Synthesis and Characterization of Heterobimetallic Organolanthanide Complexes Bearing Aryloxide-N-Heterocyclic Carbene Ligands

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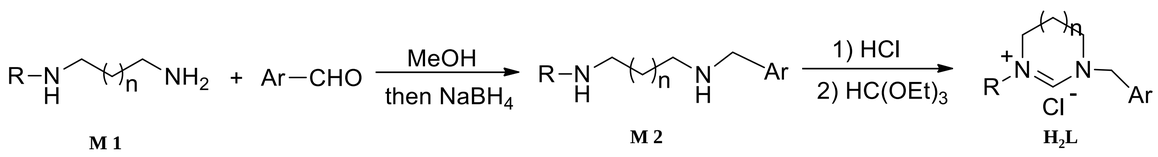
Abstract

A series of unsymmetrical o-hydroxyaryl imidazolinium proligands were synthesized. Four kinds of heterobimetallic organolanthanide complexes supporting by N-(2,4,6- trimethylaniline)-N'-(2-hydroxynaphenylmethyl)imidazolinium chloride (H_2L1) and N-(2,4,6- trimethylaniline)-N'-(2-hydroxyphenylmethyl)imidazolinium chloride (H_2L2) were prepared. Their structure were characterized by ^1H NMR and X-ray diffration. These heterobimetallic organolanthanide complexes show high activity for the ring-opening polymerization of ε- caprolactone.

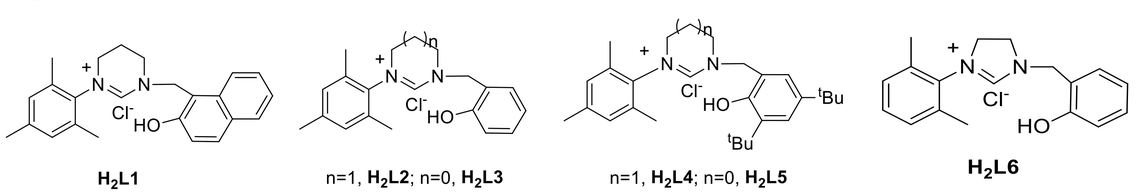
Synthesis of o-Hydroxyaryl Imidazolinium Proligands



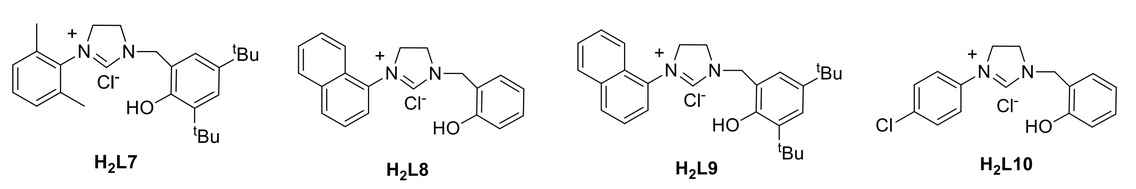
M 1 M 2 H_2L

Scheme 1. Synthesis of o-Hydroxyaryl Imidazolinium Proligands.

In this work, we develop an efficient method to synthesis the o-hydroxyaryl imidazolinium proligands depicted in scheme 1. The N-monoarylated 1,2-diamin or 1,3-diamin M1 were prepared according to the literature procedure,[1] which was condenced with aldehyde Ar-CHO generating an inamine intermediate. Then $NaBH_4$ was added to yield the unsymmetrical disubstituted 1,2-diamine or 1,3-diamine M2. After concentrated HCl was added to a stirred solution of M2,the solvent was then evaporated under reduced pressure after 30min, leaving a white solid in the flask. Subsequent cyclization using $HC(OEt)_3$ and a few drops of HCOOH provided the desired unsymmetrical o-hydroxyaryl imidazolinium proligands H_2L. What's more, we also tried different R and Ar substituent to obtain a series of proligands H_2L(Scheme 2) according to procedures in scheme 1.



H_2L1 n=1, H_2L2; n=0, H_2L3 n=1, H_2L4; n=0, H_2L5 H_2L6

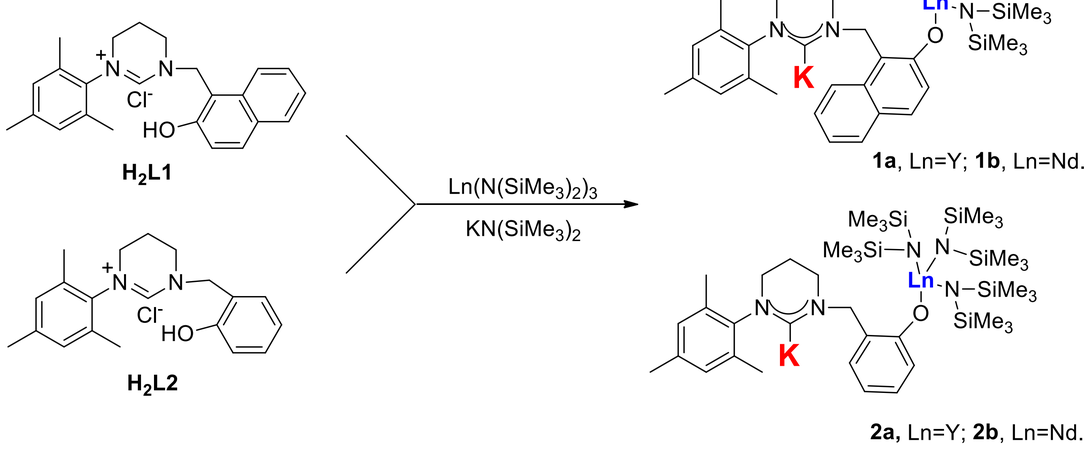


H_2L7 H_2L8 H_2L9 H_2L10

Scheme 2. Structures of o-Hydroxyaryl Imidazolinium Proligands.

Synthesis of Organolanthanide Complexes

The family of N-heterocyclic carbene rare earth-metal complexes is expanding rapidly rely on a diverse range of NHC-based ligands.[2] However, the potassium NHC complexes are still relatively rare.[3] Herein we report an simple and efficent way to obtain of heterobimetallic organolanthanide complexes containing potassium NHC and rare earth amide (Scheme 3), and the o-hydroxyaryl imidazolinium ligands are appropriate to this reaction.



H_2L1 **1a**, Ln=Y; **1b**, Ln=Nd. H_2L2 **2a,** Ln=Y; **2b**, Ln=Nd.

Scheme 3. Synthesis of heterobimetallic organolanthanide complexes.

A stirred solution of H_2L1 in toluene was treated with 1 equiv. of $Ln[N(SiMe_3)_2]_3$ and 2 equiv. of $KN(SiMe_3)_2$. The reaction mixture was stirred overnight at room temperature. Crystals were grown from a hexane/toluene solvent mixture at -20˚C in 2-3 days. Complex 1a could be synthesized by treating H_2L1 with $Y[N(SiMe_3)_2]_3$, however reactions of H_2L1 and $Nd[N(SiMe_3)_2]_3$ to yield complex 1b. Complexes 2a and 2b was synthesized similarly by replacing H_2L2 with H_2L1, and we also obtained the corresponding crystal of complex 2a with yttrium and 2b with neodymium.

These heterobimetallic organolanthanide complexes are active for the ring-opening polymerization of ε-caprolactone. Complex 1b has been used to initiate the polymerization of ε-caprolactone in toluene at 25˚C, reaching PCL with a number average molecular weight of 177000 and M_w/M_n of 1.32. It seems that these complexes have potential to yield PCL with high molecular weight and moderate molecular weight distribution. A detailed investigation of the catalytic performance of these complexes is in process.

Characterization

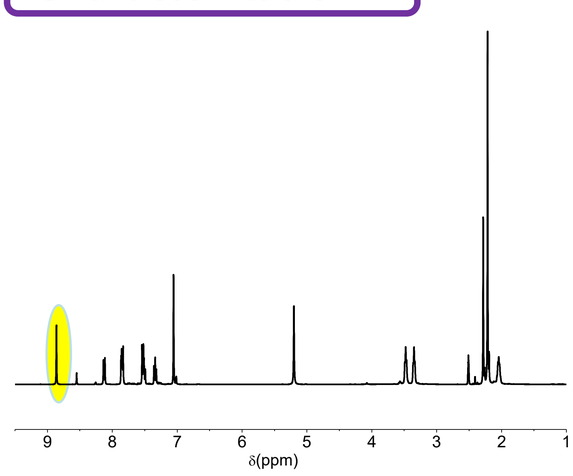


Figure 1. ^1H NMR spectrum of proligand **H_2L1** in DMSO.

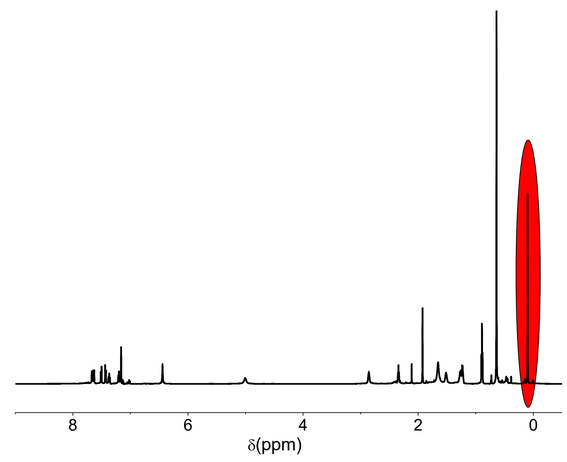


Figure 2. ^1H NMR spectrum of complex **1a** in C_6D_6.

As shown in Figure 1, the ylidene proton NHC-H displayed a typical singlet resonance in the downfield region, δ 8.67, which disappeared in^1H NMR spectrum of complex 1a showed in Figure 2. Otherwise, the signal appearing in upfiled region, δ 0.64/δ 0.1, indicating the formation of heterobimetallic organolanthanide complex 1a.

X-ray structure of complexes were obtained as well showed in Figure 3-6. These complexes had a solvated monomeric structure. Potassium NHC and rare earth tri(amide) could be found in all structures.

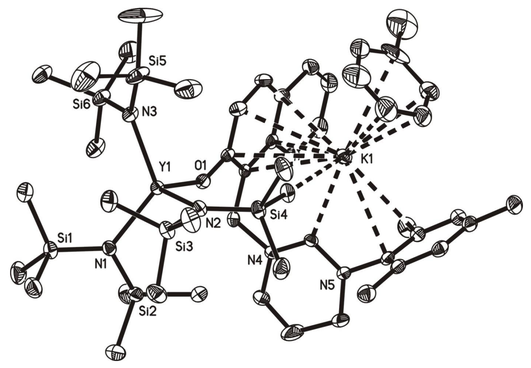


Figure 3. X-ray structure of complex **1a**, with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

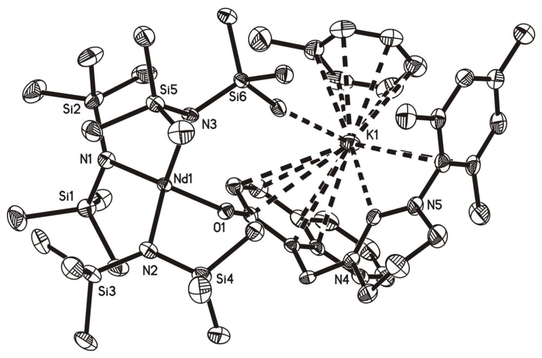


Figure 4. X-ray structure of complex**1b**, with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

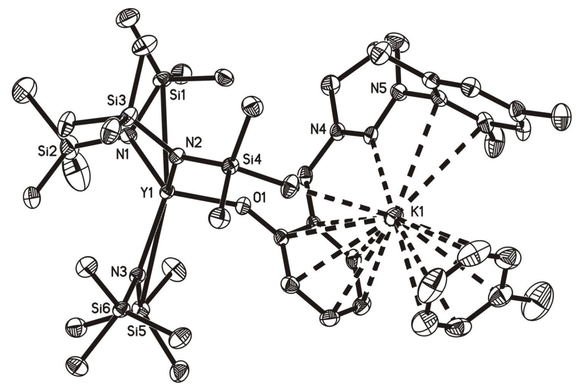


Figure 5. X-ray structure of complex **2a**, with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

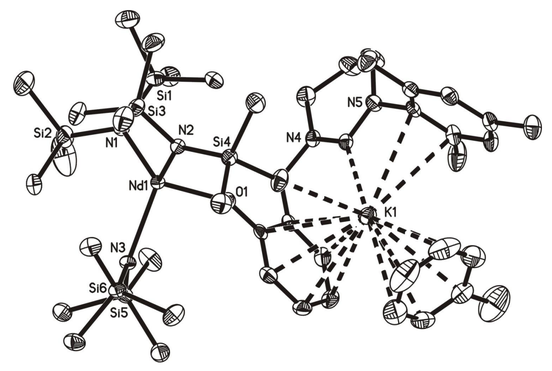


Figure 6. X-ray structure of complex **2b**, with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Conclusions

1. An efficient method was developed to synthesis the o-hydroxyaryl imidazolinium proligands. A series of unsymmetrical o-hydroxyaryl imidazolinium proligands were synthesized and determined by ^1H NMR and ^{13}C NMR.
2. Four kinds of heterobimetallic organolanthanide complexes containing potassium NHC and rare earth amide were obtained, and their sructure were characterized by ^1H NMR and X-ray diffration.
3. These heterobimetallic organolanthanide complexes show high activity for polymerization of ε-caprolactone.

References & Acknowledgments

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2. M. Zhang, X. Ni and Z. Shen, *Organometallics*.**2014**, 33, 6861.
3. P. L. Arnold, M. Rodden and C. Wilson, *Chem. Commun*.**2005**,13, 1743.

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