

# A Study of Ligand Coordination at Lanthanide and Group 4 Metal Centers by MALDI-TOF Mass Spectrometry

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**Summary:** Reactions of lanthanide amide reagents  $\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_3$  (where Ln = Sm, Gd, Ho or Yb) with amine-bis(phenol) ligands were probed using inert atmosphere MALDI-TOF mass spectrometry (MS) (anthracene matrix); the technique rapidly confirms ligand coordination, giving excellent agreement with theoretical isotope patterns for lanthanide(amine-phenolate) fragments. Spectra on isolated lanthanide amine-bis(phenolate) amido complexes are similar to those seen from small scale parallel reactions of metal amides and protonated ligands. Although in all cases molecular ion peaks are not observed, peaks for lanthanide arene complexes,  $[\text{M} + \text{arene}]^+$ , formed *in situ* are seen. The lack of molecular ion peak is due to difficulties in ionizing  $\text{Ln}^{3+}$  complexes by charge-transfer. However, if Nujol is used to disperse the analyte and matrix prior to analysis rather than toluene, arene adducts are not observed. Similar phenol-derived ligands can be reacted with diamagnetic  $\text{M}(\text{NMe}_2)_4$  (where M = Ti

or Zr) and amine-phenolate complex formation is again confirmed easily by MALDI-TOF MS or LDI-TOF MS (no matrix). These complexes were also characterized by NMR spectroscopy and elemental analysis on isolated samples.

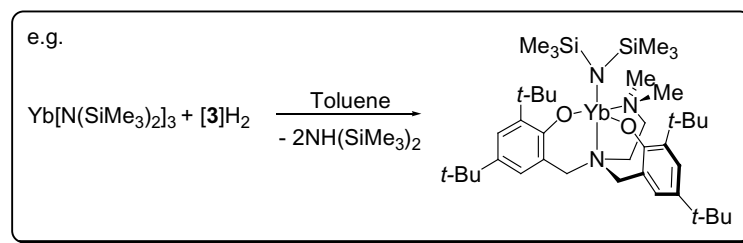
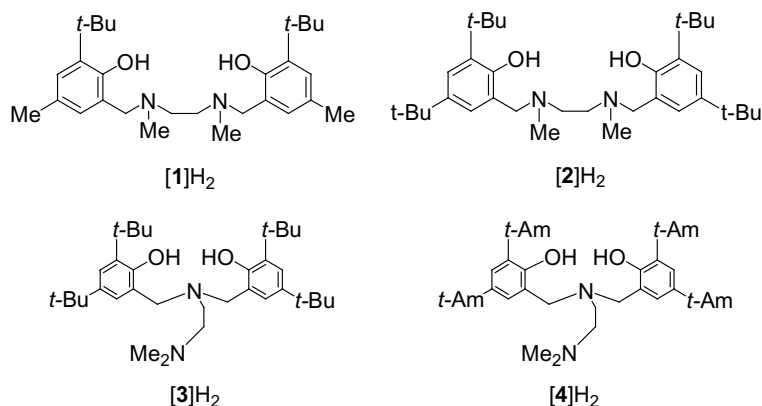
**KEYWORDS** Lanthanide, Group 4 metals, transamination, MALDI mass spectrometry, phenolate-amine ligand, arene complex, charge-transfer ionization

At present many researchers are investigating anionic ligands containing ‘hard’ nitrogen and oxygen donor atoms as alternatives to cyclopentadienyl ligands in early transition metal and lanthanide chemistry.<sup>1</sup> In particular, amine-bis(phenol) ligands in combination with group 3 metals and lanthanides are active initiators in the ring opening polymerization of lactones,<sup>2</sup> with group 4 and 5 metals also displaying high activity in this reaction at the same time as usually being excellent  $\alpha$ -olefin polymerization catalysts.<sup>3</sup> Whereas the characterization of the diamagnetic early transition metal species is possible using  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopies, the characterization of organolanthanide species (with the exception of  $\text{Y}^{3+}$ ,  $\text{La}^{3+}$ ,  $\text{Lu}^{3+}$  and  $\text{Yb}^{2+}$ ) is heavily dependent on the growth of single crystals and X-ray crystallographic structure determination. NMR spectroscopy is widely used throughout the field of organometallic chemistry, but this method is not as useful when applied to paramagnetic lanthanide compounds.<sup>2a,b,e,f,h,i</sup> To remedy this situation, characterization methods which have recently been applied to neutral organometallic complexes, namely MALDI-TOF MS,<sup>4</sup> need to be used in the field of organolanthanide chemistry where they may be able to provide valuable data.

Here we report the use of MALDI-TOF MS for investigating coordination reactions for a series of lanthanide amide reagents,  $\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_3$  (where  $\text{Ln} = \text{Sm}, \text{Gd}, \text{Ho}, \text{Yb}$ ) with amine-bis(phenol) ligands, Chart 1. These elements were chosen as they represent a range in  $\text{Ln}^{3+}$  ion sizes from across the lanthanide series. Additionally, they are all paramagnetic ( $\text{Sm}^{3+} f^5$ ,  $\text{Gd}^{3+} f^7$ ,  $\text{Ho}^{3+} f^{10}$ ,  $\text{Yb}^{3+} f^{13}$ ) and their complexes are difficult to study using conventional NMR based characterization techniques. Although mass spectrometry has been used to study moisture-stable lanthanide complexes,<sup>5</sup> such as MRI contrast agents, it has not been used for catalytic, metallo-organic lanthanide species that are typically extremely

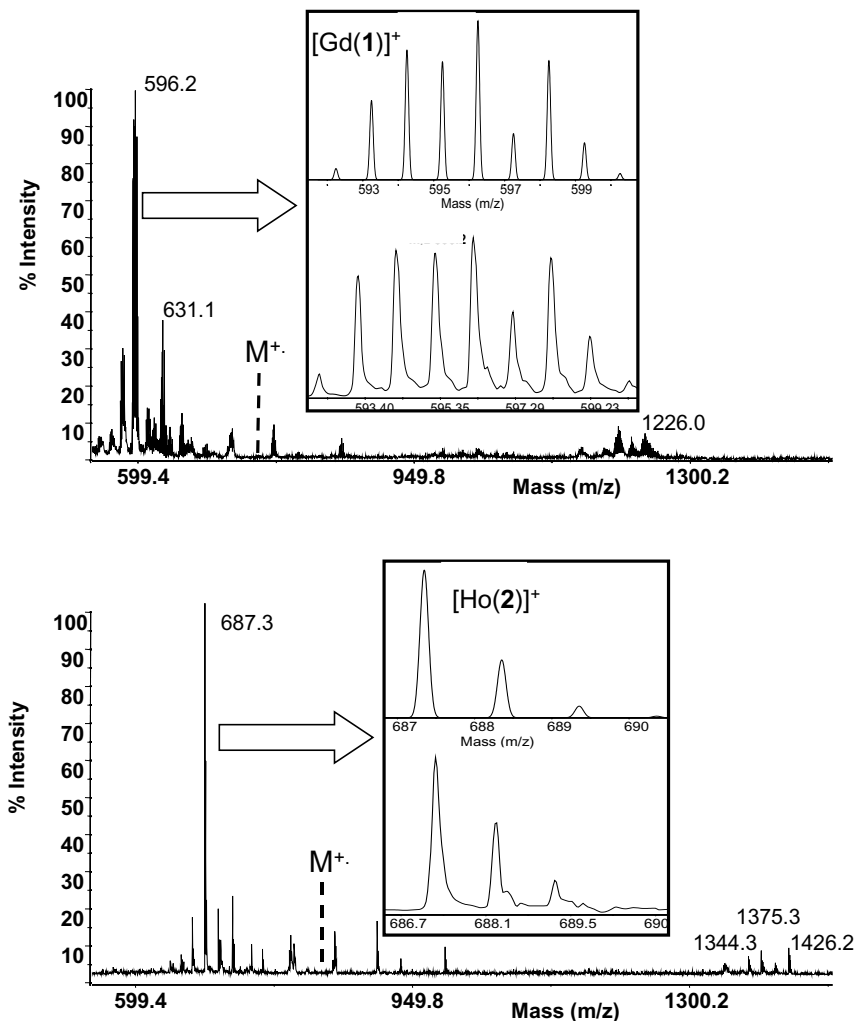
moisture sensitive. A recent communication has highlighted the versatility of this mass spectrometric technique in studying reactions of catalytically active metal centers,<sup>4</sup> including a highly reactive  $Ti^{3+}$  polymerization catalyst. For most transition metals, ionization of the compounds proceeds through a charge-transfer mechanism where the metal centers are redox active, e.g.  $Ti^{3+}/Ti^{4+}$ , using pyrene or anthracene as the matrix.

**Chart 1.** Amine-bis(phenol) ligands used in this study with  $Ln\{N(SiMe_3)_2\}_3$  reagents

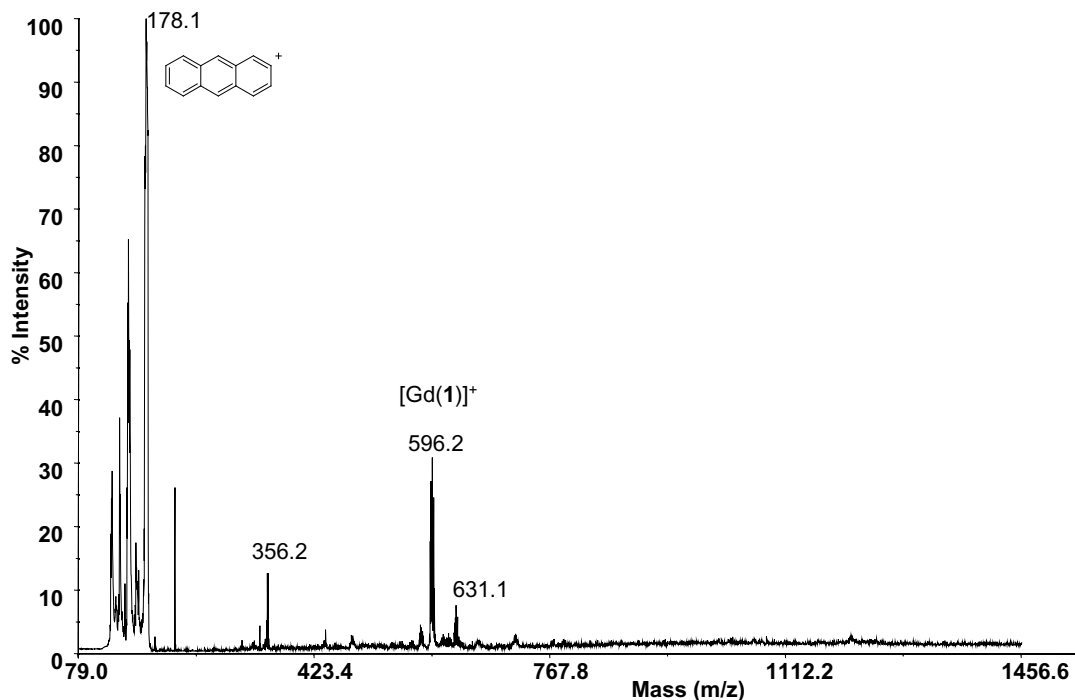


$Ln$  amide reagents and amine-phenol ligands<sup>6,7</sup> readily react to yield phenolate complexes<sup>2a,h</sup> and therefore, we decided these reactions would be amenable to the assessment of MALDI-TOF MS in metallo-organic lanthanide chemistry. These reactions can also be performed on a millimolar scale in a glove box. MALDI-TOF MS of isolated metal complexes (authenticated by elemental analyses) was performed by preparing the samples in a glove box and transferring the sample plate to the spectrometer using a glove bag.<sup>8</sup> In addition to optimizing the parameters of the instrument, it was important to screen the amount of matrix used. LDI-TOF MS (no matrix) did not afford interpretable spectra, but only a small amount of a neutral matrix (1:1 anthracene:analyte) was required to get spectra with good

signal-to-noise ratio. Initial experiments using larger concentrations of matrix (10:1 anthracene:analyte) gave spectra dominated by matrix ions.<sup>9</sup> Previous investigations of organometallic species using MALDI-TOF MS have used larger ratios of matrix to analyte.<sup>4</sup> In our study the ligands may absorb the laser energy and play a role in ionization of samples. Although the sample plate was exposed briefly to the air (five to twenty seconds) when being placed in the spectrometer, we did not observe any products of hydrolysis reactions in our MS experiments. However, when plates were intentionally exposed to air for five to twenty minutes, the resulting spectra contained no high mass peaks and the only assignable signals were for the protonated ligands. For all spectra obtained in this study, efforts were made to optimize the signal-to-noise ratio, however, increasing the number of laser shots accumulated or ratios of analyte:matrix did not provide improved spectra. In fact, a steady deterioration in signal-to-noise ratio was seen upon increasing shots from 60 to 100 and higher.



**Figure 1.** Mass spectra of isolated [1]GdN(SiMe<sub>3</sub>)<sub>2</sub> and [2]HoN(SiMe<sub>3</sub>)<sub>2</sub>, insets contain isotope patterns for the fragment [Ln(amine-phenolate)]<sup>+</sup>, simulated (top) and observed (bottom). Expected position of intact [Ln(amine-phenolate)N(SiMe<sub>3</sub>)<sub>2</sub>]<sup>+</sup> indicated by dotted line.

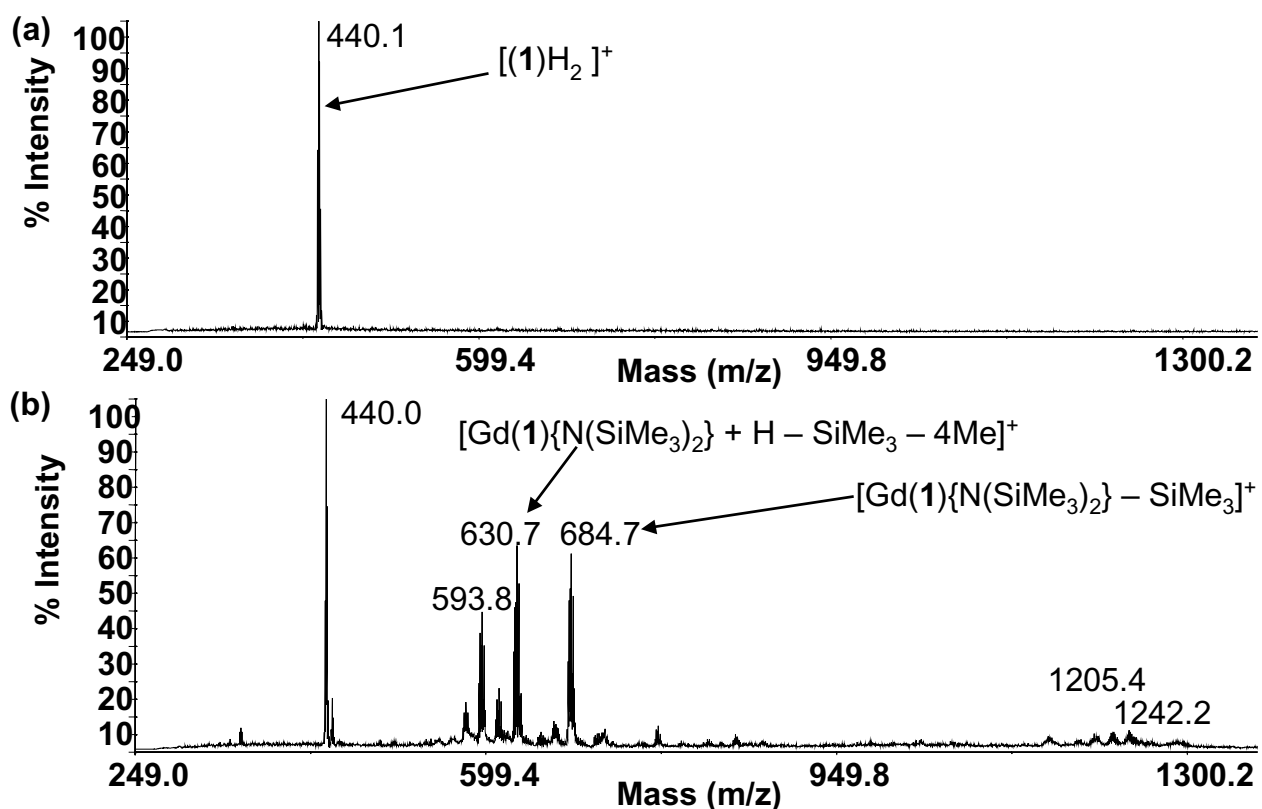


**Figure 2.** Mass spectrum of isolated  $[1]\text{GdN}(\text{SiMe}_3)_2$  obtained using Nujol to disperse matrix (anthracene) and analyte.

The most intense peaks (outside of the matrix region) in the spectra of the metal complexes were readily assigned to  $[\text{Ln}(\text{amine-phenolate})]^+$  fragments, Figures 1 and 2. Molecular ion peaks were not observed but other peaks could be assigned to  $[\text{M-SiMe}_3]^+$  and  $[\text{M-R}]^+$  (e.g.  $[\text{M-C}_4\text{H}_9]^+$ ).<sup>10</sup> In the work of Fogg and co-workers,<sup>4</sup> Cu(II) complexes resisted one-electron oxidation to yield the cation *via* electron-transfer MALDI, as the metal center is in its highest common oxidation state. Therefore, it is not so surprising that no molecular ion peaks for intact lanthanide(amine-phenolate)bis(trimethylsilyl)amido complexes were observed as the metal center cannot be further oxidized. However, it should also be noted that amine-bis(phenolate) ligands can be non-innocent and are themselves redox active, as has been demonstrated in their iron chemistry,<sup>11</sup> and the ligands may play a role in the ionization mechanism. Typically, all peaks with  $m/z$  between that of the ligand and the expected peak for the intact complex could be interpreted through their isotope patterns and mass. However, the spectra also contained a cluster of less intense peaks between  $m/z$  1000 and 1300 if toluene was used to deposit the analyte and matrix on the sample plate. In contrast, if Nujol (paraffin oil) was used to prepare a mull of matrix and analyte for analysis, the spectra obtained did not contain these

high mass clusters of peaks (Figure 2). It has been proposed by Fogg and co-workers that this approach to sample preparation may lead to better shot-to-shot reproducibility of mass spectra of transition metal complexes.<sup>4</sup> We have experienced this ourselves and in future studies we will focus on this sample preparation method.

We were intrigued by the origin of the unexpected high mass peaks formed when toluene was used in the sample preparation. Therefore, a further series of reactions was performed to see if this was a general mass spectrometric trend for lanthanide species supported by amine-phenolate ligands, and attempts were made to identify these species by  $m/z$  and isotope pattern matching.



**Figure 3.** (a) Mass spectrum of  $[1]H_2$  alone; (b) Mass spectrum of  $[1]GdN(SiMe_3)_2$  identified *in situ* from a reaction mixture containing  $Gd\{N(SiMe_3)_2\}_3$  and  $[1]H_2$ .

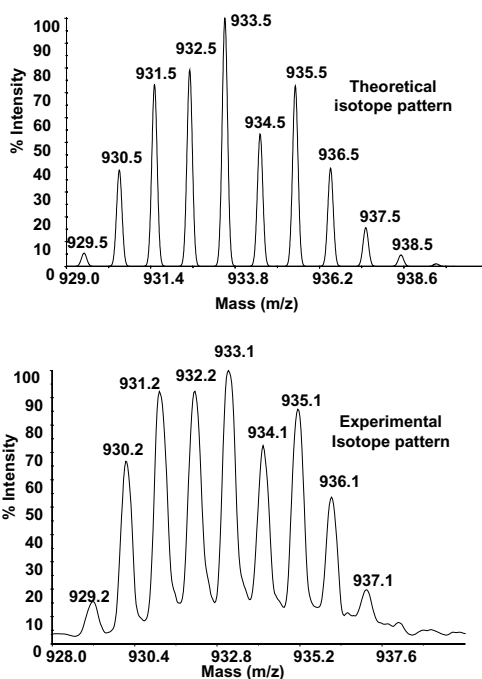
When analyzing reaction mixtures, Figure 3, spectra of the free ligand analyzed from a sample spotted on the same plate immediately confirmed that a reaction had occurred.<sup>12</sup> However, in contrast to the free ligands that can be ionized by charge transfer, the lanthanide amide reagents alone did not yield

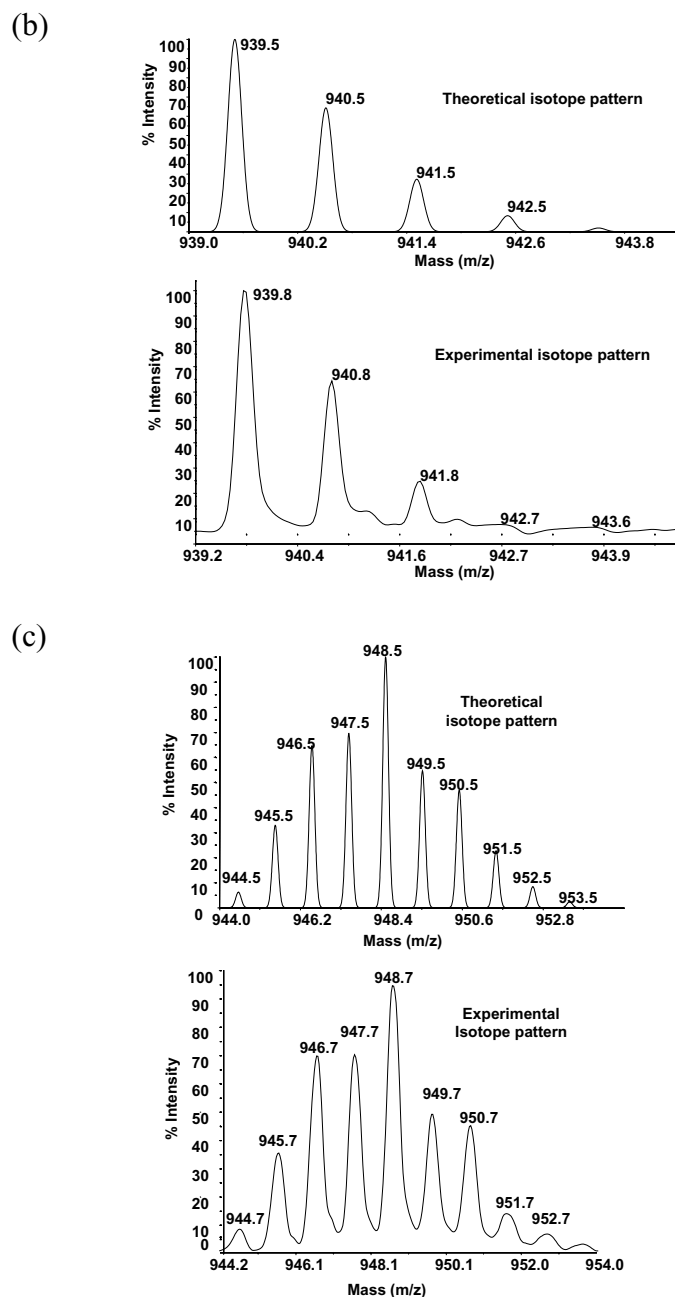
spectra. There are two reasons for this: their volatility in the spectrometer prior to analysis<sup>12</sup> and also their inability to undergo charge transfer ionization. The spectra of the pure ligands show peaks at  $m/z$  corresponding to the molecular weights of the ligands, in this case  $m/z$  440. The isotopic pattern of the peaks is in agreement with the relative amounts of  $^{12}\text{C}$  and  $^{13}\text{C}$  in the compound. The mass spectra obtained from the reaction mixtures show series of peaks consistent with the expected product and are only slightly more complex than those of isolated complexes. In particular, all mixtures studied to date show a peak corresponding to loss of an amido group and the presence of a  $[\text{Ln}(\text{amine-phenolate})]^+$  ion. Also, as Sm, Gd and Yb each possess 7 naturally occurring isotopes and Ho exists as only 1 naturally occurring isotope,  $^{165}\text{Ho}$ ,<sup>6</sup> characteristic isotope patterns were seen, Figure 3, and were extremely valuable in elucidating the molecular formulae and thereby, the species present. In agreement with the spectra of isolated complexes, in addition to the expected region of peaks ( $m/z$  600-800), higher mass peaks ( $m/z >900$ ) were seen in all examples studied, these were particularly evident in some samples such as the reaction of  $\text{Yb}\{\text{N}(\text{SiMe}_3)_2\}_3$  with  $[\mathbf{4}]\text{H}_2$ . None of these high mass peaks could be assigned to zwitterionic species where two amine-bis(phenol) molecules have coordinated to the metal center, analogous to those recently crystallographically characterized by Mountford and co-workers.<sup>2a</sup> We propose that the high mass peaks can be attributed to arene complexes formed *in situ* during the analysis, Table 1. Good matches of the theoretical and experimental isotope patterns (Figure 3) for the monometallic toluene species suggests that toluene, which co-crystallized with the samples during preparation, has become associated with the coordinatively unsaturated Ln metal center during mass spectrometric analysis. Previously, adduct formations have been observed by Fogg and co-workers in the spectra of coordinatively unsaturated two-coordinate Pd and Au complexes.<sup>4</sup> As large lanthanide metal centers have a tendency to form complexes with high-coordination numbers (6 to 12), perhaps it is not surprising that adducts are seen in all our spectra. In the solid-state, similar lanthanide complexes typically coordinate a Lewis basic solvent e.g. THF or DME to form 6 or 7 coordinate monomeric species.<sup>2i</sup> Additionally, the toluene adduct species are not observed in spectra obtained using a Nujol mull sample preparation method. We also propose that in our study,  $[\text{Ln}(\text{amine-phenolate})]^+$  species



formed *in situ* react in the gas phase within the ion source region with gaseous anthracene to yield bimetallic adducts through scavenging of neutral gas-phase anthracene molecules. This results in the appearance of a range of high  $m/z$  peaks in our experiments that have isotope patterns in agreement with bimetallic species. Large amounts of anthracene cations were observed in all mass spectra obtained during this study, for example see Figure 2. However, this region is not shown in most spectra as it generally does not provide any useful information. Therefore, although polyaromatic hydrocarbons such as anthracene are generally considered inert, they can affect the results obtained in MALDI-TOF analyses with metals that form stable arene adducts or are significantly coordinatively unsaturated.

(a)





**Figure 4.** Experimental and theoretical isotope patterns for toluene adduct peaks (a)  $[\text{Gd}(\mathbf{1})\text{N}(\text{SiMe}_3)_2 + \text{toluene} + \text{H}]^+$ , (b)  $[\text{Ho}(\mathbf{3})\text{N}(\text{SiMe}_3)_2 + \text{toluene}]^+$  and (c)  $[\text{Yb}(\mathbf{3})\text{N}(\text{SiMe}_3)_2 + \text{toluene}]^+$ .

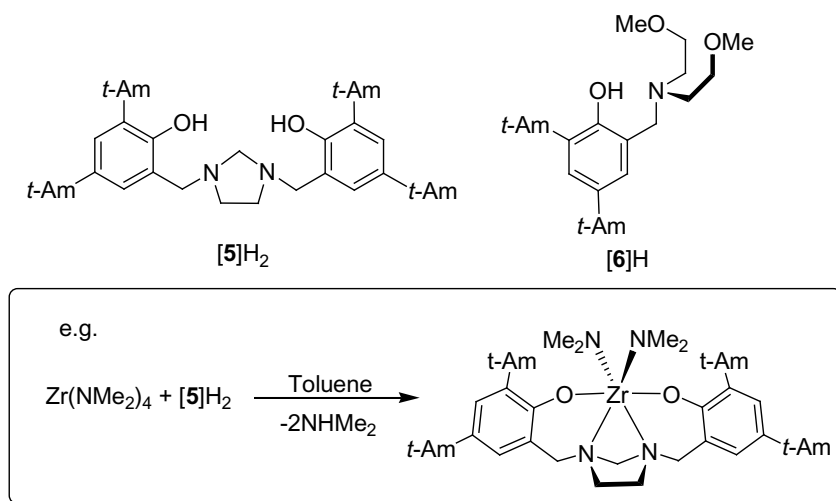
**Table 1.** Ln-arene adducts detected by MALDI-TOF MS.

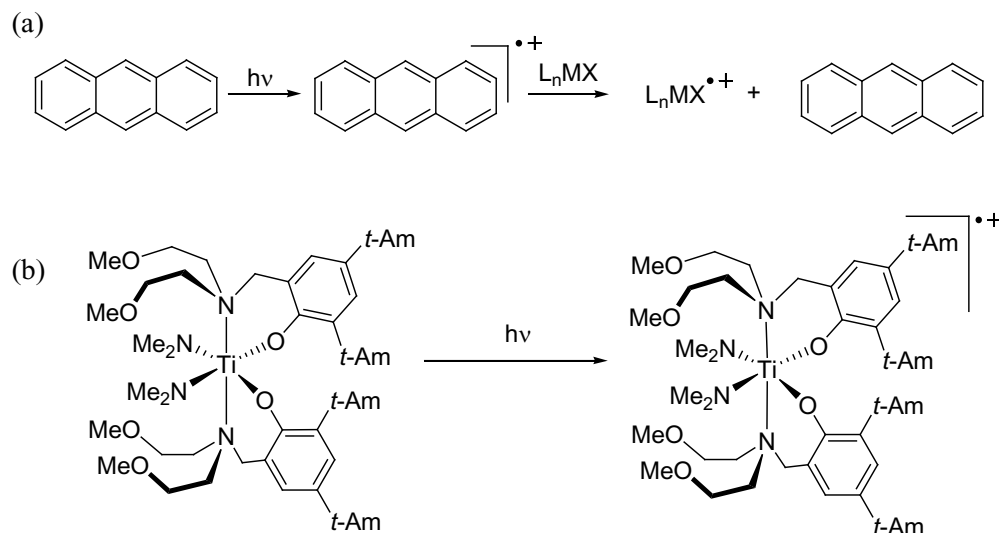
Ln	Ligand	$m/z$	Assignment
Gd	$[\mathbf{1}]^{2-}$	1298	$[\text{Gd}_2(\mathbf{1})_2 + \text{anthracene} - t\text{-Bu} - \text{Me}]^+$

Gd	[1] <sup>2-</sup>	1242	[Gd <sub>2</sub> (1) <sub>2</sub> + anthracene - 2 <i>t</i> -Bu - Me] <sup>+</sup>
Gd	[3] <sup>2-</sup>	932	[Gd(3)N(SiMe <sub>3</sub> ) <sub>2</sub> + toluene] <sup>+</sup>
Gd	[4] <sup>2-</sup>	1220	[Gd <sub>2</sub> (4) <sub>2</sub> + anthracene - 6 <i>t</i> -Am - 2H] <sup>+</sup>
Ho	[4] <sup>2-</sup>	1233	[Ho <sub>2</sub> (4) <sub>2</sub> + anthracene - 6 <i>t</i> -Am] <sup>+</sup>
Ho	[3] <sup>2-</sup>	940	[Ho(3)N(SiMe <sub>3</sub> ) <sub>2</sub> + toluene] <sup>+</sup>
Yb	[3] <sup>2-</sup>	948	[Yb(3)N(SiMe <sub>3</sub> ) <sub>2</sub> + toluene] <sup>+</sup>
Yb	[4] <sup>2-</sup>	1089	[Yb(4)N(SiMe <sub>3</sub> ) <sub>2</sub> + anthracene - H] <sup>+</sup>

The reactions of Ti(NMe<sub>2</sub>)<sub>4</sub> and [{Zr(NMe<sub>2</sub>)<sub>3</sub>(μ-NMe<sub>2</sub>)<sub>2</sub>}]<sub>2</sub>, referred to as Zr(NMe<sub>2</sub>)<sub>4</sub> from herein, were also studied using MALDI-TOF MS with similar substituted phenol ligands, Chart 2. The chemistry of these metals is related to the lanthanides in that the resulting species are reactive in a similar way (moisture sensitive, polymerization catalysts) and are usually dominated by their maximum oxidation state and therefore, exist as *d*<sup>0</sup> metal ions. However, in contrast to the lanthanides that can achieve coordination numbers of up to twelve, the coordination numbers of Zr and Ti are typically in the range of four to six. As described above, adduct formation was observed in the mass spectra of the lanthanide complexes and therefore, by studying metals that typically have lower coordination numbers, the mass spectra of their complexes may be less complicated and easier to interpret.

**Chart 2.** Amine-phenol ligands used in this study with Ti(NMe<sub>2</sub>)<sub>4</sub> and Zr(NMe<sub>2</sub>)<sub>4</sub> reagents





**Scheme 1** (a) Ionization by charge-transfer in MALDI-TOF mass spectrometry with arene matrices,<sup>4</sup> (b) Proposed direct ionization in LDI-TOF of Ti-phenolate complexes, the radical is likely delocalised on the phenolate ligand and the positive charge on the metal center.

Reactions were performed using group 4 amido complexes,  $Ti(NMe_2)_4$  and  $Zr(NMe_2)_4$ . As Zr has 5 stable isotopes ( $^{90}Zr$  to  $^{96}Zr$ ) and Ti has 5 stable isotopes ( $^{46}Ti$  to  $^{50}Ti$ ),<sup>6</sup> we reasoned useful information on metal:ligand formulations should be obtained.<sup>14</sup> Using a methodology similar to the lanthanide experiments, metal precursors and ligands were mixed in vials in a glove box and then analyzed. As in the spectra of ligands **1-4**, [**5**] $H_2$  and [**6**] $H$  afford spectra with relatively few peaks and the highest mass peak represents the molecular weight of the ligand,  $m/z$  563 and  $m/z$  379 respectively. As noted above, amine-bis(phenolate) ligands can be non-innocent and redox active. Therefore, charge-transfer may occur at the ligand rather than at the metal center under the MALDI and LDI conditions employed to yield phenoxy radical species. Indeed, this must be the ionization mechanism when spectra of the protonated ligands are obtained. The spectrum from the reaction mixture of  $Zr(NMe_2)_4$  and [**5**] $H_2$  showed a peak at  $m/z$  740 assigned to [**5**] $Zr(NMe_2)_2$  but additional peaks were also evident at higher  $m/z$ . These high mass peaks have been assigned to dimeric species and fragments on the basis of their  $m/z$  and isotope patterns. The  $^1H$  NMR spectrum of a white crystalline compound isolated through a preparative scale reaction suggests a formulation of [**5**] $_2Zr(NMe_2)_2$  for this compound. However, a

dimeric complex  $\{[\mathbf{5}]_2\text{Zr}(\text{NMe}_2)_2\}_2$  would also afford the same NMR spectrum in solution and *via* elemental analysis the monomer and dimer have the same empirical formulae. The mass spectrometric data suggest that  $\{[\mathbf{6}]_2\text{Zr}(\text{NMe}_2)_2\}_2$  is present (at least in the gas phase) and therefore, provides some practical information regarding this transamination reaction in the absence of crystallographic data. In contrast, the spectrum from the reaction mixture of  $\text{Ti}(\text{NMe}_2)_4$  and  $[\mathbf{5}]\text{H}_2$  did not exhibit any readily assignable peaks.  $^1\text{H}$  NMR spectra of a reaction mixture also failed to provide any interpretable data. This may be caused by the large bite angle and the rigid imidazolidine backbone of  $[\mathbf{5}]\text{H}_2$ . For the formation of monomeric species, this ligand is not compatible with the small ionic radius of  $\text{Ti}^{4+}$  as it cannot effectively chelate the metal center.

In all our mass spectrometric studies, metal reagents and ligands were reacted in an approximately 1:1 ratio. The spectrum from the reaction mixture of  $\text{Zr}(\text{NMe}_2)_4$  and  $[\mathbf{6}]\text{H}$  shows a peak at  $m/z$  600 assigned to  $[\mathbf{6}]\text{Zr}(\text{NMe}_2)_3$ , however, there is also evidence for  $[\mathbf{6}]_2\text{Zr}(\text{NMe}_2)_2$ ,  $m/z$  934 and the dimer  $\{[\mathbf{6}]_2\text{Zr}(\text{NMe}_2)_2\}_2$ ,  $m/z$  1869. Therefore, mass spectra of this reaction mixture suggest that a mixture of products formed and this is confirmed by the presence of two  $-\text{NMe}_2$  resonances in the  $^1\text{H}$  NMR spectrum of said reaction mixture. In contrast, the spectrum from the reaction mixture of  $\text{Ti}(\text{NMe}_2)_4$  and  $[\mathbf{6}]\text{H}$  did not show a peak for  $[\mathbf{6}]\text{Ti}(\text{NMe}_2)_3$  but fragments assignable to a parent species containing two  $[\mathbf{6}]$  ligands,  $[\mathbf{6}]_2\text{Ti}(\text{NMe}_2)_2$ , were observed. Interestingly, a better signal-to-noise ratio was achieved when no matrix was used in these experiments. It is worth noting that no high mass peaks were observed in this spectrum and, therefore, as would be expected for the smaller Ti metal center, no dimeric species were formed. To confirm the interpretation of this spectrum, a reaction of  $[\mathbf{6}]\text{H}$  and  $\text{Ti}(\text{NMe}_2)_4$  was performed on a preparative scale. Although, the metal precursor and ligand were mixed in a 1:1 mole ratio, the complex  $[\mathbf{6}]_2\text{Ti}(\text{NMe}_2)_2$  was formed exclusively and in quantitative yield with respect to  $[\mathbf{6}]\text{H}$  as evidenced by  $^1\text{H}$  NMR spectroscopy and elemental analysis.

In this preliminary study, we have shown that ligand coordination reactions of moisture-sensitive lanthanide reagents can be screened using MALDI-TOF MS and this approach could be extended to the characterization of other water-sensitive paramagnetic complexes.<sup>11</sup> These preliminary reactions were

performed on a sub-fifty millimolar scale and thereby consumption of metal precursors, ligands and solvents was reduced. Therefore, such approaches will become especially valuable as chemists develop more sustainable approaches to chemical research. Using ‘conventional’ techniques for paramagnetic complexes e.g. X-ray crystallography and magnetic measurements, data are difficult or impossible to obtain on such a scale. Intriguingly, arene adducts of lanthanide metals were observed and formed *in-situ* during the MS experiment, but this could be avoided if samples were prepared as Nujol mulls rather than using the dried drop method from toluene solution. The technique also provides insight into ligand compatibility and metal complex nuclearity when significant differences in ion size exist (Zr<sup>4+</sup> cf. Ti<sup>4+</sup>). The chemistry of imidazolidine bridged bis(phenol) ligands is relatively unexplored,<sup>15</sup> but these initial studies show that such a sterically demanding and rigid ligand is not compatible with metals possessing a small ionic radius. Furthermore, dimeric dimethylamido bridged Zr species are observed using MALDI-TOF MS and can be distinguished from their corresponding monomers. Although these initial studies are promising, a more thorough study is required in order to ascertain the generality of this method and results, therefore, experiments are ongoing in this regard. For example, the chemistry of redox active lanthanide complexes (Sm<sup>+2/+3</sup>, Ce<sup>+3/+4</sup>) and the spectra of species with ‘innocent’ ligands need to be investigated. Also, tandem MS-MS data may provide further evidence for the *in situ* formation of Ln-arene adducts.

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**Supporting Information Available:** Full details of experimental procedures, characterization data and mass spectrometric analyses. This material is available free of charge *via* the Internet at

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9 In general, spectra presented in this communication are shown without the low  $m/z$  region displayed so these matrix ions (anthracene,  $m/z$  178) are not shown.

10 In all spectra, clusters of peaks were seen at each mass that represent the natural isotopic abundances of the elements in a particular compound or fragment. Therefore, where ‘peak’ is mentioned in this paper, this corresponds to the envelope of peaks that represent all isotopes present in the compound and the  $m/z$  of each peak represents the most intense peak within the polyisotopic group.

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12 A toluene solution of  $\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_3$  (approx. 3  $\mu\text{mol}$ ) was added to a vial containing a solution of ligand (approx. 4.5  $\mu\text{mol}$ ) and stirred overnight. From the reaction mixture, a sample for MALDI-TOF analysis was prepared using an anthracene matrix and the dried droplet method. On the same analysis plate (10  $\times$  10 spots available) and using the same matrix, samples of the lanthanide reagent alone and the ligand alone were also prepared. The spectra of all samples were recorded in linear and reflectron positive modes but, as expected, reflectron mode gave cleaner, more easily interpretable spectra. Lanthanide tris(bis(trimethylsilyl)amido) complexes are volatile.<sup>6a</sup> Sublimation temperatures are in the range 70-90 °C at  $10^{-4}$  Torr. In the spectrometer used here, the sample plate is subjected to a vacuum of  $10^{-8}$  Torr or greater and therefore, a lack of signal in spectral of the lanthanide reagents is likely due to their volatility in the MS chamber prior to laser ablation and analysis.

13 Performing electrospray mass spectrometry on such species would be difficult because they would be particular sensitive to contaminants in the tubing.

14 It should be noted that polyisotopic elements are not essential to the success of this technique in characterizing such species, however, a fingerprint isotope pattern is often helpful for definitive assignments.

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## A Study of Ligand Coordination at Lanthanide and Group 4 Metal Centers by MALDI-TOF Mass Spectrometry

Nduka Ikpo, Samantha M. Butt, Kayla L. Collins and Francesca M. Kerton

MALDI-TOF MS rapidly confirms the coordination of amine-phenolate ligands to lanthanides, Ti and Zr. Arene-lanthanide species are formed *in situ*. Direct Laser Desorption Ionization (LDI-TOF) is possible with some Ti species.

