

## Pnictogen–Silicon Analogues of Benzene

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### Supporting Information

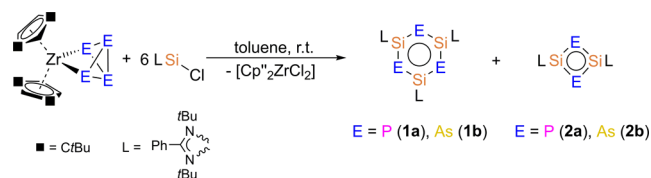
**ABSTRACT:** Since the discovery of the first “inorganic benzene” (borazine, B<sub>3</sub>N<sub>3</sub>H<sub>6</sub>), the synthesis of other noncarbon derivatives is an ongoing challenge in Inorganic Chemistry. Here we report on the synthesis of the first pnictogen–silicon congeners of benzene, the triarsa- and the triphospha-trisilabenzene [(PhC(NtBu)<sub>2</sub>)<sub>3</sub>Si<sub>3</sub>E<sub>3</sub>] (E = P (**1a**), As (**1b**)) by a simple metathesis reaction. These compounds are formed by the reaction of [Cp<sup>''</sup><sub>2</sub>Zr(η<sup>1:1</sup>-E<sub>4</sub>)] (E = P, As; Cp<sup>''</sup> = C<sub>5</sub>H<sub>3</sub>tBu<sub>2</sub>) with [PhC(NtBu)<sub>2</sub>SiCl] in toluene at room temperature along with the silicon pnictogen congeners of the cyclobutadiene, [(PhC(NtBu)<sub>2</sub>)<sub>2</sub>Si<sub>2</sub>E<sub>2</sub>] (E = P (**2a**), As (**2b**)), which is unprecedented for the arsenic system **2b**. All compounds were comprehensively characterized, and density functional theory calculations were performed to verify the stability and the aromatic character of the triarsa- and the triphospha-trisilabenzene.

Since the discovery of benzene by Faraday in 1825 and the postulation of its structure and aromatic character by Kekulé in 1865/66, the term “aromaticity” was mainly attributed to organic compounds.<sup>1</sup> A molecule was considered as “aromatic” when it possessed a planar structure, 4*n* + 2 π-electrons and a special stability due to the electronic delocalization of its π-electrons.<sup>2</sup> In 1926, Stock et al. reported on the synthesis of borazine B<sub>3</sub>N<sub>3</sub>H<sub>6</sub>.<sup>3</sup> This compound was described as a six-membered ring, showing a high stability toward air and higher temperatures. Even if the aromatic character is controversially discussed and the reactivity differs from that of benzene, B<sub>3</sub>N<sub>3</sub>H<sub>6</sub> and related compounds are regarded as “inorganic benzene” due to their structural analogy and similar physical properties as compared to C<sub>6</sub>H<sub>6</sub>.<sup>4</sup> While there are many examples of substituting one, two, or three CH moieties of the benzene ring (e.g., with N, P, O, etc.), only few examples of synthesized noncarbon derivatives are known so far. One example is the class of cyclotriphosphaazatrienes N<sub>3</sub>P<sub>3</sub>R<sub>6</sub>.<sup>5</sup> These compounds possess a planar six-membered ring structure with formally six π-electrons. However, theoretical studies revealed divergent results.<sup>4c,6</sup> The aromatic stabilization energy (ASE) favors an aromatic character of such phosphazenes, whereas the magnetic susceptibility exaltation (MSE) and the nucleus-independent chemical shift (NICS) contradict the aromaticity.<sup>4c</sup> In contrast, the class of boraxines E<sub>3</sub>Q<sub>3</sub>H<sub>3</sub> (E = B, Al, Ga; Q = O, S) is considered as not aromatic.<sup>4c</sup> In the 1980s and 90s, the Power

group succeeded in synthesizing “heavy” borazines (REE'R')<sub>3</sub> (E = N, E' = Al, Ga; E = P, E' = B, Ga) and (GeNR)<sub>3</sub>.<sup>7</sup> They used the bulky substituents R and R' such as mesityl, diisopropylphenyl, and others to stabilize the central group 13/pnictogen ring systems. Calculations of the ASE, MSE, and NICS values resulted in triboratriphoshabenzene being regarded as aromatic.<sup>4c</sup> In 2010, the group of Scheschkewitz synthesized a derivative of hexasilabenzene Si<sub>6</sub>Tip<sub>6</sub> (Tip = 2,4,6-triisopropylphenyl).<sup>8</sup> Even if the molecule does not possess a planar structure, it is assumed to be aromatic also shown by experimental charge density studies.<sup>9</sup> Already in 1977, Chivers and Bojes reported on the synthesis of the trisulphur trinitride anion S<sub>3</sub>N<sub>3</sub><sup>−</sup>, which is formally a 10π electron aromatic ring system.<sup>10</sup> Moreover, many other possible combinations of inorganic analogues with main group elements were only predicted by computational studies.<sup>4c,11</sup> The ongoing interest in synthesizing new carbon-free aromatic ring systems is further reflected in recent reports<sup>12</sup> about, e.g., the formal analogue of Cp<sup>+</sup>, [(PhC(NtBu)<sub>2</sub>)<sub>3</sub>Si<sub>3</sub>PCMe]Cl,<sup>13</sup> and the P<sub>2</sub>N<sub>3</sub><sup>−</sup> anion as Cp<sup>−</sup> congener.<sup>14</sup> Therefore, it is reasonable to consider whether other element combinations, especially those containing group 14 congeners, are able to form 6π electron systems.

We have now found that the triarsa- and triphosphatrisilabenzene [(PhC(NtBu)<sub>2</sub>)<sub>3</sub>Si<sub>3</sub>E<sub>3</sub>] (E = P (**1a**), As (**1b**)) can be easily prepared under mild conditions by simple transfer reactions using [Cp<sup>''</sup><sub>2</sub>Zr(η<sup>1:1</sup>-E<sub>4</sub>)] (E = P, As). Such reactions enable the synthesis of metastable compounds due to the mild reaction conditions and were, for instance, demonstrated by the preparation of AsP<sub>3</sub>.<sup>15</sup> The reaction of the monochlorosilylene [PhC(NtBu)<sub>2</sub>SiCl] with [Cp<sup>''</sup><sub>2</sub>Zr(η<sup>1:1</sup>-P<sub>4</sub>)] in toluene at room temperature leads within 12 h to the formation of the triphosphatrisilabenzene **1a** and [(PhC(NtBu)<sub>2</sub>)<sub>2</sub>Si<sub>2</sub>P<sub>2</sub>] (**2a**) (Scheme 1). Additionally, we succeeded in the synthesis of the arsenic analogues [(PhC(NtBu)<sub>2</sub>)<sub>3</sub>Si<sub>3</sub>As<sub>3</sub>] (**1b**) and the four-

Scheme 1. Synthesis of **1a,b** and **2a,b**

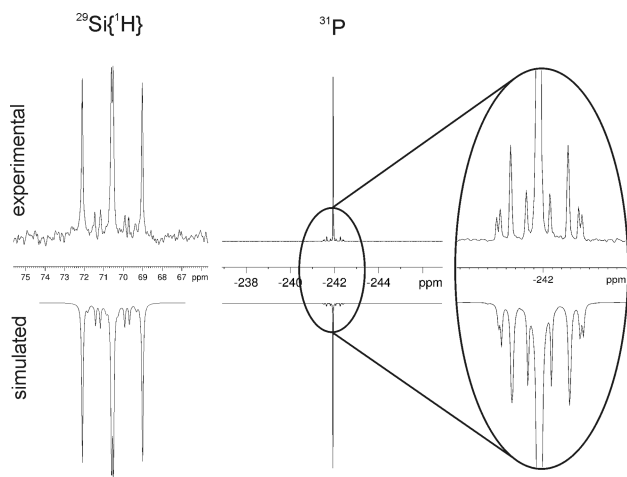


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membered ring compound  $[(\text{PhC}(\text{NtBu})_2)_2\text{Si}_2\text{As}_2]$  (**2b**) under the same reaction conditions by using  $[\text{Cp}^*\text{Zr}(\eta^{1-1}\text{-As}_4)]$ .<sup>16</sup>

The  $^{31}\text{P}$  NMR spectrum of the crude mixture of the first mentioned reaction indicates the formation of  $[(\text{PhC}(\text{NtBu})_2)_3\text{Si}_3\text{P}_3]$  (**1a**) as the major product along with  $[(\text{PhC}(\text{NtBu})_2)_2\text{Si}_2\text{P}_2]$  (**2a**) (the latter was recently synthesized starting from  $[\text{PhC}(\text{NtBu})_2\text{SiCl}]$  and  $\text{P}_4$  or  $\text{LiP}(\text{SiMe}_3)_2$ )<sup>17</sup> and an unidentified product in an overall 2:1:1 integral ratio (Figure S1).<sup>18</sup> In the  $^{31}\text{P}$  NMR spectrum, **1a** shows a singlet at  $-241.9$  ppm with a higher order spectrum for the  $^{29}\text{Si}$  satellites (Figure 1). This signal is strongly high field shifted compared to the four-

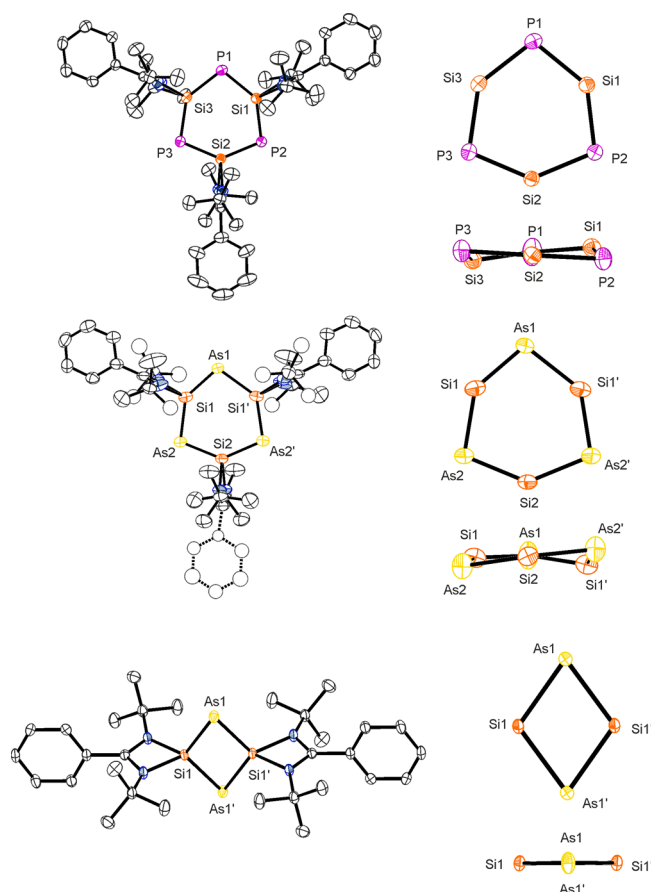


**Figure 1.**  $^{29}\text{Si}\{^1\text{H}\}$  (left),  $^{31}\text{P}$  (middle), and enlarged  $^{31}\text{P}$  (right) NMR spectrum of **1a** in  $\text{C}_6\text{D}_6$ . Experimental (up) and simulated (down) data are displayed.

membered ring compound **2a** ( $-166$  ppm). However, this value is in good agreement with the calculated one of  $-219.6$  ppm, which is also true for all other experimentally found chemical shifts reported in the following.<sup>18</sup> The higher order spectrum of the  $^{29}\text{Si}$  satellites was simulated resulting in  $^1J_{\text{PSi}}$  coupling constants of 119.0 and 117.3 Hz, respectively, and a  $^3J_{\text{PSi}}$  coupling constant of 7.0 Hz.

The higher order  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of **1a** displays a pseudo doublet-of-doublet at  $+70.6$  ppm (Figure 1). Compared to **2a**, it is shifted downfield by about 45 ppm. The arsenic ring compounds **1b** and **2b** could also be isolated from the reaction mixture. The found  $^{29}\text{Si}$  chemical shift of the singlets at  $+70.4$  ppm for **1b** and at  $+3.1$  ppm for **2b** are in agreement with the calculated values, and, like the phosphorus analogues, the  $^{29}\text{Si}$  chemical shift of the four-membered ring is high field shifted, compared to **1b**. Furthermore, the molecular ion peaks of **1a**, **1b**, and **2b**, respectively, were detected by mass spectrometry at  $m/z = 870.4$ ,  $m/z = 1002.0$ , and  $m/z = 668.3$ , respectively.

The molecular structures of **1a** and **1b** were confirmed by single crystal X-ray diffraction analysis (Figure 2).<sup>18</sup> The central structural motif for both compounds is a nearly planar six-membered ring of alternating pnictogen and silicon atoms. The  $\text{E}_3\text{Si}_3$  ( $\text{E} = \text{P}, \text{As}$ ) rings are slightly twisted due to the presence of the ligands. Additionally, the hexagon of the pnictogen and silicon atoms possesses a visible angular distortion. In **1a**, the averaged angle at the phosphorus atoms ( $103.4^\circ$ ) is more acute, while the one at the silicon atoms ( $135.2^\circ$ ) is more obtuse as compared to the angle in an undistorted ideal hexagon ( $120^\circ$ ) like benzene. A similar situation is found for **1b**, the averaged angles at the arsenic and silicon atoms are shrunken ( $101.9^\circ$  for

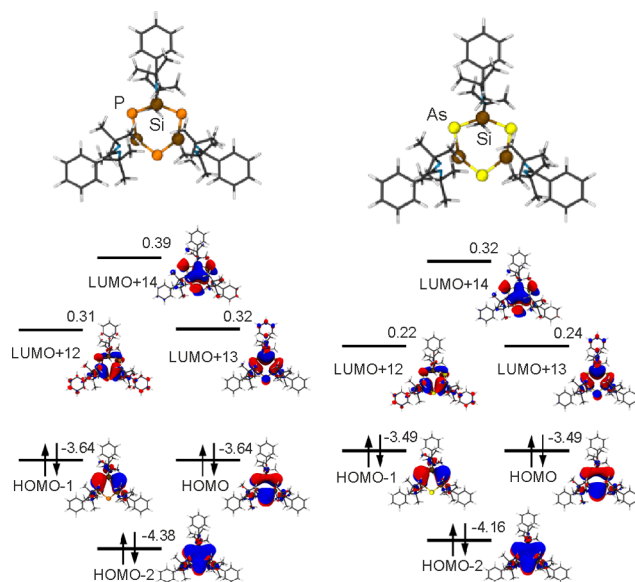


**Figure 2.** Molecular structure of  $[(\text{PhC}(\text{NtBu})_2)_3\text{Si}_3\text{P}_3]$  (**1a**, top),  $[(\text{PhC}(\text{NtBu})_2)_3\text{Si}_3\text{As}_3]$  (**1b**, middle), and  $[(\text{PhC}(\text{NtBu})_2)_2\text{Si}_2\text{As}_2]$  (**2b**, bottom) in the solid-state. Hydrogen atoms are omitted for reasons of clarity; the ellipsoids are at the 50% probability level. In the case of disorder, only the main part is depicted. On the right side the top- and side-view of the central units are depicted. Selected bond lengths [ $\text{\AA}$ ] and angles [ $^\circ$ ] for **1a**: P1–Si3 2.1512(12), P1–Si1 2.1603(13), P2–Si2 2.1514(12), P2–Si1 2.1608(13), P3–Si3 2.1549(12), P3–Si2 2.1588(12), Si3–P1–Si1 102.68(5), Si2–P2–Si1 103.53(5), Si3–P3–Si2 103.92(5), P1–Si1–P2 135.31(5), P2–Si2–P3 134.68(5), P1–Si3–P3 135.62(6); **1b**: As1–Si1 2.157(3), As1–Si1' 2.367(3), As2–Si2 2.2606(6), As2–Si1 2.2630(10), Si1–As1–Si1' 101.21(5), Si2–As2–Si1 102.72(4), As1–Si1–As2 139.31(7), As2–Si2–As2' 135.20(6); **2b**: As1–Si1 2.2782(6), As1–Si1' 2.2844(6), Si1–As1–Si1' 71.39(2), As1–Si1–As1' 108.61(2).

As) and widened ( $134.6^\circ$  for Si), respectively, as compared to the interior angle of a regular hexagon. However, these observations are in agreement with the different orbital hybridization between phosphorus and arsenic, respectively, and silicon as shown by the results of natural bond orbital analysis NBO.<sup>18</sup> Regarding the distances in **1a**, the phosphorus–silicon bond lengths vary slightly between 2.1530(13)–2.1589(12)  $\text{\AA}$  and 2.1512(12)–2.1608(13)  $\text{\AA}$ , respectively, for the two independent molecules and are in-between a single bond (2.24–2.27  $\text{\AA}$ ) and a double bond distance (2.06–2.09  $\text{\AA}$ ).<sup>19</sup> They are slightly shortened compared to the bond lengths in the four-membered  $\text{P}_2\text{Si}_2$  ring in **2a**.<sup>17</sup> For the arsenic analogue **1b**, the As–Si bond lengths (2.1573(3)–2.367(3)  $\text{\AA}$ ) are also in-between a single and a double bond length.<sup>19</sup> All these features are in good agreement with the presence of an aromatic ring system. In contrast to the reported aromatic species  $(\text{REE}'\text{R}')_3$  ( $\text{E} = \text{N}, \text{E}' = \text{Al}, \text{Ga}; \text{E} = \text{P}, \text{E}' = \text{B}, \text{Ga}$ ) and  $(\text{GeNR})_3$ ,<sup>7</sup> the central units of **1a** and **1b** are only

substituted by three amidinato groups bound to the silicon atoms, while no substituents at the pnictogen atoms are present. Additionally, Figure 2 shows the molecular structure of **2b**. The central structural motif of **2b** is a planar  $\text{Si}_2\text{As}_2$  four-membered ring with As–Si bond lengths of 2.2782(6) and 2.2844(6) Å, respectively, which are in-between an As–Si single and an As–Si double bond length. This fact is an indication of a conjugated  $4\pi$ -electron system formally required for antiaromaticity. Compared to a perfect rectangle, the angles at the As ( $71.39(2)^\circ$ ) and Si ( $108.61(2)^\circ$ ) atoms are strongly narrowed and widened, respectively. This was also observed for the isostructural phosphorus analogue.<sup>17</sup> The silicon-substituted amidinato moieties are orthogonally arranged to the central  $\text{As}_2\text{Si}_2$  unit. This structural motif is also found for the recently published germanium phosphorus compound  $[\text{L}^{\text{H}}_2\text{Ge}_2\text{P}_2]$  ( $\text{L}^{\text{H}} = \text{CH}(\text{CHNDipp})_2$ ,  $\text{Dipp} = 2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$ ).<sup>20</sup>

To elucidate the aromatic character of the unprecedented products **1** and **2**, density functional theory (DFT) calculations were applied. For reasons of comparability, the same calculations were performed on the phosphorus analogue **2a**, which are in good agreement with the reported values.<sup>11e,17</sup> Both **1a** and **1b** show  $C_2$  symmetric structures with the central  $\text{E}_3\text{Si}_3$  unit ( $\text{E} = \text{P}, \text{As}$ ), only slightly distorted from planarity with the distortion as measured by the Si–E–Si–E dihedral angles (Table S3) of at most  $7^\circ$ . Calculations employing model compounds  $\text{H}_3\text{Si}_3\text{P}_3$  and  $\text{H}_3\text{Si}_3\text{As}_3$  reveal that this distortion is caused by the presence of bulky  $\text{PhC}(\text{N}t\text{Bu})_2$  ligands. For the phosphorus compound **1a**, a planar structure was predicted by Yang et al.<sup>11e</sup> In our calculations, the fully planar,  $D_{3h}$  symmetric structures of **1** (Table S3) are higher order saddle points with six imaginary frequencies of about  $30\text{ cm}^{-1}$  involving rotations of  $t\text{Bu}$  groups. These structures are only 2.9 and 4.3 kJ/mol less stable than the  $C_2$  symmetric configurations of **1a** and **1b**, respectively. In the case of **2**,  $D_2$  symmetric structures with planar configurations of the central  $\text{E}_2\text{Si}_2$  unit were found (Table S4). A planar  $\text{P}_2\text{Si}_2$  unit in **2a** showing almost identical structure parameters had already been reported earlier.<sup>17</sup> Table S5 shows the calculated NICS(0) and NICS(1) values for **1** and **2** along with a comparison to the corresponding values in  $\text{H}_3\text{Si}_3\text{E}_3$ ,  $\text{H}_2\text{Si}_2\text{E}_2$ , and benzene. The values for the phosphorus compounds are similar to the reported ones.<sup>11e,17</sup> For **1a** and **1b**, the NICS values are lower than for benzene, indicating a weak aromatic character of the central E–Si units, and they change only slightly, when  $\text{PhC}(\text{N}t\text{Bu})_2$  ligands are replaced by H atoms. In agreement with a previous report,<sup>11e</sup> we find that the negative NICS values for the four-membered rings of **2a** and **2b** change sign when  $\text{PhC}(\text{N}t\text{Bu})_2$  ligands are replaced by H atoms. This points to strong shielding effects of the ligands and indicates a weak antiaromatic character of the  $\text{Si}_2\text{E}_2$  unit. The aromatic character of the central  $\text{E}_3\text{Si}_3$  unit ( $\text{E} = \text{P}, \text{As}$ ) is further confirmed by the inspection of the molecular  $\pi$  orbitals of **1a** and **1b** shown in Figure 3. The shape and distribution of the orbitals are virtually identical for both title compounds. They consist of three occupied and three virtual  $\pi$  orbitals with shapes similar to benzene. In occupied orbitals, the contribution of  $p_z(\text{E})$  is smaller than that of the  $p_z(\text{Si})$ . This situation is reversed for unoccupied orbitals. The HOMO–LUMO gap is 3.95 and 3.71 eV (314 and 334 nm) for **1a** and **1b**, respectively. Calculations for benzene at the same level of theory yield a HOMO–LUMO gap of 5.12 eV (242 nm). The energy gap for **1a** is by 1.44 eV smaller than the one reported by Yang et al.<sup>11e</sup> using a hybrid exchange–correlation functional. This is owed to the well-known tendency toward underestimation of band gaps by GGA functionals.<sup>21</sup> However, our value for the HOMO–



**Figure 3.** Molecular  $\pi$  orbitals of  $[(\text{PhC}(\text{N}t\text{Bu})_2)_3\text{Si}_3\text{P}_3]$  (**1a**, left) and  $[(\text{PhC}(\text{N}t\text{Bu})_2)_3\text{Si}_3\text{As}_3]$  (**1b**, right). Energy values are in eV.

LUMO gap of **1a** is in very good agreement with the value obtained from the UV/vis spectrum (332 nm). Additionally, the compounds **1** and **2** show virtually the same Si–E ( $\text{E} = \text{P}, \text{As}$ ) bond configurations as indicated by the WBI and NBO (Table S7 and Table S8). In both central  $\text{E}_3\text{Si}_3$  and  $\text{E}_2\text{Si}_2$  units, significant differences between the s- and p-contributions to the  $\sigma(\text{Si}-\text{E})$  NBOs were found for Si and E. Similarly, the total WBI calculated for Si is significantly higher than those of P and As, indicating different hybridization states of Si and E. The conjugated  $\pi$ -electron system along with a weak aromatic and antiaromatic character of the central  $\text{E}_3\text{Si}_3$  and  $\text{E}_2\text{Si}_2$  units, respectively, is clearly confirmed by similarities of the WBI and NBO occupations of  $\sigma$ ,  $\pi$ , and  $\pi^*$  orbitals with comparable values calculated for the benzene molecule. Further confirmation of the aromatic character of the  $\text{E}_3\text{Si}_3$  unit is provided by the aromatic stabilization energy (ASE) evaluated as the energy change of the homodesmotic reaction shown in Figure S14. The calculated ASE is 59.2 kJ/mol for  $\text{Si}_3\text{P}_3$  and 54.0 kJ/mol for  $\text{Si}_3\text{As}_3$ . By comparison, the ASE of benzene evaluated using the same setup is 93.5 kJ/mol, which is in excellent agreement with the experimental value of  $89.0 \pm 3.8$  inferred from experiment.<sup>22</sup>

In summary, we have shown a simple synthetic route for the preparation of unprecedented silicon–phosphorus and silicon–arsenic benzene-like and cyclobutadiene-like molecules possessing less bulky substituents. All compounds were comprehensively characterized by nuclear magnetic resonance spectroscopy, mass spectrometry, and single crystal X-ray diffraction analysis. The pnictogen–silicon analogues of benzene possess an only slightly distorted six-membered  $\text{Si}_3\text{E}_3$  ring system with pnictogen–silicon bond lengths in-between a single and a double bond as expected for conjugated aromatic ring systems. Computational studies verify an aromatic character of the title compounds. For the cyclobutadiene derivatives, a very weak antiaromatic character is found, in agreement with previous computational studies. Together with the all-pnictogen analogue of  $\text{Cp}^-$ ,  $\text{P}_2\text{N}_3^-$ ,<sup>14</sup> the novel silicon–pnictogen congeners of benzene  $[(\text{PhC}(\text{N}t\text{Bu})_2)_3\text{Si}_3\text{E}_3]$  ( $\text{E} = \text{P}, \text{As}$ ) give an insight into the chemistry of inorganic aromatic systems and aromaticity in



general, 150 years after Kekulé's first report on aromatic compounds.<sup>1b</sup>

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b07389.

Experimental section, crystallographic and computational details, and spectra (PDF)

Compound 1a (CIF)

Compound 1a (PDF)

Compound 1b (CIF)

Compound 1b (PDF)

Compound 2b (CIF)

Compound 2b (PDF)

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### Notes

The authors declare no competing financial interest.

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