Synthesis and Structure of Crystalline $[\mathrm{K\{Sn(CH_2Bu^t)_3\}(\eta\text{-}C_6H_5Me)_3}]$ and the First NMR Spectral Observation of $^{119}\mathrm{Sn}$–$^{39}\mathrm{K}$ Coupling†

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Treatment of $[\mathrm{Sn_2(CH_2Bu^t)_6}]$ with K in tetrahydrofuran (thf) at 25 °C affords crystalline $[\mathrm{K\{Sn(CH_2Bu^t)_3\}(thf)_2}]$ **1**, which with toluene gives $[\mathrm{K\{Sn(CH_2Bu^t)_3\}(\eta^6\text{-}C_6H_5Me)_3}]$ **2**, the X-ray structure of **2** at 295 K revealing that potassium is in a distorted tetrahedral environment (taking each of the η^6-toluene molecules as occupying a single site), with l(K–Sn) 3.548(3) Å and l(K–C) ranging from 3.21 to 3.72 Å; a solid state ^{119}Sn cross-polarisation magic angle spinning (CP-MAS) NMR spectral study of **2** provides the first observation of direct ^{119}Sn–^{39}K coupling.

As recently noted by Wright and coworkers, despite the important role of tri(hydrocarbyl)stannyl–alkali metal complexes as organic synthetic auxiliaries,[1] or their use as $\mathrm{\bar{S}nR_3}$ ligand-transfer reagents {as in the synthesis of $[\mathrm{Zr(\eta\text{-}C_5H_5)_2(Cl)(SnPh_3)}]$[2] or $[\mathrm{Yb\{Sn(CH_2Bu^t)_3\}_2(thf)}]$, thf = tetrahydrofuran)[3]}, little is known relating to their isolation or structural characterisation in solution or the solid state.

We now report (*i*) the preparation (Scheme 1) of the monomeric, crystalline, hydrocarbon-soluble complexes $[\mathrm{K\{Sn(CH_2Bu^t)_3\}(thf)_2}]$ **1** and $[\mathrm{K\{Sn(CH_2Bu^t)_3\}(\eta^6\text{-}PhMe)_3}]$ **2**;‡ (*ii*) their NMR spectral characterisation in $\mathrm{C_6D_6}$ **1** or $[^2\mathrm{H_8}]$toluene **2**;§ (*iii*) the cross-polarisation magic angle spinning (CP-MAS) ^{119}Sn NMR spectrum of solid **2** (Fig. 1), showing the first example of direct ^{119}Sn–^{39}K coupling;§ and (*iv*) the X-ray structure¶ of **2**, Fig. 2, showing potassium remarkably to have 19 non-hydrogen nearest neighbours (Sn + 18C) at distances of < 3.75 Å.

$$\mathrm{K} \xrightarrow{\text{i}} \underset{\mathbf{1}}{[\mathrm{K\{Sn(CH_2Bu^t)_3\}(thf)_2}]} \xrightarrow{\text{ii}} \underset{\mathbf{2}}{[\mathrm{K\{Sn(CH_2Bu^t)_3\}(\eta^6\text{-}C_6H_5Me)_3}]}$$

Scheme 1 *Reagents and conditions*: i, 1/2 $\mathrm{Sn_2(CH_2Bu^t)_6}$, naphthalene, thf, 25 °C, 16 h (then removal of volatiles *in vacuo* and recrystallisation from thf; 97% yield); ii, PhMe, 25 °C, 10 min. Alternatively,‡ **2** was obtained without isolating crystalline **1**.

The method of preparing **1** (i in Scheme 1, 97%, satisfactory C/H analyses) had previously been used (but without its

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† No reprints available.

‡ *Preparation of* **2**: A suspension of K (0.22 g, 5.89 mmol) in thf (150 cm^3) containing $\mathrm{Sn_2(CH_2Bu^t)_6}$ (1.7 g, 2.94 mmol) and naphthalene (0.09 g) was stirred at *ca.* 25 °C for 12 h. Volatiles were removed at 25 °C/10^{-2} mmHg. The residual yellow solid was extracted into toluene (*ca.* 60 cm^3), the extract was concentrated (to *ca.* 25 cm^3) *in vacuo* and cooled (−30 °C) to yield yellow crystals of **2** (3.09 g, 5.06 mmol), m.p. 171 °C.

§ NMR chemical shifts (δ) {at 300 K in $\mathrm{C_6D_6}$ for **1** and $[^2\mathrm{H_8}]$PhMe for **2**, for ^{1}H at 250 MHz, ^{13}C at 125.8 MHz, and ^{119}Sn at 186.5 MHz}, ^{1}H: **1** 1.06 (s, 6H), 1.28 (m, 8H), 1.40 (s, 27H), 3.54 (m, 8H), and **2** 1.31 (s, 6H), 1.50 (s, 27H), 2.30 (s, 9H), 7.30 (m, 15H); $^{13}\mathrm{C}\{^1\mathrm{H}\}$: **1** 35.0 ($\mathrm{CH_3}$), 33.07 ($\mathrm{CH_2}$), 31.4 (C), 25.72 (thf), 67.75 (thf), and **2** 21.20 ($\mathrm{C_6H_5}\mathit{C}\mathrm{H_3}$), 31.50 (C), 33.20 ($\mathrm{CH_2}$), 35.20 ($\mathrm{CH_3}$), 124.15 ($\mathrm{C_1}$), 125.21 ($\mathrm{C_{2.6}}$), 127.20 ($\mathrm{C_{3.5}}$), 128.50 ($\mathrm{C_4}$); $^{119}\mathrm{Sn}\{^1\mathrm{H}\}$: **1** −221 (s), and **2** −221 (s). The ^{119}Sn CP-MAS spectrum for solid **2**: δ −211 [q, $^1J(^{119}\mathrm{Sn}\text{–}^{39}\mathrm{K})$ 289 Hz].

¶ *Crystal data* for **2** [*T* 295 K, Enraf-Nonius CAD-4 diffractometer, Mo-Kα radiation (λ = 0.71069 Å)], no crystal decay, full-matrix least-squares refinement with non-hydrogen atoms (other than carbons of PhMe) anisotropic. Hydrogen atoms fixed: C atoms of toluene isotropic (attempts to refine them anisotropically led to their positions becoming unstable); $w = \sigma^{-2}(F)$. $\mathrm{C_{36}H_{57}KSn}$, $M = 647.6$, monoclinic, space group $P2_1/c$, $a = 10.886(2)$, $b = 35.095(16)$, $c = 10.139(2)$ Å, $\beta = 91.65(2)$, $U = 3871.7$ Å^3, $Z = 4$, $D_c = 1.11$ g cm^{-3}, $F(000) = 1368$, μ(Mo-Kα) = 7.8 cm^{-1}, specimen, 0.3 × 0.3 × 0.3 mm. 3703 Unique reflections for $2 < \theta < 25°$, of which 2234 with $|F^2| > 2\sigma(F^2)$ were used in the refinement; $R = 0.058$, $R_W = 0.072$, $S = 2.0$. 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.

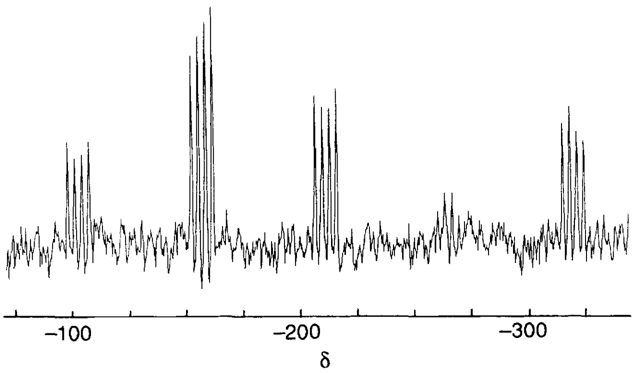

Fig. 1 ^{119}Sn CP-MAS NMR spectrum of **2**; * denotes isotropic shift

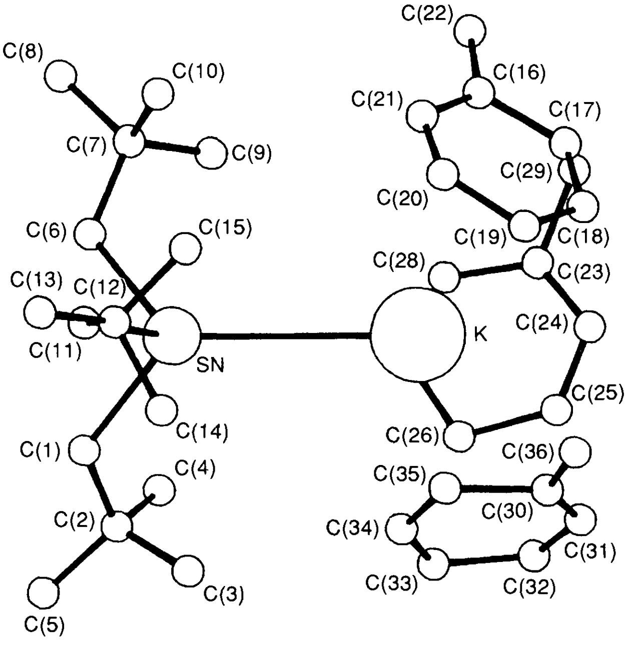

Fig. 2 X-Ray structure of [K{Sn(CH_2Bu^t)$_3$}(η^6-C_6H_5Me)$_3$] **2** with atom numbering scheme. Selected intramolecular bond lengths (Å) and angles (°): K–Sn 3.548(3), K–M1 3.13, K–M2 3.35, K–M3 3.41, K–Sn–C(1) 125.0(4), K–Sn–C(6) 122.5(4), K–Sn–C(11) 124.6(3), Sn–K–M1 113.3, Sn–K–M2 110.6, Sn–K–M3 107.7 [where M1, M2, and M3 are the mid-points of the C(16) to C(21), C(23) to C(28), and C(30) to C(35) rings, respectively].

isolation or formulation as **1**) in the course of the synthesis of [Yb{Sn(CH_2Bu^t)$_3$}$_2$(thf)$_2$].[3] It is noteworthy that crystallisation of **1** from toluene yielded **2**, thereby demonstrating a surprising toluene/thf displacement reaction.‡

The $^{119}Sn\{^1H\}$ NMR spectrum of **2** in [$^2H_8$]toluene§ revealed a single signal at δ −221; ^{119}Sn–^{39}K coupling was not observed, probably due to the low site symmetry at the quadrupolar ^{39}K nucleus. In contrast, such coupling for **2** was observed in the solid-state CP-MAS NMR spectrum, as a 1 : 1 : 1 : 1 quartet at δ_{iso} −211, $^1J(^{119}Sn$–$^{39}K)$ 289 Hz, Fig. 1.

The molecular structure at 295 K of crystalline [K{Sn(CH_2Bu^t)$_3$}(η^6-C_6H_5Me)$_3$] **2**, Fig. 2, shows that the potassium is in a distorted tetrahedral environment, with the three toluene molecules coordinated to K in an η^6-fashion, av. *l*(K–M) 3.30 Å, av. Sn–K–M 110.5°, and *l*(K–Sn) 3.548(3) Å (M being the mid-point of the aromatic ring). The tin environment, relative to the α-carbons of the neopentyl groups, is pyramidal with av. C–Sn–C 91.7°, indicating that the tin–carbon bonds have little s-character.

The sole prior examples of X-ray-characterised crystalline tri(hydrocarbyl)stannyl–alkali metal complexes were [Li($SnPh_3$)(pmdeta)] **3**,[1] [Sn(η-C_5H_5)$_2$(μ-η-C_5H_5){Na(pmdeta)}] **4**,[4] [K(18-crown-6][$SnPh_3$] **5**,[5] and [Li(dioxane)$_4$][Li{Sn($CH_2C(CH)_3O$)$_3$}$_2$] **6**;[6] the lead analogue of **3** has been reported[7] [pmdeta = ($Me_2NCH_2CH_2$)$_2$NMe]. The geometry associated with the SnC_3 fragment in each of **2**, **3**, **5** and **6** is broadly similar, with the av. C–Sn–C angle being 96.1(2)° in **3**,[1] 96.9° in **5**,[5] and *ca.* 90° in **6**.[6] However, the closest K···Sn contact in **5** is >6 Å;[5] in **3**, *l*(Li–Sn)$_{av}$ is 2.871(7) Å [the ^{119}Sn NMR spectrum was not recorded, but $^1J(^7Li$–$^{119/117}Sn)$ of *ca.* 412 Hz was observed in the ^7Li NMR spectrum at −90 °C].[1]

Related crystalline stannyl–alkali metal complexes to have been described are [Sn(μ-OAr)$_3$Li] [Ar = $C_6H_3Ph_2$-2,6 with *l*(Sn···Li) 2.784(4) Å],[8] [K{Sn($OsiPh_3$)$_3$}(dme)] [dme = ($MeOCH_2$)$_2$, with av. *l*(K–Sn) 3.470(4) Å and δ(^{119}Sn) in thf −360.5],[9] [K(18-crown-6)(η^2-PhMe)$_2$][K{Sn($OSiPh_3$)$_3$}$_2$(18-crown-6] **7** [with *l*(K–Sn) 3.4894(9) Å],[9] [Sn(OBu^t)(μ-OBu^t)M(OBu^t)M(μ-OBu^t)Sn(OBu^t)] (M = Li or Na) [av. *l*(Sn···Na) 3.45 Å],[10] and [M{Sn(OBu^t)$_3$}]$_\infty$ (M = K, Rb, or Cs).[10]

Alkali-metal–arene ion–dipole interactions have been described as present in certain 'liquid clathrates' such as K[$Al_2Me_6(NO_3)$]7C_6H_6 yielding crystals of K[$AlMe_3$(ONO_2)(η^6-C_6H_6)].[11] The coordination of more than one arene molecule to an alkali metal is unusual, but recent examples include **7** (η^2-PhMe),[9] [Lu{CH($SiMe_3$)$_2$}$_3$(μ-Cl)K(η^6-PhMe)$_2$][12] and [K(μ_3-$OSiMe_2Ph$)(η^6-C_6H_6)]$_4$.[13] In such K(η^6- arene) complexes, the K–C distance has been in the range 3.18 to 3.59 Å. The binding energy of benzene to K^+ has been calculated as *ca.* 80 kJ mol^{-1}.[14]

The crystalline hydrocarbon-soluble [K{$SnNp_3$}(η^6-PhMe)$_3$] **2** is thus far unique in stannyl–alkali metal complex chemistry, and even among mononuclear group 14–group 1 compounds in being free from *O*- or *N*-centred ligands.

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References

1 D. Reed, D. Stalke and D. S. Wright, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1459.
2 B. M. Kingston and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 1972, 69.
3 F. G. N. Cloke, C. I. Dalby, P. B. Hitchcock, H. Karamallakis and G. A. Lawless, *J. Chem. Soc., Chem. Commun.*, 1991, 779.
4 M. G. Davidson, D. Stalke and D. S. Wright, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1226.
5 T. Birchall and J. A. Vetrone, *J. Chem. Soc., Chem. Commun.*, 1988, 877.
6 M. Veith, C. Ruloff, V. Huch and F. Töllner, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1381.
7 D. R. Armstrong, M. G. Davidson, D. Moncrieff, D. Stalke and D. S. Wright, *J. Chem. Soc., Chem. Commun.*, 1992, 1413.
8 G. D. Smith, P. E. Fanwick and I. P. Rothwell, *Inorg. Chem.*, 1989, **28**, 618.
9 M. J. McGeary, R. H. Cayton, K. Folting, J. C. Huffman and K. G. Caulton, *Polyhedron*, 1992, **11**, 1369.
10 M. Veith and R. Rösler, *Z. Naturforsch., Teil B*, 1986, **41**, 1071.
11 J. L. Atwood, *J. Inclusion Phenom.*, 1985, **3**, 13; C. Schade and P. v. R. Schleyer, *Adv. Organomet. Chem.*, 1987, **27**, 169; and references cited therein.
12 C. J. Schaverien and J. B. van Mechelen, *Organometallics*, 1991, **10**, 1704.
13 G. R. Fuentes, P. S. Coan, W. E. Streib and K. G. Caulton, *Polyhedron*, 1991, **10**, 2371.
14 J. Sunner, K. Nishizawa and P. Kebarle, *J. Phys. Chem.*, 1981, **85**, 1814.