derstanding the chemistry and properties of these materials.

Experimental Section

^{13}C NMR spectra were obtained on a Varian FT-80A instrument equipped with a 10-mm ^{13}C–^{1}H switchable probe and the standard temperature controller. Samples in sealed tubes with toluene-d_8 as lock solvent were excited with a 45° pulse every second with full proton decoupling. Only 512 points were taken at a spectral width of 500 Hz in most cases. The free induction decays were zero filled to 1024 points before Fourier transformation with no additional line broadening added in the data processing. Each sample required 2000–4000 pulses to accumulate sufficient signal to noise for further data analysis.

The temperature was measured by the exchange method: an open 10-mm NMR tube containing about 2 mL of cooking oil and an immersed copper constantan thermocouple was allowed to equilibrate in the spectrometer with the decoupler on before measurement of the thermocouple voltage with a potentiometer sensitive to ±0.001 mV. Temperatures were read from standard tables. The samples were also allowed to equilibrate for 15 min before any data acquisition.

^{1}H NMR spectra were obtained on a Varian T60 NMR spectrometer. ^{27}Al NMR spectra were obtained on a Varian XL200 spectrometer using resonance frequency at (4.7 T) 52.128 MHz. Since we were interested only in peak width, the chemical shifts were not obtained.

Samples of Al_2Et_6 were obtained from Texas Alkyls and used as received. $Na[Al_2Et_6F]$ was prepared[2] by heating Al_2Et_6 (2.0 mol) with anhydrous NaF (1.0 mol) under rigorously purified inert atmosphere.

Appendix

The derivation follows Matteson.[14]

$$Na[Al_2Et_6F] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Na[AlEt_3F] + AlEt_3$$

$$Al_2Et_6 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2[AlEt_3]$$

Let Q = the fraction of ethyl groups on $AlEt_3$ that have come from $Na[Al_2Et_6F]$. As $AlEt_3$ dimerizes, $-d[Et_{2:1}]/dt = 6Qk_2[Al_2Et_6]$. Also, $-d[Et_{TEA}]/dt = 6(1 - Q)k_1[Na[Al_2Et_6F]]$. But, $-d[Et_{2:1}]/dt = -d[Et_{TEA}]/dt$. So, $6Qk_2[Al_2Et_6] = 6(1 - Q)k_1[Na[Al_2Et_6F]]$.

$$Q = \frac{[Na[Al_2Et_6F]]}{(k_2/k_1)[Al_2Et_6] + [Na[Al_2Et_6F]]} \tag{3}$$

The lifetimes are

$$1/\tau_{2:1} = \frac{-d[Et_{2:1}]}{6dt[Na[Al_2Et_6F]]} = \frac{k_2Q[Al_2Et_6]}{[Na[Al_2Et_6F]]} \tag{1}$$

$$1/\tau_{TEA} = \frac{-d[Et_{TEA}]}{6dt[Al_2Et_6]} = k_2Q \tag{2}$$

Gas-Phase Reactions of Yttrium and Lanthanum Ions with Alkanes by Fourier Transform Mass Spectrometry

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The gas-phase reactions of Y^+ and La^+ with linear, branched, and cyclic alkanes are reported. Dehydrogenation is predominant for ethane and propane while dehydrogenation and carbon–carbon bond cleavage occur for linear and branched alkanes larger than C_3. As was observed for the other group 3 metal ion, Sc^+, both Y^+ and La^+ form characteristic dialkyl ions. Evidence is given for two different $YC_4H_6^+$ and $LaC_4H_6^+$ isomeric structures. Reaction with cyclopropane gives predominant dehydrogenation products. The observation of $LaCH_2^+$ from cyclopropane implies $D°(La^+–CH_2) > 93$ kcal/mol. Only dehydrogenation products are observed for cyclopentane and cyclohexane. In general, the primary reactions of Y^+ and La^+ are found to be similar to those of Sc^+. The secondary reactions of La^+, however, are found to be considerably slower than those for Sc^+ and Y^+.

Introduction

In recent years, a number of laboratories have demonstrated that transition-metal ions are highly reactive with organics in the gas phase.[1-16] There has been considerable interest in these reactions from both the standpoint of the fundamental chemistry involved as well as the practical applications of transition-metal ions as selective chemical ionization reagents for analytical mass spectrometry.[1,13,14] Thus far, most of the attention has focussed on the interactions of first-row groups 8–10 transition-metal ions Fe^+, Co^+, and Ni^+ with simple hydrocarbons[4-6,8,11-14] and has resulted in a good understanding of the processes and

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mechanisms involved in these reactions. Studies involving the early transition metals or the second- and third-row transition-metal ions have been much fewer, but those that have been conducted have provided interesting comparisons.[2,3,6,10,15,16]

In particular in a recent report by Tolbert and Beauchamp, Sc^+ was shown to exhibit a unique reactivity with alkanes.[10] First, formation of dialkyl products of the general form $Sc(C_nH_{2n+2})^+$ was observed with butane and larger alkanes, which is not seen for the other first-row transition metals. Second, Sc^+ was observed to dehydrogenate alkanes by a 1,3-process compared to the other first-row metals where 1,2- and 1,4-dehydrogenations occur. Two factors pertaining to the electronic structure of Sc^+ were cited for this unique reactivity: (a) only two valence electrons are available, making the formation of more than two strong σ bonds unlikely, and (b) the absence of additional d electrons on the metal center reduces the binding energy of acceptors in scandium(III) intermediates. By analogy, the other group 3 metals Y^+ and La^+ would also be expected to exhibit the same unique reactivity and, as described in this paper, this is in fact what is observed. Subtle differences in reactivity between the three metals do occur, however, and these are also discussed.

Experimental Section

The theory, instrumentation, and methodology of ion cyclotron resonance (ICR) spectrometry[17,18] and Fourier transform mass spectrometry[19-21] have been discussed elsewhere. Experiments were performed by using both a homebuilt frequency-swept capacitance bridge ICR and a Nicolet prototype FTMS-1000 Fourier transform mass spectrometer 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 FTMS cell was constructed in our laboratory and includes a $^1/_4$ in. diameter hole in one of the transmitter plates which permits irradiation with various light sources.

Y^+ and La^+ were generated by focussing the beam of a pulsed Nd-YAG laser onto metal targets mounted on the rear wall of the ICR (or FTMS) cell. Laser ionization can produce ions which are kinetically or electronically excited.[22,23] Some of the minor products observed in this study may be attributed to these species. The product ion distributions are reproducible to within ±10% absolute. Secondary reactions were observed by first using swept double-resonance ejection procedures to isolate the primary product ions. The selected ions were then permitted to react with the sample gas and the products detected.

Reagents were obtained from commercial sources and used as supplied except for several freeze–pump–thaw cycles to remove noncondensable gases immediately prior to their introduction into the spectrometer. Typical sample pressures were $(1-6) \times 10^{-7}$ torr as measured with a Bayard-Alpert ionization gauge. Reaction times (trapping time) were selectively varied from a minimum of 50 ms to a maximum of 2 s, allowing both primary and higher order reaction products to be observed. In order to reduce space–charge effects in the conventional ICR, a background of high-purity N_2 was maintained in the spectrometer at a pressure of 6×10^{-6} torr.

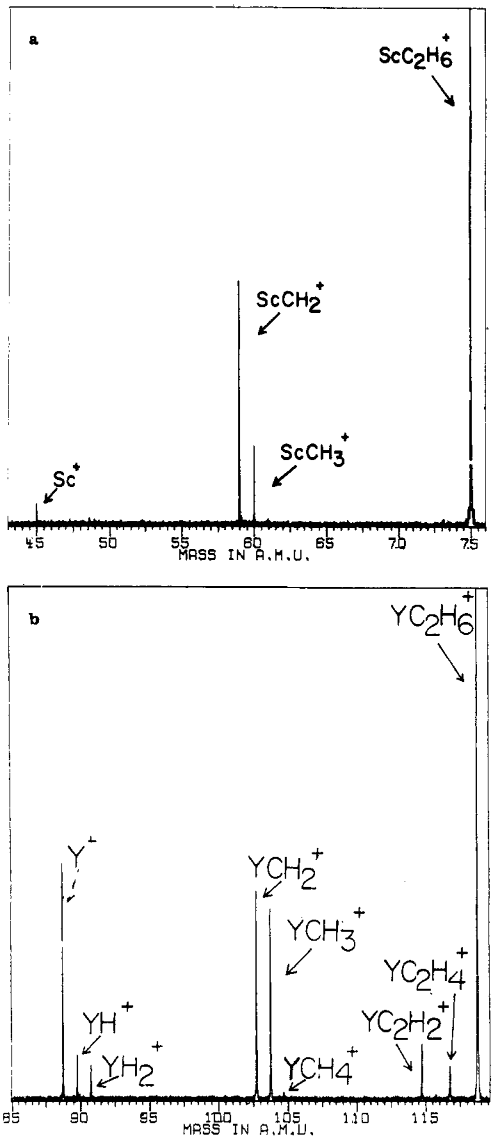

Figure 1. a. Collision-induced dissociation spectrum of $ScC_2H_6^+$ at 21-eV collision energy. (Note: no additional products were observed at 21-eV energy.) b. Collisional-induced dissociation of $YC_2H_6^+$ at 65-eV collision energy.

For collision-induced dissociation experiments using the FTMS,[21,24] argon was used as the collision gas. It was maintained in the spectrometer at a static pressure of 5×10^{-6} torr. The collision energy of the ions can be varied, typically between 0 and 100 eV. The CID spectrum changes as a function of collision energy as expected, favoring low-energy fragmentations such as rearrangements at low collision energies and high-energy fragmentations (often direct cleavage processes) at higher collision energies. In addition, because FTMS CID occurs by a multiple-collision process, isomerization can occur prior to dissociation yielding spectra that are not very diagnostic. Therefore, while CID spectra of many of the major ions were obtained, most of the structures are necessarily assigned as "reasonable" as opposed to proven and, thus, the resulting mechanistic conclusions must be considered tentative.

Results and Discussion

La^+ is very reactive with oxygen and LaO^+ is observed even at a background pressure of 1×10^{-8} torr. In addition, background oxygen can displace ligands to form LaO^+ from

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Table I. Primary Product Ion Distributions and Neutrals Lost for Reactions of Group 3 M$^+$ with Linear Alkanes

alkane	neutral (s) lost	ion	Sc^{+a}	Y^{+a}	La^+
methane	no reaction				
ethane	$2H_2$	$MC_2H_2^+$	29		
	H_2	$MC_2H_4^+$	71	100	100
n-propane	CH_4	$MC_2H_4^+$	27		
	$2H_2$	$MC_3H_4^+$		25	15
	H_2	$MC_3H_6^+$	73	75	85
n-butane	C_3H_6	MCH_4^+		3	
	C_2H_4	$MC_2H_6^+$	28	35	19
	CH_4, H_2	$MC_3H_4^+$	2	3	
	$2H_2$	$MC_4H_6^+$	16	47	77
	H_2	$MC_4H_8^+$	54	12	4
n-pentane	C_3H_8, H_2	$MC_2H_2^+$		2	
	C_3H_6	$MC_2H_6^+$		10	10
	C_2H_6, H_2	$MC_3H_4^+$		2	
	C_2H_6	$MC_3H_6^+$		16	3
	C_2H_4	$MC_3H_8^+$	51	12	4
	CH_4, H_2	$MC_4H_6^+$	13	14	5
	CH_4	$MC_4H_8^+$	9		
	$3H_2$	$MC_5H_6^+$		6	3
	$2H_2$	$MC_5H_8^+$	8	34	75
	H_2	$MC_5H_{10}^+$	19	4	
n-hexane	C_4H_{10}, H_2	$MC_2H_2^+$			2
	C_4H_{10}	$MC_2H_4^+$		1	
	C_4H_8	$MC_2H_6^+$		8	3
	C_3H_8	$MC_3H_6^+$		6	4
	C_3H_6	$MC_3H_8^+$	9	6	7
	C_2H_6, H_2	$MC_4H_6^+$	20	8	5
	C_2H_6	$MC_4H_8^+$	36	14	4
	C_2H_4	$MC_4H_{10}^+$	7	2	2
	CH_4, $2H_2$	$MC_5H_6^+$		4	2
	CH_4, H_2	$MC_5H_8^+$		7	6
	CH_4	$MC_5H_{10}^+$	4		
	$4H_2$	$MC_6H_6^+$		3	
	$3H_2$	$MC_6H_8^+$	2	30	53
	$2H_2$	$MC_6H_{10}^+$	22	10	12
	H_2	$MC_6H_{12}^+$		1	

[a] Results taken from ref 7.

Table II. Primary Product Distributions and Neutrals Lost for Reactions of Group 3 M$^+$ with Branched Alkanes

alkane	neutral (s) lost	ion	Sc^+	Y^{+a}	La^{+b}
isobutane	C_2H_4	$MC_2H_6^+$	5^a	12	14
	CH_4, H_2	$MC_3H_4^+$		5	
	$2H_2$	$MC_4H_6^+$	9	66	86
	H_2	$MC_4H_8^+$	86	17	
neopentane	C_3H_6	$MC_2H_6^+$		23	28
	CH_4, H_2	$MC_4H_6^+$	15^a	65	72
	CH_4	$MC_4H_8^+$	14		
	H_2	$MC_5H_{10}^+$	71	12	
2,2-dimethylbutane	C_4H_{10}, H_2	$MC_2H_2^+$			1
	C_4H_8	$MC_2H_6^+$		7	5
	C_3H_8,H_2	$MC_3H_4^+$	1^b		
	C_3H_6	$MC_3H_8^+$	1	3	1
	C_2H_6, H_2	$MC_4H_6^+$	20	4	2
	C_2H_6	$MC_4H_8^+$	2	16	
	CH_4, $2H_2$	$MC_5H_6^+$	2		
	CH_4, H_2	$MC_5H_8^+$	70	69	91
	$2H_2$	$MC_6H_{10}^+$	2		
	H_2	$MC_6H_{12}^+$	2	1	
2,3-dimethylbutane	C_4H_8	$MC_2H_6^+$	1^b	2	1
	C_3H_8, H_2	$MC_3H_4^+$	2	1	
	C_3H_8	$MC_3H_6^+$	1	1	
	C_3H_6	$MC_3H_8^+$	1	1	
	C_2H_6, H_2	$MC_4H_6^+$	7	1	
	C_2H_6	$MC_4H_8^+$	3	2	
	CH_4, $2H_2$	$MC_5H_6^+$	1		
	CH_4, H_2	$MC_5H_8^+$	44	20	4
	$2H_2$	$MC_6H_{10}^+$	40	72	95

[a] Results taken from ref 7. [b] Results in this study.

Table III. Primary Product Ion Distribution and Neutrals Lost for Reactions of Group 3 M$^+$ with Cyclic Alkanes

alkane	neutral (s) lost	ion	Sc^+	Y^{+a}	La^+
cyclopropane	C_2H_4	MCH_2^+			69
	CH_4	$MC_2H_2^+$	3		
	H_2	$MC_3H_4^+$	97	100	31
cyclobutane	C_2H_6	$MC_2H_2^+$	16	38	12
	C_2H_4	$MC_2H_4^+$	16		
	CH_4	$MC_3H_4^+$		4	
	$2H_2$	$MC_4H_4^+$	41	28	81
	H_2	$MC_4H_6^+$	27	30	7
cyclopentane	$2H_2$	$MC_5H_6^+$	100	100	100
cyclohexane	$3H_2$	$MC_6H_6^+$	89	100	100
	$2H_2$	$MC_6H_8^+$	11		

[a] Results taken from ref 7.

many product ions. Fortunately, LaO^+ is not very reactive with hydrocarbons presumably because La^+ uses its two valence electrons to form two bonds with oxygen atom. Thus, there are no electrons remaining to form σ bonds with carbon or hydrogen, inhibiting insertion into C–C and C–H bonds. Therefore, although LaO^+ appears in many cases, it does not present a serious problem in the study.

In general, reactions of Y^+ and La^+ with alkanes are very similar to those reported for Sc^+.[7,10] Both dehydrogenation and C–C cleavage products are observed. The most distinctive similarity is that all three of these group 3 metal ions react with acyclic alkanes larger than C_3 to form dialkyl metal ions, whereas the analogous reaction does not occur for any of the other metal ions studied in the gas phase to date. Tables I–III list the primary product distributions for the alkanes studied with Y^+ and La^+. For comparison, results for Sc^+ are also listed. In order to avoid the systematic differences in the product ion abundances obtained from different instrument systems, the results listed for scandium were obtained in our laboratory,[7] instead of using those obtained earlier on an ion beam instrument.[10] In addition, the reactions of Sc^+ with 2,2-dimethylbutane, 2,3-dimethylbutane, and cyclics listed in the tables had not been investigated by using the ion beam instrument. In general, the results obtained in our laboratory are in good agreement with those obtained from the ion beam instrument, with the exception of a few of the minor peaks.

Linear Alkanes. Methane, Ethane, and Propane. As is the case for Sc^+,[7,10] no reaction was observed for methane with Y^+ and La^+ at CH_4 pressures up to 4×10^{-5} torr and trapping times up to 2 sec. Y^+ and La^+ do, however, react with ethane to produce $MC_2H_4^+$ as the only product ion in reaction 1, indicating that $D°(M^+–C_2H_4)$ > 33 kcal/mol.[25] Sc^+ is different from Y^+ and La^+ in also

$$M^+ + C_2H_6 \xrightarrow{100\%} MC_2H_4^+ + H_2 \text{ (M =Y, La)} \quad (1)$$

giving some $ScC_2H_2^+$.[7,10] There appears to be a regular trend in going down the group from Sc^+ to La^+ for the secondary reactions. While $ScC_2H_4^+$ and $ScC_2H_2^+$ are both very reactive with ethane, $YC_2H_4^+$ only reacts very slowly, and $LaC_2H_4^+$ is not observed to react. The rapid decrease in reactivity for secondary reactions down the group is apparently due to the size effect since all three complex ions should have similar electronic structures.

CID of the $YC_2H_4^+$ and the $LaC_2H_4^+$ formed by reaction 1 results in predominant dehydrogenation to give $MC_2H_2^+$ at lower energies (below 58 eV) and predominant loss of the entire ligand at higher energy. Interestingly, minor

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[25] Supplemental thermochemistry taken from: Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data Suppl.* 1977, *6*.

amounts of LaC_2^+, LaH^+, and I -H_2^+ were also observed at higher energies. This is in contrast to $MC_2H_4^+$ (M = Fe, Co, Ni) where exclusive loss of C_2H_4 is observed over the entire energy range studied.[4]

Y^+ and La^+ react with propane according to reactions 2 and 3 to generate, presumably, M^+–propene and M^+–allene, respectively. Sc^+ behaves differently in also giving $ScC_2H_4^+$ as a product ion.[7,10] Assuming that reactions 2 and 3 are exothermic yields $D°(M^+\text{–propene}) > 30$ kcal/mol and $D°(M^+\text{–allene}) > 71$ kcal/mol. There is again a consistent change in reactivity for secondary reactions. Although secondary reactions were observed for each of the scandium primary product ions,[7] only one yttrium product ion, $YC_3H_6^+$, was observed to undergo secondary reactions 4 and 5, while no secondary reactions were observed for the lanthanum primary product ions. CID of the $YC_3H_6^+$ ion results in the loss of H_2 as the major product at low energy to produce $YC_3H_4^+$. CID of $YC_3H_4^+$ results in the loss of H_2 at low energy and the loss of C_2H_2 and C_3H_4 at higher energy. CID on $LaC_3H_6^+$ also yields predominantly the single dehydrogenation product $LaC_3H_4^+$ at low energy (below 12 eV kinetic energy). As the collision energy is increased, further dehydrogenation and carbon–carbon chain cleavage become more important. The CID results at 43 eV for $LaC_3H_6^+$ are given in reactions 6–11. These results are in direct contrast to the analogous group 8 species $MC_3H_6^+$ (M = Fe, Co, Ni), where CID yields exclusive loss of C_3H_6.[4]

$$
\begin{array}{llllll}
 & & & Y^+ & La^+ & \\
M^+ + C_3H_8 & \longrightarrow & MC_3H_6^+ + H_2 & 75\% & 85\% & (2) \\
 & \longrightarrow & MC_3H_4^+ + 2H_2 & 25\% & 15\% & (3)
\end{array}
$$

$$
\begin{array}{llll}
YC_3H_6^+ + C_3H_8 & \xrightarrow{75\%} & Y(C_6H_{12})^+ + H_2 & (4) \\
 & \xrightarrow{25\%} & Y(C_6H_{10})^+ + 2H_2 & (5)
\end{array}
$$

$$
\begin{array}{llll}
LaC_3H_6^+ \xrightarrow{\text{CID}} & \xrightarrow{22\%} & La^+ \bullet C_3H_6 & (6) \\
 & \xrightarrow{35\%} & LaCH_2^+ + C_2H_4 & (7) \\
 & \xrightarrow{1\%} & LaC_2H_2^+ + CH_4 & (8) \\
 & \xrightarrow{2\%} & LaC_3^+ + 3H_2 & (9) \\
 & \xrightarrow{37\%} & LaC_3H_2^+ + 2H_2 & (10) \\
 & \xrightarrow{3\%} & LaC_3H_4^+ + H_2 & (11)
\end{array}
$$

n-Butane. More interesting results are obtained when group 3 metal ions react with acyclic alkanes larger than propane. As first reported for Sc^+,[10] dialkylmetal complexes are also formed by Y^+ and La^+ with these alkanes. The predominant reactions of Y^+ and La^+ with n-butane are shown in eq 12–14. An interesting trend in the $MC_4H_8^+$ ion intensity can be seen in Table I. While it is the base peak for Sc^+, it is much less abundant than the butadiene complex base peak for Y^+, and only a minor peak in the reaction of La^+. This trend, in which higher multiple dehydrogenation products are observed down the group, appears to be somewhat general.

$$
\begin{array}{llllll}
 & & & Y^+ & La^+ & \\
M^+ + n\text{-}C_4H_{10} & \longrightarrow & MC_4H_8^+ + H_2 & 12\% & 4\% & (12) \\
 & \longrightarrow & MC_4H_6^+ + 2H_2 & 47\% & 77\% & (13) \\
 & \longrightarrow & MC_2H_6^+ + C_2H_4 & 35\% & 19\% & (14)
\end{array}
$$

Scheme I

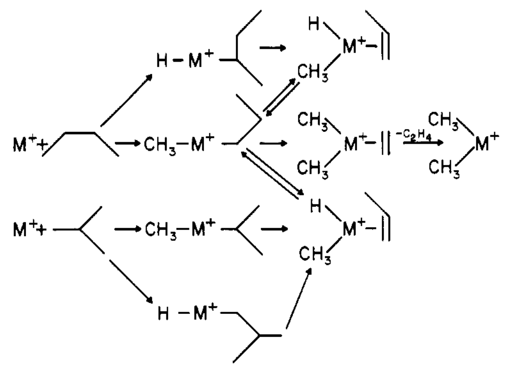
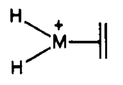


Table IV. Distributions for Neutral Losses from Y^+ and La^+ Reaction with n-Butane-1,1,1,4,4,4-d_6

neutral (s) lost	Y^+	La^+
H_2	1	0
HD	8	5
$2H_2$ or D_2	0	1
HD + H_2	3	32
2HD (H_2 + D_2)	41	37
HD + D_2	3	5
(CH_5D)	1	0
(CH_2D_4)	2	0
(CHD_5)	1	0
C_2H_4	22	6
C_2H_3D	3	4
$C_2H_2D_2$	3	4
C_2HD_3	7	6
$C_3H_4D_2$	1	0
$C_3H_3D_3$	3	0
$C_3H_2D_4$	1	0
C_3HD_5	trace	0

Scheme I depicts a mechanism for the formation of $MC_2H_6^+$ from n-butane in analogy for that reported earlier for Sc^+.[10] This mechanism involves the oxidative addition of M^+ across a terminal C–C bond to form a methyl–M^+–propyl complex intermediate. A β-methyl shift onto the metal ion then occurs generating a dimethylethene complex. Elimination of ethene then occurs to generate the observed dimethylmetal ion. Reaction of Y^+ and La^+ with n-butane-1,1,1,4,4,4-d_6 (listed in Table IV) supports this mechanism since the elimination of C_2H_4 (with the formation of $MC_2D_6^+$) is the major neutral loss observed when the dimethyl ion is formed. Some scrambling is observed, however, as evidenced by the losses of C_2H_3D, $C_2H_2D_2$, and C_2HD_3. A similar observation for Sc^+ was rationalized by invoking a reversible olefin insertion as shown in Scheme I. This mechanism also explains the observation of dialkyl ions from longer linear alkanes as well as from branched alkanes as discussed below.

Possible structures of the $MC_2H_6^+$ product observed for the reaction of Y^+ and La^+ with n-butane are given below (structures I–III). While the analogous dimethyl structure III was assigned for $ScC_2H_6^+$ on thermodynamic grounds,[10] the thermochemistry for Y^+ and La^+ has not yet been determined. The structure of the $MC_2H_6^+$ ion, therefore, was probed via ion–molecule reactions, H/D exchange, and collision-induced dissociation.



I

$H\text{—}\overset{+}{M}\text{—}C_2H_5$

II

$CH_3\text{—}\overset{+}{M}\text{—}CH_3$

III

No incorporation of deuterium into the $YC_2H_6^+$ ion was found to occur when the ion was trapped for 2 s in the presence of D_2 at a pressure of 5×10^{-6} torr. This result

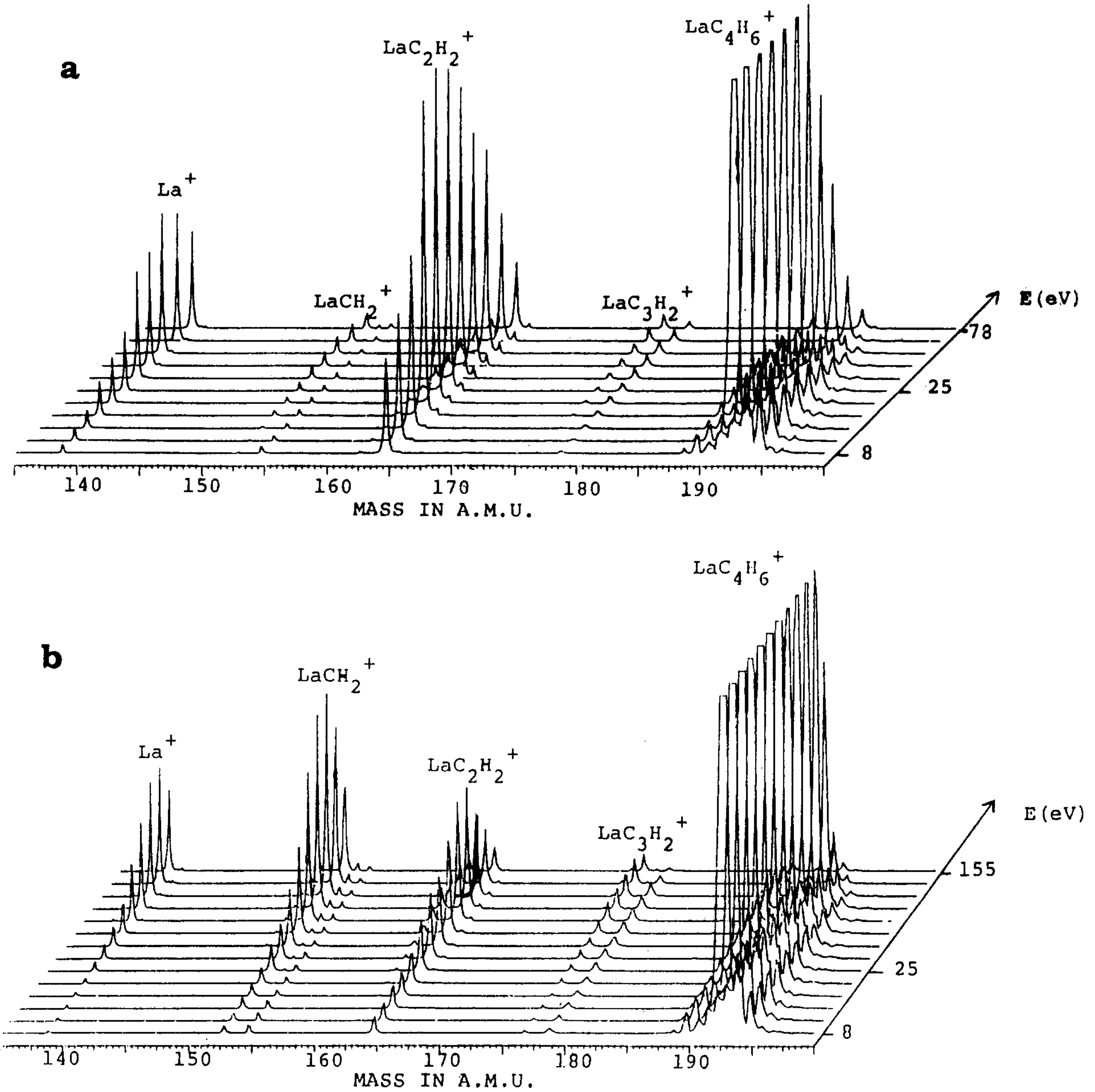


Figure 2. a. CID of $LaC_4H_6^+$ from La^+ reaction with *n*-butane. b. CID of $LaC_4H_6^+$ from La^+ reaction with isobutane.

is consistent with the dimethyl structure III, since deuterium exchange might have been expected to occur for structures I and II in which there is a metal–hydride bond; however, these results are not conclusive since FeH^+ does not undergo H/D exchange with deuterium.[6] No ligand exchange was found to occur with 1-butene, propene, or benzene probably ruling out the dihydride–ethene complex I.

Collision-induced dissociation of $YC_2H_6^+$ yields predominantly the loss of CH_4, CH_3, and C_2H_6 while, as shown in Figure 1a, these are the exclusive losses observed for $ScC_2H_6^+$. The reductive elimination of CH_4 is a known decomposition pathway of metal–alkyl complexes[26] and stable yttrium–alkyl bonds have also been observed in the condensed phase as well.[27] Thus, these results are consistent with dimethyl structures. Observation of additional peaks corresponding to $YC_2H_4^+$, $YC_2H_2^+$, YH_2^+, and YH^+ in Figure 1b and not observed for $ScC_2H_6^+$, however, indicates that for $YC_2H_6^+$ structures I and II may also be present or, at very least, are easily accessible isomeric forms upon activation. The dimethyl structure is also the most likely for $LaC_2H_6^+$ based on similar CID results to that of $YC_2H_6^+$. CID of $LaC_2H_6^+$ yields La^+, $LaCH_2^+$, $LaCH_3^+$, $LaC_2H_2^+$, and $LaC_2H_4^+$ as well as minor amounts of LaH^+ and LaH_2^+. Observation of LaH^+, LaH_2^+, and $LaC_2H_4^+$ again suggests that structures I and II might also be involved in some stages during the CID process. This would involve the coupling of the dimethyl groups. Finally, $D°(M^+–2CH_3)$ must be larger than 111 kcal/mol in order for reaction 14 to be exothermic.[25]

The structure of $MC_4H_6^+$ produced in reaction 13 was probed via CID. The major decomposition products observed in the CID spectrum of $YC_4H_6^+$ correspond to the loss of C_2H_4 and the elimination of the entire ligand with nearly equal abundances at low energies (30 eV). At higher energies (60 eV), the loss of C_4H_6 is the dominant process. Additionally, direct reaction of Y^+ with 1,3-butadiene produces loss of C_2H_4 as the major product. These results suggest that the structure of $YC_4H_6^+$ is yttrium–butadiene. In analogy to what was observed for $YC_4H_6^+$, the loss of C_2H_4 from $LaC_4H_6^+$ to form $LaC_2H_2^+$ is predominant over the CID energy range (8–78 eV) studied as shown in Figure

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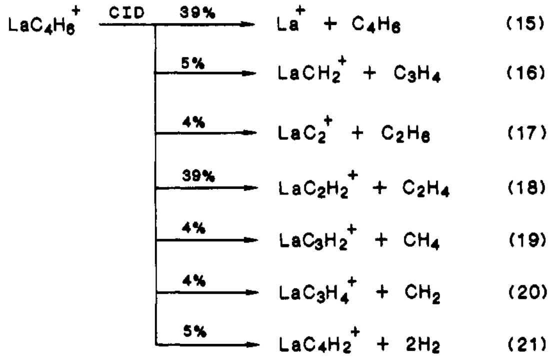
(26) Schrock, R. R.; Parshall, G. W. *Chem. Rev.* **1976**, *76*, 243.

(27) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pierce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* 54.

Table V. Alkyl Product Ions Observed for the Reaction of Y^+ with Linear Alkanes. Observed Product Ions (Percent of Primary Products)

alkane	$YC_2H_6^+$	$YC_3H_8^+$	$YC_4H_{10}^+$	$YC_5H_{12}^+$	$YC_6H_{14}^+$	$YC_7H_{16}^+$	$YC_8H_{18}^+$
methane	...	...	...	...	...	...	...
ethane	...	...	...	...	...	...	...
n-propane	...	...	...	...	...	...	...
n-butane	35	...	...	...	...	...	...
n-pentane	10	12	...	...	...	...	...
n-hexane	8	6	2	...	...	...	...
n-heptane	7	9	4	...	...	...	...
n-octane	2	8	6	...	...	...	...
n-nonane	2	3	7	4	...	...	...
n-decane	2	2	3	5	4	...	...
n-dodecane	1	2	4	4	2	3	2

2a. The CID results at 62-eV kinetic energy are given by eq 15–21. Again, these results are considerably different from the group 8 $MC_4H_6^+$ species (M = Fe, Co, Ni) where C_4H_6 loss is observed exclusively.[4]



$$LaC_4H_6^+ \xrightarrow{\text{CID}\ 39\%} La^+ + C_4H_6 \qquad (15)$$

$$\xrightarrow{5\%} LaCH_2^+ + C_3H_4 \qquad (16)$$

$$\xrightarrow{4\%} LaC_2^+ + C_2H_6 \qquad (17)$$

$$\xrightarrow{39\%} LaC_2H_2^+ + C_2H_4 \qquad (18)$$

$$\xrightarrow{4\%} LaC_3H_2^+ + CH_4 \qquad (19)$$

$$\xrightarrow{4\%} LaC_3H_4^+ + CH_2 \qquad (20)$$

$$\xrightarrow{5\%} LaC_4H_2^+ + 2H_2 \qquad (21)$$

The reaction of La^+ with *n*-butane-*1,1,1,4,4,4*-d_6 gives a predominant peak corresponding to $LaC_4H_2D_4^+$. These results also support a lanthanum–butadiene ion structure. Its formation can be easily explained by two consecutive hydrogen eliminations following an initial C–H bond insertion. Finally, observation of reaction 13 implies $D°(M^+\text{–butadiene}) > 57$ kcal mol^{-1}.[25]

***n*-Pentane and *n*-Hexane.** Reactions of Y^+ and La^+ with both *n*-pentane and *n*-hexane are characterized by an abundance of dehydrogenation products as well as carbon-chain cleavages and multiple-loss products. The elimination of $2H_2$ and $3H_2$ from *n*-pentane and *n*-hexane, respectively, are the single most abundant neutral losses observed for these reactions. Other neutral losses (and primary product ions) are given in Table I.

Dialkylyttrium ions are also observed for both of these alkanes. With *n*-pentane, $MC_2H_6^+$ and $MC_3H_8^+$ are observed, while for *n*-hexane, $MC_2H_6^+$, $MC_3H_8^+$, and $MC_4H_{10}^+$ are formed. Loss of ethene from either *n*-pentane or *n*-hexane could arise by initial oxidative insertion of M^+ into the C_3–C_4 bond on pentane or hexane followed by a β-methyl shift of the C_1 methyl group onto the metal center, forming a dialkylethene complex. This ion could then eliminate ethene (as proposed for butane in Scheme I) to produce the observed dialkyl ions. This mechanism is supported by the results of a labeling experiment using *n*-pentane-*3,3*-d_2 with Y^+ in which the elimination of $C_2H_2D_2$ is a dominant loss for the formation of the methylethylyttrium ion.

It is interesting to note that $MC_4H_{10}^+$ from the reaction with *n*-hexane is formed in relatively low abundance (2% of the total primary product distribution). This could indicate that the methyl–propyl ion is susceptible to an additional loss of ethene by the same mechanism proposed for the formation of the dimethyl species from *n*-butane in Scheme I.

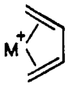
In addition to the multiple-loss scheme just mentioned, the formation of the other dialkyl ions ($MC_2H_6^+$ from pentane and $MC_2H_6^+$ and $MC_3H_8^+$ from hexane) can be explained by a reversible olefin insertion mechanism similar to the one shown in Scheme I. With pentane, for example, initial insertion of the metal ion into the first C–C bond with a subsequent β-hydride transfer onto the metal center would generate a methyl–hydride–butene intermediate complex. This complex can then undergo an olefin insertion which converts the butene ligand to a secondary butyl ligand that can then undergo a β-methyl shift onto the metal, forming a dialkylpropene intermediate. Elimination of the propene then results in the formation of the dimethyl species. Experiments with *n*-pentane-*3,3*-d_2 displayed only a minor amount of deuterium incorporation into the dimethylyttrium ion which is consistant with the proposed mechanism.

***n*-Heptane through *n*-Dodecane.** Reactions with larger alkanes up to *n*-dodecane (except for undecane) were also studied with Y^+. These reactions are chiefly characterized by carbon-chain cleavage products and multiple-loss products. For all of these alkanes, a large number of reaction products are observed with, for example, 32 products being observed for *n*-dodecane. Abundant secondary reactions occur for all of the larger alkanes.

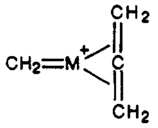
The most interesting observation with these large alkanes is that for *n*-heptane and *n*-octane the dialkyl product ion with the greatest number of carbon atoms is $YC_4H_{10}^+$. Beginning with *n*-nonane, the largest dialkyl ions correspond to the loss of C_4H_8 from the parent alkane. A summary of the yttrium–dialkyl ions observed with each of the linear alkanes is given in Table V. This trend cannot be explained at this time.

Branched Alkanes. Isobutane. All three metal ions react rapidly with isobutane to give the products shown in Table II. The dimethyl species were again observed for all three metals. It is interesting to note the decrease of $MC_4H_8^+$ intensity and the increase of $MC_4H_6^+$ intensity from scandium to lanthanum.

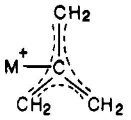
The $MC_4H_6^+$ ion structure was investigated by CID and specific ion–molecule reactions. Three possible structures for this ion include IV–VI.



IV



V



VI

The CID spectra of the $MC_4H_6^+$ from isobutane at a series of different kinetic energies easily distinguishes it from the isomeric butadiene ion (Figure 2). Although both ions give similar fragmentation products, the relative fragmentation abundances are quite different. While MCH_2^+ is an insignificant fragmentation pathway over the energy range (8–78 eV) studied for the butadiene complex, it is an important pathway and becomes predominant at higher CID energy (above 70 eV) for the $MC_4H_6^+$ generated from isobutane. For example, its CID spectrum gives the results shown in eq 22–29. This tends to exclude the possibility of rearrangement to the butadiene structure IV.

	Y^+ (40 eV)	La^+ (62 eV)	
$MC_4H_6^+ \xrightarrow{CID} M^+ + C_4H_6$	34%	13%	(22)
$\rightarrow MCH_2^+ + C_3H_4$	23%	35%	(23)
$\rightarrow MC_2^+ + C_2H_6$	0%	3%	(24)
$\rightarrow MC_2H_2^+ + C_2H_4$	20%	28%	(25)
$\rightarrow MC_3H_2^+ + CH_4$	0%	4%	(26)
$\rightarrow MC_3H_4^+ + CH_2$	9%	3%	(27)
$\rightarrow MC_4H_2^+ + 2H_2$	0%	8%	(28)
$\rightarrow MC_4H_4^+ + H_2$	14%	6%	(29)

While the CID experiments consistently and reproducibly showed the difference between the two $LaC_4H_6^+$ ions, surprisingly, repeated attempts at studying the secondary reactions of the ions with reagents such as acetonitrile, 1,3-butadiene, methanol, methyl iodide, benzene, and H/D exchange experiments with C_3D_6 failed to distinguish between structures IV and VI. Part of the difficulty was that the two ions react slowly to give secondary reactions. For the few cases where the secondary reactions were fast enough to be conveniently observed, they appeared to react identically. For example, cyclohexene reacts with $LaC_4H_6^+$ from both *n*-butane and isobutane to give $LaC_6H_6^+$ and $La(C_4H_6)(C_6H_6)^+$ ions in about the same relative abundance. These results suggest two possibilities: either the two isomeric ions have very similar reactivities or the $LaC_4H_6^+$ from one or both sources are a mixture of the two forms.

A rough thermodynamic consideration can provide some insight into this problem. A simple Hückel molecular calculation predicts that trimethylenemethane is a diradical, and its resonance energy is only about 1β less than that for butadiene.[10] In addition, symmetry considerations predict that M^+ can form two σ-bonds with trimethylenemethane while only two π bonds can be formed with butadiene in structure IV. Thus, structure IV may not be energetically favored over structure VI, and rearrangement from the latter to the former is not favored. Although thermodynamic data for yttrium and lanthanum are not available, estimated values in Tolbert and Beauchamp's paper do support the argument for the scandium case.[10] While the energy for two alkyl σ bonds to Sc^+ is around 120 kcal/mol, the bond energy between Sc^+ and ethylene is only about 40 kcal/mol. Since Y^+ and La^+ have a similar valence electronic structure to Sc^+, a parallel relationship in bond energy is expected. In contrast, for the later transition-metal ions, more electrons are available for back-donation. Thus, π-bonds between these metal ions and butadiene should be stronger, and the formation of structure IV over VI may actually be favored. This has been observed in the cobalt case. Co^+ reacts with isobutene to give $CoC_4H_6^+$ ion which does have the cobalt–butadiene structure, despite the multistep rearrangements required to give this structure.[27] An $FeC_4H_6^+$ is generated by electron impact on trimethylenemethane–iron–tricarbonyl, which exhibits distinctly different chemical and photochemical behavior than the Fe^+–butadiene species, however, suggesting that a trimethylenemethane structure is stable.[28]

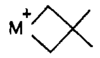
On the basis of the above results and arguments, we suggest that the two ions are probably of different structures with similar reactivities.

Finally, in order to distinguish between structures V and VI, the ion complex was allowed to react with CH_3CN. If structure V is correct, the displacement of the allene ligand would be possible, producing $MCH_2(CH_3CN)^+$. However, this was not observed. Furthermore, in the reaction of cyclohexene with the $MC_4H_6^+$ ion, neither $MCH_2(C_6H_6)^+$ nor $M(C_3H_4)(C_6H_6)^+$ was observed. Thus, although the failure to observe ligand displacement does not constitute absolute proof of a structure, the trimethylene–methane structure VI appears to be the most reasonable structure.

Finally, the formation of $YC_2H_6^+$ and $LaC_2H_6^+$ from isobutane is illustrated by Scheme I in analogy to Sc^+.

Neopentane. Neopentane provides a test for the 1,3-dehydrogenation mechanism since no β-hydrogen exists for 1,2-dehydrogenation. Although the single dehydrogenation product predominates for Sc^+,[7,10] it becomes far less important for Y^+ and is not observed for La^+. Instead, $MC_4H_6^+$ intensity was observed to increase down the group, again demonstrating the tendency for heavier metal ions within the group to give higher abundances of multiple loss products.

Since no β-hydrogen is available, the reaction might proceed by a 1,3-dehydrogenation following initial C–H bond insertion generating a metallocyclobutane intermediate (structure VII) which can then decompose to give the observed product ions. Alternatively, the reaction may proceed by an initial C–C bond insertion.



VII

The structure of $MC_4H_6^+$ formed from neopentane was investigated by CID. The result is identical with that observed from isobutane within experimental error, suggesting this might also be the trimethylenemethane structure VI.

Cyclopropane. Cyclopropane reacts with the group 3 metal ions as indicated in Table III. The reaction of cyclopropane with Y^+ occurs readily eliminating a single molecule of H_2 exclusively (reaction 30). Y^+ is one of the

$$Y^+ + \triangle \xrightarrow{100\%} YC_3H_4^+ + H_2 \qquad (30)$$

few transition-metal ions that reacts with cyclopropane in the gas phase.[2,3,29,30] CID of the $YC_3H_4^+$ ion formed by this reaction produces the loss of H_2 exclusively at low energy (30 eV). At higher CID energies, the loss of C_2H_2 and C_3H_4 are also observed. These results mimic the CID spectra of $YC_3H_4^+$ generated from both *n*-propane and propene, strongly indicating that in the reaction of Y^+ with cyclopropane, the ring is opened, generating an yttrium–allene complex instead of an yttrium–cyclopropene ion. These results suggest that Y^+ inserts into the weak C–C bonds of cyclopropane generating a metallacyclobutane which can subsequently rearrange to Y^+–propene.[6] This complex retains sufficient energy to then eliminate H_2.

The secondary reactions with cyclopropane are very slow but are observable. One of the most interesting secondary products corresponds to the elimination of two H_2 molecules, forming Y^+–C_6H_6 (reaction 31). CID of this ion at

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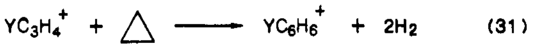
(28) Hettich, R. L.; Freiser, B. S., unpublished results.

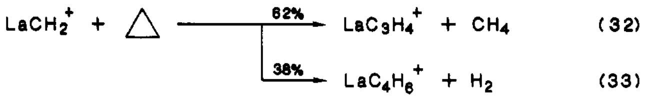
(29) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* 1981, *103*, 6628.

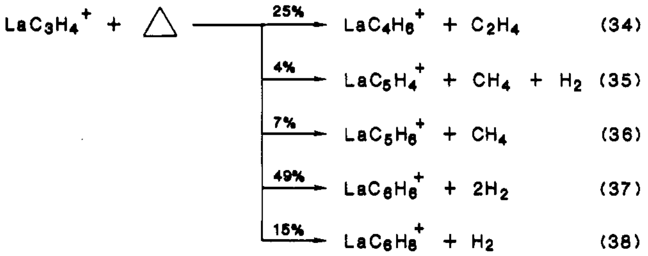
(30) Peake, D. A.; Gross, M. L.; Ridge, D. P. *J. Am. Chem. Soc.* 1984, *106*, 4307.



low energies results in products that correspond to the losses of H_2 and C_6H_6. These are the same losses observed in the CID spectrum of the yttrium–benzene ion, indicating that the $YC_6H_6^+$ formed in the secondary reaction with cyclopropane may also be a benzene complex.

La^+ reacts with cyclopropane to form $LaCH_2^+$, suggesting that $D°(La^+–CH_2^+) > 93$ kcal/mol, consistent with the photodissociation result of $D°(La^+–CH_2) = 106 \pm 5$ kcal/mol.[31] Both primary product ions for La^+ give secondary reactions as shown in reactions 32 and 33 for $LaCH_2^+$ and reactions 34–38 for $LaC_3H_4^+$.

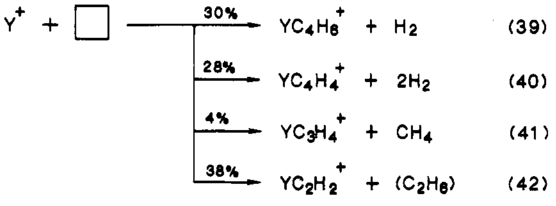




The $LaCH_2^+$ is believed to have a lanthanum–methylidene structure. Its CID at lower energy (below 51 eV) yields La^+ exclusively. At higher energies (e.g. 125 eV), a minor peak corresponding to loss of hydrogen to give LaC^+ was observed.

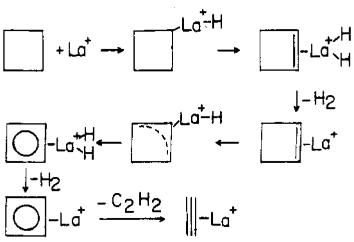
The structure of $LaC_3H_4^+$ from reaction 32 was studied by both H/D exchange and CID. $LaC_3H_4^+$ reacts with C_2D_4 to give four H/D exchanges, which is the same as that observed for the $LaC_3H_4^+$ ion generated from propene. CID of these two ions gave fragmentation and intensity results identical within experimental error, indicating that the cyclopropane ring is opened during the reaction generating a metal–allene structure.

Cyclobutane. Although hydrogen eliminations are the principal processes involved in the reaction of Y^+ with cyclobutane, some carbon–carbon bond cleavage products are also formed, reactions 39–42. The products observed

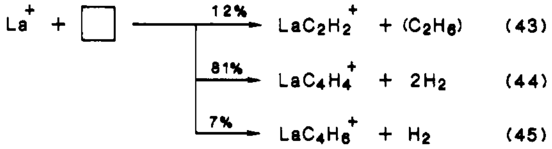


for the primary reactions with cyclobutane can be explained by the insertion of Y^+ into a C–C bond, generating a metallacyclopentane species, followed by two β-hydride shifts onto the metal center and subsequent loss of H_2 as has been postulated for Fe^+, Co^+, and Ni^+.[5] This scheme would presumably result in the formation of an yttrium–butadiene complex which can then undergo subsequent elimination of another molecule of hydrogen or C_2H_4 to form $YC_4H_4^+$ or $YC_2H_2^+$, respectively. This is consistant with the primary products formed by the reaction of Y^+ with 1,3-butadiene in which H_2 (32%) and C_2H_4 (68%) are eliminated.

Scheme II

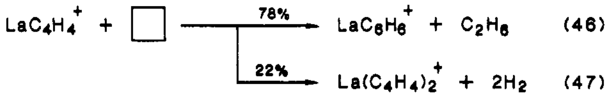


La^+ reacts with cyclobutane as indicated in reactions 43–45. Interestingly, the mechanism proposed above to

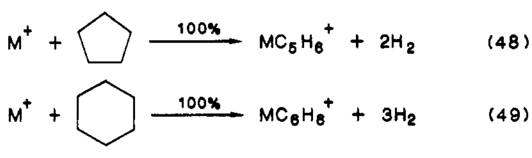


explain the reactions of Y^+ with cyclobutane does not explain the product ion abundance distribution for La^+. According to the mechanism, the reaction proceeds by initial C–C bond insertion by Y^+ to generate a metallacyclopentane species followed by dehydrogenation to give yttrium–butadiene ion. The butadiene complex can then decompose to give the other observed products. Because CID of the lanthanum–butadiene ion does not give a significant $LaC_4H_4^+$ fragment, however, $LaC_4H_4^+$ may not be formed through a butadiene intermediate. The reaction may actually proceed by single and double dehydrogenation to give the lanthanum cyclobutene and cyclobutadiene species as indicated in Scheme II. Many examples have been observed where a transition-metal atom significantly stabilizes the otherwise elusive cyclobutadiene ligand, presumably because the metal ion can contribute two more electrons to allow the ligand to achieve a stable aromatic configuration.[13] The structure of $LaC_4H_4^+$ was studied by H/D exchange and CID. No H/D exchange was observed between the ion and C_2D_4. If the ion has a diacetylene structure, ligand displacement by C_2D_4 to give $La(C_2H_2)(C_2D_2)^+$ should occur. This, however, was not observed. Unfortunately, an attempt to form $La(C_2H_2)_2^+$ directly from La^+ and ethylene was unsuccessful because further reaction of $LaC_2H_2^+$ with ethylene is extremely slow. CID of the $LaC_4H_4^+$ ion yields predominantly $LaC_2H_2^+$ as well as two minor ions, La^+ and LaC_2^+. These CID results are clearly different than those from the $LaC_4H_4^+$ ion isolated from butadiene where formation of $LaC_4H_2^+$ was a significant CID fragmentation pathway, again suggesting La^+–butadiene is not the intermediate involved in the reaction between La^+ and cyclobutane.

Like the $LaC_3H_4^+$ from cyclopropane, $LaC_4H_4^+$ also gives secondary reactions as shown in reactions of 46 and 47.



Cyclopentane and Cyclohexane. Dehydrogenation is the only process observed for cyclopentane and cyclohexane as shown in reactions 48 and 49. These reactions



probably proceed through consecutive dehydrogenations following initial carbon–hydrogen bond insertion, with no

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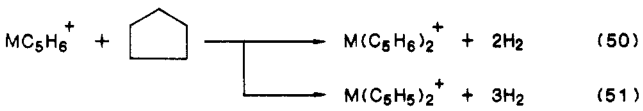
[31] Hettich, R. L.; Freiser, B. S., submitted for publication in *J. Am. Chem. Soc.*

carbon-carbon bond insertion or carbon skeleton rearrangement occurring.

$MC_5H_6^+$ reacts readily as shown in reactions 50 and 51.



The two product ions probably have structures corresponding to dicyclopentadiene and metallocene complexes, respectively. Although Sc^+-benzene and Y^+-benzene ions react further to give dibenzene metal ions,[7,10] this secondary reaction was not observed in their lanthanum counterpart, consistent with the general pattern that secondary reactions are slower as one goes down the group 3 metals.

The $LaC_5H_6^+$ ion structure was confirmed through isotope exchange and CID experiments. No H/D exchange with C_2D_4 was observed, suggesting a lanthanum cyclopentadiene structure, instead of a lanthanum cyclopentadienyl hydride structure. CID at 38 eV gives a predominant $LaC_5H_4^+$ ion as well as two small peaks corresponding to La^+ and $LaC_3H_2^+$. This result is consistent with the cyclopentadiene structure, as opposed to an acyclic structure where CID would produce a great variety of cleavage fragments.

The $LaC_6H_6^+$ CID gives a predominant peak corresponding to the loss of the whole ligand and two minor peaks with the formulae LaC_2^+ and $LaC_6H_4^+$, consistent with a lanthanum-benzene structure.

Conclusion

The reactions of La^+ with alkanes are very similar to that of its first- and second-row congeners, Sc^+ and Y^+. Their similarity in reactivity toward alkanes well demonstrates their similar electronic structures. In analogy with Sc^+ and Y^+, La^+ exhibits very high reactivity toward alkanes. While multiple dehydrogenation is the predominant process for Y^+ and La^+ with small alkanes, abundant carbon-carbon bond and dehydrogenation product ions are formed for acyclic alkanes larger than C_3. Particularly interesting is the formation of dialkyl ions. Only ring-cleaved product ions are formed for Y^+ and La^+ reacting with cyclopropane, while dehydrogenation is predominant for larger cyclic alkanes. Second-row transition-metal ions such as Rh^+,[2] Y^+, and Nb^+[32] display enhanced ability to dehydrogenate, and La^+ seems to further this trend as compared to Sc^+ and Y^+. This suggests a possible generalization that down the periodic table of d-block elements, gas-phase monovalent positive ions tend to exhibit a greater ability to dehydrogenate alkanes. Also interesting is the apparent formation of two distinct $YC_4H_6^+$ and $LaC_4H_6^+$ ions, one believed to have the butadiene structure generated from *n*-butane and the other having the trimethylenemethane structure generated from isobutane or neopentane.

Another interesting trend is the decreased tendency for primary product ions to participate in secondary reactions down the group. While secondary reactions are facile for Sc^+ and Y^+ reactions with alkanes, with the latter being usually slower, only three C_3–C_5 cyclic alkanes react with their lanthanum primary product ions rapidly enough to give secondary product ions observable under our experimental conditions.

Finally, this work has provided preliminary information on a number of reaction mechanisms. Further detailed studies are underway in our laboratory to test the conclusions drawn in this study.

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Registry No. La^+-CH_2, 105039-61-0; Sc^+, 14336-93-7; Y^+, 14782-34-4; La^+, 14175-57-6; CH_4, 74-82-8; C_2H_6, 74-84-0; C_3H_8, 74-98-6; *n*-C_4H_{10}, 106-97-8; *n*-pentane, 109-66-0; *n*-hexane, 110-54-3; *n*-heptane, 142-82-5; *n*-dodecane, 112-40-3; isobutane, 75-28-5; neopentane, 463-82-1; cyclopropane, 75-19-4; cyclobutane, 287-23-0; cyclopentane, 287-92-3; cyclohexane, 110-82-7; *n*-octane, 111-65-9; *n*-nonane, 111-84-2; *n*-decane, 124-18-5.

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[32] (32) Buckner, S.; MacMahan, T.; Freiser, B. S., unpublished results.

Theoretical Study of the Hydrogenation of Metal-Ligand π Bonds: Reaction of Cl_2TiCH_2 with H_2 To Form Cl_2TiHCH_3

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Correlated ab initio theoretical calculations at the valence double ζ plus polarization level are used to study the addition of dihydrogen across a titanium-carbon π bond. We find the reaction occurs with a small activation energy ($\Delta H^{\ddagger}_{300K}$ = 10.5 kcal/mol) from a weakly bound H_2 adduct complex (ΔH_{300K} = 3.8 kcal/mol). The reaction is also fairly exothermic (ΔH_{300K} = 21.5 kcal/mol). The explanation for the small barrier is precisely the same as for previously studied four-center 2 + 2 reactions. The geometry of the transition state for this reaction (and related four-center 2 + 2 reactions) is quite similar to related organic radical plus bond reactions.

Introduction

There are few documented examples of the hydrogenation of metal-ligand multiple bonds (eq 1a-c),[1-3] despite the analogy to other more common metal-ligand four-center 2 + 2 reactions. This paucity is due to either

$$M{=}CR_2 + H_2 \rightarrow M(H)(CHR_2) \qquad (1a)$$

$$M{=}NX + H_2 \rightarrow M(H)(NHX) \qquad (1b)$$

$$M{=}O + H_2 \rightarrow M(H)(OH) \qquad (1c)$$

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[1] (1) Schrock, R. R. *Science (Washington, D.C.)* **1983**, *219*, 13-18.

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