

Supplementary data

Experimental Procedures.

General. All manipulations were performed under an atmosphere of nitrogen using standard Schlenk techniques. Toluene, hexanes, THF, and diethyl ether were distilled from sodium benzophenone ketyl and degassed before use. Methanol was distilled from magnesium methoxide and degassed before use. Dehydrated acetonitrile was purchased from Wako Pure Chemical Industry, Ltd., and degassed before use. Deuterated solvents were degassed by three freeze-pump-thaw cycles and stored over 4A molecular sieves. $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-NPh})(\mu_2\text{-CH}_2)]$ (**1**)¹ and $[\text{PdMeCl}(\text{cod})]$ ² were prepared according to the literature. $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{PMe}_3)_2]$ was generated in situ from *cis*- $[\text{PtCl}_2(\text{PMe}_3)_2]$ and sodium naphthalenide under ethylene atmosphere. Other chemicals were obtained from commercial sources.

NMR spectra were recorded on a JEOL ECP500 NMR spectrometer operating at 500.16 (¹H), 202.48 (³¹P), 125.78 (¹³C) MHz; chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane or 85% phosphoric acid. IR spectra were recorded on a JASCO FT-IR spectrometer. Elemental analyses were performed on a Perkin Elmer CHNS series II microanalyzer. Mass spectra were measured on a JEOL JMS-700 spectrometer.

Preparation of $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-CH}_2)(\mu_3\text{-NPh})\text{Pt}(\text{PMe}_3)_2]$ (2**).** To a stirred suspension of *cis*- $[\text{PtCl}_2(\text{PMe}_3)_2]$ (209 mg, 0.5 mmol) in THF (20 mL) was added sodium naphthalenide (2.5 mL, 0.5 M solution in THF) at room temperature with continuous bubbling of ethylene into the suspension.³ The solution of $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{PMe}_3)_2]$ thus obtained was added to a solution of $[(\text{Cp}^*\text{Ru})_2(\mu_2\text{-NPh})(\mu_2\text{-CH}_2)]$ (**1**) (292 mg, 0.5 mmol) in THF (10 mL). The reaction mixture was stirred for 63 h at room temperature, and then evaporated to dryness. The residue was extracted with 40 mL of toluene, and the extract was concentrated to 2 mL. Slow diffusion of acetonitrile (6 mL) to the concentrated extract afforded **2** as black blocks, which were collected by filtration, washed with 3 mL of acetonitrile, and

then dried in vacuo. Yield 144 mg. The supernatant solution was evaporated to dryness, and recrystallization of the residue from toluene/acetonitrile (1 mL/8 mL) afforded second crop. Total yield 317 mg, 69%. Anal. Calcd for $C_{33}H_{55}NP_2Ru_2Pt$: C, 42.85; H, 5.99; N, 1.51. Found: C, 42.29; H, 6.02; N, 1.62. 1H NMR (C_6D_6): δ 10.17 (s, 1H, μ_2 -CH₂), 10.08 (s, 1H, μ_2 -CH₂), 7.23-6.97 (m, 5H, Ph), 1.71 (s, 30H, Cp*), 1.34 (m, 9H, PMe₃). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 170.7 (m, μ_2 -CH₂), 167.1 (m, Ph), 127.0 (s, Ph), 126.8 (m, Ph), 120.3 (s, Ph), 85.5 (s, C₅Me₅), 23.0 (m, PMe₃), 21.5 (m, PMe₃), 11.2 (s, C₅Me₅). $^{31}P\{^1H\}$ NMR (C_6D_6): δ -32.1 (d with ^{195}Pt satellites, $^2J_{P-P} = 28.9$ Hz, $^1J_{Pt-P} = 3856$ Hz), -32.8 (d with ^{195}Pt satellites, $^2J_{P-P} = 28.9$ Hz, $^1J_{Pt-P} = 3301$ Hz). FAB MS: 925 m/z (M^+).

Preparation of [(CpRu*)₂(μ_2 -CH₂)(μ_3 -NPh)(μ_2 -H)Pt(PMe₃)₂][CF₃SO₃] (3).** To a solution of **2** (66 mg, 0.07 mmol) in THF (10 mL) was added CF₃SO₃H (6.4 mL, 0.07 mmol) at room temperature, which caused an immediate color change from brown to green. The solution was concentrated to 1 mL and hexanes (6 mL) was layered onto the concentrated solution. Dark green prisms that deposited were collected by filtration and dried in vacuo. Yield 48 mg, 72%. Anal. Calcd for $C_{34}H_{56}NO_3F_3SP_2Ru_2Pt$: C, 37.99; H, 5.25; N, 1.30. Found: C, 37.89; H, 5.02; N, 1.29. 1H NMR (C_6D_6): δ 10.41 (s with ^{195}Pt satellites, $^3J_{Pt-H} = 18$ Hz, 1H, μ_2 -CH₂), 9.69 (d with ^{195}Pt satellites, $^3J_{Pt-H} = 18$ Hz, $^3J_{H-H} = 2.8$ Hz, 1H, μ_2 -CH₂), 7.35–6.96 (m, 5H, Ph), 1.78 (d, $^2J_{P-H} = 9$ Hz, 9H, PMe₃), 1.62 (d, $^2J_{P-H} = 9$ Hz, 9H, PMe₃), 1.58 (s, 30H, Cp*), -14.7 (dd with ^{195}Pt satellites, $^1J_{Pt-H} = 604$ Hz, $^2J_{P-H} = 98$ and 15 Hz, 1H, μ_2 -H). $^{13}C\{^1H\}$ NMR (acetone-*d*₆): δ 165.5 (s, μ_2 -CH₂), 154.4 (s, Ph), 129.0 (s, Ph), 125.8 (m, Ph), 124.1 (s, Ph), 90.5 (s, C₅Me₅), 20.9 (m, PMe₃), 17.5 (m, PMe₃), 11.0 (s, C₅Me₅). $^{31}P\{^1H\}$ NMR (C_6D_6): δ -27.5 (d with ^{195}Pt satellites, $^2J_{P-P} = 22$ Hz, $^1J_{Pt-P} = 2955$ Hz), -32.8 (d with ^{195}Pt satellites, $^2J_{P-P} = 22$ Hz, $^1J_{Pt-P} = 3557$ Hz).

Preparation of [(CpRu*)₂(μ_2 -CH₂)(μ_3 -NPh)(μ_2 -H)PtH(PMe₃)] (4).** A solution of **2** (243 mg, 0.25 mmol) in toluene (10 mL) was pressurized with H₂ (5 atm) in a stainless autoclave and the mixture

was stirred at room temperature for 69 h. Concentration of the solution to ca. 2 mL followed by slow diffusion of methanol (10 mL) afforded **4** as dark green blocks, which were collected by filtration and dried in vacuo. Yield 80 mg, 36%. Anal. Calcd for $C_{30}H_{48}NPRu_2Pt$: C, 42.35; H, 5.69; N, 1.65. Found: C, 42.11; H, 6.01; N, 1.77. 1H NMR (C_6D_6): δ 9.98 (d with ^{195}Pt satellites, $^3J_{Pt-H} = 20$ Hz, $^3J_{H-H} = 3$ Hz, 1H, μ_2 -CH₂), 9.85 (s with ^{195}Pt satellites, $^3J_{Pt-H} = 20$ Hz, 1H, μ_2 -CH₂), 7.77–6.39 (m, 5H, Ph), 1.61 (s, 30H, Cp*), 1.44 (d, $^2J_{P-H} = 9$ Hz, 9H, PMe₃), –3.70 (dd with ^{195}Pt satellites, $^1J_{Pt-H} = 1511$ Hz, $^2J_{H-H} = 31$ Hz, $^2J_{P-H} = 11$ Hz, 1H, Pt–H), –15.79 (m with ^{195}Pt satellites, $^1J_{Pt-H} = 460$ Hz, 1H, μ_2 -H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ –27.14 (s with ^{195}Pt satellites, $^1J_{Pt-P} = 3352$ Hz).

Preparation of [(CpRu*)₂(μ_2 -NPh)(μ_3 -CH)PdCl]₂ (**5**).** A solution of [PdMeCl(cod)] (48 mg, 0.18 mmol) in THF (5 mL) was added to a solution of **1** (100 mg, 0.18 mmol) in THF (5 mL). The mixture was stirred at room temperature for 18 h, and then concentrated to ca. 1 mL. Slow diffusion of hexanes (5 mL) to the concentrated solution afforded **5** as brown platelets, which were collected by filtration and dried in vacuo. Yield 92 mg, 73%. Anal. Calcd for $C_{54}H_{72}N_2Cl_2Ru_4Pd_2$: C, 45.13; H, 5.05. Found: C, 44.67; H, 5.30. 1H NMR (C_6D_6): δ 15.1 (s, 2H, μ_3 -CH), 7.17–6.98 (m, 10H, Ph), 1.82 (s, 60H, Cp*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 362.9 (s, μ_3 -CH), 169.5 (s, Ph), 127.6 (s, Ph), 123.3 (s, Ph), 116.9 (s, Ph), 95.4 (s, C_5Me_5), 11.2 (s, C_5Me_5).

X-ray Crystallography. Reflection data were collected at 296 K with a Rigaku RAXIS Rapid diffractometer equipped with an imaging plate detector. The frame data were processed using the Rigaku PROCESS-AUTO program,⁵ and the reflection data were corrected for absorption with the ABSCOR program.⁶ The structures were solved by direct method and refined on F^2 by full-matrix least-squares method with the SHELX97 program package.⁷ Anisotropic refinement was applied to all non-hydrogen atoms. Hydrogen atoms were located at the calculated positions and treated as riding models, except for the hydride ligand in **3** which was found in the final difference Fourier map and refined isotropically.

References

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