Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Materials

Selective Dimerization of a Trinuclear Mixed-Metal Sandwich Complex: Construction of an Axially Chiral Metal Skeleton

Hiroshige Yamaura, Koji Yamamoto, Tetsuro Murahashi*

Department of Chemical Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552, Japan.

Table of Contents

Experimental Section

General Consideration. All manipulations were conducted under a nitrogen atmosphere using standard Schlenk or dry-box technique. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on 400 MHz instruments (JEOL JNM-ECZ400S). The chemical shifts were referenced to the residual resonances of deuterated solvents. Elemental analyses were performed on a PerkinElmer 2400II series CHN analyzer. X-ray crystal data were collected by Rigaku RAXIS-RAPID imaging plate diffractometer. ESI-MS spectra were recorded on Bruker micrOTOF ESI-TOF. Unless specified, all reagents were purchased from commercial suppliers and used without purification. Acetonitrile, nitromethane, dichloromethane, toluene, diethyl ether, CD_3NO_2 and CD_3CN were purified according to the standard procedures. $Pd_2(dba)_3\cdot CHCl_3$,[S1] $Pt_2(dba)_3\cdot CHCl_3$,[S2] $Pt(styrene)_2Cl_2$,[S3] $[C_7H_7][BF_4]$,[S4] $[Pd_2Pt(C_7H_7)_2(CH_3CN)_3][BF_4]_2$ (**2**),[S5] and $[PdPt_2(C_7H_7)_2(CH_3CN)_3][BF_4]_2$ (**3**)[S5] were prepared according to the literature.

Synthesis of $[Pd_2Pt(C_7H_7)_2(Ph\text{-}C{\equiv}C\text{-}Ph)(CH_3CN)_2][BF_4]_2$ (2a): Complex **2** (106.8 mg, 1.20 x 10^{-1} mmol) and diphenylacetylene (214.9 mg, 1.21 mmol) were dissolved in nitromethane. The mixture was stirred for 30 min at room temperature and evaporated *in vacuo*. The resultant solid was dissolved in nitromethane. After filtration, the filtrate was reprecipitated with toluene to afford a red powder of complex **2a** (103.1 mg, 1.01 x 10^{-1} mmol, 84% yield). ^{1}H NMR (400 MHz, CD_3NO_2, 25 °C) δ 7.45 (t, J = 7.4 Hz, 2H, H_2), 7.38 (t, J = 7.4 Hz, 4H, H_3), 7.14 (d, J = 7.4 Hz, 4H, H_4), 4.85 (s, 14H, H_1). $^{13}C\{^{1}H\}$ NMR (100.5 MHz, CD_3NO_2, 25 °C) δ 133.3 (singlet with a ^{195}Pt satellite doublet, $J_{C\text{-}Pt}$ = 46 Hz, C_4) 131.6 (s, C_2), 130.5 (s, C_3), 123.8 (singlet with a ^{195}Pt satellite doublet, $J_{C\text{-}Pt}$ = 38 Hz, C_5), 78.9 (s, C_6), 78.2 (s, C_1).

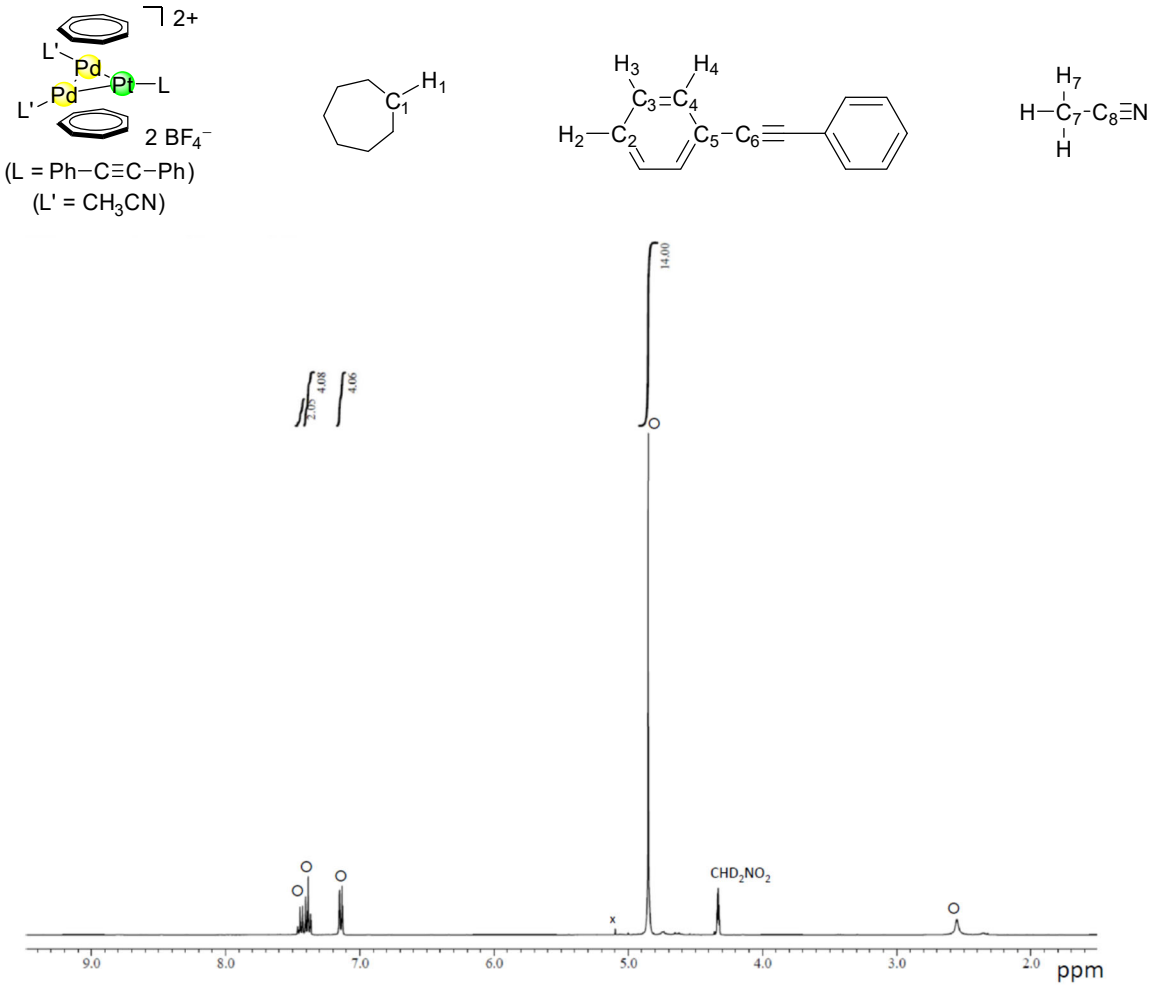
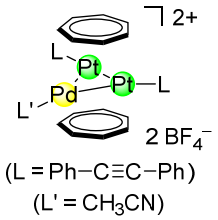
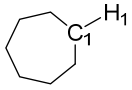
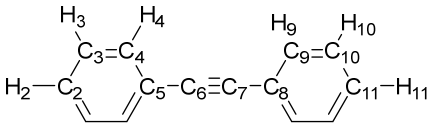


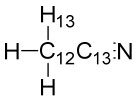
Figure S1. ^{1}H NMR spectrum of complex **2a**. ○ = $[Pd_2Pt(C_7H_7)_2(Ph\text{-}C{\equiv}C\text{-}Ph)(CH_3CN)_2][BF_4]_2$, x = impurities.

Synthesis of $[PdPt_2(C_7H_7)_2(Ph\text{-}C{\equiv}C\text{-}Ph)_2(CH_3CN)][BF_4]_2$ (3a): Complex **3** (112.2 mg, 1.15 x 10^{-1} mmol) and diphenylacetylene (409.9 mg, 2.30 mmol) were dissolved in nitromethane. The mixture was stirred for 30 min at room temperature and evaporated *in vacuo*. The resultant solid was dissolved in nitromethane. After filtration, the filtrate was reprecipitated with toluene to afford a brown powder of complex **3a**. Recrystallization from nitromethane/toluene gave crystals of complex **3a** (116.4 mg, 9.31 x 10^{-2} mmol, 81% yield). ^{1}H NMR (400 MHz, CD_3NO_2, 25 °C) δ 7.56-7.47 (m, 4H, H_2 and H_{11}), 7.43 (m, 8H, H_3 and H_{10}), 7.23 (d, J = 6.8 Hz, 8H, H_4 and H_9), 4.72 (s, 14H, H_1). ^{13}C{^{1}H} NMR (101 MHz, CD_3NO_2, 25 °C) δ 134.2 (s, C_9), 133.1 (s, C_4), 132.1 (s, C_{11}), 131.9 (s, C_2), 130.9 (s, C_3 or C_{10}), 130.5 (s, C_3 or C_{10}), 124.0 (s, C_5 or C_8), 123.9 (s, C_5 or C_8), 79.4 (s, C_6 and C_7), 70.3 (s, C_1).









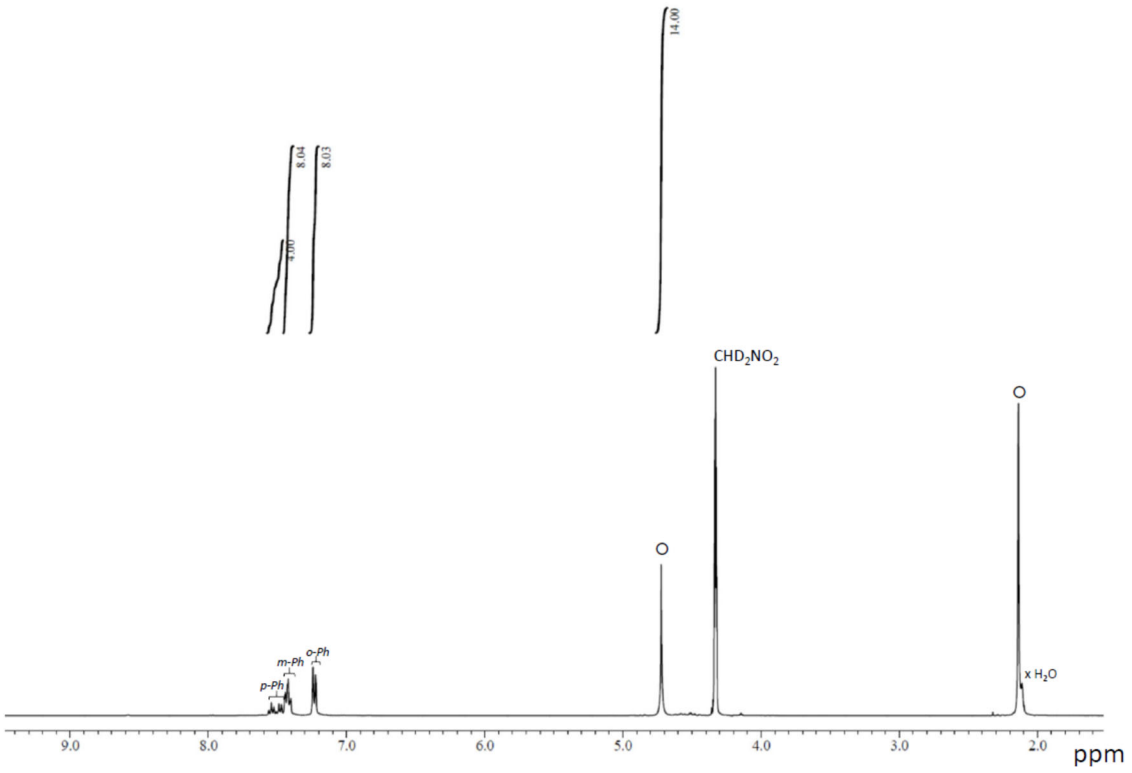


Figure S2. ^{1}H NMR spectrum of complex **3a**. ○ = $[PdPt_2(C_7H_7)_2(Ph\text{-}C{\equiv}C\text{-}Ph)_2(CH_3CN)][BF_4]_2$.

Synthesis of $[Pd_4Pt_2(C_7H_7)_4(CH_3CN)_4][BF_4]_2$ (4): To an acetonitrile solution of $[Pd_2Pt(C_7H_7)_2(CH_3CN)_3][BF_4]_2$ (**2**) (315.8 mg, 3.56 x 10^{-1} mmol) was added Cp_2Co (69.6 mg, 3.68 x10^{-1} mmol), and stirred for 3 h at room temperature. The reaction mixture was filtered through Celite and toluene was added to the filtrate to give a dark purple solid. The precipitate was dissolved in acetonitrile and reprecipitated by toluene four times to afford a dark purple powder of complex **4**. Recrystallization from acetonitrile/diethyl ether gave crystals of complex **4** (201.7 mg, 1.33 mmol, 75% yield). ^{1}H NMR (400 MHz, CD_3CN, 25 °C) δ 3.85 (singlet with a ^{195}Pt satellite doublet, $J_{H\text{-}Pt}$ = 8.8 Hz, 28H, H_1). $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3CN, 25 °C) δ 64.6 (singlet with a ^{195}Pt satellite doublet, $J_{C\text{-}Pt}$ = 12 Hz, C_1). Anal. Calcd. for $C_{36}H_{40}B_2F_8N_4Pd_4Pt_2$: C, 28.48; H, 2.66; N, 3.69.

Found: C, 28.47; H, 2.65; N, 3.91.

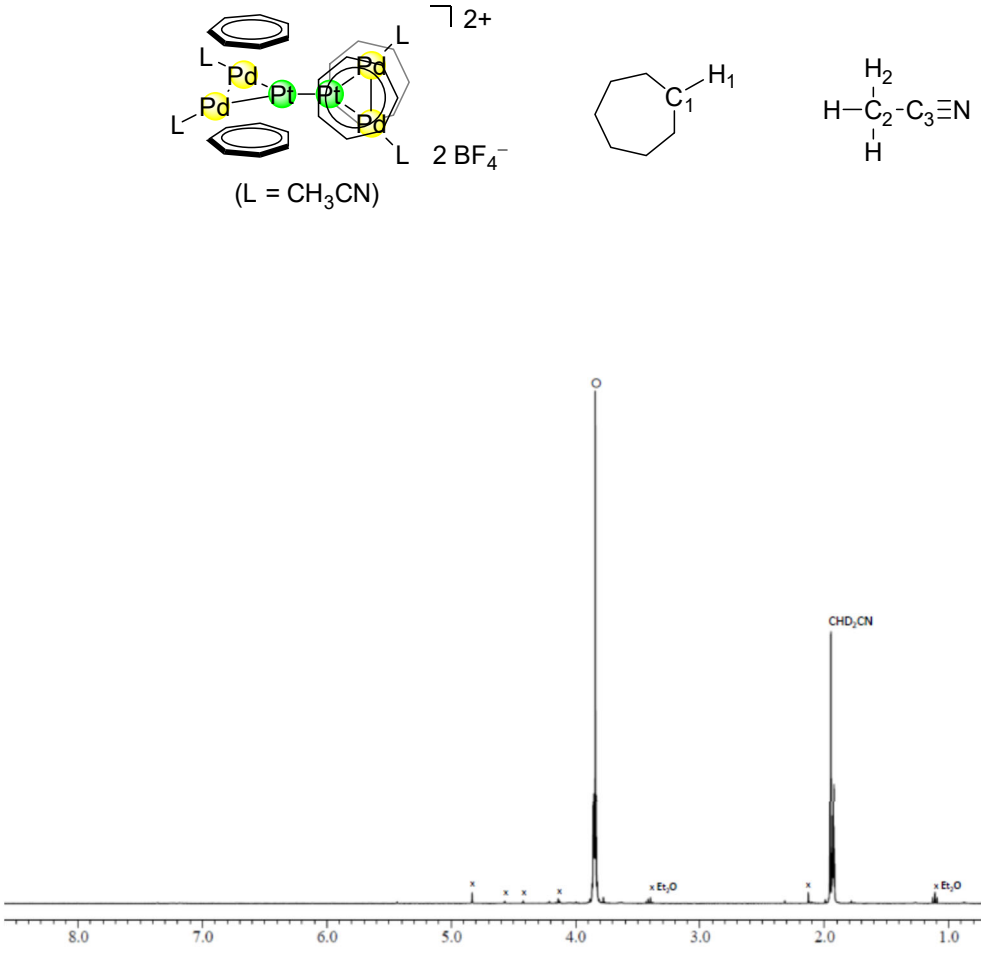
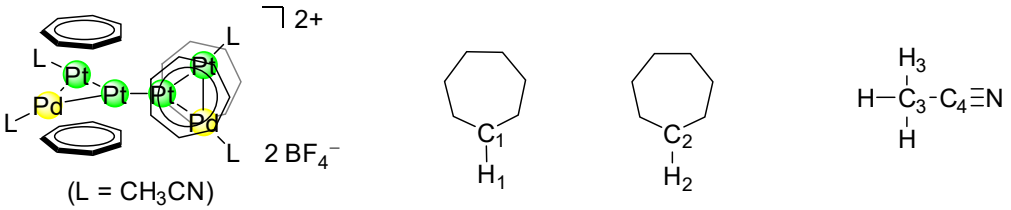


Figure S3. ^{1}H NMR spectrum of complex **4**. ○ = $[Pd_4Pt_2(C_7H_7)_4(CH_3CN)_4][BF_4]_2$, x = impurities.

Synthesis of $[Pd_2Pt_4(C_7H_7)_4(CH_3CN)_4][BF_4]_2$ (5): To an acetonitrile solution of $[PdPt_2(C_7H_7)_2(CH_3CN)_3][BF_4]_2$ (**3**) (131.0 mg, 1.34 x 10^{-1} mmol) was added Cp_2Co (28.4 mg, 1.50 x 10^{-1} mmol), and stirred for 72 h at room temperature. The reaction mixture was filtered through Celite, and toluene was added toluene to the filtrate to give a dark brown solid. The precipitate was dissolved in acetonitrile and reprecipitated with toluene

three times to afford a dark brown powder of complex **5** (51.7 mg, 3.05 x 10^{-2} mmol, 46% yield). ^{1}H NMR (400 MHz, CD_3CN, 25 °C) δ 3.95 (s, 14H, H_1), 3.74 (s, 14H, H_2), 1.95 (s, 12H, H_2). $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3CN, 25 °C) δ 118.3 (s, C_4), 58.4 (singlet with a ^{195}Pt satellite doublet, $J_{C\text{-}Pt}$ = 15 Hz, C_2), 57.9 (singlet with a ^{195}Pt satellite doublet, $J_{C\text{-}Pt}$ = 16 Hz, C_1), 1.32 (s, C_3). Anal. Calcd. for $C_{36}H_{40}B_2F_8N_4Pd_2Pt_4$: C, 25.50; H, 2.38; N, 3.30. Found: C, 25.89; H, 2.45; N, 3.41.



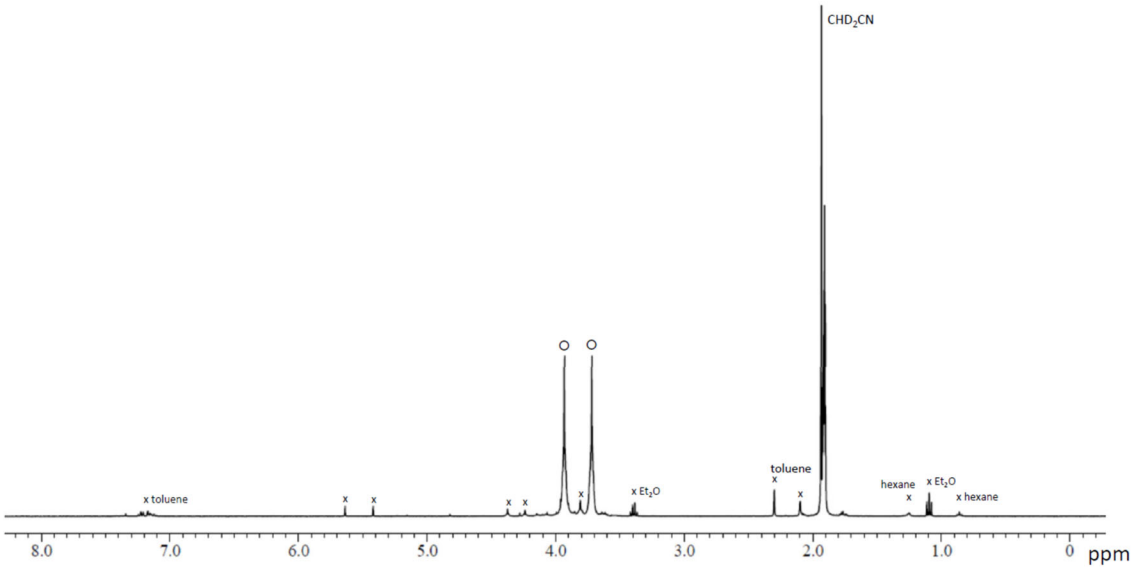
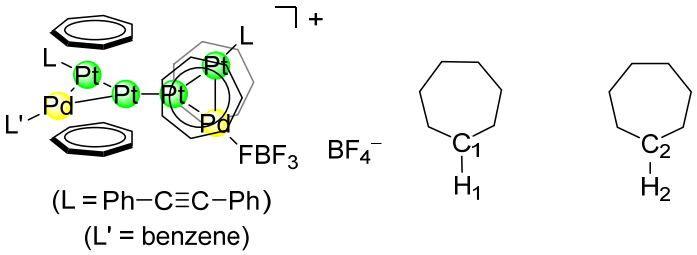


Figure S4. ^{1}H NMR spectrum of complex **5**. ○ = $[Pd_2Pt_4(C_7H_7)_4(CH_3CN)_4][BF_4]_2$, x = impurities.

Synthesis of $[Pd_2Pt_4(C_7H_7)_4(Ph\text{-}C{\equiv}C\text{-}Ph)_2(CH_3CN)_2][BF_4]_2$ (5a): Complex **5** (55.3 mg, 3.26 x 10^{-2} mmol) and diphenylacetylene (31.3 mg, 0.176 mmol) were dissolved in nitromethane. The mixture was stirred for 1 h at room temperature and evaporated *in vacuo*. The resultant solid was dissolved in nitromethane. After filtration, toluene was added to the filtrate to give a dark green precipitate. The precipitate was washed with toluene to afford a dark green powder of complex **5a** (40.4 mg, 2.05 x 10^{-2} mmol, 63% yield). Recrystallization from nitromethane/benzene gave crystals of complex **5a'**. ^{1}H NMR (400 MHz, CD_3CN, 25 °C) δ 7.55 (m, 4H, *o*–Ph), 7.47 (m, 6H, *m*–Ph and *p*–Ph), 7.37 (s, 6H, benzene), 7.36 (s, 6H, *m*–Ph and *p*–Ph), 7.06 (m, 4H, *o*–Ph), 4.31 (s, 14H, H_1), 4.26 (s, 14H, H_2). $^{13}C\{^{1}H\}$ NMR (100.5 MHz, CD_3NO_2, 25 °C) δ 134.4 (s, *o*–Ph), 133.6 (s, *o*–Ph), 130.8 (s, *p*–Ph), 130.6 (s, *p*–Ph), 130.2 (s, *m*–Ph), 130.1 (s, *m*–Ph), 129.7 (s, benzene), 126.6 (s, *ipso*-Ph), 126.2 (s, *ipso*-Ph), 82.3(s, C≡C), 61.9 (s, C_2), 61.2 (s, C_1). Anal. Calcd. for $C_{62}H_{54}B_2F_8Pd_2Pt_4{\cdot}C_6H_6$: C, 39.96; H, 2.96. Found: C, 39.57; H, 2.59.



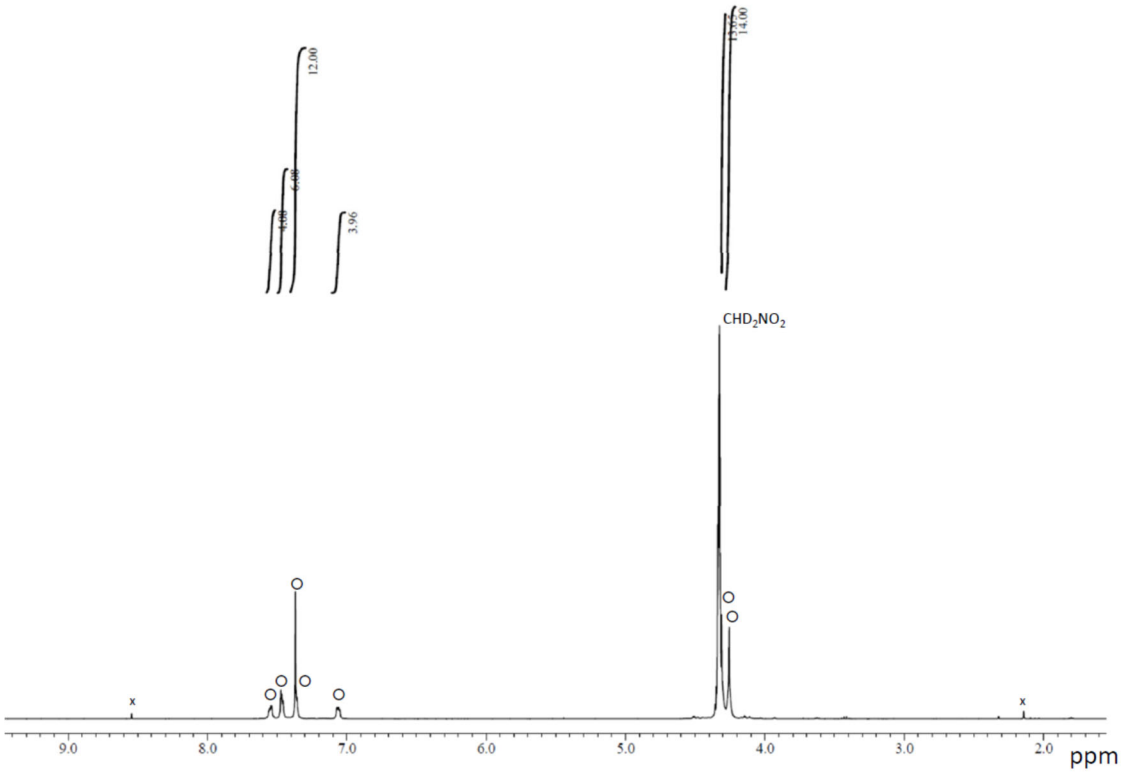


Figure S5. ^{1}H NMR spectrum of complex **5a'**. ○ = $[Pd_2Pt_4(C_7H_7)_4(Ph\text{-}C{\equiv}C\text{-}Ph)_2(CH_3CN)_2][BF_4]_2$, x = impurities.

Generation of $[Pd_2Pt_4(C_7H_7)_4(PMe_2Ph)_4][BF_4]_2$ (5b): To a CD_3CN solution of complex **5** (7.8 mg, 8.0 x 10^{-3} mmol) was added PMe_2Ph_2 (4.6 μL, 3.2 x 10^{-4} mmol) at ambient temperature. Reaction mixture was monitored by NMR measurement.

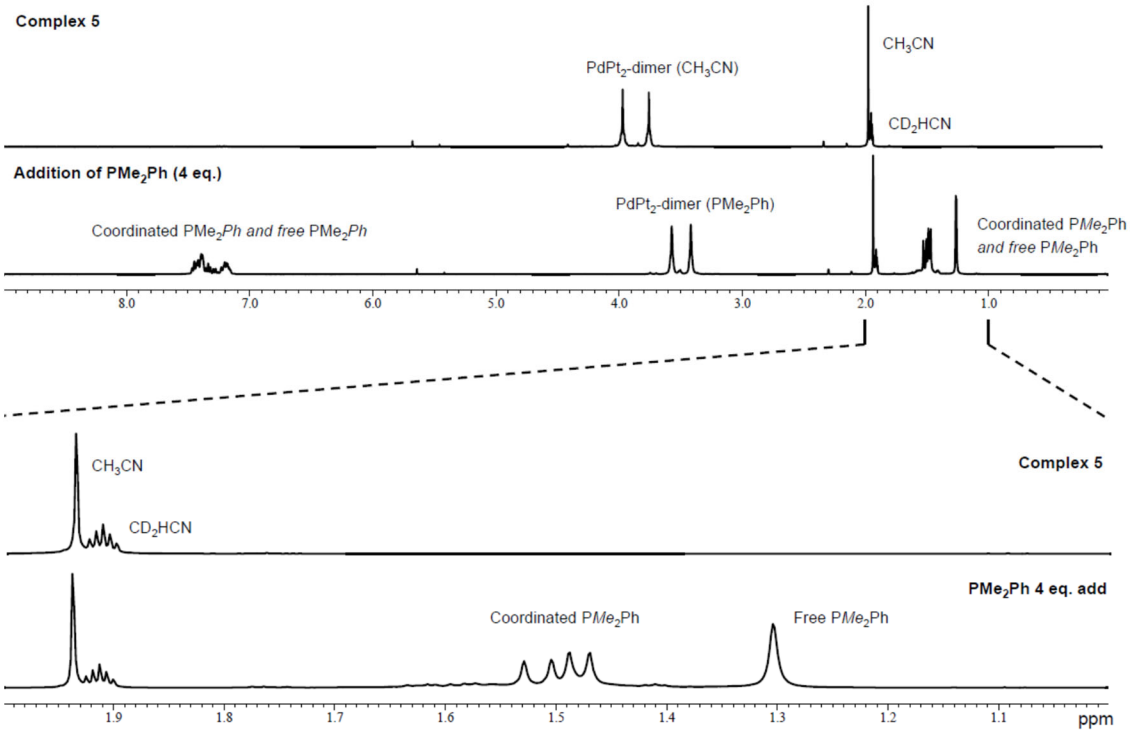


Figure S6. ^1H NMR spectrum of complex **5b**.

Electrochemical Measurements: The cyclic voltammograms were obtained by ALS 600A electrochemical analyzer. The cell was placed in a grove box under an atmosphere of N_2. A 1.6 mm diameter Pt working electrode, Pt wire counter electrode, and Ag/Ag^+ reference electrode were used. The electrochemical measurement was made in CH_3CN with 1.0 mM of complex **2** or **3** and [*n*-Bu_4N][BF_4] (0.1 M). A scan rate is 0.1 V s^{-1}.

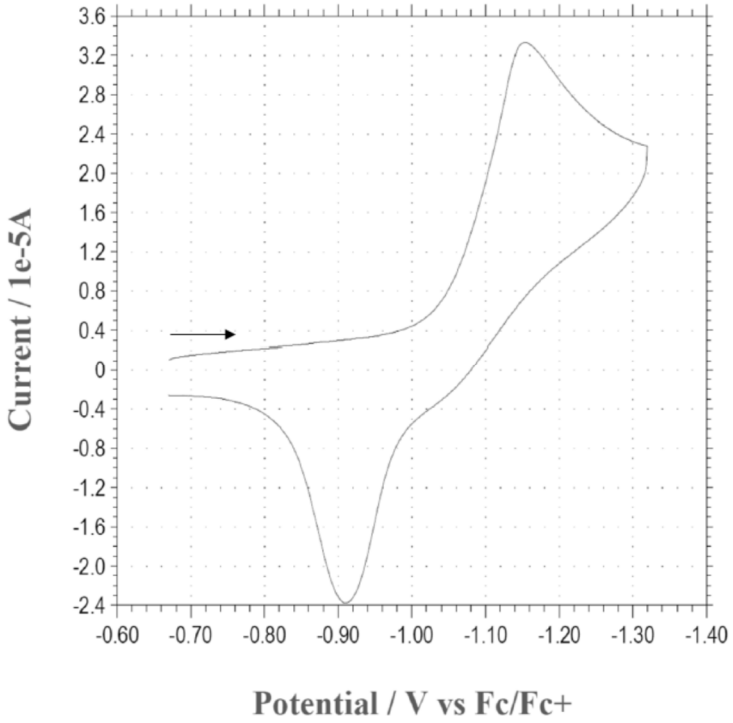


Figure S7. The cyclic voltammogram of $[Pd_2Pt(C_7H_7)_2(CH_3CN)_3][BF_4]_2$ (**2**) in CH_3CN. An arrow indicates sweep direction.

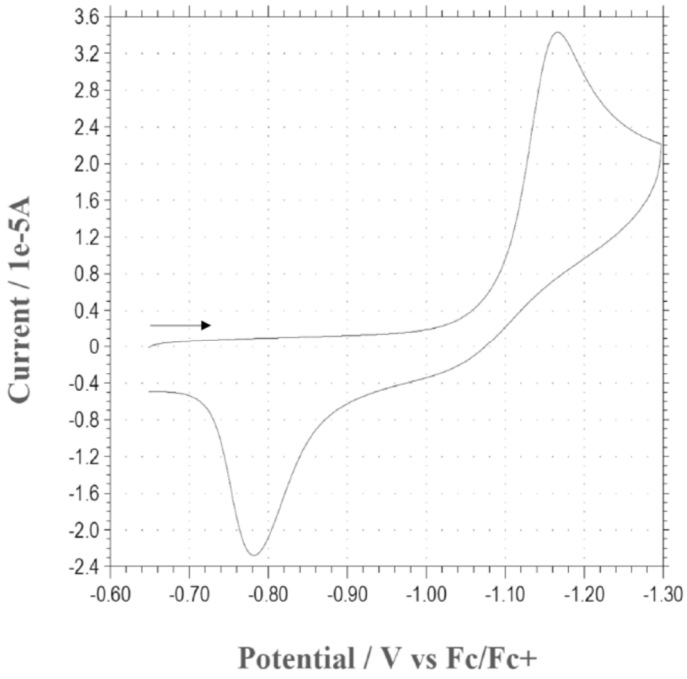


Figure S8. The cyclic voltammogram of $[PdPt_2(C_7H_7)_2(CH_3CN)_3][BF_4]_2$ (**3**) in CH_3CN. An arrow indicates sweep direction.

Computational Details: All calculations were carried out with Gaussian09 program package (Revision D.01).[S6] Geometrical optimization was performed with DFT method using the M06 functional.[S7] Core electrons of Pd and Pt were replaced with Stuttgart-Dresden-Bonn relativistic effect core potentials (ECPs) and their valence electrons were represented by (8s7p6d)/[6s5p3d] basis set.[S8] Usual 6-311G(d) basis sets were used for other atoms.[S9] The optimized structures of $[(\mu_3\text{-}C_7H_7)_2(HCN)_2PdPtPt–PtPdPt(\mu_3\text{-}C_7H_7)_2(HCN)_2]^{2+}$ (**5''-PtPt**) and $[(\mu_3\text{-}C_7H_7)_2(HCN)_2Pt_2Pd–PdPt_2(\mu_3\text{-}C_7H_7)_2(HCN)_2]^{2+}$ (**5''-PdPd**) were depicted in Figures S9 and S10. Cartesian coordinates of the optimized geometries of **5''-PtPt** and **5''-PdPd** were shown in Tables S1 and S2. The Gibbs energies (298.15 K, 1 atm) of **5''-PtPt** and **5''-PdPd** were summarized in Table S3.

Table S1. Cartesian coordinates (in Å) of the optimized geometry of [(μ_3-C_7H_7)$_2$(HCN)$_2$PdPtPt–PtPdPt(μ_3-C_7H_7)$_2$(HCN)$_2$]$^{2+}$ (**5''-PtPt**).

Symbol	X	Y	Z
Pd	-3.7558380	-1.2345824	1.0809715
Pd	3.7525087	1.1019167	1.2167628
N	-5.5264038	2.1088610	-1.8338108
N	-4.6896909	-2.7924452	2.4591708
N	5.5400086	-1.8799357	-2.0527974
N	4.6664347	2.4935060	2.7734794
C	-4.4757305	-0.9785823	-1.9341837
C	-4.4591744	-2.0302620	-0.9798887
C	-3.3344807	-2.7751960	-0.5030157
C	-1.9823501	-2.5699530	-0.7634054
C	-1.3382000	-1.5759480	-1.5545984
C	-1.9651970	-0.5295113	-2.2967442
C	-3.3556656	-0.2900554	-2.5116148
C	-4.3987173	1.8198662	1.2120331
C	-4.4111455	0.7419418	2.1343593
C	-3.2995538	0.1371185	2.8012467
C	-1.9404281	0.3605551	2.6081250
C	-1.2688565	1.2374625	1.7049330
C	-1.8777505	2.1332143	0.7730597
C	-3.2627922	2.4297794	0.5819835
C	3.2849659	-2.4811355	0.3015349
C	1.8965648	-2.2183182	0.5119615
C	1.2730533	-1.4440543	1.5378576
C	1.9298555	-0.6744304	2.5426622
C	3.2848964	-0.4579936	2.7704774
C	4.4074700	-0.9697736	2.0461487
C	4.4107348	-1.9345111	1.0052255
C	3.3466531	0.5700835	-2.4604188
C	1.9568706	0.7858844	-2.2138479
C	1.3346956	1.7456616	-1.3579996
C	1.9853410	2.6410746	-0.4608169
C	3.3388436	2.8111504	-0.1847875
C	4.4600194	2.1247599	-0.7490685
C	4.4707357	1.1901410	-1.8176848
C	-6.2663239	2.7714185	-2.4048408
C	-5.2759355	-3.5282789	3.1136607
C	6.2977713	-2.4659418	-2.6812143
C	5.2384203	3.1594240	3.5102946
H	-5.4364180	-0.8069439	-2.4176245
H	-5.4312407	-2.4723980	-0.7681875
H	-3.5723895	-3.6941176	0.0302724
H	-1.3103830	-3.2999198	-0.3112255

H	-0.2947942	-1.7680152	-1.7968103
H	-1.3036064	0.0193891	-2.9662581
H	-3.5851884	0.3396937	-3.3695104
H	-5.3406818	2.3575925	1.1135480
H	-5.3875840	0.5063907	2.5537420
H	-3.5524613	-0.4948245	3.6511030
H	-1.2853673	-0.2095411	3.2673923
H	-0.2168107	1.4195528	1.9176150
H	-1.1993453	2.8528695	0.3169616
H	-3.4622245	3.3684696	0.0675471
H	3.4977725	-3.3540444	-0.3133132
H	1.2265952	-2.8794899	-0.0363367
H	0.2209054	-1.6584978	1.7180266
H	1.2646705	-0.1961899	3.2618692
H	3.5239047	0.0758354	3.6888696
H	5.3789272	-0.7774043	2.4980742
H	5.3589184	-2.4477950	0.8515342
H	3.5700033	0.0392667	-3.3845117
H	1.2923909	0.3195008	-2.9403845
H	0.2948522	1.9749472	-1.5825041
H	1.3179657	3.3164856	0.0750909
H	3.5821158	3.6631784	0.4478962
H	5.4337421	2.5361680	-0.4890140
H	5.4286151	1.0738355	-2.3226793
H	5.7775257	3.7825905	4.1989253
H	-6.9599144	3.3911829	-2.9414814
H	-5.8287138	-4.2156890	3.7260982
H	7.0082863	-3.0155398	-3.2696856
Pt	-1.3817973	0.0991359	-0.1530092
Pt	-4.0922918	0.8246197	-0.7267321
Pt	1.3805090	-0.0830910	-0.1671458
Pt	4.0959275	-0.7325538	-0.8156991

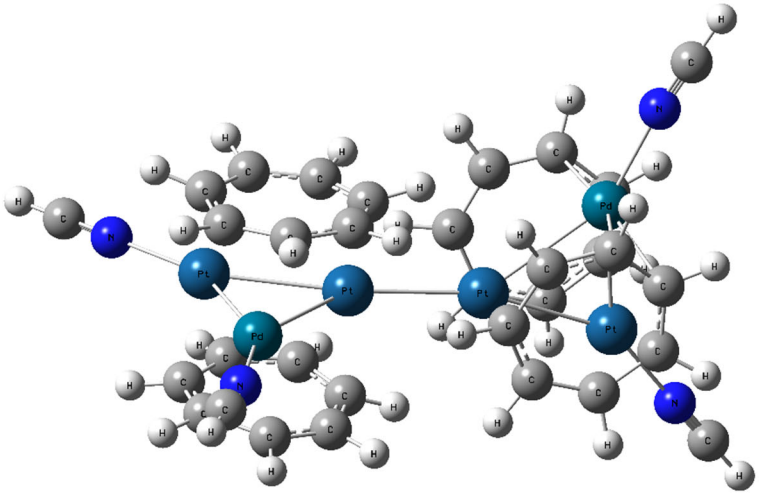


Figure S9. The optimized geometry of $[(\mu_3\text{-}C_7H_7)_2(HCN)_2PdPtPt–PtPdPt(\mu_3\text{-}C_7H_7)_2(HCN)_2]^{2+}$ (**5''-PtPt**).

Table S2. Cartesian coordinates (in Å) of the optimized geometry of $[(\mu_3\text{-}C_7H_7)_2(HCN)_2Pt_2Pd–PdPt_2(\mu_3\text{-}C_7H_7)_2(HCN)_2]^{2+}$ (**5''-PdPd**).

Symbol	X	Y	Z
N	5.2250750	-2.3043070	2.1539690
N	4.5920310	2.5026150	-2.4739510
N	-4.5958510	-2.4798750	-2.4946570
N	-5.2238090	2.2854740	2.1748870
C	4.3433540	-1.9658580	-1.0211500
C	4.3351240	-0.9180160	-2.0038110
C	3.1870950	-0.3626400	-2.6711710
C	1.8283570	-0.5847130	-2.4210280
C	1.1899760	-1.4414220	-1.4907440
C	1.8295030	-2.3089200	-0.5663650
C	3.2080890	-2.5896870	-0.3995150
C	4.5000360	0.9113250	1.9531120
C	4.4884160	1.9279930	0.9373140
C	3.3510080	2.6726220	0.4653870
C	1.9951870	2.4957080	0.7654410
C	1.3581000	1.5809430	1.6378850
C	1.9883320	0.5873410	2.4331650
C	3.3688270	0.3312260	2.6236450
C	-3.1838900	0.3847010	-2.6658310
C	-1.8253190	0.6062620	-2.4121400

C	-1.1889400	1.4575140	-1.4757970
C	-1.8307230	2.3169150	-0.5453490
C	-3.2095080	2.5943950	-0.3775530
C	-4.3436640	1.9740720	-1.0047550
C	-4.3331720	0.9348040	-1.9964050
C	-3.3534190	-2.6774170	0.4423040
C	-1.9972960	-2.5039050	0.7422080
C	-1.3582600	-1.5971820	1.6219090
C	-1.9864500	-0.6095760	2.4260420
C	-3.3668660	-0.3537620	2.6200680
C	-4.4990170	-0.9275960	1.9459390
C	-4.4895680	-1.9354930	0.9213870
C	5.8884330	-2.9823100	2.7962530
C	5.0870040	3.2352720	-3.2025620
C	-5.0934340	-3.2048390	-3.2291640
C	-5.8870880	2.9586010	2.8223500
H	5.2829600	-2.5099650	-0.9370050
H	5.2856150	-0.7618740	-2.5108630
H	3.4026840	0.2122450	-3.5702670
H	1.1550100	-0.0310080	-3.0767510
H	0.1192040	-1.5886920	-1.6289080
H	1.1652300	-2.9793530	-0.0221040
H	3.4255790	-3.5006010	0.1559700
H	5.4623240	0.7602670	2.4402230
H	5.4553890	2.3898340	0.7459030
H	3.5841170	3.5769680	-0.0942660
H	1.3288060	3.2075890	0.2773500
H	0.3095610	1.7793550	1.8553750
H	1.3298970	0.0619800	3.1247750
H	3.6056800	-0.2670900	3.5019920
H	-3.3975130	-0.1829370	-3.5699730
H	-1.1507570	0.0578290	-3.0710380
H	-0.1181230	1.6068080	-1.6116610
H	-1.1679820	2.9830140	0.0059830
H	-3.4286330	3.5001130	0.1857550
H	-5.2840050	2.5162970	-0.9167890
H	-5.2827780	0.7824630	-2.5063080
H	-3.5878470	-3.5766420	-0.1250050
H	-1.3319920	-3.2122240	0.2475290
H	-0.3096480	-1.7985160	1.8364880
H	-1.3269810	-0.0909650	3.1217860
H	-3.6024020	0.2368110	3.5039930
H	-5.4607170	-0.7798580	2.4352640
H	-5.4572940	-2.3943450	0.7267500
H	-6.5108710	3.5875310	3.4291680

H	6.5126090	-3.6160490	3.3976470
H	5.5526310	3.9212880	-3.8850550
H	-5.5606800	-3.8837320	-3.9176490
Pt	4.0415470	-0.9371310	0.8826440
Pt	-3.8228230	-1.0000040	-0.9977640
Pt	3.8225410	1.0086940	-0.9893340
Pt	-4.0409270	0.9297830	0.8910280
Pd	-1.3622490	0.1195040	0.2556810
Pd	1.3620550	-0.1233440	0.2562930

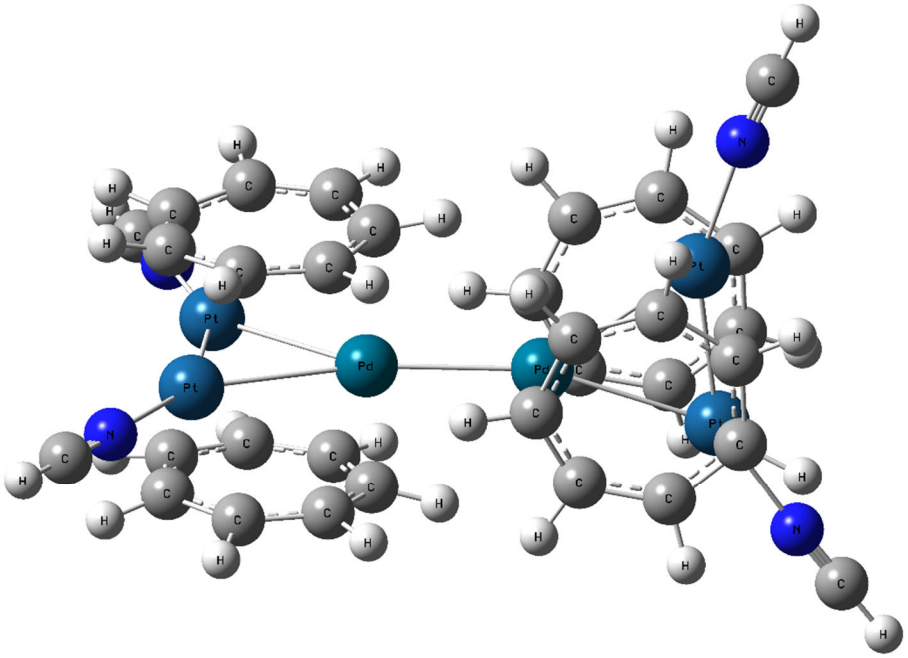


Figure S10. The optimized geometry of $[(\mu_3\text{-}C_7H_7)_2(HCN)_2Pt_2Pd–PdPt_2(\mu_3\text{-}C_7H_7)_2(HCN)_2]^{2+}$ (**5''-PdPd**).

Table S3. The summary of Gibbs energies of **5''-PtPt** and **5''-PdPd**.

Model Complex	Sum of electronic and thermal Free Energies (Hartree/Particle)	ΔG (298.15 K, 1 atm) (kcal/mol)
Complex **5''-PtPt**	-2189.261648	-
Complex **5''-PdPd**	-2189.243546	11.4

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 nitrogen stream at 123(2), 143(2) or 153(2) K. All measurements were performed on a R-AXIS RAPID imaging plate with graphite-monochromated Mo-Kα (0.71075 Å) radiation. The structure was solved by direct method (SIR 92[S10] or SIR97[S11]) and refined on F^2 by full-matrix least-squares methods; using SHELXL 97, 2014/1 or 2018/3.[S12] 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 $[\Sigma w(Fo^2 - Fc^2)^2]$ ($w = 1 / [\sigma^2 (Fo^2) + (aP)^2 + bP]$), where $P = (\mathrm{Max}(Fo^2,0) + 2Fc^2) / 3$ with $\sigma^2(Fo^2)$ from counting statistics. The function $R1$ and $wR2$ were $(\Sigma||Fo| - |Fc||) / \Sigma|Fo|$ and $[\Sigma w(Fo^2 - Fc^2)^2 / \Sigma(wFo^4)]^{1/2}$, respectively. The ORTEP-3 program was used to draw the molecule.[S13] Crystal data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Database Center: CCDC 2094329 (**2a'**), CCDC 2094330 (**3a'**), CCDC 2094331 (**4**), and CCDC 2094332 (**5a'**).

X-ray Crystallographic Data

Crystal data for **2a'**: $C_{30}H_{27}B_2F_8NPd_2Pt$, M_r = 983.05, *monoclinic*, space group $P2_1$ (no. 4). a = 9.0000(17) Å, b = 11.736(2) Å, c = 14.406(3) Å, β = 90.775(4)º, Z = 2, V = 1521.5(5) Å^3, F(000) = 932, D_c = 2.146 g cm^{-3}, μ(MoKα) = 58.093 cm^{-1}, T = 153 K, 22815 reflections collected, 6885 unique (R_{int} = 0.1127), 397 variables refined with 5156 reflections with $I > 2\sigma(I)$ to R = 0.0879. CCDC 2094329.

Crystal data for **3a'**: $C_{42}H_{36}B_2F_8OPdPt_2$, M_r = 1226.91, *triclinic*, space group P-1 (no. 2). a = 10.2863(3) Å, b = 10.8987(4) Å, c = 17.5682(5) Å, α = 104.1710(9)º, β = 103.2030(9)º, γ = 92.3928(11)º, Z = 2, V = 1849.13(10) Å^3, F(000) = 1160, D_c = 2.204 g cm^{-3}, μ(MoKα) = 81.04 cm^{-1}, T = 153 K, 35926 reflections collected, 6957 unique (R_{int} = 0.0947), 506 variables refined with 6296 reflections with $I > 2\sigma(I)$ to R = 0.0501. CCDC 2094330.

Crystal data for **4**: $C_{36}H_{40}B_2F_8N_4Pd_4Pt_2$, M_r = 1518.12, *triclinic*, space group P-1 (no. 2). a = 11.4221(4) Å, b = 13.8137(4) Å, c = 14.3901(4) Å, α = 83.8592(8)º, β = 76.9542(9)º, γ = 71.2097(9)º, Z = 2, V = 2092.55(11) Å^3, F(000) = 1412, D_c = 2.409 g cm^{-3}, μ(MoKα) = 84.09 cm^{-1}, T = 143 K, 30310 reflections collected, 7365 unique (R_{int} = 0.0893), 509 variables refined with 6878 reflections with $I > 2\sigma(I)$ to R = 0.0388. CCDC 2094331.

Crystal data for **5a'**: $C_{71}H_{63}B_2F_8Pd_2Pt_4$, M_r = 2083.05, *triclinic*, space group P-1 (no. 2). a = 12.7384(3) Å, b = 15.0444(4) Å, c = 16.3890(4) Å, α = 89.1192(7)º, β = 80.0982(7)º, γ = 75.3532(7)º, Z = 2, V = 2992.19(12) Å^3, F(000) = 1950, D_c = 2.312 g cm^{-3}, μ(MoKα) = 99.36 cm^{-1}, T = 123 K, 71514 reflections collected, 13682 unique (R_{int} = 0.0580), 784

variables refined with 12530 reflections with $I > 2\sigma(I)$ to $R = 0.0257$. CCDC 2094332.

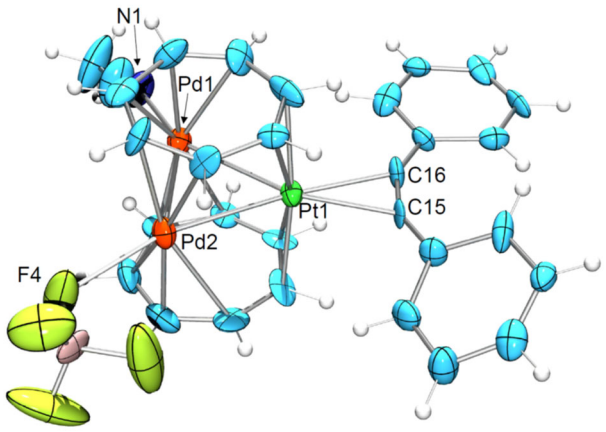


Figure S11. ORTEP of complex **2a'**

Table S4. Selected Bond Distances (Å)

Pd1–Pt1	2.791(2)	Pt1–C16	2.19(2)
Pd2–Pt1	2.714(3)	C15–C16	1.34(4)
Pd1–Pd2	2.750(3)	Pt1–Pd1–Pd2	58.65(7)
Pd1–N1	2.17(3)	Pt1–Pd2–Pd1	61.44(7)
Pd2–F4	2.48(3)	Pd1–Pt1–Pd2	59.91(7)
Pt1–C15	2.20(2)		

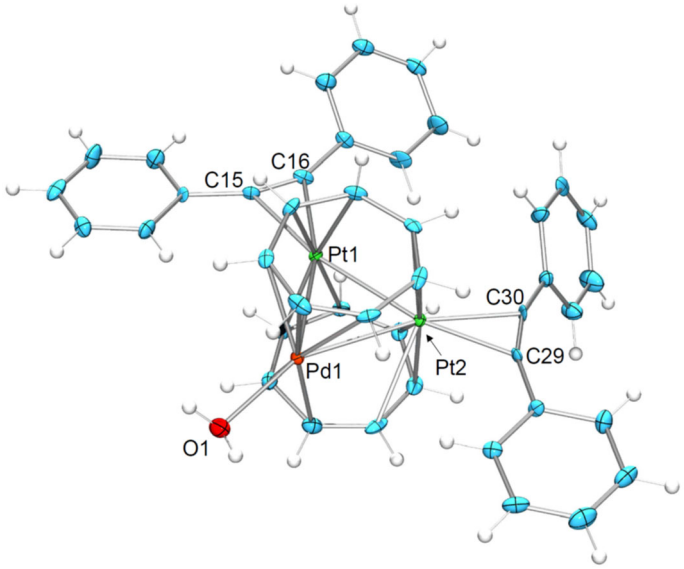


Figure S12. ORTEP of complex **3a'**

Table S5. Selected Bond Distances (Å)

Pd1–Pt1	2.7950(11)	Pt2–C30	2.183(13)
Pd1–Pt2	2.7405(11)	C15–C16	2.130(18)
Pt1–Pt2	2.7691(7)	C29–C30	2.25(2)
Pd1–O1	2.268(11)	Pd1–Pt1–Pt2	59.01(3)
Pt1–C15	2.225(13)	Pd1–Pt2–Pt1	60.96(3)
Pt1–C16	2.222(12)	Pt1–Pd1–Pt2	60.02(2)
Pt2–C29	2.188(13)		

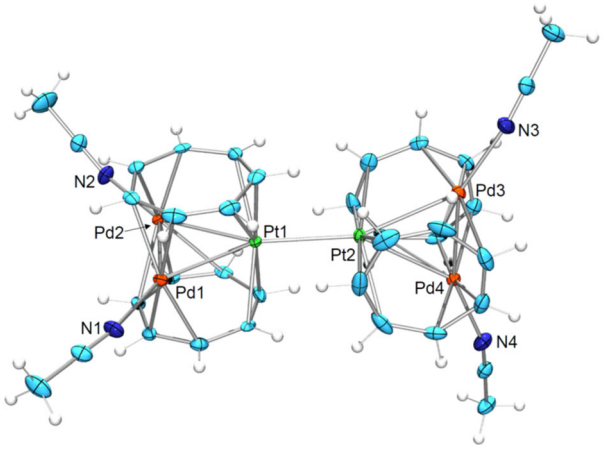


Figure S13. ORTEP of complex **4**

Table S6. Selected Bond Distances (Å)

Pd1–Pd2	2.7034(7)	Pd3–N3	2.194(6)
Pd1–Pt1	2.7931(6)	Pd4–N4	2.203(6)
Pd2–Pt1	2.8132(5)	Pt1–Pd1–Pd2	61.544(16)
Pd3–Pd4	2.6850(7)	Pt1–Pd2–Pd1	60.797(15)
Pd3–Pt2	2.7984(5)	Pd1–Pt1–Pd2	57.659(15)
Pd4–Pt2	2.8449(6)	Pt2–Pd3–Pd4	62.466(16)
Pt1–Pt2	2.6793(3)	Pt2–Pd4–Pd3	60.721(16)
Pd1–N1	2.167(7)	Pd3–Pt2–Pd4	56.813(16)
Pd2–N2	2.227(6)		

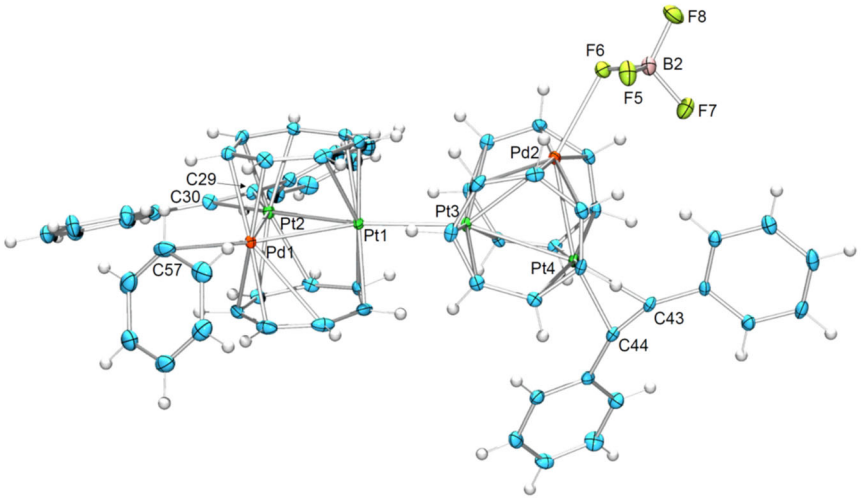


Figure S14. ORTEP of complex **5a'**

Table S7. Selected Bond Distances (Å)

Pd1–Pt1	2.8540(3)	Pt4–C43	2.167(4)
Pd1–Pt2	2.7324(4)	Pt4–C44	2.163(4)
Pd2–Pt3	2.8325(4)	Pt1–Pd1–Pt2	59.854(8)
Pd2–Pt4	2.6889(4)	Pt1–Pt2–Pd1	62.240(8)
Pt1–Pt2	2.7891(2)	Pd1–Pt1–Pt2	57.906(8)
Pt1–Pt3	2.6935(2)	Pt3–Pd2–Pt4	60.698(8)
Pt3–Pt4	2.7925(2)	Pt3–Pt4–Pd2	62.195(8)
Pd1–C57	2.612(5)	Pd2–Pt3–Pt4	57.107(8)
Pd2–F6	2.457(3)	Pd1–Pt1–Pt3	148.156(9)
Pt2–C29	2.182(4)	Pt1–Pt3–Pt4	160.806(9)
Pt2–C30	2.176(5)		

References

[S1] T. Ukai, H. Kawazura, Y. Ishii, J. K. Bonnet, J. A. Ibers, *J. Organomet. Chem.* **1974**, *65*, 253.

[S2] a) K. Moseley, R. M. Maitlis, *J. Chem. Soc., Dalton Trans.* **1974**, 169. b) W. J. Cherwinski, B. F. G. Johnson, J. Lewis, *J. Chem. Soc., Dalton Trans.* **1974**, 1405. c) H. Tanaka, H. Kawazura, *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2815. d) L. N. Lewis, T. A. Krafft, J. C. Huffman, *Inorg. Chem.* **1992**, *31*, 3555.

[S3] A. Albinati, W. R. Caseri, P. S. Pregosin, *Organometallics* **1987**, *6*, 788.

[S4] K. Conrow, *Org. Syn. Coll.* **1973**, *5*, 1138.

[S5] T. Murahashi, K. Usui, Y. Tachibana, S. Kimura, *Chem. Eur. J.* **2012**, *18*, 8886.

[S6] Gaussian09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, **2013**.

[S7] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215.

[S8] D. Andrae, U. Häußermann, M. Dolg, H. Stoll, H. Preuß, *Theor. Chim. Acta* **1990**, *77*, 123.

[S9] (a) A. D. Becke, *Phys. Rev.* **1988**, *A38*, 3098. (b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648. (c) S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200. (d) C. Lee, W. Yang, R. G. Parr, *Phys. Rev.* **1988**, *B37*, 785 (e) B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* **1989**, *157*, 200.

[S10] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 435.

[S11] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, G. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999,** *32,* 115-119.

[S12] a) G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112. b) G. M. Sheldrick, *Acta Crystallogr.* **2015**, *C71*, 3-8.

[S13] L. J. Farrugia, *J. Appl. Crystallogr.* **2012**, *45*, 849.