A Delocalized Hypervalent Silyl Radical Supported by Amidinate and Iminob substituents

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ABSTRACT: The reaction of the amidinate silylsilylene with a functionalized dianinochlorosilyl substituent \( [\text{LSiSi(Cl)}(\text{NtBu})_2C(\text{H})\text{Ph}] \) (1, \( L = \text{PhC(NtBu)}_2 \)) with \( \text{ArN}=\text{C}=\text{NAr} (\text{Ar} = \text{2,6-}p\text{Pr}_2C_6H_3) \) in toluene afforded the delocalized hypervalent silyl radical \( [\text{LSiSi}^+(\mu-CNAr)_2] \text{Si}([\text{NtBu}]_2C(\text{H})\text{Ph}] \) (2). It possesses a hypervalent silyl radical, which delocalizes throughout the \( \text{Si}_2\text{C}_2 \) ring.

Silyl radicals are one of the most important intermediates in chemistry. However, they have very short lifetimes and their existence 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 cyclo-tetrasilylenyl radical, in which the radical is delocalized in the allylic-type \( \text{Si}_2 \) skeleton.

Following this example, the stable silyl radical \( [(\text{Bu}_3\text{Si})_2\text{Si}]^- \) was prepared by the oxidation of the corresponding silyl anion \( [(\text{Bu}_3\text{Si})_2\text{Si}]^- \), in which the radical is localized on the three-coordinate silicon centre. Moreover, \( [(\text{Bu}_3\text{MeSi})_2\text{Si}]^- \) was found to be an electrochemical energy storage system. 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, disilene cation radical and disilene anion radicals, which comprise a multiple-bonded silicon radical and sterically hindered silyl ligands, were isolated. In addition, the silylene anion radical \( [(\text{Bu}_3\text{MeSi})_2\text{Si}]^- \), which has a low valent silicon radical centre, was also synthesized.

 nevertheless, the stable phenyl substituted silyl radical \( [(\text{Bu}_3\text{MeSi})_2(\text{Ph})\text{Si}]^- \) exhibits an equilibrium with its silene derivative in solution, which is formed similarly to a dimer of Gomberg’s radical (Ph,C=).\(^9\) When the phenyl substituent is replaced by more sterically hindered aryl substituents such as \( 4\text{-}\text{BuS}_{2}C_6H_3 \), the stable aryl-substituted silyl radicals were isolated. Moreover, phenylene- or imino-bridged multisilyl radicals, for example, \( p \cdot m\cdot [(\text{Bu}_2\text{MeSi})_2\text{Si}]^-\text{C}_6\text{H}_4 \) and \([(\text{Me}_3\text{Si})_2\text{H}_2\text{Si}]^+\text{µ-NC}_6\text{H}_4^{-3,5-}\text{Me}_2\text{C}_6\text{H}_3 \], 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 \( [(\text{Bu}_3\text{Si})_2\text{Si}]^+(\text{Im}_3\text{Me}) \) \( (\text{Im}_3\text{Me} = \text{C}(\text{N}(\text{Me})\text{CMe})_2 \) was isolated by coordinating the silylene radical cation with the N-heterocyclic carbene.\(^12\) In addition, the NHC-disilicon cation \( \text{Si}^+(\text{Im}_3\text{Me})_2 \) \( (\text{Im}_3\text{Me} = \text{C}(\text{N}(\text{Ar})\text{CH})_2 \) ) which is the cationic counterpart of the disilylene radical anion \( \text{Si}^-\text{R}_2 \) was synthesized.\(^13\) In these examples, the spin density is mainly localized at the silicon centre. In contrast, cAAC-centered radicals \( \text{cAAC} = \text{cyclic alkyl (amino) carbene} \) such as \( \text{cAAC}_\text{Me}^-\text{Si}(\text{Cl})_2\cdot\text{cAAC}_\text{Me}^- \) \( (\text{cAAC}_\text{Me} = \text{C}(\text{CH})_2(\text{Me})_2\text{NAr}, \text{Ar} = 2,6-p\text{Pr}_2\text{C}_6\text{H}_3 \) ) \( , \text{cAAC}_\text{Me}^-\text{SiCl}_2 \), \( \text{cAAC}_\text{Me}^-\text{SiCl}_3 \) \( (\text{cAAC}_\text{Me}^-\text{SiCl}_2\cdot\text{cAAC}_\text{Me}^-, \text{cAAC}_\text{Me}^-\text{SiCl}_3\cdot\text{PPh}_3 \) in which the spin densities are resided on the C 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 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 \( 2,4\text{-diimino}-1,3\text{-disilacyclobutanoediy} \) \( [\text{LSi}^+(\mu-CNAr)_2\text{Si}L] \) \( (L = \text{PhC(NtBu)}_2 \), Figure 5) by the reaction of the silicon(IV) dimer \( [\text{LSi}]_2 \) with \( \text{ArN}=\text{C}=\text{NAr} \).\(^16\) This is the first stable example comprising two hypervalent silyl radicals, which extensively delocalize throughout the Si,C 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)]2Si·L is replaced by a spacer, a novel hypervalent silyl radical, which coordinates to an amidinate substituent, could be isolated.

![Diagram of the singlet delocalized 2,4-diimino-1,3-disilacyclobutanediyl](image)

**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.[9,10] They exist in very shallow potential energy minima and dissociate rapidly by simple bond cleavages.[10] As such, stable hypervalent main-group radicals are scarcely known.[9,10,11] 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](image)

**Scheme 1.** Synthesis of compound 2

The amidinato silylsilylene with a functionalized diaminochlorosilyl substituent [LSiSi(C)(NtBu)C(Ph)Ph] (1) was reacted with ArN=C=NR in toluene (Scheme 1). The green reaction mixture was filtered and the filtrate was concentrated under reduced pressure. It was analysed by 1H and 29Si NMR and EPR spectroscopy. No EPR signal was observed. The 1H and 29Si NMR spectra of the mother liquor show a mixture of unidentified products and unreacted ArN=C=NR (see the Supporting Information). In addition, the 1H NMR spectrum of the mother liquor shows a singlet (δ 5.77 ppm) for the NtBuCHPh proton of the amidino "(NtBu)C(Ph)Ph" ligand. Along with the upfield 29Si NMR signals of the mother liquor, the by-products in the mother liquor could be a mixture of silanes bonded with amidinate "Ph(NtBu)" and/or amidino "Ph(H)C(NtBu)" ligands. However, an attempt to separate the mixture by recrystallisation 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)]2Si·L, 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 ·N-Ar and Cl· radical further undergo oxidative addition reactions with 1 to form a mixture of silanes bonded with amidinate "Ph(C(NtBu))", and/or amidino "(NtBu)C(Ph)Ph" ligands. Such a proposal can further be supported by the fact that compound 1 can undergo an oxidative addition and Cl-shift reaction.[21,22] For example, the oxidative addition of 1 with ArN3, which generates a nitrene ·NAr intermediate, afforded the silaimine.[21,22] Also underwent a Cl-shift reaction with azobenzene to form the 1,2-diaza-3,4-disilacyclobutane.[20,21] Besides our work, the Cl· radical elimination is also known in other main-group element complexes.[21,22]
C29 (1.82(4) Å) and Si1-C (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-Ni (1.289(5) Å) bond lengths are approximately intermediate between the C=N double and C-N(sp²) single bond lengths. These results indicate that the radical is mainly delocalized throughout the NiCl-Si-C29N4 skeleton.

![Figure 3](image)

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

<table>
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<th>Table 1. The spin Hamiltonian parameters of compound 2</th>
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<td>giso / MHz</td>
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[i] giso = 2.0082; tcorr = 4.5 ns; N = number of equivalent nuclei.

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 ¹⁴N 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 ¹⁴N (a₀ = 186.4 MHz), less than 1% s-orbital spin density is calculated on each nitrogen nucleus (0.6, 0.8 and 0.3% on each N₁, N₂ and N₃, respectively). The hyperfine coupling to the final unique Hₙ proton was calculated as aiso = 0.3 MHz and could not be resolved experimentally. Despite the DFT predicted aiso 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 ²⁹Si (4.7% spin active). These DFT predicted hyperfine values indicate an asymmetric spin density over the Si atoms, as was previously observed for the NH₃-stabilised silicon hydride [(Iₐ)H₂Si[(Iₐ)]:.24 The small ²⁹Si aiso 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 (tcorr) 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 based on the crystal structure (Table 1), performed in ORCA 3.0.36 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 Si₃C₃ ring. Accordingly, the natural spin densities are mainly found in the Si and Nnimino atoms (Table S1). The highest occupied molecular orbital (HOMO) shows primarily the σ orbitals of the Si₃C₃ ring. Moreover, the Wiberg bond index of the Si-C bonds (Si-C: 0.88, 0.85; Si2-C: 0.68, 0.72) illustrates that the radical is mainly delocalized along the NiCl-Si-C29N4 skeleton, which is consistent with the spin Hamiltonian parameters of the ¹⁴N₁ and ¹⁴N₃ nuclei.

![Figure 4](image)

Figure 4. (a) The natural spin density of supporting 2, (b) the SOMO (isovalue = 0.04) of 2 showing the delocalization of radical throughout the Si₃C₃ ring, and (c) the HOMO of 2 showing the σ orbitals of the Si₃C₃ ring.

In conclusion, the first example of the delocalized hypervalent silyl radical [LSi{μ-CNAr}$_2$Si{(N(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(Bu)$_2$)C(H)Ph}] (1) with ArN=C=NR in toluene. X-ray crystallography, EPR spectroscopy and theoretical studies show conclusively that the hypervalent silyl radical is stabilized by the delocalization throughout the Si₃C₃ 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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REFERENCES

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Author Contributions
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(30) For the details of DFT calculations, see the Supporting Information.
The reaction of the amidinato silylsilylene 1 with ArN=C=NAr (Ar = 2,6-iPr₂C₆H₃) in toluene afforded the delocalized hypervalent silyl radical 2.