



Synthesis and Characterization of N-Heterocyclic Carbene Bis(phenolate) Lanthanide Complexes and Their Applications in Ring-opening Polymerization of L-Lactide

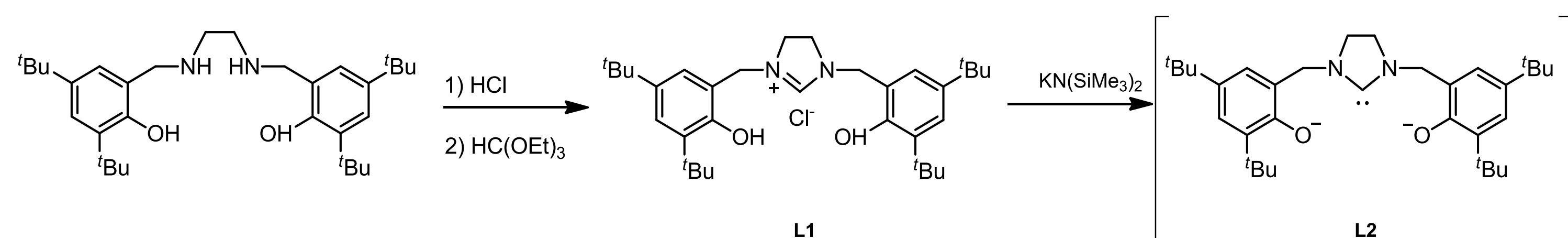
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Abstract

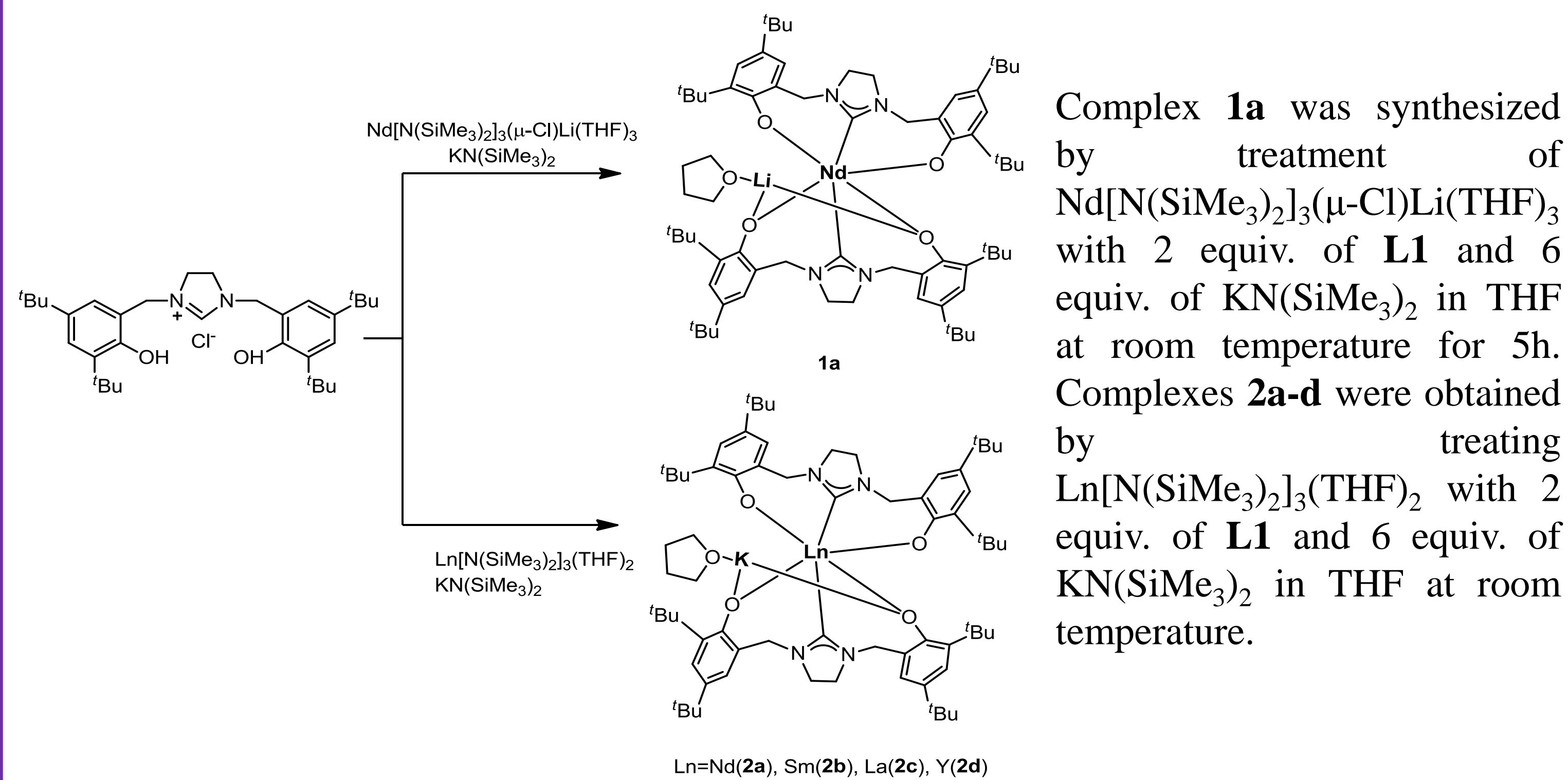
A series of bis(phenolate) lanthanide complexes supported by 1,3-bis[O-4,6-di-*t*-Bu-C₆H₂-2-CH₂][CH(NCH₂CH₂N)]⁺Cl⁻ (**L1**) and 1,3-bis[O-4,6-di-*t*-Bu-C₆H₂-2-CH₂][C(NCH₂CH₂N)] (**L2**) were prepared and applied in the polymerization of L-lactide. Results showed that N-heterocyclic carbene (NHC) complexes (**1a**, **2a-d**) had good to high activity while imidazolium-bridged lanthanide complexes (**3a-c**) had no activity towards L-lactide polymerization.

Synthesis



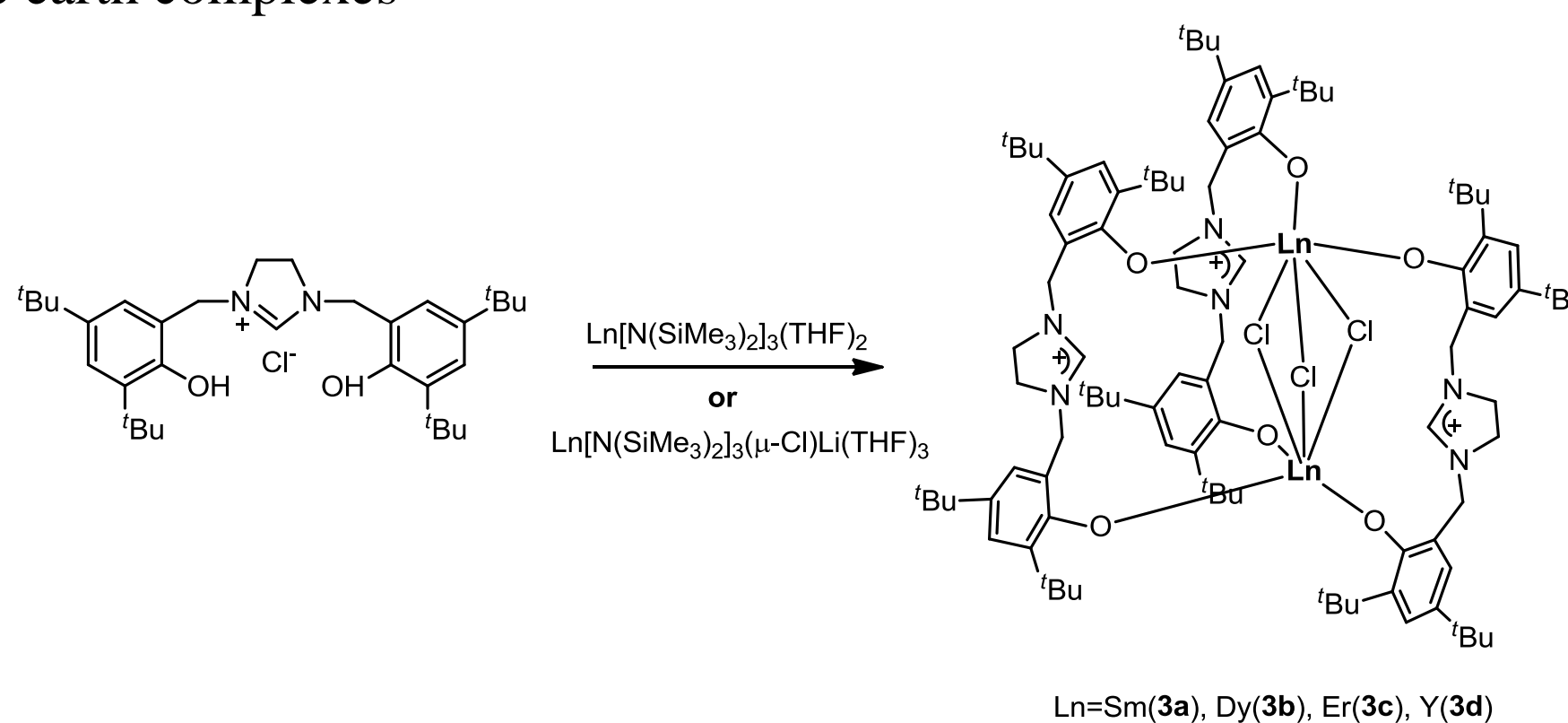
Scheme 1 Synthesis of ligands

The ligands used in this work were prepared according to the general pathway^[1] depicted in Scheme 1. N,N'-bis(3,5-di-*tert*-butyl-2-hydroxyphenylmethyl)imidazolium chloride (**L1**) was obtained as a N-Heterocyclic carbene precursor. NHC ligand **L2** was obtained *in situ* by treatment **L1** with KN(SiMe₃)₂ for deprotonation.



Scheme Synthesis of NHC bis(phenolate) rare earth complexes

Complexes **3a-c** could be synthesized by treating **L1** with Ln[N(SiMe₃)₂]₃(THF)₂ or with Ln[N(SiMe₃)₂]₃(μ-Cl)Li(THF)₃ in THF at room temperature for 5h. Most likely, the structures of complexes **3a-c** were isotypical, forming non-NHC structures.



Scheme 3 Synthesis of imidazolium-bridged bis(phenolate) rare earth complexes

Characterization

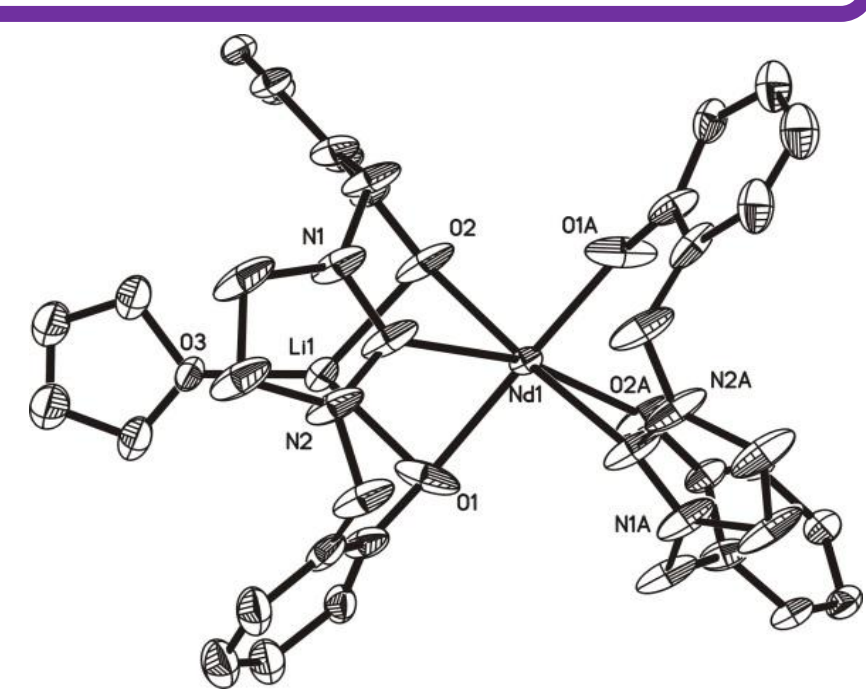


Figure 1. X-ray structure of complex **1a**, with 30% probability thermal ellipsoids. Hydrogen atoms and *t*-butyl groups are omitted for clarity.

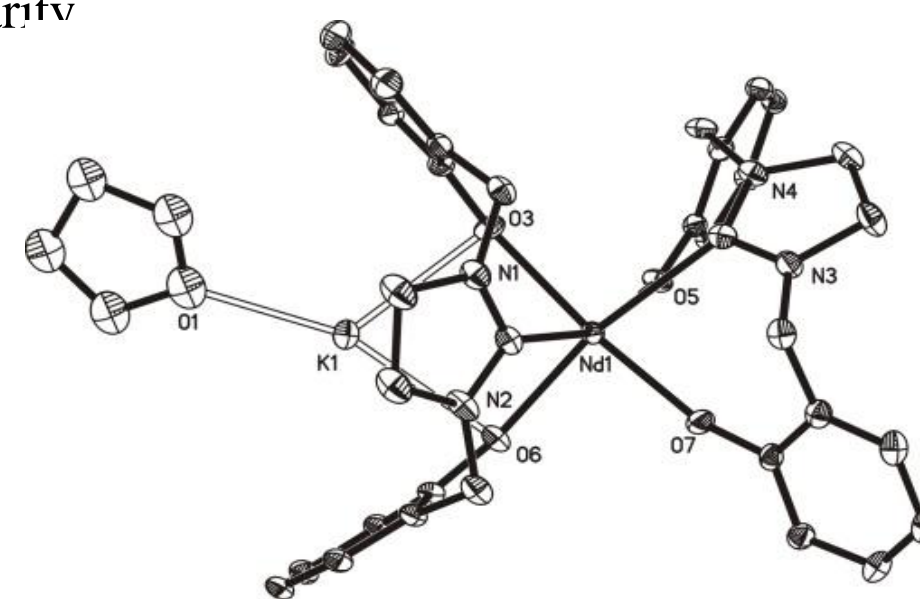


Figure 2. X-ray structure of complex **2a**, with 30% probability thermal ellipsoids. Hydrogen atoms and *t*-butyl groups are omitted for clarity.

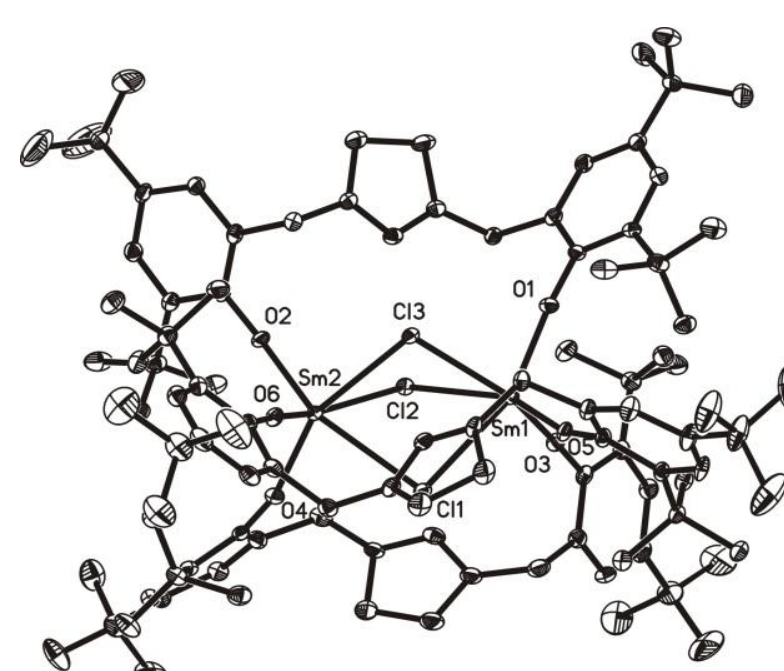


Figure 3. X-ray structure of complex **3a**, with 30% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

In Figure 1, the ligand adopted a tridentate coordination mode. The geometry at the metal center could be best described as trigonal antiprism with two oxygen atoms and one C_{carbene} on one planar. In structure, **2a** differentiated **1a** in alkali metal. The structures of complexes **2a** and **2c** were isotypical.

As shown in Figure 3, each ligand coordinated to the metal center in a bidentate mode, and the two samarium atoms were bridged by three chlorines. The geometry at the metal center could be best described as trigonal antiprism. The structures of complexes **3a-c** were isotypical.

Ring-opening polymerization of L-Lactide

Table 1. Polymerization of L-Lactide by Complexes **1a**, **2a-d**

Entry	Initiator	[M] ₀ /[I] ₀	t(min)	Yield(%) ^b	M _n ^c (×10 ⁴)	M _n ^{theor} (×10 ⁴)	PDI
1	1a	1:1000	5	35	0.7	5.0	1.19
2	1a	1:1000	30	90	1.7	13.0	1.33
3	1a	1:1000	1 h	92	1.8	13.3	1.38
4 ^d	1a	1:1000	30	40	0.7	5.8	1.18
5	1a	1:1500	1h	86	2.1	18.6	1.41
6	1a	1:2000	2 h	61	2.1	17.6	1.40
7	2a	1:1000	5	80	1.3	11.5	1.31
8	2a	1:1000	30	93	1.7	13.4	1.57
9 ^d	2a	1:1000	1 h	50	0.8	7.1	1.34
10	2a	1:2000	2 h	80	1.5	23.0	1.25
11	2b	1:1000	30	69	1.4	10.0	1.32
12	2c	1:1000	5	57	1.0	8.14	1.43
13	2d	1:1000	1 h	67	1.3	9.7	1.44

^aGeneral polymerization conditions: toluene as the solvent, [L-LA]= 1 mol/L. ^bYield: weight of polymer obtained/weight of monomer used. ^cMeasured by GPC relative to polystyrene standards with Mark-Houwink factor of 0.58. ^dIn THF.

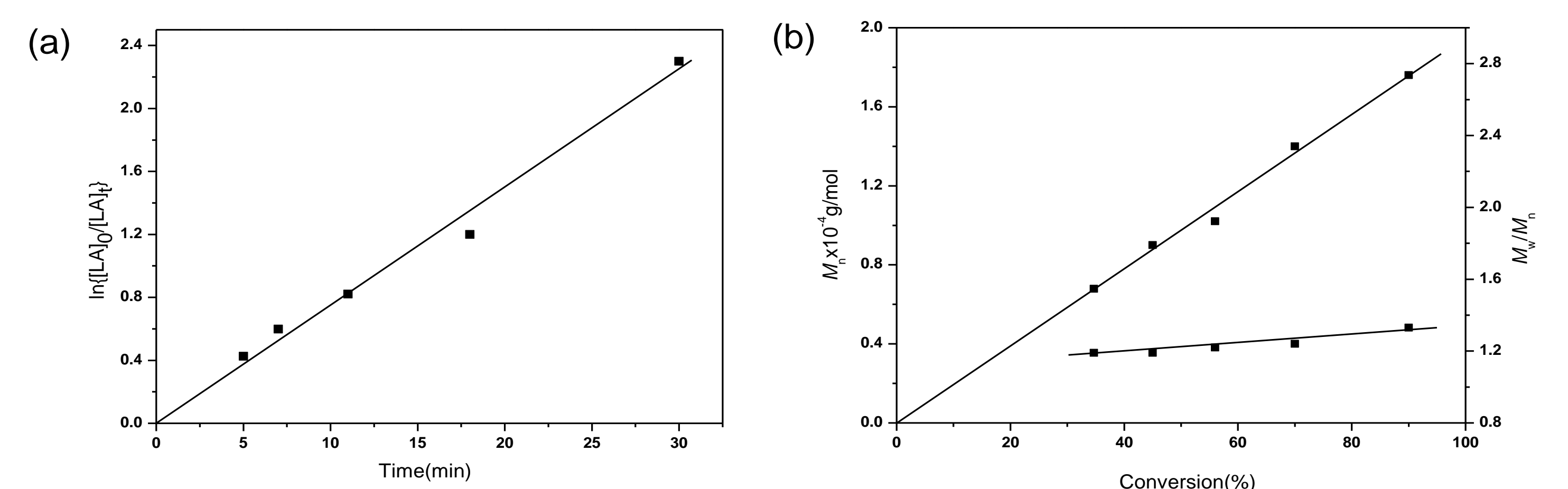


Figure 4. (a) Semilogarithmic plot of L-LA conversion versus time using complex **1a** as the initiator (linear fit, R=0.987); (b) M_n versus L-LA conversion using complex **1a** as the initiator (linear fit, R=0.985). Conditions: toluene, 70 °C, [LA]₀/[Ln]₀=1000 and [LA]₀ = 1 M.

Polymerization of L-lactide was carried out and polymerization data was collected in Table 1. NHC bis(phenolate) complexes (**1a**, **2a-d**) showed good to high activity towards the polymerization of L-lactide. In comparison, imidazolium-bridged bis(phenolate) lanthanide complexes (**3a-c**) had no activity towards the polymerization of L-lactide. The NHC moiety was found to involve in the initiation of the ROP of L-LA, by way of abstracting the methine hydrogen of L-LA, and a coordination-insertion polymerization mechanism was suggested. The reason for the difference in activity of complex **1a** and **2a** might attribute to the difference in electronic configurations and charge density of lithium and potassium cations as well as their steric effect. Figure 4 indicated that the polymerization in this system occurred in a controllable fashion.

Conclusions

1. A series of NHC bis(phenolate) complexes and imidazolium-bridged bis(phenolate) complexes were synthesized and their structural features had been determined by X-ray diffraction and NMR analysis.
2. The activity of the complexes was evaluated in the ring-opening polymerization of L-lactide. Bis(phenolate) N-heterocyclic carbene complexes were highly efficient initiators for L-lactide polymerization while imidazolium-bridged bis(phenolate) complexes showed no activity.

References & Acknowledgments

1. Min, K. S.; Weyhermüller, T.; Bothe, E.; Wieghardt, K., *Inorganic Chemistry* **2004**, 43, 2922-2931.

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