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C_2-symmetric bis(oxazolinato) complexes of yttrium and lanthanum † ‡

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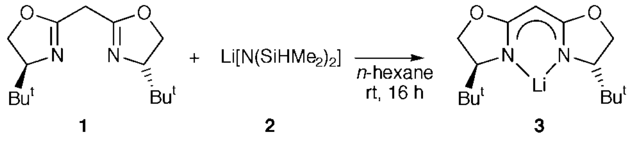
Chiral 2,2′-methylene-bis[(4*S*)-4-*tert*-butyl-2-oxazoline] reacts with $Ln[N(SiHMe_2)_2]_3(thf)_2$ (Ln = Y, La) *via* an extended silylamide route to yield the first mono- and bis-(bisoxazolinato) complexes, potentially relevant to enantioselective catalysis.

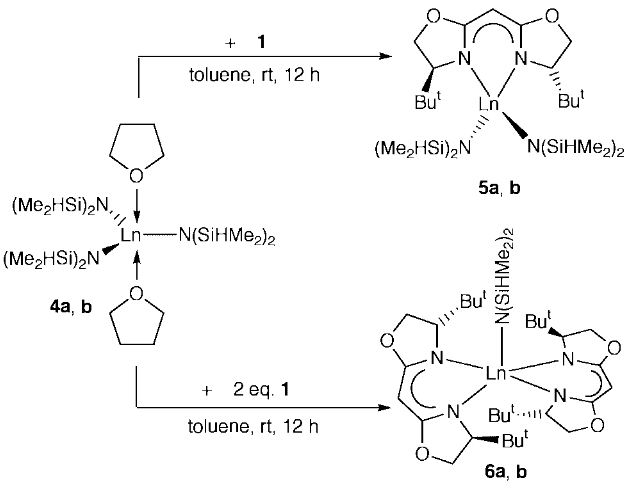
Chelating nitrogen donor ligands provide a versatile and prolific metal co-ordination, uniquely suited for stereoselective synthesis.[1] In particular, chiral bis(oxazoline) (BOX) ligation has been demonstrated to be highly efficient in, *e.g.*, enantioselective cyclopropanation, (hetero) Diels–Alder reactions or several nucleophilic addition reactions to carbonyl functions.[2] Although BOX ligands are easily deprotonated only a few examples comprising magnesium,[3] titanium,[4] zinc,[5] copper[6] and rhodium[7] complexes have been reported and structurally characterised.[6b,7] As organolanthanide mediated catalysis increasingly benefits from anionic ancillary nitrogen donor co-ordination,[8,9] our interest was drawn to bis(oxazolinato) (*d*-BOX) complexes of the rare earth elements, the synthesis and characterisation of which we wish to report herein.

We anticipated the mild reaction conditions of an "extended silylamide route"[8] to be a viable synthetic pathway. The feasibility of this specialised deprotonation reaction was initially verified for a Li(*d*-BOX) system. According to Scheme 1, commercially available 2,2′-methylene-bis[(4*S*)-4-*tert*-butyl-2-oxazoline] **1** (BOX-Bu^t) was reacted with lithium bis(dimethylsilyl)amide **2** to yield the desired lithium bis(oxazolinato) complex **3** as an analytically pure white powder in nearly quantitative yield (see SUP 57678). Both ^{1}H NMR (integral of the methine proton) as well as infrared spectroscopy (absence of the characteristic Si–H stretching band) showed the deprotonation of **1** to proceed even more efficiently than in the presence of more reactive lithium alkyl compounds.



Scheme 1 Deprotonation of 2,2′-methylene-bis[(4*S*)-4-*tert*-butyl-2-oxazoline] **1**.

Taking into account the different sizes of rare earth metal ions, for the syntheses of rare earth metal complexes of *d*-BOX-Bu^t, yttrium and lanthanum were chosen as examples for a small and a large cation.§[10] The precursor amide complexes $Ln[N(SiHMe_2)_2]_3(thf)_2$ (**4a**, Ln = Y; **4b**, Ln = La)[11] were reacted with one equivalent of **1** as shown in Scheme 2 (see SUP 57678). After crystallisation from toluene, compounds [(*d*-BOX-Bu^t)-Ln{N(SiHMe$_2$)$_2$}$_2$] **5a, b** were obtained in good yields (60–70%). Interestingly, the lanthanide centre lost its thf as shown by elemental analysis GC/MS analysis of the evaporated volatiles. This is probably due to the good donor capabilities of bis(oxazolinato) ligands, however, it also could result from interaction with the sterically demanding *tert*-butyl groups.



Scheme 2 Syntheses of various lanthanide bis(oxazolinato) complexes **5a**,**b** and **6a**,**b** [Ln = Y **a**, La **b**] according to the extended silylamide route.

The ^{1}H NMR spectra of **5a**,**b** show a singlet for the methine proton at $\delta = 4.69$ (**5a**) and 4.65 (**5b**), respectively. Co-ordination of the chiral ligand renders the formerly enantiotopic SiHMe$_2$ groups diastereotopic, resulting in a doubled set of signals [$\delta = 0.32/0.31$ (**5a**) and 0.34/0.33 (**5b**)]. This was further revealed by ^{13}C NMR spectroscopy [$\delta = 3.0/2.8$ (**5a**) and 3.1/2.9 (**5b**)]. Evidence for β(Si–H) agostic interactions frequently observed in similar compounds[12] was not obtained from spectroscopic data. Neither the chemical shift of the SiH protons [$\delta = 5.09$ (**5a**) and 5.07 (**5b**)] nor the bands of the ν(Si–H) vibration [$\tilde{\nu} = 2060$ (**5a**) and 2009 cm^{-1} (**5b**)] are indicative of such an interaction.

These findings were further supported by an X-ray crystallographic study performed on the yttrium derivative **5a**.¶ The molecule as depicted in Fig. 1 lies on a crystallographic C_2-symmetry axis, the yttrium centre being co-ordinated in a distorted tetrahedral fashion. A similar all-nitrogen co-ordination geometry was recently described in the aminotroponiminate (ATI) complex [(ATI)Y{N(SiMe$_3$)$_2$}$_2$].[9b] The silylamide ligands in **5a** are orientated away from the *tert*-butyl groups of the conformationally rigid C_2-symmetric *d*-BOX-Bu^t ligand, thus avoiding steric hindrance. The two oxazoline rings are twisted relative to each other by 12.4°. The Y–N(1) silylamide bond distance of 2.222(6) Å is comparable to those in the five-co-

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† Dedicated to Professor Don Bradley on the occasion of his 75th Birthday.

‡ *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/4287/

Also available: experimental details for the preparation and characterisation of compounds **3**, **5a**, **b** and **6a**, **b**. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/4287/, otherwise available from BLDSC (No. SUP 57678, 5 pp.) or the RSC library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).

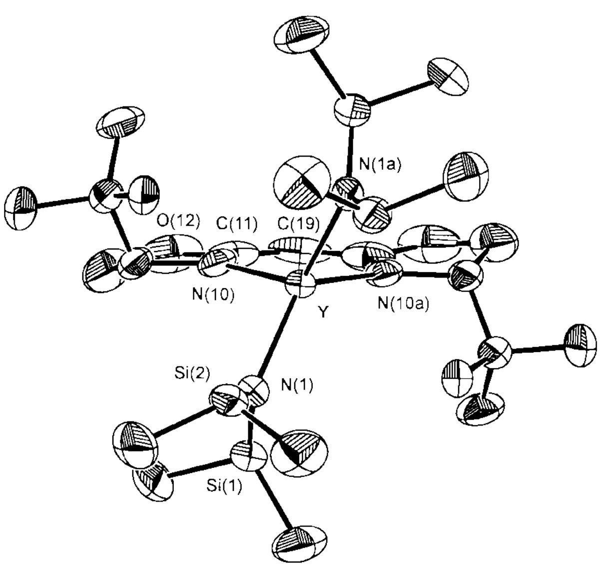

Fig. 1 Molecular structure of **5a** (PLATON).[15] Hydrogen atoms are omitted for reasons of clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected distances [Å] and angles [°]: Y–N(1) 2.222(6), Y–N(10) 2.288(5); N(1)–Y–N(1a) 126.4(2), N(1)–Y–N(10) 97.1(2), N(10)–Y–N(10a) 82.0(2), Y–N(1)–Si(1) 113.4(3), Y–N(1)–Si(2) 118.9(3), Si(1)–N(1)–Si(2) 127.7(4).

ordinated precursor amide complex [2.229(4)–2.276(4) Å] and in four-co-ordinated Y[N(SiHMe$_2$)$_2$]$_3$(1,3-dimethylimidazolin-2-ylidene) [2.237(6)–2.248(6) Å].[13] The angles at the silylamide nitrogen do not show any peculiarities: the minor deviation from ideal sp^2 geometry cannot be attributed to a significant β(Si–H) agostic interaction. The N(10)–Y–N(10a) bite angle of the *six*-membered chelate formed by the *d*-BOX-Bu^t ligand amounts to 82.0(2)° [*cf.* 69.0(1)° in the *five*-membered chelate [(ATI)Y{N(SiMe$_3$)$_2$}$_2$].[9b] The Y–N(10) distance of 2.288(5) Å appears only slightly elongated compared to that of the Y–N(1) silylamide bond length, in contrast to other monoanionic charge-delocalised N$_2$-ligands [*e.g.*, Y–N$_{\text{ATI}}$ = 2.315(3) Å in [(ATI)Y{N(SiMe$_3$)$_2$}$_2$].[9] Although a disordering problem of the six-membered chelate in **5a** excludes a detailed discussion, a conjugation is suggested comparable to that found in copper and rhodium *d*-BOX complexes exhibiting elongated N(10)–C(11) and shortened C(11)–C(19) distances.[6b,7]

The synthesis of the bis(oxazolinato) complexes [(*d*-BOX-Bu^t)$_2$Ln{N(SiHMe$_2$)$_2$}] **6a**,**b** was accomplished in a completely analogous manner as depicted in Scheme 2 by reaction of the precursor amide complexes with two equivalents of **1** (see SUP 57678). The NMR spectroscopic characterisation of the compounds obtained in good yields after crystallisation (70–80%) again revealed two sets of signals for the diastereotopic SiHMe$_2$ groups, except for the ^{1}H NMR spectrum of **6b**. Also, β(Si–H) agostic interactions were not present in **6a**,**b** [$\tilde{\nu}$ = 2057 (**6a**) and 2096 cm^{-1} (**6b**)]. The exchange of the third bis(dimethylsilyl)amide by this *d*-BOX ligand leading to homoleptic bis(oxazolinato) complexes could not be achieved. While the reaction did not proceed further than compounds **6a**,**b** at ambient temperature, refluxing in toluene apparently led to decomposition. We assume that three *tert*-butyl substituted *d*-BOX ligands are sterically too demanding even for the larger lanthanum ion, which documents their enhanced steric bulk compared to that of the structurally related β-diketonate ligands in Ln(thd)$_3$ complexes (thd = 2,2,6,6-tetramethyl-3,5-heptanedionate).[14]

In summary, we have prepared the first rare earth metal complexes carrying chiral deprotonated bis(oxazoline) ligands. The newly synthesized heteroleptic bis(oxazolinato) complexes are stable towards ligand redistribution and exhibit high solubility in aliphatic hydrocarbons which is in accordance with their mononuclear composition. Preliminary investigations indicate that the remaining bis(dimethylsilyl) groups provide excellent tools for immobilisation or transformation into chiral cationic derivatives. Future work will address both the co-ordination chemistry of differently substituted BOX ligands and their use as precursors to catalytically active species.

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Notes and references

§ Recently, rare earth metal triflate complexes Ln(OTf)$_3$ were used in the presence of chiral BOX systems for the asymmetric synthesis of (α-chloroalkyl)boronates and revealed to be superior to Cu(OTf)$_2$ and Zn(OTf)$_2$ congeners.[10]

¶ Crystal data for **5a**: C$_{23}$H$_{53}$N$_4$O$_2$Si$_4$Y, M = 618.95, orthorhombic, space group $P2_12_12$, a = 11.0695(4) Å, b = 11.4615(6) Å, c = 13.8026(7) Å, V = 1751.18(14) Å^3, Z = 2, ρ_{calc} = 1.176 g cm^{-3}, F(000) = 662, μ(Mo-Kα) = 1.83 mm^{-1}, λ = 0.71073 Å, T = 193(2) K. The 31760 reflections measured on a Nonius Kappa CCD area detector diffractometer yielded 3470 unique data (θ_{max} = 26.37°, R_{int} = 0.058). Preliminary positions of heavy atoms were found by direct methods, while positions of the other non-hydrogen atoms were determined from successive Fourier difference maps coupled with initial isotropic least squares refinement. The hydrogen atoms were placed in calculated positions and included in the structure factor calculation but not refined. The final refinement on F^2 converged at $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2} = 0.1441$ on all data, conventional $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.0576$ on F values of 3430 reflections having $F_o^2 > 2\sigma(F_o^2)$, GOF = 1.207 for all F^2 values and 163 refined parameters. Largest difference peak and hole (e Å^{-3}): 0.848, −0.708. CCDC reference number 186/1728. See http://www.rsc.org/suppdata/dt/1999/4287/ for crystallographic files in .cif format.

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