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

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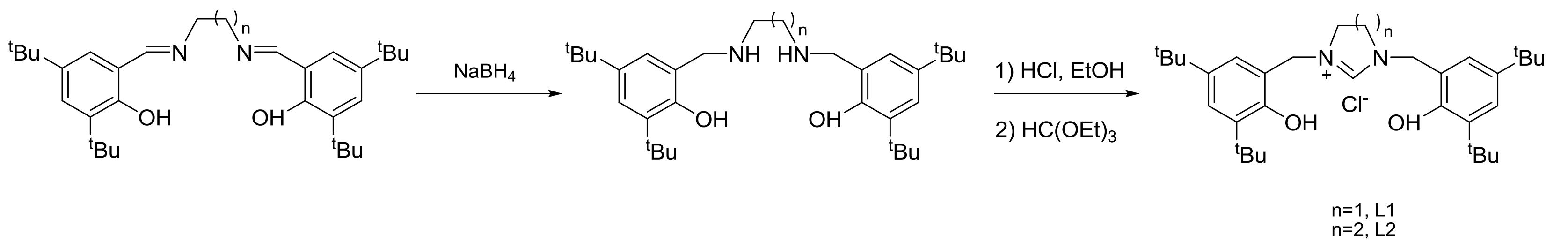
Abstract

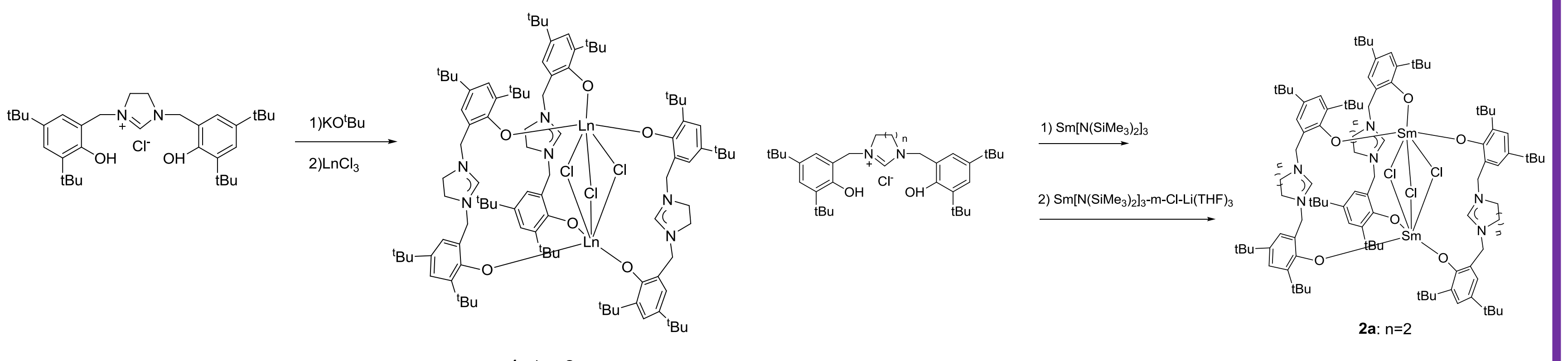
A series of bisphenolate lanthanide complexes supported by N,N'-bis(3,5-di-tert-butyl-2-hydroxyphenylmethyl)imidazolinium chloride (L1) and N,N'-bis(3,5-di-tert-butyl-2-hydroxyphenylmethyl)tetrahydro-pyrimidinium chloride (L2) were prepared and applied in the polymerization of L-Lactide. Results show that tricloride bridged lanthanide complexes (**1a-c**, **2a**) have no activity towards polymerization while N-heterocyclic carbene (NHC) complexes show high activity.

Synthesis



Scheme 1

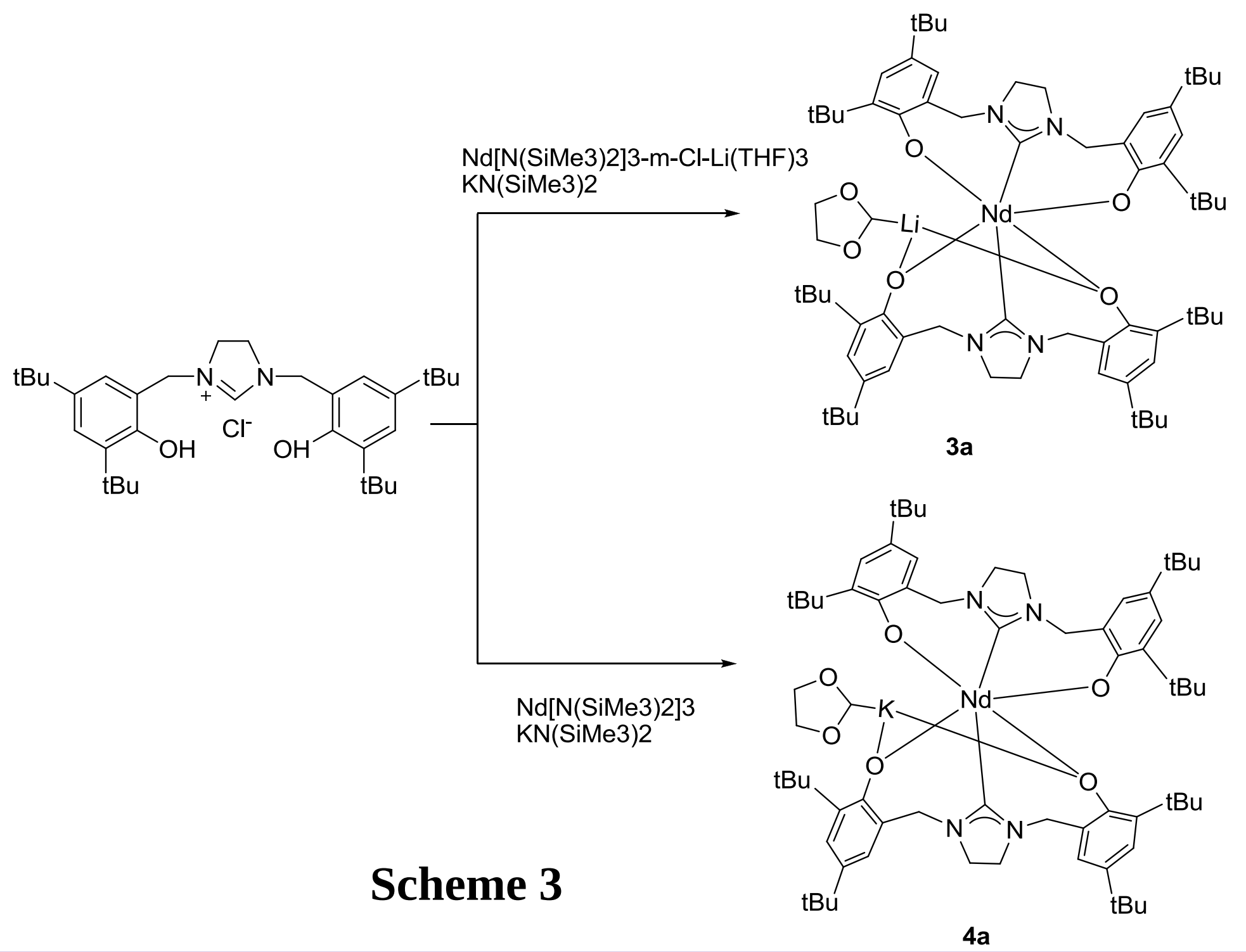
The ligands used in this work were prepared according to the general pathway[1] depicted in Scheme 1. N,N'-bis(3,5-di-tert-butyl-2-hydroxyphenylmethyl)imidazolinium chloride (L1) was obtained as a N-Heterocyclic carbene precursor, and N,N'-bis(3,5-di-tert-butyl-2-hydroxyphenylmethyl)tetrahydro- pyrimidinium chloride (L2) was obtained similarly.



1a: Ln= Sm
1b: Ln= Dy
1c: Ln= Er

Scheme 2

L1 was treated with 3 equiv. of KO^{t}Bu at ambient temperature for 2h, and subsequently treated with 2 equiv. of $LnCl_3$ at 70°C to give the product in a high yield. Most likely, the structures of complex **1a-c** are isotypical, forming non-NHC structures. Complexes **1a** could be synthesized by treating L1 with $Sm[N(SiMe_3)_2]_3$ or with $Sm[N(SiMe_3)_2]_3$-μ-Cl-$Li(THF)_3$. Complex **2a** was synthesized similarly by replacing L2 with L1.



Scheme 3

Complex **3a** was synthesized by treatment of $Nd[N(SiMe_3)_2]_3$-μ-Cl-$Li(THF)_3$ with 2 equiv. of L3 and 6 equiv. of $KN(SiMe_3)_2$ in THF at room temperature for 5h. Complex **4a** was obtained by treating $Nd[N(SiMe_3)_2]_3$ with 2 equiv. of L3 and 6 equiv. of $KN(SiMe_3)_2$ in THF at room temperature.

Characterization

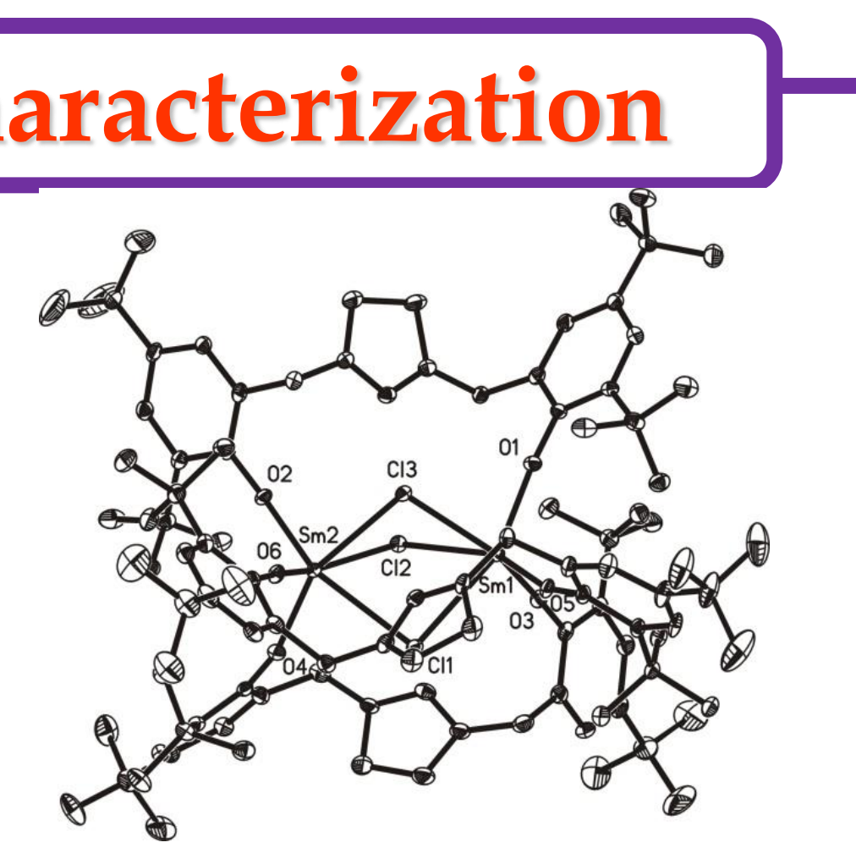


Figure 1. X-ray structure of complex **1a**, with 35% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

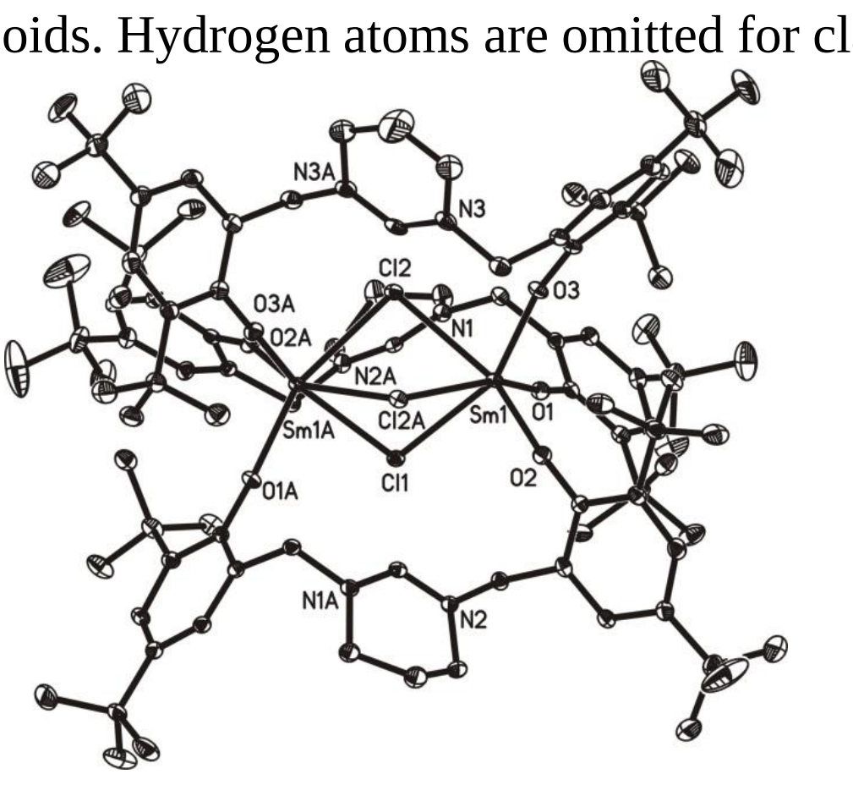


Figure 2. X-ray structure of complex **2a**, with 35% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

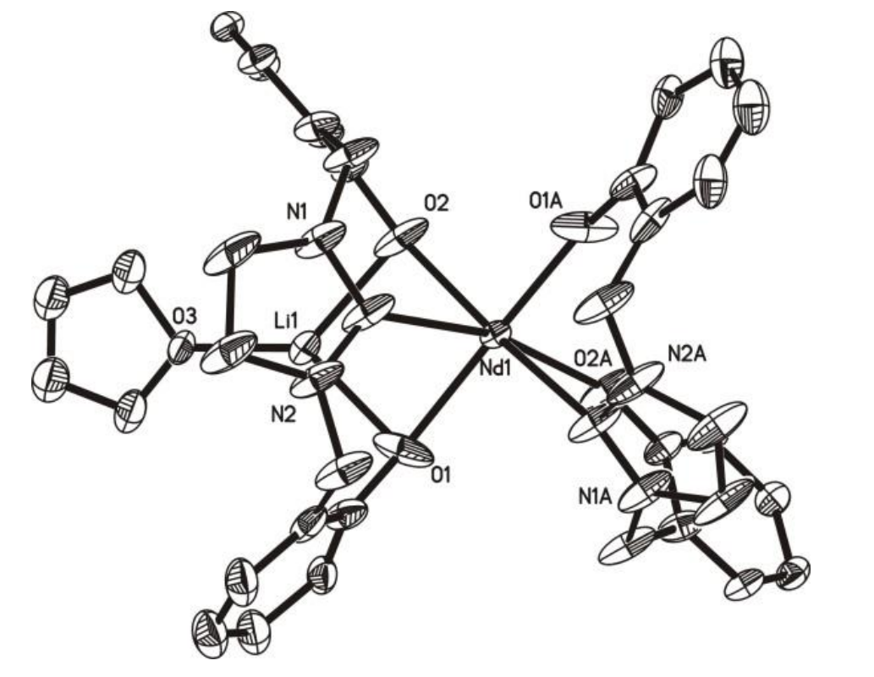


Figure 3. X-ray structure of complex **3a**, with 35% probability thermal ellipsoids. Hydrogen atoms and t-butyl groups are omitted for clarity.

As shown in Figure 1, each ligand coordinates to the metal centers in a bidentate mode, and the two samarium atoms are bridged by three chlorines. The geometry at the metal center can be best described as trigonal antiprism. The structures of complex **1a-c** are isotypical.

Complex **2a** has a almost similar strucure with **1a**, but with a more contact structure.

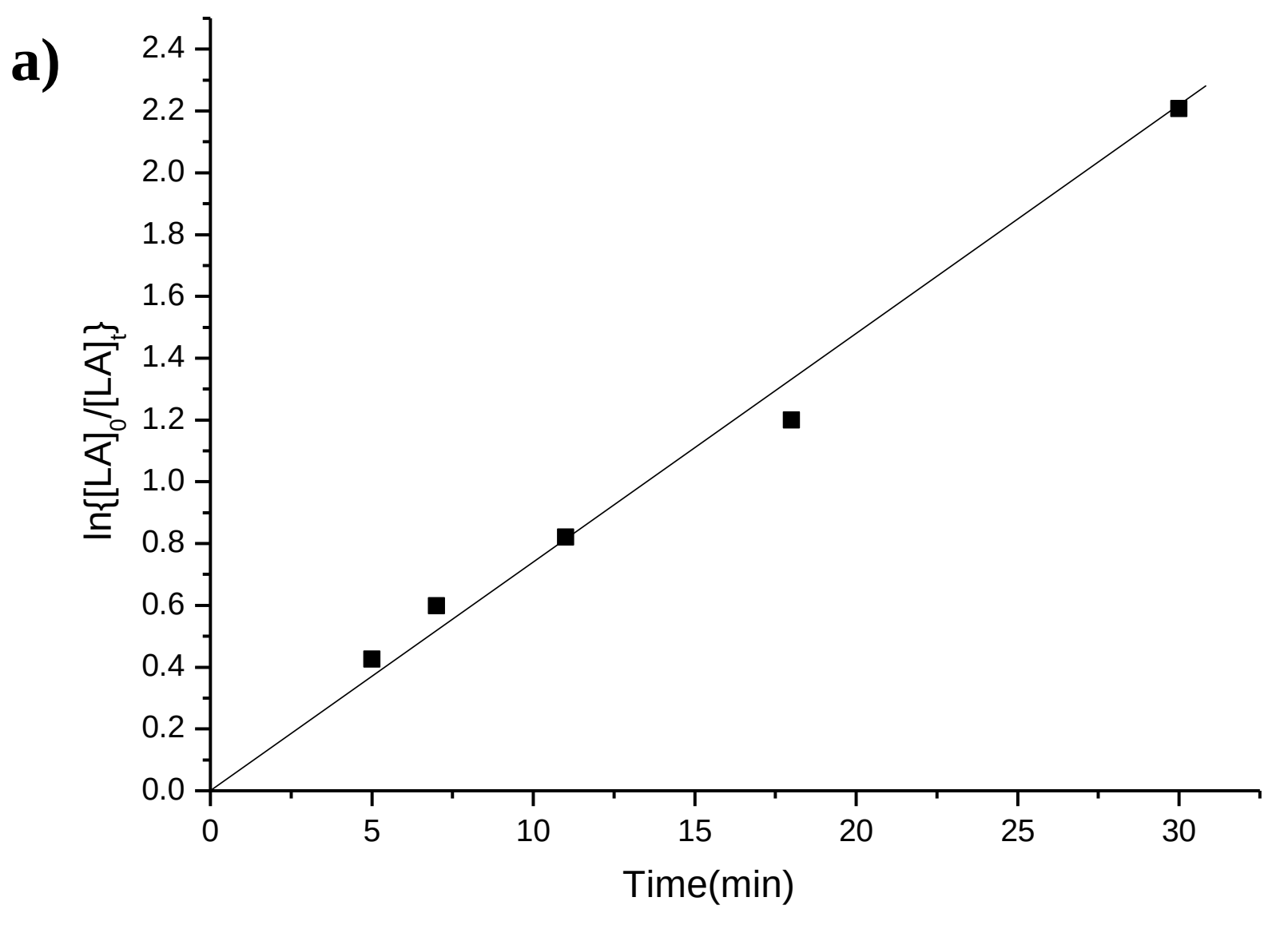
In Figure 3, the ligand adopts a tridentate coordination mode. Unlike a bridging 5-membered imidazolinium, hydrogen atom on the imidazolium ring was deprotonated by $KN(SiMe_3)_2$ thus forming a N-Heterocyclic Carbene structure. The geometry at the metal center can be best described as trigonal antiprism with two oxygen atoms and one $C_{carbene}$ on one planar.

Ring-opening polymerization of L-Lactide

Table 1. Polymerization of L-Lactide by Complexes 3a-4a

Entry	Initiator	$[M]_0/[I]_0$	T(°C)	t(min)	Yield(%)[b]	M_n^c(×10^4)	PDI
1	**3a**	1:500	25	30	73	1.3	1.44
2	**3a**	1:500	50	30	80	1.8	1.54
3	**3a**	1:500	70	30	94	1.5	1.54
4	**3a**	1:1000	70	5	35	0.7	1.19
5	**3a**	1:1000	70	7	45	0.9	1.19
6	**3a**	1:1000	70	11	56	1.0	1.22
7	**3a**	1:1000	70	18	70	1.4	1.24
8	**3a**	1:1000	70	30	89	1.7	1.10
9	**3a**	1:1000	70	1 h	92	1.8	1.38
10[d]	**3a**	1:1000	70	30	40	0.7	1.18
11	**3a**	1:2000	70	2 h	61	2.1	1.40
12	**4a**	1:1000	70	5	80	1.3	1.31
13	**4a**	1:1000	70	20	90	1.6	1.52
14	**4a**	1:1000	70	30	93	1.7	1.57
15[d]	**4a**	1:1000	70	1 h	50	0.7	1.34
16	**4a**	1:2000	70	2 h	80	1.5	1.25

[a]General polymerization conditions: toluene as the solvent, [L-LA]= 1 mol/L. [b]Yield: weight of polymer obtained/weight of monomer used. [c]Measured by GPC relative to polystyrene standards with Mark-Houwink factor of 0.58. [d]In THF.



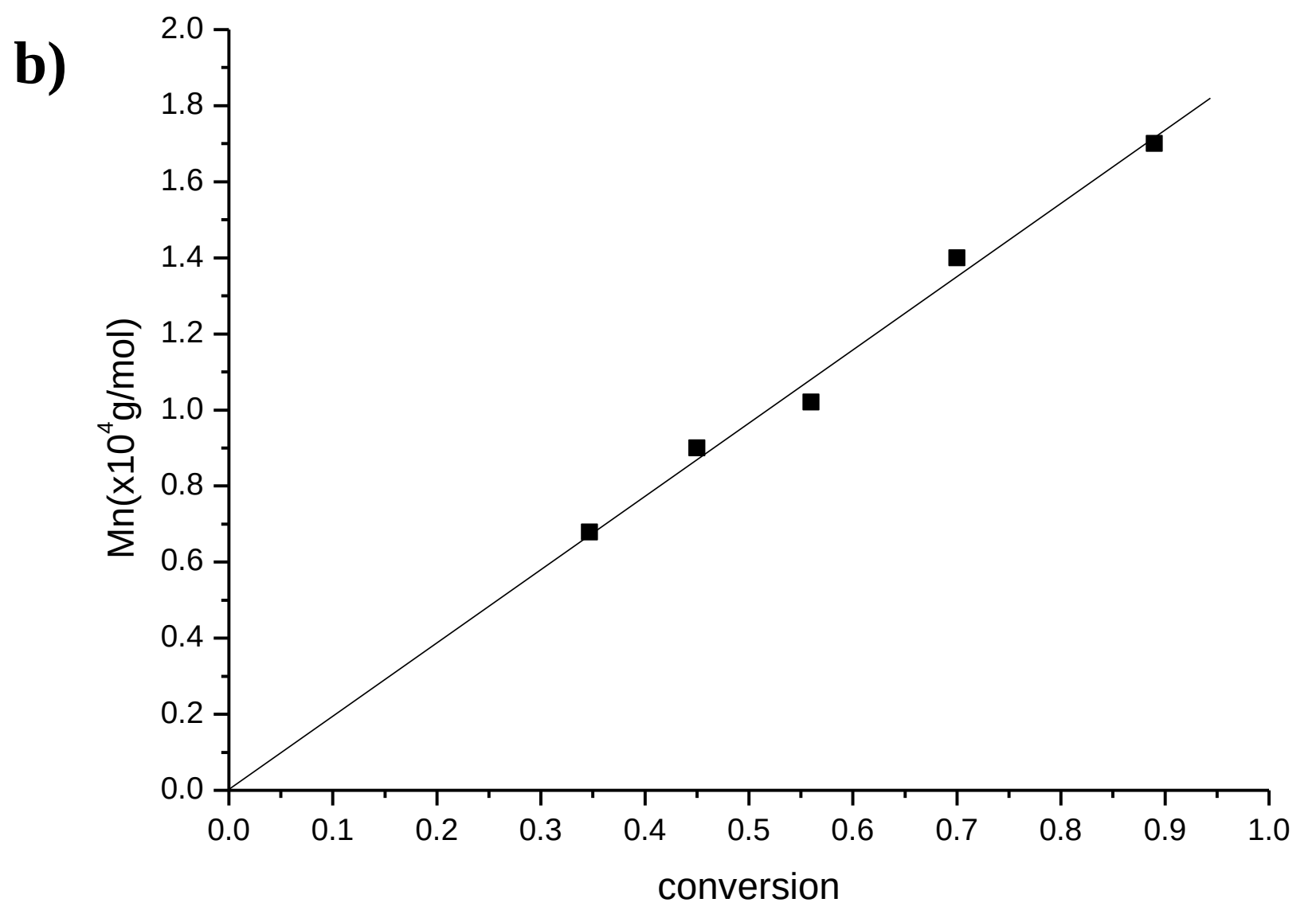


Figure 4. (a) Semilogarithmic plot of L-LA conversion versus time using complex **3a** as the initiator (linear fit, R=0.987); (b) Mn versus L-LA conversion using complex **3a** as the initiator (linear fit, R=0.985). Conditions: toluene, 70 °C, $[LA]_0$ /$[Ln]_0$=1000 and $[LA]_0$ = 1 M.

Polylactide is one of the most desirable biodegradable polymers, and it has received great attention for their biodegradability as well as their practical applications[2]. Polymerization of L-Lactide was carried out and polymerization data was collected in Table 1. Tricloride bridged bis(phenolate) lanthanide complexes (**1a-c**, **2a**) barely show activity towards the polymerization of L-Lactide and it might due to the nature of compact structure and large steric effect. Metal centers are embraced tightly by large ligands, thus cyclic monomers are too large for insertion. In comparison, NHC bis(phenolate) complexes (**3a**, **4a**) show high activity towards the polymerization of L-Lactide.

Conclusions

1. A series of tricloride bis(phenolate) complexes and NHC bis(phenolate) complexes were synthesized and their structural features have been determined by X-ray diffraction.
2. The activity of the complexes was evaluated in the ring–opening polymerization of L-Lactide. Tricloride bis(phenlate) complexes barely show activity while bis(phenolate) N-heterocyclic carbene complexes are highly efficient initiators for L-LA polymerization.

References & Acknowledgments

1. Min, K. S.; Weyhermüller, T.; Bothe, E.; Wieghardt, K., *Inorganic Chemistry* **2004**, 43, 2922-2931.
2. Zhang Z, .Xu X, Yao Y, Luo Y, etc., *Inorganic Chemistry* **2009**, 48, 5715-5724.

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