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Planar lithium silolide: aromaticity, with significant contribution of non-classical resonance structures†

Csaba Fekete,[ab] Ilona Kovács,*[a] László Nyulászi *[ab] and Tamás Holczbauer[c]

The first planar lithium silolide characterized by X-ray crystallography is reported. The structural data, NMR and DFT results reveal high aromatic character, with the unusual dominance of non-classical resonance structures.

The cyclopentadienide ion is a textbook example for a planar aromatic compound alongside benzene.[1a] The replacement of a carbon atom by silicon results in the silacyclopentadienyl (silolide) anion,[1b–f] for which the planarity and the apparently related aromaticity are far from being trivial. There are only two single crystal X-ray structures available for silolide anions. One is for the 1-trimethylsilyl-tetramethyl-derivative,[2a] and the second for a benzanulated silolide.[2b] Silicon is pyramidal in both cases. Clearly, silyl anions are highly pyramidal,[3a] likewise the isoelectronic phosphanes.[3b] Since all known phospholes are also non-planar,[4] the structural similarity for the isoelectronic silolide anion is also expected. Computational studies have also predicted that silolide is pyramidal;[5] however, even with the non-planar silicone a moderate aromaticity was reported for the parent compound,[5a] furthermore the presence of the countercation has a flattening effect on silicon.[5] A noteworthy feature of the calculated planar silolide structure was the equalization of the C–C distances, the Cβ–Cβ′ bond being slightly (by 0.008 Å) shorter than Cα–Cβ.[5a] Accordingly, for the planar silolide the "**b**" resonance structure had larger (30%) weight than the classical "**a**" (17%) according to a natural resonance theory (NRT) study (Fig. 1).[5d]

For silolide dianions, where the pyramidalization problem does not occur (*cf.* with thiophene), all experimental[2a,6a–d] and computational[6e,f] evidence indicate significant aromaticity. Considerable aromaticity was, however, concluded in a single case, namely for 1-*t*Bu-tetraphenylsilolide on the basis of NMR evidence.[7] The significant shift (downfield in ^{29}Si and upfield in ^{13}C NMR) with respect to the neutral precursor disilane was attributed to cyclic delocalization.[7] Unfortunately, for this particular silolide, no X-ray structure could be obtained,[7] thus it remains unclear whether or not the NMR observations are indeed related to planarization. For the structurally characterized pyramidal 1-trimethylsilyl-tetramethylsilolide, both ^{29}Si and ^{13}C NMR results are consistent with the negative charge localized on the silicon.[2a]

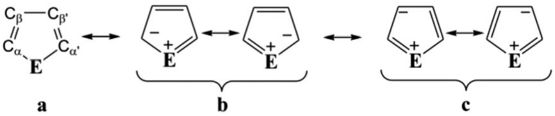

Fig. 1 Resonance structures for planar heteroaromatic five membered rings, with different heteroelements. E can be S, PR, or SiR^- (R:H, alkyl, aryl, *etc.*). The numbering of the ring atoms is shown on resonance structure **a**.

The situation is further complicated by the fact that for 1-Me-tetraphenylsilolide the dimerization of the anion was reported, yielding tricyclic systems with a central 1,3-disilacyclobutane ring.[8] While no planar silolide has been reported to date, Sekiguchi's 1,2,3-trisilacyclopentadienide and 1,2-disila-3-germacyclopentadienide anions have been shown to exhibit planar X-ray structures with equalized bond lengths, and with ^{29}Si NMR data indicating aromaticity.[9] Furthermore, nearly planar transition metal (Zr, Hf or Ru) complexed silolides were also synthetized.[10]

In a computational search for planar silolide anions we revealed that due to the charge stabilizing effect, π–acceptor SiH_3 groups at the α carbons enhance the planarity and aromaticity of the naked silolide ring considerably.[5d] This effect was already noted on the related phosphole with SiH_3[11] and BH_2[12] substituents, and the charge stabilizing effect was also shown in the case of the silyl-substituted stannole dianion.[13] Furthermore, the α-silyl groups enhanced the relative weight of the **b** type resonance structure.[5d] η^5-Coordination of the Li

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[a] *Department of Inorganic and Analytical Chemistry, Budapest University of Technology and Economics, Szt. Gellért tér 4, Budapest, H-1111, Hungary. E-mail: ikovacs@mail.bme.hu*
[b] *MTA-BME Computation Driven Chemistry Research Group, Hungary. E-mail: nyulaszi@mail.bme.hu*
[c] *Institute of Organic Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, POB. 206, H-1519 Budapest, Hungary*

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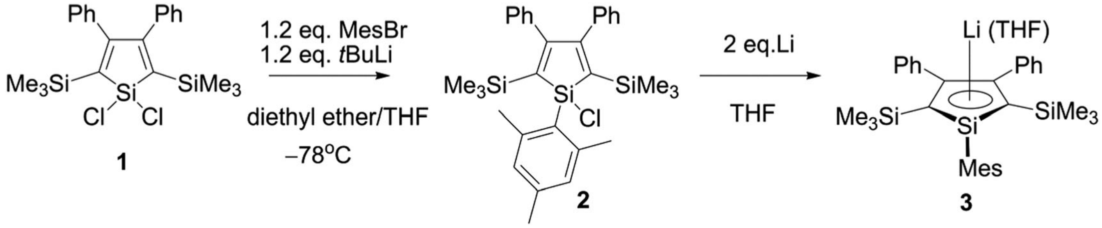


Scheme 1 Preparation of **3**.

(with some covalent character) had a further flattening effect on the pyramidal silicon, and for the 1H- and the 1-Me compounds the planar structure was by only 1 kcal mol^{-1} less stable than the non-planar minimum.[5d] Accordingly, it can be expected that with this substituent pattern the planarization of the parent ring system might be possible. Herein we describe the successful synthesis and structural characterization of the first planar 2,5-trimethylsilyl substituted silolide anion, which exhibits high aromaticity and dominating non-classical resonance structures with $\mathrm{Si{=}C}$ character.

Our initial synthetic efforts to characterize or isolate the silyl-substituted silolide anion from 1-methyl- or 1-*tert*-butylsilol remained unsuccessful, yielding a mixture of different products according to NMR measurements, which was attributed to the simultaneous presence of the monomeric anion, its dimer[8] and also to the subsequently formed decomposition products. In order to suppress the dimerization reaction, we decided to choose a more bulky substituent at the ring Si atom. We selected the bulky[14] mesityl substituent, with some reported[14b] flattening effect on phosphole. Our preliminary DFT calculations showed that with this substituent pattern the η^5-lithiosilole contact ion pair is indeed effectively planar (see below) and accordingly, we targeted the synthesis of this compound.

To obtain the aimed silolide, the previously synthesized[6f] 1,1-dichlorosilole (**1**) was used as the starting material (Scheme 1). Treating **1** with 1.2 equivalents of mesityl lithium (prepared from mesityl bromide and *t*BuLi) resulted in **2** which was isolated by distillation at reduced pressure, followed by recrystallization from hexane. The THF solution of **2** was then reacted with **2** equivalents of lithium at RT for one day. Crystals suitable for X-ray diffraction were obtained in a concentrated diethyl ether solution of **3** at −30 °C. The yellow air-sensitive crystal of **3** contains two independent molecules in the asymmetric unit. In both structures the five-membered rings are effectively planar, the sums of the angles around the silicon are 358.4° and 356.8° respectively, and also the skeletal distances of the five-membered rings are similar. The main difference between the two structures is the position of the mesityl group, with 88.6° dihedral angle to the silolide ring (Fig. 2); however, for the other molecule the corresponding dihedral angle is 59.0° (Fig. S30–S31 in ESI†). Optimizations at M06-2X/6-31+G(2d,p) from both geometries resulted in a near perpendicular mesityl arrangement. The geometries obtained (Table S1 in ESI†) are in good agreement with the X-ray data.

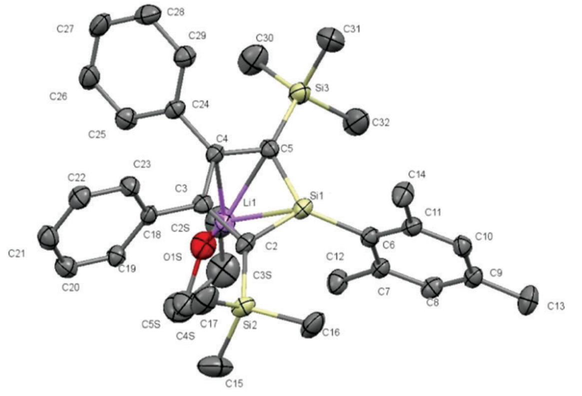


Fig. 2 Molecular structure of **3** in the solid state. Ellipsoids are set to 50% probability; hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Si(1)–C(5) 1.796(5); Si(1)–C(2) 1.784(5); Si(1)–Li(1) 2.517(8); C(2)–C(3) 1.455(6); C(3)–C(4) 1.417(6); C(4)–C(5) 1.451(6).

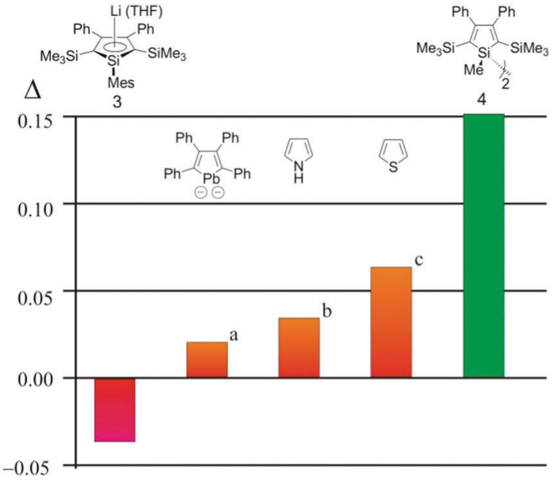


Fig. 3 Difference of the CαCβ and CβCβ′ distances (Δ in Å) in five membered heterocycles. Aromatic compounds with equalized bond lengths[1a] are shown in red, the non-aromatic silole (**4**) with green. (a ref. 18; b ref. 19; c ref. 20).

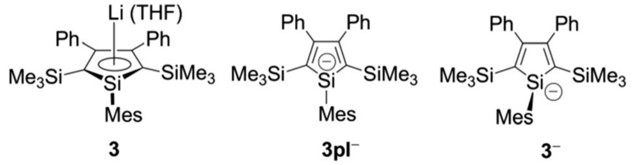
While in 1,1-bissilol **4** (Fig. 3) the average Si–C distance is 1.885 Å[15] (typical single bond range is 1.87–1.89 Å),[16a] the ring Si–C bonds in **3** (1.796(5) and 1.784(5) Å) are significantly shorter exhibiting considerable double bond ($\mathrm{Si{=}C}$ typically 1.70–1.76 Å)[16b] character, despite the usual lengthening of the bonds in anionic compounds. The enhanced $\mathrm{Si{=}C}$ character is not surprising, and C-silyl-substitution at the $\mathrm{Si{=}C}$ bond is known to have a stabilizing effect.[17] Altogether, the Si lone pair is heavily involved in the π-system. The C–C distances (Fig. 2) are considerably equalized, a sign of aromaticity, and their difference is slightly larger than those in silolide,[6a,d] germolide[2a] or stannolide[18] dianions and is comparable to that in pyrrole,[19] being smaller than that for thiophene[20] (Fig. 3). Most importantly, the Cβ–Cβ′ distance is by 0.036(8) Å shorter than the average of Cα–Cβ and Cα′–Cβ′ (in agreement with the computed results – see ESI†). This bond length distribution is unusual among the five-membered heteroaromatic systems and is in accordance with the increased contribution of the non-classical resonance structures **b** and **c** (Fig. 1) dominating over the classical **a** as evidenced from NBO calculations (**a**: 15%, **b**: 37% and **c**: 47%). Also Bader analysis shows increased Si–Cα and Cβ–Cβ′ ellipticities (Fig. S22 in ESI†). In five-membered heterocycles the aromaticity (and the stabilization) stems from the dative interaction between the heteroatom lone pair and the π* LUMO of the Cβ–Cβ′ bonding butadiene moiety.[14b] Thus, for **3** the HOMO (see Fig. S24 in ESI†) get stabilized and has Cβ–Cβ′ bonding, shortening this distance. For the other orbital pair, the LUMO is destabilized. Since the electropositive silicon is a strong π-donor,[5d] the aromaticity is high, and the butadiene unit becomes negatively charged with dominating "**b**" and "**c**" structures.

^{29}Si NMR measurements showed a highly downfield chemical shift for the ring silicon (+65.7 ppm) compared to the starting 1-mesityl-1-chlorosilole (**2**) (+17.0 ppm), while the ring carbons possess highly upfield chemical shifts (see Table 1), in accordance with the increased delocalization as was discussed above. It is noteworthy that silenes with an isolated Si═C double bond have also ^{29}Si chemical shifts in the same region,[21] supporting also the increased contribution of the "**b**" and "**c**" resonance structures.

Further evidence for the aromaticity was obtained from the ^{1}H NMR behavior of 3,4-phenyl rings, which – from apparent steric reasons – occupy an out-of-plane position (see Fig. 2), making the *ortho* hydrogens susceptible to the effect of a possible ring current. Comparing **3** to **2**, the chemical shifts of the *meta* and *para* hydrogens remain nearly unchanged, and the signal of the *ortho* hydrogens appears downfield (in **2**: *o*-H: 6.83–6.96 ppm; *m*- and *p*-H: 7.03–7.12 ppm; in **3**: *o*-H: 7.32 ppm, *m*-H: 7.08 ppm, *p*-H: 6.96 ppm). The ^{7}Li NMR chemical shift of **3** in a C_6D_6 solution (−5.6 ppm) is in the region of the η^5-coordinated aromatic half sandwich contact ion pairs,[22] again in accordance with the aromatic ring current. The calculated ^{29}Si and ^{13}C NMR chemical shifts of **3** (using the calculated signals of the trimethylsilyl group as an internal reference – see Tables S2 and S3 in ESI†) were in a good agreement with those of the measured ones, supporting also the above assignment.

Adding one equivalent of 12-crown-4 to the C_6D_6 solution of **3** resulted in a brownish-red precipitate, which became soluble upon THF addition. The ^{7}Li NMR showed only one signal at −0.2 ppm, and this was assigned to the 12-crown-4 coordinated Li ion,[23] resulting in a solvent separated silolide anion and a 12-crown-4 coordinated Li ion. The ^{29}Si NMR signal is then shifted somewhat upfield (by 5.7 ppm) to +60.0 ppm. To evaluate the origin of this effect, we calculated the ^{29}Si NMR shifts of **3** (+66.6 ppm in excellent agreement with the experimental value), and also that of the naked silolide anion **3**$^-$ (+37.3 ppm). Since the calculated structure of **3**$^-$ (Fig. 4) turned out to be non-planar, we considered the effect of the planarization on the ^{29}Si NMR shift, calculating also the planar naked anion **3pl**$^-$ (+73.8 ppm). This was a first order saddle point at B3LYP/6-31+G(d,2p) by only 1.3 kcal mol^{-1} higher in energy than **3**$^-$. At the M06-2X/6-31+G(d,2p) level (note that this functional accounts for some dispersion interaction apparently present in **3**$^-$), the planar **3pl**$^-$ structure is also a minimum, but only with 0.3 kcal mol^{-1} above the other non-planar form, indicating a highly flexible structure. Since the decomplexation of **3** to **3**$^-$ resulted in a small upfield shift, we have to consider that in the solution phase the structure of **3**$^-$ is slightly non-planar, and the two (energetically identical) enantiomeric forms are in a dynamic equilibrium on the rather flat potential energy surface centered about the planar **3pl**$^-$. The comparison of the NMR results for the calculated **3**$^-$ and **3pl**$^-$ shows that the observed values are much closer to those calculated for the planar structure, indicating a small contribution of the non-planar structure(s) in the solution phase for the naked anion. Accordingly, while **3** (in C_6D_6 solution) has magnetically different *ortho* methyl and *meta* hydrogens on the mesityl ring and therefore split ^{13}C and ^{1}H signals, in the crown-ether containing solution these signals merged together. Further evidence for the significant contribution of the planar structure comes from the ^{13}C NMR spectra. The chemical shifts for the 12-crown-4 containing solution of **3** show a better agreement with the calculated chemical shifts of **3pl**$^-$, compared with the non-planar **3**$^-$ (Tables S2 and S3 in ESI†). Especially informative is the HMBC assigned high field shifted α-carbon signal (Fig. S13 in ESI†), which is very sensitive to the planarity about Si, in an apparent relationship with the increasing energy of the LUMO (see above), decreasing the paramagnetic contribution. A similar effect was shown on flattened heavy ruthenocenes.[14d]

The calculated aromaticity indices (Bird indices and NICS (1) values in Table 2) indicate that all molecules possess high aromatic character, even without the Li$^+$ countercation, which again was shown to have a beneficial effect on the planarity and aromaticity as was previously reported.[5c,d] It is noteworthy that in the naked silolide monoanion (**3**$^-$) with the slightly pyramidal arrangement around the silicon, the aromaticity indices do not show significant decrease.



3 **3pl**$^-$ **3**$^-$

Fig. 4 Structures of **3**, **3pl**$^-$, and **3**$^-$.

Table 1 Ring ^{29}Si and ^{13}C NMR chemical shifts (δ), and their changes Δ($\delta_3 - \delta_2$) upon formation of **3** from the precursor **2** [in ppm]

Atom	2[a]	3[b]	Δ($\delta_3 - \delta_2$)
δSi_{ring}	17.0	65.7	+48.7
$\delta C_{2,5}$	143.9	103.1	−40.8
$\delta C_{3,4}$	168.1	135.0	−33.1

[a] In $CDCl_3$ external reference TMS. [b] In C_6D_6 external reference TMS.

Table 2 M06-2X/6-31+G(d,2p) Bird index (I_5) and NICS (1) values of **3**, **3**$^-$, and **3pl**$^-$

	I_5[a]	ASS[b]	NICS (1)[c] [ppm]
3	90	356.9	−8.2
3$^-$	65	324.0	−6.7/−7.7
3pl$^-$	81	360.0	−6.8

[a] For details, see S24 in the ESI. [b] Angle sum at Si [°]. [c] B3LYP/pcS-2//M06-2X/6-31+G(d,2p).

In summary, we have reported the first structurally characterized planar aromatic lithium silolide (**3**) with α-trimethylsilyl substituents and a bulky mesityl group at Si. Structural parameters indicate significant bond length equalization. This results in a high Bird index, indicating aromaticity, together with the calculated NICS (1) value and all experimental NMR evidence. The experimentally obtained Cβ–Cβ′ distance is significantly shorter than Cα–Cβ, showing the dominance of the non-classical "**b**" and "**c**" type resonance structures, with significant Si═C double bond character. Theoretical (NRT and Bader-analysis) studies as well as ^{29}Si NMR results corroborate these finding. Further studies on the effect of aromatic stabilization and the reactivity of this and other planar silolides are in progress.

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Conflicts of interest

There are no conflicts to declare.

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