

Synthesis and structure of $[\{\text{Sn}(\mu\text{-PCy})\}_3(\text{Na}\cdot\text{PMDETA})_2]$, containing an electron-deficient $[\{\text{Sn}(\mu\text{-PCy})\}_3]^{2-}$ dianion†

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The reaction of CyPHNa with $\text{Sn}(\text{NMe}_2)_2$ in the presence of PMDETA (= $\{\text{Me}_2\text{NCH}_2\text{CH}_2\}_2\text{NMe}$) gives the title compound $[\{\text{Sn}(\mu\text{-PCy})\}_3(\text{Na}\cdot\text{PMDETA})_2]$ (**1**), containing an electron-deficient $[\{\text{Sn}(\mu\text{-PCy})\}_3]^{2-}$ dianion with a novel two-electron, three centre (2e–3c) bonding arrangement.

The reactions of Group 15 dimethylamido reagents, like $\text{E}(\text{NMe}_2)_3$ (E = As–Bi), with alkali metal primary phosphides (RPHM; M = Li, Na) provide a low-temperature, solution route for the deposition of technologically important alkali metal/Group 15 alloys.^{1,2} These reactions occur through the initial formation of electron-precise cages³ which decompose *via* coupling of the phosphide groups⁴ into Zintl compounds, M_3E_7 , and cyclophosphanes, $[\text{RP}]_n$. The formation of P–P single bonds in this process (having the greatest homoatomic single bond energy of all of the Group 15 elements) provides the principal thermodynamic driving force. Our initial studies of the Group 14 reagent $\text{Sn}(\text{NMe}_2)_2$ with RPHLi suggest similar reaction characteristics to the Group 15 reagents.⁵ Despite the considerable knowledge gained so far from these combined studies, however, the precise mechanism by which electron-precise cage arrangements are converted into metallic cages is unclear. We report here the isolation of the new model intermediate $[\{\text{Sn}(\mu\text{-PCy})\}_3(\text{Na}\cdot\text{PMDETA})_2]$ (**1**) (Cy = cyclohexyl, PMDETA = $(\text{Me}_2\text{NCH}_2\text{CH}_2)_2\text{NMe}$), whose electron-deficient Sn...Sn bonded $[\{\text{Sn}(\mu\text{-PCy})\}_3]^{2-}$ dianion gives a key insight into the alloy-forming process.

Compound **1** is obtained from the reaction of CyPHNa (3 equiv.) with $\text{Sn}(\text{NMe}_2)_2$ (1 equiv.) in the presence of the Lewis base donor PMDETA (ESI^\dagger). Although the yield of **1** is low (11%), the formation of the complex is entirely reproducible under these conditions. ³¹P NMR spectroscopic studies of the reaction mixture show that although **1** is a major product, a complicated mixture of species is present at the end of the reaction (including the cyclophosphane $[\text{CyP}]_4$ and unreacted CyPHNa and CyPH_2). The ³¹P NMR behaviour of the complex is highly solvent dependent. The ³¹P NMR spectrum in THF consists of two poorly-resolved multiplets [at δ –65.2, –184.6 (*ca.* 1 : 1)], with only minor changes in the spectrum occurring with temperature. In DMSO solvent at rt two well-resolved singlets are observed [at δ –37.8, –72.7 (*ca.* 1:2)], with ^{119,117}Sn satellites being found for each. Since no coupling between the P environments is observed, the behaviour of **1** in both solvents probably indicates the presence of ion-paired (down-field) and ion-separated (up-field) $[\{\text{Sn}(\mu\text{-PCy})\}_3]^{2-}$ dianions.

A low-temperature X-ray crystallographic study of **1** (ESI^\dagger) shows that the complex exists as discrete molecules in the solid

state, arising from the ion-pairing of the $[\{\text{Sn}(\mu\text{-PCy})\}_3]^{2-}$ dianion with two $[\text{Na}\cdot\text{PMDETA}]^+$ cations (Fig. 1). One of the Na^+ cations [$\text{Na}(2)$] is bonded to the three Sn centres on one face of the cyclic $[\{\text{Sn}(\mu\text{-PCy})\}_3]^{2-}$ dianion. The bonding contacts between this cation and Sn(1) [3.231(1) Å] and Sn(3) [3.388(1) Å] are within the range of values found previously in the few structurally characterized Sn–Na bonded complexes reported,⁶ while the remaining contact to Sn(2) [3.619(2) Å] is consistent with a weaker interaction. The second Na^+ cation [$\text{Na}(1)$] is bonded to two of the μ_2 -P atoms on the other face of the dianion [P(2)–Na(1) 2.924(1), P(3)–Na(1) 2.910(1) Å].⁷

The Sn–P bond lengths within the Sn_3P_3 ring of the $[\{\text{Sn}(\mu\text{-PCy})\}_3]^{2-}$ dianion fall in a relatively narrow range [2.5570(8)–2.5852(8) Å], and are typical of Sn–P bonds found

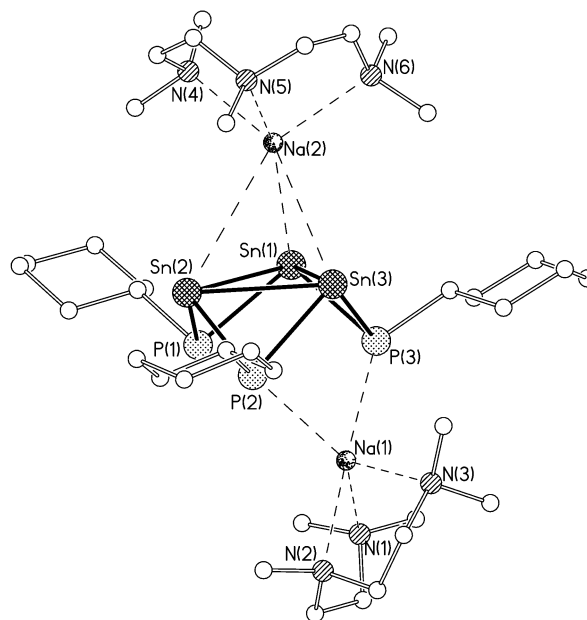


Fig. 1 Molecular structure of **1**. H-atoms, disorder in one of the PMDETA ligands and lattice solvation by toluene molecules have been omitted for clarity. Key bond lengths (Å) and angles (°): Sn(1)–P(1) 2.5611(8), Sn(1)–P(3) 2.5570(8), Sn(1)–Sn(2) 3.1824(3), Sn(1)–Sn(3) 3.1983(3), Sn(1)–Na(2) 3.231(1), Sn(2)–P(1) 2.5742(8), Sn(2)–P(2) 2.5636(8), Sn(2)–Sn(3) 3.1502(3), Sn(2)–Na(2) 3.619(2), Sn(3)–P(2) 2.5790(8), Sn(3)–P(3) 2.5852(8), Sn(3)–Na(2) 3.388(1), P(2)–Na(1) 2.924(1), P(3)–Na(1) 2.910(1), Na(2)–N(PMDETA) 2.423(4)–2.53(3), Na(1)–N(PMDETA) 2.469(3)–2.494(3), Sn(2)–Sn(1)–Sn(3) 59.169(6), Sn(1)–Sn(2)–Sn(3) 60.668(6), Sn(2)–Sn(3)–Sn(1) 60.163(6), P(1)–Sn(1)–P(3) 97.71(3), P(1)–Sn(2)–P(2) 97.49(3), P(2)–Sn(3)–P(3) 93.10(2), Sn(1)–P(1)–Sn(2) 76.59(2), Sn(2)–P(2)–Sn(3) 75.55(2), Sn(1)–P(3)–Sn(3) 76.92(2). CCDC 194980.

† Electronic supplementary information (ESI) available: experimental procedure, crystallographic data and *ab initio* calculations. See <http://www.rsc.org/suppdata/cc/b3/b300522d/>

in structurally characterised Sn^{II} phosphides.^{5,8} The Sn–Sn contacts in this unit [Sn(1)–Sn(2) 3.1824(3), Sn(1)–Sn(3) 3.1823(3), Sn(2)–Sn(3) 3.1502(3) Å] are within the range of values found in Sn–Sn bonded complexes [mean 2.91 Å]⁹ and are typical of Sn–Sn bond lengths present in electron-deficient Zintl ions.¹⁰ However, these bonds are considerably longer than those found in multiply-bonded Sn compounds such as [Ph(2,6-Trip₂)Sn–Sn(2,6-Trip)Ph][–] [2.782(1)–2.824(1) Å] (Trip = 2,4,6-Ph₃C₆H₂)^{6b,11} or [R₂Sn=SnR₂] [2.77–2.83 Å].¹² Evidence for the importance of Sn–Sn bonding in **1** is seen in the unusually acute Sn–P–Sn angles within the [Sn(μ–PCy)₃]^{2–} dianion [75.55(2)–76.92(2)°]. The latter are consistent with only limited hybridisation of the *s* and *p* orbitals on the P and Sn centres.

Model *ab initio* MO calculations of the isolated [Sn(μ–PMe)₃]^{2–} dianion (**1a**) and the neutral complex [Sn(μ–PMe)₃Na₂] (**1b**) were used to probe the bonding present in **1** (ESI†).¹³ The structures of both species at the HF and DFT (B3LYP and MPW1K) levels are in good agreement with the solid-state structure of **1**. Natural bond orbital (NBO) analysis was performed on the B3LYP wavefunction.^{19,20} The NBO analysis of **1a** and **1b** indicates the existence of a 2e–3c Sn₃ bond. The occupancy of the 2e–3c NBO in **1a** is 1.975 while in **1b** the occupancy drops to 1.810. The character of this NBO is primarily constructed from *p*-natural atomic orbitals (NAO) on Sn, each Sn contributing 1/3 of a bond to this NBO. This NBO has the highest doubly occupied NBO energy and can be compared to the HOMO molecular orbital found in **1a** and **1b** (Fig. 2). Associated with this bonding 2e–3c NBO are two degenerate, anti-bonding Sn₃ NBO's. These anti-bonding NBO's play an important role in delocalization of charge within the dianion, having occupancy of 0.115 (coming mostly from donation from the Sn–P NBO's).

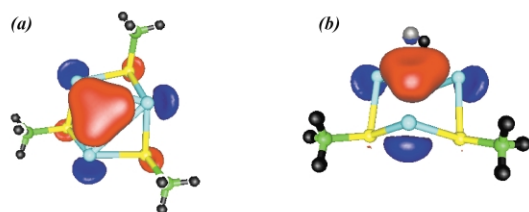


Fig. 2 DFT(B3LYP)/cc-pvtz calculations of the HOMO of a) the discrete [Sn(μ–PMe)₃]^{2–} dianion (**1a**), and b) the neutral [Sn(μ–PMe)₃Na₂] molecule (**1b**).

In summary, studies of the [Sn(μ–PCy)₃]^{2–} anion show that it has an unprecedented bonding arrangement for a main group metal phosphide complex. The delocalized Sn₃ unit of **1** can be regarded an incipient Zintl ion, a view which provides a possible mechanistic insight into the ultimate formation of Zintl compounds from electron-precise *p*-block element phosphide cages.

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