

ic, space group  $P2_1/c$ ,  $a = 14.627(2)$ ,  $b = 14.762(2)$ ,  $c = 20.654(2)$  Å,  $\beta = 97.923(4)^\circ$ ,  $V = 4417.1(8)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{calcd}} = 1.679$  g cm<sup>-3</sup>,  $2\theta_{\text{max}} = 55^\circ$ , room temperature,  $F(000) = 2248$ ,  $\mu = 15.81$  cm<sup>-1</sup>, Rigaku RAXIS-RAPID imaging plate area detector, MoK $\alpha$  radiation ( $\lambda = 0.7107$  Å), graphite monochromator, 17753 measured reflections, Lorentz polarization and absorption corrections (transmission factors: 0.3044–0.7289), full-matrix least-squares refinement based on  $|F|$ , 461 parameters, H atoms except for those for HCl/H<sub>2</sub>O included with fixed parameters,  $R = 0.052$  and  $R_w = 0.076$  ( $w = 1/\sigma^2 F_o$ ) for 6248 observed reflections [ $I > 3\sigma(I)$ ], max./min. residual electron density 0.78/–1.26 e<sup>-</sup> Å<sup>-3</sup>. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-134168 (**5a**) and -134169 (**6a**·HCl·H<sub>2</sub>O·MeCN). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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## Synthesis of Mixed-Metal High-Nuclearity Clusters by Fusion of Anionic Ruthenium Carbido Clusters through Palladium Units

Takayuki Nakajima, Atsushi Ishiguro, and Yasuo Wakatsuki\*

High-nuclearity cluster complexes, in particular heterometallic clusters, have attracted considerable interest because of their diverse properties.<sup>[1, 2]</sup> One example is their application as precursors for metal dispersions with discrete metal atom composition, which may be useful as heterogeneous catalysts.<sup>[3]</sup> The fusion of two smaller cluster units through different metal atoms should provide a straightforward method to increase the nuclearity of carbonyl clusters efficiently. A large number of fusions of transition metal clusters by treatment of the cluster anions with cations or halides of Cu,<sup>[4]</sup> Ag,<sup>[5, 6]</sup> Au,<sup>[4e, 7]</sup> and Hg<sup>[7d, 8]</sup> to give a “sandwiching” of these metal atoms between two cluster units have been reported. In contrast, the reactions of cluster anions with cation or halide of Group 10 transition metals have been known to give giant clusters comprising two different transition metals, for example, [Ni<sub>38</sub>Pt<sub>6</sub>(CO)<sub>48</sub>(H)<sub>6–n</sub>]<sup>n–</sup>,<sup>[9]</sup> [Pd<sub>33</sub>Ni<sub>9</sub>(CO)<sub>41</sub>(PPh<sub>3</sub>)<sub>6</sub>]<sup>4–</sup>,<sup>[10]</sup> [Ni<sub>36</sub>Pt<sub>4</sub>(CO)<sub>45</sub>]<sup>6–</sup>,<sup>[11]</sup> and [Fe<sub>6</sub>Pd<sub>6</sub>(CO)<sub>24</sub>H]<sup>3–</sup>.<sup>[12]</sup> In these examples, considerable fragmentation and recombination of the original cluster component appear to be the important factors. Herein we report on the coupling of ruthenium carbido carbonyl clusters through palladium species to give high-nuclearity Ru/Pd mixed-metal complexes of “sandwich cluster” type structure. This is similar to the many cases of Group 11 and 12 metals as linking agents, rather than the unpredictable cluster formation by fragmentation and spontaneous assembly pathways. Incorporation of a Group 10 transition metal as a linking agent in sandwiching products should greatly widen the scope of the fusion route as a method for the rational synthesis of large heterometallic clusters, particularly in terms of their application as potential precursors for tailored alloy catalysts. This investigation is significant in that ruthenium and palladium are utilized as heterogeneous catalysts in a wide variety of industrial reactions.<sup>[13]</sup>

Treatment of the pentanuclear ruthenium carbido anion [Ru<sub>5</sub>C(CO)<sub>14</sub>]<sup>2–</sup> (cation: PPN=N(PPh<sub>3</sub>)<sub>2</sub><sup>+</sup>) with two equivalents of [Pd(C<sub>3</sub>H<sub>5</sub>)Cl]<sub>2</sub> in THF at room temperature for 12 h gave dark red crystals of a neutral cluster with the composition [Pd<sub>8</sub>Ru<sub>10</sub>C<sub>2</sub>(CO)<sub>27</sub>(C<sub>3</sub>H<sub>5</sub>)<sub>4</sub>] (**1**) in 52% yield. X-ray structural analysis (Figure 1) revealed that the molecule has two pseudo mirror planes, one of which passes through Pd2, Pd5, Ru11, and Ru21 and the other through Pd7, Pd8, C20, O21, C8, and C11.

The Pd<sub>8</sub> core, which is flanked on each side by a square-pyramidal Ru<sub>5</sub> core, consists of two coplanar fused squares, Pd1–Pd2–Pd5–Pd4 and Pd2–Pd3–Pd6–Pd5, and two Pd atoms, Pd7 and Pd8, which cap each of the squares from the same

[\*] Dr. Y. Wakatsuki, Dr. T. Nakajima, Dipl.-Chem. A. Ishiguro  
RIKEN (The Institute of Physical and Chemical Research)  
Wako-shi, Saitama 351-0198 (Japan)  
Fax: (+81) 484-62-4665  
E-mail: waky@postman.riken.go.jp

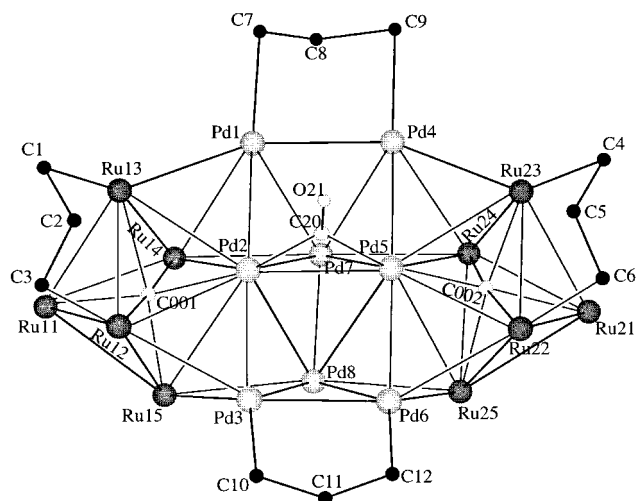


Figure 1. Structure of **1** in the crystal (26 CO ligands omitted for clarity). Four Pd–Ru bonds (Pd7–Ru14, Pd7–Ru24, Pd8–Ru15, Pd8–Ru25) and one Pd–Pd bond (Pd2–Pd5) have bridging CO, and four Pd–Ru bonds (Pd1–Ru13, Pd3–Ru12, Pd4–Ru23, Pd6–Ru22) have semibridging CO ligands, while all other CO ligands are terminal and bonded to Ru atoms. Selected interatomic distances [Å] and angles [°]: Pd1–Ru13 2.865(2), Pd1–Ru14 2.977(2), Pd2–Ru12 2.888(2), Pd2–Ru13 2.872(2), Pd2–Ru14 3.037(1), Pd2–Ru15 3.162(2), Pd3–Ru12 2.839(2), Pd3–Ru15 2.956(1), Pd4–Ru23 2.800(2), Pd4–Ru24 2.973(2), Pd5–Ru22 2.874(1), Pd5–Ru23 2.880(2), Pd5–Ru24 3.199(2), Pd5–Ru25 3.079(2), Pd6–Ru22 2.845(2), Pd6–Ru25 2.941(2), Pd7–Ru14 2.757(2), Pd7–Ru24 2.809(2), Pd8–Ru15 2.820(2), Pd8–Ru25 2.780(2), Pd1–C7 2.08(2), Pd4–C9 2.14(2), Ru12–C3 2.23(1), Ru13–C1 2.23(2); Pd2–C001–Ru11 179.8(8), Pd5–C002–Ru21 176.0(8).

side of the fused square plane and are in bonding distance (2.720(2) Å). There are 20 Pd–Ru bonds in the structure (Figure 1), and as a consequence of these Pd–Ru bonding interactions, the basal planes of the Ru pyramids tilt toward the Pd7–Pd8 bond. The dihedral angles between the basal planes and the fused Pd squares are 68.89(4) and 71.12(4)°, respectively. Four  $\mu_2\text{-}\eta^3\text{-C}_3\text{H}_5$  groups are located on the Pd1–Pd4, Pd3–Pd6, Ru12–Ru13, and Ru22–Ru23 bonds. The  $^1\text{H}$  NMR spectrum shows sets of signals for the Ru-allyl<sup>[14]</sup> and Pd-allyl groups; these signals do not change even at 80 °C. The  $^{13}\text{C}$  NMR spectrum exhibits two moderately broad peaks ( $\delta$  = 198.2 and 196.8; ratio 1:2) in the CO region. These can be assigned to CO ligands that interact with the Pd atoms and to those that are bonded solely to Ru atoms.

By using the hexanuclear ruthenium carbido anion  $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$  as the starting carbonyl cluster, the reactions with the palladium cation  $[\text{Pd}(\text{CH}_3\text{CN})_4]^{2+}$  proceeded smoothly; however, the number of palladium atoms incorporated in the product complexes was found to be dependent on reaction conditions. Refluxing  $[\text{PPN}]_2[\text{Ru}_6\text{C}(\text{CO})_{16}]$  in  $\text{CH}_2\text{Cl}_2$  with about one equivalent of  $[\text{Pd}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$  for 4 h under air afforded a dark red oil. Subsequent treatment of the latter with  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  resulted in crystals of  $[\text{PPN}]_2[\text{Pd}_2\text{Ru}_{12}\text{C}_2(\text{CO})_{30}]$  (**2**) in 33% yield. Reaction of the same reactants in the same feeding ratio in THF at room temperature for 12 h but under argon gave dark red crystals of the composition  $[\text{PPN}]_2[\text{Pd}_4\text{Ru}_{12}\text{C}_2(\text{CO})_{32}]$  (**3**). The yield of this reaction was 34% based on the starting ruthenium complex and 68% based on the palladium cation used. The use of excess  $[\text{Pd}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$  gives a much worse yield of

**3**. Refluxing a solution of **3** in  $\text{CH}_2\text{Cl}_2$  under air did not give **2** but resulted in gradual decomposition of **3** to an intractable material.

The molecular structure of **2** determined by X-ray structure analysis (Figure 2) shows that the two  $\text{Ru}_6$  octahedra are linked through two palladium atoms. The  $\text{Ru}_6$  skeleton retains

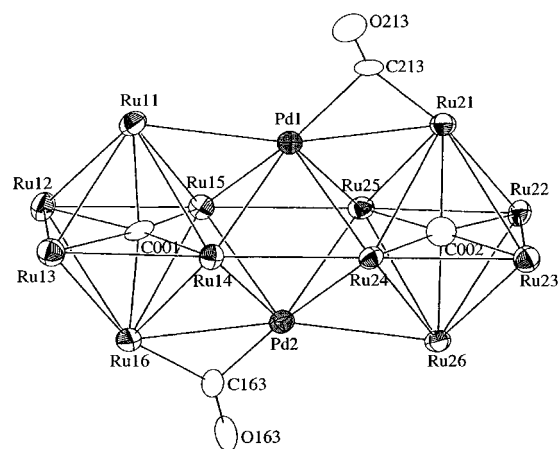


Figure 2. Structure of the anion of **2** in the crystal. The CO ligands, except those bridging the Pd–Ru bonds, are omitted for clarity; all other CO ligands are bonded solely to Ru atoms. Selected interatomic distances [Å] and angles [°]: Pd1–Ru11 2.836(1), Pd1–Ru14 2.754(1), Pd1–Ru15 2.788(1), Pd1–Ru21 2.786(1), Pd1–Ru24 2.735(1), Pd1–Ru25 2.767(1), Pd2–Ru14 2.759(1), Pd2–Ru15 2.722(1), Pd2–Ru16 2.762(1), Pd2–Ru24 2.797(1), Pd2–Ru25 2.762(1), Pd2–Ru26 2.848(1), Ru14–Ru15 3.215(2), Ru24–Ru25 3.212(2); Ru11–Pd1–Ru21 165.83(3), Ru16–Pd2–Ru26 165.87(3), Ru12–Ru13–Ru14 94.48(3), Ru13–Ru12–Ru15 93.31(3).

its original octahedral geometry except that the edge that interacts with the palladium atoms is broken; the Ru14–Ru15 and Ru24–Ru25 distances are 3.215(2) and 3.212(2) Å, respectively. Each palladium atom has six heterometallic bonds, four to the ruthenium atoms of the broken Ru–Ru edges and two to apical ruthenium atoms.

Complex **3** (Figure 3) contains two additional palladium atoms. The  $\text{Pd}_4$  skeleton adopts the form of a bent square (angle 107.5°; nonbonded Pd2–Pd3 distance 3.485(2) Å). The two  $\text{Ru}_6$  octahedra have local structures similar to those in **2** but their relative orientation is now twisted, in terms of the broken Ru–Ru edges, by almost 90° from that in **2**.

Apparently, formation of these heterometallic cluster complexes does not result from a simple combination reaction between cationic and anionic complexes but is accompanied by partial redox reactions. Formation of **1** may be viewed formally as the result of the reaction between two molecules of  $[\text{Ru}_5\text{C}(\text{CO})_{14}]^{2-}$  and four molecules of the “ $\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}$ ” species, in which four atoms of  $\text{Pd}^0$  are further incorporated. In the synthesis of **2** and **3**, the neutral ruthenium cluster  $[\text{Ru}_6\text{C}(\text{CO})_{17}]$  is always obtained as a minor product (ca. 20%). Cyclic voltammetric studies in  $\text{CH}_3\text{CN}$  with  $[\text{Cp}_2\text{Fe}]/[\text{Cp}_2\text{Fe}^+]$  ( $\text{Cp} = \text{C}_5\text{H}_5^-$ ) as reference gave  $E_p(\text{reduction})$  of  $[\text{Pd}(\text{CH}_3\text{CN})_4]^{2+}$  at  $-0.14$  V, while  $E_p(\text{oxidation})$  for  $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$  was  $-0.01$  V. The oxidation peak of the cluster anion is, however, broad and the lower part of the voltammogram is extended over  $-0.14$  V, suggesting that only gentle reduction of the palladium cation by the cluster anion is

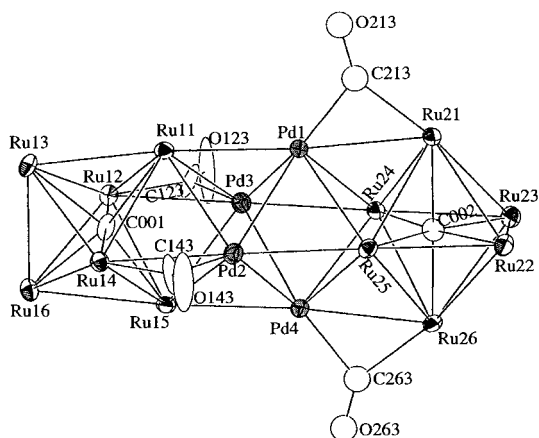


Figure 3. Structure of the anion of **3** in the crystal. The CO ligands, except those bridging the Pd–Ru bonds, are omitted for clarity; all other CO ligands are bonded solely to Ru atoms. Selected interatomic distances [Å]: Pd1–Pd2 2.825(4), Pd1–Pd3 2.720(2), Pd2–Pd3 3.485(2), Pd2–Pd4 2.744(2), Pd3–Pd4 2.824(3), Pd1–Ru11 2.774(2), Pd1–Ru21 2.740(2), Pd1–Ru24 2.902(2), Pd1–Ru25 2.840(3), Pd2–Ru11 2.833(3), Pd2–Ru14 2.750(2), Pd2–Ru15 2.905(2), Pd2–Ru25 2.763(2), Pd3–Ru11 2.916(2), Pd3–Ru12 2.748(2), Pd3–Ru15 2.833(3), Pd3–Ru24 2.764(2), Pd4–Ru15 2.771(2), Pd4–Ru24 2.820(4), Pd4–Ru25 2.909(3), Pd4–Ru26 2.744(2), Ru11–Ru15 3.458(4), Ru24–Ru25 3.454(2).

possible. By employing  $[\text{Fe}(\text{C}_5\text{H}_5)_2]^+$  as an “innocent” oxidant that does not chemically react with the cluster anion or cluster species being oxidized, the reaction with one equivalent of  $[\text{Ru}_5\text{C}(\text{CO})_{14}]^{2-}$  at  $0^\circ\text{C}$  was found to give the self-condensation product  $[\text{Ru}_{10}\text{C}_2(\text{CO})_{24}]^{2-}$  in a 83 % yield. The same complex was previously prepared by pyrolysis of  $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$  at  $210^\circ\text{C}$  in 35 % yield.<sup>[15]</sup> The investigation of the transformation of these high-nuclearity heterometallic clusters into supported fine metal particles of Ru/Pd alloy is now in progress.

## Experimental Section

All reactions (except the synthesis of **2**) were carried out in dry solvents under purified argon. The products were purified by column chromatography on silica gel and crystallized from  $\text{CH}_2\text{Cl}_2/\text{hexane}$  (**1**) or from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (**2** and **3**). All data collections for X-ray analysis were made on a Rigaku RAXIS-IV imaging plate diffractometer with graphite-monochromated  $\text{MoK}\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation. Structures were solved by direct methods, expanded using Fourier techniques, and refined by full-matrix least-squares. All calculations were performed by using the teXsan crystallographic software package (Molecular Structure Corporation 1992). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-135943, CCDC-135944, and CCDC-135945. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

**1:** Yield 52 %; dark red plates;  $^1\text{H}$  NMR (270 MHz,  $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta = 4.25$  (d,  $J = 4.8 \text{ Hz}$ , 2H, *syn*-H, Pd-allyl), 4.17 (m, 1H, central-H, Pd-allyl), 3.39 (d,  $J = 7.0 \text{ Hz}$ , 2H, *syn*-H, Ru-allyl), 2.89 (d,  $J = 12.0 \text{ Hz}$ , 2H, *anti*-H, Pd-allyl), 1.99 (m, 1H, central-H, Ru-allyl), 0.37 (d,  $J = 13.0 \text{ Hz}$ , 2H, *anti*-H, Ru-allyl);  $^{13}\text{C}$  NMR (500 MHz,  $[\text{D}_8]\text{toluene}$ ,  $25^\circ\text{C}$ ):  $\delta = 198.2$  (CO), 196.8 (CO), 108.2 (allyl-terminal), 80.4 (allyl-terminal), 65.9 (allyl-central), 59.2 (allyl-central); IR ( $\text{CH}_2\text{Cl}_2$ ):  $\tilde{\nu}(\text{CO}) = 2072$  (m), 2036 (s), 2023 (s)  $\text{cm}^{-1}$ ; elemental analysis (%) calcd for  $\text{C}_{41}\text{H}_{20}\text{O}_{27}\text{Pd}_8\text{Ru}_{10}$ : C 17.54, H 0.72; found: 17.43, H 0.79. Crystal data for **1**·3  $\text{CH}_2\text{Cl}_2$ :  $M_r = 3062.45$ , monoclinic, space group  $P2_1/n$  (no. 14),  $a = 21.557(2)$ ,  $b = 14.515(4)$ ,  $c = 21.931(3) \text{ \AA}$ ,

$\beta = 101.092(8)^\circ$ ,  $V = 6733(2) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 3.019 \text{ g cm}^{-3}$ ,  $\mu = 45.61 \text{ cm}^{-1}$ , data collection at  $-100^\circ\text{C}$ ,  $R1 = 0.051$ ,  $R2 = 0.049$  for 7401 data with  $I > 4\sigma(I)$ .

**2:** Yield 33 %; dark red plates; IR ( $\text{CH}_2\text{Cl}_2$ ):  $\tilde{\nu}(\text{CO}) = 2038$  (s), 2008 (s)  $\text{cm}^{-1}$ ; elemental analysis (%) calcd for  $\text{C}_{105}\text{H}_{62}\text{Cl}_2\text{N}_2\text{O}_{30}\text{Pd}_4\text{Ru}_{12}$  (one  $\text{CH}_2\text{Cl}_2$  molecule as solvent of crystallization): C 36.53, H 1.81, N 0.81; found: C 36.46, H 1.77, N 0.83. Crystal data for **2**·2  $\text{CH}_2\text{Cl}_2$ :  $M_r = 3537.01$ , monoclinic, space group  $Cc$  (no. 9),  $a = 38.271(5)$ ,  $b = 9.973(4)$ ,  $c = 36.093(5) \text{ \AA}$ ,  $\beta = 123.592(8)^\circ$ ,  $V = 11475(5) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 2.047 \text{ g cm}^{-3}$ ,  $\mu = 20.58 \text{ cm}^{-1}$ , data collection at  $-100^\circ\text{C}$ ,  $R1 = 0.043$ ,  $R2 = 0.054$  for 9619 data with  $I > 3\sigma(I)$ .

**3:** Yield 34 % (based on Ru), 68 % (based on Pd); dark red plates; IR ( $\text{CH}_2\text{Cl}_2$ ):  $\tilde{\nu}(\text{CO}) = 2033$  (s), 2021 (s), 2002 (sh)  $\text{cm}^{-1}$ ; elemental analysis (%) calcd for  $\text{C}_{106}\text{H}_{60}\text{N}_2\text{O}_{32}\text{Pd}_4\text{Ru}_{12}$ : C 35.00, H 1.66, N 0.77; found: C 34.90, H 1.62, N 0.72. Crystal data for **3**:  $M_r = 3635.97$ , monoclinic, space group  $Cc$  (no. 9),  $a = 23.979(3)$ ,  $b = 31.343(8)$ ,  $c = 19.177(2) \text{ \AA}$ ,  $\beta = 128.613(6)^\circ$ ,  $V = 11262 \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calcd}} = 2.144 \text{ g cm}^{-3}$ ,  $\mu = 23.13 \text{ cm}^{-1}$ , data collection at  $-100^\circ\text{C}$ ,  $R1 = 0.054$ ,  $R2 = 0.058$  for 7430 data with  $I > 4\sigma(I)$ .

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