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Coupling of propargylsilanes with Fischer carbene chromium complexes: a new synthesis of conjugated dienes

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Abstract

The reaction of propargylsilanes with Fischer carbene complexes has been examined. If the silane-containing carbon is secondary the predominant pathway involves formation of conjugated dienes through a 1,2-silicon shift process of the initially formed vinylcarbene complex intermediate. If a primary propargylsilane is employed, the silicon does not shift and normal alkyne-Fischer carbene coupling processes are observed. The process is moderately stereoselective, resulting in the *E* enol ether and *Z* alkenylsilane.

Keywords: Carbene complexes; Chromium; Alkynes; Silicon migration; Dienes

1. Introduction

The instability of Fischer carbene complexes that contain an α-silyl group is well-known [1]. Deliberate attempts to prepare this class of compounds often result in their conversion to 1-alkoxy-1-silylalkenes. Most of the stable α-silylcarbene complexes feature additional stabilizing influences such as a tungsten metal or amino substitution at the carbene carbon. In one case, the room-temperature conversion of an α-silylcarbene complex to an alkenylsilane was observed and measured kinetically. Based on these observations, a program to examine the reaction between propargylsilanes and Fischer carbene complexes was initiated (Scheme 1) [2]. This reaction would afford an intermediate carbene complex (**3**) that features an α-trimethylsilyl group. A conjugated diene-enol ether (**4**) would result if these complexes undergo the silyl migration process in reference 1. Alternatively, if propargylsilanes successfully undergo annulation processes, then silylated products useful for further transformations would be obtained. For example, the Dötz benzannulation reaction [3] using a propargylsilane and a phenylcarbene complex would afford a benzylsilane (e.g. **5**). Alternatively, the cyclopentannulation reaction of a cyclopropylcarbene complex and a propargylsilane would lead to a cyclopentadienone **6** [4], which would then likely rearrange to fulvene **7** after a 1,7-silicon shift [5]. The conversion of **6** to **7** (R^1 = H) is a highly exothermic process according to DFT calculations ($\Delta H = -7.9$ kcal/mol) [6] (see Fig. 1).

2. Results

General methods for preparation of propargylsilanes and carbene complexes are depicted in Scheme 2. Propargylsilanes were prepared through the double-deprotonation of terminal alkynes followed by reaction with one mole of trimethylsilyl chloride [7]. The most generally efficient procedure involves the treatment of the

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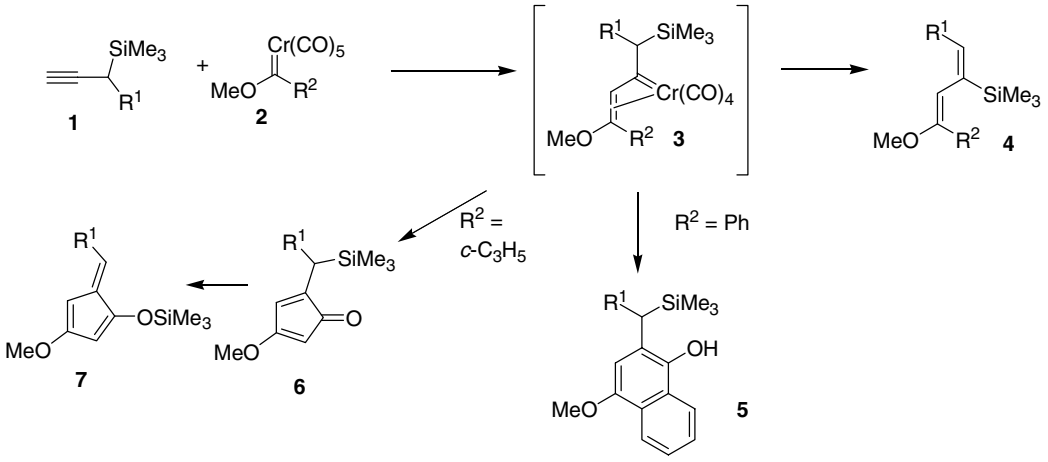
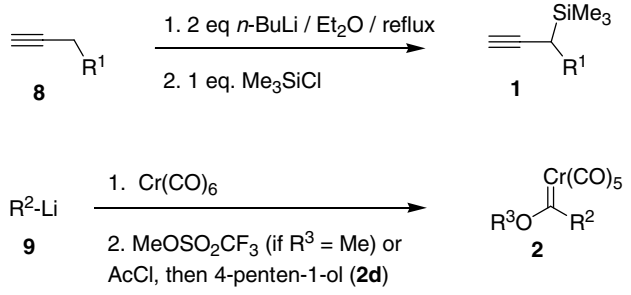


Scheme 1.

a R^1 = Ph
b R^1 = n-C_3H_7
c R^1 = H

Fig. 1. Substituent letter codes for compounds **1**, **5**–**7**.



Scheme 2.

terminal alkyne with two equivalents of n-butyllithium in refluxing ether. Carbene complexes were prepared from the corresponding organolithium reagents according to the method of Fischer (see Fig. 2).

Initially the coupling of cyclopropylcarbene complex **2a** and propargylsilane **1a** was examined (Table 1, entry A). This coupling afforded an isomeric mixture (83:17 ratio) of diene **4a**. No cyclopentannulation products (e.g. **6a** or **7a**) were isolated from this reaction. The coupling of the propargylsilane derived from 1-hexyne (**1b**) with cyclopropylcarbene complex **2a** was also examined. A similar process was observed, resulting in the formation of an isomeric mixture (76:15:9 ratio) of diene **4e** (Entry E). Various carbene complexes were tested in their reaction with propargylsilanes. In most of the cases, diene formation was the exclusive reaction process. Other processes are not competitive with the diene synthesis. As noted in Entries C and G, benzannulation hypothetically resulting in naphthols (**5a** or **5b**) does not occur. A more severe test, triene synthesis from alkenylcarbene complexes (Entries H–J) was also successful. Competing benzannulation was not observed in any of the reaction in Entries H–J. Intramolecular cyclopropanation was also non-competitive with the diene synthesis (Entry D). Failure of the diene synthesis was noted in the reaction process involving simple propargylsilane **1c** (Entry K and Scheme 3). This reaction afforded exclusively the Dötz benzannulation product **5c** and none of the expected diene derivative **4k**.

a R^2 = c-C_3H_5, R^3 = Me
b R^2 = Me, R^3 = Me
c R^2 = Ph, R^3 = Me
d R^2 = Me, R^3 = -$(CH_2)_3CH{=}CH_2$
e R^2 = -$CH{=}CHCH_3$, R^3 = Me
f R^2 = -$C(CH_3){=}CH_2$, R^3 = Me
g R^2 = (5,6-dihydropyran)-2-yl, R^3 = Me

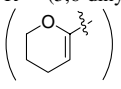
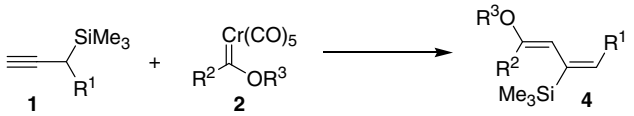


Fig. 2. Substituent letter codes for compound **2**.

3. Discussion

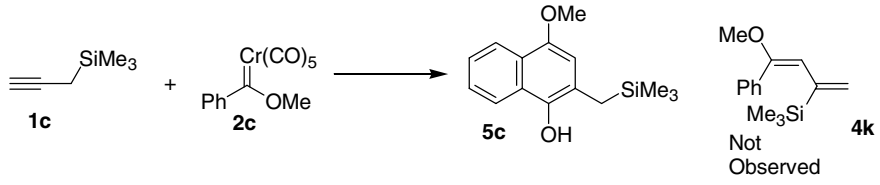
The major isomers of the diene adducts were assigned as E enol ethers based on well-documented trends in the chromium carbene–alkyne coupling [9] and based on the chemical shifts of the enol ether carbon atoms in the major isomers [10] (Table 2). Note that in the cases where a direct comparison can be made (Entries A, C, and G), the chemical shift of asterisked carbon for the major diene stereoisomer is about 10 ppm less than the analogous carbon one of the minor stereoisomers. Based on these chemical shift trends, the minor isomer in Entry A has been assigned as the E, Z isomer [8]. In Entries C and G, one of the minor isomers has been assigned

Table 1
Synthesis of dienes through coupling of propargylsilanes with Fischer carbene complexes



Entry[a] (Reactants)	R^1	R^2	R^3	Yield[b] (%)	Isomer ratio[c,d,e]
A (**1a** + **2a**)	Phenyl	*c*-C_3H_5	Methyl	80	83:17
B (**1a** + **2b**)	Phenyl	Methyl	Methyl	78	63:19:18
C (**1a** + **2c**)	Phenyl	Phenyl	Methyl	82	63:20:17
D (**1a** + **2d**)	Phenyl	Methyl	–$(CH_2)_3$ CH=CH_2	90	77:23
E (**1b** + **2a**)	*n*-C_3H_7	c-C_3H_5	Methyl	90	76:15:9
F (**1b** + **2b**)	*n*-C_3H_7	Methyl	Methyl	85	76:15:9
G (**1b** + **2c**)	*n*-C_3H_7	Phenyl	Methyl	75	56:25:19
H (**1b** + **2e**)	*n*-C_3H_7	*trans*-CH=$CHCH_3$	Methyl	70	72:14:14
I (**1b** + **2f**)	*n*-C_3H_7	–$C(CH_3)$=CH_2	Methyl	72	69:25:6
J (**1b** + **2g**)	*n*-C_3H_7	(5,6-dihydropyran)-2-yl	Methyl	80	84:16
K (**1c** + **2c**)	H	Phenyl	Methyl	0	–[f]

[a] Entry letters correlate with R^1–R^3 substituents for compound **4** and intermediates **3**, **12**, **15**, and **16**.
[b] The yield refers to the combined yield of all stereoisomers; complete separation was impossible in most cases.
[c] The major isomer was the *E*, *E* isomer [8].
[d] The minor isomer(s) was assumed to differ from the major isomer in the configuration at one (not both) double bonds.
[e] See Tables 2 and 3 and the experimental for specific discussions on the stereochemical assignments of minor isomers in Entries A, C, and G.
[f] See Scheme 3.



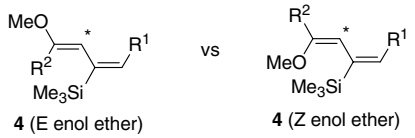
Scheme 3.

as the *E*, *Z* isomer, and the other has been assigned as the *Z*, *Z* isomer.

Assignment of stereochemistry to the alkenylsilane functionality was more difficult. Protiodesilylation of the isomeric mixture from Entry C led to a mixture of three dienes (structure **10**, Table 3) in an identical ratio to those obtained in the carbene coupling. The observed couplings are depicted in Table 3. Only Minor Isomer 1 affords a product consistent with trans coupling between H'_B and H'_C (J = 15.6 Hz). This coupling in the product derived from the other isomers is consistent with cis coupling (J = 11.2 and 11.6 Hz). These values suggest that the *E* alkenylsilane is the major isomer produced as a result of the carbene coupling. This stereochemistry is consistent with that observed in previous conversion of α-silylcarbene complexes to alkenylsilanes [1] and is consistent with other reaction processes that transform carbene complexes into alkenes [11]. In the other cases where three isomers were obtained, the two minor isomers were assumed to differ in the configuration at one and not both of the alkene units.

The mechanism for the formation of dienes is depicted in Scheme 4. After formation of the vinylcarbene complex **3**, migration of silicon occurs to afford the diene derivative. The Dötz benzannulation reaction, which requires

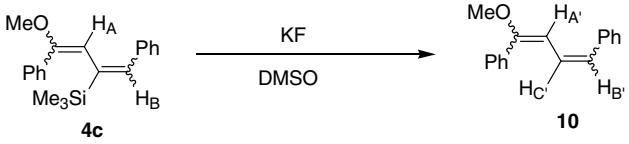
Table 2
NMR data for isomer comparisons



4 (E enol ether) **4** (Z enol ether)

Compound	*C δ (major isomer)	*C δ (2nd isomer)	*C δ (3rd isomer)
Entry A (**4a**)	96.1	105.4	
Entry B (**4b**)	96.7		
Entry C (**4c**)	102.1	106.0	114.0
Entry D (**4d**)	97.6		
Entry E (**4e**)	95.5		
Entry F (**4f**)	96.4		
Entry G (**4g**)	105.6	111.3	105.8

Table 3
Observed couplings in the protiodesilylation of isomeric compounds **4c**



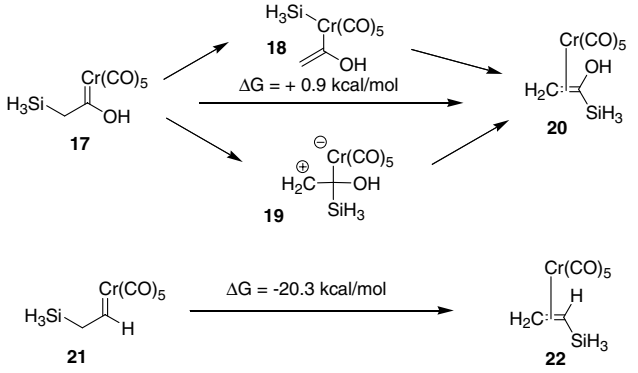
4c **10**

Isomer[a]	δH_A	δH_B	$\delta H'_A$	$\delta H'_B$	$\delta H'_C$
Major (*E*, *E*)	5.61	6.69	6.14 (d, J = 11.2)	6.20 (d, J = 11.2)	6.30 (t, J = 11.2)
Minor 1 (*E*, *Z*)	5.90	6.80	5.75 (d, J = 10.6)	6.49 (d, J = 15.6)	6.89 (dd, J = 15.6, 10.6)
Minor 2 (*Z*, *E*)	6.16	6.96	6.47 (d, J = 11.6)	6.51 (d, J = 11.6)	6.77 (t, J = 11.6)

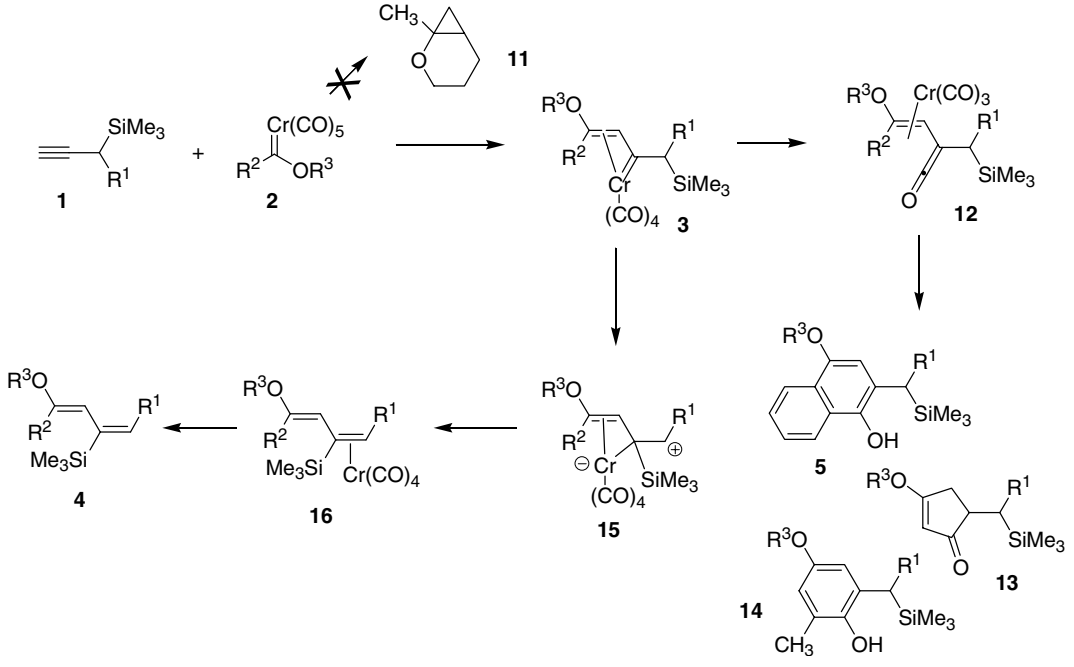
[a] The second letter refers to the alkenylsilane stereochemistry in **4c**, the letter would be opposite for diene **10**.

CO insertion to form a ketene (**12**), is not competitive with diene formation since the silicon migration process occurs prior to any CO insertion. The cyclopentannulation likely has a similar requirement [4]. The diene synthesis was also favored over intramolecular cyclopropanation. Apparently this process is easily intercepted by coordination of the alkyne to a coordinatively unsaturated carbene complex intermediate [12].

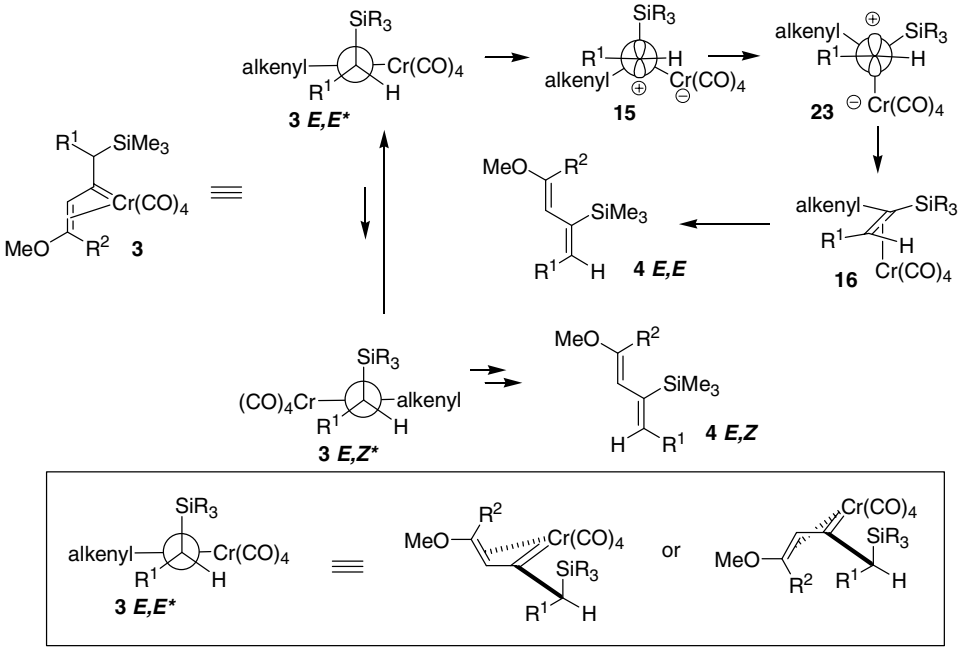
Synthesis of a diene (**4k**) was not observed in the coupling of simple propargylsilane **1c** with phenylcarbene complex **2c**. Only the benzannulation product **5c** was isolated from this reaction. The diene synthesis likely fails in this case because the silicon shift process is less favorable. In the coupling of **1c** and **2c**, silyl migration from the alkenylcarbene complex intermediate (**3k**) generates a primary-like carbocation intermediate (**15k**) A similar observation was noted in [3 + 2]-cycloadditions of allenylsilanes. In these cases, the cycloaddition process failed for allenylsilanes devoid of an alkyl group alpha to the silane group [13].



Scheme 5.



Scheme 4.



Scheme 6.

Mechanistically, both a concerted 1,2-migration of silicon and a 1,3-shift of silicon followed by reductive elimination have been proposed as likely mechanisms for transformation of α-silylcarbene complexes to alkenylsilane–metal complexes. Evaluation of this process was attempted computationally using DFT calculations on the simple systems **17** and **21** (see Scheme 5). All attempts to effect energy minimization on the intermediates **18** and **19** resulted in structures identical to **20**. Energy minimizations performed on other seven-coordinate pentacarbonylchromium complexes analogous to **18** also failed; an attempt to minimize *cis*-$Me_2Cr(CO)_5$ resulted in $Cr(CO)_5$ coordinated to a C–H bond of ethane [14]. Unsuccessful minimization of **19** is not surprising since it can be viewed as an extreme resonance form of **20** [15]. The 1,2-shift mechanism is favored due to the unique failure of the diene synthesis employing the simple propargylsilane **1c** and the instability of $R_2Cr(CO)_5$ species. Transformation of the α-silylcarbene complex to an alkenylsilane-$Cr(CO)_5$ complex was slightly endothermic for the hydroxycarbene complex **17** but considerably exothermic for the non-oxygenated carbene complex **21**. In both carbene complexes **17** and **21**, a nearly perfect overlap of the carbon–silicon bond and the *p*-orbital at the carbene carbon was noted in the energy-minimized structures.

The stereochemistry of alkenylsilane formation is rationalized in Scheme 6. Two conformers featuring overlap of the carbene p-orbital with the carbon–silicon bond can be envisaged; these have been labeled ***3 E,E**** and ***3 E,Z****. Conformer ***3 E.Z**** is predicted to be less stable due to steric interaction between the $Cr(CO)_4$ unit and the R^1 substituent [16]. Silicon migration from the more stable conformer ***3 E,E**** would initially provide zwitterionic intermediate **15**. Hyperconjugation from the more electropositive element chromium can be achieved through a 60° rotation of the chromium-bearing carbon leading to intermediate **23** [17], which can be viewed as an extreme resonance form of alkene chromium complex **16**. Decomplexation of chromium provides the *E,E* isomer of diene **4**. If the minor conformer ***3 E,Z**** proceeds through the same reaction sequence, the *E,Z* isomer of diene **4** would be produced.

4. Conclusion

The coupling of propargylsilanes and carbene complexes readily affords diene derivatives featuring enol ether and alkenylsilane functionalities. A mechanism involving alkyne insertion followed by rapid 1,2-migration of silicon and decomplexation of chromium has been proposed and supported through analysis of the scope of the reaction and through theoretical calculations. The only failure noted was the coupling of carbene complexes with the unsubstituted propargylsilane **1c**.

5. Experimental [18]

5.1. Starting materials

The following were prepared according to literature procedures: 3-phenyl-3-trimethylsilyl-1-propyne (**1a**)

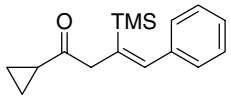
[7], 3-trimethylsilyl-1-hexyne (**1b**) [7], cyclopropylcarbene complex **2a** [19], methylcarbene complex **2b** [20], phenylcarbene complex **2c** [21], pentenyloxycarbene complex **2d** [22], 1-propenylcarbene complex **2e** [23], 2-propenylcarbene complex **2f** [24], and pyranylcarbene complex **2g** [25]. The simple propargylsilane 3-trimethylsilylpropyne is commercially available.

5.2. General procedure for the coupling of carbene complexes with propargylsilanes

A solution of carbene complex (1.0 eq) and propargylsilane (1.5 eq) in dioxane or THF was heated at reflux until a routine TLC indicated complete consumption of the starting carbene complex (typically 2–3 h). The reaction mixture was allowed to cool to room temperature and hexane (10 mL) was added. The green solution was filtered through a bed of Celite and washed with 4:1 hexane: ethyl acetate. Removal of the solvent on a rotary evaporator afforded the crude diene product. At this point the isomer ratio was determined through examination of peaks in the region δ 5–7 of the ^{1}H NMR spectrum. Final purification was achieved by Flash chromatography on triethylamine-treated silica gel [26] using pure hexane as the eluent. Due to difficulty in separation, spectral data are reported for the mixture of isomers. The exceptions are Entries A, D, and J, where the *E* and *Z* isomers were separable.

5.3. Coupling of carbene complex **2a** with propargylsilane **1a** (Table 1, Entry A)

The general procedure was followed using cyclopropylcarbene complex **2a** (0.055 g, 0.20 mmol) and propargylsilane **1a** (0.056 g, 0.30 mmol) in dioxane (10 mL). Final purification using hexane as the eluent afforded a single fraction identified as an 83:17 mixture of dienes **4a** (0.043 g, 80%). A small portion of this sample (0.020 g) was applied to a preparative TLC plate and could be separated into two bands. The minor (less polar) fraction was tentatively assigned as the *Z*, *E* isomer based on the relatively large difference in the δ of the enol ether proton (5.33) vs. the same proton in the major (*E*, *E*) isomer (5.10). ^{1}H NMR ($CDCl_3$): δ 7.42–7.16 (m, 5H), 6.58 (s, 1H), 5.33 (s, 1H), 3.66 (s, 3H), 1.47 (m, 1H), 0.78–0.69 (m, 2H), 0.59–0.54 (m, 2H), 0.09 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 156.2, 139.8, 138.9, 136.6, 129.3, 127.8, 126.6, 105.4, 54.9, 14.1, 12.1, 5.7, 1.0, −0.5; IR (CH_2Cl_2): 1631 (m) cm^{-1}. This product was not further characterized, but was hydrolyzed using aqueous concentrated hydrochloric acid to afford ketone **24**. ^{1}H NMR ($CDCl_3$): δ 7.42–7.23 (m, 5H), 7.07 (s, 1H), 3.65 (s, 2H), 2.05 (m, 1H), 1.12–1.04 (m, 2H), 0.95–0.86 (m, 2H), 0.20 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 209.3, 141.2, 137.8, 128.3, 128.2, 127.8, 127.0, 45.4, 20.2, 11.0, 0.2, −1.4; IR (CH_2Cl_2): 1700 cm^{-1}; Mass Spec. (EI): 258 (M, 6), 243 (100), 215 (3), 159 (5), 141 (3), 115 (7), 73 (42); HRMS: Calc. for $C_{16}H_{22}OSi$ 258.1439. Found 258.1442. The more polar fraction was assigned as the *E*, *E* isomer. ^{1}H NMR ($CDCl_3$): δ 7.57–7.11 (m, 5H), 6.67 (d, 1H, J = 2.0 Hz), 5.10 (d, 1H, J = 2.0 Hz), 3.53 (s, 3H), 1.40 (m, 1H), 0.59–0.50 (m, 2H), 0.30–0.20 (m, 2H), 0.16 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 153.9, 140.9, 138.9, 137.4, 129.1, 128.7, 127.9, 126.8, 96.1, 54.6, 11.6, 5.2, 4.2, 0.2, −1.5; IR (CH_2Cl_2): 1631 (s) cm^{-1}; Mass Spec. (EI): 272 (M, 37), 229 (22), 225 (5), 167 (6), 141 (7), 105 (11), 73 (100); HRMS: Calc. for $C_{17}H_{24}OSi$ 272.1596. Found 272.1586.



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5.4. Coupling of carbene complex **2b** with propargylsilane **1a** (Table 1, Entry B)

The general procedure was followed using methylcarbene complex **2b** (0.050 g, 0.20 mmol) and propargylsilane **1a** (0.056 g, 0.30 mmol) in dioxane (10 mL). Final purification using hexane as the eluent afforded a single fraction identified as a 63:19:18 mixture of dienes **4b** (0.038 g, 78%). ^{1}H NMR ($CDCl_3$): major (*E*, *E*) isomer: δ 6.62 (s, 1H), 5.10 (s, 1H), 3.60 (s, 3H), minor isomers: δ 6.62 (s, 1H), 6.58 (s, 1H), 5.36 (s, 1H), 5.22 (s, 1H), 3.53 (s, 3H), 3.49 (s, 3H); the following peaks are overlapping in all three isomers: δ 7.49–7.41 (m, 2H), 7.28–7.15 (m, 3H), 1.45 (s, 3H), 0.12 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 151.8, 141.2, 138.8, 137.2, 128.7, 128.0, 127.7, 126.9, 126.7, 125.2, 104.2, 96.7, 54.5, 17.0, −1.8, −3.4; IR (CH_2Cl_2): 1644 (m); Mass Spec. (EI): 246 (M, 7), 217 (47), 189 (13), 143 (8), 105 (29), 73 (100); HRMS: Calc. for $C_{15}H_{22}OSi$ 246.1440. Found 246.1439.

5.5. Coupling of carbene complex **2c** with propargylsilane **1a** (Table 1, Entry C)

The general procedure was followed using phenylcarbene complex **2c** (0.062 g, 0.20 mmol) and propargylsilane **1a** (0.055 g, 0.30 mmol) in dioxane (10 mL). Final purification using hexane as the eluent afforded a single fraction identified as a 63:20:17 mixture of dienes **4c** (0.050 g, 82%). ^{1}H NMR ($CDCl_3$): major (*E*, *E*) isomer: δ 6.69 (d, 1 H, J = 2.4 Hz), 5.61 (d, 1H, J = 2.4 Hz), 3.80 (s, 3H), *E*, *Z* isomer: δ 6.80 (d, 1H, J = 1.9 Hz), 5.90 (d, 1H, J = 1.9 Hz), 3.51 (s, 3H); *Z*, *E* isomer: δ 6.96 (d, 1H, J = 1.8 Hz), 6.16 (d, 1H, J = 1.8 Hz), 3.75 (s, 3H); the following peaks are overlapping in all three isomers: δ 7.67–7.11 (m, 10H), 0.14 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 155.3, 154.2, 153.6, 145.7, 141.3, 140.4, 139.6, 139.0,

138.8, 138.6, 136.9, 136.6, 136.3, 129.5, 129.4, 128.8, 128.4, 128.2, 127.7, 127.0, 126.8, 126.1, 125.0, 114.0, 106.0, 102.1, 58.5, 55.9, 55.7, 0.0, −0.7, −3.0; IR (CH_2Cl_2): 1624 (m); Mass Spec. (EI): 308 (M, 29), 293 (100), 234 (24), 203 (15), 145 (8), 102 (8) 73 (73); HRMS: Calc. for $C_{20}H_{24}OSi$ 308.1596. Found 308.1582.

5.6. Coupling of carbene complex **2d** with propargylsilane **1a** (Table 1, Entry D)

The general procedure was followed using pentenyloxycarbene complex **2d** (0.066 g, 0.20 mmol) and propargylsilane **1a** (0.056 g, 0.30 mmol) in dioxane (10 mL). Final purification using hexane as the eluent afforded a single fraction identified as a 77:23 mixture of dienes **4d** (0.054 g, 90%). A sample of the pure major (*E*, *E*) isomer was obtained via preparative TLC. ^{1}H NMR ($CDCl_3$): δ 7.45 (d, 2 H, J = 8.0 Hz), 7.28–7.10 (m, 3H), 6.60 (d, 1H, J = 1.9 Hz), 5.91 (ddt, 1H. J = 16.9, 10.2, 6.9 Hz), 5.08 (d, 1H, J = 1.9 Hz), 5.05 (br d, 1H, J = 16.9 Hz), 4.99 (br d, 1H, J = 10.2 Hz), 3.73 (t, 2H, J = 6.5 Hz), 2.17 (br q, 2H, J = 6.5 Hz), 1.78 (quintet, 2H, J = 6.5 Hz), 1.42 (s, 3H), 0.12 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 151.3, 141.4, 139.0, 138.0, 137.1, 128.8, 128.0, 126.7, 115.0, 97.6, 66.0, 30.3, 28.2, 17.2, −1.7; IR (CH_2Cl_2): 1640 cm^{-1}; Mass Spec. (EI): 300 (M, 32), 231 (4), 216 (12), 141 (5), 115 (7), 73 (100); HRMS: Calc. for $C_{19}H_{28}OSi$ 300.1909. Found 300.1918. The stereochemistry of the minor isomer could not be reliably assigned due to overlapping peaks in the alkene region of the ^{1}H NMR spectrum.

5.7. Coupling of carbene complex **2a** with propargylsilane **1b** (Table 1, Entry E)

The general procedure was followed using cyclopropylcarbene complex **2a** (0.055 g, 0.20 mmol) and propargylsilane **1b** (0.046 g, 0.30 mmol) in dioxane (10 mL). Final purification using hexane as the eluent afforded a single fraction identified as a 76:15:9 mixture of dienes **4e** (0.043 g, 90%). ^{1}H NMR ($CDCl_3$): major (*E*, *E*) isomer: δ 5.78 (td, 1H, J = 6.7, 1.7 Hz), 4.82 (br s, 1H), 3.48 (s, 3 H), *E*, *Z* isomer: δ 6.09 (td, 1H, J = 7.6, 1.8 Hz), 5.03 (br s, 1H), 3.62 (s, 3H), *Z*, *E* isomer: 5.67 (dt, 1H, J = 6.8, 1.5 Hz), 5.06 (br s, 1H), 3.43 (s, 3H), the following peaks are overlapping in all isomers: δ 2.10 (m, 2H), 1.48–1.20 (m, 3H), 0.88 (t, 3H, J = 7.2 Hz), 0.72–0.63 (m, 2H), 0.44–0.49 (m, 2H), 0.04 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 155.9, 154.2, 153.8, 149.5, 141.3, 138.0, 95.5, 55.4, 32.3, 31.2, 22.4, 19.6, 13.9, 11.3, 4.0, 0.0, −1.5, −1.7; IR (CH_2Cl_2): 1696 (m), 1640 (m) cm^{-1}; Mass Spec. (EI): 238 (M, 7), 181 (17), 155 (11), 107 (29), 73 (100); HRMS: Calc. for $C_{14}H_{26}OSi$ 238.1753. Found 238.1764.

5.8. Coupling of carbene complex **2b** with propargylsilane 1b (Table 1, Entry F)

The general procedure was followed using methylcarbene complex **2b** (0.050 g, 0.20 mmol) and propargylsilane **1b** (0.046 g, 0.30 mmol) in dioxane (10 mL). Final purification using hexane as the eluent afforded a single fraction identified as a 76:15:9 mixture of dienes **4f** (0.037 g, 85%). ^{1}H NMR ($CDCl_3$): major (*E, E*) isomer: δ 5.73 (dt, 1H, J = 6.7, 1.7 Hz), 4.80 (br s, 1H), 3.54 (s, 3H), *E*, *Z* isomer: δ 5.88 (dt, 1H, J = 6.8, 1.6 Hz), 5.01 (br s, 1H), 3.50 (s, 3H), *Z*, *E* isomer: 5.65 (dt, 1H, J = 6.5, 1.5 Hz), 5.10 (br s, 1H), 3.52 (s, 3H), the following peaks are overlapping in all isomers: δ 1.95 (m, 2H), 1.58 (s, 3H), 1.45–1.27 (m, 2H), 0.90 (t, 3H, J = 7.8 Hz), 0.05 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 152.4, 147.6, 144.9, 140.9, 138.3, 102.6, 96.4,54.3, 54.0, 33.5, 32.2, 23.2, 22.3, 17.0, 14.0, 13.8, 0.2, −1.5, −2.5; IR (CH_2Cl_2): 1636 (m) cm^{-1}; Mass Spec. (CI): 213 (M + 1, 17), 73 (100); HRMS: Calc. for $C_{12}H_{25}OSi$ 213.1675. Found 213.1681.

5.9. Coupling of carbene complex **2c** with propargylsilane **1b** (Table 1, Entry G)

The general procedure was followed using phenylcarbene complex **2c** (0.062 g, 0.20 mmol) and propargylsilane **1b** (0.046 g, 0.30 mmol) in dioxane (10 mL). Final purification using hexane as the eluent afforded a single fraction identified as a 56:25:19 mixture of dienes **4g** (0.041 g, 75%). ^{1}H NMR ($CDCl_3$): major (*E E*) isomer: δ 5.80 (dt, 1H, J = 7.7, 1.9 Hz), 5.40 (br s, 1H), 3.65 (s, 3H), *E*, *Z* isomer: δ 5.80 (overlaps with *E, E*), 5.25 (br s, 1H), 3.50 (s, 3H), *Z*, *E* isomer: 5.65 (dt, 1H, J = 6.7, 2.0 Hz), 5.40 (overlaps with *E*, *E*), 3.62 (s, 3H), the following peaks are overlapping in all isomers: δ 7.37–7.20 (m, 5H), 1.98 (m, 2 H), 1.58 (s, 3H), 1.14 (m, 2H), 0.71 (t, 3H, J = 7.2 Hz), 0.10 (s, 9 H); ^{13}C NMR ($CDCl_3$): δ 154.1, 153.8, 146.9, 142.7, 136.9, 134.7, 129.4, 128.3, 127.7, 127.6, 127.1, 126.3, 125.8, 111.3, 105.8, 105.6, 55.5, 55.2, 34.3, 22.6, 13.9, 13.7, 1.0, 0.3, −0.7, −1.1; IR (CH_2Cl_2): 1630 (m) cm^{-1}; Mass Spec. (CI): 274 (M, 3), 259 (27), 201 (7), 171 (6), 141 (14), 89 (24), 73 (100); HRMS: Calc. for $C_{17}H_{26}OSi$ 274.1753. Found 274.1736.

5.10. Coupling of carbene complex **2e** with propargylsilane **1b** (Table 1, Entry H)

The general procedure was followed using 1-propenylcarbene complex **2e** (0.276 g, 1.0 mmol) and propargylsilane **1b** (0.231 g, 1.50 mmol) in THF (100 mL). Final purification using hexane as the eluent afforded a single fraction identified as a 72:14:14 mixture of trienes **4h** (0.165 g, 70%). ^{1}H NMR ($CDCl_3$): major (*E*, *E*, *E*) (enol ether, alkenylsilane, original

alkene) isomer: δ 5.95 (dq, 1H, J = 15.6, 6.7 Hz), 5.83 (d, 1H, J = 15.6 Hz), 5.80 (td, 1H, J = 6.7, 2.0 Hz), 4.97 (br s, 1H), 3.62 (s, 3H), (*E*, *Z*, *E*) isomer: δ 5.31 (br s, 1H), 3.45 (s, 3H) (all other alkene H's obscured by major isomer), (*Z*, *E*, *E*) isomer: δ 3.46 (s, 3H) (all alkene H's obscured by peaks for the major isomer), the following peaks are overlapping in all isomers: δ 2.15–1.89 (m, 2H), 1.77 (d, 3 H, J = 6.7 Hz), 1.42 (sextet, 2H, J = 7.0 Hz), 0.85 (t, 3H, J = 7.0 Hz), 0.03 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 151.2, 144.1, 143.8, 142.0, 141.7, 137.9,134.2, 133.5, 131.0, 124.9, 124.6, 100.0, 56.5, 54.7, 51.0, 49.0, 45.1, 42.0, 33.5, 31.5, 22.3, 22.2, 19.2, 18.0, 13.8, −1.5, −1.7; IR (CH_2Cl_2): 1681 (m), 1630 (m) cm^{-1}; Mass Spec. (EI): 238 (M, 4), 223 (7), 209 (3), 195 (4), 181 (6), 165 (11), 73 (100); HRMS (CI): Calc. for $C_{14}H_{27}OSi$ 239.1831. Found 239.1847.

5.11. Coupling of carbene complex **2f** with propargylsilane **1b** (Table 1, Entry I)

The general procedure was followed using 1-propenylcarbene complex **2f** (0.276 g, 1.00 mmol) and propargylsilane **1b** (0.231 g, 1.50 mmol) in THF (100 mL). Final purification using hexane as the eluent afforded a single fraction identified as a 69:25:6 mixture of trienes **4i** (0.172 g, 72%). ^{1}H NMR ($CDCl_3$): δ 5.80 (td, 1H, J = 6.7, 1.4 Hz), 5.61 (br s, 1H), 5.26 (br d, 1H, J = 1.4 Hz), 4.91 (br s, 1H), 3.47 (s, 3H), 2.06 (t, 2H, J = 6.7 Hz), 1.87 (br s, 3H), 1.37 (sextet, 2 H, J = 6.7 Hz), 0.87 (t, 3H, J = 6.7 Hz), 0.09 (s, 9H); the following peaks can be attributed to minor isomers: δ 3.47 (s, 3H, 2nd most isomer), 3.44 (s, 3H, minor isomer) ^{13}C NMR ($CDCl_3$): δ 142.6, 140.7, 138.5, 132.6, 127.3, 124.0, 113.1, 112.1, 58.9, 41.8, 33.0, 29.7, 22.2, 20.1, 18.6, 13.9, −1.6, −2.4; IR (CH_2Cl_2): 1578 (m) cm^{-1}; Mass Spec. (EI): 239 (M + 1, 6), 224 (18), 106 (14), 73 (100); HRMS: Calc. for $C_{14}H_{27}OSi$ 239.1831. Found 239.1817.

5.12. Coupling of carbene complex **2g** with propargylsilane **1b** (Table 1, Entry J)

The General Procedure was followed using carbene complex **2g** (0.302 g, 1.00 mmol) and propargylsilane **1b** (0.231 g, 1.50 mmol) in THF (100 mL). Final purification using hexane as the eluent afforded a single fraction identified as a 84:16 mixture of trienes **4j** (0.220 g, 80%). Further purification using preparative TLC and partial band cutting provided a pure sample of the major (*E*, *E*) stereoisomer. ^{1}H NMR ($CDCl_3$): δ 5.65 (dt, 1H, J = 6.7, 2.0 Hz), 5.13 (br s, 1H), 4.90 (t, 1H, J = 3.9 Hz), 3.96 (t, 2H, J = 5.1 Hz), 3.58 (s, 3H), 2.05 (m, 2H), 1.77 (m, 2H), 1.75 (m, 4H), 1.37 (m, 2H), 0.88 (t, 3H, J = 7.2 Hz), 0.03 (s, 9H); ^{13}C NMR ($CDCl_3$): δ 149.4, 148.3, 142.6, 136.4, 110.1, 98.3, 68.1, 59.0, 32.9, 22.4, 22.3, 20.6, 13.9, −0.9; MS (EI): 280 (M), 265, 251, 237, 207; HRMS: Calc. for $C_{16}H_{28}O_2Si$ 280.1859. Found 280.1869.

5.13. Coupling of carbene complex **2c** with propargylsilane **2c** (Table 1, Entry K)

The general procedure was followed using carbene complex **2c** (0.375 g, 1.20 mmol) and propargyltrimethylsilane (**1c**) (0.113 g, 1.00 mmol) in THF (10 mL). Final purification by flash chromatography on untreated silica gel using 9:1 hexane:ethyl acetate as the eluent afforded a single fraction identified as naphthol **5c** (0.162 g, 62%). ^{1}H NMR ($CDCl_3$): δ 8.15 (d, 1H, J = 8.1 Hz), 7.99 (d, 1H, J = 8.1Hz); 7.42 (m, 2H), 6.43 (s, 1H), 4.45 (s, 1H), 3.92 (s, 3H), 2.17 (s, 2H), 0.05 (s, 9 H) ^{13}C NMR ($CDCl_3$): δ 149.3, 140.3, 125.8, 125.7, 124.1, 124.0, 121.9, 120.3, 119.9, 106.9, 55.7, 21.4, −1.5; MS (EI): 260 (M, 12), 244 (4), 243 (40), 229 (8), 171 (9), 73 (100); HRMS: Calc. for $C_{15}H_{12}O_2Si$ 260.1234. Found 260.1236.

5.14. Fluoride-induced protiodesilylation and hydrolysis of **4c**

Desilylation was effected using a literature procedure [27]. A solution of diene **4c** (0.100 g, 0.324 mmol, 63:20:17 mixture of stereoisomers) in DMSO (5 mL) was heated to 40–45 °C under nitrogen using an oil bath. Potassium fluoride dihydrate (0.092 g, 0.972 mmol) was added and the mixture was stirred at this temperature until disappearance of the starting compound was verified by TLC analysis (about 6 h). The mixture was poured into a mixture of water and ether in a separatory funnel. The aqueous layer was extracted two times with ether. The combined ether layers were washed once with saturated aqueous ammonium chloride solution and dried over sodium sulfate. After evaporation of the solvent, a 63:20:17 mixture of diene stereoisomers was obtained. The crude reaction mixture was analyzed by ^{1}H NMR to determine the stereochemistry of the process. ^{1}H NMR ($CDCl_3$): major (*E*, *Z*) [28] isomer: δ 6.30 (t, 1H, J = 11.2 Hz), 6.20 (d, 1 H, J = 11.2 Hz), 6.14 (d, 1H, J = 11.2 Hz), 2nd most abundant (*E*, *E*) isomer: 6.89 (dd, 1 H, J = 15.6, 10.6 Hz), 6.49 (d, 1H, J = 15.6 Hz), 5.75 (d, 1H, J = 10.6 Hz), minor (*Z*, *E*) isomer: δ 6.77 (t, 1H, J = 11.6 Hz), 6.51 (d, 1H, J = 11.6 Hz), 6.47 (d, 1H, J = 11.6 Hz). After the NMR analysis, the mixture was dissolved in dichloromethane (25 mL) and concentrated aqueous hydrochloric acid (0.5 mL) was added. The reaction mixture was stirred at 25 °C until all starting material had been consumed according to TLC analysis (about 1 h). Water (20 mL) was added and the mixture was extracted with dichloromethane. The organic layer was washed once with saturated aqueous sodium bicarbonate solution, dried over sodium sulfate, and the solvent was removed on a rotary evaporator. Final

purification was achieved by flash chromatography on silica gel using 9:1 hexane:ethyl acetate as eluent. A single fraction was isolated and identified as 1,4-diphenyl-3-buten-2-one (0,055 g, 76%). M.p. 89.5–90.7 °C (lit 92.0–93.0 °C); ^{1}H NMR ($CDCl_3$): δ 8.17–7.85 (m, 2H), 7.65–7.12 (m, 3H), 6.60–6.41 (m, 2H), 3.89 (d, 2H, J = 5.2 Hz); irradiate as δ 3.89: δ 6.55 (d, J = 16.0 Hz), 6.45 (d, 1H, J = 16.0 Hz); IR (CH_2Cl_2): 1684 (s), 1598 (m) cm^{-1}. The spectral data were in agreement with those previously reported for this compound [29].

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