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Adventures in Tin(II) phosphinidene chemistry; insights into the mechanism of P–P and Sn–Sn bond formation

Review

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Abstract

The reactions of the Sn(II) dimethylamido reagent Sn(NMe₂)₂ with alkali metal primary phosphides [RPHM] give a range of heterometallic Sn(II) phosphinidene compounds, depending on the organic substituents (R) and the alkali metal (M). For less sterically demanding substituents and/or for the heavier alkali metals, the formation of P–P and Sn–Sn bonded complexes occurs. Structural studies of the reaction products with a range of R-groups and alkali metals cast light on the mechanisms involved in this new type of reaction. © 2005 Elsevier B.V. All rights reserved.

Keywords: Alkali metal; Phosphorus; Mechanisms; Tin(II)

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1. Background

During investigations of the synthesis of little-studied Group 15 phosphinidene compounds, formed by reactions of the Group 15 reagents $E(NMe_2)_3$ with alkali metal primary phosphides [RPHM] (E = Group 15 element, M = alkali metal), we found unexpectedly that complexes such as the heterometallic cage [{Sb(PCy)_3}_2Li_6 · (Me_2NH)_6] (1) (Cy = cyclohexyl) decompose from the solution state at just above room temperature to give Sb–Sb bonded Zintl compounds containing the Sb₇³⁻ anion (Scheme 1) [1]. This new type of reaction is apparently driven thermodynamically by the energy of the P–P single bond, which at 210 kJ mol⁻¹ is the highest homoatomic single bond energy in Group 15. This is illustrated by the isolation of heterocyclic intermediates containing $[(RP)_n$ - Sb]⁻ anions from reactions of this type at low temperature and by the final formation of cyclophosphanes, *cylo*-[RP]_n, which are produced together with the Zintl compounds [2]. Interestingly, the lower value of the N–N single bond (167 kJ mol⁻¹) underlies the thermodynamic stability of the imido analogue of 1, $[{Sb(NCy)_3}_2-Li_6 \cdot (Me_2NH)_2](2)$, which is indefinitely stable at room temperature under N₂ atmosphere and is a source of the [Sb(NCy)₃]³⁻ anion [3].

A major interest in this type of reaction is the potential to deposit thin metal films for various applications in electronic devices. For example, alkali metal antimonate thin films are

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a key component in photodiode tubes [4]. In addition, the generalisation of this kind of reaction elsewhere (for other main group, and transition metals) provides exciting prospects not only for the low-temperature synthesis of materials but for uncovering new structural chemistry and patterns of reactivity. This short review describes recent extension of the work on Group 15 phosphinidene compounds to related Sn(II) chemistry. This work not only indicates the generality of this type of reaction, but also provides important new insights into the type of mechanism involved in P–P and metal–metal bond formation.

2. Extension to Sn(II) phosphinidene chemistry

Prior to the studies of Sn(II) phosphinidenes very little detail of the mechanism of the decomposition reactions of Group 15 phosphinidene complexes into Zintl compounds was known, apart from the fact that the heterocyclic intermediates were of fundamental importance in the delivery of the Group 15 atoms into the framework of the Zintl compounds. Despite this, a range of synthetic studies of Group 15 phosphinidenes had revealed two important general trends in reactivity [1a]. The first apparently relates to the nature of the substituents. In particular, it was found that aromatic substituents promote the formation of Zintl compounds. In fact, the reactions of primary phosphides [RPHM] (M = alkali metal) with Group 15 reagents $E(NMe_2)_3$ (E = As, Sb, Bi) only give cage compounds (like 1) or heterocyclic intermediates (Scheme 1)

if aliphatic R groups are present. These reactions generally lead to the immediate formation of Zintl compounds even at low temperature (<0 °C) if an aromatic R group is present. The second trend relates to the alkali metal (M), that the formation of Zintl compounds in the reactions of E(NMe₂)₃ with [RPHM] is encouraged as Group 1 is descended. In the absence of knowledge of the mechanism of this new type of reaction, however, the reasons for these trends were not understood.

Our first task with the related Sn(II) chemistry was to assess whether the same two reactivity trends would be observed in the reactions of the Sn(II) reagent Sn(NMe₂)₂ with RPHM as were found for Group 15. The 1:3 reactions of lithium aliphatic primary phosphides [RPHLi] with Sn(NMe₂)₂ in thf give [{Sn(μ -PR})}₂-(μ -PR)]₂(Li · thf)₄ [R = ^{*t*}Bu (**2**) (Fig. 1); Cy (**3**)], containing metallocyclic [{Sn(μ -PR})}₂(μ -PR)]₂⁴⁻ tetraanions (Fig. 1b) [5]. Interestingly, these anions are valence-isoelectronic and isostructural with the neutral Group 15 compounds [{P(μ -NR})}₂(μ -NR)]₂ (R = ^{*i*}Pr, ^{*t*}Bu) (Fig. 2b) [6] and the Group 13 tetraanions of the type [{MeE(μ -PR)}₂-(μ -PR)]₂⁴⁻ [E = A1 (4) [7], In (5) [8]; R = Cy] (Fig. 2c). More significantly, however, no P–P bond formation has occurred in the framework of the Sn(II) tetraanions of **2** and **3**.

In contrast to reactions involving aliphatic phosphides as precursors, the 1:3 reaction of $Sn(NMe_2)_2$ with the aromatic primary phosphide [MesPHLi] (Mes = 2,4,6-Me_3C_6H_2) gives [{ $Sn(\mu$ -PMes)}_2(MesPPMes)](Li · TMEDA)_2 (5)



Fig. 1. (a) Structure of $[{Sn(\mu-P'Bu)}_2(\mu-P'Bu)]_2(Li \cdot THF)_4$ (2) and (b) the $[{Sn(\mu-P'Bu)}_2(\mu-P'Bu)]_2^4$ tetraanion.



Fig. 2. Valence-isoelectronic and isostructural p-block frameworks: (a) the $[{Sn(\mu-PR)}_2(\mu-PR)]_2^{4-}$ tetraanions of 2 and 3, (b) the neutral Group 15 compounds $[{P(\mu-NR)}_2(\mu-PR)]_2$, and (c) the Group 13 tetraanions $[{MeE(\mu-PR)}_2(\mu-PR)]_2^{4-}$.

(Fig. 3a), containing the $[{Sn(\mu-PMes)}_2(MesPPMes)]^2$ -dianion in which P–P bond formation has occurred (Fig. 3b) [5].

The structural studies of **4** and **5** provided the first indication that the reactivity pattern for Sn(II) phosphinidenes is similar overall to that found previously for Group 15. However, in addition the resemblance of the framework of the metallocyclic $[\{Sn(\mu-PR)\}_2(\mu-PR)]_2^{4-}$ tetraanion of **4** with the $[\{Sn(\mu-PMes)\}_2(MesPPMes)]_2^{2-}$ dianion of **5** gave us an early hint that a common mechanism may be involved in the formation of both. According to the proposed mechanism shown in Scheme 2, [9] the $[\{Sn(\mu-PR)\}_2(\mu-PR)]_2^{4-}$ tetraanion and $[\{Sn(\mu-PMes)\}_2-$ (MesPPMes)]²⁻ dianion arise from a common pathway involving intermediates of the type $[Sn(PR)_2]^{2-}$ (A) and $[RPHSn(\mu-PR)]_2$ (B). Key steps are the condensation of two molecules of B (with the elimination of two molecules of RPH₂) giving the tetraanion, whereas the dianion would be obtained by the elimination of H₂ from B.

An explanation for the observed dependence of the outcome of the reactions on the organic substituents and the alkali metal present came initially from studies of reactions involving sodium phosphide precursors. In particular, the reaction of MesPHNa with $Sn(NMe_2)_2$ gives a complex containing the stannate trianion $[Sn{P(2-CH_2)(4,6-Me_2-C_6H_2)}(PMes)]^{3-}$ (6), resulting from intermolecular deprotonation of an *ortho*-CH₃ group from an intermediate of type *A* in Scheme 2 (Scheme 3) [10]. Thus, the formation of a $[{Sn(\mu-PMes)}_2(\mu-MesPPMes)]^{2-}$ dianion [formed in the analogous reaction of MesPHLi with Sn(NMe₂)₂ in **5**] is prevented. Interestingly, this reaction bears a close relationship to the intramolecular rearrangement of the Zr-phosphinidene intermediate [Cp*₂Zr=PMes] (7) (Scheme 4), reported previously by Stephan and co-workers [11].

Most importantly, however, the formation of 6 suggests that the basicity and/or nucleophilicty of the alkali metal primary phosphides [RPHM] might be the key factor influencing the results of their reactions with $Sn(NMe_2)_2$. On this basis it would be expected that the more sterically demanding the organic substituent, the lower the nucleophilicity of the phosphide anion RPH⁻, and that it is not the aromaticity or otherwise of the R group that influences the direction of the mechanism followed in Scheme 2. In addition to the steric demands of the R-groups, moving down Group 1 would be expected to result in more polar P–M bonds and hence in an increase in the nucleophilicity and bascity of the RPH⁻ anion. A good example illustrating the effect of polarity of the P-M bonds on the reaction products is the series of reactions of Sn(NMe₂)₂ with CyPHM (M = Na, K, Rb). For M = Na, the two major products obtained are $[{Sn(\mu-PCy)}_2(CyPPCy)](Na \cdot PMD)$ ETA_2 (8) [PMDETA = (Me_2NCH_2CH_2)_2NMe] (Fig. 4a)



Fig. 3. (a) Structure of $[{Sn(\mu-PMes)}_2(MesPPMes)](Li \cdot TMEDA)_2 (5), (b) the <math>[{Sn(\mu-PMes)}_2(MesPPMes)]^2 - dianion.$



Scheme 2.



Scheme 3.





[12] and $[\{Sn(\mu-PCy)\}_3(Na \cdot 2PMDETA)]$ (9) (Fig. 5) [13] (depending on the reaction stoichiometry employed). Complex 8 contains a $[\{Sn(\mu-PCy)\}_2(CyPPCy)]^{2^-}$ dianion (Fig. 4b) like that of complex 5, while 9 contains an unusual $[\{Sn(\mu-PCy)\}_3]^{2^-}$ dianion (Fig. 5b). MO calculations on this species show that it has a 2e,3c bonding arrangement in which two electrons are delocalised over three Sn p orbitals, with a one-third bond order for the three Sn...Sn contacts (Fig. 6). The electronic structure of this species, which can be regarded as part way between the electron precise arrangements of Sn(II) phosphinidene cages and the delocalised electron structure of a metal, is related to that of the cycloproponium cation and *tris*- homoaromatics of boron reported by Siebert and von Schleyer [14].

Irrespective of the stoichiometry, the analogous reaction of $Sn(NMe_2)_2$ with CyPHK gives $[Sn_2(\mu-PCy)(\mu-CyP-PCy)_2](K \cdot 2thf)_2$ (10) (Fig. 7a) [12], containing a $[Sn_2(\mu-PCy)(\mu-CyPPCy)_2]^2-$ dianion in which the two Sn(II) centres are bridged by two CyPPCy ligands and by a single PCy group (Fig. 7b). The corresponding reaction of CyP-HRb with Sn(NMe_2)_2 gives [{(CyP)_3Sn(PHCy)}Rb · PMD-ETA] (11) (Fig. 8a), containing a $[(CyP)_3Sn(PHCy)]^$ anion (Fig. 8b) which can be seen as analogous to the heterocyclic intermediates found in reactions of Group 15 reagents with alkali metal phosphides [RPHM] [12].



Fig. 4. (a) Structure of $[{Sn(\mu-PCy)}_2(CyPPCy)](Na \cdot PMDETA)_2$ (8), and (b) the $[{Sn(\mu-PCy)}_2(CyPPCy)]^2$ diamon of 8.



Fig. 5. (a) Structure of $[\{Sn(\mu-PCy)\}_3(Na \cdot 2PMDETA)](9)$, and (b) the 2e, 3c bonding arrangement of the $[\{Sn(\mu-PCy)\}_3]^{2-1}$ dianion of 9.



Fig. 6. (a) The HOMO of the isolated $\left[Sn(\mu\text{-PMe})\right]_3^{2-}$ dianion and (b) valence-bond description of the dianion.

There is clearly a general increase in the extent of P–P bond formation in going from the structure of the Li-derivative $[{Sn(\mu-PCy)}_2(\mu-PCy)]_2(\text{Li} \cdot \text{THF})_4$ (3) to the heavier alkali metals [5].

Although full mechanistic details are not available as yet, it can be seen that many of the species formed can be related directly to the mechanism portrayed Scheme 2, which is modified by the resulting increase in the nucleophilicity of the RPH⁻ anions (resulting from the increase in polarity of the P–M bonds as Group 1 is descended). For

example, a possible mechanism for the formation of the framework of the $[Sn_2(\mu-PCy)(\mu-CyPPCy)_2]^2$ dianion of **10** is nucleophilic attack of the $[{Sn(\mu-PCy)}_2(CyPPCy)]^2$ dianion (found in **8**) followed by elimination of H₂ (Scheme 5). The $[{Sn(\mu-PCy)}_3]^2$ dianion of **9** may also arise from the $[{Sn(\mu-PCy)}_2(CyPPCy)]^2$ dianion (Scheme 5).

The product of the reaction of PhPHLi with $Sn(NMe_2)_2$ is of particular interest in respect to the above mechanism [15]. The resulting complex [{(PhP–PPh)Sn(µ-PPh)}₂(Na · PMDETA)₄] (**12**) (in the presence of PMDETA) contains a [(PhP–PPh)Sn(µ-PPh)]₂^{4–} tetraanion in which insertion of a PhP-group into the framework of a [{Sn(µ-PPh)}₂-(PhP–PPh)]^{2–} dianion (like the dianion of **10**) has occurred (Scheme 6).

The greater steric bulk of the 'Bu group compared to the Cy group results in a large difference in the reactions of $Sn(NMe_2)_2$ with 'BuPHM (M = Li, Na, K). No such P–P or Sn–Sn bond formation occurs in any of these reactions. The majority of the structurally characterised products obtained contain the $[Sn_3(\mu-P'Bu)_4]^{2-}$ dianion, such as the ion-paired Na complex $[{Sn_3(\mu-P'Bu)_4}(Na \cdot PMD-ETA)(Na \cdot PMDETA \cdot thf)]$ (12) (Fig. 9a) and the



Fig. 7. (a) Structure of $[Sn_2(\mu-PCy)(\mu-CyPPCy)_2](K \cdot 2thf)_2$ (10) and (b) the $[Sn_2(\mu-PCy)(\mu-CyPPCy)_2]^{2-}$ dianion of the complex.



Fig. 8. (a) Structure of $[{(CyP)_3Sn(PHCy)}Rb \cdot PMDETA]$ (11) and (b) the $[(CyP)_3Sn(PHCy)]^-$ anion of the complex.





ionseparated K complex $[{Sn_3(\mu-P'Bu)_4}_2K_3]^- [K(thf)_6]^+$ (13) (Fig. 9b) [16]. Interestingly, as far as the potential mechanistic relationship between the various products formed is concerned, the $[Sn_3(\mu-P'Bu)_4]^{2-}$ dianion can be seen to result from reaction of an intermediate of type *B* in Scheme 2 with Sn(NMe₂)₂ (Scheme 7).

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Fig. 9. (a) Structure of the Na complex $[{Sn_3(\mu-P'Bu)_4}(Na \cdot PMDETA)(Na \cdot PMDETA \cdot thf)]$ (12) and (b) the K complex $[{Sn_3(\mu-P'Bu)_4}_2K_3]^-[K(thf)_6]^+$ (13).



Scheme 7.

3. Future prospects

Studies of the reactions of $Sn(NMe_2)_2$ with alkali metal primary phosphides [RPHM] suggest that the majority of the resulting Sn(II) phosphinidene frameworks produced can be understood in terms of a simple set of related mechanisms. The exact course of the reactions depends to a large extent on the basicity and nucleophilicity of the phosphide anion [RPH⁻], hence the observed dependence of the reactions involving Groups 14 and 15 on the steric bulk of the organic substituents (R) and the alkali metal (M). Future work will involve extensive spectroscopic and theoretical analysis of such reactions (combined with continuing structural investigations) in order to elucidate the mechanisms involved further. So far, the reactions of $Sn(NMe_2)_2$ with RPHM have been explored only at around room temperature. A particular future target will be the investigation of the thermolysis reactions of the Sn(II) phosphinidene frameworks described above, in order to obtain Sn–Sn bonded Zintl compounds (in an analogous manner to the chemistry involved with Group 15). Some evidence for the formation of compounds of this type has been seen already in the electron-deficient $[Sn(\mu-PCy)]_3^{2-}$ dianion of 9 (Fig. 5).

Viewed from a different angle, the studies of the reactions of Groups 14 and 15 have shown that mixtures of alkali metal organometallics with p-block dimethylamido reagents function as powerful superbases. An interesting area for future studies will be the application of these mixed-base



Fig. 10. Comparison of MesPH₂ with 2-amino-phenylphosphine (LH₄).



Fig. 11. Structure of the paramagnetic complex 15.



systems in the deprotonation reactions with organic and organometallic precursors. Prompted by the observed activation of the *ortho*-CH₃ groups of MesPH₂ in the unusual stannate anion $[Sn{P(2-CH_2)(4,6-Me_2C_6H_2)}]$ (PMes)]³⁻ (6) (Scheme 3), we recently explored the reaction of the deprotonation of structurally related 2-amino-phenylphosphine (LH₄) with "BuLi/Sn(NMe₂)₂ (Fig. 10) [17].

Remarkably, it was found that the reaction of LH_4 with ^{*n*}BuLi/Sn(NMe₂)₂ results in complete deprotonation of the PH₂ and NH₂ groups, resulting in the paramagnetic complex **15** (Fig. 11) containing L³⁻ and L⁴⁻ anions (Scheme 8).

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