

A leaving group strategy for the selective functionalisation of an imido Sn(II) cubane

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Controlled hydrolysis of the cubane $[\text{Sn}^t\text{Bu}]_4$ with H_2O in thf-MeCN provides a direct route to the oxo complex $[\text{Sn}_4(\text{N}^t\text{Bu})_3\text{O}]$, reaction of which with naphNHLi (naph = 1-naphthyl) gives the heteroleptic cubane $[\text{Sn}_4(\text{N}^t\text{Bu})_3(\text{Nnaph})]$ as the sole product.

In original studies by Veith,¹ imido Sn(II) cubanes of the type $[\text{SnNR}]_4$ **1** were found to be readily accessible from the reaction of $[\{\text{Me}_2\text{Si}^t\text{Bu}\}_2\text{Sn}]$ with primary amines.² These species prove to be valuable precursors for the preparation of heterometallic complexes containing Sn(II) imido and phosphinidene anions, such as $[\text{Li}\cdot\text{thf}]_4[\{\text{Sn}(\mu\text{-PCy})\}_2(\mu\text{-PCy})_2]$ in which the four Li^+ cations are coordinated by a metallacyclic $[\{\text{Sn}(\mu\text{-PCy})\}_2(\mu\text{-PCy})_2]^{4-}$ unit.³ However, although it has been found that the *intact* oxo cubane $[\text{Sn}_4(\text{N}^t\text{Bu})_3\text{O}]$ **2** can function as an ether-like donor ligand in the adduct $[\{\text{Sn}_4(\text{N}^t\text{Bu})_3\text{O}\}\cdot\text{AlMe}_3]$,⁴ nothing has so far been reported concerning the reactivity or synthetic utility of the cubane itself.

A current interest of ours has involved uncovering new synthetic strategies which will allow the selective synthesis of a range of main group complexes.⁵ In contrast to the previous report that the oxo cubane $[\text{Sn}_4(\text{N}^t\text{Bu})_3\text{O}]$ **2** cannot be obtained from the hydrolysis of $[\text{Sn}^t\text{Bu}]_4$ **1a** with H_2O ,^{5a} we have now found that **2** is readily prepared in high yield from this reaction *if* MeCN-thf is employed as the solvent (rather than solely thf as used in the previous study). This discovery facilitates a leaving group strategy by which imido cubanes **1** can be converted regioselectively into monosubstituted, heteroleptic cubanes $[\text{Sn}_4(\text{NR})_3(\text{NR}^*)]$, as exemplified by the formation of $[\text{Sn}_4(\text{N}^t\text{Bu})_3(\text{Nnaph})]$ **3** (naph = 1-naphthyl) from the controlled hydrolysis of $[\text{Sn}^t\text{Bu}]_4$ with H_2O followed by the substitution of the oxo group of **2** with naphNHLi .† The latter reaction relies on the greater polarity of the Sn–O bonds compared to the Sn–N bonds in **2** and is driven thermodynamically by the formation of LiOH (Scheme 1). It is noteworthy that **3** cannot be obtained from the reaction of the cubane **1** with naphNHLi under similar conditions and that the reaction of **1** with excess naphNHLi results in $[\text{Li}(\text{thf})_4][(\text{N}^t\text{Bu})\text{Sn}_3(\text{Nnaph})_3\text{Li}\cdot\text{thf}]^-$ only after reflux.³ As far as we are aware, although hydrolytic substitution reactions of organo-oxo compounds of Sn(IV) with amines and alcohols have been employed in the preparation of amide and alkoxide complexes,⁶ the reaction of a metallated primary amine or similar species (with the elimination of LiOH) is a novel one.

The low-temperature crystal structure of **3**‡ shows it to consist of discrete cubane units, $[\text{Sn}_4(\text{N}^t\text{Bu})_3(\text{Nnaph})]$ (Fig. 1). Despite the incorporation of one different imido substituent into the cubane framework, only minor distortions in the Sn_4N_4 core have been introduced. The internal angles at the Sn (mean 81.1°) and N (mean 98.3°) centres are similar to those observed previously in $[\text{Sn}^t\text{Bu}]_4$ ^{1d} and other homoleptic cubanes.² However, although the majority of the Sn–N bonds of the core fall in a similar range to those present in $[\text{Sn}^t\text{Bu}]_4$,^{1d} the bonds to the aryl-imido group are on the whole longer [Sn(2,3,4)–N(4) 2.218(4)–2.224(4) Å; cf. 2.181(4)–2.203(4) Å for the other Sn–N bonds]. This pattern can be seen as arising from the

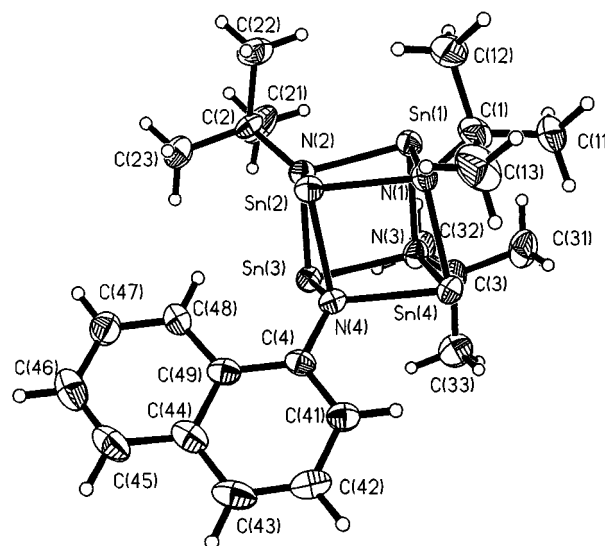
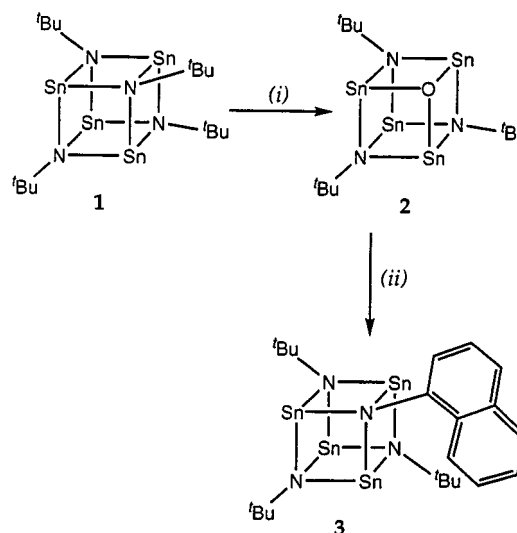


Fig. 1 ORTEP¹⁰ drawing of the structure of **3**. Thermal ellipsoids are at the 40% probability level. Selected bond lengths (Å) and angles ($^\circ$): Sn(1)–N(1) 2.197(4), Sn(1)–N(2) 2.203(4), Sn(1)–N(3) 2.199(4), Sn(2)–N(1) 2.185(4), Sn(2)–N(2) 2.187(4), Sn(2)–N(4) 2.224(4), Sn(3)–N(2) 2.199(4), Sn(3)–N(3) 2.181(4), Sn(3)–N(4) 2.218(4), Sn(4)–N(1) 2.194(4), Sn(4)–N(3) 2.191(4), Sn(4)–N(4) 2.219(4), C(4)–N(4) 1.415(7); range N–Sn–N 80.7(1)–81.7(2) (mean 81.1), range Sn–N–Sn 97.6(2)–99.7(2) (mean 98.3).



Scheme 1 (i) H_2O (1 equivalent), MeCN-thf , -78°C , $-^t\text{BuNH}_2$; (ii) naphNHLi , thf , $-\text{LiOH}$.

greater electron acceptor ability of the naph group compared to the ^tBu groups, allowing some degree of dispersion of the negative charge on the naphN imido centre into the aromatic

substituent and resulting in correspondingly weaker Sn–N bonds.

The synthetic strategy outlined above furnishes a potential route to a range of compounds of the type $[\text{Sn}_4(\text{NR})_3\text{X}]$ (e.g., X = NH, PH, S) not previously accessible, using the corresponding cubane precursors $[\text{SnNR}]_4$ which are readily prepared. Complex **3** is the first example of a heteroleptic imido Sn(II) cubane to be prepared and structurally characterised. The synthetic methodology involved (a leaving group strategy which is related to that commonly employed in organic synthesis) provides a rare if not unprecedented example of the selective structural modification of an oligomeric main group cage.

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Notes and references

† Synthesis of **2**. $[\text{SnN}^t\text{Bu}]_4$ **1a** (1.25 mmol) was prepared by the *in situ* reaction of $t\text{BuNH}_2$ (0.53 ml, 5.0 mmol) with $[\text{Sn}(\text{NMe}_2)_2]$ ⁷ (1.03 g, 5 mmol) in thf (20 ml). To this solution at -78°C was added dropwise a solution of H_2O (0.02 ml, 1.1 mmol) in MeCN (10 ml, distilled over CaH_2). After full addition the mixture was allowed to warm slowly to room temperature and stirred (2 h) before filtration to remove a white precipitate. The solvent was removed under vacuum to obtain **2** as a lemon yellow powder. Yields of up to 0.78 g (89%) were obtained using this method. ^1H NMR (250 MHz, d_6 -benzene, $+25^\circ\text{C}$): δ 1.34 (Me of $t\text{Bu}$) (Found: C, 20.2; H, 3.9; N, 5.8. Calc. for $[\text{Sn}_4\text{ON}_3\text{C}_{12}\text{H}_{27}]$: C, 20.5; H, 3.8; N, 6.0%).

Synthesis of **3**. A solution of naphNHLi (0.71 mmol) was prepared by the addition of $n\text{BuLi}$ (0.47 ml, 1.5 mol dm^{-3} solution in hexanes) to a solution of naph NH_2 (0.102 g, 0.71 mmol) in toluene (5 ml)–thf (5 ml). The solution was added to a solution of **2** (0.59 g, 0.71 mmol). After stirring at room temperature (30 min) the solution was filtered. The solvent was removed under vacuum and was replaced by thf (3 ml) and Et_2O (4 ml). Storage at -15°C (4 d) gave brown crystals of **3**. Yield 0.21 (36%). ^1H NMR (250 MHz, d_8 -toluene, $+25^\circ\text{C}$): δ 8.23 [d, 1H, $J = 8.2$, C(2)–H], 7.72 [dd, 1H, $J = 9.3$, 1.5 Hz, C(9)–H], 7.32 [m, 5H, C(3,4,6,7,8)–H], 1.48 (s, 27H, $t\text{Bu}$) (Found: C, 32.2; H, 4.2; N, 6.8. Calc. for $[\text{Sn}_4\text{N}_4\text{C}_{22}\text{H}_{34}]$: C, 31.8; H, 4.1; N, 5.8%).

‡ Crystal data for **3**: $\text{C}_{22}\text{H}_{34}\text{N}_4\text{Sn}_4$, $M = 829.29$, monoclinic, space group $P\bar{1}$ (no. 2), $a = 8.670(5)$, $b = 9.703(5)$, $c = 16.815(9)$ Å, $\alpha = 75.71(3)$, $\beta = 81.36(4)$, $\gamma = 81.72(4)^\circ$, $U = 1347(1)$ Å³, $Z = 2$, $\rho_{\text{calc.}} = 2.045$ Mg m⁻³, $\lambda = 0.71073$ Å, $T = 180(2)$ K, $\mu(\text{Mo-K}\alpha) = 3.682$ mm⁻¹, $F(000) = 788$. Data were collected on a Stoe AED diffractometer using an oil-coated rapidly-cooled crystal⁸ of dimensions $0.40 \times 0.28 \times 0.16$ mm by the ω - θ method ($3.56 \leq \theta \leq 22.50^\circ$). Of a total of 5293 collected reflections, 3505 were independent ($R_{\text{int}} = 0.032$). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to final values of $R_1[F > 4\sigma(F)] = 0.023$ and $wR_2 = 0.057$ (all data);⁹ largest peak and hole in the final difference map 0.715 and -0.665 e Å⁻³. CCDC reference number 186/1362. See <http://www.rsc.org/suppdata/dt/1999/1043/> for crystallographic files in .cif format.

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