Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 690 (2005) 5922–5928
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Stereoselective [3+2+2] cycloaddition utilizing optically active binuclear Fischer carbene complexes with alkynes

Ken Kamikawa [a,*], Yasunori Shimizu [a], Hiroyuki Matsuzaka [a], Motokazu Uemura [b,*]

[a] Department of Chemistry, Graduate School of Science, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan
[b] Kyoto Pharmaceutical University, Misasagi, Yamashina, Kyoto 640-8412, Japan

Received 10 June 2005; received in revised form 22 July 2005; accepted 22 July 2005
Available online 31 August 2005

Abstract

The reaction of optically active α,β-unsaturated binuclear Fischer carbene complexes with alkynes gave planar chiral cycloheptatriene chromium complexes via [3+2+2] cycloaddition with high diastereoselectivity.

Keywords: Fischer carbene; Cycloaddition; Planar chirality; Arene chromium complex

1. Introduction

The Fischer carbene complex is one of the most versatile organometallic reagents for organic synthesis [1]. In recent years, a number of novel reactions using Fischer carbene complexes have been reported [2]. One of the major classes of reactions utilizing α,β-unsaturated Fischer carbene complexes is cycloaddition reactions, which provides four-, five-, and six-membered carbo- or heterocyclic compounds, and important advances have been reported [1]. Recently, Barluenga developed interesting [3+2+2] cycloaddition reactions of α,β-unsaturated Fischer carbene complexes with alkynes giving seven-membered carbocyclic compounds [3]. For the asymmetric variation of these reactions, various chiral Fischer carbene complexes have been developed to date [4]. On the other hand, we have developed the new entry of optically active α,β-unsaturated binuclear Fischer carbene complexes with planar chirality of arene chromium complex [5]. The advantage of these chiral Fischer carbene complexes are that a chiral auxiliary can be introduced close to the reaction site effectively blocking one face of the α,β-unsaturated double bond of the carbene complex. As a continuation of our studies on asymmetric reactions utilizing the planar chirality of arene chromium complex, we examined the asymmetric variation of the [3+2+2] cycloaddition reaction developed by Barluenga utilizing chiral binuclear Fischer carbene complexes.

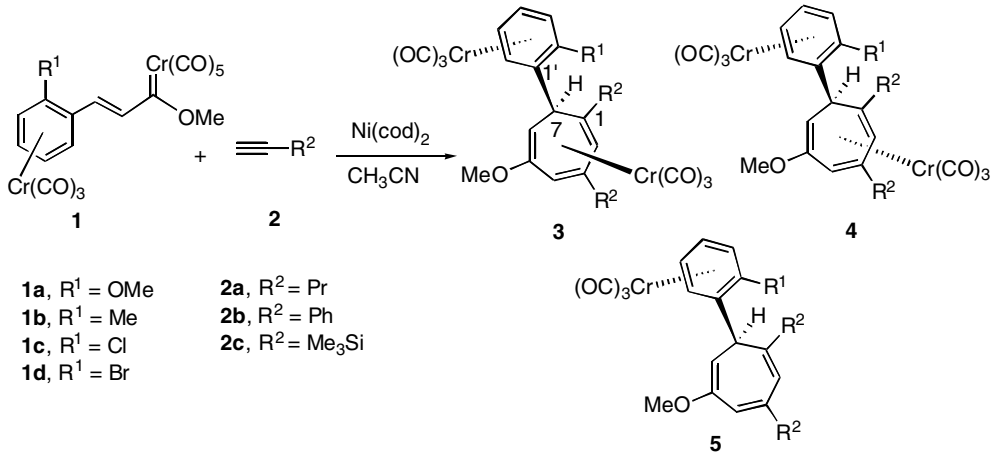
2. Results and discussion

Initially, we examined the reaction of binuclear Fischer carbene complex **1a** ($[\alpha]_D^{24} - 3400$ (*c* 0.001, $CHCl_3$)) with 1-pentyne (**2a**) (3.0 equiv) in the presence of a stoichiometric amount of $Ni(cod)_2$ (1.1 equiv). The resulting solution was stirred for 2 h at −10 °C and then warmed to 20 °C over 2 h. It was found that bis-tricarbonylchromium-coordinated 7-aryl cycloheptatriene derivative **3aa** ($[\alpha]_D^{20} + 40$ (*c* 0.08, $CHCl_3$)) was obtained via the [3+2+2] cycloaddition in 47% yield with high diastereoselectivity (dr = >98:<2) (Table 1, entry 1).

* Corresponding authors. Fax: +81 72 254 9931 (K. Kamikawa)/+81 75 595 4763 (M. Uemura).
E-mail addresses: kamikawa@c.s.osakafu-u.ac.jp (K. Kamikawa), muemura@mb.kyoto-phu.ac.jp (M. Uemura).

0022-328X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2005.07.089

Table 1
Stereoselective [3+2+2] cyclization reaction utilizing chiral binuclear Fischer carbene complexes



Entry	Complex **1**	Acetylene **2**	Product **3**	Yield (%) of **3**	Product **4**	Yield (%) of **4**	dr (**3**/**4**)	Product **5**	Yield (%) of **5**
1	**1a**	**2a**	**3aa**	47		–	>98/<2		–
2	**1a**	**2b**	**3ab**	28		–	>98/<2	**5ab**	25
3	**1a**	**2c**	**3ac**	27	**4ac**	27	1/1	**5ac**	10
4	**1b**	**2a**	**3ba**	67		–	>98/<2		–
5	**1c**	**2a**	**3ca**	36		–	91/9		–
6	**1d**	**2a**	**3da**	41		–	91/9		–

When phenylacetylene (**2b**) was used as the alkyne, heptatriene chromium complex **3ab** was obtained in high diastereoselectivity along with chromium-free product **5ab** (25%) (entry 2). However, when trimethylsilyl acetylene (**2c**) was used, a diastereomeric mixture was obtained in 1:1 ratio (entry 3). High stereoselectivity at the benzylic position was still observed even in this case.

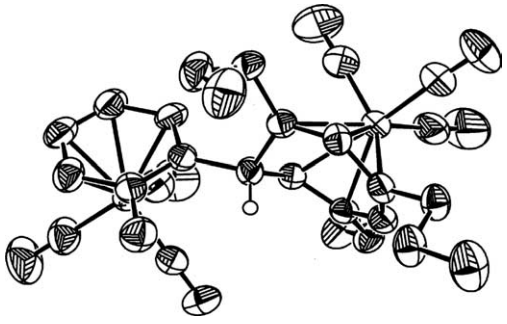
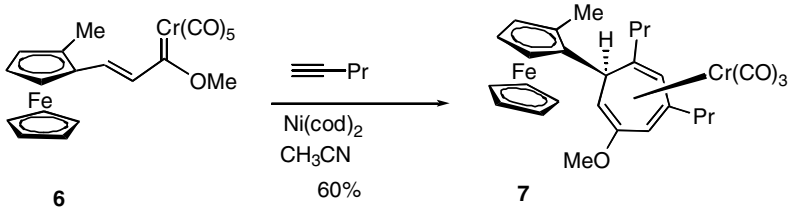


Fig. 1. X-ray structure of **3ba**.

The diastereomers were confirmed to be **3ac** and **4ac**, respectively, having opposite planar chirality of the cycloheptatriene chromium complex, as mono-demetallation of both diastereomers **3ac** and **4ac** gave an identical (arene)chromium complex **5ac** [6]. When other arene chromium complexes with different *ortho* substituents were used, the cycloaddition reaction with 1-pentyne proceeded also with high diastereoselectivity (entries 4–6). The stereochemistry of **3ba** was determined by X-ray analysis, which has an *endo* relationship between the chromium-coordinated arene ring and the tricarbonylchromium fragment of the heptatriene ring (Fig. 1).

Similarly, α,β-unsaturated Fischer carbene complex **6** with planar chiral ferrocene was treated with 1-pentyne to give a cycloheptatriene chromium complex **7** under the same conditions as a single diastereomer in 60% yield (Scheme 1) and its relative stereochemistry was confirmed by X-ray analysis (Fig. 2).

We propose a reaction mechanism for this stereoselective [3+2+2] cycloaddition in Scheme 2. In order to



Scheme 1. Stereoselective [3+2+2] cyclization reaction utilizing a planar chiral ferrocene.

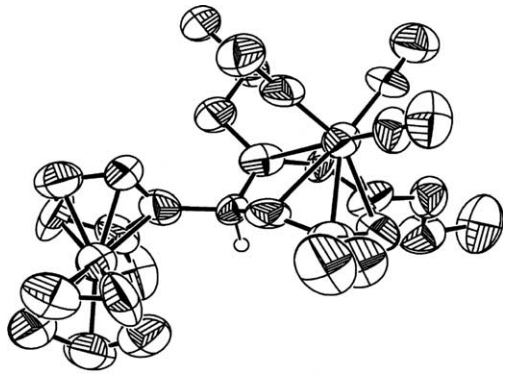
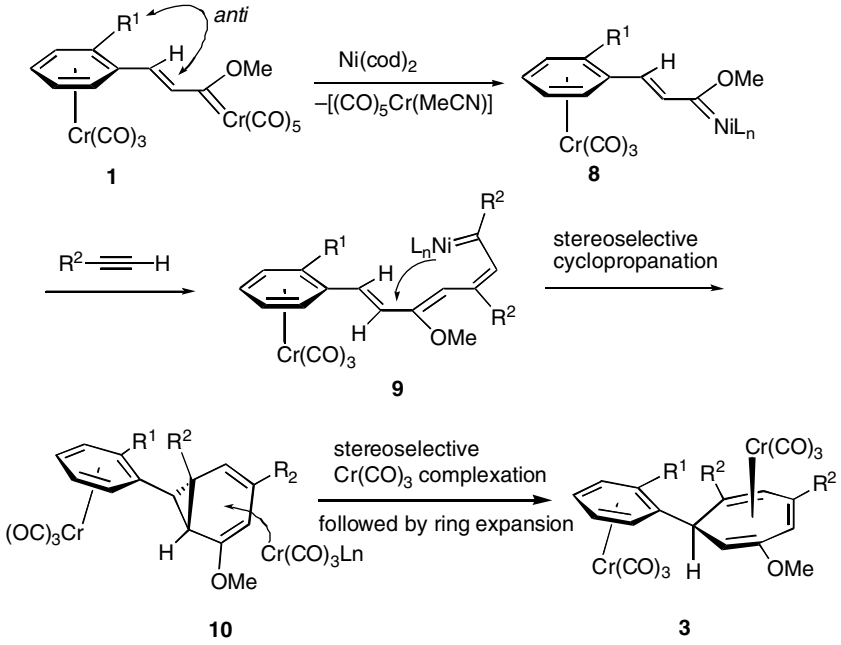


Fig. 2. X-ray structure of **7**.

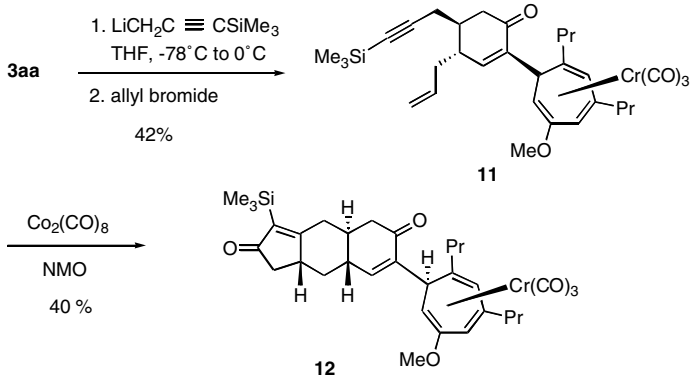
minimize steric repulsion, the α,β-unsaturated double bond is believed to take *anti* orientation with respect to the *ortho* substituent of the arene chromium complex [7]. In the presence of stoichiometric amount of Ni(cod)$_2$, the carbene moiety would be transferred from chromium to nickel to afford **8** [3,8]. The regioselective double alkyne insertion into the nickel–carbon bond of **8** could generate **9** [9], in which stereoselective cyclopropanation from the *exo* side of the coordinated arene would proceed to form norcaradiene intermediate **10**. The diene part of intermediate **10** could be stereoselectively coordinated with a CrLn fragment from a convex face of the bicyclic system and subsequent ring expansion [10] would produce the bis-tricarbonylchromium coordinated compound **3** as a single diastereomer. With trimethylsilyl acetylene (Table 1, entry 3), non-selectivity of the planar chirality on the cycloheptatriene ring is a quite unique result. In this case, the ring expansion of norcaranadiene intermediate might be occurred prior to the chromium coordination due to a steric effect between the chromium-coordinated arene ring and R^2 ($SiMe_3$) group on the cyclopropane ring, and the resulting cycloheptatriene could be coordinated with chromium ligand from both sides of the triene ring to give 1:1 mixture of diastereomers.

With the binuclear chromium complexes with two planar chiralities in hand, we further examined the stereoselective transformation of both tricarbonylchromium-coordinated rings of the complex **3**. Initially, the stereoselective transformation of the planar chiral arene ring was examined by conducting of nucleophilic addition reaction. Thus, binuclear complex **3aa** was treated with 3-trimethylsilylpropargyl lithium and then with allyl bromide. Chemo- and regioselective propargyl lithium addition to the chromium coordinated η^6-anisole gave the anionic cyclohexadienyl intermediate which can be readily trapped with allyl bromide [11]. After decomplexation of the cyclohexadiene intermediate and subsequent in situ hydrolysis, was obtained *trans*-disubstituted cyclohexenone **11** as a single diastereomer (Scheme 3). Furthermore, an intramolecular Pauson-Khand reaction was carried out by treatment with $Co_2(CO)_8$ to give tricyclic diketone **12** as a single diastereomer. The relative stereochemistry of the newly generated chiral center of **12** was determined by X-ray analysis (Fig. 3). The tricarbonylchromium fragment of the cycloheptatriene ring bounds to the heptatriene ring without influence in a series of these reactions.

We next examined the stereoselective transformation of the chromium-coordinated heptatriene ring.



Scheme 2. Proposed reaction mechanism.



Scheme 3. Stereoselective functionalization of the planar chiral arene chromium complex.

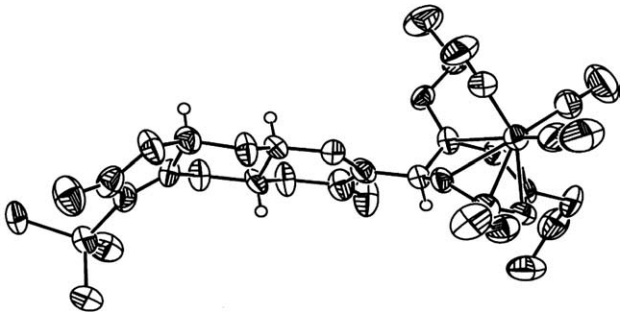


Fig. 3. X-ray structure of **12**.

To this end, we examined transition metal promoted higher-order cycloaddition reactions, such as $[6\pi + 4\pi]$ and $[6\pi + 2\pi]$, utilizing cycloheptatriene chromium tricarbonyl for the synthesis of medium ring size [12]. Binuclear chromium complex **3aa** was reacted with methyl acrylate in hexane under irradiation of UV light. The $[6\pi + 2\pi]$ cycloaddition reaction proceeded smoothly at room temperature to give product **13** as a single diastereomer in 73% yield (Scheme 4). The planar chirality of cycloheptatriene chromium tricarbonyl **3aa** was effectively utilized in the generation of three chiral centers on the $[6\pi + 2\pi]$ cycloaddition product. The stereo- and regiochemistry of the cycloaddition product **13** were determined by NMR techniques (^{1}H–^{1}H, ^{1}H–^{13}C COSY, HMBC, DEPT, NOESY). Cross peaks were observed between aromatic proton and methine proton at the 7-position, and between methylene proton at the 8-position and methine proton at the 1-position by NOESY experiment. It was found that those relationships are coincided with those report by Rigby [12]. In this way, tricarbonylchromium-coordinated both rings can be independently functionalized by using distinct properties of chromium complexes, and these compounds could be obtained as optically active forms.

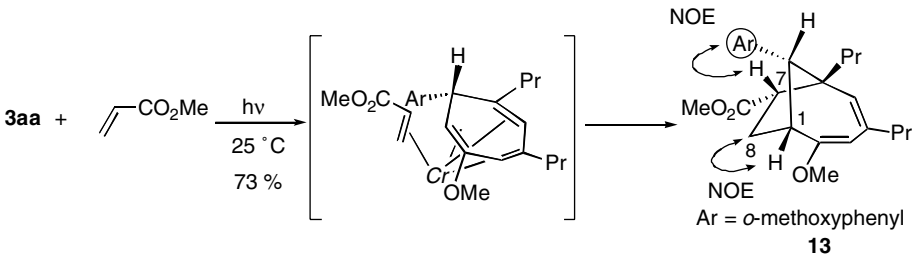
3. Conclusion

In conclusion, we have demonstrated the synthesis of optically pure cycloheptatriene chromium complexes by the diastereoselective [3+2+2] cycloaddition reaction developed by Barluenga, utilizing binuclear α,β-unsaturated Fischer carbene complexes and alkynes. The chromium-coordinated both rings were stereo- and chemoselectively functionalized by utilizing distinct properties of the chromium complexes. Further exploration of the synthetic utility is in progress.

4. Experimental

4.1. General procedure for stereoselective [3+2+2] cycloaddition

To a solution of binuclear complex **1** (0.10 mmol) and alkyne **2** (0.30 mmol) in dry acetonitrile (2.0 mL) was added a solution of $Ni(cod)_2$ (0.11 mmol) in dry acetonitrile (2.0 mL) via a cannulla at −10 °C. The reaction



Scheme 4. Stereoselective functionalization of the planar chiral cycloheptatriene chromium complex.

mixture was stirred for 1.5 h and gradually warmed to 20 °C. Then the reaction mixture was extracted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$, filtrated and concentrated at reduced pressure. The residue was purified by silica gel chromatography to give the cyclized product.

4.1.1. Complex **3aa**

$[\alpha]_D^{20} + 40$ (*c* 0.08, $CHCl_3$); mp. 145 °C (decomposition); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (3H, t, $J = 7.3$ Hz), 1.14 (3H, t, $J = 7.3$ Hz), 1.71–1.80 (1H, m), 1.83–2.00 (3H, m), 2.61–2.70 (1H, m), 2.72–2.81 (3H, m), 2.91 (1H, dd, $J = 2.2$, 2.9 Hz), 3.52 (3H, s), 3.58 (3H, s), 4.05 (1H, s), 4.41 (1H, s), 4.94 (1H, d, $J = 6.5$ Hz), 5.15 (1H, t, $J = 6.5$ Hz), 5.59 (1H, t, $J = 6.5$ Hz), 6.00 (1H, d, $J = 2.2$ Hz), 6.07 (1H, d, $J = 6.5$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.83, 13.93, 20.75, 26.00, 32.76, 36.47, 36.74, 43.21, 55.53, 55.84, 72.48, 76.58, 77.11, 82.72, 85.99, 92.39, 93.62, 94.63, 97.53, 99.73, 114.58, 141.61, 142.23, 232.21; IR ($CHCl_3$) 3404, 2965, 2874, 1966, 1896, 1466 cm^{-1}. Anal. Calc. for $C_{27}H_{28}Cr_2O_8$: C, 55.48; H, 4.83. Found: C, 55.68; H, 4.85%.

4.1.2. Complex **3ab**

Mp. 119 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.17 (1H, d, $J = 4.7$ Hz), 3.52 (1H, dd, $J = 2.0$, 4.7 Hz), 3.58 (3H, s), 3.62 (3H, s), 4.74 (1H, t, $J = 6.4$ Hz), 4.93 (1H, d, $J = 6.4$ Hz), 5.19 (1H, s), 5.28 (1H, dd, $J = 0.9$, 6.4 Hz), 5.60 (1H, dt, $J = 0.9$, 6.4 Hz), 6.51 (1H, d, $J = 2.0$ Hz), 7.08–7.16 (4H, m), 7.26–7.44 (4H, m), 7.64–7.66 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.35, 29.76, 33.83, 41.16, 42.60, 55.50, 55.96, 65.87, 74.43, 83.33, 88.54, 95.22, 95.47, 95.71, 99.51, 100.26, 103.59, 109.52, 127.02, 127.35, 128.58, 128.88, 130.29, 138.41, 141.34, 141.49, 142.64, 232.67; IR ($CHCl_3$) 3391, 2932, 2361, 2339, 1968, 1890, 1599, 1460 cm^{-1}; MS (relative intensity) *m/z* 652 (M^+, 8), 568 (35), 516 (8), 484 (78), 454 (12), 432 (100), 417 (26), 402 (18); HRMS calc. for $C_{33}H_{24}O_8Cr_2$ 652.0268. Found: 652.0307.

4.1.3. Complex **3ba**

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 (3H, t, $J = 6.8$ Hz), 1.14 (3H, t, $J = 6.8$ Hz), 1.25–1.94 (4H, m), 1.83 (3H, s), 2.30 (1H, d, $J = 2.0$ Hz), 2.63–2.82 (4H, m), 2.90 (1H, s), 3.52 (3H, s), 4.46 (1H, d, $J = 2.0$ Hz), 5.11 (1H, d, $J = 6.2$ Hz), 5.42 (1H, t, $J = 6.2$ Hz), 5.48 (1H, t, $J = 6.2$ Hz), 5.89 (1H, d, $J = 6.2$ Hz), 6.01 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 14.0, 18.7, 20.8, 26.1, 35.8, 36.1, 36.8, 43.2, 55.4, 80.9, 90.8, 92.6, 92.8, 93.6, 93.7, 97.7, 108.3, 109.2, 114.6, 142.3, 198.9, 232.5; IR ($CHCl_3$) 2964, 2361, 2340, 1966, 1900, 1601, 1458 cm^{-1}. Anal. Calc. for $C_{27}H_{28}O_7Cr_2$: C, 57.04; H, 4.96. Found: C, 57.12; H, 5.15%.

4.1.4. Complex **3ca**

Mp. 123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (3H, t, $J = 7.2$ Hz), 1.14 (3H, t, $J = 7.2$ Hz), 0.92–0.99 (2H, m), 1.69–1.78 (1H, m), 1.87–2.04 (3H, m), 2.64–2.71 (2H, m), 2.69 (1H, d, $J = 3.5$ Hz), 2.91 (1H, d, $J = 3.5$ Hz), 3.52 (3H, s), 4.47 (1H, s), 5.31 (1H, dt, $J = 0.9$, 6.3 Hz), 5.43 (1H, dd, $J = 1.0$, 6.3 Hz), 5.53 (1H, dt, $J = 1.0$, 6.3 Hz), 5.94 (1H, dd, $J = 0.9$, 6.3 Hz), 6.03 (1H, d, $J = 2.0$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.10, 13.8, 14.0, 20.6, 26.2, 35.3, 36.6, 37.3, 43.3, 55.4, 80.9, 89.1, 90.6, 92.2, 92.5, 92.8, 97.5, 106.2, 114.5, 114.8, 142.3, 230.8; IR ($CHCl_3$) 2963, 2933, 2874, 2372, 2311, 1981, 1969, 1903, 1698 cm^{-1}. Anal. Calc. for $C_{26}H_{25}O_7ClCr_2$: C, 53.03; H, 4.28. Found: C, 53.06; H, 4.31%.

4.1.5. Complex **3da**

Mp. 117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (3H, t, $J = 7.3$ Hz), 1.14 (3H, t, $J = 7.3$ Hz), 1.18–1.25 (2H, m), 1.70–1.78 (1H, m), 1.89–2.05 (3H, m), 2.63 (1H, d, $J = 3.4$ Hz), 2.62–2.69 (1H, m), 2.71–2.81 (1H, m), 3.52 (3H, s), 3.89 (1H, s), 4.48 (1H, s), 5.37 (1H, t, $J = 6.1$ Hz), 5.46 (1H, t, $J = 6.1$ Hz), 5.55 (1H, d, $J = 6.1$ Hz), 5.89 (1H, d, $J = 6.1$ Hz), 6.03 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.09, 13.73, 14.08, 20.45, 26.17, 35.27, 36.41, 40.12, 43.22, 55.40, 80.99, 89.92, 91.78, 92.61, 93.02, 93.95, 97.37, 102.69, 114.75, 142.24, 230.89; IR ($CHCl_3$) 2962, 2934, 2873, 2361, 1968, 1903, 1616, 1453 cm^{-1}. Anal. Calc. for $C_{26}H_{25}O_7BrCr_2$: C, 49.30; H, 3.98. Found: C, 49.35; H, 3.85%.

4.1.6. Complex **5ac**

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.03 (9H, s), 0.05 (9H, s), 3.39 (1H, d, $J = 8.3$ Hz), 3.66 (3H, s), 3.69 (3H, s), 4.32 (1H, s), 4.81 (1H, t, $J = 6.4$ Hz), 5.00 (1H, d, $J = 6.4$ Hz), 5.42 (1H, t, $J = 6.4$ Hz), 5.66 (1H, d, $J = 6.4$ Hz), 6.15 (1H, s), 6.30 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.00, 1.22, 56.66, 57.11, 57.27, 75.60, 85.86, 95.67, 98.88, 102.69, 107.28, 111.79, 120.69, 128.62, 130.49, 135.19, 144.01, 156.89, 234.95; IR ($CHCl_3$) 3011, 2956, 2911, 2838, 1963, 1885, 1612, 1529, 1463 cm^{-1}; MS (relative intensity) *m/z* 508 (M^+, 4), 424 (49), 409 (17), 304 (11), 256 (9), 236 (9), 69 (100); HRMS calc. for $C_{24}H_{32}O_5Si_2Cr$: 508.1194. Found: 508.1212.

4.1.7. Complex **7**

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.75 (3H, t, $J = 7.3$ Hz), 1.04–1.08 (2H, m), 1.14 (3H, t, $J = 7.3$ Hz), 1.55–1.62 (1H, m), 1.64 (3H, s), 1.69–1.80 (1H, m), 1.82–1.97 (2H, m), 2.26 (1H, d, $J = 3.9$ Hz), 2.58–2.68 (1H, m), 2.72–2.79 (1H, m), 3.29 (1H, s), 3.54 (3H, s), 4.02 (5H, s), 4.12 (1H, s), 4.16 (1H, s), 4.38 (1H, s), 4.45 (1H, s), 6.02 (1H, d, $J = 2.2$ Hz); IR ($CHCl_3$) 2961, 2931, 2872, 1965, 1899, 1872, 1602, 1464 cm^{-1}; MS

(relative intensity) *m/z* 540 (M^+, 20), 456 (77), 454 (15), 264 (55), 149 (55), 69 (100); HRMS calc. for $C_{28}H_{32}O_4CrFe$: 540.1055. Found: 540.1056.

4.1.8. Complex 11

To a solution of 1-trimthylsilyl propyne (54 mg, 0.48 mmol, 1.4 equiv) in THF (1.0 mL), a solution of *t*-BuLi (0.027 mL, 0.39 mmol, 1.46 M in pentane) was added at −78 °C. The mixture was stirred for 2 h at −78 °C. Complex **3aa** (200 mg, 0.34 mmol) was dissolved in THF (1.0 mL) and added to the solution. The resulting solution was gradually warmed up to 0 °C over 2 h, then kept at this temperature for additional 3 h. After cooling to −78 °C, allyl bromide (0.030 mL, 3.4 mmol, 10 equiv) was added and the solution was warmed up to ambient overnight. The solvent was removed in vacuo, the residue was diluted with ether and filtrated over silica gel. After evaporation of the solvent in vacuo, the residue was diluted with THF (2.0 mL). Monohydrated *p*-toluenesulfonic acid (65 mg, 0.34 mmol) was added to the solution and stirred for 1 h at ambient temperature. The resulting mixture was extracted with ether, washed with sat. $NaHCO_3$, water and sat. NaCl, and dried over $MgSO_4$. The filtrate was evaporated in vacuo, and the residue was purified by chromatography (hexane:ethylacetate, 9:1) to give complex **11** (84 mg, 42% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.16 (9H, s), 0.87 (3H, t, $J = 7.3$ Hz), 0.88–0.93 (1H, m), 1.05–1.13 (2H, m), 1.12 (3H, t, $J = 7.3$ Hz), 1.67–1.76 (1H, m), 1.82–1.97 (3H, m), 2.11–2.18 (1H, m), 2.31–2.40 (2H, m), 2.45–2.53 (3H, m), 2.56–2.64 (3H, m), 2.68 (1H, d, $J = 4.3$ Hz), 2.71–2.78 (1H, m), 2.81–2.85 (1H, m), 3.35 (3H, s), 4.39 (1H, s), 5.17–5.23 (2H, m), 5.77–5.87 (1H, m), 5.94 (1H, d, $J = 1.2$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.05, 13.78, 14.04, 21.10, 23.56, 25.96, 31.74, 36.12, 36.47, 36.86, 39.32, 41.78, 43.27, 54.68, 83.34, 88.72, 91.93, 92.09, 97.96, 102.63, 114.52, 118.19, 134.24, 138.32, 142.14, 151.66, 196.93; IR ($CHCl_3$) 2962, 2934, 2873, 2172, 1965, 1894, 1711, 1673, 1163, 1016, 922, 846 cm^{-1}; MS (relative intensity) *m/z* 586 (M^+, 1), 502 (80), 461 (100), 391 (2), 350 (2), 310 (3); HRMS calc. for $C_{32}H_{42}O_5SiCr$: 586.2206. Found: 586.2194.

4.1.9. Complex 12

To a solution of complex **11** (20 mg, 0.034 mmol) in CH_2Cl_2 (2.0 mL), $Co_2(CO)_8$ (17.5 mg, 0.051 mmol) was added as a solid. The resulting mixture was stirred for 3 h at ambient temperature. NMO (0.078 mL, 0.34 mmol, 4.8 M solution in water) was added and stirred at ambient temperature overnight, then filtrate over silica. After evaporation of the solvent in vacuo, the residue was purified by chromatography (hexane:ethylacetate, 10:1) to give complex **12** (8.3 mg, 40% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.21 (9H, s), 0.88 (3H, t, $J = 7.5$ Hz), 1.13 (3H, t, $J = 7.5$ Hz), 1.23–1.32 (3H, m), 1.72–1.80 (1H, m), 1.83–1.94 (4H, m), 2.05 (1H, dd, $J = 2.5$, 18.7 Hz), 2.25 (1H, t, $J = 12.8$ Hz), 2.34 (1H, dd, $J = 6.3$, 13.9 Hz), 2.56–2.68 (7H, m), 2.72–2.79 (1H, m), 2.88–2.96 (1H, m), 3.03 (1H, dd, $J = 3.7$, 13.4 Hz), 3.37 (3H, s), 4.39 (1H, s), 5.96 (1H, d, $J = 2.2$ Hz), 7.14 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.00, 14.24, 14.42, 21.07, 26.41, 32.37, 36.44, 36.76, 37.09, 39.9, 41.8, 41.92, 42.53, 43.71, 45.21, 46.42, 55.37, 83.39, 92.41, 98.23, 115.07, 138.76, 139.61, 142.7, 143.20, 151.19, 186.22, 196.67, 212.07; IR ($CHCl_3$) 2964, 2930, 1965, 1895, 1678, 1596, 1455 cm^{-1}; MS (relative intensity) *m/z* 614 (M^+, 5), 530 (100), 478 (43), 435 (46), 368 (45), 340 (29); HRMS calc. for $C_{33}H_{42}O_6SiCr$, 614.2156. Found: 614.2161.

4.1.10. Compound 13

A mixture of complex **3aa** (58 mg, 010 mmol) and methyl acrylate (1.9 g, 22 mmol) in hexane (60 mL) was irradiated by medium pressure Hg vapor lamp (Pyrex filter) at ambient temperature for 36 h. The resulting solution was filtrated and evaporated in vacuo. The residue was purified by chromatography to give **13** (29 mg, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.66 (3H, t, $J = 6.8$ Hz), 0.93 (3H, t, $J = 7.1$ Hz), 0.93–1.00 (2H, m), 1.13–1.15 (2H, m), 1.30–1.34 (1H, m), 1.42–1.48 (2H, m), 1.90–2.01 (3H, m), 2.72 (1H, dd, $J = 3.2$, 13.2 Hz), 3.10 (1H, d, $J = 10.5$ Hz), 3.47 (3H, s), 3.61 (3H, s), 3.77 (3H, s), 4.41 (1H, s), 4.57 (1H, s), 5.36 (1H, s), 6.84 (1H, d, $J = 7.8$ Hz), 6.90 (1H, t, $J = 7.8$ Hz), 7.06 (1H, dd, $J = 1.2$, 7.8 Hz) 7.18 (1H, dt, $J = 1.2$, 7.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.92, 15.03, 18.47, 22.61, 39.56, 43.52, 44.36, 45.89, 51.53, 51.62, 52.09, 54.38, 54.78, 55.22, 96.29, 110.14, 120.33, 126.93, 127.20, 130.37, 130.72, 132.50, 156.76, 163.74, 173.56; IR ($CHCl_3$) 2999, 2958, 2933, 2871, 2837, 1735, 1463, 1438, 1243, 1201 cm^{-1}; MS (relative intensity) *m/z* 398 (M^+, 15), 383 (2), 369 (3), 355 (3), 339 (2), 312 (2), 279 (3), 269 (5), 69 (100); HRMS calc. for $C_{25}H_{34}O_4$, 398.2458. Found: 398.2455.

4.2. Crystal sturcture

CCDC number 272083 for **3ba**: Crystal data: empirical formula, $C_{27}H_{28}O_7Cr_2$, $M = 568.51$, red block, monoclinic, space group, $P2_1/n$ (No. 14), $a = 11.159(1)$ Å, $b = 18.420(1)$ Å, $c = 12.960(1)$ Å, $V = 2648.8(4)$ Å^3, $Z = 4$, $D_{calc} = 1.426$ g/cm^3, $F(000) = 1176.00$, μ(Mo Kα) = 8.63 cm^{-1}.

CCDC number 274090 for **7**: Crystal data: empirical formula, $C_{28}H_{30}O_4CrFe$, $M = 538.39$, red block, orthorhombic, space group, $Pna2_1$ (No. 33), $a = 14.066(3)$ Å, $b = 11.517(3)$ Å, $c = 16.251(4)$ Å, $V = 2648.8(4)$ Å^3, $Z = 4$, $D_{calc} = 1.358$ g/cm^3, $F(000) = 1120.00$, μ(Mo Kα) = 9.93 cm^{-1}.

CCDC number 273173 for **12**: Crystal data: empirical formula, $C_{33}H_{42}O_6SiCr$, $M = 614.77$, red block,

orthorhombic, space group, $P2_12_12_1$ (No. 19), $a = 10.0935(9)$ Å, $b = 15.249(2)$ Å, $c = 21.321(2)$ Å, $V = 3281.6(6)$ Å^3, $Z = 4$, $D_{calc} = 1.244$ g/cm^3, $F(000) = 1304.00$, μ(Mo Kα) = 4.26 cm^{-1}.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 14078101, Reaction Control of Dynamic Complexes) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

[1] (a) M.P. Doyle, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 12, Pergamon Press, New York, 1995, pp. 387–420;
(b) W.D. Wulff, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 12, Pergamon, New York, 1995, pp. 469–547;
(c) L.S. Hegedus, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 12, Pergamon Press, New York, 1995, pp. 549–600;
(d) J. Barluenga, J. Flórez, F.J. Fañanás, J. Organomet. Chem. 624 (2001) 5;
(e) A. de Meijere, H. Schirmer, M. Duetsch, Angew. Chem., Int. Ed. 39 (2000) 3964;
(f) M.A. Sierra, Chem. Rev. 100 (2000) 3591;
(g) R. Aumann, Eur. J. Org. Chem. (2000) 17;
(h) J.W. Herndon, Tetrahedron 56 (2000) 1257;
(i) K.-H. Dötz (Ed.), Metal Carbons in Organic Synthesis, Topics in Organometallic Chemistry, vol. 13, Springer, Berlin, 2004;
(j) G. Bertrand (Guest Ed.); J. Organomet. Chem. 617/618 (2001) 3.

[2] (a) Some selected recent references: T. Miura, N. Iwasawa, J. Am. Chem. Soc. 124 (2002) 518;
(b) H. Kagoshima, T. Okamura, T. Akiyama, J. Am. Chem. Soc. 123 (2001) 7182;
(c) N. Iwasawa, M. Shido, H. Kusama, J. Am. Chem. Soc. 123 (2001) 5814;
(d) J. Barluenga, F. Aznar, M.A. Palomero, Angew. Chem., Int. Ed. 39 (2000) 4346;
(e) J. Barluenga, F. Aznar, I. Gutiérrez, A. Martín, S. García-Granda, M.A. Llorca-Baragaño, J. Am. Chem. Soc. 122 (2000) 1314;
(f) J. Barluenga, A. Ballesteros, J. Santamaría, R. Bernardo de la Rúa, E. Rubio, M. Tomás, J. Am. Chem. Soc. 122 (2000) 12874;
(g) J. Barluenga, F. Rodríguez, F.J. Fañanás, E. Rubio, Angew. Chem., Int. Ed. 38 (1999) 3084.

[3] (a) J. Barluenga, P. Barrio, L.A. López, M. Tomás, S. García-Granda, C. Alvarez-Rúa, Angew. Chem., Int. Ed. 42 (2003) 3008;
(b) J. Barluenga, R. Vicente, P. Barrio, L.A. López, M. Tomás, J. Borge, J. Am. Chem. Soc. 126 (2004) 14354.

[4] (a) W.D. Wulff, Organometallics 17 (1998) 3116;
(b) K.H. Dötz, P. Tomuschat, Chem. Soc. Rev. 28 (1999) 187;
(c) J. Barluenga, K. Muñiz, M. Tomás, A. Ballesteros, S. García-Granda, Organometallics 22 (2003) 1756.

[5] K. Kamikawa, A. Tachibana, Y. Shimizu, K. Uchida, M. Furusho, M. Uemura, Org. Lett. 6 (2004) 4307.

[6] A solution of heptatriene chromium complex **3ac** and **4ac**, respectively, in acetonitrle was stirred under CO pressure (75 bar) at 25 °C for 72 h to give an identical mono-(arene)chromium complex **5ac** (50%).

[7] (a) A. Solladié-Cavallo, in: L.S. Liebeskind (Ed.), Advances in Metal–Organic Chemistry, vol. 1, JAI Press, Greenwich, CT, 1989, pp. 99–133;
(b) S.G. Davies, T.D. McCarthy, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 12, Pergamon Press, Oxford, 1995, pp. 1039– 1070.

[8] (a) For chromium–metal exchange reaction of alkoxy Fischer carbene complexes, see: J. Barluenga, L.A. López, O. Löber, S. García-Granda, C. Alvarez-Rúa, J. Borge, M. Tomás, Angew. Chem., Int. Ed. 40 (2001) 3392;
(b) M.A. Sierra, J.C. del Amo, J.M. Mancheño, M. Gómez-Gallego, J. Am. Chem. Soc. 123 (2001) 851;
(c) I. Göttker–Schnetmann, R. Aumann, Organometallics 20 (2001) 346;
(d) E.O. Fischer, H.-J. Beck, C.G. Kreiter, J. Lynch, J. Müller, E. Winkler, Chem. Ber. 105 (1972) 162;
(e) R. Aumann, E.O. Fischer, Chem. Ber. 114 (1981) 1853.

[9] J.J. Eisch, A.A. Aradi, M.A. Lucarelli, Y. Qian, Tetrahedron 54 (1998) 1169.

[10] A.A. Jarzecki, J. Gajewski, E.R. Davidson, J. Am. Chem. Soc. 121 (1999) 6928.

[11] A. Quattropani, G. Anderson, G. Bernardinelli, E.P. Kündig, J. Am. Chem. Soc. 119 (1997) 4773.

[12] (a) J.H. Rigby, Acc. Chem. Res. 26 (1993) 579;
(b) J.H. Rigby, in: L.S. Liebeskind (Ed.), Advances in Metal–Organic Chemistry, vol. 4, JAI Press, Greenwich, CT, 1995, pp. 89–127;
J.H. Rigby, in: L.A. Paquette (Ed.), Organic Reactions, vol. 49, Wiley, New York, 1997, pp. 331–425;
J.H. Rigby, Tetrahedron 55 (1999) 4521.