Platinum-Catalyzed Reactions of 2,3-Bis(diisopropylsilyl)thiophene with Alkynes

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Supporting Information

ABSTRACT: The reactions of 2,3-bis(diisopropylsilyl)thiophene (1) with diphenylacetylene, phenylacetylene, trimethylsilylacetylene, and mesitylacetylene have been reported. The reactions of 1 with diphenylacetylene and phenylacetylene in the presence of a catalytic amount of tetrakis(triphenylphosphine)platinum(0) at 80 °C gave [1,4]-disilino[2,3-b]thiophene derivatives. With trimethylsilylacetylene, 1 afforded two types of products arising from sp-hybridized C−H bond activation of the acetylene, together with [1,3]disilolo[4,5-b]thiophene derivatives. A similar treatment of 1 with mesitylacetylene produced two regioisomers of products arising from the C−H bond activation of mesitylacetylene. Theoretical calculations for the intramolecular reactions of 10a and 10b are also discussed.

1. INTRODUCTION

It is well-known that reactions of organosilanes with unsaturated compounds in the presence of a catalytic amount of transition-metal complexes can be employed for the synthesis of various organosilicon compounds.1 In these reactions, the silyl-transition-metal complexes would be formed as reactive species. For example, the benzodisilaplatinacyclopentene derivatives are produced by reactions of 1,2-bis(hydrosilyl)benzenes with platinum complexes, and their chemical properties have been widely examined by Tanaka et al., Nagashima et al., and other chemists.2−8

We have reported that the platinum-catalyzed reactions of tetraethyl-substituted benzodisilacyclobutene with alkynes such as diphenylacetylene, 3-hexyne, and phenylacetylene readily produce the respective 1:1 adducts, benzodisilacyclobutene derivatives, in high yield.9−11 On the other hand, platinum-catalyzed reactions of tetraisopropyl-substituted benzodisilacyclobutene with the same alkynes afford two types of products, benzodisilacyclohexadienes and benzodisilacyclopentenes.12,13

Recently, we have demonstrated that the platinum-catalyzed reactions of 2,3-bis(diethylsilyl)thiophene with alkynes such as diphenylacetylene, 3-hexyne, and phenylacetylene afford the respective 1:1 adducts, benzodisilacyclohexadiene derivatives, in high yield.9−11 On the other hand, platinum-catalyzed reactions of tetraisopropyl-substituted benzodisilacyclobutene with the same alkynes afford two types of products, benzodisilacyclohexadienes and benzodisilacyclopentenes.12,13

We first examined the reactions of 1 with diphenylacetylene. Treatment of compound 1 with diphenylacetylene in the presence of Pt(PPh3)4 in refluxing benzene for 96 h gave 1,1,4,4-tetraisopropyl-2,3-diphenyl-1,4-dihydro-[1,4]disilino[2,3-b]thiophene (2) in 80% yield (Scheme 2). The structure of 2 was verified by spectroscopic analysis. The mass spectrum for 2 shows parent ions at m/z 488, corresponding to the calculated molecular weight of C30H40Si2S. The 1H NMR spectrum of 2...
shows septet signals at 1.33 and 1.34 ppm, attributable to the methine protons in the isopropyl groups at silicon; four doublet signals at 0.80, 0.81, 1.04, and 1.09 ppm, attributable to the methyl protons of the isopropyl groups; two doublet signals at 7.39 and 7.76 ppm, attributable to the thienylene protons; and signals attributed to the phenyl protons. The $^{29}$Si NMR spectrum for 2 shows signals at $-10.6$ and $-9.2$ ppm.

On the basis of the results obtained from the platinum-catalyzed dehydrogenative double silylation of various unsaturated compounds with bis(hydrosilane)s, the formation of adduct 2 obtained from the platinum-catalyzed reaction of 1 with diphenylacetylene may be explained as follows: (1) oxidative addition of the platinum species to one of the Si–H bonds in 1; (2) dehydrogenation to give the bis(silyl)platinum complex (3); (3) insertion of a triple bond of alkynes into a platinum–silicon bond to produce the platinum complex (4); (4) reductive elimination of 2 from the Pt complex (Scheme 3).

Unfortunately, compound 1 did not react with phenyltrimethylsilylacetylene and bis(trimethylsilyl)acetylene. The starting compound 1 was recovered quantitatively.

Next, we investigated the platinum-catalyzed reaction of 1 with monosubstituted alkynes under the same conditions as described above. Treatment of 1 with phenylacetylene at 80 °C indicated that 1:1 cyclic adducts as a mixture of two regioisomers, namely, 1,1,4,4-tetraisopropyl-3-phenyl-1,4-dihydro-[1,4]disilino[2,3-b]-thiophene (5a) and 1,1,4,4-tetraisopropyl-2-phenyl-1,4-dihydro-[1,4]disilino[2,3-b]thiophene (5b), were produced in a ratio of 3:1 in 60% yield, along with unreacted starting compound 1 (40%) (Scheme 4). All attempts to separate 5a and 5b were unsuccessful, but their structures were verified by spectroscopic analysis of the mixture.

The regioselective formation of 5a and 5b in the platinum-catalyzed reaction of 1 with monosubstituted alkynes can be best explained by a series of reactions similar to the reaction shown in Scheme 3. Namely, the regioselective addition of a Pt–Si bond in the intermediate similar to 3 to the carbon–carbon triple bond of monosubstituted acetylene affords predominantly 1,1,5,5-tetraisopropyl-3-phenyl-1,5-dihydro-[1,2,5]platinadisilepino-[3,4-b]thiophene as the intermediate. It has been reported that the introduction of electron-withdrawing substituents on the silicon atom in the silyl–platinum complexes enhances the Pt–Si bond. In the present reactions, the Pt–Si bond of the Pt–Si–C–C moiety is probably weaker than that of the Pt–Si–C–S moiety (sulfur has higher electronegativity than carbon) and the former migrates to the less hindered carbon atom in the coordinated monosubstituted alkyne to produce insertion product 5a.

When a mixture of 1 and trimethylsilylacetylene in the presence of Pt(PPh$_3$)$_4$ catalyst was heated to reflux in benzene for 20 h, four products were obtained. We separated these products...
from the reaction mixture by column chromatography and identified them as (E)- and (Z)-1,1,3,3-tetraisopropyl-2-\((\text{trimethylsilyl})\text{methylene}\)-2,3-dihydro-1\(H\)-[1,3]disilolo[4,5-\(b\)]thiophene (6\(a\),\(b\)), (2-\((\text{diisopropyl})\text{silyl}\)thiophen-3-yl)diisopropyl((trimethylsilyl)ethynyl)silane (7), and (3-\((\text{diisopropyl})\text{silyl}\)thiophen-2-yl)diisopropyl((trimethylsilyl)ethyl)silane (8) by mass spectrometry (MS) and \(^1\text{H}\), \(^{13}\text{C}\), and \(^{29}\text{Si}\) NMR spectroscopy (Scheme 4). Unfortunately, all attempts
to separate 6a and 6b were unsuccessful. The ratio of 6a and 6b was determined to be 1.6:1 by $^1$H NMR spectrometric analysis. Compounds 7 and 8 were isolated by column chromatography. The $^1$H NMR spectrum of 7 shows a singlet signal at 0.22 ppm attributed to trimethylsilyl protons and a triplet signal at 4.28 ppm attributed to a proton on the silicon atom along with isopropyl and thienyl protons. The $^{13}$C NMR spectrum of 7 reveals a resonance at $-0.16$ ppm, attributed to trimethylsilyl carbons, and two resonances at 108.70 and 118.17 ppm, attributed to sp-hybridized carbons as well as isopropyl and thienyl carbons. The $^1$H NMR spectrum of 8 shows a singlet signal at 0.21 ppm, attributed to trimethylsilyl protons, and a double of triplet signal at 4.46 ppm ($^3J = 3.6$ Hz, $^5J = 0.8$ Hz), attributed to an Si–H proton along with isopropyl and thienyl protons. The $^{13}$C NMR spectrum of 8 reveals a resonance at $-0.10$ ppm, attributed to trimethylsilyl carbons, and two resonances at 109.90 and 119.38 ppm, attributed to the sp-hybridized carbons as well as isopropyl and thienyl carbons.

Scheme 5 illustrates a possible mechanistic interpretation of the observed reaction course for products 7 and 8. The formation of 7 and 8 can be understood in terms of the Pt atom into the sp-hybridized C–H bond of the acetylene leading to 9, followed by the reductive elimination of the C–Si bond to give complexes 10a and 10b.

To confirm whether or not compounds 6a and 6b were produced from compounds 7 and 8 by intramolecular hydrosilation, we carried out reactions of 7 and 8 with a catalytic amount of the platinum complex. Thus, the reaction of 7 with 6 mol % of tetrakis(triphenylphosphine)platinum(0) at 80 °C for 130 h produced 6a and 6b in the ratio of 1.2:1 in 47% combined yield, in addition to the starting compound 7 and its isomer 8 in the ratio of 3:1 (Scheme 6). The presence of 8 in this reaction obviously indicates the production of intermediates 11a and 11b (Scheme 7). A similar reaction of 8 in the presence of the platinum catalyst produced 6a and 6b in the ratio of 1.3:1 in 49% combined yield, along with the starting compound 8 and its isomer 7 in the ratio of 5:1. These reactions indicate that compounds 6a and 6b must come from the intramolecular hydrosilation of 7 and 8.

Next, we investigated the reaction of 1 with mesitylacetylene. Thus, when a mixture of 1 and mesitylacetylene in the presence of the same catalyst was heated to reflux in benzene for 4 h, a mixture of the regioisomers was obtained in an almost quantitative yield (Scheme 8). The regioisomers were separated using column chromatography and assigned as [2-(diisopropylsilyl)thiophen-3-yl]diisopropyl(mesitylethynyl)silane (12) and [3-(diisopropylsilyl)thiophen-2-yl]diisopropyl-(mesitylethynyl)silane (13) by MS and $^1$H, $^{13}$C, and $^{29}$Si NMR spectroscopy.

2.1. Theoretical Calculations. We carried out density functional theory (DFT) calculations to investigate the energy and structural changes from 7 and 8 to 6a and 6b. Gaussian09 program package was employed together with the Becke-three-parameter-Lee–Yang–Parr hybrid functional. The Los Alamos effective core potentials were used for Si, S, and Pt atoms along with the corresponding valence basis sets. For the H and C atoms, the Dunning–Huzinaga full double-basis set was employed.
The calculated species are Pt complexes, that is, 10a, 10b, 11a, and 11b, shown in Scheme 7, and their transition states (TS’s) are labeled as TS(10−11a) and TS(10−11b). Furthermore, 10a and 10b mutually convert through TS(10−14a), 14a, TS(14a−14b), 14b, and TS(14−10b), as shown in Scheme 9, and these structures were also investigated. In the calculations, TS is searched first. Then, the intrinsic reaction coordinate (IRC) analysis is carried out at each TS for both directions, that is, the reactant and product sides. Because the IRC analysis for the whole reaction path is very time consuming, it is limited to the...
neighborhood of TS’s, and normal optimization runs are followed at the end points of IRC analysis. Finally, we confirmed that the reaction path is seamlessly connected from the reactant, via TS, to the product.

Figure 2. Optimized structures for TS(10−14a) and 14a (left), TS(10−14b) and 14b (right), and TS(14a−14b) (bottom center). Total energy of 10a is taken as the zero of relative energy.
The optimized structures for 10a, TS(10–11a), and 11a are shown in the left column and 10b, TS(10–11b), and 11b are shown in the right column of Figure 1. Figure 2 shows the optimized structures for TS(10–14a) and 14a in the left column and TS(10–14b) and 14b in the right column. TS(14a–14b) is a junction between the a- and b-series and shown at the center. For all of the intermediate species, the optimized structures are well-described by the line drawing structures shown in Schemes 7 and 9. A noticeable point is that a weak interaction between the C=C group and the Pt atom is suggested in 10a and 10b.

The energy changes for all reaction paths are shown in Figure 3. The total energy of 10a is taken as zero. Among the TS's, TS(10–11a) and TS(10–11b) are the highest, and the conversions from 10a to 11a and 10b to 11b are the rate-determining step. This means that compounds in the a- and b-series can mix with each other because the energies for TS(10a–14a), TS(14a–14b), and TS(10–14b) are lower than those for TS(10–11a) and TS(10–11b). The conversion from 14a to 14b proceeds by an internal rotation of the Si–C–Pt group. The energy difference between the corresponding compounds in the a- and b-series is relatively small (at maximum, 16.3 kJ mol⁻¹ between 10a and 10b). Thus, the energetics for the a- and b-series reactions resemble each other, and the two sets of reactions occur in parallel.

3. CONCLUSIONS

We describe here the preparation and platinum-catalyzed reactions of 2,3-bis(diisopropylsilyl)thiophene. The reactions of 2,3-bis(diisopropylsilyl)thiophene 1 with diphenylacetylene in the presence of a catalytic amount of Pt(PPh₃)₄ proceeded to give cyclic products such as 2. A similar treatment of 1 with monosubstituted alkenes bearing less bulky substituents such as phenylacetylene afforded regioisomers of the cyclic products, whereas with alkenes bearing bulky substituents, 1 gives products arising from sp-hybridized C–H bond activation of the alkenes. In the intramolecular reactions of 10a and 10b, the theoretical calculations indicate that the conversion from 14a to 14b or 14b to 14a proceeds with the internal rotation of the Si–C–Pt group.

4. EXPERIMENTAL SECTION

4.1. General Procedure. All reactions of 2,3-bis(diisopropylsilyl)thiophene 1 were carried out under an atmosphere of dry nitrogen. Yields of the products were determined by analytical gas–liquid chromatography (GLC) with the use of tridecane or pentadecane as an internal standard on the basis of the starting compound used. NMR spectra were recorded on a JEOL model JMS-700 instrument. Column chromatography was performed using Wakogel C-300 (WAKO).

4.2. Preparation of 2,3-Bis(diisopropylsilyl)thiophene 1. In a 200 mL three-necked flask fitted with a stirrer, a reflux condenser, and a dropping funnel were placed 1.75 g (72.0 mmol) of magnesium, 11.2 g (74.3 mmol) of chlorodisopropylsilane, and 0.411 g (4.59 mol) of copper(I) cyanide in 10 mL of dry THF. To this mixture was added dropwise a solution of 5.94 g (20.6 mmol) of 2-bromo-3-iodothiophene in 10 mL of dry THF. The mixture was heated to reflux for 4 h. The resulting magnesium salts were removed by filtration and washed with ether. The solvent was evaporated, and the residue was distilled under reduced pressure to give 2.35 g (37% yield) of 2,3-bis(diisopropylsilyl)thiophene 1: bp 77–80 °C/2 torr; anal. calcd for C₂₆H₂₅Si₂S: C, 61.46; H, 10.32. Found: C, 61.16; H, 10.01. MS m/z 312 (M⁺); ¹H NMR δ(CDCl₃) 0.96 (d, 6H, MeCH, J = 7.6 Hz), 1.01 (d, 6H, MeCH, J = 7.6 Hz), 1.06 (d, 6H, MeCH, J = 7.6 Hz), 1.07 (d, 6H, MeCH, J = 7.6 Hz), 1.15–1.28 (m, 4H, CHMe), 4.24 (t, 1H, HSi, J = 3.6 Hz), 4.36 (t, 1H, HSi, J = 3.6 Hz), 7.29 (d, 1H, thienyl ring proton, J = 4.4 Hz), 7.67 (d, 1H, thienyl ring proton, J = 4.4 Hz); ¹³C NMR δ(CDCl₃) 12.25, 11.72 (CHMe); 18.79 (2C), 18.84, 18.93 (MeCH); 130.05, 142.04, 143.82 (thienyl ring carbons); ²⁹Si NMR δ(CDCl₃) −3.52, −3.09.

4.2.1. Platinum-Catalyzed Reaction of 1 with Diphenylacetylene. In a 30 mL two-necked flask fitted with a reflux condenser were placed 0.310 g (0.991 mmol) of 1, 0.355 g (1.99 mmol) of diphenylacetylene, and 0.411 g (4.59 mol) of Pt(PPh₃)₄ in 15 mL of dry benzene. The mixture was heated to reflux for 96 h. The mixture was analyzed by GLC as being 2 (80% yield), along with starting compound 1 (20% yield). The solvent benzene was evaporated, and the residue was chromatographed on a silica gel column using hexane as the eluent: HR-MS: calc'd for C₇₀H₆₈Si₄S: 848.2389; found: 848.2378. MS m/z 488 (M⁺); ¹H NMR δ(CDCl₃) 0.80 (d, 6H, MeCH, J = 7.6 Hz), 0.81 (d, 6H, MeCH, J = 7.6 Hz), 1.04 (d, 6H, MeCH, J = 7.6 Hz), 1.09 (d, 6H, MeCH, J = 7.6 Hz), 1.33 (sep, 2H, CHMe, J = 7.6 Hz), 1.34 (sep, 2H, CHMe, J = 7.6 Hz), 6.85–6.90 (m, 4H, phenyl ring protons), 6.91–6.96 (m, 2H, phenyl ring protons), 7.04 (dt, 4H, phenyl ring protons, J = 7.8, 0.9 Hz), 7.39 (d, 1H, thienyl ring proton, J = 4.4 Hz), 7.76 (d, 1H, thienyl ring proton, J = 4.4 Hz); ¹³C NMR δ(CDCl₃) 11.98, 12.44 (CHMe), 17.62, 17.85, 17.87, 18.04 (MeCH), 125.14, 125.22, 127.28, 127.31, 128.47, 128.56, 129.87, 132.75, 141.44, 143.99, 144.05, 144.16, 156.36, 157.62 (phenyl, thienyl ring and olefinic carbons); ²⁹Si NMR δ(CDCl₃) −10.6, −9.2.
4.2.2. **Platinum-Catalyzed Reaction of 1 with Phenylacetylene.** In a 30 mL two-necked flask fitted with a reflux condenser were placed 0.312 g (0.988 mmol) of 1, 0.205 g (2.01 mmol) of phenylacetylene, and 0.0649 g (0.0522 mmol) of \( \text{Pt}(\text{PPh}_3)_3 \) in 15 mL of dry benzene. The mixture was heated to reflux for 73 h. The mixture was analyzed by GLC as being 5a and 5b (60% combined yield), together with starting compound 1 (40% yield). The ratio of 5a and 5b was determined to be 3:1 by \(^1\)H NMR spectroscopic analysis. For 5a and 5b: HR-MS: calcd for \( \text{C}_{21}\text{H}_{40}\text{Si}_3\text{S} \) 408.2159, found: 408.2141. MS hexane as the eluent. For 5a and 5b (60% combined yield) and 5a (97% combined yield) and 7 (97% combined yield). The ratio of 7 and 8 in the reaction mixture was determined to be 3:1 by \(^1\)H NMR spectroscopic analysis. All spectral data for 6a, 6b, 7, and 8 were identical to those of the authentic samples.

4.2.3. **Platinum-Catalyzed Reaction of 1 with Trimethylsilylacetylene.** In a 30 mL two-necked flask fitted with a reflux condenser were placed 0.309 g (0.988 mmol) of 1, 0.215 g (2.19 mmol) of trimethylsilylacetylene, and 0.0640 g (0.0514 mmol) of \( \text{Pt}(\text{PPh}_3)_3 \) in 15 mL of dry benzene. The mixture was heated to reflux for 20 h. The mixture was analyzed by GLC as being 6a and 6b (22% combined yield) and 7 and 8 (71% combined yield). The ratio of 6a and 6b in the reaction mixture was determined to be 1:6 by \(^1\)H NMR spectroscopic analysis. The ratio of 7 and 8 in the reaction mixture was determined to be 1:1 by \(^1\)H NMR spectroscopic analysis. The solvent benzene was evaporated, and the residue was chromatographed on a silica gel column using hexane as the eluent. For 6a and 6b: HR-MS: calcd for \( \text{C}_{23}\text{H}_{36}\text{Si}_2\text{S} \) 412.2076, found: 412.2059. MS m/z 365 (M^+ - \text{SiH}) \( \equiv 4.4 \) Hz (thienyl ring carbons); 29Si NMR \( \delta(\text{DCDCl}) = -10.4(\text{Sa}), -8.84(\text{Sb}), -8.76(\text{Sb}), -7.51(\text{Sa}) \).
2H, Mes-H), 7.32 (d, 1H, thienyl ring proton, J = 4.4 Hz), 7.66 (d, 1H, thienyl ring proton, J = 4.4 Hz); 13C NMR δ(CDCl₃) 11.98, 14.26, (HCMe), 18.53, 18.90, 18.98, 19.11 (MeCH), 21.31, 21.36 (Mes-Me), 96.45, 106.24 (Cmes), 120.17, 127.53, 130.59, 134.78, 138.05, 140.07, 142.05, 143.63 (mesityl and thienyl ring carbons); 29Si NMR δ(CDCl₃) −12.59, 13.97 (CHSi), 18.51, 18.72, 18.76, 18.90 (CHmes), 21.30, 31.35 (Mes-Me), 97.68, 105.65 (Cmes), 120.32, 127.55, 129.54, 137.01, 137.93, 140.82, 140.97, 144.60 (thienyl and mesityl ring carbons); 31P NMR δ(CDCl₃) −2.86, −3.32.

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01628.

**REFERENCES**

We thank grants-in-aid or Scientific Research program (No. 26410061) from the Ministry of Education, Science, Sports, and Culture of Japan, and Wesco Science Promotion Foundation.

**ACKNOWLEDGMENTS**

We gratefully acknowledge the financial support from the Ministry of Education, Science, Sports, and Culture of Japan and Wesco Science Promotion Foundation.

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**Notes**

The authors declare no competing financial interest.

**REFERENCES**

1. Corey, J. Y. Reactions of hydrosilanes with transition metal complexes. *Chem. Rev.* 2016, 116, 11291–11435.
2. Tanaka, M.; Uchimaru, Y.; Lautenschlager, H.-J. Platinum-complex-catalyzed dehydrogenative double silylation of acetylenes, dienes, and olefins with bis(hydrosilanes). *Organometallics* 1991, 10, 16–18.
3. Uchimaru, Y.; Lautenschlager, H.-J.; Wynd, A. J.; Tanaka, M.; Goto, M. Platinum-catalyzed dehydrogenative double silylation of carbonyl compounds with o-bis(dimethylsilyl)benzene. *Organometallics* 1992, 11, 2639–2643.
4. Tanaka, M.; Uchimaru, Y.; Lautenschlager, H.-J. Platinum complex-catalyzed dehydrogenative double silylation of olefins and dienes with o-bis(dimethylsilyl)benzene. *J. Organomet. Chem.* 1992, 428, 1–12.
5. Tanaka, M.; Uchimaru, Y. Dehydrogenative double silylation of acetylenes with bis(hydrosilane) compounds. *Bull. Soc. Chim. Fr.* 1992, 129, 667–675.
6. Uchimaru, Y.; El Sayed, A. M. M.; Tanaka, M. Selective arylation of a silicon-hydrogen bond in o-bis(dimethylsilyl)benzene via carbon-hydrogen bond activation of arenes. *Organometallics* 1993, 12, 2065–2069.
7. Tsutsui, H.; Sunada, Y.; Nagashima, H. Novel disilaplatinacyclopentenes bearing dialkylsulfide ligands: Preparation, characterization, and mechanistic consideration of hydrosilane reduction of carboxamides by bifunctional organohydrosilanes. *Organometallics* 2011, 30, 68–76.
8. Eaborn, C.; Metham, T. N.; Piccock, A. Some platinum complexes containing chelating bis(silyl) ligands. *J. Organomet. Chem.* 1973, 63, 107–117.
9. Ishikawa, M.; Naka, A.; Ohshita, J. Platinum-catalyzed reactions of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene. *Organometallics* 1993, 12, 4987–4992.
10. Okada, A.; Shinohara, K.; Naka, M.; Ishikawa, M. Synthesis and platinum- and palladium-Catalyzed reactions of benzodisilacyclobutenes and benzobis(disilacyclobutene)s: new development of transition-metal-catalyzed reactions, stereochemistry and theoretical studies. *Dalton Trans.* 2016, 45, 3210–3235.
11. Ishikawa, M.; Tanaka, M. Thermolysis, photolysis, and transition-metal-catalyzed reactions of 3,4-benzo-1,1,2,2-tetraethyl-1,2-disilacyclobut-3-ene. *Synlett* 1995, 1995, 794–802.
12. Ishikawa, M.; Okada, T.; Kunai, A.; Ishikawa, M. Platinum-catalyzed reactions of 3,4-benzo-1,1,2,2-tetra(isopropyl)-1,2-disilacyclobut-3-ene with mono- and di-substituted alkynes. *J. Organomet. Chem.* 1997, 547, 149–156.
13. Ishikawa, M.; Naka, A.; Yoshizawa, K. The chemistry of benzodisilacyclobutenes and benzobis(disilacyclobutene)s: new development of transition-metal-catalyzed reactions, stereochemistry and theoretical studies. *Dalton Trans.* 2016, 45, 3210–3235.