

Supplementary Materials

Bis-cyclooctatetraene Tripalladium Sandwich Complexes

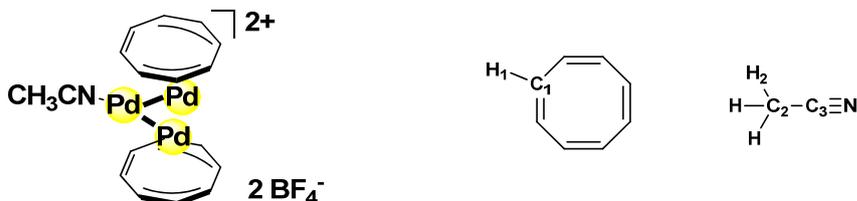
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Experimental Section

General Consideration. All manipulations were conducted under a nitrogen atmosphere using standard Schlenk or drybox techniques. ^1H , $^{13}\text{C}\{^1\text{H}\}$ NMR 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, or the Analytical Center, Faculty of Engineering, Osaka University. ESI-MS analyses were performed by Bruker micrOTOF ESI-TOF. X-ray crystal data were collected by Rigaku RAXIS-RAPID Imaging Plate diffractometer. Unless specified, all reagents were purchased from commercial suppliers and used without purification. Nitromethane, diethyl ether, dichloromethane, benzene, acetonitrile, CD_3NO_2 , and CD_2Cl_2 were purified according to the standard procedures. $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ ¹ and $\text{Pd}_2(\text{dba})_3$ ² were prepared according to the literature.

Synthesis of $[\text{Pd}_3(\mu_3\text{-C}_8\text{H}_8)_2(\text{CH}_3\text{CN})][\text{BF}_4]_2$ (1-CH₃CN**):** To a solution of $\text{Pd}_2(\text{dba})_3$ (200 mg, 0.193 mmol) in CH_2Cl_2 was added cyclooctatetraene (131 μL , 1.16 mmol) and $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ (244 mg, 0.386 mmol). After stirring at room temperature for 1h, the resultant brown precipitate was collected and washed with CH_2Cl_2 . The crude product was then dissolved in CH_3NO_2 , and CH_3CN (61 μL , 1.16 mmol) was added. After stirring for 5 min at room temperature, the mixture was filtered, and to the filtrate was added Et_2O to afford a dark brown powder of **1-CH₃CN** (221 mg, 77% yield). ^1H NMR (400 MHz, CD_3NO_2 , 25 °C): δ 5.43 (16H, s, H₁), 2.43 (3H, s, H₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CD_3NO_2 , 25 °C): δ 83.7 (s, C₁), 3.1 (s, C₂). An ESI-MS spectrum is shown in Figure S1.



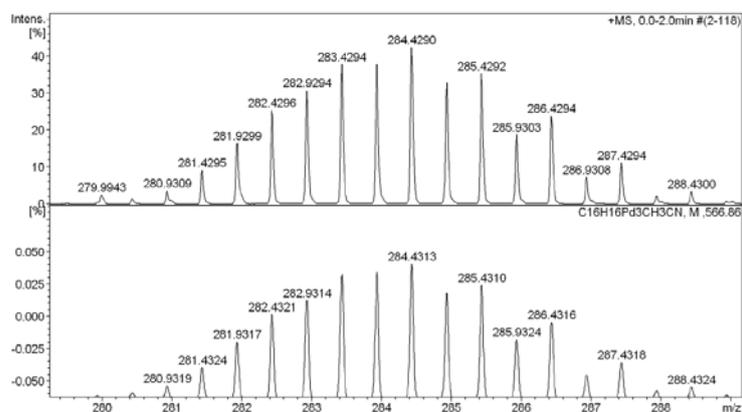
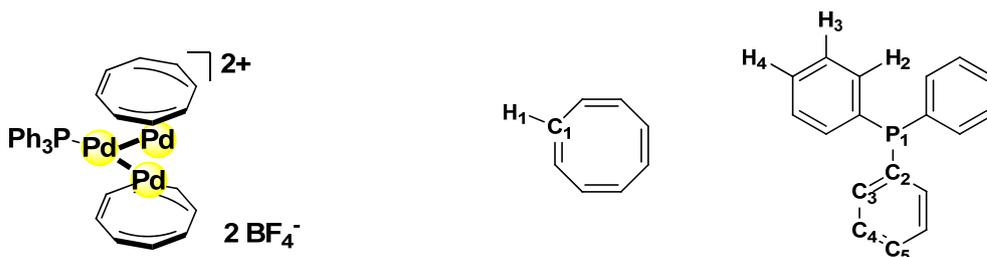


Figure S1. Experimental (top) and calculated (bottom) ESI(+)-mass spectra of $[\text{Pd}_3(\mu_3\text{-cyclooctatetraene})_2(\text{CH}_3\text{CN})][\text{BF}_4]_2$ (**1-CH₃CN**).

Synthesis of $[\text{Pd}_3(\mu_3\text{-C}_8\text{H}_8)_2(\text{PPh}_3)][\text{BF}_4]_2$ (1-PPh₃**):** To a CH_3NO_2 solution of **1-CH₃CN** (100 mg, 0.135 mmol) was added PPh_3 (35.4 mg, 0.135 mmol), and the mixture was stirred for 5 min. The reaction mixture was filtered, and the filtrate was concentrated in vacuo. Addition of Et_2O gave the dark purple precipitate. Recrystallization from $\text{CH}_3\text{NO}_2/\text{benzene}$ gave **1-PPh₃** (85 mg, 66% yield). ^1H NMR (400 MHz, CD_3NO_2 , 25 °C): δ 7.80-7.75 (15H, m, PPh_3), 5.27 (16H, s, H_1). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CD_3NO_2 , 25 °C): δ 135.8-131.1 (PPh_3), 81.8 (s, C_1). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_3NO_2 , 25 °C): δ 29.9. An ESI-MS spectrum is shown in Figure S2. Anal. Calcd. for $\text{C}_{34}\text{H}_{31}\text{B}_2\text{F}_8\text{P}_1\text{Pd}_3 \cdot \text{CH}_3\text{NO}_2$: C, 41.03; H, 3.35; N, 1.37. Found: C, 40.54; H, 3.41; N, 0.74.



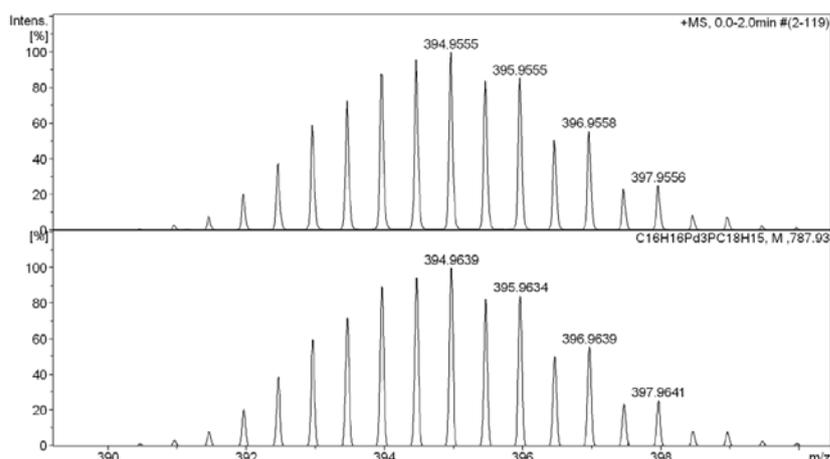
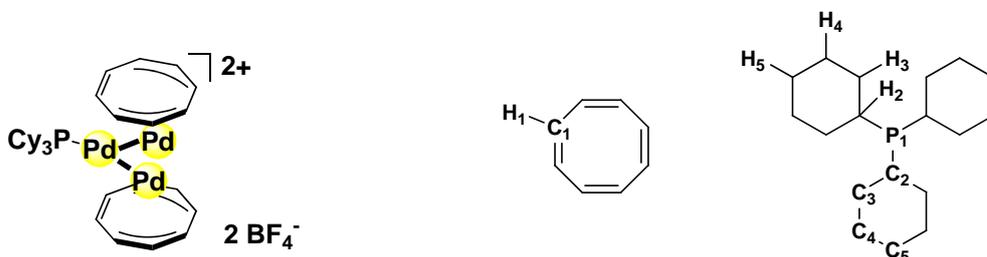


Figure S2. Experimental (top) and calculated (bottom) ESI(+)-mass spectra of $[\text{Pd}_3(\mu_3\text{-cyclooctatetraene})_2(\text{PPh}_3)][\text{BF}_4]_2$ (**1-PPh₃**).

Synthesis of $[\text{Pd}_3(\mu_3\text{-C}_8\text{H}_8)_2(\text{PCy}_3)][\text{BF}_4]_2$ (1-PCy₃**):** To a CH_3NO_2 solution of **1-CH₃CN** (107.5 mg, 0.145 mmol) was added PCy_3 (40.6 mg, 0.145 mmol), and the mixture was stirred for 1 h. The reaction mixture was filtered, and the filtrate was concentrated in vacuo. Addition of Et_2O gave the dark purple precipitate. Recrystallization from $\text{CH}_2\text{Cl}_2/\text{hexane}$ gave **1-PCy₃** (88.1 mg, 62% yield). ^1H NMR (400 MHz, CD_3NO_2 , 25 °C): δ 5.43 (16H, s, H₁), 2.49 (3H, m, H₂), 2.08 (6H, m, H₃ or H₄), 1.91 (6H, m, H₃ or H₄), 1.79 (3H, m, H₅), 1.48-1.68 (12H, m, H₃, H₄), 1.35 (3H, m, H₅). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, CD_3NO_2 , 25 °C): δ 80.4 (s, C₁), 36.0 (d, $J = 14$ Hz, C₂), 32.1 (s, C₃ or C₄) 28.6 (d, $J = 10$ Hz, C₃ or C₄) 27.3 (s, C₅). $^{31}\text{P}\{^1\text{H}\}$ NMR (160.3 MHz, CD_3NO_2 , 25 °C): δ 43.6 (s, P₁). An ESI-MS spectrum is shown in Figure S3. Anal. Calcd. For. $\text{C}_{34}\text{H}_{49}\text{B}_2\text{F}_8\text{PPd}_3 \cdot 0.5\text{CH}_2\text{Cl}_2$: C, 40.46; H, 4.92. Found: C, 40.32; H, 5.26.



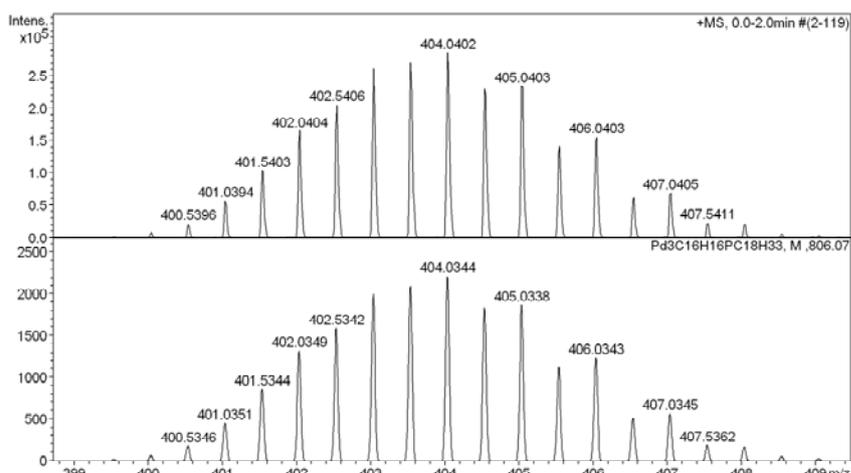
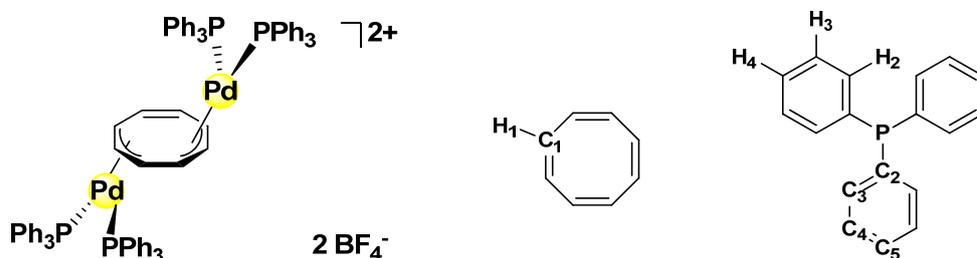


Figure S3. Experimental (top) and calculated (bottom) ESI(+)-mass spectra of $[\text{Pd}_3(\mu_3\text{-cyclooctatetraene})_2(\text{PCy}_3)][\text{BF}_4]_2$ (**1-PCy₃**).

Synthesis of $[\text{Pd}_2(\mu\text{-C}_8\text{H}_8)(\text{PPh}_3)_4][\text{BF}_4]_2$ (4-PPh₃**):** The complex **4-PPh₃** was isolated by the following method. To a CH_3CN_3 solution of $[\text{Pd}_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-C}_8\text{H}_8)(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ (88.5 mg, 0.131 mmol) was added PPh_3 (137.0 mg, 0.522 mmol), and the mixture was stirred for 1 h. The reaction mixture was filtered, and the filtrate was concentrated in vacuo. Addition of Et_2O gave the orange precipitate. Recrystallization from $\text{CH}_3\text{CN}/\text{ether}$ gave $[\text{Pd}_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-C}_8\text{H}_8)(\text{PPh}_3)_4][\text{BF}_4]_2$ (126.3 mg, 63% yield). ^1H NMR (400 MHz, CD_3NO_2 , 25 °C): δ 7.47 (12H, t, $J = 7$ Hz, H_4), δ 7.34 (24H, dd, $J = 7$ Hz, $J = 7$ Hz, H_3), δ 7.20 (24H, m, H_2), δ 4.54 (8H, s, H_1). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, CD_3NO_2 , 25 °C): δ 134.9 (s, C_5), 132.8 (s, C_3), 131.2 (t, $J = 24$ Hz, C_2) 130.5 (s, C_4) 100.4 (s, C_1). $^{31}\text{P}\{^1\text{H}\}$ NMR (160.3 MHz, CD_3NO_2 , 25 °C): δ 25.2 (s, P_1). An ESI-MS spectrum is shown in Figure S4. Anal. Calcd. For. $\text{C}_{80}\text{H}_{68}\text{B}_2\text{F}_8\text{P}_4\text{Pd}_2$: C, 62.40; H, 4.83. Found: C, 62.05; H, 4.45.



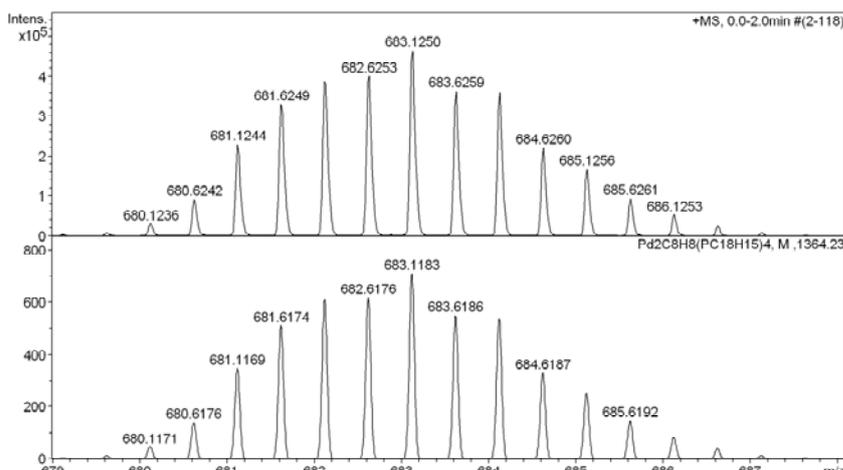


Figure S4. Experimental (top) and calculated (bottom) ESI(+)-mass spectra of $[\text{Pd}_2(\mu\text{-}\eta^3\text{-}\eta^3\text{-cyclooctatetraene})(\text{PPh}_3)_4][\text{BF}_4]_2$ (**4-PPh₃**).

X-ray Crystallographic Data

Crystal data for **1-H₂O·H₂O·C₆H₆**: $\text{C}_{22}\text{H}_{26}\text{B}_2\text{F}_8\text{O}_2\text{Pd}_2$, $M_r = 815.25$, monoclinic, space group $P2_1/n$ (no. 14), $a = 10.0392(6)$, $b = 16.352(1)$, $c = 14.6824(8)$ Å, $\beta = 93.420(2)^\circ$, $V = 2405.9(3)$ Å³, $Z = 4$, $F(000) = 1576$, $D_c = 2.251$ g cm⁻³, $\mu(\text{MoK}\alpha) = 23.025$ cm⁻¹, $T = 123$ K, 22510 reflections collected, 5472 unique ($R_{\text{int}} = 0.0545$), 334 variables refined with 4221 reflections with $I > 3\sigma(I)$ to $R = 0.054$. CCDC 904367.

For the crystal structure of **1-H₂O**, a relatively large residual electron density was observed at (0.93344, 0.56154, 0.24500), which is located closely to the heavy metal atom (Pd1).

Crystal data for **4-PPh₃**: $\text{C}_{80}\text{H}_{68}\text{P}_4\text{B}_2\text{F}_8\text{O}_2\text{Pd}_2$, $M_r = 1539.64$, monoclinic, space group $C2/c$ (no. 15), $a = 25.3856(12)$, $b = 24.7751(10)$, $c = 11.8833(6)$ Å, $\beta = 93.6780(10)^\circ$, $V = 7458.4(6)$ Å³, $Z = 4$, $F(000) = 3296$, $D_c = 1.447$ g cm⁻³, $\mu(\text{MoK}\alpha) = 7.03$ cm⁻¹, $T = 123$ K, 36530 reflections collected, 8540 unique ($R_{\text{int}} = 0.0764$), 408 variables refined with 5150 reflections with $I > 2\sigma(I)$ to $R = 0.073$. CCDC 962478.

For the crystal structure of **4-PPh₃**, four methylene chloride molecules in the unit cell are disordered. The contribution to the scattering arising from the presence of disordered molecules in the crystals was removed by use of the utility SQUEEZE in the

PLATON software package.³ Additional details on PLATON/SQUEEZE can be found in the CIF of complex **4-PPh₃**.

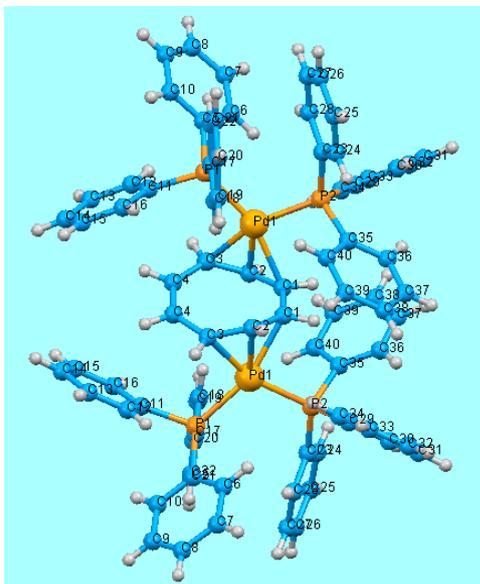


Figure S5. A ball and stick drawing of **4-PPh₃** (BF₄ anions were omitted). For the duplicate atom labels, one set of the atom labels are at (1-x, y, 1/2-z).

References

- 1 T. Murahashi, T. Nagai, T. Okuno, T. Matsutani, H. Kurosawa, *Chem. Commun.* **2000**, 1689.
- 2 H. Ukai, H. Kawazura, Y. Ishii, *J. Organomet. Chem.* 1974, **65**, 253.
- 3 A. L. Spec, *Acta Cryst.* 2009, **D65**, 148.