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Rhodium-Catalyzed Carbon-Silicon Bond Activation for Synthesis of Benzosilole Derivatives

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ABSTRACT: A rhodium-catalyzed coupling reaction of 2-trimethylsilylphenylboronic acid with internal alkynes is developed for the synthesis of 2,3-disubstituted benzosilole derivatives. A range of functional groups, encompassing ketones, esters, amines, aryl bromides, and heteroarenes, are compatible, which provides rapid access to diverse benzosiloles. Sequential two-fold coupling enables modular synthesis of asymmetrically substituted 1,5-dihydro-1,5-disila-s-indacene, a π -extended molecule of interest in organic electronics. In terms of the mechanism, the reaction involves cleavage of a C(alkyl)-Si bond in a trialkylsilyl group, which normally requires extremely harsh conditions for activation. Mechanistic studies including effects of substituents, reveal that C-Si bond cleavage does not proceed through a hypercoordinated silicon species, but rather through a rhodium-mediated activation process. The potential use of the reaction in catalytic asymmetric synthesis of Si-chiral benzosiloles is also demonstrated.

formation

Introduction

Organosilicon compounds occupy a prominent position in the field of organic chemistry, and their use covers synthetic reagents and organic materials.¹⁻⁴ The method development for the synthesis of organosilicon compounds therefore continues to attract interest. To construct new carbon-silicon (C-Si) bonds, halosilanes or hydrosilanes are typically used as the silicon source,¹⁻⁵ but the tetraorganosilanes formed are normally unreactive and cannot be transformed further. If a C-Si bond transformation is achieved, new synthetic strategies that enable access to intricate silicon-containing architectures become possible (Scheme 1).

Scheme 1. C-Si Transformation Enables New Synthetic Strategy



The reactivity of a C-Si bond depends greatly on the hybridization of the carbon atom attached to the silicon: $C(sp^2)$ -Si, C(sp)-Si and C(allyl)-Si bonds can be cleaved relatively easily, compared with C(alkyl)-Si, because of the hyperconjugative interactions with neighboring π -bonds.^{6,7} C(alkyl)-Si bonds incorporated in a strained ring, i.e., silacyclopropanes⁸ and silacyclobutanes,⁹ are exceptionally reactive, affording ring-opened products under mild conditions. Catalytic trans-

Me₃Si(CH₂)₃SO₃Na^{10b} are also reported. A more general strategy for activating C(alkyl)-Si bonds is conversion to penta- or hexacoordinated silicon species by adding an external or internal nucleophile.¹¹ For instance, an Me-Si bond in pentacoordinate Me₃SiF₂⁻ can be cleaved under palladium-catalyzed conditions, thus serving as a methyl donor in the cross-coupling process.¹² Nucleophiles, such as alkoxides¹³ and carbonyl oxygens,¹⁴ can be used to activate C(alkyl)-Si bonds to facilitate alkyl group transfer in cross-coupling processes when the nucleophiles are attached to the silicon atom (internal coordination). This intramolecular activation strategy is useful in the context of the synthesis of silacycles via C(alkyl)-Si bond cleavage. A tethered alcohol has been reported to promote intramolecular substitution at the silicon via the cleavage of a C(alkyl)-Si bond.¹⁵ In these cases, stoichiometric amount of a base is generally required to generate an alkoxide, which can form hypercoordinated silicon species by intramolecular attack. Shindo reported that carbonyl oxygen can also serve as a tethered nucleophile in the iodine-promoted cyclization of (Z)- β silvlacrylic acid derivatives.¹⁶ Cramer recently reported a skeletal rearrangement including the cleavage of a C(alkyl)-Si bond by catalytically generated rhodium alkoxide.¹⁷ Carbon nucleophiles, such as organolithium and magnesium, also promote displacement at a silicon center.¹⁸ In this transformation, a new C-Si bond is formed by cleaving a inert C(alkyl)-Si bond. In 2002, van Klink and Bickelhaupt reported that intramolecular nucleophilic substitution by a tethered Grignard reagent occurs at a trimethylsilyl group to form dibenzosilole (Scheme 2a).¹⁹ Xi extensively investigated this reaction using organolithium reagents and established a general protocol for the synthesis of a range of silole derivatives (Scheme 2b).^{20,21} Recently, Shirakawa and Hayashi applied

bonds

in

SiMe₄^{10a}

and

of Me-Si

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this process to the synthesis of benzosilole derivatives by combining it with iron-catalyzed carbolithiation reaction of alkynes.²²

Scheme 2. Intramolecular Nucleophilic Substitution at a Silicon Center for the Synthesis of Silole Scaffold



In 1992, Ojima reported that the rhodium-catalyzed reaction of diyne **1** with $HSi'BuMe_2$ under an atmosphere of CO affords silole **2**, in which an Me-Si bond derived from hydrosilane is cleaved (Scheme 3).²³ This reaction is notable in that the C(alkyl)-Si bond cleavage occurs in the absence of a strongly nucleophilic activator, suggesting that the intermediacy of hypercoordinated silicon species is unlikely, and that catalytic activation of C(alkyl)-Si is involved. In spite of its mechanistic uniqueness and potential use as a catalytic method for the synthesis of siloles, the report contains this one isolated example, and further investigation have never been reported.

Scheme 3. Ojima's Rhodium-Catalyzed Silylative Cyclization of Diyne via the Cleavage of a Me-Si Bond



In 2009, our group reported a novel rhodium-catalyzed coupling reaction of 2-trimethylsilylphenylboronic acid and internal alkynes, leading to the formation of benzosilole derivatives (Scheme 4).²⁴ The most salient feature of this reaction is the involvement of the activation of the Me-Si bond under catalytic and virtually neutral conditions. Following our preliminary report, several catalytic reactions that proceed via the activation of C(alkyl)-Si bonds have appeared.^{25,26} Xi demonstrated that palladium is also a competent catalyst for a similar process.²⁵ Matsuda has developed an intermolecular variant of Ojima's reaction (Scheme 3) using disilane, in place of hydrosilane.²⁶ In this article, we provide a full account of our study of rhodium-catalyzed benzosilole synthesis via the cleavage of a C-Si bond, including the scope of both coupling partners, mechanistic investigation of the C-Si bond cleavage, and applications in the construction of stereogenic silicon centers through catalytic enantioselective C-Si bond activation.

Scheme 4. Rhodium-Catalyzed Coupling of 2-Trimethysilylphenylboronic Acid with Alkynes



It is worth noting that siloles and their benzo-fused analogs are attractive synthetic targets. Siloles (silacyclopentadienes) have received much attention as useful building blocks of π -conjugated organic materials because of their unique electronic properties, resulting from their low-lying LUMO levels, derived from $\sigma^* - \pi^*$ conjugation in the ring.²⁷ Additionally, their benzo-fused analogs,28 dibenzosiloles (silafluorenes)²⁹ and benzosiloles (silaindenes),³⁰ are also known to be promising candidates for organic materials. Various applications of silole-containing organic electronic devices such as light-emitting diodes,³¹ field-effect transistors,³² solar cells,³³ and fluorescent sensors³⁴ have been intensively studied. Traditionally, silole derivatives have been synthesized under harsh reaction conditions, using stoichiometric amount of strong reducing reagent,³⁵ highly basic organometallic reagents³⁶ or other reactive reagents.^{37,38} A serious drawback of these procedures is narrow functional group toleration as a result of the vigorous reaction conditions, which limits the diversity of the accessible products. This limitation has been overcome, in part, by the recent development of transition metal-catalyzed meth-ods, including nickel,³⁹ palladium,^{25,40} iridium,⁴¹ ruthenium,⁴² gold,⁴³ and rhodium^{26,44} catalysis. Nevertheless, further development of versatile and convergent catalytic methods is still necessary for the exploration of new functional materials.

Results and Discussion

Previously, we reported rhodium-catalyzed transformations of nitriles through the cleavage of carbon-cyano bonds with the aid of organosilicon reagents.⁴⁵ During the course of the study, we examined the rhodium-catalyzed reaction of nitrile 3 with hexamethyldisilane, expecting that a putative key intermediate 4 might be intercepted by a pendant chloroarene moiety to form 5. However, we observed no proof for the formation of 5. Instead, dibenzosilole 6 was isolated in 27% yield (55% of 3 was recovered) (Scheme 5). What intrigued us most was that one of the methyl groups in a trimethylsilyl group was eliminated during the formation of 6. At the time we initiated these studies, C(alkyl)-Si bond cleavage by transition-metal catalysis was rare.^{14a,23} Silole derivatives are attractive synthetic targets because of their characteristic photophysical properties, as mentioned above.³¹⁻³⁴ We therefore decided to pursue the rhodium-mediated dibenzosilole formation reaction in more detail.

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A hypothetical pathway to 6 is outlined in Scheme 6. According to our previous findings,45 rhodium-mediated decyanative silvlation initially occurs to form silvlated compound 7. Arylrhodium species 8 was subsequently generated through the activation of an Ar-Cl bond. If arylrhodium 8 undergoes an intramolecular cyclization by substituting a methyl group on the silicon center, dibenzosilole 6 is produced. As described in the Introduction, such a displacement at silicon is known to proceed when strong nucleophiles, such as organolithium or magnesium, are used.¹⁹⁻²¹ However, it was uncertain whether transition metal species such as arylrhodium could promote a similar substitution reaction.

N SiMe₃

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Scheme 6. A Plausible Pathway for Dibenzosilole 6



To verify the feasibility of our hypothesis, especially the competence of organorhodium species in the C-Si bond cleavage, we turned our attention to the use of boronic acid 9 as a more suitable precursor to the arylrhodium 8 on the basis of a well-established boron to rhodium transmetallation process.⁴⁶ Boronic acid 9 was therefore subjected to conditions typical of those used for the generation of arylrhodium species, i.e., [RhCl(cod)]₂ (5 mol%) and base (2 equiv) in dioxane/H₂O (100/1) at 100 °C (Table 1). When Na₂CO₃ was added as a base, the expected dibenzosilole 6 was obtained in 89% yield through the cleavage of an Me-Si bond (entry 1). Yields were

Table 1. Rhodium-Catayzed Cyclization of Boronic Acid 9 via Cleavage of Me-Si Bond^a



^a Reaction conditions: 9 (0.5 mmol), [RhCl(cod)]₂ (0.025 mmol), base (1.0 mmol), dioxane (1 mL), H₂O (10 µL), at 100 °C for 15 h. ^b Isolated yield.

The formation of 6, shown in Table 1, clearly suggests that an arylrhodium(I) intermediate can activate a suitably positioned C-Si bond of a trimethylsilyl group and induce cyclization to form a silole skeleton. To further exploit this new reactivity of arylrhodium(I) species toward a silvl group in the synthesis of more demanding targets, we designed an annulative coupling of 2-trimethylsilylphenylboronic acid (10a) with an alkyne to build benzosilole derivatives (Scheme 7). According to the pioneering work of Hayashi and coworkers,^{47a} arylrhodium 11 generated from 10a should add across an alkyne to form alkenylrhodium 12, which would then undergo cyclization through displacement at a silicon center, as for arylrhodium 8. Although this carborhodation/cyclization strategy has often been employed using arylboronic acids bearing an ortho electrophiles, such as carbonyl, cyano, electron-deficient alkenes, and halide groups,^{46,48} its application to *ortho*-silylsubstituted phenylboronic acids has never been reported.

Scheme 7. Rhodium-Catalyzed Two-Component Coupling Reaction of o-Trimethylsilylphenylboronic Acid and **Internal Alkyne**



As shown in Table 2, the designed annulation was reaction achieved by conducting the of 2trimethylsilylphenylboronic acid (10a) and diphenylacetylene (13a) under identical conditions to those used for intramolecular cyclization (Table 1). The yield of benzosilole 14a was significantly affected by the base used. When inorganic bases such as Na₂CO₃ were used, 14a was obtained in low to moderate yield due to the formation of undesired protodeboronated product (entry 1-3). A significant increase in yield was observed when amine bases were used (entries 4-6). Notably, when DABCO was used, the annulative coupling proceeded even at ambient temperature, producing 14a in 69% yield (entry 7).

Table 2.	Rhodium-Catalyzed	Two-Component	Coupling
of 10a wit	h 13a: Effect of Base a	and Temperature ^a	

B(OH) ₂ + SiMe ₃	Ph Ph	[RhCl base dioxa	(cod)] ₂ 5 mol% ne/H ₂ O (100/1)		Ph Ph Si Me
10a	13a	15 N		1	4a
entry	base		temp. (°C)	yield (%) ^b	
1	Na ₂ C	O_3	100	45 ^c	
2	K ₂ CC	D ₃	100	38 ^c	
3	Cs_2C	:O ₃	100	5 ^c	
4	NEt ₃		100	88	
5	DAB	CO	100	97	
6	DAB	CO	80	95	
7	DAB	CO	rt	69	

^{*a*} Reaction conditions: **10a** (0.5 mmol), **13a** (1.0 mmol), [RhCl(cod)]₂ (0.025 mmol), base (1.0 mmol), dioxane (1 mL), H₂O (10 μ L) for 15 h. ^{*b*} Isolated yield. ^{*c*} GC yield.

The scope of the alkyne partner is shown in Table 3. Not only diphenylacetylene (13a, entry 1), but other substituted diarylacetylenes 13b-13f produced the corresponding benzosiloles (entries 2-6). The high functional group compatibility of the reaction gives rapid access to 2,3-diaryl-susbstituted benzosilole derivatives bearing a range of electron-donating (entries 2 and 3) and -withdrawing groups (entries 4-6). Of note is the applicability of ketone groups, which are incompatible with the highly basic conditions typically used for the synthesis of silole derivatives.^{35,36} Moreover, bromoaryls, which cannot survive under conventional palladium-based cross-coupling conditions, are readily introduced by this rhodium-catalyzed protocol (entry 4). The obtained 14d serves as a versatile platform for more elaborated benzosilole derivatives. Fused aromatics such as naphthyl, as well as heteroarenes, including thiophene and pyridine, were also incorporated (entries 7-9). Aliphatic alkynes also serve as excellent components in this annulative coupling to produce dialkylsubstituted benzosiloles (entries 10-12). The reaction tolerates a propargylic ether functionality, which is potentially reactive under rhodium catalysis⁴⁹ (entry 13). Cyclic alkyne 13n underwent annulation to form a twelve-membered cycloalkanefused benzosilole 14n (entry 14). Several electronically or sterically-biased unsymmetrical alkynes were also incorporated, delivering the corresponding benzosiloles regioselectively. For instance, the use of alkylphenylacetylenes regioselectively yielded benzosiloles bearing an aryl group at the 2position as the major product. (entries 15 and 16). Although terminal alkynes failed to react in this coupling, silyl-protected alkynes 13q-13s successfully participated to give the corresponding benzosiloles. When 1-(trimethysilyl)propyne 13q was used, benzosilole bearing a trimethylsilyl group at the 2position was obtained with high yield and regioselectivity (86%, 11:1) (entry 17). Trimethylsilylphenylacetylene (13r) was also efficiently incorporated, favoring a 2-silyl isomer, albeit with diminished selectivity (94%, 2:1; entry 18). The regioselectivity in this specific case was readily improved (10:1) by using a more bulky triethylsilyl protecting group

without any loss of yield (entry 19). Benzosiloles bearing an ester group at the 2-position were also accessible using alkynyl esters (entries 20 and 21).

Synthetic methods for benzosiloles are dominated by intramolecular processes, ^{30,35c,40n,42a,b,43} in which the product diversity relies on the structures of the starting compounds. In contrast, the reaction established here is an intermolecular twocomponent annulation. A wide range of substituted benzosiloles can therefore be prepared simply by changing the structure of the alkyne component, as demonstrated in Table 3. This modular nature of the present method is particularly valuable when applied to the synthesis of compound libraries. Having traditionally inaccessible benzosiloles⁵⁰ in hand has a significant impact on the exploration of new organic functional materials, given the unique optoelectronic properties of aryl-substituted siloles.^{31-34,51} Some of the 2,3-diarylsubstituted benzosiloles synthesized in this study exhibited solid-state photoluminescence, and the wavelength of the maximum absorption can be tuned by the functional groups introduced (see SI for details).

Table 3. Scope of Alkynes^a

$\begin{bmatrix} B(OH)_2 \\ SiMe_3 \end{bmatrix} + \begin{bmatrix} R^1 \\ R^2 \\ R^2 \end{bmatrix}$ 10a 13a-u	[RhCl(cod)] ₂ 5 mol% DABCO dioxane/H ₂ O (100/1) 80 °C, 15 h	R ¹ Si Me Me 14a-u
entry	product	yield (%) ^b
1 R	R=H (14a)	95
2 ^c	NMe ₂ (14b)	90
3ª	OMe (14c)	61
4	—∖ Br (14d)	85
5 ^e	/ R AC (14e)	56
6 _{Me} Me	CF ₃ (14f)	97
7 Ar	Ar = 1-naphthyl (14g)	99
8 ^f Ar	3-pyridyl (14h)	65
9 ^f Me Me	2-thiophenyl (14i)	65
10	Alk = Et (14j)	94
11 Alk	Pr (14k)	90
12 🗍 🖌 🔪 – Alk	Bu (14I)	98
13 ^g Si	CH ₂ OMe (14m)	76
14 Me Me	−(CH ₂) ₁₀ − (14n)	95
15	— R = Me (140)	94 (12:1) ^h
16 Si	Bu (14p)	93 (13:1) ^h
Me	· · ·	. ,
17 R	$R = Me_i(S_i = SiMe_a)$ (1	4 a) 86 (11 ⁻ 1) ^h
18 () Si	Ph (Si = SiMe ₂) (1	$ 4\mathbf{r}\rangle = 94 (2.1)^h$
19 Me Me	Ph (Si = SiEta) (14	1s) 95 (10:1) ^h
	(,
20 ^{<i>i</i>,<i>j</i>}	R = Me (14t)	44
	² Me Ph (14 u)	44 (5:1) ^h
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59 60 ^{*a*} Reaction conditions: **10a** (0.5 mmol), **13** (1.0 mmol), [RhCl(cod)]₂ (0.025 mmol), DABCO (1.0 mmol), dioxane (1 mL), H₂O (10 μL) at 80 °C for 15 h. ^{*b*} Isolated yield. ^{*c*} **10a** (0.2 mmol), **13b** (0.4 mmol), [RhCl(cod)]₂ (0.01 mmol), DABCO (0.4 mmol), dioxane (0.4 mL), H₂O (4 μL). ^{*d*} **13c** (0.6 mmol), DMF (1 mL). ^{*e*} **13e** (0.6 mmol), NEt₃ (1.0 mmol) in place of DABCO. ^{*f*} [RhCl(cod)]₂ (0.05 mmol) at 100 °C for 72 h. ^{*g*} **13m** (2.0 mmol) and [RhCl(cod)]₂ (0.05 mmol). ^{*h*} The values in parenthesis refer to the ratio of regioisomers determined by NMR. ^{*i*} **13** (2.0 mmol), [RhCl(cod)]₂ (0.05 mmol), Na₂CO₃ (1.0 mmol) in place of DABCO. ^{*j*} At 100 °C. ^{*k*} At 130 °C.

In the course of the investigation to determine the scope of the arylsilane component, we encountered difficulties in purifying some of the starting arylboronic acids. We therefore pursued the possibility of directly using protected boronic acid substrates, which can be purified by chromatography (Table 4). Neopentyl glycolate 10b and catecholate 10c could be employed as surrogates for the boronic acid **10a** under the same reaction condition (entries 1-3). However, when bulkier pinacolate ester 10d was used, the reaction was sluggish, and 10d remained after 15 h. Increasing the amount of water effectively promoted the conversion of 10d, and the yield of 14a was raised to 86% (entry 4). The use of boronate esters offers significant synthetic advantages over the use of boronic acids, because boronate esters are readily available by transition metal-catalyzed borylation, especially through C-X⁵² or C-H⁵³ bond activation.

Table 4. Effect of Substituents on the Boron Moiety^a



^{*a*} Reaction conditions: **10** (0.5 mmol), **13a** (1.0 mmol), [RhCl(cod)]₂ (0.025 mmol), DABCO (1.0 mmol), dioxane (1 mL), H₂O (10 μL) at 80 °C for 15 h. ^{*b*} Isolated yield. ^{*c*} Dioxane (1 mL), H₂O (67 μL) (dioxane/H₂O = 15/1).

Having established that boronate esters are good substrates, we next synthesized several substituted boronate esters and conducted rhodium-catalyzed coupling with **13a** (Table 5). The π -extended silole **15** was assembled using a naphthalenebased substrate. Introduction of electron-donating and electron-withdrawing substituents into the benzosilole framework was also achieved, as in **16** and **17**. Moreover, our synthetic method for benzosiloles was successfully applied to the construction of simple silole structure. Thus, the reaction of alkenylboronate ester **18**, which is readily prepared by palladium-catalyzed silylboration of ethynylbenzene,⁵⁴ with **13a** furnished trisubstituted silole **19** under the standard reaction condition (eq. 1). In this case, a Ph-Si bond of diphenylmethylsilyl group is selectively cleaved (*vide infra* for selectivity issues regarding the silicon substituent). Since the regioselectivity of a silylboration across a terminal alkyne is controllable,⁵⁵ regioselective synthesis of various trisubstituted siloles would be possible by sequential silylboration/rhodium-catalyzed annulation with unsymmetrical alkynes (see entries 15-21 in Table 3).







^{*a*} Reaction conditions: **10** (0.5 mmol), **13a** (1.0 mmol), [RhCl(cod)]₂ (0.025 mmol), DABCO (1.0 mmol), dioxane (1 mL), H₂O (10 μL) at 80 °C for 15 h. ^{*b*} Dioxane (1 mL), H₂O (67 μL) (dioxane/H₂O = 15/1).

A plausible catalytic cycle of the reaction of boronic acid 10a and alkyne 13 is depicted in Scheme 8. Rhodium hydroxide I is initially generated from rhodium(I) chloride with the aid of water and base and serves as a catalytically active species. Rhodium complex I is subsequently converted into arylrhodium II by transmetallation with boronic acid 10a, followed by insertion of alkyne 13, leading to alkenylrhodium III. The cyclization of III then occurs with cleavage of an Me-Si bond in a trimethylsilyl group to form benzosilole 14, along with methylrhodium IV. The hydrolysis of methylrhodium IV regenerates rhodium hydroxide I with evolution of methane.⁵⁶ The methane generation during the catalytic cycle was confirmed by ¹H NMR spectroscopy. The resonance indicative of methane ($\delta = 0.20$ ppm) was observed when the reaction was run in a sealed tube and monitored by ¹H NMR spectroscopy (see SI for the detail). When unsymmetrical alkynes are used, the regioselectivity is determined in the step of the insertion of alkynes (II→III). The regioselectivities observed with unsymmetrical alkynes in this study (entries 15-21 in Table 3) suggest that the formation of alkenylrhodium III, which bears a bulkier or more electron-withdrawing substituent at the α position, i.e., R^2 in Scheme 8, is favored. The trend in regiochemistry is in accord with that observed in reported catalytic

Scheme 8. Plausible Catalytic Cycle



It is important to note that alkenylrhodium intermediate III can follow several alternative pathways on the basis of the reported reactivity of organorhodium(I) species (Scheme 9). In addition to the Me-Si bond cleavage process that leads to the formation of benzosilole 14 (path 1), alkenylrhodium III could undergo 1,4-migration of a rhodium center to form V,⁵⁷ which should eventually be protonated to form arylsilane VI (path 2). However, we did not observe this type of byproduct in all cases investigated in this study. In addition, there are several reports where other pathways predominate over 1,4rhodium migration via C-H activation.^{17,47b} On the basis of these observations and literature, we consider that the rate of path 2 is relatively slow compared with that of path 1 under our rhodium-catalyzed conditions. Another alternative pathway that intermediate III could follow is the oxidative addition of the Ar-Si bond, which affords rhodium(III) intermediate VII (path 3). Subsequent C(alkenyl)-Si bond-forming reductive elimination from VII would result in the formation of arylrhodium VIII. This unique silicon/rhodium transposition process was reported by Cramer.¹⁷ The resultant arylrhodium VIII can follow two possible pathways. One is protonation, which affords alkenylsilane IX (path 3-1). However, we can exclude this path since no IX was observed experimentally. Another pathway involves the Me-Si bond cleavage, which should afford identical products as path 1 (path 3-2). Based on the Cramer's work¹⁷ as well as our own observation that a silyl group at the vinylic position can participate the silole formation (eq 1), this represents another possible pathway to silole 14.

(Please refer page 12 for Scheme 9. This is a two-column artwork.)



^a Reaction conditions: 10 (0.5 mmol), 13a (1.0 mmol), [RhCl(cod)]₂ (0.025 mmol), DABCO (1.0 mmol), dioxane (1 mL), H₂O (67 µL), at 80 °C for 15 h. ^b Isolated yield. ^c Ratio of the products (21/14a) determined by GC. ^d NMR yield. ^e Ratio of the products (25/14a) determined by NMR.

Our proposed catalytic cycle consists of relatively wellestablished elementary processes involving rhodium(I), except for the C-Si cleavage step (III \rightarrow 14). To better understand this elusive but intriguing process, we next investigated the scope of the silicon substituents in boronate ester 10. Boronate esters possessing sterically and electronically different silvl groups

Table 6. Scope of Silicon Substituents^a

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59 60 were prepared and exposed to rhodium-catalyzed coupling with 13a under the optimized conditions (Table 6). A more hindered triethylsilyl-substituted substrate 10h successfully afforded the corresponding benzosilole 20 via cleavage of an Et-Si bond, although the yield was slightly decreased compared to that using a trimethylsilyl substrate 10b (entry 1). The sensitivity of C-Si bond substitution to steric effects led us to examine a series of dimethylalkylsilyl (SiMe₂R) groups. As we expected, selective cleavage of methyl over bulkier alkyl groups was observed. For example, a substrate bearing an SiMeⁿBu group, as in **10i**, smoothly underwent annulative coupling to form siloles 21 and 14a in a ratio of 93/7 (entry 2). Exclusive cleavage of Me is observed when the bulkier i-Pr, t-Bu and benzyl groups are employed (entries 3-5). A phenyl group on the silicon atom was next examined in order to determine the relative reactivities between C(sp³)-Si and C(sp²)-Si bond. The reaction of a substrate possessing a dimethylphenylsilyl group (SiMe₂Ph) resulted in a mixture of 25 and 14a in a ratio of 59/41, suggesting that cleavage of both Me-Si and Ph-Si bonds occurs competitively under the catalytic conditions (entry 6).⁵⁸ Phenyl cleavage occurred exclusively over methyl cleavage when a diphenylmethylsilyl (SiMePh₂) group was introduced into the substrate (entry 7).

The substitution aptitude observed with SiMe₂Bn and SiMe₂Ph groups (entries 5 and 6 in Table 6) contrasts with that observed with the C-Si substitution reactions using organolithium reagents. It was reported that the cleavage of a C-Si bond by an organolithium species occurred via pentacoordinated organosilicate **26** (eq 2).²⁰⁻²¹ In this system, when a substrate bearing SiMe₂Bn or SiMe₂Ph is used, a benzyl or phenyl group is predominantly eliminated over a methyl group, presumably because the thermodynamic stabilities of concurrently produced organolithium species (Li⁺R⁻) determine the selectivity of the collapse of organosilicate **26**.



In stark contrast, a kinetic factor primarily determines the selectivity in C-Si cleavage in our rhodium-catalyzed annulation. In the case of SiMe₂Bn, a methyl group, which is small, is exclusively cleaved, and the benzyl group remains intact (entry 5 in Table 6). In the case of SiMe₂Ph, kineticallyfavored Me cleavage is competitive with a thermodynamically-favored Ph cleavage, and a mixture of the two benzosiloles is produced (entry 6 in Table 6).⁵⁹ These prominent differences among the reactivities of the silicon substituents exclude a mechanistic scenario in which a discrete pentacoordinated silicate species is involved as an intermediate in the rhodiumcatalyzed benzosilole formation. Although the exact mechanism for the rhodium-catalyzed C-Si bond cleavage remains elusive at present, a concerted pathway such as σ -bond metathesis through a four-centered transition state 27 may account for the observed selectivity for the C-Si cleavage in the rhodium-catalyzed cyclocoupling, in which a less hindered C-Si bond is expected to be cleaved preferentially (eq 3). 60



To shed further light on the mechanism of C-Si bond cleavage, we investigated the electronic effect of the Ar group of SiMe₂Ar on the selectivity for Me-Si and Ar-Si cleavage. Boronate esters containing a series of *para*-substituted arenes on the silicon atom 100-10u were prepared, and reacted with 13a under the standard conditions (Table 7). All the substituents examined were tolerated, and the corresponding benzosiloles derived from Me-Si bond cleavage (A) and Ar-Si bond cleavage (B) were obtained in each case. The ratio of the products (A/B in Table 7) varied depending on the electronic nature of the arene moiety on silicon atom.⁶¹ Based on these results, the selectivity for Ar-Si bond cleavage [B/(A/2+B)], which is an index for the preference of Ar-Si cleavage relative to Me-Si cleavage was calculated. The Hammett plot of the selectivity $[\mathbf{B}/(\mathbf{A}/2+\mathbf{B})]$ against σ_p value afforded two intersecting lines as shown in Figure 1. A positive ρ value (+0.12) was obtained with electron-donating groups, whereas electrondeficient aryl groups resulted in a negative ρ value (-0.28).⁶²

Table 7. Electronic Effect of Aryl Group on Silicon Substituents^a



^{*a*} Reaction conditions: **10** (0.5 mmol), **13a** (1.0 mmol), [RhCl(cod)]₂ (0.025 mmol), DABCO (1.0 mmol), dioxane (1 mL), H₂O (67 μ L), at 80 °C for 15 h. ^{*b*} NMR yield. ^{*c*} The ratio of the products was determined by NMR after chromatography.







A convex line in the Hammett plot usually suggests a change in the rate-determining step with electronic variation of the substituents.⁶³ On the basis of the Hammett studies, we propose that the rhodium-catalyzed Ar-Si bond cleavage is not a concerted mechanism, but an asynchronous electrophilic aromatic substitution mechanism (eq 4).⁶⁴ Thus, the intramolecular electrophilic attack of the alkenylrhodium 35 on the aryl group on the silicon center initially generates an areniumlike intermediate 36^{65} (step a). Migration of the alkenyl moiety on the rhodium to a silicon atom and the simultaneous cleavage of an arenium-silicon bond produce benzosilole 14a and arylrhodium 37 (step b). The Hammett behavior is rationalized by assuming a change in the turnover-limiting step as a result of varying the electronics of the leaving aryl group. In the negative slope region (red dashed line), electrophilic attack of the rhodium (step a) is rate-determining, because a more electrondonating group accelerates the formation of an Ar-Si cleaved product. In contrast, the cyclization stage (step b) becomes rate-determining in the positive slope region (blue dashed line). because the presence of highly electron-rich arene renders step a significantly facile and reversible. However, the electrondonating group decelerate step b in turn by stabilizing the partially positive intermediate 36, thereby exhibiting a positive ρ value. In this mechanistic scenario, the rate of Ar-Si cleavage relative to Me-Si cleavage decreases when the absolute value of $\sigma_{\rm p}$ of the substituent is high, regardless of its sign.



Having successfully examined preparative and mechanistic aspects of the rhodium-catalyzed benzosilole synthesis, we next directed our attention to the synthesis of more intricate silole derivatives that are otherwise inaccessible. We envi-

sioned that the synthesis of 1,5-dihydro-1,5-disila-s-indacene skeleton, in which two siloles are fused with a benzene core, would be possible by a two-fold annulation, hopefully incorporating two different alkynes. The analogous ladder-type ring-fused siloles are among the most attractive targets as organic electronic materials because of their widely π conjugated coplanar structures.⁶⁶ Establishing a general convergent protocol for the synthesis of these silole-fused polyaromatics would therefore lead to numerous application. We chose disilyl-substituted phenylboronate ester bearing a bromo group, i.e., **39**, as an appropriate platform for sequential silole formation. The boronate 39 was readily prepared from commercially available 1,4-dibromobenzene (38) in three steps (See SI for details). The boronate ester 39 was then assembled with 4-octyne (13k) under the optimal conditions for the rhodium-catalyzed annulation, affording benzosilole 40 in excellent yield, without loss of the bromo functionality. The bromo moiety served as a handle for the introduction of a boryl group via the palladium-catalyzed Miyaura borylation,⁵² furnishing the boronate 41. The second rhodium-catalyzed annulation with diphenylacetylene (13a) delivered the expected 1,5dihydro-1,5-disila-s-indacene derivative 42 with excellent efficiency. The mild nature of our protocol allowed for the synthesis of densely functionalized intermediate 40, thereby enabling the incorporation of two different alkynes into the silole structure in a sequential manner.

Scheme 10. Synthesis of Asymmetrically Substituted 1,5-Dihydro-1,5-disila-s-indacene Derivative by Sequential Introduction of Two Different Alkynes



As demonstrated in Table 6, when a SiMe₂R group is used in our rhodium-catalyzed annulation, selective cleavage of an Me-Si bond occurs to form benzosiloles bearing a silicon stereogenic center. If enantiotopic methyl groups can be discriminated by adding a suitable chiral ligand, the catalytic asymmetric construction of benzosiloles is possible. The available methods for constructing a silicon-stereocenter are considerably limited compared with those for carbon-based chiral centers. Although several classical methods for preparing Sichiral compounds using stoichiometric amounts of chiral sources are known,⁶⁷ the catalytic asymmetric methods for such compounds remains underdeveloped.⁶⁸ With regard to catalytic asymmetric synthesis of chiral siloles, there was no

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59 60 Ph

'Pr

Mé

22*

46% (98% ce)

Ρh

(5)

example of the synthesis of siloles bearing a silicon stereocenter, at the time when we initiated our study.⁶⁹ Recently, Shintani and Hayashi reported a notable catalytic asymmetric synthesis of silicon-stereogenic dibenzosiloles via palladiumcatalyzed enantioselective intramolecular C-H bond arylation.⁷⁰

Our approach focused on the investigation of chiral ligands that can induce enantioselective Me-Si bond cleavage in the reaction of 10j with 13a. The highly sterically congested nature of substrate 10j renders the application of typical chiral ligands difficult. After much work on ligand screening and optimization of the reaction conditions (See SI for details of the optimization studies), we identified Imamoto's⁷¹ QuinoxP* as an effective ligand, producing benzosilole 22* bearing a chiral silicon center with almost perfect enantioselectivity (98% ee) (eq 5). Nevertheless, the efficiency of the reaction was significantly lowered as a result of the inherent steric bulkiness imposed by this chiral phosphine ligand, thereby limiting the application of other alkynes to this catalytic asymmetric variant.⁷² Although this means there is still much room for improvement, a benzosilole containing stereogenic silicon center was synthesized for the first time by harnessing our own rhodium-catalyzed carbon-silicon bond activation strategy.

> $[RhCl(C_2H_4)_2]_2$ 5mol% (S,S)-QuinoxP* 11mol%

dioxane/H2O (5/1)



Na₂CO₃

80 °C, 15 h

Ph

Ρh

13a

Conclusions

 \cap

10j

'n

SiMe₂ⁱPr

We have developed a rhodium-catalyzed coupling of 2silylphenylboronic acids with alkynes for the synthesis of benzosilole derivatives. From the preparative viewpoint, our protocol has two notable advantages over classical methods. One is high functional compatibility. The mildness of the catalytic conditions employed keeps reactive functional groups, such as ketones, esters and halides (Cl, and Br), intact during the silole formation process. The other aspect is the convergent nature of the protocol. A diverse range of benzosiloles are rapidly accessible simply by changing the structure of the alkyne coupling partner. These advantages also enable the synthesis of asymmetrically substituted 1,5-dihydro-1,5-disila-s-indacene. From the mechanistic viewpoint, the present reaction involves the activation of C-Si bonds, especially those in trialkylsilyl groups. A thorough investigation of the reactivity order of the silicon substituents excluded conventional mechanistic manifold, in which C-Si bond cleavage occurs from activated, hypercoordinated silicon species. The potential use in the catalytic asymmetric synthesis of Si-chiral benzosiloles is also demonstrated. Further exploration of catalytic methods that

can transform inert C-Si bonds are underway in our laboratory. $^{73}\!\!$

ASSOCIATED CONTENT

Supporting Information. Detailed experimental procedures and characterization of new compounds are available free of charge via the Internet at http://pubs.acs.org.

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Table of Contents artwork