Synthesis, structure and reactivity of $[\mathrm{Yb}(\eta\text{-}\mathrm{C_5Me_5})\{\mathrm{Si(SiMe_3)_3}\}(\mathrm{thf})_2]$

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The reaction of $[\mathrm{Yb}(\eta\text{-}\mathrm{C_5Me_5})_2(\mathrm{OEt_2})]$ with 1 equiv. of $[\mathrm{Li}\{\mathrm{Si(SiMe_3)_3}\}(\mathrm{thf})_3]$ in toluene affords $[\mathrm{Yb}(\eta\text{-}\mathrm{C_5Me_5})\{\mathrm{Si(SiMe_3)_3}\}(\mathrm{thf})_2]$ 1 in high yield; a single-crystal X-ray analysis and multinuclear ^{171}Yb and ^{29}Si NMR spectroscopic data for 1 are reported.

Since their proposed role in the catalytic dehydrocoupling of primary silanes to polysilanes, much interest has recently focused on the exploration of chemistry of lanthanide–silicon-bonded species.[1] Nevertheless only three routes to such compounds are known, and four complexes have been structurally characterised (Scheme 1, Table 1).[2–5]

We now report the synthesis and molecular structure of $[\mathrm{Yb}(\eta\text{-}\mathrm{C_5Me_5})\{\mathrm{Si(SiMe_3)_3}\}(\mathrm{thf})_2]$ **1**. The reaction of $[\mathrm{Yb}(\eta\text{-}\mathrm{C_5Me_5})_2(\mathrm{OEt_2})]$ with 1 equiv. of $[\mathrm{Li}\{\mathrm{Si(SiMe_3)_3}\}(\mathrm{thf})_3]$ in toluene afforded **1** in high yield (75%).† The elimination of $\mathrm{LiC_5Me_5}$ has been previously employed for complexes of main-group[6,7] and lanthanide[8] elements in substitution reactions in which the $\mathrm{C_5Me_5}^-$ group was replaced by alkyl, alkoxide or amide but not, to our knowledge, by silyl derivatives. **1** was initially characterised by its ^{171}Yb NMR spectrum, in toluene solution, which displayed a single resonance at δ 421 with satellites corresponding to $^1J(^{171}\mathrm{Yb}\text{–}^{29}\mathrm{Si})$ 829 Hz [Fig. 1(*a*)]. The ^{29}Si NMR spectrum [Fig. 1(*b*)] comprised two resonances at δ −2.9 and −158, the latter assigned to $\mathrm{Si(SiMe)_3}$ possessing satellites confirming the previously measured $^1J(^{171}\mathrm{Yb}\text{–}^{29}\mathrm{Si})$ coupling and also displaying $^1J(^{29}\mathrm{Si}\text{–}^{29}\mathrm{Si})$ 26 Hz; the former, assigned to $\mathrm{Si(\mathit{Si}Me)_3}$ showed a $^2J(^{29}\mathrm{Si}\text{–}^{171}\mathrm{Yb})$ coupling of 11.5 Hz and a $^1J(^{29}\mathrm{Si}\text{–}^{13}\mathrm{C})$ coupling of 40 Hz. The ^{13}C NMR spectrum of **1** revealed $^2J(^{13}\mathrm{C}\text{–}^{29}\mathrm{Si})$ of 8 Hz for $\mathrm{Si(SiMe)_3}$ and a $^1J(^{13}\mathrm{C}\text{–}^{171}\mathrm{Yb})$ coupling of 10 Hz for $\mathrm{C_5Me_5}$.

Recrystallisation of **1** from hexane afforded orange needles. The molecular structure was determined from a single-crystal X-ray diffraction study (Fig. 2).‡ The ligand geometry about the Yb atom is distorted tetrahedral, with the angle between the bulky silyl substituent and the $^-\mathrm{C_5Me_5}$ centroid, M–Yb–Si(1), expanded to 128° and a corresponding compression of the angle O(1)–Yb–O(2) to 89° (M defines the centroid of the $^-\mathrm{C_5Me_5}$ ring). The Yb–Si(1) distance, 3.032(3) Å, is somewhat shorter than that reported for the other previously recorded $\mathrm{Yb^{II}}$–Si compound and longer than that in the other three Ln–Si compounds (Table 1). The Yb–M distance, 2.380(2) Å, and the average cyclopentadienyl ring C–C lengths and angles are unexceptional [1.38(5) Å, 108(3)°]. The $\mathrm{Si(SiMe)_3}$ group is

Table 1 Selected structural data for lanthanide–silicon-containing compounds

Compound	Ln–Si/Å	Ref.
$[\mathrm{Li(dme)_3}][\mathrm{Sm}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{SiMe_3})_2]$	2.880(2)	2
$[\mathrm{Li(dme)_3}][\mathrm{Sm}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{SiMe_3})_2]$	2.888(2)	3
$[\{\mathrm{Sm}(\eta\text{-}\mathrm{C_5Me_5})_2[\mathrm{SiH(SiMe_3)_2}]\}_2]$	3.052(8)	4
$[\mathrm{Yb(SiPh_3)_2(thf)_4}]$	3.158(2)	5
$[\mathrm{Yb}(\eta\text{-}\mathrm{C_5Me_5})\{\mathrm{Si(SiMe_3)_3}\}(\mathrm{thf})_2]$ **1**	3.032(3)	This work

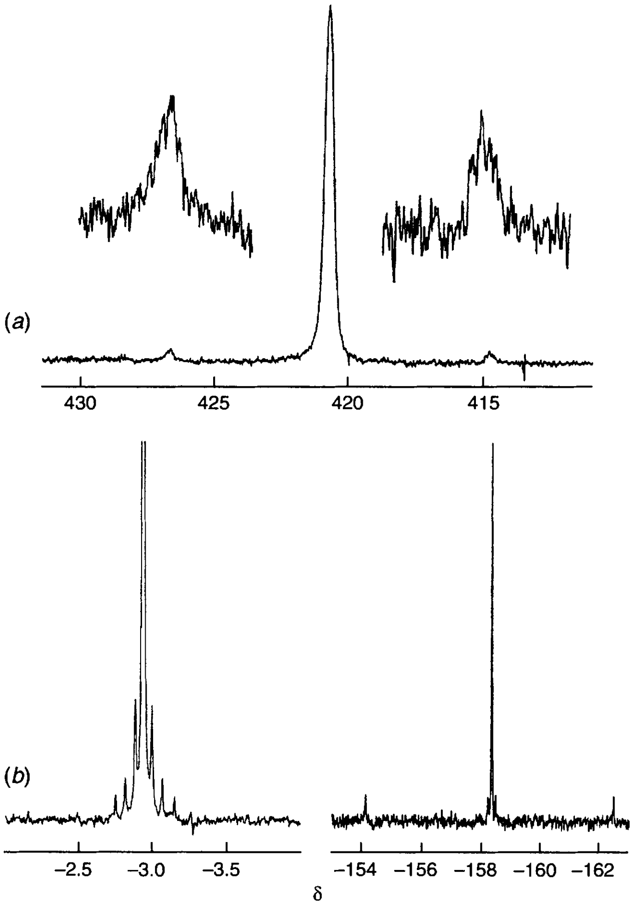
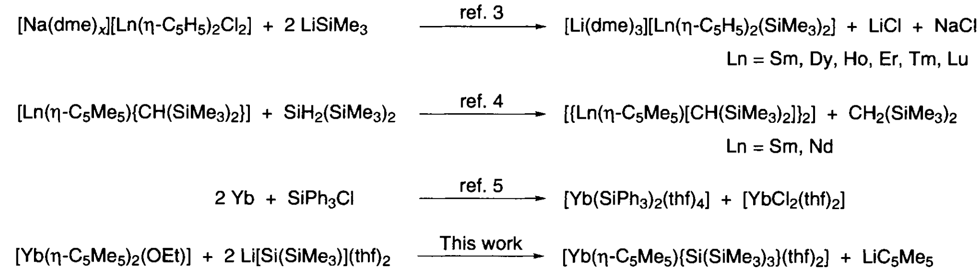


Fig. 1 $^{171}\mathrm{Yb}\{^1\mathrm{H}\}$ (*a*) and $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ (*b*) NMR spectra of **1**



$$[\mathrm{Na(dme)}_x][\mathrm{Ln}(\eta\text{-}\mathrm{C_5H_5})_2\mathrm{Cl_2}] + 2\,\mathrm{LiSiMe_3} \xrightarrow{\text{ref. 3}} [\mathrm{Li(dme)_3}][\mathrm{Ln}(\eta\text{-}\mathrm{C_5H_5})_2(\mathrm{SiMe_3})_2] + \mathrm{LiCl} + \mathrm{NaCl}$$

$$\mathrm{Ln = Sm, Dy, Ho, Er, Tm, Lu}$$

$$[\mathrm{Ln}(\eta\text{-}\mathrm{C_5Me_5})\{\mathrm{CH(SiMe_3)_2}\}] + \mathrm{SiH_2(SiMe_3)_2} \xrightarrow{\text{ref. 4}} [\{\mathrm{Ln}(\eta\text{-}\mathrm{C_5Me_5})[\mathrm{CH(SiMe_3)_2}]\}_2] + \mathrm{CH_2(SiMe_3)_2}$$

$$\mathrm{Ln = Sm, Nd}$$

$$2\,\mathrm{Yb} + \mathrm{SiPh_3Cl} \xrightarrow{\text{ref. 5}} [\mathrm{Yb(SiPh_3)_2(thf)_4}] + [\mathrm{YbCl_2(thf)_2}]$$

$$[\mathrm{Yb}(\eta\text{-}\mathrm{C_5Me_5})_2(\mathrm{OEt})] + 2\,\mathrm{Li}[\mathrm{Si(SiMe_3)}](\mathrm{thf})_2 \xrightarrow{\text{This work}} [\mathrm{Yb}(\eta\text{-}\mathrm{C_5Me_5})\{\mathrm{Si(SiMe_3)_3}\}(\mathrm{thf})_2] + \mathrm{LiC_5Me_5}$$

Scheme 1 Synthetic routes to Ln–Si bonded species disordered equally between two different orientations related by a rotation of 35° about the Yb–Si bond and with shared sites for 2/3 of the methyl groups. A similar disorder has been observed for the Sm derivative, $[\{Sm(\eta\text{-}C_5Me_5)_2[SiH(SiMe_3)_2]\}_2]$.[4]

When monitored by ^{171}Yb NMR spectroscopy, the addition of a second equivalent of $[LiSi(SiMe_3)_3(thf)_3]$ to **1** showed a new resonance at δ 875, which is assigned to the disubstituted product $[Yb\{Si(SiMe_3)_3\}(thf)_n]$ **2**. Its ^{29}Si NMR spectrum revealed the $\mathit{Si}(SiMe)_3$ resonance at δ −147, with the $Si(\mathit{Si}Me_3)_2$ signal coincident with that of **1**. Attempts to improve the conversion of **1** to **2** above 30%, either by addition of a large excess of the lithium silyl or by heating (**2** decomposed above *ca.* 40 °C), failed. The following features of **1** are noteworthy. (*i*) The stability of the $^{-}C_5Me_5$ ligand in **1** to further substitution, coupled with the NMR spectroscopically active ^{171}Yb centre, makes **1** an ideal substrate to study the reactivity of the Ln–Si bond. (*ii*) Compound **1** is the first example of a half-sandwich lanthanide(II)–silyl compound, $LnCp^xX$. (*iii*) **1** is also the first $LnCp^xX$ compound which is monomeric. (*iv*) The present study also provides the first measurements of $^1J(^{171}Yb\text{–}^{29}Si)$.

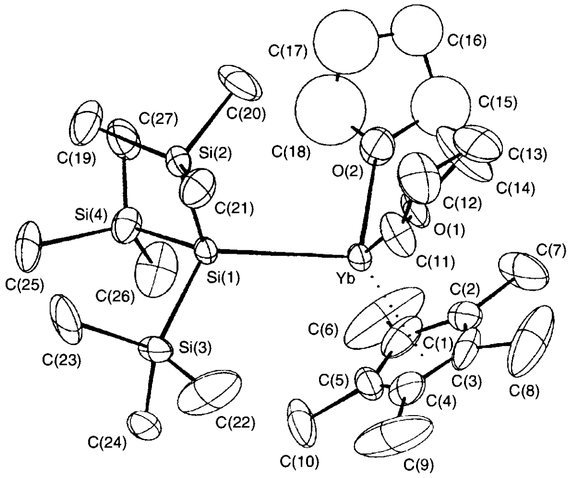


Fig. 2 The molecular structure of $[Yb(\eta\text{-}C_5Me_5)\{Si(SiMe_3)_3\}(thf)_2]$ **1** and atom numbering scheme with selected bond lengths (Å) and angles (°): Yb–M 2.380(2), Yb–Si(1) 3.032(3), Yb–O(1) 2.388(9), Yb–O(2) 2.371(10), Yb–C(1) 2.660(14), Yb–C(2) 2.670(13), Yb–C(3) 2.648(13), Yb–C(4) 2.63(2), Yb–C(5) 2.65(2), M–Yb–Si(1) 128.4(4), M–Yb–O(1) 113.8(2), M–Yb–O(2) 115.2(6), Si(1)–Yb–O(1) 98.6(2), Si(1)–Yb–O(2) 103.8(3), O(2)–Yb–O(1) 89.1(4). M denotes the centroid of the ring C(1)–C(5).

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Footnotes

† *Synthesis* of $[Yb(\eta\text{-}C_5Me_5)\{Si(SiMe_3)_3\}(thf)_2]$. To a Schlenk tube containing a solution of $[Yb(\eta\text{-}C_5Me_5)_2(OEt_2)]$ (0.56 g, 1.08 mmol) in toluene (150 ml) at −78 °C was added slowly a toluene solution (60 ml) of $[Li\{Si(SiMe_3)_3\}(thf)_3]$ (0.45 g, 0.96 mmol). Upon warming to *ca.* −30 °C, a gradual colour change from dark brown to red was accompanied by the formation of an off-white precipitate. After stirring at room temperature for 24 h, the mixture was filtered and the solvent removed from the filtrate *in vacuo*. The residue was washed with ice-cold hexane and afforded **1** (0.62 g, 74.5%) as a dark orange powder. Recrystallisation from hexane afforded orange needles, decomp. *ca.* 60 °C. ^1H NMR (C_6D_6, 400.13 MHz): δ 0.59 (s, 27 H), 1.40 (br s, 8 H), 2.37 (s, 15 H), 3.54 (br s, 8 H); $^{13}C\{^1H\}$ NMR (20% C_6D_6 in toluene, 125.72 MHz): δ 6.70 [$^1J(^{13}C\text{–}^{29}Si)$ 40.3, $^2J(^{13}C\text{–}^{29}Si)$ 8.1 Hz], 11.54 [$^1J(^{13}C\text{–}^{13}C)$ 4.3 Hz], 25.61, 69.87, 113.29 [$^1J(^{13}C\text{–}^{171}Yb)$ 10.3 Hz]; $^{29}Si\{^1H\}$ NMR (20% C_6D_6 in toluene, 99.32 MHz): δ −2.94, −158.3; ^{171}Yb NMR (20% C_6D6 in toluene, 70.02 MHz): δ 421.

‡ *Crystal data* for $[Yb(\eta\text{-}C_5Me_5)\{Si(SiMe_3)_3\}(thf)_2]$: $C_{27}H_{58}O_4Si_4Yb$, Crystallographic measurements were made on an Enraf-Nonius CAD4 diffractometer using (Mo-Kα) radiation, $\lambda = 0.71073$ Å. The structure was solved by direct methods and refined on F^2 by the full-matrix least-squares procedure, $T = 173(2)$ K. Specimen 0.4 × 0.4 × 0.05 mm, $M = 700.1$, monoclinic, space group $P2_1/n$ (non-standard no. 14), $a = 11.848(3)$, $b = 17.039(4)$, $c = 18.098(9)$ Å, $\beta = 103.04(3)°$, $U = 3559(2)$ Å^3, $D_c = 1.31$ g cm^{-3}, $Z = 4$. For reflections with $2 < \theta < 25°$, $R(F) = 0.068$ for 3898 observed reflections $[I > 2\sigma(I)]$ and $wR(F^2) = 0.185$ for all 6559 reflections. Atomic coordinates, bond lengths and angles, and thermal parameters hve been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/233.

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