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Utility of Electrospray Mass Spectrometry for the Characterization of Air-Sensitive Organolanthanides and Related Species[1]

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The utility of electrospray mass spectrometry for the characterization of air-sensitive lanthanide complexes has been examined. A wide variety of lanthanide complexes were studied as acetonitrile solutions, including divalent and trivalent compounds, neutral and cationic species, and complexes with cyclopentadienyl as well as alternative ancillary ligands. The spectra are sensitive to the composition of the complex and the oxidation potential of the lanthanide ion. The $[(C_5Me_5)_2Ln][BPh_4]$ (Ln = Nd, Sm, Y, Tm) complexes form the solvated parent ions $[(C_5Me_5)_2Ln(MeCN)_x]^+$, whereas $[Zr_2(O^iPr)_9]Ln(C_5H_5)$ (Ln = Sm, Yb) forms the unsolvated parent ion $\{[Zr_2(O^iPr)_9]Ln(C_5H_5)\}^+$. $[(C_5Me_5)_2Ln(MeCN)_x]^+$ ions are also observed in the spectra of $(C_5Me_5)_2Ln(C_3H_5)$ (Ln = Sm, Y) and $(C_5Me_5)_2Ln(THF)_x$ (Ln = Sm, Eu, Yb). $[(C_5Me_5)Ln(\mu\text{-}I)(THF)_2]_2$ (Ln = Sm, Yb, Eu) and $LnI_2(THF)_2$ (Ln = Sm, Yb, Eu) gave differing sets of ions, depending on the specific metal. The spectra of bimetallic compounds, $[(C_5Me_5)Ln(THF)_x]_2(C_8H_8)$ (Ln = Sm, Yb), are more complicated.

Introduction

Mass spectroscopy is a powerful characterization tool for a variety of chemical species, but for organometallic complexes of the electropositive lanthanide metals, the utility of conventional mass spectral techniques is sometimes limited. Organolanthanide complexes frequently do not have the volatility and thermal stability profiles that would allow for characterization of the parent ions. In addition, many organolanthanides are sufficiently air sensitive that they often decompose before they can be conveniently introduced into the spectrometer. In practice, characterization of lanthanide complexes by mass spectral techniques[2] is much less routine than analysis of organic compounds by these methods.

Electrospray mass spectroscopy (ESMS)[3] has the potential to overcome some of the problems previously plaguing organolanthanide mass spectroscopy. This technique allows the introduction of samples in solution protected from air contamination and avoids the requirements of volatility and thermal stability, common for gas-phase methods. Recently, air-sensitive zirconium complexes have been characterized by this method,[4] and we are aware of a few reports on this technique with lanthanide complexes,[5] but ESMS has not been broadly explored in the organolanthanide area.

We initially examined the utility of ESMS in organolanthanide chemistry by studying a series of organolanthanide cations which we recently synthesized.[6] Since these complexes contain a stable cationic component, they seemed to be ideal first candidates for ESMS studies. The useful information obtained encouraged us to extend our study to the more difficult divalent organolanthanides,[7] since these often display the extremes of high reactivity among organolanthanide complexes. We have chosen pentamethylcyclopentadienyl complexes for this study, since this ligand is so common in organolanthanide chemistry and it is air sensitive in these systems. Results are also reported on air-sensitive, noncyclopentadienyl lanthanide complexes, both to evaluate the ESMS technique and to study the behavior of alternative ancillary ligands under these conditions.

Experimental Section

The complexes $[(C_5Me_5)_2Ln][BPh_4]$ (Ln = Tm, Nd, Sm),[6] $[(C_5Me_5)_2Y][BPh_4]$,[8] $[(C_5Me_5)_2Sm][B(C_6F_5)_4]$,[8] $(C_5Me_5)_2Ln(THF)_2$ (Ln = Eu, Sm),[9] $(C_5Me_5)_2Yb(THF)$,[10] $[(C_5Me_5)Sm(THF)_2]_2$-

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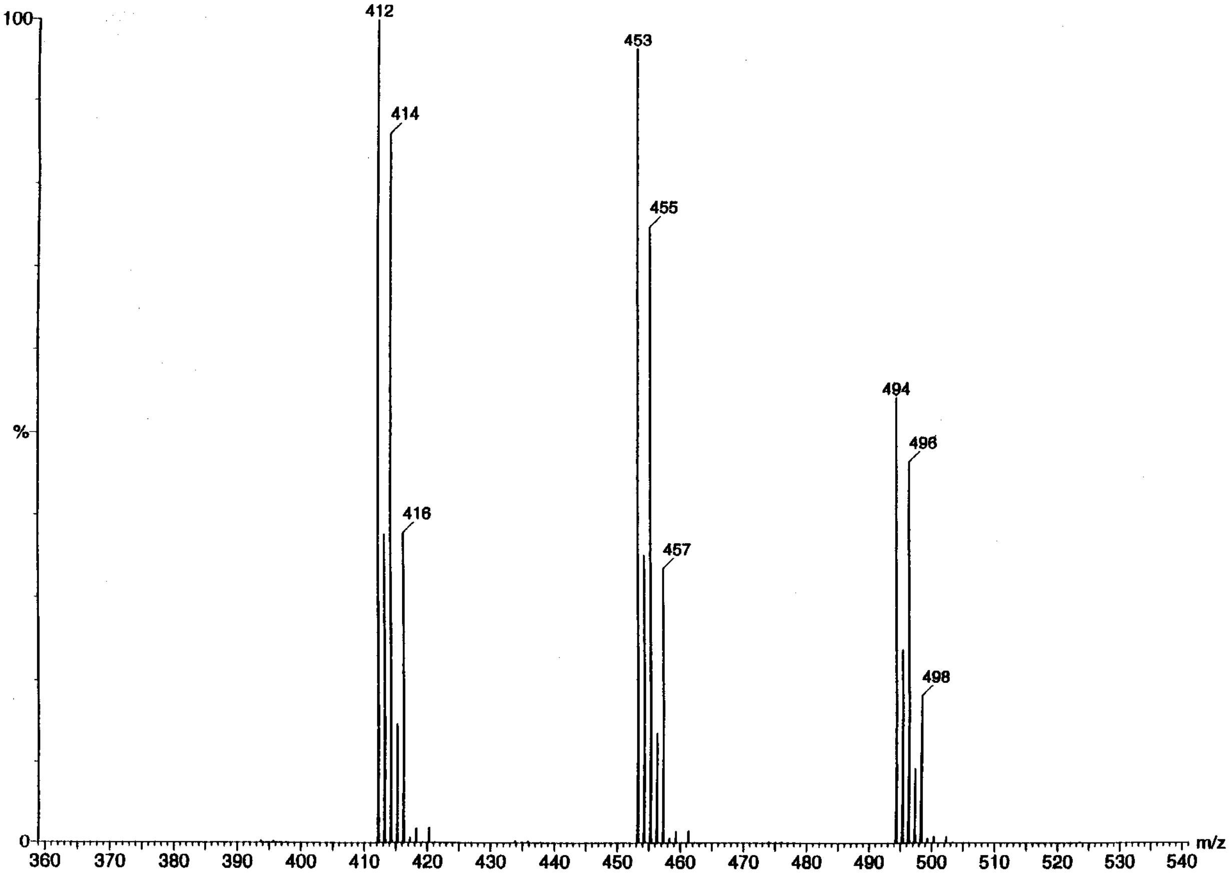

Figure 1. ESMS of $[(C_5Me_5)_2Nd][BPh_4]$ with *m/z* 412, 453, and 494 corresponding to the $[(C_5Me_5)_2Nd(MeCN)_x]^+$ ($x = 0-2$) ions.

(C_8H_8),[11] $[(C_5Me_5)Yb(THF)]_2(C_8H_8)$,[12] $(C_5Me_5)Ln(C_8H_8)$ (Ln = Sm, Yb, Ce),[11,13] $[(C_5Me_5)Ln(\mu\text{-}I)(THF)_2]_2$ (Ln = Eu, Sm, Yb),[14−16] $LnI_2(THF)_2$ (Ln = Eu, Yb, Sm),[17] $\{[Zr_2(O^iPr)_9]Ln(\mu\text{-}I)\}_2$ (Ln = Eu, Yb, Sm),[18] $[Zr_2(O^iPr)_9]Ln(C_5H_5)$ (Ln = Sm, Yb),[19] $\{[Zr_2(O^iPr)_9]Yb\}\{BPh_4\}$,[20] $(C_5Me_5)_2Ln(C_3H_5)$ (Ln = Sm, Y),[6] and $[Y(salen')(\mu\text{-}Cl)(THF)]_2$[21] were prepared as previously described. Anhydrous acetonitrile (99.8%) was purchased from Aldrich and used without further purification.

Typical Sample Analysis. In a nitrogen-containing glovebox, a sample approximately 2 mg in size was weighed into a vial. This sample was then subjected to multiple dilutions in acetonitrile until an approximate concentration of 60−100 μg/mL was reached. A 50 μL aliquot of acetonitrile was taken up into a 250 μL Model 1725 gastight syringe (Hamilton) followed by 150 μL of sample solution and finally another 50 μL aliquot of acetonitrile. This syringe was transported to the mass spectrometer in a rubber-septum-capped Schlenk flask under nitrogen. The sample was introduced via a syringe pump operating at 20 μL/min. The ESMS was a Micromass Model LCT with a Z-spray source. The capillary voltage was 3200 V, and the sample cone and extraction cone voltages were 40 and 10 V, respectively. The cone voltage was maintained at 40 V, which was intended to reduce fragmentation. Changing the capillary voltage affected the relative intensities of the solvation products but did not otherwise change the spectra.

Results

Representative electrospray mass spectra are shown in Figures 1−6, and data are summarized in Tables 1−8 (Cp* = C_5Me_5).

Trivalent $(C_5Me_5)_2LnZ$ Complexes. Compounds containing the $[(C_5Me_5)_2Ln]^+$ fragment seemed like the ideal first candidates for ESMS studies, since the parent ions were already present as stable cationic species. In addition, this series is available across the lanthanides; therefore, the effect of metal size could be studied in a single class of molecules. The syntheses of $[(C_5Me_5)_2Ln][BPh_4]$ have been described for Ln = Sm, Nd, and Tm,[6] and the yttrium analogue can be made similarly.

The electrospray mass spectrum of $[(C_5Me_5)_2Nd][BPh_4]$ (Figure 1) contained three major peak envelopes which correspond to the ions $[(C_5Me_5)_2Nd(MeCN)_x]^+$ (*x*

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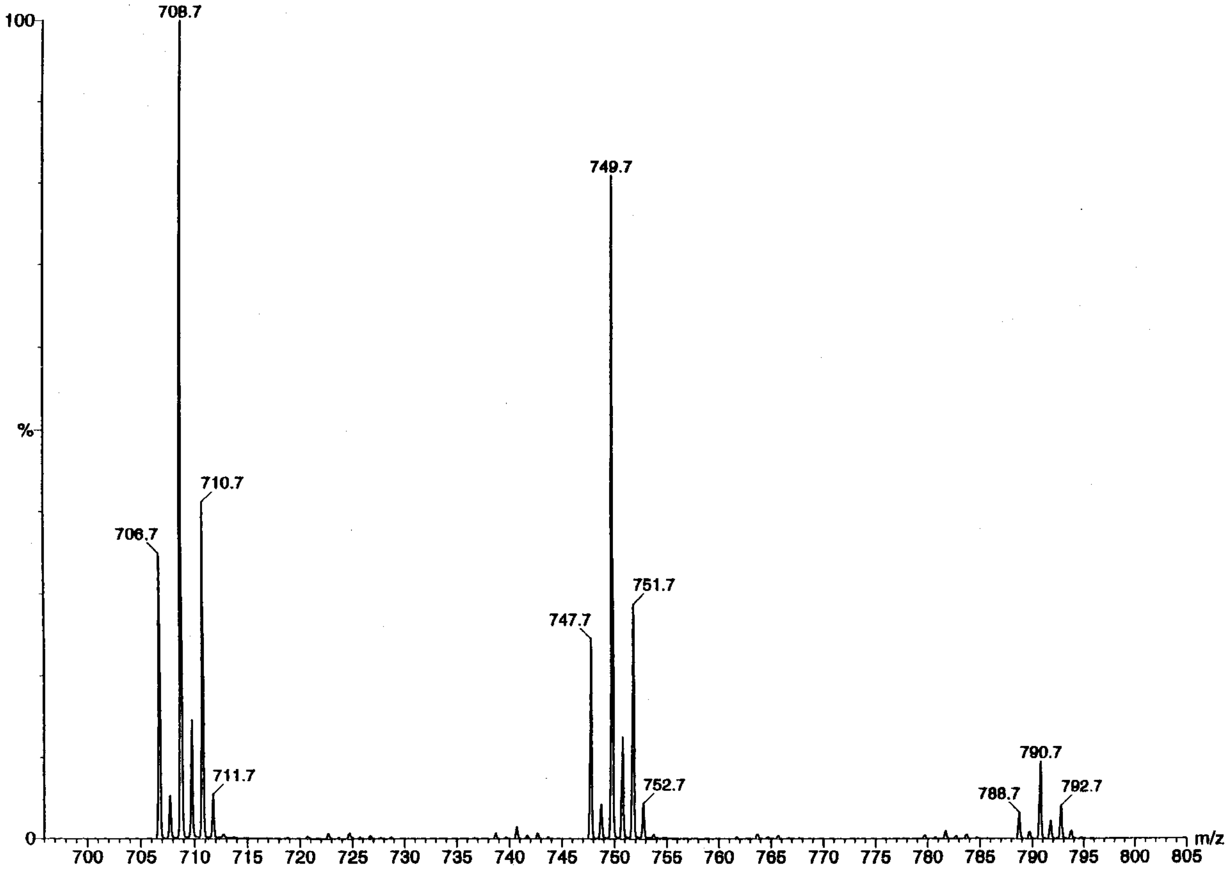

Figure 2. ESMS of $(C_5Me_5)_2Eu(THF)_2$ showing *m/z* 708, 749, and 790 corresponding to polymetallic $[(C_5Me_5)_3Eu_2(MeCN)_x]^+$ ($x = 0-2$) ions.

$= 0-2$) (Table 1). Each envelope has the isotopic pattern characteristic of a monometallic neodymium complex (^{142}Nd, 27.13%; ^{143}Nd, 12.18%; ^{144}Nd, 23.80%; ^{145}Nd, 8.30%; ^{146}Nd, 17.19%; ^{148}Nd, 5.76%; ^{150}Nd, 5.64%). The Sm, Y, and Tm analogues gave similar peak envelopes, and $[BPh_4]^-$ was observed in the negative ion spectra in each case. The ESMS of $[(C_5Me_5)_2Sm][B(C_6F_5)_4]$ was identical with that of $[(C_5Me_5)_2Sm][BPh_4]$, except that the $[B(C_6F_5)_4]^-$ anion was observed in the negative ion spectrum. A series of ions similar to those obtained from $[(C_5Me_5)_2Ln][BPh_4]$ were obtained from the allyl complexes, $(C_5Me_5)_2Ln(C_3H_5)$ (Ln = Sm, Y) (Table 2).

Divalent $(C_5Me_5)_2Ln(THF)_x$ Systems. Since $(C_5Me_5)_2Sm(THF)_2$ is an extremely reactive, low-valent lanthanide compound,[7] it seemed to be a challenging candidate for ESMS characterization. The samarium complex was studied, as well as the europium[9] and ytterbium[10] analogues, since these compounds comprise a series in which the effect of changes in reduction potential could be evaluated. The Ln(III)/Ln(II) reduction potentials for the divalent lanthanides vs NHE are as follows: Eu, −0.35 V; Yb, −1.1 V; Sm, −1.5 V.[22]

Examination of the least reducing europium system revealed two series of peaks consistent with formally divalent species. The more intense peaks corresponded to $[(C_5Me_5)Eu(MeCN)_x]^+$ ($x = 0-3$) (Table 3) and the others to polymetallic ions of the formula $[(C_5Me_5)_3Eu_2(MeCN)_x]^+$ ($x = 0-2$) (Figure 2).

The spectra of $(C_5Me_5)_2Sm(THF)_2$ and $(C_5Me_5)_2Yb(THF)$ differ from those of the europium system in that only one major envelope was observed for each system and the peaks correspond to the trivalent dicyclopentadienyl ions $[(C_5Me_5)_2Ln(MeCN)_x]^+$ (Ln = Sm, Yb; $x = 0-2$) (Table 3). Hence, the more reactive Sm(II) and Yb(II) become oxidized in the ESMS experiment. In the samarium case, these peaks are identical with those found for $[(C_5Me_5)_2Sm][B(aryl)_4]$ (aryl = C_6H_5, C_6F_5) and $(C_5Me_5)_2Sm(C_3H_5)$ (Tables 1 and 2). The unsolvated metallocene, $(C_5Me_5)_2Sm$, gave the same spectrum as the THF solvate, as expected since $(C_5Me_5)_2Sm$ readily adds bases and would enter the spectrometer as $(C_5Me_5)_2Sm(MeCN)_x$.

$[(C_5Me_5)Ln([\mu\text{-}I)(THF)_2]_2$ Complexes. In another series of divalent lanthanide pentamethylcyclopentadienyl complexes, the samarium compound, $[(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$, gave a single set of peak envelopes for the $[(C_5Me_5)_2Sm(MeCN)_x]^+$ ($x = 0-2$) ions (Table 4). The formation of bis(cyclopentadienyl) ions from a monocyclopentadienyl precursor may seem unusual, but this has been seen before in gas-phase Fourier transform ion cyclotron resonance (FTICR) studies of Sm/C_5Me_5H systems.[23] In contrast, the spectrum of $[(C_5Me_5)Yb(\mu\text{-}I)(THF)_2]_2$ contains one set of peaks analogous to the Sm peaks and also a second set corresponding to the doubly charged ions, $[(C_5Me_5)Yb(MeCN)_x]^{2+}$ ($x = 4, 5$).

The europium analogue $[(C_5Me_5)Eu(\mu\text{-}I)(THF)_2]_2$ has a third type of spectrum: four peak envelopes corresponding to the divalent ions $[(C_5Me_5)Eu(MeCN)_x]^+$ (x

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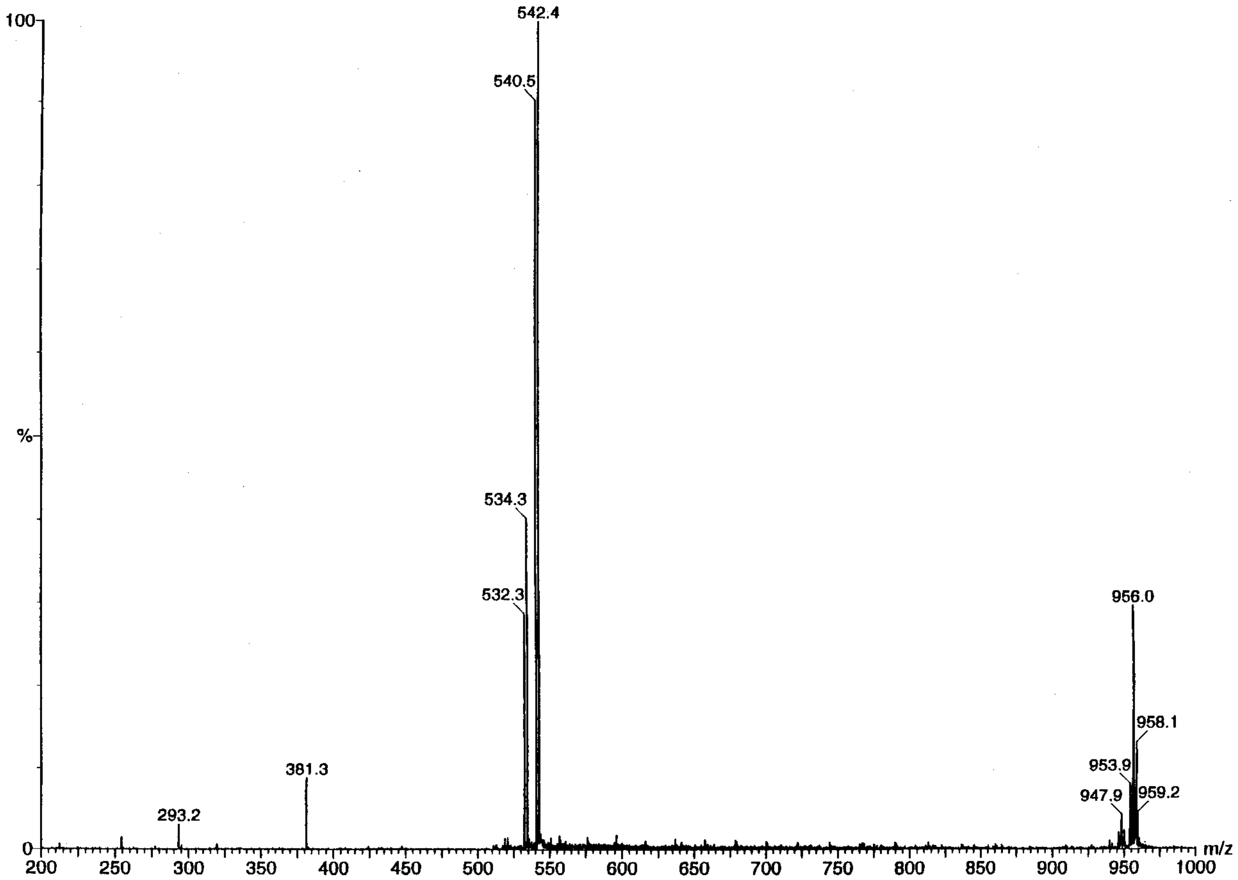

Figure 3. Negative ion ESMS of $[(C_5Me_5)Eu(\mu\text{-}I)(THF)_2]_2$ showing I_3^- at *m*/*z* 381, $[(C_5Me_5)EuI_2]^-$ at *m*/*z* 542, and $[Eu_2I_3(C_5Me_5)_2]^-$ at *m*/*z* 956.

= 0−3) are observed. These ions are equivalent in composition to the second set of ytterbium ions, but they are singly charged and contain divalent Eu^{2+}, not trivalent Yb^{3+}.

The negative ion spectra of the $[(C_5Me_5)Ln(\mu\text{-}I)(THF)_2]_2$ complexes contained I_3^- for each compound in this series. In the europium case, two sets of europium-based signals were also observed which match the isotopic distribution expected for the divalent anionic compounds $[(C_5Me_5)EuI_2]^-$ and $[(C_5Me_5)_2Eu_2I_3]^-$ (Figure 3).

$LnI_2(THF)_2$ Complexes. The ESMS spectra of the divalent $LnI_2(THF)_2$ series had I_3^- in the negative ion spectrum in each case, but the positive ion spectra differed as a function of the oxidation potential of the metal (Table 5). The spectra of $EuI_2(THF)_2$ and $YbI_2(THF)_2$ contained peaks for the divalent ions $[EuI(MeCN)_x]^+$ (x = 0, 1) and $[YbI(MeCN)_x)]^+$ (x = 0−3), respectively. However, the Yb spectrum had an additional set of peaks for the doubly charged, divalent $[Yb(MeCN)_6]^{2+}$ ion.

The spectrum of $SmI_2(THF)_2$ changed over time. The first positive ion spectrum which was recorded had only one series of peaks for the divalent $[SmI(MeCN)_x]^+$ (x = 0−5) ions, similar to those observed for Eu and Yb. However, a second positive ion spectrum showed a decrease in intensity of the divalent signals and a new series of peaks of much stronger intensity at *m*/*z* 446 and 487 for the trivalent $[SmI_2(MeCN)_x]^+$ (x = 0, 1) ions.

Bimetallic, Triple-Decked Divalent $[(C_5Me_5)Ln(THF)_x]_2(C_8H_8)$ Complexes and Trivalent $(C_5Me_5)Ln(C_8H_8)$ Metallocenes. The divalent bimetallic $[(C_5Me_5)Ln(THF)_x]_2(C_8H_8)$ complexes (Ln = Sm, Yb)[11,12] were examined, since isolation of the parent ions was expected to be a challenge: the more reactive Sm and Yb complexes have a tendency to readily form $(C_5Me_5)Ln(C_8H_8)$ as a byproduct in reduction reactions.[12,13] In addition, it was of interest to see if the other fragment formed in the reactions of these bimetallic complexes, $[(C_5Me_5)Ln]^{n+}$, could be observed by ESMS. The likely fragmentation products, $(C_5Me_5)Ln(C_8H_8)$, which can be synthesized independently,[13] were also examined.

The spectrum of $(C_5Me_5)Sm(C_8H_8)$ (Table 6) contains the $[(C_5Me_5)_2Sm(MeCN)_x]^+$ ions seen in the spectra of other compounds containing the $(C_5Me_5)_2Sm$ unit (Tables 1−3) and in the ESMS of $[(C_5Me_5)Sm(\mu\text{-}I)(THF)_2]_2$ (Table 4). A much lower intensity series is found at *m*/*z* 867.8 and 908.7 which appears to arise from Sm_2 species on the basis of the isotope patterns. In contrast, $(C_5Me_5)Yb(C_8H_8)$ shows a much more extensive series of signals (Figure 4). The major series of peaks matches the divalent monocyclopentadienyl formula $[(C_5Me_5)Yb(MeCN)_x]^+$ (x = 0−3). A low mass peak is observed which matches $[Yb]^+$ on the basis of the isotope pattern and doubly charged ion peaks were identified for divalent $[Yb(MeCN)_6]^{2+}$ and trivalent $[(C_5Me_5)Yb(MeCN)_x]^{2+}$ (x = 4, 5). A polymetallic isotope pattern was also observed which matches the theoretical pattern for divalent $[(C_5Me_5)Yb_2(C_8H_8)(MeCN)_x]^+$ (x = 2, 3). These latter ions could be related to the family of bimetallic, triple-decked lanthanide compounds, $[(C_5Me_5)Ln(solvent)_x]_2(C_8H_8)$.[11,12] Finally, peaks were observed at *m*/*z* 991.5 and 1032.5

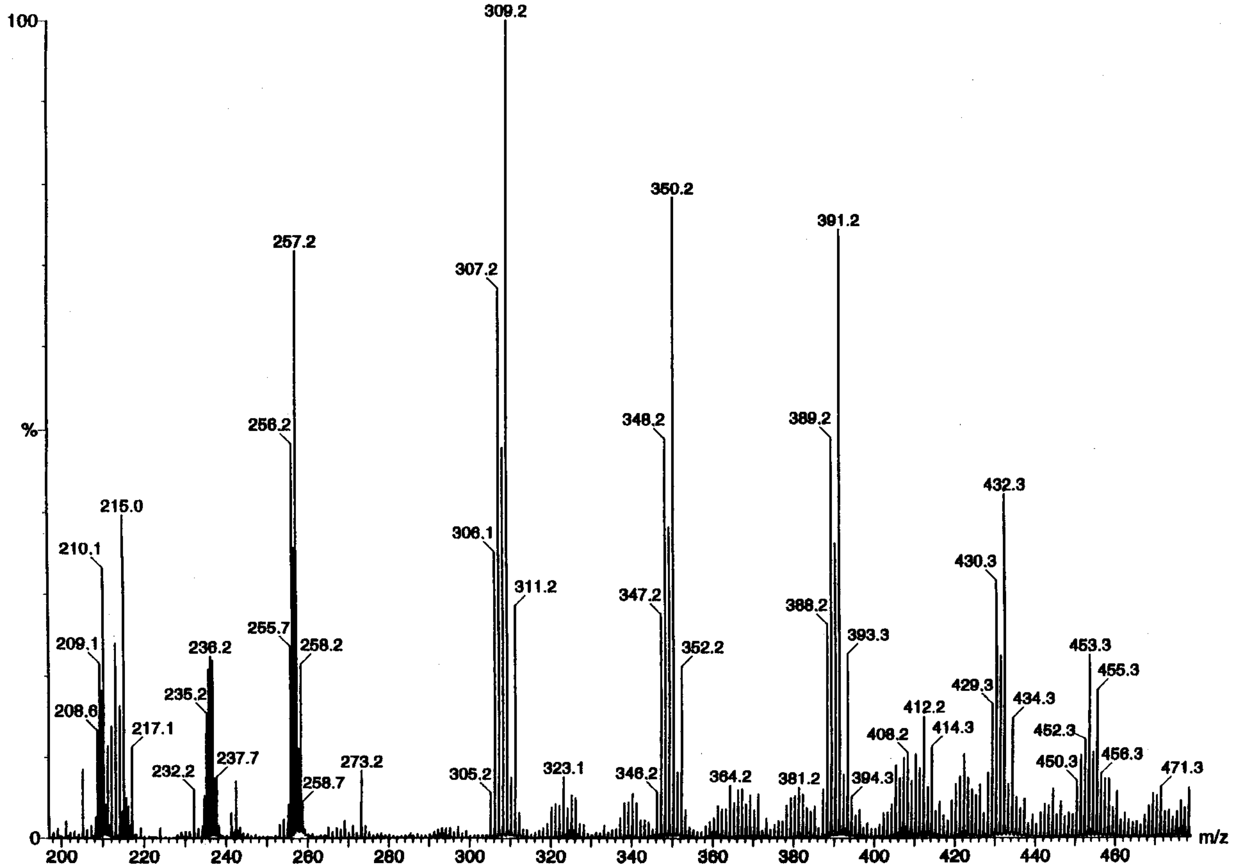

Figure 4. ESMS of $(C_5Me_5)Yb(C_8H_8)$ in MeCN with trivalent and divalent peak envelopes.

which appear to contain at least three ytterbium centers. They are separated by *m*/*z* 41, consistent with loss of acetonitrile from the higher mass peak to the lower mass one. The cerium compound, $(C_5Me_5)Ce(C_8H_8)$, which has no readily accessible divalent state, had a much simpler spectrum. Only one series of peaks for the $[(C_5Me_5)_2Ce(MeCN)_x]^+$ ($x = 0, 1, 2$) ions was observed.

The spectrum of bimetallic $[(C_5Me_5)Sm(THF)_2]_2(C_8H_8)$ (Table 7) revealed only one major series of peaks identical with those observed in the spectrum of $(C_5Me_5)Sm(C_8H_8)$. Again the more reactive Sm(II) complex is observed to oxidize under ESMS conditions. The fact that the spectrum of $[(C_5Me_5)Sm(THF)_2]_2(C_8H_8)$ is the same as that of its common reaction product, $(C_5Me_5)Sm(C_8H_8)$, indicates that its reductive reactivity in the ESMS systems has similarities to that in solution. No evidence for a $[(C_5Me_5)Sm]^{n+}$ fragment was observed, however.

The ESMS of $[(C_5Me_5)Yb(THF)]_2(C_8H_8)$ was not only complex, but it changed over time (Figure 5). The first positive ion spectrum, recorded within 120 s of sample introduction, had three major features. The most prominent peaks corresponded to the trivalent series $[(C_5Me_5)_2Yb(MeCN)_x]^+$ ($x = 0, 1, 2$). This is similar to the $[(C_5Me_5)Sm(THF)_2]_2(C_8H_8)$ system, but differs from the $(C_5Me_5)Yb(C_8H_8)$ spectrum which does not contain this ion. Also observed in smaller quantities were $[Yb]^+$ and two series of doubly charged ions previously found in the spectrum of $(C_5Me_5)Yb(C_8H_8)$: $[Yb(MeCN)_x]^{2+}$ ($x = 5, 6$) and $[(C_5Me_5)Yb(MeCN)_x]^{2+}$ ($x = 4, 5$). The second positive ion spectrum, recorded 5 min after the run was started, showed diminished $[(C_5Me_5)_2Yb(MeCN)_x]^+$ peaks and larger signals for'the divalent ions $[(C_5Me_5)Yb(MeCN)_x]^+$ ($x = 0-3$), found in the spectrum of $(C_5Me_5)Yb(C_8H_8)$. In addition, new doubly charged ions were observed at *m*/*z* 128.0 and 148.6 for $[Yb(MeCN)_x]^{2+}$ ($x = 2, 3$).

Altering the voltage over time led to no change in the population of different oxidation states, although the flow rate of sample introduction had a profound effect. At low flow rates (approximately 25 μL/min), the spectra consisted of only the trivalent $[(C_5Me_5)_2Yb(MeCN)_x]^+$ ions. However, at higher flow rates (greater than 100 μL/min), the prominent species became the divalent ions $[(C_5Me_5)Yb(MeCN)_x]^+$, although the trivalent $[(C_5Me_5)_2Yb(MeCN)_x]^+$ ions are still present.

Dizirconium Nonaisopropoxide Complexes. Complexes of the tetradentate, monoanionic dizirconium nonaisopropoxide ligand, $[Zr_2(O^iPr)_9]^-$ (dzni), were also studied, since this cyclopentadienide replacement often provides complexes which are more soluble than their cyclopentadienyl analogues. The spectra of $(dzni)Ln(C_5H_5)$ (Ln = Sm, Yb) contained only one family of peaks corresponding to the unsolvated trivalent parent ion, $[(dzni)Ln(C_5H_5)]^+$ (Figure 6, Table 8). The remaining peaks in the spectrum can be attributed to the breakdown of the dzni ligand, with most having a common difference of *m*/*z* 28. Similar peaks were observed in the spectrum of K(dzni).

Bimetallic dzni complexes were also studied. Each member of the $\{[Zr_2(O^iPr)_9]Ln(\mu\text{-}I)]\}_2$ series (Ln = Eu, Yb, Sm)[18] gave a similar spectrum (Table 8). The signals corresponded to the divalent, mono-dzni ions [(dzni)Ln-

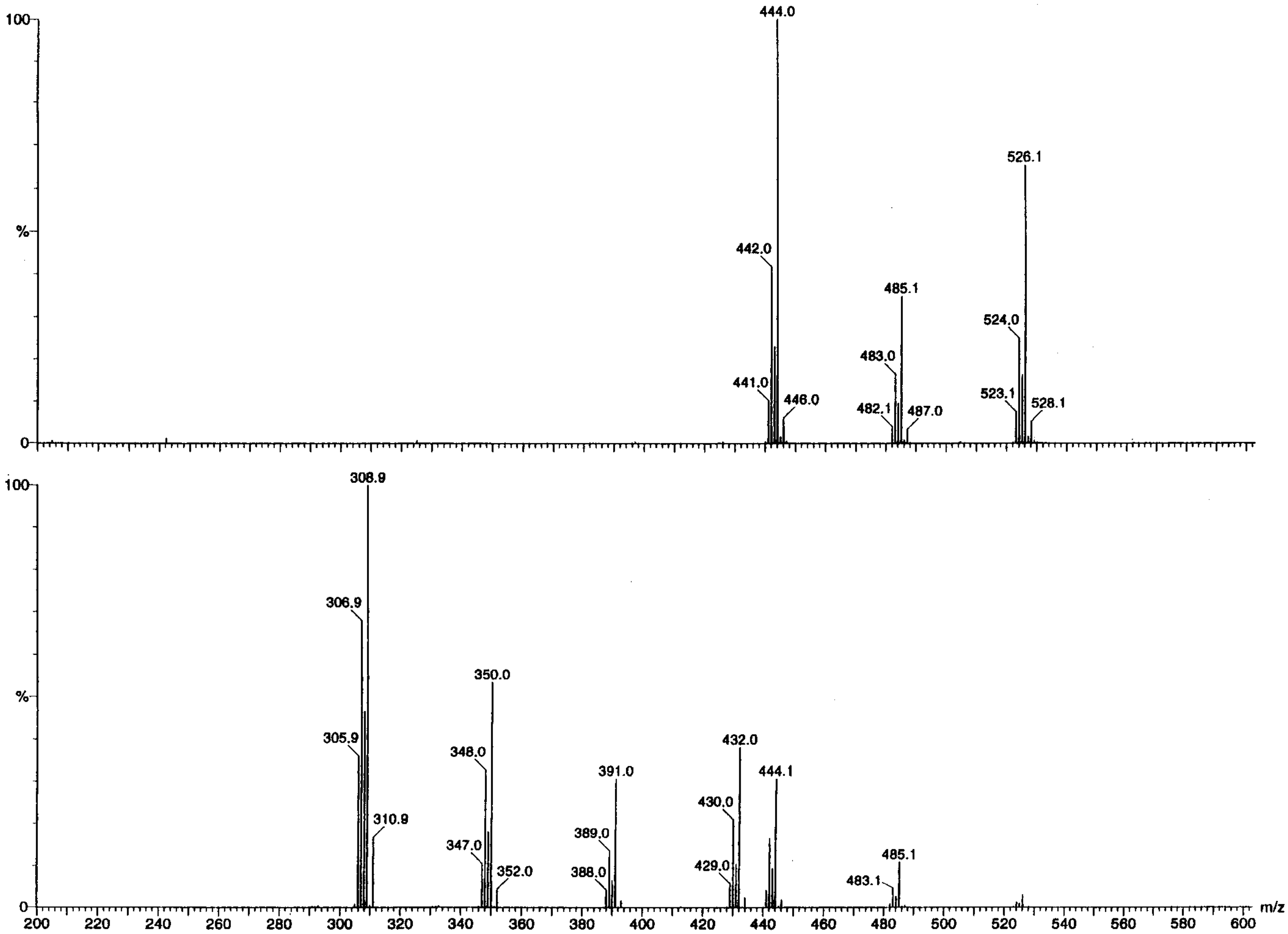

Figure 5. ESMS of $[(C_5Me_5)Yb(THF)]_2(C_8H_8)$ in MeCN as a function of flow rate (low flow rate, top; high flow rate, bottom).

$(MeCN)_x]^+$ ($x = 0, 1$). As with other iodide-containing complexes, the I_3^- ion was observed in all the negative ion spectra of the $[(dzni)Ln(\mu\text{-}I)]_2$ compounds. The $[(dzni)Yb(THF)_2][BPh_4]$ salt[20] was also examined and formed the $[(dzni)Yb(MeCN)]^+$ ($x = 0, 1$) ions as expected.

Schiff Base Complexes. A series of yttrium complexes of the dianionic substituted-salen ligand *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)ethylenediamine (salen′; $C_{32}H_{46}N_2O_2$) was also studied.[24] The yttrium complex $[(salen')Y(\mu\text{-}Cl)(THF)]_2$ was used as a precursor to complexes formulated as $[(salen')Y(THF)_x][BPh_4]$, $[(salen')Y(OSO_2CF_3)(THF)_x]$, $[(salen')Y(C_5Me_5)]$, and $[(salen')Y(OC_6H_3\text{-}{}^tBu\text{-}2,6)(THF)]$.[25] $[(salen')Y([\mu\text{-}Cl)(THF)]_2$ shows peaks for $[(salen')Y(MeCN)_x]^+$ at *m*/*z* 620 and 661 ($x = 1, 2$), as did the other four salen′ complexes. No evidence of any other ligand was present.

Discussion

The results described above clearly show that ESMS is a viable technique which can be valuable for obtaining information on the composition of reactive, air-sensitive organolanthanide complexes. The complexes can be conveniently introduced into the system without decomposition, and parent ions can be obtained from complexes as reactive as $(C_5Me_5)_2Sm(THF)_2$.

These results indicate that the behavior of organolanthanide and related compounds under these conditions can be quite varied, depending on their composition. Too few data are available to make any definitive generalizations, but it appears that some classes of compounds will readily form parent ions and solvated parent ions. However, for other types of compounds, information on only some of the components can be obtained by ESMS. With acetonitrile as the solvent, formation of MeCN adducts occurs in almost all cases. This is expected, since MeCN is a good ligand for the lanthanides[26] and may actually help stabilize the ions observed. The observation of higher molecular weight ions in the gas phase suggests that ESMS can be used to probe particularly favorable polymetallic combinations for the lanthanides.

Three series of compounds produced relatively clean parent ion or solvated parent spectra: divalent $(C_5Me_5)_2Ln(THF)_x$ (Ln = Sm, Eu, Yb), divalent $(dnzi)Ln(C_5H_5)$ (Ln = Sm, Yb), and trivalent $[(C_5Me_5)_2Ln][BPh_4]$ (Ln = Nd, Sm, Y, Tm). The C_5Me_5 complexes generated MeCN adducts, while the dzni-based ions were solvate-free. Earlier studies of dzni complexes showed that the dzni ligand could stabilize solvate-free species.[12,18] For the $[(C_5Me_5)_2Ln]^+$ series, it appears that the ESMS data are independent of the anion.

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(25) To be submitted for publication.
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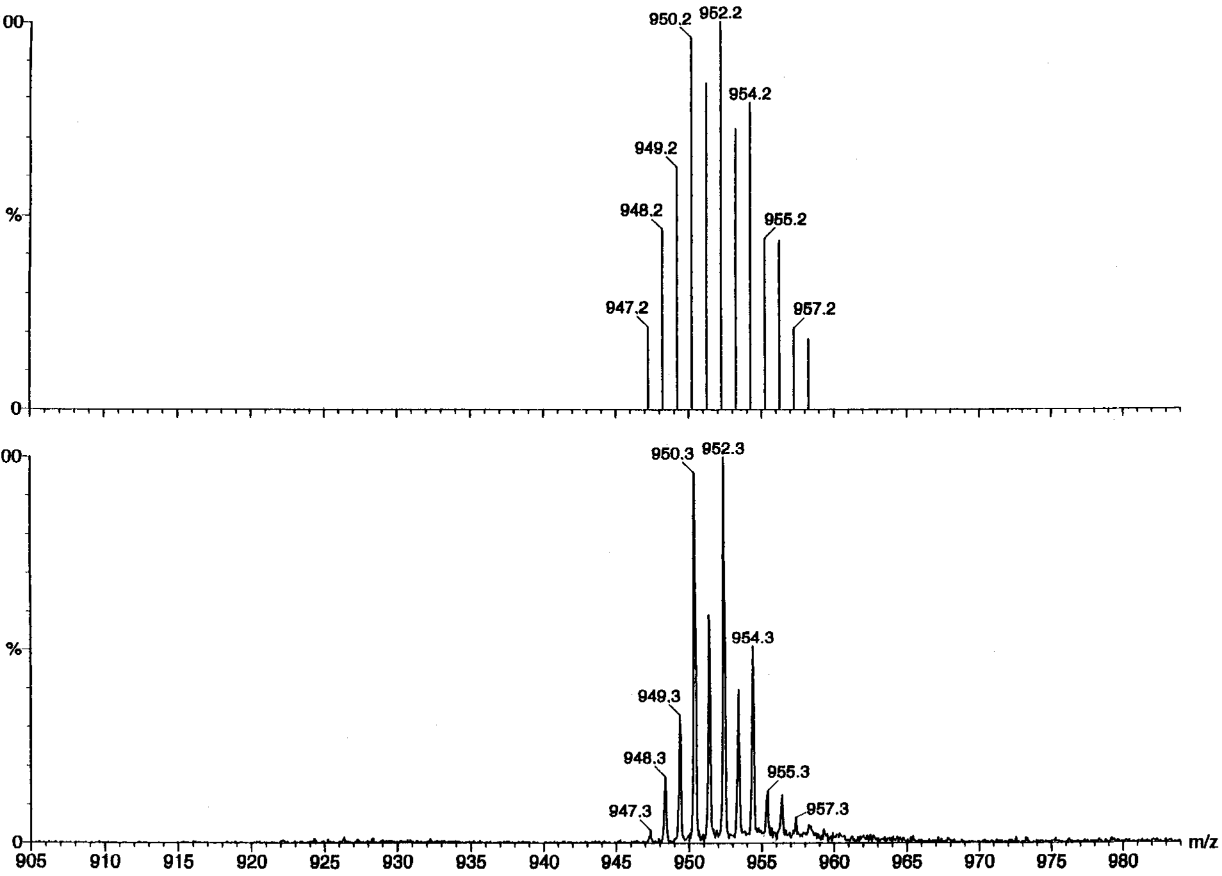

Figure 6. ESMS of [(dzni)Yb(C_5H_5)] in MeCN (bottom) compared with theoretical isotope distribution (top).

Table 1. Electrospray Mass Spectroscopic Data (*m/z*) for $[(C_5Me_5)_2Ln]^+[B(aryl)_4]$

	Ln, aryl				
assignt	Nd, C_6H_5	Sm, C_6H_5	Y, C_6H_5	Tm, C_6H_5	Sm, C_6F_5
$[Cp^*_2Ln]^+$	412	422	359	439	422
$[Cp^*_2Ln(MeCN)]^+$	453	463	400	480	463
$[Cp^*_2Ln(MeCN)_2]^+$	494	504	441	521	504

Table 2. Electrospray Mass Spectroscopic Data (*m/z*) for $[(C_5Me_5)_2Ln(C_3H_5)]$

assignt	Sm	Y
$[Cp^*_2Ln]^+$	422	359
$[Cp^*_2Ln(MeCN)]^+$	463	400
$[Cp^*_2Ln(MeCN)_2]^+$	504	441
$[Cp^*_2Ln(MeCN)_3]^+$		482

Table 3. Electrospray Mass Spectroscopic Data (*m/z*) for $[(C_5Me_5)_2Ln(THF)_x]$

assignt	Sm	Eu	Yb
$[Cp^*Ln]^+$		287	
$[Cp^*Ln(MeCN)]^+$		328	
$[Cp^*Ln(MeCN)_2]^+$		369	
$[Cp^*Ln(MeCN)_3]^+$		410	
$[Cp^*_2Ln]^+$	422		444
$[Cp^*_2Ln(MeCN)]^+$	463		485
$[Cp^*_2Ln(MeCN)_2]^+$	504		526
$[Cp^*_3Ln_2]^+$		708	
$[Cp^*_3Ln_2(MeCN)]^+$		749	
$[Cp^*_3Ln_2(MeCN)_2]^+$		790	

Table 4. Electrospray Mass Spectroscopic Data (*m/z*) for $[(C_5Me_5)Ln(\mu\text{-}I)(THF)_2]$

assignt	Sm	Yb	Eu
$[Cp^*_2Ln]^+$	422		
$[Cp^*_2Ln(MeCN)]^+$	463	485	
$[Cp^*_2Ln(MeCN)_2]^+$	504	526	
$[Cp^*_2Ln(MeCN)_3]^+$			
$[Cp^*Ln]^+$			285
$[Cp^*Ln(MeCN)]^+$			326
$[Cp^*Ln(MeCN)_2]^+$			367
$[Cp^*Ln(MeCN)_3]^+$			408
$[Cp^*Ln(MeCN)_4]^{2+}$		236	
$[Cp^*Ln(MeCN)_5]^{2+}$		257	
I_3^-	381	381	381
$[Cp^*LnI_2]^-$			542
$[Cp^*_2LnI_3]^-$			956

Table 5. Electrospray Mass Spectroscopic Data (*m/z*) for $[LnI_2(THF)_2]$

assignt	Sm[a]	Yb	Eu
$[LnI]^+$	278	300	279
$[LnI(MeCN)]^+$	319	341	320
$[LnI(MeCN)_2]^+$	360	382	
$[LnI(MeCN)_3]^+$	401	423	
$[LnI(MeCN)_4]^+$	442		
$[LnI(MeCN)_5]^+$	483		
$[Ln(MeCN)_6]^{2+}$		210	

[a] Time dependent.

The other types of complexes gave spectra containing primarily ions of the metal attached only to the polydentate, stabilizing ancillary ligands. Hence, the $(C_5Me_5)_2Ln(C_3H_5)$ and $[(salen')YZ(THF)_x]$ (Z = Cl, BPh_4, OSO_2CF_3, C_5Me_5, $OC_6H_3\text{-}^tBu\text{-}2,6$) systems gave only $[(C_5Me_5)_2Ln(MeCN)_x]^+$ and $[(salen')Y(MeCN)_x]^+$ ions, respectively. The C_3H_5, Cl, and OAr ligands were lost and not detected in either the positive or negative ion spectra. Similarly, $[(dzni)Ln(\mu\text{-}I)]^2$ gave only the $[(dzni)Ln(MeCN)]^+$ ions. In the case of [(salen′)-

Table 6. Electrospray Mass Spectroscopic Data (*m*/*z*) for [$(C_5Me_5)Ln(C_8H_8)$]

assignt	Ce	Sm	Yb
Ln^+			174
$[Ln(MeCN)_6]^{2+}$			210
$[Cp^*Ln(MeCN)_4]^{2+}$			236
$[Cp^*Ln(MeCN)_5]^{2+}$			257
$[Cp^*Ln]^+$			309
$[Cp^*Ln(MeCN)]^+$			350
$[Cp^*Ln(MeCN)_2]^+$			391
$[Cp^*Ln(MeCN)_3]^+$			432
$[Cp^*_2Ln]^+$	410	422	
$[Cp^*_2Ln(MeCN)]^+$	451	463	
$[Cp^*_2Ln(MeCN)_2]^+$	492	504	
$[Cp^*Ln_2(C_8H_8)(MeCN)_2]^+$		867	667
$[Cp^*Ln_2(C_8H_8)(MeCN)_3]^+$		908	708

Table 7. Electrospray Mass Spectroscopic Data (*m*/*z*) for [$(C_5Me_5)Ln(THF)_x]_2(C_8H_8)$]

assignt	Sm	Yb[a]
$[Ln]^+$		174
$[Ln(MeCN)_5]^{2+}$		189
$[Ln(MeCN)_6]^{2+}$		210
$[Cp^*Ln]^+$		309
$[Cp^*Ln(MeCN)]^+$		350
$[Cp^*Ln(MeCN)_2]^+$		391
$[Cp^*Ln(MeCN)_3]^+$		432
$[Cp^*_2Ln]^+$	422	444
$[Cp^*_2Ln(MeCN)]^+$	463	485
$[Cp^*_2Ln(MeCN)_2]^+$	504	526
$[Cp^*Ln(MeCN)_4]^{2+}$		236
$[Cp^*Ln(MeCN)_5]^{2+}$		257

[a] Time dependent.

Table 8. Electrospray Mass Spectroscopic Data (*m*/*z*) for [$Zr_2(O^iPr)_9$] Lanthanide Complexes

assignt	Sm	Eu	Yb
$[Zr_2(O^iPr)_9]Ln(C_5H_5)$			
$[(dzni)Ln(C_5H_5)]^+$	930		952
$\{[Zr_2(O^iPr)_9]Ln(\mu\text{-}I)\}_2$			
$[(dzni)Ln]^+$	864	865	887
$[(dzni)Ln(MeCN)]^+$	905	906	928
I_3^-	381	381	381

$Y(C_5Me_5)$], the salen′ ancillary ligand predominated over C_5Me_5.

The bimetallic complexes tended to be more unpredictable. Hence, the 1:1 C_5Me_5/Ln complex $[(C_5Me_5)Sm(THF)_2]_2(C_8H_8)$, gave ions with a 2:1 C_5Me_5/Ln ratio and the spectrum of the Yb analogue was shown to be time and flow rate dependent. The $(C_5Me_5)Ln(C_8H_8)$ (Ln = Ce, Sm, Yb) spectra were also not straightforward in that 2:1 C_5Me_5/Ln ions were formed. Preliminarily, it appears that a lanthanide attached to a full complement of stabilizing ancillary ligands, i.e., $[(C_5Me_5)_2]^{2-}$, $[salen']^{2-}$, or $[Zr_2(O^iPr)_9]^-$ can give spectra containing these fragments. With less ancillary ligand saturation, the results are more variable.

The results obtained for the divalent series of complexes $(C_5Me_5)_2Ln(THF)_x$, $[(C_5Me_5)Ln(\mu\text{-}I)(THF)_2]_2$, $[(C_5Me_5)Ln(THF)_x]_2(C_8H_8)$, and $LnI_2(THF)_2$ follow the stability of these divalent oxidation states. Hence, the most stable divalent state, Eu(II), gives divalent ions in the ESMS system, while the most reactive, Sm(II), gave trivalent products. The Yb complexes were of intermediate stability, exhibiting both divalent and trivalent ions in a variety of complexes.

Conclusion

Electrospray mass spectroscopy can be used to characterize highly reactive, air-sensitive organolanthanide complexes. In some cases, e.g. the $[(C_5Me_5)_2Ln]^+$ cations, parent ions are readily formed. In other cases, e.g. the $(C_5Me_5)Ln(C_8H_8)$ system, ligand redistribution can occur. When this happens, the observed ions do not represent the formulas of the precursors but do provide information about the components in the system. Some ligands, however, may be "ESMS silent", as was seen for all compounds with the allyl ligand $[C_3H_5]^-$ and the majority of compounds with the cyclooctatetraenide ligand $[C_8H_8]^{2-}$. These preliminary data suggest that ESMS can be very helpful as an ancillary means of characterization, in that it will indicate components and in favorable cases the parent ions. This technique must be used in conjunction with other methods of characterization, but as more data are acquired about the types of compounds that give parent ions, it can become a reliable way to obtain information about products from organolanthanide reactions.

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