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Interconnected Bis-Silylenes: A New Dimension in Organosilicon Chemistry

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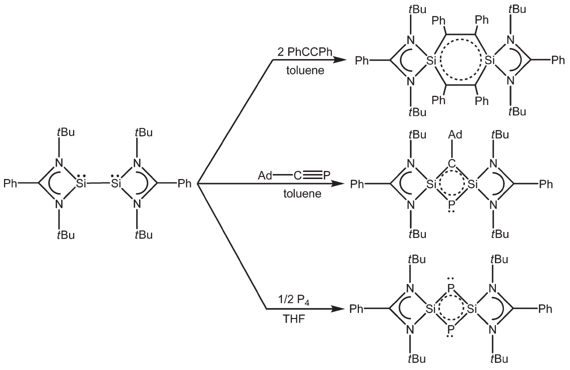
CONSPECTUS



The past two decades have brought remarkable advances in organosilicon chemistry with the isolation of stable silylenes, persila-allene, and disilynes. The extension of this list gives an impression that it will continue to flourish. The judicious employment of sterically appropriate ligands has enabled the synthesis and isolation of compounds with low-valent silicon. Recently, for example, interconnected bis-silylenes were isolated where the two Si atoms are connected by a σ-bond and each Si atom is possessing a lone pair of electrons. The formal oxidation state of each Si atom in the interconnected bis-silylene is $+1$, so bis-silylenes can be considered as the valence isomers of disilynes. In this Account, we describe the synthesis of interconnected bis-silylenes and assess their potential as a new building block in organosilicon chemistry.

In 2009, we reported the isolation of a bis-silylene ($(PhC(N\textit{t}Bu)_2)_2Si_2$) stabilized by a sterically bulky benz-amidinato ligand with *t*Bu substituents on the nitrogen atoms. Prior to our work, Robinson and co-workers described the synthesis of a N-heterocyclic carbene stabilized bis-silylene. In following years, just two more interconnected bis-silylenes have been reported. Density functional theory calculations to establish the geometric and electronic structures of the reported bis-silylenes have shown that the Wiberg bond index (WBI) for all the reported bis-silylenes is ~ 1.

The synthesis of stable $(PhC(N\textit{t}Bu)_2)_2Si_2$ prompted explorations of its reactivity. An important facet of silylene chemistry involves oxidative addition at the Si(II) center with unsaturated substrates, a reaction also available for bis-silylenes. Due to the three reaction sites (two lone pairs of electrons and a labile Si(I)–Si(I) single bond) in the interconnected bis-silylenes, we expect novel product formation. A labile Si–Si bond facilitates the reactions of $(PhC(N\textit{t}Bu)_2)_2Si_2$ with diphenyl alkyne or adamantyl phosphaalkyne which afforded 1,4- disilabenzene and 1,3-disilacarbaphosphide (CSi_2P) derivatives, respectively. The former is a noteworthy addition to the silicon analogues of benzene, and the latter serves as a heavy cyclobutadiene. With white phosphorus, a cyclic Si_2P_2 derivative, an analogue of cyclobutadiene was obtained. The most predominant structural feature of these heavy cyclobutadienes is the presence of two-coordinate P atoms.

1. Introduction

The synthesis of the first disilene[1] ($Mes_2Si{=}SiMes_2$ (Mes = 2,4,6-$Me_3C_6H_2$)) (**1**) and silene[2] $(Me_3Si)_2Si{=}C(OSiMe_3)$-2-Ad (Ad = adamantyl) (**2**) in 1981 heralded the burgeoning chemistry of the multiply bonded compounds with low-valent silicon atoms. The realization that steric protection could be employed to overcome the kinetic instability facilitated the progress of chemistry with low-valent heavier group 14 elements.[3–9] Few of the noteworthy achievements include the isolation of silicon analogues of allene (**3**),[3] 1,3-butadienes (**4**–**6**),[4] and alkynes (**7**–**10**) (Chart 1).[5]

Another important advancement realized in organosilicon chemistry is the synthesis of silylenes,[6] which are the heavier analogues of carbenes. Ever since the first isolation of N-heterocyclic silylene **11** (Chart 1) by West and co-workers[7] in 1994, they have constituted an active area of research with increasing focus toward compounds with two such low-valent silicon centers in a single molecule termed

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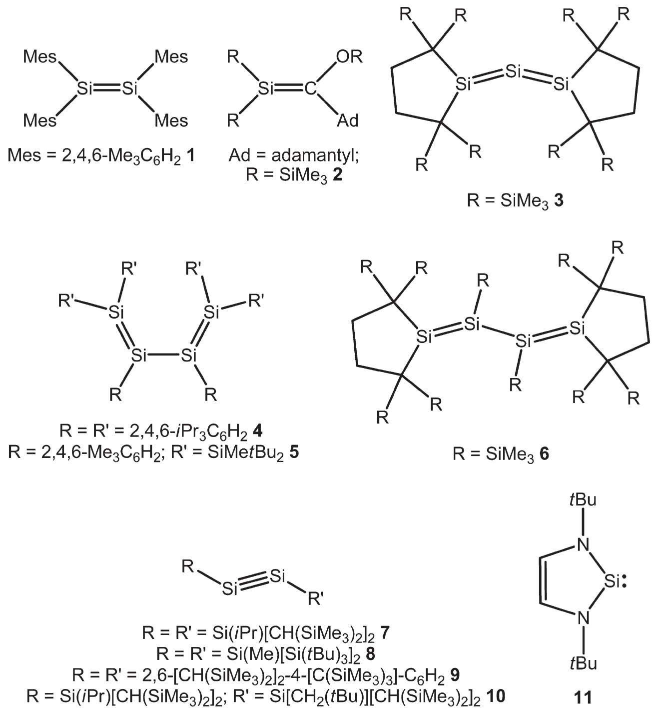
CHART 1. Structures of Compounds **1**−**11**



generally as "*bis-silylenes*". Two types of bis-silylenes can be envisaged: (a) "*interconnected bis-silylenes*" where the two low-valent silicon atoms are adjacent to each other and connected by a single bond (type **A**) and (b) "*spacer-separated bis-silylenes*" in which the low-valent silicon atoms are separated by a suitable spacer (type **B**) (Chart 2).

The low-valent silicon centers in the type **A** and **B** bis-silylenes possess formally +1 and +2 oxidation states, respectively. Moreover, type **A** bis-silylene is the valence isomer of disilyne. Though the idea to isolate bis-silylenes began from the time when the first N-heterocyclic silylene was synthesized, it took almost a decade of efforts to realize it. The first spacer-separated bis-silylene **12** and inter-connected bis-silylene **15** (Chart 3) were reported by the groups of Lappert[8a] and Robinson[9] in 2005 and 2008, respectively. Despite this initial success, only few new bis-silylenes of either type have been isolated to date.[8−12] Two noteworthy synthetic developments related to spacer separated bis-silylenes are the isolation of **13** and **14**. In **13**, the two Si(II) centers are supported by benz-amidinato ligands and separated by an oxygen atom.[8b] Compound **14** is the first example of a bis-silylene having two-coordinate silicon atoms which are separated by nitrogen atoms.[8c] The bulky N-aryl substituents ($Ar^1 = 2,6\text{-}Ar_2C_6H_3$; $Ar = 2,6\text{-}iPr_2C_6H_3$) protect the lone pair of electrons on silicon. With respect to the interconnected bis-silylenes, only three more are known including bis-silylene **16** (Chart 3) reported by our group in 2009.[10] The other two examples **17** and **18** (Chart 3) were synthesized in 2011 by Jones et al.[11a] and Baceiredo et al.,[12] respectively. These limited developments reveal that the chemistry of bis-silylenes is still in an early stage of development. Therefore, we have launched a research program during the last 3 years focusing on the features of the interconnected bis-silylene **16**. This Account will preview our findings on the synthetic, spectroscopic, structural, and reactivity features of bis-silylene **16**. Apart from that, the essential aspects of the bis-silylenes **15**, **17**, and **18** will also be highlighted.

CHART 2. Pictorial Representation of Interconnected and Spacer-Separated Bis-Silylenes

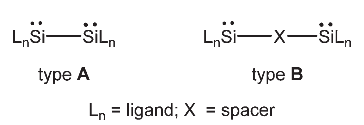
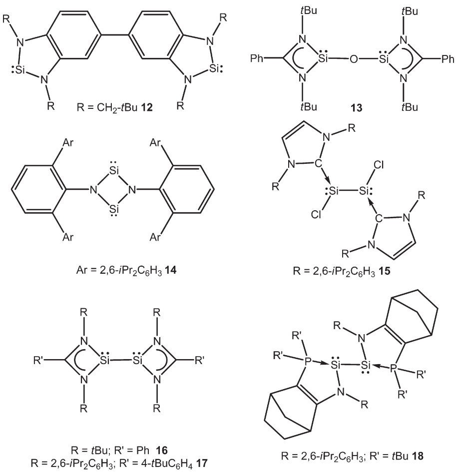


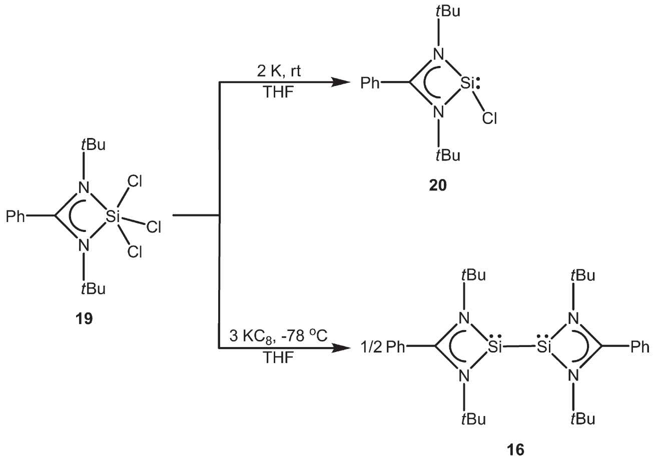
CHART 3. Spacer-Separated **12**−**14** and Interconnected **15**−**18** Bis-Silylenes



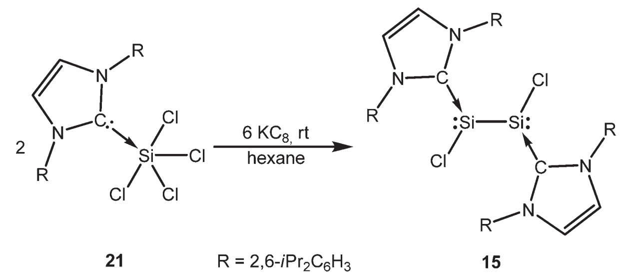
2. Synthetic, Spectroscopic, and Structural Aspects of Interconnected Bis-Silylenes 15−18

The synthesis of the bis-silylene **16** (as well as of compounds **15**, **17**, and **18**) follows the traditional synthetic route (dehalogenation of halosilanes with a suitable reducing agent) to isolate a silylene. The reduction of trichlorosilane complex **19** with 2 equiv of finely divided potassium at room temperature gave the first functionalized silylene complex **20**[13] and with 3 equiv of potassium graphite (KC_8) at −78 °C afforded the bis-silylene complex **16** as an orange-red solid (Scheme 1).[10] This is similar to the synthetic methodology adopted for the isolation of the bis-silylene **15** stabilized by a N-heterocyclic carbene,

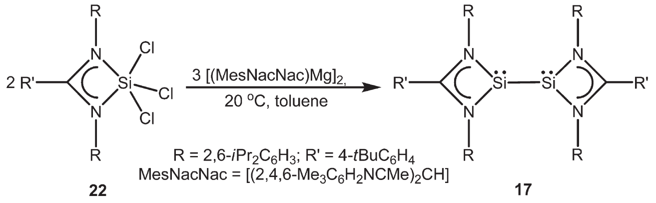
SCHEME 1. Synthesis of First Functionalized Silylene **20** and Base-Stabilized Bis-Silylene **16**



SCHEME 2. Synthesis of Bis-Silylene **15** with N-Heterocyclic Carbene Donors



SCHEME 3. Synthesis of Bis-Silylene **17**

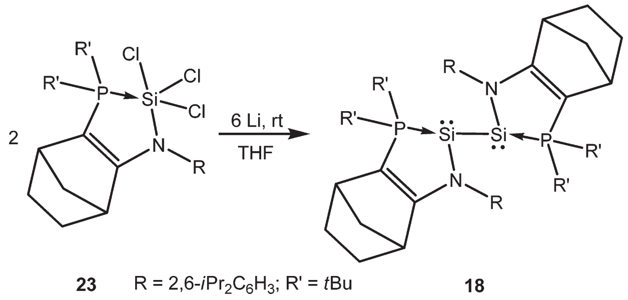


1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene. Accordingly, when the N-heterocyclic carbene → $SiCl_4$ adduct **21** was reduced with 3 equiv of KC_8 in *n*-hexane, compound **15** was obtained as a major product (Scheme 2).[9]

In contrast, for the synthesis of bis-silylenes **17** and **18**, the reducing agents are different from that of KC_8. **17** was obtained by reacting the trichlorosilane complex **22** with a Mg(I) dimer, $[(MesNacNac)Mg]_2$ (MesNacNac = $[(2,4,6\text{-}Me_3C_6H_2NCMe)_2CH]$)[11b] in a ratio of 1:1.5 at 20 °C (Scheme 3).

The reduction of the trichlorosilane derivative **23** with 3 equiv of lithium at room temperature in tetrahydrofuran (THF) afforded the bis-silylene **18** stabilized by the trivalent phosphorus atoms of the phophine moieties. (Scheme 4).[12]

SCHEME 4. Synthesis of Bis-Silylene **18** with Phosphorus Donors



The color, yield, and ^{29}Si NMR resonances of compounds **15**−**18** are summarized in Table 1. It reveals that the yield of bis-silylene **17** is higher compared to those of other bis-silylenes. This is presumably due to the usage of a homogeneous reducing agent such as the Mg(I) dimer.[11b] All the bis-silylenes **15**−**18** were characterized in the solid-state by single crystal X-ray diffraction studies, and their molecular structure shows the presence of a silicon−silicon single bond (Table 1).

The Si−Si bond lengths in the bis-silylenes **17** [2.489(2) Å] and **16** (Figure 1) [2.413(2) Å] are substantially longer than the sum of the Si−Si covalent radii [2.34 Å][14] and the Si−Si single bond length found in α-silicon [2.36 Å].[15] The Si−Si bond lengths in **18** [2.331(1) Å] and **15** [2.393(3) Å] are slightly shorter and longer than that seen in α-silicon,[15] respectively. Nevertheless, the Si−Si bond lengths in **15**−**18** are significantly longer than those found in their valence isomers, **7** [2.0622(9) Å], **8** [2.108(5) Å], and **10** [2.0569(12) Å].[5] Each of the low-valent silicon atoms in the bis-silylenes **15**−**18** exhibits a distorted tetrahedral geometry, if the lone pair of electrons is taken into consideration.

The bis-silylenes **15-17** display a *gauche*-bent conformation, akin to the analogous bis-germylene $[PhC(NtBu)_2Ge]_2$.[16] In contrast, the bis-silylene **18** adopts a *cis*-bent geometry with a N−Si−Si−N torsion angle of 4.9°.[12]

In order to probe the nature of the silicon−silicon bond in the bis-silylenes **15**−**18**, density functional theory calculations were carried out. The natural bonding orbital (NBO) analysis on **16** shows that the two low-valent silicon centers are connected by a σ-bond with high *p*-character (*s*, 18.27%; *p*, 81.73%) and are characterized by the Wiberg bond index (WBI) of 0.9768. Interestingly, the nonbonded electron density on each of the silicon centers in **16** is found to reside in an orbital with 65% *s*-character.[17] Thus, the lack of directionality associated with the *s*-orbitals and the geometrical constrain around the low-valent silicon centers of **16** force the lone pair of electrons on the Si(I) centers to remain

TABLE 1. Essential Synthetic and Structural Features Regarding the Interconnected Bis-Silylenes **15**–**18**

cmpd	**15**	**16**	**17**	**18**
yield (%)	6.1	5.1	91	13.4
color	dark-red	orange-red	deep-blue	red
^{29}Si NMR resonance (C_6D_6, ppm)	38.4	76.3	96.9	−18.5
Si–Si bond length (Å)	2.393(3)	2.413(2)	2.489(2)	2.331(1)
geometry	*gauche*	*gauche*	*gauche*	*cis*
dihedral angle (deg)	133.5	96.4	103.9	4.9

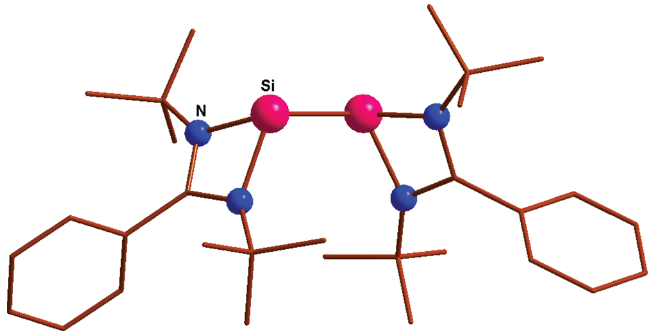


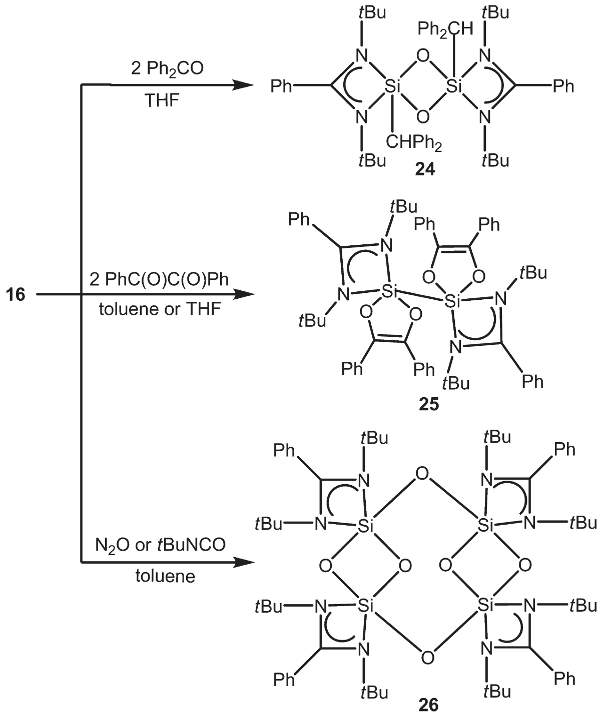
FIGURE 1. Molecular structure of the bis-silylene **16**.

preferentially nonbonded. Moreover, to unequivocally prove the absence of any π-bonding in the Si(I)–Si(I) bond of **16**, chemical shift anisotropy (CSA) value (which is an indicator for the presence of π-bond) was calculated. A CSA value of 80.5 ppm for **16** against the CSA value of 362.6 ppm for $H_2Si{=}SiH_2$ beyond doubt implies that the Si(I)–Si(I) bond in **16** does not have a multiple-bond character.[17] These features are similar to those of bis-silylene **15**. The NBO analysis on **15** showed that the Si–Si bond has a predominate *p*-character (*s*, 12.1% *p*, 87.4%) with a WBI of 0.94.[9] The nonbonding electron density on each of the low-valent silicon centers also resides in an orbital with maximum *s*-character (*s*, 68.3%; *p*, 31.6%). Similarly, the NBO analysis on **17** showed that the Si–Si bond has 88.7% *p*-character whereas the lone pair orbitals of the low-valent silicon centers contain 72.6% *s*-character.[11a] In contrast to bis-silylenes **15**–**17**, the WBI of **18** is found to be 1.262 and is greater than that obtained for the bis-silylenes **15**–**17**. This disparity stems from the enhanced negative hyper-conjugative π-interaction between the two silicon centers (n_{Si}–σ^*_{Si}),[12] rather than between phosphorus and silicon centers (n_{Si}–σ^*_{P}).

3. Reactivity Studies on the Interconnected Bis-Silylene 16

The successful synthesis of the interconnected bis-silylenes **15**–**18** has created a unique opportunity to explore their chemistry, and thereby has opened up a new field in organosilicon chemistry. At the outset, it is important to understand what kind of new reactivity can be expected from these compounds versus simple silylenes, and from where will it emanate. To answer this, let us recollect the typical reactivity of the N-hetrocyclic silylene such as insertion into polar bonds, oxidative addition with reagents such as S, Se, and Te, and coordination with Lewis acids which is based on the lone pair of electrons on the low-valent silicon center. As the interconnected bis-silylenes have two such stereochemically active lone pairs of electrons, it is natural to expect that they will also display similar reactivity. Nevertheless, based on their electronic structure (discussed vide supra), it can be foreseen that novel reactivity can arise from the labile σ-bond that connects the two Si(I) centers. It was this reaction site that has motivated us to pursue the reactivity of interconnected bis-silylenes with the hope to develop novel synthetic routes to elusive target molecules in organosilicon chemistry. Accordingly, we have studied the reaction of **16** with benzophenone, benzil, nitrogen dioxide, *tert*-butyl

SCHEME 5. Reaction of **16** with Ketones, N_2O, and *t*BuNCO



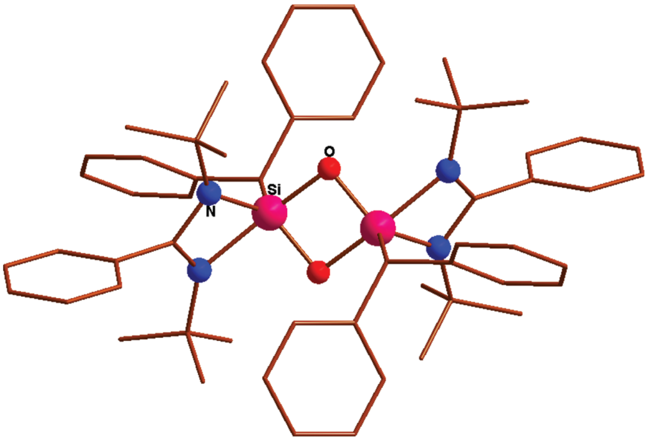


FIGURE 2. Molecular structure of compound **24**.

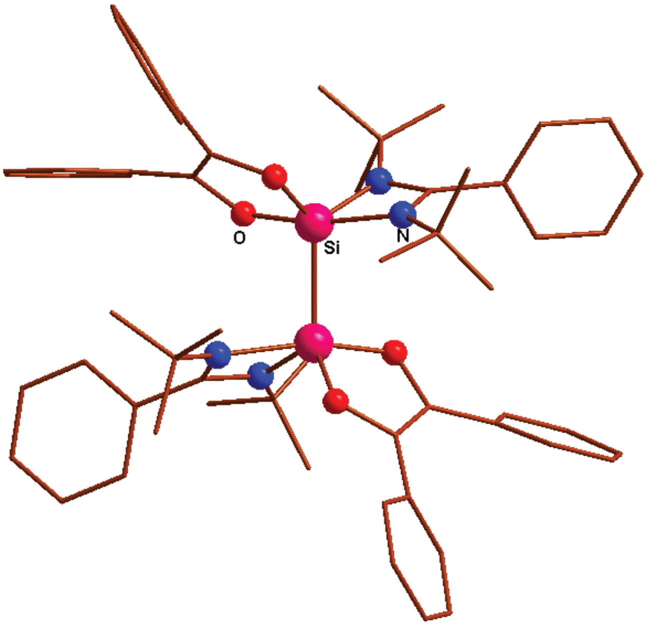


FIGURE 3. Molecular structure of compound **25**.

isocyanate, cyclooctatetraene, diphenylalkyne, phosphaalkyne, and white phosphorus. The reactivity of **16** with bromine, selenium, and phenylalkyne is also included for discussion. Surprisingly, the reactivity of the other bis-silylenes **15**, **17**, and **18** is not well established except for the reaction of **18** with CO_2.

a. Reaction with Oxygen Containing Reagents. In this section, the reaction of bis-silylenes **16** with benzophenone, benzil, N_2O, *tert*-butyl isocyanate will be briefly discussed. A common feature seen in all these reactions is the loss of both the lone pair of electrons and Si(I)–Si(I) σ-bond barring the benzil reaction where the Si(I)–Si(I) single bond is retained. The reaction of **16** with 2 equiv of benzophenone abstracted

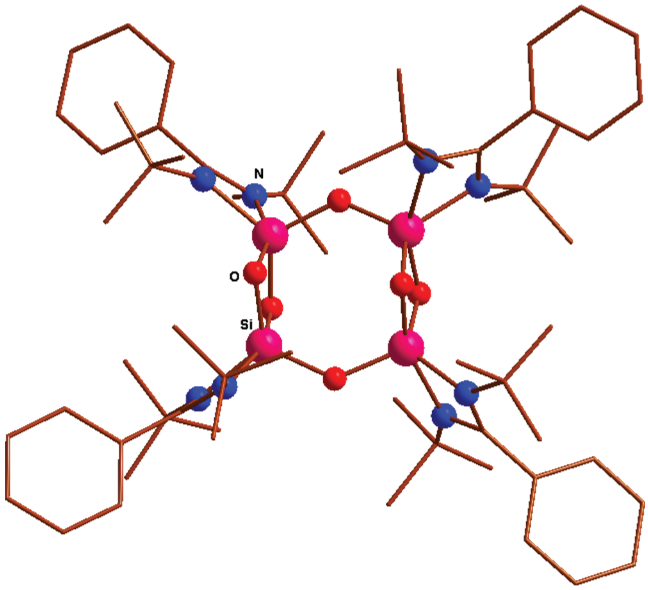
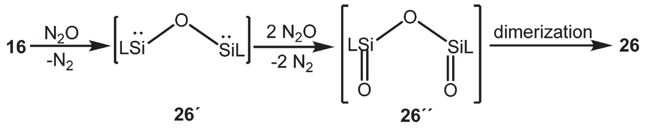


FIGURE 4. Molecular structure of compound **26**.

SCHEME 6. Tentative Mechanism for the Formation of **26**, L=PhC(N*t*Bu)$_2$



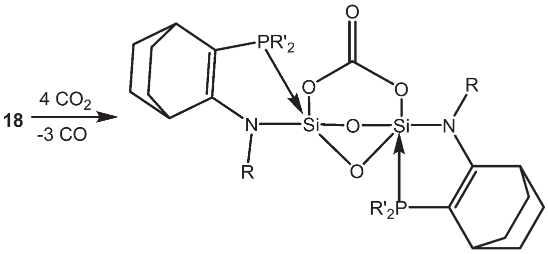
two protons from the THF molecules to afford compound **24** with a Si_2O_2 four-membered ring (Scheme 5).[18]

When the same reaction was carried out in toluene, it did not furnish **24** and led to a mixture of insoluble products, which could not be identified. Treatment of **16** with 1, 2-diketone in toluene or THF afforded compound **25** that contains two SiO_2C_2 rings connected by a Si–Si single bond (Scheme 5).[19] The molecular structure of compounds **24** and **25** (Figures 2 and 3) clearly shows the planar Si_2O_2 and SiO_2C_2 rings. All the silicon atoms in **24** and **25** are pentacoordinated and possess a trigonal bipyramidal geometry around them.[18,19] The Si–Si bond length [2.362(7) Å] in **25** is less than that in **16** [2.413(2) Å] and is probably due to the elimination of the lone-pair lone-pair repulsion.

The reaction of **16** (Scheme 5) with either N_2O or *t*BuNCO yielded compound **26** with two four-membered Si_2O_2 rings linked together by two oxygen atoms (Figure 4).[18] A proposed mechanism suggests that an intermediate (26′′) is formed (Scheme 5). It dimerizes to **26** due to the high polarity of the Si═O double bond.[20]

Baceiredo and co-workers reacted **18** with 4 equiv of CO_2 to afford a carboxylato bis-silicate complex **27** with the

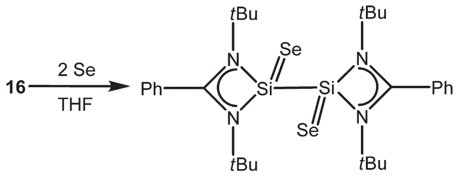
SCHEME 7. Reaction of **18** with CO_2



R = 2,6-$iPr_2C_6H_3$; R' = *t*Bu

27

SCHEME 8. Reaction of **16** with Selenium



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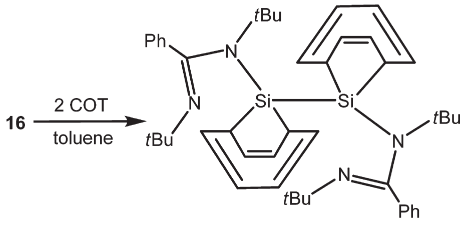
SCHEME 9. Reaction of **16** with COT



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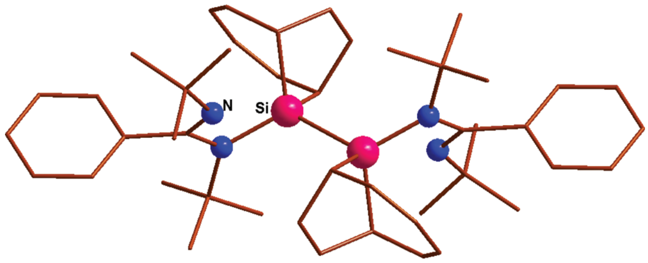
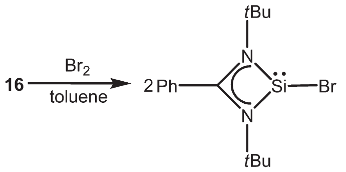


FIGURE 5. Molecular structure of compound **29**.

SCHEME 10. Reaction of **16** with Bromine



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elimination of three CO molecules (Scheme 7).[12] The molecular structure of **27** reveals the presence of a central tricyclic structure and a distorted trigonal bipyramidal geometry around the silicon centers.[12]

b. Reaction with Selenium. To investigate the reactions of **16** with heavier chalcogens, it was treated with sulfur and selenium. Upon analysis of the product obtained from the reaction of **16** with sulfur, a most abundant peak was observed at *m/z* 324 (that corresponds to half of LSi(S)−S−Si(S)L) in EI-MS, and indicates the formation of the expected product, but authentication by structural studies is still pending. However, the reaction of **16** with Se in THF afforded the di(silaneselone) **28** which was structurally characterized (Scheme 8).[21]

The ^{77}Se NMR spectrum of **28** shows a singlet at $\delta = -322.9$ ppm. The average Si═Se bond length [2.134 Å] in **28** is comparable to that seen in base stabilized silaneselones[22a,b] but longer than that in dialkylsilaneselone [2.0963(5) Å].[22c] The Si−Si bond length [2.384(3) Å] in **28** is slightly shorter than that in **16** [2.413(2) Å].

c. Reaction with COT. A reaction of **16** with COT (cyclooctatetraene) in toluene at room temperature (Scheme 9) resulted in compound **29** as a pale-yellow colored solid.[23]

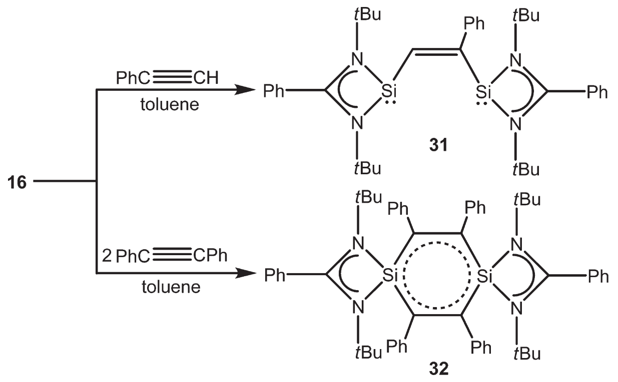
Interestingly, in this reaction, the Si−Si single bond is preserved but one of two Si−N bonds in each ligand was cleaved (Figure 5). The Si−Si bond [2.415(7)] Å in **29** is almost the same in length with that present in **16** [2.413(2) Å].

d. Reaction with Bromine. Treatment of **16** with bromine in toluene for 2 h readily accessed the amidinatosilylene monobromide **30** as the sole product (Scheme 10) by a facile Si(I)−Si(I) bond cleavage and without oxidative addition at the low-valent silicon centers.[17] The ^{29}Si NMR resonance of **30** ($\delta = 18.6$ ppm) is very close to that observed for chloride analogue **20** ($\delta = 14.6$ ppm).[13]

The structural studies on **30** show that its Si−Br bond length [2.326(3) Å] is very similar to the length of Si(II)−Br bonds [2.361(8) and 2.338(8) Å] present in $LSiBr_2$ (L = 1,3-bis-(2,6-$iPr_2C_6H_3$)imidazol-2-ylidene).[24]

e. Reaction with Alkynes. Silicon analogues of benzene are sparsely known,[25a−e] and there is no stable example of a 1,4-disilabenzene.[25f,g] Also, there is no report of a conversion of interconnected bis-silylene to a spacer-separated one. These two lacunas have been resolved in the reaction of **16** with alkynes. The reaction of **16** with phenylalkyne (in a 1:1 ratio) and diphenylalkyne (in a 1:2 ratio) in toluene led to the formation of *cis*-1,2-disilylenylethene **31**[26] and 1,4-disilabenzene **32** (Scheme 11).[27] The ^{29}Si

SCHEME 11. Reaction of **16** with Phenyl and Diphenylalkyne



NMR spectrum of **31** displayed two singlet resonances ($\delta = 15.1$ and 29.5 ppm) for its nonequivalent silicon centers, whereas, in the case of **32** the ^{29}Si NMR studies show that the silicon centers are equivalent ($\delta = -18.05$ ppm). It must be mentioned that the possibility of **32** being a 1,4-disilacyclohexadiene diradical has been ruled out by performing EPR studies at elevated temperatures.

Further structural confirmation of compounds **31** and **32** (Figure 6) comes from the single crystal X-ray diffraction studies. Both the silicon atoms in **31** adopt a distorted trigonal pyramidal geometry and show the expected Si–C bond length [1.905(2) and 1.927(2) Å].[18,19,28] In the structure of **32**, a distorted tetrahedral geometry prevails around the silicon atoms although the 1,4-disilabenzene ring is almost planar, and this is an important factor that contributes to the enhanced stability of **32**. The average Si–C bond length [1.800(3) Å] in **32**[27] is shorter than the usual Si–C single bond length[18,19,28] (1.86–1.93 Å), longer than that of the Si=C double bond (1.764 Å) present in **2**,[2] and matches excellently with that of Sekiguchi's 1,2-disilabenzene derivative (1.80 and 1.79 Å).[25c] To supplement the EPR studies performed to disprove a 1,4-disilacyclohexadiene diradical structure of **32**, theoretical calculations were also carried out. The results showed (a) a doubly occupied HOMO and an unoccupied LUMO, respectively, and (b) an energy difference of 10.61 kcal/mol between the singlet and triplet states of **32**.[27] These findings affirm and augment the experimental studies. To investigate the aromaticity in **32,** NICS at 1 Å above the plane of 1,4-disilabenzene ring was calculated (−3.64) and demonstrates that the molecule is slightly aromatic.

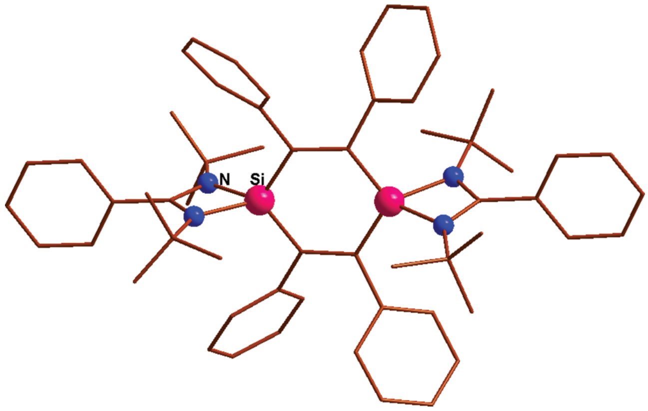


FIGURE 6. Molecular structure of compound **32**.

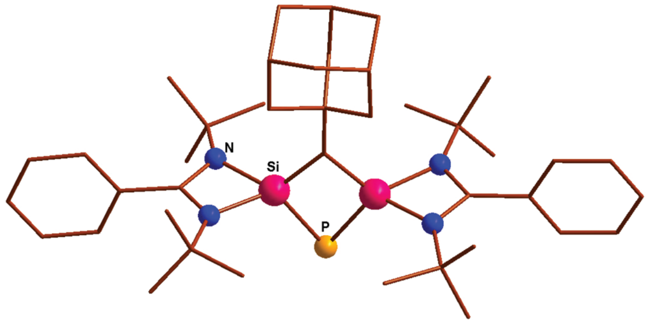


FIGURE 7. Molecular structure of compound **33**.

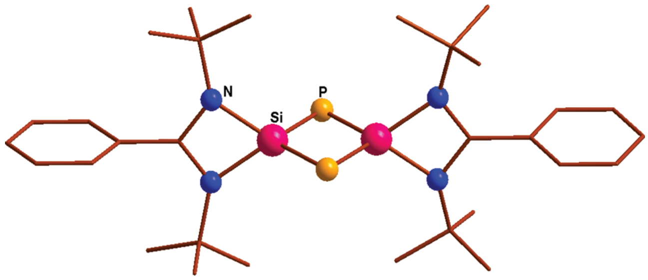
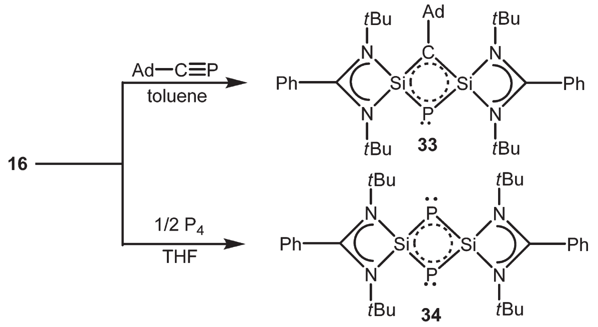


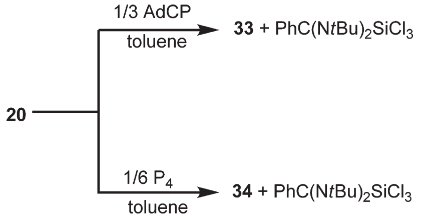
FIGURE 8. Molecular structure of compound **34**.

f. Reaction with Phosphaalkyne and Elemental Phosphorus. Like benzene being a characteristic example of aromatic compounds, cyclobutadiene is a classic antiaromatic compound. Though few examples (vide supra) of stable silabenzenes[25a–e] are reported, there was no example of a silacyclobutadiene until 2010 perhaps due to the instability associated with antiaromaticity. Bertrand proposed that the degree of aromaticity or antiaromaticity will decrease if elements of the third or higher rows replace one or more carbon atom(s) of the carbacycles and thereby make the system relatively unstable or stable, respectively.[29] The validity of this statement with respect to aromaticity can be immediately seen from the aforementioned example of 1,4-disilabenzene **32** [whose NICS(1) is −3.64 against the benzene NICS(1) of −10].[27] Simultaneously, it hinted at the possibility to isolate stable cyclobutadiene analogues by having three or four heavier main-group elements in the ring. In fact, the

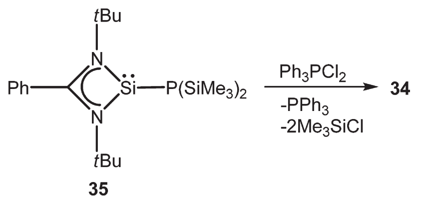
SCHEME 12. Reaction of **16** with Adamantyl Phosphaalkyne and Phosphorus



SCHEME 13. Synthesis of Compounds **33** and **34** from **20**



SCHEME 14. Synthesis of Compound **34** from **35**



realization of this concept came from the reaction of **16** with adamantyl phosphaalkyne and elemental phosphorus. Addition of a toluene solution of adamantyl phosphaalkyne to a toluene solution of **16** at −30 °C in 1:1 molar ratio resulted in **33** whereas the reaction of **16** and white P_4 in 2:1 molar ratio afforded **34** (Scheme 12).[30] Both **33** and **34** are structurally characterized and can be considered as heavier cyclobutadienes. Interestingly, both these compounds **33** and **34** can be accessed from **20** (Scheme 13) and the latter can also be derived from $PhC(NtBu)_2SiP(SiMe_3)_2$ (**35**) (Scheme 14).[31]

The core of **33** (Figure 7) and **34** (Figure 8) has a CSi_2P and Si_2P_2 four-membered ring, respectively. The average Si−C bond length in **33** (1.7821 Å) and the average Si−P bond length (2.17 Å) in **33** and **34** are in agreement with expected values.

The predominant structural feature of these two compounds is the presence of naked phosphorus atoms. To prove their two-coordination, solid-state NMR spectroscopic studies were carried out and the cross-polarization (CP) build-up patterns were analyzed. This study gave the clear corroboration for the presence of naked phosphorus atom(s) in **33** and **34** by showing that none of the phosphorus atoms is protonated.[30] Theoretical investigations were also performed to derive the additional bonding features of compounds **33** and **34**. The NBO analysis of **33** showed the presence of the following natural charges on the atoms of its CSi_2P ring: −0.75 (for P), +1.56 (for each Si), and −1.44 (for C). For the atoms in the Si_2P_2 ring of **34**, the values are +1.12 (for each Si) and −0.69 (for each P). These values clearly demonstrate the zwitterionic character of the CSi_2P and Si_2P_2 rings of **33** and **34**. The electron localizability index (ELI-d) for **33** and **34** reveals that there are two lone pairs of electrons present at the phosphorus atom(s). The NICS(1) values [for **33** (−4.17) and **34** (−2.56)] also clearly show that the four-membered rings of **33** and **34** with the naked phosphorus atom(s) have no antiaromatic character.

4. Conclusion and Future Scope

The successful synthesis of interconnected bis-silylenes **15**−**18** is viewed as an important advancement in organosilicon chemistry. Though different reducing agents are used, they are all isolated by reducing the corresponding halosilane complexes. Structural and theoretical studies have shown the presence of a labile Si(I)−Si(I) σ-bond in the bis-silylenes **15**−**18** with predominant *p*-character. The successful syntheses of bis-silylenes **15**−**18** will inspire further research for the synthesis of additional examples of interconnected bis-silylenes with other stabilizing ligands. In this regard, the isolation of an interconnected bis-silylene stabilized only by kinetic means will bring further richness and diversity.

The synthesis of the bis-silylenes has made it possible to investigate their novel reactivity that arises from the presence of a Si(I)−Si(I) single bond. However, the reactivity studies remain limited with the exception of bis-silylene **16**. It is expected that this situation will ease out with the synthetic strategies that offer the bis-silylenes at higher yields as in the case of **17**. The investigations by our group and others into **16** have resulted in various striking findings. Few of those include the isolation of a new class of silicon−oxygen ring containing compounds such as **24**−**26** in the reaction with oxygen containing reagents, the first stable 1,4-disilabenze **32** obtained from the diphenyl alkyne reaction, and the hitherto unknown heavier analogues **33** and **34** of cyclobutadiene realized in the reactions with phosphaalkyne and phosphorus. Motivated by these results, we have intensified our efforts on **16** with the ambition to obtain silicon analogue of 1,2-diketone. The unusual compounds like 1,4-disilabenzene (**32**) that accentuates the importance of the interconnected bis-silylene **16** are now ready for reactivity studies. The heavier cyclobutadiene analogues **33** and **34** are also prepared for the reactivity studies.

With respect to antiaromatic compounds of silicon, two remarkable discoveries were brought to the fore very recently. Tamao et al. described the isolation of a planar rhombic charge separated tetrasilacyclobutadiene stabilized by the appropriately designed bulky 1,1,7,7-tetraethyl-3,3,5,5-tetramethyl-*s*-hydrindacen-4-yl (EMind) group.[32] Parallel to this, we have isolated a new type of spacer arranged bis-silylene $(ArNSi)_2$ ($Ar^1 = 2,6\text{-}Ar_2C_6H_3$; $Ar = 2,6\text{-}i\text{Pr}_2C_6H_3$) (**14**) containing a Si_2N_2 four-membered ring.[8c] It is also important to mention that the synthesis of stable silylene with nitrogen substitution remained a challenge for the organosilicon chemist and bis(dialkylamino) silylenes (alkyl = *i*Pr, TMS) reported so far are either stable at low temperature[33] or in solution.[34] In this respect, **14** is the first example of a bis-silylene with two-coordinate Si(II) atoms. Note that no carbon analogue to **14** with two-coordinate carbon atoms bridged by NR groups has been isolated so far.

The reactivity study with transition metal complexes is still at its infancy and requires new input. This may produce a variety of silylidyne complexes which could emerge as important organometallic compounds, in light of the highlighted value of transition metal alkylidyne complexes in organometallic and organic chemistry by Fischer and Schrock in their Nobel Prize lectures.[35]

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BIOGRAPHICAL INFORMATION

Sakya S. Sen was born in Kolkata, India in 1983. He obtained his M.Sc. degree from IIT Kharagpur in 2006. Then he joined the University of Göttingen as a doctoral student under the supervision of Prof. Dr. Herbert W. Roesky and received the title Dr. rer. nat. in 2010. During his tenure as a doctoral student, he worked on the preparation and reaction of compounds with heavier group 14 elements in low oxidation states with an emphasis on silicon. Dr. Sen has coauthored more than 20 research publications in leading scientific journals.

Shabana Khan was born in Faizabad, India in 1979. She received her Ph.D. in 2008 from IIT Delhi. In 2009, Dr. Khan took up a fellowship of Deutscher Akademischer Austausch Dienst in the group of Prof. Dr. Herbert W. Roesky, and since then she has been working as a postdoctoral fellow in the chemistry of compounds with low valent silicon atoms.

Selvarajan Nagendran was born in Virudhunagar, India in 1974. He obtained his Ph.D. degree from IIT Kanpur. Currently, he is working as an assistant professor in the Department of Chemistry, IIT-Delhi, India, and is interested in the chemistry of compounds with low valent group 13 and 14 elements. He has coauthored over 30 research papers in peer reviewed international journals.

Herbert W. Roesky was born in 1935 in Laukischken. He obtained his doctorate from University of Göttingen. After working at Du Pont in the United States, he returned to Göttingen and finished his habilitation. Then he became a professor at the Johann-Wolfgang-Goethe-Universität, Frankfurt am Main in 1971. He moved to University of Göttingen in 1980 and was the director of Institute for Inorganic Chemistry until 2004. He is primarily known for his pioneering work on fluorides of both transition and main group elements. His current research interest is focused on the synthesis and reactivity of compounds with heavier group 13 and 14 elements in low oxidation states. More than 1200 peer-reviewed papers, articles, patents, and books record his research activity in the areas of Inorganic Chemistry and Material sciences.

FOOTNOTES

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REFERENCES

1 West, R.; Fink, M. J.; Michl, J. Tetramesityldisilene, a stable compound containing a silicon-silicon double bond. *Science* **1981**, *214*, 1343–1344.

2 Brook, A. G.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Kallury, R. K. A solid silaethene: isolation and characterization. *Chem. Commun.* **1981**, 191–192.

3 Ishida, S.; Iwamoto, T.; Kira, M. A stable silicon-based allene analogue with a formally sp-hybridized silicon atom. *Nature* **2003**, *421*, 725–727.

4 (a) Weidenbruch, M.; Willms, S.; Saak, W.; Henkel, G. Hexaaryltetrasilabuta-1,3-diene: a molecule with conjugated $Si{=}Si$ double bonds. *Angew. Chem., Int. Ed.* **1997**, *36*, 2503–2504. (b) Ichinohe, M.; Sanuki, K.; Inoue, S.; Sekiguchi, A. Disilenyllithium from tetrasila-1,3-butadiene: a silicon analogue of a vinyllithium. *Organometallics* **2004**, *23*, 3088–3090.

5 (a) Sekiguchi, A.; Kinjo, R.; Ichinohe, M. A stable compound containing a silicon-silicon triple bond. *Science* **2004**, *305*, 1755–1757. (b) Wiberg, N.; Vasisht, S. K.; Fischer, G.; Mayer, P. A relatively stable disilyne $RSi{\equiv}SiR$ ($R = SiMe(Si\mathit{t}Bu_3)_2$). *Z. Anorg. Allg. Chem.* **2004**, *630*, 1823–1828. (c) Sasamori, T.; Hironaka, K.; Sugiyama, Y.; Takagi, N.; Nagase, S.; Hosoi, Y.; Furukawa, Y.; Tokitoh, N. Synthesis and reactions of a stable 1,2-diaryl-1,2-dibromodisilene: a precursor for substituted disilenes and a 1,2-diaryldisilyne. *J. Am. Chem. Soc.* **2008**, *130*, 13856–13857. (d) Murata, Y.; Ichinohe, M.; Sekiguchi, A. Unsymmetrically substituted disilyne $Dsi_2\mathit{i}PrSi\text{-}Si{\equiv}Si\text{-}SiNpDsi_2$ ($Np = CH_2\mathit{t}Bu$): synthesis and characterization. *J. Am. Chem. Soc.* **2010**, *132*, 16768–16770.

6 (a) Haaf, M.; Schmedake, T. A.; West, R. Stable silylenes. *Acc. Chem. Res.* **2000**, *33*, 704–714. (b) Ottosson, H.; Steel, P. G. Silylenes, silenes, and disilenes: novel silicon-based reagents for organic synthesis? *Chem.—Eur. J.* **2006**, *12*, 1576–1585. (c) Nagendran, S.; Roesky, H. W. The chemistry of aluminum(I), silicon(II), and germanium(II). *Organometallics* **2008**, *27*, 457–492. (d) Mandal, S. K.; Roesky, H. W. Interstellar molecules: guides for new chemistry. *Chem. Commun.* **2010**, *46*, 6016–6041. (e) Asay, M.; Jones, C.; Driess, M. N-Heterocyclic carbene analogues with low-valent group 13 and group 14 elements: syntheses, structures, and reactivities of a new generation of multitalented ligands. *Chem. Rev.* **2011**, *111*, 354–396. (f) Yao, S.; Xiong, Y.; Driess, M. Zwitterionic and

donor-stabilized N-heterocyclic silylenes (NHSis) for metal-free activation of small molecules *Organometallics* **2011**, *30*, 1748–1767.

7 Denk, M.; Lennon, R.; Hayashi, R.; West, R.; Belyakov, A. V.; Verne, H. P.; Haaland, A.; Wagner, M.; Metzler, N. Synthesis and structure of a stable silylene. *J. Am. Chem. Soc.* **1994**, *116*, 2691–2692.

8 (a) Gehrhus, B.; Hitchcock, P. B.; Lappert, M. F. Synthesis of a stable biphenyl-bis(carbene) and -bis(silylene) $[M\{(NCH_2Bu\mathit{t})_2C_6H_3\text{-}3,4\}]_2$ (M = C or Si). *Z. Anorg. Allg. Chem.* **2005**, *631*, 1383–1386. (b) Wang, W.; Inoue, S.; Yao, S.; Driess, M. An isolable bis-silylene oxide ("disilylenoxane") and its metal coordination. *J. Am. Chem. Soc.* **2010**, *132*, 15890–15892. (c) Ghadwal, R. S.; Roesky, H. W.; Pröpper, K.; Dittrich, B.; Klein, S.; Frenking, G. A dimer of silaisonitrile with two-coordinate silicon atoms. *Angew. Chem., Int. Ed.* **2011**, *50*, 5374–5378.

9 Wang, Y.; Xie, Y.; Wei, P.; King, R. B.; Schaefer, H. F., III; Schleyer, P. v. R.; Robinson, G. H. A stable silicon(0) compound with a Si═Si double bond. *Science* **2008**, *321*, 1069–1071.

10 Sen, S. S.; Jana, A.; Roesky, H. W.; Schulzke, C. A remarkable base-stabilized bis(silylene) with a silicon(I)-silicon(I) bond. *Angew. Chem., Int. Ed.* **2009**, *48*, 8536–8538.

11 (a) Jones, C.; Bonyhady, S. J.; Holzmann, N.; Frenking, G.; Stasch, A. Preparation, characterization, and theoretical analysis of group 14 element(I) dimers: a case study of magnesium(I) compounds as reducing agents in inorganic synthesis. *Inorg. Chem.* **2011**, *50*, 12315–12325. (b) Green, S. P.; Jones, C.; Stasch, A. Stable magnesium(I) compounds with Mg-Mg bonds. *Science* **2007**, *318*, 1754–1757.

12 Gau, D.; Rodriguez, R.; Kato, T.; Saffon-Merceron, N.; de Cózar, A.; Cossío, F. P.; Baceiredo, A. Synthesis of a stable disilyne bisphosphine adduct and its non-metal-mediated CO_2 reduction to CO. *Angew. Chem., Int. Ed.* **2011**, *50*, 1092–1096.

13 (a) So, C.-W.; Roesky, H. W.; Magull, J.; Oswald, R. B. Synthesis and characterization of $[PhC(N\mathit{t}Bu)_2]SiCl$: a stable monomeric chlorosilylene. *Angew. Chem., Int. Ed.* **2006**, *45*, 3948–3950. (b) Sen, S. S.; Roesky, H. W.; Stern, D.; Henn, J.; Stalke, D. High yield access to silylene RSiCl ($R{=}PhC(N\mathit{t}Bu)_2$) and its reactivity toward alkyne: synthesis of stable disilacyclobutene. *J. Am. Chem. Soc.* **2010**, *132*, 1123–1126.

14 Corey, J. Y. In *The chemistry of organic silicon compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Vol. 1, Chap. 1.

15 Nesper, R.; Currao, A.; Wengert, S. In *Organosilicon chemistry II: from molecules to materials*; Auner, N., Weis, J., Eds.; VCH: Weinheim, Germany, 1996; p 469.

16 Nagendran, S.; Sen, S. S.; Roesky, H. W.; Koley, D.; Grubmüller, H.; Pal, A.; Herbst-Irmer, R. RGe(I)Ge(I)R compound ($R{=}PhC(N\mathit{t}Bu)_2$) with a Ge−Ge single bond and a comparison with the gauche conformation of hydrazine. *Organometallics* **2008**, *27*, 5459–5463.

17 Yeong, H.-X.; Lau, K.-C.; Xi, H.-W.; Lim, K. H.; So, C.-W. Reactivity of a disilylene $[\{PhC(NBu\mathit{t})_2\}Si]_2$ toward bromine: synthesis and characterization of a stable monomeric bromosilylene. *Inorg. Chem.* **2010**, *49*, 371–373.

18 Sen, S. S.; Tavčar, G.; Roesky, H. W.; Kratzert, D.; Hey, J.; Stalke, D. Synthesis of a stable four-membered Si_2O_2 ring and a dimer with two four-membered Si_2O_2 rings bridged by two oxygen atoms, with five-coordinate silicon atoms in both the ring systems. *Organometallics* **2010**, *29*, 2343–2347.

19 Tavčar, G.; Sen, S. S.; Roesky, H. W.; Hey, J.; Kratzert, D.; Stalke, D. Reaction of a bis-silylene (LSi-SiL, L = $PhC(N\mathit{t}Bu)_2$) and a heteroleptic chloro silylene (LSiCl) with benzil: formation of bis(siladioxolene) and monosiladioxolene analogue with five-coordinate silicon atoms in both ring systems. *Organometallics* **2010**, *29*, 3930–3935.

20 Kimura, M.; Nagase, S. The quest of stable silanones: substituent effects. *Chem. Lett.* **2001**, 1098–1099.

21 Zhang, S.-H.; Yeong, H.-X; So., C.-W. Reactivity of a silylsilylene bearing a functionalized diaminochlorosilyl substituent. *Chem.—Eur. J.* **2011**, *17*, 3490–3499.

22 (a) Yao, S.; Xiong, Y.; Driess, M. N-heterocyclic carbene (NHC)-stabilized silanechalcogenones: NHC→Si(R_2)═E (E═O, S, Se, Te). *Chem.—Eur. J.* **2011**, *17*, 1281–1288. (b) Mitra, A.; Wojcik, J. P.; Lecoanet, D.; Müller, T.; West, R. A bis(silaselenone) with two donor-stabilized Si═Se bonds from an unexpected stereoconvergent hydrolysis of a diselenadisiletane. *Angew. Chem., Int. Ed.* **2009**, *48*, 4069–4072. (c) Iwamoto, T.; Sato, K.; Ishida, S.; Kabuto, C.; Kira, M. Synthesis, properties, and reactions of a series of stable dialkyl-substituted silicon−chalcogen doubly bonded compounds. *J. Am. Chem. Soc.* **2006**, *128*, 16914–16920.

23 Sen, S. S.; Khan, S.; Kratzert, D.; Roesky, H. W.; Stalke, D. Reaction of a base-stabilized bis(silylene) $[PhC(N\mathit{t}Bu)_2Si]_2$ with cyclooctatetraene without cleavage of the Si−Si bond. *Eur. J. Inorg. Chem.* **2011**, 1370–1373.

24 Filippou, A.; Chernov, O.; Schnakenburg, G. $SiBr_2$(Idipp): A stable N-heterocyclic carbene adduct of dibromosilylene. *Angew. Chem., Int. Ed.* **2009**, *48*, 5687–5690.

25 (a) Wakita, K.; Tokitoh, N.; Okazaki, R.; Nagase, S. Synthesis and properties of an overcrowded silabenzene stable at ambient temperature. *Angew. Chem., Int. Ed.* **2000**, *39*, 634–636. (b) Kabe, Y.; Ohkubo, K.; Ishikawa, H.; Ando, W. 1,4-Disila(dewar-benzene) and 1,4-disilabenzene: valence isomerization of bis(alkylsilacyclopropenyl)s. *J. Am. Chem. Soc.* **2000**, *122*, 3775–3776. (c) Kinjo, R.; Ichinohe, M.; Sekiguchi, A.; Takagi, N.; Sumimoto, M.; Nagase, S. Reactivity of a disilyne RSi≡SiR ($R{=}S\mathit{i}Pr[CH(SiMe_3)_2]_2$) toward π-bonds: stereospecific addition and a new route to an isolable 1,2-disilabenzene. *J. Am. Chem. Soc.* **2007**, *129*, 7766–7767. (d) Abersfelder, K.; White, A. J. P.; Rzepa, H. S.; Scheschkewitz, D. A tricyclic aromatic isomer of hexasilabenzene. *Science* **2010**, *327*, 564–566. (e) Abersfelder, K.; White, A. J. P.; Berger, R. J. F.; Rzepa, H. S.; Scheschkewitz, D. A stable derivative of the global minimum on the Si_6H_6 potential energy surface. *Angew. Chem., Int. Ed.* **2011**, *50*, 7936–7939. (f) Rich, J. D.; West, R. Evidence for the intermediacy of hexamethyl-1,4-disilabenzene. *J. Am. Chem. Soc.* **1982**, *104*, 6884–6886. (g) Maier, G.; Schöttler, K.; Reisenauer, H. P. 1,4-Disilabenzol. - Dimethoxysilylen als idealer Synthesebaustein. *Tetrahedron Lett.* **1985**, *26*, 4079–4082.

26 Yeong, H.-X; Xi, H.-W.; Lim, K. H.; So, C.-W. Synthesis and characterization of an amidinate-stabilized cis-1,2-disilylenylethene [cis-LSi{C(Ph)═C(H)} SiL] and a singlet delocalized biradicaloid $[LSi(\mu_2\text{-}C_2Ph_2)_2SiL]$. *Chem.—Eur. J.* **2010**, *16*, 12956–12961.

27 Sen, S. S.; Roesky, H. W.; Meindl, K.; Stern, D.; Henn, J.; Stückl, A. C.; Stalke, D. Synthesis, structure, and theoretical investigation of amidinato supported 1,4-disilabenzene. *Chem. Commun.* **2010**, *46*, 5873–5875.

28 (a) Kaftory, M.; Kapon, M.; Botoshansky, M. In *The chemistry of organic silicon compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, Chapter 5. (b) Ghadwal, R. S.; Sen, S. S.; Roesky, H. W.; Granitzka, M.; Kratzert, D.; Merkel, S.; Stalke, D. Convenient access to monosilicon epoxides with pentacoordinate silicon. *Angew. Chem., Int. Ed.* **2010**, *49*, 3952–3955.

29 Bertrand, G. Ylidic four π electron four-membered λ^5-phosphorus heterocycles: electronical isomers of heterocyclobutadienes. *Angew. Chem., Int. Ed.* **1998**, *37*, 270–281.

30 Sen, S. S.; Khan, S.; Roesky, H. W.; Kratzert, D.; Meindl, K.; Henn, J.; Stalke, D.; Demers, J.-P.; Lange, A. Zwitterionic Si-C-Si-P and Si-P-Si-P four-membered rings with two-coordinate phosphorus atoms. *Angew. Chem., Int. Ed.* **2011**, *50*, 2322–2325.

31 Inoue, S.; Wang, W.; Präsang, C.; Asay, M.; Irran, E.; Driess, M. An ylide-like phosphasilene and striking formation of a 4π-electron, resonance-stabilized 2,4-disila-1,3-diphosphacyclobutadiene. *J. Am. Chem. Soc.* **2011**, *133*, 2868–2871.

32 Suzuki, K.; Matsuo, T.; Hashizume, D.; Fueno, H.; Tanaka, K.; Tamao, K. A planar rhombic charge-separated tetrasilacyclobutadiene. *Science* **2011**, *331*, 1306–1309.

33 Lee, G.-H.; West, R.; Müller, T. Bis[bis(trimethylsilyl)amino]silylene, an unstable divalent silicon compound. *J. Am. Chem. Soc.* **2003**, *125*, 8114–8115.

34 Tsutsui, S.; Sakamoto, K.; Kira, M. Bis(diisopropylamino)silylene and its dimer. *J. Am. Chem. Soc.* **1998**, *120*, 9955–9956.

35 (a) Fischer, E. O. Auf dem Weg zu Carben- und Carbin-Komplexen. *Angew. Chem.* **1974**, *86*, 651–682. (b) Schrock, R. R. Multiple metal−carbon bonds for catalytic metathesis reactions. *Angew. Chem., Int. Ed.* **2006**, *45*, 3748–3759.