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Enantioselective Synthesis, Crystal Structure, and Photophysical Properties of a 1,1′-Bitriphenylene-Based Sila[7]helicene

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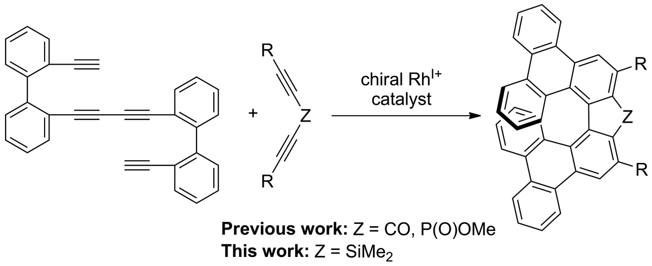
A 1,1′-bitriphenylene-based sila[7]helicene was synthesized with a high *ee* value by enantioselective double [2+2+2] cycloaddition of a biaryl-linked tetrayne with a silicon-linked bis(propargylic alcohol) as a key step. This sila[7]helicene exhibited a high tolerance toward racemization, which could be explained by the X-ray crystal structure analysis. With respect to the photophysical properties, this sila[7]helicene exhibited a relatively high fluorescence quantum yield and circularly polarized luminescence activity.

Introduction

Silafluorene derivatives have attracted much attention in materials chemistry because of their use for organic electroluminescent compounds.[1] There have been several reports on the transition-metal-catalyzed synthesis of silafluorenes.[2–4] For example, several research groups have reported the intra- and intermolecular cross-coupling reactions to produce silafluorenes.[2] Murakami and co-workers reported a conceptually different strategy, the iridium-catalyzed [2+2+2] cycloaddition of silicon-linked diynes with monoynes, for the synthesis of silafluorenes.[3] On the other hand, our research group reported the enantioselective synthesis of 1,1′-bitriphenylene-based carbo- and phospha[7]-helicenes by the rhodium-catalyzed double [2+2+2] cycloaddition of a biaryl-linked tetrayne with carbonyl- or phosphorus-linked diynes (Scheme 1).[5–11] We anticipated that the rhodium-catalyzed double [2+2+2] cycloaddition of the biaryl-linked tetrayne with a silicon-linked diyne would afford an 1,1′-bitriphenylene-based sila[7]helicene (Scheme 1). Recently, Nozaki, Nakano, and co-workers reported the synthesis of an enantiopure 3,3′-biphenanthrene-based sila[7]helicene[12] by the platinum-catalyzed intramolecular double hydroarylation followed by resolution with chiral HPLC,[4] while the enantioselective synthesis of the sila[7]helicene has not been achieved. In this paper, we disclose the enantioselective synthesis, crystal structure, and photophysical properties of the 1,1′-bitriphenylene-based sila[7]helicene.



Scheme 1. Enantioselective synthesis of 1,1′-bitriphenylene-based [7]helicenes by rhodium-catalyzed [2+2+2] cycloadditions.

Results and Discussion

Our research group previously reported that a silyl-substituted propargylic alcohol is a highly reactive substrate in the rhodium-catalyzed [2+2+2] cycloaddition with a biaryl-linked diyne (Scheme 2).[13]

Thus, silicon-linked bis(propargylic alcohol) **2** was selected as a cycloaddition partner of the biaryl-linked tetrayne **3**. Diyne **2** was readily prepared in two steps through the silylation of protected propargylic alcohol **1** followed by deprotection (Scheme 3). Various cationic rhodium(I)/axially chiral biaryl bisphosphine complexes

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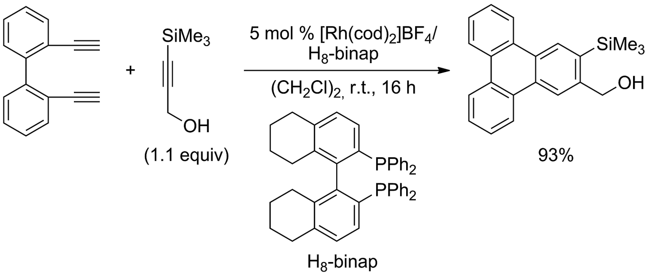


Scheme 2. Rhodium-catalyzed [2+2+2] cycloaddition of a biaryl-linked diyne with a silyl-substituted propargylic alcohol.

were screened for the reaction of tetrayne **3**[5] and diyne **2** at room temperature for 16 hours, which revealed that the use of a cationic rhodium(I)-BAr$^F{}_4$/(*S*)-segphos complex shows the highest catalytic activity, while not the desired sila[7]helicene but biaryl (+)-**4** was obtained with a high *ee* value (Scheme 3).

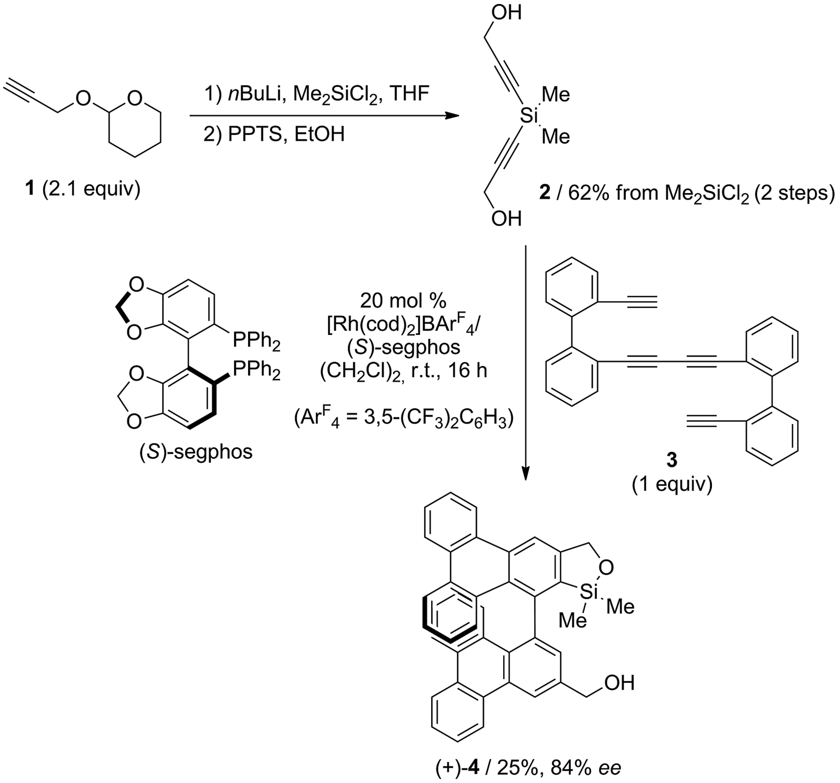
It is well known that transition-metal complexes react with aryl[2-(hydroxymethyl)phenyl]dimethylsilanes to form [1,2]oxasilole derivatives through transmetallation of in situ generated tetraorganosilicon intermediates.[14] In order to minimize the formation of the undesired biaryl (+)-**4**, the same reaction was conducted for 1 hour to give the desired 1,1′-bitriphenylene-based sila[7]helicene (+)-**5** in 18% yield with 85% *ee* (Scheme 4) along with (+)-**4** in ca. 10% yield. The use of the BF_4^- counteranion improves the enantioselectivity, but the product yield decreases (Scheme 4). The optical rotation value (1378°) of **5**, which is calculated as 100% *ee*, was close to that (1087°) of the 1,1-bitriphenylene-based carbo[7]helicene,[5] but significantly smaller than that (2980°) of the 3,3-biphenanthrene-based sila[7]helicene.[4]

For comparison, the rhodium-catalyzed double [2+2+2] cycloaddition of biaryl-linked diyne **6** with **2** was examined (Scheme 5). Interestingly, not the corresponding C–Si bond cleavage product **8** but the double [2+2+2] cycloaddition product **7** was obtained in good yields. Therefore, steric strain of sila[7]helicene **5** might facilitate C–Si bond cleavage.

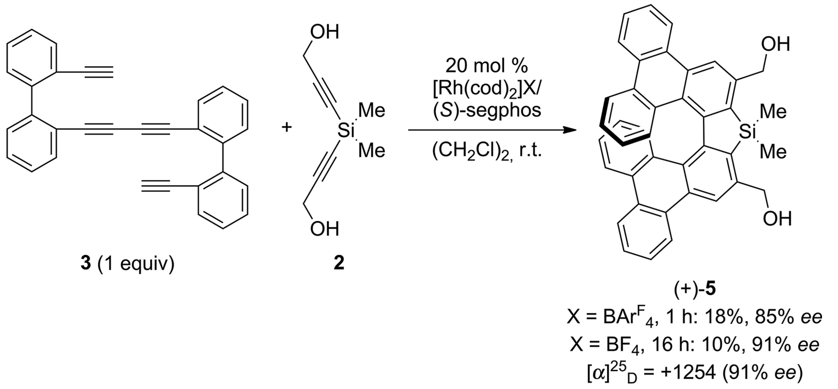
In order to confirm the formation of (+)-**4** from (+)-**5**, the reaction of (+)-**5** with the cationic rhodium(I)-BAr$^F{}_4$/(*S*)-segphos complex was examined. Indeed, (+)-**4** was generated in good yield without racemization at room temperature (Scheme 6).

We previously reported that the racemization of a carbonyl-linked 1,1′-bitriphenylene proceeds in $(CH_2Cl)_2$ solution at 80 °C.[5] The thermal stability of 1,1′-bitriphenylene-based sila[7]helicene **5** toward racemization was examined, which revealed that no racemization was observed in $(CH_2Cl)_2$ solution at 80 °C for 24 hours. This observation is consistent with the recent report by Nozaki, Nakano, and co-workers, which discloses the extraordinarily high tolerance of the phenanthrene-based sila[7]helicene toward racemization.[4]

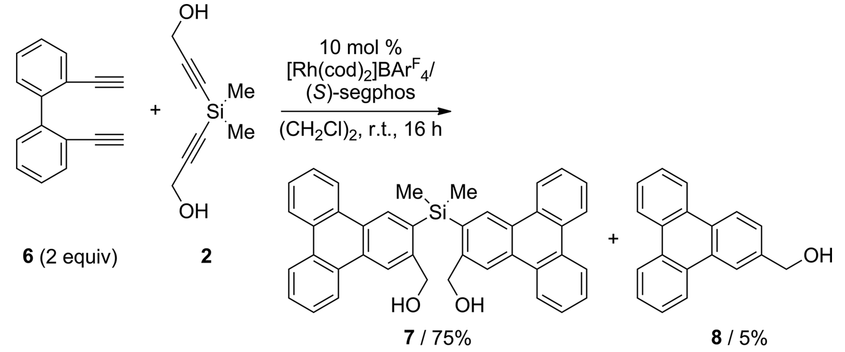
The X-ray crystal structure of enantiopure (+)-**5** is shown in Figure 1. The angle between two formal C=C double bonds of the annelated cyclopentadiene fragment is 48.1°, which is larger than that for the carbonyl-linked 1,1′-bitriphenylene (37.2°)[5] and close to that of the 3,3-biphenanthrene-based sila[7]helicene (53°).[4] This feature accounts



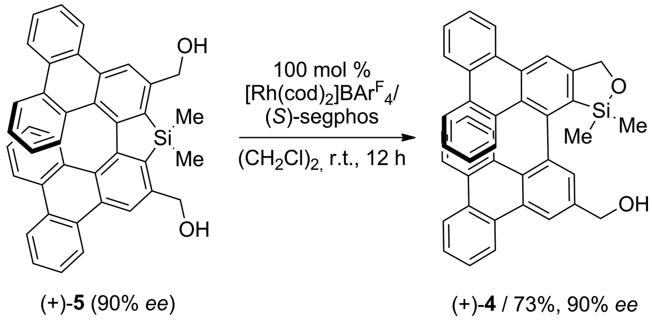
Scheme 3. Enantioselective synthesis of 1,1′-bitriphenylene-based biaryl **4** by rhodium-catalyzed [2+2+2] cycloaddition.



Scheme 4. Enantioselective synthesis of 1,1′-bitriphenylene-based sila[7]helicene (+)-**5** by rhodium-catalyzed [2+2+2] cycloaddition.

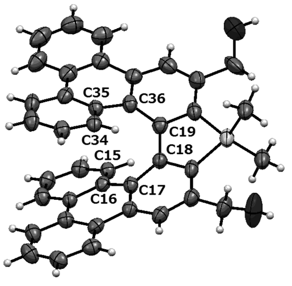


Scheme 5. Rhodium-catalyzed [2+2+2] cycloaddition of biaryl-linked diyne **6** with silicon-linked bis(propargylic alcohol) **2**.



Scheme 6. Rhodium-mediated formation of (+)-**4** from (+)-**5**.

for the higher tolerance of **5** towards racemization. On the other hand, the sum of the five dihedral angles [C15–C16–C17–C18, C16–C17–C18–C19, C17–C18–C19–C36, C18–C19–C36–C35, and C19–C36–C35–C34] is 119.1°, which is significantly larger than those for the carbonyl-linked 1,1′-bitriphenylene (90.7°)[5] and the 3,3-biphenanthrene-based sila[7]helicene (99.5°).[4] Therefore, triphenylene-based sila[7]helicene **5** is more distorted than the carbonyl-linked 1,1′-bitriphenylene and 3,3-biphenanthrene-based sila[7]helicene. The absolute configuration of (+)-**5** was determined to be *P* by the anomalous dispersion method.[15]



C–C bonds	Dihedral angle (°)
C15–C16–C17–C18	26.6
C16–C17–C18–C19	22.9
C17–C18–C19–C36	24.1
C18–C19–C36–C35	20.5
C19–C36–C35–C34	25.1

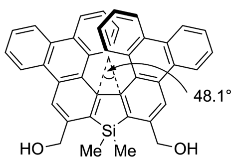


Figure 1. X-ray crystal structure analysis of enantiopure (+)-**5** with ellipsoids at 30% probability.

Absorption and emission spectra of **5** are shown in Figure 2. The absorption maximum of **5** is 269 nm, which is longer than that for the 3,3-biphenanthrene-based sila[7]helicene (ca. 260 nm)[4] presumably because of the more extended delocalization of the π-electrons over triphenylene than phenanthrene. Compound **5** exhibits a strong blue luminescence with λ_{max} = 482 nm, which is also longer than that for the 3,3-biphenanthrene-based sila[7]helicene (450 nm).[4] The fluorescence quantum yield of **5** in $CHCl_3$ is relatively high (15%) for helicene derivatives,[16] although those of the 3,3-biphenanthrene-based sila[7]helicene (23%)[4] and the 1,1-bitriphenylene-based carbo[7]helicene (32%)[5] are higher.

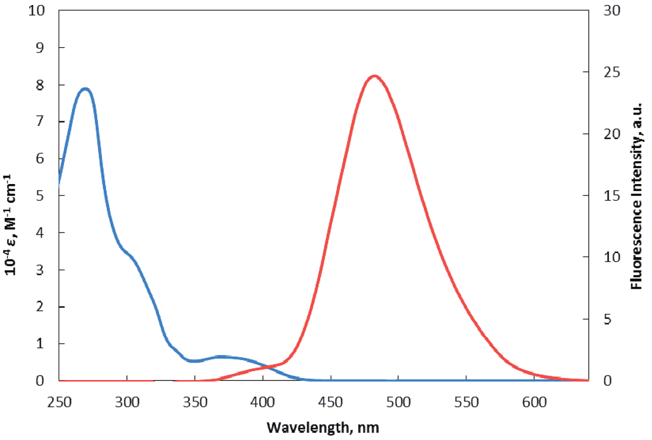


Figure 2. UV/Vis (blue line) and fluorescence (red line) spectra of **5** at 7.8×10^{-6} M in $CHCl_3$ at 25 °C.

The corresponding circular dichroism (CD) spectra of (+)-**5** (91% *ee*) and (–)-**5** (91% *ee*) in $CHCl_3$ is shown in Figure 3. It was found that these enantiomers show strong Cotton effects, which are mirror images. Thus, we attempted to measure circularly polarized luminescence (CPL) of (+)-**5**, as shown in Figure 3.[17] The value is g_{lum} = –0.016 at 482 nm, which is larger than that for the 3,3-biphenanthrene-based sila[7]helicene (g_{lum} = –0.0035 at 470 nm)[4] but smaller than that for the 1,1-bitriphenylene-based carbo[7]helicene (g_{lum} = –0.030 at 428 nm).[5,18]

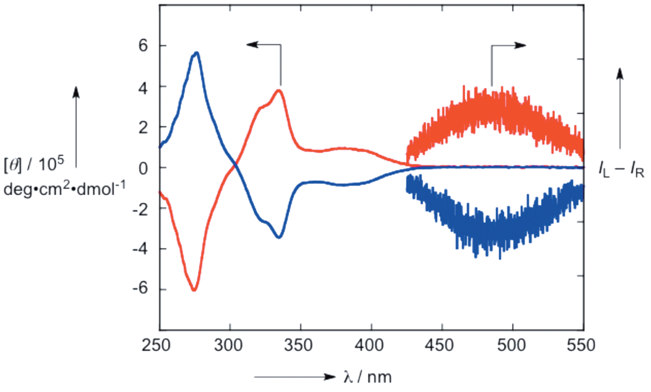


Figure 3. CD and CPL spectra of (+)-**5** (blue) and (–)-**5** (red) in $CHCl_3$ at 25 °C.

Conclusions

We have achieved the first enantioselective synthesis of a sila[7]helicene through the double [2+2+2] cycloaddition of a biaryl-linked tetrayne with a silicon-linked bis(propargylic alcohol) as a key step. The thus obtained 1,1′-bitriphenylene-based sila[7]helicene exhibits a high tolerance toward racemization, which could be explained by the X-ray crystal structure analysis. With respect to the photophysical properties, this sila[7]helicene exhibits a relatively high fluorescence quantum yield and circularly polarized luminescence activity.

Experimental Section

Typical Procedure: (Scheme 4). Under an atmosphere of argon, $[Rh(cod)_2]BAr^F{}_4$ (11.8 mg, 0.010 mmol) and (*S*)-segphos (6.1 mg, 0. 010 mmol) were dissolved in CH_2Cl_2, and the mixture was stirred at room temperature for 10 min. H_2 was introduced to the resulting solution in a Schlenk tube. After the mixture was stirred at room temperature for 1 h, it was concentrated to dryness. To a $(CH_2Cl)_2$ (1.0 mL) solution of the residue and **2** (8.4 mg, 0.0500 mmol) was added a $(CH_2Cl)_2$ (1.0 mL) solution of **3** (20.1 mg, 0.0500 mmol). The mixture was stirred at room temperature for 1 h. The resulting solution was concentrated and purified by a preparative TLC (hexane/ethyl acetate/CH_2Cl_2/CH_3OH = 100:60:60:3) to give (+)-**5** (5.1 mg, 0.0091 mmol, 18% yield, 85% *ee*).

Supporting Information (see footnote on the first page of this article): Experimental procedures, characterization data, and copies of the ^1H NMR and ^{13}C NMR spectra are presented.

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