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A Delocalized Hypervalent Silyl Radical Supported by Amidinate and Imino Substituents

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Supporting Information Placeholder

ABSTRACT: The reaction of the amidinato silylsilylene with a functionalized diaminochlorosilyl substituent [LSiSi(Cl){(N*t*Bu)$_2$C(H)Ph}] (**1**, L = PhC(N*t*Bu)$_2$) with ArN=C=NAr (Ar = 2,6-*i*Pr$_2$C$_6$H$_3$) in toluene afforded the delocalized hypervalent silyl radical [LSi$^\bullet$(μ-CNAr)$_2$Si{(N*t*Bu)$_2$C(H)Ph}] (**2**). It possesses a hypervalent silyl radical, which delocalizes throughout the Si$_2$C$_2$ ring.

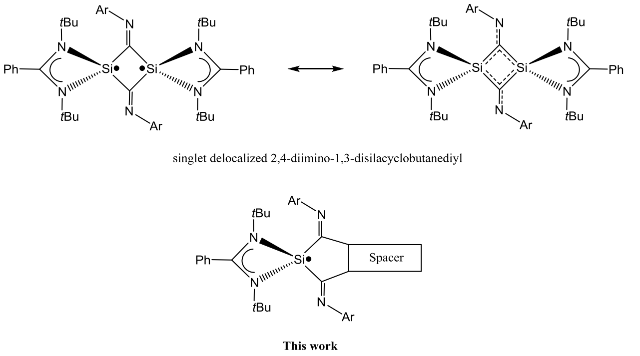
Silyl radicals are one of the most important intermediates in chemistry.[1] However, they have very short lifetimes and their existences have only previously been evidenced by EPR spectroscopy or trapping reactions. Their lifetimes can be prolonged by incorporating sterically hindered substituents at the silicon radical centres, where they are protected from undergoing typical radical reactions, such as dimerization, hydrogen abstraction and disproportionation. The successful isolation of stable silyl radicals opens up many new opportunities because stable radicals can serve as “building blocks” for new materials which may possess a unique combination of magnetic, electrochemical, and photochemical properties. The most spectacular example of such a compound is the cyclotetrasilenyl radical, in which the radical is delocalized in the allylic-type Si$_3$ skeleton.[2] Following this example, the stable silyl radical [(*t*Bu$_2$MeSi)$_3$Si·] was prepared by the oxidation of the corresponding silyl anion [(*t*Bu$_2$MeSi)$_3$SiNa], in which the radical is localized on the three-coordinate silicon centre.[3] Moreover, [(*t*Bu$_2$MeSi)$_3$Si·] was found to be an electrochemical energy storage system.[4] The common features of the abovementioned examples are that the silicon radical centres are three-coordinate and stabilized by sterically hindered silyl ligands. Subsequently, the stable disilene anion radical,[5] disilene cation radical[6] and disilyne anion radical,[7] which comprise a multiple-bonded silicon radical and sterically hindered silyl ligands, were isolated. In addition, the silylene anion radical [(*t*Bu$_2$MeSi)$_2$Si:]$^{\bullet -}$, which has a low valent silicon radical centre, was also synthesized.[8]

In contrast, isolable silyl radicals containing other substituents, such as alkyl, aryl, and heteroatom substituents, are scarcely found. For example, the amino substituted silyl radical [(*t*BuHN)(*t*BuMe$_2$Si)$_2$Si·] has a very short half lifetime and can only be characterized by EPR spectroscopy.[1g] Moreover, the stable phenyl substituted silyl radical [(*t*Bu$_2$MeSi)$_2$(Ph)Si·] exhibits an equilibrium with its silene derivative in solution, which is formed similarly to a dimer of Gomberg’s radical (Ph$_3$C·).[9] When the phenyl substituent is replaced by more sterically hindered aryl substituents such as 4-*t*BuC$_6$H$_4$, 4-PhC$_6$H$_4$, 3,5-*t*Bu$_2$C$_6$H$_3$, the stable aryl-substituted silyl radicals were isolated.[9] Moreover, phenylene- or imino-bridged multisilyl radicals, for example, *p*- and *m*-[{(*t*Bu$_2$MeSi)$_2$Si$^\bullet$}$_2$C$_6$H$_4$] and [{(Me$_3$Si)$_2$HC}$_2$*i*PrSi$^\bullet${μ-NC$_6$H$_3$-3,5-Me$_2$}]$_2$ were isolated, which possess singlet and triplet biradical and singlet biradicaloid characters, respectively.[10]

Recently, several research groups demonstrated the interaction of silicon radicals and N-heterocyclic carbenes (NHCs) resulting in unprecedented structural and electronic properties, which lead to a dispute over their bonding situations.[11] The stable NHC-silyl radical cation [(*t*Bu$_3$Si)$_2$Si$^\bullet$(I$_{\mathrm{Me}}$)]$^+$ (I$_{\mathrm{Me}}$ = :C{N(Me)CMe}$_2$) was isolated by coordinating the silylene radical cation with the N-heterocyclic carbene.[12] In addition, the NHC-disilicon cation [Si$_2$(I$_{\mathrm{Ar}}$)$_2$]$^+$ (I$_{\mathrm{Ar}}$ = :C{N(Ar)CH}$_2$), which is the cationic counterpart of the disilyne radical anion [Si$_2$R$_2$]$^-$, was synthesized.[13] In these examples, the spin density is mainly localized at the silicon centre. In contrast, various cAAC-centered radicals (cAAC = cyclic alkyl(amino) carbene) such as [cAAC$_{\mathrm{Me}}$$^\bullet$-Si(Cl)$_2$-cAAC$_{\mathrm{Me}}$$^\bullet$] (cAAC$_{\mathrm{Me}}$ = :C(CH$_2$)(CMe$_2$)$_2$NAr, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$),[14] [cAAC$_{\mathrm{Me}}$$^\bullet$-SiCl$_3$],[15] [cAAC$_{\mathrm{Me}}$$^\bullet$-(SiCl)$_2$-cAAC$_{\mathrm{Me}}$$^\bullet$],[16] and [cAAC$_{\mathrm{Me}}$$^\bullet$-SiCl$_2PPh_2$],[17] in which the spin densities are resided on the C$_{\mathrm{carbene}}$ atom, were formed by coordinating the corresponding silicon radicals with cAAC. Their different electronic properties are due to the stronger donating and improved accepting abilities of cAAC in comparison with NHC. Due to strong C$_{\mathrm{carbene}}$-Si bonds, the parent silicon radical intermediates in the aforementioned examples have to date not been observed in solution.

Recently, our research group isolated the amidinate-stabilized singlet delocalized 2,4-diimino-1,3-disilacyclobutanediyl [LSi$^\bullet$(μ-CNAr)$_2$Si$^\bullet$L] (L = PhC(N*t*Bu)$_2$, Figure 1) by the reaction of the silicon(I) dimer [LSi:]$_2$ with ArN=C=NAr.[18] This is the first stable example comprising two hypervalent silyl radicals, which extensively delocalize throughout the Si$_2$C$_2$ four-membered ring and exocyclic C=N bonds, resulting in singlet biradicaloid character. The delocalization is illustrated by X-ray crystallography and the biradicaloid character is evidenced by

DFT calculations. If one of the [LSi·] moieties in [LSi•(μ-CNAr)$_2$Si•L] is replaced by a spacer, a novel hypervalent silyl radical, which coordinates to an amidinate substituent, could be isolated.

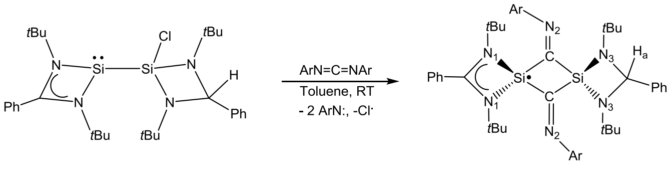


singlet delocalized 2,4-diimino-1,3-disilacyclobutanediyl

This work

Figure 1. The singlet delocalized 2,4-diimino-1,3-disilacyclobutanediyl and proposed hypervalent silyl radical

Hypervalent main-group radicals have been postulated as reactive intermediates in the homolytic substitution chemistry for the formation of carbon-heteroatom bonds.[19a,b] They exist in very shallow potential energy minima and dissociate rapidly by simple bond cleavages.[19c] As such, stable hypervalent main-group radicals are scarcely known.[19d,e] It is anticipated that hypervalent silyl radicals should be worthwhile synthetic targets not only for fundamental bonding studies, but also for their potential application in radical substitution and addition reactions. In this paper, we report for the first time the synthesis and characterization of a delocalized hypervalent silyl radical supported by amidinate and imino ligands.



Scheme 1. Synthesis of compound **2**

The amidinato silylsilylene with a functionalized diaminochlorosilyl substituent [LSiSi(Cl){(N*t*Bu)$_2$C(H)Ph}] (**1**) was reacted with ArN=C=NAr in toluene (Scheme 1). The green reaction mixture was filtered and the filtrate was concentrated to afford the delocalized hypervalent silyl radical [LSi•(μ-CNAr)$_2$Si{(N*t*Bu)$_2$C(H)Ph}] (**2**) as a highly air- and moisture-sensitive red crystalline solid. Compound **2** was characterized by EPR spectroscopy and X-ray crystallography (see below). The mother liquor was filtered and the solvent was removed under reduced pressure. It was analysed by ^{1}H and ^{29}Si NMR and EPR spectroscopy. No EPR signal was observed. The ^{1}H and ^{29}Si NMR spectra of the mother liquor show a mixture of unidentified products and unreacted ArN=C=NAr (see the Supporting Information). In addition, the ^{1}H NMR spectrum of the mother liquor shows a singlet (δ 5.77 ppm) for the N$_2$C*H*Ph proton of the amido "(N*t*Bu)$_2$C(H)Ph" ligand. Along with the upfield ^{29}Si NMR signals of the mother liquor, the byproducts in the mother liquor could be a mixture of silanes bonded with amidinate "PhC(NtBu)$_2$" and/or amido "Ph(H)C(N*t*Bu)$_2$" ligands. However, an attempt to separate the mixture by recrystallization failed. No X-ray quality crystals were grown over a year. Based on the mechanism for the formation of the 2,4-diimino-1,3-disilacyclobutanediyl [LSi•(μ-CNAr)$_2$Si•L],[18] it is proposed that the Si-Si bond in **1** undergoes an insertion reaction with ArN=C=NAr, which then eliminates two nitrene intermediates :N-Ar and a Cl· radical to form **2**. The nitrene intermediates :NAr and Cl· radical further undergo oxidative addition reactions with **1** to form a mixture of silanes bonded with amidinate "PhC(NtBu)$_2$" and/or amido "(N*t*Bu)$_2$C(H)Ph" ligands. Such a proposal can further be supported by the fact that compound **1** can undergo an oxidative addition and Cl-shift reaction.[20] For example, the oxidative addition of **1** with ArN$_3$, which generates a nitrene :NAr intermediate, afforded the silaimine.[20] **1** also underwent a Cl-shift reaction with azobenzene to form the 1,2-diaza-3,4-disilacyclobutane.[20] Besides our work, the Cl· radical elimination is also known in other main-group element complexes.[21]

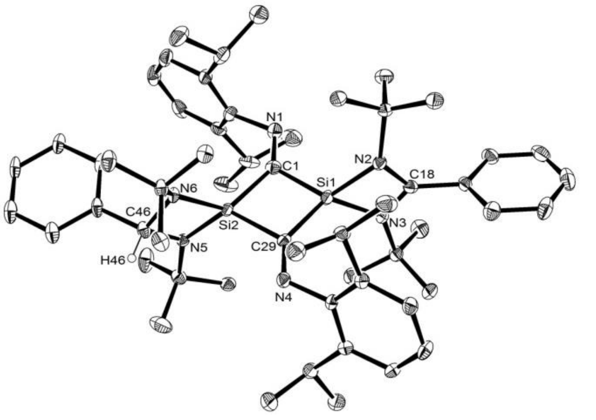


Figure 2. Molecular structure of **2** with thermal ellipsoids at the 25% probability level. Disorder in phenyl ring and hydrogen atoms is omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1-C1 1.854(4), Si1-C29 1.821(4), Si2-C1 1.886(4), Si2-C29 1.905(3), C1-N1 1.289(5), C29-N4 1.323(5), Si1-N2 1.823(3), Si1-N3 1.837(3), N2-C18 1.354(4), N3-C18 1.339(5), Si2-N5 1.725(3), Si2-N6 1.736(3), N5-C46 1.472(4), N6-C46 1.473(5), C1-Si1-C29 87.53(16), Si1-C29-Si2 94.34(16), C29-Si2-C1 84.22(16), Si2-C1-Si1 93.90(17), Si1-C1-N1 125.9(3), Si2-C1-N1 140.2(3), Si1-C29-N4 140.4(3), Si2-C29-N4 125.3(3), C29-Si1-N2 128.74(15), C29-Si1-N3 124.55(15), C1-Si1-N2 122.70(16), C1-Si1-N3 126.98(16), Si1-N3-C18 90.8(2), N3-C18-N2 106.2(3), C18-N2-Si1 90.9(2), N2-Si1-N3 72.12(14), C29-Si2-N5 124.96(14), C29-Si2-N6 121.67(15), C1-Si2-N5 124.92(15), C1-Si2-N6 128.82(15), N5-Si2-N6 78.37(13), Si2-N6-C46 92.1(2), N6-C46-N5 95.9 (3), C46-N5-Si2 92.6(2).

Compound **2** was analysed by X-ray crystallography (Figure 2). The *R*1 value is large (R1 = 0.0985) as red crystals of **2** are not stable during mounting. The Si$_2$C$_2$ four-membered ring is planar and the sum of the interior bond angles is 360°. The amidinate ligand is bidentate coordinated to the Si1 atom, which adopts a tetrahedral geometry. The amido ligand is bonded to the Si2 atom, which adopts a tetrahedral geometry. Moreover, the Si1-N2-C18-N3 ring is planar and tilted with respect to the Si$_2$C$_2$ four-membered ring (dihedral angle = 85.8°). The Si2-N5-C46-N6 ring is also tilted with respect to the Si$_2$C$_2$ four-membered ring (dihedral angle = 86.6°). The C46 atom adopts a tetrahedral geometry, which is different from the planar C18 atom. The Si2-C1 (1.886(4) Å) and Si2-C29 bonds (1.905(3) Å) are typical Si-C single bonds. In addition, the Si1-

C29 (1.821(4) Å) and Si1-C1 (1.854(4) Å) bond lengths are intermediate between the Si-C single (1.87 Å) and double (1.70 Å) bond lengths.[22] The C29-N4 (1.323(5) Å) and C1-N1 (1.289(5) Å) bond lengths are approximately intermediate between the C=N double and C-N(sp^2) single bond lengths. These results indicate that the radical is mainly delocalized throughout the N1C1-Si1-C29N4 skeleton.

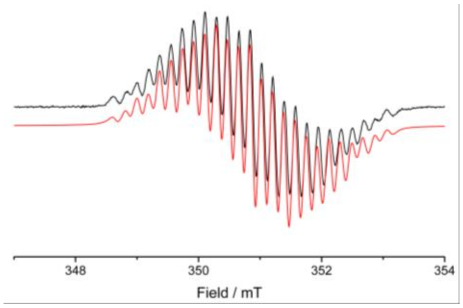


Figure 3. The X-band EPR spectrum (298 K) of compound **2** (black) experimental; (red) simulation

Table 1. The spin Hamiltonian parameters of compound 2

	$^{14}N_1$	$^{14}N_2$	$^{14}N_3$	$^{1}H_a$
[i]n	2	2	2	1
[ii]a_{iso} / MHz				
Expt	10.5	15.0	6.0	<1.0
DFT	11.0	14.8	5.7	1.3

[i] g_{iso} = 2.0082; t_{corr} = 4.5 ns; [i]n = number of equivalent nuclei. [ii] ± 0.1 MHz. Labelled nuclei are shown in Scheme 1.

A solution of compound **2** in toluene was characterized by EPR spectroscopy. The isotropic continuous-wave (CW) EPR spectrum (black line) and the corresponding simulation (red line) are shown in Figure 3. A satisfactory fit to the experimental data was achieved using the spin Hamiltonian parameters listed in Table 1. The simulation was performed using the Easyspin toolbox for Matlab.[23] The simulation revealed the contributions from three different sets of two-equivalent nitrogen ^{14}N nuclei (for labelling, see Scheme 1). These values indicate a slight excess of spin density on the amidinate ligand in comparison to the amido ligand, although from the theoretical isotropic hyperfine constant of ^{14}N (a_o = 1816 MHz), less than 1% s-orbital spin density is calculated on each nitrogen nucleus (0.6, 0.8 and 0.3% on each N_1, N_2 and N_3, respectively). The hyperfine coupling to the final unique H_a proton was calculated as a_{iso} = 0.3 MHz and could not be resolved experimentally. Despite the DFT predicted a_{iso} values of 22.5 and 4.1 MHz on Si1 and Si2 respectively, no hyperfine interaction could be detected to the silicon nuclei due to the low natural abundance of spin-active ^{29}Si (4.7% spin active). These DFT predicted hyperfine values indicate an asymmetric spin density over the Si atoms, as was previously observed for the NHC-stabilised silicon hydride $[(I_{Ar})HSiSi(I_{Ar})]^{\bullet}$.[24] The small ^{29}Si a_{iso} values correspond to only 0.5 and 0.1 % s-orbital spin density, indicating a localization of the unpaired electron in a p-orbital, in good agreement with the density functional calculations (*vide infra*). A rotation correlation time (t_{corr}) of 4.5 ns indicates intermediate rotational dynamics of the paramagnetic species in solution (on a timescale similar to the EPR timescale), resulting in slight broadening of the EPR spectrum.[25] The experimental spin Hamiltonian parameters are in excellent agreement with DFT-calculated hyperfine coupling values based on the crystal structure (Table 1), performed in ORCA 3.0.3[26] using the hybrid PBE0 functional,[27] and a basis set consisting of EPR-II on C, H and N,[28] and def2-TZVP on Si.[29]

To understand the bonding nature in compound **2**, density functional calculations were conducted. The optimized geometry (UB3PW91/6-31+G(d) level, see the Supporting Information) is in good agreement with the X-ray crystallographic data.[30] The singly occupied molecular orbital (α-SOMO, Figure 4b) comprises σ* orbitals of Si-N bonds and π* orbitals of the C=N double bonds. Along with its Mulliken spin density, they precisely shows that the radical is delocalized throughout the Si_2C_2 ring. Accordingly, the natural spin densities are mainly found in the Si and N_{imino} atoms (Table S1). The highest occupied molecular orbital (HOMO) shows primarily the σ orbitals of the Si_2C_2 ring. Moreover, the Wiberg bond index of the Si-C bonds (Si1-C: 0.88, 0.85; Si2-C: 0.68, 0.72) illustrates that the radical is mainly delocalized along the N1C1-Si1-C29N4 skeleton, which is consistent with the spin Hamiltonian parameters of the $^{14}N_1$ and $^{14}N_3$ nuclei.

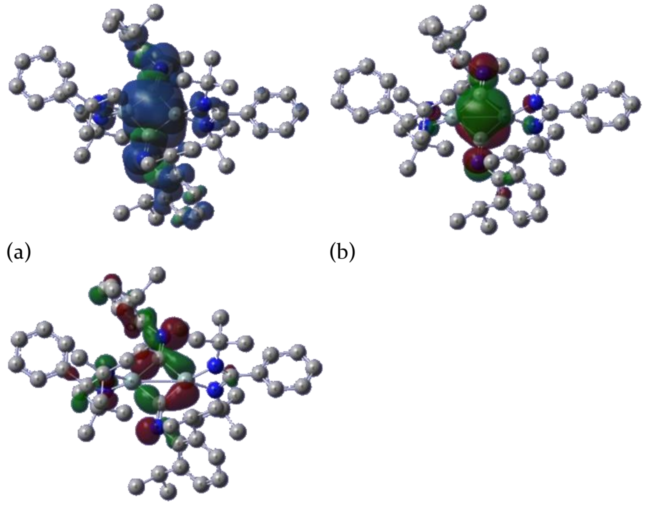

(a)
(b)
(c)

Figure 4. (a) The natural spin density of compound **2**, (b) the SOMO (isovalue = 0.04) of **2** showing the delocalization of radical throughout the Si_2C_2 ring, and (c) the HOMO of **2** showing the σ orbitals of the Si_2C_2 ring.

In conclusion, the first example of the delocalized hypervalent silyl radical [LSi$^{\bullet}$(μ-CNAr)$_2$Si{(N*t*Bu)$_2$C(H)Ph}] (**2**), which is supported by the amidinate and imino substituents, was synthesized by the reaction of the amidinato silylsilylene [LSiSi(Cl){(N*t*Bu)$_2$C(H)Ph}] (**1**) with ArN=C=NAr in toluene. X-ray crystallography, EPR spectroscopy and theoretical studies show conclusively that the hypervalent silyl radical is stabilized by the delocalization throughout the Si_2C_2 ring. The isolation of the by-products, theoretical studies of the mechanism and the reactivity of compound **2** are currently under investigation.

ASSOCIATED CONTENT

Supporting Information

Experimental procedure, selected DFT calculation results, X-ray crystallographic data of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. S.-H.Z. synthesized compound **2**. E.C. performed EPR spectroscopy. H.-W.X. performed DFT calculations. Y.L. analyzed the crystallographic data.

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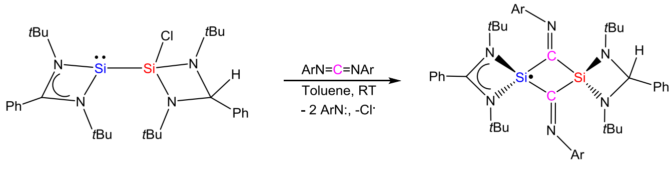

1 **2**

The reaction of the amidinato silylsilylene **1** with ArN=C=NAr (Ar = 2,6-$i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3$) in toluene afforded the delocalized hypervalent silyl radical **2**.