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

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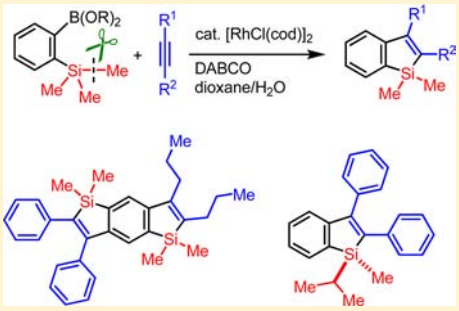
Supporting Information

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 2-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.

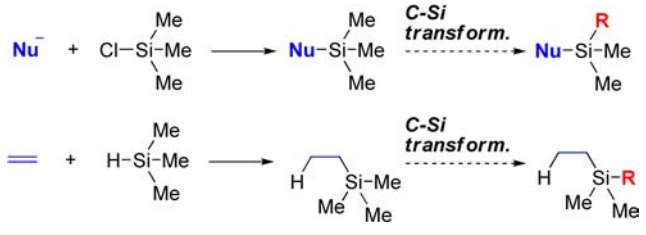


INTRODUCTION

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).

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., silacyclopropanes[8] and silacyclobutanes,[9] are exceptionally reactive, affording ring-opened products under mild conditions. Catalytic transformation of Me–Si bonds in $SiMe_4$[10a] and $Me_3Si(CH_2)_3SO_3Na$[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 $Me_3SiF_2^-$ can be cleaved under palladium-catalyzed conditions, thus serving as a methyl donor in the cross-coupling process.[12] Nucleophiles, such as alkoxides[13] 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 cleavage of a C(alkyl)–Si bond.[15] In these cases, a 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-silylacrylic 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

Scheme 1. C–Si Transformation Enables New Synthetic Strategy



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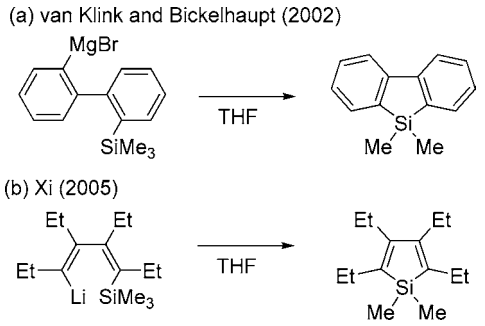
center.[18] In this transformation, a new C−Si bond is formed by cleaving an inert C(alkyl)−Si bond. In 2002, van Klink and Bickelhaupt reported that intramolecular nucleophilic substitution by a tethered Grignard reagent occurs at a trimethylsilyl group to form dibenzosilole (Scheme 2a).[19] Xi

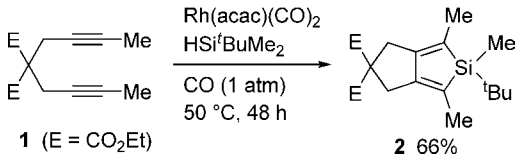
Scheme 2. Intramolecular Nucleophilic Substitution at a Silicon Center for the Synthesis of Silole Scaffold



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

In 1992, Ojima reported that the rhodium-catalyzed reaction of diyne **1** with HSi^tBuMe_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

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

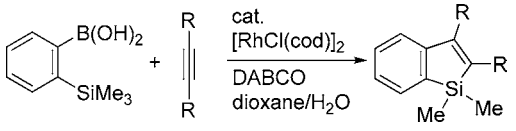


1 (E = CO_2Et) **2** 66%

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 has never been reported.

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

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



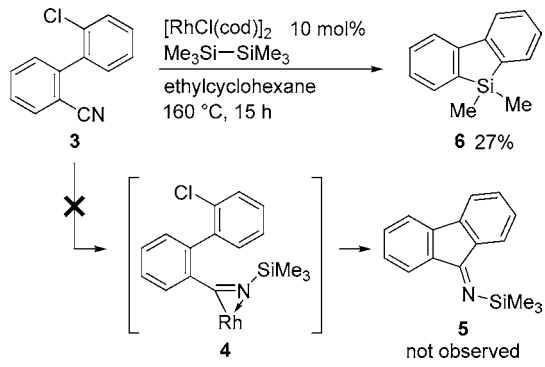
the activation of C(alkyl)−Si bonds have appeared.[25,26] Xi demonstrated that palladium is also a competent catalyst for a similar process.[25] Matsuda has developed an intermolecular variant of Ojima's reaction (Scheme 3) using disilane, in place of hydrosilane.[26] In this article, we provide a full 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.

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 sensors[34] have been intensively studied. Traditionally, silole derivatives have been synthesized under harsh reaction conditions, using a stoichiometric amount of strong reducing reagent,[35] highly basic organometallic reagents,[36] 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 methods, 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

Scheme 5. Initial Discovery of C−Si Bond Cleavage



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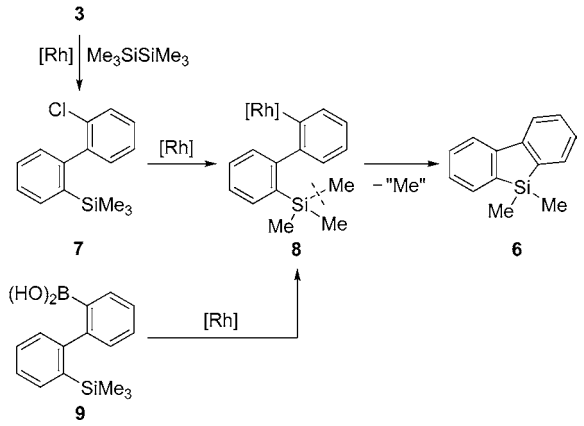
studies, C(alkyl)−Si bond cleavage by transition-metal catalysis was rare.[14a,23] Silole derivatives are attractive synthetic targets because of their characteristic photophysical properties, as mentioned above.[31−34] We therefore decided to pursue the rhodium-mediated dibenzosilole formation reaction in more detail.

A hypothetical pathway to **6** is outlined in Scheme 6. According to our previous findings,[45] rhodium-mediated

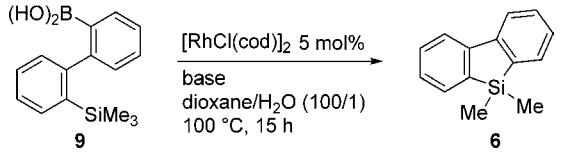
Scheme 6. A Plausible Pathway for Dibenzosilole 6



decyanative silylation initially occurs to form silylated 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.

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 transmetalation 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/H_2O (100/1) at 100 °C (Table 1). When Na_2CO_3 was added as a

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



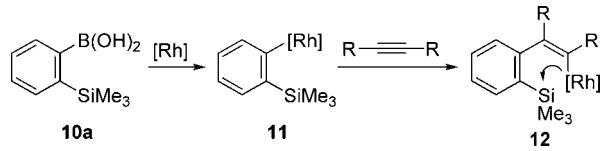
entry	base	yield (%)[b]
1	Na_2CO_3	89
2	NEt_3	97
3	DABCO	96

[a]Reaction conditions: **9** (0.5 mmol), $[RhCl(cod)]_2$ (0.025 mmol), base (1.0 mmol), dioxane (1 mL), H_2O (10 μL), at 100 °C for 15 h. [b]Isolated yield.

base, the expected dibenzosilole **6** was obtained in 89% yield through the cleavage of an Me−Si bond (entry 1). Yields were further improved by using organic bases such as triethylamine or 1,4-diazabicyclo[2,2,2]octane (DABCO) (entries 2 and 3).

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 silyl 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 co-

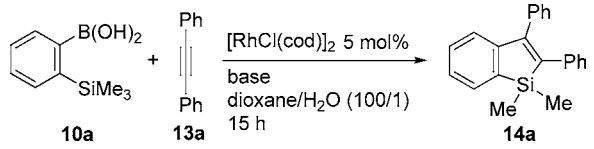
Scheme 7. Rhodium-Catalyzed Two-Component Coupling Reaction of *o*-Trimethylsilylphenylboronic Acid and Internal Alkyne



workers,[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* electrophile, such as carbonyl, cyano, electron-deficient alkenes, and halide groups,[46,48] its application to *ortho*-silyl-substituted phenylboronic acids has never been reported.

As shown in Table 2, the designed annulation was achieved by conducting the reaction of 2-trimethylsilylphenylboronic

Table 2. Rhodium-Catalyzed Two-Component Coupling of 10a with 13a: Effect of Base and Temperature[a]



entry	base	temp (°C)	yield (%)[b]
1	Na_2CO_3	100	45[c]
2	K_2CO_3	100	38[c]
3	Cs_2CO_3	100	5[c]
4	NEt_3	100	88
5	DABCO	100	97
6	DABCO	80	95
7	DABCO	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), H_2O (10 μL) for 15 h. [b]Isolated yield. [c]GC yield.

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 Na_2CO_3 were used, **14a** was obtained in low to moderate yield due to the formation of an undesired protodeboronated product (entries 1−3). A significant increase in yield was observed when amine bases were used (entries 4−6). Notably, when DABCO was used, the

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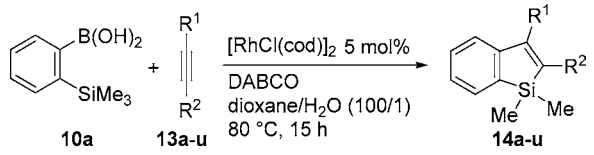
annulative coupling proceeded even at ambient temperature, producing **14a** in 69% yield (entry 7).

The scope of the alkyne partner is shown in Table 3. Not only diphenylacetylene (**13a**, entry 1) but also other substituted

Table 3. Scope of Alkynes[a]



10a 13a-u 14a-u

entry	product	yield (%)[b]
1	R = H (**14a**)	95
2[c]	NMe_2 (**14b**)	90
3[d]	OMe (**14c**)	61
4	Br (**14d**)	85
5[e]	Ac (**14e**)	56
6	CF_3 (**14f**)	97
7	Ar = 1-naphthyl (**14g**)	99
8[f]	3-pyridyl (**14h**)	65
9[f]	2-thienyl (**14i**)	65
10	Alk = Et (**14j**)	94
11	Pr (**14k**)	90
12	Bu (**14l**)	98
13[g]	CH_2OMe (**14m**)	76
14	$-(CH_2)_{10}-$ (**14n**)	95
15	R = Me (**14o**)	94 (12:1)[h]
16	Bu (**14p**)	93 (13:1)[h]
17	R = Me (*Si* = $SiMe_3$) (**14q**)	86 (11:1)[h]
18	Ph (*Si* = $SiMe_3$) (**14r**)	94 (2:1)[h]
19	Ph (*Si* = $SiEt_3$) (**14s**)	95 (10:1)[h]
20[i,j]	R = Me (**14t**)	44
21[i,k]	Ph (**14u**)	44 (5:1)[h]

[a]Reaction conditions: **10a** (0.5 mmol), **13** (1.0 mmol), $[RhCl(cod)]_2$ (0.025 mmol), DABCO (1.0 mmol), dioxane (1 mL), H_2O (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), H_2O (4 μL). [d]**13c** (0.6 mmol), DMF (1 mL) in place of dioxane. [e]**13e** (0.6 mmol), NEt_3 (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 parentheses refer to the ratio of regioisomers determined by NMR. [i]**13** (2.0 mmol), $[RhCl(cod)]_2$ (0.05 mmol), Na_2CO_3 (1.0 mmol) in place of DABCO. [j]At 100 °C. [k]At 130 °C.

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 dialkyl-substituted benzosiloles (entries 10−12). The reaction tolerates a propargylic ether functionality, which is potentially reactive under rhodium catalysis[49] (entry 13). Cyclic alkyne **13n** underwent annulation to form a 12-membered cycloalkane-fused 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 2-position 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 2-position 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 two-component 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 benzosiloles[50] 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-diaryl-substituted 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 Supporting Information (SI) for details).

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 conditions (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

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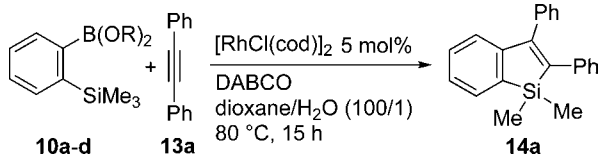
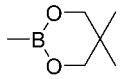
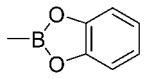
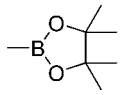
Table 4. Effect of Substituents on the Boron Moiety[a]



10a-d 13a 14a

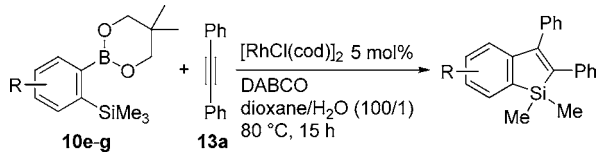
entry	$B(OR)_2$		yield (%)[b]
1	$-B(OH)_2$	(**10a**)	95
2		(**10b**)	96
3		(**10c**)	95
4		(**10d**)	56 (86)[c]

[a]Reaction conditions: **10** (0.5 mmol), **13a** (1.0 mmol), $[RhCl(cod)]_2$ (0.025 mmol), DABCO (1.0 mmol), dioxane (1 mL), H_2O (10 μL) at 80 °C for 15 h. [b]Isolated yield. [c]Dioxane (1 mL), H_2O (67 μL) (dioxane/H_2O = 15/1).

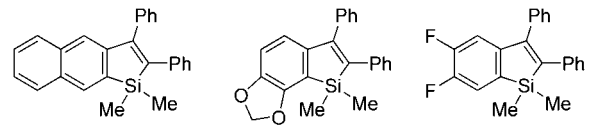
acids, because boronate esters are readily available by transition-metal-catalyzed borylation, especially through C–X[52] or C–H[53] bond activation.

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

Table 5. Scope of *o*-Trimethylsilylarylboronic Esters[a]



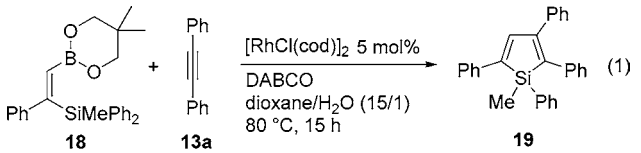
10e-g 13a



15 90% **16** 65%[b] **17** 67%

[a]Reaction conditions: **10** (0.5 mmol), **13a** (1.0 mmol), $[RhCl(cod)]_2$ (0.025 mmol), DABCO (1.0 mmol), dioxane (1 mL), H_2O (10 μL) at 80 °C for 15 h. [b]Dioxane (1 mL), H_2O (67 μL) (dioxane/H_2O = 15/1).

π-extended silole **15** was assembled using a naphthalene-based substrate. Introduction of electron-donating and -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 structures. 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 conditions (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

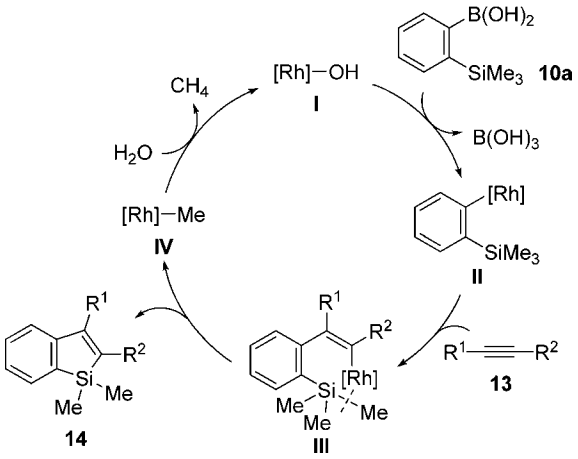


18 **13a** 2 equiv **19** 69% (NMR yield) (1)

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 plausible catalytic cycle of the reaction of boronic acid **10a** and alkyne **13** is depicted in Scheme 8. Rhodium hydroxide **I** is

Scheme 8. Plausible Catalytic Cycle



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 transmetalation 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 ^{1}H NMR spectroscopy. The resonance indicative of methane (δ = 0.20 ppm) was observed when the reaction was run in a sealed tube and monitored by ^{1}H NMR spectroscopy (see SI for the detail). When unsymmetrical alkynes are used, the regioselectivity is determined in the insertion of alkynes step (**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 reactions via carborhodation of arylrhodium **II** across alkynes.[46]

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

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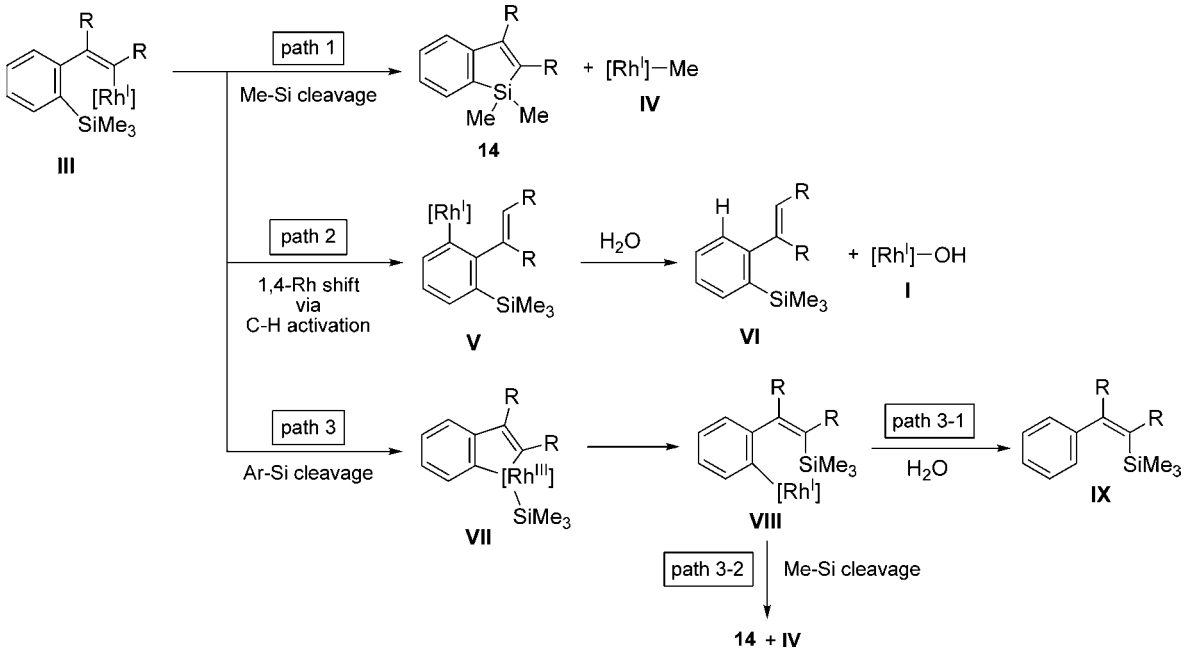
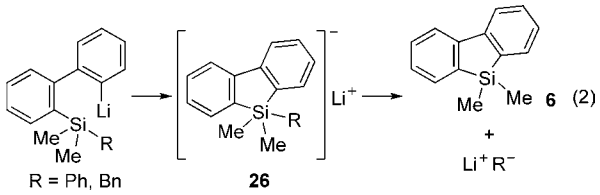
Scheme 9. Possible Reactions That Intermediate III Undergoes



where other pathways predominate over 1,4-rhodium 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 work[17] 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**.

Our proposed catalytic cycle consists of relatively well-established elementary processes involving rhodium(I), except for the C−Si cleavage step (**III**→**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 silyl groups 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 ($SiMe_2R$) groups. As we expected, selective cleavage of methyl over bulkier alkyl groups was observed. For example, a substrate bearing a $SiMe_2{}^nBu$ 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 the $C(sp^3)$−Si and $C(sp^2)$−Si bond. The reaction of a substrate possessing a dimethylphenylsilyl group ($SiMe_2Ph$) 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 ($SiMePh_2$) group was introduced into the substrate (entry 7).

The substitution aptitude observed with the $SiMe_2Bn$ and $SiMe_2Ph$ 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 $SiMe_2Bn$ or $SiMe_2Ph$ 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 intermediate **26**.

In stark contrast, a kinetic factor primarily determines the selectivity in C−Si cleavage in our rhodium-catalyzed annulation. In the case of $SiMe_2Bn$, a methyl group, which is small, is exclusively cleaved, and the benzyl group remains intact (entry 5 in Table 6). In the case of $SiMe_2Ph$, kinetically favored 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

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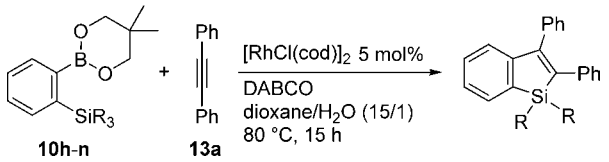
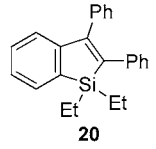
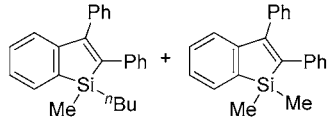
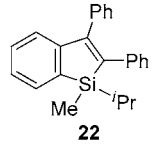
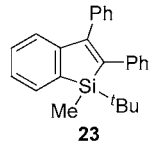
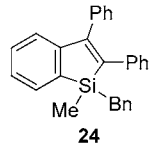
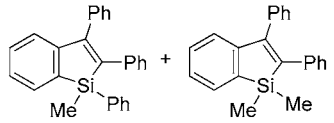
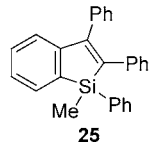
Table 6. Scope of Silicon Substituents[a]

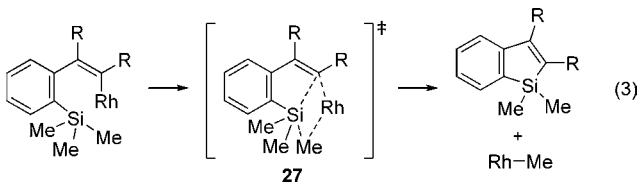


entry	SiR_3	product	yield (%)[b]
1	$SiEt_3$ (**10h**)	 **20**	68
2	$SiMe_2{}^nBu$ (**10i**)	 **21** + **14a**	89 (93/7)[c]
3	$SiMe_2{}^iPr$ (**10j**)	 **22**	88
4	$SiMe_2{}^tBu$ (**10k**)	 **23**	75
5	$SiMe_2Bn$ (**10l**)	 **24**	88
6	$SiMe_2Ph$ (**10m**)	 **25** + **14a**	88[d] (59/41)[e]
7	$SiMePh_2$ (**10n**)	 **25**	79

[a]Reaction conditions: **10** (0.5 mmol), **13a** (1.0 mmol), $[RhCl(cod)]_2$ (0.025 mmol), DABCO (1.0 mmol), dioxane (1 mL), H_2O (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.

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 rhodium-catalyzed 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]

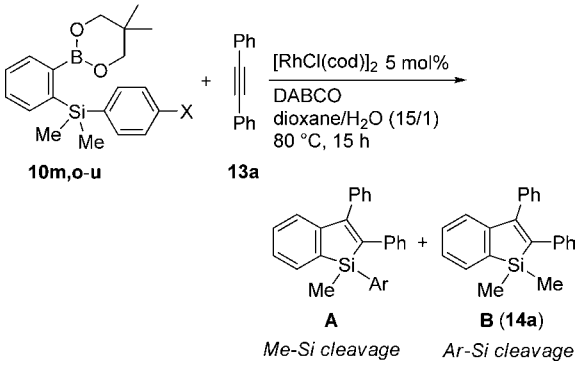
To shed further light on the mechanism of C−Si bond cleavage, we investigated the electronic effect of the Ar group of



(3)

$SiMe_2Ar$ on the selectivity for Me−Si and Ar−Si cleavage. Boronate esters containing a series of *para*-substituted arenes on the silicon atom **10o**−**10u** were prepared and reacted with **13a** under the standard conditions (Table 7). All the

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



entry	X	A + B (%)[b]		A/B[c]
1	NMe_2 (**10o**)	96	(**28** + **14a**)	60/40
2	OBu (**10p**)	77	(**29** + **14a**)	51/49
3	OMe (**10q**)	94	(**30** + **14a**)	50/50
4	Me (**10r**)	89	(**31** + **14a**)	49/51
5	H (**10m**)	88	(**25** + **14a**)	59/41
6	F (**10s**)	82	(**32** + **14a**)	62/38
7	Cl (**10t**)	81	(**33** + **14a**)	67/33
8	CF_3 (**10u**)	75	(**34** + **14a**)	73/27

[a]Reaction conditions: **10** (0.5 mmol), **13a** (1.0 mmol), $[RhCl(cod)]_2$ (0.025 mmol), DABCO (1.0 mmol), dioxane (1 mL), H_2O (67 μL), at 80 °C for 15 h. [b]NMR yield. [c]The ratio of the products was determined by NMR after chromatography.

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 the 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 [**B**/(**A**/2 + **B**)] against the 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 electron-deficient aryl groups resulted in a negative ρ value (−0.28).[62]

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 arenium-

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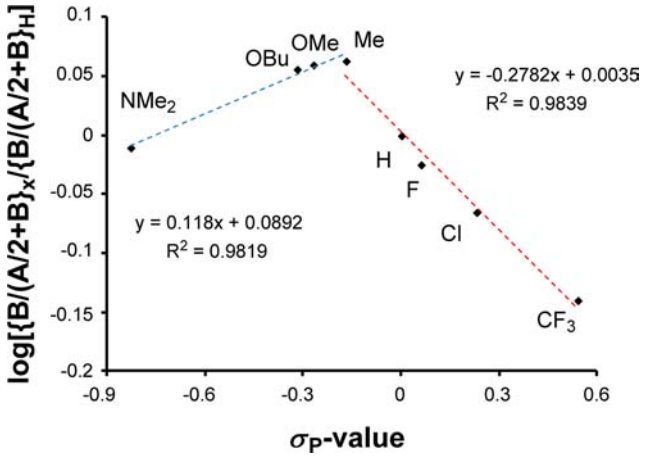
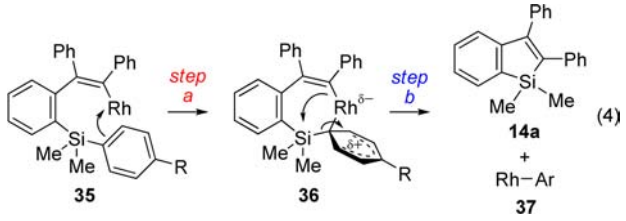


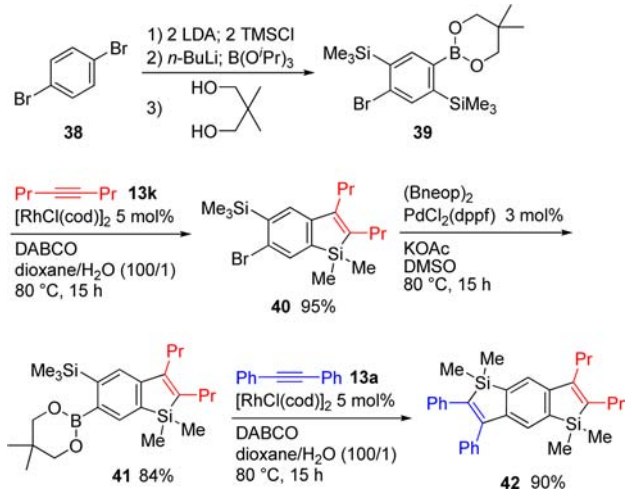
Figure 1. Hammett plot for selectivity of Ar−Si bond cleavage.



like 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 electron-donating 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 electron-donating group decelerates 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 σ_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 envisioned that the synthesis of the 1,5-dihydro-1,5-disila-*s*-indacene skeleton, in which two siloles are fused with a benzene core, would be possible by a twofold 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 applications. 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 (Scheme 10; see SI for details). The boronate ester **39** was then assembled

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



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 1,5-dihydro-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.

As demonstrated in Table 6, when a $SiMe_2R$ 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 Si-chiral compounds using stoichiometric amounts of chiral sources are known,[67] catalytic asymmetric methods for such compounds remain underdeveloped.[68] With regard to catalytic asymmetric synthesis of chiral siloles, there was no example of the synthesis of siloles bearing a silicon stereocenter at the time we initiated our study.[69] Recently, Shintani and Hayashi reported a notable catalytic asymmetric synthesis of silicon-stereogenic dibenzosiloles via palladium-catalyzed 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's[71] 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

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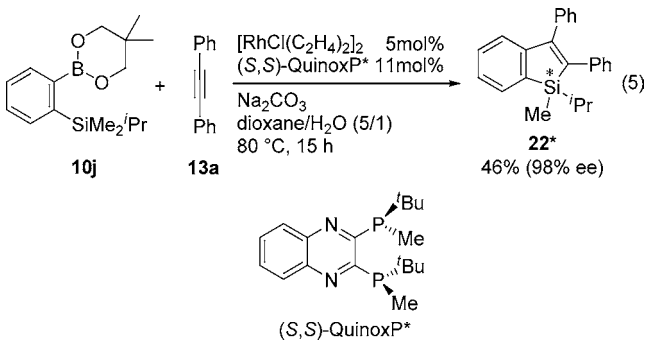

this chiral phosphine ligand, thereby limiting the application of other alkynes to this catalytic asymmetric variant.[72] Although this means there is still much room for improvement, a benzosilole containing stereogenic silicon center was synthesized for the first time by harnessing our own rhodium-catalyzed carbon−silicon bond activation strategy.

CONCLUSIONS

We have developed a rhodium-catalyzed coupling of 2-silylphenylboronic acids with alkynes for the synthesis of benzosilole derivatives. From the preparative viewpoint, our protocol has two notable advantages over classical methods. One possesses 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 the 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 is underway in our laboratory.[73]

ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures and characterization of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley: New York, 2000.
(2) *The Chemistry of Organic Silicon Compounds*, Vol. *1*; Pati, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Vol. *2*; Rappoport, Z., Apeloig, Y., Eds.; 1998.
(3) Colvin, E. W. *Silicon Reagents in Organic Synthesis*; Academic Press: London, 1988.
(4) Weber, W. P. *Silicon Reagents in Organic Synthesis*; Springer: Berlin, 1983.
(5) Yamamoto, K.; Hayashi, T. In *Transition Metals for Organic Synthesis*, 2nd ed.; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, 2004; Vol. *2*, pp 167−191.
(6) Hosomi, A. *Acc. Chem. Res.* **1988**, *21*, 200.
(7) Fleming, I.; Barbero, A.; Walter, D. *Chem. Rev.* **1997**, *97*, 2063.
(8) Franz, A. K.; Woerpel, K. A. *Acc. Chem. Res.* **2000**, *33*, 813.
(9) Reviews: (a) Matsumoto, K.; Oshima, K.; Utimoto, K. *J. Synth. Org. Chem. Jpn.* **1996**, *54*, 289. (b) Hirano, K.; Yorimitsu, H.; Oshima, K. *Chem. Commun.* **2008**, 3234.
(10) (a) Heyduk, A. F.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2003**, *125*, 6366. (b) Yu, M.; Fu, X. *J. Am. Chem. Soc.* **2011**, *133*, 15926.
(11) (a) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371. (b) Tamao, K. *Proc. Jpn. Acad., Ser. B* **2008**, *84*, 123. Hypercoordinate silicon species in cross-couplings: (c) Nakao, Y.; Hiyama, T. *Chem. Soc. Rev.* **2011**, *40*, 4893.
(12) (a) Hatanaka, Y.; Hiyama, T. *Tetrahedron Lett.* **1988**, *29*, 97. Other examples of fluoride-promoted activation of C(alkyl)−Si bonds in cross-coupling processes: (b) Matsuhashi, H.; Kuroboshi, M.; Hatanaka, Y.; Hiyama, T. *Tetrahedron Lett.* **1994**, *35*, 6507. (c) Matsuhashi, H.; Asai, S.; Hirabayashi, K.; Hatanaka, Y.; Mori, A.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 437.
(13) (a) Nakao, Y.; Takeda, M.; Matsumoto, T.; Hiyama, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 4447. The tethered alkoxide can also promote C(sp^2)−Si bond cleavage in cross-coupling processes: (b) Nakao, Y.; Imanaka, H.; Sahoo, A. K.; Yada, A.; Hiyama, T. *J. Am. Chem. Soc.* **2005**, *127*, 6952. (bb) Nakao, Y.; Sahoo, A. K.; Imanaka, H.; Yada, A.; Hiyama, T. *Pure Appl. Chem.* **2006**, *78*, 435. (c) Nakao, Y.; Sahoo, A. K.; Yada, A.; Chen, J.; Hiyama, T. *Sci. Technol. Adv. Mater.* **2006**, *7*, 536. (d) Nakao, Y.; Imanaka, H.; Chen, J.; Yada, A.; Hiyama, T. *J. Organomet. Chem.* **2007**, *692*, 585. (e) Nakao, Y.; Ebata, S.; Chen, J.; Imanaka, H.; Hiyama, T. *Chem. Lett.* **2007**, *36*, 606. (f) Nakao, Y.; Chen, J.; Imanaka, H.; Hiyama, T.; Ichikawa, Y.; Duan, W.-L.; Shintani, R.; Hayashi, T. *J. Am. Chem. Soc.* **2007**, *129*, 9137. (g) Nakao, Y.; Chen, J.; Tanaka, M.; Hiyama, T. *J.*

Am. Chem. Soc. **2007**, *129*, 11694. (h) Shintani, R.; Ichikawa, Y.; Hayashi, T.; Chen, J.; Nakao, Y.; Hiyama, T. *Org. Lett.* **2007**, *9*, 4643. (i) Nakao, Y.; Takeda, M.; Chen, J.; Hiyama, T.; Ichikawa, Y.; Shintani, R.; Hayashi, T. *Chem. Lett.* **2008**, *37*, 290. (j) Nakao, Y.; Takeda, M.; Chen, J.; Hiyama, T. *Synlett* **2008**, 774. (k) Chen, J.; Tanaka, M.; Sahoo, A. K.; Takeda, M.; Yada, A.; Nakao, Y.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **2010**, *83*, 554. (l) Tang, S.; Takeda, M.; Nakao, Y.; Hiyama, T. *Chem. Commun.* **2011**, *47*, 307.

(14) (a) Rauf, W.; Brown, J. M. *Angew. Chem., Int. Ed.* **2008**, *47*, 4228. A similar strategy for C(sp^2)−Si activation: (b) Shindo, M.; Matsumoto, K.; Shishido, K. *Synlett* **2005**, 176. (c) Matsumoto, K.; Shindo, M. *Adv. Synth. Catal.* **2012**, *354*, 642.

(15) Selected examples: (a) Yamamoto, Y.; Takeda, Y.; Akiba, K.-y. *Tetrahedron Lett.* **1989**, *30*, 725. (b) Kirmse, W.; Sollenbohmer, F. *J. Chem. Soc., Chem. Commun.* **1989**, 774. (c) Eaborn, C.; Hitchcock, P. B. *J. Chem. Soc., Perkin Trans. 2* **1991**, 1137. (d) Taguchi, H.; Ghoroku, K.; Tadaki, M.; Tsubouchi, A.; Takeda, T. *Org. Lett.* **2001**, *3*, 3811. (e) Tipparaju, S. K.; Mandal, S. K.; Sur, S.; Puranik, V. G.; Sarkar, A. *Chem. Commun.* **2002**, 1924. (f) Horie, H.; Kajita, Y.; Matsubara, S. *Chem. Lett.* **2009**, *38*, 116. (g) Tsubouchi, A.; Matsuda, H.; Kira, T.; Takeda, T. *Chem. Lett.* **2009**, *38*, 1180.

(16) Shindo, M.; Matsumoto, K.; Shishido, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 104.

(17) (a) Seiser, T.; Cramer, N. *Angew. Chem., Int. Ed.* **2010**, *49*, 10163. (b) Cramer, N.; Seiser, T. *Synlett* **2011**, 449.

(18) Early examples: (a) Wittenberg, D.; Gilman, H. *J. Am. Chem. Soc.* **1958**, *80*, 2677. (b) Gilman, H.; Gorsich, R. D. *J. Am. Chem. Soc.* **1958**, *80*, 3243. (c) Ishikawa, M.; Tabohashi, T.; Sugisawa, H.; Nishimura, K.; Kumada, M. *J. Organomet. Chem.* **1983**, *250*, 109.

(19) van Klink, G. P. M.; de Boer, H. J. R.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F.; Spek, A. L. *Organometallics* **2002**, *21*, 2119.

(20) (a) Wang, Z.; Fang, H.; Xi, Z. *Tetrahedron Lett.* **2005**, *46*, 499. (b) Xi, Z. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 1021. (c) Wang, C.; Luo, Q.; Sun, H.; Guo, X.; Xi, Z. *J. Am. Chem. Soc.* **2007**, *129*, 3094. (d) Yu, N.; Wang, C.; Zhao, F.; Liu, L.; Zhang, W.-X.; Xi, Z. *Chem.—Eur. J.* **2008**, *14*, 5670. (e) Luo, Q.; Wang, C.; Gu, L.; Zhang, W.-X.; Xi, Z. *Chem.—Asian J.* **2010**, *5*, 1120.

(21) Related reports from other groups: (a) Hudrlik, P. F.; Dai, D.; Hudrlik, A. M. *J. Organomet. Chem.* **2006**, *691*, 1257. (b) Wu, W.; Xu, L.; Shi, J.; Qin, X.; Wang, H. *Organometallics* **2009**, *28*, 1961. (c) Zhao, J.; Qiu, D.; Shi, J.; Wang, H. *J. Org. Chem.* **2012**, *77*, 2929.

(22) Shirakawa, E.; Masui, S.; Narui, R.; Watabe, R.; Ikeda, D.; Hayashi, T. *Chem. Commun.* **2011**, *47*, 9714.

(23) Ojima, I.; Fracchiolla, D. A.; Donovan, R. J.; Banerji, P. *J. Org. Chem.* **1994**, *59*, 7594.

(24) (a) Tobisu, M.; Onoe, M.; Kita, Y.; Chatani, N. *J. Am. Chem. Soc.* **2009**, *131*, 7506. Related germole synthesis: (b) Tobisu, M.; Baba, K.; Chatani, N. *Org. Lett.* **2011**, *13*, 3282.

(25) (a) Liang, Y.; Zhang, S.; Xi, Z. *J. Am. Chem. Soc.* **2011**, *133*, 9204. (b) Liang, Y.; Geng, W.; Wei, J.; Xi, Z. *Angew. Chem., Int. Ed.* **2012**, *51*, 1934.

(26) Matsuda, T.; Suda, Y.; Fujisaki, Y. *Synlett* **2011**, 813.

(27) Reviews: (a) Yamaguchi, S.; Tamao, K. *J. Chem. Soc., Dalton Trans.* **1998**, 3693. (b) Yamaguchi, S.; Tamao, K. *J. Organomet. Chem.* **2002**, *653*, 223. (c) Hissler, M.; Dyer, P. W.; Reau, R. *Coord. Chem. Rev.* **2003**, *244*, 1. (d) Chen, J.; Cao, Y. *Macromol. Rapid Commun.* **2007**, *28*, 1714. (e) Liu, J.; Lam, J. W. Y.; Tang, B. Z. *J. Inorg. Organomet. Polym. Mater.* **2009**, *19*, 249. (f) Corey, J. Y. *Adv. Organomet. Chem.* **2011**, *59*, 1.

(28) Corey, J. Y. *Adv. Organomet. Chem.* **2011**, *59*, 181.

(29) (a) Wong, W. W. H.; Holmes, A. B. *Adv. Polym. Sci.* **2008**, *212*, 85. (b) Shimizu, M.; Tatsumi, H.; Mochida, K.; Oda, K.; Hiyama, T. *Chem.—Asian J.* **2008**, *3*, 1238. (c) Wong, W. W. H.; Hooper, J. F.; Holmes, A. B. *Aust. J. Chem.* **2009**, *62*, 393. (d) Ohshita, J. *Macromol. Chem. Phys.* **2009**, *210*, 1360. (e) Shimizu, M.; Mochida, K.; Katoh, M.; Hiyama, T. *J. Phys. Chem. C* **2010**, *114*, 10004. (f) Shimizu, M.; Mochida, K.; Hiyama, T. *J. Phys. Chem. C* **2011**, *115*, 11265. (g) Shimizu, M.; Hiyama, T. *Synlett* **2012**, *23*, 973.

(30) (a) Ilies, L.; Tsuji, H.; Sato, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2008**, *130*, 4240. (b) Ilies, L.; Tsuji, H.; Nakamura, E. *Org. Lett.* **2009**, *11*, 3966. (c) Ilies, L.; Sato, Y.; Mitsui, C.; Tsuji, H.; Nakamura, E. *Chem.—Asian J.* **2010**, *5*, 1376.

(31) (a) Tamao, K.; Uchida, M.; Izumizawa, T.; Furukawa, K.; Yamaguchi, S. *J. Am. Chem. Soc.* **1996**, *118*, 11974. (b) Uchida, M.; Izumizawa, T.; Nakano, T.; Yamaguchi, S.; Tamao, K.; Furukawa, K. *Chem. Mater.* **2001**, *13*, 2680. (c) Chen, J.; Law, C. C. W.; Lam, J. W. Y.; Dong, Y.; Lo, S. M. F.; Williams, I. D.; Zhu, D.; Tang, B. Z. *Chem. Mater.* **2003**, *15*, 1535. (d) Lee, S. H.; Jang, B.-B.; Kafafi, Z. H. *J. Am. Chem. Soc.* **2005**, *127*, 9071. (e) Zhan, X.; Haldi, A.; Risko, C.; Chan, C. K.; Zhao, W.; Timofeeva, T. V.; Korlyukov, A.; Antipin, M. Y.; Montgomery, S.; Thompson, E.; An, Z.; Domercq, B.; Barlow, S.; Kahn, A.; Kippelen, B.; Bredas, J.-L.; Marder, S. R. *J. Mater. Chem.* **2008**, *18*, 3157. (f) Li, L.; Xu, C.; Li, S. *Tetrahedron Lett.* **2010**, *51*, 622. (g) Chen, J.; Xie, Z.; Lam, J. W. Y.; Law, C. C. W.; Tang, B. Z. *Macromolecules* **2003**, *36*, 1108. (h) Liu, M. S.; Luo, J.; Jen, A. K. Y. *Chem. Mater.* **2003**, *15*, 3496. (i) Chan, K. L.; McKiernan, M. J.; Towns, C. R.; Holmes, A. B. *J. Am. Chem. Soc.* **2005**, *127*, 7662. (j) Wang, F.; Luo, J.; Chen, J.; Huang, F.; Cao, Y. *Polymer* **2005**, *46*, 8422. (k) Wang, E.; Li, C.; Mo, Y.; Zhang, Y.; Ma, G.; Shi, W.; Peng, J.; Yang, W.; Cao, Y. *J. Mater. Chem.* **2006**, *16*, 4133. (l) Wang, E.; Li, C.; Zhuang, W.; Peng, J.; Cao, Y. *J. Mater. Chem.* **2008**, *18*, 797. (m) Liu, Z.; Zou, J.; Chen, J.; Huang, L.; Peng, J.; Cao, Y. *Polymer* **2008**, *49*, 1604.

(32) (a) Wang, F.; Luo, J.; Yang, K.; Chen, J.; Huang, F.; Cao, Y. *Macromolecules* **2005**, *38*, 2253. (b) Usta, H.; Lu, G.; Facchetti, A.; Marks, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 9034. (c) Lu, G.; Usta, H.; Risko, C.; Wang, L.; Facchetti, A.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **2008**, *130*, 7670. (d) Beaujuge, P. M.; Pisula, W.; Tsao, H. N.; Ellinger, S.; Müllen, K.; Reynolds, J. R. *J. Am. Chem. Soc.* **2009**, *131*, 7514.

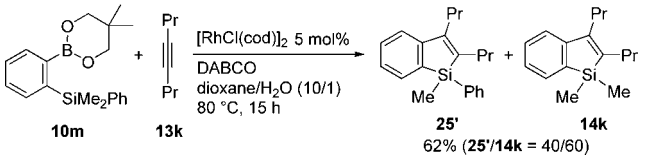
(33) (a) Mi, B.; Dong, Y.; Li, Z.; Lam, J. W. Y.; Häussler, M.; Sung, H. H. Y.; Kwok, H. S.; Dong, Y.; Williams, I. D.; Liu, Y.; Luo, Y.; Shuai, Z.; Zhu, D.; Tang, B. Z. *Chem. Commun.* **2005**, 3583. (b) Hou, J.; Chen, H.-Y.; Zhang, S.; Li, G.; Yang, Y. *J. Am. Chem. Soc.* **2008**, *130*, 16144. (c) Duan, C.; Cai, W.; Huang, F.; Zhang, J.; Wang, M.; Yang, T.; Zhong, C.; Gong, X.; Cao, Y. *Macromolecules* **2010**, *43*, 5262. (d) Chu, T.-Y.; Lu, J.; Beaupré, S.; Zhang, Y.; Pouliot, J.-R. m.; Wakim, S.; Zhou, J.; Leclerc, M.; Li, Z.; Ding, J.; Tao, Y. *J. Am. Chem. Soc.* **2011**, *133*, 4250. (e) Song, J.; Du, C.; Li, C.; Bo, Z. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 4267. (f) Welch, G. C.; Perez, L. A.; Hoven, C. V.; Zhang, Y.; Dang, X.-D.; Sharenko, A.; Toney, M. F.; Kramer, E. J.; Nguyen, T.-Q.; Bazan, G. C. *J. Mater. Chem.* **2011**, *21*, 12700. (g) Wang, H.; Gao, J.; Tong, W.; Qian, Q.; Lin, K.; Liu, F. *Polym. Chem.* **2012**, *3*, 2794.

(34) (a) Sohn, H.; Sailor, M. J.; Magde, D.; Trogler, W. C. *J. Am. Chem. Soc.* **2003**, *125*, 3821. (b) Sanchez, J. C.; DiPasquale, A. G.; Rheingold, A. L.; Trogler, W. C. *Chem. Mater.* **2007**, *19*, 6459. (c) Sanchez, J. C.; Urbas, S. A.; Toal, S. J.; DiPasquale, A. G.; Rheingold, A. L.; Trogler, W. C. *Macromolecules* **2008**, *41*, 1237. (d) Liu, J.; Zhong, Y.; Lam, J. W. Y.; Lu, P.; Hong, Y.; Yu, Y.; Yue, Y.; Faisal, M.; Sung, H. H. Y.; Williams, I. D.; Wong, K. S.; Tang, B. Z. *Macromolecules* **2010**, *43*, 4921. (e) Yang, J.; Aschemeyer, S.; Martinez, H. P.; Trogler, W. C. *Chem. Commun.* **2010**, *46*, 6804. (f) Shen, X.; Zhang, G.; Zhang, D. *Org. Lett.* **2012**, *14*, 1744. (g) Zhang, L.-H.; Jiang, T.; Wu, L.-B.; Wan, J.-H.; Chen, C.-H.; Pei, Y.-B.; Lu, H.; Deng, Y.; Bian, G.-F.; Qiu, H.-Y.; Lai, G.-Q. *Chem.—Asian J.* **2012**, *7*, 1583.

(35) For examples: (a) Tamao, K.; Yamaguchi, S.; Shiro, M. *J. Am. Chem. Soc.* **1994**, *116*, 11715. (b) Yamaguchi, S.; Xu, C.; Tamao, K. *J. Am. Chem. Soc.* **2003**, *125*, 13662. (c) Xu, C.; Wakamiya, A.; Yamaguchi, S. *Org. Lett.* **2004**, *6*, 3707. (d) Xu, C.; Wakamiya, A.; Yamaguchi, S. *J. Am. Chem. Soc.* **2005**, *127*, 1638.

(36) For examples: (a) Xi, C.; Huo, S.; Afifi, T. H.; Hara, R.; Takashashi, T. *Tetrahedron Lett.* **1997**, *38*, 4099. (b) Mouri, K.; Wakamiya, A.; Yamada, H.; Kajiwara, T.; Yamaguchi, S. *Org. Lett.* **2006**, *9*, 93. (c) Chen, R.-F.; Fan, Q.-L.; Zheng, C.; Huang, W. *Org. Lett.* **2006**, *8*, 203. (d) Li, L.; Xiang, J.; Xu, C. *Org. Lett.* **2007**, *9*, 4877. See also refs 19−22 and 30.

(37) (a) Wrackmeyer, B. *Coord. Chem. Rev.* **1995**, *145*, 125. (b) Wrackmeyer, B. *Heteroat. Chem.* **2006**, *17*, 188. (c) Dierker, G.; Ugolotti, J.; Kehr, G.; Fröhlich, R.; Erker, G. *Adv. Synth. Catal.* **2009**, *351*, 1080.
(38) (a) Furukawa, S.; Kobayashi, J.; Kawashima, T. *J. Am. Chem. Soc.* **2009**, *131*, 14192. (b) Furukawa, S.; Kobayashi, J.; Kawashima, T. *Dalton Trans.* **2010**, *39*, 9329.
(39) (a) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 9263. (b) Ishikawa, M.; Sugisawa, H.; Harata, O.; Kumada, M. *J. Organomet. Chem.* **1981**, *217*, 43. (c) Ishikawa, M.; Matsuzawa, S.; Higuchi, T.; Kamitori, S.; Hirotsu, K. *Organometallics* **1985**, *4*, 2040. (d) Tamao, K.; Yamaguchi, S.; Shiozaki, M.; Nakagawa, Y.; Ito, Y. *J. Am. Chem. Soc.* **1992**, *114*, 5867.
(40) (a) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Organomet. Chem.* **1975**, *86*, C27. (b) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3879. (c) Seyferth, D.; Duncan, D. P.; Vick, S. C. *J. Organomet. Chem.* **1977**, *125*, C5. (d) Seyferth, D.; Vick, S. C.; Shannon, M. L.; Lim, T. F. O.; Duncan, D. P. *J. Organomet. Chem.* **1977**, *135*, C37. (e) Seyferth, D.; Shannon, M. L.; Vick, S. C.; Lim, T. F. O. *Organometallics* **1985**, *4*, 57. (f) Ikenaga, K.; Hiramatsu, K.; Nasaka, N.; Matsumoto, S. *J. Org. Chem.* **1993**, *58*, 5045. (g) Palmer, W. S.; Woerpel, K. A. *Organometallics* **1997**, *16*, 1097. (h) Palmer, W. S.; Woerpel, K. A. *Organometallics* **1997**, *16*, 4824. (i) Palmer, W. S.; Woerpel, K. A. *Organometallics* **2001**, *20*, 3691. (j) Ohmura, T.; Masuda, K.; Suginome, M. *J. Am. Chem. Soc.* **2008**, *130*, 1526. (k) Shimizu, M.; Mochida, K.; Hiyama, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 9760. (l) Mochida, K.; Shimizu, M.; Hiyama, T. *J. Am. Chem. Soc.* **2009**, *131*, 8350. (m) Yabusaki, Y.; Ohshima, N.; Kondo, H.; Kusamoto, T.; Yamanoi, Y.; Nishihara, H. *Chem.—Eur. J.* **2010**, *16*, 5581. (n) Ouyang, K.; Liang, Y.; Xi, Z. *Org. Lett.* **2012**, *14*, 4572.
(41) (a) Matsuda, T.; Kadowaki, S.; Goya, T.; Murakami, M. *Org. Lett.* **2006**, *9*, 133. (b) Shibata, T.; Uchiyama, T.; Yoshinami, Y.; Takayasu, S.; Tsuchikama, K.; Endo, K. *Chem. Commun.* **2012**, *48*, 1311.
(42) (a) Matsuda, T.; Kadowaki, S.; Murakami, M. *Chem. Commun.* **2007**, 2627. (b) Matsuda, T.; Yamaguchi, Y.; Murakami, M. *Synlett* **2008**, 561. (c) Matsuda, T.; Yamaguchi, Y.; Ishida, N.; Murakami, M. *Synlett* **2010**, 2743.
(43) (a) Matsuda, T.; Kadowaki, S.; Yamaguchi, Y.; Murakami, M. *Chem. Commun.* **2008**, 2744. (b) Matsuda, T.; Yamaguchi, Y.; Shigeno, M.; Sato, S.; Murakami, M. *Chem. Commun.* **2011**, *47*, 8697.
(44) Ureshino, T.; Yoshida, T.; Kuninobu, Y.; Takai, K. *J. Am. Chem. Soc.* **2010**, *132*, 14324.
(45) (a) Tobisu, M.; Kita, Y.; Chatani, N. *J. Am. Chem. Soc.* **2006**, *128*, 8152. (b) Tobisu, M.; Kita, Y.; Ano, Y.; Chatani, N. *J. Am. Chem. Soc.* **2008**, *130*, 15982. (c) Tobisu, M.; Nakamura, R.; Kita, Y.; Chatani, N. *J. Am. Chem. Soc.* **2009**, *131*, 3174. (d) Tobisu, M.; Nakamura, R.; Kita, Y.; Chatani, N. *Bull. Korean Chem. Soc.* **2010**, *31*, 582. (e) Kita, Y.; Tobisu, M.; Chatani, N. *Org. Lett.* **2010**, *12*, 1864. A related reaction using diboron: (f) Tobisu, M.; Kinuta, H.; Kita, Y.; Rémond, E.; Chatani, N. *J. Am. Chem. Soc.* **2012**, *134*, 115.
(46) (a) Fagnou, K.; Lautens, M. *Chem. Rev.* **2003**, *103*, 169. (b) Hayashi, T.; Yamasaki, K. *Chem. Rev.* **2003**, *103*, 2829. (c) Miura, T.; Murakami, M. *Chem. Commun.* **2007**, 217.
(47) (a) Hayashi, T.; Inoue, K.; Taniguchi, N.; Ogasawara, M. *J. Am. Chem. Soc.* **2001**, *123*, 9918. (b) Zhang, W.; Liu, M.; Wu, H.; Ding, J.; Cheng, J. *Tetrahedron Lett.* **2008**, *49*, 5214.
(48) (a) Harada, Y.; Nakanishi, J.; Fujihara, H.; Tobisu, M.; Fukumoto, Y.; Chatani, N. *J. Am. Chem. Soc.* **2007**, *129*, 5766. (b) Miyamoto, M.; Harada, Y.; Tobisu, M.; Chatani, N. *Org. Lett.* **2008**, *10*, 2975. (c) Morimoto, T.; Yamasaki, K.; Hirano, A.; Tsutsumi, K.; Kagawa, N.; Kakiuchi, K.; Harada, Y.; Fukumoto, Y.; Chatani, N.; Nishioka, T. *Org. Lett.* **2009**, *11*, 1777.
(49) Shimada, M.; Harumashi, T.; Miura, T.; Murakami, M. *Chem.—Asian J.* **2008**, *3*, 1035.
(50) All the silole derivatives in Table 3, except for **14a**, **14p**, and **14r**, are new compounds, whose synthesis was enabled by the development of the present method.
(51) (a) Yamaguchi, S.; Endo, T.; Uchida, M.; Izumizawa, T.; Furukawa, K.; Tamao, K. *Chem.—Eur. J.* **2000**, *6*, 1683. (b) Zhan, X.; Barlow, S.; Marder, S. R. *Chem. Commun.* **2009**, 1948.
(52) Ishiyama, T.; Miyaura, N. *Chem. Rec.* **2004**, *3*, 271.
(53) (a) Cho, J.-Y.; Tse, M. K.; Holmes, D.; Maleczka, R. E.; Smith, M. R., III; Ishiyama, T.; Takagi, J.; Ishida, K.; Miyaura, N.; Anastasi, N. R.; Hartwig, J. F.; Kellogg, R. M. *Chemtracts* **2002**, *15*, 195. (b) Mkhalid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*, 890.
(54) (a) Suginome, M.; Nakamura, H.; Ito, Y. *Chem. Commun.* **1996**, 2777. (b) Onozawa, S.; Hatanaka, Y.; Tanaka, M. *Chem. Commun.* **1997**, 1229. (c) Suginome, M.; Matsuda, T.; Nakamura, H.; Ito, Y. *Tetrahedron* **1999**, *55*, 8787. (d) Da Silva, J. C. A.; Birot, M.; Pillot, J.-P.; Pétraud, M. *J. Organomet. Chem.* **2002**, *646*, 179. (e) Suginome, M.; Noguchi, H.; Hasui, T.; Murakami, M. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 323. (f) Ohmura, T.; Suginome, M. *Bull. Chem. Soc. Jpn.* **2009**, *82*, 29.
(55) Ohmura, T.; Oshima, K.; Taniguchi, H.; Suginome, M. *J. Am. Chem. Soc.* **2010**, *132*, 12194.
(56) (a) Kloek, S. M.; Heinekey, D. M.; Goldberg, K. I. *Angew. Chem., Int. Ed.* **2007**, *46*, 4736. (b) Hanson, S. K.; Heinekey, D. M.; Goldberg, K. I. *Organometallics* **2008**, *27*, 1454. (c) Slaney, M. E.; Anderson, D. J.; Ferguson, M. J.; McDonald, R.; Cowie, M. *Organometallics* **2012**, *31*, 2286.
(57) Ma, S.; Gu, Z. *Angew. Chem., Int. Ed.* **2005**, *44*, 7512.
(58) The selectivity of the product derived from **10m** is also affected by the substituent on the alkyne. When 4-octyne (**13k**) was used in place of **13a**, the ratio of the products (**25′**/**14k**) was 40/60.



(59) Interestingly, a methyl group is exclusively cleaved over a phenyl group in a similar palladium-catalyzed reaction reported by Xi, suggesting that the nature of the intermediate(s) are substantially different between palladium and rhodium. See ref 25.
(60) An oxidative addition/reductive elimination sequence via a Rh(III) intermediate could be an alternative mechanism. In general, these pathways are difficult to discriminate experimentally: Hartwig, J. F. *Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 2010; p 285.
(61) The ratio of **A**/**B** was invariable during the course of the reaction.
(62) This outcome is also inconsistent with the pentacoordinated silicate mechanism, in which the aryl group bearing an electron-withdrawing group is likely to be cleaved more facilely rather than an alkyl group. François, C.; Boddaert, T.; Durandetti, M.; Querolle, O.; Van Hijfte, L.; Meerpoel, L.; Angibaud, P.; Maddaluno, J. *Org. Lett.* **2012**, *14*, 2074.
(63) Anslyn, E. K.; Dougherty, D. A. *Modern Physical Organic Chemistry*; University Science Book: Sausalito, CA, 2006; p 448.
(64) General reviews for S_EAr of arylsilanes: (a) Eaborn, C. *J. Organomet. Chem.* **1975**, *100*, 43. (b) Bennetau, B.; Dunogues, J. *Synlett* **1993**, 171. The S_EAr mechanism is proposed in the transmetalation process of hypercoordinated silicon species: (c) Hatanaka, Y.; Goda, K.; Okahara, Y.; Hiyama, T. *Tetrahedron* **1994**, *50*, 8301. (d) Denmark, S. E.; Smith, R. C.; Chang, W.-T. T. *Tetrahedron* **2011**, *67*, 4391.
(65) The σ_p rather than σ^+ showed better correlation in our Hammett study. Thus, we suggest that the intermediate **36** is likely to possess a partially positive charge, rather than a discrete arenium cation. See the SI for details.
(66) (a) Yamaguchi, S.; Xu, C.; Okamoto, T. *Pure Appl. Chem.* **2006**, *78*, 721. (b) Fukazawa, A.; Yamaguchi, S. *Chem.—Asian J.* **2009**, *4*, 1386. (c) Wu, J.-S.; Cheng, Y.-J.; Lin, T.-Y.; Chang, C.-Y.; Shih, P.-I.; Hsu, C.-S. *Adv. Funct. Mater.* **2012**, *22*, 1711.
(67) Reviews: (a) Oestreich, M. *Synlett* **2007**, 1629. (b) Weickgenannt, A.; Mewald, M.; Oestreich, M. *Org. Biomol. Chem.* **2010**, *8*,

1497. (c) Xu, L.-W.; Li, L.; Lai, G.-Q.; Jiang, J.-X. *Chem. Soc. Rev.* **2011**, *40*, 1777. Selected recent examples: (d) Tomooka, K.; Nakazaki, A.; Nakai, T. *J. Am. Chem. Soc.* **2000**, *122*, 408. (e) Strohmann, C.; Hornig, J.; Auer, D. *Chem. Commun.* **2002**, 766. (f) Trzoss, M.; Shao, J.; Bienz, S. *Tetrahedron: Asymmetry* **2004**, *15*, 1501. (g) Rendler, S.; Auer, G.; Oestreich, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 7620. (h) Rendler, S.; Auer, G.; Keller, M.; Oestreich, M. *Adv. Synth. Catal.* **2006**, *348*, 1171. (i) Rendler, S.; Oestreich, M.; Butts, C. P.; Lloyd-Jones, G. C. *J. Am. Chem. Soc.* **2007**, *129*, 502. (j) Igawa, K.; Takada, J.; Shimono, T.; Tomooka, K. *J. Am. Chem. Soc.* **2008**, *130*, 16132 (one catalytic example is included). (k) Oka, N.; Nakamura, M.; Soeda, N.; Wada, T. *J. Organomet. Chem.* **2009**, *694*, 2171. (l) Däschlein, C.; Gessner, V. H.; Strohmann, C. *Chem.—Eur. J.* **2010**, *16*, 4048. (m) Igawa, K.; Kokan, N.; Tomooka, K. *Angew. Chem., Int. Ed.* **2010**, *49*, 728. (n) Weickgenannt, A.; Mohr, J.; Oestreich, M. *Tetrahedron* **2012**, *68*, 3468.

(68) (a) Corriu, R. J. P.; Moreau, J. J. E. *Tetrahedron Lett.* **1973**, *14*, 4469. (b) Hayashi, T.; Yamamoto, K.; Kumada, M. *Tetrahedron Lett.* **1974**, *15*, 331. (c) Corriu, R. J. P.; Moreau, J. J. E. *J. Organomet. Chem.* **1974**, *64*, C51. (d) Corriu, R. J. P.; Moreau, J. J. E. *J. Organomet. Chem.* **1975**, *85*, 19. (e) Corriu, R. J. P.; Moreau, J. J. E. *J. Organomet. Chem.* **1976**, *120*, 337. (f) Ohta, T.; Ito, M.; Tsuneto, A.; Takaya, H. *J. Chem. Soc., Chem. Commun.* **1994**, 2525. (g) Schmidt, D. R.; O'Malle, S. J.; Leighton, J. L. *J. Am. Chem. Soc.* **2003**, *125*, 1190. (h) Yasutomi, Y.; Suematsu, H.; Katsuki, T. *J. Am. Chem. Soc.* **2010**, *132*, 4510. (i) Shintani, R.; Moriya, K.; Hayashi, T. *J. Am. Chem. Soc.* **2011**, *133*, 16440. (j) Shintani, R.; Moriya, K.; Hayashi, T. *Org. Lett.* **2012**, *14*, 2902. (k) Kurihara, Y.; Nishizawa, M.; Yamanoi, Y.; Nishihara, H. *Chem. Commun.* **2012**, *48*, 11564. (l) Igawa, K.; Yoshihiro, D.; Ichikawa, N.; Kokan, N.; Tomooka, K. *Angew. Chem., Int. Ed.* **2012**, DOI: 10.1002/anie.201207361.

(69) A few axially chiral silole derivatives are known: (a) Yasuike, S.; Iida, T.; Okajima, S.; Yamaguchi, K.; Seki, H.; Kurita, J. *Tetrahedron* **2001**, *57*, 10047. (b) Yamauchi, K.; Tamura, N.; Seiki, T.; Kuninobu, Y.; Takai, K. *Chemical Society Japan Annual Meeting* **2012**, 1C8−45. Related axially chiral silacycle: (c) Tamao, K.; Nakamura, K.; Ishii, H.; Yamaguchi, S.; Shiro, M. *J. Am. Chem. Soc.* **1996**, *118*, 12469. Helically chiral siloles (silahelicenes) have also been reported; see ref 41b.

(70) Shintani, R.; Otomo, H.; Ota, K.; Hayashi, T. *J. Am. Chem. Soc.* **2012**, *134*, 7305.

(71) Imamoto, T.; Sugita, K.; Yoshida, K. *J. Am. Chem. Soc.* **2005**, *127*, 11934.

(72) 4-Octyne and 1-phenyl-1-hexyne afforded a complicated mixture when exposed to the conditions shown in eq 5.

(73) During the reviewing process of our manuscript, catalytic Ar−Si bond activation through intramolecular substitution by an oxygen-based nucleophile has been reported: (a) Shintani, R.; Maciver, E. E.; Tamakuni, F.; Hayashi, T. *J. Am. Chem. Soc.* **2012**, *134*, 16955 (asymmetric). (b) Fujihara, T.; Tani, Y.; Semba, K.; Terao, J.; Tsuji, Y. *Angew. Chem., Int. Ed.* **2012**, *51*, 11487.