HETEROCYCLES, Vol. 104, No. 2, 2022, pp. 389 - 396. © 2022 The Japan Institute of Heterocyclic Chemistry
Received, 9th November, 2021, Accepted, 22nd November, 2021, Published online, 30th November, 2021
DOI: 10.3987/COM-21-14585

REACTION OF AN OVERCROWDED 1,2-DIARYL-1,2-DIBROMODISILENE WITH 1-VINYLCYCLOHEPTA-1,3,5-TRIENE: ISOLATION OF A 2-VINYLSILACYCLOPROPANE DERIVATIVE AND ITS THERMAL CONVERSION TO A SILACYCLOPENT-3-ENE DERIVATIVE

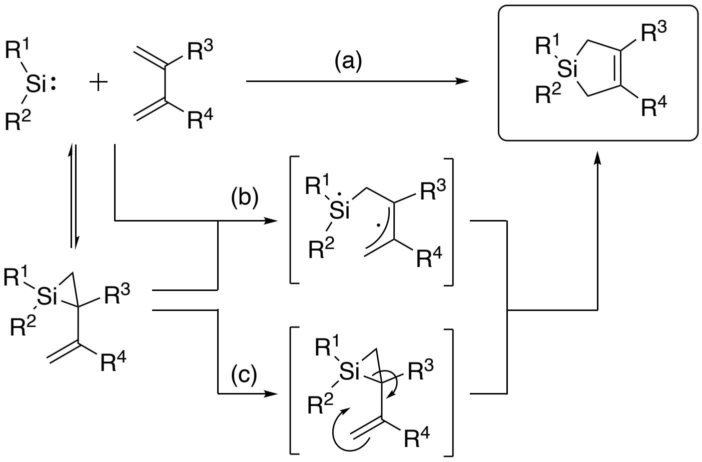
Taku Oshiro,[a] Yoshiyuki Mizuhata,[a,b]* and Norihiro Tokitoh[a,b]*

[a]Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan. E-mail: tokitoh@boc.kuicr.kyoto-u.ac.jp
[b]Integrated Research Consortium on Chemical Sciences, Gokasho, Uji, Kyoto 611-0011, Japan.

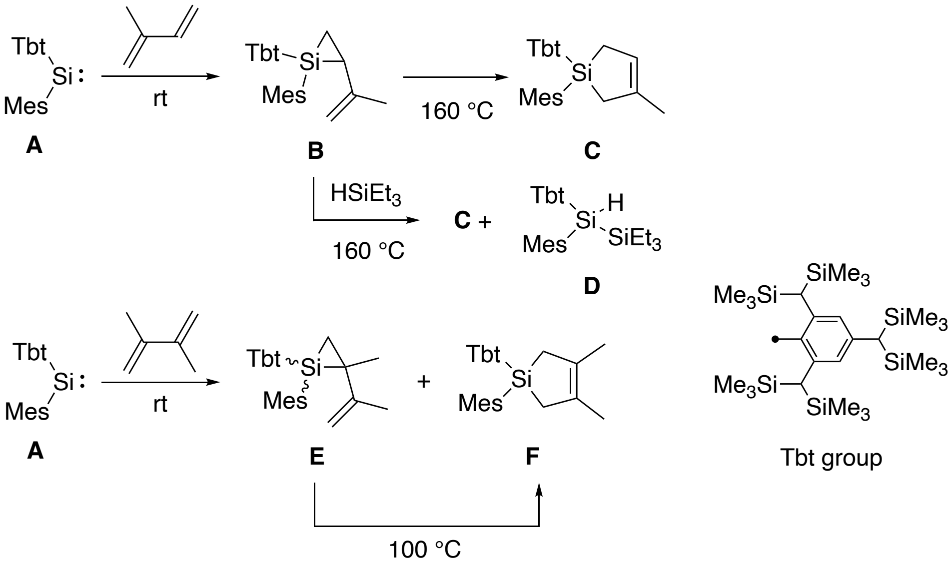
In memory of Prof. Wataru Ando

Abstract – We examined the reactions of a bulky aryl-substituted 1,2-dibromodisilene with 1-vinylcyclohepta-1,3,5-triene to investigate the reaction mechanism of a bromosilylene with a buta-1,3-diene. The reaction proceeded selectively with the exocyclic vinyl group and gave the corresponding [1+2]-adduct, *i.e.,* 2-cyclohepta-1,3,5-trien-1-ylsilacyclopropane derivative, as an isolable compound. The following thermal reaction of the adduct resulted in the stereo-selective formation of a 1,2,4,8a-tetrahydrocyclohepta[*b*]silole skeleton, the formal [1+4]-adduct between the bromosilylene and 1-vinylcyclohepta-1,3,5-triene. Several experimental verifications suggested that the conversion of the [1+2]- to [1+4]-adducts proceeded via 1,3-sigmatropic rearrangement.

Silylenes, silicon analogues of carbene, have an ambiphilic character derived from the vacant p orbital and the lone pair on the silicon atom leading to their characteristic reactivity. It is well-known that silylenes are useful building blocks for silicon-containing cyclic compounds. Silylenes react with alkenes to produce silacyclopropanes, *i.e.,* the [1+2]-cycloadducts; with buta-1,3-dienes to form silacyclopent-3-enes, *i.e.,* the [1+4]-cycloadducts. The reaction mechanism for the [1+4]-cycloaddition has been debated for years and is considered as follows: path (a) the direct [1+4]-cycloaddition,[1] path (b) via diradical intermediate,[2] and path (c) 1,3-sigmatropic rearrangement of vinyl silacyclopropane[3] (Scheme 1). According to the results of theoretical calculations by Gasper *et al.*, dimethylsilylene and diphenylsilylene react with buta-1,3-dienes to form 2-vinylsilacyclopane skeleton initially, and the following regeneration of the corresponding silylene via retro-[1+2]-reaction results in the formation of silacyclopent-3-ene via path (a) the direct [1+4] cycloaddition.[4] On the other hand, Boganov *et al.* proposed that the reactions of halogen-substituted silylenes proceed via path (c) the 1,3-sigmatropic rearrangement of 2-vinylsilacyclopropane.[5] Thus, 2-vinylsilacyclopropanes should be important intermediates. In general, however, these reactions proceed promptly to give thermodynamically favored silacyclopent-3-enes, and the successful observation of the conversion from detectable 2-vinylsilacyclopropane to silacyclopent-3-ene had been limited to our previous report using bulky silylene **A**, Tbt(Mes)Si: (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl) (Scheme 2).[1a,6] This reaction proceeded via the silylene-regeneration process, as in the cases of dimethylsilylene and diphenylsilylene, and the proposed mechanism was supported by the thermal reaction of 2-vinylsilacyclopropane **B** in the presence of $HSiEt_3$ giving the expected silylene-insertion product, $Tbt(Mes)Si(H)SiEt_3$ **D**, together with the silacyclopent-3-ene derivative **C**.

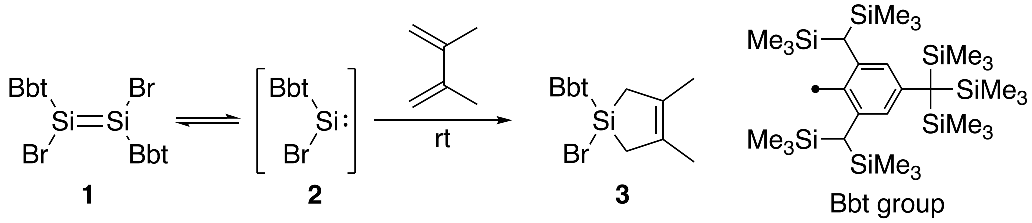


Scheme 1. Reaction pathways proposed for the reactions of silylenes with buta-1,3-dienes

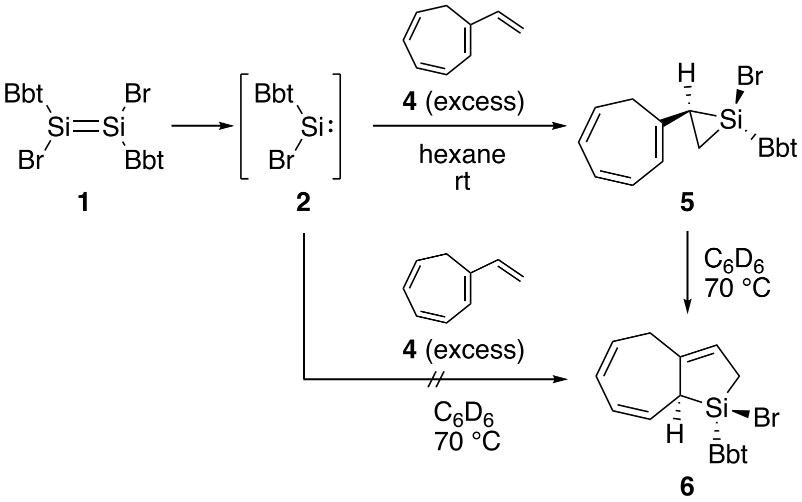


Scheme 2. Reactions of silylene **A** with buta-1,3-dienes

On the other hand, we have already reported the reactivity of a stable 1,2-dibromodisilene having bulky aryl substituents, (*E*)-Bbt(Br)Si=Si(Br)Bbt (**1**, Bbt = 2,6-bis[trimethylsilylmethyl]-4-[tris(trimethylsilyl)-methyl]phenyl).[7] Disilene **1** reacted as bromosilylene **2** with various trapping reagents at ambient temperature to give the corresponding adducts. It means that disilene **1** dissociates into bromosilylenes **2** in solution under mild conditions.[8] The product in the reaction of disilene **1** with 2,3-dimethylbuta-1,3-diene is silacyclopent-3-ene derivative **3** containing a halogen-substituted silicon atom suitable for further modification (Scheme 3). Since this reaction showed no intermediate, it is still unclear experimentally whether bromosilylene **2** undergoes addition with buta-1,3-dienes by direct [1+4]-cycloaddition or stepwise formation of **3** via the [1+2]-cycloaddition as proposed by theoretical calculations.[5] During the course of our studies on the construction of silicon-containing azulene skeleton, we found the reaction of disilene **1** with 1-vinylcyclohepta-1,3,5-triene **4** having four conjugated double bonds, resulting in the site-selective formation of 2-vinylsilacyclopropane derivative **5** and the following stereo-selective isomerization to silacyclopent-3-ene derivative **6** (Scheme 4).



Scheme 3. Reaction of silylene **1** with 2,3-dimethylbuta-1,3-dienes



Scheme 4. Reactions of bromosilylene **2** with 1-vinylcyclohepta-1,3,5-triene **4**

The reaction of dibromodisilene **1** with an excess amount of 1-vinylcyclohepta-1,3,5-triene **4** in hexane at ambient temperature resulted in quantitative, regioselective, and stereoselective formation of compound **5** (Scheme 4). Compound **5** was fully characterized by ^{1}H, ^{13}C and ^{29}Si NMR and high-resolution mass spectrometry, and its molecular structure was finally confirmed by X-ray crystallography (Figure 1a). The crystal structure of **5** showed severe disorder (83:17) on the part except for the substituent (See Figure S11), and hence the structural parameters were poor in accuracy. Bbt-substituent was found to locate at the opposite side of the cycloheptatriene ring toward the SiC_2 ring, and therefore, the stereoselectivity leading to **5** is probably due to the steric hindrance between the cycloheptatriene-ring and Bbt. The bond lengths in the silacyclopropane moiety [Si1–C1 = 1.848(12), Si–C2 = 1.866(5), C1–C2 = 1.548(14) Å, observed for the major part of disordered structures] are within the range of those reported for non-fused silacyclopropanes (Si–C: 1.822 to 1.960 Å; C–C: 1.508 to 1.642 Å).[9] The ^{29}Si NMR signal of the silicon atom in the SiC_2 ring of **5** was observed at –53.4 ppm, whose up-field shifted chemical shift indicates the silacyclopropane structure of **5**.

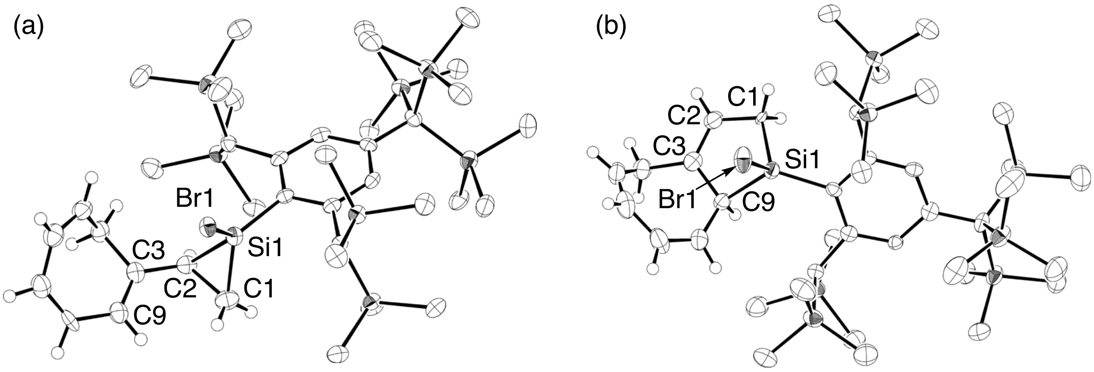
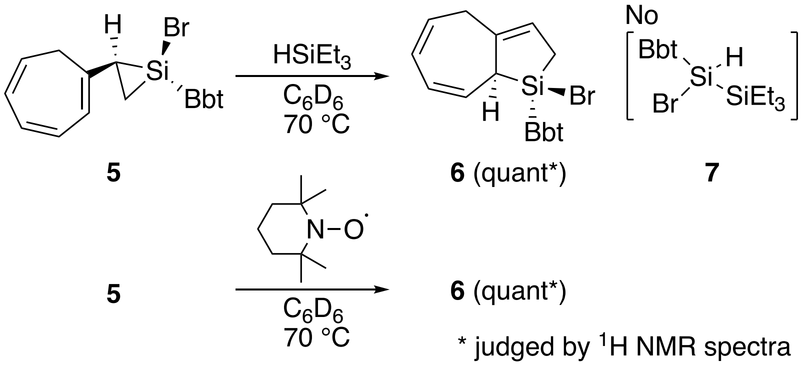


Figure 1. Thermal ellipsoid plots (50% probability) of compounds **5** (a) and **6** (b). Hydrogen atoms on Bbt subsitituents were omitted for clarity.

Heating of the C_6D_6 solution of **5** at 70 °C for 30 h afforded compound **6** stereoselectively, which is a typical [1+4]-cycloadduct of a silylene with a buta-1,3-diene (Scheme 4). The structure of **6** was also confirmed by single-crystal X-ray diffraction analysis, showing the bicyclic structure with fused five- and seven-membered rings (Figure 1b). Although the low crystal quality (due to the unresolvable inversion disorder of the bicyclic part) precluded detailed discussion of structural parameters, the bicyclic system of **6** showed a folded boat conformation and the bromine atom situated inside the curved surface and at the anti-position towards the methine proton. The stereoselectivity might be derived from the bulkiness of Bbt group, preventing the opposite configuration of Br and Bbt groups. The ^{29}Si NMR signal of the ring silicon atom in **5** appeared at 27.4 ppm, which is within the range of the reported ones in 1-bromo-1-silacyclopent-3-enes (−8.0 to 38.0 ppm).[8,10]

To clarify the reaction mechanism, several experiments were performed. When disilene **1** reacted with **4** at 70 °C in C_6D_6 without isolation of **5**, the reaction gave a complicated mixture containing neither **5** nor **6** (Scheme 4). It suggested that the reaction of intermediary bromosilylene **2** with **4** under harsh conditions showed no selectivity and that the selective formation of **5** is necessary to give **6**. Importantly, thermal conversion of **5** to **6** in the presence of $HSiEt_3$ proceeded without the formation of insertion product **7** (Scheme 5), indicating that the silylene-regeneration process proposed in the case from **B** to **C** can be ruled out. We have already revealed the formation of **7** in the reaction of **1** with $HSiEt_3$ at ambient temperature.[8] As described in the previous theoretical investigations by Boganov *et al.*, it suggested that halogen substitution affects the reactivity of the silylene and the adduct. Similarly, the coexistence of TEMPO (2,2,6,6-tetramethylpiperidine 1-oxyl) did not affect the conversion of **5** to **6** (Scheme 5), indicating that the radical mechanism as shown in Scheme 1b can also be excluded. Therefore, it can be concluded that this formal [1+4]-cycloaddition between bromosilylene **2** with **4** should proceed via the [1+2]-cycloadduct, 2-vinylsilacyclopropane derivative **5**, and the subsequent 1,3-sigmatropic rearrangement. It was also supported by the fact that only the peaks of **5** and **6** were detected during the monitoring of the reaction by ^{1}H NMR. This rearrangement is possible when the cycloheptatriene ring is semi-rotated and the C3–C9 double bond and the C2–Si1 bond are close to each other based on the conformation of **5** shown in Figure 1 and Scheme 4. Since there is an energy barrier to the rotation around the C2–C3 bond leading to the rearrangeable conformation, compound **5** can be isolated and heating would give compound **6**.



Scheme 5. Thermal reactions of **5** in the presence of $HSiEt_3$ or TEMPO

In conclusion, we have succeeded in the synthesis and isolation of vinylsilacyclopropane derivative **5** by the reaction of bromosilylene **2** with 1-vinylcyclohepta-1,3,5-triene **4**. Compound **5** thus obtained was found to undergo thermal isomerization to give the ring-fused bicyclic compound **6** containing a silacyclopent-3-ene skeleton, regarded as the [1+4]-cycloadduct between **2** and **4**. Moreover, it was possible to experimentally clarify that the [1+4]-cycloaddition between bromosilylene with buta-1,3-diene proceeds stepwise via 1,3-sigmatropic rearrangement of [1+2]-cycloadduct, the mechanism of which was proposed by theoretical calculations of Boganov and co-workers.[5]

EXPERIMENTAL

GENERAL

All the manipulations were performed under a dry argon atmosphere using standard Schlenk techniques or gloveboxes. Solvents were purified by the Ultimate Solvent System, Glass Contour Company[11] (hexane) or by trap-to-trap distillation from a potassium mirror prior to use (C_6D_6). ^{1}H, ^{13}C, and ^{27}Si NMR spectra were measured on a JEOL AL-300 spectrometer (^{1}H: 300 MHz, ^{13}C: 75 MHz, ^{29}Si: 59.6 MHz) or on a Bruker Avance NEO 400N (Nano-Bay) NMR spectrometer (^{1}H: 400 MHz, ^{13}C: 100 MHz, ^{29}Si: 79.5 MHz). Signals arising from residual partially hydrogenated C_6D_5H (7.15 ppm for ^{1}H), C_6D_6 (128.06 ppm for ^{13}C), and $SiMe_4$ (0.0 ppm for ^{29}Si) were used as an external standard. ^{1}H and ^{13}C NMR signals were assigned with the aids of the ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, and ^{1}H-^{13}C HMBC spectra. Melting points were determined on a BUCHI Melting Point M-565 apparatus and uncorrected. High-Resolution mass spectrometry data were obtained on a Bruker Daltonics microTOF forcus-Kci with an IonSence DART®-SVP ion source. (*Z*)-Bbt(Br)Si=Si(Br)Bbt **1**[7] and 1-vinylcyclohepta-1,3,5-triene **4**[12] were prepared according to the literatures.

Synthesis of 5

To a solution of dibromodisilene **1** (95.3 mg, 0.065 mmol) in *n*-hexane (5.0 mL), an excess amount of 1-vinylcyclohepta-1,3,5-triene (>5 eq.) were added at room temperature. After stirring for 4 h at room temperature, color of the solution changed from yellow to colorless. The solvent and excess 1-vinylcyclohepta-1,3,5-triene were removed to afford **5** as colorless crystals (118.6 mg, 0.130 mmol, quant.). ^{1}H NMR δ (400 MHz, C_6D_6, 298 K) 0.25 (br, 36H), 0.32 (s, 27H), 1.33 (t, ^3J = 12.0 Hz, 1H), 1.59 (dd, ^2J = 12.0 Hz, ^3J = 10.4 Hz, 1H), 2.44 (t, ^3J = 10.8 Hz, 1H), 2.53 (dd, ^2J = 12.4 Hz, ^3J = 6.8 Hz, 1H), 2.85 (dd, ^2J = 12.4 Hz, ^3J = 6.8 Hz, 1H), 2.96 (br, 2H), 5.57 (dd, ^3J = 6.8, 9.2 Hz, 1H), 6.17 (d, ^3J = 6.0 Hz, 1H), 6.26 (dd, ^3J = 5.6, 9.2 Hz, 1H), 6.52 (dd, ^3J = 5.6, 11.2 Hz, 1H), 6.62 (dd, ^3J = 6.0, 11.2 Hz, 2H), 6.95 (s, 2H). ^{13}C NMR (100 MHz, C_6D_6, 298 K) δ 1.81, 5.54, 12.4, 23.3, 29.0, 33.1, 119.3, 120.96, 126.5, 127.4, 128.6, 131.1, 134.9, 150.0. As seen in other systems with a Bbt group, some of aromatic ring carbons and *o*-benzyl carbons of Bbt group were severely broadened and could not be observed. Normally, these can be observed by increasing the temperature, but in this system, it was not possible because the reaction to **6** proceeded at elevated temperature. We tried to detect them by using long-range correlations at room temperature but could not observe any significant correlation. ^{29}Si NMR (79.5 MHz, C_6D_6, 298 K) δ –53.4, 1.2, 2.5. DART-TOF MS: *m*/*z* calcd for $C_{39}H_{77}BrSi_8$: 851.3416; ([M+H]$^+$); found: 851.3440.

Synthesis of 6

5 (26.0 mg, 30.4 μmol) and C_6D_6 (0.5 mL) were charged in a Young NMR tube. The mixture was left to stand at 70 °C for 30 h. The solvent was removed to afford **6** (25.9 mg, 30.2 μmol, 99%). **6**: colorless crystals, mp 106 °C. ^{1}H NMR δ (400 MHz, C_6D_6, 298 K) 0.25 (s, 18H), 0.28 (s, 18H), 0.33 (s, 27H), 2.34 (br, 2H), 2.39 (s, 2H), 2.77 (dd, ^2J = 10.6 Hz, ^3J = 3.6 Hz, 1H), 2.97 (dd, ^2J = 10.6 Hz, ^3J = 3.6 Hz, 1H), 3.51 (br, 1H), 5.35 (br, 1H), 5.87 (dt, J = 4.5, 8.1 Hz, 1H), 5.94 (dd, J = 3.6, 8.1 Hz, 1H), 6.17 (ddd, J = 2.1, 3.9, 9.0 Hz, 1H), 6.58 (dd, J = 3.6, 8.1 Hz, 1H), 6.93 (s, 2H). ^{13}C NMR (100 MHz, C_6D_6, 298 K) δ 2.11, 2.39, 5.80, 22.79, 28.26, 30.31, 35.31, 42.58, 120.29, 127.58, 128.32, 129.60, 131.02, 132.61, 148.76, 152.20, 152.68. ^{29}Si NMR (79.5 MHz, C_6D_6, 298 K) δ 1.1, 2.1, 2.6, 27.4. DART-TOF MS: *m*/*z* calcd for $C_{39}H_{77}BrSi_8$: 851.3416; ($[M+H]^+$); found: 851.3372.

X-Ray Diffraction Studies of 5 and 6

Suitable crystals were mounted in Fomblin® Y oil on a glass fiber. For **5**, low-temperature (103 K) data were collected on a RIGAKU Saturn70 CCD system with VariMax Mo Optics using MoKα radiation (λ = 0.71073 Å) with φ- and ω-scans. For **6**, low-temperature (90 K) data were collected on a Bruker D8 VENTURE system with IμS Diamond Mo Optics using MoKα radiation (λ = 0.71073 Å) with ϕ- and ω-scans. An empirical absorption correction was applied to the diffraction data using SCALE3 ABSPACK[13] for **5** and SADABS-2016/2[14] for **6**. Structures were solved by using SHELXT-2014/5[15] and refined against F^2 on all data by full-matrix least squares with SHELXL-2018/1.[16] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U_{eq} value of the atoms they are linked to (1.5 times for methyl groups). Details of the data quality and a summary of the residual values of the refinements for all structures are contained within Table S1. Deposition numbers 2120758 (for **5**) and 2120759 (for **6**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

ACKNOWLEDGEMENTS

This work was supported by KAKENHI (JP24109013, JP26620028, JP19H05528, JP18H01963, and JP19H05635), Integrated Research Consortium on Chemical Science (IRCCS). This study was supported by the Joint Usage/Research Center [JURC, Institute for Chemical Research (ICR), Kyoto University] by providing access to a Bruker Avance III 600 NMR spectrometer. The authors are furthermore grateful for computation time, which was provided by the Super Computer System (ICR, Kyoto University). Elemental analyses were carried out at the Microanalytical Laboratory of the ICR (Kyoto University).

REFERENCES AND NOTES

1. (a) N. Takeda, T. Kajiwara, H. Suzuki, R. Okazaki, and N. Tokitoh, *Chem. Eur. J.*, 2003, **9**, 3530; (b) M. Kira, *J. Chem. Sci.*, 2012, **124**, 1205.
2. D. Lei, R. Hwang, and P. P. Gaspar, *J. Organomet. Chem.*, 1984, **271**, 1.
3. W. H. Atwell and D. R. Weyenberg, *J. Am. Chem. Soc.*, 1968, **90**, 3438.
4. M. Nag and P. P. Gaspar, *Organometallics*, 2009, **28**, 5612.
5. S. S. Rynin, V. I. Faustov, S. E. Boganov, M. P. Egorov, and O. M. Nefedov, *J. Organomet. Chem.*, 2010, **695**, 2345.
6. N. Takeda, N. Tokitoh, and R. Okazaki, *Chem. Lett.*, 2000, **29**, 622.
7. T. Sasamori, K. Hironaka, Y. Sugiyama, N. Takagi, S. Nagase, Y. Hosoi, Y. Furukawa, and N. Tokitoh, *J. Am. Chem. Soc.*, 2008, **130**, 13856.
8. J. S. Han, T. Sasamori, Y. Mizuhata, and N. Tokitoh, *Chem. Asian J.*, 2012, **7**, 298.
9. (a) G. L. Delker, Y. Wang, G. D. Stucky, R. L. Lambert Jr., C. K. Hass, and D. Seyferth, *J. Am. Chem. Soc.*, 1976, **98**, 1779; (b) M. Ishikawa, S. Matsuzawa, H. Sugisawa, F. Yano, S. Kamitori, and T. Higuchi, *J. Am. Chem. Soc.*, 1985, **107**, 7706; (c) D. H. Pae, M. Xiao, M. Y. Chiang, and P. P. Gaspar, *J. Am. Chem. Soc.*, 1991, **113**, 1281; (d) W. Ando, W. Shiba, T. Hidaka, K. Morihashi, and O. Kikuchi, *J. Am. Chem. Soc.*, 1997, **119**, 3629; (e) M. E. Lee, H. M. Cho, Y. M. Lim, J. K. Choi, C. H. Park, S. E. Jeong, and U. Lee, *Chem. Eur. J.*, 2004, **10**, 377; (f) T. M. Klapötke, S. K. Vasisht, and P. Mayer, *Z. Anorg. Allg. Chem.*, 2009, **635**, 2447; (g) R. Rodriguez, D. Gau, T. Kato, N. Saffon-Merceron, A. D. Cózar, F. P. Cossío, and A. Baceiredo, *Angew. Chem. Int. Ed.*, 2011, **50**, 10414; (h) K. R. Pichaandi, J. T. Mague, and M. J. Fink, *J. Organomet. Chem.*, 2011, **696**, 1957; (i) H. M. Cho, K. Bok, S. H. Park, Y. M. Lim, M. E. Lee, M. Choi, and K. M. Lee, *Organometallics*, 2012, **31**, 5227.
10. (a) R. Boukherroub, V. Dejean, G. Manuel, and W. P. Weber, *Main Group Met. Chem.*, 1995, **18**, 67; (b) M. E. Lee, H. M. Cho, M. S. Ryu, C. H. Kim, and W. Ando, *J. Am. Chem. Soc.*, 2001, **123**, 7732.
11. A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, and F. J. Timmers, *Organometallics*, 1996, **15**, 1518.
12. (a) T. Asao, S. Kuroda, and K. Kato, *Chem. Lett.*, 1978, **7**, 41; (b) M. Aga, K. Okada, and M. Oda, *Tetrahedron Lett.*, 1986, **27**, 5653.
13. SCALE3 ABSPACK - Oxford Diffraction Ltd.
14. L. Krause, R. Herbst-Irmer, G. M. Sheldrick, and D. Stalke, *J. Appl. Cryst.*, 2015, **48**, 3.
15. G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3.
16. G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3.