Asymmetric Catalysis

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Rhodium-Catalyzed Asymmetric Synthesis of Silicon-Stereogenic Dibenzosiloles by Enantioselective [2+2+2] Cycloaddition**

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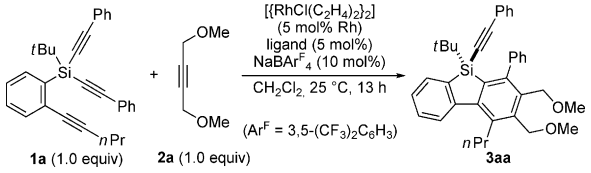
Abstract: *A rhodium-catalyzed asymmetric synthesis of silicon-stereogenic dibenzosiloles has been developed through a [2+2+2] cycloaddition of silicon-containing prochiral triynes with internal alkynes. High yields and enantioselectivities have been achieved by employing an axially chiral monophosphine ligand, and the present catalysis is also applicable to the asymmetric synthesis of a germanium-stereogenic dibenzogermole. Preliminary studies on the optical properties of these compounds are also described.*

Dibenzosiloles are widely found as a structural motif in various useful materials,[1] such as light-emitting diodes,[2] thin-film transistors,[3] solar cells,[4] and detectors for explosives,[5] because of their optoelectronic properties derived from the π-conjugated system. Several efficient synthetic methods for dibenzosiloles using transition-metal catalysts have therefore been actively developed in recent years.[6] In contrast, the preparation of enantioenriched chiral dibenzosiloles has been scarcely investigated[7] despite their potential future applications, for example as materials for circularly polarized luminescence (CPL).[8] This lack of available methods is presumably due to the planar nature of these compounds except at the silicon atom. However, the introduction of chirality at the silicon center, particularly in a catalytic asymmetric manner, is not a trivial task compared with the construction of carbon stereocenters.[9–11] In fact, only two intramolecular approaches have been reported for the transition-metal-catalyzed enantioselective synthesis of dibenzosiloles.[7a,b] In this context, herein we describe the first intermolecular asymmetric synthesis of silicon-stereogenic dibenzosiloles through a rhodium-catalyzed [2+2+2] cycloaddition of silicon-containing prochiral triynes with internal alkynes.[12,13]

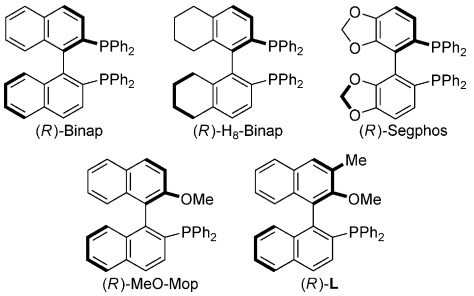
Initially, we employed prochiral triyne **1a**, which has two identical alkynyl groups on the silicon atom, as a model substrate for the rhodium-catalyzed [2+2+2] cycloaddition with 1,4-dimethoxy-2-butyne (**2a**) in the presence of (*R*)-Binap[14] as the ligand (Table 1, entry 1). The reaction proceeded at 25 °C to give the desired silicon-stereogenic dibenzosilole **3aa** in 74% yield, but the enantiomeric excess was only 18%.[15] The change of ligand to (*R*)-H_8-Binap[16] resulted in even lower enantioselectivity (9% *ee*; entry 2), whereas the use of (*R*)-Segphos[17] improved the enantioselectivity to 73% *ee* (Table 1, entry 3). Compared to these axially chiral bisphosphine ligands that are typically used for rhodium-catalyzed asymmetric [2+2+2] cycloaddition reactions,[12] (*R*)-MeO-mop,[18] an axially chiral monophosphine

Table 1: The effect of the ligand in the rhodium-catalyzed asymmetric [2+2+2] cycloaddition of **1a** with **2a**.



Entry	Ligand	Yield [%][a]	*ee*[b]
1	(*R*)-Binap	74	18
2	(*R*)-H_8-Binap	83	9
3	(*R*)-Segphos	95	73
4	(*R*)-MeO-Mop	63	80
5	(*R*)-**L**	98	88

[a] Yield of isolated product. [b] Determined by chiral HPLC on a Chiralpak IF-3 column with hexane/2-propanol = 500:1 v/v.



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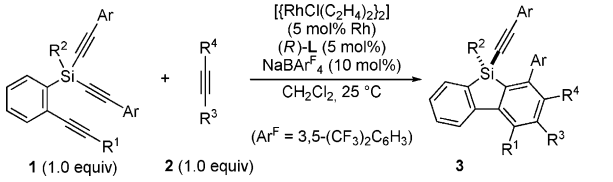
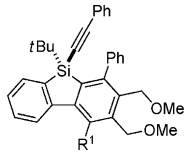
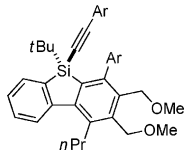
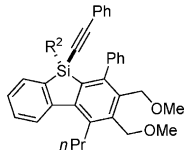
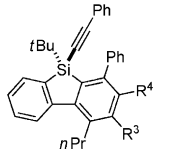
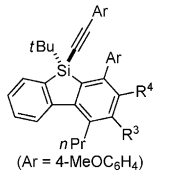
ligand, gave **3aa** with higher enantioselectivity (80% *ee*; entry 4). By introducing a methyl group at the 3′-position of (*R*)-MeO-mop ((*R*)-**L**),[19] the enantioselectivity of **3aa** was further improved to 88% *ee* in 98% yield (entry 5).[20]

Under the conditions described in Table 1 entry 5, various silicon-stereogenic dibenzosiloles can be synthesized with high yields and enantioselectivities as summarized in Table 2.

Table 2: Reaction scope of the rhodium-catalyzed asymmetric synthesis of dibenzosiloles **3**.

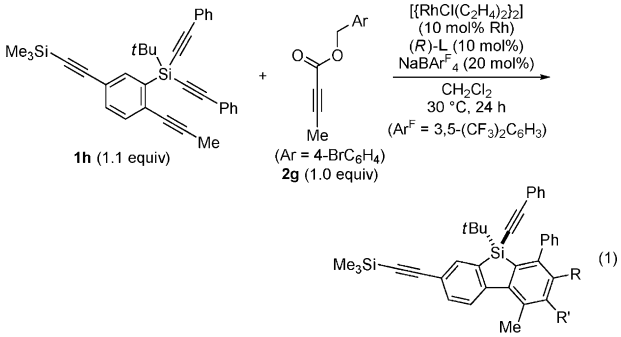


1 (1.0 equiv) **2** (1.0 equiv) **3**

Entry	Product		Yield [%][a]	*ee*[b]
1		**3aa** (R^1 = *n*Pr)	98	88
2		**3ba** (R^1 = Me)	96	91
3		**3ca** (R^1 = *i*Bu)	99	86
4		**3da** (Ar = 4-MeOC$_6$H$_4$)	91	89
5[c]		**3ea** (Ar = 4-ClC$_6$H$_4$)	72	85
6		**3fa** (R^2 = Cy)	95	85
7		**3ga** (R^2 = Ph)	91	59
8		**3ab** (R^3 = R^4 = CH_2OAc)	80	87
9[c]		**3ac** (R^3 = R^4 = 4-MeOC$_6$H$_4$)	92	88
10[d]		**3ad** (R^3 = Me, R^4 = $CH_2CMe(CO_2Me)_2$)	90	88
11[e]		**3ae** (R^3 = Me, R^4 = CO_2Me)	91[f]	88
12	 (Ar = 4-MeOC$_6$H$_4$)	**3df** (R^3 = Ph, R^4 = Me)	60	96
		3df′ (R^3 = Me, R^4 = Ph)	26	77

[a] Yield of isolated product. [b] Determined by chiral HPLC. [c] The reaction was conducted at 30 °C. [d] The regioselectivity was 99:1. [e] The regioselectivity was 93:7. [f] Yield of the isolated major regioisomer.

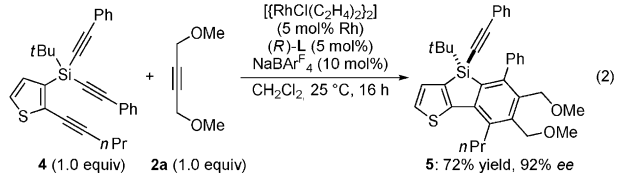
Thus, the 1-pentynyl group on **1a** (entry 1) can be replaced by other alkynyl groups, such as 1-propynyl (**1b**) and 4-methyl-1-pentynyl (**1c**) groups to give **3ba** and **3ca** in high yields with 86–91% *ee* (entries 2 and 3). Triynes having two identically substituted arylethynyl groups on the silicon atom (**1d** and **1e**) are also suitable substrates for the reaction with alkyne **2a** to give **3da** and **3ea** with similar enantiomeric excesses (85–89% *ee*; entries 4 and 5). Replacement of the *tert*-butyl group on the silicon atom of **1a** by the less bulky cyclohexyl group (**1f**) provides the corresponding dibenzosilole **3fa** with a relatively high *ee* value of 85% (entry 6), but the use of the phenyl-substituted variant (**1g**) results in the formation of dibenzosilole **3ga** with significantly lower enantioselectivity (59% *ee*; entry 7). With regard to the internal alkyne, symmetrical alkynes, such as **2a**, 1,4-diacetoxy-2-butyne (**2b**), and bis(4-methoxyphenyl)acetylene (**2c**), as well as unsymmetrical alkynes, such as dimethyl 2-(2-butynyl)-2-methylmalonate (**2d**), methyl tetrolate (**2e**), and 1-phenyl-1-propyne (**2f**), can be employed for the present catalysis to give **3aa**–**3ae** and **3df**/**3df′** in high yields (80–92% yield) with up to 96% *ee* (entries 8–12). It is worth mentioning that the reactions of **1a** with unsymmetrical **2d** and **2e** proceed with high regioselectivity to give **3ad** (99:1; entry 10) and **3ae** (93:7; entry 11) respectively,[21] although the reaction of **1d** with **2f** gives a 70:30 mixture of regioisomers (entry 12).[22] More functionalized dibenzosiloles **3hg**/**3hg′** bearing polymerizable sites through the (sila-)Sonogashira coupling can also be prepared enantioselectively (96% *ee* and 70% *ee*, respectively) as shown in Eq. (1) with moderate regioselectivity (76:24).[21,23] In addition to triynes **1**, thiophene-tethered triyne **4** can also react with alkyne **2a**, leading to the formation of benzosilolothiophene **5** in 72% yield with 92% *ee* [Eq. (2)].



1h (1.1 equiv) **2g** (1.0 equiv) (Ar = 4-BrC$_6$H$_4$)

3hg (R = Me, R′ = CO_2CH_2Ar): 72% yield, 96% *ee*
3hg′ (R = CO_2CH_2Ar, R′ = Me): 23% yield, 70% *ee*

(1)

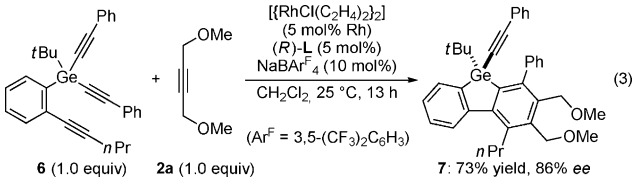


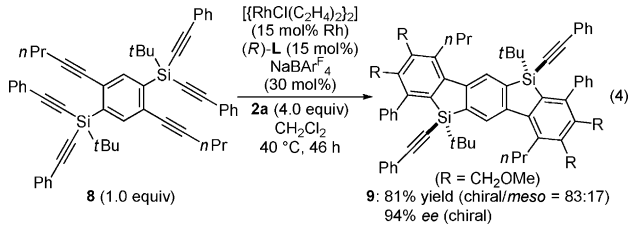
4 (1.0 equiv) **2a** (1.0 equiv) **5**: 72% yield, 92% *ee*

(2)

We have also found that the present asymmetric catalysis can be applied to the preparation of enantioenriched germanium-stereogenic dibenzogermoles by employing germanium-containing prochiral triynes as substrates. For example, the reaction of triyne **6** with alkyne **2a** under our standard conditions gives dibenzogermole **7** in 73% yield with 86% *ee* [Eq. (3)]. To our knowledge, this result demonstrates the first example of the enantioselective construction of a germanium stereogenic center under transition-metal catalysis.[24] Furthermore, the reaction of prochiral hexayne

8 gives doubly cyclized product **9** in an 81% combined yield of chiral and *meso* isomers (ratio = 83:17) with 94% *ee* for the chiral isomer through the twofold enantioselective [2+2+2] cycloaddition with alkyne **2a** [Eq. (4)].





Having established the catalytic asymmetric synthesis of various dibenzosiloles and related compounds, we examined the optical properties of these compounds, considering the lack of literature precedent for the study of the optical properties of silicon-stereogenic dibenzosiloles. In our preliminary investigation, we focused on comparing the properties of **3aa** and chiral **9**. As summarized in Table 3, the UV/Vis absorption and emission band maxima are red-shifted for doubly cyclized (*R*,*R*)-**9** compared to dibenzosilole (*R*)-**3aa**. Additionally, the absolute quantum yield of (*R*,*R*)-**9** was significantly higher than that of (*R*)-**3aa** (0.54 vs. 0.19).[25] We also examined the CD spectra of these compounds and found that (*R*)-**3aa** showed a relatively weak negative Cotton effect at $\lambda = 259$ nm ($\Delta\varepsilon = -3.0\,\text{M}^{-1}\text{cm}^{-1}$), whereas (*R*,*R*)-**9** showed stronger positive and negative Cotton effects at $\lambda = 282$ nm ($\Delta\varepsilon = +7.3\,\text{M}^{-1}\text{cm}^{-1}$) and $\lambda = 256$ nm ($\Delta\varepsilon = -10.8\,\text{M}^{-1}\text{cm}^{-1}$), respectively (Figure 1). Based on these data, we attempted to measure the circularly polarized luminescence (CPL) of (*R*,*R*)-**9**, but, unfortunately, the CPL activity was only close to the measurement limit ($g_{lum} \sim 10^{-4}$) for this particular compound.[26]

Table 3: Optical properties of compounds **3aa** and **9** in CH_2Cl_2 at 25 °C.

Compound	UV/Vis absorption λ_{max}/nm ($\varepsilon/10^4$ M^{-1}cm^{-1})	Emission λ_{max}/nm[a]	Φ_F[a]
(*R*)-**3aa** (88% *ee*)	245 (10.1), 330 (0.7)[b]	358[c]	0.19[c]
(*R*,*R*)-**9** (94% *ee*)	256 (9.2), 331 (3.6), 368 (1.9)[d]	404[e]	0.54[e]

[a] Excited at $\lambda = 250$ nm. [b] At 1.1×10^{-5} M. [c] At 2.3×10^{-6} M. [d] At 5.7×10^{-6} M. [e] At 2.2×10^{-6} M.

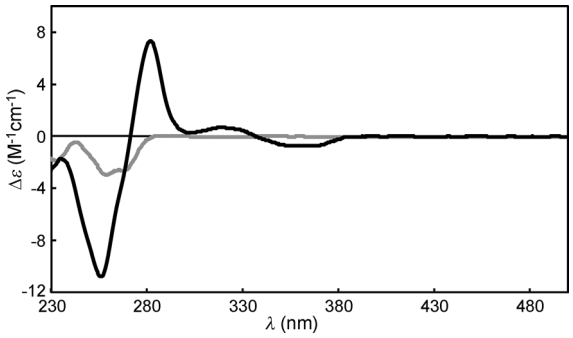


Figure 1. CD spectra of (*R*)-**3aa** (gray line; 1.1×10^{-5} M) and (*R*,*R*)-**9** (black line; 5.7×10^{-6} M) in CH_2Cl_2 at 25 °C.

In summary, we have developed a rhodium-catalyzed asymmetric synthesis of silicon-stereogenic dibenzosiloles through a [2+2+2] cycloaddition of silicon-containing prochiral triynes with internal alkynes. High yields and enantioselectivities have been achieved by employing axially chiral monophosphine (*R*)-**L** as the ligand, and this process could also be applied to the asymmetric synthesis of a germanium-stereogenic dibenzogermole. We have also conducted preliminary investigations on the optical properties of these compounds. Future studies will be directed toward further expansion of the scope of this catalysis including the synthesis of more CPL-active compounds.

Experimental Section

General procedure for Table 2: A solution of [{RhCl(C$_2$H$_4$)$_2$}$_2$] (1.5 mg, 7.7 μmol Rh) and (*R*)-**L** (3.6 mg, 7.5 μmol) in CH_2Cl_2 (0.50 mL) were stirred for 20 min at 25 °C, and a mixture of triyne **1** (0.150 mmol), alkyne **2** (0.150 mmol), and NaBAr$^F_4$ (13.3 mg, 15.0 μmol) in CH_2Cl_2 (0.50 mL) was added to it with additional CH_2Cl_2 (0.50 mL). The reaction mixture was stirred for 13–23 h at 25 °C, and this was directly passed through a pad of silica gel with EtOAc. After removal of the solvent under vacuum, the residue was purified by silica gel preparative TLC to afford compound **3**.

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