Supplementary Materials

Oxidative Dinuclear Addition of a Pd^{I}–Pd^{I} Moiety to Arenes: Generation of μ-η^3:η^3-Arene Pd^{II}_2 Species

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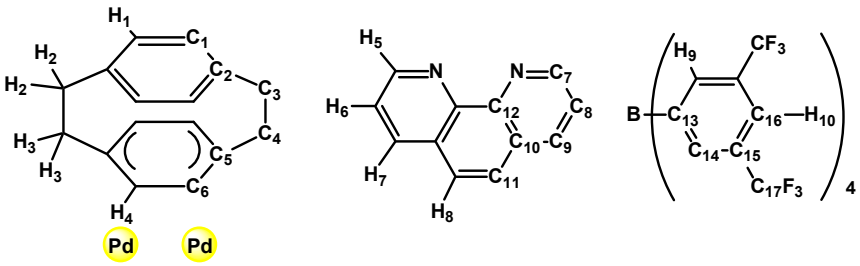
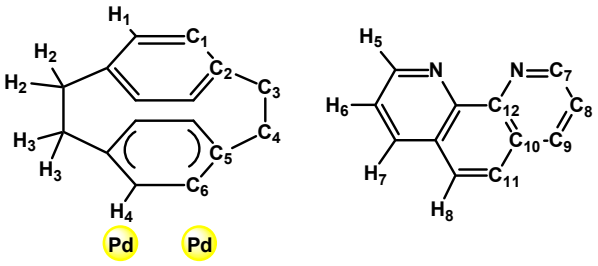
Experimental Section

General Consideration. All manipulations were conducted under a nitrogen atmosphere using standard Schlenk or drybox techniques. ^{1}H, $^{13}C\{^{1}H\}$ NMR spectra were recorded on and 400 MHz (JEOL GSX-400, Brucker DPX-400) 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 Analytical Center, Faculty of Engineering, Osaka University. 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, Et_2O, *n*-hexane, dichloromethane, benzene, toluene, CD_3NO_2, CD_2Cl_2, and CD_3CN were purified according to the standard procedures. $[Pd_2(CH_3CN)_6][BF_4]_2$,[1] $NaB(Ar^F)_4$,[2] and $[Pd_2(\mu\text{-}[2.2]paracyclophane)_2(CH_3CN)_2][B(Ar^F)_4]_2$[3] were prepared according to the literature.

Synthesis of $[Pd_2(\mu\text{-}[2.2]paracyclophane)(phen)_2][B(Ar^F)_4]_2$ (3′): To a solution of $[Pd_2(\mu\text{-}[2.2]paracyclophane)_2(CH_3CN)_2][B(Ar^F)_4]_2$ (183 mg, 0.075 mmol) in CH_2Cl_2 was added 1,10-phenanthoroline (27.0 mg, 0.150 mmol), and the mixture was stirred for 1 h at room temperature. Crystallization from CH_3NO_2/toluene gave yellow crystals of **3′** (106 mg) in 58% yield. ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 8.63 (4H, br s, H_5), 8.11 (4H, d, J = 8 Hz ,H_7), 7.74 (16H, s, H_9), 7.55 (8H, s, H_{10}), 7.52 (4H, s, H_8), 7.42 (4H, m, H_6), 7.31 (4H, s, H_1), 5.06 (4H, s, H_4), 3.23 (4H, dd, J = 6 Hz, J = 5 Hz, H_2), 2.80 (4H, dd, J = 6 Hz, J = 5 Hz, H_3). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, CD_2Cl_2, 25 °C): δ 162.2 (q, J = 50 Hz, C_{13}), 154.0 (s, C_7), 144.1 (s, C_{12}), 140.0 (s, C_9), 139.1 (s, C_2), 135.2 (s, C_{14}), 131.9 (s, C_1), 129.9 (s, C_{10}), 129.3 (m, C_{15}), 127.8 (s, C_{11}), 125.9 (s, C_8), 125.0 (q, J = 271 Hz, C_{17}), 122.2 (s, C_5), 117.9 (m, C_{16}), 76.9 (s, C_6), 35.1 (s, C_4), 34.5 (s, C_3). Anal. Calcd. For. $C_{104}H_{56}B_2F_{48}N_4Pd_2$: C, 49.81; H, 2.25; N, 2.23. Found: C, 49.81; H, 2.32; N, 2.23.

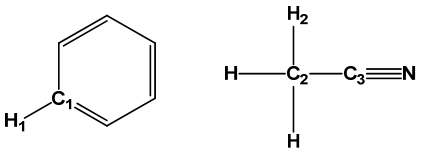


Synthesis of $[Pd_2(\mu\text{-}[2.2]paracyclophane)(phen)_2][BF_4]_2$ (3): To a suspension of [2.2]paracyclophane (95.2 mg, 0.46 mmol) in CH_3NO_2 was added $[Pd_2(CH_3CN)_6][BF_4]_2$ (102 mg, 0.16 mmol), and stirred at room temperature for 30 min. To the brown solution was then added 1,10-phenanthoroline (57.0 mg, 0.32 mmol). The mixture was stirred for 30 min at room temperature. The reaction mixture was concentrated in vacuo, and the mixture was filtered. Crystallization from CH_3NO_2/benzene gave crystals of **3** (124 mg) in 80% yield. ^{1}H NMR (400 MHz, CD_3NO_2, 25 °C): δ 8.91 (4H, d, J = 4 Hz, H_5), 8.30 (4H, d, J = 8 Hz, H_7), 7.68 (4H, s, H_8), 7.58 (4H, dd, J = 8 Hz, J = 5 Hz, H_6), 7.40 (4H, s, H_1), 5.41 (4H, s, H_4), 3.24 (4H, m, H_2), 2.91 (4H, m, H_3). ^{13}C{^{1}H} NMR (100.6 MHz, CD_3NO_2, 25 °C): δ 156.1 (s, C_7), 145.0 (s, C_{12}), 140.9 (s, C_9), 140.8 (s, C_2), 132.9 (s, C_1), 130.8 (s, C_{10}), 128.5 (s, C_{11}), 127.1 (s, C_8), 122.5 (s, C_5), 78.7 (s, C_6), 35.4 (s, C_4), 35.1 (s, C_3). $C_{40}H_{32}B_2F_8N_4Pd_2 \cdot CH_3NO_2$: C, 48.46; H, 3.47; N, 6.89. Found: C, 48.44; H, 3.59; N, 6.38.

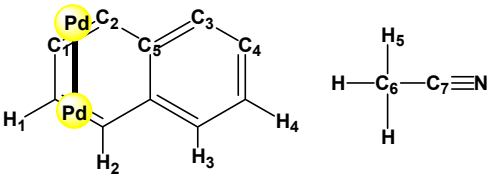


Synthesis of $[Pd_2(\mu\text{-benzene})_2(CH_3CN)_2][BF_4]_2$ (4): To a solution of $[Pd_2(CH_3CN)_6][BF_4]_2$ (344 mg, 0.54 mmol) in CH_3NO_2 was added benzene, and the resultant brown precipitates were collected and dried in vacuum. This treatment was repeated ten times. The brown powder was dissolved in CH_3NO_2, and filtered. Addition of benzene to the filtrate gave brown **4** (148 mg) in 44% yield. ^{1}H NMR (400 MHz, CD_3NO_2, 25 °C): δ 7.35 (12H, s, H_1), 2.56 (6H, s, H_2). No change of the

shape of the benzene proton signal was observed at -20 °C. $^{13}C\{^{1}H\}$ NMR (100.6 MHz, CD_3NO_2, 25 °C): δ 126.1 (s, C_3), 112.9 (s, C_1), 3.4 (s, C_2). Anal. Calcd. For. $C_{14}H_{18}B_2F_8N_2Pd_2 \cdot CH_3NO_2$: C, 29.77; H, 3.09; N, 6.13. Found: C, 30.12; H, 2.97; N, 6.67.



Synthesis of $[Pd_2(\mu$–naphthalene$)_2(CH_3CN)_2][BF_4]_2$ (5): To a solution of naphthalene (1.01 g, 7.89 mmol) in CH_3NO_2 was added $[Pd_2(CH_3CN)_6][BF_4]_2$ (198 mg, 0.312 mmol), and the mixture was stirred for 1 h at ambient temperature. The solution was filtered, and the filtrate was concentrated in vacuo. Addition of Et_2O gave a yellow-orange precipitate, which was then washed with Et_2O and *n*-hexane. Recrystallization from CH_3NO_2/CH_2Cl_2 gave reddish orange microcrystals of **5** (158 mg) in 70% yield. ^{1}H NMR (600 MHz, CD_3NO_2, –20 °C): δ 7.84 (4H, br, H_2), 7.81 (4H, br, H_3), 7.49 (4H, br, H_4), 6.71 (4H, br, H_1), 2.69 (6H, s, H_5). Variable temperature ^{1}H NMR spectra were shown in Figure S1. $^{13}C\{^{1}H\}$ NMR (151 MHz, CD_3NO_2, -20 °C): δ 132.6 (s, C_4), 130.8 (s, C_5), 129.3 (s, C_3), 126.0 (s, C_7), 97.4 (s, C_2), 94.7 (s, C_1), 2.9 (s, C_6). Anal. Calcd. For. $C_{24}H_{22}B_2F_8N_2Pd_2$: C, 39.77; H, 3.06; N, 3.86. Found: C, 39.21; H, 2.90; N, 3.84.



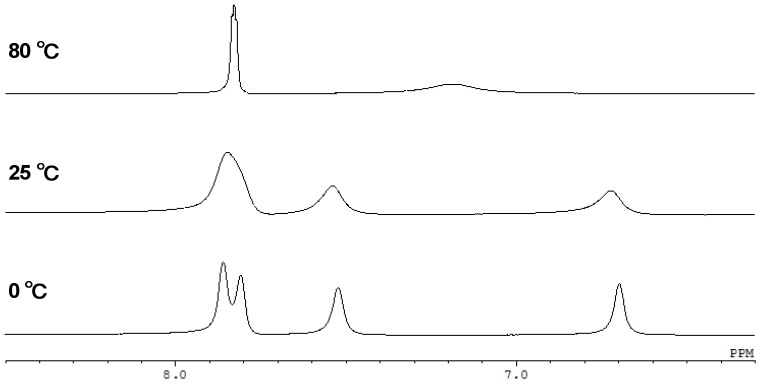
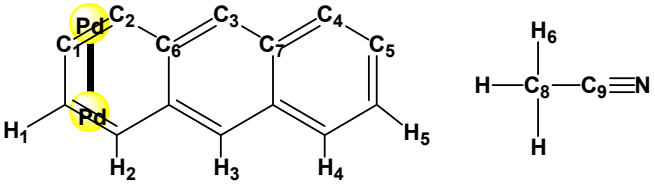


Figure S1. Variable temperature ^{1}H NMR spectra of $[Pd_2(\mu\text{–naphthalene})_2(CH_3CN)_2][BF_4]_2$ (**5**) in CD_3NO_2.

Synthesis of $[Pd_2(\mu\text{–anthracene})_2(CH_3CN)_2][BF_4]_2$ (6): To a suspension of anthracene (849 mg, 4.76 mmol) in CH_3NO_2 was added $[Pd_2(CH_3CN)_6][BF_4]_2$ (311 mg, 0.490 mmol), and the mixture was stirred for 1 h at ambient temperature. The solution was filtered, and the filtrate was concentrated in vacuo. Addition of Et_2O gave a dark purple precipitate, which was then washed with Et_2O and *n*-hexane. Recrystallization from CH_3NO_2/CH_2Cl_2 gave a dark purple powder of **6** (241 mg) in 60% yield. ^{1}H NMR (600 MHz, CD_3NO_2, -20 °C): δ 8.29 (4H, s, H_3), 7.88 (4H, br, H_2), 7.63 (4H, dd, J = 6 Hz, J = 2 Hz, H_4), 7.47 (4H, dd, J = 7 Hz, J = 3 Hz, H_5), 6.53 (4H, dd, J = 5 Hz, J = 3 Hz, H_1), 2.74 (6H, s, H_6). Variable temperature ^{1}H NMR spectra were shown in Figure S2. ^{13}C{^{1}H} NMR (100.6 MHz, CD_3NO_2, 25 °C): δ 134.3 (s, C_6 or C_7), 130.4 (s, C_5), 129.6 (s, C_3), 128.8 (s, C_4), 126.8 (s, C_6 or C_7), 126.0 (s, C_9), 98.6 (s, C_2), 91.5 (s, C_1), 2.9 (s, C_8). Anal. Calcd. For. $C_{32}H_{26}B_2F_8N_2Pd_2$: C, 46.59; H, 3.18; N, 3.40. Found: C, 45.91; H, 2.95; N, 3.51.



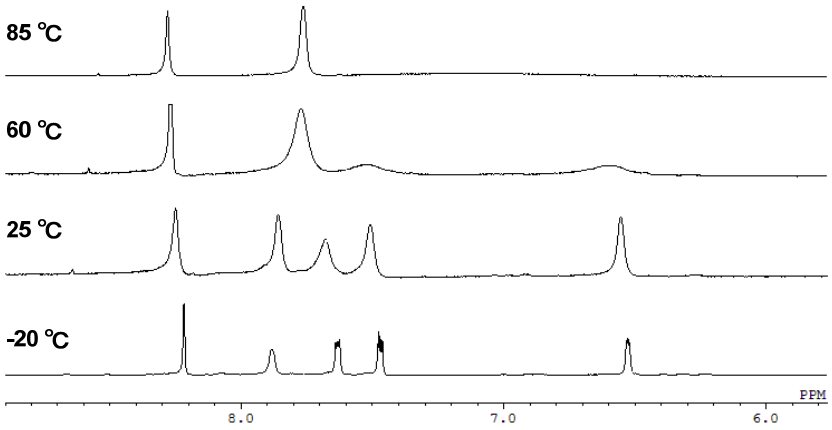
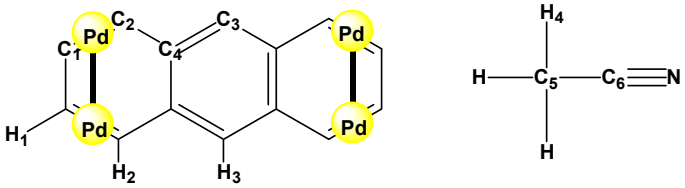


Figure S2. Variable temperature ^{1}H NMR spectra of $[Pd_2(\mu\text{–anthracene})_2(CH_3CN)_2][BF_4]_2$ (**6**) in CD_3NO_2.

Synthesis of $[Pd_4(\mu\text{–anthracene})_2(CH_3CN)_4][BF_4]_4$ (7): To a suspension of anthracene (56.3 mg, 0.32 mmol) in CH_3NO_2 was added $[Pd_2(CH_3CN)_6][BF_4]_2$ (200 mg, 0.320 mmol), and the mixture was stirred for 1 h at ambient temperature. The volatiles were removed by evaporation under vacuum. Then the residues were dissolved in CH_3NO_2 and then volatiles were removed by evaporation under vacuum again. Then the CH_3NO_2 solution of the residues was filtered. Crystallization from CH_3NO_2/toluene gave a dark brown powder of **7** (149 mg) in 73% yield. ^{1}H NMR (400 MHz, CD_3NO_2, 25 °C): δ 10.09 (4H, s, H_3), 8.74 (8H, m, H_2), 6.38 (8H, m, H_1), 3.03 (12H, br, H_4). $^{13}C\{^{1}H\}$ NMR (100.6 MHz, CD_3NO_2, 25 °C): δ 135.0 (s, C_4), 128.9 (s, C_3), 98.9 (s, C_2), 96.5 (s, C_1). Anal. Calcd. For. $C_{36}H_{32}B_4F_{16}N_4Pd_4$: C, 33.43; H, 2.49; N, 4.33. Found: C, 32.65; H, 2.49; N, 3.92.



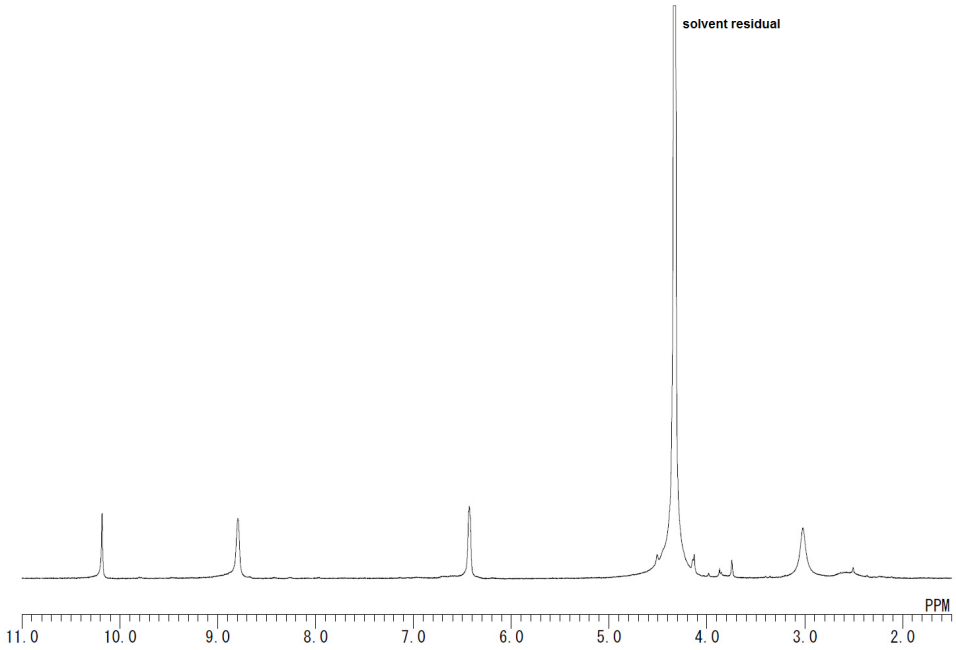
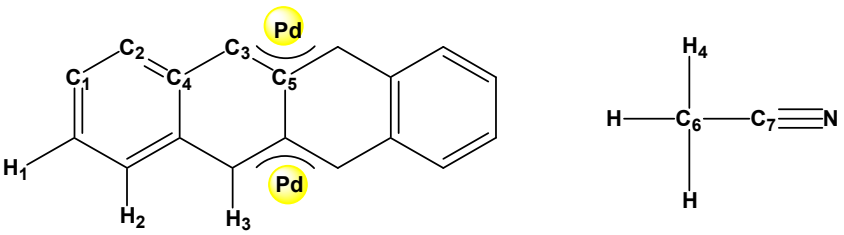


Figure S3. A ^{1}H NMR spectrum of **[Pd$_4$(μ–anthracene)$_2$(CH$_3$CN)$_4$][BF$_4$]$_4$ (7)** in CD_3NO_2.

Synthesis of [Pd$_2$(μ–tetracene)(CH$_3$CN)$_4$][BF$_4$]$_2$ (8): To a suspension of tetracene (51.4 mg, 0.225 mmol) in CH_3NO_2 was added $[Pd_2(CH_3CN)_6][BF_4]_2$ (127 mg, 0.201 mmol), and the mixture was stirred for 4 h at ambient temperature. The solution was filtered, and the filtrate was concentrated in vacuo. Addition of Et_2O gave a yellow precipitate, which was then washed with Et_2O. Recrystallization from CH_3NO_2/benzene/CH_3CN gave orange needle crystals of **8** (85 mg) in 54% yield. ^{1}H NMR (400 MHz, CD_3NO_2, 25 °C): δ 8.11 (4H, dd, J = 5 Hz, J = 3 Hz, H_2), 7.77 (4H, dd, J = 5 Hz, J = 3 Hz, H_1), 6.21 (4H, s, H_3), 2.10 (12H, s, H_4). ^{13}C{^{1}H} NMR (100.6 MHz, CD_3NO_2, 25 °C): δ 132.0 (s, C_4), 129.1 (s, C_2), 128.1 (s, C_1), 120.2 (s, C_7), 106.4 (s, C_5), 73.8 (s, C_3), 3.7 (s, C_6). Anal. Calcd. For. $C_{26}H_{24}B_2F_8N_4Pd_2$·$C_9H_{12}$: C, 46.75; H, 4.04; N, 6.23. Found: C, 46.84; H, 4.11; N, 6.08.



Synthesis of $[Pd_2(\mu\text{–pentacene})(CH_3CN)_4][BF_4]_2$ (9): To a suspension of pentacene (206 mg, 0.74 mmol) in CH_3NO_2 was added $[Pd_2(CH_3CN)_6][BF_4]_2$ (423 mg, 0.67 mmol), and the mixture was stirred for 5 h at 51 °C. The solution was filtered. Addition of toluene gave a yellow precipitate, which was then washed with toluene and Et_2O. Recrystallization from CH_3NO_2/benzene gave yellow crystals of **9** (444 mg) in 80% yield. ^{1}H NMR (600 MHz, CD_3NO_2, -20 °C): δ 8.64 (2H, s, H_5), 8.10 (2H, dd, J = 5 Hz, J = 3 Hz, H_2), 8.05 (2H, dd, J = 6 Hz, J = 3 Hz, H_6), 7.78 (2H, dd, J = 6 Hz, J = 3 Hz, H_1), 6.62 (2H, dd, J = 6 Hz, J = 3 Hz, H_7), 6.19 (2H, s, H_4), 6.16 (2H, s, H_3), 2.0 (6H, br s, H_8), 1.9 (6H, br s, H_8). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_3NO_2, 25 °C): δ 135.6 (s, C_{10}), 135.1 (s, C_{13}), 133.0 (s, C_5), 132.7 (s, C_2), 132.1 (s, C_{12}), 131.7 (s, C_1), 129.6 (s, C_6 and C_7), 123.5 (s, C_9), 108.6 (s, C_{11}), 76.2 (s, C_3), 74.4 (s, C_4), 2.2 (s, C_9). Anal. Calcd. For. $C_{30}H_{26}B_2F_8N_4Pd_2$: C, 43.46; H, 3.16; N, 6.76. Found: C, 43.07 H, 3.46; N, 5.84.

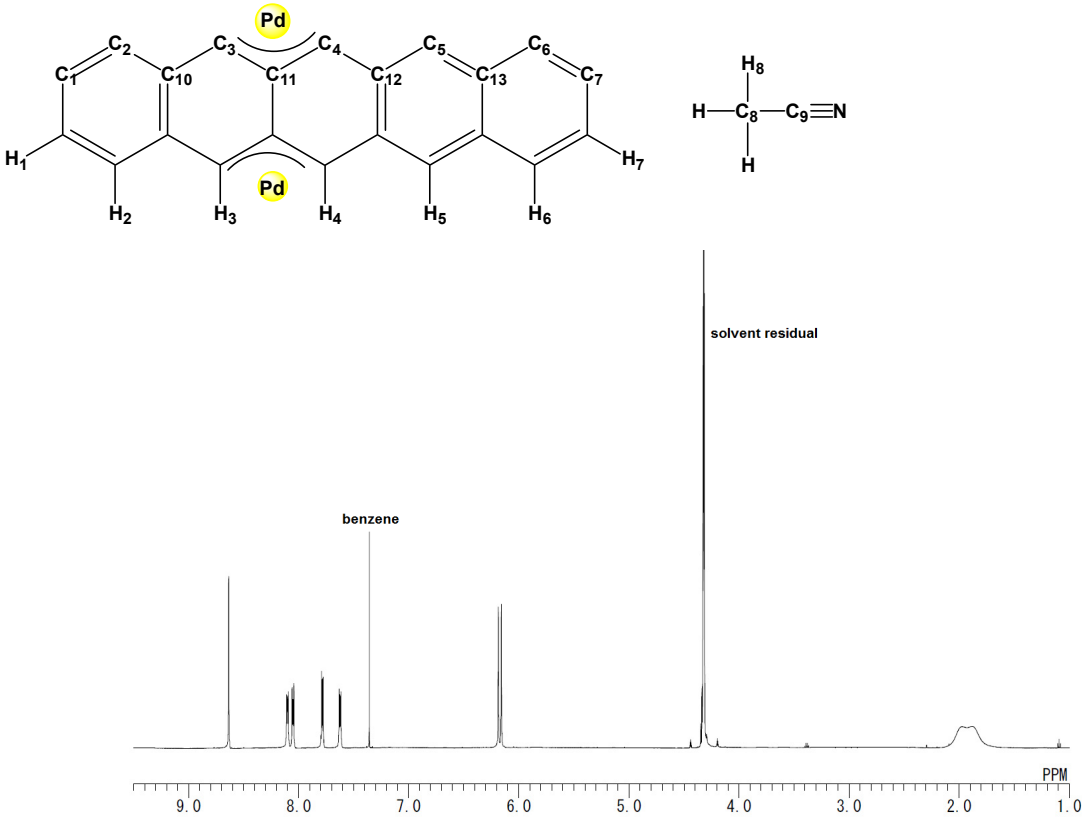


Figure S4. A ^{1}H NMR spectrum of $[Pd_2(\mu\text{–pentacene})(CH_3CN)_4][BF_4]_2$ (**9**) in CD_3NO_2 at -20 °C.

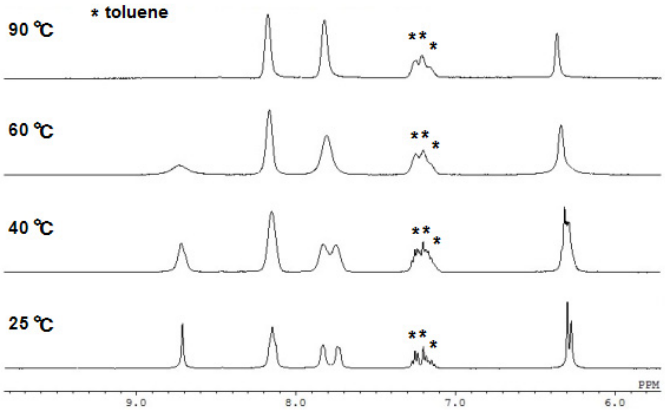


Figure S5. Variable temperature ^{1}H NMR spectra of $[Pd_2(\mu$–pentacene$)(CH_3CN)_4][BF_4]_2$ (**9**) in CD_3NO_2.

Synthesis of $[Pd_2(\mu$-anthracene$)(phen)_2][BF_4]_2$ (10): To a solution of $[Pd_2(CH_3CN)_6][BF_4]_2$ (100 mg, 0.16 mmol) in CH_3NO_2 was slowly added a CH_2Cl_2 solution of anthracene (28.2 mg, 0.16 mmol) and 1,10-phenanthoroline (57.0 mg, 0.32 mmol). The mixture was stirred for 1 h at room temperature. The reaction mixture was filtered, and crystallization from CH_3NO_2/toluene gave orange needle crystals of **10** (10.0 mg, 7 % yield). ^{1}H NMR (400 MHz, CD_3NO_2, 25 °C): δ 8.65 (2H, dd, J = 5 Hz, J = 1 Hz, H_{13}), 8.41 (4H, m, H_1, H_4), 8.23 (2H, dd, J = 8 Hz, J = 1 Hz, H_{11}), 8.13 (4H, m, H_5, H_8), 7.57 (8H, m, H_6, H_9, H_{10}, H_{12}), 7.32 (2H, dd, J = 8.4 Hz, J = 5.2 Hz, H_7), 6.13 (2H, t, J = 3.6 Hz, H_2), 6.05 (2H, s, H_3). ^{13}C NMR (100.6 MHz, CD_3NO_2, 25 °C): δ 153.2 (s, C_{17}), 149.2 (s, C_8), 145.3 (s, C_{18}), 144.1 (s, C_{19}), 141 (s, C_{10}, C_{15}), 135.8 (s, C_5), 135.6 (s, C_1), 133.7 (s, C_6), 131.9 (s, C_7), 130.5 (s, C_{14}), 130.3 (s, C_{11}), 128.6 (s, C_{12} or C_{13}), 128.5 (s, C_{12} or C_{13}), 127.7 (s, C_{16}), 126.8 (s, C_9), 110.6 (s, C_3), 74.6 (s, C_2), 70.4 (s, C_4). Anal. Calcd. For. $C_{38}H_{26}B_2F_8N_4Pd_2$: C, 49.34; H, 2.83; N, 5.95. Found: C, 48.76; H, 3.61; N, 5.95.

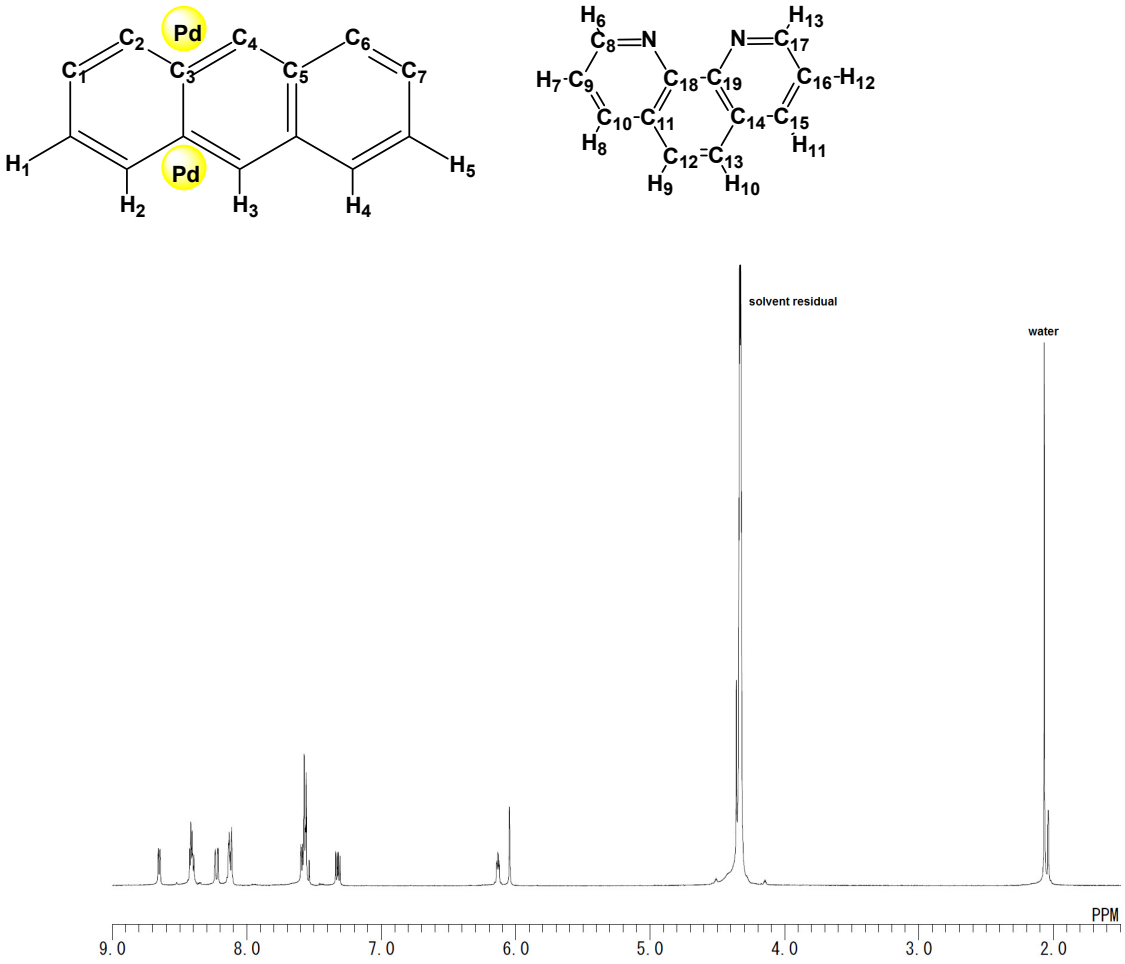


Figure S6. A ^{1}H NMR spectrum of $[Pd_2(\mu\text{-anthracene})(phen)_2][BF_4]_2$ (**10**) in CD_3NO_2.

Computational Details

All calculations were carried out with Gaussian03 program package (Revision C.02).[4] Geometrical optimization was carried out initially with DFT method (B3LYP).[5] Core electrons of Pd were replaced with Stuttgart-Dresden-Bonn relativistic effect core potentials (ECPs) and its valence electrons were represented by (8s7p6d)/[6s5p3d] basis set.[6] 6-311G(d) basis sets were used for other atoms.[7]

The results of the Natural Charge Analyses on $[Pd_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-acene})(HCN)_4]^{2+}$ were shown in Table S1. Cartesian coordinates of the optimized geometries of the model compounds $[Pd_2(naphthalene)(HCN)_4]^{2+}$, $[Pd_2(anthracene)(HCN)_4]^{2+}$, $[Pd_2(tetracene)(HCN)_4]^{2+}$, and $[Pd_2(pentacene)(HCN)_4]^{2+}$ were shown in Tables S2, S3, S4, and S5.

Table S1. **Charge distribution in $[Pd_2(\mu\text{-}\eta^3\text{:}\eta^3\text{-acene})(HCN)_4]^{2+}$ based on the Natural Population Analyses at the B3LYP level**

complex	acene	$[Pd(HCN)_2]_2$
$[Pd_2(C_{10}H_8)_2(HCN)_4]^{2+}$	+0.333	+1.667
$[Pd_2(C_{14}H_{10})_2(HCN)_4]^{2+}$	+0.397	+1.603
$[Pd_2(C_{18}H_{12})_2(HCN)_4]^{2+}$	+0.445	+1.555
$[Pd_2(C_{22}H_{14})_2(HCN)_4]^{2+}$	+0.489	+1.511

Table S2. Cartesian coordinates of $[Pd_2(naphthalene)(HCN)_4]^{2+}$

Pd1	1.98	−0.00005	0.11182	H17	2.4525	−1.29955	−2.01219
Pd2	−1.97998	0.00003	0.1119	H18	2.45255	1.29942	−2.01219
C3	3.13545	−2.33127	2.10312	H19	−2.45262	−1.29945	−2.0121
C4	3.13566	2.33169	2.10238	H20	−2.45257	1.29952	−2.0121
C5	−3.13555	−2.33166	2.10258	N21	2.65942	−1.54438	1.42082
C6	−3.13552	2.33176	2.10255	N22	2.65945	1.54426	1.42083
C7	1.42739	−1.23567	−1.65412	N23	−2.65942	−1.54428	1.42092
C8	1.42744	1.23559	−1.65413	N24	−2.65934	1.54436	1.42094
C9	0.68073	−2.46235	−1.52796	H25	3.58561	−3.06828	2.73998
C10	0.68083	2.46231	−1.528	H26	3.58575	3.06747	2.74071
C11	0.7226	−0.00002	−1.75714	H27	−3.58564	−3.06771	2.74061
C12	−0.68088	−2.46233	−1.52794	H28	−3.58561	3.0676	2.74081
C13	−0.68079	2.46233	−1.52797	H29	1.2257	−3.39886	−1.49942
C14	−0.72266	0	−1.75711	H30	−1.22588	−3.39881	−1.49938
C15	−1.4275	−1.23561	−1.65406	H31	1.22583	3.3988	−1.49947
C16	−1.42745	1.23565	−1.65408	H32	−1.22575	3.39884	−1.49942

Table S3. Cartesian coordinates of $[Pd_2(anthracene)(HCN)_4]^{2+}$

Pd1	0.54701	1.92474	0.13179	C20	−1.16803	−1.4331	−1.20133
Pd2	0.54745	−1.9246	0.13186	H21	1.13878	2.45795	−2.2854

C3	3.37998	3.05471	1.36034	H22	−3.53732	2.4817	−0.44248
C4	−1.07094	2.96825	2.78568	H23	−1.31157	2.46444	−1.51576
C5	3.38098	−3.05396	1.35971	H24	−3.53674	−2.48253	−0.44238
C6	−1.0702	−2.96839	2.78582	H25	1.13935	−2.45776	−2.28531
C7	−3.52361	1.3969	−0.41375	H26	−1.311	−2.46479	−1.51567
C8	1.18363	1.42679	−1.94311	N27	2.42182	2.587	0.94208
C9	−1.16836	1.43279	−1.20139	N28	−0.5302	2.53706	1.87281
C10	2.38827	0.68087	−2.20636	N29	2.42242	−2.58642	0.94218
C11	−4.67038	0.69961	−0.06291	N30	−0.52961	−2.5371	1.87292
C12	−2.34775	0.71124	−0.75657	H31	4.27657	3.49689	1.74949
C13	−0.02658	0.72611	−1.66874	H32	−1.57499	3.37633	3.63997
C14	−4.67022	−0.70069	−0.06288	H33	4.27708	−3.49596	1.75019
C15	2.38843	−0.68039	−2.20633	H34	−1.57421	−3.37657	3.64009
C16	−2.34759	−0.7118	−0.75654	H35	−5.57538	1.23966	0.19095
C17	−3.52328	−1.39773	−0.41369	H36	−5.57509	−1.24094	0.191
C18	−0.02641	−0.72617	−1.66871	H37	3.28832	1.22659	−2.46504
C19	1.18396	−1.42658	−1.94306	H38	3.28861	−1.22591	−2.46499

Table S4. Cartesian coordinates of $[Pd_2(tetracene)(HCN)_4]^{2+}$

Pd1	−0.00007	1.87398	0.44358	C23	1.23047	−1.432	−1.36116
Pd2	0.00002	−1.87395	0.44366	C24	−1.23028	−1.43208	−1.36121
C3	2.34134	2.90769	2.50852	H25	3.71818	2.48212	−1.36981
C4	−2.34196	2.90789	2.50789	H26	5.8526	1.24054	−1.39284
C5	2.34187	−2.90791	2.50794	H27	1.27002	2.46873	−1.68803
C6	−2.34193	−2.90757	2.50806	H28	−3.71819	2.48192	−1.3699
C7	3.71431	1.39725	−1.33962	H29	−1.27004	2.46865	−1.68815
C8	4.91343	0.70029	−1.35749	H30	5.85266	−1.24029	−1.39279
C9	−3.71426	1.39705	−1.33971	H31	3.7183	−2.48198	−1.36971
C10	1.2304	1.43202	−1.36122	H32	−3.71806	−2.48217	−1.3698
C11	−1.23035	1.43197	−1.36127	H33	1.27015	−2.46872	−1.68793
C12	2.4902	0.71121	−1.30658	H34	−1.26991	−2.46878	−1.68806
C13	−4.91335	0.70003	−1.35759	N35	1.54873	2.47936	1.8012

C14	4.91346	−0.70008	−1.35746	N36	−1.54891	2.47959	1.80106
C15	−2.49013	0.71108	−1.30664	N37	1.54881	−2.4793	1.80131
C16	0.00004	0.72974	−1.46286	N38	−1.54883	−2.4795	1.80115
C17	−4.91332	−0.70034	−1.35757	H39	3.08314	3.31328	3.16819
C18	2.49024	−0.71113	−1.30655	H40	−3.08234	3.31331	3.16926
C19	3.71438	−1.3971	−1.33957	H41	3.08262	−3.31363	3.16872
C20	−2.49009	−0.71126	−1.30661	H42	−3.08244	−3.31281	3.1694
C21	−3.71419	−1.39729	−1.33966	H43	−5.85255	1.24023	−1.39295
C22	0.00008	−0.7298	−1.46283	H44	−5.85248	−1.24059	−1.39292

Table S5. Cartesian coordinates of $[Pd_2(pentacene)(HCN)_4]^{2+}$

Pd1	−0.68332	−1.84969	0.51603	C26	−0.43613	0.73165	−1.38603
Pd2	−0.68307	1.84975	0.51565	C27	−1.66939	1.43122	−1.4421
C3	−3.2797	−2.86195	2.27521	C28	0.77215	1.43488	−1.13682
C4	1.38333	−2.84619	2.87762	H29	−4.1347	−2.48197	−1.7748
C5	−3.27995	2.86118	2.2747	H30	−6.24828	−1.24056	−2.07635
C6	1.38258	2.84874	2.87705	H31	5.69946	−2.49206	−0.68774
C7	−4.13506	−1.39701	−1.74635	H32	−1.66712	−2.47126	−1.76071
C8	−5.32149	−0.70033	−1.92003	H33	7.81789	−1.24077	−0.54767
C9	5.69414	−1.407	−0.6766	H34	3.22892	−2.48593	−0.88753
C10	6.87502	−0.70824	−0.60067	H35	0.84137	−2.47636	−1.44265
C11	3.22399	−1.40001	−0.85785	H36	−6.2482	1.24054	−2.07655
C12	−1.66948	−1.43145	−1.4418	H37	7.81797	1.24013	−0.54794
C13	0.77206	−1.43516	−1.13651	H38	−4.13454	2.48186	−1.77523
C14	−2.92518	−0.71102	−1.55587	H39	5.69963	2.49153	−0.68827
C15	4.45608	−0.71905	−0.75505	H40	3.22908	2.48552	−0.88806
C16	−5.32145	0.70027	−1.92015	H41	−1.66698	2.47099	−1.76114
C17	2.0199	−0.72099	−0.94628	H42	0.84155	2.47598	−1.44326
C18	6.87507	0.70765	−0.60082	N43	−2.39798	−2.44167	1.67662
C19	−0.43617	−0.73192	−1.38587	N44	0.68598	−2.43236	2.06844
C20	4.45612	0.71859	−0.7552	N45	−2.3977	2.4416	1.67643

C21	−2.92513	0.71086	−1.556	N46	0.68586	2.43336	2.06812
C22	−4.13497	1.39691	−1.7466	H47	−4.1048	−3.2597	2.83239
C23	5.69423	1.40647	−0.6769	H48	2.03372	−3.23803	3.63442
C24	2.01995	0.72065	−0.94644	H49	−4.1041	3.25835	2.83371
C25	3.22408	1.39961	−0.85816	H50	2.03254	3.24189	3.63354

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X-ray Crystallographic Data for $[Pd_2(\mu\text{–}[2.2]paracyclophane)_2(phen)_2][BF_4]_2$ (3)

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{49.50}H_{41}B_2F_8N_{4.50}OPd_2$
Formula Weight	1101.31
Crystal Color, Habit	orange, block
Crystal Dimensions	0.100 X 0.100 X 0.100 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 17.4255(7) Å b = 23.633(1) Å c = 21.2105(9) Å β = 98.028(2) ° V = 8649.2(6) Å^3
Space Group	$P2_1/c$ (#14)
Z value	8
D_{calc}	1.691 g/cm^3
F_{000}	4412.00
μ(MoKα)	9.126 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	110 exposures
ω oscillation Range (χ=45.0, ϕ=30.0)	130.0 - 190.0°
Exposure Rate	160.0 sec./°
ω oscillation Range (χ=45.0, ϕ=180.0)	0.0 - 160.0°
Exposure Rate	160.0 sec./°
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2\theta_{max}$	55.0°
No. of Reflections Measured	Total: 79121 Unique: 19201 (R_{int} = 0.0939)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.501 - 0.913)

C. Structure Solution and Refinement

Structure Solution	Patterson Methods (DIRDIF99 PATTY)
Refinement	Full-matrix least-squares on F
Function Minimized	Σ w (|Fo| - |Fc|)^2
Least Squares Weights parameters	Chebychev polynomial with 3 4.6291,1.2093,3.6902,
$2\theta_{max}$ cutoff	55.0^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00σ(I))	10553
No. Variables	1289
Reflection/Parameter Ratio	8.19
Residuals: R (I>3.00σ(I))	0.0496
Residuals: wR (I>3.00σ(I))	0.0571
Goodness of Fit Indicator	1.120
Max Shift/Error in Final Cycle	0.157
Maximum peak in Final Diff. Map	1.58 e$^-$/Å^3
Minimum peak in Final Diff. Map	-0.99 e$^-$/Å^3

X-ray Crystallographic Data for $[Pd_2(\mu\text{–naphthalene})_2(CH_3CN)_2][BF_4]_2$ (5)

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{24}H_{22}B_2F_8N_2Pd_2$
Formula Weight	724.86
Crystal Color, Habit	red, block
Crystal Dimensions	0.200 X 0.200 X 0.150 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 9.643(3) Å b = 11.957(4) Å c = 13.585(4) Å α = 63.325(6) ° β = 81.360(6) ° γ = 69.636(5) ° V = 1312.1(6) Å^3
Space Group	P-1 (#2)
Z value	2
D_{calc}	1.835 g/cm^3
F_{000}	708.00
μ(MoKα)	14.451 cm^{-1}

B. Intensity Measurements

Diffractometer	R-AXIS RAPID
Radiation	MoKα (λ = 0.71075 Å) graphite monochromated
Voltage, Current	50kV, 40mA
Temperature	23.0°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	80.0 sec./°
ω oscillation Range (χ=45.0, ϕ=180.0)	0.0 - 160.0°
Exposure Rate	80.0 sec./°
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2\theta_{max}$	54.8°
No. of Reflections Measured	Total: 12761 Unique: 5874 (R_{int} = 0.0656)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.542 - 0.805)

C. Structure Solution and Refinement

Structure Solution	Patterson Methods (DIRDIF99 PATTY)
Refinement	Full-matrix least-squares on F
Function Minimized	Σ w (|Fo| - |Fc|)^2
Least Squares Weights parameters	Chebychev polynomial with 3 2.3880,2.2307,1.3110,
$2\theta_{max}$ cutoff	54.8^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00σ(I))	4127
No. Variables	355
Reflection/Parameter Ratio	11.63
Residuals: R (I>3.00σ(I))	0.0533
Residuals: wR (I>3.00σ(I))	0.0613
Goodness of Fit Indicator	0.960
Max Shift/Error in Final Cycle	0.149
Maximum peak in Final Diff. Map	1.21 e$^-$/Å^3
Minimum peak in Final Diff. Map	-0.75 e$^-$/Å^3

X-ray Crystallographic Data for $[Pd_2(\mu\text{–tetracene})(CH_3CN)_4][BF_4]_2$ (8)

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{32.50}H_{32.50}B_2F_8N_{4.50}OPd_2$
Formula Weight	888.55
Crystal Color, Habit	orange, platelet
Crystal Dimensions	0.200 X 0.200 X 0.100 mm
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 10.2184(7) Å b = 13.876(1) Å c = 25.846(2) Å α = 89.238(2) ° β = 81.877(2) ° γ = 78.169(2) ° V = 3550.5(5) Å^3
Space Group	P-1 (#2)
Z value	4
D_{calc}	1.662 g/cm^3
F_{000}	1764.00
μ(MoKα)	10.890 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	72 exposures
ω oscillation Range (χ=45.0, ϕ=0.0)	0.0 - 180.0°
Exposure Rate	140.0 sec./°
ω oscillation Range (χ=45.0, ϕ=210.0)	0.0 - 180.0°
Exposure Rate	140.0 sec./°
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2\theta_{max}$	55.0°
No. of Reflections Measured	Total: 53334 Unique: 16181 (R_{int} = 0.1161)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.468 - 0.897)

C. Structure Solution and Refinement

Structure Solution	Patterson Methods (DIRDIF99 PATTY)
Refinement	Full-matrix least-squares on F
Function Minimized	Σ w (|Fo| - |Fc|)^2
Least Squares Weights parameters	Chebychev polynomial with 3 6.5805,0.6492,4.7262,
$2\theta_{max}$ cutoff	55.0^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00σ(I))	6089
No. Variables	954
Reflection/Parameter Ratio	6.38
Residuals: R (I>3.00σ(I))	0.0599
Residuals: wR (I>3.00σ(I))	0.0704
Goodness of Fit Indicator	1.111
Max Shift/Error in Final Cycle	0.057
Maximum peak in Final Diff. Map	1.70 e$^-$/Å^3
Minimum peak in Final Diff. Map	-1.08 e$^-$/Å^3

X-ray Crystallographic Data for $[Pd_2(\mu\text{–pentacene})(CH_3CN)_4][BF_4]_2$ (9)

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{33.50}H_{30}B_2F_8N_4Pd_2$
Formula Weight	875.04
Crystal Color, Habit	orange, block
Crystal Dimensions	0.200 X 0.100 X 0.100 mm
Crystal System	monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 13.4428(5) Å b = 24.2164(9) Å c = 10.8013(5) Å β = 101.052(1) ° V = 3451.0(3) Å^3
Space Group	$P2_1/c$ (#14)
Z value	4
D_{calc}	1.684 g/cm^3
F_{000}	1732.00
μ(MoKα)	11.167 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	100.0 sec./°
ω oscillation Range (χ=45.0, ϕ=270.0)	0.0 - 160.0°
Exposure Rate	100.0 sec./°
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2\theta_{max}$	54.9°
No. of Reflections Measured	Total: 33650 Unique: 7876 (R_{int} = 0.0699)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.497 - 0.894)

C. Structure Solution and Refinement

Structure Solution	Patterson Methods (DIRDIF99 PATTY)
Refinement	Full-matrix least-squares on F
Function Minimized	Σ w (|Fo| - |Fc|)^2
Least Squares Weights	1/[0.0010Fo^2+1.0000σ(Fo^2)]
2θ_{max} cutoff	54.9^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>3.00σ(I))	3841
No. Variables	480
Reflection/Parameter Ratio	8.00
Residuals: R (I>3.00σ(I))	0.0455
Residuals: wR (I>3.00σ(I))	0.0607
Goodness of Fit Indicator	1.362
Max Shift/Error in Final Cycle	0.195
Maximum peak in Final Diff. Map	0.73 e$^-$/Å^3
Minimum peak in Final Diff. Map	-0.88 e$^-$/Å^3