

## A New Ligand Environment in Organolanthanoid Chemistry: Sterically Hindered, Chelating Diolato Ligands and the X-Ray Structure of $[\text{La}\{(\text{CH}(\text{SiMe}_3)_2)\{1,1'-(2\text{-OC}_6\text{H}_2\text{Bu}^t\text{-}3,5)_2\}(\text{thf})_3\}]$ (thf = tetrahydrofuran)

Colin J. Schaverien,<sup>\*a</sup> Nicolaas Meijboom<sup>a</sup> and A. Guy Orpen<sup>b</sup>

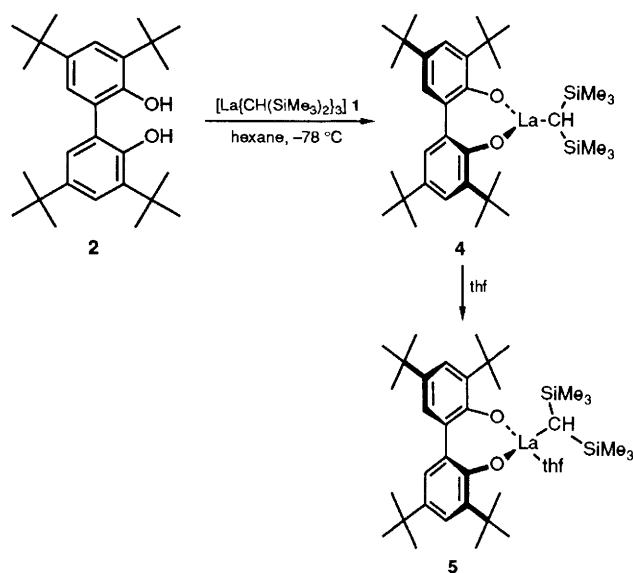
<sup>a</sup> Koninklijke/Shell Laboratorium Amsterdam (Shell Research B. V.), PO Box 3003, 1003 AA Amsterdam, The Netherlands

<sup>b</sup> School of Chemistry, University of Bristol, Bristol BS8 1TS, UK

$[\text{La}\{\text{CH}(\text{SiMe}_3)_2\}_3]$  **1** reacts with 1 equiv. of 3,3',5,5'-tetra-*tert*-butylbiphenyl-2,2'-diol **2** to afford the monomeric chelate  $[\text{La}\{\text{CH}(\text{SiMe}_3)_2\}\{1,1'-(2\text{-OC}_6\text{H}_2\text{Bu}^t\text{-}3,5)_2\}]$  **4**, whose mono-**5**, and crystallographically characterised tris-thf adducts **6** have been synthesized; its reaction with 3,3'-bis(triphenylsilyl)-1,1'-binaphthyl-2,2'-diol **3c** affords  $[\text{La}\{\text{CH}(\text{SiMe}_3)_2\}\{1,1'-(2\text{-OC}_{10}\text{H}_5\text{SiPh}_3\text{-}3)_2\}(\text{OEt}_2)]$  **7**.

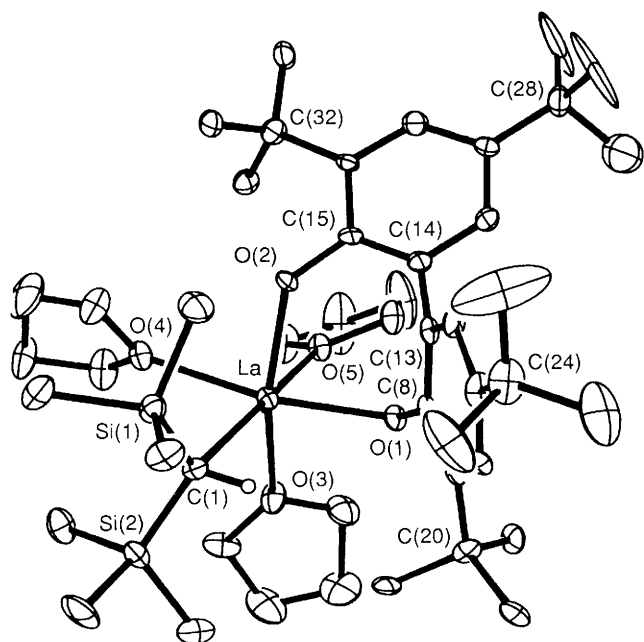
Despite the compatibility of alkoxides with high-valent transition metals, binaphtholate and related ligands have been little used in early transition metal chemistry<sup>1</sup> and not at all in lanthanoid chemistry. This is in spite of the well established synthetic utility of chiral main-group binaphtholato complexes in enantiospecific synthesis.<sup>2</sup> Furthermore, functionalized binaphthol ligands are useful chiral auxiliaries for asymmetric homo-<sup>3</sup> and hetero-Diels–Alder,<sup>4</sup> ene<sup>5</sup> and Claisen reactions,<sup>6</sup> the enantioselective activation of carbonyl compounds occurring by complexation to these bulky, chiral Lewis acids. Incorporation of a sterically hindered, chiral binaphthol ligand into a lanthanoid alkyl framework may afford a new class of lanthanoid complex that could effect stereospecific transformations.<sup>7</sup>

To prepare discrete, mononuclear lanthanoid complexes of potential utility, the mild protonolysis of  $[\text{La}\{\text{CH}(\text{SiMe}_3)_2\}_3]$  **1**<sup>8</sup> with sterically hindered, chiral, chelating diols was explored.† Thus 3,3',5,5'-tetra-*tert*-butylbiphenyl-2,2'-diol

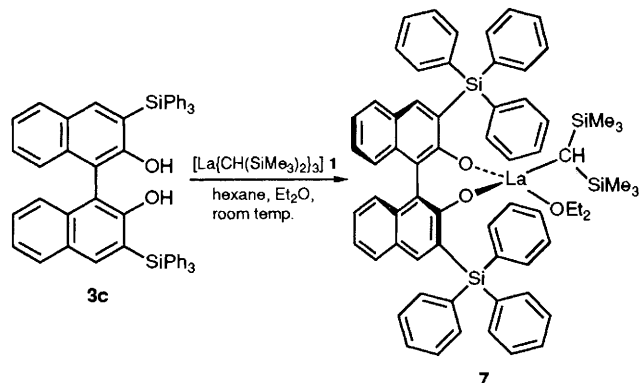


Scheme 1

† Analogous reactions with  $[\text{M}\{\text{CH}(\text{SiMe}_3)_2\}_3]$  ( $\text{M} = \text{Y}, \text{Lu}$ ) were, surprisingly, uniformly unsuccessful.



**Fig. 1** Perspective view of the molecular structure of **6**. Selected bond lengths (Å) La–C(1) 2.676(13), La–O(1) 2.271(9), La–O(2) 2.216(7), La–O(3) 2.654(10), La–O(4) 2.656(10), La–O(5) 2.724(10), La...C(8) 3.096(13) Å. Angles (°) O(1)–La–O(2) 88.1(3), O(2)–La–O(3) 149.1(3), O(1)–La–O(4) 157.6(3), O(3)–La–O(5) 67.8(3), La–C(1)–Si(1) 118.7(6), La–C(1)–Si(2) 116.5(7)°. Torsion angle C(8)–C(13)–C(14)–C(15) 72.9(1.9)°.



**Scheme 2**

**2**,<sup>9</sup> and binaphthol ligands of varying steric bulk, 3,3'-(SiR<sub>3</sub>)<sub>2</sub>-1,1'-bi-{2-C<sub>10</sub>H<sub>5</sub>OH}<sub>2</sub> (R<sub>3</sub> = Me<sub>3</sub>, **3a**; Ph<sub>2</sub>Me, **3b**; Ph<sub>3</sub>, **3c**<sup>10</sup> were used.

Reaction of **1**<sup>8</sup> with **2** in hexane at –78 °C selectively affords the highly sensitive (to air and moisture), extremely hexane-soluble chelate [La{CH(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>{1,1'-(2-OC<sub>6</sub>H<sub>2</sub>But<sub>2</sub>-3,5)}<sub>2</sub>]**4**‡ (Scheme 1). The <sup>1</sup>H NMR spectrum (C<sub>6</sub>D<sub>6</sub>, 25 °C) shows equivalent SiMe<sub>3</sub> groups at δ 0.15 with the methyne proton at

δ –1.46. In the <sup>13</sup>C NMR spectrum, the methyne carbon resonates at δ 59.4 (*J*<sub>CH</sub> 95 Hz), shifted downfield from that found<sup>11</sup> (δ 44.6) in [La(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>{CH(SiMe<sub>3</sub>)<sub>2</sub>}], suggesting a more electrophilic lanthanum environment in **4**. Addition of tetrahydrofuran (thf; 1.2 equiv) to **4** in hexane led to precipitation of the crystalline mono-thf adduct **5**.

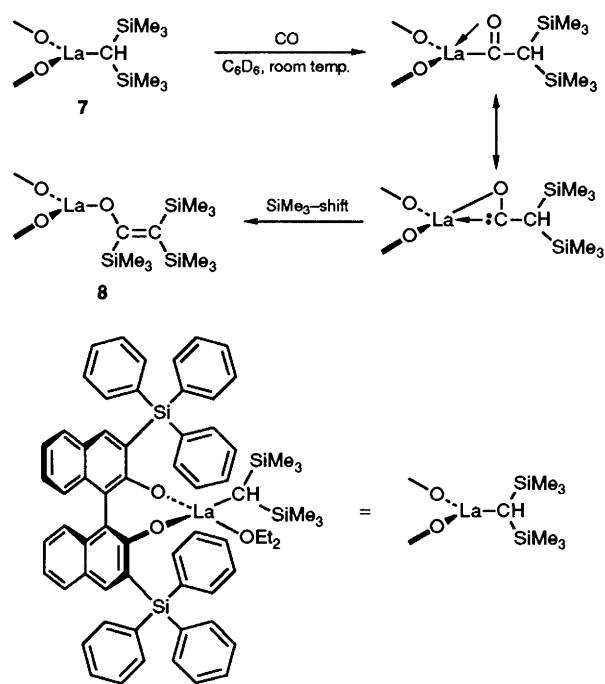
To determine the influence of the chelating alkoxide on the lanthanum coordination sphere, the X-ray crystal structure§ of the tris-thf adduct [La{CH(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>{1,1'-(2-OC<sub>6</sub>H<sub>2</sub>But<sub>2</sub>-3,5)}<sub>2</sub>](thf)<sub>3</sub> (prepared by the addition of 3 equiv. thf to **4**) **6** was determined (Fig. 1). It shows a highly distorted octahedral geometry around the lanthanum atom which is ligated by an α-bonded alkyl group [La–C(1) 2.676(13) Å], three thf ligands [La–O(3) 2.654(10); La–O(4) 2.656(10); La–O(5) 2.724(10) Å], and the chelating alkoxide. The La–O(thf) distances are, as expected, significantly longer than those of the chelating bis-phenoxide [La–O(1) 2.271(9); La–O(2) 2.216(7) Å]. The longest distance [La–O(5)] is *trans* to the alkyl group. The shorter La–O bond in the chelating ligand is associated with the larger La–O–C angle [La–O(2)–C(15) 132.9(7)° vs. La–O(1)–C(8) 113.6(7)°], consistent with more π-donation from O to La for O(2) than O(1). The relatively small La–O(1)–C(8) angle leads to a La...C(8) distance of only 3.096(13) Å, implying some bonding interaction between these atoms.

The chelating bis-phenoxide is sterically quite undemanding, allowing coordination of three facial thf molecules in **6**. Hence, the sterically hindered, chelating binaphthol ligands **3a–3c** were investigated. These provide a stereochemically rigid ligand framework, a prerequisite for induction of asymmetry at the lanthanum centre. The importance of steric bulk in determining stereoregular alkene insertion catalysed by Zr complexes has been alluded to,<sup>7b</sup> this serving to maximize the energy difference between the two diastereoisomers inducing enantiomorphic site-control based on catalyst chirality. Reaction of **1**<sup>8</sup> with **3a** and **3b** under a variety of conditions did not afford an isolable product; however, reaction (Scheme 2) of **1**<sup>8</sup> with **3c** in 1:2 mixture of ether and hexane¶ (20 h; 25 °C) gave the binaphtholato complex **7** in 65% isolated yield. The intrinsic chirality of the complex is reflected in the <sup>1</sup>H and <sup>13</sup>C NMR resonances of the CH(SiMe<sub>3</sub>)<sub>2</sub> group, two diastereotopic SiMe<sub>3</sub> groups being observed. The chirality of the ligand is caused by the lack of free rotation about the C–C bond between the two naphthyl rings; this, in principle, also applies to the phenyl rings in **5**. Diastereotopic SiMe<sub>3</sub> groups were, however, not observed in **5**, even at –70 °C. Hence a mechanism has to be invoked in which the two enantiomers of the biphenolato unit are exchanged. This could occur by a biphenolato 'flipping' mechanism in solution, which may also involve thf dissociation from **5**. This implies that the biphenolato ligand may not be suitable for stereoselective transformations. In contrast, the more sterically demanding binaphtholato unit in **7** is effectively 'locked' into its conformation

§ *Crystal data* for **6**: C<sub>47</sub>H<sub>83</sub>LaO<sub>5</sub>Si<sub>2</sub>, *M* = 923.26, monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 11.145(2), *b* = 20.599(5), *c* = 22.535(7) Å, β = 98.89(2)°, *V* = 5111(2) Å<sup>3</sup>, *Z* = 4, *F*(000) = 1960 electrons, *T* = 200 K, *D*<sub>c</sub> = 1.21 g cm<sup>–3</sup>, μ(Mo–Kα) = 9.2 cm<sup>–1</sup>. Full-matrix least-squares refinement for 4864 independent reflections [*I* ≥ 3σ(*I*)] collected between 4.0 ≤ 2θ ≤ 47.5° and 510 parameters converged at *R* = 0.071, *R*<sub>w</sub> = 0.101. All non-hydrogen atoms [except C(25')–C(27')] were assigned anisotropic displacement parameters and refined without positional restraints. All hydrogen atoms were constrained to idealised positions, and assigned fixed isotropic displacement parameters. The relatively high *R* values reflect the problems of integrating intensities in the presence of a small satellite crystal. Atomic coordinates, bond lengths and angles, and thermal parameters, have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

¶ The reaction is crucially dependent on the solvent choice. This is the only suitable combination we have found.

‡ *Selected NMR data*. **4**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>4</sub>): δ 7.55 (d, *J* 2.5 Hz, 2H), 7.43 (d, *J* 2.5 Hz, 2H), 1.65 (s, 18H), 1.32 (s, 18H), 0.15 (s, 18H, SiMe<sub>3</sub>) and –1.46 [s, 1H, CH(SiMe<sub>3</sub>)<sub>2</sub>]; <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 59.4 (d, *J* 95 Hz, CH), 4.7 (q, SiMe<sub>3</sub>). **7**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 8.18 (s, 2H), 7.87 (m, 12H), 7.53 (m, 4H), 7.18 (m, 22H), –0.13 (s, 9H, SiMe<sub>3</sub>), –0.24 (s, 9H, SiMe<sub>3</sub>) and –1.29 [s, 1H, CH(SiMe<sub>3</sub>)<sub>2</sub>]; <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 57.2 (d, *J* 95 Hz, CH), 4.75 (q, SiMe<sub>3</sub>) and 4.62 (q, SiMe<sub>3</sub>). **8**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 8.12 (s, 2H), 4.56 (s, 1H, CH), 0.06 (s, 9H, SiMe<sub>3</sub>) and –0.12 (s, 9H, SiMe<sub>3</sub>); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 187.1 [s, La–OC(SiMe<sub>3</sub>)], 107.1 (d, *J* 136 Hz, CHSiMe<sub>3</sub>), 1.6 (q, SiMe<sub>3</sub>) and –1.3 (q, SiMe<sub>3</sub>). Satisfactory elemental analyses were obtained for compounds **5** (C, H, Si, La) and **7** (C, H, La).



Scheme 3

In preliminary reactivity studies,  $[\text{La}\{\text{CH}(\text{SiMe}_3)_2\}\{1,1'-(2\text{-OC}_{10}\text{H}_5\text{SiPh}_3\text{-}3)_2\}(\text{OEt}_2)]$  **7** readily reacted (Scheme 3) with excess CO to give a red solution from which the unusual lanthanum enolate  $[\text{La}\{\text{OC}(\text{SiMe}_3)=\text{CHSiMe}_3\}\{1,1'-(2\text{-OC}_{10}\text{H}_5\text{SiPh}_3\text{-}3)_2\}]$  **8** was isolated quantitatively. Complex **8** arises from relatively facile 1,2- $\text{SiMe}_3$  migration from the oxycarbene intermediate  $[\text{La}\{\sigma,\eta^2\text{-OC-CH}(\text{SiMe}_3)_2\}]$ , promoted by the oxophilicity of lanthanum. Similar  $\text{SiMe}_3$  migratory insertion reactions promoted by CO insertion have been observed.<sup>12</sup>

We have shown for the first time that sterically hindered chelating binaphtholato and biphenolato ligands provide a disproportionation-resistant|| coordination sphere compatible

|| Disproportionation and alkoxide exchange reactions take place readily for non-chelating alkoxides. For example, reaction of **1** with  $\text{HOC}_6\text{H}_3\text{Bu}_2$  (2 equiv.), or  $[\text{La}(\text{OC}_6\text{H}_3\text{Bu}_2)_3]$  with  $\text{LiCH}(\text{SiMe}_3)_2$  (1 equiv.), does not afford putative  $[\text{La}(\text{OC}_6\text{H}_3\text{Bu}_2)_2\{\text{CH}(\text{SiMe}_3)_2\}]$ , but a complex mixture of products.

with the lanthanoid alkyl fragment. The chelating alkoxide framework in the binaphtholato complex **7**, but not in the less sterically hindered biphenolato complex **5**, provides a stereochemically rigid ligand framework. Subsequent work further addresses the reactivity of **7**.

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