

Electronic Supplementary Information

Palladium(II) mononuclear and palladium(II)/ruthenium(II) heterodinuclear complexes containing 2-quinoly-substituted (pyridine-2-carbonyl)hydrazone

Asami Mori,^a Takayoshi Suzuki,^{a,b,*} Yuichi Nakatani,^a Yukinari Sunatsuki,^a Masaaki Kojima^a and Kiyohiko Nakajima^{c,*}

^a Department of Chemistry, Faculty of Science, Okayama University, Okayama 700-8530, Japan.

E-mail: suzuki@okayama-u.ac.jp; fax: +81-86-251-7900

^b Photosynthesis Research Center, Graduate School of Natural Science and Technology, Okayama University, Okayama 700-8530, Japan.

^c Department of Chemistry, Aichi University of Education, Kariya, Aichi 448-8542, Japan.

E-mail: knakajim@aecc.aichi-edu.ac.jp

Experimental details

General: All reagents and solvents were commercially available and used without further purification. The starting materials, [PdCl₂(cod)]¹ and HL², were prepared according to the literature methods. A mixture of *E*- and *Z*-isomers (58:42) of HL was used for preparation of the palladium(II) complexes.

Synthesis of complexes

[PdCl₂{L-κN(quinoline),κN(hydrazone),κN(pyridine)}] (1): To an acetonitrile solution (15 mL) of a mixture of *E*- and *Z*-isomers of HL (96.7 mg, 0.35 mmol) was added Et₃N (48.7 μL, 0.35 mmol) and [PdCl₂(cod)] (99.9 mg, 0.35 mmol); the mixture was stirred to dissolve [PdCl₂(cod)] completely. Then, the mixture was allowed to stand for several days at room temperature. The reddish crystalline product precipitated was collected by filtration and dried in air. Yield: 140 mg (96%). Anal. Calcd for C₁₆H₁₁ClN₄OPd: C, 46.07; H, 2.66; N, 13.43%. Found: C, 45.99; H, 2.09; N, 13.37%. ¹H NMR (CDCl₃): δ 9.38 (d, *J* = 5.6 Hz, 1H), 9.35 (d, *J* = 8.8 Hz, 1H), 8.34 (d, *J* = 8.3 Hz, 1H), 8.22 (d, *J* = 7.7 Hz, 1H), 8.09 (td, *J* = 7.6, 1.5 Hz, 1H), 7.81 (ddd, *J* = 8.0, 6.3, 1.6 Hz, 1H), 7.78 (d, *J* = 6.8 Hz, 1H), 7.64 (ddd, *J* = 5.3, 4.2, 3.7 Hz, 1H), 7.60 (ddd, *J* = 7.5, 5.7, 1.7 Hz, 1H), 7.57 (d, *J* = 8.3 Hz, 1H), 7.48 (s, 1H, azomethine-H). The single-crystals of **1**•0.5CH₃CN suitable for X-ray analysis were directly picked up from the reaction solution, and those of **1**•0.5CH₂Cl₂ were obtained from a dichloromethane solution of **1** by slow evaporation at ambient temperature.

[PdCl₂{HL'-κN(hydrazone),κN(pyridine)}] (2): Solid [PdCl₂(cod)] (37.5 mg, 0.13

mmol) was added to an acetonitrile solution (8.5 mL) of a mixture of *E*- and *Z*-isomers of HL (36.2 mg, 0.13 mmol), and the mixture was stirred to dissolve [PdCl₂(cod)] completely. To the reaction mixture was diffused diisopropyl ether vapor. After 1 d at ambient temperature yellow platelet crystals of **2**•0.5CH₃CN•H₂O were obtained as well as reddish crystalline solids of **1**•0.5CH₃CN. These crystals were separated under the microscope and used for X-ray analysis and spectroscopic measurements. Because of the poor solubility of **2** in common (deuterated) organic solvents, ¹H NMR spectrum of **2** could not be measured.

trans(Cl,Cl)-[PdCl(μ-L)RuCl₂(PPh₃)₂] (3): Complex **1** (41.7 mg, 0.10 mmol) was dissolved in dichloromethane (15 mL) on heating, and [RuCl₂(PPh₃)₃] (95.9 mg, 0.10 mmol) was then added to the solution. After stirring the mixture for 3 h at room temperature, the solvent was evaporated (to ca. 5 mL) under reduced pressure. Hexane (15 mL) was added to the concentrate, affording a green precipitate, which was collected by filtration and dried in air. Yield: 110 mg (99%). Anal. Calcd for C₅₂H₄₁Cl₃N₄OP₂PdRu•0.5CH₂Cl₂: C, 54.54; H, 3.66; N, 4.85%. Found: C, 54.66; H, 3.48; N, 4.69%. ¹H NMR (CDCl₃): δ 9.19 (d, *J* = 8.4 Hz, 2H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.97 (td, *J* = 1.4, 7.8 Hz, 1H), 7.80 (dd, *J* = 4.9, 1.7 Hz, 1H), 7.80 (t, *J* = 5.2 Hz, 1H), 7.69 (t, *J* = 7.2 Hz, 4H), 7.59 (t, *J* = 8.1 Hz, 6H), 7.53 (t, *J* = 6.7 Hz, 1H), 7.44 (ddd, *J* = 9.8, 8.5, 1.3 Hz, 6H), 7.17 (t, *J* = 4H), 7.06 (dd, *J* = 11.2, 1.6 Hz, 6H), 7.06 (td, *J* = 13.5, 1.9 Hz, 6H), 6.86 (t, *J* = 6.8 Hz, 1H), 6.30 (d, *J* = 8.5 Hz, 1H) ppm. ³¹P NMR (CDCl₃): δ = 47.27 (d, *J*_{P,P} = 35 Hz), 37.79 (d). Green prismatic crystals suitable for X-ray analysis were deposited by slow diffusion of layered hexane into a dichloromethane solution of the crude product.

Measurements

Proton and phosphorus-31 NMR spectra were recorded on a Varian NMR System 400-MR spectrometers. The ¹H and ³¹P NMR chemical shifts were referenced to the residual solvent peak and the external 85% H₃PO₄, respectively. Cyclic voltammograms were measured using a BAS 100B/W electrochemical workstation with dichloromethane solutions containing Bu₄NClO₄ (0.1 M) as a supporting electrolyte, at scan rate of 100 mV s⁻¹. The three-electrode system consisting of a glassy carbon working, a platinum wire auxiliary, and an Ag/Ag⁺ (Ag/0.01 M AgNO₃) reference electrodes were used. UV-vis absorption spectra were recorded on a Jasco V-550 spectrophotometer.

Crystallography

Each single-crystal of complexes **1**•0.5CH₃CN, **1**•0.5CH₂Cl₂ and **3**•2CH₂Cl₂ was glued on a top of glass fiber. The X-ray diffraction data were obtained at 25(1) °C using a Rigaku SCXmini CCD detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). A single-crystal of complex **2**•0.5CH₃CN•H₂O was mounted with a cryoloop and flash cooled using a cold nitrogen

stream. The X-ray diffraction data were obtained at $-110(1)$ °C using a Rigaku VariMax diffractometer with a Saturn CCD detector. The data were processed using the Process-Auto or the CrystalClear software package,³ and the numerical absorption corrections were applied.⁴ The structures were solved using the direct method employing the SIR2004, SIR2011,⁵ or SHELXS97⁶ software package and refined on F^2 (with all independent reflections) using the SHELXL97 or SHELXL2013 software package.⁶ All non-H atoms were refined anisotropically. In the analyses for $1 \cdot 0.5\text{CH}_3\text{CN}$ and $1 \cdot 0.5\text{CH}_2\text{Cl}_2$ all H-atoms were refined isotropically, while those of $3 \cdot 2\text{CH}_2\text{Cl}_2$ were placed at the theoretical positions and treated using riding models. For the analysis of $2 \cdot \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$, the quinolinium H-atom was located in a D-synthesis map and refined isotropically, but the other H-atoms in the complex molecule were theoretically introduced and treated using riding models. H atoms of the solvated CH_3CN and H_2O molecules were not included in the calculation. All calculations were carried out using the CrystalStructure software package.⁷

The crystal data are collected in Table S1, and selected structural parameters are listed in Table S2.

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Table S1. Crystallographic Data

Abbreviation	1 •0.5CH ₃ CN	1 •0.5CH ₂ Cl ₂	2 •0.5CH ₃ CN•H ₂ O	3 •2CH ₂ Cl ₂
Formula	C ₁₇ H _{12.5} Cl ₂ N _{4.5} OPd	C _{16.5} H ₁₂ Cl ₂ N ₄ OPd	C ₁₇ H _{15.5} Cl ₂ N _{4.5} O ₂ Pd	C ₅₄ H ₄₅ Cl ₇ N ₄ OP ₂ PdRu
<i>FW</i>	437.67	459.61	492.14	1283.56
<i>T</i> / K	298(1)	298(1)	163(1)	298(1)
Colour, shape	Orange, prism	Orange, prism	Yellow, platelet	Green, prism
Crystal size / mm	0.20 × 0.13 × 0.06	0.30 × 0.30 × 0.20	0.20 × 0.10 × 0.02	0.30 × 0.20 × 0.10
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group, <i>Z</i>	<i>C2/c</i> , 8	<i>C2/c</i> , 8	<i>C2/c</i> , 8	<i>P1</i> , 2
<i>a</i> / Å	10.9736(2)	22.4138(4)	27.991(6)	10.7286(5)
<i>b</i> / Å	13.3638(2)	9.6592(2)	7.563(2)	15.3170(8)
<i>c</i> / Å	21.7523(4)	17.3560(3)	17.189(6)	17.1968(9)
<i>α</i> / deg.	90	90	90	93.998(2)
<i>β</i> / deg.	90.796(1)	118.589(1)	95.354(15)	101.667(1)
<i>γ</i> / deg.	90	90	90	91.621(2)
<i>V</i> / Å ³	3189.65(10)	3299.42(11)	3623.0(18)	2758.2(2)
<i>D_x</i> / Mg m ⁻³	1.823	1.675	1.814	1.545
<i>F</i> (000)	1736	1816	1960	1288
<i>μ</i> (Mo K _α) / mm ⁻¹	1.345	1.461	1.346	1.039
<i>T</i> _{min} , <i>T</i> _{max}	0.775, 0.9248	0.697, 0.782	0.852, 0.973	0.746, 0.903
<i>R</i> _{int}	0.0327	0.0158	0.0314	0.0721
Refln./param. ratio	3663/276	3761/271	4140/253	12577/631
<i>R</i> 1 [<i>F</i> _o ² > 2σ(<i>F</i> _o ²)]	0.0255	0.0202	0.0355	0.0647
<i>wR</i> 2 (all refln)	0.0596	0.0532	0.0966	0.1525
GoF	1.051	1.086	1.099	1.054

Table S2. Selected structural parameters of complexes **1**, **2**, **3** and the related Ru complex, **4**.^a

	1 •0.5CH ₃ CN	1 •0.5CH ₂ Cl ₂	2 •0.5CH ₃ CN•H ₂ O	3 •2CH ₂ Cl ₂	4
Pd1—Cl1 (Cl3 for 3)	2.3359(6)	2.3391(5)	2.2956(11)	2.3140(18)	—
Pd1—Cl2	—	—	2.3145(12)	—	—
Pd1—N1	2.0438(18)	2.0379(16)	—	2.036(4)	—
Pd1—N3	1.9669(18)	1.9660(15)	2.071(2)	1.983(5)	—
Pd1—N4	2.0361(18)	2.0393(16)	2.020(3)	2.034(5)	—
Ru1—Cl1	—	—	—	2.4150(16)	2.430(1)
Ru1—Cl2	—	—	—	2.4113(17)	2.400(1)
Ru1—P1	—	—	—	2.3172(13)	2.313(1)
Ru1—P2	—	—	—	2.3369(15)	2.331(1)
Ru1—O1	—	—	—	2.133(4)	2.163(3)
Ru1—N2	—	—	—	2.146(5)	2.143(4)
O1—C11	1.212(3)	1.216(2)	1.238(4)	1.250(7)	1.245(6)
N3—C11	1.378(3)	1.375(2)	1.367(4)	1.336(7)	1.341(6)
N3—Pd1—Cl1 (Cl3)	168.85(6)	169.24(5)	166.26(14)	166.26(14)	—
N4—Pd1—Cl2	—	—	176.65(8)	—	—
N1—Pd1—N4	171.20(7)	169.28(6)	—	171.87(19)	—
τ_4^a	0.14	0.15	0.12	0.15	—
plane(CAH) ^b vs. plane(qn) ^c	27.0(1)	29.6(1)	2.3(1)	20.4(2)	16.5(2)
plane(CAH) vs. plane(py) ^d	15.9(1)	18.9(1)	2.4(1)	12.2(3)	3.2(2)
plane(qn) vs. plane(py)	41.22(7)	45.6(1)	3.9(1)	31.1(2)	18.5(2)

^aRef. 1. ^bDefined by N2, N3, C11 and O1. ^cDefined by N1, C1, C2, C3, C4, C5, C6, C7, C8, and C9. ^dDefined by N4, C12, C13, C14, C15 and C16.

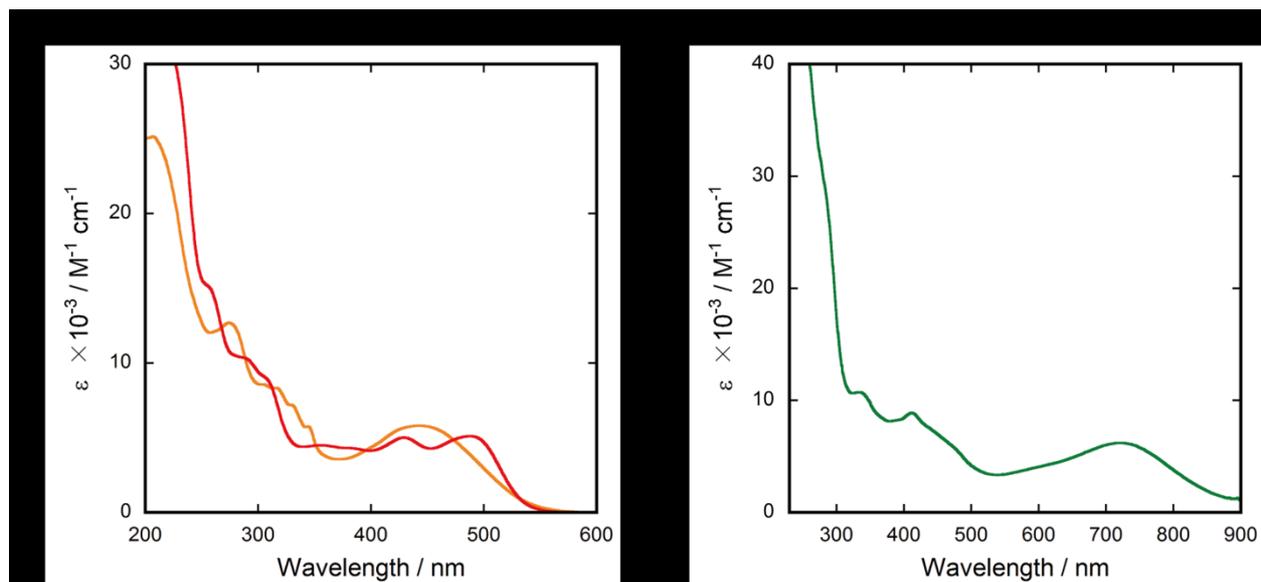


Figure S1 Absorption spectra of (a) complexes **1** (red) and **2** (orange) and (b) complex **3** (green) in acetonitrile at room temperature (~ 25 °C).

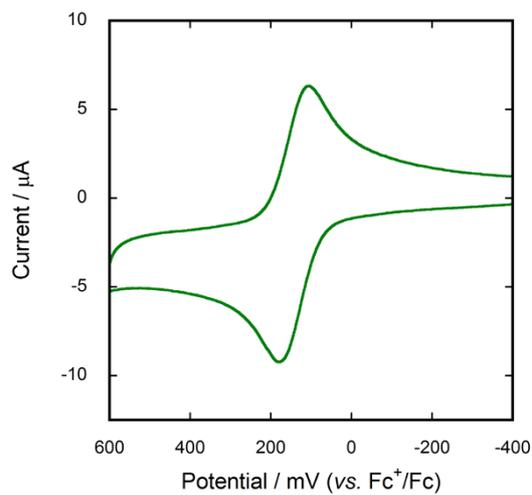


Figure S2 Cyclic voltammogram of complex **3** in dichloromethane at room temperature (~ 25 °C). $\Delta E_p = 75$ mV ($\Delta E_p = E_{pa} - E_{pc}$).

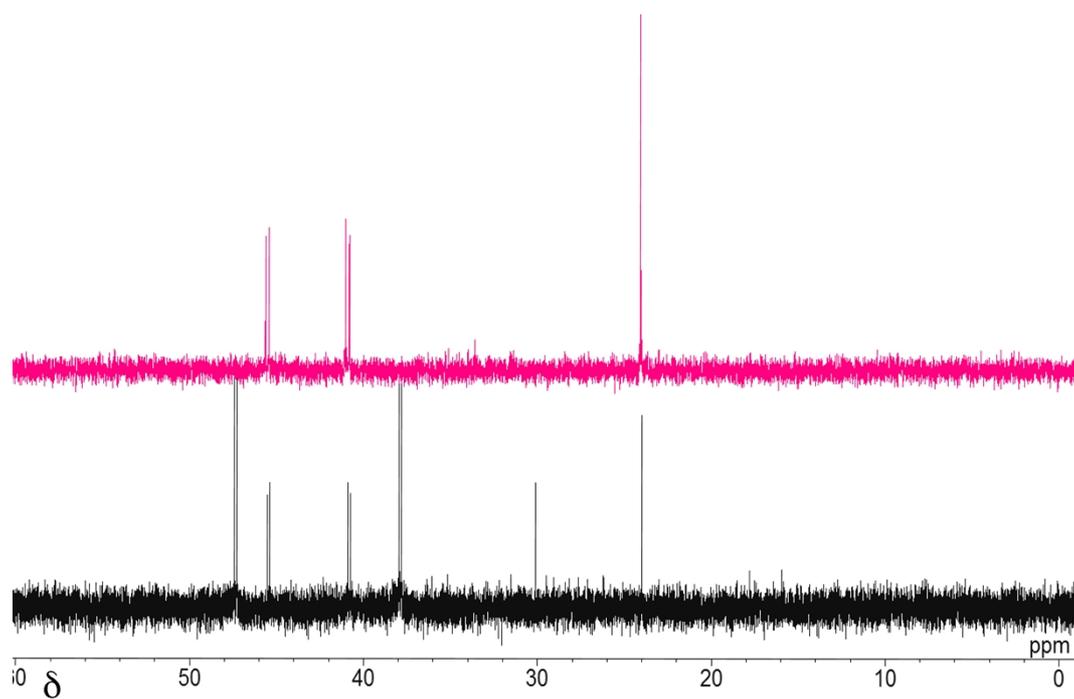


Figure S3. ^{31}P NMR spectra of complex **3** in CDCl_3 . Lower (black) spectrum was measured after ca. 1 h when a crude reaction product from complex **1** and $[\text{RuCl}_2(\text{PPh}_3)_3]$ in dichloromethane for 3 h (see: Experimental section) was dissolved in CDCl_3 . Upper (purple) was a spectrum of a prolonged (~ 10 h) reaction product from the same precursors in dichloromethane.