

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/263322696>

Cyclic Alkyl(amino) Carbene Stabilized Biradical of Disilicontetrachloride

ARTICLE in JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · JUNE 2014

Impact Factor: 12.11 · DOI: 10.1021/ja505817u · Source: PubMed

CITATIONS

8

READS

223

5 AUTHORS, INCLUDING:



Birger Dittrich

Heinrich-Heine-Universität Düsseldorf

187 PUBLICATIONS 2,389 CITATIONS

SEE PROFILE



Bholanath Maity

Indian Institute of Science Education and Re...

15 PUBLICATIONS 88 CITATIONS

SEE PROFILE



Debasis Koley

Indian Institute of Science Education and Re...

47 PUBLICATIONS 969 CITATIONS

SEE PROFILE



Herbert W Roesky

Gesellschaft für wissenschaftliche Datenvera...

781 PUBLICATIONS 13,449 CITATIONS

SEE PROFILE

Communication

Cyclic Alkyl(amino) Carbene Stabilized Biradical of Disilicontetrachloride

Kartik Chandra Mondal, Birger Dittich, Bholanath Maity, Debasis Koley, and Herbert W Roesky

J. Am. Chem. Soc., **Just Accepted Manuscript** • Publication Date (Web): 19 Jun 2014

Downloaded from <http://pubs.acs.org> on June 21, 2014

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



ACS Publications
High quality. High impact.

Cyclic Alkyl(amino) Carbene Stabilized Biradical of Disilcontetrachloride

Kartik Chandra Mondal,[†] Birger Dittrich,^{*,§} Bholanath Maity,[‡] Debasis Koley,^{*,‡} and Herbert W. Roesky^{*,†}

[†]Institut für Anorganische Chemie, Georg-August-Universität, Tammannstraße 4, 37077 Göttingen, Germany

[§]Martin-Luther-King-Platz 6, Raum AC 15c (Erdgeschoss), 20146 Hamburg, Germany

[‡]Dept. of Chemical Sciences, Indian Institute of Science Education and Research Kolkata, Mohanpur Campus, Mohanpur - 741252, India

Supporting Information Placeholder

ABSTRACT: One and a half decades ago the formation of Si_2Cl_4 from the intermediate species SiCl_2 was theoretically predicted to be exothermic. The hypothetical Si_2Cl_4 has never been experimentally synthesized and isolated. Herein we report that the Si_2Cl_4 species was stabilized as singlet biradical $(\text{Cy-cAAC}\cdot)_2\text{Si}_2\text{Cl}_4$ utilizing two cAAC carbenes. This compound is stable, isolable, and storable at room temperature under an inert atmosphere. The electronic structure and bonding were studied by theoretical calculations which revealed that the molecule possesses a singlet biradical ground state with an unpaired electron on each carbene carbon atom having opposite spin.

Silicontetrachloride, disiliconhexachloride, acyclic, and cyclic siliconperchlorides are well known. They are chemical textbook examples¹ and have received importance for industrial applications.² However, to the best of our knowledge a Si_2Cl_4 has never been published as a possible intermediate of $[\text{SiCl}_2]_x$ formation during the dechlorination process of SiCl_4 .³ The dechlorination reaction is an important technical process, due to the formation of SiCl_4 as a side product during the reduction of HSiCl_3 to Si with hydrogen gas. It is well known that in the presence of a base HSiCl_3 can produce dichlorosilylene which can be trapped as $(\text{NHC})\text{SiCl}_2$ ^{4a-b} by N-heterocyclic carbene (NHC). In the presence of triethylamine, Si_2Cl_6 produces SiCl_4 and $\text{Si}_6\text{Cl}_{14}$.^{4c} The exact mechanism is not known.^{4d} Hexachlorodisilane (Si_2Cl_6) undergoes disproportionation to produce SiCl_4 and SiCl_2 both of which were trapped by NHC too.^{4e} SiCl_2 could also be generated from Si_3Cl_8 in the presence of tertiary amine.^{3d} None of the proposed mechanisms involves the formation of Si_2Cl_4 . However, the theoretical calculation showed that the dissociation of Si_2Cl_4 into two SiCl_2 is endothermic by 17 kcal/mol.^{3c} This means the formation of Si_2Cl_4 from SiCl_2 is favorable. In 2003, Boganov et al. suggested that the dimerization of 2 SiCl_2 to Si_2Cl_4 is energetically favorable over complexation between SiCl_2 and molecular N_2 .^{3c} This was concluded from the quantum chemical calculations and experimentally at low-temperature by an argon-nitrogen matrix isolation of pyrolysis product ($\text{N}_2\text{-SiCl}_2$) from Si_2Cl_6 . Two structures (*trans*-olefin and bridged structure; Scheme S1) of Si_2Cl_4 were theoretically predicted. The calculated dimerization energy (2 $\text{SiCl}_2 \rightarrow \text{Si}_2\text{Cl}_4$) is -8.6 kcal/mol⁻¹ for *trans*-olefin structure and only -1.2 kcal/mol⁻¹ for a bridged structure.^{3c} Gaseous SiCl_2 is known for a long time but it condenses to polymeric $(\text{SiCl}_2)_n$. The stability and properties of the latter were investigat-

ed.^{3a,3b,3d,3f} In 1998 the X-ray single crystal structures of a cyclic^{5a} and an acyclic^{5b} polymeric perchloropolysilane $(\text{SiCl}_2)_n$ were reported by West et al. The generation of SiCl_2 ^{6a-c} and reactivity of Si_2Cl_6 ^{6d-i} has been studied. It is worth to mention that the isolation and characterization of Si_2Cl_4 at room temperature are not achieved yet.

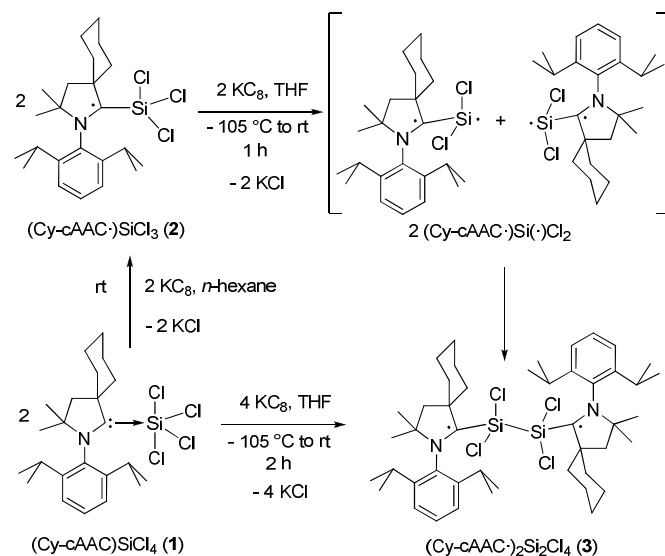
NHC can stabilize several low coordinate unstable intermediate species via strong σ -donation.^{4a-b} The above mentioned $(\text{NHC})\text{SiCl}_2$ was exclusively obtained from the reaction of HSiCl_3 with two equivalents of NHC under the elimination of $\text{NHC}\cdot\text{HCl}$ (Scheme S2).^{4b} This means formation of $(\text{NHC})\text{SiCl}_2$ from reaction of NHC and SiCl_2 (generated *in situ*). Alternatively, $(\text{NHC})\text{SiCl}_2$ (**B**) was also prepared via the reduction of the adduct $(\text{NHC})\text{SiCl}_4$ (**A**) with two equivalents of KC_8 under the elimination of two equivalents of KCl. Theoretical calculations on $(\text{NHC})\text{SiCl}_2$ (**B**) showed that NHC forms a strong donor NHC \rightarrow Si σ -bond and the lone pair of electrons of NHC-silylenedichloride, $(\text{NHC})(\text{Si}(\cdot)\text{Cl}_2)$ resides on the silicon atom in the singlet ground state.^{4b} The lone pair of electrons on the silicon atom of **B** can be even donated to the acceptor molecules.^{4e} Moreover, NHC and cAAC stabilized $(\text{L})\text{ECl}_2$ (L = NHC, for E = Si, Ge, Sn; ^{2c,4b,7-8} L = cAAC for Ge, Sn) are known.⁹ Recently we published the $(\text{NHC})\text{SiCl}_2$ ^{4a-b} and two polymorphs of composition $(\text{cAAC}\cdot)_2\text{Si}_2\text{Cl}_4$ ¹⁰ (cAAC = cyclic alkyl(amino) carbene). In view of the prominent role, which a $\text{Cl}_2\text{SiSiCl}_2$ molecule might play, we targeted the preparation of this unknown molecule. We utilized $(\text{Cy-cAAC}\cdot)\text{SiCl}_3$ ($\text{Cy-cAAC} = \text{:C}(\text{CH}_2)(\text{CMe}_2)(\text{C}_6\text{H}_{10})\text{N-2,6-}i\text{Pr}_2\text{C}_6\text{H}_3$) as a precursor instead of $(\text{NHC})\text{SiCl}_2$, because treatment of the latter with cAAC resulted exclusively in the formation of $(\text{cAAC}\cdot)_2\text{Si}_2\text{Cl}_4$.¹⁰

NHC and cAAC are inherently different from each other since the HOMO-LUMO energy gap is smaller for the latter one. This can play a pivotal role for their unusual cAAC-silylene chemistry. NHC carbene provides strong σ -donation and acts as a weak π -acceptor due to the presence of two σ -withdrawing and π -donating N-atoms leading to a weaker bond strength between NHC and silicon atom when compared with that of cAAC.¹¹

When the cyclic alkyl(amino) carbene (cAAC) is used instead of the NHC: one π -donating and σ -withdrawing N-atom is replaced by one σ -donating quaternary C-atom. Thus the cAAC becomes a stronger σ -donor and π -acceptor when compared with that of NHC.¹¹ Several radical species of main

group elements such as PN^+ , P_2^+ , phosphinyl radical cation, H-B^+ , CO^+ , and ketene with biradical character were stabilized with cAAC:¹² (Cy-cAAC)SiCl₄ (**1**) was reduced to the mono radical (Cy-cAAC·)SiCl₃ (**2**) by one equivalent of KC_8 .¹³ A NHC analogue of **2** is not known. The stronger π -acceptor property of Cy-cAAC is the reason why it stabilizes such radical species. Having (Cy-cAAC·)SiCl₃ (**2**) in hand, it was intriguing to carry out the reduction of (Cy-cAAC·)SiCl₃ (**2**) with another equivalent of KC_8 to obtain (Cy-cAAC·)₂Si₂Cl₄ (**3**) (Scheme 1). In this communication we report the synthesis, characterization, and theoretical calculations of the 1,4-biradical (Cy-cAAC·)₂Si₂Cl₄ (**3**).

Scheme 1. Synthetic Routes of (Cy-cAAC·)₂Si₂Cl₄ (**3**).



Compound (Cy-cAAC·)₂Si₂Cl₄ (**3**) was synthesized by controlling the reaction temperature and the molar ratio of the precursor and reducing agent (Scheme 1). A 1:1 molar mixture of precursor (Cy-cAAC·)SiCl₃ (**2**) and KC_8 was cooled to -105 °C using a frozen THF bath and separately the solvent was also cooled to the same temperature. Both were mixed together via a canula and the resultant solution was stirred for fifteen minutes at this temperature. Then the temperature was slowly raised to room temperature for another thirty minutes and within the next fifteen minutes a dark green solution of compound **3** was obtained (Scheme 1). The volume of the solvent was reduced and stored at -32 °C in a freezer to form dark green blocks of **3** in 85% yield. Alternatively compound **3** can also be prepared via the reduction of precursor (Cy-cAAC)SiCl₄ (**1**) instead of **2** (Scheme 1) by two equivalents of KC_8 . This reduction should be carried out also at low temperature to exclusively obtain compound **3** otherwise a mixture of several compounds (unreacted **1**, **2**, **3**, and (Cy-cAAC)₂Si₂Cl₄)^{10,14} is produced. The reaction is very rapid when KC_8 is employed as a reducing agent and hence the control of temperature is necessary. Compound **3** can be prepared within one hour at much higher temperature (0 °C) via the reduction of **1** by $\text{Li}^+(\text{NiPr}_2)^-$ in THF. After completion of the reaction the solvent was removed and product **3** was extracted with *n*-hexane. The concentrated solution was stored at 0 °C in a refrigerator to form big blocks of **3**.

The solution of **3** is stable at -32 to 0 °C for about three months. The crystals of **3** are stable at room temperature for more than four months in an inert atmosphere. Compound **3** melts in the temperature range of 93 to 94 °C. ²⁹Si NMR spectrum of **3** shows a resonance at 3.3 ppm which is down field shifted when compared to the reported value (-3.9 ppm)^{6b} for a polymeric perchloropolysilane (SiCl₂)_n. The UV-vis spectrum of **3** was recorded in THF which shows absorption bands at 222, 272, 305, 410, 552, 605 nm (see SI) while fluorescent mono radical **2** (precursor) and related dark blue colored biradical (Cy-cAAC·)₂SiCl₂ absorb at 263, 304, 337, 405,¹³ and 260, 308, 405, 582^{10b} nm respectively.

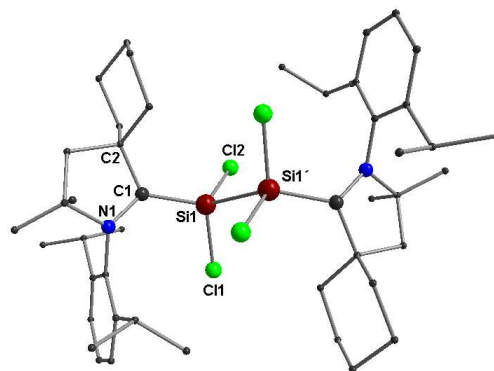


Figure 1. Molecular structure of compound **3**. H-atoms are omitted for clarity. Selected experimental [calculated at the BP86/def2-SVP level for the ground state] bond lengths [Å] and angles [°]. Si1-Si1' 2.454(3) [2.416], Si1-C1 1.846(5) [1.845], C1-N1 1.376(6) [1.379], Si1-Cl1 2.061(2) [2.085], Si1-Cl2 2.068(2) [2.099]; C2-C1-N1 109.5(4) [109.9], C2-C1-Si1 122.6(3) [124.2], N1-C1-Si1 123.9(3) [123.5], C1-Si1-Cl1 106.71(16) [107.5], C1-Si1-Cl2 109.63(16) [109.5], C1-Si1-Si1' 125.95(17) [124.3], Cl1-Si1-Cl2 102.43(9) [103.7], Cl1-Si1-Si1' 108.23(11) [108.1], Cl2-Si1-Si1' 101.52(10) [101.9].

Compound **3** crystallizes in space group *P*-1 with a center of symmetry arranged in between two silicon atoms of the molecule. Both the silicon atoms adopt a distorted tetrahedral geometry. Each silicon atom is bound to one carbene carbon atom, two chlorines and one silicon atom. The selected bond lengths and angles are given in caption of Figure 1. The values are in good agreement with those of the previously calculated values for a *trans*-olefin structure of the optimized discrete Si₂Cl₄ molecule (Scheme S1). The Si₂Cl₄ unit of **3** adopts a *trans*-olefin like configuration as predicted by Swihart et al.^{3c} and Boganov et al.^{3e} to be the most stable form. The Si-Si bond distance in **3** is 2.454(3) Å which is close to that of hypothetical Si₂Cl₄ (2.446 Å, Scheme S1).^{3c} Generally, the average Si-Si single bond distance is close to 2.35 Å.^{3,6,14} The Si-Si single bond distance of 2.424(8) Å^{5b} has been reported for polymeric perchloropolysilane (SiCl₂)_n. The C_{cAAC}-Si bond distance of **3** is 1.846(5) Å which is close to that found for precursor (Cy-cAAC·)SiCl₃ (**2**) (1.8193(8)) and biradical (Cy-cAAC·)₂SiCl₂ (1.854(2), 1.843(2) Å). The C_{cAAC}-N bond distance of **3** is 1.376(6) Å which is very close to that of the mono radical **2** (138.27(10) Å)¹³ and slightly smaller than those of SiCl₂ bridged singlet biradical (Cy-cAAC·)₂SiCl₂ (1.400(2), 1.403(2) Å).^{10b} The carbenes of **3** are oriented in a *trans*-position with respect to the central Si₂Cl₄ unit with C-Si-Si-C torsion angle of 180°. The carbene carbon atom adopts a near

trigonal planar geometry with a sum of angles (356°) which is far from that of $(\text{Me}_2\text{-cAAC-H})_2\text{O}$ (330.26°) (see SI of ref. 9a) but close to those of the mono radical **2** (357.33°) and the biradical $(\text{Cy-cAAC})_2\text{SiCl}_2$ (354.8° , 355.7°).^{10,13} In comparison the sum of the angles of free cAAC is 359.9° ,^{10b} suggesting a C-Si covalent electron-sharing single bond between the carbene carbon atom and the silicon atom of **3**. The entire mentioned bond data suggest that **3** contains two unpaired electrons, one on each carbene carbon atom retaining the radical character like precursor **2**. Hence **3** can be considered as a Si_2Cl_4 bridged carbon centered 1,4-biradical.

We have performed DFT calculations to illustrate the electronic structure and bonding scenario of compound **3**. Two possible bonding situations were previously shown for a similar type of compound $(\text{Cy-cAAC})_2\text{SiCl}_2$.¹⁰ If the ligand Cy-cAAC involves in donor-acceptor type bonding to the SiCl_2 unit ($\text{C}\rightarrow\text{Si}$) then the molecule will be a closed-shell singlet, whereas when a covalent bonding (C-Si) exists, the biradical state will be stabilized. We have optimized the geometry (taken from the crystal structure) at Mo6-2X/SVP level of theory and found that the singlet electronic state is less stable than the triplet by 7.5 kcalmol^{-1} (Mo6-2X/TZVP//Mo6-2X/SVP level). Further optimization of the geometry **3** using the broken symmetry formalism reveals that the biradical singlet state is 2.8 kcalmol^{-1} lower in energy than the triplet state. The optimized geometrical parameters of the biradical singlet state of **3** exhibit closer resemblance with the crystal structure than the closed-shell singlet and triplet electronic states (Table S4 and Figure S3). For further validation the CASSCF(2,2)/SVP method was employed for the optimization of geometry **3** in the singlet state. The coefficient values for the three singlet components are $0.80(2/0)$, $-0.60(0/2)$, $0.0(1/1)$, and the diagonal elements of the final one electron symbolic density matrix are 1.3 and 0.7, respectively. These results indicate that the stable form of compound **3** contains two unpaired electrons with opposite sign. Similar results were also obtained from fragment analysis (Figure S4), where two Cy-cAAC ligands in the triplet state combine with two triplet SiCl_2 units resulting in the biradical species **3** (see Figure 2). Thus **3** can be considered as a singlet 1,4-biradical.¹⁵ The unpaired electrons are stabilized by coupling with the neighbouring lone-pair of the nitrogen atoms in cAAC. In the singlet electronic state of Si_2Cl_4 unit, the Si=Si bond is longer (2.424 \AA) than a typical Si-Si bond (2.362 \AA), a characteristic feature for non-classical double bond exhibiting trans-bent geometry resulting from σ - π mixing.¹⁶ Surprisingly, in compound **3** the Si-Si bond distance is 2.416 \AA although the SiCl_2 sub-units combining to form the Si_2Cl_4 fragment are in triplet states (Figure 2). This typical bonding scenario can be explained taking resort to the NBO analysis. Under bond formation of the free Si_2Cl_4 unit with two carbene ligands (L), the electron density on silicon atoms is reduced ($\Delta q_{\text{Si}}=0.402\text{ e}$) and successively the bond occupancy of Si-Si decreased by 0.073 e resulting to an elongated Si-Si bond (2.416 \AA) with respect to the normal bond length (2.319 \AA in Si_2Cl_6 molecule). Mulliken spin density distribution plot of singlet biradical and triplet form entails that the two unpaired electrons are localized at the C(carbene) of the Cy-cAAC donor ligand (Figure 2 and Figure S5). The radical intermediate $(\text{Cy-cAAC})_2\text{Si}(\cdot)\text{Cl}_2$ formed during the reaction depicted in Scheme 1 possesses a singlet ground state. Dimerization of two such species to form the

1,4-biradical **3** is favorable with an exothermicity of -30.9 kcal/mol ($\Delta G_{298} = -14.7\text{ kcal/mol}$, refer to Figure S4). In order to exemplify the role of interaction between the Si-Si bond and the carbon radical centers in stabilizing the biradical **3**, we have optimized the structure with hydrogen atoms saturating the radical centers (**3-2H**, refer to Figure S6).¹⁵ Formation of such species from its monomers is stabilized by -70.1 kcal/mol , which is -3.3 kcal/mol less exothermic with respect to the formation of **3** from its monomeric triplet fragments. This indicates the stabilization influence, though less, with the σ bond and the radical centers.

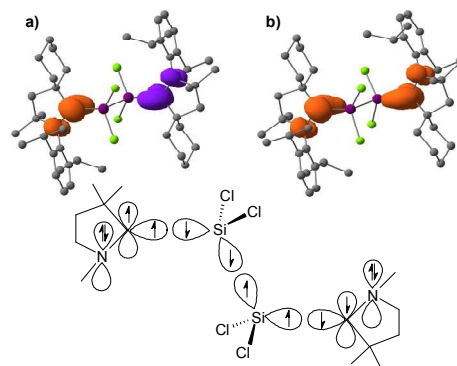


Figure 2. Computed Mulliken spin density plot (top, isosurface = 0.006 au) of **3** in a) biradical singlet and b) triplet state at UMo6-2X/TZVP//UMo6-2X/SVP level of theory. Bonding orbitals (bottom) in fragments of compound **3**.

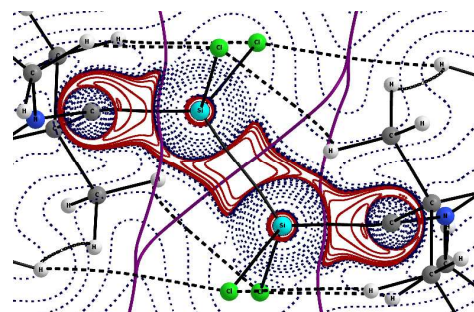


Figure 3. Contour plot of Laplacian distribution [$\nabla^2\rho(r)$] in the C1-Si1-Si1' plane of **3**. Solid lines indicate the areas of the charge concentration ($\nabla^2\rho(r) < 0$) while dotted lines mean the charge depletion ($\nabla^2\rho(r) > 0$). The range of contours of the Laplacian is -8×10^2 to $+8\times 10^2$. Solid lines connecting atomic nuclei (black) are the bond paths and those lines (purple) separating the atomic basins indicate the zero-flux surface crossing the molecular plane.

Calculated Laplacian distribution [$\nabla^2\rho(r)$, see computational details] of the C1-Si1-Si1' plane of **3** is shown in Figure 3 (Ni-C1-Si1 plane in Figure S7). We have noticed the charge concentration of lone pair at the C(carbene) (solid lines) and charge depletion at the silicon end (dotted lines). The C(carbene)-Si bonds are polarized towards the carbon atom. This type of bonding situation was also supported by the NBO results where C(carbene) atom has contributed $\sim 70\%$ electron to the C(carbene)-Si bond.

In conclusion we have shown the hypothetical Si_2Cl_4 can be stabilized by two cyclic alkyl(amino) carbenes with a general

formula of (Cy-cAAC)₂Si₂Cl₄ (**3**). (Cy-cAAC)SiCl₄ (**1**) or (Cy-cAAC)₂SiCl₃ (**2**) were utilized as a precursor. The reduction of **1** or **2** was carried out in THF at low temperature with calculated equivalents of KC₈ (Scheme 1). The crystals of compound **3** are dark green in color and stable at room temperature in an inert atmosphere. **3** melts in the temperature range of 93–94 °C. Organic linker bridged TEMPO- or nitroxide-based biradicals are studied.¹⁷ However, Si₂Cl₄ bridged 1,4-biradical such as **3** is an unprecedented species. Theoretical calculations were performed to study the electronic structure and the bonding of **3** which revealed that **3** possesses a singlet 1,4-biradical spin ground state with an unpaired electron on each carbene carbon atom having opposite spin. Calculations employing broken symmetry formalism revealed that the biradical singlet state of **3** is 2.8 kcalmol⁻¹ lower in energy than the triplet state. **3** adopts a *trans*-olefin configuration (Figure 1) similar to what was previously predicted for the hypothetical Si₂Cl₄ molecule (Scheme S1) formed via favourable dimerization of SiCl₂.

ASSOCIATED CONTENT

Supporting Information

Syntheses of **3**, UV-vis, crystal structure determination, and theoretical details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

hroesky@gwdg.de

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

Dedicated to Professor Alan H. Cowley on the occasion of his 80th birthday. H. W. R. thanks the Deutsche Forschungsgemeinschaft (DFG RO 224/60-I) for financial support. B.M. is thankful to the CSIR for SRF fellowship. D.K. acknowledges the IISER-Kolkata for start-up grant and the SERB for a DST fast track fellowship (SR/FT/CS-72/2011).

REFERENCES

- Holleman, A. F.; Wiberg, E.; Wiberg, N. *Lehrbuch der Anorganischen Chemie*, 1995.
- Simmler, W. "Silicon Compounds, Inorganic", *Ullmann's Encyclopedia of Industrial Chemistry*, Weinheim: Wiley-VCH, 2005, doi:10.1002/14356007.a24_001.
- (a) Schmeisser, M.; Voss, P.; *Z. Anorg. Allg. Chem.* **1964**, 334, 50–56. (b) Schenk, P. W.; Bloching, H. Z. *Anorg. Allg. Chem.* **1964**, 334, 57–65. (c) Swihart, M. T.; Carr, R. W. *J. Phys. Chem. A* **1998**, 102, 785–792. (d) Meyer-Wegner, F.; Nadj, A.; Bolte, M.; Auner, N.; Wagner, M.; Holthausen, M. C.; Lerner, H.-W.; *Chem. Eur. J.* **2011**, 17, 4715–4719 and ref. herein. (e) Lalov, A. V.; Boganov, S. E.; Faustov, V. I.; Egorov, M. P.; Nefedov, O. M. *Russ. Chem. Bull.* **2003**, 52, 526–538; DOI: 10.1023/A:1023973815486. (f) P. L. Timms, *Inorg. Chem.* **1968**, 7, 387–389.
- (a) Ghadwal, R. S.; Azhakar, R.; Roesky, H. W. *Acc. Chem. Res.* **2013**, 46, 444–456. (b) Ghadwal, R. S.; Roesky, H. W.; Merkel, S.; Henn, J.; Stalke, D. *Angew. Chem. Int. Ed.* **2009**, 48, 5683–5686; *Angew. Chem.* **2009**, 121, 5793–5796; and references therein. (c) Kaczmarczyk, A.; Urry, G. *J. Am. Chem. Soc.* **1960**, 82, 751–752. (d) Urry, G. *Acc. Chem. Res.* **1970**, 3, 306–312. (e) Tavčar, G.; Sen, S. S.; Azhakar, R.; Thorn, A.; Roesky, H. W. *Inorg. Chem.* **2010**, 49, 10199–10202.
- (a) Koe, J. R.; Powell, D. R.; Buffry, J. J.; West, R. *Polyhedron* **1998**, 17, 1791–1793. (b) Koe, J. R.; Powell, D. R.; Buffry, J. J.; Hayase, S.; West, R. *Angew. Chem. Int. Ed.* **1998**, 37, 1441–1442; *Angew. Chem.* **1998**, 110, 1514–1515.
- (a) Benkeser, R. A. *Acc. Chem. Res.* **1971**, 4, 94–100. (b) Kang, S.-H.; Han, J. S.; Lee, M. E.; Yoo, B. R.; Jung, I. N. *Organometallics* **2003**, 22, 2551–2553. (c) So, C.-W.; Roesky, H. W.; Magull, J.; Oswald, R. B. *Angew. Chem., Int. Ed.* **2006**, 45, 3948–3950; *Angew. Chem.* **2006**, 118, 4052–4054. (d) Martens, R.; du Mont, W.-W.; *Chem. Ber.* **1992**, 125, 657–658. (e) Martens, R.; du Mont, W.-W. *Chem. Ber.* **1993**, 126, 115–117. (f) Zanin, A.; Karnop, M.; Jeske, J.; Jones, P. G.; du Mont, W.-W. *J. Organomet. Chem.* **1994**, 475, 95–98. (g) Herzog, U.; Richter, R.; Brendler, E.; Roewer, G.; *J. Organomet. Chem.* **1996**, 507, 221–228. (h) Müller, L.-P.; du Mont, W.-W.; Jeske, J.; Jones, P. G.; *Chem. Ber.* **1995**, 128, 615–619. (i) du Mont, W.-W.; Müller, L.; Martens, R.; Papathomas, P. M.; Smart, B. A.; Robertson, H. E.; Rankin, D. W. H. *Eur. J. Inorg. Chem.* **1999**, 1381–1392.
- (a) Sidiropoulos, A.; Jones, C.; Stasch, A.; Klein, S.; Frenking, G. *Angew. Chem., Int. Ed.* **2009**, 48, 9701–9704; *Angew. Chem.* **2009**, 121, 9881–9884. (b) Thimer, K. C.; Al-Rafia, S. M. I.; Ferguson, M. J.; McDonald, R.; Rivard, E. *Chem. Commun.* **2009**, 7119–7121.
- Schäfer, A.; Weidenbruch, M.; Saak, W.; Pohl, S. J. *Chem. Soc., Chem. Commun.*, **1995**, 1157–1158.
- (a) Li, Y.; Mondal, K. C.; Roesky, H. W.; Zhu, H.; Stollberg, P.; Herbst-Irmer, R.; Stalke, D.; Andrada, D. M. *J. Am. Chem. Soc.* **2013**, 135, 12422–12428. (b) Singh, A. P.; Samuel, P. P.; Mondal, K. C.; Roesky, H. W.; Sidhu, N. S.; Dittrich, B. *Organometallics* **2013**, 32, 354–357.
- (a) Mondal, K. C.; Roesky, H. W.; Schwarzer, M. C.; Frenking, G.; Tkach, I.; Wolf, H.; Kratzert, D.; Herbst-Irmer, R.; Niepötter, B.; Stalke, D. *Angew. Chem. Int. Ed.* **2013**, 52, 1801–1805; *Angew. Chem.* **2013**, 125, 1845–1850. (b) Mondal, K. C.; Samuel, P. P.; Tretiakov, M.; Singh, A. P.; Roesky, H. W.; Stückl, A. C.; Niepötter, B.; Carl, E.; Wolf, H.; Herbst-Irmer, R.; Stalke, D. *Inorg. Chem.* **2013**, 52, 4736–4743. (c) Mondal, K. C.; Roesky, H. W.; Schwarzer, M. C.; Frenking, G.; Niepötter, B.; Wolf, H.; Herbst-Irmer, R.; Stalke, D. *Angew. Chem. Int. Ed.* **2013**, 52, 2963–2967; *Angew. Chem.* **2013**, 125, 3036–3040.
- (a) Martin, D.; Soleilhavoup, M.; Bertrand, G. *Chem. Sci.* **2011**, 2, 389–399. (b) Martin, D.; Melaimi, M.; Soleilhavoup, M.; Bertrand, G. *Organometallics*, **2011**, 30, 5304–5313.
- See review: Martin, C. D.; Soleilhavoup, M.; Bertrand, G. *Chem. Sci.* **2013**, 4, 3020–3030.
- Mondal, K. C.; Roesky, H. W.; Stückl, A. C.; Ehret, F.; Kaim, W.; Dittrich, B.; Maity, B.; Koley, D. *Angew. Chem. Int. Ed.* **2013**, 52, 11804–11807; *Angew. Chem.* **2013**, 125, 12020–12023.
- Mondal, K. C.; Roesky, H. W.; Dittrich, B.; Holzmänn, N.; Hermann, M.; Frenking, G.; Meents, A. *J. Am. Chem. Soc.* **2013**, 135, 15990–15993.
- Hoffmann, R. *Acc. Chem. Res.* **1971**, 4, 1–9.
- For details on non-classical double bonds refer: (a) Trinquier, G.; Malrieu, J.-P. *J. Am. Chem. Soc.* **1987**, 109, 5303–5315. (b) Trinquier, G.; Malrieu, J.-P. *J. Am. Chem. Soc.* **1989**, 111, 5916–5921 and references therein.
- (a) Komaguchi, K.; Iida, T.; Goh, Y.; Ohshita, J.; Kunai, A.; Shiotani, M. *Chem. Phys. Lett.* **2004**, 387, 327–331. (b) Ohshita, J.; Iida, T.; Ohta, N.; Komaguchi, K.; Shiotani, M.; Kunai, A. *Org. Lett.* **2002**, 4, 403–406.

Cyclic Alkyl(amino) Carbene Stabilized Biradical of Disilicontetrachloride

