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Gas-Phase Synthesis and FT/ICR Mass Spectrometric Characterization of Sandwich Complexes of Sc^+, Y^+, and Lanthanide Ions with 1,3,5-Tri-*tert*-butylbenzene

Winnie W. Yin,[†] Alan G. Marshall,*[,†,‡] Joaquim Marçalo,[§] and Anto'nio Pires de Matos*[,§]

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, and Department Quimica, ICEN, LNETI, 2686 Sacavêm Codex, Portugal

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Abstract: Gas-phase reactions of Sc^+, Y^+, and lanthanide metal ions (M^+) with 1,3,5-tri-*tert*-butylbenzene (L) have been investigated at 10^{-6} to 10^{-7} Torr by means of FT/ICR mass spectrometry in the first systematic study in which all of the lanthanide series elements (except for Pm^+) are included. For Sm^+, Eu^+, Tm^+, and Yb^+, sandwich complex ions, ML_2^+, are formed by successive addition of intact ligand. The other metal ions activate C–H and C–C bonds, reacting with the *tert*-butyl group to form product ions with elimination of hydrogen, methane, and other neutrals. For all of the lanthanide series ions, the primary ion–molecule reaction pathway is controlled by the metal ion electronic configuration and the 4f to 5d promotion energy of the ion.

Introduction

During the past decade, several research groups have demonstrated the high reactivity of transition metal ions with organic molecules in the gas phase.[1-11] These reactions are of major interest both from the standpoint of the fundamental chemistry involved and the practical application for synthesis of transition metal complexes with organic molecules.[12,13] However, most of the attention has focused on the interactions of first-row transition metal ions such as Fe^+, Co^+, and Ni^+ with simple hydrocarbons and has resulted in a good understanding of the processes and mechanisms involved in these reactions.[2,6,14] The limited prior studies involving the early transition metals, the second- and third-row transition metal ions, and the lanthanide ions have provided equally interesting comparisons.[5,8]

Beauchamp *et al.* used ion beam techniques to study the reactions of scandium with alkanes[4] and praseodymium, europium, and gadolinium with alkanes and alkenes: Eu^+ was non-reactive; Pr^+ reacted only with alkenes; and Gd^+ exhibited reactivity similar to that of Sc^+.[15] Specifically, for the reaction of scandium, yttrium, and lanthanum ions with alkanes up to C_6, dehydrogenation and carbon–carbon bond cleavage were observed by Freiser *et al.* by FT/ICR mass spectrometry for linear and branched alkanes larger than C_3, whereas reaction with cyclopentane gave predominantly dehydrogenation products.[5] In complementary guided ion beam studies by Armentrout *et al.*[8] of reactions of Sc^+, Y^+, La^+, and Lu^+ with methane and ethane, the major products in the endothermic methane reaction were MCH_2^+ at low energy and MH^+ at high energy, with small amounts of MCH_3^+. Single and double dehydrogenation of ethane were exothermic for Sc^+, Y^+, and La^+ but endothermic for Lu^+.

In the condensed phase, Cloke *et al.* recently reported the metal vapor synthesis (MVS) of the first authentic examples of zero oxidation state lanthanide complexes, the bis(η-arene) sandwich compounds $[Ln(\eta\text{-}Bu^t{}_3(C_6H_3))_2]$,[16,17] as well as complexes with Sc, Y, and group 4, 5, and 6 elements.[18,19] With the lanthanides, different stabilities among members of the series were observed. However, he was unable to stabilize any complex with uranium.[20] To date, the only characterized uranium η-arene complexes are the uranium(III)–aluminium chloride with empirical formula $UAl_3Cl_{12}\cdot C_6H_6$,[21] the η-arene uranium(IV) complexes $[U(C_6Me_6)Cl_2(\mu\text{-}Cl)_3UCl_2(C_6Me_6)]AlCl_4$ and $U(C_6Me_6)Cl_2(\mu\text{-}Cl)_3UCl_2(\mu\text{-}Cl)_3UCl_2\text{-}(C_6Me_6)$,[22] and η-arene uranium(III) borohydrides (η-mesitylene)$U(BH_4)_3$ and $(C_6Me_6)U(BH_4)_3$.[23]

Successful detection of analogous reactions in the gas phase can provide considerable insight into condensed-phase behavior. For example, for the reaction of U^+ with tri-*tert*-butylbenzene (Bz′), the sandwich complex $U(Bz')_2^+$ and products resulting from CH_4 elimination were obtained.[24] Another example is Dunbar *et al.*'s comparison[11] of gas-phase and condensed-phase synthesis and reactivity of metallocyclotriynes: M(tribenzocy-

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* Authors to whom correspondence may be addressed.

[†] The Ohio State University.

[‡] Present address: National High Magnetic Field Laboratory, 1800 East Paul Dirac Drive, Tallahassee, FL 32312-4005.

[§] ICEN.

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clotriyne)$^+$ and M(tribenzocyclotriyne)$_2^+$ for first-row d-transition metals were formed in the gas phase, and no neutral leaving groups were observed.

In this work we are specifically interested in comparing the results obtained by Cloke *et al.*[16,17,19,25] on the stability and bonding of bis(η^6-1,3,5-*t*-Bu$_3$C$_6$H$_3$)lanthanide complexes prepared by metal vapor synthesis with the present results of the gas-phase reactions of Sc$^+$, Y$^+$, and all the lanthanide ions (except Pm$^+$) with the same ligand. A brief comparison of gas-phase reactions with prior work is also addressed.

The work reported here constitutes the first systematic study of the reactivities of *all* (except Pm$^+$) of the lanthanide ions (plus Y$^+$ and Sc$^+$) with the *same* organic molecule (1,3,5-tri-*tert*-butylbenzene). Fourier transform ion cyclotron resonance mass spectrometry[26–42] is ideally suited for this purpose, because abundant lanthanide ions may be produced by laser desorption/ionization and trapped for extended periods to produce various species whose time-evolution and reactivity may be monitored at high mass resolving power to facilitate identification of products.

Experimental Section

All experiments in Columbus, OH, were performed on a Nicolet FTMS-2000 FT/ICR mass spectrometer (Extrel FTMS Millipore Corp., Madison, WI), operating at 3 T, connected to an all-glass heated inlet system (Brunfeldt, Bartlesville, OK) and interfaced to a Nd:YAG (1.064 μm) laser (model YAG660A, Continuum, Santa Clara, CA). Experiments in Sacavém, Portugal, were performed with an Extrel FTMS-2001 FT/ICR mass spectrometer, also operating at 3 T, interfaced to a Nd:YAG (1.064 μm) laser (GCR-11, Spectra Physics, Mountain View, CA). Rare earth metals (and metal oxides) were obtained from Aldrich Chemical Co. (Milwaukee, WI), Ventron GmbH (Karlsruhe, Germany), and Research Chemicals (Phoenix, AR). For the more oxophilic lanthanides, the ligand 1,3,5-tri-*tert*-butylbenzene (Aldrich Chemical Co., Milwaukee, WI) was sublimed and transferred to the instrument under argon.

Rare earth positive ions were generated by means of laser desorption from a piece of metal or from metal oxide powder which was mounted on the automatic probe near the front trapping plate of the source side of the dual cell ion trap where the Nd:YAG laser was focused. The solid ligand (1,3,5-tri-*tert*-butylbenzene) was dissolved in methanol or acetone and put on the back side of the probe tip which was dried in air before being admitted into the vacuum chamber of the instrument. The vapor pressure of the ligand was sufficiently high that probe heating was not required to produce a sufficient number of molecules in the gas phase for ion–molecule reactions. For some experiments the ligand was introduced through an Extrel batch inlet which includes a leak valve (model 120, Andonian Cryogenics, Inc., Newtonville, MA). The ligand pressure on the source side of a dual source/analyzer ion trap was typically in the range of 10^{-7}–10^{-6} Torr as measured by ion gauges.

Rate constants were measured by observing the pseudo-first-order decay of the metal ion FT mass spectral peak magnitude as a function of time at constant ligand pressure. Pressure calibration was based on the reaction of CH$_3$COCH$_3^+$ with CH$_3$COCH$_3$[43] and included corrections for reactant gas ionization efficiency;[44,45] the molecular polarizability of 1,3,5-tri-*tert*-butylbenzene was estimated by the method of Miller.[46] Ions formed by laser desorption may exhibit a broad distribution of kinetic and electronic energies.[47] However, semilog kinetic plots showed highly linear decay for all of the ions studied, consistent with predominantly ground state ions. Moreover, the use of a 500 ms thermalization period, with pulsed valve introduction of argon, for the reactions of some metal ions did not change any rate constants or product distributions.

For collision-induced dissociation (CID) experiments, we introduced argon gas through either a leak valve or a pulsed valve (model 9-338-900, General Valve Co., Fairfield, NJ) at a pressure of $\sim 5 \times 10^{-7}$ Torr and excited the ions in question to a lab-frame translational energy of ~10–50 eV.[48,49]

Ions generated from a given laser pulse were allowed to pass into the ion trap by grounding the source trap plate for 2 ms after the laser pulse; the trapping potential was then raised to 1 V for 5 ms to 3 s to provide an ion thermalization and/or ion–molecule reaction period. (In the Sacavém experiments, the source trap plate was not grounded after the laser pulse.) Coherent ion cyclotron motion was then excited by frequency-sweep irradiation over a bandwidth from d.c to several hundred kHz to 1 MHz at a sweep rate of 1.4 kHz to 2 kHz per μs at an rf amplitude of 57–78 $V_{(p\text{-}p)}$. Direct-mode detection over the same bandwidth generated either 16K or 32K time domain data points, to which another 16K or 32K zeroes were added before discrete Fourier transformation. No apodization (windowing) was used. Each mass spectrum was obtained from a single laser shot, and data were acquired on the source side of the dual source/analyzer ion trap in each case.

Results and Discussion

Pathways for Gas-Phase Lanthanide Ion Complexation and/or Reaction with 1,3,5-Tri-*tert*-butylbenzene. In Table 1, we summarize the products obtained in the reactions of Sc$^+$, Y$^+$, and all of the lanthanide ions (except Pm$^+$) with 1,3,5-tri-*tert*-butylbenzene. Figures 1 and 2 illustrate the two types of behavior observed for the various metal (M) ions: either the ligand associates intact with the ion (e.g., Yb$^+$ in Figure 1) or there is elimination of H$_2$ and CH$_4$ or other neutrals (Figure 2 for Ho$^+$) indicating C–H and/or C–C bond activation, probably of the *tert*-butyl group. Previous studies of Sc$^+$, Y$^+$, La$^+$, and Gd$^+$ reactions with a branched alkane, namely neopentane, have also shown this type of reactivity.[5,15] The observed primary products, ML$^+$ or [ML – H$_2$]$^+$, [ML – CH$_4$]$^+$, ... (L = 1,3,5-tri-*tert*-butylbenzene), react further to form species of the type ML$_2^+$ or [ML$_2$ – H$_2$]$^+$, [ML$_2$ – CH$_4$]$^+$, [ML$_2$ – C$_5$H$_{12}$]$^+$, and others. For ions of the second half of the lanthanide series, species with three ligands minus fragments are formed at a sufficiently long reaction period. In some cases, species containing oxygen are formed, in particular for the oxophilic metals at the beginning of the lanthanide series.

The two types of behavior described above may be represented by the following equations:

$$M^+ + L \rightarrow ML^+ \xrightarrow{+L} ML_2^+ \tag{1}$$

M = Sm, Eu, Tm, Yb

and

$$M^+ + L \rightarrow [ML - H_2]^+ + [ML - CH_4]^+ + \ldots \xrightarrow{+L} [ML_2 - H_2]^+ + [ML_2 - CH_4]^+ + [ML_2 - C_5H_{12}]^+ + \ldots \tag{2}$$

M = Sc, Y, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er, Lu

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Table 1. Principal Products of Reaction of Sc^+, Y^+, and the Lanthanide Ions (Ln^+) with 1,3,5-Tri-*tert*-butylbenzene

M^+	Sc^+	Y^+	La^+	Ce^+	Pr^+	Nd^+	Sm^+	Eu^+	Gd^+	Tb^+	Dy^+	Ho^+	Er^+	Tm^+	Yb^+	Lu^+
(a) Primary Reaction Products																
ML^+							100	100			24	10	3	100	100	4
$(ML - H_2)^+$	3	12							11	12	7	14	31			71
$(ML - 2H_2)^+$		6														
$(ML - CH_4)^+$	7	12	83	83	91	95			74	77	69	69	63			14
$(ML - CH_4 - H_2)^+$	10	40								4		4	3			11
$(ML - CH_4 - 2H_2)^+$		4														
$(ML - 2CH_4)^+$	67	18	17	17	9	5			15	7		3				
$(ML - 2CH_4 - H_2)^+$	3	6														
$(ML - 3CH_4)^+$	10	2														
(b) Secondary Reaction Products																
ML_2^+							100	100			13	2		100	100	
$(ML_2 - H_2)^+$		2							3	5	4	13	17			37
$(ML_2 - 2H_2)^+$		1							2							
$(ML_2 - CH_4)^+$	2		56	50	77	83			10	18	34	18	9			
$(ML_2 - CH_4 - H_2)^+$	2	17		3					13	10	4	14	18			13
$(ML_2 - CH_4 - 2H_2)^+$	2	4														2
$(ML_2 - 2CH_4)^+$	43	8	33	34	8	9			8	3						
$(ML_2 - 2CH_4 - H_2)^+$		10														
$(ML_2 - 3CH_4)^+$	9															
$(ML_2 - C_4H_8)^+$		3							3	3	2	2	4			4
$(ML_2 - C_4H_{10})^+$		4							3	5		4	8			28
$(ML_2 - C_4H_{10} - H_2)^+$		3														
$(ML_2 - C_5H_{12})^+$	4	13	6	5	15	8			51	51	43	45	44			7
$(ML_2 - C_5H_{12} - H_2)^+$	4	20	3	3						2		2				9
$(ML_2 - C_5H_{12} - CH_4)^+$	30	15	2	5					7	3						
$(ML_2 - C_5H_{12} - 2CH_4)^+$	4															

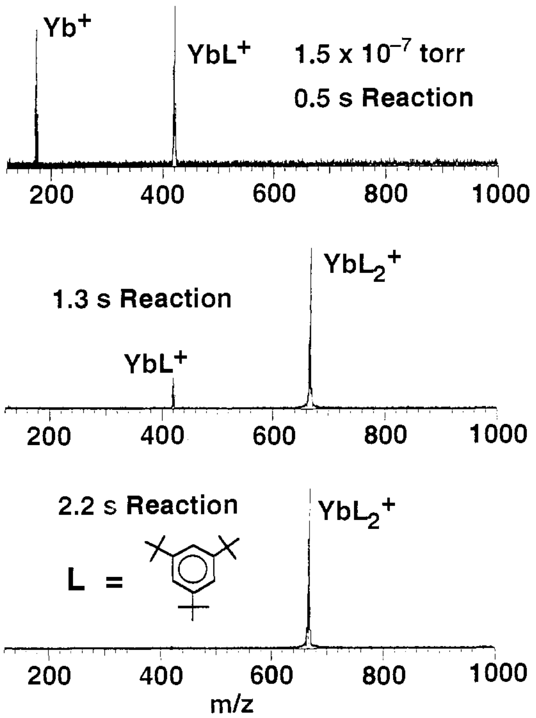

Figure 1. FT/ICR mass spectra of the ionic products of the reaction of Yb^+ with 1,3,5-tri-*tert*-butylbenzene (L) at 1.5 × 10^{-7} Torr, following each of three different reaction periods. Note the successive addition of two ligands and the absence of C–H or C–C activation products. The time-evolution of the ionic species in this reaction is shown in Figure 3.

Figure 3 shows the variation of the relative abundances of Yb^+, YbL^+, and YbL_2^+ with ion–molecule reaction period. Figure 4 shows the variation of the relative abundances of Ho^+, HoL^+, $[HoL - H_2]^+$, $[HoL - CH_4]^+$, HoL_2^+, $[HoL_2 - H_2]^+$, $[HoL_2 - CH_4]^+$, ... with reaction period. The data plotted in these figures are in accord with eqs 1 and 2. Adduct formation (eq 1) is most probably the result of infrared radiative stabilization of the collision complex, since the low experimental pressure (<10^{-7} Torr if the ionization efficiency of the ligand is taken into account) makes collisional deactivation very unlikely. Moreover the rate constants for adduct formation (for Sm, Eu, Tm, and Yb) did not show any noticeable pressure dependence (see below).

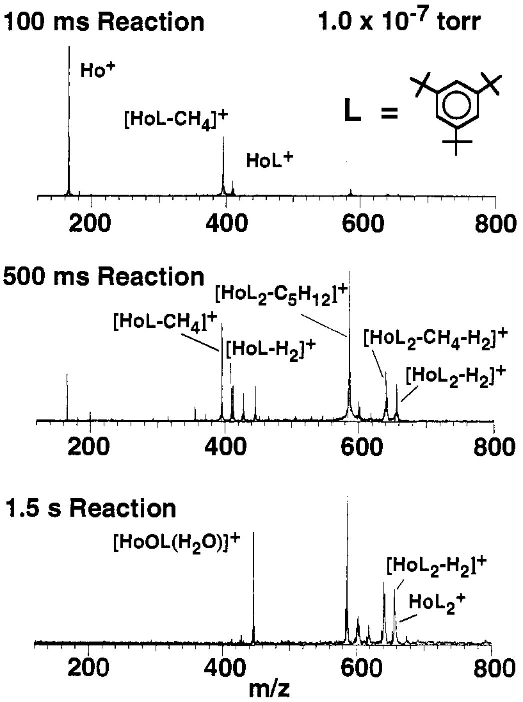

Figure 2. Spectra of the ionic products of the reaction of Ho^+ with 1,3,5-tri-*tert*-butylbenzene (L) at 1.5 × 10^{-7} Torr, following each of three different reaction periods. Note the additional reaction channels compared to Yb^+ in Figure 1.

Dunbar *et al.* observed for the reaction of metal ions with a cyclotriyne that the ligands are added one after another and remain

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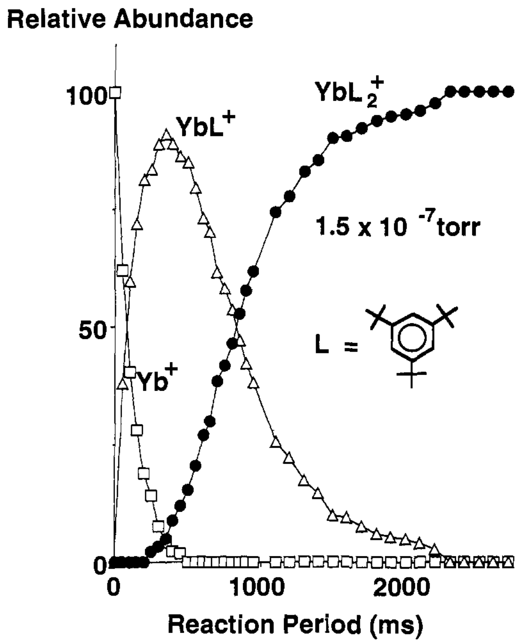

Figure 3. Time-evolution of the relative abundances of the principal ionic species in the Yb^+ reaction of Figure 1.

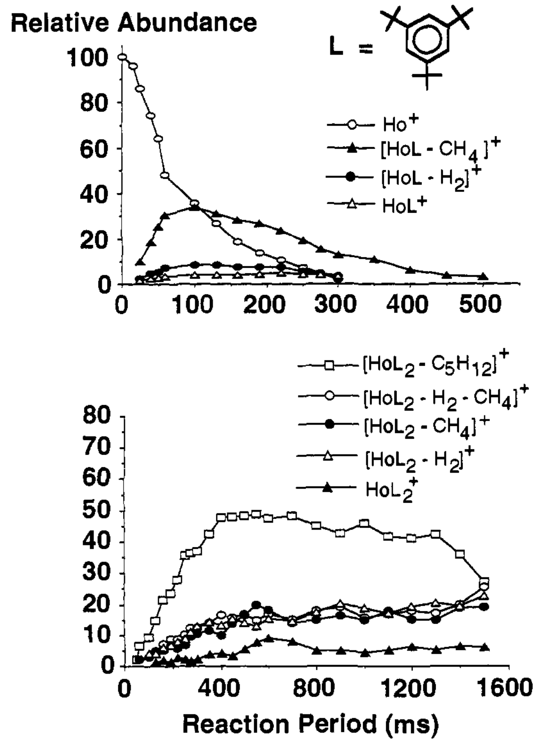

Figure 4. Time-evolution of the relative abundances of the principal ionic species in the Ho^+ reaction of Figure 2.

intact; they explained the adduct formation in terms of infrared radiative stabilization and estimated bond energies of the adducts, concluding that the first ligand is more strongly bonded than the second.[11] Here, collision-induced dissociation (CID) experiments at ~10–50 eV (laboratory frame) of YbL_2^+ gave YbL^+ and of YbL^+ gave Yb^+, indicating that in the ML^+ and ML_2^+ species, the ligands remain intact.

In the cases for which activation of the ligand is observed (eq 2), a second ligand may add without further fragmentation: e.g., as observed for $[HoL_2 - H_2]^+$ and $[HoL_2 - CH_4]^+$, as indicated by CID experiments with these species which gave $[HoL - H_2]^+$ and $[HoL - CH_4]^+$, respectively. However, in most cases the addition of a second ligand leads to the loss of more neutrals. For example, double resonance experiments performed for the Ho^+ reactions showed that $[HoL - C_5H_{12}]^+$ is formed in the reaction of $[HoL - CH_4]^+$ with a second ligand.

Scheme 1 shows possible mechanisms for the dehydrogenation and demethanation of 1,3,5-tri-*tert*-butylbenzene. In general, dehydrogenation of alkanes is believed to proceed by initial C–H oxidative addition to the metal center followed by hydrogen atom transfer to the metal and reductive elimination of H_2. Elimination of CH_4 can originate from either C–H or C–C activation.[50] C–C activation can also lead to dehydrogenation[2] as has been shown by Freiser and co-workers for Sc^+ ions.[51]

In Scheme 1, the probable interaction of the metal ions with the aromatic ring in some species is not indicated. Thermochemical estimates based on the available bond dissociation enthalpies of M^+–H and M^+–C bonds[13] and of C–H and C–C bonds[13,52] indicate that C–H insertion is less exothermic by approximately 100 kJ mol^{-1} for Sc^+, Y^+, La^+, and Gd^+ ions, due to the weak C–C bond of a *tert*-butyl group attached to an aromatic ring (since the M^+–C and M^+–H bond strengths are comparable). It is interesting to note that for the Lu^+ ion, C–H insertion is endothermic if the interaction with the aromatic ring is not considered. The available bond dissociation enthalpy data[4,13,51,52] also allow us to estimate the enthalpies of the demethanation and dehydrogenation reactions considered in Scheme 1. The demethanation reactions are the most exothermic with the exception of the formation of the methylallyl species by dehydrogenation, for which a similar exothermicity was estimated. Possible interaction with the arene ring does not influence this comparison.

Kinetics of the Reactions of Lanthanide Ions with 1,3,5-Tri-*tert*-butylbenzene. The two types of reactivity described in the previous section (namely, activation of the ligand or adduct formation) may be represented for the primary reaction by the following scheme:[53] Scheme 2 indicates the two pathways available for product formation: the activated complex, $(ML^+)^*$, may undergo stabilization by collisions or by infrared radiative emission to form ML^+, with an effective rate constant k_{add},[54] or the activated complex may undergo unimolecular decomposition to give $(ML - XH)^+ + XH$, with a rate constant k_{act}. The apparent rate constant, k, for the reaction of M^+ with L is thus

$$k = \frac{k_f(k_{add} + k_{act})}{(k_{add} + k_{act} + k_b)} \qquad (3)$$

in which k_f is usually assumed to be equal to the Langevin bimolecular rate constant, k_L.[55] In Table 2, we report the values of the apparent rate constants, k, for the reactions of Sc^+, Y^+, and the lanthanide ions. The experimental rate constants in some cases exceed the Langevin rate constant, in part because of the uncertainty in the absolute rate pressure determination (the ion gauge sensitivity for 1,3,5-tri-*tert*-butylbenzene was derived in

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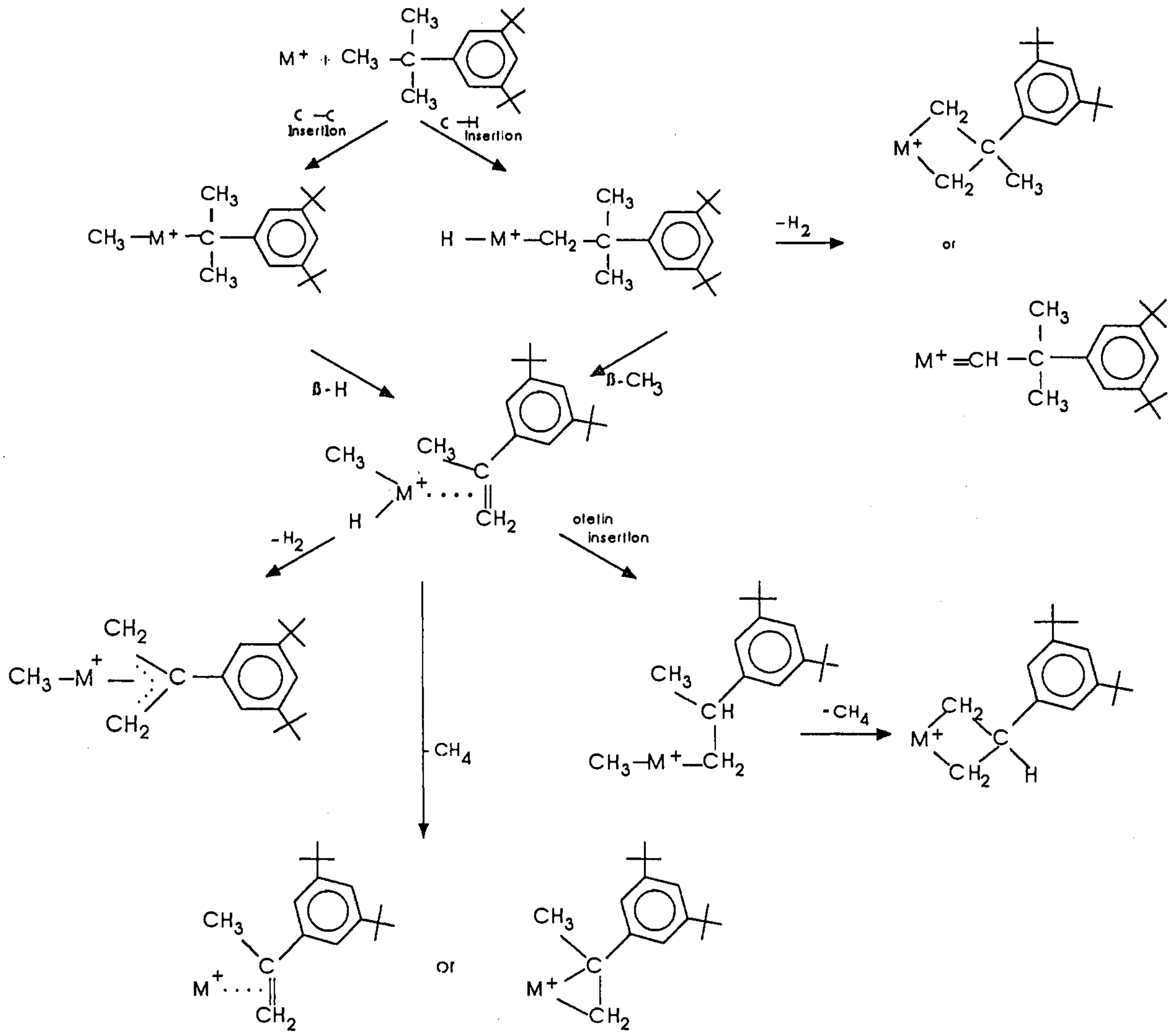
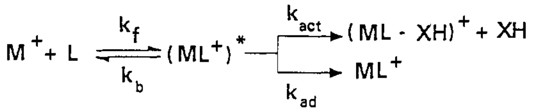
Scheme 1



Scheme 2



$$M^+ + L \underset{k_b}{\overset{k_f}{\rightleftharpoons}} (ML^+)^* \begin{cases} \xrightarrow{k_{act}} (ML\cdot XH)^+ + XH \\ \xrightarrow[k_{ad}]{} ML^+ \end{cases}$$

X = H, R

turn from an estimated molecular polarizability) and in part due to underestimation of the Langevin rate constant in the calculation of the reaction efficiency arising from a large anisotropic polarizability and the presence of a quadrupole moment in 1,3,5-tri-*tert*-butylbenzene.[46,56-62] Although the above factors can lead to a 50% *systematic* error in reaction efficiency, the *relative* magnitudes of the rate constants and reaction efficiencies should still be correct. The presence of excited electronic states or excess kinetic energy in the metal ion could in general lower the rate constant relative to that for reaction of thermalized ions; however, semilog kinetic plots of log[M^+] vs time did not exhibit noticeable nonlinearity, nor did the introduction of a thermalization period in the reaction sequence for some of the ions affect the rate constants. A significant lowering of the rate constants was observed only if the metal ions were purposely subjected to prior rf excitation at the ion cyclotron frequency. As seen from Table 2, the rate constants follow the order $Sc^+ > Y^+ > Ln^+$ as previously observed by other authors for reactions with different hydrocarbons.[5,15,63]

In spite of the uncertainties in the determination of the reaction efficiencies listed in Table 2, we believe that all of the reactions have high efficiency. According to eq 3, a high efficiency, k/k_f, indicates that $k_b \ll (k_{add} + k_{act})$, implying high efficiency for both adduct formation (which is the only reaction observed for Sm, Eu, Tm, and Yb ions, and which most probably results from radiative stabilization of the activated complex, since the rate constants for these metal ions were found to be pressure-independent) and the reactions leading only to activation products observed for Sc^+, Y^+, La^+-Nd^+, Gd^+, and Tb^+ ions. For the remaining metal ions, Dy^+, Ho^+, Er^+, and Lu^+, both types of reaction are observed, but with less efficient adduct formation.

Prior Examples of Gas-Phase Lanthanide Ion-Molecule Chemistry. It is instructive to compare the present gas-phase lanthanide chemistry with several prior examples of gas-phase reactions of hydrocarbons with group 3 and lanthanide ions. For example, Sc^+ reactions with alkanes were studied by Tolbert and Beauchamp;[4] Schilling and Beauchamp used ion beam techniques to characterize the reactions of Pr^+, Eu^+, and Gd^+ with alkanes,

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Table 2. Apparent Rate Constants and Efficiencies for the Reaction of Sc, Y, and the Lanthanide Ions with 1,3,5-Tri-*tert*-butylbenzene

M^+	Sc^+	Y^+	La^+	Ce^+	Pr^+	Nd^+	Sm^+	Eu^+	Gd^+	Tb^+	Dy^+	Ho^+	Er^+	Tm^+	Yb^+	Lu^+
k^a	5.3	2.3	2.0	1.7	1.4	1.3	1.1	0.8	1.0	1.1	1.1	1.7	1.0	1.3	1.1	0.9
k/k_L	2.5	1.4	1.4	1.2	1.0	0.9	0.8	0.6	0.8	0.8	0.8	1.3	0.8	1.0	0.8	0.7

[a] $\times 10^{-9}$ cm^3 molecule^{-1} s^{-1}.

Table 3. Ground-State Electronic Configurations for the Atom and the Positive Ion of Each Lanthanide Element[8,66]

element	atom ground state	ion ground state
Sc	d^1s^2	d^1s^1
Y	d^1s^2	s^2
La	d^1s^2	d^2
Ce	$f^1d^1s^2$	f^1d^2
Pr	f^3s^2	f^3s^1
Nd	f^4s^2	f^4s^1
Sm	f^6s^2	f^6s^1
Eu	f^7s^2	f^7s^1
Gd	$f^7d^1s^2$	$f^7d^1s^1$
Tb	f^9s^2	f^9s^1
Dy	$f^{10}s^2$	$f^{10}s^1$
Ho	$f^{11}s^2$	$f^{11}s^1$
Er	$f^{12}s^2$	$f^{12}s^1$
Tm	$f^{13}s^2$	$f^{13}s^1$
Yb	$f^{14}s^2$	$f^{14}s^1$
Lu	$f^{14}d^1s^2$	$f^{14}s^2$

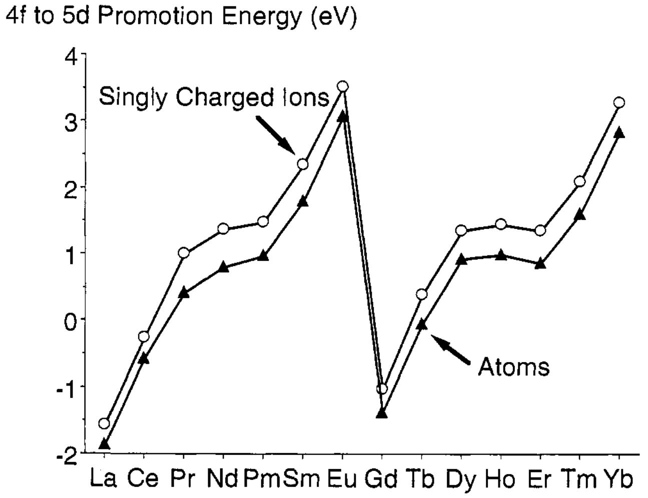

Figure 5. Promotion energy from $4f^n5d^06s^k$ to $4f^{n-1}5d^16s^k$ (k = 1 for singly-charged ion; k = 2 for neutral element) for the lanthanides.[66] Other potentially relevant promotion energies are the following: Y^+ $5s^2 \rightarrow 5s^14d^1$, 0.148 eV; La^+ $5d^2 \rightarrow 6s^15d^1$, 0.195 eV; Lu^+ $6s^2 \rightarrow 6s^15d^1$, 1.628 eV; Ce^+ $4f^15d^2 \rightarrow 4f^16s^15d^1$, 0.295 eV.[8,66]

cycloalkanes and alkenes[15] and compared the results with prior FT/ICR/MS results from Huang *et al.*[5] on reactions of Sc^+, Y^+, and La^+ with alkanes. Eu^+ was shown to be nonreactive; Pr^+ was unreactive with alkanes and reacted only with alkenes; Gd^+ exhibited a reactivity similar to that of the group 3 transition metal cations.

Beauchamp *et al.* found that first-row transition metal ions with ground states derived from the $3d^n4s^1$ configuration have strong metal–hydrogen and metal–methyl bonds.[4,64] Sc^+, with a ground state derived from the $3d^14s^1$ configuration, is also expected to form a strong σ-bond to both H and CH_3. In fact both Sc^+ and Gd^+ reacted readily with hydrocarbons. Beauchamp *et al.* also stated that Eu^+ and Pr^+ are nonreactive because their ground-state electronic configurations are f^ns^1, whereas activation of C–C and C–H bonds in alkanes requires the formation of two strong σ-bonds by the metal (f-electrons do not participate in the bonding); the reactivity of Pr^+ with alkenes could be enhanced by the interaction of the alkene π-system with the metal ion d-orbitals. Irikura and Beauchamp recently showed that for third-row transition metal ions as well, the electronic structures are important to the understanding of their reactivities with hydrocarbons.[65]

Effect of f → d Promotion Energy on Reactivity. Table 3 lists the ground-state electronic configurations for the neutral atom and positive ion of Sc, Y, and each of the lanthanides.[66] Figure 5 shows the electronic promotion energies for the $f^ns^k \rightarrow f^{n-1}d^1s^k$ (k = 1, 2) transitions for the lanthanide series. If the electronic configuration, d^1s^1, is necessary for the ion to insert into a C–C or C–H bond, then the larger $f^ns^1 \rightarrow f^{n-1}d^1s^1$ promotion energy for Sm^+, Eu^+, Tm^+, and Yb^+ would account for the lack of reactivity (except for adduct formation) of these metal ions with the ligand, L. [The exchange energies (high spin coupling) lost upon bond formation were not considered in the discussion as no values are available for the lanthanide ions. Calculation of the exchange energies related to work in progress (J. P. Leal, J. Marçalo, A. Pires de Matos, A. G. Marshall, W. W. Yin, N. M. Edelstein, and N. Kaltsoyannis, unpublished results) on the reactivity of the lanthanide ions with several arenes shows that in the case of 1,3,5-tri-*tert*-butylbenzene, they do not need to be invoked to explain the general trends in reactivity.] On the other hand, the ground-state electronic configurations for Sc^+ and Gd^+ are already d^1s^1. Moreover, d^1s^1 is easily accessible for Y^+ and the other lanthanides (except Sm^+, Eu^+, Tm^+, and Yb^+). Thus, we expect (and find) C–C and/or C–H activation in these cases. Schilling and Beauchamp previously found that Eu^+ and Pr^+ were unreactive with alkanes.[15] We find that although Eu^+ is nonreactive, Pr^+ reacts with tri-*tert*-butylbenzene; the interaction of the arene π-system with the metal ion could favor the latter reactivity. Finally, it is interesting to note that for the previously observed reaction of uranium ions with tri-*tert*-butylbenzene,[24] ion species resulting from CH_4 elimination were observed (the promotion energy from the ground-state electronic configuration of U^+, $5f^37s^2$ to $5f^37s^16d^1$ is 0.04 eV[67]), consistent with the requirement for two non-f valence electrons for such reactivity.

A tentative explanation for the different reactivities is based on Figure 6 which shows various hypothetical reaction coordinate diagrams for the insertion of M^+ into C–C and C–H bonds. In contrast to the reaction of L with neutral metal atom, for which there is a high barrier to activation of C–C and C–H bonds at the coordinatively unsaturated transition metal center, the ion-induced dipole (and also ion quadrupole in the case of an arene) attraction can lower the energy of the chemically activated adduct to allow the C–H and C–C bond insertion reaction to proceed.[15] Thus, the ions with highest promotion energies (namely, Sm^+, Eu^+, Tm^+, and Yb^+) are predicted (and observed) to be least reactive, forming only ML^+ and ML_2^+ adducts.

Having accounted for the unreactive lanthanides (Sm^+, Eu^+, Tm^+, and Yb^+), we may now return to Table 1 to distinguish between the reaction product distributions for Sc^+, Y^+, and the first and second halves of the lanthanide series: in the primary reactions, no residual ML^+ is observed and only demethanation products are formed for first half lanthanides, whereas residual

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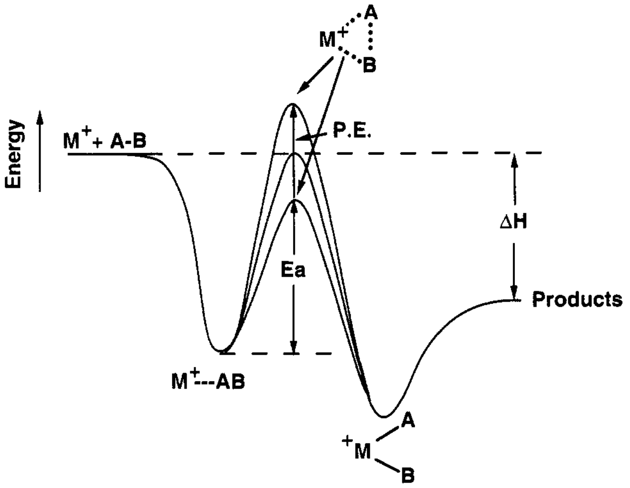

Figure 6. Schematic potential energy along the reaction path for insertion of M^+ into a C–H or C–C bond for an ion with low (bottom curve), intermediate (middle curve), or high (top curve) $f^ns^1 \rightarrow f^{n-1}d^1s^1$ promotion energy. (For Y, La, Ce, and Lu, the promotion energy corresponds to $s^2 \rightarrow d^1s^1$ or $d^2 \rightarrow d^1s^1$.) Proceeding from left to right, the potential energy of the reactants initially decreases as they approach due to their ion–induced dipole attraction and in the case of an arene to interaction between the metal ion d-orbitals and the π-system of the ligand.[69] The additional energy (P.E.) required to promote a metal ion electron from $f^ns^1 \rightarrow f^{n-1}d^1s^1$ effectively increases the activation energy barrier height (E_a). Thus, reactivity of M^+ ions toward insertion into a C–H or C–C bond is expected to decrease with increasing $f^ns^1 \rightarrow f^{n-1}d^1s^1$ promotion energy.

ML^+ (except for Gd^+ and Tb^+) as well as both demethanation and dehydrogenation are observed for the second half lanthanides; however, no residual ML^+ is formed for Gd^+ and Tb^+; and for Sc^+ and Y^+, multiple losses of neutrals are favored. The cases in which residual ML^+ is observed correspond to ions with larger promotion energies.

The differences in reactivity along the lanthanide series and for Sc^+ and Y^+ stem mainly from differences in the f → d promotion energies (and exchange energies) as just discussed, but also from other factors such as the decrease in orbital size with the lanthanide contraction (which affects mainly the s-orbitals)[65,68] and lanthanide ion size (its decrease along the series results in a deeper electrostatic potential well—see Figure 6; Sc^+ is smaller than any of the lanthanides and Y^+ is similar in size to Er^+).

Comparison between Gas-Phase and Condensed-Phase Lanthanide Chemistry. As noted in the Introduction, we are interested in comparing the present gas-phase ion–molecule chemistry to metal vapor synthesis[17] of the (neutral) ML_2 complexes (L = tri-*tert*-butylbenzene). Can the analogous ML_2^+ complexes be prepared in the gas phase to provide insight into the condensed-phase behavior?

In prior work reported by Cloke *et al.*, reactions were carried out by first co-condensing the metal vapor with an excess of tri-*tert*-butylbenzene ligand at low temperature and then letting the mixture warm up. Stable sandwich compounds were obtained for Y, Nd, Gd, Tb, Dy, Ho, Er, and Lu. The La complex decomposed above 0 °C and the Pr complex above 40 °C. Sandwich compounds for Ce, Eu, Tm, and Yb could not be isolated. For Sm, the observed ML_2 product decomposed above –30 °C. These stability trends were explained by a simple bonding model in which a d^1s^2 configuration is required either in the ground state or in an easily accessible excited state of the lanthanide atom. Thus, for Sm, Eu, Tm, and Yb, which have a f^ns^2 ground-state configuration and a high $f^ns^2 \rightarrow f^{n-1}d^1s^2$ promotion energy (see Figure 5), no stable compounds were obtained. A sandwich scandium(0) compound was also reported by the same authors[19] as well as a scandium(II) species obtained by activation of one of the methyl groups of a *tert*-butyl ring substituent. In contrast, we observe a high yield of ML_2^+ species for gas-phase (rather than condensed-phase) reactions of lanthanide ions (rather than neutrals) only when the $f^ns^1 \rightarrow f^{n-1}d^1s^1$ promotion energy is too high to permit facile C–C and C–H activation, namely for Sm^+, Eu^+, Tm^+, and Yb^+.

In summary, reactions of either neutral metal atoms or metal ions can be explained by a (different) simple bonding model based on the transition state energy. Work is in progress to study the reactivity of the lanthanide ions toward other types of arenes as well as the electron ionization or laser desorption/ionization of bulk samples of neutral sandwich complexes, ML_2.

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