

Synthesis, structure and reactivity of dinuclear rare earth metal bis(*o*-aminobenzyl) complexes bearing 1,4-phenylenediamidinate co-ligand

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General Remarks All manipulations were performed under an inert atmosphere of purified nitrogen with rigorous exclusion of air and moisture using standard Schlenk techniques and a nitrogen filled glovebox operating at less than 1 ppm oxygen and 1 ppm moisture. Solvents (toluene, hexane, and THF) were distilled from sodium/benzophenone ketyl, and dried over fresh Na chips in the glovebox. Bis(2,6-diisopropylphenyl) carbodiimide was obtained from Tokyo Chemical Industry Co., Ltd and used without purification. CH₃C₆H₄NMe₂-*o*, ⁿBuLi (2.5 mol/L in hexane) were purchased from Acros and used without purification. Phenyl isocyanate and phenyl isothiocyanate were purchased from Dar Rui and distilled from P₂O₅ before being used. C₆D₆ was obtained from Cambridge Isotope and dried by sodium chips. LnCl₃ (Ln = Y, Lu, Sc)^[1] were prepared according to literature procedures. ¹H NMR and ¹³C NMR spectra were recorded on a JEOL ECA-400 NMR spectrometer (FT, 400 MHz for ¹H; 100 MHz for ¹³C) in C₆D₆ at room temperature in C₆D₆. GPC data were collected on a Waters 1515 Breeze GPC system using a polystyrene standard in THF.

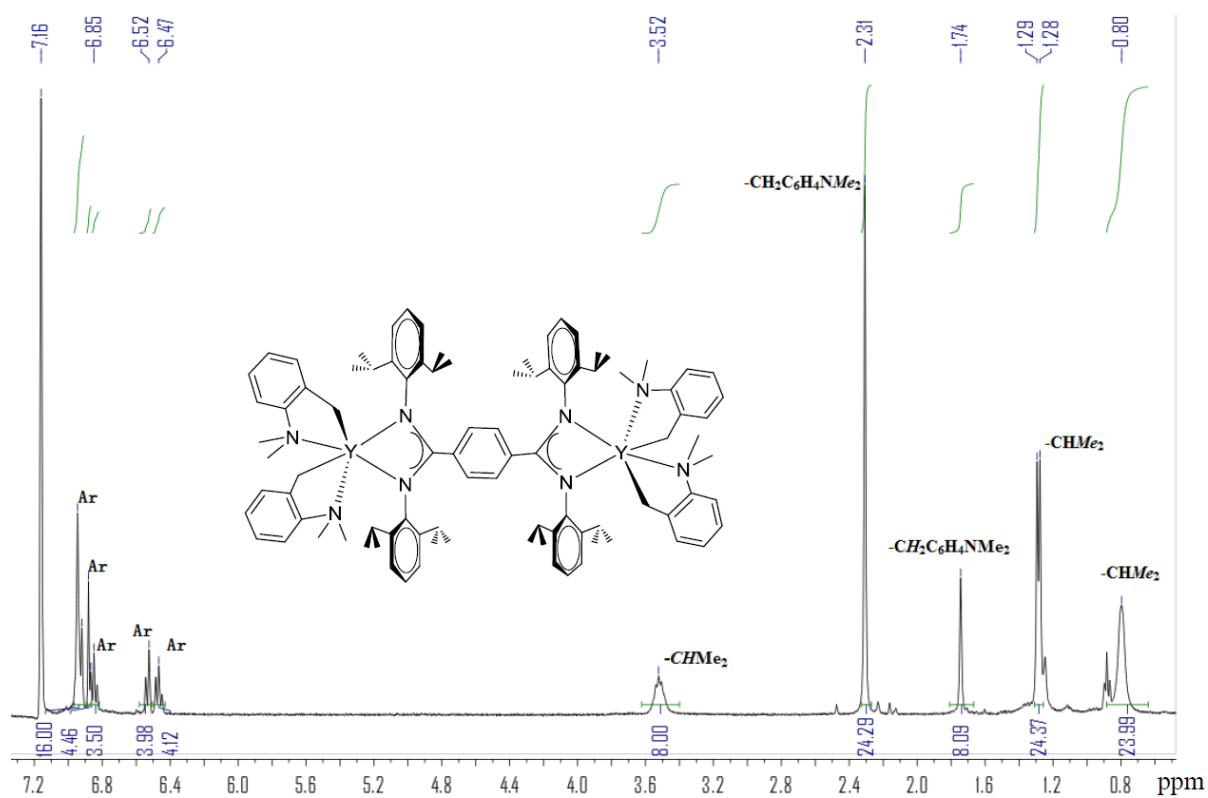


Figure S1. ¹H NMR spectrum of **2a** (1,4-C₆H₄[C(NR)₂Y(*o*-CH₂C₆H₄NMe₂)₂]₂ (R = 2,6-ⁱPr₂-C₆H₃)) obtained in C₆D₆ at 60°C.

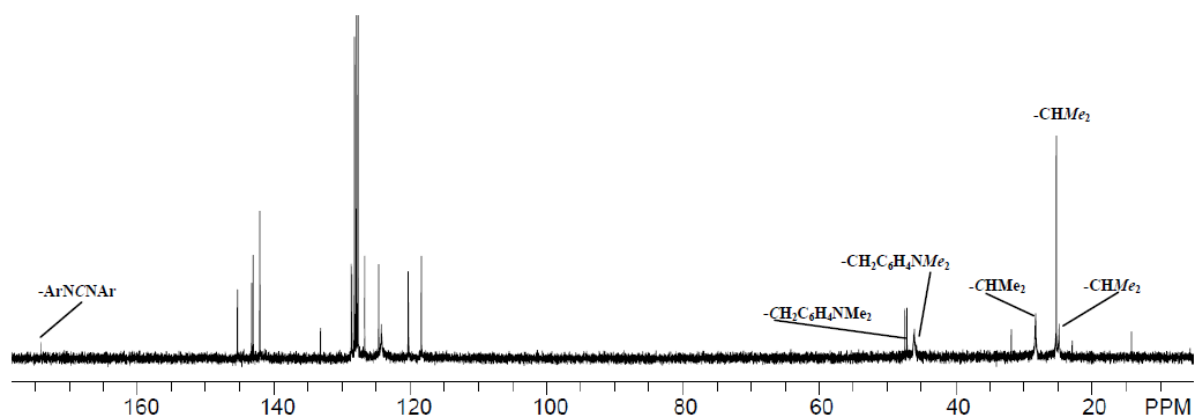


Figure S2. ^{13}C NMR spectrum of **2a** ($1,4\text{-C}_6\text{H}_4[\text{C}(\text{NR})_2\text{Y}(\text{o-CH}_2\text{C}_6\text{H}_4\text{NMe}_2)_2]_2$) obtained in C_6D_6 at room temperature.

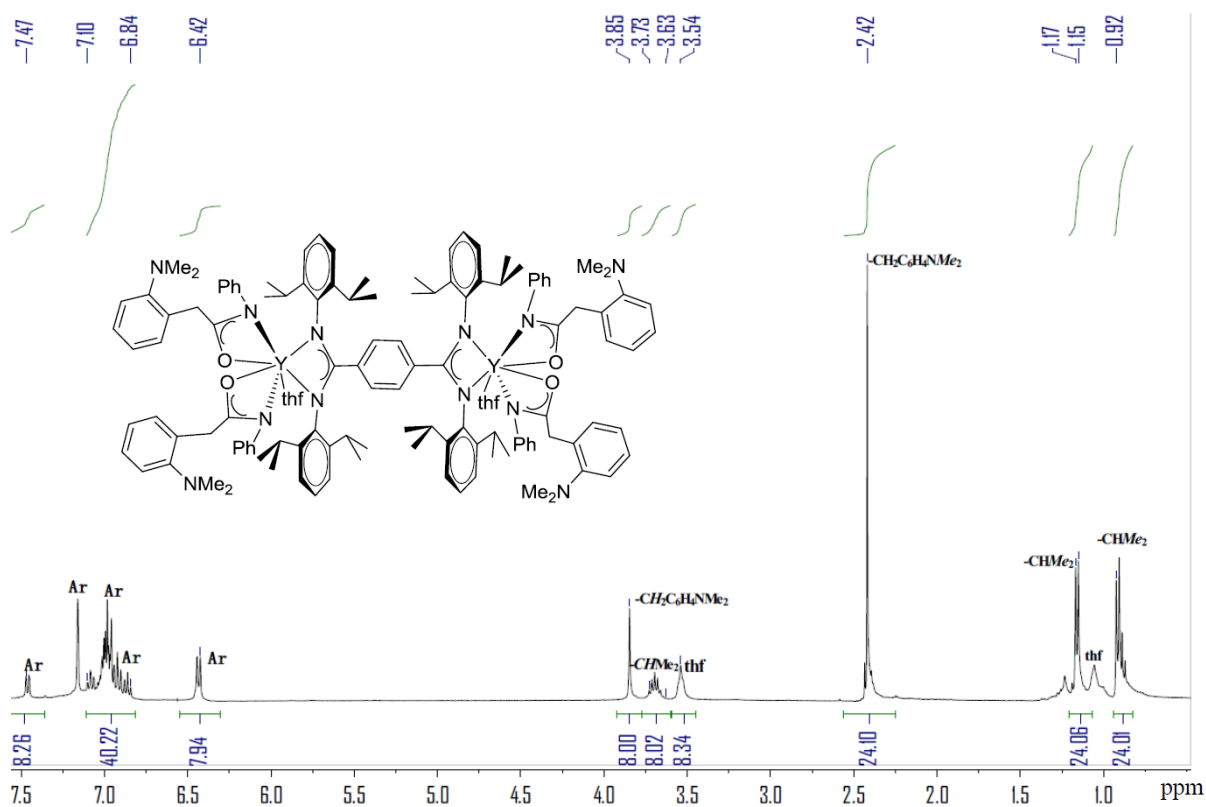


Figure S3. ^1H NMR spectrum of **3a** ($1,4\text{-C}_6\text{H}_4[\text{C}(\text{NR})_2\text{Y}\{\text{OC}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-o})\text{NPh}\}_2(\text{THF})_2$) obtained in C_6D_6 at room temperature.

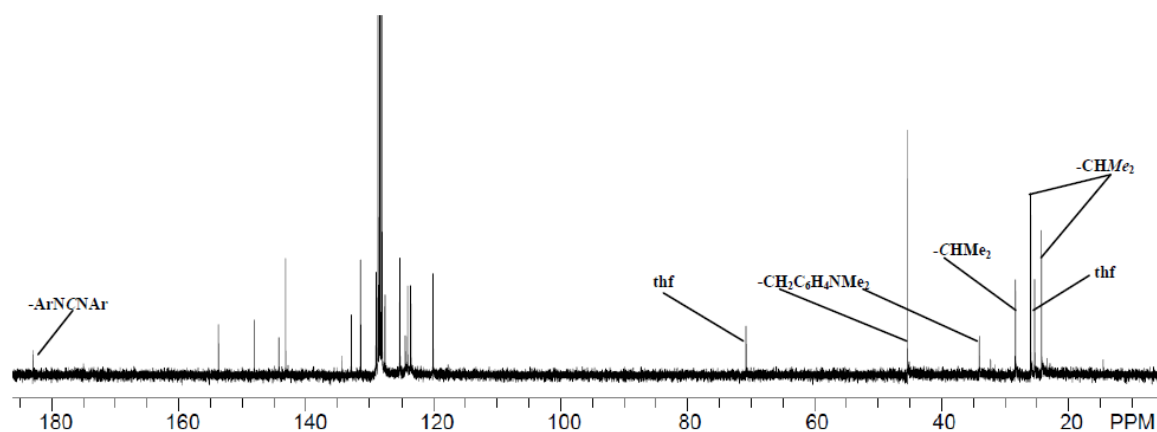


Figure S4. ^{13}C NMR spectrum of **3a** ($1,4\text{-C}_6\text{H}_4[\text{C}(\text{NR})_2\text{Y}\{\text{OC}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)\text{NPh}\}_2(\text{THF})_2$) obtained in C_6D_6 at room temperature.

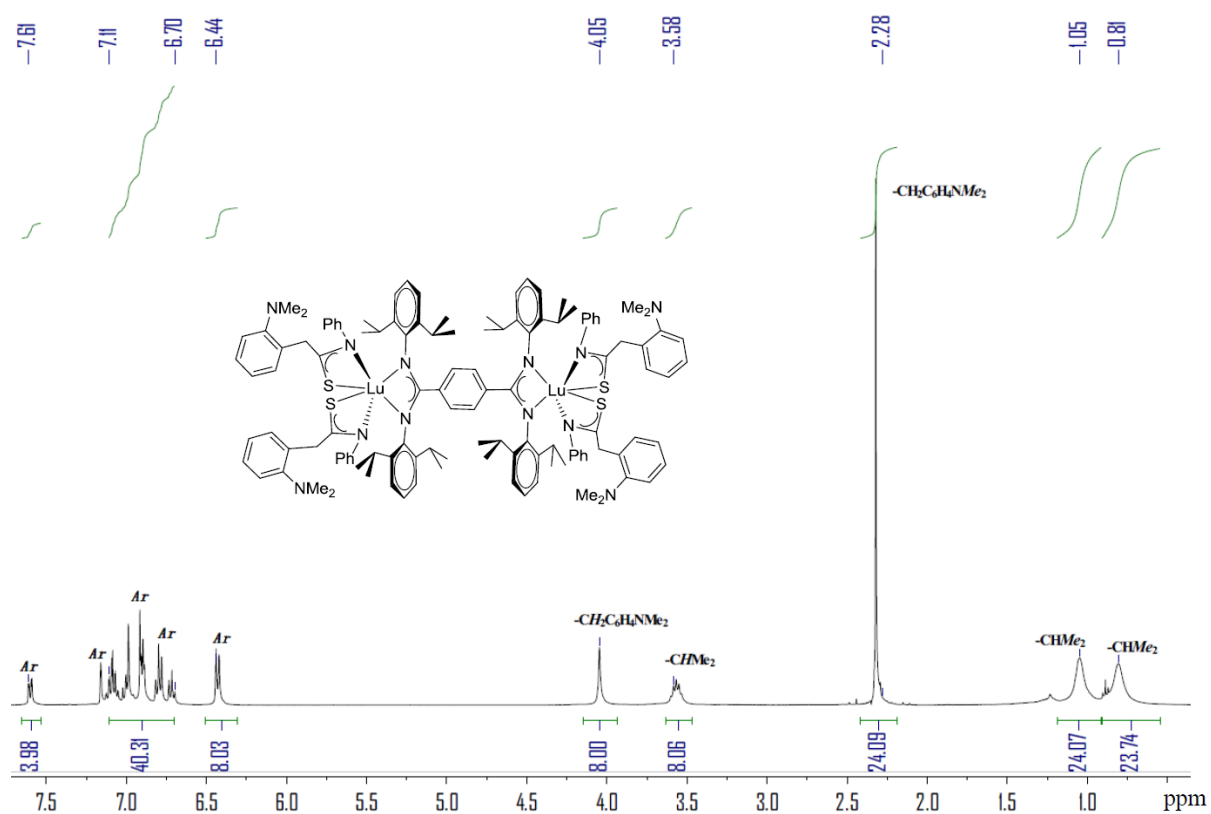


Figure S5. ^1H NMR spectrum of **4b** ($1,4\text{-C}_6\text{H}_4[\text{C}(\text{NR})_2\text{Lu}\{\text{SC}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)\text{NPh}\}_2(\text{THF})_2$) obtained in C_6D_6 at room temperature.

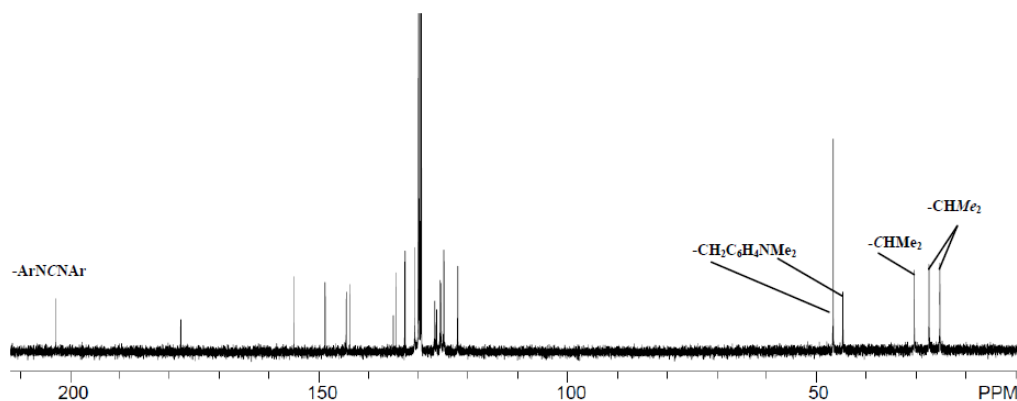


Figure S6. ^{13}C NMR spectrum of **4b** ($1,4\text{-C}_6\text{H}_4[\text{C}(\text{NR})_2\text{Lu}\{\text{SC}(\text{CH}_2\text{C}_6\text{H}_4\text{NMe}_2\text{-}o)\text{NPh}\}_2(\text{THF})_2$) obtained in C_6D_6 at room temperature.

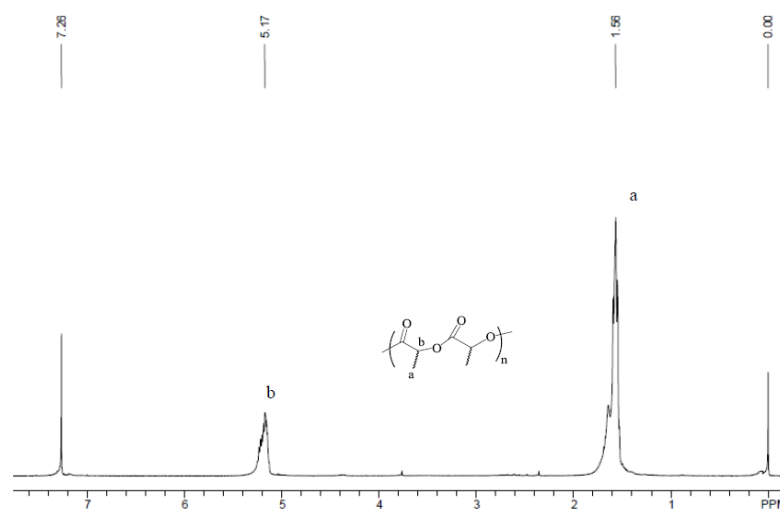


Figure S7. Representative ^1H NMR spectrum of isolated PLA (400 MHz, CDCl_3).

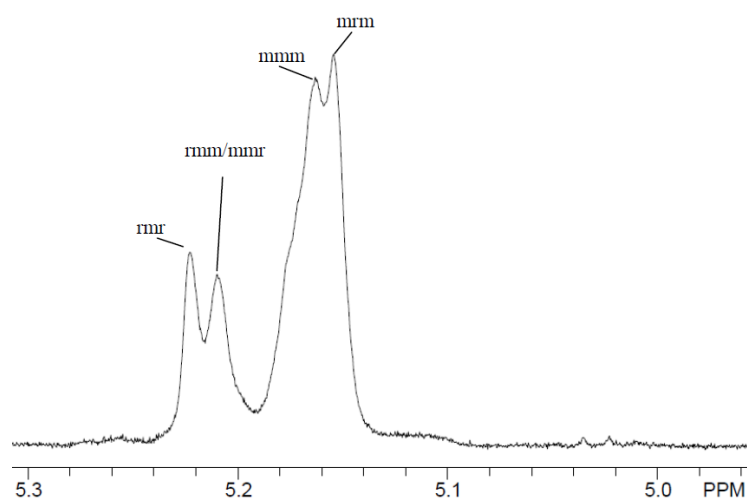


Figure S8. Homocoupled ^1H NMR spectrum of the methine region of heterotactic PLA prepared (500 MHz, CDCl_3). P_r is the probability of a racemic placement between monomer units. (i.e. (R,R)-PLA followed by (S,S)-PLA, or

vice versa). The expressions for the tetrad concentrations in terms of P_r , assuming Bernoullian statistics and the absence of transesterification, are as follows^[2,3]: $[mmm] = (2(1 - P_r)^2 + P_r(1 - P_r))/2$; $[mrm] = (P_r^2 + P_r(1 - P_r))/2$; $[mmr] = [rmm] = (P_r(1 - P_r))/2$; $[rmr] = P_r^2/2$.

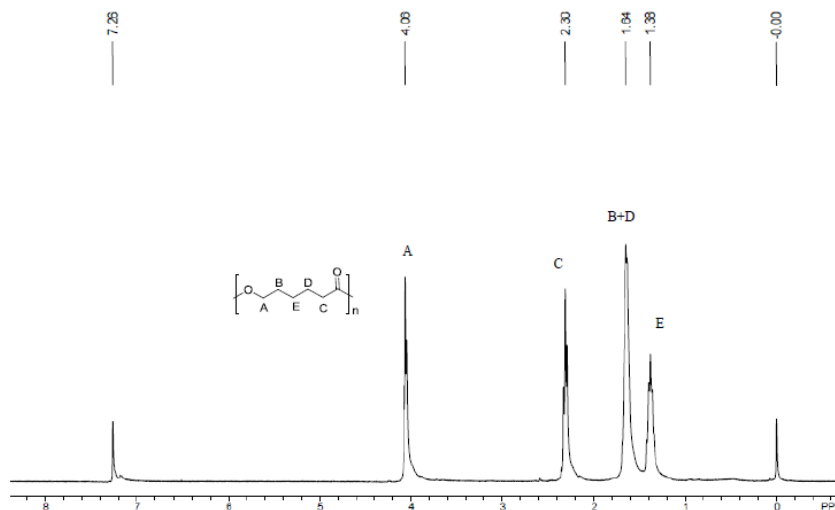


Figure S9. Representative ¹H NMR spectrum of isolated PCL(400 MHz, CDCl₃).

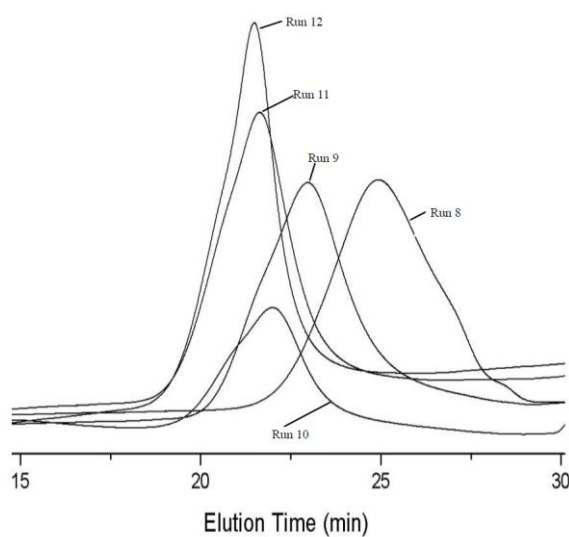


Figure S10. GPC curves of the PCL obtained by the complex **2a** (table 2 entries 8-12).

X-ray Crystallographic structure determinations

All crystals for X-ray analysis were obtained as described in the preparations. Suitable crystals were sealed in the thin-wall glass capillaries under a microscope in the glovebox. Data collection was performed using a Bruker SMART APEX (at 293 K) diffractometer with a CCD area detector using graphite-monochromated MoK_α radiation ($\lambda=0.71073\text{\AA}$). The determination of crystal class and unit cell was carried out by using the SMART program package. The raw frame data were processed using SAINT³³ and SADABS³⁴ to yield the reflection data file. The structure was solved by using the SHELXTL program³⁵ Refinement was performed on F^2 anisotropically by the full-matrix least-squares method for all the non-hydrogen

atoms. The analytical scattering factors for neutral atoms were used throughout the analysis. Except for the hydrogen atoms on bridging carbons, hydrogen atoms were placed at the calculated positions and included in the structure calculation without further refinement of the parameters. The hydrogen atoms on bridging carbons were located by difference Fourier syntheses and their coordinates and isotropic parameters were refined. The residual electron densities were of no chemical significance. The disordered toluene molecules within the crystal lattice are not crystallographically well defined and are squeezed by the PLATON program. Details about this SQUEEZE are given in the cif files. Crystal data, data collection, and processing parameters for complexes **1**, **3b**, and **4a** are summarized in Table 3. CCDC-840581 (**1**), 840582 (**3b**), 840583 (**4a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Selected bond lengths [Å] and angles [°] for complexes **1**, **3b**, **4a**.

	1	3b	4a
C–N(av.)	1.350(4)	–	–
C=N(av.)	1.294(5)	–	–
C=N _{amidinate} (av.)	–	1.341(7)	1.335(4)
Ln–N _{PhNCO₂S} (av.)	–	2.385(5)	2.406(3)
Ln–N _{amidinate} (av.)	–	2.331(5)	2.363(3)
Ln–O/S(av.)	–	2.266(4)	2.708(1)
N–C–N _{amidine} (av)	122.3(4)	–	–
N–C–N _{amidinate} (av)	–	113.9(5)	113.7(4)
N–Ln–N _{amidinate} (av)	–	57.63(2)	56.4(1)
O/S–Lu–N _{PhNCO₂S} (av)	–	56.62(2)	60.71(8)

[1] R. W. Stotz, G. A. Melson, *Inorg. Chem.*, 1972, **11**, 1720.

[2] J. E. Kasperczyk, *Macromolecules*, 1995, **28**, 3937.

[3] J. Coudane, C. Ustariz-Peyret, G. Schwach, M. Vert, *J. Polym. Sci. Polym. Chem. Ed.*, 1997, **35**, 1651.