

Note

# Thermal and photochemical reactions of Fischer carbene complexes with trialkylsilyl-substituted alkynes

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## Abstract

Thermal reaction of Fischer carbene complexes with triisopropylsilyl (TIPS) substituted alkynes in benzene afforded TIPS-substituted vinylketenes or 2-TIPS-substituted cyclobutenones as major products while photochemical reaction of Fischer carbene complexes with trimethylsilyl (TMS) substituted alkynes in acetonitrile afforded 3-TMS-substituted cyclobutenones.

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## 1. Introduction

The thermal benzannulation of Fischer carbene complexes with alkynes, commonly known as the Dötz reaction, have been extensively studied and widely utilized to generate substituted aromatic ring systems [1]. Recently, Moser have discovered the interrupted Dötz benzannulation of Fischer carbene complexes with trialkylsilyl-substituted alkynes afforded silyl vinylketenes [2] which can function as versatile four-carbon building blocks in synthesis of highly substituted carbocyclic and heterocyclic compounds via [4+1] [2a,3] and [4+2] [4] annulations. However, the scope of the thermal reaction of Fischer carbene complexes with trialkylsilyl-substituted alkynes has not been extensively studied. On the other hand, the photochemistry of Fischer carbene complexes has experienced an enormous development in the past decades and the photochemical reactions of Fischer carbene complexes with imine, alkene, diene, ketone and aldehyde have been well documented [5]. Low-temperature photolysis of  $[\text{W}(\text{CO})_5\{\text{C}(\text{OMe})\text{Ph}\}]$  in the presence of alkynes leads to spectroscopically observable alkyne–carbene adducts [6] and

photolytic reaction of chromium imine–carbene complexes with alkynes results in 2*H*-pyrrole derivatives [7]. However, the photochemical [2+2] reaction of Fischer carbene complexes with alkynes has not yet been explored. We reported herein for the first time the photochemical [2+2] reaction of the Fischer carbene complexes with trialkylsilyl-substituted alkynes.

## 2. Results and discussion

### 2.1. Thermal reaction of Fischer carbene complexes with TIPS-substituted alkynes

The Fischer carbene complexes **1a–d** were prepared according to the literature [8a]. The initial investigation of the thermal reaction of Fischer carbene complexes **1a–d** with TIPS-substituted alkynes bearing a phenyl ring was indicated in Fig. 1.

The degassed solution of Fischer carbene complexes **1a–c** and various TIPS-substituted alkynes containing a phenyl group in benzene was heated at reflux under argon for 24 h affording the TIPS-vinylketenes complexed with  $\text{Cr}(\text{CO})_3$  moiety (Table 1, entries 1–3) or the  $\text{Cr}(\text{CO})_3$  free TIPS-vinylketenes (Table 1, entries 4 and 5) in moderate to good yield [8b].

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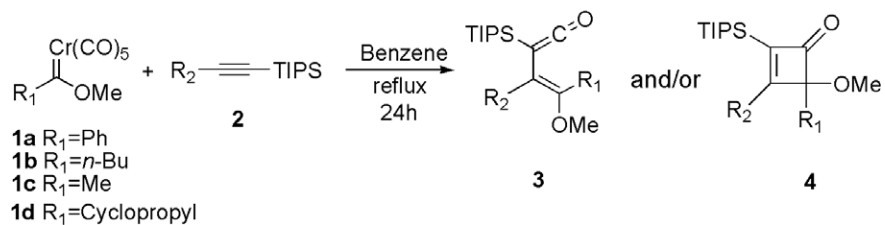


Fig. 1. Thermal reaction of Fischer carbene complexes with TIPS-substituted alkynes containing a phenyl ring.

Table 1  
Thermal reaction of **1a–d** with TIPS-substituted alkynes

Entry	Carbene complex	Alkyne	Product	Yield <sup>a</sup> [%]
1	<b>1a</b>			48
2	<b>1b</b>			33
3	<b>1a</b>			60
4	<b>1c</b>			59
5	<b>1a</b>			65
6	<b>1d</b>			<b>3f</b> : 32 <b>4a</b> : 30
7	<b>1c</b>			66
8	<b>1b</b>			73

<sup>a</sup> Isolated yield.

Interestingly, when the cyclopropyl methoxy chromium Fischer carbene complex **1d** reacted with TIPS-substituted phenyl acetylene under the same thermal reaction conditions, TIPS vinylketene **3f** was obtained in 32% yield along with 30% of the 2-TIPS-substituted cyclobutenone **4a** (Table 1, entry 6).

Due to the significance of cyclobutenones in organic chemistry [9] and encouraged by the previous results, we investigated the thermal reaction of the Fischer carbene complexes with TIPS-substituted alkynes without a phenyl group to explore the scope of the interrupted Dötz benzannulation. Surprisingly, Fischer carbene complex **1c** and **1b** reacted with TIPS-substituted cyclopropyl acetylene and TIPS-substituted furan-2-yl acetylene afforded 2-TIPS-substituted cyclobutenone **4b** and **4c** as sole product respectively (Table 1, entries 7 and 8). The regiochemistry of cyclobutenones **4a**, **4b** and **4c** could be established by the NOE enhancement between the cyclopropyl methylene proton and the methyl group on the cyclobutenone ring of **4b**.

The proposed mechanism accounted for the thermal reaction of Fischer carbene complexes with TIPS-substituted alkynes was outlined in Fig. 2.

Decarbonylation of Fischer carbene complex **1** followed by coordination of the TIPS-substituted alkyne **2** forms the alkyne–carbene complex intermediate **5**. Subsequent alkyne insertion of **5** results in the metallacycle intermediate **6**, which undergoes ring opening to generate the intermediate **7** [10]. When the R<sub>2</sub> contains a phenyl group, CO insertion of **7** results in silyl vinylketene **3A** with the Cr(CO)<sub>3</sub> moiety coordinated to the phenyl ring. The Cr(CO)<sub>3</sub> moiety in **3A** can be removed through ligand exchange with the benzene solvent to afford **3B** [2]. When the R<sub>2</sub> does not contain a phenyl group, CO insertion of

intermediate **7** generates the η<sup>4</sup>-vinylketene complexed intermediate **8** [2a,10–12]. The cyclobutenone **4** is formed from ring closure of the Cr(CO)<sub>3</sub> complexed intermediate **8** [1a].

## 2.2. Photochemical reaction of Fischer carbene complexes with TMS-substituted alkynes

Initially, Fischer carbene complex **1a** was irradiated in the presence of *tert*-butyl dimethylsilyl (TBS) or TIPS-substituted phenyl acetylene under argon. Disappointingly, the reaction only led to decomposition of **1a**. When the alkyne was switched to phenyl acetylene, the similar disappointing result was observed. While **1a** was photolyzed in the presence of TMS-substituted phenyl acetylene in DME under argon, a new product **9a** was obtained in 10% yield (see Fig. 3). According to the IR spectra of **9a**, the silyl vinylketene structure was excluded because **9a** did not have the characteristic ketene band at 2080 cm<sup>-1</sup>.

As shown in Table 2, a variety of reaction conditions were screened to maximize the cyclobutenone **9a** formation. Photolysis of **1a** in the presence of TMS-substituted phenyl acetylene in benzene or ethyl acetate, disappointingly, gave none of the desired product (Table 2, entries 2 and 3). A variety of other solvents were screened (Table 2, entries 4–7), but the desired product was obtained in

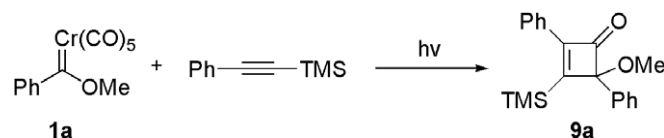


Fig. 3. Photochemical reaction of **1a** with TMS-substituted alkyne.

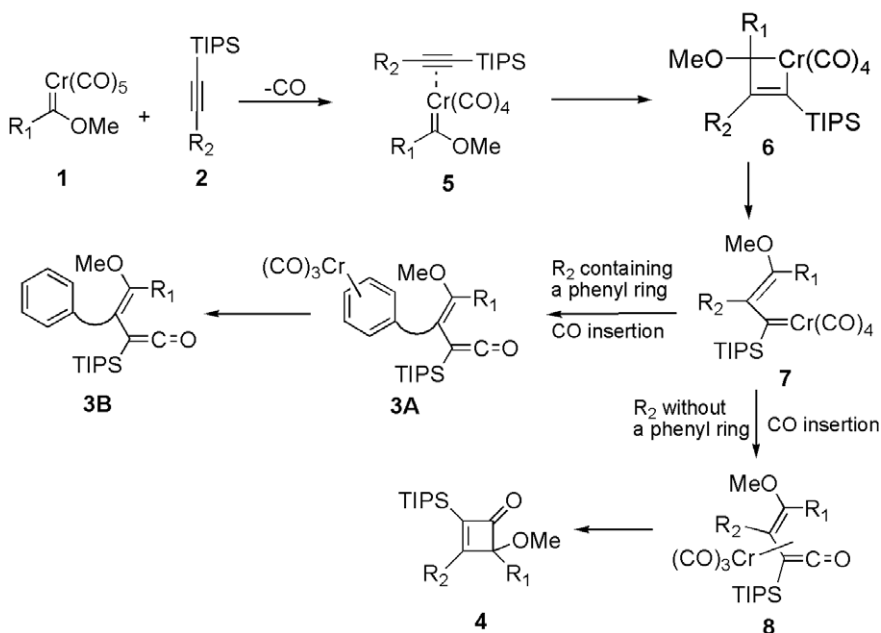


Fig. 2. Proposed mechanism for the thermal reaction of Fischer carbene complexes with TIPS-substituted alkynes.

Table 2  
Photolysis of **1a** to **9a** under different reaction conditions

Entry	Solvent	Adduct	Yield of <b>9a</b> <sup>a</sup> [%]
1	DME		10
2	Ethyl acetate		0
3	Benzene		0
4	Dioxane		18
5	<i>n</i> -Hexane		15
6	Trifluoromethyl benzene		13
7	Acetonitrile/dioxane = 1:2		18
8	Diethyl ether		39
9	Acetonitrile		43
10	Acetonitrile	PPh <sub>3</sub>	28
11	Acetonitrile	CuBr	15
12	Acetonitrile	CF <sub>3</sub> SO <sub>3</sub> Cu	28

<sup>a</sup> Isolated yield.

low yield. While the photochemical reaction was carried out in acetonitrile, the best yield of **9a** (43%) was obtained in all solvents screened. Adducts such as PPh<sub>3</sub>, CuBr and CF<sub>3</sub>SO<sub>3</sub>Cu in acetonitrile (Table 2, entries 10–12), to our surprise, lowered the yield.

Similarly, **9b** was obtained in 46% in acetonitrile from **1a** and TMS-substituted hexyne (Fig. 4).

The regiochemistry of above two cyclobutenones was confirmed by transformation of **9b** to a known compound [13]. To our surprise, they are 3-TMS-substituted cyclobutenones, in which the regiochemistry was different and complementary to the 2-TIPS-substituted cyclobutenone obtained from the thermal reaction.

The mechanism of this 3-TMS-substituted cyclobutenone-forming reaction is unknown at present. The plausible mechanism is shown in Fig. 5.

The Fischer carbene complex **1a** is initially irradiated into the metal-to-ligand charge transfer (MLCT) state

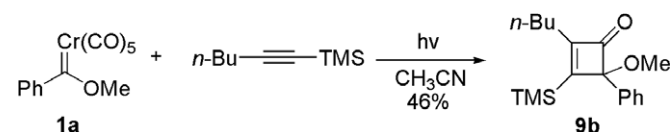


Fig. 4. Photochemical reaction of **1a** with TMS-substituted hexyne.

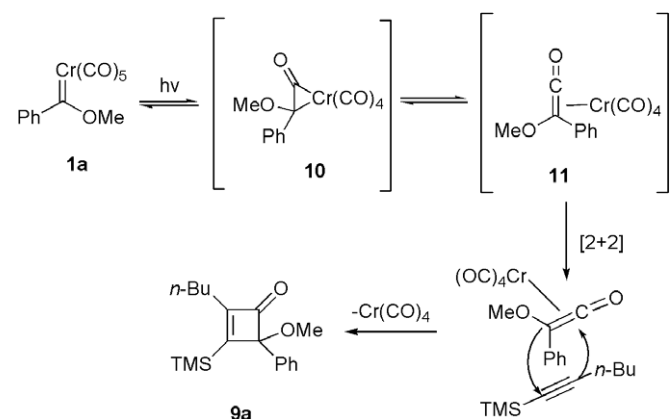


Fig. 5. Proposed mechanism for photochemical reaction of Fischer carbene complexes with TMS-substituted alkynes.

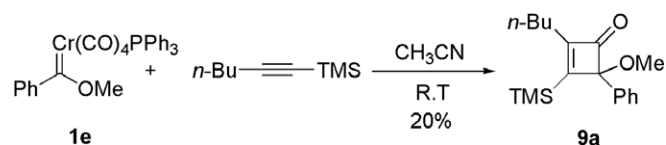


Fig. 6. [2+2] reaction of TMS-substituted hexyne and carbene complex **1e**.

[5b,14]. Excitation into this state results in the formation of the metalacycle intermediate **10** or the chromium–ketene complex **11** [5b,14a,14b]. The metal–ketene complex **11** undergoes [2+2] cyclization to afford the cyclobutenone **9a** in a similar way to the photochemical [2+2] reaction of Fischer carbene complexes with olefins [5b,15]. The silyl group which can enhance the electron density of the alkyne is necessary because the alkyne serves as the nucleophilic part in the photochemical [2+2] reaction with the metal–ketene complex **11** [16]. The similar result was observed in the photochemical [2+2] cyclization of Fischer carbene complexes with olefins where the electron-rich olefins underwent the [2+2] reaction smoothly while the electron-poor olefins did not give the cyclobutanone product [15e]. On the other hand, the steric hindrance of the bulky TBS group may prevent the [2+2] cyclization to give the cyclobutenone product. This could account for the failure of the reaction of **1a** with phenyl acetylene or TBS-substituted phenyl acetylene.

Interestingly, when the carbene complex **1e** was stirred in the presence of TMS-substituted hexyne in acetonitrile under argon at room temperature for 20 h, 3-TMS-substituted cyclobutenone **9a** was also obtained in 20% yield (see Fig. 6).

### 3. Conclusions

The thermal and the photochemical reactions of Fischer carbene complexes with trialkylsilyl-substituted alkynes were investigated in this paper. In the thermal reaction of Fischer carbene complexes with TIPS-substituted alkynes, the silyl vinylketenes generated smoothly when the TIPS-substituted alkynes contained a phenyl ring. On the contrary, 2-TIPS-substituted cyclobutenones could be obtained if the TIPS-substituted alkynes did not bear a phenyl group. Finally, the photochemical [2+2] reaction of the Fischer carbene complexes with the TMS-substituted alkynes in acetonitrile afforded the 3-TMS-substituted cyclobutenones.

### 4. Experimental

#### 4.1. General information

<sup>1</sup>H NMR spectra and <sup>13</sup>C NMR spectra were recorded on VARIAN INOVA (500 MHz) spectrometer. Chemical shifts were reported in ppm relative to (CH<sub>3</sub>)<sub>4</sub>Si (0 ppm,

$^1\text{H}$ ) or  $\text{CDCl}_3$  (77.0 ppm,  $^{13}\text{C}$ ). IR spectra were recorded on Thermo Nicolet AVATAR 360 spectrometer. Mass spectra were recorded on Bruker Daltonics Inc., APEX II FT-ICRMS (FAB). Glassware was dried in oven overnight then flame dried prior to use. Thin layer chromatography (TLC) was performed on Silica Gel 60 F254 plates and visualized with UV light and  $\text{KMnO}_4$  stain. Reactions were conducted under argon atmosphere unless otherwise noted. Benzene was distilled from calcium hydride prior to use.

#### 4.2. General procedure for thermal reactions of Fischer carbene complexes with TIPS-substituted alkynes

A degassed solution of the appropriate Fischer carbene complex (1.0 equiv.) and silyl-substituted alkyne (1.8 equiv.) in benzene was heated at reflux under argon atmosphere for 24 h. Upon cooling to room temperature, the solution was concentrated under reduced pressure, and the residue was purified via flash chromatography ( $\text{SiO}_2$ , 30:1 petroleum ether/ethyl acetate) to afford the silyl vinylketenes or the cyclobutenones.

##### 4.2.1. Silyl vinylketene **3a**

Carbene complex (312 mg, 1.0 mmol) and alkyne (514 mg, 1.8 mmol) were subjected to the general procedure, affording silyl vinylketene **3a** (272 mg, 48% yield). IR (neat):  $\nu$  2946, 2867, 2084, 1959, 1877, 1741, 1593, 1539, 1462, 1252, 1124  $\text{cm}^{-1}$ . 500 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.41–7.37 (m, 3H), 7.33–7.32 (m, 2H), 6.07 (d,  $J = 7.0$  Hz, 2H), 5.21 (d,  $J = 7.0$  Hz, 2H), 3.73 (s, 3H), 3.37 (s, 3H), 0.88–0.79 (m, 21H). 125 MHz  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  234.0, 180.1, 157.9, 141.2, 135.0, 129.8, 129.1, 128.5, 103.9, 102.9, 97.0, 78.4, 58.0, 55.9, 18.5, 14.6, 12.5. HRMS (FAB):  $m/z$  calc. for  $\text{C}_{30}\text{H}_{36}\text{CrO}_6\text{Si}$ : 572.1686. Found: 572.1683.

##### 4.2.2. Silyl vinylketene **3b**

Carbene complex (280 mg, 1.0 mmol) and alkyne (403 mg, 1.8 mmol) were subjected to the general procedure, affording silyl vinylketene **3b** (180 mg, 33% yield) as a yellow oil. IR (neat):  $\nu$  2951, 2867, 2080, 1964, 1889, 1739, 1596, 1525, 1460, 1382, 1307, 1257, 1211, 1156, 1064, 973, 879, 804  $\text{cm}^{-1}$ . 500 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.33 (d,  $J = 16.0$  Hz, 1H), 6.16 (d,  $J = 15.5$  Hz, 1H), 5.55–5.54 (m, 2H), 5.32–5.31 (m, 3H), 3.63 (s, 3H), 2.54 (t,  $J = 8.0$  Hz, 2H), 1.50–1.47 (m, 2H), 1.40–1.36 (m, 2H), 1.26–1.21 (m, 3H), 1.15–1.11 (m, 18H), 0.95 (t,  $J = 7.5$  Hz, 3H). 125 MHz  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  233.3, 177.8, 160.8, 129.2, 128.4, 128.2, 124.5, 109.2, 107.0, 92.4, 92.0, 91.8, 56.8, 29.7, 29.0, 23.0, 18.8, 14.1, 13.0, 9.4. HRMS (FAB):  $m/z$  calc. for  $\text{C}_{29}\text{H}_{40}\text{CrO}_5\text{Si}$ : 548.2050. Found: 548.2043.

##### 4.2.3. Silyl vinylketene **3c**

Carbene complex (312 mg, 1.0 mmol) and alkyne (540 mg, 1.8 mmol) were subjected to the general procedure, affording silyl vinylketene **3c** (351 mg, 60% yield) as a yellow oil. IR (neat):  $\nu$  2944, 2866, 2082, 1971, 1893,

1636, 1598, 1461, 1420, 1256, 1158, 1105, 1073, 997  $\text{cm}^{-1}$ . 500 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.40 (5H), 5.43–5.39 (m, 4H), 5.26 (1H), 4.33 (s, 2H), 4.25 (s, 2H), 3.34 (s, 3H), 1.09–0.93 (m, 21H). 125 MHz  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  232.9, 180.4, 157.0, 134.4, 129.9, 128.9, 128.3, 108.3, 108.2, 93.1, 92.9, 92.7, 91.6, 70.4, 69.7, 58.0, 18.6, 12.7, 12.2. HRMS (FAB):  $m/z$  calc. for  $[\text{C}_{31}\text{H}_{38}\text{CrO}_6\text{Si}+\text{Na}]^+$ : 609.1740. Found: 609.1746.

##### 4.2.4. Silyl vinylketene **3d**

Carbene complex (250 mg, 1.0 mmol) and alkyne (520 mg, 1.8 mmol) were subjected to the general procedure, affording silyl vinylketene **3d** (219 mg, 59% yield) as a colorless oil. IR (neat):  $\nu$  2944, 2866, 2085, 1647, 1598, 1585, 1495, 1463, 1381, 1299, 1235, 1154, 1075, 1029, 1006, 939, 882  $\text{cm}^{-1}$ . 500 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.26–7.23 (m, 2H), 6.93–6.89 (m, 3H), 4.60 (s, 2H), 3.58 (s, 3H), 2.05 (s, 3H), 1.21–1.13 (m, 3H), 1.09–1.08 (m, 18H). 125 MHz  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  179.0, 158.7, 154.4, 129.2, 120.3, 114.9, 104.8, 65.5, 56.3, 18.5, 14.8, 12.6, 11.3. HRMS (FAB):  $m/z$  calc. for  $[\text{C}_{22}\text{H}_{34}\text{O}_3\text{Si}+\text{Na}]^+$ : 397.2175. Found: 397.2170.

##### 4.2.5. Silyl vinylketene **3e**

Carbene complex (312 mg, 1.0 mmol) and alkyne (520 mg, 1.8 mmol) were subjected to the general procedure, affording silyl vinylketene **3e** (283 mg, 65% yield) as a colorless oil. IR (neat):  $\nu$  2944, 2866, 2085, 1598, 1494, 1462, 1287, 1238, 1170, 1107, 1074, 1030, 1003, 881  $\text{cm}^{-1}$ . 500 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.41–7.33 (m, 5H), 7.30–7.27 (m, 2H), 7.00 (dd,  $J = 8.5$  Hz,  $J = 1.0$  Hz, 2H), 6.94 (t,  $J = 7.5$  Hz, 1H), 4.78 (s, 2H), 3.35 (s, 3H), 0.91–0.89 (m, 21H). 125 MHz  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  179.7, 158.7, 156.5, 134.1, 129.8, 129.3, 128.6, 128.5, 128.0, 120.6, 115.0, 107.6, 66.6, 57.7, 18.5, 12.2, 11.7. HRMS (FAB):  $m/z$  calc. for  $\text{C}_{27}\text{H}_{36}\text{O}_3\text{Si}$ : 436.2434. Found: 436.2431.

##### 4.2.6. Silyl vinylketene **3f** and cyclobutenone **4a**

Carbene complex (276 mg, 1.0 mmol) and alkyne (464 mg, 1.8 mmol) were subjected to the general procedure, affording silyl vinylketene **3f** (162 mg, 32% yield). IR (neat):  $\nu$  2084, 1963, 1887  $\text{cm}^{-1}$ . 300 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 5.79–5.77 (m, 2H), 5.27–5.25 (m, 3H), 3.62 (s, 3H), 1.81–1.76 (m, 1H), 1.17–1.07 (m, 21H), 0.96–0.88 (m, 2H), 0.80–0.75 (m, 2H). 75.5 MHz  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 233.4, 178.4, 159.9, 110.5, 107.1, 95.7, 91.9, 57.8, 18.7, 13.8, 12.9, 12.8, 7.6. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR data consistent with the literature [2a] and the cyclobutenone **4a** (152 mg, 30% yield). IR (neat):  $\nu$  2945, 2866, 1973, 1903, 1739, 1542, 1456, 1070, 882  $\text{cm}^{-1}$ . 300 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  6.14–6.04 (m, 1H), 5.93–5.82 (m, 1H), 5.72–5.58 (m, 1H), 5.35–5.21 (m, 2H), 3.44 (s, 3H), 1.54–1.29 (m, 4H), 1.23–1.00 (m, 18H), 0.97–0.82 (m, 2H), 0.76–0.64 (m, 2H). 75.5 MHz  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  230.8, 196.0, 184.0, 152.1, 102.0, 95.1, 94.9, 94.5, 92.6, 88.5, 88.3, 53.1, 18.8, 18.7, 14.6, 12.0, 4.0, 3.0. HRMS (FAB):  $m/z$  calc. for  $\text{C}_{26}\text{H}_{34}\text{CrO}_5\text{Si}$ : 506.1581. Found: 506.1589.

#### 4.2.7. Cyclobutenone **4b**

Carbene complex (250 mg, 1.0 mmol) and alkyne (400 mg, 1.8 mmol) were subjected to the general procedure, affording cyclobutenone **4b** (203 mg, 66% yield). IR (neat):  $\nu$  2942, 2865, 1740, 1554, 1459, 1368, 1303, 1234, 1124, 1093, 1063  $\text{cm}^{-1}$ . 500 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.27 (s, 3H), 2.09–2.04 (m, 1H), 1.38 (s, 3H), 1.37–1.30 (m, 4H), 1.23–1.18 (m, 3H), 1.11–1.09 (m, 18H). 125 MHz  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  198.6, 151.0, 97.9, 52.5, 21.1, 18.6, 18.5, 15.2, 11.2, 10.7, 9.9. HRMS (FAB):  $m/z$  calc. for  $\text{C}_{18}\text{H}_{32}\text{O}_2\text{Si}$ : 308.2172. Found: 308.2165.

#### 4.2.8. Cyclobutenone **4c**

Carbene complex (215 mg, 0.73 mmol) and alkyne (340 mg, 1.3 mmol) were subjected to the general procedure, affording cyclobutenone **4c** (201 mg, 73% yield). IR (neat):  $\nu$  2931, 2865, 1748, 1600, 1516, 1455, 1388, 1300, 1125, 1084, 1021  $\text{cm}^{-1}$ . 500 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.74–7.73 (m, 1H), 7.05–7.04 (m, 1H), 6.62–6.61 (m, 1H), 3.25 (s, 3H), 2.02–1.96 (m, 1H), 1.86–1.80 (m, 1H), 1.56–1.49 (m, 3H), 1.30–1.25 (m, 4H), 1.08 (d,  $J = 7.5$  Hz, 18H), 0.82 (t,  $J = 7.0$  Hz, 3H). 125 MHz  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  198.4, 172.4, 148.2, 148.1, 146.9, 118.3, 113.6, 102.7, 53.1, 33.4, 28.2, 23.6, 19.3, 14.4, 12.0. HRMS (FAB):  $m/z$  calc. for  $\text{C}_{22}\text{H}_{36}\text{O}_3\text{Si}$ : 376.2434. Found: 376.2428.

#### 4.3. General procedure for photochemical reactions of Fischer carbene complexes with TMS-substituted alkynes

A degassed solution of the appropriate Fischer carbene complex (1.0 equiv.) and silyl-substituted alkyne (2.0 equiv.) in acetonitrile in a quartz tube charged with glass beads was irradiated with a 20-W Vitalite under argon at room temperature for 24 h. The red solution turned light-yellow and heterogeneous. After filtered through a bed of Celite, the solution was concentrated under reduced pressure and purified via flash chromatography ( $\text{SiO}_2$ , 30:1 petroleum ether/ethyl acetate) to afford the cyclobutenone.

##### 4.3.1. Cyclobutenone **9a**

A degassed solution of the Fischer carbene complex (390 mg, 1.25 mmol) and the alkyne (375 mg, 2.50 mmol) in 15 ml acetonitrile was irradiated under argon for 24 h. After filtered via Celite, the solution was concentrated under reduced pressure and purified via flash chromatography ( $\text{SiO}_2$ , 30:1 petroleum ether/ethyl acetate) to afford the cyclobutenone **9a** (173 mg, 43% yield). 500 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.83–7.81 (m, 2H), 7.48–7.42 (m, 5H), 7.35–7.31 (m, 2H), 7.28–7.23 (m, 1H), 3.52 (s, 3H), 0.25 (s, 9H). 125 MHz  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  192.0, 181.8, 162.9, 138.9, 130.3, 129.9, 129.0, 128.6, 128.5, 128.0, 126.2, 104.3, 53.3, –1.2. HRMS (FAB):  $m/z$  calc. for  $\text{C}_{20}\text{H}_{22}\text{O}_2\text{Si}$ : 322.1389. Found: 322.1387.

##### 4.3.2. Cyclobutenone **9b**

A degassed solution of the Fischer carbene complex (390 mg, 1.25 mmol) and the alkyne (385 mg, 2.50 mmol)

in 15 ml acetonitrile was irradiated under argon for 24 h. After filtered via Celite, the solution was concentrated under reduced pressure and purified via flash chromatography ( $\text{SiO}_2$ , 30:1 petroleum ether/ethyl acetate) to afford the cyclobutenone **9b** (174 mg, 46% yield) as a yellowish oil. IR (neat):  $\nu$  2957, 2934, 2873, 2830, 1750, 1493, 1449, 1251, 1197, 1135, 1078, 1019, 843  $\text{cm}^{-1}$ . 500 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.34–7.20 (m, 5H), 3.45 (s, 3H), 2.45–2.31 (m, 2H), 1.71–1.54 (m, 2H), 1.48–1.29 (m, 2H), 0.92 (t,  $J = 7.0$  Hz, 3H), 0.15 (s, 9H). 125 MHz  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  193.6, 184.1, 169.3, 138.8, 128.1, 127.6, 125.8, 103.7, 52.9, 29.9, 25.8, 22.8, 13.7, –1.3. HRMS (FAB):  $m/z$  calc. for  $\text{C}_{18}\text{H}_{26}\text{O}_2\text{Si}$ : 302.1702. Found: 302.1709.

#### 4.4. Reaction of **1e** with TMS-substituted hexyne at room temperature

A degassed solution of the Fischer carbene complex **1e** (480 mg, 0.88 mmol) and the alkyne (271 mg, 1.76 mmol) in 10 ml acetonitrile was stirred at room temperature under argon for 20 h. After filtered via Celite, the solution was concentrated under reduced pressure and purified via flash chromatography ( $\text{SiO}_2$ , 30:1 petroleum ether/ethyl acetate) to afford the cyclobutenone **9a** (55 mg, 20% yield).

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