

Supporting Information

Contiguous multiple π -coordination of π -conjugated polyenes: chain-length dependent ^{13}C NMR chemical shifts and bonding nature of polyene-(palladium chain) sandwich clusters

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General Considerations. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques or dry-box technique. ^1H , ^{13}C NMR spectra were recorded on either the 270- (JEOL GSX-270), 400- (JEOL GSX-400, JEOL ECP-400), or 600 MHz (Varian UNITY-INOVA 600) instruments. The chemical shifts were referenced to the residual resonances of deuterated solvents. Elemental analyses were performed in Analytical Center, Faculty of Engineering, Osaka University. Unless specified, all reagents were purchased from commercial suppliers and used without purification. CH_2Cl_2 was distilled from CaH_2 prior to use. 1,10-diphenyl-1,3,5,7,9-decapentaene (**Pen**) and 1,14-diphenyl-1,3,5,7,9,11,13-tetradecaheptaene (**Hep**) were prepared according to the literature method,^{S1} and purified with Soxhlet's extractor prior to use. $\text{Pd}_2(\text{dba})_3$,^{S2} $\text{NaB}(\text{Ar}^{\text{F}})_4$,^{S3} and $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$,^{S4} were prepared according to the literature. $[\text{Pd}_m\{\text{Ph}(\text{CH}=\text{CH})_{m+1}\text{Ph}\}_2][\text{B}(\text{Ar}^{\text{F}})_4]_2$ ($m = 3$, **Pd3Tet**; $m = 5$, **Pd5Hex**) were prepared according to the literature.^{S5}

Synthesis of $[\text{Pd}_4\{\text{Ph}(\text{CH}=\text{CH})_5\text{Ph}\}_2][\text{B}(\text{Ar}^{\text{F}})_4]_2$ (Pd4Pen**):** To a suspension of $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ (343 mg, 0.543 mmol) in CH_2Cl_2 was added 1,10-diphenyl-1,3,5,7,9-decapentaene (**Pen**) (486 mg, 1.71 mmol) and $\text{Pd}_2(\text{dba})_3$ (572 mg, 0.553 mmol). The suspension was stirred overnight at room temperature. To the resultant orange suspension was added $\text{NaB}(\text{Ar}^{\text{F}})_4$ (962 mg, 1.09 mmol), and the mixture was stirred for 15 min at room temperature. Then, the reaction mixture was filtered and crystallization from CH_2Cl_2 /n-hexane gave orange powders of **Pd4Pen** (1.09 g, 74% yield). mp. 280 °C (decomposed). ^1H NMR (CD_2Cl_2) for meso isomer: $\delta = 7.66$ (br, 16H, $\text{B}(\text{Ar}^{\text{F}})_4$), 7.49 (br s, 8H, $\text{B}(\text{Ar}^{\text{F}})_4$), 7.45 (m, 4H, *p*-Ph), 7.10 (t, $J = 7.8$ Hz, 8H, *m*-Ph), 6.94 (d, $J = 7.2$ Hz, 8H, *o*-Ph), 6.30 (d, $J = 13.5$ Hz, 4H, H_1), 5.30 (dd, $J = 13.8$ Hz, $J = 10.8$ Hz, 4H, H_2), 3.06 (m, 4H, H_3), 3.00 (m, 4H, H_4), 2.82 (m, 4H, H_5). ^1H NMR (CD_2Cl_2) for rac isomer: $\delta = 7.66$ (br, 16H, $\text{B}(\text{Ar}^{\text{F}})_4$), 7.49 (brs, 8H, $\text{B}(\text{Ar}^{\text{F}})_4$), 7.47 (m, 4H, *p*-Ph), 7.31 (t, $J = 7.8$ Hz, 8H, *m*-Ph), 7.12 (d, $J = 7.0$ Hz, 8H, *o*-Ph), 5.71 (dd, $J = 13.6$ Hz, $J = 11.1$ Hz, 4H, H_2), 5.51 (d, $J = 13.6$ Hz, 4H, H_1), 3.13 (m, 4H, H_4), 2.81 (m, 4H, H_5), 2.69 (m, 4H, H_3). $^{13}\text{C}\{^1\text{H}\}$ NMR data are shown in Tables 1 and 2. Anal. Calcd for $\text{Pd}_4\text{C}_{108}\text{H}_{64}\text{B}_2\text{F}_{48}$: C, 47.64; H, 2.37. Found: C, 47.40; H, 2.52.

Synthesis of $[\text{Pd}_6\{\text{Ph}(\text{CH}=\text{CH})_7\text{Ph}\}_2][\text{B}(\text{Ar}^{\text{F}})_4]_2$ (Pd6Hep**):** To a suspension of $[\text{Pd}_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ (155 mg, 0.245 mmol) in CH_2Cl_2 was added 1,14-diphenyl-1,3,5,7,9,11,13-tetradecaheptaene (**Hep**) (228 mg, 0.679 mmol) and $\text{Pd}_2(\text{dba})_3$ (503 mg, 0.486 mmol). The suspension was stirred for 2 days at room temperature. To the resultant orange-brown suspension was added $\text{NaB}(\text{Ar}^{\text{F}})_4$ (435 mg, 0.491 mmol) and the mixture was stirred for 15 min at room temperature. Then, the reaction mixture was filtered and crystallization from $\text{CH}_2\text{Cl}_2/\text{n-hexane}$ gave orange powders of **Pd6Hep** (395 mg, 53% yield). ^1H NMR (CD_2Cl_2) for meso isomer: δ = 7.65 (br, 16H, $\text{B}(\text{Ar}^{\text{F}})_4$), 7.42 (br, 8H, $\text{B}(\text{Ar}^{\text{F}})_4$), 7.35 (m, 4H, *p*-Ph), 7.10 (t, J = 7.8 Hz, 8H, *m*-Ph), 6.99 (d, J = 7.8 Hz, 8H, *o*-Ph), 6.03 (d, J = 13.2 Hz, 4H, H_1), 5.32 (overlap with solvent residual, 4H, H_2), 3.24 (m, 4H, H_4), 3.24 (m, 4H, H_6), 2.84 (m, 4H, H_7), 2.71 (m, 4H, H_3), 2.46 (m, 4H, H_5). ^1H NMR (CD_2Cl_2) for rac isomer: δ = 7.65 (br, 16H, $\text{B}(\text{Ar}^{\text{F}})_4$), 7.42 (br, 8H, $\text{B}(\text{Ar}^{\text{F}})_4$), 7.39 (m, 4H, *p*-Ph), 7.33 (t, J = 7.8 Hz, 8H, *m*-Ph), 7.17 (d, J = 7.8 Hz, 8H, *o*-Ph), 5.58 (dd, J = 13.8 Hz, J = 11.7 Hz, 4H, H_2), 5.18 (d, J = 13.8 Hz, 4H, H_1), 3.18 (m, 4H, H_4), 3.13 (m, 4H, H_6), 3.00 (m, 4H, H_7), 2.61 (m, 4H, H_5), 2.46 (m, 4H, H_3). $^{13}\text{C}\{^1\text{H}\}$ NMR data are shown in Tables 1 and 2. Anal. Calcd for $\text{Pd}_6\text{C}_{116}\text{H}_{72}\text{B}_2\text{F}_{48}$: C, 44.09; H, 2.47. Found: C, 44.30; H, 2.49.

Table S1. Cartesian coordinates (in Å) of the optimized geometry of $[\text{Pd}_3(\text{C}_8\text{H}_{10})_2]^{2+}$.

Symbol	X	Y	Z
C	-0.6104262	-2.0863955	0.3592251
C	0.6115333	-2.0858785	-0.3602578
C	-0.6106269	2.0864074	0.3591695
C	0.6112597	2.0855949	-0.3604030
Pd	-0.0003607	-0.0000517	0.0003947
H	0.5940809	-2.2199604	-1.4451647
H	0.5937634	2.2195934	-1.4453184
H	-0.5930295	2.2218482	1.4439072
H	-0.5929625	-2.2218111	1.4439666
C	-1.8849381	2.0454440	-0.2988301
H	-1.9062003	2.1254246	-1.3891479
C	1.8855417	2.0459274	0.2978045
H	1.9067612	2.1271349	1.3880377
C	-1.8846551	-2.0453561	-0.2989243
H	-1.9057829	-2.1252274	-1.3892474
C	1.8857764	-2.0461289	0.2979784
H	1.9069814	-2.1273321	1.3882131
C	-3.1208254	-2.0884367	0.4198319
H	-3.1114390	-2.2804570	1.4931518
C	3.1218813	-2.0879586	-0.4208861
H	3.1126264	-2.2789237	-1.4944003
C	3.1216151	2.0882182	-0.4210906
H	3.1122232	2.2791950	-1.4946016
C	-3.1210108	2.0884571	0.4200929
H	-3.1115677	2.2806648	1.4933791
Pd	2.7896489	0.0000050	-0.0005428
Pd	-2.7902263	0.0000129	0.0013238
C	-4.2952222	1.6220430	-0.1973611
H	-4.4016923	1.6505579	-1.2812029
C	4.2955219	1.6219914	0.1968761
H	4.4017745	1.6512395	1.2807231
C	4.2956042	-1.6215048	0.1972165
H	4.4017484	-1.6508238	1.2810717
C	-4.2949989	-1.6222790	-0.1979014
H	-4.4012093	-1.6507267	-1.2817704
H	-5.2116356	-1.5651753	0.3808567
H	-5.2117329	1.5647490	0.3815718
H	5.2121994	-1.5627825	-0.3814543
H	5.2120672	1.5634965	-0.3818974

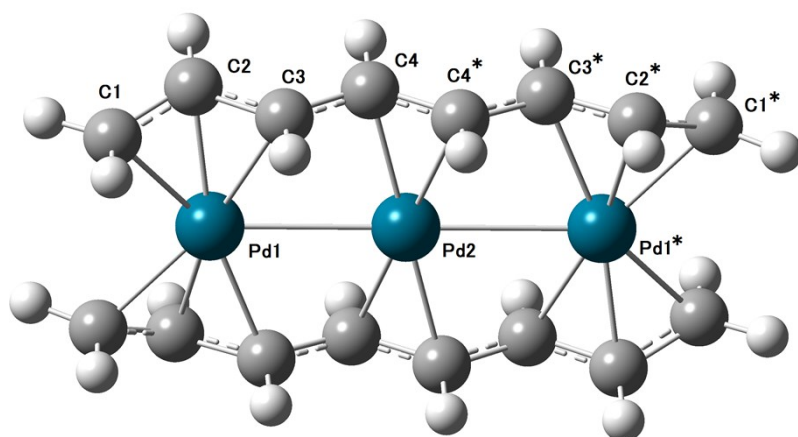


Figure S1. The optimized geometry of $[\text{Pd}_3(\text{C}_8\text{H}_{10})_2]^{2+}$.

Table S2. Selected bond lengths (Å) and angles (°) of $[\text{Pd}_3(\text{C}_8\text{H}_{10})_2]^{2+}$.

Pd1–Pd2	2.790	C1–C2	1.406
Pd1–C1	2.222	C2–C3	1.431
Pd1–C2	2.156	C3–C4	1.435
Pd1–C3	2.257	C4–C4*	1.418
Pd2–C4	2.203	Pd1–Pd2–Pd1	180.0

Table S3. Cartesian coordinates (in Å) of the optimized geometry of $[\text{Pd}_3(\text{C}_6\text{H}_8)_2(\text{py})_2]^{2+}$.

Symbol	X	Y	Z
C	0.3440008	-0.6151947	2.0567973
C	-0.3440008	0.6151947	2.0567973
C	0.3440008	-0.6151947	-2.0567973
C	-0.3440008	0.6151947	-2.0567973
Pd	0.0000000	0.0000000	0.0000000
H	-1.4291761	0.6208693	2.1876251
H	-1.4291761	0.6208693	-2.1876251
H	1.4291761	-0.6208693	-2.1876251
H	1.4291761	-0.6208693	2.1876251
C	-0.3440008	-1.8818934	-2.0742123
H	-1.4302389	-1.8695540	-2.1756228
C	0.3440008	1.8818934	-2.0742123
H	1.4302389	1.8695540	-2.1756228
C	-0.3440008	-1.8818934	2.0742123
H	-1.4302389	-1.8695540	2.1756228
C	0.3440008	1.8818934	2.0742123
H	1.4302389	1.8695540	2.1756228
C	0.3326768	-3.1015167	2.1448715
H	1.4101567	-3.1137512	2.3057061
H	-0.2107752	-3.9975828	2.4270786
C	-0.3326768	3.1015167	2.1448715
H	-1.4101567	3.1137512	2.3057061
H	0.2107752	3.9975828	2.4270786
C	-0.3326768	3.1015167	-2.1448715
H	-1.4101567	3.1137512	-2.3057061
H	0.2107752	3.9975828	-2.4270786
C	0.3326768	-3.1015167	-2.1448715
H	1.4101567	-3.1137512	-2.3057061
H	-0.2107752	-3.9975828	-2.4270786
Pd	-0.0859132	2.8258097	0.0000000
Pd	0.0859132	-2.8258097	0.0000000
C	0.8744220	5.6768127	0.0000000
C	-1.4547105	5.5337108	0.0000000
C	0.8234490	7.0700869	0.0000000
H	1.8202785	5.1435068	0.0000000
C	-1.5743960	6.9225314	0.0000000
H	-2.3279074	4.8887192	0.0000000
C	-0.4192697	7.7088834	0.0000000
H	1.7495390	7.6363945	0.0000000
H	-2.5627628	7.3713821	0.0000000
H	-0.4859876	8.7927440	0.0000000
C	1.4547105	-5.5337108	0.0000000

C	-0.8744220	-5.6768127	0.0000000
C	1.5743960	-6.9225314	0.0000000
H	2.3279074	-4.8887192	0.0000000
C	-0.8234490	-7.0700869	0.0000000
H	-1.8202785	-5.1435068	0.0000000
C	0.4192697	-7.7088834	0.0000000
H	2.5627628	-7.3713821	0.0000000
H	-1.7495390	-7.6363945	0.0000000
H	0.4859876	-8.7927440	0.0000000
N	-0.2482884	4.9187513	0.0000000
N	0.2482884	-4.9187513	0.0000000

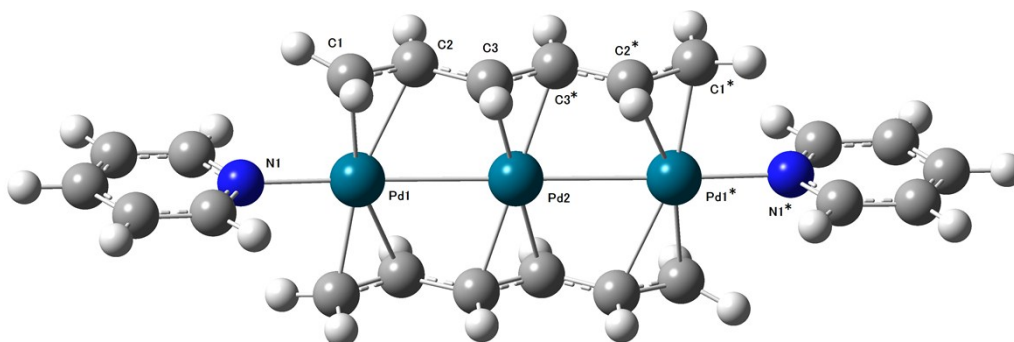


Figure S2. The optimized geometry of $[\text{Pd}_3(\text{C}_6\text{H}_8)_2(\text{py})_2]^{2+}$.

Table S4. Selected bond lengths (Å) and angles (°) of $[\text{Pd}_3(\text{C}_6\text{H}_8)_2(\text{py})_2]^{2+}$.

Pd1–Pd2	2.827	C1–C2	1.397
Pd1–N1	2.099	C2–C3	1.442
Pd1–C1	2.177	C3–C3*	1.410
Pd1–C2	2.319	Pd1–Pd2–Pd1*	180.0
Pd2–C3	2.174	N1–Pd1–Pd2	177.3

Table S5. Cartesian coordinates (in Å) of the optimized geometry of $[\text{Pd}_2(\text{C}_6\text{H}_8)_2]^{2+}$.

Symbol	X	Y	Z
H	-0.8281447	3.2794792	1.6044849
H	0.9347113	3.8317039	1.4516048
C	0.6775342	1.7839388	2.0763817
H	1.7408636	1.6199577	2.2542589
C	-0.2284912	0.6785367	2.0843178
H	-1.3011503	0.8682456	2.1838761
C	0.2284912	-0.6785367	2.0843178
H	1.3011503	-0.8682456	2.1838761
C	-0.6775342	-1.7839388	2.0763817
H	-1.7408636	-1.6199577	2.2542589
C	-0.2284912	-3.0150305	1.5673818
H	0.8281447	-3.2794792	1.6044849
H	-0.9347113	-3.8317039	1.4516048
C	0.2284912	3.0150305	-1.5673818
H	-0.8281447	3.2794792	-1.6044849
H	0.9347113	3.8317039	-1.4516048
C	0.6775342	1.7839388	-2.0763817
H	1.7408636	1.6199577	-2.2542589
C	-0.2284912	0.6785367	-2.0843178
H	-1.3011503	0.8682456	-2.1838761
C	0.2284912	-0.6785367	-2.0843178
H	1.3011503	-0.8682456	-2.1838761
C	-0.6775342	-1.7839388	-2.0763817
H	-1.7408636	-1.6199577	-2.2542589
C	-0.2284912	-3.0150305	-1.5673818
H	0.8281447	-3.2794792	-1.6044849
H	-0.9347113	-3.8317039	-1.4516048
Pd	0.1633514	1.4249824	0.0000000
Pd	-0.1633514	-1.4249824	0.0000000

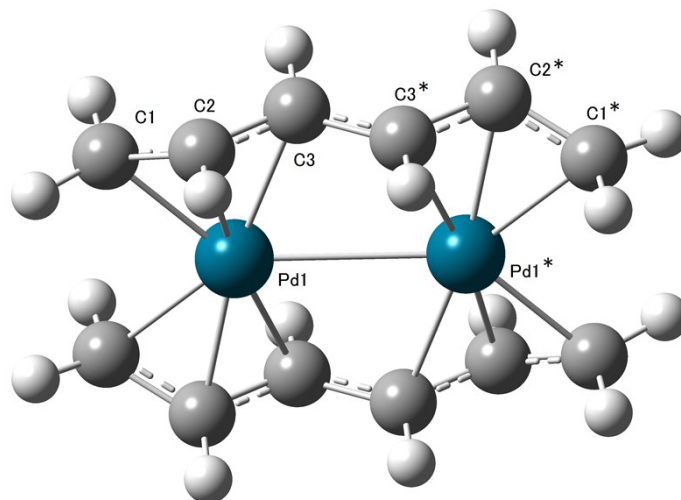


Figure S3. The optimized geometry of $[\text{Pd}_2(\text{C}_6\text{H}_8)_2]^{2+}$.

Table S6. Selected bond lengths (Å) of $[\text{Pd}_2(\text{C}_6\text{H}_8)_2]^{2+}$.

Pd1–Pd1*	2.869	C1–C2	1.406
Pd1–C1	2.234	C2–C3	1.429
Pd1–C2	2.169	C3–C3*	1.432
Pd1–C3	2.248		

Table S7. Cartesian coordinates (in Å) of the optimized geometry of $[\text{Pd}_4(\text{C}_{10}\text{H}_{12})_2]^{2+}$.

Symbol	X	Y	Z
C	-0.2353673	5.5679319	1.6556291
H	-1.3200495	5.6650355	1.6709297
C	0.3847712	4.3858800	2.0997456
H	1.4546331	4.3837851	2.3108680
C	-0.3138785	3.1378250	2.0324470
C	0.3551022	1.8721630	2.1004940
C	-0.3407755	0.6353419	2.0527365
C	0.3407755	-0.6353419	2.0527365
C	-0.3551022	-1.8721630	2.1004940
C	0.3138785	-3.1378250	2.0324470
C	-0.3847712	-4.3858800	2.0997456
C	0.2353673	-5.5679319	1.6556291
H	0.3353161	6.4910372	1.6405895
H	-1.4060429	3.1465469	2.0789703
H	1.4368264	1.8676276	2.2585206
H	-1.4276720	0.6324022	2.1708435
H	1.4276720	-0.6324022	2.1708435
H	-1.4368264	-1.8676276	2.2585206
H	1.4060429	-3.1465469	2.0789703
H	-1.4546331	-4.3837851	2.3108680
H	1.3200495	-5.6650355	1.6709297
H	-0.3353161	-6.4910372	1.6405895
C	-0.2353673	5.5679319	-1.6556291
H	-1.3200495	5.6650355	-1.6709297
C	0.3847712	4.3858800	-2.0997456
H	1.4546331	4.3837851	-2.3108680
C	-0.3138785	3.1378250	-2.0324470
C	0.3551022	1.8721630	-2.1004940
C	-0.3407755	0.6353419	-2.0527365
C	0.3407755	-0.6353419	-2.0527365
C	-0.3551022	-1.8721630	-2.1004940
C	0.3138785	-3.1378250	-2.0324470
C	-0.3847712	-4.3858800	-2.0997456
C	0.2353673	-5.5679319	-1.6556291
H	0.3353161	6.4910372	-1.6405895
H	-1.4060429	3.1465469	-2.0789703
H	1.4368264	1.8676276	-2.2585206
H	-1.4276720	0.6324022	-2.1708435
H	1.4276720	-0.6324022	-2.1708435
H	-1.4368264	-1.8676276	-2.2585206
H	1.4060429	-3.1465469	-2.0789703
H	-1.4546331	-4.3837851	-2.3108680

H	1.3200495	-5.6650355	-1.6709297
H	-0.3353161	-6.4910372	-1.6405895
Pd	0.0174586	4.1225630	0.0000000
Pd	-0.0174586	-4.1225630	0.0000000
Pd	-0.0279625	-1.3530866	0.0000000
Pd	0.0279625	1.3530866	0.0000000

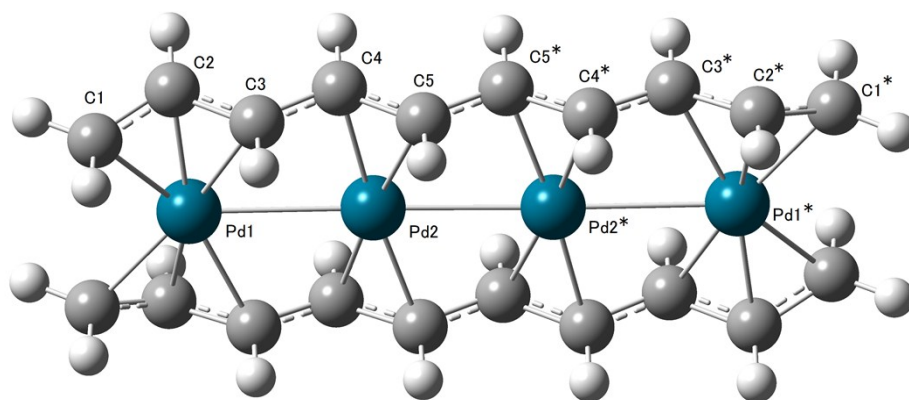


Figure S4. The optimized geometry of $[\text{Pd}_4(\text{C}_{10}\text{H}_{12})_2]^{2+}$.

Table S8. Selected bond lengths (Å) and angles (°) of $[\text{Pd}_4(\text{C}_{10}\text{H}_{12})_2]^{2+}$.

Pd1–Pd2	2.770	C1–C2	1.407
Pd2–Pd2*	2.707	C2–C3	1.432
Pd1–C1	2.212	C3–C4	1.433
Pd1–C2	2.148	C4–C5	1.420
Pd1–C3	2.283	C5–C5*	1.442
Pd2–C4	2.188	Pd1–Pd2–Pd2*	178.6
Pd2–C5	2.206	Pd1*–Pd2*–Pd2	178.6

Table S9. Cartesian coordinates (in Å) of the optimized geometry of $[\text{Pd}_5(\text{C}_{12}\text{H}_{14})_2]^{2+}$.

Symbol	X	Y	Z
C	-0.6223736	-2.0712417	0.3424991
C	0.6225133	-2.0712129	-0.3419653
C	-0.6225354	2.0702958	0.3422216
C	0.6224998	2.0701309	-0.3420584
Pd	-0.0000215	-0.0005487	0.0001214
H	0.6313632	-2.2140375	-1.4258894
H	0.6315275	2.2129915	-1.4259752
H	-0.6315467	2.2133417	1.4261122
H	-0.6313223	-2.2142587	1.4263887
C	-1.8912651	2.0363731	-0.3435143
H	-1.8827195	2.1239969	-1.4332751
C	1.8912332	2.0361733	0.3436767
H	1.8827119	2.1239061	1.4334258
C	-1.8911543	-2.0366938	-0.3431514
H	-1.8826594	-2.1243863	-1.4329068
C	1.8913829	-2.0371052	0.3435353
H	1.8830832	-2.1247510	1.4332940
C	-3.1356327	-2.1114720	0.3412928
H	-3.1357648	-2.2941032	1.4191510
C	3.1356781	-2.1118189	-0.3411732
H	3.1356689	-2.2944809	-1.4190223
C	3.1356689	2.1111842	-0.3407835
H	3.1357523	2.2938908	-1.4186300
C	-3.1357561	2.1113976	0.3408799
H	-3.1358956	2.2940895	1.4187282
Pd	2.6836166	-0.0003577	-0.0546776
Pd	-2.6836215	-0.0000567	0.0548336
C	-4.3972489	2.0215589	-0.3306660
H	-4.4004284	2.0437167	-1.4234712
C	4.3972095	2.0215243	0.3307060
H	4.4004127	2.0437675	1.4235085
C	4.3972586	-2.0210191	0.3300908
H	4.4006356	-2.0433507	1.4228916
C	-4.3971192	-2.0211319	-0.3301817
H	-4.4003478	-2.0434650	-1.4229841
C	5.6522102	2.1064727	-0.3560847
H	5.6532046	2.3319189	-1.4231195
C	6.8404945	1.6779013	0.2644447
H	6.9330793	1.6843258	1.3494236
H	7.7664492	1.6934462	-0.3013490
C	-5.6523319	2.1062969	0.3559955
H	-5.6534933	2.3317247	1.4230321
C	-6.8405171	1.6777418	-0.2647547

H	-6.9329523	1.6842882	-1.3497465
H	-7.7665494	1.6932041	0.3009140
C	-5.6522277	-2.1055234	0.3564918
H	-5.6534041	-2.3307012	1.4235789
C	-6.8403840	-1.6770991	-0.2644102
H	-6.9327219	-1.6839581	-1.3494076
H	-7.7664348	-1.6923328	0.3012300
C	5.6522718	-2.1054032	-0.3567779
H	5.6532523	-2.3305726	-1.4238681
C	6.8405446	-1.6769429	0.2638797
H	6.9330942	-1.6837620	1.3488567
H	7.7664812	-1.6922350	-0.3019457
Pd	5.4367130	0.0005161	-0.0232189
Pd	-5.4367517	0.0003484	0.0229393

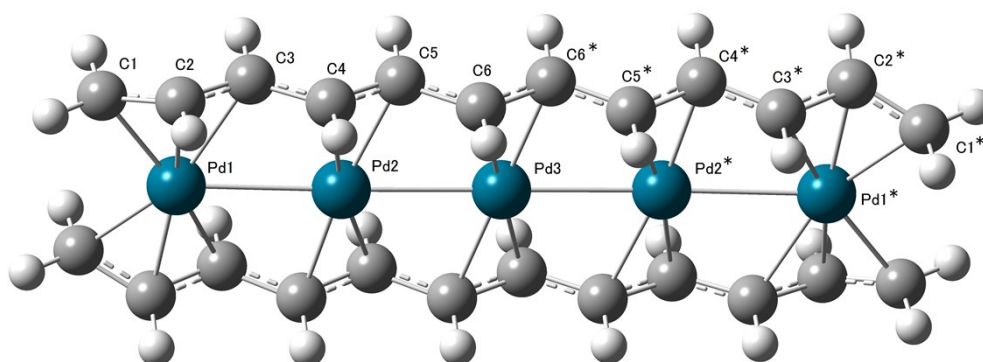


Figure S5. The optimized geometry of $[\text{Pd}_5(\text{C}_{12}\text{H}_{14})_2]^{2+}$.

Table S10. Selected bond lengths (Å) and angles (°) of $[\text{Pd}_5(\text{C}_{12}\text{H}_{14})_2]^{2+}$.

Pd1–Pd2	2.753	C1–C2	1.407
Pd2–Pd3	2.684	C2–C3	1.433
Pd1–C1	2.206	C3–C4	1.432
Pd1–C2	2.143	C4–C5	1.422
Pd1–C3	2.300	C5–C6	1.443
Pd2–C4	2.178	C6–C6*	1.421
Pd2–C5	2.221	Pd1–Pd2–Pd3	178.2
Pd3–C6	2.189	Pd2–Pd3–Pd2*	180.0

Table S11. Cartesian coordinates (in Å) of the optimized geometry of [Pd₃(s-cis-C₈H₁₀)₂]²⁺.

Symbol	X	Y	Z
C	0.7107269	2.0931904	0.9337462
C	-0.7122906	2.0938947	0.9304482
C	0.7130621	-2.0961649	0.9256763
C	-0.7116207	-2.0980052	0.9298187
Pd	-0.0000597	-0.0012663	0.9317835
H	1.1953660	-2.2994245	1.8845485
H	1.1930495	2.2947831	1.8928218
C	1.5668090	-2.0175983	-0.2213772
H	1.1342299	-2.0458092	-1.2236497
C	1.5632341	2.0170104	-0.2155186
H	1.1284312	2.0468003	-1.2166668
C	2.9872396	2.1002064	-0.0931323
H	3.4269130	2.3367723	0.8765124
C	2.9906958	-2.0987885	-0.0951810
H	3.4283926	-2.3362021	0.8751571
Pd	2.5714103	0.0005618	-0.2599664
C	3.8080818	-1.6221814	-1.1360694
H	3.4491939	-1.6120769	-2.1643162
C	3.8030470	1.6271269	-1.1369514
H	3.4414626	1.6177274	-2.1643048
H	4.8797421	1.6032913	-0.9995019
H	4.8843537	-1.5960761	-0.9956499
C	-1.5654363	-2.0209731	-0.2175198
C	-1.5650137	2.0197597	-0.2177286
C	-2.9892956	-2.1048888	-0.0918064
C	-3.8079837	-1.6308245	-1.1329952
C	-2.9890327	2.1015190	-0.0919905
C	-3.8061509	1.6296508	-1.1352750
Pd	-2.5706797	0.0017128	-0.2620899
H	-1.1931908	-2.3031232	1.8885289
H	-1.1953996	2.2952695	1.8892087
H	-3.4267551	-2.3419602	0.8786450
H	-4.8843459	-1.6070166	-0.9928189
H	-4.8826404	1.6053188	-0.9963623
H	-3.4458115	1.6221228	-2.1630392
H	-1.1316710	2.0499254	-1.2194910
H	-1.1322084	-2.0495416	-1.2193829
H	-3.4489847	-1.6210559	-2.1612039
H	-3.4274249	2.3362902	0.8786498

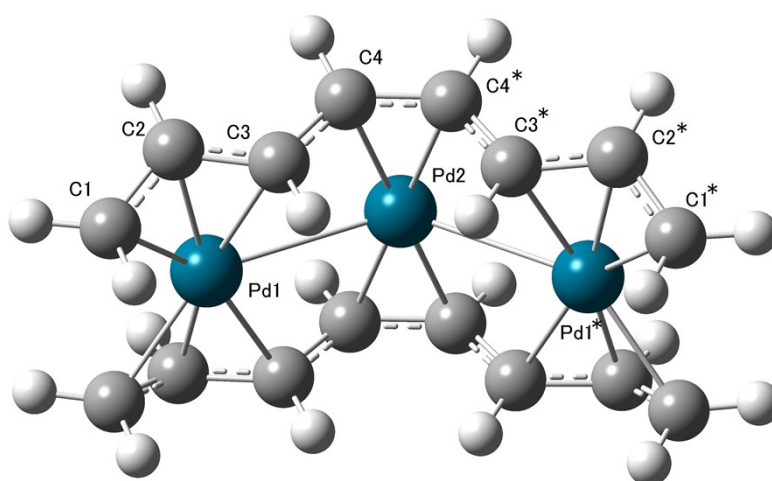


Figure S6. The optimized geometry of $[\text{Pd}_3(\text{s-cis-C}_8\text{H}_{10})_2]^{2+}$.

Table S12. Selected bond lengths (Å) and angles (°) of $[\text{Pd}_3(\text{s-cis-C}_8\text{H}_{10})_2]^{2+}$.

Pd1–Pd2	2.834	C1–C2	1.407
Pd1–C1	2.221	C2–C3	1.432
Pd1–C2	2.147	C3–C4	1.433
Pd1–C3	2.255	C4–C4*	1.423
Pd2–C4	2.212	Pd1–Pd2–Pd1	130.2

Table S13. Cartesian coordinates (in Å) of the optimized geometry of $[\text{Pd}_3(\text{HCN})_8]^{2+}$.

Symbol	X	Y	Z
Pd	0.0000000	0.0000000	2.6292498
Pd	0.0000000	0.0000000	0.0000045
Pd	0.0000000	0.0000000	-2.6292382
N	0.0000000	0.0000000	4.8449170
N	-1.9470475	0.5283808	2.4736369
N	1.9470475	-0.5283808	2.4736369
N	-0.0000682	1.9838874	0.0000075
N	0.0000682	-1.9838874	0.0000075
N	-1.9470343	-0.5284596	-2.4736842
N	0.0000000	0.0000000	-4.8449013
N	1.9470343	0.5284596	-2.4736842
C	0.0000000	0.0000000	6.0130209
H	0.0000000	0.0000000	7.0862343
C	3.0732979	-0.8332480	2.5185361
H	4.1075942	-1.1135852	2.5642806
C	-3.0732979	0.8332480	2.5185361
H	-4.1075942	1.1135852	2.5642806
C	0.0001107	-3.1511568	-0.0000250
H	0.0001228	-4.2237356	0.0000303
C	-0.0001107	3.1511568	-0.0000250
H	-0.0001228	4.2237356	0.0000303
C	-3.0732667	-0.8333585	-2.5185467
H	-4.1075468	-1.1137572	-2.5642947
C	3.0732667	0.8333585	-2.5185467
H	4.1075468	1.1137572	-2.5642947
C	0.0000000	0.0000000	-6.0130058
H	0.0000000	0.0000000	-7.0862193

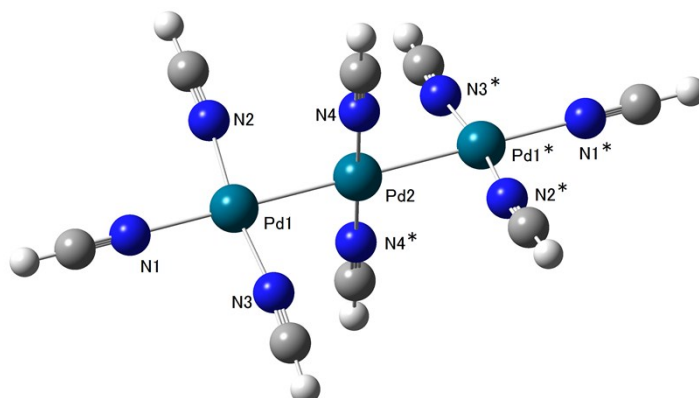


Figure S7. The optimized geometry of $[\text{Pd}_3(\text{HCN})_8]^{2+}$.

Table S14. Selected bond lengths (Å) and angles (°) of [Pd₃(HCN)₈]²⁺.

Pd1–Pd2	2.629	Pd2–N4	1.984
Pd1–N1	2.216	Pd1–Pd2–Pd1*	180.0
Pd1–N2	2.023	N2–Pd1–Pd2–N4	74.8
Pd1–N3	2.023	N4–Pd2–Pd1*–N2*	74.8

Table S15. Cartesian coordinates (in Å) of the optimized geometry of $[\text{Pd}_3(\text{PhC}_8\text{H}_8\text{Ph})_2]^{2+}$.

Symbol	X	Y	Z
C	-0.6397350	-2.1539630	0.3038290
C	0.6398370	-2.1540160	-0.3032120
C	-0.6584310	2.0223460	0.2610260
C	0.6582500	2.0223350	-0.2611040
Pd	-0.0000250	-0.0695460	0.0000880
H	0.7139400	-2.2791590	-1.3870150
H	0.8057970	2.1612250	-1.3354370
H	-0.8059810	2.1612590	1.3353560
H	-0.7138630	-2.2789690	1.3876450
C	-1.8223430	1.9667540	-0.5831320
H	-1.6669550	2.0204620	-1.6646130
C	1.8221450	1.9666910	0.5830530
H	1.6667600	2.0203460	1.6645350
C	-1.8601290	-2.1114650	-0.4560300
H	-1.7955030	-2.2240890	-1.5422640
C	1.8602390	-2.1114450	0.4566190
H	1.7956490	-2.2237470	1.5428850
C	-3.1393410	-2.1182140	0.1700450
H	-3.1864210	-2.2733790	1.2477490
C	3.1394240	-2.1183150	-0.1694970
H	3.1864410	-2.2737780	-1.2471590
C	3.1562510	2.0483290	0.0839660
H	3.3364590	2.3088310	-0.9593750
C	-3.1564620	2.0483100	-0.0840550
H	-3.3366880	2.3087920	0.9592820
Pd	2.7252360	-0.0510060	0.3268560
Pd	-2.7250700	-0.0509860	-0.3268940
C	-4.2244840	1.6309870	-0.9152330
H	-4.0193430	1.6118560	-1.9909430
C	4.2243500	1.6311540	0.9151250
H	4.0193090	1.6120720	1.9908560
C	4.2963060	-1.7170360	0.5418820
H	4.2470320	-1.7679620	1.6342360
C	-4.2961540	-1.7170770	-0.5415060
H	-4.2468030	-1.7682700	-1.6338440
C	-5.6256550	-1.6140380	0.0279650
C	-5.8851630	-1.7615090	1.4106910
C	-6.7053410	-1.3743660	-0.8499780
C	-7.1950970	-1.7386350	1.8820420
H	-5.0770730	-1.9390080	2.1169340

C	-8.0140930	-1.3408020	-0.3686040
H	-6.5158000	-1.2730580	-1.9170210
C	-8.2626640	-1.5203560	0.9972910
H	-7.3898340	-1.8860940	2.9410700
H	-8.8392460	-1.1812210	-1.0568710
H	-9.2840870	-1.5195110	1.3691600
C	5.6257870	-1.6140520	-0.0276860
C	5.8853850	-1.7626490	-1.4102780
C	6.7053950	-1.3733910	0.8500850
C	7.1953180	-1.7397650	-1.8816220
H	5.0773870	-1.9411190	-2.1163730
C	8.0141420	-1.3398170	0.3687090
H	6.5158010	-1.2712780	1.9170430
C	8.2628010	-1.5204260	-0.9970300
H	7.3901320	-1.8881410	-2.9405090
H	8.8392320	-1.1794530	1.0568680
H	9.2842290	-1.5195950	-1.3688840
C	-5.6211350	1.6264140	-0.5348640
C	-6.5893720	1.8159900	-1.5462840
C	-6.0391060	1.4851180	0.8066210
C	-7.9358440	1.9587370	-1.2113410
H	-6.2719590	1.9175060	-2.5830190
C	-7.3882470	1.6062300	1.1302180
H	-5.3107400	1.2906480	1.5920340
C	-8.3382220	1.8490470	0.1255900
H	-8.6710630	2.1465640	-1.9891330
H	-7.7066450	1.5077970	2.1643210
H	-9.3864020	1.9658720	0.3888160
C	5.6209720	1.6265690	0.5345840
C	6.0387420	1.4841020	-0.8068400
C	6.5893300	1.8173100	1.5456560
C	7.3878020	1.6051350	-1.1307920
H	5.3102620	1.2886520	-1.5919120
C	7.9357120	1.9600410	1.2103310
H	6.2720820	1.9197550	2.5823490
C	8.3378910	1.8491500	-0.1265600
H	7.7060390	1.5057550	-2.1648530
H	8.6710230	2.1488140	1.9878100
H	9.3860140	1.9658810	-0.3900560

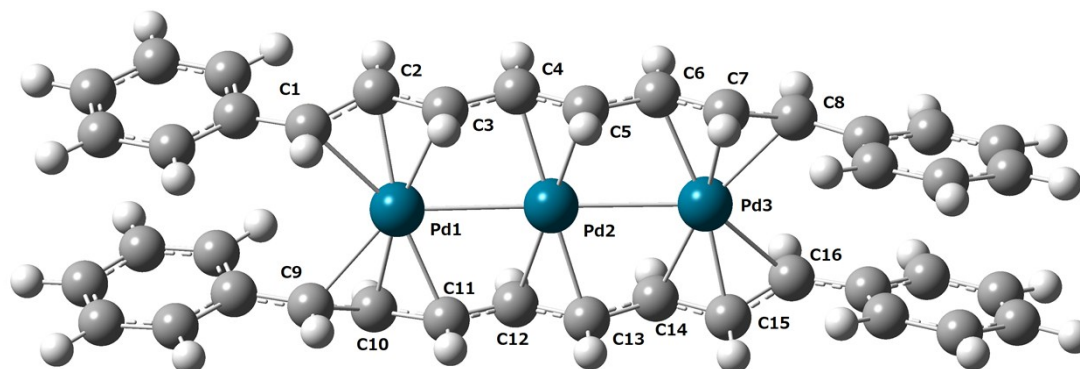


Figure S8. The optimized geometry of $[\text{Pd}_3(\text{PhC}_8\text{H}_8\text{Ph})_2]^{2+}$.

Table S16. Selected bond lengths (Å) and angles (°) of $[\text{Pd}_3(\text{PhC}_8\text{H}_8\text{Ph})_2]^{2+}$.

Pd1–Pd2	2.745	C1–C2	1.416
Pd2–Pd3	2.745	C2–C3	1.424
Pd1–C1	2.300	C3–C4	1.438
Pd1–C2	2.166	C4–C5	1.416
Pd1–C3	2.238	C5–C6	1.438
Pd1–C9	2.329	C6–C7	1.424
Pd1–C10	2.157	C7–C8	1.416
Pd1–C11	2.225	C9–C10	1.416
Pd2–C4	2.201	C10–C11	1.427
Pd2–C5	2.201	C11–C12	1.439
Pd2–C12	2.209	C12–C13	1.416
Pd2–C13	2.209	C13–C14	1.439
Pd3–C6	2.238	C14–C15	1.427
Pd3–C7	2.166	C15–C16	1.416
Pd3–C8	2.300	Pd1–Pd2–Pd3	179.2
Pd3–C14	2.225		
Pd3–C15	2.157		
Pd3–C16	2.329		

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