Two Triorganostannate Complexes synthesised from Bis(cyclopentadienyl)tin(II); Structural Variation Between $[Mg(thf)_6]^{2+}2[Sn(\eta^3\text{-}C_5H_5)_3]^-$ and $[Li(thf)_4]^+[Sn(C_{13}H_9)_3]^-$ (thf = tetrahydrofuran, $C_{13}H_9$ = fluorenyl)

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Nucleophilic *addition* of $Mg(C_5H_5)_2$ to $Sn(C_5H_5)_2$ (1:2) in tetrahydrofuran (thf) gave $[Mg(thf)_6]^{2+}$ $2[Sn(\eta^3\text{-}C_5H_5)_3]_2$ **1** whereas the reaction of fluorenyllithium (2 or 3 equivalents) resulted in nucleophilic *substitution* of both C_5H_5 ligands and in the formation of $[Li(thf)_4]^+[Sn(C_{13}H_9)_3]^-$ **2**; the anion of **1** is essentially planar whereas that in **2** has a distorted-pyramidal structure.

We have been interested in p-block metal organometallic compounds[1] and particularly in those containing reactive heavy metal fragments.[2] Our interests in triorgano-stannates and -plumbates, which are valuable precursors in organic synthesis,[3] led to the synthesis of the [Ph_3E–Li(pmdeta)] complexes [E = Sn or Pb; pmdeta = $(Me_2NCH_2CH_2)_2NMe$] which contain the first structurally authenticated early main-group metal–heavy p-block metal bonds.[2a,b] More recently we have been interested in the synthetic utility of heavy p-block metal cyclopentadienide complexes as precursors to organometallics and metalate complexes. Nucleophilic *addition* of $Na(C_5H_5)$ to $Sn(C_5H_5)_2$ and in the presence of pmdeta (1:1:1) produces ion-contacted $[(C_5H_5)_2Sn(\mu\text{-}\eta^5\text{-}C_5H_5)Na(pmdeta)]$ which contains an unusual trigonal-planar 'paddle-wheel' ion linked to a Na^+ centre.[2c] However, nucleophilic *substitution* of one C_5H_5 occurs when $LiN{=}C(NMe_2)_2$ is treated with $Sn(C_5H_5)_2$ and the dimeric mixed-ligand complex $[\{Sn(\eta^3\text{-}C_5H_5)[\mu\text{-}N{=}C(NMe_2)_2]\}_2]$ is formed.[1b]

We here report the synthetic applications of both nucleophilic addition and substitution of $Sn(C_5H_5)_2$ in the syntheses of two ion-separated triorganostannate complexes in which very different anion geometries are observed. Nucleophilic addition of $Mg(C_5H_5)_2$ to $Sn(C_5H_5)_2$ (1:2) in tetrahydrofuran (thf) produces $[Mg(thf)_6]^{2+}2[Sn(\eta^3\text{-}C_5H_5)_3]^-$ **1**.† In contrast, reaction of fluorenyllithium $Li(C_{13}H_9)$ with $Sn(C_5H_5)_2$ (2 or 3 equivalents) in thf leads to disubstitution followed by addition of a third $C_{13}H_9$ ligand and in the formation of $[Li(thf)_4]^+$-$[Sn(C_{13}H_9)_3]^-$ **2**. The formation of the latter, which has a distorted-pyramidal structure, illustrates the use of nucleophilic substitution of $Sn(C_5H_5)_2$ in the synthesis of triorganostannate reagents in general.

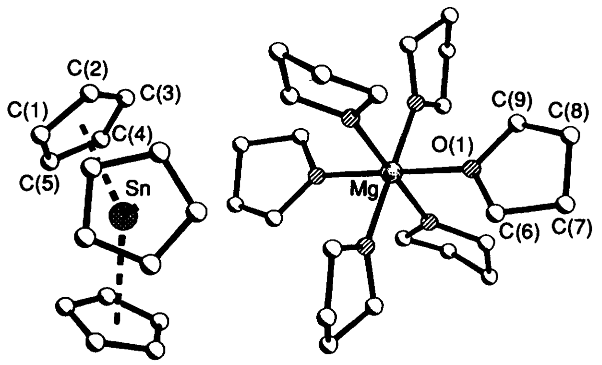

Fig. 1 Structure of **1** in the asymmetric unit {only one of the $[Mg(thf)_6]^{2+}$ ions is shown}. All H atoms omitted for clarity. Bond lengths (Å) and angles (°): Sn–C(1) 2.621(2), Sn–C(2) 2.862(2), Sn–C(3) 3.126(3), Sn–C(4) 3.092(2), Sn–C(5) 2.805(2), mean Cp(centroid)–Sn 2.571 (Sn *ca.* 0.29 Å out of the C_5H_5 mean plane), mean Mg–O 2.094(1) Å; Cp(centroid)–Sn–Cp(centroid) 118.8, mean O–Mg–O 90.0(4)°

Crystallographic studies were undertaken on **1** and **2**.‡ Complex **1** has an ion-separated structure (Fig. 1) in which there is one lattice-bound thf per formula unit (not shown)

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† The compound $Mg(C_5H_5)_2$ (Strem; 0.31 g, 2.0 mmol) was dissolved in dry thf (6 cm^3). A solution of $Sn(C_5H_5)_2$[4] (1.00 g, 4 mmol, in 2.5 cm^3 thf) was added at 20 °C. The faintly cloudy solution was filtered and thf (15 cm^3) was added to the filtrate. Storage at 20 °C (24 h) gave cubic colourless, air-sensitive crystals of **1**. Isolation and placing under vacuum [*ca.* 10^{-2} atm (*ca.* 10^3 Pa), 15 min] gave a powder from which the thf of solvation, which is seen in the crystal structure of **1**, has been completely removed. For unsolvated material: first batch yield 42% (0.92 g, 0.85 mmol), m.p. 57–60 °C to colourless oil; satisfactory elemental analyses (C, H, N) for all samples; IR (Nujol mull) 3075 cm^{-1} (C–H str, C_5H_5) disappearing on exposure to air; ^1H NMR (25 °C, 250 MHz, $[^2H_8]$thf): δ 5.26 (s, 15 H, J_{SnH} = 15.6 Hz, C_5H_5), *ca.* 3.30 (m, 24 H, thf) and *ca.* 1.45 (m, 24 H, thf).

A solution of fluorene (Aldrich, 1.25 g, 7.5 mmol) in dry thf (7.0 cm^3) was treated at 0 °C with a solution of $LiBu^n$ (4.7 cm^3, 1.6 mol dm^{-3} in hexanes, 7.5 mmol). To the bright orange solution produced was added $Sn(C_5H_5)_2$ (0.63 g, 2.5 mmol) in 1.4 cm^3 of thf) at −5 °C and the mixture allowed to warm to 20 °C. Stirring gave a mass of orange-yellow powder which was dissolved upon gentle heating. Storage at 20 °C (24 h) gave yellow air-sensitive and thermally unstable crystalline rods of compound **2**. First batch yield 50% (1.14 g, 1.25 mmol); 2:1 reaction of $Li(C_{13}H_9)$ with $Sn(C_5H_5)_2$ gave **2** in *ca.* 40% yield [based on $Li(C_{13}H_9)$ consumed] in an identical manner to that described above; decomp. to black solid *ca.* 130 °C. Satisfactory elemental analyses were obtained (C, H, N) although some problems with loss of Li-co-ordinated thf were experienced. IR (Nujol mull): 3020w (aryl and C_5H_5 C–H), 1606m and *ca.* 1590w cm^{-1} (aryl C$\cdots$C str). ^1H NMR (25 °C, 250 MHz, $[^2H_8]$thf): δ 6.72 [d, 6 H, H(1)], 6.45 [d, 6 H, H(4)], 6.25 (td, 6 H) and 6.18 (td, 6 H) [H(2) and H(3)], 3.82 (s, 3 H, α-CH), *ca.* 3.55 (m, 16 H, thf) and *ca.* 1.72 (m, 16 H, thf).

‡ Crystal data: $C_{54}H_{78}MgO_6Sn_2$ **1**·thf, *M* = 1156.96, rhombohedral, space group $R\bar{3}$, *a* = *b* = 14.472(2), *c* = 22.811(5) Å, *U* = 4137.4(12) $Å^3$, *Z* = 3, D_c = 1.393 Mg m^{-3}, *F*(000) = 1806, λ = 0.710 73 Å, *T* = 153 K, μ(Mo-Kα) = 96.7 cm^{-1}. Data were collected on a Siemens-Stoe AED diffractometer using an oil-coated rapidly cooled crystal of dimensions 0.4 × 0.3 × 0.3 mm by the θ–ω method (8 ⩽ 2θ ⩽ 52°). Of 7959 reflections collected, 1804 were unique. The structure was solved by direct methods (SHELXS 92)[5] and refined by full-matrix least squares based on F^2 with all data to *R*1 and *wR*2 of 0.017 and 0.039 respectively. The H atoms of C_5H_5 were refined freely in chemically equivalent groups, those of $Mg(thf)_6$ were refined geometrically with *U* refined freely. The lattice-bound thf was refined as a rigid group. Residual electron density +2.66, −2.45 e $Å^{-3}$. *M*

$C_{55}H_{59}LiO_4Sn$ **2**, *M* = 909.65, monoclinic space group $P2_1/c$ (no. 14), *a* = 10.284(2), *b* = 16.815(3), *c* = 27.311(5) Å, β = 100.51(3)°, *U* = 4643.5(15) $Å^3$, *Z* = 4, D_c = 1.301 Mg m^{-3}, *F*(000) = 1896, λ = 0.710 73 Å, *T* = 153 K, μ(Mo-Kα) = 5.95 cm^{-1}. Data were collected as above on a crystal of dimensions 0.33 × 0.31 × 0.28 mm (5 ⩽ 2θ ⩽ 50°). Of 8793 reflections collected, 8316 were unique. The structure was solved by direct methods (SHELXTL PLUS)[6] and refined by full-matrix least squares based on F^2 and 7682 reflections with $I > 2\sigma(I)$ to *R*1 and *wR*2 of 0.1097 and 0.2969 respectively (SHELX 92).[5] Hydrogen atoms not found in the difference maps were placed in idealised positions and allowed to ride on the relevant carbon atom. Both the thf and the fluorenyl rings showed some disorder, and only the Sn, Li, O and the ordered C atoms were refined anisotropically. Residual electron density +1.68, −1.82 e $Å^{-3}$. Atomic coordinates, thermal parameters and bond lengths and angles for **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

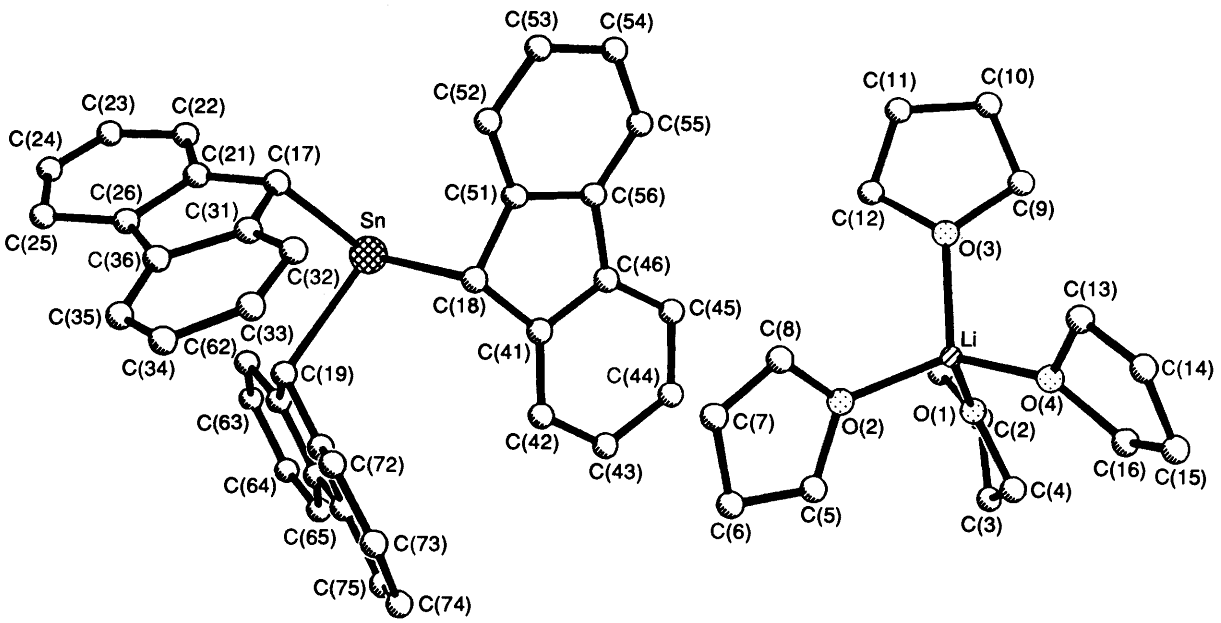

Fig. 2 Structure of **2** in the asymmetric unit. All H atoms omitted for clarity. Bond lengths (Å) and angles (°): Sn–C(17) 2.353(10), Sn–C(18) 2.350(10), Sn–C(19) 2.341(10), mean Li–O 1.93(3) Å; C(17)–Sn–C(18) 93.9(3), C(18)–Sn–C(19) 102.9(4), C(19)–Sn–C(17) 91.3(4), mean O–Li–O 110(2)°

which is lost when **1** is placed under vacuum. The complex contains a triorganostannate ion $[Sn(\eta^3-C_5H_5)_3]^-$ in which the three ligands are attached equivalently in an η^3-bonding mode [centroid Cp–Sn 2.571(1) Å]. Although a similar fragment has been observed in the ion-contacted complex $[(C_5H_5)_2Sn(\mu-\eta^5-C_5H_5)Na(pmdeta)]$[2c] it was not completely clear whether the latter is best rationalised as a triorganostannate $Na^+[Sn(C_5H_5)_3]^-$ or as a loose complex between the two neutral fragments $Sn(C_5H_5)_2$ and $Na(C_5H_5)$. The structure of **1** verifies that the $[Sn(C_5H_5)_3]^-$ anion has a true existence. To our knowledge, this is the first example of an unassociated or uncontacted species containing three π-bonded ligands attached to Sn.[2c,7]

The anion in compound **1** is significantly more distorted than that in $[(C_5H_5)_2Sn(\mu-\eta^5-C_5H_5)Na(pmdeta)]$ (Sn *ca.* 0.29 Å out of the C_5H_5 centroid plane of **1**, *cf.* only *ca.* 0.14 Å in the latter). This distortion corresponds to a ring-slip parameter of *ca.* 6.5° in **1**. There is also a change in hapticity of the C_5H_5 ligands from η^5 in the ion-contacted species to η^3 in **1**. Both the increased distortion of the anion away from trigonal planar and the change in hapticity are consistent with an increase in lone pair character on Sn in **1**.

The relationship between the anion geometry, the ligand hapticity and the lone-pair character on Sn is clearly seen in the essentially pyramidal geometry of the anion within $[Li(thf)_4]^+[Sn(C_{13}H_9)_3]^-$ **2** (Fig. 2). Pyramidal geometries have been observed for a variety of ion-separated and -contacted triorganostannate complexes in the solid state, *e.g.* within ion-separated $[K(18\text{-crown-}6)]^+[SnPh_3]^-$ [average C–Sn–C 96.9(2)°][8] (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane) and in contacted $[Ph_3Sn–Li(pmdeta)]$ [average C–Sn–C 96.1(2)°].[2a] However, there is a marked distortion in the geometry of the fluorenyl ligands in the anion of **2**. Although these groups have approximately equal C–Sn bond lengths [average 2.35(1) Å], presumably for steric reasons, their associated angles about Sn are not the same. Notably C(19)–Sn–C(18) 102.9(4)° is large compared to the (*ca.* 96°) angles observed in the few (C–Sn bonded) triorganostannates so far structurally characterised.[2a,c,9,10]

The difference in reactivity of $Sn(C_5H_5)_2$ observed in the syntheses of **1** and **2** is evidently a consequence of the nucleophilicity and steric bulk of the reagents employed. Hence *addition* of the weakly nucleophilic $C_5H_5^-$ occurs in the synthesis of **1**, whereas *disubstitution* followed by addition of the highly nucleophilic $C_{13}H_9^-$ occurs in the synthesis of **2**. It should be noted in relation to the latter that nucleophilic disubstitution of $Sn(C_5Me_5)_2$ occurs preferentially with bulky nucleophiles such as $(Me_3Si)_2CHLi$ but further addition does not ensue presumably for steric reasons.[8] Where nucleophiles of intermediate strength are employed, such as in the synthesis of $[\{Sn(\eta^3-C_5H_5)[\mu-N{=}C(NMe_2)_2]\}_2]$ from $LiN{=}C(NMe_2)_2$ and $Sn(C_5H_5)_2$, monosubstitution at Sn is most likely.[1b] We are finding that a range of triorganostannates can be prepared in an analogous way to that used in the synthesis of **2**. This method potentially provides a clean and efficient way of making these reagents in general.

Acknowledgements

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