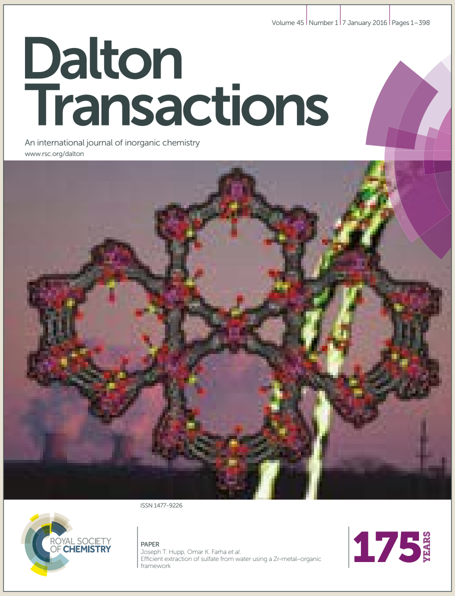
Dalton Transactions

This article can be cited before page numbers have been issued, to do this please use: T. Sugahara, J. Guo, D. hashizume, T. Sasamori, S. Nagase and N. Tokitoh, *Dalton Trans.*, 2018, DOI: 10.1039/C8DT03081B.



DOI: 10.1039/C8DT03081B

Journal Name

COMMUNICATION

The Selective Formation of a 1,2-Disilabenzene from the Reaction of a Disilyne with Phenylacetylene[#]

Received 00th January 20xx,
Accepted 00th January 20xx

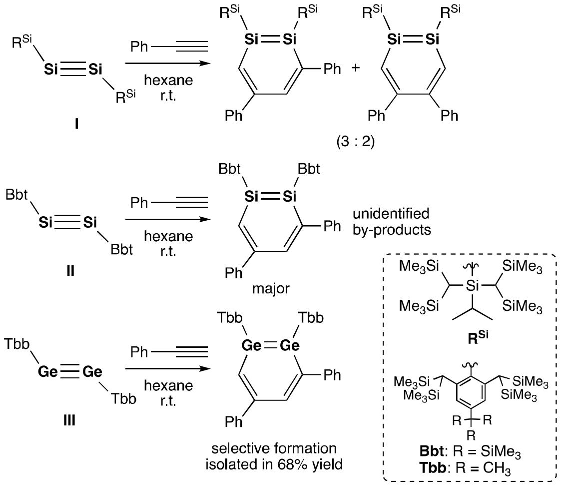
DOI: 10.1039/x0xx00000x

www.rsc.org/

Tomohiro Sugahara,[a] Jing-Dong Guo,[a,b] Daisuke Hashizume,[c] Takahiro Sasamori,*[d] Shigeru Nagase,[e] and Norihiro Tokitoh[a,b]

A stable 3,5-diphenyl-1,2-disilabenzene was selectively synthesized by the reaction between the isolabe disilyne TbbSi≡SiTbb (Tbb = 2,6-[CH(SiMe$_3$)$_2$]$_2$-4-*t*-Bu-phenyl) with phenylacetylenes. Its molecular structure and physical properties were examined and compared to those of the 1,2-disilabenzene that was obtained from the reaction between TbbSi≡SiTbb and acetylene. Moreover, a plausible formation mechanism for this reaction is discussed.

Among the simple organic hydrocarbon molecules, benzene occupies a unique position given its characteristic aromaticity. This aromaticity arises from the delocalization of its six π-electrons, which is the most distinguishing feature relative to linear or cyclic π-conjugated systems.[1] Benzene analogues that incorporate at least one heavier group 14 element have generated much interest not only with respect to a comparison with the all-carbon system of benzene, but also with regard to creating novel building blocks for optelectronic materials, regardless of the difficulties associated with isolating such species on account of their intrinsically high susceptibility toward self-oligomerization.[2] Recently, the synthesis and isolation of stable metallabenzenes that include heavier group 14 elements have been accomplished by using bulky substituents, which allowed examining their unique physical and chemical properties.[3,4] Among these, 1,2-disilabenzenes are one of the most fascinating targets, especially with respect to the effect of replacing a C=C with a Si=Si unit in the 6π aromatic system of benzene, considering the unique π-electron character of disilenes (R$_2$Si=SiR$_2$)[5] relative to olefins (R$_2$C=CR$_2$). The only synthetic route to 1,2-disilabenzenes involves the reaction of an isolable disilyne (RSi≡SiR) with acetylenes, *i.e.*, a formal [2+2+2] cycloaddition (Scheme 1).[6] Sekiguchi reported the first successful isolation of a stable 1,2-disilabenzene from the reaction of the stable disilyne R^{Si}Si≡SiR^{Si} (**I**; R^{Si} = Si(*i*Pr)[CH(SiMe$_3$)$_2$]$_2$)[7] with phenylacetylene.[6a] However, the separation and purification of the two-isomers obtained, *i.e.*, 3,5-diphenyl- and 4,5-diphenyl-1,2-disilabenzene is problematic due to their instability under atmospheric conditions.



Scheme 1. Synthesis of 1,2-disila- and 1,2-digerma-benzenes.

We have already reported the synthesis of stable 1,2-disilabenzenes[6b] from the reactions of the stable diaryldisilyne BbtSi≡SiBbt (**II**; Bbt = 2,6-[CH(SiMe$_3$)$_2$]$_2$-4-[C(SiMe$_3$)$_3$]-phenyl)[8] with acetylenes. The reaction of disilyne **II** with phenylacetylene resulted in the predominant formation of the corresponding 3,5-diphenyl-1,2-disilabenzene together with unidentified by-products, which prevented us from purifying 3,5-diphenyl-1,2-disilabenzene and acquiring detailed structural information. Conversely, the reaction of the stable

---

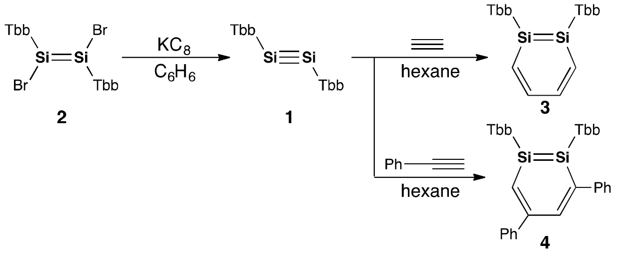
[a] Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan
[b] Integrated Research Consortium on Chemical Sciences, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan.
[c] RIKEN Center for Emergent Matter Science (CEMS), 2-1 Hirosawa, Wako, Saitama 351-0198, Japan
[d] Graduate School of Natural Sciences, Nagoya City University, Nagoya, Aichi 467-8501, Japan.
[e] Fukui Institute for Fundamental Chemistry, Kyoto University, Sakyo-ku, Kyoto 606-8103, Japan

Electronic Supplementary Information (ESI) available: [Experimenatal procedures, chemical data of the newly obtained compounds, a cif file, and coordinates of the optimized structures]. See DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/C8DT03081B

diaryldigermyne TbbGe≡GeTbb (**III**; Tbb = 2,6-[CH(SiMe$_3$)$_2$]$_2$-4-*t*Bu-phenyl)[9] with phenylacetylene proceeded selectively to afford the corresponding 3,5-diphenyl-1,2-digermabenzene.[10] Thus, the regioselectivity of the formation of 1,2-dimetallabenzenes should depend on the features of the substituents on the dimetallyne precursors. Herein, we report reactions of Tbb-substituted disilyne with acetylenes, which lead in some cases to the selective formation of 1,2-disilabenzenes. Calculated mechanisms for the formation of Tbb- and R^{Si}- substituted 3,5- and 4,5-diphenyl-1,2-disilabenzenes are also described.

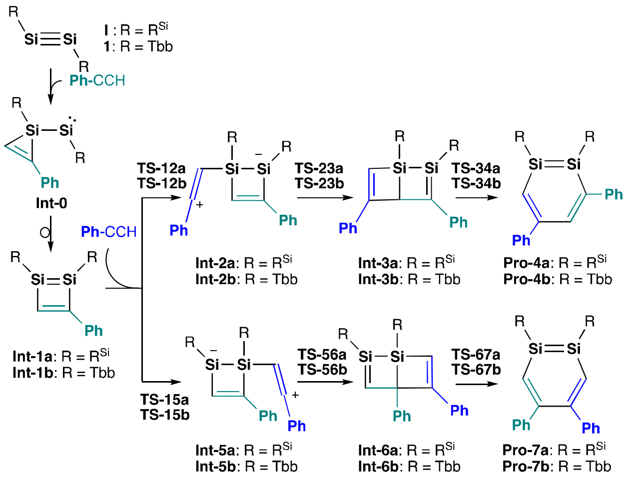
In accordance with the synthetic procedures for TbbGe≡GeTbb (**III**), Tbb-substituted disilyne TbbSi≡SiTbb (**1**) was prepared by the reduction of the corresponding dibromodisilene **2** (Scheme 2).[11] Isolated disilyne **1** was fully characterized using spectroscopic and X-ray diffraction techniques. Disilyne **1** exhibits structural features that are similar to those of the previously reported stable disilynes **I** and **II**,[7,8,12] *i.e.*, **1** exhibits a short SI≡Si bond length [2.1050(15) Å] and a considerable *trans*-bent structure [Si–Si–C angle: 131.42(9)°], suggesting substantial Si≡Si triple-bond character. In solution, the triply bonded silicon nuclei in **1** show a characteristic ^{29}Si NMR signal at δ_{Si} = 16.2, which is comparable to that of **II** (δ_{Si} = 16.7).[8] These physical properties of **1** suggest a negligible electronic perturbation of the Si≡Si moiety by the Tbb groups, which stands in contrast to the case of the Bbt groups.



Scheme 2. Synthesis of disilyne **1** and its subsequent reactions with acetylenes to afford 1,2-disilabenzenes **3** and **4**.

Exposure of an *n*-hexane solution of **1** to acetylene gas (1 atm) at r.t. resulted in a color change from dark to light yellow within 10 minutes, and 1,2-disilabenzene **3** was isolated in quantitative yield similar to the case of **II**. In contrast to the reaction of Tbb-substituted digermyne **III** with acetylene, which furnished a 9,10-digermabarrelene by-product,[9] no Si-containing by-product was observed in the crude mixture. Subsequently, **1** was treated with phenylacetylene in *n*-hexane at room temperature. The reaction smoothly furnished 3,5-diphenyl-1,2-disilabenzene **4** in quantitative yield.

The observed regioselectivity should represent a manifestation of the remarkable difference between the cases of silyl-substituted disilyne **I** and Tbb-substituted disilyne **1**. The reaction mechanism for the formal [2+2+2] cycloaddition of disilynes with two molecules of phenylacetylene has already been investigated theoretically. Initially, a formal [2+2] cycloaddition between the Si≡Si moiety of the disilyne and the C≡C moiety of phenylacetylene should afford 3-phenyl-1,2-disilacyclobutadienes (**Int-1**) *via* the electrophilic attack of the Si≡Si moiety toward the C≡C π-bond followed by an intramolecular ring expansion (Scheme 3).[4,6a,9b,13]



Scheme 3. Plausible mechanism for the formation of 1,2-disilabenzenes from a disilyne and phenylacetylene.

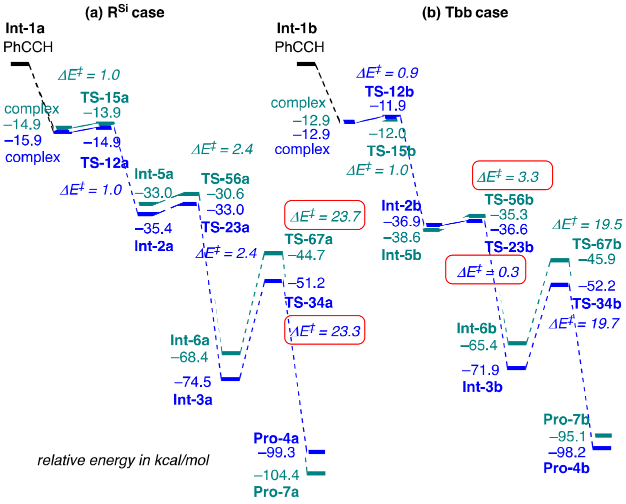


Figure 1. Potential energy surfaces of the reactions of **Int-1** with phenylacetylene.[14] (a) R = R^{Si} (**Int-1a**) case, (b) R = Tbb (**Int-1b**) case.

The subsequent reaction, *i.e.*, the insertion of the C≡C moiety of phenylacetylene into the Si–C bond of **Int-1** should be the regioselectivity-determining step (Scheme 3).[14] In both cases, i.e. R = R^{Si} or Tbb, the entire process consists of three steps: (i) the addition of PhCCH (**Int-1** → **Int-2/5**), (ii) a ring-closure (**Int-2/5** → **Int-3/6**), and (iii) an isomerization (**Int-3/6** → **Pro-4/7**). According to these processes, the insertion of phenylacetylene into the 1,4-Si–C bond of **Int-1** would furnish 3,5-diphenyl-1,2-disilabenzenes (**Pro-4a,b**), while that into the 2,3-Si–C bond would generate 4,5-diphenyl-1,2-disilabenzenes (**Pro-7a,b**). However, the selectivity can hardly be rationalized in terms of the thermodynamic stability of **Pro-4** and **Pro-7**, given that the predominant product for R = R^{Si} (**Pro-4a**) is by 5.1 kcal/mol less stable than the minor product **Pro-7a**.

View Article Online
DOI: 10.1039/C8DT03081B

Therefore, we calculated the potential energy surface (PES) for **Int-1** to **Pro-4** and **Pro-7** for R = R^{Si} and Tbb (Figure 1). For R = R^{Si}, the reactions should proceed with almost the same barriers toward **Pro-4a** and **Pro-7a**. However, the barriers in the final steps, *i.e.*, (iii) the isomerization from disila-Dewar-benzenes **Int-3a**/**6a** to 1,2-disilabenzenes **Pro-4a**/**7a**, show a slight difference, where the process from **Int-3a** to **Pro-4a** is by 0.4 kcal/mol more favorable than that from **Int-6a** to **Pro-7a**. These results can be used to rationalize the experimental results in terms of a competitive formation of **Pro-4a** and **Pro-7a** in a 3:2 ratio in the reaction between disilyne **I** and phenylacetylene. Conversely, for R = Tbb, a different reaction barrier was found in (ii) the ring-closure process from **Int-2b**/**5b** to **Int-3b**/**6b** between the PESs for **Pro-4b** and **Pro-7b**, while the barriers in the other steps, *i.e.*, (i) and (iii) are almost identical for **Pro-4b** and **Pro-7b**. Higher barriers were calculated for the pathway from **Int-5b** to **Int-6b** (3.3 kcal/mol) relative to that from **Int-2b** to **Int-3b** (0.3 kcal/mol), and the difference (3.0 kcal/mol) should be sufficient to afford **Pro-4b** exclusively with absolute selectivity.

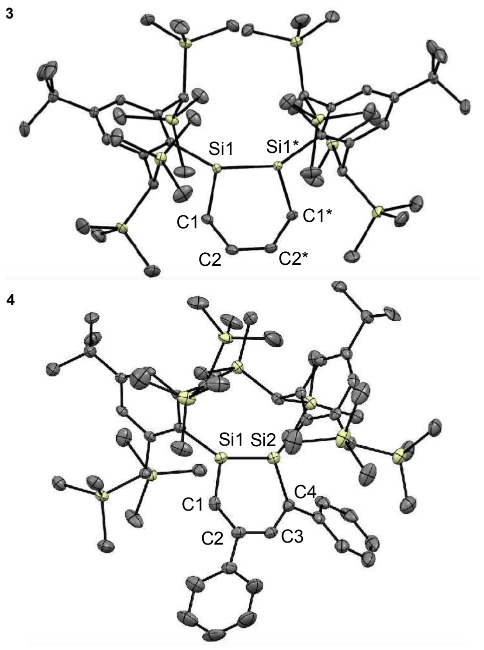


Figure 2. Molecular structures of **3** (top) and **4** (bottom). (ORTEP drawings at 50% probability level; solvent molecules and hydrogen atoms omitted for clarity.)[15]

The structural parameters of **3** and **4** were unambiguously determined by single-crystal X-ray diffraction analyses (Figure 2 and Table 1).[15] Notably, disilabenzene **3** exhibits a crystallographic C_2 axis through the central ring similar to 1,2-Tbb_2-1,2-digermabenzene.[9] The bond angle sums around the Si atoms in the $[Si_2C_4]$ ring [**3**: 355.5˚; **4**: 356.7˚/355.7˚] indicate an almost planar geometry as in the case of 1,2-Bbt_2-1,2-disilabenzenes. In addition, the internal angle sums in the six-membered $[Si_2C_4]$ rings (**3**: 719.9˚; **4**: 719.2˚) suggest planarity that is similar to that in benzene, which stands in contrast to the slightly bent structure of 1,2-Tbb_2-1,2-digermabenzene (8.6˚).[9] The Si–Si, Si–C, and C–C bond lengths fall between the corresponding single and double bond lengths,[16] suggesting a partial delocalization of the 6π electrons over the $[Si_2C_4]$ rings. Considering these structural parameters in their entirety, it seems feasible to conclude that these disilabenzenes exhibit considerable aromaticity on account of the cyclic conjugation systems with 6π-electrons.

Table 1. Experimentally observed and theoretically calculated structural parameters.

	3	$\mathbf{3_{calc}}^*$	**4**	$\mathbf{4_{calc}}^*$
Si1–Si1*/Si2 [Å]	2.2094(6)	2.2308	2.2093(14)	2.2303
Si1–C1 [Å]	1.8094(12)	1.7998	1.785(4)	1.7909
Si2–C4 [Å]	-----	-----	1.833(4)	1.8293
C1–C2 [Å]	1.3733(17)	1.3753	1.384(5)	1.3920
C3–C4 [Å]	-----	-----	1.388(5)	1.3940
C2–C2*/C3 [Å]	1.413(3)	1.4047	1.415(5)	1.4155
internal angles of the $[Si_2C_4]$ ring [˚]	719.9	719.8	719.2	718.5

* calculated at the B3PW91/6-31G(2d,p) level of theory.

The ^{29}Si NMR spectra of **3** and **4** revealed characteristic signals for their $[Si_2C_4]$ rings in the lower-field region (**3**: 61.7 ppm; **4**: 59.7/72.7 ppm). The chemical shifts were reproduced by GIAO calculations[17] (**3**: 55.2 ppm; **4**: 55.6/74.5 ppm), which suggests that disilabenzenes **3** and **4** retain in solution the structures observed in the crystalline state in solution. In addition, the lower-field shifted NMR resonances for the ^{1}H and ^{13}C nuclei in the six-membered $[Si_2C_4]$ rings (δ_H = 7.7-8.1, δ_C = 131-146) suggest the existence of a ring current in the 1,2-disilabenzene rings. NICS-scan calculations[18,19] on the optimized structures support the considerable aromaticity of disilabenzene **3** [NICS(0.6) = –8.3, $NICS_{zz}$(1.1) = –20.9].[19] Moreover, we carried out TD-DFT calculations,[19] which revealed the electron-transitions of $\mathbf{3_{calc}}$ (374 nm, f = 0.227; 368 nm, f = 0.057) and $\mathbf{4_{calc}}$ (416 nm, f = 0.159; 385 nm, f = 0.138) that were assigned to the contamination of some $\pi\rightarrow\pi^*$ transitions of the $[Si_2C_4]$ disilabenzene moieties. These calculated absorptions are in good agreement with the observed λ_{max} values for **3** (397 nm, ε = 5100; 363 nm, ε = 8400) and **4** (442 nm, ε = 9,300; 385 nm, ε = 11,000). The broadened absorption of the *n*-hexane solution of 1,2-Bbt_2-1,2-disilabenzene (λ_{max} = 378 nm) should most likely be interpreted in terms of an overlap of the two characteristic absorptions similar to the cases of **3** and **4**.

Conclusions

In summary, we have synthesized and isolated 1,2-disilabenzenes **3** and **4** from the reactions of the stable disilyne TbbSi≡SiTbb (**1**) with acetylenes. It should be noted that the reaction of **1** with phenylacetylene afforded the 3,5-diphenyl-1,2-disilabenzene selectively, which stands in contrast to the reaction of the silyl-substituted disilyne with phenylacetylene.

View Article Online
DOI: 10.1039/C8DT03081B

While the reaction mechanisms are similar to the Tbb- and R^{Si}-substituted cases, the absolute regioselectivity of the former could be explained based on detailed theoretical calculations. The experimentally observed physical properties of **3** and **4** as well as the results from the theoretical calculations suggest considerable levels of aromaticity.

Acknowledgements

This work was supported by JSPS KAKENHI grants JP15H03777, 15K13640, and JP20109013 from MEXT (Japan), a Grant-in-Aid for Research at Nagoya City University, the Joint Usage/Research Center (JURC, Institute for Chemical Research (ICR), Kyoto University), the Integrated Research Consortium on Chemical Science (IRCCS), and Kyoto University Research Coordination Alliance (KURCA), and the Collaborative Research Program of Institute for Chemical Research, Kyoto University (grant No. 2015-99). T. Sugahara gratefully acknowledges support from a grant-in-aid for JSPS fellows (JP16J05501). The XRD measurements on **3** were carried out at JASRI and BL02B1 in SPring-8 (2016B1716). We would like to thank Mr. Toshiaki Noda and Ms. Hideko Natsume at Nagoya University for the expert manufacturing of custom-tailored glassware.

Notes and references

Dedicated to Emeritus Professor Kohei Tamao on the occasion of his 77th birthday.

1 V. J. Minkin, M. N. Glukhovtsev and B. Y. Simkin, in *Aromaticity and Antiaromaticity; Electronic and Structual Aspects*, Wiley-Interscience, 1994.

2 (a) G. Maier, G. Mihm and H. P. Reisenauer, *Chem. Ber.*, 1982, **115**, 801-803. (b) B. Solouki, P. Rosmus, H. Bock and G. Maier, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 51-52. (c) G. Maier, G. Mihm and H. P. Reisenauer, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 52-53. (d) C. L. Kreil, O. L. Chapman, G. T. Burns and T. J. Barton, *J. Am. Chem. Soc.*, 1980, **102**, 841-842. (e) G. Maier, K. Schöttler and H. P. Reisenauer, *Tetrahedron Lett.*, 1985, **26**, 4079-4082. (f) G. Märkl and P. Hofmeister, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 789-790. (g) G. Märkl and W. Schlosser, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 963-965. (h) G. Märkl and D. Rudnick, *Tetrahedron Lett.*, 1980, **21**, 1405-1408. (i) G. Märkl, D. Rudnick, R. Schulz and A. Schweig, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 221-222. (j) P. Jutzi, M. Meyer, H. P. Reisenauer and G. Maier, *Chem. Ber.*, 1989, **122**, 1227-1230.

3 (a) N. Tokitoh, *Acc. Chem. Res.*, 2004, **37**, 86-94. (b) N. Tokitoh, *Bull. Chem. Soc. Jpn.*, 2004, **77**, 429-441. (c) Y. Mizuhata, S. Fujimori, T. Sasamori and N. Tokitoh, *Angew. Chem., Int. Ed.*, 2017, **56**, 4588-4592.

4 S. Nagase, *Bull. Chem. Soc. Jpn.*, 2014, **87**, 167-195.

5 (a) R. West, M. J. Fink and J. Michl, *Science*, 1981, **214**, 1343-1344. (b) T. Sasamori and N. Tokitoh, *Bull. Chem. Soc. Jpn.*, 2013, **86**, 1005-1021. (c) R. C. Fishcher and P. P. Power, *Chem. Rev.*, 2010, **110**, 3877-3923. (d) V. Ya Lee and Sekiguchi, in *Organometallic Compounds of Low-Coordinate Si, Ge, Sn and Pb: From Phantom Species to Stable Compounds*, Wiley & Sons, New York, 2010. (e) M. Kira and T. Iwamoto, *Adv. Organomet. Chem.*, 2006, **54**, 73-148.

6 (a) R. Kinjo, M. Ichinohe, A. Sekiguchi, N. Takagi, M. Sumimoto and S. Nagase, *J. Am. Chem. Soc.*, 2007, **129**, 7766-7767. (b) J. S. Han, T. Sasamori, Y. Mizuhata and N. Tokitoh, *Dalton Trans.,* 2010, 9238-9240.

7 A. Sekiguchi, R. Kinjo and M. Ichinohe, *Science*, 2004, **315**, 1755-1757.

8 T. Sasamori, K. Hironaka, Y. Sugiyama, N. Takagi, S. Nagase, Y. Hosoi, Y. Furukawa and N. Tokitoh, *J. Am. Chem. Soc.*, 2008, **130**, 13856-13857.

9 (a) T. Sasamori, T. Sugahara, T. Agou, J.-D. Guo, S. Nagase, R. Streubel and N. Tokitoh, *Organometallics*, 2015, **34**, 2106-2109. (b) T. Sugahara, J.-D. Guo, Y. Karatsu, Y. Furukawa, A. E. Ferao, S. Nagase and N. Tokitoh, *Bull. Chem. Soc. Jpn.*, 2016, **89**, 1375-1384.

10 T. Sugahara, J.-D. Guo, T. Sasamori, S. Nagase and N. Tokitoh, *Angew. Chem., Int. Ed.*, 2018, **57**, 3499-3503.

11 T. Agou, N. Hayakawa, T. Sasamori, T. Matsuo, D. Hashizume and N. Tokitoh, *Chem.-Eur. J.*, 2014, **20**, 9246-9249.

12 S. Ishida, R. Sugawara, Y. Misawa and T. Iwamoto, *Angew. Chem., Int. Ed.*, 2013, **52**, 12869-12873.

13 (a) C. Cui, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 2004, **126**, 5062-5063. (b) N. Y. Tashkandi, L. C. Pavelka, C. A. Caputo, P. D. Boyle, P. P. Power and K. M. Baines, *Dalton Trans.*, 2016, **45**, 7226-7230. (c) L. Zhao, C. Jones and G. Frenking, *Chem.-Eur. J.*, 2015, **21**, 12405-12413.

14 B3PW91-D3(BJ)/lanl2dz+d for Si, 6-31G(d) for C,H. Frequency calculations and IRC calculations to confirm the PESs were carried out at the B3PW91-D3(BJ)/3-21G* level of theory.

15 Crystallographic data for **1:** $C_{48}H_{98}Si_{10}$, FW 956.16, crystal size $0.15 \times 0.12 \times 0.08$ mm^3, –170 ˚C, λ = 0.71073 Å, monoclinic, *C*2/*c* (#15), a = 19.8244(4) Å, b = 12.3683(2) Å, c = 27.2326(5) Å, β = 104.974(2)˚, V = 6450.5(2) $Å^3$, Z = 4, D_{calcd} = 0.985 g cm^{-3}, μ = 0.230 mm^{-1}, θ_{max} = 27.997˚, refl./param. = 7700/277, GOF = 1.239, Completeness = 99.8%, R_1 [$I>2\sigma(I)$] = 0.0529, wR_2 (all data) = 0.1240, largest diff. peak and hole 0.643 and –0.332 e.$Å^{-3}$. CCDC-1830586. **3:** $C_{52}H_{102}Si_{10}\cdot C_6H_6$, FW 1086.34, crystal size $0.40 \times 0.35 \times 0.20$ mm^3, –183 ˚C, λ = 0.3024(1) Å, orthorhombic, *Pnna*(#52), a = 18.1857(3) Å, b = 30.4174(5) Å, c = 12.6976(2) Å, V = 7023.8(2) $Å^3$, Z = 4, D_{calcd} = 1.027 g cm^{-3}, μ = 0.035 mm^{-1}, θ_{max} = 11.325˚, refl./param. = 7977/351, GOF = 1.062, Completeness = 98.9%, R_1 [$I>2\sigma(I)$] = 0.0348, wR_2 (all data) = 0.0973, largest diff. peak and hole 0.71 and –0.23 e $Å^{-3}$. CCDC-1830587. **4:** $C_{64}H_{110}Si_{10}$, FW 1160.41, crystal size $0.11 \times 0.06 \times 0.06$ mm^3, –170 ˚C, λ = 0.71073 Å, triclinic, space group *P*–1 (#2), a = 13.2542(4) Å, b = 14.3679(5) Å, c = 20.4533(7) Å, α = 85.985(3)˚,⍰β = 89.418(2)˚,⍰γ = 66.661(3)˚, V = 3565.4(2) $Å^3$, Z = 2, D_{calcd} = 1.081 g cm^{-3}, μ = 0.219 mm^{-1}, θ_{max} = 24.999˚, refl./param. = 12508/625, GOF = 1.057, Completeness = 99.6%, R_1 [$I>2\sigma(I)$] = 0.0622, wR_2 (all data) = 0.1594, largest diff. peak and hole 0.815 and –0.435 e $Å^{-3}$. CCDC-1830588.

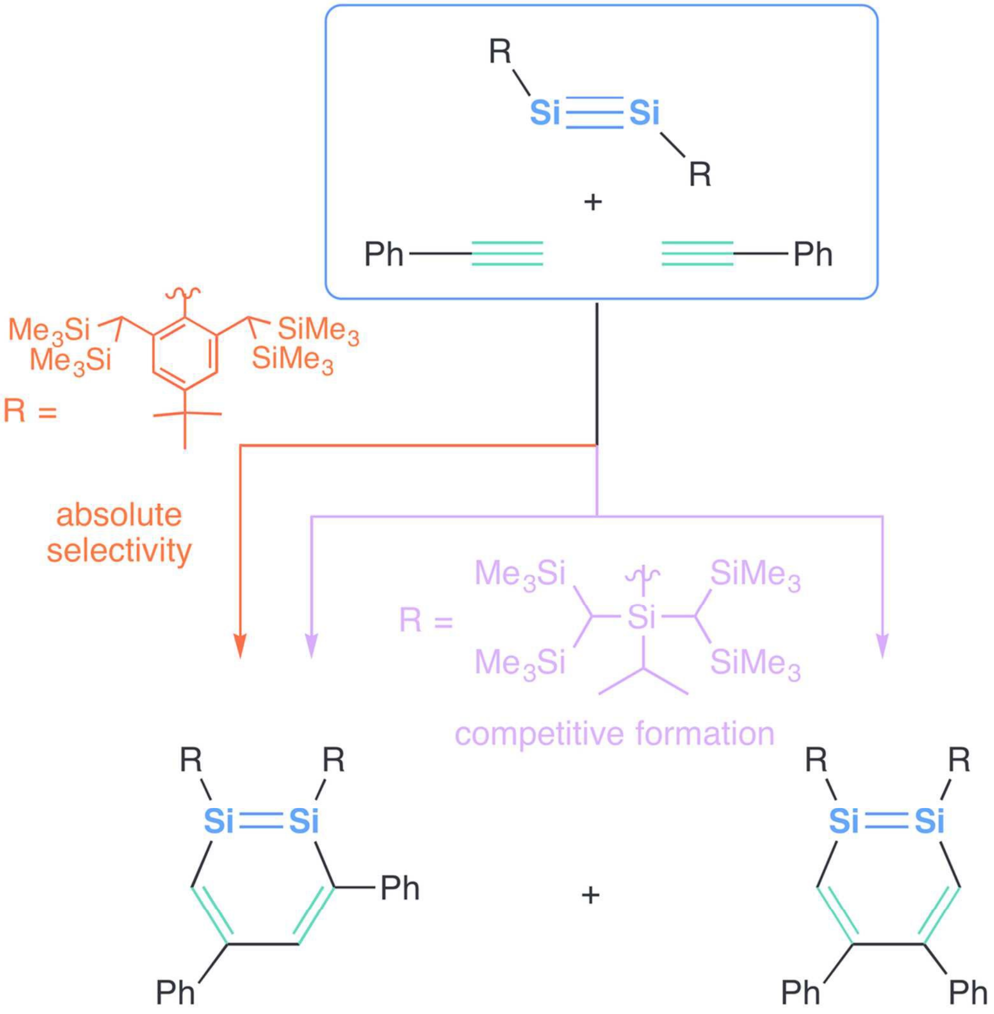
16 M. Kaftrory, M. Kapon and M. Botoshansky, in *The Chemistry of Organic Silicon Compounds*, 1998, **2**, Chapter 5.

17 HCTH407/6-311G(3df,p)//B3PW91/6-31G(2d,p)

18 A. Stanger, *J. Org. Chem.*, 2006, **71**, 883-893.

19 (GIAO- or TD-)B3PW91/6-311G(3df,p)//B3PW91/6-31G(2d,p)

View Article Online
DOI: 10.1039/C8DT03081B



106x107mm (300 x 300 DPI)