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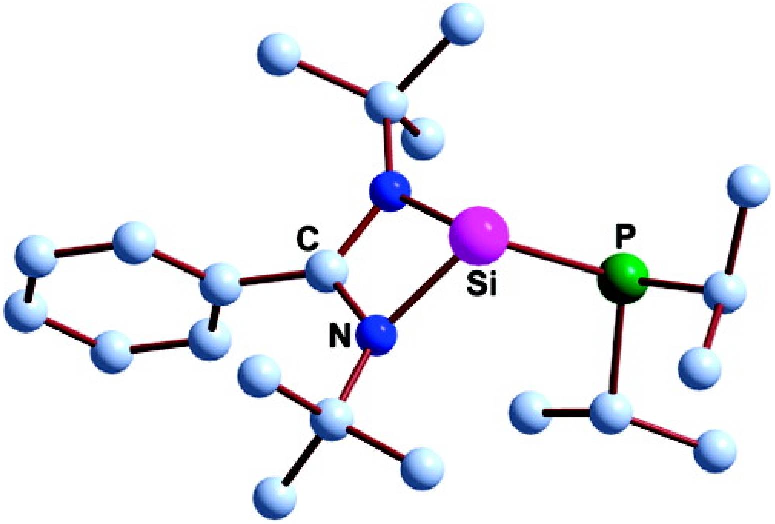
*J. Am. Chem. Soc.*, **2007**, 129 (39), 12049-12054• DOI: 10.1021/ja074019e • Publication Date (Web): 11 September 2007



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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Published on Web 09/11/2007

# Synthesis and Structures of Heteroleptic Silylenes

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***Abstract:*** The reaction of benzamidinato silicon trichloride $[\{\mathrm{PhC(NR)_2}\}\mathrm{SiCl_3}]$ [R = $\mathrm{Bu}^t$ (**1**), $\mathrm{SiMe_3}$ (**2**)] with 2 equiv of potassium in THF afforded mononuclear chlorosilylene $[\{\mathrm{PhC(NBu}^t)_2\}\mathrm{SiCl}]$ (**3**) and $[\{\mathrm{PhC(NSiMe_3)_2}\}_2\mathrm{SiCl_2}]$ (**4**), respectively. Compound **4** was formed by the disproportionation of unstable $[\{\mathrm{PhC(NSiMe_3)_2}\}\mathrm{SiCl}]$. The reaction of $[\{\mathrm{PhC(NBu}^t)_2\}\mathrm{SiCl_3}]$ (**1**) with 1 equiv of LiR (R = $\mathrm{NMe_2}$, $\mathrm{OBu}^t$, $\mathrm{OPr}^i$, $\mathrm{PPr}^i_2$) in THF yielded $[\{\mathrm{PhC(NBu}^t)_2\}\mathrm{SiCl_2R}]$ [R = $\mathrm{NMe_2}$ (**5**), $\mathrm{OBu}^t$ (**6**), $\mathrm{OPr}^i$ (**7**), $\mathrm{PPr}^i_2$ (**8**)]. Treatment of **5**−**8** with 2 equiv of potassium in THF resulted in the novel heteroleptic silylene $[\{\mathrm{PhC(NBu}^t)_2\}\mathrm{SiR}]$ [R = $\mathrm{NMe_2}$ (**9**), $\mathrm{OBu}^t$ (**10**), $\mathrm{OPr}^i$ (**11**), $\mathrm{PPr}^i_2$ (**12**)]. Compounds **4**, **9**, and **12** have been analyzed by X-ray crystallography.

## Introduction

In the past 20 years the chemistry of stable silylene has attracted much attention due to the carbene-like properties.[1] The first example of a stable silylene $[\mathrm{Si}\{\mathrm{N(Bu}^t)\mathrm{CHCHN(Bu}^t)\}]$ was reported by West's group in 1994.[2] However, only a handful of room-temperature stable silylene complexes were then synthesized and structurally characterized.[3] They are kinetically stabilized by nitrogen-containing bulky ligands. One of the main stabilizing factors is the donation of lone pair electrons from the nitrogen atom to the vacant p orbital at the silicon(II) center. All of them can be synthesized by the reduction of dihalidesilane precursor with alkali metals, since mononuclear $\mathrm{SiCl_2}$ is not available at room temperature. Gaseous silicon dichloride can be prepared by the reaction of silicon with silicon tetrachloride at high temperatures. It is unstable and polymerizes to insoluble perchloropolysilane $(\mathrm{SiCl_2})_n$.[4] It is well-known that silylene complexes with small substituents such as Me, Ph, or even $\mathrm{NPr}^i_2$ are regarded as reactive intermediates.[5] Recently, we have communicated the synthesis of the first stable mononuclear chlorosilylene $[\{\mathrm{PhC(NBu}^t)_2\}\mathrm{SiCl}]$ by reduction of $[\{\mathrm{PhC(NBu}^t)_2\}\mathrm{SiCl_3}]$ (**1**).[6] We anticipate that reactive silylene can be stabilized with the aid of the bulky benzamidinate ligand $\{\mathrm{PhC(NBu}^t)_2\}$. Herein, we report the synthesis and structures of $[\{\mathrm{PhC(NBu}^t)_2\}\mathrm{SiNMe_2}]$, $[\{\mathrm{PhC(NBu}^t)_2\}\mathrm{SiOR}]$ (R = $\mathrm{Bu}^t$, $\mathrm{Pr}^i$), and $[\{\mathrm{PhC(NBu}^t)_2\}\mathrm{SiPPr}^i_2]$.

## Results and Discussion

In our previous communication, we reported the synthesis of novel chlorosilylene $[\{\mathrm{PhC(NBu}^t)_2\}\mathrm{SiCl}]$ (**3**) by the reaction of benzamidinato silicon trichloride $[\{\mathrm{PhC(NBu}^t)_2\}\mathrm{SiCl_3}]$ (**1**) with 2 equiv of potassium in THF.[6] Compound **3** is stable in the solid and solution state under an inert atmosphere at room temperature. Similar benzamidinato silicon trichloride $[\{\mathrm{PhC(NSiMe_3)_2}\}\mathrm{SiCl_3}]$ (**2**) can be prepared from the reaction of $[\mathrm{LiN(SiMe_3)_2}]$ with PhCN and $\mathrm{SiCl_4}$.[7] The reduction of **2** with 2 equiv of potassium in THF for 1.5 days did not afford mononuclear chlorosilylene $[\{\mathrm{PhC(NSiMe_3)_2}\}\mathrm{SiCl}]$; instead the formation of a six-coordinate $[\{\mathrm{PhC(NSiMe_3)_2}\}_2\mathrm{SiCl_2}]$ (**4**) was observed, which is confirmed by NMR spectroscopy and single-crystal X-ray structural analysis (see the Supporting Information) (Scheme 1). The reaction pathway suggested that $[\{\mathrm{PhC(NSiMe_3)_2}\}\mathrm{SiCl}]$ is unstable, maybe due to the $\mathrm{SiMe_3}$ ligands compared to the bulkier $\mathrm{Bu}^t$ groups in **3**. The $^{29}\mathrm{Si}$ NMR of **4**

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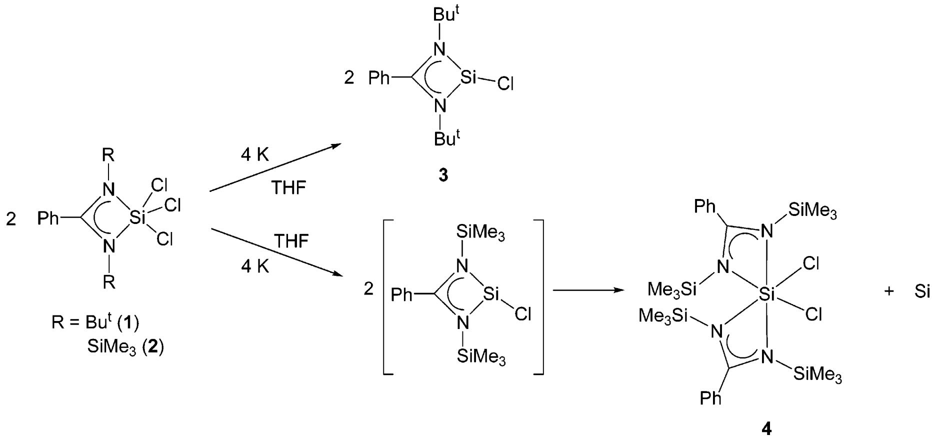
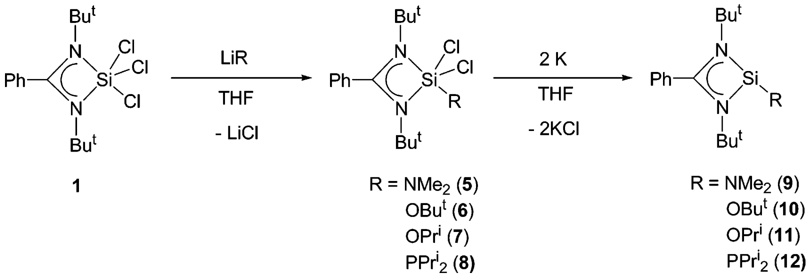
**10.1021/ja074019e CCC: $37.00 © 2007 American Chemical Society**

***Scheme 1.*** Synthesis of **3** and **4**



***Scheme 2.*** Synthesis of **5**−**12**



exhibits three resonances, which correspond to the $SiCl_2$ (−175.98 ppm) and two resonances for the nonequivalent $SiMe_3$ groups (1.19 and 4.39 ppm). Similar six-coordinate [{MeC(NPr$^i$)$_2$}$_2$SiCl$_2$] has been synthesized by the reaction of [{MeC(NPr$^i$)$_2$}$_2$Li·THF] with $SiCl_4$.[8] [{MeC(NPr$^i$)$_2$}$_2$SiCl$_2$] shows remarkable stability. It cannot be reduced by potassium and is stable upon heating in toluene at 100 °C for several days.

Chlorosilylene [{PhC(NSiMe$_3$)$_2$}SiCl] was calculated by the B3LYP[9] hybrid functional as implemented in the Gaussian program package[10] with cc-pvtz basis sets for all the geometry optimizations at the DFT level of theory. The detailed coordinates of the resulting optimized structure are given in the Supporting Information. It shows that the disproportionation of [{PhC(NSiMe$_3$)$_2$}SiCl] to [{PhC(NSiMe$_3$)$_2$}$_2$SiCl$_2$] (**4**) and Si is favorable with $\Delta H = -65$ kcal/mol.

Attempted reduction of less sterically hindered benzamidinato silicon trichloride [{PhC(NR′)$_2$}SiCl$_3$] (R′ = Pr$^i$, cyclohexyl) with potassium under various conditions resulted in a mixture of products. It is suggested that chlorosilylene cannot be stabilized without sterically hindered substituents at the benzamidinate ligand. However, when the phenyl ring in [{PhC(NBu$^t$)$_2$}SiCl$_3$] (**1**) is replaced by alkyl substituents such as Bu$^t$ or Pr$^i$, the reduction is not successful. The results suggested that the phenyl ring at the benzamidinate ligand stabilizes the electron density within the highly delocalized benzamidinato ring system. Therefore, the benzamidinate ligand "{PhC(NBu$^t$)$_2$}" is applied to stabilize the reactive silylene.

The reaction of **1** with 1 equiv of LiR (R = NMe$_2$, OBu$^t$, OPr$^i$, PPr$^i_2$) in THF afforded [{PhC(NBu$^t$)$_2$}SiCl$_2$R] [R = NMe$_2$ (**5**), OBu$^t$ (**6**), OPr$^i$ (**7**), PPr$^i_2$ (**8**)], respectively (Scheme 2). Compounds **5**−**8** were obtained as colorless crystalline solids and have been confirmed by NMR spectroscopy, electron impact mass spectrometry (EI-MS), and elemental analysis. The $^1H$ and $^{13}C$ NMR spectra of **5**−**8** correspond to the benzamidinate ligand. The $^{29}Si$ NMR spectra of **5**−**8** [$\delta$ −87.2 (**5**), −112.2 (**6**), −107.7 (**7**), −78.6 (**8**)] indicate pentacoordination at the silicon.[11]

Treatment of **5**−**8** with 2 equiv of potassium in THF for 17 h afforded the novel heteroleptic silylene [{PhC(NBu$^t$)$_2$}SiR] [R = NMe$_2$ (**9**), OBu$^t$ (**10**), OPr$^i$ (**11**), PPr$^i_2$ (**12**)] (Scheme 2). Compounds **9**−**12** were isolated as colorless crystalline solids with good solubility in diethyl ether, toluene, and tetrahydrofuran. They are stable in solution or in the solid state at room temperature under an inert atmosphere. Heteroleptic silylenes are rare. In contrast, germanium analogues, such as [{HC(CMeNAr)$_2$}GeX] (Ar = 2,6-Pr$^i_2$C$_6$H$_3$; X = H, Me, Bu$^n$, OH),[12] [MamxGeX] [Mamx = methylamino-methyl-*m*-xylyl; X = Me, Bu$^n$, Bu$^t$, C≡CPh, OBu$^t$, N$_3$, N(SiMe$_3$)$_2$],[13] [{Pr$^i_2$ATI}GeX] (ATI = aminotroponiminate; X = N$_3$, OSO$_2$CF$_3$)[14] are extensively investigated.

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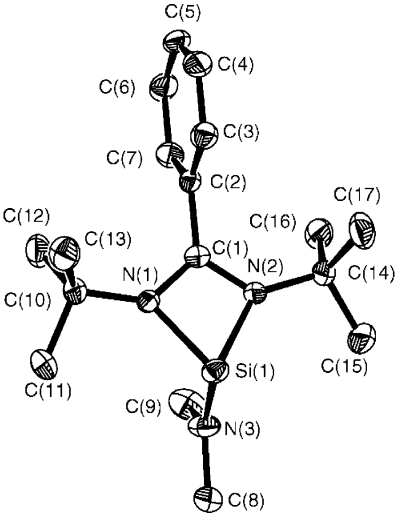

***Figure 1.*** Molecular structure of **9**. Thermal ellipsoids are set at the 50% probability level. H atoms are omitted for clarity.

Compound **9** is the first example of a room-temperature stable system containing a dimethylamine group attached to a silicon(II) center. Until now, only cyclic diaminosilylenes have been isolated.[3a−d,f,g] West's group has reported the synthesis of $[\{(Me_3Si)_2N\}_2Si]$, but this compound is only stable at low temperature.[15] Similarly, the existence of $[(Pr^{i}_{2}N)_2Si]$ generated photochemically from 3-bis(diisopropylamino)-1,2-bis(trimethylsilyl)-3-silacyclopropane was confirmed by trapping experiments.[5d] It is suggested that the benzamidinate ligand stabilizes the reactive Si(II)−NMe$_2$ bond.

The $^{29}$Si NMR spectrum of **9** exhibits one singlet ($\delta$ −2.62 ppm) which shows an upfield shift when compared with that of $[\{PhC(NBu^{t})_2\}SiCl]$ ($\delta$ 14.6 ppm).[6] It is assumed that the lone pair electrons of NMe$_2$ are donated to the vacant p orbital at the silicon(II) center so that the deshielding of the silicon atom is reduced. The $^1$H NMR spectrum at 298 K displays one broad resonance ($\delta$ 2.59 ppm) corresponding to the N*Me*$_2$ group. This may be due to the rotation of the NMe$_2$ group at the silicon center in solution. At 233 K, the rotation slowed down and the $^1$H NMR spectrum exhibits two sharp singlets ($\delta$ 2.43 and 2.70 ppm).

The molecular structure of **9** is shown in Figure 1. Compound **9** crystallizes in the space group *Pc* (Table 1); it is a mononuclear heteroleptic silylene. The benzamidinate ligand is bonded in a N,N′ chelate to the silicon center, and the latter displays a trigonal pyramidal geometry (Table 1). The sum of bond angles at the silicon center is 274.4° and 274.1° in two independent molecules. The four-membered Si(1)−N(1)−C(1)−N(2) ring is planar, and the phenyl ring is orthogonally arranged to this plane. The Si(1)−N(3) bond distance (1.724(2), 1.722(2) Å) in **9** is slightly shorter than the theoretical calculated value of $[\{(Me_3Si)_2N\}_2Si]$ (1.779 Å).[15] Similarly, it is shorter than those in cyclic diaminosilylenes $[Si\{N(CH_2Bu^{t})\}_2C_6H_3$-1,2-H-4] (1.752(3), 1.747(3) Å)[3a] and $[HC\{C(Me)NAr\}\{C(CH_2)NAr\}Si]$ (Ar = 2,6-$Pr^{i}_{2}C_6H_3$) (1.734, 1.735(1) Å)[3g] (Table 2).

Compound **9** was investigated by means of quantum chemical calculations (Table 3). The molecule was first fully optimized with the DFT-variant B3LYP[9] as implemented in the Gaussian program package[10] employing the 6-31G basis set expanded with additional double-diffuse functions.[16] The calculated structural parameters (Si(1)−N(1) 1.941 Å, Si(1)−N(3) 1.758 Å, N(1)−C(10) 1.477 Å, N(3)−C(8) 1.453 Å; N(3)−Si(1)−N(2) 103.28°, N(2)−Si(1)−N(1) 67.24°, C(1)−Si(1)−N(1) 91.92°, C(8)−N(3)−C(9) 113.03°) are in good agreement with the crystallographic data. The natural bond orbital (NBO) analysis shows that none of the bonds formed by silicon are stable since most of the electronic density is on the nitrogen atoms (Table 3).[17] The stability of these bonds results from the redistribution of electronic density out of the phenyl group over the nitrogen atoms of the benzamidinate ring to the silicon and the attached NMe$_2$ substituent. This strengthening can be seen in the donor−acceptor interactions. The Si(1)−N(1) and Si(1)−N(2) bonds are stabilized by 14 kcal/mol each through the interaction with an antibonding C(1)−C(2) orbital. The Si(1)−N(3) bond gains 26 kcal/mol by interacting with the antibonding Si(1)−N(1) and Si(1)−N(2) orbitals.

***Table 1.*** Crystallographic Data for Compounds **9** and **12**

| | **9** | **12** |
|---|---|---|
| formula | $C_{17}H_{29}N_3Si$ | $C_{21}H_{37}N_2PSi$ |
| molecular weight | 303.5 | 376.6 |
| color | colorless | colorless |
| cryst syst | monoclinic | monoclinic |
| space group | *Pc* | *P*2(1) |
| *a* (Å) | 9.147(8) | 9.062(2) |
| *b* (Å) | 18.235(2) | 10.209(2) |
| *c* (Å) | 12.117(1) | 12.720(3) |
| $\beta$ (deg) | 111.94(4) | 94.17(3) |
| *V* (Å$^3$) | 1874.8(3) | 1173.8(4) |
| *Z* | 4 | 2 |
| $d_{calcd}$ (g cm$^{-3}$) | 1.075 | 1.066 |
| *M* (mm$^{-1}$) | 0.124 | 0.174 |
| *F*(000) | 664 | 412 |
| cryst size (mm) | 0.40 × 0.35 × 0.25 | 0.50 × 0.50 × 0.20 |
| 2$\theta$ range (deg) | 2.13−30.51 | 2.25−29.16 |
| index range | $-13 \le h \le 13$,<br>$-26 \le k \le 26$,<br>$-17 \le l \le 17$ | $-12 \le h \le 12$,<br>$-13 \le k \le 13$,<br>$0 \le l \le 17$ |
| no. of rflns collected | 35157 | 6303 |
| R1, wR2 ($I > 2(\sigma)I$) | 0.0493, 0.0720 | 0.0283, 0.0671 |
| R1, wR2 (all data) | 0.0935, 0.0798 | 0.0322, 0.0683 |
| goodness of fit, $F^2$ | 0.881 | 0.962 |
| no. of data/restraints/params | 11222/2/395 | 6303/1/374 |
| largest diff peaks, eÅ$^{-3}$ | 0.575 and −0.280 | 0.202 and −0.151 |

***Table 2.*** Selected Bond Distances (angstroms) and Angles (deg) for Compounds **9** and **12**

| | | | |
|---|---|---|---|
| | $[\{PhC(NBu^{t})_2\}SiNMe_2]$ (**9**) | | |
| Si(1)−N(1) | 1.905(1) | Si(1)−N(2) | 1.893(1) |
| Si(1)−N(3) | 1.724(2) | C(1)−N(1) | 1.335(2) |
| C(1)−N(2) | 1.342(2) | | |
| N(1)−Si(1)−N(3) | 102.8(7) | N(2)−Si(1)−N(3) | 103.4(7) |
| N(1)−Si(1)−N(2) | 68.3(6) | Si(1)−N(1)−C(1) | 91.8(1) |
| N(1)−C(1)−N(2) | 105.6(1) | | |
| | $[\{PhC(NBu^{t})_2\}SiPPr^{i}_{2}]$ (**12**) | | |
| Si(1)−P(1) | 2.307(8) | Si(1)−N(1) | 1.881(1) |
| Si(1)−N(2) | 1.875(1) | C(5)−N(1) | 1.345(2) |
| C(5)−N(2) | 1.335(2) | | |
| N(1)−Si(1)−P(1) | 107.4(4) | N(2)−Si(1)−P(1) | 99.8(4) |
| N(1)−Si(1)−N(2) | 69.3(5) | Si(1)−N(2)−C(5) | 92.2(8) |
| N(2)−C(5)−N(1) | 105.7(1) | C(5)−N(1)−Si(1) | 91.6(8) |

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*Table 3.* Selected Calculated Data of **9**

| bond | occupancy | MO 1 | contr.[a] | type | MO 2 | contr.[a] | type |
|---|---|---|---|---|---|---|---|
| C(1)−N(1 ) | 1.98157 | C(1) | 39.88% | s(31.08%)<br>$p^{2.21}$(68.83%) | N(1) | 60.12% | s(35.09%)<br>$p^{1.85}$(64.86%) |
| N(1)−C(1 0) | 1.98153 | N(1) | 62.12% | s(36.82%)<br>$p^{1.72}$(63.15%) | C(10) | 37.88% | s(21.50%)<br>$p^{3.65}$(78.36%) |
| C(1)−C(2) | 1.97202 | C(1) | 49.53% | s(36.12%)<br>$p^{1.77}$(63.85%) | C(2) | 50.47% | s(30.36%)<br>$p^{2.29}$(69.61%) |
| Si(1)−N(1 ) | 1.88686 | Si(1) | 10.07% | s(8.41%)<br>$p^{7.52}$(63.21%)<br>$d^{3.38}$(28.39%) | N(1) | 89.93% | s(28.07%)<br>$p^{2.56}$(71.91%) |
| Si(1)−N(2 ) | 1.89098 | Si(1) | 9.74% | s(8.41%)<br>$p^{7.51}$(63.22%)<br>$d^{3.37}$(28.37%) | N(2) | 90.26% | s(27.61%)<br>$p^{2.62}$(72.37%) |
| Si(1)−N(3 ) | 1.96381 | Si(1) | 14.41% | s(13.47%)<br>$p^{6.23}$(83.87%)<br>$d^{0.20}$(2.66%) | N(3) | 85.59% | s(38.47%)<br>$p^{1.60}$(61.50%) |
| N(3)−C(8 ) | 1.99250 | N(3) | 60.86% | s(30.90%)<br>$p^{2.24}$(69.07%) | C(8) | 39.14% | s(25.08%)<br>$p^{2.98}$(74.80%) |

[a] contr. = contribution.

Compounds **10** and **11** are alkoxide-substituted silylenes. In 1989, Maier et al. synthesized the dimethoxysilylene intermediate [$Si(OMe)_2$] by the pyrolysis of hexamethoxydisilane.[18] Its existence can be demonstrated by the trapping reactions with dimethylacetylene or 2,3-dimethylbutadiene. Recently, a siloxyl silylene [$HC\{C(Me)NAr\}_2SiOSi(H)\{NArC(CH_2)\}\{NArC(Me)\}CH$] has been synthesized by the reaction of [$HC\{C(Me)NAr\}\{C(CH_2)NAr\}Si$] with $H_2O$.[19] Compounds **10** and **11** have been confirmed by NMR spectroscopy, EI-MS, and elemental analysis. The $^1H$ and $^{13}C$ NMR spectra of **10** and **11** display one set of resonances due to the ligand backbone and alkoxide substituent. The $^{29}Si$ NMR spectra of **10** and **11** exhibit one singlet [$\delta$ −5.19 ppm (**10**), $\delta$ −13.4 ppm (**11**)] which are slightly upfield shifted when compared with that of **9**. However, X-ray structure analysis of **10** and **11** were unsuccessful due to nonmerohedral twinning.

Short-lived or stable diphosphino silylenes [$Si(PR_2)_2$] are rare. Only bis(diphosphinomethanide) silylene [$Si\{(PMe_2)_2C(SiMe_3)\}_2$] has been reported, although this molecule has a tetracoordinated silicon atom.[20] With the aid of a benzamidinate ligand, a novel silylene consisting of a small phosphino substituent [$\{PhC(NBu^t)_2\}SiPPr^i_2$] (**12**) with three-coordinate silicon was isolated. The $^{31}P$ NMR spectrum of **12** shows one singlet ($\delta$ −16.5 ppm) which exhibits an upfield shift when compared with that of tetracoordinate [$Si\{(PMe_2)_2C(SiMe_3)\}_2$] ($\delta$ −5.2 ppm) and pentacoordinate [$\{PhC(NBu^t)_2\}SiCl_2PPr^i_2$] (**8**) ($\delta$ 1.86 ppm).[20] The $^{29}Si$ NMR spectrum of **12** exhibits a doublet ($\delta$ 56.2 ppm, $J_{Si-P}$ = 154 Hz) which shows a downfield shift as compared with that of five-coordinate [$\{PhC(NBu^t)_2\}SiPPr^i_2Cl_2$] ($\delta$ −78.6 ppm, $J_{Si-P}$ = 68.6 Hz) and three-coordinate [$\{PhC(NBu^t)_2\}SiCl$] silicon ($\delta$ 14.6 ppm).[6] The two-coordinate silicon chemical shift of N-heterocyclic silylenes is in the range from +78 to +119 ppm.[2,3]

The molecular structure of **12** (Figure 2) is similar to that of **9**. Compound **12** crystallizes in the space group *P*2(1) (Table 1); it is a mononuclear phosphino silylene. The benzamidinate ligand is bonded in a N,N′ chelate to the silicon center. The angle of N(2)−Si(1)−P(1) (107.4°) is larger than that of N(1)−Si(1)−P(1) (99.8°). The silicon center displays a distorted trigonal pyramidal geometry. The sum of bond angles at the silicon center is 276.5°. The Si(1)−P(1) bond distance in **12** (2.307(8) Å) is slightly longer when compared with that in tetracoordinate silicon of [$Si\{(PMe_2)_2C(SiMe_3)\}_2$] (2.271(4) Å)[20] (Table 2).

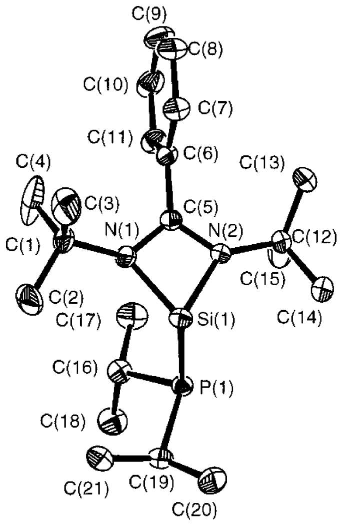

*Figure 2.* Molecular structure of **12**. Thermal ellipsoids are set at the 50% probability level. H atoms are omitted for clarity.

Compound **12** was analyzed by quantum theoretical calculation using DFT-variant B3LYP employing a basis set termed 6-31G(d′,p′).[9] The coordinates of the optimized structure are given in the Supporting Information. The NBO analysis was carried out to explain the bonding between N−Si and Si−P.[17] The calculated bond can be described as c1 × hybrid1 + c2 × hybrid2, where the coefficients c1 and c2 denote the polarization coefficient. The calculated N−Si bond is $0.9296 \times sp^{2.59}(N) + 0.3686 \times sp^{9.74}$, whereas the calculated Si−P bond is $0.5479 \times sp^{9.50}(Si) + 0.8365 \times sp^{2.29}(P)$. From the polarization coefficient, larger electronic density can be found on P than on Si. The formation of ionic species in solution might be possible due to the donor−acceptor interactions between the localized orbitals. This may account for the downfield shift of the $^{29}Si$ NMR resonance of **12**. The interaction of a filled bonding donor orbital with an empty antibonding acceptor orbital weakens the bond belonging to the acceptor NBO. One of the Si−N bonds

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is weakened by the interaction with Si−P, P−C, and Si−N′ bonding donor orbitals. In conclusion, this result indicates that the interaction of **12** with metal carbonyl fragments will predominately occur at the phosphorus rather than at the silicon atom. Interpretation for supporting this assumption is in progress in our laboratory.

## Experimental Section

All manipulations were carried out under an inert atmosphere of dinitrogen gas by standard Schlenk techniques. Solvents were dried over and distilled from Na/K alloy prior to use. $\mathrm{LiPPr}^i{}_2$[21] was prepared as described in the literature. $\mathrm{LiNMe_2}$, $\mathrm{LiOBu}^t$, and $\mathrm{LiOPr}^i$ were purchased from Aldrich Chemicals and used without further purification. The $^1$H, $^{13}$C, $^{31}$P, and $^{29}$Si spectra were recorded on a Bruker Avance 500 instrument. The NMR spectra were recorded in THF-$d_8$ or $C_6D_6$, and the chemical shifts $\delta$ are relative to $\mathrm{SiMe_4}$ and 85% $H_3PO_4$ for $^1$H, $^{13}$C, $^{29}$Si, and $^{31}$P, respectively. Elemental analyses were performed by the Institut für Anorganische Chemie, Universität Göttingen. Melting points were measured in a sealed glass tube and were not corrected.

**[{PhC(NSiMe$_3$)$_2$}$_2$SiCl$_2$] (4).** THF (50 mL) was added to a mixture of **2** (2.10 g, 5.28 mmol) and finely divided potassium (0.41 g, 10.6 mmol) at ambient temperature. The resulting red mixture was stirred for 1.5 days. The solvent was then removed in vacuo, and the residue was extracted with $\mathrm{Et_2O}$/hexane (1:1, 20 mL). The insoluble solid was filtered off, and the red filtrate was concentrated to yield colorless crystals of **4** at −30 °C. $^1$H NMR ($C_6D_6$): $\delta = 0.11$ (s, 9H, SiMe$_3$), 0.34 (s, 9H, SiMe$_3$), 6.88−7.02 (m, 3H, Ph), 7.25−7.38 (m, 2H, Ph). $^{29}$Si{$^1$H} NMR ($C_6D_6$): $\delta = -175.98$ (SiCl$_2$), 1.19 (SiMe$_3$), 4.39 (SiMe$_3$).

**[{PhC(NBu$^t$)$_2$}SiCl$_2$NMe$_2$] (5).** A solution of $\mathrm{LiNMe_2}$ (0.44 g, 8.61 mmol) in THF (50 mL) was added dropwise to **1** (3.15 g, 8.61 mmol) in THF (20 mL) at −78 °C. The reaction mixture was stirred at room temperature for 2 days. Volatiles of the mixture were removed under reduced pressure, and the residue was extracted with $\mathrm{Et_2O}$. After filtration and concentration of the filtrate, **5** was obtained as colorless crystals at −30 °C. Yield: 1.17 g (36.3%). Mp 120.7 °C. Elemental Anal. found (%): C, 54.36; H, 7.73; N, 11.07. Calcd for $\mathrm{C_{17}H_{29}Cl_2N_3Si}$: C, 54.53; H, 7.81; N, 11.22. $^1$H NMR ($C_6D_6$): $\delta = 1.18$ (s, 18H, Bu$^t$), 2.76 (s, 6H, Me), 6.73−6.98 (m, 5H, Ph). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta = 31.8$ (C*Me*$_3$), 38.9 (NMe$_2$), 55.1 (*C*Me$_3$), 127.5, 127.7, 127.8, 128.5, 128.9, 129.8 (Ph), 170.9 (N*C*N). $^{29}$Si{$^1$H} NMR ($C_6D_6$): $\delta = -87.2$. EI-MS *m*/*z*: 374 [M$^+$].

**[{PhC(NBu$^t$)$_2$}SiCl$_2$OBu$^t$] (6).** An analogous experimental procedure as for **5** was used. The reaction of $\mathrm{LiOBu}^t$ (0.72 g, 8.97 mmol) with **1** (3.28 g, 8.97 mmol) afforded **6** as colorless crystals. Yield: 2.75 g (76.0%). Mp 117.8 °C. Elemental Anal. found (%): C, 56.41; H, 7.86; N, 6.74. Calcd for $\mathrm{C_{19}H_{32}Cl_2N_2OSi}$: C, 56.56; H, 7.99; N, 6.94. $^1$H NMR ($C_6D_6$): $\delta = 1.24$ (s, 18H, NBu$^t$), 1.68 (s, 9H, OBu$^t$), 6.72−6.94 (m, 5H, Ph). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta = 31.7$ (OC*Me*$_3$), 31.9 (C*Me*$_3$), 55.4 (*C*Me$_3$), 75.7 (O*C*Me$_3$), 127.7, 128.7, 129.8, 133.5 (Ph), 170.4 (N*C*N). $^{29}$Si{$^1$H} NMR ($C_6D_6$): $\delta = -112.2$. EI-MS *m*/*z*: 404 [M$^+$].

**[{PhC(NBu$^t$)$_2$}SiCl$_2$OPr$^i$] (7).** An analogous experimental procedure as for **5** was used. The reaction of **1** (3.49 g, 9.54 mmol) with $\mathrm{LiOPr}^i$ (0.63 g, 9.54 mmol) in THF afforded **7** as colorless crystals. Yield: 2.23 g (60.0%). Mp 103.2 °C. Elemental Anal. found (%): C, 55.29; H, 7.43; N, 7.01. Calcd for $\mathrm{C_{18}H_{30}Cl_2N_2OSi}$: C, 55.52; H, 7.76; N, 7.19. $^1$H NMR ($C_6D_6$): $\delta = 1.23$ (s, 18H, Bu$^t$), 1.33−1.42 (d, 6H, CH*Me*$_2$), 4.93−5.08 (sept, 1H, C*H*Me$_2$), 6.71−6.93 (m, 5H, Ph). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta = 25.9$ (CH*Me*$_2$), 32.4 (C*Me*$_3$), 56.1 (*C*Me$_3$), 67.6 (*C*HMe$_2$), 128.3, 128.4, 128.5, 129.2, 130.4, 133.6 (Ph), 172.3 (N*C*N). $^{29}$Si{$^1$H} NMR ($C_6D_6$): $\delta = -107.7$. EI-MS *m*/*z*: 389 [M$^+$].

**[{PhC(NBu$^t$)$_2$}SiCl$_2$PPr$^i{}_2$] (8).** An analogous experimental procedure as for **5** was used. The reaction of **1** (3.35 g, 9.16 mmol) with $\mathrm{LiPPr}^i{}_2$ (1.14 g, 9.16 mmol) in THF afforded **8** as colorless crystals. Yield: 1.07 g (26.2%). Mp 134.2 °C. Elemental Anal. found (%): C, 56.10; H, 8.07; N, 5.98. Calcd for $\mathrm{C_{21}H_{37}Cl_2N_2PSi}$: C, 56.36; H, 8.33; N, 6.26. $^1$H NMR (THF-$d_8$): $\delta = 1.26-1.40$ (s + d + d, 30 H, Bu$^t$ + CH*Me*$_2$), 2.32−2.51 (td, 2H, C*H*Me$_2$), 7.41−7.53 (m, 5H, Ph). $^{13}$C{$^1$H} NMR (THF-$d_8$): $\delta = 23.5$ (*C*HMe$_2$), 23.7 (*C*HMe$_2$), 25.0 (CH*Me*$_2$), 25.6 (CH*Me*$_2$), 32.5 (C*Me*$_3$), 57.1 (*C*Me$_3$), 128.6, 130.0, 131.1, 134.6, (Ph), 172.5 (N*C*N). $^{31}$P{$^1$H} NMR (THF-$d_8$) $\delta = 1.86$. $^{29}$Si{$^1$H} NMR (THF-$d_8$): $\delta = -78.6$ (d, $J_{\mathrm{Si-P}} = 68.6$ Hz). EI-MS *m*/*z*: 448 [M$^+$].

**[{PhC(NBu$^t$)$_2$}SiNMe$_2$] (9).** THF (50 mL) was added to a mixture of **5** (1.17 g, 3.12 mmol) and finely divided potassium (0.24 g, 6.24 mmol) at ambient temperature. The resulting red mixture was stirred for 17 h. The solvent was then removed in vacuo, and the residue was extracted with $\mathrm{Et_2O}$ (50 mL). The insoluble solid was filtered off, and the red filtrate was concentrated to yield colorless crystals of **9**. Yield: 0.39 g (41.1%). Mp 87 °C. Elemental Anal. found (%): C, 67.13; H, 9.41; N, 13.68. Calcd for $\mathrm{C_{17}H_{29}N_3Si}$: C, 67.27; H, 9.63; N, 13.84. $^1$H NMR (THF-$d_8$, 25 °C): $\delta = 1.01$ (s, 18H, Bu$^t$), 2.59 (br, 6H, Me), 7.23−7.47 (m, 5H, Ph). $^{13}$C{$^1$H} NMR (THF-$d_8$, 25 °C): $\delta = 31.7$ (C*Me*$_3$), 52.9 (*C*Me$_3$), 128.5, 128.6, 128.9, 130.1, 131.1, 135.6 (Ph), 161.7 (N*C*N). $^1$H NMR (THF-$d_8$, −40 °C): $\delta = 1.10$ (s, 18H, Bu$^t$), 2.43 (s, 3H, Me), 2.70 (s, 3H, Me), 7.32−7.53 (m, 5H, Ph). $^{13}$C{$^1$H} NMR (THF-$d_8$, −40 °C): $\delta = 31.5$ (C*Me*$_3$), 36.1, 41.3 (N*Me*$_2$), 52.8 (*C*Me$_3$), 128.7, 128.8, 130.3, 131.1, 135.3 (Ph), 161.9 (N*C*N). $^{29}$Si{$^1$H} NMR ($C_6D_6$, 25 °C): $\delta = -2.62$. EI-MS *m*/*z*: 304 [M$^+$].

**[{PhC(NBu$^t$)}SiOBu$^t$] (10).** THF (50 mL) was added to a mixture of **6** (2.75 g, 6.82 mmol) and finely divided potassium (0.53 g, 13.6 mmol) at ambient temperature. The resulting orange mixture was stirred for 17 h. The solvent was then removed in vacuo, and the residue was extracted with $\mathrm{Et_2O}$ (50 mL). The insoluble solid was filtered off. The orange filtrate was concentrated and stored at 4 °C to yield colorless crystals of **10**. Yield: 1.17 g (51.6%). Mp 114.5 °C. Elemental Anal. found (%): C, 68.47; H, 9.52; N, 8.21. Calcd for $\mathrm{C_{19}H_{32}N_2OSi}$: C, 68.62; H, 9.70; N, 8.42. $^1$H NMR ($C_6D_6$): $\delta = 1.21$ (s, 18H, Bu$^t$), 1.59 (s, 9H, OBu$^t$), 6.78−6.97 (m, 4H, Ph), 7.05−7.12 (m, 1H, Ph). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta = 31.7$ (C*Me*$_3$), 32.8 (OC*Me*$_3$), 52.8 (*C*Me$_3$), 71.6 (O*C*Me$_3$), 127.3, 127.6, 127.7, 128.8, 129.7, 134.5 (Ph), 162.7 (N*C*N). $^{29}$Si{$^1$H} NMR ($C_6D_6$): $\delta = -5.19$. EI-MS *m*/*z*: 333 [M$^+$].

**[{PhC(NBu$^t$)$_2$}SiOPr$^i$] (11).** An analogous experimental procedure as for **10** was used. The reaction of **7** (2.23 g, 5.73 mmol) and finely divided potassium (0.45 g, 11.5 mmol) afforded colorless crystals of **11**. Yield: 0.72 g (45.4%). Mp 73.9 °C. Elemental Anal. found (%): C, 67.65; H, 9.21; N, 8.47. Calcd for $\mathrm{C_{18}H_{30}N_2OSi}$: C, 67.87; H, 9.49; N, 8.79. $^1$H NMR ($C_6D_6$): $\delta = 1.17$ (s, 18H, Bu$^t$), 1.33−1.42 (d, 6H, CH*Me*$_2$), 4.31−4.52 (sept, 1H, C*H*Me$_2$), 6.80−7.01 (m, 4H, Ph), 7.02−7.11 (m, 1H, Ph). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta = 26.9$ (CH*Me*$_2$), 31.8 (C*Me*$_3$), 52.89 (*C*Me$_3$), 65.2 (*C*HMe$_2$), 127.6, 127.9, 129.3, 130.2, 134.4, 134.5 (Ph), 163.7 (N*C*N). $^{29}$Si{$^1$H} NMR ($C_6D_6$): $\delta = -13.4$. EI-MS *m*/*z*: 319 [M$^+$].

**[{PhC(NBu$^t$)$_2$}SiPPr$^i{}_2$] (12).** An analogous experimental procedure as for **9** was used. The reaction of **8** (1.07 g, 2.39 mmol) and finely divided potassium (0.19 g, 4.78 mmol) afforded colorless crystals of **12**. Yield: 0.47 g (52.2%). Mp 63.5 °C. Elemental Anal. found (%): C, 66.71; H, 9.83; N, 7.27. Calcd for $\mathrm{C_{21}H_{37}N_2PSi}$: C, 66.98; H, 9.90; N, 7.44. $^1$H NMR ($C_6D_6$): $\delta = 1.21$ (s, 18H, Bu$^t$), 1.44−1.47 (d, 6H, CH*Me*$_2$), 1.50−1.54 (d, 6H, CH*Me*$_2$), 2.48 (m, 2H, C*H*Me$_2$), 6.87−7.01 (m, 4H, Ph), 7.21 (m, 1H, Ph). $^{13}$C{$^1$H} NMR ($C_6D_6$): $\delta = 23.2$ (*C*HMe$_2$), 23.3(*C*HMe$_2$), 23.4 (CH*Me*$_2$), 23.5 (CH*Me*$_2$), 31.9 (C*Me*$_3$), 53.6 (*C*Me$_3$), 127.6, 128.3, 128.5, 129.6, 130.2 (Ph), 155.5 (N*C*N). $^{31}$P{$^1$H}NMR ($C_6D_6$) $\delta = -16.5$. $^{29}$Si{$^1$H} NMR ($C_6D_6$): $\delta = 56.2$ (d, $J_{\mathrm{Si-P}} = 154$ Hz). EI-MS *m*/*z*: 377 [M$^+$].

**X-ray Data Collection and Structural Refinement.** Intensity data for compounds **9** and **12** were collected using a Bruker SMART CCD

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area detector and Stoe IPDS 2T, respectively, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The crystals of **9** and **12** were measured at 133(2) and 170(2) K, respectively. The structures were solved by direct phase determination (SHELXS-97) and refined for all data by full-matrix least-squares methods on $F^2$.[22] All non-hydrogen atoms were subjected to anisotropic refinement. Methyl hydrogens were included using idealized rigid groups allowed to rotate but not tip; other H were generated geometrically and allowed to ride on their respective parent atoms. A summary of X-ray data is given in Table 1. (X-ray structure and crystal data for **4** are given in the Supporting Information.)

**Acknowledgment.** Dedicated to Professor Robert West. This work was supported by the Göttinger Akademie der Wissenschaften. C.-W.S. thanks the Alexander von Humboldt Stiftung for a Research Fellowship. The authors are grateful to Professor Frank T. Edelmann for the measurement of X-ray data. C.-W.S. thanks Mr. Ying Yang for the measurement of NMR data. We thank the referees for their valuable suggestions.

**Supporting Information Available:** Complete ref 10, complete atomic coordinates, anisotropic displacement coefficients, and isotropic displacement coefficients for hydrogen atoms and summary of crystal data, data collection, and refinement for **9** and **12**, calculated structure atomic coordinates of the unstable silylenes, **4** and **12**, X-ray data (CIF) of **9**, **12**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

JA074019E

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