

## Oxidative addition reactions and stereochemistry on rhodium/4,5-bis(2-oxazoliny)xanthene complexes

Hirofumi Uchimura<sup>a</sup>, Jun-ichi Ito<sup>a</sup>, Seiji Iwasa<sup>b</sup>, Hisao Nishiyama<sup>a,\*</sup>

<sup>a</sup> Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Chikusa, Nagoya 464-8603, Japan

<sup>b</sup> School of Materials Science, Toyohashi University of Technology, Tempaku-cho, Toyohashi 441-8580, Japan

Received 22 February 2006; received in revised form 20 April 2006; accepted 24 April 2006

Available online 30 August 2006

### Abstract

The oxidative addition reactions on 4,5-bis(2-oxazoliny)-(2,7-di-*tert*-butyl-9,9-dimethyl)-9*H*-xanthene (Xabox)/rhodium(I) complex were examined using chloroacetate and substituted diynes to give stereoselectively the corresponding methoxycarbonylmethyl-rhodium(III) complex and rhodacyclopentadiene complexes, respectively. The rhodacycle complex **7** catalyzed the cyclotrimerization of the diynes and alkynes to give arene derivatives.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Oxazoline; *N,O,N*-Ligand; Rhodacycle; Rhodium

### 1. Introduction

Attention has been focused on xanthene skeleton as a new ligand motif, providing a variety of bidentate P,P-system with larger bite-angles; for example, Xantphos [1]. Since Haenel et al. reported 9,9-dimethyl-4,5-bis(diphenylphosphino)-xanthene as a bidentate phosphine ligand, many analogues have been synthesized and applied to catalytic reactions such as hydroformylation, cross-coupling reaction, amination reactions, and so on [2]. Other xanthene–bidentate system of P,N and N,N were also prepared for asymmetric palladium-catalyzed allylation [3], and bis(amidinato)xanthene *N,N*-ligand was clarified about coordination profiles [4]. Most of the xanthene-based ligands so far reported act as a bidentate ligand, so that the center oxygen atoms are not incorporated into the coordination. In this context, 4,5-bis(2-oxazoliny)dibenzofuran (DBFOX) can play as a tridentate *N,O,N*-ligand in a meridional manner [5]. In this report, we disclose a new

type of xanthene-based *N,O,N*-ligand, 4,5-bis(2-oxazoliny)xanthene (Xabox) with a facial configuration and its rhodium complexes obtained by stereoselective oxidative additions with chloroacetate and diynes. In this context, we have already reported chiral Xabox derivatives and the application for the asymmetric catalytic 1,3-dipolar cycloaddition of nitrones and enones with nickel-salt catalysts [6] (Chart 1).

### 2. Results and discussion

#### 2.1. Synthesis of Xabox and $RhCl_3(Xabox)$

The ligand Xabox **2** was readily synthesized in three steps by chlorination of a commercially available xanthene dicarboxylic acid **1** in thionyl chloride, condensation with 2-aminethanol, and oxazoline formation with methanesulfonyl chloride and triethylamine (Scheme 1). Treatment of Xabox with rhodium trichloride in an ethanol solution at 60 °C gave  $RhCl_3(Xabox)$  (**3**) in 95% yield. On the basis of <sup>1</sup>H NMR analysis, the proton signal of dimethyl groups on the xanthene skeleton appears as two singlets at 1.64 (3H) and 1.90 (3H) ppm, respectively. In

\* Corresponding author. Fax: +81 52 789 3209.

E-mail address: [hnishi@apchem.nagoya-u.ac.jp](mailto:hnishi@apchem.nagoya-u.ac.jp) (H. Nishiyama).

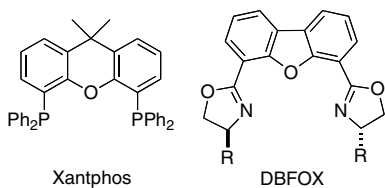


Chart 1.

addition, the protons of the oxazoline rings appear as four sets of multiplet signals. The complex **3** should therefore be concluded to have a facial configuration of Xabox (Scheme 2).

### 2.2. Oxidative addition of chloroacetate

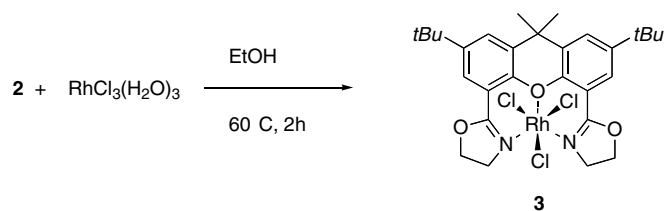
We have already found an oxidative addition of organohalides, such as dichloromethane, chloroform, and chloroacetate, to an in situ generated Rh(I)–nitrogen ligand adduct to form stable Rh(III) alkyl complexes [7]. Therefore, in order to study stereochemistry around the facial circumstance of Xabox in an oxidative addition reaction, we examined the reaction of in situ generated Rh(I)–Xabox complex. We could not confirm an exact structure of the in situ complex, facial-tridentate or bidentate coordination of Xabox on the rhodium species, by NMR analysis of a mixture of Rh(I)Cl(COE)<sub>2</sub>/2 (COE = cyclooctene) and Xabox, because of the complicated signals. We then examined the subsequent reaction with organic halides. Although the reaction of RhCl(COE)<sub>2</sub>/2 and Xabox with dichloromethane did not give **4**, the reaction with methyl chloroacetate (excess) in THF proceeded smoothly to give a sole product (70% yield), which proved to be  $\sigma$ -symmetric on the basis of NMR study. Therefore, it is assumed that the methoxycarbonylmethyl group appears at *trans* position toward the oxygen atom of the xanthene skeleton;  $\delta$  6.79 (d,  $J_{\text{Rh-C}} = 28.0$  Hz, Rh–CH<sub>2</sub>CO<sub>2</sub>Me). Thus, we have found the stereoselective oxidative addition on the facial system. The alkyl complex **5** is thermally stable compound (Scheme 3).

### 2.3. Metallacycle formation

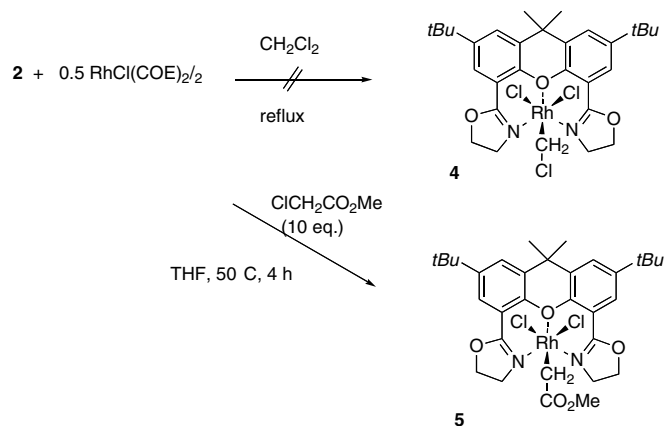
We previously found metallacycle formation by the reaction of diynes and an in situ generated Rh(I)–nitrogen ligand adduct [8]. In order to study stereochemistry around

the facial circumstance of Xabox in the metallacycle formation, we examined the reaction of in situ generated Rh(I)–Xabox complex and the symmetric diyne dimethyl ester **6** (Scheme 4). The reaction proceeded smoothly at 30 °C for 24 h to give the adduct **7** in 73% yield. The structure proved to be not  $\sigma$ -symmetric, because the protons of dimethyl ester groups appear at  $\delta$  3.08 (s, 3H) and 3.78 (s, 3H) ppm, respectively. Thus, the proton signal of one methyl group shows high-magnetic field shift, probably because of anisotropic effect by the xanthene ring. The facial structure of **7** could be unambiguously confirmed by X-ray analysis (Fig. 1). The bond lengths of Rh–C31 and Rh–C36 are 1.984 and 2.009 Å, respectively, and that of Rh–O is 2.363 Å (Table 1). The Rh–C bond *trans* to the Xabox–oxygen atom is a little shorter than that of *trans* to the Xabox–nitrogen atom.

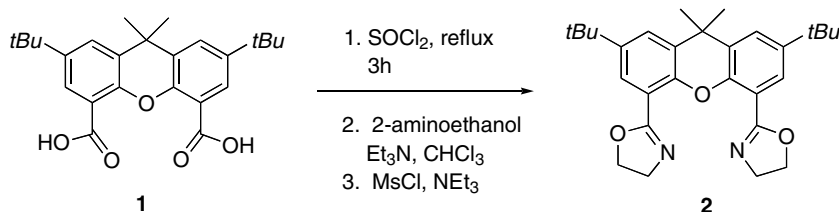
Next, the use of the unsymmetrical diyne **8** also afforded a sole product **9** in 66% yield. As the proton signal of the methyl group appears at higher magnetic field,  $\delta$  3.05 (s,



Scheme 2.



Scheme 3.



Scheme 1.

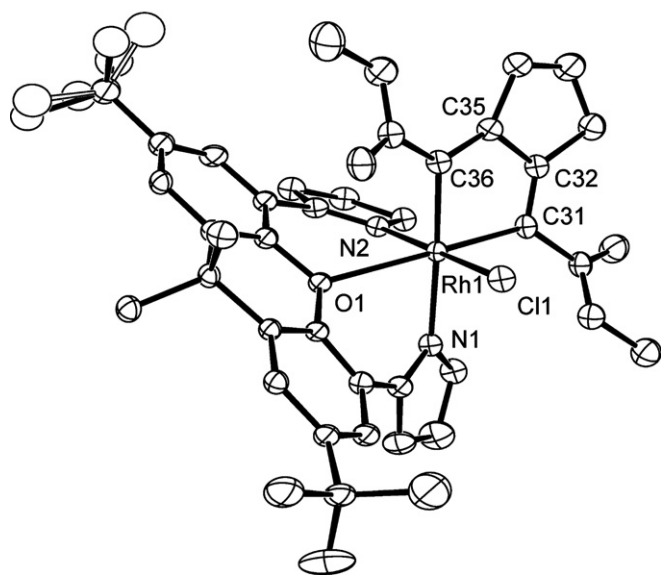
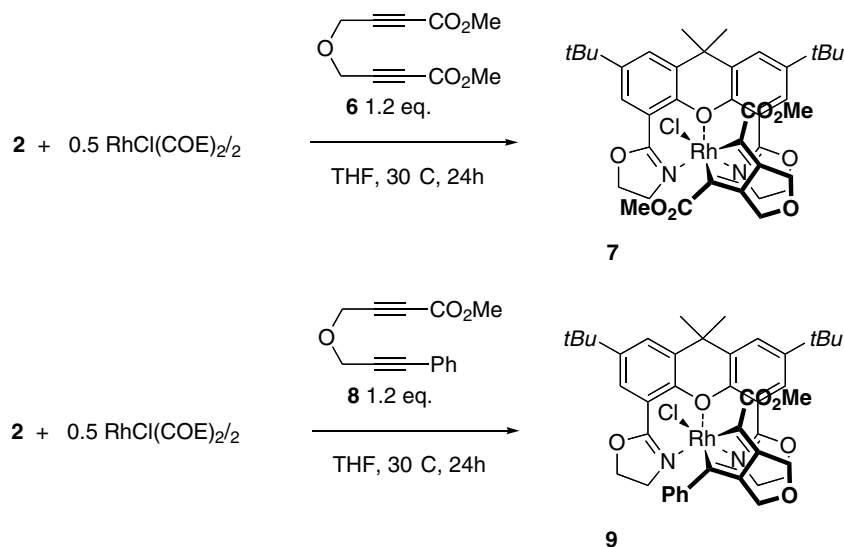


Fig. 1. The molecular structure of molecule A in 7 shown with 40% probability ellipsoids.

3H) ppm, the complex may have the structure that the PhC group appears at the *trans* position toward the oxygen atom of the xanthene skeleton.

#### 2.4. Cyclotrimerization with the complex 7 as a catalyst

The diynes **6** and **11** were subjected to a cyclotrimerization with phenylacetylene in the presence of the complex **7** (5 mol%) as a catalyst, respectively (Scheme 5). The reaction of **6** proceeded smoothly at 80 °C to give the adduct **10** in 86% yield. The monoester **11** similarly gave the adduct of the regio-isomers **12a** and **12b** in the ratio of 60:40 in 58% yield. Thus, the metallacycle complex proved to be active for the cyclization reaction.

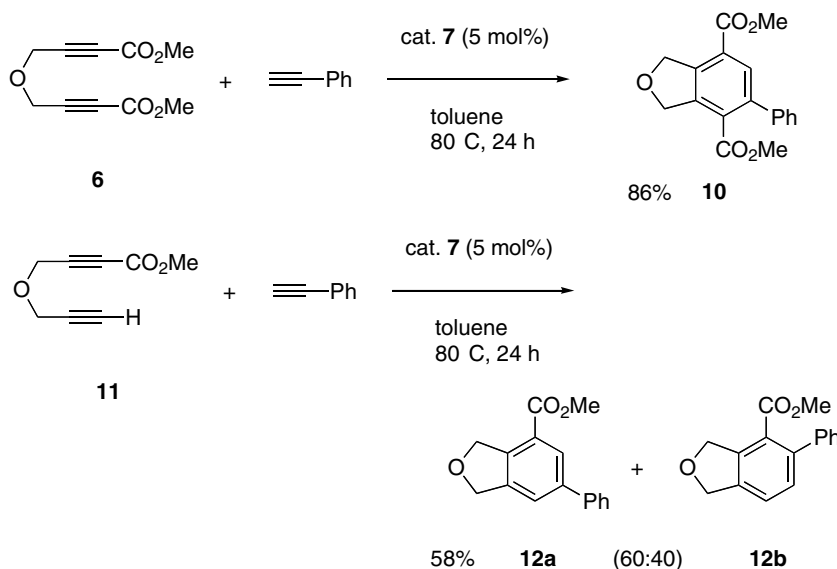
Table 1  
Selected bond distances (Å) and bond angles (°) for 7

Molecule A			
Rh1–Cl1	2.3294(10)	N2–Rh1–N1	90.96(13)
Rh1–N1	2.172(3)	N2–Rh1–O1	78.79(11)
Rh1–N2	2.045(3)	N1–Rh1–O1	76.27(11)
Rh1–O1	2.363(3)	N2–Rh1–Cl1	174.53(10)
Rh1–C31	1.984(4)	N1–Rh1–Cl1	91.49(9)
Rh1–C36	2.009(4)	C31–Rh1–C36	80.78(17)
C31–C32	1.354(6)	C32–C31–Rh1	113.7(3)
C32–C35	1.441(6)	C31–C32–C35	116.2(4)
C35–C36	1.365(6)	C36–C35–C32	113.7(4)
		C36–C35–Rh1	114.0(3)
Molecule B			
Rh2–Cl2	2.3267(10)	N4–Rh2–N3	90.38(13)
Rh2–N3	2.179(3)	N4–Rh2–O9	79.46(11)
Rh2–N4	2.032(3)	N3–Rh2–O9	76.90(12)
Rh2–O9	2.311(3)	N4–Rh2–Cl2	176.05(10)
Rh2–C70	1.995(4)	N3–Rh2–Cl2	87.75(9)
Rh2–C75	2.024(4)	C70–Rh2–C75	81.27(18)
C70–C71	1.363(6)	C71–C70–Rh2	113.5(3)
C71–C74	1.442(7)	C70–C71–C74	115.8(4)
C74–C75	1.350(7)	C75–C74–C71	115.5(4)
		C74–C75–Rh2	113.3(3)

### 3. Experimental

#### 3.1. General comments

<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained at 25 °C on a Varian Mercury 300 spectrometer. <sup>1</sup>H NMR chemical shifts are reported in δ units, in ppm relative to the singlet at 7.26 ppm for chloroform. <sup>13</sup>C NMR spectra are reported in terms of chemical shift (δ, ppm) relative to the triplet at δ = 77.0 ppm for CDCl<sub>3</sub> as an internal standard. Infrared spectra were recorded on a JASCO FT/IR-230 spectrometer. Absolute toluene and THF were purchased from TCI. Column chromatography was performed with a silica gel



Scheme 5.

column (Merck Silica gel 60). 2,7-Di-*tert*-butyl-9,9-dimethylxanthene-4,5-dicarboxylic acid was purchased from Aldrich.

### 3.2. Synthesis of ligand and complexes

#### 3.2.1. Xabox (**2**)

A mixture of the xanthene dicarboxylic acid **1** (1.04 g, 2.54 mmol) and thionyl chloride (10 mL) was refluxed for 3 h. Thionyl chloride was removed under reduced pressure to give the acid chloride as a white solid. A  $\text{CHCl}_3$  (20 mL) solution of the acid chloride was then added to the solution of 2-aminoethanol (448 mg, 7.33 mmol) and triethylamine (2.1 mL) in  $\text{CHCl}_3$  (15 mL). The mixture was stirred for 12 h at room temperature. After concentration of the solvent, the residue was purified by silica-gel column chromatography (hexane/ethyl acetate then  $\text{CH}_2\text{Cl}_2$ /methanol as eluent) to give the xanthene diamide of 1.20 g (2.42 mmol, 95%) as white solid; TLC,  $R_f = 0.53$  (ethyl acetate/methanol = 10:1); m.p. 200–201 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.35 (s, 18H), 1.66 (s, 6H), 2.95 (bs, 2H), 3.71 (dd,  $J = 4.8, 5.1$  Hz, 4H), 3.87 (dd,  $J = 4.8, 5.1$  Hz, 4H), 7.56 (d,  $J = 2.4$  Hz, 2H), 7.76 (d,  $J = 2.4$  Hz, 2H), 7.74–7.82 (m, 2H) ppm.  $^{13}\text{C}$  NMR (75.5 Hz,  $\text{CDCl}_3$ ):  $\delta$  31.48 ( $\text{C}(\text{CH}_3)_3$ ), 34.57, 34.95, 55.30 (C–O), 67.48 (C–N), 116.36, 124.67, 125.82, 130.59, 145.21, 147.27, 163.81 (C=N) ppm. IR (KBr disk):  $\nu = 3342, 1642, 1533, 1433$   $\text{cm}^{-1}$ . Anal. Calc.  $\text{C}_{29}\text{H}_{40}\text{N}_2\text{O}_5$  requires: C, 70.13; H, 8.12; N, 5.64. Found: C, 70.10; H, 8.11; N, 5.55%.

To the solution of the xanthene diamide (1.20 g, 2.42 mmol) in dichloromethane (50 mL) was added triethylamine (3.4 mL) and then methanesulfonyl chloride (0.41 mL, 5.32 mmol). The mixture was stirred for 2 h at room temperature. The mixture was poured into aq  $\text{K}_2\text{CO}_3$  solution (2 N) at 0 °C, and was extracted with dichloromethane. After the organic layer was dried over

$\text{Na}_2\text{SO}_4$  and concentrated, the residue was purified by recrystallization with dichloromethane and ether to give the xanthene bisoxazoline (Xabox) **2** (940 mg, 2.04 mmol) in 84% yield (total yield, 80%) as white solid; m.p. > 300 °C.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.33 (s, 18H), 1.63 (s, 6H), 4.12 (dd,  $J = 4.6, 9.3$  Hz, 4H), 4.49 (dd,  $J = 4.6, 9.3$  Hz, 4H), 7.50 (d,  $J = 2.5$  Hz, 2H), 7.61 (d,  $J = 2.5$  Hz, 2H) ppm.

$^{13}\text{C}$  NMR (75.5 Hz,  $\text{CDCl}_3$ ):  $\delta$  31.54 ( $\text{C}(\text{CH}_3)_3$ ), 32.73 ( $\text{C}(\text{CH}_3)_2$ ), 34.72, 34.79, 43.43 (O–C), 62.65 (N–C), 121.48, 125.48, 126.08, 130.08, 145.64, 146.15, 167.70 (C=N) ppm. IR (KBr disk):  $\nu = 1655, 1450, 1360$   $\text{cm}^{-1}$ . Anal. Calc.  $\text{C}_{29}\text{H}_{36}\text{N}_2\text{O}_3$  requires: C, 75.62; H, 7.88; N, 6.08. Found: C, 75.69; H, 7.82; N, 6.13%.

#### 3.2.2. $\text{RhCl}_3$ (Xabox) (**3**)

A mixture of Xabox (**2**) (448 mg, 0.12 mmol) and  $\text{RhCl}_3(\text{H}_2\text{O})_3$  (35.8 mg, 0.12 mmol) in ethanol was stirred for 2 h at 60 °C to give orange precipitate, which was filtered and washed with hexane and ether. The solid was dried under reduced pressure to give the complex **3** (68.5 mg, 0.10 mmol) in 85% yield; orange solid, m.p. > 300 °C; lower solubility in  $\text{CDCl}_3$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.34 (s, 18H), 1.64 (s, 3H), 1.90 (s, 3H), 4.15 (m, 2H), 4.78 (m, 2H), 4.80 (m, 2H), 5.05 (m, 2H), 7.63 (d,  $J = 2.3$  Hz, 2H), 7.82 (d,  $J = 2.3$  Hz, 2H) ppm. IR (KBr disk):  $\nu = 1612, 1467, 1375$   $\text{cm}^{-1}$ . Anal. Calc.  $\text{C}_{29}\text{H}_{36}\text{N}_2\text{O}_3$  requires: C, 52.00; H, 5.42; N, 4.18. Found: C, 51.90; H, 5.53; N, 4.19%.

#### 3.2.3. $\text{RhCl}_2$ (Xabox)( $\text{CH}_2\text{CO}_2\text{Me}$ ) (**5**)

To a mixture of Xabox (36.8 mg, 0.08 mmol) and  $[\text{RhCl}(\text{COE})_2]_2$  (28.7 mg, 0.04 mmol) in THF (1 mL) was added methyl chloroacetate (0.07 mL, 0.80 mmol). The mixture was stirred for 4 h at 50 °C. After concentration,

the residue was purified by silica-gel column chromatography ( $\text{CH}_2\text{Cl}_2/\text{MeOH} = 100:1-100:5$  as eluent) to give the complex **5** (39.4 mg, 0.056 mmol) in 70% yield as yellow solid; dec. 250 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.33 (s, 18H), 1.63 (s, 3H), 1.92 (s, 3H), 3.60 (s, 3H), 3.94 (d,  $J = 3.6$  Hz, 2H), 3.98–4.06 (m, 2H), 4.60 (m, 2H), 4.71–3.79 (m, 4H), 7.66 (d, 2.1 Hz, 2H), 7.75 (d,  $J = 2.4$  Hz, 2H) ppm.  $^{13}\text{C}$  NMR (75.5 Hz,  $\text{CDCl}_3$ ):  $\delta$  6.79 (d,  $J = 28.0$  Hz,  $\text{CH}_2\text{-Rh}$ ), 22.71, 31.41 ( $\text{C}(\text{CH}_3)_3$ ), 32.21, 34.96, 36.09, 50.89 ( $\text{CH}_3\text{-O}$ ), 55.04 ( $\text{CH}_2\text{-O}$ ), 67.31 ( $\text{CH}_2\text{-N}$ ), 114.29, 125.72, 126.10, 134.64, 147.99, 148.44, 163.70 ( $\text{C}=\text{N}$ ), 183.45 (d,  $J = 3.1$  Hz,  $\text{Rh-C-CO}$ ) ppm. IR (KBr disk):  $\nu = 1690, 1626, 1449\text{ cm}^{-1}$ . Anal. Calc.  $\text{C}_{32}\text{H}_{41}\text{Cl}_2\text{N}_2\text{O}_5\text{Rh}$  requires: C, 54.32; H, 5.84; 3.96. Found: C, 54.30; H, 5.85; N, 3.90%.

### 3.2.4. $\text{RhCl}(\text{Xabox})(\text{C}_{10}\text{H}_{10}\text{O}_5)$ (**7**)

A mixture of Xabox (23.1 mg, 0.05 mmol) and  $[\text{RhCl}(\text{COE})_2]_2$  (17.9 mg, 0.025 mmol), and the diyne **6** (10.7 mg, 0.051 mmol) in THF (2 mL) was stirred for 24 h at 30 °C. After concentration, the residue was purified by silica-gel column chromatography ( $\text{CH}_2\text{Cl}_2/\text{MeOH} = 100:1-100:5$  as eluent) to give the complex **7** (29.7 mg, 0.0367 mmol) in 73% yield as orange solid; dec. 204 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.31 (s, 3H), 1.33 (s, 15H), 1.75 (s, 3H), 1.90 (s, 3H), 3.08 (s, 3H), 3.78 (s, 3H), 3.83–3.96 (m, 2H), 4.08–4.20 (m, 1H), 4.25–4.90 (m, 10H), 7.61 (d,  $J = 2.4$  Hz, 1H), 7.62 (d,  $J = 2.4$  Hz, 1H), 7.65 (d,  $J = 2.4$  Hz, 1H), 7.68 (d,  $J = 2.4$  Hz, 1H), 7.72 (d,  $J = 2.4$  Hz, 1H) ppm.  $^{13}\text{C}$  NMR (75.5 Hz,  $\text{CDCl}_3$ ):  $\delta$  30.22, 31.29 ( $\text{C}(\text{CH}_3)_3$ ), 31.30 ( $\text{C}(\text{CH}_3)_3$ ), 32.74, 34.65, 34.69, 35.44, 50.15 ( $\text{CH}_3\text{-O}$ ), 50.99 ( $\text{CH}_3\text{-O}$ ), 55.86 ( $\text{CH}_2\text{-O}$ ), 56.89 ( $\text{CH}_2\text{-O}$ ), 67.10, 67.22, 69.85, 69.58, 70.04, 70.48, 112.46, 115.43, 125.24, 126.11, 126.86, 128.16, 131.44, 132.00, 132.73, 134.35, 145.93, 146.37, 146.49, 146.59, 147.05, 148.73, 149.16, 163.30 (d,  $\text{C}=\text{N}$ ), 166.42 ( $\text{C}=\text{N}$ ), 168.8 ( $\text{C}=\text{O}$ ), 169.3 ( $\text{C}=\text{O}$ ) ppm. IR (KBr disk):  $\nu = 1662, 1453, 1378\text{ cm}^{-1}$ . Anal. Calc.  $\text{C}_{39}\text{H}_{46}\text{ClN}_2\text{O}_8\text{Rh}$  requires: C, 57.89; H, 5.73; 3.46. Found: C, 57.90; H, 5.88; N, 3.38%.

### 3.2.5. $\text{RhCl}(\text{Xabox})(\text{C}_{14}\text{H}_{12}\text{O}_3)$ (**9**)

A mixture of Xabox (46.1 mg, 0.10 mmol) and  $[\text{RhCl}(\text{COE})_2]_2$  (35.9 mg, 0.050 mmol), and the diyne **6** (27.4 mg, 0.12 mmol) in THF (2 mL) was stirred for 24 h at 30 °C. After concentration, the residue was purified by silica-gel column chromatography ( $\text{CH}_2\text{Cl}_2/\text{MeOH} = 100:1-100:5$  as eluent) to give the complex **7** (29.7 mg, 0.0367 mmol) in 73% yield as orange solid; dec. 240 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.34 (s, 9H), 1.35 (s, 9H), 1.80 (s, 3H), 1.87 (s, 3H), 2.73 (ddd,  $J = 3.3, 9.6, 12.6$  Hz, 1H), 3.05 (s, 3H), 3.28 (ddd,  $J = 3.3, 12.9, 13.2$  Hz, 1H), 3.73–3.92 (m, 2H), 4.23–4.46 (m, 4H), 4.61–4.84 (m, 4H), 7.21–7.32 (m, 3H), 7.61–7.66 (m, 3H), 7.69–7.72 (m, 3H).  $^{13}\text{C}$  NMR (75.5 Hz,  $\text{CDCl}_3$ ):  $\delta$  28.99, 31.39 ( $\text{C}(\text{CH}_3)_3$ ), 32.92, 34.75, 35.62, 50.05 ( $\text{CH}_3\text{-O}$ ), 54.83 ( $\text{CH}_2\text{-O}$ ), 57.10 ( $\text{CH}_2\text{-O}$ ), 65.08, 66.84 ( $\text{CH}_2\text{-N}$ ), 67.17 ( $\text{CH}_2\text{-N}$ ), 70.82,

112.89, 115.47, 125.33, 125.95, 126.94, 127.78, 128.07, 132.54, 132.77, 146.03, 146.45, 147.00, 147.05, 149.75, 152.04 (d,  $J = 38.1$  Hz), 153.47, 162.94 ( $\text{C}=\text{N}$ ), 163.66 ( $\text{C}=\text{N}$ ), 169.34, 169.84 ppm. IR (KBr disk):  $\nu = 1632, 1457, 1228\text{ cm}^{-1}$ . Anal. Calc.  $\text{C}_{43}\text{H}_{48}\text{ClN}_2\text{O}_6\text{Rh}$  requires: C, 62.43; H, 5.58; 3.39. Found: C, 62.44; H, 5.90; N, 3.44%.

### 3.3. X-ray analysis of **7**

Single crystals of **7** for X-ray analysis were obtained from slow diffusion of a  $\text{CH}_2\text{Cl}_2$  solution into hexane at room temperature. A crystal was mounted on a glass fiber, and diffraction data were collected in  $\theta$  ranges at 173 K with a Bruker SMART APEX CCD diffractometer with graphite-monochromated  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ). Data were collected on 1321 oscillation images with oscillation range of 0.3°. Cell refinement and data reduction were performed using the SAINTPLUS program package. Intensity data were corrected for Lorentz-polarization effects and an empirical absorption. The structure was solved by the Patterson method and refined by full-matrix least-square on  $F^2$  by using the SHELXTL program package. The  $^t\text{Bu}$  groups attached to C(10) and C(43) are disordered over two positions, which were refined in the ratio of 60:40 and 53:47, respectively. The hydrogen atoms were included in calculated positions and refined by using a riding mode. The crystallographic data and refinement parameters were summarized in Table 2. Crystallographic data for the structural analyses has been deposited with the Cambridge Crystallographic Data Centre; CCDC No. 299102. Copies of this information may be obtained free

Table 2  
Crystallographic data and refinement parameters for **7**

Empirical formula	$\text{C}_{39}\text{H}_{46}\text{Cl}_5\text{N}_2\text{O}_8\text{Rh}$
Formula weight	950.94
Crystal color, habit, dimension (mm)	Yellow, prism, $0.4 \times 0.2 \times 0.2$
Crystal system	Triclinic
Space group	$P\bar{1}$ (#2)
$a$ (Å)	13.9108(16)
$b$ (Å)	14.0766(17)
$c$ (Å)	23.962(3)
$\alpha$ (°)	94.404(3)
$\beta$ (°)	99.211(2)
$\gamma$ (°)	99.991(3)
$V$ (Å <sup>3</sup> )	4535.0(9)
$Z$	4
$D_{\text{calcd}}$ (g cm <sup>-3</sup> )	1.393
$\mu$ (mm <sup>-1</sup> )	0.719
Temperature (K)	153(2)
$2\theta_{\text{max}}$ (°)	55
Max/min transmission	1.000000/0.573353
No. total of reflections measured	32,574
No. of unique data	20,718
No. of observed ( $I > 2\sigma(I)$ )	15,584
$R_1$ ( $I > 2\sigma(I)$ )	0.0620
$wR_2$ ( $I > 2\sigma(I)$ )	0.1609
$R_1$ (all data)	0.0845
$wR_2$ (all data)	0.1763
Parameters/restraints	1037/0
Goodness of fit	1.037

of the charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1 EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk. or <http://www.ccdc.cam.ac.uk>).

### 3.4. Cyclotrimerization reaction

The reaction was performed with the diyne (0.2 mmol), phenylacetylene (1.6 mmol), and the catalyst **7** (5 mol%, 8 mg) in toluene (2 mL) at 80 °C for 24 h. After concentration of the solvent, the residue was purified by silica-gel column chromatography (hexane/ethyl acetate as eluent) to give the corresponding dihydroisobenzofuran derivatives **10** and **12**, respectively; for spectroscopic analysis, see Supporting information of Ref. [8].

### Acknowledgements

H.N. gratefully acknowledges financial supports from the Ministry of Education, Culture, Sports, Science and Technology, Japan (Reaction Control of Dynamic Complexes, No. 420) and DAIKO Foundation.

### References

- [1] (a) P.C.J. Kamer, P.W.N.M. van Leeuwen, J.N.H. Reek, *Acc. Chem. Res.* 34 (2001) 895; (b) P.W.N.M. van Leeuwen, P.C.J. Kamer, J.N.H. Reek, *Pure Appl. Chem.* 71 (1999) 1443.
- [2] (a) S. Hillebrand, J. Bruckmann, C. Krüger, M.W. Haenel, *Tetrahedron Lett.* 36 (1995) 75; (b) M. Kranenburg, Y.E.M. van der Burgt, P.C.J. Kamer, P.W.N.M. van Leeuwen, K. Goubitz, J. Fraanje, *Organometallics* 14 (1995) 3081; (c) C. Botteghi, C. dei Ngri, S. Paganelli, M.J. Marchetti, *Mol. Catal. A: Chem.* 551 (1998) 165; (d) I.D. Rio, N. Ruiz, C. Claver, L. van der Veen, P.W.N.M. van Leeuwen, *J. Mol. Catal.* 161 (2000) 39; (e) M. Kranenburg, P.C.J. Kamer, P.W.N.M. van Leeuwen, *Eur. J. Inorg. Chem.* (1998) 155; (f) J. Yin, S.L. Buchwald, *Org. Lett.* 2 (2000) 1101; (g) K.W. Anderson, M. Mendez-Perez, J. Priego, S.L. Buchwald, *J. Org. Chem.* 68 (2003) 9563; (h) L. Yin, S.L. Buchwald, *J. Am. Chem. Soc.* 124 (2002) 124.
- [3] G. Malaisé, L. Barloy, J.A. Osborn, *Tetrahedron Lett.* 42 (2001) 7417.
- [4] J.R. Hagadorn, *Chem. Commun.* (2001) 2144.
- [5] S. Kanemasa, Y. Oderaotoshi, J. Tanaka, E. Wada, *J. Am. Chem. Soc.* 120 (1998) 12355.
- [6] S. Iwasa, Y. Ishima, H.S. Widagdo, K. Aoki, H. Nishiyama, *Tetrahedron Lett.* 45 (2004) 2121.
- [7] H. Nishiyama, M. Horihata, T. Hirai, S. Wakamatsu, K. Itoh, *Organometallics* 10 (1991) 2706; Related papers for tridentate N-ligand-Rh species: H.F. Haarman, J.M. Ernsting, M. Kranenburg, H. Kooijman, N. Veldman, A.L. Spec, P.W.N.M. van Leeuwen, K. Vrieze, *Organometallics* 16 (1997) 887; S. Nüchel, P. Burger, *Organometallics* 20 (2001) 4359.
- [8] H. Nishiyama, E. Niwa, T. Inoue, Y. Ishima, K. Aoki, *Organometallics* 21 (2002) 2572.