

# Synthesis and Characterization of an Amidinate-Stabilized *cis*-1,2-Disilylenylethene [*cis*-LSi{C(Ph)=C(H)}SiL] and a Singlet Delocalized Biradicaloid [LSi( $\mu_2$ -C<sub>2</sub>Ph<sub>2</sub>)<sub>2</sub>SiL]\*\*

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**Abstract:** The synthesis and characterization of novel *cis*-1,2-disilylenylethene [*cis*-LSi{C(Ph)=C(H)}SiL] (**2**; L = PhC(N*t*Bu)<sub>2</sub>) and a singlet delocalized biradicaloid [LSi( $\mu_2$ -C<sub>2</sub>Ph<sub>2</sub>)<sub>2</sub>SiL] (**3**) are described. Compound **2** was prepared by the reaction of [{PhC(N*t*Bu)<sub>2</sub>}Si:]<sub>2</sub> (**1**) with one equivalent of PhC≡CH in toluene. Compound **3** was synthesized by the reaction of **1** with two equivalents

of PhC≡CPh in toluene. The results suggest that the reaction proceeds through an [LSi{C(Ph)=C(Ph)}SiL] intermediate, which then reacts with another molecule of PhC≡CPh to form **3**.

**Keywords:** density functional calculations · N ligands · radicals · silicon · silylene

Compounds **2** and **3** have been characterized by X-ray crystallography and NMR spectroscopy. X-ray crystallography and DFT calculations of **3** show that the singlet biradicals are stabilized by the amidinate ligand and the delocalization within the “Si( $\mu_2$ -C<sub>2</sub>Ph<sub>2</sub>)<sub>2</sub>Si” six-membered ring.

## Introduction

Stable heavier Group 14 dicarbene analogues of composition RE<sub>2</sub>-E<sub>2</sub>R (R = supporting ligand; E = low valent Si, Ge, Sn, Pb) have attracted much attention in the past few years.<sup>[1]</sup> These compounds comprise of an E<sub>2</sub>-E<sub>2</sub> single bond and a lone pair of electrons at each E atom. The formal oxidation state of each E atom is +1. They can be synthesized successfully by incorporating sterically hindered substituents at the heavier Group 14 elements. For example, the amidinate-stabilized disilylene and digermylene {[R<sup>1</sup>C(NR<sup>2</sup>)<sub>2</sub>]E<sub>2</sub>}<sub>2</sub> (E = Si or Ge, R<sup>1</sup> = Ph, R<sup>2</sup> = *t*Bu; E = Ge, R<sup>1</sup> = *t*Bu, R<sup>2</sup> = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>),<sup>[1a,c,d]</sup> N-heterocyclic carbene-stabilized dichlorodisilylene R → (Cl)Si-Si(Cl) ← R [R = :C{N(2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)CH<sub>2</sub>}]<sup>[1e]</sup> and diaryldistannylene [Ar\*Sn]<sub>2</sub> [Ar\* =

2,6-(Me<sub>2</sub>NCH<sub>2</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sup>[1g]</sup> were reported and structurally characterized. That heavier dicarbene analogues have unprecedented electronic structure prompted our interest in exploring their chemical reactivity. In our previous communication, we report the synthesis and characterization of a stable bromosilylene [{PhC(N*t*Bu)<sub>2</sub>}SiBr] from the reaction of [{PhC(N*t*Bu)<sub>2</sub>}Si:]<sub>2</sub> with bromine.<sup>[2]</sup> Recently, Roesky and co-workers have reported the reaction of [{PhC(N*t*Bu)<sub>2</sub>}Si:]<sub>2</sub> with Ph<sub>2</sub>CO to form a four-membered Si<sub>2</sub>O<sub>2</sub> ring with five-coordinate silicon atoms.<sup>[3]</sup> Leung et al. have prepared the germanium analogue of a dithiocarboxylic acid anhydride [{R<sup>3</sup>Ge(S)}<sub>2</sub>S] [R<sup>3</sup> = N(SiMe<sub>3</sub>)C(Ph)C(SiMe<sub>3</sub>)(C<sub>2</sub>H<sub>4</sub>N-2)] by the reaction of [R<sup>3</sup>Ge:]<sub>2</sub> with elemental sulfur.<sup>[1b]</sup>

Herein, we report the synthesis and characterization of a *cis*-1,2-disilylenylethene [*cis*-LSi{C(Ph)=C(H)}SiL] (**2**; L = PhC(N*t*Bu)<sub>2</sub>) and a singlet delocalized biradicaloid [LSi( $\mu_2$ -C<sub>2</sub>Ph<sub>2</sub>)<sub>2</sub>SiL] (**3**) by the reaction of [LSi-SiL] (**1**) with phenylacetylene and diphenylacetylene, respectively. The theoretical studies of **3** are also described to understand its bonding nature.

## Results and Discussion

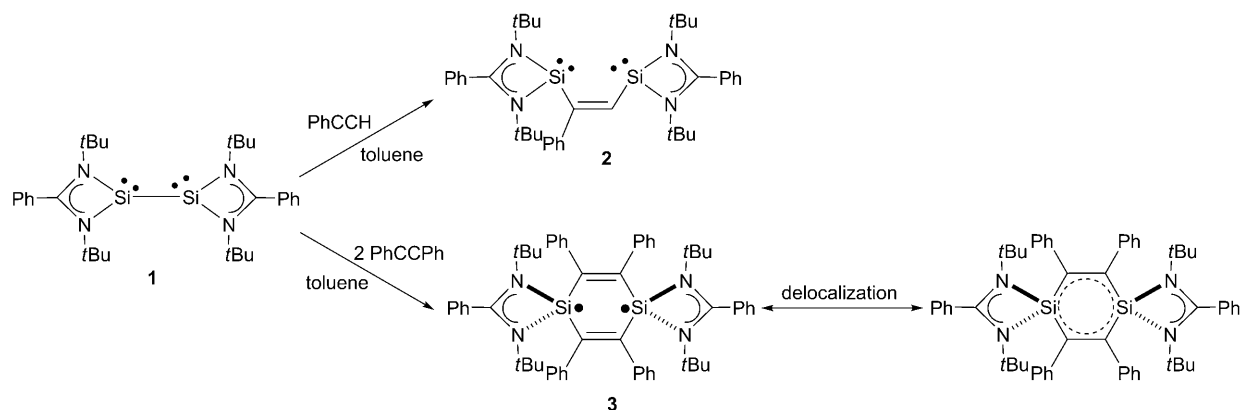
The reaction of **1** with one equivalent of PhC≡CH in toluene for 2 h afforded the novel *cis*-1,2-disilylenylethene [*cis*-LSi{C(Ph)=C(H)}SiL] (**2**; L = PhC(N*t*Bu)<sub>2</sub>) (Scheme 1). Its stereoisomer, *trans*-1,2-disilylenylethene, was not observed.

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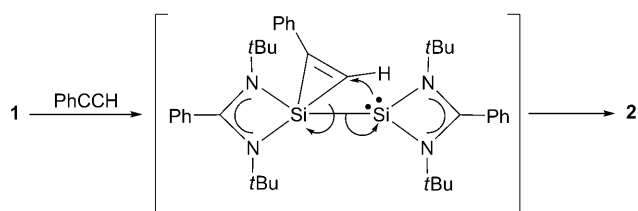
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\*\*] L = PhC(N*t*Bu)<sub>2</sub>

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Scheme 1. Synthesis of compounds **2** and **3**.

The reaction may proceed through a [1+2] cycloaddition of a Si<sup>I</sup> center in **1** with PhCCH to form a silacyclopropene intermediate, which then undergoes an insertion with another Si<sup>I</sup> center to form **2** (Scheme 2). Recently, we reported that the reaction of **1** with one equivalent of bromine formed a

Scheme 2. Proposed mechanism for the formation of **2**.

stable monomeric bromosilylene [LSiBr].<sup>[2]</sup> In contrast, the reaction of **1** with two equivalents of PhC≡CH in toluene afforded a mixture of products that cannot be identified. Tokitoh and co-workers showed that the reaction of [BbtSi≡SiBbt] (Bbt = C<sub>6</sub>H<sub>2</sub>-2,6-{CH(SiMe<sub>3</sub>)<sub>2</sub>}-4-[C(SiMe<sub>3</sub>)<sub>3</sub>]) with ethylene may proceed through a disilylene intermediate [BbtSi(CH<sub>2</sub>CH<sub>2</sub>)SiBbt] to form a bis(silacyclopropane).<sup>[4]</sup> Power and co-workers have reported that the reaction of [ArMMAr] [M = Ge or Sn; Ar = C<sub>6</sub>H<sub>3</sub>-2,6-(C<sub>6</sub>H<sub>3</sub>-2,6-*i*Pr<sub>2</sub>)<sub>2</sub>] with PhN=NPh resulted in the complete cleavage of the MM bond and a lone pair of electrons was found at the metal centers in the product [ArM{(Ph)N=N(Ph)}MAr].<sup>[5]</sup> On the other hand, there is no reaction between **1** and Me<sub>3</sub>SiC≡CH or Me<sub>3</sub>SiC≡CSiMe<sub>3</sub> in toluene.

Compound **2** is isolated as a highly air- and moisture-sensitive yellow crystalline solid which is soluble in toluene. It is stable in the solid state at room temperature under an inert atmosphere. Compound **2** has been characterized by elemental analysis, spectroscopic methods and X-ray crystallography. The <sup>1</sup>H NMR spectrum of **2** displays resonances due to the amidinate ligand and -C(H)=C(Ph)- substituent. The <sup>29</sup>Si NMR spectrum of **2** displays two singlets at δ = 15.1 and 29.5 ppm for the non-equivalent silicon centers, which

show a downfield shift relative to that of [{PhC(N*t*Bu)<sub>2</sub>]SiR] [R = NMe<sub>2</sub>, δ = -2.62 ppm; R = OiPr, δ = -13.4 ppm].<sup>[6]</sup> The <sup>29</sup>Si NMR signals of **2** are comparable to the theoretical <sup>29</sup>Si NMR chemical shift (δ = 22.7, 49.6 ppm) at the B3LYP/6-31+G(d) level.

The molecular structure of **2** with an atomic numbering scheme is shown in Figure 1. The amidinate ligands are bonded in an *N,N'*-chelate fashion to the silicon centers and

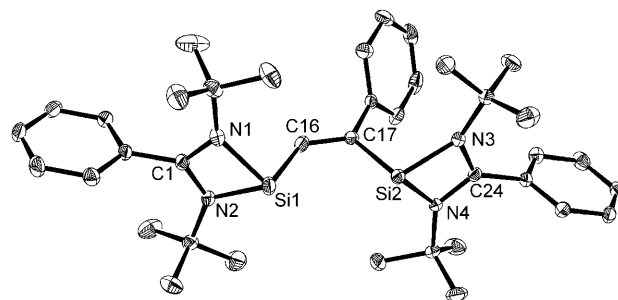


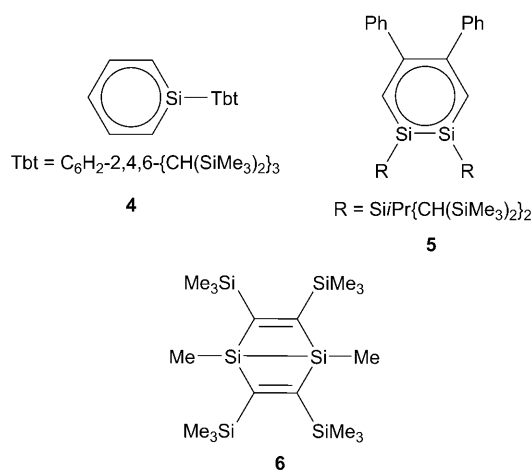
Figure 1. ORTEP drawing of compound **2** (50% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Si1–N1 1.875(1), Si1–N 1.886(1), Si1–C16 1.905(2), Si2–N3 1.877(1), Si2–N4 1.874(1), Si2–C17 1.927(2), C16–C17 1.346(2), C1–N1 1.333(2), C1–N 1.343(2), C24–N3 1.335(2), C24–N4 1.343(2); N1–Si1–N2 69.07(6), N1–Si1–C16 95.54(7), N–Si1–C16 98.48(7), Si1–C16–C17 125.48(13), C16–C17–Si2 118.88(12), N3–Si2–N4 69.34(6), N3–Si2–C17 101.03(6), N4–Si2–C17 99.08(6).

display a trigonal pyramidal geometry. The sum of the bond angles at the Si1 and Si2 atoms are 263.1 and 269.5°, respectively. They are comparable with that of the three-coordinated chlorosilylene [{PhC(N*t*Bu)<sub>2</sub>]SiCl] (260.7°).<sup>[7]</sup> This geometry is consistent with a stereoactive lone pair at the silicon centers. The Si1 atom is displaced from the N1–C1–N2 least-squares plane by 0.282 Å, whereas the Si2 atom is displaced from the N3–C24–N4 least-squares plane by 0.337 Å. The Si1–C16 (1.905(2) Å) and Si2–C17 (1.927(2) Å) bonds are slightly shorter than the Si<sup>II</sup>–C<sub>aryl</sub> bond (1.973(2) Å) in

$[\text{Si}\{\text{C}_6\text{H}_3\text{-}2,6\text{-(Trip)}_2\}(\eta^3\text{-Cp}^*)]$  (Trip = 2,4,6-*i*Pr<sub>3</sub>C<sub>6</sub>H<sub>2</sub>).<sup>[8]</sup> The Si1–C16 and Si2–C17 bonds are comparable with the Si<sup>IV</sup>–C(sp<sup>2</sup>) bonds (average 1.901 Å) in  $[(\text{Me}_2\text{HSi})_2\text{C}=\text{C}(\text{SiHMe}_2)_2]$ .<sup>[9]</sup> The C16–C17 bond (1.346(2) Å) is a typical C=C double bond (1.34 Å). The C–N bond lengths (C1–N1 = 1.333(2), C1–N2 = 1.343(2), C24–N3 = 1.335(2), C24–N4 = 1.343(2) Å) are approximately intermediate between the C=N double and C–N(sp<sup>2</sup>) single bond lengths. This geometry shows considerable delocalization throughout the N1–C1–N2 and N3–C24–N4 skeletons.

The reaction of **1** with one or two equivalents of PhC≡CPh in toluene for 2 h afforded  $[\text{LSi}(\mu_2\text{-C}_2\text{Ph}_2)_2\text{SiL}]$  (**3**). The results suggest that the reaction proceeds through a  $[\text{LSi}\{\text{C}(\text{Ph})=\text{C}(\text{Ph})\}\text{SiL}]$  intermediate, which then reacts with another molecule of PhC≡CPh to afford a biradicaloid. The radicals are stabilized by the amidinate ligand and the delocalization within the “Si(μ<sub>2</sub>-C<sub>2</sub>Ph<sub>2</sub>)<sub>2</sub>Si” six-membered ring, as confirmed by X-ray crystallography and DFT calculations. Similarly, the reaction of  $[\text{ArGeGeAr}]$  with HC≡CSiMe<sub>3</sub> afforded a 1,4-digermbenzene intermediate with considerable diradical character, which then underwent a cycloaddition with a flanking aryl ring on the terphenyl ligand.<sup>[10]</sup> Stable singlet biradicaloid  $[\text{ArGe}(\mu\text{-NSiMe}_3)_2\text{GeAr}]$  was synthesized by the reaction of  $[\text{ArGeGeAr}]$  with N<sub>3</sub>SiMe<sub>3</sub>.<sup>[11]</sup> Recently, Ando and co-workers reported that a stable 1,4-disila(Dewar-benzene) **6** was synthesized successfully by heating a dimethyldisilacyclopropenyl.<sup>[12]</sup> The 1,4-disila(Dewar-benzene) **6** underwent a photochemical valence isomerization to a 1,4-disilabenzene intermediate, which was trapped by butadiene to form a [4+2] cycloaddition product.

Compound **3** is isolated as a highly air- and moisture-sensitive dark red crystalline solid, which is soluble in CH<sub>2</sub>Cl<sub>2</sub> and THF. It is stable in the solid state at room temperature under an inert atmosphere. When crystals of **3** dissolve in [D<sub>8</sub>]toluene, [D<sub>6</sub>]benzene, [D<sub>2</sub>]dichloromethane, [D<sub>5</sub>]pyridine or [D<sub>8</sub>]THF at room temperature, the solution decomposes after 1 day to give a white precipitate. The isolation of products from these solutions is currently under investigation. Compound **3** is stable in [D<sub>8</sub>]1,4-dioxane at room temperature. The <sup>1</sup>H NMR spectrum displays resonances for the *t*Bu and phenyl protons. The <sup>29</sup>Si{<sup>1</sup>H} NMR shows a singlet at δ = –51.0 ppm, which shows an upfield shift as compared with the <sup>29</sup>Si NMR spectrum of the 1,2-disilabenzene **5** in [D<sub>6</sub>]benzene (δ = 99.2 ppm)<sup>[14]</sup> and silabenzene **4** in [D<sub>12</sub>]cyclohexane (δ = 92.5 ppm).<sup>[13]</sup> The <sup>29</sup>Si{<sup>1</sup>H} NMR signal lies between the three-coordinate silicon in **2** (δ = 15.1 and 29.5 ppm) and the five-coordinate silicon in  $[\{\text{PhC}(\text{N}t\text{Bu})_2\}\text{SiCl}_3]$  (δ = –98.6 ppm).<sup>[7]</sup> The results suggest that compound **3** is a singlet biradicaloid instead of a 1,4-disilabenzene derivative. The UV/Vis spectrum of **3** in CH<sub>2</sub>Cl<sub>2</sub> at room temperature shows absorption bands at 431 nm in the visible light region and at 299, 295, 281 and 266 nm in the ultraviolet region. The absorption band of **3** in the visible light region shows a bathochromic shift compared with that of the 1,4-disilabenzene  $[\text{1,4-Si}_2\text{C}_4\text{H}_6]$  (408, 396, 385, 340, 275 nm) in low-temperature Ar matrices.<sup>[15]</sup>



The molecular structure of **3** is shown in Figure 2. The phenyl rings on the Si(μ<sub>2</sub>-C<sub>2</sub>Ph<sub>2</sub>)<sub>2</sub>Si ring are disordered. The disordered phenyl rings (C17A–C22A) are omitted for clarity in Figure 2. Moreover, in the asymmetric unit, there are two disordered toluene molecules, which are treated by SQUEEZE/PLATON (for details, see the Supporting Information). Several attempts to obtain more precise structural parameters were unsuccessful.

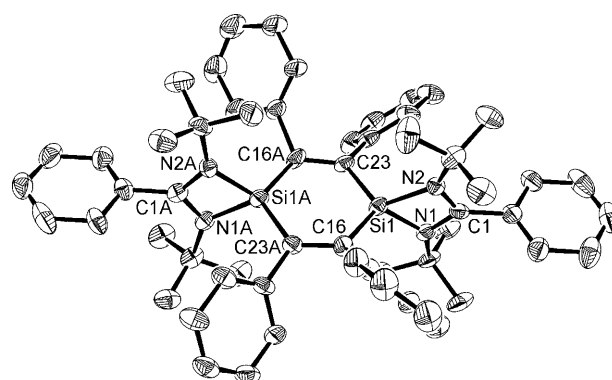


Figure 2. ORTEP drawing of compound **3** (30% thermal ellipsoids). Hydrogen atoms and the disordered phenyl ring (C17A–C22A) are omitted for clarity. Selected bond lengths (Å) and angles (°): Si1–C16 1.821(4), Si1–C23 1.819(3), C16–C23A 1.384(5), Si1–N1 1.807(3), Si1–N2 1.819(3), C1–N1 1.339(5), C1–N2 1.339(5); C16–Si1–C23 114.8(2), Si1–C16–C23A 123.4(2), Si1–C23–C16A 121.4(2), N1–Si1–N2 72.3(1), Si1–N1–C1 91.2(2), N1–C1–N2 105.9(3), C1–N2–Si1 90.7(2).

The Si(μ<sub>2</sub>-C<sub>2</sub>Ph<sub>2</sub>)<sub>2</sub>Si ring is almost planar (the dihedral angle of Si1A–C23A–C16–Si1 = 7.43°) and the sum of the interior angles is 719.2°. The amidinate ligands are bonded in an *N,N'*-chelate fashion to the silicon centers, which display a tetrahedral geometry. Unlike **2**, the Si1 atom in **3** is displaced from the N1–C1–N2 least-squares plane by 0.021 Å. Thus, the Si1–N1–C1–N2 ring is planar and almost perpendicular to the “Si(μ<sub>2</sub>-C<sub>2</sub>Ph<sub>2</sub>)<sub>2</sub>Si” ring (dihedral angle = 87.0°). The amidinate rings are tilted (dihedral angle: 5.98°). The

phenyl rings on the  $\text{Si}(\mu_2\text{-C}_2\text{Ph}_2)_2\text{Si}$  ring are also tilted and staggered (dihedral angle of  $\text{C17-C16-C23A-C24A}=35.5^\circ$ ; for the disordered phenyl ring ( $\text{C17A-C22A}$ ), dihedral angle of  $\text{C17A-C16-C23A-C24A}=2.67^\circ$ ). According to the theoretical calculations, the tilted phenyl rings provide additional stabilization due to the conjugation between the phenyl rings and the  $\text{C}=\text{C}$  double bonds on the  $\text{Si}(\mu_2\text{-C}_2\text{Ph}_2)_2\text{Si}$  ring. The  $\text{C16-C23A}$  bond ( $1.384(5)$  Å) is similar to that in benzene ( $1.39\text{--}1.40$  Å), **4** ( $1.381(6)\text{--}1.399(6)$  Å)<sup>[13]</sup> and **5** ( $1.389(6)$ ,  $1.386(6)$ ,  $1.452(6)$  Å).<sup>[14]</sup> The  $\text{C16-C23A}$  bond is longer than the  $\text{C16-C17}$  bond ( $1.346(2)$  Å) in **2**. The  $\text{Si1-C16}$  ( $1.821(4)$  Å) and  $\text{Si1-C23}$  ( $1.819(3)$  Å) bond lengths are almost equal to each other and intermediate between the  $\text{Si-C}$  single ( $1.87$  Å) and double ( $1.70$  Å) bond lengths.<sup>[16]</sup> The  $\text{Si1-C16}$  and  $\text{Si1-C23}$  bonds are significantly shorter than those in **2** ( $1.905(2)$ ,  $1.927(2)$  Å) and the 1,4-disila(Dewar-benzene) **6** (average  $1.938$  Å).<sup>[12]</sup> They are longer than those in **5** ( $1.804(4)$ ,  $1.799(5)$  Å)<sup>[14]</sup> and **4** ( $1.765(4)$ ,  $1.770(4)$  Å).<sup>[13]</sup> The  $\text{Si1-Si1A}$  distance ( $3.343$  Å) is significantly longer than the  $\text{Si-Si}$  bond length ( $2.248(2)$  Å) in **6**.<sup>[12]</sup> This suggests that there is no  $\text{Si-Si}$  interaction in **3**. The results suggest that the singlet biradicals are stabilized by the delocalization within the  $\text{Si}(\mu_2\text{-C}_2\text{Ph}_2)_2\text{Si}$  six-membered ring. The  $\text{Si-N}$  bonds (average  $1.813$  Å) in **3** are shorter than those in **2** (average  $1.878$  Å). The  $\text{C-N}$  bond lengths ( $\text{C1-N1}=1.339(5)$  Å,  $\text{C1-N2}=1.339(5)$  Å) in **3** are approximately intermediate between the  $\text{C=N}$  double and  $\text{C-N}(\text{sp}^2)$  single bond lengths. This geometry shows considerable delocalization throughout the  $\text{N1-C1-N2}$  skeleton.

To understand the bonding nature in compound **3**, it was investigated by means of quantum chemical calculations. The theoretical calculations of **3** were performed by means of DFT<sup>[17]</sup> B3LYP<sup>[18]</sup> with the 6-31G(d) basis set as implemented in the Gaussian 03 program<sup>[19]</sup> due to the large molecular structure of **3**. The calculated structural parameters ( $\text{Si1-C16}$   $1.813$  Å,  $\text{Si1-N1}$   $1.910$  Å,  $\text{C16-C23A}$   $1.432$  Å,  $\text{C1-N1}$   $1.341$  Å;  $\text{C16-Si1-C23}$   $114.6^\circ$ ,  $\text{Si1-C16-C23A}$   $122.6^\circ$ ,  $\text{N1-Si1-N}$   $68.8^\circ$ ) are in good agreement with the crystallographic data except the  $\text{Si1-N1}$  bond. The 6-31G(d) basis set does not include the diffused function for electron delocalization, and advanced multiple polarization functions, although there are  $\pi_{\text{C}=\text{C}} \rightarrow \sigma^*_{\text{Si-N}}$ ,  $\pi_{\text{C}=\text{N}} \rightarrow \sigma^*_{\text{Si-C}}$ , and  $\rho_{\text{N}} \rightarrow \sigma^*_{\text{Si-C}}$  donor-acceptor interactions around the  $\text{Si1-N1}$  bond. Therefore, the calculated  $\text{Si1-N1}$  bond ( $1.9103$  Å) is slightly longer than the crystallographic data.<sup>[20]</sup> Moreover, the calculated dihedral angle of the phenyl rings at the  $\text{Si}(\mu_2\text{-C}_2\text{Ph}_2)_2\text{Si}$  ring ( $17.2^\circ$ ) shows deviation

from the crystallographic data, which is due to the substantial disorder of the phenyl rings on the  $\text{Si}(\mu_2\text{-C}_2\text{Ph}_2)_2\text{Si}$  ring in the X-ray structure of **3**.

The energy difference between the singlet and triplet state of **3** is calculated (Figure S1 and S2, see the Supporting Information). The singlet state of **3** is more stable than the triplet state by  $12.2$  kcal mol<sup>-1</sup>. The calculated  $\text{Si}(\mu_2\text{-C}_2\text{Ph}_2)_2\text{Si}$  ring in the triplet state is not planar (the dihedral angle of  $\text{SiCCSi}=20.3^\circ$ ), whereas that in the singlet state is almost planar (the dihedral angle of  $\text{SiCCSi}=4.84^\circ$ ). The results are consistent with the crystallographic data. It is suggested that compound **3** is a singlet biradicaloid.

The nucleus-independent chemical shift at  $1$  Å (NICS(1)) above the center of the  $\text{Si}(\mu_2\text{-C}_2\text{Ph}_2)_2\text{Si}$  ring in **3** ( $\delta=-3.5$  ppm) shows that there is an electron delocalization within the  $\text{Si}(\mu_2\text{-C}_2\text{Ph}_2)_2\text{Si}$  six-membered ring.<sup>[21]</sup> In contrast, the NICS(1) of benzene ( $\delta=-11.2$  ppm) and the simple 1,4-disilabenzene derivative ( $1,4\text{-Si}_2\text{C}_4\text{H}_6$ ) ( $\delta=-7.9$  ppm) at the B3LYP/6-31G(d) level shows aromaticity. The natural-bond-orbital (NBO) analysis<sup>[22]</sup> (Table 1) shows that the delocali-

Table 1. Pertinent bonds and the respective atomic hybridization, contribution (Contr.), occupancy, and Wiberg bond index of compound **3**.

Bond	Atom 1	Contr. %	Hybrid Type	Atom 2	Contr. %	Hybrid Type	Occupancy	Wiberg index
$\text{Si1-N1}$ ( $\sigma$ )	Si	15.0	$\text{sp}^{4.28}$	N	85.0	$\text{sp}^{2.47}$	1.94	0.41
$\text{Si1-N1}$ ( $\sigma^*$ )	Si	85.0	$\text{sp}^{4.28}$	N	15.0	$\text{sp}^{2.47}$	0.24	–
$\text{Si1-C16}$ ( $\sigma$ )	Si	25.1	$\text{sp}^{2.15}$	C	74.9	$\text{sp}^{1.95}$	1.93	0.94
$\text{C16-C23A}$ ( $\sigma$ )	C	50.0	$\text{sp}^{1.83}$	C	50.0	$\text{sp}^{1.83}$	1.96	1.34
$\text{C16-C23A}$ ( $\pi$ )	C	50.0	p	C	50.0	p	1.81	–
$\text{C16-C23A}$ ( $\pi^*$ )	C	50.0	p	C	50.0	p	0.59	–
$\text{C1-N1}$ ( $\sigma$ )	C	39.5	$\text{sp}^{2.15}$	N	60.5	$\text{sp}^{1.89}$	1.98	1.39
$\text{C1-N1}$ ( $\pi$ )	C	25.1	p	N	74.9	p	1.95	–

zation system of the  $\text{Si}(\mu_2\text{-C}_2\text{Ph}_2)_2\text{Si}$  ring in **3** is comprised of the  $\pi$  and  $\pi^*$  orbitals of the  $\text{C16-C23A}$  and  $\text{C16A-C23}$  bonds (total electron occupancy for  $\pi=3.62$ ; for  $\pi^*=1.18$ ) and the  $\sigma^*$  orbitals of the  $\text{Si1-N1}$ ,  $\text{Si1-N}$ ,  $\text{Si1A-N1A}$ , and  $\text{Si1A-N2A}$  bonds (total electron occupancy=0.97). The  $\pi$  orbitals of the  $\text{C16-C23A/C16A-C23}$  bonds form  $\pi\text{-}\sigma^*$  conjugation with the  $\sigma^*$  orbitals of the  $\text{Si-N}$  bonds (second order perturbation stabilizing energy:  $5.15$  or  $4.44$  kcal mol<sup>-1</sup>) (Table S1, see the Supporting Information). The results suggest that the radicals are stabilized by the amidinate ligand and the delocalization within the  $\text{Si}(\mu_2\text{-C}_2\text{Ph}_2)_2\text{Si}$  six-membered ring.

In the calculated structure of **3**, the amidinate rings are tilted with respect to the  $\text{Si}(\mu_2\text{-C}_2\text{Ph}_2)_2\text{Si}$  ring (dihedral angle of  $\text{N-Si-Si-N}$ :  $12.4^\circ$ ). The phenyl rings on the  $\text{Si}(\mu_2\text{-C}_2\text{Ph}_2)_2\text{Si}$  ring are also tilted and staggered. The resulting structure is

a stable minimum. When the amidinate and phenyl rings are perpendicular to the  $\text{Si}(\mu_2\text{-C}_2\text{Ph}_2)_2\text{Si}$  ring (dihedral angle of the amidinate rings =  $0^\circ$ ,  $D_{2h}$  symmetry), the resulting structure is less stable than compound **3** by  $57.0 \text{ kcal mol}^{-1}$ . When the amidinate rings are tilted and the phenyl rings are perpendicular to the  $\text{Si}(\mu_2\text{-C}_2\text{Ph}_2)_2\text{Si}$  ring, the resulting structure is less stable than compound **3** by  $35.8 \text{ kcal mol}^{-1}$ . When the phenyl rings on the  $\text{Si}(\mu_2\text{-C}_2\text{Ph}_2)_2\text{Si}$  six-membered ring are tilted, this results in the  $\pi$  orbitals of the phenyl rings forming  $\pi\text{-}\pi^*$  conjugation with the  $\pi^*$  orbitals of the C16–C23A/C16A–C23 bonds (total second order perturbation stabilizing energy:  $19.7 \text{ kcal mol}^{-1}$ ) (Table S1, see the Supporting information). This conjugation effect provides an additional stabilization in compound **3**.

Since the Si1–N1–C1–N2 ring is planar, this leads to  $\pi_{\text{C=N}} \rightarrow \sigma_{\text{Si-C}}^*$  and  $\rho_{\text{N}} \rightarrow \sigma_{\text{Si-C}}^*$  hyperconjugation around the Si–N bonds (the sum of second order perturbation stabilizing energy of  $\pi_{\text{C=N}} \rightarrow \sigma_{\text{Si-C}}^*$  and  $\rho_{\text{N}} \rightarrow \sigma_{\text{Si-C}}^* = 4.78$  or  $4.65 \text{ kcal mol}^{-1}$ ). The electronic delocalization ( $\pi_{\text{C=N}} \rightarrow \sigma_{\text{Si-C}}^*$  and  $\rho_{\text{N}} \rightarrow \sigma_{\text{Si-C}}^*$ ) shortens the Si–N bonds, although **3** has a substantial population in the Si–N  $\sigma^*$  orbitals and steric hindrance arising from the substituents. Similar hyperconjugation is not found in compound **2**, in which the amidinate Si–N–C–N ring is not planar. The calculated Si–N bonds (1.927, 1.924, 1.923, 1.916 Å) in **2** at the B3LYP/6-31G(d) level are longer than those in **3**. The results are consistent with the X-ray data of **2** and **3**, in which the Si–N bonds (average 1.813 Å) in **3** are shorter than those in **2** (average 1.878 Å).

The calculated enthalpies of reaction for compounds **2** and *cis*-[LSi{C(Ph)=C(Ph)}SiL] show that compound **2** is more stable than [LSi{C(Ph)=C(Ph)}SiL] by  $14.5 \text{ kcal mol}^{-1}$  (**2**:  $\Delta H_{\text{reaction}}^0 = -35.5 \text{ kcal mol}^{-1}$ ; [LSi{C(Ph)=C(Ph)}SiL]:  $\Delta H_{\text{reaction}}^0 = -21.0 \text{ kcal mol}^{-1}$ ) in view of thermodynamics. The higher stability of compound **2** means that it may not undergo further reaction with another molecule of  $\text{PhC}\equiv\text{CH}$  to form a singlet delocalized biradicaloid in the reaction of **1** with  $\text{PhC}\equiv\text{CH}$ .

## Conclusion

A novel *cis*-1,2-disilylenylethene **2** has been synthesized successfully by the reaction of **1** with one equivalent of phenylacetylene. Moreover, a singlet delocalized biradicaloid **3** has been synthesized successfully by the reaction of **1** with two equivalents of diphenylacetylene. X-ray crystallography and DFT calculations show that the singlet biradicals are stabilized by the amidinate ligand and the delocalization within the  $\text{Si}(\mu_2\text{-C}_2\text{Ph}_2)_2\text{Si}$  six-membered ring.<sup>[24]</sup>

## Experimental Section

**General procedure:** All manipulations were carried out under an inert atmosphere of argon by using standard Schlenk techniques in an argon filled glove box. Solvents were dried over and distilled over Na/K alloy prior to use. Compound **1** was prepared as described in the literature.<sup>[14]</sup>

The  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$  NMR spectra were recorded on a JEOL ECA 400 spectrometer. The chemical shifts  $\delta$  are relative to  $\text{SiMe}_4$  for  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{29}\text{Si}$ . Elemental analyses were performed by the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured in sealed glass tubes and were not corrected.

**Compound 2:**  $\text{PhC}\equiv\text{CH}$  (22.5  $\mu\text{L}$ , 0.21 mmol) was added dropwise to a solution of **1** (0.11 g, 0.21 mmol) in toluene (16 mL) at ambient temperature and stirred for 2 h. After filtration and concentration of the filtrate, **2** was obtained as yellow crystals (0.02 g; 13.6%). M.p.  $115^\circ\text{C}$ ;  $^1\text{H}$  NMR (395.9 MHz,  $[\text{D}_6]\text{benzene}$ ,  $25^\circ\text{C}$ ):  $\delta = 1.15$  (s, 18H, *t*Bu), 1.22 (s, 18H, *t*Bu), 6.88–7.16 (m, 10H, C=C(H)+Ph), 7.36–7.40 (m, 3H, Ph), 7.54–7.58 ppm (m, 3H, Ph);  $^{13}\text{C}$  NMR (99.5 MHz,  $[\text{D}_6]\text{benzene}$ ,  $25^\circ\text{C}$ ):  $\delta = 31.1$  ( $\text{CMe}_3$ ), 31.7 ( $\text{CMe}_3$ ), 52.7 ( $\text{CMe}_3$ ), 52.9 ( $\text{CMe}_3$ ), 125.4, 128.3, 128.5, 128.6, 128.8, 130.3, 130.6, 134.9, 135.1, 150.1 (Ph), 157.1 ((Ph)C=C(H)), 158.2 ((Ph)C=C(H)), 170.8 (NCN), 173.9 ppm (NCN);  $^{29}\text{Si}$  NMR (78.7 MHz,  $[\text{D}_6]\text{benzene}$ ,  $25^\circ\text{C}$ ):  $\delta = 15.1$ , 29.5 ppm; elemental analysis calcd (%) for  $\text{C}_{38}\text{H}_{52}\text{N}_4\text{Si}_2$ : C 73.50, H 8.45, N 9.03; found: C 73.28, H 8.16, N 8.75. Crystal data for **2** ( $\text{C}_{45}\text{H}_{60}\text{N}_4\text{Si}_2$ ):  $M_r = 713.15$ ;  $a = 10.3544(2)$ ,  $b = 13.7776(3)$ ,  $c = 17.4384(5)$  Å;  $\alpha = 111.101(2)$ ,  $\beta = 90.966(2)$ ,  $\gamma = 111.998(1)^\circ$ ;  $V = 2118.6(9)$  Å<sup>3</sup>;  $Z = 2$ ; space group  $P1$  (triclinic);  $T = 103(2)$  K;  $\lambda = 0.71073$  Å;  $\mu = 0.118 \text{ mm}^{-1}$ ;  $\rho_{\text{calcd}} = 1.118 \text{ g cm}^{-3}$ ;  $F(000) = 772$ ; 46961 measured reflections, 13055 independent reflections and 473 refined parameters;  $R1 = 0.0509$ ,  $wR2 = 0.1293$  ( $I > 2\sigma(I)$ ); largest diff. peak and hole  $0.424/-0.324 \text{ e } \text{Å}^{-3}$ .

**Compound 3:** A solution of  $\text{PhC}\equiv\text{CPh}$  (0.073 g, 0.42 mmol) in toluene (1.2 mL) was added dropwise to a solution of **1** (0.11 g, 0.21 mmol) in toluene (16.2 mL) at ambient temperature. After stirring for 2 h, a dark red suspension was formed. Dichloromethane ( $\approx 10 \text{ mL}$ ) was added. The resulting solution was filtered and concentrated to obtain dark-red crystals of **3**. After two hours, the mother liquid was filtered; otherwise the dark red crystals decomposed slowly to give a yellow precipitate. Yield: 0.103 g (47.0%). M.p.  $153^\circ\text{C}$  (dec);  $^1\text{H}$  NMR (399.5 MHz,  $[\text{D}_8]1,4\text{-dioxane}$ ,  $25^\circ\text{C}$ ):  $\delta = 0.983$  (s, 36H, *t*Bu), 6.81–6.91 ppm (m, 30H, Ph);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.4 MHz,  $[\text{D}_8]1,4\text{-dioxane}$ ,  $25^\circ\text{C}$ ):  $\delta = 31.7$  ( $\text{CMe}_3$ ), 66.08 ( $\text{CMe}_3$ ), 125.20, 128.10, 128.15, 128.29, 128.40, 128.89, 129.44, 130.22, 131.50, 138.80 (Ph), 158.46 ((Ph)C=C(Ph)), 181.29 ppm (NCN);  $^{29}\text{Si}\{^1\text{H}\}$  NMR (79.4 MHz,  $[\text{D}_8]1,4\text{-dioxane}$ ,  $25^\circ\text{C}$ ):  $\delta = -51.0$  ppm; UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 266 (19744), 281 (14596), 295 (13047), 299 (13933), 431 nm ( $2223 \text{ mol}^{-1} \text{ m}^2 \text{ cm}^{-1}$ ); elemental analysis calcd (%) for  $\text{C}_{58}\text{H}_{66}\text{N}_4\text{Si}_2$ : C 79.59, H 7.61, N 6.41; found: C 79.32, H 7.51, N 6.24. Crystal data for **3** ( $\text{C}_{72}\text{H}_{82}\text{N}_4\text{Si}_2$ ):  $M_r = 1059.60$ ;  $a = 13.8659(2)$ ,  $b = 13.8659(2)$ ,  $c = 28.2606(6)$  Å;  $\alpha = 90$ ,  $\beta = 90$ ,  $\gamma = 120^\circ$ ;  $V = 4705.5(1)$  Å<sup>3</sup>;  $Z = 3$ ; space group  $P3(1)21$  (trigonal);  $T = 173(2)$  K;  $\lambda = 0.71073$  Å;  $\mu = 0.101 \text{ mm}^{-1}$ ;  $\rho_{\text{calcd}} = 1.122 \text{ g cm}^{-3}$ ;  $F(000) = 1710$ ; 29415 measured reflections, 5553 independent reflections and 350 refined parameters;  $R1 = 0.0743$ ,  $wR2 = 0.2156$  ( $I > 2\sigma(I)$ ); largest diff. peak and hole  $0.437/-0.323 \text{ e } \text{Å}^{-3}$ .

**X-ray data collection and structural refinement:** The crystal data were collected on a Bruker APEX II diffractometer. The structures were solved by direct phase determination (SHELXS-97) and refined for all data by full matrix least squares methods on  $F^2$ .<sup>[25]</sup> All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to reside in their respective parents atoms; they were assigned appropriate isotopic thermal parameters and included in the structure-factor calculations. SQUEEZE/PLATON was employed to treat two highly disordered toluene molecules in the asymmetric unit of **3**. The toluene molecules were removed from the model, but included in the empirical formula. Additional PLATON/SQUEEZE details can be found in the Supporting Information and the CIF file of **3**. CCDC-757725 (**3**) and 757726 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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