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Direct synthesis of dialkylarylvinylsilane derivatives: metathesis of dialkylaryl-iso-propenylsilane and its application to tetracyclic silacycle dye synthesis†

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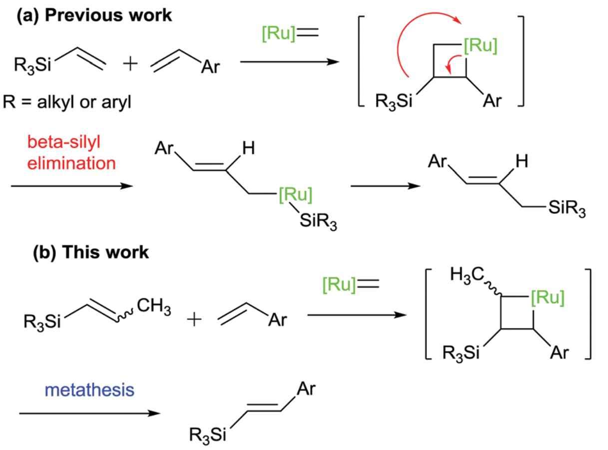
The metathesis of dialkylarylvinylsilane, which has not been accomplished to date, is achieved using dialkylaryl-iso-propenylsilane as a substrate. In addition, we discovered that the reason why the metathesis of a ruthenium carbene complex and dialkylarylvinylsilane is difficult is the formation of a carbide complex.

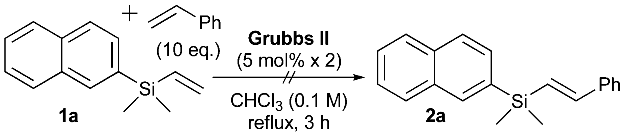
Diene and enyne metatheses in their various versions (ring-closing metathesis, RCM; ring-opening metathesis, ROM; and cross-metathesis, CM) have emerged as major tools for the synthesis of complex molecules.[1] Furthermore, olefinic double bonds bearing heteroatom substituents (*e.g.*, vinyl halides,[2] enol ethers,[3] enamides,[4] vinylboranes,[5] vinylsilanes, *etc.*) offer vast functionalization possibilities.[6] However, systems in which the dialkylarylsilyl group is maintained have been limited due to the decomposition of the ruthena-cyclobutane intermediate as a result of beta-trialkylsilyl elimination (Scheme 1a).[7]

In this communication, we describe unprecedented CM, RCM and enyne metathesis (EM) of dialkylaryl-iso-propenylsilane derivatives, which have a methyl substituent at the beta position of the silicon atom to prevent unwanted beta-silyl elimination. Using this method, we can obtain the very same products that we have tried to synthesize from vinylsilane derivatives (Scheme 1b).



Scheme 1 Reaction of trialkylvinylsilane and a ruthenium carbene catalyst.

First, in order to confirm that the metathesis reaction of dialkylarylvinylsilane does not proceed, the experiment shown in Scheme 2 was performed. A solution of dimethylvinylnaphthylsilane (**1a**), styrene (10 eq.) and a Grubbs II catalyst (5 mol%) in chloroform was refluxed for 1 hour and then an additional 5 mol% Grubbs II catalyst was added to the mixture. The target CM reaction did not proceed.



Scheme 2 Attempted cross-metathesis of compound **1a**.

Next, dimethylnaphthyl-iso-propenylsilane (**1b**), having a methyl substituent at the beta position of the silicon atom to prevent unwanted beta-silyl elimination, was subjected to the same reaction conditions as in Scheme 2, and as a result the corresponding CM product **2a** was obtained in 45% yield (Table 1, entry 1). When the solvent was replaced by toluene, which has a higher boiling point, the yield of **2a** was improved to 75% (entry 2). The yield of **2a** decreased when 10 mol% Grubbs II catalyst was added at the start of the reaction (entry 3). When 9 mol% Grubbs II catalyst was added in three portions, hourly, and 10 eq. of styrene was added in two portions, the yield of **2a** was 62% (entry 4). Further investigation was carried out and, by using a more concentrated solvent of 0.2 M and adding the Grubbs II catalyst in three portions, the yield of **2a** was improved to 85% (entry 5). When the styrene was reduced to

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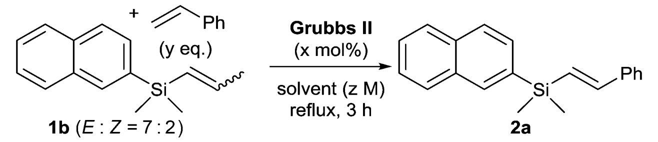
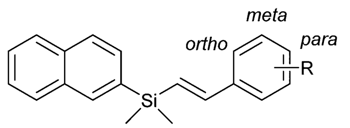
Table 1 Optimization of reaction conditions for cross-metathesis of compound **1b**



1b (*E* : *Z* = 7 : 2) **2a**

Entry	*x*	*y*	Solvent	*z*	Yield (%)
1	5 × 2	10	$CHCl_3$	0.1	45
2	5 × 2	10	Toluene	0.1	75
3	10	10	Toluene	0.1	61
4	3 × 3	5 × 2	Toluene	0.1	62
5	3 × 3	10	Toluene	0.2	85
6	3 × 3	5	Toluene	0.2	76
7	3 × 3	3	Toluene	0.2	65



2a R = H (85%) **2e** R = *o* - Cl (52%) **2i** R = *p* - COMe (43%, 68%[a])
2b R = *o* - OMe (97%) **2f** R = *m* - Cl (63%) **2j** R = *p* - CO_2Me (51%)
2c R = *m* - OMe (84%) **2g** R = *p* - Cl (69%) **2k** R = *p* - NO_2 (35%)
2d R = *p* - OMe (90%) **2h** R = *p* - OAc (88%) **2l** R = *p* - NHBoc (59%)
[a] The reaction was performed in glove-box.

Scheme 3 Effect of substituents on the aromatic ring in styrene.

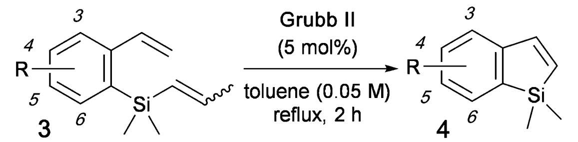
5 eq. and 3 eq., the yield of **2a** gradually decreased to 76% and 65%, respectively (entries 6 and 7).[8]

Then, the substrate coverage of this reaction was investigated based on the optimal conditions obtained (Scheme 3). This was examined using the compound with electron-donating and electron-withdrawing groups in the *ortho*, *meta* or *para* position on the benzene ring of styrene. As a result, CM products **2b**, **2c** and **2d** were obtained with high yields of 97%, 84% and 90%, respectively, for substrates substituted with an electron-donating group. With an electron-withdrawing group, the reaction proceeded with a moderate yield of 69% (**2g**) in the *para* position, 63% (**2f**) in the *meta* position and 52% (**2e**) in the *ortho* position.

A silole ring is used as an organic electroluminescent or pigment material because of its high electron acceptability.[9] We therefore applied the metathesis reaction described above and synthesized a silole skeleton using intramolecular RCM[10] and EM. Furthermore, we synthesized fluorescent substances using a one-pot intramolecular EM/Diels–Alder/oxidation reaction.

The RCM reaction of compound **3** was performed based on the optimum conditions for the CM reaction in Table 2. Because the boiling point of the cyclized substance was low in the substrate with no substituent on the benzene ring, we started with the 4-methoxy substrate **3a**. As a result of various investigations, it was found that when a solution of **3a** and the Grubbs II catalyst (5 mol%) in toluene (0.05 M) was refluxed for 2 hours, the corresponding RCM product **4a** was obtained in 91% yield (Table 2, entry 1). The RCM of a substrate with a methoxy or chloro substituent at the 3-position hardly proceeded, giving the corresponding product in 35% and 25% yield, respectively; most of the starting material remained, probably due to steric hindrance in the RCM (entries 2 and 5). The same reaction with a substituent at the 4-, 5- or 6-position on the substrate proceeded more smoothly, although an electron-donating group accelerated the reaction more than an electron-withdrawing group.

Table 2 Ring-closing metathesis of compound **3**



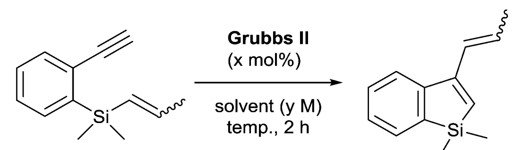
3 **4**

Entry	Substrate			Product	
		R =	*E* : *Z*=		Yield (%)
1	**3a**	4-OMe	4 : 1	**4a**	91
2	**3b**	3-OMe	18 : 1	**4b**	35
3	**3c**	5-OMe	1.8 : 1	**4c**	Quant.
4	**3d**	6-OMe	11 : 5	**4d**	63
5	**3e**	3-Cl	12 : 1	**4e**	25
6	**3f**	4-Cl	1 : 1	**4f**	62
7	**3g**	5-Cl	E only	**4g**	80
8	**3h**	3-F	1.8 : 1	**4h**	Trace
9	**3i**	4-F	20 : 1	**4i**	Trace
10	**3j**	5-F	4 : 1	**4j**	42

The boiling point of fluoro-substituted benzosiloles is rather low, so most of these could not be obtained. However, benzosilole with a fluoro substituent at the 5-position was obtained in 42% yield, although the conversion rate by crude nuclear magnetic resonance (NMR) was almost 100%.

Next, the conditions of the EM reaction were examined (Table 3). A solution of compound **5a** and Grubbs II catalyst (3 mol%) in 0.05 M toluene was refluxed for 2 hours to obtain EM product **6a** in 30% yield (entry 1). At this time, a dimer of compound **6a** was formed in addition to the raw material. When chloroform was used as the solvent, the formation of the dimer was not suppressed and product **6a** was obtained in 32% yield (entry 2). The reaction did not proceed when dichloromethane was used as the solvent (entry 3). Lowering the reaction temperature to 45 °C, increasing the amount of catalyst to 5 mol% and using chloroform as the solvent improved the product yield to 60% (entry 4). Furthermore, the yield remained fairly high at 57% even when the reaction

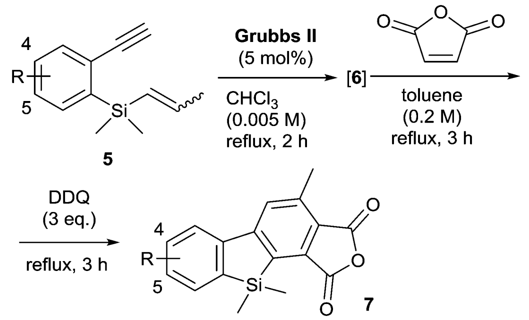
Table 3 Enyne metathesis of compound **5a**



5a (*E* : *Z* = 10 : 1) **6a**

Entry	*x*	Solvent	*y*	Temp. (°C)	Product yield (%)	*E* : *Z* =
1	3	Toluene	0.05	Reflux	30	6 : 1
2	3	$CHCl_3$	0.05	Reflux	32	5 : 1
3	3	CH_2Cl_2	0.05	Reflux	Trace	—
4	5	$CHCl_3$	0.05	45	60	4 : 1
5	5	$CHCl_3$	0.005	Reflux	57	5 : 1

Table 4 One-pot enyne metathesis/Diels–Alder/oxidation reaction of compound **5** to produce compound **7**



Entry	Substrate			Product				
		R =	$E:Z$ =		Yield (%)	λ_{abs} (nm)	λ_{em} (nm)	ϕ
1	**5a**	H	10 : 1	**7a**	52	343	400	0.41
2	**5b**	4-OMe	10 : 1	**7b**	35	363	442	0.32
3	**5c**	5-OMe	10 : 1	**7c**	48	371	466	0.53
4	**5d**	4-Me	10 : 1	**7d**	24	348	415	0.37
5	**5e**	5-Me	10 : 1	**7e**	21	354	470	0.58
6	**5f**	4-F	10 : 1	**7f**	39	350	392	0.50
7	**5g**	5-F	3 : 1	**7g**	38	345	406	0.51

solution was heated to reflux and the concentration was lowered to 0.005 M (entry 5).

According to the reaction conditions for the synthesis of polycyclic silicon-containing six-membered ring compounds that we reported previously,[11] silicon-containing five-membered tetracyclic compound **7a** was obtained through a one-pot EM/Diels–Alder/oxidation reaction from compound **5a** (Table 4, entry 1). The substrate application range was investigated and the yield for the three steps was 35% (compound **7b**) in the 4-methoxy group, 48% (compound **7c**) in the 5-methoxy group, 24% in the 4-methyl group (compound **7d**), 21% in the 5-methyl group (compound **7e**), 39% in the 4-fluoro group (compound **7f**) and 38% in the 5-fluoro group (compound **7g**).

Table 4 also shows the optical properties of compound 7 in chloroform (see also Fig. 1). As a whole, it was found that for substrates with an electron-donating group at the 5-position, the maximum fluorescence wavelength is shifted to longer wavelengths and the fluorescence quantum yield becomes higher (0.58 at most). We also found that fluorescence quantum yields give good results even for substrates with electron-withdrawing groups.

^{31}P-NMR experiments were carried out to obtain structural information in view of the fact that the metathesis reaction of dialkylarylvinylsilane (**1a**) does not proceed due to a structural change in the Grubbs II catalyst.

First, the Grubbs II catalyst, compound **1b** (3 eq.) and deuterated chloroform solvent were heated to 50 °C (Fig. 2).

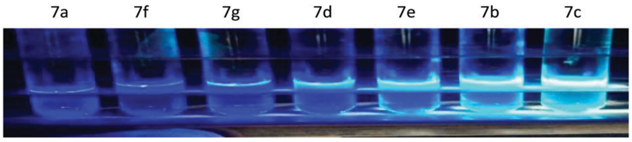


Fig. 1 Fluorescence of compound **7** under 365 nm irradiation.

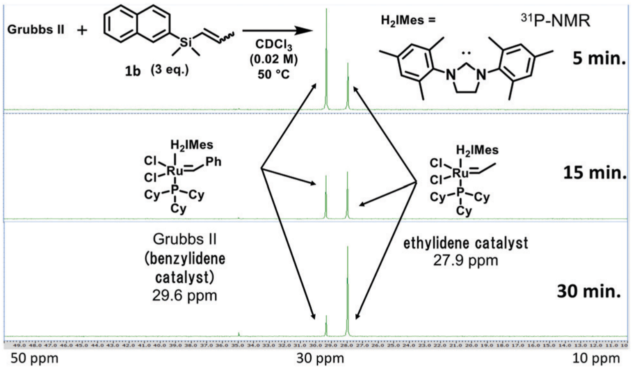


Fig. 2 ^{31}P-NMR of compound **1b** and Grubbs II catalyst.

Five minutes after the start of heating, a peak different from the 29.6 ppm Grubbs II catalyst peak[12] appeared at 27.9 ppm. As time passed, this peak increased, so after 30 minutes when the reaction solution was isolated and purified by column chromatography the peak at 27.9 ppm was in agreement with that in the literature[13] for an ethylidene complex. From this, it was found that in the present reaction the ethylidene complex became an active species as the metathesis proceeded.

Subsequently, the same ^{31}P-NMR experiment was performed using compound **1a** to investigate the structural change of the Grubbs II catalyst (Fig. 3). Five minutes after the start of the reaction, a peak thought to be the peak for a benzylidene complex was observed around 29.3 ppm, alongside the 29.6 ppm Grubbs II catalyst peak. This peak is considered to be the peak for a ruthenium catalyst having a similar skeleton to the Grubbs II catalyst: the peak and the chemical shift are hardly changed. After 15 minutes (20 minutes after the start of the reaction), the peak of the Grubbs II catalyst disappeared and new peaks appeared at around 34.9 ppm and 13 ppm, in addition to the 29.3 ppm peak. The 13 ppm peak is considered to be the peak for temporarily released tricyclohexylphosphine, but it was not clear what the 34.9 ppm peak indicates. Therefore, 30 minutes after the start of the reaction the solution was subjected to isolation and purification by column chromatography, with subsequent recrystallization and X-ray crystal structure analysis. As a result,

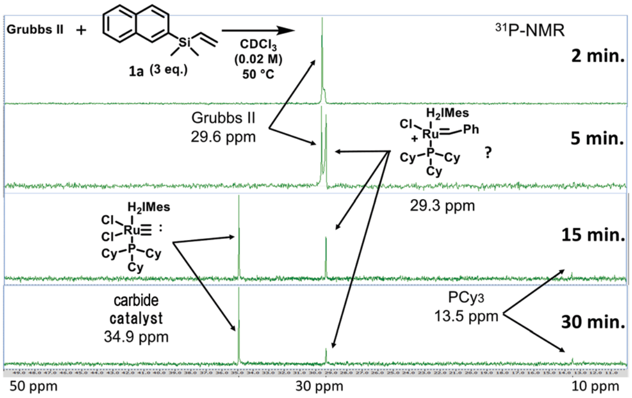


Fig. 3 ^{31}P-NMR of compound **1a** and Grubbs II catalyst.

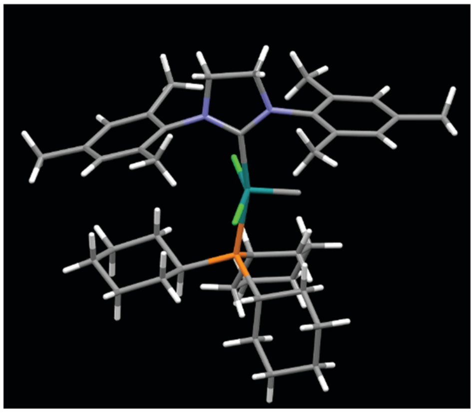


Fig. 4 X-ray crystal structure analysis of the carbide catalyst.[15]

the peak at 34.9 ppm was found to be the peak for a carbide complex derived from the Grubbs II catalyst (Fig. 4).[14]

From the result of this carbide complex and ^{31}P-NMR described above, the Grubbs II catalyst is considered to be rapidly converted to a carbide complex when it reacts with a dialkylarylvinylsilane such as **1a**, and loses activity as a metathesis catalyst.[7] On the other hand, when the Grubbs II catalyst reacted with substituted dialkylarylvinylsilane, having a methyl substituent at the beta position of the silicon atom, such as dimethylnaphthyl-iso-propenylsilane (**1b**), beta-silyl elimination of the ruthenacyclobutane intermediate did not proceed and the expected metathesis product was yielded probably due to the effect of steric hindrance.

Improved understanding of catalyst decomposition, particularly those pathways operating for the most vulnerable active species, is critical to guide process implementation and catalyst redesign.

In summary, although the metathesis reaction of dialkylarylvinylsilane has been difficult to date, it was found that the metathesis reaction proceeds when using dialkylaryl-iso-propenylsilane, having a methyl substituent at the beta position of the silyl atom to prevent unwanted beta-silyl elimination, as a substrate. We have also succeeded in synthesizing polycyclic silicon-containing cyclic compounds by combining EM, Diels–Alder and oxidation reactions. Furthermore, our findings showed that vinylsilane changed the Grubbs II catalyst to a carbide catalyst and that its catalytic activity was inactivated during metathesis.

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Conflicts of interest

There are no conflicts to declare.

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15 The X-ray crystal structural data of the carbide catalyst were deposited (CCDC 1938337)†.