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The First Structurally Authenticated Divalent Lanthanide Stannyl Derivative

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The reaction between YbI_2 and $K[Sn(CH_2Bu^t)_3]$ affords the diamagnetic ytterbium bis-stannyl derivative $[Yb(SnNep_3)_2(thf)_2]$ **1** (Nep = 2,2-dimethylpropyl and thf = tetrahydrofuran) which has been characterised by multinuclear NMR spectroscopy (^{119}Sn and ^{171}Yb) and X-ray crystallography: reaction of **1** with two equivalents of ArOH (ArOH = 2,6-di-*tert*-butyl-4-methylphenol) or C_5Me_5H results in the elimination of $Sn(CH_2Bu^t)_3H$ to afford the known complexes $[Yb(OAr)_2(thf)_2]$ and $[Yb(C_5Me_5)_2(thf)_2]$ respectively whereas the reaction with one equivalent of ArOH or C_5Me_5 results in the formation of the novel mixed ligand complexes $[Yb(OAr)\{Sn(CH_2Bu^t)_3\}(thf)_2]$ and $[Yb(C_5Me_5)\{(Sn(CH_2Bu^t)_3\}(thf)_2]$.

The chemistry of the +II oxidation state derivatives of the lanthanides Sm, Eu and Yb has received considerable interest recently due to their unique reactivity, especially as selective reducing agents and in the activation of small molecules.[1] Exploration of the Yb^{II} oxidation state has been considerably facilitated by the development, by one of us, of ^{171}Yb NMR.[2] Thus, we were particularly interested in the synthesis of Yb^{II} complexes containing bonds between ytterbium and spin active main group elements, both for NMR studies and also for their potential reactivity. Herein we report the first bis-stannyl derivative of a divalent lanthanide, including the first Yb–Sn bond to be structurally characterised and a similarly unique measurement of Yb–Sn coupling constants. Furthermore we also provide a synthetic route to the mixed

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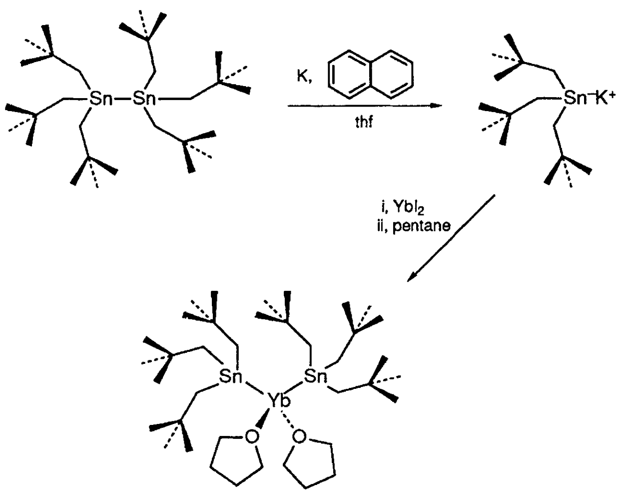

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Scheme 1

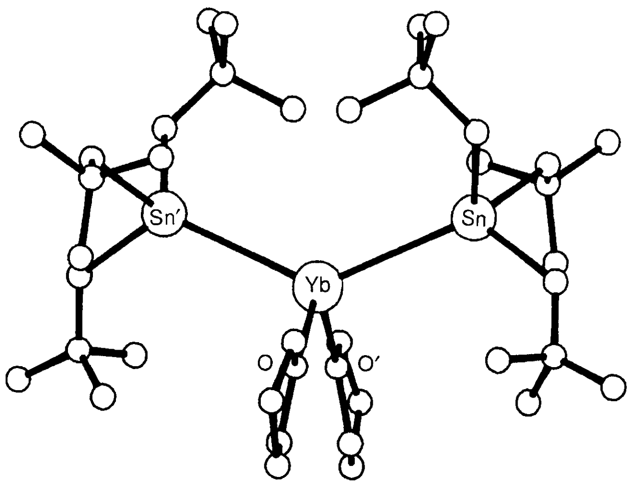

Fig. 1 The X-ray structure of **1**. Selected bond lengths (Å): Yb–Sn, 3.216(1); Yb–O, 2.345(7). Selected bond angles (°): Sn–Yb–Sn', 132.34(3); O–Yb–O', 102.4(2); Sn–Yb–O 106.6(2); Sn–Yb–O', 102.7(2). The molecule lies on a crystallographic twofold rotation axis.

ligand derivatives of Yb^{II}. To date, few lanthanide–tin bonds have been reported; the ytterbium(III) complex [Yb(η-$C_5H_5)_2(SnPh_3)(thf)_2$] is known[3a] but has not been structurally authenticated, and the only ytterbium(II) complexes, Bu_3SnYbI and Ph_3SnYbI, are ill-characterised.[3b] The reaction of YbI_2 and K[$SnNep_3$] (Nep = 2,2-dimethylpropyl) in tetrahydrofuran (thf) affords orange, crystalline [$Yb(SnNep_3)_2(thf)_2$], **1**, in 60% yield after recrystallisation from pentane (see Scheme 1).†

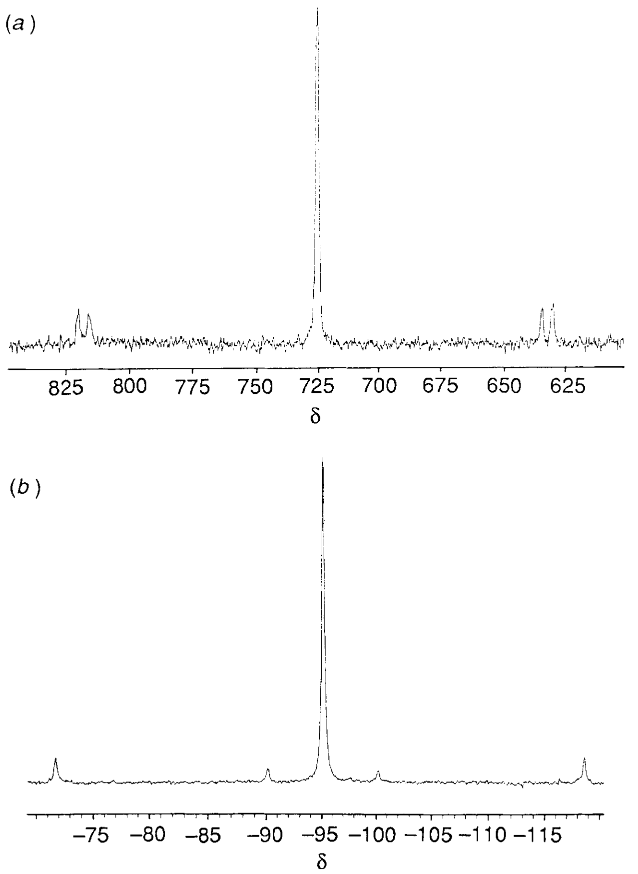

Fig. 2 (*a*) The ^{171}Yb NMR spectrum of **1**; (*b*) the ^{119}Sn NMR spectrum of **1**

A single crystal X-ray study[4]‡ of **1** has been carried out and the results are shown in Fig. 1. Noteworthy features of the structure are the pseudo tetrahedral geometry about the Yb atom and the apparently long Yb–Sn bond of 3.2 Å, although the dearth of any precedents in lanthanide chemistry coupled with the lack of reported values for either covalent or van der Waals radii for Yb makes interpretation of this bond length ambiguous. However, we note that the Hf–Sn distance in the Hf^{II} complex [Hf(η-PhMe)$_2$(SnMe$_3$)$_2$] is 2.95 Å,[5] and Hf^{II} would be expected to be similar in size to Yb^{II}.

The ^{171}Yb NMR spectrum of **1** in toluene reveals a single resonance at δ 725 with ^{119}Sn and ^{117}Sn satellites. Similarly the

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† To a Schlenk tube containing 100 ml of extremely dry thf and a potassium mirror (0.24 g, 6 mmol) was added all at once solid hexaneopentylditin (1.99 g, 3 mmol) and solid naphthalene (0.748 g, 6 mmol), with stirring. When all the potassium had been consumed, to the resultant deep-green solution of potassium(trineopentylstannyl) was added solid ytterbium diiodide (1.41 g, 3.3 mmol). The resultant deep-brown solution was stirred at room temperature for 2 days, filtered, and the solvent and naphthalene removed under vacuum. Extraction of the residue with n-pentane, filtration, and slow cooling of the filtrate to 0 °C afforded dark-orange crystals of **1** (1.8 g, 60%). Extremely facile loss of thf from **1** precluded meaningful microanalysis.

^{1}H NMR (C_7D_8, 500.13 MHz, 298 K): δ 3.71 (br s, 8H, thf), 1.40 (br s, 8H, thf), 1.20 [s, 54H, $CH_2C(CH_3)_3$], 1.14 [s, 12H, $CH_2C(CH_3)_3$]. ^{13}C NMR {^{1}H} (C_7D_8, 125.77 MHz, 298 K): δ 69.2 (thf), 39.55 [$CH_2C(CH_3)_3$], 34.95 [$CH_2C(CH_3)_3$], 32.97 [$CH_2C(CH_3)_3$].

‡ *Crystal data*: $C_{38}H_{82}O_2Sn_2Yb$, $M = 981.5$, monoclinic, space group *C2/c*, $a = 13.726(6)$, $b = 18.154(7)$, $c = 19.989(8)$ Å, $\beta = 105.37(3)°$, $U = 4802.8$ Å^3, $Z = 4$, $D_c = 1.36$ g cm^{-3}; F(000) = 1984. Monochromated Mo-Kα radiation, $\lambda = 0.71069$ Å, $\mu = 29.9$ cm^{-1}.

Data were collected using a crystal *ca.* 0.5 × 0.5 × 0.5 mm, sealed in a capillary under argon (along with a trace of the mother liquor), on an Enraf-Nonius CAD4 diffractometer in the θ-2θ mode with $\Delta\theta = (0.8 + 0.35\tan\theta)°$ and a maximum scan time of one minute. A total of 4231 unique reflections for $2 < \theta < 25°$ and +h +k ±1, and 1900 reflections with $|F^2| > 3\sigma(F^2)$, where $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{1/2}L\rho$ (Lρ = Lorentz polarisation), were used in refinement. A correction (max. 1.33, min. 0.65) was applied for absorption using DIFABS[4] after isotropic refinement.

The structure was solved by routine heavy-atom methods and non-hydrogen atoms refined anisotropically by full-matrix least-squares. Hydrogen atoms were held fixed at calculated positions with $U_{iso} = 1.3\ U_{eq}$ for the parent carbon atom. With a weighting scheme of $w = 1/\sigma^2(F)$, the final residuals were $R = 0.036$, $R_w = 0.046$, with a ratio of observations to variables of 10 : 1, and $S = 1.4$. Programs from the Enraf-Nonius SDP-Plus package were run on a micro Vax II computer. 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.

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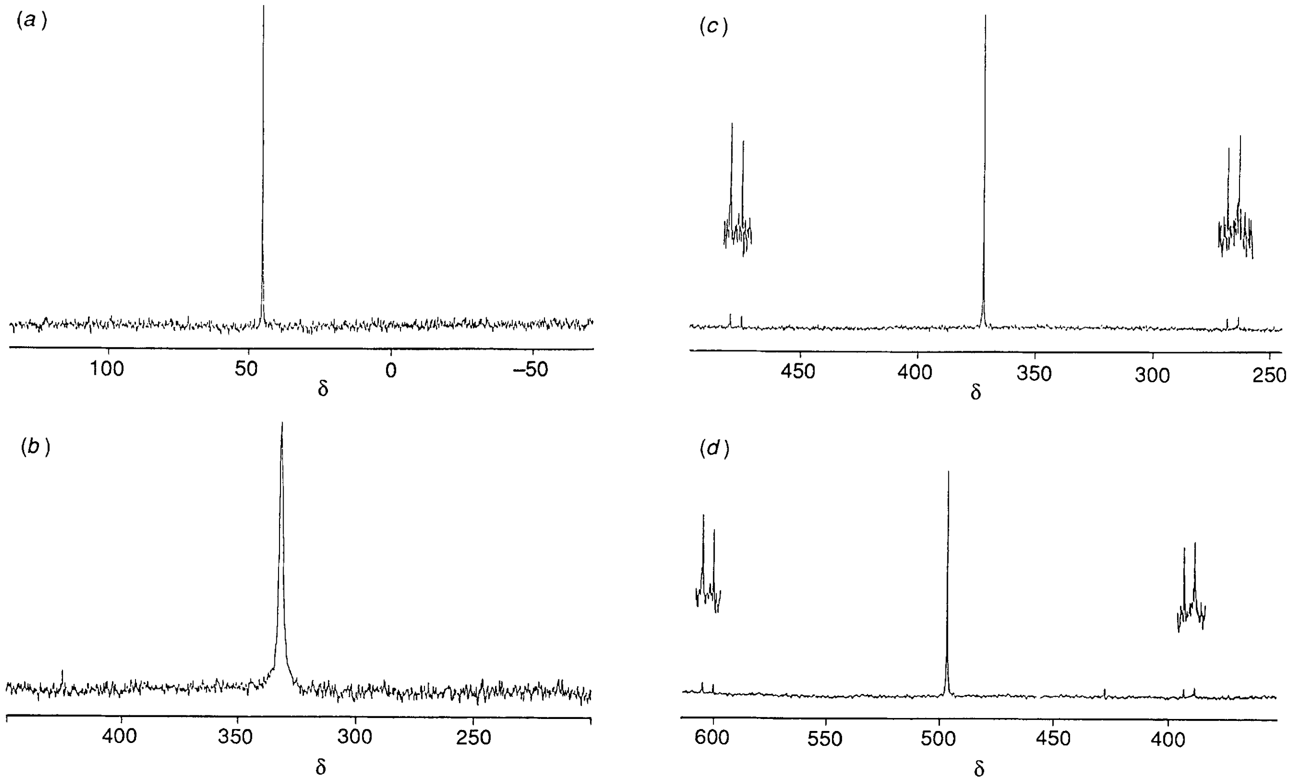

Fig. 3 The ^{171}Yb spectra of; (*a*) [Yb(C_5Me_5)$_2$(thf)$_2$]; (*b*) [Yb(OAr)$_2$(thf)$_2$]; (*c*) [Yb(C_5Me_5){Sn(CH_2Bu^t)$_3$}(thf)$_2$]; and (*d*) [Yb(OAr)-{Sn(CH_2Bu^t)$_3$}(thf)$_2$]

^{119}Sn spectrum consists of another singlet, at δ −95, with accompanying ^{117}Sn and ^{171}Yb couplings.§

The incipient basicity of the trineopentyltin group in **1** suggests that the latter will afford a wide range of Yb^{II} complexes, by reaction with protic reagents. For example, the addition of two equivalents of either C_5Me_5H [eqn. (1)] or ArOH [eqn. (2)] (where C_5Me_5H = 1,2,3,4,5-pentamethylcyclopentadiene and ArOH = 2,6-di-*tert*-butyl-4-methylphenol) affords the previously reported [Yb(C_5Me_5)$_2$(thf)$_2$][6] and [Yb(OAr)$_2$(thf)$_2$][7] respectively [by ^{171}Yb NMR, see Fig. 3(*a*) and (*b*)]¶ with the concomitant generation of two equivalents of SnNep$_3$H. The potential for the synthesis of mixed ligand complexes which retain one trineopentyltin group is demonstrated by NMR tube reactions between **1** and only one equivalent of either C_5Me_5H, [eqn. (3)] or ArOH [eqn. (4)]. The ^{171}Yb NMR spectrum for reaction (3) reveals a new resonance at δ 372‖ intermediate in chemical shift between those of **1** and [Yb(C_5Me_5)$_2$2thf], and similarly that for reaction (4) exhibits a new resonance at δ 497‖ intermediate between those for **1** and [Yb(OAr)$_2$-(thf)$_2$]. The corresponding ^{119}Sn spectra exhibit only ^1J (Sn–^{171}Yb) couplings with no ^2J (Sn–^{117}Sn) present, thus further confirming the formation of the mono-stannyl complexes [Yb(C_5Me_5){Sn(CH_2Bu^t)$_3$}(thf)$_2$] and [Yb(OAr){Sn-(CH_2Bu^t)$_3$}(thf)$_2$]. Further characterisation of the latter and other related derivatives, together with the preparation of the lead and silicon analogues of **1**, are in progress.

$$\mathbf{1} + 2\,C_5Me_5H \rightarrow [Yb(C_5Me_5)_2(thf)_2] + 2\,Sn(CH_2Bu^t)_3H \quad (1)$$

$$\mathbf{1} + 2\,ArOH \rightarrow [Yb(OAr)_2(thf)_2] + 2\,Sn(CH_2Bu^t)_3H \quad (2)$$

$$\mathbf{1} + 1\,C_5Me_5H \rightarrow [Yb(C_5Me_5)\{Sn(CH_2Bu^t)_3\}_3(thf)_2] + Sn(CH_2Bu^t)_3H \quad (3)$$

$$\mathbf{1} + 1\,ArOH \rightarrow [Yb(OAr)\{Sn(CH_2Bu^t)_3\}_3(thf)_2] + Sn(CH_2Bu^t)_3H \quad (4)$$

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§ ^{171}Yb NMR {^{1}H} (C_7D_8, 43.77 MHz, 298 K): δ 725 [*J* (Yb–^{119}Sn) 8627, *J* (Yb–^{117}Sn) 8254 Hz]. ^{119}Sn NMR {^{1}H} (C_7D_8, 93.27 MHz, 298 K): δ −95 [*J* (Sn–^{171}Yb) 8627, ^2J (Sn–^{117}Sn) 1872 Hz].

¶ ^{171}Yb NMR {^{1}H} (C_7D_8, 43.77 MHz, 298 K): δ 45 [Yb(C_5Me_5)$_2$(thf)$_2$]; δ 331 [Yb(OAr)$_2$(thf)$_2$].

‖ ^{171}Yb NMR {^{1}H} (C_7D_8, 43.77 MHz, 298 K): δ 372 [*J* (Yb–^{119}Sn) 9479, *J* (Yb–^{117}Sn) 9058 Hz]; δ 497 [*J* (Yb–^{119}Sn) 8783, *J* (Yb–^{117}Sn) 8396 Hz].