A New Ligand Environment in Organolanthanoid Chemistry: Sterically Hindered, Chelating Diolato Ligands and the X-Ray Structure of [La{(CH(SiMe$_3$)$_2$}{1,1′-(2-OC$_6$H$_2$Bu$^t_2$-3,5)$_2$}(thf)$_3$] (thf = tetrahydrofuran)

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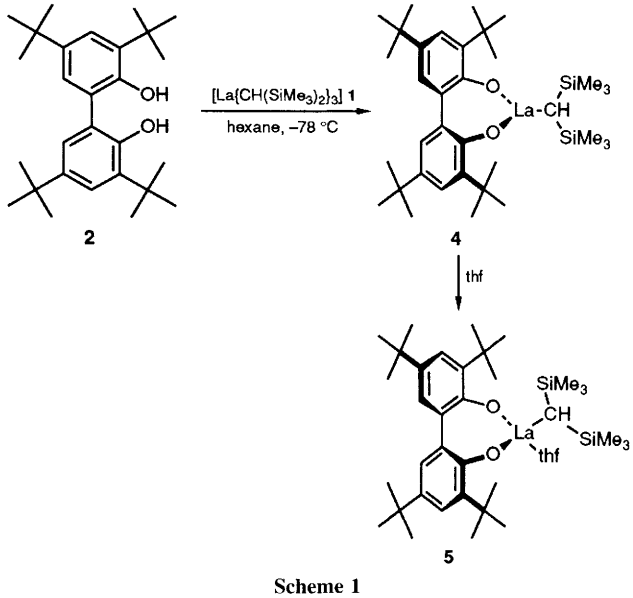
[La{CH(SiMe$_3$)$_2$}$_3$] **1** reacts with 1 equiv. of 3,3′,5,5′-tetra-*tert*-butylbiphenyl-2,2′-diol **2** to afford the monomeric chelate [La{CH(SiMe$_3$)$_2$}{1,1′-(2-OC$_6$H$_2$Bu$^t_2$-3,5)$_2$}] **4**, whose mono- **5**, and crystallographically characterised tris-thf adducts **6** have been synthesized; its reaction with 3,3′-bis(triphenylsilyl)-1,1′-binaphthyl-2,2′-diol **3c** affords [La{CH(SiMe$_3$)$_2$}{1,1′-(2-OC$_{10}$H$_5$SiPh$_3$-3)$_2$}(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[1] 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.[2] Furthermore, functionalized binaphthol ligands are useful chiral auxiliaries for asymmetric homo-[3] and hetero-Diels–Alder,[4] ene[5] and Claisen reactions,[6] 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.[7]

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



2 **4** **5**

Scheme 1

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

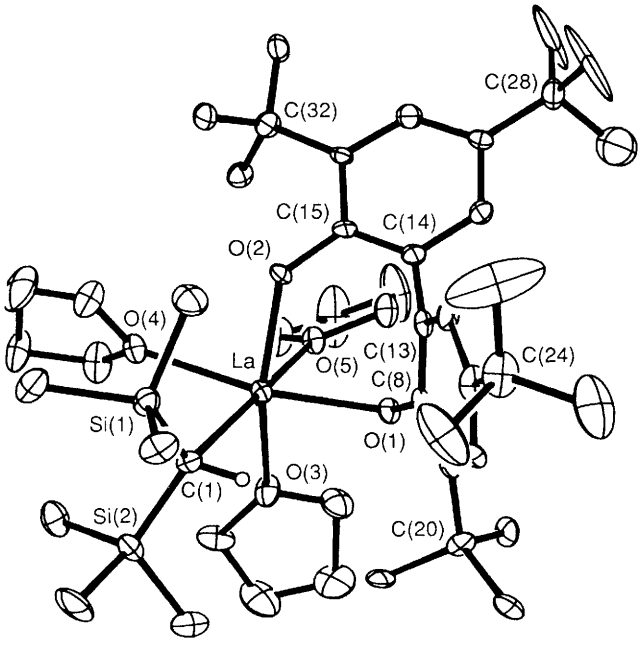
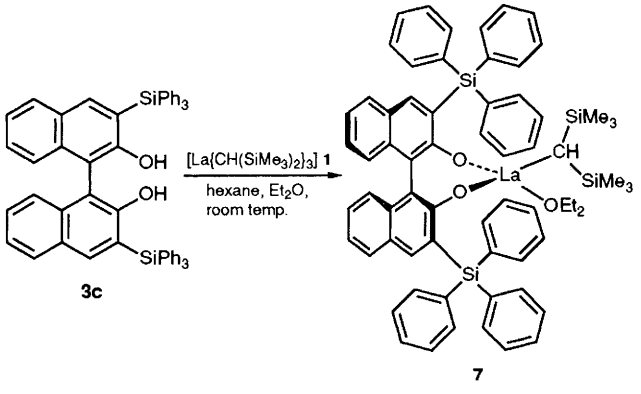


Fig. 1 Perspective view of the molecular structure of **6**. Selected bond lengths (Å) La–C(1) 2.676(13), La–O(1) 2.271(9), La–O(2) 2.216(7), La–O(3) 2.654(10), La–O(4) 2.656(10), La–O(5) 2.724(10), La···C(8) 3.096(13) Å. Angles (°) O(1)–La–O(2) 88.1(3), O(2)–La–O(3) 149.1(3), O(1)–La–O(4) 157.6(3), 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,[9] and binaphthol ligands of varying steric bulk, 3,3′-$(SiR_3)_2$-1,1′-bi-$\{2\text{-}C_{10}H_5OH\}_2$ (R_3 = Me_3, **3a**; Ph_2Me, **3b**; Ph_3, **3c**[10] were used.

Reaction of **1**[8] with **2** in hexane at −78 °C selectively affords the highly sensitive (to air and moisture), extremely hexane-soluble chelate [La{CH(SiMe$_3$)$_2$}{1,1′-(2-$OC_6H_2Bu^t_2$-3,5)$_2$}] **4**‡ (Scheme 1). The ^{1}H NMR spectrum (C_6D_6, 25 °C) shows equivalent $SiMe_3$ groups at δ 0.15 with the methyne proton at δ −1.46. In the ^{13}C NMR spectrum, the methyne carbon resonates at δ 59.4 (J_{CH} 95 Hz), shifted downfield from that found[11] (δ 44.6) in [La(C_5Me_5)$_2${CH($SiMe_3$)$_2$}], 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**.

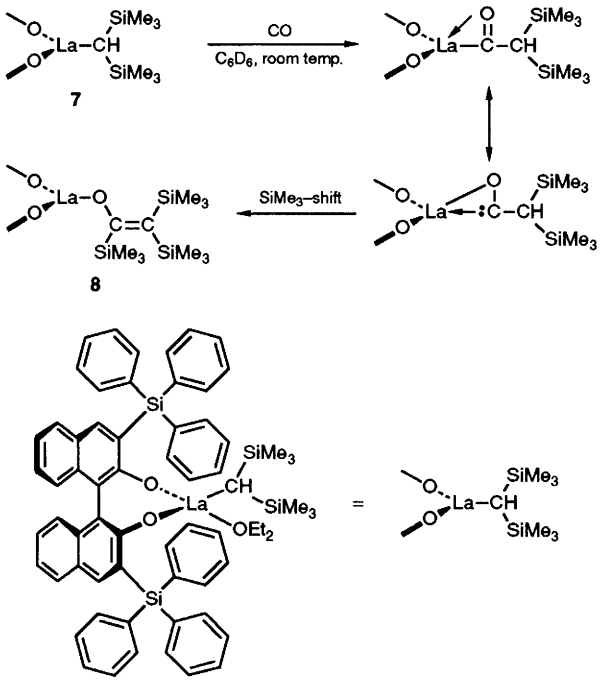
To determine the influence of the chelating alkoxide on the lanthanum coordination sphere, the X-ray crystal structure§ of the tris-thf adduct [La{CH($SiMe_3$)$_2$}{1,1′-(2-$OC_6H_2Bu^t_2$-3,5)$_2$}(thf)$_3$] (prepared by the addition of 3 equiv. thf to **4**) **6** was determined (Fig. 1). It shows a highly distorted octahedral geometry around the lanthanum atom which is ligated by a σ-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,[7b] this serving to maximize the energy difference between the two diastereoisomers inducing enantiomorphic site-control based on catalyst chirality. Reaction of **1**[8] with **3a** and **3b** under a variety of conditions did not afford an isolable product; however, reaction (Scheme 2) of **1**[8] 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 ^{1}H and ^{13}C NMR resonances of the CH($SiMe_3$)$_2$ group, two diastereotopic $SiMe_3$ 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 $SiMe_3$ 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 biphenolate '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

‡ *Selected NMR data*. **4**: ^{1}H NMR (C_6D_4): 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, $SiMe_3$) and −1.46 [s, 1H, C*H*($SiMe_3$)$_2$]; ^{13}C NMR (C_6D_6): δ 59.4 (d, *J* 95 Hz, CH), 4.7 (q, $SiMe_3$). **7**: ^{1}H NMR (C_6D_6): δ 8.18 (s, 2H), 7.87 (m, 12H), 7.53 (m, 4H), 7.18 (m, 22H), −0.13 (s, 9H, $SiMe_3$), −0.24 (s, 9H, $SiMe_3$) and −1.29 [s, 1H, C*H*($SiMe_3$)$_2$]; ^{13}C NMR (C_6D_6): δ 57.2 (d, *J* 95 Hz, CH), 4.75 (q, $SiMe_3$) and 4.62 (q, $SiMe_3$). **8**: ^{1}H NMR (C_6D_6): δ 8.12 (s, 2H), 4.56 (s, 1H, CH), 0.06 (s, 9H, $SiMe_3$) and −0.12 (s, 9H, $SiMe_3$); ^{13}C NMR (C_6D_6): δ 187.1 [s, La–OC($SiMe_3$)], 107.1 (d, *J* 136 Hz, C*H*$SiMe_3$), 1.6 (q, $SiMe_3$) and −1.3 (q, $SiMe_3$). Satisfactory elemental analyses were obtained for compounds **5** (C, H, Si, La) and **7** (C, H, La).

§ *Crystal data* for **6**: $C_{47}H_{83}LaO_5Si_2$, *M* = 923.26, monoclinic, space group $P2_1/n$, *a* = 11.145(2), *b* = 20.599(5), *c* = 22.535(7) Å, β = 98.89(2)°, *V* = 5111(2) Å^3, *Z* = 4, *F*(000) = 1960 electrons, *T* = 200 K, D_c = 1.21 g cm^{-3}, μ(Mo-Kα) = 9.2 cm^{-1}. Full-matrix least-squares refinement for 4864 independent reflections [$I \geqslant 3\sigma(I)$] collected between $4.0 \leqslant 2\theta \leqslant 47.5°$ and 510 parameters converged at R = 0.071, R_w = 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.



Scheme 3

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

We have shown for the first time that sterically hindered chelating binaphtholato and biphenolato ligands provide a disproportionation-resistant‖ coordination sphere compatible 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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‖ Disproportionation and alkoxide exchange reactions take place readily for non-chelating alkoxides. For example, reaction of **1** with HOC$_6$H$_3$Bu$^t_2$ (2 equiv.), or [La(OC$_6$H$_3$Bu$^t_2$)$_3$] with LiCH(SiMe$_3$)$_2$ (1 equiv.), does not afford putative [La(OC$_6$H$_3$Bu$^t_2$)$_2$}{CH(SiMe$_3$)$_2$}], but a complex mixture of products.

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