

# Reactivities governed by a single metal atom M in mixed-metal highnuclearity clusters having $[\text{Ru}_5\text{M}(\text{C})]$ core (M = Co, Rh, Pd): Site-nonspecific, site-selective, and chemo-selective variations in the $\text{SO}_2$ -trapping reactions

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## Abstract

The  $\text{SO}_2$  substitution for a CO ligand of the hexa-nuclear carbonyl complexes having  $\text{Ru}_5\text{M}(\text{C})$  type carbido-metal core,  $[\text{PPN}][\text{Ru}_5\text{Co}(\text{C})(\text{CO})_{16}]$  (**2**),  $[\text{PPN}][\text{Ru}_5\text{Rh}(\text{C})(\text{CO})_{16}]$  (**3**), and  $\text{Ru}_5\text{Pd}(\text{C})(\text{CO})_{16}$  (**4**), is dramatically affected by the kind of metal atom M: **2** (M = Co) is reactive but not site-selective, **3** (M = Rh) is reactive and site-selective, whereas **4** (M = Pd) is not reactive at all even though **4** can easily react with  $\text{PPh}_3$  to give the substitution products.

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**Keywords:** Mixed-metal highnuclearity; Clusters; Carbonyl clusters; Sulfur dioxide;  $^{59}\text{Co}$  NMR

## 1. Introduction

In our continuous study to find efficient catalysts for reduction of  $\text{SO}_2$ , one of the main polluting species contained in various exhaust gases, we previously examined a metal dispersed Ru/TiO<sub>2</sub> system using H<sub>2</sub> as the reducing gas [1]. When the carbido carbonyl cluster complex  $[\text{PPN}]_2[\text{Ru}_6(\text{C})(\text{CO})_{16}]$  (**1**) (PPN = N(PPh<sub>3</sub>)<sub>2</sub>) was employed as the precursor, the resulting nano metal-particle catalyst had a unique high performance at even below 200 °C. From the perspective of coordination chemistry, it is interesting to note that **1** reacts with  $\text{SO}_2$ , by the help of Me<sub>3</sub>NO, at ambient temperatures to give very stable complexes  $[\text{PPN}]_2[\text{Ru}_6(\text{C})(\text{CO})_{15}(\text{SO}_2)]$  and  $[\text{PPN}]_2[\text{Ru}_6(\text{C})(\text{CO})_{14}(\text{SO}_2)_2]$  [2].

We become interested if alloyed metal nano-scale dispersion prepared from mixed-metal clusters can show some specific reactivity in the  $\text{SO}_2$ -reduction system. As a model reaction of such systems, we decided to substitute one heterometal atom for one of the Ru atoms in **1** and systematically checked the reactivity of the mixed-metal clusters toward  $\text{SO}_2$ . Whether  $\text{SO}_2$  molecule prefers interaction specifically with M rather with Ru, or if it favors coordination to Ru, would be one of the determining factors for the positive or negative reactivity effected by the alloy as compared with corresponding homo-metallic Ru catalysts, particularly in the very early stage of the reaction [3].

## 2. Results and discussion

### 2.1. Synthesis of $[\text{Ru}_5\text{M}]$ (M = Co, Rh, Pd) type clusters

Recently, synthesis and structural characterization of  $[\text{PPN}][\text{Ru}_5\text{Co}(\text{C})(\text{CO})_{16}]$  (**2**) was reported [4]. We prepared

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**2** in higher yield (98%) via a different route, i.e. the reaction of **1** with  $\text{Co}_2(\text{CO})_8$  at room temperature in THF (see Section 3). The red-crystalline rhodium analog  $[\text{PPN}][\text{Ru}_5\text{Rh}(\text{C})(\text{CO})_{16}]$  (**3**) was prepared by the reaction of **1** with  $\text{Rh}_2(\text{CO})_4\text{Cl}_2$  at room temperature in THF in 87% yield. X-ray analysis of **3** has proved a solid-state structure shown in Fig. 1, which is identical to that of **2**. The important bond lengths and angles are listed in Table 1. The  $\nu(\text{CO})$  frequency of **3**, which appeared at  $2021\text{ cm}^{-1}$ , is higher by  $28\text{ cm}^{-1}$  as compared to cluster **1**. A derivative of **3** with a 1,5-cyclooctadiene (cod) ligand coordinated to Rh,  $[\text{PPN}][\text{Ru}_5\text{Rh}(\text{C})(\text{CO})_{14}(\text{cod})]$  (**3'**), was also prepared from the reaction of  $[\text{PPN}]_2[\text{Ru}_5(\text{C})(\text{CO})_{14}]$  and  $[\text{Rh}(\text{cod})(\text{NH}_3)_2]\text{PF}_6$  in THF at room temperature. The complex was isolated in 79% yield and structurally characterized (Fig. 2 and Table 2) [5].

The smooth replacement of Co with Pd is effected by the room temperature reaction of **2** with  $[\text{Pd}(\text{MeCN})_4][\text{BF}_4]_2$ ,

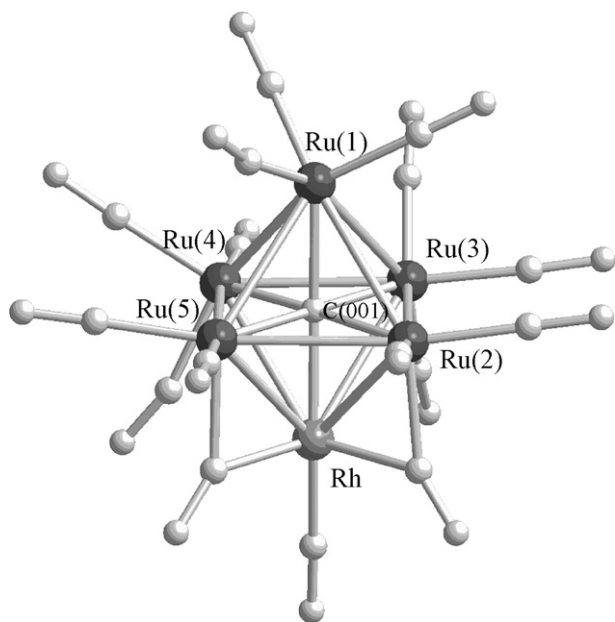


Fig. 1. Crystal structure of the cluster anion of **3**.

Table 1  
Selected bond lengths (Å) and angles (°) for  $[\text{PPN}][\text{Ru}_5\text{Rh}(\text{C})(\text{CO})_{16}]$  (**3**)

| Bond lengths   |           |                |           |
|----------------|-----------|----------------|-----------|
| Ru(1)–Ru(2)    | 2.9429(6) | Ru(3)–Rh       | 2.9779(8) |
| Ru(1)–Ru(3)    | 2.8564(6) | Ru(4)–Rh       | 2.9481(7) |
| Ru(1)–Ru(4)    | 2.8903(6) | Ru(5)–Rh       | 2.7983(6) |
| Ru(1)–Ru(5)    | 2.9452(6) | Ru(1)–C(001)   | 2.036(4)  |
| Ru(2)–Ru(3)    | 2.9229(5) | Ru(2)–C(001)   | 2.047(4)  |
| Ru(2)–Ru(5)    | 2.9303(6) | Ru(3)–C(001)   | 2.064(4)  |
| Ru(3)–Ru(4)    | 2.8650(6) | Ru(4)–C(001)   | 2.051(4)  |
| Ru(4)–Ru(5)    | 2.8857(5) | Ru(5)–C(001)   | 2.044(4)  |
| Ru(2)–Rh       | 2.7822(6) | Rh–C(001)      | 2.044(4)  |
| Bond angles    |           |                |           |
| Ru(2)–Rh–Ru(3) | 60.87(2)  | Ru(3)–Rh–Ru(4) | 57.82(2)  |
| Ru(4)–Rh–Ru(5) | 60.22(1)  | Ru(5)–Rh–Ru(2) | 63.35(2)  |
| Ru(2)–Rh–Ru(4) | 91.25(2)  | Ru(3)–Rh–Ru(5) | 90.58(2)  |

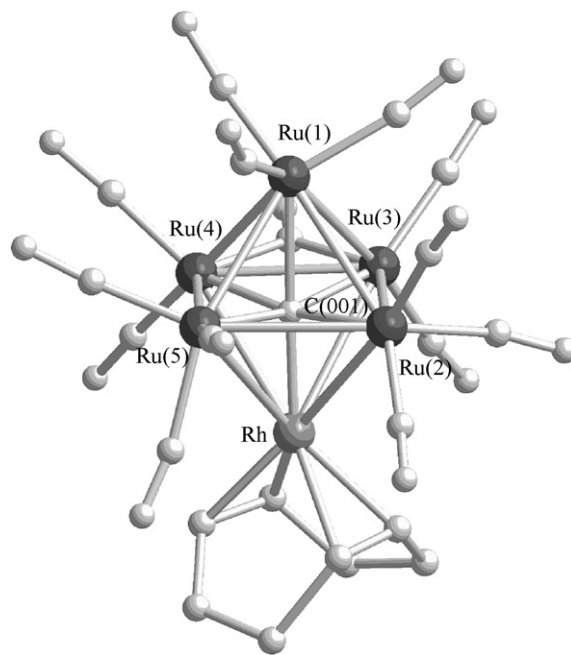


Fig. 2. Crystal structure of the cluster anion of **3'**.

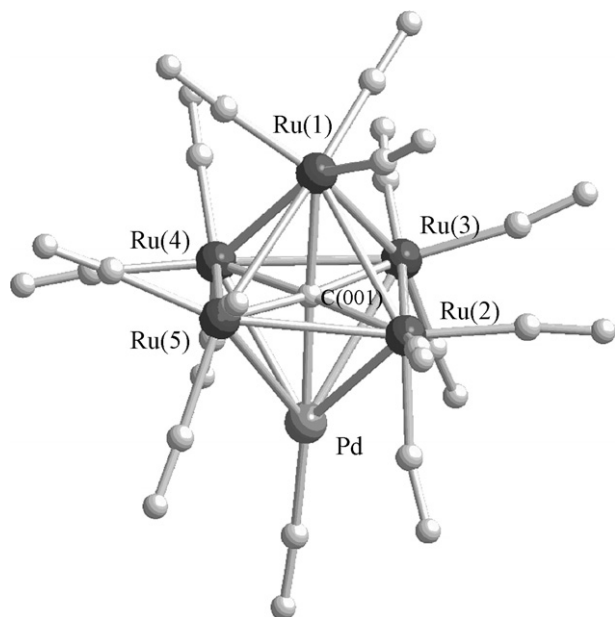
Table 2  
Selected bond lengths (Å) and angles (°) for  $[\text{PPN}][\text{Ru}_5\text{Rh}(\text{C})(\text{CO})_{14}(\text{cod})]$  (**3'**)

| Bond lengths   |           |                |           |
|----------------|-----------|----------------|-----------|
| Ru(1)–Ru(2)    | 2.829(3)  | Ru(3)–Rh       | 2.998(4)  |
| Ru(1)–Ru(3)    | 2.934(2)  | Ru(4)–Rh       | 2.996(2)  |
| Ru(1)–Ru(4)    | 2.887(4)  | Ru(5)–Rh       | 2.864(2)  |
| Ru(1)–Ru(5)    | 2.834(4)  | Ru(1)–C(001)   | 2.15(2)   |
| Ru(2)–Ru(3)    | 2.963(2)  | Ru(2)–C(001)   | 2.05(2)   |
| Ru(2)–Ru(5)    | 2.879(3)  | Ru(3)–C(001)   | 2.03(2)   |
| Ru(3)–Ru(4)    | 2.796(3)  | Ru(4)–C(001)   | 2.07(2)   |
| Ru(4)–Ru(5)    | 2.940(2)  | Ru(5)–C(001)   | 2.05(2)   |
| Ru(2)–Rh       | 2.977(4)  | Rh–C(001)      | 2.00(2)   |
| Bond angles    |           |                |           |
| Ru(2)–Rh–Ru(3) | 59.46(9)  | Ru(3)–Rh–Ru(4) | 55.61(8)  |
| Ru(4)–Rh–Ru(5) | 60.19(6)  | Ru(5)–Rh–Ru(2) | 59.04(8)  |
| Ru(2)–Rh–Ru(4) | 87.04(10) | Ru(3)–Rh–Ru(5) | 88.03(11) |

which gave after purification with column chromatography, the red-crystalline neutral cluster complex  $\text{Ru}_5\text{Pd}(\text{C})(\text{CO})_{16}$  (**4**) in 72% yield. The solid-state structure of **4**, determined by single-crystal X-ray analysis (Fig. 3 and Table 3), is identical to that of platinum analog  $\text{Ru}_5\text{Pt}(\text{C})(\text{CO})_{16}$  [6]. Synthesis of  $[\text{Ru}_5\text{M}]$  ( $\text{M} = \text{Co}, \text{Rh}, \text{Pd}$ ) type clusters is summarized in Scheme 1.

## 2.2. Reaction of $[\text{Ru}_5\text{M}]$ ( $\text{M} = \text{Co}, \text{Rh}, \text{Pd}$ ) type clusters with $\text{SO}_2$

We reported previously that trapping of gaseous  $\text{SO}_2$  on **1** was a rather easy reaction though it needed help of  $\text{Me}_3\text{NO}$  to remove CO ligand [2]. It is now found that the reaction of the Co-containing cluster **2** with  $\text{SO}_2$  takes place more smoothly by simply mixing the two reactants at

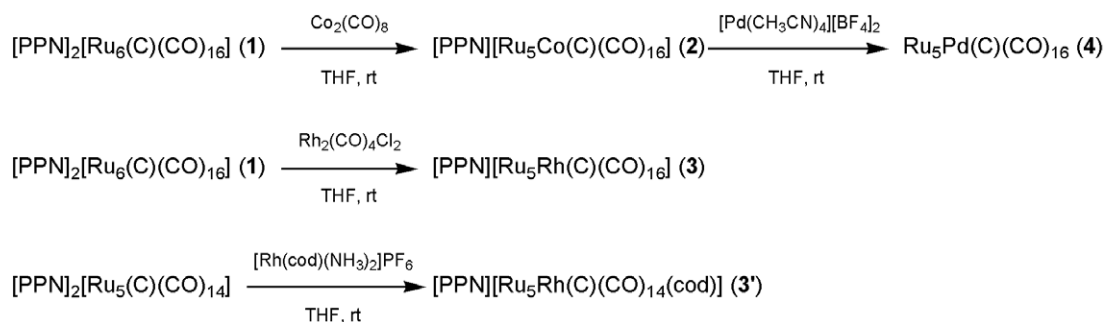
Fig. 3. Crystal structure of the cluster of **4**.Table 3  
Selected bond lengths (Å) and angles (°) for Ru<sub>5</sub>Pd(C)(CO)<sub>16</sub> (**4**)

| Bond lengths   |           |                |           |
|----------------|-----------|----------------|-----------|
| Ru(1)–Ru(2)    | 2.8927(6) | Ru(3)–Pd       | 2.9855(6) |
| Ru(1)–Ru(3)    | 2.8431(5) | Ru(4)–Pd       | 2.8619(6) |
| Ru(1)–Ru(4)    | 2.8808(5) | Ru(5)–Pd       | 2.9750(5) |
| Ru(1)–Ru(5)    | 2.8291(6) | Ru(1)–C(001)   | 2.073(5)  |
| Ru(2)–Ru(3)    | 2.8713(6) | Ru(2)–C(001)   | 2.037(5)  |
| Ru(2)–Ru(5)    | 2.8973(6) | Ru(3)–C(001)   | 2.063(5)  |
| Ru(3)–Ru(4)    | 2.8973(6) | Ru(4)–C(001)   | 2.051(5)  |
| Ru(4)–Ru(5)    | 2.9499(5) | Ru(5)–C(001)   | 2.067(5)  |
| Ru(2)–Pd       | 2.9409(9) | Pd–C(001)      | 2.027(5)  |
| Bond angles    |           |                |           |
| Ru(2)–Pd–Ru(3) | 57.95(1)  | Ru(3)–Pd–Ru(4) | 59.36(2)  |
| Ru(4)–Pd–Ru(5) | 60.68(1)  | Ru(5)–Pd–Ru(2) | 58.64(1)  |
| Ru(2)–Pd–Ru(4) | 89.52(2)  | Ru(3)–Pd–Ru(5) | 87.53(2)  |

room temperature in CH<sub>2</sub>Cl<sub>2</sub>. When the reaction was stopped after **2** was consumed completely (after 7–8 h), the resulting product was found to be a mixture of two complexes having the empirical formulae [PPN][Ru<sub>5</sub>Co(C)(CO)<sub>15</sub>(SO<sub>2</sub>)] (**5**) and [PPN][Ru<sub>5</sub>Co(C)(CO)<sub>14</sub>(SO<sub>2</sub>)<sub>2</sub>]

(**6**). Since separation of **5** and **6** was difficult, the reaction had to be stopped while **2** was still remaining to get pure **5**, or the reaction mixture was allowed to stand longer time (12 h) in order to get pure **6**. In this way pure **5** and **6** were obtained in 30% and 65% yield, respectively. The patterns of the IR spectra in the region for the terminally coordinated CO ligands of **2**, **5** and **6** are quite similar, but positions of these peaks in **5** and **6** appeared at 2032 and 2041 cm<sup>-1</sup> respectively, which shifted 11 and 20 cm<sup>-1</sup> to higher energy from the corresponding peaks of the parent complex **2** (2021 cm<sup>-1</sup>). This observation indicates a steady decrease of electron charge in the cluster core by the introduction of SO<sub>2</sub> ligand(s). Crystallinity of these complexes was not suitable for X-ray diffraction analysis, though the preliminary X-ray data for **6** (*R* = 10%) indicated the solid-state structure similar to that of the Rh analogue **8** (*vide infra*). The <sup>59</sup>Co NMR gave some information concerning their structure in solution (Fig. 4). As expected, the NMR of **6** showed a single peak at –3597 ppm (Fig. 4b). Spectrum of **5** (Fig. 4a) consists of three peaks, of which the one at –3597 ppm is due to contaminating **6**. The presence of two more peaks attributable to **5** indicates that it is a mixture of two regio-isomers. Since the parent **2** has <sup>59</sup>Co NMR peak at –2632 ppm, the peak at –3004 ppm was assigned to the isomer (**5-1**) with an SO<sub>2</sub> molecule occupying the position away from Co, whereas the peak at –3363 ppm is attributed to (**5-2**) which has μ<sub>2</sub>-SO<sub>2</sub> directly bonded to Co. Based on the peak intensities, isomer ratio is approximately 3/2. Consequently, the incoming SO<sub>2</sub> showed no appreciable site-preference in the reaction with **2**.

In striking contrast, a single product formulated as [PPN][Ru<sub>5</sub>Rh(C)(CO)<sub>15</sub>(SO<sub>2</sub>)] (**7**) was isolated in 93% yield on treatment of complex **3** with SO<sub>2</sub> under a condition similar to that for the reaction of **2**. X-ray analysis of red-crystalline **7** revealed the structure with the μ<sub>2</sub>-SO<sub>2</sub> ligand bridging a Rh–Ru hetero-metallic bond (Fig. 5 and Table 4). The S-bridged Rh–Ru distance (2.8145(9) Å), metal-S distances (2.228(1), 2.316(1) Å), and metal-S-metal angle (75.37(3)°) are similar to those found in hexaruthenium carbido clusters Ru<sub>6</sub>(C)(CO)<sub>16</sub>(SO<sub>2</sub>) and [PPN]<sub>2</sub>[Ru<sub>6</sub>(C)(CO)<sub>15</sub>(SO<sub>2</sub>)] [2]. Unlike the case of the cobalt analogue, **7** is stable and does not show any further reaction with SO<sub>2</sub>. This is probably due to a kinetic reason, because **3**'



Scheme 1.

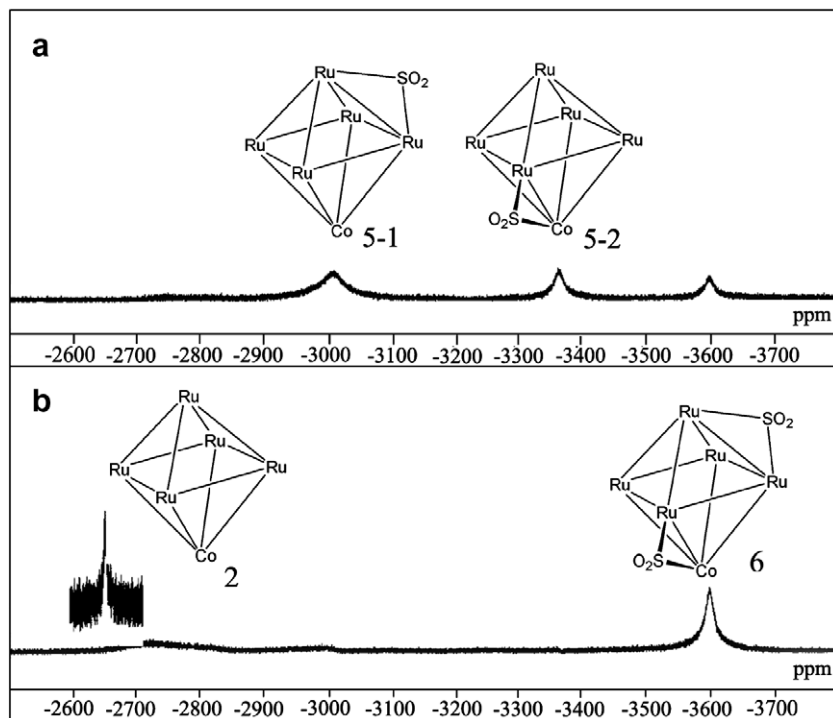
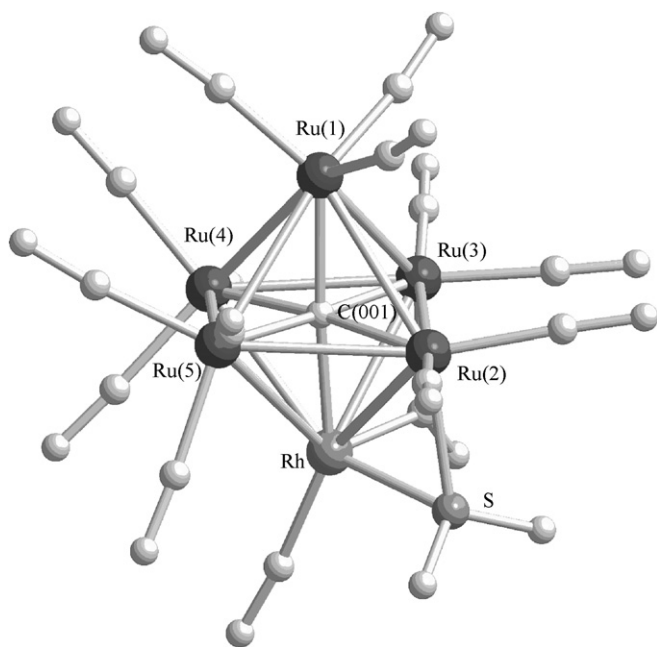
Fig. 4.  $^{59}\text{Co}$  NMR spectra for 2, 5-1, 5-2, and 6.

Fig. 5. Crystal structure of the cluster anion of 7.

easily reacted with gaseous  $\text{SO}_2$  at room temperature to give quite stable  $[\text{PPN}][\text{Ru}_5\text{Rh}(\text{C})(\text{CO})_{14}(\text{SO}_2)_2]$  (**8**), which is closely related to **6**, in 65% isolated yield. As expected, X-ray single-crystal analysis evidenced that the second  $\text{SO}_2$  unit bridges a Ru–Ru bond away from the Rh atom

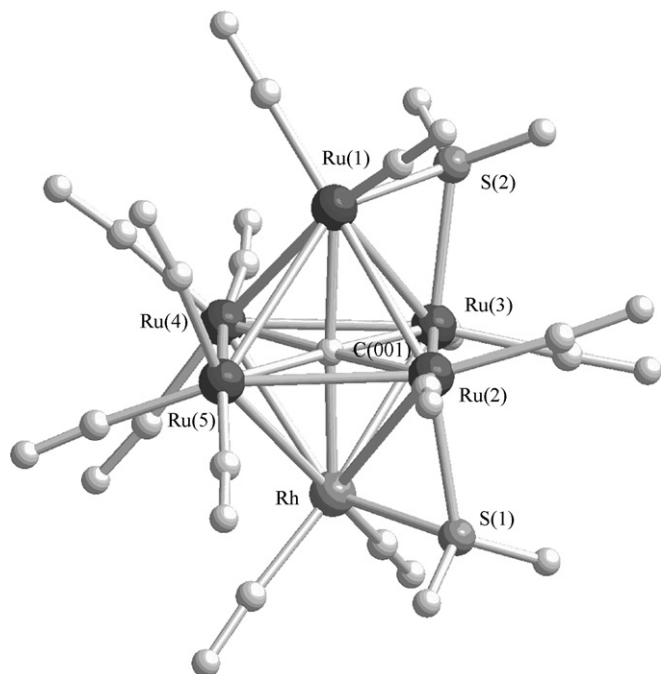
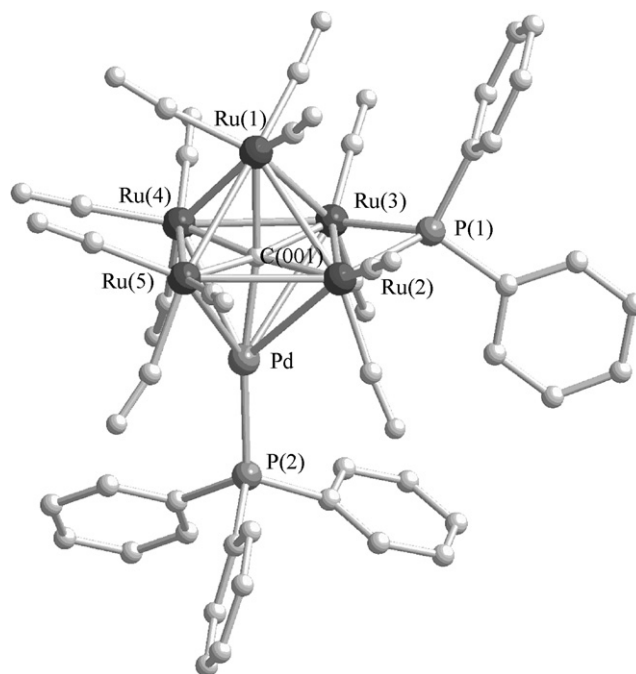
Table 4

Selected bond lengths (Å) and angles (°) for  $[\text{PPN}][\text{Ru}_5\text{Rh}(\text{C})(\text{CO})_{15}(\text{SO}_2)]$  (**7**)

| Bond lengths   |           |                |           |
|----------------|-----------|----------------|-----------|
| Ru(1)–Ru(2)    | 2.9412(4) | Ru(3)–Rh       | 2.7872(4) |
| Ru(1)–Ru(3)    | 2.9019(5) | Ru(4)–Rh       | 2.8613(4) |
| Ru(1)–Ru(4)    | 2.9484(4) | Ru(5)–Rh       | 3.0413(4) |
| Ru(1)–Ru(5)    | 2.8376(4) | Ru(1)–C(001)   | 2.029(3)  |
| Ru(2)–Ru(3)    | 2.9477(4) | Ru(2)–C(001)   | 2.036(2)  |
| Ru(2)–Ru(5)    | 2.9117(4) | Ru(3)–C(001)   | 2.057(3)  |
| Ru(3)–Ru(4)    | 2.9065(4) | Ru(4)–C(001)   | 2.063(2)  |
| Ru(4)–Ru(5)    | 2.8376(4) | Ru(5)–C(001)   | 2.048(3)  |
| Ru(2)–Rh       | 2.8148(4) | Rh–C(001)      | 2.050(3)  |
| Ru(2)–S        | 2.315(1)  | Rh–S           | 2.284(1)  |
| Bond angles    |           |                |           |
| Ru(2)–Rh–Ru(3) | 63.50(1)  | Ru(3)–Rh–Ru(4) | 61.92(1)  |
| Ru(4)–Rh–Ru(5) | 57.37(1)  | Ru(5)–Rh–Ru(2) | 59.48(1)  |
| Ru(2)–Rh–Ru(4) | 92.33(1)  | Ru(3)–Rh–Ru(5) | 89.40(2)  |
| Ru(2)–S–Rh     | 75.38(3)  |                |           |

(Fig. 6 and Table 5). Such a geometry was also observed in  $[\text{PPN}]_2[\text{Ru}_6(\text{C})(\text{CO})_{14}(\text{SO}_2)_2]$  [**2**].

The reactivity of the Pd-containing complex **4** toward  $\text{SO}_2$  has been found to be much lower than those of **1–3**: it did not react with excess  $\text{SO}_2$  at ambient temperature, even in the presence of excess  $\text{Me}_3\text{NO}$ . Heating of **4** with  $\text{SO}_2$  at 80 °C in  $\text{CH}_2\text{Cl}_2$  resulted in simply gradual decomposition. It is noteworthy that the homo-metallic neutral cluster  $\text{Ru}_6\text{C}(\text{CO})_{17}$  (**1'**) reacts with  $\text{SO}_2$  at room temperature to give an  $\text{SO}_2$ -substituted product in good yield [**2**].

Fig. 6. Crystal structure of the cluster anion of **8**.Fig. 7. Crystal structure of the cluster anion of **9**.Table 5  
Selected bond lengths (Å) and angles (°) for [PPN][Ru<sub>5</sub>Rh(C)(CO)<sub>14</sub>(SO<sub>2</sub>)<sub>2</sub>] (**8**)

| <i>Bond lengths</i> |          |                  |           |
|---------------------|----------|------------------|-----------|
| Ru(1)–Ru(2)         | 2.875(3) | Ru(3)–Rh         | 2.856(2)  |
| Ru(1)–Ru(3)         | 2.873(2) | Ru(4)–Rh         | 2.994(3)  |
| Ru(1)–Ru(4)         | 2.838(2) | Ru(5)–Rh         | 2.844(2)  |
| Ru(1)–Ru(5)         | 3.018(2) | Ru(1)–C(001)     | 2.044(19) |
| Ru(2)–Ru(3)         | 2.964(2) | Ru(2)–C(001)     | 2.052(19) |
| Ru(2)–Ru(5)         | 2.917(2) | Ru(3)–C(001)     | 2.090(10) |
| Ru(3)–Ru(4)         | 2.906(2) | Ru(4)–C(001)     | 2.05(2)   |
| Ru(4)–Ru(5)         | 2.834(2) | Ru(5)–C(001)     | 2.021(11) |
| Ru(2)–Rh            | 2.877(2) | Rh–C(001)        | 2.045(19) |
| Ru(2)–S(1)          | 2.314(9) | Rh–S(1)          | 2.353(8)  |
| Ru(1)–S(2)          | 2.392(5) | Ru(3)–S(2)       | 2.268(8)  |
| <i>Bond angles</i>  |          |                  |           |
| Ru(2)–Rh–Ru(3)      | 62.26(6) | Ru(3)–Rh–Ru(4)   | 59.52(6)  |
| Ru(4)–Rh–Ru(5)      | 58.01(6) | Ru(5)–Rh–Ru(2)   | 61.32(5)  |
| Ru(2)–Rh–Ru(4)      | 88.61(8) | Ru(3)–Rh–Ru(5)   | 92.20(7)  |
| Ru(2)–S(1)–Rh       | 76.1(2)  | Ru(1)–S(2)–Ru(3) | 76.1(2)   |

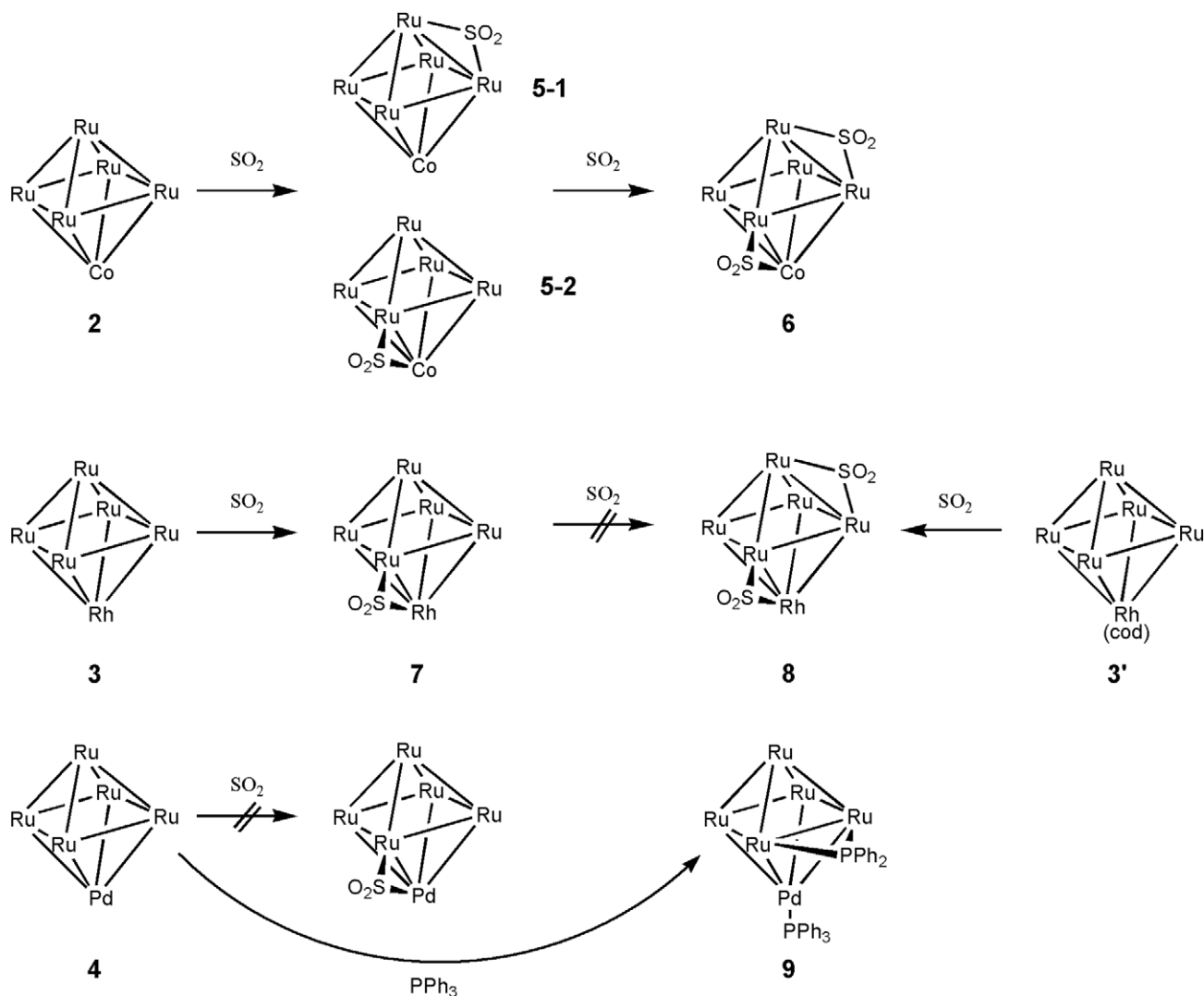
To address whether the CO ligands in complex **4** are bound to the metal core too strongly to undergo any substitution reactions, the reaction with excess PPh<sub>3</sub> was examined in hexane at room temperature. After 24 h, red precipitate was purified to give the product [PPh<sub>4</sub>][Ru<sub>5</sub>Pd(C)(CO)<sub>13</sub>(μ<sub>2</sub>-PPh<sub>2</sub>)(PPh<sub>3</sub>)] (**9**) in 56% isolated yield, which resulted from substitution of CO and concomitant disproportionation of PPh<sub>3</sub>. The structure of complex **9** determined by X-ray analysis is shown in Fig. 7 while important bond lengths and angles are listed in Table 6. Since Ru<sub>6</sub>(C)(CO)<sub>17</sub> is equally reactive with PPh<sub>3</sub> to give a simple mono-substitution product [7], the high ability

Table 6  
Selected bond lengths (Å) and angles (°) for [PPh<sub>4</sub>][Ru<sub>5</sub>Pd(C)(CO)<sub>13</sub>(μ<sub>2</sub>-PPh<sub>2</sub>)(PPh<sub>3</sub>)] (**9**)

| <i>Bond lengths</i> |           |                  |           |
|---------------------|-----------|------------------|-----------|
| Ru(1)–Ru(2)         | 2.8998(6) | Ru(3)–Pd         | 3.1700(6) |
| Ru(1)–Ru(3)         | 2.8637(7) | Ru(4)–Pd         | 2.9040(6) |
| Ru(1)–Ru(4)         | 2.8467(8) | Ru(5)–Pd         | 2.8409(7) |
| Ru(1)–Ru(5)         | 2.8248(6) | Ru(1)–C(001)     | 2.128(5)  |
| Ru(2)–Ru(3)         | 2.7892(5) | Ru(2)–C(001)     | 2.041(4)  |
| Ru(2)–Ru(5)         | 2.9465(5) | Ru(3)–C(001)     | 2.055(4)  |
| Ru(3)–Ru(4)         | 2.8842(6) | Ru(4)–C(001)     | 2.025(4)  |
| Ru(4)–Ru(5)         | 2.9244(6) | Ru(5)–C(001)     | 2.059(4)  |
| Ru(2)–Pd            | 3.0085(7) | Pd–C(001)        | 2.046(5)  |
| Ru(2)–P(1)          | 2.291(2)  | Ru(3)–P(1)       | 2.297(2)  |
| Pd–P(2)             | 2.300(2)  |                  |           |
| <i>Bond angles</i>  |           |                  |           |
| Ru(2)–Pd–Ru(3)      | 53.59(1)  | Ru(3)–Pd–Ru(4)   | 56.49(2)  |
| Ru(4)–Pd–Ru(5)      | 61.19(2)  | Ru(5)–Pd–Ru(2)   | 60.41(1)  |
| Ru(2)–Pd–Ru(4)      | 86.69(2)  | Ru(3)–Pd–Ru(5)   | 85.86(2)  |
| Ru(2)–P(1)–Ru(3)    | 74.48(3)  | Ru(3)–Ru(2)–P(1) | 52.63(3)  |
| Ru(2)–Ru(3)–P(1)    | 52.46(3)  |                  |           |

of **4** to distinguish SO<sub>2</sub> and PPh<sub>3</sub> is remarkable. The related platinum complex Ru<sub>5</sub>Pt(C)(CO)<sub>15</sub>(PMe<sub>2</sub>Ph) has been known to form by the reaction of the platinum analog Ru<sub>5</sub>Pt(C)(CO)<sub>16</sub> with PMe<sub>2</sub>Ph [8].

In the present SO<sub>2</sub>-involved reactions, it is thus obvious that one hetero-metal atom M (M = Co, Rh, Pd) has dramatic influence on the reactivity of five neighboring Ru atoms in molecular cluster complexes [9]. Further investigation is in progress to examine the reactivity of nano-scale metal alloy particles derived from these mixed-metal cluster complexes [10]. Reaction of [Ru<sub>5</sub>M] (M = Co, Rh, Pd) type clusters with SO<sub>2</sub> is summarized in Scheme 2.



Scheme 2.

### 3. Experimental

All reactions were carried out in dry solvents under purified argon. Solvents were purified by standard methods and freshly distilled from Na-benzophenone or CaH<sub>2</sub> under argon before use. The starting materials and complexes [PPN]<sub>2</sub>[Ru<sub>5</sub>(C)(CO)<sub>14</sub>] [11], [PPN]<sub>2</sub>[Ru<sub>6</sub>(C)(CO)<sub>16</sub>] [12], [Rh(cod)(NH<sub>3</sub>)<sub>2</sub>PF<sub>6</sub>] [13], and [Pd(MeCN)<sub>4</sub>][BF<sub>4</sub>]<sub>2</sub> [14] were obtained by published procedures. All other reagents were commercially obtained. <sup>59</sup>Co NMR spectra were measured on a JEOL JNM-400 spectrometer with K<sub>3</sub>[Co(CN)<sub>6</sub>]/D<sub>2</sub>O as the external standard for 0 ppm. IR spectra were recorded on a Perkin–Elmer FT-1650 spectrometer using a CaF<sub>2</sub> liquid cell. All data collections for X-ray analysis were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation. Crystallographic data are given in Tables 7 and 8. Structures were solved by direct methods, expanded using Fourier techniques, and refined by full-matrix least squares. All calculations were

performed using the TEXSAN crystallographic software package of Molecular Structure Corporation (1992). All non-hydrogen atoms were refined with anisotropic atomic displacement parameters (anisotropically), unless otherwise noted. All carbon and oxygen atoms in the complex 3' were refined isotropically. One of four phenyl groups of 9 in the counter cation was treated as a rigid group. All hydrogen atoms were placed in idealized positions, assigned isotropic displacement parameters and allowed to ride on the parent carbons.

#### 3.1. Synthesis of [PPN][Ru<sub>5</sub>Co(C)(CO)<sub>16</sub>] (2)

A mixture of [PPN]<sub>2</sub>[Ru<sub>6</sub>(C)(CO)<sub>16</sub>] (1) (150 mg, 0.070 mmol) and Co<sub>2</sub>(CO)<sub>8</sub> (72 mg, 0.210 mmol) in THF (15 ml) was stirred at room temperature for 5 h. The solvent was evaporated under reduced pressure and the residual dark-red solid was chromatographed on SiO<sub>2</sub> (deactivated with 10 wt% H<sub>2</sub>O). The dark-red solution eluted with Hex/CH<sub>2</sub>Cl<sub>2</sub> = 1:4 was collected and evapo-

Table 7  
Crystallographic data for complexes [PPN][Ru<sub>5</sub>RhC(CO)<sub>16</sub>] (3), [PPN][Ru<sub>5</sub>RhC(CO)<sub>14</sub>(cod)] (3') and Ru<sub>5</sub>PdC(CO)<sub>16</sub> (4)

|   | 3   | 3'  | 4  |
|---|---|---|--|
| Chemical formula                                  | C <sub>53</sub> H <sub>30</sub> NO <sub>16</sub> P <sub>2</sub> RhRu <sub>5</sub> | C <sub>59</sub> H <sub>42</sub> NO <sub>14</sub> P <sub>2</sub> RhRu <sub>5</sub> | C <sub>17</sub> O <sub>16</sub> PdRu <sub>15</sub> |
| Formula weight                                    | 1607.02   | 1659.18   | 1071.9   |
| Crystal system                                    | Orthorhombic  | Monoclinic  | Monoclinic   |
| Space group                                       | <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>                             | <i>P</i> 2 <sub>1</sub>   | <i>P</i> 2 <sub>1</sub> / <i>n</i>                 |
| <i>a</i> (Å)                                      | 15.489(4)   | 9.406(2)  | 9.5343(6)  |
| <i>b</i> (Å)                                      | 17.265(7)   | 38.606(11)  | 36.032(2)  |
| <i>c</i> (Å)                                      | 21.077(2)   | 15.786(3)   | 15.108(1)  |
| $\beta$ (°)                                       |   | 91.983(13)  | 92.329(1)  |
| <i>V</i> (Å <sup>3</sup> )                        | 5636(3)   | 5729.2(2)   | 5185.9(6)  |
| <i>Z</i>  | 4   | 4   | 8  |
| Crystal size                                      | 0.25 × 0.20 × 0.15  | 0.25 × 0.12 × 0.07  | 0.29 × 0.22 × 0.13                                 |
| <i>d</i> <sub>calc</sub> (g cm <sup>-3</sup> )    | 1.894   | 1.924   | 2.746  |
| $\mu$ (cm <sup>-1</sup> )                         | 17.16   | 16.88   | 35.92  |
| Full matrix least square                          | <i>F</i> <sup>2</sup>   | <i>F</i>  | <i>F</i> <sup>2</sup>                              |
| Reflections collected                             | 346641  | 21164   | 38978  |
| Unique reflections                                | 14373   | 12699   | 13995  |
| Reflections observed [ <i>I</i> > 2σ( <i>I</i> )] | 9689  | 8700  | 8659   |
| <i>R</i> <sub>1</sub>                             | 0.0409  | 0.0730  | 0.0571   |
| <i>wR</i> <sub>2</sub>                            | 0.1188  | 0.1294  | 0.1433   |

Table 8  
Crystallographic data for complexes [PPN][Ru<sub>5</sub>RhC(CO)<sub>15</sub>(SO<sub>2</sub>)] (7), [PPN][Ru<sub>5</sub>RhC(CO)<sub>14</sub>(SO<sub>2</sub>)<sub>2</sub>] (8) and [PPh<sub>4</sub>][Ru<sub>5</sub>PdC(CO)<sub>13</sub>(μ<sub>2</sub>-PPh<sub>2</sub>)(PPh<sub>3</sub>)] (9)

|   | 7   | 8  | 9  |
|---|---|--|--|
| Chemical formula                                  | C <sub>52</sub> H <sub>30</sub> NO <sub>17</sub> P <sub>2</sub> RhRu <sub>5</sub> S | C <sub>51</sub> H <sub>30</sub> NO <sub>18</sub> P <sub>2</sub> S <sub>2</sub> RhRu <sub>5</sub> | C <sub>68</sub> H <sub>45</sub> O <sub>13</sub> P <sub>3</sub> PdRu <sub>5</sub> |
| Formula weight                                    | 1643.1  | 1679.1   | 1774.77  |
| Crystal system                                    | Triclinic   | Triclinic  | Triclinic  |
| Space group                                       | <i>P</i> $\bar{1}$  | <i>P</i> $\bar{1}$   | <i>P</i> $\bar{1}$   |
| <i>a</i> (Å)                                      | 14.7468(9)  | 19.163(15)   | 12.765(1)  |
| <i>b</i> (Å)                                      | 16.6767(6)  | 19.623(9)  | 15.227(1)  |
| <i>c</i> (Å)                                      | 11.7539(8)  | 18.617(3)  | 18.030(2)  |
| $\alpha$ (°)                                      | 99.009(1)   | 103.23(2)  | 76.558(2)  |
| $\beta$ (°)                                       | 92.572(1)   | 104.24(1)  | 79.010(2)  |
| $\gamma$ (°)                                      | 80.196(1)   | 115.00(4)  | 78.103(2)  |
| <i>V</i> (Å <sup>3</sup> )                        | 2812.8(3)   | 5692(5)  | 3297.8(5)  |
| <i>Z</i>  | 2   | 4  | 2  |
| Crystal size                                      | 0.57 × 0.42 × 0.12  | 0.36 × 0.25 × 0.14   | 0.28 × 0.21 × 0.11   |
| <i>d</i> <sub>calc</sub> (g cm <sup>-3</sup> )    | 1.95  | 1.959  | 1.787  |
| $\mu$ (cm <sup>-1</sup> )                         | 17.93   | 17.77  | 15.18  |
| Full matrix least square                          | <i>F</i> <sup>2</sup>   | <i>F</i>   | <i>F</i> <sup>2</sup>  |
| Reflections collected                             | 32257   | 59581  | 56414  |
| Unique reflections                                | 15121   | 25927  | 19995  |
| Reflections observed [ <i>I</i> > 2σ( <i>I</i> )] | 13748   | 10813  | 14874  |
| <i>R</i> <sub>1</sub>                             | 0.0399  | 0.0888   | 0.0474   |
| <i>wR</i> <sub>2</sub>                            | 0.1055  | 0.1507   | 0.1304   |

rated to dryness to yield red solid of [PPN][Ru<sub>5</sub>Co(C)(CO)<sub>16</sub>] (2) (108 mg, 97%). Analytically pure sample was obtained by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>–MeOH as red plates. IR  $\nu$ (CO) (CH<sub>2</sub>Cl<sub>2</sub>) 2019(s), 1995(w) cm<sup>-1</sup>. Anal. Calc. for C<sub>53</sub>H<sub>30</sub>CoNO<sub>16</sub>P<sub>2</sub>Ru<sub>5</sub>, C, 40.73; H, 1.93; N, 0.90. Found C, 40.69; H, 1.97; N, 0.86%. <sup>59</sup>Co NMR (94.86 MHz, CD<sub>2</sub>Cl<sub>2</sub>) –2632 ppm ( $\Delta_{1/2}$  = 1115 Hz).

Procedure for the synthesis of 3, 3' and 4 is quite similar to that described for 2.

### 3.2. Synthesis of [PPN][Ru<sub>5</sub>Rh(C)(CO)<sub>16</sub>] (3)

A mixture of [PPN]<sub>2</sub>[Ru<sub>6</sub>(C)(CO)<sub>16</sub>] (1) (200 mg, 0.093 mmol) and Rh<sub>2</sub>(CO)<sub>4</sub>Cl<sub>2</sub> (29 mg, 0.075 mmol) in

THF (20 ml) was stirred for 12 h. After chromatographic purification (CH<sub>2</sub>Cl<sub>2</sub>) and recrystallization (CH<sub>2</sub>Cl<sub>2</sub>–MeOH), [PPN][Ru<sub>5</sub>Rh(C)(CO)<sub>16</sub>] (3) (130 mg, 87%) was obtained as red plates. IR  $\nu$ (CO) (CH<sub>2</sub>Cl<sub>2</sub>) 2021(s) cm<sup>-1</sup>. Anal. Calc. for C<sub>53</sub>H<sub>30</sub>O<sub>16</sub>P<sub>2</sub>RhRu<sub>5</sub>: C, 39.61; H, 1.88; N, 0.87. Found C, 39.43; H, 1.89; N, 0.79%.

### 3.3. Synthesis of [PPN][Ru<sub>5</sub>Rh(C)(CO)<sub>14</sub>(cod)] (3')

A mixture of [PPN]<sub>2</sub>[Ru<sub>5</sub>(C)(CO)<sub>14</sub>] (200 mg, 0.101 mmol) and [Rh(cod)(NH<sub>3</sub>)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> (75 mg, 0.201 mmol) in THF (50 ml) was stirred for 12 h. After chromatographic purification (CH<sub>2</sub>Cl<sub>2</sub>) and recrystallization (CH<sub>2</sub>Cl<sub>2</sub>–Hex), [PPN][Ru<sub>5</sub>Rh(C)(CO)<sub>14</sub>(cod)] (3') (132 mg, 79%) was

obtained as red plates. IR  $\nu(\text{CO})$  ( $\text{CH}_2\text{Cl}_2$ ) 2045(w), 1993(s)  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{59}\text{H}_{42}\text{NO}_{14}\text{P}_2\text{RhRu}_5$ : C, 42.71; H, 2.55; N, 0.84. Found: C, 42.68; H, 2.54; N, 0.84%.

### 3.4. Synthesis of $[\text{PPN}][\text{Ru}_5\text{Pd}(\text{C})(\text{CO})_{16}]$ (**4**)

A mixture of  $[\text{PPN}][\text{Ru}_5\text{Co}(\text{C})(\text{CO})_{16}]$  (**2**) (100 mg, 0.073 mmol) and  $[\text{Pd}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$  (155 mg, 0.367 mmol) in THF (60 ml) was stirred for 12 h. After chromatographic purification (Hex/ $\text{CH}_2\text{Cl}_2$  = 1:4) and recrystallization ( $\text{CH}_2\text{Cl}_2$ –Hex),  $\text{Ru}_5\text{Pd}(\text{C})(\text{CO})_{16}$  (**4**) (57 mg, 72%) was obtained as red plates. IR  $\nu(\text{CO})$  ( $\text{CH}_2\text{Cl}_2$ ) 2058(s), 2026(w)  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{17}\text{O}_{16}\text{Ru}_5\text{Pd}$ : C, 19.05; H, 0.00; N, 0.00. Found C, 19.07; H, 0.00; N, 0.00%.

### 3.5. Synthesis of $[\text{PPN}][\text{Ru}_5\text{Co}(\text{C})(\text{CO})_{15}(\text{SO}_2)]$ (**5**)

After bubbling  $\text{SO}_2$  for 10 min into a solution of  $[\text{PPN}][\text{Ru}_5\text{Co}(\text{C})(\text{CO})_{16}]$  (**2**) (100 mg, 0.064 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 ml), the resulting mixture was stirred at room temperature for 4 h. The solvent was evaporated under reduced pressure and the residual dark-red solid was chromatographed on  $\text{SiO}_2$  (deactivated with 10 wt%  $\text{H}_2\text{O}$ ). The first red solution eluted with Hex/ $\text{CH}_2\text{Cl}_2$  = 1:2 was collected and evaporated to dryness to yield red solid of  $[\text{PPN}][\text{Ru}_5\text{Co}(\text{C})(\text{CO})_{16}]$  (**2**) (15 mg). The second dark-red solution eluted with  $\text{CH}_2\text{Cl}_2$  was collected and evaporated to dryness to yield red solid of  $[\text{PPN}][\text{Ru}_5\text{Co}(\text{C})(\text{CO})_{15}(\text{SO}_2)]$  (**5**) (26 mg, 30%). Analytically pure sample was obtained by recrystallization from  $\text{CH}_2\text{Cl}_2$ –MeOH as red plates. IR  $\nu(\text{CO})$  ( $\text{CH}_2\text{Cl}_2$ ) 2032(s)  $\text{cm}^{-1}$ ;  $\nu(\text{SO})$  (KBr) 1065(s)  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{52}\text{H}_{30}\text{CoNO}_{17}\text{P}_2\text{Ru}_5\text{S}$ : C, 39.06; H, 1.89; N, 0.88. Found: C, 39.02; H, 1.89; N, 0.84%.  $^{59}\text{Co}$  NMR (94.86 MHz,  $\text{CD}_2\text{Cl}_2$ )  $-3004$  ( $\Delta_{1/2}$  = 4272 Hz) (**5-1**),  $-3363$  ( $\Delta_{1/2}$  = 1709 Hz) (**5-2**).

Procedure for the synthesis of **6**, **7** and **8** is quite similar to that described for **5**.

### 3.6. Synthesis of $[\text{PPN}][\text{Ru}_5\text{Co}(\text{C})(\text{CO})_{14}(\text{SO}_2)_2]$ (**6**)

After bubbling  $\text{SO}_2$  into a solution of  $[\text{PPN}][\text{Ru}_5\text{Co}(\text{C})(\text{CO})_{16}]$  (**2**) (100 mg, 0.064 mmol) in  $\text{CH}_2\text{Cl}_2$  (40 ml), the resulting mixture was stirred for 12 h. After chromatographic purification ( $\text{CH}_2\text{Cl}_2$ /THF = 8:1) and recrystallization ( $\text{CH}_2\text{Cl}_2$ –MeOH),  $[\text{PPN}][\text{Ru}_5\text{Co}(\text{C})(\text{CO})_{14}(\text{SO}_2)_2]$  (**6**) (68 mg, 65%) (57 mg, 72%) was obtained as red plates. IR  $\nu(\text{CO})$  ( $\text{CH}_2\text{Cl}_2$ ) 2041(s)  $\text{cm}^{-1}$ ;  $\nu(\text{SO}_2)$  (KBr) 1068(s)  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{51}\text{H}_{30}\text{CoNO}_{18}\text{P}_2\text{Ru}_5\text{S}_2$ : C, 37.46; H, 1.85; N, 0.86. Found: C, 37.02; H, 1.89; N, 0.89%.  $^{59}\text{Co}$  NMR (94.86 MHz,  $\text{CD}_2\text{Cl}_2$ )  $-3597$  ppm ( $\Delta_{1/2}$  = 1566 Hz).

### 3.7. Synthesis of $[\text{PPN}][\text{Ru}_5\text{Rh}(\text{C})(\text{CO})_{15}(\text{SO}_2)]$ (**7**)

After bubbling  $\text{SO}_2$  into a solution of  $[\text{PPN}][\text{Ru}_5\text{Rh}(\text{C})(\text{CO})_{16}]$  (**3**) (50 mg, 0.031 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 ml), the resulting mixture was stirred for 12 h. After chromatographic

purification ( $\text{CH}_2\text{Cl}_2$ /THF = 8:1) and recrystallization ( $\text{CH}_2\text{Cl}_2$ –MeOH),  $[\text{PPN}][\text{Ru}_5\text{Rh}(\text{C})(\text{CO})_{15}(\text{SO}_2)]$  (**7**) (47 mg, 93%) was obtained as red plates. IR  $\nu(\text{CO})$  ( $\text{CH}_2\text{Cl}_2$ ) 2031(s)  $\text{cm}^{-1}$ ;  $\nu(\text{SO}_2)$  (KBr) 1064(s)  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{52}\text{H}_{30}\text{NO}_{17}\text{P}_2\text{RhRu}_5\text{S}$ : C, 38.01; H, 1.84; N, 0.85. Found: C, 37.81; H, 1.89; N, 0.77%.

### 3.8. Synthesis of $[\text{PPN}][\text{Ru}_5\text{Rh}(\text{C})(\text{CO})_{14}(\text{SO}_2)_2]$ (**8**)

After bubbling  $\text{SO}_2$  into a solution of  $[\text{PPN}][\text{Ru}_5\text{Rh}(\text{C})(\text{CO})_{14}(\text{cod})]$  (**3'**) (80 mg, 0.048 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 ml), the resulting mixture was stirred for 12 h. After chromatographic purification ( $\text{CH}_2\text{Cl}_2$ /THF = 8:1) and recrystallization ( $\text{CH}_2\text{Cl}_2$ –MeOH),  $[\text{PPN}][\text{Ru}_5\text{Rh}(\text{C})(\text{CO})_{14}(\text{SO}_2)_2]$  (**8**) (66 mg, 82%) was obtained as red plates. IR  $\nu(\text{CO})$  ( $\text{CH}_2\text{Cl}_2$ ) 2041(s)  $\text{cm}^{-1}$ ;  $\nu(\text{SO})$  (KBr) 1068(s)  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{51}\text{H}_{30}\text{NO}_{18}\text{P}_2\text{RhRu}_5\text{S}_2$ : C, 36.48; H, 1.80; N, 0.83. Found: C, 36.41; H, 1.71; N, 0.55%.

### 3.9. Synthesis of $[\text{PPh}_4][\text{Ru}_5\text{Pd}(\text{C})(\text{CO})_{13}(\mu_2\text{-PPh}_2)(\text{PPh}_3)]$ (**9**)

A mixture of  $\text{PdRu}_5(\text{C})(\text{CO})_{16}$  (50.0 mg, 0.047 mmol) and  $\text{PPh}_3$  (122.4 mg, 0.47 mmol) in Hex (80 ml) was stirred at room temperature for 24 h. The solvent was evaporated under reduced pressure and the dark-red residue was chromatographed on  $\text{SiO}_2$  (deactivated with 10 wt%  $\text{H}_2\text{O}$ ). The dark-red solution eluted with  $\text{CH}_2\text{Cl}_2$ /Hex = 1:2 was collected and evaporated to dryness to yield red solid of  $[\text{PPh}_4][\text{Ru}_5\text{Pd}(\text{C})(\text{CO})_{13}(\mu_2\text{-PPh}_2)(\text{PPh}_3)]$  (**9**) (46 mg, 56%). Analytically pure sample was obtained by recrystallization from  $\text{CH}_2\text{Cl}_2$ –Hex as red plates. IR  $\nu(\text{CO})$  ( $\text{CH}_2\text{Cl}_2$ ) 2037m, 1995s, 1977sh, 1934w  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{68}\text{H}_{45}\text{O}_{13}\text{P}_3\text{PdRu}_5$ : C, 46.02; H, 2.56; N, 0.00. Found: C, 46.13; H, 2.52; N, 0.00%.

## 4. Supplementary material

CCDC 635713, 635714, 635715, 635716, 635717 and 635718 contain the supplementary crystallographic data for **3**, **3'**, **4**, **7**, **8** and **9**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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