Synthesis and Structure of [{Sn_2(μ-PMes)$_3$}K_2·3THF]$_\infty$, Exhibiting Multifunctional Coordination of [Sn_2(μ-PMes)$_3$]$^{2-}$ Anions to K^+

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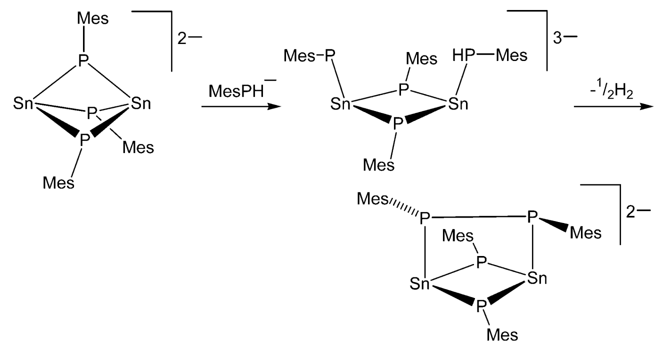
Received June 25, 2004

*Summary: The reaction of Sn(NMe$_2$)$_2$ with MesPHK (1:2) in THF gives the title compound [{Sn$_2$(μ-PMes)$_3$}-K$_2$·3THF]$_\infty$ (**1**), having a polymeric structure in the solid state in which the [Sn$_2$(μ-PMes)$_3$]$^{2-}$ dianions behave as multifunctional σ(Sn), σ(P), and π-arene donors to K$^+$ cations. The trigonal-bipyramidal core arrangement of the [Sn$_2$(μ-PMes)$_3$]$^{2-}$ dianion represents a monomeric unit of the metallacyclic tetraanions [{Sn(μ-PR)}$_2$-(μ-PR)]$_2$$^{4-}$ and of valence-isoelectronic group 14 and 15 species of the type [{MeE(μ-PR)}$_2$(μ-PR)]$^{4-}$ (E = Al, In) and [{P(μ-NR)}$_2$(μ-NR)]$_2$.*

The dimeric phosphazane [{P(μ-N^{i}Pr)}$_2$(μ-N^{i}Pr)]$_2$ (Figure 1a), reported by Scherer and co-workers in 1980,[1] represents an archetypal main-group framework. The more recent structural characterization of complexes containing the valence-isoelectronic tetraanions [{Sn(μ-PR)}$_2$(μ-PR)]$_2$$^{4-}$ [2] and [{MeE(μ-PR)}$_2$(μ-PR)]$_2$$^{4-}$ (E = group 13 metal)[3] (Figure 1b,c, respectively) has revealed that this dimeric macrocyclic arrangement occurs for a range of other p-block elements. Our interest in this area has been stimulated in particular by the potentially extensive coordination chemistry exhibited by these species and by the growing realization that larger macrocyclic homologues of this type may also be accessible. These features have been illustrated recently by the characterization of the trimeric Sb(III) imido trianion [{Sb(μ-NCy)}$_2$(μ-N)]$_3$$^{3-}$[4] and the neutral tetrameric phosphazane [{P(μ-N^{t}Bu)}$_2$(μ-NH)]$_4$,[5] having the same toroidal architecture as the dimeric relatives. The study reported here describes the first monomeric homologue of this class of compounds, a [Sn$_2$(μ-PR)$_3$]$^{2-}$ dianion that is directly related to metallacyclic [{Sn(μ-PR)}$_2$(μ-PR)]$_2$$^{4-}$ tetraanions.

The title compound [{Sn$_2$(μ-PMes)$_3$}K$_2$·3THF]$_\infty$ (**1**) was obtained in 26% yield from the reaction of

Scheme 1



Sn(NMe$_2$)$_2$ with MesPHK (1:2) in THF.[6] The [Sn$_2$(PMes)$_3$]$^{2-}$ dianion of **1** represents a monomeric unit of the previously reported metallacyclic tetraanions [{Sn(μ-PR)}$_2$(μ-PR)]$_2$$^{4-}$, obtained from the reactions of Sn(NMe$_2$)$_2$ with ^{t}BuPHLi or CyPHLi (1:2 or 1:3) in THF.[2b] It is interesting to note that the reaction of Sn(NMe$_2$)$_2$ and MesPHLi (1:2 or 1:3) in the presence of TMEDA (Me$_2$NCH$_2$CH$_2$NMe$_2$) gives the [Sn(μ-PMes)}$_2$-(MesPPMes)]$^{2-}$ dianion, whose [MesPPMes]$^{2-}$ ligand formally results from the insertion of a PMes group into one of the Sn−P bonds of the [Sn$_2$(PMes)$_3$]$^{2-}$ dianion of **1**.[2b] The presence of TMEDA in this reaction presumably enhances the nucleophilicity of the MesPH$^-$ anion sufficiently for attack of one of the Sn(II) centers of the [Sn$_2$(PMes)$_3$]$^{2-}$ dianion to occur (Scheme 1).[9] The ^{1}H and ^{31}P NMR spectra of **1** in THF indicate that a number of

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(6) Synthesis of **1**: to a stirred solution of PhCH$_2$K[7] (0.7 g, 5.15 mmol) in THF (20 mL) at −78 °C was added MesPH$_2$[8] (0.742 g, 0.7 mL, 4.9 mmol). The reaction mixture was stirred at −78 °C for 15 min and then warmed to room temperature and stirred for a further 6 h, producing a red solution. This solution was cooled to −78 °C, and Sn(NMe$_2$)$_2$ (0.518 g, 2.5 mmol) in THF (10 mL) was added. The reaction mixture was stirred at room temperature (16 h) to give a red solution. The solvent was removed under vacuum, and the crude product was crystallized from THF/toluene (7 mL:3mL) at −15 °C. Yield: 0.32 g (26%). Dec pt: 110 °C. IR (Nujol, NaCl; ν/cm^{-1}): major bands at 1093 (s), 1019 (s), 780 (s) (air exposure results in the appearance of a P−H stretching band at 2360 cm^{-1}). ^{1}H NMR (500.2 MHz, d_8-THF, 25 °C): δ 6.62 (s), 6.57 (s), 6.51 (s) (total ca. 2H, aryl C−H), 3.61 (mult, THF), 2.6−2.0 (collection of singlets, ca. 18H, *o*- and *p*-Me), 1.79 (mult, THF) (samples contain variable amounts of THF). ^{31}P{^{1}H} NMR (161.975 MHz, d_8-THF, 25 °C): −145.5 (br s), −155.0 (br s) (unidentified hydrolysis product at −131.3, t. J_{P-P} = 105.3 Hz with $J_{^{117,119}Sn-^{31}P}$ = 1368.8 Hz (satellites) (J_{P-H}= 194.4 Hz from the ^{1}H-coupled spectrum)). Anal. Found: C, 45.0; H, 5.1; P, 9.2, Calcd for **1**(−3THF): C, 45.3; H, 5.2; P, 10.6.

10.1021/om0495372 CCC: $27.50
Publication on Web 09/16/2004

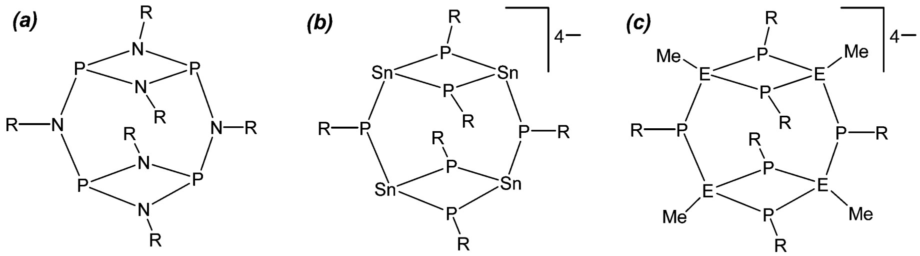

Figure 1. Valence-isoelectronic macrocycles.

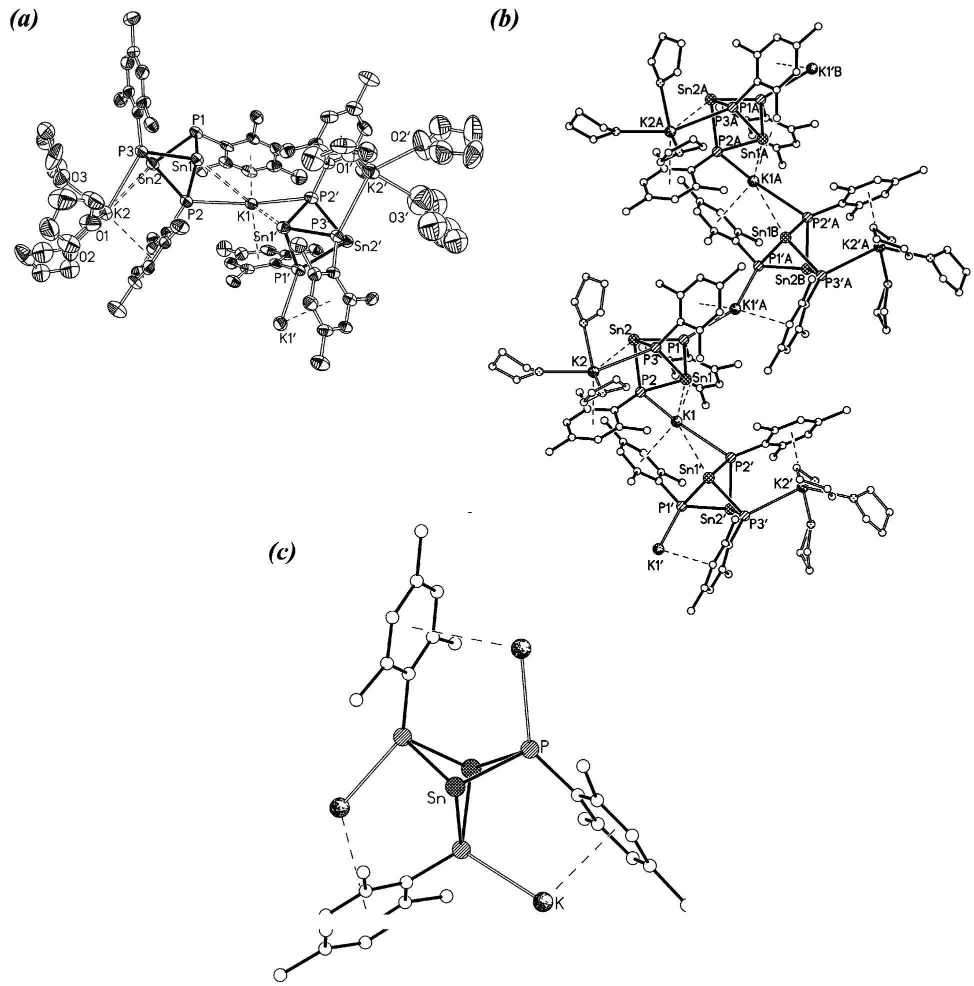

Figure 2. (a) Asymmetric unit in the crystal of **1**. Thermal ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. Key bond lengths (Å) and angles (deg): Sn(1)−P(1) = 2.667(3), Sn(1)−P(2) = 2.629(3), Sn(1)−P(3) = 2.606(3), Sn(2)−P(1) = 2.618(3), Sn(2)−P(2) = 2.628(3), Sn(2)−P(3) = 2.667(3), Sn(1′)−P(1′) = 2.648(3), Sn(1′)−P(2′) = 2.647(3), Sn(1′)−P(3) = 2.619(3), Sn(2′)−P(1′) = 2.628(3), Sn(2′)−P(2′) = 2.632(3), Sn(2′)−P(3′) = 2.654(3), Sn(1)−K(1) = 4.016(2), Sn(1′)−K(1) = 3.845(2), K(1)−P(2) = 3.185(4), K(1)−P(2′) = 3.235(4), K(1)−C range 3.125(9)−3.22-(1), Sn(2)−K(2) = 3.821(3), P(3)−K(2) = 3.354(4), K(2)−C range 3.04(1)−3.52(1), K(1′)−P(1) = 3.402(4), K(1′)−C range 3.27(1)−3.51(9), K(2′)−P(3′) = 3.268(4), K(2′)−C = 3.10−3.52(1), P−Sn(1,1′,2,2′)−P range 80.59(9)−84.88(9), Sn−P(1,2,3,1′,2′,3′)−Sn range 79.40(8)−79.91(8). (b) Part of the infinite polymeric chain structure of **1** running parallel to the *a* axis (K(1′A)−P(1), K(1′)−P(1B) = 3.398(4) Å). (c) Mode of coordination of the three K^+ cations by each of the anions of **1**, with additional K···Sn bonding augmenting the π-arene and σ(P) bonding. Symmetry transformations used to generate equivalent atoms: (A) $x - 1, y, z$; (**B**) $x + 1, y, z$.

solution species are present. This situation is complicated by the extreme moisture sensitivity and/or reactivity of the compound in solution, which leads to unavoidable formation of a decomposition product (containing the SnPHMes functionality).[6] The absence of a P−H stretching band in the IR spectrum of solid **1** shows that this species is not a contaminant in the reaction product itself.

The low-temperature X-ray structure of **1** shows that the asymmetric unit contains two crystallographically

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(9) Related enhancement of the basicity of the $MesPH^-$ ion has been observed in the reaction of MesPHNa with $Sn(NMe_2)_2$ in the presence of TMEDA, resulting in the deprotonation of a Me group of the Mes ligands; see: McPartlin, M.; Woods, A. D.; Pask, C. M.; Vogler, T.; Wright, D. S. *Chem. Commun.* **2003**, 1524.

independent $[Sn_2(PMes)_3]^{2-}$ dianions linked via a K^+ cation (K(1), Figure 2a). This double unit associates further to give an infinite-chain polymeric arrangement parallel to the crystallographic *a* axis via bridging of a second independent K^+ cation (K(1′) at $x - 1$, y, z; Figure 2b).[10] The two remaining K^+ cations (K(2) and K(2′)) are found in "terminal" positions and are coordinated by three THF ligands. The Sn−P bonds within $[Sn_2(PMes)_3]^{2-}$ dianions (range 2.606(3)−2.667(3) Å) and the angles at the Sn centers (range 80.59(9)−84.88(9)°) are typical of those found in Sn(II) phosphinidine compounds.[2,11] The acute angles at the Sn(II) centers are consistent with the presence of a stereochemically active metal lone pair which possess a high degree of s character, directed exo to the trigonal-bipyramidal cage arrangement of the anions. The very acute internal angles at the P centers of the dianions (79.40(8)−79.91(8)°) are at the lower range of the values previously observed in Sn(II) phosphinidines. The trigonal-bipyramidal core arrangement of the framework of the $[Sn_2(PMes)_3]^{2-}$ dianion of **1** is rare for main-group nitrogen and phosphorus compounds, the closest structural analogue being the neutral phosphinidine $[(^tBuSi)_2(\mu\text{-}PCy)_3]$.[12]

Perhaps the most interesting feature of **1** is the use of the full range of σ(Sn), σ(P), and π-arene metal bonding modes available to the $[Sn_2(PMes)_3]^{2-}$ dianions in the structure. Overall, each of the $[Sn_2(PMes)_3]^{2-}$ anions coordinates three K^+ cations with local approximate C_3 symmetry (Figure 2c), with the coordination of the two independent anions differing largely in the extent of Sn···K interactions involved. The two cations K(2) and K(2′) have similar environments; in addition to coordination by three THF ligands they are bonded to a P center (K(2′,2)−P(3′,3) = 3.268(4)−3.354(4) Å) and π-bonding to a Mes ring (range 3.04(1)−3.52(1) Å[13]). In the case of K(2), however, the Sn−P bond coordinates in a "side-on" mode involving an additional interaction with Sn(2) (Sn(2)−K(2) = 3.821(3) Å). In bridging the two independent $[Sn_2(PMes)_3]^{2-}$ dianions K(1) also uses "side-on" coordination of two Sn−P bonds (Sn(1,1′)−K(1) = 3.845(2)−4.016(2) Å, P(2,2′)−K(1) = 3.185(4)−3.235(4) Å) and a π-interaction with a Mes group from each of the dianions (range 3.13(1)−3.22(1) Å[13]). The "side-on" interactions of Sn−P bonds with K(1) and K(2) in the structure of **1** are unprecedented. The Sn−K and P−K bond lengths involved compare to ranges of 3.59−4.15 Å[14] (cf. 3.821(3)−4.016(2) Å in **1**) and 3.04−3.66 Å[15] (cf. 3.185(4)−3.354(4) Å), respectively, observed in previously characterized compounds containing these individual bonding types. The coordination of K(1′), in linking of the structure into a polymer, is similar to that of K(1), but in this case no Sn−K bonding occurs, with the cation being bonded only to two P centers (P(1′,1A′)−K(1′) = 3.398(4)−3.402(4) Å) and π-bonded to two Mes groups (3.27(1)−3.514(9) Å[13]).

In summary, the $[Sn_2(PMes)_3]^{2-}$ dianion has a unique structural arrangement for a Sn(II) phosphinidine which represents a monomeric homologue of a broad class of related main-group macrocycles. The multifunctional capabilities of the $[Sn_2(PMes)_3]^{2-}$ dianion (illustrated in the structure of **1**) and, indeed, its potential to oligomerize into higher cyclic homologues in response to metal coordination should lead to interesting coordination chemistry in the future.

Acknowledgment. We gratefully acknowledge the EPSRC (F.G., S.M.H., M.McP., C.M.P., D.S.W.), The Cambridge European Trust (F.G.), The Newton Trust (F.G.), St. Catharine's College (Fellowship for A.D.W.), and Churchill and Fitzwilliam Colleges (Fellowship for A.D.H.) for financial support. We also thank Dr. J. Davies for collecting data on **1**.

Supporting Information Available: Tables of crystallographic data for **1**; these data are also available as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Crystal data for **1**: $C_{78}H_{114}K_4O_6P_6Sn_4$, M_r = 1964.68, monoclinic, space group $P2_1/n$, $Z = 4$, a = 12.5487(2) Å, b = 23.4701(4) Å, c = 30.4697(6) Å, β = 96.8740(10)°, V = 8909.4(3) Å^3, μ(Mo Kα) = 1.448 mm^{-1}, ρ_{calcd} = 1.465 Mg m^{-3}, T = 180(2) K. Data were collected on a Nonius KappaCCD diffractometer. Of a total of 37 772 reflections collected, 10 802 were unique (R_{int} = 0.081). The structure was solved by direct methods and refined by full-matrix least squares on F^2.[16] Final R1 = 0.069 ($I > 2\sigma(I)$) and wR2 = 0.135 (all data).

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