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# Reactions of Stable *N*-Heterocyclic Silylenes with Ketones and 3,5-Di-*tert*-butyl-*o*-benzoquinone

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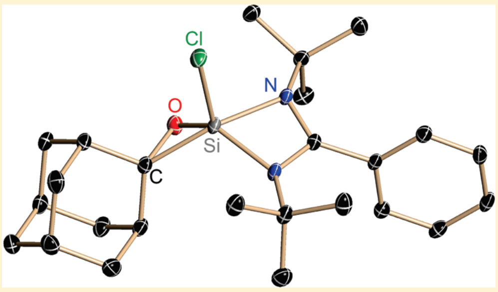
S *Supporting Information*

**ABSTRACT:** The reactions of **L** [PhC(N$t$Bu)$_2$SiCl] and **L′** [CH{(C=CH$_2$)(CMe)(2,6-$i$Pr$_2$C$_6$H$_3$N)$_2$}Si] with monoketones and quinone have been examined. The reaction of **L** with 2-adamantanone furnishes a [1 + 2]−cycloaddition product **1**, whereas with 3,5-di-*tert*-butyl-*o*-benzoquinone leads to the [1 + 4]−cycloaddition product **2**. The treatment of **L′** with 3,5-di-*tert*-butyl-*o*-benzoquinone gives [1 + 4]−cycloaddition product **3**, and the reaction with acylferrocene yields compound **4**. Compounds **1**−**4** were characterized by single crystal X-ray structural analysis, NMR spectroscopy, EI−MS spectrometry, and elemental analysis.



## INTRODUCTION

Silylenes are silicon analogues of carbenes and exist with neutral divalent silicon atoms.[1] The first stable *N*-heterocyclic silylene (NHSi) was reported by West et al.,[2] in 1994. Since then, many stable NHSis[1b−d,3] and other silylenes have been isolated.[4] The reactivity pattern of NHSis is quite comparable with that of the N-heterocyclic carbenes (NHCs), where the latter led to many applications in chemistry.[5,6] Silylenes have two nonbonding electrons in the HOMO which possess nucleophilic character, and an empty 3p-orbital as the LUMO which causes electrophilic properties. They possess both nucleophilic and electrophilic reactive sites at the same silicon atom, therefore they are ambiphilic and behave as Lewis acids as well as Lewis bases.[7] Owing to this, there is an extensive research activity going on in the chemistry of NHSis, which is very challenging (insertion: C−H,[8] N−H,[9] O−H,[10] S−H,[9a] P−P,[11] N−Si,[12] C−F,[13] C−X (Cl, Br, I),[14] Si−Cl,[14] P−H,[15] As−H,[15] addition,[8a,9c,9d,16] metal complexes,[17] Lewis acids[18]). In addition, the reactions of silylenes with organic substrates lead to a number of interesting new organosilicon compounds, which are otherwise difficult to achieve.[1e,f] Recently, we became interested in the reactivity studies of silylenes **L** [PhC(N$t$Bu)$_2$SiCl] and **L′** [CH{(C=CH$_2$)(CMe)(2,6-$i$Pr$_2$C$_6$H$_3$N)$_2$}Si] toward organic substrates.[3b,9b−9d,13,19] Inspired by the diverse reactivity shown by silylenes with ketones,[8a,9d,16a,19a,19d] we report herein the reactions of silylenes **L** and **L′** with 2-adamantanone, 3,5-di-*tert*-butyl-*o*-benzoquinone, and acylferrocene. The reaction of **L** with 2-adamantanone favors a [1 + 2]−cycloaddition product **1**, whereas with 3,5-di-*tert*-butyl-*o*-benzoquinone leads to [1 + 4]−cycloaddition product **2**. Treatment of **L′** with 3,5-di-*tert*-butyl-*o*-benzoquinone affords the [1 + 4]−cycloaddition product **3**, and the reaction with acylferrocene gives compound **4**.

## RESULTS AND DISCUSSION

Compounds **1** and **2** were obtained in good yield when **L** was treated with 2-adamantanone and 3,5-di-*tert*-butyl-*o*-benzoquinone in 1:1 ratio as shown in Scheme 1, whereas compounds **3** and **4** were formed upon reaction of **L′** with 3,5-di-*tert*-butyl-*o*-benzoquinone and acylferrocene in 1:1 ratio (Scheme 2). Compounds **1**−**4** were unequivocally established by single crystal X-ray structural analyses. Furthermore, all structures were fully characterized by NMR spectroscopy, EI−MS, and elemental analysis.

The reaction of **L** with an equimolar amount of 2-adamantanone resulted in silaoxirane **1**. Compound **1** is soluble in toluene and benzene and insoluble in *n*-hexane and *n*-pentane. It is stable both in the solid state as well as in solution without any decomposition under an inert gas atmosphere. The $^{29}$Si NMR spectrum of **1** shows a single resonance at $\delta$ −104.80 ppm, which is upfield shifted when compared with that of **L** ($\delta$ 14.6 ppm).[3a] The $t$Bu protons of compound **1** in the $^1$H NMR spectrum exhibit a singlet which is observed at $\delta$ 1.16 ppm and is downfield shifted compared to that of **L** ($\delta$ 1.08 ppm). In addition, **1** shows its molecular ion in the mass spectrum at $m/z$ 444.

The silaoxirane product **1** was unambiguously established by single crystal X-ray structural analysis. **1** crystallizes in the triclinic space group $P2_1/c$, and the molecular structure is shown in Figure 1. We propose that the reaction of **L** with 2-adamantanone followed the [1 + 2]−cycloaddition reaction. The silicon atom is in a distorted square pyramidal geometry, made up from two nitrogen atoms, a single oxygen atom, a carbon atom, and a chlorine atom. The structural index $\tau$ which defines the extent of deviation from trigonal bipyramidal to square pyramidal geometry ($\tau = 1$ for perfect trigonal bipyramidal; $\tau = 0$ for perfect square based pyramid[20]) is 0.14, indicating strong deviation from the regular TBP geometry and closer to square pyramidal geometry. Such a silicon atom with almost distorted square pyramidal geometry is rare.[21] There is little change in the N−Si−N bite angle at the silicon atom with the backbone ligand. In **1** it is

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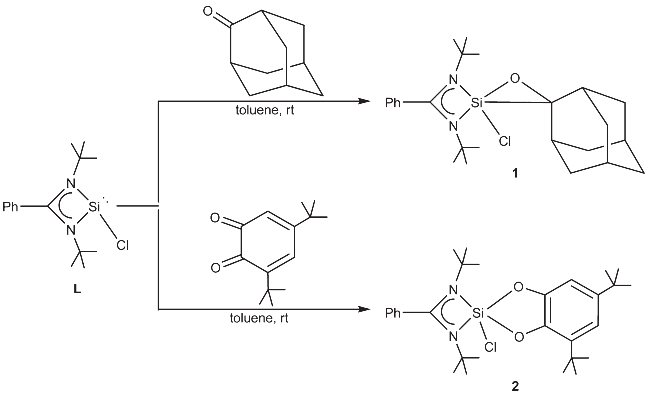
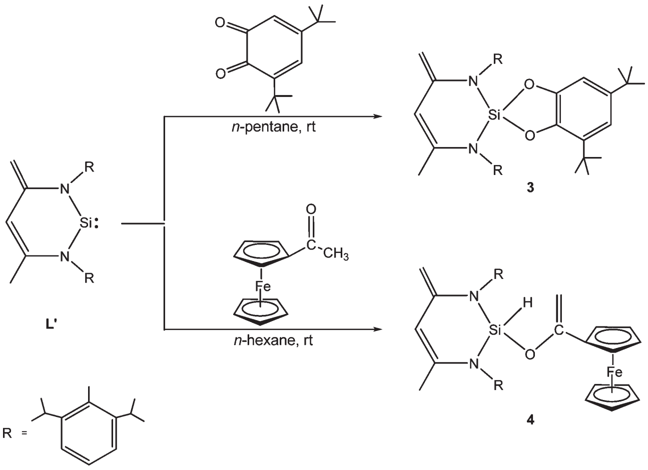
**Scheme 1. Synthesis of 1 and 2**



**Scheme 2. Synthesis of 3 and 4**



70.48(5)°, whereas in **L** it is 71.15(7)°. There is shortening of the Si−Cl bond length (2.0930(5) Å) in **1** when compared to that of **L** [Si−Cl of **L** 2.156(1) Å]. The angles of the newly formed OSiC three-membered ring are O−Si−C (52.26(6)°), Si−C−O (57.22(6)°), and C−O−Si (70.52(7)°). Correspondingly, the bond distances within the three-membered ring are Si−O (1.6462(11) Å), O−C (1.5485(17) Å), and Si−C (1.8461(15) Å). These values are quite comparable to those of other silaoxirane compounds reported in the literature.[16a,19a]

Treatment of **L** with 3,5-di-*tert*-butyl-*o*-benzoquinone afforded the [1 + 4]−cycloaddition product **2**. Compound **2** is soluble in all common organic solvents. Similar to **1**, it is stable both in the solid state as well as in solution under an inert gas atmosphere. Like **1**, the $^{29}$Si NMR spectrum of **2** is upfield shifted with a single resonance at $\delta$ −94.58 ppm. The *t*Bu protons for compound **2** in the $^{1}$H NMR spectrum show a single resonance at $\delta$ 1.24 ppm. In addition, the *t*Bu protons of the 3,5-di-*tert*-butyl-*o*-benzoquinone exhibit resonances at 1.34 and 1.69 ppm. Compound **2** shows its molecular ion in the mass spectrum at *m*/*z* 514.

The [1 + 4]−cycloaddition product **2** was confirmed by single crystal X-ray structural analysis. Compound **2** crystallizes in the orthorhombic space group $P2_12_12_1$, and the molecular structure is depicted in Figure 2. The right absolute structure is confirmed by the refinement of the Flack-x-parameter to 0.03(5).[22] Compared to **1**, the silicon atom is also pentacoordinate, made up of two nitrogen atoms, two oxygen atoms, and a chlorine atom. The coordination polyhedron of the central silicon atom is located halfway between that of a trigonal bipyramid and a square pyramid with $\tau$ = 0.50. Like in **1**, there is a small variation of the N−Si−N bite angle (70.00(7)°) at the silicon atom with the backbone ligand. The Si−Cl bond length is 2.0858(8) Å, and the distances of Si(1)−O(1) and Si(1)−O(2) are 1.7204(14) Å and 1.6906(14) Å, respectively.

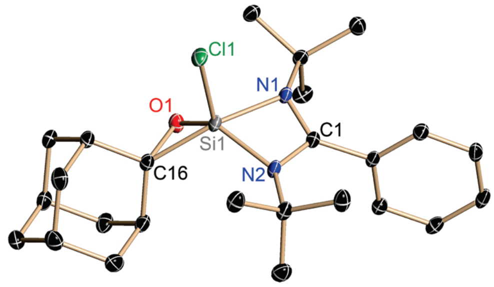


**Figure 1.** Molecular structure of **1**. The anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si(1)−N(1) 1.8997(13), Si(1)−N(2) 1.8176(13), Si(1)−O(1) 1.6462(11), Si(1)−Cl(1) 2.0930(5), Si(1)−C(16) 1.8461(15), O(1)−C(16) 1.5485(17), C(1)−N(1) 1.3188(18), C(1)−N(2) 1.3559(18), O(1)−Si(1)−N(2) 131.79(6), O(1)−Si(1)−C(16) 52.26(6), N(2)−Si(1)−C(16) 114.56(6), O(1)−Si(1)−N(1) 98.50(6), N(2)−Si(1)−N(1) 70.48(5), C(16)−Si(1)−N(1) 146.59(6), O(1)−Si(1)−Cl(1) 117.33(4), N(2)−Si(1)−Cl(1) 110.73(5), C(16)−Si(1)−Cl(1) 109.40(5), N(1)−Si(1)−Cl(1) 98.08(4), C(16)−O(1)−Si(1) 70.52(7), O(1)−C(16)−Si(1) 57.22(6).

However, the reaction of 3,5-di-*tert*-butyl-*o*-benzoquinone with **L′** afforded the [1 + 4]−cycloaddition product **3**. It is soluble in *n*-hexane, *n*-pentane, toluene, and benzene. In addition, it is stable both in the solid state as well as in solution. The $^{29}$Si NMR spectrum of **3** shows a single resonance ($\delta$ −49.36 ppm), which is shifted upfield compared to that of **L′** ($\delta$ 88.4 ppm).[3c] The $\gamma$−C*H* proton for compound **3** in the $^{1}$H NMR spectrum is observed at $\delta$ 5.38 ppm and is upfield shifted when compared with that of **L′** ($\delta$ 5.44 ppm). The NCC$H_2$ protons in **3** exhibit sharp singlets at 3.42 and 4.02 ppm ($\delta$ for **L′** = 3.32 and 3.91 ppm). Compound **3** shows its molecular ion in the mass spectrum at *m*/*z* 664.4.

Compound **3** crystallizes in the triclinic space group $P\bar{1}$, and the structure is shown in Figure 3. In **3**, the silicon atom is tetracoordinate in a distorted tetrahedral geometry comprising two nitrogen atoms (from the supporting ligand) and two oxygen atoms. The silicon atom is dislocated from $N_2C_3$ ligand plane by 0.304(2) Å. There is a shortening of bonds observed between the Si atom and the nitrogen atoms of the supporting ligand. The average bond distance between Si−N$_{av}$ in **3** is 1.6992(18) Å, whereas in **L′** it is 1.7345(10) Å. The bite angle (N−Si−N) at the silicon atom with the backbone ligand is 106.06(8)°, compared to 99.317(54)° in **L′**. The bond lengths Si1−O1 (1.6647(15) Å) and Si1−O2 (1.6607(15) Å) are indicating single bonds.[23] The newly formed $SiC_2O_2$ five-membered ring is nearly orthogonal arranged to the $SiN_2C_3$ six-membered ring. The dihedral angle between the two planes is 85.68(5)°.

The reaction of **L′** with an equimolar amount of acylferrocene in *n*-hexane at room temperature proceeds rapidly with the formation

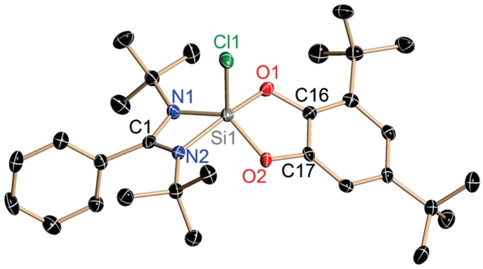


**Figure 2.** Molecular structure of **2**. The anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si(1)−N(2) 1.9060(18), Si(1)−N(1) 1.8164(18), Si(1)−O(1) 1.7204(14), Si(1)−Cl(1) 2.0858(8), Si(1)−O(2) 1.6906(14), O(1)−C(16) 1.378(2), C(1)−N(1) 1.362(3), C(1)−N(2) 1.3606(3), O(2)−C(17) 1.375(2), C(16)−C(17) 1.389(3), O(2)−Si(1)−O(1) 90.59(7), O(2)−Si(1)−N(1) 131.49(8), O(1)−Si(1)− N(1) 99.30(7), O(2)−Si(1)−N(2) 88.38(7), O(1)−Si(1)−N(2) 164.15(7), N(1)−Si(1)−N(2) 70.00(7), O(2)−Si(1)−Cl(1) 116.01(6), O(1)−Si(1)−Cl(1) 98.05(5), N(1)−Si(1)−Cl(1) 109.43(6), N(2)−Si(1)−Cl(1) 96.61(6).

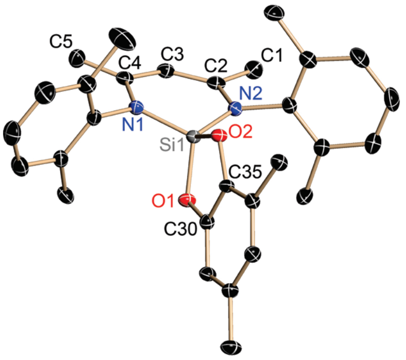


**Figure 3.** Molecular structure of **3**. The anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): N(1)−Si(1) 1.6955(18), N(2)−Si(1) 1.7028(17), O(1)−Si(1) 1.6647(15), O(2)−Si(1) 1.6607(15), C(35)−O(2) 1.396(2), C(30)−O(1) 1.385(2), C(30)−C(35) 1.387(3), C(1)−C(2) 1.477(3), C(4) − C(5) 1.364(3), O(2)−Si(1)−O(1) 96.04(7), O(2)−Si(1)−N(1) 118.62(8), O(1)−Si(1)−N(1) 110.09(8), O(2)−Si(1)−N(2) 109.28(8), O(1)−Si(1)−N(2) 117.13(8), N(1)−Si(1)−N(2) 106.06(8), C(35)−O(2)−Si(1) 108.91(12), C(30)−O(1)−Si(1) 108.87(12), C(30)−C(35)−O(2) 112.51(17), O(1)−C(30)−C(35) 113.37(17).

of an orange−red colored solution of compound **4**. Like **3**, compound **4** is soluble in *n*-hexane, *n*-pentane, toluene, and benzene. Furthermore, **4** is stable both in the solid state as well as in solution for a long period of time without any decomposition under an inert gas atmosphere. Similar to **3**, the $^{29}$Si NMR spectrum of **4** shows a single upfield resonance ($\delta$ −51.25 ppm). The $\gamma$−C*H* proton for compound **4** exhibits a single resonance, which is observed at $\delta$ 5.35 ppm in its $^1$H NMR spectrum. The Si−H proton shows a single resonance ($\delta$ 5.28 ppm), which was confirmed by $^1$H−$^{29}$Si HSQC experiment. The $C{=}CH_2$ unit of **4** results in two doublets (2.83 and 4.26 ppm) with $J$ = 2 Hz. The NCC$H_2$ protons in **4** resonate at $\delta$ 3.45 and $\delta$ 4.02 ppm. The unsubstituted cylcopentadienyl part of the ferrocenyl unit exhibits a single resonance ($\delta$ 3.90 ppm), while the substituted part of the ferrocenyl unit exhibits multiplets ($\delta$ 3.11 (1H), 3.54(1H), 3.72(1H), and 3.78(1H)). Moreover compound **4** exhibits its molecular ion in the mass spectrum at $m/z$ 672.

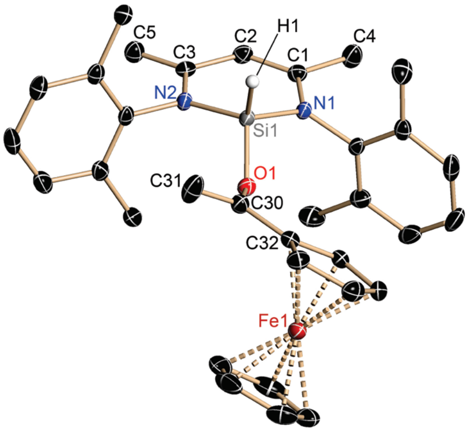


**Figure 4.** Molecular structure of **4**. The anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms are omitted for clarity except over silicon atom. Selected bond lengths (Å) and angles (deg): N(1)−Si(1) 1.7192(15), N(2)−Si(1) 1.7215(15), O(1)−Si(1) 1.6446(12), Si(1)−H(1) 1.457(19), C(30)−O(1) 1.383(2), C(30)−C(32) 1.476(3), C(30)−C(31) 1.322(3), C(1)−C(4) 1.476(3), C(3)−C(5) 1.375(3), O(1)− Si(1)−N(1) 108.56(7), O(1)−Si(1)−N(2) 112.37(7), N(1)−Si(1)−N(2) 103.88(7), O(1)−Si(1)−H(1) 104.9(8), N(1)−Si(1)−H(1) 115.0(8), N(2)−Si(1)−H(1) 112.3(8), C(30)−O(1)−Si(1) 125.51(11), C(31)−C(30)−O(1) 121.72(17), O(1)−C(30)−C(32) 113.34(15).

Compound **4** crystallizes in the triclinic space group *C*2*c* and the molecular structure is shown in Figure 4. The silicon atom is in a distorted tetrahedral geometry, made up from two nitrogen atoms, one oxygen atom, and a hydrogen atom. The two nitrogen atoms are derived from the chelating ligand. There is a little deviation in the distance between the Si atom and the nitrogen atoms of the supporting ligand. The average Si−N$_{av}$ bond distance in **4** is 1.7204(15). The bite angle at the silicon atom with the backbone ligand is 103.88(7)°. The Si1−O1 bond length is 1.6446(12) Å and C30−O1 is 1.383(2) Å. The distance C30−C31 of 1.3222(3) Å indicates a C═C double bond. The position of the silicon bound hydrogen atom was taken from the difference Fourier map and refined freely to a Si−H distance of 1.457(19) Å, which is quite comparable with that of similar reported compounds.[24] The silicon atom is dislocated from the N$_2$C$_3$ plane by 0.362(2) Å.

## ■ CONCLUSION

We have shown the versatile reactivity of silylenes **L** and **L′** toward monoketones and quinone. The reaction of **L** with 2-adamantanone and 3,5-di-*tert*-butyl-*o*-benzoquinone furnish a [1 + 2]−cycloaddition product **1** and [1 + 4]−cycloaddition product **2**, respectively. Treatment of **L′** with 3,5-di-*tert*-butyl-*o*-benzoquinone and acylferrocene leads to [1 + 4]−cycloaddition product **3** and compound **4**, respectively.

## ■ EXPERIMENTAL SECTION

All manipulations were carried out in an inert atmosphere of dinitrogen using standard Schlenk techniques and in a dinitrogen filled glovebox. Solvents were purified by MBRAUN solvent purification system MB SPS-800. All chemicals were purchased from Aldrich and used without further purification. **L** was prepared as reported in literature.[3c]

Table 1. Crystal and Structure Refinement Parameters for Compounds 1, 2, 3, and 4

| parameters | 1 | 2 | 3·0.5pentane | 4 |
|---|---|---|---|---|
| empirical formula | $C_{25}H_{37}ClN_2OSi$ | $C_{29}H_{43}ClN_2O_2Si$ | $C_{45.5}H_{66}N_2O_2Si$ | $C_{41}H_{52}FeN_2OSi$ |
| CCDC no. | CCDC 824154 | CCDC 824155 | CCDC 824156 | CCDC 824157 |
| formula wt | 445.11 | 515.19 | 701.09 | 672.79 |
| temperature/K | 90 (2) | 100 (2) | 100 (2) | 100 (2) |
| wavelength/Å | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| crystal system | monoclinic | orthorhombic | triclinic | monoclinic |
| space group | $P2_1/c$ | $P2_12_12_1$ | $P\bar{1}$ | $C2c$ |
| unit cell dimensions | $a$ = 15.4914 (14) Å | $a$ = 10.8117 (10) Å | $a$ = 12.9856 (9) Å | $a$ = 21.2031 (5) Å |
| | $b$ = 11.6071 (10) Å | $b$ = 14.4507 (14) Å | $b$ = 12.9963 (9) Å | $b$ = 10.0796 (2) Å |
| | $c$ = 13.5417 (12) Å | $c$ = 18.4194 (18) Å | $c$ = 13.3486 (9) Å | $c$ = 35.5186 (8) Å |
| | $\alpha$ = 90° | $\alpha$ = 90° | $\alpha$ = 73.1430(10)° | $\alpha$ = 90° |
| | $\beta$ = 104.728 (2)° | $\beta$ = 90° | $\beta$ = 79.4280(10)° | $\beta$ = 104.5550° |
| | $\gamma$ = 90° | $\gamma$ = 90° | $\gamma$ = 88.4660(10)° | $\gamma$ = 90° |
| volume, $Z$ | 2354.9 (4) $Å^3$, 4 | 2877.8 (3) $Å^3$, 4 | 2118.5 (3) $Å^3$, 2 | 7347.4 (3) $Å^3$, 8 |
| density (calcd) | 1.255 $g/cm^3$ | 1.189 $g/cm^3$ | 1.098 $g/cm^3$ | 1.216 $g/cm^3$ |
| absorption coefficient | 0.233 $mm^{-1}$ | 0.202 $mm^{-1}$ | 0.092 $mm^{-1}$ | 0.476 $mm^{-1}$ |
| $F$ (000) | 960 | 1112 | 766 | 2880 |
| crystal size | 0.16 × 0.12 × 0.05 $mm^3$ | 0.07 × 0.07 × 0.07 $mm^3$ | 0.12 × 0.08 × 0.06 $mm^3$ | 0.12 × 0.10 × 0.08 $mm^3$ |
| $\theta$ range for data collection | 1.36–27.20° | 1.79–26.03° | 1.60–26.75° | 1.98–25.35° |
| limiting indices | $-19 \leq h \leq 19$, | $-12 \leq h \leq 13$, | $-16 \leq h \leq 16$, | $-25 \leq h \leq 20$, |
| | $-14 \leq k \leq 14$, | $-17 \leq k \leq 17$, | $-16 \leq k \leq 16$, | $-12 \leq k \leq 9$, |
| | $-17 \leq l \leq 17$ | $-22 \leq l \leq 22$ | $-16 \leq l \leq 16$ | $-42 \leq l \leq 41$ |
| reflections collected | 39086 | 29073 | 59261 | 58971 |
| independent reflections | 5224 ($R_{int}$ = 0.0305) | 5657 ($R_{int}$ = 0.0549) | 8992 ($R_{int}$ = 0.0269) | 6648 ($R_{int}$ = 0.0340) |
| completeness to $\theta$ | 99.9% ($\theta$ = 27.20) | 99.7% ($\theta$ = 26.03) | 99.7% ($\theta$ = 26.75) | 98.8% ($\theta$ = 25.35) |
| refinement method | full-matrix least-squares on $F^2$ | full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| data/restraints/parameters | 5224/0/277 | 5663/0/359 | 8992/143/485 | 6648/0/428 |
| goodness-of-fit on $F^2$ | 1.122 | 1.038 | 1.028 | 1.037 |
| final $R$ indices [$I > 2\sigma(I)$] | $R1$ = 0.0366, $wR2$ = 0.0942 | $R1$ = 0.0351, wR2 = 0.0729 | $R1$ = 0.0439, $wR2$ = 0.1090 | $R1$ = 0.0335, $wR2$ = 0.0774 |
| $R$ indices (all data) | $R1$ = 0.0403, $wR2$ = 0.0964 | $R1$ = 0.0427, $wR2$ = 0.0764 | $R1$ = 0.0535, $wR2$ = 0.1151 | $R1$ = 0.0407, $wR2$ = 0.0809 |
| absolute structure parameter | | 0.03(5) | | |
| largest diff peak and hole | 0.373 and −0.322 $eÅ^{-3}$ | 0.193 and −0.203 $eÅ^{-3}$ | 0.455 and −0.557 $eÅ^{-3}$ | 0.420 and −0.370 $eÅ^{-3}$ |

$^1$H and $^{29}$Si NMR spectra were recorded with Bruker Avance DPX 200, Bruker Avance DRX 300, Bruker Avance DRX 400, or a Bruker Avance DRX 500 spectrometer, using $C_6D_6$ as solvent. Chemical shifts ($\delta$) are given relative to $SiMe_4$. EI–MS spectra were obtained using a Finnigan MAT 8230 instrument. Elemental analyses were performed by the Institut für Anorganische Chemie, Universität Göttingen. Melting points were measured in a sealed glass tube on a Büchi B-540 melting point apparatus.

**Synthesis of 1.** Toluene (60 mL) was added to a 100 mL Schlenk flask containing **L** (0.29 g, 0.98 mmol) and 2-adamantanone (0.15 g, 1.00 mmol). The reaction mixture was stirred at room temperature for 12 h. The solution was filtered, and the solvent was reduced in vacuo to about 30 mL and stored at −32 °C in a freezer for 2 days to obtain colorless single crystals of **1**; (0.31 g, 70%); mp 171–174 °C (decomp). Elemental analysis (%) calcd for $C_{25}H_{37}ClN_2OSi$ (445.11): C, 67.46; H, 8.38; N, 6.29. Found: C, 67.29; H, 8.25; N, 6.38. $^1$H NMR (200 MHz, $C_6D_6$, 25 °C): $\delta$ 1.16 (s, 18H, 2 × $C(CH_3)_3$), 1.66–1.69 (m, 2H, $C_{10}H_{14}$), 1.88 (s, 2H, $C_{10}H_{14}$), 1.98–2.07 (m, 4H, $C_{10}H_{14}$), 2.20 (br, 2H, $C_{10}H_{14}$), 2.58 (br, 2H, $C_{10}H_{14}$), 2.98 (br, 2H, $C_{10}H_{14}$), 6.80–6.94 (m, 5 H, $C_6H_5$) ppm. $^{29}Si\{^1H\}$ NMR (59.63 MHz, $C_6D_6$, 25 °C): $\delta$ −104.80 ppm. EI–MS: *m/z* 444.0 ($M^+$).

**Synthesis of 2.** Toluene (60 mL) was added to a 100 mL Schlenk flask containing **L** (0.25 g, 0.85 mmol) and 3,5-di-*tert*-butyl-*o*-benzoquinone (0.19 g, 0.86 mmol). The green-colored reaction mixture was stirred at room temperature for 12 h. The solution was filtered, and the solvent was reduced in vacuo to 20 mL and stored in a freezer at −32 °C for 3 days to obtain colorless single crystals of **2**; (0.32 g, 73%); mp 150–153 °C (decomp). Elemental analysis (%) calcd for $C_{29}H_{43}ClN_2O_2Si$ (515.20): C, 67.61; H, 8.41; N, 5.44. Found: C, 67.27; H, 8.51; N, 5.36. $^1$H NMR (200 MHz, $C_6D_6$, 25 °C): $\delta$ 1.24 (s, 18H, 2 × $C(CH_3)_3$), 1.34 (s, 9H, $C(CH_3)_3$), 1.69 (s, 9H, $C(CH_3)_3$), 6.79–7.26 (m, 7H, $C_6H_5$ and $C_6H_2$) ppm; $^{29}Si\{^1H\}$ NMR (79.49 MHz, $C_6D_6$, 25 °C): $\delta$ −94.58 ppm. EI–MS: *m/z* 514.0 ($M^+$).

**Synthesis of 3.** *n*-Pentane (60 mL) was placed in a 100 mL Schlenk flask containing **L′** (0.24 g, 0.54 mmol) and 3,5-di-*tert*-butyl-*o*-benzoquinone (0.12 g, 0.54 mmol). The reaction mixture was stirred at room temperature for 12 h. The solution was filtered, and the solvent was reduced in vacuo to 10 mL and stored in a freezer at −32 °C for a week to obtain colorless single crystals of **3**. For elemental analysis, **3**·0.5pentane was treated under vacuum for 6 h to remove the pentane molecule; (0.28 g, 78%); mp 135–138 °C (decomp). Elemental analysis (%) calcd for $C_{43}H_{60}N_2O_2Si$ (665.03): C, 77.66; H, 9.09; N, 4.21. Found: C, 77.70; H, 9.15; N, 4.15. $^1$H NMR (500 MHz, $C_6D_6$, 25 °C): $\delta$ 0.69 (d, 3H, $J$ = 7 Hz, $CH(CH_3)_2$), 1.00 (s, 9H, $C(CH_3)_3$), 1.08 (d, 3H, $J$ = 7 Hz, $CH(CH_3)_2$), 1.14 (s, 9H, $C(CH_3)_3$), 1.29 (d, 3H, $J$ = 7 Hz, $CH(CH_3)_2$), 1.37 (m, 6H, 2 × $CH(CH_3)_2$), 1.44 (s, 3H, $NCCH_3$) 1.48 (m, 6H, 2 × $CH(CH_3)_2$), 1.56 (d, 3H, $J$ = 7 Hz, $CH(CH_3)_2$), 3.30 (m, 1H, $J$ = 7 Hz, $CH(CH_3)_2$), 3.42 (s, 1H, $NCCH_2$), 3.64 (m, 1H, $J$ = 7 Hz, $CH(CH_3)_2$), 3.83 (m, 1H, $J$ = 7 Hz, $CH(CH_3)_2$), 4.02 (s, 1H, $NCCH_2$), 5.38 (s, 1H, $\gamma{-}CH$), 6.69 (br, 1H, $C_6H_2$), 6.86 (br, 1H, $C_6H_2$), 6.98−7.14 (m, 6 H, 2 x $i\mathrm{Pr}_2C_6H_3$) ppm. $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR (79.49 MHz, $C_6D_6$, 25 °C): $\delta$ −49.36 ppm. EI−MS: $m/z$ 664.4 ($M^+$).

**Synthesis of 4.** *n*-Hexane (60 mL) was placed in a 100 mL Schlenk flask containing **L′** (0.24 g, 0.54 mmol) and acylferrocene (0.12 g, 0.53 mmol). The orange red colored reaction mixture was stirred at room temperature for 12 h. The solution was filtered, and the solvent was reduced in vacuo to 40 mL and stored in a freezer at −32 °C for 12 h to obtain reddish−orange colored single crystals of **4**; (0.26 g, 72%); mp 212−215 °C (decomp). Elemental analysis (%) calcd for $C_{41}H_{52}FeN_2OSi$ (672.79): C, 73.19; H, 7.79; N, 4.16. Found: C, 72.85; H, 7.89; N, 4.00. $^1$H NMR (300 MHz, $C_6D_6$, 25 °C): $\delta$ 1.02 (d, 3H, $J$ = 7 Hz, $CH(CH_3)_2$), 1.06 (d, 3H, $J$ = 7 Hz, $CH(CH_3)_2$), 1.26−1.29 (2*d*, 6H, 2 × $CH(CH_3)_2$), 1.30 (d, 3H, $J$ = 7 Hz, $CH(CH_3)_2$), 1.44 (d, 3H, $J$ = 7 Hz, $CH(CH_3)_2$), 1.49 (s, 3H, $NCCH_3$), 1.52 (d, 3H, $J$ = 7 Hz, $CH(CH_3)_2$), 1.56 (d, 3H, $J$ = 7 Hz, $CH(CH_3)_2$), 2.83 (d, 1H, $J$ = 2 Hz, $C{=}CH_2$), 3.11 (m, 1H, $C_5H_4$), 3.40 (m, 1H, $J$ = 7 Hz, $CH(CH_3)_2$), 3.45 (s, 1H, $NCCH_2$), 3.54 (m, 2H, $CH(CH_3)_2$, $C_5H_4$), 3.72 (m, 1H, $C_5H_4$), 3.78 (m, 1H, $C_5H_4$), 3.84 (m, 2H, $J$ = 7 Hz, 2 × $CH(CH_3)_2$), 3.90 (s, 5H, $C_5H_5$), 4.02 (s, 1H, $NCCH_2$), 4.26 (d, 1H, $J$ = 2 Hz, $C{=}CH_2$), 5.28 (s, 1H, Si$H$), 5.35 (s, 1H, $\gamma{-}CH$), 6.97−7.30 (m, 6 H, 2 × $i\mathrm{Pr}_2C_6H_3$) ppm. $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR (59.62 MHz, $C_6D_6$, 25 °C): $\delta$ −51.25 ppm. EI−MS: $m/z$ 672 ($M^+$).

**Crystal Structure Determination.** Suitable single crystals for X−ray structural analysis of **1**, **2**, **3**, and **4** were mounted at low temperature in inert oil under argon atmosphere by applying the X-Temp2 device.[25] The data were collected on a Bruker D8 three circle diffractometer equipped with a SMART APEX II CCD detector and an INCOATEC Mo microfocus source with INCOATEC Quazar mirror optics.[26] The data were integrated with SAINT,[27] and an empirical absorption correction with SADABS[28] was applied. The structures were solved by direct methods (SHELXS-97) and refined against all data by full-matrix least-squares methods on $F^2$ (SHELXL-97).[29] All non-hydrogen-atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their $U_{\mathrm{iso}}$ values constrained to 1.5 $U_{\mathrm{eq}}$ of their pivot atoms for terminal sp$^3$ carbon atoms and 1.2 times for all other carbon atoms (Table 1).

## ■ ASSOCIATED CONTENT

**Ⓢ Supporting Information.** CIFs for **1**(CCDC−824154), **2**(CCDC−824155), **3**(CCDC−824156), and **4**(CCDC−824157). This material is available free of charge via the Internet at http://pubs.acs.org.

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