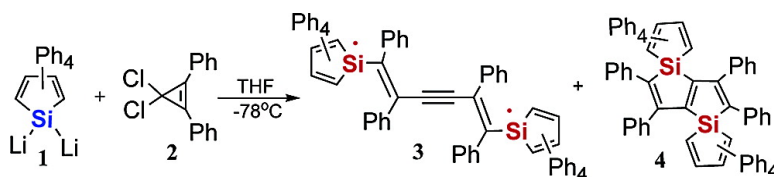


A Disilapentalene and a Stable Diradical from the Reaction of a Dilithiosilole with a Dichlorocyclopropene

Irina S. Touloukhonova, Thomas C. Stringfellow, Sergei A. Ivanov, Artem Masunov, and Robert West

J. Am. Chem. Soc., **2003**, 125 (19), 5767-5773 • DOI: 10.1021/ja020763h • Publication Date (Web): 16 April 2003

Downloaded from <http://pubs.acs.org> on March 26, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 4 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

A Disilapentalene and a Stable Diradical from the Reaction of a Dilithiosilole with a Dichlorocyclopropene

Irina S. Touloukhonova,[†] Thomas C. Stringfellow,[†] Sergei A. Ivanov,[†]
Artem Masunov,[‡] and Robert West*[†]

Contribution from the Organosilicon Research Center, Department of Chemistry,
University of Wisconsin, Madison, Wisconsin 53706, and T-12 Theoretical Division,
Los Alamos National Lab, Los Alamos, New Mexico 87544

Received May 31, 2002; E-mail: west@chem.wisc.edu

Abstract: The reaction of 1,1-dilithio-2,3,4,5-tetraphenylsilole (**1**) with 1,1-dichloro-2,3-diphenylcyclopropene (**2**) leads to the novel 1,4-disila-1,4-dihydropentalene (**4**), as well as an exceptionally stable diradical for which the structure **3** is suggested. The diradical is unreactive toward water, methanol, and chloroform; upon heating it transforms into **4**. Structure **3** for the paramagnetic species is proposed on the basis of EPR data and theoretical calculations. The *trans-trans* isomer of diradical **3** was calculated to be more stable than its *cis-cis* isomer. The strong and stable EPR signal in the reaction mixture is probably due to the *trans-trans* isomer of diradical **3** in the triplet state. A reaction scheme describing the formation of **3** and **4** is presented.

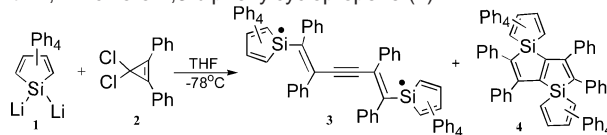
Introduction

Silole dianions are attractive subjects for investigation from both theoretical and synthetic points of view. The structure of silole dianions has been discussed extensively in the literature, and the aromatic character of silole dianions was clearly shown in several publications.^{1–5} However, reactions of these dianions have mainly been limited to those with simple electrophiles,^{6–9} which were often used as trapping agents. Here we report the reaction of 1,1-dilithio-2,3,4,5-tetraphenylsilole (**1**) with 1,1-dichloro-2,3-diphenylcyclopropene (**2**), which leads to two quite unexpected products, **3** and **4** (Scheme 1).

Results and Discussion

A bright red, strongly paramagnetic solution is obtained in the reaction of **1** with **2**. After separation of byproduct lithium chloride and evaporation of solvent, the resulting dark red solid shows a strong EPR signal which persists for many months, even when exposed to air. The spin quantity was determined to be 3.21×10^{19} spins in a solution of 0.040 g of the solid product in 0.7 mL of benzene, corresponding to a 75% conversion to a diradical such as **3** (evidence for the structural assignment of **3**

Scheme 1. Reaction of 1,1-Dilithio-2,3,4,5-tetraphenylsilole (**1**) with 1,1-Dichloro-2,3-diphenylcyclopropene (**2**)



will be presented later). The free radical product was quite stable in a vacuum. After storage at room temperature for 2.5 years, the spin concentration of a sealed sample of the reaction mixture decreased by a factor of 3. When a similar sample was stored exposed to air, the spin concentration decreased by a factor of 5 after 4 months. In both cases the radical had undergone conversion to **4**.

When the reaction solution was opened to air and immediately separated by column chromatography and preparative GPC (toluene elution), 25% of compound **4** was isolated. If on the other hand the solution was heated to 80 °C for 24 h and then chromatographed, 65% of **4** was recovered. Thus it appears that the diradical converts to **4**, slowly at ambient temperature and rapidly at 80 °C. The diradical is unreactive toward water, methanol, or chloroform. When it was heated in the presence of any of those trapping agents, the major product was **4**.

The molecular structure of **4** was determined by X-ray crystallography (Figure 1).

The disilapentalene ring is nearly planar with slight deviations of the silicon atoms from the plane, by 0.12 Å. The two silole rings attached *spiro* to the disilapentalene ring are perpendicular to the disilapentalene plane. The bond distances and angles of the silole moiety (Si(1)–C(2)–C(3)–C(4)–C(5)) of **4** are quite similar to those of other perphenylated siloles.^{10,11} In the

[†] University of Wisconsin.

[‡] Los Alamos National Lab.

- (1) Hong, J.-H.; Boudjouk, P.; Castellino, S. *Organometallics* **1994**, *13*, 3387.
- (2) Goldfuss, B.; Schleyer, P. von R. *Organometallics* **1995**, *14*, 1553.
- (3) West, R.; Sohn, H.; Bankwitz, U.; Calabrese, J.; Apeloig, Y.; Müller, T. *J. Am. Chem. Soc.* **1995**, *117*, 11608.
- (4) West, R.; Sohn, H.; Bankwitz, U.; Powell, D. R.; Müller, T.; Apeloig, Y. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1002.
- (5) Freeman, W. P.; Tilley, T. D.; Yap, G. P. A.; Rheingold, A. L. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 882.
- (6) Freeman, W. P.; Tilley, T. D.; Liable-Sands, L. M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 10457.
- (7) Choi, S.-B.; Boudjouk, P.; Wei, P. *J. Am. Chem. Soc.* **1998**, *120*, 5814.
- (8) Choi, S.-B.; Boudjouk, P.; Hong, J.-H. *Organometallics* **1999**, *18*, 2919.
- (9) Joo, W.-C.; Hong, J.-H.; Choi, S. B.; Son, H.-E. *J. Organomet. Chem.* **1990**, *391*, 27.

- (10) Sohn, H.; Huddleston, R.; Powell, D. R.; West, R. *J. Am. Chem. Soc.* **1999**, *121*, 2325.

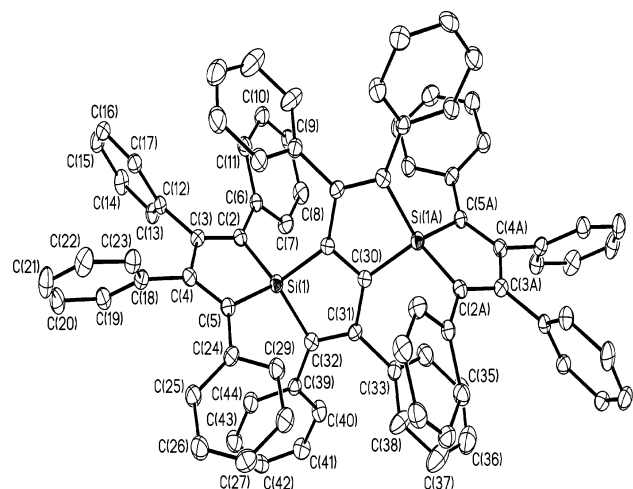


Figure 1. ORTEP drawing (50% thermal ellipsoids) of pentalene **4**. Hydrogen atoms are omitted for clarity.

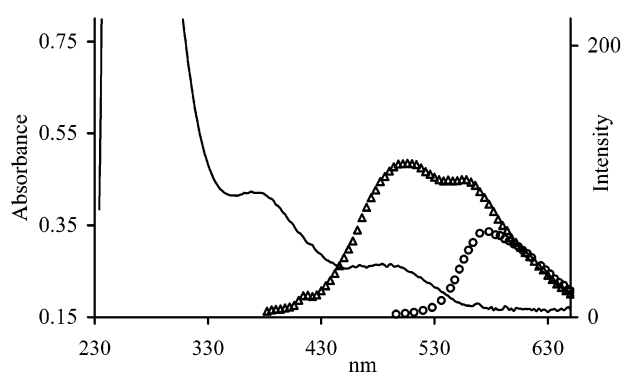
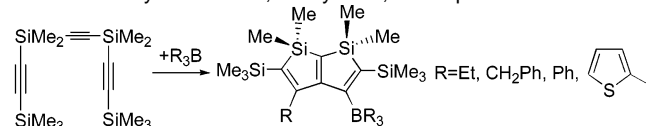


Figure 2. UV-vis and fluorescence spectra of **4**. (—) Absorbance of **4**; ($\Delta\Delta\Delta$) emission of **4** (excited at 370 nm); ($\circ\circ\circ$) emission of **4** (excited at 486 nm).

Scheme 2. Synthesis of 1,6-Dihydro-1,6-disilapentalenes¹²



disilapentalene component, the formal single bond (C(30)–C(31) 1.487(4) Å) is shorter than the corresponding bond in the external silole (C(3)–C(4) 1.519(5) Å). This difference is consistent with increased conjugation in the disilapentalene system. The exocyclic bonds to phenyl rings are also slightly shorter for the pentalene moieties than for the silole rings.

The only other disilapentalenes reported in the literature are 1,6-dihydro-1,6-disilapentalenes, synthesized by Wrackmeyer and co-workers by ring closure from triynes (Scheme 2).¹² No crystal structures were obtained for these compounds.

Compound **4** showed unusual photophysical properties. The UV-vis absorption and fluorescence spectra of **4** are illustrated in Figure 2. **4** has absorption bands at 250, 370 ($\epsilon = 5660$) and 484 ($\epsilon = 730$) nm. Most perphenylated siloles have bands at 250 nm, due to the phenyl groups, and 360 nm, attributed to the silole moiety.^{10,11,13} Thus in **4** the silole band near 360 nm

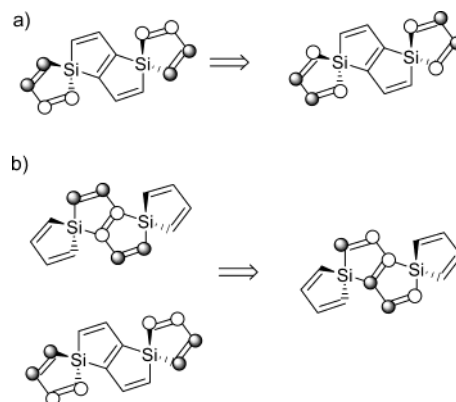


Figure 3. (a) HOMO \rightarrow (LUMO + 2) transition in **4a**; (b) (HOMO – 2) + HOMO \rightarrow LUMO transition in **4a**. All molecular orbitals possess π -symmetry and are represented here by only one of their top lobes.

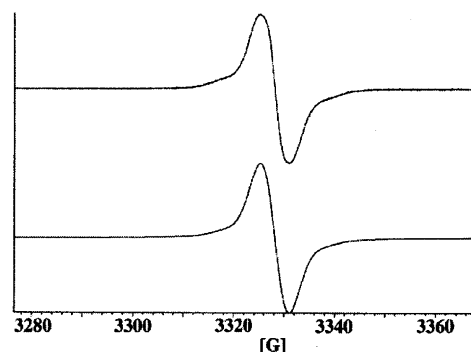


Figure 4. EPR spectrum of the reaction mixture in benzene at room temperature (top) and the simulated spectrum of the reaction mixture (bottom).

is shifted 10 nm to the red, and a new long-wavelength band appears at 484 nm.

The UV-vis spectrum of **4a** (a model of disilapentalene **4**, where all phenyl groups are replaced by hydrogen atoms) was calculated at the TD-B3LYP/6-311++G(d,p) level of theory. Two transitions with nonzero intensity were found at 376 and 430 nm. The first of these two transitions corresponds to the HOMO \rightarrow LUMO+2 excitation, which is the excitation from the π -system to the π^* -system of two five-membered cycles, which are perpendicular to the plane of the bicycle (Figure 3a). The second transition occurs from both HOMO-2 and HOMO to the LUMO and corresponds to the excitation from both the π -system of the two five-membered rings and the π -system of the bicycle onto the π^* -system of the bicycle (Figure 3b).

In the fluorescence spectrum disilapentalene **4** has a broad emission band with two maxima around 506 and 554 nm (excited at 370 nm). A first maximum at 506 nm can be attributed to emission by the silole moiety, and a second maximum at 554 nm might be assigned to emission by the disilapentalene ring. When **4** was excited at 486 nm, a broad emission band was observed at $\lambda_{\text{max}} = 576$ nm. The Stokes shift for the red emission of **4** is relatively large (90 nm).

Electron Paramagnetic Resonance Studies. The EPR spectrum of a reaction mixture solution at room temperature (Figure 4, upper trace) showed a single resonance at $g = 2.0026$, with a peak-to-peak line width $\Delta B_{\text{pp}} = 5.7$ G, flanked by apparent satellite peaks with approximately 18 G separation. The experimental spectrum is reasonably well simulated (Figure 4, lower trace) with hyperfine splitting constants $a_1(^{129}\text{Si}) = 16.0$

(11) Sanji, T.; Sakai, T.; Kabuto, C.; Sakurai, H. *J. Am. Chem. Soc.* **1998**, *120*, 4552.

(12) Wrackmeyer, B.; Kehr, G.; Süß, J.; Molla, E. *J. Organomet. Chem.* **1998**, *562*, 207.

(13) Tang, B. Z.; Zhan, X.; Yu, G.; Lee, P. P. S.; Liu, Y.; Zhu, D. *J. Mater. Chem.* **2001**, *11*, 2974.

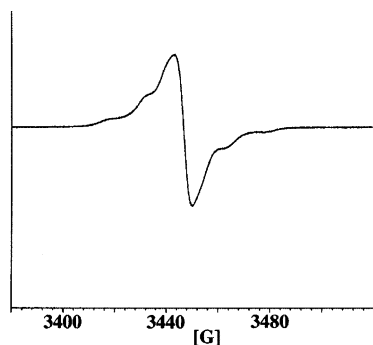


Figure 5. Room-temperature EPR spectrum of the reaction mixture as a solid.

g and $a_2(^{13}\text{C}) = 14.0$ G and a line shape with 40% Gaussian character. The Gaussian nature of the line shape is likely due to unresolved hyperfine coupling to phenyl protons,¹⁴ owing to spin-exchange broadening; attempts to adjust the solution concentration in order to obtain spectra with resolved proton hyperfine splitting were unsuccessful. Density functional calculations for the 2,3,4,5-tetraphenylsilole radical anion¹⁵ predict hyperfine-splitting parameters of 0.7, 1.6, and 2.2 G for interaction with protons from one pair of phenyl substituents and 0.1, 0.2, and 0.2 G for the protons of the other pair of phenyl groups. That such a set of electron–nuclear interactions with 20 protons could lead to a very dense and potentially unresolvable spectrum is further confirmed by spectral simulation using the calculated splitting parameters and individual Lorentzian lines of 1.4 G width.

Data were acquired under various conditions in an effort to characterize the radical species as monoradical or diradical in nature and, if a diradical, to determine whether a triplet-state or biradical description is more appropriate.¹⁶ The reaction mixture was examined at room temperature and 77 K in amorphous solid form. To avoid a signal from the glass sample tube in the half-field region, quartz EPR sample tubes were used.

At room temperature, a dominant central peak of 5.8 G width was observed in the $g = 2$ (single-quantum) region, flanked by smaller components characteristic of a dipolar line shape pattern ($D = 28$ G, $E = 2$ G), indicating the presence of a triplet-state diradical (Figure 5).¹³

The intensity of the central resonance can be attenuated by application of greater incident microwave power, making the contribution of the dipolar component relatively more pronounced. The dipolar line shape component is well simulated with the parameters $D = 28$ G and $E = 2$ G; from D the average interelectron distance is calculated¹³ to be $\langle r \rangle = 9.98$ Å. No half-field (double-quantum) resonance was detected at room temperature; however, at 77 K a weak half-field signal was observed (Figure 6). For the $g = 2$ region at 77 K, the central resonance broadened slightly to 8 G and the distinctive features of the dipolar line shape were lost, at least in part due to line broadening (Figure 5). At both room temperature and 77 K, only a very slight asymmetry of the line shape was detected, indicating a negligible anisotropy of the g tensor for the diradical in the amorphous solid.

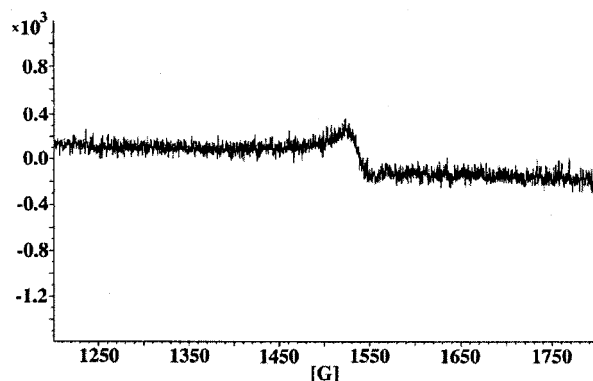
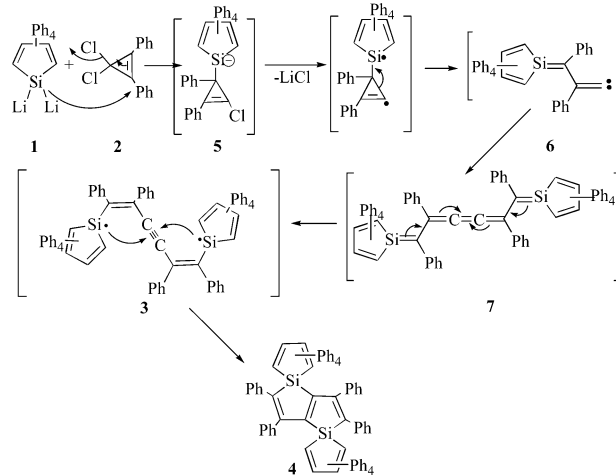


Figure 6. Half-field (double-quantum) resonance of the reaction mixture at 77 K.

Scheme 3. Possible Mechanism for the Formation of 4



Formation of 4. A possible mechanism for the reaction leading to **4** is shown in Scheme 3. The first step involves attack of dianion **1** on the carbon–carbon double bond of **2** with expulsion of chloride ion to give nonisolable chlorocyclopropene intermediate **5**.

Subsequent spontaneous loss of LiCl with concomitant rupture of the cyclopropene ring affords the intermediate carbene **6**, which could dimerize to form the unstable bis(silene)butatriene **7**. The intermediate cumulene **7** cannot be planar because of strong interactions between phenyl rings in 1,4 positions. Twisting of the silole rings to relieve this steric hindrance would favor the diradical **3**, which might exist as three different isomers: *trans*–*trans*, *trans*–*cis*, and *cis*–*cis*. Cyclization of the *cis*–*cis* isomer of **3** could provide the final product **4**. There are precedents for several of the proposed steps in the mechanism. Similar reactions of different nucleophiles on the carbon–carbon double bond of 1,1-dichlorocyclopropenes have been reported.^{17,18} Also, dianion **1** attacks the carbon–carbon double bond in 2,3-diphenylcyclopropenone, leading to rearrangements with the formation of a silaspirotropyliene.¹⁹ The analogous formation of a dihydropentalene and a vinylpentafulvene through a vinyl carbene as a possible intermediate was observed in the reaction of sodium cyclopentadienide with 1,2,3-tris[(*tert*-butyl)thio]cyclopropenylium tetrafluoroborate (Scheme 4).²⁰

(14) Weil, J. A.; Bolton, J. R.; Wertz, J. E. *Electron Paramagnetic Resonance: Elementary Theory and Practical Applications*; Wiley: New York, 1994.

(15) Faustov, V. I.; Egorov, M. P.; Nefedov, O. M.; Molin, Yu. N. *Phys. Chem. Chem. Phys.* **2000**, *2*, 4293.

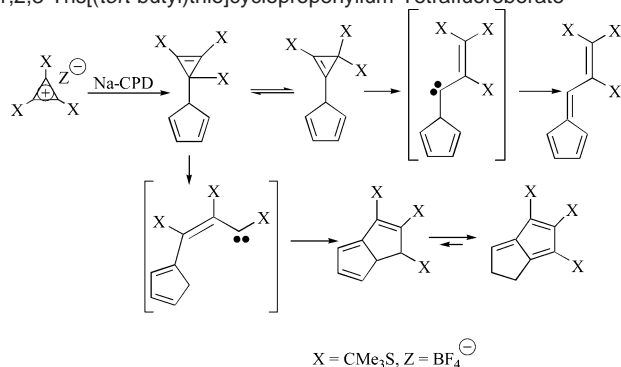
(16) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

(17) Melloni, G.; Ciabattini, J. *Chem. Commun.* **1968**, 1505.

(18) Murata, I.; Nakazawa, T.; Shima, K. *Chem. Lett.* **1972**, 669.

(19) Sohn, H.; Merritt, J.; Powell, D. R.; West, R. *Organometallics* **1997**, *16*, 5133.

Scheme 4. Reaction of Sodium Cyclopentadienide with 1,2,3-Tris[(*tert*-butyl)thio]cyclopropenylium Tetrafluoroborate²⁰



Theoretical Calculations of Diradical 3. Theoretical calculations for the proposed diradical were performed at two different levels of theory.^{21–23} To simplify the calculations, the model molecule **3a** was chosen in which hydrogen atoms were substituted for all the phenyl groups. Two initial geometries were considered: (1) a “flat” conformation, where **3a** is lying in one plane and (2) a “turned” conformation, where the five-membered rings of **3a** are twisted along the Si1–C5 bond to be perpendicular to the C6–C7–C8 plane. The actual diradical **3** cannot be planar, because of repulsions between phenyl groups at the 2,7 and 2',7' positions (Figure 7). Three geometrical isomers are possible: (a) *trans–trans*, (b) *trans–cis*, and (c) *cis–cis*.

First, the geometries of *trans–trans* and *cis–cis* isomers of **3a** in the triplet state and in both “flat” and “turned” conformations were optimized at the UB3LYP/6-31G** level²¹ using broken symmetry (BS) technique.^{22a} This technique is based on a UHF, Guess=Mix method to build a single determinant description of the open-shell singlet state using orbitals localized on different magnetic centers bearing electrons of opposite spin. While a single determinant description of a triplet state is fairly accurate, the BS state is spin contaminated and lies between low- and high-spin eigenstates of the S² spin operator. As a result, BS-HF underestimates the singlet–triplet gap. In contrast, the BS-B3LYP approach usually results in low spin contamination and gives a reliable description of the geometry and spin

polarization effects in biradicals.^{22b} However, the BS-B3LYP level tends to overestimate the extent of delocalization of the magnetic orbitals, leading to overestimation of the singlet–triplet gap.^{22c} For this reason we employed complete active space multireference perturbation theory (MR-PT2) to estimate the singlet–triplet energy gap. All bond lengths and major angles for the optimized structures are given in the Supporting Information.²⁴

Relative DFT energies of the triplet states for both *trans–trans* and *cis–cis* isomers and singlet states for the *trans–trans* isomer of **3a** in both conformations are presented in Table 1. The energy differences between triplet states of *trans–trans* and *cis–cis* isomers were found to be only 0.8 and 3.6 kcal/mol (favoring the *trans–trans* isomer) for “flat” and “turned” conformations, respectively, indicating that thermodynamically the formation of both isomers is quite possible. We believe that the *trans–cis* isomer of **3a** would have energy somewhere between that of the *trans–trans* and *cis–cis* isomers. For that reason the *trans–cis* isomer was not studied.

Estimation of the singlet–triplet energy gap and some bond lengths obtained for “flat” *cis–cis* **3a** at the RB3LYP/6-31G** and BS-B3LYP/6-31G** levels²⁵ are presented in Table 2.

Apparently, forcing a closed-shell configuration of the singlet in the RB3LYP geometry optimization resulted in the geometry that is best described as a cumulene-like form **7a**, a “precursor” for **3a** in the proposed mechanism (see Scheme 3). Thus the Si1–C2 and Si1–C5 single bonds (1.836 Å) are longer than the Si1–C6 bond (1.760 Å), and the C2–C3 and C4–C5 double bonds (1.364 Å) are shorter than the C6–C7 bond (1.414 Å).

For comparison, important bond lengths of the “turned” triplet of **3a** are also presented in Table 2. The Si1–C6 and C7–C8 bonds in the “turned” triplet are expected to be single bonds, while C6–C7 would be a double bond since unpaired electrons cannot be delocalized over the SiC₆Si chain due to their orthogonality to the π-system of the molecule. In the UB3LYP-optimized molecule the Si1–C6 and C7–C8 bonds lengthen, while the C6–C7 and C8–C8' bonds shorten, which indicates that the cumulene-like representation of **3a** acquires more biradical character. Significant deviation of the ⟨S²⟩ value from zero in the UB3LYP case highlights the noticeable contribution of the biradical form into the singlet wave function.

It is also worth mentioning that DFT finds BS singlet and triplet (T) states of the “turned” conformer of *trans–trans* **3a** to be degenerate. This spin degeneracy turns out to be the characteristic of the system (vide infra). The “turned” conformer of *trans–trans* **3a** can be viewed as a system with two noninteracting radical centers.

To estimate correctly the singlet–triplet gap for **3a** in the “turned” conformation, multireference CASSCF and MR-MP2 calculations²³ were performed for the triplet, as well as for the

- (20) Guggisberg, von D.; Bigler, P.; Neuenschwander, M.; Engel, P. *Helv. Chim. Acta* **1989**, *72*, 1506.
- (21) (a) All DFT and TD-DFT calculations were performed using the Gaussian-98 package: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, A.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98* (Revision A.1); Gaussian, Inc.: Pittsburgh, PA, 1998. (b) QM/MM calculations were performed using the Gaussian 98 ONIOM (AMI: UFF) option.
- (22) (a) Nudelman, L. *J. Chem. Phys.* **1981**, *74*, 5737. (b) Barone, V.; Crescenzi, O.; Impropa, R. *Quant. Struct.–Act. Relat.* **2002**, *21*, 105. (c) Cabrero, J.; Calzado, C. J.; Maynau, D.; Caballol, R.; Malrieu, J. P. *J. Phys. Chem. A* **2002**, *106*, 8146.
- (23) Geometry optimizations at CAS (10,10)/6-31G* and single-point calculations at MR-PT2 (10,10)/6-31G* levels were performed using the PC GAMESS version of the GAMESS (US) QC package: (a) Granovsky, Alex A. URL: <http://classic.chem.msu.su/gran/gamess/index.html>. (b) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. J.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. *J. Comput. Chem.* **1993**, *14*, 1347.

- (24) IR frequency calculations confirmed that the “flat” triplet state of **3a** is the true minimum. The “turned” triplet state of **3a** is found to be a two-dimensional saddle point. However, analysis of the imaginary vibrations revealed that they correspond to symmetric and antisymmetric rotations of SiC₅ cycles about the Si–C5 and Si–C5' bonds. This was expected since the molecule was locked in the “turned” configuration by the symmetry restrictions. However, the presence of phenyl substituents instead of H atoms in **3** would not allow the molecule to adopt the “flat” conformation due to the phenyl...phenyl repulsion. The restrictions on the conformation, imposed by phenyl groups in **3**, were simulated in **3a** by “locking” the molecule in the “turned” conformation by imposing C_{2v} symmetry.
- (25) IR calculations for both restricted and unrestricted singlet of the “flat” **3a** confirmed that both geometries converged to true minima.

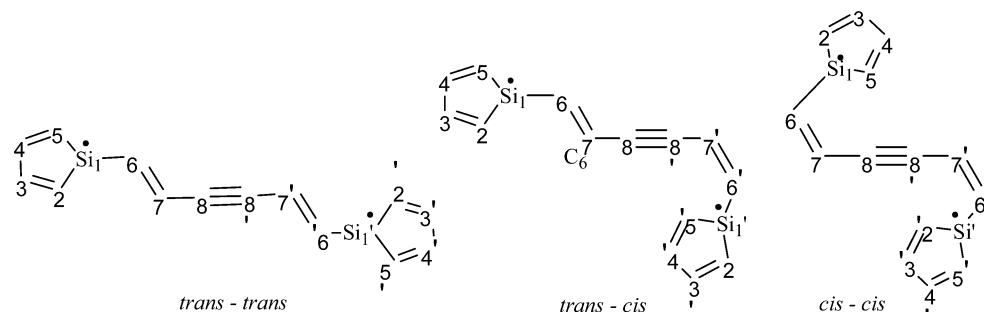


Figure 7. Possible conformers of diradical **3a**, the hydrogen-substituted model of **3**.

Table 1. Relative Energies (kcal/mol) of Some Isomers of **3a** in Singlet and Triplet States, Calculated by B3LYP/6-31G** Level

state: ^a	conformation					
	"flat"			"turned"		
isomer	CSS	BSS	T	CSS	BSS	T
<i>trans-trans</i> 3a	0	-0.6	23.6	57.2	33.1	33.1
<i>cis-cis</i> 3a	<i>b</i>	<i>b</i>	24.4	<i>c</i>	<i>b</i>	29.9
iso-pentalene 8	-22.4					
disilapentalene 4a	-51.5					

^a CSS, closed shell singlet; BSS, broken symmetry singlet; T, triplet.
^b Was not calculated. ^c Converged to iso-pentalene (vide infra).

Table 2. Important Bond Lengths (Å) and Relative Energies (kcal/mol) for Triplet and Singlet States of "Flat" and "Turned" Conformers of *trans-trans* Isomer of **3a**

conformer	state ^a	Si1-C6	C6-C7	C7-C8	C8-C8'	ΔE , kcal/mol
"flat"	CSS ($\langle S^2 \rangle = 0$)	1.760	1.414	1.360	1.249	0.6
"flat"	BSS ($\langle S^2 \rangle = 0.48$)	1.775	1.402	1.373	1.242	0.0
"flat"	T ($\langle S^2 \rangle = 2$)	1.815	1.369	1.407	1.223	23.6
"turned"	T ($\langle S^2 \rangle = 2$)	1.867	1.354	1.417	1.219	33.5

^a CSS, close-shell singlet; BSS, broken-symmetry singlet; T, triplet.

Table 3. Relative Energies (kcal/mol) of the Two Conformers of **3a** in Singlet and Triplet States, Calculated at the MR-MP2(10,10)/6-31G**/CAS(10,10)/6-31G* Level

state: ^a	conformation					
	"flat"			"turned"		
isomer	CSS	OSS	T	CSS	OSS	T
CAS(10,10)/6-31G*	14.7	14.9	16.8	0.0	0.1	0.0
MR-MP2(10,10)/6-31G*	8.7	3.8	0.0	10.1	10.1	10.1

^a CSS, closed-shell singlet; OSS, open-shell singlet; T, triplet.

open- and closed-shell singlet states with no symmetry constraints imposed on the wave function. Results of these calculations are presented in Table 3.

As in the case of DFT calculations, the multiconfigurational treatment (after including dynamical correlation correction) also finds the "flat" conformation of **3a** to be energetically preferred over the "turned" one by about 2–10 kcal/mol (depending on the multiplicity of compared conformations). But unlike BS-B3LYP, multireference perturbation theory (MR-MP2) predicts the triplet to be the most stable species. MR-MP2 also confirms the singlet–triplet degeneracy found by DFT for the "turned" conformer of the *trans-trans* isomer of **3a**. The HOMO and LUMO of this conformer consist primarily of p-orbitals of Si atoms and adjacent C atoms of the rings. Orthogonality between these p-orbitals and the π -system of the carbon chain ensures the lack of interaction between two radical centers. Apparently, spin polarization along the chain of σ -bonds

is not sufficient to remove the resulting singlet–triplet degeneracy²⁶ in **3a**.

Despite the failure to predict the relative stability of the "flat" spin states, DFT calculations give useful insights into the isomerization behavior of molecule **3**. Attempts to optimize the geometry of the "turned" conformation of the *cis-cis* isomer of **3a** (B3LYP/6-31G(d,p)) in the restricted singlet state lead to the convergence of its initial geometry to **8**, an isomer of disilapentalene **4a** (Figure 8). Disilapentalene **4a** itself was found to be 29.1 kcal/mol more stable than its isomer **8** and 84.6 kcal/mol more stable than the triplet *trans-trans* "turned" isomer of **3a**.

Another attempt at geometry optimization for the "turned" *cis-cis* isomer of **3a** in the restricted singlet state was performed, starting with a distorted initial conformation. The distortion was introduced by bending the C7–C8≡C8'–C7' chain in a zigzag fashion (angle C7–C8≡C8' is 160°), so C8 and C8' would be further from Si1 and Si1', respectively, than they were in the previous initial guess (Figure 9).

In this case the structure of the singlet *cis-cis* "turned" isomer of **3a** converged to disilapentalene **4a**. Conversion of the *trans-trans* isomer of diradical **3** into **4** is inhibited by the *cis-trans* isomerization barrier. It is therefore plausible that the triplet *cis-cis* "turned" isomer of **3** spontaneously condenses into **4** after the triplet \Rightarrow singlet spin-flip and an attack by the Si atom of the most remote sp-hybridized carbon.

The distance between Si atoms in the *trans-trans* isomer is 9.60 Å. These data are in good agreement with the average interelectron distance ($r = 9.98$ Å) calculated from the dipolar splitting parameter D of the room-temperature EPR spectrum of the amorphous solid reaction mixture. The isotropic hyperfine splitting constants a/G for ²⁹Si for isomers of diradical **3a** were calculated to be -50.7 G (for **3a**, "turned") and -13.5 G (**3a**, "flat") with UB3LYP/6-311G(2df,2pd). These data are in satisfactory agreement with the hyperfine splitting constant $a_1(^{29}\text{Si}) = 16.0$ G used for the simulation of experimental spectra because the actual geometry of diradical **3**, bearing bulky phenyl groups, will be somewhere between these proposed two idealized "flat" and "turned" conformations.

Conclusions

Both the EPR observations and theoretical calculations are consistent with our formulation of the diradical as the *trans*, *trans* isomer of **3**. The "flat" conformation would be preferred over the "turned" form, but cannot be achieved due to steric repulsions. Most likely the molecule adopts an intermediate conformation between the "flat" and the 90° "turned" form. The

(26) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

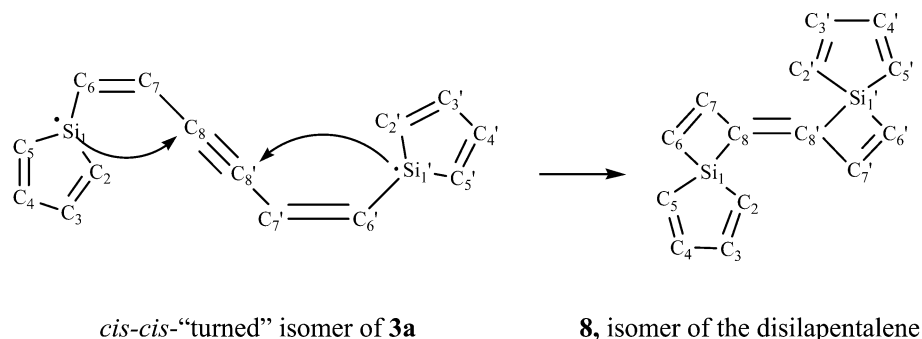


Figure 8.

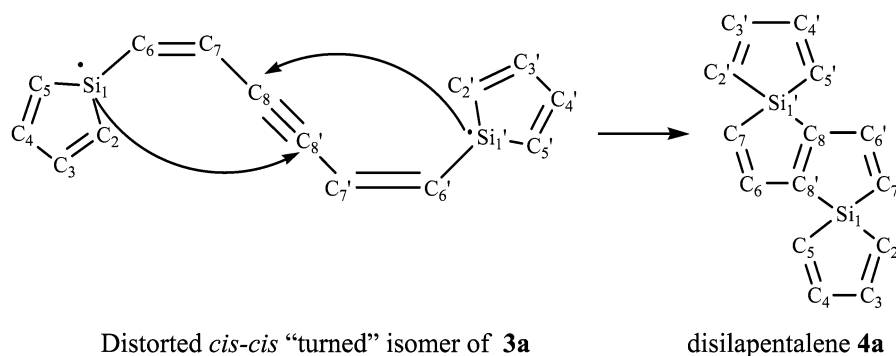


Figure 9.

triplet state is expected to be the ground state for **3**, with a small triple–singlet energy gap. The conversion of the diradical to **4** upon heating can be explained by thermal isomerization to the *cis, cis* form, which cyclizes to **4**.

Why is diradical **3** so remarkably unreactive? Its stability can perhaps be explained by steric hindrance, as well as delocalization of the unpaired electrons over the silole ring. Silole anion radicals are well known and quite stable although highly reactive.¹⁵ However neutral silole radicals have apparently not been reported. Our results suggest that the study of such radicals may be very worthwhile.

Experimental Section

General Procedures. All reactions were carried out using a standard Schlenk line under a nitrogen or argon gas atmosphere. ¹H, ¹³C, and ²⁹Si NMR spectra were recorded at 20 °C on a Varian INOVA-500 spectrometer working at 500.00 MHz for ¹H, 125.75 MHz for ¹³C, and 99.38 MHz for ²⁹Si in CDCl₃. The chemical shifts are expressed in ppm using TMS as an internal standard (¹H, ¹³C, and ²⁹Si data). UV–vis and fluorescence spectra were recorded on a HP 8452 UV–visible spectrophotometer and F-4500 fluorescence spectrophotometer, respectively. The quantum yield ($\Phi_f = 0.08$) for **4** was measured in heptane solution. Quinine sulfate in 0.1 N sulfuric acid was used as a standard.²⁷

EPR data were acquired with a Bruker ESP 300E X-band spectrometer using 100 kHz modulation frequency. A gaussmeter calibrated with solid DPPH was used to measure the field strength for *g*-value determination. Acquisition parameters were adjusted on a case-by-case basis to provide sufficient spectral resolution. Low-temperature data were acquired at 77 K by immersion of the sample into a quartz dewar insert containing liquid nitrogen. The spin concentration was determined by careful integration of the EPR signal standardized with that of TEMPO solution. Quartz EPR sample tubes were used.

The matrix-assisted laser desorption/ionization (MALDI) mass spectra were obtained using a Bruker REFLEX II (Billerica, MA)

equipped with a 337 nm nitrogen laser, a reflection, and delayed extraction. Acceleration voltage is 25 kV.

X-ray Data Collection and Structural Refinement of 4. Intensity data for this compound were collected using a Bruker SMART CCD area detector (1) mounted on a Bruker Platform goniometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The sample was cooled to 133(2) K. The monoclinic space group *P2(1)/n* (# 14) was determined by systematic absences and statistical tests and verified by subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods on *F*². Hydrogen atom positions were initially determined by geometry and refined by a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters.

Reaction of 1,1-Dilithio-2,3,4,5-tetraphenylsilole with 1,1-Dichloro-2,3-diphenylcyclopropane. 1,1-Dichloro-2,3-diphenylcyclopropane (**2**) was prepared according to a literature procedure.²⁸ 1,1-Dilithio-2,3,4,5-tetraphenyl-1-silacyclopentadiene (**1**) was prepared from 1,1-dichloro-2,3,4,5-tetraphenyl-1-silole (0.5 g, 2.2 mmol) in 7.5 mL of THF and Li (0.033 g, 4.8 mmol) in an argon atmosphere as described previously.³ A solution of **2** (0.58 g, 2.2 mmol) in 10 mL of THF was added to **1** (2.2 mmol in 10 mL of THF) at –78 °C. The reaction mixture immediately turned dark red. After warming the reaction mixture to room temperature over 2 h, THF was evaporated in vacuo and the residue was dissolved in benzene and filtered to remove LiCl. Evaporation of the solvent gave a dark red powder. The EPR spectrum of the solid and its benzene solution showed strong signals assigned to diradical **3**.

Reactivity of Diradical 3 toward MeI, MeOH, Me₃SiCl, CHCl₃, or water. A reaction mixture was prepared by the procedure described above and was treated with excess MeI (or MeOH, water, Me₃SiCl, or CHCl₃) at –78 °C and allowed to warm to room temperature. The solvent and excess MeI (or other reagents) were removed and the residue was dissolved in benzene and filtered to remove LiCl. In the case of water or MeOH the organic layer was separated and dried with MgSO₄. After evaporation of the solvent a dark red powder was

(27) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.(28) Tobey, S.; West, R. *J. Am. Chem. Soc.* **1964**, *86*, 4215.

obtained. The EPR spectrum of the solid and its benzene solution showed strong signals assigned to diradical **3**.

The reaction mixture prepared as described above was treated with excess methanol or water at $-78\text{ }^{\circ}\text{C}$ and then heated to $70\text{--}80\text{ }^{\circ}\text{C}$ for 24 h. Analyses of the reaction mixture by NMR spectroscopy showed the presence of only one silicon-containing product, disilapentalene **4**.

Preparation of Disilapentalene 4. A solution of **2** (0.58 g, 2.2 mmol) in 10 mL of THF was added to **1** (2.2 mmol in 10 mL of THF) at $-78\text{ }^{\circ}\text{C}$. The reaction mixture immediately turned dark red. After heating for 24 h at $80\text{ }^{\circ}\text{C}$ and evaporation of THF, the crude solid was dissolved in benzene and washed with a saturated aqueous solution of ammonium chloride. The organic layer was dried with MgSO_4 , and the residue was purified by column chromatography (benzene–hexane (10:1) elution). A dark red compound was obtained (1.4 g, 1.2 mmol, 60%). Further purification by preparative GPC (toluene elution) and crystallization from benzene at room temperature afforded bright red crystals of **4**: mp $360\text{--}361\text{ }^{\circ}\text{C}$. ^{29}Si NMR (CDCl_3 , 99.38 MHz): δ -21.865 . ^1H NMR (CDCl_3 , 500.0 MHz): δ $7.23\text{--}8.18$ (br, m, Ph). ^{13}C NMR (CDCl_3 , 125.38 MHz): δ $130.33\text{--}135.06$ (m, silole carbons); $136.36\text{--}147.30$ (br, m, Ph). HRMS (MALDI) calcd for $\text{C}_{86}\text{H}_{60}\text{Si}_2$ 1149.57, found 1149.43. Anal. Calcd for $\text{C}_{86}\text{H}_{60}\text{Si}_2$: C, 89.85; H, 5.26. Found: C, 89.67; H, 5.53.

MALDI Mass Spectra of Diradical 3 and Disilapentalene 4. To find evidence for the presence of diradical **3**, matrix-assisted laser desorption/ionization (MALDI) mass spectra for disilapentalene **4** and for the fresh reaction mixture containing a strong paramagnetic signal were recorded and compared.

The MALDI mass spectrum of disilapentalene **4** without matrix showed only one peak at $1149.1\text{ }m/z$ corresponding to the product **4**. The MALDI mass spectrum of **4** in the presence of α -cyano-4-

hydroxycinnamic acid includes an intense peak at $1338.0\text{ }m/z$ that can be interpreted as a complex of **4** with matrix as well as a less intense peak for **4** at $1149.1\text{ }m/z$.

The MALDI mass spectrum of the paramagnetic reaction mixture in the presence of α -cyano-4-hydroxycinnamic acid has a very intense peak at $592.2\text{ }m/z$ and only traces of the signal at $1149.1\text{ }m/z$ of **4**. When the mass spectrum of the same sample was recorded in the presence of anthracene, the peak at $592.2\text{ }m/z$ disappeared and only a weak signal at $1149.1\text{ }m/z$ of disilapentalene **4** was observed. The appearance of the signal at $592.2\text{ }m/z$ can be explained by the splitting of the diradical **3** in the presence of α -cyano-4-hydroxycinnamic acid, which might take place during laser irradiation, and subsequent addition of water present in the matrix.

Acknowledgment. The authors are grateful to Dr. Anna Krylov and Dr. Martha M. Vestling for valuable discussions. This work was supported by grants from the National Science Foundation.

Supporting Information Available: Tables of bond lengths and angles, complete atomic coordinates, anisotropic displacement coefficients, and isotropic displacement coefficients for hydrogen atoms and summary of crystal data, data collection, and refinement for **4** and results of theoretical calculations of geometry optimizations of diradical **3a**, its conformers, and isomers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA020763H