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Pyramidanes

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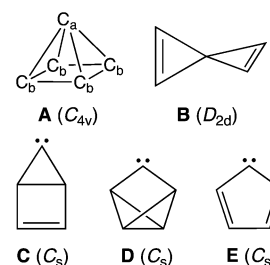
Supporting Information

ABSTRACT: Pyramidane is an elusive but highly desirable target for synthetic chemists that has attracted a great deal of attention because of its nonclassical structure and unusual bonding features. Although well studied on theoretical grounds, neither the parent all-carbon pyramidane nor its derivatives containing heavier group 14 elements have ever been isolated and characterized. In this Communication, we report on the synthesis and structural elucidation of the first stable representatives of this class of highly strained polyhedral compounds: germa- and stannapyramidanes $\text{Ge}[\text{C}_4(\text{SiMe}_3)_4]$ and $\text{Sn}[\text{C}_4(\text{SiMe}_3)_4]$. The peculiar structural and bonding features of these compounds are verified by combined experimental and computational analyses, showing these derivatives to be nonclassical neutral compounds with a very large contribution of ionic character.

As a geometrical object, the square pyramid, with its regular shape, is one of the fundamental polyhedra. Man-made square-pyramidal structures—again thanks to their highly symmetrical appearance—were first built long ago in many parts of the world: the Egyptian pyramid of Cheops is probably the most famous example. Therefore, it comes as no surprise that such appealing pyramidal shapes have long been very attractive, yet posed a major challenge for synthetic chemists. However, the aesthetic appeal of square pyramids is not the only (and by no means the main) feature that drives chemists' curiosity to synthesize such elusive compounds. Their very unusual structural and bonding properties, which cannot be adequately described by classical bonding theory and contribute to its further development, are the most fascinating aspect, motivating chemists in experimental pursuits.

In chemistry, the compound possessing the shape of a square pyramid is called *pyramidane* (known also as tetracyclo-[2.1.0.0^{1,3}.0^{2,5}]pentane or [3.3.3.3]fenestrane), the simplest organic system with a pyramidal C atom featuring inverted tetrahedral geometry¹ (Chart 1). There are two principal modes of such inverted tetrahedral (so-called “umbrella”) configuration of the tetracoordinate C atom: propellane-type^{2,3} and pyramidane-type.^{4,5} Although fascinating synthetic targets, neither pyramidane **A** nor its structural isomers, spiro-pentadiene **B** and cyclic/polycyclic carbenes **C**, **D**, and **E** (Chart 1),

Chart 1. The Most Important Isomers Found on the C_5H_4 Potential Energy Surface^a



^a**A**, pyramidane (C_a , apical atom; C_b , basal atom); **B**, spiro-pentadiene; **C**, bicyclo[2.1.0]pent-2-en-5-ylidene; **D**, tricyclo[2.1.0.0^{2,5}]pent-3-ylidene; and **E**, cyclopentadienylidene. H atoms are not shown; symmetry point group is shown in parentheses.

have ever been isolated as stable compounds, despite being thoroughly studied computationally.^{4a–k} [For **B**, its all-silicon version, spiro-pentasiladiene, $\text{Si}_5(\text{SiR}_3)_4$ ($\text{R}_3\text{Si} = \text{Si}(\text{SiMe}_2^t\text{Bu})_3$), has been reported.⁶]

The predicted high kinetic stability of pyramidane with respect to its decomposition and rearrangements suggests that the synthesis of pyramidane is feasible.^{4k} Although all four structures **B–E** (Chart 1) were suggested to serve as potential precursors for pyramidane **A**,^{4k} the bicyclo[2.1.0]pent-2-en-5-ylidene **C** seems to be the most appropriate, given its reasonably accessible barrier to thermal rearrangement (16.3 kcal/mol at the CCSD(T)/DZP level), and accordingly its expected ready isomerization to pyramidane.^{4j} We reasoned that such a transient bicyclic carbene of type **C** could be generated by the coupling of the tetrakis(trimethylsilyl)-cyclobutadiene dianion salt $[\eta^4-(\text{Me}_3\text{Si})_4\text{C}_4]^{2-} \cdot [\text{Li}^+(\text{thf})]_2$ ($1^{2-} \cdot [\text{Li}^+(\text{thf})]_2$)⁷ with readily available dioxane (diox) complexes of dichlorogermylene and dichlorostannylene. Based on this strategy, we succeeded in isolating pyramidanes incorporating heavier group 14 elements at the apex, and here we report their synthesis and structural characterization and computational studies of the structure and bonding nature of these nonclassical compounds.

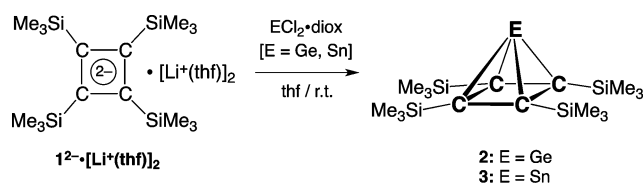
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The reaction of $1^{2-} \cdot [\text{Li}^+(\text{thf})]_2$ with both $\text{GeCl}_2 \cdot \text{diox}$ and $\text{SnCl}_2 \cdot \text{diox}$ produced the germa- and stannapyramidane derivatives **2** and **3** nearly quantitatively (Scheme 1).⁸

Scheme 1. Synthesis of the Germa- and Stannapyramidanes **2 and **3****



Both **2** and **3** showed highly symmetrical compositions, both in solution and in the solid state. Thus, their C_6D_6 solutions showed only one set of resonances in all NMR spectra (^1H , ^{13}C , ^{29}Si , and ^{119}Sn); moreover, the Sn atom at the apex of the square pyramid in **3** was found to be extraordinarily shielded, being observed at -2441.5 ppm.⁹ The last value closely approaches those of the stannocene derivatives, with their record high-field tin resonances appearing in the range from -2100 to -2300 ppm.¹⁰

In its crystalline state, stannapyramidane **3** (germapyramidane **2** exhibited very similar features) showed a practically planar C_4 -base ($\text{C1}-\text{C2}-\text{C1\#}-\text{C3}$) with a negligible folding of 0.6° and tetrahaptoordinated Sn1 apex (Figure 1).⁸ There is

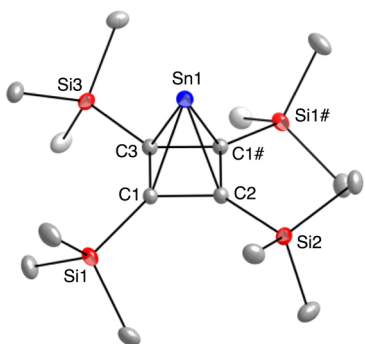


Figure 1. ORTEP view of the stannapyramidane **3**. Thermal ellipsoids are given at the 30% probability level; H atoms are not shown. Selected bond lengths (Å): Sn1–C1 = 2.3432(16), Sn1–C2 = 2.339(2), Sn1–C3 = 2.342(2), C1–C2 = 1.485(2), C1–C3 = 1.482(2), C1–Si1 = 1.8774(17), C2–Si2 = 1.862(2), C3–Si3 = 1.868(2). Selected bond angles (deg): C1–Sn1–C2 = 36.97(5), C1–Sn1–C3 = 36.88(5), C1–Sn1–C1# = 53.04(8), C2–Sn1–C3 = 53.39(8), C1–C2–C1# = 89.62(18), C1–C3–C1# = 89.81(18), C2–C1–C3 = 90.28(13). Folding angle of the C1–C2–C1#–C3 ring (deg): 0.58.

no alternation in the endocyclic C–C bond lengths of 1.485(2) and 1.482(2) Å, and these values are very close to those of the “inverted” sandwich and half-sandwich cyclobutadiene dianion alkali and alkaline earth metal derivatives, for which a remarkable 6π -electron aromaticity was demonstrated: Li salt $1^{2-} \cdot [\text{Li}^+(\text{thf})]_2$, 1.485(10)–1.507(9) Å,⁷ and Mg salt $[\eta^4-(\text{Me}_3\text{Si})_4\text{C}_4]^{2-} \cdot [\text{Mg}^{2+}(\text{thf})_3]$ (**4**), 1.474(5)–1.513(5) Å.¹¹ Based on these structural similarities of the neutral pyramidane **3** and ionic salts **1** and **4**, one can propose the important extent of the π -electron delocalization within the C_4 -ring of **3**, which implies that in **3** (and in **2**) the p-block element (Sn or Ge) plays the rather unusual role of the s-block element (Li, Mg).

Another striking structural peculiarity of **3** is its markedly stretched Sn–C bonds of 2.339(2)–2.3432(16) Å, values that exceed the sum of the Sn and C covalent single-bond radii of 2.15 Å¹² by ca. 9%. These geometrical features are in line with those theoretically predicted for the parent pyramidane $\text{C}[\text{C}_4\text{H}_4]$, whose structural trends are dominated by the presence of the inverted tetrahedral apical carbon: (1) exceptionally long distances from the apical to the base atoms with a bond order of 0.75, and (2) remarkable base–apex charge separation and presence of a lone pair at the apex.^{4a–k} Our own computations also gave very long interatomic distances of 2.389 Å for the Sn–C bonds in **3** (2.166 Å for the Ge–C bonds in **2**).¹³ Moreover, optimized structures of both germa- and stannapyramidanes **2** and **3** manifest a remarkable charge separation within the molecule, with the apical atom charged positively (+0.69 for Ge in **2** and +0.87 for Sn in **3**) and base C atoms charged negatively (−0.65 in **2** and −0.68 in **3**) [natural population analysis (NPA) charges], which is not unexpected given the greatly differing electronegativities of Ge and Sn vs C atoms (2.01 and 1.96 vs 2.55, Pauling scale).¹⁴

To obtain further insight into the particular bonding situation of pyramidanes **2** and **3**, it is instructive to look at the molecular orbital (MOs) interaction diagram for the model stannapyramidane $\text{Sn}[\text{C}_4\text{H}_4]$ (**3'**) [germapyramidane $\text{Ge}[\text{C}_4\text{H}_4]$ (**2'**) as well as the real compounds **2** and **3** showed a similar MO interaction mode] (Figure 2). The orbital

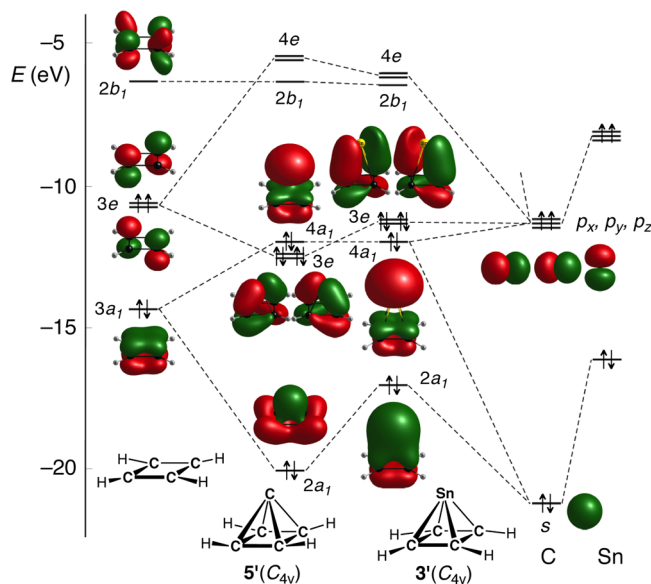


Figure 2. MO interaction diagram visualizing the formation of the most important orbitals from fragment orbitals, computed by the extended Hückel's method for the model pyramidanes $\text{C}[\text{C}_4\text{H}_4]$ (**5'**) and $\text{Sn}[\text{C}_4\text{H}_4]$ (**3'**). Only bonding interactions are shown.

interaction in the hypothetical all-carbon pyramidane $\text{C}[\text{C}_4\text{H}_4]$ (**5'**) is also shown on this diagram to facilitate understanding of the similarities and differences between the organic **5'** and organometallic **3'**. In the pyramidane **5'**, the overall stabilization mainly comes from the formation of two doubly degenerate highest-occupied MOs (HOMOs), HOMO–1 and HOMO–2 ($3e$), whereas the presence of a lone pair at the apex is clearly seen in the HOMO ($4a_1$). Although in the heteronuclear **3'** the principal orbitals are of the same type as those of homonuclear **5'**, there is an important distinction

between them, namely, the order of the two highest occupied MOs, $3e$ and $4a_1$, which are reversed in the “heavy” pyramidine $3'$; the doubly degenerate $3e$ orbital represents now HOMO and HOMO–1, whereas the lone pair orbital $4a_1$ is HOMO–2. This leads to an overall system destabilization because of the increase in the energy level of the four-electron $3e$ orbital caused by the poorer overlap between the cyclobutadiene $3e$ π -orbitals and apical Sn p_x and p_y atomic orbitals. Accordingly, the apex–base orbital interaction in stannapyramidine $3'$, although similar to that in pyramidine $5'$, is substantially weaker. This conclusion agrees well with the exceedingly low values of the apical–basal atoms bond order in both **2** and **3** (Wiberg bond indices), only 0.48 for the Ge–C bonds in **2** and 0.42 for the Sn–C bonds in **3**, which are much lower than the values for the basal–basal C–C bonds, 1.16 in **2** and 1.18 in **3**. [In sharp contrast, the $C_{\text{apical}}-C_{\text{basal}}$ bond order in the parent all-carbon pyramidine $5'$ is substantially greater, at 0.70 (1.10 for the $C_{\text{basal}}-C_{\text{basal}}$ bond order).]

Bader topological analysis based on the Atoms in Molecules (AIM) method^{15a,b} showed the presence of bonding paths between the basal C and apical Sn atoms (see Figure S7; for the related paper, see ref 16). Quantitative analysis of the electron density $\rho(r)$ and the Laplacian of the electron density $\nabla^2\rho(r)$ indicates that, in the prototypical pyramidine $5'$, both basal–basal and basal–apical C–C bonds are covalent [large $\rho(r)$ and negative $\nabla^2\rho(r)$; Table 1].^{17,18} In sharp contrast, the hybrid

Table 1. Topological Analysis (AIM) Data of the C_4 -Based Pyramidanes, Parent Pyramidine $5'$, Germapyrimidanes **2' and **2**, and Stannapyrimidanes $3'$ and **3**^a**

pyramidine $E[C_4R_4]$	$E_{\text{apical}}-C_{\text{basal}}$ bonds		$C_{\text{basal}}-C_{\text{basal}}$ bonds	
	$\rho(r)$	$\nabla^2\rho(r)$	$\rho(r)$	$\nabla^2\rho(r)$
$C[C_4H_4]$ ($5'$)	0.168	–0.016	0.271	–0.616
$Ge[C_4H_4]$ ($2'$)	0.073	0.120	0.271	–0.624
$Ge[C_4(SiMe_3)_4]$ (2)	0.072	0.120	0.254	–0.532
$Sn[C_4H_4]$ ($3'$)	0.055	0.140	0.251	–0.644
$Sn[C_4(SiMe_3)_4]$ (3)	0.056	0.144	0.237	–0.568

^aB3LYP/6-311+G(d,p) for $5'$, $2'$, and **2**; B3LYP/3-21G for $3'$ and **3**. $\rho(r)$ is electron density; $\nabla^2\rho(r)$ is the Laplacian of electron density (a.u.).

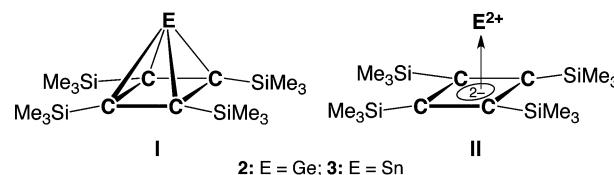
stannapyrimidine $3'$ showed very different electronic properties for apex–base bonds [small $\rho(r)$ and positive $\nabla^2\rho(r)$, indicative of the high degree of their ionicity], whereas the C–C bonds within the C_4 -base in $3'$ are classical covalent bonds (the same holds true for pyrimidanes $2'$, **2**, and **3**).

This AIM outcome well corroborates with the results of the Electron Localization Function (ELF) computations of pyrimidanes $5'$, $2'$, **2**, $3'$, and **3**, which confirm the presence of the apex–base bonding interactions and progressive increase in the degree of ionicity (seen in the values of N , basin population) of the latter on going from $5'$ (0.67) to $2'$ (0.58) and $3'$ (0.47) (see Table S11 and Figure S8).

Thus, all experimental (very long E–C bonds, square-planar shape of the C_4 -base, and striking similarity of the NMR spectra of **2** and **3**) and computational (MO interaction mode, trends in the magnitudes and signs of $\rho(r)$ and $\nabla^2\rho(r)$ from AIM calculations) results point to a very important degree of ionicity for the $E_{\text{apical}}-C_{\text{basal}}$ bonds in **2** and **3**. Such a trend, together with the very strong apex–base charge separation in both molecules (see above: NPA charges), leads us to the overall

conclusion of the crucial contribution of the cyclobutadiene dianion–apical atom dication ionic structure $[(Me_3Si)_4C_4]^{2-} \rightarrow E^{2+}$ (**II**) to the total composition of the formally neutral pyrimidanes **2** and **3** (Scheme 2; for the related Ge^{2+} complex with [2.2.2]cryptand, see ref 19).

Scheme 2. Resonance Forms of Pyrimidanes **2 and **3**: Covalent Form I and Ionic Form II**



In accord with such a contribution of pyrimidanes **2** and **3** as the group 14 element dicationic derivatives of the cyclobutadiene dianion, they react in the same way as a dilithium salt, $1^{2-} \cdot [Li^+(\text{thf})]_2$, giving identical products (e.g., forming $\{[\eta^4-(Me_3Si)_4C_4]Ru(CO)_3\}$ with $[Ru(CO)_3Cl_2]_2$).²⁰

Nearly 40 years after the beginning of theoretical studies on pyrimidanes, the first stable all-group 14 element-containing compounds of this fascinating class of highly strained small cages have finally been prepared as readily available materials. With only one heavier group 14 element at the apex of the square pyramid, these compounds represent a closest approach to still unprecedented all-carbon pyrimidanes. Given their nonclassical apex–base bonding interaction mode, one would expect that such compounds could serve as sophisticated models for further development of a modern theory of chemical bonding. In addition, if one considers pyramidal structures as the bridge between organic and organometallic chemistry,^{4b} then the use of pyrimidanes as precursors for novel transition metal complexes featuring cyclobutadiene ligands could be envisaged.

■ ASSOCIATED CONTENT

● Supporting Information

Experimental and computational details, complete reference 13, and X-ray crystallographic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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(8) Details of experimental procedures and spectral and crystallographic data for compounds **2** and **3** are given in the Supporting Information.

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