



## Synthesis and reactivity of *N*-aryl substituted *N*-heterocyclic silylenes<sup>☆</sup>

P. Zark<sup>a</sup>, A. Schäfer<sup>a</sup>, A. Mitra<sup>b</sup>, D. Haase<sup>a</sup>, W. Saak<sup>a</sup>, R. West<sup>b</sup>, T. Müller<sup>a,\*</sup>

<sup>a</sup> Institut für Reine und Angewandte Chemie, Carl von Ossietzky Universität Oldenburg, Carl von Ossietzky Strasse 9-11, 26129 Oldenburg, Federal Republic of Germany

<sup>b</sup> Organosilicon Research Center, Department of Chemistry, University of Wisconsin, 1101 University Avenue, Madison, WI 53706, USA

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### ABSTRACT

The synthesis of two *N*-aryl substituted 2-silaimidazolidenes **9a**, **b** by metal-reduction of the appropriate silicon(IV) heterocycles is reported. Structural as well as spectroscopic data obtained for the *N*-aryl substituted *N*-heterocyclic silylenes (NHSi) are very close to those obtained previously for their *N*-alkyl substituted counterparts. NHSis **9a**, **b** are used as starting materials for the synthesis of a series of dichalcogenadisiletanes **19–24** and for a mono silylene tungsten complex **29**. The reactivity studies revealed only marginally differences between the *N*-aryl substituted NHSis **9a**, **b** and previously described *N*-alkyl substituted silylenes.

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## 1. Introduction

Stable silylenes **1–8** [1–11] are known for several years and most of the well-characterized examples are *N*-heterocyclic silylenes (NHSi), in which the di-coordinated silicon atom is substituted by two nitrogen atoms. Although the synthesis of NHSis **1** [1], **2a** [2], **3a** [4] were reported already 15 years ago, the chemistry of these compounds and their use in synthesis is still very limited, in particular when compared with the analogous *N*-heterocyclic carbenes. The extremely bulky and inflexible substituents at the nitrogen atoms are one of the reasons for the limited use of NHSis **1**, **2a**, **3**. In the course of our investigation of low coordinated silicon cations the quest for stable silylenes with different substitution patterns at nitrogen arose. Therefore, we established convenient synthetic routes which afford *N*-aryl substituted silylenes **9** in moderate to high isolated yields and studied the principal reactivity of these NHSis versus Brønsted acids, chalcogens and reactive transition metal complexes (Charts 1 and 2).

## 2. Results and discussion

### 2.1. Syntheses

A low yield synthesis of the Dipp (Dipp: 2,6-di-*iso*-propyl-phenyl) substituted silylene **9a** has been reported earlier [12] and the less-bulky substituted NHSi **9b** was previously unknown. Follow-

ing the general scheme for the synthesis of *N*-heterocyclic carbene analogues, we considered the reduction of *N*-aryl substituted 1,4-diazabutadienes **10** by lithium metal and subsequent cyclization of the dianion **11** with silicon(IV)chloride as a viable synthetic route to the *N*-heterocyclic dichloride **12** (see Scheme 1). Reductive elimination of the dichlorides **12** would then afford the NHSi **9a**, **b**. Following this lead, the dichloride **12a** was synthesized in a 20 g scale by treatment of diazabutadiene **10a** with 2.2 eq. lithium in thf at 0 °C, addition of tetrachlorosilane to the resulting suspension of dianion **11a** in thf at liquid nitrogen temperature and subsequent warming of the reaction mixture to room temperature.

The synthesis of the analogue Xyl (Xyl: 2,6-dimethylphenyl) substituted diaminedichlorosilane **12b** proved to be more demanding. At temperatures below  $T = -45$  °C the solubility of the intermediate dilithiodiazabutadiene **11b** in thf is low and reaction with silicon tetrachloride yielded a mixture of the disilylated product **14** and the *N*-heterocyclic silyldichloride **12b** (Scheme 2). When the reaction is performed at 0 °C, instead, the spiro compound **13** was the only isolated product (Scheme 2). Performing the reaction at  $T = -40$  °C and using diluted solutions of **11b** allowed however the isolation of dichloride **12b** in high yields. In a similar way the dibromide **15** was obtained by reaction of **11b** with silicon tetrabromide (Scheme 2).

For the subsequent reduction step of the dichlorides **12** by alkali metals a careful monitoring of the reaction by <sup>1</sup>H NMR is warranted since over-reduction and decomposition easily occurs and purification of the NHSis proved to be tedious. We found, that the reduction of dichloride **12a** with lithium naphthalide in thf at room temperature affords the NHSi **9a** in high yields (Scheme 3), while using the same reaction conditions NHSi **9b** was produced only in low yields in a not tractable product mixture together with

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\* Corresponding author. Tel.: +49 (441) 798 3874; fax: +49 (441) 798 3352.

E-mail address: [thomas.mueller@uni-oldenburg.de](mailto:thomas.mueller@uni-oldenburg.de) (T. Müller).

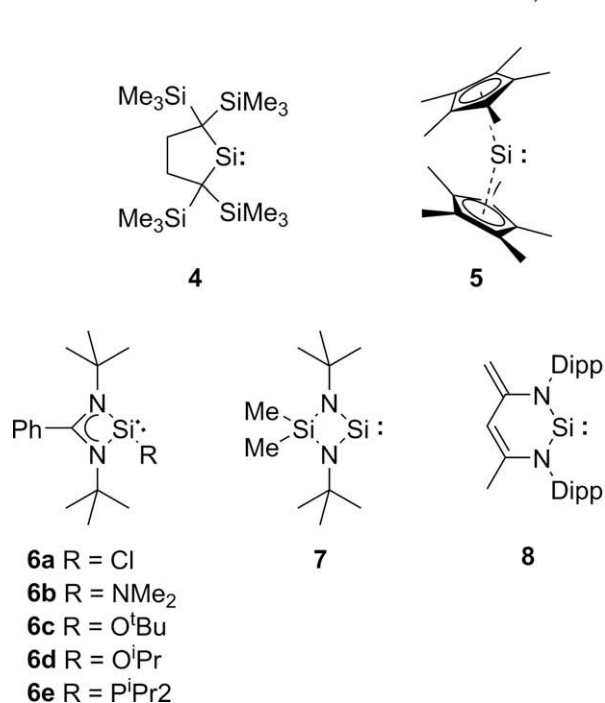
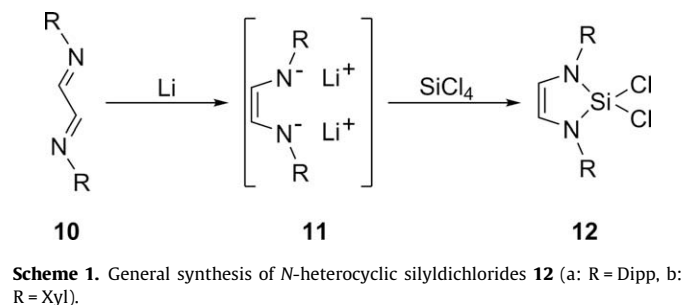
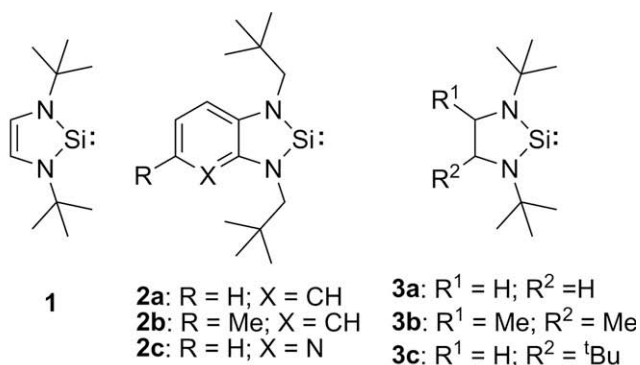


Chart 1.

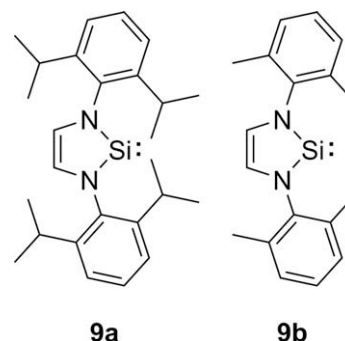
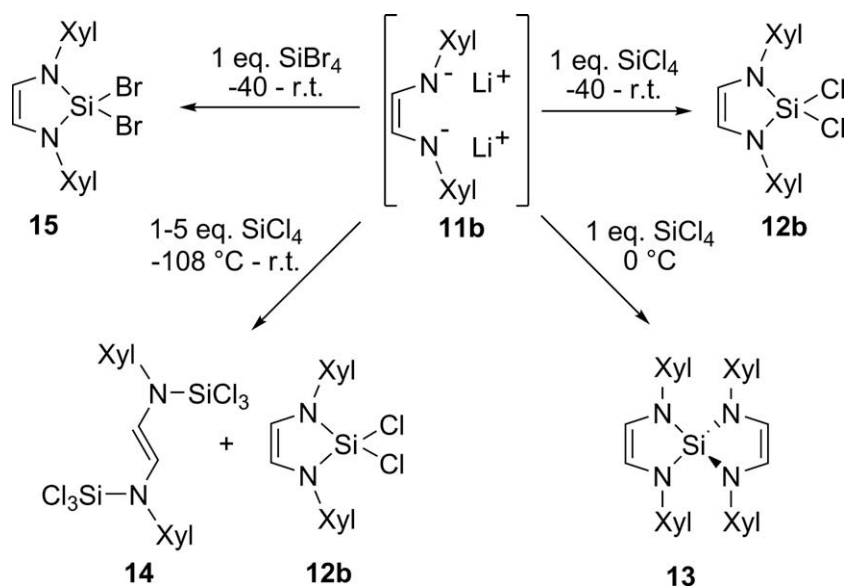


Chart 2.

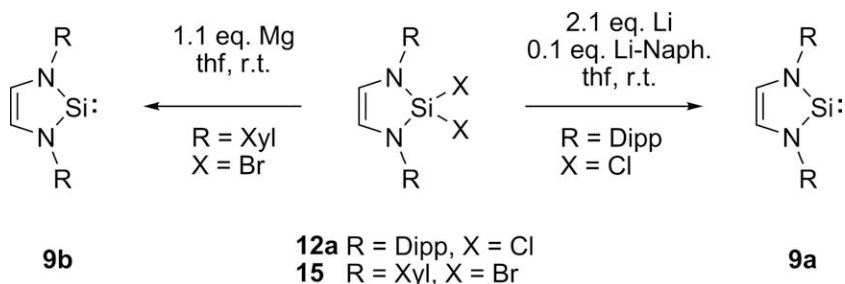
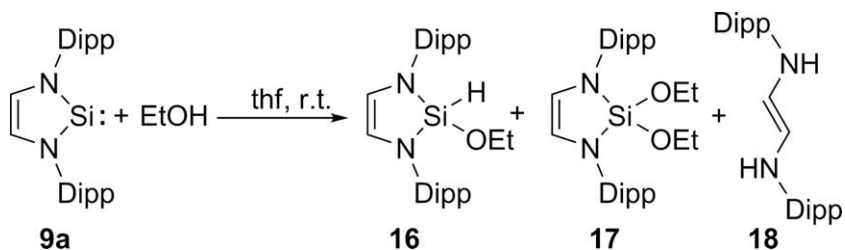
elemental silicon, compound **11b** and the spiro compound **13**. On the other hand the dibromide **15** was reduced by magnesium to give the NHSi **9b** in high isolated yields (80%). Using the less reactive magnesium as reductant over-reduction does not occur, therefore monitoring of the reaction course is not needed in this case. Crystals from NHSis **9** which proved to be suitable for X-ray diffraction analysis were obtained in both cases from *n*-hexane solution at  $-20\text{ }^{\circ}\text{C}$ .

## 2.2. Reactivity

The reactivity of the *N*-alkyl substituted heterocyclic silylenes **1**, **2a**, **3a** is well investigated and is documented in several literature



**Scheme 2.** Reaction of dilithiated diazabutadiene **11b** with silicon tetrahalides at various temperatures.

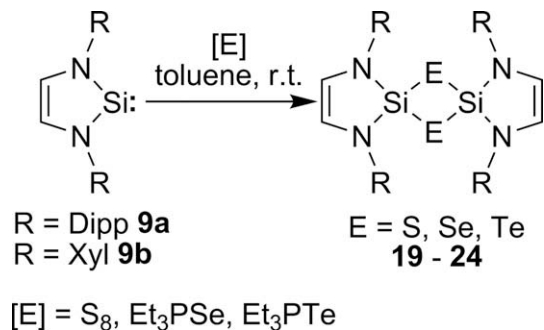
Scheme 3. Synthesis of NHSi **9a, b**.Scheme 4. Reaction of NHSi **9a** with ethanol.

overviews [13–16]. Their reactivity is dominated by the Lewis base character which is conferred by the lone electron pair at the silicon atom. On the other hand, the conjugation between the lone pairs at the nitrogen atoms and the 3p(Si) orbital dramatically decrease the Lewis acidity of the NHSi to such an extent, that even with strong bases such as triethylamine and pyridine no reaction occurs. The formation of a complex with a *N*-heterocyclic carbene is the only well documented example for a Lewis acid like reactivity of silylene **2a** [17]. The most important reaction mode for silylenes **1, 2a, 3a** is oxidative addition to give tetracoordinated silicon(IV) compounds [18–21]. For these transformations concerted [19] as well as stepwise radical mechanisms [20–22] are suggested. We examined several reactions which are characteristic for silylenes to review the effect of the *N*-aryl substituent on the reactivity of NHSis **9**.

Unlike non-stabilized silylenes but similar to their *N*-alkyl substituted counterparts, silylenes **9** do not react with silanes such as Et<sub>3</sub>SiH even at elevated temperatures. That is <sup>1</sup>H and <sup>29</sup>Si NMR spectra of the reaction mixture indicate even after 12 h at room temperature only the presence of the starting material. In the same way, like NHSis **1–3** and unlike typical silylenes the NHSis **9** did not show any [1,4]-cycloaddition reactivity versus 2,3-dimethyl-butadiene and in contrast to NHSi **1** [23] also no activity in polymerization of alkenes. As a test case for the stability and chemical behaviour of aryl substituted NHSi **9** versus H acidic compounds, silylene **9a** was treated with 1 eq. ethanol at room temperature. The NMR spectroscopic results indicate the formation of three main compounds **16, 17, 18**, which integrate in the <sup>1</sup>H NMR and in GC to 1:2:1, see Scheme 4. These three compounds were identified in the mixture by their characteristic NMR spectroscopic data and by their mass spectra obtained from GC/MS. While the formation of ethoxysilanes **16, 17** is as anticipated, based on the experience with *N*-alkyl substituted silylenes [24] the formation of the degradation product, enamin **18**, is unexpected and hints to lower stability of the Si–N linkage in **9a** versus Brønsted acids.

In analogy to the reactivity of NHSi **1–3** versus chalcogens, the *N*-aryl substituted silylenes **9** afford dichalcogena–disiletanes **19–24** by reaction with elemental sulphur, Et<sub>3</sub>PSe or Et<sub>3</sub>PTe in low to moderate yields (Scheme 5 and Table 1). Crystals of compounds **19–22**, which were suitable for X-ray diffraction analysis were

grown from *n*-hexane/thf solutions at –20 °C over a period of several days. The use of phospho chalcogenides instead of the elemental chalcogens Se and Te permitted shorter reaction times and allowed lower reaction temperatures. Previous low temperature NMR investigations of the reaction of NHSi **1** with sulfur reported by West and colleagues suggested the presence of a reactive intermediate for which a silathione structure was put forward [24]. In addition the groups of Kira and Tokitoh reported the synthesis and characterization of donor-free heavy silachalcogenons R<sub>2</sub>Si=E (E = S, Se, Te) by reaction of silylenes with chalcogens [25]. Recently several other groups reported the isolation of intra-, or intermolecularly stabilized heavy silaketones [26–29]. Our attempts to use the modified steric requirements of *N*-aryl substituted NHSis **9** to stabilize or to trap putative silachalcogenon

Scheme 5. Synthesis of dichalcogena-disiletanes **19–24**.

**Table 1**  
Syntheses and yields of dichalcogena-disiletanes **19–24**.

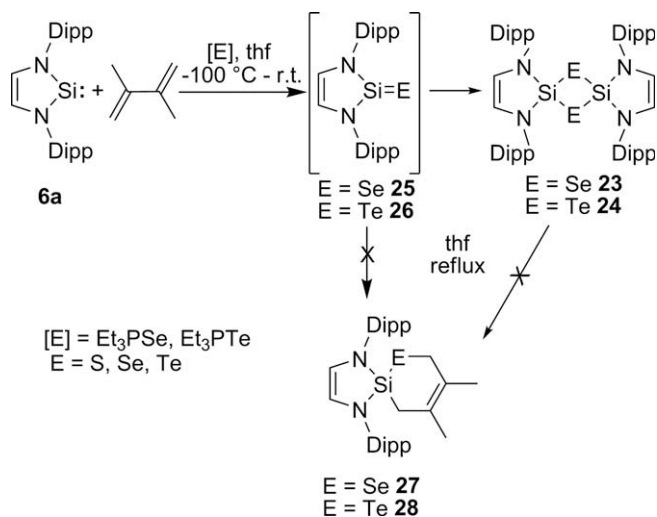
Compound	R	E	Reaction	Yield (%)
<b>19</b>	Xyl	S	<b>6b</b> + S <sub>8</sub>	45
<b>20</b>	Xyl	Se	<b>6b</b> + Et <sub>3</sub> PSe	50
<b>21</b>	Xyl	Te	<b>6b</b> + Et <sub>3</sub> PTe	46
<b>22</b>	Dipp	S	<b>6a</b> + S <sub>8</sub>	82
<b>23</b>	Dipp	Se	<b>6a</b> + Et <sub>3</sub> PSe	69
<b>24</b>	Dipp	Te	<b>6a</b> + Et <sub>3</sub> PTe	5

intermediates failed however. That is, reactions of NHSi **9a** with  $\text{Et}_3\text{PE}$  ( $\text{E} = \text{Se}, \text{Te}$ ) at temperatures as low as  $-100^\circ\text{C}$  in the presence of 2,3-dimethyl-butadiene give as only detectable products disiletanes **23** and **24**. In particular no bicyclic products **27**, **28** which would result from a [4 + 2] cycloaddition reaction between the butadiene and the putative heavy silanones **25**, **26** were observed (Scheme 6). In addition the disiletanes **23**, **24** are stable towards cycloreversion up to temperatures  $T = 65^\circ\text{C}$  as no trapping products, **27**, **28**, were detected even after heating to reflux in thf for 12 h in the presence of excess 2,3-dimethyl-butadiene (Scheme 6).

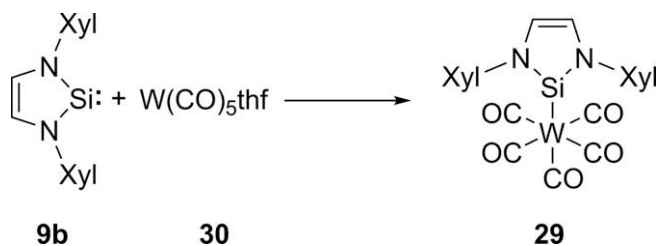
The nucleophilic properties of *N*-heterocyclic silylenes are underlined by their ability to form transition metal complexes with group 6 and group 8 metals [30,31]. As an example for a transition metal complex having a *N*-aryl substituted silylene as ligand, the deep violet tungsten pentacarbonyl complex  $\text{W}(\text{CO})_5(\mathbf{9b})$ , **29**, was synthesized by reaction of NHSi **9b** with  $\text{W}(\text{CO})_5(\text{thf})$ , **30** (Scheme 7). The particular advantage of using the solvent complex **30** is the exclusive formation of the mono silylene complex **29**, indicated by only one signal in the  $^{29}\text{Si}$  NMR spectra ( $\delta^{29}\text{Si} = 109.1$ ,  $^1J_{\text{Si,W}} = 164$  Hz). In reactions using  $\text{W}(\text{CO})_6$  as starting material complex **29** is formed in a mixture with a second species which features a Si–W linkage. This new product became noticeable by an additional  $^{29}\text{Si}$  NMR signal at  $\delta^{29}\text{Si} = 111.7$  ( $^1J_{\text{Si,W}} = 198$  Hz).

### 2.3. Spectroscopic properties

Selected NMR data for the NHSis **9**, and the tungsten silylene complex **29** are compared in Table 2 with those obtained for the Si(IV) containing diazasilacyclopentenes **12**, **13**, **15**, and with dis-



Scheme 6. Formation of disiletanes **23**, **24** in the presence of 2,3-dimethylbutadiene.



Scheme 7. Synthesis of the NHSi tungsten carbonyl complex **29**.

Table 2

Selected NMR data of compounds NHSi **9**, diazasilacyclopentenes **12**, **13**, **15**, disiletanes **19–24** and silylene complex **29**.

Compound	R	$\delta^1\text{H}(\text{NCH})$	$\delta^{13}\text{C}(\text{NCH})$	$\delta^{29}\text{Si}$	Other nuclei
<b>9b</b>	Xyl	6.27	124.1	76.5	$\delta^{15}\text{N} = -190.7$
<b>9a</b>	Dipp	6.48	125.4	75.9	$\delta^{15}\text{N} = -196.3$
<b>12a</b>	Dipp	5.73	125.1	-38.4	$\delta^{15}\text{N} = -297.8$
<b>12b</b>	Xyl	5.51	118.5	-41.0	
<b>13</b>	Xyl	5.38	117.5	-48.1	
<b>15</b>	Xyl	5.53	119.5	-64.9	$\delta^{15}\text{N} = -290.1$
<b>19</b>	Xyl	5.49	118.3	-39.5	
<b>20</b>	Xyl	5.37	118.7	-63.0	$\delta^{77}\text{Se} = 186.0$
<b>21</b>	Xyl	5.28	119.0	-137.9	$\delta^{125}\text{Te} = 483.0$
				$(^1J_{\text{Si,Te}} = 315 \text{ Hz})$	
<b>22</b>	Dipp	5.63	124.1	-38.8	
<b>23</b>	Dipp	5.64	124.1	-61.7	$\delta^{77}\text{Se} = 197.3$
<b>24</b>	Dipp	5.60	124.3	-131.2	$\delta^{125}\text{Te} = 451.9$
				$(^1J_{\text{Si,Te}} = 310 \text{ Hz})$	
<b>29</b>	Xyl	6.07	124.7	109.1	$\delta^{15}\text{N} = -209.3$
				$(^1J_{\text{Si,W}} = 163 \text{ Hz})$	

iletanes **19–24**. All Si(IV) compounds are characterized by  $^1\text{H}$  NMR chemical shift for the NCH hydrogen atom of  $\delta^1\text{H}(\text{NCH}) = 5.28\text{--}5.73$ . Compared to the Xyl substituted heterocycles the NCH proton of the Dipp substituted analogous species resonate at slightly lower field ( $\Delta\delta^1\text{H}(\text{NCH}) = 0.14\text{--}0.32$ ). The NHSis **9** are characterized by a significant low field shift of this  $^1\text{H}$  resonance by  $\Delta\delta^1\text{H}(\text{NCH}(\text{Si(II)}/\text{Si(IV)})) = 0.75$  (**9a**) and 0.76 (**9b**) compared to the corresponding silyldichlorides **12**. This low energy shift is less pronounced as reported for NHSi **1** ( $\Delta\delta^1\text{H}(\text{NCH}(\text{Si(II)}/\text{Si(IV)})) = 1.02$ ) [1] but still remarkable. The deshielding of the NCH protons in *N*-heterocyclic silylenes such as **1** and **9** was put forward as an indication of cyclic conjugation across the five-membered heterocycle [32]. For the tungsten silylene complex **29** this low field shift is smaller but still noticeable ( $\Delta\delta^1\text{H}(\text{NCH}(\text{Si(II)}/\text{Si(IV)})) = 0.46$ ). The analysis of the  $^{13}\text{C}$  NMR shift data obtained for the  $\text{sp}^2$  hybridized NCH carbon atoms in compounds **9**, **12**, **13**, **15**, **19–24**, **29** is of little informative value. The substituent effect of the different aryl groups attached to nitrogen atom on  $\delta^{13}\text{C}(\text{NCH})$  is as large as the effect of the different oxidation states of the inner-cyclic silicon atom. More instructive is a comparison of the nitrogen NMR chemical shift of the silyldihalides **12a** and **15** with that obtained for NHSis **9**. The replacement of the tetracoordinated silicon center in **12a** and **15** by a di-coordinated silicon atom in **9** results in a marked deshielding of the ring nitrogen atoms by approximately 100 ppm. The  $^{15}\text{N}$  NMR signal is transferred from a chemical shift region typical for aromatic enamines to a region characteristic for imidazols [33]. This deshielding of the nitrogen atoms in NHSis **9** suggests a certain degree of multiple bonding between the innercyclic nitrogen and carbon atoms. Obviously, the effect of metal complexation on  $\delta^{15}\text{N}$  NMR chemical shift is relatively small, since for the tungsten complex **29**  $\delta^{15}\text{N} = -209.3$  is detected, still in the chemical shift region typical for NHSi (i.e.  $\delta^{15}\text{N}$  (**1**) =  $-170$   $\delta^{15}\text{N}$  (**2a**) =  $-225$ ). The strongly deshielded  $^{29}\text{Si}$  resonances of NHSis **9** at  $\delta^{29}\text{Si} = 75.9$  (**9a**) and 76.5 (**9b**) are very close to that reported for their *N*-*t*-butyl substituted counterpart **1** ( $\delta^{29}\text{Si}$  (**1**) = 78.3) [34,35] and are clearly the most significant and characteristic NMR spectroscopic parameters for this class of compounds. In the series of disiletanes **19–24** a marked high field shift of the  $^{29}\text{Si}$  NMR resonance is noticed along the chalcogen series which places the  $^{29}\text{Si}$  NMR signal of the tellurium compounds **21**, **24** in an unusual high field region for tetracoordinated silicon compounds (i.e.  $\delta^{29}\text{Si}$  (**21**) =  $-137.9$   $\delta^{29}\text{Si}$  (**24**) =  $-131.2$ ). The low field  $^{29}\text{Si}$  NMR resonance of silylene pentacarbonyl tungsten complex **29** ( $\delta^{29}\text{Si} = 109.1$ ) is very close to that found for the tetracarbonyl complex *trans*- $\text{W}(\text{CO})_4(\mathbf{1})_2$  ( $\delta^{29}\text{Si} = 97.8$ ) and is located at the high field end of the chemical shift region previously reported

for base-free  $\eta^1$ -silylene tungsten complexes ( $\delta^{29}\text{Si} = 380.9\text{--}97.8$ ) [30,36–39]. The large value of the  $^1J_{\text{Si,W}}$  coupling constant of 163 Hz testifies the direct Si–W linkage. Due to the limited number of reported values [36,39] the size of the  $^1J_{\text{Si,W}}$  coupling constant can not be securely correlated to the degree of bonding between the silicon and tungsten atoms in complex **29**.

Silylenes **9a**, **b** are pale yellow substances and accordingly they show absorptions in the UV–vis spectra also in the visible region (**9a**:  $\lambda_{\text{max}}$  (*n*-hexane): 225, 268, 278, 290, 374, 452; **9b**:  $\lambda_{\text{max}}$  (*n*-hexane): 225, 268, 278, 289, 382, 462). The comparison with the UV data obtained for the 2-silaimidazoles **12a** and **15** suggests that the chromaticity of the silylenes is solely due to the *N*-arylated silaimidazole moiety (**12a**:  $\lambda_{\text{max}}$  (*n*-hexane): 225, 268, 278, 291, 374, 452; **15**: 225, 268, 278, 291, 385, 462). A distinct UV band which could be assigned to the lone pair Si $\rightarrow$ 3p(Si) transmission was not detected in the UV–vis spectra of silylenes **9a**, **b**, most probably due to the low intensity of this formally forbidden band.

#### 2.4. Crystal structure data

The molecular structures of silylenes **9a**, **b** in the crystal are shown in Figs. 1 and 2 and pertinent data for NHSi **9b** are summarized in Table 3. The basic structural feature in both molecules is the central planar five-membered  $\lambda^2$ -2-sila-1,3-diazole ring (dihedral angles CCNSi =  $-2.7\text{--}3.0^\circ$ ) with the aryl substituents at the nitrogen atoms oriented almost perpendicular to the heterocycle (dihedral angles  $\text{C}_8\text{C}_3\text{NSi}$   $95.7\text{--}106.1^\circ$ ). Crystals of NHSi **9a** show a statistical side disorder (see Fig. 3) which prevents a careful analysis of the structural data. In this case the crystal symmetry of the monoclinic space group  $C2/c$  generates a centre of inversion at the midpoint of the two nitrogen atoms and allows for two different orientations of the five membered heterocycle in the crystal. In

**Table 3**

Experimental structural parameters of compounds **9b**, **15**, **19–22** and **29** (bond distances *d* in pm, bond angles  $\alpha$  in  $^\circ$ ), all data are given as average values of chemical identical linkages). Selected data for NHSi **1** is also given for comparison [43].

Compound	<i>d</i> (C,C)	<i>d</i> (C,N)	<i>d</i> (N,Si)	$\alpha$ (NSiN)	<i>d</i> (SiX)	$\alpha$ (XSiX)
<b>1</b>	132.0	138.8	174.7	88.1		
<b>9b</b>	131.8	138.5	174.7	87.6		
<b>15</b>	133.4	142.2	171.4	93.7	222.8 <sup>a</sup>	101.2 <sup>a</sup>
<b>19</b>	133.3	141.7	171.9	92.6	213.1 <sup>b</sup>	96.7 <sup>b</sup>
<b>20</b>	132.8	141.9	172.0	92.7	228.0 <sup>c</sup>	97.6 <sup>c</sup>
<b>21</b>	133.0	142.1	173.2	92.7	251.5 <sup>d</sup>	98.2 <sup>d</sup>
<b>22</b>	133.2	141.8	171.8	92.9	213.5 <sup>b</sup>	96.4 <sup>b</sup>
<b>29</b>	138.2	138.6	171.8	90.3	245.6 <sup>e</sup>	

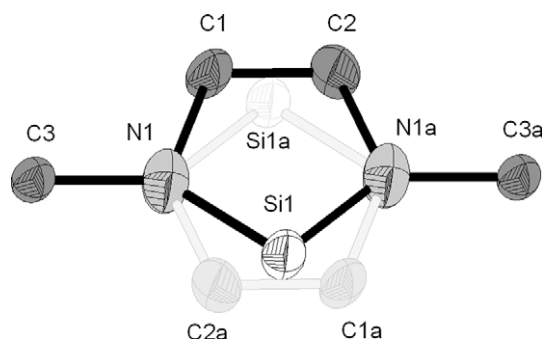
<sup>a</sup> X = Br.

<sup>b</sup> X = S.

<sup>c</sup> X = Se.

<sup>d</sup> X = Te.

<sup>e</sup> X = W.

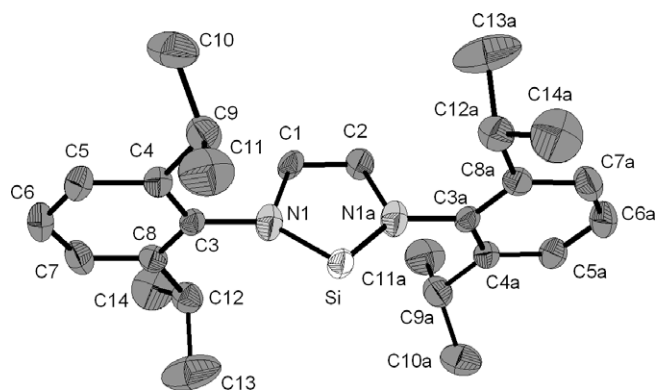


**Fig. 3.** Statistical side disorder in the crystal structure of silylene **9a**, only the central five membered ring and the *ipso* atoms of the Dipp-substituents are shown.

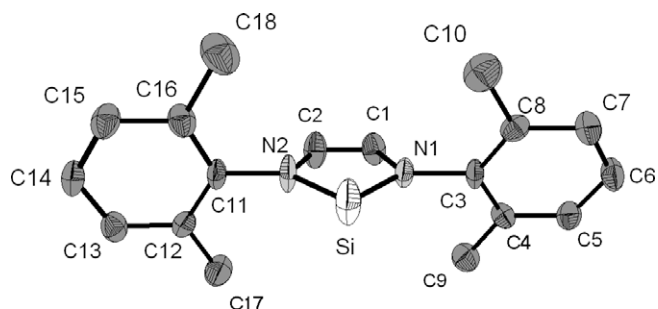
contrast, crystals of the *N*-aryl substituted silylene **9b** show no disorder and the crystal structure was refined to high accuracy. The bond parameter of NHSi **9b** are nearly identical to those obtained previously for the *N*-alkyl substituted NHSi **1** (see Table 3) [40]. This indicates a negligible substituent effect on the structure of the central  $\lambda^2$ -2-sila-1,3-diazole ring when the substituent at the nitrogen atom is changed from alkyl to bulky aryl groups. The most notable differences in the molecular structures of NHSi **9b** and its precursor compound, the cyclic dibromide **15**, are the shorter innercyclic CN bonds and the longer SiN bonds in NHSi **9b**. While the long SiN bond is a result of the divalency of the silicon atom in NHSi **9b**, the shorter CN bond suggests a bond order larger than one, in qualitative agreement with the  $^{15}\text{N}$  NMR results.

Fig. 4 shows as an example for the tricyclic disiletanes, the molecular structure of the ditellura-disiletane **21** in the crystal. Pertinent data for all structurally experimentally investigated disiletanes are summarized in Table 3. Inspection of the bond parameters reveals the close structural similarity between these compounds. Bond lengths and bond angles of the planar five-membered rings are nearly identical. In all investigated cases also the central four-membered 1,3-disiletane rings are planar and in the case of the selenium **20** and sulfur compounds **19**, **22** they are oriented nearly orthogonal to both diazasilacyclopentene cycles. In the case of the tellurium compound **21** the rings are tilted. That is, the planes of the central four-membered ring and five-membered ring form a torsion angle of  $75^\circ$ . The silicon-chalcogen distances and the innercyclic bond angles found in the experimental structures of disilaetanes **19–22** are very similar to those found for related compounds [24,41,42].

Fig. 5 shows the molecular structure of the silylene pentacarbonyl tungsten complex **29**. The compound crystallizes in the



**Fig. 1.** Molecular structure of silylene **9a** in the crystal (hydrogen atoms are omitted; ellipsoids are drawn at 50% probability).



**Fig. 2.** Molecular structure of silylene **9b** in the crystal (hydrogen atoms are omitted; ellipsoids are drawn at 50% probability).

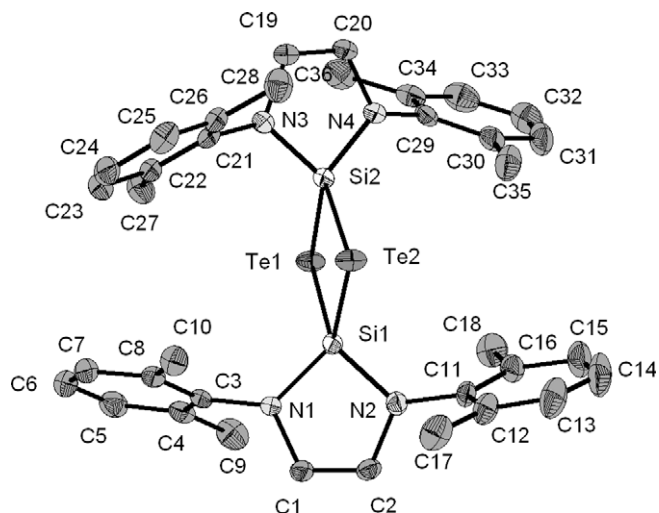


Fig. 4. Molecular structure of the tellurium compound **21** in the crystal (hydrogen atoms are omitted; ellipsoids are drawn at 50% probability).

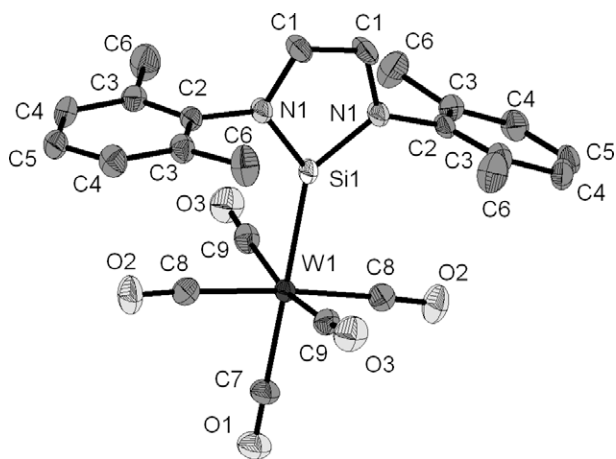


Fig. 5. Molecular structure of the tungsten pentacarbonyl silylene complex **29** in the crystal (hydrogen atoms are omitted; ellipsoids are drawn at 50% probability).

space group  $Cmcm$  and the molecules are located on the Wyckoff position  $c$  ( $m2m$ ). The planar five-membered ring and two of the *cis*-carbonyl groups are located in one mirror plane. The orthogonal *cis*-carbonyl ligands are placed in the second mirror plane and the *N*-aryl substituent are oriented perpendicular relative to the central diazasilole ring. The bond lengths and angles in the diazasilole ring are nearly identical compared to those in the free silylene **9b** with the exception of a slightly elongated C=C bond in complex **29**. The Si–W bond is short ( $d(\text{SiW}) = 245.62(16)$  pm), regarding the range of typical Si–W bonds ( $d(\text{SiW}) = 238.9\text{--}270.8$  pm) [43]. It is in the same range as reported previously for the tetracarbonyl tungsten complex *trans*  $\text{W}(\text{CO})_4(\mathbf{1})_2$  ( $d(\text{SiW}) = 247.1$  pm) but it is significantly longer than the Si–W bond found in  $\eta^1$ -silylene tungsten complexes with non-stabilized silylenes ( $d(\text{SiW}) = 235$  pm [37] and 238.5 pm [36]). The CO bond lengths of the *cis*-carbonyl groups ( $d(\text{CO}) = 114.18(62)$  and 113.97(62) pm) are close to the bond length in  $\text{W}(\text{CO})_6$  with 113.9 pm [44], while the *trans* CO bond is markedly shortened for about 4 pm ( $d(\text{CO}) = 109.90(72)$  pm). Concomitantly the *trans* W–CO bond ( $d(\text{W–CO}^{\text{trans}}) = 207.75(58)$  pm) is the longest W–C bond in the molecule ( $d(\text{W–CO}^{\text{cis}}) = 204.32(51)$ , 205.10(48) pm). This indicates the weakest degree of W–C  $\pi$ -back bonding for this group and a

relative strong back bonding for the Si–W bond. Finally, the Tollman angle for NHSi **9b** was established with a value of 123.7° close to that reported for NHSi **1**.

### 3. Conclusion

The multi-gramme synthesis of two silylenes, **9a**, **b**, of the 2-silaimidazolidene type which have aryl substituents at the ring nitrogen atoms is reported. The investigations revealed no significant differences in structures, spectroscopic properties or reactivities of these new NHSis to those of previously known *N*-alkyl substituted silylenes, such as **1**. Minor differences such as deviating solubility and modified spatial requirements around the low coordinated silicon atom, however, might be of importance for their further application in synthesis and catalysis.

### 4. Experimental

#### 4.1. General information

All procedures were carried out in oven-dried glassware under inert argon atmosphere using Schlenk techniques. Benzene, toluene, thf, hexane and triethylsilane were distilled from sodium. Ethanol was dried as described in literature [45].  $[\text{D}_6]$ Benzene,  $[\text{D}_8]$ toluene and  $[\text{D}_1]$ chloroform were stored over molecular sieves. All reagents were obtained from commercial suppliers and were used without further purification. Tetrabromosilane [46], triethylphosphane selenide [47], -telluride [48] and the 1,4-diazabutadienes **10a**, **b** [50] were prepared according to literature procedures. IR spectra were recorded on a Bruker Vector 22 spectrometer. UV–vis spectra were obtained on a Zeiss (Jena) Specord 100 spectrometer. Mass spectra and high resolution mass spectra were carried out on a Finnigan-MAT95 spectrometer with electron impact ionization (EI) and chemical ionization (CI), using *iso*-butane. GC–MS studies were performed on a thermo focus, DSQ. NMR spectra were recorded on a Bruker DRX 500 and DRX 300.  $^1\text{H}$  NMR spectra were calibrated using residual protio signals of the solvent as internal reference  $\delta^1\text{H}$  ( $\text{C}_6\text{D}_5\text{H}$ ) = 7.20,  $\delta^1\text{H}$  ( $\text{C}_6\text{D}_5\text{CD}_2\text{H}$ ) = 2.03,  $\delta^1\text{H}$  ( $\text{CHCl}_3$ ) = 7.24 and  $^{13}\text{C}$  NMR spectra using the central line of the solvent signal  $\delta^{13}\text{C}$  ( $\text{C}_6\text{D}_6$ ) = 128.0,  $\delta^{13}\text{C}$  ( $\text{C}_6\text{D}_5\text{CD}_3$ ) = 20.4,  $\delta^{13}\text{C}$  ( $\text{CDCl}_3$ ) = 77.0.  $^{15}\text{N}$ ,  $^{29}\text{Si}$ ,  $^{77}\text{Se}$ ,  $^{125}\text{Te}$  NMR spectra were calibrated using external standards.  $^{15}\text{N}$  NMR:  $\delta^{15}\text{N}$  ( $\text{Me}_2\text{NCHO}$ ) =  $-267.5$  versus  $\text{CH}_3\text{NO}_2$ .  $^{29}\text{Si}$  NMR:  $\delta^{29}\text{Si}$  ( $\text{Me}_2\text{SiHCl}$ ) = 11.1 versus TMS.  $^{77}\text{Se}$  NMR:  $\delta^{77}\text{Se}$  ( $\text{Ph}_2\text{Se}_2$ ) = 275.0 versus  $\text{Me}_2\text{Se}$ .  $^{125}\text{Te}$  NMR:  $\delta^{125}\text{Te}$  ( $\text{Ph}_2\text{Te}_2$ ) = 422.0 versus  $\text{Me}_2\text{Te}$ . The definite assignment of the signals resulted from DEPT and 2D H,H COSY, H,C HMQC, H,C HMBC and H,N HMBC ( $^3J_{\text{N,H}} = 10$  Hz) measurements. Single-crystal X-ray diffraction data for compound **9a**, **9b**, **15**, **19–24** and **29** were recorded on a STOE-IPDS-diffractometer using Mo  $K\alpha$  ( $\lambda = 71.073$  pm) radiation at 153 K. Structural solutions were obtained with direct methods using SHELXS-97 [51] and refined SHELXL-97 [51]. All shown molecular structures designed with DIAMOND. Crystallographic data are summarized in Table 4.

#### 4.2. Synthesis of 1,3-bis(2,6-diisopropylphenyl)-1,3-diaza-2,2-dichloro-2-silacyclopent-4-ene, **12a**

Lithium (387 mg, 55.9 mmol), cut into small pieces was added to a solution of **10a** (10 g, 26.6 mmol) in thf (110 mL,  $c = 236$  mmol  $\text{L}^{-1}$ ) at 0 °C. The cooling bath was removed and the mixture was stirred for 16 h. Excess of lithium was removed with a pincer and the reaction mixture was frozen using a liquid nitrogen bath. Tetrachlorosilane (15.5 mL, 133 mmol), pre cooled to  $-25$  °C, was added in one portion. After the addition was completed the mixture was allowed to warm to room temperature and stirred for

**Table 4**  
Crystallographic data of compound **9**, **15**, **19–22** and **29**.

Compound	<b>9b</b>	<b>9a</b>	<b>15</b>	<b>19</b>
Formula	SiN <sub>2</sub> C <sub>2</sub> H <sub>2</sub> (C <sub>8</sub> H <sub>9</sub> ) <sub>2</sub>	Si(N <sub>2</sub> C <sub>2</sub> H <sub>2</sub> )(C <sub>12</sub> H <sub>17</sub> ) <sub>2</sub>	SiBr <sub>2</sub> (N <sub>2</sub> C <sub>2</sub> H <sub>2</sub> )(C <sub>8</sub> H <sub>9</sub> ) <sub>2</sub>	Si <sub>2</sub> S <sub>2</sub> (N <sub>2</sub> C <sub>18</sub> H <sub>20</sub> ) <sub>2</sub>
CCSD number	731875	731877	731876	731881
Empirical formula	C <sub>18</sub> H <sub>20</sub> N <sub>2</sub> Si	C <sub>26</sub> H <sub>36</sub> N <sub>2</sub> Si	C <sub>18</sub> H <sub>20</sub> Br <sub>2</sub> N <sub>2</sub> Si	C <sub>36</sub> H <sub>40</sub> N <sub>4</sub> S <sub>2</sub> Si <sub>2</sub>
M <sub>f</sub>	292.45	404.66	452.27	649.02
T (K)	153(2)	153(2)	153(2)	153(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	8.3255(14)	20.1834(13)	9.8400(7)	11.0010(2)
<i>b</i> (Å)	10.526(2)	6.5053(7)	14.0110(6)	14.3957(4)
<i>c</i> (Å)	11.109(2)	20.1801(14)	13.7925(10)	21.6609(5)
$\alpha$ (°)	99.14(3)	90	90	90
$\beta$ (°)	105.25(2)	102.61(1)	95.070(9)	96.466(2)
$\gamma$ (°)	112.91(2)	90	90	90
V <sub>UC</sub> (Å <sup>3</sup> )	826.9(4)	2585.7(4)	1894.1(2)	3408.55(14)
Z	2	4	4	4
$\rho_{\text{calc}}$ (mg m <sup>-3</sup> )	1.175	1.039	1.586	1.265
$\mu$ (mm <sup>-1</sup> )	0.138	0.104	4.344	0.258
F(0 0 0)	312	880	904	1376
Crystal size (mm <sup>3</sup> )	0.22 × 0.11 × 0.02	0.50 × 0.47 × 0.29	0.60 × 0.32 × 0.08	0.28 × 0.12 × 0.02
$\theta$ Range (°)	2.49–26.25	2.59–26.09	2.54–26.23	3.51–28.04
Index ranges	–9 ≤ <i>h</i> ≤ 9 –13 ≤ <i>k</i> ≤ 13 –13 ≤ <i>l</i> ≤ 13	–23 ≤ <i>h</i> ≤ 24 –7 ≤ <i>k</i> ≤ 8 –24 ≤ <i>l</i> ≤ 24	–12 ≤ <i>h</i> ≤ 12 –17 ≤ <i>k</i> ≤ 17 –17 ≤ <i>l</i> ≤ 17	–13 ≤ <i>h</i> ≤ 14 –17 ≤ <i>k</i> ≤ 19 –27 ≤ <i>l</i> ≤ 28
Reflections collected	10334	10846	20099	31681
Independent reflections	3077 [R <sub>int</sub> = 0.1608]	2384 [R <sub>int</sub> = 0.0515]	3738 [R <sub>int</sub> = 0.0681]	8216 [R <sub>int</sub> = 0.1008]
Observed reflections	916 [ <i>I</i> > 2σ( <i>I</i> )]	1498 [ <i>I</i> > 2σ( <i>I</i> )]	2547 [ <i>I</i> > 2σ( <i>I</i> )]	4338 [ <i>I</i> > 2σ( <i>I</i> )]
Completeness to $\theta = 25.00^\circ$	94.1%	93.8%	97.8%	99.4%
Absorption correction	None	None	Numerical	None
Maximum and minimum transmission	0.9973 and 0.9704	0.9705 and 0.9500	0.7226 and 0.1803	0.9943 and 0.9324
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	3077/0/194	2384/0/149	3738/0/212	8216/0/405
Goodness-of-fit (GOF) on F <sup>2</sup>	0.584	1.034	0.831	0.974
Final R indices [ <i>I</i> > 2σ( <i>I</i> )]	R <sub>1</sub> = 0.0442 wR <sub>2</sub> = 0.0625	R <sub>1</sub> = 0.0558 wR <sub>2</sub> = 0.1224	R <sub>1</sub> = 0.0276 wR <sub>2</sub> = 0.0534	R <sub>1</sub> = 0.0534 wR <sub>2</sub> = 0.1013
R indices (all data)	R <sub>1</sub> = 0.1814 wR <sub>2</sub> = 0.0818	R <sub>1</sub> = 0.0919 wR <sub>2</sub> = 0.1307	R <sub>1</sub> = 0.0513 wR <sub>2</sub> = 0.0567	R <sub>1</sub> = 0.1363 wR <sub>2</sub> = 0.1263
Largest difference in peak and hole (e Å <sup>-3</sup> )	0.152 and –0.208	0.148 and –0.136	0.528 and –0.609	0.408 and –0.340
	<b>20</b>	<b>21</b>	<b>22</b>	<b>29</b>
Formula	Se <sub>2</sub> Si <sub>2</sub> (N <sub>2</sub> C <sub>18</sub> H <sub>20</sub> ) <sub>2</sub>	Si <sub>2</sub> Te <sub>2</sub> (N <sub>2</sub> C <sub>18</sub> H <sub>20</sub> ) <sub>2</sub> ½ (C <sub>7</sub> H <sub>8</sub> )	Si <sub>2</sub> S <sub>2</sub> (N <sub>2</sub> C <sub>26</sub> H <sub>36</sub> ) <sub>2</sub>	W(CO) <sub>5</sub> Si(N <sub>2</sub> C <sub>2</sub> H <sub>2</sub> (C <sub>8</sub> H <sub>9</sub> ) <sub>2</sub> )
CCSD number	731879	731880	731878	731882
Empirical formula	C <sub>36</sub> H <sub>40</sub> N <sub>4</sub> Se <sub>2</sub> Si <sub>2</sub>	C <sub>39.5</sub> H <sub>44</sub> N <sub>4</sub> Si <sub>2</sub> Te <sub>2</sub>	C <sub>52</sub> H <sub>72</sub> N <sub>4</sub> S <sub>2</sub> Si <sub>2</sub>	C <sub>23</sub> H <sub>20</sub> N <sub>2</sub> O <sub>5</sub> SiW
M <sub>f</sub>	742.82	886.17	873.44	616.35
T (K)	153(2)	153(2)	153(3)	153(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>Cmcm</i>
<i>a</i> (Å)	11.1542(2)	11.3582(4)	20.8619(5)	9.7089(5)
<i>b</i> (Å)	14.3715(6)	11.0611(5)	15.2564(4)	14.3926(5)
<i>c</i> (Å)	21.6091(13)	30.9109(9)	15.9470(4)	17.1781(5)
$\alpha$ (°)	90	90	90	90
$\beta$ (°)	95.371	96.241(4)	94.733(2)	90
$\gamma$ (°)	90	90	90	90
V <sub>UC</sub> (Å <sup>3</sup> )	3448.8(3)	3860.5(2)	5058.3(2)	2400.40(16)
Z	4	4	4	4
$\rho_{\text{calc}}$ (mg m <sup>-3</sup> )	1.431	1.525	1.147	1.706
$\mu$ (mm <sup>-1</sup> )	2.245	1.606	0.190	4.897
F(0 0 0)	1520	1764	1888	1200
Crystal size (mm <sup>3</sup> )	0.45 × 0.27 × 0.13	0.60 × 0.24 × 0.08	0.31 × 0.20 × 0.11	0.50 × 0.26 × 0.13
$\theta$ Range (°)	2.83–26.15	1.96–26.10	2.77–28.96	2.53–28.21
Index ranges	–13 ≤ <i>h</i> ≤ 13 –17 ≤ <i>k</i> ≤ 17 –26 ≤ <i>l</i> ≤ 26	–14 ≤ <i>h</i> ≤ 14 –13 ≤ <i>k</i> ≤ 13 –37 ≤ <i>l</i> ≤ 36	–28 ≤ <i>h</i> ≤ 28 –20 ≤ <i>k</i> ≤ 20 –21 ≤ <i>l</i> ≤ 21	–12 ≤ <i>h</i> ≤ 12 –19 ≤ <i>k</i> ≤ 19 –21 ≤ <i>l</i> ≤ 22
Reflections collected	31555	33050	73816	18725
Independent reflections	6695 [R <sub>int</sub> = 0.0741]	7180 [R <sub>int</sub> = 0.0650]	13287 [R <sub>int</sub> = 0.0616]	1585 [R <sub>int</sub> = 0.0784]
Observed reflections	3865 [ <i>I</i> > 2σ( <i>I</i> )]	5462 [ <i>I</i> > 2σ( <i>I</i> )]	8288 [ <i>I</i> > 2σ( <i>I</i> )]	1585 [ <i>I</i> > 2σ( <i>I</i> )]
Completeness to $\theta = 25.00^\circ$	97.3%	94.4%	99.3%	97.6%
Absorption correction	Numerical	Numerical	None	Numerical
Maximum and minimum transmission	0.7590 and 0.4315	0.8823 and 0.4458	0.9797 and 0.9427	0.5685 and 0.1933
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	6695/0/405	7180/3/415	13287/0/557	1585/0/93

Table 4 (continued)

	20	21	22	29
Goodness-of-fit (GOF) on $F^2$	0.601	0.928	1.001	1.042
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0239$ $wR_2 = 0.0358$	$R_1 = 0.0307$ $wR_2 = 0.0763$	$R_1 = 0.0399$ $wR_2 = 0.0886$	$R_1 = 0.0199$ $wR_2 = 0.0473$
$R$ indices (all data)	$R_1 = 0.0573$ $wR_2 = 0.0389$	$R_1 = 0.0440$ $wR_2 = 0.0807$	$R_1 = 0.0922$ $wR_2 = 0.1122$	$R_1 = 0.0221$ $wR_2 = 0.0478$
Largest difference in peak and hole ( $e \text{ \AA}^{-3}$ )	0.312 and $-0.55$	1.586 and $-0.919$	0.340 and $-0.314$	3.477 and $-0.690$

one hour. The solvent was evaporated in vacuum, the residue was treated with *n*-hexane and the remaining salts were removed by filtration. Finally, the solvent was evaporated in vacuum until incipient crystallization. Storage of the solution at  $-20^\circ\text{C}$  results in quantitative crystallization of the product. Yield: 7.91 g (16.6 mmol, 62%).  $^1\text{H}$  NMR (500.133 MHz, 300 K,  $\text{C}_6\text{D}_6$ ):  $\delta = 1.20$  (d, 12H,  $\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{H,H}} = 6.8$  Hz), 1.36 (d, 12H,  $\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{H,H}} = 6.8$  Hz), 3.69 (sept., 4H,  $\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{H,H}} = 6.8$  Hz), 5.73 (s, 2H, NCH), 7.13–7.22 (m, 6H,  $\text{C}_6\text{H}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.758 MHz, 300 K,  $\text{C}_6\text{D}_6$ ):  $\delta = 24.5$  ( $\text{CH}(\text{CH}_3)_2$ ), 24.9 ( $\text{CH}(\text{CH}_3)_2$ ), 28.6 ( $\text{CH}(\text{CH}_3)_2$ ), 118.6 (CH), 125.1 (NCH), 129.4 (CH), 134.3 ( $\text{C}^q$ ), 147.9 ( $\text{C}^q$ ).  $^{15}\text{N}\{^1\text{H}\}$  INEPT NMR (50.678 MHz, 300 K,  $\text{C}_6\text{D}_6$ ):  $\delta = -297.8$ .  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99.362 MHz, 300 K,  $\text{C}_6\text{D}_6$ ):  $\delta = -38.4$ . UV–vis (*n*-hexane):  $\lambda_{\text{max}}$  [nm] = 225, 268, 278, 291, 374, 452 (shoulder).

#### 4.3. Synthesis of 1,3-bis(2,6-dimethylphenyl)-1,3-diaza-2,2-dichloro-2-silacyclopent-4-ene, **12b**

Similar to the preparation of **12a** using a solution of **10b** in thf with a concentration of  $c = 75 \text{ mmol L}^{-1}$ . Tetrachorosilane was added at  $T = -40^\circ\text{C}$ . Yield: 65%.  $^1\text{H}$  NMR (300.132 MHz, 303 K,  $\text{C}_6\text{D}_6$ ):  $\delta = 2.46$  (s, 12H  $\text{CH}_3$ ), 5.51 (s, 2H, NCH), 7.00 (s, 6H,  $\text{C}_6\text{H}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.773 MHz, 300 K,  $\text{C}_6\text{D}_6$ ):  $\delta = 18.9$  ( $\text{CH}_3$ ), 118.5 (NCH), 127.4 ( $\text{C}^{\text{para}}$ ), 129.0 ( $\text{C}^{\text{meta}}$ ), 137.7 ( $\text{C}^{\text{ipso}}$ ), 138.4 ( $\text{C}^{\text{ortho}}$ ).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99.357 MHz, 300 K,  $\text{C}_6\text{D}_6$ ):  $\delta = -41.0$ . GC/MS: RT: 12.80 min,  $m/z$  (%) 362.1 (5) [**12b** $^+$ ], 132.0 (72) [ $\text{C}_9\text{H}_{10}\text{N}^+$ ], 105.0 (100) [ $\text{C}_6\text{H}_9^+$ ].

#### 4.4. Reaction of **10b** with lithium and tetrachorosilane at $0^\circ\text{C}$

Similar to the preparation of **12a** using a solution of **10b** in thf with  $c = 236 \text{ mmol L}^{-1}$ . Tetrachorosilane was added at  $0^\circ\text{C}$ . After evaporation of the reaction solvent thf, the residue was extracted with toluene. After recrystallization from toluene the spiro compound 1,4,6,9-tetrakis(2,6-dimethylphenyl)-1,4,6,9-tetraaza-5-silaspiro[4,4]nona-2,7-diene, **13** was isolated. Yield: 10%.  $^1\text{H}$  NMR (300.132 MHz, 303 K,  $\text{C}_6\text{D}_6$ ):  $\delta = 2.09$  (s, 24H  $\text{CH}_3$ ), 5.38 (s, 4H, NCH), 6.97 (s, 12H,  $\text{C}_6\text{H}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.773 MHz, 300 K,  $\text{C}_6\text{D}_6$ ):  $\delta = 19.2$  ( $\text{CH}_3$ ), 117.5 (NCH), 125.7 ( $\text{C}^{\text{para}}$ ), 129.0 ( $\text{C}^{\text{meta}}$ ), 137.1 ( $\text{C}^{\text{ipso}}$ ), 143.1 ( $\text{C}^{\text{ortho}}$ ).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99.357 MHz, 300 K,  $\text{C}_6\text{D}_6$ ):  $\delta = -48.1$ . GC/MS: RT: 21.68 min,  $m/z$  (%) 556.3 (100) [**13** $^+$ ], 292.1 (58) [**10b** $^+$ ].

#### 4.5. Reaction of **10b** with lithium and tetrachorosilane at $-70^\circ\text{C}$

Similar to the preparation of **12a** using a solution of **10b** in thf with  $c = 236 \text{ mmol L}^{-1}$  was used. Tetrachorosilane was added at  $-70^\circ\text{C}$ . A 1:2 mixture of 1,4-bis(2,6-dimethylphenyl)-1,4-bis(trichlorosilyl)-1,4-diaza-butane-2-ene, **14** and **12b** was isolated and no further separation was performed.  $^1\text{H}$  NMR (300.132 MHz, 303 K,  $\text{C}_6\text{D}_6$ ):  $\delta = 2.27$  (s, 24H,  $\text{CH}_3$ , **14**), 2.46 (s, 12H  $\text{CH}_3$ , **12b**), 5.51 (s, 2H, NCH, **12b**), 5.93 (s, 2H, NCH, **14**), 6.91 (s, 6H,  $\text{C}_6\text{H}_3$ , **14**), 7.00 (s, 6H,  $\text{C}_6\text{H}_3$ , **12b**).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.773 MHz, 300 K,  $\text{C}_6\text{D}_6$ ):  $\delta = 18.5$  ( $\text{CH}_3$ , **14**), 18.9 ( $\text{CH}_3$ , **12b**), 117.0 (NCH, **14**), 118.5

(NCH, **12b**), 127.4 ( $\text{C}^{\text{para}}$ , **12b**), 127.8 ( $\text{C}^{\text{para}}$ , **14**), 129.0 ( $\text{C}^{\text{meta}}$ , **12b**), 129.4 ( $\text{C}^{\text{meta}}$ , **14**), 137.4 ( $\text{C}^{\text{ipso}}$ , **14**), 137.7 ( $\text{C}^{\text{ipso}}$ , **12b**), 138.3 ( $\text{C}^{\text{ortho}}$ , **14**), 138.4 ( $\text{C}^{\text{ortho}}$ , **12b**).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99.357 MHz, 300 K,  $\text{C}_6\text{D}_6$ ):  $\delta = -41.0$ . (NNSiCl<sub>2</sub>, **12b**),  $-30.0$  (NSiCl<sub>3</sub>, **14**). 12.80 min,  $m/z$  (%) 362.1 (5) [**12** $^+$ ], 132.0 (72) [ $\text{C}_9\text{H}_{10}\text{N}^+$ ], 105.0 (100) [ $\text{C}_6\text{H}_9^+$ ], 13.20 min,  $m/z$  (%) 531.9 (32) [**14** $^+$ ]; 265.9 (100) [ $\text{C}_9\text{H}_5\text{Cl}_4\text{N}_2\text{Si}_2^+$ ], 132.0 (62) [ $\text{C}_9\text{H}_{10}\text{N}^+$ ], 105.0 (84) [ $\text{C}_6\text{H}_9^+$ ].

#### 4.6. Synthesis of 1,3-bis(2,6-dimethylphenyl)-1,3-diaza-2,2-dibromo-2-silacyclopent-4-ene, **15**

Lithium (551 mg, 79.4 mmol), which was cut into small pieces, was added to a solution of **10b** (10 g, 37.8 mmol) in thf (500 mL,  $c = 75 \text{ mmol L}^{-1}$ ) at  $0^\circ\text{C}$ . The cooling bath was removed and the mixture was stirred for 16 h. Excess of lithium was removed by a pincer and the mixture was cooled to  $-40^\circ\text{C}$ . Degassed tetrabromosilane (4.7 mL, 37.7 mmol) was added in one portion. When the addition was completed the mixture was allowed to warm to room temperature and stirred for one hour. The solvent was evaporated in vacuum, the residue was treated with *n*-hexane and the salts were removed by filtration. Finally, the solvent was evaporated in vacuum until incipient crystallization. Crystals suitable for single-crystal X-ray diffraction were obtained after complete crystallization at  $-20^\circ\text{C}$ . Yield: 9.55 g (21.1 mmol, 63%).  $^1\text{H}$  NMR (500.133 MHz, 300 K,  $\text{C}_6\text{D}_6$ ):  $\delta = 2.50$  (s, 12H,  $\text{CH}_3$ ), 5.53 (s, 2H, NCH), 7.01 (m, 6H,  $\text{C}_6\text{H}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.758 MHz, 300 K,  $\text{C}_6\text{D}_6$ ):  $\delta = 19.5$  ( $\text{CH}_3$ ), 119.5 (NCH), 127.4 ( $\text{C}^{\text{para}}$ ), 129.1 ( $\text{C}^{\text{meta}}$ ), 137.7 ( $\text{C}^{\text{ipso}}$ ), 138.3 ( $\text{C}^{\text{ortho}}$ ).  $^{15}\text{N}\{^1\text{H}\}$  INEPT NMR (50.678 MHz, 300 K,  $\text{C}_6\text{D}_6$ ):  $\delta = -290.1$ .  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99.362 MHz, 300 K,  $\text{C}_6\text{D}_6$ ):  $\delta = -64.9$ . EI MS  $m/z$  (%): 453.8 (23) [**15** $^{+4}$ ], 451.8 (51) [**15** $^{+2}$ ], 449.8 [**15** $^+$ ] (20), 121.0 (100) [ $\text{C}_8\text{H}_9\text{NH}_2^+$ ]. EI HRMS calc. for [ $^{12}\text{C}_{18}^{1}\text{H}_{20}^{29}\text{Br}_2^{14}\text{N}_2^{28}\text{Si}$ ]  $m/z$  449.9763, found  $m/z$  449.9763.

#### 4.7. Synthesis of 1,3-bis(2,6-dimethylphenyl)-1,3-diaza-2-silacyclopent-4-en-2-ylidene, **9b**

A mixture of magnesium turnings (620 mg, 25.6 mmol) and **15** (10.52 g, 23.3 mmol) were stirred in thf (150 mL) at room temperature until the magnesium was consumed. The complete reduction of **15** is verified by  $^1\text{H}$  NMR. The solvent was evaporated in vacuum, the residue was dissolved in *n*-hexane and the salts were removed by filtration. Finally, the solvent was evaporated in vacuum until incipient crystallization. Crystals suitable for single-crystal X-ray diffraction were obtained after complete crystallization from *n*-hexane at  $-20^\circ\text{C}$ . Yield: 6.01 g (20.6 mmol, 80%).  $^1\text{H}$  NMR (500.133 MHz, 300 K,  $\text{C}_6\text{D}_6$ ):  $\delta = 2.27$  (s, 12H,  $\text{CH}_3$ ), 6.27 (s, 2H, NCH), 7.07 (m, 6H,  $\text{C}_6\text{H}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.772 MHz, 300 K,  $\text{C}_6\text{D}_6$ ):  $\delta = 18.5$  ( $\text{CH}_3$ ), 124.1 (NCH), 126.7 ( $\text{C}^{\text{para}}$ ), 128.6 ( $\text{C}^{\text{meta}}$ ), 135.2 ( $\text{C}^{\text{ortho}}$ ), 142.8 ( $\text{C}^{\text{ipso}}$ ).  $^{15}\text{N}\{^1\text{H}\}$  INEPT NMR (50.683 MHz, 300 K,  $\text{C}_6\text{D}_6$ ):  $\delta = 190.7$ .  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99.362 MHz, 300 K,  $\text{C}_6\text{D}_6$ ):  $\delta = 76.5$ . CI MS  $m/z$  (%): 602.4 (2) [**9b** $_2$ + $\text{H}_2\text{O}^+$ ], 349.3 (19) [**9b**+ $\text{C}_4\text{H}_9^+$ ], 293.3 (100) [**9b**+ $\text{H}^+$ ]. CI HRMS calc. for [ $^{12}\text{C}_{18}^{1}\text{H}_{20}^{14}\text{N}_2^{28}\text{Si}$ ]  $m/z$  293.1474, found  $m/z$  293.1476. UV–vis (*n*-hexane):  $\lambda_{\text{max}}$  [nm] = 225, 268, 278, 289, 385, 462 (shoulder).



#### 4.8. Synthesis of 1,3-bis(2,6-diisopropylphenyl)-1,3-diaza-2-silacyclopent-4-en-2-ylidene, **9a**

Naphthalene (420 mg, 3.2 mmol) was dissolved in thf (150 mL) and lithium (228.3 mg, 32.9 mmol), cut into small pieces, was added. When the green color of lithium naphthalide appeared, silyl dichloride **12a** (7.11 g, 14.9 mmol), dissolved in thf (40 mL) was slowly added. The mixture was stirred at room temperature for 20 h. The reduction of **12a** was monitored by  $^1\text{H}$  NMR. After the reduction was completed the solvent was evaporated in vacuum, the residue was treated with *n*-hexane and the salts were removed by filtration. Finally, the solvent was evaporated in vacuum until incipient crystallization. Crystals suitable for single-crystal X-ray diffraction were obtained after complete crystallization from *n*-hexane at  $-20^\circ\text{C}$ . Yield: 4.37 g (10.8 mmol, 72%).  $^1\text{H}$  NMR (500.133 MHz, 300 K,  $\text{C}_6\text{D}_5\text{CD}_3$ ):  $\delta = 1.22$  (d, 12H,  $\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{H,H}} = 6.7$  Hz), 1.30 (d, 12H,  $\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{H,H}} = 6.7$  Hz), 3.29 (sept., 2H,  $\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{H,H}} = 6.7$  Hz), 6.48 (s, 2H, NCH), 7.11–7.27 (m, 6H,  $\text{C}_6\text{H}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.758 MHz, 300 K,  $\text{C}_6\text{D}_6$ ):  $\delta = 24.4$  ( $\text{CH}(\text{CH}_3)_2$ ), 25.6 ( $\text{CH}(\text{CH}_3)_2$ ), 28.7 ( $\text{CH}(\text{CH}_3)_2$ ), 123.7 ( $\text{C}^{\text{meta}}$ ), 125.4 (NCH), 127.8 ( $\text{C}^{\text{para}}$ ), 139.3 ( $\text{C}^{\text{ipso}}$ ), 146.0 ( $\text{C}^{\text{ortho}}$ ).  $^{15}\text{N}\{^1\text{H}\}$  INEPT NMR (50.678 MHz, 300 K,  $\text{C}_6\text{D}_6$ ):  $\delta = -196.3$ .  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99.362 MHz, 300 K,  $\text{C}_6\text{D}_6$ ):  $\delta = 75.9$ . UV-vis (*n*-hexan):  $\lambda_{\text{max}}$  [nm] = 225, 268, 278, 290, 374 (shoulder).

#### 4.9. General method to synthesize the silicon chalcogene four-membered ring compounds **19–24**

The corresponding silylene **9** (0.5 mmol) and the chalcogene source (octasulfur 0.0625 mmol, triethylphosphane selenide, -telluride, 0.5 mmol) were dissolved in toluene and stirred 16 h at room temperature. The solvent was evaporated in vacuum and the residue was dried under reduced pressure.

##### 4.9.1. Di- $\mu$ -sulfo-di-1,3-bis(2,6-dimethylphenyl)-1,3-diaza-2-silacyclopent-4-en-2-ylidene, **19**

From silylene **9b** by reaction with elemental sulphur. Colorless crystals for single-crystal X-ray diffraction were obtained after recrystallization and storage at  $-20^\circ\text{C}$ . For recrystallization the solid was suspended in *n*-hexane (2 mL) and thf was added until a homogenous solution was obtained at room temperature. Yield: 149 mg (0.23 mmol, 45%).  $^1\text{H}$  NMR (500.133 MHz, 300 K,  $\text{C}_6\text{D}_5\text{CD}_3$ ):  $\delta = 2.21$  (s, 24H,  $\text{CH}_3$ ), 5.49 (s, 4H, NCH), 7.02 (m, 12H,  $\text{C}_6\text{H}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.773 MHz, 300 K,  $\text{C}_6\text{D}_5\text{CD}_3$ ):  $\delta = 19.0$  ( $\text{CH}(\text{CH}_3)_2$ ), 118.3 (NCH), 126.3 ( $\text{C}^{\text{para}}$ ), 128.8 ( $\text{C}^{\text{meta}}$ ), 133.3 ( $\text{C}^{\text{ortho}}$ ), 139.4 ( $\text{C}^{\text{ipso}}$ ).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99.357 MHz, 300 K,  $\text{C}_6\text{D}_5\text{CD}_3$ ):  $\delta = -39.5$ . CI MS  $m/z$  (%): 705.5 (11) [**19**+ $\text{C}_4\text{H}_9^+$ ], 650.4 (43) [**19**+2], 649.4 (79) [**19**+1], 648.4 (100) [**19**+]. CI HRMS calc. for [ $^{12}\text{C}_{36}^1\text{H}_{40}^{14}\text{N}_4^{32}\text{S}_2^{28}\text{Si}_2$ ]  $m/z$  648.2233, found  $m/z$  648.2242.

##### 4.9.2. Di- $\mu$ -seleno-di-1,3-bis(2,6-dimethylphenyl)-1,3-diaza-2-silacyclopent-4-en-2-ylidene, **20**

From silylene **9b** by reaction with triethylphosphane selenide. Colorless crystals for single-crystal X-ray diffraction were obtained after recrystallization and storage at  $-20^\circ\text{C}$ . For recrystallization the solid was suspended in *n*-hexane (2 mL) and thf was added until a homogenous solution was obtained at room temperature. Yield: 185 mg (0.25 mmol, 50%)  $^1\text{H}$  NMR (500.133 MHz, 300 K,  $\text{C}_6\text{D}_5\text{CD}_3$ ):  $\delta = 2.13$  (s, 24H,  $\text{CH}_3$ ), 5.37 (s, 4H, NCH), 6.84–6.95 (m, 12H,  $\text{C}_6\text{H}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.773 MHz, 300 K,  $\text{C}_6\text{D}_5\text{CD}_3$ ):  $\delta = 19.5$  ( $\text{CH}_3$ ), 118.7 (NCH), 126.2 ( $\text{C}^{\text{para}}$ ), 128.7 ( $\text{C}^{\text{meta}}$ ), 137.3 ( $\text{C}^{\text{ortho}}$ ), 139.7 ( $\text{C}^{\text{ipso}}$ ).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99.357 MHz, 300 K,  $\text{C}_6\text{D}_5\text{CD}_3$ ):  $\delta = -63.0$ .  $^{77}\text{Se}\{^1\text{H}\}$  NMR (95.397 MHz, 300 K,  $\text{C}_6\text{D}_5\text{CD}_3$ ):  $\delta = 186.0$ . CI MS  $m/z$  (%): 801.3 (10) [**20**+ $\text{C}_4\text{H}_9^+$ ], 745.2 (72) [**20**+1], 744.2 (70) [**20**+], 742.2 (71) [**20**+2]. CI HRMS calc. for [ $^{12}\text{C}_{36}^1\text{H}_{40}^{14}\text{N}_4^{80}\text{Se}_2^{28}\text{Si}_2$ ]  $m/z$  744.1122, found  $m/z$  744.1112.

##### 4.9.3. Di- $\mu$ -telluro-di-1,3-bis(2,6-dimethylphenyl)-1,3-diaza-2-silacyclopent-4-en-2-ylidene, **21**

From silylene **9b** by reaction with triethylphosphane telluride. Oxygen and water sensitive, red crystals for single-crystal X-ray diffraction were obtained after complete crystallization from [ $\text{D}_8$ ]toluene at  $-20^\circ\text{C}$ . For recrystallization the solid was suspended in *n*-hexane (2 mL) and thf was added until a homogenous solution was obtained at room temperature. Yield: 193 mg (0.23 mmol, 46%).  $^1\text{H}$  NMR (500.133 MHz, 300 K,  $\text{C}_6\text{D}_5\text{CD}_3$ ):  $\delta = 2.18$  (s, 24H,  $\text{CH}_3$ ), 5.28 (s, 4H, NCH), 6.88–6.95 (m, 12H,  $\text{C}_6\text{H}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.773 MHz, 300 K,  $\text{C}_6\text{D}_5\text{CD}_3$ ):  $\delta = 20.4$  ( $\text{CH}_3$ ), 119.0 (NCH), 126.4 ( $\text{C}^{\text{para}}$ ), 128.9 ( $\text{C}^{\text{meta}}$ ), 137.3 ( $\text{C}^{\text{ortho}}$ ), 140.1 ( $\text{C}^{\text{ipso}}$ ).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99.357 MHz, 300 K,  $\text{C}_6\text{D}_5\text{CD}_3$ ):  $\delta = -137.9$  ( $J_{\text{Si,Te}} = 314$  Hz).  $^{125}\text{Te}\{^1\text{H}\}$  NMR (157.845 MHz, 300 K,  $\text{C}_6\text{D}_5\text{CD}_3$ ):  $\delta = 483.0$  ( $J_{\text{Si,Te}} = 315$  Hz). CI MS  $m/z$  (%): 844.2 (58) [**23**+], 842.2 (96) [**21**+2], 840.1 (100) [**21**+4], 838.1 (68) [**21**+6]. CI HRMS calc. for [ $^{12}\text{C}_{36}^1\text{H}_{40}^{14}\text{N}_4^{28}\text{Si}_2^{130}\text{Te}_2$ ]  $m/z$  844.0926, found  $m/z$  844.0938. UV-vis (thf):  $\lambda_{\text{max}}$  [nm] = 216, 246, 251, 259, 266, 345 (shoulder), 450.

##### 4.9.4. Di- $\mu$ -sulfo-di-1,3-bis(2,6-diisopropylphenyl)-1,3-diaza-2-silacyclopent-4-en-2-ylidene, **22**

From silylene **9a** by reaction with elemental sulphur. Colorless crystals for single-crystal X-ray diffraction were obtained after recrystallization and storage at  $-20^\circ\text{C}$ . For recrystallization the solid was suspended in *n*-hexane (2 mL) and thf was added until a homogenous solution was obtained at room temperature. Yield: 144 mg (0.2 mmol, 82%).  $^1\text{H}$  NMR (500.133 MHz, 300 K,  $\text{C}_6\text{D}_6$ ):  $\delta = 1.15$  (d, 24H,  $\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{H,H}} = 6.8$  Hz), 1.17 (d, 24H,  $\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{H,H}} = 6.8$  Hz), 3.49 (sept., 8H,  $\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{H,H}} = 6.8$  Hz), 5.63 (s, 4H, NCH), 7.05–7.22 (m, 12H,  $\text{C}_6\text{H}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.773 MHz, 300 K,  $\text{C}_6\text{D}_6$ ):  $\delta = 23.6$  ( $\text{CH}(\text{CH}_3)_2$ ), 26.3 ( $\text{CH}(\text{CH}_3)_2$ ), 28.8 ( $\text{CH}(\text{CH}_3)_2$ ), 120.1 ( $\text{C}^{\text{meta}}$ ), 124.1 (NCH), 127.6 ( $\text{C}^{\text{para}}$ ), 137.3 ( $\text{C}^{\text{ipso}}$ ), 148.0 ( $\text{C}^{\text{ortho}}$ ).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99.361 MHz, 300 K,  $\text{C}_6\text{D}_6$ ):  $\delta = -38.8$ . CI MS  $m/z$  (%): 872.8 (80) [**22**+ $\text{H}^+$ ], 871.8 (100) [**22**+], 377.0 (95) [ $\text{C}_{26}\text{H}_{36}\text{N}_2+\text{H}^+$ ], 178.0 (84) [ $\text{C}_{12}\text{H}_{17}\text{NH}_2+\text{H}^+$ ]. CI HRMS calc. for [ $^{12}\text{C}_{52}^1\text{H}_{72}^{14}\text{N}_4^{32}\text{S}_2^{28}\text{Si}_2$ ]  $m/z$  872.4737, found  $m/z$  872.4738.

##### 4.9.5. Di- $\mu$ -seleno-di-1,3-bis(2,6-diisopropylphenyl)-1,3-diaza-2-silacyclopent-4-en-2-ylidene, **23**

From silylene **9a** by reaction with triethylphosphane selenide. Colorless solid were isolated after recrystallization and storage at  $-20^\circ\text{C}$ . For recrystallization the solid was suspended in *n*-hexane (2 mL) and thf was added until a homogenous solution was obtained at room temperature. Yield: 165 mg (0.17 mmol, 69%).  $^1\text{H}$  NMR (500.133 MHz, 300 K,  $\text{C}_6\text{D}_6$ ):  $\delta = 1.18$  (d, 48H,  $\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{H,H}} = 6.7$  Hz), 3.50 (sept., 8H,  $\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{H,H}} = 6.7$  Hz), 5.64 (s, 4H, NCH), 7.08–7.24 (m, 12H,  $\text{C}_6\text{H}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.773 MHz, 300 K,  $\text{C}_6\text{D}_6$ ):  $\delta = 23.7$  ( $\text{CH}(\text{CH}_3)_2$ ), 26.5 ( $\text{CH}(\text{CH}_3)_2$ ), 29.0 ( $\text{CH}(\text{CH}_3)_2$ ), 120.2 ( $\text{C}^{\text{meta}}$ ), 124.1 (NCH), 127.6 ( $\text{C}^{\text{para}}$ ), 137.3 ( $\text{C}^{\text{ipso}}$ ), 148.2 ( $\text{C}^{\text{ortho}}$ ).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99.362 MHz, 300 K,  $\text{C}_6\text{D}_6$ ):  $\delta = -61.7$ .  $^{77}\text{Se}\{^1\text{H}\}$  NMR (95.402 MHz, 300 K,  $\text{C}_6\text{D}_6$ ):  $\delta = 197.3$ . CI MS  $m/z$  (%): 871.8 (7) [**23**+ $\text{C}_4\text{H}_9^+$ ], 967.4 (100) [**23**+ $\text{H}^+$ ], 379.0 (38) [ $\text{C}_{26}\text{H}_{38}\text{N}_2+\text{H}^+$ ], 178.0 (20) [ $\text{C}_{12}\text{H}_{17}\text{NH}_2+\text{H}^+$ ]. CI HRMS calc. for [ $^{12}\text{C}_{52}^1\text{H}_{72}^{14}\text{N}_4^{80}\text{Se}_2^{28}\text{Si}_2$ ]  $m/z$  968.3626, found  $m/z$  968.3629.

##### 4.9.6. Di- $\mu$ -telluro-di-1,3-bis(2,6-diisopropylphenyl)-1,3-diaza-2-silacyclo-pent-4-en-2-ylidene, **24**

From silylene **9a** by reaction with triethylphosphane telluride. A red solid was isolated after recrystallization and storage at  $-20^\circ\text{C}$ . For recrystallization the solid was suspended in *n*-hexane (2 mL) and thf was added until a homogenous solution was obtained at room temperature. Yield: 26 mg (25  $\mu\text{mol}$ , 5%)  $^1\text{H}$  NMR (500.133 MHz, 300 K,  $\text{C}_6\text{D}_6$ ):  $\delta = 1.18$  (d, 24H,  $\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{H,H}} = 6.6$  Hz), 1.26 (d, 24H,  $\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{H,H}} = 6.6$  Hz), 3.47 (sept., 8H,  $\text{CH}(\text{CH}_3)_2$ ,  $^3J_{\text{H,H}} = 6.6$  Hz), 5.60 (s, 4H, NCH), 7.14–7.29 (m,

12H, C<sub>6</sub>H<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.758 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>): δ = 24.2 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.1 (CH(CH<sub>3</sub>)<sub>2</sub>), 29.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 120.0 (C<sup>meta</sup>), 124.3 (NCH), 127.6 (C<sup>para</sup>), 137.4 (C<sup>ipso</sup>), 148.3 (C<sup>ortho</sup>). <sup>29</sup>Si{<sup>1</sup>H} NMR (99.354 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>): δ = -131.2 (<sup>1</sup>J<sub>Si,Te</sub> = 310 Hz). <sup>125</sup>Te{<sup>1</sup>H} NMR (157.861 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>): δ = 451.9 (<sup>1</sup>J<sub>Si,Te</sub> = 309 Hz). CI MS *m/z* (%): 1063.7 (0.2) [**24**+H<sup>+</sup>], 379.3 (19) [C<sub>26</sub>H<sub>38</sub>N<sub>2</sub>+H<sup>+</sup>], 178.2 (16) [C<sub>12</sub>H<sub>17</sub>NH<sub>2</sub>+H<sup>+</sup>]. CI HRMS calc. for [<sup>12</sup>C<sub>52</sub><sup>1</sup>H<sub>72</sub><sup>14</sup>N<sub>4</sub><sup>28</sup>Si<sub>2</sub><sup>130</sup>Te<sub>2</sub>] *m/z* 1068.3430, found 1068.3430. UV-vis (thf): λ<sub>max</sub> [nm] = 215, 246, 251, 257, 266, 350 (shoulder), 450.

#### 4.9.7. Synthesis of **23** and **24** in presence of 2,3-dimethyl-butadiene

Compound **9a** (400 mg, 0.98 mmol) and 2,3-dimethyl-1,3-butadiene (0.56 mL, 4.9 mmol) were dissolved in thf (30 mL). At -100 °C the corresponding triethylphosphane chalcogenide, dissolved in thf (10 mL), was added slowly. The mixture was warmed slowly to room temperature and stirred for additional 24 h. The analysis of the reaction mixture by <sup>1</sup>H NMR only showed the formation of the corresponding four-membered hetero cycles **23** and **24**. The mixture was heated to reflux for another 12 h. Finally, the thf was evaporated in vacuum and the residue was dried under reduced pressure. NMR spectroscopy indicated only the formation of **23** and **24**.

#### 4.10. Synthesis of the silylene tungsten pentacarbonyl complex, **29**

The W(CO)<sub>5</sub>(thf) complex **30** was prepared according to literature [52] by UV irradiation of W(CO)<sub>6</sub> (1.203 g, 3.42 mmol) in thf. Silylene **9b** (1 g, 3.42 mmol) was dissolved in thf (50 mL) and added to the solution of W(CO)<sub>5</sub>(thf) **30**. The mixture was stirred over night at room temperature. Finally, the solvent was evaporated in vacuum and recrystallized twice from *n*-hexane. Deep violet crystals suitable for single-crystal X-ray diffraction were obtained after complete crystallization from *n*-hexane at -20 °C. Yield: 984 mg (1.6 mmol, 47%). <sup>1</sup>H NMR (499.873 MHz, 305 K, C<sub>6</sub>D<sub>6</sub>) δ = 2.26 (s, 12H, CH<sub>3</sub>), 6.07 (s, 2H, NCH), 7.03 (m, 6H, C<sub>6</sub>H<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (125.706 MHz, 305 K, C<sub>6</sub>D<sub>6</sub>) δ = 18.1 (CH<sub>3</sub>), 124.7 (NCH), 127.8 (C<sup>para</sup>), 128.2 (C<sup>meta</sup>), 135.6 (C<sup>ortho</sup>), 139.6 (C<sup>ipso</sup>), 193.7 (CO, <sup>1</sup>J<sub>C,W</sub> = 120.8 Hz), 196.6 (CO, <sup>1</sup>J<sub>C,W</sub> = 144.3 Hz). <sup>15</sup>N{<sup>1</sup>H} INEPT NMR (50.651 MHz, 305 K, C<sub>6</sub>D<sub>6</sub>) δ = 170.9. <sup>29</sup>Si{<sup>1</sup>H} NMR (99.311 MHz, 305 K, C<sub>6</sub>D<sub>6</sub>) δ = 109.1 (<sup>1</sup>J<sub>Si,W</sub> = 163.6 Hz). CI MS *m/z* (%) 616.1 (100) [**29**<sup>+</sup>], 560.2 (22) [**29**-2CO<sup>+</sup>], 532.2 (20) [**29**-3CO<sup>+</sup>], 266.3 (16) [C<sub>18</sub>H<sub>22</sub>N<sub>2</sub><sup>+</sup>], CI HRMS calc. for [<sup>12</sup>C<sub>23</sub><sup>1</sup>H<sub>21</sub><sup>14</sup>N<sub>2</sub><sup>16</sup>O<sub>5</sub><sup>28</sup>Si<sup>184</sup>W] *m/z* 617.0730, found *m/z* 617.0710. IR(nujol) ν = 2069 cm<sup>-1</sup>, 2011 cm<sup>-1</sup>, 1980 cm<sup>-1</sup>.

#### 4.11. Reaction of **9a** with ethanol

Silylene **9a** (400 mg, 0.98 mmol) was dissolved in thf (2 mL). A solution of ethanol (57 μL, 0.98 mmol) in thf (2 mL) was added slowly. The reaction mixture was stirred for 16 h. Finally, the solvent was evaporated in vacuum and the residue was dried under reduced pressure. Yield 214 mg: The percentage of the three contained products was calculated by integration of GC spectra of the GC/MS experiments: 13.8% **17**, 34.4% **16**, 15.7% **18**. The remaining 35% are a mixture of five unidentified products. <sup>1</sup>H NMR (500.133 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>): δ = 0.85 (t), 0.99 (t), 1.12 (t), 1.21 (d), 1.27 (d), 1.31 (d), 1.34 (d), 1.35 (d), 1.38 (d), 1.42 (d), 3.46 (q), 3.48 (sept.), 3.66 (sept.), 3.76 (q), 3.80 (q), 3.91 (sept.), 5.71 (s), 5.79 (s), 7.14–7.29 (m). <sup>13</sup>C{<sup>1</sup>H} NMR (125.773 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>): δ = 18.1, 18.3, 18.4, 23.1, 23.9, 24.4, 25.2, 25.7, 26.2, 28.1, 28.2, 28.5, 30.1, 58.6, 59.2, 59.8, 117.2, 118.1, 119.0, 123.9, 124.0, 124.2, 124.9, 126.0, 127.4, 138.3, 138.9, 140.9, 142.8, 147.9, 148.4, 148.8. <sup>29</sup>Si{<sup>1</sup>H} NMR INEPT (99.357 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>): δ = -38.6, -63.4. <sup>29</sup>Si NMR INEPT (99.362 MHz, 300 K, C<sub>6</sub>D<sub>6</sub>): δ = -38.6 (d, <sup>1</sup>J<sub>Si,H</sub> = 270 Hz). GC/MS: RT: 22.81 min, *m/z* (%) 450.2

(100) [**16**<sup>+</sup>]; RT: 23.15 min, *m/z* (%) 378.2 (32) [**18**<sup>+</sup>]; RT: 24.02 min, *m/z* (%) 494.3 (100) [**17**<sup>+</sup>].

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.10.034.

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