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gem-Selective Cross-Dimerization and Cross-Trimerization of Alkynes with Silylacetylenes Promoted by a Rhodium–Pyridine–*N*-Heterocyclic Carbene Catalyst

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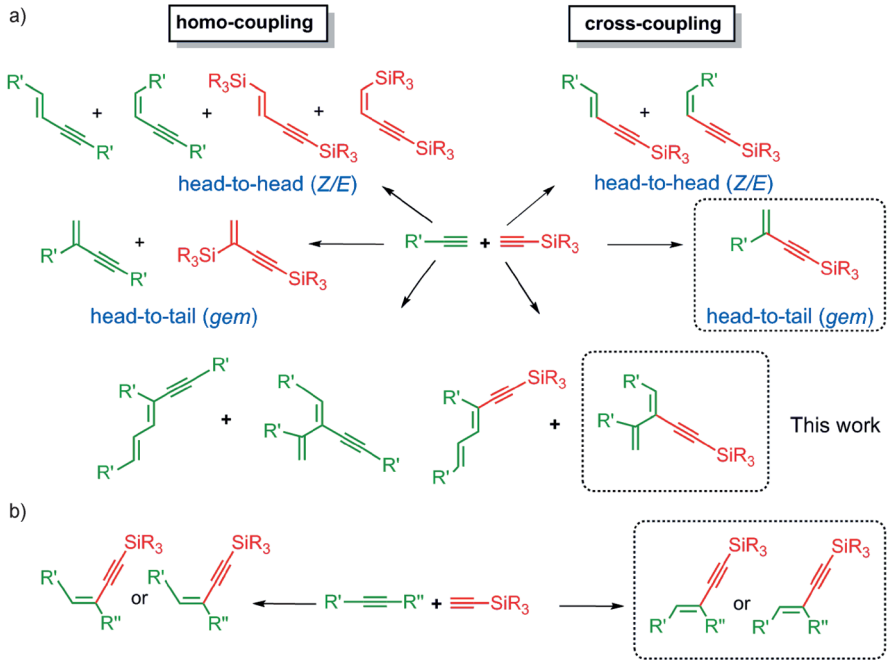
The *gem*-selective cross-dimerization and -trimerization of silylacetylenes with alkynes through C–H activation using a rhodium(I)–pyridine–*N*-heterocyclic carbene catalyst have been developed. This reaction is applied to various aliphatic or aromatic terminal alkynes, internal alkynes, and *gem*-1,3-disubsituted enynes to afford the corresponding enynes and dienynes with high regio- and stereoselectivities and in good isolated yields (up to 91%).

Introduction

The presence of 1,3- or 1,4-disubstituted enynes as key structural units in many biologically active molecules, polymers, or photoactive compounds has stimulated the interest in seeking for new and simple synthetic routes.[1] The metal-catalyzed homodimerization of terminal alkynes to selectively synthesize *E*-, *Z*-, and *gem*-enynes has been studied in depth.[2] However, the cross-dimerization of two alkynes is more limited because of the competitive homo- and oligodimerization reactions. In this context, different chemo-, regio-, and stereoselectivities have been achieved with Ir,[3] Ni,[4] Pd,[5] Rh,[6] Ru,[7] Ti,[8] and Co[9] catalysts, among others.[10] The cross-dimerization of silylacetylenes as a donor acetylene group with unactivated internal alkynes has been disclosed.[4, 5f, 6b,c, 7a, 9c] In contrast, the addition of silylacetylenes to terminal alkynes is challenging because of the competitive homodimerization reaction, particularly for aromatic acetylenes that present comparable acidity (Scheme 1).[11] Although several Ru,[7b] Rh,[6d] and Ir[3b] metal complexes selectively catalyzed the head-to-head cross-dimerization and afforded both *Z* and *E* isomers, reports on the formation of head-to-tail products are scarce.[5f, 8a] In contrast, the selective cross-trimerization of three alkynes by combining silylacetylene and internal alkynes leading to 1,3-dien-5-ynes has been performed with Ni[4, 12] and Pd[5c] catalysts. However, the formation of selective (2-alkynyl)-*gem*-1,3-dienes with a combination of three terminal alkynes has not been reported till date.



Scheme 1. Possible products of the cross-coupling of silylacetylene derivatives with alkynes: a) terminal and b) internal. Compounds prepared herein are shown in dashed boxes. R, R′, R″ = alkyl, aryl.

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Our research group has been developing new efficient and selective catalytic systems based on Rh–*N*-heterocyclic carbene (NHC) metal complexes for C–C and C–heteroatom coupling reactions.[13] Dinuclear compounds of type [Rh(μ-Cl)(NHC)(η^2-olefin)]$_2$ (**1**) have been revealed as valuable starting materials for the preparation of mononuclear complexes of type RhCl(NHC)(η^2-olefin)(L) (**2**) via simple bridge cleavage with a nucleophilic ligand.[13d–h] These derivatives demonstrated excellent performance in catalytic alkyne hydrothiolation[13d,h] and in the preparation of 4*H*-quinolizines through C–H activation.[13e] It has also been found that the complex [RhCl(IPr)(η^2-coe)(py)] (**2a**) [IPr = 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-carbene, coe = cyclooctene, and py = pyridine] promotes the selective homodimerization of alkynes to head-to-tail enynes, in which the chemo- and regioselectivity is controlled by the addition of pyridine.[13f] Herein, we report an efficient chemo-, regio-, and stereoselective Markovnikov-type cross-dimerization and -trimerization involving trimethylsilylacetylene and aliphatic and aromatic terminal alkynes, internal alkynes, and *gem*-1,3-disubstituted enynes.

Results and Discussion

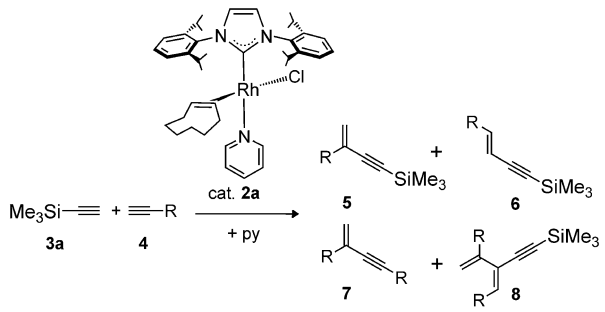
Cross-dimerization of trimethylsilylacetylene with terminal alkynes

The catalytic system **2a** + 10 equiv. of pyridine[14] was tested for the cross-dimerization of trimethylsilylacetylene (**3a**) with phenylacetylene (**4a**) (Table 1 and Scheme 2). At 40 °C, the reaction is fully selective to head-to-tail (*gem*) phenylacetylene homodimerization product **7a** (Table 1, entry 1). However, we observed that selectivity changes dramatically with the temperature. At 60 °C, a 37% of phenylacetyl–trimethylsilylacetylene cross-dimerization product **5a** and a 50% of phenylacetylene homodimerization derivative **7a** were obtained (entry 2). At 80 °C, the cross-coupled compound **5a** was the major product (81%) along with a 5% of the homodimerization product **7a** (entry 3). In both cases, the formation of the trimer **8a** (≈14%), resulting from the coupling of two molecules of phenylacetylene with trimethylsilylacetylene, was also observed as a byproduct. The observed temperature effect over the selectivity is probably due to a modification of the overall kinetic parameters, which indicates that at high temperature the C–H activation plays a pre-eminent role and thus favors cross-dimerization. Moreover, an excess amount of pyridine accelerates the cross-dimerization to form **5a** with high chemo- and regioselectivity. Notably, if dinuclear complexes **1**, lacking a pyridine ligand, were used as catalysts, no dimerization products were formed; however, the presence of cyclotrimers was observed, as described in our previous work.[13f]

Table 1. Temperature screening for the cross-dimerization of trimethylsilylacetylene (**3a**) with phenylacetylene (**4a**) catalyzed by **2a** + 10 equiv. of pyridine.[a]

Entry	*t* [h]	*T* [°C]	Conversion [%]	Selectivity [%]			
				5a	**6a**	**7a**	**8a**
1	3	40	65	18	–	82	–
2	3	60	99	37	–	50	13
3	2	80	99	81	–	5	14

[a] Reaction conditions: 0.5 mL of C_6D_6, 0.2 mmol of **3a**, 0.2 mmol of **4a**, 0.01 mmol of catalyst **2a** + 0.1 mmol of pyridine.



Scheme 2. Catalytic transformation of alkynes with **2a** + 10 equiv. of pyridine (py). R = alkyl, aryl.

The unequivocal characterization of the head-to-tail cross-dimerization product **5a** was accomplished by comparison with the reported ^{1}H and ^{13}C{^{1}H} NMR data[15] and the heteronuclear correlation ^{1}H–^{13}C HMBC experimental data. The more significant part of the 2D NMR spectrum is shown in Figure 1. The

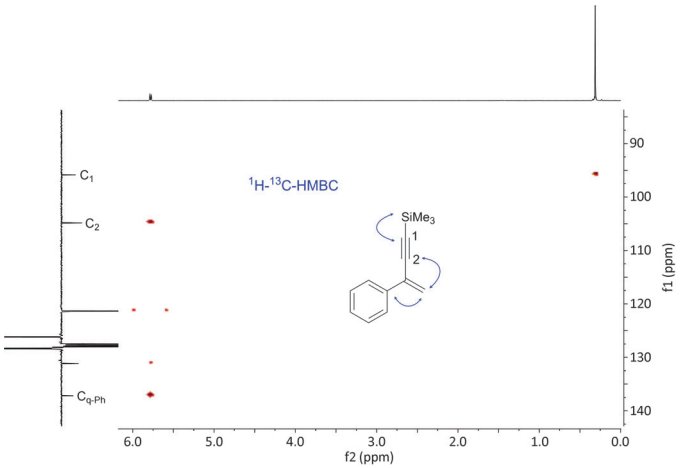
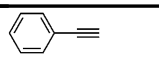
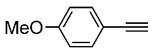
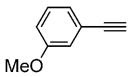
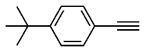
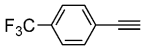
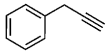
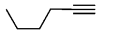
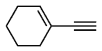
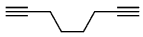


Figure 1. ^{1}H–^{13}C HMBC spectrum of compound **5a** in C_6D_6.

terminal olefinic protons (δ = 5.80 and 5.77 ppm) correlates with one C sp atom (δ = 104.8 ppm), whereas, more significantly, the other alkynyl carbon atom (δ = 95.9 ppm) interacts with the protons of the trimethylsilyl group (δ = 0.31 ppm) and not with the aromatic protons, discarding the phenyl–alkynyl connectivity. A correlation between the geminal protons and the *ipso*-phenyl quaternary carbon (δ = 137.3 ppm) was also observed (see the Supporting Information).

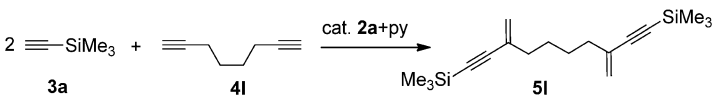
We have then studied the scope of the cross-dimerization reaction between terminal alkynes and trimethylsilylacetylene (Table 2). In general, full alkyne conversion was attained in 1–4 h, which gave the corresponding *gem*-1,3-disubstituted enynes (**5**) in good isolated yields (up to 80%). Cross-coupled *E*-enynes (**6**), homodimerization derivatives (**7**), and *gem*-dien-

Table 2. Catalytic cross-dimerization of alkynes with trimethylsilylacetylene (**3a**) mediated by **2a** + 10 equiv. of pyridine.[a]

Entry	Alkyne		*t* [h]	Conversion [%]	Selectivity [%] 5	6	7	8	Yield [%]
1		**4a**	2	99	81	–	5	14	71 (**5a**)
2		**4b**	1	99	91	–	4	5	83 (**5b**)
3		**4c**	2	99	85	–	–	15	78 (**5c**)
4		**4d**	2	99	86	–	10	4	76 (**5d**)
5		**4e**	1	92	–	–	98[c]	–	0 (**5e**)
6		**4f**	2	99	82	–	3	15	70 (**5f**)
7		**4g**	3	99	75	12	8	5	68 (**5g**)
8		**4h**	4	90	81	11	6	2	74 (**5h**)
9		**4i**	4	95	80	12	–	8	70 (**5i**)
10		**4j**	5	98	83	–	4	13	71 (**5j**)
11		**4k**	3	99	78	–	22	–	60 (**5k**)
12		**4l**	4	99	86	14[d]	–	–	80 (**5l**)

[a] Reaction conditions: 0.5 mL of C_6D_6, 0.2 mmol of **3a**, 0.2 mmol of **4**, 0.01 mmol of catalyst **2a** + 0.1 mmol of pyridine at 80 °C; [b] Isolated yield of **5**; [c] 2% of *E*-homodimer was also observed.[d] *E*/*gem* isomer

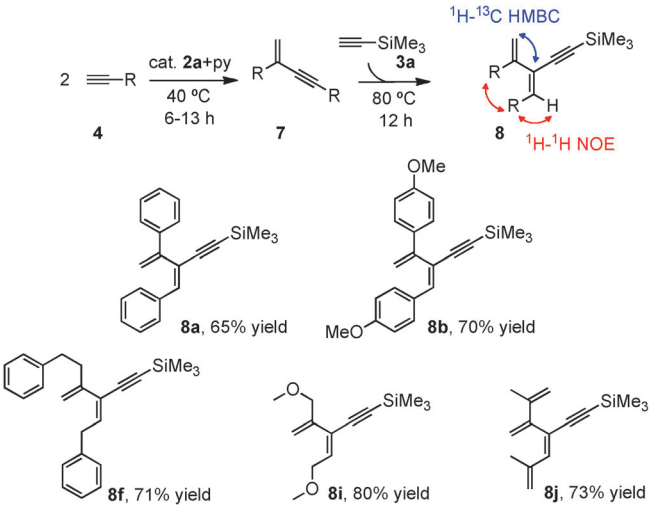
yne trimers (**8**) were also formed in variable amounts. As a general trend, aromatic alkynes react faster than aliphatic alkynes (Table 2, entries 1–4 vs. entries 6–12). Phenylacetylene was completely consumed after 2 h, and *gem*-**5a** was formed with 81% selectivity (entry 1). The substituted phenylacetylenes bearing an electron-donating group such as –OMe, at either the *para* or the *meta* position, or *tert*-butyl demonstrate high regioselectivities and good yields (entries 2–4). However, the *para*-CF_3-substituted substrate **4e** gave exclusively the homodimerization product **7e**. In the case of aliphatic alkynes, head-to-tail products were obtained as the major product (>75%). In contrast to aromatic alkynes, *E*-enynes (**6**) were also formed in some cases (<15%). Thus, 1-benzylacetylene was transformed in 2 h, which gave 82% *gem*-**5f** (entry 6). 1-Hexyne reacted in 3 h and gave 75% *gem*-**5g** and 12% *E*-**6g** as major products (entry 7). Terminal alkynes bearing $-NMe_2$ and –OMe groups were also cross-dimerized with **3a** to form **5h** and **i** in good yields and high regioselectivities (entries 8 and 9). The reaction worked equally well with functionalized enynes such as 2-methyl-1-buten-3-yne and 1-cyclohexenylacetylene to give *gem*-dienynes **5j** and **k**, respectively, in good yields and high regioselectivities (entries 10 and 11). 1,7-Octadiyne reacted with 2 equiv. of **3a** and afforded the *gem*-bis-enyne **5l** in good yield because of a double cross-dimerization process (entry 12 and Scheme 3).



Scheme 3. Double cross-dimerization of 2 equiv. of trimethylsilylacetylene with 1 equiv. of 1,7-dioctyne.

Cross-trimerization of terminal alkynes with trimethylsilylacetylene

In some cases, aromatic and aliphatic trimers **8** were also formed as secondary products (Table 2). Most probably, these derivatives result from the homocoupling reaction of the corresponding terminal alkyne and a subsequent cross-trimerization with trimethylsilylacetylene. Thus, this process could be a straightforward way to construct π-conjugated systems. To promote the formation of (*E*)-(2-alkynyl)-(1,3-disubstituted)-1,3-butadiene derivatives (**8**) as major products, we performed the reaction in two steps. In the first step, the homodimerization reaction of the corresponding terminal alkyne was performed under reaction conditions of our previously reported work using 5 mol% of catalyst **2a** and 10 equiv. of pyridine at 40 °C in C_6D_6.[13f] In the second step, trimethylsilylacetylene was added and the crude mixture heated at 80 °C for 12 h to form *gem*-1,3-dienynes in good isolated yields and high regioselectivity (Scheme 4). The structure of the dienynes was confirmed by performing ^1H–^{13}C HMBC and ^1H–^1H NOE NMR experiments (see the Supporting Information). Reactions of aromatic substituted *gem*-1,3-enynes **7** gave good yields of the expected *gem*-dienyne products, for example, **8a** and **b**. Unfortunately, compound **8e** could

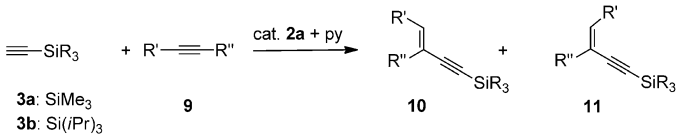


Scheme 4. Rh-catalyzed cross-trimerization of terminal alkynes with trimethylsilylacetylene through the formation of 1,3-*gem*-enynes.

not be obtained owing to the decomposition of dienyne **7e**, bearing a *para*-C_6H_4–CF_3 substituent, under the reaction conditions. The aliphatic substituted *gem*-1,3-enyne arising from benzylacetylene gave **8f**, which was isolated in 71% yield. Heteroatom-substituted and olefin-functionalized alkynes also underwent the coupling reaction towards the head-to-tail trimers **8i** and **j**, respectively.

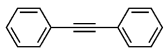
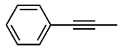
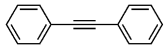
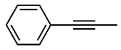
Cross-dimerization of trialkylsilylacetylenes with internal alkynes

The efficiency of catalyst **2a** was demonstrated for the cross-dimerization of internal alkynes (**9**) with trimethylsilylacetylene (**3a**) and triisopropylsilylacetylene (**3b**) (Scheme 5 and Table 3).



Scheme 5. Cross-dimerization of trialkylsilylacetylenes with internal alkynes. R′, R″ = alkyl, aryl.

Table 3. Cross-dimerization of silylacetylenes with internal alkynes.[a]

Entry	Alkyne		3	*T* [h]	Conversion [%]	Molar ratio **10**/**11**	Yield[b] [%]
1		**9a**	**3a**	12	71	90/10	64 (**10a**)
2		**9b**	**3a**	1	99	100/–	91 (**10b**)
3		**9c**	**3a**	3	92	(100/–)[c]/–	83 (**10c**)
4		**9a**	**3b**	32	93	80/20	76 (**10d**)
5		**9b**	**3b**	24	92	82/18	75 (**10e**)
6		**9c**	**3b**	44	90	(40/60)[d]/–	81 (**10f**)[d]

[a] Reaction conditions: 0.5 mL of C_6D_6, 0.2 mmol of **3a** or **b**, 0.2 mmol of **9**, 0.01 mmol of catalyst **2a** + 0.1 mmol of pyridine at 80 °C; [b] Isolated yield; [c] (*E*)-1-Trimethylsilyl-3-phenylpent-3-en-1-yne derivative as the major regioisomer; [d] Isolated as a mixture of regioisomers.

Both silylacetylenes reacted with 3-hexyne (**9a**) and diphenylacetylene (**9b**) to give preferentially the *syn*-addition products *E*-enynes **10**, which were isolated in moderate to high yields. The formation of thermodynamically more stable *Z*-enynes **11** resulted from the isomerization of **10**, as observed at prolonged reaction times. Alkyne **3a** was slightly more reactive and selective than **3b** (Table 3, entries 1 and 2 vs. entries 4 and 5). An unsymmetrical internal alkyne such as 1-phenyl-1-propyne (**9c**) reacted with **3a** and gave preferentially *E*-1-trimethylsilyl-3-phenylpent-3-en-1-yne in high yield (entry 3). In contrast, the reaction of **9c** with **3b** afforded a mixture of *E* regioisomers in a ratio of 40/60 (3-phenyl/4-phenyl; entry 6).

Mechanism of cross-dimerization and -trimerization of terminal alkynes

A plausible mechanism for head-to-tail cross-dimerization (step a) and head-to-tail cross-trimerization (step b) is shown in Scheme 6. This reaction probably proceeds by a mechanism similar to that proposed for the Rh-catalyzed dimerization of terminal alkynes.[13f] The first step involves the substitution of the cyclooctene ligand by the alkyne and the subsequent oxidative addition generates Rh^{III}–alkynyl–hydride intermediates. Then, the insertion of alkyne or *gem*-1,3-enyne can proceed via two pathways: carbometalation via 1,2 insertion (path I) or hydrometalation via 2,1 insertion (path II). Finally, reductive elimination affords the corresponding enynes or dienynes and the coordination of a second alkyne or *gem*-1,3-enynes to the metal regenerates the Rh^{I} active species. The selectivity outcome is governed by two key facts: 1) The C–H activation of trimethylsilylacetylene in the first step is favored compared with that of aromatic or aliphatic alkynes owing to its higher acidity,[11] and 2) the bulkier trimethylsilyl group hinders the insertion step for this substrate, thus, aliphatic and aromatic alkynes react faster. The increase in acidity of the alkyne through incorporation of a $-CF_3$ group in 1-ethynyl-4-(trifluoromethyl)-benzene (**4e**) could explain the observed preferential homodimerization of this alkyne. Finally, note the beneficial effect of using an excess of pyridine, which plays a crucial role in the catalytic cycle for the stabilization of Rh–alkynyl–hydride intermediates.[13f]

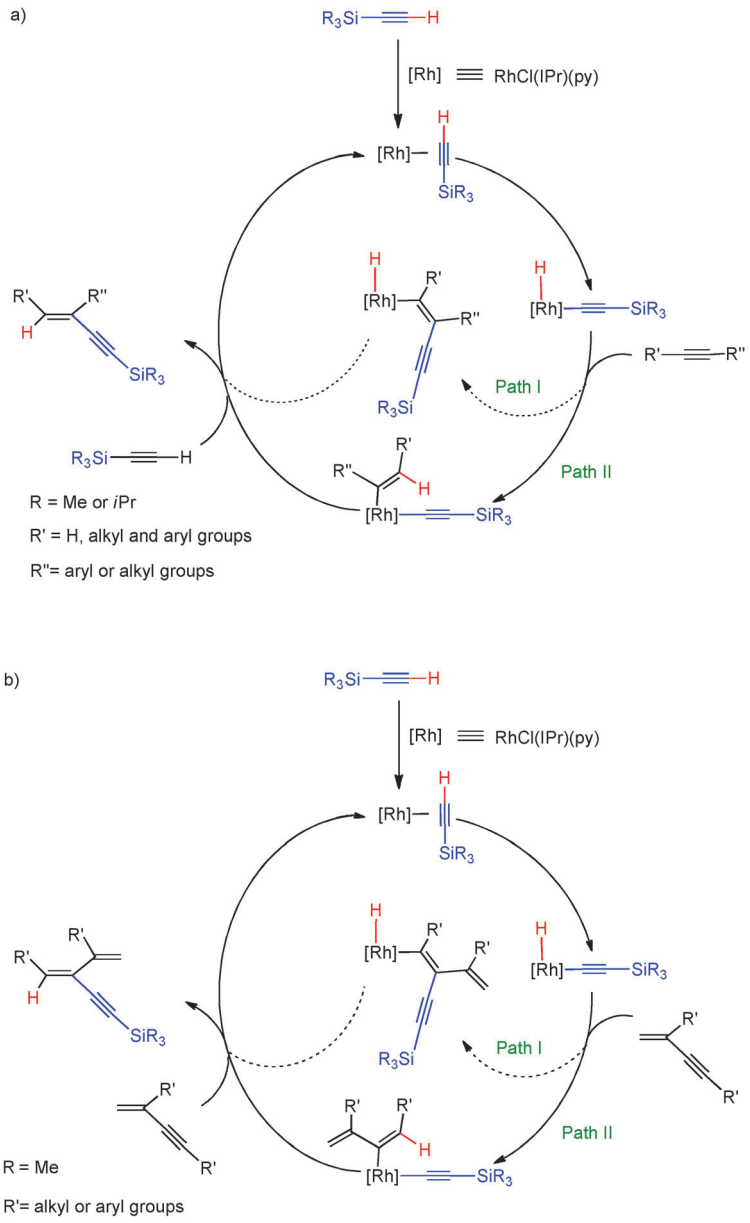
Conclusions

We have described an efficient protocol for the selective head-to-tail cross-dimerization and -trimerization of silylacetylenes with alkynes promoted by a Rh–*N*-heterocyclic carbene catalyst. This catalytic system is an alternative for the synthesis of elaborated enynes and dienynes, which are difficult to prepare by using other available methods. The reaction could be applied to various terminal alkynes, symmetrical and unsymmetrical internal alkynes, and *gem*-1,3-disubstituted enynes with substituents of different electronic character.

Experimental Section

General

All reactions were performed with rigorous exclusion of air by applying Schlenk techniques. All reagents were commercially available and used as received, except for phenylacetylene, which was distilled under Ar and stored over molecular sieves. Organic solvents were dried by using standard methods and distilled under Ar before use or obtained oxygen- and water-free with a Solvent Purification System (Innovative Technologies). The starting complexes $[Rh(\mu\text{-}Cl)(IPr)(\eta^2\text{-coe})]_2$ (**1a**)[16] and **2**[13d] were prepared as described previously in the literature. The ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded with either a Bruker ARX 300 MHz or a Bruker 400 MHz instrument. Chemical shifts for ^1H and $^{13}C\{^1H\}$ NMR spectra were



Scheme 6. Plausible mechanism for the cross-dimerization and -trimerization of alkynes.

referenced to residual solvent peaks. Spectral assignments were accomplished by performing a combination of ^{1}H–^{1}H COSY, ^{13}C-APT, and ^{1}H–^{13}C HSQC and HMBC NMR experiments. The GC–MS spectra were recorded with an Agilent 5973 mass selective detector interfaced to an Agilent 6890 series gas chromatograph system equipped with an HP-5MS 5% phenyl methyl siloxane column (30 m×250 mm with a 0.25 mm film thickness).

Catalytic cross-dimerization of silylacetylenes with terminal or internal alkynes

An NMR tube containing a solution of catalyst **2a** (0.01 mmol, 5 mol%) in C_6D_6 (0.5 mL) was treated with silylacetylene (**3a** or **b**, 0.2 mmol), terminal alkyne (**4**, 0.2 mmol) or internal alkyne (**9**, 0.2 mmol), and pyridine (0.1 mmol) and heated at 80 °C. The conversion was monitored with an NMR apparatus and quantified by the integration of the ^{1}H NMR signals of the aliphatic or aromatic alkyne and the products formed.

Isolation of *gem*-1,3-disubstituted enynes

General procedure: A solution of catalyst **2a** (0.02 mmol), pyridine (0.2 mmol), silylacetylene (**3a** or **b**, 0.4 mmol), and terminal alkyne (**4**, 0.4 mmol) or internal alkyne (**9**, 0.4 mmol) in toluene (10 mL) was placed in a Schlenk tube and stirred at 80 °C for the time indicated in Table 1. The solution was analyzed by using GC–MS to quantify the remaining substrate and was later concentrated under reduced pressure, affording a crude residue, which was purified by using column chromatography on silica gel (70–230 mesh) and eluted with hexane–diethyl ether (99:1) to isolate the corresponding products.

Isolation of *gem*-1,3-disubstituted dienyne derivatives

General procedure: A solution of catalyst **2a** (0.02 mmol), terminal alkyne (**4**, 0.4 mmol), and pyridine (0.2 mmol) in toluene (10 mL) was placed in a Schlenk tube and stirred at 40 °C. Upon conversion of the corresponding alkyne into *gem*-1,3-enyne (**7**), trimethylsilylacetylene (**3a**, 0.2 mmol) was added and the solution was heated at 80 °C for 12 h. The solution was concentrated under reduced pressure, affording a crude residue, which was purified by using column chromatography on silica gel (70–230 mesh) and eluted with hexane–diethyl ether (90:10) to isolate the corresponding dienynes (**8**).

NMR data

See the Supporting Information for full NMR data of all compounds.

1-Trimethylsilyl-3-phenylbut-3-en-1-yne (**5a**): Isolated as a light yellow oil; yield 71%; ^{1}H NMR (400 MHz, C_6D_6, 298 K): $\delta = 7.81$ (d, $J_{H-H} = 8.3$ Hz, 2H; H_{o-Ph}), 7.23 (dd, $J_{H-H} = 8.3$, 7.4 Hz, 2H; H_{m-Ph}), 7.18 (t, $J_{H-H} = 7.4$ Hz, 1H; H_{p-Ph}), 5.80 and 5.77 (both d, $J_{H-H} = 1.0$ Hz, 2H; H_4), 0.31 ppm (s, 9H; SiMe); $^{13}C\{^{1}H\}$ APT NMR plus HSQC and HMBC (100 MHz, C_6D_6, 298 K): $\delta = 137.3$ (s, C_{q-Ph}), 131.1 (s, C_3), 128.5 and 128.4 (both s, $C_{m,p-Ph}$), 126.2 (s, C_{o-Ph}), 121.5 (s, C_4), 104.7 (s, C_2), 88.8 (s, C_1), −0.3 ppm (s, SiMe); GC–MS: *m/z* (%): 200 [M^+], 185 [M^+−Me], 170, 145, 129, 105.

(***E***)-1-Trimethylsilyl-3-benzylidene-4-phenylpent-4-en-1-yne (**8a**): Isolated as a colorless oil; yield 65%; ^{1}H NMR (400 MHz, C_6D_6, 298 K): $\delta = 7.42$ (d, $J_{H-H} = 8.2$ Hz, 2H; $H_{o-Ph\beta}$), 7.15 (d, $J_{H-H} = 8.0$ Hz, 2H; $H_{o-Ph\alpha}$), 7.09 (s, 1H; H_6), 6.93 (dd, $J_{H-H} = 8.2$ Hz, 7.6, 2H; $H_{m-Ph\beta}$), 6.89 (t, $J_{H-H} = 7.6$ Hz, 1H; $H_{p-Ph\beta}$), 6.75 (dd, $J_{H-H} = 8.0$ Hz, 7.6, 2H; $H_{m-Ph\alpha}$), 6.72 (t, $J_{H-H} = 7.6$ Hz, 1H; $H_{p-Ph\alpha}$), 5.40 and 5.25 (both d, $J_{H-H} = 1.0$ Hz, 2H; H_5), 0.00 ppm (s, 9H; SiMe); $^{13}C\{^{1}H\}$ APT NMR plus HSQC and HMBC (100 MHz, C_6D_6, 298 K): $\delta = 145.6$ (s, C_4), 139.4 (s, C_6), 138.0 (s, $C_{q-Ph\beta}$), 136.0 (s, $C_{q-Ph\alpha}$), 129.4 (s, $C_{o-Ph\alpha}$), 128.7 and 128.6 (both s, $C_{m,p-Ph\beta}$), 128.3 and 128.2 (both s, $C_{m,p-Ph\alpha}$), 126.8 (s, $C_{o-Ph\beta}$), 124.6 (s, C_3), 116.2 (s, C_5), 107.8 (s, C_2), 92.0 (s, C_1), 0.0 ppm (s, SiMe); HRMS (ESI): *m/z*: calcd for $C_{21}H_{22}Si$: 303.1564[M^++1]; found: 303.1544.

(*E*)-1-Trimethylsilyl-3,4-diphenylbut-3-en-1-yne (**10b**): Isolated as a colorless oil; yield (91%); ^{1}H NMR (400 MHz, C_6D_6, 298 K): $\delta = 7.55$ (d, $J_{H-H} = 8.1$ Hz, 2H; H_{o-Ph}), 7.30 (s, 1H; H_4), 7.15–7.07 (m, 6H; H_{Ph}), 6.98 (d, $J_{H-H} = 8.1$ Hz, 2H; H_{o-Ph}), 0.32 ppm (s, 9H; SiMe); $^{13}C\{^1H\}$ APT NMR plus HSQC and HMBC (100 MHz, C_6D_6, 298 K): $\delta =$ 137.8 and 136.2 (both s, C_{q-Ph}), 137.6 (s, C_4), 129.5, 129.2, 128.6, 128.2, 127.8, and 127.7 (all s, C_{Ph}), 124.7 (s, C_3), 108.4 (s, C_2), 94.5 (s, C_1), −0.1 ppm (s, SiMe); HRMS (ESI): *m/z*: calcd for $C_{19}H_{20}Si$: 277.1407 [M^++1]; found: 277.1426.

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