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

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Controlled hydrolysis of the cubane $[SnN^tBu]_4$ with H_2O in thf–MeCN provides a direct route to the oxo complex $[Sn_4(N^tBu)_3O]$, reaction of which with naphNHLi (naph = 1-naphthyl) gives the heteroleptic cubane $[Sn_4(N^tBu)_3(Nnaph)]$ as the sole product.

In original studies by Veith,[1] imido Sn(II) cubanes of the type $[SnNR]_4$ **1** were found to be readily accessible from the reaction of $[\{Me_2SiN^tBu\}_2Sn]$ 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 $[Li{\cdot}thf]_4[\{Sn(\mu\text{-}PCy)\}_2(\mu\text{-}PCy)]_2$ in which the four Li^+ cations are coordinated by a metallacyclic $[\{Sn(\mu\text{-}PCy)\}_2(\mu\text{-}PCy)]_2^{4-}$ unit.[3] However, although it has been found that the *intact* oxo cubane $[Sn_4(N^tBu)_3O]$ **2** can function as an ether-like donor ligand in the adduct $[\{Sn_4(N^tBu)_3O\}{\cdot}AlMe_3]$,[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 $[Sn_4(N^tBu)_3O]$ **2** cannot be obtained from the hydrolysis of $[SnN^tBu]_4$ **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 $[Sn_4(NR)_3(NR')]$, as exemplified by the formation of $[Sn_4(N^tBu)_3(Nnaph)]$ **3** (naph = 1-naphthyl) from the controlled hydrolysis of $[SnN^tBu]_4$ 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 $[Li(thf)_4]^+[(^tBuN)Sn_3(Nnaph)_3Li{\cdot}thf]^-$ 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, $[Sn_4(N^tBu)_3(Nnaph)]$ (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 $[SnN^tBu]_4$[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 $[SnN^tBu]_4$,[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 greater electron acceptor ability of the naph group compared to the ^{t}Bu groups, allowing some degree of dispersion of the negative charge on the naphN imido centre into the aromatic

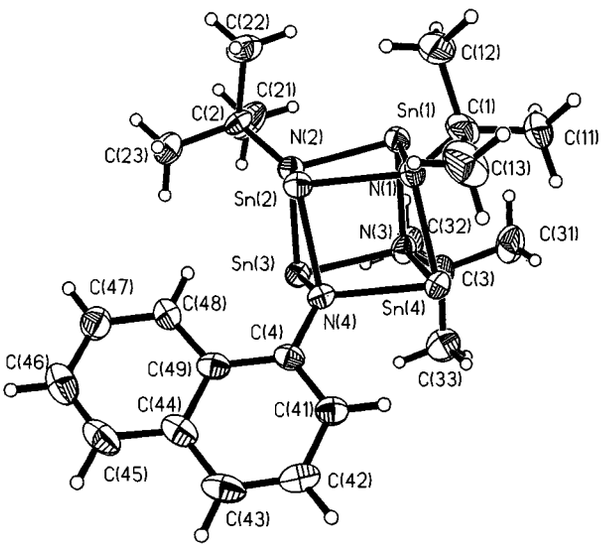
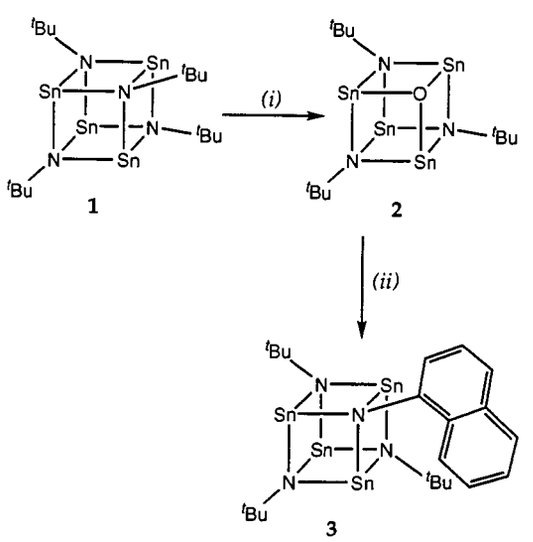


Fig. 1 ORTEP[10] drawing of the structure of **2**. Thermal ellipsoids are at the 40% probability level. Selected bond lengths (Å) and angles (°): Sn(1)–N(1) 2.197(4), Sn(1)–N(2) 2.203(4), Sn(1)–N(3) 2.199(4), Sn(2)–N(1) 2.185(4), Sn(2)–N(2) 2.187(4), Sn(2)–N(4) 2.224(4), Sn(3)–N(2) 2.199(4), Sn(3)–N(3) 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, $-{}^tBuNH_2$; (*ii*) naphNHLi, thf, −LiOH.

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 $[Sn_4(NR)_3X]$ (*e.g.*, X = NH, PH, S) not previously accessible, using the corresponding cubane precursors $[SnNR]_4$ 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**. $[SnN^tBu]_4$ **1a** (1.25 mmol) was prepared by the *in situ* reaction of $^tBuNH_2$ (0.53 ml, 5.0 mmol) with $[Sn(NMe_2)_2]$[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. ^{1}H NMR (250 MHz, d_6-benzene, +25 °C): δ 1.34 (Me of ^{t}Bu) (Found: C, 20.2; H, 3.9; N, 5.8. Calc. for $[Sn_4ON_3C_{12}H_{27}]$: 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}BuLi (0.47 ml, 1.5 mol dm^{-3} solution in hexanes) to a solution of $naphNH_2$ (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%). ^{1}H NMR (250 MHz, d_8-toluene, +25 °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}Bu) (Found: C, 32.2; H, 4.2; N, 6.8. Calc. for $[Sn_4N_4C_{22}H_{34}]$: C, 31.8; H, 4.1; N, 5.8%).

‡ Crystal data for **3**: $C_{22}H_{34}N_4Sn_4$, M = 829.29, monoclinic, space group $P\bar{1}$ (no. 2), a = 8.670(5), b = 9.703(5), c = 16.815(9) Å, α = 75.71(3), β = 81.36(4), γ = 81.72(4)°, U = 1347(1) Å^3, Z = 2, $\rho_{calc.}$ = 2.045 Mg m^{-3}, λ = 0.71073 Å, T = 180(2) K, μ(Mo-Kα) = 3.682 mm^{-1}, F(000) = 788. Data were collected on a Stoe AED diffractometer using an oil-coated rapidly-cooled crystal[8] of dimensions 0.40 × 0.28 × 0.16 mm by the ω–θ method (3.56 ≤ θ ≤ 22.50°). Of a total of 5293 collected reflections, 3505 were independent (R_{int} = 0.032). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to final, values of $R1[F > 4\sigma(F)]$ = 0.023 and $wR2$ = 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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