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Journal of Organometallic Chemistry 645 (2002) 228–234
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Synthesis of 2-pyranylidene or (2-furyl)carbene–chromium complexes from conjugated enyne carbonyl compounds with $Cr(CO)_5(THF)$

Koji Miki, Tomomi Yokoi, Fumiaki Nishino, Kouichi Ohe *, Sakae Uemura *

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

Received 21 August 2001; received in revised form 18 September 2001; accepted 23 September 2001

Abstract

The reaction of β-ethynyl α,β-unsaturated esters or amides with $Cr(CO)_5(L)$ ($L = Et_2O$, THF), derived from chromium hexacarbonyl, gives 2-pyranylidene–chromium complexes in good yields. The conjugated ene-carbonyl-vinylidene complex is a key intermediate to these Fischer-type oxacarbene complexes. In contrast, β-ethynyl α,β-unsaturated ketones react with $Cr(CO)_5(THF)$ to give (2-furyl)carbene complexes via nucleophilic attack of the carbonyl oxygen atom to the intermediate π-alkyne–chromium complexes. Some chemical transformation, such as [4 + 2] type cyclization of 2-pyranylidene complexes with alkynes and aldehyde formation from (2-furyl)carbene complexes, has also been described. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Chromium; Pyranylidene; Furylcarbene; Vinylidene

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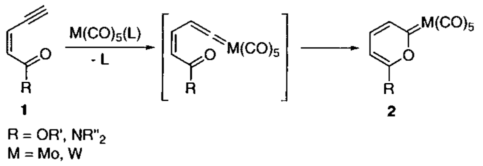
1. Introduction

Transition metal carbene complexes, especially Fischer-type oxacarbene complexes, have been widely studied and applied to synthetic organic chemistry as versatile organometallic reagents [1,2]. Typical oxacarbene complexes like $(CO)_5M{=}C(OR)R'$ are readily prepared by the reaction of metal hexacarbonyl with a range of organolithium and organomagnesium reagents. Nucleophilic addition of an alcohol to the α- and β-carbons of a vinylidene–metal complex ($M = C_\alpha = C_\beta$, M = Cr, Mo, W) also leads to the formation of oxacarbene complexes in catalytic and stoichiometric reactions [3–5]. We have recently reported that 2-pyranylidene–molybdenum and –tungsten complexes, as cyclic Fischer-type oxacarbene complexes, were prepared from $M(CO)_5(L)$ (M = Mo, W; L = THF, NEt_3) and β-ethynyl α,β-unsaturated esters or amides via nucleophilic attack of the carbonyl oxygen to the α-carbon of a vinylidene–metal intermediate (Scheme 1) [6,7]. However, the preparation of 2-pyranylidene–chromium complexes from $Cr(CO)_5(L)$ ($L = Et_2O$, THF), which was prepared by photo-irradiation, was unsuccessful. The complex $Cr(CO)_5(NMe_3)$ [8] prepared from $Cr(CO)_6$ and trimethylamine-*N*-oxide in situ was only slightly effective for the preparation of 2-pyranylidene–chromium complex. After we investigated the optimal conditions to obtain 2-pyranylidene–chromium complexes, we found that the reaction of β-ethynyl α,β-unsaturated esters or amides with $Cr(CO)_5(solv)$, which was prepared from $Cr(CO)_6$ by irradiation in a suitable solvent, in the presence of Et_3N as an additive gave effectively the corresponding pyranylidene–chromium complexes. In sharp contrast with this result, the reaction of β-ethynyl α,β-unsaturated ketones with $Cr(CO)_5(THF)$ afforded new (2-furyl)carbene–



Scheme 1.

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* Corresponding authors. Tel.: +81-75-753-5687; fax: +81-75-753-3573.

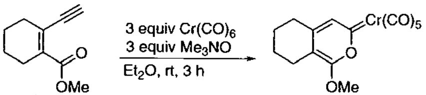
E-mail address: uemura@scl.kyoto-u.ac.jp (S. Uemura).

0022-328X/02/$ - see front matter
PII: S0022-328X(01)01328-6

chromium complexes. The 5-*exo*-dig nucleophilic cyclization in a π-alkyne complex of the ketone with $Cr(CO)_5$ might be responsible for the formation of nonstabilized carbene complexes. 2-Pyranylidene–chromium complexes undergo [4 + 2] type cycloaddition with dimethyl acetylenedicarboxylate followed by demetallation to give tetralin derivatives, while (2-furyl)carbene–chromium complexes react with molecular oxygen to give the corresponding furfurals.

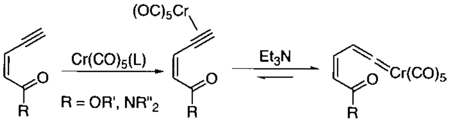
2. Results and discussion

We have reported that 2-pyranylidene–tungsten or –molybdenum complexes were prepared from β-ethynyl α,β-unsaturated esters or amides with $W(CO)_5(THF)$ [9] or $Mo(CO)_5(NEt_3)$ [8]. However, the corresponding pyranylidene–chromium complexes could not be prepared under similar conditions using $Cr(CO)_5(Et_2O)$ or $Cr(CO)_5(THF)$. When we examined the reaction with these chromium complexes in more detail, we found that the reaction of β-ethynyl α,β-unsaturated ester **1a** with $Cr(CO)_6$ and $Me_3N^+O^-$ gave 2-pyranylidene–chromium complex **2a** in 9% yield (Eq. (1)). We considered that trimethylamine, which is generated from the reaction between $Cr(CO)_6$ and $Me_3N^+O^-$ might play some role in the formation of pyranylidene complex. Then we tried the reaction using an amine as an additive. The reaction of **1a** with $Cr(CO)_5(Et_2O)$ in the absence of triethylamine gave none of **2a** (Table 1). However, the reaction proceeded in the presence of triethylamine to give complex **2a** in 27% isolated yield together with the recovered **1a** (30–50%). The use of THF instead of Et_2O as a solvent gave a better yield of **2a**. The reactions of other substrates with $Cr(CO)_5(THF)$ in the presence of triethylamine were next examined, typical results of which being shown in Table 2.



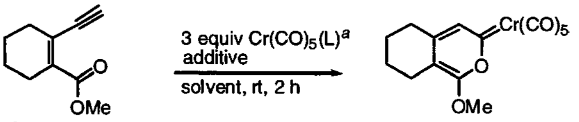
1a 2a (9% yield) (1)

Reactions of **1a** with a lesser amount of $Cr(CO)_5(THF)$ gave lower yields of **2a** in 15% (1.2 equivalents of Cr) and 33% (2.0 equivalents of Cr), respectively (entries 1 and 2). The reaction of an amide **1b** with $Cr(CO)_5(THF)$ at room temperature for 0.5 h also gave the corresponding 2-pyranylidene–chromium complex **2b** in 68% yield (entry 4). The ester **1c** and the amide **1d** gave similar complexes **2c** and **2d** in 69 and 50% yields, respectively (entries 5 and 6). At present, we assume that triethylamine facilitates the formation of a vinylidene–chromium intermediate from a π-alkyne–chromium complex (Scheme 2) [7b].



Scheme 2.

Table 1
Preparation of **2a**

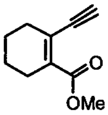
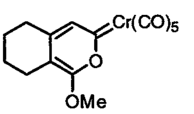
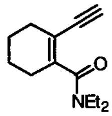
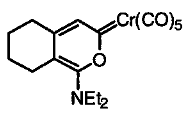
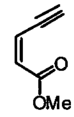
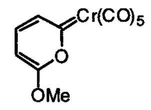
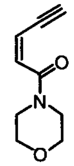
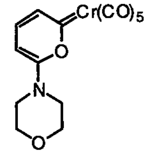


1a (0.2 mmol) **2a**

Solvent	Additive	Isolated yield (%)
Et_2O (30 ml)		
Et_2O (30 ml)	Et_3N (0.1 ml)	27
THF (20 ml)	Et_3N (0.1 ml)	62

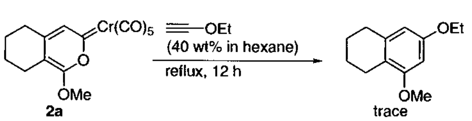
[a] The solution of $Cr(CO)_5(L)$ was prepared by irradiating $Cr(CO)_6$ (in Et_2O or THF) for 4 h with a high-pressure Hg lamp.

Table 2
Preparation of pyranylidene–chromium complexes from conjugated enyne carbonyls and $Cr(CO)_5(THF)$ [a,b]

entry	1	product	yield (%)[c]
1[d]	 **1a**	 **2a**	15
2[e]	**1a**	**2a**	33
3	**1a**	**2a**	62
4[f]	 **1b**	 **2b**	68
5[f]	 **1c**	 **2c**	69
6[f]	 **1d**	 **2d**	50

[a] Reactions were carried out with **1** (0.2 mmol) at room temperature for 2 h under Ar. [b] The solution of $Cr(CO)_5(L)$ was prepared by irradiating a solution of $Cr(CO)_6$ (0.6 mmol) and triethylamine (0.1 ml) in THF (20 ml) for 4 h with a high-pressure Hg lamp. [c] Isolated yield. [d] **1a** (0.5 mmol). [e] **1a** (0.3 mmol). [f] Reaction time was 0.5 h.

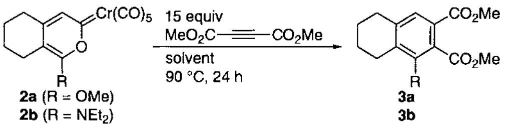
The structure of pyranylidene–chromium complexes represents α-metallopyrone. Therefore, we envisaged cycloaddition reaction of these 2-pyranylidene–chromium complexes with dienophiles. The reaction of **2a** with an excess amount of dimethyl acetylenedicarboxylate (DMAD, 15 equivalents) gave the tetralin derivative **3a** in 26% isolated yield (Table 3). The use of solvent, i.e., toluene, did not positively affect the reaction. The reaction in DMSO resulted in demetallation leading to the formation of compound **1a** in 59% yield. The complex **2b** also reacted with DMAD to give the corresponding tetralin derivative **3b** in 25% yield. However, the reaction of **2a** with an electron-rich dienophile, i.e., ethyl ethynyl ether, gave only a trace amount of tetralin derivative as one isomer (Eq. (2)). The transformation was explained by assuming [4 + 2] cycloaddition reaction between 2-pyranylidene–chromium complex and the acetylene followed by a pericyclic demetallation of chromium hexacarbonyl (Scheme 3).



(2)

Next, we examined the reactions of β-ethynyl α,β-unsaturated ketone instead of β-ethynyl α,β-unsaturated ester or amide with chromium and tungsten carbonyls. When 2-ethynyl-1-cyclohexenyl phenyl ketone (**4a**) was treated with three equivalents of $Cr(CO)_5(THF)$ in the presence of triethylamine, the corresponding 2-pyranylidene–chromium complex **2e** was obtained only in 8% yield together with many unidentified products (Eq. (3)). On the other hand, in the absence of triethylamine the reaction of **4a** with three equivalents of $Cr(CO)_5(THF)$ did not afford **2e**, and instead (2-furyl)carbene–chromium **5a** was isolated in 52% yield as a blue solid (Eq. (4)) [10]. The complex **5a** is marginally stable during purification with silica gel column chromatography. 2-Thienyl ketone **4b** also gave the corresponding (2-furyl)carbene–chromium complex **5b** in 59% yield. When **4a** was treated with three equivalents of $W(CO)_5(THF)$, (2-furyl)carbene–tungsten complex **5c** was isolated in 56% yield [11] (Eq. (4)).

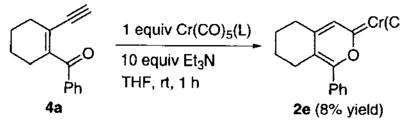
Table 3
Reaction of pyranylidene–chromium complex with dimethyl acetylene dicarboxylate



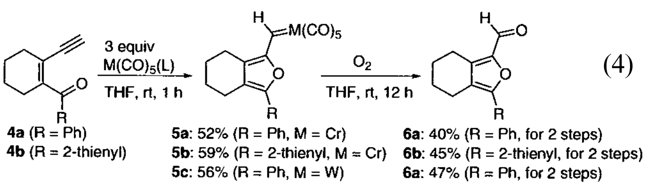
Entry	Substrate	Solvent	Product	Yield (%) [a]
1	**2a**	–	**3a**	26
2	**2b**	–	**3b**	25
3	**2a**	Toluene	**3a**	9
4	**2a**	Dioxane	**3a**	0
5	**2a**	DMSO	**3a**	0 [b]

[a] Isolated yield.

[b] An enyne carbonyl compound **1a** was obtained in 59% yield.



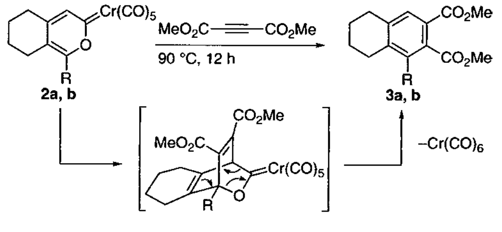
(3)



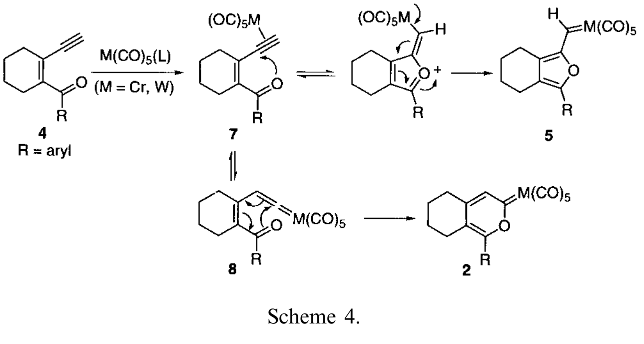
(4)

However, in the reaction of an alkyl vinyl ketone, such as ethyl 2-ethynyl-1-cyclohexenyl ketone (R = Et in **4**), we could not succeed in the isolation of the corresponding (2-furyl)carbene complex. These complexes **5a**–**5c** were stored for several days under N_2 atmosphere, but they gradually decomposed in $CDCl_3$ or under oxygen atmosphere. When the isolated carbene complex **5a** was stirred in THF under oxygen atmosphere, furfural derivative **6a** was obtained in 76% yield. The displacement of metal carbonyl moiety with the oxygen atom in carbene complex by molecular oxygen is a well-known process [12]. Most plausible pathway from **4** to **5** is shown in Scheme 4.

In the pre-equilibrium between a π-alkyne complex **7** and a vinylidene complex **8**, 5-*exo*-dig cyclization takes place as a favorable process to give the furylcarbene



Scheme 3.



Scheme 4.

complex. The presence of triethylamine, which may promote the isomerization of a π-alkyne complex to a vinylidene complex, in fact, precluded the formation of the (2-furyl)carbene complex. The mode of the complex formation is also attributed to the difference in the reactivity of carbonyl functionality of β-ethynyl α,β-unsaturated carbonyl compounds.

3. Conclusions

We have demonstrated that 2-pyranylidene–chromium complexes were prepared from β-ethynyl α,β-unsaturated esters and amides in the presence of triethylamine. In sharp contrast, the reaction of β-ethynyl α,β-unsaturated ketones with $M(CO)_5(THF)$ (M = Cr, W) gave (2-furyl)carbene complexes selectively via nucleophilic attack of a carbonyl oxygen to a π-alkyne complex. Some chemical transformation of newly prepared 2-pyranylidene–chromium complexes and (2-furyl)carbene–chromium and tungsten complexes has been described: [4 + 2] type cyclization with alkynes in the former cases and aldehyde formation in the latter cases, respectively.

4. Experimental

4.1. General

Tetrahydrofuran (THF) and Et_2O were distilled from sodium benzophenone ketyl under Ar. Analytical thin-layer chromatographies (TLC) were performed with silica gel 60 Merck F-254 plates. Column chromatographies were performed with Merck silica gel 60. The NMR spectra were measured for solutions in $CDCl_3$ or THF-d_8 with Me_4Si as an internal standard (^1H and ^{13}C) and the following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet. IR spectra were recorded with a FT-IR spectrometer. Melting points (m.p.) are uncorrected. Elemental analyses were performed at Microanalytical Center of Kyoto University. All new compounds were prepared and fully characterized.

*4.2. Synthesis of 2-pyranylidene–chromium complex **2** from **1** or **4a***

*4.2.1. 2-Pyranylidene–chromium complex **2a** from **1a***

A solution of $Cr(CO)_6$ (0.13 g, 0.60 mmol) in THF (20 ml) and Et_3N (0.1 ml) under Ar was irradiated by a Hg lamp (350 nm) at room temperature (r.t.) for 4 h. To this orange solution under Ar was added a solution of **1a** (33 mg, 0.20 mmol) in THF (1 ml) by a syringe. The mixture was stirred at r.t. for 0.5–2 h. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane–EtOAc (v/v = 10:1) as an eluent to afford **2a** (44 mg, 62% yield) as an orange solid, m.p. 91.5–94.3 °C. IR (KBr, cm^{-1}): 1897, 1935, 1976, 2053. ^1H-NMR ($CDCl_3$, 300 MHz, 25 °C): $\delta = 1.72$–1.84 (m, 4H), 2.38–2.49 (m, 2H), 2.55–2.64 (m, 2H), 4.32 (s, 3H), 7.33 (s, 1H). ^{13}C-NMR ($CDCl_3$, 75 MHz, 25 °C): $\delta = 20.4$, 21.2, 21.4, 29.0, 56.9, 108.2, 134.7, 154.9, 171.9, 218.6 (Cr–*C*O), 223.4 (Cr–*C*O), 251.0 (Cr = *C*). HRMS (FAB); *m*/*z*: 355.9995 ([M^+], calc. for $C_{15}H_{12}CrO_7$: 355.9988).

*4.2.2. 2-Pyranylidene–chromium complex **2b** from **1b***

An orange solid (68% yield), m.p. 118.4–121.5 °C. IR (KBr, cm^{-1}): 1888, 1909, 1965, 2045. ^1H-NMR ($CDCl_3$, 300 MHz, 25 °C): $\delta = 1.36$ (t, $J = 6.9$ Hz, 6H), 1.69–1.79 (m, 4H), 2.44–2.50 (m, 2H), 2.53–2.60 (m, 2H), 3.63 (q, $J = 6.9$ Hz, 4H), 6.96 (s, 1H). ^{13}C-NMR ($CDCl_3$, 75 MHz, 25 °C): $\delta = 13.7$, 21.1, 22.6, 25.4, 29.5, 44.7, 108.6, 132.0, 151.2, 170.1, 219.3 (Cr–*C*O), 223.9 (Cr–*C*O), 240.7 (Cr=*C*). Anal. Calc. for $C_{18}H_{19}CrNO_6$: C, 54.41; H, 4.82; N, 3.53. Found: C, 54.27; H, 5.03; N, 3.40%.

*4.2.3. 2-Pyranylidene–chromium complex **2c** from **1c***

An orange solid (69% yield), m.p. 71.0–73.5 °C. IR (KBr, cm^{-1}): 1898, 1917, 1976, 2053. ^1H-NMR ($CDCl_3$, 300 MHz, 25 °C): $\delta = 4.32$ (s, 3H), 6.15 (d, $J = 8.1$ Hz, 1H), 7.15 (dd, $J = 8.1$, 8.1 Hz, 1H), 7.68 (d, $J = 8.1$ Hz, 1H). ^{13}C-NMR ($CDCl_3$, 75 MHz, 25 °C): $\delta = 57.0$, 96.9, 134.1, 139.6, 175.0, 217.9 (Cr–*C*O), 223.4 (Cr–*C*O), 269.6 (Cr=*C*). HRMS (FAB); *m*/*z*: 301.9518 ([M^+], calc. for $C_{11}H_6CrO_7$: 301.9519).

*4.2.4. 2-Pyranylidene–chromium complex **2d** from **1d***

An orange solid (50% yield), m.p. 128.3–129.5 °C. IR (KBr, cm^{-1}): 1906, 1966, 2052. ^1H-NMR ($CDCl_3$, 300 MHz, 25 °C): $\delta = 3.75$–3.87 (m, 8H), 6.00 (m, 1H), 6.97 (m, 1H), 7.26 (m, 1H). ^{13}C-NMR ($CDCl_3$, 75 MHz, 25 °C): $\delta = 44.7$, 65.9, 95.4, 129.4, 137.6, 169.2, 218.7 (Cr–*C*O), 223.8 (Cr–*C*O), 258.1 (Cr=*C*). HRMS (FAB); *m*/*z*: 356.9934 ([M^+], calc. for $C_{14}H_{11}CrNO_7$: 356.9941).

*4.2.5. 2-Pyranylidene–chromium complex **2e** from **4a***

The ketone **4a** (0.13 g, 0.60 mmol) and Et_3N (1.0 ml) were used. A red solid (8% yield), m.p. 132.0–134.6 °C. IR (KBr, cm^{-1}): 1918, 1974, 2051. ^1H-NMR (THF-d_8, 300 MHz, 25 °C): $\delta = 1.78$–1.91 (m, 4H), 2.76–2.84 (m, 4H), 7.56–7.62 (m, 3H), 7.79–7.86 (m, 2H), 7.95 (s, 1H); ^{13}C-NMR (THF-d_8, 75 MHz, 25 °C): $\delta = 22.0$, 23.0, 26.2, 29.6, 124.8, 129.6, 129.7, 132.0, 133.1, 141.0, 150.6, 175.5, 219.2 (Cr–*C*O), 224.3 (Cr–*C*O), 268.8 (Cr=*C*). HRMS (FAB); *m*/*z*: 402.0185 ([M^+], calc. for $C_{20}H_{14}CrO_6$: 402.0196).

4.3. Typical procedure for [4 + 2] type cycloaddition of **2**

4.3.1. Dimethyl 5,6,7,8-tetrahydro-1-methoxy-2,3-naphthalenedicarboxylate **(3a)**

A mixture of complex **2a** (0.034 g, 0.095 mmol) and dimethyl acetylenedicarboxylate (0.2 ml, 1.6 mmol) in a sealed tube was stirred at 90 °C for 12 h under N_2. The mixture was subjected to column chromatography on SiO_2 with hexane–EtOAc (v/v = 10:1) as an eluent to afford **3a** (7 mg, 0.025 mmol, 26% yield) as a colorless liquid. ^{1}H-NMR ($CDCl_3$, 300 MHz, 25 °C): $\delta = 1.77$–1.84 (m, 4H), 2.74–2.82 (m, 4H), 3.79 (s, 3H), 3.86 (s, 3H), 3.94 (s, 3H), 7.52 (s, 1H). ^{13}C-NMR ($CDCl_3$, 75 MHz, 25 °C): $\delta = 22.2$, 22.4, 23.7, 29.3, 52.3, 52.6, 61.7, 125.3, 126.6, 127.2, 136.9, 140.4, 155.0, 165.8 (*C*O), 168.4 (*C*O).

4.3.2. Dimethyl 1-diethylamino-5,6,7,8-tetrahydro-2,3-naphthalenedicarboxylate **(3b)**

A yellow liquid (25% yield). ^{1}H-NMR ($CDCl_3$, 300 MHz, 25 °C): $\delta = 1.00$ (t, $J = 7.2$ Hz, 6H), 1.72–1.82 (m, 4H), 2.65–2.75 (m, 2H), 2.75–2.86 (m, 2H), 2.90–3.12 (m, 4H), 3.85 (s, 3H), 3.89 (s, 3H), 7.57 (s, 1H). ^{13}C-NMR ($CDCl_3$, 75 MHz, 25 °C): $\delta = 14.4$, 22.4, 22.6, 26.6, 29.6, 47.4, 52.1, 52.2, 124.7, 128.1, 134.9, 139.4, 144.2, 146.8, 166.2 (*C*O), 169.8 (*C*O).

4.4. Synthesis of furylcarbene complexes **5**

4.4.1. Chromium complex **5a**

A solution of $Cr(CO)_6$ (0.13 g, 0.60 mmol) in THF (20 ml) under Ar was irradiated by a Hg lamp (350 nm) at r.t. for 4 h. To the yellow solution under Ar was added a solution of **4a** (42 mg, 0.20 mmol) in THF (1 ml) by a syringe. The mixture was stirred at r.t. for 0.5 h. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane–EtOAc (v/v = 10:1) as an eluent to afford **5a** (42 mg, 0.10 mmol, 52% yield) as a blue solid. IR (KBr, cm^{-1}): 651, 826, 1934, 1994, 2045. ^{1}H-NMR (THF-d_8, 300 MHz, 25 °C): $\delta = 1.84$–2.00 (m, 4H), 2.75–2.83 (m, 2H), 2.95–3.04 (m, 2H), 7.60–7.69 (m, 3H), 8.16–8.25 (m, 2H), 13.5 (s, 1H). ^{13}C-NMR (THF-d_8, 75 MHz, 25 °C): $\delta = 23.0$, 24.0, 24.1, 24.4, 127.7, 128.8, 129.9, 130.8, 132.9, 138.4, 168.2, 171.7, 219.6 (Cr–*C*O), 233.9 (Cr–*C*O), 284.4 (Cr=*C*). HRMS (FAB); *m*/*z*: 402.0195 ([M$^+$], calc. for $C_{20}H_{14}CrO_6$: 402.0219).

4.4.2. Chromium complex **5b**

A blue solid (59% yield). IR (KBr, cm^{-1}): 1933, 1970, 2041. ^{1}H-NMR (THF-d_8, 300 MHz, 25 °C): $\delta =$ 1.73–1.90 (m, 4H), 2.66 (t, $J = 3.9$ Hz, 2H), 2.77 (t, $J = 3.9$ Hz, 2H), 7.27–7.31 (m, 1H), 7.88–7.94 (m, 2H), 13.0 (s, 1H). ^{13}C-NMR (THF-d_8, 75 MHz, 25 °C): $\delta = 21.5$, 21.6, 22.2, 22.7, 125.3, 129.2, 130.3, 131.5, 132.8, 137.2, 163.3, 169.9, 218.2 (Cr–*C*O), 232.3 (Cr–*C*O), 276.4 (Cr=*C*). HRMS (FAB); *m*/*z*: 407.9756 ([M$^+$], calc. for $C_{19}H_{12}CrO_6S$: 407.9760).

4.4.3. Tungsten complex **5c**

A solution of $W(CO)_6$ (0.21 g, 0.60 mmol) in THF (20 ml) under Ar was irradiated by a Hg lamp (350 nm) at r.t. for 4 h. To the yellow solution under Ar was added a solution of **4a** (42 mg, 0.2 mmol) in THF (1 ml) by a syringe. The mixture was stirred at r.t. for 0.5 h. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography on SiO_2 with hexane–EtOAc (v/v = 10:1) as an eluent to afford **5c** (60 mg, 0.11 mmol, 56% yield) as a blue solid. IR (KBr, cm^{-1}): 580, 677, 825, 1920, 1934, 2052. ^{1}H-NMR (THF-d_8, 300 MHz, 25 °C): $\delta = 1.94$–2.10 (m, 4H), 2.54–2.60 (m, 2H), 3.07–3.13 (m, 2H), 7.64–7.78 (m, 3H), 8.26–8.32 (m, 2H), 13.3 (s, 1H). ^{13}C-NMR (THF-d_8, 75 MHz, 25 °C): $\delta = 21.3$, 22.5, 22.5, 23.5, 127.4, 127.9, 129.5, 129.8, 131.5, 141.7, 166.5, 171.3, 198.1 (W–*C*O), 210.2 (W–*C*O), 247.8 (W=*C*). HRMS (FAB); *m*/*z*: 534.0300 ([M$^+$], calc. for $C_{20}H_{14}WO_6$: 534.0286).

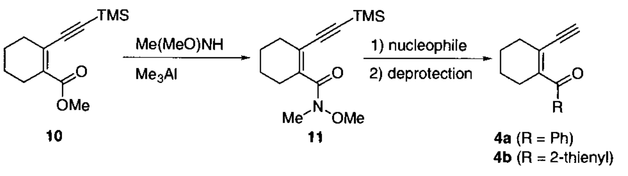
4.5. Synthesis of furfural derivatives **6**

4.5.1. Furfural **6a**

A solution of **5a** (22 mg, 0.054 mmol) in THF (5 ml) was stirred at r.t. under O_2 atmosphere for 12 h. The solvent was removed under reduced pressure and the residue was subjected to column chromatography on SiO_2 with hexane–EtOAc (v/v = 8:1) as an eluent to afford **6a** (9.2 mg, 0.041 mmol, 76% yield) as a white solid, m.p. 91.3–94.8 °C. IR (KBr, cm^{-1}): 696, 773, 828, 1650, 1669. ^{1}H-NMR (THF-d_8, 300 MHz, 25 °C): $\delta = 1.73$–1.86 (m, 4H), 2.81–2.87 (m, 2H), 2.87–2.93 (m, 2H), 7.31–7.38 (m, 1H), 7.41–7.49 (m, 2H), 7.76–7.81 (m, 2H), 9.73 (s, 1H). ^{13}C-NMR (THF-d_8, 75 MHz, 25 °C): $\delta = 22.8$, 23.4, 23.9, 24.4, 122.6, 124.7, 127.1, 129.9, 130.2, 132.1, 147.8, 152.9, 178.2 (*C*HO). HRMS (FAB); *m*/*z*: 227.1067 ([M + H$^+$], calc. for $C_{15}H_{14}O_2$: 227.1072).

4.5.2. Furfural **6b**

A white solid (76% yield), m.p. 100.5–101.6 °C. IR (KBr, cm^{-1}): 698, 819, 853, 1445, 1635, 1663. ^{1}H-NMR (THF-d_8, 300 MHz, 25 °C): $\delta = 1.75$–1.90 (m, 4H), 2.68–2.76 (m, 2H), 2.87–2.94 (m, 2H), 7.14 (dd, $J =$ 3.6, 4.8 Hz, 1H), 7.42 (d, $J = 4.8$ Hz, 1H), 7.47 (d, $J = 3.6$ Hz, 1H), 9.69 (s, 1H). ^{13}C-NMR (THF-d_8, 75 MHz, 25 °C): $\delta = 22.7$, 23.1, 23.5, 24.1, 121.6, 126.6, 128.2, 129.3, 134.0, 136.7, 147.4, 149.6, 177.8 (*C*HO). Anal. Calc. for $C_{13}H_{12}O_2S$: C, 67.21; H, 5.21. Found: C, 66.97; H, 5.17%.



Scheme 5.

4.6. *Synthesis of substrates*

Methyl 2-(trimethylsilyl)-1-cyclohexenecarboxylate (**10**) was prepared from cyclohexanone in several steps: see the supporting information of Ref. [6a] (Scheme 5).

4.6.1. *N-Methyl N-methoxy 2-(trimethylsilyl)-1-cyclohexenecarboxamide (**11**) [13]*

A solution of methyl 2-(trimethylsilylethynyl)-1-cyclohexenecarboxylate (**10**) (3.6 g, 15 mmol) in benzene (5 ml) was added to benzene (40 ml) and hexane (45 ml) solution of $Me_2AlNMe(OMe)$ prepared from a hexane solution of Me_3Al (45 ml, 45 mmol) and *N*,*O*-dimethylhydroxylamine hydrochloride (4.4 g, 45 mmol). The resulting solution was heated under reflux for 3 h. The reaction mixture was cooled down to r.t., and hydrolyzed by slow and cautious addition of 1.0 N HCl (30 ml). The upper organic layer was separated, and the aqueous layer was extracted with EtOAc (30 ml × 3). The organic extracts were combined, washed with brine, and dried over $MgSO_4$. The solvent was removed under reduced pressure to give the residual liquid, which was subjected to column chromatography on SiO_2 with hexane–EtOAc (v/v = 4:1) as an eluent to afford *N*-methyl *N*-methoxy 2-(trimethylsilyl)-1-cyclohexenecarboxamide (**11**) (3.6 g, 14 mmol, 92% yield) as a pale yellow liquid. IR (KBr, cm^{-1}): 845, 1659 (C=O), 2144 (C≡C). ^1H-NMR ($CDCl_3$, 300 MHz, 25 °C): $\delta =$ 0.12 (s, 9H), 1.57–1.65 (m, 4H), 2.14–2.27 (m, 4H), 3.23 (s, 3H), 3.71 (s, 3H). ^{13}C-NMR (CD_2Cl_2, 100 MHz, −25 °C): $\delta = -0.1$ (Si*C*H_3), −0.1 (Si*C*H_3), 21.5 (*C*H_2), 21.5 (*C*H_2), 21.8 (*C*H_2), 21.9 (*C*H_2), 26.5 (*C*H_2), 26.7 (*C*H_2), 28.8 (*C*H_2), 29.5 (*C*H_2), 31.8 (N*C*H_3), 35.7 (N*C*H_3), 60.3 (O*C*H_3), 62.0 (O*C*H_3), 96.4 (*C*≡), 97.2 (*C*≡), 103.0 (*C*≡), 104.5 (*C*≡), 116.7 (*C* =), 119.4 (*C* =), 140.0 (*C* =), 143.1 (*C* =), 166.4 (*C* = O), 170.8 (*C* = O) as a mixture of rotamers. Anal. Calc. for $C_{14}H_{23}NO_2Si$: C, 63.35; H, 8.73; N, 5.28. Found: C, 63.07; H, 8.47; N, 5.21%.

4.7. *Preparation of β-ethynyl-α,β-unsaturated carbonyl compounds **4***

4.7.1. *2-Ethynyl-1-cyclohexenyl phenyl ketone (**4a**)*

To a solution of **11** (0.47 g, 2.0 mmol) in THF (10 ml) was added preformed phenylmagnesium bromide (4.2 mmol) in THF (15 ml) at 0 °C, and the mixture was stirred at r.t. for 4 h. The reaction mixture was poured into saturated NH_4Cl solution (30 ml), and the aqueous layer was extracted with EtOAc (20 ml × 3). The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure and then 1 N KOH solution (2.0 ml) was added to the residue in MeOH (20 ml) at r.t. After stirring for 0.5 h, this solution was poured into saturated NH_4Cl solution (50 ml). The aqueous layer was extracted with EtOAc (20 ml × 3) and the combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was subjected to column chromatography on SiO_2 with hexane–EtOAc (v/v = 20:1) as an eluent to afford **4a** (0.22 g, 1.0 mmol, 52% yield) as a colorless liquid. IR (neat, cm^{-1}): 648, 690, 709, 732, 916, 1662 (C = O), 2093 (C≡C), 3292 (≡C–H). ^1H-NMR ($CDCl_3$, 300 MHz, 25 °C): $\delta = 1.71–1.77$ (m, 4H), 2.28–2.38 (m, 4H), 2.81 (s, 1H), 7.40–7.48 (m, 2H) 7.50–7.57 (m, 1H), 7.85–7.92 (m, 2H). ^{13}C-NMR ($CDCl_3$, 75 MHz, 25 °C): $\delta = 21.4$, 21.8, 27.3, 29.8, 82.2, 82.3, 119.8, 128.5, 129.5, 133.2, 136.0, 145.8, 199.0 (*C*O). HRMS (FAB); *m*/*z*: 211.1119 ([M + H^+], calc. for $C_{15}H_{14}O$: 211.1123).

4.7.2. *2-Ethynyl-1-cyclohexenyl 2-thienyl ketone (**4b**)*

To a solution of thiophene (0.46 ml, 6.0 mmol) in THF (5 ml) was added *n*-BuLi (4 ml, 1.6 M in hexane, 6.4 mmol) at 0 °C under N_2, and the mixture was stirred at r.t. for 2 h. This mixture was added to a solution of **10** (0.80 g, 3.0 mmol) in THF (5 ml) at 0 °C, and the mixture was stirred at r.t. for 10 min. The reaction mixture was poured into saturated NH_4Cl solution (20 ml), and the aqueous layer was extracted with EtOAc (10 ml × 3). The combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure and then K_2CO_3 (1.0 g, 7.5 mmol) was added to the residue in MeOH (30 ml) at r.t. After stirring for 12 h, this solution was poured into saturated NH_4Cl solution (100 ml). The aqueous layer was extracted with EtOAc (30 ml × 3) and the combined organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was subjected to column chromatography on SiO_2 with hexane–EtOAc (v/v = 20:1) as an eluent to afford **4b** (0.28 g, 1.3 mmol, 43% yield) as a colorless liquid. IR (neat, cm^{-1}): 643, 734, 774, 856, 1262, 1285, 1411, 1644 (C=O), 2094 (C≡C), 2935, 3288 (≡C–H). ^1H-NMR ($CDCl_3$, 300 MHz, 25 °C): $\delta = 1.71–1.77$ (m, 4H), 2.28–2.40 (m, 4H), 2.92 (s, 1H), 7.13 (dd, $J = 4.2$, 4.2 Hz, 1H), 7.68 (d, $J = 4.2$ Hz, 2H). ^{13}C-NMR ($CDCl_3$, 75 MHz, 25 °C): $\delta = 21.4$, 21.7, 27.3, 29.7, 82.0, 82.2, 119.4, 128.1, 134.6, 134.7, 143.0, 145.8, 191.2 (*C*O). HRMS (FAB); *m*/*z*: 217.0685 ([M + H^+], calc. for $C_{13}H_{12}OS$: 217.0687).

Acknowledgements

We thank Mr Yasuaki Hisamoto in our department for measuring HRMS spectra. This research was supported on Priority Areas (A) "Exploitation of Multi-Element Cyclic Molecules" from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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