

Synthesis and crystal structures of triruthenium clusters containing phosphinidene ligands

Taeko Kakizawa

College of Science and Engineering, Kanto Gakuin University, Mitsuurahigashi, Kanazawa-ku, Yokohama, Kanagawa 236-8501, Japan. E-mail: kg100683@kanto-gakuin.ac.jp

Received: September 02, 2019; accepted: November 12, 2019

Abstract: The manipulation of trinuclear ruthenium clusters $[\text{Ru}_3(\text{CO})_9(\mu\text{-H})_2(\mu_3\text{-PMes})]$ (**1**) with PH_2Ph in refluxing hexane produces $[\text{Ru}_3(\text{CO})_8(\text{PH}_2\text{Ph})(\mu\text{-H})_2(\mu_3\text{-PMes})]$ (**2**) where PH_2Ph coordinates as a terminal ligand. Cluster **2** is converted to $[\text{Ru}_3(\text{CO})_9(\mu_3\text{-PMes})(\mu_3\text{-PPh})]$ (**3**) when heated in a toluene solution in the presence of CO. This study provides the solutions of the X-ray structures for clusters **2** and **3**.

Keywords: cluster; X-ray crystal structure; ruthenium; phosphinidene.

1. INTRODUCTION

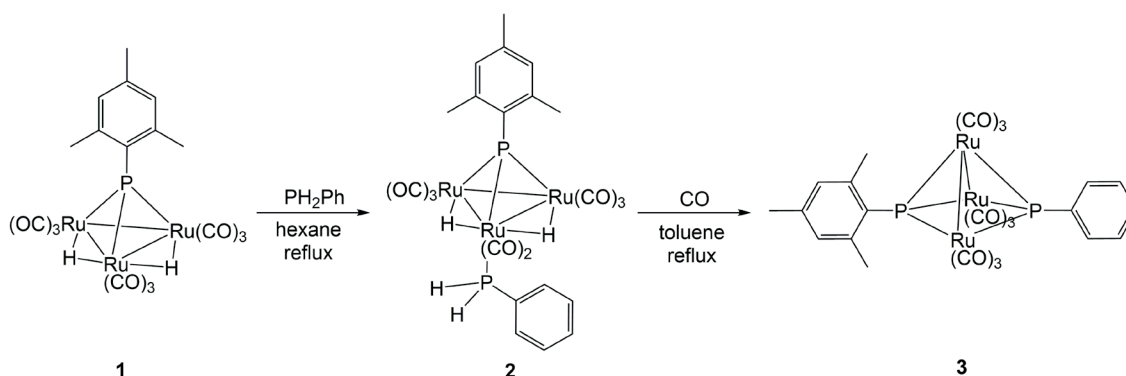
Phosphinidene is a versatile ligand that bridges transition metals in several coordination modes [1,2]. Many transition metal clusters with phosphinidene ligands have been reported along with their chemical properties, structures, and preparation methods [3–6]. I previously reported the synthesis of phosphinidene-capped, ruthenium, carbonyl clusters and their expansion reactions using the produced clusters as building blocks containing more ligands or vertices [7,8]. The reactions demonstrated that the phosphinidene ligand is beneficial in preserving the ruthenium cluster core. Cluster expansion reactions are useful for preparing large, complicated molecules. In this study, stepwise formation of triruthenium clusters containing two types of phosphinidene ligands is examined, beginning with the reaction of a phosphinidene-capped cluster with a terminal phosphine ligand. Clusters produced via these methods were analyzed by X-ray studies.

2. EXPERIMENTAL

All procedures were performed under a dry nitrogen atmosphere using Schlenk techniques. Before usage, toluene and hexane were distilled from sodium benzophenone ketyl. Dichloromethane was evaporated over calcium hydride and purified by trap-to-trap distillation, and benzene- d_6 was dried over potassium mirrors. ^1H and ^{31}P NMR spectra were obtained using a Bruker AVANCE 300 spectrometer and IR spectra were obtained using a HORIBA FT-730 spectrometer. Elemental analyses were performed at the Instrumental Analysis Center for Chemistry, Tohoku University. The Ru_3 cluster $[\text{Ru}_3(\text{CO})_9(\mu\text{-H})_2(\mu_3\text{-PMes})]$ (**1**) was prepared as previously reported [7]. All other reagents were purchased and used without further purification.

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

Ru_3 cluster **1** (50 mg, 0.071 mmol) and PH_2Ph (10 mg, 0.091 mmol) were dissolved in 20 mL of hexane, and the solution was refluxed overnight. The solvent was evaporated at low pressure and the resulting yellow residue was dissolved in tetrahydrofuran (THF). The THF solution was adsorbed onto Celite™ and the solvent was removed under low pressure. The Celite was then placed on a silica gel column (2 cmφ/4 cm) in a hexane/toluene (5/1) mixture under N_2 pressure. A yellow fraction with a yield of 57% (32 mg, 0.041 mmol) was collected as cluster **2**. ^1H NMR (300 MHz, CD_2Cl_2): δ –18.80 (brn, 2H, $\mu\text{-H}$), 2.24 (s, 3H, $p\text{-CH}_3$), 2.67 (s, 6H, $o\text{-CH}_3$), 5.85 (brd, 2H, $J_{\text{PH}} = 144.6$ Hz, PH), 6.91–7.39 (m, 7H, ArH). $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 CD_2Cl_2): δ –68.9 (d, $J_{\text{pp}} = 113.6$ Hz, PH_2Ph), 233.2 (d, $J_{\text{pp}} = 113.6$ Hz,



Scheme 1. Synthetic scheme for compounds **2** and **3**

PMes). IR ν_{CO} (KBr, cm^{-1}): 2077 (s), 2043 (s), 2033 (vs), 2008 (m), 1997 (s), 1989 (s), 1968 (s). Anal. Calcd for $\text{C}_{23}\text{H}_{20}\text{O}_8\text{P}_2\text{Ru}_3$: C, 34.99; H 2.55. Found: C, 35.05; H, 2.69.

Synthesis of $[\text{Ru}_3(\text{CO})_9(\mu_3\text{-PMes})(\mu_3\text{-PPh})]$ (3)

Cluster **2** (30 mg, 0.038 mmol) was dissolved in toluene (20 mL) and refluxed overnight under a CO atmosphere. Silica gel chromatography was performed using the methods discussed above and compound **3** was obtained as a yellow fraction with a 42% yield (13 mg, 0.016 mmol) along with several unidentified products. ^1H NMR (300 MHz, C_6D_6): δ 1.91 (s, 3H, *p*- CH_3), 2.74 (s, 3H, *o*- CH_3), 2.75 (s, 3H, *o*- CH_3), 6.59–7.55 (m, 7H, ArH). IR

ν_{CO} (KBr, cm^{-1}): 2056 (s), 2034 (s), 2008 (s), 1996 (s), 1984 (s), 1979 (s).

X-ray diffraction data were collected at 150(2) K with a Rigaku R-Axis RAPID imaging plate using Mo radiation ($\lambda = 0.71069$ Å). The structural identification and refinement were performed using the SHELXL-97 software [9]. Two H atoms bridging Ru atoms and two H atoms on the P atom observed in cluster **2** within a difference-Fourier map were freely refined. All other H atoms were placed at geometrically calculated positions, i.e., C–H = 0.95 or 0.98 Å. Crystallographic data from the structural analyses are available at the Cambridge Crystallographic Data Center, CCDC 1950762 and 1950763.

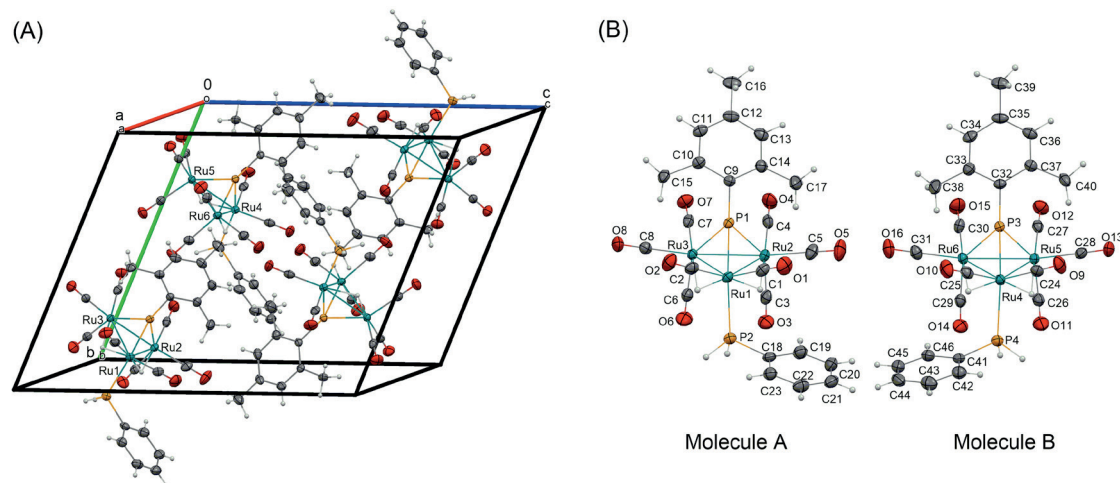


Figure 1. (A) Packing of $[\text{Ru}_3(\text{CO})_8(\text{PH}_2\text{Ph})(\mu\text{-H})_2(\mu_3\text{-PMes})]$ (**2**) along the *a* axis and (B) the structure of the two independent molecules, A and B, of cluster **2**. The thermal ellipsoids are shown at 50% probability.

3. RESULTS AND DISCUSSION

The thermal reaction of $[\text{Ru}_3(\text{CO})_9(\mu\text{-H})_2(\mu_3\text{-PMes})]$ (**1**) with PH_2Ph in a hexane solution formed the complex $[\text{Ru}_3(\text{CO})_8(\text{PH}_2\text{Ph})(\mu\text{-H})_2(\mu_3\text{-PMes})]$ (**2**) (Scheme 1). X-ray analysis suggests that complex **2** is crystallized in the triclinic crystal system with P-1 space group. Complex **2** crystallized with two independent molecules in an asymmetric unit (Figure 1A). The structure of cluster **2** maintains a phosphinidene-capped, triangular, and pyramidal core, in which the PH_2Ph moiety coordinates as a terminal phosphine ligand (Figure 1B). The phenyl groups of the two independent molecules, A and B, are inclined in di-

fferent directions (Fig. 1B), probably due to intermolecular interactions of aromatic rings (Figure 2). Selected bond lengths and angles for cluster **2** are presented in Table 1. The Ru–Ru bond intervals containing hydrogen bridges, i.e., Ru1–Ru2, Ru1–Ru3, Ru4–Ru5, and Ru4–Ru6, are slightly longer than those without hydrogen bridges, i.e., Ru2–Ru3 and Ru5–Ru6, for molecules A and B, respectively.

Heating complex **2** in a toluene solution under CO atmosphere produced $[\text{Ru}_3(\text{CO})_9(\mu_3\text{-PMes})(\mu_3\text{-PPh})]$ (**3**). The crystalline structure of **3** is depicted in Figure 3, with selected bond lengths and angles presented in Table 2. The complex **3** is crystallized in the monoclinic crystal system with $P2_1/c$ space group. It

Table 1. Selected bond lengths [Å] and angles [°] for molecules A and B of complex **2**.

Molecule A		Molecule B	
Ru1–Ru2	2.9270(4)	Ru4–Ru5	2.9345(3)
Ru1–Ru3	2.9319(3)	Ru4–Ru6	2.9342(3)
Ru2–Ru3	2.8035(3)	Ru5–Ru6	2.8035(3)
Ru1–P1	2.3243(8)	Ru4–P3	2.3261(8)
Ru2–P1	2.3178(8)	Ru5–P3	2.3215(8)
Ru3–P1	2.3218(8)	Ru6–P3	2.3152(8)
Ru1–P2	2.3622(8)	Ru4–P4	2.3627(8)
Ru2–Ru1–Ru3	57.176(8)	Ru5–Ru4–Ru6	57.071(8)
Ru1–Ru2–Ru3	61.499(8)	Ru4–Ru5–Ru6	61.459(9)
Ru1–Ru3–Ru2	61.325(9)	Ru4–Ru6–Ru5	61.470(8)

contains a square, pyramidal Ru₃P₂ core, with a distorted square base comprising two phosphorus atoms, two ruthenium atoms, and a capped Ru(CO)₃ moiety. The pyramidal core possesses two different phosphinidene ligands, i.e., μ₃-PMes and μ₃-PPh. The creation of Ru₃P₂ clusters containing two types of phosphinidene ligands is possible through several synthetic approaches

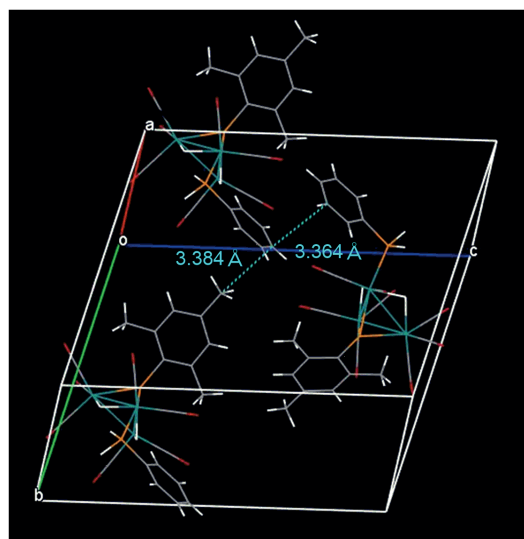


Figure 2. Partial packing of **2**. The pale blue dashed lines are C16–C21 (3.384 Å) and C21–C45 (3.364 Å).

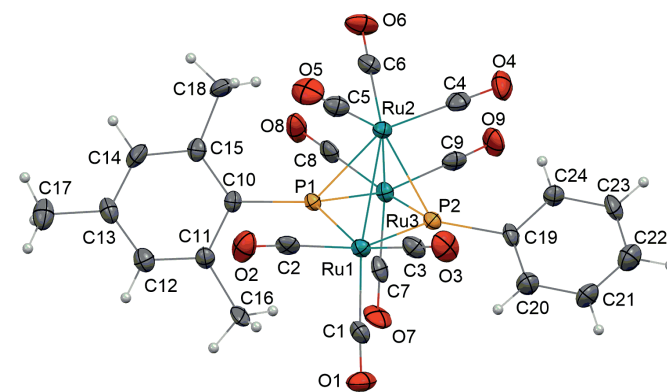


Figure 3. The structure of [Ru₃(CO)₉(μ₃-PMes)(μ₃-PPh)] (**3**). Thermal ellipsoids are shown at 50% probability.

Table 2. Selected bond lengths [Å] and angles [°] for complex **3**.

Ru1–Ru2	2.8700(10)	Ru2–Ru3	2.8766(10)
Ru1–P1	2.363(2)	Ru1–P2	2.315(2)
Ru2–P1	2.391(2)	Ru2–P2	2.383(2)
Ru3–P1	2.357(2)	Ru3–P2	2.331(2)
Ru1–Ru2–Ru3	82.23(3)	Ru1–P1–Ru3	106.37(9)
P1–Ru2–P3	69.89(8)	Ru1–P2–Ru3	108.86(9)

In conclusion, the thermal reaction between complex **1** and PH₂Ph formed trinuclear ruthenium, complex **2**, incorporating PH₂Ph as a terminal phosphine ligand. Subsequent thermolysis of complex **2**, in the presence of CO, produced asymmetric Ru₃P₂, i.e., cluster **3**. X-ray analyses of clusters **2** and **3** revealed that compound **2** crystallized with two independent molecules in an asymmetric unit, while the Ru₃P₂ cluster **3** combined two different phosphinidene ligands into a molecule.

Acknowledgments

This study was supported in part by a Waseda University Grant for Special Research Projects (project number 2017K-199). The author thanks Dr. H. Hashimoto and Professor H. Tobita for their useful assistance.

4. REFERENCES

- [1] García, M. E.; García-Vivó, D.; Ramos, A.; and Ruiz, M. A. *Coord. Chem. Rev.* **2017**, 330, 1.
- [2] Huttner, V. G. and Knoll, K. *Angew. Chem.* **1987**, 99, 765.
- [3] Field, J. S.; Haines, R. J.; and Smit, D. N. *J. of Organomet. Chem.* **1986**, 304, C17.
- [4] Sanchez-Nieves, J.; Sterenberg, B. T.; Udachin, K. A. and Carty, A. J. *Inorg. Chim. Acta* **2003**, 350, 486.
- [5] Bartsch, R.; Blake, A. J.; Johnson, B. F. G.; Jones, P. G.;

Müller, C.; Nixon, J. F.; Nowotny, M.; Schmutzler, R.; and Shephard, D. S. *Phosphorus, Sulfur Silicon Relat. Elem.* **1996**, 115, 201.

[6] Deeming, A. J.; Doherty, S.; and Powell, N. I. *Inorg. Chim. Acta* **1992**, 198–200, 469.

[7] Kakizawa, T.; Hashimoto, H.; and Tobita, H. *J. Organomet. Chem.* **2006**, 691, 726.

[8] Kakizawa, T.; Hashimoto, H.; and Tobita, H. *Inorg. Chim. Acta* **2015**, 425, 7.

[9] Sheldrick, G. M. *Acta Cryst.* **2008**, A64, 112.

[10] Freytag, M.; Edlmann, F. T.; Ernst, L.; Jones, P. G.; and Schmutzler, R. *Z. Anorg. Allg. Chem.* **2004**, 630, 377.

[11] Scheer, M.; Krug, J.; Kramkowski, P.; and Corrigan J. F. *Organometallics* **1997**, 16, 5917.



This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Communications in Inorganic Synthesis is sponsored and supported by: Universidad de Santiago de Chile.