Journal of Organometallic Chemistry 696 (2011) 3987–3991

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Ring-closing metathesis within chromium-coordination sphere: Facile access to phosphine-chelate (π-arene)chromium complexes☆

Masamichi Ogasawara [a,*], Wei-Yi Wu [b], Sachie Arae [a], Tomotaka Morita [b], Susumu Watanabe [a], Tamotsu Takahashi [a,**], Ken Kamikawa [b,***]

[a] Catalysis Research Center and Graduate School of Life Science, Hokkaido University, Kita-ku, Sapporo 001-0021, Japan
[b] Department of Chemistry, Graduate School of Science, Osaka Prefecture University, Sakai Osaka 599-8531, Japan

ARTICLE INFO

Article history:
Received 9 April 2011
Received in revised form
4 May 2011
Accepted 6 May 2011

Keywords:
(π-Arene)chromium complex
Alkenylphosphine
Ring-closing metathesis
Ruthenium-carbene complex

ABSTRACT

A variety of phosphine-chelate (π-arene)chromium complexes were prepared in good to excellent yields by the ring-closing metathesis reaction of [η^6-(ω-alkenyl)benzene][(ω-alkenyl)phosphine]chromium(0) dicarbonyl complexes catalyzed by the Grubbs' ruthenium–carbene complexes.

1. Introduction

Since the discovery of well-defined metathesis catalysts, olefin metathesis has been widely recognized as a versatile and powerful tool in organic chemistry and material science [1]. Due to the excellent functional group tolerance of the Schrock's Mo- [2] and the Grubbs' Ru-catalysts [3], they have been utilized in modulation of a wide range of organic compounds. In the last decade, organometallic compounds have emerged as a novel class of substrates in olefin metathesis, and the Mo- and the Ru-catalysts show good versatility in the transformation of the organometallic substrates as well [4]. The metathesis reactions of the organometallics have provided the unique ways to interesting structures which are otherwise difficult to access [4,5]. The majority of the earlier works in this field is on the ferrocene platforms, which can partly be attributed to their chemical robustness, and the metathesis studies on other organometallics are still rather limited.

In organometallic chemistry, (η^6-arene)chromium complexes are one of the most useful compounds because not only of their unique reactivity but also of their usefulness as chiral building blocks based on planar-chirality [6]. In this article, we wish to report preparation of the phosphine-chelate (η^6-arene)chromium complexes by the Ru-catalyzed ring-closing metathesis. This type of bridged (η^6-arene)chromium species is relatively rare and all the precedented examples are prepared by ligation of a preformed phosphine-tethered arene to a chromium center [7].

The RCM studies on the arene-chromium compounds were previously reported by Sarkar and coworkers [8]. In their system, the two alkenyl side chains are arranged on the arene ring. The reaction cites are remote from the chromium-coordination spheres and the (η^6-arene)chromium moieties exist outside of the newly formed rings (the *exo*-cyclization mode; Scheme 1). In other words, the *exo*-mode cyclization is a process converting the single ligand by the RCM reaction. On the other hand, the RCM reaction of (η^6-arene) chromium species described here proceeds within the chromium-coordination spheres connecting the two coordinating ligands (an η^6-arene and a phosphine), which leads to the formation of the chromium-containing ring systems (the *endo*-cyclization mode).

2. Results and discussion

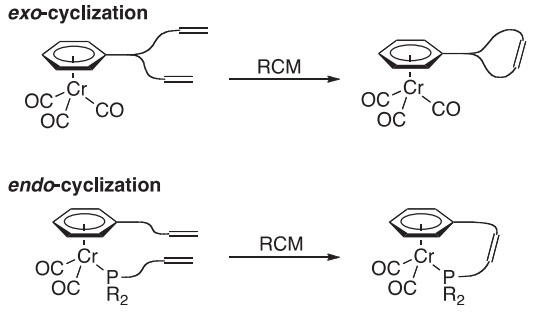
2.1. Preparation of (η^6-ω-alkenylbenzene)Cr(CO)$_2$(ω-alkenylphosphine) complexes **1**

A series of η^6-ω-alkenylbenzene/ω-alkenylphosphine–chromium complexes were prepared by a photo-induced ligand exchange

☆ Dedicated to Professor Kenneth G. Caulton on the occasion of his 70th birthday.

* Corresponding author. Tel.: +81 11 706 9154; fax: +81 11 706 9150.
** Corresponding author. Tel.: +81 11 706 9149; fax: +81 11 706 9150.
*** Corresponding author. Tel.: +81 72 254 9721; fax: +81 72 254 9931.
E-mail addresses: ogasawar@cat.hokudai.ac.jp (M. Ogasawara), tamotsu@cat.hokudai.ac.jp (T. Takahashi), kamikawa@c.s.osakafu-u.ac.jp (K. Kamikawa).

0022-328X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2011.05.006

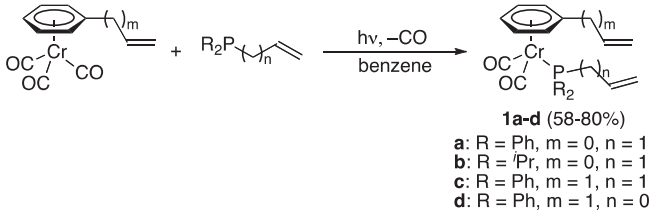


Scheme 1. Two reaction modes of RCM on chromium-arene platforms.

reaction as illustrated in Scheme 2 [9]. Photoirradiation of a preformed (η^6-ω-alkenylbenzene)chromium(0) tricarbonyl complex in benzene with a high-pressure mercury lamp in the presence of an excess (1.5 equiv. to Cr) appropriate ω-alkenylphosphine (ω-alkenyl = vinyl or allyl) induces a ligand exchange between CO and the phosphine to give a dicarbonyl(alkenylphosphine)chromium complex in moderate to good yields (58–80%). The complexes are red to yellow poorly crystalline solids. They are slightly air-sensitive but easily purified by silica gel chromatography under nitrogen.

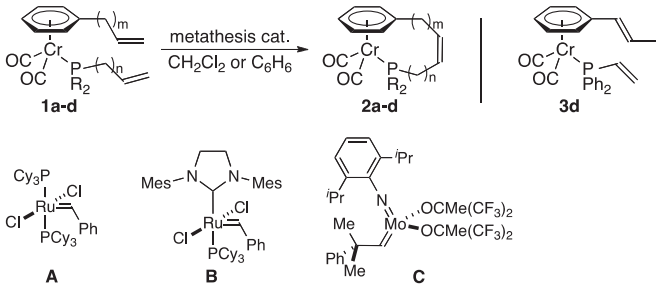
2.2. Preparation of phosphine-chelate (η^6-arene)chromium(0) complexes by ruthenium-catalyzed ring-closing metathesis

It was found that the η^6-styrene/allyldiphenylphosphine complex **1a** was an excellent substrate for the *endo*-mode ring-closing metathesis. A reaction of **1a** with the 1st generation Grubbs' catalyst (**A**; 10 mol %) in dichloromethane at 25 °C was complete within 6 h and the NMR analysis of the reaction mixture showed nearly quantitative formation of the desired phosphine-chelate complex **2a**. The pure RCM product **2a** was isolated in 93% yield as a yellow crystalline solid by silica gel chromatography (Table 1, entry 1). The Cr complex **1b**, which is with a diisopropylphosphino moiety in place of the PPh_2 unit, is equally reactive as **1a** under the identical reaction conditions (entry 2). The isolated yield of **2b** (82%) is slightly lower than that of **2a**, that can be attributed to the lower stability of **2b** toward oxidation due to the more electron-donating phosphine (i.e., the higher electron density at the chromium center). The RCM reaction of the substrate **1c**, which is with an η^6-allylbenzene, was tardier and the product **2c** was obtained in 60% yield (entry 3). The use of the 2nd generation Grubbs' catalyst (**B**) was found to be more effective for the reaction of **1c**, and the yield of **2c** was improved to 71% (entry 4). Note that the reactions of **1c** (entries 3 and 4) are not so clean as those of **1a** and **1b**, and several uncharacterized byproducts were detected in the ^1H and ^{31}P NMR spectra of the reaction mixtures. Some of the byproducts can be ascribed to results of intermolecular cross-metathesis. Among the byproducts from the reaction of **1c**, about 5% of **2a** was observed. The formation of the "shortened" chelate complex **2a** can



Scheme 2. Preparation of η^6-ω-alkenylbenzene/ω-alkenylphosphine–chromium complexes **1**.

Table 1
Ring-closing metathesis of preparing phosphine-chelate (η^6-arene)chromium(0) complexes.[a]



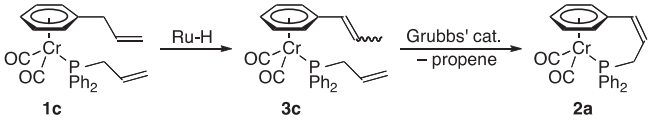
entry	Substrate **1**	Catalyst (mol %)	Solvent	Time (h)	Temp (°C)	Yield of **2** (%)[b]
1	**1a**	**A** (10)	CH_2Cl_2	6	25	93 (**2a**)
2	**1b**	**A** (10)	CH_2Cl_2	6	25	82 (**2b**)
3	**1c**	**A** (10)	CH_2Cl_2	18	25	60 (**2c**)
4	**1c**	**B** (10)	CH_2Cl_2	18	25	71 (**2c**)
5	**1d**	**A** (10)	CH_2Cl_2	18	25	0[c]
6	**1d**	**B** (10)	CH_2Cl_2	18	50	0
7	**1d**	**C** (10)	C_6H_6	18	80	0[d]

[a] The reaction was carried out in the given solvent under argon with initial concentration of **1** at 0.1 mol/L in the presence of the indicated catalyst (10 mol %).
[b] Isolated yield by silica gel chromatography.
[c] The unreacted substrate **1d** was recovered in >80%.
[d] The major product was **3d** in 68%.

be rationalized as depicted in Scheme 3. Isomerization of the substrate **1c**, which was likely promoted by a Ru-hydride species derived by decomposition of the Grubbs catalysts [10], gives the (η^6-propenylbenzene)chromium complex **3c**, and following RCM of **3c** afforded **2a** with elimination of propene [11].

On the other hand, the RCM reaction of the η^6-allylbenzene/vinyldiphenylphosphine complex **1d**, which was expected to produce the C_3-bridged phosphine-chelate (η^6-arene)chromium complex **2d**, did not afford the cyclized product under the conditions examined. With the ruthenium catalyst **A** (10 mol %) at 25 °C, the unreacted substrate was recovered in >80% yield (entry 5). Under the more severe conditions, i. e. with the catalyst **B** at 50 °C, consumption of **1d** was observed in a certain extent, but the desired chelate complex **2d** was not found in the reaction mixture (entry 6). The Mo catalyst **C**, which is known to be powerful for sterically congested substrates, was not effective for the reaction of **1d** either. More than 95% of **1d** was consumed at 80 °C during 18 h in the presence of **C** (10 mol %), however, the main product (68%) from the reaction was the isomerized complex **3d** and no RCM product was detected (entry 7). It seems that the diphenylphosphino group adjacent to the vinyl moiety exerts a steric effect which suppresses the formation of **2d**.

In general, ring sizes and substitution patterns are two of the most important factors for success of RCM. The results shown above imply that an η^6-vinylarene and an allylphosphine are the best combination for the high-yield preparation of the phosphine-chelate (π-arene)chromium species by *endo*-cyclization RCM.



Scheme 3. Plausible pathway from **1c** to **2a**.

A distinctive color change was observed during the ring-closing metathesis of **1a** and **1b**. The color of the η^6-styrene complexes (**1a** and **1b**) is bright red, while that of the η^6-allylbenzene complexes (**1c** and **1d**) is light yellow. The darker colors in **1a** and **1b** can be explained by the conjugation of the vinyl groups and the η^6-arene moieties in these two complexes. On the other hand, all of the RCM products **2a-c** are light yellow in color as **1c** and **1d**. In **2a** and **2b**, the η^6-arene and the bridging α,ω-alkenylene moieties are not conjugating anymore due to their non-coplanar orientation (see their crystal structures; vide infra), which cancels the red-shift detected in **1a** and **1b**. In accordance with this, the complex **3d**, which has an η^6-(β-methylstyrene) ligand, is bright red as **1a** and **1b**.

The non-chelate Cr-complexes **1a-d** and **3d** show the ^{31}P NMR resonances between δ 82.4 to δ 84.9, which is the typical range for this type of complexes. On the other hand, the ^{31}P NMR signals of **2a** and **2b** are detected at δ 104.6 and δ 119.8, respectively. This unusual lower field shift of the ^{31}P-NMR resonances would be ascribed to the distorted geometries of the phosphorus atoms in **2a** and **2c** in response to the ring strain due to the shorter C_3-chain between the η^6-phenyl and diphenylphosphino groups. Indeed, the distortion can be seen in the crystal structure of **2a** (see the next section). The C_4-bridged complex **2c**, of which three-dimensional structure is close to the ideal piano-stool geometry, does not show the lower field shift in its ^{31}P NMR spectrum (δ 75.8).

2.3. X-ray crystal structures of *2a* and *2c*

Single crystals of **2a** and **2c** suitable for X-ray crystallography were grown from ethyl acetate/hexane at low temperature. Their ORTEP drawings are shown in Figs. 1,2, along with selected bond lengths and angles (see the Supporting Information for details). The structure of **2a** clearly displays the distorted conformation of the molecule as suggested by the ^{31}P NMR spectrum. The Cr(1)-P(1)–C(1) angle is 110.4(1)°, which is much smaller than the angles of Cr(1)-P(1)–C(12) (116.8(1)°) and Cr(1)-P(1)–C(18) (121.6(1)°).

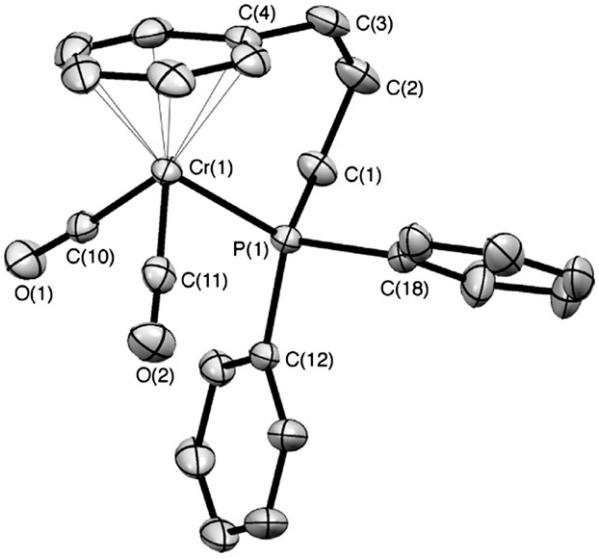


Fig. 1. ORTEP drawing of **2a** with 30% thermal ellipsoids. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cr(1)–P(1) = 2.271(1), Cr(1)–C(4) = 2.201(4), P(1)–C(1) = 1.842(3), C(1)–C(2) = 1.509(6), C(2)–C(3) = 1.303(6), C(3)–C(4) = 1.492(5), Cr(1)-(η^6-arene) = 1.689; P(1)–Cr(1)–C(4) = 84.6(1), Cr(1)–P(1)–C(1) = 110.4(1), Cr(1)–P(1)–C(12) = 116.8(2), Cr(1)–P(1)–C(18) = 121.6(1), Cr(1)–C(4)–C(3) = 130.3(3).

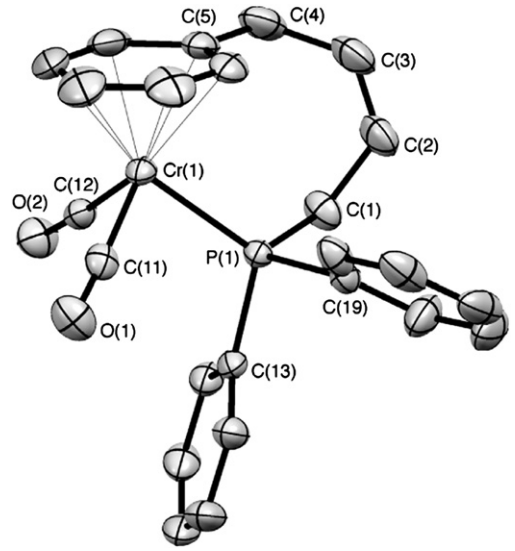


Fig. 2. ORTEP drawing of **2c** with 30% thermal ellipsoids. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cr(1)–P(1) = 2.2871(8), Cr(1)–C(5) = 2.224(2), P(1)–C(1) = 1.847(2), C(1)–C(2) = 1.501(4), C(2)–C(3) = 1.310(5), C(3)–C(4) = 1.490(5), C(4)-C(5) = 1.491(4), Cr(1)-(η^6-arene) = 1.693; P(1)–Cr(1)–C(5) = 95.08(7), Cr(1)–P(1)–C(1) = 115.61(8), Cr(1)–P(1)–C(13) = 115.29(8), Cr(1)–P(1)–C(19) = 120.34(8), Cr(1)–C(5)–C(4) = 131.2(2).

Thus, the geometry around the P(1) atom in **2a** is far from the ideal tetrahedral orientation. In contrast, the three Cr(1)-P(1)-carbon angles in **2c** are in the range 115.29(8)-120.34(8)°. Likewise, due to the skewed chelate ring in **2a**, the C(4)-Cr(1)-P(1) angle in **2a** (84.6(1)°) is considerably smaller than the C(5)-Cr(1)-P(1) angle in **2c** (95.08(7)°). The Cr–P distances are 2.271(1) Å in **2a** and 2.2871(8) Å in **2c** respectively, which are approximately 5% shorter than the Cr–P distance in an analogous non-chelate complex (η^6-benzene)$Cr(CO)_2(PPh_2CH_2Ph)$ (2.4015(14) Å) [12]. Other bond lengths and angles in **2a** and **2c** are within the normal range.

2.4. Origin of high reactivity of *1a* and *1b* in RCM

As described in the section 2.3, the RCM product **2a** contains the distortion originated in the shorter chelate chain. Comparison between the two structures suggests that the strain energy in **2a** is probably larger than that in **2c**. Corollary of these observations is that relative thermodynamic stability of the RCM products cannot account for the higher reactivity of **1a** and **1b** than **1c** in the RCM reaction. Most likely, the RCM reactions of **1a-c** are under kinetic control. With a shorter alkenyl substituent (vinyl group) on the η^6-arene in **1a** and **1b**, the probability of meeting the two olefinic termini becomes higher leading to the higher yields of **2a** and **2b** than **2c**. Alternatively, the higher yields of **2a**/**2b** could be explained by the greater reactivity of the η^6-styrene moieties in **1a** and **1b** than the η^6-allylbenzene in **1c** [13,14].

3. Conclusions

In conclusion, we have successfully achieved efficient *endo*-cyclization within the coordination sphere of the (η^6-arene)chromium complexes by the RCM reaction. The reactivity of the substrates is strongly affected by length of the olefinic tethers, and choice of suitable alkenyl substituents is important for higher yields of the RCM products. Future outlook: explorations of the asymmetric synthesis of planar-chiral (η^6-arene)chromium complexes are in progress.

4. Experimental section

4.1. General

All anaerobic and/or moisture sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or with glovebox techniques under prepurified argon. ^{1}H NMR (at 400 MHz) and ^{13}C NMR (at 101 MHz) chemical shifts are reported in ppm downfield of internal tetramethylsilane. ^{31}P NMR (at 162 MHz) chemical shifts are externally referenced to 85% H_3PO_4. Tetrahydrofuran and benzene were distilled from benzophenone-ketyl under nitrogen prior to use. Dichloromethane was distilled from CaH_2 under nitrogen prior to use. The chromium tricarbonyl complexes (η^6-arene)Cr(CO)$_3$ [15], $(PCy_3)_2Cl_2$-Ru(=CHPh) [3b], $(H_2IMes)(PCy_3)Cl_2Ru(=CHPh)$ [16], and Mo(=CHCMe$_2$Ph)(=NC$_6$H$_3$-2,6-^{i}Pr$_2$)(OC(CF$_3$)$_2$Me)$_2$ [1a,17] were prepared according to the reported methods. All the other chemicals were obtained from commercial sources.

4.2. Preparation of nonbridged (η^6-arene)Cr(CO)$_2$(phosphine) **1**

A chromium tricarbonyl complex (1 mmol) and an appropriate alkenylphosphine (1.5 mmol) were dissolved in benzene (10 mL) under an argon atmosphere. The solution was irradiated with mercury lamp and stirred for 7 h at room temperature. The resulting red color solution was filtrate and concentrated under reduced pressure. The crude product was purified by silica gel chromatography to give the target compound in 58–80% yield. The characterization data of the complexes are given below.

4.2.1. (η^6-Vinylbenzene)(allyldiphenylphosphine)chromium(0) dicarbonyl (**1a**)

Yield: 68%. ^{1}H NMR (C_6D_6): δ 3.06–3.11 (m, 2H), 4.20–4.29 (m, 3H), 4.46–4.49 (m, 2H), 4.70–4.76 (m, 1H), 4.82–4.86 (m, 1H), 4.93 (dd, J = 10.7 and 0.6 Hz, 1H), 5.23 (dd, J = 17.4 and 0.6 Hz, 1H), 5.66–5.77 (m, 1H), 5.96 (dd, J = 17.4 and 10.7 Hz, 1H), 7.00–7.11 (m, 6H), 7.45–7.50 (m, 4H). ^{13}C{^{1}H} NMR (C_6D_6): δ 40.4 (d, J_{PC} = 22.7 Hz), 87.4 (s), 89.2 (s), 90.0 (s), 99.4 (s), 113.3 (s), 118.9 (d, J_{PC} = 10.0 Hz), 128.1 (d, J_{PC} = 8.3 Hz), 129.1 (d, J_{PC} = 2.0 Hz), 131.4 (d, J_{PC} = 5.0 Hz), 132.6 (d, J_{PC} = 10.0 Hz), 135.8 (s), 140.4 (d, J_{PC} = 28.4 Hz), 240.6 (d, J_{PC} = 20.7 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 82.4 (s). IR (KBr) 1654, 1542 cm^{-1}. Anal. Calcd for $C_{25}H_{23}CrO_2P$: C, 68.49; H, 5.29. Found: C, 68.47; H, 5.44. EI-HRMS Calcd for $C_{25}H_{23}CrO_2P$: 438.0841. Found: 438.0842.

4.2.2. (η^6-Vinylbenzene)(allyldiisopropylphosphine)chromium(0) dicarbonyl (**1b**)

Yield: 80%. ^{1}H NMR (C_6D_6): δ 0.94 (dd, J = 13.9 and 7.2 Hz, 6H), 1.00 (dd, J = 12.6 and 7.2 Hz, 6H), 1.69–1.78 (m, 2H), 2.48 (t, J = 7.4 Hz, 2H), 4.44–4.51 (m, 3H), 4.61–4.63 (m, 2H), 4.91–5.00 (m, 3H), 5.33 (d, J = 17.6 Hz, 1H), 5.77–5.89 (m, 1H), 6.12, (dd, J = 17.6 and 10.8 Hz, 1H). ^{13}C{^{1}H} NMR (C_6D_6): δ 18.7 (d, J_{PC} = 3.0 Hz), 19.0 (s), 28.9 (d, J_{PC} = 14.8 Hz), 34.3 (d, J_{PC} = 16.9 Hz), 85.1 (s), 87.1 (s), 87.4 (s), 98.0 (s), 113.0 (s), 117.2 (d, J_{PC} = 7.4 Hz), 134.0 (d, J_{PC} = 6.5 Hz), 136.3 (s), 241.5 (d, J_{PC} = 19.8 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 84.9 (s). IR (KBr) 1880, 1826 cm^{-1}. Anal. Calcd for $C_{21}H_{31}CrO_2P$: C, 61.61; H, 7.35. Found: C, 61.71; H, 7.42. EI-HRMS Calcd for $C_{19}H_{27}CrO_2P$: 370.1154. Found: 370.1149.

4.2.3. (η^6-Allylbenzene)(allyldiphenylphosphine)chromium(0) dicarbonyl (**1c**)

Yield: 58%. ^{1}H NMR (C_6D_6): δ 2.90 (dt, J = 6.7 and 1.3 Hz, 2H), 3.11 (t, J = 7.9 Hz, 2H), 4.05–4.09 (m, 1H), 4.15–4.16 (m, 2H), 4.32–4.36 (m, 2H), 4.70–4.77 (m, 1H), 4.83–4.89 (m, 2H), 4.91–4.93 (m, 1H), 5.68–5.81 (m, 2H), 7.00–7.10 (m, 6H), 7.47–7.52 (m, 4H). ^{13}C{^{1}H} NMR (C_6D_6): δ 39.4 (s), 40.6 (d, J_{PC} = 22.6 Hz), 88.2 (s), 88.6 (s), 91.2 (s), 105.5 (d, J_{PC} = 0.9 Hz), 116.9 (s), 118.8 (d, J_{PC} = 10.0 Hz), 128.1 (d, J = 8.1 Hz), 129.0 (d, J_{PC} = 2.1 Hz), 131.6 (d, J_{PC} = 5.0 Hz), 132.6 (d, J_{PC} = 9.7 Hz), 136.6 (s), 140.6 (d, J_{PC} = 28.3 Hz), 240.8 (d, J_{PC} = 20.6 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 83.5 (s). IR ($CHCl_3$) 1879, 1825, 1092 cm^{-1}. Anal. Calcd for $C_{26}H_{25}CrO_2P$: C, 69.02; H, 5.57. Found: C, 69.04; H, 5.62. EI-HRMS Calcd for $C_{26}H_{25}CrO_2P$: 452.0997. Found: 452.0995.

4.2.4. (η^6-Allylbenzene)(diphenylvinylphosphine)chromium(0) dicarbonyl (**1d**)

Yield: 74%. ^{1}H NMR (C_6D_6): δ 2.93 (d, J = 6.8 Hz, 2H), 4.10–4.14 (m, 1H), 4.22–4.23 (m, 2H), 4.37–4.41 (m, 2H), 4.88–4.94 (m, 2H), 5.44 (td, 17.8 and 1.7 Hz, 1H), 5.56 (ddd, J = 35.7, 11.8, and 1.7 Hz, 1H), 5.79 (ddt, J = 17.8, 9.6, and 6.8 Hz, 1H), 6.54 (ddd, J = 17.8, 17.2, and 11.8 Hz, 1H), 6.99–7.10 (m, 6H), 7.53–7.58 (m, 4H). ^{13}C{^{1}H} NMR (C_6D_6): δ 39.4 (s), 88.1 (s), 88.5 (s), 91.2 (s), 105.5 (d, J_{PC} = 0.9 Hz), 117.0 (s), 127.2 (d, J_{PC} = 4.4 Hz), 128.3 (d, J_{PC} = 8.9 Hz), 129.2 (d, J_{PC} = 2.1 Hz), 132.7 (d, J_{PC} = 10.4 Hz), 136.5 (s), 138.9 (d, J_{PC} = 33.1 Hz), 140.1 (d, J_{PC} = 34.3 Hz), 240.4 (d, J_{PC} = 21.0 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 84.3 (s). IR (KBr) 1877, 1820 cm^{-1}. Anal. Calcd for $C_{25}H_{23}CrO_2P$: C, 68.49; H, 5.29. Found: C, 68.77; H, 5.45. EI-HRMS Calcd for $C_{25}H_{23}CrO_2P$: 438.0841. Found: 438.0835.

4.3. General procedure for the ring-closing metathesis of **1**

A solution of the chromium complex **1** (0.50 mmol) and the Grubbs' catalyst (50 μmol; 10 mol%) in CH_2Cl_2 (5 mL) was stirred at 25 °C for 6–18 h under a nitrogen atmosphere. The resulting solution was concentrated under reduced pressure. The residue was purified by silica gel chromatography to give the cyclized product.

4.3.1. [η^6-(3-Diphenylphosphinopropenyl)benzene-P]chromium(0) dicarbonyl (**2a**)

^{1}H NMR (C_6D_6): δ 2.56 (ddd, J = 8.9, 5.8, and 1.7 Hz, 2H), 4.01–4.04 (m, 2H), 4.32–4.36 (m, 1H), 4.71–4.75 (m, 2H), 5.39 (ddt, J = 13.1, 11.0, and 5.8 Hz, 1H), 6.03 (ddt, J = 11.0, 3.0, and 1.7 Hz, 1H), 6.99–7.04 (m, 2H), 7.06–7.11 (m, 4H), 7.47–7.52 (m, 4H). ^{13}C{^{1}H} NMR (C_6D_6): δ 30.8 (d, J_{PC} = 14.1 Hz), 80.8 (d, J_{PC} = 0.9 Hz), 85.6 (s), 91.0 (d, J_{PC} = 1.1 Hz), 100.4 (d, J_{PC} = 3.0 Hz), 128.2 (d, J_{PC} = 9.1 Hz), 128.6 (d, J_{PC} = 12.6 Hz), 128.8 (s), 129.1 (d, J_{PC} = 2.1 Hz), 132.2 (d, J_{PC} = 10.0 Hz), 140.4 (d, J_{PC} = 35.0 Hz), 238.5, (d, J_{PC} = 18.9 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 104.6 (s). IR ($CHCl_3$) 1890, 1831 cm^{-1}. Anal. Calcd for $C_{23}H_{19}CrO_2P$: C, 67.32; H, 4.67. Found: C, 67.02; H, 4.87. EI-HRMS Calcd for $C_{23}H_{19}CrO_2P$: 410.0528. Found: 410.0530.

4.3.2. [η^6-1-(3-Diisopropylphosphino-2-propenyl)benzene-P] chromium(0) dicarbonyl (**2b**)

^{1}H NMR (C_6D_6): δ 0.88 (dd, J = 12.5 and 7.0 Hz, 6H), 1.00 (dd, J = 14.5 and 7.2 Hz, 6H), 1.62–1.66 (m, 2H), 1.80–1.92 (m, 2H), 4.12–4.14 (m, 2H), 4.40–4.47 (m, 3H), 5.46–5.55 (m, 1H), 5.98–6.01 (m, 1H). ^{13}C{^{1}H} NMR (C_6D_6): δ 17.2 (d, J_{PC} = 0.6 Hz), 18.4 (d, J_{PC} = 3.0 Hz), 22.0 (d, J_{PC} = 6.8 Hz), 28.9 (d, J_{PC} = 19.8 Hz), 81.6 (s), 88.1 (d, J_{PC} = 1.5 Hz), 88.8 (s), 96.5 (d, J_{PC} = 2.4 Hz), 129.2 (s), 241.5 (d, J_{PC} = 17.3 Hz), 241.0 (d, J_{PC} = 18.0 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 119.8 (s). IR ($CHCl_3$) 1870, 1815 cm^{-1}. Anal. Calcd for $C_{17}H_{23}CrO_2P$: C, 59.64; H, 6.77. Found: C, 59.30; H, 6.81. EI-HRMS Calcd for $C_{19}H_{27}CrO_2P$: 342.0841. Found: 342.0839.

4.3.3. [η^6-(4-Diphenylphosphinobut-2-enyl)benzene-P] chromium(0) dicarbonyl (**2c**)

^{1}H NMR (C_6D_6): δ 2.84 (d, J = 7.6 Hz, 2H), 3.07 (dd, J = 9.4 and 7.3 Hz, 1H), 4.46–4.54 (m, 3H), 4.60–4.62 (m, 2H), 5.21–5.35 (m, 2H), 7.01–7.06 (m, 2H), 7.10–7.14 (m, 4H), 7.45–7.50 (m, 4H). ^{13}C{^{1}H} NMR (C_6D_6): δ 31.3 (s), 32.8 (d, J_{PC} = 11.6 Hz), 85.4 (s), 85.8 (d, J_{PC} = 0.7 Hz), 90.4 (s), 97.0 (s), 126.5 (d, J_{PC} = 8.6 Hz), 128.1 (d,

J_{PC} = 8.6 Hz), 128.9 (d, J_{PC} = 2.0 Hz), 129.1 (d, J_{PC} = 3.7 Hz), 132.1 (d, J_{PC} = 10.0 Hz), 142.0 (d, J_{PC} = 34.0 Hz), 239.6 (d, J_{PC} = 20.0 Hz). ^{31}P {^{1}H} NMR (C_6D_6): δ 75.8 (s). IR ($CHCl_3$) 1883,1824 cm^{-1}. Anal. Calcd for $C_{24}H_{21}CrO_2P$: C, 67.92; H, 4.99. Found: C, 67.75; H, 5.10. EI-HRMS Calcd for $C_{24}H_{21}CrO_2P$: 424.0684. Found: 424.0678.

4.3.4. (η^6-1-Propenylbenzene)(diphenylvinylphosphine) chromium(0) dicarbonyl (**3d**)

^{1}H NMR (C_6D_6): δ 1.55 (d, J = 5.1 Hz, 3H), 4.28–4.31 (m, 1H), 4.36–4.39 (m, 2H), 4.51–4.53 (m, 2H), 5.40–5.75 (m, 4H), 6.55 (ddd, J = 18.1, 17.4, and 11.9 Hz, 1H), 6.99–7.10 (m, 6H), 7.54–7.58 (m, 4H). ^{13}C{^{1}H} NMR (C_6D_6): δ 18.2 (s), 86.8 (s), 89.1 (s), 89.5 (s), 101.3 (d, J_{PC} = 0.9 Hz), 125.9 (s), 127.1 (d, J_{PC} = 4.4 Hz), 128.2 (d, J_{PC} = 8.8 Hz), 129.1 (d, J_{PC} = 2.0 Hz), 129.6 (s), 132.9 (d, J_{PC} = 10.6 Hz), 138.9 (d, J_{PC} = 32.9 Hz), 140.0 (d, J_{PC} = 33.8 Hz), 240.5 (d, J_{PC} = 20.9 Hz). ^{31}P {^{1}H} NMR (C_6D_6): δ 84.0 (s). IR (KBr) 1883, 1831 cm^{-1}. EI-HRMS Calcd for $C_{25}H_{23}CrO_2P$: 438.0841. Found: 438.0841.

4.4. X-ray crystallography of **2a**

CCDC number 820585. Crystal data: empirical formula, $C_{23}H_{19}O_2PCr$, M = 410.35, orange needles, monoclinic, space group, $P2_1/C$, a = 12.636(3)Å, b = 11.302(3)Å, c = 14.075(3)Å, V = 1953.6(8) Å^3, Z = 4, D_c = 1.395 g/cm^3, $F(000)$ = 848.0, μ(Mo Kα) = 0.682 mm^{-1}, T = 296 K, R_1 = 0.0547 ($I > 2\sigma(I)$), wR_2 = 0.1865 ($I > 2\sigma(I)$), S = 1.018, number of collected data = 18502, number of refined parameters = 245. Data collection was carried out using the RIGAKU RAXIS RAPID, and SHELXL97 programs were used for the structure solution and refinement.

4.5. X-ray crystallography of **2c**

CCDC number 820584. Crystal data: empirical formula, $C_{24}H_{21}O_2PCr$, M = 424.38, orange needles, monoclinic, space group, $P2_1/c$, a = 12.704(6)Å, b = 11.357(4)Å, c = 14.368(5)Å, V = 2023.9(13)Å^3, Z = 4, D_c = 1.393 g/cm^3, $F(000)$ = 880.0, μ(Mo Kα) = 0.661 mm^{-1}, T = 296 K, R_1 = 0.0404 ($I > 2\sigma(I)$), wR_2 = 0.1104 ($I > 2\sigma(I)$), S = 1.018, number of collected data = 19345, number of refined parameters = 253. Data collection was carried out using the RIGAKU RAXIS RAPID, and SHELXL97 programs were used for the structure solution and refinement.

Acknowledgments

This work was supported by the Cooperative Research Program from the Catalysis Research Center, Hokkaido University (Grant #10A0002) and a Grant-in-Aid for Scientific Research on Innovative Areas from MEXT, Japan (to MO and KK).

Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2011.05.006.

References

[1] (a) A.H. Hoveyda Chapter 2.3, in: R.H. Grubbs (Ed.), Handbook of Metathesis, vol. 2, Wiley-VCH, Weinheim, 2003, p. 128;
(b) J. Cossy, S. Arseniyadls, C. Meyer (Eds.), Metathesis in Natural Product Synthesis, Wiley-VCH, Weinheim, 2010.
[2] (a) R.R. Schrock, J.S. Murdzek, G.C. Bazan, J. Robbins, M. DiMare, M. O'Regan, J. Am. Chem. Soc. 112 (1990) 3875;
(b) R.R. Schrock Chapter 1.3, in: R.H. Grubbs (Ed.), Handbook of Metathesis, vol. 1, Wiley-VCH, Weinheim, 2003, p. 8.
[3] (a) S.T. Nguyen, L.K. Johnson, R.H. Grubbs, J.W. Ziller, J. Am. Chem. Soc. 114 (1992) 3974;
(b) P. Schwab, R.H. Grubbs, J.W. Ziller, J. Am. Chem. Soc. 118 (1996) 100;
(c) M. Scholl, S. Ding, C.W. Lee, R.H. Grubbs, Org. Lett. 1 (1999) 953;
(d) S.T. Nguyen, T.M. Trnka Chapter 1.6, in: R.H. Grubbs (Ed.), Handbook of Metathesis, vol. 1, Wiley-VCH, Weinheim, 2003, p. 61.
[4] E.B. Bauer, J.A. Gladysz Chapter 2.11, in: R.H. Grubbs (Ed.), Handbook of Metathesis, vol. 2, Wiley-VCH, Weinheim, 2003, p. 403.
[5] Examples of Enantio-/Diastereo-Selective Preparation of Chiral Metallocenes:
(a) A.J. Locke, C. Jones, C.J. Richards, J. Organomet. Chem. 637–639 (2001) 669;
(b) M. Ogasawara, T. Nagano, T. Hayashi, J. Am. Chem. Soc 124 (2002) 9068, J. Am. Chem. Soc. 124 (2002) 12626;
(c) M. Ogasawara, S. Watanabe, L. Fan, K. Nakajima, T. Takahashi, Organometallics 25 (2006) 5201;
(d) M. Ogasawara, S. Watanabe, K. Nakajima, T. Takahashi, Pure Appl. Chem. 80 (2008) 1109;
(e) M. Ogasawara, S. Watanabe, K. Nakajima, T. Takahashi, J. Am. Chem. Soc. 132 (2010) 2136.
[6] (a) L.-X. Dai, T. Tu, S.-L. You, W.-P. Deng, X.-L. Hou, Acc. Chem. Res. 36 (2003) 659;
(b) A. Togni, N. Bieler, U. Burckhardt, C. Knöllner, G. Pioda, R. Schneider, A. Schnyder, Pure Appl. Chem. 71 (1999) 1531;
(c) M.F. Semmelhack, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 12, Elsevier Science, Oxford, 1995, p. 979;
(d) M.F. Semmelhack, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 12, Elsevier Science, Oxford, 1995, p. 1017;
(e) S.G. Davies, T.D. McCarthy, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 12, Elsevier Science, Oxford, 1995, p. 1039;
(f) H.-G. Schmalz, S. Siegel, in: C. Bolm, M. Beller (Eds.), Transition Metals for Fine Chemicals and Organic Synthesis, vol. 1, VCH, Weinheim, 1998, p. 550;
(g) K.P. Kaliappan, E.P. Kündig, Chem. Rev. 100 (2000) 2917;
(h) E.P. Kündig (Ed.), Transition Metal Arene π-Complexes in Organic Synthesis and Catalysis, Topics in Organometallic Chemistry, vol. 7, Springer, Berlin, 2004, pp. 21–30.
[7] (a) A.N. Nesmeyanov, V.V. Krivykh, P.V. Petrovskii, M.I. Rybinskaya, Dokl. Akad. Nauk SSSR 231 (1976) 110;
(b) A.N. Nesmeyanov, V.V. Krivykh, M.I. Rybinskaya, Dokl. Akad. Nauk SSSR 239 (1978) 1363;
(c) A.N. Nesmeyanov, Y.T. Struchkov, V.G. Andrianov, V.V. Krivykh, M.I. Rybinskaya, J. Organomet. Chem. 164 (1979) 51;
(d) A.N. Nesmeyanov, V.V. Krivykh, G.A. Panosyan, P.V. Petrovskii, M.I. Rybinskaya, J. Organomet. Chem. 164 (1979) 159;
(e) A.N. Nesmeyanov, V.V. Krivykh, M.I. Rybinskaya, J. Organomet. Chem. 164 (1979) 167;
(f) A.N. Nesmeyanov, Y.T. Struchkov, V.G. Andrianov, V.V. Krivykh, M.I. Rybinskaya, J. Organomet. Chem. 166 (1979) 211;
(g) W.R. Jackson, I.D. Rae, M.G. Wong, Aust. J. Chem. 37 (1984) 1563;
(h) W.R. Jackson, I.D. Rae, M.G. Wong, Aust. J. Chem. 39 (1986) 303.
[8] B.C. Maity, V.M. Swamy, A. Sarkar, Tetrahedron Lett. 42 (2001) 4373.
[9] W. Strohmeier, H. Hellmann, Chem. Ber. 63 (1963) 2859.
[10] (a) S.E. Lehman Jr., J.E. Schwendeman, P.M. O'Donnell, K.B. Wagener, Inorg. Chim. Acta 345 (2003) 190;
(b) B. Schmidt, Eur. J. Org. Chem. (2004) 1865.
[11] The formation of propene could not be detected due to the low yield (5%) of **2a**.
[12] J. Geicke, I.-P. Lorenz, K. Polborn, Inorg. Chim. Acta 272 (1998) 101.
[13] D.R. Lane, C.M. Beavers, M.M. Olmstead, N.E. Schore, Organometallics 28 (2009) 6789.
[14] Although this Possibility could not be Ruled Out, We Prefer the Explanation as the Kinetic Control, because the yields of [4]ferrocenophanes (from 1,1′-diallylferrocenes) are generally higher than those of [5]ferrocenophanes (from 1-allyl-1′-butenylferrocenes) in the analogous RCM reactions of producing the bridged ferrocenes. See: (a) M. Ogasawara, S. Watanabe, K. Nakajima, T. Takahashi, Organometallics 27 (2008) 6565;
(b) Ref. 5e.
[15] (a) M.D. Rausch, G.A. Moser, E.J. Zaiko, A.L. Lipman, J. Organomet. Chem. 23 (1970) 185;
(b) E.P. Kündig, C. Perret, S. Spichiger, G. Bernardinelli, J. Organomet. Chem. 286 (1985) 183;
(c) M.L.H. Green, M. Wagner, J. Chem. Soc. Dalton Trans. (1996) 2467.
[16] (a) T.M. Trnka, J.P. Morgan, M.S. Sanford, T.E. Wilhelm, M. Scholl, T.-L. Choi, S. Ding, M.D. Day, R.H. Grubbs, J. Am. Chem. Soc. 125 (2003) 2546;
(b) S.B. Garber, J.S. Kingsbury, B.L. Gray, A.H. Hoveyda, J. Am. Chem. Soc. 122 (2000) 8168.
[17] H.H. Fox, J.-K. Lee, L.Y. Park, R.R. Schrock, Organometallics 12 (1993) 759.