

Synthesis and structure of $[\{\text{Sn}_4(\text{NBu}^t)_3\text{P}\}\{\text{Sn}_4(\text{NBu}^t)_3(\text{OSiMe}_3)\}]$; a low-oxidation state p-block metal complex containing a P^{3-} anion

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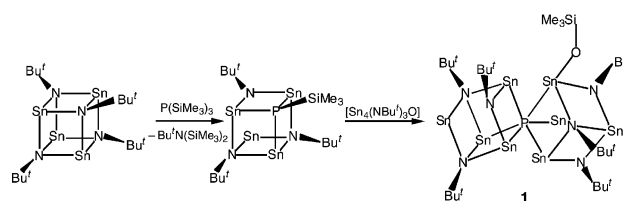
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The complex $[\{\text{Sn}_4(\text{NBu}^t)_3\text{P}\}\{\text{Sn}_4(\text{NBu}^t)_3(\text{OSiMe}_3)\}]$ **1** is the first example of a low-oxidation state p-block metal complex containing a P^{3-} anion.

In contrast to transition metal complexes containing bare P^{3-} ions,¹ the analogous complexes of the heaviest (most metallic) p-block elements have been almost unexplored.² Among the very few complexes of this type so far structurally characterised are $[(\text{Cp}^*\text{Al})_6\text{P}_4]$,^{2e} $[(\text{Me}_3\text{Si})_3\text{CGa}]_3\text{P}_4$ ^{2f} and $[\{\text{Me}_2\text{Sn}\}_n\text{P}_2]$ ($n = 5^{2b}$ or 6^{2c}), all of which contain the Group 13 and 14 elements in their highest oxidation states (*i.e.* corresponding to the formal loss of the valence s and p electrons). Two of the main synthetic strategies used to generate these species are the reactions of high-oxidation state organometallic dihydrides with P_4 ^{2b,c} or oxidative addition of low-oxidation state organometallics with P_4 .^{2e,f} Norman and coworkers recently showed that the binary Group 15 phosphides EP ($\text{E} = \text{Sb}, \text{Bi}$) can be generated by the reactions of $\text{E}(\text{NMe}_2)_3$ with $\text{P}(\text{SiMe}_3)_3$,³ a process which is driven thermodynamically by the formation of Si–N bonds. However, although the related reactions of transition metal halides with trimethylsilyl phosphines have been used to generate molecular transition metal phosphides,^{1*i,j*} neither this reaction nor reactions involving amides or imides have previously been used in the generation of molecular main group metal species containing the P^{3-} anion.⁴ Our interest in the synthesis and coordination chemistry of Sn^{II} oxo cubanes such as $[\text{Sn}_4(\text{NBu}^t)_3\text{O}]$ ^{5,6} led us to investigate new approaches to the isoelectronic Group 15 anions $[\text{Sn}_4(\text{NR})_3\text{E}]^-$ ($\text{E} = \text{N}, \text{P}$). Herein we report the synthesis and structure of $[\{\text{Sn}_4(\text{NBu}^t)_3\text{P}\}\{\text{Sn}_4(\text{NBu}^t)_3(\text{OSiMe}_3)\}]$, a Sn^{II} phosphide which formally contains a $[\text{Sn}_4(\text{NBu}^t)_3\text{P}]^-$ anion.

The reaction of $[\text{SnNBu}^t]_4$ (1 equiv.) with an excess of $\text{P}(\text{SiMe}_3)_3$ in $\text{THF}-\text{PhCH}_3$ was undertaken initially in order to obtain the substituted cubane $[\text{Sn}_4(\text{NBu}^t)_3(\text{PSiMe}_3)]$ [via elimination of $\text{Bu}^t\text{N}(\text{SiMe}_3)_2$]. However, unexpectedly the title complex $[\{\text{Sn}_4(\text{NBu}^t)_3\text{P}\}\{\text{Sn}_4(\text{NBu}^t)_3(\text{OSiMe}_3)\}]$ **1** was obtained as the only isolable crystalline product (in low yield). The incorporation of the O centre within the OSiMe_3 group of **1** was confirmed by the subsequent structural characterisation of the complex, and is supported by the observation of a Si–O stretching band in the IR spectrum at 1175 cm^{-1} .⁷ The low solubility of the complex once isolated precluded more extensive investigations of its solution structure. However, the observation of only two Bu^t resonances in the ^1H NMR spectrum of **1** (δ 1.15 and 1.11) suggests that the behaviour of the complex in solution is far from simple. The likely pathway to **1** involves the addition reaction of $[\text{Sn}_4(\text{NBu}^t)_3(\text{PSiMe}_3)]$ and the oxo cubane $[\text{Sn}_4(\text{NBu}^t)_3\text{O}]$ (as depicted in Scheme 1). It was assumed that the latter species arose from trace hydrolysis of the imido Sn^{II} cubane $[\text{SnNBu}^t]_4$ during storage of the reaction mixture; a previously established route to the oxo cubane.⁶ This view is supported by the isolation of **1** from the reaction of $[\text{SnNBu}^t]_4$ (1 equiv.) and an excess of $\text{P}(\text{SiMe}_3)_3$, followed by addition of $[\text{Sn}_4(\text{NBu}^t)_3\text{O}]$ (1 equiv.).[†] Significantly, attempts



Scheme 1

to prepare the complex by reaction of $[\text{Sn}_4(\text{NBu}^t)_3\text{O}]$ (2 equiv.) with $\text{P}(\text{SiMe}_3)_3$ (1 equiv.) failed to produce **1**, indicating that the imido cubane $[\text{SnNBu}^t]_4$ is involved in the initial step.

The X-Ray crystallographic study of **1** shows that molecules of the complex consist of a pseudo 'double-cubane' $\text{Sn}_8(\text{NBu}^t)_6\text{P}$ core (Fig. 1),[‡] in which the two $\text{Sn}_4(\text{NBu}^t)_3$ cubane subunits are linked together by a P^{3-} ion. Although other Group 13 and 14 metal complexes containing the P^{3-} ion have been structurally characterised,² **1** is the first example in

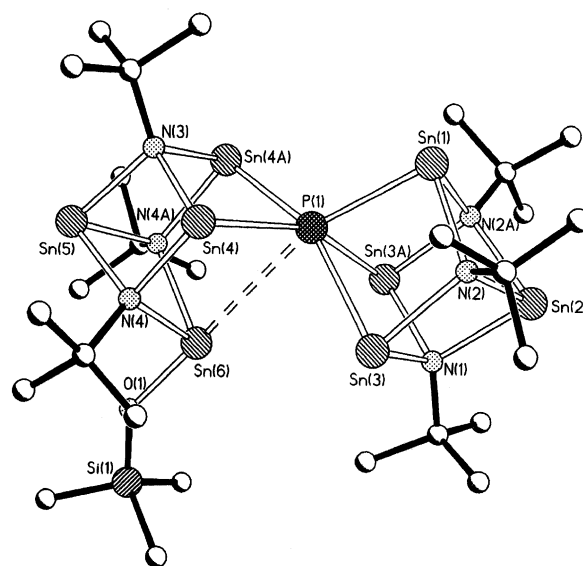


Fig. 1 The cage structure of **1**. H-atoms have been omitted for clarity. Key bond lengths (Å) and angles ($^\circ$): Sn(1)–P(1) 2.580(4), Sn(1)–N(2) 2.219(7), Sn(1)–N(2) 2.219(8), Sn(2)–N(1) 2.20(1), Sn(2)–N(2,2A) 2.219(8), Sn(3)–P(1) 2.725(3), Sn(3)–N(1) 2.207(6), Sn(3)–N(2) 2.235(7), Sn(4)–P(1) 2.630(3), Sn(4)–N(3) 2.198(7), Sn(4)–N(4) 2.177(7), Sn(5)–N(3) 2.22(1), Sn(5)–N(4,4A) 2.187(7), Sn(6)–P(1) 3.298(4), Sn(6)–N(4) 2.265(8), Sn(6)–N(4A) 2.265(7), Sn(6)–O(1) 1.981(9), Si(1)–O(1) 1.64(1); Sn–N–Sn range 96.9(3)–107.0(3), N–Sn–N range 78.1(3)–81.4(3), N–Sn–P range 82.2(2)–98.3(2), Sn(1)–P(1)–Sn(3) 84.8(1), Sn(1)–P(1)–Sn(4) 118.0(1), Sn(2)–P(1)–Sn(3) 98.8(3), Sn(3)–P(1)–Sn(3A) 101.3(4), Sn(3)–P(1)–Sn(4) 94.70(5), Sn(3)–P(1)–Sn(4A) 155.4(2), Sn(4)–P(1)–Sn(4A) 82.7(1), N(4)–Sn(6)–O(1) 99.8(3), Sn(6)–O(1)–Si(1) 140.5(7).

which the p-block metal is in a low-oxidation state (*i.e.* in which the metal lone-pair of electrons is retained).

Although they occur over fairly broad ranges, the Sn–N bond lengths [2.177(7)–2.265(8) Å] and Sn–N–Sn [96.9(3)–107.0(3)°] and N–Sn–N [78.1(3)–81.4(3)°] angles in **1** are similar to those found in structurally characterised imido Sn(II) cubanes of the type [SnNR]₄ [*cf.* Sn–N range 2.15(1)–2.34(2) Å, Sn–N–Sn mean 98.4°, N–Sn–N mean 81.9°].^{5,8} An unusual feature of **1** is the distorted six-coordinate geometry of the P^{3–} centre. The five Sn–P bonds involved with Sn(1) [2.580(4) Å], Sn(3,3A) [2.725(3) Å] and Sn(4,4A) [2.630(3) Å] fall within the range previously reported for bonds between anionic (R₂P[–] and RP^{2–}) P centres and Sn^{II} (2.60–2.80 Å).^{9,10} However, the remaining contact with the chemically distinct tin centre Sn(6) [3.298(3) Å] [which is bonded to the O centre of an Me₃SiO group [Sn–O 1.981(9) Å]¹¹] is clearly much weaker, and is around the value which could be estimated for that between a neutral phosphine (R₃P) and Sn^{II}.¹⁰ The weakness of this contact is consistent with the absence of a vacant p orbital on Sn(6) and the apparent orientation of the metal lone pair towards the core of **1**. The coordination number of the Sn(II) centre and range of Sn–P distances in **1** are similar to that found in the NaCl-type lattice structure of tetragonal SnP [with Sn–P bond lengths of 2.55(6), 2.74(1) and 3.41(1) Å].¹² However, the bonding pattern in **1** is markedly different to that found in all previously reported molecular p-block metal compounds containing P^{3–} anions, which have three-coordinate P atoms and electron-precise metal–P bonding.² Two bonding schemes may be used to rationalise the Sn₅P unit in **1**. Although the description of the structure of **1** as a donor complex of the [Sn₄(NBU^t)₃P][–] anion and a [Sn₄(NBU^t)₃(OSiMe₃)⁺ fragment is an attractive one [*i.e.* containing a 2e–3c bond between P(1) and Sn(4) and (4A)], a model involving a 2e–3c bond with Sn(3) and Sn(3A) appears to be most consistent with the variation of the Sn–P bond lengths in the complex.

In conclusion, the first low-oxidation state p-block metal complex containing a P^{3–} anion has been prepared. The synthetic route used in its preparation ('silyl/imido elimination') exemplifies a new, potentially broad-ranging approach to a variety of molecular main group as well as transition metal species containing 'bare' P centres.

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Notes and references

† *Synthesis of 1*: [SnNBU^t]₄ (0.42 mmol) was prepared *in situ* by reaction of Bu^tNH₂ (0.18 mL, 1.70 mmol) with Sn(NMe₂)₂ (0.35 g, 1.70 mmol) in PhCH₃ (15 mL). The reaction mixture was brought to reflux briefly and stirred (2 h), to give a bright yellow solution. To this solution was added P(SiMe₃)₃ (0.42 mL, 1.45 mmol, excess) at room temperature. Immediately, a solution of [Sn₄(NBU^t)₃O] (0.44 mmol) in THF (10 mL) was added. Stirring at room temperature (20 min) produced a deep red solution. Filtration followed by reduction of the solvent under vacuum (to ca. 3 mL) and storage (18 °C, 3 d) gave deep red cubic crystals of **1**. These were washed with Et₂O (2 × 5 mL) prior to analysis. Yield 0.090g (14%). Decomp. 153 °C to black solid. IR (Nujol mull), $\nu_{\text{max}}/\text{cm}^{-1}$ 1355m, 1250m, 1237w, 1175s (Si–O str.), 1092s, 1021s, 937m, 916m, 899w, 871w, 822s(sh), 801vs (air exposure led to a gradual loss of the bands at 1175, 937, 916, 899 and 822 cm^{–1} and to a change in color from red to yellow). ¹H NMR (+25 °C, 400.132 MHz, [D₈]-THF): δ = 1.15 (s, 18H, Bu^tN), 1.11 (s, 36H, Bu^tN), 0.11 (s, 9H, Me₃Si). ³¹P NMR (+25 °C, 161.976 MHz, [D₈]-THF): δ = +245.0 (s, poorly resolved shoulders). Anal. Found: C, 21.7; H, 4.2; N 5.4. Calc.: C 21.7; H, 4.2; N, 5.6%.

‡ *Crystal data for 1*: C₂₇H₆₃N₆OPSiSn₈, *M* = 1496.42, monoclinic, space group *Cm*, *Z* = 2, *a* = 13.453(3), *b* = 15.280(3), *c* = 12.736(3) Å, β = 116.00(3)°, *V* = 2353.1(8) Å³, *D_c* = 2.109 Mg m^{–3}, $\mu(\text{Mo–K}\alpha)$ = 4.257

mm^{–1}, *T* = 220(2) K. Data were collected on a Nonius Kappa CCD diffractometer. Of a total of 10543 reflections collected, 5244 reflections were independent (*R*_{int} = 0.021). The structure was solved by direct methods and refined by full-matrix least squares on *F*². Final *R*₁ = 0.043 [for 4605 reflections *I* > 2σ(*I*)] and *wR*₂ = 0.193 (all data).¹³ CCDC 182/1887. See <http://www.rsc.org/suppdata/cc/b0/b008108f/> for crystallographic files in cif format.

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