Supporting Information for:

Clusters as Building Blocks: Linking Heteronuclear Rhodium-Platinum Clusters

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Page S2-S3: Syntheses of $[Rh_8Pt_2(CO)_{21}(dppm)_2]$ (**1**) and $[Rh_6Pt_4(CO)_{16}(dppm)_3]$ (**2**).

*Synthesis of [$Rh_8Pt_2(CO)_{21}(dppm)_2$] (**1**) and [$Rh_6Pt_4(CO)_{16}(dppm)_3$] (**2**).*

$[Rh_6(CO)_{15}NCMe]$ [1], $[Rh_6(CO)_{15}][NBu_4]_2$ [2], $[PtCldppm]_2$ [3] and $[Pt_2(CO)_3(dppm)_2]$ [4] were prepared according to published procedures. All reactions were carried out using standard Schlenk technique under an atmosphere of dry, oxygen free nitrogen or carbon monoxide using solvents, which were freshly distilled from appropriate drying agents. Infrared spectra were recorded using a Nicolet Magna 550 FTIR spectrometer. ^1H, $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker AM 500 and Varian Unity 500 instruments. The products purification was performed using column chromatography with Silica 5-40 mesh Merck Kieselgel 60.

Reaction of $[Rh_6(CO)_{15}][NBu_4]_2$ with $[PtCldppm]_2$.

In a typical experiment, $[PtCldppm]_2$ (82 mg, 0.067 mmol) was suspended in 7 cm^3 of anhydrous methanol and CO was bubbled through the suspension under vigorous stirring. Within 10-15 min, the suspension turned into a transparent yellow solution, which was then added drop-wise to the solid $[Rh_6(CO)_{15}][NBu_4]_2$ complex (100 mg, 0.066 mmol) under CO. A red crystalline precipitate immediately separated from the reaction mixture, which was then stirred under CO for ten minutes. Degassed tetrahydrofurane (4 cm^3) were added to give dark red solution, which was stirred under CO for extra 30 min. The solvents were removed from the reaction mixture in *vacuo*. The precipitate formed was dissolved in 3 cm^3 of chloroform, diluted with 2 cm^3 of hexane (leaving some insoluble dark oily material) and transferred onto chromatographic column (2.5*7 cm, eluant chloroform/hexane/diethyl ether 30/50/2). Two main red bands were separated in the order of elution: - $Rh_2Pt_2(CO)_6(dppm)_2$ (**1**), (19 mg), $Rh_8Pt_2(CO)_{21}(dppm)_2$ (**2**) (45 mg). $Rh_2Pt_2(CO)_6(dppm)_2$,), IR (CH_2Cl_2): ν(CO), cm^{-1}, 2027s, 2006s, 1810s, br. ^1H NMR ($CDCl_3$), δ: broad multiplet of the phenyl rings 6.18-7.93 ppm. $^{31}P\{^1H\}$ ($CDCl_3$, 35°C) δ -12.4, [^1J(Pt-P) = 3257 Hz]; 5.50, [^1J(Rh-P) = 135 Hz]. FAB-MS (m/z): 1533 [M^+] (calculated 1532) and [M^+-nCO], n=1-6. $Rh_8Pt_2(CO)_{21}(dppm)_2$, IR ($CH_2Cl_2$): ν(CO), cm^{-1}, 2088m, 2077w, 2054s, 2021mw, 1972vw, 1865w, 1787m, br. ^1H NMR ($CDCl_3$), δ: broad multiplet of the phenyl rings 6.51-7.87 ppm. $^{31}P\{^1H\}$ ($CDCl_3$, 35°C), δ: -22.8 [^1J(Pt-P) = 2550 Hz]; -16.5 [^1J(Pt-P) = 3390 Hz]; -8.8 [^1J(Rh-P) = 160 Hz, ^3J(P-P) = 156 Hz]; -7.45 [^1J(Pt-P) = 3150 Hz, ^3J(P-P) = 156 Hz]. Single crystals of **2** suitable for X-ray analysis were grown by vapour phase diffusion of hexane into methanolic solution of the complex at room temperature.

Reaction of $[Rh_6(CO)_{15}NCMe]$ with $[Pt_2(CO)_3(dppm)_2]$.

$Rh_6(CO)_{15}(NCMe)$ (50 mg, 0.046 mmol) was dissolved in 25 cm^3 of dichloromethane and solution was cooled to – 80 ^{0}C (acetone bath). N_2 was bubbled through the solution for 20-25 min and crystalline $Pt_2(CO)_3(dppm)_2$ (118 mg, 0.095 mmol) was then added. The reaction mixture was allowed to reach room temperature under stirring when a brown crystalline precipitate was formed as a fine suspension. The suspension was diluted with 4 cm^3 of hexane and reduced to in volume under *vacuo* to ca. 10 – 8 cm^3. Red-violet solution was decanted and precipitate was washed with 3 cm^3 of methanol. The precipitate containing crude product was dissolved in 10 cm^3 of dichloromethane and the solution obtained was then filtered leaving on the filter some insoluble dark grey-greenish material. Solvent was removed in *vacuo* to give brown crystalline complex $[Rh_6Pt_4(CO)_{16}(dppm)_3]$ (**3**). For spectroscopic measurements complex (**3**) was purified chromatographically. Crude complex was dissolved in 3 cm^3 of CH_2Cl_2 and diluted with 1.5

cm^3 of hexane. Dark suspension was filtered, clear solution was transferred onto chromatographic column (2.5*5 cm, eluant CH_2Cl_2/hexane 2/1). The complex **(3)** was separated as main red-brownish band. IR (CH_2Cl_2): ν(CO), cm^{-1}, 2083m, 2050s, 2020m, 1977m, br, 1772m, br. ^1H NMR ($CDCl_3$), δ: broad multiplet of the phenyl rings 6.76-7.16 ppm. $^{31}P\{^1H\}$ ($CDCl_3$, 25°C) = -4.8, [^1J(Pt-P) = 2970 Hz, ^2J(Pt-P) = 450 Hz, ^3J(P-P) = 195 Hz].

Single crystals of **2** suitable for X-ray diffraction study were grown by slow diffusion of hexane into dichloromethane solution at 5 ^{0}C.

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