Electronic Supplementary Information

Molecular tectonics: hierarchical organization of heterobimetallic coordination networks into heterotrimetallic core-shell crystals

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Experimental part

Materials and general techniques

IR spectra were recorded on a FT-ATR Spectrometer PE apparatus.
Microanalyses were performed by the Service de Microanalyses de la Fédération de Recherche Chimie, Université de Strasbourg, Strasbourg, France. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded at 298 K on a Bruker AV300 spectrometer, with the solvent peak as the internal reference.

Synthesis

Analytical grade solvents were purchased and used without further purification. All commercially available products were used without further purification.
cis-$Pt(PPh_3)_2Cl_2$ was synthesized following an adapted literature procedure,[1] and 3-ethynylpyridine was obtained from a commercial source.

Compound *trans*-$[Pt(C{\equiv}CPy)_2(PPh_3)_2]$ (1):

cis-$Pt(PPh_3)_2Cl_2$ (150 mg, 0.19 mmol, 1 eq.) and 3-ethynylpyridine (39 mg, 0.38 mmol, 2 eq.) were dissolved in a degassed THF/Et_3N mixture (1/1, 8 mL). After refluxing for 2 days at 65°C, the solution was evaporated to dryness and the residue was purified by column chromatography (SiO_2, CH_2Cl_2/acetone 1/0 to 8/2) and recrystallized from CH_2Cl_2/cyclohexane 2/1 mixture. The compound **1** was obtained in 63% yield (110 mg) as a yellow solid.
^{1}H-NMR (CD_2Cl_2, 300 MHz, δ ppm): 7.42 (d; J = 5.3 Hz; 2H); 7.11(m; 12H; Ph); 6.75(m; 20H); 6.19(dd; J = 7.8 Hz, J = 5.3 Hz; 2H); 5.84(d; J = 7.8 Hz; 2H).
^{13}C-NMR (CD_2Cl_2, 75 MHz, δ ppm): 131.3; 124.6; 117.7; 114.9; 110.4; 107.9; 105.0; 102.2; 100.2.
^{31}P-NMR (CD_2Cl_2, 125 MHz, δ ppm): 20.1 ($J_{P\text{-}Pt}$ = 2626 Hz). MS (ESI): m/z calcd for $C_{50}H_{38}N_2P_2PtH^+$ $(M+H)^+$ 924.22 g/ mol ; Found 924.24 g/ mol. Anal. Calcd. for $C_{50}H_{38}N_2P_2Pt$: C, 65.00; H, 4.15; N, 3.03. Found: C, 64.34; H, 4.27; N, 2.85.

Crystallisations conditions for 1

In a 5 mL vial, compound **1** (8 mg, 8.66 μmol) was dissolved in $C_2H_4Cl_2$ (4 mL). The vial was placed into a closed jar containing pentane (6-8 mL). Yellow crystals, suitable for X-ray analysis, were obtained after 3 days by vapour diffusion.

Crystallisations conditions of 1-$ZnCl_2$

In a 5 mL tube, compound **1** (1.5 mg, 1.62 μmol) was dissolved in 1 mL of $C_2H_4Cl_2$. $ZnCl_2$ (5 mg, 37 μmol) was dissolved in 1 mL of MeOH and was gently layered on the top of the solution containing the tecton **1**. Colourless crystals, suitable for X-ray analysis, were obtained after 1 week.
Anal. Calcd. for $C_{50}H_{38}Cl_2N_2ZnP_2Pt$ $(C_2H_4Cl_2)_{1.56}$: C, 52.53 %; H, 3.67 %; N, 2.30 %; Found: C, 52.55 %; H, 3.62 %; N, 2.26 %.
IR data (cm^{-1}): ν = 1589, 1476, 1435, 1234, 1184, 1099, 997, 817, 710, 690, 654, 510.

Crystallisations conditions for 1-$CoCl_2$

In a 5 mL tube, compound **1** (1.5 mg, 1.62 μmol) was dissolved in 1 mL of $C_2H_4Cl_2$. $CoCl_2$ (5 mg, 38 μmol) was dissolved in 1 mL of MeOH and was gently layered on top of a crystallization tube containing the tecton **1**. Blue crystals, suitable for X-ray analysis, were obtained after 1 week

[1] R. Pryadun, D. Sukumaran, R. Bogadi, J. D. Atwood,. *J. Am. Chem. Soc*,. **2004**, *126*, 12414-12420

Anal. Calcd. for $C_{50}H_{38}Cl_2N_2CoP_2Pt$. $(C_2H_4Cl_2)_{0.99}$: C, 54.21%; H, 3.67 %; N, 2.43 %; Found: C, 54.18%; H, 3.64 %; N, 2.23 %.
IR data (cm^{-1}): ν = 1563, 1475, 1435, 1403, 1233, 1183, 1099, 1052, 1027, 816, 709, 689, 509.

Crystallisations conditions for 1-$CoBr_2$

In a 5 mL tube, compound **1** (1.5 mg, 1.62 µmol) was dissolved in 1 mL of $C_2H_4Cl_2$. $CoBr_2$ (5 mg, 23 µmol) was dissolved in 1 mL of MeOH and was gently layered on the top of the solution containing the tecton **1**. Blue crystals, suitable for X-ray analysis, were obtained after 1 week.
Anal. Calcd. for $C_{50}H_{38}Br_2N_2CoP_2Pt$: C, 52.56 %; H, 3.35 %; N, 2.45 %; Found: C, 52.82 %; H, 3.45%; N, 2.32 %.
IR data (cm^{-1}): ν = 1566, 1588, 1475, 1435, 1402, 1235, 1184, 1099, 1051, 1027, 816, 743, 710, 689, 509.

Generation of 1-$ZnCl_2$@1-$CoBr_2$ (or $CoCl_2$) core-shell crystals

Preformed crystals **1**-$CoBr_2$ (or **1**-$CoCl_2$) (approximately 0.1 x 0.06 x 0.02 mm) were placed in a 1:1 mixture of $C_2H_4Cl_2$: MeOH (3 mL) containing the tecton **1** (1 mg / mL) and $ZnCl_2$ (5 mg / mL). After a few days, the blue seed crystals **1**-$CoBr_2$ (or **1**-$CoCl_2$) were converted into bicolour crystals, with a colourless shroud around the blue seed crystal.

Characterization of the 1-$ZnCl_2$@1-$CoBr_2$ (or 1-$ZnCl_2$@1-$CoCl_2$) core-shell crystals

X-ray diffraction on core-shell crystals of the **1**-$ZnCl_2$@**1**-$CoBr_2$ (or **1**-$ZnCl_2$@**1**-$CoCl_2$) has been performed in order to check the crystalline nature of the core-shell crystals and to determine cell parameters. The data led to an average unit cell metrics (table 3) lying between the pure crystals **1**-$ZnCl_2$ and **1**-$CoBr_2$ (or **1**-$CoCl_2$).
Taking advantage of the difference in colour between the core (blue) and shroud (colourless) crystals, the core-shell crystals were cut affording two crystalline phases corresponding to **1**-$ZnCl_2$ and **1**-$CoBr_2$ (or **1**-$CoCl_2$). X-ray diffraction on each phase revealed cell parameters close to those obtained independently for the pure crystals (see table S2).

X-Ray Crystallography

X-ray Diffraction on microcrystalline powder

Powder X-ray diffraction (XRPD) diagrams were collected on a Bruker D8 diffractometer using monochromatic Cu-K□ radiation with a scanning range between 3.8 and 40° using a scan step size of 2°/mn.
As already demonstrated and currently admitted, for all compounds, discrepancies in intensity between the observed and simulated patterns are due to preferential orientations of the microcrystalline powders.

X-ray diffraction on Single-Crystal (Table S1)

Data were collected at 173(2) K on a Bruker APEX8 CCD Diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using graphite-monochromated Mo-Kα (λ= 0.71073 Å) radiation. For both structures, diffraction data were corrected for absorption. Structures were solved using SHELXS-97 and refined by full matrix least-squares on F^2 using SHELXL-97. The hydrogen atoms were introduced at calculated positions and not refined (riding model).[2] They can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif. CCDC: 1508100-1508103.

[2] Sheldrick, G. M.: *Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.

Formula	**1** $C_{50}H_{38}N_2P_2Pt$	**1**-$ZnCl_2$ $C_{50}H_{38}Cl_2N_2ZnP_2Pt$	**1**-$CoCl_2$ $C_{50}H_{38}Cl_2N_2CoP_2Pt$	**1**-$CoBr_2$ $C_{50}H_{38}Br_2N_2CoP_2Pt$
Molecular weight	923.85	1060.12	1053.68	1142.60
Crystal system	orthorhombic	Triclinic	Triclinic	Triclinic
Space group	P*bca*	P-1	P-1	P-1
a(Å)	18.2714(4)	9.5502(4)	9.5376(4)	9.5894(3)
b(Å)	9.6175(2)	9.6247(4)	9.6186(4)	9.6957(4)
c(Å)	22.3182(5)	24.0632(8)	24.0705(11)	24.1720(9)
α(deg)	90	95.2473(10)	95.2427(18)	95.1270(10)
β(deg)	90	91.6860(10)	91.7776(18)	91.4850(10)
γ(deg)	90	98.5240(11)	98.5725(18)	98.3100(11)
V($Å^3$)	3921.87(15)	2176.16(15)	2172.15(16)	2213.20(14)
Z	4	2	2	2
Colour	yellow	colourless	Blue	Blue
Crystal dim (mm^3)	0.050 x 0.060 x 0.060	0.050 x 0.060 x 0.070	0.050 x 0.050 x 0.060	0.050 x 0.050 x 0.060
D_{calc} (gcm^{-3})	1.565	1.618	1.611	1.715
F(000)	1840	1048	1042	1114
μ (mm^{-1})	3.698	3.995	3.833	5.446
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Number of data meas.	42714	20373	62688	33971
Number of data with I> $2_{\sigma(I)}$	5576 [R(int) = 0.0381]	11327 [R(int) = 0.0270]	11597 [R(int) = 0.0360]	11919 [R(int) = 0.0373]
R	R1 = 0.0218, wR2 = 0.0651	R1 = 0.0363, wR2 = 0.0797	R1 = 0.0290, wR2 = 0.0550	R1 = 0.0326, wR2 = 0.0769
R_W	R1 = 0.0444, wR2 = 0.0827	R1 = 0.0509, wR2 = 0.0850	R1 = 0.0455, wR2 = 0.0597	R1 = 0.0422, wR2 = 0.0811
GOF	1.025	1.025	1.036	1.020
Largest diff. peak and hole (e.Å-3)	0.478 and -0.545	2.072 and -1.188	1.036 and -0.868	2.188 and -2.024

Table S1: Crystallographic parameters recorded at 173 K for **1** and **1**-MX_2 (M = Co and Zn and X = Cl or Br), **1**-$CoBr_2$.