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Gas Phase Chemistry of Bis(pentamethylcyclopentadienyl)samarium

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The gas phase chemistry of bis(pentamethylcyclopentadienyl)samarium, $(C_5Me_5)_2Sm$, was studied by Fourier transform ion cyclotron resonance mass spectrometry (FTICR/MS). Positive electron impact (EI) spectra showed the formation of $(C_5Me_5)_2Sm^+$, $(C_5Me_5)Sm^+$, and Sm^+. All three ions reacted with $(C_5Me_5)_2Sm$ by charge transfer, as verified by double-resonance techniques, and $(C_5Me_5)Sm^+$ also formed the $(C_5Me_5)_3Sm_2^+$ ion in a condensation reaction with neutral $(C_5Me_5)_2Sm$. The laser desorption/ionization (LDI) spectra showed, in addition to $(C_5Me_5)_2Sm^+$, $(C_5Me_5)Sm^+$, and Sm^+, the formation of $(C_5Me_4H)Sm^+$ and $(C_5Me_4CH_2)Sm^+$. The latter species most probably involves a tetramethylfulvenide ligand. Access to all of the ionic species cited here could also be obtained by reacting laser-desorbed Sm^+ ions with pentamethylcyclopentadiene, C_5Me_5H. $(C_5Me_4CH_2)Sm^+$, $(C_5Me_4H)Sm^+$, and $(C_5Me_5)Sm^+$ were formed as primary products, and the metallocene ion $(C_5Me_5)_2Sm^+$ resulted from the rapid addition of C_5Me_5H to $(C_5Me_4CH_2)Sm^+$.

Introduction

Recently, considerable attention has been given to the previously unexplored gas phase chemistry of lanthanide cations. Gas phase reactions of lanthanide ions with arenes,[1,2] alkanes,[3,4] and alkenes[3−5] have been reported and suggest that the reactivity along the lanthanide series is strongly dependent on the electronic configuration of each lanthanide ion and the magnitude of the promotion energies to reactive configurations. In an effort to further explore the chemistry of organolanthanide species and to begin to connect the gas phase results with condensed-phase chemistry, we have conducted FTICR/MS[6−8] studies of the gas phase ion chemistry of the Sm/C_5Me_5 system. This system was chosen because $(C_5Me_5)_2Sm$,[9−11] with its strong reduction potential and unusual "bent sandwich" structure, has been shown to have a rich chemistry: it can bind substrates and effect reactions that traditionally were not thought to be possible with lanthanide compounds.[12−14] As a result, extensive chemistry has developed for compounds containing the Sm/C_5Me_5 combination, which provides valuable data useful in interpreting the gas phase chemistry observed. In addition, since $(C_5Me_5)_2Sm$ is volatile, gas phase studies can be conducted starting from a molecular precursor, i.e., from $(C_5Me_5)_2Sm$, as well as from the combination of metal-derived Sm^+ with pentamethylcyclopentadiene.

We report here the electron impact (EI) and laser desorption/ionization (LDI) spectra of $(C_5Me_5)_2Sm$ and connect them with the reactivity of Sm^+ with C_5Me_5H. These experiments show how ligated samarium ions are formed in the gas phase and how the initially formed species react.

Experimental Section

All FTICR/MS experiments were performed with an FT/MS (Madison, WI) Model 2001-DT spectrometer, equipped with a 3.0 T superconducting magnet and interfaced to a Spectra-Physics Quanta-Ray GCR-11 pulsed Nd:YAG laser operating at the fundamental wavelength (1064 nm).

The air-sensitive, volatile complex $(C_5Me_5)_2Sm$[9,10] was prepared by the published procedure and transferred to the automatic solids probe of the instrument under argon. EI spectra were obtained at a probe temperature of 120 °C, while no heating was used for LDI spectra. The samarium metal ions were produced by LDI of a commercially obtained pure metal piece mounted on the solids probe. C_5Me_5H, predried with CaH_2, was introduced into the spectrometer through a leak valve. All experiments were carried out on the "source" side of the dual ion trap of the instrument. Neutral pressures,

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measured by an ion gauge, were in the range of 3×10^{-8} to 3×10^{-7} Torr.

Reaction pathways were established by double-resonance methods, and the isolation of the desired ions was achieved with the SWIFT technique.[15] Rate constants were determined by observing the pseudo-first-order decay of the reactant ion intensities as a function of time at constant neutral reagent pressure. Pressure calibration was made by using the reaction of $CH_3COCH_3^+$ with CH_3COCH_3[16] and included corrections for the ionization efficiencies of the neutral reagents;[17] the molecular polarizability of C_5Me_5H was estimated by the method of Miller.[18] For the experiments involving $(C_5Me_5)_2Sm$, the Langevin rate constant (k_L) estimated by Richardson and coworkers[19a] for the reaction couple $(C_5Me_5)_2Fe^+/(C_5Me_5)_2Fe$ (1.1×10^{-9} cm^3 molecule^{-1} s^{-1}) was used to obtain estimates of the molecular polarizability and ionization efficiency of $(C_5Me_5)_2Fe$, which were then used for $(C_5Me_5)_2Sm$. As a further test of the pressure calibration procedure in the case of samarocene, a few experiments with ferrocene were performed and were satisfactorily checked against reported kinetic data on the gas phase chemistry of this metallocene.[19,20] In spite of the preceding precautions, we believe that the uncertainties in the pressure calibration procedure can lead to errors in the absolute rate constants that may be higher than 50% in the case of the experiments involving samarocene; in the case of the reactions of Sm^+ ions with C_5Me_5H, the errors are probably lower. The relative rate constants for each type of experiment have estimated errors of ±20%.

Collisional cooling of the reactant ions was performed in all cases and involved 0.5−1 s collisional periods with argon introduced into the vacuum chamber through General Valve Corporation Series 9 pulsed solenoid valves to maximum pressures of $\sim 10^{-6}$ Torr. Collision-induced dissociation (CID) experiments were carried out by excitation of the ions in question to lab-frame energies of ~10−50 eV and pulsed-valve introduction of argon.

Results and Discussion

Electron Ionization and Positive Ion Chemistry of $(C_5Me_5)_2Sm$. Positive EI spectra of $(C_5Me_5)_2Sm$ at 3×10^{-8} to 1×10^{-7} Torr and 70 eV electron beam energies showed the formation of $(C_5Me_5)_2Sm^+$, $(C_5Me_5)Sm^+$, and Sm^+ as major products and $(C_5Me_4H)Sm^+$, $SmCH_3^+$, SmH^+, and $C_5Me_5H^+$ as minor products (<3%). At lower electron beam energies, fragmentation decreased as expected, and at 6−10 eV the molecular ion $(C_5Me_5)_2Sm^+$ dominated the spectra, with small contributions from $(C_5Me_5)Sm^+$ and Sm^+. No negative ion spectra could be obtained under different electron beam conditions (variation of electron energy and intensity as well as duration).

If a delay time was introduced between ion formation and detection in the positive ion mode, the formation of a new ion, identified as $(C_5Me_5)_3Sm_2^+$, was observed, as shown in the spectrum of Figure 1. This species, for which a "triple-decker sandwich" structure can be reasonably expected, has no known counterpart in condensed-phase samarium chemistry.

In Figure 2, the evolution in time of the relative abundances of the major ionic species formed after 70 eV electron ionization of $(C_5Me_5)_2Sm$ is presented. Double-resonance experiments revealed that the overall variation of the ion abundances with time corresponded to the superposition of several processes. The primary reactions were the self-charge exchange reaction of $(C_5Me_5)_2Sm^+$ with the neutral metallocene (eq 1), the charge transfer reactions of $(C_5Me_5)Sm^+$ and Sm^+ with the neutral metallocene (eqs 2a and 3, respectively), and the condensation reaction of $(C_5Me_5)Sm^+$ with $(C_5Me_5)_2Sm$ to form the $(C_5Me_5)_3Sm_2^+$ ion (eq 2b). $(C_5Me_5)Sm^+$ also reacted with neutral $(C_5Me_5)_2Sm$ to give $(C_5Me_5)_2Sm_2^+$, but this was a minor process. The ionization of $(C_5Me_5)_2Sm$ in the electron transfer processes also led to fragmentation, giving rise to small quantities of $(C_5Me_5)Sm^+$ and Sm^+, which again reacted with the neutral metallocene.

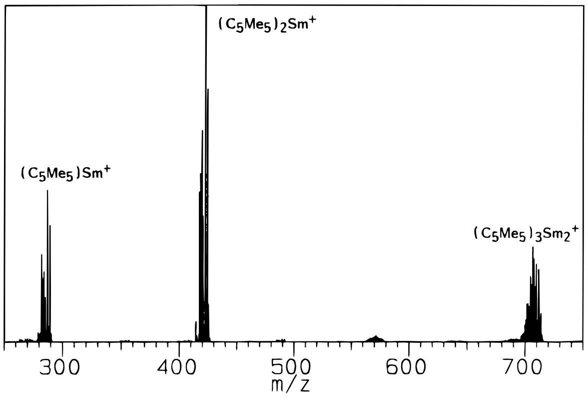

Figure 1. Positive ion mass spectrum of $(C_5Me_5)_2Sm$ at 5×10^{-8} Torr, 0.3 s after 70 eV electron ionization.

$$(C_5Me_5)_2Sm^+ + (C_5Me_5)_2Sm \rightarrow (C_5Me_5)_2Sm + (C_5Me_5)_2Sm^+ \quad (1)$$

$$(C_5Me_5)Sm^+ + (C_5Me_5)_2Sm \rightarrow (C_5Me_5)_2Sm^+ + (C_5Me_5)Sm \quad (2a)$$

$$(C_5Me_5)Sm^+ + (C_5Me_5)_2Sm \rightarrow (C_5Me_5)_3Sm_2^+ \quad (2b)$$

$$Sm^+ + (C_5Me_5)_2Sm \rightarrow (C_5Me_5)_2Sm^+ + Sm \quad (3)$$

In the double-resonance experiments, the ions containing ^{152}Sm and ^{12}C isotopes at *m/z* 422 (from $(C_5Me_5)_2Sm^+$), 287 (from $(C_5Me_5)Sm^+$), and 152 (from Sm^+), formed by low-energy (8−15 eV) EI of the neutral metallocene, were isolated and, after collisional cooling with argon (and reisolation), were allowed to react with the neutral samarocene. The spectra obtained for each of these reactions showed that the samarium atoms in the product ions originated exclusively from the neutral reactant. This indicated that the reactions in fact corresponded to electron transfer processes and there were no ligand (or metal) exchanges involved.

The positive ion chemistry of $(C_5Me_5)_2Sm$ shows striking similarities to that observed by Beauchamp and co-workers in ICR experiments with the archetypical metallocene $(C_5H_5)_2Fe$[20] and (in part) with $(C_5H_5)_2Ni$.[21] Self-charge exchange reactions were later identified and thoroughly studied by Richardson and co-work-

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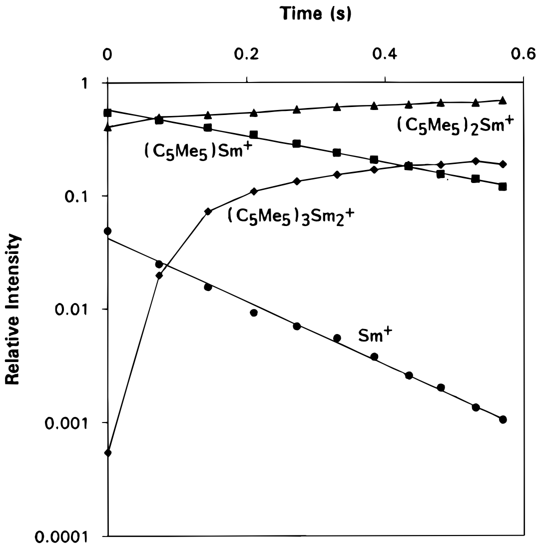

Figure 2. Temporal variation of positive ion abundances in 7 × 10^{-8} Torr of $(C_5Me_5)_2Sm$ following 70 eV electron ionization.

ers[19,22] (and also by Freiser *et al.*[23]) for ferrocene, nickelocene, and several other d-transition element metallocenes using FTICR techniques. Metal exchange reactions between transition metal cations and metallocenes with different central metals, in competition with charge exchange, have been described by Freiser and co-workers.[24]

The rate constants of reactions 1−3 were determined from the data collected in the double-resonance experiments described earlier by using the method of Richardson *et al.*,[19] in which the relative abundances of ejected and nonejected isotopes are taken into account to obtain the decaying reactant ion intensities. For reaction 1, an efficiency, $k/k_L = 0.27$, was determined that, given the estimated experimental errors and the probable errors in the determination of k_L (see Experimental Section), is comparable to the maximum expected efficiency of 0.50 for a self-charge exchange reaction,[19] indicating that reaction 1 probably occurs at a rate close to the capture rate.

For processes 2 and 3, reaction efficiencies well above the anticipated collisional efficiencies were obtained: $k/k_L = 5.3$ for reaction 2 and $k/k_L = 11.6$ for reaction 3. A faster rate than the Langevin rate limit could indicate that a long-range electron jump mechanism, in which an ion/molecule complex does not form, might be effective. The absence of metal exchange processes competing with charge transfer could support this long-range mechanism. However, other factors may lead to overestimation of the rates of reactions 2 and 3, namely, experimental errors in the pressure calibration procedure or underestimation of the value of k_L. In addition, as stated in the Experimental Section, the molecular polarizability of $(C_5Me_5)_2Sm$ was approximated by that of $(C_5Me_5)_2Fe$, although differences exist between the two complexes in terms of size and structure. Moreover, inefficient collisional cooling of the reactant ions might be occurring, although low electron beam energies have been used for the ionization of $(C_5Me_5)_2Sm$.

In spite of the uncertainties in the absolute values of the efficiencies of reactions 1−3, their relative magnitudes should be fairly reliable, and they follow the order that could be expected from a thermoneutral process like the self-charge exchange reaction 1 and exothermic processes like the electron transfer reactions 2a and 3 [IE(Sm) = 5.631 eV,[25] IE($(C_5Me_5)_2Sm$) = 5.4 eV[26]]. According to the model developed by Richardson to interpret gas phase electron transfer reactions,[19] the rate constants markedly depend on the exoergicity of the reactions, with the height of the central barrier of the double-well potential surface being reduced for exothermic processes. In the case of reactions 2a and 3, inefficient cooling of the reactant ions could further increase the exoergicity of the electron transfer processes, contributing to the rather large relative efficiencies of these reactions compared to reaction 1.

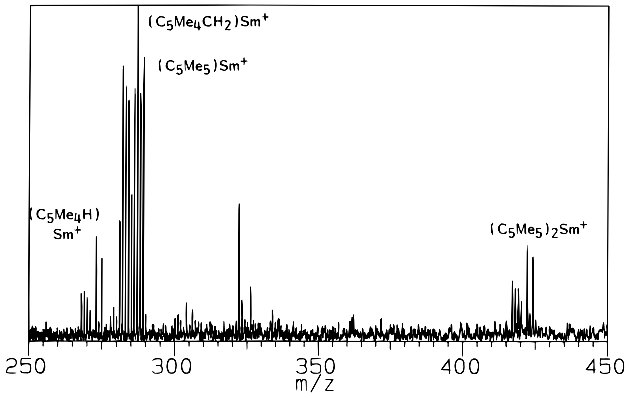

Figure 3. Positive ion laser desorption/ionization mass spectrum of $(C_5Me_5)_2Sm$ showing the formation of $(C_5Me_4CH_2)Sm^+$ and $(C_5Me_4H)Sm^+$.

Laser Desorption/Ionization of $(C_5Me_5)_2Sm$. Positive LDI spectra of $(C_5Me_5)_2Sm$ showed mainly the formation of $(C_5Me_5)_2Sm^+$, $(C_5Me_5)Sm^+$, and Sm^+, but in some cases the formation of $(C_5Me_4H)Sm^+$ and $(C_5Me_4CH_2)Sm^+$ was also observed, as shown in Figure 3. The species $(C_5Me_4CH_2)Sm^+$ most probably involves a tetramethylfulvenide ligand, whose formation from C_5Me_5 in condensed-phase organolanthanide chemistry is well documented, namely, in the decomposition of the samarium complex $[(C_5Me_5)_2Sm(\mu\text{-}H)]_2$ to form $[(C_5Me_5)_2Sm(\mu\text{-}H)(\mu\text{-}CH_2C_5Me_4)Sm(C_5Me_5)]$[27] and in the thermolysis of the complexes $[(C_5Me_5)_2LnCH(SiMe_3)_2]$ (Ln = Y, La, Ce).[28]

Reactivity of Sm^+ with C_5Me_5H. Access to all of the ionic species observed by LDI (and most of the ones formed by EI) of $(C_5Me_5)_2Sm$ could also be obtained by reacting laser-desorbed Sm^+ ions with pentamethylcyclopentadiene, C_5Me_5H. $(C_5Me_4CH_2)Sm^+$, $(C_5Me_4H)Sm^+$, and $(C_5Me_5)Sm^+$ were formed as primary products, and $(C_5Me_5)_2Sm^+$ was formed as a secondary product in a rapid addition reaction of C_5Me_5H to $(C_5Me_4CH_2)Sm^+$.

Figure 4 shows spectra obtained at two different times in the reaction of isolated $^{152}Sm^+$ ions with C_5Me_5H, which illustrate the formation of $(C_5Me_5)_2Sm^+$ as a secondary product. As a confirmation that this product

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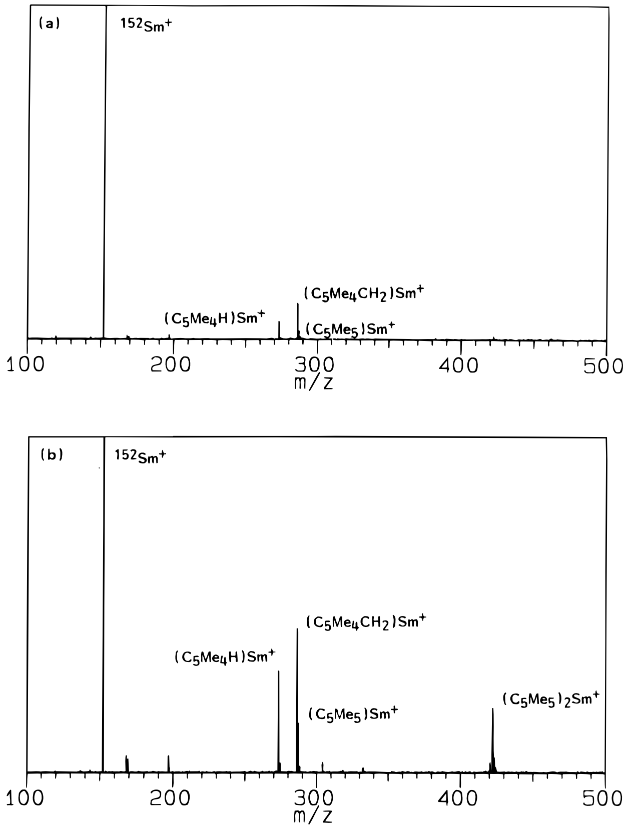

Figure 4. Mass spectra obtained in the reaction of $^{152}Sm^+$ with 1.0×10^{-7} Torr of C_5Me_5H: (a) 0.2 s; (b) 1 s.

was in fact the bis(pentamethylcyclopentadienyl)samarium cation, CID experiments were performed with this ion and with the authentic $(C_5Me_5)_2Sm^+$ ion formed by EI of the samarocene complex. In both cases, the formation of $(C_5Me_5)Sm^+$ at low energies and that of Sm^+ at higher energies were the only fragmentation processes observed.

The reactions of each of the primary product ions formed by $^{152}Sm^+$ with C_5Me_5H were studied, allowing the construction of Scheme 1, which shows the product ion distributions as well as the reaction efficiencies, k/k_{ADO}, that were obtained. Here, k_{ADO} represents the collisional rate constant determined by the "Average Dipole Orientation" procedure,[29] using a molecular polarizability for C_5Me_5H that was estimated by Miller's additivity method[18] and a dipole moment that was considered to be similar to the one tabulated for cyclopentadiene.[30]

The relative efficiencies of the secondary reactions, indicated in Scheme 1, support the formulation of the $(C_5Me_4CH_2)Sm^+$ ion as a fulvenide species, since it forms $(C_5Me_5)_2Sm^+$ from C_5Me_5H instead of an adduct. In comparison, the cyclopentadienyl ions $(C_5Me_5)Sm^+$ and $(C_5Me_4H)Sm^+$ are involved in less efficient condensation or ligand exchange processes.

The formation of $(C_5Me_4CH_2)Sm^+$, $(C_5Me_4H)Sm^+$, and $(C_5Me_5)Sm^+$ as primary products indicates that two types of processes might be simultaneously operative in the Sm^+/C_5Me_5H reaction. "Direct" reactions that eliminate CH_3 or H radicals and form the monocyclopentadienylsamarium ions occur, as well as reactions involving C−H insertion, followed by H_2 elimination and formation of the presumed tetramethylfulvenide species.

Scheme 1

(1) ($k/k_{ADO} = 0.48$)	$Sm^+ + C_5Me_5H \rightarrow (C_5Me_5)Sm^+ + H$	(5%)
	$\rightarrow (C_5Me_4H)Sm^+ + CH_3$	(40%)
	$\rightarrow (C_5Me_4CH_2)Sm^+ + H_2$	(55%)
(2a) ($k/k_{ADO} = 0.17$)	$(C_5Me_5)Sm^+ + C_5Me_5H \rightarrow (C_5Me_5)(C_5Me_5H)Sm^+$	(100%)
(2b) ($k/k_{ADO} = 0.18$)	$(C_5Me_4H)Sm^+ + C_5Me_5H \rightarrow (C_5Me_4H)(C_5Me_5H)Sm^+$	(5%)
	$\rightarrow (C_5Me_5)Sm^+ + C_5Me_4H_2$	(95%)
(2c) ($k/k_{ADO} = 0.38$)	$(C_5Me_4CH_2)Sm^+ + C_5Me_5H \rightarrow (C_5Me_5)_2Sm^+$	(90%)
	$\rightarrow (C_5Me_4CH_2)_2Sm^+ + H_2$	(10%)

It is instructive, at this point, to compare these results with the known data on the reactivity of Sm^+ ions with different hydrocarbons. With arenes, ranging from benzene to tri-*tert*-butylbenzene, only adduct formation reactions were observed.[1,2] With alkanes and alkenes the Sm^+ ions were unreactive, and only with 1,4-cyclohexadiene, a molecule for which the loss of H_2 to form benzene is exothermic by 25 kJ/mol,[25] did Sm^+ induce dehydrogenation to form $Sm(C_6H_6)^+$.[4] These studies compared the reactivities of all of the lanthanide series ions, which revealed a strong dependence on the ground state electronic configurations of the ions and the magnitudes of the promotion energies to reactive configurations. The reduced reactivity of Sm^+ was correlated with the high promotion energy from the $4f^6\,6s^1$ ground state to a reactive $4f^5\,5d^1\,6s^1$ configuration.

Although there is no thermochemical data available to fully interpret the reactivity of Sm^+ with C_5Me_5H, it can be reasonably assumed by using data for cyclopentadiene and methylcyclopentadiene[21,30,31] that the thermodynamics is more favorable for the Sm^+/C_5Me_5H reaction than for the reactions with arenes, alkanes, and alkenes. These data lead to values of 298−328 kJ/mol (depending on the source) for $D(C_5H_5{-}H)$ and 292 kJ/mol for $D(C_5H_5{-}CH_3)$ and to a ΔH of 128 kJ/mol for the process methylcyclopentadiene → fulvene + hydrogen. These values are lower than the C−H and $C{-}CH_3$ bond dissociation enthalpies in typical arenes, alkanes, and alkenes [$D(C{-}H)$ is 464 kJ/mol in benzene, 410 kJ/mol in propane, and 361 kJ/mol in propene, and $D(C{-}CH_3)$ is 426 kJ/mol in toluene, 359 kJ/mol in propane, and 311 kJ/mol in 1-butene].[31]

Preliminary studies of the reactivities of other lanthanide metal ions with C_5Me_5H have shown that, in this case, differences along the 4f series also exist[32] and are in agreement with the previous reports on Ln^+ reactivity with hydrocarbons.

With d-transition metal cations there are no reports of reactivity studies with C_5Me_5H, but Jacobson and Freiser have described a few reactions of Fe^+ and Co^+ with other cyclopentadienes from which some comparisons can be drawn. Both metal ions react with cyclopentadiene (C_5H_6) to form $(C_5H_5)M^+$,[33,34] and Co^+ dehydrogenates methylcyclopentadiene ($C_5H_5CH_3$) to form

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a $CoC_6H_6^+$ species, which was identified as the Co(fulvene)$^+$ ion.[34] $(C_5H_5)Co^+$ reacts with C_5H_6 (and also with cyclopentene) to give the bis(cyclopentadienyl)cobalt ion $(C_5H_5)_2Co^+$.[34] In the case of the Sm^+/C_5Me_5H system, three primary reaction channels were observed, while the secondary reactions involving the cyclopentadienyl ions $(C_5Me_4H)Sm^+$ and $(C_5Me_5)Sm^+$ with C_5Me_5H occurred only by ligand exchange or condensation processes. More adequate comparisons with d-transition metal ion reactivity would necessarily require experiments with pentamethylcyclopentadiene.

A final comparison can be made between the gas phase synthesis of $(C_5Me_5)_2Sm^+$ described in this work and the original preparation of $(C_5Me_5)_2Sm(THF)_2$ by the metal vapor synthesis technique (MVS).[11] In the condensed-phase reaction sequence, an intermediate product could be isolated and was characterized as $(C_5Me_5)Sm(H)(THF)_2$, a species that is the direct product of the insertion of a Sm atom into the C_5Me_5-H bond. In the gas phase synthesis of $(C_5Me_5)_2Sm^+$, the reaction proceeds through the tetramethylfulvenide ion $(C_5Me_4CH_2)Sm^+$, although the formation of a $(C_5Me_5)Sm(H)^+$ species can be postulated, which by H_2 elimination then leads to $(C_5Me_4CH_2)Sm^+$. As could be expected, the very different reaction conditions of the gas phase and the MVS experiments give rise to different relative stabilities of the possible intermediates along the reaction coordinate.

Conclusions

The first gas phase ion chemistry experiments involving a lanthanide metallocene, in this case $(C_5Me_5)_2Sm$, showed that remarkable similarities exist with the gas phase behavior of d-transition element metallocenes, despite the differences in covalency traditionally thought to exist between metallocenes of transition metals and lanthanides. The similarities in electron transfer chemistry and the formation of “triple-decker sandwich” species are particularly noteworthy. The decamethylsamarocene ion $(C_5Me_5)_2Sm^+$ can also 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, $(C_5Me_4CH_2)Sm^+$. These experiments demonstrate that several ligated samarium ions can be readily accessed under these conditions and will be available for gas phase studies of the reactivity of organosamarium species.

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