

Supplementary Materials

Trinuclear Palladium Addition to Unsaturated Carbocycles

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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, and the Analytical Center, Faculty of Engineering, Osaka University. High-resolution 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 $\text{NaB}(\text{Ar}^{\text{F}})_4$,² and $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{PF}_6]_2$ ³ were prepared according to the literature.

Synthesis of $[\text{Pd}_3(\mu_3\text{-[2.2]paracyclophane})(\text{phen})_3][\text{BF}_4]_2$ (3**):** To a solution of $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ (100 mg, 0.16 mmol) in a mixture of CH_2Cl_2 (ca. 40 mL) and CH_3CN (ca. 5 mL) was added [2.2]paracyclophane (165 mg, 0.79 mmol) and $\text{Pd}_2(\text{dba})_3$ (82 mg, 0.079 mmol), and the mixture was stirred for 1 h at room temperature. Addition of 1,10-phenanthroline (85 mg, 0.47 mmol) to the mixture resulted in precipitation of a red powder. After the volatiles were removed in vacuo, the red powder was dissolved in nitromethane, and the solution was filtrated. Addition of Et_2O to the filtrate gave a red powder. Recrystallization from CH_3NO_2 /benzene gave red crystals of **3** (93.5 mg) in 48% yield. ^1H NMR(400 MHz, CD_3NO_2 , 25 °C): δ 9.66 (br, 1H, H7), 9.62 (br, 2H, H15), 8.84 (d, $^3J = 6$ Hz, 1H, H9), 8.61 (br, 4H, H17, H20 or 22), 8.30 (m, 1H, H8), 8.04 (d, $^3J = 8.8$ Hz, 1H, H10), 7.99 (d, $^3J = 8.8$ Hz, 2H, H20 or 22), 7.93 (d, $^3J = 8.8$ Hz, 2H, H18 or 19), 7.86 (m, 2H, H16), 7.71 (m, 4H, H11, H12 or 14, H18 or 19), 7.53 (s, 2H, H2), 7.41 (s, 2H, H1), 7.32 (m, 1H, H12 or 14), 6.74 (m, 2H, H21), 5.95 (m, 1H, H13), 4.78 (s, 2H, H5), 4.75 (s, 2H, H6), 3.17 (m, 4H, H3), 2.78 (m, 4H, H4). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CD_3NO_2 , 25 °C) δ 155.1 (s, C26 or 28), 153.8 (s, C19), 153.3 (s, C16 or 18), 150.8 (s, C9), 146.6 (s), 146.5(s), 146.2

(s), 140.6 (s, C7), 140.2 (s, C21), 139.9 (s, C11), 139.1 (s, C26 or 28), 138.3 (s, C14 or 16 or 18), 133.0 (s, C2), 132.8 (s, C1), 132.0 (s), 131.4 (s) 130.7 (s), 130.4 (s), 129.7 (s), 128.6 (s, C23 or 24) 128.6 (s, C23 or 24), 128.5 (s, C13), 127.3 (s, C10), 126.9 (s, C20), 125.4 (s, C27), 125.0 (s, C17), 106.0 (s, C8), 68.9 (s, C6), 67.7 (s, C5), 37.7 (s, C4), 35.3 (s, C3). Anal. Calcd. For. $C_{52}H_{40}B_2F_8N_6Pd_3 \cdot CH_3NO_2$: C, 48.86; H, 3.33; N, 7.53. Found: C, 48.34; H, 3.37; N, 6.76.

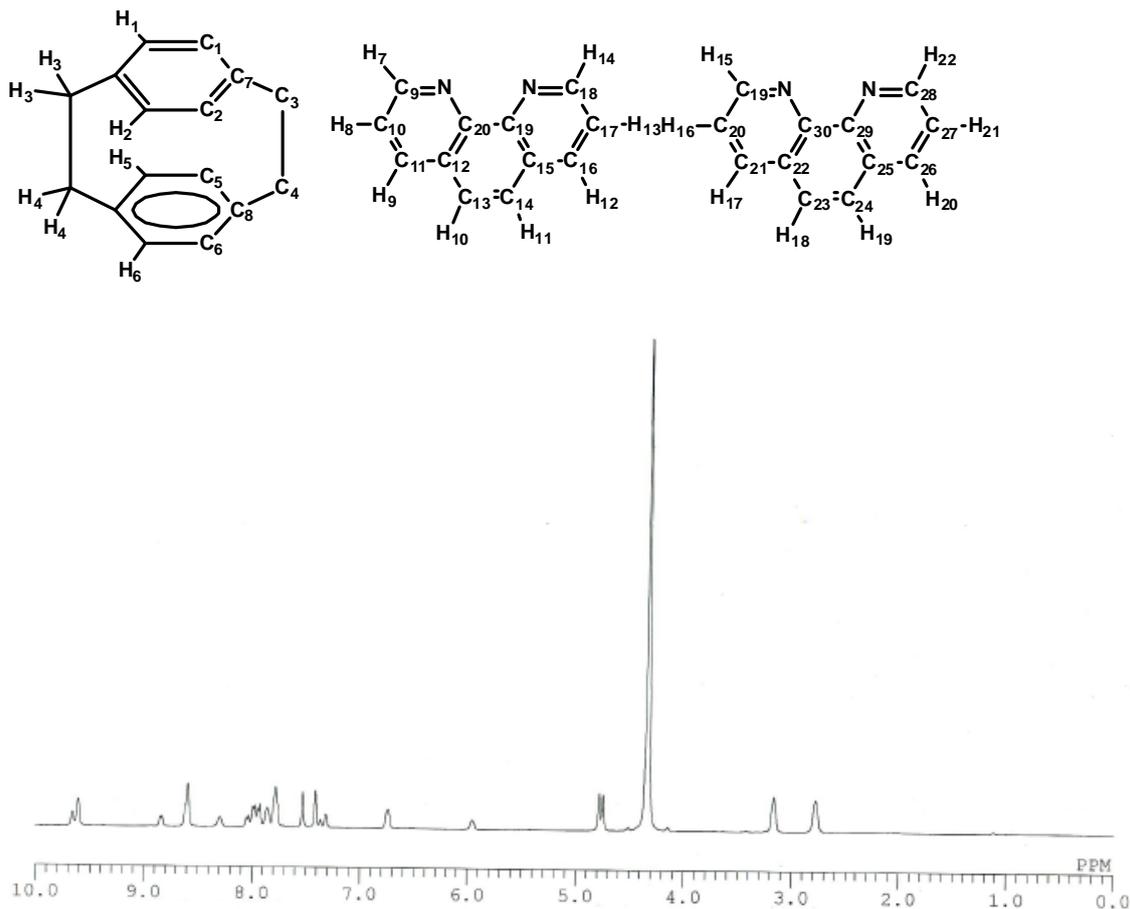
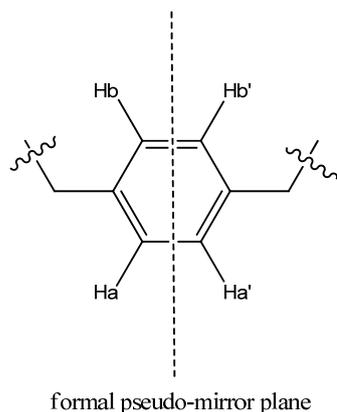


Figure S1. A 1H NMR spectrum of $[Pd_3(\mu_3\text{-}[2.2]\text{paracyclophane})(\text{phen})_3][BF_4]_2$ (**3**) in CD_3NO_2 at 25 °C.

The $B(\text{Ar}^F)_4$ salt $[Pd_3(\mu_3\text{-}[2.2]\text{paracyclophane})(\text{phen})_3][B(\text{Ar}^F)_4]_2$ (**3'**), which was generated in CD_2Cl_2 by treatment of **3** with $NaB(\text{Ar}^F)_4$ showed a dynamic 1H NMR behavior (Figure S2). As described in the main text, the well-separated signals could not be obtained in the range of the temperature down to -90 °C, and the signals of the phen protons were very broad at 90 °C. Presumably, two or more dynamic processes are involved in the processes. The 1H NMR spectral change in the temperature range of -90 °C to 20 °C might involve an exchange process

which resulted in the averaging of two sets of phen ligands as well as of pairs of the coordinated or uncoordinated arene protons, as to make a formal pseudo-mirror plane in a molecule. The two coordinated arene signals or the two uncoordinated arene signals without $^3J_{\text{H-H}}$ coupling at 23 °C may indicate that the chemical environments around two ipso carbons of the cyclophane become equivalent on the NMR time scale. In this case, the hydrogen atoms H_a and H_a' are equivalent, as are the hydrogen atoms H_b and H_b' .



A few explanations for the NMR aspects are possible. Firstly, one major barrier to the structural change appears to come from steric interactions within the tripalladium-arene complex, particularly around the (phen)Pd1–Pd2(phen) framework. Secondly, the singlet pattern of the coordinated and uncoordinated arene protons at 23 °C may exclude a situation that dynamic processes result in different bonding and/or structural environments about the two ipso-carbons in each arene of the paracyclophane ligand. Thirdly, the facts that the NMR signals for two of three Pd(phen) units in **3'** are averaged at 23 °C and those for another Pd(phen) unit are not involved in the exchange event suggest that the dynamic NMR behavior may arise from the rapid exchange between two of three Pd(phen) units. One possible dynamic process, which is consistent with the observed signal pattern and variable temperature NMR behavior, is the rapid exchange between Pd3(phen) and one of the Pd(phen) units of the Pd₂ framework. In the process, the Pd1(phen) unit or the Pd2(phen) unit moves fluxionally between the two allylic coordination site (Scheme S1). It is known that intermolecular allyl ligand exchange between a μ -allyl Pd–Pd complex [Pd₂(μ -allyl)(PPh₃)₂(μ -Cl)] and a mononuclear allyl Pd complex [Pd(allyl)(PPh₃)Cl] proceeds in an equilibrium manner.

On the other hand, the ¹H NMR spectral change in the temperature range of 30 °C to 90 °C gives rise to averaging of all four protons of the coordinated or uncoordinated arene to a single signal. Significant broadening of the all phen proton signals may suggest that all three Pd(phen) units are involved in the exchange process.

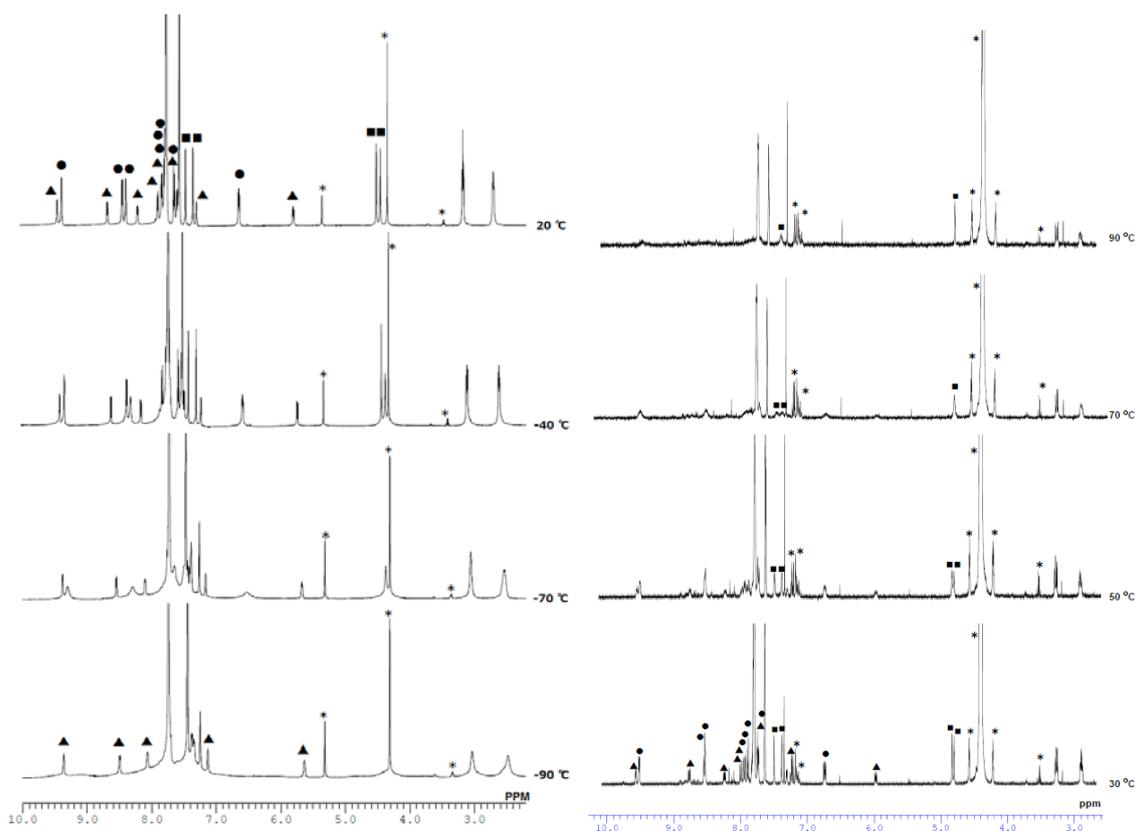
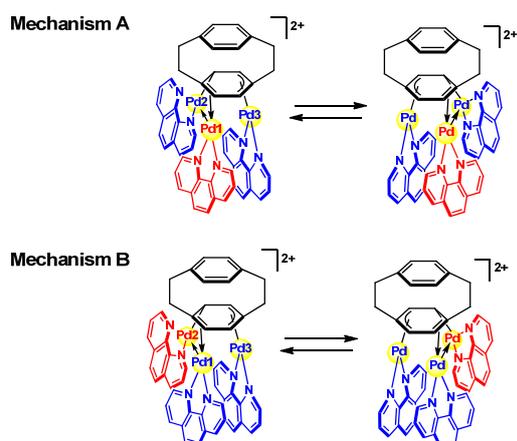
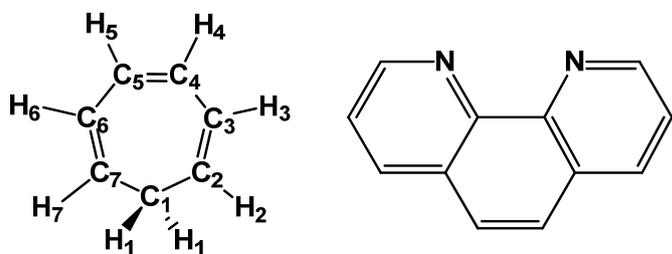


Figure S2. Variable Temperature ^1H NMR spectra of **3'** (left: $-90 \sim 20\text{ }^\circ\text{C}$ in CD_2Cl_2 ; right: $30 \sim 90\text{ }^\circ\text{C}$ in CD_3NO_2) (\blacktriangle = a set of phen, \bullet = a set of phen, \blacksquare = arene protons, * = dichloromethane, nitromethane, toluene, and Et_2O).



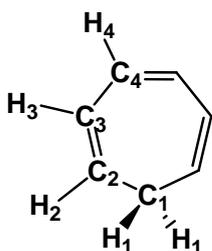
Scheme S1. Possible mechanisms for the dynamic behavior of **3'**. One of the two $\text{Pd}(\text{phen})$ units (red) in the Pd-Pd moiety [mechanism A, $\text{Pd1}(\text{phen})$; mechanism B, $\text{Pd2}(\text{phen})$] moves between the two π -allylic sites.

Synthesis of $[\text{Pd}_3(\mu_3\text{-C}_7\text{H}_8)(\text{phen})_3][\text{BF}_4]_2$ (5**):** To a solution of $[\text{Pd}_3(\mu_3\text{-C}_7\text{H}_8)_2(\text{CH}_3\text{CN})_3][\text{BF}_4]_2$ (**4**) (100 mg, 0.125 mmol) in CH_3NO_2 (ca. 3 mL) was added 1,10-phenanthroline (67.5 mg, 0.370 mmol) at room temperature. The mixture was stirred for 5 min, and the mixture was filtered. Crystallization from CH_3NO_2 /benzene gave **5** (59.3 mg, 42% yield). ^1H NMR (400 MHz, CD_3NO_2 , 25 °C): δ 9.96 (d, $^3J = 4.5$ Hz, 1H, phen), 9.54 (d, $^3J = 5.0$ Hz, 1H, phen), 9.50 (d, $^3J = 5.0$ Hz, 1H, phen), 9.44 (d, $^3J = 5.0$ Hz, 1H, phen), 9.00 (d, $^3J = 8.3$ Hz, 1H, phen), 8.79 (d, $^3J = 8.0$ Hz, 1H, phen), 8.41 (m, 2H, phen), 8.34 (d, $^3J = 8.5$ Hz, 1H, phen), 8.25 (m, 3H, phen), 8.09 (d, $^3J = 8.5$ Hz, 1H, phen), 8.01 (d, $^3J = 9.0$ Hz, 1H, phen), 7.83 (d, $^3J = 8.8$ Hz, 1H, phen), 7.78-7.74 (m, 3H, phen), 7.71 (d, $^3J = 8.0$ Hz, 1H, phen), 7.64 (d, $^3J = 8.8$ Hz, 1H, phen), 7.36 (m, 1H, phen), 7.19 (dd, $^3J = 5.0$ and 8.0 Hz, 1H, phen), 6.69 (dd, $^3J = 4.8, 7.9$ Hz, 1H, phen), 5.95 (dd, $^3J = 5.0$ and 8.3 Hz, 1H, phen), 5.66 (dd, $^3J = 8.0$ and 9.0 Hz, 1H, H₅), 5.35 (dd, $^3J = 8.0$ and 9.0 Hz, 1H, H₆), 4.99 (dd, $^3J = 8.0$ and 7.0 Hz, 1H, H₇), 4.94 (dd, $^3J = 8.3$ and 8.0 Hz, 1H, H₄), 4.78 (dd, $^3J = 8.3$ and 9.5 Hz, 1H, H₃), 3.63 (m, 1H, H₂), 3.32 (ddd, $^2J = 19.3$ Hz, $^3J = 7.0$ and 2.5 Hz, 1H, H₁), 2.31 (m, 1H, H₁). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, CD_3NO_2 , 25 °C): δ 157.7 (s, phen), 154.2 (s, phen), 153.9 (s, phen), 153.2 (s, phen), 152.4 (s, phen), 150.9 (s, phen), 147.6 (s, phen), 147.4 (s, phen), 146.8 (s, phen), 145.7 (s, phen), 145.2 (s, phen), 140.7 (s, phen), 140.3 (s, phen), 140.0 (s, phen), 139.7 (s, phen), 139.3 (s, phen), 138.3 (s, phen), 132.0 (s, phen), 131.9 (s, phen), 131.6 (s, phen), 131.5 (s, phen), 130.4 (s, phen), 130.2 (s, phen), 129.7 (s, phen), 129.0 (s, phen), 128.9 (s, phen), 128.8 (s, phen), 128.7 (s, phen), 128.6 (s, phen), 128.5 (s, phen), 127.8 (s, phen), 127.7 (s, phen), 127.0 (s, phen), 126.2 (s, phen), 125.7 (s, phen), 125.0 (s, phen), 100.3 (s, C₆), 85.3 (s, C₅), 76.3 (s, C₇), 73.4 (s, C₃), 54.5 (s, C₄), 40.5 (s, C₂), 31.7 (s, C₁). Anal. Calcd. for $\text{C}_{43}\text{H}_{32}\text{B}_2\text{F}_8\text{N}_6\text{Pd}_3$: C, 45.88; H, 2.87; N, 7.47. Found: C, 45.36; H, 3.07; N, 7.28.

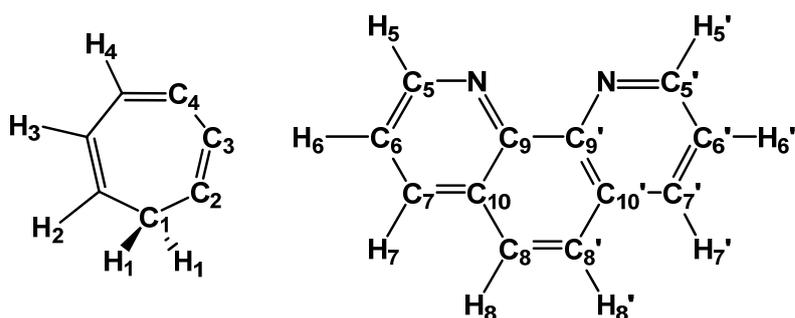


Synthesis of $[\text{Pd}_2(\mu\text{-C}_7\text{H}_8)(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ (6-CH₃CN**):** To solution of $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ (200.3 mg, 0.32 mmol) in CH_3NO_2 (ca. 4 mL) was added

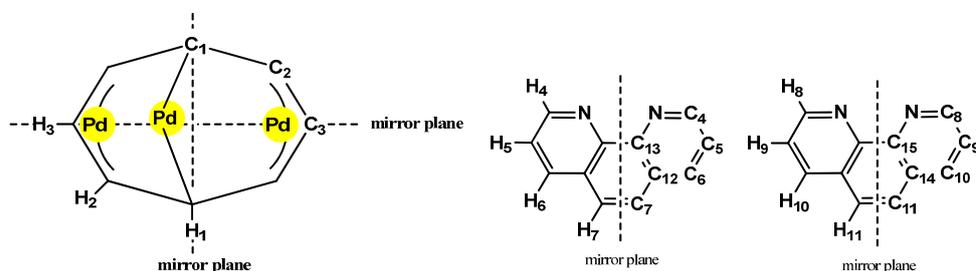
cycloheptatriene (29.5 mg, 0.32 mmol, 33.0 μ L) at room temperature. The mixture was stirred for 30 min, and mixture was filtered. Adding CH_2Cl_2 and Et_2O , the solution was cooled at $-20\text{ }^\circ\text{C}$ to give **6-CH₃CN** (114.1 mg, 56%). ^1H NMR (400 MHz, CD_3CN , $25\text{ }^\circ\text{C}$): δ 5.41 (m, 2H, H₄), 5.16 (m, 2H, H₃), 5.05 (m, 2H, H₂), 2.19 (m, 1H, H₁), 1.52 (m, 1H, H₁). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, CD_3CN , $25\text{ }^\circ\text{C}$): δ 104.16 (s, C₃), 83.12 (s, C₂), 79.52 (s, C₄), 32.32 (s, C₁). Anal. Calcd. for $\text{C}_{15}\text{H}_{20}\text{B}_2\text{F}_8\text{N}_4\text{Pd}_2$: C, 28.03; H, 3.14; N, 8.72. Found: C, 27.69; H, 3.03; N, 8.44.



Synthesis of $[\text{Pd}_2(\mu\text{-C}_7\text{H}_8)(\text{phen})_2][\text{BF}_4]_2$ (6-phen**):** To solution of $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ (99.9 mg, 0.16 mmol) in CH_3NO_2 (ca. 8 mL) was added cycloheptatriene (14.29 mg, 0.16 mmol, 16.0 μ L) at room temperature, and the mixture was stirred for 30 min. 1,10-phenanthroline (57.0 mg, 0.32 mmol) was added and the reaction mixture was stirred for 1h. The reaction mixture was filtered and concentrated in vacuo. Addition of Et_2O to the solution gave the crude product. Crystallization from CH_3NO_2 /toluene gave **6-phen** (94.9 mg, 71%). ^1H NMR (400 MHz, CD_3NO_2 , $25\text{ }^\circ\text{C}$): δ 9.14 (dd, $^3J = 4.8\text{ Hz}$, $^4J = 1.5\text{ Hz}$, 2H, H₅), 8.96 (dd, $^3J = 5.0\text{ Hz}$, $^4J = 1.3\text{ Hz}$, 2H, H_{5'}), 8.39 (dd, $^3J = 8.3\text{ Hz}$, $^4J = 1.3\text{ Hz}$, 2H, H_{7'}), 8.33 (dd, $^3J = 8.3\text{ Hz}$, $^4J = 1.5\text{ Hz}$, 2H, H₇), 7.75 (s, 4H, H₈ and H_{8'}), 7.69 (dd, $^3J = 5.0$ and 8.3 Hz , 2H, H_{6'}), 7.66 (dd, $^3J = 4.8$ and 8.3 Hz , 2H, H₆), 6.11 (m, 2H, H₄), 5.68 (m, 2H, H₃), 5.20 (m, 2H, H₂), 3.00 (dt, $^2J = 22.6\text{ Hz}$, $^3J = 3.7\text{ Hz}$, 1H, H₁), 2.22 (dt, $^2J = 22.6\text{ Hz}$, $^3J = 3.9\text{ Hz}$, 1H, H₁). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, CD_3NO_2 , $25\text{ }^\circ\text{C}$): δ 155.7 (s, C₅), 153.8 (s, C_{5'}), 145.5 (s, C_{9'}), 144.7 (s, C₉), 141.3 (s, C_{7'}), 141.0 (s, C₇), 130.9 (s, C_{10'}), 130.6 (s, C₁₀), 128.9 (s, C₈), 128.7 (s, C_{8'}), 127.7 (s, C₆), 127.5 (s, C_{6'}), 106.8 (s, C₃), 82.4 (s, C₄), 78.2 (s, C₂), 31.8 (s, C₁). Anal. Calcd. for $\text{C}_{24}\text{H}_{25}\text{B}_1\text{F}_4\text{N}_2\text{Pt}_3$: C, 44.38; H, 2.88; N, 6.68. Found: C, 43.99; H, 2.96; N, 6.66.



Synthesis of $[\text{Pd}_3(\mu_3\text{-C}_8\text{H}_8)(\text{phen})_3][\text{BF}_4]_2$ (8**):** To a solution of cyclooctatetraene (48.6 mg, 0.47 mmol) in CH_3NO_2 was added $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ (268 mg, 0.42 mmol) and 1,10-phenanthroline (153 mg, 0.85 mmol). Subsequently, $\text{Pd}_2(\text{dba})_3$ (219 mg, 0.21 mmol) and 1,10-phenanthroline (76.3 mg, 0.42 mmol) were added to the reaction mixture. The mixture was stirred at ambient temperature for 2 h to give a deep blue solution. The mixture was filtered, and the filtrate was concentrated in vacuo. Addition of toluene afforded a deep blue powder of **8** (413 mg, 0.36 mmol) in 86% yield. ^1H NMR (400 MHz, CD_3NO_2 , 25 °C): δ 9.16 (4H, dd, $J = 5$ Hz, $J = 1$ Hz, H_4), 8.48 (2H, dd, $J = 5$ Hz, $J = 1$ Hz, H_8), 8.26 (4H, dd, $J = 10$ Hz, $J = 1$ Hz, H_6), 8.01 (2H, dd, $J = 10$ Hz, $J = 1$ Hz, H_{10}), 7.66 (4H, dd, $J = 10$ Hz, $J = 5$ Hz, H_5), 7.60 (4H, s, H_7), 7.43 (2H, s, H_{11}), 7.39 (2H, dd, $J = 10$ Hz, $J = 5$ Hz, H_9), 6.37 (4H, t, $J = 6$ Hz, H_2), 6.03 (2H, t, $J = 6$ Hz, H_3), 2.42 (2H, t, $J = 6$ Hz, H_1). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CD_3NO_2 , 25 °C): δ 156.0 (s, C_4), 148.6 (s, C_8), 145.3 (s, C_{13}), 144.6 (s, C_{15}), 139.4 (s, C_6), 138.8 (s, C_{10}), 130.9 (s, C_{12}), 130.0 (s, C_{14}), 128.1 (s, C_7), 127.8 (s, C_{11}), 126.4 (s, C_5), 125.6 (s, C_9), 106.6 (s, C_3), 93.5 (s, C_2), 22.1 (s, C_1). Anal. Calcd. for $\text{C}_{44}\text{H}_{32}\text{B}_2\text{F}_8\text{N}_6\text{Pd}_3 \cdot \text{CH}_3\text{NO}_2$: C, 45.09; H, 2.94; N, 8.18. Found: C, 45.55; H, 3.08; N, 7.82.



The PF_6 salt $[\text{Pd}_3(\mu_3\text{-cyclooctatetraene})(\text{phen})_3][\text{PF}_6]_2$ (**5'**) was obtained by a similar method using $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{PF}_6]_2$ as the starting material. Anal. Calcd. for $\text{C}_{44}\text{H}_{32}\text{P}_2\text{F}_{12}\text{N}_6\text{Pd}_3 \cdot$

CH₃NO₂: C, 42.14; H, 2.57; N, 6.70. Found: C, 41.80; H, 2.72; N, 6.75.

Synthesis of [Pd₂(μ-C₈H₈)(phen)₂][BF₄]₂ (9-phen): To a solution of cyclooctatetraene (50 mg, 0.48 mmol) in CH₃NO₂ was added [Pd₂(CH₃CN)₆][BF₄]₂ (304 mg, 0.48 mmol) and 1,10-phenanthroline (173 mg, 0.96 mmol). The mixture was filtered, and crystallization from CH₃NO₂/benzene gave a yellow powder of **9-phen** (175 mg, 0.21 mmol) in 43% yield. ¹H NMR spectra of **9-phen** at 25 °C showed broad signals for phen and COT protons due to a dynamic process of **9-phen** (Figure S3). ¹H and ¹³C{¹H} NMR assignment by using Variable Temperature measurement with aid of COSY and HSQC was done for **9-phen** (see below). Anal. Calcd. For C₃₂H₂₄B₂F₈N₄Pd₂: C, 45.16; H, 2.84; N, 6.58. Found: C, 44.92; H, 3.03; N, 6.73.

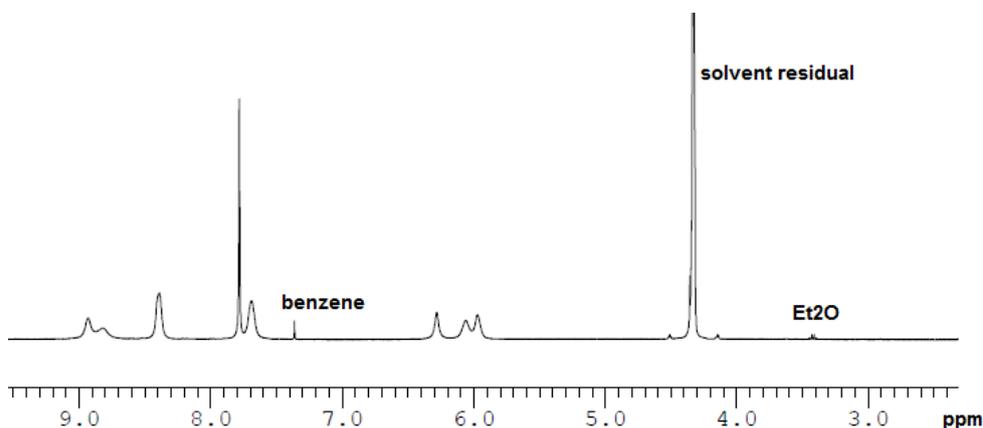


Figure S3. A ¹H NMR spectrum of [Pd₂(μ-C₈H₈)(phen)₂][BF₄]₂ (**9-phen**).

The B(Ar^F)₄ salt [Pd₂(μ-C₈H₈)(phen)₂][B(Ar^F)₄]₂ (**9'-phen**) was obtained by treatment of **9-phen** with NaB(Ar^F)₄ (2 equiv.) in CH₂Cl₂. ¹H NMR (600 MHz, CD₂Cl₂, -60 °C): For the COT protons; δ 5.97-5.93 (4H, br), 5.74 (1H, br), 5.64 (2H, br), 2.82 (1H, br). 13 resonances were observed for phen protons (three signals overlap with those of B(Ar^F)₄ anions). ¹³C{¹H} NMR (151 MHz, CD₂Cl₂, -60 °C): For the COT carbons; δ 145.8 (s), 129.4 (s), 110.0 (s), 102.0 (s), 92.3 (s), 92.2 (s) 75.7 (s), 47.5 (s).

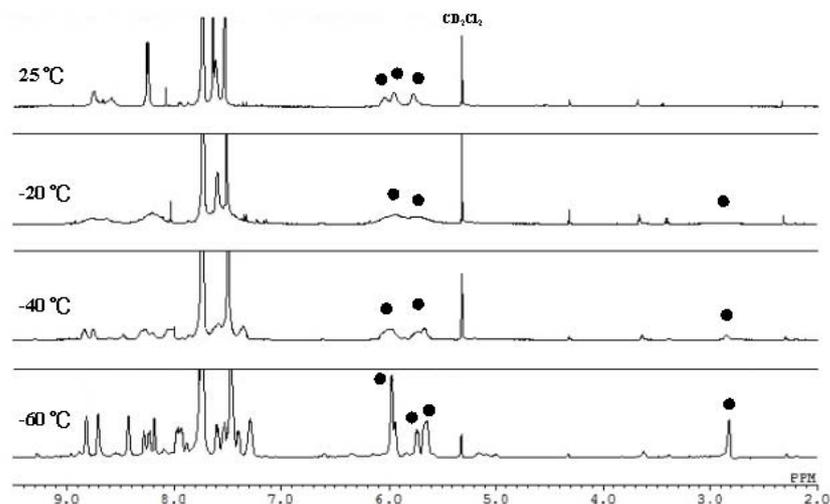


Figure S4. Variable Temperature ^1H NMR spectra of **9'-phen** in CD_2Cl_2 .

Synthesis of $[\text{Pd}_3(\mu_3\text{-dihydropentalenediyl})(\text{phen})_3][\text{BF}_4]_2$ (10**):** A deep blue solution of $[\text{Pd}_3(\mu\text{-cyclooctatetraene})(\text{phen})_3][\text{BF}_4]_2$ (36.6 mg, 0.032 mmol) in CH_3NO_2 was heated at 55 $^\circ\text{C}$ for 5 h. The resultant red mixture was filtered, and the volatiles were removed in vacuo. Crystallization from $\text{CH}_3\text{CN}/\text{CH}_3\text{NO}_2/\text{benzene}$ gave orange microcrystals of **6** (28.1 mg) in 77% yield. A ^1H NMR spectrum (400 MHz, CD_3NO_2 , 25 $^\circ\text{C}$) is shown in Figure S4. At 25 $^\circ\text{C}$, only averaged signals were observed except for central allylic protons, due to the dynamic process of **10**. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR assignment by using Variable Temperature measurement with aid of COSY and HSQC was done for **10'** (see below). ESI-MS spectrum is shown in Figure S5. Anal. Calcd. for $\text{C}_{44}\text{H}_{32}\text{B}_2\text{F}_8\text{N}_6\text{Pd}_3$: C, 46.45; H, 2.84; N, 7.39. Found: C, 45.59; H, 3.08; N, 7.36.

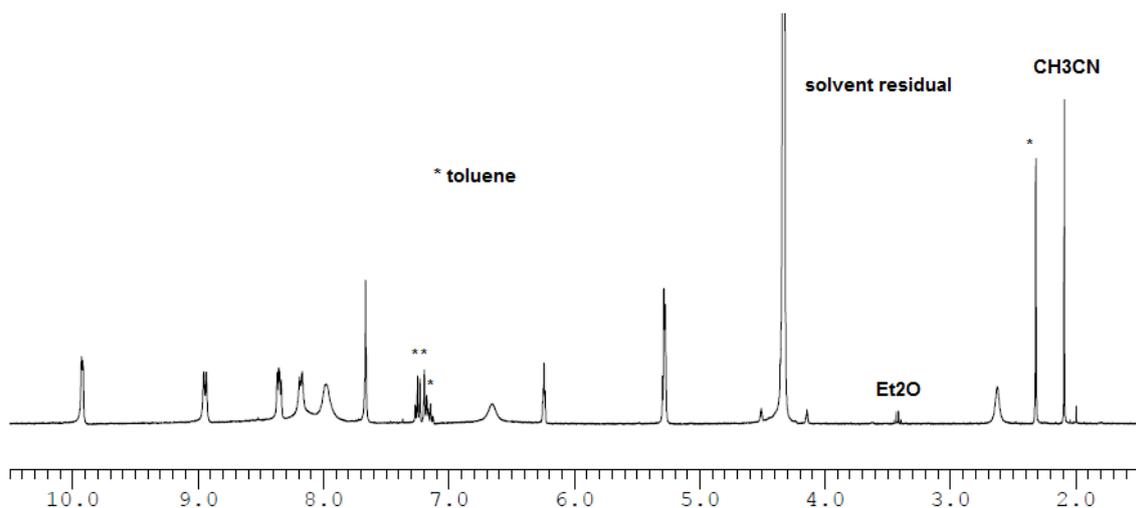


Figure S5. A ^1H NMR spectrum of $[\text{Pd}_3(\mu_3\text{-dihydropentalenediyl})(\text{phen})_3][\text{BF}_4]_2$ (**10**) in CD_3NO_2 at $25\text{ }^\circ\text{C}$.

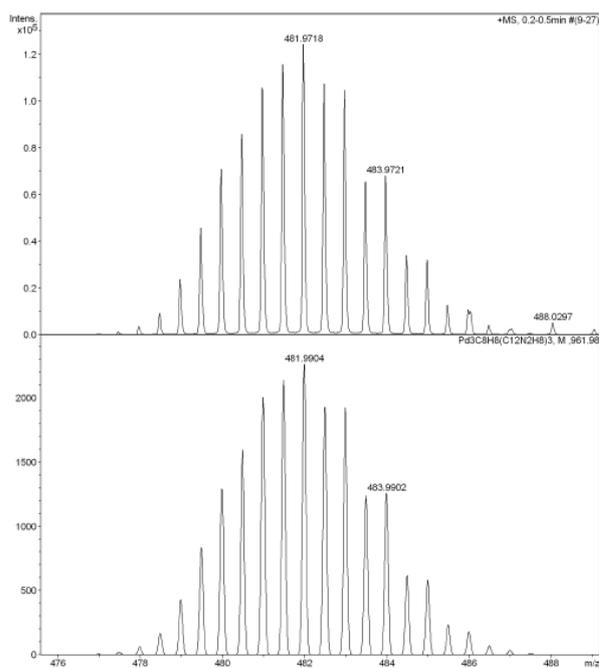
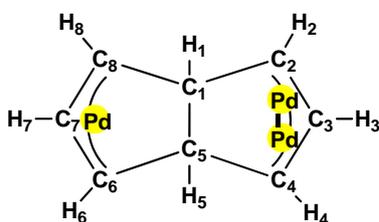


Figure S6. Experimental (top) and calculated (bottom) ESI(+)-mass spectrum of $[\text{Pd}_3(\mu_3\text{-dihydropentalenediyl})(\text{phen})_3][\text{BF}_4]_2$ (**10**).

The $\text{B}(\text{Ar}^{\text{F}})_4$ salt $[\text{Pd}_3(\mu_3\text{-dihydropentalenediyl})(\text{phen})_3][\text{B}(\text{Ar}^{\text{F}})_4]_2$ (**10'**) was obtained by treatment of **10** with $\text{NaB}(\text{Ar}^{\text{F}})_4$ (2 equiv.) in CH_2Cl_2 . ^1H NMR (600 MHz, CD_2Cl_2 , $-60\text{ }^\circ\text{C}$): δ 9.66 (1H, d, $J = 4$ Hz, phen), 9.59 (1H, d, $J = 4$ Hz, phen), 8.93 (1H, d, $J = 5$ Hz, phen), 8.72

(1H, d, $J = 8$ Hz, phen), 8.63 (1H, d, $J = 5$ Hz, phen), 8.58 (1H, d, $J = 8$ Hz, phen), 8.20 (1H, dd, $J = 8$ Hz, $J = 5$ Hz, phen), 8.13-8.10 (2H, m, phen), 7.97 (1H, d, $J = 8$ Hz, phen), 7.80-7.78 (2H, m, phen), 7.75 (B(Ar^F)₄), 7.58-7.56 (2H, m, phen), 7.45-7.43 (B(Ar^F)₄ + phen), 7.39 (1H, d, $J = 8$ Hz, phen), 7.35-7.30 (2H, two d, $J = 9$ Hz, phen), 7.18 (1H, d, $J = 4$ Hz, phen), 7.07 (1H, dd, $J = 8$ Hz, $J = 5$ Hz, phen), 6.85 (1H, d, $J = 4$ Hz, phen), 6.57 (1H, dd, $J = 8$ Hz, $J = 5$ Hz, phen), 6.14 (1H, phen), 5.93 (1H, br s, H7), 5.55 (1H, dd, $J = 8$ Hz, $J = 5$ Hz, phen), 5.12 (1H, t, $J = 5$ Hz, H3), 4.92 (1H, br s, H6 or H8), 4.80 (1H, br s, H6 or H8), 4.46 (1H, t, $J = 5$ Hz, H2), 3.82 (1H, br t, H4), 2.62 (br t, H5), 2.35 (br t, H1). ¹³C{¹H} NMR (151 MHz, CD₂Cl₂, -80 °C): δ 105.6 (s, C7), 81.1 (s, C3), 81.1 (s, C6 or C8), 79.5 (s, C6 or C8), 57.4 (s, C5), 56.2 (s, C1), 52.1 (s, C2), 46.0 (s, C4).



The dynamic NMR behavior observed for **10** and **10'** might be due to the exchange between two Pd-phen moieties of the Pd-Pd unit.

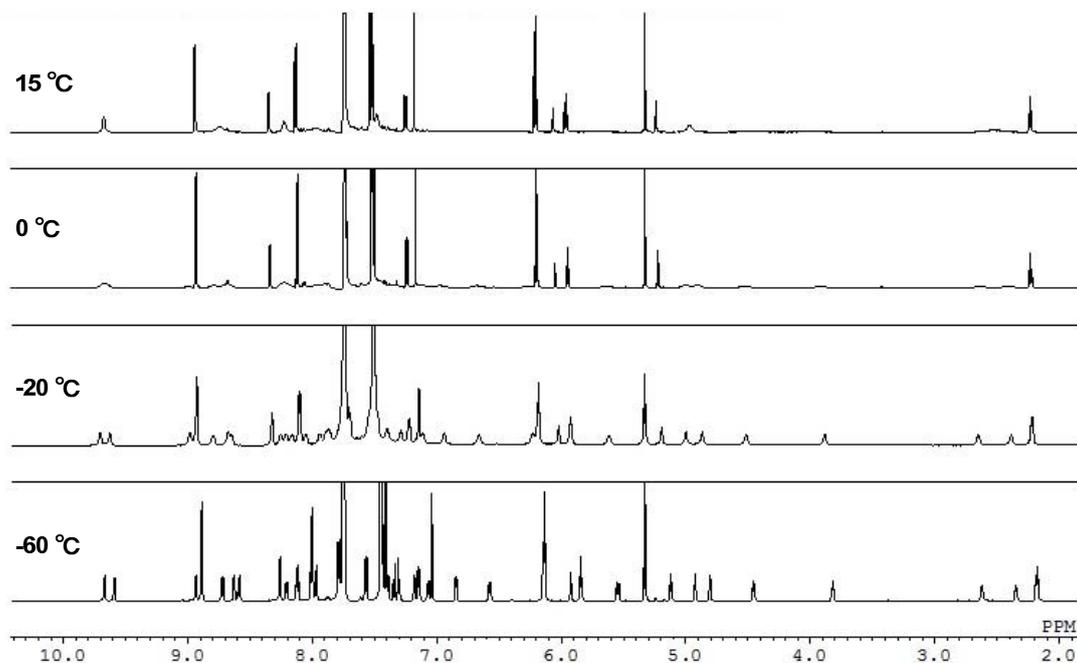


Figure S7. Variable Temperature ¹H NMR spectra of **10'** in CD₂Cl₂.

Synthesis of $[\text{Pd}_2(\mu\text{-dihydropentalenediyl})(\text{phen})_2][\text{BF}_4]_2$ (11**):** To a solution of $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ (272 mg, 0.43 mmol) in CH_3NO_2 was added COT (44.7 mg, 0.43 mmol) and 2 equiv of 1,10-phenanthroline (155 mg, 0.86 mmol). To the mixture was added 5 mol% of $\text{Pd}(\text{dba})(\text{phen})$ (25.7 mg, 0.021 mmol). The mixture was heated at 60 °C for 6 h, and filtered. The filtrate was concentrated in vacuo. Crystallization from CH_3NO_2 /benzene gave an orange powder of **11** (266 mg) in 73% yield. ^1H NMR (400 MHz, CD_3NO_2 , 25 °C): δ 9.01 (4H, dd, $J = 5$ Hz, $J = 1$ Hz, H4), 8.27 (4H, dd, $J = 8$ Hz, $J = 1$ Hz, H6), 7.68 (4H, s, H7), 7.60 (4H, dd, $J = 8$ Hz, $J = 5$ Hz, H5), 6.70 (2H, t, $J = 3$ Hz, H3), 5.64 (4H, t, $J = 2$ Hz, H2), 2.34 (2H, m, H1). A ^1H NMR spectrum is shown in Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CD_3NO_2 , 25 °C): δ 155.4 (s, C4), 144.7 (s, C9), 140.9 (s, C6), 130.5 (s, C8), 128.6 (s, C7), 127.3 (s, C5), 115.6 (s, C3), 83.3 (s, C2), 58.9 (s, C1). ESI-MS spectrum is shown in Figure S7. Anal. Calcd. for $\text{C}_{32}\text{H}_{24}\text{B}_2\text{F}_8\text{N}_4\text{Pd}_2$: C, 45.16; H, 2.84; N, 6.58. Found: C, 46.14; H, 3.40; N, 6.43.

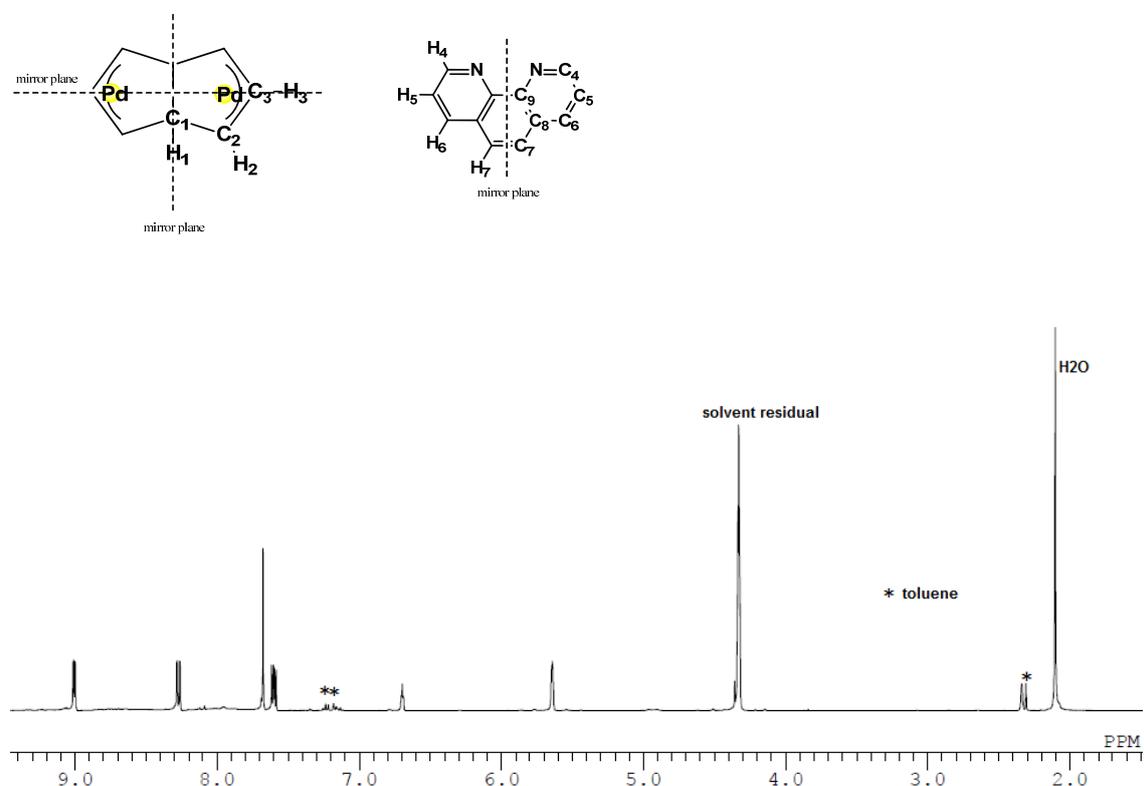


Figure S8. A ^1H NMR spectrum of $[\text{Pd}_2(\mu\text{-dihydropentalenediyl})(\text{phen})_2][\text{BF}_4]_2$ (**11**) in CD_3NO_2 .

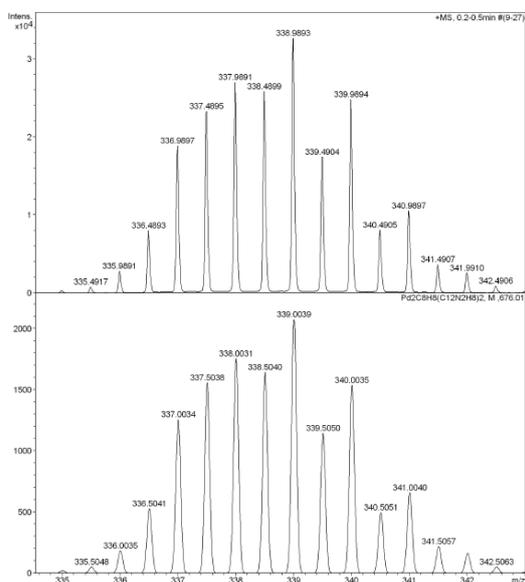
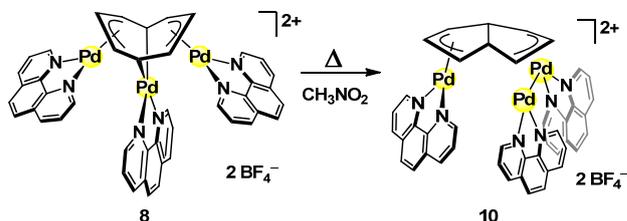


Figure S9. Experimental (top) and calculated (bottom) ESI(+)-mass spectra of $[\text{Pd}_2(\mu\text{-dihydropentalenediyl})(\text{phen})_2][\text{BF}_4]_2$ (**11**).

Kinetic Data for the conversion of **8** to **10**.



The sample of **8** (1.0×10^{-4} M) was prepared in a drybox in CH_3NO_2 , and change of the absorbance at 700 nm was monitored. The rate constant was independent on the concentration of **8** at 60 °C (1.0×10^{-4} M, $k = 2.21 \times 10^{-4} \text{ s}^{-1}$; 2.0×10^{-4} M, $k = 2.19 \times 10^{-4} \text{ s}^{-1}$; 3.0×10^{-4} M, $k = 2.15 \times 10^{-4} \text{ s}^{-1}$).

Table S1. Rate constants and half -lives for the conversion of **8** to **10**.

temp. /°C	rate const. k / s^{-1}	$t_{1/2} / \text{min}$
70	6.21×10^{-4}	19
65	3.38×10^{-4}	34
60	2.21×10^{-4}	52
55	1.12×10^{-4}	103

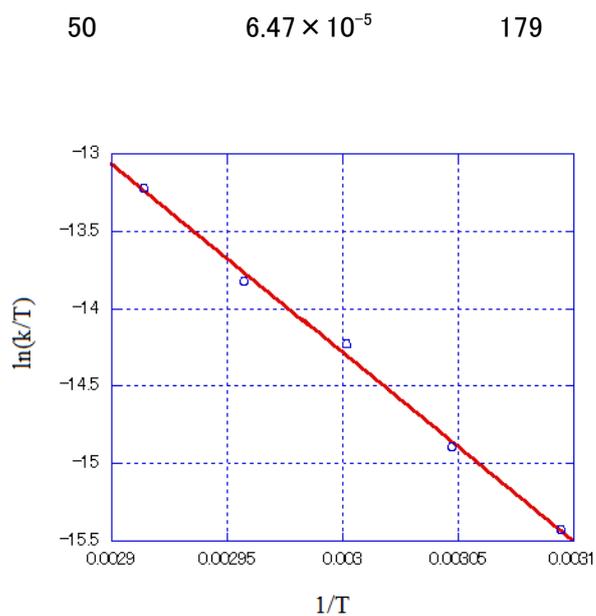


Figure S10. An Eyring Plot for the conversion of **8** to **10**.

References

- (1) T. Murahashi, T. Nagai, T. Okuno, T. Matsutani, H. Kurosawa, *Chem. Commun.* **2000**, 1689.
- (2) N. A. Yakelis, R. G. Bergman, *Organometallics*, **2005**, *24*, 3579.
- (3) T. Murahashi, K. Shirato, A. Fukushima, K. Takase, T. Suenobu, S. Fukuzumi, S. Ogoshi, H. Kurosawa, *Nat. Chem.* **2012**, *4*, 52.

X-ray Crystallographic Data for [Pd₃(μ₃-[2.2]paracyclophane)(phen)₃][BF₄]₂ (3)

A. Crystal Data

Empirical Formula	C ₅₄ H ₄₉ B ₂ F ₈ N ₈ O ₄ Pd ₃
Formula Weight	1366.84
Crystal Color, Habit	red, block
Crystal Dimensions	0.180 X 0.180 X 0.150 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 16.270(2) Å b = 16.700(2) Å c = 22.126(3) Å α = 81.787(3) ° β = 71.232(3) ° γ = 64.084(3) ° V = 5120(1) Å ³
Space Group	P-1 (#2)
Z value	4
D _{calc}	1.773 g/cm ³
F ₀₀₀	2724.00
μ(MoKα)	11.293 cm ⁻¹

B. Intensity Measurements

Diffractometer	R-AXIS RAPID
Radiation	MoKα (λ = 0.71075 Å) graphite monochromated
Voltage, Current	50kV, 40mA
Temperature	-150.0°C
Detector Aperture	280 x 256 mm
Data Images	74 exposures
ω oscillation Range (χ=45.0, φ=0.0)	130.0 - 190.0°
Exposure Rate	100.0 sec./°
ω oscillation Range (χ=45.0, φ=180.0)	0.0 - 162.0°
Exposure Rate	100.0 sec./°
Detector Position	127.00 mm
Pixel Size	0.100 mm
2θ _{max}	55.0°
No. of Reflections Measured	Total: 51000 Unique: 23379 (R _{int} = 0.0300)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.597 - 0.844)

C. Structure Solution and Refinement

Structure Solution	Patterson Methods (DIRDIF99 PATTY)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\sum w (F_o^2 - F_c^2)^2$
Least Squares Weights	$w = 1 / [\sigma^2(F_o^2) + (0.0503 \cdot P)^2 + 24.2543 \cdot P]$ where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$
$2\theta_{\text{max}}$ cutoff	55.0°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	23379
No. Variables	1409
Reflection/Parameter Ratio	16.59
Residuals: R1 ($I > 2.00\sigma(I)$)	0.0450
Residuals: R (All reflections)	0.0538
Residuals: wR2 (All reflections)	0.1254
Goodness of Fit Indicator	1.076
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	1.73 e ⁻¹ Å ³
Minimum peak in Final Diff. Map	-1.39 e ⁻¹ Å ³

X-ray Crystallographic Data for [Pd₃(μ₃-cycloheptatriene)(phen)₃][BF₄]₂ (5)

A. Crystal Data

Empirical Formula	C ₅₀ H ₄₁ B ₂ F ₈ N ₇ O ₂ Pd ₃
Formula Weight	1264.73
Crystal Color, Habit	orange, block
Crystal Dimensions	0.200 X 0.100 X 0.100 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 12.978(5) Å b = 14.106(5) Å c = 14.993(6) Å α = 83.662(6) ° β = 65.457(4) ° γ = 70.420(6) ° V = 2351(2) Å ³
Space Group	P-1 (#2)
Z value	2
D _{calc}	1.786 g/cm ³
F ₀₀₀	1252.00
μ(MoKα)	12.180 cm ⁻¹

B. Intensity Measurements

Diffractometer	R-AXIS RAPID
Radiation	MoKα (λ = 0.71075 Å) graphite monochromated
Voltage, Current	50kV, 40mA
Temperature	-150.0°C
Detector Aperture	280 x 256 mm
Data Images	55 exposures
ω oscillation Range (χ=45.0, φ=90.0)	130.0 - 190.0°
Exposure Rate	120.0 sec./°
ω oscillation Range (χ=45.0, φ=270.0)	0.0 - 160.0°
Exposure Rate	120.0 sec./°
Detector Position	127.40 mm
Pixel Size	0.100 mm
2θ _{max}	55.0°
No. of Reflections Measured	Total: 23216 Unique: 10707 (R _{int} = 0.0801)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.550 - 0.885)

C. Structure Solution and Refinement

Structure Solution	Patterson Methods (DIRDIF99 PATTY)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\sum w (F_o^2 - F_c^2)^2$
Least Squares Weights parameters	Chebyshev polynomial with 3 1986.6000,2772.2400,821.8180,
$2\theta_{\max}$ cutoff	55.00
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I > 2.00\sigma(I)$)	5576
No. Variables	667
Reflection/Parameter Ratio	8.36
Residuals: R1 ($I > 2.00\sigma(I)$)	0.0503
Residuals: wR2 ($I > 2.00\sigma(I)$)	0.0992
Goodness of Fit Indicator	0.739
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	1.26 e-/Å ³
Minimum peak in Final Diff. Map	-1.15 e-/Å ³

X-ray Crystallographic Data for $[\text{Pd}_2(\mu\text{-cycloheptatriene})(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ (6- CH_3CN)

A. Crystal Data

Empirical Formula	$\text{C}_{16}\text{H}_{22}\text{B}_2\text{Cl}_2\text{F}_8\text{N}_4\text{Pd}_2$
Formula Weight	727.69
Crystal Color, Habit	yellow, block
Crystal Dimensions	0.200 X 0.200 X 0.100 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 6.9325(8) Å b = 21.863(2) Å c = 17.529(2) Å $\beta = 103.236(3)^\circ$ V = 2586.2(5) Å ³
Space Group	P2 ₁ /c (#14)
Z value	4
D _{calc}	1.869 g/cm ³
F ₀₀₀	1416.00
$\mu(\text{MoK}\alpha)$	16.676 cm ⁻¹

B. Intensity Measurements

Diffractometer	R-Axis RAPID
Radiation	MoK α ($\lambda = 0.71075$ Å) graphite monochromated
Voltage, Current	50kV, 40mA
Temperature	-150.0°C
Detector Aperture	280 x 256 mm
Data Images	44 exposures
ω oscillation Range ($\chi=45.0$, $\psi=120.0$)	130.0 - 190.0°
Exposure Rate	100.0 sec./°
ω oscillation Range ($\chi=45.0$, $\psi=270.0$)	0.0 - 160.0°
Exposure Rate	100.0 sec./°
Detector Position	127.40 mm
Pixel Size	0.100 mm
2 θ_{max}	54.9°
No. of Reflections Measured	Total: 20167 Unique: 4552 ($R_{\text{int}} = 0.0989$)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.039 - 0.846)

C. Structure Solution and Refinement

Structure Solution	Patterson Methods (DIRDIF99 PATTY)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\sum w (F_o^2 - F_c^2)^2$
Least Squares Weights	$w = 1 / [\sigma^2(F_o^2) + (0.1573 \cdot P)^2 + 1.2421 \cdot P]$ where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$
$2\theta_{\text{max}}$ cutoff	50.0 ^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	4552
No. Variables	311
Reflection/Parameter Ratio	14.64
Residuals: R1 ($I > 2.00\sigma(I)$)	0.0654
Residuals: R (All reflections)	0.0984
Residuals: wR2 (All reflections)	0.2433
Goodness of Fit Indicator	1.075
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	1.36 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-2.68 e ⁻ /Å ³

X-ray Crystallographic Data for [Pd₂(μ-cycloheptatriene)(phen)₂][BF₄]₂ (6-phen)

A. Crystal Data

Empirical Formula	C ₃₂ H ₂₇ B ₂ F ₈ N ₅ O ₂ Pd ₂
Formula Weight	900.00
Crystal Color, Habit	orange, block
Crystal Dimensions	0.200 X 0.200 X 0.150 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 11.016(2) Å b = 12.327(2) Å c = 13.836(2) Å α = 113.360(4) ° β = 104.512(4) ° γ = 102.553(4) ° V = 1560.2(4) Å ³
Space Group	P-1 (#2)
Z value	2
D _{calc}	1.916 g/cm ³
F ₀₀₀	888.00
μ(MoKα)	12.434 cm ⁻¹

B. Intensity Measurements

Diffractometer	R-AXIS RAPID
Radiation	MoKα (λ = 0.71075 Å) graphite monochromated
Voltage, Current	50kV, 40mA
Temperature	-150.0°C
Detector Aperture	280 x 256 mm
Data Images	44 exposures
ω oscillation Range (χ=45.0, φ=0.0)	130.0 - 190.0°
Exposure Rate	100.0 sec./°
ω oscillation Range (χ=45.0, φ=180.0)	0.0 - 160.0°
Exposure Rate	100.0 sec./°
Detector Position	127.40 mm
Pixel Size	0.100 mm
2θ _{max}	54.9°
No. of Reflections Measured	Total: 12298 Unique: 5460 (R _{int} = 0.0576)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.625 - 0.830)

C. Structure Solution and Refinement

Structure Solution	Patterson Methods (DIRDIF99 PATTY)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\sum w (F_o^2 - F_c^2)^2$
Least Squares Weights	$w = 1 / [\sigma^2(F_o^2) + (0.0001 \cdot P)^2 + 36.4146 \cdot P]$ where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$
$2\theta_{\text{max}}$ cutoff	50.0 $^\circ$
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	5460
No. Variables	461
Reflection/Parameter Ratio	11.84
Residuals: R1 ($I > 2.00\sigma(I)$)	0.0750
Residuals: R (All reflections)	0.0955
Residuals: wR2 (All reflections)	0.2036
Goodness of Fit Indicator	1.172
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	1.61 e-/Å ³
Minimum peak in Final Diff. Map	-1.90 e-/Å ³

X-ray Crystallographic Data for [Pd₃(μ₃-cyclooctatetraene)(phen)₃][PF₆]₂ (8')

A. Crystal Data

Empirical Formula	C ₄₈ H ₃₈ F ₁₂ N ₈ P ₂ Pd ₃
Formula Weight	1336.01
Crystal Color, Habit	blue, platelet
Crystal Dimensions	0.100 X 0.100 X 0.050 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 11.8333(7) Å b = 14.0677(7) Å c = 15.8338(8) Å α = 70.703(2) ° β = 89.832(2) ° γ = 70.362(2) ° V = 2325.6(2) Å ³
Space Group	P-1 (#2)
Z value	2
D _{calc}	1.908 g/cm ³
F ₀₀₀	1316.00
μ(MoKα)	13.124 cm ⁻¹

B. Intensity Measurements

Diffractometer	R-Axis RAPID
Radiation	MoKα (λ = 0.71075 Å)
Voltage, Current	50kV, 24mA
Temperature	-170.0°C
Detector Aperture	280 x 256 mm
Data Images	55 exposures
ω oscillation Range (χ=45.0, φ=0.0)	130.0 - 190.0°
Exposure Rate	30.0 sec./°
ω oscillation Range (χ=45.0, φ=180.0)	0.0 - 160.0°
Exposure Rate	30.0 sec./°
Detector Position	127.40 mm
Pixel Size	0.100 mm
2θ _{max}	55.0°
No. of Reflections Measured	Total: 22744 Unique: 10598 (R _{int} = 0.0551)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.535 - 0.936)

C. Structure Solution and Refinement

Structure Solution	Patterson Methods (DIRDIF99 PATTY)
Refinement	Full-matrix least-squares on F ²
Function Minimized	$\sum w (F_o^2 - F_c^2)^2$
Least Squares Weights	$w = 1 / [\sigma^2(F_o^2) + (0.2000 \cdot P)^2 + 0.0000 \cdot P]$ where $P = (Max(F_o^2, 0) + 2F_c^2)/3$
2 θ_{max} cutoff	55.0 ^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	10598
No. Variables	660
Reflection/Parameter Ratio	16.06
Residuals: R1 (I>2.00 σ (I))	0.0599
Residuals: R (All reflections)	0.0748
Residuals: wR2 (All reflections)	0.2102
Goodness of Fit Indicator	0.830
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	1.42 e ⁻ Å ³
Minimum peak in Final Diff. Map	-3.29 e ⁻ Å ³

X-ray Crystallographic Data for [Pd₃(μ₃-dihydropentalenediyl)(phen)₃][BF₄]₂ (10)

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	C ₅₀ H ₄₁ B ₂ F ₈ N ₉ Pd ₃
Formula Weight	1260.74
Crystal Color, Habit	yellow, block
Crystal Dimensions	0.100 X 0.080 X 0.080 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 10.708(3) Å b = 15.246(4) Å c = 16.514(4) Å α = 115.265(5) ° β = 98.940(5) ° γ = 98.087(6) ° V = 2343(1) Å ³
Space Group	P-1 (#2)
Z value	2
D _{calc}	1.787 g/cm ³
F ₀₀₀	1248.00
μ(MoKα)	12.200 cm ⁻¹

B. Intensity Measurements

Diffractometer	R-AXIS RAPID
Radiation	MoKα (λ = 0.71075 Å) graphite monochromated
Voltage, Current	50kV, 40mA
Temperature	-150.0°C
Detector Aperture	280 x 256 mm
Data Images	88 exposures
ω oscillation Range (χ=45.0, φ=0.0)	130.0 - 190.0°
Exposure Rate	150.0 sec./°
ω oscillation Range (χ=45.0, φ=180.0)	0.0 - 160.0°
Exposure Rate	150.0 sec./°
Detector Position	127.40 mm
Pixel Size	0.100 mm
2θ _{max}	55.0°
No. of Reflections Measured	Total: 19078 Unique: 8968 (R _{int} = 0.0702)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.501 - 0.907)

C. Structure Solution and Refinement

Structure Solution	Patterson Methods (DIRDIF99 PATTY)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma w (F_o^2 - F_c^2)^2$
Least Squares Weights	$w = 1 / [\sigma^2(F_o^2) + (0.0993 \cdot P)^2 + 13.8518 \cdot P]$ where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$
$2\theta_{\text{max}}$ cutoff	52.0°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	8968
No. Variables	651
Reflection/Parameter Ratio	13.78
Residuals: R1 ($I > 2.00\sigma(I)$)	0.0813
Residuals: R (All reflections)	0.1198
Residuals: wR2 (All reflections)	0.2118
Goodness of Fit Indicator	1.049
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	2.75 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-1.06 e ⁻ /Å ³