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Formation and Rearrangement of Sn^{II} Phosphanediide Cages

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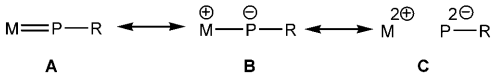
Abstract: The room-temperature reactions of $Sn(NMe_2)_2$ with less sterically demanding primary phosphines (RPH_2) give the homoleptic phosphanediide compounds $[SnPR]_n$ in high yields (R = *t*Bu (**1a**), cyclohexyl (**1b**), 1-adamantyl (**1c**)). However, the room-temperature reaction of Mes^*PH_2 (Mes^* = 2,4,6-$tBu_3C_6H_2$) with $Sn(NMe_2)_2$ gives the model intermediate $[\{SnPMes^*\}_2(\mu\text{-}NMe_2)SnP(H)Mes^*]$ (**3**), together with the product of complete deprotonation $[SnPMes^*]_3$ (**4**). Phosphorus–phosphorus bonded products are produced in these reactions at elevated temperatures. If the reaction producing **1a** is heated to reflux then [*t*BuP(H)P(H)*t*Bu] is produced as the major product (together with tin metal). The novel octanuclear cage $[\{SnPtBu\}_7Sn(PtBu)_3]$ (**2**) can also be isolated in low yield, resulting from formal addition of the heterocyclic stannylene $[(tBuP)_3Sn]$ to a Sn–P single bond of the *intact* structure of **1a**. Prolonged heating of the reaction producing **3** and **4** leads to the formation of the diphosphene $[PMes^*]_2$ (**5**) and tin metal. The X-ray structures of the heptamer **1a** ($n = 7$), octanuclear **2** and trinuclear **3** are reported.

Keywords: bond formation · dehydrocoupling · phosphorus · tin · X-ray diffraction

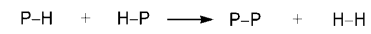
Introduction

In contrast to the transition-metal species, the bonding situation in main group compounds that contain (formally) RP^{2-} ligands is noticeably more polar. For this reason transition-metal compounds commonly contain a high degree of P–M multiple bonding and are described as phosphinidenes (resonance form A, Scheme 1). Main group counterparts are more properly described as phosphanediides, reflecting the greater polarity in the metal–phosphorus bonds (resonance forms B and C, Scheme 1). A further impact of this polarity is seen in the formation of normally highly-aggregated cages for main group phosphanediides, in which the RP^{2-} ligands bridge the metals.[1–3] Examples of large main group cages of this type are numerous.[1–3] Only in rare cases has multiple bonding been seen, where there is electronic and/or steric stabilisation.[4]



Scheme 1. Resonance forms of a metal phosphinidene/phosphanediide (M = metal atom).

Our current interest in the chemistry of tin(II) phosphanediides stems from the realisation that their reactivity has some striking similarities to the behaviour of transition-metal phosphinidenes.[5,6] This can to some extent be seen as a result of the greater degree of covalency involved in metal–ligand bonding as compared to more electropositive early main group metals (resonance form B, Scheme 1). Like transition-metal relatives,[6] p-block phosphanediides are active in dehydrogenic P–P bond formation (Scheme 2),[5] producing a similar range of products by closely related reaction mechanisms.



Scheme 2. Dehydrogenic P–P bond formation.

In on-going studies we are exploring the potential applications of p-block phosphanediides in a range of other bond-forming reactions involving unsaturated and electrophilic organic substrates. Transition-metal phosphinidenes have so far dominated this area,[6] and little is known about the reac-

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tivity of main group counterparts.[7] Tin(II) phosphanediides are of particular interest as reagents in this regard since they are rare examples of neutral homoleptic main group phosphanediides. This should allow the study of the reactivity of the RP functionality without the complications that may arise through competing ligand reactions. However, to date comparatively little is known even about the structural chemistry of neutral Sn^{II} phosphanediides compounds, and only the tetramer $[SnPSitBu_3]_4$,[3d] hexamer $[SnPSiiPr_3]_6$[3c] and heptamer $[SnPSiiPr_3]_7$[3f] have been structurally characterised.

In the current paper, we present a simple way of making Sn^{II} phosphanediides $[SnPR]_n$ containing aliphatic groups (R), and thus, providing key and easily prepared reagents for the future. We also explore the thermal decomposition of these species, revealing that P–P coupling reactions occur in this process.

Results and Discussion

Previous routes to neutral $[SnPR]_n$ compounds have involved 1) salt exchange reactions of R_3SiPLi_2 with $SnCl_2$ and 2) acid–base reactions of SnR'_2 [$R' = N(SiMe_3)_2$, 2,4,6-$(CF_3)_3C_6H_2$] with R_3SiPH_2.[3d,c,f] Noticeably, there are no previous reports of compounds containing simple aliphatic R groups. Pertinent to this, some time ago we found that the readily prepared Sn^{II} reagent $Sn(NMe_2)_2$ is an extremely potent base that can be used to obtain Sn^{II}–imido compounds through deprotonation of a broad range of amines, RNH_2 (Scheme 3).[8,9] Importantly, this reaction is successful

$$4Sn(NMe_2)_2 + 4\,RNH_2 \longrightarrow [SnNR]_4 + 8Me_2NH$$

Scheme 3.

even at room temperature for very un-acidic primary amines, containing aliphatic R groups in which there is no potential for electronic stabilisation of the RN^{2-} functionality. It can be noted that weaker bases such as $Sn\{N(SiMe_3)_2\}_2$ require far more forcing conditions to give complete reaction (i.e., in the melt at 50–60 °C or at reflux in *n*-hexane), and are therefore not suitable for the synthesis of thermally unstable compounds.[10]

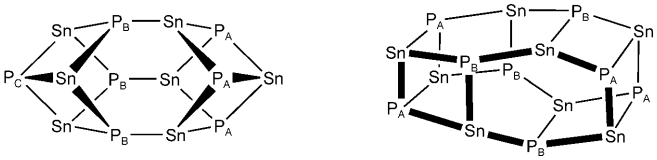
Clearly the use of $Sn(NMe_2)_2$ should be extendable to the corresponding aliphatic phosphines, providing a low-temperature route to Sn^{II} phosphanediides. In practice, the reactions of $Sn(NMe_2)_2$ with primary phosphines (RPH_2) are markedly solvent dependent, reactions occurring only slowly in *n*-hexane but rapidly in THF at room temperature. In the case of THF as the solvent, clear solutions are formed after stirring for 16 h at room temperature. For R = *t*Bu, Cy (cyclohexyl) and 1-Ad (adamantyl), removal of the solvent under vacuum produces orange powders of $[SnPR]_n$ (R = *t*Bu (**1a**), Cy (**1b**), 1-Ad (**1c**), in 78–84 % yields, Scheme 4)

$$n\,Sn(NMe_2)_2 + n\,RPH_2 \longrightarrow [SnPR]_n + 2n\,Me_2NH$$

Scheme 4.

(see the Experimental Section). These materials are highly pure and free from residual lattice solvent, as revealed by elemental analysis. No solid products were isolated, however, in the case of R = Ph an impure orange oil was formed by complete removal of the solvent.

Only in the case of **1a** we were able to grow single crystals suitable for X-ray crystallography, which showed that **1a** is a heptameric cage with a similar structure to the previously reported heptamer $[SnP(SiiPr_3)]_7$ (see later, Figure 1). The room-temperature $^{31}P\{^1H\}$ NMR spectra of **1a** in THF or toluene show four resonances at $\delta = -81.8$ (s), -81.7 (s), -167.5 (d) and -410.6 ppm (s), together with $^{117/119}Sn$–^{31}P satellites for each. Whereas the resonances at $\delta = -81.8$ (s), -167.5 (d) and -410.6 ppm (s) retain a relative ratio of 3:3:1 at all concentrations, the resonance at $\delta = -81.7$ ppm noticeably increases in intensity with dilution. The overall appearance of the ^{31}P NMR spectra of **1a** is similar to the $^{31}P\{^1H\}$ NMR spectrum of the previously reported heptamer $[SnP(SiiPr_3)]_7$ ($\delta = -243.9$ (s), -294.9 (s) and -373.0 ppm (s)),[3f] although with considerable differences in the chemical shifts involved, caused by changing the $SiiPr_3$ group for a *t*Bu group in **1a**. The three resonances at $\delta = -81.8$ (s), -167.5 (d) and -410.6 ppm (s) in **1a** can be assigned to the intact heptamer. Referring to the core arrangement of the heptamer shown in Scheme 5 (left), these three P shifts correspond to P_A, P_B and P_C (i.e., ratio 3:3:1, the same as that found in the ^{31}P NMR spectrum). However, the presence of the additional, concentration-dependent resonance at $\delta = -81.7$ ppm for **1a** shows that there is significant dissociation of the heptamer in solution. Although cryoscopic molecular mass measurements were restricted by the relatively low solubility of $[SnPtBu]_n$ (**1a**) in benzene, the measured degree of association (*n*) of 3.54 ± 0.24 (0.02 mol dm^{-3}) is consistent with the presence of a smaller oligomer in solution.



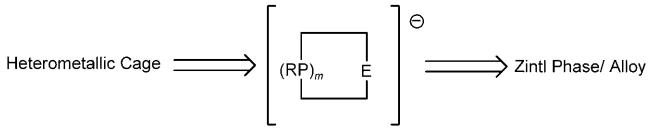
Scheme 5. Core structure of the heptamers **1a** and **1c** (left) and of the proposed octamer **1b** (right).

The $^{31}P\{^1H\}$ NMR spectrum of **1c** is also dominated by three resonances, $\delta = +33.4$ (t), -18.2 (t) and -205.4 ppm (ddd) (ratio ca. 3:3:1). This is consistent with the presence of a heptameric structure similar to that found for **1a**, but with a greater degree of magnetic inequivalence of the phosphorus atoms. Thus, the lone phosphorus atom (P_C,

Scheme 5) is split by three inequivalent P atoms (P_B), whereas the resonances for P_A and P_B are split into apparent (broad) triplets with $^2J(^{31}P,^{31}P)$ coupling to the nearest-neighbour P atoms within the Sn_3P_3 rings of the core. Although of relatively low solubility, cryoscopic molecular mass measurements in benzene provide evidence for dissociation of **1c** in solution, with the association state (n) being 3.69 ± 0.72 (0.01 mol dm^{-3}). Consistent with this, other unidentified solution species are also observed in the $^{31}P\{^1H\}$ spectrum of **1c** at room temperature, notably at $\delta = -2.3$ ppm (s).

The appearance of the $^{31}P\{^1H\}$ NMR spectrum of **1b** in THF is considerably different from those of **1a** or **1c**, and suggests that this compound does not adopt a heptameric structure. Analysis of the spectrum is complicated by the apparent instability of **1b** in solution, as witnessed by the presence of decomposition products even in freshly prepared samples (most notably a trace amount of CyP(H)–P(H)Cy, two AA′BB′ multiplets in the ^{1}H-coupled NMR at $\delta = -84.7$ and -88.0 ppm). However, the major solution species is characterised by two resonances at $\delta = -38.0$ (br d) and -1.0 ppm (dd) (relative ratio ca. 1:1). Bearing in mind the lower steric demands of the Cy group compared to *t*Bu and 1-Ad, it is likely that **1c** is a higher oligomer than a heptamer. Indeed, the ^{31}P NMR spectrum is consistent with an AA′BB′ system that would occur with an octameric arrangement for **1c** (Scheme 5, right). Similar octameric arrangements have been seen before for other main group compounds.[11]

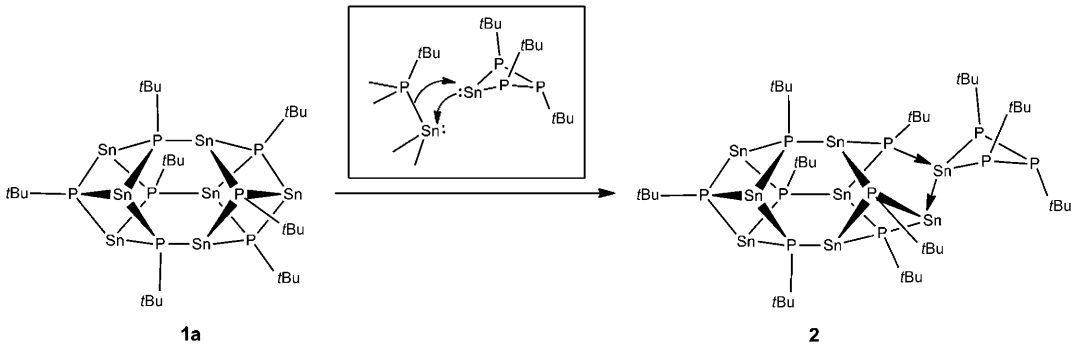
Solid **1a**, **1b** and **1c** are relatively stable at room temperature under dry, O_2-free N_2 for days, decomposing only slowly at this temperature to give metallic-looking residues. This intrigued us, as previous studies have shown that heterometallic group 15/alkali metal phosphanediides compounds (e.g., $[\{Sb(PCy)_3\}_2(Li{\cdot}NHMe_2)_6]$[12]) decompose into Zintl ions and metallic alloys.[13] As illustrated in Scheme 6, this process occurs through heterocyclic anions of the type $[(RP)_mE]^-$ and is driven by the thermodynamics of P–P single-bond formation. We wondered whether similar chemistry was occurring in the thermal decomposition of **1a–c**. In order to test this, the reaction producing **1a** was followed in an NMR tube in [D$_8$]THF with heating to reflux for 16 h under N_2. After this time the $^{31}P\{^1H\}$ NMR spectrum showed that decomposition of **1a** had indeed occurred, with the formation of a number of phosphorus-containing products ($\delta = 39.7$–-75 ppm). However, by far the major product formed is the P–P-coupled diphosphane [*t*BuP(H)P(H)*t*Bu] ($\delta = 59.3$ ppm (d, $^1J(^{31}P,^{31}P) = 184$ Hz; appearing as the expected AA′BB′ pattern in the ^{1}H-coupled spectrum).[14] The formation of [CyP(H)P(H)Cy] as a decomposition product was also noted earlier in the ^{31}P NMR spectroscopic studies of **1b** (see above).



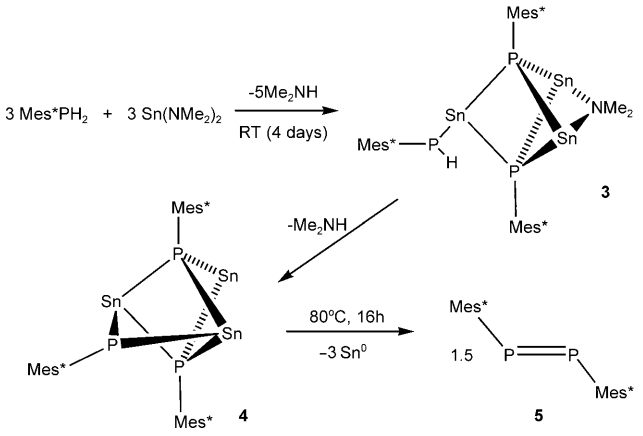
Scheme 6.

Closer inspection of the in situ ^{31}P NMR spectrum also reveals the presence of an A_2B spin system ($\delta = -12.7$ (t), -46.0 ppm (d, $^1J(^{31}P,^{31}P) = 231$ Hz)), suggesting the formation of a heterocyclic $[(t\text{BuP})_3\text{Sn}]$ ring unit. On one occasion we were able to isolate a few amber crystals of the new cage $[\{\text{SnP}t\text{Bu}\}_7\text{Sn}(\text{P}t\text{Bu})_3]$ (**2**) from a scaled-up reaction in a Schlenk tube (1 mmol scale in 20 mL THF). Owing to the low yield of **2** it was only characterised by X-ray crystallography (see later, Figure 3). The structure of **2** is apparently derived from addition of the heterocyclic stannylene $[(t\text{BuP})_3\text{Sn}]$ to one of the Sn–P bonds of the intact structure of **1a** (Scheme 7). The in situ NMR experiments of the decomposition of **1a** and the isolation of **2** provide indications of the close relationship between the chemistry of Sn^{II} phosphanediides and the previously reported studies of other main group systems involving P–P bond formation.

In order to assess the effects of increased steric demands on the structure of the formed Sn^{II} phosphanediide, we also investigated the 1:1 stoichiometric reaction of $Sn(NMe_2)_2$ with Mes*PH_2 (Mes* = 2,4,6-*t*Bu$_3$C$_6$H$_2$) at $-78\,^\circ$C in toluene. Orange crystals of the heteroleptic, trinuclear cage $[\{\text{SnPMes*}\}_2(\mu\text{-NMe}_2)\text{SnP(H)Mes*}]$ (**3**) are deposited slowly by storage at room temperature (Scheme 8). This result is of particular interest in relation to our previous studies of the reactions of $Sn(NMe_2)_2$ with primary amines (RNH_2), which normally give the cubanes $[\text{SnNR}]_4$ where the R group is less sterically demanding (e.g., R = *t*Bu, Cy).[8] However, for



Scheme 7. Formation of **2**.



Scheme 8.

more sterically encumbered amines the trinuclear intermediates are generated [{Sn(μ-NR)$_2$}{Sn(μ-NMe$_2$)}$_2$] [R = Mes (1,2,3-Me$_3$C$_6$H$_2$), Dipp (2,6-*i*Pr$_2$C$_6$H$_4$)].[9] Compound **3** can be seen as a model intermediate in the formation of cages like **1a–c**, containing single- and double-deprotonated RP^{2-} and RPH^{-} ligands.

^{1}H and ^{31}P NMR spectroscopic studies of **3** in benzene (Figure 1a) show that the species is intact in solution, having a structure that is much the same as that found later

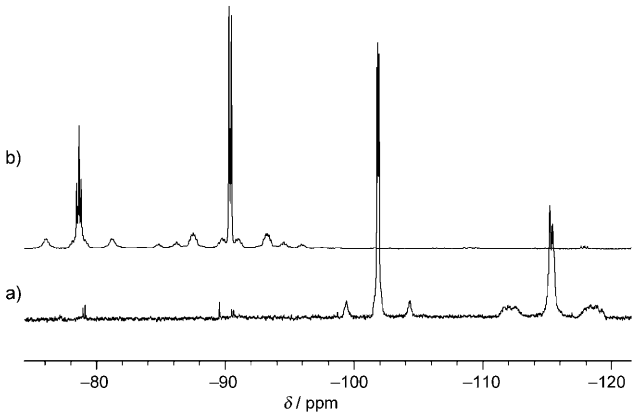
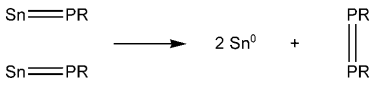


Figure 1. ^{31}P{^{1}H} NMR spectra of a) crystals of **3** in benzene and b) the mother liquor from which **3** was obtained, showing the formation of **4** (an identical spectrum is obtained if the reaction is heated briefly to 40 °C).

in the solid state (see later, Figure 4). The proton-coupled ^{31}P NMR spectrum of **3** is particularly diagnostic, showing two major resonances due to the Mes*PH and the Mes*P groups. The P atom of the Mes*PH group in **3** generates as expected a doublet of triplets as a result of $^{1}J(^{31}P,H)$ and $^{2}J(^{31}P,^{31}P)$ coupling, whereas the relatively broad resonance for the Mes*P groups is narrowly split into two singlets due to the apparent magnetic inequivalence of the two μ_3-P centres. The fact that this is not the result of $^{2}J(^{31}P,^{31}P)$ coupling can be seen from the separation of these singlets (ca. 33 Hz), which does not conform to the $^{2}J(^{31}P,^{31}P)$ coupling constant found for the Mes*PH resonance ($^{2}J(^{31}P,^{31}P) =$ 13.5 Hz). Although the ^{1}H NMR spectrum of **3** is complicated in the aromatic and CH_3 regions, the P–H proton of the Mes*PH group appears as the expected doublet of triplets due to a combination of ^{1}J and $^{2}J(^{31}P,^{31}P)$ coupling, and is again consistent with the intact structure of **3**.

Interestingly, the ^{31}P NMR spectrum of the reaction heated to 40 °C or of the mother liquor from which crystals of **3** are obtained show that none of **3** remains in solution (Figure 1b). Instead, a new species is produced, as seen by the presence of a doublet ($\delta = -90.4$ ppm) and a triplet ($\delta = -78.6$ ppm).[15] The coupling constant involved (32 Hz) is too small to be a $^{2}J(^{31}P,^{31}P)$ coupling constant, as would be found within a P_3Sn heterocyclic ring unit like that present in the structure of **2** (see previous discussion). The fact that no further splitting of either resonance occurs in the proton-coupled spectrum indicates that the new species is $[SnPMes]_3$ (**4**), resulting from completion of the deprotonation reaction and having a closely related structure to **3** (Scheme 8). The formation of **4** suggests that **3** is a kinetic product of the reaction, which is effectively trapped by slow crystallisation from the reaction mixture when it is formed. If the reaction is heated further to 80 °C for 16 h, the previously characterised P=P bonded diphosphene $[Mes^*P]_2$ (**5**)[16] is obtained in approximately 50 % yield ($\delta = +$ 495 ppm) together with tin metal.[17] This reaction can be regarded conceptually as akin a metathesis reaction (Scheme 9).



Scheme 9.

Despite repeated attempts, we were unable to grow single crystals of either **1b** or **1c**. However, storage of a solution of **1a** in THF for 3 days at −20 °C gave crystals of sufficient quality for X-ray diffraction. In the solid state **1a** exists as a heptameric Sn^{II} phosphanediide cage, comprising of Sn_2P_2 and Sn_3P_3 ring units (Figure 2). The core structure can be viewed as coming about by the fusing of two Sn_3P_4 and Sn_4P_3 heterocubane fragments, and is the same as that found previously in the heptamer $[SnESi{i}Pr_3]_7$ (E = P, As), obtained from the reaction of iPr$_3$SiELi$_2$ with SnCl$_2$.[3f] The Sn–P bond lengths (range 2.573(5)–2.670(5) Å) and P-Sn-P (range 77.7(2)–104.2(2)°) and Sn-P-Sn (range 93.0(2)–134.6(2)°) bond angles in **1a** fall over large ranges, having a slightly more distorted structure than in $[SnPSi{i}Pr_3]_7$ (Sn–P range 2.623(3)–2.658(3) Å, P-Sn-P range 83.4(1)–101.3(1)°, Sn-P-Sn range 96.2(1)–133.5(1)°). However, the overall pattern of bond lengths and angles in both compounds are similar, with the largest of the core angles at Sn and P being found within the P_3Sn_3 ring units and the smallest occurring within the P_2Sn_2 units.

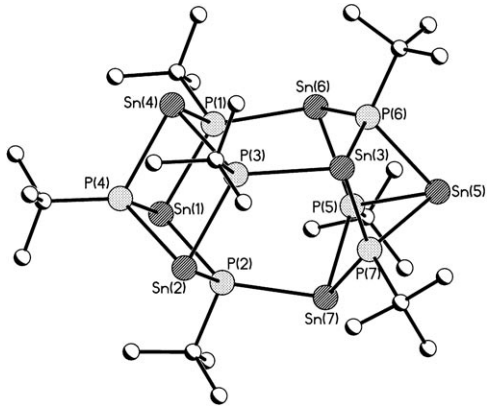


Figure 2. Structure of the heptamer **1a**. H atoms are omitted for clarity. Selected bond length [Å] and angles [°]: Sn−P range 2.573(5)–2.670(5), P-Sn-P range 77.7(2)–104.2(2), Sn-P-Sn range 93.0(2)-134.6(2).

The molecular structure of **2** is that of an octanuclear Sn_8 cage (Figure 3), which appears to arise from the insertion of the heterocyclic stannylene $[(t\text{BuP})_3\text{Sn}]$ into the Sn(5)−P(6) bond of the intact structure of **1a**. Overall, the addition of the stannylene unit to the structure of **1a** has comparatively little effect on the majority of the bond lengths and angles

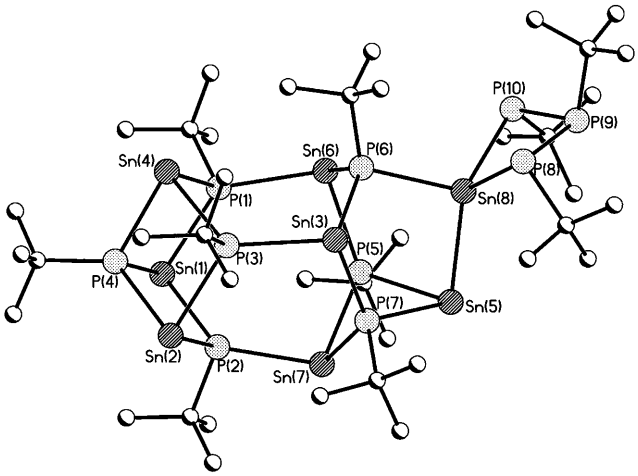


Figure 3. Structure of the octanuclear compound **2**. H atoms are omitted for clarity. Key bond lengths [Å] and angle [°]: Sn−P [Sn_7P_7 fragment] range 2.576(2)–2.667(1), Sn(8) −P(6), 2.560(2), Sn(8) −P(8) 2.548(2), Sn(8) −P(10) 2.552(2), Sn(5) −Sn(8) 2.880(1), P-Sn-P [Sn_7P_7 fragment] range 75.25(5)–104.96(5), Sn-P-Sn [Sn_7P_7 fragment] range 82.87(4)–131.09(6), P(6)-Sn(8)-Sn(5) 98.78(4), P(8)-Sn(8)-P(10) 81.37(6).

involved within the surviving Sn_7P_7 core (Sn−P range 2.576(2)–2.667(1) Å, P-Sn-P range 75.25(5)–104.96(5)°, Sn-P-Sn range 82.87(4)–131.09(6)°), except those associated with Sn(5) and P(6). Surprisingly, the formally dative P→Sn bond P(8)−Sn(8) (2.548(2) Å) is significantly shorter than the other Sn−P bonds in **2**. The dative Sn(8)→Sn(5) bond (2.880(1) Å), although considerably shorter than that in $[\text{ArSn}^{\text{II}}\rightarrow\text{Sn}^{\text{II}}\{1,8\text{-}(\text{NR})_2\text{C}_{10}\text{H}_6\}]$ $(\text{Ar}=2,6\text{-}(\text{Me}_2\text{N})_2\text{C}_6\text{H}_3)$ (3.087(2) Å),[18] is similar to those found in $[(\text{Me}_3\text{Si})_3\text{Sn}\rightarrow\text{Sn}\{2\text{-}[(\text{Me}_3\text{Si})_2\text{C}]\text{C}_5\text{H}_4\text{N}\}]$ (2.8689(5) Å)[19] and $[\{[\text{Sn(L)}\text{-}(\text{NMe}_2\text{Li(thf)})][\text{Sn(L)Li(thf)}_3]\text{Sn}\}_2]$ $(\text{L}=1\text{-}N\text{-}2\text{-P-C}_6\text{H}_4)$ (2.885(1) Å).[20] The tetravalent Sn^{II} centre Sn(8) has a highly distorted tetrahedral geometry, with bond angles in the range 81.37(6)–128.75(4)°. The most acute of these angles is found within the P_3Sn ring unit. This ring unit is similar to that found in the Sn^{II} anion $[(\text{CyP})_3\text{SnP(H)Cy}]^-$, containing a trivalent, pyramidal Sn^{II} centre with a correspondingly more acute P-Sn-P angle (74.4(1)°).[3j]

Compound **3** has a trinulcear arrangement, containing phosphanediide (Mes*P) and phosphido (Mes*PH) groups (Figure 4a). The structure is composed of a trigonal bipyramidal Sn_3P_2 core, capped at the axial positions by two Mes*P groups. Sn(2) and Sn(3) are bridged by a μ-NMe_2 group, whereas Sn(1) has a terminal Mes*PH group. Therefore, all three Sn^{II} centres attain pyramidal geometries with stereochemically-active lone pairs. There is clearly a significant amount of steric congestion within this arrangement, judging by the distortion of the axial Mes*P ligands away from the terminal Mes*PH group. Indeed, the aromatic C_6 rings of these ligands are noticeably puckered and the P atom lies significantly out of the mean plane of each of the C_6 rings (by ca. 27°). This distortion is, however, not unprecedented for other phosphanediide and phophinidene compounds, for example, in the Sn^{IV} and Ga^{III} dimers $[\text{Me}_2\text{Sn}(\mu\text{-PMes*})]_2$ and $[\text{Me}_2\text{Ga}(\mu\text{-PMes*})]_2$, where very similar distortion of the Mes*P groups is observed.[21] In **3**, this appears to result from the steric confrontation between the *ortho*-*t*Bu substituents on the Mes*PH groups and those on the Mes*P groups (as seen in Figure 4b).

Conclusion

In conclusion, we have shown that 1) simple aliphatic Sn^{II} phosphanediides can be prepared in high yields by the 1:1 stoichiometric reactions of primary phosphines (RPH_2) with $Sn(NMe_2)_2$ at room temperature, 2) these reactions can be limited by the presence of bulky substituents, indicating that the phosphanediide cages are formed by stepwise build up and 3) that the Sn^{II} phosphanediides are relatively thermally stable but decompose either by prolonged storage at room temperature or by heating to give P−P or P=P bonded products through a mechanism that appears to be related to other main group-mediated dehydrogenic coupling reactions. With this work done, the next step is to use the neutral Sn^{II} phosphanediides as precursors in reactions with organic electrophiles and unsaturated species, and to assess the relationship between these and the transition-metal counterparts.

Experimental Section

All reactions were performed under dry, O_2-free argon on a standard vacuum line in an efficient fume cupboard. $t\text{BuPH}_2$ and Mes*PH_2 were prepared by following the literature route[22,23] and CyPH_2 was acquired

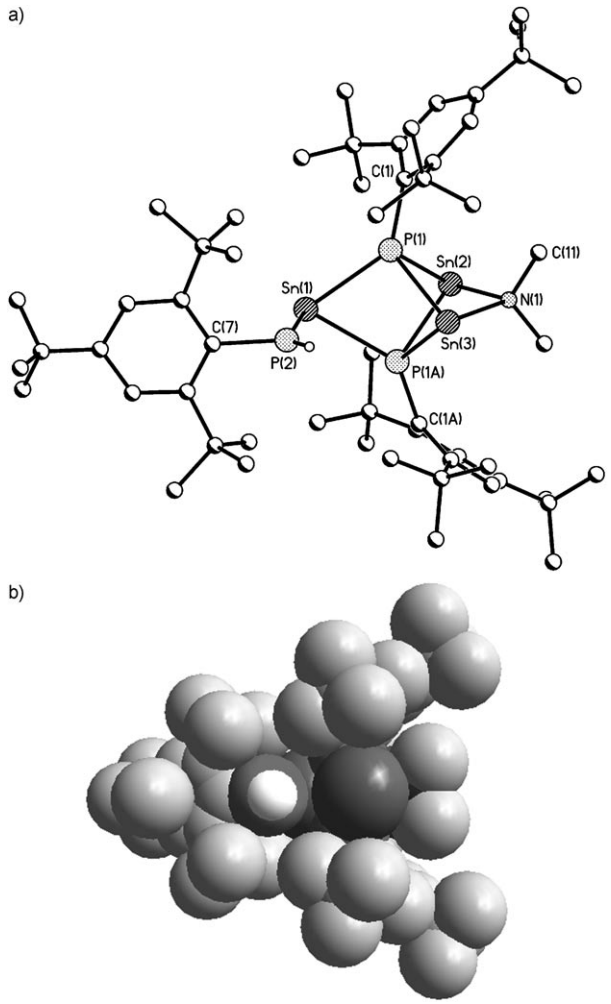


Figure 4. a) Structure of the trinulcear cage **3** and b) space-filling diagram showing the proximity of the *ortho*-*t*Bu substituents on the Mes*PH and Mes*P groups. The orientation of the molecule is the same in a) and b). Selected bond lengths [Å] and angles [°]: Sn(1)–P(2) 2.640(2), Sn(1) – P(1) 2.686(1), Sn(2) –P(1) 2.630(1), Sn(2) –N(1) 2.229(8), Sn(3) –P(1) 2.619(2), Sn(3) –N(1) 2.263(8), Sn(3) –P(1) 2.619(2), Sn(2)-N(1)-Sn(3) 94.6(2), Sn-P(1)-Sn range 77.97(4)–98.63(5), P(1)-Sn-P(1A) range 67.00(6)–68.96(6), P(1)-Sn(1)-P(2) 96.35(5). Symmetry transformations used to generate equivalent atoms (A): $x, -y+1, z$.

commercially (Aldrich). ^{1}H, ^{31}P NMR spectra were obtained by using a Bruker DPX 500 MHz NMR spectrometer. ^{31}P NMR spectra were referenced to an external standard of 85% H_3PO_4/D_2O and ^{1}H NMR spectra were referenced internally to the solvent peaks. Samples were run in [D_8]THF or [D_6]benzene, which were dried further by storage over a Na mirror for 48 h. Elemental analysis (C, H) was obtained by using an Exeter CE-440. In situ ^{31}P NMR samples were recorded in the reaction solvents by using a [D_6]acetone capillary to obtain a lock. Despite repeated attempts we were unable to obtain ^{119}Sn NMR spectra of all of the compounds, even though $^1J(^{31}P,^{119/117}Sn)$ coupling was present (as noted later in the this section). This is probably due to the relatively low solubility of the compounds and to relaxation. Elemental samples (1–2 mg) were placed in pre-weighed, air-tight aluminium boats in the glove box prior to analysis.

Synthesis of [*t*BuPSn]$_7$ (1a): *t*BuPH$_2$ (0.25 mL, 2.0 mmol) was added to a solution of Sn(NMe$_2$)$_2$ (416 mg, 2.0 mmol) in THF (20 mL) at room temperature and was left to stir for 16 h. The solution was filtered through Celite and the solvent removed to give a red-brown powder of **1a** (350 mg, 1.68 mmol of the monomer, 84%). Red crystals of the **1a** were formed after storing a solution at −20 °C for 3 days. Decomp. 212 °C; ^{1}H NMR (400.14 MHz, +25 °C, [D_8]THF): $\delta = 0.85$–1.10 ppm (collection of overlapping doublets); ^{31}P{^{1}H} NMR (161.98 MHz, +25 °C, [D_8]THF): $\delta = -80.7$ (s, $^1J(^{31}P,^{119/117}Sn) = 1018$ Hz, 1571 Hz), −167.5 (d, $^2J(^{31}P,^{31}P) \approx 7$ Hz, $^1J(^{31}P,^{119/117}Sn) = 733$, 1107 Hz), −410.6 ppm (br s); elemental analysis calcd for C_4H_9PSn: C 23.2, H 4.4; found: C 23.0, H 4.8.

Synthesis of [CyPSn]$_n$ (1b): CyPH$_2$ (0.2 mL, 1.51 mmol) was added to a solution of Sn(NMe$_2$)$_2$ (300 mg, 1.44 mmol) in THF (12 mL) at room temperature and was left to stir for 16 h. The solution was filtered through Celite and the solvent removed in vacuum to give **1b** as a red-brown powder (280 mg, 1.20 mmol of the monomer, 83%). Decomp. 169 °C; ^{1}H NMR (400.14 MHz, +25 °C, [D_8]THF): $\delta = 1.0$–3.2 ppm (overlapping br m, Cy); ^{31}P NMR (161.98 MHz, +25 °C, [D_8]THF): $\delta = -38.0$ (br d), −1.0 ppm (dd, $^1J(^{31}P,^{119/117}Sn)$ coupling was present but poorly resolved); elemental analysis calcd for $C_6H_{11}PSn$: C 31.0, H 4.8; found: C 31.4, H 5.3.

Synthesis of [AdPSn]$_n$ (1c): AdPH$_2$ (1.44 mL of a 1 mol dm^{-3} solution in THF, 1.44 mmol) was added to a solution of Sn(NMe$_2$)$_2$ (300 mg, 1.44 mmol) in THF (12 mL) at room temperature and was left to stir for 16 h. The solution was filtered through Celite and the solvent removed in vacuum to give the product as a red solid (320 mg, 1.12 mmol of the monomer, 78%). M.p. 150 °C; ^{1}H NMR (400.14 MHz, +25 °C, [D_8]THF): $\delta = 1.4$–3.0 ppm (overlapping br m., 1-Ad); ^{31}P NMR (161.98 MHz, +25 °C, [D_8]THF): $\delta = 33.4$ (t, $^2J(^{31}P,^{31}P) = 29$ Hz, $^1J(^{31}P,^{119/117}Sn) = 1270$ Hz), −18.2 (t, $^2J(^{31}P,^{31}P) = 17$ Hz), −205.4 ppm (ddd, ratio ca. 3:3:1); elemental analysis calcd for $C_{10}H_{15}PSn$: C 42.2,H 5.3; found: C 41.1, H 5.8.

Synthesis of 3: To a solution of Sn(NMe$_2$)$_2$ (103 mg, 0.5 mmol) in toluene (10 mL) was dropwise added a solution of Mes*PH$_2$ in toluene (0.5 mL, 1 mol dm^{-3}) at −78 °C. The reaction was allowed to reach room temperature while stirring, forming an orange solution. It was then stored at room temperature for 4 days during which time the reaction continues slowly with the solution darkening and with gradually depositing of orange crystals of **3** (70 mg, 33%). ^{1}H NMR (400.14 MHz, +25 °C, [D_6]benzene): $\delta = 7.8$–7.5 (collection of s, Mes* C-H aryl), 5.27 (dt, $^1J(^{31}P,H) = 206$ Hz, $^3J(^{31}P,H) = 6.7$ Hz, Mes*PH), 2.2–1.3 ppm (collection of s, Mes* *t*Bu/Me$_2$N); ^{31}P NMR (161.97 MHz, +25 °C, [D_6]benzene): $\delta = -101.8$ (dt, $^3J(^{31}P,^{31}P) = 13.5$ Hz, $^1J(^{31}P,H) = 199$ Hz, $^1J(^{31}P,^{119/117}Sn) = 800$ Hz, Mes*PH), −115.2 (s, $^1J(^{31}P,^{119/117}Sn \approx 1050$ Hz, Mes*P), −115.4 ppm (s. Mes*P); elemental analysis calcd for $C_{56}H_{88}P_3SnN$: C 55.9, H 7.7, P 2.4; found: C 56.0, H 7.8, P. The ^{31}P{^{1}H} and proton-coupled NMR spectra of the mother liquor were recorded by using a [D_6]acetone capillary to obtain a lock. Compound **4**, ^{31}P NMR (161.97 MHz, +25 °C, [D_6]acetone, capillary in THF): $\delta = -90.4$ (d, $^1J(^{31}P,H) = 32$ Hz, $^1J(^{31}P,^{119/117}Sn) = 931$ Hz), −78.6 ppm (t, $^1J(^{31}P,H) = 32$ Hz, $^1J(^{31}P,^{119/117}Sn) = 830$ Hz) (see also reference [16]).

X-ray crystallography for 1a, 2 and 3: Data for all complexes were collected on a Nonius Kappa CCD diffractometer and solved by direct methods and refined by full-matrix least squares on F^2.[24] All of the compounds contain a half molecule of toluene in the lattice, which is disordered over two 50:50 symmetry-related sites. One of the *t*Bu groups in the structure of **3** was also disordered over two 50:50 sites by rotation. Crystals of **3** form as merohedral twins; details on the treatment of the twinned data are given in the cif file. CCDC-769305 (**1a**), CCDC-769306 (**2**) and CCDC-769307 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Table 1 contains details of the structure refinement.

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Table 1. Details of the data collections and structure refinements of **1a**·0.5 toluene, **2**·0.5 toluene and **3**·0.5 toluene.[a]

	1a·toluene	**2**·toluene	**3**·0.5 toluene
chemical formula	$C_{31.5}H_{67}P_7Sn_7$	$C_{47}H_{98}P_{10}Sn_8$	$C_{59.50}H_{98}NP_3Sn_3$
M_W	1493.62	400.51	1276.37
crystal system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P21/n$	$C2m$
unit cell dimensions			
a [Å]	10.6194(4)	19.011(4)	27.489(6)
b [Å]	11.1446(5)	17.173(3)	24.490(5)
c [Å]	21.9224(12	22.205(4)	9.880(2)
α [°]	90.8288(18)	–	–
β [°]	92.430(2	100.01(3)	106.62(3)
γ [°]	96.8327(16)	–	–
V [Å^3]	2573.3(2)	7139(2)	6373(2)
Z	2	4	4
ρ_{calcd} [Mg m^{-3}]	1.927	1.789	1.330
$\mu(Mo_{K\alpha})$ [mm^{-1}]	3.579	3.002	1.276
reflections collected	20873	88276	7783
independent reflections (R_{int})	6167 (0.117)	14571 (0.054)	7783
$R1$, $wR2$ [$I>2\sigma(I)$]	0.073, 0.173	0.026, 0.066	0.048, 0.112
$R1$, $wR2$ (all data)	0.115, 0.189	0.038, 0.074	0.060, 0.121

[a] Data in common, $\lambda = 0.71073$ Å, $T = 180(2)$ K.

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