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Access to a Stable Si_2N_2 Four-Membered Ring with Non-Kekulé Singlet Biradical Character from a Disilyne

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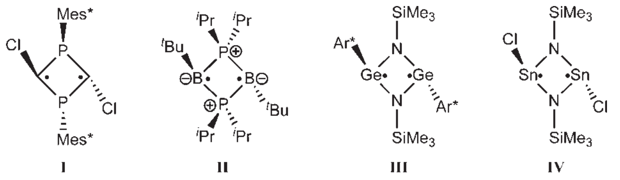
Supporting Information

ABSTRACT: The reactions of 1,1,4,4-tetrakis[bis(trimethylsilyl)methyl]-1,4-diisopropyltetrasila-2-yne **1** with an equivalent amount of *trans*- and *cis*-3,3′,5,5′-tetramethylazobenzenes produced a Si_2N_2 four-membered ring biradicaloid [$RSi(\mu\text{-}NAr)_2SiR$] **2** (R = $Si^iPr[CH(SiMe_3)_2]_2$, Ar = 3,5-$Me_2C_6H_3$), which was isolated as air- and moisture-sensitive dark purple crystals. Compound **2** displays no EPR signal, and the molecular structure of **2** was characterized by NMR spectroscopy and X-ray crystallography, revealing that **2** has a planar centrosymmetric Si_2N_2 four-membered ring. The Si1−Si1′ distance is 2.63380(9) Å, and there is no bond interaction between the Si1 and Si1′ atoms of **2**. The reactions of **2** with methanol and carbon tetrachloride show that **2** has both closed-shell and radical-type reactivity.

Biradicals are important chemical species that have been postulated by theorists and experimentalists as reactive intermediates; however, typical organic biradicals are too unstable to isolate.[1] However, since Niecke and co-workers reported the first isolable carbon-centered four-membered cyclic biradical, 1,3-diphosphacyclobutane-2,4-diyl $Mes^*P(\mu\text{-}CCl)_2PMes^*$ (Mes^* = 2,4,6-$^tBu_3C_6H_2$) (**I**) in 1995,[2] several additional C_2P_2 four-membered ring biradicals and their reactivities have been reported (Chart 1).[3] Recently, Bertrand and co-workers also reported the synthesis and reactivities of boron-centered B_2P_2 four-membered ring biradicals, such as $^iPr_2P(\mu\text{-}B^tBu)_2P^iPr_2$ (**II**), which have non-Kekulé singlet biradical character.[4] In the field of heavier group 14 elements, germanium- and tin-centered four-membered cyclic biradical species, $Ar^*Ge(\mu\text{-}NSiMe_3)_2GeAr^*$ (Ar^* = 2,6-$Dipp_2C_6H_3$, Dipp = 2,6-$^iPr_2C_6H_3$) (**III**)[5] and $ClSn(\mu\text{-}NSiMe_3)_2SnCl$ (**IV**),[6] were also reported by Power's and Lappert's groups in 2004 (Chart 1). Thus, four-membered cyclic systems with heteroatoms have been shown to be beneficial for the stabilization of biradicaloids.[7] However, one of the most important silicon analogues of four-membered ring biradicals has remained elusive because of the synthetic difficulty in preparing such molecules.

In 2004, we succeeded in synthesizing the first isolable disilyne **1**, RSi≡SiR (R = $Si^iPr[CH(SiMe_3)_2]_2$),[8,9] and we are currently investigating its reactivity toward a variety of reactants: alkenes,[10] alkynes,[10] RLi (R = ^tBu, Me),[11] alkali metals,[11a,12] nitriles,[13] silylcyanides,[14] amines,[15a,b] 9-borabicyclo[3.3.1]nonane (9-BBN),[15a,c] 1,3,4,5-tetramethylimidazol-2-ylidene (NHC),[16] 4-dimethylaminopyridine (DMAP).[17] Wiberg's and Tokitoh's groups also reported the synthesis of disilynes and their reactivity toward C−C multiply bonded compounds.[18] These reactions not only demonstrate the chemistry of the Si≡Si bond but also allow access to unsaturated organosilicon compounds, which are difficult to make by traditional methods. Thus, we concluded that disilynes are good precursors for the synthesis of numerous types of unsaturated organosilicon compounds.[7] We present here the reaction of disilyne **1** with azobenzene derivatives, providing a new member of a stable Si_2N_2 four-membered ring biradicaloid [$RSi(\mu\text{-}NAr)_2SiR$] **2** (Ar = 3,5-$Me_2C_6H_3$), which was characterized by spectroscopic data and X-ray crystallography. In addition, we also report its unique reactivity toward methanol and carbon tetrachloride, showing that **2** has both closed-shell and radical-type reactivity.

Chart 1. Isolable Four-Membered Cyclic Biradicals I, II, III, and IV



Ar^* = 2,6-$Dipp_2C_6H_3$, Dipp = 2,6-$^iPr_2C_6H_3$

The reaction of disilyne **1** with 1 equiv of *trans*-3,3′,5,5′-tetramethylazobenzene in THF at room temperature under light-shielded conditions gave a dark purple solution of $RSi(\mu\text{-}NAr)_2SiR$ (**2**). The reaction proceeded slowly, and it took 24 h for completion. However, the reaction was very fast and complete within 5 min when *cis*-3,3′,5,5′-tetramethylazobenzene was used.[19] Recrystallization from THF afforded air- and moisture-sensitive dark purple crystals of **2** in 58% yield (Scheme 1).[20,21] Recently, Power's group reported the reaction of the germanium and tin alkyne analogues Ar^*EEAr^* with azobenzene; however, these reactions gave only hydrazine derivatives $Ar^*E\{(Ph)\text{-}NN(Ph)\}EAr^*$.[22]

The molecular structure of **2** determined by X-ray analysis is shown in Figure 1.[20] In brief, the gross structural features of **2** are geometrically similar to those of germanium and tin analogues **III** and **IV**. Compound **2** has a perfectly planar centrosymmetric Si_2N_2 four-membered ring. The geometry at the nitrogen atoms is trigonal-planar (sum of interligand angles = 359.9°), and that of the silicon atoms is pyramidal (sum of interligand angles = 317.8°). The Si−N bond lengths of 1.7654(14) and 1.7644(14) Å are slightly longer than the typical range for Si−N single bond

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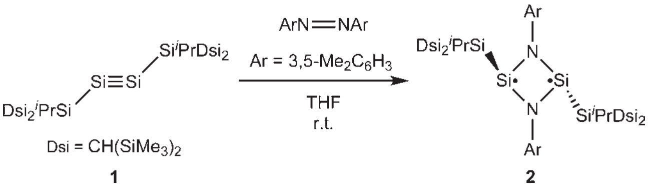
Scheme 1. Reactions of Disilyne 1 with *trans*- and *cis*-3,3′,5,5′-Tetramethylazobenzenes, Giving a Biradicaloid [RSi(μ-NAr)$_2$SiR] 2 (R = Si^{i}Pr[CH(SiMe$_3$)$_2$]$_2$, Ar = 3,5-Me$_2$C$_6$H$_3$)



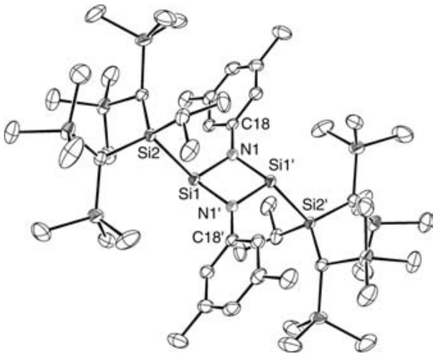
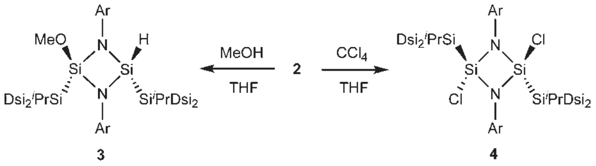


Figure 1. ORTEP drawing of **2** (50% thermal ellipsoids). Hydrogen atoms and a THF molecule as a crystallization solvent are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1−N1, 1.7654(14); Si1−N1′, 1.7644(14); Si1−Si1′, 2.6380(9); Si1−Si2, 2.4836(6); N1−C18, 1.4140(19); N1−Si1−N1′, 83.27(6); N1−Si1−Si2, 120.82(5); N1′−Si1−Si2, 113.72(5); Si1−N1−Si1′, 96.73(6); Si1−N1−C18, 132.28(11); Si1′−N1−C18, 130.90(11).

lengths (1.713 Å).[23] The Si1···Si1′ distance of 2.6380(9) Å is notably longer than a normal Si−Si single bond length (2.341 Å),[23] but it is slightly shorter than the sterically elongated Si−Si single bond of the disilane ^{t}Bu$_3$Si−Si^{t}Bu$_3$ (2.697 Å).[24] Despite this, the "atoms in molecules" (AIM) analysis of the model compound **2′** (using SiMe$_3$ and Ph groups instead of Si^{i}Pr[CH(SiMe$_3$)$_2$]$_2$ and 3,5-Me$_2$C$_6$H$_3$, respectively), which predicts geometrical features that are similar to those found in the X-ray structure of **2**, showed no bond-critical point between the skeletal Si atoms. Therefore, there is no bond interaction between the Si1 and Si1′ atoms of **2**.

Because biradicaloid **2** displays no EPR signal and normal ^{1}H, ^{13}C, and ^{29}Si NMR signals at room temperature, **2** has a singlet ground state. The large singlet−triplet energy gap ($\Delta E_{\mathrm{S-T}}$ = 12.8 kcal mol^{-1}) calculated for model compound **2′** also supports a singlet ground state for **2**.[20] In the ^{29}Si NMR spectrum of **2**, measured by an inverse-gate pulse sequence, a signal for the skeletal silicon atoms was observed at 19.4 ppm, which lies in the range of typical sp^3 silicon atoms and shows that **2** also has pyramidalized skeletal Si atoms in solution. Calculations using the GIAO method for the model compound **2′** agreed with the observed value (14.7 ppm for the skeletal Si). The UV−vis spectrum of **2** in hexane shows a strong absorption maximum at 529 nm (ε = 32 000 M^{-1} cm^{-1}),[20] which is very similar to that of **III** (521 nm). According to the calculated absorption maxima of **2′** using the TD-DFT method, the strong absorption maximum of **2** is assigned to the overlap of two $\pi-\pi^*$ electronic transitions of the Si$_2$N$_2$ four-membered ring (HOMO−1 → LUMO and HOMO → LUMO).

Scheme 2. Reaction of the Biradicaloid 2 with Methanol and Carbon Tetrachloride



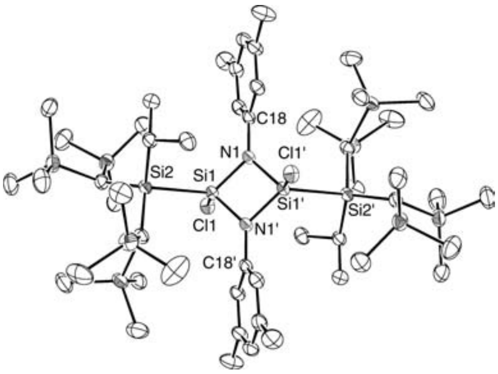


Figure 2. ORTEP drawing of **4** (50% thermal ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si1−N1, 1.7479(14); Si1−N1′, 1.7536(13); Si1−Cl1, 2.0909(6); Si1−Si1′, 2.5889(8); Si1−Si2, 2.4676(6); N1−C18, 1.425(2); N1−Si1−N1′, 84.65(6); N1−Si1−Si2, 117.30(5); N1′−Si1−Si2, 123.11(5); Si1−N1−Si1′, 95.35(6); Si1−N1−C18, 133.94(11); Si1′−N1−C18, 130.65(11).

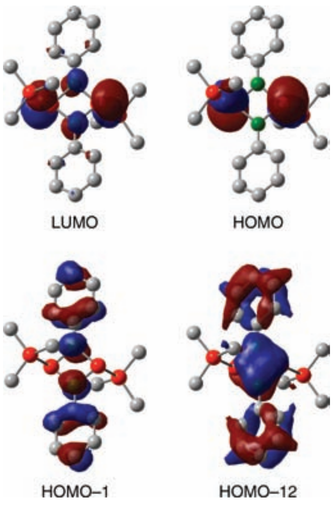


Figure 3. Frontier Kohn−Sham orbitals of Me$_3$SiSi(μ-NPh)$_2$SiSiMe$_3$ **2′** at the B3LYP/6-31G(d) level.

When **2** was reacted with MeOH at room temperature in THF, the purple color of the solution disappeared to give *cis*-adduct **3** as colorless crystals in 65% yield (Scheme 2).[20] In contrast, **2** also reacted with CCl$_4$, which is a well-known silyl-radical scavenger, in THF to give *trans*-adduct **4** as colorless crystals in 55% yield (Scheme 2, Figure 2).[20] These reactivity studies indicate that **2** has both closed-shell and radical-type reactivity. Breher and co-workers recently reported that pentasila[1.1.1]propellane Si_5Mes_6 has a similar biradicaloid reactivity.[25]

Although **2** has remarkably pyramidalized skeletal silicon atoms, there are also six π-electrons in the Si_2N_2 four-membered ring (two lone-pair electrons on the nitrogen atoms and two radical electrons on the silicon atoms). Therefore, biradicaloid **2** is expected to be an aromatic compound. The calculated frontier orbitals of **2′** include the four π-orbitals, with six π-electrons in the Si_2N_2 four-membered ring corresponding to 6π-aromatic character, as depicted in Figure 3. The HOMO is the singlet biradical orbital of the skeletal silicon atoms, which shows a nonbonding combination centered on the silicon atoms. The HOMO−1 corresponds to the lone pairs on the skeletal nitrogen atoms with a contribution from the π-orbitals of the phenyl groups, and the HOMO−12 and LUMO are the corresponding bonding and antibonding π-orbitals of the Si_2N_2 four-membered ring. The calculated NICS value of **2′** is negative [−9.9 for NICS(0) and −4.2 for NICS(1)], which shows the aromaticity of **2**.[26,27] However, the Si−N bond lengths of **4** (1.7479(14) and 1.7536(13) Å) are slightly shorter than those of **2** (1.7654(14) and 1.7644(14) Å), despite the breaking of the 6π aromaticity of the Si_2N_2 four-membered ring by the addition of two chlorine atoms. Therefore, we concluded that biradicaloid **2** has some aromatic character,[27] but the aromatic character is too small to affect the Si−N bond length in the Si_2N_2 four-membered ring.

In summary, we report a new synthetic strategy for a Si_2N_2 four-membered ring biradicaloid [RSi(μ-NAr)$_2$SiR] **2** by the reaction of disilyne **1** with azobenzene derivatives. In contrast to the reaction of the germanium and tin alkyne analogues Ar*EEAr* with azobenzene to produce hydrazine derivatives, disilyne **1** produces a Si_2N_2 four-membered ring biradicaloid by cleavage of the two π-bonds in **1**. The spectroscopic data and the molecular structure determined by X-ray crystallography of **2** as well as reactivity with MeOH and CCl_4 show that **2** has a non-Kekulé singlet biradicaloid character.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. The experimental procedures of **2**, **3**, and **4**; UV−vis spectral chart of **2**; computational results on the model compounds **2′** and **4′**; table of crystallographic data including atomic positional and thermal parameters for **2** and **4** (PDF/CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) The reaction mechanism of **1** with azobenzene derivatives to form **2** is not clear at this moment; however, the first step of the reaction is σ-coordination of the nitrogen lone pair electrons of the azobenzene to the in-plane LUMO ($\pi_{\mathrm{in}}{}^*$) of **1**, as reported in the reaction of **1** with amines (see ref 15a,15b). This is also in agreement with the faster reaction rate observed for the *cis*-isomer as compared to the *trans*-isomer. This has also been seen in the case of *cis*- and *trans*-2-butenes (see ref 10).

(20) For the experimental procedures, spectral data of **2**−**4**, and crystal data of **2** and **4**, UV−vis chart of **2**, and details of the theoretical studies of **2′** and **4′**, see the Supporting Information.

(21) Disilyne **1** reacts with azobenzene, and NMR analysis of the reaction mixture showed the presence of a similar product. However, the product cannot be isolated because of its instability and low yield.

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(27) The NICS value of the model compound **4′** (using $\mathrm{SiMe_3}$ and Ph groups instead of $\mathrm{Si^{\mathit{i}}Pr[CH(SiMe_3)_2]_2}$ and 3,5-$\mathrm{Me_2C_6H_3}$, respectively) is also negative (−8.0 for NICS(0) and −2.1 for NICS(1)), due to the influence of the σ-electrons in the four-membered ring (see ref 26b). The NICS value of **2′** is slightly more negative compared with that of **4′**, suggesting that the magnitude of π aromaticity in **2** is very small. For the discussion of the aromaticity in systems with σ-electrons, see ref 26b.