

Synthesis, structure, and reactivities of the Ru–Co heterobimetallic complex. Molecular structures of  $\text{Cp}^*\text{Ru}(\text{CO})_2(\mu_2\text{-CO})\text{Co}(\text{CO})_3$ ,  $\text{Cp}^*\text{Ru}(\mu_2\text{-CO})_2(\mu_2\text{-dppm})\text{Co}(\text{CO})_2$ ,  $\text{Cp}^*\text{Ru}(\text{CNBu}')(\text{CO})(\mu_2\text{-CO})\text{Co}(\text{CO})_3$ , and  $\text{Cp}^*(\text{CO})\text{Ru}\{\eta^2:\eta^4-\mu_2\text{-C}(\text{Tol})\text{CHC}(\text{Tol})\text{CH}\}\text{Co}(\text{CO})_2$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ,  $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ ,  $\text{Tol} = \text{C}_6\text{H}_4\text{Me}$ )

Hiroyuki Matsuzaka\*, Koji Ichikawa, Tomohiro Ishioka, Haru Sato, Takashi Okubo, Tomohiko Ishii, Masahiro Yamashita, Mitsuru Kondo<sup>1</sup>, Susumu Kitagawa<sup>1</sup>

*Department of Chemistry, Graduate School of Science, Tokyo Metropolitan University, Minami-osawa, Hachioji, Tokyo 192-0397, Japan*

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## Abstract

Treatment of  $\text{Cp}^*\text{Ru}(\text{CO})_2\text{Cl}$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) with  $\text{NaCo}(\text{CO})_4$  produces the metal–metal bonded heterobimetallic complex  $\text{Cp}^*\text{Ru}(\text{CO})_2(\mu_2\text{-CO})\text{Co}(\text{CO})_3$  (**2b**). Substitution of the CO ligands by the  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$  (dppm) leads to the isolation of  $\text{Cp}^*\text{Ru}(\mu_2\text{-CO})_2(\mu_2\text{-dppm})\text{Co}(\text{CO})_2$  (**3**) whereas that by  $\text{Bu}'\text{NC}$  gives  $\text{Cp}^*\text{Ru}(\text{CO})(\text{CNBu}')(\mu_2\text{-CO})\text{Co}(\text{CO})_3$  (**4**). Stoichiometric head-to-tail dimerization of *p*-tolylacetylene at the bimetallic site of **2b** proceeds to form the dinuclear metallacyclopentadiene complex  $\text{Cp}^*(\text{CO})\text{Ru}\{\eta^2:\eta^4-\mu_2\text{-C}(\text{Tol})\text{CHC}(\text{Tol})\text{CH}\}\text{Co}(\text{CO})_2$  (**5**) in which two alkyne molecules are coupled to form a ruthenacyclopentadiene core which coordinates to the  $\text{Co}(\text{CO})_2$  fragment. On the other hand, catalytic head-to-head coupling of methyl propiolate in the presence of **2b** yields (*E*)- $(\text{MeO}_2\text{C})\text{CH}=\text{CH}(\text{C}\equiv\text{CCO}_2\text{Me})$  (**6**). The molecular structures of **2b**, **3**, **4**, and **5** have been determined by X-ray crystallography. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Heterobimetallic complex; Ruthenium; Cobalt; Alkyne; Dinuclear metallacyclopentadiene; Enyne

## 1. Introduction

The chemistry of heteronuclear metal–metal bonded compounds has been a major subject of recent research interest due to the inherent catalytic potential of mixed–metal complexes [1]. The Fe–Co heterobimetallic complex  $\text{CpFe}(\text{CO})(\mu_2\text{-CO})_2\text{Co}(\text{CO})_3$  (**1a**;  $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ), one of the examples of this class, was originally

reported by Joshi and Pauson [2], and the molecular structures of **1a** [3] and  $(\text{indenyl})\text{Fe}(\text{CO})(\mu_2\text{-CO})_2\text{Co}(\text{CO})_3$  [4] have been established. Subsequent studies revealed that the CO ligands terminally bonded to the Co atom in **1a** were selectively substituted by  $\text{PMePh}_2$  or dienes to give  $\text{CpFe}(\text{CO})(\mu_2\text{-CO})_2\text{Co}(\text{CO})_2(\text{PMePh}_2)$  [5],  $\text{CpFe}(\text{CO})(\mu_2\text{-CO})_2\text{Co}(\text{CO})(\text{CH}_2\text{-CMeCMe-CH}_2)$  [6], and  $\text{CpFe}(\text{CO})(\mu_2\text{-CO})_2\text{Co}(\text{CO})(\text{norbondadiene})$  [7], respectively. In sharp contrast, the chemistry of  $\text{CpRu}(\text{CO})_2\text{Co}(\text{CO})_4$  (**2a**) has been surprisingly less developed to date, partially because **2a** can be isolated only in very poor yield (ca. 10%) [8]. We have recently found that  $\text{Cp}^*\text{Ru}(\text{CO})_2(\mu_2\text{-CO})\text{Co}(\text{CO})_3$  (**2b**), the  $\text{Cp}^*$  analog of **2a**, is readily obtained in high yield [9], which prompted us to investigate its chemical reactivity. Here we describe details on preparation and structure of **2b**

\* Corresponding author. Tel.: +81-426-77-2551; fax: +81-426-77-2525.

*E-mail addresses:* matsuzaka-hiroyuki@c.metro-u.ac.jp (H. Matsuzaka), kitagawa@sbchem.kyoto-u.ac.jp (S. Kitagawa)

<sup>1</sup> Present address: Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan. Tel.: +81-75-753-5652; fax: +81-75-753-4979.

together with its phosphine and isocyanide substituted derivatives  $\text{Cp}^*\text{Ru}(\mu_2\text{-CO})_2(\mu_2\text{-dppm})\text{Co}(\text{CO})_2$  (**3**;  $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ ) and  $\text{Cp}^*\text{Ru}(\text{CO})(\text{CNBu}^i)(\mu_2\text{-CO})\text{Co}(\text{CO})_3$  (**4**). Also reported is the dimerization reaction of terminal alkynes induced by **2b**, which selectively affords either the dinuclear metallacyclopentadiene complex  $\text{Cp}^*(\text{CO})\text{Ru}\{\eta^2\text{-}\eta^4\text{-}\mu_2\text{-C}(\text{Tol})\text{CHC}(\text{Tol})\text{CH}\}\text{Co}(\text{CO})_2$  (**5**) or (*E*)-enyne (*E*)-(MeO<sub>2</sub>C)CH=CH(C≡CCO<sub>2</sub>-Me) (**6**) depending upon the nature of the alkyne.

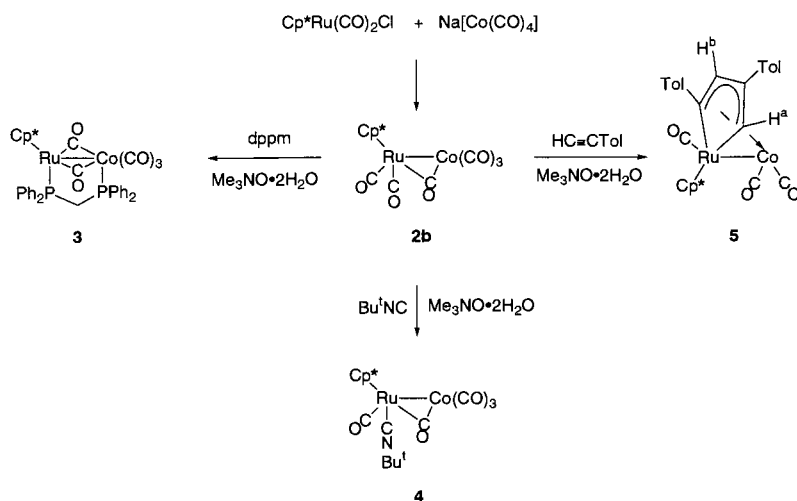
## 2. Results and discussion

A yellow–brown THF solution of  $\text{Cp}^*\text{Ru}(\text{CO})_2\text{Cl}$  gradually turned to an orange suspension upon treatment with  $\text{NaCo}(\text{CO})_4$  (one equivalent) over 4 days at 50°C. Work-up of the reaction mixture resulted in the isolation of  $\text{Cp}^*\text{Ru}(\text{CO})_2(\mu_2\text{-CO})\text{Co}(\text{CO})_3$  (**2b**) as an orange microcrystalline solid (86%, Scheme 1), which was both spectroscopically and crystallographically characterized. The <sup>1</sup>H-NMR spectrum of **2b** shows a characteristic resonance of  $\text{Cp}^*$  protons at  $\delta$  1.94. The IR spectrum indicates the presence of terminal and bridging CO ligands both in the solid state and in THF solution [10]. This is in sharp contrast with the fact that all CO ligands in **2a** are terminally bonded to the metal atoms [8]. The mass spectrum (FAB) of **2b** shows a parent ion peak at  $m/z = 464$   $\{(M+1)^+\}$  together with resonances due to the sequential loss of six CO groups. These spectral data are fully consistent with the crystal structure of **2b** (vide infra). It is interesting to note that the reaction of  $\text{Cp}^*\text{Ru}(\text{CO})_2\text{Cl}$  with  $\text{NaCo}(\text{CO})_4$  readily afforded **2b** (86%), whereas that of  $\text{CpRu}(\text{CO})_2\text{Cl}$  gave **2a** only in very low yield (10%) [8b]. Treatment of  $\text{Cp}^*\text{Fe}(\text{CO})\text{Cl}$  with  $\text{NaCo}(\text{CO})_4$  produced the related

complex  $\text{Cp}^*\text{Fe}(\text{CO})(\mu_2\text{-CO})_2\text{Co}(\text{CO})_3$  (**1b**, 39%), which was recently isolated by Akita et al. as one of the thermolysis products of the trinuclear cluster  $(\eta^2\text{-}\eta^2\text{-}\mu_2\text{-Fp}^*\text{C}\equiv\text{CH})\text{Co}_2(\text{CO})_6$  ( $\text{Fp}^* = \text{Cp}^*\text{Fe}(\text{CO})_2$ ) and has been structurally defined [11].

An ORTEP drawing of **2b** is depicted in Fig. 1, and selected bond distances and angles are given in Table 2. Fig. 1 clearly shows the dinuclear structure of **2b** where the  $\text{Cp}^*\text{Ru}(\text{CO})_2$  unit and the  $\text{Co}(\text{CO})_4$  fragment are joined by the direct Ru–Co bond (2.7445(6) Å), the distance of which is in the range of a typical Ru–Co single bond (2.59–2.79 Å) [12]. The semi-bridging C(3)O(3) ligand is bonded more strongly to Co than to Ru [Co(1)–C(3), 1.817(4) Å; Ru(1)–C(3), 2.206(3) Å] and the O(3) atom is tilted towards Ru [Co(1)–C(3)–O(3), 148.5(3)°; Ru(1)–C(3)–O(3), 126.3°]. The bonding mode of the  $\mu_2\text{-CO}$  ligand in **2b** is in sharp contrast to that observed in **1b** [11]. Thus, the semi-bridging CO ligand in **1b** is bonded more strongly to Fe than to Co (Fe–C, 1.834(3) Å; Co–C, 2.225(3) Å) and the oxygen atom is tilted toward Co [Fe–C–O, 153.3(3)°; Co–C–O, 128.0(2)°]. Complex **1b** has another  $\mu_2\text{-CO}$  which is coordinated to Fe and Co in an essentially symmetrical manner.

Treatment of **2b** with  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$  (dppm, one equivalent) and  $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$  (one equivalent) in refluxing THF produced  $\text{Cp}^*\text{Ru}(\mu_2\text{-CO})_2(\mu_2\text{-dppm})\text{Co}(\text{CO})_2$  (**3**, 79%, Scheme 1), which was isolated as orange columnar crystals and both spectroscopically and crystallographically characterized. The <sup>1</sup>H-NMR spectrum of **3** shows a triplet due to the methylene protons of dppm at  $\delta$  2.15, together with signals attributed to the  $\text{Cp}^*$  ( $\delta$  1.59) and phenyl protons. The <sup>31</sup>P{<sup>1</sup>H}-NMR spectrum of **3** exhibits two resonances at  $\delta$  55.1 (Ru–P) and 42.1 (Co–P). The latter signal is



Scheme 1.

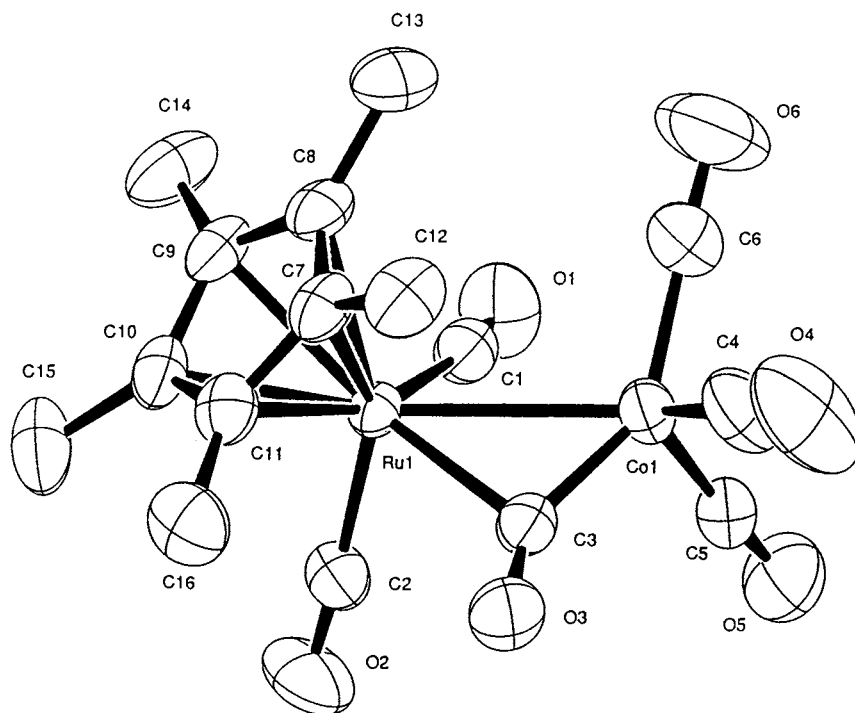


Fig. 1. Molecular structure of **2b** drawn at the 50% probability level.

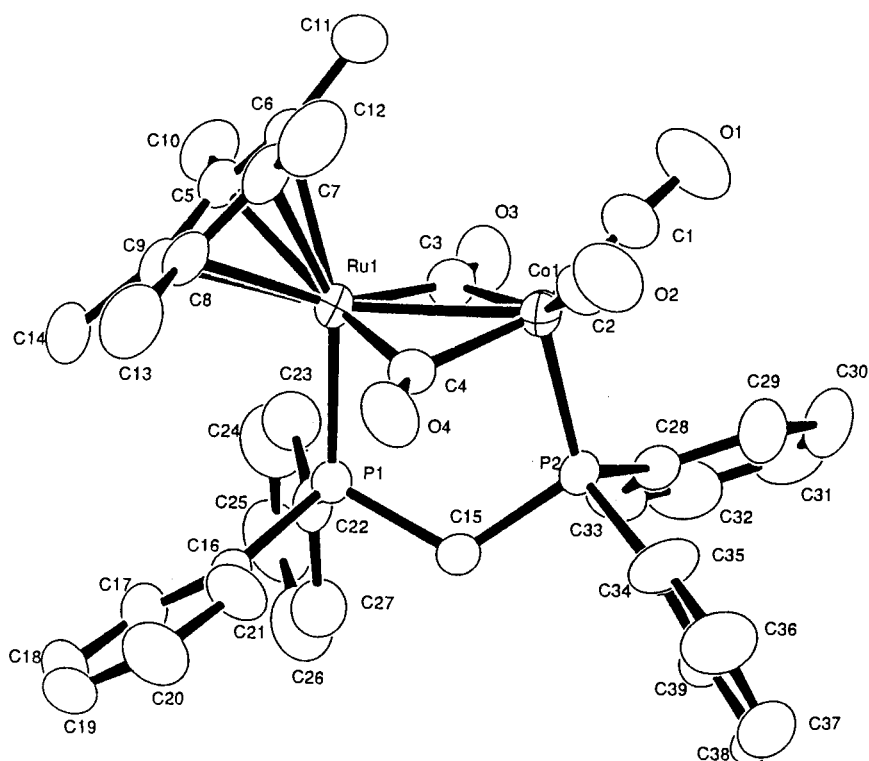


Fig. 2. Molecular structure of **3** drawn at the 50% probability level.

markedly broader than the former one owing to the effects of the quadrupole moment of the cobalt nucleus to which it is directly bonded. The IR spectrum of **3** indicates the existence of both terminal ( $\nu_{\text{CO}}$  1985, 1932

$\text{cm}^{-1}$ ) and bridging ( $\nu_{\text{CO}}$  1728  $\text{cm}^{-1}$ ) CO ligands. These spectral data are fully consistent with its crystal structure depicted in Fig. 2. The dppm ligand bridges the two metal atoms to form the common five-mem-

bered framework. The C(4)O(4) ligand bridges Ru and Co in an essentially symmetrical manner as is evident from the similar M–C(4) distances [Ru(1)–C(4), 2.014(4) Å; Co(1)–C(4), 1.958(4) Å] and M–C(4)–O(4) angles [Ru(1)–C(4)–O(4), 137.7(4)°; Co(1)–C(4)–O(4), 137.7(3)°]. On the other hand, the C(3)O(3) group is bonded more strongly to Ru than to Co [Ru(1)–C(3), 1.917(5) Å; Co(1)–C(3), 2.226(5) Å] and the O(3) atom is tilted toward Co [Ru(1)–C(3)–O(3), 149.9(4)°; Co(1)–C(3)–O(3), 129.9(4)°]. These bridging modes of two  $\mu_2$ -CO ligands are similar to those observed for **1b** (vide supra) [11]. The intramolecular distance between Ru and Co is 2.6733(7) Å, which indicates a direct bonding interaction between the two metal atoms [12].

Substitution of the CO ligand in **2b** also proceeded with Bu'NC (five equivalents) in the presence of Me<sub>3</sub>NO·2H<sub>2</sub>O (one equivalent) to form the monosubstituted species Cp\*Ru(CO)(CNBu')(μ<sub>2</sub>-CO)Co(CO)<sub>3</sub> **4**, which was isolated as orange needles and both spectroscopically and crystallographically characterized. The <sup>1</sup>H-NMR spectrum of **4** shows two singlets at  $\delta$  1.44 (9H, Bu') and 1.87 (15H, Cp\*). The IR spectrum of **4** exhibits  $\nu_{\text{CO}}$  resonances at 2027, 1956, and 1794 cm<sup>-1</sup>, which are lower by approximately 20 cm<sup>-1</sup> compared with those observed for the parent **2b**. The key to the structural assignment of **4** from the IR spectrum is the absence of a set of two resonances due to the symmetric and anti symmetric stretching of two CO groups terminally bonded to Ru in *cis* configuration. These spectral data indicate that one of the two COs terminally bonded to Ru is selectively substituted by the Bu'NC ligand (Scheme 1), which is unambiguously confirmed by X-ray diffraction analysis. The crystal lattice con-

tains two crystallographically independent formula units. An ORTEP drawing of them is given in Fig. 3, which clearly shows that the Bu'NC ligand coordinates to Ru and occupies the pseudo-*cis* position to the  $\mu_2$ -CO unit in both molecules.

Complex **2b** reacted with HC≡CTol (five equivalents) in the presence of Me<sub>3</sub>NO·2H<sub>2</sub>O to yield the dinuclear metallacyclopentadiene complex Cp\*(CO)Ru{ $\eta^2$ : $\eta^4$ - $\mu_2$ -C(Tol)CHC(Tol)CH}Co(CO)<sub>2</sub> (**5**) (95%, Scheme 1), which was isolated as orange columnar crystals and spectroscopically characterized. The molecular structure of **5** has been further defined by X-ray crystallography. The <sup>1</sup>H-NMR spectrum of **5** exhibits two resonances at  $\delta$  8.00 and 6.90 (d, 1H each, <sup>4</sup>J<sub>HH</sub> = 2.5 Hz) due to the H<sup>a</sup> and H<sup>b</sup> protons (Scheme 1) of the metallacyclopentadiene framework. An ORTEP drawing of **5** is shown in Fig. 4, and selected bond distances and angles are given in Table 5. Two HC≡CTol molecules are coupled in a head-to-tail manner on the bimetallic site to form the ruthenacyclopentadiene core which is coordinated to the Co(CO)<sub>2</sub> fragment. The four carbon atoms C(1)–C(4) are essentially coplanar. However, the metallacycle ring in **5** is not planar as commonly observed for other dinuclear metallacyclopentadiene systems [13] but is bent with a fold angle of 17.7° (angle between the Ru(1)–C(1)–C(4) and C(1)–C(2)–C(3)–C(4) planes). Examples containing the folded five-membered rings are still limited.[14]. The distance between the two metal atoms in **5** is 2.627(1) Å, indicating the existence of a Ru–Co single bond.[12].

On the other hand, reaction of **2b** with HC≡CCO<sub>2</sub>Me occurred in a quite different manner. Thus, catalytic head-to-head dimerization of the alkyne readily pro-

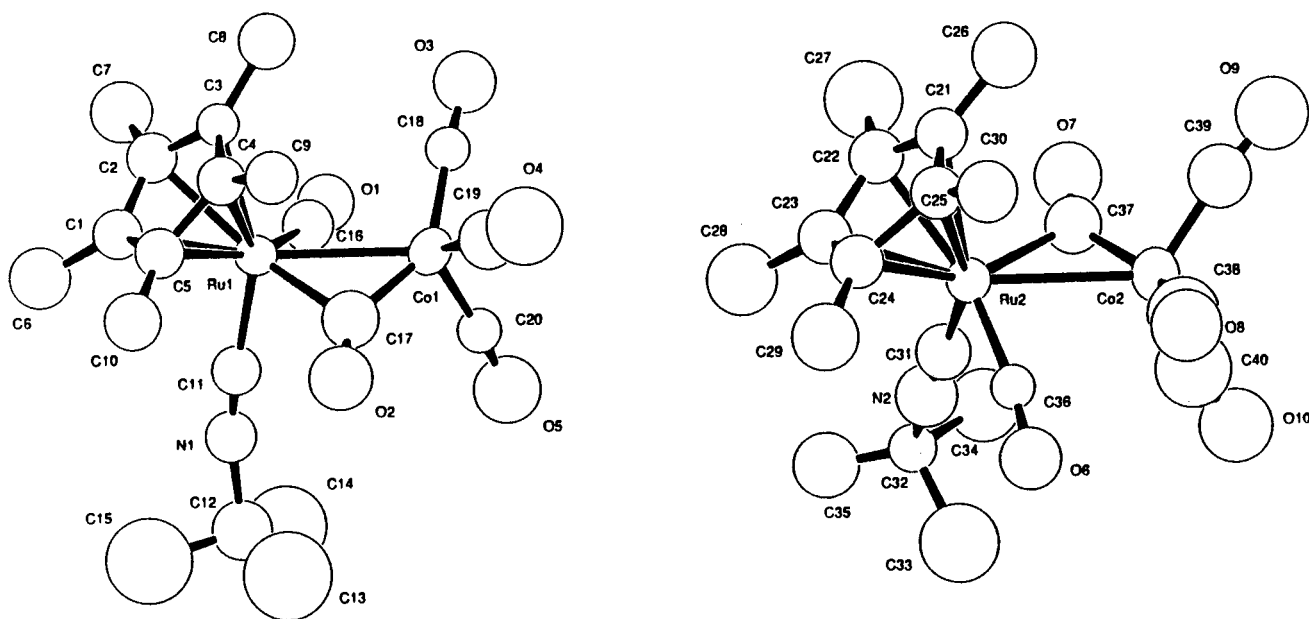


Fig. 3. Molecular structure of **4** drawn at the 50% probability level.

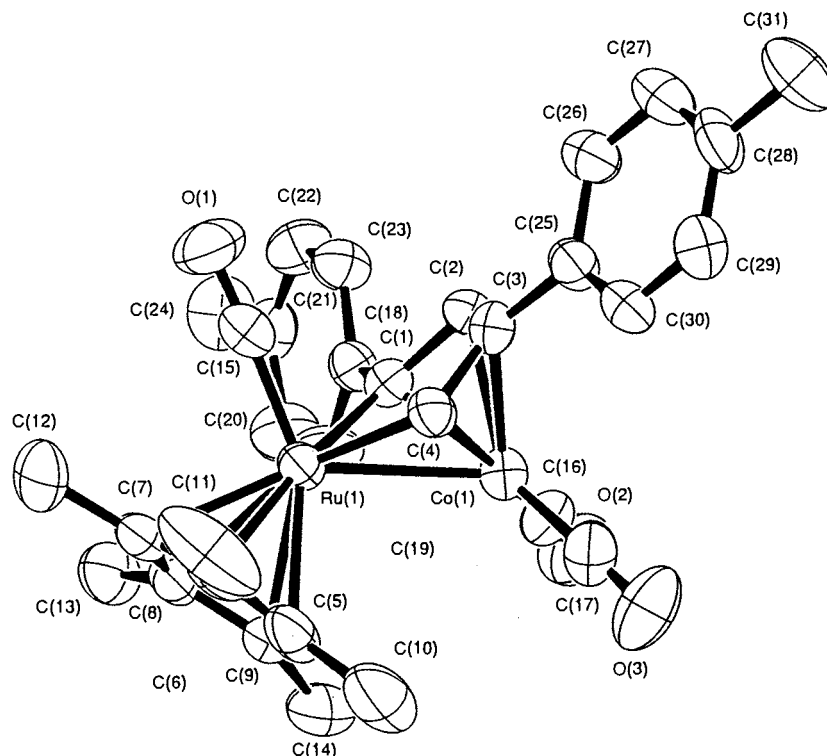
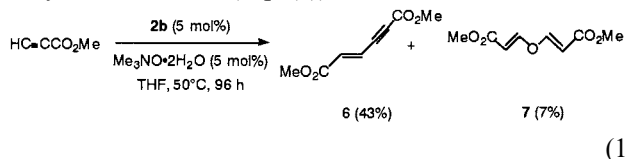


Fig. 4. Molecular structure of **5** drawn at the 50% probability level.

ceeded at 50°C in the presence of 5 mol% of **2b** and  $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$  to give (*E*)-(MeO<sub>2</sub>C)CH=CH(C≡CCO<sub>2</sub>Me) (**6**, 43%) together with (*E,E*)-(MeO<sub>2</sub>C)CH=CHOCH=CH(CO<sub>2</sub>Me) (**7**, 7%), both of which were isolated as white microcrystalline solids and spectroscopically characterized (Eq. (1)).



It is of interest to note that carbon–carbon bond formation between the alkyne molecules exclusively produces **6** and neither the corresponding (*Z*)-enyne nor the head-to-tail dimers were detected during this reaction. Several examples of selective head-to-head coupling of terminal alkynes to form *trans*-enyne have appeared in the literature [15]. There is great interest at the present time in head-to-head, tail-to-tail and head-to-tail coupling of alkyne and alkynyl groups at bimetallic and polymeric centers because of the possibility of generating new molecular wires and molecular switches. The role of the metals and orientation of the yne (ynyl) functionality at the metal centers in directing such coupling reactions is crucial [16]. It is noteworthy that cyclotrimerization of  $\text{HC}\equiv\text{CCO}_2\text{Me}$  did not proceed under these conditions. This is the most commonly observed coupling product in transition metal-catalyzed oligomerization of alkynes [17].  $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$  is essen-

tial for this dimerization. Only a trace amount of cyclotrimerization products were detected when the reaction was carried out without  $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ . The dialkenyl ether **7** can be formally derived from two alkyne molecules and  $\text{H}_2\text{O}$ . In fact, the yield of **7** was increased up to 29% when the reaction was carried out in the presence of a stoichiometric amount of  $\text{H}_2\text{O}$  (50 mol% of the alkyne), whereas the reaction in the presence of carefully dried  $\text{Me}_3\text{NO}$  gave only 1% of **7**. These results suggest that  $\text{H}_2\text{O}$  plays a critical role in the formation of **7**. However we must await further investigation to elucidate the detailed reaction mechanism. It is not certain at this stage whether a heterobimetallic complex **2b** or a mononuclear species derived from **2b** is the active catalyst. The <sup>1</sup>H-NMR analysis indicated the absence of **2b** in the crude reaction mixture but several Cp\* resonances were also observed around δ 2 ppm.

### 3. Experimental

#### 3.1. General

Complexes  $\text{Cp}^*\text{Ru}(\text{CO})_2\text{Cl}$  [18] and  $\text{NaCo}(\text{CO})_4$  [19] were prepared according to the published methods. The reagents  $\text{Bu}'\text{NC}$ ,  $\text{HC}\equiv\text{CTol}$ , and  $\text{HC}\equiv\text{CCO}_2\text{Me}$  were obtained commercially, degassed, and stored over 4 Å molecular sieves, whereas dppm was obtained commercially and used without further purification. Solvents

were dried by refluxing over Na–benzophenone ketyl (THF, benzene, hexane), or CaH<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub>) 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-500 spectrometer, and mass spectra were recorded on a JEOL AX-505H spectrometer. Elemental analyses were performed at the Elemental Analysis Laboratory, Department of Chemistry, Tokyo Metropolitan University.

### 3.2. Preparation of **2b**

To a THF (10 ml) solution of Cp\*Ru(CO)<sub>2</sub>Cl (1.425 g, 4.346 mmol) was added NaCo(CO)<sub>4</sub> (0.843 g, 4.346 mmol) in THF (20 ml) and the reaction mixture was stirred for 4 days at 60°C, during which time the original yellow–brown solution gradually turned to a n orange suspension. After removal of the solvent, the resulting residue was extracted with hexane and purified by chromatography on alumina with benzene/hexane (3/7). Evaporation of the solvent from a single orange band gave **2b** as an analytically pure orange microcrystalline solid (1.73 g, 86%). Complex **2b** was quite soluble in common organic solvents. Single crystals suitable for X-ray diffraction analysis were obtained by recrystallization from MeOH–water. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 1.94(s, Cp\*). IR (THF, cm<sup>-1</sup>): ν<sub>CO</sub> 2053(s), 2004(s), 1971(s), 1817(w). MS(FAB), *m/z* = 464 {(M + 1)<sup>+</sup>}. Anal. Found: C, 41.67; H, 3.51. Calc. for C<sub>16</sub>H<sub>15</sub>CoO<sub>6</sub>Ru: C, 41.47; H, 3.26%.

### 3.3. Preparation of **1b**

Cp\*Fe(CO)<sub>2</sub>Cl was prepared in 79% yield by analogous procedures to those reported for Cp-Fe(CO)<sub>2</sub>Cl [20]. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 1.77(s, Cp\*). IR (THF, cm<sup>-1</sup>): ν<sub>CO</sub> 2024(s), 1973(s). To a THF (20 ml) solution of Cp\*Fe(CO)<sub>2</sub>Cl (320 mg, 1.13 mmol) was added NaCo(CO)<sub>4</sub> (220 mg, 1.13 mmol) and the mixture was stirred overnight at 50°C. After removal of the solvent, the residue was extracted with benzene and chromatographed on silica gel with benzene. Evaporation of the solvent from a single orange band afforded **1b** as a dark brown microcrystalline solid (184 mg, 39%).

### 3.4. Reaction of **2b** with *dppm*

To a THF (10 ml) solution of **2b** (185 mg, 0.399 mmol) was added Me<sub>3</sub>NO·2H<sub>2</sub>O (44 mg, 0.399 mmol) and *dppm* (153 mg, 0.399 mmol) and the solution was refluxed overnight. After removal of the solvent, the resulting residue was extracted with benzene. Removal of the solvent gave an orange solid which was recrystallized from benzene–hexane to afford **3** as orange

columnar crystals (251 mg, 79%). <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>) δ 7.49–6.95 (m, 20H, Ph), 2.15 (t, 2H, <sup>2</sup>J<sub>PH</sub> = 9.2 Hz, PCH<sub>2</sub>P), 1.59 (s, 15H, Cp\*). IR (THF, cm<sup>-1</sup>) ν<sub>CO</sub> 1985(s), 1932(s), 1728(m). <sup>31</sup>P{<sup>1</sup>H}-NMR δ 55.1(d, <sup>2</sup>J<sub>PP</sub> = 101 Hz, Ru–P), 42.1 (brs, Co–P). Anal. Found: C, 59.19; H, 4.80. Calc. for C<sub>39</sub>H<sub>37</sub>CoO<sub>4</sub>P<sub>2</sub>Ru: C, 59.16; H, 4.71%.

### 3.5. Reaction of **2b** with *Bu<sup>t</sup>NC*

To a mixture of **2b** (87 mg, 0.19 mmol) and Me<sub>3</sub>NO·2H<sub>2</sub>O (21 mg, 0.19 mmol) in THF (10 ml) was added Bu<sup>t</sup>NC (79 mg, 0.95 mmol) and the solution was stirred for 6 h at room temperature. After removal of the solvent, the residue was purified by chromatography on alumina with 3:7 benzene–hexane. Evaporation of the solvent from a single yellow band gave a yellow solid which was recrystallized from hexane to afford **4** as orange needles (64 mg, 65%). <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 1.87 (s, 15H, Cp\*), 1.44 (s, 9H, Bu<sup>t</sup>). IR (THF, cm<sup>-1</sup>): ν<sub>NC</sub> 2145, ν<sub>CO</sub> 2027(s), 1956(s), 1794(w). Anal. Found: C, 46.15; H, 4.41; N, 2.54. Calc. for C<sub>20</sub>H<sub>24</sub>CoNO<sub>3</sub>Ru: C, 46.33; H, 4.67; N, 2.70%.

### 3.6. Reaction of **2b** with *HC≡CTol*

Complex **2b** (306 mg, 0.660 mmol) was reacted with a mixture of HC≡CTol (372 mg, 3.20 mmol) and Me<sub>3</sub>NO·2H<sub>2</sub>O (73 mg, 0.660 mmol) in THF at 60°C for 12 h. After removal of the solvent, the residue was purified by chromatography on alumina with hexane. Evaporation of the solvent from a single orange band afforded **5** as an orange microcrystalline solid (95%). Single crystals for structural analysis were prepared by recrystallization from hexane. <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 8.00 (d, 1H, *J* = 2.5 Hz, H<sup>a</sup>), 7.47, 7.37 (d, 2H each, *J* = 8.2 Hz, aryl), 7.14–7.12 (m, 4H, aryl), 6.90 (d, 1H, *J* = 2.5 Hz, H<sup>b</sup>), 2.37, 2.34 (s, 3H each, C<sub>6</sub>H<sub>4</sub>Me), 2.02 (s, 15H, Cp\*). IR (hexane): ν<sub>CO</sub> 2010 (vs), 1970 (vs), 1956 (vs). Anal. Found: C, 61.31; H, 5.24. Calc. for C<sub>31</sub>H<sub>31</sub>CoO<sub>3</sub>Ru: C, 60.87; H, 5.11%.

### 3.7. Reaction of **2b** with *HC≡CCO<sub>2</sub>Me*

A THF (20 ml) solution containing **2b** (95 mg, 0.21 mmol), Me<sub>3</sub>NO·2H<sub>2</sub>O (23 mg, 0.21 mmol), and HC≡CCO<sub>2</sub>Me (353 mg, 4.20 mmol) was stirred at 50°C for 96 h. After removal of the solvent, the residue was chromatographed on silica gel first with CH<sub>2</sub>Cl<sub>2</sub> to elute **6** then with 1:3 THF–hexane to elute **7**. Evaporation of the solvent gave **6** (152 mg, 43%) and **7** (27 mg, 7%), respectively. **7**: <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 7.58, 5.66 (d, 2H each, *J* = 12.2 Hz, alkenyl), 3.74 (s, 6H, OMe). <sup>13</sup>C-NMR (CDCl<sub>3</sub>) δ 166.4 (CO), 157.3 (–O–C=C), 104.0 (–O–C=C), 51.6 (OMe). IR (KBr: cm<sup>-1</sup>): ν<sub>CO</sub>

Table 1  
Crystal and data collection parameters for complexes **2b**, **3**, **4**, and **5**

	<b>2b</b>	<b>3</b>	<b>4</b>	<b>5</b>
Formula	C <sub>16</sub> H <sub>15</sub> O <sub>6</sub> CoRu	C <sub>39</sub> H <sub>37</sub> O <sub>4</sub> P <sub>2</sub> CoRu	C <sub>40</sub> H <sub>48</sub> Co <sub>2</sub> N <sub>2</sub> O <sub>10</sub> Ru <sub>2</sub>	C <sub>31</sub> H <sub>31</sub> O <sub>3</sub> CoRu
Molecular weight	463.29	791.67	1036.83	611.59
Space group (crystal system)	<i>P</i> 1 (triclinic)	<i>P</i> 2 <sub>1</sub> / <i>a</i> (monoclinic)	<i>Pca</i> 21 (orthorombic)	<i>P</i> $\bar{1}$ (triclinic)
Crystal color	Orange	Orange	Orange	Dark orange
Unit cell dimensions				
<i>a</i> (Å)	9.219(2)	17.284(2)	16.810(10)	10.681(3)
<i>b</i> (Å)	12.301(2)	11.941(2)	8.634(7)	14.722(4)
<i>c</i> (Å)	8.4515(7)	17.678(2)	32.24(1)	9.443(2)
$\alpha$ (°)	90.94(1)			100.18(2)
$\beta$ (°)	109.164(9)	105.687(8)		99.42(2)
$\gamma$ (°)	90.63(1)			105.06(2)
Cell volume (Å <sup>3</sup> )	905.0(2)	3512.7(7)	4678(9)	1376.5(8)
<i>Z</i>	2	4	4	2
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.700	1.497	1.472	1.475
<i>F</i> (000) electrons	460	1616	2096	624
$\mu$ (Mo–K $\alpha$ ) <sub>calc</sub> (cm <sup>-1</sup> )	17.77	10.33	13.82	11.81
Crystal dimensions (mm)	0.40 × 0.20 × 0.20	0.30 × 0.30 × 0.20	0.20 × 0.30 × 0.30	0.35 × 0.35 × 0.25
Reflections measured	± <i>h</i> , + <i>k</i> , ± <i>l</i>	+ <i>h</i> , – <i>k</i> , ± <i>l</i>	– <i>h</i> , + <i>k</i> , – <i>l</i>	± <i>h</i> , + <i>k</i> , ± <i>l</i>
Used data ( <i>I</i> = 3 $\sigma$ ( <i>I</i> ))	3829	4793	2547	2683
No. of parameters refined	217	424	245	325
<i>R</i>	0.032	0.038	0.057	0.044
<i>R</i> <sub>w</sub>	0.039	0.035	0.069	0.036
GoF	4.09	1.71	0.67	2.05

1717. MS (EI), 186 [M<sup>+</sup>]. Anal. Found: C, 51.81; H, 5.26. Calc. for C<sub>8</sub>H<sub>10</sub>O<sub>5</sub>: C, 51.61; H, 5.41%.

### 3.8. X-ray crystallography of **2b**, **3**, and **5**

Suitable crystals of **2b**, **3**, **4**, and **5** were mounted on glass fibers. Diffraction measurements were made on a Rigaku AFC-7R automated four-circle diffractometer by using graphite-monochromated Mo–K $\alpha$  radiation ( $\nu = 0.71069$  Å). The unit cells were determined and refined by a least-squares method using 20 independent reflections. Data were collected with an  $\omega$ –2 $\theta$  scan technique. If  $\sigma(F)/F$  was more than 0.1, a scan was repeated up to five times and the results were added to the first scan. Three standard reflections were monitored at every 150 measurements. 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 [21]. In the reduction of data, Lorentz polarization and empirical absorption corrections ( $\psi$  scan) were made.

The structures were solved by a combination of heavy-atom Patterson methods (**2b**, **5**) or by direct methods (SHELXL-86 for **3**, SIR-92 for **4**) and Fourier synthesis (DIRDIF). All the non-hydrogen atoms were refined anisotropically for **2b**, **3**, and **5**. For **4**, Ru and Co atoms were refined anisotropically whereas other non-hydrogen atoms were refined isotropically. All the

Table 2  
Selected bond distances (Å) and angles (°) for **2b**<sup>a</sup>

Bond distances			
Ru(1)–Co(1)	2.7445(6)	Ru(1)–C(1)	1.899(4)
Ru(1)–C(2)	1.890(4)	Ru(1)–C(3)	2.206(3)
Ru(1)–C(7)	2.281(3)	Ru(1)–C(8)	2.258(3)
Ru(1)–C(9)	2.239(3)	Ru(1)–C(10)	2.225(3)
Ru(1)–C(11)	2.239(3)	Co(1)–C(3)	1.817(4)
Co(1)–C(4)	1.755(5)	Co(1)–C(5)	1.800(4)
Co(1)–C(6)	1.806(5)	O(1)–C(1)	1.136(4)
O(2)–C(2)	1.131(4)	O(3)–C(3)	1.174(4)
O(4)–C(4)	1.141(5)	O(5)–C(5)	1.133(5)
O(6)–C(6)	1.128(5)		
Bond angles			
Co(1)–Ru(1)–C(1)	68.3(1)	Co(1)–Ru(1)–C(2)	103.7(1)
Co(1)–Ru(1)–C(3)	41.31(9)	C(1)–Ru(1)–C(2)	90.8(2)
C(1)–Ru(1)–C(3)	103.9(1)	C(2)–Ru(1)–C(3)	83.1(1)
Ru(1)–Co(1)–C(3)	53.3(1)	Ru(1)–Co(1)–C(4)	129.4(2)
Ru(1)–Co(1)–C(5)	111.0(1)	Ru(1)–Co(1)–C(6)	99.0(1)
C(3)–Co(1)–C(4)	90.1(2)	C(3)–Co(1)–C(5)	103.3(2)
C(3)–Co(1)–C(6)	146.2(2)	C(4)–Co(1)–C(5)	110.6(2)
C(4)–Co(1)–C(6)	96.8(2)	C(5)–Co(1)–C(6)	105.1(2)
Ru(1)–C(1)–O(1)	168.6(3)	Ru(1)–C(2)–O(2)	175.6(3)
Ru(1)–C(3)–O(3)	85.4(1)	Ru(1)–C(3)–O(3)	126.0(3)
Co(1)–C(3)–O(3)	148.5(3)	Co(1)–C(4)–O(4)	177.5(5)
Co(1)–C(5)–O(5)	175.5(4)	Co(1)–C(6)–O(6)	176.8(5)

<sup>a</sup> Estimated S.D.s in the least significant figure are given in parentheses.

Table 3  
Selected bond distances (Å) and angles (°) for **3**<sup>a</sup>

<i>Bond distances</i>			
Ru(1)–Co(1)	2.6733(7)	Ru(1)–P(1)	2.304(1)
Ru(1)–C(3)	1.917(5)	Ru(1)–C(4)	2.014(4)
Ru(1)–C(5)	2.273(4)	Ru(1)–C(6)	2.238(4)
Ru(1)–C(7)	2.256(4)	Ru(1)–C(8)	2.270(4)
Ru(1)–C(9)	2.250(4)	Co(1)–P(2)	2.190(1)
Co(1)–C(1)	1.768(5)	Co(1)–C(2)	1.749(5)
Co(1)–C(3)	2.226(5)	Co(1)–C(4)	1.958(4)
O(1)–C(1)	1.149(5)	O(2)–C(2)	1.157(5)
O(3)–C(3)	1.167(5)	O(4)–C(4)	1.177(4)
<i>Bond angles</i>			
Co(1)–Ru(1)–P(1)	93.91(3)	Co(1)–Ru(1)–C(3)	55.1(1)
Co(1)–Ru(1)–C(4)	46.8(1)	P(1)–Ru(1)–C(3)	86.0(1)
P(1)–Ru(1)–C(4)	84.8(1)	C(3)–Ru(1)–C(4)	100.1(2)
Ru(1)–Co(1)–P(2)	98.46(4)	Ru(1)–Co(1)–C(1)	118.1(2)
Ru(1)–Co(1)–C(2)	121.5(2)	Ru(1)–Co(1)–C(3)	44.9(1)
Ru(1)–Co(1)–C(4)	48.6(1)	P(2)–Co(1)–C(1)	105.1(2)
P(2)–Co(1)–C(2)	116.2(2)	P(2)–Co(1)–C(3)	86.6(1)
P(2)–Co(1)–C(4)	91.9(1)	C(1)–Co(1)–C(2)	97.3(2)
C(1)–Co(1)–C(3)	80.1(2)	C(1)–Co(1)–C(4)	160.6(2)
C(2)–Co(1)–C(3)	156.6(2)	C(2)–Co(1)–C(4)	83.0(2)
C(3)–Co(1)–C(4)	91.9(2)	Ru(1)–P(1)–C(15)	112.7(1)
Co(1)–P(2)–C(15)	111.7(1)	Co(1)–C(1)–O(1)	176.5(5)
Co(1)–C(2)–O(2)	177.4(4)	Ru(1)–C(3)–Co(1)	80.0(2)
Ru(1)–C(3)–O(3)	149.9(4)	Co(1)–C(3)–O(3)	129.9(4)
Ru(1)–C(4)–Co(1)	84.6(2)	Ru(1)–C(4)–O(4)	137.7(4)
Co(1)–C(4)–O(4)	137.7(3)	P(1)–C(15)–P(2)	117.3(2)

<sup>a</sup> Estimated S.D.s in the least significant figure are given in parentheses.

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 1–5.

#### 4. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 132706 for **2b**, 132707 for **3**, 134377 for **4**, and 132708 for **5**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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Table 4  
Selected bond distances (Å) and angles (°) for **4**<sup>a</sup>

<i>Bond distances</i>			
Ru(1)–Co(1)	2.735(4)	Ru(1)–C(1)	2.21(2)
Ru(1)–C(2)	2.22(2)	Ru(1)–C(3)	2.23(2)
Ru(1)–C(4)	2.28(2)	Ru(1)–C(5)	2.26(2)
Ru(1)–C(11)	1.94(3)	Ru(1)–C(16)	1.92(3)
Ru(1)–C(17)	2.10(3)	Ru(2)–Co(2)	2.743(4)
Ru(2)–C(21)	2.26(2)	Ru(2)–C(22)	2.22(2)
Ru(2)–C(23)	2.19(2)	Ru(2)–C(24)	2.25(2)
Ru(2)–C(25)	2.27(3)	Ru(2)–C(31)	1.97(3)
Ru(2)–C(36)	1.80(2)	Ru(2)–C(37)	2.12(3)
Co(1)–C(17)	1.83(3)	Co(1)–C(18)	1.73(2)
Co(1)–C(19)	1.70(3)	Co(1)–C(20)	1.74(2)
Co(2)–C(37)	1.81(3)	Co(2)–C(38)	1.94(5)
Co(2)–C(39)	1.69(3)	Co(2)–C(40)	1.76(5)
<i>Bond angles</i>			
Co(1)–Ru(1)–C(11)	101.7(8)	Co(1)–Ru(1)–C(16)	69.6(8)
Co(1)–Ru(1)–C(17)	41.9(9)	C(11)–Ru(1)–C(16)	87(1)
C(11)–Ru(1)–C(17)	83(1)	C(16)–Ru(1)–C(17)	106(1)
Co(2)–Ru(2)–C(31)	100.1(7)	Co(2)–Ru(2)–C(36)	70.5(7)
Co(2)–Ru(2)–C(37)	41.3(7)	C(31)–Ru(2)–C(36)	87(1)
C(31)–Ru(2)–C(37)	81(1)	C(36)–Ru(2)–C(37)	106(1)
Ru(1)–Co(1)–C(17)	50.1(9)	Ru(1)–Co(1)–C(18)	97.8(7)
Ru(1)–Co(1)–C(19)	127(1)	Ru(1)–Co(1)–C(20)	111.9(7)
C(17)–Co(1)–C(18)	144(1)	C(17)–Co(1)–C(19)	91(1)
C(17)–Co(1)–C(20)	99(1)	C(18)–Co(1)–C(19)	99(1)
C(18)–Co(1)–C(20)	110(1)	C(19)–Co(1)–C(20)	109(1)
Ru(1)–C(17)–Co(1)	88(1)	Ru(1)–C(17)–O(2)	127(2)
Co(1)–C(17)–O(2)	145(3)	Ru(1)–C(11)–N(1)	175(2)
Ru(2)–Co(2)–C(37)	50.5(8)	Ru(2)–Co(2)–C(38)	100(1)
Ru(2)–Co(2)–C(39)	125.0(9)	Ru(2)–Co(2)–C(40)	108(2)
C(37)–Co(2)–C(38)	148(2)	C(37)–Co(2)–C(39)	92(1)
C(37)–Co(2)–C(40)	99(2)	C(38)–Co(2)–C(39)	97(2)
C(38)–Co(2)–C(40)	104(2)	C(39)–Co(2)–C(40)	117(2)
Ru(2)–C(37)–Co(2)	88(1)	Ru(2)–C(37)–O(7)	129(2)
Co(2)–C(37)–O(7)	142(2)	Ru(2)–C(31)–N(2)	178(2)

<sup>a</sup> Estimated S.D.s in the least significant figure are given in parentheses.

Table 5  
Selected bond distances (Å) and angles (°) for **5**<sup>a</sup>

<i>Bond distances</i>			
Ru(1)–Co(1)	2.627(1)	Ru(1)–C(1)	2.101(7)
Ru(1)–C(4)	2.049(7)	Co(1)–C(1)	2.023(7)
Co(1)–C(2)	2.084(7)	Co(1)–C(3)	2.124(7)
Co(1)–C(4)	2.045(7)	C(1)–C(2)	1.438(9)
C(2)–C(3)	1.40(1)	C(3)–C(4)	1.421(9)
<i>Bond angles</i>			
Co(1)–Ru(1)–C(1)	49.1(2)	Co(1)–Ru(1)–C(4)	50.0(2)
C(1)–Ru(1)–C(4)	76.7(3)	Ru(1)–Co(1)–C(1)	51.8(2)
Ru(1)–Co(1)–C(2)	77.5(2)	Ru(1)–Co(1)–C(3)	77.0(2)
Ru(1)–Co(1)–C(4)	50.1(2)	C(1)–Co(1)–C(2)	41.0(3)
C(1)–Co(1)–C(3)	70.8(3)	C(1)–Co(1)–C(4)	78.6(3)
C(2)–Co(1)–C(3)	38.8(3)	C(2)–Co(1)–C(4)	69.2(3)
C(3)–Co(1)–C(4)	39.8(3)	Ru(1)–C(1)–Co(1)	79.1(3)
Ru(1)–C(1)–C(2)	113.3(5)	Co(1)–C(1)–C(2)	71.8(4)
Co(1)–C(2)–C(1)	67.2(4)	Co(1)–C(2)–C(3)	72.2(4)
C(1)–C(2)–C(3)	116.0(7)	Co(1)–C(3)–C(2)	69.1(4)
Co(1)–C(3)–C(4)	67.1(4)	C(2)–C(3)–C(4)	112.7(6)
Ru(1)–C(4)–Co(1)	79.8(3)	Ru(1)–C(4)–C(3)	117.3(5)
Co(1)–C(4)–C(3)	73.1(4)		

<sup>a</sup> Estimated S.D.s in the least significant figure are given in parentheses.



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