinylcyclohexane (reaction 88). This ion fragments mainly via loss



(88)

of H_2 with loss of C_2H_2 and C_2H_4 at higher energies. The similar fragmentation patterns of $NbC_8H_8^+$ produced from 1-butene and vinylcyclohexane suggest that these ions may have the same structure. The difference in fragmentation patterns from $NbC_8H_8^+$ produced from ethene indicates that the ion from vinylcyclohexane has an intact carbon skeleton (structure XVI).



XVI

This is reasonable considering Nb^+ preferentially activates C–H bonds. Formation of structure XVI from 1-butene requires coupling of the ligands. A mechanism for this reaction is shown in Scheme IV. After initial formation of $NbC_4H_4^+$, dehydrogenation of a second butene ligand, followed by a Diels–Alder type coupling of the ligands and dehydrogenation of the subsequent ligand results in formation of $NbC_8H_8^+$.[34] Interestingly, $NbC_6H_6^+$ produced from 1-butene undergoes CID to produce the same fragments as $NbC_6H_6^+$ produced from cyclohexane, loss of H_2, C_2H_4, and C_6H_6. This ion is accounted for in Scheme IV by dealkylation of the coupled ligand, instead of dehydrogenation.

$NbC_{12}H_{12}^+$, the terminal product in reaction 69, undergoes

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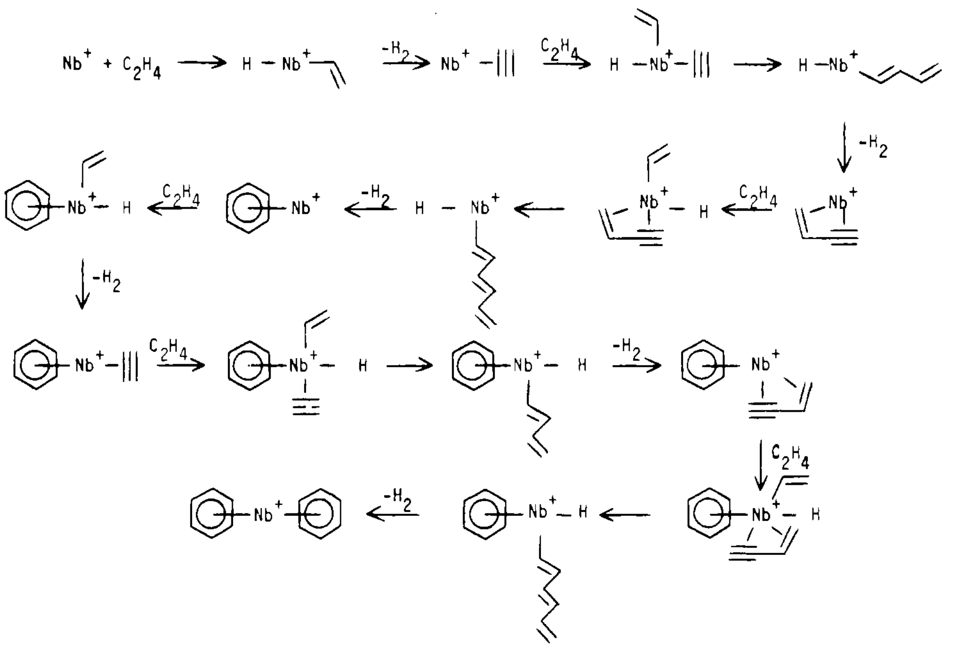
(33) ΔH_f(benzyne) taken from: Moini, M.; Leroi, G. E. *J. Phys. Chem.* **1986**, *90*, 4002.

(34) Metal assisted Diels–Alder reactions in gas-phase organometallic ion complexes have been previously proposed; see ref 14a and 32.

Scheme V

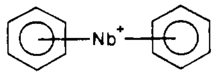


collisional activation predominantly via loss of H_2, C_6H_6, and C_6H_8 (reactions 89–92). However, $NbC_{12}H_{12}^+$ generated from reaction of Nb^+ with cyclohexane undergoes CID via pathways 93–97.

$$\begin{array}{llrr} & & \text{40-eV laboratory energy} & \\ NbC_{12}H_{12}^+ \xrightarrow{Ar} & NbC_{12}H_{10}^+ + H_2 & 55\% & (89) \\ & NbC_8H_6^+ + C_4H_6 & 6\% & (90) \\ & NbC_6H_6^+ + C_6H_6 & 31\% & (91) \\ & NbC_6H_4^+ + C_6H_8 & 8\% & (92) \end{array}$$

$$\begin{array}{llrr} & & \text{40-eV laboratory energy} & \\ NbC_{12}H_{12}^+ \xrightarrow{Ar} & NbC_{12}H_{10}^+ + H_2 & 9\% & (93) \\ & NbC_8H_6^+ + C_4H_6 & 3\% & (94) \\ & NbC_6H_6^+ + C_6H_6 & 47\% & (95) \\ & NbC_6H_4^+ + C_6H_8 & 28\% & (96) \\ & NbC_4H_2^+ + C_8H_{10} & 13\% & (97) \end{array}$$

These variations could be attributed to differences in internal energy of the two ions since they were formed from different precursors, or the ions could have different structures. Reactions 96 and 97 most likely result from the subsequent dissociation of $NbC_6H_6^+$ from reaction 95 (see reactions 75 and 76). The ion produced from cyclohexane most likely has a Nb^+–bis(benzene) structure (XVII).



XVII

The large number of C_2H_2 units incorporated on the Nb^+ center in reaction 69 is unusual and would seem to require coupling of the ligands to avoid coordinative saturation. Also, the CID results for each of the ions produced in reaction 69 are similar to those for the corresponding $NbC_nH_n^+$ initially produced from a C_n hydrocarbon (i.e. $NbC_6H_6^+$ appears to have the same structure whether produced from ethene or cyclohexane). A mechanism for these results is shown in Scheme V. All of the ionic structures are consistent with the CID results. Initially, Nb^+ inserts into a vinylic C–H bond in C_2H_4, followed by a β-H migration and reductive elimination of H_2 to produce a Nb^+–acetylene complex. Reaction of this ion with C_2H_4 also proceeds by initial oxidative addition of a C–H bond to the metal center. The next step, however, is a migratory insertion of C_2H_2 into the Nb^+–vinylidene bond, which couples the ligands. β-H migration and elimination of H_2 produces the Nb^+ (but-1-en-3-yne) ion. This ion reacts with C_2H_4 in a similar manner. After initial oxidative addition of the C–H bond, the C_4 ligand undergoes migratory insertion into the Nb^+–vinylidene bond, with subsequent dehydrocyclization of the C_6 ligand to produce Nb^+(benzene). Nb^+(benzene) can react with C_2H_4 three more times by an analogous mechanism to produce $NbC_{12}H_{12}^+$, which does not react further with C_2H_4. The final product may have a $Nb^+(c\text{-}C_6H_6)_2$ structure. However, the differences in CID intensities for this ion compared to the ion produced from cyclohexane may indicate that the final product in Scheme V does not undergo dehydrocyclization. A linear C_6 structure would be expected to lose H_2 upon collisional activation more readily than the bis(benzene) structure, in agreement with the observed results. $NbC_{12}H_{12}^+$ produced from ethene does not react further with ethene, which may be due to coordinative saturation about the metal center.

Conclusion

The reactions of Nb^+ with alkanes and alkenes in the gas phase have been studied by using FTMS. Nb^+ is observed to be very reactive toward C–H bond insertion processes. The reactivity with alkanes is characterized by extensive dehydrogenation, similar to that of Ta^+. CID of $NbC_4H_6^+$ generated from *n*-butane, isobutane, and ethane indicates the presence of two isomeric structures, with the ion generated from ethane producing similar fragments to that from *n*-butane. The ion from ethane is proposed to come from a ligand coupling mechanism. Ligand coupling is also observed in the reaction of Nb^+ with ethene, which generates $NbC_{2n}H_{2n}^+$ (n = 1–6), and the reaction of Nb^+ with 1-butene. The other main reaction pathway is dehydrocyclization of larger alkanes. This type of reaction is used to generate $Nb(Cp)^+$ from *n*-pentane and $Nb(benzene)^+$ from *n*-hexane.

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