

## Supplementary Materials

### **Bridging $\pi$ -Coordination of Pyrrole and Indole over a Pd<sup>I</sup>–Pd<sup>I</sup> Bond**

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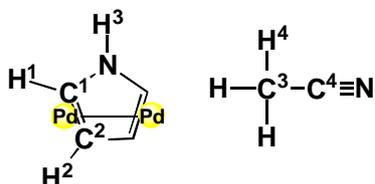
## Experimental Details

### General Consideration.

All manipulations were conducted under a nitrogen atmosphere using standard Schlenk or drybox techniques.  $^1\text{H}$ ,  $^{13}\text{C}$  nuclear magnetic resonance spectra were recorded on 400 MHz (JEOL GSX-400, Bruker DPX-400), 500 MHz (JEOL JNM-A500), and 600 MHz (Varian Unity-Inova 600) instruments. The chemical shifts were referenced to the residual resonances of deuterated solvents. Elemental analyses were performed at the Instrument Center, Institute for Molecular Science, and at the Analytical Center, Faculty of Engineering, Osaka University. X-ray crystal data were collected by Rigaku Saturn70 diffractometer. Unless specified, all reagents were purchased from commercial suppliers and used without purification. Nitromethane, diethyl ether, dichloromethane, benzene, acetonitrile,  $\text{CD}_3\text{NO}_2$ , and  $\text{CD}_2\text{Cl}_2$  were purified according to the standard procedures.  $[\text{Pd}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ <sup>1</sup>,  $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ <sup>2</sup> and  $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{PF}_6]_2$ <sup>3</sup> were prepared according to the literature.

### Synthesis of $[\text{Pd}_2(\mu\text{-pyrrole})_2(\text{CH}_3\text{CN})_2][\text{BF}_4]_2$ (**3-H**)

To a solution of  $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$  (186 mg, 0.29 mmol) in  $\text{CH}_3\text{NO}_2$  was added pyrrole (39.3 mg, 0.59 mmol). After stirring at room temperature for 30 min, the reaction mixture was filtered and the filtrate was concentrated in vacuo. Addition of toluene gave brownish orange precipitates, which was collected, washed with  $\text{Et}_2\text{O}$  and dried in vacuo. Orange powder of **3-H** was obtained (121 mg, 69% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{NO}_2$ , 25 °C)  $\delta$  9.46 (br s, 4H, H3), 7.99 (s, 6H, 1H), 6.21 (s, 4H, H2), 2.43 (s, 6H, H4).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.5 MHz,  $\text{CD}_3\text{NO}_2$ , 25 °C)  $\delta$  = 124.2 (s, C4), 107.6 (s, C1), 85.4 (s, C2), 2.9 (s, C3). Anal. Calcd. for  $\text{C}_{12}\text{H}_{16}\text{B}_2\text{F}_8\text{N}_4\text{Pd}_2$ : C, 28.87; H, 2.63; N, 9.20. Found: C, 28.91; H, 2.68; N, 9.30.



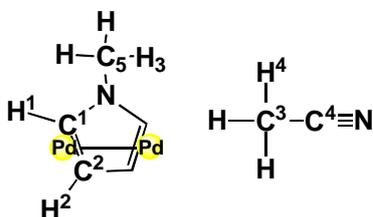
### Synthesis of $[\text{Pd}_2(\mu\text{-pyrrole})_2(\text{CH}_3\text{CN})_2][\text{PF}_6]_2$ (**3'-H**)

To a solution of  $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{PF}_6]_2$  (100 mg, 0.134 mmol) in  $\text{CH}_3\text{NO}_2$  was added pyrrole (19.2  $\mu\text{L}$ , 0.277 mmol). After stirring at room temperature for 10 min, the reaction mixture was filtered and the filtrate was concentrated in vacuo. The

precipitates obtained by addition of toluene to the concentrated filtrate was collected and washed with Et<sub>2</sub>O and dried in vacuo to give orange powder of **3'-H** (61.3 mg, 61% yield). <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>NO<sub>2</sub>, 25 °C) δ 9.35 (br s, H3), 7.99 (s, 2H, H1), 6.21 (s, 4H, H2), 2.42 (s, 4H, H4). The single crystal suitable to X-ray diffraction analysis was obtained by recrystallization from CH<sub>3</sub>NO<sub>2</sub>/benzene at room temperature.

### Synthesis of [Pd<sub>2</sub>(μ-*N*-methylpyrrole)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> (**3'-Me**)

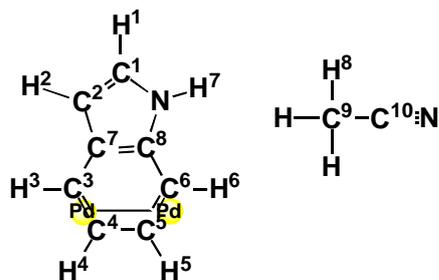
To a solution of [Pd<sub>2</sub>(CH<sub>3</sub>CN)<sub>6</sub>][PF<sub>6</sub>]<sub>2</sub> (100 mg, 0.134 mmol) in CH<sub>3</sub>NO<sub>2</sub> was added *N*-methylpyrrole (24.6 μL, 0.276 mmol). After stirring for 10 min at room temperature, the reaction mixture was filtrated and the filtrate was concentrated in vacuo. After addition of toluene, the resultant precipitate was collected, washed with Et<sub>2</sub>O, and dried in vacuo to give **3'-Me** as an orange powder (74.2 mg, 72% yield). <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>NO<sub>2</sub>, 25 °C) δ 7.81 (s, 4H, H1), 6.16 (s, 4H, H2), 3.56 (s, 6H, H3), 2.40 (s, 6H, H4). <sup>13</sup>C{<sup>1</sup>H} NMR (100.5 MHz, CD<sub>3</sub>NO<sub>2</sub>, 25 °C) δ 124.1 (s, C4), 111.3 (s, C1), 85.9 (s, C2), 36.7 (s, C5), 2.8 (s, C3). Anal. Calcd. for C<sub>14</sub>H<sub>20</sub>P<sub>2</sub>F<sub>12</sub>N<sub>4</sub>Pd<sub>2</sub>: C, 22.51; H, 2.70; N, 7.50. Found: C, 22.64; H, 2.76; N, 7.28. The single crystal suitable to X-ray diffraction analysis was obtained by recrystallization from CH<sub>3</sub>NO<sub>2</sub>/benzene at room temperature.



### Synthesis of [Pd<sub>2</sub>(μ-indole)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> (**4**)

To a solution of [Pd<sub>2</sub>(CH<sub>3</sub>CN)<sub>6</sub>][PF<sub>6</sub>]<sub>2</sub> (150 mg, 0.200 mmol) in CH<sub>3</sub>NO<sub>2</sub> was added a CH<sub>3</sub>NO<sub>2</sub> solution of indole (46.9 mg, 0.400 mmol). After stirring for 30 min, the reaction mixture was filtrated and the filtrate was concentrated in vacuo. Addition of toluene gave precipitates which was collected, washed with Et<sub>2</sub>O, and dried in vacuo. The complex **7** was obtained as dark brown powder (105.6 mg, 64% yield). The complex **7** was obtained as a mixture of two isomers. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>NO<sub>2</sub>, 25 °C) δ 10.13 (br s, Isomer A, H7), 10.09 (br s, Isomer B, H7), 7.68-7.62 (m, Isomers A and B, two among H3, H4, H5, and H6), 7.32 (s, Isomers A and B, H1), 6.72 (Isomers A and B, H2), 6.27 (br s, Isomers A and B, two among H3, H4, H5, and H6), 2.61 (s, Isomers A and B, H8). <sup>13</sup>C{<sup>1</sup>H} NMR (100.5 MHz, CD<sub>3</sub>NO<sub>2</sub>, 25 °C) δ 133.8 (s, C7 or C8), 133.6 (s, C7 or C8), 131.5 (s, C1), 131.1 (s, C1), 127.3 (s, C7 or C8), 127.0 (s, C7

or C8), 107.2 (s, C2), 107.2 (s, C2), 94.6 (s, C3, C4, C5, or C6), 94.4 (s, C3, C4, C5, or C6), 91.9 (s, C3, C4, C5, or C6), 91.3 (s, C3, C4, C5, or C6), 91.3 (s, C3, C4, C5, or C6), 90.8 (s, C3, C4, C5, or C6), 88.0 (s, C3, C4, C5, or C6), 87.3 (s, C3, C4, C5, or C6), 3.3 (s, C9). Anal. Calcd. for  $C_{20}H_{20}P_2F_{12}N_4Pd_2$ : C, 29.32; H, 2.46; N, 6.84. Found: C, 29.01; H, 2.70; N, 6.72. The single crystal suitable to X-ray diffraction analysis was obtained by recrystallization from  $CH_3NO_2$ /benzene at room temperature.



### Crystal structure determination

All data were obtained on a Rigaku Saturn70 diffractometer with graphite monochromated Mo-K $\alpha$  radiation. Calculations were carried out with the CrystalStructure crystallographic software package of Rigaku. The structures were solved by Patterson methods. The nonhydrogen atoms except for those of solvent molecules were refined anisotropically. All hydrogens were sited at calculated positions.

Crystal data for **3'-H**: C<sub>12</sub>H<sub>16</sub>F<sub>12</sub>N<sub>4</sub>P<sub>2</sub>Pd<sub>2</sub>,  $M_r = 719.01$ , monoclinic, space group  $P2_1/n$  (no. 14),  $a = 8.016(2)$ ,  $b = 8.174(2)$ ,  $c = 15.789(4)$  Å,  $\beta = 90.039(4)^\circ$ ,  $V = 1034.6(5)$  Å<sup>3</sup>,  $Z = 2$ ,  $F(000) = 692$ ,  $D_c = 2.308$  g cm<sup>-3</sup>,  $\mu(\text{MoK}\alpha) = 20.087$  cm<sup>-1</sup>, Temperature = 123 K, 6961 reflections collected, 1705 unique ( $R_{\text{int}} = 0.0275$ ), 145 variables refined with 1556 reflections with  $I > 2\sigma(I)$  to  $R_1 = 0.054$ . CCDC 904113.

Crystal data for **3'-Me·2CH<sub>3</sub>NO<sub>2</sub>**: C<sub>16</sub>H<sub>26</sub>F<sub>12</sub>N<sub>6</sub>O<sub>4</sub>P<sub>2</sub>Pd<sub>2</sub>,  $M_r = 869.15$ , triclinic, space group  $P-1$  (no. 2),  $a = 7.7670(11)$ ,  $b = 10.1048(13)$ ,  $c = 10.601(2)$  Å,  $\alpha = 111.900(5)^\circ$ ,  $\beta = 109.527(5)^\circ$ ,  $\gamma = 90.519(4)^\circ$ ,  $V = 719.0(2)$  Å<sup>3</sup>,  $Z = 1$ ,  $F(000) = 426$ ,  $D_c = 2.007$  g cm<sup>-3</sup>,  $\mu(\text{MoK}\alpha) = 14.758$  cm<sup>-1</sup>, Temperature = 123 K, 4200 reflections collected, 2107 unique ( $R_{\text{int}} = 0.0171$ ), 196 variables refined with 1923 reflections with  $I > 2\sigma(I)$  to  $R_1 = 0.030$ . CCDC 904114.

Crystal data for **4-C<sub>i</sub>**: C<sub>20</sub>H<sub>20</sub>F<sub>12</sub>N<sub>4</sub>P<sub>2</sub>Pd<sub>2</sub>,  $M_r = 819.13$ , triclinic, space group  $P-1$  (no. 2),  $a = 7.934(2)$ ,  $b = 8.982(3)$ ,  $c = 9.950(3)$  Å,  $\alpha = 103.254(2)^\circ$ ,  $\beta = 107.386(3)^\circ$ ,  $\gamma = 101.872(2)^\circ$ ,  $V = 629.3(3)$  Å<sup>3</sup>,  $Z = 1$ ,  $F(000) = 398$ ,  $D_c = 2.161$  g cm<sup>-3</sup>,  $\mu(\text{MoK}\alpha) = 16.662$  cm<sup>-1</sup>, Temperature = 123 K, 3875 reflections collected, 1938 unique ( $R_{\text{int}} = 0.0122$ ), 181 variables refined with 1837 reflections with  $I > 2\sigma(I)$  to  $R_1 = 0.034$ . CCDC 904115.

## References

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3. T. Murahashi, K. Shirato, A. Fukushima, K. Takase, T. Suenobu, S. Fukuzumi, S. Ogoshi, H. Kurosawa, *Nature Chem.* 2012, **4**, 52.