Supporting Information for:

"Design and synthesis of tetranuclear cluster monophosphine-cyclopalladated ferrocenylpyrimidinone complexes from the palladium-catalyzed hydroxylation of chloropyrimidine"

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Experimental

General: All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. All other chemicals were commercially available expect for chloromercuriferrocene which was prepared according to the published procedures.[1] Elemental analyses were determined with a Carlo Erba 1160 Elemental Analyzer. IR spectra were collected on a Bruker VECTOR22 spectrophotometer in KBr pellets. ^{1}H, ^{31}P $\{^{1}H\}$ NMR spectra were recorded on a Bruker DPX-400 spectrometer in $CDCl_3$ with TMS as an internal standard. Mass spectra were measured on a LC-MSD-Trap-XCT instrument.

Synthesis of 4-chloro-6-pyrimidinylferrocene (1)

In a flask equipped with reflux condenser and gas inlet chloromercuriferrocene (1 mmol), 4,6-dichloropyrimidine (1.1 mmol), NaI (2 mmol) and $Pd(PPh_3)_4$ (0.05 mmol), 18 ml absolute THF and 12 ml absolute Me_2CO were placed under N_2 atmosphere. The reaction mixture was then placed in an oil bath and heated at 80 °C for 6 h, cooled and quenched with water. The organic layer was separated and the aqueous layer was extracted with dichloromethane, then the combined organic layers were washed with water, dried over $MgSO_4$, filtered, and the solvent was removed on a rotary evaporator. The product was separated by passing through a short silica gel column with CH_2Cl_2 / petroleum ether solution (2:1) as eluent. The second band was collected and afforded the red solid **1**, yield

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63%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.73 (s, 1H, $C_4H_2N_2Cl$–H), 7.30 (s, H, $C_4H_2N_2Cl$–H), 4.97 (s, 2H, C_5H_4), 4.56 (s, 2H, C_5H_4), 4.09 (s, 5H, C_5H_5). IR (KBr, cm^{-1}): 3075, 1568, 1520, 1486, 1428, 1349, 1320, 1289, 1122, 852, 818, 765. Anal. Calcd for $C_{14}H_{11}ClFeN_2$: C, 56.32; H, 3.71; N, 9.38. Found: C, 56.52; H, 3.83; N 9.22. MS-ESI$^+$: *m/z* 298.9 ([M+H]$^+$).

General procedure for the synthesis of the cyclopalladated ferrocenylpyrimidine monophosphine complexes 2 and 4

A mixture of **1** (1 mmol), Li_2PdCl_4 (1.1 mmol) and NaOAc (1 mmol) in 20 ml of dry methanol was stirred for 24 h at room temperature. The red solids (yield: 86%) were collected by filtration and washed several times with methanol. Without further purification, it was treated with monophosphine ligands (1.1 mmol) in dry CH_2Cl_2 at room temperation for 1 hour. The product was separated by passing through a short silica gel column with CH_2Cl_2 as eluent. The first band was collected and afforded the corresponding monophosphine-cyclopalladated ferrocenylpyrimidine complexes **2** and **4**.

[PdCl{[(η^5-C_5H_5)]Fe[(η^5-C_5H_3)-$N_2C_4H_2$-Cl]}(PPh_3)] (2). Red solid, yield 87%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.61 (s, 1H, $C_4H_2N_2Cl$–H), 7.76–7.81 (m, 6H, Ph–H), 7.38–7.45 (m, 9H, Ph–H), 7.17 (s, 1H, $C_4H_2N_2Cl$–H), 4.72 (s, 1H, C_5H_3), 4.31 (s, 1H, C_5H_3), 3.74 (s, 5H, C_5H_5), 3.52 (s, 1H, C_5H_3). ^{31}P { ^{1}H } NMR (162 MHz, CDCl$_3$): δ 37.52. IR (KBr, cm^{-1}): 3436, 3053, 1576, 1518, 1485, 1434, 1360, 1297, 1128, 1097, 1002, 822, 783, 748, 695. Anal. Calcd for $C_{33}H_{28}Cl_2FeN_2PPd$: C, 55.30; H, 3.94; N, 3.91. Found: C, 55.56; H, 4.13; N 3.71. MS-ESI$^+$: *m/z* 678.6 ([M–Cl]$^+$).

[PdCl{[(η^5-C_5H_5)]Fe[(η^5-C_5H_3)-$N_2C_4H_2$-Cl]}(PCy_3)] (4). Red solid, yield 85%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.68 (s, 1H, $C_4H_2N_2Cl$–H), 7.19 (s, 1H, $C_4H_2N_2Cl$–H), 4.78 (s, 1H, C_5H_3), 4.61 (s, 1H, C_5H_3), 4.47 (s, 1H, C_5H_3), 4.11 (s, 5H, C_5H_5), 2.55 (m, 3H, P-($CHC_5H_{10})_3$), 2.05-2.21 (m, 6H, PCy_3), 1.56-1.86 (m, 15H, PCy_3), 1.28-1.35 (m, 9H, PCy_3). ^{31}P { ^{1}H } NMR (162 MHz, CDCl$_3$): δ 47.57. IR (KBr, cm^{-1}): 3457, 3075, 2927, 2850, 1575, 1519, 1487, 1445, 1417, 1357, 1297, 1266, 1128, 1003, 912, 850, 820, 782,

731. Anal. Calcd for $C_{33}H_{46}Cl_2FeN_2PPd$: C, 53.93; H, 6.31; N, 3.81. Found: C, 54.16; H, 6.47; N 3.62. MS-ESI$^+$: *m/z* 699.9 ([M–Cl]$^+$).

General procedure for the synthesis of tetranuclear cluster monophosphine-cyclopalladated ferrocenylpyrimidinone complexes 3 and 5.

In a flask equipped with reflux condenser and gas inlet **2** or **4** (1 mmol) and KOH (4 mmol), 10 ml dioxane were placed under N_2 atmosphere. The reaction mixture was then placed in an oil bath and heated at 100 °C for 10 h, cooled and quenched with water. The organic layer was separated and the aqueous layer was extracted with dichloromethane, then the combined organic layers were washed with water, dried over $MgSO_4$, filtered, and the solvent was removed on a rotary evaporator. The product was separated by passing through a short silica gel column with CH_2Cl_2 / petroleum ether solution (2:1) as eluent. The first band was collected and afforded the corresponding tetranuclear cluster monophosphine-cyclopalladated ferrocenylpyrimidinone complexes **3** and **5**.

[Pd{[(η^5-C_5H_5)]Fe[(η^5-C_5H_3)-$N_2C_4H_2O$]}PPh_3)]$_4$ (3). Red solid, yield 91%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80–7.75 (m, 15H, Ph–H), 6.85 (s, 1H, $C_4H_2N_2Cl$–H), 4.03 (d, 2H, C_5H_3), 3.60 (s, 5H, C_5H_5), 3.28 (s, 1H, C_5H_3). ^{31}P { ^{1}H } NMR (162 MHz, $CDCl_3$): δ 38.17. IR (KBr, cm^{-1}): 3437, 3055, 1622, 1511, 1481, 1441, 1405, 1342, 1308, 1246, 1190, 1098, 1028, 843, 747, 697. Anal. Calcd for $C_{128}H_{100}Fe_4N_8O_4P_4Pd_4$: C, 59.42; H, 3.90; N, 4.33. Found: C, 59.68; H, 4.11; N 4.12. MS-ESI$^+$: *m/z* 2609.9 ([M+Na]$^+$).

[Pd{[(η^5-C_5H_5)]Fe[(η^5-C_5H_3)-$N_2C_4H_2O$]}PCy_3)]$_4$ (5). Red solid, yield 86%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.32 (s, 1H, $C_4H_2N_2Cl$–H), 6.25 (s, 1H, $C_4H_2N_2Cl$–H), 4.53 (s, 1H, C_5H_3), 4.32 (s, 1H, C_5H_3), 4.12 (s, 1H, C_5H_3), 4.10 (s, 5H, C_5H_5), 2.52 (m, 3H, P-(C*H*C_5H_{10})$_3$), 2.03-2.18 (m, 6H, PCy_3), 1.53-1.81 (m, 15H, PCy_3), 1.23-1.31 (m, 9H, PCy_3). ^{31}P { ^{1}H } NMR (162 MHz, $CDCl_3$): δ 48.36. IR (KBr, cm^{-1}): 3452, 2926, 2851, 1659, 1618, 1553, 1445, 1374, 1313, 1177, 1107, 923, 818, 735. Anal. Calcd for $C_{128}H_{172}Fe_4N_8O_4P_4Pd_4$: C, 57.80; H, 6.52; N, 4.21. Found: C, 57.96; H, 6.65; N 4.02. MS-ESI$^+$: *m/z* 2655.5 ([M]$^+$).

X-ray diffraction studies

Crystallographic data for **3** were collected on a Bruker SMART APEX-II CCD diffractometer with Mo-Ka radiation (λ = 0.071073Å). The data were corrected for Lorentz-polarization factors as well as for absorption. Structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 with the SHELX-97 program.[2] All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in geometrically calculated positions. Crystal data for **3**: $C_{128}H_{100}Fe_4N_8O_4P_4Pd_4$, $M = 2587.04$, Tetragonal, P4(2)/n, $a = 17.7245(9)$ Å, $b = 17.7245(9)$ Å, $c = 22.880(2)$ Å, $\alpha = \beta = \gamma = 90^{\circ}$. $V = 7187.9(9)$ Å^3, $Z = 2$, $D_{\mathrm{Calc}} = 1.195$ Mg/m^3, 54649 reflections measured, 6696 unique reflections with $I > 2\sigma(I)$, $R_1 = 0.0453$, $wR_2 = 0.0821$. CCDC 779859.

References

1 M. Rausch, M. Vogel, H. Rosenberg, *J. Org. Chem.* 1957, *22*, 900.

2 G. M. Sheldrick, *SHELXL-97*, *Program for refinement of crystal structure*, University of Göttingen, Germany, 1997.