A water soluble and air-stable tripalladium cluster.

Fu-Ming Yang, Po-Yuan Chen, Chun-Chin Lee, Yi-Hong Liu, Shie-Ming Peng, Pi-Tai Chou and Shiuh-Tzung Liu*

Supporting information

Experimental Section

General information. All reactions and manipulations steps were performed under a dry nitrogen atmosphere. Tetrahydrofuran was distilled under nitrogen from sodium benzophenone ketyl. Dichloromethane and acetonitrile were dried over CaH_2 and distilled under nitrogen. Other chemicals and solvents were of analytical grade and were used after degassed process. Nuclear magnetic resonance spectra were recorded on a Bruker AVANCE 400 spectrometer. Chemical shifts are given in parts per million relative to Me_4Si. UV-Vis spectra were recorded on a Shimatzu PC 2100 spectrometer. Ligand **bpnp** was prepared according to the reported method.[1]

Complex 1. A mixture of **bpnp** (239, 0.84 mmol), $PdCl_2(PhCN)_2$ (400 mg, 0.90 mmol) and $Pd_2(dba)_3$ (390 mg, 0.43 mmol) in dichloromethane was heated to reflux for 8 h under nitrogen atmosphere. Upon cooling, the reaction mixture was filtered to collect dark solid, which was extracted with hot methaol. The methanol extract was concentrated to yield dark red solid (273 mg, 63 %). ^{1}H NMR(400 MHz, D_2O): δ 7.50 (m, 2H), 7.82 (d, J = 4.8 Hz, 1H), 8.08 (t, J = 8 Hz, 1H), 8.20 (t, J = 8 Hz, 1H), 8.39 (d, J = 8 Hz, 1H), 8.64 (m, 2H), 8.75 (d, J = 8 Hz, 1H), 8.92 (d, J = 8.8 Hz, 1H), 9.18 (m, 2H); UV-Vis (MeOH): λmax (log ε [$dm^3mol^{-1}cm^{-1}$]) = 248 (4.46), 265 (4.42), 290 (3.56), 302 (4.30), 335 (4.30), 360 (4.34), 467 (3.37). ESI-MS for [M-Cl][+]: Calcd. m/z = 990.83, found m/z = 991.02; Conductivity (2.5 x 10^{-4} M in CH_3OH, 25℃) : 169 ($ohm^{-1}cm^2mole^{-1}$). Anal. Calcd for $C_{36}H_{24}Cl_4N_8Pd_3$:C, 41.99; H, 2.35; N, 10.88. Found: C, 42.34; H, 2.62; N, 10.51.

[{Pd$_3$(bpnp)$_2$Cl$_2$}(CoCl$_4$)]. A mixture of **1** (10 mg, 0.01 mmol) and $CoCl_2$ (3 mg, 0.01 mmol) in metahnol (1 mL) was stirred at room temperature for 30 min. After removal of solvent, the residue was washed with acetone (1 mL x 2) and recrystallized from methano/ethanol to yield the desired complex as brown crystalline solid (11 mg, 95 %):^{1}H NMR(400 MHz, D_2O) : δ 6.99(s,1H), 7.27(s,1H),

7.55(s,1H), 7.70(s,1H), 7.91(s,1H), 8.14(s,2H), 8.49(s,2H), 8.77(s,1H), 9.17(s,2H); UV-Vis (H_2O):

λ_{max}(logε [$dm^3mol^{-1}cm^{-1}$]) = 248 (4.51), 265 (4.37), 290 (3.53), 302 (4.28), 335 (4.32), 360 (4.36), 481

(3.63). Anal. Calcd for $C_{36}H_{24}Cl_6CoN_8Pd_3$: C, 39.29; H, 2.09; N, 9.66. Found: C, 38.93; H, 2.63; N,

9.49.

[Pd₃(bpnp)₂Cl₂](PF₆)₂ (2). The procedure is similar to that for the preparation of

[{Pd₃(bpnp)₂Cl₂}(CoCl₄)] except NaPF₆ was used. ^{1}H NMR (400 MHz, d₆-acetone) δ 9.33-9.30 (m,

4H), 9.20 (d, J = 8.9 Hz, 2H), 9.07 (d, J = 8.1 Hz, 2H), 8.99 (d, J = 8.9 Hz, 2H), 8.93 (d, J = 5.4 Hz,

2H), 8.88 (d, J = 8.1 Hz, 2H), 8.46 (t, J = 7.8 Hz, 2H), 8. 39 (d, J = 7.8 Hz, 2H), 8.32 (d, J = 5.4 Hz,

2H), 7.95 (m, 2H), 7.68 (m, 2H). Anal. Calcd for $C_{36}H_{24}Cl_2F_{12}N_8P_2Pd_3 \cdot (H_2O)$: C, 34.13; H, 2.07; N,

8.85. Found: C, 33.97; H, 1.87; N, 8.35.

[{Pd₃(bpnp)₂(OH)₂}(PF₆)₂]. A solution of **1** (10 mg, 0.01 mmol) in basic aqueous solution (pH = 12)

was stirred at room temperature for 7 days, and then NaPF₆ (7 mg, 0.04 mmol) was added with stirring

for 3 h. After removal of solvent, the residue was washed with acetone (1 mL x 2) and re-crystallized

from CH_2Cl_2/methanol to yield the desired complex as a brown crystalline solid (11 mg, 88%): [1]H

NMR (400 MHz, D_2O): δ 9.18 (d, 2H, J = 8.0 Hz), 9.16 (d, 2H, J = 8.0 Hz), 9.01 (d, 2H, J = 8.0 Hz),

8.87 (d, 2H, J = 8.0 Hz), 8.76 (d, 2H, J = 8.0 Hz), 8.70 (d, 2H, J = 8.0 Hz), 8.70 (d, 2H, J = 8.0 Hz),

8.43 (t, 2H, J = 8.0 Hz), 8.33 (t, 2H, J = 8.0 Hz), 8.20 (d, 2H, J = 4.0 Hz), 8.03 (d, 2H, J = 4.0 Hz),

7.87 (dd, 1H, J = 4.0, 8.0 Hz, *py*), 7.64 (dd, 1H, J = 4.0, 8.0 Hz). Anal. Calcd for

$C_{36}H_{26}F_{12}N_8O_2P_2Pd_3 \cdot (H_2O)_2$: C, 34.65; H, 2.42; F, 18.27; N, 8.98. Found: C, 34.21; H, 2.47; N, 9.13.

Crystallography.

Crystals suitable for X-ray determination were obtained for **1** and **[{Pd₃(bpnp)₂Cl₂}(CoCl₄)]** by

recrystallization at room temperature. Cell parameters were determined either by a Oxford Diffraction

Gemini A diffractometer. The structure was solved using the SHELXS-97 program[2] and refined using

the SHELXL-97 program[3] by full-matrix least-squares on $F2$ values. Crystal data of

[{Pd₃(bpnp)₂Cl₂}(CoCl₄)]. $C_{36}H_{24}Cl_6CoN_8Pd_3 \cdot (C_2H_5OH)_2 \cdot (CH_3OH)$, Mw = 1159.46, Orthorhombic;

space group Pbca; a = 19.4036(3), b = 18.7413(2), c = 23.7872(3) Å; α = β = γ = 90°; V = 8650.2(2) Å³; Z = 8; $\rho_{calcd.}$ = 1.781 Mgm⁻³; F(000) 4504; Crystal size 0.20 x 0.20 x 0.15 mm³, reflections collected: 53323; independent reflections: 9916 [R(int) = 0.0326]; θ range 3.14 to 27.50°; goodness-of-fit on F^2 0.915; final R indices [I>2σ(I)]: R1 = 0.0241, wR2 = 0.0654; R indices (all data): R1 = 0.0361, wR2 = 0.0677.

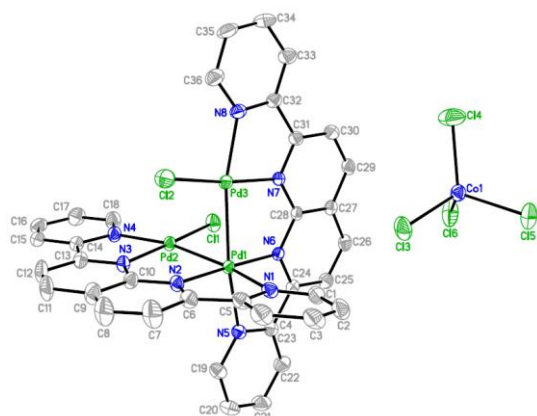**Figure S1** ORTEP plot of [{Pd₃(**bpnp**)₂Cl₂}(CoCl₄)] at the 50% probability level.

Theoretical calculation.

The calculation is performed with the Gaussian 09 program package.[4] The ground state geometry optimization is using density functional theory (DFT) at B3LYP/LANL2DZ (Pd) and 6-31G* (H, C, N, Cl) level. We use dimethylformamide (DMF) as solvent. The solvation effect is based on conductor-like polarizable continuum model (C-PCM), as was implemented in the Gaussian 09 program. We then adopt the Mulliken population analysis that provides a method of estimating partial atomic charges based on the linear combination of atomic orbital (LCAO).[5] The calculated HOMO and LUMO for complex **1** are shown in Table S1.

Table S1. The calculated frontier orbital and energy level of HOMO and LUMO for complex **1**

HOMO (-6.28 eV)　　　　　　LUMO (-3.52 eV)
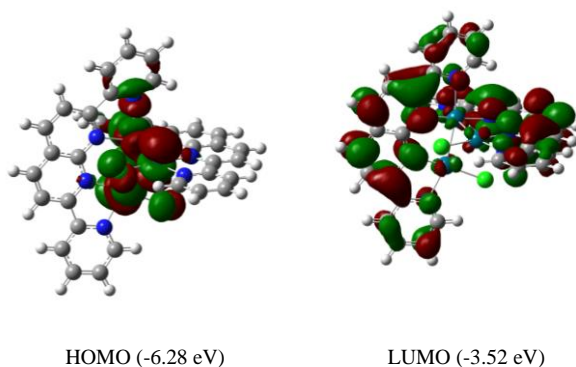
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