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Journal of Organometallic Chemistry 625 (2001) 133–139

Journal of Organometallic Chemistry

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Synthesis, structure and reactivities of the dinuclear μ-η^1:η^6-arylethynyl ruthenium complexes [Cp(PR$_3$)$_2$Ru(μ-η^1:η^6-C≡CC$_6$H$_4$Me-*p*)RuCp*]·Cl (R = Ph, Me; Cp = η^5-C$_5$H$_5$, Cp* = η^5-C$_5$Me$_5$). The molecular structure of [Cp(PPh$_3$)$_2$Ru(μ-η^1:η^6-C≡CC$_6$H$_4$Me-*p*)RuCp*]·PF$_6$

Hiroyuki Matsuzaka [a,*], Hironobu Okimura [a], Yoshiyuki Sato [a], Tomohiko Ishii [a], Masahiro Yamashita [a], Mitsuru Kondo [a,1], Susumu Kitagawa [1,a], Moto-o Shiro [b], Mikio Yamasaki [b]

[a] *Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Minami-osawa, Hachioji, Tokyo 192-0397, Japan*
[b] *X-ray Research Laboratory, Rigaku Corporation, 3-9-12 Matsubara-cho, Akishima, Tokyo 196-8666, Japan*

Received 6 July 2000; received in revised form 11 September 2000; accepted 13 September 2000

Abstract

Treatment of [Cp(PR$_3$)$_2$Ru(C≡CC$_6$H$_4$Me-*p*) (**1a**, R = Ph **1b**, R = Me; Cp = η^5-C$_5$H$_5$) with [Cp*Ru(μ$_3$·Cl)]$_4$ (Cp* = η^5-C$_5$Me$_5$) selectively produced the novel dinuclear μ-η^1:η^6- arylethynyl complex Cp(PR$_3$)$_2$Ru(μ-η^1:η^6-C≡CC$_6$H$_4$Me-*p*)RuCp*] (**2**·Cl: **2a**, R = Ph; **2b**, R = Me). Protonation of **2**·OTf (OTf = OSO$_2$CF$_3$) by TfOH afforded the corresponding vinylidene complex [Cp(PR$_3$)$_2$Ru(μ-η^1:η^6-C=CHC$_6$H$_4$Me-*p*)RuCp*]·[OTf]$_2$ (**3**·[OTf]$_2$: **3a**, R = Ph; **3b**, R = Me), which regenerated **2**·OTf upon treatment with LiBHEt$_3$. Reaction of **2a**·Cl with I$_2$ and subsequent anion metathesis with AgBF$_4$ produced the iodovinylidene complex [Cp(PPh$_3$)$_2$Ru(μ-η^1:η^6-C=CIC$_6$H$_4$Me-*p*)RuCp*]·[BF$_4$]$_2$ (**4**·[BF$_4$]$_2$), whereas similar treatment of **2b**·PF$_6$ yielded the iodo/arylethynyl complex [Cp(I)(PMe$_3$)$_2$Ru(μ-η^1:η^6-C≡CC$_6$H$_4$Me-*p*)RuCp*]·[PF$_6$]$_2$ (**5**·[PF$_6$]$_2$). Substitution of one of the PPh$_3$ ligands in **2a**·OTf proceeded under 1 atm of CO to form [Cp(PPh$_3$)(CO)Ru(μ-η^1:η^6-C≡CC$_6$H$_4$Me-*p*)RuCp*]·OTf (**6**·OTf). The molecular structure of **2a**·PF$_6$ was determined by X-ray crystallography.

Keywords: Dinuclear complexes; Ruthenium; Arylethynyl; Vinylidene; Iodovinylidene; X-ray crystal structures

1. Introduction

Reactions of arenes with organometallic species to form η^6-arene complexes have found numerous application in organic synthesis [1,2]. Recently transformation of the mononuclear η^6-arene compounds to the dinuclear μ-η^1:η^6-structures offers a new set of polynuclear complexes with σ,π-bridging ligands [3]. This process generally proceeds via initial lithiation of the coordinated arene and subsequent reaction with organometallic compounds having halogen ligands. Another general route involves treatment of η^6-haloarene complexes with anionic organometallic nucleophiles. We have previously reported alternative approach to the σ,π-bridging system containing a η^6-aryl group, which includes the reaction of a mononuclear arylethynyl complex Cp(PPh$_3$)$_2$Ru(C≡CC$_6$H$_4$Me-*p*) (**1a**; Cp = η^5-C$_5$H$_5$) with a precursor of a coordinatively unsaturated species [Cp*Ru(μ3-Cl)]$_4$ (Cp* = η^5-C$_5$Me$_5$) [4,5]. This type of reaction is expected to produce a new family of polynuclear complexes in which metal centers are joined by organic ligands with conjugated π-electron systems. Here we describe details on preparation and structure of the diruthenium μ-η^1:η^6-arylethynyl complex [Cp(PR$_3$)$_2$Ru(μ-η^1:η^6-C≡CC$_6$H$_4$Me-*p*)RuCp*]·

* Corresponding author. Fax: +81-426-772525.
E-mail address: matsuzaka-hiroyuki@c.metro-u.ac.jp (H. Matsuzaka).

[1] Present address: Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan.

0022-328X/01/$ - see front matter
PII: S0022-328X(00)00811-1

Cl (**2**·Cl: **2a**, R = Ph; **2b**, R = Me). Also reported are its reactions with electrophiles to form the corresponding dinuclear vinylidene, iodovinylidene, and iodo/ethynyl structures, as well as facile substitution of one of the PPh_3 ligands in **2a**·Cl with CO.

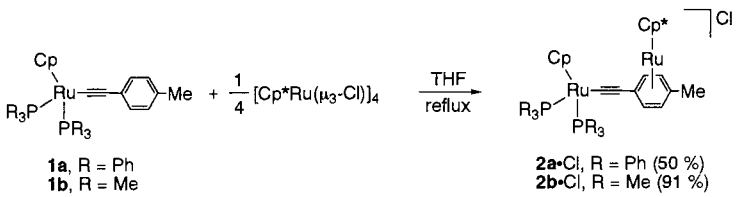
2. Results and discussion

2.1. Preparation and structure of the dinuclear μ-η^1:η^6-arylethynyl complex **2**·Cl

A dark red solution of a mixture of $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ and $Cp(PR_3)_2Ru(C{\equiv}CC_6H_4Me\text{-}p)$ (**1a**, R = Ph; **1b**, R = Me; molar ratio, 1:4) in refluxing THF gradually turned to a yellow–brown suspension. Work up of the reaction mixture resulted in the isolation of the novel dinuclear μ-η^1:η^6-arylethynyl complex $[Cp(PR_3)_2Ru(\mu\text{-}\eta^1{:}\eta^6\text{-}C{\equiv}CC_6H_4Me\text{-}p)RuCp^*]$·Cl (**2**·Cl: **2a**, R = Ph; **2b**, R = Me) in good yield, which was spectroscopically characterized (Eq. (1)). The molecular structure of **2a**·PF_6 was further determined by X-ray crystallography.

The ^{1}H-NMR spectrum of **2a**·Cl exhibits two singlets at δ 4.36 and 1.95 ppm assigned to the Cp and Cp* protons, respectively, together with the signals due to the PPh_3 and tolyl groups. Key to the structural assignment of **2a**·Cl is the characteristic resonances at δ 5.82 and 5.23 (2H each, $J = 6.1$ Hz) in ABq pattern due to the aryl protons of the μ-η^1:η^6-$C{\equiv}CC_6H_4Me$-*p* moiety, which appear significantly upfield compared to those of **1a**. Similar upfield shift was observed in the mononuclear η^6-arene complexes [1–3]. The IR spectrum of **2a**·Cl shows a $\nu_{C\equiv C}$ absorption at 2071 cm^{-1}, which is consistent with that observed for the parent arylethynyl complex **1a** (2068 cm^{-1}). The ^{1}H-NMR and IR spectra of **2b**·Cl are essentially similar to those for **2a**·Cl (see Section 3), and fully consistent with the crystal structure of **2a**·PF_6 (vide infra).

An ORTEP drawing of a cationic part of **2a**·PF_6 is given in Fig. 1, and pertinent crystallographic details are set out in Tables 1 and 2. Fig. 1 clearly shows the dinuclear structure of the **2a**$^+$ cation, where two Ru atoms are bridged by the $C{\equiv}CC_6H_4Me$-*p* group. Almost linear alkynyl moiety (Ru(1)–C(1)–C(2), 175.6(4)°; C(1)–C(2)–C(3), 174.8(5)°) terminally bound to the



(1)

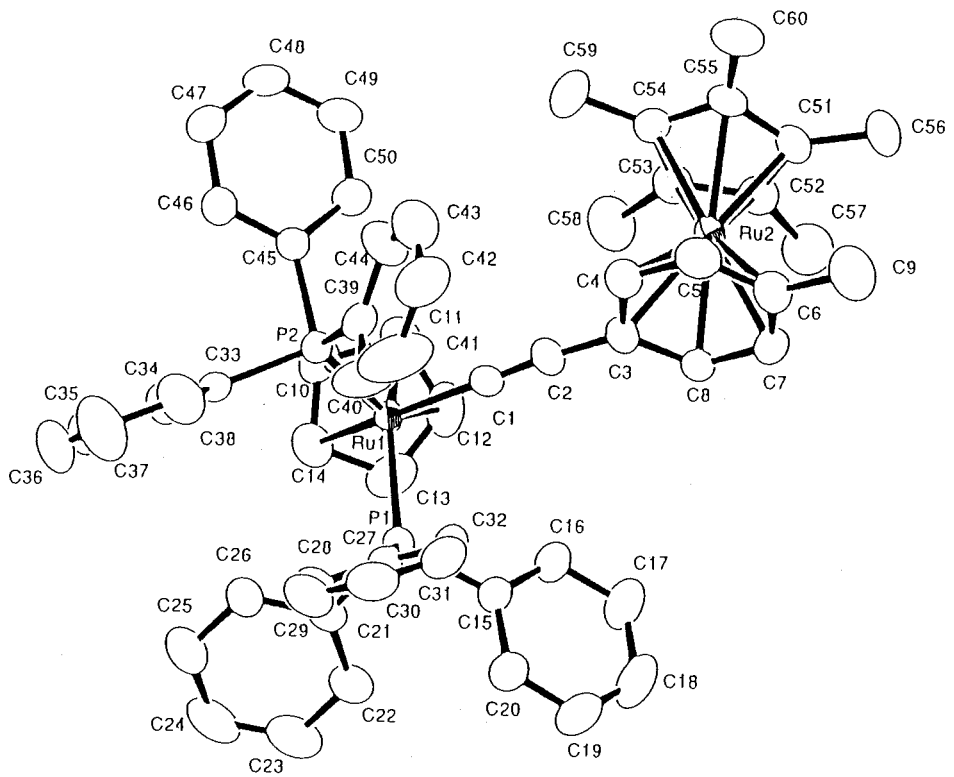
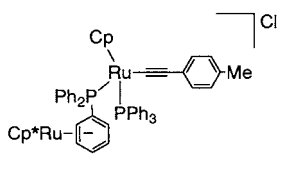


Fig. 1. Molecular structure of a cationic part of **2a**·PF_6 drawn at the 50% probability level.

Table 1
Crystal and data collection parameters for complexes **2a**·PF_6

Empirical formula	$C_{60}H_{57}F_6P_3Ru_2$	D_{calc} (gcm^{-3})	1.488
Formula weight	1187.16	$F(000)$ electrons	2416
Space group (crystal system)	$P2_1/n$ (monoclinic)	μ (Mo–K_α) calc. (cm^{-1})	7.21
Crystal color	Yellow	Crystal dimensions (mm)	$0.60 \times 0.30 \times 0.30$
a (Å)	14.7239(2)	Reflections measured	$+h, +k, \pm l$
b (Å)	18.5463(2)	Used data ($I > 3\sigma(I)$)	6978
c (Å)	20.0903(4)	Number of parameters refined	640
β (°)	104.9924(9)	R	0.042
Cell volume ($Å^3$)	5299.3	R_w	0.047
Z	4	Goodness-of-fit	3.25

'$Cp(PPh_3)_2Ru$' unit coordinates to the 'Cp^*Ru' fragment in a η^6-manner through its tolyl ring. The distance of carbon–carbon triple bond (C(l)–C(2), 1.200(6) Å) is apparently shorter than that reported for $Cp(PPh_3)_2Ru(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CPh)CuCl$ (1.242(13) Å) [6] or $CpRu(PMe_3)_2(\mu\text{-}\eta^1{:}\eta^6\text{-}C{\equiv}CH)WCp(CO)(\eta^2\text{-}PhC{\equiv}CPh)$ (1.25(2) Å) [7], and compares well to the values observed for terminal arylethynyl complexes such as $Cp(PPh_3)_2Ru(C{\equiv}CPh)$ (**1c**) (1.214(7) Å) [8] or Cp(dppe)Ru(C≡CPh) (1.204(5) Å) [9]. The intramolecular Ru···Ru distance of 6.36 Å clearly indicates the absence of bonding interaction between these two Ru atoms. The most characteristic feature of the structure of $\mathbf{2a}^+$ cation is that the arylethynyl ligand bridges two metal centers not in a common $\eta^1{:}\eta^2$-fashion, but in a $\eta^1{:}\eta^6$-manner, presumably due to the steric hinderance around the Ru atom in **1a**. The related $\mu\text{-}\eta^1{:}\eta^5$-cyclopentadienylethynyl complex $Cp(PPh_3)_2Ru(\mu\text{-}\eta^1{:}\eta^5\text{-}C{\equiv}CC_5H_4)MCp$ (M = Fe, Ru) was recently prepared by treatment of $Cp(PPh_3)_2RuCl$ with ferrocenyl- or ruthenocenylacetylene [10]. It is of interest to note that the tolyl unit in **2a**·Cl selectively coordinates to the Cp^*Ru^+ cation. Triphenylphospine has been known to serve as a η^6-arene ligand for the $CpRu^+$ fragment. Thus, heating $CpRu(PPh_3)_2Cl$ in ethylene glycol and subsequent addition of $NaBPh_4$ produced $[Cp(Cl)(PPh_3)Ru\{PPh_2(\eta^6\text{-}C_6H_5)\}RuCp]\cdot BPh_4$ and $[CpRu(\eta^6\text{-}C^6H^5)PPh_2]\cdot BPh_4$ [11]. On the other hand, complex **2a′**·Cl, the isomeric form of **2a**·Cl, was not detected in our case. The Cp^*Ru^+ cation is selectively bonded to the less sterically hindered arene unit



2a′·Cl

2.2. Reactivities of 2^+ with HOTf I_2, and CO

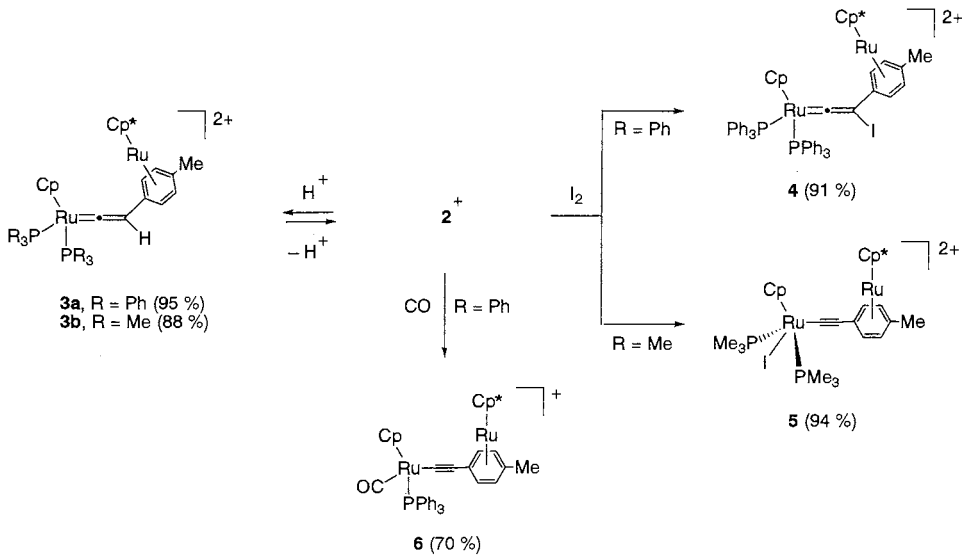
Protonation of **2**·OTf [12] with TfOH gave the corresponding dinuclear vinylidene complex $[Cp(PR_3)_2Ru(\mu\text{-}\eta^1{:}\eta^6\text{-}C{=}CHC_6H_4Me\text{-}p)RuCp^*]\cdot[OTf]_2$ (3·$[OTf]_2$: **3a**, R = Ph; **3b**, R = Me), which was isolated as orange plates in almost quantitative yield and spectroscopically characterized (Scheme 1). The ^{1}H-NMR spectrum of **3a**·$[OTf]_2$ shows a singlet at δ 5.02 due to the proton attached to the C^β of the vinylidene ligand. The $^{13}C\{^1H\}$-NMR spectrum exhibits a characteristic resonance at δ 346.0 assigned to the C^α of the vinylidene moiety. In its IR spectrum, a $\nu_{C=C}$ absorption appears at 1640 cm^{-1}. These spectral features are well consistent with the mononuclear vinylidene complexes derived from **1c** [13]. The spectral data of **3b**·$[OTf]_2$ are essentially similar to those of **3a**·$[OTf]_2$. Addition of $LiBHEt_3$ to a CH_2Cl_2 solution of **3**·$[OTf]_2$ did not yield the corresponding dinuclear alkenyl complex $[Cp(PR_3)_2Ru(\mu\text{-}\eta^1{:}\eta^6\text{-}CH{=}CHC_6H_4Me\text{-}p)RuCp^*]\cdot[OTf]$, but reproduced the parent **2**·OTf quantitatively. Similar deprotonation reaction was also observed with NaOMe.

Reaction of the $\mathbf{2}^+$ cation with I_2 smoothly proceeded to give two types of products depending on the PR_3 ligand. Thus, addition of I_2 to a CH_2Cl_2 solution of **2a**·Cl and subsequent anion metathesis with $AgBF_4$ yielded the dinuclear iodovinylidene complex $[Cp(PPh_3)_2Ru(\mu\text{-}\eta^1{:}\eta^6\text{-}C{=}ClC_6H_4Me\text{-}p)RuCp^*]\cdot[BF_4]_2$ (**4**·$[BF_4]_2$) [12], which was isolated as dark green blocks

Table 2
Selected bond distances and angles for **2a**·PF_6[a]

Distances (Å)			
Ru(l)–P(l)	2.297(l)	Ru(l)–P(2)	2.311(l)
Ru(l)–C(l)	1.997(4)	Ru(l)–C(10)	2.235(4)
Ru(l)–C(11)	2.230(5)	Ru(l)–C(12)	2.241(5)
Ru(l)–C(13)	2.236(4)	Ru(l)–C(14)	2.252(4)
Ru(2)–C(3)	2.272(4)	Ru(2)–C(4)	2.212(5)
Ru(2)–C(5)	2.203(5)	Ru(2)–C(6)	2.232(5)
Ru(2)–C(7)	2.206(5)	Ru(2)–C(8)	2.197(4)
C(l)–C(2)	1.200(6)	C(2)–C(3)	1.428(6)
Angles (°)			
P(1)–Ru(1)–P(2)	101.37(4)	P(1)–Ru(1)–C(1)	89.9(1)
P(2)–Ru(1)–C(1)	86.6(l)	Ru(1)–C(1)–C(2)	175.6(4)
C(1)–C(2)–C(3)	174.8(5)		

[a] Estimated standard deviations in the least significant figure are given in parentheses.



Scheme 1.

and spectroscopically characterized (Scheme 1). The $^{13}C\{^1H\}$-NMR spectrum of **4**·$[BF_4]_2$ exhibits a resonance at δ 345.8 due to the C^{α}, of the iodovinylidene unit, whereas its IR spectrum shows a $\nu_{C=C}$ band at 1617 cm^{-1}. On the other hand, similar treatment of **2b**·PF_6 [14] with I_2 and subsequent anion metathesis with $AgPF_6$ selectively afforded the dinuclear iodo/ethynyl complex $[Cp(I)(PMe_3)_2Ru(\mu\text{-}\eta^1\text{:}\eta^6\text{-}C{\equiv}CC_6H_4Me\text{-}p)RuCp^*]\cdot[PF_6]_2$ (**5**·$[PF_6]_2$), which was obtained as dark red plates and spectroscopically characterized (Scheme 1). The IR spectrum of **5**·$[PF_6]_2$ shows a $\nu_{C=C}$ absorption at 2114 cm^{-1}, which is consistent with that observed for **2b**·Cl (2052 cm^{-1}). The ^1H-NMR spectrum of **5**·$[PF_6]_2$ shows a characteristic signal for the PMe_3 protons at δ 2.34, while the Cp resonance is at the unusually low-field position of δ 6.13. The $^{31}P\{^1H\}$-NMR spectrum exhibits one peak at δ 12.37 assigned to PMe_3, which indicates that the two PMe_3 ligands occupy the mutually *trans* disposition as shown in Scheme 1. Similar oxidative transformation of the mononuclear Ru(II) complex bearing PMe_3 ligands was previously reported by Bruce et al. [15]. Thus, $Cp(PMe_3)_2RuCl$ reacts with Cl_2 in the presence of $[NH_4][PF_6]$ to give $[Cp(PMe_3)_2RuCl_2][PF_6]$, in which the two PMe_3 ligands are mutually *trans* to each other on the basis of the ^1H and $^{31}P\{^1H\}$-NMR criteria.

Substitution of one of the PPh_3 ligands in **2a**·OTf readily proceeded at room temperature (r.t.) under 1 atm of CO to give $[Cp(PPh_3)(CO)Ru(\mu\text{-}\eta^1\text{:}\eta^6\text{-}C{\equiv}CC_6H_4Me\text{-}p)]\cdot OTf$ (**6**·OTf), which was isolated as yellow needles and spectroscopically characterized (Scheme 1). The IR spectrum of **6**·OTf shows a ν_{CO} absorption at 1952 cm^{-1} together with a $\nu_{C=C}$ absorption at 2095 cm^{-1}. The ^1H-NMR spectrum of **6**·OTf exhibits a characteristic set of four doublets at δ 5.86, 5.42, 5.24 and 4.80 assigned to the aromatic protons of the tolyl group. The substitution reaction in **1c** to give $Cp(PPh_3)(CO)Ru(C{\equiv}CPh)$ (**7**) was reported to require much more forcing conditions (under 100 atm of CO at 105°C) [16]. We have also confirmed that the substitution process in **1c** proceeds quite slowly under 1 atm of CO at r.t., and a small amount of **7** was detected by IR analysis of the reaction mixture. It is noteworthy that the substitution reaction in **2a**·OTf occurs under extremely milder conditions compared to those for **1c**, which suggests that the Cp^*Ru^+ fragment attached to the arylethynyl unit in the $\mathbf{2a}^+$ cation sufficiently increases the steric hindrance around the Ru center bearing the two PPh_3 ligands and could facilitate this transformation. In sharp contrast, the corresponding substituted product was never detected during the reaction of **2b**·OTf with CO under similar conditions, from which **2b**·OTf was quantitatively recovered.

Further studies are in progress on preparation and properties of homo- and heterodinuclear complexes containing a $\mu\text{-}\eta^1\text{:}\eta^6$-arylethynyl or related unsaturated organic ligands with conjugated π-electron systems.

3. Experimental

Complexes **1a** [17] and **lb** [18] were prepared according to the published methods. The reagents HOTf, I_2, $LiBHEt_3$, and CO were obtained commercially and used without further purification. Solvents were dried by refluxing over Na–benzophenone ketyl (THF, hexane), CaH_2 (CH_2Cl_2), $Mg(OEt)_2$ (EtOH), or K_2CO_3 (acetone) and freshly distilled prior to use. All manipulations were performed with standard Schlenk tube techniques. IR spectra were recorded on a Hitachi I-5040 spectrometer. NMR spectra were obtained on a JEOL Lambda-506 spectrometer. Elemental analyses

were performed at Elemental Analysis Laboratory, Department of Chemistry, Tokyo Metropolitan University.

3.1. Preparation of [Cp(PPh$_3$)$_2$Ru(μ-η^1:η^6-C≡CC$_6$H$_4$Me-p)RuCp*]·Cl (**2a**·Cl)

To a THF (10 ml) suspension of [Cp*Ru([μ3-Cl)]$_4$ (0.337 g, 0.310 mmol) was added **1a** (1.00 g, 1.24 mmol) in THF (10 ml), and the mixture was refluxed for 2 days, during which time the original dark red solution turned to a yellow–brown suspension. After filtration, the resultant solid was extracted with CH_2Cl_2 (5 ml) and purified by chromatography on basic alumina. Elution with CH_2Cl_2 gave unreacted **1a**. A yellow band was successively obtained upon elution with EtOH–THF (3/7, v/v), from which **2a**·Cl was isolated as yellow plates (0.668 g, 50%) after evaporation of the solvent and recrystallization of the residue from CH_2Cl_2–hexane (3:5 ml). ^{1}H-NMR ($CDCl_3$) δ 7.36–7.09 (m, 30H, Ph), 5.82, 5.23 (d, 2H each, $J = 6.1$ Hz, C$_6$*H*$_4$Me), 4.36 (s, 5H, Cp), 2.25 (s, 3H, C$_6$H$_4$*Me*), 1.95 (s, 15H, Cp*). ^{13}C{^{1}H}-NMR ($CDCl_3$) δ 137.7, 137.4 (t, $J_{PC} = 21.9$ Hz, P*Ph*$_3$ (ipso)), 135.3 (t, $J_{PC} = 24.4$ Hz, Ru–C≡*C*C$_6$H$_4$Me), 133.0 (t, $J_{PC} = 5.6$ Hz, P*Ph*$_3$ (ortho)), 128.5 (P*Ph*$_3$ (para)), 126.9 (t, $J_{PC} = 5.0$ Hz, P*Ph*$_3$ (meta)), 104.7, 93.9, 87.4, 85.0 (*C*$_6$H$_4$Me), 96.6 (Ru–C≡*C*C$_6$H$_4$Me), 93.8 (Cp), 17.9 (C$_6$H$_4$*Me*), 9.58 (C$_5$*Me*$_5$). IR (KBr) $\nu_{C\equiv C}$ 2071 cm^{-1}. Anal. Calc. for $C_{60}H_{57}ClP_2Ru_2 \cdot CH_2Cl_2$: C, 63.01; H, 5.11. Found: C, 62.73; H, 5.18%.

3.2. Preparation of [Cp(PMe$_3$)$_2$Ru(μ-η^1:η^1-C≡CC$_6$H$_4$Me-p)RuCp*]·Cl (**2b**·Cl)

To a THF (10 ml) suspension of [Cp*Ru(μ3-Cl)$_4$ (0.142 g, 0.131 mmol) was added **lb** (0.225 g, 0.519 mmol) in THF (10 ml), and the mixture was refluxed for 2 days. After filtration, the resultant solid was washed with THF (3 ml, three times), dried in vacuo, and extracted with $CHC1_3$ (3 ml, three times). Evaporation of the solvent afforded a gray solid, which was recrystallized from CH_2Cl_2–hexane (3:10) to give **2b**·Cl as yellow plates (0.333 mg, 91%). ^{1}H-NMR ($CDCl_3$) δ 5.75, 5.37 (d, 2H each, $J = 6.5$ Hz, C$_6$*H*$_4$Me), 4.69 (s, 5H, Cp), 2.18 (s, 3H, C$_6$H$_4$*Me*), 1.92 (s, 15H, Cp*), 1.47 (t, 18H, $J = 8.9$ Hz, P*Me*$_3$) [19]. ^{13}C{^{1}H}-NMR ($CDCl_3$) δ 139.0 (t, $J_{PC} = 24.4$ Hz, Ru–*C*≡CC$_6$H$_4$Me), 98.1, 94.4, 87.3, 86.7 (*C*$_6$H$_4$Me), 95.5 (Ru–C≡*C*C$_6$H$_4$Me), 93.1 (Cp), 80.5 (*C*$_5$Me$_5$), 22.1 (t, $J_{PC} = 15.6$ Hz, P*Me*$_3$), 17.4 (C$_6$H$_4$*Me*), 9.04 (C$_5$*Me*$_5$). ^{31}P{^{1}H]-NMR ($CDCl_3$) δ 12.37. IR (KBr) $\nu_{C\equiv C}$ 2060 cm^{-1}. Anal. Calc. for $C_{30}H_{45}ClP_2Ru_2$: C, 51.08; H, 6.43. Found: C, 50.68; H, 6.35%.

3.3. Preparation of [Cp(PR$_3$)$_2$Ru(μ-η^1:η^6-C=CHC$_6$H$_4$Me-p)RuCp*]·[OTf]$_2$ (**3**·[OTf]$_2$)

A yellow CH_2Cl_2 solution of **2a**·OTf obtained quantitatively by reaction of **2a**·Cl (0.181 g, 0.168 mmol) with AgOTf (0.043 g, 0.168 mmol) in CH_2Cl_2 immediately changed to a red solution when added HOTf (0.015 ml, 0.168 mmol). After the mixture was stirred for 30 min at r.t., the solvent was removed under reduced pressure. The resultant residue was washed with hexane (5 ml, four times) and recrystallized from THF–hexane (10:10 ml) to give **3a**·[OTf]$_2$ as orange plates (0.219 g, 95%). ^{1}H-NMR ($CDCl_3$) δ 7.42–6.96 (m, 30H, Ph), 5.95, 5.76 (d, 2H each, $J = 6.1$ Hz, C$_6$*H*$_4$Me), 5.42 (s, 5H, Cp), 5.02 (s, 1H, C=C*H*C$_6$H$_4$Me), 2.08 (s, 3H, C$_6$H$_4$*Me*), 1.98 (s, 15H, Cp*). ^{13}C{^{1}H}-NMR ($CDCl_3$) δ 346.0 (t, $J_{PC} = 16.3$ Hz, Ru=*C*=CHC$_6$H$_4$Me), 133.0–129.1 (P*Ph*$_3$), 111.8 (Ru=C=*C*HC$_6$H$_4$Me), 85.1 (Cp), 88.3 (*C*$_5$Me$_5$), 99.0, 95.7, 95.5, 93.1 (*C*$_6$H$_4$Me), 18.2 (*C*$_6$H$_4$Me), 10.0 (C$_5$*Me*$_5$). IR (KBr) $\nu_{C=C}$ 1631 cm^{-1}. Anal. Calc. for $C_{62}H_{58}F_6O_6P_2Ru_2S_2$: C, 54.84; H, 4.60. Found: C, 54.97; H, 4.49%. Complex **3b**·[OTf]$_2$ was obtained analogously. Yield, 88%. ^{1}H-NMR ($CDCl_3$) δ 5.94, 5.66 (d, 2H each, $J = 6.1$ Hz, C$_6$*H*$_4$Me), 5.85 (s, 1H, C=C*H*C$_6$H$_4$Me), 5.64 (s, 5H, Cp), 2.11 (s, 3H, C$_6$H$_4$*Me*), 1.95 (s, 15H, Cp*), 1.67 (t, 18H, $J = 10.1$ Hz, P*Me*$_3$). ^{13}C{^{1}H}-NMR ($CDCl_3$) δ 341.2 (t, $J_{PC} = 16.3$ Hz, Ru=*C*=CHC$_6$H$_4$Me), 107.0 (Ru=C=*C*HC$_6$H$_4$), 98.4 (*C*$_5$Me$_5$), 96.8 (Cp), 95.3, 92.4, 88.1, 87.3 (*C*$_6$H$_4$Me), 22.68 (t, $J_{PC} = 16.1$ Hz, P*Me*$_3$), 18.2 (C$_6$H$_4$*Me*), 10.1 (C$_5$*Me*$_5$). ^{31}P{^{1}H}-NMR ($CDCl_3$) δ 5.57. IR (KBr) $\nu_{C=C}$ 1632 cm^{-1}. Anal. Calc. for $C_{32}H_{46}F_6O_6P_2Ru_2S_2$: C, 39.66; H, 4.78. Found: C, 39.39; H, 4.65%.

3.4. Preparation of [Cp(PPh$_3$)2Ru(μ-η^1:η^6-C=CIC$_6$H$_4$Me-p)RuCp*]·[BF$_4$]$_2$ (**4**·[BF$_4$]$_2$)

A yellow THF (10 ml) solution of **2a**·Cl (0.100 g, 0.093 mmol) was immediately turned to a dak red suspension when added I_2 (0.075 g, 0.295 mmol), then gradually changed to a dark green suspension. The mixture was stirred for 1 day at r.t. and $AgBF_4$ (0.036 g, 0.186 mmol) was added. After removal of the solvent, the residue was washed with hexane until excess I_2 was completely removed, extracted with CH_2Cl_2, and recrystallized from CH_2Cl_2–hexane (3:10 ml) to give **4**·[BF$_4$]$_2$ as dark green blocks (0.114 g, 91%). ^{1}H-NMR ($CDCl_3$) δ 7.52–6.91 (m, 30H, Ph), 5.79, 5.70 (d, 2H each, $J = 6.3$ Hz, C$_6$*H*$_4$Me), 5.40 (s, 5H, Cp), 2.11 (s, 3H, C$_6$*H*$_4$Me), 2.00 (s, 15H, Cp*). ^{13}C{^{1}H}-NMR ($CDCl_3$) δ 345.8 (t, $J_{PC} = 15.7$ Hz, Ru=*C*=CIC$_6$H$_4$Me), 133.6–129.0 (PPh$_3$), 100.12 (Ru=C=*C*IC$_6$H$_4$), 98.9, 98.0, 87.9, 83.0 (*C*$_6$H$_4$Me), 97.0 (Cp), 96.4 (*C*$_5$Me$_5$), 18.0 (C$_6$H$_4$*Me*), 10.3 (C$_5$*Me*$_5$). IR (CH_2Cl_2) $\nu_{C=C}$ 1617 cm^{-1}. Anal. Calc. for $C_{60}H_{57}B_2F_8IP_2Ru_2$: C, 53.66; H, 4.28. Found: C, 54.36; H, 4.38%.

3.5. Preparation of [Cp(I)(PMe_3)$_2$Ru(μ:η^1-η^6-C≡CC_6H_4Me-p)RuCp*]·[PF_6]$_2$ (**5**·[PF_6]$_2$)

A yellow CH_2Cl_2 solution of **2b**·PF_6 prepared by the reaction of **2b**·Cl (0.180 g, 0.255 mmol) with $AgPF_6$ (0.064 g, 0.255 mmol) in CH_2Cl_2 rapidly turned to an orange–red suspension when added I_2 (0.181 g, 0.709 mmol). After the mixture was stirred for 6 h at r.t., the solvent was removed under reduced pressure and the residue was dissolved in acetone (10 ml). To this solution was added $AgPF_6$ (0.064 mg, 0.255 mmol) and the resultant mixture was stirred for 12 h at r.t. After removal of the solvent, the residue was washed with hexane until excess I_2 was completely removed, extracted with acetone (3 ml, four times), and recrystallized from acetone–hexane (10:20 ml) to give **5**·[PF_6]$_2$ as dark red plates (0.258 g, 94%). ^{1}H-NMR (acetone-d_6) δ 6.13 (s, 5H, Cp), 6.05, 5.94 (d, 2H each, $J = 6.1$ Hz, C_6H_4Me), 2.34 (t, 18H, $J_{PH} = 11.0$ Hz, PMe_3), 2.23 (s, 3H, C_6H_4Me), 1.99 (s, 15H, Cp*). ^{13}C{^{1}H}-NMR (acetone-d_6) δ 102.1 (t, $J_{PC} = 37.5$ Hz, RuC=CC$_6$H$_4$Me), 102.3 (Ru–C=CC$_6$H$_4$Me), 97.4 (Cp), 97.1, 90.9, 89.7, 89.4 (C_6H_4Me), 95.7 (C_5Me_5), 23.0 (t, $J_{PC} = 20.6$ Hz, PMe_3), 18.7 (C_6H_4Me), 11.0 (C_5Me_5). ^{31}P{^{1}H}-NMR (acetone-d_6) δ 1.46 (PMe_3), -144.4 (sep $J_{PF} = 706$ Hz, PF_6^-). IR (KBr) $\nu_{C\equiv C}$ 2114 cm^{-1}. Complex **5**·[PF_6]$_2$ is somewhat unstable and satisfactory elemental analysis was not obtained.

3.6. Preparation of [Cp(PPh_3)(CO)Ru(μ-η^1:η^6-C≡CC_6H_4Me-p)RuCp*]·OTf (**6**·OTf)

To a CH_2Cl_2 (20 ml) solution of **2a**·OTf prepared from **2a**·Cl (0.100 g, 0.093 mmol) and AgOTf (0.024 g, 0.093 mmol) was bubbled CO for 15 min and the mixture was stirred for 1 week at r.t. After removal of the solvent, the resultant solid was recrystallized from CH_2Cl_2–Et_2O (2:5 ml) to give **6**·OTf as yellow needles (0.062 g, 70%). ^{1}H-NMR ($CDCl_3$) δ 7.95–7.10 (m, 15H, Ph), 5.86, 5.42, 5.24, 4.80 (d, 1H each, $J = 6.0$ Hz, C_6H_4Me), 5.00 (s, 5H, Cp), 2.10 (s, 3H, C_6H_4Me), 1.83 (s, 15H, Cp*). ^{13}C{^{1}H}-NMR ($CDCl_3$) δ 203.0 (d, $J_{PC} = 17.5$ Hz, CO), 135.5–128.2 (PPh_3), 115.7 (d, $J_{PC} = 22.5$ Hz, Ru–C≡CC_6H_4Me), 103.1 (Ru–C≡CC$_6$H$_4$Me), 97.5, 94.8, 94.3, 92.4, 89.0, 88.5 (C_6H_4Me), 94.6 (Cp), 87.3 (C_5Me_5), 18.1 (C_6H_4Me), 9.68 (C_5Me_5). IR (KBr) $\nu_{C\equiv C}$ 2095, ν_{CO} 1952 cm^{-1}. Anal. Calc. for $C_{44}H_{42}F_{30}O_4PRu_2S$: C, 61.74; H, 4.95. Found: C, 61.97; H, 4.53%.

3.7. X-ray crystal structure analysis of **2a**·PF_6

Suitable crystals of **2a**·PF_6 were mounted on glass fibers. Diffraction measurements were made on a Rigaku RAXIS II imaging plate area detector with graphite-monochromated Mo–K_α radiation $\lambda =$ 0.71069 Å). Data were collected at a temperature of 23 ± 1°C to a maximum 2θ value of 49.8°. All data processing was performed on a Silicon Graphics Iris Indigo computer with the TEXSAN program (Rigaku, Tokyo). Neutral scattering factors were obtained from the standard source [20]. The structures were solved by heavy-atom Patterson methods and expanded using Fourier synthesis (DIRDIF). All the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were fixed at the calculated positions (C–H = 0.95 Å) and were not refined. The crystallographic data and selected structural parameters are summarized in Tables 1 and 2.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC 140835. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the Grant-in-Aid for Scientific Research on Priority Area No. 284-11120246 from The Ministry of Education, Science, Sports and Culture, Japan.

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