Convergent syntheses of [$Sn_7\{C_6H_3\text{-}2,6\text{-}(C_6H_3\text{-}2,6\text{-}{}^iPr_2)_2\}_2$]: a cluster with a rare pentagonal bipyramidal motif

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Two complementary synthetic routes to a pentagonal bipyramidal Sn_7 cluster, Sn_7Aryl_2 (Aryl = terphenyl ligand), are reported.

Stable polyhedral clusters of the heavier group 14 elements are found either as highly charged anionic Zintl compounds E_m^{x-},[1] or as ligand-stabilized clusters of the formula E_mR_n ($m \geqslant n$).[2] Some of these species reveal structural similarities to Zintl anions, although there is no formal electronic correspondence between them.[3] In recent years, it has been shown that sterically demanding terphenyl ligands[4] can stabilize tetrel (group 14 element) clusters with unusual structures. For example, the neutral clusters Sn_9Ar_3,[5] Sn_8Ar_4,[6] $Ge_4(GeAr)_2$[3] and the mixed tetrel cluster $Sn_4(GeAr)_2$[7] (Ar = terphenyl ligands) have been isolated. Other bulky ligand systems have also proven effective at tetrel cluster stabilization, as exemplified by the germanium species $Ge_8[N(SiMe_3)_2]_6$,[8] the tin cluster $Sn_2[Sn(2,6\text{-diethylphenyl})_2]_3$[9] and the silylated lead cluster $Pb_{10}[Si(SiMe_3)_3]_6$.[10] Building upon previous work, we now report the synthesis of Sn_7 cluster $Sn_5(SnAr')_2$ (**1**) ($Ar' = C_6H_3\text{-}2,6\text{-}(C_6H_3\text{-}2,6\text{-}{}^iPr_2)_2$) by two independent synthetic strategies. Compound **1** features a pentagonal bipyramidal framework, an arrangement that is rare for main group elements, and, to our knowledge, was previously unknown for clusters of group 14 elements.

By following a pre-established reductive coupling protocol, **1** was prepared by the reduction of a 4 : 1 mixture of Ar′SnCl[11] and $SnCl_2$ with KC_8 (one equiv. of K per halide) in THF.† Compound **1** was isolated as orange crystals from cold (−20 °C) hexanes in a low yield of 15%, and was characterized by a combination of X-ray crystallography,‡ NMR (^1H, $^{13}C\{^1H\}$ and ^{119}Sn) and UV-vis spectroscopy.

The X-ray crystal structure of **1** is illustrated in Fig. 1, and reveals a central, planar, pentagonal Sn_5 core of non-ligand-bearing tin atoms (Sn3 to Sn7), capped at each side of the Sn_5 plane by two SnAr′ groups (Sn1 and Sn2). The average Sn–Sn distance in the Sn_5 ring is 2.959(4) Å, while the internal angles within this pentagon are in the range 107.02(5) to 109.28(4)° (107.98(10)° average) and correspond closely to the expected value of $3\pi/5 = 108°$ for a planar structure. Furthermore, the angular sum of the internal ring angles in **1** is 539.90(10)° ($\Sigma°_{pentagon} = 3\pi$ or 540°). The apical C(1)–Sn(1)···Sn(2)–C(30) array deviates slightly from linearity; however, the Sn_7 unit itself has an overall geometry that approaches D_{5h} symmetry. Compound **1** crystallizes in the $P2_1/c$ space group, with each Sn atom within the highly symmetric pentagonal bipyramidal Sn_7 unit located as a crystallographically-independent entity. Thus, the nearly ideal D_{5h} symmetry of the Sn_7 framework is not crystallographically imposed.

The distances between the two aryl-substituted tin atoms, Sn(1) and Sn(2), and the remaining central tin ring atoms range from 2.95 to 3.03 Å. The Sn–Sn separation between the axial Sn(1) and Sn(2) atoms is *ca.* 0.3 Å longer, with an observed length of 3.32(7) Å. For comparison, the Sn–Sn distances in **1** are longer than that found in elemental tin (2.80 Å).[12] However, they are similar to those in related cluster $Sn_8Ar^{\#}_4$ (2.853(2)–3.107(2) Å) ($Ar^{\#} = C_6H_3\text{-}2,6\text{-}(C_6H_2\text{-}2,4,6\text{-}Me_3)_2$).[6] The Sn–C distances are 2.181(6) and 2.190(6) Å, and within expected values.[13] Interestingly, the two terphenyl groups in **1** are staggered with respect to each other, and there is a dihedral angle of 66.7° between the planes of the central rings.

Fortunately, **1** retains its structure in solution and was soluble enough in C_6D_6 to permit the acquisition of multinuclear NMR spectra. The ^1H and $^{13}C\{^1H\}$ NMR data for **1** consisted of the expected ligand-based resonances, while the $^{119}Sn\{^1H\}$ NMR spectrum displayed two signals at δ 419.5 and 529.7, respectively. The latter, more intense, resonance has been tentatively assigned to the five magnetically-equivalent tin centers in the Sn_5 ring core,

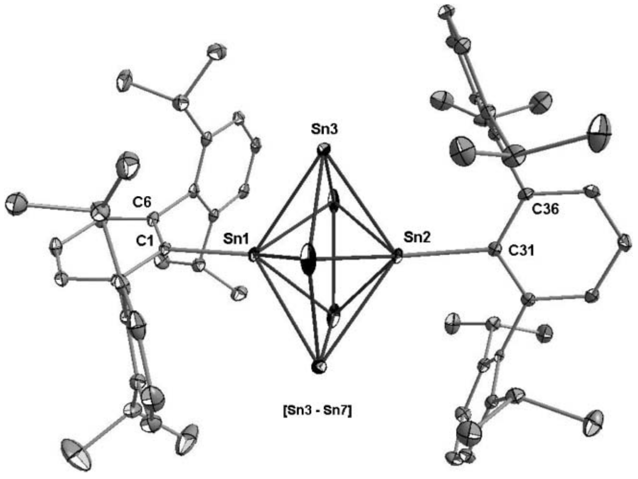

Fig. 1 Thermal ellipsoid plot (30% probability level) for $Sn_5(SnAr')_2$ (**1**). Hydrogen atoms and disordered Sn_5 ring atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Sn(1)···Sn(2) 3.32(7), Sn(1,2)–ring tin atoms [Sn(3) to Sn(7)] 2.9464(14) to 3.0263(4), Sn(1)–C(1) 2.190(6), Sn(2)–C(31) 2.181(6); C(1)–Sn(1)–Sn(2) 176.0(2), Sn(1)–Sn(2)–C(31) 175.3(2). Average internal angle in the central Sn_5 ring: 107.98(10)°.

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and the more shielded signal at δ 419.5 to the ligand-bearing tin atoms. For comparison, mixed cluster $Sn_4[GeAr^{\#}]_2$ shows a tin resonance at δ 1583,[7] while the tin cluster $Sn_8Ar^{\#}_4$ shows two signals at δ 751.7 and 483.1.[6] The UV-vis spectrum of **1** (hexanes) consisted of two broad shoulders at 422 and 484 nm.

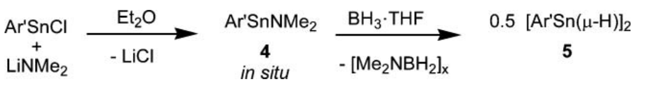
The pentagonal Sn_5 structural motif has been observed as part of the drum-like decastanna[5]prismane,[14] $(SnAryl)_{10}$ (Aryl = 2,6-diethylphenyl), and in the Zintl species Na_8BaSn_6 (**2**).[15] Compound **2** contains a planar formal Sn_5^{6-} unit with a mean Sn–Sn distance of 2.91(5) Å. Apart from **1**, the trielide Zintl anion Tl_7^{7-} represents the only other known example of an isolated pentagonal bipyramidal M_7 unit (M = main group element), and is found in the Zintl phase $K_{10}Tl_7$ (**3**).[16] The Tl_7^{7-} anion in this cluster is isoelectronic to a neutral Sn_7 molecule, and the apical Tl–Tl distance is 3.46(2) Å, exceeding the sum of the covalent radius of Tl (2.94 Å) by 17%. The apical Sn–Sn distance in **1** (3.32(7) Å) is also *ca.* 17% longer than the sum of the covalent radii for tin (*ca.* 2.8 Å), indicating that similar M_7 geometries are found in **1** and **3**.[12] As already mentioned, the angles about the Sn atoms in the Sn_5 core (averaging 107.98(10)°) are close to the anticipated value of 108° for an ideal pentagon. A similar geometry has been noted in the mixed pentagonal bipyramidal cluster $[Pb_5\{Mo(CO)_3\}_2]^{4-}$, where the angles about the planar Pb_5 array are in the range 106.84(1) to 108.57(1)°.[17]

The almost perfect bicapped pentagon is the most prominent feature of **1**. By applying Wade's rules,[18] a *closo* structure is predicted if $2n + 2$ electrons (n = number of vertices) are present in the metal framework. The unsubstituted tin atoms in the Sn_5 unit each provide 2 electrons, while each SnAr′ group supplies 3 electrons, giving the requisite number of 16 electrons for a *closo* structure with seven vertices. Moreover, the uniformity of the Sn–Sn distances is in agreement with Wade's rules, which predict equal bond distances in closed deltahedral structures.[19]

Concurrent with our studies of low-valent main group hydrides, we have explored the thermolysis of species of the form ArSnH as a possible entry into new tin-rich clusters.[5,20] To investigate this area further, we have prepared the tin(II) hydride $[Ar'Sn(\mu\text{-}H)]_2$ (**5**) and explored its thermolysis chemistry.

Compound **5** was prepared by a new two-step procedure,† whereby the *in situ*-generated tin(II) amide $Ar'Sn\text{–}NMe_2$ (**4**) (from Ar′SnCl[11] and $LiNMe_2$ in ether) was treated with a slight excess of $BH_3{\cdot}THF$, resulting in a rapid NMe_2/H exchange reaction[21] to give **5** as a sparingly soluble orange solid (85% yield from Ar′SnCl; Scheme 1). Tin(II) hydride **5** was characterized by X-ray crystallography, and NMR and UV-vis spectroscopy.

The structure of **5** is presented in Fig. 2, and consists of a centrosymmetric dimer with Sn–H distances of 1.82(8) and 1.99(8) Å, respectively, and a Sn···Sn separation of 3.1260(11) Å. The tin center has pyramidal coordination with a C_{ipso}–Sn–H angle of 99(2)° and C_{ipso}–Sn–Sn angle of 98.11(15)°. These metrical parameters are similar to those observed for the only other known aryltin(II) hydride, $[Ar^*Sn(\mu\text{-}H)]_2$ (**6**) ($Ar^* = C_6H_3\text{-}2,6\text{-}(C_6H_2\text{-}2,4,6\text{-}{}^iPr_3)_2$), which has a Sn–Sn distance of 3.1192(3) Å and a C_{ipso}–Sn–H angle of 93.28(5)°.[20]



Scheme 1 Preparation of the tin(II) hydride $[Ar'Sn(\mu\text{-}H)]_2$ (**5**).

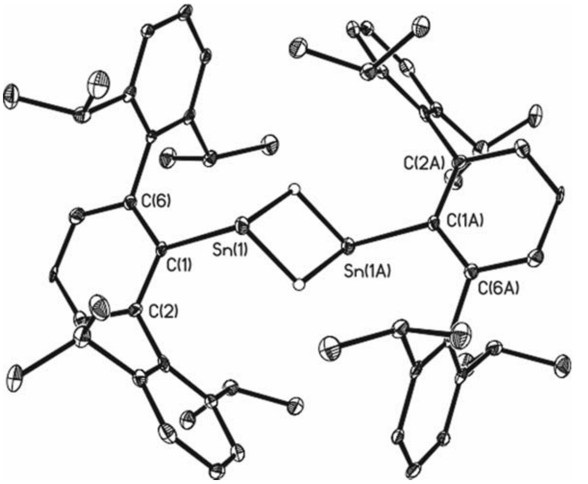
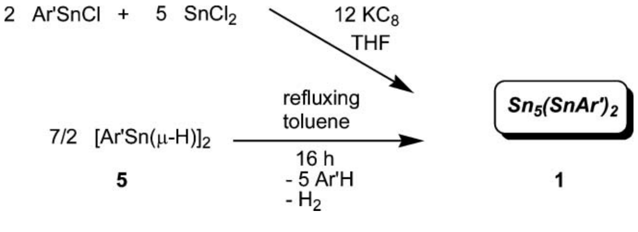


Fig. 2 Molecular structure of $[Ar'Sn(\mu\text{-}H)]_2$ (**5**), with thermal ellipsoids at the 30% probability level. Carbon-bound hydrogen atoms are not shown, and alphabetized atom labels indicate symmetry-generated atoms ($-x$, $-y$, $1 - z$). Selected bond lengths (Å) and angles (°): Sn(1)–Sn(1A) 3.1260(11), Sn(1)–C(1) 2.221(6), Sn(1)–H(1) 1.82(8), Sn(1)–H(1A) 1.99(8); C(1)–Sn(1)–Sn(1A) 98.11(15), C(1)–Sn(1)–H(1) 99(2).

When compound **5** was heated for 16 h in refluxing toluene,† the initially orange slurry dissolved and the solution became dark green. Near the completion of the thermolysis reaction, the solution had changed to amber. Work-up of the reaction mixture, including filtration and crystallization of the product from hexanes, yielded large, well-formed orange crystals, which were identified as the title Sn_7 cluster **1** (25% yield with respect to Sn; Scheme 2) using a combination of X-ray crystallography and NMR spectroscopy.

According to Scheme 2, the synthesis of **1** could involve the formation of H_2 and Ar′H by-products. Indeed, we were able to isolate Ar′H as the major side-product from the mother liquor of the reaction mixture and compare its ^1H and $^{13}C\{^1H\}$ NMR spectra with those of an authentic sample. The low yields of **1** from both routes suggest that other tin-containing species might also be formed, and we are currently investigating these reactions in more detail.



Scheme 2 Convergent syntheses of $Sn_5(SnAr')_2$ (**1**).

The synthesis of **1** *via* the thermolysis of tin(II) hydride **5** represents a complementary route to the reduction of $SnCl_2$/Ar′SnCl mixtures with KC_8. It is important to mention that changing the nature of the ligand in the ArSnH precursor has a dramatic impact on the product obtained upon thermolysis. For example, we have previously shown that $[Ar^*Sn(\mu\text{-}H)]_2$ (**6**) can be converted into tricapped cluster $Sn_9Ar^*_3$.[5] We anticipate that the thermolysis of new low-valent hydrides will be a useful and general route for obtaining new cluster archetypes.

In conclusion, a rare example of a pentagonal bipyramidal main group cluster has been prepared using two independent methods. With the aid of the complementary synthetic strategies reported, it is anticipated that tailoring of the ligand environment and element type should lead to the discovery of unprecedented cluster arrangements.

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Notes and references

† All manipulations were carried out under strictly anhydrous and anaerobic conditions.

Preparation of $Sn_5(SnAr')_2$ (**1**): Ar′SnCl[11] (0.55 g, 1.0 mmol) and $SnCl_2$ (0.048 g, 0.25 mmol) were mixed in 30 mL of de-gassed THF, and added as a slurry to a cold (−78 °C) suspension of KC_8 (0.058 g, 1.5 mmol of K) in 30 mL of THF. The reaction mixture was allowed to warm slowly to room temperature and stirred for 5 h. The solvent was then removed under reduced pressure and the residue extracted with 50 mL of hexanes. The mixture was filtered, the volume of the filtrate reduced to *ca.* 40 mL and then stored at *ca.* −20 °C. After 24 h, compound **1** was isolated as orange crystals (0.045 g, 15% yield with respect to Sn). ^{1}H NMR (C_6D_6): δ 0.46 (d, 24H, $^3J_{HH}$ = 6.6 Hz, CH(CH_3)$_2$), 1.44 (d, 24H, $^3J_{HH}$ = 6.6 Hz, CH(CH_3)$_2$), 2.8–3.2 (br, 8H, CH(CH$_3$)$_2$), 6.16 (d, 4H, $^3J_{HH}$ = 7.5 Hz, *m*-C$_6H_3$), 6.22 (t, 2H, $^3J_{HH}$ = 7.5 Hz, *p*-C$_6H_3$), 7.38 (d, 8H, $^3J_{HH}$ = 8.2 Hz, *m*-Dipp) and 7.63 (t, 4H, $^3J_{HH}$ = 8.2 Hz, *p*-Dipp). ^{13}C{^{1}H} NMR (C_6D_6): δ 24.3 (CH(CH_3)$_2$), 25.7 (CH(CH_3)$_2$), 30.1 (CH(CH$_3$)$_2$), 123.6, 128.8, 130.1, 140.0, 145.6, 146.9, 166.3 and 169.8 (Ar*C*). ^{119}Sn{^{1}H} NMR (C_6D_6, ref. to $SnMe_4$): δ 419.5 (*Sn*–Ar′) and 529.7 (Sn_5 ring). Mp (°C): 248–251 (decomp.). UV-vis (hexanes, nm [ε, M^{-1} cm^{-1}]): 422 (shoulder) and 484 (shoulder).

Preparation of $[Ar'Sn(\mu\text{-}H)_2]$ (**5**): To a mixture of Ar′SnCl[11] (2.90 g, 5.27 mmol) and $LiNMe_2$ (0.275 g, 5.33 mmol) was added 60 mL of cold (*ca.* −30 °C) Et_2O. The reaction was then warmed to room temperature and stirred for 5 h to give a yellow-orange solution over a white precipitate (LiCl). The reaction mixture was then filtered and BH_3·THF (5.30 mL, 1.0 M solution in THF, 5.3 mmol) added dropwise to the filtrate. Upon addition of BH_3·THF, a deep green-blue solution was seen that afforded an orange microcrystalline precipitate. After stirring for 30 min, the reaction volume was concentrated to *ca.* 7 mL and the mother liquor decanted from the orange precipitate. The product was dried under vacuum to afford **5** in moderate yield (2.32 g, 85% based on Ar′SnCl). Crystals of suitable quality for X-ray diffraction studies were subsequently obtained from benzene (*ca.* 7 °C). ^{1}H NMR (C_6D_6): δ 0.93 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH(CH_3)$_2$), 1.02 (d, 12H, $^3J_{HH}$ = 6.6 Hz, CH(CH_3)$_2$), 1.04 (d, 12H, $^3J_{HH}$ = 6.6 Hz, CH(CH_3)$_2$), 1.11 (d, 12H, $^3J_{HH}$ = 6.6 Hz, CH(CH_3)$_2$), 3.00 (overlapping septets, 8H, CH(CH$_3$)$_2$), 7.03 (d, 4H, $^3J_{HH}$ = 7.5 Hz, ArH), 7.10 (m, 10H, ArH), 7.30 (t, 4H, $^3J_{HH}$ = 7.5 Hz, ArH) and 9.13 (s, 2H, $^1J_{SnH}$ = *ca.* 89 Hz, SnH). ^{119}Sn NMR (C_6D_6): δ 657 (br, $\Delta\omega_{1/2}$ = *ca.* 270 Hz). Mp (°C): 181–183 (decomp.). UV-vis (benzene, nm [ε, M^{-1} cm^{-1}]): 595 (70). IR (Nujol, cm^{-1}): Sn–H stretching mode likely to have been obscured by ligand vibrations.

Synthesis of ***1*** *via the thermolysis of* **5**: An orange slurry of **5** (0.542 g, 1.05 mmol) in 15 mL of de-gassed toluene was heated to reflux for 16 h. The resulting amber-red solution was cooled to room temperature and then filtered to remove the trace amounts of tin metal that had formed. The volatiles were then removed and the orange-red residue re-dissolved in 15 mL of hexanes. Storage of this solution at *ca.* −20 °C afforded a crop of orange crystals that were identified as $Sn_5(SnAr')_2$ (**1**) (0.062 g, 25% yield with respect to Sn) by X-ray crystallography, and ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. Ar′H was identified in the hexane-soluble fraction. Data for Ar′H: ^{1}H NMR (C_6D_6): δ 1.12 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH(CH_3)$_2$), 1.13 (d, 12H, $^3J_{HH}$ = 6.9 Hz, CH(CH_3)$_2$), 2.90 (septet, 4H, $^3J_{HH}$ = 6.9 Hz, CH(CH$_3$)$_2$) and 7.03–7.30 (m, 9H, ArH). ^{13}C{^{1}H} NMR (C_6D_6): δ 24.4 (CH(CH_3)$_2$), 24.5 (CH(CH_3)$_2$), 30.8 (CH(CH$_3$)$_2$), 122.9, 128.3, 128.4, 131.5, 139.7, 141.1, 146.2 and 146.9 (Ar*C*).

‡ Details of the X-ray diffraction studies:

1·hexane: $C_{66}H_{88}Sn_7$, M = 1712.19, monoclinic, $P2_1/c$, orange block, a = 15.6747(5), b = 17.1734(5), c = 24.6446(7) Å, β = 99.012(10)°, V = 6552.1(3) A^3, Z = 4, T = 90(2) K, 86311 total reflections, 15043 independent (R_{int} = 0.0241), $R1$ (obs. data) = 0.0350, w$R2$ (all data) = 0.0914. CCDC 651569. The large residual electron densities were due to rotational disorder of the central Sn_5 moiety, of which three orientations could be refined (0.83 : 0.075 : 0.095 ratio) and summed to full occupancy. The tin atoms in the two minor components were restrained to adopt similar Sn–Sn distances and thermal parameters as the major residue. It is possible that the disorder in the Sn_5 core could be due to libration, and future work will involve a theoretical investigation of this phenomenon.

5: $C_{60}H_{76}Sn_2$, M = 1034.59, triclinic, P-1, orange block, a = 9.2996(16), b = 12.814(12), c = 12.938(2) Å, α = 110.141(3), β = 98.399(3), γ = 110.940(3)°, V = 1286.6(4) Å^3, Z = 1, T = 90(2) K, 4763 total reflections, 4677 independent (R_{int} = 0.0704), $R1$ (obs. data) = 0.0554, w$R2$ (all data) = 0.1658. CCDC 651570.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b709446a

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