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Synthesis and structural characterisation of novel linked bis(B-diketiminato) rare earth metal complexes[†]

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Rare earth metal complexes based on novel linked $bis(\beta$ diketiminato) ligands have been prepared via amine elimination and their structural characterisation revealed that the linker unit has significant influence on the geometry and coordination mode of the ancillary ligand.

The chemistry of rare earth metal complexes has been stimulated over the last two decades due to their high catalytic activity for various organic transformations1 and polymer synthesis.2 Noncyclopentadienyl ligand sets have attracted considerable interest as they are easy to modify with respect to steric demand and electronic properties.3 One promising ancillary ligand set is the family of β -diketiminato ligands,⁴ which has been successfully applied in transition metal catalyst systems.^{5,6}

Catalyst systems of the three-valent rare earth metals commonly comprise of two monoanionic ancillary ligands controlling the reactivity as well as one reactive amido or alkyl group. Analogous to the ansa-metallocene ligand set, we envisioned to accommodate two linked β -diketiminato ligands in the coordination sphere of the metal. Linking the two β-diketiminato moieties should increase complex stability, with the additional benefit of an anchor for potential stereoselective control by utilising chiral linkers.9

Ethylene- and cyclohexyl-linked bis(\beta-diketiminato) ligands with different sterically demanding aromatic substituents were prepared in a two-step standard condensation route (Scheme 1).

+ 2 ArNH₂ _____ À١ 5-fold excess H₂L¹ : Ar = 2,4,6-Me₃C₆H₂ H_2L^2 : Ar = 2,6-*i*Pr₂C₆H₃ H_2L^3 : Ar = 2,4,6-Me_3C_6H_2 H_2L^4 : Ar = 2,6-*i*Pr_2C_6H_3

Scheme 1 Reagents and conditions: (i) 150 °C, 24 h; (ii) [Et₃O]⁺[BF₄]⁻; (iii) Et₃N, diamine, CH₂Cl₂, 25 °C.

The new ligands $H_2L^1-H_2L^4$ reacted cleanly with trisamido complexes $[Ln{N(SiMe_3)_2}]$ (Ln = La, Y) to form the desired linked bis(β -diketiminato) complexes 1–4 (Scheme 2).⁷ Whereas reactions of the ethylene-linked ligands H_2L^1 and H_2L^2 proceeded readily at 60-75 °C, the more rigid cyclohexyl-linked ligands H₂L³ and H₂L⁴ required higher temperatures.⁸

† Electronic supplementary information (ESI) available: Experimental procedures and characterising data for all new complexes. See http://www.rsc.org/suppdata/dt/b5/b501930c/

[Ln{N(SiMe₃)₂}₃] ii Me₃Si SiMe₃ SiMe₃ Me₃Si R R¹R 'n2 1a Ln = La, R¹ = R² = Me $3 R^1 = R^2 = Me$ 1b Ln = Y, R¹ = R² = Me **4** $R^1 = iPr, R^2 = H$ **2a** Ln = La, R¹ = *i*Pr, R² = H **2b** Ln = Y, $R^1 = iPr$, $R^2 = H$

Scheme 2 Reagents and conditions: (i) 1 equiv. H_2L^1 (Ln = La: 60 °C, 30 min; Ln = Y: 70 °C, 24 h) or H_2L^2 (Ln = La: 75 °C, 4.5 d; Ln = Y: 95 °C, 5 d); (ii) Ln = La, 1 equiv. H_2L^3 (65 °C, 24 h) or H_2L^4 (95 °C, 4 d).

X-Ray crystallographic analyses of 2a and 4 confirmed their monomeric structures (Figs. 1 and 2).‡ In both complexes lanthanum is coordinated in a distorted square pyramidal fashion, in which the amido ligand occupies the apical position and the two linked β -diketiminato moieties form the basis. However, the overall geometry of the linked $bis(\beta$ -diketiminato) ligand differs significantly when exchanging the ethylene linker unit in 2a for the trans-cyclohexyl unit in 4. Whereas the two aromatic substituents have a cisoid arrangement in 2a, pointing away from the apical amido group, they are oriented in a transoid fashion in 4 with one aromatic substituent pointing away from the amido group and the other aromatic substituent pointing towards the amido group. This significant change in ligand geometry is inflicted by a slight decrease of the dihedral angle of the linker unit (N2–C–C–N3) from $49.3(4)^{\circ}$ in **2a** (-53.1(5)° for the second independent molecule) to 42.25(19) in 4.

In complex 2a the two β -diketiminato moieties display different bonding modes. The β-diketiminato fragment consisting of N1, N2 and C11–C13 is bonded in a η^2 fashion with the lanthanum atom being situated only 1.235 Å out of the N_2C_3 plane and rather long La \cdots C distances (3.45–3.73 Å). The other β -diketiminato moiety is tilted significantly towards a η^5 bonding mode. The metal is more displaced from the N_2C_3 plane (1.883 Å) and La \cdots C contacts are shorter (3.01–3.18 Å). While both La–N bonds in the η^2 bound β -diketiminato moiety are almost identical (2.536(3) and 2.557(3) Å), they vary by almost 0.17 Å for the tilted β -diketiminato ligand (2.559(3) vs. 2.394(3) Å).

Contrary to the findings for complex 2a, both β -diketiminato moieties in complex 4 are bound in the η^5 bonding mode with



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Fig. 1 Molecular structure of one of the two independent molecules of 2a. Selected bond lengths (Å) and bond angles (°): La1–N1 2.557(3), La1–N2 2.536(3), La1–N3 2.394(3), La1–N4 2.559(3), La1–N10 2.425(3), La1–C16 3.014(3); N1–La1–N2 72.33(9), N1–La1–N4 119.95(9), N3–La1–N4 72.06(9), N2–La1–N3 65.47(9), N4–La1–N10 123.36(9), N3–La1–N10 98.16(10), N2–La1–N10 112.22(10), N1–La1–N10 105.01(10), N2–C14–C15–N3 49.3(4); N₂C₃ plane–La1 1.235 (ring 1) and 1.883 (ring 2).



Fig. 2 Molecular structure of 4. Selected bond lengths (Å) and bond angles (°): La1–N1 2.4977(15), La1–N2 2.4340(14), La1–N3 2.5063(15), La1–N4 2.5939(15), La1–N10 2.4543(15), La1–C11 3.0554(18), La1–C12 3.0469(18), La1–C13 2.9690(17), La1–C16 3.036(2); N1–La1–N2 72.15(5), N1–La1–N4 132.85(5), N3–La1–N4 73.45(5), N2–La1–N3 63.72(5), N4–La1–N10 97.34(5), N3–La1–N10 133.96(5), N2–La1–N10 100.05(5), N1–La1–N10 118.20(5), N2–C21–C26–N3 42.25(19); N₂C₃ plane–La1 1.941 (ring 1) and 1.940 (ring 2).

the lanthanum atom being displaced by 1.94 Å out of the N₂C₃ plane and short La \cdots C contacts (2.97–3.06 Å for ring 1, 3.04–3.19 Å for ring 2). The La–N bonds within the β -diketiminato moiety vary less dramatically by only 0.06–0.09 Å (2.4977(15) vs. 2.4340(14) Å and 2.5939(15) vs. 2.5063(15) Å).

We are currently investigating the catalytic properties of these novel linked bis(β -diketiminato) complexes for hydroamination^{1d,e} and copolymerisation of epoxides and CO₂.^{5b,10} The drastic difference in ligand geometry of ethylenelinked *vs.* cyclohexyl-linked ligands should be reflected in their reactivity and stereoselectivity. Furthermore, we are exploring other linker units in order to better understand the factors governing the binding mode of the β -diketiminato ligands in these systems.

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Notes and references

 $\ddagger Crystallographic data$ for **2a**: C₄₅H₇₇LaN₅Si₂, $M_r = 883.21$, crystal size $0.30 \times 0.30 \times 0.30$ mm, triclinic, space group $P\overline{1}$, a = 11.816(2), b = 19.038(4), c = 22.377(5) Å, $a = 92.67(3), \beta = 102.60(3), \gamma = 102.60(3), \gamma$ 99.47(3)°, V = 4827.7(17) Å³, Z = 4, $D_c = 1.215$ g cm⁻³, F(000) = 1868, Mo-Ka radiation ($\lambda = 0.71073$ Å), T = 173(2) K, $\mu = 0.968$ mm⁻¹ The 41058 reflections measured on a Nonius Kappa CCD system yielded 22127 independent reflections ($R_{int} = 0.0335$), $R_1 (I > 2\sigma(I)) =$ 0.0383, wR_2 (all data) = 0.1174. The asymmetric unit contains two independent molecules as well as one molecule of isohexane, which showed strong non-resolvable disorder of all atoms. The isohexane was refined by using distance restraints; no hydrogen atoms have been added to the refinement model. CCDC reference number 262110. Crystallographic data for 4: $C_{46}H_{76}LaN_5Si_2$, $M_r = 894.21$, crystal size $0.20 \times 0.20 \times 0.20$ mm, triclinic, space group $P\bar{1}$, a = 11.6019(1), b = 12.3156(1), c = 18.3663(2) Å, $a = 89.618(1), \beta = 79.329(1),$ $= 69.595(1)^{\circ}$, V = 2412.28(4) Å³, Z = 2, $D_c = 1.231$ g cm⁻³, F(000) = 944, Mo-Ka radiation ($\lambda = 0.71073$ Å), T = 173(2) K, $\mu = 0.970$ mm⁻¹, The 21572 reflections measured on a Nonius Kappa CCD system yielded 11064 independent reflections ($R_{int} = 0.0159$), $R_1 (I > 2\sigma(I)) = 0.0243, wR_2$ (all data) = 0.0669. CCDC reference number 265749. See http://www.rsc.org/suppdata/dt/b5/b501930c/ for crystallographic data in CIF or other electronic format.

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- 8 The complexes were generally prepared in toluene solution, except for complex **1a**, where the reaction temperature and solubility of the ethylene-linked ligand permitted the use of hexanes.
- 9 For related linked aminotroponiminate complexes of the rare earth metals, see: M. R. Bürgstein and P. W. Roesky, *Organometallics*, 2003, 22, 1372, and references cited therein.
- 10 Preliminary experiments indicate that complex 3 copolymerises cyclohexene oxide and CO₂ with low activity (60 °C, 41 atm CO₂ TOF = 5 h⁻¹, 87% carbonate linkages, overall TON = 90, $M_n = 3940$, $M_w/M_n = 7.3$). We are indebted to Prof. J. Okuda and Dr. K. Beckerle (RWTH Aachen) for obtaining the GPC data.