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Isolable *p*- and *m*-[(^{t}Bu$_2$MeSi)$_2$Si]$_2$C$_6$H$_4$: Disilaquinodimethane vs Triplet Bis(silyl radical)

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S *Supporting Information*

ABSTRACT: Isomeric *p*- and *m*-disilaquinodimethanes **2** and **4** were synthesized by the reductive dehalogenation of the corresponding *p*- and *m*-bis(halosilyl)benzenes **1** and **3**, respectively, and were isolated and structurally characterized. The X-ray diffraction and solid-state NMR studies of **2** revealed its singlet quinodimethane structure featuring two exocyclic Si=C double bonds with some singlet biradical contribution. In contrast, the X-ray crystallography and EPR measurements of **4** disclosed its biradical nature, described as a triplet ground state bis(silyl radical).

Organic free radicals are open-shell species featuring an unpaired electron and are ubiquitous in a variety of chemical transformations. To date, a number of free radicals have been classified as persistent or even isolable species, in which the highly reactive odd-electron centers are stabilized by either thermodynamic or kinetic means.[1] On the other hand, the high-spin molecules possessing several radical centers in a single molecule and serving as model compounds for the design of organic ferromagnetic materials[1,2] are more challenging, especially from the viewpoint of potential communication between the radical centers. Among the most representative examples of such species, one can mention *p*- and *m*-quinodimethane derivatives, of which the *para*-isomer is known to possess a singlet ground state with a closed-shell quinoid form,[3] whereas the *meta*-isomer was shown to manifest a robust triplet ground state.[4]

The heavy analogues of organic free radicals featuring an unpaired electron on a silicon, germanium, tin, or lead atom as the key reactive intermediates in a number of organometallic transformations represent another important synthetic challenge.[5] Although the first persistent radicals of the type [(Me$_3$Si)$_2$CH]$_3$E$^\bullet$ (E = Si, Ge, Sn) were reported by Lappert and coworkers as early as 1973,[6] the isolation and structural characterization of the first stable cyclotrigermenyl radical was reported by Power et al. in 1997,[7a] and then the stable silyl radical was achieved in 2001 with the synthesis of a cyclotetrasilenyl radical.[7b] Since then, several other representatives of isolable silyl,[8] germyl,[8,9] stannyl,[10] and plumbyl[11] radicals have been reported, including neutral acyclic nonconjugated radicals, cyclic radicals, and charged radical species (such as silylene anion-radical, disilene anion-radical and cation-radical, and disilyne anion-radical) as well as singlet biradicaloid species.[12] However, despite such recent advances in the field, oligo-radicals with two (or more) heavy group 14 element radical centers have remained elusive. In this paper, we report the synthesis and structural identification of the isomeric *p*- and *m*-disilaquinodimethanes **2** and **4**, of which the former is classified as having a predominantly singlet ground-state *p*-disilaquinodimethane form featuring two exocyclic Si=C bonds, whereas the latter was found to represent a triplet ground-state bis(silyl radical).

1,4-Bis(bromosilyl)benzene derivative **1** was reduced with 2 equiv of KC$_8$ in dry THF at −78 °C, forming 3,6-bis[bis(di-*tert*-butylmethylsilyl)silylidene]cyclohexa-1,4-diene (**2**), which was isolated from pentane as air-sensitive purple crystals in 23% yield (Scheme 1). Likewise, the *meta*-isomer, 1,3-bis[bis(di-*tert*-butylmethylsilyl)silyl]benzene-1′,1″-diyl (**4**), was prepared by reduction of the corresponding precursor, 1,3-bis(iodosilyl)benzene derivative **3**, and isolated by recrystallization from pentane as air-sensitive yellow crystals in 29% yield (Scheme 1).[13,14] The electronic spectra of isomeric **2** and **4** were distinctly different (see the Supporting Information). Thus, the longest wavelength absorption of **2** was remarkably red-shifted compared with that of **4** (**2**, 555 nm (ε 6800) vs **4**, 414 nm (ε 870), 433 nm (ε 780)),[14] pointing to different electronic structures for **2** and **4**. Such a distinction was demonstrated by X-ray crystallographic studies, which revealed that in their crystalline form these two isomers have quite different geometries. Thus, **2** exhibited a disilaquinodimethane structure with trigonal-planar configuration at the Si1 and Si1$^\#$ atoms (sum of the bond angles 359.96°) and coplanar alignment of the 3p(Si) and 2p(C) (aromatic ring) orbitals, allowing their effective π-conjugation (Figure 1, left).[14] The Si1−C1 bond of 1.8174(14) Å is notably shorter than typical Si−C(aryl) single bonds (1.879 Å),[15] although longer than the Si=C bonds in previously reported silenes (1.702−1.775 Å).[16] Within the six-membered ring, C−C bond alternation characteristic of the cyclohexa-1,4-diene system was observed, C1−C2 = 1.423(2) Å, C1−C3$^\#$ = 1.422(2) Å, C2−C3 = 1.3700(19) Å, although the extent of such alternation ($\Delta \approx 0.05$ Å) was smaller than that of the carbon analogue, tetraphenylparaquinodimethane ($\Delta = 0.10$ Å).[3b] These structural features of **2** imply that its structure is best described as the predominant contribution of the closed-shell quinoid form with some (but by no means full) contribution of the singlet bis(silyl radical) character. The solid-state ^{13}C and ^{29}Si NMR spectra of **2** are also in accord with its formulation as the *p*-disilaquinodimethane derivative: the resonances observed at 156.3 ppm (^{13}C NMR) and 91.1 ppm (^{29}Si NMR) are typical for the doubly bonded C and Si atoms of stable silenes Si=C.[16]

In contrast, in **4** the 3p(Si) and 2p(C) (aromatic ring) orbitals are orthogonal to each other, an arrangement that prevents their

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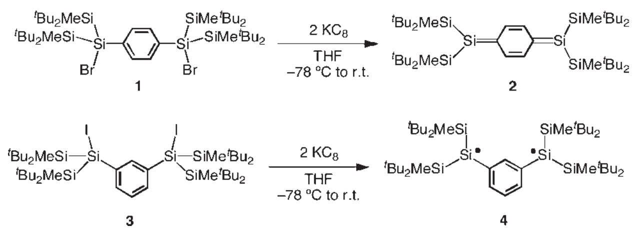
Scheme 1. Synthesis of the Disilaquinodimethane 2 and Bis(silyl radical) 4



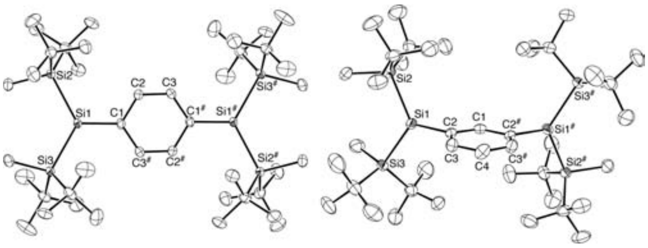


Figure 1. (Left) ORTEP drawing of **2** (50% probability level). One of the *tert*-butyl groups on Si3 is disordered, and the minor contribution (occupancy factor 0.299) and hydrogen atoms are omitted for clarity. # indicates the following symmetry transformation: $-x$, $-y+1$, $-z$. Selected bond lengths (Å) and angles (deg): Si1−Si2 = 2.3675(6), Si1−Si3 = 2.3737(6), Si1−C1 = 1.8174(14), C1−C2 = 1.423(2), C1−C3$^\#$ = 1.422(2), C2−C3 = 1.3700(19). Si2−Si1−Si3 = 122.86(2), Si2−Si1−C1 = 117.52(5), Si3−Si1−C1 = 119.58(5), Si1−C1−C2 = 120.66(11), Si1−C1−C3$^\#$ = 124.39(11), C2−C1−C3$^\#$ = 114.94(12), C1−C2−C3 = 122.78(13), C2−C3−C1$^\#$ = 122.29(13). (Right) ORTEP drawing of **4** (50% probability level). Hydrogen atoms are omitted for clarity. # indicates the following symmetry transformation: $-x+1/2$, $-y+1/2$, z. Selected bond lengths (Å) and angles (deg): Si1−Si2 = 2.3554(14), Si1−Si3 = 2.3524(14), Si1−C2 = 1.9108(19), C1−C2 = 1.387(3), C1−C2$^\#$ = 1.387(3), C2−C3 = 1.395(5), C3−C4 = 1.386(4), C4−C3$^\#$ = 1.386(4). Si2−Si1−Si3 = 122.21(5), Si2−Si1−C2 = 117.15(5), Si3−Si1−C2 = 119.29(5), C2−C1−C2$^\#$ = 123.2(4), Si1−C2−C1 = 120.8(3), Si1−C2−C3 = 121.73(17), C1−C2−C3 = 117.5(2), C2−C3−C4 = 121.0(3), C3−C4−C3$^\#$ = 119.7(4).

π-bonding, although the geometry at both Si1 and Si1$^\#$ atoms is still nearly trigonal-planar (sum of the bond angles 358.65°) (Figure 1, right).[14] Accordingly, the Si1−C2 and Si1$^\#$−C2$^\#$ bonds of 1.9108(19) Å were no longer shortened, and C−C bond alternation was not observed within the six-membered ring, pointing to its 6π-electron aromaticity. Such structural peculiarities of **4** permit its classification as a bis(silyl radical) bridged by a *m*-phenylene group, and indeed computations showed the preference for the triplet ground state of **4** over its singlet state by ~20 kcal/mol.[17] Such an assumption on the spin multiplicity of **4** was further corroborated by its EPR measurements. The EPR spectrum of **4** (Figure 2) measured at 80 K in 3-methylpentane showed characteristic signals at 335.2 mT ($g = 2.0034$). As is well known, the EPR resonances of triplet biradicals are split by the magnetic dipole−dipole interaction between unpaired electrons (zero-field splitting, ZFS).[19] Accordingly, the EPR signal of **4** was split into six lines with the ZFS parameters $D = 6.4 \times 10^{-3}$ cm^{-1} (13.8 mT) and $E = 0.80 \times 10^{-3}$ cm^{-1} (1.72 mT). The average distance between the unpaired electrons in **4** was thus estimated as 5.89 Å, assuming the point-dipole approximation, a value that is close to the distance of 5.72 Å determined from the X-ray crystal structure, indicating that in **4** the two unpaired electrons reside mainly on the silicon atoms. A resonance at 167.4 mT was observed in a characteristic half-field region corresponding to a forbidden $\Delta m = 2$ transition. The temperature-dependent EPR measurements of this signal intensity revealed that it follows the Curie law (see the Supporting Information),[18] indicating that **4** represents a triplet ground-state biradical, despite the perpendicular arrangement of its *m*-phenylene π-orbitals and 3p(Si) orbitals holding unpaired electrons, in contrast to the coplanar conjugated system of these orbitals in the carbon analogue.[1,2]

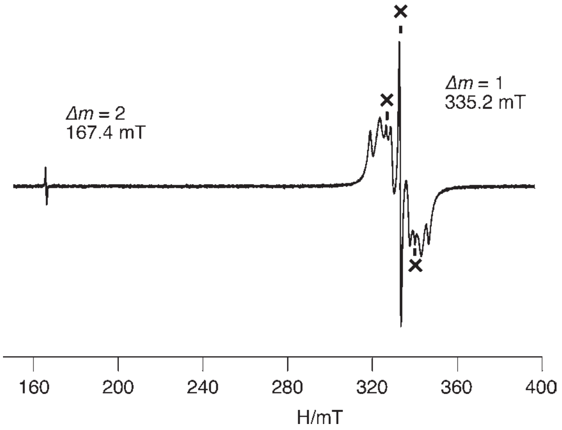
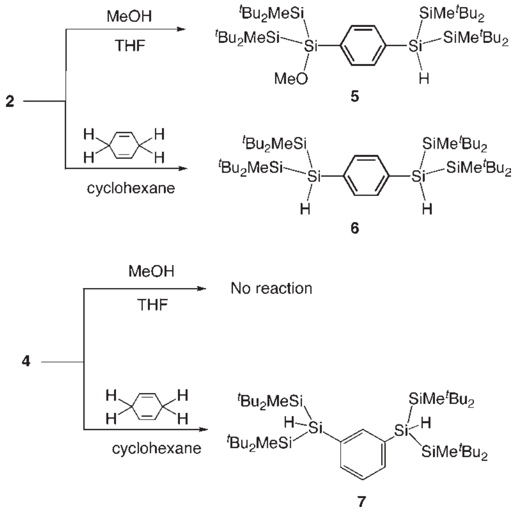


Figure 2. EPR spectrum of **4** in 3-methylpentane at 80 K. The peaks marked by × are due to a monosilyl radical impurity.

Scheme 2. Reactivity of the Disilaquinodimethane 2 and Bis(silyl radical) 4



In accord with their differing structures, **2** and **4** react differently with MeOH and 1,4-cyclohexadiene (Scheme 2). Thus, **2** is reactive toward both MeOH (as a typical reagent for silenes) to give the 1,6-adduct **5** and 1,4-cyclohexadiene (as a hydrogen donor) to give the hydrogen-abstraction product **6** in quantitative yields.[14] These results indicate that **2** has both a Si═C double bond and bis(silyl radical) reactivity. On the other hand, although **4** failed to react with MeOH, it quantitatively reacted with 1,4-cyclohexadiene to form *m*-bis(hydrosilyl)benzene **7**,[14] indicating that **4** has only bis(silyl radical) reactivity.

In summary, we have succeeded in the synthesis, isolation, and structural characterization of the first stable *p*- and *m*-disilaquinodimethane derivatives, **2** and **4**. Their noticeable differences are the alignments of the 3p(Si) and 2p(C) (aromatic ring) orbitals. The former exhibited a nearly planar arrangement, giving a *p*-disilaquinodimethane structure, whereas the latter exhibited an orthogonal arrangement, leading to a diradical structure with a triplet ground state.

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental procedures and spectral data for compounds **1**−**7**; tables of crystallographic data, including atomic positional and thermal parameters, and CIF files for **2** and **4**; UV−vis spectral charts of **2** and **4**; temperature-dependent EPR spectral chart of **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) For temperature-dependent EPR measurements of **4**, see the Supporting Information.

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