

Ruthenium-catalysed double *trans*-hydrosilylation of 1,4-diarylbuta-1,3-diyne leading to 2,5-diarylsiloles†‡

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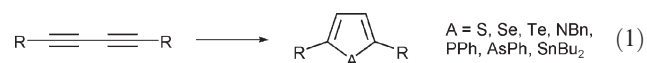
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Dihydrosilanes undergo double *trans*-hydrosilylation with 1,4-diarylbuta-1,3-diyne in the presence of a cationic ruthenium catalyst to afford 2,5-diarylsiloles: in particular, 9-silafluorene is a good hydrosilylating agent to produce spiro-type siloles in good yield.

Studies on the synthesis of heteroles and metalloles continue to be of great importance owing to their unique photophysical and electronic properties.¹ 2,5-Disubstituted heteroles of group 14–16 elements can be synthesised by [4 + 1]-type annulation reactions of 1,3-diyne with appropriate group 14–16 element compounds (eqn (1)).² For example, a thermal reaction of hexa-2,4-diyne with dibutyltin dihydride affords the corresponding stannole.^{2g} However, no [4 + 1]-type annulation reaction of 1,3-diyne producing siloles has been reported. Ever increasing interest in silicon-based σ - and π -conjugated molecules³ prompted us to explore an efficient process for the preparation of siloles from 1,3-diyne. We herein wish to report a new synthesis of 2,5-diarylsiloles by means of catalytic double hydrosilylation.⁴



Hydrosilylation of alkynes is catalysed by various transition metal complexes, and in most cases, *cis* adducts are formed.⁵ However, a synthesis of silole derivatives by hydrosilylation of 1,3-diyne necessitates a *trans* addition process. Trost *et al.* reported that ruthenium complex, [Cp*Ru(MeCN)₃]PF₆ (**1**), catalyses *trans*-hydrosilylation of alkynes.⁶ We tried to apply this catalyst to the reaction of 1,3-diyne and dihydrosilanes (Table 1). No reaction occurred when 1,4-diphenylbuta-1,3-diyne (**2a**) was treated with Et₂SiH₂ (**3a**, 3 equiv.) in the presence of **1** (20 mol%) in 1,2-dichloroethane (entry 1). Only a trace amount of silole was obtained when PhMeSiH₂ (**3b**) was used (entry 2). Gratifyingly, the desired double hydrosilylation of **2a** occurred with Ph₂SiH₂ (**3c**) to afford 1,1,2,5-tetraphenylsilole (**4ac**) in 51% yield (entry 3).^{7,8} 9-Silafluorene (**3d**)⁹ was found to be a better hydrosilylating agent to produce spiro-type silole **4ad** in 79% yield (entry 4).¹⁰ The reaction proceeded efficiently to give **4ad** in 75% yield even with 1.5 equiv. of **3d** (entry 5). The yield of **4ad** decreased to 58% with 10 mol% of the catalyst (entry 6).

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‡ This paper is dedicated to the late Professor Yoshihiko Ito in appreciation of his inspiring mentorship.

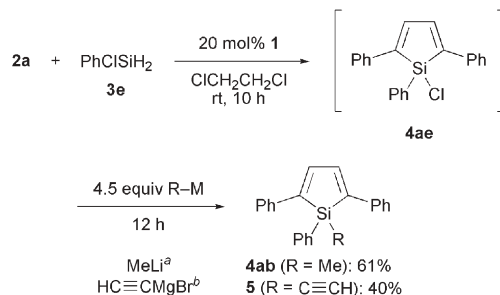
Table 1 Reaction of 1,4-diphenylbuta-1,3-diyne (**2a**) with dihydrosilanes **3a–d** in the presence of [Cp*Ru(MeCN)₃]PF₆ (**1**)^a

Entry	Dihydrosilane		Silole	
	3 (R ₂ SiH ₂)	Equiv.	mol% Ru	4 Yield ^b
1	3a (Et ₂ SiH ₂)	3.0	20	4aa 0%
2	3b (PhMeSiH ₂)	3.0	20	4ab trace
3	3c (Ph ₂ SiH ₂)	3.0	20	4ac 51%
4	3d (9-silafluorene)	3.0	20	4ad 79%
5	3d	1.5	20	4ad 75%
6	3d	3.0	10	4ad 58%

^a Diyne **2a** and silane **3** were reacted in 1,2-dichloroethane at rt for 10 h in the presence of **1**. ^b Isolated yield by preparative TLC.

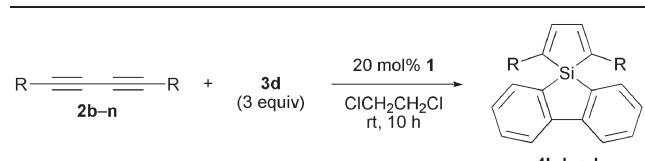
Chloro(phenyl)silane (**3e**) also successfully participated in the reaction with **2a** to produce 1-chlorosilole derivative **4ae** (Scheme 1). The following treatment with methylolithium afforded 1-methyl-1-phenylsilole **4ab** in 61% yield, which was difficult to obtain through a direct double hydrosilylation process using **3b**. Ethynylation of **4ae** with HC≡CMgBr gave ethynylsilole **5** (40%).¹¹

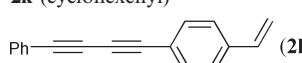
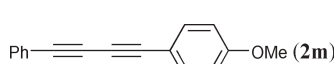
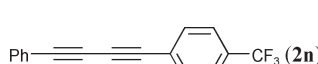
Thus, the double hydrosilylation of 1,3-diyne provides a new synthetic route to 2,5-diarylsiloles. Next, a wide variety of 1,3-diyne were subjected to the double *trans*-hydrosilylation reaction with **3d** (Table 2).§ Some results obtained with **3c** are included therein.



Scheme 1 Reagents and conditions: ^a MeLi, Et₂O, -78 °C ~ rt, ^b HC≡CMgBr, THF, 0 ~ 50 °C.

Table 2 Ruthenium-catalysed double *trans*-hydrosilylation of 1,3-diyne **2b–n** with 9-silafluorene (**3d**)^a

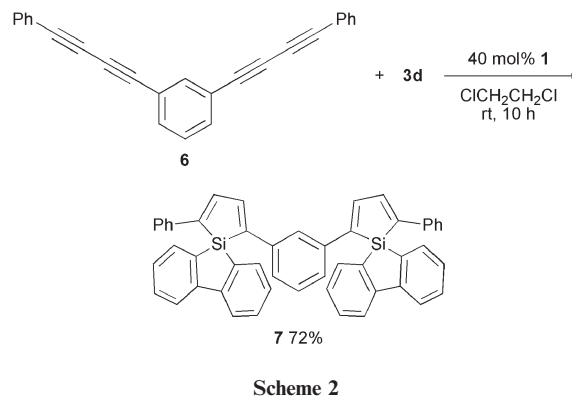


Entry	1,3-diyne 2 (R)	Silole 4	%yield ^{b,c}
1	2b (2-naphthyl)	4bd	59 (55)
2	2c (4-MeC ₆ H ₄)	4cd	77 (65)
3	2d (4-MeOC ₆ H ₄)	4dd	78 (75)
4	2e (4-MeCOC ₆ H ₄)	4ed	25
5	2f (4-FC ₆ H ₄)	4fd	65
6	2g (3-BrC ₆ H ₄)	4gd	71
7	2h (4-Me ₃ SiC ₆ H ₄)	4hd	62
8	2i (3-(pin)BC ₆ H ₄) ^d	4id	73
9	2j (3-thienyl)	4jd	76 (67)
10	2k (cyclohexenyl)	4kd	50
11	 (2l)	4ld	63
12	 (2m)	4md	56
13	 (2n)	4nd	69

^a Reaction conditions: **2** (1 equiv.), **3d** (3 equiv.), **1** (20 mol%), 1,2-dichloroethane, rt, 10 h. ^b Isolated yield. ^c Yields in parentheses are results with Ph₂SiH₂ (**3c**). ^d pin = pinacolato (–OCMe₂CMe₂O–).

2-Naphthyl-substituted 1,3-diyne **2b** afforded the corresponding silole **4bd** in 59% yield (entry 1), whereas 1-naphthyl-substituted 1,3-diyne failed to react with **3d** presumably due to steric reasons. 1,3-Diyne (**2c** and **2d**) having electron-donating groups on the *para* positions of the phenyl rings provided the siloles (**4cd** and **4dd**) in good yields (entries 2 and 3). In contrast, introduction of electron-withdrawing acetyl groups significantly retarded the reaction (entry 4). Various heteroatom functionalities including halogens, silicon, and boron on the phenyl rings survived unscathed under the reaction conditions (entries 5–8). Other sp² carbon-substituted diynes like bis(3-thienyl)butadiyne **2j** and dicyclohexenylbutadiyne **2k** worked well (entries 9 and 10). On the other hand, hexa-2,4-diyne (R = Me) failed to react with **2d**, and 1,4-bis(trimethylsilyl)buta-1,3-diyne (R = SiMe₃) afforded a complex mixture of products. These results suggest that 1,3-diyne with the 1- and 4-carbons being connected to sp² carbons are suitable substrates for the present silole forming reaction. The reaction of unsymmetrical 1,3-diyne was also examined. 1-Phenyl-4-(4-vinylphenyl)buta-1,3-diyne (**2l**) furnished silole **4ld** with the vinyl group remaining intact (entry 11). Siloles **4md** (R = OMe) and **4nd** (R = CF₃) having electronically biased aryl groups were produced by hydrosilylation of the corresponding unsymmetrical 1,3-diyne **2m** and **2n** (entries 12 and 13).

The incorporation of silole cores into a π -conjugated backbone is of particular interest because silole-containing oligomers and polymers have been regarded as promising electron-transporting



materials. Thus, the present reaction was applied to the synthesis of extended π -conjugated silole derivatives. *m*-Bis(diyne)benzene **6** that possess two 1,3-diyne moieties reacted with two molecules of silane **3d** to provide *m*-phenylenebissilole **7** (Scheme 2).

As another approach to extend silole-containing π -conjugation, we carried out polymerization by a cross-coupling reaction. Suzuki–Miyaura coupling of diborylsilole **4id** with 1,4-dibromobenzene **8** in the presence of a palladium catalyst furnished alternating copolymer **9** in 99% yield (Scheme 3).

Selected photophysical and thermal data for the produced siloles are shown in Table 3. Tetraphenylsilole **4ac** exhibits its absorption maximum at 382 nm and fluorescence maximum at 467 nm. Substitution of the –SiPh₂– moiety with silafluorenylene causes red shifts of both the absorption and fluorescence maxima. Siloles **4ac** and **4gd** have high quantum efficiencies (Φ_F) of 0.64 and 0.65, respectively. Introduction of the spiro linkage increases the glass transition temperature (T_g) and melting point (T_m); **4hd** has T_g of 90 °C and **4jd** has T_m of 233 °C.

The production of 2,5-diarylsiloles from 1,3-diyne and dihydrosilanes can be accounted for by assuming that the initial ruthenium-catalysed *trans*-hydrosilylation is followed by the second intramolecular hydrosilylation in a *trans* fashion (Scheme 4).¹² In order to support this assumption, 2-alkynylphenylsilane **10** was prepared and subjected to the reaction conditions. Intramolecular hydrosilylation occurred in a *trans* fashion to give 1-silaindene **11** in 72% yield (eqn (2)).¹³ This experiment corroborates the successive double hydrosilylation mechanism.

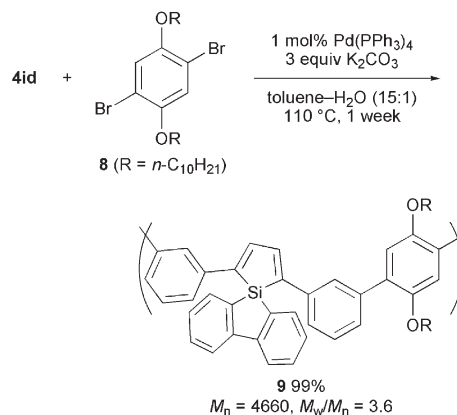
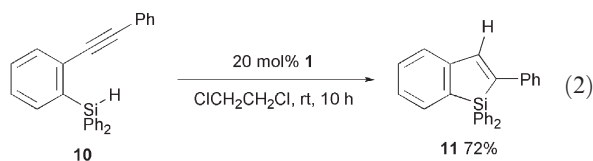
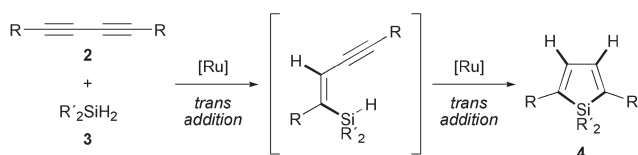


Table 3 Photophysical and thermal properties of siloles

Silole	UV-vis ^a		fluorescence ^b		T _g (°C)	T _m (°C)
	λ _{abs} (nm)	log ε	λ _{em} (nm)	Φ _F		
4ac	382	4.26	467	0.64	35	169
4ad	391	4.12	490	0.35	65	197
4gd	390	4.24	488	0.65	52	157
4hd	401	4.34	500	0.31	90	203
4jd	398	3.95	493	0.26	81	233

^a Measured in CHCl₃. ^b Measured in hexane. Determined with reference to quinine sulfate in 0.1 N H₂SO₄ and anthracene in EtOH (excited at 250 nm).



In summary, we have discovered a new double *trans*-hydrosilylation reaction of 1,3-diyne catalysed by a cationic ruthenium complex. The reaction enabled the rapid assembly of 2,5-diarylsiloles from readily available starting materials under mild conditions.

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Notes and references

§ General procedure: To a solution of [Cp**Ru*(MeCN)₃]PF₆ (**1**, 30.3 mg, 0.060 mmol) in 1,2-dichloroethane (1.5 mL) was added a solution of 1,4-diphenylbuta-1,3-diyne (**2a**, 60.7 mg, 0.30 mmol) and 9-silafluorene (**3d**, 164.1 mg, 0.90 mmol) in 1,2-dichloroethane (1.5 mL). After being stirred

under an argon atmosphere for 10 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was purified by thin-layer chromatography (hexane:AcOEt = 10 : 1) to give 2',5'-diphenylspiro[9-silafluorene-9,1'-silole] (**4ad**, 91.4 mg, 79%).

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