



# Linking of phosphinidene-capped triruthenium carbonyl clusters with diphosphine ligands



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## ABSTRACT

A phosphinidene-capped triruthenium cluster  $\text{Ru}_3(\text{CO})_9(\mu\text{-H})_2(\mu_3\text{-PMes})$  (**1**, Mes = mesityl = 2,4,6-trimethylphenyl) reacted with diphosphines to afford linked clusters  $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu_3\text{-PMes})]_2(\mu\text{-dppe})$  (**2a**, dppe = 1,2-bis(diphenylphosphino)ethane),  $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu_3\text{-PMes})]_2(\mu\text{-dppa})$  (**2b**, dppa = bis(diphenylphosphino)acetylene), and  $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu_3\text{-PMes})]_2(\mu\text{-dppf})$  (**2c**, dppf = 1,1'-bis(diphenylphosphino)ferrocene) in high yields. The molecular structures of **2a** and **2c** were confirmed by single-crystal X-ray diffraction.

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## 1. Introduction

Metal clusters consisting of structurally well-defined polynuclear cores are attractive synthetic targets in the field of synthetic metal-cluster chemistry due to their expected unique properties such as various coordination modes [1a–c], electrochemical properties [1], and catalytic advantages [1e]. Connection of cluster units with some spacer ligands is a useful method to construct such large clusters [2,3]. However, it is important to consider selective and high-yield synthesis of connected or linked large clusters as it is sometimes prevented by fragmentation caused by metal–metal bond cleavage or pyrolysis, and/or intramolecular coordination of bridging ligands [3,4]. For example, the reaction of  $\text{Ru}_3(\text{CO})_{12}$  with 0.5 equiv of bis(diphenylphosphino)acetylene (dppa) produced  $[\text{Ru}_3(\text{CO})_{11}]_2(\mu\text{-dppa})$  in 71% yield; however, the resulting compound thermally decomposed to afford  $\text{Ru}_5(\mu_5\text{-}\kappa^3\text{C,C,P-C}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_{13}$  upon heating (90 °C, 1 h) [3b]. A similar reaction of  $\text{Ru}_3(\text{CO})_{12}$  with 1,1'-bis(diphenylphosphino)ferrocene (dppf) predominantly gave intramolecularly coordinated products such as  $\text{Ru}_3(\text{CO})_{10}(\text{dppf})$  [3f]. A linked cluster  $[\text{Ru}_3(\text{CO})_{11}]_2(\mu\text{-dppf})$  was only obtained in 9.4% yield.

We previously reported the X-ray crystal structure of a phosphinidene-capped triruthenium cluster,  $\text{Ru}_3(\text{CO})_9(\mu\text{-H})_2(\mu_3\text{-PMes})$  (**1**, Mes = mesityl = 2,4,6-trimethylphenyl) and its regioselective

monosubstitution reaction with  $\text{PH}_2\text{Mes}$  to produce  $\text{Ru}_3(\text{CO})_8(\text{PH}_2\text{Mes})(\mu\text{-H})_2(\mu_3\text{-PMes})$  quantitatively under hexane refluxing [5]. During the reaction, the trinuclear cluster core remained intact probably due to the existence of the bridging phosphinidene ligand. Almost no redistribution or decomposition of the cluster core was observed under heating. In addition, the  $\mu_3\text{-PMes}$  group presumably allows selectivity for monosubstitution reaction because of increased bulk. Therefore, we applied this high-yield thermal reaction to some bidentate phosphines to build up large clusters containing **1** as a cluster unit. Here we report the synthesis of clusters formulated as  $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu_3\text{-PMes})]_2(\mu\text{-diphosphine})$  and their X-ray crystal structures.

## 2. Experimental

### 2.1. Materials and methods

All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Toluene and hexane were distilled from sodium-benzophenone ketyl just before use. Dichloromethane was dried over calcium hydride and purified by trap-to-trap distillation. Toluene-*d*<sub>8</sub> was dried over potassium mirrors and vacuum transferred to nuclear magnetic resonance (NMR) tubes directly before use. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded on a Bruker AVANCE 300 spectrometer. <sup>1</sup>H NMR chemical shifts were referenced to a residual proton signal of CD<sub>2</sub>Cl<sub>2</sub> (δ 5.32) or toluene-*d*<sub>8</sub> (δ 2.09). <sup>13</sup>C{<sup>1</sup>H} NMR chemical shifts

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were referenced to the carbon signal of  $\text{CD}_2\text{Cl}_2$  ( $\delta$  53.4).  $^{31}\text{P}\{^1\text{H}\}$  NMR chemical shifts were referenced to the signal of 85%  $\text{H}_3\text{PO}_4$  aqueous solution ( $\delta$  0) used as an external standard. Infrared (IR) spectra were measured on a HORIBA FT-730 spectrometer. Elemental analyses were performed at the Research and Analytical Center for Giant Molecules, Tohoku University. Complex  $\text{Ru}_3(\text{CO})_9(\mu\text{-H})_2(\mu_3\text{-PMes})$  (**1**) was prepared according to the literature method [5]. All other reagents including 1,2-bis(diphenylphosphino)ethane (dppe), dppe, dppa, and dppf were purchased and used as received.

## 2.2. Synthesis of the clusters

### 2.2.1. Synthesis of $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu_3\text{-PMes})]_2(\mu\text{-dppe})$ (**2a**)

A hexane solution (15 mL) of  $\text{Ru}_3(\text{CO})_9(\mu\text{-H})_2(\mu_3\text{-PMes})$  (**1**) (45 mg, 0.064 mmol) and dppe (13 mg, 0.033 mmol) was refluxed overnight. The solvent was evaporated and the resulting yellow residue was extracted with tetrahydrofuran (THF). The THF solution was adsorbed on Celite and the solvent was removed under reduced pressure. The Celite was placed on the top of the column, which was charged with silica gel (2 cm  $\phi \times$  4 cm), and eluted with hexane/toluene (2/1) under  $\text{N}_2$  pressure. A yellow fraction was collected to give  $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu_3\text{-PMes})]_2(\mu\text{-dppe})$  (**2a**) in 72% yield (40 mg, 0.023 mmol).

**2a:**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -18.88 (dd, 4H,  $^2J_{\text{PH}} = 15.4$  Hz,  $^2J_{\text{PH}} = 11.3$  Hz, RuH), 2.25 (s, 6H, *p*- $\text{CH}_3$ ), 2.31 (s, 4H,  $\text{CH}_2$ ), 2.63 (s, 12H, *o*- $\text{CH}_3$ ), 6.93 (d, 4H,  $^4J_{\text{PH}} = 3.6$  Hz,  $\text{C}_6\text{H}_2\text{Me}_3$ ), 7.22–7.45 (m, 20H, PPh).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  26.2 (d,  $^2J_{\text{PP}} = 110.6$  Hz, PPh<sub>2</sub>), 230.8 (d,  $^2J_{\text{PP}} = 110.6$  Hz, PMes).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  21.7 (s, *p*-Me), 26.7 (d,  $J_{\text{PC}} = 12.1$  Hz, *o*-Me), 29.1 (br m, PCH<sub>2</sub>), 129.4 (m), 130.3 (d,  $J_{\text{PC}} = 8.3$  Hz), 131.2 (s), 132.3 (m), 134.2 (d,  $J_{\text{PC}} = 40.0$  Hz), 140.8 (d,  $J_{\text{PC}} = 3.8$  Hz), 142.4 (d,  $J_{\text{PC}} = 8.3$  Hz) (Ph), 190.8 (s), 192.0 (m), 196.7 (m), 200.7 (m), 201.3 (s) (CO). IR  $\nu_{\text{CO}}$  (KBr,  $\text{cm}^{-1}$ ): 2072 (s), 2031 (vs), 2011 (s), 1990 (s), 1971 (s), 1961 (s). *Anal. Calc.* for  $\text{C}_{60}\text{H}_{50}\text{O}_{16}\text{P}_4\text{Ru}_6$ : C, 41.01; H, 2.87. Found: C, 40.66; H, 3.10%.

### 2.2.2. Synthesis of $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu_3\text{-PMes})]_2(\mu\text{-dppa})$ (**2b**)

The complex  $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu_3\text{-PMes})]_2(\mu\text{-dppa})$  (**2b**) was prepared in 91% yield in a procedure similar to that described in Section 2.2.1 using dppa instead of dppe.

**2b:**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -18.52 (dd, 4H,  $^2J_{\text{PH}} = 15.0$  Hz,  $^2J_{\text{PH}} = 13.4$  Hz, RuH), 2.24 (s, 6H, *p*- $\text{CH}_3$ ), 2.67 (s, 12H, *o*- $\text{CH}_3$ ), 6.95 (d, 4H,  $^4J_{\text{PH}} = 3.6$  Hz,  $\text{C}_6\text{H}_2\text{Me}_3$ ), 7.30–7.54 (m, 20H, PPh).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.32 (d,  $^2J_{\text{PP}} = 117.7$  Hz, PPh<sub>2</sub>), 234.9 (d,  $^2J_{\text{PP}} = 117.7$  Hz, PMes).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  21.2 (s, *p*-Me), 26.6 (d,  $J_{\text{PC}} = 11.3$  Hz) (*o*-Me), 106.6 (dd,  $J_{\text{PC}} = 60.5$  Hz,  $J_{\text{PC}} = 4.1$  Hz, PCCP), 129.5 (d,  $J_{\text{PC}} = 11.3$  Hz), 130.4 (d,  $J_{\text{PC}} = 8.3$  Hz), 130.9 (s), 131.4 (m), 131.9 (d,  $J_{\text{PC}} = 13.6$  Hz), 133.4 (d,  $J_{\text{PC}} = 49.5$  Hz), 141.1 (m), 142.5 (d,  $J_{\text{PC}} = 9.2$  Hz) (Ph), 190.8 (m), 190.6 (m), 200.5 (m), 201.2 (s), 202.4 (m) (CO). IR  $\nu_{\text{CO}}$  (KBr,  $\text{cm}^{-1}$ ): 2073 (s), 2035 (vs), 2017 (s), 1996 (s), 1977 (s), 1969 (s). *Anal. Calc.* for  $\text{C}_{60}\text{H}_{46}\text{O}_{16}\text{P}_4\text{Ru}_6$ : C, 41.10; H, 2.64. Found: C, 41.23; H, 2.82%.

### 2.2.3. Synthesis of $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu_3\text{-PMes})]_2(\mu\text{-dppf})$ (**2c**)

The complex  $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu_3\text{-PMes})]_2(\mu\text{-dppf})$  (**2c**) was prepared in 92% yield by a procedure similar to that described in Section 2.2.1 using dppf instead of dppe.

**2c:**  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  -18.49 (dd, 4H,  $^2J_{\text{PH}} = 15.4$  Hz,  $^2J_{\text{PH}} = 15.2$  Hz, RuH), 2.25 (s, 6H, *p*- $\text{CH}_3$ ), 2.68 (s, 12H, *o*- $\text{CH}_3$ ), 3.95 (d, 4H,  $^3J_{\text{PH}} = 1.5$  Hz, Cp), 4.39 (s, 4H, Cp), 6.96 (d, 4H,  $^4J_{\text{PH}} = 3.9$  Hz,  $\text{C}_6\text{H}_2\text{Me}_3$ ), 7.12–7.32 (m, 20H, PPh).  $^{31}\text{P}\{^1\text{H}\}$  NMR (121 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  22.1 (d,  $^2J_{\text{PP}} = 120.3$  Hz, PPh<sub>2</sub>), 229.3 (d,  $^2J_{\text{PP}} = 120.3$  Hz, PMes).  $^{13}\text{C}\{^1\text{H}\}$  NMR (75.5 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  21.2 (s, *p*-Me), 26.7 (d,  $J_{\text{PC}} = 11.3$  Hz, *o*-Me), 74.5 (d,  $J_{\text{PC}} = 6.9$  Hz), 75.2 (d,  $J_{\text{PC}} = 12.7$  Hz),

79.7 (d,  $J_{\text{PC}} = 44.8$  Hz) (Cp), 128.6 (d,  $J_{\text{PC}} = 9.1$  Hz), 130.4 (s), 130.5 (s), 131.0 (s), 132.9 (d,  $J_{\text{PC}} = 11.3$  Hz), 136.7 (d,  $J_{\text{PC}} = 44.8$  Hz), 140.9 (m), 142.5 (d,  $J_{\text{PC}} = 8.0$  Hz) (Ph), 191.1 (s), 192.4 (m), 196.8 (m), 200.9 (s), 201.6 (s) (CO). IR  $\nu_{\text{CO}}$  (KBr,  $\text{cm}^{-1}$ ): 2071 (s), 2031 (vs), 2013 (s), 2002 (s), 1982 (s), 1973 (s), 1959 (s). *Anal. Calc.* for  $\text{C}_{68}\text{H}_{54}\text{FeO}_{16}\text{P}_4\text{Ru}_6$ : C, 42.69; H, 2.84. Found: C, 42.53; H, 3.01%.

## 2.3. Thermal stability testing of cluster compounds

Clusters **2a**, **2b**, and **2c** were placed in Pyrex NMR tubes (5 mm o.d.), and toluene-*d*<sub>8</sub> (ca. 0.5 mL) was vacuum transferred under high vacuum. The NMR tubes were flame-sealed and heated in the oil bath. The  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were periodically collected to determine the degree of decomposition over time.

## 2.4. X-ray crystal structure analysis

### 2.4.1. X-ray crystal structure determination of **2a** and **2c**

The crystals of **2a** and **2c** suitable for X-ray crystal structure determination were mounted on a glass fiber. The intensity data were collected on a RIGAKU RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo  $K\alpha$  radiation to a maximum  $2\theta$  value of 55.0 at 150 K. A total of 44 images, corresponding to 220.0° oscillation angles, were collected with two different goniometer settings. Exposure time was 1.30 min per degree. Readout was performed in the 0.100 mm pixel mode. Numerical absorption corrections were applied on the crystal shape. The structures were solved by Patterson and Fourier transform methods. All non-hydrogen atoms were refined by full-matrix least-squares techniques with anisotropic displacement parameters based on  $F^2$  with all reflections. The positions of hydrogen atoms directly attached to ruthenium atoms in **2a** and **2c** were found by difference Fourier synthesis and refined with isotropic thermal parameters. All other hydrogen atoms were placed at their geometrically calculated positions and added to the structure factor calculations without refinement. All calculations were performed using SHELXS and SHELXL [6].

**2a:** The final residue  $R_1$  and the weighted  $wR_2$  were  $R_1 = 0.0715$  and  $wR_2 = 0.1622$  for 7244 reflections with  $I > 2\sigma(I)$ . Crystallographic data are listed in Table S1.1.

**2c:** The final residue  $R_1$  and the weighted  $wR_2$  were  $R_1 = 0.0456$  and  $wR_2 = 0.1386$  for 15249 reflections with  $I > 2\sigma(I)$ . Crystallographic data are listed in Table S1.2.

## 3. Results and discussion

A hexane solution of **1** and 0.5 equiv. of dppe was refluxed overnight to afford  $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu_3\text{-PMes})]_2(\mu\text{-dppe})$  (**2a**) in 72% yield (Scheme 1). Complexes  $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu_3\text{-PMes})]_2(\mu\text{-dppa})$  (**2b**) and  $[\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu_3\text{-PMes})]_2(\mu\text{-dppf})$  (**2c**) were also prepared by reactions of **1** with dppa and dppf in 91% and 92% yields, respectively. Complexes **2a** and **2c** are fairly thermally stable. They survived at 90 °C and started to decompose upon heating at 130 °C. The half-lives of **2a** and **2c** at 130 °C are estimated to be ca. 4 days. Complex **2b** is less thermally stable and its half-life at 90 °C is ca. 1.5 days.

Complexes **2a–c** were fully characterized by elemental analysis, NMR, and IR spectroscopy. X-ray crystal structures of **2a** and **2c** were determined. The crystallographic data are shown in Table 1. However, good crystals of **2b** were not obtained in spite of a number of trials. An ORTEP diagram of **2a** is presented in Fig. 1. It is clearly shown that two  $\text{Ru}_3$  cluster units,  $\text{Ru}_3(\text{CO})_8(\mu\text{-H})_2(\mu_3\text{-PMes})$ , are connected with a dppe ligand in an *anti* geometry with respect to the dppe ligand. There is an inversion center at the middle of the ethylene chain of the dppe ligand. The selected

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