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Stabilisation of an *ortho*-deprotonated mesityl group within the unusual [{2,4,6-$Me_3C_6H_2P$}{4,6-$Me_2C_6H_2$(2-CH_2)P}Sn]$^{3-}$ stannate ion†

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The reaction of 2,4,6-$Me_3C_6H_2PHNa$ with Sn(NMe_2)$_2$ (3 : 1 equivalents, respectively) results in the formation of the unusual [{2,4,6-$Me_3C_6H_2P$}{4,6-$Me_2C_6H_2$(2-CH_2)P}Sn]$^{3-}$ stannate trianion in the heterometallic cage [{2,4,6-$Me_3C_6H_2P$}{4,6-$Me_2C_6H_2$(2-CH_2)P}Sn]Na_3·2TMEDA]$_4$ (1), in which unprecedented *ortho*-Me deprotonation of a [2,4,6-$Me_3C_6H_2P$]$^{2-}$ ligand has occurred.

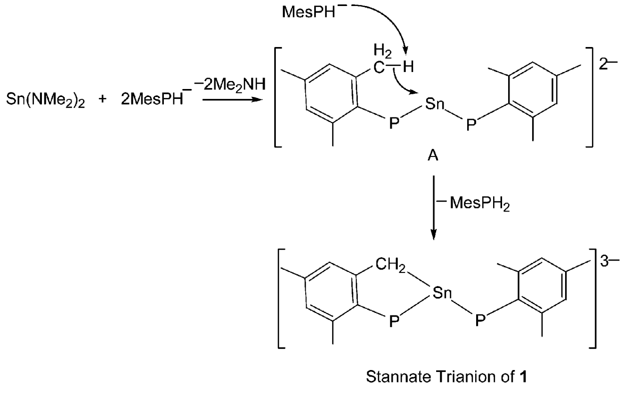
The development of transition metal mediated synthesis of organic compounds is a major and ever-growing field of study.[1] Although transition metal complexes containing metal-imido (M = NR) functionality have extensive applications in organic synthesis,[2] the reactivity of metal-phosphinidene counterparts (M=PR) has remained relatively unexplored. Stephan and coworkers showed that the primary phosphides [Cp*$_2$Zr(PHR)$_2$] are synthons for the transient phosphinidenes [Cp*Zr=PR], generated *via* intramolecular deprotonation and loss of RPH_2.[3] For R = Ph, addition of $PhPH_2$ to the Zr=P bond results in the formation of the P–P coupled product [Cp*$_2$Zr(PPh)$_n$].[3b] However, this pathway is slower for the more sterically demanding R = Mes (2,4,6-$Me_3C_6H_2$), which undergoes intramolecular proton transfer from an *ortho*-Me group to the P centre to give the phosphametallocycle [Cp*$_2$Zr{PH(2-CH_2)(4,6-$Me_2C_6H_2$)}].[3] Surprisingly, our recent investigations have shown that p-block metal phosphinidenes can exhibit a similar reactivity pattern to their transition metal counterparts.[4] For example, the thermally-unstable complexes [{Sb(PR)$_3$}$_2$Li$_6$] (R = ^{t}Bu, Cy)[5] rapidly form P–P coupled heterocycles of the type [(RP)$_n$Sb]$^-$ at room temperature, before the ultimate formation of Zintl compounds.[6] We now report an even closer link between the chemistry of transition metal and main group metal phosphinidenes, a C–H bond activation reaction which is related to that involved in the formation of [Cp*$_2$Zr{PH(2-CH_2)(4,6-$Me_2C_6H_2$)}].

We had shown previously that, unlike reactions involving aliphatic phosphides, the reactions of Sn(NMe_2)$_2$ with MesPHLi gives a P–P coupled product, containing the [{Sn(μ-PMes)}$_2$(MesPPMes)]$^{2-}$ dianion.[7] Using the same optimal stoichiometry in the reaction of Sn(NMe_2)$_2$ with MesPHNa (1 : 3 equivalents) in TMEDA–toluene (TMEDA = $Me_2NCH_2CH_2NMe_2$) gives the new cage [{2,4,6-$Me_3C_6H_2P$}{4,6-$Me_2C_6H_2$(2-CH_2)P}Sn]Na_3·2TMEDA]$_4$ (**1**) (in 20% first-batch yield).† This complex contains an unusual [{2,4,6-$Me_3C_6H_2P$}{4,6-$Me_2C_6H_2$(2-CH_2)P}Sn]$^{3-}$ stannate ion, in which one of the *ortho*-Me groups of the Mes group has been deprotonated. The formation of this trianion is shown, in particular, by the presence of two doublets in the ^{31}P NMR spectrum of **1** [δ = −162.1, −162.8 ($^2J_{PP}$ = 44.0 Hz)] and by the appearance of a CH_2 resonance in the ^1H NMR spectrum (δ = 3.58).

The mechanism of formation of this anion (Scheme 1) is likely to be similar to that involved in [Cp*$_2$Zr{PH(2-CH_2)(4,6-$Me_2C_6H_2$)}],[3] the only difference being that the formation of the stannate involves intermolecular, rather than intramolecular, deprotonation of the Me group (involving $MesPH^-$ as a base). As a result, a [4,6-$Me_2C_6H_2$(2-CH_2)P]$^{3-}$ ligand is generated in the case of **1**, as opposed to a [4,6-$Me_2C_6H_2$(2-CH_2)PH]$^{2-}$ ligand. The activation effect of (generally O or N) donor substituents on *ortho*-C–H and -CH_3 groups towards deprotonation by organolithium and related bases has been known for some time.[8] What is surprising in the formation of **1**, however, is that the deprotonation of a highly charged $MesP^{2-}$ ligand is apparently accomplished by a such a poor $MesPH^-$ base. Primary evidence for the involvement of MesPHNa in the *ortho*-metallation step comes from *in situ* ^{31}P NMR studies, showing that MesPHNa present at the beginning of the reaction is converted into $MesPH_2$ in the final reaction solution. The key to this process, we believe, is the stabilisation of the additional charge within the initially vacant Sn orbital of intermediate **A** (Scheme 1). This option presumably shifts what would otherwise be an unfavourable equilibrium to the right.

The solid-state structure of **1** (Fig. 1(*a*)) is that of an elaborate, C_2-symmetric cage containing a $Sn_4P_8Na_{12}$ core (Fig. 1(*b*)).‡ In addition, there is a total of four toluene molecules present in the lattice for each molecule of **1**. Of the four [{2,4,6-$Me_3C_6H_2P$}{4,6-$Me_2C_6H_2$(2-CH_2)P}Sn]$^{3-}$ trianions present in each molecule, two are crystallographically-independent and are the two possible enantiomers of the [{2,4,6-$Me_3C_6H_2P$}{4,6-$Me_2C_6H_2$(2-CH_2)P}Sn]$^{3-}$ trianion with opposite chirality at Sn(1) and Sn(2). The CH_2–Sn [2.225(5)–2.243(6) Å] and Sn–P [2.564(2)–2.608(2) Å] bond lengths within these anions fall over relatively narrow ranges (being typical of single bonds[9]). Although highly distorted [with C–Sn–P and P–Sn–P angles in the range 82.0(2)–107.9(2)°], the pyramidal geometries of the Sn centres of both trianions suggest the presence of a stereochemically-active metal lone pair. To our knowledge, the [{2,4,6-$Me_3C_6H_2P$}{4,6-$Me_2C_6H_2$(2-CH_2)P}Sn]$^{3-}$ trianion of **1** is the highest charged stannate ion known.

The [{2,4,6-$Me_3C_6H_2P$}{4,6-$Me_2C_6H_2$(2-CH_2)P}Sn]$^{3-}$ trianions within the core of **1** coordinate the twelve Na^+ cations using a combination of π-arene–, P– and Sn–Na bonding. In the



Scheme 1 Likely mechanism of formation of the [{2,4,6-$Me_3C_6H_2P$}{4,6-$Me_2C_6H_2$(2-CH_2)P}Sn]$^{3-}$ trianion in **1**.

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† Electronic supplementary information (ESI) available: synthesis of **1**. See http://www.rsc.org/suppdata/cc/b3/b303390m/

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cases of Na(1,1A), Na(2,2A) and Na(6,6A), skeletal bonding to a total of three Sn or P centres within the cage is augmented by η^3- or η^1-arene interactions with 2,4,6-$Me_3C_6H_2$ or 4,6-$Me_2C_6H_2$(2-CH_2)P groups [C···Na range 2.661(2)–3.064(2) Å].[10] Na(6,6A) and Na(5,5A) are located at the centre of the cage and are involved in the association of the two symmetry-related halves of the molecule, *via* Na–P bonding within a P_4Na_4 unit. In the case of Na(5,5A), further π-arene interactions appear unnecessary since this cation is already bonded to four skeletal P centres within the core. Na(4,4A) and Na(6,6A) possess relatively short bonds to the Sn centres of stannate ions [Sn(1)–Na(4) 3.288(2), Sn(2)–Na(4) 3.146(2), Sn(2)–Na(6) 3.183(2) Å], which are in a similar range to structurally authenticated Sn–Na bonds observed previously [*ca.* 3.07–3.24 Å[11]]. These interactions occur at the vacant coordination site of the Sn centres of the anions, in the approximate direction of the Sn pair. For Na(4,4A), two Sn–Na bonds are formed with the Sn centres of the independent stannate ions of the cage, with this Na^+ cation bridging the Sn(2,2A)–P(4,4A) bond of one anion. The cage architecture of **1** (Fig. 1(*b*)) can be regarded (pictorially) as being constructed from the 'stacking' of four five-membered SnP_3N_2 rings [*i.e.*, Sn(1)Na(4)P(4)Na(3)P(3), Sn(2)Na(6)P(1)Na(5)P(2), *etc.*], with the remaining four Na^+ cations [Na(1,1A) and Na(2,2A)] being directed *exo* to the cage.

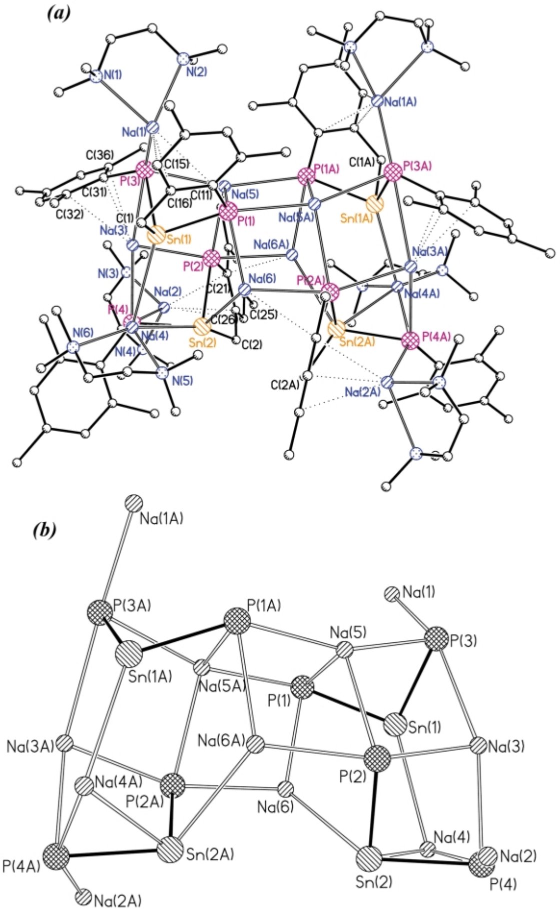

Fig. 1 (*a*) Structure of exact C_2 symmetry of the heterometallic cage molecules of **1** in **1**·(4tol). H-atoms and lattice toluene molecules have been omitted for clarity. Key bond lengths (Å) and angles (°): Sn(1)–P(1) 2.565(2), Sn(1)–P(3) 2.583(2), Sn(1)–C(1) 2.243(6), Sn(2)–P(2) 2.558(2), Sn(2)–P(4) 2.608(2), Sn(2)–C(2) 2.225(5), Na(1)–P(3) 2.823(3), Na(1)···C(11,15,16) 2.661(2)–2.855(2), Na(2)–P(4) 2.812(3), Na(2)···C(21,25,26) 2.679(2)–3.064(2), Na(3)–P(2,3,4) 2.806(3)–3.210(3), Na(3)···C(31,32,36) 2.627(2)–3.035(2), Na(4)–Sn(1) 3.288(2), Na(4)–Sn(2) 3.146(2), Na(4)–P(4) 2.985(3), Na(5)–P(1,2, 3,1A) 2.897(3)–3.043(5), Na(6)–Sn(2) 3.183(2), Na(6)–P(1,2A) 2.841(3)–2.856(3), Na(6)···C(21) 2.972(2), P(1)–Sn(1)–P(3) 91.58(6), P(2)–Sn(2)–P(4) 88.34(6), C–Sn(1,2)–P range 82.01(5)–107.9(2); (*b*) the $Sn_4P_8Na_{12}$ core.

In conclusion, this study reveals an unexpectedly close link between a reaction system involving Sn(II) and one involving a transition metal. The new stannate trianion generated within the novel cage structure of **1** is the highest charged stannate reported so far.

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Notes and references

‡ *Crystal data for* **1**·(4tol); $C_{136}H_{212}N_{12}Na_{12}P_8Sn_4$, M = 3013.58, monoclinic, space group $C2/c$, Z = 4, a = 30.072(6), b = 18.257(4), c = 31.229(6) Å, β = 99.06(3)°, V = 16931(6) Å^3, μ(Mo-Kα) = 0.733 mm^{-1}, T = 293(2) K. Data were collected on a Nonius Kappa CCD diffractometer. Of a total of 49036 reflections collected, 14739 were independent (R_{int} = 0.056). Final $R1$ = 0.062 [$I > 2\sigma(I)$] and $wR2$ = 0.172 (all data).[12] CCDC 207020. See http://www.rsc.org/suppdata/cc/b3/b303390m/ for crystallographic data in .cif or other electronic format.

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