Synthesis, structure and hydrosilylation activity of neutral and cationic rare-earth metal silanolate complexes[†]

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Rare-earth metal alkyl tri(*tert*-butoxy)silanolate complexes $[Ln{\mu,\eta^2-OSi(O^tBu)_3}(CH_2SiMe_3)_2]_2$ (Ln = Y(1), Tb(2), Lu(3)) were prepared *via* protonolysis of the appropriate tris(alkyl) complex [Ln(CH₂SiMe₃)₃(thf)₂] with tri(*tert*-butoxy)silanol in pentane. Crystal structure analysis revealed a dinuclear structure for 1 with square pyramidal geometry at the yttrium centre. The silanolate ligand coordinates in an η²-bridging coordination mode giving a 4-rung truncated ladder and non-crystallographic inversion centre. Addition of two equiv. of 12-crown-4 to a pentane solution of 1 or **3** respectively gave $[Ln{OSi(O'Bu)_3}(CH_2SiMe_3)_2(12\text{-crown-4})]\cdot 12\text{-crown-4}(Ln = Y (4), Lu (5)).$ Crystal structure analysis of **5** showed a slightly distorted octahedral geometry at the lutetium centre. The silanolate ligand adopts an η^{l} -terminal coordination mode, whilst the crown ether unit coordinates in an unusual κ^3 -fashion. Reaction of 1–3 with [NEt₃H]⁺[BPh₄]⁻ in thf yielded the cationic derivatives $[Ln{OSi(O'Bu)_3}(CH_2SiMe_3)(thf)_4]^+[BPh_4]^- (Ln = Y (6), Tb (7) and Lu (8));$ coordination of crown ether led to compounds of the form $[Ln{OSi(O'Bu)_3}(CH_2SiMe_3)(L)(thf)_n]^+[BPh_4]^- (Ln = Y, Lu, L = V, Lu$ 12-crown-4, n = 1 (9, 10); Ln = Y, Lu, L = 15-crown-5, n = 0 (11, 12)). Reaction of 1 with [NMe₂PhH]⁺- $[B(C_6F_5)_4]^-$, $[Al(CH_2SiMe_3)_3]$ or BPh₃ in the gave the ion pairs $[Y{OSi(O^tBu)_3}(CH_2SiMe_3)(thf)_4]^+[A]^ ([A]^- = [B(C_6F_5)_4]^- (13), [Al(CH_2SiMe_3)_4]^- (14), [BPh_3(CH_2SiMe_3)]^- (15)),$ whilst two equiv. $[NMe_2PhH]^+[BPh_4]^-$ with 1 in thf produced the dicationic ion triple $[Y{OSi(O^tBu)_3}(thf)_6]^{2+}[BPh_4]^-$ (16). Crystal structure analysis revealed that 16 is mononuclear with pentagonal bipyramidal geometry at the yttrium centre. The silanolate ligand coordinates in an η^{l} -terminal fashion. All diamagnetic compounds have been characterized by NMR spectroscopy. 1, 3, 4, 6 and 13 were tested as olefin hydrosilylation pre-catalysts with a variety of substrates; 1 was found to be highly active in 1-decene hydrosilylation.

Introduction

Neutral rare-earth metal dialkyl complexes incorporating a single monoanionic spectator ligand $[Ln(L_nX)R_2L'_m]$ $(L_nX = monoan$ ionic ligand, L'_m = neutral ligand)¹ and cationic rare-earth metal mono(alkyl) complexes $[Ln(L_nX)RL'_m]^+[A]^-$ (A = anion)² are of increasing importance in organo-rare-earth metal chemistry. For instance, recent studies of cationic rare-earth metal alkyl complexes incorporating trimethylsilylmethyl and methyl ligands have implicated the dicationic methyl complex as the active species in ethylene and 1-hexene polymerisation.³ Many heteroleptic neutral and cationic rare-earth metal alkyls rely on the Cp-ligand framework to stabilise the metal centre, although recently non-Cp ligands based on alkoxy, aryloxy, amido and related functionalities have also been applied.⁴ More specifically, rare-earth and transition metal complexes of ligands derived from silanol [SiR₃(OH)], silanediol $[SiR_2(OH)_2]$, α, ω -siloxanediol $[O(SiR_2OH)_2]$, silanetriol $[SiR(OH)_3]$ and incompletely condensed silses quioxane $[SiRO_{3/2}]_{2n}$ have been used as soluble "model compounds" for silica-supported catalysts,⁵ or in some cases as molecular precursors for the preparation of metal silicate materials.⁶ Despite this interest and although the first transition metal complexes containing the monoanionic tri(*tert*-butoxy)silanolate ligand were reported in 1969,⁷ rare-earth metal examples are limited to La complexes that model silicate-grafted rare-earth metal aluminates active in iso-prene polymerisation,⁸ homoleptic tris{tri(*tert*-butoxy)silanolate} complexes,⁹ pre-catalysts for the ring-opening of lactones¹⁰ and various Sm species.¹¹ Cationic rare-earth metal siloxy complexes are not known^{2,4} and Group 4 analogues are rather scarce.¹² We present here neutral and cationic rare-earth metal alkyl complexes supported by the tri(*tert*-butoxy)silanolate ligand and their assessment as pre-catalysts for olefin hydrosilylation.

Results and discussion

Neutral complexes

The syntheses of $[Ln \{\mu, \eta^2-OSi(O'Bu)_3\}(CH_2SiMe_3)_2]_2$ (Ln = Y (1), Tb (2), Lu (3)) cleanly proceeded from equimolar amounts of the appropriate rare-earth metal tris(alkyl) $[Ln(CH_2SiMe_3)_3(thf)_2]^{13}$ and the silanol HOSi(O'Bu)_3 in pentane at room temperature (Scheme 1).¹⁴ 1–3 are highly soluble in all common aliphatic, aromatic and ethereal solvents and represent rare examples of thf-free non-cyclopentadienyl rare-earth metal alkyl complexes.⁴

Institute of Inorganic Chemistry, RWTH Aachen University, Landoltweg 1, D-52074, Aachen, Germany. E-mail: jun.okuda@ac.rwth-aachen.de † Electronic supplementary information (ESI) available: VT and ¹H NMR spectra of 1, 4, 9, 16; time-conversion plots for catalytic hydrosilylation, molecular structure of [Sc{OSi(O'Bu)₃}(CH₂SiMe₃)₂]. See DOI: 10.1039/b512285f



X-Ray diffraction quality crystals of 1 were grown by evaporation of a hexamethyldisiloxane solution at room temperature. 1 is dimeric in the crystalline state, with bridging silanolate oxygen atoms between the yttrium centres, which are related by a noncrystallographic inversion centre (Fig. 1, Table 1).¹⁵ The Y–C bond lengths (Y(1)–C(1) = 2.386(5), Y(1)–C(5) = 2.366(5) Å) are within the 2.35(1)–2.45(2) Å range typical of neutral yttrium trimethylsilylmethyl complexes (Table 2).¹⁶ The geometry at each yttrium centre is best described as square pyramidal, with one trimethylsilylmethyl group occupying the apical position. As well as the puckered 4-membered ring (dihedral angle Y(2)–O(2)– O(6)–Y(1) = 161.08(14)°) described by these yttrium and oxygen atoms, there are also two other 4-membered rings on either

 Table 1
 Crystal data for 1, 5 and 16^a

side, arising from the chelation of one *tert*-butoxy functionality to each metal, giving overall a 4-rung truncated ladder. This second set of 4-membered rings is almost flat (dihedral angle $Y(1)-O(1)-O(2)-Si(3) = 177.76(18)^{\circ}$ and Y(2)-O(5)-O(6)-Si(6) = $174.7(2)^{\circ}$) but extremely strained at the metal (O(1)-Y(1)-O(2) = $62.33(11)^{\circ}$). The central core is asymmetric, with the Y(1)-O(6) and Y(2)-O(2) chelate-free edge contacts shorter than Y(1)-O(2) and Y(2)-O(6). There is a slight elongation of the Si-O separation for the two atoms involved in the 4-membered chelate (Si(6)-O(5) = 1.674(4) vs. Si(6)-O(6) = 1.615(3), Si(6)-O(7) = 1.609(4), Si(6)-O(8) = 1.603(3) Å and Si(3)-O(1) = 1.675(44)vs. Si(3)-O(2) = 1.613(3), Si(3)-O(3) = 1.603(3), Si(3)-O(4) = 1.611(3) Å).

	1	5	16
Chemical formula	$C_{40}H_{98}O_8Si_6Y_2$	$C_{28}H_{65}LuO_8Si_3 \cdot C_8H_{16}O_4$	$C_{84}H_{115}B_2O_{10}SiY \cdot C_4H_8O$
Formula weight	1053.54	965.26	1495.48
T/K	110(2)	110(2)	110(2)
λ/Å	0.71073	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2_1/n$ (no. 14)	Triclinic, P1 (no. 2)	Monoclinic, $P2_1/c$ (no. 14)
a/Å	15.406(3)	11.9494(7)	13.0500(12)
b/Å	20.736(4)	13.9573(9)	25.186(2)
c/Å	19.089(4)	14.4939(9)	25.083(2)
$a/^{\circ}$	90	86.7120(10)	90
β/°	103.003(4)	76.0020(10)	94.606(2)
y/°	90	88.5490(10)	90
$V/Å^3$	5942(2)	2341.5(3)	8217.6(12)
Ζ	4	2	4
$D_{\text{Calc}}/\text{Mg m}^{-3}$)	1.178	1.369	1.209
$R(F_0^2), R_w(F_0^2) [I > 2\sigma(I)]$	0.0661, 0.1216	0.0392, 0.0967	0.0479, 0.0969
$R(F_0^2), R_w(F_0^2)$ (all data)	0.167, 0.1511	0.0459, 0.1109	0.1011, 0.1144

^{*a*} $R(F_0^2)$ and $Rw(F_0^2)$ are the final R indices.

Table 2Selected bond lengths (Å) and angles (°) for 1, 5 and 16

1		5		16		
$\begin{array}{c} Y(1)-C(1) \\ Y(1)-C(5) \\ Y(1)-O(1) \\ Y(1)-O(2) \\ Y(1)-O(6) \\ C(1)-Y(1)-C(5) \\ O(2)-Y(1)-O(6) \\ O(1)-Y(1)-O(2) \\ O(1)-Si(3)-O(2) \end{array}$	2.386(5) 2.366(5) 2.352(3) 2.370(3) 2.211(3) 113.2(2) 73.59(12) 62.33(11) 95.99(17)	Lu-C(9) Lu-C(13) Lu-O(1) Lu-O(2) Lu-O(3) Lu-O(9) O(2)-Lu-O(9) C(13)-Lu-O(3) C(9)-Lu-O(1)	$\begin{array}{c} 2.374(4)\\ 2.373(4)\\ 2.445(3)\\ 2.370(3)\\ 2.477(3)\\ 2.060(3)\\ 154.19(13)\\ 159.42(14)\\ 154.41(14)\end{array}$	$\begin{array}{c} Y-O(1) \\ Y-O(5) \\ Y-O(6) \\ Y-O(7) \\ Y-O(8) \\ Y-O(9) \\ Y-O(10) \\ O(1)-Y-O(10) \\ O(1)-Si \end{array}$	$\begin{array}{c} 2.0705(15)\\ 2.4257(15)\\ 2.3802(15)\\ 2.3892(15)\\ 2.3730(15)\\ 2.4216(16)\\ 2.4102(15)\\ 178.72(6)\\ 162.30(9)\\ \end{array}$	



Fig. 1 Molecular structure of 1 (ellipsoids drawn at the 50% probability level, hydrogen atoms and methyl groups omitted for clarity).

A mixture of terminal- η^1 -coordinating and bridging- η^2 coordinating modes were observed in the series of seven crystallographically characterized Sm compounds recently published.^{11b} No terminal- η^2 - or bridging- η^1 -coordinating modes of this ligand have been found for the rare-earth metals.⁸⁻¹¹ However, since the homoleptic zinc and hafnium compounds co-crystallise as two isomeric forms $[M{\eta^2-OSi(O^tBu)_3}{\eta^1-OSi(O^tBu)_3}_3]$ and $[M{\eta^1-OSi(O^tBu)_3}_3]$ $OSi(O^{t}Bu)_{3}_{4}$ (M = Zr, Hf: isotypic), the energy difference between terminal η^1 - and η^2 -coordination modes may be rather small.17 Asymmetric bimetallic central cores involving two or more bridging silanolate oxygen atoms are common across the above series of Sm compounds.^{11b} In $[Sm{\mu,\eta^2-OSi(O'Bu)_3}{\eta^1 OSi(O^{t}Bu)_{3}_{2}_{2}$, in which one chelate arm coordinates each metal centre, and $[Cp*Sm{\mu,\eta^2-OSi(O'Bu)_3}_3Sm]$, in which all three chelates appear at the non-Cp Sm centre, the longer Sm-O bond is always at the four-membered ring created by the chelate. Furthermore, in a similar manner to 1 all Sm compounds show an elongation of the chelating Si-O separation with respect to the other Si-O distances. The elongated Si-O and M-O contacts can be assigned to charge delocalisation across the 4membered M–O–Si–O ring. A similar elongation at the chelating Si–O unit was observed for $[La{\mu,\eta^2-OSi(O^tBu)_3}](\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)(\mu-MeAlMe_2)($ Me_2AIMe_2 , whilst an asymmetric M_2O_2 core was also observed for [Nd(OSiH^tBu₂)₂(µ-OSiH^tBu₂)]₂, which may chelate via an agostic Nd-H interaction.9 Dimerization in 1 may formally occur

via lone pair donation from two oxygen atoms at the same η^1 coordinated silanolate ligand ("**B**", Scheme 1) or by the union of two terminally-bonded η^2 -complexes ("**A**", Scheme 1).

1 and 3 give rise to single resonances for all chemically equivalent groups at room temperature in C_7D_8 in the ¹H and ¹³C{¹H} NMR spectra; characteristic doublets were seen for the yttrium methylene groups of 1 ($\delta_{\rm H}$ – 0.33 ppm, $J(\rm YH)$ = 3.4 Hz; $\delta_{\rm C}$ 39.5 ppm, J(YC) = 43.0 Hz). At low temperature, the coordination of one *tert*-butoxy group to the yttrium centre is resolved (ΔG^{\ddagger} = 51.5 ± 0.1 kJ mol⁻¹), giving rise to two singlets of rather different chemical shift values ($\Delta \delta = 0.15$ ppm) in a 2 : 1 ratio in the ¹H NMR spectrum, consistent with the X-ray data. Furthermore, at low temperature the diastereotopic yttrium methylene protons give rise to an AB quartet (J(HH) = 11.0 Hz, J(YH) coupling not resolved, $\Delta G^{\ddagger} = 52.6 \pm 0.1 \text{ kJ mol}^{-1}$). A single resonance was noted in the ²⁹Si NMR spectra for the silanolate ligand in the neutral species 1, within the range reported for the free ligand and other similar silanols, whose chemical shift values show a small solvent dependency.¹⁸ The ⁸⁹Y NMR spectrum of 1 (C₆D₆, 298 K: $\delta_{\rm Y}$ 863.2 ppm) gave a single resonance of a similar chemical shift value to the previously reported neutral tris(alkyl) complex $[Y(CH_2SiMe_3)_3(thf)_2].^{19}$

Temperature-dependent behaviour in solution has been noted for $[Zn{OSi(O'Bu)_3}_2]_2$, which is dimeric in the solid state with inequivalent bridging and terminal η^1 - and η^2 -coordinated silanolate units.²⁰ At room temperature in C₇D₈ a single resonance was observed for the *tert*-butoxy groups in the ${}^{1}H$ and ${}^{13}C{}^{1}H$ NMR spectra, assigned to a monomeric formulation, whilst at low temperature two singlets of intensity ratio 1 : 1 were observed. The existence of a stable, monomeric, terminally η^1 -coordinated structure for 1 is highly unlikely however, given the ubiquity of thf or other ethers when the trimethylsilylmethyl ligand is used;¹⁻⁴ base-free 3-coordinate rare-earth metal alkyl compounds are known commonly only for the larger bis(trimethylsilyl)methyl ligand, e.g. $[Ln{CH(SiMe_3)_2}_3]^{21}$ Thus a dimeric (or higher order) structure in aromatic solution is the most likely, with the rapidly exchanging tert-butoxy groups "frozen-out" within the dinuclear structure at lower temperatures.

Two resonances of 2 : 1 intensity arising from the *tert*-butoxy groups of very similar chemical shift value ($\Delta \delta = 0.02$ ppm) were observed for 1 and 3 in thf-d₈ solution at room temperature; the *tert*-butoxy region of the ¹H NMR spectrum of 1 remained essentially unchanged at -70 °C. Three separate sets of signals of varying intensity arising from the LnCH₂SiMe₃ (Ln = Y, Lu) groups were also observed in both the ¹H and {¹H}¹³C NMR spectra of both 1 and 3. After 24 h at room temperature, the

two upfield resonances arising from both **1** and **3** remained in a 1 : 4 ratio, but the downfield resonance had almost disappeared. We assume that the downfield resonance represents the dimeric species, which is slowly broken-up into monomeric units by thf. At $-70 \,^{\circ}$ C, an AB quartet of doublets ($\delta_{\rm H} - 1.05 \,\text{ppm}$, $J(\text{HH}) = 11.3 \,\text{Hz}$, $J(\text{YH}) = 2.4 \,\text{Hz}$, $\Delta G^{\ddagger} = 47.3 \pm 0.1 \,\text{kJ} \,\text{mol}^{-1}$) and a doublet ($\delta_{\rm H} - 0.92 \,\text{ppm}$, d, $J(\text{YH}) = 2.7 \,\text{Hz}$) were observed for **1**.²²

The addition of different amounts of thf to a C_6D_6 solution of 1 at room temperature gave both the thf-adduct of the dimeric complex and the monomeric thf-complex[†] (Scheme 2). Two equiv. of thf gave a small low-frequency shift of the Y-CH₂SiMe₃ group resonances from the thf-free compound 1 ($\delta_{\rm H} - 0.27$ ppm (CH₂), 0.37 ppm (SiMe₃)) to the dimeric species with coordinated thf $(\delta_{\rm H} - 0.35 \text{ ppm (CH}_2), 0.33 \text{ ppm (SiMe}_3))$. A small amount of monomeric thf-adduct ($\delta_{\rm H} - 0.71$ ppm (CH₂), 0.27 ppm (SiMe₃)) was also observed. This complex predominated in the presence of 25 equiv. of thf ($\delta_{\rm H} - 0.73$ ppm (CH₂), 0.29 ppm (SiMe₃)). When 40 equiv. of thf were added, three different peaks of varying intensity around $\delta_{\rm H} - 0.75$ ppm were observed, in a similar manner to the spectrum of 1 in thf-d₈. The extent to which the monomeric or dimeric structures are preferred was only slightly affected by heating to 80 °C. $[Cp*Sm{\mu,\eta^2-OSi(O'Bu)_3}_3Sm]$ gives rise to a single broad peak ($\delta_{\rm H}$ 3.10 ppm) for the *tert*-butoxy groups in C₆D₆ at room temperature and to additional signals arising from the same groups when dissolved in thf-d₈ ($\delta_{\rm H}$ 2.08, 1.50, 3.20 ppm),^{11b} an effect attributed to the formation of the monomeric complexes $[SmCp^{*}{OSi(O^{t}Bu)_{3}}(thf)_{x}]$ and $[Sm{OSi(O^{t}Bu)_{3}}_{2}(thf)_{x}]$.



The crown-ether adducts $[Ln{OSi(O'Bu)_3}(CH_2SiMe_3)_2(12-crown-4)] \cdot (12-crown-4)_n$ (Ln = Y (4), Lu (5)) were isolated from 1 and 3 with 2 equiv. of 12-crown-4 respectively in pentane at -30 °C. The extra equivalent of 12-crown-4 (n = 1 by NMR spectroscopy and EA for 4 and 5), was presumably promoted by the low temperature conditions and cannot be excluded by using stoichiometric amounts of this reagent. The use of $[Y(CH_2SiMe_3)_3(12-crown-4)]^{23}$ as a starting material for 4 failed to give a pure product.

Crystals of **5** suitable for X-ray diffraction were grown in pentane at -30 °C. **5** is monomeric in the crystalline state and the silanolate ligand adopts an η^1 -terminal coordination mode (Fig. 2). Only three oxygens of the 12-crown-4 unit coordinate to the metal centre. This κ^3 -bonding mode was observed for [Sc(CH₂SiMe₃)₃(12-crown-4)]¹⁹ but not for [Ln(CH₂SiMe₃)₃(12-crown-4)] (Ln = Y, Lu), which are isostructural and exhibit symmetrical κ^4 -coordination of 12-crown-4.²³ The geometry at the lutetium centre is distorted octahedral, the O(2)–Lu–O(9), C(13)–Lu–O(3) and C(9)–Lu–O(1) angles are all slightly less than 180° (Table 2). The Lu–C bond lengths (Lu–C(9) = 2.374(4), Lu–C(13) = 2.373(4) Å) are within the 2.29(2)–2.40(1) Å range typical of lutetium trimethylsilylmethyl



Fig. 2 Molecular structure of 5 (ellipsoids drawn at the 50% probability level, hydrogen atoms and lattice 12-crown-4 omitted for clarity, only one of two disordered positions at O(11) and O(12) shown).

complexes,²⁴ whilst the Lu–O(12-crown-4) separations (Lu–O(1) = 2.445(3), Lu–O(2) = 2.370(3), Lu–O(3) = 2.477(3) Å) are slightly shorter than those in the previously reported seven-coordinate tris(alkyl) complex [Lu(CH₂SiMe₃)₃(12-crown-4)] (Lu–O(12-crown-4): 2.52(1)–2.60(1) Å).²³

In both aromatic and chlorinated hydrocarbon solution the neutral 12-crown-4 compounds 4 and 5 give rise to an AB quartet in the ¹H NMR spectrum (4 (C_7D_8): J(HH) = 11.5 Hz, J(YH) = 3.2 Hz; 5 (C₆D₆): J(HH) = 11.7 Hz) in a similar manner to the low temperature case for 1. Y-H coupling was also resolved for 4 (J(YH) = 3.2 Hz). Surprisingly given the asymmetrical κ^3 -coordination mode of 12-crown-4 shown in the crystal structure of 5, two higher-order multiplets were observed in the ¹H NMR spectrum (4 (C_7D_8): δ_H 2.80, 3.68 ppm; 5 (C_6D_6): $\delta_{\rm H}$ 2.95, 3.81 ppm) suggestive of symmetrical κ^4 -coordination of 12-crown-4.²³ Either the crown ether adopts a κ^3 -coordination mode in solution with a "carousel" rotation that is rapid on the NMR timescale, as observed for [Sc(CH₂SiMe₃)₃(12-crown-4)],¹⁹ or greater coordination sphere flexibility in solution allows for a κ^4 -coordination mode. Trace amounts of 1 and 3 respectively were also noted in the spectra. Integration of the spectra indicated one free and one coordinated 12-crown-4 per metal centre, consistent with elemental analysis and the result of the crystal structure determination for 5.25 In thf-d₈ a single, broad resonance was observed for the 12-crown-4 unit of 4 ($\delta_{\rm H}$ 3.66 ppm), whilst two resonances arising from the Y–CH₂ group were found ($\delta_{\rm H} - 0.95$, -0.79 ppm, d, J(YH) = 2.9 Hz), in a similar manner to 1 in thf-d₈. We attribute this to fluxional 12-crown-4 coordination, as previously observed for [Y(CH₂SiMe₃)₃(12-crown-4)].²³

Monocationic complexes

The cationic alkyl species $[Ln {OSi(O'Bu)_3}(CH_2SiMe_3)(thf)_4]^+ [BPh_4]^-$ (Ln = Y (6), Tb (7), Lu (8)) were isolated from an equimolar thf solution of 1–3 respectively and $[NEt_3H]^+ [BPh_4]^-$ (Scheme 1). Furthermore, a suspension of 6 or 8 in heptane with a slight excess of 12-crown-4 or 15-crown-5 yielded the crown ether-adducts $[Ln{OSi(O'Bu)_3}(CH_2SiMe_3)(12$ -crown-4)(thf)]+ $[BPh_4]^-$ (Ln = Y (9), Lu (10)) and $[Ln{OSi(O'Bu)_3}(CH_2SiMe_3)(15$ -crown-5)]+ $[BPh_4]^-$ (Ln = Y (11), Lu (12)) respectively as colourless microcrystals. The ion pairs 6–12 are highly soluble in chlorinated and ethereal solvents, but insoluble in aromatic and aliphatic hydrocarbons. Monocationic thf-complexes of yttrium supported by the anions $[B(C_6F_5)_4]^-$ (13), $[Al(CH_2SiMe_3)_4]^-$ (14) and $[BPh_3(CH_2SiMe_3)]^-$ (15) were also synthesized and characterized by NMR spectroscopy. Whilst the synthesis of 15 proceeded rapidly at room temperature, 14 required 24 h for complete conversion to the cation. Synthesis of the 12-crown-4 supported yttrium monocationic complex 9 was also possible at room temperature in thf-d₈ from 4 with one equiv. of $[NEt_3H]^+[BPh_4]^-$ with concomitant SiMe4 formation.

We observed that the ions in compounds 6, 8-15 are separated by solvent molecules in solution, since NMR spectroscopy (¹H, ${}^{13}C{}^{1}H$, ${}^{11}B$, ${}^{19}F$, ${}^{27}Al$) gave rise to resonances indicative of highsymmetry anions. Furthermore, the ¹¹B chemical shift values for the $[{\rm BPh}_4]^-$ anion were independent of the cation present. Two resonances of very similar chemical shift value were found for the silanolate group of the monocationic species (14: δ_{si} – 99.6 ppm, d, J(YSi) = 10.6 Hz and 100.1 ppm, d, J(YSi) = 9.6 Hz), consistentwith the observations in the ¹H and ¹³C{¹H} NMR spectra of two tert-butoxy resonances of slightly different chemical shift values. The ⁸⁹Y NMR spectrum of 14 (thf-d₈, 298 K: $\delta_{\rm Y}$ 666.2 ppm) gave a single resonance of a similar chemical shift value to the previously reported cationic bis(alkyl) complexes [Y(CH₂SiMe₃)₂(thf)₄]⁺[A]⁻, the low frequency shift with respect to 1 consistent with increasing nuclear charge and with the reported pattern for cationic yttrium complexes.19

¹H NMR studies of the monocationic species 6, 8–15 in thf- d_8 and CD₂Cl₂ revealed two resonances arising from the tert-butoxy groups of very similar chemical shift values ($\Delta \delta = 0.02$ ppm). Two clearly resolved peaks of different intensity arising from Ln-CH₂ and SiMe₃ protons were observed in the ¹H NMR spectrum in thf-d₈ and CD₂Cl₂ for all diamagnetic monocationic complexes, the relative intensities of which are a sensitive function of the metal and anion, whilst 9-12 gave rise to corresponding sets of resonances for the diastereotopic protons at the crown ether ligand. The diastereotopic Y-CH₂ protons were not resolved at the low temperature limit for 6 in thf-d₈ or CD₂Cl₂. The high intensity resonances arise from the respective title compounds, the ¹H and $^{13}C{^{1}H}$ NMR chemical shift values for which show a slight anion dependency (Table 3), which has been observed in our previous studies of rare-earth metal alkyl cations.¹⁹ The J(YC) coupling constants are also much larger for the monocationic compounds **6**, **13–15** than for the neutral compound **1**, which is also consistent with our earlier observations of similar compounds and can be assigned to a shorter Y–C separation.¹⁹ The low intensity resonances were assigned on the basis of their chemical shift values as minor bis(alkyl) $[Ln(CH_2SiMe_3)_2(thf)_n]^+[A]^-$ and bis(silanolate) $[Ln{OSi(O'Bu)_3}_2(thf)_n]^+[A]^-$ impurities (Scheme 3). An equilibrium between major and minor compounds in solution can be excluded, since their ratios do not change with temperature in common NMR solvents. Major and minor products were noted, but the very similar solubility of the three species prevented their separation by re-crystallisation.²⁶



The bis(alkyl) co-product may form by reaction of the Lewis or Brønsted acid with the silanolate functionality rather than the alkyl group, as noted in the attack of MAO at the Ti– or Zr–silsesquioxane bond in $[MCp''{(c-C_5H_9)_7Si_8O_{13}}(CH_2Ph)_2]$ $(Cp'' = C_5H_3(SiMe_3)_2)^{27}$ However, the ¹H, ¹¹B and ²⁷Al NMR spectroscopic studies for **6**, **8–15** indicated the formation of $[Al(CH_2SiMe_3)_4]^-$ and $[BPh_3(CH_2SiMe_3)]^-$ alone,¹⁹ while the known yttrium tris(silanolate) species $[Y{OSi(O'Bu)_3}_3(thf)_{0.5}]$ failed to react with BPh₃ or $[NEt_3H]^+[BPh_4]^-$ in the at room temperature overnight.²⁸

Redistribution of $[Ln(CH_2SiMe_3)_2(thf)_n]^+[A]^-$ to give a mixture of cationic bis(alkyl) and bis(silanolate) species is possible; such processes have been recognised for some time for rare-earth metal complexes.²⁹ Furthermore, although the siloxyaluminium alkyl cations $[Al_2\{\mu$ -OSi(OR)_3]_2Me_3(NMe_2Ph)]^+[B(C_6F_5)_4]^- (R = 'Bu, SiMe_3) and $[Al_2\{\mu$ -OSi('BuMe_2)]_2Me_3(NMe_2Ph)]^+[B(C_6F_5)_4]^-, prepared by the addition of half an equiv. per aluminium of $[NMe_2PhH]^+[B(C_6F_5)_4]^-$ to the dimeric species $[Al\{\mu$ -OSi(OR)_3]Me_2]_2 and $[Al_{\{\mu$ -OSi('BuMe_2)}]Me_2]_2, are stable

Table 3 Selected NMR data for neutral, mono- and dicationic Y tri(tert-butoxy)silanolate complexes

	Compound	δ (¹ H) LnCH ₂ [ppm]	J(YH)/Hz	δ (¹³ C) LnCH ₂ [ppm]	J(YC)/Hz	δ (⁸⁹ Y) [ppm]			
	Neutral vttrium complexes								
	$1(C_6D_6)$	-0.33	3.4	39.5	43.0	863.2			
	1 (thf-d ₈)	-1.03, -1.00, -0.92	3.1-3.4	22.3, 26.7	45.1, 38.6	_			
	Monocationic yttrium complexes								
	$6 (thf-d_8)$	-0.86	3.4	29.6	47.6	_			
	13 (thf- d_8)	-0.79	3.4	30.1	46.0	_			
	14 (thf-d ₈)	-0.83	3.4	30.2	46.3	666.2			
	15 (thf-d ₈)	-0.88	3.4		_	_			
Dicationic yttrium complexes									
	$16(C_5D_5N)$		_			133.6			

at room temperature,³⁰ reaction of the similar dimeric species $[(AlMe_2)_2\{\mu$ -OSi(1,3,5-C₆H₂Me₃)₃ $(\mu$ -Me)] with one equiv. per aluminium of $[NMe_2PhH]^+[B(C_6F_5)_4]^-$ gave redistribution to $[AlMe_2(NMe_2Ph)_2]^+[B(C_6F_5)_4]^-$, $[Al\{OSi(1,3,5$ -C₆H₂Me₃)₃ $\}_2Me]$ and other minor products.³¹

We sought a rational synthesis of the monocationic species $[Lu{OSi(O'Bu)_3}_2(thf)_4]^+[BPh_4]^-$ using $[Lu(CH_2SiMe_3)_2(thf)_4]^+$ $[BPh_4]^-$ as a starting material¹⁹ in order to compare its NMR data with those above. Thus reaction of $[Lu(CH_2SiMe_3)_2(thf)_4]^+$ $[BPh_4]^-$ with two equiv. of HOSi(O'Bu)_3 in thf gave $[Lu{OSi(O'Bu)_3}_2(thf)_4]^+$ [BPh_4]⁻ as a microcrystalline solid in 84% yield. The signals arising from the *tert*-butoxy methyl groups in both the ¹H and ¹³C{¹H} NMR spectra correspond exactly with one of the two resonances observed for these groups in the spectra of 7.³²

Dicationic complex

A thf solution of the yttrium alkyl **1** with two equiv. of $[NMe_2PhH]^+[BPh_4]^-$ gave the thf-soluble alkyl-free dication $[Y{OSi(O'Bu)_3}(thf)_6]^{2+}[BPh_4]^{-}_2$ (**16**) in 65% yield. The dicationic species **16** in thf-d₈ gave two resonances arising from the *tert*-butoxy groups of very similar chemical shift value ($\Delta \delta = 0.01$ ppm). A single, sharp resonance was observed for the *tert*-butoxy groups in C₅D₅N, whilst a single resonance was noted in the ²⁹Si NMR spectrum (thf-d₈, 298 K: $\delta_{si} - 103.3$ ppm, d, J(YSi) = 9.9 Hz). The ⁸⁹Y NMR spectrum of **16** (C₅D₅N, 298 K: δ_Y 133.6 ppm) gave a single resonance highly shifted to lower frequency with respect to the neutral and monocationic complexes. **16** reacted with one equiv. of LiCH₂SiMe₃ in thf-d₈ to give immediate formation of a mixture of **6** and **1** at room temperature; addition of a second equiv. of LiCH₂SiMe₃ yielded **1** (Scheme 4).³³



Despite repeated attempts in a variety of solvents, it was not possible to grow X-ray quality crystals of the alkyl cations 6-15. However, X-ray crystallography of crystals of 16 (see Fig. 3) grown at -30 °C in thf indicated that this compound is monomeric in the crystalline state, adopting a slightly distorted pentagonal bipyramidal geometry $(O(1)-Y-O(10) = 178.72(6)^{\circ})$. The Y-O(Si) bond length (2.0705(15) Å, Table 2) is as expected somewhat shorter than that found in the neutral congener 1; the Y–O(thf) bond lengths in 16 are within the normal range reported for Y-O(thf) bond lengths at cationic yttrium centres.³⁴ The apical silanolate functionality is η^{1} -coordinated (Y–O(^tBu) = 4.7393(15) (O2), 4.2170(15) (O3), 4.4066(16) (O4) Å, Fig. 3) and cants slightly away from linearity $(Y-O(1)-Si = 162.30(9)^{\circ})$. This bend in the Y-O(1)-Si axis and the pseudo mirror plane that bisects O(3) and O(4) through O(2)–Si–O(1)–Y (torsion angle = $176.1(3)^{\circ}$) results in two inequivalent sets of *tert*-butoxy groups (O(4) = O(3) (*cis* to Y) $\neq O(2)$ (*trans* to Y)), the torsion angles involving



Fig. 3 Molecular structure of **16** (ellipsoids drawn at the 50% probability level, hydrogen atoms, borate anions and lattice THF omitted for clarity).

O(3)–Si–O(1)–Y and O(4)–Si–O(1)–Y being 52.6(3)° and 64.5(3)° respectively. Terminal η^1 -coordinated silanolate units are known for both Sm and Gd, whilst there are no terminal η^2 -coordinated silanolate units reported for the rare-earth metals.^{8–11}

Olefin hydrosilylation

Catalytic olefin hydrosilylation using rare-earth metal complexes has recently been developed, although there are relatively few active pre-catalysts free of Cp-ligands known.35 Whilst a comparative study of olefin hydroamination with neutral and cationic rare-earth metal complexes has been reported,³⁶ no such studies concerning hydrosilylation have yet appeared in the literature.² We found that a catalytic amount of 1 in C₆D₆ gave complete hydrosilylation of 1-decene by PhSiH₃ (40 equiv., 100%) linear product) at room temperature after 2 h. Very high initial conversions are observed and the percentage conversion after a given time varies little between 10 and 40 equiv. with the same solvent volume (see ESI[†] for time-conversion plots).³⁷ Neither catalytic amounts of 4 in C_6D_6 , 6 in thf-d₈, 13 in C_6D_6 nor $1/B(C_6F_5)_3$ in C_6D_6 gave measurable activities under the same conditions. A catalytic quantity of 13 in C₆D₅Br gave 30% conversion after 20 h at room temperature (43 equiv, 100% linear product). Piers et al. have noted that, in the case of $[Sc{ArNC(Me)CHC(Me)NAr}(Me)(solv)]^+[B(C_6F_5)_4]^-$ (Ar = 2,6- $iPr_2C_6H_3$), C_6H_5Br coordinates much more weakly to the metal centre than C_6H_6 , which may explain the difference in reactivity noted between these two solvents in hydrosilylation with 13 as pre-catalyst.38

Hydrosilylation of 40 equiv. of 1-decene catalysed by **3** required 6 days for 90% conversion. Hydrosilylation of styrene (20 equiv.) with **1** in C_6D_6 gave 30% conversion to a mixture of regioisomers after 18 h at room temperature, but failed to show significant further conversion 2 days later. A deep yellow colouration was observed during the course of this reaction, likely to arise from metal–ligand charge transfer due to coordination of the aromatic ring to the relatively open metal centre.³⁹

A series of reactions were carried out in order to probe the nature of the active species derived from 1 and 13. 1 reacted completely with 2 equiv. PhSiH₃ after 3 h at 25 °C with co-formation of PhSiH₂(CH₂SiMe₃). Addition of 20 equiv. of 1-decene and PhSiH₃ to this solution initiated olefin hydrosilylation at a reduced rate from that observed directly from the alkyl complex. The formation of PhSiH₂(CH₂SiMe₃) supports the hypothesis of a hydride intermediate, however no Y–H signals were observed in the ¹H NMR spectrum.⁴⁰

The inactivity of the cationic species under most conditions was also explored by NMR-scale reactions. 6 reacted completely with 2 equiv. of PhSiH₃ in thf-d₈ after 24 h at 25 °C with concomitant $PhSiH_2(CH_2SiMe_3)$ evolution, as did 13 in C_6D_6 , however neither any reactivity of these solutions with 1-decene, nor any hydride resonances were observed. Addition of one equiv. of $B(C_6F_5)_3$ to a C_6D_6 solution of 1 gave rapid and complete loss of all Y-CH₂ resonances in the ¹H NMR spectrum and yielded highly complicated ¹⁹F and ¹H NMR spectra. The yttrium tris(silanolate) species $[Y{OSi(O'Bu)_3}_3(thf)_{0.5}]$ reacted with 1.5 equiv. of $B(C_6F_5)_3$ in C_6D_6 to give, according to NMR spectroscopy, the "inorganic" contact-ion pair [Y{OSi- $(O^{\iota}Bu)_{3}\}_{2}\{\mu\text{-}OSi(O^{\iota}Bu)_{3}\}B(C_{6}F_{5})_{3}(thf)_{\textit{n}}]^{41} \ \text{ and } \ [B(C_{6}F_{5})_{3}(thf)].^{42}$ Thus not only is the postulated alkyl cation $[Y{OSi(O^tBu)_3}]$ - $(CH_2SiMe_3)(C_6D_6)_n]^+[B(C_6F_5)_3(CH_2SiMe_3)]^-$ likely to rapidly decompose on formation at room temperature, but also the Y-O(silanolate) bond is subject to attack by $B(C_6F_5)_3$ in aromatic solvents.

Conclusions

We have demonstrated that stable, thf-free neutral rare-earth metal dialkyl complexes $[Ln{\mu,\eta^2-OSi(O'Bu)_3}(CH_2SiMe_3)_2]_2$ can be prepared from the appropriate rare-earth metal tris(alkyl) complex with tri(tert-butoxy)silanol for Ln = Y, Tb and Lu. We have also shown that monocationic, mono(alkyl) complexes $[Ln{OSi(O'Bu)_3}(CH_2SiMe_3)(thf)_4]^+[A]^-$ (Ln = Y, Tb, Lu) are isolable species with a variety of anions, although they are contaminated by a small amount of the rearranged bis(alkyl) and bis(silanolate) monocations. It is also possible to synthesize an yttrium silanolate dication $[Y{OSi(O^tBu)_3}(thf)_6]^{2+}[BPh_4]^{-2}$ reaction of which with two equiv. of trimethylsilylmethyl lithium regenerates the neutral bis(alkyl) species. Whilst hydrosilylation of 1-decene with the neutral yttrium complex $[Y{\mu,\eta^2}$ - $OSi(O^{t}Bu)_{3}$ (CH₂SiMe₃)₂]₂ proceeds rapidly at room temperature in C_6D_6 solution, the analogous lutetium complex gives a very slow reaction under identical conditions. Hydrosilylation catalysis using the monocationic yttrium complexes appears to depend on the extent of the ion pair separation, as both the nature of the solvent and the anion influenced the activity.

Experimental

General

All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. thf and toluene were distilled from sodium benzophenone ketyl. Pentane and heptane were purified by distillation from sodium/triglyme benzophenone ketyl. Anhydrous trichlorides of scandium, yttrium, terbium and lutetium (ALFA or Strem) were used as received. All other chemicals were commercially available and used after appropriate purification. NMR spectra were recorded on a Varian Unity 500 spectrometer (1H, 500 MHz, 13C, 125.6 MHz, ¹¹B, 160.3 MHz, ²⁹Si, 99.2, ²⁷Al, 130.2, ¹⁹F 470.1 MHz) or on a Bruker DRX 400 spectrometer (89Y, 19.6 MHz). Chemical shifts for ¹H and ¹³C NMR spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane.¹¹B NMR spectra were referenced externally to a 1 M solution of NaBH₄ in D₂O. ¹⁹F NMR spectra were referenced externally to CCl₃F. ²⁷Al spectra were referenced externally to a 1.1 M solution of Al(NO₃)₃ in D₂O. ²⁹Si spectra were referenced externally to a 1% solution of SiMe₄ in CDCl₃. ⁸⁹Y spectra were referenced externally to a 1 M solution of YCl₃ in D₂O. Elemental analyses were performed by the Microanalytical Laboratory of the Johannes Gutenberg-University, Mainz, Germany. The results show values low for carbon content, despite acceptable H and Ln measurements. We ascribe this difficulty, also observed by other workers, to the extreme sensitivity of the material and to the possibility of metal carbide formation during combustion.⁴³ Metal analysis was performed by complexometric titration and gave satisfactory results for all compounds.44 The sample (20 to 30 mg) was dissolved in acetonitrile (2 mL) and titrated with a 0.005 M aqueous solution of EDTA using xylenol orange as indicator and a 1 M ammonium acetate buffer solution (20 mL).

Syntheses

 $[Y{OSi(O'Bu)_3}(CH_2SiMe_3)_2]$ (1). A solution of HOSi-(O'Bu)₃ (536 mg, 2025 µmol) in pentane (20 mL) was added to a solution of $[Y(CH_2SiMe_3)_3(thf)_2]$ (1002 mg, 2025 µmol) in pentane (20 mL) at 25 °C and stirred for 1 h. The volatiles were removed under reduced pressure and the resultant slightly sticky, colourless solid dissolved in hexamethyldisiloxane (20 mL). Removal of all volatiles under reduced pressure and drying in vacuo resulted in a colourless, microcrystalline solid (925 mg, 1800 µmol, 90%). Crystals suitable for X-ray diffraction were grown by slow evaporation to dryness of a concentrated hexamethyldisiloxane solution. Found: C, 43.94, 43.82; H, 9.62, 9.44; Y, 16.74. $C_{20}H_{49}O_4Si_3Y$ requires: C, 45.60; H, 9.38; Y, 16.88%. δ_H (C₇D₈, 298 K) -0.33 (d, J(YH) = 3.36 Hz, 2 × 2 H, YCH₂SiMe₃), 0.30 (s, 2 × 9 H, YCH₂SiMe₃), 1.49 (s, 3 × 9 H, SiOC(CH₃)₃). $\delta_{\rm H}$ (C₇D₈, 213 K) -0.27 (d, 2 × 1 H, J(HH) = 11.0 Hz, YCH₂SiMe₃), -0.21 (d, 2 × 1 H, J(HH) = 11.0 Hz, YCH₂SiMe₃), 0.45 (s, 2 × 9 H, YCH₂SiMe₃), 1.39 (s, 2 \times 9 H, free SiOC(CH₃)₃), 1.54 (s, 1×9 H, coordinated SiOC(CH₃)₃). The J(YH) coupling was not resolved at the low temperature limit. $\delta_{\rm H}$ (thf-d₈, 298 K) -1.03 (d, 1.05×2 H, J(YH) = 3.1 Hz, YCH_2SiMe_3), -1.00 $(d, 0.4 \times 2 H, J(YH) = 3.4 Hz, YCH_2SiMe_3), -0.92 (d, 0.55 \times 10^{-10} Hz)$ $2 \text{ H}, J(\text{YH}) = 3.1 \text{ Hz}, \text{YCH}_2\text{SiMe}_3), -0.14, -0.13 \text{ (major)}, -0.09$ (s, 2×9 H, YCH₂SiMe₃), 1.30 (s, 1×9 H, SiOC(CH₃)₃), 1.32 (s, 2 × 9 H, SiOC(CH₃)₃). $\delta_{\rm H}$ (thf-d₈, 203 K) -1.09 (d, 1.5 × 1 H, J(HH) = 11.3 Hz, YCH_2SiMe_3 , -1.04 (d, 0.1×2 H, $J(YH) = 2.4 \text{ Hz}, YCH_2SiMe_3), -1.00 \text{ (d, } 1.5 \times 1 \text{ H}, J(HH) =$ 11.3 Hz, YCH₂SiMe₃), -0.92 (d, 0.4×2 H, J(YH) = 2.7 Hz, YCH_2SiMe_3 , -0.12, -0.07 (s, 2 × 9 H, YCH_2SiMe_3), 1.30 (s, 1×9 H, SiOC(CH₃)₃), 1.34 (s, 2×9 H, SiOC(CH₃)₃). $\delta_{\rm C}$ (C₆D₆, 298 K) 4.7 (YCH₂SiMe₃), 31.8 (SiOC(CH₃)₃), 39.5 (d, J(YC) = 43.0 Hz, YCH₂SiMe₃), 77.0 (SiOC(CH₃)₃). δ_c (thf-d₈, 298 K) 4.4,

4.6 (major), 4.8 (YCH₂Si*Me*₃), 22.3 (minor) (d, *J*(YC) = 45.1 Hz, Y*C*H₂SiMe₃), 26.7 (major) (d, *J*(YC) = 38.6 Hz, Y*C*H₂SiMe₃), 32.1 (major), 32.2 (SiOC(*C*H₃)₃), 71.2, 71.3 (major) (SiOC(*C*H₃)₃). δ_{si} (C₆D₆, 298 K) -4.12, -4.16 (CH₂SiMe₃), -95.85 (YOSi). δ_{Y} (C₆D₆, 298 K) 863.2.

[Tb{OSi(O'Bu)₃}(CH₂SiMe₃)₂] (2). A solution of HOSi-(O'Bu)₃ (88 mg, 333 µmol) in pentane (10 mL) was added to a solution of [Tb(CH₂SiMe₃)₃(thf)₂] (188 mg, 333 µmol) in pentane (10 mL) at 25 °C and stirred for 30 min. The volatiles were removed under reduced pressure and the resultant slightly sticky, colourless solid dissolved in hexamethyldisiloxane (25 mL). Removal of 15 mL solvent under reduced pressure and recrystallisation at -30 °C resulted in a colourless, crystalline solid (160 mg, 268 µmol, 81%). Found: Tb 26.00, C₂₀H₄₉O₄Si₃Tb requires: Tb, 26.63%.

 $[Lu{OSi(O'Bu)_3}(CH_2SiMe_3)_2]$ (3). A solution of HOSi-(O'Bu)₃ (520 mg, 1966 µmol) in pentane (15 mL) was added to a solution of [Lu(CH₂SiMe₃)₃(thf)₂] (1142 mg, 1966 µmol) in pentane (15 mL) at 25 °C and stirred for 30 min. The volatiles were removed under reduced pressure and the resultant slightly sticky, colourless solid dissolved in hexamethyldisiloxane (25 mL). Removal of 15 mL solvent under reduced pressure and recrystallisation at -30 °C resulted in a colourless, crystalline solid (578 mg, 944 µmol, 48%). Found: C, 35.19; H, 7.59; Lu, 28.64. C₂₀H₄₉LuO₄Si₃ requires: C, 39.20; H, 8.06; Lu, 28.55%. δ_H $(C_6D_6, 298 \text{ K}) - 0.49 \text{ (s, } 2 \times 2 \text{ H, } LuCH_2SiMe_3), 0.38 \text{ (s, } 2 \times 2 \text{ H, } LuCH_2SiMe_3)$ 9 H, LuCH₂SiMe₃), 1.49 (s, 3 × 9 H, SiOC(CH₃)₃). $\delta_{\rm H}$ (thf-d₈, 298 K) -1.16 (s, 1.35×2 H, LuCH₂SiMe₃), -1.15 (s, 0.45×10^{-1} 2 H, LuCH₂SiMe₃), -1.14 (s, 0.2×2 H, LuCH₂SiMe₃), -0.10(major), -0.09 (s, 2 × 9 H, LuCH₂SiMe₃), 1.31 (s, 1 × 9 H, SiOC(CH₃)₃), 1.32 (s, 2 × 9 H, SiOC(CH₃)₃). $\delta_{\rm C}$ (C₆D₆, 298 K) $5.1 (LuCH_2SiMe_3), 32.0 (SiOC(CH_3)_3), 45.9 (LuCH_2SiMe_3).$ The peak arising from SiOC(CH₃)₃ was not detected.

 $[Y{OSi(O'Bu)_3}(CH_2SiMe_3)_2(12\text{-crown-4})] \cdot 12\text{-crown-4}$ (4). A solution of 12-crown-4 (200 mg, 1140 µmol) in pentane (5 mL) was added to a solution of 1 (300 mg, 570 µmol) in pentane (5 mL) and vigorously shaken. After removal of trace colourless, insoluble impurities by filtration, the clear, colourless solution was cooled overnight to -30 °C. Removal of the supernatant liquid and drying for 30 min at 298 K yielded the title compound as colourless crystals (200 mg, 228 µmol, 80%). Found: C, 45.78; H, 8.68; Y, 10.03. $C_{36}H_{81}O_{12}Si_3Y$ requires: C, 49.18; H, 9.29; Y, 10.11%. δ_H $(CD_2Cl_2, 298 \text{ K}) - 1.04 \text{ (dd}, J(HH) = 11.2 \text{ Hz}, J(YH) = 3.2 \text{ Hz},$ 2×1 H, YCH₂SiMe₃), -0.88 (dd, J(HH) = 11.2 Hz, J(YH) = $3.2 \text{ Hz}, 2 \times 1 \text{ H}, \text{YCH}_2\text{SiMe}_3), -0.12 (s, 2 \times 9 \text{ H}, \text{YCH}_2\text{Si}Me_3),$ 1.32 (s, 3×9 H, SiOC(CH₃)₃), 3.62 (s, 16 H, 12-crown-4), 3.72, 4.22 (m, 16 H, 12-crown-4). $\delta_{\rm H} (C_7 D_8, 298 \text{ K}) - 0.64 \text{ (dd, } J(\rm HH) =$ 11.2 Hz, J(YH) = 3.2 Hz, 2×1 H, YCH_2SiMe_3 , -0.47 (dd, $J(HH) = 11.2 \text{ Hz}, J(YH) = 3.2 \text{ Hz}, 2 \times 1 \text{ H}, YCH_2SiMe_3), 0.32$ $(s, 2 \times 9 \text{ H}, \text{YCH}_2\text{Si}Me_3), 1.53 (s, 3 \times 9 \text{ H}, \text{SiOC}(CH_3)_3), 3.44 (s,$ 16 H, 12-crown-4), 2.88, 3.73 (m, 16 H, 12-crown-4). $\delta_{\rm H}$ (thf-d₈, 298 K) -0.95 (d, 1.7×2 H, J(YH) = 2.9 Hz, YCH₂SiMe₃), -0.79 $(d, 0.3 \times 2 H, J(YH) = 2.9 Hz, YCH_2SiMe_3), -0.12 (s, 1.7 \times 9 H)$ YCH_2SiMe_3 , -0.12 (s, 0.3×9 H, YCH_2SiMe_3), 1.32 (s, 1×9 H, SiOC(CH₃)₃), 1.34 (s, 2×9 H, SiOC(CH₃)₃), 3.44 (s (br), 32 H, 12-crown-4). $\delta_{\rm C}$ (C₆D₆, 298 K) 5.2 (YCH₂SiMe₃), 27.4 (d, J(YC) = 40.1 Hz, YCH₂SiMe₃), 32.4 (SiOC(CH₃)₃), 67.1, 71.1 (12-crown-4), 71.2 (SiOC(CH₃)₃). δ_C (thf-d₈, 298 K) 5.0 (YCH₂SiMe₃), 26.6

 $(d, J(YC) = 43.8 \text{ Hz}, YCH_2SiMe_3), 32.4, 32.5 (SiOC(CH_3)_3), 71.2$ (br) (12-crown-4), 71.4 (SiOC(CH_3)_3).

[Lu{OSi(O'Bu)₃}(CH₂SiMe₃)₂(12-crown-4)]-12-crown-4 (5). A solution of 12-crown-4 (52 mg, 294 µmol) in pentane (1 mL) was added to a solution of **3** (90 mg, 147 µmol) in pentane (2 mL) and vigorously shaken. After removal of trace colourless, insoluble impurities by filtration, the clear, colourless solution was cooled to -30 °C for 3 days. Removal of the supernatant liquid and drying for 30 min at 298 K yielded the title compound as colourless crystals (80 mg, 82 µmol, 56%). Found: Lu, 17.17. C₃₆H₈₁LuO₁₂Si₃ requires: Lu, 18.13%. $\delta_{\rm H}$ (C₆D₆, 298 K) -0.73 (d, J(HH) = 11.7 Hz, 2 × 1 H, LuCH₂SiMe₃), -0.56 (d, J(HH) = 11.7 Hz LuCH₂SiMe₃), 0.39 (s, 2 × 9 H, LuCH₂SiMe₃), 1.53 (s, 3 × 9 H, SiOC(CH₃)₃), 3.49 (s, 16 H, 12-crown-4), 2.94, 3.80 (m, 16 H, 12-crown-4). $\delta_{\rm C}$ (C₆D₆, 298 K) 5.2 (YCH₂SiMe₃), 32.0 (LuCH₂SiMe₃), 32.3 (SiOC(CH₃)₃), 68.1, 71.3, 71.5 (12-crown-4).

 $[Y{OSi(O^{t}Bu)_{3}}(CH_{2}SiMe_{3})(thf)_{4}]^{+}[BPh_{4}]^{-}$ (6). A solution of $[NEt_3H]^+[BPh_4]^-$ (401 mg, 952 µmol) in thf (15 mL) was added to a solution of 1 (501 mg, 952 µmol) in thf (15 mL) at 0 °C and stirred for 1 h at the same temperature. The volatiles were removed under reduced pressure and the resultant colourless solid dried for 2 h in vacuo to give a colourless, microcrystalline solid (901 mg, 860 µmol, 90%). Found: C, 62.13, 62.01; H, 8.69, 8.91; Y, 8.30. $C_{56}H_{90}BO_8Si_2Y$ requires: C, 64.23; H, 8.66; Y, 8.49%. δ_H (thf-d₈, 298 K) $-0.86 (d, J(YH) = 3.4 \text{ Hz}, 1.25 \times 2 \text{ H}, YCH_2 \text{SiMe}_3), -0.78$ $(d, J(YH) = 3.1 \text{ Hz}, 0.75 \times 2 \text{ H}, YCH_2SiMe_3), -0.09, -0.06 (s, -0.06)$ 9 H, YCH₂SiMe₃), 1.32, 1.33 (s, 3×9 H, SiOC(CH₃)₃), 6.73 (t, J(HH) = 7.2 Hz, 4 H, 4-Ph), 6.86 (m, 8 H, 3-Ph), 7.27 (s (br), 8 H,2-Ph). $\delta_{\rm H}$ (CD₂Cl₂, 298 K) -0.86 (d, J(YH) = 3.4 Hz, 1.25 × 2 H, YCH_2SiMe_3 , -0.10 (s, 9 H, YCH_2SiMe_3), 1.29, 1.31 (s, 3 × 9 H, SiOC(CH₃)₃), 1.97 (s, 4×4 H, β -thf), 3.99 (s, 4×4 H, α -thf), 6.87 $(t, J(HH) = 7.0 \text{ Hz}, 4 \times 1 \text{ H}, 4\text{-Ph}), 7.02 (m, 4 \times 2 \text{ H}, 3\text{-Ph}), 7.30$ (m (br), 4 × 2 H, 2-Ph). $\delta_{\rm H}$ (CD₂Cl₂, 263 K) -0.88 (d, J(YH) = $3.4 \text{ Hz}, 1.25 \times 2 \text{ H}, \text{YC}H_2\text{SiMe}_3), -0.77 \text{ (d}, J(\text{YH}) = 3.1 \text{ Hz},$ 0.75×2 H, YCH₂SiMe₃), -0.10, -0.06 (s, 9 H, YCH₂SiMe₃), 1.28, 1.30 (s, 3×9 H, SiOC(CH₃)₃), 1.99 (s, 4×4 H, β -thf), 4.01 $(s, 4 \times 4 \text{ H}, \alpha\text{-thf}), 6.89 (t, J(\text{HH}) = 7.2 \text{ Hz}, 4 \times 1 \text{ H}, 4\text{-Ph}), 7.04$ $(m, 4 \times 2 H, 3-Ph), 7.30 (m (br), 4 \times 2 H, 2-Ph). \delta_{C} (thf-d_{8}, 298 K)$ 3.9, 4.1 (YCH₂SiCH₃), 29.6 (d, J(YC) = 47.6 Hz, YCH₂SiCH₃), 32.0, 32.1 (SiOC(CH₃)₃), 72.0, 72.1 (SiOC(CH₃)₃), 121.6 (Ph-4), 125.5 (Ph-3), 136.9 (Ph-2), 164.9 (q, J(BC) = 49.6 Hz, Ph-1). $\delta_{\rm B}$ $(thf-d_8, 298 \text{ K}) - 6.6.$

[Tb{OSi(O'Bu)₃}(CH₂SiMe₃)(thf)₄]*[BPh₄]⁻ (7). A solution of [NEt₃H]⁺[BPh₄]⁻ (113 mg, 268 µmol) in thf (15 mL) was added to a solution of 2 (160 mg, 268 µmol) in thf (15 mL) at -78 °C and stirred for 30 min at 0 °C and overnight at room temperature. The volatiles were removed under reduced pressure and the resultant colourless, waxy solid dried for 30 min *in vacuo* and washed with pentane (2 × 15 mL) to give a colourless, microcrystalline solid (200 mg, 179 µmol, 67%). Found: Tb, 14.01, C₅₆H₉₀BO₈Si₂Tb requires: Tb, 14.23%.

[Lu{OSi(O'Bu)₃}(CH₂SiMe₃)(thf)₄]⁺[BPh₄]⁻ (8). A solution of [NEt₃H]⁺[BPh₄]⁻ (379 mg, 898 μ mol) in thf (20 mL) was added to a solution of 3 (550 mg, 898 μ mol) in thf (20 mL) at 0 °C and stirred for 1 h at the same temperature. The volatiles were removed under reduced pressure and the resultant colourless solid dried for 2 h *in vacuo* to give a colourless, microcrystalline

solid (810 mg, 715 μmol, 80%). Found: C, 57.12; H, 8.56; Lu, 15.25. $C_{56}H_{90}BLuO_8Si_2$ requires: C, 59.35; H, 8.00; Lu, 15.44%. $\delta_{\rm H}$ (CD₂Cl₂, 298 K) –1.00 (major), –0.97 (s, 2 H, LuCH₂SiMe₃), –0.06 (major), –0.04 (s, 9 H, LuCH₂SiMe₃), 1.29, 1.32 (s, 3 × 9 H, SiOC(CH₃)₃), 1.97 (s, 4 × 4 H, β-thf), 3.99 (s, 4 × 4 H, α-thf), 6.87 (t, *J*(HH) = 7.0 Hz, 4 × 1 H, 4-Ph), 7.02 (m, 4 × 2 H, 3-Ph), 7.30 (m (br), 4 × 2 H, 2-Ph). $\delta_{\rm C}$ (CD₂Cl₂, 298 K) 4.0, 4.3 (major) (LuCH₂SiCH₃), 25.7 (β-thf), 32.0, 32.1 (SiOC(CH₃)₃), 32.8 (LuCH₂SiCH₃), 71.7 (α-thf), 72.1, 72.2 (SiOC(CH₃)₃), 122.1 (Ph-4), 126.0 (Ph-3), 136.4 (Ph-2), 164.3 (q, *J*(BC) = 50.0 Hz, Ph-1). $\delta_{\rm B}$ (thf- d_8 , 298 K) –6.6.

 $[Y{OSi(O'Bu)_3}(CH_2SiMe_3)(12-crown-4)(thf)]^+[BPh_4]^-(9).$ A solution of 12-crown-4 (39 mg, 220 µmol) in heptane (1 mL) was added to a suspension of 5 (202 mg, 193 µmol) in heptane (10 mL) and stirred rapidly for 1 h at room temperature. The supernatant liquid was removed and the resultant colourless microcrystalline solid dried in vacuo for 1 h to give 6 (166 mg, 170 µmol, 89%). Found: C, 61.18, 60.97; H, 8.59, 8.45; Y, 8.81. C₅₂H₈₂BO₉Si₂Y requires: C, 62.02; H, 8.21; Y, 8.83%. δ_H (CD₂Cl₂, 298 K) -0.98 $(d, J(YH) = 2.8 Hz, 0.88 \times 2 H, YCH_2SiMe_3), -0.86 (d, J(YH) =$ $3.1 \text{ Hz}, 0.12 \times 2 \text{ H}, \text{YCH}_2\text{SiMe}_3), -0.13 \text{ (major)}, -0.12 \text{ (minor)}$ (s, 9 H, YCH₂SiMe₃), 1.27, 1.29 (s, 3×9 H, SiOC(CH₃)₃), 1.97 (s, 1 × 4 H, β -thf), 3.32, 3.74 (m, 0.88 × 16 H, 12-crown-4), 3.38, $3.96 \text{ (m, } 0.16 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12, 3.66 \text{ (m, } 0.02 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12 \times 16 \text{ H, } 12\text{-crown-4}\text{)}, 3.12 \times 16 \text{-crown-4}\text{)}, 3.12 \times 16 \text{-crown-4}\text{)}, 3.12 \times 16 \text{-crown-4}\text{)}, 3.12 \times 16 \text{-crown-4}\text{)}, 3.12 \times 16 \text{-crown-4}\text{)$ 12-crown-4), 4.07 (s, 1 × 4 H, α -thf), 6.93 (t, J(HH) = 7.3 Hz, 4 H, 4-Ph), 7.08 (m, 4 \times 2 H, 3-Ph), 7.38 (m (br), 4 \times 2 H, 2-Ph). $\delta_{\rm C}$ $(CD_2Cl_2, 298 \text{ K}) 3.9 (YCH_2SiCH_3), 25.7 (\beta-thf), 27.8 (d, J(YC) =$ 44.6 Hz, YCH₂SiCH₃), 31.8 (SiOC(CH₃)₃), 67.7 (α-thf), 68.0, 70.0, 71.5, 71.6, 71.6 (12-crown-4, SiOC(CH₃)₃), 122.4 (Ph-4), 126.1 (Ph-3), 136.3 (Ph-2), 164.3 (q, J(BC) = 49.7 Hz, Ph-1). $\delta_{\rm B}$ (CD₂Cl₂, 298 K) -6.7.

 $[Lu{OSi(O^{t}Bu)_{3}}(CH_{2}SiMe_{3})(12-crown-4)(thf)]^{+}[BPh_{4}]^{-}$ (10). A solution of 12-crown-4 (31 mg, 178 µmol) in heptane (1 mL) was added to a suspension of 7 (202 mg, 178 µmol) in heptane (10 mL) and stirred rapidly for 1 h at room temperature. The supernatant liquid was removed and the resultant colourless microcrystalline solid washed with a 1:5 thf: heptane mixture and dried in vacuo for 1 h (148 mg, 145 µmol, 81%). Found: C, 53.23; H, 6.86; Lu, 15.71. C₅₂H₈₂BLuO₉Si₂ requires: C, 57.13; H, 7.56; Lu, 16.01%. δ_H $(CD_2Cl_2, 298 \text{ K}) - 1.14 \text{ (br, major)}, -1.10 \text{ (s, 2 H, LuCH}_2SiMe_3),$ -0.13 (major), -0.11 (s, 9 H, LuCH₂SiMe₃), 1.26, 1.28 (s, 3 × 9 H, SiOC(CH₃)₃), 1.97 (s, 4 H, β -thf), 3.05–4.30 (m, 20 H, 12crown-4 and thf), 6.93 (t, J(HH) = 7.2 Hz, $4 \times 1 \text{ H}$, 4-Ph), 7.07 (m, 4 × 2 H, 3-Ph), 7.37 (m (br), 4 × 2 H, 2-Ph). $\delta_{\rm C}$ (thf-d₈, 298 K) 4.2 (LuCH₂SiCH₃), 25.7 (α-thf), 30.9 (LuCH₂SiCH₃), 31.8, 31.9 (SiOC(*C*H₃)₃), 67.1, 67.9, 68.1, 68.2, 70.1 (12-crown-4, β-thf), 71.7, 71.8 (SiOC(CH₃)₃), 121.6 (Ph-4), 125.5 (Ph-3), 136.9 (Ph-2), 164.9 $(q, J(BC) = 49.0 \text{ Hz}, \text{Ph-1}). \delta_{B} (\text{thf-d}_{8}, 298 \text{ K}) - 6.6.$

[Y{OSi(O'Bu)₃}(CH₂SiMe₃)(15-crown-5)]⁺[BPh₄]⁻ (11). A solution of 15-crown-5 (49 mg, 220 μmol) in heptane (1 mL) was added to a suspension of **5** (201 mg, 178 μmol) in heptane (10 mL) and stirred rapidly for 1 h at room temperature. The supernatant liquid was removed and the resultant colourless microcrystalline solid dried *in vacuo* for 1 h to give **8** (142 mg, 140 μmol, 76%). Trace thf was noted in the ¹H NMR spectrum (0.25 equiv.). Found: C, 60.32, 60.33; H, 8.50, 8.42; Y, 8.87. C₅₀H₇₈BO₉Si₂Y requires: C, 61.34; H, 8.03; Y, 9.08%. δ_H (CD₂Cl₂, 298 K) –0.93

(d, J(YH) = 3.1 Hz, $0.7 \times 2 \text{ H}$, $YCH_2\text{SiMe}_3$), -0.89 (d, J(YH) = 3.4 Hz, $0.3 \times 2 \text{ H}$, $YCH_2\text{SiMe}_3$), -0.12 (major), -0.09 (minor) (s, 9 H, YCH_2Si Me_3), 1.28, 1.30 (s, $3 \times 9 \text{ H}$, SiOC(CH_3)₃), 3.54, 3.94 (m, $0.7 \times 20 \text{ H}$, 15-crown-5), 3.61, 4.15 (m, $0.3 \times 20 \text{ H}$, 15-crown-5), 3.45, 3.75 (m, $0.05 \times 20 \text{ H}$, 15-crown-5), 6.93 (t, J(HH) = 7.3 Hz, $4 \times 1 \text{ H}$, 4-Ph), 7.07 (m, $4 \times 2 \text{ H}$, 3-Ph), 7.37 (m (br), $4 \times 2 \text{ H}$, 2-Ph). δ_{C} (CD₂Cl₂, 298 K) 4.1 (YCH₂SiCH₃), 26.3 (d, J(YC) = 45.5 Hz, YCH₂SiCH₃), 32.0 (SiOC(CH_3)₃), 69.2, 69.4, 69.6, 71.6, 71.7 (15-crown-5, SiOC(CH_3)₃), 122.4 (Ph-4), 126.2 (Ph-3), 136.3 (Ph-2), 164.2 (q, J(BC) = 49.7 Hz, Ph-1). δ_{B} (CD₂Cl₂, 298 K) –6.7.

 $[Lu{OSi(O^{t}Bu)_{3}}(CH_{2}SiMe_{3})(15-crown-5)]^{+}[BPh_{4}]^{-}$ (12). A solution of 15-crown-5 (41 mg, 186 µmol) in heptane (1 mL) was added to a suspension of 7 (204 mg, 180 µmol) in heptane (10 mL) and stirred rapidly for 1 h at room temperature. The supernatant liquid was removed and the resultant colourless microcrystalline solid washed with a 1:5 thf: heptane mixture and dried in vacuo for 1 h (143 mg, 134 µmol, 72%). Found: C, 55.57; H, 8.47; Lu, 16.32. C₅₀H₇₈BLuO₉Si₂ requires: C, 56.38; H, 7.38; Lu, 16.43%. δ_H (CD₂Cl₂, 298 K) -1.18, -1.11 (major) (s, 2 H, LuCH₂SiMe₃), -0.12 (major), -0.09 (s, 9 H, LuCH₂SiMe₃), 1.28, 1.30 (s, 3 × 9 H, SiOC(CH₃)₃), 3.54, 3.95 (m, 0.62×20 H, 15-crown-5), 3.61, 4.15 (m, 0.26×20 H, 15-crown-5), 3.45, 3.75 (m, 0.12×20 H, 15crown-5), 6.92 (t, J(HH) = 7.0 Hz, $4 \times 1 \text{ H}$, 4-Ph), 7.06 (m, $4 \times 1 \text{ H}$) 2 H, 3-Ph), 7.36 (m (br), 4 \times 2 H, 2-Ph). $\delta_{\rm C}$ (CD₂Cl₂, 298 K) 4.3 (LuCH₂SiCH₃), 29.1 (major), 36.8 (LuCH₂SiCH₃), 31.9, 32.0 (SiOC(CH₃)₃), 69.2, 69.5, 69.7, 69.9, 70.5 (15-crown-5), 71.6, 71.7 (SiOC(CH₃)₃), 122.4 (Ph-4), 126.1 (Ph-3), 136.3 (Ph-2), 164.3 (q, J(BC) = 49.0 Hz, Ph-1). $\delta_{\rm B}$ (thf-d₈, 298 K) -6.6.

 $[Y{OSi(O^{t}Bu)_{3}}(CH_{2}SiMe_{3})(thf)_{4}]^{+}[B(C_{6}F_{5})_{4}]^{-}$ (13). A solution of 1 in thf (30 mL) was added to $[NMe_2PhH]^+[B(C_6F_5)_4]^-$ (200 mg, 379 µmol) and stirred for 10 min at this temperature, 30 min at 0 °C and 15 min at room temperature. The volatiles were removed under reduced pressure and the resultant pale yellow oil dried for 30 min in vacuo. Pentane was added and the resultant oily dispersion stirred for 30 min at room temperature, cooled to -78 °C, at which temperature a colourless microcrystalline solid was observed. Removal of the liquid phase via cannula and drying of the solid *in vacuo* gave **10** as a colourless, microcrystalline solid (440 mg, 313 µmol, 83%). Found: C, 44.65; H, 3.89; Y, 6.54. C₅₆H₇₀BF₂₀O₈Si₂Y requires: C, 47.80; H, 5.01; Y, 6.32%. δ_H (C₆D₆, 298 K after 18 h at 298 K) -0.86 (d, J(YH) = 3.4 Hz, 1.5×2 H, YCH_2SiMe_3 , -0.80 (d, J(YH) = 3.1 Hz, 0.5×2 H, YCH_2SiMe_3), 0.16, 0.18 (s, 9 H, YCH₂SiMe₃), 1.31 (s, 3×9 H, SiOC(CH₃)₃), 1.51 (s, 4 \times 4 H, β -thf), 3.66 (s, 4 \times 4 H, α -thf). $\delta_{\rm H}$ (thf-d₈, 298 K) -0.79 (d, J(YH) = 3.4 Hz, 1.5×2 H, YCH_2SiMe_3), -0.69 (d, J(YH) = 3.4 Hz, 0.5×2 H, YCH_2SiMe_3), 0.09, 0.02 (s, 9 H, YCH₂SiMe₃), 1.32, 1.33 (s, 3×9 H, SiOC(CH₃)₃). $\delta_{\rm C}$ $(thf-d_8, 298 \text{ K}) 3.8, 4.0 \text{ (major)} (YCH_2SiCH_3), 30.1 \text{ (d, } J(YC) =$ 46.0 Hz, YCH₂SiCH₃), 31.8, 31.9, 32.0 (SiOC(CH₃)₃), 71.7, 72.1, 72.2 (SiOC(CH₃)₃), 125.0 (m (br), C₆F₅-1), 137.9 (m, C₆F₅-3, C₆F₅-4), 148.9 (d, ${}^{1}J_{CF} = 243.4$ Hz, C₆F₅-2). δ_{B} (thf-d₈, 298 K) -16.7. $\delta_{\rm F}$ (C₆D₆, 298 K after 18 h at 298 K) -166.2, -162.1, -131.6. $\delta_{\rm F}$ (thf-d₈, 298 K) -168.5, -165.0, -132.8. $\delta_{\rm Si}$ (thf-d₈, 298 K) -0.2 (CH₂SiMe₃), -99.8 (d, J(YSi) = 9.7 Hz, SiOC(CH₃)₃), 100.2 $(SiOC(CH_3)_3).$

 $[Y{OSi(O^{\dagger}Bu)_{3}}(CH_{2}SiMe_{3})(thf)_{4}]^{+}[Al(CH_{2}SiMe_{3})_{4}]^{-}$ (14). A solution of Al(CH₂SiMe₃)₃ (241 mg, 835 µmol) in thf (0.5 mL) was added to a thf solution (2 mL) of 1 (440 mg, 835 µmol) at room temperature and left for 24 h at this temperature. The volatiles were removed from the resultant pale green solution and the resultant pale green/yellow oil dried for 1 h in vacuo. Due to the difficulty of handling this material, the yield and elemental analysis were not determined. $\delta_{\rm H}$ (thf-d₈, 298 K) -1.29 (m (br), 4×2 H, AlCH₂SiMe₃), -0.83 (d, J(YH) = 3.4 Hz, 1.75 × 2 H, YCH₂SiMe₃), -0.74 (d, J(YH) = 3.1 Hz, 0.25×2 H, YCH_2SiMe_3 , -0.17 (s, 4 × 9 H, AlCH₂SiMe₃), -0.13, -0.08 (s, 9 H, YCH₂SiMe₃), 1.27, 1.29 (s, 3 × 9 H, SiOC(CH₃)₃). $\delta_{\rm C}$ $(thf-d_8, 298 \text{ K}) 1.7 (sextet, AlCH_2SiMe_3, J(AlC) = 63.0 \text{ Hz}), 2.8,$ 3.9, 4.0 (AlCH₂Si Me_3 , YCH₂Si Me_3), 30.2 (d, J(YC) = 46.3 Hz, YCH₂SiCH₃), 31.9, 32.0 (SiOC(CH₃)₃), 72.0, 72.1 (SiOC(CH₃)₃). δ_{A1} (thf-d₈, 298 K) 150.1. δ_{Si} (thf-d₈, 298 K) -0.2 (CH₂SiMe₃), -99.6 (d, J(YSi) = 10.6 Hz, $SiOC(CH_3)_3$), 100.1 (d, J(YSi) =9.6 Hz, SiOC(CH₃)₃). $\delta_{\rm Y}$ (thf- d_8 , 298 K) 666.2.

[Y{OSi(O'Bu)₃}(CH₂SiMe₃)(thf)₄]⁺[BPh₃(CH₂SiMe₃)]⁻ (15). thf-d₈ was added to a mixture of 1 (50 mg, 95 μmol) and BPh₃ (23 mg, 95 μmol) at room temperature. Spectra were measured after standing for 30 min at room temperature. $\delta_{\rm H}$ (thf-d₈, 298 K) -0.88 (d, J(YH) = 3.4 Hz, 1 × 2 H, YCH₂SiMe₃), -0.80 (d, J(YH) = 3.1 Hz, 1 × 2 H, YCH₂SiMe₃), -0.48 (s, 1 × 9 H, BCH₂SiMe₃), -0.09, -0.06 (s, 9 H, YCH₂SiMe₃), 0.18 (q, J(BH) = 5.0 Hz, 1 × 2 H, BCH₂SiMe₃), 1.33, 1.32 (s, 3 × 9 H, SiOC(CH₃)₃), 6.66 (t, J(HH) = 7.2 Hz, 4 × 1 H, 4-Ph), 6.83 (m, 4 × 2 H, 3-Ph), 7.37 (m (br), 4 × 2 H, 2-Ph). $\delta_{\rm B}$ (thf-d₈, 25 °C) -10.4 (major), 73.3 (minor).

 $[Y{OSi(O^{t}Bu)_{3}}(thf)_{6}]^{2+}[BPh_{4}]^{-}_{2}$ (16). thf (20 mL) was added to a mixture of 1 (263 mg, 500 μ mol) and [NMe₂PhH]⁺[BPh₄]⁻ (552 mg, 1250 μ mol) at -78 °C, warmed slowly to room temperature and stirred overnight. The volatiles were removed under reduced pressure and the resultant pale yellow oil dried for 30 min in vacuo. This solid was washed with diethyl ether (20 mL) and heptane (20 mL) and dried for 1 h in vacuo to yield a fine, off-white powder (460 mg, 323 µmol, 65%). Single crystals were grown from a highly concentrated thf solution at -30 °C. Found: C, 63.76; H, 7.12; Y, 6.52. C₈₄H₁₁₅B₂O₁₀SiY requires: C, 70.88; H, 8.14; Y, 6.25%. $\delta_{\rm H}$ (thf-d₈, 298 K) 1.31, 1.32 (s, 3 × 9 H, SiOC(CH₃)₃), 6.76 (t, J(HH) = 7.0 Hz, 8 × 1 H, 4-Ph), 6.90 (m, 8 × 2 H, 3-Ph), 7.29 (m (br), 8 × 2 H, 2-Ph). $\delta_{\rm H}$ (C₅D₅N, 298 K) 1.52 (s, 3×9 H, SiOC(CH₃)₃), 1.62 (m, 6×4 H, β -thf), 3.66 (s, 6×4 H, α -thf), 7.10 (t, J(HH) = 7.0 Hz, 8×1 H, 4-Ph), 7.26 (m, 8 × 2 H, 3-Ph), 8.05 (m (br), 8 × 2 H, 2-Ph). $\delta_{\rm C}$ (thf-d₈, 298 K) 32.2, 32.3 (SiOC(CH₃)₃), 73.4, 72.2 (SiOC(CH₃)₃), 121.9 (Ph-4), 125.7 (Ph-3), 136.9 (Ph-2), 164.9 (q, J(BC) = 49.8 Hz, Ph-1). $\delta_{\rm C}$ (C₅D₅N, 298 K) 26.0 (β-thf), 32.2, 32.4 (SiOC(CH₃)₃), 68.0 (α-thf), 72.4, 73.2 (SiOC(CH₃)₃), 122.5 (Ph-4), 126.3 (Ph-3), 137.3 (Ph-2), 164.0 (q, J(BC) = 48.7 Hz, Ph-1). δ_B (thf-d₈, 298 K) -6.6. $\delta_{\rm B}$ (C₅D₅N, 298 K) -4.25. $\delta_{\rm Si}$ (thf-d₈, 298 K) -103.3 (d, J(YSi) = 9.9 Hz, YOSi). δ_Y (C₅D₅N, 298 K) 133.6.

Hydrosilylation

In a typical experiment, an NMR tube was charged with 0.03 mmol pre-catalyst, 0.30–1.20 mmol PhSiH₃, 0.30–1.20 mmol olefin and 0.5 mL C₆D₆. In order to determine the progress of the reaction,

¹H NMR spectra with relatively short delay and acquisition times (typically $d_1 = 0.2$ s, nt = 32) were taken at regular intervals and the degree of conversion calculated from the relative intensities of the product and starting material resonances.

Crystallography

X-Ray diffraction data were collected on a Bruker CCD platform diffractometer equipped with a CCD detector. The SMART program package was used to determine the unit-cell parameters and for data collection; the raw frame data was processed using SAINT and SADABS to yield the reflection data file.⁴⁵ Subsequent calculations were carried out using the SHELXS and SHELXL programs.⁴⁶ Analytical scattering factors for neutral atoms were used throughout the analysis.⁴⁷ The structures of 1, **5** and **16** were solved by direct methods and Fourier difference analyses. Hydrogen atoms were included at calculated positions. The structure of [Sc{OSi(O'Bu)₃}(CH₂SiMe₃)₂],¹⁵† was solved by isotypic replacement using the coordinates of **1**.

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For crystallographic data in CIF or other electronic format see DOI: 10.1039/b512285f

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References and notes

- 1 S. Arndt and J. Okuda, Chem. Rev., 2002, 102, 1953.
- 2 S. Arndt and J. Okuda, Adv. Synth. Catal., 2005, 347, 339.
- 3 (a) S. Arndt, T. P. Spaniol and J. Okuda, Angew. Chem., Int. Ed., 2003, 42, 5075; (b) B. D. Ward, S. Bellemin-Laponnaz and L. H. Gade, Angew. Chem., Int. Ed., 2005, 44, 1668.
- 4 (a) W. E. Piers and D. J. H. Emslie, *Coord. Chem. Rev.*, 2002, 233, 131;
 (b) F. T. Edelmann, D. M. M. Freckmann and H. Schumann, *Chem. Rev.*, 2002, 102, 1851; (c) J. Gromada, J. F. Carpentier and A. Mortreux, *Coord. Chem. Rev.*, 2004, 248, 397.
- 5 (a) F. J. Feher, J. Am. Chem. Soc., 1986, 108, 3850; (b) W. A. Hermann, R. Anwander and V. Dufaud, Angew. Chem., Int. Ed. Engl., 1994, 33, 1285; (c) R. Murugavel, A. Voigt, M. G. Walawalkar and H. W. Roesky, Chem. Rev., 1996, 96, 2205; (d) J. Annand, H. C. Aspinall and A. Steiner, Inorg. Chem., 1999, 38, 3941; (e) L. King and A. C. Sullivan, Coord. Chem. Rev., 1999, 189, 19; (f) H. C. Aspinall and J. Annand, J. Chem. Soc., Dalton Trans., 2000, 1867; (g) G. G. Hlatky, Chem. Rev., 2000, 100, 1347; (h) H. C. L. Abbenhuis, Chem. Eur. J., 2000, 6, 25; (i) V. Lorenz, A. Fischer, S. Giessman, J. W. Gilje, Y. K. Gunko, K. Jacob and F. T. Edelmann, Coord. Chem. Rev., 2000, 206-207, 321; (j) Y. K. Gunko, R. Reilly, F. T. Edelmann and H. G. Schmidt, Angew. Chem., Int. Ed., 2001, 40, 1279; (k) V. Lorenz, A. Fischer and F. T. Edelmann, J. Organomet. Chem., 2002, 647, 245; (1) R. Duchateau, Chem. Rev., 2002, 102, 3525; (m) C. Copéret, M. Chabanas, R. P. Saint-Arroman and J.-M. Basset, Angew. Chem., Int. Ed., 2003, 42, 156; (n) R. W. J. M. Hanssen, R. A. van Santen and H. C. L. Abbenhuis, Eur. J. Inorg. Chem., 2004, 675.
- 6 (a) K. W. Terry and T. D. Tilley, *Chem. Mater.*, 1991, 3, 1001; (b) K. W. Terry, P. K. Ganzel and T. D. Tilley, *Chem. Mater.*, 1992, 4, 1290; (c) R. Murugavel, V. Chandrasekhar and H. W. Roesky, *Acc. Chem. Res.*, 1996, 29, 183; (d) R. Murugavel, M. Bhattachargee and H. W. Roesky, *Appl. Organomet. Chem.*, 1997, 13, 227; (e) J. Jarupatrakorn, M. P. Coles and T. D. Tilley, *Chem. Mater.*, 2005, 17, 1818.

- 7 (a) Y. Abe and I. Kijima, Bull. Chem. Soc. Jpn., 1969, 42, 1148; (b) Y. Abe and I. Kijima, Bull. Chem. Soc. Jpn., 1970, 43, 466; (c) I. Kijima, T. Yamamoto and Y. Abe, Bull. Chem. Soc. Jpn., 1971, 44, 3193; (d) Y. Abe, K. Hayama and I. Kijima, Bull. Chem. Soc. Jpn., 1972, 45, 1258.
- 8 A. Fischbach, M. G. Klimpel, M. Widenmeyer, E. Herdtweck, W. Scherer and R. Anwander, *Angew. Chem.*, *Int. Ed.*, 2004, 43, 2234.
- 9 A. Fischbach, G. Eickerling, W. Scherer, E. Herdtweck and R. Anwander, Z. Naturforsch., Teil B, 2004, 1353.
- 10 (a) S. Ko, Y. Wakatsuki and M. Nishiura (Institute of Physical and Chemical Research, Japan), Jpn. Pat., 11 255 776 A2, 1999S. Ko, Y. Wakatsuki and M. Nishiura, Chem. Abstr., 1999, 131, 229166; (b) M. Nishiura, Z. Hou, T. Imamoto and Y. Wakatsuki, Kidorui, 1998, 32, 294.
- 11 (a) Z. Hou and Y. Wakatsuki, J. Organomet. Chem., 2002, 647, 61; (b) M. Nishiura, Z. Hou and Y. Wakatsuki, Organometallics, 2004, 23, 1359.
- 12 (a) R. Duchateau, R. A. van Santen and G. P. A. Yap, Organometallics, 2000, 19, 809; (b) M. D. Skowronska-Ptasinska, R. Duchateau, R. A. van Santen and G. P. A. Yap, Organometallics, 2001, 20, 3519; (c) G. Jimenez, P. Royo, T. Cuenca and M. Galakhov, Organometallics, 2001, 20, 5237; (d) V. Amo, R. Andrés, E. de Jesús, F. J. de la Mata, J. C. Flores, R. Gómez, M. P. Gómez-Sal and J. F. C. Turner, Organometallics, 2005, 24, 2331.
- [Ln(CH₂SiMe₃)₃(thf)_n] (n = 2 for Ln = Lu, Sc; n = 2, 3 for Ln = Y, Tb) were prepared according to literature procedures: (a) M. F. Lappert and R. Pearce, J. Chem. Soc., Chem. Commun., 1973, 126; (b) W. J. Evans, J. C. Brady and J. W. Ziller, J. Am. Chem. Soc., 2001, 123, 7711; (c) H. Schumann, D. M. M. Freckmann and S. Dechert, Z. Anorg. Allg. Chem., 2002, 628, 2422.
- 14 Synthesis of the scandium analogue was hampered by the formation of various by-products tentatively assigned by NMR spectroscopy and complexometric titration as $[Sc{OSi(O'Bu)_3}_2(CH_2SiMe_3)]$ and $[Sc{OSi(O'Bu)_3}_3]$. The successful synthesis required thf solvent and low temperature conditions to give $[Sc{OSi(O'Bu)_3}(CH_2SiMe_3)_2]$ in a very low yield.
- 15 The molecular structure of [Sc{OSi(O'Bu)₃}(CH₂SiMe₃)₂] is isotypic to that of **1**. Selected bond lengths (Å) and angles (°): Sc(1)–C(1) 2.225(3), Sc(1)–C(5) 2.192(3), Sc(1)–O(1) 2.207(2), Sc(1)–O(2) 2.213(2), Sc(1)–O(6) 2.063(2); C(1)–Sc(1)–C(5) 109.96(13), O(1)–Sc(1)–O(2) 66.57(8), O(2)–Sc(1)–O(6) 74.69(8), O(1)–Si(3)–O(2) 94.64(11). Further details are given in the ESI⁺.
- 16 D. J. Emslie, W. E. Piers, M. Parvez and R. McDonald, Organometallics, 2002, 21, 4226 and references cited therein.
- 17 K. W. Terry, C. G. Lugmair and T. D. Tilley, J. Am. Chem. Soc., 1997, 119, 9745.
- 18 J. Beckmann, D. Dakternieks, A. Duthie, M. L. Larchin and E. R. T. Tiekink, *Appl. Organomet. Chem.*, 2003, 17, 52.
- 19 B. R. Elvidge, S. Arndt, P. M. Zeimentz, T. P. Spaniol and J. Okuda, *Inorg. Chem.*, 2005, 44, 6777.
- 20 K. Su, T. D. Tilley and M. J. Sailor, J. Am. Chem. Soc., 1996, 118, 3459.
- 21 P. B. Hitchcock, M. F. Lappert, R. G. Smith, R. A. Bartlett and P. P. Power, J. Chem. Soc., Chem. Commun., 1988, 1007.
- 22 Coalescence of a second low intensity resonance was also observed at a similar temperature, but the coupling pattern at low temperature was obscured by the larger multiplet. See ESI† for VT spectra.
- 23 S. Arndt, P. M. Zeimentz, T. P. Spaniol, J. Okuda, M. Honda and K. Tatsumi, *Dalton Trans.*, 2003, 3622.
- 24 (a) [LuCp₂(CH₂SiMe₃)(thf)]: Lu-C = 2.376(16) Å, see: H. Schumann, W. Genthe and N. Bruncks, Angew. Chem., Int. Ed. Engl., 1981, 20, 129; H. Schumann, W. Genthe, N. Bruncks and J. Pickardt, Organometallics, 1982, 1, 1194; (b) [Li(thf)₃]*[Lu(η⁵-C₅Me₅)-(CH₂SiMe₃){CH(SiMe₃)₂}Cl]⁻: Lu-C = 2.314(18), 2.344(18) Å (two crystallographically independent molecules), see: H. van der Heijden, P. Pasman, E. J. M. de Boer, C. J. Schaverien and A. G. Orpen, Organometallics, 1989, 8, 1459; (c) [(C₆H₃(Me₂NCH₂)₂-2,6)Lu(µ-Cl)(CH₂SiMe₃)]₂: Lu-C = 2.39(3) Å, see: M. P. Hogerheide, D. M. Grove, J. Boersma, J. T. B. H. Jastrzebski, H. Kooijman, A. L. Spek and G. van Koten, Chem. Eur. J., 1995, 1, 343; (d) [Li(thf)₄]*[Lu(CH₂SiMe₃)₂(OC₆H₃'Bu₂-2,6)₂]⁻: 2thf: Lu-C = 2.29(2), 2.42(3) Å, see: W. J. Evans and R. N. R. Broomhall-Dillard, J. Organomet. Chem., 1998, 569, 89; (e) [Lu(CH₂SiMe₃)₃(thf)₂]: Lu-C = 2.346(3) 2.380(3) Å, see: H. Schumann, D. M. M. Freckmann and S. Dechert, Z. Anorg. Allg. Chem., 2002, 628, 2422;

(f) $[Lu(CH_2SiMe_3)_2(12\text{-crown-4})(thf)]^+[B(CH_2SiMe_3)Ph_3]^-: Lu-C = 2.340(2), 2.354(2) Å, see: S. Arndt, T. P. Spaniol and J. Okuda,$ *Chem. Commun.* $, 2002, 896; (g) <math>[Lu(CH_2SiMe_3)_3(12\text{-crown-4})]: Lu-C = 2.36(1) - 2.40(1) Å, see ref. 15; (h) <math>[Ln\{\eta^5:\eta^1-C_3Me_4SiMe_2(OC_4H_3-2)](CH_2SiMe_3)_2(thf)]: Lu-C = 2.374(4), 2.381(4) Å, see: S. Arndt, T. P. Spaniol and J. Okuda,$ *Organometallics*, 2003,**22**, 775.

- 25 The waxy off-white solid tentatively assigned as the 15-crown-5 analogue of **4**, synthesized in an analogous manner, gave rise to very similar resonances to **4** in the ¹H NMR spectrum for the alkyl and silanolate groups (C_6D_6), however the crown ether region was rather poorly resolved. Selected NMR data: δ_H (C_6D_6 , 298 K) –0.58 (dd, J(HH) = 11.0 Hz, J(YH) = 3.2 Hz, 2×1 H, YCH₂SiMe₃), -0.48 (dd, J(HH) = 11.0 Hz, J(YH) = 3.2 Hz, 2×1 H, YCH₂SiMe₃), 0.42 (s, 2×9 H, YCH₂SiMe₃), 1.55 (s, 3×9 H, SiOC(CH₃)₃), 3.15, 3.49, 3.66 (s (br), 20 H, 15-crown-5). δ_C (C_6D_6 , 298 K) 5.1 (YCH₂SiMe₃), 28.8 (d, J(YC) = 40.7 Hz, YCH_2 SiMe₃), 32.3 (SiOC(CH₃)₃), 69.6 ((br), 15-crown-5), 71.4 (SiOC(CH₃)₃).
- 26 Complexometric titration gave results for all cationic species consistent with the alkyl-silanolate formulation, although simple rearrangement does not affect the elemental composition.
- 27 (a) R. Duchateau, U. Cremer, R. J. Harmsen, S. I. Mohamud, H. C. L. Abbenhuis, R. A. van Santen, A. Meetsma, S. K.-H. Thiele, M. F. H. van Tol and M. Krankenburg, *Organometallics*, 1999, **18**, 5447; (b) R. Duchateau, H. C. L. Abbenhuis, R. A. van Santen, S. K.-H. Thiele and M. F. H. van Tol, *Organometallics*, 1998, **17**, 5222.
- 28 The synthesis of $[Y{OSi(O'Bu)_3}_3]$ from $[Y{N(SiMe_3)_2}_3]$ and HOSi(O'Bu)_3 has been reported: R. Anwander, *Top. Organomet. Chem.*, 1999, **2**, 1. We found that the use of $[Y(CH_2SiMe_3)_3(thf)_2]$ under similar conditions led to the inclusion of a small amount of thf: $[Y{OSi(O'Bu)_3}_3(thf)_n]$ (n = 0.5-0.6) after recrystallisation from pentane.
- 29 (a) T. D. Tilley, A. Zalkin, R. A. Andersen and D. H. Templeton, *Inorg. Chem.*, 1981, **20**, 551; (b) H. C. Aspinall, D. C. Bradley, M. B. Hursthouse, K. D. Sales, N. P. C. Walker and B. Hussain, *J. Chem. Soc.*, *Dalton Trans.*, 1989, 623.
- 30 O. Wrobel, F. Schaper, U. Wieser, H. Gregorius and H. H. Brintzinger, Organometallics, 2003, 22, 1320.
- 31 O. Wrobel, F. Schaper and H. H. Brintzinger, *Organometallics*, 2004, 23, 900.
- 32 An attempted synthesis of [Lu{OSi(O'Bu)₃}(CH₂SiMe₃)(thf)₄]⁺[BPh₄]⁻ from equimolar amounts of HOSi(O'Bu)₃ and [Lu(CH₂SiMe₃)₂-(thf)₃]⁺[BPh₄]⁻ in thf gave a very poor yield of an impure colourless microcrystalline solid. The major product was assigned as [Lu{OSi(O'Bu)₃}₂(thf)₄]⁺[BPh₄]⁻ by 'H NMR spectroscopy, although some low intensity Lu–CH₂SiMe₃ resonances were also detected. The attempted synthesis of [Lu{OSi(O'Bu)₃}₂(CH₂SiMe₃)(thf)_n] from two equiv. of HOSi(O'Bu)₃ and [Lu(CH₂SiMe₃)₃(thf)₂] resulted in a mixture of products both in C₆D₆ at room temperature and pentane at -78 °C.
- 33 Similar reactivity of [Ln(C₅Me₅)₂]*[BPh₄]⁻ compounds has been demonstrated: (a) W. J. Evans, C. A. Seibel and J. W. Ziller, J. Am. Chem. Soc., 1998, 120, 6745; (b) W. J. Evans, J. M. Perotti and J. W. Ziller, J. Am. Chem. Soc., 2005, 127, 3894.
- 34 (a) [Y(CH₂SiMe₃)₂(thf)₄]⁺[Al(CH₂SiMe₃)₄]⁻, 2.354(4)–2.479(4) and [Y(CH₃)(thf)₆]²+[BPh₄]⁻, 2.352(3)–2.427(3): ref. 2; (b) [YCl(OCMe₃)-(thf)₅]⁺[BPh₄]⁻, 2.391(5)–2.422(5): W. J. Evans, J. M. Olofson and J. W. Ziller, J. Am. Chem. Soc., 1990, **112**, 2308; (c) [YCl₂(thf)₅]⁺[YCl₄(thf)₂]⁻, 2.368(5)–2.382(6): P. Sobota, J. Utko and S. Szafert, *Inorg. Chem.*, 1994, **33**, 5203; (d) [YCl₂(thf)₅]⁺[C₂B₉H₁₂]⁻, 2.309(7)–2.401(7): K. Y. Chiu, Z. Y. Zhang, T. C. W. Mak and Z. W. Xie, J. Organomet. Chem., 2000, **614**, 107.
- 35 (a) T. Sakakura, H.-J. Lautenschlaeger and M. Tanaka, J. Chem. Soc., Chem. Commun., 1991, 40; (b) G. A. Molander and M. Julius, J. Org. Chem., 1992, 57, 6347; (c) P.-J. Fu, L. Brard, Y. Li and T. J. Marks, J. Am. Chem. Soc., 1995, 117, 7157; (d) T. I. Gountchev and T. D. Tilley, Organometallics, 1999, 18, 5661; (e) A. A. Trifonov, T. P. Spaniol and J. Okuda, Dalton Trans., 2004, 2245 and references cited therein.
- 36 F. Lauterwasser, P. G. Hayes, S. Bräse, W. E. Piers and L. L. Schafer, *Organometallics*, 2004, 23, 2234.
- 37 Under comparative conditions, the neutral tris(alkyl) [Y(CH₂SiMe₃)₃-(thf)₂] very rapidly deposited an off-white, insoluble solid. ¹H NMR spectroscopy of the supernatant liquid indicated 90% hydrosilylated olefin (linear product), 10% non-hydrosilylated olefin.
- 38 P. G. Hayes, W. E. Piers and M. Parvez, J. Am. Chem. Soc., 2003, 125, 5622.

- 39 (a) P. Voth, S. Arndt, T. P. Spaniol, J. Okuda, A. J. Ackermann and M. L. H. Green, Organometallics, 2003, 22, 65; (b) P. Voth, T. P. Spaniol and J. Okuda, Organometallics, 2003, 22, 3921.
- 40 M. Ephritikine, Chem. Rev., 1997, 97, 2193.
- 41 Selected NMR data for $[Y{OSi(O'Bu)_3}_2 \{\mu OSi(O'Bu)_3\}B(C_6F_5)_{5^-}(thf)_n]/[B(C_6F_5)_3(thf)]: \delta_H (C_6D_6, 298 K) 1.31, 1.42, 1.54, 1.57 (s, 9 × 9 H and 0.5 × 4 H, SiOC(CH_3)_3, \beta-thf), 3.77 (0.5 × 4 H, \alpha-thf). <math>\delta_B (C_6D_6, 298 K) -5.2 (thf B(C_6F_5)_3), 3.0 (OSi(O'Bu)_3 B(C_6F_5)_3). \delta_F (C_6D_6, 298 K) -129.8, -132.6, -154.4, -162.3, -164.5, -167.4.$
- 42 (a) L. H. Doerrer and M. L. H. Green, J. Chem. Soc., Dalton Trans., 1999, 4325; (b) L. H. Doerrer, A. J. Graham, D. Haussinger and M. L. H. Green, J. Chem. Soc., Dalton Trans., 2000, 813.
- 43 (a) J. P. Mitchell, S. Hajela, S. K. Brookhart, K. I. Hardcastle, L. M. Henling and J. E. Bercaw, J. Am. Chem. Soc., 1996, 118,

1045; (b) S. Bambirra, M. J. R. Brandsma, E. A. C. Brussee, A. Meetsma, B. Hessen and J. H. Teuben, *Organometallics*, 2000, **19**, 3197.

- 44 S. Arndt, T. P. Spaniol and J. Okuda, *Organometallics*, 2003, 22, 775 and references therein.
- 45 ASTRO, SAINT and SADABS. Data Collection and Processing Software for the SMART System, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, 1996.
- 46 (a) G. M. Sheldrick, SHELXS-86, Program for Crystal Structure Solution, University of Göttingen, Germany, 1986; (b) G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
- 47 International Tables for X-Ray Crystallography, Kluwer Academic Publishers, Dordrecht, 1992, vol. C.