

Supporting Information

Bridging Coordination of Acenaphthylene to a Pd₃ Chain or a Pd₄ Sheet Clusters

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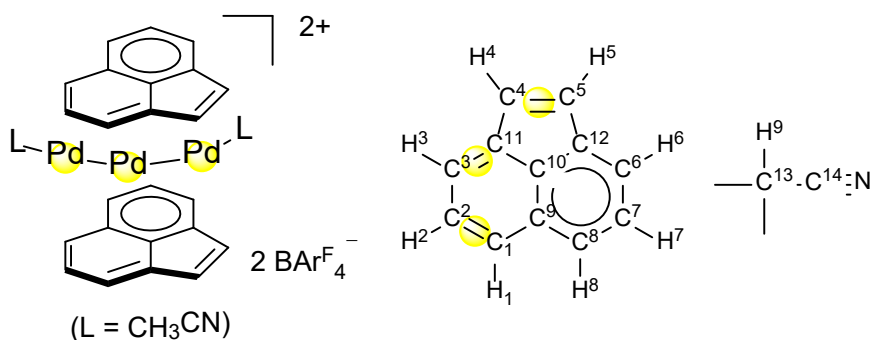
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Experimental Section

General Procedures. All manipulations were conducted under a nitrogen atmosphere using standard Schlenk or dry-box technique. ^1H (400 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (100 MHz) NMR spectra were recorded on JEOL JNM-ECS400. The chemical shifts were referenced to the residual resonances of deuterated solvents. Elemental analyses were performed at the Instrument Center of Institute for Molecular Science. X-ray crystal data were collected by Rigaku R-Axis RAPID diffractometer, or Rigaku XtaLAB Synergy diffractometer equipped with a HyPix-6000HE Hybrid Photon Counting (HPC) detector with graphite-monochromated Mo-K α (0.71075 Å) radiation. Unless specified, all reagents were purchased from commercial supplier and used without purification. Nitromethane, dichloromethane, *n*-hexane, toluene, CD_3NO_2 , and CD_2Cl_2 were purified according to the standard procedures. $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$,^[S1] $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$,^[S2] $\text{NaBAR}^{\text{F}}_4$,^[S3] and $[\text{Pd}_3(\mu_3\text{-anisole})(\mu_3\text{-COT})(\text{CH}_3\text{CN})_3][\text{PF}_6]_2$ (**2**)^[S4] were prepared according to the literature.

Synthesis of $[\text{Pd}_3(\mu_3\text{-acenaphthylene})_2(\text{CH}_3\text{CN})_2][\text{BAR}^{\text{F}}_4]_2$ (1**):** To a dichloromethane solution of acenaphthylene (245 mg, 1.61 mmol) was added $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ (215 mg, 3.40×10^{-1} mmol) and $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (176 mg, 1.70×10^{-1} mmol) at ambient temperature, and the mixture was stirred for 10 min. $\text{NaBAR}^{\text{F}}_4$ (602 mg, 6.79×10^{-1} mmol) was added to the reaction mixture, and the mixture was stirred for 30 min. After filtration of the reaction mixture, the filtrate was concentrated, reprecipitated with *n*-hexane, dried *in vacuo* to afford complex **1** (640 mg, 2.63×10^{-1} mmol, 77% yield). The complex **1** was crystallized from CH_2Cl_2 /hexamethyldisiloxane. A mixture of two isomers (91:9); major isomer: ^1H NMR (400 MHz, CD_3NO_2 , 0 °C) δ 8.02 (d, $^3J = 7.2$ Hz, 2H, H¹),

7.86 (s, 16H, *o*-Ar^F), 7.68 (m, 2H, H⁵), 7.66 (s, 8H, *p*-Ar^F), 7.22 (d, ³*J* = 7.2 Hz, 2H, H⁶), 7.00 (d, ³*J* = 8.0 Hz, 2H, H⁸), 6.79 (dd, ³*J* = 8.0, 8.0 Hz, 2H, H⁷), 6.77 (dd, ³*J* = 6.4, 6.4 Hz, 2H, H²), 5.97 (d, ³*J* = 4.4 Hz, 2H, H⁴), 5.76 (d, ³*J* = 6.0 Hz, 2H, H³), 2.72 (s, 6H, H⁹). The proton signal for H⁵ was overlapped with the signal for Ar^F group. ¹³C{¹H} NMR (101 MHz, CD₃NO₂, 0 °C): δ 163.2 (q, ¹*J*_{C-B} = 50 Hz, *i*-Ar^F), 136.8 (s, C¹²), 136.1 (s, *o*-Ar^F), 132.0 (s, C¹⁰), 131.3 (s, C⁷), 130.2 (q, ²*J*_{C-F} = 31 Hz, *m*-Ar^F), 127.3 (s, C¹⁴), 126.2 (s, C⁶), 126.0 (s, C⁸), 125.3 (s, C⁹), 123.1 (q, ¹*J*_{C-F} = 273 Hz, CF₃), 118.9 (s, *p*-Ar^F), 100.4 (s, C²), 90.1 (s, C¹), 90.0 (s, C⁴), 89.8 (s, C¹¹), 87.3 (s, C⁵), 84.1 (s, C³), 3.7 (s, C¹³). minor isomer: ¹H NMR (400 MHz, CD₃NO₂, 0 °C) δ 7.86 (s, 16H, *o*-Ar^F), 7.72 (d, ³*J* = 3.6 Hz, 2H, H⁵), 7.66 (s, 8H, *p*-Ar^F), 7.04 (d, ³*J* = 8.0 Hz, 2H, acenaphthylene), 6.82 (m, 2H, H² or H³), 6.66 (dd, ³*J* = 6.8, 6.8 Hz, 2H, H² or H³), 6.13 (d, ³*J* = 3.6 Hz, 2H, H⁴), 5.82 (d, ³*J* = 6.8 Hz, 2H, H³), 2.72 (s, 6H, H⁹). The proton signals for H¹, H⁶, H⁷, and H⁸ was overlapped with the signal for major isomer and Ar^F group. Anal. Calcd. For. C₉₂H₄₆B₂F₄₈N₂Pd₃·CH₂Cl₂: C, 44.38; H, 1.92; N, 1.11. Found: C, 44.53; H, 2.02; N, 1.05.



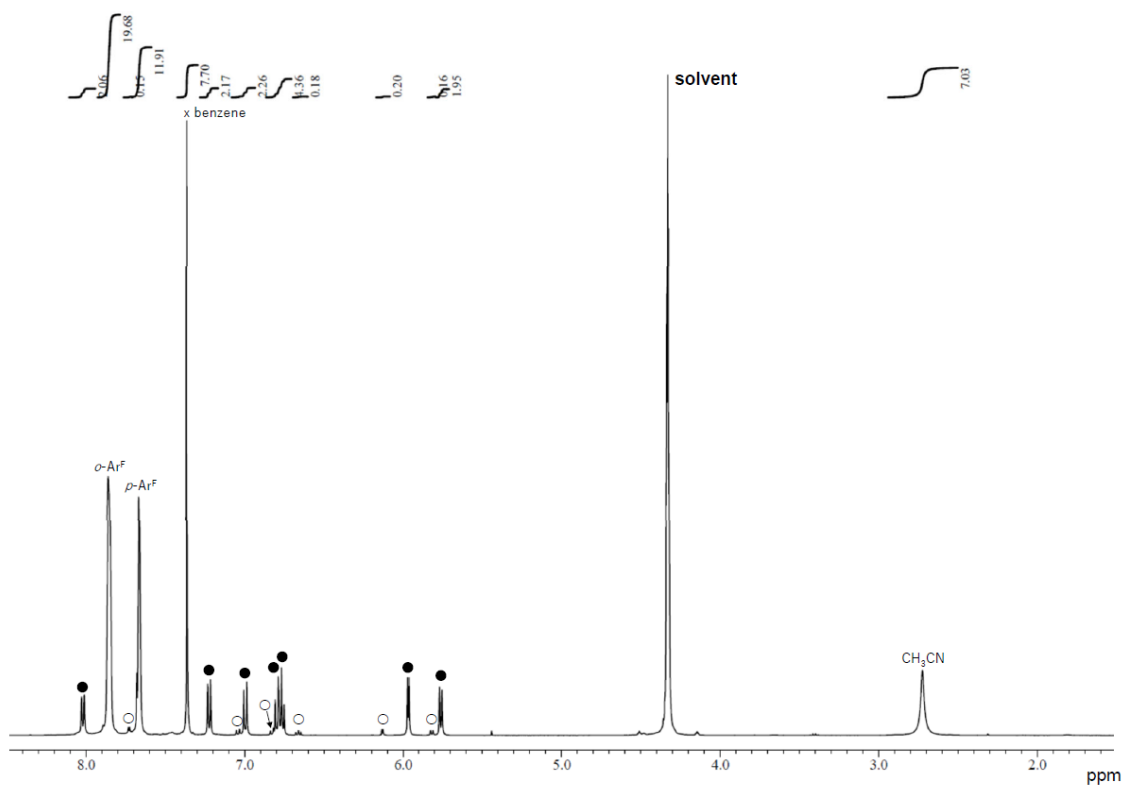


Figure S1. ^1H NMR spectrum of complex **1**. ● = major isomer of $[\text{Pd}_3(\mu_3\text{-acenaphthylene})_2(\text{CH}_3\text{CN})_2][\text{BAr}^{\text{F}}_4]_2$, ○ = minor isomer of $[\text{Pd}_3(\mu_3\text{-acenaphthylene})_2(\text{CH}_3\text{CN})_2][\text{BAr}^{\text{F}}_4]_2$, x = benzene.

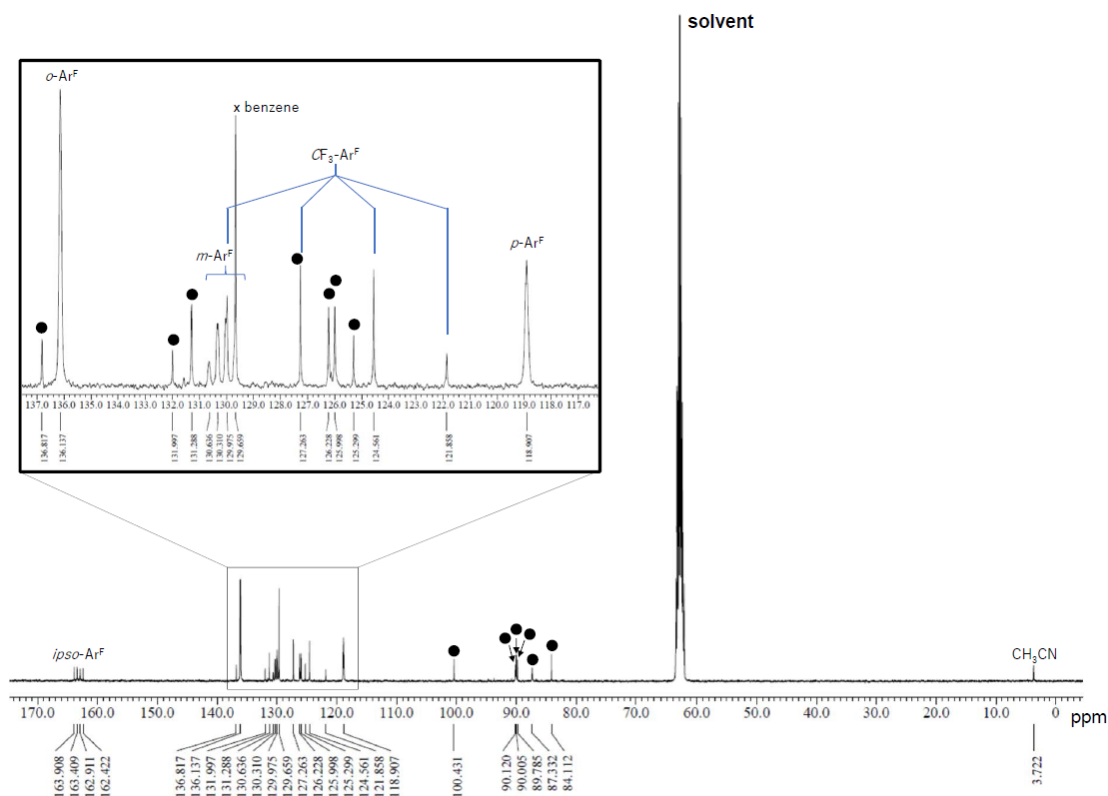
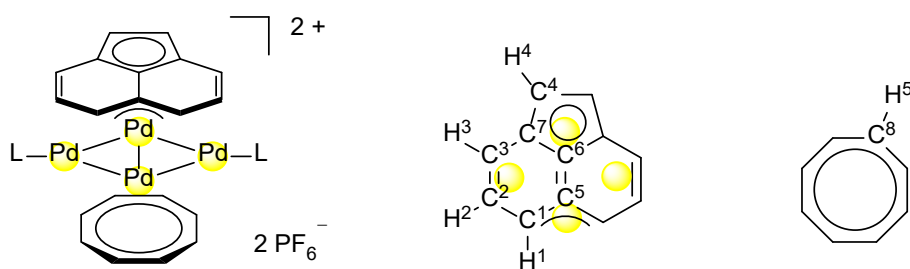


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex **1**. ● = major isomer of $[\text{Pd}_3(\mu_3\text{-acenaphthylene})_2(\text{CH}_3\text{CN})_2][\text{BAr}^{\text{F}}_4]$, x = benzene.

Synthesis of $[\text{Pd}_4(\mu_4\text{-acenaphthylene})(\mu_4\text{-COT})(\text{L})_2][\text{PF}_6]_2$ (L = MeCN (**3**), PPh_3 (**3'**)):

To a nitromethane solution of $[\text{Pd}_3(\mu_3\text{-anisole})(\mu_3\text{-COT})(\text{CH}_3\text{CN})_3][\text{PF}_6]_2$ (300 mg, 3.18×10^{-1} mmol) was added acenaphthylene (242 mg, 1.59 mmol) at ambient temperature, and the mixture was stirred for 1 h at 60 °C. The reaction mixture was evaporated *in vacuo*. The resulting solid was dissolved in nitromethane, and the solution was filtered through Celite. The filtrate was reprecipitated with toluene, washed with toluene and *n*-hexane, and dried *in vacuo* to afford complex **3** (205 mg, 1.94×10^{-1} mmol, 92% yield). ^1H NMR (400 MHz, CD_3NO_2 , 25 °C) δ 6.23 (2H, dd, $^3J = 6.0, 6.0$ Hz, H^2), 6.12 (2H, d, $^3J = 6.0$ Hz, H^3), 5.76 (2H, s, H^4), 5.39 (2H, d, $^3J = 6.0$ Hz, H^1), 4.50 (8H, s, H^5), 2.33

(6H, s, CH₃CN). ¹³C{¹H} NMR (101 MHz, CD₃NO₂, 25 °C): δ 124.9 (s, CH₃CN), 111.3 (s, C⁴), 108.6 (s, C⁶), 101.5 (s, C⁷), 87.1 (s, C²), 86.9 (s, C⁵), 80.2 (s, C³), 79.6 (s, C¹), 67.0 (s, C⁸), 2.8 (s, CH₃CN). To a nitromethane solution of **2** (50.0 mg, 4.74 x 10⁻² mmol) was added acenaphthylene (24.9 mg, 9.49 x 10⁻² mmol) at ambient temperature, and the mixture was stirred for 10 min. The reaction mixture was evaporated *in vacuo*. The filtrate was layered with n-hexane, and the two-layer solution was stood overnight. The precipitate was collected, dried *in vacuo*, and washed with benzene and n-hexane to afford complex **3'** (48.7 mg, 3.25 x 10⁻² mmol, 69% yield). ¹H NMR (400 MHz, CD₃NO₂, 25 °C) δ 7.70 (dd, ³J = 8.0, 8.0 Hz, 6H, *p*-PPh₃), 7.62 (dd, ³J = 8.0, 6.8 Hz, 12H, *m*-PPh₃), 7.56-7.51 (m, 12H, *o*-PPh₃), 6.07 (m, 2H, H³), 5.72 (dd, ³J = 6.0, 6.0 Hz, 2H, H²), 5.46 (s, 2H, H⁴), 4.59 (d, ³J = 6.0 Hz, 2H, H¹), 3.93 (s, 8H, H⁵). ¹³C{¹H} NMR (101 MHz, CD₃NO₂, 25 °C): δ 135.2 (m, *o*-PPh₃), 133.3 (s, *p*-PPh₃), 130.9 (m, *m*-PPh₃), 130.1 (d, ¹J_{C-P} = 39 Hz, *ipso*-PPh₃), 111.9 (s, C⁴), 109.7 (s, C⁶), 97.2 (s, C⁷), 86.9 (s, C⁵), 84.8 (s, C²), 77.1 (s, C³), 76.4 (s, C¹), 65.4 (s, C⁸). ³¹P{¹H} NMR (162 MHz, CD₃NO₂, 25 °C) δ 19.7 (PPh₃), -144.1 (sept, ¹J_{P-F} = 707 Hz, PF₆). Anal. Calcd. For. C₅₆H₄₆F₁₂P₄Pd₃: C, 44.94; H, 3.10. Found: C, 44.71; H, 3.11.



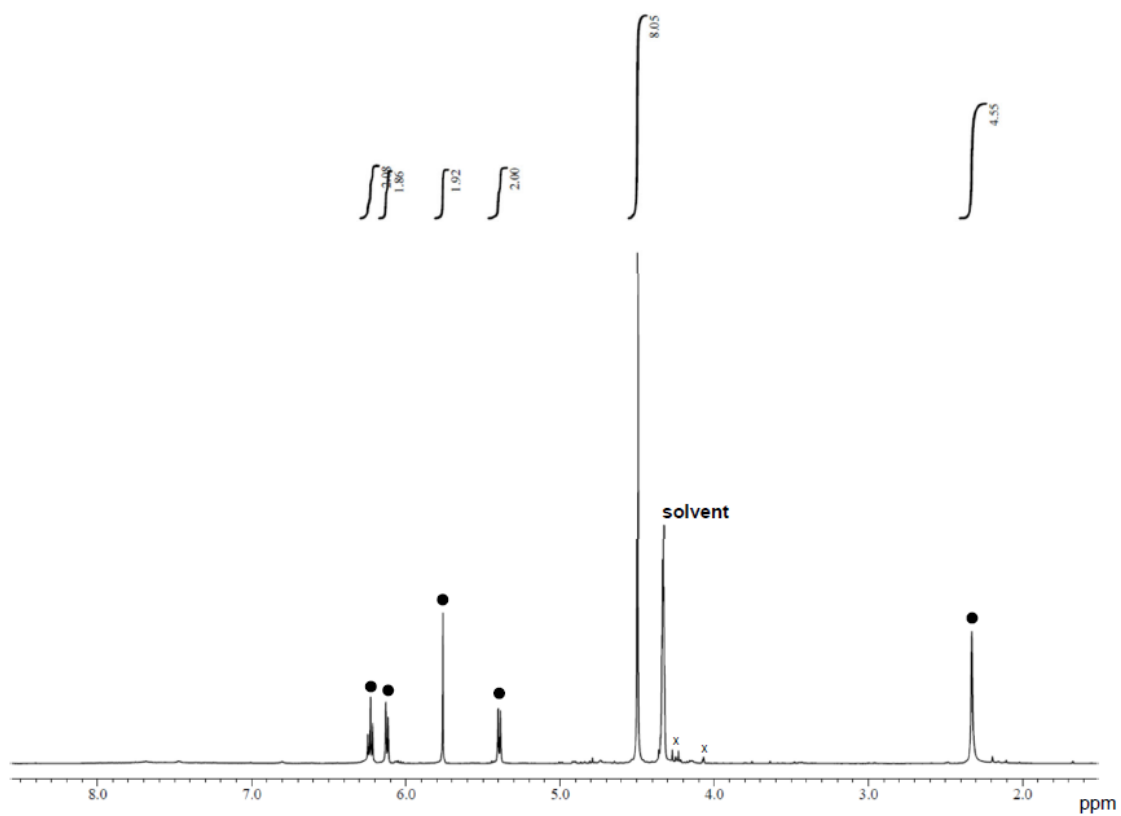


Figure S3. ^1H NMR spectrum of complex **3**. $\bullet = [\text{Pd}_4(\mu_4\text{-acenaphthylene})(\mu_4\text{-COT})(\text{CH}_3\text{CN})_2][\text{PF}_6]_2$.
 x = impurities.

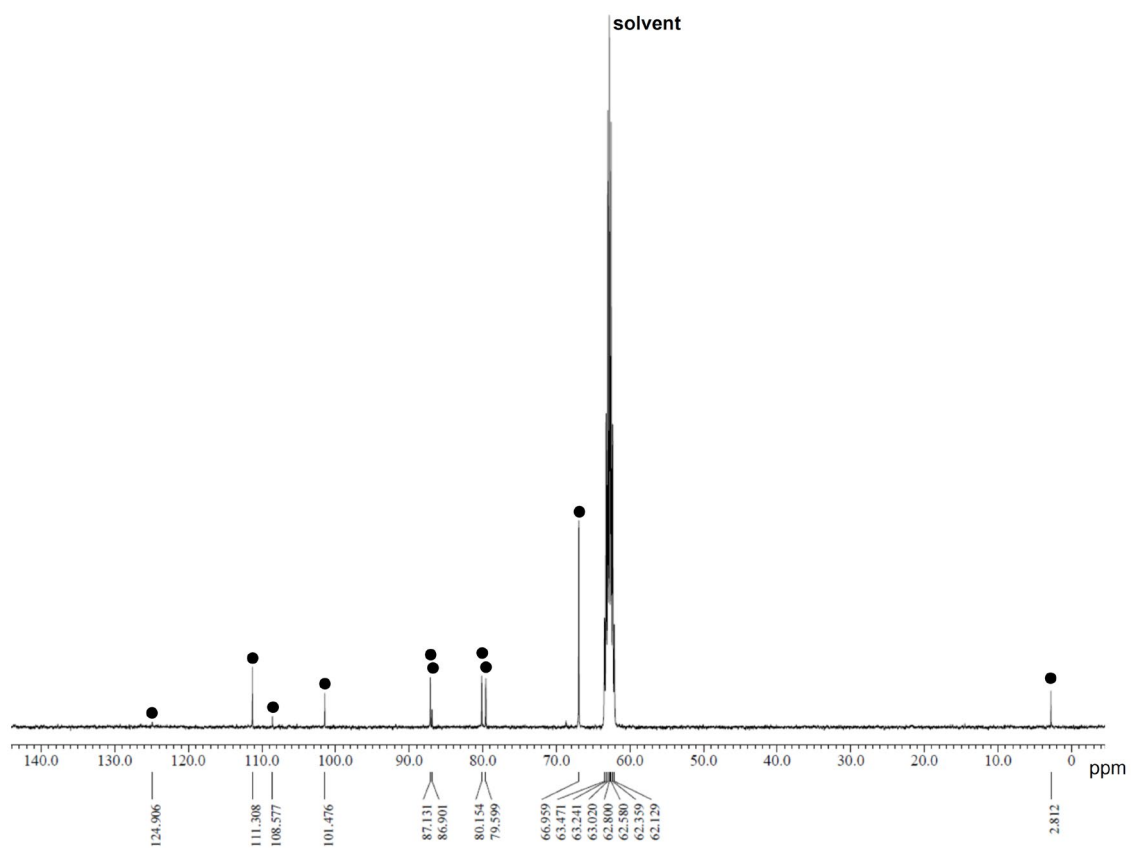


Figure S4. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex **3**. • = $[\text{Pd}_4(\mu_4\text{-acenaphthylene})(\mu_4\text{-COT})(\text{CH}_3\text{CN})_2][\text{PF}_6]_2$.

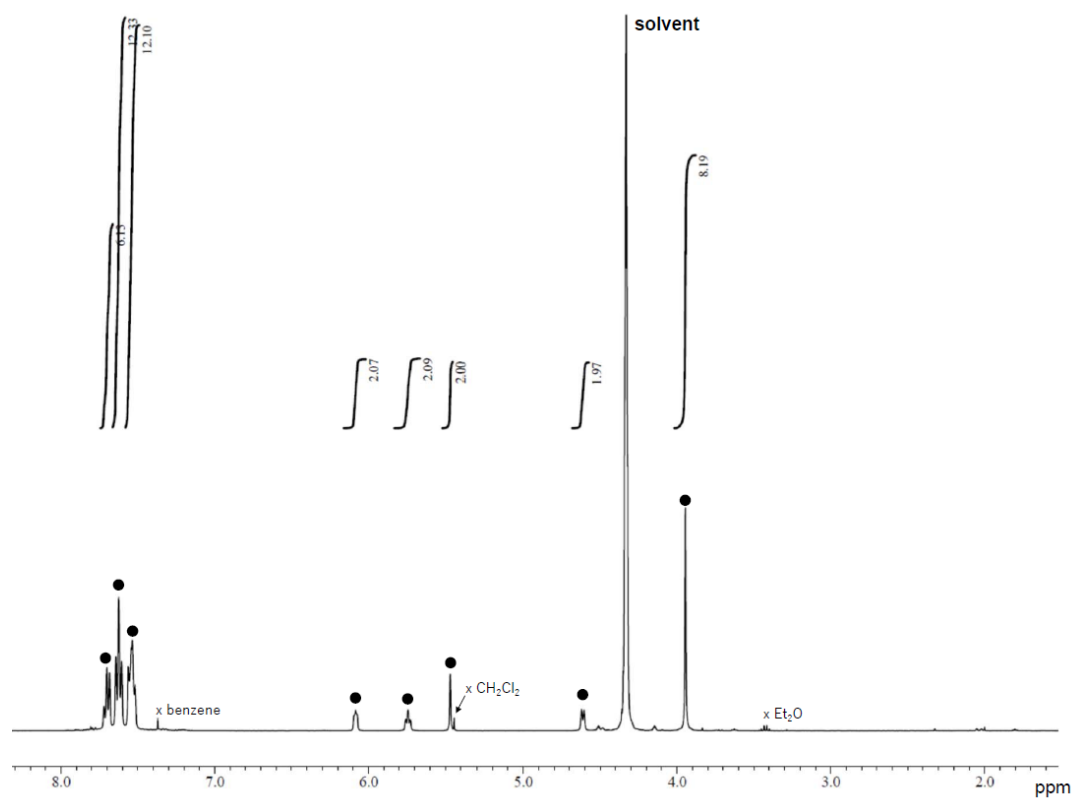


Figure S5. ^1H NMR spectrum of complex $3'$. ● = $[\text{Pd}_4(\mu_4\text{-acenaphthylene})(\mu_4\text{-COT})(\text{PPh}_3)_2][\text{PF}_6]_2$. x = impurities.

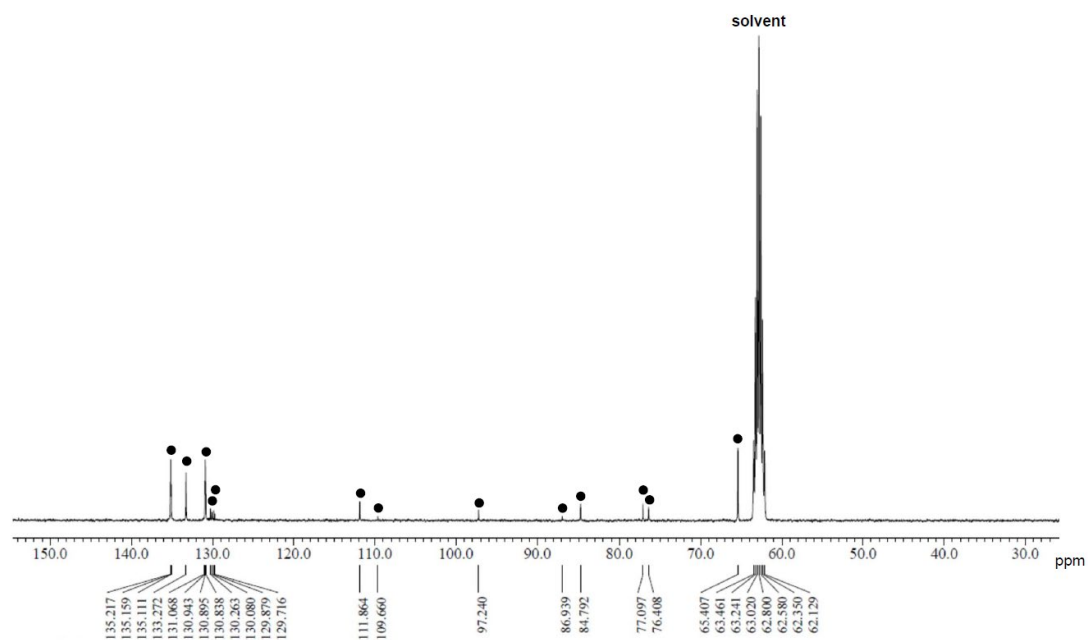


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex $3'$. ● = $[\text{Pd}_4(\mu_4\text{-acenaphthylene})(\mu_4\text{-COT})(\text{PPh}_3)_2][\text{PF}_6]_2$.

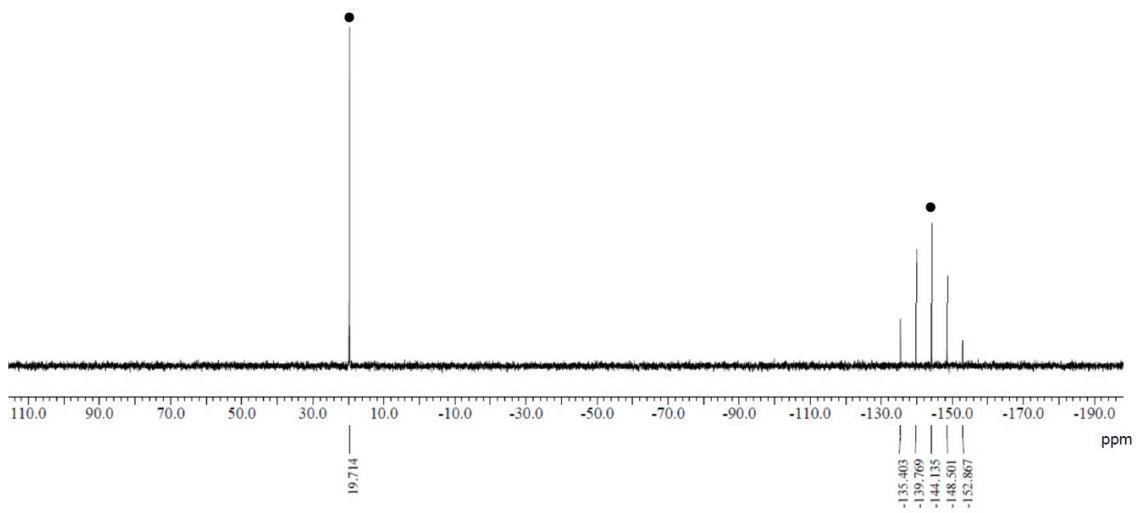


Figure S7. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of complex **3'**. ● = $[\text{Pd}_4(\mu_4\text{-acenaphthylene})(\mu_4\text{-COT})(\text{PPh}_3)_2][\text{PF}_6]_2$.

Computational Details: All calculations were carried out with Gaussian09 program package (Revision D.01).^[S5] Geometrical optimization was performed with DFT method using the M06 functional.^[S6] Core electrons of Pd were replaced with Stuttgart-Dresden-Bonn relativistic effect core potentials (ECPs) and their valence electrons were represented by (8s7p6d)/[6s5p3d] basis set.^[S7] Usual 6-311G(d) basis sets were used for other atoms.^[S8] The optimized structures of eclipsed-[Pd₃(μ₃-acenaphthylene)₂(HCN)₂]²⁺ (**1'**), staggered-[Pd₃(μ₃-acenaphthylene)₂(HCN)₂]²⁺ (**1''**), [Pd₄(μ₄-acenaphthylene)(μ₄-COT)(HCN)₂]²⁺ (**3''**), and acenaphthylene were depicted in Figures S8-S11. Cartesian coordinates of the optimized geometries of **1'**, **1''**, **3''** and acenaphthylene were shown in Tables S1-S4.

Table S1. Cartesian coordinates (in Å) of the optimized geometry of eclipsed-[Pd₃(μ₃-acenaphthylene)₂(HCN)₂]²⁺ (**1'**).

Symbol	X	Y	Z
C	-1.3998090	2.2981260	1.0082630
C	-0.1543000	2.2306610	0.3784830
C	1.0680440	2.2827610	1.0329210
C	1.0209690	2.4190880	2.4340410
C	-0.2025700	2.4884470	3.0772080
C	-1.4264390	2.4267430	2.3836690
C	-2.4134540	2.2009520	-0.0626470
C	-1.7542750	2.1210840	-1.2983110
C	-0.3223240	2.1166060	-1.0485690
H	1.9422480	2.4871100	3.0087940
H	-0.2221350	2.6086350	4.1568310
H	-2.3614310	2.4963430	2.9345530
H	-3.4518820	2.4957110	0.0500580
H	-2.2172080	2.2369600	-2.2720470
C	2.2421930	2.2254730	0.1917150
C	2.1068650	2.1583110	-1.2057100
H	2.9917680	2.2715250	-1.8274950
C	0.8331640	2.0834410	-1.8532890
H	3.2113050	2.4842020	0.6141630
H	0.7836210	2.1412540	-2.9384910
C	-1.3997840	-2.2981540	1.0082490
C	-0.1542790	-2.2306710	0.3784630
C	1.0680690	-2.2827740	1.0328920
C	1.0210040	-2.4191210	2.4340100
C	-0.2025300	-2.4884980	3.0771840
C	-1.4264050	-2.4267910	2.3836540
C	-2.4134370	-2.2009720	-0.0626530
C	-1.7542660	-2.1210760	-1.2983200
C	-0.3223130	-2.1165950	-1.0485860
H	1.9422870	-2.4871460	3.0087560
H	-0.2220880	-2.6087000	4.1568050
H	-2.3613930	-2.4964060	2.9345420
H	-3.4518620	-2.4957370	0.0500570
H	-2.2172030	-2.2369480	-2.2720540
C	2.2422130	-2.2254650	0.1916780
C	2.1068750	-2.1582830	-1.2057450
H	2.9917760	-2.2714780	-1.8275360
C	0.8331680	-2.0834100	-1.8533140
H	3.2113310	-2.4841890	0.6141150
H	0.7836180	-2.1412080	-2.9385160
Pd	0.0915850	0.0000100	-1.3564000
Pd	-2.4913070	-0.0000100	-0.4121100

Pd	2.4904390	0.0000100	-0.2215970
N	-4.4390330	-0.0000130	0.4617820
N	4.4021170	0.0000260	0.7615400
C	5.4580640	0.0000060	1.2031420
H	6.4517700	-0.0000100	1.6150220
C	-5.5185670	0.0000300	0.8414970
H	-6.5343870	0.0000470	1.1946140

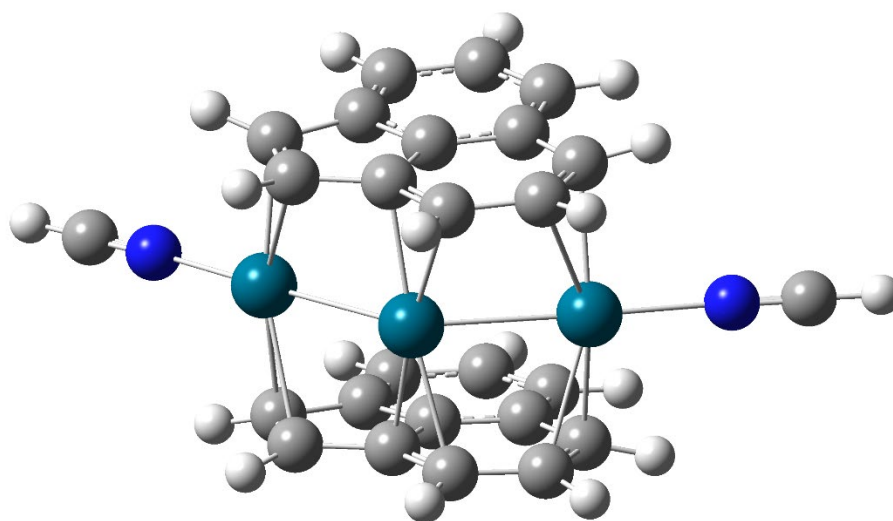


Figure S8. The optimized geometry of eclipsed- $[\text{Pd}_3(\mu_3\text{-acenaphthylene})_2(\text{HCN})_2]^{2+}$ (**1'**).

Table S2. Cartesian coordinates (in Å) of the optimized geometry of staggered-[Pd₃(μ₃-acenaphthylene)₂(HCN)₂]²⁺ (**1''**).

Symbol	X	Y	Z
C	0.3003790	2.1352090	-1.0624610
C	0.1256490	2.2537290	0.3624820
C	-1.1005190	2.3044950	1.0089350
C	-2.2686240	2.2355980	0.1613660
C	-2.1296020	2.1440660	-1.2322680
C	-0.8497200	2.0618310	-1.8699510
C	1.7294170	2.1247270	-1.3050800
C	2.3883370	2.1964520	-0.0643820
C	1.3680880	2.3117930	0.9996850
H	-3.2420470	2.4846910	0.5789150
H	-3.0091060	2.2534280	-1.8621110
H	-0.7947090	2.0932400	-2.9561780
H	2.2004860	2.2197930	-2.2771340
H	3.4254990	2.4979570	0.0467350
C	-1.0607950	2.4410410	2.4100040
C	0.1595420	2.5041550	3.0608660
H	0.1726410	2.6221610	4.1408530
C	1.3873680	2.4359050	2.3758310
H	-1.9849180	2.5096900	2.9799920
H	2.3197060	2.4945720	2.9327190
C	-1.3676470	-2.3132540	0.9984410
C	-0.1252620	-2.2543200	0.3612480
C	1.1009370	-2.3055050	1.0076150
C	1.0613360	-2.4433170	2.4085380
C	-0.1589780	-2.5071520	3.0594170
C	-1.3868250	-2.4385230	2.3744890
C	-2.3880020	-2.1967800	-0.0654670
C	-1.7290570	-2.1235420	-1.3061230
C	-0.3000090	-2.1341580	-1.0635540
H	1.9855090	-2.5122800	2.9784120
H	-0.1720360	-2.6259210	4.1393200
H	-2.3191160	-2.4977710	2.9313800
H	-3.4250930	-2.4986680	0.0454540
H	-2.2002870	-2.2176040	-2.2782010
C	2.2690570	-2.2358870	0.1601230
C	2.1301030	-2.1433560	-1.2335080
H	3.0093770	-2.2531320	-1.8635950
C	0.8501100	-2.0599500	-1.8710150
H	3.2424550	-2.4854650	0.5774680
H	0.7951450	-2.0904790	-2.9572740
Pd	-0.0000770	0.0006940	-1.3652440
Pd	-2.4907510	0.0008770	-0.3079260

Pd	2.4904300	-0.0013980	-0.3089980
N	-4.3934200	0.0055100	0.6752280
N	4.3924900	-0.0034260	0.6761500
C	5.4467740	0.0115090	1.1213030
H	6.4391640	0.0247840	1.5358030
C	-5.4482040	-0.0082410	1.1192380
H	-6.4409500	-0.0206980	1.5329110

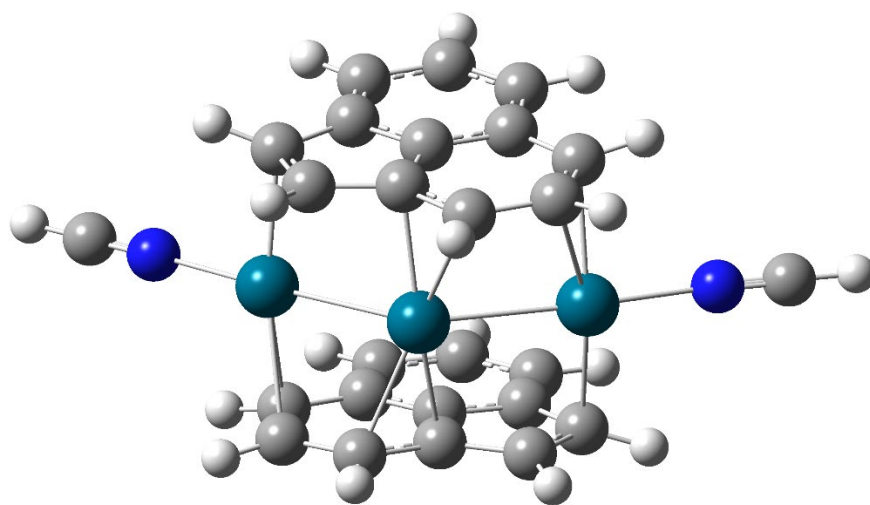


Figure S9. The optimized geometry of staggered-[Pd₃(μ₃-acenaphthylene)₂(HCN)₂]²⁺ (**1''**).

Table S3. Cartesian coordinates (in Å) of the optimized geometry of [Pd₄(μ₄-acenaphthylene)(μ₄-COT)(HCN)₂]²⁺ (**3''**).

Symbol	X	Y	Z
Pd	-0.0007252	-0.6705089	-1.4398625
Pd	2.3431380	-0.2653831	0.0043958
N	4.5511143	-0.5143623	0.2184240
C	5.6849438	-0.6477364	0.3088514
Pd	0.0004447	0.5872968	1.2863661
C	0.0007995	2.1027338	-0.4892542
C	-0.0000883	1.4969009	-1.7791177
C	1.2792652	1.1684645	-2.3217828
C	2.4474431	1.4435631	-1.5700745
C	2.4146498	2.0589106	-0.2858333
C	1.1638000	2.4193285	0.2586601
H	1.3728198	0.8330158	-3.3523096
H	3.4127826	1.2977560	-2.0485406
H	3.3455115	2.3589668	0.1892035
C	-1.7194001	-1.8121109	1.5159135
C	-1.7201614	-2.4115143	0.2437653
C	-0.7083345	-2.6503220	-0.7493741
C	0.7047656	-2.6511262	-0.7501104
C	1.7179648	-2.4131902	0.2418042
C	1.7191898	-1.8139049	1.5140060
C	0.7065688	-1.2129543	2.3457930
C	-0.7052556	-1.2124213	2.3467173
H	-2.6672051	-1.9255411	2.0430969
H	-2.6680521	-2.8891609	-0.0067571
H	-1.1239329	-3.1340629	-1.6336130
H	1.1189056	-3.1353147	-1.6347941
H	2.6651202	-2.8917533	-0.0097759
H	2.6673951	-1.9284696	2.0402130
H	1.1217545	-0.8662194	3.2919815
H	-1.1189988	-0.8653757	3.2934209
H	6.7499898	-0.7713259	0.3927632
C	-1.2802812	1.1694951	-2.3204395
C	-1.1612006	2.4203728	0.2598234
C	-2.4129538	2.0609368	-0.2833214
H	-3.3431029	2.3617777	0.1926160
C	-2.4474997	1.4456076	-1.5675402
H	-3.4133948	1.3007627	-2.0451731
H	-1.3751834	0.8341403	-3.3508765
C	0.6881034	3.0595784	1.4911445
C	-0.6837415	3.0602469	1.4917979
H	-1.3185107	3.4772803	2.2646599
H	1.3239938	3.4759507	2.2634417

Pd	-2.3431824	-0.2632273	0.0064190
N	-4.5516342	-0.5145179	0.2165552
C	-5.6853979	-0.6494996	0.3054166
H	-6.7503842	-0.7745853	0.3878753

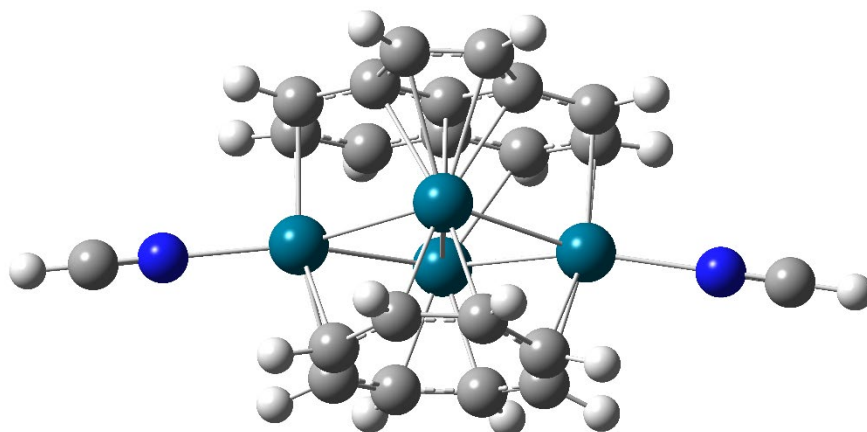


Figure S10. The optimized geometry of $[\text{Pd}_4(\mu_4\text{-acenaphthylene})(\mu_4\text{-COT})(\text{HCN})_2]^{2+}$ (**3''**).

Table S4. Cartesian coordinates (in Å) of the optimized geometry of acenaphthylene.

Symbol	X	Y	Z
C	0.0000000	0.0000000	-0.1414570
C	0.0000000	0.0000000	1.2463484
C	0.0000000	1.2743282	1.8694337
C	0.0000000	2.4140554	1.0995373
C	0.0000000	2.3761491	-0.3183657
C	0.0000000	1.1558094	-0.9471698
H	0.0000000	1.3479860	2.9559341
H	0.0000000	3.3846227	1.5912086
H	0.0000000	3.3102624	-0.8777307
C	0.0000000	-1.2743282	1.8694337
C	0.0000000	-1.1558094	-0.9471698
C	0.0000000	-2.3761491	-0.3183657
H	0.0000000	-3.3102624	-0.8777307
C	0.0000000	-2.4140554	1.0995373
H	0.0000000	-3.3846227	1.5912086
H	0.0000000	-1.3479860	2.9559341
C	0.0000000	0.6774982	-2.3321390
C	0.0000000	-0.6774982	-2.3321390
H	0.0000000	-1.3127458	-3.2118649
H	0.0000000	1.3127458	-3.2118649

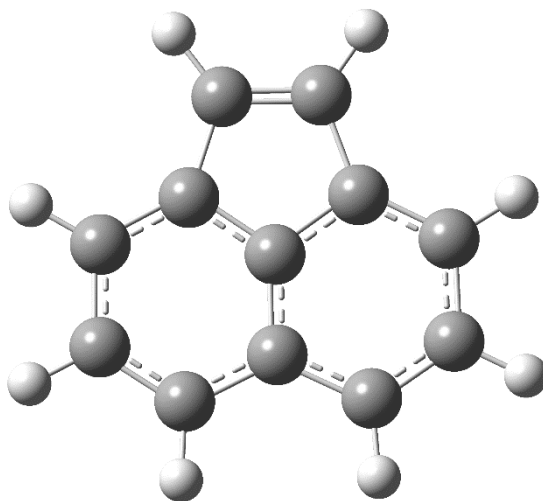


Figure S11. The optimized geometry of acenaphthylene.

X-ray Crystallographic analyses: A crystal of suitable dimensions was mounted on a CryoLoop (Hampton Research Corp.) with a layer of paraton-N oil and placed in a cold nitrogen stream. All measurements were performed on a R-Axis RAPID imaging plate, or Rigaku XtaLAB Synergy diffractometer equipped with a HyPix-6000HE Hybrid Photon Counting (HPC) detector with graphite-monochromated Mo-K α (0.71075 Å) radiation. The structure was solved by direct method (SHELXT)^[S9] and refined on F^2 by full-matrix least-squares methods; using SHELXL 2017/1.^[S10] Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\sum w(F_o^2 - F_c^2)^2]$ ($w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$), where $P = (\text{Max}(F_o^2, 0) + 2F_c^2) / 3$ with $\sigma^2(F_o^2)$ from counting statistics. The function $R1$ and $wR2$ were $(\sum ||F_o| - |F_c||) / \sum |F_o|$ and $[\sum w(F_o^2 - F_c^2)^2 / \sum (wF_o^4)]^{1/2}$, respectively. The ORTEP-3 program was used to draw the molecule.^[S11] Crystal data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Database Centre: CCDC 2116562 and 2116563.

X-ray Crystallographic Data

Crystal data for **1**: $C_{101}H_{55}B_2F_{48}N_2Pd_3$, $M_r = 2549.30$, *monoclinic*, space group $P2_1/c$ (no. 14). $a = 14.5164(6)$ Å, $b = 27.9490(10)$ Å, $c = 24.4264(10)$ Å, $\beta = 102.9552(12)^\circ$, $Z = 4$, $V = 9658.0(7)$ Å³, $F(000) = 5020$, $D_c = 1.753$ g cm⁻³, $\mu(\text{MoK}\alpha) = 6.96$ cm⁻¹, $T = 129$ K, 134093 reflections collected, 21915 unique ($R_{\text{int}} = 0.0741$), 1371 variables refined with 15410 reflections with $I > 2\sigma(I)$ to $R = 0.0763$. CCDC 2116562.

Crystal data for **3'**: $C_{71}H_{61}F_{12}P_4Pt_2 \cdot 0.5CH_2Cl_2$, $M_r = 1734.21$, *triclinic*, space group $P-1$ (no. 2). $a = 10.7362(4)$ Å, $b = 18.4776(6)$ Å, $c = 19.2924(6)$ Å, $\alpha = 115.3717(9)^\circ$, $\beta = 97.0350(12)^\circ$, $\gamma = 90.4714(12)^\circ$, $Z = 2$, $V = 3424.1(2)$ Å³, $F(000) = 1720$, $D_c = 1.682$ g cm⁻³, $\mu(\text{MoK}\alpha) = 12.41$ cm⁻¹, $T = 165$ K, 60364 reflections collected, 15467 unique ($R_{\text{int}} = 0.0647$), 837 variables refined with 12308 reflections with $I > 2\sigma(I)$ to $R = 0.0668$. CCDC 2116563.

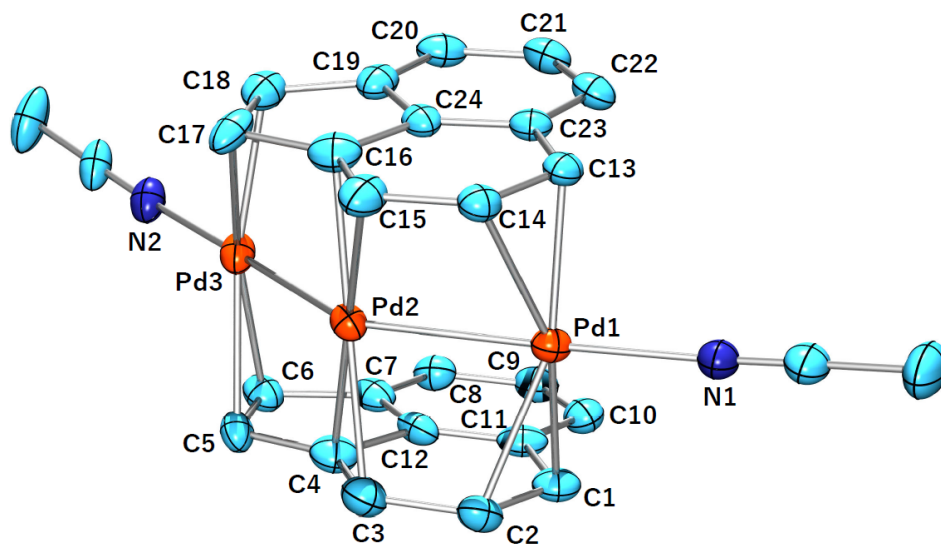


Figure S12. ORTEP of complex 1.

Table S5. Selected bond distances (Å) and angles (°).

Pd1–Pd2	2.5968(7)	C6–C7	1.489(10)
Pd2–Pd3	2.6693(7)	C7–C8	1.387(9)
Pd1–N1	2.092(6)	C7–C12	1.376(9)
Pd3–N2	2.089(6)	C8–C9	1.403(10)
Pd1–C1	2.237(6)	C9–C10	1.381(10)
Pd1–C2	2.314(6)	C10–C11	1.418(9)
Pd1–C13	2.215(5)	C11–C12	1.378(10)
Pd1–C14	2.350(6)	C13–C14	1.405(9)
Pd2–C3	2.190(7)	C13–C23	1.454(8)
Pd2–C4	2.129(6)	C14–C15	1.443(10)
Pd2–C15	2.232(7)	C15–C16	1.353(11)
Pd2–C16	2.159(7)	C16–C17	1.502(10)
Pd3–C5	2.331(6)	C16–C24	1.442(10)
Pd3–C6	2.208(6)	C17–C18	1.395(11)
Pd3–C17	2.344(6)	C18–C19	1.473(10)
Pd3–C18	2.200(6)	C19–C20	1.377(10)
C1–C2	1.380(9)	C19–C24	1.409(9)
C1–C11	1.467(9)	C20–C21	1.397(10)
C2–C3	1.475(10)	C21–C22	1.378(10)
C3–C4	1.366(10)	C22–C23	1.403(9)
C4–C5	1.458(10)	C23–C24	1.392(9)
C4–C12	1.482(9)	Pd1–Pd2–Pd3	138.67(2)
C5–C6	1.400(9)		

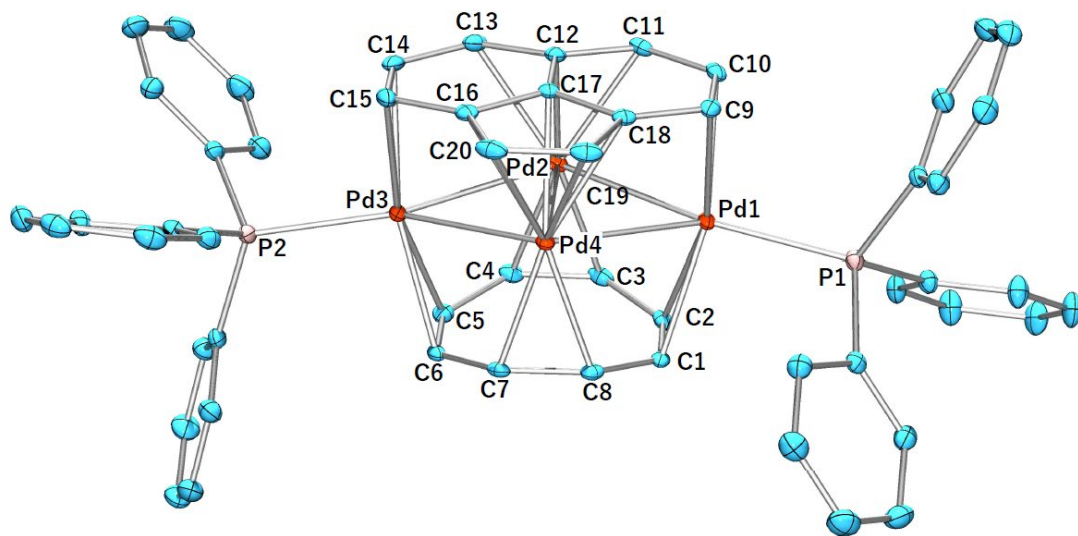


Figure S13. ORTEP of complex 3'.

Table S6. Selected bond distances (Å) and angles (°).

Pd1–Pd2	2.7628(7)	C1–C2	1.405(11)
Pd1–Pd4	2.7853(7)	C2–C3	1.457(11)
Pd2–Pd3	2.7766(7)	C3–C4	1.413(10)
Pd2–Pd4	2.9131(7)	C4–C5	1.454(10)
Pd3–Pd4	2.7921(7)	C5–C6	1.417(11)
Pd1–P1	2.3379(17)	C6–C7	1.427(11)
Pd3–P2	2.3578(18)	C7–C8	1.421(10)
Pd1–C1	2.282(6)	C8–C1	1.433(10)
Pd1–C2	2.205(7)	C9–C10	1.425(11)
Pd1–C9	2.282(7)	C10–C11	1.434(11)
Pd1–C10	2.260(7)	C11–C12	1.425(11)
Pd2–C3	2.189(7)	C12–C13	1.416(11)
Pd2–C4	2.147(7)	C12–C17	1.426(11)
Pd2–C11	2.356(7)	C13–C14	1.425(11)
Pd2–C12	2.118(7)	C14–C15	1.413(12)
Pd2–C13	2.327(7)	C15–C16	1.426(11)
Pd3–C5	2.242(7)	C16–C17	1.429(10)
Pd3–C6	2.227(7)	C16–C20	1.457(12)
Pd3–C14	2.320(7)	C17–C18	1.431(10)
Pd3–C15	2.290(8)	C18–C19	1.452(11)
Pd4–C7	2.186(6)	C19–C20	1.381(12)
Pd4–C8	2.152(6)	Pd1–Pd2–Pd3	116.41(2)
Pd4–C16	2.324(7)	Pd1–Pd4–Pd3	115.16(2)
Pd4–C17	2.250(7)	Pd2–Pd1–Pd4	63.345(19)
Pd4–C18	2.308(7)	Pd2–Pd3–Pd4	63.084(18)
Pd4–C19	2.472(8)		
Pd4–C20	2.472(8)		

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