Reactivity of Lanthanide, Group 2, and Group 3 Metal and Metal Oxide Cations with Pentamethylcyclopentadiene: Gas-Phase Synthesis of Cyclopentadienyl Cations

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The gas-phase reactivity of lanthanide ($Ln^+ = La^+-Lu^+$), group 2 (Ca^+, Sr^+, and Ba^+), and group 3 (Sc^+ and Y^+) cations, and of their corresponding monoxide ions MO^+, with pentamethylcyclopentadiene (C_5Me_5H) was studied by Fourier transform ion cyclotron resonance mass spectrometry. The reactivity of Eu^+, Tm^+, Yb^+, and the alkaline earth metal ions was similar to that observed previously for Sm^+, namely formation of the fulvenide ion $M(C_5Me_4CH_2)^+$ as the main primary product and the metallocene ion $M(C_5Me_5)_2^+$ as the main secondary product. With Sc^+, Y^+, and the remaining lanthanide series ions, several other species were observed in the primary reactions, corresponding to single and multiple losses of neutral molecules such as H_2 and CH_4. These differences in reactivity appear to correlate with the accessibility of reactive excited state electron configurations of the metal ions. In the case of the metal oxide cations MO^+, the reactivity with pentamethylcyclopentadiene appears to be determined by the strength of the M^+-O bonds. The ions with the strongest bonds, LaO^+, CeO^+, PrO^+, and NdO^+, formed $M(C_5Me_5)(OH)^+$ as the sole primary product, which reacted further, eliminating water, to give the metallocene ion $M(C_5Me_5)_2^+$. ScO^+, YO^+, and the lanthanide series ions SmO^+, GdO^+-TmO^+, and LuO^+ yielded $MO(C_5Me_4CH_2)^+$ and $M(C_5Me_4CH_2)^+$ as the primary products in addition to $M(C_5Me_5)(OH)^+$. These metal oxides gave $M(C_5Me_4CH_2)_2^+$ and $M(C_5Me_5)_2^+$ as secondary products. The ions with the weakest M^+-O bonds, EuO^+, YbO^+, CaO^+, SrO^+, and BaO^+, formed MOH^+ as a primary product and $M(C_5Me_5)^+$ as a secondary product.

Introduction

In the last two decades, an extensive chemistry has developed for organolanthanide compounds containing the pentamethylcyclopentadienyl ligand, C_5Me_5.[1−4] In an effort to further explore the chemistry of organolanthanide species, we have recently described the first gas-phase ion chemistry experiments involving a lanthanide metallocene, namely the bis(pentamethylcyclopentadienyl)samarium complex, $Sm(C_5Me_5)_2$, which showed remarkable similarities with the gas-phase behavior of d transition element metallocenes.[5] In that study, we also observed that the decamethylsamarocene ion, $Sm(C_5Me_5)_2^+$, could be obtained by gas-phase synthesis from Sm^+ ions and C_5Me_5H in a two-step process involving the intermediacy of a tetramethylfulvenide species, $Sm(C_5Me_4CH_2)^+$. As a logical sequence to this observation, in the present paper we report a Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR/MS)[6−8] study of the reactions of the remaining lanthanide series cations ($Ln^+ = La^+-Nd^+$, Eu^+-Lu^+) with C_5Me_5H, complemented by studies of related group 2 (Ca^+, Sr^+, and Ba^+) and group 3 (Sc^+ and Y^+) metal ions. In condensed-phase organometallic chemistry, group 2 and group 3 elements have closely accompanied the divalent and trivalent lanthanide chemistry involving the C_5Me_5 ligand.[9] As we probed the conditions for the formation of $M(C_5Me_5)_2^+$ species and since laser desorption/ionization of metal targets often forms MO^+ ions, we discovered that the metal oxide ions, MO^+, could also play an important role in these systems. Consequently, we have also examined reactions of lanthanide, group 2, and group 3 metal oxide ions with C_5Me_5H. These results add to the data available on the gas-phase reactivity of lanthanide cations with hydrocarbons and other organic molecules, an area which has been receiving considerable attention lately.[10−24]

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Table 1. Primary Product Distributions (%) of the Reactions of Lanthanide, Group 2, and Group 3 Metal Ions with Pentamethylcyclopentadiene

	M^+																		
product ion	La^+	Ce^+	Pr^+	Nd^+	$Sm^{+\,a}$	Eu^+	Gd^+	Tb^+	Dy^+	Ho^+	Er^+	Tm^+	Yb^+	Lu^+	Sc^+	Y^+	Ca^+	Sr^+	Ba^+
$M(C_5Me_5)^+$					5	17						2	9				4	15	29
$M(C_5Me_4CH_2)^+$	12	11	36	38	55	51	15	14	30	32	23	86	87	32	2	2	49	72	31
$M(C_5Me_5H-2H_2)^+$	27	28	15	10			36	29	21	18	31			24	34	36			
$M(C_5Me_5H-3H_2)^+$	17	16	4	6			6	13	8	10	6			12	9	20			
$M(C_5Me_4H)^+$					40	32						2	4				47	13	40
$M(C_5Me_5H-CH_4)^+$	12	13	32	27			20	19	25	23	28	10		15	7	21			
$M(C_5Me_5H-CH_4,H_2)^+$	11	12	4	7			12	14	6	9	3			6	24	8			
$M(C_5Me_5H-CH_4,2H_2)^+$	5	4					3	4							3	2			
$M(C_5Me_5H-C_2H_6)^+$	7	8	9	12			6	7	10	8	9			11	12	7			
$M(C_5Me_5H-C_2H_6,H_2)^+$	4	3					2								4	2			
$M(C_5Me_5H-C_3H_8)^+$	5	6													5	2			

[a] From ref 5.

Experimental Section

All experiments were performed in a Finnigan FT/MS (Madison, WI) 2001-DT FT-ICR mass spectrometer, equipped with a 3 T superconducting magnet and interfaced with a Spectra-Physics Quanta-Ray GCR-11 Nd:YAG laser operated at the fundamental wavelength (1064 nm). The lanthanide and group 3 metal ions were produced by direct laser desorption/ionization (LDI) of commercially obtained pure metal pieces, while the alkaline earth ions were formed by LDI of hydroxide pellets, all mounted on the solids probe of the instrument. The metal oxide ions were either produced by LDI of the oxide layer on the surface of the metal samples or, in the case of the alkaline earth and of the less oxophilic lanthanide metals, by reaction of the metal ion with N_2O introduced into the vacuum chamber through General Valve series 9 pulsed solenoid valves. Isolation of the desired ions was achieved with the SWIFT technique.[25] Pentamethylcyclopentadiene, predried with CaH_2, was introduced into the spectrometer through an Andonian Cryogenics leak valve. All experiments were carried out on the "source" side of the dual ion trap of the instrument.

Neutral pressures, measured by an ion gauge, were in the range from 3×10^{-8} to 3×10^{-7} Torr. Pressure calibration was made using the reactions $CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$[26] and $CH_3COCH_3^+ + CH_3COCH_3 \rightarrow$ products[27] and included a correction for the ionization efficiency of pentamethylcyclopentadiene,[28] based on a molecular polarizability estimated by Miller's additivity method.[29] Rate constants were determined from the pseudo-first-order decay of the reactant ion relative intensity as a function of time at constant reagent pressure. These constants are reported as reaction efficiencies, that is, as fractions of the average dipole orientation theory (ADO) collisional rates,[30] calculated using a dipole moment considered to be similar to the one tabulated for cyclopentadiene.[31] Uncertainties in the pressure calibration procedure may lead to errors in the absolute rate constants that we estimate to be ±50%, but the relative magnitudes of the reaction efficiencies should have errors lower than 20%.

Thermalization of the reactant ions was performed for all of the reactions and typically involved 1 s collisional cooling periods after the introduction of argon into the vacuum chamber through pulsed valves to maximum pressures of $\sim 10^{-5}$ Torr; in the case of the metal oxide ions produced by reaction with N_2O, this gas was used for thermalization since it does not react with the MO^+ ions formed. Reaction sequences were identified by means of double-resonance and MS/MS techniques. Collision-induced dissociation (CID) experiments were carried out by excitation of the ions in question to lab-frame energies of ~10−80 eV and pulsed-valve introduction of argon.

Results and Discussion

Reactivity of Lanthanide, Group 2, and Group 3 Metal Ions with Pentamethylcyclopentadiene. In Table 1 we summarize the primary product distributions obtained in the reactions of all of the lanthanide series ions, $Ln^+ = La^+-Lu^+$ (except Pm^+), of the group 3 ions Sc^+ and Y^+, and of the alkaline-earth ions Ca^+, Sr^+, and Ba^+ with pentamethylcyclopentadiene; in Table 2 we present the corresponding reaction efficiencies, k/k_{ADO}.

Table 1 shows that the metal ions examined fall into two distinct groups on the basis of the reaction pathways traversed. One group of metal ions, Sm^+,[5] Eu^+, Tm^+, Yb^+, and the group 2 ions, Ca^+, Sr^+, and Ba^+, form the $M(C_5Me_4CH_2)^+$ ion as the main primary product, with variable contributions from $M(C_5Me_5)^+$ and $M(C_5Me_4H)^+$ ions and from $M(C_5Me_4)^+$ in the case of Tm^+. The second group of metal ions, the remainder of the lanthanide ions, as well as the group 3 ions, Sc^+ and Y^+, give rise to a large number of products that correspond to single and multiple losses of neutral

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Table 2. Efficiencies (k/k_{ADO}) of the Reactions of Lanthanide, Group 2, and Group 3 Metal Ions with Pentamethylcyclopentadiene

	La^+	Ce^+	Pr^+	Nd^+	$Sm^{+\,a}$
k/k_{ADO}	0.79	0.80	0.54	0.54	0.48
	Eu^+	Gd^+	Tb^+	Dy^+	Ho^+
k/k_{ADO}	0.50	0.74	0.67	0.56	0.54
	Er^+	Tm^+	Yb^+	Lu^+	Sc^+
k/k_{ADO}	0.60	0.45	0.32	0.68	0.77
	Y^+	Ca^+	Sr^+	Ba^+	
k/k_{ADO}	0.77	1.04	0.30	0.39	

[a] From ref 5.

species, such as H_2, CH_4, and other small hydrocarbon molecules, and at the same time do not lead to the formation of $M(C_5Me_5)^+$ and $M(C_5Me_4H)^+$ ions.

These differences in reactivity appear to correlate with the accessibility of reactive excited state electron configurations of the metal ions. For the lanthanide series ions, recent work[12,16–24] has shown that the ability of these ions to activate C−H or C−C in hydrocarbons correlates with the magnitude of the excitation energies[32,33] from the ground state electron configurations, generally $4f^n6s^1$, to configurations with two unpaired non-f electrons, $4f^{n-1}6s^15d^1$. The lanthanide ions with the largest excitation energies, Sm^+, Eu^+, Tm^+, and Yb^+, are precisely the ones found in the first group of metal ions in terms of reactivity with C_5Me_5H. These ions, along with the group 2 metal ions, form primarily $M(C_5Me_4CH_2)^+$ ions in their reactivities with C_5Me_5H. The fact that the group 2 metal ions are similar to the lanthanide ions with high excitation energies confirms the validity of this model, as those ions have only one s valence electron beyond the rare gas configuration. In contrast, the group 3 ions, which have easily accessible d^1s^1 configurations[13] and are very reactive with hydrocarbons,[34] have a reactivity similar to that of the more reactive lanthanide ions.

In our previous work describing the reactivity of Sm^+ with C_5Me_5H,[5] we pointed out that two types of mechanisms could be simultaneously operative in the formation, as primary products, of the ions $Sm(C_5Me_5)^+$, $Sm(C_5Me_4H)^+$, and $Sm(C_5Me_4CH_2)^+$ (for which evidence was presented that it corresponded to a tetramethylfulvenide species). “Direct” reactions eliminating CH_3 or H radicals to form the monocyclopentadienyl metal ions were possible, as well as reactions involving C−H insertion, followed by H_2 elimination and formation of the presumed tetramethylfulvenide species. The results obtained in the present work, namely the similarity of the reactivity patterns of the alkaline-earth metal ions and of Sm^+, Eu^+, Tm^+, and Yb^+ argue against the possibility of an insertion mechanism to be operative for these ions, since this requires a second valence electron not available to the alkaline-earth metal ions. A direct mechanism in which elimination of either CH_3 and H radicals or a hydrogen molecule can be envisioned if a strong initial interaction between the metal ion and the neutral pentamethylcyclopentadiene is established within the adduct complex. This would correspond to an increase of the ion−neutral complex lifetime and could facilitate either the breaking of the weak C−CH_3 and C−H bonds, with concomitant radical losses, or the elimination of H_2 with formation of the tetramethylfulvene, which is a thermodynamically favorable process (see below). On the other hand, insertion into the C−H or/and C−C bonds of pentamethylcyclopentadiene appears to be a reasonable first step in the case of Sc^+, Y^+, and the more reactive lanthanide ions; the absence of the two product ions that clearly indicate a direct mechanism, $M(C_5Me_5)^+$ and $M(C_5Me_4H)^+$, is in line with this hypothesis.

There is not enough data available for C_5Me_5H to fully define the thermochemistry of the M^+/C_5Me_5H systems in this study.[31,35,36] However, it can be reasonably assumed that rather weak C−H and C−CH_3 bonds are present in C_5Me_5H, based on data for cyclopentadiene and methylcyclopentadiene that lead to values of 298−328 kJ/mol (depending on the source) for $D(C_5H_5{-}H)$, of 292 kJ/mol for $D(C_5H_5{-}CH_3)$, and a ΔH of 128 kJ/mol for the process methylcyclopentadiene → fulvene + hydrogen.[31,35,36] The favorability of the thermodynamics, in conjunction with the large polarizability[29] (and a small dipole moment[31]) of pentamethylcyclopentadiene which lead to a significant amount of energy available in the collision complexes, are the probable driving forces for the appreciable reactivity observed for all of the ions studied. This explains why the alkaline-earth ions and the lanthanide ions with high $f^ns^1 \rightarrow f^{n-1}s^1d^1$ excitation energies can form products.

The reaction efficiencies presented in Table 2 apparently are in agreement with the above considerations, as the less reactive ions show smaller efficiencies. The high kinetic efficiency of Ca^+ constitutes an exception, but probably derives from a high charge density of the ion that gives rise to a strong initial ion−neutral interaction.

The products of secondary reactions with C_5Me_5H are summarized in Table 3. The primary products of the reactions of C_5Me_5H with the ions Eu^+, Tm^+, Yb^+, Ca^+, Sr^+, and Ba^+ showed similar reactivities to that observed previously in the samarium case:[5] formation of the $M(C_5Me_5)_2^+$ ion from the $M(C_5Me_4CH_2)^+$ ion (with a minor contribution from $M(C_5Me_4CH_2)_2^+$ [37]), adduct formation in the case of the $M(C_5Me_5)^+$ ion, and ligand exchange plus adduct formation in the case of the $M(C_5Me_4H)^+$ ion. Convincing evidence was presented in the case of Sm^+ for the formulation of $M(C_5Me_5)_2^+$ as the metallocene.[5] The absence of stable trivalent states for the alkaline-earth elements could raise doubts concerning the ligation of the cyclopentadienyl moieties in the group 2 $M(C_5Me_5)_2^+$ products. These species can be alternatively formulated as $M(C_5Me_4CH_2)(C_5Me_5H)^+$, in which both ligands are neutral and the alkaline-earth metal ions are in a formal +1 oxidation state. CID

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(37) Although the structure of this species is not known, it is interesting to consider that it could be an *ansa*-metallocene cation with a CH_2CH_2 bridge. An alternative with a trivalent oxidation state would be a fulvene−fulvenide complex.

Table 3. Secondary Products in the Reactions of Lanthanide, Group 2, and Group 3 Metal Ions with Pentamethylcyclopentadiene

		M^+	
reactant ion	ionic products	La^+-Nd^+, Gd^+-Er^+, Lu^+, Sc^+, Y^+	Sm^+,[a] Eu^+, Tm^+, Yb^+, Ca^+, Sr^+, Ba^+
$M(C_5Me_5)^+$	$M(C_5Me_5)(C_5Me_5H)^+$	−	+
$M(C_5Me_4CH_2)^+$	$M(C_5Me_5)_2{}^+$	+	+
	$M(C_5Me_4CH_2)_2{}^+$	+	+
$M(C_5Me_5H-2H_2)^+$	$M(C_5Me_4CH_2)_2{}^+$	+	−
$M(C_5Me_5H-3H_2)^+$	*b*	+	−
$M(C_5Me_4H)^+$	$M(C_5Me_4H)(C_5Me_5H)^+$	−	+
	$M(C_5Me_5)^+$	−	+
$M(C_5Me_5H-CH_4)^+$	$M(C_5Me_4H)(C_5Me_5)^{+\,c}$	+	−
$M(C_5Me_5H-CH_4,H_2)^+$	*b*	+	−
$M(C_5Me_5H-CH_4,2H_2)^+$	*b*	+	−
$M(C_5Me_5H-C_2H_6)^+$	$M(C_5Me_4H)_2{}^{+\,c}$	+	−
$M(C_5Me_5H-C_2H_6,H_2)^+$	*b*	+	−
$M(C_5Me_5H-C_3H_8)^+$	*b*	+	−

[a] From ref 5. [b] These ions form adducts with C_5Me_5H like the other products in the table, but possible structures are less certain. [c] This is one possible structure.

Table 4. Primary Product Distributions (%) of the Reactions of Lanthanide, Group 2, and Group 3 Oxide Ions with Pentamethylcyclopentadiene

	MO^+																		
product ion	LaO^+	CeO^+	PrO^+	NdO^+	SmO^+	EuO^+	GdO^+	TbO^+	DyO^+	HoO^+	ErO^+	TmO^+	YbO^+	LuO^+	ScO^+	YO^+	CaO^+	SrO^+	BaO^+
MOH^+						52							100				100	100	100
$M(OH)(C_5Me_5)^+$	100	100	100	100	10		10	27	21	14	8	15		23	14	22			
$MO(C_5Me_4CH_2)^+$					14		17	25	45	55	67	66		40	48	49			
$MO(C_4Me_4)^+$							8	14	5	14	10	15		20	24	15			
$M(C_5Me_4CH_2)^+$					76	48	65	34	29	17	15	4		17	14	14			

experiments made in the case of Ca showed the formation of $M(C_5Me_5)^+$ as the only fragment, indicating that the metallocene ions could also be formed for the alkaline-earth metals. However, interconversion of the possible structures under the conditions of the CID experiments has to be considered, and the observed fragmentation could just correspond to a thermochemically favored exit channel.

For the more reactive metal ions, the yield of the metallocene species in the secondary reactions with C_5Me_5H is rather low, due to the large number of primary products besides $M(C_5Me_4CH_2)^+$; all of these products add new C_5Me_5H molecules in the secondary reactions, with contributions from single dehydrogenation processes as well.

Several of the reactions observed have condensed-phase analogs. The existence of lanthanide metallocene cations is well-established in the condensed phase,[38] as are reactions of fulvenide complexes with sources of active hydrogen to form C_5Me_5 ligands.[39,40] Lanthanide-based C−H activation is also known in solution, but C−C cleavage is less common.[41]

Reactivity of Lanthanide, Group 2, and Group 3 Oxide Ions with Pentamethylcyclopentadiene. In Table 4 we present the primary product distributions obtained in the reactions of all of the lanthanide oxide ions, $LnO^+ = LaO^+-LuO^+$ (except PmO^+), of the group 3 oxide ions ScO^+ and YO^+, and of the alkaline-earth oxide ions CaO^+, SrO^+, and BaO^+ with pentamethylcyclopentadiene; in Table 5 we show the corresponding reaction efficiencies, k/k_{ADO}.

Table 5. Efficiencies (k/k_{ADO}) of the Reactions of Lanthanide, Group 2, and Group 3 Oxide Ions with Pentamethylcyclopentadiene

	LaO^+	CeO^+	PrO^+	NdO^+	SmO^+
k/k_{ADO}	0.57	0.57	0.49	0.46	0.57
	EuO^+	GdO^+	TbO^+	DyO^+	HoO^+
k/k_{ADO}	0.68	0.62	0.66	0.72	0.73
	ErO^+	TmO^+	YbO^+	LuO^+	ScO^+
k/k_{ADO}	0.75	0.78	0.88	0.77	0.65
	YO^+	CaO^+	SrO^+	BaO^+	
k/k_{ADO}	0.54	1.89	1.44	1.15	

In Table 4 three main types of reactivity can be distinguished. First, the lanthanide oxide ions LaO^+, CeO^+, PrO^+, and NdO^+ form a single condensation product ion $MC_5Me_5OH^+$. This product can be formulated as $M(OH)(C_5Me_5)^+$ or $MO(C_5Me_5H)^+$. Although CID experiments with the Pr species showed the formation of PrO^+ and $Pr(C_5Me_4CH_2)^+$ fragments, we believe that these experiments are not conclusive, as under the FTICR/MS experimental conditions rearangements generally occur and elimination of the stable neutrals C_5Me_5H and H_2O could be favored. The second type of reactivity pattern is that the alkaline-earth oxide ions, YbO^+ and in part EuO^+, yield MOH^+. Finally, the remaining metal oxide ions give $M(OH)(C_5Me_5)^+$ and three other product ions that correspond to the elimination of H_2, $MO(C_5Me_4CH_2)^+$, of C_2H_4 (or C_2H_2, H_2), $MO(C_4Me_4)^+$, and H_2O, $M(C_5Me_4CH_2)^+$.

In a recent comprehensive review of the gas-phase chemistry of transition metal oxide ions by Schröder and Schwarz[43] (and also in a recent work of the same group comparing the reactivity of $CeO_2{}^+$ and CeO^+ ions with hydrocarbons[21]), it can be seen that the driving forces

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Table 6. Bond Dissociation Enthalpies $D(M^+{-}O)$ (kJ/mol) of the Lanthanide, Group 2, and Group 3 Oxide Ions[a]

	LaO^+	CeO^+	PrO^+	NdO^+	SmO^+
$D(M^+{-}O)$	866(±14)	867(±16)	801(±20)	756(±16)	582(±16)
	EuO^+	GdO^+	TbO^+	DyO^+	HoO^+
$D(M^+{-}O)$	389(±18)	754(±17)	733(±16)	600(±43)	597(±27)
	ErO^+	TmO^+	YbO^+	LuO^+	ScO^+
$D(M^+{-}O)$	589(±23)	535(±22)	389(±13)	560(±20)	689(±6)
	YO^+	CaO^+	SrO^+	BaO^+	
$D(M^+{-}O)$	752(±18)	324(±20)	299(±23)	389(±10)	

[a] From ref 35, except ScO^+ from ref 44. Revised values of $D(M^+{-}O)$ for the lanthanide oxide ions can be found in ref 42 and 45.

in the reactivity of metal oxide ions are the strengths of the $M^+{-}O$ bonds and the nature of the bonding. In Table 6 we collected the values of the $D(M^+{-}O)$ bond energies from one of the available sources[35] for all of the metals used in this work. It is readily apparent that the ions with the strongest bonds are precisely the ones that are only involved in the formation of the condensation product $M(OH)(C_5Me_5)^+$, $LaO^+{-}NdO^+$, while the ions with the weakest bonds, CaO^+, SrO^+, BaO^+, YbO^+, and EuO^+, are the ones that react by H-atom abstraction to form MOH^+; the remaining ions show a more varied chemistry, inducing several bond-breaking processes.

It is instructive, at this point, to compare the $M^+{-}O$ bond energies in Table 6 with the $M^+{-}OH$ bond energies available in the case of the alkaline-earth metal ions (436, 443, and 533 kJ/mol for M = Ca, Sr, and Ba, respectively[35]) and scandium (499 kJ/mol[44]) and see that $M^+{-}OH$ bonds are stronger than $M^+{-}O$ bonds for the group 2 metal ions, while the opposite occurs in the case of Sc^+. In the lanthanide series, it can be reasonably expected that at least Eu^+ and Yb^+ will have stronger bonds to OH than to O.

The variation of the $M^+{-}O$ bond energies along the lanthanide series is related to the trend defined by the $f^ns^1 \rightarrow f^{n-1}s^1d^1$ excitation energies of the metal ions.[45] In a simple, qualitative description of the bonding in the lanthanide monoxide cations, one could then consider that the $M^+{-}O$ bonds formally range from a double bond to a single bond on going from the species with the stronger bonds ($LaO^+{-}NdO^+$) to the species with the weaker bonds (EuO^+ and YbO^+). These bonds can be of higher order if electron density can be donated from the oxygen lone pairs into empty d orbitals in the metal ion, but in the monoxide cations with weak $M^+{-}O$ bonds, a certain radical character of the oxygen can be considered, which could then be responsible for the H-atom abstraction processes observed.[43,46] In the case of the alkaline-earth monoxide cations, a similar description of the bonding (and a similar reactivity) could be expected due to the fact that only one metal ion s electron is available for bonding with oxygen. The two extreme cases just discussed admit intermediate characters of the $M^+{-}O$ bonds that can lead to the reactivity observed for the remaining metal oxide ions. In any case, the nature of the organic reagent, with its large polarizability and the favorable thermodynamics discussed in the previous section, makes an important contribution to the varied reactivity observed.

The values of the reaction efficiencies presented in Table 5 also show some dependence on the relative magnitudes of the $M^+{-}O$ bond energies. This is especially apparent in the case of the alkaline-earth metal oxide ions, which have rate constants k that even surpass the collisional rates k_{ADO}. Uncertainties in the pressure calibration procedure (see Experimental Section), limitations of the ADO model used,[30] which for instance does not take into account the polarizability anisotropy of the neutral reagent,[47,48] and ineffective thermalization of the reagent ions (see Experimental Section) could all contribute to the high values of k/k_{ADO} found. Relevant to this problem is some very recent work on the limitations of polarization models of ion−molecule collisions.[49]

Table 7 shows the secondary products formed in the metal oxide ion reactions with C_5Me_5H. The primary product ion $M(OH)(C_5Me_5)^+$ reacts by eliminating water leading to the metallocene ion $M(C_5Me_5)_2{}^+$. CID experiments with $Pr(C_5Me_5)_2{}^+$ showed $Pr(C_5Me_5)^+$ as the only fragment at low energies. Elimination of water is also observed in the secondary reactions of the MOH^+ ions, with formation of $M(C_5Me_5)^+$ ions (which then add a C_5Me_5H molecule). In the case of $MO(C_5Me_4CH_2)^+$ and $MO(C_4Me_4)^+$, water elimination yields $M(C_5Me_4CH_2)_2{}^+$ and $M(C_4Me_4)(C_5Me_4CH_2)^+$, respectively. The $M(C_5Me_4CH_2)^+$ ion, as observed before in the study of the metal ions, reacts with C_5Me_5H to give the metallocene $M(C_5Me_5)_2{}^+$ as the major product and also $M(C_5Me_4CH_2)_2{}^+$.

For the metal oxide ion reactions there are fewer analogs in organolanthanide solution chemistry. Little is known about the reactivity of lanthanide oxide and hydroxide complexes in solution.[50]

Conclusions

This study shows that starting from either the metal cation M^+ or from the corresponding monoxide ion MO^+ access to lanthanide and related group 2 and group 3 cyclopentadienyl species could be easily obtained. Several interesting ionic species were identified that deserve further study in terms of their reactivity with organic substrates. In addition, this work provides further examples confirming the relevance of the

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Table 7. Secondary Products in the Reactions of Lanthanide, Group 2, and Group 3 Oxide Ions with Pentamethylcyclopentadiene

		MO$^+$				
reactant ion	ionic products	LaO$^+$−NdO$^+$	SmO$^+$	EuO$^+$	GdO$^+$−TmO$^+$, LuO$^+$, ScO$^+$, YO$^+$	YbO$^+$, CaO$^+$, SrO$^+$, BaO$^+$
MOH$^+$	M(C$_5$Me$_5$)$^+$	−	−	+	−	+
M(OH)(C$_5$Me$_5$)$^+$	M(C$_5$Me$_5$)$_2$$^+$	+	+	−	+	−
MO(C$_5$Me$_4$CH$_2$)$^+$	M(C$_5$Me$_4$CH$_2$)$_2$$^+$	−	+	−	+	−
MO(C$_4$Me$_4$)$^+$	M(C$_4$Me$_4$)(C$_5$Me$_4$CH$_2$)$^+$	−	−	−	+	−
M(C$_5$Me$_4$CH$_2$)$^+$	M(C$_5$Me$_5$)$_2$$^+$	−	+	+	+	−
	M(C$_5$Me$_4$CH$_2$)$_2$$^+$	−	+	+	+	−

accessibility of reactive electronic configurations to the reactivity of lanthanide metal ions with organic molecules. This evidently applies not only to metal ions but also to metal oxide ions. Clearly, oxo ligation introduces important differences in gas-phase reactivity, and these differences must be considered in any experiment in which metal oxide ions are present along with metal ions. Similar conclusions also apply to group 2 ions, and it is evident that alkaline-earth oxide ions are also potentially interesting species for gas-phase studies.

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