Electronic Supplementary Information for Dalton Transactions

Formation of $[PtPd_2(\mu_3\text{-}X)_2(P\text{-}P)(\eta\text{-}dppmX)_2]^{2+}$ (X= S, Se; P-P=dppe, 2 x PPh_3) Aggregates Through Activation of the Chalcogen-Rich $[PtX_4]$ Ring by Pd^I-Pd^I Bond

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Experimental

General Methods and Materials

All reactions were carried out with standard Schlenk techniques under an inert atmosphere of nitrogen. The following compounds were synthesized according to published procedures: Na_2Se_2[1], $Pd_2Br_2(dppm)_2$[2] and $Pt_2Cl_2(dppm)_2$[3]. All other reagents were of analytical grade and were used as received. The ligand Bis(diphenylphosphino)methane (dppm), 2-(Diphenylphosphino)pyridine (dppy), 1,2-Bis(diphenylphosphino)ethane (dppe), Triphenylphosphine (PPh_3), Selenium powder, element sulfur, Platinum Chloride ($PtCl_2$) and Ammonium Hexafluorophosphate (NH_4PF_6) were purchased from Sigma-Aldrich. ^1H and ^{31}P NMR spectra were recorded on Bruker ACF 300 and Bruker AMX 500 spectrometers, with chemical shifts (δ) reported relative to Me_4Si. ESI mass spectra were obtained using a Finnigan LCQ. Elemental analyses were performed on a Perkin-Elmer PE 2400 elemental analyzer at the Department of Chemistry, National University of Singapore.

Syntheses

$[Pt(\eta\text{-}Se)_4(dppe)]$ 3: An ethanol (5ml) solution of Na_2Se_2(46 mg, 0.23 mmol) was added to a suspension of $PtCl_2$(dppe)(50 mg, 0.075 mmol) in EtOH(5 ml). The mixture was stirred for 5 h, after which the solvent was removed and the residue dried *in vacuo*. An aliquot of THF (15 ml) was introduced to give a red suspension which was filtered to give a bright red solution. Evaporation gave a solid residue that was vacuum dried and washed successively by Et_2O (30 ml) and hexane (30 ml). Recrystallization from THF gave bright red crystals of **1.2** (24.2 mg, 35%). ESI-MS (MeOH/H_2O): m/z (%) 969 ($[M+2MeOH+H]^+$, 100%); $^{31}P\{^1H\}$NMR ($CDCl_3$): δp = 47.1 ppm(s) ($J_{Pt\text{-}P}$ = 2804 Hz);

Complexes **4-7** were synthesized by the following method: $[M_2L_2(dppm)_2]$ (0.024 mmol) was added into a solution of $[PtS_4(P\text{-}P)]$ (0.024 mmol) with a molar ratio of 1:1 in MeOH. The mixture was stirred for 5 h and filtered by celite to obtain a clear yellow solution. NH_4PF_6 (0.05 mmol) was added, turning the solution into a suspension. The precipitate was washed with deionized water and diethyl ether using vacuum suction filtration to yield powder of **4-7**.

$[PdPt(\mu_3\text{-}S)_2(PPh_3)_2(\eta\text{-}dppmS)_2](PF_6)_2$ 4. ESI-MS (MeOH/H_2O): m/z (%) 913 ($[M]^{2+}$, 75%), 931.2 ($[M+MeOH]^{2+}$, 100%); ^{1}H-NMR($CDCl_3$): δ= 3.5 ppm (m, 4H; CH_2 of dppm), 7.1-8.0 ppm (m, 70H; phenyl); $^{31}P\{^1H\}$NMR ($CDCl_3$): δp = -43.0 ppm (d), 17.2 ppm ($^1J_{(Pt\text{-}P)}$= 3173 Hz), 22.4 ppm ($^1J_{(Pt\text{-}P)}$= 2790 Hz), 43.9 ppm; Element analysis: calcd (%) for C86H74F12P8Pd2PtS4.CH2Cl2(2200.96): C 47.40, H 3.54; Found (%): C 47.42, H 3.72. Yield: 35 mg, 70%.

$[Pt_3(\mu_3\text{-}S)_2(PPh_3)_2(\eta\text{-}dppmS)_2](PF_6)_2$ 5. ESI-MS (MeOH/H_2O): m/z (%) 986 ($[M\text{-}S]^{2+}$, 100%), 1103 ($[M]^{2+}$, 45%); ^{1}H-NMR($CDCl_3$): δ= 3.5 ppm (m, 4H; CH_2 of dppm), 7.1-7.9 ppm (m, 70H; phenyl); $^{31}P\{^1H\}$NMR ($CDCl_3$): δp = -55.3 ppm ($^1J_{(Pt\text{-}P)}$= 2712 Hz), -53.8 ppm ($^2J_{(Pt\text{-}P)}$= 2712 Hz), 10.0 ppm ($^1J_{(Pt\text{-}P)}$= 3253 Hz), 16.1 ppm ($^2J_{(Pt\text{-}P)}$= 3333 Hz), 43.9 ppm; Element analysis: calcd (%) for C86H74F12P8Pt3S4.H2O.CH2Cl2(2397.10): C 43.54, H 3.28; Found (%): C 43.40, H 3.29. Yield: 25 mg, 46%.

$[PdPt(\mu_3\text{-}S)_2(dppe)(\eta\text{-}dppmS)_2](PF_6)_2$ 6. ESI-MS (MeOH/H_2O): m/z (%) 851 ($[M]^{2+}$, 100%); ^{1}H-NMR($CDCl_3$): δ = 2.49 ppm (d, 4H; CH2 of dppe), 3.48 ppm (m, 4H; CH_2 of dppm), 7.1-7.8 ppm (m, 60H; phenyl); $^{31}P\{^1H\}$NMR ($CDCl_3$): δp = -43.8 ppm (d), 42.1 ppm (m, $^1J_{(Pt\text{-}P)}$= 2905 Hz), 43.3 ppm ($^1J_{(Pt\text{-}P)}$= 3114 Hz), 42.8 ppm; Element analysis: calcd (%) for C76H68F12P8Pd2PtS4.CH2Cl2.H2O(2092.93): C 44.12, H 3.46; Found (%): C 44.07; H 3.22. Yield: 40 mg, 72%.

$[Pt_3(\mu_3\text{-}S)_2(dppe)(\eta\text{-}dppmS)_2](PF_6)_2$ 7. ESI-MS (MeOH/H_2O): m/z (%) 940 ($[M]^{2+}$, 100%), 924 ($[M\text{-}S]^{2+}$, 80%); ^{1}H-NMR($CDCl_3$): δ = 2.4 ppm (d, 4H; CH2 of dppe), 3.5 ppm (m, 4H; CH_2 of dppm), 7.1-7.9 ppm (m, 60H; phenyl); $^{31}P\{^1H\}$NMR ($CDCl_3$): δp = -53.04 ppm ($^1J_{(Pt\text{-}P)}$= 2065 Hz), 42.01 ppm ($^1J_{(Pt\text{-}P)}$ = 3175 Hz), 45.00 ppm; Element analysis: calcd (%) for C76H68F12P8Pt3S4.4CH3CN(2333.19): C 43.21, H 3.45; Found(%): C43.50, H 3.36. Yield: 27 mg, 45%.

Complexes **8-9** were synthesized by the following method: Solid $M_2L_2(dppm)_2$ (0.022mmol) was added to a CH_2Cl_2 solution of $PtSe_4(dppe)$ (0.022mmol) with ratio of 1:1. The mixture was stirred for 5 h and filtered by celite to obtain a clear red solution. After vacuum dried and changed solvent to MeOH, solid NH_4PF_6 was added to turn a solution intosuspension. The dark red precipitate was allowed to settle, collected by suction filtration and washed with deionized water and Et_2O to yield powder of **8** and **9**.

[PdPt(μ_3-Se)$_2$(dppe)(η-dppmSe)$_2$](PF$_6$)$_2$ 8. ESI-MS (MeOH/H_2O): m/z (%) 945.5 ($[M]^{2+}$, 100%); ^{1}H-NMR($CDCl_3$): δ = 2.6 ppm (d, 4H; CH2 of dppe), 3.5 ppm (m, 4H; CH_2 of dppm), 7.1-8.0 ppm (m, 60H; phenyl); Element analysis: calcd (%) for C76H68F12P8Pd2PtSe4.2CH2Cl2.H2O(2368.66): C 39.55, H 3.15; Found(%): C 39.61, H 3.24. Red crystals of $\{PtSe_2[PdSe(dppm)]_2(dppe)\}(PF_6)_2$ suitable for X-ray crystallographic analysis were obtained from slow diffusion in the mixture of CH_2Cl_2 /hexane. Yield: 31 mg, 65%.

[Pt$_3$(μ_3-Se)$_2$(dppe)(η-dppmSe)$_2$](PF$_6$)$_2$ 9. ESI-MS (MeOH/H_2O): m/z (%) 1074 ($[M+2MeOH]^{2+}$, 85%), 1034 ($[M+2MeOH-Se]^{2+}$, 80%), 995 ($[M+2MeOH-2Se]^{2+}$, 100%), 956 ($[M+2MeOH-3Se]^{2+}$, 70%); ^{1}H-NMR($CDCl_3$): δ = 2.4 ppm (d, 4H; CH2 of dppe), 3.5 ppm (m, 4H; CH_2 of dppm), 7.1-7.9 ppm (m, 60H; phenyl); $^{31}P\{^1H\}$NMR ($CDCl_3$): δp = -56.9ppm (m, $^1J_{(Pt-P)}$= 2867 Hz), 38.6 ppm (d), 42.8ppm (m, $^1J_{(Pt-P)}$ = 3268 Hz); Element analysis: calcd (%) for C76H68F12P8Pt3Se4.CH2Cl2.H2O(2462.83): C 37.58, H 2.95; Found(%): C 37.42, H 2.87. Yield: 22 mg, 42%.

X-ray Crystal Structure Determination and Refinement

The selected bond lengths and angles for complexes **8** are given in Table 1. All measurements were made on a Bruker AXS SMART APEX diffractometer equipped with a CCD area detector by using $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). The software SMART[4] was used for the collection of data frames, for indexing reflections, and to determine lattice parameters; SAINT[4] was used for the integration of the intensity of the reflections and for scaling; SADABS[5] was used for empirical absorption correction; and SHELXTL[6] was used for space group and structure determination, refinements, graphics, and structure reporting. The structure was refined by full-matrix least squares on F^2 with anisotropic thermal

parameters for non-hydrogen atoms. A summary of crystallographic parameters for the data collections and refinements is given in Table 2.

Table 1 Selected bond lengths Å and angles ° for **8**

Pt(1)-P(1)	2.241(2)	Pd(2)-Se(4)	2.412(5)
Pt(1)-P(2)	2.261(2)	Pd(2)-Se(6)	2.457(4)
Pt(1)-Se(4)	2.451(8)	Pd(3)-Se(7)	2.458(1)
Pt(1)-Se(5)	2.492(2)	Pd(3)-Se(5)	2.485(8)
Se(6)-P(4)	2.174(2)	Se(7)-P(6)	2.173(2)
Pd(3)-Se(4)	2.415(3)	Pd(3)-Se(5)	2.485(8)
Pd(2)-Se(5)	2.482(1)	Pd(2)-P(3)	2.261(2)
Pd(3)-P(5)	2.246(2)	Pd(2)-Pd(3)	3.2414(9)
Pt(1)-Pd(3)	3.1218(12)		
P(1)-Pt(1)-P(2)	85.59(8)	P(1)-Pt(1)-Se(4)	93.06(6)
Se(4)-Pt(1)-Se(5)	80.33(3)	Se(4)-Pd(2)-Se(5)	173.44(6)
Pd(2)-Se(4)-Pd(3)	84.35(3)	Pd(2)-Se(5)-Pd(3)	81.46(3)
P(4)-Se(6)-Pd(2)	100.46(6)	P(5)-Pd(3)-Se(7)	93.68(6)

Table 2 Crystallographic data and refinement for complex **8**

Complex	**8**		
Empirical formula	$C_{77}H_{70}Cl_2F_{12}P_8Pd_2PtSe_4$	Formula weight	2265.72
Temperature [K]	223(2)	Wavelength [Å]	0.71073
Crystal system	Monoclinic	Space group	P2(1)/c
a [Å]	13.701(3)	*b* [Å]	18.914(7)
c [Å]	32.456(1)	*α* [°]	90
β [°]	100.41(4)	*γ* [°]	90
Volume [Å^3]	8272.6(5)	Z	4
Density (calculated) [Mg/m3]	1.819	Absorption coefficient [mm^{-1}]	4.165

Reflections collected	58501	Independent reflections	18994
R_{int}	0.0795	R (F, $F^2 > 2\sigma$)	0.0591
R_w (F^2, all data)	0.1320	Parameters	982
Goodness-of-fit on F^2	0.960	Largest diff. peak and hole [e Å^{-3}]	2.050, -1.079

Reference

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