

Synthesis of Ru–Pt and Ru–Pd mixed-metal imido clusters from a diruthenium imido-methylene scaffold $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-NPh})(\mu_2\text{-CH}_2)]^\dagger$

Shin Takemoto, Hidenobu Morita, Ken Kamikawa and Hiroyuki Matsuzaka*

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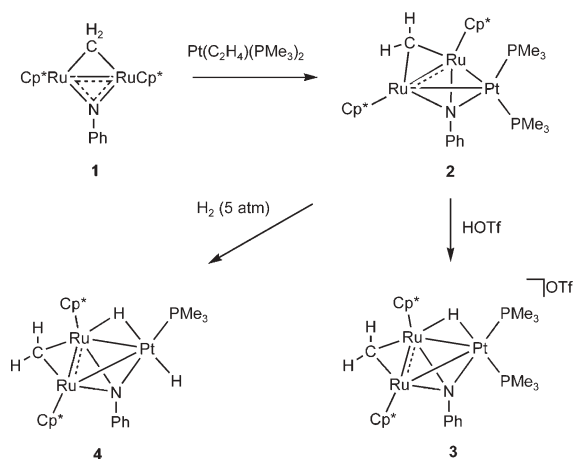
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The diruthenium μ_2 -imido μ_2 -methylene complex $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-NPh})(\mu_2\text{-CH}_2)]$ serves as a bifunctional scaffold for cluster synthesis, producing a μ_3 -imido Ru_2Pt cluster $[(\text{Cp}^*\text{Ru})_2(\mu_3\text{-NPh})(\mu_2\text{-CH}_2)\text{Pt}(\text{PMe}_3)_2]$ on treatment with $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{PMe}_3)_2]$ and a μ_3 -methylidyne Ru_4Pd_2 cluster $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-NPh})(\mu_3\text{-CH})\text{PdCl}]_2$ with $[\text{PdMeCl}(\text{cod})]$.

Bimetallic catalysts containing ruthenium and platinum are widely used in petrochemical industry. For example, supported Ru/Pt/alumina catalysts are useful for petroleum reforming,¹ and Ru–Pt electrodes are used to catalyze methanol oxidation in fuel cells.^{2–5} Soluble Ru–Pt mixed-metal clusters have consequently attracted much attention since they may provide insights into the behavior of heterogeneous Ru–Pt surfaces.^{6–21} Additionally, Ru–Pt and Ru–Pd mixed-metal clusters have recently been shown to be precursors of supported bimetallic nanoparticles that exhibit high catalytic activity for certain hydrogenation reactions.^{22,23}

We have recently synthesized a novel diruthenium complex $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-NPh})(\mu_2\text{-CH}_2)]$ (**1**; $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) containing bridging imido and methylene ligands.²⁴ The inherent reactivity of these ligands^{25,26} as well as the unsaturated nature of the diruthenium core have allowed us to explore the chemistry of **1**. Metal imido clusters containing low-oxidation-state platinum group metals are rare,^{27–31} and the heteronuclear ones are represented only by those derived from the monomeric iridium imido complex $[\text{Cp}^*\text{Ir}(\text{NBu}^1)]$ ³² and the di- and trinuclear anionic rhodium imido species $[\text{Rh}_2(\mu_2\text{-NAr})_2\text{L}_4]^{2-}$ ($\text{L} = \text{CO}, 1/2\text{cod}$) and $[\text{Rh}_3(\mu_3\text{-NAr})_2(\text{CO})_6]^-$.^{33,34} We now report the selective transformation of **1** into Ru_2Pt and $(\text{Ru}_2\text{Pd})_2$ mixed-metal clusters. These clusters represent the first examples of Ru–Pt and Ru–Pd heterobimetallic imido clusters. It is also notable that both μ_3 -imido-bridged and μ_3 -methylidyne-bridged³⁵ heterotrinuclear structures are constructed from a single precursor **1**.

As outlined in Scheme 1, the diruthenium complex **1** cleanly reacts with a Pt(0) complex $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PMe}_3)_2]$ in THF at room temperature to produce the μ_3 -imido-bridged Ru_2Pt cluster **2**. The synthetic strategy is related to that employed by Bergman *et al.* for the synthesis of the Zr–Ir imido complex $[\text{Cp}_2\text{Zr}(\mu_2\text{-NBu}^1)\text{IrCp}^*]$.³² The cluster **2** was isolated in 69% yield as air-sensitive dark brown plates, and characterized by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, elemental analysis, and a preliminary X-ray study. The ^1H NMR



Scheme 1 Synthesis and reactivity of the Ru–Pt mixed-metal cluster **2**.

spectrum of **2** shows two diastereotopic methylene resonances at δ 10.2 and 10.1, along with a single Cp^* resonance at δ 1.71. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum exhibits two mutually coupled doublets at δ –32.1 and –32.8 ($^2J_{\text{PP}} = 28.9$ Hz) with $^1J_{\text{PtP}}$ coupling of 3856 and 3301 Hz, respectively. These data are fully consistent with the μ_3 -imido heterotriangular structure, with the edge-bridging methylene between the two ruthenium atoms and with two inequivalent trimethylphosphines on platinum. The 46 valence electron count for **2** suggests some unsaturation in the Ru_2Pt core.

Protonation of **2** with trifluoromethanesulfonic acid in THF affords a cationic hydride cluster $[(\text{Cp}^*\text{Ru})_2(\mu_3\text{-NPh})(\mu_2\text{-CH}_2)(\mu_2\text{-H})\text{Pt}(\text{PMe}_3)_2]\text{CF}_3\text{SO}_3$ (**3**), which was isolated in 72% yield as dark green prisms, and identified by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy, elemental analysis, and X-ray crystallography. The structure of the cationic part is shown in Fig. 1. The hydride ligand was found in the final difference Fourier map. One face of the Ru_2Pt triangle is capped by the μ_3 -imido nitrogen, and from the other side, the methylene and hydride ligands bridge the Ru–Ru and one of the Ru–Pt edges, respectively. The methylene carbon, the imido nitrogen, and the two ruthenium atoms are nearly coplanar, as in the diruthenium complex **1**, and the short Ru–Ru distance (2.5774(4) Å) suggests a double bond order as proposed for **1**.²⁴ The hydride-bridged Ru–Pt edge has a Ru–Pt distance of 2.7518(3) Å, which can be attributable to a Ru–H–Pt three-center two-electron bond, whereas the other Ru–Pt edge shows a long Ru–Pt separation (3.0082(4) Å).³⁶ Without considering any Ru–Pt interactions, the platinum has a square planar geometry, indicating a formal oxidation state of Pt(II). In contrast to the solid-state structure, in which two ruthenium atoms are inequivalent, the ^1H NMR spectrum of **3** exhibits only one

Department of Chemistry, Graduate School of Science, Osaka Prefecture University, Gakuen cho 1-1, Sakai, Osaka, 599-8531, Japan. E-mail: matuzaka@c.s.osakafu-u.ac.jp; Fax: 81-72-254-9931; Tel: 81-72-254-9696

† Electronic supplementary information (ESI) available: preparation and characterization details. See DOI: 10.1039/b517222e

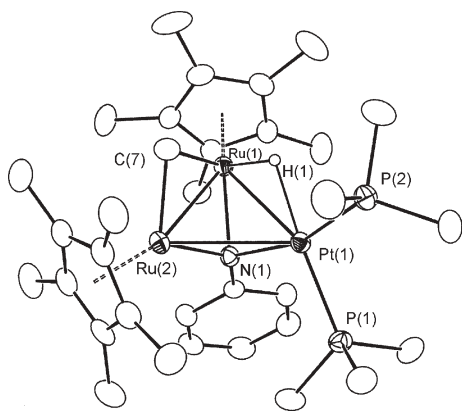
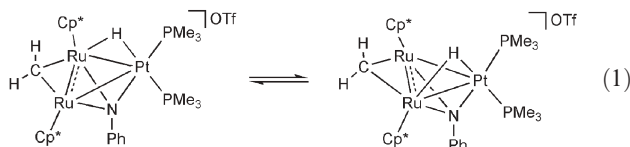


Fig. 1 Thermal ellipsoid plot of the cationic part of **3**. Ellipsoids are drawn at 30% probability level and hydrogen atoms except for H(1) are omitted for clarity. Selected bond lengths (Å): Ru(1)–Ru(2), 2.5774(4); Pt(1)–Ru(1), 2.7518(3); Pt(1)–Ru(2), 3.0082(4); Ru(1)–C(7), 2.025(4); Ru(2)–C(7), 2.025(4); Ru(1)–N(1), 2.029(3); Ru(2)–N(1), 2.045(3); Pt(1)–N(1), 2.066(3); Pt(1)–P(1), 2.2841(11); Pt(1)–P(2), 2.2673(10).

Cp* resonance over the temperature range of 20 to -80 °C. We may assume a fast site exchange between the two ruthenium centers in solution (eqn (1)) with retention of the Ru–(μ_2 -H)–Pt structure, since the $^1J_{\text{PtH}}$ coupling of 604 Hz for the hydride resonance (δ -14.7) falls within a range of those observed for other platinum μ_2 -hydride complexes.³⁷



The cluster **2** reacts with H₂ (5 atm) at room temperature to afford the dihydride cluster [(Cp*Ru)₂(μ_3 -NPh)(μ_2 -CH₂)(μ_2 -H)PtH(PMe₃)] (**4**), which was isolated in 36% yield and characterized by both spectroscopic and crystallographic methods (Scheme 1). The ¹H NMR spectrum shows two hydride resonances at δ -3.70 (dd; $^2J_{\text{PH}} = 11$ Hz, $^2J_{\text{HH}} = 31$ Hz, $^1J_{\text{PtH}} = 1511$ Hz) and -15.79

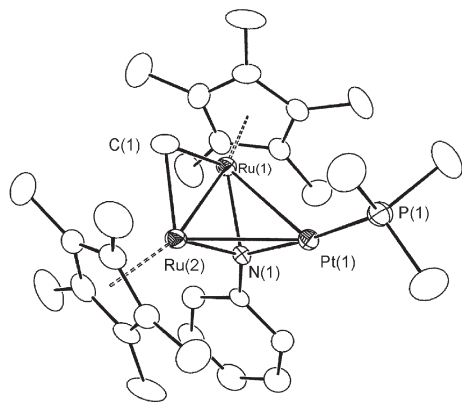
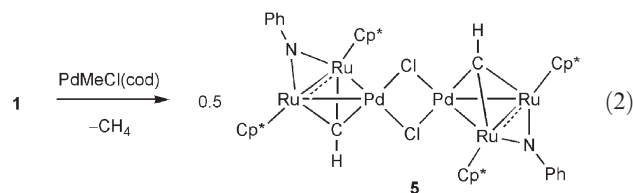


Fig. 2 Thermal ellipsoid plot of **4**. Ellipsoids are drawn at 30% probability level and hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ru(1)–Ru(2), 2.5625(9); Pt(1)–Ru(1), 2.7878(8); Pt(1)–Ru(2), 2.9193(8); Ru(1)–C(1), 2.044(6); Ru(2)–C(1), 2.034(6); Ru(1)–N(1), 2.039(4); Ru(2)–N(1), 2.024(5); Pt(1)–N(1), 2.037(5); Pt(1)–P(1), 2.2081(17).

(m, $^1J_{\text{PtH}} = 460$ Hz) in equal intensity, and the $^1J_{\text{PtH}}$ values are diagnostic of their assignment as terminal and bridging hydrides, respectively.³⁷ Furthermore, the coupling pattern of the terminal hydride resonance (dd) as well as the appearance of a single phosphorus resonance in the ³¹P{¹H} NMR spectrum (δ -27.1 , s, $^1J_{\text{PtP}} = 3352$ Hz) are consistent with the existence of only one trimethylphosphine in the molecule. The X-ray crystallographic study (Fig. 2) revealed a Ru₂Pt trinuclear framework analogous to that of **3**, displaying one short (2.7878(8) Å, Ru(1)–Pt(1)) and one long (2.9193(8) Å, Ru(2)–Pt(1)) Ru–Pt distances. The almost linear P(1)–Pt(1)–N(1) linkage (angle = 173.67(13)°) indicates a *trans* arrangement of the two hydride ligands on a square-planar platinum centre. The facile displacement of a trimethylphosphine in **2** by dihydrogen is rather unexpected. Additionally, the isolation of **4** contrasts well to the hydrogenation of **1**, which results in the complete hydrogenolysis of both Ru–NPh and Ru–CH₂ bonds to give [(Cp*Ru)₂(μ_2 -H)₄]³⁸ under similar reaction conditions.



In contrast to the formation of the μ_3 -imido heterotrinnuclear structure **2** as described above, treatment of **1** with a Pd(II) complex [PdMeCl(cod)]³⁹ leads to cleavage of a methylene C–H bond to afford a μ_3 -methylidyne-bridged heterohexanuclear cluster [(Cp*Ru)₂(μ_2 -NPh)(μ_3 -CH)Pd(μ_2 -Cl)]₂ (**5**, 73%), whose structure was unequivocally determined by a single-crystal X-ray diffraction (eqn (2); Fig. 3). The cluster **5** is a chloro-bridged dimer of the trinuclear Ru₂Pd fragment {(Cp*Ru)₂(μ_2 -NPh)(μ_3 -CH)Pd}, and the molecule sits on a crystallographic inversion centre. The Ru–Ru distance of 2.5936(11) Å is comparable to that of **1** and suggests a Ru–Ru double bond character. The Ru–Pd distances of 2.6733(13) and 2.6815(13) Å correspond to Ru–Pd single bonds,⁹ whereas the long Pd–Pd separation (3.540 Å) indicates the absence of bonding interaction between these atoms. It is interesting to note that the cluster **5** still contains μ_2 -imido group on the Ru–Ru edges, whose reactivity may be investigated.

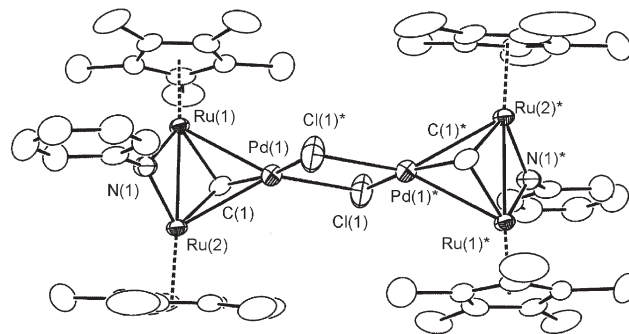


Fig. 3 Thermal ellipsoid plot of **5**. Ellipsoids are drawn at 30% probability level and hydrogen atoms are omitted for clarity. The asterisk in the atom labels indicates atoms at equivalent position (1 $-x$, 1 $-y$, $-z$). Selected bond lengths (Å): Ru(1)–Ru(2), 2.5936(11); Pd(1)–Ru(1), 2.6733(13); Pd(1)–Ru(2), 2.6815(13); Ru(1)–C(1), 1.984(10); Ru(2)–C(1), 1.987(11); Pd(1)–C(1), 1.943(12); Ru(1)–N(1), 1.894(8); Ru(2)–N(1), 1.905(8); Pd(1)–Cl(1), 2.582(5); Pd(1)–Cl(1)*, 2.460(4).

In summary, the diruthenium imido-methylene complex **1** has been shown to be a versatile starting material for the synthesis of Ru–Pt and Ru–Pd mixed-metal imido clusters. It turned out that **1** can selectively produce either μ_3 -imido- or μ_3 -methylidyne-bridged heterotrinnuclear structures depending on the nature of the incoming metal fragments. Further studies on the reactivity of **2–5** as well as the preparation of other mixed-metal clusters are now in progress.‡

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Notes and references

‡ Crystallographic data for **3**: $C_{34}H_{56}NO_3F_3P_2SRu_2Pt$, Fw = 1075.03, monoclinic, space group $P2_1/n$, $a = 15.0174(7)$, $b = 13.6700(5)$, $c = 19.3130(10)$ Å, $\beta = 90.840(2)^\circ$, $V = 3964.3(3)$ Å³, $T = 296$ K, $Z = 4$, $\mu(\text{MoK}\alpha) = 1.801$ mm⁻¹, 37335 reflections measured, 9081 unique ($R_{\text{int}} = 0.0393$), $R1 = 0.0299$, $wR2 = 0.0738$, GOF = 1.031. Crystallographic data for **4**: $C_{30}H_{48}NPRu_2Pt$, Fw = 850.89, monoclinic, space group $P2_1/n$, $a = 10.825(3)$, $b = 17.604(5)$, $c = 16.735(4)$ Å, $\beta = 92.64(3)^\circ$, $V = 3185.6(15)$ Å³, $T = 296$ K, $Z = 4$, $\mu(\text{MoK}\alpha) = 1.774$ mm⁻¹, 28092 reflections measured, 6763 unique ($R_{\text{int}} = 0.0456$), $R1 = 0.0361$, $wR2 = 0.0999$, GOF = 1.216. Crystallographic data for **5**: $C_{34}H_{72}N_2Cl_2Ru_4Pd_2$, Fw = 1437.12, triclinic, space group $P\bar{1}$, $a = 8.515(3)$, $b = 10.9474(2)$, $c = 16.620(5)$ Å, $\alpha = 106.02(2)$, $\beta = 92.442(9)$, $\gamma = 112.13(4)^\circ$, $V = 1360.5(7)$ Å³, $T = 296$ K, $Z = 1$, $\mu(\text{MoK}\alpha) = 1.863$ mm⁻¹, 13372 reflections measured, 6171 unique ($R_{\text{int}} = 0.0513$), $R1 = 0.0771$, $wR2 = 0.2082$, GOF = 1.042. CCDC 292722–292724. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b517222e

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