# Rhodium-Catalyzed Stitching Reaction: Convergent Synthesis of Quinoidal Fused Oligosiloles

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**S** *Supporting Information*

**ABSTRACT:** Quinoidal fused oligosiloles, a new family of silicon-bridged π-conjugated compounds, have been synthesized for the first time based on a new synthetic strategy, a stitching reaction. Multiple carbon−carbon bonds can be formed consecutively between two oligo-(silylene-ethynylene)s under rhodium catalysis in a stitching manner, and up to five siloles have been fused in a quinoidal form. Physical properties of these oligosiloles have also been investigated to find a unique trend in their LUMO levels, which become higher with longer π-conjugation.

Silicon-bridged π-conjugated organic molecules such as dibenzosiloles and related compounds constitute a useful class of compounds in the field of materials science due to their unique optoelectronic properties.[1] The most typical synthetic method of this family of compounds is based on the generation of a dimetalated π-conjugated precursor, followed by the reaction with a dichlorosilane to introduce the bridging silicon atom as illustrated in Scheme 1a.[2] Although this method is reliable, the accessible skeletons are inherently limited, which also limits potential future applications of silicon-bridged π-conjugated materials due to the narrow structural diversity. For example, even structurally simple compounds such as fused oligosiloles and their analogs would be difficult to access with this synthetic approach.[3] To partially overcome this problem, an efficient synthesis of fused bis(silole)s, bis-silicon-bridged stilbene homologues, was devised by Yamaguchi and Tamao in 2003, and they disclosed high luminescence properties of these compounds.[4] Surprisingly, however, three or more siloles have never been fused consecutively to date despite the promising electronic properties predicted by computation,[5] and no single report on the synthesis of quinoidal fused oligosiloles has ever been made as far as we are aware.[6] In this context, herein we describe the development of a rhodium-catalyzed stitching reaction between two different oligo(silylene-ethynylene)s for the first synthesis of quinoidal fused oligosiloles and investigation of their physical properties.[7]

To achieve an efficient synthesis of quinoidal fused oligosilole **C**, we devised a reaction between two oligo(silylene-ethynylene)s **A** and **B**, one of which (**A**) contains an arylmetal moiety on one end and a haloarene moiety on the other end, under rhodium catalysis to stitch them together through a pathway illustrated in Scheme 1b. Thus, initial transmetalation of the arylmetal moiety of **A** to rhodium(I) generates arylrhodium

**Scheme 1.** (a) Conventional Synthetic Method of Silicon-Bridged π-Conjugated Compounds and (b) New Quinoidal Fused Oligosiloles C and Their Synthetic Approach through the Rhodium-Catalyzed "Stitching Reaction" between Oligo(silylene-ethynylene)s A and B
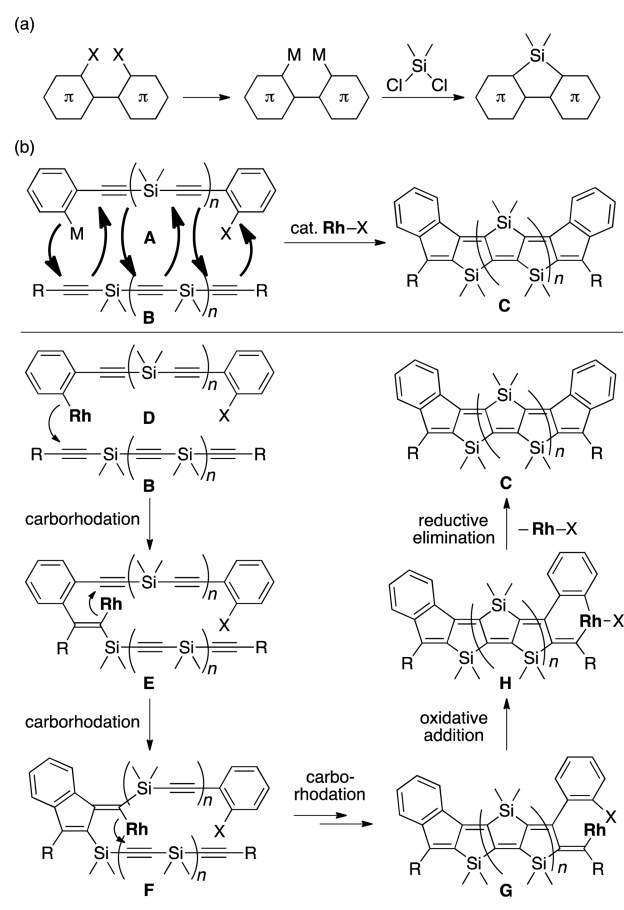


**D**, which undergoes intermolecular carborhodation to the alkyne at the terminal position of **B** to give alkenylrhodium **E**.[8] This then undergoes five-membered ring-forming carborhodation to the nearest alkyne (originally on **A**) to give a new alkenylrhodium species **F**.[9] Repeating the five-membered ring-forming carborhodation in a stitching manner back and forth eventually arrives at alkenylrhodium **G**, bearing a haloarene moiety at a nearby

position. Oxidative addition of aryl–X bond to alkenylrhodium in **G** produces six-membered alkenyl(aryl)rhodium **H**, reductive elimination of which leads to quinoidal fused oligosilole **C** along with regeneration of rhodium(I).[10]

To realize the above-mentioned synthetic strategy for quinoidal fused oligosiloles, we chose boronic acid ester as M and bromide as X and initiated our study using a combination of the simplest model substrates, 2-(2-bromophenylethynyl)-phenylboronic acid ester **1a** and diphenyldi(1-propynyl)silane **2a**, toward the synthesis of a new class of silicon-bridged $\pi$-conjugated pentacyclic compound, diindenosilole **3a**, under rhodium catalysis through the formation of four carbon–carbon bonds consecutively. After some investigation, we found that the expected reaction proceeded to give desired product **3a** in a moderate yield of 44% when the reaction of **1a** (1.3 equiv) with **2a** (1.0 equiv) was conducted in the presence of [Rh(OH)(cod)]$_2$ (8 mol % Rh) as a catalyst and Cs$_2$CO$_3$ (1.5 equiv) as a base in dioxane/H$_2$O (50/1) at 80 °C for 20 h (Table 1, entry 1).

**Table 1. Rhodium-Catalyzed Stitching Reaction of 1a with 2a: Reaction Conditions**
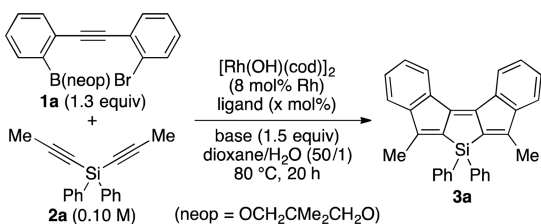


| entry | ligand ($x$ mol %) | base | yield (%)[a] |
|-------|--------------------|------|--------------|
| 1 | none | Cs$_2$CO$_3$ | 44 |
| 2 | binap (10) | Cs$_2$CO$_3$ | 12 |
| 3 | cod (10) | Cs$_2$CO$_3$ | 82 |
| 4 | **cod (42)** | **Cs$_2$CO$_3$** | 87 (79)[b] |
| 5 | cod (42) | Na$_2$CO$_3$ | 79 |
| 6 | cod (42) | Et$_3$N | 62 |
| 7 | cod (42) | dabco | 56 |

[a]Determined by $^1$H NMR against internal standard (MeNO$_2$). [b]Isolated yield.

Although the use of binap (10 mol %) as an external ligand retarded the reaction progress (12% yield; entry 2), addition of cod (10 mol %) was beneficial to improve the yield significantly (82% yield; entry 3), and somewhat higher yield was achieved by employing 42 mol % of cod (87% yield (79% isolated yield); entry 4). Other bases such as Na$_2$CO$_3$, Et$_3$N, and dabco (1,4-diazabicyclo[2.2.2]octane) could also be used, but the yield of **3a** became lower than the reaction with Cs$_2$CO$_3$ (56–79% yield; entries 5–7).

Under the conditions described in Table 1, entry 4, several diindenosiloles **3** can be synthesized in moderate to high yields (Table 2). For example, substituents on the silicon atom of **2** can be either diaryl (entry 1), aryl/alkyl (entry 2), or dialkyl (entry 3), although diaryl groups are better suited for higher reactivity. With regard to alkyne substituents of **2**, not only methyl but also aryl groups are tolerated as demonstrated in entries 4–6, but the substrate with terminal alkynes results in a complex mixture. In addition to parent compound **1a**, dichlorinated variant **1b** can also be employed, which allows for further functionalization at this position (entry 7). It is worth mentioning that 4-bromophenyl group is compatible as shown in entry 6, indicating that the reaction does not commence with oxidative addition of a

**Table 2. Rhodium-Catalyzed Stitching Reaction of 1 with 2**
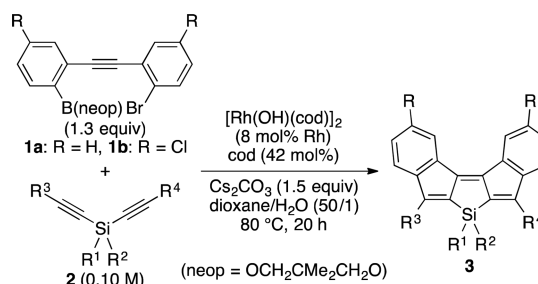


| entry | 1 | 2 | product | yield (%)[a] |
|-------|-----|------------------------------------------------|---------|--------------|
| 1 | 1a | 2a (R$^1$ = R$^2$ = Ph, R$^3$ = R$^4$ = Me) | 3a | 79 |
| 2 | 1a | 2b (R$^1$ = Ph, R$^2$ = R$^3$ = R$^4$ = Me) | 3b | 70 |
| 3 | 1a | 2c (R$^1$ = R$^2$ = iPr, R$^3$ = R$^4$ = Me) | 3c | 58 |
| 4 | 1a | 2d (R$^1$ = R$^2$ = R$^3$ = R$^4$ = Ph) | 3d | 61 |
| 5 | 1a | 2e (R$^1$ = R$^2$ = Ph, R$^3$ = Me, R$^4$ = 4-MeOC$_6$H$_4$) | 3e | 80 |
| 6 | 1a | 2f (R$^1$ = R$^2$ = Ph, R$^3$ = Me, R$^4$ = 4-BrC$_6$H$_4$) | 3f | 73 |
| 7[b] | 1b | 2a | 3g | 64 |

[a]Isolated yield. [b]1.0 equiv of **1b**, 2.0 equiv of **2a**, 1.0 equiv of Cs$_2$CO$_3$ were used with 30 mol % Rh in anhydrous dioxane.

C–Br bond to rhodium, supporting the proposed reaction pathway via initial transmetalation of aryl group from M (boron) to rhodium as proposed in Scheme 1b.[10]

The present stitching reaction is also applicable to the synthesis of longer quinoidal fused oligosilole **6** containing three silicon atoms by the reaction of **4** and **5** as shown in eq 1. Six
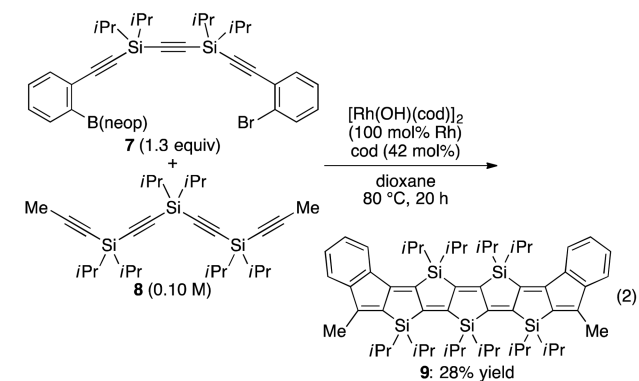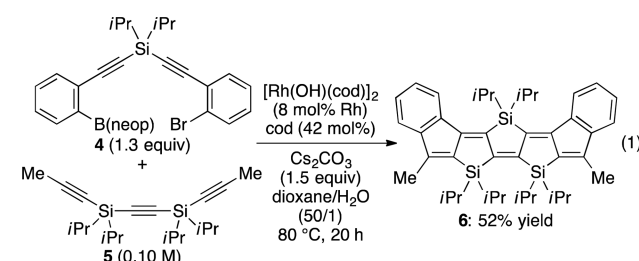


carbon–carbon bonds were successfully formed consecutively between these substrates in the presence of a catalytic amount of rhodium to give heptacyclic compound **6** in 52% isolated yield. Furthermore, synthesis of nonacyclic oligosilole **9** having five silicon atoms was attempted by employing substrates **7** and **8** (eq 2). Although the use of a catalytic amount of rhodium resulted in only 8% yield, 28% isolated yield of **9** was obtained through the formation of eight carbon–carbon bonds in the presence of a stoichiometric amount of rhodium under anhydrous conditions.
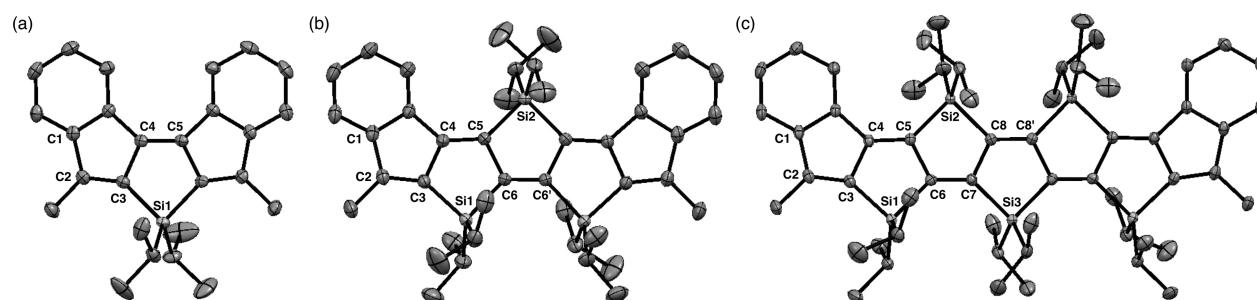
**Figure 1.** X-ray crystal structure of compounds (a) **3c**, (b) **6**, and (c) **9**. Hydrogen atoms are omitted for clarity.

We have also investigated the structural and physical properties of these quinoidal fused oligosiloles, which could also be considered as model compounds for *cis–transoid* oligoacetylenes fixed in a planar form.[11,12] As shown in Figure 1, X-ray crystal structures of compounds **3c**, **6**, and **9** were obtained, and selected bond distances are compiled in Table 3.[13]

**Table 3. Selected Bond Distances (Å) for Compounds 3c, 6, and 9**

|  | 3c | 6 | 9 |
|---|---|---|---|
| C1−C2 | 1.476(2) | 1.473(2) | 1.473(3) |
| C2−C3 | 1.356(2) | 1.361(2) | 1.358(3) |
| C3−C4 | 1.487(2) | 1.482(2) | 1.483(3) |
| C4−C5 | 1.368(2) | 1.373(2) | 1.365(3) |
| C5−C6 | — | 1.478(2) | 1.488(3) |
| C6−C7(C6′) | — | 1.375(2) | 1.375(3) |
| C7−C8 | — | — | 1.482(3) |
| C8−C8′ | — | — | 1.375(4) |

For all of these three compounds, it was confirmed that vertical carbon−carbon bonds (C1−C2, C3−C4, C5−C6, C7−C8) are single bonds (1.473−1.488 Å) and horizontal carbon−carbon bonds (C2−C3, C4−C5, C6−C7(C6′), C8−C8′) are double bonds (1.356−1.375 Å) as predicted by the proposed reaction mechanism. In other words, stitched portions of the molecules are conjugated with alternating carbon−carbon single and double bonds with high planarity by the bridging silicon atoms.

The UV−vis spectra of these three compounds are shown in Figure 2, and molar absorption coefficient $\varepsilon$ at >400 nm becomes larger in the order of the number of silole unit, and the maximum wavelength of absorbance also becomes longer in this order.[14] In
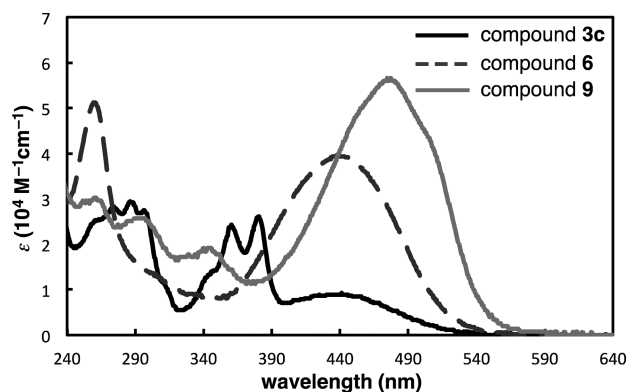


**Figure 2.** UV−vis spectra of compounds **3c** (black line; at $3.8 \times 10^{-6}$ M), **6** (dark-gray broken line; at $4.2 \times 10^{-6}$ M), and **9** (gray line; at $1.5 \times 10^{-6}$ M) in $CH_2Cl_2$ at 25 °C.

terms of photoluminescence properties, none of these compounds turned out to be emissive at all.

Comparison of electrochemical data of compounds **3c**, **6**, and **9** using cyclic voltammetry is summarized in Table 4. The

**Table 4. Electrochemical Data of Compounds 3c, 6, and 9**

| compd | $E_{ox}^{1/2}$ (V)$^{a,b}$ | $E_{red}^{1/2}$ (V)$^{a,c}$ | HOMO (eV)$^{d,e}$ | LUMO (eV)$^{e,f}$ |
|---|---|---|---|---|
| 3c | 0.90 | −1.90 | −5.70 [−5.37] | −2.90 [−2.22] |
| 6 | 0.55 | −2.01 | −5.35 [−4.99] | −2.79 [−2.15] |
| 9 | 0.34 | −2.07 | −5.14 [−4.79] | −2.73 [−2.11] |

$^a$Values are against Fc/Fc$^+$. $^b$In $CH_2Cl_2$. $^c$In THF. $^d$HOMO = −(4.8 + $E_{ox}^{1/2}$). $^e$Values in brackets are calculated at the B3LYP/6-31G(d) level of theory.[16,17] $^f$LUMO = −(4.8 + $E_{red}^{1/2}$).

oxidation potential becomes lower in the order of **3a**, **6**, and **9** as expected due to the higher HOMO level for the longer π-conjugation system. Surprisingly, however, the reduction potential also becomes lower in this order, indicating that the LUMO level becomes higher for the longer π-conjugation, which is quite an unusual phenomenon, and we are unaware of such examples reported in the literature. This trend was reproduced by the DFT calculation as well (values in brackets in Table 4; see the Supporting Information (SI) for the calculated frontier orbital profiles).[15] Although currently we do not fully understand the origin of this trend in LUMO levels, it might have to do with the presence of carbon−silicon bonds of the diisopropylsilyl groups at the bridges, because the same calculated trend was observed for dimethylsilyl variants of these compounds but was not observed for dihydrosilyl variants which lack the carbon−silicon bonds (see the SI for details).

In summary, we have synthesized quinoidal fused oligosiloles for the first time based on a new synthetic strategy, a stitching reaction. Multiple carbon−carbon bonds can be formed consecutively between two oligo(silylene-ethynylene)s under rhodium catalysis in a stitching manner and up to five siloles have been fused in a quinoidal form. We have also investigated the physical properties of these oligosiloles and found a unique trend in their LUMO levels, which become higher with longer π-conjugation. Future studies will be directed toward improvement and expansion of this synthetic strategy as well as further investigation and understanding of the properties of the newly synthesized π-conjugated compounds.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

procedures and compound characterization data (PDF) and (CIF). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b00082.

Experimental details and data; complete ref 15 (PDF)

X-ray data (CIF)
X-ray data (CIF)
X-ray data (CIF)

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### Notes
The authors declare no competing financial interest.

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