

Synthesis of parent amido (NH₂)-bridged dinuclear complexes of ruthenium and iridium by stepwise transfer hydrogenation of μ -azido complexes

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Experimental Details

Caution. Transition-metal azido complexes are potentially explosive, so that should be handled with great caution, although we did not have any accident in the following reactions.

General. All manipulations were performed under an atmosphere of argon using standard Schlenk technique unless otherwise specified. Solvents were dried by refluxing over sodium benzophenone ketyl (THF, toluene, diethyl ether and hexane), CaH₂ (CH₂Cl₂ and 2-propanol) and distilled before use. Acetone, 1,2-dichloromethane and pentane (anhydrous) were purchased from Kanto Chemical and used as received. [(CymRuCl)₂(μ -N₃)₂]¹ (Cym = η^6 -*p*-cymene) and [(Cp*IrCl)₂(μ -H)₂]² were prepared according to the literature. ¹H NMR (300.4 MHz) were recorded in C₆D₆ from on a JEOL JNM-LA300 spectrometer; chemical shifts are referenced to the residual nondeuterated benzene at δ 7.15. Infrared spectra were recorded on a JASCO FT/IR-610 spectrometer. Elemental analysis were performed by the Analytical Facility at the Research Laboratory of Resources Utilization, Tokyo Institute of Technology or on a Perkin-Elmer 2400II CHN analyzer.

Preparation of [(CymRuCl)₂(μ -NH₂)(μ -N₃)] (1a). To a solution of [(CymRuCl)₂(μ -N₃)₂] (299.7 mg, 0.4791 mmol) in THF (30 mL) were added 2-propanol (10 mL) and Na₂CO₃ (101.5 mg, 0.9576 mmol) and stirred for 31 h at room temperature. The resultant reddish orange solution was evaporated to dryness, and extracted with toluene (60 mL). Recrystallization from CH₂Cl₂/diethyl ether (3 mL/15 mL) afforded **1a** as reddish orange crystals (178.5 mg, 0.2977 mmol, 62%). δ_{H} 1.02 (d, 12H, ³J_{HH} = 6.9 Hz, CH(CH₃)₂), 1.88 (s, 6H, C₆H₄CH₃), 2.70 (m, 2H, CH(CH₃)₂), 4.58, 4.66, 4.73, 4.85 (d, 2H each, ³J_{HH} = 5.5 Hz, C₆H₄). ν_{max} (KBr)/cm⁻¹ 3246, 3328 (NH), 2041 (N₃). Anal. Calcd for C₂₀H₃₀Cl₂N₄Ru₂: C, 40.07; H, 5.04; N, 9.35. Found: C, 39.93; H, 5.09; N, 9.29.

Preparation of [(Cp*IrCl)₂(μ -N₃)₂]. To a solution of [(Cp*IrCl)₂]₂ (2.0029 g, 2.5140 mmol) in acetone (60 mL) was added NaN₃ (327.1 mg, 5.0315 mmol) and the mixture was stirred for 12 h at room temperature. After removal of the solvent in vacuo, the residue was extracted with 1,2-dichloroethane/CH₂Cl₂ (80 mL, 1:2 v/v). Recrystallization from dichloroethane/diethyl ether (10 mL/40 mL) afforded the title compound as orange crystals (1.8802 g, 2.3217 mmol, 92%). δ_{H} 1.35 (s, 30H, Cp*). ν_{max} (KBr)/cm⁻¹ 2060 (N₃). Anal. Calcd for C₂₀H₃₂Cl₂Ir₂N₄: C, 29.66; H, 3.73; N, 10.38. Found: C, 29.60; H, 3.64; N, 10.20.

Preparation of [(Cp*IrCl)₂(μ -NH₂)(μ -N₃)] (1b). To a solution of [(Cp*IrCl)₂(μ -N₃)₂] (302.3 mg, 0.3733 mmol) in THF (35 mL) was

added 2-propanol (29 μ L, 0.373 mmol) and stirred for 5 h at 50 °C. After removal of the solvent in vacuo, the residue was recrystallized from THF/pentane (5 mL/20 mL) at -30 °C. The brown crystals of **1b** that formed were filtered off and dried in vacuo (217.2 mg, 0.2771 mmol, 74%). δ_{H} 1.39 (s, 30H, Cp*). ν_{max} (KBr)/cm⁻¹ 3311, 3349 (NH), 2055 (N₃). The elemental analysis reproducibly gave a nitrogen value slightly less than the calculated one, which may be ascribed to facile loss of the azido nitrogens. Anal. Calcd for C₂₀H₃₂Cl₂Ir₂N₄: C, 30.65; H, 4.11; N, 7.15. Found: C, 31.09; H, 4.15; N, 6.56.

Preparation of [(CymRuCl)₂(μ -NH₂)(μ -H)] (2a). (a) To a solution of [(CymRuCl)₂(μ -N₃)₂] (48.4 mg, 0.0774 mmol) in toluene (12 mL) were added 2-propanol (3 mL) and triethylamine (22 μ L, 0.16 mmol), and the mixture was stirred for 14 h at 80 °C. The resultant red solution was evaporated to dryness, and extracted with toluene (18 mL). Recrystallization from THF/pentane (1 mL/5 mL) at -30 °C afforded **2a** as reddish orange crystals (26.7 mg, 0.0478 mmol, 62%). δ_{H} -11.08 (s, 1H, Ru₂H), 1.24, 1.25 (d, 12H each, ³J_{HH} = 6.7 Hz, CH(CH₃)₂), 2.02 (s, 6H, C₆H₄CH₃), 2.80 (m, 2H, CH(CH₃)₂), 3.74 (br, 2H, NH₂), 4.68, 4.74, 4.94, 5.07 (d, 2H each, ³J_{HH} = 5.5 Hz, C₆H₄). ν_{max} (KBr)/cm⁻¹ 3356, 3447 (NH). Anal. Calcd for C₂₀H₃₁Cl₂NRu₂: C, 43.01; H, 5.59; N, 2.51. Found: C, 43.31; H, 5.65; N, 2.46.

(b) To a solution of **1a** (40.4 mg, 0.0674 mmol) in THF (10 mL) were added 2-propanol (3 mL) and triethylamine (10 μ L, 0.067 mmol) and stirred for 5 days at 50 °C. The resultant red solution was evaporated to dryness, and extracted with toluene (18 mL). Recrystallization from THF/pentane (1 mL/5 mL) at -30 °C afforded **2a** as reddish orange crystals (15.3 mg, 0.0274 mmol, 41%).

Preparation of [(Cp*IrCl)₂(μ -NH₂)(μ -H)] (2b). (a) To a solution of [(Cp*IrCl)₂(μ -N₃)₂] (57.3 mg, 0.0708 mmol) in THF (10 mL) were added 2-propanol (3 mL) and Na₂CO₃ (15.0 mg, 0.142 mmol), and the mixture was stirred in the dark for 24 h at 50 °C. The resultant orange solution was evaporated to dryness, and extracted with toluene (12 mL). Recrystallization from THF/hexane (2 mL/8 mL) at -30 °C afforded **2b** as orange crystals (44.3 mg, 0.0596 mmol, 84%). δ_{H} -14.84 (s, 1H, Ir₂H), 1.74 (s, 30H, Cp*), 3.09 (br, 2H, NH₂). ν_{max} (KBr)/cm⁻¹ 3294, 3278 (NH). Anal. Calcd for C₂₀H₃₃Cl₂Ir₂N: C, 32.34; H, 4.48; N, 1.89. Found: C, 32.14; H, 4.50; N, 1.85.

(b) To a solution of **1b** (52.0 mg, 0.0663 mmol) in THF (8 mL) were added 2-propanol (1 mL) and Na₂CO₃ (14.0 mg, 0.133 mmol) and the mixture was stirred for 6 h at 50 °C. The resultant yellow solution was evaporated to dryness, and extracted with toluene (12

100 mL). Recrystallization from THF/pentane (2.5 mL/10 mL) at –
30 °C afforded **2b** as orange crystals (32.1 mg, 0.0432 mmol, 65%).
(c) To a solution of [(Cp*IrCl)₂(μ-H)₂] (302.5 mg, 0.4156 mmol) in
THF (50 mL) was added NaN₃ (27.0 mg, 0.415 mmol) and
105 [(C₂H₅)₃NH]Cl (120.0 mg, 0.8718 mmol), and the mixture was
stirred for 13 h at 50 °C. The resultant red orange solution was
evaporated to dryness, and extracted with toluene (60 mL).
Recrystallization from THF/diethyl ether (4 mL/15 mL) afforded
2b as orange crystals (66.1 mg, 0.089 mmol, 21%).

110 **X-ray Diffraction Studies.** Diffraction experiments were
performed on a Rigaku Saturn CCD area detector with graphite
monochromated Mo-Kα radiation (λ = 0.710 70 Å). Single
crystals suitable for X-ray analyses were mounted on glass fibers.
Intensity data were corrected for Lorentz–polarization effects and
115 for absorption.

Structure solution and refinements were carried out by using the
CrystalStructure program package.³ The heavy-atom positions
were determined by a direct methods program (SIR92⁴ for **1a** and
2a, SIR2002⁵ for **2b**) and remaining non-hydrogen atoms were
120 found by subsequent Fourier syntheses. All non hydrogen atoms
were refined anisotropically by full-matrix least-squares techniques
based on F². All hydrogen atoms except for the hydride hydrogen
atom in **2a** and **2b** were placed at calculated positions and included
in the final stages of the refinements. The hydride hydrogens were
125 found in Fourier syntheses and refined with fixed (**2a**) or isotropic
(**2b**) thermal parameters. The atomic scattering factors were taken
from ref 6, and anomalous dispersion effects were included; the
values of Δf' and Δf'' were taken from ref 7. The data completeness

value for **2a** (93%) proved to be lower than standard due to the
130 mosaicity of the crystal.

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