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COMMUNICATION

Rhodium-Catalysed Synthesis of Multi-Substituted Silylindenes from Aryl Alkynes and Hydrosilanes via C-H Bond Activation

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We successfully developed a first rhodium-catalysed synthesis of multi-substituted silylindenes from 2 equivalents of aryl alkynes and 1 equivalent of hydrosilanes in moderate to good yields via C-H bond activation. The silyl groups of the obtained silylindenes could be converted to several other functional groups.

Organosilicon compounds are important reagents,¹ organic functional materials,² and bioactive molecules.³ Therefore, many reactions for the synthesis of organosilicon compounds have been developed.⁴ Among them, transition metal-catalysed hydrosilylation of alkynes is well established for synthesizing alkenylsilanes (Fig. 1a).⁵

We are interested in developing synthetic reactions of heteroatom-containing π -conjugated molecules via C-H bond activation, and have reported several reactions,^{6,7} such as the synthesis of dibenzosilole derivatives⁸ and dibenzosilole equivalents with a Lewis acid-base interaction.⁹ We considered that if C-H bond activation occurs at the phenyl group on the silicon atom of an alkenyl-metal intermediate **A** before reductive elimination of the catalyst from intermediate **A**, benzosiloles would be formed (Fig. 1b). Surprisingly, silylindenes and alkenylsilanes were obtained, but the attempted benzosiloles were not produced at all (Fig. 1c).¹⁰ We were interested in forming silylindenes because rhodium complexes are well-known catalysts for hydrosilylation of alkynes with hydrosilanes (Fig. 1a),⁵ and this is the first example of the synthesis of silylindenes from aryl alkynes and hydrosilanes.

We first investigated reactions with several transition metal complexes and ligands using diphenylacetylene (**1a**) and dimethyl(phenyl)silane (**2a**) as substrates (Table 1). Reactions between **1a** and **2a** did not produce silylindene **3a** in the presence of catalytic amounts of a manganese, rhenium, iron, ruthenium, or cobalt catalyst in toluene at 150 °C for 24 h (entries 1-7). When the reaction was performed using Wilkinson's catalyst, silylindene **3a**, which was formed from 2 equivalents of **1a** and 1 equivalent of **2a**, was obtained in 46% yield (entry 8).¹¹⁻¹⁴ Silylindenes are used as ligands of catalysts for olefin polymerization,¹⁵ and several syntheses of silylindenes have been reported.¹⁶ Most of these, however, (e.g., 1*H*-inden-3-yltrimethylsilane) decompose easily due to the formation of indanones upon oxidation with oxygen.¹⁷

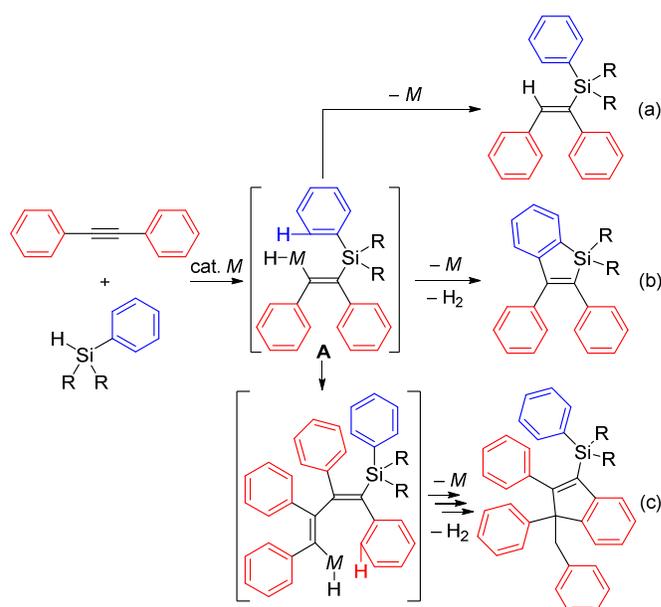
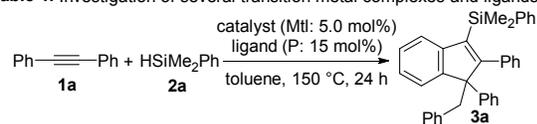


Fig. 1 Possible organosilicon compounds derived from alkynes and hydrosilanes.

Therefore, examples of isolation of 3-silylindenes are still rare. When the catalytic system was changed to a mixture of $[\text{RhCl}(\text{cod})_2]$ and PPh_3 , the yield of **3a** slightly increased and we selected this combination as the best catalytic system (entry 9). In the case of trialkylphosphines, such as tricyclohexylphosphine and trimethylphosphine, the yields of **3a** drastically decreased (entries 10 and 11). Reactions using an electron-deficient triarylphosphine or PPh_3 gave similar results, but the yield of **3a** decreased to 30% when an electron-rich triarylphosphine was used (entries 12 and 13). When the reaction was performed using a bidentate phosphine ligand, such as DPPE (1,2-bis(diphenylphosphino)ethane), **3a** was not formed at all (entry 14). The yield of **3a** was moderate when a mixture of a rhodium olefin complex and PPh_3 was used (entry 15). A cationic rhodium complex and $[\text{Cp}^*\text{RhCl}_2]_2$ gave unsatisfactory results (entries 16 and 17). Iridium complexes did not provide **3a** (entries 18 and 19).

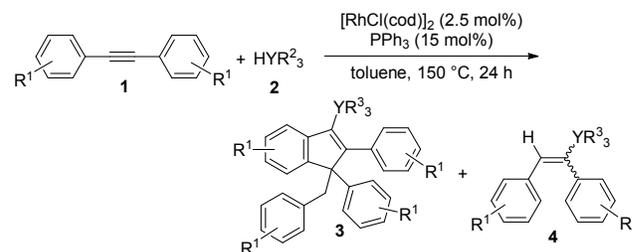
Table 1. Investigation of several transition metal complexes and ligands^a

Entry	Catalyst	Ligand	Yield (%) ^b
1	Mn ₂ (CO) ₁₀	none	<1
2	Re ₂ (CO) ₁₀	none	<1
3	Fe(CO) ₅	none	<1
4	Ru ₃ (CO) ₁₂	none	<1
5	[RuCl ₂ (<i>p</i> -cymene)] ₂	none	<1
6	Co ₂ (CO) ₈	none	<1
7	CoCl(PPh ₃) ₃	none	<1
8	RhCl(PPh ₃) ₃	none	46
9	[RhCl(cod)] ₂	PPh ₃	50 (47) ^{c,d}
10	[RhCl(cod)] ₂	PCy ₃	21
11	[RhCl(cod)] ₂	PMe ₃	11
12	[RhCl(cod)] ₂	P(4-OMeC ₆ H ₄) ₃	30
13	[RhCl(cod)] ₂	P(4-CF ₃ C ₆ H ₄) ₃	49
14	[RhCl(cod)] ₂	DPPE	<1
15	[RhCl(coe)] ₂	PPh ₃	47
16	[Rh(cod)] ₂ OTf	PPh ₃	37
17	[Cp*RhCl ₂] ₂	none	<1
18	Ir ₄ (CO) ₁₂	none	<1
19	[IrCl(cod)] ₂	PPh ₃	<1

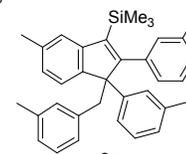
^a **1a** (2.0 equiv). ^b ¹H NMR yield using 1,1,2,2-tetrachloroethane as an internal standard. ^c Isolated yield. ^d (*E*)-(1,2-Diphenylvinyl)-dimethyl(phenyl)silane (**4a**) was obtained in 19% isolated yield.

The substrate scope of alkynes, hydrosilanes, and hydrogermane was investigated (Table 2). Reaction of diphenylacetylene (**1a**) with triethoxysilane (**2b**) gave silylindene **3b** and alkenylsilane **4b** in 76% NMR yield and 8% isolated yield, respectively (entry 1). Because silylindene **3b** was unstable for further purification, the isolated yield of **3b** decreased to 48% (entry 1).¹⁸ Trialkylhydrosilanes **2c** and **2d** gave the corresponding silylindenes **3c** and **3d** in 40% and 46% yields, respectively (entries 2 and 3). A more sterically bulky hydrosilane, such as *tert*-butyldimethylsilane (**2e**), was also suitable for the reaction and silylindene **3e** was obtained in 33% yield (entry 4). We then investigated the substituents of aryl alkynes. Reactions using aryl alkynes bearing electron-donating groups gave silylindenes **3f–3h** in 30–51% yield (entries 5–7). Notably, the thioether moiety, which usually works as a catalyst poison, was compatible with this reaction (entry 7). Moreover, silylindene bearing an *N,N*-dimethylamino group **3i** was obtained in 25% yield despite the presence of strong electron-rich functional groups (entry 8). Aryl alkynes with electron-withdrawing groups also produced silylindenes **3j** and **3k** in 36% and 52% yields, respectively (entries 9 and 10). Aryl alkynes **1h** and **1i** with ethoxycarbonyl or trimethylsilyl groups, which could be used for further transformations, were tolerant to the reaction conditions (entries 11 and 12). An aryl alkyne with methyl groups at the *meta*-position, **1j**, provided a single regioisomer **3n** in 59% yield (entry 13). Interestingly, the reaction also proceeded using tributylgermane (**2f**), and the corresponding germylindene **3o** was produced in 21% yield (entry 14).¹⁹

To elucidate the reaction mechanism, we performed a deuterium-labelling experiment using a deuterated diphenylacetylene **1a-D₁₀**. Silylindene **3p-D₂₀** was obtained in 70% yield and the percent deuterium incorporated at the benzylic position was 89% (Eq. (1)).²⁰

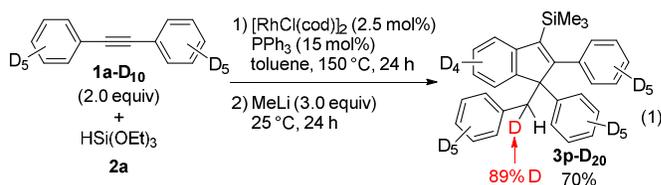
Table 2. Rhodium-catalysed synthesis of silylindenes using several hydrosilanes, hydrogermane, and aryl alkynes^a

Entry	R ¹	1	YR ² ₃	2	YR ³ ₃	Yield (%)		
						3	4	3 + 4
1	H	1a	Si(OEt) ₃	2b	Si(OEt) ₃	3b 48 (76) ^b	4b 8	56
2		1a	SiEt ₃	2c	SiEt ₃	3c 40	4c 38	78
3		1a	Si ^{<i>t</i>} Bu ₃	2d	Si ^{<i>t</i>} Bu ₃	3d 46	4d 50	96
4		1a	SiMe ₂ ^{<i>t</i>} Bu	2e	SiMe ₂ ^{<i>t</i>} Bu	3e 33	4e 30	63
5 ^c	4-Me	1b	2b	SiMe ₃	3f 30	4f 24	54	
6 ^c	4-OMe	1c	2b	SiMe ₃	3g 44	4g 26	70	
7 ^c	4-SMe	1d	2b	SiMe ₃	3h 51	4h 25	76	
8 ^d	4-NMe ₂	1e	2c	SiEt ₃	3i 25	4i 47	72	
9 ^c	4-CF ₃	1f	2b	SiMe ₃	3j 36	4j 18	54	
10 ^c	4-OCF ₃	1g	2b	SiMe ₃	3k 52	4k 27	79	
11 ^d	4-SiMe ₃	1h	2c	SiEt ₃	3l 39	4l 23	62	
12 ^d	4-CO ₂ Et	1i	2c	SiEt ₃	3m 36	4m 38	74	
13 ^c	3-Me	1j	2b	SiMe ₃	3n 59	4n 24	83	



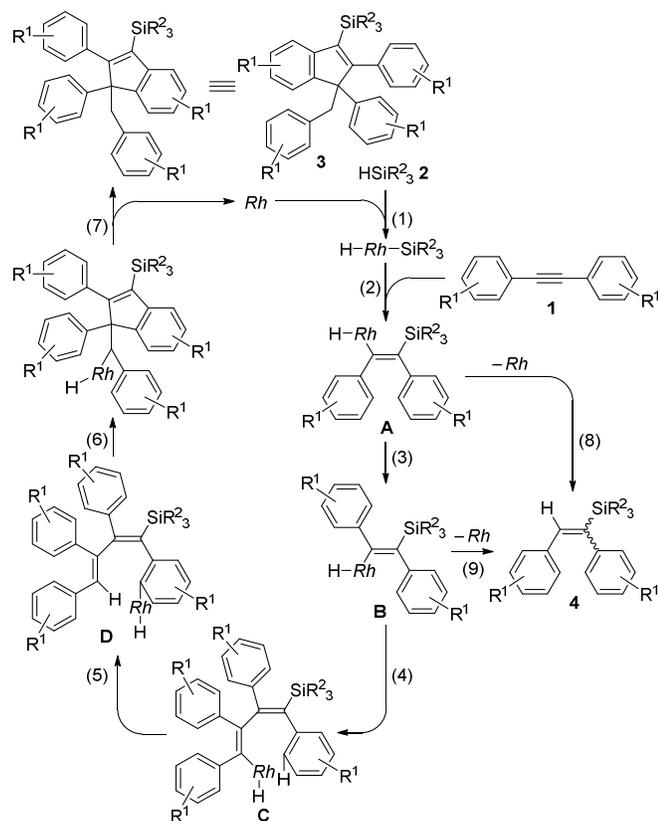
14	1a	Ge ^{<i>n</i>} Bu ₃	2f	Ge ^{<i>n</i>} Bu ₃	3o 21	4o 41	62
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^a **1** (2.0 equiv). ^b ¹H NMR yield using 1,1,2,2-tetrachloroethane as an internal standard. ^c A product was isolated after treatment with MeLi. ^d HSiEt₃:alkyne = 2:1.

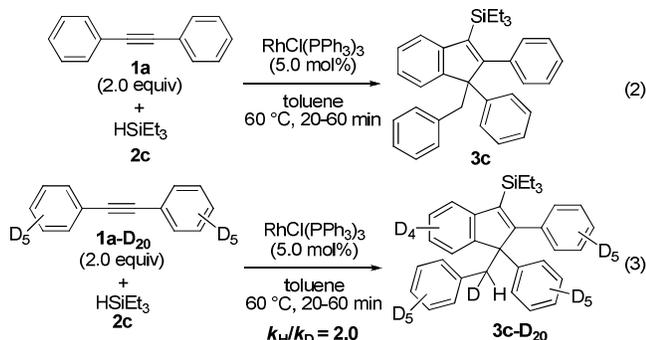


Based on the result in Eq. (1), we propose a mechanism for the rhodium-catalysed formation of multisubstituted silylindene **3** (Scheme 1).²¹ (1) oxidative addition of hydrosilane **2** to a rhodium catalyst; (2) first insertion of alkyne **1** into a rhodium-silicon bond;²² (3) isomerisation from *Z*-olefin **A** to *E*-olefin **B**;²³ (4) second insertion of alkyne **1** into the formed rhodium-carbon bond of **B**; (5) 1,6-migration from intermediate **C** (C-H bond activation);²⁴ (6) insertion of the olefin moiety of intermediate **D** into the formed rhodium-carbon bond; and (7) reductive elimination to give **3** and regenerate the rhodium catalyst. Alkenyl silanes **4** were formed by reductive elimination of the rhodium catalyst from intermediates **A** and **B** ((8) and (9)).

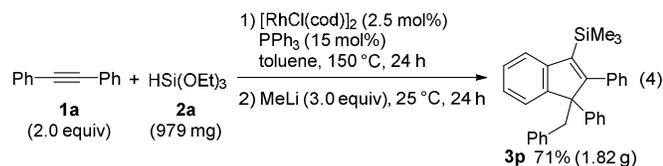
Kinetic studies performed using Wilkinson's catalyst²⁵ revealed that the value of the kinetic isotope effect, k_H/k_D , was 2.0 (Eqs. (2) and (3)). This result indicates that the second oxidative addition at the *ortho*-C-H bond of intermediate **C** (step 5) was the rate-determining step of the reaction.



Scheme 1. Plausible reaction mechanism for formation of multi-substituted silylindenes **3**.

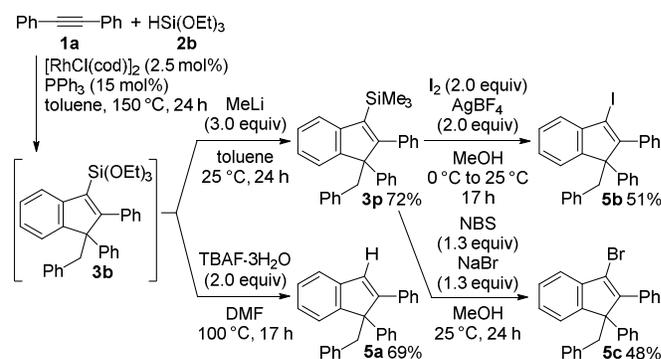


The yield of silylindene **3p** was high, even in gram scale. Treatment of diphenylacetylene (**1a**) with 979 mg of hydrosilane **2a** produced 1.82 g of **3p** in 71% yield [Eq. (4); **2a**, 41.1 mg; **3p**, 77.5 mg, 72% yield].



Finally, we investigated transformations of silylindenes (Scheme 2). Triethoxysilylindene **3b** was converted to trimethylsilylindene **3p** by treating **3b** with methylolithium. Desilylation of **3b** proceeded to give multi-substituted indene **5a**.²⁶ These transformations were carried out in one-pot from alkyne **1a** and hydrosilane **2b** without isolation of **3b**. We also investigated transformations of trimethylsilylindene **3p**. Silver-mediated desilylation and iodination gave iodoindene **5b** in 51% yield.²⁷ On the other hand, bromoindene

5c was obtained in 48% yield by bromination of **3p** with *N*-bromosuccinimide and NaBr.²⁸



Scheme 2. Several transformations of silylindenes **3** and **5**.

Conclusions

In summary, we successfully synthesised multi-substituted silylindenes via rhodium catalysis from 2 equivalents of internal alkynes and 1 equivalent of hydrosilanes in moderate to good yields. This is the first example of the synthesis of silylindenes from aryl alkynes and hydrosilanes via C-H bond activation. By the similar reaction, the corresponding germylindene was also obtained using a hydrogermane as a substrate. Kinetic isotope effect experiments revealed that C-H bond activation of the aromatic rings was the rate-determining step. Silylindenes were obtained in good yield even in gram scale. The silyl groups of the obtained silylindenes could be converted to several other functional groups. We expect that this reaction will contribute to organosilicon chemistry and become a useful method for synthesising silylindenes and indene derivatives.

Notes and references

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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- 18 We found that a reaction between diphenylacetylene (**1a**) and triethoxysilane (**2b**) at 150 °C finished within 1 h. For further investigations, the reaction time was 24 h.
- 19 A reaction between 1-methoxy-4-((4-(trifluoromethyl)phenyl)ethynyl)benzene and triethoxysilane, followed by the treatment of the reaction mixture with methylolithium, produced the corresponding silylindene in 48% yield as a mixture of inseparable regioisomers. Other alkynes, such as bis(2-tolyl)acetylene, bis(1-naphthyl)acetylene, bis(4-pyridyl)acetylene, bis(2-thienyl)acetylene, 1-phenyl-1-propyne, and ethynylbenzene, did not give the desired silylindenes.
- 20 A reaction between diphenylacetylene (**1a**) and dimethyl(phenyl)silane (**2a**) in the presence of 5 equivalents of D₂O under the similar reaction conditions in Table 1, entry 9 gave silylindene **3a** in 43% yield without incorporation of a deuterium atom.
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