

Electronic Supporting information for:

Palladium carbene complexes as persistent radicals

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1 X-ray data for compounds {2}₂, 3-6, 8, 9, 11, 12

X-Ray crystal structure of {[PC(sp²)P]PdI}₂·½Et₂O ({2}₂·½Et₂O). Single crystals were obtained as green blocks from a concentrated diethyl ether solution at –34 °C in the glovebox. Crystal and refinement data for {2}₂·½Et₂O: C₁₀₄H₁₅₄I₄OP₈Pd₄; M_r = 2601.23; Monoclinic; space group *P*2₁/*c*; *a* = 16.2343(6) Å; *b* = 15.9423(6) Å; *c* = 20.8753(8) Å; α = 90°; β = 94.7040(14)°; γ = 90°; *V* = 5384.6(4) Å³; *Z* = 2; *T* = 120(2) K; λ = 0.71073 Å; μ = 1.967 mm^{–1}; *d*_{calc} = 1.604 g·cm^{–3}; 131164 reflections collected; 9479 unique (*R*_{int} = 0.0363); giving *R*₁ = 0.0257, *wR*₂ = 0.0662 for 8389 data with [*I* > 2σ(*I*)] and *R*₁ = 0.0314, *wR*₂ = 0.0733 for all 9479 data. Residual electron density (e[–]·Å^{–3}) max/min: 0.964/–1.540.

X-Ray crystal structure of [PC*(sp²)P]PdBr (3). Single crystals were obtained as dichroic orange-green rhomboids from a concentrated diethyl ether solution at –35 °C in the glovebox. Crystal and refinement data for 3: C₂₅H₃₆BrP₂Pd; M_r = 584.79; Monoclinic; space group *P*2₁/*n*; *a* = 12.5686(12) Å; *b* = 13.9781(13) Å; *c* = 14.9939(14) Å; α = 90°; β = 97.3300(18)°; γ = 90°; *V* = 2612.7(4) Å³; *Z* = 4; *T* = 120(2) K; λ = 0.71073 Å; μ = 2.372 mm^{–1}; *d*_{calc} = 1.487 g·cm^{–3}; 33653 reflections collected; 4601 unique (*R*_{int} = 0.0528); giving *R*₁ = 0.0258, *wR*₂ = 0.0542 for 3834 data with [*I* > 2σ(*I*)] and *R*₁ = 0.0375, *wR*₂ = 0.0569 for all 4601 data. Residual electron density (e[–]·Å^{–3}) max/min: 0.617/–0.548.

X-Ray crystal structure of [PC(sp³)HP]PdBr (4). Single crystals were obtained as cream rhomboids from a concentrated diethyl ether solution at –35 °C in the glovebox. Crystal and refinement data for 4: C₂₅H₃₇BrP₂Pd; M_r = 585.80; Monoclinic; space group *P*2₁/*n*; *a* = 11.2438(8) Å; *b* = 13.7677(10) Å; *c* = 17.4246(12) Å; α = 90°; β = 106.9775(12)°; γ = 90°; *V* = 2579.8(3) Å³; *Z* = 4; *T* = 120(2) K; λ = 0.71073 Å; μ = 2.402 mm^{–1}; *d*_{calc} = 1.508 g·cm^{–3}; 33493 reflections collected; 4546 unique (*R*_{int} = 0.0524); giving *R*₁ = 0.0348, *wR*₂ = 0.0742 for 3801 data with [*I* > 2σ(*I*)] and *R*₁ = 0.0463, *wR*₂ = 0.0776 for all 4546 data. Residual electron density (e[–]·Å^{–3}) max/min: 1.970/–1.106.

X-Ray crystal structure of [PC*(sp²)P]PdCl (5). Single crystals were obtained as green rhomboids from a concentrated diethyl ether solution at –35 °C in the glovebox. Crystal and refinement data for 5: C₂₅H₃₆ClP₂Pd; M_r = 540.33; Monoclinic; space group *P*2₁/*n*; *a* = 11.6639(11) Å; *b* = 13.5934(13) Å; *c* = 16.5680(16) Å; α = 90°; β = 105.1159(14)°; γ = 90°; *V* = 2536.0(4) Å³; *Z* = 4; *T* = 120(2) K; λ = 0.71073 Å; μ = 0.973 mm^{–1}; *d*_{calc} = 1.415 g·cm^{–3}; 36052 reflections collected; 4436 unique (*R*_{int} = 0.0430); giving *R*₁ = 0.0240, *wR*₂ = 0.0523 for 3928 data with [*I* > 2σ(*I*)] and *R*₁ = 0.0298, *wR*₂ = 0.0541 for all 4436 data. Residual electron density (e[–]·Å^{–3}) max/min: 0.664/–0.356.

X-Ray crystal structure of [PC(CH₂)P]Pd(PMe₃) (6). Single crystals were obtained as orange blocks from a concentrated *n*-pentane at –35 °C in the glovebox. Crystal and refinement data for 6: C₂₉H₄₇P₃Pd; M_r = 594.98; Monoclinic; space group *P*2₁/*n*; *a* = 10.3086(7) Å; *b* = 24.0617(16) Å; *c* = 12.5709(8) Å; α = 90°; β = 107.5771(18)°; γ = 90°; *V* = 2972.5(3) Å³; *Z* = 4; *T* = 120(2) K; λ = 0.71073 Å; μ = 0.801 mm^{–1}; *d*_{calc} = 1.329 g·cm^{–3}; 71407 reflections collected; 5233 unique (*R*_{int} = 0.0510); giving *R*₁ = 0.0220, *wR*₂ = 0.0495 for 4714 data with [*I* > 2σ(*I*)] and *R*₁ = 0.0257, *wR*₂ = 0.0512 for all 5233 data. Residual electron density (e[–]·Å^{–3}) max/min: 0.407/–0.292.

X-Ray crystal structure of [PC(CH₃)HP]PdCl₂ (8). Single crystals were obtained as yellow needles from a concentrated dichloromethane solution at −35 °C in the glovebox. Crystal and refinement data for **8**: C₂₆H₄₀Cl₂P₂Pd; M_r = 591.82; Monoclinic; space group *C2/c*; *a* = 13.0569(14) Å; *b* = 16.8080(14) Å; *c* = 31.261(3) Å; α = 90°; β = 93.209(2)°; γ = 90°; V = 6849.8(11) Å³; Z = 8; T = 120(2) K; λ = 0.71073 Å; μ = 0.801 mm^{−1}; d_{calc} = 1.148 g·cm^{−3}; 38696 reflections collected; 6002 unique (R_{int} = 0.0536); giving R₁ = 0.0372, wR₂ = 0.0751 for 5140 data with [I > 2σ(I)] and R₁ = 0.0457, wR₂ = 0.0779 for all 6002 data. Residual electron density (e[−]·Å^{−3}) max/min: 0.596/−0.503.

X-Ray crystal structure of [PC(CH₃)P]PdCl (9). Single crystals were obtained as yellow cubes from a concentrated diethyl ether solution at −35 °C in the glovebox. Crystal and refinement data for **9**: C₂₆H₃₉ClP₂Pd; M_r = 555.36; Monoclinic; space group *P2₁/c*; *a* = 11.2685(8) Å; *b* = 20.7303(14) Å; *c* = 23.1605(16) Å; α = 90°; β = 99.2340(13)°; γ = 90°; V = 5340.2(6) Å³; Z = 8; T = 120(2) K; λ = 0.71073 Å; μ = 0.926 mm^{−1}; d_{calc} = 1.382 g·cm^{−3}; 62725 reflections collected; 9411 unique (R_{int} = 0.0607); giving R₁ = 0.0419, wR₂ = 0.0827 for 7826 data with [I > 2σ(I)] and R₁ = 0.0557, wR₂ = 0.0867 for all 9411 data. Residual electron density (e[−]·Å^{−3}) max/min: 0.851/−0.547.

X-Ray crystal structure of [PC(sp³)HP]PdI (11). Single crystals were obtained as light yellow plates from a concentrated diethyl ether solution at −35 °C in the glovebox. Crystal and refinement data for **11**: C₂₅H₃₇IP₂Pd; M_r = 632.79; Monoclinic; space group *C2/c*; *a* = 29.176(6) Å; *b* = 12.515(2) Å; *c* = 22.247(4) Å; α = 90°; β = 105.315(4)°; γ = 90°; V = 7835(2) Å³; Z = 12; T = 120(2) K; λ = 0.71073 Å; μ = 2.025 mm^{−1}; d_{calc} = 1.609 g·cm^{−3}; 55501 reflections collected; 6893 unique (R_{int} = 0.0219); giving R₁ = 0.0235, wR₂ = 0.0511 for 6564 data with [I > 2σ(I)] and R₁ = 0.0252, wR₂ = 0.0519 for all 6893 data. Residual electron density (e[−]·Å^{−3}) max/min: 1.412/−1.244.

X-Ray crystal structure of [PC(sp³)H₂P]PdBr₂·CH₂Cl₂ (12·CH₂Cl₂). Single crystals were obtained as orange cubes from a concentrated dichloromethane solution at −35 °C in the glovebox. Crystal and refinement data for **12·CH₂Cl₂**: C₅₁H₇₈Br₄Cl₂P₄Pd₂; M_r = 1418.35; Monoclinic; space group *P2₁/n*; *a* = 10.3876(9) Å; *b* = 16.2993(14) Å; *c* = 17.0895(15) Å; α = 90°; β = 103.4770(14)°; γ = 90°; V = 2813.8(4) Å³; Z = 2; T = 120(2) K; λ = 0.71073 Å; μ = 3.721 mm^{−1}; d_{calc} = 1.674 g·cm^{−3}; 50587 reflections collected; 4956 unique (R_{int} = 0.0399); giving R₁ = 0.0185, wR₂ = 0.0423 for 4411 data with [I > 2σ(I)] and R₁ = 0.0239, wR₂ = 0.0435 for all 4956 data. Residual electron density (e[−]·Å^{−3}) max/min: 0.371/−0.325.

2 Magnetic moment for $\{[\text{PC}(\text{sp}^2)\text{P}]\text{PdI}\}_2$ ($\{2\}_2$)

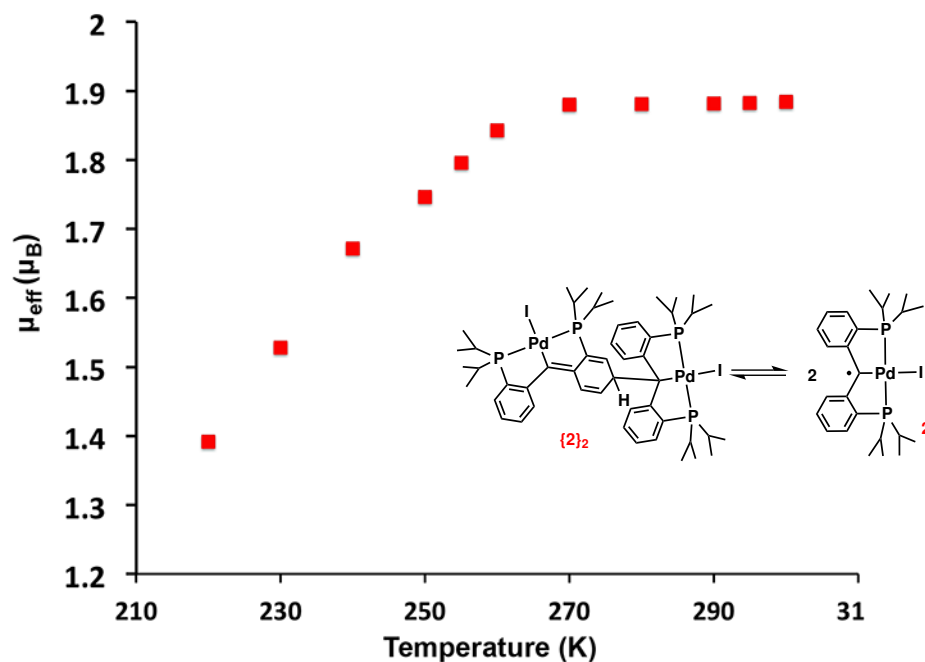


Figure S1. Magnetic moment for $\{2\}_2$ as a function of temperature (Evans method, C_6D_6).

3 Cyclic Voltammetry

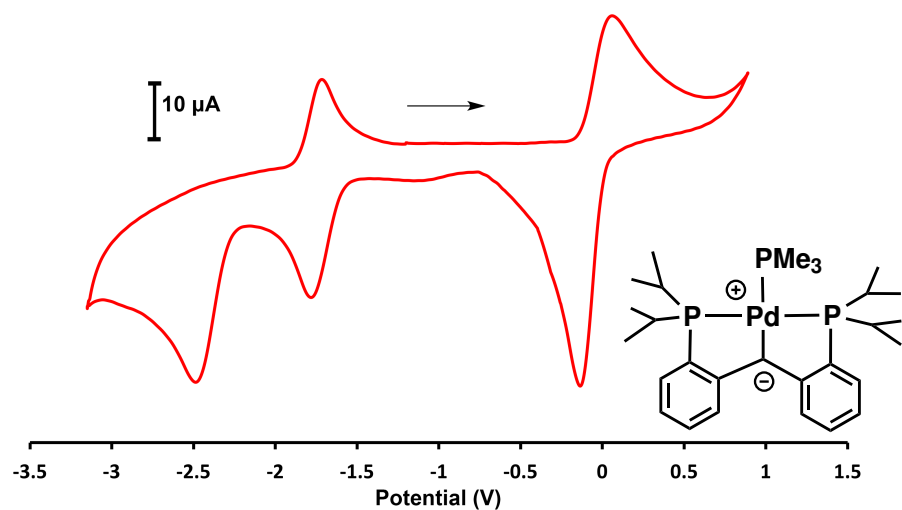


Figure S2. Cyclic voltammogram of $[\text{PC}(\text{sp}^2)\text{P}]\text{Pd}(\text{PMe}_3)$ (**1**) at 100 mV/s, 1 mM in 0.1 M $[\text{nBu}_4\text{N}][\text{PF}_6]$ in THF, $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$ corrected.

4 EPR Spectra

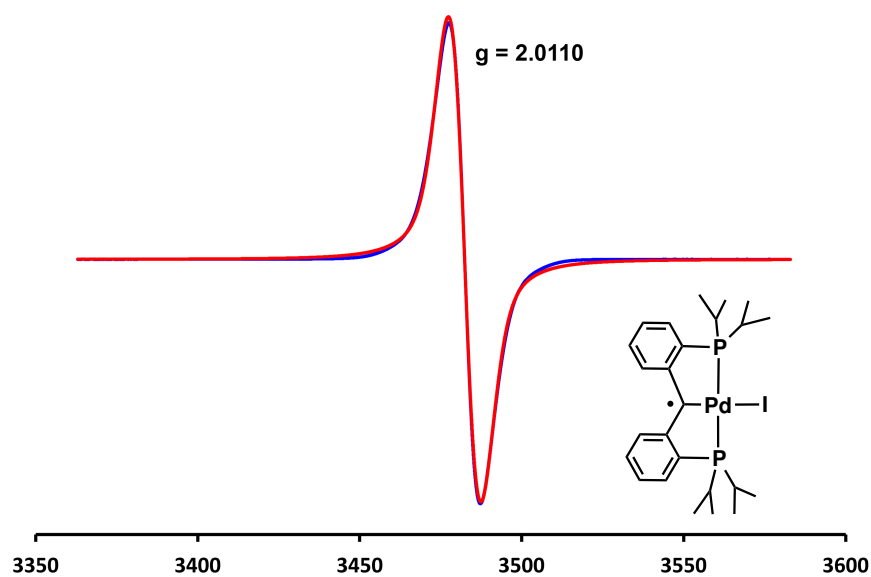


Figure S3. EPR spectrum of [PC[•](sp²)P]PdI (**2**) (1 mM solution in toluene, 298 K), $\Delta H_{pp} = 10.0$ G; the blue line represents the experimental data and the red line represents the simulated spectrum.

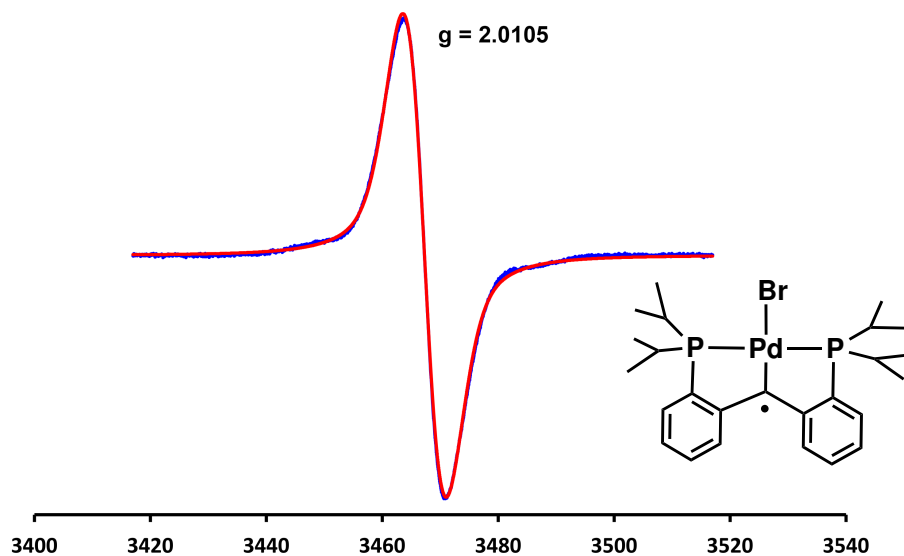


Figure S4. EPR spectrum of [PC[•](sp²)P]PdBr (**3**) (1 mM solution in toluene, 298 K), $\Delta H_{pp} = 7.5$ G; the blue line represents the experimental data and the red line represents the simulated spectrum.

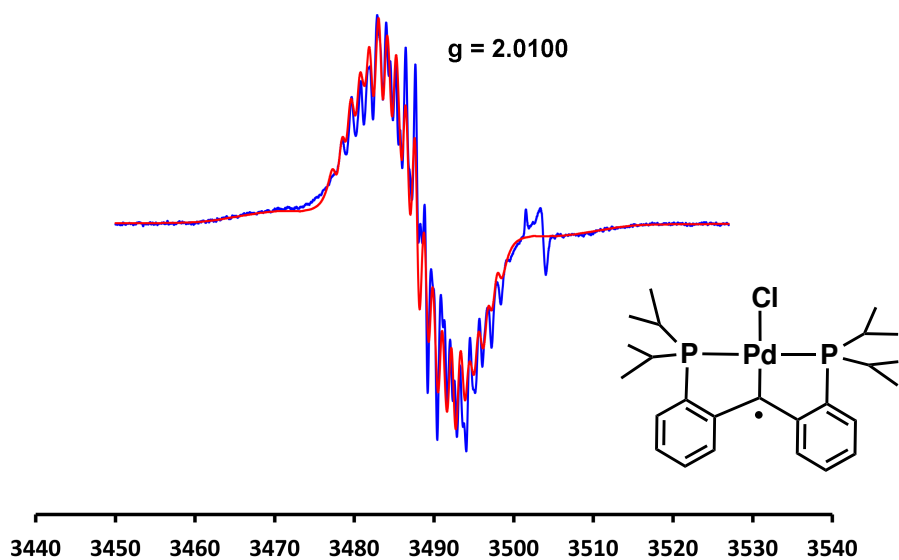


Figure S5. EPR spectrum of [PC[•](sp²)P]PdCl (**5**) at 298 K (100 μ M solution in toluene); the blue line represents the experimental data and the red line represents the simulation with the following parameters: $a_1(2H) = 4.5$ G; $a_2(2H) = 2.6$ G; $a_3(2H) = 2.1$ G; $a_4(2H) = 1.2$ G; $g = 2.0100$, individual linewidth 0.8 G (lorentzian lineshape), relative intensity 77.67% for the nonmagnetic Pd isotope species; $a_1(2H) = 4.5$ G, $a_2(2H) = 2.6$ G, $a_3(2H) = 2.1$ G, $a_4(2H) = 1.2$ G, $a(^{105}\text{Pd}) = 6.0$ G, individual linewidth 1.7 G, relative intensity 22.33% for the ^{105}Pd species. The small satellite peak on the right comes from the quartz sample tube.

5 Complete Reference 24

24. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, 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, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *Gaussian, Inc.*, Wallingford CT, 2004.

6 DFT Results

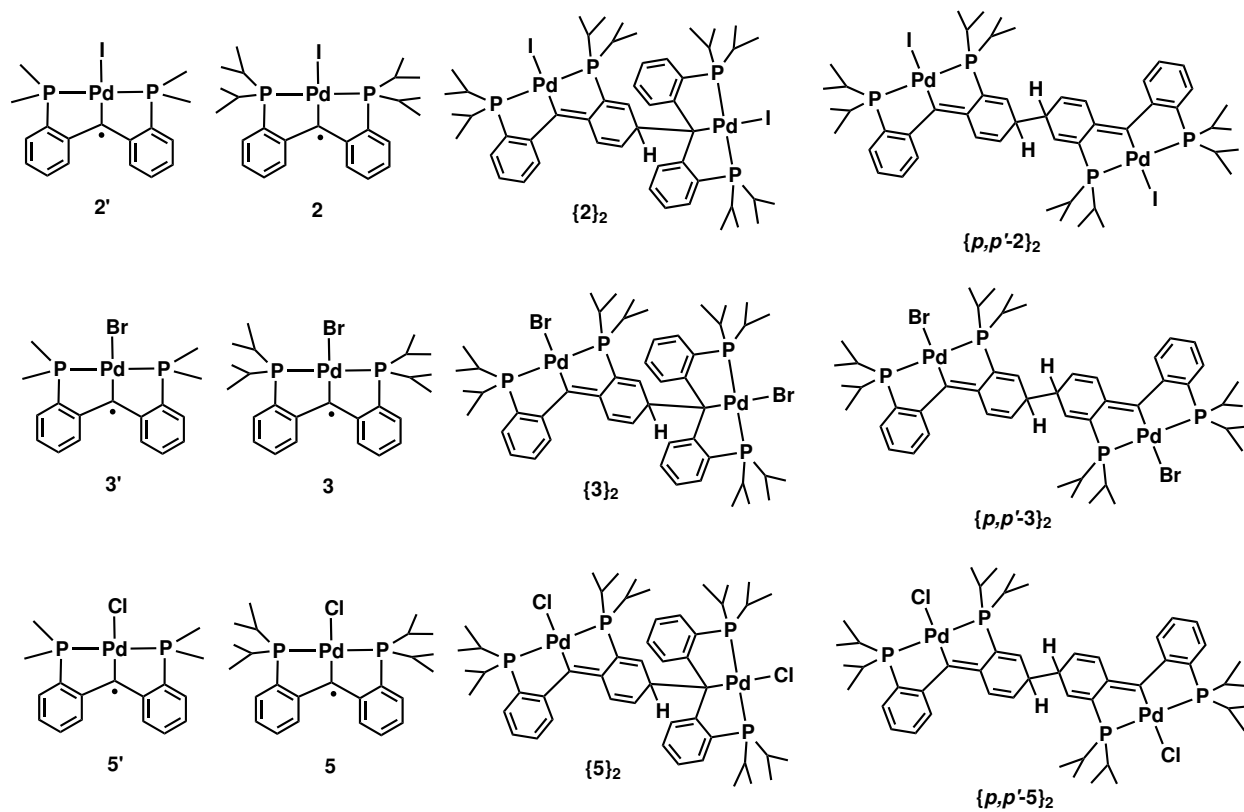


Figure S6. Computed molecules.

6.1 {[PC(sp²)P]PdI}₂ ({2}₂)

Table S1. Optimized coordinates for {[PC(sp²)P]PdI}₂ ({2}₂).

atom	x	y	z
Pd	3.782800	-0.200187	-0.256172
P	4.026958	1.407714	-2.076560
P	4.090199	-1.009851	1.941575
C	2.559016	1.337554	0.638793
I	4.962089	-2.438263	-1.442177
C	5.811178	-0.681159	2.733384
H	5.671573	-0.873930	3.807701
C	6.216618	0.796881	2.550489
H	5.461461	1.484439	2.948748
H	6.369166	1.033918	1.491427
H	7.160582	0.984778	3.080369
C	6.888091	-1.637611	2.176198
H	7.856604	-1.404763	2.639792
H	6.990430	-1.528434	1.090616
H	6.663411	-2.691010	2.381565
C	3.702958	-2.852073	2.328847
H	4.382629	-3.372420	1.641145
C	2.257122	-3.178261	1.908239
H	2.094186	-2.943585	0.850759
C	2.684636	-0.051193	4.277140
H	1.534846	-2.618426	2.515763
H	2.063453	-4.250070	2.050888
C	3.988351	-3.323268	3.772677
H	3.250192	-2.929142	4.481093
H	3.917277	-4.419259	3.807117
H	4.990639	-3.051618	4.124174
C	5.820961	1.635020	-2.752956
H	5.825726	2.634763	-3.214598
C	6.165718	0.584616	-3.832362
H	5.478167	0.609397	-4.687074
H	6.153587	-0.426403	-3.412092
H	7.175641	0.783969	-4.216965
C	6.848500	1.603411	-1.602743
H	6.640815	2.365765	-0.842958
H	6.851737	0.618288	-1.121712
H	7.854379	1.787914	-2.004608
C	2.968265	1.641183	-3.694576

Continued on next page

Table S1. – continued from previous page

atom	x	y	z
H	3.718309	1.832994	-4.473787
C	1.994385	2.838490	-3.663845
H	1.489276	2.912572	-4.637253
H	2.506288	3.788955	-3.477264
H	1.218168	2.720511	-2.899452
C	2.241830	0.318001	-4.032969
H	1.772090	0.394241	-5.023461
H	1.451405	0.102463	-3.302746
H	2.926101	-0.538195	-4.038317
C	2.922099	0.096344	2.893011
C	2.267483	1.102617	2.137631
C	1.318196	1.904805	2.825823
H	0.772387	2.665260	2.279954
C	1.055275	1.736495	4.194531
H	0.315403	2.368367	4.680838
C	1.751985	0.764700	4.936347
H	1.567070	0.640004	6.000370
H	3.224181	-0.803798	4.844258
C	1.192833	1.310565	-0.219442
H	1.552957	1.294799	-1.259680
C	3.280604	2.667711	0.341065
C	3.816368	2.914223	-0.961055
C	4.317411	4.182960	-1.305095
C	4.369929	5.223691	-0.358986
C	3.925531	4.970665	0.949544
C	3.382765	3.717011	1.286766
H	3.033830	3.560874	2.300772
H	3.990730	5.747310	1.708478
H	4.775733	6.194484	-0.631772
H	4.710759	4.359579	-2.303869
C	0.365078	0.049880	-0.053054
C	0.322633	2.551157	-0.115809
H	0.817456	3.507358	-0.276287
H	0.922813	-0.883171	-0.094499
C	-0.989985	0.042507	0.062781
C	-1.793245	1.275150	0.214399
C	-1.020529	2.523346	0.079688
H	-1.569534	3.460306	0.062453
C	-3.167787	1.213781	0.427758
C	-3.967079	2.375233	0.905183
C	-5.355020	2.474820	0.589982
C	-6.118173	3.576390	1.016269

Continued on next page

Table S1. – continued from previous page

atom	x	y	z
C	-5.543881	4.583395	1.814591
C	-4.197086	4.460157	2.206975
C	-3.425342	3.374111	1.765108
H	-2.404086	3.273174	2.116522
H	-3.753031	5.201199	2.868184
H	-6.144124	5.424390	2.152375
H	-7.172435	3.643612	0.759785
P	-2.055023	-1.509555	0.074036
Pd	-4.201216	-0.504744	-0.046412
P	-6.073383	0.973072	-0.273740
I	-5.525091	-2.819056	-0.847462
C	-7.735101	0.663962	0.638474
H	-8.223248	1.646341	0.717173
C	-8.656712	-0.297359	-0.143684
H	-8.178547	-1.272870	-0.283962
H	-9.584581	-0.449029	0.425161
H	-8.933056	0.094666	-1.130324
C	-6.528418	1.493449	-2.065205
C	-5.237817	1.808139	-2.853079
H	-4.537596	0.965593	-2.824630
H	-4.727924	2.689390	-2.442164
H	-5.485768	2.017655	-3.902552
C	-7.535707	2.661255	-2.142258
H	-7.102619	3.583210	-1.735103
H	-7.792212	2.853105	-3.193310
H	-8.469942	2.449108	-1.608058
C	-7.444349	0.134102	2.060570
H	-6.954757	-0.845939	2.012320
H	-6.800744	0.815825	2.630236
H	-8.388002	0.018260	2.611160
C	-1.568723	-2.503766	1.635648
H	-0.484225	-2.655614	1.565908
C	-1.875780	-1.675464	2.901722
H	-1.561270	-2.235847	3.793139
H	-1.347897	-0.714317	2.900402
H	-2.951494	-1.477097	2.985307
C	-2.280018	-3.875091	1.664057
H	-1.996690	-4.413259	2.579338
H	-3.369600	-3.756817	1.658384
H	-6.983426	0.587560	-2.488316
C	-1.591557	-2.590987	-1.444179
H	-2.359693	-3.375438	-1.409016

Continued on next page

Table S1. – continued from previous page

atom	x	y	z
C	−1.801231	−1.780503	−2.741701
H	−1.107568	−0.931323	−2.799930
H	−2.827502	−1.402773	−2.808948
H	−1.619524	−2.427639	−3.610286
C	−0.193075	−3.244942	−1.400166
H	−0.009104	−3.793526	−0.468856
H	0.610359	−2.511732	−1.535929
H	−0.111758	−3.966356	−2.224917
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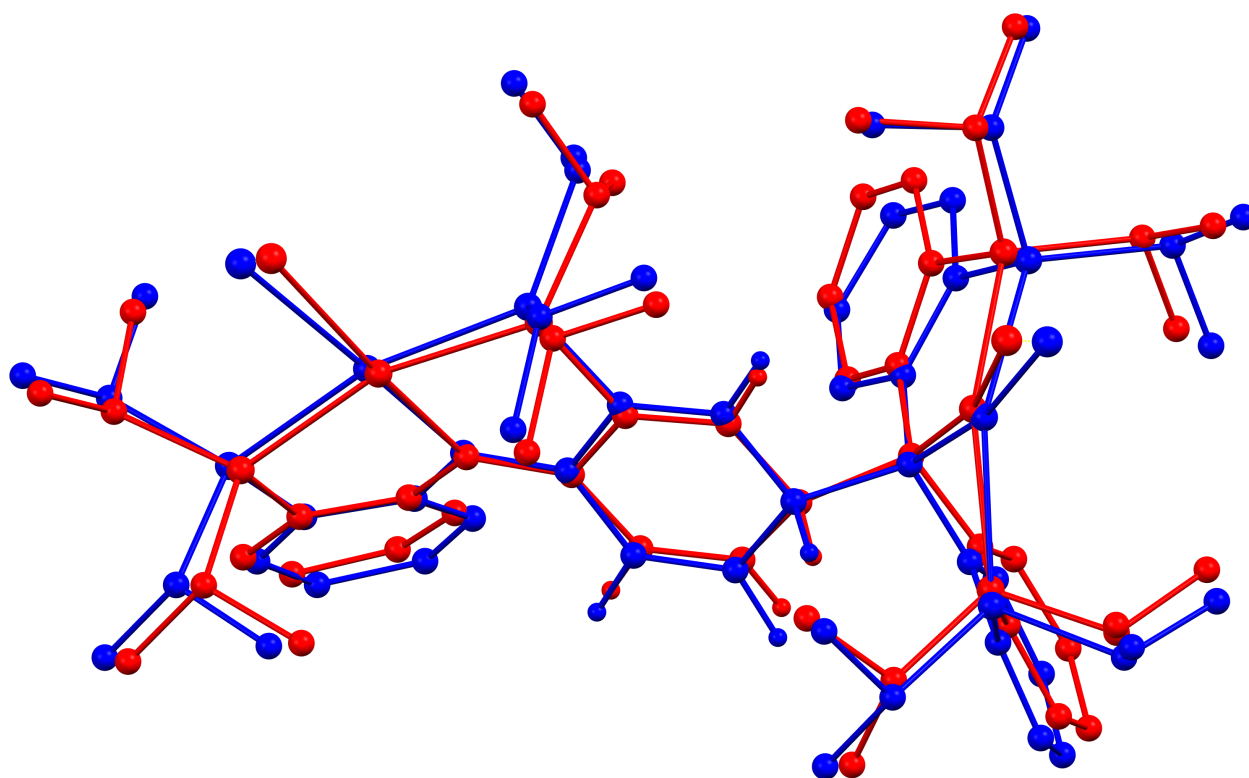


Figure S7. Overlaid structures for $\{[\text{PC}(\text{sp}^2)\text{P}]\text{PdI}_2\}_2$ (**2**)₂ (red: X-ray, blue: optimized).

Table S2. Selected distances (Å) and angles (°) for the optimized geometry and the crystal structure of $\{[\text{PC}(\text{sp}^2)\text{P}]\text{PdI}\}_2$ (**2**)₂.

Distance	Calcd.	X-Ray	Angle	Calcd.	X-Ray
Pd(1)–I(1)	2.794	2.6851(3)	I(1)–Pd(1)–C(1)	170.24	167.42(8)
Pd(2)–I(2)	2.784	2.6868(3)	I(2)–Pd(2)–C(2)	176.37	177.19(9)
Pd(1)–C(1)	2.159	2.127(3)	I(1)–Pd(1)–P(11)	99.72	100.04(2)
Pd(2)–C(2)	2.061	2.043(3)	I(1)–Pd(1)–P(12)	93.75	95.99(2)
Pd(1)–P(11)	2.441	2.3359(9)	I(2)–Pd(2)–P(21)	95.32	94.63(2)
Pd(1)–P(12)	2.362	2.2686(9)	I(2)–Pd(2)–P(22)	96.54	98.75(2)
Pd(2)–P(21)	2.373	2.2728(8)	P(11)–Pd(1)–P(12)	155.03	155.64(3)
Pd(2)–P(22)	2.396	2.3104(9)	P(11)–Pd(1)–C(1)	84.07	83.20(9)
C(1)–C(54)	1.614	1.588(4)	P(21)–Pd(2)–P(22)	166.60	163.58(3)
C(1)–C(11)	1.542	1.529(4)	P(21)–Pd(2)–C(2)	83.56	82.65(9)
C(1)–C(21)	1.545	1.530(4)	P(12)–Pd(1)–C(1)	86.11	85.13(9)
C(54)–C(53)	1.517	1.496(4)	P(22)–Pd(2)–C(2)	84.22	84.06(9)
C(53)–C(52)	1.360	1.345(4)	C(51)–C(2)–C(61)	123.01	123.6(3)
C(52)–C(51)	1.479	1.465(4)	C(21)–C(1)–C(54)	110.71	109.1(3)
C(51)–C(56)	1.474	1.465(4)	C(11)–C(1)–C(54)	107.93	107.8(2)
C(56)–C(55)	1.358	1.339(4)	C(11)–C(1)–C(21)	114.00	115.5(3)
C(55)–C(54)	1.519	1.508(4)	Pd(1)–C(1)–C(54)	104.33	103.74(19)
C(2)–C(51)	1.392	1.380(4)	C(51)–C(2)–Pd(2)	119.78	120.8(2)
C(2)–C(61)	1.489	1.481(4)	C(61)–C(2)–Pd(2)	117.08	115.6(2)

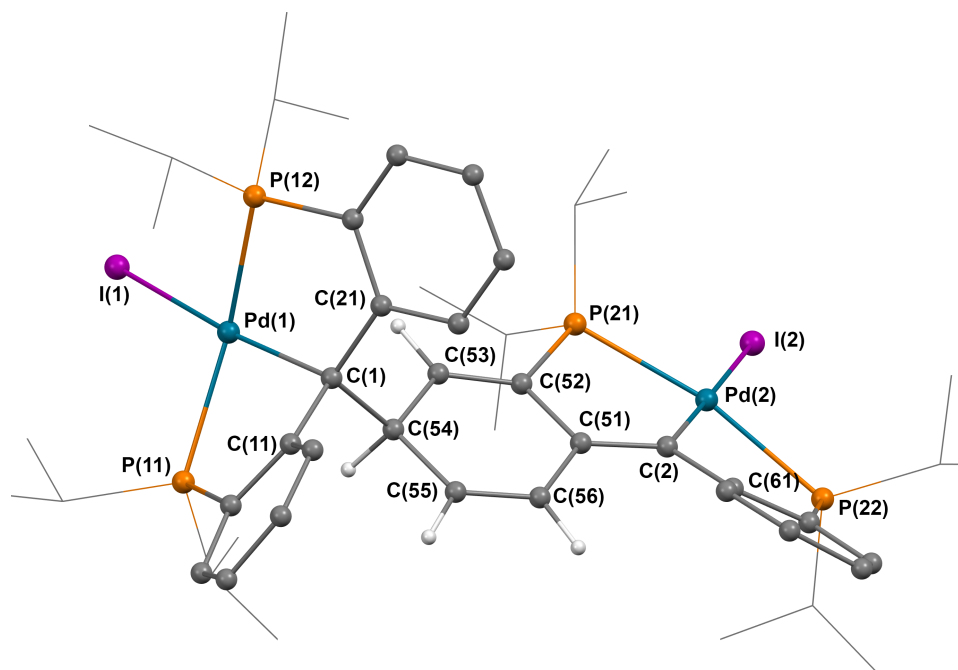


Figure S8. Optimized geometry for $\{[\text{PC}(\text{sp}^2)\text{P}]\text{PdI}\}_2$ (**2**)₂.

6.2 $\{p,p'\text{-[PC(sp}^2\text{)P]PdI}\}_2$ ($\{p,p'\text{-2}\}_2$)

Table S3. Optimized coordinates for $\{p,p'\text{-[PC(sp}^2\text{)P]PdI}\}_2$ ($\{p,p'\text{-2}\}_2$).

atom	x	y	z
C	-6.504565	2.938936	-0.215188
C	-5.144848	2.543000	-0.373098
C	-4.243832	3.516065	-0.896617
C	-4.653831	4.834257	-1.148796
C	-5.982300	5.228211	-0.894610
C	-6.905054	4.267314	-0.440585
C	-4.731525	1.143955	-0.080733
C	-3.426699	0.800089	0.264217
C	-2.979018	-0.606621	0.223070
C	-1.680873	-0.970150	0.397014
C	-0.561663	0.010605	0.682607
C	-1.113675	1.383522	0.989959
C	-2.401866	1.744303	0.750285
P	-4.369513	-1.805310	-0.174151
C	-3.861938	-2.642745	-1.820844
C	-4.797039	-3.822047	-2.168257
P	-7.699124	1.550877	0.189606
C	-9.118164	1.851080	-1.077246
C	-8.613055	1.487867	-2.491746
Pd	-6.204573	-0.302361	-0.104061
I	-8.130067	-2.314697	-0.082570
C	-4.402762	-3.173161	1.171112
C	-3.178795	-4.116471	1.190870
C	-8.418772	1.966759	1.929043
C	-7.308772	2.497050	2.863948
C	-9.115908	0.737554	2.557261
C	-10.416447	1.091825	-0.731032
C	-4.643035	-2.528586	2.554218
C	-3.839052	-1.587961	-2.949091
H	-7.941708	4.560661	-0.287722
H	-6.300935	6.250967	-1.079404
H	-3.941748	5.550424	-1.552796
H	-3.227043	3.224205	-1.135805
H	-6.516930	1.748304	2.996641
H	-6.848980	3.416152	2.485123
H	-7.738144	2.710450	3.852294
H	-9.159438	2.764130	1.761300

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Table S3. – continued from previous page

atom	x	y	z
H	-9.544596	1.021441	3.528573
H	-9.918766	0.334345	1.933802
H	-8.398164	-0.074133	2.721317
H	-9.316613	2.932491	-1.035073
H	-10.857376	1.431417	0.213721
H	-11.155874	1.270165	-1.524026
H	-10.239085	0.012437	-0.669043
H	-9.388337	1.728166	-3.232030
H	-8.397605	0.414826	-2.558269
H	-7.704982	2.041784	-2.759201
H	-5.298090	-3.749394	0.900940
H	-3.801895	-1.886811	2.847269
H	-4.751487	-3.315628	3.312656
H	-5.558438	-1.926639	2.556236
H	-2.280387	-3.602715	1.552884
H	-3.380328	-4.946659	1.882053
H	-2.960530	-4.554015	0.208949
H	-2.839028	-3.016306	-1.663326
H	-3.164644	-0.754375	-2.718861
H	-4.842520	-1.177521	-3.116195
H	-3.499527	-2.054789	-3.883707
H	-4.758793	-4.621506	-1.418635
H	-4.497119	-4.252154	-3.133643
H	-5.838463	-3.489995	-2.248086
H	-2.723795	2.748702	1.010580
H	-0.435569	2.104909	1.442607
H	-1.389849	-2.013791	0.312909
H	0.024864	-0.352333	1.542992
C	0.498783	0.042453	-0.537846
C	1.045446	-1.333837	-0.840886
H	-0.086691	0.404751	-1.398958
C	1.622769	1.017853	-0.252320
C	2.333173	-1.699775	-0.607015
C	2.918068	0.647882	-0.077124
C	3.366483	-0.756454	-0.138484
H	0.362800	-2.054275	-1.287995
H	1.337813	2.065861	-0.173869
H	2.647985	-2.706245	-0.867338
C	4.688925	-1.093682	0.140287
P	4.307167	1.858541	0.307908
C	5.127236	-2.494173	0.381314
C	6.472927	-2.886365	0.114307

Continued on next page

Table S3. – continued from previous page

atom	x	y	z
C	6.873646	-4.229079	0.238917
C	5.978358	-5.202797	0.720305
C	4.679217	-4.811748	1.099891
C	4.261127	-3.482592	0.933436
P	7.624913	-1.474522	-0.312923
H	7.886441	-4.523980	-0.021342
H	6.298481	-6.235979	0.828475
H	3.994355	-5.541009	1.526905
H	3.265465	-3.195884	1.254483
Pd	6.147696	0.363220	0.053007
C	3.902076	2.591340	2.043004
C	4.010631	3.264258	-0.973613
C	4.761446	4.571443	-0.644126
C	4.374567	2.744062	-2.382582
H	2.927894	3.455813	-0.933702
C	5.134057	3.309728	2.642530
H	3.092002	3.319032	1.878663
C	3.405602	1.488152	3.003621
C	8.296092	-1.874314	-2.064593
C	9.123641	-1.538804	0.885706
H	9.663279	-0.618204	0.625010
C	8.629410	-1.406133	2.342846
C	10.067406	-2.749286	0.713153
C	9.421307	-0.901448	-2.480349
H	8.698771	-2.896723	-2.001595
C	7.132522	-1.860895	-3.080021
I	8.169295	2.271460	-0.100392
H	7.503824	-2.160269	-4.069471
H	6.330155	-2.551572	-2.794021
H	6.704242	-0.854837	-3.167032
H	9.759565	-1.148891	-3.495978
H	9.066278	0.135370	-2.477581
H	10.291591	-0.956232	-1.815323
H	4.124394	3.507676	-3.131808
H	5.449130	2.537953	-2.450051
H	3.827173	1.827862	-2.635239
H	4.580303	5.298570	-1.447870
H	4.417072	5.023540	0.293586
H	5.841758	4.401348	-0.578544
H	10.977502	-2.579772	1.304899
H	9.607745	-3.673604	1.082440
H	10.377039	-2.903303	-0.327452

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Table S3. – continued from previous page

atom	x	y	z
H	9.492763	-1.344437	3.019076
H	8.030145	-0.498515	2.475127
H	8.024548	-2.271936	2.642270
H	4.863106	3.743123	3.615441
H	5.956213	2.601743	2.798220
H	5.516720	4.112263	2.005959
H	3.193470	1.930916	3.986321
H	2.492770	1.002741	2.642297
H	4.172837	0.715470	3.141101

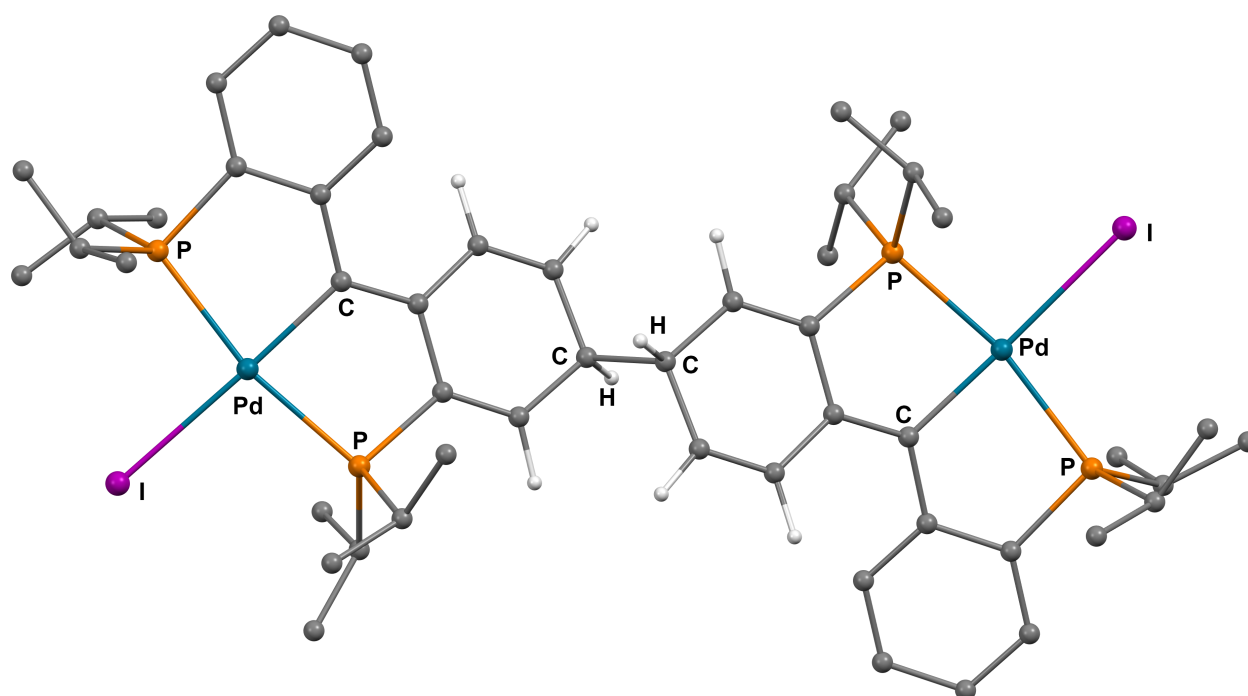


Figure S9. Optimized geometry for $\{p,p'-[PC(sp^2)P]PdI\}_2$ ($\{p,p'-2\}_2$).

6.3 [PC[•](sp²)P]PdI (2)

Table S4. Optimized coordinates for [PC[•](sp²)P]PdI (2).

atom	x	y	z
Pd	-0.047428	-0.336933	-0.021538
P	2.314178	-0.111216	-0.242191
P	-2.408665	-0.031872	0.252013
C	-0.015497	1.711373	-0.025248
I	-0.012672	-3.123864	-0.015889
C	1.234436	2.397589	0.305717
C	2.485282	1.702763	0.183669
C	3.706161	2.359810	0.402858
C	3.735091	3.703391	0.828783
C	2.515566	4.377781	1.050342
C	1.293030	3.745105	0.790881
H	0.369476	4.277140	0.993148
H	2.521079	5.398067	1.427987
H	4.684022	4.202265	1.007824
H	4.644528	1.833033	0.253272
C	-1.240699	2.425462	-0.389895
C	-1.255048	3.752748	-0.930795
C	-2.454871	4.395813	-1.261877
C	-3.694353	3.750346	-1.067033
C	-3.706489	2.427687	-0.579017
C	-2.508874	1.765863	-0.271768
H	-4.660794	1.919098	-0.457630
H	-4.625503	4.254142	-1.313199
H	-2.426501	5.398750	-1.682504
H	-0.314929	4.257147	-1.126741
C	-3.181593	-0.127689	2.015115
C	-2.764100	-1.436203	2.726011
C	-2.774311	1.101886	2.856756
H	-1.683070	1.157021	2.963408
H	-3.121474	2.041954	2.414576
H	-3.207327	1.014285	3.862547
H	-4.272451	-0.119097	1.866410
H	-3.252454	-1.488497	3.709008
H	-3.030742	-2.334556	2.161946
H	-1.678893	-1.462049	2.878093
C	-3.652360	-0.892521	-0.937133
C	-4.042252	-2.316526	-0.486624

Continued on next page

Table S4. – continued from previous page

atom	x	y	z
C	-3.067761	-0.893992	-2.367384
H	-4.551028	-0.257457	-0.917949
H	-4.562875	-2.319806	0.478529
H	-4.723385	-2.751704	-1.231064
H	-3.161141	-2.963906	-0.413881
H	-3.809627	-1.301689	-3.067644
H	-2.171573	-1.523839	-2.414154
H	-2.801718	0.115486	-2.703764
C	3.326479	-1.135174	1.027466
C	3.168314	-0.337316	-1.944102
H	3.069481	-2.166093	0.749269
C	2.785358	-0.874738	2.450487
H	2.948157	0.166805	2.757184
H	3.305694	-1.525528	3.166217
H	1.713506	-1.094085	2.510691
C	4.860185	-0.958781	0.960112
H	5.170772	0.013813	1.359208
H	5.335054	-1.731222	1.580692
H	5.258220	-1.064300	-0.056503
C	2.415096	0.480102	-3.016215
H	4.180786	0.078520	-1.829423
C	3.262448	-1.830179	-2.329213
H	2.356231	1.543471	-2.754478
H	1.393504	0.102557	-3.147309
H	2.937381	0.394056	-3.978750
H	3.871136	-2.407599	-1.622967
H	3.722952	-1.922379	-3.322394
H	2.268731	-2.291364	-2.365452

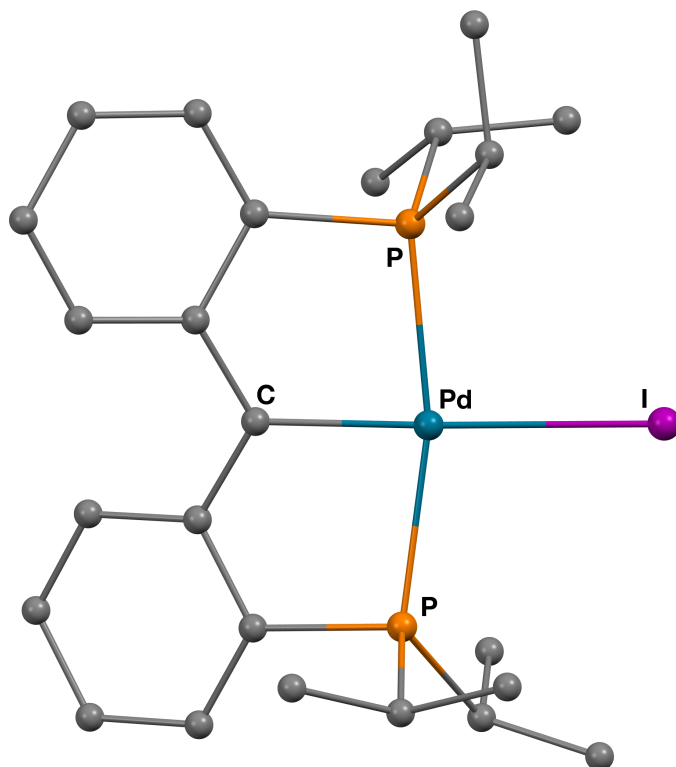


Figure S10. Optimized geometry for $[\text{PC}^\bullet(\text{sp}^2)\text{P}]\text{PdI}$ (**2**).

6.4 Calculated energies for $[\text{PC}^\bullet(\text{sp}^2)\text{P}]\text{PdI}$ (**2**) and corresponding dimers

		Energy (hartree)	Energy loss (kcal/mol)
$[\text{PC}^\bullet(\text{sp}^2)\text{P}]\text{PdI}$ (2)		-11125.396903	—
$\{[\text{PC}(\text{sp}^2)\text{P}]\text{PdI}\}_2$ ({2}) ₂)		-2250.785894	4.96
$\{p,p'\text{-}[\text{PC}(\text{sp}^2)\text{P}]\text{PdI}\}_2$ ({p,p'-2}) ₂)		-2250.76912	14.49

6.5 [Me₂PC[•](sp²)PMe₂]PdI (2')

Table S5. Optimized coordinates for [Me₂PC[•](sp²)PMe₂]PdI (2').

atom	x	y	z
C	-0.031108	-0.016835	0.015152
C	-0.027816	0.001792	1.416416
C	1.193959	0.065679	2.163228
C	2.408273	0.042061	1.396324
C	2.397381	0.044988	-0.005134
C	1.177432	0.027524	-0.711706
P	3.964051	-0.079648	2.424639
C	4.930817	1.514206	2.167430
C	1.259091	0.084204	3.627302
C	0.148662	0.520412	4.478642
C	0.111832	0.125723	5.859262
C	-0.939406	0.500212	6.707124
C	-1.982886	1.321845	6.233961
C	-1.938880	1.779904	4.900127
C	-0.901979	1.391728	4.041030
P	1.610572	-0.837920	6.423076
C	2.133249	-0.090356	8.065134
Pd	2.997657	-0.533349	4.533483
I	5.335609	-1.363243	5.751769
C	1.024366	-2.566868	6.879448
C	5.033808	-1.392731	1.612419
H	-0.971207	-0.080655	1.945104
H	-0.978725	-0.079179	-0.515589
H	1.170507	0.019796	-1.798454
H	3.334278	0.038643	-0.559384
H	-0.872176	1.798719	3.036159
H	-2.711155	2.453270	4.534449
H	-2.792334	1.619656	6.895195
H	-0.945927	0.176032	7.746295
H	5.907428	-1.564354	2.248248
H	4.463046	-2.323047	1.544357
H	5.353530	-1.082419	0.611087
H	3.071358	-0.561668	8.372965
H	2.308773	0.980234	7.927581
H	1.366927	-0.242412	8.833785
H	5.844394	1.471503	2.768654
H	5.187903	1.646393	1.110276

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Table S5. – continued from previous page

atom	x	y	z
H	4.322718	2.358235	2.504424
H	1.887394	-3.155526	7.205925
H	0.278664	-2.524993	7.681516
H	0.585607	-3.039203	5.996204

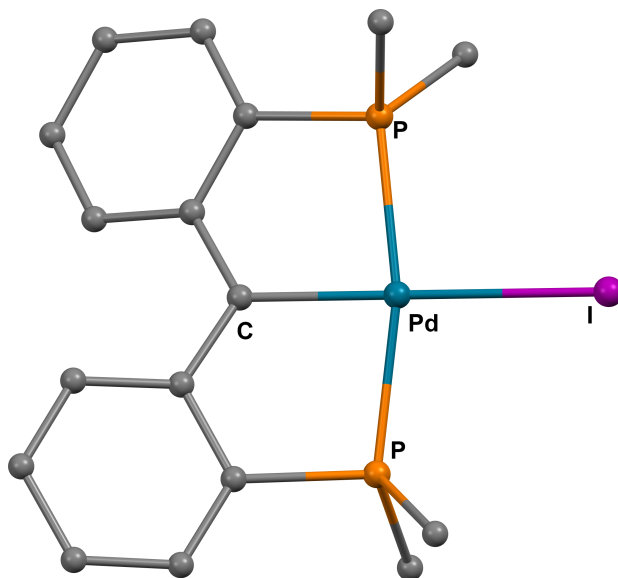


Figure S11. Optimized geometry for $[\text{Me}_2\text{PC}^*(\text{sp}^2)\text{PMe}_2]\text{PdI}$ (**2'**).

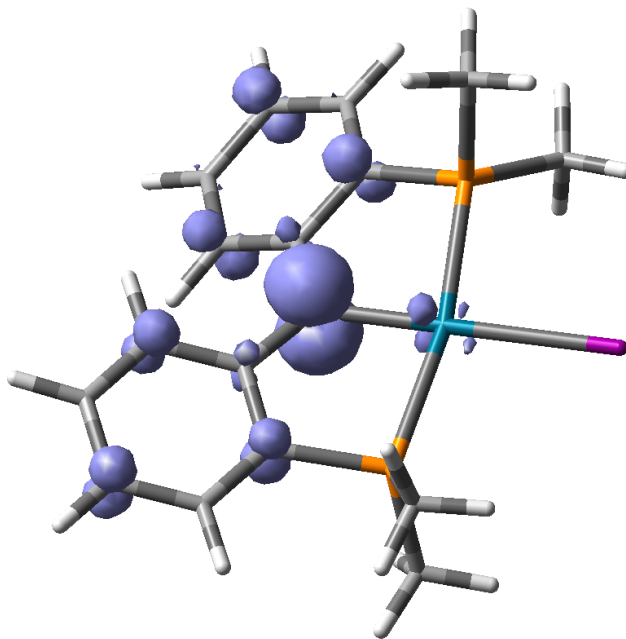


Figure S12. Spin density for $[\text{Me}_2\text{PC}^*(\text{sp}^2)\text{PMe}_2]\text{PdI}$ (**2'**).

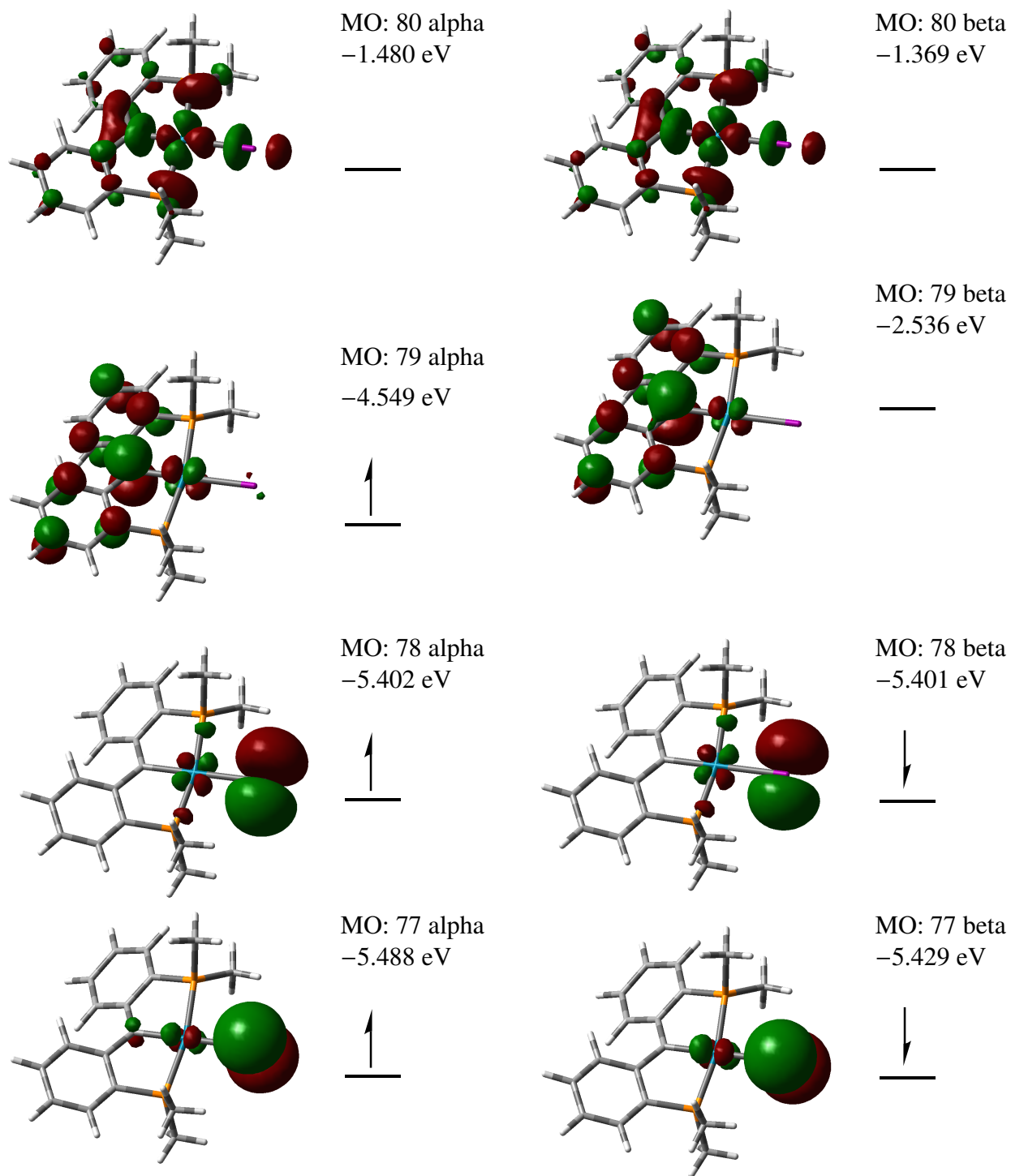


Figure S13. Frontier molecular orbitals for [Me₂PC[•](sp²)PMe₂]PdI (2').

6.6 [PC[•](sp²)P]PdBr (3)

Table S6. Optimized coordinates for [PC[•](sp²)P]PdBr (3).

atom	x	y	z
C	-2.523749	1.541582	-0.271242
C	-1.261254	2.213428	-0.391645
C	-1.289297	3.538012	-0.938071
C	-2.495517	4.166221	-1.275021
C	-3.728523	3.508164	-1.081302
C	-3.727625	2.188064	-0.586119
C	-0.028459	1.510623	-0.027427
C	1.219502	2.204678	0.297147
C	2.474169	1.513746	0.180991
C	3.692135	2.175566	0.401519
C	3.715486	3.521930	0.819041
C	2.492984	4.193933	1.031315
C	1.273045	3.555579	0.773115
P	2.308982	-0.301219	-0.239085
C	3.166509	-0.550215	-1.934379
C	3.227713	-2.049391	-2.303265
P	-2.403755	-0.251356	0.260331
C	-3.619073	-1.152046	-0.924006
C	-3.034300	-1.136957	-2.354268
Pd	-0.046341	-0.529920	-0.023534
Br	0.008132	-3.153402	-0.044946
C	3.296727	-1.332721	1.041652
C	4.832011	-1.167396	0.989924
C	-3.166599	-0.362507	2.026094
C	-2.801067	0.885640	2.859436
C	-2.692951	-1.651406	2.738379
C	-3.943000	-2.590503	-0.465363
C	2.741511	-1.067812	2.458457
C	2.430745	0.272359	-3.014701
H	0.347493	4.085940	0.970445
H	2.494078	5.216912	1.401677
H	4.662124	4.025003	0.998493
H	4.632366	1.649724	0.259227
H	-4.676136	1.668348	-0.465633
H	-4.664233	4.000378	-1.333551
H	-2.476941	5.167419	-1.700342
H	-0.354569	4.051791	-1.135462

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Table S6. – continued from previous page

atom	x	y	z
H	-1.712031	0.981955	2.960103
H	-3.184929	1.810010	2.414391
H	-3.225274	0.787271	3.868010
H	-4.257911	-0.396647	1.884825
H	-3.171338	-1.719665	3.725267
H	-2.928271	-2.560786	2.178205
H	-1.606297	-1.633423	2.881758
H	-4.543252	-0.554541	-0.906133
H	-4.472649	-2.611582	0.494774
H	-4.593519	-3.066087	-1.212320
H	-3.029757	-3.189828	-0.378127
H	-3.760286	-1.574672	-3.053077
H	-2.115610	-1.733829	-2.396726
H	-2.805274	-0.119699	-2.694494
H	3.032055	-2.361022	0.760585
H	2.908479	-0.027596	2.767559
H	3.248453	-1.722809	3.179994
H	1.667473	-1.279133	2.505219
H	5.144275	-0.190756	1.378311
H	5.295756	-1.933752	1.626299
H	5.240204	-1.289560	-0.020852
H	4.187249	-0.154289	-1.822663
H	2.393732	1.339245	-2.763272
H	1.401592	-0.085201	-3.142793
H	2.951517	0.166368	-3.976060
H	3.837270	-2.628528	-1.599084
H	3.671009	-2.162137	-3.302062
H	2.225065	-2.492266	-2.317080

Table S7. Selected distances (Å) and angles (°) for the optimized geometry and the crystal structure of [PC[•](sp²)P]PdBr (**3**).

Distance	Calcd.	X-Ray	Angle	Calcd.	X-Ray
Pd–Br	2.624	2.5117(4)	P(1)–Pd–P(2)	167.68	166.96(3)
Pd–P(1)	2.376	2.2891(7)	C–Pd–Br	178.21	175.31(15)
Pd–P(2)	2.391	2.2783(7)	P(2)–Pd–Br	94.30	94.93(2)
Pd–C	2.041	2.020(3)	C(11)–C–C(21)	123.01	123.0(3)
C–C(11)	1.464	1.467(4)	C(11)–C–Pd	118.75	118.1(2)
C–C(21)	1.465	1.463(4)	C(21)–C–Pd	118.22	118.7(2)

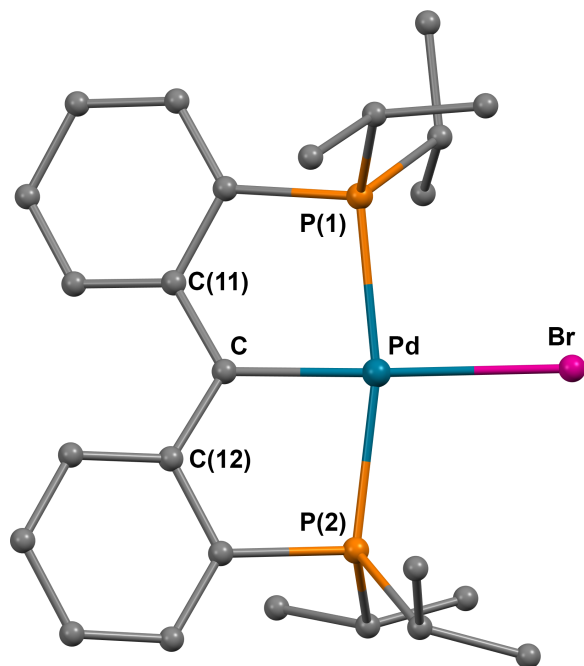


Figure S14. Optimized geometry for $[\text{PC}^*(\text{sp}^2)\text{P}]\text{PdBr}$ (**3**).

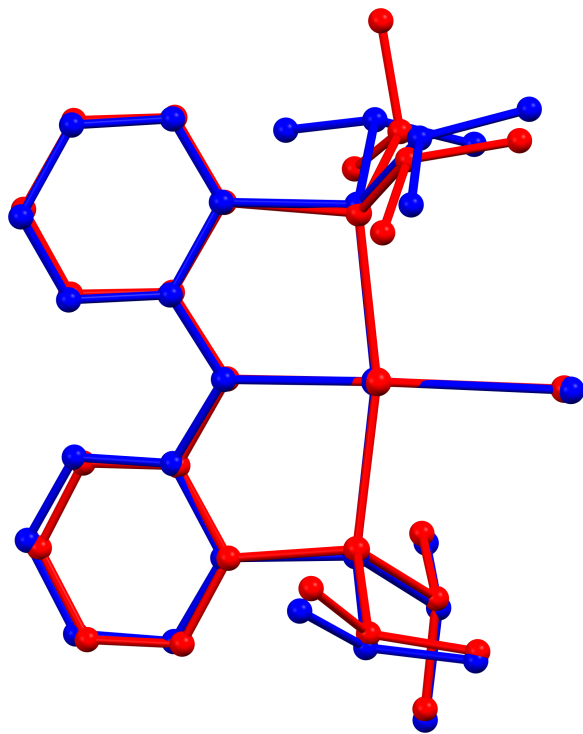


Figure S15. Overlaid structures for $[\text{PC}^*(\text{sp}^2)\text{P}]\text{PdBr}$ (**3**) (red: X-ray, blue: optimized).

6.7 {[PC(sp²)P]PdBr}₂ ({**3**)₂)

Table S8. Optimized coordinates for {[PC(sp²)P]PdBr}₂ ({**3**)₂).

atom	x	y	z
C	-3.431432	2.782678	2.270227
C	-3.989782	1.971788	1.239762
C	-5.386126	2.123303	0.984168
C	-6.142484	3.108925	1.643392
C	-5.551616	3.941078	2.612366
C	-4.194673	3.752875	2.938406
C	-3.199677	0.931763	0.522721
Pd	-4.241630	-0.646222	-0.278539
Br	-5.509009	-2.627472	-1.437927
P	-6.123117	0.818805	-0.139754
C	-6.682432	1.675145	-1.763587
C	-7.727230	2.793458	-1.558236
C	-1.825991	1.030398	0.312579
C	-1.029957	-0.147084	-0.100506
C	0.325810	-0.124565	-0.210948
C	1.162947	1.135268	-0.093767
C	0.296949	2.334375	0.247984
C	-1.046725	2.275750	0.431637
C	2.504065	0.967159	0.793735
C	3.190639	2.347233	0.892750
C	3.764978	2.946103	-0.271916
C	4.234630	4.271901	-0.244143
C	4.216617	5.023020	0.946109
C	3.733211	4.418927	2.118968
C	3.222082	3.108209	2.086453
P	4.066886	1.798440	-1.735643
C	3.086635	2.438888	-3.290261
C	2.560581	1.225323	-4.092354
P	-2.106266	-1.655671	-0.420447
C	-1.701657	-2.357531	-2.158858
C	-0.311028	-3.012815	-2.302456
Pd	3.824367	-0.230337	-0.405522
Br	5.216833	-1.882483	-1.913905
P	4.057044	-1.607859	1.490614
C	2.808426	-0.835159	2.645689
C	2.512176	-1.358081	3.923632
C	1.532266	-0.762064	4.733001

Continued on next page

Table S8. – continued from previous page

atom	x	y	z
C	0.846814	0.368614	4.251055
C	1.164935	0.905947	2.993825
C	2.163312	0.332287	2.161914
C	5.882143	2.209222	-2.244929
C	6.863183	1.883748	-1.099904
C	5.727474	-1.476251	2.430409
C	6.858217	-2.220484	1.686543
C	3.732561	-3.489931	1.298626
C	3.920548	-4.339947	2.575175
C	6.080338	0.007490	2.670706
C	2.348009	-3.723923	0.663902
C	6.281736	1.470593	-3.542596
C	1.963812	3.452245	-2.983314
C	-1.614369	-2.991035	0.856627
C	-2.357814	-4.315992	0.573143
C	-7.724386	0.263767	0.757648
C	-7.347854	-0.509266	2.041498
C	-8.624359	-0.585772	-0.167744
C	-5.443327	2.190055	-2.528225
C	-1.892523	-2.473589	2.284678
C	-1.931153	-1.264211	-3.225244
H	5.551648	-1.957334	3.404502
H	5.299346	0.528835	3.236470
H	6.221073	0.535701	1.720475
H	7.016177	0.074118	3.242118
H	7.805280	-2.071936	2.223232
H	6.975343	-1.844862	0.663946
H	6.676787	-3.300128	1.622454
H	4.495381	-3.771065	0.560240
H	2.262135	-3.199916	-0.294130
H	1.545586	-3.385580	1.331890
H	2.203948	-4.796737	0.477008
H	3.111572	-4.170391	3.295796
H	3.894654	-5.403894	2.301806
H	4.878582	-4.154980	3.075392
H	5.889717	3.294636	-2.432297
H	5.643286	1.734749	-4.394758
H	6.240285	0.385333	-3.399446
H	7.312930	1.742776	-3.807405
H	6.601706	2.404671	-0.171295
H	6.877746	0.804599	-0.908802
H	7.877845	2.191559	-1.388561

Continued on next page

Table S8. – continued from previous page

atom	x	y	z
H	3.850469	2.951678	-3.891642
H	1.538997	3.811257	-3.931393
H	2.329211	4.322227	-2.426534
H	1.146442	3.003589	-2.408399
H	2.117287	1.566388	-5.038179
H	1.785787	0.688172	-3.530146
H	3.354847	0.506108	-4.322571
H	0.625101	1.778729	2.645535
H	0.071237	0.835371	4.854201
H	1.303050	-1.174179	5.712568
H	3.044162	-2.230718	4.290999
H	1.555916	1.328607	-1.103740
H	2.841653	2.678897	3.005830
H	3.743532	4.965971	3.059206
H	4.597684	6.040953	0.959916
H	4.656645	4.717119	-1.142792
H	0.795337	3.300919	0.280517
H	0.877617	-1.032051	-0.447840
H	-1.590110	3.200862	0.599579
H	-2.402448	2.621584	2.572657
H	-3.735702	4.349992	3.723430
H	-6.145846	4.692039	3.126750
H	-7.204164	3.213589	1.433879
H	-8.257036	1.184350	1.038674
H	-8.090925	-1.474825	-0.522932
H	-9.510133	-0.915453	0.392658
H	-8.975462	-0.023037	-1.042013
H	-4.721227	1.385110	-2.705890
H	-4.935043	2.987381	-1.969836
H	-5.750551	2.599463	-3.500277
H	-7.300574	3.636384	-1.000643
H	-8.050835	3.174990	-2.536456
H	-8.621471	2.441828	-1.028826
H	-6.824575	-1.439142	1.788988
H	-6.703874	0.081640	2.704409
H	-8.260073	-0.769570	2.595629
H	-0.533276	-3.142567	0.738256
H	-1.568785	-3.225347	3.017800
H	-1.355370	-1.540991	2.494222
H	-2.964846	-2.293344	2.431145
H	-2.103409	-5.050283	1.349875
H	-3.444166	-4.169029	0.578479

Continued on next page

Table S8. – continued from previous page

atom	x	y	z
H	-7.133531	0.856267	-2.340713
H	-2.481365	-3.120613	-2.285912
H	-1.224855	-0.432234	-3.105089
H	-2.951811	-0.870216	-3.169278
H	-1.785432	-1.692672	-4.225989
H	-0.115227	-3.767619	-1.531441
H	0.493658	-2.268686	-2.272971
H	-0.251025	-3.516548	-3.277135
H	-2.085458	-4.747039	-0.397843

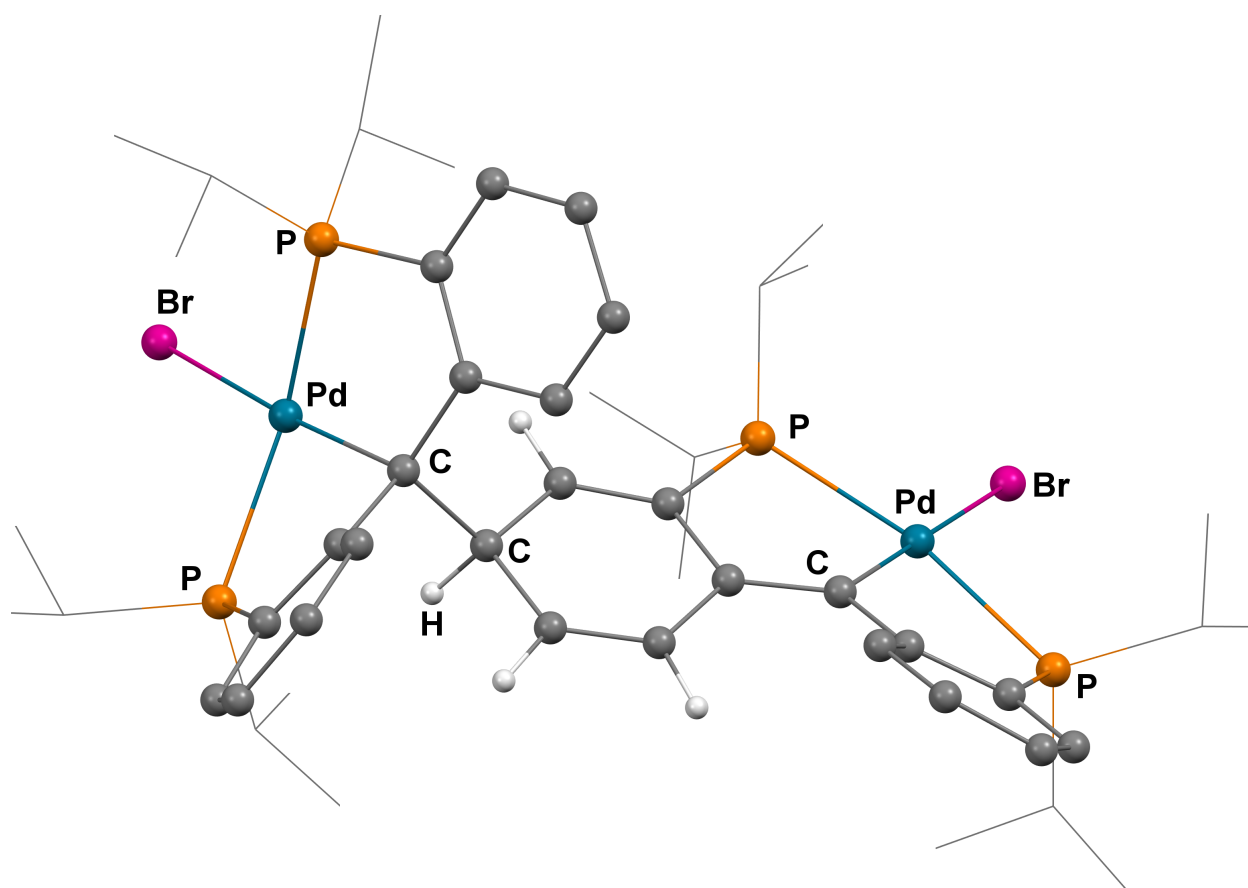


Figure S16. Optimized geometry for {[PC(sp²)P]PdBr₂]₂ (**3**)₂).

6.8 $\{p,p'\text{-[PC(sp}^2\text{)P]PdBr}}\}_2$ ($\{p,p'\text{-3}\}_2$)

Table S9. Optimized coordinates for $\{p,p'\text{-[PC(sp}^2\text{)P]PdBr}}\}_2$ ($\{p,p'\text{-3}\}_2$).

atom	x	y	z
C	4.425733	-3.350583	0.929137
C	5.237183	-2.318765	0.373617
C	6.597136	-2.646500	0.088081
C	7.062208	-3.969405	0.199609
C	6.219128	-4.987464	0.683536
C	4.907769	-4.659882	1.080595
C	4.730695	-0.937510	0.148535
Pd	6.117148	0.577009	0.044784
Br	7.940470	2.453070	-0.159100
P	7.676352	-1.178357	-0.335792
C	9.172361	-1.154068	0.864840
C	10.176051	-2.317302	0.705189
C	3.390177	-0.656824	-0.109501
C	2.391062	-1.641561	-0.566267
C	1.087391	-1.328006	-0.788411
C	0.487926	0.026057	-0.485373
C	1.573424	1.045915	-0.206589
C	2.883840	0.728317	-0.041791
C	-0.567863	-0.045596	0.737476
C	-1.655681	-1.059923	0.445908
C	-2.961425	-0.733073	0.255992
C	-3.449664	0.661437	0.294283
C	-2.458787	1.632586	0.796616
C	-1.163423	1.307975	1.049225
C	-4.760356	0.969470	-0.064135
Pd	-6.182342	-0.514077	-0.118789
Br	-7.934872	-2.467739	-0.142885
P	-4.314171	-1.966422	-0.161915
C	-4.360977	-3.330771	1.183977
C	-4.644842	-2.688859	2.559907
P	4.226745	1.993521	0.324179
C	3.892003	3.381223	-0.963728
C	4.243755	2.850468	-2.371980
C	-5.213805	2.357319	-0.356475
C	-6.588913	2.708440	-0.219725
C	-7.031084	4.021480	-0.455877
C	-6.133683	5.012617	-0.895884

Continued on next page

Table S9. – continued from previous page

atom	x	y	z
C	-4.788000	4.664069	-1.124338
C	-4.337519	3.360641	-0.863783
P	-7.737730	1.279571	0.167574
C	-8.489608	1.639476	1.904400
C	-9.101160	0.358241	2.518860
C	-3.776406	-2.804835	-1.796481
C	-3.732150	-1.752710	-2.926501
C	-4.716790	-3.978328	-2.152355
C	-9.158878	1.509396	-1.106327
C	-10.393142	0.639309	-0.782952
C	-8.617670	1.211586	-2.522814
C	-3.123656	-4.254896	1.231571
C	-7.420900	2.237125	2.846766
C	3.828665	2.729037	2.058271
C	3.356501	1.625813	3.030845
C	8.376566	-1.514262	-2.086804
C	7.218588	-1.559705	-3.107625
C	5.063548	3.461533	2.635751
C	4.647174	4.691521	-0.654443
C	9.434481	-0.456983	-2.475096
C	8.669137	-1.030552	2.319791
H	-8.080364	4.277813	-0.323712
H	-6.483626	6.023465	-1.089405
H	-4.093588	5.403944	-1.516227
H	-3.307467	3.103790	-1.085677
H	-6.577271	1.545350	2.970118
H	-7.028079	3.191358	2.479271
H	-7.864044	2.406827	3.837506
H	-9.283520	2.384438	1.740393
H	-9.566489	0.605284	3.483335
H	-9.858986	-0.103148	1.879744
H	-8.325676	-0.396394	2.693052
H	-9.442225	2.571159	-1.045160
H	-10.871169	0.932353	0.159466
H	-11.136181	0.761068	-1.583125
H	-10.123305	-0.421494	-0.725974
H	-9.402536	1.409472	-3.265552
H	-8.325342	0.158144	-2.606660
H	-7.749487	1.833719	-2.771778
H	-5.243049	-3.916917	0.892242
H	-3.823696	-2.030290	2.871904
H	-4.756286	-3.476777	3.317047

Continued on next page

Table S9. – continued from previous page

atom	x	y	x
H	-5.571764	-2.105508	2.537611
H	-2.238253	-3.722512	1.599360
H	-3.320820	-5.081140	1.928717
H	-2.885559	-4.698729	0.257024
H	-2.758200	-3.184667	-1.624196
H	-3.060872	-0.919372	-2.686210
H	-4.732018	-1.341636	-3.112692
H	-3.376556	-2.222163	-3.853786
H	-4.678779	-4.783935	-1.409214
H	-4.420742	-4.401612	-3.121860
H	-5.757383	-3.641386	-2.225219
H	-2.812943	2.625588	1.058875
H	-0.511408	2.045854	1.513498
H	-1.334475	-2.095343	0.366332
H	0.030990	-0.393006	1.595454
H	-0.114596	0.363408	-1.344986
H	0.430238	-2.076748	-1.227189
H	1.248299	2.082241	-0.126782
H	2.742808	-2.635187	-0.828399
H	8.085512	-4.212921	-0.072681
H	6.588286	-6.005257	0.780807
H	4.262787	-5.423216	1.510182
H	3.421973	-3.113524	1.265103
H	2.808768	3.568143	-0.910841
H	3.010048	3.448672	1.901641
H	9.664091	-0.209827	0.594574
H	8.847150	-2.507975	-2.040355
H	7.613099	-1.813460	-4.100835
H	6.463854	-2.308869	-2.839270
H	6.723279	-0.583466	-3.176776
H	9.773722	-0.641483	-3.503584
H	9.016179	0.554799	-2.423262
H	10.315371	-0.486127	-1.822189
H	3.978135	3.604222	-3.125855
H	5.319766	2.654585	-2.447539
H	3.703000	1.926340	-2.609590
H	4.460998	5.410622	-1.464191
H	4.311074	5.154042	0.281262
H	5.727523	4.517363	-0.595684
H	11.070714	-2.103546	1.306078
H	9.757116	-3.262409	1.070668
H	10.503169	-2.457212	-0.332294

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Table S9. – continued from previous page

atom	x	y	z
H	9.526915	−0.917211	2.996497
H	8.023767	−0.153280	2.439655
H	8.108467	−1.922540	2.628555
H	4.804383	3.895935	3.611364
H	5.894767	2.761587	2.779647
H	5.428035	4.264662	1.989493
H	3.153047	2.071041	4.014271
H	2.444086	1.128914	2.684210
H	4.133670	0.861774	3.161654

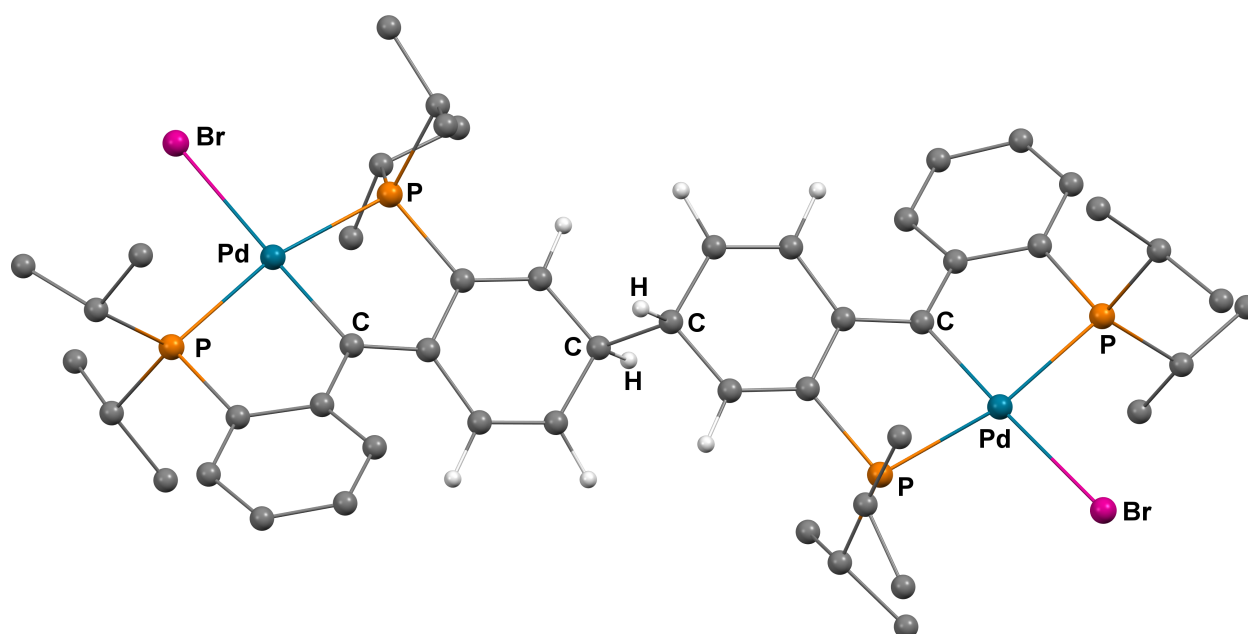
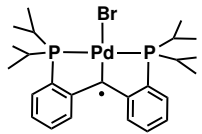
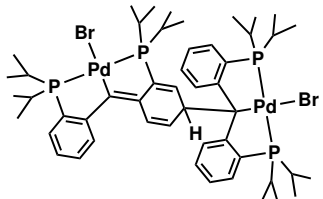
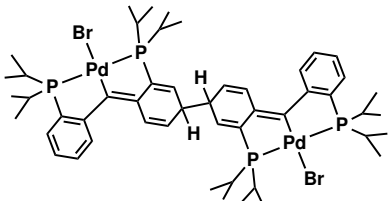


Figure S17. Optimized geometry for $\{p,p'\text{-[PC(sp}^2\text{)P]PdBr}\}_2$ ($\{p,p'\text{-3}\}_2$).

6.9 Calculated energies for $[\text{PC}^\bullet(\text{sp}^2)\text{P}]\text{PdBr}$ (**3**) and corresponding dimers

		Energy (hartree)	Energy loss (kcal/mol)
$[\text{PC}^\bullet(\text{sp}^2)\text{P}]\text{PdBr}$ (3)		-1127.178084	—
$\{[\text{PC}(\text{sp}^2)\text{P}]\text{PdBr}\}_2$ (3) ₂)		-2254.345893	6.45
$\{p,p'-[\text{PC}(\text{sp}^2)\text{P}]\text{PdBr}\}_2$ (p,p'-3) ₂)		-2254.328477	17.38

6.10 [Me₂PC[•](sp²)PMe₂]PdBr (3')

Table S10. Optimized coordinates for [Me₂PC[•](sp²)PMe₂]PdBr (3').

atom	x	y	z
C	0.001362	0.001603	-0.006068
C	0.000391	0.002264	1.427140
C	1.289194	0.001383	2.062617
C	2.477383	0.081278	1.323694
C	2.443074	0.123262	-0.085181
C	1.194343	0.060512	-0.739119
C	-1.214015	-0.064724	2.245777
Pd	-1.052732	-0.760324	4.164700
Br	-0.847494	-1.645464	6.605170
P	1.227598	-0.198378	3.919299
C	1.890658	1.391457	4.676455
C	-2.537804	0.340116	1.762952
C	-2.750335	1.253315	0.678985
C	-4.039896	1.611019	0.262912
C	-5.179939	1.079482	0.902188
C	-5.003560	0.212707	2.000122
C	-3.716739	-0.132846	2.434713
P	-3.371079	-1.158327	3.957828
C	-4.507945	-0.522265	5.310329
C	-3.999245	-2.898788	3.616191
C	2.516010	-1.488072	4.369837
H	-1.895723	1.716005	0.197422
H	-4.159793	2.317846	-0.555374
H	-6.178305	1.354497	0.572368
H	-5.878205	-0.170325	2.522988
H	-0.938508	-0.093345	-0.538960
H	1.154104	0.044411	-1.826177
H	3.365633	0.175246	-0.657310
H	3.438874	0.089738	1.834154
H	-4.238382	-1.024743	6.244133
H	-4.346209	0.552303	5.433201
H	-5.560578	-0.711864	5.071137
H	2.414546	-1.710734	5.436263
H	2.316924	-2.401454	3.802342
H	3.530413	-1.133562	4.154183
H	-3.792799	-3.524399	4.490248
H	-5.075916	-2.891020	3.411535

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Table S10. – continued from previous page

atom	x	y	z
H	-3.465821	-3.306945	2.753251
H	1.849303	1.304926	5.766771
H	2.923334	1.573472	4.357684
H	1.258275	2.226385	4.362150

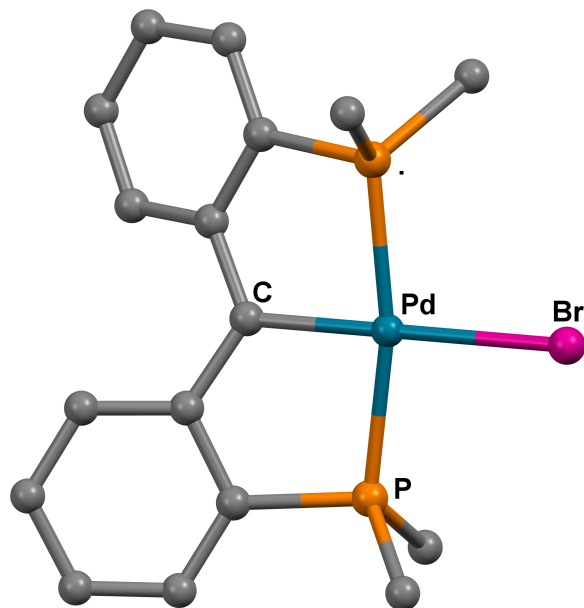


Figure S18. Optimized geometry for $[\text{Me}_2\text{PC}^\bullet(\text{sp}^2)\text{PMe}_2]\text{PdBr}$ (**3'**).

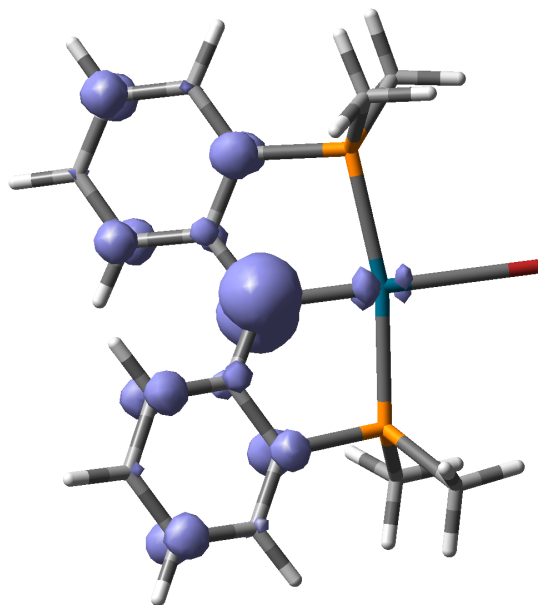


Figure S19. Spin density for $[\text{Me}_2\text{PC}^\bullet(\text{sp}^2)\text{PMe}_2]\text{PdBr}$ (**3'**).

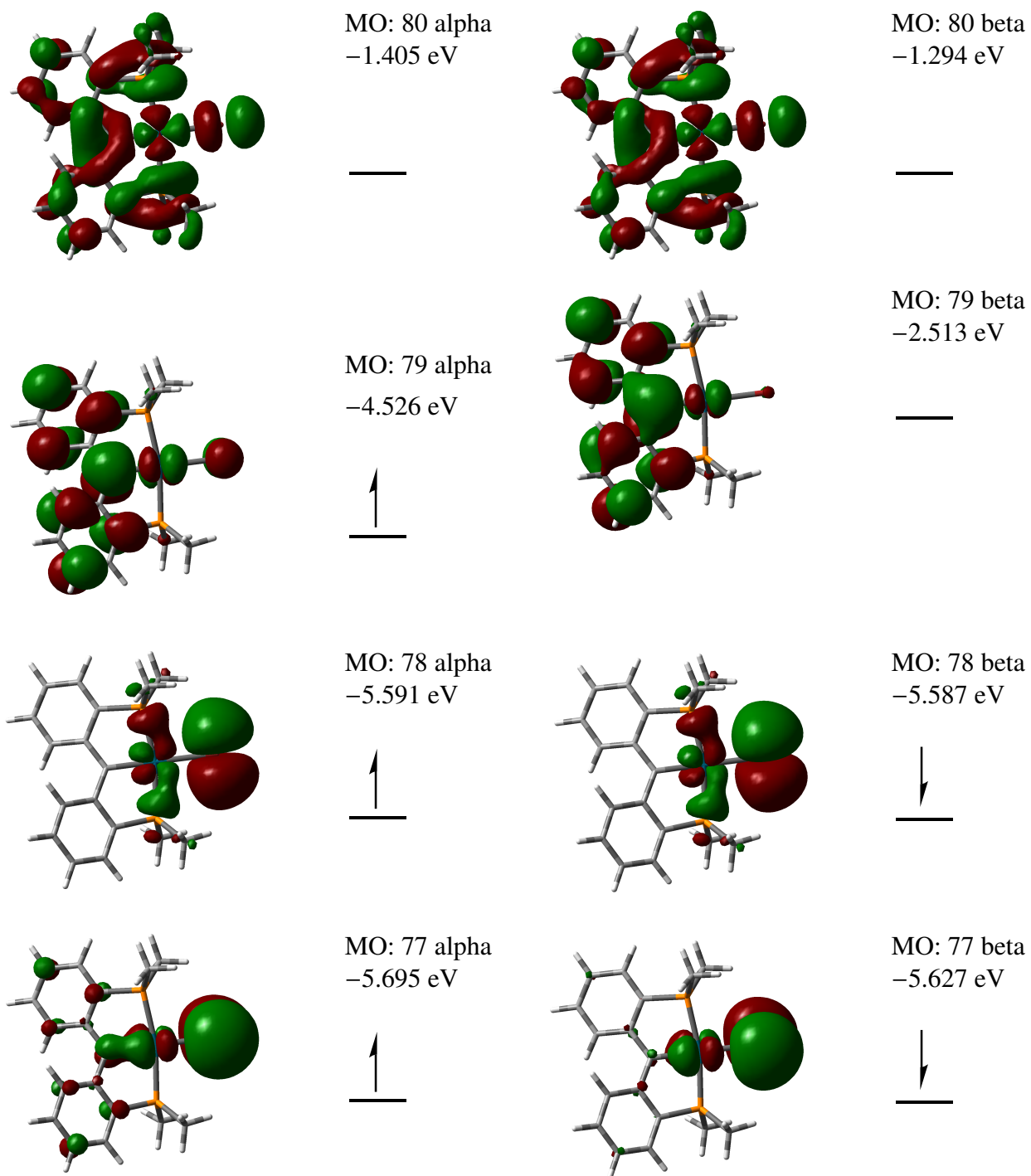


Figure S20. Frontier molecular orbitals for [Me₂PC[•](sp²)PMe₂]PdBr (**3'**).

6.11 [PC•(sp²)P]PdCl (5)

Table S11. Optimized coordinates for [PC•(sp²)P]PdCl (5).

atom	x	y	z
C	-2.533971	1.317523	-0.266066
C	-1.276613	2.002126	-0.381027
C	-1.317489	3.328138	-0.922988
C	-2.529122	3.943827	-1.264003
C	-3.756008	3.271553	-1.080027
C	-3.743198	1.950522	-0.587457
C	-0.036888	1.307492	-0.021397
C	1.210155	2.006726	0.299085
C	2.468125	1.319926	0.180852
C	3.684039	1.984012	0.405396
C	3.703519	3.329690	0.825414
C	2.478912	3.998264	1.036228
C	1.260641	3.357128	0.776359
P	2.306607	-0.493531	-0.243779
C	3.153001	-0.758939	-1.940420
C	3.168282	-2.261472	-2.303566
P	-2.395244	-0.473786	0.261194
C	-3.570697	-1.414321	-0.928161
C	-3.012741	-1.331691	-2.366903
Pd	-0.041496	-0.726136	-0.025537
Cl	0.029648	-3.206109	-0.070665
C	3.278905	-1.540088	1.034736
C	4.815410	-1.388433	0.987768
C	-3.165882	-0.623611	2.020721
C	-2.907256	0.652684	2.850766
C	-2.600510	-1.869723	2.743184
C	-3.775911	-2.882811	-0.492563
C	2.719872	-1.278391	2.450610
C	2.432125	0.080275	-3.017954
H	0.333850	3.884866	0.974920
H	2.476975	5.020841	1.407749
H	4.648527	3.834812	1.007704
H	4.625508	1.459658	0.264579
H	-4.685744	1.418015	-0.474936
H	-4.695424	3.753915	-1.337503
H	-2.519346	4.946571	-1.686032
H	-0.387943	3.852978	-1.115633

Continued on next page

Table S11. – continued from previous page

atom	x	y	z
H	-1.830201	0.836558	2.958500
H	-3.360276	1.542000	2.399371
H	-3.328785	0.524418	3.857174
H	-4.249553	-0.744180	1.869213
H	-3.103586	-1.989938	3.712713
H	-2.729951	-2.791851	2.169417
H	-1.525746	-1.751187	2.924667
H	-4.534487	-0.884190	-0.882183
H	-4.283707	-2.962136	0.476519
H	-4.402154	-3.393820	-1.236816
H	-2.815521	-3.408143	-0.432165
H	-3.718952	-1.805774	-3.062262
H	-2.056689	-1.863940	-2.435628
H	-2.859468	-0.295266	-2.691025
H	3.003600	-2.563860	0.747224
H	2.892293	-0.241101	2.766443
H	3.218853	-1.941066	3.170762
H	1.644255	-1.482737	2.490256
H	5.134809	-0.411553	1.370286
H	5.271462	-2.154424	1.630145
H	5.224961	-1.520403	-0.021317
H	4.185007	-0.391183	-1.836821
H	2.427221	1.148688	-2.770274
H	1.392196	-0.248506	-3.136198
H	2.941822	-0.043757	-3.983062
H	3.774768	-2.852566	-1.606568
H	3.591498	-2.390384	-3.309010
H	2.154095	-2.677911	-2.296934

Table S12. Selected distances (Å) and angles (°) for the optimized geometry and the crystal structure of [PC⁺(sp²)P]PdCl (**5**).

Distance	Calcd.	X-Ray	Angle	Calcd.	X-Ray
Pd–Cl	2.481	2.3884(6)	P(1)–Pd–P(2)	168.18	165.30(2)
Pd–P(1)	2.370	2.2751(6)	C–Pd–Cl	178.00	175.61(8)
Pd–P(2)	2.385	2.2977(6)	P(1)–Pd–Cl	93.90	94.32(2)
Pd–C	2.034	2.005(2)	C(11)–C–C(21)	123.18	122.2(2)
C–C(11)	1.465	1.461(3)	C(11)–C–Pd	118.66	118.78(17)
C–C(21)	1.466	1.446(3)	C(21)–C–Pd	118.13	118.87(17)

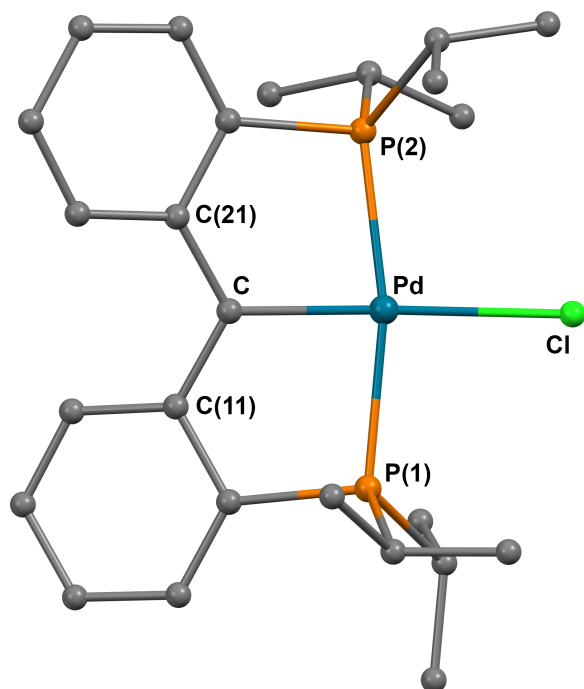


Figure S21. Optimized geometry for $[\text{PC}^*(\text{sp}^2)\text{P}]\text{PdCl}$ (**5**).

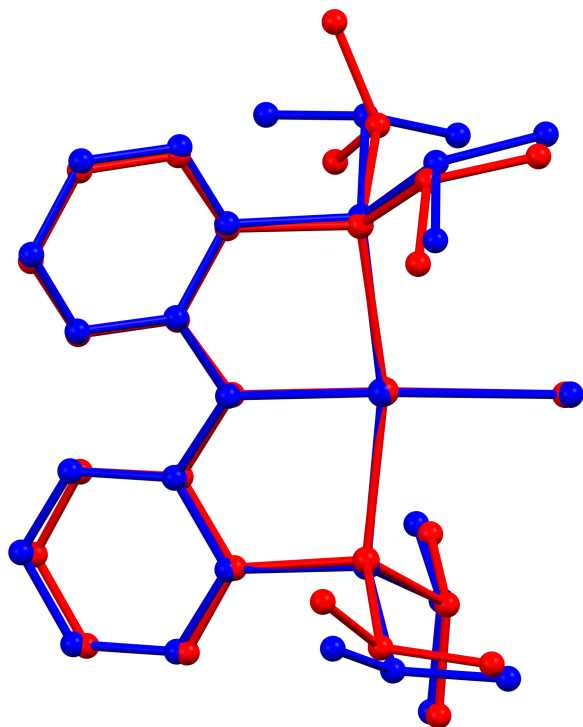


Figure S22. Overlaid structures for $[\text{PC}^*(\text{sp}^2)\text{P}]\text{PdCl}$ (**5**) (red: Xray, blue: optimized).

6.12 {[PC(sp²)P]PdCl}₂ ({5}₂)

Table S13. Optimized coordinates for {[PC(sp²)P]PdCl}₂ ({5}₂).

atom	x	y	z
C	3.526384	-2.022297	2.738419
C	4.048486	-1.467370	1.534512
C	5.440754	-1.663742	1.282779
C	6.228282	-2.459321	2.133642
C	5.673382	-3.045702	3.286724
C	4.321119	-2.801223	3.594380
C	3.230291	-0.622338	0.618639
Pd	4.237998	0.752416	-0.512651
Cl	5.388394	2.411704	-1.957049
P	6.125119	-0.661553	-0.142840
C	6.607234	-1.880863	-1.544084
C	7.679294	-2.914385	-1.135847
C	1.854280	-0.773441	0.460540
C	1.042092	0.274098	-0.200373
C	-0.310985	0.201241	-0.319007
C	-1.129534	-1.015821	0.068358
C	-0.253746	-2.080791	0.704555
C	1.088066	-1.962217	0.874243
C	-2.498545	-0.669427	0.852853
C	-3.174567	-1.999505	1.253282
C	-3.709082	-2.862566	0.245482
C	-4.179428	-4.147628	0.571670
C	-4.196995	-4.596800	1.905497
C	-3.749580	-3.729627	2.916421
C	-3.240244	-2.458763	2.591016
P	-3.966925	-2.095991	-1.455342
C	-2.919354	-3.065416	-2.778788
C	-2.333555	-2.061025	-3.799419
P	2.099583	1.701476	-0.818418
C	1.709868	2.054235	-2.660854
C	0.316013	2.654446	-2.943108
Pd	-3.803432	0.182788	-0.612205
Cl	-5.203693	1.318773	-2.337194
P	-4.112151	1.959200	0.893008
C	-2.880106	1.511530	2.222896
C	-2.624690	2.327152	3.347488
C	-1.660261	1.956440	4.297855

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Table S13. – continued from previous page

atom	x	y	z
C	-0.949298	0.755824	4.113584
C	-1.225569	-0.068249	3.011289
C	-2.206796	0.274788	2.043315
C	-5.761667	-2.617317	-1.923291
C	-6.779441	-2.053202	-0.910180
C	-5.808005	2.038827	1.792515
C	-6.916651	2.583001	0.863607
C	-3.810095	3.732596	0.228969
C	-3.954264	4.871417	1.262510
C	-6.173886	0.649542	2.357415
C	-2.455782	3.797627	-0.503258
C	-6.105815	-2.164213	-3.361486
C	-1.826506	-3.985666	-2.194161
C	1.624294	3.263899	0.176797
C	2.398878	4.491414	-0.356022
C	7.760638	0.096037	0.503131
C	7.439633	1.142687	1.593851
C	8.565889	0.724279	-0.657925
C	5.336122	-2.567510	-2.090035
C	1.893087	3.025361	1.678395
C	1.967275	0.782231	-3.498135
H	-5.661815	2.732892	2.634438
H	-5.394843	0.253182	3.019166
H	-6.330942	-0.069730	1.545692
H	-7.105658	0.722531	2.934683
H	-7.878159	2.558289	1.394631
H	-7.005234	1.977357	-0.045423
H	-6.732928	3.619402	0.555598
H	-4.603711	3.820129	-0.524978
H	-2.412295	3.057027	-1.308642
H	-1.621495	3.624324	0.188953
H	-2.324380	4.792707	-0.949932
H	-3.112832	4.883489	1.965550
H	-3.953170	5.835863	0.736149
H	-4.887822	4.812450	1.835108
H	-5.772227	-3.717868	-1.875686
H	-5.430492	-2.590715	-4.114000
H	-6.070520	-1.071818	-3.438616
H	-7.124230	-2.494731	-3.608737
H	-6.566758	-2.379643	0.114723
H	-6.776009	-0.957708	-0.942440
H	-7.788385	-2.398990	-1.175007

Continued on next page

Table S13. – continued from previous page

atom	x	y	x
H	-3.657484	-3.697245	-3.292118
H	-1.367022	-4.559037	-3.011665
H	-2.228032	-4.698517	-1.465415
H	-1.028107	-3.417128	-1.704410
H	-1.855354	-2.603719	-4.626605
H	-1.573264	-1.423972	-3.329503
H	-3.102716	-1.401551	-4.217588
H	-0.665504	-0.988724	2.892819
H	-0.186267	0.457693	4.829168
H	-1.462959	2.591838	5.157665
H	-3.176730	3.252483	3.485070
H	-1.487899	-1.451266	-0.877450
H	-2.889914	-1.821002	3.394126
H	-3.787774	-4.040070	3.958362
H	-4.577737	-5.585678	2.147963
H	-4.574393	-4.794705	-0.209046
H	-0.741126	-3.016037	0.972686
H	-0.874149	1.022972	-0.756464
H	1.639775	-2.812150	1.264664
H	2.502081	-1.805661	3.021860
H	3.890279	-3.203094	4.508938
H	6.291207	-3.648231	3.947756
H	7.286083	-2.599992	1.924681
H	8.339347	-0.724512	0.952407
H	7.967396	1.480290	-1.179787
H	9.463646	1.212284	-0.254297
H	8.895554	-0.023531	-1.390491
H	4.587235	-1.830310	-2.400886
H	4.879553	-3.217130	-1.331725
H	5.593385	-3.188948	-2.958548
H	7.299763	-3.592632	-0.361309
H	7.947442	-3.527228	-2.007730
H	8.599851	-2.444574	-0.767720
H	6.863992	1.973135	1.167891
H	6.865693	0.711313	2.423311
H	8.375621	1.548091	2.002124
H	0.546072	3.414084	0.028189
H	1.597527	3.915468	2.250747
H	1.326721	2.169408	2.063834
H	2.959949	2.841811	1.857079
H	2.170553	5.365885	0.268608
H	3.481040	4.317860	-0.328539

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Table S13. – continued from previous page

atom	x	y	z
H	7.012462	-1.223957	-2.325876
H	2.485135	2.788327	-2.918753
H	1.268900	-0.022192	-3.231827
H	2.991898	0.421191	-3.356404
H	1.831498	1.011825	-4.563670
H	0.103928	3.538145	-2.329926
H	-0.482718	1.920715	-2.781657
H	0.264887	2.964095	-3.996115
H	2.128783	4.737466	-1.390168

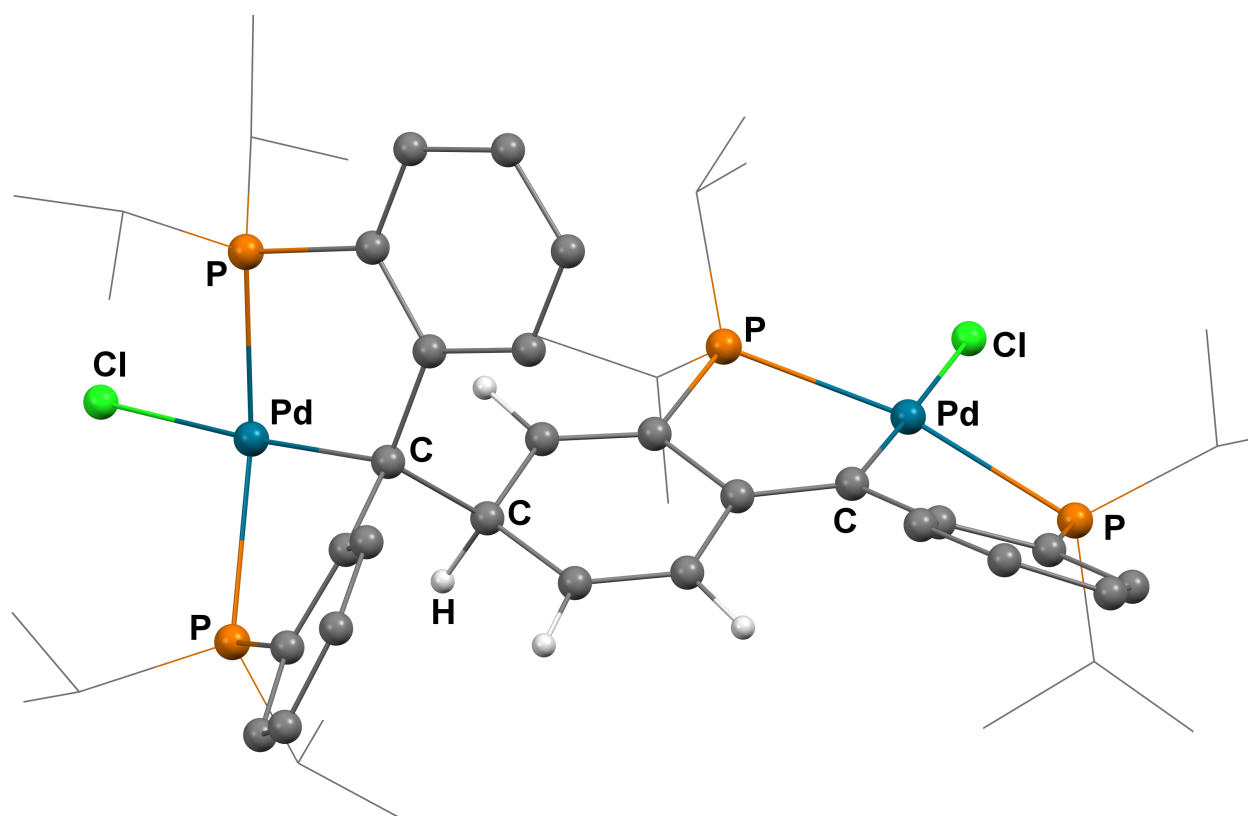


Figure S23. Optimized geometry for {[PC(sp²)P]PdCl₂]₂ (**5**)₂).

6.13 $\{p,p'\text{-[PC(sp}^2\text{)P]PdCl}_2\}_2$ ($\{p,p'\text{-5}\}_2$)

Table S14. Optimized coordinates for $\{p,p'\text{-[PC(sp}^2\text{)P]PdCl}_2\}_2$ ($\{p,p'\text{-5}\}_2$).

atom	x	y	z
C	4.593542	-3.184905	0.941779
C	5.348943	-2.115349	0.378777
C	6.723379	-2.375377	0.089140
C	7.256072	-3.671954	0.206790
C	6.467653	-4.729372	0.698426
C	5.142421	-4.467221	1.097674
C	4.772702	-0.760629	0.152686
Pd	6.079267	0.814059	0.026890
Cl	7.703751	2.670767	-0.237068
P	7.722757	-0.855245	-0.342850
C	9.211229	-0.731674	0.859994
C	10.280781	-1.836087	0.711359
C	3.417777	-0.546072	-0.097480
C	2.463013	-1.578487	-0.543022
C	1.145995	-1.326281	-0.765763
C	0.485753	0.002634	-0.477138
C	1.523860	1.072122	-0.203963
C	2.847018	0.815071	-0.036555
C	-0.571523	-0.105081	0.741135
C	-1.625337	-1.152495	0.439930
C	-2.939099	-0.864927	0.241211
C	-3.472474	0.513973	0.284738
C	-2.514813	1.513537	0.794633
C	-1.211375	1.228172	1.053268
C	-4.792925	0.781079	-0.072687
Pd	-6.157744	-0.744275	-0.149400
Cl	-7.748969	-2.648272	-0.201044
P	-4.250397	-2.134928	-0.196093
C	-4.291665	-3.507499	1.139612
C	-4.617026	-2.882095	2.513953
P	4.132399	2.140650	0.314835
C	3.753727	3.509636	-0.977210
C	4.086429	2.971225	-2.387355
C	-5.296063	2.155375	-0.353747
C	-6.683705	2.455234	-0.213900
C	-7.176725	3.749560	-0.451193
C	-6.317843	4.774326	-0.891451

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Table S14. – continued from previous page

atom	x	y	z
C	-4.959179	4.478110	-1.116913
C	-4.458559	3.192663	-0.857208
P	-7.771008	0.981562	0.175682
C	-8.512107	1.264094	1.931768
C	-8.954198	-0.081898	2.554399
C	-3.690976	-2.957521	-1.829699
C	-3.631648	-1.897366	-2.951369
C	-4.637135	-4.122389	-2.201382
C	-9.229240	1.140629	-1.061417
C	-10.375260	0.158090	-0.730456
C	-8.701945	0.920324	-2.497080
C	-3.035214	-4.403935	1.203035
C	-7.497393	1.980078	2.850554
C	3.733639	2.876312	2.047661
C	3.277868	1.773113	3.027812
C	8.445779	-1.139523	-2.091900
C	7.293639	-1.254806	-3.113876
C	4.969827	3.618925	2.610505
C	4.511512	4.824047	-0.688682
C	9.429206	-0.006911	-2.466611
C	8.696631	-0.626047	2.312481
H	-8.235701	3.963324	-0.320211
H	-6.706140	5.770776	-1.086544
H	-4.293316	5.244681	-1.507091
H	-3.419234	2.976100	-1.079058
H	-6.575806	1.391269	2.949272
H	-7.227178	2.974385	2.478770
H	-7.932047	2.094189	3.852994
H	-9.391814	1.910681	1.790346
H	-9.437886	0.107639	3.522788
H	-9.651519	-0.638486	1.922124
H	-8.086642	-0.730359	2.722421
H	-9.598317	2.173396	-0.964626
H	-10.844529	0.377477	0.236396
H	-11.152644	0.241146	-1.502376
H	-10.011861	-0.876244	-0.717942
H	-9.518025	1.072704	-3.216487
H	-8.331199	-0.105056	-2.613210
H	-7.890930	1.613684	-2.750242
H	-5.156320	-4.108594	0.827109
H	-3.822232	-2.200152	2.843504
H	-4.716820	-3.677508	3.264947

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Table S14. – continued from previous page

atom	x	y	z
H	-5.561323	-2.328155	2.477846
H	-2.166165	-3.850801	1.579625
H	-3.221120	-5.233978	1.898759
H	-2.776324	-4.842862	0.231432
H	-2.676522	-3.344609	-1.651696
H	-2.960631	-1.067766	-2.697733
H	-4.628311	-1.482324	-3.145969
H	-3.267130	-2.361235	-3.877985
H	-4.601078	-4.938602	-1.469686
H	-4.344551	-4.533269	-3.177156
H	-5.676534	-3.779618	-2.266511
H	-2.900287	2.494578	1.057833
H	-0.584715	1.984659	1.522568
H	-1.272837	-2.177770	0.357397
H	0.034462	-0.435156	1.600874
H	-0.127217	0.305763	-1.342201
H	0.522871	-2.108908	-1.195168
H	1.153914	2.093866	-0.132469
H	2.858198	-2.557782	-0.796938
H	8.290199	-3.863939	-0.066145
H	6.888717	-5.726407	0.799908
H	4.538562	-5.260345	1.533053
H	3.580308	-2.998120	1.280964
H	2.670330	3.691024	-0.906649
H	2.909300	3.590261	1.895911
H	9.647713	0.237210	0.582003
H	8.983362	-2.098921	-2.053064
H	7.704136	-1.469947	-4.109683
H	6.592822	-2.057481	-2.853513
H	6.731153	-0.314877	-3.171996
H	9.774392	-0.150866	-3.499514
H	8.945858	0.974340	-2.393807
H	10.313793	0.009422	-1.817920
H	3.799841	3.716268	-3.142239
H	5.163214	2.786760	-2.479655
H	3.551901	2.039443	-2.608485
H	4.314926	5.536524	-1.501761
H	4.186439	5.294042	0.247340
H	5.592470	4.648589	-0.641186
H	11.153707	-1.576052	1.325957
H	9.909710	-2.804992	1.066453
H	10.629747	-1.952386	-0.322072

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Table S14. – continued from previous page

atom	x	y	z
H	9.543138	-0.452852	2.990722
H	7.995950	0.209282	2.421667
H	8.191766	-1.548496	2.628050
H	4.719149	4.051828	3.588920
H	5.807693	2.924678	2.743977
H	5.320087	4.423972	1.958792
H	3.078170	2.220119	4.011216
H	2.367068	1.267240	2.689846
H	4.062394	1.015931	3.155421

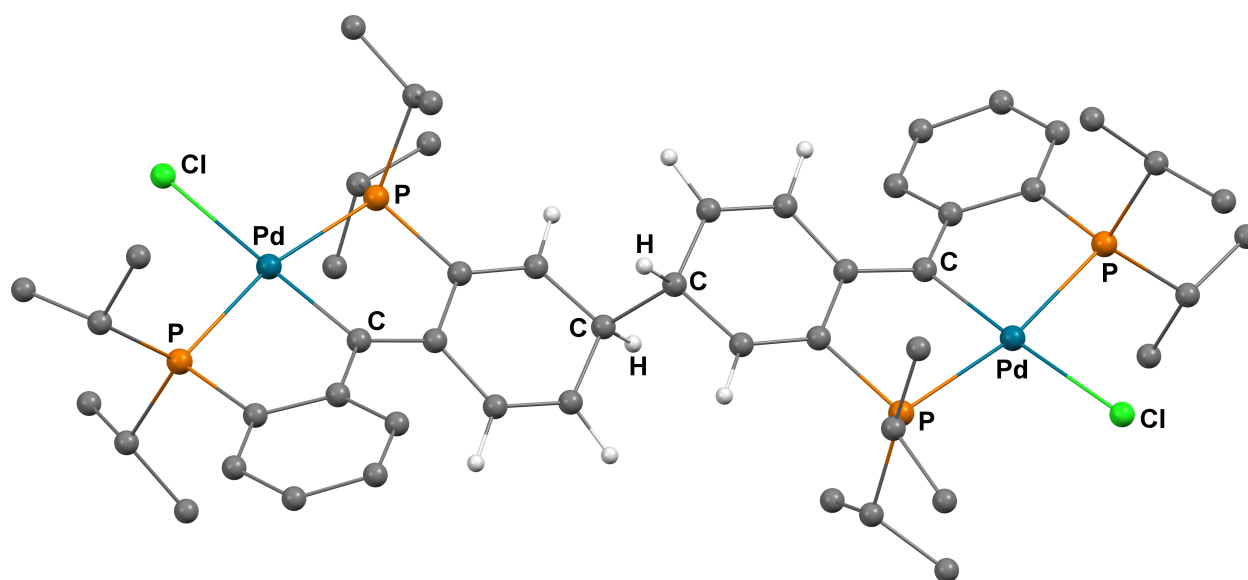
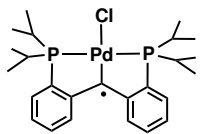
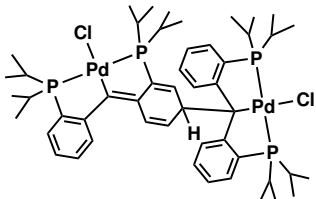
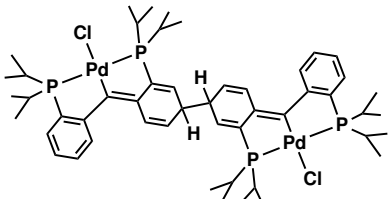


Figure S24. Optimized geometry for $\{p,p'-[PC(sp^2)P]PdCl_2\}_2$ ($\{p,p'-5\}_2$).

6.14 Calculated energies for $[\text{PC}^\bullet(\text{sp}^2)\text{P}]\text{PdCl}$ (**5**) and corresponding dimers

		Energy (hartree)	Energy loss (kcal/mol)
$[\text{PC}^\bullet(\text{sp}^2)\text{P}]\text{PdCl}$ (5)		-1128.9587254	—
$\{[\text{PC}(\text{sp}^2)\text{P}]\text{PdCl}\}_2$ (5) ₂)		-2257.904652	8.03
$\{p,p'-[\text{PC}(\text{sp}^2)\text{P}]\text{PdCl}\}_2$ (p,p'-5) ₂)		-2257.886631	19.34

6.15 [Me₂PC[•](sp²)PMe₂]PdCl (5')

Table S15. Optimized coordinates for [Me₂PC[•](sp²)PMe₂]PdCl (5').

atom	x	y	z
C	0.001736	0.003468	-0.011651
C	0.000206	0.005071	1.421448
C	1.289249	0.004683	2.057319
C	2.477685	0.082664	1.318574
C	2.443738	0.122861	-0.090350
C	1.194994	0.060804	-0.744413
C	-1.214469	-0.062727	2.240369
Pd	-1.053654	-0.756342	4.153711
Cl	-0.859618	-1.593209	6.462299
P	1.224649	-0.189176	3.913897
C	1.893347	1.399639	4.668084
C	-2.538615	0.341633	1.756846
C	-2.751642	1.255451	0.673641
C	-4.041355	1.614138	0.258820
C	-5.181349	1.083023	0.898619
C	-5.004691	0.214852	1.995389
C	-3.717751	-0.132022	2.428599
P	-3.369447	-1.161820	3.947428
C	-4.490153	-0.528575	5.314183
C	-4.003516	-2.899923	3.605023
C	2.499338	-1.486668	4.379390
H	-1.897157	1.717991	0.191652
H	-4.161473	2.321532	-0.558965
H	-6.179749	1.359122	0.569779
H	-5.879066	-0.168686	2.518417
H	-0.938071	-0.091065	-0.544782
H	1.155008	0.043962	-1.831485
H	3.366414	0.173367	-0.662440
H	3.438966	0.091366	1.829510
H	-4.205663	-1.031733	6.243126
H	-4.327330	0.545975	5.436211
H	-5.546021	-0.718871	5.090529
H	2.382478	-1.706487	5.444782
H	2.299014	-2.399565	3.811456
H	3.519268	-1.141374	4.175421
H	-3.793144	-3.528521	4.476069
H	-5.081423	-2.890000	3.406980

Continued on next page

Table S15. – continued from previous page

atom	x	y	z
H	-3.476114	-3.306826	2.737758
H	1.847824	1.317132	5.758604
H	2.928113	1.575807	4.352764
H	1.266238	2.236697	4.348802

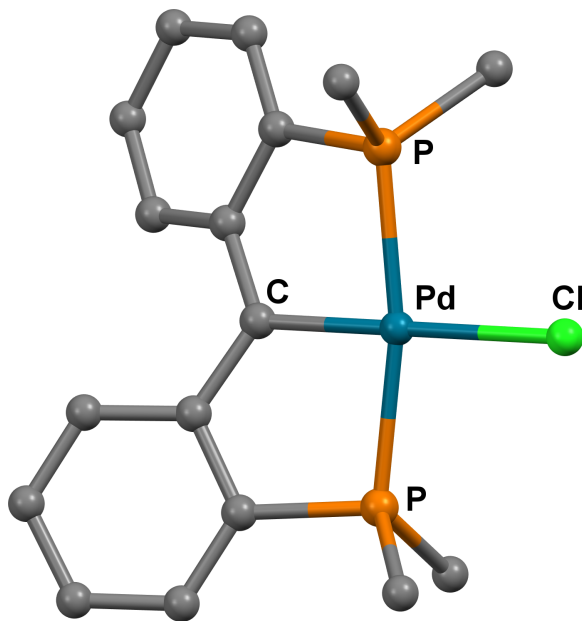


Figure S25. Optimized geometry for $[\text{Me}_2\text{PC}^*(\text{sp}^2)\text{PMe}_2]\text{PdCl}$ (**5'**).

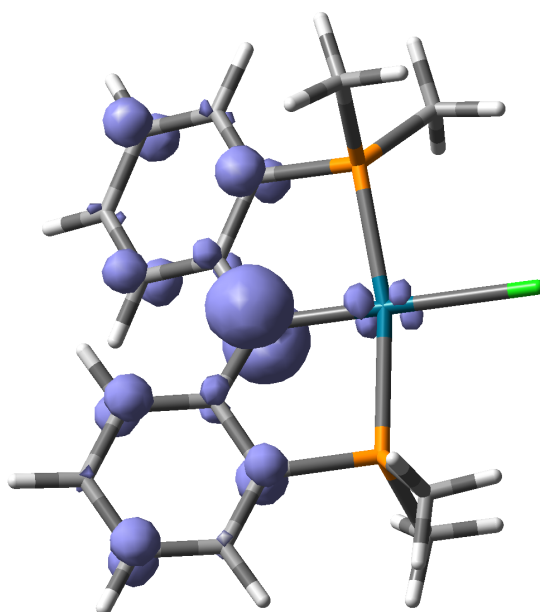


Figure S26. Spin density for $[\text{Me}_2\text{PC}^*(\text{sp}^2)\text{PMe}_2]\text{PdCl}$ (**5'**).

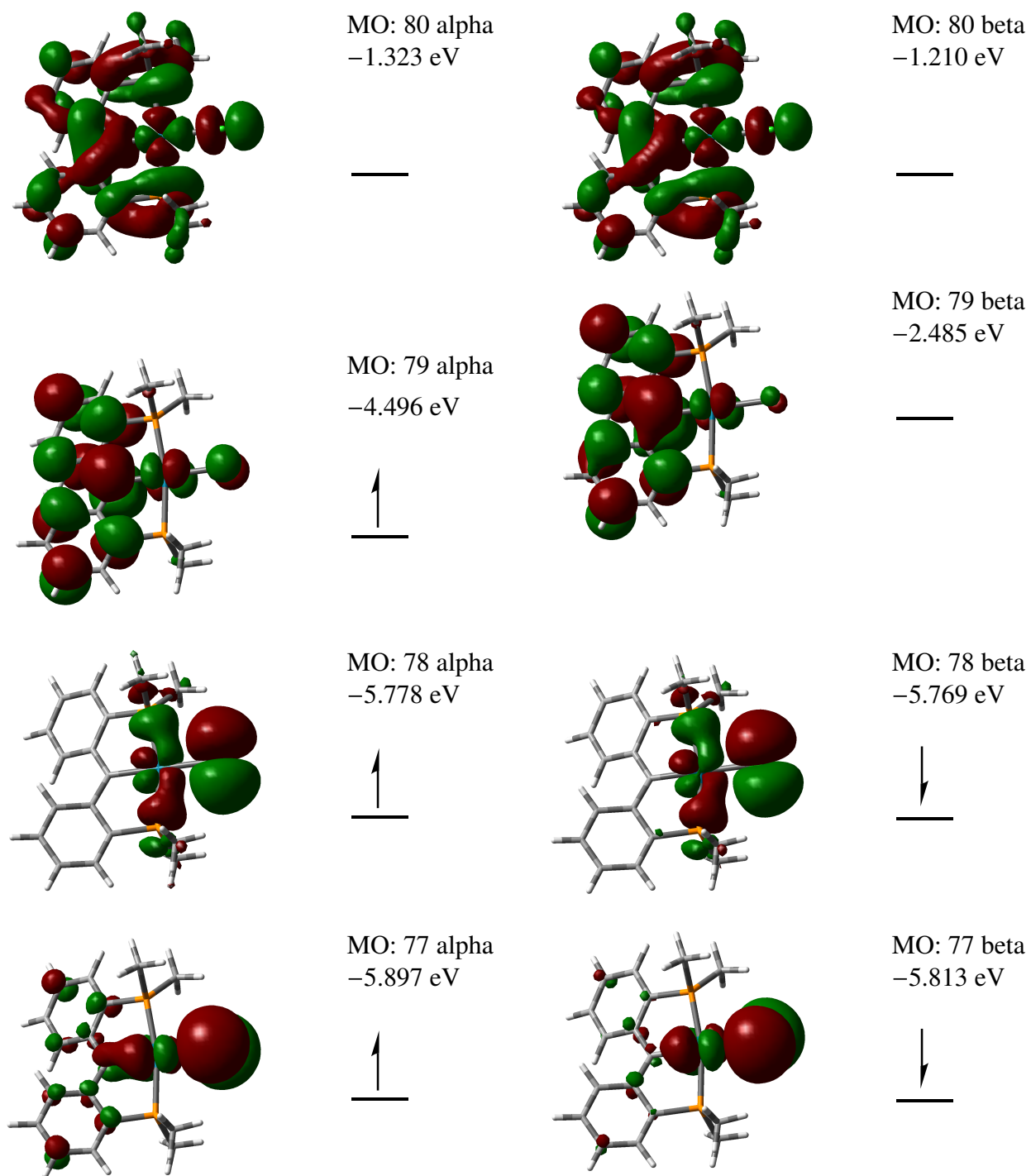


Figure S27. Frontier molecular orbitals for [Me₂PC[•](sp²)PMe₂]PdCl (**5'**).

7 NMR Spectra

7.1 NMR Spectra for $[\text{PC}^*(\text{sp}^2)\text{P}]\text{PdI}$ (**2**) and $\{[\text{PC}(\text{sp}^2)\text{P}]\text{PdI}\}_2$ (**2**)₂

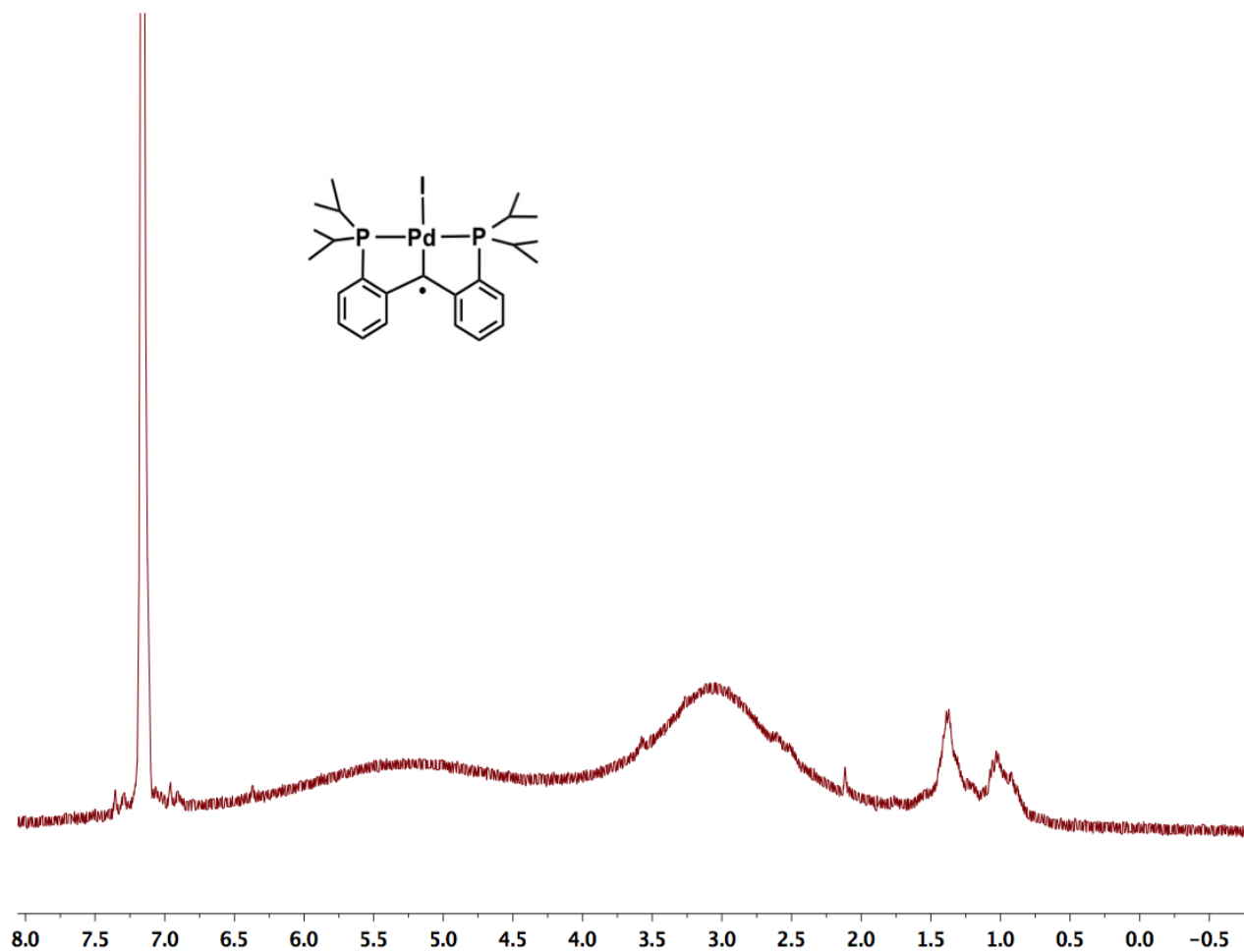


Figure S28. ^1H NMR spectrum (293 K) for $[\text{PC}^*(\text{sp}^2)\text{P}]\text{PdI}$ (**2**).

7.2 NMR Spectra for [PC(sp³)HP]PdBr (4)

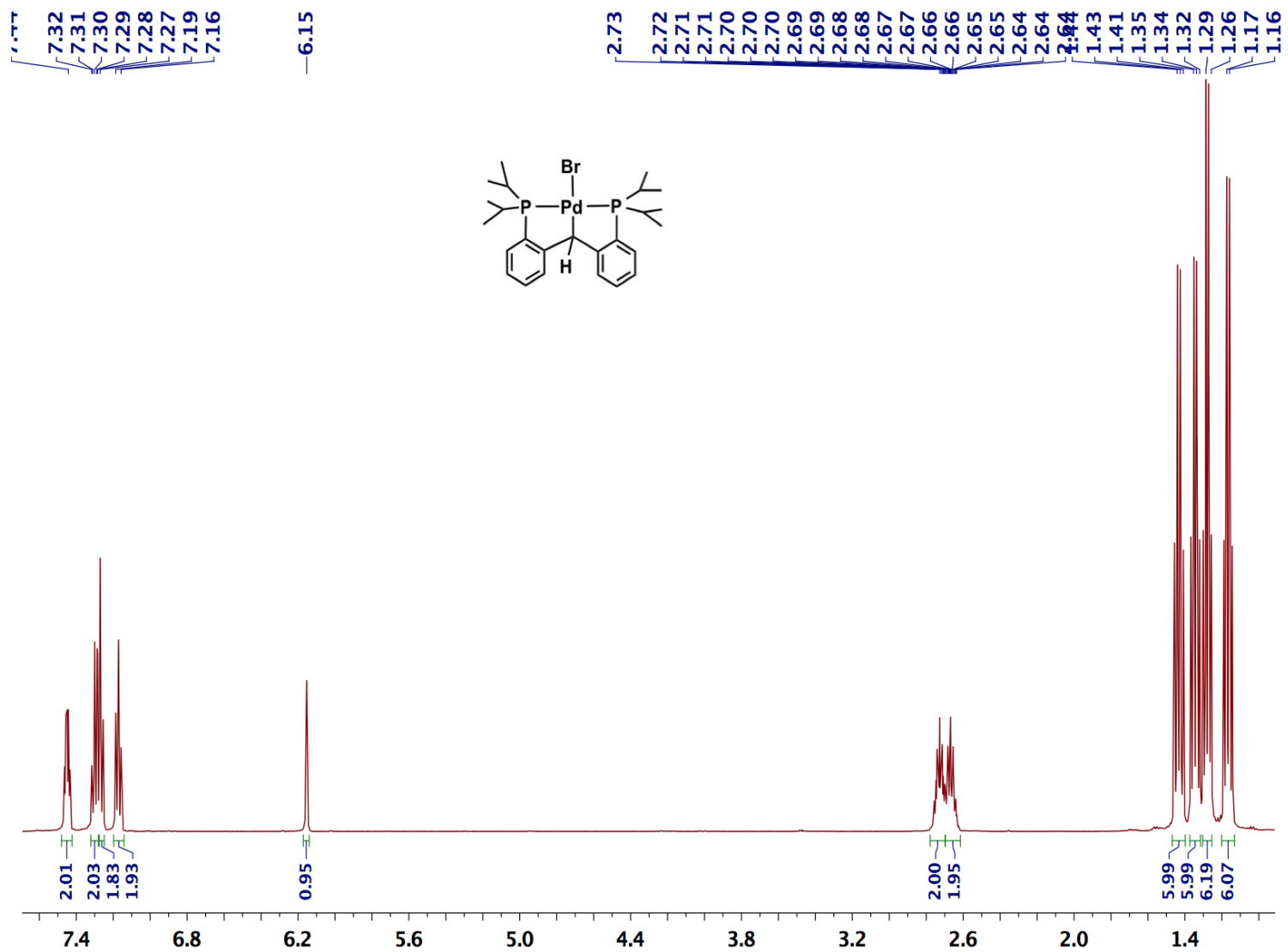


Figure S29. ¹H NMR spectrum for [PC(sp³)HP]PdBr (4).

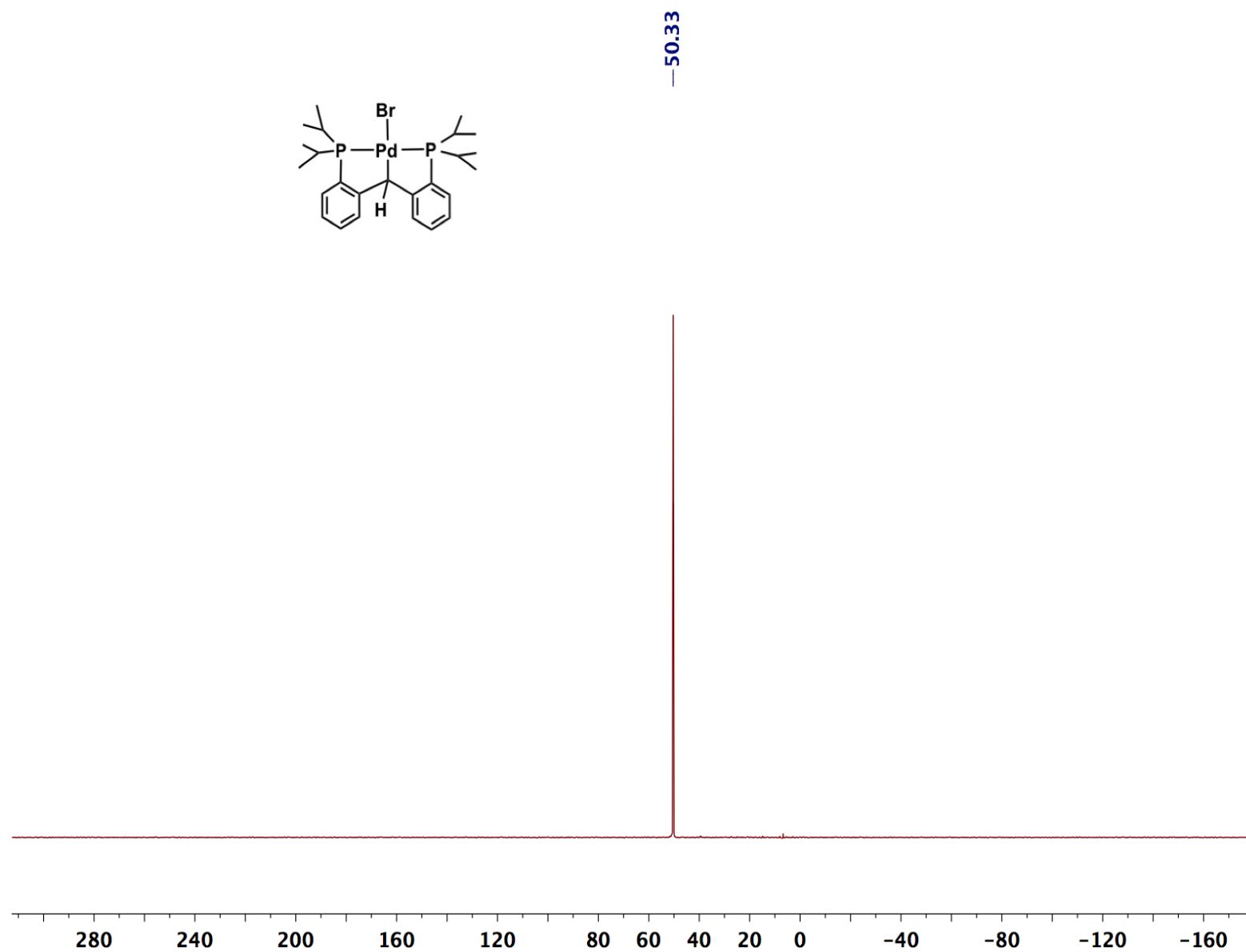


Figure S30. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for [PC(sp³)HP]PdBr (**4**).

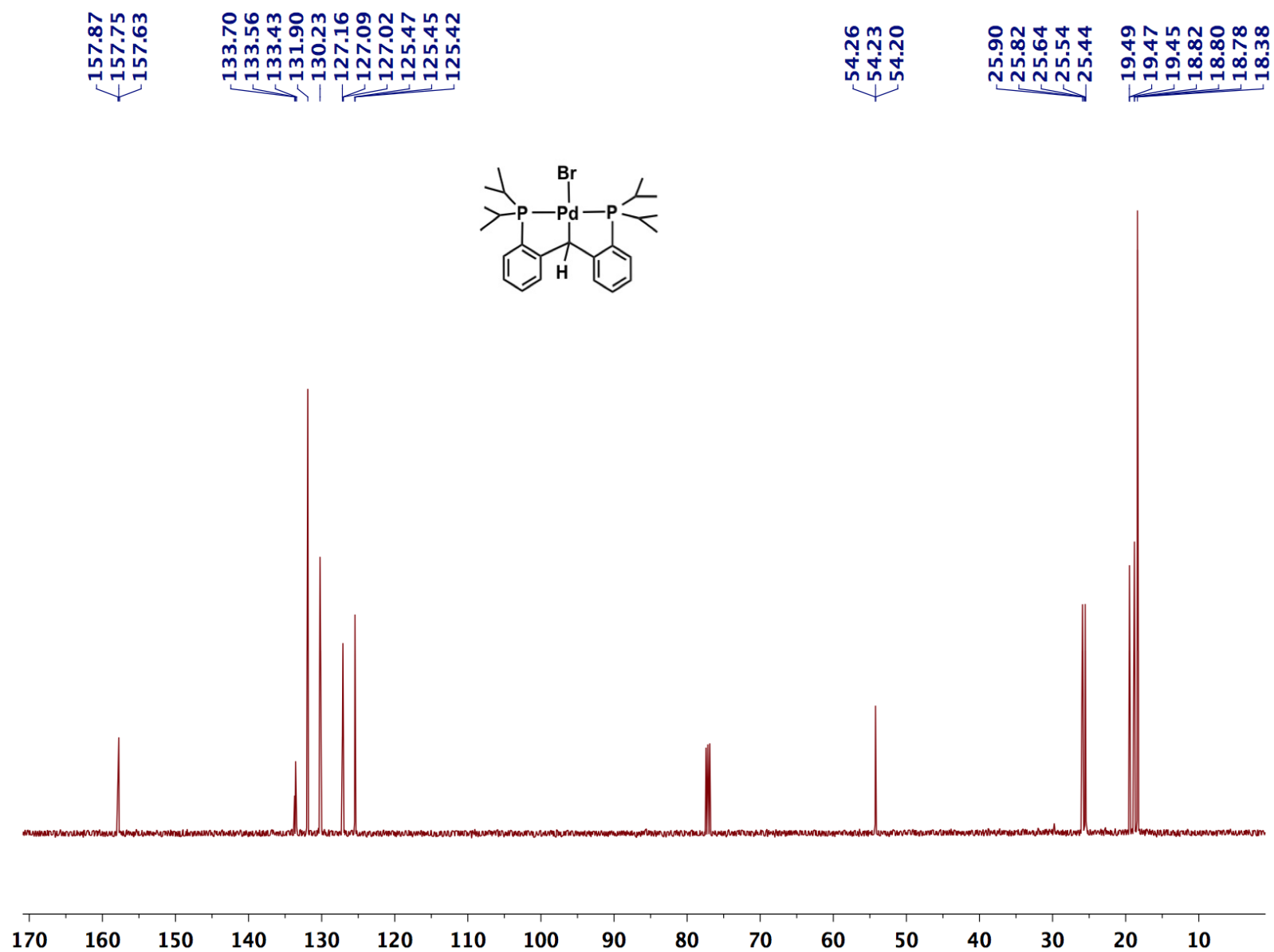


Figure S31. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for [PC(sp³)HP]PdBr (4).

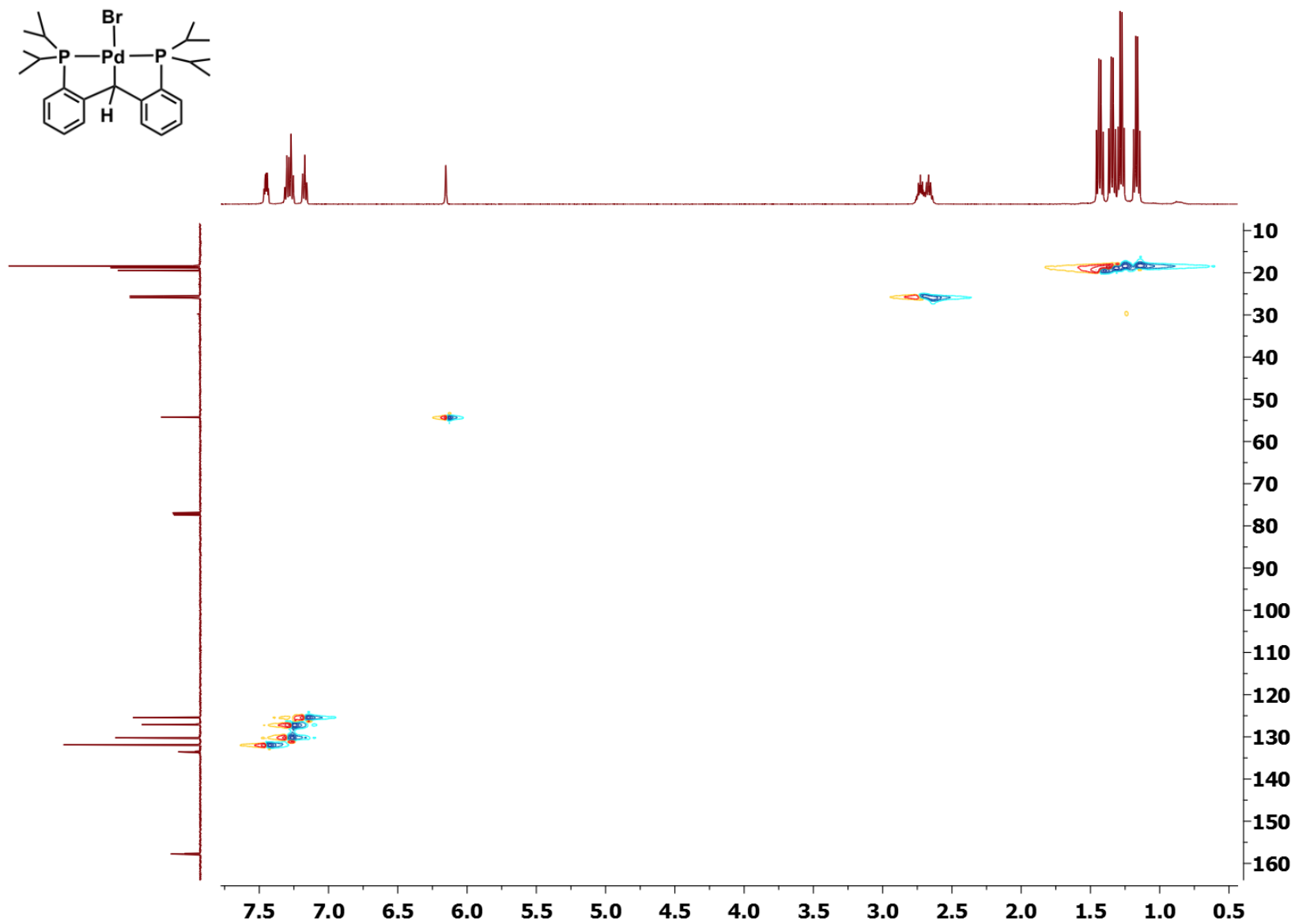


Figure S32. ¹H-¹³C HSQC NMR spectrum for [PC(sp³)HP]PdBr (4).

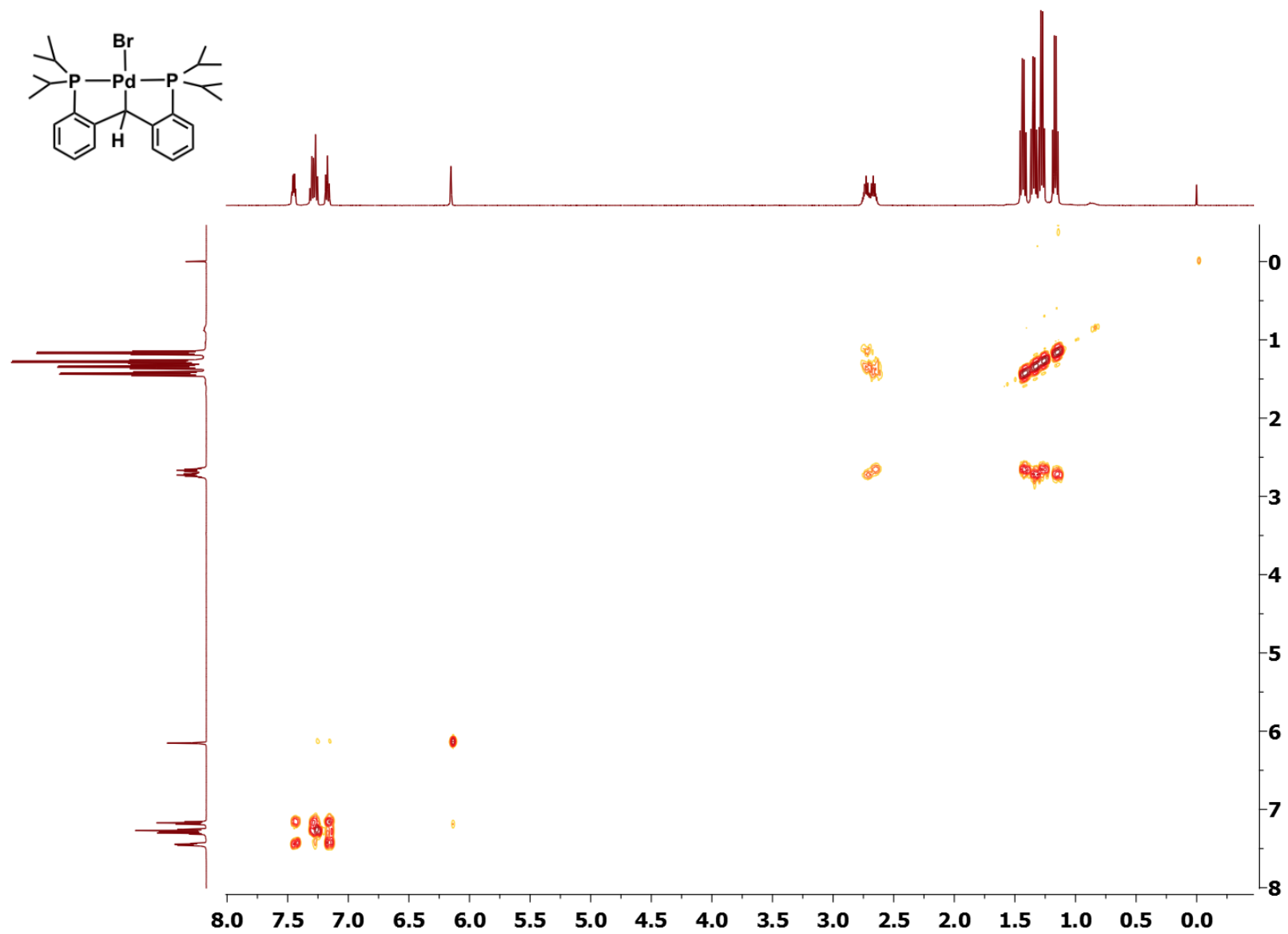


Figure S33. ¹H-¹H COSY NMR spectrum for [PC(sp³)HP]PdBr (4).

7.3 NMR Spectra for [PC(CH₂)P]Pd(PMe₃) (6)

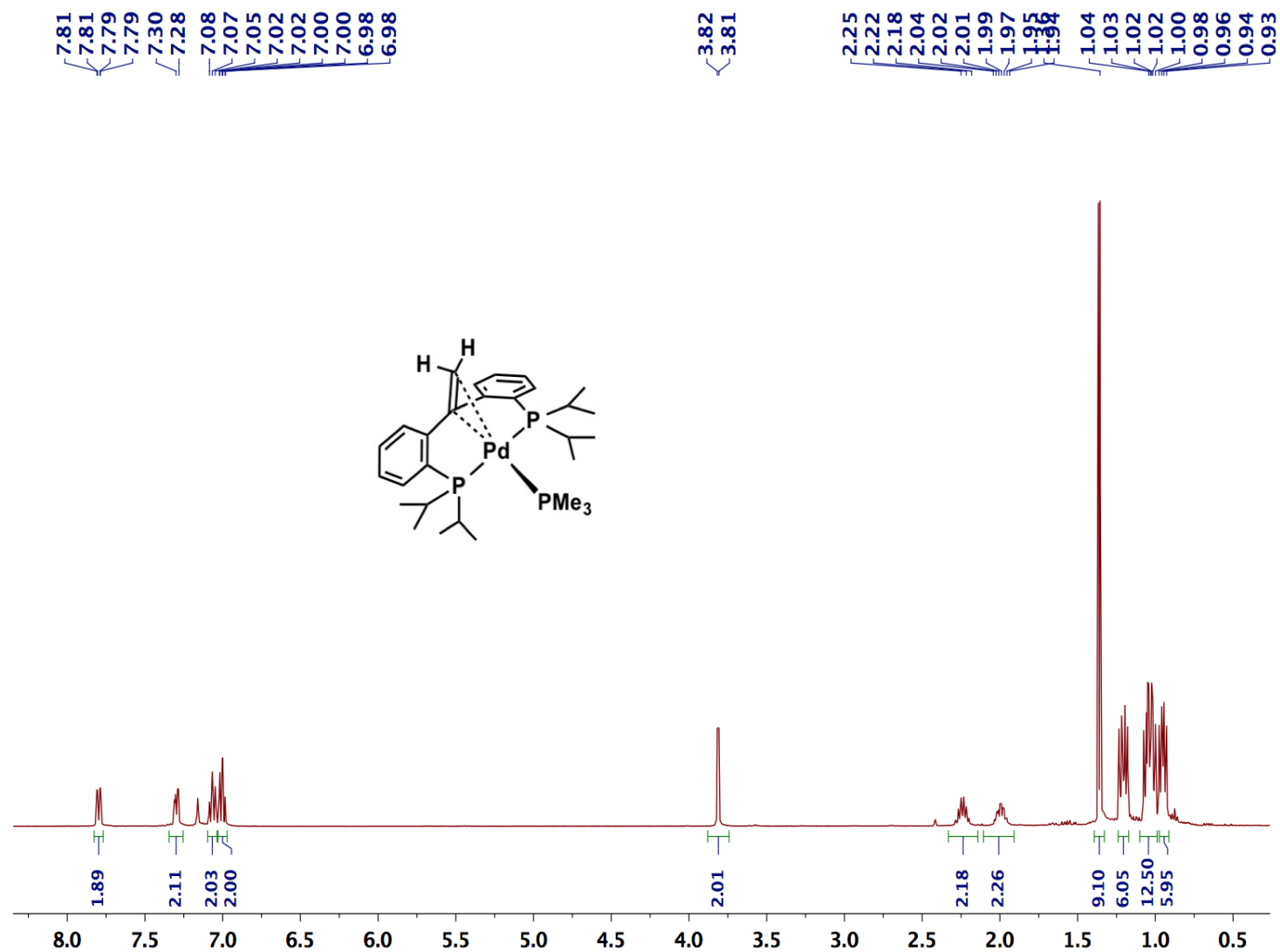


Figure S34. ¹H NMR spectrum for [PC(CH₂)P]Pd(PMe₃) (6).

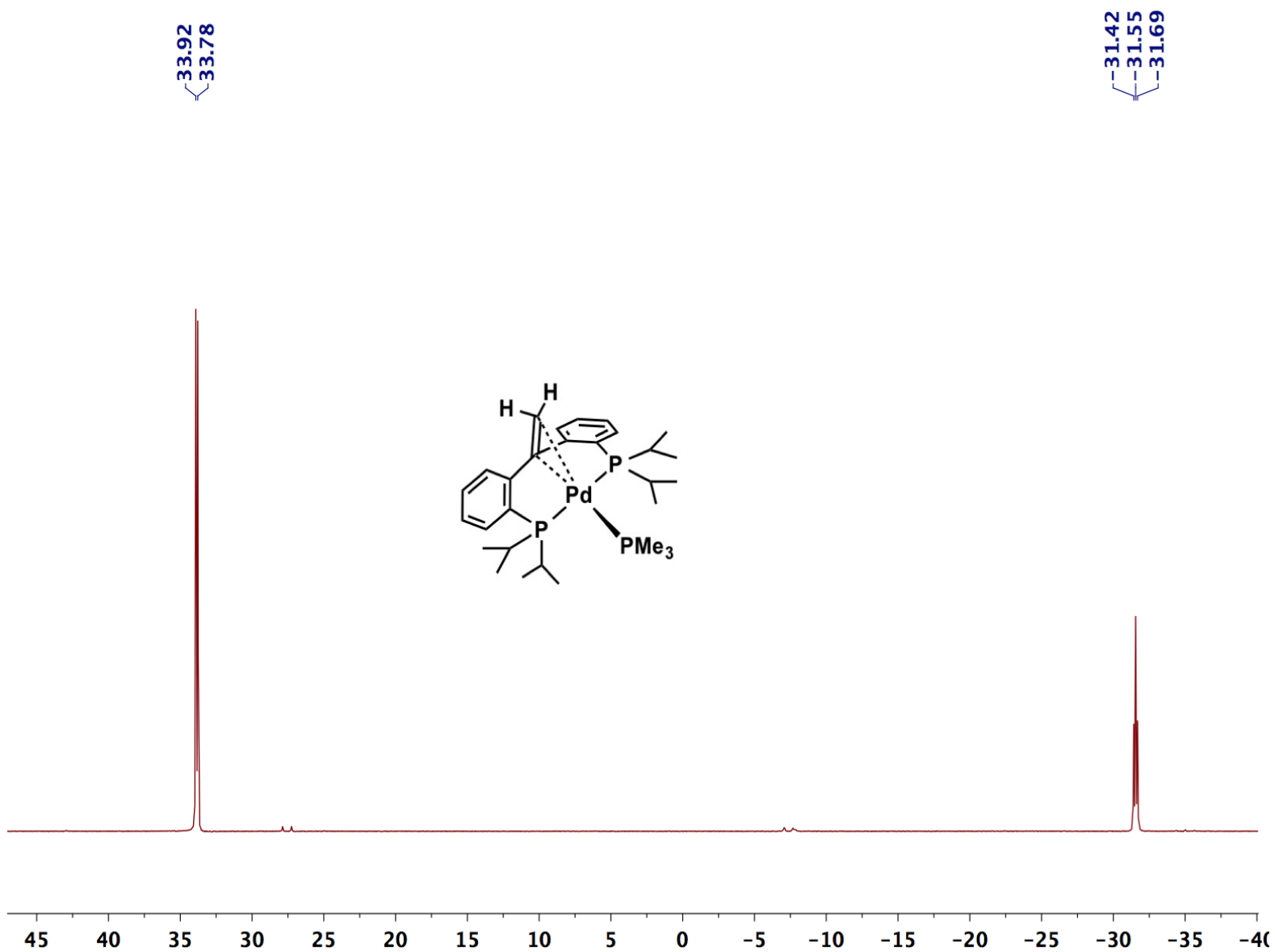


Figure S35. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for $[\text{PC}(\text{CH}_2)\text{P}]\text{Pd}(\text{PMe}_3)$ (6).

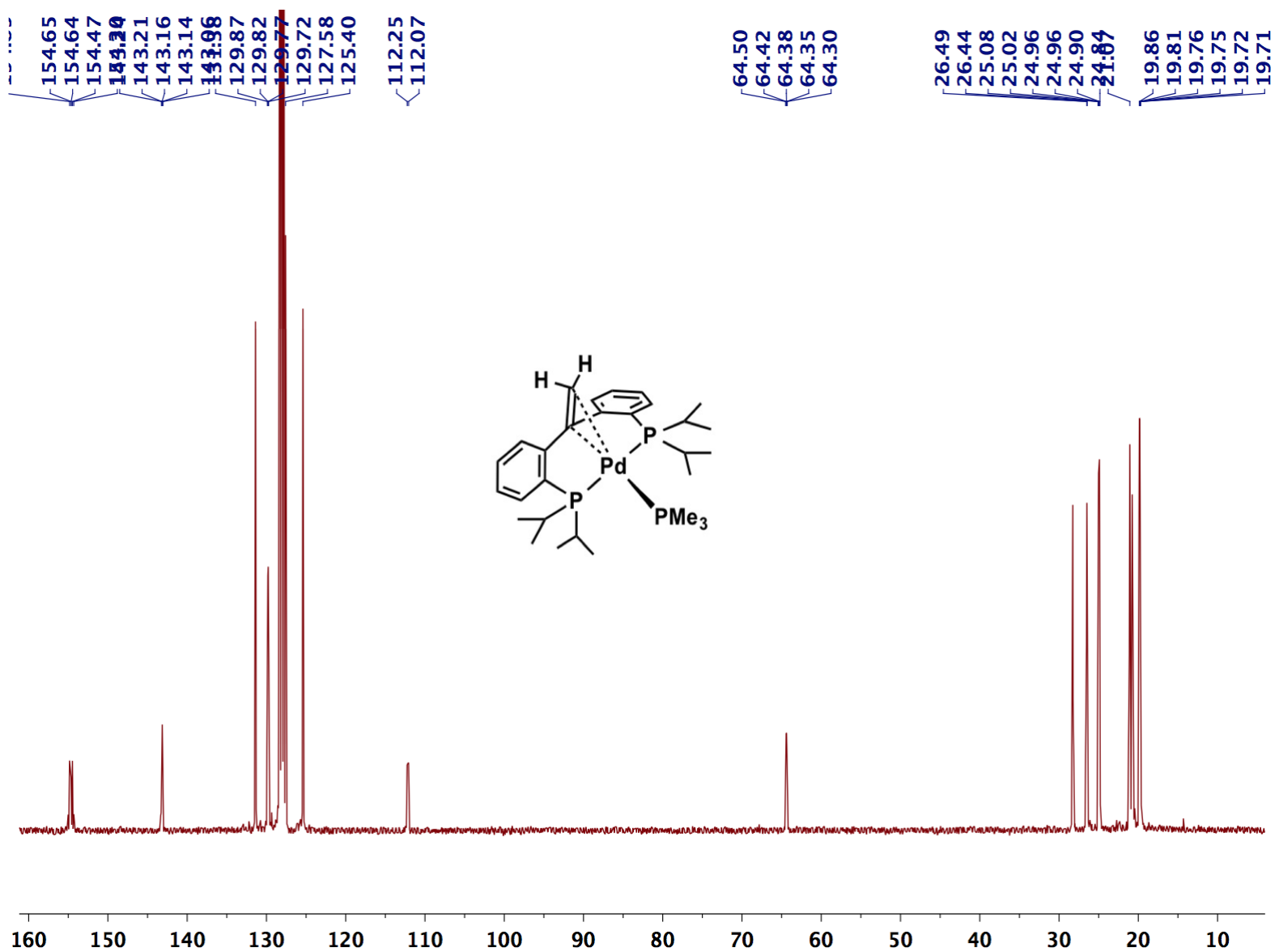


Figure S36. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for $[\text{PC}(\text{CH}_2)\text{P}]\text{Pd}(\text{PMe}_3)$ (6).

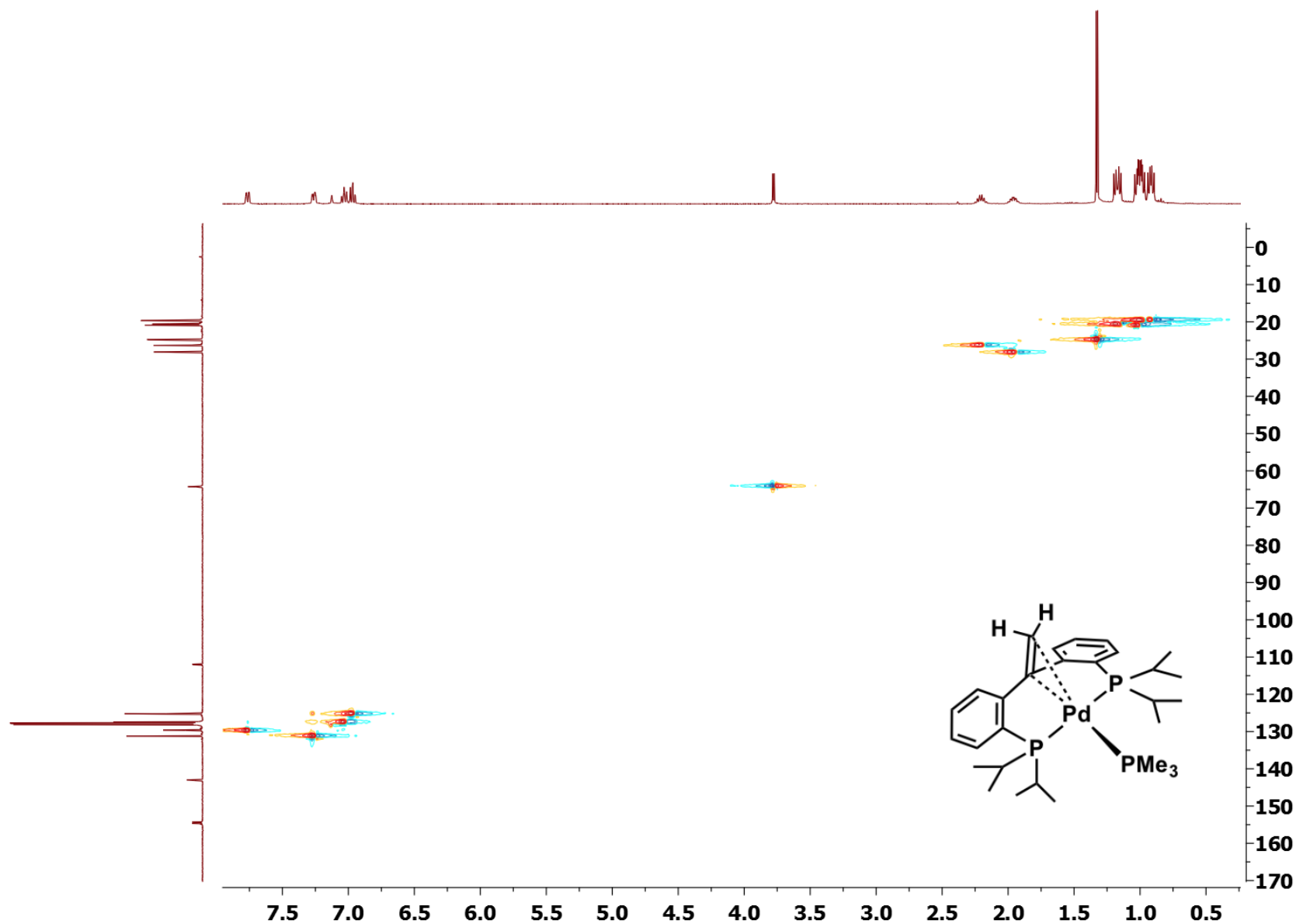


Figure S37. ^1H - ^{13}C HSQC NMR spectrum for $[\text{PC}(\text{CH}_2)\text{P}]\text{Pd}(\text{PMe}_3)$ (6).

7.4 NMR Spectra for 1,1-bis(2-bromophenyl)ethan-1-ol

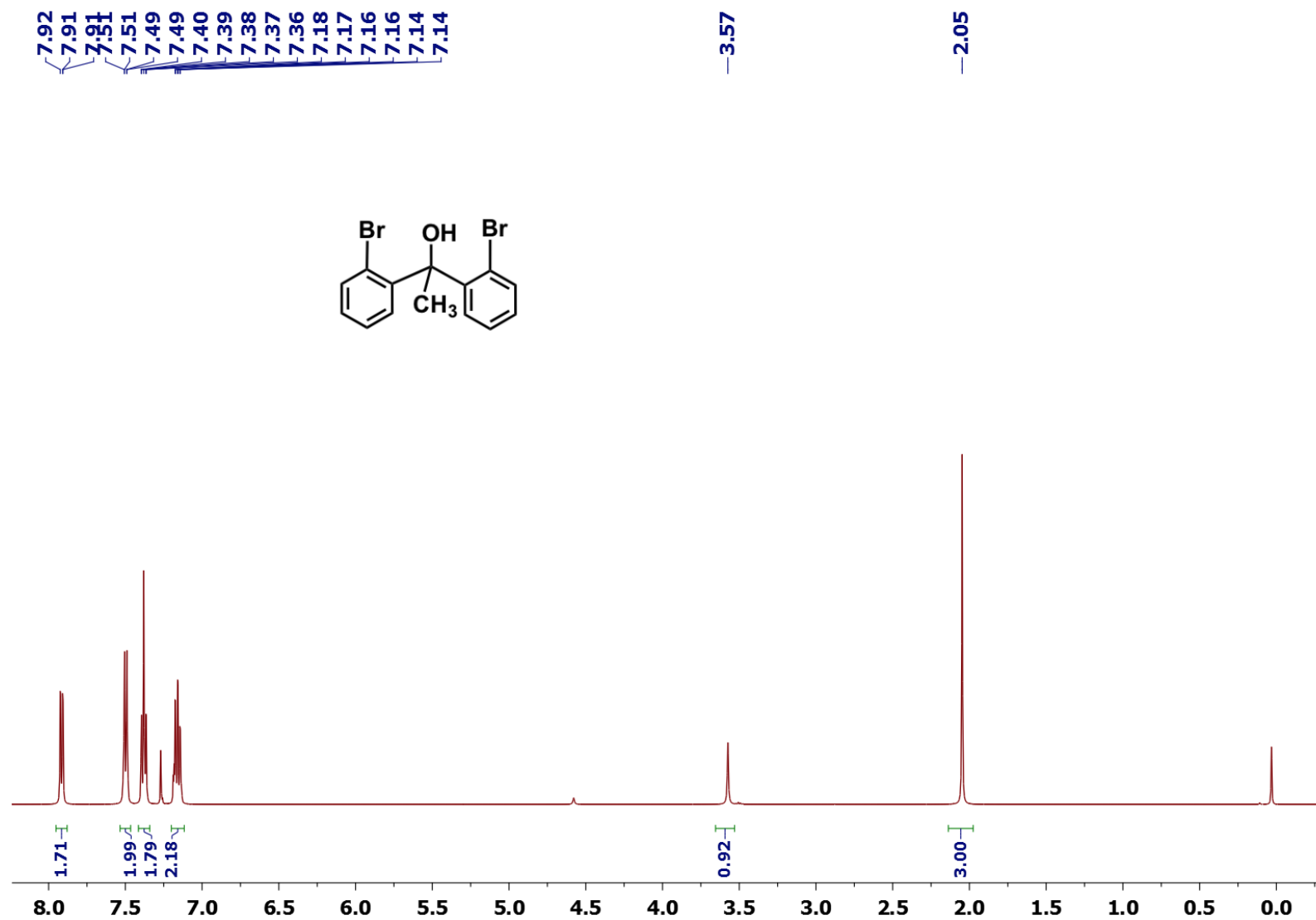


Figure S38. ¹H NMR spectrum for 1,1-bis(2-bromophenyl)ethan-1-ol.

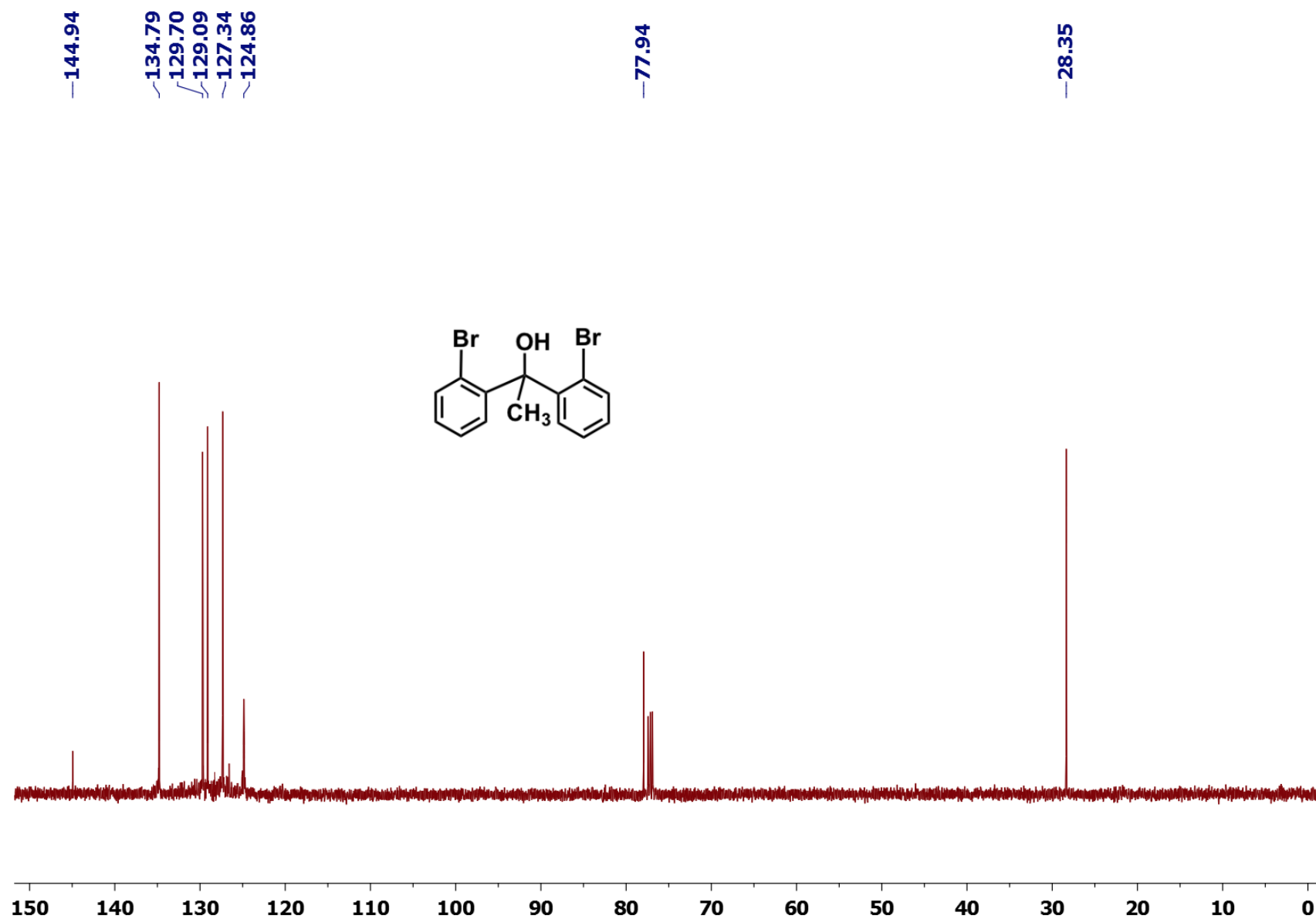


Figure S39. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for 1,1-bis(2-bromophenyl)ethan-1-ol.

7.5 NMR Spectra for 1,1-bis(2-bromophenyl)ethane

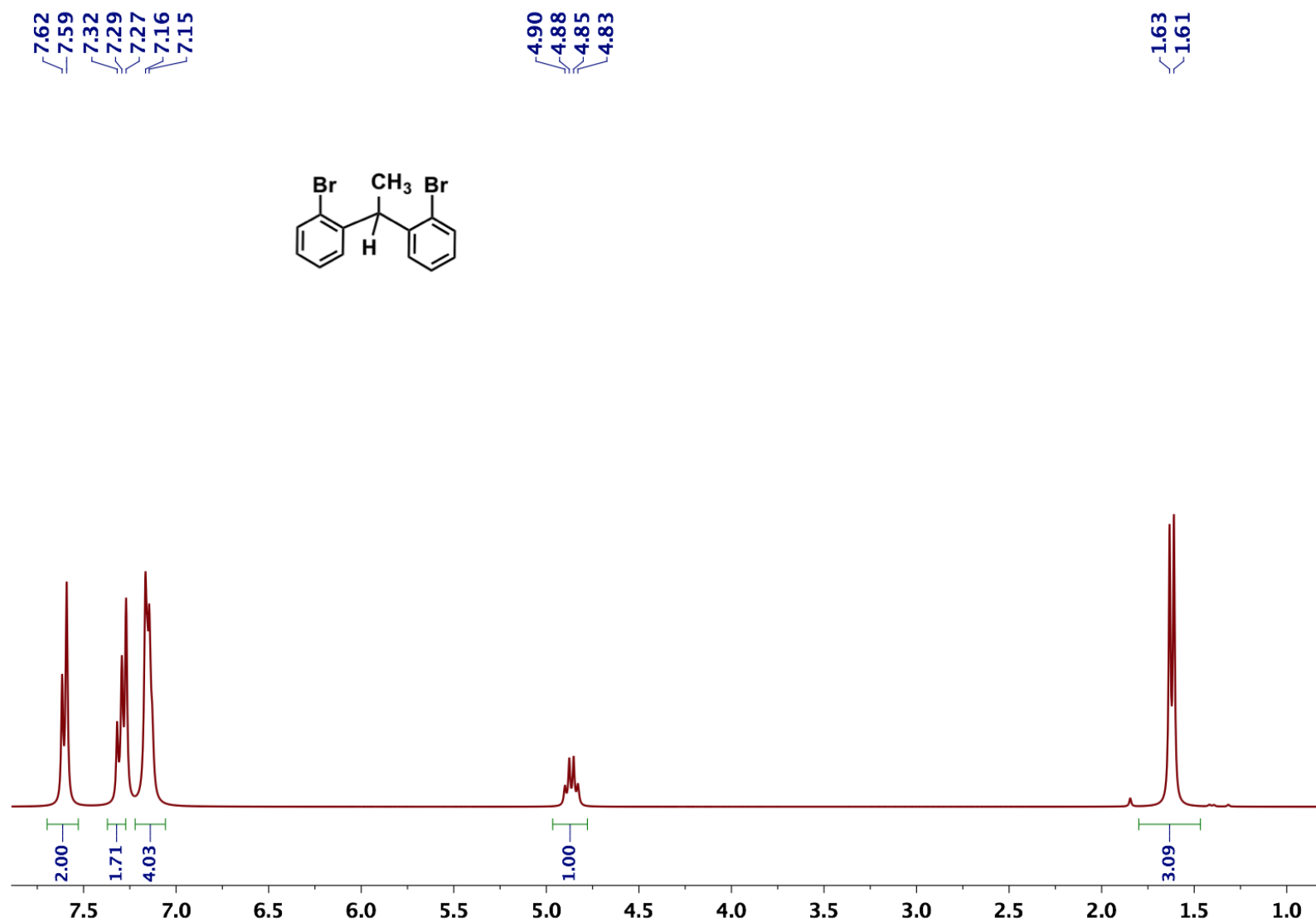


Figure S40. ^1H NMR spectrum for 1,1-bis(2-bromophenyl)ethane.

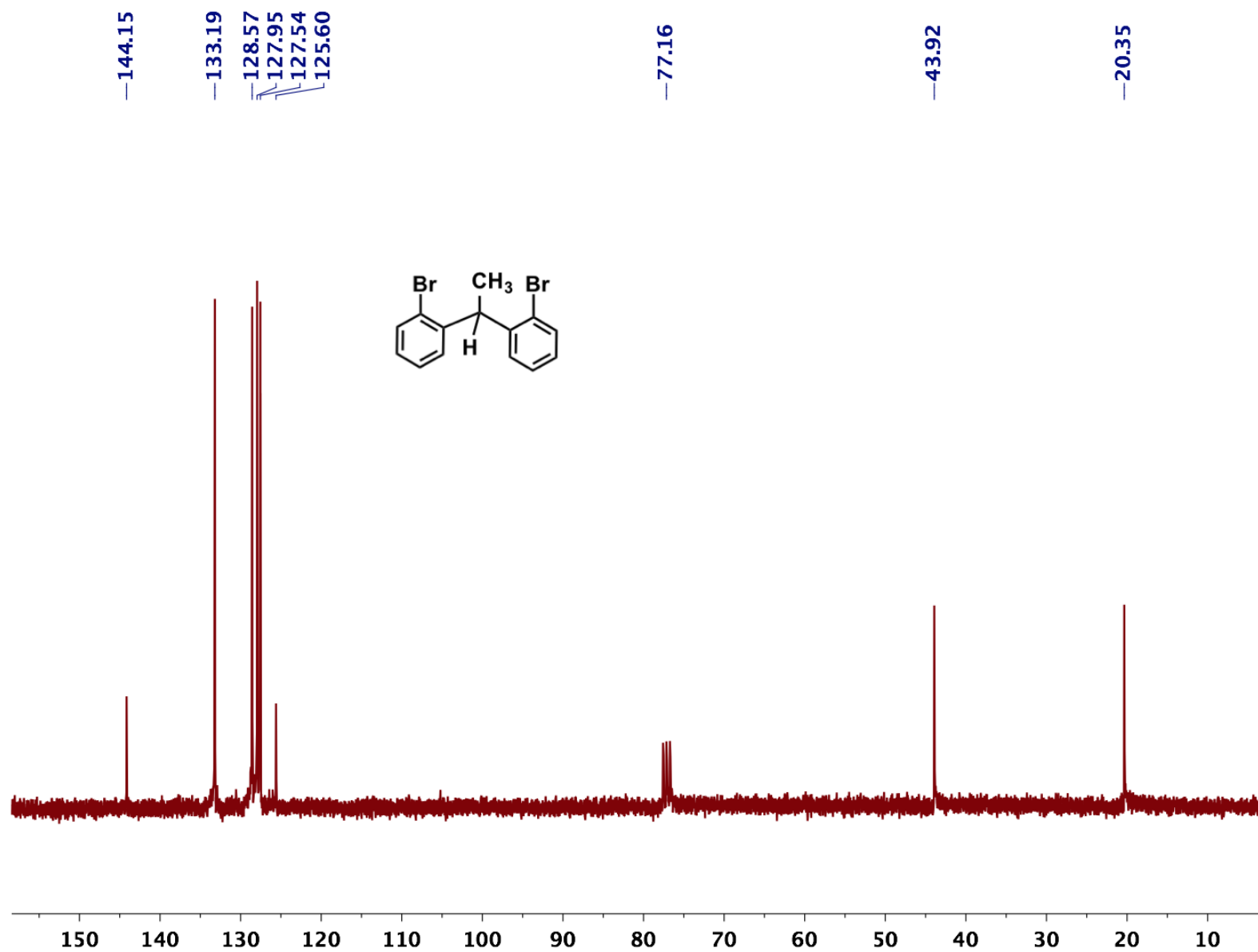


Figure S41. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for 1,1-bis(2-bromophenyl)ethane.

7.6 NMR Spectra for PC(CH₃)HP (7)

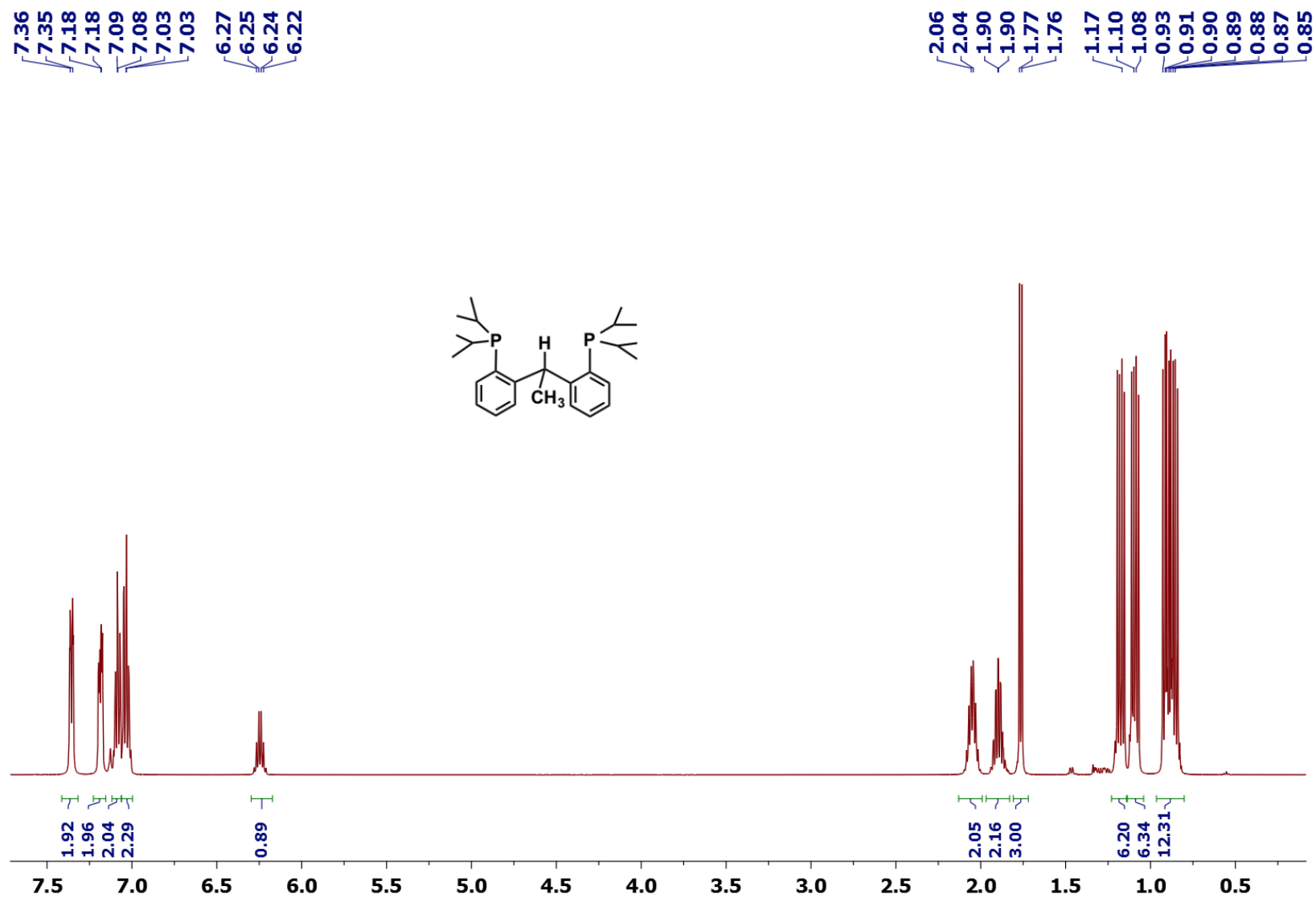


Figure S42. ¹H NMR spectrum for PC(CH₃)HP (7).

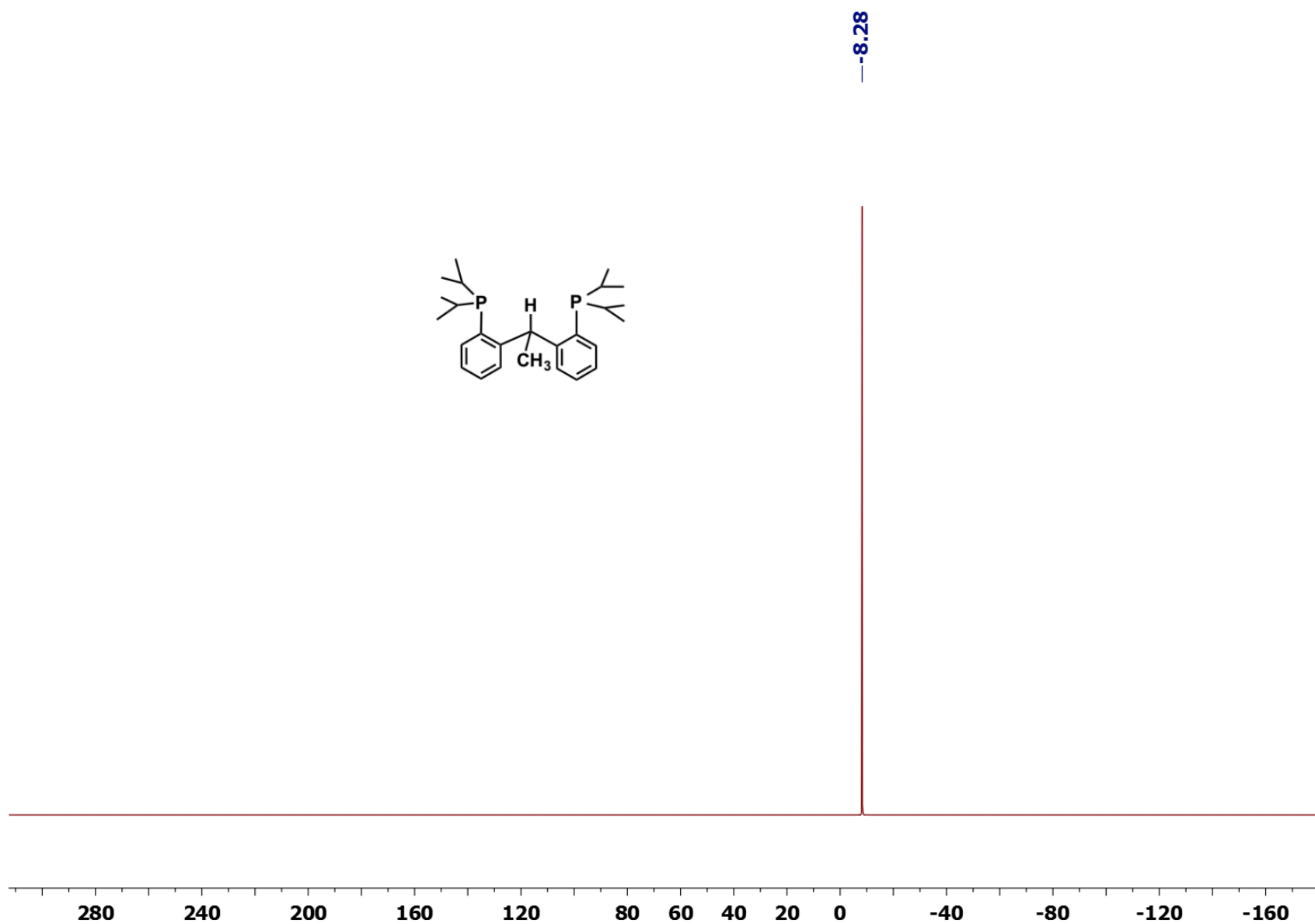


Figure S43. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for PC(CH₃)HP (7).

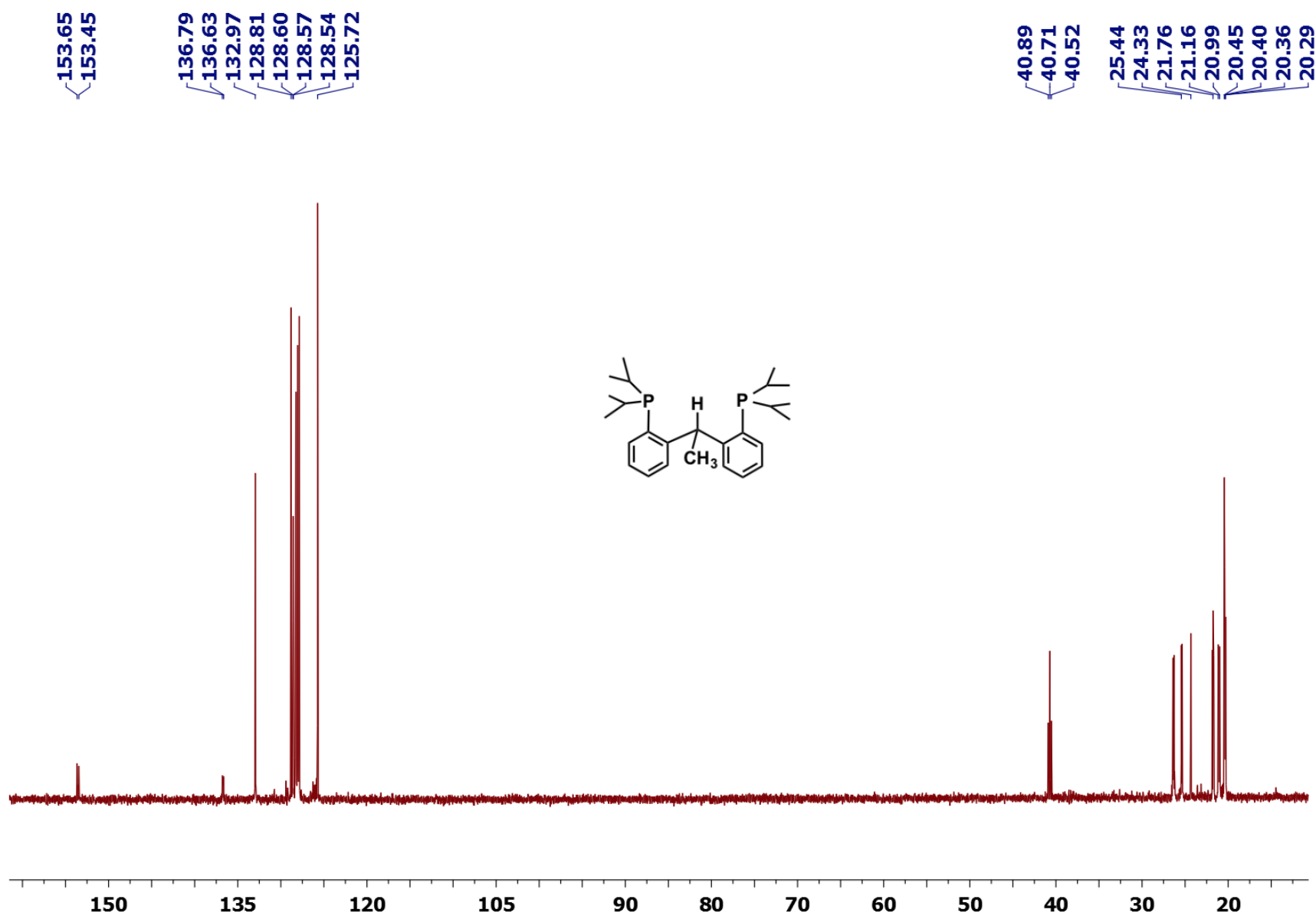


Figure S44. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for PC(CH₃)HP (7).

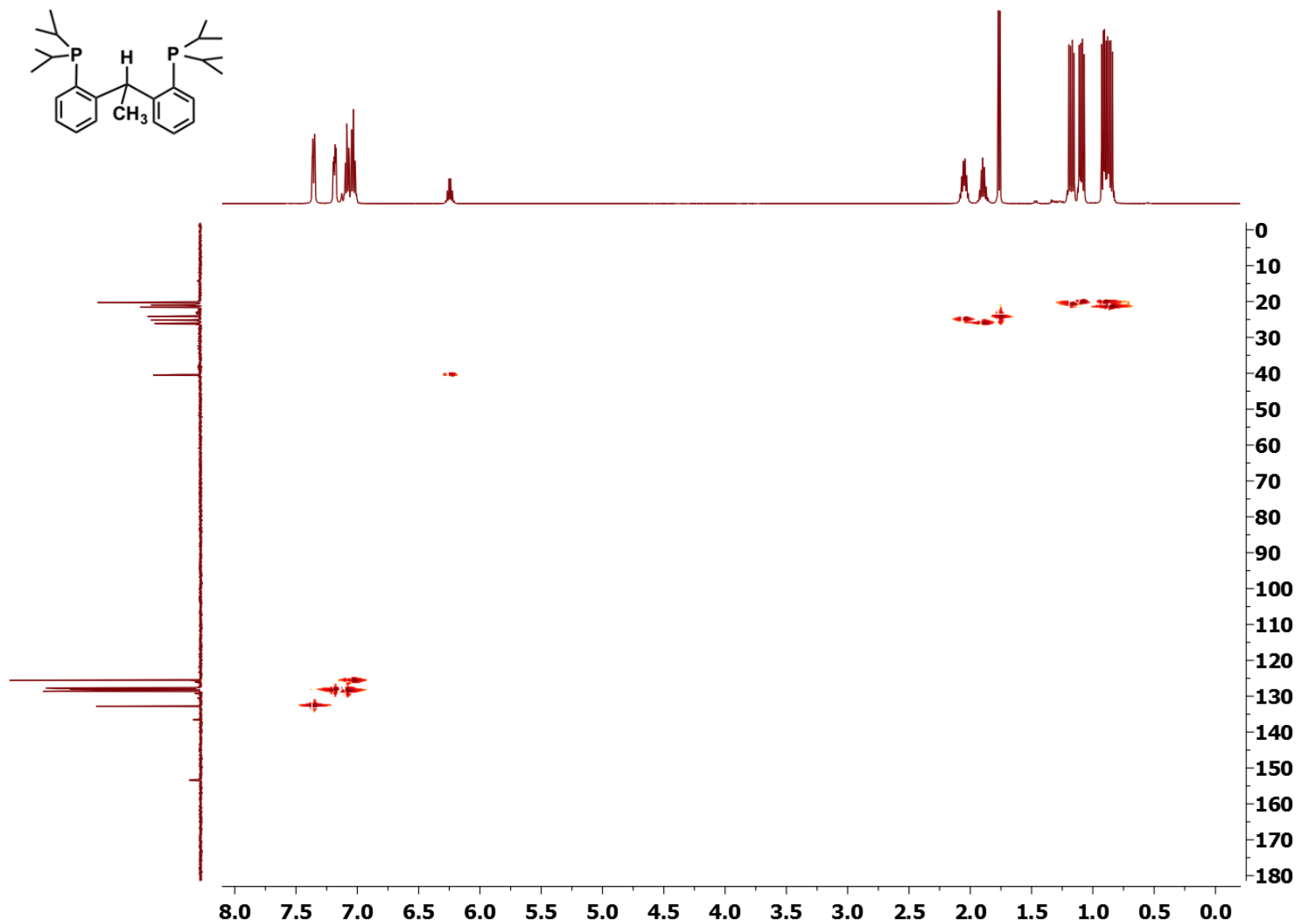


Figure S45. ^1H - ^{13}C HSQC NMR spectrum for PC(CH₃)HP (7).

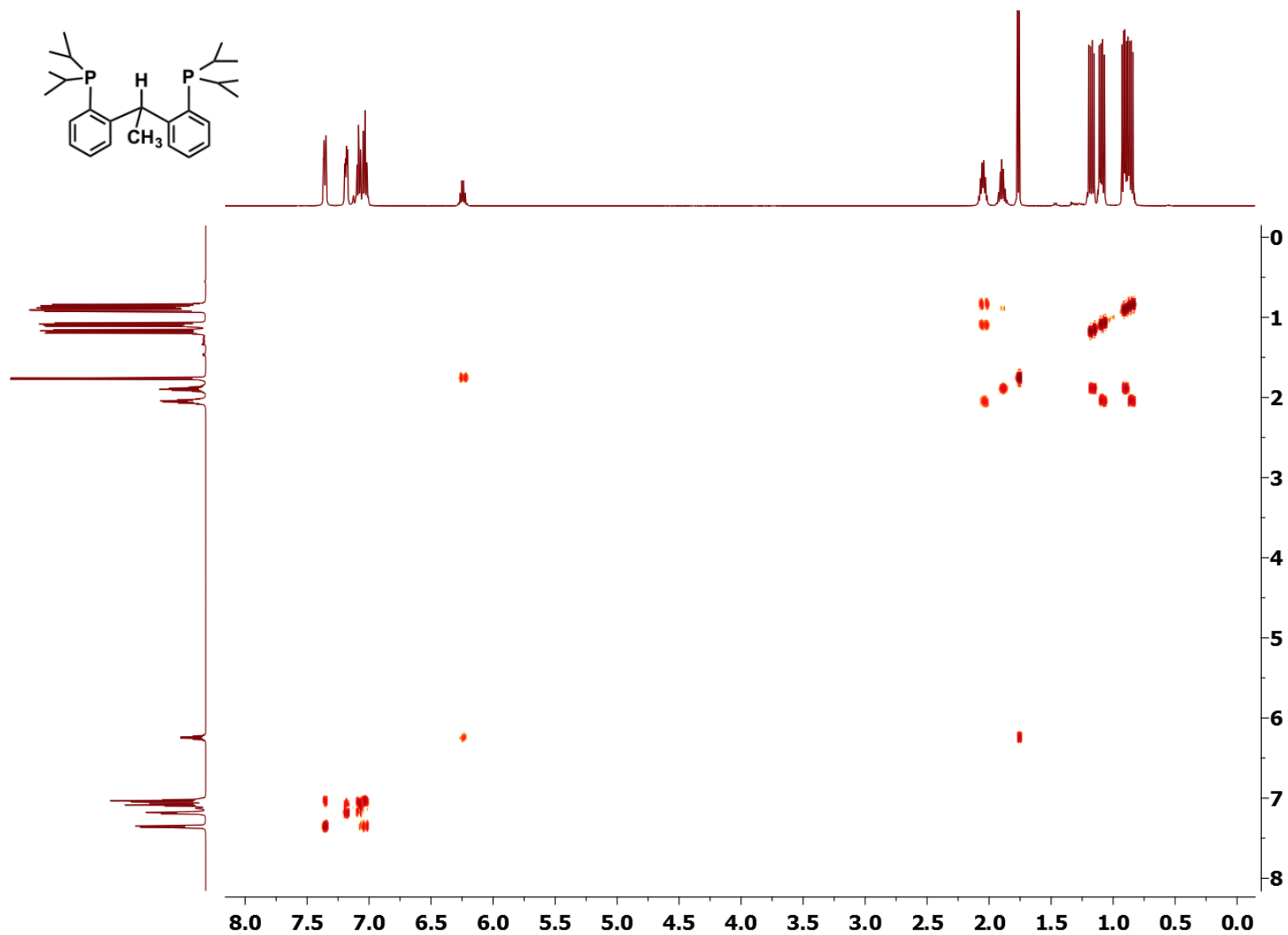


Figure S46. ^1H - ^1H COSY NMR spectrum for PC(CH₃)HP (7).

7.7 NMR Spectra for [PC(CH₃)HP]PdCl₂ (8)

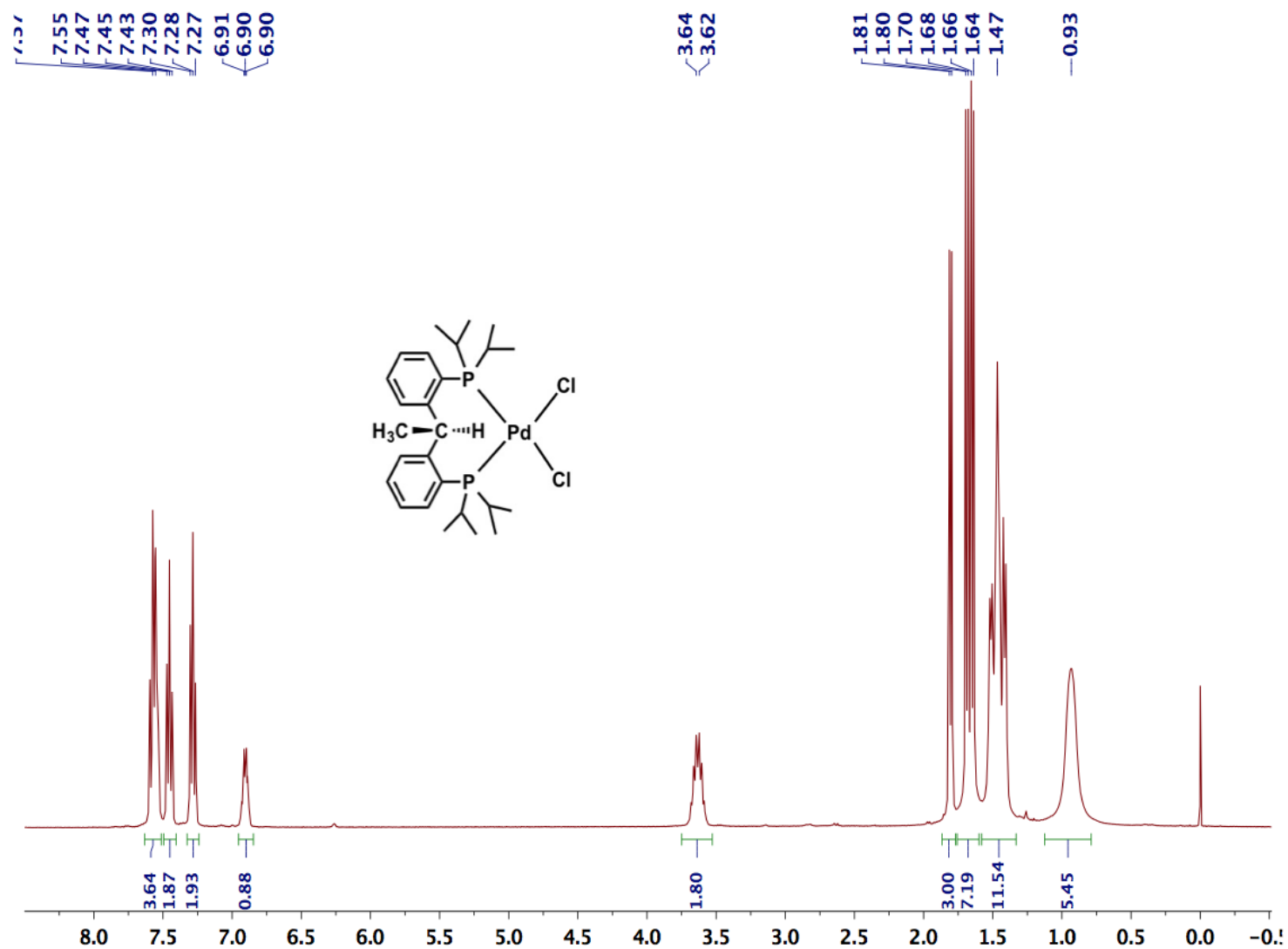


Figure S47. ¹H NMR spectrum (290 K) for [PC(CH₃)HP]PdCl₂ (8).

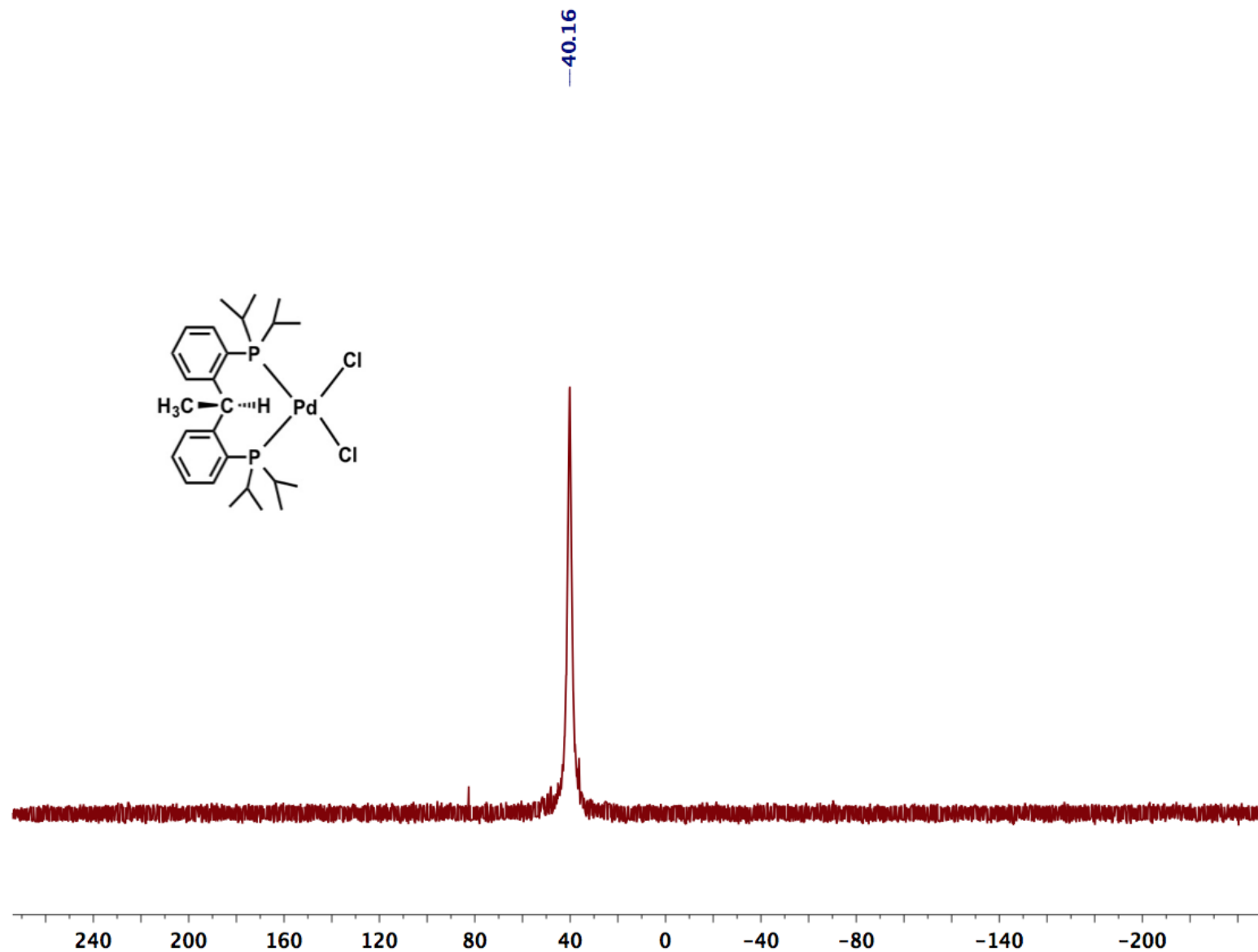


Figure S49. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (290 K) for $[\text{PC}(\text{CH}_3)\text{HP}]\text{PdCl}_2$ (**8**).

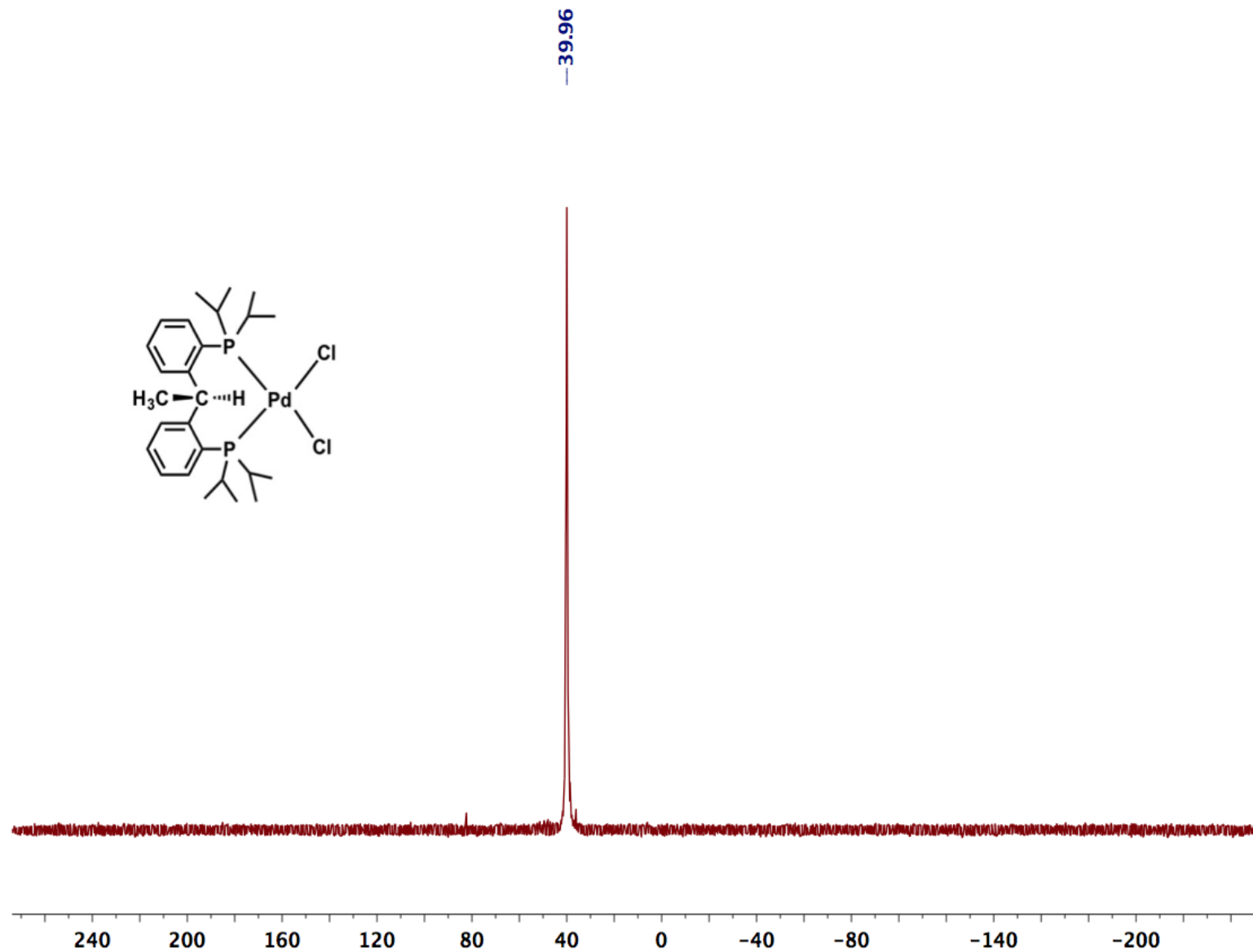


Figure S50. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (320 K) for $[\text{PC}(\text{CH}_3)\text{HP}]\text{PdCl}_2$ (**8**).

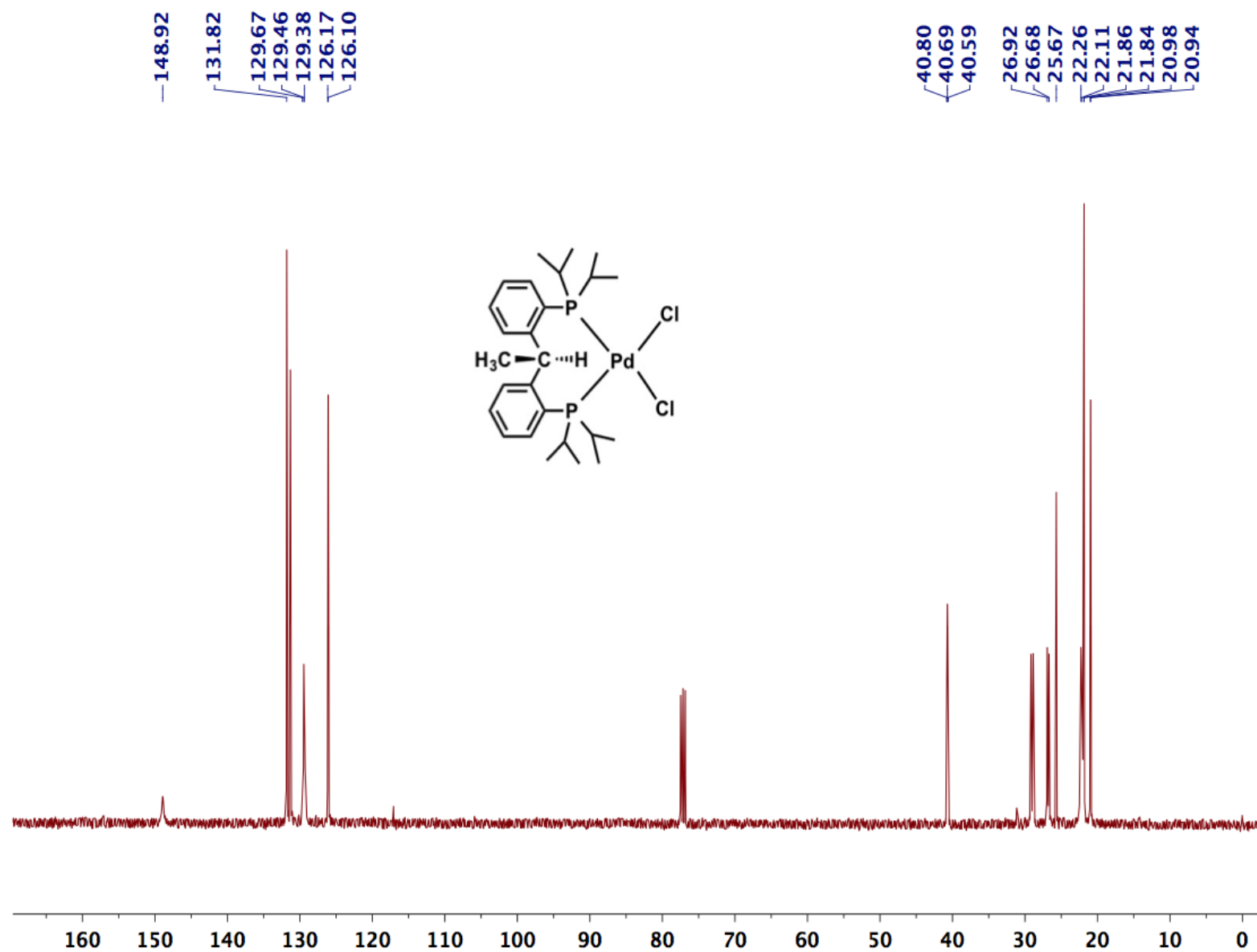
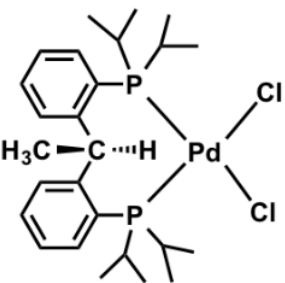


Figure S51. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (290 K) for $[\text{PC}(\text{CH}_3)\text{HP}]\text{PdCl}_2$ (8).



-S81-

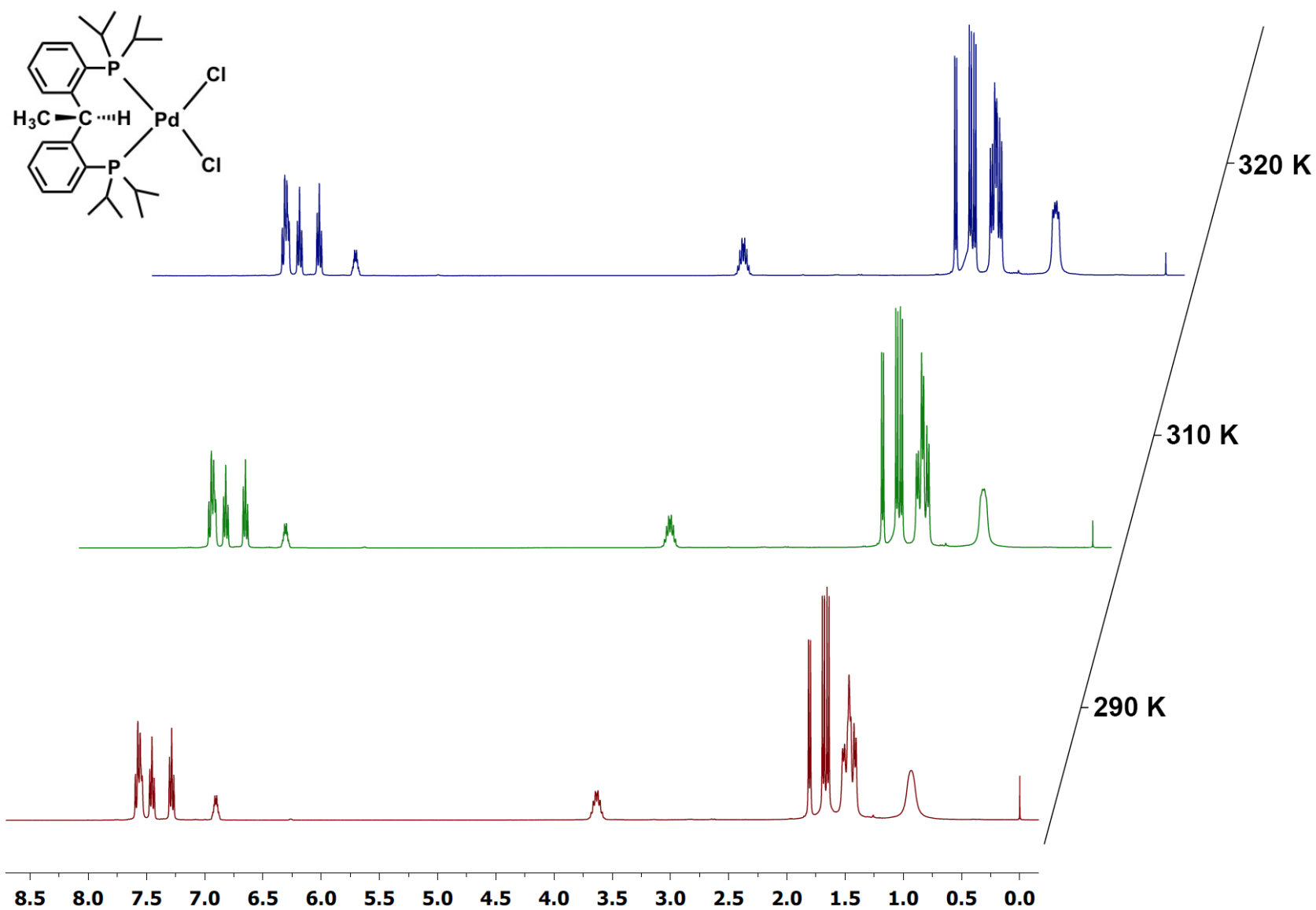


Figure S53. Variable temperature ^1H NMR spectra for $[\text{PC}(\text{CH}_3)\text{HP}]\text{PdCl}_2$ (8).

7.8 NMR Spectra for [PC(CH₃)P]PdCl (9)

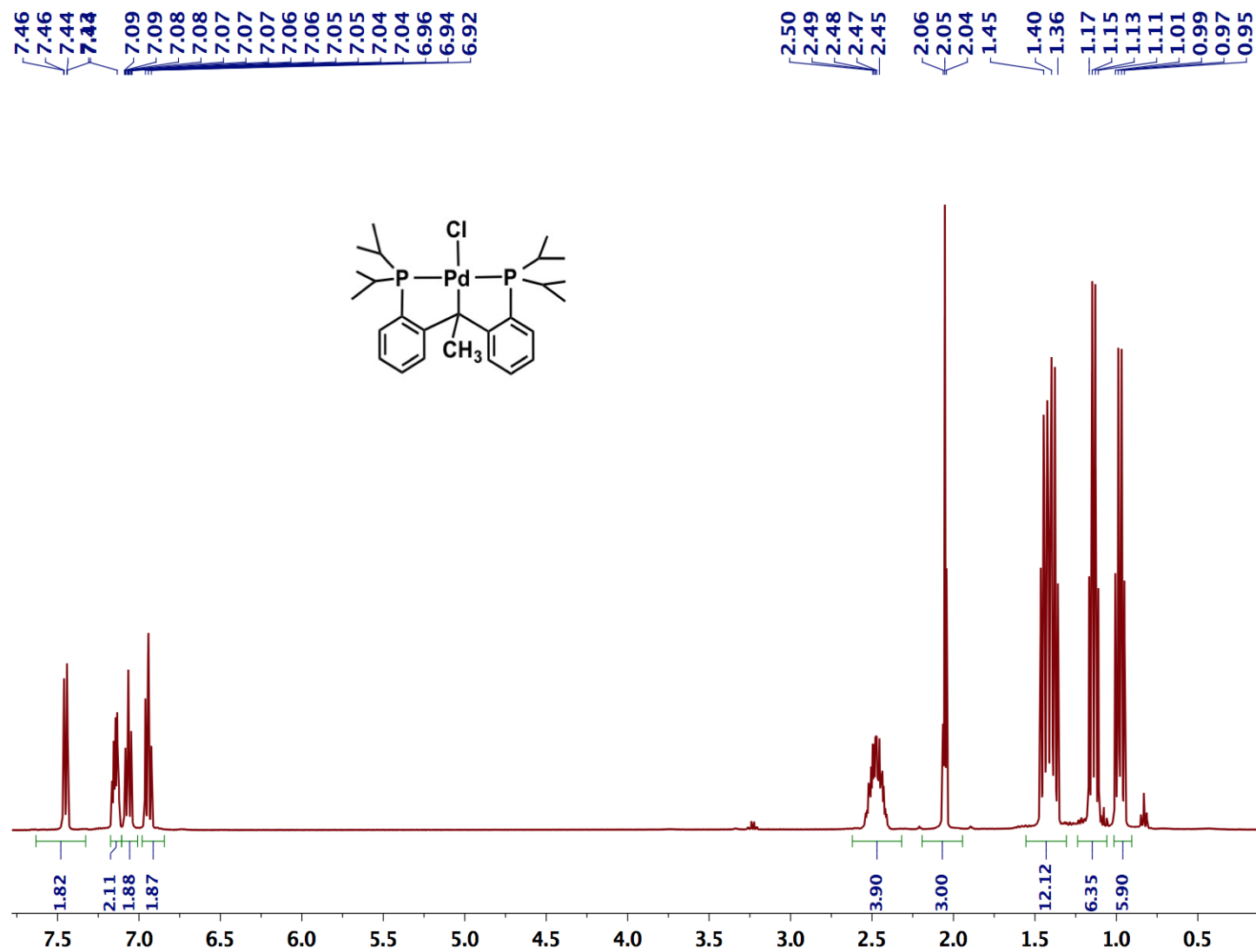


Figure S54. ¹H NMR spectrum for [PC(CH₃)P]PdCl (9).



Figure S55. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for $[\text{PC}(\text{CH}_3)\text{P}]\text{PdCl}$ (9).

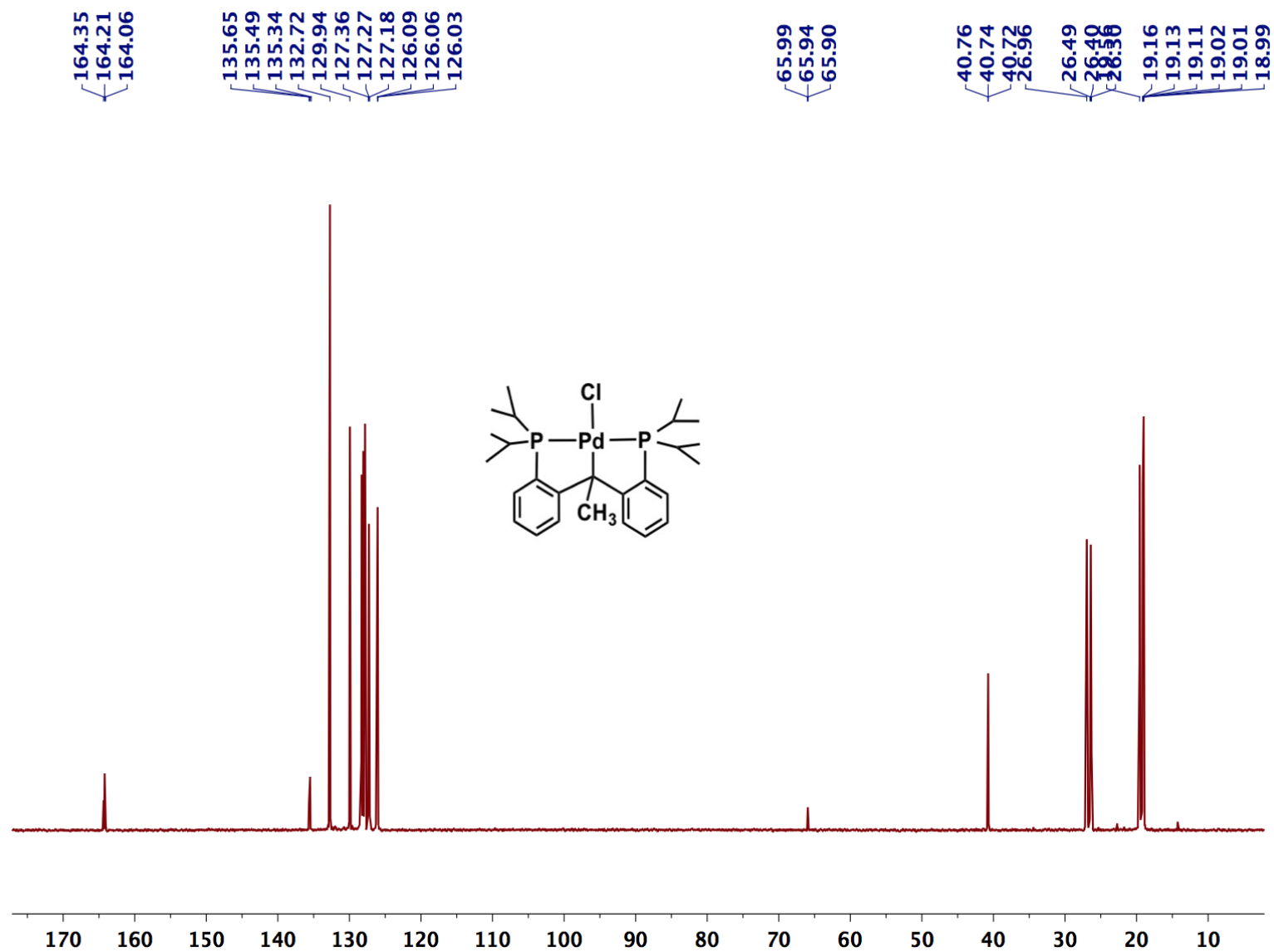


Figure S56. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for [PC(CH₃)P]PdCl (9).

7.9 NMR Spectra for [PC(sp³)HP]PdI (11)

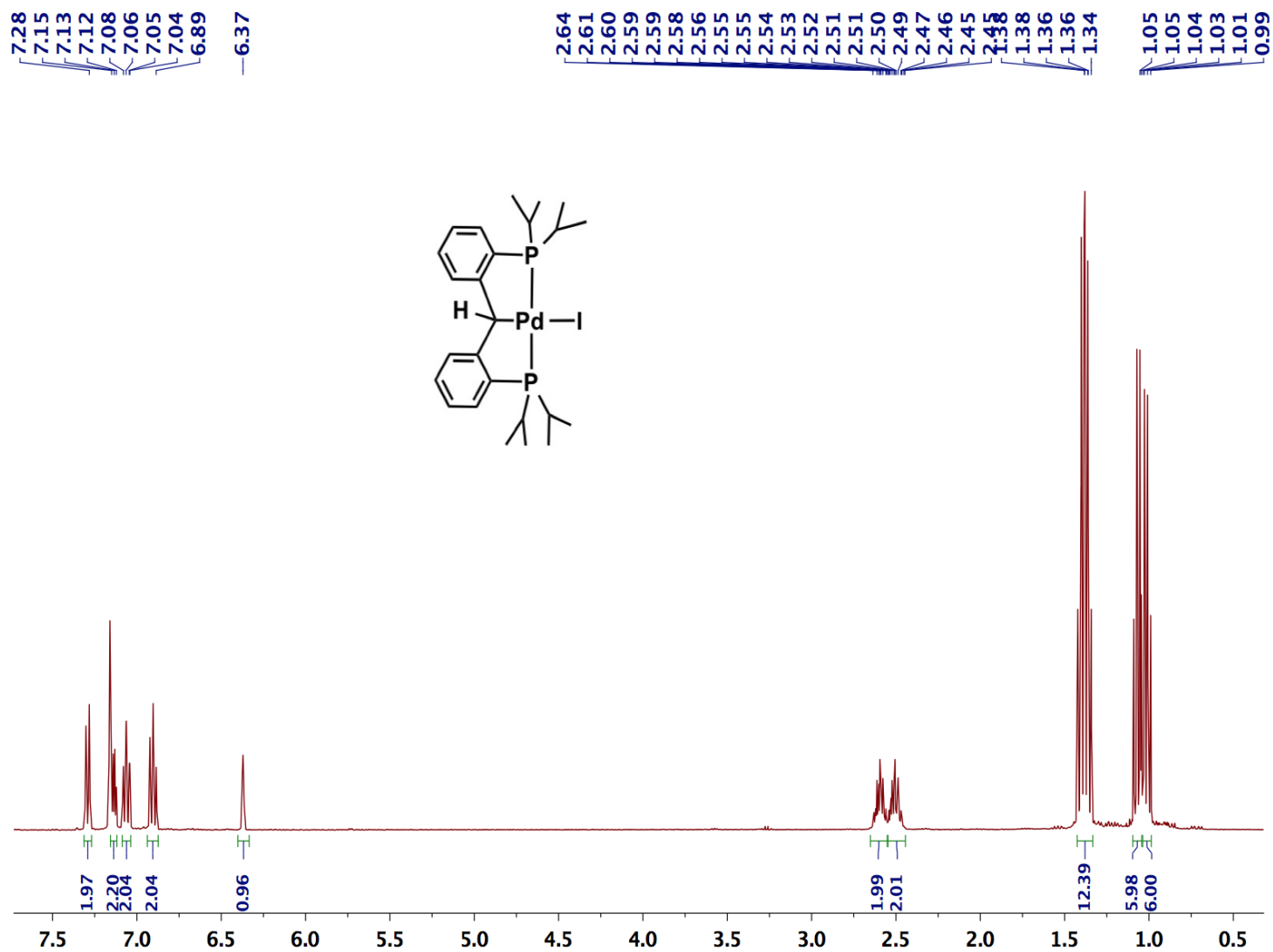


Figure S57. ¹H NMR spectrum for [PC(sp³)HP]PdI (11).

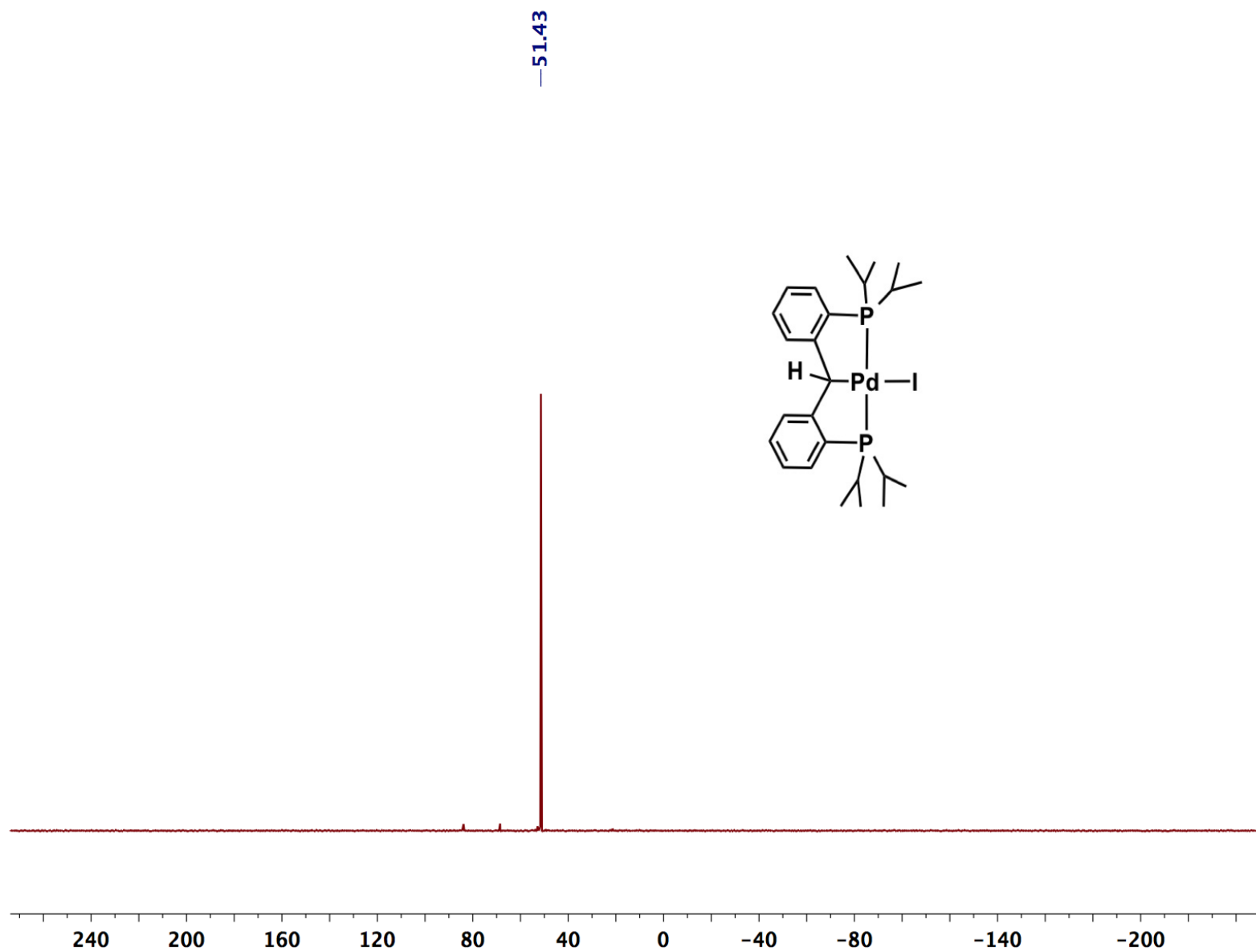


Figure S58. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for [PC(sp³)HP]PdI (**11**).

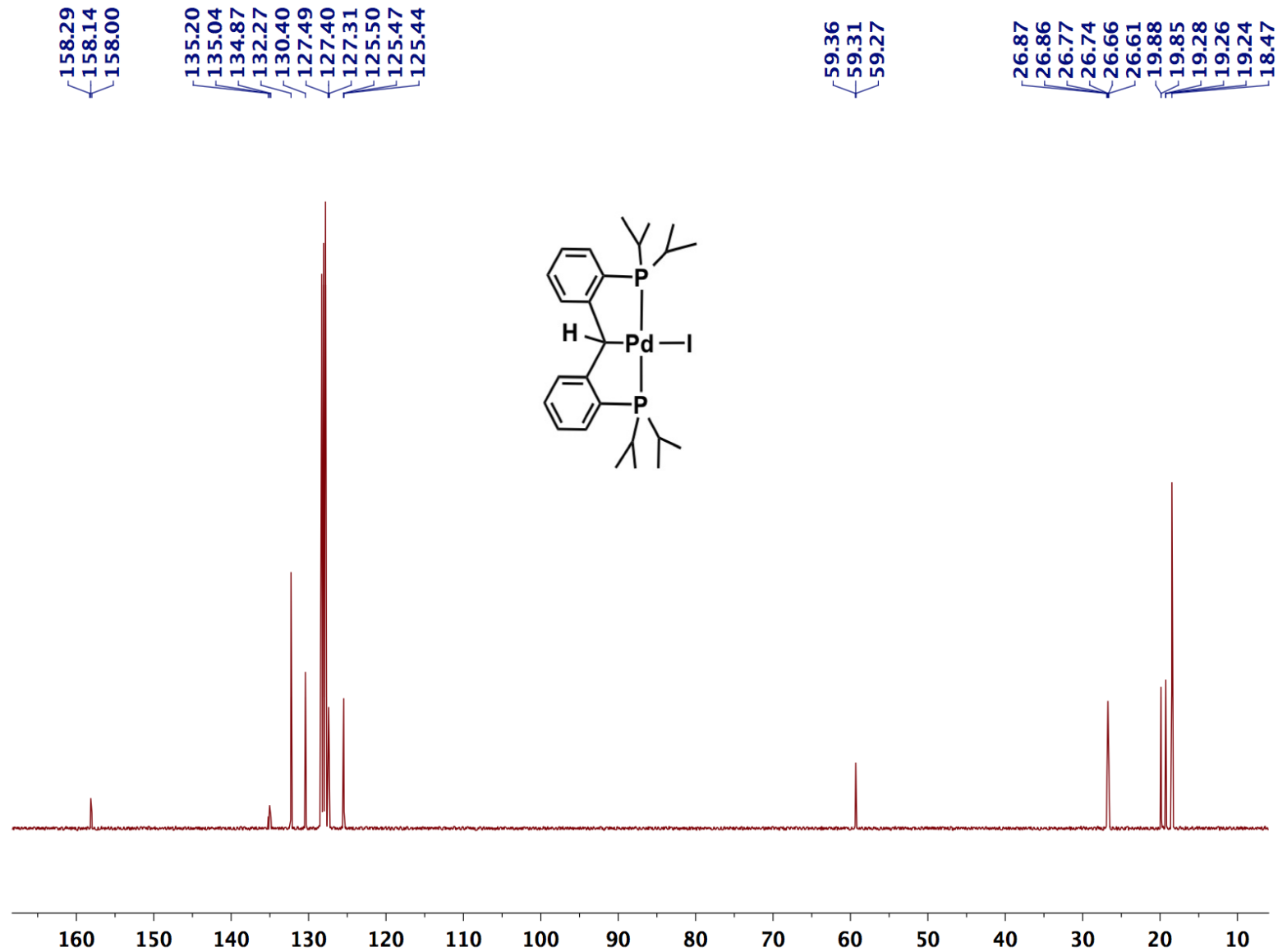


Figure S59. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for [PC(sp³)HP]PdI (11).

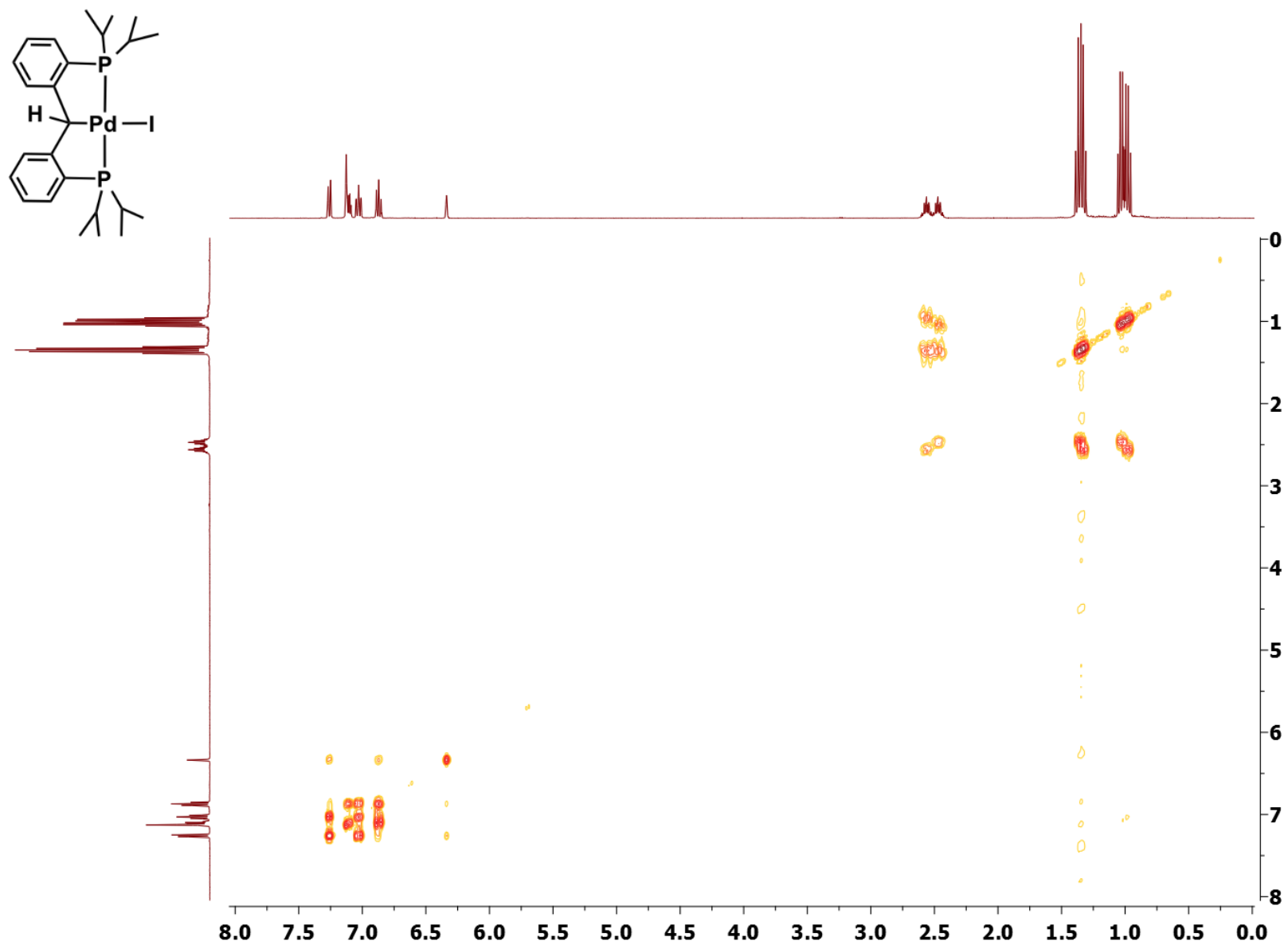


Figure S60. ^1H - ^1H COSY NMR spectrum for [PC(sp³)HP]PdI (11).

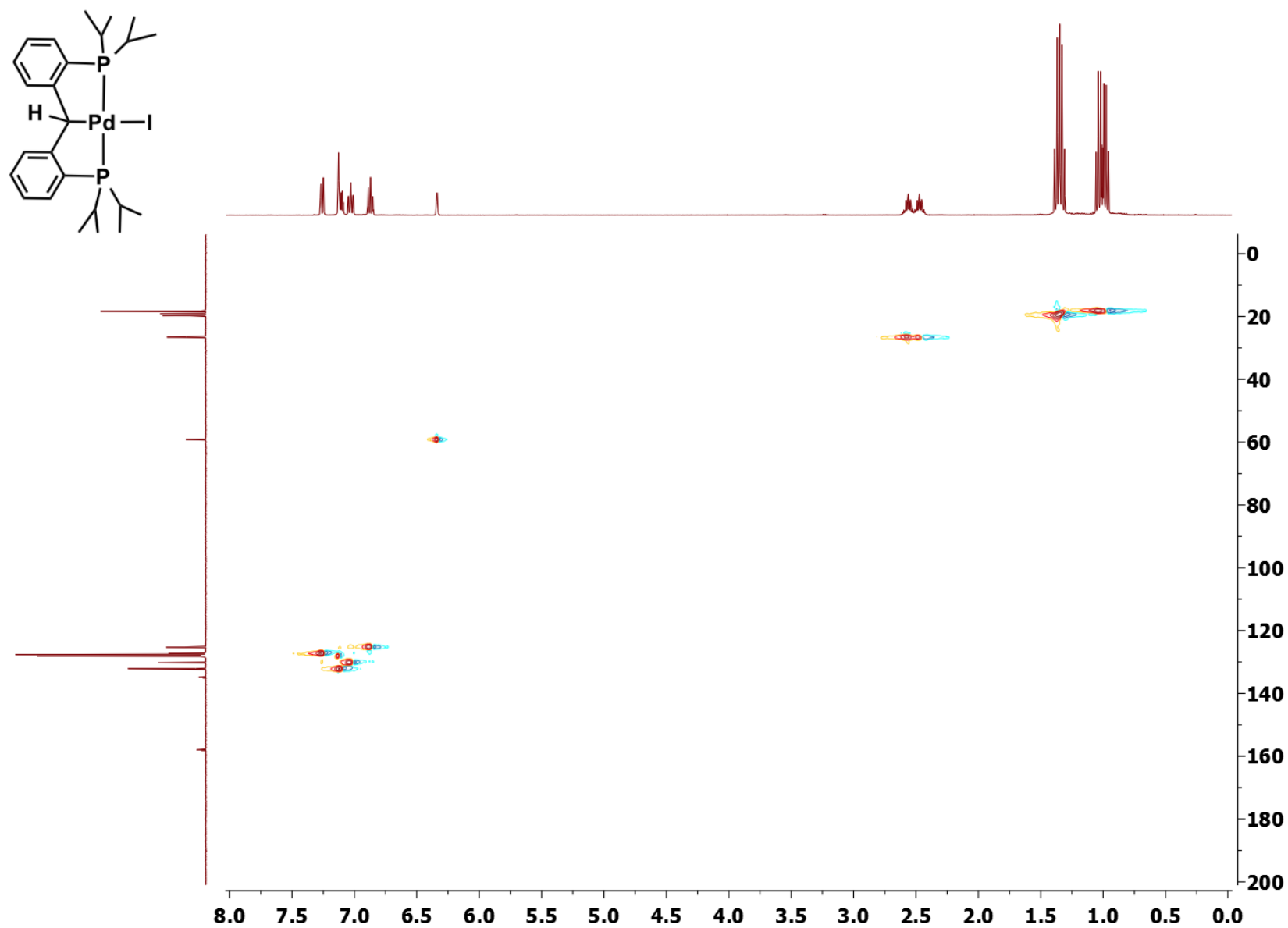


Figure S61. ^1H - ^{13}C HSQC NMR spectrum for [PC(sp³)HP]PdI (**11**).

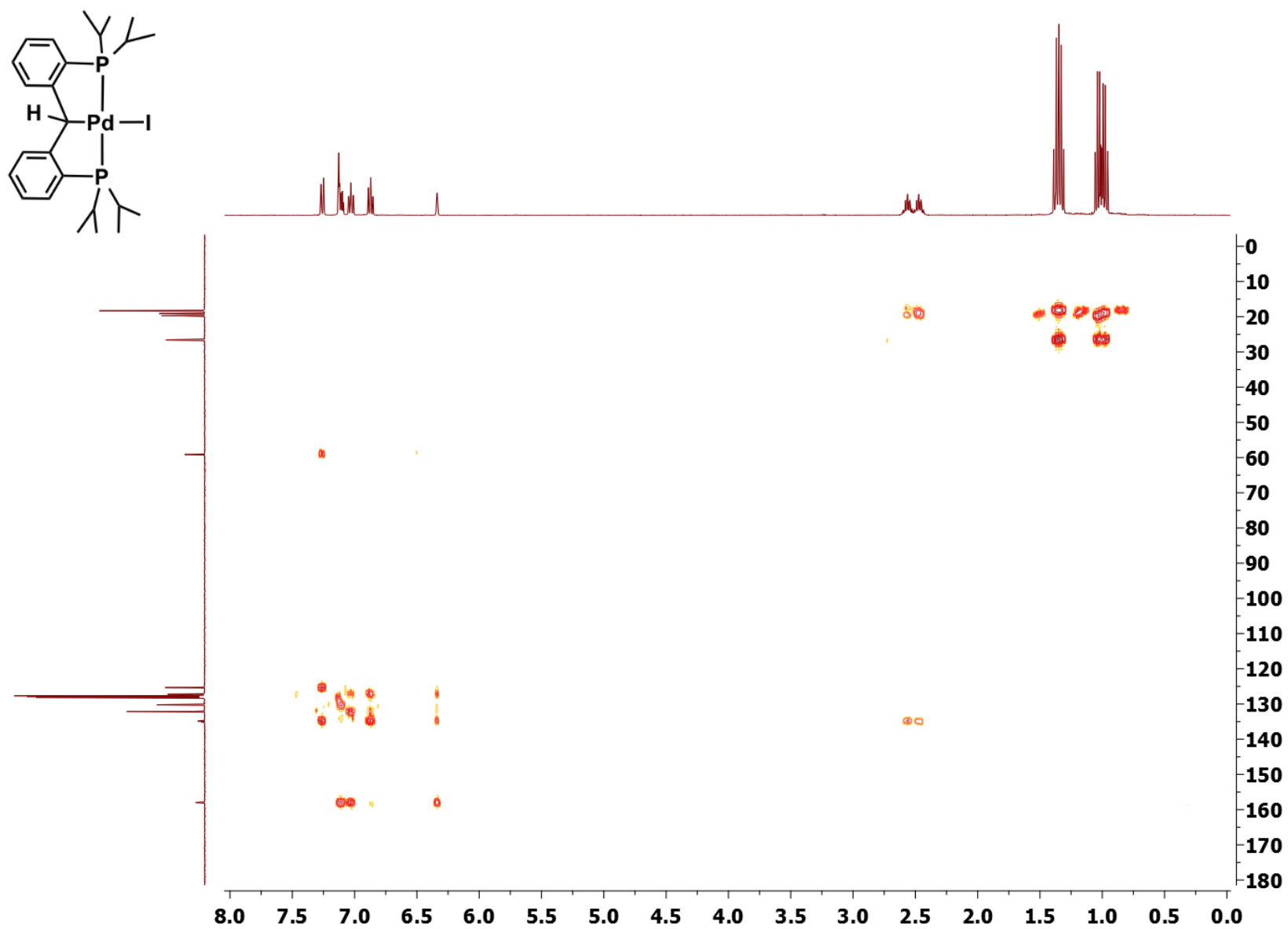


Figure S62. ¹H-¹³C HMBC NMR spectrum for [PC(sp³)HP]PdI (11).

7.10 NMR Spectra for [PC(sp³)H₂P]PdBr₂ (12)

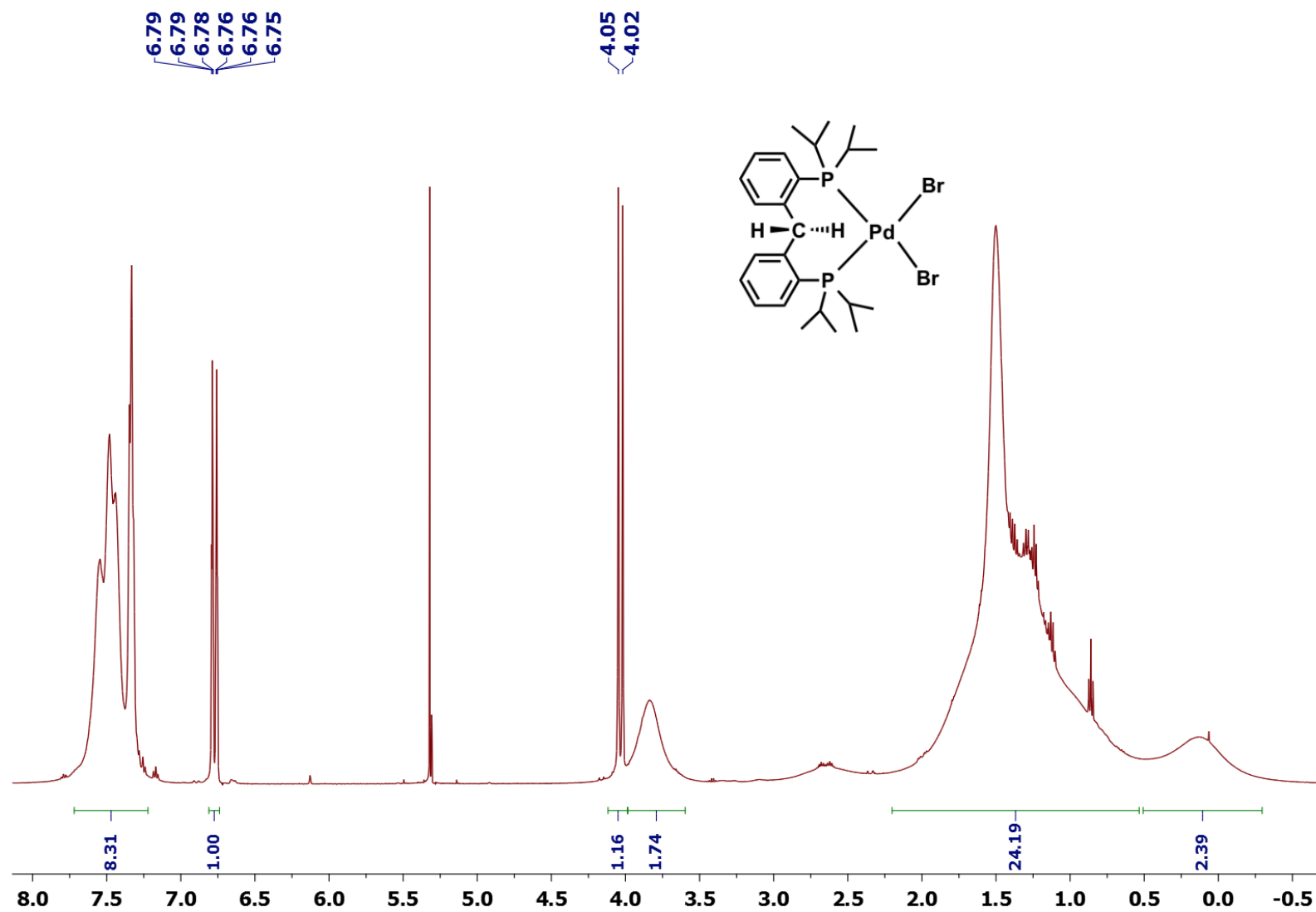


Figure S63. ¹H NMR spectrum (298 K) for [PC(sp³)H₂P]PdBr₂ (12).

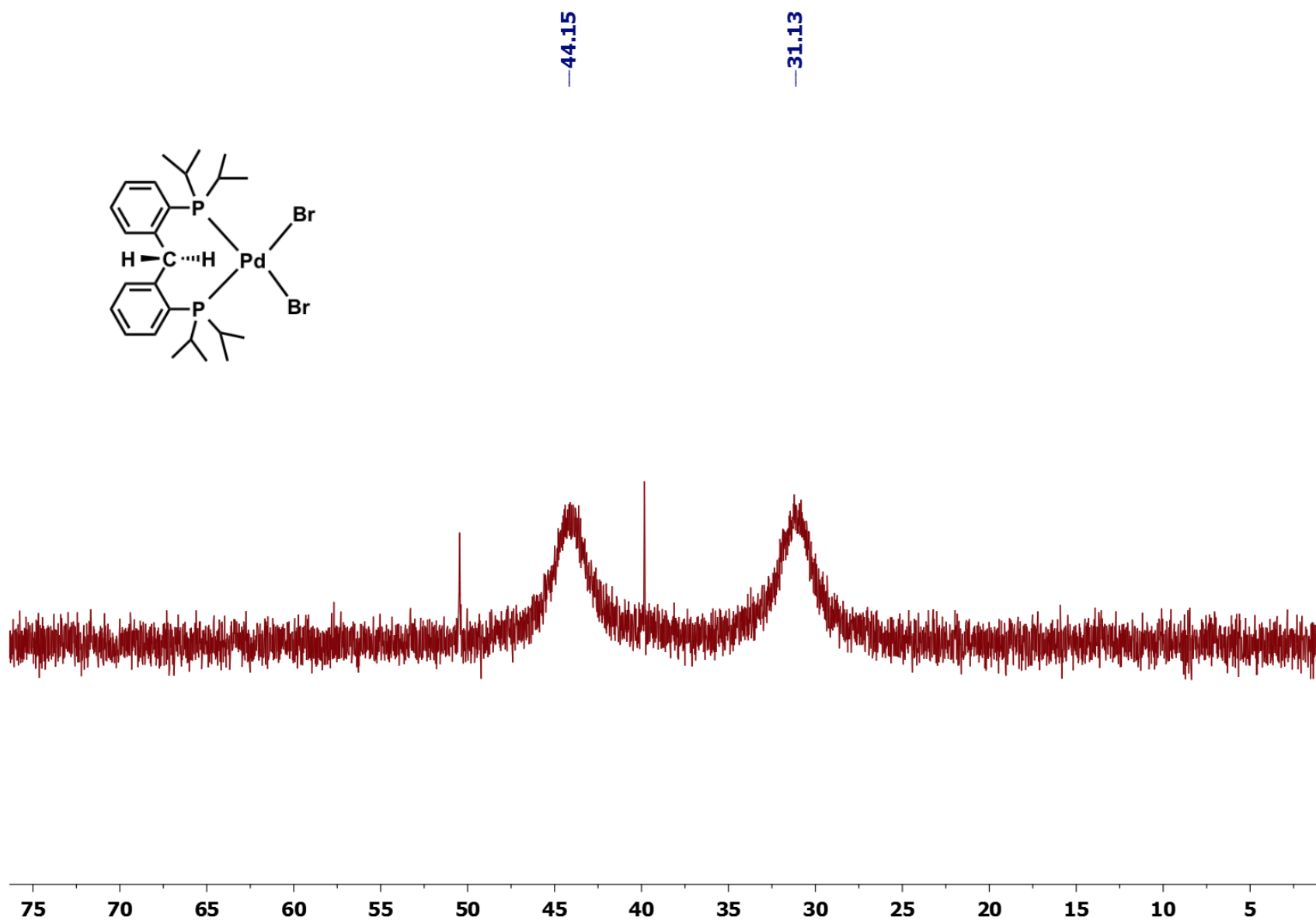


Figure S64. $^{31}P\{^1H\}$ NMR spectrum (298 K) for $[PC(sp^3)H_2P]PdBr_2$ (**12**).

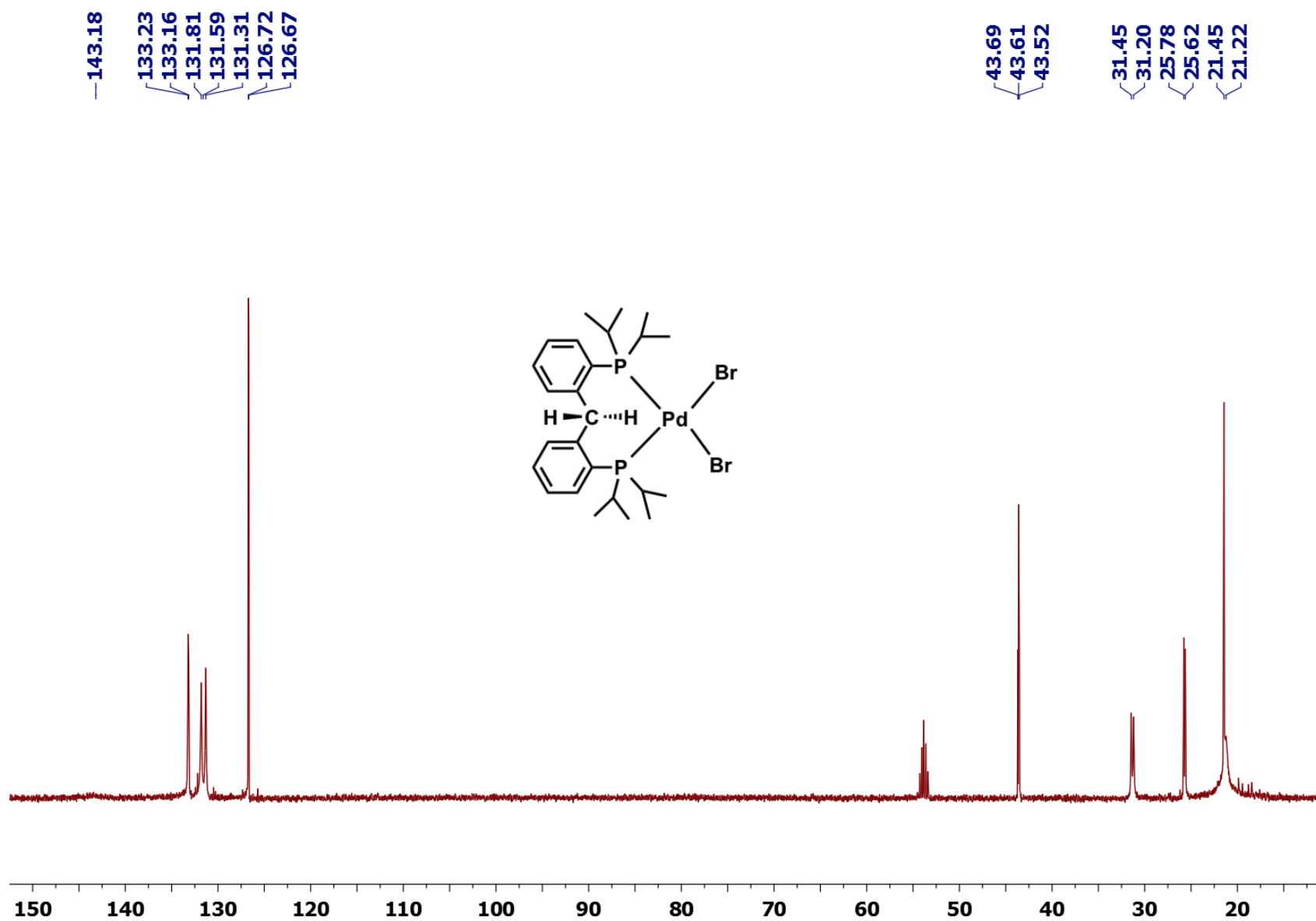


Figure S65. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (298 K) for $[\text{PC}(\text{sp}^3)\text{H}_2\text{P}]\text{PdBr}_2$ (12).

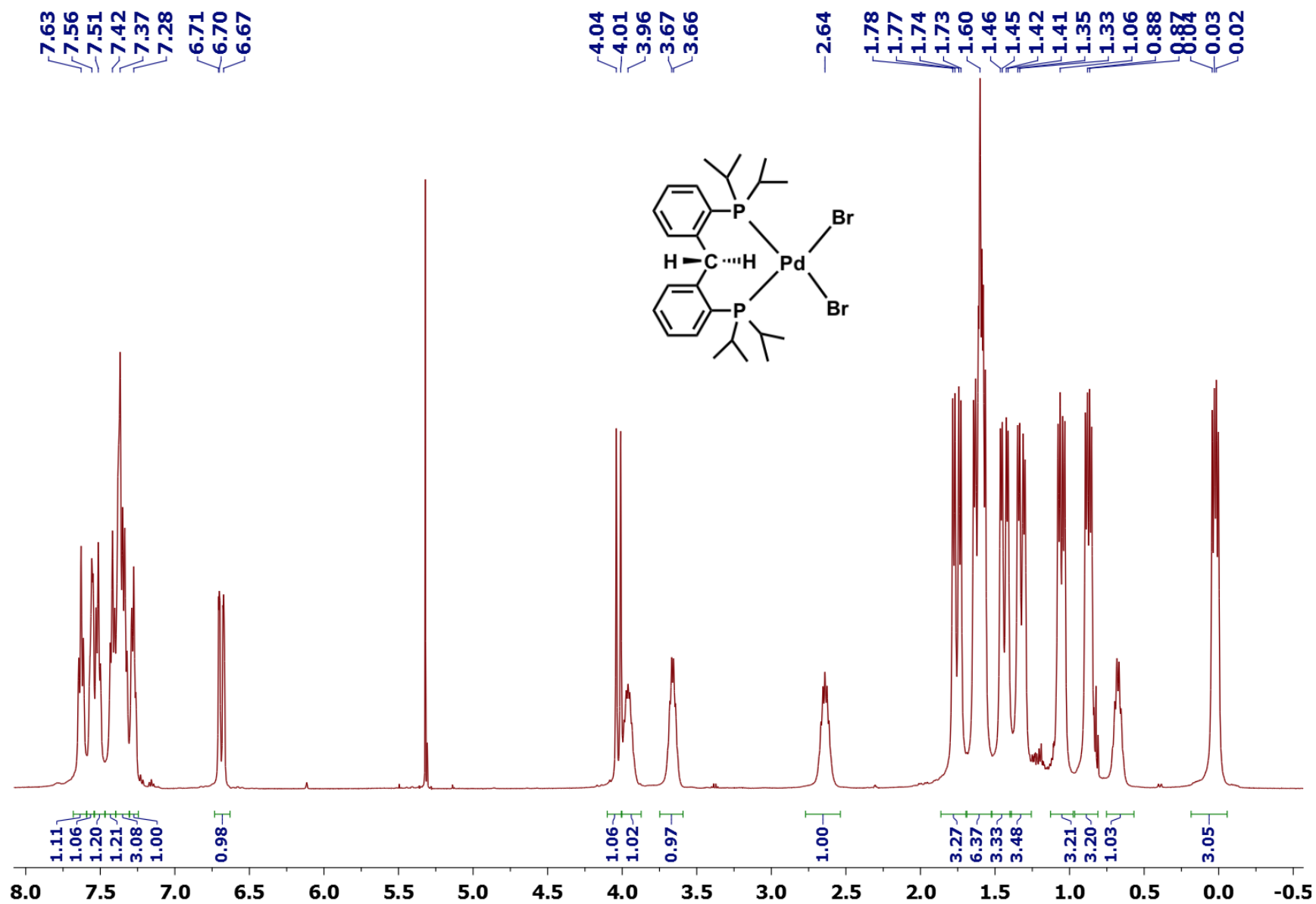


Figure S66. ¹H NMR spectrum (248 K) for [PC(sp³)H₂P]PdBr₂ (12).

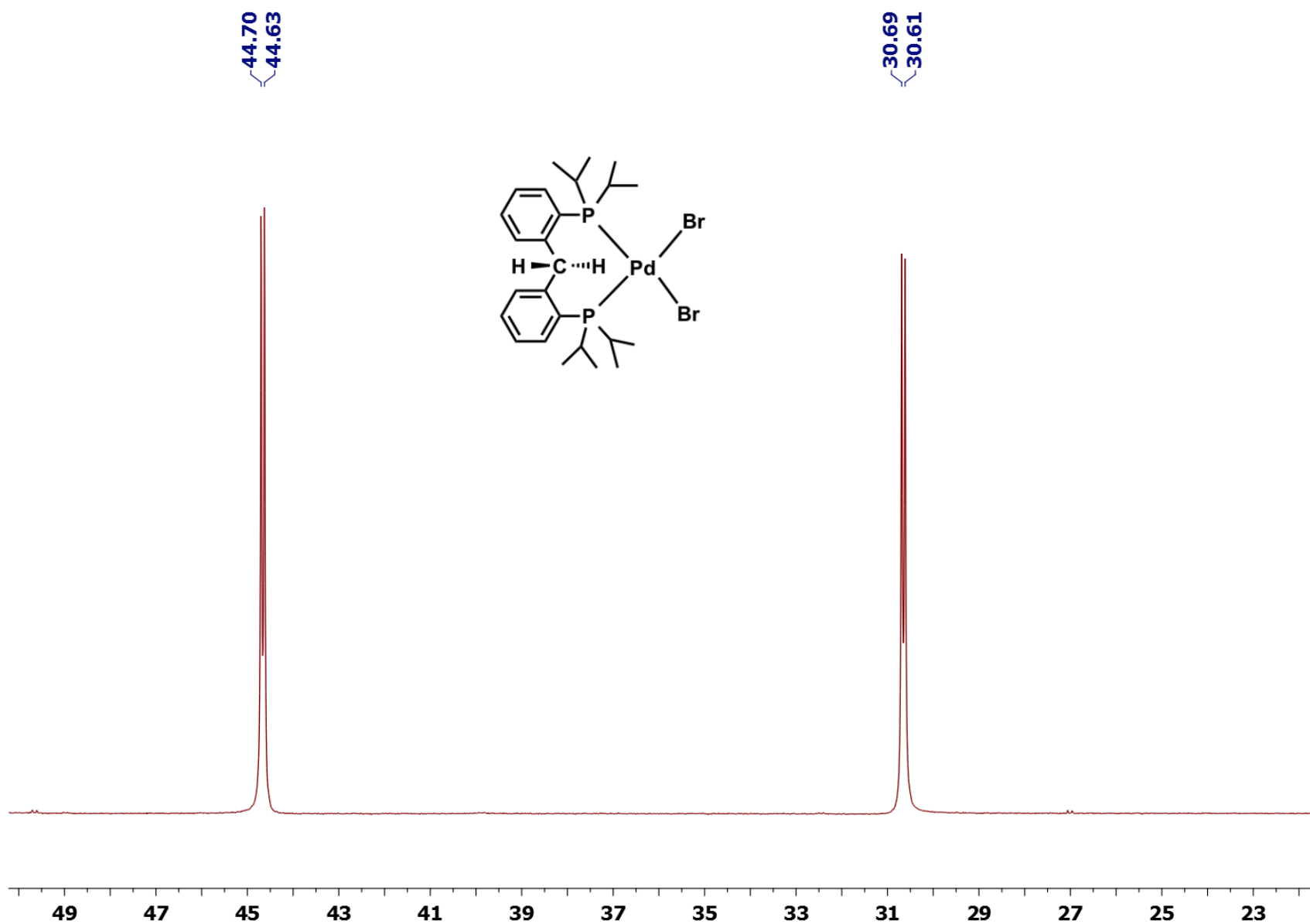


Figure S67. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (248 K) for $[\text{PC}(\text{sp}^3)\text{H}_2\text{P}]\text{PdBr}_2$ (12).

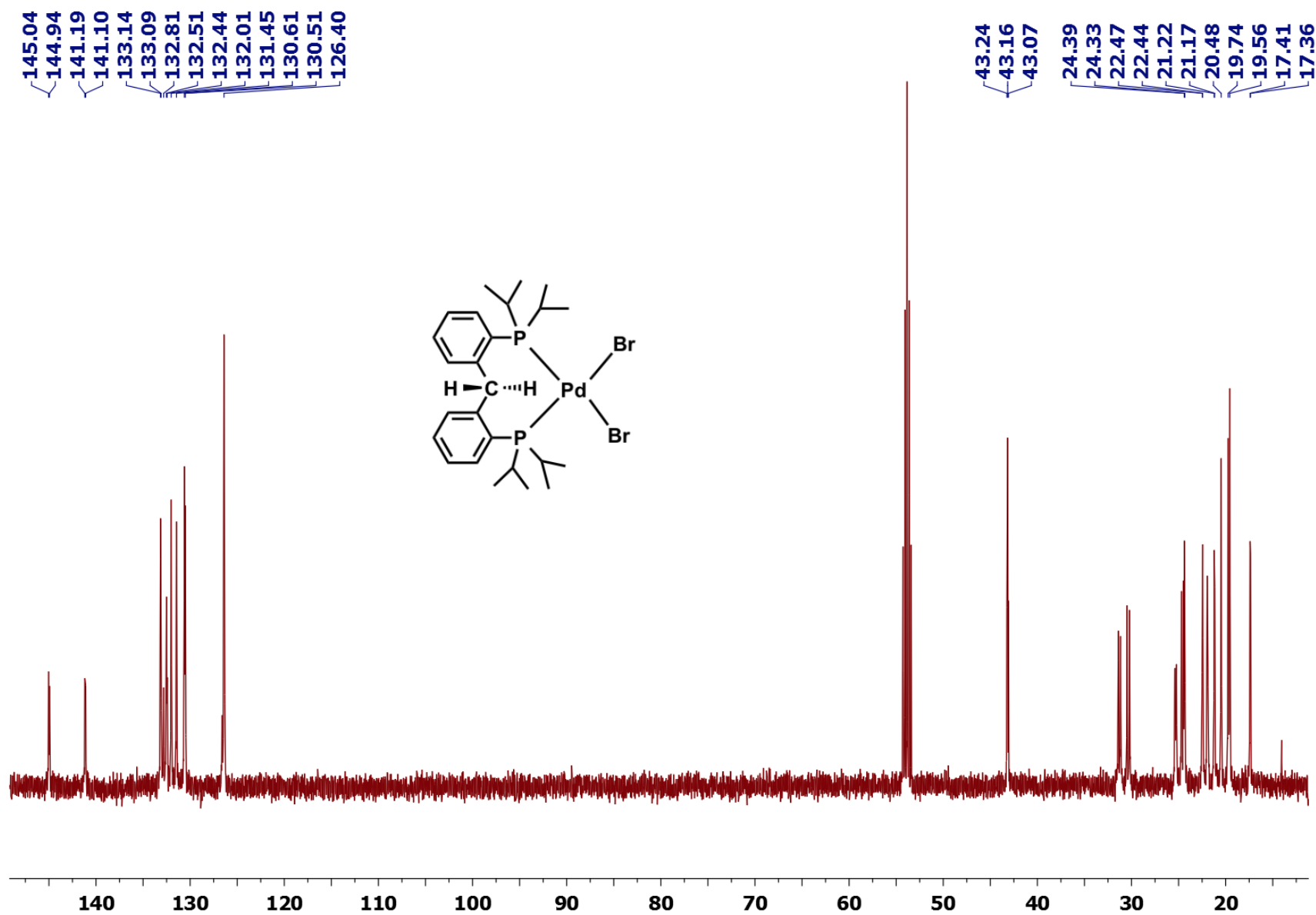


Figure S68. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (248 K) for $[\text{PC}(\text{sp}^3)\text{H}_2\text{P}]\text{PdBr}_2$ (12).

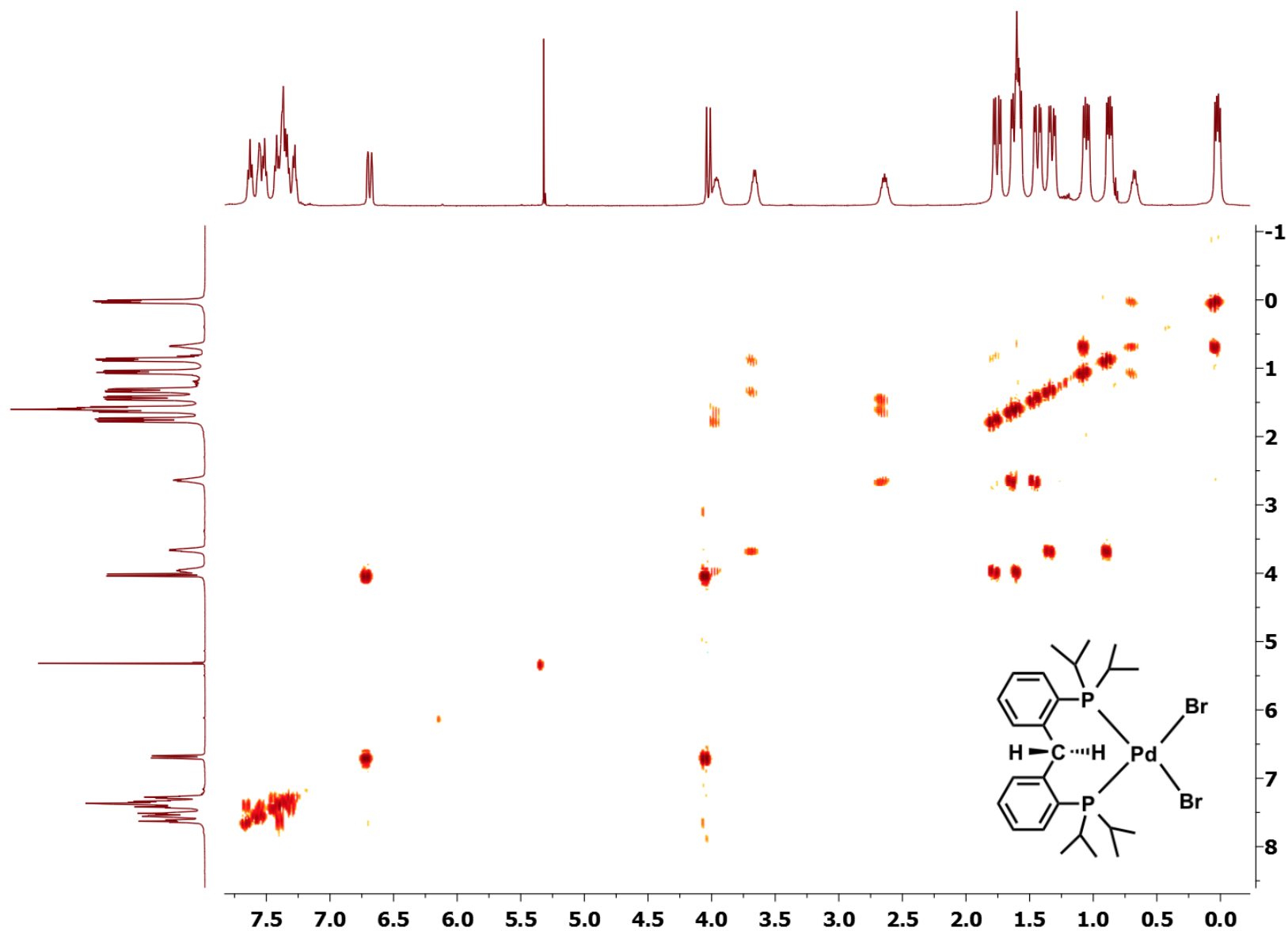


Figure S69. 1H - 1H COSY NMR spectrum (248 K) for $[PC(sp^3)H_2P]PdBr_2$ (**12**).

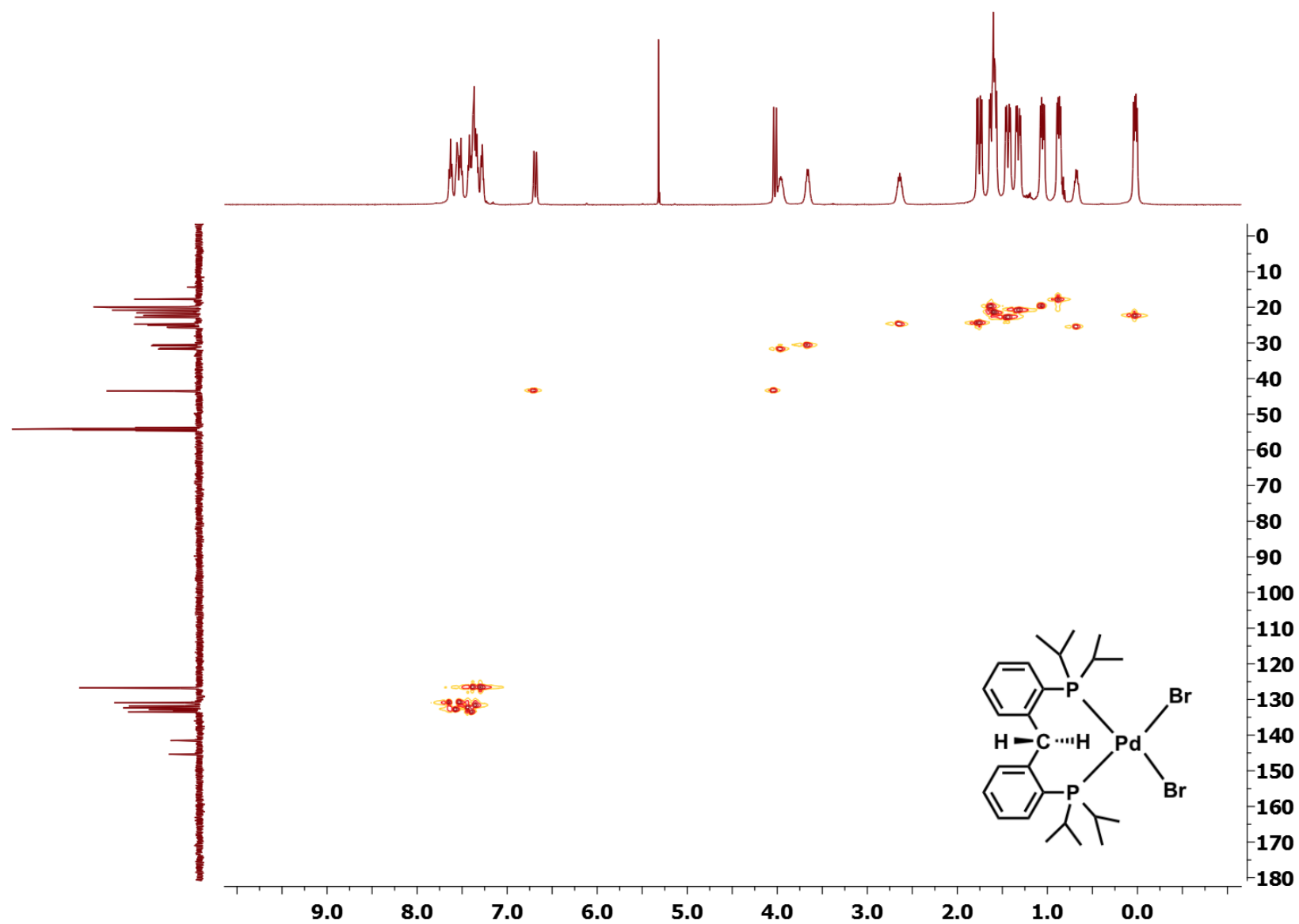


Figure S70. ^1H - ^{13}C HSQC NMR spectrum (248 K) for $[\text{PC}(\text{sp}^3)\text{H}_2\text{P}]\text{PdBr}_2$ (12).

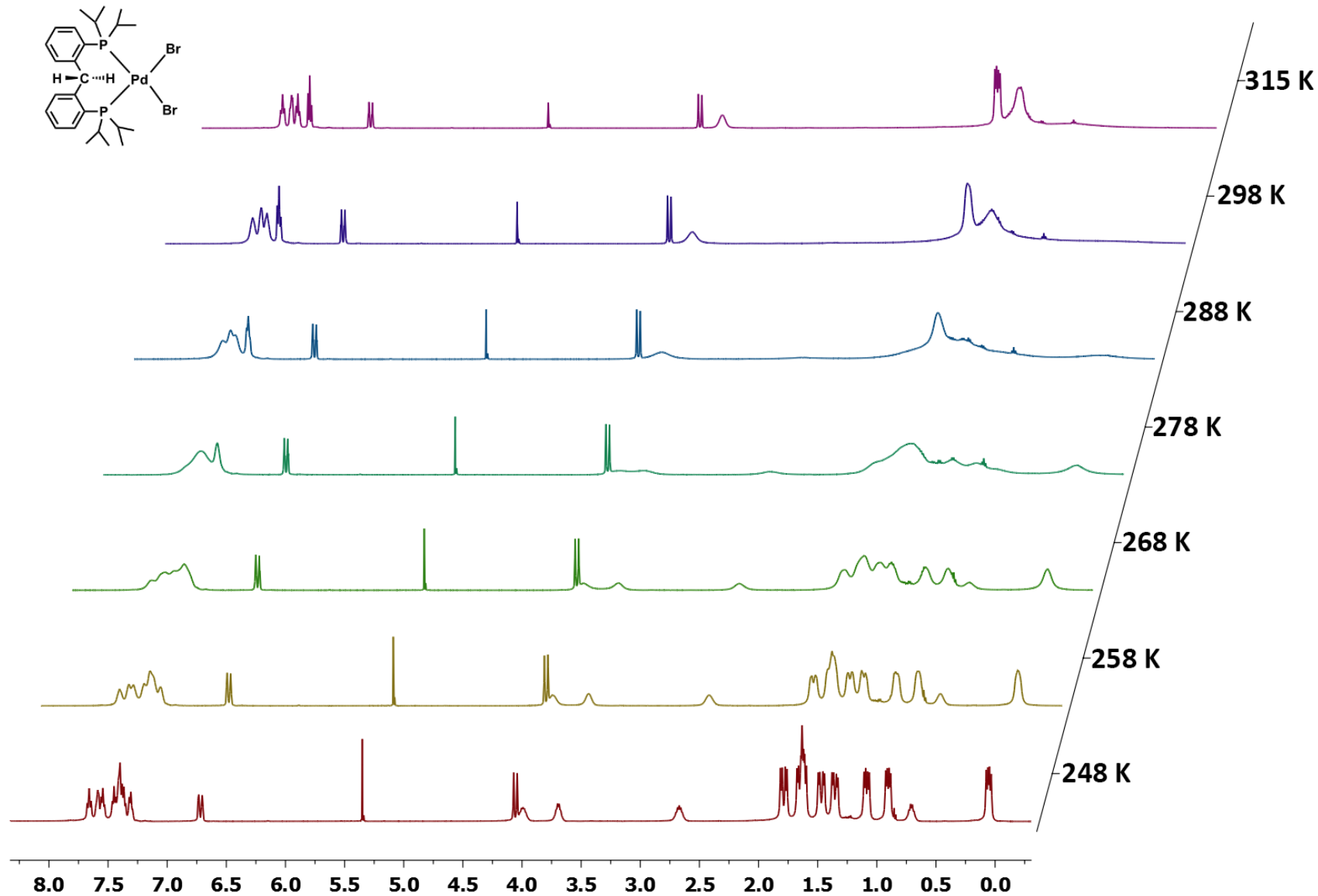


Figure S71. Variable temperature ^1H NMR spectra for $[\text{PC}(\text{sp}^3)\text{H}_2\text{P}]\text{PdBr}_2$ (12).

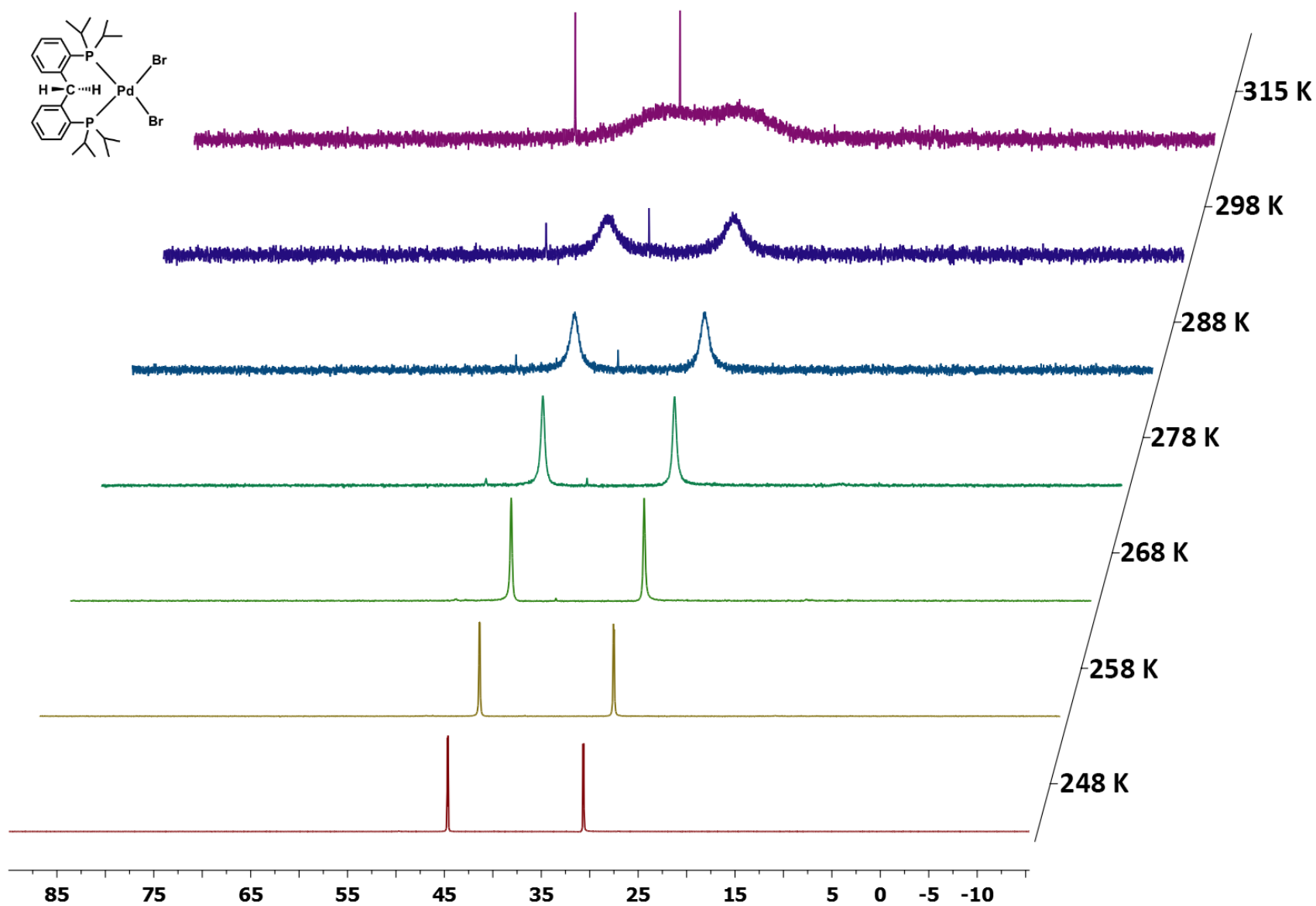


Figure S72. Variable temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for $[\text{PC}(\text{sp}^3)\text{H}_2\text{P}]\text{PdBr}_2$ (12).

8 Crystallographic tables

8.1 Crystal data for $\{[\text{PC}(\text{sp}^2)\text{P}]\text{PdI}\}_2 \cdot \frac{1}{2}\text{Et}_2\text{O} (\{2\}_2 \cdot \frac{1}{2}\text{Et}_2\text{O})$

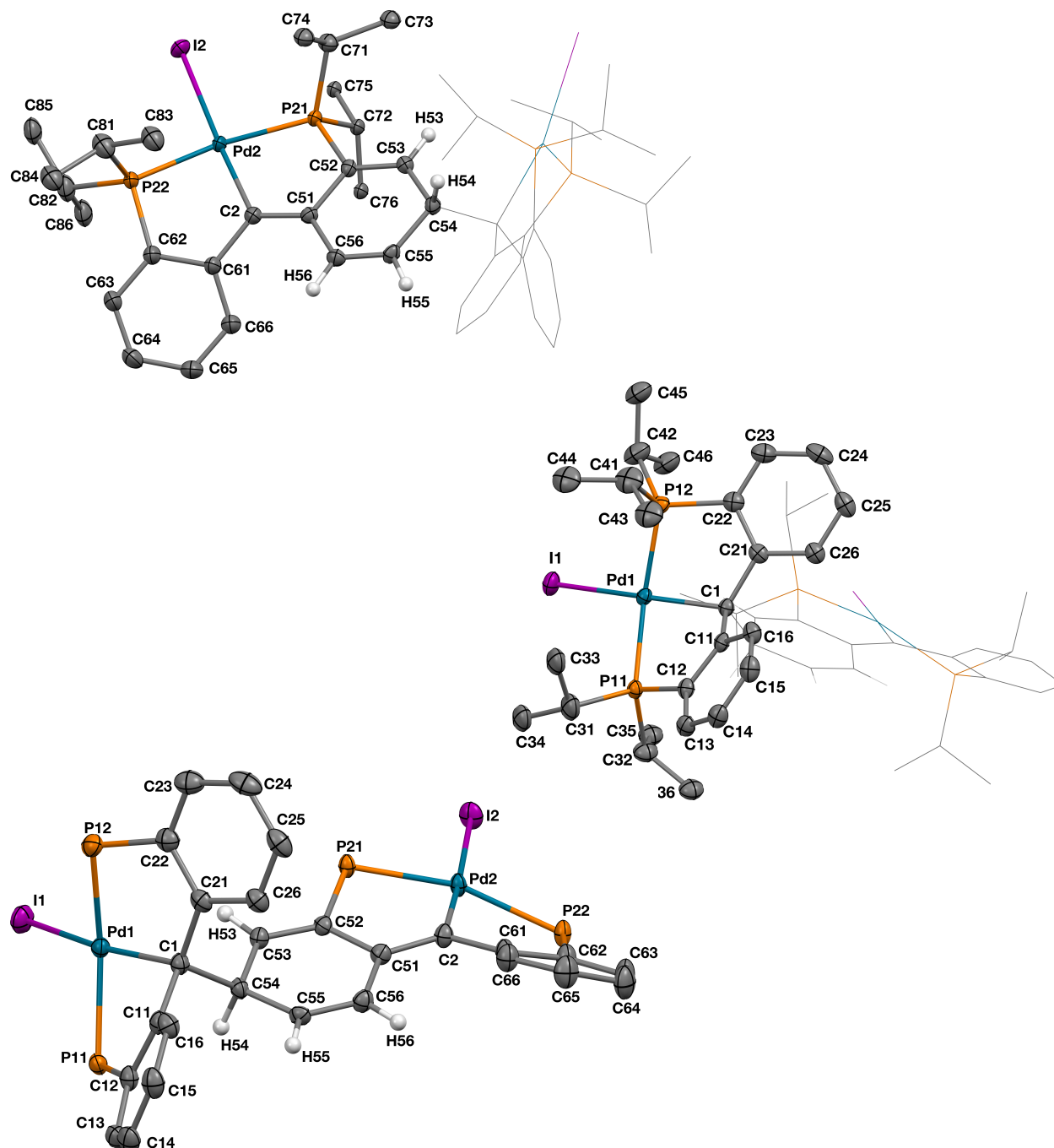


Figure S73. Thermal-ellipsoid representation of $\{[\text{PC}(\text{sp}^2)\text{P}]\text{PdI}\}_2 \cdot \frac{1}{2}\text{Et}_2\text{O} (\{2\}_2 \cdot \frac{1}{2}\text{Et}_2\text{O})$ at 50% probability. Most hydrogen atoms and the solvent were omitted for clarity.

Table S16. Crystal data and structure refinement for $\{[\text{PC}(\text{sp}^2)\text{P}]\text{PdI}\}_2 \cdot \frac{1}{2} \text{Et}_2\text{O} (\{\mathbf{2}\}_2 \cdot \frac{1}{2} \text{Et}_2\text{O})$.

Identification code:	cc218c	
Empirical formula:	$\text{C}_{104}\text{H}_{154}\text{I}_4\text{OP}_8\text{Pd}_4$	
Formula weight:	2601.23	
Temperature:	120(2) K	
Wavelength:	0.71073 Å	
Crystal system:	Monoclinic	
Space group:	$P2_1/c$	
Unit cell dimensions:	$a = 16.2343(6)$ Å	$\alpha = 90^\circ$
	$b = 15.9423(6)$ Å	$\beta = 94.7040(14)^\circ$
	$c = 20.8753(8)$ Å	$\gamma = 90^\circ$
Volume:	5384.6(4) Å ³	
Z:	2	
Density (calculated):	1.604 g·cm ⁻³	
Absorption coefficient (μ):	1.967 mm ⁻¹	
F(000):	2604	
Crystal size:	0.11 × 0.09 × 0.08 mm ³	
θ range for data collection:	1.26 to 25.00°	
Index ranges:	$-19 \leq h \leq 19, -18 \leq k \leq 18, -24 \leq l \leq 24$	
Reflections collected:	131164	
Independent reflections:	9479 [$R_{\text{int}} = 0.0363$]	
Completeness to $\theta = 25.00^\circ$:	100.0 %	
Absorption correction:	Semi-empirical from equivalents	
Max. and min. transmission:	0.7457 and 0.6774	
Refinement method:	Full-matrix least-squares on F^2	
Data / restraints / parameters:	9479 / 0 / 477	
Goodness-of-fit on F^2 :	1.113	
Final R indices [$I > 2\sigma(I)$]:	$R_1 = 0.0257, wR_2 = 0.0662$	
R indices (all data):	$R_1 = 0.0314, wR_2 = 0.0733$	
Largest diff. peak and hole:	0.964 and $-1.540 \text{ e}^- \cdot \text{Å}^{-3}$	

Table S17. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for $\{[\text{PC}(\text{sp}^2)\text{P}]\text{PdI}\}_2 \cdot \frac{1}{2} \text{Et}_2\text{O}$ ($\{\mathbf{2}\}_2 \cdot \frac{1}{2} \text{Et}_2\text{O}$). $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

atom	x	y	z	$U(\text{eq})$
C(1)	0.33153(19)	0.1629(2)	0.26023(15)	0.018(1)
I(1)	0.12423(1)	0.16406(2)	0.08361(1)	0.029(1)
Pd(1)	0.22869(2)	0.16102(2)	0.19020(1)	0.017(1)
C(2)	0.65139(19)	0.1826(2)	0.16751(15)	0.019(1)
I(2)	0.66719(1)	0.27749(1)	−0.04575(1)	0.024(1)
Pd(2)	0.66143(1)	0.22217(2)	0.07538(1)	0.016(1)
P(11)	0.23227(5)	0.01697(5)	0.21072(4)	0.019(1)
O(9)	1.0000	0.5000	0.0000	0.066(1)
C(11)	0.31086(19)	0.1016(2)	0.31291(15)	0.019(1)
P(12)	0.21527(5)	0.29868(6)	0.21480(4)	0.022(1)
C(12)	0.27613(19)	0.0236(2)	0.29410(15)	0.021(1)
C(13)	0.2660(2)	−0.0388(2)	0.33990(16)	0.025(1)
C(14)	0.2852(2)	−0.0230(2)	0.40492(17)	0.027(1)
C(15)	0.3137(2)	0.0553(2)	0.42348(17)	0.028(1)
C(16)	0.3272(2)	0.1167(2)	0.37838(16)	0.024(1)
P(21)	0.52317(5)	0.24298(5)	0.07745(4)	0.016(1)
C(21)	0.3566(2)	0.2511(2)	0.28317(15)	0.020(1)
P(22)	0.79370(5)	0.16841(6)	0.09114(4)	0.019(1)
C(22)	0.3109(2)	0.3221(2)	0.26250(16)	0.023(1)
C(26)	0.4284(2)	0.2652(2)	0.32375(15)	0.022(1)
C(25)	0.4539(2)	0.3450(2)	0.34195(16)	0.028(1)
C(24)	0.4079(3)	0.4141(2)	0.32028(18)	0.033(1)
C(23)	0.3364(2)	0.4023(2)	0.28094(17)	0.031(1)
C(31)	0.1304(2)	−0.0329(3)	0.2190(2)	0.037(1)
C(32)	0.2875(2)	−0.0652(2)	0.16639(18)	0.031(1)
C(33)	0.0769(2)	0.0241(3)	0.2566(2)	0.037(1)
C(94)	0.9289(18)	0.5887(19)	0.0616(15)	0.108(10)
C(95)	1.0890(15)	0.3932(19)	−0.0434(16)	0.065(6)
C(93)	0.9310(7)	0.5430(7)	0.0062(6)	0.069(4)
C(92)	1.0090(7)	0.4463(7)	−0.0482(5)	0.049(4)
C(34)	0.0857(2)	−0.0566(3)	0.1540(2)	0.037(1)
C(35)	0.3185(2)	−0.0296(2)	0.10504(17)	0.031(1)
C(36)	0.3536(2)	−0.1114(2)	0.20680(18)	0.031(1)
C(43)	0.1484(3)	0.2641(3)	0.3310(2)	0.042(1)
C(42)	0.1923(3)	0.3773(3)	0.1509(2)	0.038(1)
C(41)	0.1338(3)	0.3170(3)	0.2707(2)	0.042(1)
C(44)	0.0489(3)	0.3012(3)	0.2365(2)	0.042(1)
C(46)	0.2626(2)	0.3799(3)	0.1068(2)	0.038(1)
C(45)	0.1684(3)	0.4648(2)	0.1697(2)	0.038(1)

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Table S17. – continued from previous page

atom	x	y	x	U(eq)
C(54)	0.40429(19)	0.1232(2)	0.22377(15)	0.017(1)
C(55)	0.48277(19)	0.1020(2)	0.26418(15)	0.018(1)
C(56)	0.5591(2)	0.1184(2)	0.24773(15)	0.020(1)
C(61)	0.7302(2)	0.1756(2)	0.20820(15)	0.021(1)
C(62)	0.8043(2)	0.1615(2)	0.17839(16)	0.023(1)
C(63)	0.8796(2)	0.1527(2)	0.21527(17)	0.028(1)
C(64)	0.8836(2)	0.1621(3)	0.28144(18)	0.033(1)
C(65)	0.8124(2)	0.1815(3)	0.31108(17)	0.030(1)
C(66)	0.7373(2)	0.1873(2)	0.27527(16)	0.024(1)
C(71)	0.4632(2)	0.1953(2)	0.00745(16)	0.022(1)
C(72)	0.47774(19)	0.3463(2)	0.08870(14)	0.016(1)
C(73)	0.3694(2)	0.2063(2)	0.00217(16)	0.022(1)
C(74)	0.4863(2)	0.1024(2)	0.00464(16)	0.022(1)
C(75)	0.49276(18)	0.4059(2)	0.03365(14)	0.016(1)
C(76)	0.50863(18)	0.3843(2)	0.15335(14)	0.016(1)
C(81)	0.8056(2)	0.0622(2)	0.0581(2)	0.033(1)
C(82)	0.8875(2)	0.2260(2)	0.07079(19)	0.032(1)
C(83)	0.7333(2)	0.0070(2)	0.07329(19)	0.033(1)
C(84)	0.8881(2)	0.0195(2)	0.08015(19)	0.033(1)
C(85)	0.9016(2)	0.2189(2)	−0.00022(19)	0.032(1)
C(86)	0.8834(2)	0.3164(2)	0.09231(19)	0.032(1)
C(53)	0.42313(19)	0.17205(19)	0.16555(15)	0.017(1)
C(52)	0.50027(19)	0.18573(19)	0.14881(14)	0.016(1)
C(51)	0.5754(2)	0.16236(19)	0.18845(15)	0.017(1)
H(13)	0.2459	−0.0925	0.3265	0.030
H(14)	0.2786	−0.0655	0.4360	0.032
H(15)	0.3244	0.0676	0.4679	0.034
H(16)	0.3479	0.1699	0.3924	0.029
H(26)	0.4605	0.2184	0.3392	0.027
H(25)	0.5030	0.3526	0.3693	0.033
H(24)	0.4254	0.4691	0.3324	0.040
H(23)	0.3044	0.4495	0.2663	0.037
H(31)	0.1403	−0.0857	0.2443	0.044
H(32)	0.2449	−0.1080	0.1523	0.037
H(33A)	0.0654	0.0761	0.2325	0.055
H(33B)	0.1060	0.0373	0.2984	0.055
H(33C)	0.0247	−0.0043	0.2632	0.055
H(94A)	0.9791	0.6229	0.0679	0.162
H(94B)	0.9260	0.5506	0.0981	0.162
H(94C)	0.8803	0.6253	0.0583	0.162
H(95A)	1.0917	0.3604	−0.0829	0.078
H(95B)	1.0887	0.3551	−0.0065	0.078

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Table S17. – continued from previous page

atom	x	y	x	U(eq)
H(95C)	1.1371	0.4303	−0.0377	0.078
H(93A)	0.8841	0.5031	0.0037	0.083
H(93B)	0.9222	0.5817	−0.0308	0.083
H(92A)	1.0068	0.4787	−0.0888	0.058
H(92B)	0.9612	0.4076	−0.0512	0.058
H(34A)	0.0785	−0.0064	0.1270	0.055
H(34B)	0.0314	−0.0804	0.1608	0.055
H(34C)	0.1185	−0.0981	0.1326	0.055
H(35A)	0.3343	−0.0758	0.0776	0.047
H(35B)	0.3666	0.0063	0.1160	0.047
H(35C)	0.2746	0.0035	0.0821	0.047
H(36A)	0.3748	−0.1575	0.1817	0.047
H(36B)	0.3304	−0.1342	0.2450	0.047
H(36C)	0.3989	−0.0728	0.2200	0.047
H(43A)	0.1490	0.2046	0.3192	0.063
H(43B)	0.1041	0.2743	0.3592	0.063
H(43C)	0.2017	0.2792	0.3535	0.063
H(42)	0.1434	0.3549	0.1239	0.045
H(41)	0.1366	0.3773	0.2839	0.050
H(44A)	0.0387	0.3417	0.2014	0.063
H(44B)	0.0066	0.3076	0.2670	0.063
H(44C)	0.0467	0.2441	0.2189	0.063
H(46A)	0.2739	0.3230	0.0921	0.057
H(46B)	0.3122	0.4028	0.1303	0.057
H(46C)	0.2467	0.4156	0.0696	0.057
H(45A)	0.1502	0.4968	0.1310	0.057
H(45B)	0.2162	0.4927	0.1921	0.057
H(45C)	0.1233	0.4619	0.1981	0.057
H(54)	0.3823	0.0682	0.2069	0.021
H(55)	0.4777	0.0750	0.3042	0.021
H(56)	0.6049	0.1007	0.2758	0.024
H(63)	0.9283	0.1403	0.1949	0.034
H(64)	0.9348	0.1553	0.3064	0.039
H(65)	0.8154	0.1907	0.3562	0.036
H(66)	0.6891	0.1997	0.2964	0.029
H(71)	0.4834	0.2221	−0.0317	0.027
H(72)	0.4166	0.3386	0.0889	0.019
H(73A)	0.3559	0.2658	0.0068	0.034
H(73B)	0.3459	0.1740	0.0362	0.034
H(73C)	0.3463	0.1861	−0.0399	0.034
H(74A)	0.4559	0.0762	−0.0327	0.034
H(74B)	0.4719	0.0743	0.0440	0.034

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Table S17. – continued from previous page

atom	x	y	x	U(eq)
H(74C)	0.5458	0.0970	0.0008	0.034
H(75A)	0.4735	0.3797	−0.0073	0.024
H(75B)	0.5520	0.4179	0.0340	0.024
H(75C)	0.4625	0.4583	0.0389	0.024
H(76A)	0.5684	0.3938	0.1544	0.024
H(76B)	0.4968	0.3458	0.1880	0.024
H(76C)	0.4805	0.4379	0.1592	0.024
H(81)	0.8035	0.0678	0.0103	0.040
H(82)	0.9360	0.1996	0.0957	0.039
H(83A)	0.6814	0.0331	0.0562	0.050
H(83B)	0.7331	0.0006	0.1200	0.050
H(83C)	0.7388	−0.0482	0.0535	0.050
H(84A)	0.8918	−0.0345	0.0582	0.050
H(84B)	0.8911	0.0104	0.1267	0.050
H(84C)	0.9340	0.0555	0.0696	0.050
H(85A)	0.8529	0.2398	−0.0262	0.048
H(85B)	0.9110	0.1600	−0.0110	0.048
H(85C)	0.9500	0.2523	−0.0092	0.048
H(86A)	0.9344	0.3454	0.0834	0.048
H(86B)	0.8769	0.3184	0.1386	0.048
H(86C)	0.8361	0.3441	0.0689	0.048
H(53)	0.3782	0.1946	0.1390	0.021

Table S18. Anisotropic displacement parameters ($\text{\AA}^2$) for $\{[\text{PC}(\text{sp}^2)\text{P}]\text{PdI}\}_2 \cdot \frac{1}{2} \text{Et}_2\text{O}$ (**{2}** $_2 \cdot \frac{1}{2} \text{Et}_2\text{O}$). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$.

atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C(1)	0.0152(16)	0.0200(16)	0.0180(16)	0.0006(13)	0.0029(13)	-0.0005(13)
I(1)	0.0218(1)	0.0364(1)	0.0275(1)	0.0036(1)	-0.0058(1)	0.0018(1)
Pd(1)	0.0141(1)	0.0197(1)	0.0181(1)	0.0013(1)	0.0018(1)	0.0004(1)
C(2)	0.0161(16)	0.0240(17)	0.0158(16)	-0.0003(13)	0.0018(12)	0.0007(13)
I(2)	0.0239(1)	0.0338(1)	0.0151(1)	0.0041(1)	0.0051(1)	-0.0015(1)
Pd(2)	0.0122(1)	0.0235(1)	0.0131(1)	0.0016(1)	0.0026(1)	-0.0009(1)
P(11)	0.0146(4)	0.0206(4)	0.0204(4)	0.0014(3)	0.0014(3)	-0.0028(3)
O(9)	0.045(3)	0.094(4)	0.061(3)	-0.017(3)	0.019(2)	-0.014(3)
C(11)	0.0131(15)	0.0244(17)	0.0200(16)	0.0013(13)	0.0036(12)	0.0007(13)
P(12)	0.0204(4)	0.0219(4)	0.0260(5)	0.0012(4)	0.0066(4)	0.0031(4)
C(12)	0.0154(16)	0.0264(18)	0.0205(16)	0.0001(14)	0.0043(13)	-0.0006(13)
C(13)	0.0209(17)	0.0263(18)	0.0273(18)	0.0063(15)	0.0030(14)	-0.0035(14)
C(14)	0.0223(18)	0.033(2)	0.0251(18)	0.0100(15)	0.0048(14)	-0.0020(15)
C(15)	0.0230(18)	0.042(2)	0.0201(17)	0.0019(16)	0.0044(14)	-0.0031(16)
C(16)	0.0224(18)	0.0277(19)	0.0216(17)	-0.0003(14)	0.0041(14)	-0.0040(14)
P(21)	0.0122(1)	0.0235(1)	0.0131(1)	0.0016(1)	0.0026(1)	-0.0009(1)
C(21)	0.0219(17)	0.0217(17)	0.0156(15)	-0.0006(13)	0.0065(13)	-0.0030(14)
P(22)	0.0119(4)	0.0304(5)	0.0152(4)	0.0002(3)	0.0021(3)	-0.0001(3)
C(22)	0.0252(18)	0.0243(18)	0.0209(17)	0.0009(14)	0.0065(14)	-0.0004(14)
C(26)	0.0243(18)	0.0251(18)	0.0176(16)	0.0004(13)	0.0040(14)	-0.0037(14)
C(25)	0.030(2)	0.034(2)	0.0191(17)	-0.0024(15)	0.0048(15)	-0.0115(16)
C(24)	0.049(2)	0.0240(19)	0.028(2)	-0.0054(15)	0.0085(17)	-0.0097(17)
C(23)	0.039(2)	0.0237(19)	0.0291(19)	-0.0014(15)	0.0059(16)	0.0012(16)
C(31)	0.0209(11)	0.0409(13)	0.0485(14)	0.0049(11)	0.0021(10)	-0.0082(10)
C(32)	0.0361(12)	0.0287(11)	0.0292(11)	-0.0048(9)	0.0048(9)	0.0035(9)
C(33)	0.0209(11)	0.0409(13)	0.0485(14)	0.0049(11)	0.0021(10)	-0.0082(10)
C(94)	0.11(2)	0.13(2)	0.088(18)	-0.005(13)	0.036(14)	0.030(16)
C(95)	0.039(8)	0.068(11)	0.088(18)	0.005(9)	0.010(8)	0.013(8)
C(93)	0.061(7)	0.070(7)	0.076(8)	-0.007(6)	0.001(6)	0.007(6)
C(92)	0.056(8)	0.044(6)	0.046(6)	0.005(5)	0.006(5)	0.010(5)
C(34)	0.0209(11)	0.0409(13)	0.0485(14)	0.0049(11)	0.0021(10)	-0.0082(10)
C(35)	0.0361(12)	0.0287(11)	0.0292(11)	-0.0048(9)	0.0048(9)	0.0035(9)
C(36)	0.0361(12)	0.0287(11)	0.0292(11)	-0.0048(9)	0.0048(9)	0.0035(9)
C(43)	0.0367(13)	0.0455(14)	0.0470(15)	-0.0035(11)	0.0223(12)	0.0030(11)
C(42)	0.0339(13)	0.0352(13)	0.0449(14)	0.0108(11)	0.0093(11)	0.0112(10)
C(41)	0.0367(13)	0.0455(14)	0.0470(15)	-0.0035(11)	0.0223(12)	0.0030(11)
C(44)	0.0367(13)	0.0455(14)	0.0470(15)	-0.0035(11)	0.0223(12)	0.0030(11)
C(46)	0.0339(13)	0.0352(13)	0.0449(14)	0.0108(11)	0.0093(11)	0.0112(10)
C(45)	0.0339(13)	0.0352(13)	0.0449(14)	0.0108(11)	0.0093(11)	0.0112(10)

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Table S18. – continued from previous page

atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C(54)	0.0139(15)	0.0196(16)	0.0190(16)	0.0011(13)	0.0037(12)	−0.0010(13)
C(55)	0.0203(16)	0.0182(16)	0.0157(15)	0.0047(12)	0.0056(13)	0.0008(13)
C(56)	0.0185(16)	0.0232(17)	0.0173(16)	0.0026(13)	0.0000(13)	0.0020(13)
C(61)	0.0160(16)	0.0295(19)	0.0169(16)	0.0026(13)	0.0017(13)	−0.0021(14)
C(62)	0.0166(17)	0.034(2)	0.0186(17)	0.0004(14)	0.0020(13)	−0.0007(14)
C(63)	0.0156(17)	0.045(2)	0.0234(18)	0.0006(16)	0.0007(14)	0.0012(16)
C(64)	0.0194(18)	0.051(2)	0.0266(19)	0.0040(17)	−0.0041(15)	−0.0008(17)
C(65)	0.0257(19)	0.045(2)	0.0186(17)	−0.0020(16)	−0.0018(14)	−0.0006(17)
C(66)	0.0204(18)	0.0337(19)	0.0191(17)	0.0010(14)	0.0013(14)	0.0003(15)
C(71)	0.0224(11)	0.0250(10)	0.0196(9)	−0.0021(8)	−0.0002(8)	−0.0026(8)
C(72)	0.0122(1)	0.0235(1)	0.0131(1)	0.0016(1)	0.0026(1)	−0.0009(1)
C(73)	0.0224(11)	0.0250(10)	0.0196(9)	−0.0021(8)	−0.0002(8)	−0.0026(8)
C(74)	0.0224(11)	0.0250(10)	0.0196(9)	−0.0021(8)	−0.0002(8)	−0.0026(8)
C(75)	0.0122(1)	0.0235(1)	0.0131(1)	0.0016(1)	0.0026(1)	−0.0009(1)
C(76)	0.0122(1)	0.0235(1)	0.0131(1)	0.0016(1)	0.0026(1)	−0.0009(1)
C(81)	0.0256(12)	0.0327(12)	0.0406(13)	−0.0036(10)	−0.0017(10)	0.0009(10)
C(82)	0.0179(10)	0.0400(13)	0.0392(13)	0.0051(10)	0.0077(9)	−0.0005(9)
C(83)	0.0256(12)	0.0327(12)	0.0406(13)	−0.0036(10)	−0.0017(10)	0.0009(10)
C(84)	0.0256(12)	0.0327(12)	0.0406(13)	−0.0036(10)	−0.0017(10)	0.0009(10)
C(85)	0.0179(10)	0.0400(13)	0.0392(13)	0.0051(10)	0.0077(9)	−0.0005(9)
C(86)	0.0179(10)	0.0400(13)	0.0392(13)	0.0051(10)	0.0077(9)	−0.0005(9)
C(53)	0.0149(16)	0.0201(16)	0.0167(15)	0.0001(13)	0.0009(12)	0.0005(13)
C(52)	0.0160(16)	0.0161(15)	0.0163(15)	−0.0012(12)	0.0035(12)	0.0004(12)
C(51)	0.0178(16)	0.0201(16)	0.0144(15)	0.0014(12)	0.0024(12)	0.0014(13)

Table S19. Distances [Å] for {[PC(sp²)P]PdI}₂·½ Et₂O ({**2**)₂·½ Et₂O).

atom – atom	distance	atom – atom	distance
C(1) – C(11)	1.529(4)	C(1) – C(21)	1.530(4)
C(1) – C(54)	1.588(4)	C(1) – Pd(1)	2.127(3)
I(1) – Pd(1)	2.6851(3)	Pd(1) – P(12)	2.2686(9)
Pd(1) – P(11)	2.3359(9)	C(2) – C(51)	1.380(4)
C(2) – C(61)	1.481(4)	C(2) – Pd(2)	2.043(3)
I(2) – Pd(2)	2.6868(3)	Pd(2) – P(21)	2.2728(8)
Pd(2) – P(22)	2.3104(9)	P(11) – C(12)	1.829(3)
P(11) – C(31)	1.855(4)	P(11) – C(32)	1.874(4)
O(9) – C(93)#1	1.329(11)	O(9) – C(93)	1.329(11)
O(9) – C(92)#1	1.338(11)	O(9) – C(92)	1.338(11)
C(11) – C(16)	1.392(5)	C(11) – C(12)	1.409(5)
P(12) – C(22)	1.813(4)	P(12) – C(42)	1.846(4)
P(12) – C(41)	1.857(4)	C(12) – C(13)	1.398(5)
C(13) – C(14)	1.390(5)	C(13) – H(13)	0.9500
C(14) – C(15)	1.377(5)	C(14) – H(14)	0.9500
C(15) – C(16)	1.387(5)	C(15) – H(15)	0.9500
C(16) – H(16)	0.9500	P(21) – C(52)	1.811(3)
P(21) – C(72)	1.828(3)	P(21) – C(71)	1.851(3)
C(21) – C(22)	1.402(5)	C(21) – C(26)	1.402(5)
P(22) – C(62)	1.819(3)	P(22) – C(81)	1.844(4)
P(22) – C(82)	1.856(4)	C(22) – C(23)	1.389(5)
C(26) – C(25)	1.383(5)	C(26) – H(26)	0.9500
C(25) – C(24)	1.386(5)	C(25) – H(25)	0.9500
C(24) – C(23)	1.378(6)	C(24) – H(24)	0.9500
C(23) – H(23)	0.9500	C(31) – C(33)	1.520(6)
C(31) – C(34)	1.534(6)	C(31) – H(31)	1.0000
C(32) – C(36)	1.503(5)	C(32) – C(35)	1.523(5)
C(32) – H(32)	1.0000	C(33) – H(33A)	0.9800
C(33) – H(33B)	0.9800	C(33) – H(33C)	0.9800
C(94) – C(93)	1.37(4)	C(94) – H(94A)	0.9800
C(94) – H(94B)	0.9800	C(94) – H(94C)	0.9800
C(95) – C(92)	1.55(3)	C(95) – H(95A)	0.9800
C(95) – H(95B)	0.9800	C(95) – H(95C)	0.9800
C(93) – H(93A)	0.9900	C(93) – H(93B)	0.9900
C(92) – H(92A)	0.9900	C(92) – H(92B)	0.9900
C(34) – H(34A)	0.9800	C(34) – H(34B)	0.9800
C(34) – H(34C)	0.9800	C(35) – H(35A)	0.9800
C(35) – H(35B)	0.9800	C(35) – H(35C)	0.9800
C(36) – H(36A)	0.9800	C(36) – H(36B)	0.9800
C(36) – H(36C)	0.9800	C(43) – C(41)	1.517(6)

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1,-z

Continued on next page

Table S19. – continued from previous page

atom – atom	distance	atom – atom	distance
C(43) – H(43A)	0.9800	C(43) – H(43B)	0.9800
C(43) – H(43C)	0.9800	C(42) – C(45)	1.509(6)
C(42) – C(46)	1.524(5)	C(42) – H(42)	1.0000
C(41) – C(44)	1.522(6)	C(41) – H(41)	1.0000
C(44) – H(44A)	0.9800	C(44) – H(44B)	0.9800
C(44) – H(44C)	0.9800	C(46) – H(46A)	0.9800
C(46) – H(46B)	0.9800	C(46) – H(46C)	0.9800
C(45) – H(45A)	0.9800	C(45) – H(45B)	0.9800
C(45) – H(45C)	0.9800	C(54) – C(53)	1.496(4)
C(54) – C(55)	1.508(4)	C(54) – H(54)	1.0000
C(55) – C(56)	1.339(4)	C(55) – H(55)	0.9500
C(56) – C(51)	1.465(4)	C(56) – H(56)	0.9500
C(61) – C(66)	1.408(5)	C(61) – C(62)	1.418(5)
C(62) – C(63)	1.396(5)	C(63) – C(64)	1.385(5)
C(63) – H(63)	0.9500	C(64) – C(65)	1.390(5)
C(64) – H(64)	0.9500	C(65) – C(66)	1.380(5)
C(65) – H(65)	0.9500	C(66) – H(66)	0.9500
C(71) – C(73)	1.528(5)	C(71) – C(74)	1.531(5)
C(71) – H(71)	1.0000	C(72) – C(75)	1.526(4)
C(72) – C(76)	1.526(4)	C(72) – H(72)	1.0000
C(73) – H(73A)	0.9800	C(73) – H(73B)	0.9800
C(73) – H(73C)	0.9800	C(74) – H(74A)	0.9800
C(74) – H(74B)	0.9800	C(74) – H(74C)	0.9800
C(75) – H(75A)	0.9800	C(75) – H(75B)	0.9800
C(75) – H(75C)	0.9800	C(76) – H(76A)	0.9800
C(76) – H(76B)	0.9800	C(76) – H(76C)	0.9800
C(81) – C(83)	1.522(5)	C(81) – C(84)	1.539(5)
C(81) – H(81)	1.0000	C(82) – C(86)	1.513(6)
C(82) – C(85)	1.523(5)	C(82) – H(82)	1.0000
C(83) – H(83A)	0.9800	C(83) – H(83B)	0.9800
C(83) – H(83C)	0.9800	C(84) – H(84A)	0.9800
C(84) – H(84B)	0.9800	C(84) – H(84C)	0.9800
C(85) – H(85A)	0.9800	C(85) – H(85B)	0.9800
C(85) – H(85C)	0.9800	C(86) – H(86A)	0.9800
C(86) – H(86B)	0.9800	C(86) – H(86C)	0.9800
C(53) – C(52)	1.345(4)	C(53) – H(53)	0.9500
C(52) – C(51)	1.465(4)		
Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1,-z			

Table S20. Angles [°] for {[PC(sp²)P]PdI}₂·½ Et₂O ({**2**)₂·½ Et₂O).

atom – atom – atom	angle	atom – atom – atom	angle
C(11) – C(1) – C(21)	115.5(3)	C(11) – C(1) – C(54)	107.8(2)
C(21) – C(1) – C(54)	109.1(3)	C(11) – C(1) – Pd(1)	106.2(2)
C(21) – C(1) – Pd(1)	113.7(2)	C(54) – C(1) – Pd(1)	103.74(19)
C(1) – Pd(1) – P(12)	85.13(9)	C(1) – Pd(1) – P(11)	83.20(9)
P(12) – Pd(1) – P(11)	155.64(3)	C(1) – Pd(1) – I(1)	167.42(8)
P(12) – Pd(1) – I(1)	95.99(2)	P(11) – Pd(1) – I(1)	100.04(2)
C(51) – C(2) – C(61)	123.6(3)	C(51) – C(2) – Pd(2)	120.8(2)
C(61) – C(2) – Pd(2)	115.6(2)	C(2) – Pd(2) – P(21)	82.65(9)
C(2) – Pd(2) – P(22)	84.06(9)	P(21) – Pd(2) – P(22)	163.58(3)
C(2) – Pd(2) – I(2)	177.19(9)	P(21) – Pd(2) – I(2)	94.63(2)
P(22) – Pd(2) – I(2)	98.75(2)	C(12) – P(11) – C(31)	102.49(17)
C(12) – P(11) – C(32)	110.21(16)	C(31) – P(11) – C(32)	102.30(18)
C(12) – P(11) – Pd(1)	96.89(11)	C(31) – P(11) – Pd(1)	115.43(14)
C(32) – P(11) – Pd(1)	127.02(12)	C(93)#1 – O(9) – C(93)	180.0(11)
C(93)#1 – O(9) – C(92)#1	123.2(6)	C(93) – O(9) – C(92)#1	56.8(6)
C(93)#1 – O(9) – C(92)	56.8(6)	C(93) – O(9) – C(92)	123.2(6)
C(92)#1 – O(9) – C(92)	180.0(9)	C(16) – C(11) – C(12)	117.8(3)
C(16) – C(11) – C(1)	124.1(3)	C(12) – C(11) – C(1)	118.1(3)
C(22) – P(12) – C(42)	111.73(18)	C(22) – P(12) – C(41)	104.10(18)
C(42) – P(12) – C(41)	103.62(19)	C(22) – P(12) – Pd(1)	103.29(12)
C(42) – P(12) – Pd(1)	120.70(14)	C(41) – P(12) – Pd(1)	112.40(15)
C(13) – C(12) – C(11)	120.3(3)	C(13) – C(12) – P(11)	123.5(3)
C(11) – C(12) – P(11)	115.6(2)	C(14) – C(13) – C(12)	120.6(3)
C(14) – C(13) – H(13)	119.7	C(12) – C(13) – H(13)	119.7
C(15) – C(14) – C(13)	118.9(3)	C(15) – C(14) – H(14)	120.6
C(13) – C(14) – H(14)	120.6	C(14) – C(15) – C(16)	121.1(3)
C(14) – C(15) – H(15)	119.5	C(16) – C(15) – H(15)	119.5
C(15) – C(16) – C(11)	121.1(3)	C(15) – C(16) – H(16)	119.4
C(11) – C(16) – H(16)	119.4	C(52) – P(21) – C(72)	103.66(14)
C(52) – P(21) – C(71)	108.20(15)	C(72) – P(21) – C(71)	106.24(15)
C(52) – P(21) – Pd(2)	102.22(10)	C(72) – P(21) – Pd(2)	122.92(10)
C(71) – P(21) – Pd(2)	112.41(11)	C(22) – C(21) – C(26)	116.8(3)
C(22) – C(21) – C(1)	121.7(3)	C(26) – C(21) – C(1)	121.5(3)
C(62) – P(22) – C(81)	108.33(17)	C(62) – P(22) – C(82)	104.29(17)
C(81) – P(22) – C(82)	104.79(17)	C(62) – P(22) – Pd(2)	100.14(11)
C(81) – P(22) – Pd(2)	114.33(12)	C(82) – P(22) – Pd(2)	123.64(13)
C(23) – C(22) – C(21)	121.3(3)	C(23) – C(22) – P(12)	124.4(3)
C(21) – C(22) – P(12)	114.2(3)	C(25) – C(26) – C(21)	121.9(3)
C(25) – C(26) – H(26)	119.1	C(21) – C(26) – H(26)	119.1
C(26) – C(25) – C(24)	120.1(3)	C(26) – C(25) – H(25)	120.0

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1,-z

Continued on next page

Table S20. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(24) – C(25) – H(25)	120.0	C(23) – C(24) – C(25)	119.4(3)
C(23) – C(24) – H(24)	120.3	C(25) – C(24) – H(24)	120.3
C(24) – C(23) – C(22)	120.6(3)	C(24) – C(23) – H(23)	119.7
C(22) – C(23) – H(23)	119.7	C(33) – C(31) – C(34)	110.8(3)
C(33) – C(31) – P(11)	110.1(3)	C(34) – C(31) – P(11)	112.6(3)
C(33) – C(31) – H(31)	107.7	C(34) – C(31) – H(31)	107.7
P(11) – C(31) – H(31)	107.7	C(36) – C(32) – C(35)	112.6(3)
C(36) – C(32) – P(11)	114.5(3)	C(35) – C(32) – P(11)	111.1(3)
C(36) – C(32) – H(32)	106.0	C(35) – C(32) – H(32)	106.0
P(11) – C(32) – H(32)	106.0	C(31) – C(33) – H(33A)	109.5
C(31) – C(33) – H(33B)	109.5	H(33A) – C(33) – H(33B)	109.5
C(31) – C(33) – H(33C)	109.5	H(33A) – C(33) – H(33C)	109.5
H(33B) – C(33) – H(33C)	109.5	C(93) – C(94) – H(94A)	109.5
C(93) – C(94) – H(94B)	109.5	H(94A) – C(94) – H(94B)	109.5
C(93) – C(94) – H(94C)	109.5	H(94A) – C(94) – H(94C)	109.5
H(94B) – C(94) – H(94C)	109.5	O(9) – C(93) – C(94)	115.8(14)
O(9) – C(93) – H(93A)	108.3	C(94) – C(93) – H(93A)	108.3
O(9) – C(93) – H(93B)	108.3	C(94) – C(93) – H(93B)	108.3
H(93A) – C(93) – H(93B)	107.4	O(9) – C(92) – C(95)	116.4(15)
O(9) – C(92) – H(92A)	108.2	C(95) – C(92) – H(92A)	108.2
O(9) – C(92) – H(92B)	108.2	C(95) – C(92) – H(92B)	108.2
H(92A) – C(92) – H(92B)	107.3	C(31) – C(34) – H(34A)	109.5
C(31) – C(34) – H(34B)	109.5	H(34A) – C(34) – H(34B)	109.5
C(31) – C(34) – H(34C)	109.5	H(34A) – C(34) – H(34C)	109.5
H(34B) – C(34) – H(34C)	109.5	C(32) – C(35) – H(35A)	109.5
C(32) – C(35) – H(35B)	109.5	H(35A) – C(35) – H(35B)	109.5
C(32) – C(35) – H(35C)	109.5	H(35A) – C(35) – H(35C)	109.5
H(35B) – C(35) – H(35C)	109.5	C(32) – C(36) – H(36A)	109.5
C(32) – C(36) – H(36B)	109.5	H(36A) – C(36) – H(36B)	109.5
C(32) – C(36) – H(36C)	109.5	H(36A) – C(36) – H(36C)	109.5
H(36B) – C(36) – H(36C)	109.5	C(41) – C(43) – H(43A)	109.5
C(41) – C(43) – H(43B)	109.5	H(43A) – C(43) – H(43B)	109.5
C(41) – C(43) – H(43C)	109.5	H(43A) – C(43) – H(43C)	109.5
H(43B) – C(43) – H(43C)	109.5	C(45) – C(42) – C(46)	110.6(3)
C(45) – C(42) – P(12)	118.8(3)	C(46) – C(42) – P(12)	109.8(3)
C(45) – C(42) – H(42)	105.5	C(46) – C(42) – H(42)	105.5
P(12) – C(42) – H(42)	105.5	C(43) – C(41) – C(44)	111.8(4)
C(43) – C(41) – P(12)	111.3(3)	C(44) – C(41) – P(12)	110.0(3)
C(43) – C(41) – H(41)	107.8	C(44) – C(41) – H(41)	107.8
P(12) – C(41) – H(41)	107.8	C(41) – C(44) – H(44A)	109.5
C(41) – C(44) – H(44B)	109.5	H(44A) – C(44) – H(44B)	109.5

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1,-z

Continued on next page

Table S20. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(41) – C(44) – H(44C)	109.5	H(44A) – C(44) – H(44C)	109.5
H(44B) – C(44) – H(44C)	109.5	C(42) – C(46) – H(46A)	109.5
C(42) – C(46) – H(46B)	109.5	H(46A) – C(46) – H(46B)	109.5
C(42) – C(46) – H(46C)	109.5	H(46A) – C(46) – H(46C)	109.5
H(46B) – C(46) – H(46C)	109.5	C(42) – C(45) – H(45A)	109.5
C(42) – C(45) – H(45B)	109.5	H(45A) – C(45) – H(45B)	109.5
C(42) – C(45) – H(45C)	109.5	H(45A) – C(45) – H(45C)	109.5
H(45B) – C(45) – H(45C)	109.5	C(53) – C(54) – C(55)	110.6(3)
C(53) – C(54) – C(1)	113.1(3)	C(55) – C(54) – C(1)	116.7(3)
C(53) – C(54) – H(54)	105.1	C(55) – C(54) – H(54)	105.1
C(1) – C(54) – H(54)	105.1	C(56) – C(55) – C(54)	124.8(3)
C(56) – C(55) – H(55)	117.6	C(54) – C(55) – H(55)	117.6
C(55) – C(56) – C(51)	123.0(3)	C(55) – C(56) – H(56)	118.5
C(51) – C(56) – H(56)	118.5	C(66) – C(61) – C(62)	117.0(3)
C(66) – C(61) – C(2)	123.8(3)	C(62) – C(61) – C(2)	119.0(3)
C(63) – C(62) – C(61)	120.6(3)	C(63) – C(62) – P(22)	124.4(3)
C(61) – C(62) – P(22)	114.5(2)	C(64) – C(63) – C(62)	120.5(3)
C(64) – C(63) – H(63)	119.8	C(62) – C(63) – H(63)	119.8
C(63) – C(64) – C(65)	119.6(3)	C(63) – C(64) – H(64)	120.2
C(65) – C(64) – H(64)	120.2	C(66) – C(65) – C(64)	120.3(3)
C(66) – C(65) – H(65)	119.9	C(64) – C(65) – H(65)	119.9
C(65) – C(66) – C(61)	121.7(3)	C(65) – C(66) – H(66)	119.1
C(61) – C(66) – H(66)	119.1	C(73) – C(71) – C(74)	110.7(3)
C(73) – C(71) – P(21)	117.8(2)	C(74) – C(71) – P(21)	108.2(2)
C(73) – C(71) – H(71)	106.5	C(74) – C(71) – H(71)	106.5
P(21) – C(71) – H(71)	106.5	C(75) – C(72) – C(76)	111.0(3)
C(75) – C(72) – P(21)	111.9(2)	C(76) – C(72) – P(21)	111.4(2)
C(75) – C(72) – H(72)	107.4	C(76) – C(72) – H(72)	107.4
P(21) – C(72) – H(72)	107.4	C(71) – C(73) – H(73A)	109.5
C(71) – C(73) – H(73B)	109.5	H(73A) – C(73) – H(73B)	109.5
C(71) – C(73) – H(73C)	109.5	H(73A) – C(73) – H(73C)	109.5
H(73B) – C(73) – H(73C)	109.5	C(71) – C(74) – H(74A)	109.5
C(71) – C(74) – H(74B)	109.5	H(74A) – C(74) – H(74B)	109.5
C(71) – C(74) – H(74C)	109.5	H(74A) – C(74) – H(74C)	109.5
H(74B) – C(74) – H(74C)	109.5	C(72) – C(75) – H(75A)	109.5
C(72) – C(75) – H(75B)	109.5	H(75A) – C(75) – H(75B)	109.5
C(72) – C(75) – H(75C)	109.5	H(75A) – C(75) – H(75C)	109.5
H(75B) – C(75) – H(75C)	109.5	C(72) – C(76) – H(76A)	109.5
C(72) – C(76) – H(76B)	109.5	H(76A) – C(76) – H(76B)	109.5
C(72) – C(76) – H(76C)	109.5	H(76A) – C(76) – H(76C)	109.5
H(76B) – C(76) – H(76C)	109.5	C(83) – C(81) – C(84)	110.5(3)

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1,-z

Continued on next page

Table S20. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(83) – C(81) – P(22)	110.3(3)	C(84) – C(81) – P(22)	114.2(3)
C(83) – C(81) – H(81)	107.2	C(84) – C(81) – H(81)	107.2
P(22) – C(81) – H(81)	107.2	C(86) – C(82) – C(85)	111.9(3)
C(86) – C(82) – P(22)	110.3(2)	C(85) – C(82) – P(22)	112.2(3)
C(86) – C(82) – H(82)	107.4	C(85) – C(82) – H(82)	107.4
P(22) – C(82) – H(82)	107.4	C(81) – C(83) – H(83A)	109.5
C(81) – C(83) – H(83B)	109.5	H(83A) – C(83) – H(83B)	109.5
C(81) – C(83) – H(83C)	109.5	H(83A) – C(83) – H(83C)	109.5
H(83B) – C(83) – H(83C)	109.5	C(81) – C(84) – H(84A)	109.5
C(81) – C(84) – H(84B)	109.5	H(84A) – C(84) – H(84B)	109.5
C(81) – C(84) – H(84C)	109.5	H(84A) – C(84) – H(84C)	109.5
H(84B) – C(84) – H(84C)	109.5	C(82) – C(85) – H(85A)	109.5
C(82) – C(85) – H(85B)	109.5	H(85A) – C(85) – H(85B)	109.5
C(82) – C(85) – H(85C)	109.5	H(85A) – C(85) – H(85C)	109.5
H(85B) – C(85) – H(85C)	109.5	C(82) – C(86) – H(86A)	109.5
C(82) – C(86) – H(86B)	109.5	H(86A) – C(86) – H(86B)	109.5
C(82) – C(86) – H(86C)	109.5	H(86A) – C(86) – H(86C)	109.5
H(86B) – C(86) – H(86C)	109.5	C(52) – C(53) – C(54)	123.5(3)
C(52) – C(53) – H(53)	118.2	C(54) – C(53) – H(53)	118.2
C(53) – C(52) – C(51)	124.2(3)	C(53) – C(52) – P(21)	123.6(2)
C(51) – C(52) – P(21)	112.0(2)	C(2) – C(51) – C(52)	119.1(3)
C(2) – C(51) – C(56)	127.4(3)	C(52) – C(51) – C(56)	113.5(3)
Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1,-z			

8.2 Crystal data for [PC[•](sp²)P]PdBr (3)

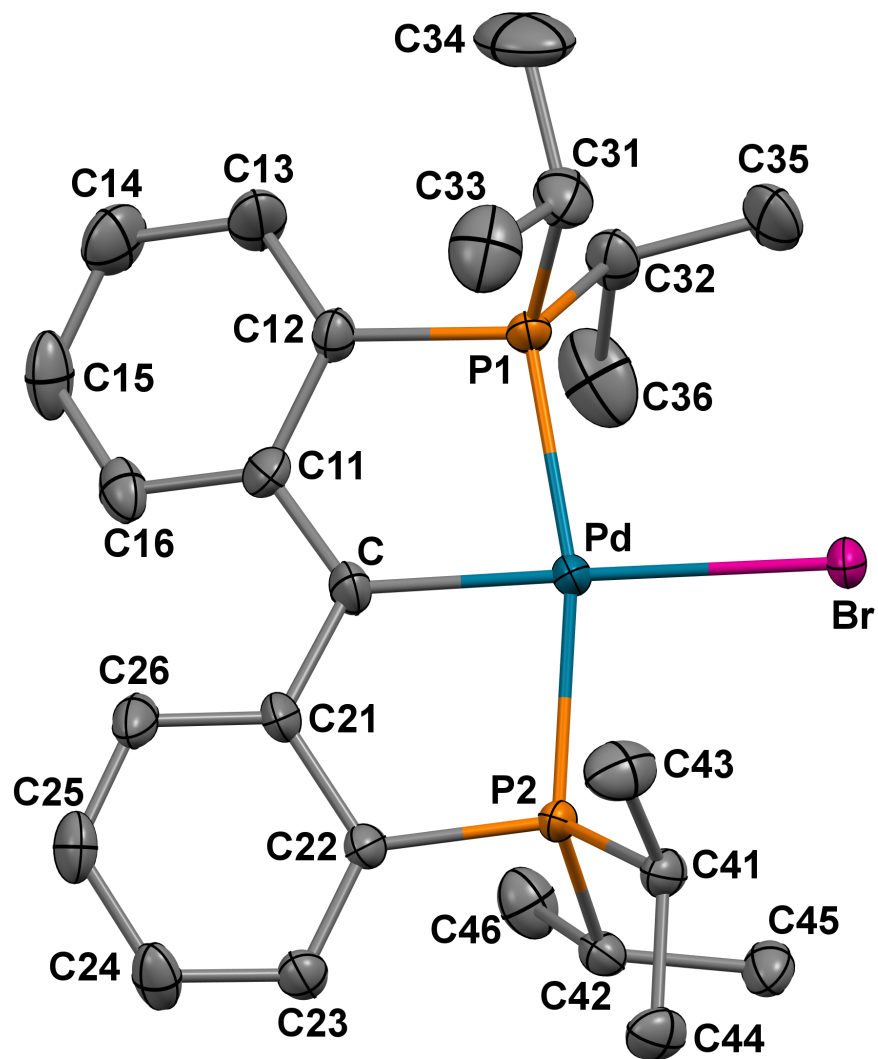


Figure S74. Thermal-ellipsoid (50% probability) representation of [PC[•](sp²)P]PdBr (3). Hydrogen atoms were omitted for clarity.

Table S21. Crystal data and structure refinement for [PC[•](sp²)P]PdBr (**3**).

Identification code:	cc277	
Empirical formula:	C ₂₅ H ₃₆ BrP ₂ Pd	
Formula weight:	584.79	
Temperature:	120(2) K	
Wavelength:	0.71073 Å	
Crystal system:	Monoclinic	
Space group:	<i>P</i> 2 ₁ / <i>n</i>	
Unit cell dimensions:	<i>a</i> = 12.5686(12) Å <i>b</i> = 13.9781(13) Å <i>c</i> = 14.9939(14) Å	$\alpha = 90^\circ$ $\beta = 97.3300(18)^\circ$ $\gamma = 90^\circ$
Volume:	2612.7(4) Å ³	
Z:	4	
Density (calculated):	1.487 g·cm ⁻³	
Absorption coefficient (μ):	2.372 mm ⁻¹	
F(000):	1188	
Crystal size:	0.09 × 0.08 × 0.07 mm ³	
θ range for data collection:	1.99 to 24.99°	
Index ranges:	−14 ≤ <i>h</i> ≤ 14, −16 ≤ <i>k</i> ≤ 16, −17 ≤ <i>l</i> ≤ 17	
Reflections collected:	33653	
Independent reflections:	4601 [<i>R</i> _{int} = 0.0528]	
Completeness to θ = 24.99°:	100.0 %	
Absorption correction:	Semi-empirical from equivalents	
Max. and min. transmission:	0.7456 and 0.6456	
Refinement method:	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters:	4601 / 0 / 270	
Goodness-of-fit on <i>F</i> ² :	1.031	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]:	<i>R</i> ₁ = 0.0258, <i>wR</i> ₂ = 0.0542	
<i>R</i> indices (all data):	<i>R</i> ₁ = 0.0375, <i>wR</i> ₂ = 0.0569	
Largest diff. peak and hole:	0.617 and −0.548 e [−] ·Å ^{−3}	

Table S22. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for [PC $\bullet$ (sp²)P]PdBr (**3**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

atom	x	y	z	U(eq)
Pd	0.46609(2)	0.67536(1)	0.28225(1)	0.022(1)
C	0.5626(3)	0.7301(3)	0.3880(3)	0.025(2)
Br	0.33607(2)	0.60275(2)	0.15975(2)	0.022(1)
P(2)	0.35448(5)	0.79619(5)	0.31262(5)	0.018(1)
P(1)	0.60486(6)	0.57043(5)	0.27643(5)	0.019(1)
C(11)	0.6776(2)	0.7085(2)	0.39585(19)	0.026(1)
C(12)	0.7106(2)	0.62699(19)	0.35196(18)	0.022(1)
C(13)	0.8179(2)	0.6013(2)	0.3607(2)	0.040(1)
C(14)	0.8942(3)	0.6566(3)	0.4114(2)	0.041(1)
C(15)	0.8636(3)	0.7393(2)	0.4501(2)	0.039(1)
C(16)	0.7581(2)	0.7659(2)	0.44299(19)	0.029(1)
C(21)	0.5161(2)	0.7942(2)	0.4498(2)	0.029(1)
C(22)	0.4175(2)	0.83952(18)	0.41989(19)	0.020(1)
C(23)	0.3745(2)	0.90667(19)	0.47272(19)	0.023(1)
C(24)	0.4240(2)	0.9260(2)	0.5588(2)	0.030(1)
C(25)	0.5164(2)	0.8765(2)	0.5920(2)	0.030(1)
C(26)	0.5620(2)	0.81261(19)	0.5386(2)	0.031(1)
C(31)	0.5865(3)	0.4469(2)	0.3139(2)	0.034(1)
C(32)	0.6617(2)	0.5635(2)	0.1692(2)	0.031(1)
C(33)	0.5474(3)	0.4495(3)	0.4060(2)	0.048(1)
C(34)	0.6825(3)	0.3812(3)	0.3145(3)	0.067(1)
C(35)	0.5962(3)	0.4993(2)	0.1011(2)	0.041(1)
C(36)	0.6660(3)	0.6650(3)	0.1335(2)	0.056(1)
C(41)	0.2199(2)	0.75156(19)	0.32807(19)	0.023(1)
C(42)	0.3372(2)	0.90126(19)	0.23770(19)	0.021(1)
C(43)	0.2325(3)	0.6685(2)	0.3953(2)	0.036(1)
C(44)	0.1401(2)	0.8257(2)	0.3534(2)	0.029(1)
C(45)	0.2627(2)	0.8796(2)	0.15154(19)	0.029(1)
C(46)	0.4476(2)	0.9329(2)	0.2169(2)	0.034(1)
H(13)	0.8391	0.5454	0.3316	0.048
H(14)	0.9673	0.6375	0.4194	0.061
H(15)	0.9166	0.7788	0.4825	0.047
H(16)	0.7389	0.8237	0.4701	0.035
H(23)	0.3107	0.9397	0.4500	0.028
H(24)	0.3950	0.9728	0.5947	0.036
H(25)	0.5482	0.8869	0.6521	0.036
H(26)	0.6259	0.7802	0.5621	0.037
H(31)	0.5273	0.4185	0.2712	0.041
H(32)	0.7364	0.5378	0.1811	0.037

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Table S22. – continued from previous page

atom	x	y	x	U(eq)
H(33A)	0.4828	0.4893	0.4031	0.072
H(33B)	0.6036	0.4765	0.4502	0.072
H(33C)	0.5306	0.3844	0.4240	0.072
H(34A)	0.7090	0.3838	0.2558	0.100
H(34B)	0.6613	0.3155	0.3266	0.100
H(34C)	0.7394	0.4018	0.3613	0.100
H(35A)	0.5227	0.5238	0.0890	0.062
H(35B)	0.5949	0.4342	0.1252	0.062
H(35C)	0.6288	0.4984	0.0451	0.062
H(36A)	0.7038	0.6652	0.0802	0.084
H(36B)	0.7042	0.7061	0.1799	0.084
H(36C)	0.5929	0.6890	0.1173	0.084
H(41)	0.1885	0.7239	0.2690	0.027
H(42)	0.3051	0.9544	0.2702	0.026
H(43A)	0.1620	0.6406	0.4003	0.055
H(43B)	0.2643	0.6922	0.4542	0.055
H(43C)	0.2793	0.6195	0.3742	0.055
H(44A)	0.1409	0.8815	0.3140	0.043
H(44B)	0.1600	0.8453	0.4160	0.043
H(44C)	0.0679	0.7978	0.3465	0.043
H(45A)	0.2612	0.9346	0.1108	0.043
H(45B)	0.1902	0.8672	0.1662	0.043
H(45C)	0.2890	0.8232	0.1223	0.043
H(46A)	0.4785	0.8828	0.1823	0.052
H(46B)	0.4946	0.9438	0.2733	0.052
H(46C)	0.4407	0.9922	0.1818	0.052

Table S23. Anisotropic displacement parameters ($\text{\AA}^2$) for $[\text{PC}^*(\text{sp}^2)\text{P}]\text{PdBr}$ (**3**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\text{h}^2\text{a}^*\text{U}_{11} + \dots + 2\text{hka}^*\text{b}^*\text{U}_{12}]$.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd	0.0192(1)	0.0198(1)	0.0234(1)	-0.0088(1)	-0.0053(1)	0.0046(1)
C	0.024(2)	0.029(3)	0.020(3)	-0.009(3)	-0.0021(2)	0.0012(2)
Br	0.0217(2)	0.0209(2)	0.0222(2)	-0.0046(1)	-0.0054(1)	-0.0008(1)
P(2)	0.0138(4)	0.0175(4)	0.0219(4)	-0.0051(3)	-0.0014(3)	0.0011(3)
P(1)	0.0150(4)	0.0215(4)	0.0214(4)	-0.0051(3)	0.0013(3)	0.0031(3)
C(11)	0.0269(17)	0.0252(16)	0.0238(16)	-0.0001(13)	-0.0063(13)	0.0052(13)
C(12)	0.0168(15)	0.0277(16)	0.0200(15)	-0.0034(12)	0.0007(12)	-0.0020(12)
C(13)	0.0197(17)	0.057(2)	0.042(2)	-0.0200(17)	0.0029(15)	0.0085(15)
C(14)	0.0207(16)	0.052(3)	0.050(2)	-0.0025(2)	0.0030(15)	-0.0037(17)
C(15)	0.0283(19)	0.059(2)	0.0287(18)	-0.0075(17)	0.0036(15)	-0.0218(17)
C(16)	0.040(2)	0.0263(17)	0.0190(16)	0.0009(13)	-0.0027(14)	-0.0061(14)
C(21)	0.0275(17)	0.0211(15)	0.0333(18)	-0.0115(13)	-0.0109(14)	0.0022(13)
C(22)	0.0184(15)	0.0161(14)	0.0247(16)	-0.0025(12)	-0.0017(12)	-0.0004(11)
C(23)	0.0187(15)	0.0253(16)	0.0259(16)	-0.0041(13)	0.0041(12)	-0.0001(12)
C(24)	0.0257(17)	0.0427(19)	0.0238(17)	-0.0124(14)	0.0072(14)	-0.0057(14)
C(25)	0.0300(18)	0.0388(19)	0.0190(16)	-0.0015(14)	-0.0032(13)	-0.0082(14)
C(26)	0.0303(18)	0.0195(16)	0.0385(19)	-0.0011(13)	-0.0138(15)	-0.0014(13)
C(31)	0.039(2)	0.0249(17)	0.0381(19)	-0.0002(14)	-0.0020(15)	-0.0036(14)
C(32)	0.0240(17)	0.0420(19)	0.0260(17)	-0.0103(14)	0.0057(13)	0.0012(14)
C(33)	0.050(2)	0.050(2)	0.044(2)	0.0122(18)	0.0046(18)	-0.0146(18)
C(34)	0.090(3)	0.037(2)	0.073(3)	0.008(2)	0.010(3)	0.031(2)
C(35)	0.041(2)	0.053(2)	0.0304(19)	-0.0200(16)	0.0059(16)	0.0056(17)
C(36)	0.080(3)	0.059(3)	0.033(2)	-0.0011(18)	0.023(2)	-0.022(2)
C(41)	0.0163(15)	0.0209(15)	0.0301(17)	-0.0030(13)	-0.0010(12)	-0.0008(12)
C(42)	0.0230(16)	0.0185(14)	0.0225(15)	-0.0042(12)	0.0033(12)	0.0009(12)
C(43)	0.0316(19)	0.0271(17)	0.052(2)	0.0078(15)	0.0075(16)	-0.0027(14)
C(44)	0.0176(15)	0.0285(17)	0.0405(19)	-0.0016(14)	0.0071(14)	-0.0004(12)
C(45)	0.0327(18)	0.0242(16)	0.0273(17)	0.0024(13)	-0.0046(14)	0.0000(13)
C(46)	0.0363(19)	0.0343(18)	0.0340(19)	-0.0037(15)	0.0097(15)	-0.0108(14)

Table S24. Distances [Å] for [PC[•](sp²)P]PdBr (**3**).

atom – atom	distance	atom – atom	distance
Pd – C	2.020(3)	Pd – P(2)	2.2783(7)
Pd – P(1)	2.2891(7)	Pd – Br	2.5117(4)
C – C(21)	1.463(4)	C – C(11)	1.467(4)
P(2) – C(22)	1.805(3)	P(2) – C(41)	1.845(3)
P(2) – C(42)	1.845(3)	P(1) – C(12)	1.814(3)
P(1) – C(31)	1.839(3)	P(1) – C(32)	1.844(3)
C(11) – C(12)	1.404(4)	C(11) – C(16)	1.409(4)
C(12) – C(13)	1.385(4)	C(13) – C(14)	1.382(4)
C(13) – H(13)	0.9500	C(14) – C(15)	1.369(5)
C(14) – H(14)	0.9500	C(15) – C(16)	1.369(4)
C(15) – H(15)	0.9500	C(16) – H(16)	0.9500
C(21) – C(26)	1.404(4)	C(21) – C(22)	1.413(4)
C(22) – C(23)	1.382(4)	C(23) – C(24)	1.386(4)
C(23) – H(23)	0.9500	C(24) – C(25)	1.388(4)
C(24) – H(24)	0.9500	C(25) – C(26)	1.373(4)
C(25) – H(25)	0.9500	C(26) – H(26)	0.9500
C(31) – C(34)	1.516(5)	C(31) – C(33)	1.525(5)
C(31) – H(31)	1.0000	C(32) – C(36)	1.519(5)
C(32) – C(35)	1.520(4)	C(32) – H(32)	1.0000
C(33) – H(33A)	0.9800	C(33) – H(33B)	0.9800
C(33) – H(33C)	0.9800	C(34) – H(34A)	0.9800
C(34) – H(34B)	0.9800	C(34) – H(34C)	0.9800
C(35) – H(35A)	0.9800	C(35) – H(35B)	0.9800
C(35) – H(35C)	0.9800	C(36) – H(36A)	0.9800
C(36) – H(36B)	0.9800	C(36) – H(36C)	0.9800
C(41) – C(44)	1.524(4)	C(41) – C(43)	1.532(4)
C(41) – H(41)	1.0000	C(42) – C(45)	1.526(4)
C(42) – C(46)	1.526(4)	C(42) – H(42)	1.0000
C(43) – H(43A)	0.9800	C(43) – H(43B)	0.9800
C(43) – H(43C)	0.9800	C(44) – H(44A)	0.9800
C(44) – H(44B)	0.9800	C(44) – H(44C)	0.9800
C(45) – H(45A)	0.9800	C(45) – H(45B)	0.9800
C(45) – H(45C)	0.9800	C(46) – H(46A)	0.9800
C(46) – H(46B)	0.9800	C(46) – H(46C)	0.9800

Table S25. Angles [°] for [PC[•](sp²)P]PdBr (**3**).

atom – atom – atom	angle	atom – atom – atom	angle
C – Pd – P(2)	83.43(10)	C – Pd – P(1)	83.61(10)
P(2) – Pd – P(1)	166.96(3)	C – Pd – Br	175.31(15)
P(2) – Pd – Br	94.93(2)	P(1) – Pd – Br	98.10(2)
C(21) – C – C(11)	123.0(3)	C(21) – C – Pd	118.7(2)
C(11) – C – Pd	118.1(2)	C(22) – P(2) – C(41)	107.88(13)
C(22) – P(2) – C(42)	106.24(12)	C(41) – P(2) – C(42)	107.87(12)
C(22) – P(2) – Pd	102.43(9)	C(41) – P(2) – Pd	111.84(9)
C(42) – P(2) – Pd	119.76(9)	C(12) – P(1) – C(31)	109.20(14)
C(12) – P(1) – C(32)	103.48(13)	C(31) – P(1) – C(32)	107.14(15)
C(12) – P(1) – Pd	101.42(9)	C(31) – P(1) – Pd	117.65(11)
C(32) – P(1) – Pd	116.67(10)	C(12) – C(11) – C(16)	117.5(3)
C(12) – C(11) – C	118.5(3)	C(16) – C(11) – C	124.0(3)
C(13) – C(12) – C(11)	120.5(3)	C(13) – C(12) – P(1)	125.0(2)
C(11) – C(12) – P(1)	114.2(2)	C(14) – C(13) – C(12)	120.4(3)
C(14) – C(13) – H(13)	119.8	C(12) – C(13) – H(13)	119.8
C(15) – C(14) – C(13)	119.5(3)	C(15) – C(14) – H(14)	120.2
C(13) – C(14) – H(14)	120.2	C(16) – C(15) – C(14)	121.2(3)
C(16) – C(15) – H(15)	119.4	C(14) – C(15) – H(15)	119.4
C(15) – C(16) – C(11)	120.7(3)	C(15) – C(16) – H(16)	119.7
C(11) – C(16) – H(16)	119.7	C(26) – C(21) – C(22)	117.1(3)
C(26) – C(21) – C	124.3(3)	C(22) – C(21) – C	118.6(3)
C(23) – C(22) – C(21)	120.9(3)	C(23) – C(22) – P(2)	125.4(2)
C(21) – C(22) – P(2)	113.6(2)	C(22) – C(23) – C(24)	120.2(3)
C(22) – C(23) – H(23)	119.9	C(24) – C(23) – H(23)	119.9
C(23) – C(24) – C(25)	119.5(3)	C(23) – C(24) – H(24)	120.2
C(25) – C(24) – H(24)	120.2	C(26) – C(25) – C(24)	120.5(3)
C(26) – C(25) – H(25)	119.8	C(24) – C(25) – H(25)	119.8
C(25) – C(26) – C(21)	121.3(3)	C(25) – C(26) – H(26)	119.3
C(21) – C(26) – H(26)	119.3	C(34) – C(31) – C(33)	111.0(3)
C(34) – C(31) – P(1)	116.1(3)	C(33) – C(31) – P(1)	108.8(2)
C(34) – C(31) – H(31)	106.8	C(33) – C(31) – H(31)	106.8
P(1) – C(31) – H(31)	106.8	C(36) – C(32) – C(35)	110.8(3)
C(36) – C(32) – P(1)	107.1(2)	C(35) – C(32) – P(1)	112.3(2)
C(36) – C(32) – H(32)	108.8	C(35) – C(32) – H(32)	108.8
P(1) – C(32) – H(32)	108.8	C(31) – C(33) – H(33A)	109.5
C(31) – C(33) – H(33B)	109.5	H(33A) – C(33) – H(33B)	109.5
C(31) – C(33) – H(33C)	109.5	H(33A) – C(33) – H(33C)	109.5
H(33B) – C(33) – H(33C)	109.5	C(31) – C(34) – H(34A)	109.5
C(31) – C(34) – H(34B)	109.5	H(34A) – C(34) – H(34B)	109.5
C(31) – C(34) – H(34C)	109.5	H(34A) – C(34) – H(34C)	109.5
H(34B) – C(34) – H(34C)	109.5	C(32) – C(35) – H(35A)	109.5

Continued on next page

Table S25. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(32) – C(35) – H(35B)	109.5	H(35A) – C(35) – H(35B)	109.5
C(32) – C(35) – H(35C)	109.5	H(35A) – C(35) – H(35C)	109.5
H(35B) – C(35) – H(35C)	109.5	C(32) – C(36) – H(36A)	109.5
C(32) – C(36) – H(36B)	109.5	H(36A) – C(36) – H(36B)	109.5
C(32) – C(36) – H(36C)	109.5	H(36A) – C(36) – H(36C)	109.5
H(36B) – C(36) – H(36C)	109.5	C(44) – C(41) – C(43)	111.6(2)
C(44) – C(41) – P(2)	116.42(19)	C(43) – C(41) – P(2)	108.63(19)
C(44) – C(41) – H(41)	106.6	C(43) – C(41) – H(41)	106.6
P(2) – C(41) – H(41)	106.6	C(45) – C(42) – C(46)	111.1(2)
C(45) – C(42) – P(2)	111.70(18)	C(46) – C(42) – P(2)	108.4(2)
C(45) – C(42) – H(42)	108.5	C(46) – C(42) – H(42)	108.5
P(2) – C(42) – H(42)	108.5	C(41) – C(43) – H(43A)	109.5
C(41) – C(43) – H(43B)	109.5	H(43A) – C(43) – H(43B)	109.5
C(41) – C(43) – H(43C)	109.5	H(43A) – C(43) – H(43C)	109.5
H(43B) – C(43) – H(43C)	109.5	C(41) – C(44) – H(44A)	109.5
C(41) – C(44) – H(44B)	109.5	H(44A) – C(44) – H(44B)	109.5
C(41) – C(44) – H(44C)	109.5	H(44A) – C(44) – H(44C)	109.5
H(44B) – C(44) – H(44C)	109.5	C(42) – C(45) – H(45A)	109.5
C(42) – C(45) – H(45B)	109.5	H(45A) – C(45) – H(45B)	109.5
C(42) – C(45) – H(45C)	109.5	H(45A) – C(45) – H(45C)	109.5
H(45B) – C(45) – H(45C)	109.5	C(42) – C(46) – H(46A)	109.5
C(42) – C(46) – H(46B)	109.5	H(46A) – C(46) – H(46B)	109.5
C(42) – C(46) – H(46C)	109.5	H(46A) – C(46) – H(46C)	109.5
H(46B) – C(46) – H(46C)	109.5		

8.3 Crystal data for [PC(sp³)HP]PdBr (4)

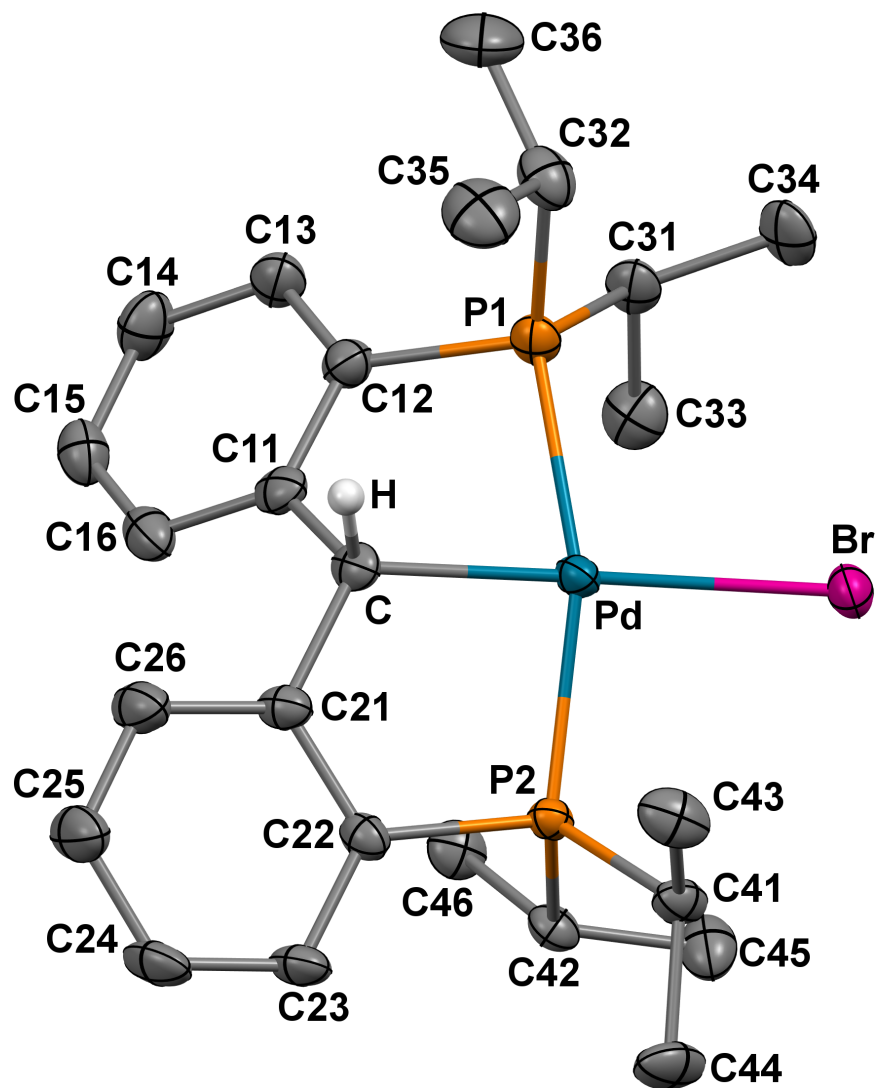


Figure S75. Thermal-ellipsoid representation of [PC(sp³)HP]PdBr (**4**) at 50% probability. Most hydrogen atoms were omitted for clarity.

Table S26. Crystal data and structure refinement for [PC(sp³)HP]PdBr (**4**).

Identification code:	cc271	
Empirical formula:	C ₂₅ H ₃₇ BrP ₂ Pd	
Formula weight:	585.80	
Temperature:	120(2) K	
Wavelength:	0.71073 Å	
Crystal system:	Monoclinic	
Space group:	<i>P</i> 2 ₁ / <i>n</i>	
Unit cell dimensions:	<i>a</i> = 11.2438(8) Å	$\alpha = 90^\circ$
	<i>b</i> = 13.7677(10) Å	$\beta = 106.9775(12)^\circ$
	<i>c</i> = 17.4246(12) Å	$\gamma = 90^\circ$
Volume:	2579.8(3) Å ³	
Z:	4	
Density (calculated):	1.508 g·cm ⁻³	
Absorption coefficient (μ):	2.402 mm ⁻¹	
F(000):	1192	
Crystal size:	0.13 × 0.10 × 0.05 mm ³	
θ range for data collection:	1.92 to 25.00°	
Index ranges:	-13 ≤ <i>h</i> ≤ 13, -16 ≤ <i>k</i> ≤ 16, -20 ≤ <i>l</i> ≤ 20	
Reflections collected:	33493	
Independent reflections:	4546 [<i>R</i> _{int} = 0.0524]	
Completeness to $\theta = 25.00^\circ$:	100.0 %	
Absorption correction:	Semi-empirical from equivalents	
Max. and min. transmission:	0.7454 and 0.6879	
Refinement method:	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters:	4546 / 0 / 270	
Goodness-of-fit on <i>F</i> ² :	1.044	
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]:	<i>R</i> ₁ = 0.0348, <i>wR</i> ₂ = 0.0742	
<i>R</i> indices (all data):	<i>R</i> ₁ = 0.0463, <i>wR</i> ₂ = 0.0776	
Largest diff. peak and hole:	1.970 and -1.106 e ⁻ ·Å ⁻³	

Table S27. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for [PC(sp³)HP]PdBr (**4**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

atom	x	y	z	U(eq)
Pd	0.02187(3)	0.65787(2)	0.18217(2)	0.019(1)
P(1)	−0.16836(10)	0.57786(7)	0.15980(6)	0.022(1)
Br	0.14254(4)	0.58796(3)	0.31483(2)	0.025(1)
C	−0.0624(4)	0.7074(3)	0.0669(2)	0.022(1)
P(2)	0.16165(9)	0.77727(7)	0.18634(6)	0.017(1)
C(11)	−0.1977(4)	0.7319(3)	0.0586(2)	0.024(1)
C(12)	−0.2653(4)	0.6656(3)	0.0910(2)	0.023(1)
C(13)	−0.3923(4)	0.6779(3)	0.0787(3)	0.029(1)
C(14)	−0.4522(4)	0.7591(3)	0.0378(3)	0.034(1)
C(15)	−0.3865(4)	0.8268(3)	0.0096(3)	0.030(1)
C(16)	−0.2606(4)	0.8131(3)	0.0189(2)	0.029(1)
C(21)	0.0106(4)	0.7824(3)	0.0343(2)	0.023(1)
C(22)	0.1203(4)	0.8214(3)	0.0840(2)	0.021(1)
C(23)	0.1880(4)	0.8894(3)	0.0539(3)	0.026(1)
C(24)	0.1467(4)	0.9163(3)	−0.0261(3)	0.033(1)
C(26)	−0.0289(4)	0.8098(3)	−0.0465(3)	0.032(1)
C(31)	−0.2339(4)	0.5750(3)	0.2457(3)	0.027(1)
C(32)	−0.1970(4)	0.4556(3)	0.1143(3)	0.032(1)
C(33)	−0.2110(4)	0.6723(3)	0.2893(3)	0.035(1)
C(34)	−0.1804(4)	0.4908(3)	0.3027(3)	0.032(1)
C(35)	−0.1365(5)	0.4462(3)	0.0470(3)	0.045(1)
C(36)	−0.3332(5)	0.4262(4)	0.0873(3)	0.051(1)
C(41)	0.3250(3)	0.7389(3)	0.2201(3)	0.023(1)
C(42)	0.1446(4)	0.8840(3)	0.2458(2)	0.021(1)
C(43)	0.3431(4)	0.6533(3)	0.1689(3)	0.032(1)
C(44)	0.4241(4)	0.8165(3)	0.2261(3)	0.036(1)
C(45)	0.1960(5)	0.8659(3)	0.3357(3)	0.034(1)
C(46)	0.0057(4)	0.9097(3)	0.2230(3)	0.027(1)
C(25)	0.0395(5)	0.8752(3)	−0.0756(3)	0.037(1)
H	−0.0666	0.6491	0.0320	0.027
H(13)	−0.4380	0.6309	0.0982	0.035
H(14)	−0.5389	0.7676	0.0294	0.041
H(15)	−0.4271	0.8835	−0.0165	0.036
H(16)	−0.2165	0.8600	−0.0021	0.035
H(23)	0.2619	0.9169	0.0883	0.032
H(24)	0.1918	0.9627	−0.0468	0.040
H(26)	−0.1031	0.7832	−0.0813	0.039
H(31)	−0.3258	0.5653	0.2241	0.032
H(32)	−0.1536	0.4084	0.1570	0.039

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Table S27. – continued from previous page

atom	x	y	x	U(eq)
H(33A)	−0.2400	0.7250	0.2505	0.052
H(33B)	−0.1218	0.6802	0.3159	0.052
H(33C)	−0.2564	0.6744	0.3294	0.052
H(34A)	−0.2018	0.4291	0.2740	0.048
H(34B)	−0.2155	0.4922	0.3480	0.048
H(34C)	−0.0898	0.4971	0.3227	0.048
H(35A)	−0.1436	0.3789	0.0278	0.067
H(35B)	−0.0484	0.4640	0.0672	0.067
H(35C)	−0.1784	0.4895	0.0027	0.067
H(36A)	−0.3791	0.4692	0.0439	0.076
H(36B)	−0.3679	0.4315	0.1326	0.076
H(36C)	−0.3406	0.3590	0.0680	0.076
H(41)	0.3393	0.7128	0.2757	0.028
H(42)	0.1907	0.9397	0.2310	0.025
H(43A)	0.3269	0.6744	0.1130	0.048
H(43B)	0.2852	0.6011	0.1716	0.048
H(43C)	0.4287	0.6294	0.1890	0.048
H(44A)	0.4241	0.8362	0.1720	0.053
H(44B)	0.5059	0.7902	0.2550	0.053
H(44C)	0.4061	0.8730	0.2551	0.053
H(45A)	0.1612	0.8053	0.3495	0.051
H(45B)	0.1731	0.9200	0.3651	0.051
H(45C)	0.2868	0.8606	0.3504	0.051
H(46A)	−0.0263	0.9182	0.1647	0.041
H(46B)	−0.0054	0.9701	0.2498	0.041
H(46C)	−0.0398	0.8571	0.2398	0.041
H(25)	0.0126	0.8925	−0.1308	0.044

Table S28. Anisotropic displacement parameters ($\text{\AA}^2$) for [PC(sp³)HP]PdBr (**4**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$.

atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Pd	0.0217(2)	0.0177(2)	0.0178(2)	0.0015(1)	0.0071(1)	-0.0036(1)
P(1)	0.0191(5)	0.0263(5)	0.0225(6)	0.0034(4)	0.0090(5)	-0.0002(4)
Br	0.0284(2)	0.0227(2)	0.0220(2)	0.0047(2)	0.0056(2)	0.0017(2)
C	0.028(2)	0.023(2)	0.015(2)	-0.0031(16)	0.0071(18)	-0.0042(17)
P(2)	0.0160(5)	0.0170(5)	0.0197(5)	0.0009(4)	0.0061(4)	-0.0014(4)
C(11)	0.027(2)	0.029(2)	0.016(2)	-0.0051(17)	0.0044(18)	-0.0080(18)
C(12)	0.021(2)	0.027(2)	0.022(2)	-0.0006(17)	0.0051(18)	-0.0029(17)
C(13)	0.024(2)	0.036(2)	0.028(2)	0.0054(19)	0.009(2)	-0.0033(19)
C(14)	0.023(2)	0.046(3)	0.033(3)	0.003(2)	0.006(2)	0.006(2)
C(15)	0.038(3)	0.028(2)	0.023(2)	0.0017(18)	0.008(2)	0.007(2)
C(16)	0.043(3)	0.022(2)	0.021(2)	-0.0006(17)	0.008(2)	-0.0036(19)
C(21)	0.025(2)	0.022(2)	0.022(2)	-0.0029(17)	0.0101(18)	-0.0061(17)
C(22)	0.027(2)	0.0189(19)	0.019(2)	0.0001(16)	0.0096(18)	-0.0017(16)
C(23)	0.030(2)	0.024(2)	0.029(2)	-0.0020(18)	0.013(2)	-0.0120(18)
C(24)	0.047(3)	0.030(2)	0.029(3)	-0.0017(19)	0.020(2)	-0.019(2)
C(26)	0.039(3)	0.035(2)	0.023(2)	-0.0009(19)	0.008(2)	-0.014(2)
C(31)	0.021(2)	0.035(2)	0.027(2)	0.0058(18)	0.0119(19)	-0.0021(18)
C(32)	0.042(3)	0.024(2)	0.033(3)	0.0018(19)	0.013(2)	0.004(2)
C(33)	0.036(3)	0.041(3)	0.031(3)	-0.003(2)	0.016(2)	0.002(2)
C(34)	0.033(3)	0.042(3)	0.029(2)	0.012(2)	0.019(2)	0.000(2)
C(35)	0.061(4)	0.034(3)	0.042(3)	-0.011(2)	0.019(3)	-0.001(2)
C(36)	0.055(4)	0.033(3)	0.060(4)	-0.007(2)	0.011(3)	-0.017(2)
C(41)	0.016(2)	0.022(2)	0.032(2)	0.0019(17)	0.0077(18)	-0.0013(16)
C(42)	0.025(2)	0.0153(18)	0.025(2)	0.0002(16)	0.0106(18)	0.0010(16)
C(43)	0.031(2)	0.024(2)	0.049(3)	-0.002(2)	0.022(2)	0.0041(19)
C(44)	0.016(2)	0.030(2)	0.058(3)	0.000(2)	0.008(2)	-0.0040(18)
C(45)	0.049(3)	0.025(2)	0.026(2)	-0.0039(18)	0.006(2)	0.004(2)
C(46)	0.026(2)	0.024(2)	0.034(3)	-0.0014(18)	0.012(2)	0.0056(18)
C(25)	0.048(3)	0.040(3)	0.022(2)	0.002(2)	0.009(2)	-0.016(2)

Table S29. Distances [Å] for [PC(sp³)HP]PdBr (**4**).

atom – atom	distance	atom – atom	distance
Pd – C	2.071(4)	Pd – P(2)	2.2608(10)
Pd – P(1)	2.3352(11)	Pd – Br	2.5057(5)
P(1) – C(12)	1.822(4)	P(1) – C(32)	1.849(4)
P(1) – C(31)	1.852(4)	C – C(11)	1.523(6)
C – C(21)	1.527(5)	C – H	1.0000
P(2) – C(22)	1.812(4)	P(2) – C(41)	1.835(4)
P(2) – C(42)	1.840(4)	C(11) – C(16)	1.394(6)
C(11) – C(12)	1.407(5)	C(12) – C(13)	1.392(6)
C(13) – C(14)	1.389(6)	C(13) – H(13)	0.9500
C(14) – C(15)	1.366(6)	C(14) – H(14)	0.9500
C(15) – C(16)	1.390(6)	C(15) – H(15)	0.9500
C(16) – H(16)	0.9500	C(21) – C(22)	1.391(5)
C(21) – C(26)	1.398(6)	C(22) – C(23)	1.402(5)
C(23) – C(24)	1.384(6)	C(23) – H(23)	0.9500
C(24) – C(25)	1.382(6)	C(24) – H(24)	0.9500
C(26) – C(25)	1.374(6)	C(26) – H(26)	0.9500
C(31) – C(33)	1.524(6)	C(31) – C(34)	1.531(6)
C(31) – H(31)	1.0000	C(32) – C(36)	1.520(7)
C(32) – C(35)	1.524(6)	C(32) – H(32)	1.0000
C(33) – H(33A)	0.9800	C(33) – H(33B)	0.9800
C(33) – H(33C)	0.9800	C(34) – H(34A)	0.9800
C(34) – H(34B)	0.9800	C(34) – H(34C)	0.9800
C(35) – H(35A)	0.9800	C(35) – H(35B)	0.9800
C(35) – H(35C)	0.9800	C(36) – H(36A)	0.9800
C(36) – H(36B)	0.9800	C(36) – H(36C)	0.9800
C(41) – C(44)	1.526(5)	C(41) – C(43)	1.528(5)
C(41) – H(41)	1.0000	C(42) – C(45)	1.525(6)
C(42) – C(46)	1.536(5)	C(42) – H(42)	1.0000
C(43) – H(43A)	0.9800	C(43) – H(43B)	0.9800
C(43) – H(43C)	0.9800	C(44) – H(44A)	0.9800
C(44) – H(44B)	0.9800	C(44) – H(44C)	0.9800
C(45) – H(45A)	0.9800	C(45) – H(45B)	0.9800
C(45) – H(45C)	0.9800	C(46) – H(46A)	0.9800
C(46) – H(46B)	0.9800	C(46) – H(46C)	0.9800
C(25) – H(25)	0.9500		

Table S30. Angles [°] for [PC(sp³)HP]PdBr (**4**).

atom – atom – atom	angle	atom – atom – atom	angle
C – Pd – P(2)	84.74(11)	C – Pd – P(1)	81.73(11)
P(2) – Pd – P(1)	160.49(4)	C – Pd – Br	173.06(11)
P(2) – Pd – Br	93.76(3)	P(1) – Pd – Br	101.28(3)
C(12) – P(1) – C(32)	109.0(2)	C(12) – P(1) – C(31)	104.12(19)
C(32) – P(1) – C(31)	105.46(19)	C(12) – P(1) – Pd	98.03(13)
C(32) – P(1) – Pd	122.51(15)	C(31) – P(1) – Pd	115.87(14)
C(11) – C – C(21)	116.4(3)	C(11) – C – Pd	109.0(3)
C(21) – C – Pd	116.1(3)	C(11) – C – H	104.6
C(21) – C – H	104.6	Pd – C – H	104.6
C(22) – P(2) – C(41)	110.95(19)	C(22) – P(2) – C(42)	104.33(17)
C(41) – P(2) – C(42)	107.96(18)	C(22) – P(2) – Pd	103.63(13)
C(41) – P(2) – Pd	114.97(13)	C(42) – P(2) – Pd	114.42(13)
C(16) – C(11) – C(12)	117.7(4)	C(16) – C(11) – C	124.9(4)
C(12) – C(11) – C	117.4(4)	C(13) – C(12) – C(11)	120.6(4)
C(13) – C(12) – P(1)	124.9(3)	C(11) – C(12) – P(1)	113.9(3)
C(14) – C(13) – C(12)	120.0(4)	C(14) – C(13) – H(13)	120.0
C(12) – C(13) – H(13)	120.0	C(15) – C(14) – C(13)	120.1(4)
C(15) – C(14) – H(14)	120.0	C(13) – C(14) – H(14)	120.0
C(14) – C(15) – C(16)	120.3(4)	C(14) – C(15) – H(15)	119.8
C(16) – C(15) – H(15)	119.8	C(15) – C(16) – C(11)	121.2(4)
C(15) – C(16) – H(16)	119.4	C(11) – C(16) – H(16)	119.4
C(22) – C(21) – C(26)	119.0(4)	C(22) – C(21) – C	120.3(3)
C(26) – C(21) – C	120.6(4)	C(21) – C(22) – C(23)	120.3(4)
C(21) – C(22) – P(2)	114.2(3)	C(23) – C(22) – P(2)	125.5(3)
C(24) – C(23) – C(22)	119.8(4)	C(24) – C(23) – H(23)	120.1
C(22) – C(23) – H(23)	120.1	C(25) – C(24) – C(23)	119.5(4)
C(25) – C(24) – H(24)	120.2	C(23) – C(24) – H(24)	120.2
C(25) – C(26) – C(21)	120.0(4)	C(25) – C(26) – H(26)	120.0
C(21) – C(26) – H(26)	120.0	C(33) – C(31) – C(34)	111.4(4)
C(33) – C(31) – P(1)	109.5(3)	C(34) – C(31) – P(1)	111.6(3)
C(33) – C(31) – H(31)	108.1	C(34) – C(31) – H(31)	108.1
P(1) – C(31) – H(31)	108.1	C(36) – C(32) – C(35)	112.1(4)
C(36) – C(32) – P(1)	114.1(3)	C(35) – C(32) – P(1)	110.3(3)
C(36) – C(32) – H(32)	106.6	C(35) – C(32) – H(32)	106.6
P(1) – C(32) – H(32)	106.6	C(31) – C(33) – H(33A)	109.5
C(31) – C(33) – H(33B)	109.5	H(33A) – C(33) – H(33B)	109.5
C(31) – C(33) – H(33C)	109.5	H(33A) – C(33) – H(33C)	109.5
H(33B) – C(33) – H(33C)	109.5	C(31) – C(34) – H(34A)	109.5
C(31) – C(34) – H(34B)	109.5	H(34A) – C(34) – H(34B)	109.5
C(31) – C(34) – H(34C)	109.5	H(34A) – C(34) – H(34C)	109.5
H(34B) – C(34) – H(34C)	109.5	C(32) – C(35) – H(35A)	109.5

Continued on next page

Table S30. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(32) – C(35) – H(35B)	109.5	H(35A) – C(35) – H(35B)	109.5
C(32) – C(35) – H(35C)	109.5	H(35A) – C(35) – H(35C)	109.5
H(35B) – C(35) – H(35C)	109.5	C(32) – C(36) – H(36A)	109.5
C(32) – C(36) – H(36B)	109.5	H(36A) – C(36) – H(36B)	109.5
C(32) – C(36) – H(36C)	109.5	H(36A) – C(36) – H(36C)	109.5
H(36B) – C(36) – H(36C)	109.5	C(44) – C(41) – C(43)	111.2(3)
C(44) – C(41) – P(2)	117.6(3)	C(43) – C(41) – P(2)	109.0(3)
C(44) – C(41) – H(41)	106.1	C(43) – C(41) – H(41)	106.1
P(2) – C(41) – H(41)	106.1	C(45) – C(42) – C(46)	110.8(3)
C(45) – C(42) – P(2)	112.1(3)	C(46) – C(42) – P(2)	107.7(3)
C(45) – C(42) – H(42)	108.7	C(46) – C(42) – H(42)	108.7
P(2) – C(42) – H(42)	108.7	C(41) – C(43) – H(43A)	109.5
C(41) – C(43) – H(43B)	109.5	H(43A) – C(43) – H(43B)	109.5
C(41) – C(43) – H(43C)	109.5	H(43A) – C(43) – H(43C)	109.5
H(43B) – C(43) – H(43C)	109.5	C(41) – C(44) – H(44A)	109.5
C(41) – C(44) – H(44B)	109.5	H(44A) – C(44) – H(44B)	109.5
C(41) – C(44) – H(44C)	109.5	H(44A) – C(44) – H(44C)	109.5
H(44B) – C(44) – H(44C)	109.5	C(42) – C(45) – H(45A)	109.5
C(42) – C(45) – H(45B)	109.5	H(45A) – C(45) – H(45B)	109.5
C(42) – C(45) – H(45C)	109.5	H(45A) – C(45) – H(45C)	109.5
H(45B) – C(45) – H(45C)	109.5	C(42) – C(46) – H(46A)	109.5
C(42) – C(46) – H(46B)	109.5	H(46A) – C(46) – H(46B)	109.5
C(42) – C(46) – H(46C)	109.5	H(46A) – C(46) – H(46C)	109.5
H(46B) – C(46) – H(46C)	109.5	C(26) – C(25) – C(24)	121.2(4)
C(26) – C(25) – H(25)	119.4	C(24) – C(25) – H(25)	119.4

8.4 Crystal data for $[\text{PC}^*(\text{sp}^2)\text{P}]\text{PdCl}$ (**5**)

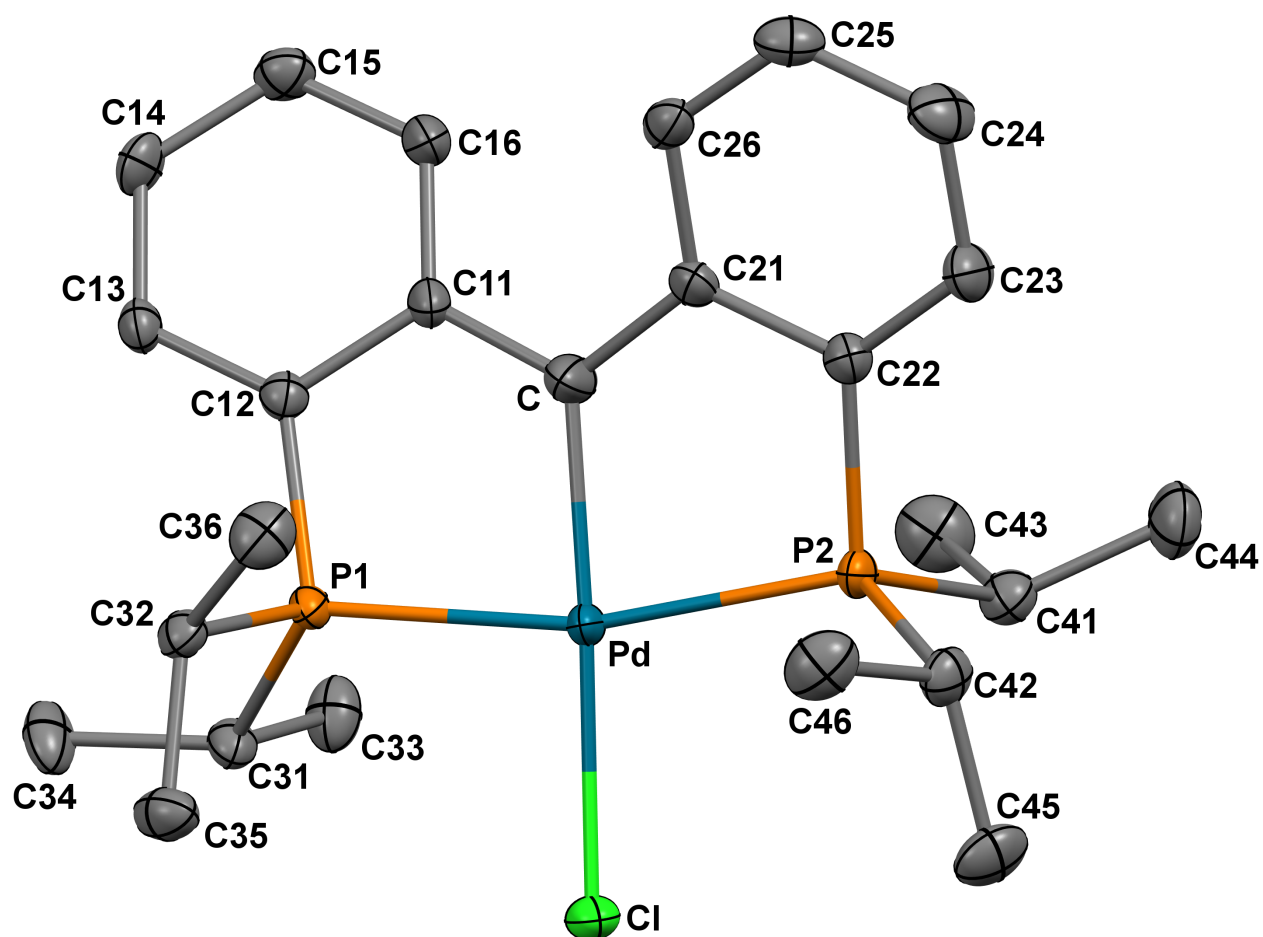


Figure S76. Thermal-ellipsoid (50% probability) representation of $[\text{PC}^*(\text{sp}^2)\text{P}]\text{PdCl}$ (**5**). Hydrogen atoms were omitted for clarity.

Table S31. Crystal data and structure refinement for [PC[•](sp²)P]PdCl (**5**).

Identification code:	cc250	
Empirical formula:	C ₂₅ H ₃₆ ClP ₂ Pd	
Formula weight:	540.33	
Temperature:	120(2) K	
Wavelength:	0.71073 Å	
Crystal system:	Monoclinic	
Space group:	<i>P</i> 2 ₁ / <i>n</i>	
Unit cell dimensions:	<i>a</i> = 11.6639(11) Å	$\alpha = 90^\circ$
	<i>b</i> = 13.5934(13) Å	$\beta = 105.1159(14)^\circ$
	<i>c</i> = 16.5680(16) Å	$\gamma = 90^\circ$
Volume:	2536.0(4) Å ³	
Z:	4	
Density (calculated):	1.415 g·cm ⁻³	
Absorption coefficient (μ):	0.973 mm ⁻¹	
F(000):	1116	
Crystal size:	0.11 × 0.09 × 0.08 mm ³	
θ range for data collection:	1.97 to 25.00°	
Index ranges:	-13 ≤ <i>h</i> ≤ 13, -16 ≤ <i>k</i> ≤ 16, -19 ≤ <i>l</i> ≤ 19	
Reflections collected:	36052	
Independent reflections:	4436 [<i>R</i> _{int} = 0.0430]	
Completeness to $\theta = 25.00^\circ$:	99.4 %	
Absorption correction:	Semi-empirical from equivalents	
Max. and min. transmission:	0.7457 and 0.6929	
Refinement method:	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters:	4436 / 0 / 270	
Goodness-of-fit on <i>F</i> ² :	1.046	
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]:	<i>R</i> ₁ = 0.0240, <i>wR</i> ₂ = 0.0523	
<i>R</i> indices (all data):	<i>R</i> ₁ = 0.0298, <i>wR</i> ₂ = 0.0541	
Largest diff. peak and hole:	0.664 and -0.356 e ⁻ ·Å ⁻³	

Table S32. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for [PC $\bullet$ (sp²)P]PdCl (**5**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

atom	x	y	z	U(eq)
Pd	0.01580(2)	0.82790(1)	0.19451(1)	0.016(1)
P(1)	0.15024(5)	0.70808(4)	0.19016(4)	0.015(1)
Cl	0.14068(5)	0.90818(4)	0.31356(3)	0.021(1)
P(2)	-0.15260(5)	0.92214(4)	0.17604(4)	0.017(1)
C	-0.0783(2)	0.7603(2)	0.09076(16)	0.031(1)
C(11)	-0.0156(2)	0.69972(16)	0.04320(15)	0.020(1)
C(12)	0.09701(19)	0.66181(16)	0.08448(14)	0.017(1)
C(13)	0.1558(2)	0.59550(16)	0.04562(14)	0.018(1)
C(14)	0.1078(2)	0.57109(17)	-0.03797(15)	0.022(1)
C(15)	0.0016(2)	0.61327(17)	-0.08147(15)	0.023(1)
C(16)	-0.0600(2)	0.67567(17)	-0.04212(15)	0.024(1)
C(21)	-0.2064(2)	0.76799(16)	0.06865(14)	0.018(1)
C(22)	-0.2590(2)	0.84699(16)	0.10216(14)	0.018(1)
C(23)	-0.3814(2)	0.85604(18)	0.08361(16)	0.025(1)
C(24)	-0.4551(2)	0.7876(2)	0.03375(16)	0.030(1)
C(25)	-0.4050(2)	0.70819(18)	0.00288(15)	0.025(1)
C(31)	0.30244(19)	0.75402(16)	0.20566(15)	0.019(1)
C(32)	0.1532(2)	0.60218(16)	0.25986(14)	0.019(1)
C(33)	0.2996(2)	0.83900(18)	0.14424(17)	0.028(1)
C(34)	0.3980(2)	0.67946(18)	0.20206(18)	0.030(1)
C(35)	0.2189(2)	0.62597(18)	0.34978(15)	0.027(1)
C(36)	0.0242(2)	0.57315(19)	0.25372(16)	0.027(1)
C(41)	-0.1519(2)	1.04615(17)	0.13154(15)	0.023(1)
C(42)	-0.2167(2)	0.93535(17)	0.26625(15)	0.022(1)
C(43)	-0.0862(2)	1.0439(2)	0.06309(17)	0.036(1)
C(44)	-0.2738(2)	1.09319(19)	0.10055(18)	0.034(1)
C(45)	-0.1491(2)	1.0115(2)	0.32843(16)	0.030(1)
C(46)	-0.2148(3)	0.83412(19)	0.30722(17)	0.033(1)
C(26)	-0.2837(2)	0.69837(17)	0.01975(14)	0.021(1)
H(13)	0.2286	0.5669	0.0760	0.022
H(14)	0.1477	0.5259	-0.0650	0.026
H(15)	-0.0294	0.5990	-0.1392	0.028
H(16)	-0.1334	0.7029	-0.0730	0.028
H(23)	-0.4153	0.9101	0.1055	0.030
H(24)	-0.5389	0.7950	0.0208	0.035
H(25)	-0.4550	0.6601	-0.0303	0.030
H(31)	0.3258	0.7834	0.2630	0.023
H(32)	0.1939	0.5460	0.2400	0.022
H(33A)	0.2744	0.8141	0.0868	0.043

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Table S32. – continued from previous page

atom	x	y	x	U(eq)
H(33B)	0.3791	0.8678	0.1542	0.043
H(33C)	0.2436	0.8893	0.1525	0.043
H(34A)	0.3881	0.6584	0.1441	0.046
H(34B)	0.3912	0.6223	0.2366	0.046
H(34C)	0.4765	0.7096	0.2232	0.046
H(35A)	0.3033	0.6362	0.3535	0.040
H(35B)	0.2101	0.5712	0.3861	0.040
H(35C)	0.1856	0.6859	0.3676	0.040
H(36A)	−0.0181	0.5630	0.1949	0.041
H(36B)	−0.0146	0.6257	0.2773	0.041
H(36C)	0.0229	0.5122	0.2850	0.041
H(41)	−0.1048	1.0891	0.1772	0.028
H(42)	−0.3011	0.9573	0.2454	0.026
H(43A)	−0.1298	1.0024	0.0168	0.054
H(43B)	−0.0063	1.0169	0.0858	0.054
H(43C)	−0.0801	1.1108	0.0426	0.054
H(44A)	−0.2648	1.1609	0.0828	0.051
H(44B)	−0.3137	1.0936	0.1458	0.051
H(44C)	−0.3212	1.0554	0.0531	0.051
H(45A)	−0.0640	0.9965	0.3426	0.046
H(45B)	−0.1771	1.0096	0.3793	0.046
H(45C)	−0.1627	1.0771	0.3034	0.046
H(46A)	−0.2575	0.7867	0.2656	0.049
H(46B)	−0.2534	0.8385	0.3531	0.049
H(46C)	−0.1324	0.8125	0.3292	0.049
H(26)	−0.2513	0.6434	−0.0021	0.025

Table S33. Anisotropic displacement parameters ($\text{\AA}^2$) for $[\text{PC}^*(\text{sp}^2)\text{P}]\text{PdCl}$ (**5**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\text{h}^2\text{a}^*\text{U}_{11} + \dots + 2\text{hka}^*\text{b}^*\text{U}_{12}]$.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd	0.0121(1)	0.0166(1)	0.0164(1)	-0.0046(1)	0.0004(1)	0.0038(1)
P(1)	0.0108(3)	0.0148(3)	0.0186(3)	-0.0024(2)	0.0019(2)	0.0011(2)
Cl	0.0214(3)	0.0189(3)	0.0192(3)	-0.0044(2)	-0.0005(2)	-0.0010(2)
P(2)	0.0135(3)	0.0178(3)	0.0185(3)	-0.0035(2)	0.0042(2)	0.0037(2)
C	0.0197(13)	0.0349(15)	0.0312(15)	-0.0150(12)	-0.0040(11)	0.0074(11)
C(11)	0.0166(12)	0.0153(11)	0.0244(13)	-0.0025(9)	-0.0001(10)	0.0038(9)
C(12)	0.0153(11)	0.0160(11)	0.0185(12)	-0.0002(9)	0.0044(9)	-0.0006(9)
C(13)	0.0146(11)	0.0166(11)	0.0234(13)	0.0008(10)	0.0042(10)	0.0032(9)
C(14)	0.0230(13)	0.0217(12)	0.0252(14)	-0.0031(10)	0.0133(11)	0.0040(10)
C(15)	0.0285(14)	0.0236(13)	0.0168(13)	-0.0002(10)	0.0054(11)	0.0002(11)
C(16)	0.0222(13)	0.0208(12)	0.0233(13)	-0.0032(10)	-0.0022(10)	0.0058(10)
C(21)	0.0187(12)	0.0198(12)	0.0141(12)	0.0003(9)	0.0010(9)	0.0030(10)
C(22)	0.0175(12)	0.0173(12)	0.0177(12)	0.0000(9)	0.0037(10)	0.0013(9)
C(23)	0.0166(12)	0.0287(14)	0.0288(14)	-0.0052(11)	0.0055(11)	0.0044(10)
C(24)	0.0169(13)	0.0412(16)	0.0303(15)	-0.0062(12)	0.0057(11)	-0.0022(11)
C(25)	0.0229(13)	0.0290(13)	0.0212(13)	-0.0029(11)	0.0038(11)	-0.0079(11)
C(31)	0.0137(11)	0.0173(11)	0.0259(13)	-0.0021(10)	0.0025(10)	-0.0010(9)
C(32)	0.0199(12)	0.0144(11)	0.0213(13)	-0.0029(9)	0.0051(10)	-0.0010(9)
C(33)	0.0249(14)	0.0207(13)	0.0430(16)	0.0038(11)	0.0148(12)	0.0008(11)
C(34)	0.0136(12)	0.0245(13)	0.0522(18)	0.0009(12)	0.0070(12)	0.0009(11)
C(35)	0.0342(15)	0.0222(13)	0.0202(13)	0.0013(10)	-0.0005(11)	-0.0023(11)
C(36)	0.0265(14)	0.0263(14)	0.0322(15)	-0.0011(11)	0.0141(12)	-0.0047(11)
C(41)	0.0239(13)	0.0199(12)	0.0251(14)	-0.0017(10)	0.0056(11)	-0.0008(10)
C(42)	0.0202(12)	0.0238(13)	0.0236(13)	-0.0034(10)	0.0105(10)	0.0025(10)
C(43)	0.0356(16)	0.0409(16)	0.0342(16)	0.0058(13)	0.0137(13)	-0.0040(13)
C(44)	0.0370(16)	0.0229(13)	0.0409(17)	0.0037(12)	0.0091(13)	0.0097(12)
C(45)	0.0360(15)	0.0338(15)	0.0267(14)	-0.0107(11)	0.0174(12)	-0.0043(12)
C(46)	0.0403(16)	0.0324(15)	0.0300(15)	-0.0006(12)	0.0160(13)	-0.0030(13)
C(26)	0.0289(14)	0.0171(12)	0.0157(12)	-0.0001(9)	0.0036(10)	0.0040(10)

Table S34. Distances [Å] for [PC[•](sp²)P]PdCl (**5**).

atom – atom	distance	atom – atom	distance
Pd – C	2.005(2)	Pd – P(1)	2.2751(6)
Pd – P(2)	2.2977(6)	Pd – Cl	2.3884(6)
P(1) – C(12)	1.811(2)	P(1) – C(31)	1.836(2)
P(1) – C(32)	1.840(2)	P(2) – C(22)	1.814(2)
P(2) – C(41)	1.841(2)	P(2) – C(42)	1.846(2)
C – C(21)	1.446(3)	C – C(11)	1.461(3)
C(11) – C(12)	1.411(3)	C(11) – C(16)	1.411(3)
C(12) – C(13)	1.389(3)	C(13) – C(14)	1.392(3)
C(13) – H(13)	0.9500	C(14) – C(15)	1.385(3)
C(14) – H(14)	0.9500	C(15) – C(16)	1.380(3)
C(15) – H(15)	0.9500	C(16) – H(16)	0.9500
C(21) – C(26)	1.409(3)	C(21) – C(22)	1.420(3)
C(22) – C(23)	1.385(3)	C(23) – C(24)	1.384(4)
C(23) – H(23)	0.9500	C(24) – C(25)	1.387(4)
C(24) – H(24)	0.9500	C(25) – C(26)	1.375(3)
C(25) – H(25)	0.9500	C(31) – C(34)	1.519(3)
C(31) – C(33)	1.534(3)	C(31) – H(31)	1.0000
C(32) – C(35)	1.522(3)	C(32) – C(36)	1.533(3)
C(32) – H(32)	1.0000	C(33) – H(33A)	0.9800
C(33) – H(33B)	0.9800	C(33) – H(33C)	0.9800
C(34) – H(34A)	0.9800	C(34) – H(34B)	0.9800
C(34) – H(34C)	0.9800	C(35) – H(35A)	0.9800
C(35) – H(35B)	0.9800	C(35) – H(35C)	0.9800
C(36) – H(36A)	0.9800	C(36) – H(36B)	0.9800
C(36) – H(36C)	0.9800	C(41) – C(44)	1.520(3)
C(41) – C(43)	1.526(3)	C(41) – H(41)	1.0000
C(42) – C(45)	1.526(3)	C(42) – C(46)	1.532(3)
C(42) – H(42)	1.0000	C(43) – H(43A)	0.9800
C(43) – H(43B)	0.9800	C(43) – H(43C)	0.9800
C(44) – H(44A)	0.9800	C(44) – H(44B)	0.9800
C(44) – H(44C)	0.9800	C(45) – H(45A)	0.9800
C(45) – H(45B)	0.9800	C(45) – H(45C)	0.9800
C(46) – H(46A)	0.9800	C(46) – H(46B)	0.9800
C(46) – H(46C)	0.9800	C(26) – H(26)	0.9500

Table S35. Angles [°] for [PC[•](sp²)P]PdCl (**5**).

atom – atom – atom	angle	atom – atom – atom	angle
C – Pd – P(1)	82.69(7)	C – Pd – P(2)	83.30(7)
P(1) – Pd – P(2)	165.30(2)	C – Pd – Cl	175.61(8)
P(1) – Pd – Cl	94.38(2)	P(2) – Pd – Cl	99.86(2)
C(12) – P(1) – C(31)	109.19(11)	C(12) – P(1) – C(32)	106.30(10)
C(31) – P(1) – C(32)	108.61(10)	C(12) – P(1) – Pd	102.35(7)
C(31) – P(1) – Pd	113.67(7)	C(32) – P(1) – Pd	116.13(8)
C(22) – P(2) – C(41)	108.61(11)	C(22) – P(2) – C(42)	104.53(11)
C(41) – P(2) – C(42)	106.27(11)	C(22) – P(2) – Pd	100.76(7)
C(41) – P(2) – Pd	118.10(8)	C(42) – P(2) – Pd	117.32(8)
C(21) – C – C(11)	122.2(2)	C(21) – C – Pd	118.87(17)
C(11) – C – Pd	118.78(17)	C(12) – C(11) – C(16)	116.9(2)
C(12) – C(11) – C	118.6(2)	C(16) – C(11) – C	124.5(2)
C(13) – C(12) – C(11)	121.5(2)	C(13) – C(12) – P(1)	125.98(18)
C(11) – C(12) – P(1)	112.51(16)	C(12) – C(13) – C(14)	119.8(2)
C(12) – C(13) – H(13)	120.1	C(14) – C(13) – H(13)	120.1
C(15) – C(14) – C(13)	119.5(2)	C(15) – C(14) – H(14)	120.3
C(13) – C(14) – H(14)	120.3	C(16) – C(15) – C(14)	120.9(2)
C(16) – C(15) – H(15)	119.5	C(14) – C(15) – H(15)	119.5
C(15) – C(16) – C(11)	121.0(2)	C(15) – C(16) – H(16)	119.5
C(11) – C(16) – H(16)	119.5	C(26) – C(21) – C(22)	117.1(2)
C(26) – C(21) – C	124.1(2)	C(22) – C(21) – C	118.6(2)
C(23) – C(22) – C(21)	120.4(2)	C(23) – C(22) – P(2)	125.73(18)
C(21) – C(22) – P(2)	113.60(16)	C(24) – C(23) – C(22)	121.1(2)
C(24) – C(23) – H(23)	119.5	C(22) – C(23) – H(23)	119.5
C(23) – C(24) – C(25)	119.2(2)	C(23) – C(24) – H(24)	120.4
C(25) – C(24) – H(24)	120.4	C(26) – C(25) – C(24)	120.7(2)
C(26) – C(25) – H(25)	119.7	C(24) – C(25) – H(25)	119.7
C(34) – C(31) – C(33)	111.4(2)	C(34) – C(31) – P(1)	117.41(16)
C(33) – C(31) – P(1)	108.10(16)	C(34) – C(31) – H(31)	106.4
C(33) – C(31) – H(31)	106.4	P(1) – C(31) – H(31)	106.4
C(35) – C(32) – C(36)	110.8(2)	C(35) – C(32) – P(1)	111.74(16)
C(36) – C(32) – P(1)	107.60(16)	C(35) – C(32) – H(32)	108.9
C(36) – C(32) – H(32)	108.9	P(1) – C(32) – H(32)	108.9
C(31) – C(33) – H(33A)	109.5	C(31) – C(33) – H(33B)	109.5
H(33A) – C(33) – H(33B)	109.5	C(31) – C(33) – H(33C)	109.5
H(33A) – C(33) – H(33C)	109.5	H(33B) – C(33) – H(33C)	109.5
C(31) – C(34) – H(34A)	109.5	C(31) – C(34) – H(34B)	109.5
H(34A) – C(34) – H(34B)	109.5	C(31) – C(34) – H(34C)	109.5
H(34A) – C(34) – H(34C)	109.5	H(34B) – C(34) – H(34C)	109.5
C(32) – C(35) – H(35A)	109.5	C(32) – C(35) – H(35B)	109.5
H(35A) – C(35) – H(35B)	109.5	C(32) – C(35) – H(35C)	109.5

Continued on next page

Table S35. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
H(35A) – C(35) – H(35C)	109.5	H(35B) – C(35) – H(35C)	109.5
C(32) – C(36) – H(36A)	109.5	C(32) – C(36) – H(36B)	109.5
H(36A) – C(36) – H(36B)	109.5	C(32) – C(36) – H(36C)	109.5
H(36A) – C(36) – H(36C)	109.5	H(36B) – C(36) – H(36C)	109.5
C(44) – C(41) – C(43)	111.4(2)	C(44) – C(41) – P(2)	114.78(17)
C(43) – C(41) – P(2)	109.55(17)	C(44) – C(41) – H(41)	106.9
C(43) – C(41) – H(41)	106.9	P(2) – C(41) – H(41)	106.9
C(45) – C(42) – C(46)	111.4(2)	C(45) – C(42) – P(2)	111.44(16)
C(46) – C(42) – P(2)	108.04(16)	C(45) – C(42) – H(42)	108.6
C(46) – C(42) – H(42)	108.6	P(2) – C(42) – H(42)	108.6
C(41) – C(43) – H(43A)	109.5	C(41) – C(43) – H(43B)	109.5
H(43A) – C(43) – H(43B)	109.5	C(41) – C(43) – H(43C)	109.5
H(43A) – C(43) – H(43C)	109.5	H(43B) – C(43) – H(43C)	109.5
C(41) – C(44) – H(44A)	109.5	C(41) – C(44) – H(44B)	109.5
H(44A) – C(44) – H(44B)	109.5	C(41) – C(44) – H(44C)	109.5
H(44A) – C(44) – H(44C)	109.5	H(44B) – C(44) – H(44C)	109.5
C(42) – C(45) – H(45A)	109.5	C(42) – C(45) – H(45B)	109.5
H(45A) – C(45) – H(45B)	109.5	C(42) – C(45) – H(45C)	109.5
H(45A) – C(45) – H(45C)	109.5	H(45B) – C(45) – H(45C)	109.5
C(42) – C(46) – H(46A)	109.5	C(42) – C(46) – H(46B)	109.5
H(46A) – C(46) – H(46B)	109.5	C(42) – C(46) – H(46C)	109.5
H(46A) – C(46) – H(46C)	109.5	H(46B) – C(46) – H(46C)	109.5
C(25) – C(26) – C(21)	121.5(2)	C(25) – C(26) – H(26)	119.3
C(21) – C(26) – H(26)	119.3		

8.5 Crystal data for [PC(CH₂)P]Pd(PMe₃) (6)

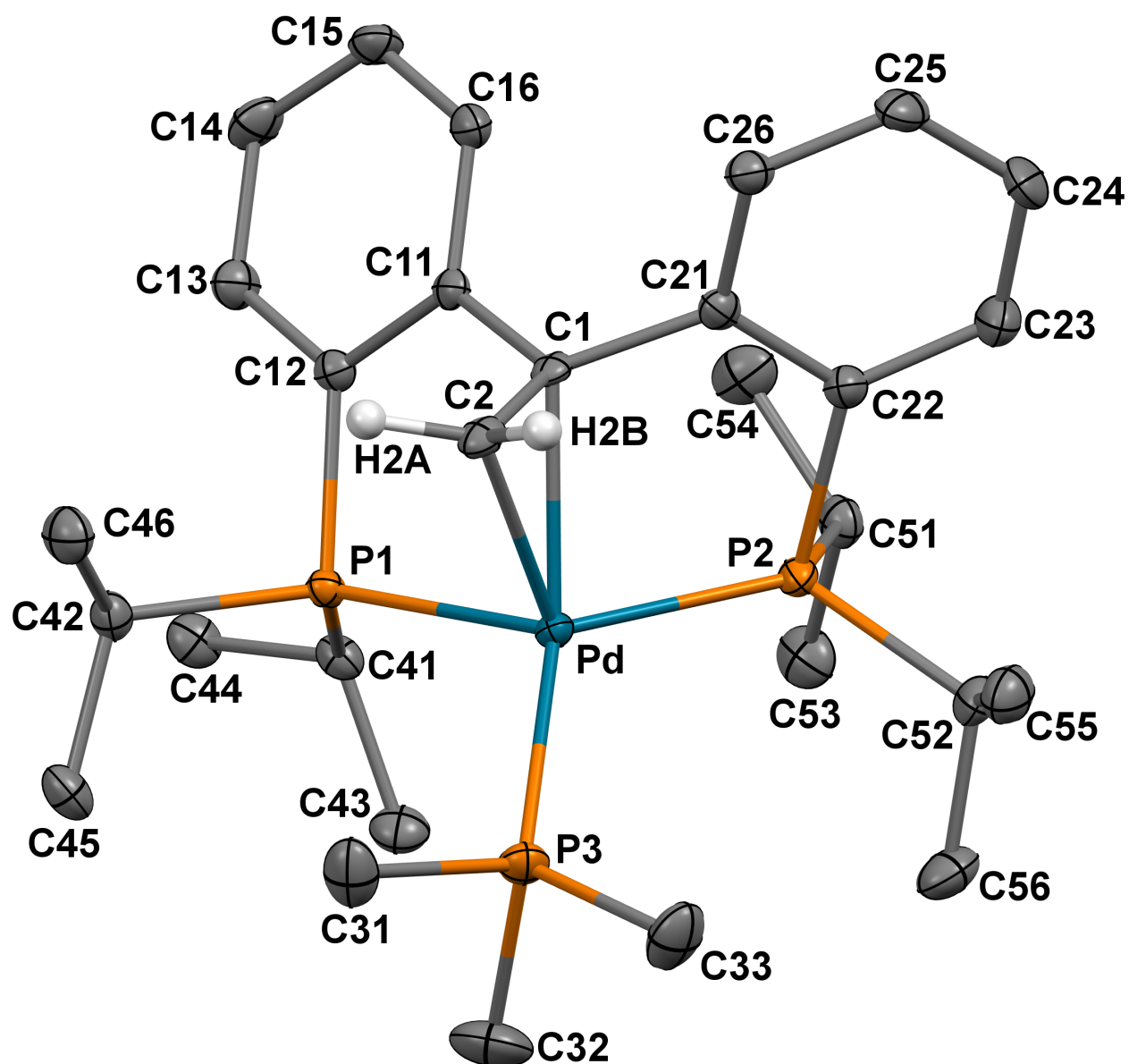


Figure S77. Thermal-ellipsoid representation of [PC(CH₂)P]Pd(PMe₃) (6) at 50% probability. Most hydrogen atoms were omitted for clarity.

Table S36. Crystal data and structure refinement for [PC(CH₂)P]Pd(PMe₃) (**6**).

Identification code:	cc252	
Empirical formula:	C ₂₉ H ₄₇ P ₃ Pd	
Formula weight:	594.98	
Temperature:	120(2) K	
Wavelength:	0.71073 Å	
Crystal system:	Monoclinic	
Space group:	<i>P</i> 2 ₁ / <i>n</i>	
Unit cell dimensions:	<i>a</i> = 10.3086(7) Å	$\alpha = 90^\circ$
	<i>b</i> = 24.0617(16) Å	$\beta = 107.5771(18)^\circ$
	<i>c</i> = 12.5709(8) Å	$\gamma = 90^\circ$
Volume:	2972.5(3) Å ³	
Z:	4	
Density (calculated):	1.329 g·cm ⁻³	
Absorption coefficient (μ):	0.801 mm ⁻¹	
F(000):	1248	
Crystal size:	0.10 × 0.08 × 0.07 mm ³	
θ range for data collection:	1.69 to 25.00°	
Index ranges:	-12 ≤ <i>h</i> ≤ 12, -28 ≤ <i>k</i> ≤ 28, -14 ≤ <i>l</i> ≤ 14	
Reflections collected:	71407	
Independent reflections:	5233 [<i>R</i> _{int} = 0.0510]	
Completeness to $\theta = 25.00^\circ$:	100.0 %	
Absorption correction:	Semi-empirical from equivalents	
Max. and min. transmission:	0.7459 and 0.7038	
Refinement method:	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters:	5233 / 0 / 309	
Goodness-of-fit on <i>F</i> ² :	1.077	
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]:	<i>R</i> ₁ = 0.0220, <i>wR</i> ₂ = 0.0495	
<i>R</i> indices (all data):	<i>R</i> ₁ = 0.0257, <i>wR</i> ₂ = 0.0512	
Largest diff. peak and hole:	0.407 and -0.292 e ⁻ ·Å ⁻³	

Table S37. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for [PC(CH₂)P]Pd(PMe₃) (**6**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

atom	x	y	z	U(eq)
Pd	0.32963(2)	0.90247(1)	0.77305(1)	0.011(1)
C(1)	0.36707(19)	0.83153(8)	0.89193(15)	0.012(1)
P(1)	0.31818(5)	0.83411(2)	0.63170(4)	0.012(1)
C(2)	0.4938(2)	0.85538(8)	0.90181(16)	0.015(1)
P(2)	0.13457(5)	0.91283(2)	0.82673(4)	0.014(1)
P(3)	0.43807(5)	0.98108(2)	0.73622(5)	0.017(1)
C(12)	0.31246(19)	0.77155(8)	0.71434(16)	0.013(1)
C(11)	0.32562(19)	0.77739(8)	0.82891(16)	0.012(1)
C(13)	0.2883(2)	0.71872(8)	0.66585(17)	0.018(1)
C(14)	0.2678(2)	0.67300(8)	0.72535(18)	0.022(1)
C(15)	0.2720(2)	0.67916(8)	0.83545(18)	0.020(1)
C(16)	0.3021(2)	0.73050(8)	0.88673(17)	0.016(1)
C(22)	0.1882(2)	0.87742(8)	0.96274(16)	0.016(1)
C(21)	0.3031(2)	0.84337(8)	0.98238(16)	0.014(1)
C(23)	0.1256(2)	0.88392(9)	1.04636(18)	0.023(1)
C(24)	0.1791(2)	0.85897(9)	1.14957(18)	0.026(1)
C(25)	0.2963(2)	0.82744(8)	1.17066(17)	0.022(1)
C(26)	0.3582(2)	0.81956(8)	1.08791(16)	0.017(1)
C(31)	0.6124(2)	0.97107(9)	0.7320(2)	0.028(1)
C(32)	0.3622(3)	1.01382(10)	0.6000(2)	0.036(1)
C(33)	0.4656(2)	1.04266(9)	0.8262(2)	0.030(1)
C(41)	0.1569(2)	0.83120(8)	0.51212(16)	0.015(1)
C(42)	0.4498(2)	0.81260(8)	0.56574(16)	0.016(1)
C(43)	0.1218(2)	0.89011(9)	0.46509(17)	0.021(1)
C(44)	0.1475(2)	0.79022(9)	0.41706(17)	0.019(1)
C(45)	0.4695(2)	0.85690(9)	0.48451(17)	0.020(1)
C(46)	0.5858(2)	0.80074(9)	0.65435(18)	0.022(1)
C(51)	−0.0360(2)	0.87909(8)	0.76584(17)	0.018(1)
C(52)	0.0845(2)	0.98315(8)	0.86488(17)	0.019(1)
C(53)	−0.1084(2)	0.89886(9)	0.64709(18)	0.025(1)
C(54)	−0.0206(2)	0.81582(9)	0.7674(2)	0.026(1)
C(55)	0.1983(2)	1.00752(9)	0.96142(18)	0.025(1)
C(56)	0.0548(2)	1.02229(9)	0.76451(19)	0.027(1)
H(2A)	0.5573	0.8331	0.8736	0.018
H(2B)	0.5387	0.8751	0.9724	0.018
H(13)	0.2860	0.7142	0.5902	0.021
H(14)	0.2509	0.6376	0.6906	0.026
H(15)	0.2542	0.6482	0.8760	0.023
H(16)	0.3070	0.7341	0.9631	0.020

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Table S37. – continued from previous page

atom	x	y	x	U(eq)
H(23)	0.0454	0.9057	1.0322	0.028
H(24)	0.1355	0.8635	1.2057	0.031
H(25)	0.3347	0.8111	1.2421	0.026
H(26)	0.4386	0.7978	1.1031	0.020
H(31A)	0.6124	0.9447	0.6726	0.042
H(31B)	0.6687	0.9564	0.8038	0.042
H(31C)	0.6495	1.0067	0.7171	0.042
H(32A)	0.3604	0.9871	0.5407	0.053
H(32B)	0.4164	1.0463	0.5929	0.053
H(32C)	0.2691	1.0256	0.5935	0.053
H(33A)	0.5180	1.0703	0.7992	0.045
H(33B)	0.5161	1.0321	0.9028	0.045
H(33C)	0.3776	1.0585	0.8248	0.045
H(41)	0.0833	0.8204	0.5449	0.018
H(42)	0.4183	0.7776	0.5228	0.019
H(43A)	0.1855	0.9012	0.4248	0.031
H(43B)	0.1287	0.9161	0.5265	0.031
H(43C)	0.0288	0.8906	0.4139	0.031
H(44A)	0.0606	0.7953	0.3586	0.029
H(44B)	0.1535	0.7521	0.4457	0.029
H(44C)	0.2226	0.7970	0.3860	0.029
H(45A)	0.5402	0.8447	0.4522	0.030
H(45B)	0.4971	0.8920	0.5246	0.030
H(45C)	0.3838	0.8623	0.4248	0.030
H(46A)	0.6524	0.7883	0.6179	0.034
H(46B)	0.5732	0.7716	0.7049	0.034
H(46C)	0.6188	0.8347	0.6970	0.034
H(51)	−0.0942	0.8891	0.8138	0.022
H(52)	0.0006	0.9794	0.8885	0.023
H(53A)	−0.0485	0.8936	0.6005	0.037
H(53B)	−0.1311	0.9384	0.6484	0.037
H(53C)	−0.1921	0.8773	0.6163	0.037
H(54A)	−0.1100	0.7987	0.7347	0.039
H(54B)	0.0180	0.8031	0.8446	0.039
H(54C)	0.0400	0.8052	0.7240	0.039
H(55A)	0.2848	1.0049	0.9445	0.037
H(55B)	0.2046	0.9867	1.0298	0.037
H(55C)	0.1784	1.0466	0.9719	0.037
H(56A)	0.1338	1.0235	0.7366	0.040
H(56B)	0.0362	1.0597	0.7872	0.040
H(56C)	−0.0246	1.0087	0.7055	0.040

Table S38. Anisotropic displacement parameters ($\text{\AA}^2$) for $[\text{PC}(\text{CH}_2)\text{P}]\text{Pd}(\text{PMe}_3)$ (**6**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$.

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd	0.0127(1)	0.0089(1)	0.0116(1)	0.0004(1)	0.0042(1)	0.0000(1)
C(1)	0.0138(10)	0.0102(9)	0.0094(9)	0.0028(7)	0.0009(8)	0.0045(8)
P(1)	0.0133(3)	0.0108(2)	0.0107(2)	-0.0003(2)	0.0040(2)	-0.0014(2)
C(2)	0.0153(10)	0.0137(10)	0.0132(10)	0.0020(8)	0.0008(8)	0.0039(8)
P(2)	0.0139(3)	0.0143(3)	0.0131(3)	0.0021(2)	0.0050(2)	0.0033(2)
P(3)	0.0195(3)	0.0117(2)	0.0213(3)	0.0006(2)	0.0078(2)	-0.0025(2)
C(12)	0.0108(10)	0.0133(10)	0.0148(10)	0.0005(8)	0.0037(8)	-0.0007(8)
C(11)	0.0093(9)	0.0130(9)	0.0154(10)	0.0019(8)	0.0049(8)	0.0022(8)
C(13)	0.0207(11)	0.0169(10)	0.0150(10)	-0.0020(8)	0.0047(9)	-0.0014(8)
C(14)	0.0231(12)	0.0119(10)	0.0289(12)	-0.0033(9)	0.0070(10)	-0.0027(9)
C(15)	0.0204(11)	0.0132(10)	0.0272(12)	0.0046(9)	0.0108(9)	-0.0018(8)
C(16)	0.0168(10)	0.0168(10)	0.0186(11)	0.0030(8)	0.0092(9)	0.0029(8)
C(22)	0.0203(11)	0.0135(10)	0.0157(10)	0.0011(8)	0.0072(9)	0.0011(8)
C(21)	0.0175(10)	0.0113(9)	0.0136(10)	-0.0017(8)	0.0056(8)	-0.0020(8)
C(23)	0.0264(12)	0.0231(11)	0.0240(12)	0.0040(9)	0.0131(10)	0.0084(10)
C(24)	0.0393(14)	0.0254(12)	0.0189(11)	0.0030(9)	0.0187(10)	0.0050(10)
C(25)	0.0338(13)	0.0179(11)	0.0140(11)	0.0038(8)	0.0085(9)	0.0023(9)
C(26)	0.0208(11)	0.0142(10)	0.0158(10)	0.0012(8)	0.0048(9)	0.0005(8)
C(31)	0.0246(12)	0.0254(12)	0.0377(14)	-0.0105(10)	0.0160(11)	-0.0097(10)
C(32)	0.0415(15)	0.0307(13)	0.0347(14)	0.0151(11)	0.0118(12)	-0.0067(11)
C(33)	0.0287(13)	0.0162(11)	0.0465(15)	-0.0092(10)	0.0146(11)	-0.0041(10)
C(41)	0.0133(10)	0.0188(10)	0.0130(10)	0.0011(8)	0.0039(8)	-0.0016(8)
C(42)	0.0166(10)	0.0166(10)	0.0172(10)	-0.0030(8)	0.0078(9)	-0.0014(8)
C(43)	0.0203(11)	0.0228(11)	0.0164(11)	0.0042(9)	0.0013(9)	0.0011(9)
C(44)	0.0187(11)	0.0225(11)	0.0148(10)	-0.0022(9)	0.0023(9)	-0.0041(9)
C(45)	0.0211(11)	0.0257(11)	0.0166(11)	-0.0011(9)	0.0094(9)	-0.0051(9)
C(46)	0.0170(11)	0.0258(12)	0.0260(12)	0.0017(9)	0.0091(9)	0.0009(9)
C(51)	0.0143(10)	0.0219(11)	0.0203(11)	0.0007(9)	0.0072(9)	0.0012(8)
C(52)	0.0197(11)	0.0177(10)	0.0217(11)	0.0006(9)	0.0083(9)	0.0061(9)
C(53)	0.0150(11)	0.0318(13)	0.0254(12)	0.0017(10)	0.0034(9)	-0.0002(9)
C(54)	0.0175(11)	0.0228(12)	0.0370(14)	0.0002(10)	0.0056(10)	-0.0038(9)
C(55)	0.0303(13)	0.0220(11)	0.0224(12)	-0.0031(9)	0.0081(10)	0.0033(10)
C(56)	0.0308(13)	0.0177(11)	0.0281(13)	0.0034(9)	0.0038(10)	0.0071(10)

Table S39. Distances [Å] for [PC(CH₂)P]Pd(PMe₃) (**6**).

atom – atom	distance	atom – atom	distance
Pd – C(1)	2.2242(18)	Pd – C(2)	2.2613(19)
Pd – P(3)	2.3140(5)	Pd – P(2)	2.3196(5)
Pd – P(1)	2.3978(5)	C(1) – C(2)	1.398(3)
C(1) – C(21)	1.504(3)	C(1) – C(11)	1.517(3)
P(1) – C(12)	1.8402(19)	P(1) – C(42)	1.864(2)
P(1) – C(41)	1.876(2)	C(2) – H(2A)	0.9900
C(2) – H(2B)	0.9900	P(2) – C(22)	1.839(2)
P(2) – C(52)	1.873(2)	P(2) – C(51)	1.877(2)
P(3) – C(31)	1.830(2)	P(3) – C(32)	1.832(2)
P(3) – C(33)	1.834(2)	C(12) – C(13)	1.399(3)
C(12) – C(11)	1.412(3)	C(11) – C(16)	1.402(3)
C(13) – C(14)	1.382(3)	C(13) – H(13)	0.9500
C(14) – C(15)	1.380(3)	C(14) – H(14)	0.9500
C(15) – C(16)	1.385(3)	C(15) – H(15)	0.9500
C(16) – H(16)	0.9500	C(22) – C(23)	1.398(3)
C(22) – C(21)	1.399(3)	C(21) – C(26)	1.398(3)
C(23) – C(24)	1.384(3)	C(23) – H(23)	0.9500
C(24) – C(25)	1.383(3)	C(24) – H(24)	0.9500
C(25) – C(26)	1.387(3)	C(25) – H(25)	0.9500
C(26) – H(26)	0.9500	C(31) – H(31A)	0.9800
C(31) – H(31B)	0.9800	C(31) – H(31C)	0.9800
C(32) – H(32A)	0.9800	C(32) – H(32B)	0.9800
C(32) – H(32C)	0.9800	C(33) – H(33A)	0.9800
C(33) – H(33B)	0.9800	C(33) – H(33C)	0.9800
C(41) – C(44)	1.530(3)	C(41) – C(43)	1.536(3)
C(41) – H(41)	1.0000	C(42) – C(46)	1.531(3)
C(42) – C(45)	1.532(3)	C(42) – H(42)	1.0000
C(43) – H(43A)	0.9800	C(43) – H(43B)	0.9800
C(43) – H(43C)	0.9800	C(44) – H(44A)	0.9800
C(44) – H(44B)	0.9800	C(44) – H(44C)	0.9800
C(45) – H(45A)	0.9800	C(45) – H(45B)	0.9800
C(45) – H(45C)	0.9800	C(46) – H(46A)	0.9800
C(46) – H(46B)	0.9800	C(46) – H(46C)	0.9800
C(51) – C(53)	1.529(3)	C(51) – C(54)	1.530(3)
C(51) – H(51)	1.0000	C(52) – C(55)	1.527(3)
C(52) – C(56)	1.529(3)	C(52) – H(52)	1.0000
C(53) – H(53A)	0.9800	C(53) – H(53B)	0.9800
C(53) – H(53C)	0.9800	C(54) – H(54A)	0.9800
C(54) – H(54B)	0.9800	C(54) – H(54C)	0.9800
C(55) – H(55A)	0.9800	C(55) – H(55B)	0.9800
C(56) – H(56B)	0.9800	C(56) – H(56C)	0.9800

Table S40. Angles [°] for [PC(CH₂)P]Pd(PMe₃) (**6**).

atom – atom – atom	angle	atom – atom – atom	angle
C(1) – Pd – C(2)	36.30(7)	C(1) – Pd – P(3)	139.94(5)
C(2) – Pd – P(3)	104.50(5)	C(1) – Pd – P(2)	82.92(5)
C(2) – Pd – P(2)	111.89(5)	P(3) – Pd – P(2)	118.946(19)
C(1) – Pd – P(1)	86.06(5)	C(2) – Pd – P(1)	92.61(5)
P(3) – Pd – P(1)	109.332(19)	P(2) – Pd – P(1)	115.868(19)
C(2) – C(1) – C(21)	117.82(17)	C(2) – C(1) – C(11)	120.48(17)
C(21) – C(1) – C(11)	116.01(16)	C(2) – C(1) – Pd	73.29(11)
C(21) – C(1) – Pd	109.62(12)	C(11) – C(1) – Pd	110.10(12)
C(12) – P(1) – C(42)	100.11(9)	C(12) – P(1) – C(41)	104.48(9)
C(42) – P(1) – C(41)	102.78(9)	C(12) – P(1) – Pd	98.37(6)
C(42) – P(1) – Pd	129.83(7)	C(41) – P(1) – Pd	116.92(6)
C(1) – C(2) – Pd	70.40(11)	C(1) – C(2) – H(2A)	116.6
Pd – C(2) – H(2A)	116.6	C(1) – C(2) – H(2B)	116.6
Pd – C(2) – H(2B)	116.6	H(2A) – C(2) – H(2B)	113.6
C(22) – P(2) – C(52)	102.07(9)	C(22) – P(2) – C(51)	99.22(9)
C(52) – P(2) – C(51)	101.46(9)	C(22) – P(2) – Pd	100.20(7)
C(52) – P(2) – Pd	120.10(7)	C(51) – P(2) – Pd	128.50(7)
C(31) – P(3) – C(32)	100.09(12)	C(31) – P(3) – C(33)	98.85(11)
C(32) – P(3) – C(33)	99.91(12)	C(31) – P(3) – Pd	115.87(8)
C(32) – P(3) – Pd	116.29(8)	C(33) – P(3) – Pd	122.09(8)
C(13) – C(12) – C(11)	118.97(18)	C(13) – C(12) – P(1)	121.94(15)
C(11) – C(12) – P(1)	119.00(14)	C(16) – C(11) – C(12)	118.04(18)
C(16) – C(11) – C(1)	119.06(17)	C(12) – C(11) – C(1)	122.89(17)
C(14) – C(13) – C(12)	121.57(19)	C(14) – C(13) – H(13)	119.2
C(12) – C(13) – H(13)	119.2	C(15) – C(14) – C(13)	119.60(19)
C(15) – C(14) – H(14)	120.2	C(13) – C(14) – H(14)	120.2
C(14) – C(15) – C(16)	119.83(19)	C(14) – C(15) – H(15)	120.1
C(16) – C(15) – H(15)	120.1	C(15) – C(16) – C(11)	121.75(19)
C(15) – C(16) – H(16)	119.1	C(11) – C(16) – H(16)	119.1
C(23) – C(22) – C(21)	119.39(18)	C(23) – C(22) – P(2)	124.73(16)
C(21) – C(22) – P(2)	115.84(15)	C(26) – C(21) – C(22)	119.14(18)
C(26) – C(21) – C(1)	119.62(17)	C(22) – C(21) – C(1)	121.24(17)
C(24) – C(23) – C(22)	120.8(2)	C(24) – C(23) – H(23)	119.6
C(22) – C(23) – H(23)	119.6	C(25) – C(24) – C(23)	119.7(2)
C(25) – C(24) – H(24)	120.2	C(23) – C(24) – H(24)	120.2
C(24) – C(25) – C(26)	120.26(19)	C(24) – C(25) – H(25)	119.9
C(26) – C(25) – H(25)	119.9	C(25) – C(26) – C(21)	120.55(19)
C(25) – C(26) – H(26)	119.7	C(21) – C(26) – H(26)	119.7
P(3) – C(31) – H(31A)	109.5	P(3) – C(31) – H(31B)	109.5
H(31A) – C(31) – H(31B)	109.5	P(3) – C(31) – H(31C)	109.5
H(31A) – C(31) – H(31C)	109.5	H(31B) – C(31) – H(31C)	109.5

Continued on next page

Table S40. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
P(3) – C(32) – H(32A)	109.5	P(3) – C(32) – H(32B)	109.5
H(32A) – C(32) – H(32B)	109.5	P(3) – C(32) – H(32C)	109.5
H(32A) – C(32) – H(32C)	109.5	H(32B) – C(32) – H(32C)	109.5
P(3) – C(33) – H(33A)	109.5	P(3) – C(33) – H(33B)	109.5
H(33A) – C(33) – H(33B)	109.5	P(3) – C(33) – H(33C)	109.5
H(33A) – C(33) – H(33C)	109.5	H(33B) – C(33) – H(33C)	109.5
C(44) – C(41) – C(43)	110.01(16)	C(44) – C(41) – P(1)	118.77(14)
C(43) – C(41) – P(1)	108.81(13)	C(44) – C(41) – H(41)	106.2
C(43) – C(41) – H(41)	106.2	P(1) – C(41) – H(41)	106.2
C(46) – C(42) – C(45)	109.76(17)	C(46) – C(42) – P(1)	110.95(14)
C(45) – C(42) – P(1)	111.35(14)	C(46) – C(42) – H(42)	108.2
C(45) – C(42) – H(42)	108.2	P(1) – C(42) – H(42)	108.2
C(41) – C(43) – H(43A)	109.5	C(41) – C(43) – H(43B)	109.5
H(43A) – C(43) – H(43B)	109.5	C(41) – C(43) – H(43C)	109.5
H(43A) – C(43) – H(43C)	109.5	H(43B) – C(43) – H(43C)	109.5
C(41) – C(44) – H(44A)	109.5	C(41) – C(44) – H(44B)	109.5
H(44A) – C(44) – H(44B)	109.5	C(41) – C(44) – H(44C)	109.5
H(44A) – C(44) – H(44C)	109.5	H(44B) – C(44) – H(44C)	109.5
C(42) – C(45) – H(45A)	109.5	C(42) – C(45) – H(45B)	109.5
H(45A) – C(45) – H(45B)	109.5	C(42) – C(45) – H(45C)	109.5
H(45A) – C(45) – H(45C)	109.5	H(45B) – C(45) – H(45C)	109.5
C(42) – C(46) – H(46A)	109.5	C(42) – C(46) – H(46B)	109.5
H(46A) – C(46) – H(46B)	109.5	C(42) – C(46) – H(46C)	109.5
H(46A) – C(46) – H(46C)	109.5	H(46B) – C(46) – H(46C)	109.5
C(53) – C(51) – C(54)	109.90(18)	C(53) – C(51) – P(2)	112.61(14)
C(54) – C(51) – P(2)	110.14(14)	C(53) – C(51) – H(51)	108.0
C(54) – C(51) – H(51)	108.0	P(2) – C(51) – H(51)	108.0
C(55) – C(52) – C(56)	109.49(18)	C(55) – C(52) – P(2)	110.22(14)
C(56) – C(52) – P(2)	110.30(14)	C(55) – C(52) – H(52)	108.9
C(56) – C(52) – H(52)	108.9	P(2) – C(52) – H(52)	108.9
C(51) – C(53) – H(53A)	109.5	C(51) – C(53) – H(53B)	109.5
H(53A) – C(53) – H(53B)	109.5	C(51) – C(53) – H(53C)	109.5
H(53A) – C(53) – H(53C)	109.5	H(53B) – C(53) – H(53C)	109.5
C(51) – C(54) – H(54A)	109.5	C(51) – C(54) – H(54B)	109.5
H(54A) – C(54) – H(54B)	109.5	C(51) – C(54) – H(54C)	109.5
H(54A) – C(54) – H(54C)	109.5	H(54B) – C(54) – H(54C)	109.5
C(52) – C(55) – H(55A)	109.5	C(52) – C(55) – H(55B)	109.5
H(55A) – C(55) – H(55B)	109.5	C(52) – C(55) – H(55C)	109.5
H(55A) – C(55) – H(55C)	109.5	H(55B) – C(55) – H(55C)	109.5
C(52) – C(56) – H(56A)	109.5	C(52) – C(56) – H(56B)	109.5
H(56A) – C(56) – H(56B)	109.5	C(52) – C(56) – H(56C)	109.5
H(56A) – C(56) – H(56C)	109.5	H(56B) – C(56) – H(56C)	109.5

8.6 Crystal data for [PC(CH₃)HP]PdCl₂ (8)

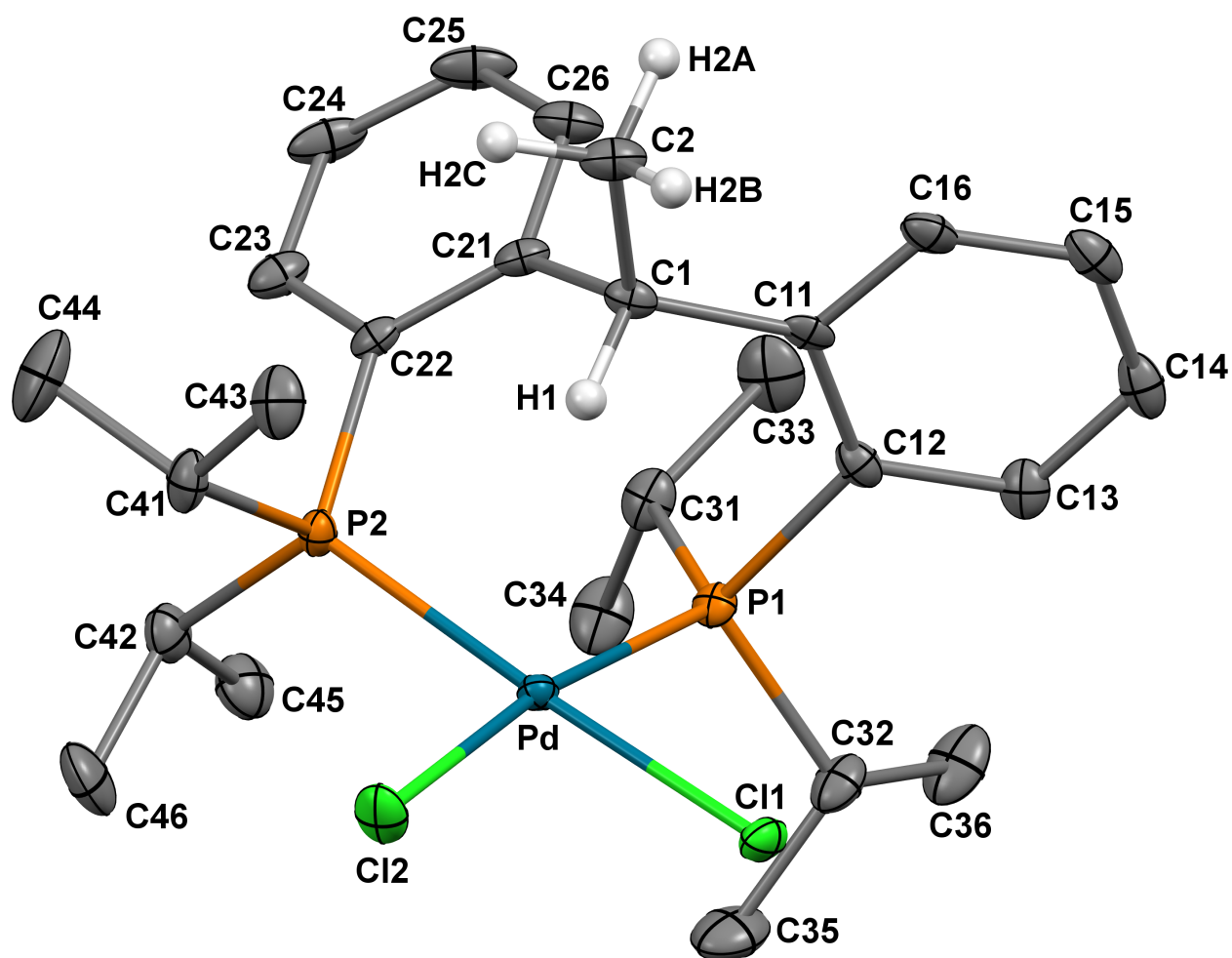


Figure S78. Thermal-ellipsoid representation of [PC(CH₃)HP]PdCl₂ (8) at 50% probability. Most hydrogen atoms were omitted for clarity.

Table S41. Crystal data and structure refinement for [PC(CH₃)HP]PdCl₂ (**8**).

Identification code:	cc251	
Empirical formula:	C ₂₆ H ₄₀ Cl ₂ P ₂ Pd	
Formula weight:	591.82	
Temperature:	120(2) K	
Wavelength:	0.71073 Å	
Crystal system:	Monoclinic	
Space group:	C2/c	
Unit cell dimensions:	$a = 13.0569(14)$ Å	$\alpha = 90^\circ$
	$b = 16.8080(14)$ Å	$\beta = 93.209(2)^\circ$
	$c = 31.261(3)$ Å	$\gamma = 90^\circ$
Volume:	6849.8(11) Å ³	
Z:	8	
Density (calculated):	1.148 g·cm ⁻³	
Absorption coefficient (μ):	0.801 mm ⁻¹	
F(000):	2448	
Crystal size:	0.11 × 0.09 × 0.08 mm ³	
θ range for data collection:	2.11 to 25.00°	
Index ranges:	−15 ≤ h ≤ 15, −19 ≤ k ≤ 19, −37 ≤ l ≤ 37	
Reflections collected:	38696	
Independent reflections:	6002 [R _{int} = 0.0536]	
Completeness to θ = 25.00°:	99.4 %	
Absorption correction:	Semi-empirical from equivalents	
Max. and min. transmission:	0.7455 and 0.6774	
Refinement method:	Full-matrix least-squares on F ²	
Data / restraints / parameters:	6002 / 0 / 289	
Goodness-of-fit on F ² :	1.051	
Final R indices [I > 2σ(I)]:	R ₁ = 0.0372, wR ₂ = 0.0751	
R indices (all data):	R ₁ = 0.0457, wR ₂ = 0.0779	
Largest diff. peak and hole:	0.596 and −0.503 e [−] ·Å ^{−3}	

Table S42. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for [PC(CH₃)HP]PdCl₂ (**8**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

atom	x	y	z	U(eq)
Pd	0.40321(2)	0.33460(2)	0.89095(1)	0.016(1)
C(1)	0.4436(2)	0.20985(19)	0.97301(10)	0.019(1)
Cl(1)	0.22633(6)	0.36860(5)	0.88942(3)	0.024(1)
P(1)	0.34981(6)	0.20549(5)	0.87347(3)	0.019(1)
C(2)	0.4730(3)	0.2126(2)	1.02138(11)	0.028(1)
Cl(2)	0.43656(7)	0.47011(5)	0.90297(3)	0.033(1)
P(2)	0.57394(6)	0.31313(5)	0.90471(3)	0.018(1)
C(12)	0.2913(2)	0.1660(2)	0.92139(10)	0.021(1)
C(11)	0.3403(2)	0.16972(19)	0.96279(10)	0.018(1)
C(13)	0.1941(3)	0.1325(2)	0.91653(12)	0.025(1)
C(14)	0.1457(3)	0.0990(2)	0.95070(13)	0.030(1)
C(15)	0.1935(3)	0.1008(2)	0.99046(12)	0.029(1)
C(16)	0.2885(3)	0.1367(2)	0.99630(12)	0.025(1)
C(21)	0.5330(2)	0.1720(2)	0.95103(10)	0.020(1)
C(22)	0.6007(2)	0.2127(2)	0.92514(10)	0.020(1)
C(23)	0.6866(3)	0.1721(2)	0.91099(11)	0.028(1)
C(24)	0.7032(3)	0.0922(2)	0.92015(12)	0.035(1)
C(25)	0.6343(3)	0.0518(2)	0.94356(12)	0.038(1)
C(26)	0.5517(3)	0.0911(2)	0.95948(12)	0.031(1)
C(31)	0.4364(3)	0.1245(2)	0.85593(11)	0.027(1)
C(32)	0.2437(3)	0.2123(2)	0.83131(11)	0.031(1)
C(33)	0.4059(3)	0.0416(2)	0.87072(15)	0.042(1)
C(34)	0.4513(3)	0.1229(3)	0.80729(12)	0.041(1)
C(35)	0.2710(3)	0.2704(3)	0.79609(13)	0.048(1)
C(36)	0.1992(3)	0.1350(3)	0.81069(14)	0.047(1)
C(41)	0.6389(3)	0.3820(2)	0.94404(12)	0.028(1)
C(42)	0.6503(3)	0.3286(2)	0.85717(12)	0.030(1)
C(43)	0.5898(3)	0.3863(2)	0.98697(13)	0.036(1)
C(44)	0.7534(3)	0.3639(3)	0.95072(16)	0.053(1)
C(45)	0.6133(3)	0.2771(3)	0.81971(13)	0.038(1)
C(46)	0.6492(3)	0.4162(3)	0.84395(15)	0.045(1)
H(1)	0.4376	0.2661	0.9627	0.022
H(2A)	0.4773	0.1582	1.0327	0.042
H(2B)	0.4208	0.2423	1.0361	0.042
H(2C)	0.5396	0.2389	1.0262	0.042
H(13)	0.1596	0.1323	0.8890	0.030
H(14)	0.0799	0.0752	0.9463	0.036
H(15)	0.1619	0.0776	1.0141	0.034
H(16)	0.3199	0.1390	1.0244	0.030

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Table S42. – continued from previous page

atom	x	y	x	U(eq)
H(23)	0.7344	0.2000	0.8948	0.033
H(24)	0.7617	0.0657	0.9103	0.042
H(25)	0.6434	−0.0035	0.9489	0.045
H(26)	0.5063	0.0626	0.9766	0.037
H(31)	0.5055	0.1356	0.8701	0.033
H(32)	0.1853	0.2376	0.8456	0.037
H(33A)	0.3414	0.0257	0.8555	0.063
H(33B)	0.3969	0.0424	0.9016	0.063
H(33C)	0.4598	0.0035	0.8645	0.063
H(34A)	0.3907	0.0994	0.7923	0.061
H(34B)	0.5119	0.0910	0.8017	0.061
H(34C)	0.4609	0.1773	0.7970	0.061
H(35A)	0.3250	0.2473	0.7794	0.071
H(35B)	0.2954	0.3205	0.8091	0.071
H(35C)	0.2101	0.2807	0.7772	0.071
H(36A)	0.1284	0.1444	0.7999	0.070
H(36B)	0.2004	0.0926	0.8322	0.070
H(36C)	0.2407	0.1191	0.7869	0.070
H(41)	0.6333	0.4365	0.9312	0.034
H(42)	0.7229	0.3135	0.8652	0.036
H(43A)	0.5156	0.3939	0.9822	0.054
H(43B)	0.6190	0.4310	1.0036	0.054
H(43C)	0.6031	0.3366	1.0028	0.054
H(44A)	0.7854	0.3663	0.9231	0.079
H(44B)	0.7626	0.3105	0.9630	0.079
H(44C)	0.7856	0.4032	0.9703	0.079
H(45A)	0.5437	0.2933	0.8099	0.058
H(45B)	0.6127	0.2212	0.8287	0.058
H(45C)	0.6594	0.2835	0.7963	0.058
H(46A)	0.6847	0.4224	0.8174	0.067
H(46B)	0.6840	0.4481	0.8666	0.067
H(46C)	0.5781	0.4344	0.8394	0.067

Table S43. Anisotropic displacement parameters ($\text{\AA}^2$) for [PC(CH₃)HP]PdCl₂ (**8**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$.

atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Pd	0.0157(1)	0.0149(1)	0.0176(1)	0.0023(1)	0.0019(1)	0.0028(1)
C(1)	0.0270(18)	0.0130(17)	0.0159(17)	-0.0017(13)	0.0024(13)	0.0041(13)
Cl(1)	0.0175(4)	0.0299(5)	0.0260(4)	0.0048(4)	0.0022(3)	0.0076(3)
P(1)	0.0197(4)	0.0217(5)	0.0142(4)	-0.0034(4)	-0.0001(3)	-0.0011(3)
C(2)	0.038(2)	0.025(2)	0.0199(18)	0.0002(15)	-0.0021(15)	0.0108(16)
Cl(2)	0.0303(5)	0.0142(4)	0.0546(6)	0.0013(4)	0.0082(4)	0.0024(3)
P(2)	0.0145(4)	0.0176(5)	0.0230(5)	-0.0019(3)	0.0026(3)	-0.0001(3)
C(12)	0.0266(17)	0.0147(17)	0.0233(17)	-0.0004(15)	0.0066(14)	-0.0004(14)
C(11)	0.0268(17)	0.0077(16)	0.0206(17)	0.0017(14)	0.0042(13)	0.0068(14)
C(13)	0.0266(19)	0.0198(19)	0.030(2)	-0.0093(15)	0.0050(15)	-0.0013(15)
C(14)	0.032(2)	0.0168(19)	0.041(2)	-0.0073(16)	0.0157(18)	-0.0044(15)
C(15)	0.037(2)	0.0169(19)	0.034(2)	0.0023(16)	0.0181(17)	0.0047(15)
C(16)	0.0315(19)	0.0167(18)	0.0266(19)	0.0055(15)	0.0053(15)	0.0069(15)
C(21)	0.0234(17)	0.0202(18)	0.0163(16)	-0.0012(14)	-0.0045(13)	0.0075(14)
C(22)	0.0177(16)	0.0224(19)	0.0185(17)	-0.0042(14)	-0.0053(13)	0.0041(14)
C(23)	0.0276(18)	0.036(2)	0.0200(18)	-0.0032(16)	-0.0029(14)	0.0099(17)
C(24)	0.041(2)	0.041(3)	0.023(2)	-0.0052(17)	-0.0014(17)	0.0274(19)
C(25)	0.060(3)	0.026(2)	0.027(2)	-0.0012(17)	-0.0025(19)	0.0245(19)
C(26)	0.045(2)	0.024(2)	0.0227(19)	0.0046(16)	0.0004(17)	0.0094(17)
C(31)	0.0270(19)	0.027(2)	0.028(2)	-0.0134(16)	0.0012(15)	0.0003(15)
C(32)	0.0252(19)	0.047(3)	0.0201(19)	-0.0084(17)	-0.0036(15)	0.0007(17)
C(33)	0.050(3)	0.023(2)	0.055(3)	-0.016(2)	0.011(2)	-0.0005(18)
C(34)	0.038(2)	0.058(3)	0.027(2)	-0.022(2)	0.0052(17)	-0.003(2)
C(35)	0.051(3)	0.070(3)	0.021(2)	0.006(2)	-0.0038(18)	0.011(2)
C(36)	0.038(2)	0.068(3)	0.033(2)	-0.026(2)	-0.0050(18)	-0.002(2)
C(41)	0.0199(18)	0.024(2)	0.040(2)	-0.0087(17)	0.0023(15)	-0.0051(15)
C(42)	0.0240(18)	0.034(2)	0.032(2)	0.0005(17)	0.0098(15)	-0.0003(16)
C(43)	0.036(2)	0.034(2)	0.038(2)	-0.0156(18)	0.0046(18)	-0.0092(17)
C(44)	0.022(2)	0.070(3)	0.065(3)	-0.030(3)	-0.004(2)	-0.004(2)
C(45)	0.041(2)	0.045(3)	0.031(2)	0.0004(19)	0.0104(18)	-0.0046(19)
C(46)	0.046(3)	0.039(3)	0.052(3)	0.007(2)	0.026(2)	-0.010(2)

Table S44. Distances [Å] for [PC(CH₃)HP]PdCl₂ (**8**).

atom – atom	distance	atom – atom	distance
Pd – P(2)	2.2754(9)	Pd – P(1)	2.3348(9)
Pd – Cl(2)	2.3452(9)	Pd – Cl(1)	2.3771(8)
C(1) – C(11)	1.526(5)	C(1) – C(21)	1.527(4)
C(1) – C(2)	1.540(5)	C(1) – H(1)	1.0000
P(1) – C(12)	1.843(3)	P(1) – C(32)	1.862(4)
P(1) – C(31)	1.871(3)	C(2) – H(2A)	0.9800
C(2) – H(2B)	0.9800	C(2) – H(2C)	0.9800
P(2) – C(22)	1.831(3)	P(2) – C(42)	1.854(3)
P(2) – C(41)	1.858(4)	C(12) – C(13)	1.390(5)
C(12) – C(11)	1.412(5)	C(11) – C(16)	1.393(5)
C(13) – C(14)	1.390(5)	C(13) – H(13)	0.9500
C(14) – C(15)	1.360(6)	C(14) – H(14)	0.9500
C(15) – C(16)	1.382(5)	C(15) – H(15)	0.9500
C(16) – H(16)	0.9500	C(21) – C(26)	1.403(5)
C(21) – C(22)	1.409(5)	C(22) – C(23)	1.404(5)
C(23) – C(24)	1.389(5)	C(23) – H(23)	0.9500
C(24) – C(25)	1.371(6)	C(24) – H(24)	0.9500
C(25) – C(26)	1.381(5)	C(25) – H(25)	0.9500
C(26) – H(26)	0.9500	C(31) – C(33)	1.528(5)
C(31) – C(34)	1.544(5)	C(31) – H(31)	1.0000
C(32) – C(35)	1.529(6)	C(32) – C(36)	1.549(6)
C(32) – H(32)	1.0000	C(33) – H(33A)	0.9800
C(33) – H(33B)	0.9800	C(33) – H(33C)	0.9800
C(34) – H(34A)	0.9800	C(34) – H(34B)	0.9800
C(34) – H(34C)	0.9800	C(35) – H(35A)	0.9800
C(35) – H(35B)	0.9800	C(35) – H(35C)	0.9800
C(36) – H(36A)	0.9800	C(36) – H(36B)	0.9800
C(36) – H(36C)	0.9800	C(41) – C(43)	1.521(5)
C(41) – C(44)	1.529(5)	C(41) – H(41)	1.0000
C(42) – C(45)	1.513(5)	C(42) – C(46)	1.530(6)
C(42) – H(42)	1.0000	C(43) – H(43A)	0.9800
C(43) – H(43B)	0.9800	C(43) – H(43C)	0.9800
C(44) – H(44A)	0.9800	C(44) – H(44B)	0.9800
C(44) – H(44C)	0.9800	C(45) – H(45A)	0.9800
C(45) – H(45B)	0.9800	C(45) – H(45C)	0.9800
C(46) – H(46A)	0.9800	C(46) – H(46B)	0.9800
C(46) – H(46C)	0.9800		

Table S45. Angles [°] for [PC(CH₃)HP]PdCl₂ (**8**).

atom – atom – atom	angle	atom – atom – atom	angle
P(2) – Pd – P(1)	99.98(3)	P(2) – Pd – Cl(2)	87.28(3)
P(1) – Pd – Cl(2)	172.10(3)	P(2) – Pd – Cl(1)	169.23(3)
P(1) – Pd – Cl(1)	86.66(3)	Cl(2) – Pd – Cl(1)	86.63(3)
C(11) – C(1) – C(21)	114.3(3)	C(11) – C(1) – C(2)	112.8(3)
C(21) – C(1) – C(2)	107.4(3)	C(11) – C(1) – H(1)	107.3
C(21) – C(1) – H(1)	107.3	C(2) – C(1) – H(1)	107.3
C(12) – P(1) – C(32)	105.75(16)	C(12) – P(1) – C(31)	105.16(16)
C(32) – P(1) – C(31)	105.98(17)	C(12) – P(1) – Pd	106.04(11)
C(32) – P(1) – Pd	108.01(13)	C(31) – P(1) – Pd	124.55(12)
C(1) – C(2) – H(2A)	109.5	C(1) – C(2) – H(2B)	109.5
H(2A) – C(2) – H(2B)	109.5	C(1) – C(2) – H(2C)	109.5
H(2A) – C(2) – H(2C)	109.5	H(2B) – C(2) – H(2C)	109.5
C(22) – P(2) – C(42)	107.93(16)	C(22) – P(2) – C(41)	105.80(17)
C(42) – P(2) – C(41)	101.38(17)	C(22) – P(2) – Pd	112.22(11)
C(42) – P(2) – Pd	113.04(12)	C(41) – P(2) – Pd	115.60(11)
C(13) – C(12) – C(11)	118.8(3)	C(13) – C(12) – P(1)	118.4(3)
C(11) – C(12) – P(1)	122.8(2)	C(16) – C(11) – C(12)	117.2(3)
C(16) – C(11) – C(1)	118.6(3)	C(12) – C(11) – C(1)	124.1(3)
C(14) – C(13) – C(12)	122.1(4)	C(14) – C(13) – H(13)	118.9
C(12) – C(13) – H(13)	118.9	C(15) – C(14) – C(13)	119.2(3)
C(15) – C(14) – H(14)	120.4	C(13) – C(14) – H(14)	120.4
C(14) – C(15) – C(16)	119.6(3)	C(14) – C(15) – H(15)	120.2
C(16) – C(15) – H(15)	120.2	C(15) – C(16) – C(11)	123.0(3)
C(15) – C(16) – H(16)	118.5	C(11) – C(16) – H(16)	118.5
C(26) – C(21) – C(22)	118.1(3)	C(26) – C(21) – C(1)	116.6(3)
C(22) – C(21) – C(1)	125.2(3)	C(23) – C(22) – C(21)	118.8(3)
C(23) – C(22) – P(2)	118.6(3)	C(21) – C(22) – P(2)	122.3(2)
C(24) – C(23) – C(22)	121.6(4)	C(24) – C(23) – H(23)	119.2
C(22) – C(23) – H(23)	119.2	C(25) – C(24) – C(23)	119.3(3)
C(25) – C(24) – H(24)	120.4	C(23) – C(24) – H(24)	120.4
C(24) – C(25) – C(26)	120.3(4)	C(24) – C(25) – H(25)	119.8
C(26) – C(25) – H(25)	119.8	C(25) – C(26) – C(21)	121.8(4)
C(25) – C(26) – H(26)	119.1	C(21) – C(26) – H(26)	119.1
C(33) – C(31) – C(34)	109.4(3)	C(33) – C(31) – P(1)	113.7(3)
C(34) – C(31) – P(1)	114.4(3)	C(33) – C(31) – H(31)	106.2
C(34) – C(31) – H(31)	106.2	P(1) – C(31) – H(31)	106.2
C(35) – C(32) – C(36)	109.5(3)	C(35) – C(32) – P(1)	110.8(3)
C(36) – C(32) – P(1)	119.3(3)	C(35) – C(32) – H(32)	105.4
C(36) – C(32) – H(32)	105.4	P(1) – C(32) – H(32)	105.4
C(31) – C(33) – H(33A)	109.5	C(31) – C(33) – H(33B)	109.5
H(33A) – C(33) – H(33B)	109.5	C(31) – C(33) – H(33C)	109.5

Continued on next page

Table S45. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
H(33A) – C(33) – H(33C)	109.5	H(33B) – C(33) – H(33C)	109.5
C(31) – C(34) – H(34A)	109.5	C(31) – C(34) – H(34B)	109.5
H(34A) – C(34) – H(34B)	109.5	C(31) – C(34) – H(34C)	109.5
H(34A) – C(34) – H(34C)	109.5	H(34B) – C(34) – H(34C)	109.5
C(32) – C(35) – H(35A)	109.5	C(32) – C(35) – H(35B)	109.5
H(35A) – C(35) – H(35B)	109.5	C(32) – C(35) – H(35C)	109.5
H(35A) – C(35) – H(35C)	109.5	H(35B) – C(35) – H(35C)	109.5
C(32) – C(36) – H(36A)	109.5	C(32) – C(36) – H(36B)	109.5
H(36A) – C(36) – H(36B)	109.5	C(32) – C(36) – H(36C)	109.5
H(36A) – C(36) – H(36C)	109.5	H(36B) – C(36) – H(36C)	109.5
C(43) – C(41) – C(44)	110.2(3)	C(43) – C(41) – P(2)	114.5(2)
C(44) – C(41) – P(2)	111.9(3)	C(43) – C(41) – H(41)	106.6
C(44) – C(41) – H(41)	106.6	P(2) – C(41) – H(41)	106.6
C(45) – C(42) – C(46)	110.1(3)	C(45) – C(42) – P(2)	112.2(3)
C(46) – C(42) – P(2)	110.7(3)	C(45) – C(42) – H(42)	107.9
C(46) – C(42) – H(42)	107.9	P(2) – C(42) – H(42)	107.9
C(41) – C(43) – H(43A)	109.5	C(41) – C(43) – H(43B)	109.5
H(43A) – C(43) – H(43B)	109.5	C(41) – C(43) – H(43C)	109.5
H(43A) – C(43) – H(43C)	109.5	H(43B) – C(43) – H(43C)	109.5
C(41) – C(44) – H(44A)	109.5	C(41) – C(44) – H(44B)	109.5
H(44A) – C(44) – H(44B)	109.5	C(41) – C(44) – H(44C)	109.5
H(44A) – C(44) – H(44C)	109.5	H(44B) – C(44) – H(44C)	109.5
C(42) – C(45) – H(45A)	109.5	C(42) – C(45) – H(45B)	109.5
H(45A) – C(45) – H(45B)	109.5	C(42) – C(45) – H(45C)	109.5
H(45A) – C(45) – H(45C)	109.5	H(45B) – C(45) – H(45C)	109.5
C(42) – C(46) – H(46A)	109.5	C(42) – C(46) – H(46B)	109.5
H(46A) – C(46) – H(46B)	109.5	C(42) – C(46) – H(46C)	109.5
H(46A) – C(46) – H(46C)	109.5	H(46B) – C(46) – H(46C)	109.5

8.7 Crystal data for [PC(CH₃)P]PdCl (9)

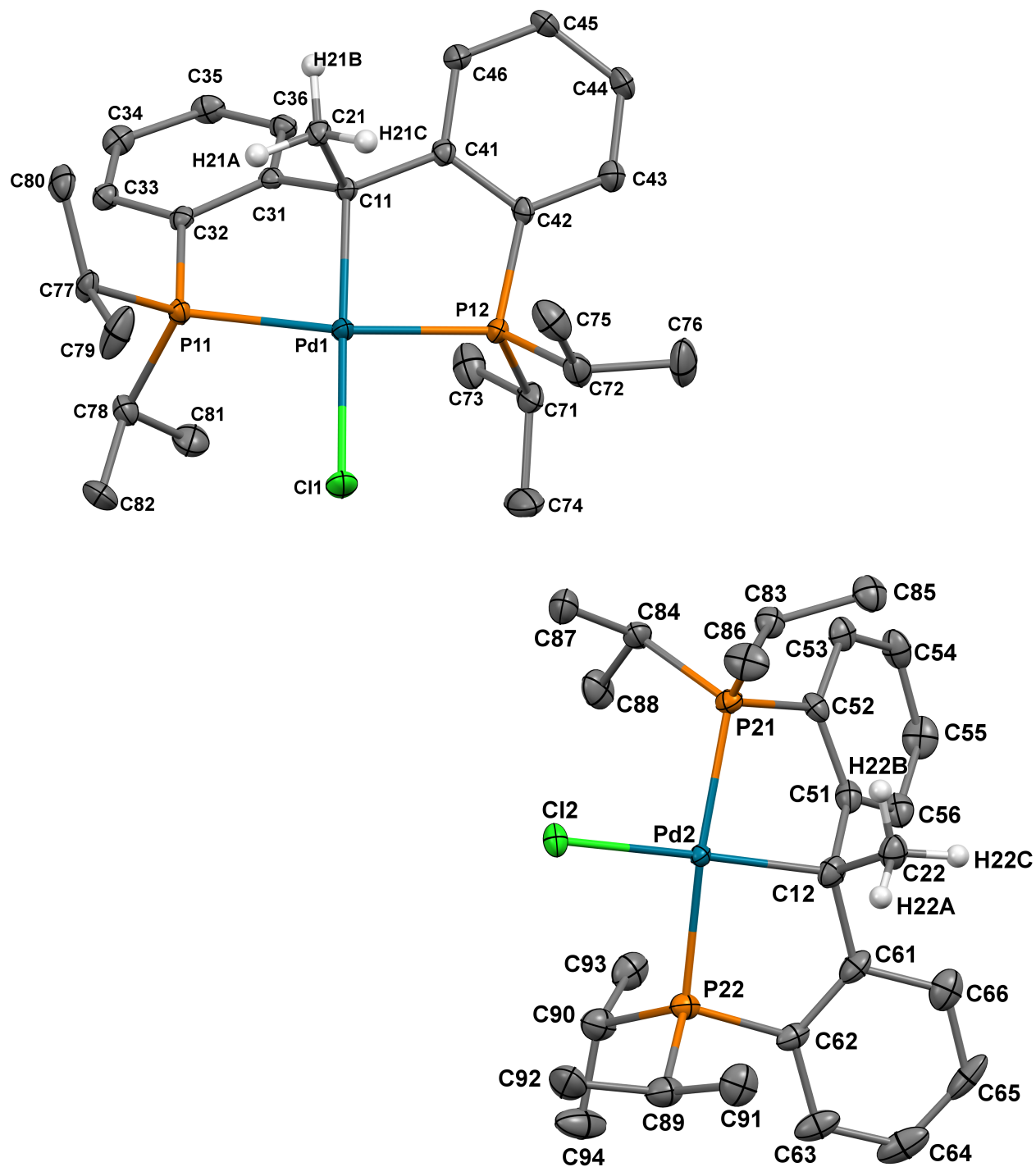


Figure S79. Thermal-ellipsoid representation (50% probability) of the two independent molecules of [PC(CH₃)P]PdCl (9). Most hydrogen atoms were omitted for clarity.

Table S46. Crystal data and structure refinement for [PC(CH₃)P]PdCl (**9**).

Identification code:	cc254	
Empirical formula:	C ₂₆ H ₃₉ ClP ₂ Pd	
Formula weight:	555.36	
Temperature:	120(2) K	
Wavelength:	0.71073 Å	
Crystal system:	Monoclinic	
Space group:	<i>P</i> 2 ₁ / <i>c</i>	
Unit cell dimensions:	<i>a</i> = 11.2685(8) Å	$\alpha = 90^\circ$
	<i>b</i> = 20.7303(14) Å	$\beta = 99.2340(13)^\circ$
	<i>c</i> = 23.1605(16) Å	$\gamma = 90^\circ$
Volume:	5340.2(6) Å ³	
Z:	8	
Density (calculated):	1.382 g·cm ⁻³	
Absorption coefficient (μ):	0.926 mm ⁻¹	
F(000):	2304	
Crystal size:	0.10 × 0.09 × 0.08 mm ³	
θ range for data collection:	1.33 to 25.00°	
Index ranges:	$-13 \leq h \leq 13, -24 \leq k \leq 24, -27 \leq l \leq 27$	
Reflections collected:	62725	
Independent reflections:	9411 [<i>R</i> _{int} = 0.0607]	
Completeness to $\theta = 25.00^\circ$:	100.0 %	
Absorption correction:	Semi-empirical from equivalents	
Max. and min. transmission:	0.7454 and 0.7137	
Refinement method:	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters:	9411 / 0 / 569	
Goodness-of-fit on <i>F</i> ² :	1.108	
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]:	<i>R</i> ₁ = 0.0419, <i>wR</i> ₂ = 0.0827	
<i>R</i> indices (all data):	<i>R</i> ₁ = 0.0557, <i>wR</i> ₂ = 0.0867	
Largest diff. peak and hole:	0.851 and -0.547 e ⁻ ·Å ⁻³	

Table S47. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for [PC(CH₃)P]PdCl (**9**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

atom	x	y	z	U(eq)
C(12)	0.5034(4)	0.2251(2)	0.47734(19)	0.030(1)
C(22)	0.6189(4)	0.1951(2)	0.4586(2)	0.033(1)
Pd(3)	0.439(2)	0.1817(7)	0.5558(4)	0.030(2)
Cl(2)	0.45948(9)	0.09518(5)	0.62723(5)	0.027(1)
Pd(2)	0.4786(2)	0.16822(9)	0.54898(5)	0.015(1)
P(22)	0.30408(10)	0.13795(5)	0.49142(5)	0.025(1)
P(21)	0.62632(10)	0.23339(5)	0.60021(5)	0.022(1)
Pd(1)	0.08191(3)	0.51140(1)	0.30826(1)	0.018(1)
Cl(1)	0.09327(10)	0.62588(5)	0.29280(5)	0.033(1)
C(11)	0.0853(3)	0.41436(18)	0.33183(17)	0.018(1)
P(11)	0.22457(9)	0.47953(5)	0.25065(5)	0.019(1)
P(12)	-0.09210(9)	0.51448(5)	0.34486(5)	0.021(1)
C(21)	0.2024(3)	0.4071(2)	0.37683(18)	0.023(1)
C(31)	0.0956(3)	0.37538(18)	0.27703(17)	0.018(1)
C(32)	0.1788(3)	0.39557(18)	0.24116(17)	0.019(1)
C(33)	0.2088(3)	0.35674(19)	0.19694(17)	0.022(1)
C(34)	0.1491(4)	0.2988(2)	0.18408(19)	0.026(1)
C(35)	0.0571(4)	0.2815(2)	0.21410(19)	0.027(1)
C(36)	0.0314(3)	0.31892(19)	0.26011(18)	0.023(1)
C(41)	-0.0164(3)	0.39225(19)	0.36368(17)	0.021(1)
C(43)	-0.2004(4)	0.4140(2)	0.40293(19)	0.029(1)
C(42)	-0.1071(3)	0.43467(19)	0.37406(18)	0.021(1)
C(44)	-0.2029(4)	0.3516(2)	0.4228(2)	0.033(1)
C(45)	-0.1115(4)	0.3094(2)	0.4147(2)	0.031(1)
C(46)	-0.0195(4)	0.3295(2)	0.38596(19)	0.027(1)
C(51)	0.5321(4)	0.2951(2)	0.49934(19)	0.029(1)
C(52)	0.6091(4)	0.3044(2)	0.55354(19)	0.025(1)
C(54)	0.6182(4)	0.4188(2)	0.5359(2)	0.036(1)
C(55)	0.5330(4)	0.4109(2)	0.4863(2)	0.039(1)
C(56)	0.4915(4)	0.3503(2)	0.4676(2)	0.035(1)
C(61)	0.4043(4)	0.2213(2)	0.42489(19)	0.033(1)
C(62)	0.3043(4)	0.1834(2)	0.42524(18)	0.027(1)
C(63)	0.2183(5)	0.1761(2)	0.3751(2)	0.041(1)
C(64)	0.2295(6)	0.2080(2)	0.3247(2)	0.053(2)
C(65)	0.3308(6)	0.2443(3)	0.3228(2)	0.048(2)
C(66)	0.4180(5)	0.2510(2)	0.3708(2)	0.041(1)
C(71)	-0.2309(4)	0.5222(2)	0.2908(2)	0.032(1)
C(72)	-0.0998(4)	0.5764(2)	0.4014(2)	0.036(1)
C(73)	-0.2332(4)	0.4705(3)	0.2438(2)	0.045(1)

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Table S47. – continued from previous page

atom	x	y	x	U(eq)
C(74)	−0.2441(5)	0.5891(3)	0.2650(3)	0.053(2)
C(75)	0.0132(5)	0.5743(3)	0.4457(2)	0.046(1)
C(76)	−0.2127(5)	0.5755(3)	0.4309(2)	0.051(2)
C(77)	0.3923(3)	0.48509(19)	0.2656(2)	0.025(1)
C(78)	0.1884(4)	0.5105(2)	0.17456(19)	0.029(1)
C(79)	0.4261(4)	0.5456(2)	0.3015(3)	0.051(2)
C(80)	0.4574(4)	0.4258(2)	0.2922(2)	0.033(1)
C(81)	0.0529(4)	0.5082(2)	0.1536(2)	0.041(1)
C(82)	0.2363(5)	0.5785(2)	0.1673(2)	0.043(1)
C(83)	0.7894(4)	0.2129(2)	0.6167(2)	0.031(1)
C(84)	0.5950(4)	0.2647(2)	0.67091(19)	0.029(1)
C(85)	0.8701(4)	0.2496(2)	0.5808(2)	0.039(1)
C(86)	0.8054(4)	0.1399(2)	0.6135(2)	0.045(1)
C(87)	0.6253(5)	0.2170(2)	0.7204(2)	0.040(1)
C(88)	0.4637(4)	0.2865(2)	0.6648(2)	0.041(1)
C(89)	0.2750(4)	0.0542(2)	0.4674(2)	0.040(1)
C(90)	0.1713(4)	0.1658(2)	0.5228(2)	0.038(1)
C(91)	0.3755(5)	0.0323(2)	0.4365(2)	0.046(1)
C(92)	0.2568(5)	0.0096(2)	0.5187(2)	0.050(1)
C(93)	0.1794(4)	0.2400(2)	0.5280(2)	0.041(1)
C(94)	0.0513(4)	0.1451(3)	0.4886(3)	0.060(2)
C(53)	0.6552(4)	0.3650(2)	0.5706(2)	0.028(1)
H(22A)	0.6031	0.1501	0.4468	0.050
H(22B)	0.6852	0.1968	0.4915	0.050
H(22C)	0.6406	0.2196	0.4256	0.050
H(21A)	0.2710	0.4222	0.3593	0.034
H(21B)	0.2141	0.3617	0.3879	0.034
H(21C)	0.1960	0.4330	0.4116	0.034
H(33)	0.2700	0.3698	0.1756	0.026
H(34)	0.1711	0.2711	0.1549	0.032
H(35)	0.0112	0.2438	0.2031	0.032
H(36)	−0.0312	0.3059	0.2806	0.028
H(43)	−0.2622	0.4433	0.4088	0.034
H(44)	−0.2668	0.3375	0.4420	0.039
H(45)	−0.1121	0.2664	0.4289	0.037
H(46)	0.0430	0.3001	0.3812	0.033
H(54)	0.6512	0.4601	0.5462	0.043
H(55)	0.5023	0.4478	0.4646	0.047
H(56)	0.4346	0.3462	0.4328	0.042
H(63)	0.1513	0.1485	0.3760	0.050
H(64)	0.1683	0.2052	0.2914	0.063
H(65)	0.3405	0.2653	0.2874	0.057

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Table S47. – continued from previous page

atom	x	y	x	U(eq)
H(66)	0.4882	0.2755	0.3681	0.050
H(71)	−0.3008	0.5143	0.3116	0.038
H(72)	−0.0998	0.6190	0.3812	0.043
H(73A)	−0.3102	0.4723	0.2173	0.067
H(73B)	−0.2234	0.4279	0.2623	0.067
H(73C)	−0.1674	0.4782	0.2216	0.067
H(74A)	−0.1748	0.5987	0.2458	0.080
H(74B)	−0.2483	0.6206	0.2961	0.080
H(74C)	−0.3180	0.5914	0.2362	0.080
H(75A)	0.0827	0.5829	0.4264	0.069
H(75B)	0.0216	0.5316	0.4640	0.069
H(75C)	0.0089	0.6071	0.4758	0.069
H(76A)	−0.2845	0.5723	0.4009	0.077
H(76B)	−0.2162	0.6152	0.4534	0.077
H(76C)	−0.2093	0.5382	0.4572	0.077
H(77)	0.4191	0.4920	0.2269	0.031
H(78)	0.2272	0.4811	0.1489	0.035
H(79A)	0.5113	0.5554	0.3018	0.077
H(79B)	0.4118	0.5387	0.3417	0.077
H(79C)	0.3770	0.5819	0.2842	0.077
H(80A)	0.4296	0.3879	0.2685	0.049
H(80B)	0.4406	0.4198	0.3321	0.049
H(80C)	0.5441	0.4312	0.2932	0.049
H(81A)	0.0357	0.5202	0.1122	0.061
H(81B)	0.0127	0.5385	0.1766	0.061
H(81C)	0.0233	0.4644	0.1586	0.061
H(82A)	0.2108	0.5930	0.1270	0.065
H(82B)	0.3243	0.5781	0.1761	0.065
H(82C)	0.2045	0.6079	0.1942	0.065
H(83)	0.8167	0.2252	0.6584	0.037
H(84)	0.6467	0.3037	0.6809	0.034
H(85A)	0.8393	0.2443	0.5390	0.059
H(85B)	0.9521	0.2324	0.5894	0.059
H(85C)	0.8707	0.2955	0.5910	0.059
H(86A)	0.7859	0.1258	0.5727	0.067
H(86B)	0.7517	0.1185	0.6369	0.067
H(86C)	0.8890	0.1287	0.6289	0.067
H(87A)	0.5830	0.1763	0.7099	0.061
H(87B)	0.6003	0.2344	0.7559	0.061
H(87C)	0.7122	0.2092	0.7275	0.061
H(88A)	0.4472	0.3184	0.6333	0.062
H(88B)	0.4494	0.3059	0.7017	0.062

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Table S47. – continued from previous page

atom	x	y	x	U(eq)
H(88C)	0.4107	0.2492	0.6556	0.062
H(89)	0.1991	0.0537	0.4384	0.048
H(90)	0.1778	0.1477	0.5632	0.045
H(91A)	0.3640	−0.0132	0.4257	0.070
H(91B)	0.4525	0.0377	0.4625	0.070
H(91C)	0.3754	0.0583	0.4011	0.070
H(92A)	0.2416	−0.0346	0.5042	0.075
H(92B)	0.1879	0.0247	0.5360	0.075
H(92C)	0.3292	0.0102	0.5484	0.075
H(93A)	0.1683	0.2591	0.4887	0.062
H(93B)	0.2585	0.2522	0.5492	0.062
H(93C)	0.1166	0.2558	0.5491	0.062
H(94A)	0.0412	0.1638	0.4493	0.089
H(94B)	−0.0136	0.1601	0.5088	0.089
H(94C)	0.0486	0.0980	0.4857	0.089
H(53)	0.7115	0.3697	0.6055	0.034

Table S48. Anisotropic displacement parameters ($\text{\AA}^2$) for [PC(CH₃)P]PdCl (**9**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$.

atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C(12)	0.031(2)	0.034(3)	0.025(2)	-0.002(2)	0.008(2)	0.005(2)
C(22)	0.037(3)	0.034(3)	0.031(3)	-0.002(2)	0.013(2)	0.002(2)
Pd(3)	0.031(5)	0.034(3)	0.025(2)	0.0032(17)	0.007(3)	0.009(4)
Cl(2)	0.0274(5)	0.0285(6)	0.0283(6)	0.0067(5)	0.0107(5)	0.0016(4)
Pd(2)	0.0137(6)	0.0186(4)	0.0144(3)	-0.0005(2)	0.0028(2)	0.0017(3)
P(22)	0.0200(5)	0.0283(6)	0.0270(6)	-0.0063(5)	0.0033(5)	0.0023(5)
P(21)	0.0233(6)	0.0228(6)	0.0195(6)	0.0005(4)	-0.0002(5)	0.0005(4)
Pd(1)	0.0165(2)	0.0152(2)	0.0240(2)	0.0013(1)	0.0072(1)	0.0004(1)
Cl(1)	0.0393(6)	0.0164(5)	0.0468(7)	0.0027(5)	0.0177(5)	0.0020(4)
C(11)	0.0129(19)	0.018(2)	0.024(2)	0.0034(17)	0.0048(17)	0.0002(15)
P(11)	0.0182(5)	0.0178(5)	0.0229(6)	-0.0002(4)	0.0078(4)	-0.0013(4)
P(12)	0.0174(5)	0.0200(5)	0.0257(6)	0.0035(5)	0.0076(4)	0.0039(4)
C(21)	0.018(2)	0.027(2)	0.023(2)	0.0025(18)	0.0034(17)	0.0042(17)
C(31)	0.0159(19)	0.018(2)	0.019(2)	0.0054(16)	0.0011(16)	0.0018(16)
C(32)	0.0137(19)	0.020(2)	0.022(2)	0.0016(17)	0.0011(16)	0.0021(16)
C(33)	0.020(2)	0.022(2)	0.023(2)	-0.0007(18)	0.0029(17)	0.0002(17)
C(34)	0.026(2)	0.026(2)	0.026(2)	-0.0030(19)	0.0000(19)	0.0015(18)
C(35)	0.024(2)	0.020(2)	0.034(3)	-0.0022(19)	-0.0007(19)	-0.0059(18)
C(36)	0.019(2)	0.021(2)	0.030(2)	0.0058(18)	0.0040(18)	-0.0009(17)
C(41)	0.017(2)	0.024(2)	0.021(2)	0.0007(17)	0.0034(17)	0.0005(17)
C(43)	0.023(2)	0.030(2)	0.036(3)	0.003(2)	0.010(2)	0.0013(19)
C(42)	0.0132(19)	0.025(2)	0.025(2)	0.0034(18)	0.0061(17)	-0.0012(16)
C(44)	0.029(2)	0.035(3)	0.038(3)	0.010(2)	0.018(2)	-0.002(2)
C(45)	0.034(3)	0.025(2)	0.035(3)	0.010(2)	0.016(2)	-0.0007(19)
C(46)	0.026(2)	0.026(2)	0.032(2)	0.009(2)	0.0097(19)	0.0068(19)
C(51)	0.026(2)	0.033(3)	0.029(2)	0.008(2)	0.008(2)	0.0035(19)
C(52)	0.018(2)	0.024(2)	0.033(3)	0.0027(19)	0.0064(18)	-0.0017(17)
C(54)	0.043(3)	0.022(2)	0.047(3)	0.001(2)	0.021(2)	0.000(2)
C(55)	0.039(3)	0.034(3)	0.047(3)	0.009(2)	0.012(2)	0.019(2)
C(56)	0.029(2)	0.038(3)	0.036(3)	0.009(2)	0.005(2)	0.005(2)
C(61)	0.040(3)	0.037(3)	0.021(2)	0.003(2)	0.000(2)	0.010(2)
C(62)	0.021(2)	0.037(3)	0.023(2)	-0.0096(19)	0.0006(18)	0.0109(19)
C(63)	0.048(3)	0.037(3)	0.034(3)	-0.011(2)	-0.010(2)	0.017(2)
C(64)	0.079(4)	0.034(3)	0.037(3)	-0.011(2)	-0.015(3)	0.024(3)
C(65)	0.083(4)	0.042(3)	0.016(2)	0.002(2)	0.003(3)	0.033(3)
C(66)	0.048(3)	0.041(3)	0.038(3)	0.002(2)	0.013(3)	0.014(2)
C(71)	0.019(2)	0.041(3)	0.036(3)	0.011(2)	0.007(2)	0.0051(19)
C(72)	0.046(3)	0.029(3)	0.038(3)	-0.003(2)	0.023(2)	-0.003(2)
C(73)	0.029(3)	0.073(4)	0.031(3)	-0.001(3)	0.003(2)	-0.005(3)
C(74)	0.037(3)	0.054(3)	0.068(4)	0.034(3)	0.011(3)	0.015(3)

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Table S48. – continued from previous page

atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C(75)	0.055(3)	0.051(3)	0.033(3)	−0.001(2)	0.011(3)	−0.015(3)
C(76)	0.054(3)	0.052(3)	0.058(4)	−0.018(3)	0.036(3)	−0.004(3)
C(77)	0.018(2)	0.023(2)	0.038(3)	−0.005(2)	0.0121(19)	−0.0023(17)
C(78)	0.034(2)	0.031(2)	0.025(2)	0.003(2)	0.013(2)	0.000(2)
C(79)	0.018(2)	0.046(3)	0.090(4)	−0.037(3)	0.010(3)	−0.008(2)
C(80)	0.017(2)	0.044(3)	0.039(3)	0.000(2)	0.008(2)	0.001(2)
C(81)	0.044(3)	0.047(3)	0.030(3)	0.009(2)	0.004(2)	0.007(2)
C(82)	0.052(3)	0.035(3)	0.047(3)	0.019(2)	0.023(3)	0.001(2)
C(83)	0.028(2)	0.034(3)	0.031(3)	0.002(2)	0.006(2)	0.003(2)
C(84)	0.031(2)	0.029(2)	0.027(2)	−0.0072(19)	0.008(2)	−0.0056(19)
C(85)	0.027(3)	0.044(3)	0.046(3)	0.003(2)	0.008(2)	0.005(2)
C(86)	0.040(3)	0.031(3)	0.060(4)	0.005(2)	−0.004(3)	0.012(2)
C(87)	0.046(3)	0.046(3)	0.031(3)	0.000(2)	0.013(2)	−0.007(2)
C(88)	0.036(3)	0.045(3)	0.049(3)	−0.011(2)	0.023(2)	0.002(2)
C(89)	0.036(3)	0.045(3)	0.037(3)	−0.009(2)	−0.001(2)	0.000(2)
C(90)	0.032(3)	0.040(3)	0.041(3)	−0.012(2)	0.009(2)	0.001(2)
C(91)	0.050(3)	0.041(3)	0.050(3)	−0.004(3)	0.015(3)	0.013(2)
C(92)	0.062(4)	0.039(3)	0.050(3)	−0.006(3)	0.010(3)	−0.020(3)
C(93)	0.037(3)	0.050(3)	0.039(3)	−0.007(2)	0.009(2)	0.014(2)
C(94)	0.026(3)	0.081(4)	0.071(4)	−0.042(3)	0.005(3)	0.001(3)
C(53)	0.025(2)	0.030(2)	0.033(3)	−0.002(2)	0.013(2)	0.0057(19)

Table S49. Distances [Å] for [PC(CH₃)P]PdCl (**9**).

atom – atom	distance	atom – atom	distance
C(12) – C(61)	1.514(6)	C(12) – C(51)	1.555(6)
C(12) – C(22)	1.566(6)	C(12) – Pd(2)	2.091(5)
C(22) – H(22A)	0.9800	C(22) – H(22B)	0.9800
C(22) – H(22C)	0.9800	Pd(3) – Pd(2)	0.57(2)
Pd(3) – P(22)	2.154(7)	Pd(3) – Cl(2)	2.425(7)
Pd(3) – P(21)	2.440(11)	Cl(2) – Pd(2)	2.3978(12)
Pd(2) – P(22)	2.2795(16)	Pd(2) – P(21)	2.3176(13)
P(22) – C(62)	1.799(5)	P(22) – C(89)	1.836(5)
P(22) – C(90)	1.856(5)	P(21) – C(52)	1.818(4)
P(21) – C(84)	1.847(4)	P(21) – C(83)	1.865(4)
Pd(1) – C(11)	2.083(4)	Pd(1) – P(12)	2.2585(10)
Pd(1) – P(11)	2.3430(10)	Pd(1) – Cl(1)	2.4065(10)
C(11) – C(31)	1.525(5)	C(11) – C(41)	1.530(5)
C(11) – C(21)	1.551(5)	P(11) – C(32)	1.819(4)
P(11) – C(78)	1.859(4)	P(11) – C(77)	1.869(4)
P(12) – C(42)	1.806(4)	P(12) – C(72)	1.845(5)
P(12) – C(71)	1.847(4)	C(21) – H(21A)	0.9800
C(21) – H(21B)	0.9800	C(21) – H(21C)	0.9800
C(31) – C(36)	1.399(5)	C(31) – C(32)	1.412(5)
C(32) – C(33)	1.387(5)	C(33) – C(34)	1.386(6)
C(33) – H(33)	0.9500	C(34) – C(35)	1.385(6)
C(34) – H(34)	0.9500	C(35) – C(36)	1.385(6)
C(35) – H(35)	0.9500	C(36) – H(36)	0.9500
C(41) – C(42)	1.398(5)	C(41) – C(46)	1.403(6)
C(43) – C(44)	1.376(6)	C(43) – C(42)	1.400(5)
C(43) – H(43)	0.9500	C(44) – C(45)	1.387(6)
C(44) – H(44)	0.9500	C(45) – C(46)	1.383(6)
C(45) – H(45)	0.9500	C(46) – H(46)	0.9500
C(51) – C(56)	1.396(6)	C(51) – C(52)	1.420(6)
C(52) – C(53)	1.392(6)	C(54) – C(55)	1.383(7)
C(54) – C(53)	1.398(6)	C(54) – H(54)	0.9500
C(55) – C(56)	1.386(7)	C(55) – H(55)	0.9500
C(56) – H(56)	0.9500	C(61) – C(62)	1.375(6)
C(61) – C(66)	1.425(6)	C(62) – C(63)	1.397(6)
C(63) – C(64)	1.366(7)	C(63) – H(63)	0.9500
C(64) – C(65)	1.373(8)	C(64) – H(64)	0.9500
C(65) – C(66)	1.367(7)	C(65) – H(65)	0.9500
C(66) – H(66)	0.9500	C(71) – C(74)	1.508(6)
C(71) – C(73)	1.524(7)	C(71) – H(71)	1.0000
C(72) – C(75)	1.503(7)	C(72) – C(76)	1.538(6)
C(72) – H(72)	1.0000	C(73) – H(73A)	0.9800

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Table S49. – continued from previous page

atom – atom	distance	atom – atom	distance
C(73) – H(73B)	0.9800	C(73) – H(73C)	0.9800
C(74) – H(74A)	0.9800	C(74) – H(74B)	0.9800
C(74) – H(74C)	0.9800	C(75) – H(75A)	0.9800
C(75) – H(75B)	0.9800	C(75) – H(75C)	0.9800
C(76) – H(76A)	0.9800	C(76) – H(76B)	0.9800
C(76) – H(76C)	0.9800	C(77) – C(80)	1.511(6)
C(77) – C(79)	1.521(6)	C(77) – H(77)	1.0000
C(78) – C(82)	1.527(6)	C(78) – C(81)	1.527(6)
C(78) – H(78)	1.0000	C(79) – H(79A)	0.9800
C(79) – H(79B)	0.9800	C(79) – H(79C)	0.9800
C(80) – H(80A)	0.9800	C(80) – H(80B)	0.9800
C(80) – H(80C)	0.9800	C(81) – H(81A)	0.9800
C(81) – H(81B)	0.9800	C(81) – H(81C)	0.9800
C(82) – H(82A)	0.9800	C(82) – H(82B)	0.9800
C(82) – H(82C)	0.9800	C(83) – C(86)	1.526(6)
C(83) – C(85)	1.530(6)	C(83) – H(83)	1.0000
C(84) – C(87)	1.512(6)	C(84) – C(88)	1.531(6)
C(84) – H(84)	1.0000	C(85) – H(85A)	0.9800
C(85) – H(85B)	0.9800	C(85) – H(85C)	0.9800
C(86) – H(86A)	0.9800	C(86) – H(86B)	0.9800
C(86) – H(86C)	0.9800	C(87) – H(87A)	0.9800
C(87) – H(87B)	0.9800	C(87) – H(87C)	0.9800
C(88) – H(88A)	0.9800	C(88) – H(88B)	0.9800
C(88) – H(88C)	0.9800	C(89) – C(91)	1.503(7)
C(89) – C(92)	1.545(7)	C(89) – H(89)	1.0000
C(90) – C(94)	1.516(6)	C(90) – C(93)	1.545(7)
C(90) – H(90)	1.0000	C(91) – H(91A)	0.9800
C(91) – H(91B)	0.9800	C(91) – H(91C)	0.9800
C(92) – H(92A)	0.9800	C(92) – H(92B)	0.9800
C(92) – H(92C)	0.9800	C(93) – H(93A)	0.9800
C(93) – H(93B)	0.9800	C(93) – H(93C)	0.9800
C(94) – H(94A)	0.9800	C(94) – H(94B)	0.9800
C(94) – H(94C)	0.9800	C(53) – H(53)	0.9500

Table S50. Angles [°] for [PC(CH₃)P]PdCl (**9**).

atom – atom – atom	angle	atom – atom – atom	angle
C(61) – C(12) – C(51)	113.5(4)	C(61) – C(12) – C(22)	107.2(4)
C(51) – C(12) – C(22)	108.9(4)	C(61) – C(12) – Pd(2)	115.6(3)
C(51) – C(12) – Pd(2)	108.3(3)	C(22) – C(12) – Pd(2)	102.7(3)
Pd(2) – Pd(3) – P(22)	95.5(9)	Pd(2) – Pd(3) – Cl(2)	80.5(8)
P(22) – Pd(3) – Cl(2)	98.0(2)	Pd(2) – Pd(3) – P(21)	71.0(9)
P(22) – Pd(3) – P(21)	160.7(10)	Cl(2) – Pd(3) – P(21)	93.3(4)
Pd(3) – Pd(2) – C(12)	98.9(6)	Pd(3) – Pd(2) – P(22)	70.2(6)
C(12) – Pd(2) – P(22)	84.48(13)	Pd(3) – Pd(2) – P(21)	95.6(6)
C(12) – Pd(2) – P(21)	84.32(13)	P(22) – Pd(2) – P(21)	160.27(13)
Pd(3) – Pd(2) – Cl(2)	86.0(6)	C(12) – Pd(2) – Cl(2)	174.7(2)
P(22) – Pd(2) – Cl(2)	95.43(6)	P(21) – Pd(2) – Cl(2)	97.20(4)
C(62) – P(22) – C(89)	105.2(2)	C(62) – P(22) – C(90)	106.4(2)
C(89) – P(22) – C(90)	107.3(2)	C(62) – P(22) – Pd(3)	105.8(2)
C(89) – P(22) – Pd(3)	132.8(5)	C(90) – P(22) – Pd(3)	97.0(7)
C(62) – P(22) – Pd(2)	103.59(15)	C(89) – P(22) – Pd(2)	122.17(18)
C(90) – P(22) – Pd(2)	111.05(17)	C(52) – P(21) – C(84)	103.0(2)
C(52) – P(21) – C(83)	108.33(19)	C(84) – P(21) – C(83)	102.8(2)
C(52) – P(21) – Pd(2)	99.67(14)	C(84) – P(21) – Pd(2)	115.79(16)
C(83) – P(21) – Pd(2)	125.09(17)	C(52) – P(21) – Pd(3)	95.9(3)
C(84) – P(21) – Pd(3)	104.6(6)	C(83) – P(21) – Pd(3)	137.9(6)
C(11) – Pd(1) – P(12)	84.81(10)	C(11) – Pd(1) – P(11)	83.77(11)
P(12) – Pd(1) – P(11)	159.73(4)	C(11) – Pd(1) – Cl(1)	172.80(11)
P(12) – Pd(1) – Cl(1)	95.63(4)	P(11) – Pd(1) – Cl(1)	97.79(4)
C(31) – C(11) – C(41)	113.9(3)	C(31) – C(11) – C(21)	109.8(3)
C(41) – C(11) – C(21)	105.6(3)	C(31) – C(11) – Pd(1)	107.1(2)
C(41) – C(11) – Pd(1)	115.6(3)	C(21) – C(11) – Pd(1)	104.3(2)
C(32) – P(11) – C(78)	101.63(19)	C(32) – P(11) – C(77)	109.87(17)
C(78) – P(11) – C(77)	102.4(2)	C(32) – P(11) – Pd(1)	97.57(13)
C(78) – P(11) – Pd(1)	112.13(14)	C(77) – P(11) – Pd(1)	130.02(14)
C(42) – P(12) – C(72)	110.7(2)	C(42) – P(12) – C(71)	102.29(19)
C(72) – P(12) – C(71)	106.8(2)	C(42) – P(12) – Pd(1)	104.71(13)
C(72) – P(12) – Pd(1)	115.38(15)	C(71) – P(12) – Pd(1)	116.12(15)
C(11) – C(21) – H(21A)	109.5	C(11) – C(21) – H(21B)	109.5
H(21A) – C(21) – H(21B)	109.5	C(11) – C(21) – H(21C)	109.5
H(21A) – C(21) – H(21C)	109.5	H(21B) – C(21) – H(21C)	109.5
C(36) – C(31) – C(32)	116.5(4)	C(36) – C(31) – C(11)	124.9(3)
C(32) – C(31) – C(11)	118.6(3)	C(33) – C(32) – C(31)	121.8(4)
C(33) – C(32) – P(11)	123.2(3)	C(31) – C(32) – P(11)	114.5(3)
C(34) – C(33) – C(32)	119.6(4)	C(34) – C(33) – H(33)	120.2
C(32) – C(33) – H(33)	120.2	C(35) – C(34) – C(33)	119.6(4)
C(35) – C(34) – H(34)	120.2	C(33) – C(34) – H(34)	120.2

Continued on next page

Table S50. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(34) – C(35) – C(36)	120.5(4)	C(34) – C(35) – H(35)	119.8
C(36) – C(35) – H(35)	119.8	C(35) – C(36) – C(31)	121.4(4)
C(35) – C(36) – H(36)	119.3	C(31) – C(36) – H(36)	119.3
C(42) – C(41) – C(46)	117.3(4)	C(42) – C(41) – C(11)	121.3(3)
C(46) – C(41) – C(11)	121.3(3)	C(44) – C(43) – C(42)	120.3(4)
C(44) – C(43) – H(43)	119.8	C(42) – C(43) – H(43)	119.8
C(41) – C(42) – C(43)	121.0(4)	C(41) – C(42) – P(12)	113.4(3)
C(43) – C(42) – P(12)	125.6(3)	C(43) – C(44) – C(45)	119.5(4)
C(43) – C(44) – H(44)	120.3	C(45) – C(44) – H(44)	120.3
C(46) – C(45) – C(44)	120.4(4)	C(46) – C(45) – H(45)	119.8
C(44) – C(45) – H(45)	119.8	C(45) – C(46) – C(41)	121.4(4)
C(45) – C(46) – H(46)	119.3	C(41) – C(46) – H(46)	119.3
C(56) – C(51) – C(52)	117.1(4)	C(56) – C(51) – C(12)	124.0(4)
C(52) – C(51) – C(12)	118.8(4)	C(53) – C(52) – C(51)	121.4(4)
C(53) – C(52) – P(21)	124.2(3)	C(51) – C(52) – P(21)	114.1(3)
C(55) – C(54) – C(53)	119.1(4)	C(55) – C(54) – H(54)	120.4
C(53) – C(54) – H(54)	120.4	C(54) – C(55) – C(56)	121.4(4)
C(54) – C(55) – H(55)	119.3	C(56) – C(55) – H(55)	119.3
C(55) – C(56) – C(51)	120.8(4)	C(55) – C(56) – H(56)	119.6
C(51) – C(56) – H(56)	119.6	C(62) – C(61) – C(66)	117.1(4)
C(62) – C(61) – C(12)	121.6(4)	C(66) – C(61) – C(12)	120.8(4)
C(61) – C(62) – C(63)	121.1(4)	C(61) – C(62) – P(22)	114.7(3)
C(63) – C(62) – P(22)	123.8(4)	C(64) – C(63) – C(62)	120.8(5)
C(64) – C(63) – H(63)	119.6	C(62) – C(63) – H(63)	119.6
C(63) – C(64) – C(65)	118.9(5)	C(63) – C(64) – H(64)	120.6
C(65) – C(64) – H(64)	120.6	C(66) – C(65) – C(64)	121.5(5)
C(66) – C(65) – H(65)	119.2	C(64) – C(65) – H(65)	119.2
C(65) – C(66) – C(61)	120.3(5)	C(65) – C(66) – H(66)	119.8
C(61) – C(66) – H(66)	119.8	C(74) – C(71) – C(73)	111.9(4)
C(74) – C(71) – P(12)	111.6(3)	C(73) – C(71) – P(12)	109.8(3)
C(74) – C(71) – H(71)	107.8	C(73) – C(71) – H(71)	107.8
P(12) – C(71) – H(71)	107.8	C(75) – C(72) – C(76)	111.5(4)
C(75) – C(72) – P(12)	109.5(3)	C(76) – C(72) – P(12)	116.3(3)
C(75) – C(72) – H(72)	106.3	C(76) – C(72) – H(72)	106.3
P(12) – C(72) – H(72)	106.3	C(71) – C(73) – H(73A)	109.5
C(71) – C(73) – H(73B)	109.5	H(73A) – C(73) – H(73B)	109.5
C(71) – C(73) – H(73C)	109.5	H(73A) – C(73) – H(73C)	109.5
H(73B) – C(73) – H(73C)	109.5	C(71) – C(74) – H(74A)	109.5
C(71) – C(74) – H(74B)	109.5	H(74A) – C(74) – H(74B)	109.5
C(71) – C(74) – H(74C)	109.5	H(74A) – C(74) – H(74C)	109.5
H(74B) – C(74) – H(74C)	109.5	C(72) – C(75) – H(75A)	109.5
C(72) – C(75) – H(75B)	109.5	H(75A) – C(75) – H(75B)	109.5

Continued on next page

Table S50. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(72) – C(75) – H(75C)	109.5	H(75A) – C(75) – H(75C)	109.5
H(75B) – C(75) – H(75C)	109.5	C(72) – C(76) – H(76A)	109.5
C(72) – C(76) – H(76B)	109.5	H(76A) – C(76) – H(76B)	109.5
C(72) – C(76) – H(76C)	109.5	H(76A) – C(76) – H(76C)	109.5
H(76B) – C(76) – H(76C)	109.5	C(80) – C(77) – C(79)	112.7(4)
C(80) – C(77) – P(11)	115.8(3)	C(79) – C(77) – P(11)	108.0(3)
C(80) – C(77) – H(77)	106.6	C(79) – C(77) – H(77)	106.6
P(11) – C(77) – H(77)	106.6	C(82) – C(78) – C(81)	110.3(4)
C(82) – C(78) – P(11)	113.3(3)	C(81) – C(78) – P(11)	110.2(3)
C(82) – C(78) – H(78)	107.6	C(81) – C(78) – H(78)	107.6
P(11) – C(78) – H(78)	107.6	C(77) – C(79) – H(79A)	109.5
C(77) – C(79) – H(79B)	109.5	H(79A) – C(79) – H(79B)	109.5
C(77) – C(79) – H(79C)	109.5	H(79A) – C(79) – H(79C)	109.5
H(79B) – C(79) – H(79C)	109.5	C(77) – C(80) – H(80A)	109.5
C(77) – C(80) – H(80B)	109.5	H(80A) – C(80) – H(80B)	109.5
C(77) – C(80) – H(80C)	109.5	H(80A) – C(80) – H(80C)	109.5
H(80B) – C(80) – H(80C)	109.5	C(78) – C(81) – H(81A)	109.5
C(78) – C(81) – H(81B)	109.5	H(81A) – C(81) – H(81B)	109.5
C(78) – C(81) – H(81C)	109.5	H(81A) – C(81) – H(81C)	109.5
H(81B) – C(81) – H(81C)	109.5	C(78) – C(82) – H(82A)	109.5
C(78) – C(82) – H(82B)	109.5	H(82A) – C(82) – H(82B)	109.5
C(78) – C(82) – H(82C)	109.5	H(82A) – C(82) – H(82C)	109.5
H(82B) – C(82) – H(82C)	109.5	C(86) – C(83) – C(85)	112.4(4)
C(86) – C(83) – P(21)	109.7(3)	C(85) – C(83) – P(21)	115.3(3)
C(86) – C(83) – H(83)	106.3	C(85) – C(83) – H(83)	106.3
P(21) – C(83) – H(83)	106.3	C(87) – C(84) – C(88)	111.1(4)
C(87) – C(84) – P(21)	112.9(3)	C(88) – C(84) – P(21)	110.0(3)
C(87) – C(84) – H(84)	107.5	C(88) – C(84) – H(84)	107.5
P(21) – C(84) – H(84)	107.5	C(83) – C(85) – H(85A)	109.5
C(83) – C(85) – H(85B)	109.5	H(85A) – C(85) – H(85B)	109.5
C(83) – C(85) – H(85C)	109.5	H(85A) – C(85) – H(85C)	109.5
H(85B) – C(85) – H(85C)	109.5	C(83) – C(86) – H(86A)	109.5
C(83) – C(86) – H(86B)	109.5	H(86A) – C(86) – H(86B)	109.5
C(83) – C(86) – H(86C)	109.5	H(86A) – C(86) – H(86C)	109.5
H(86B) – C(86) – H(86C)	109.5	C(84) – C(87) – H(87A)	109.5
C(84) – C(87) – H(87B)	109.5	H(87A) – C(87) – H(87B)	109.5
C(84) – C(87) – H(87C)	109.5	H(87A) – C(87) – H(87C)	109.5
H(87B) – C(87) – H(87C)	109.5	C(84) – C(88) – H(88A)	109.5
C(84) – C(88) – H(88B)	109.5	H(88A) – C(88) – H(88B)	109.5
C(84) – C(88) – H(88C)	109.5	H(88A) – C(88) – H(88C)	109.5
H(88B) – C(88) – H(88C)	109.5	C(91) – C(89) – C(92)	112.9(4)
C(91) – C(89) – P(22)	108.6(4)	C(92) – C(89) – P(22)	111.9(3)

Continued on next page

Table S50. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(91) – C(89) – H(89)	107.8	C(92) – C(89) – H(89)	107.8
P(22) – C(89) – H(89)	107.8	C(94) – C(90) – C(93)	111.0(4)
C(94) – C(90) – P(22)	114.6(3)	C(93) – C(90) – P(22)	107.4(3)
C(94) – C(90) – H(90)	107.9	C(93) – C(90) – H(90)	107.9
P(22) – C(90) – H(90)	107.9	C(89) – C(91) – H(91A)	109.5
C(89) – C(91) – H(91B)	109.5	H(91A) – C(91) – H(91B)	109.5
C(89) – C(91) – H(91C)	109.5	H(91A) – C(91) – H(91C)	109.5
H(91B) – C(91) – H(91C)	109.5	C(89) – C(92) – H(92A)	109.5
C(89) – C(92) – H(92B)	109.5	H(92A) – C(92) – H(92B)	109.5
C(89) – C(92) – H(92C)	109.5	H(92A) – C(92) – H(92C)	109.5
H(92B) – C(92) – H(92C)	109.5	C(90) – C(93) – H(93A)	109.5
C(90) – C(93) – H(93B)	109.5	H(93A) – C(93) – H(93B)	109.5
C(90) – C(93) – H(93C)	109.5	H(93A) – C(93) – H(93C)	109.5
H(93B) – C(93) – H(93C)	109.5	C(90) – C(94) – H(94A)	109.5
C(90) – C(94) – H(94B)	109.5	H(94A) – C(94) – H(94B)	109.5
C(90) – C(94) – H(94C)	109.5	H(94A) – C(94) – H(94C)	109.5
H(94B) – C(94) – H(94C)	109.5	C(52) – C(53) – C(54)	119.5(4)
C(52) – C(53) – H(53)	120.2	C(54) – C(53) – H(53)	120.2

8.8 Crystal data for [PC(sp³)HP]PdI (11)

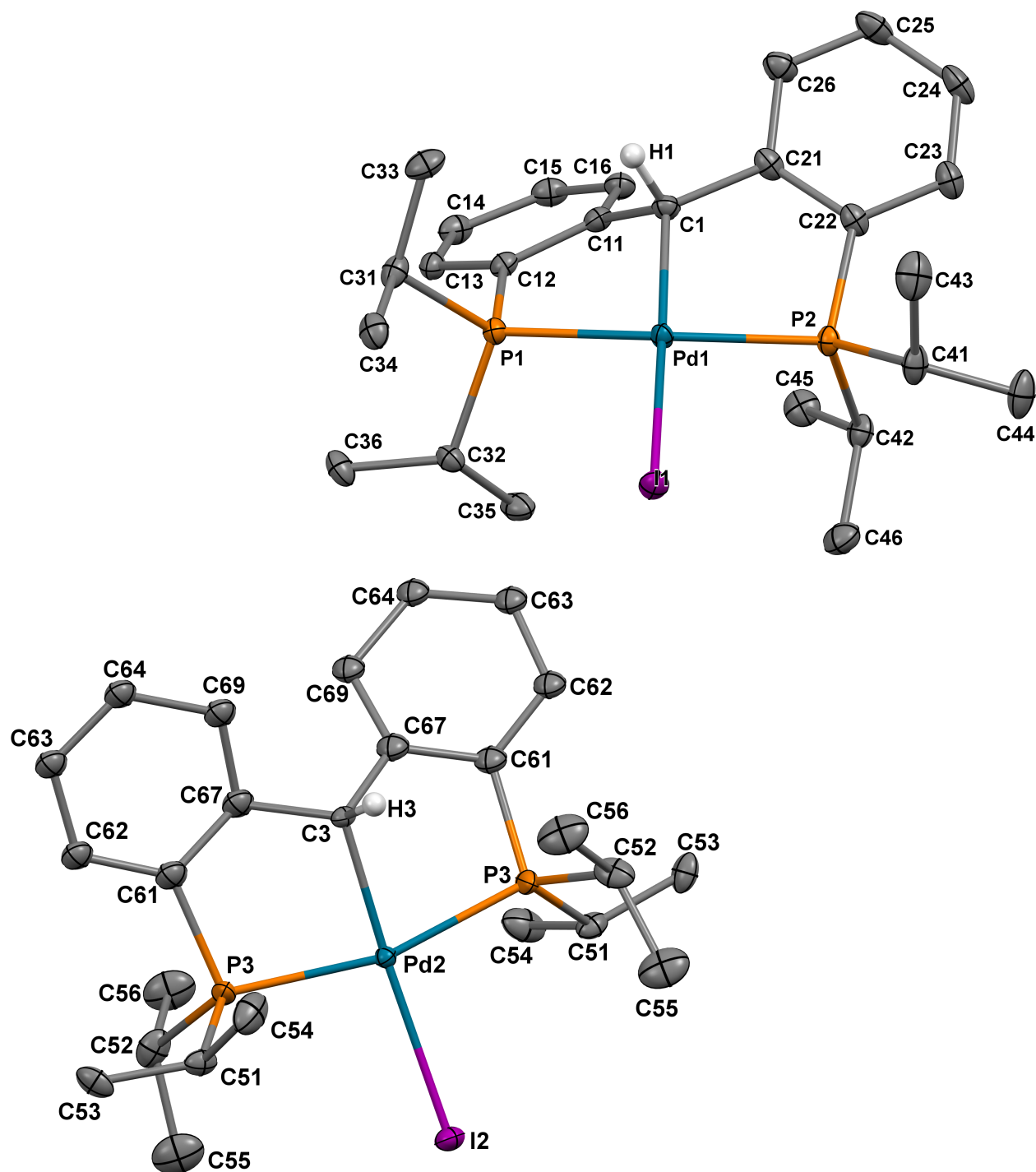


Figure S80. Thermal-ellipsoid representation for the two independent molecules of [PC(sp³)HP]PdI (11) at 50% probability. Most hydrogen atoms were omitted for clarity.

Table S51. Crystal data and structure refinement for [PC(sp³)HP]PdI (**11**).

Identification code:	cc56	
Empirical formula:	C ₂₅ H ₃₇ IP ₂ Pd	
Formula weight:	632.79	
Temperature:	120(2) K	
Wavelength:	0.71073 Å	
Crystal system:	Monoclinic	
Space group:	C2/c	
Unit cell dimensions:	$a = 29.176(6)$ Å	$\alpha = 90^\circ$
	$b = 12.515(2)$ Å	$\beta = 105.315(4)^\circ$
	$c = 22.247(4)$ Å	$\gamma = 90^\circ$
Volume:	7835(2) Å ³	
Z:	12	
Density (calculated):	1.609 g·cm ⁻³	
Absorption coefficient (μ):	2.025 mm ⁻¹	
F(000):	3792	
Crystal size:	0.02 × 0.02 × 0.01 mm ³	
θ range for data collection:	1.78 to 25.00°	
Index ranges:	$-34 \leq h \leq 34, -14 \leq k \leq 14, -26 \leq l \leq 26$	
Reflections collected:	55501	
Independent reflections:	6893 [$R_{\text{int}} = 0.0219$]	
Completeness to $\theta = 25.00^\circ$:	100.0 %	
Absorption correction:	Semi-empirical from equivalents	
Max. and min. transmission:	0.7454 and 0.6649	
Refinement method:	Full-matrix least-squares on F^2	
Data / restraints / parameters:	6893 / 0 / 384	
Goodness-of-fit on F^2 :	1.080	
Final R indices [$I > 2\sigma(I)$]:	$R_1 = 0.0235, wR_2 = 0.0511$	
R indices (all data):	$R_1 = 0.0252, wR_2 = 0.0519$	
Largest diff. peak and hole:	1.412 and -1.244 e ⁻ ·Å ⁻³	

Table S52. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for [PC(sp³)HP]PdI (**11**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

atom	x	y	z	U(eq)
C(67)	−0.0326(2)	0.2608(5)	0.2713(3)	0.027(1)
C(69)	−0.0431(2)	0.1606(5)	0.2441(3)	0.027(1)
C(66)	−0.0527(2)	0.2590(5)	0.2412(3)	0.027(1)
C(70)	−0.0660(2)	0.1541(5)	0.2216(3)	0.027(1)
C(64)	−0.09194(11)	0.1039(3)	0.24571(14)	0.027(1)
I(1)	0.27189(1)	0.64632(2)	0.36531(1)	0.024(1)
C(1)	0.39437(10)	0.4058(2)	0.46606(13)	0.019(1)
Pd(1)	0.33760(1)	0.50634(2)	0.42675(1)	0.016(1)
P(1)	0.31054(2)	0.35751(6)	0.36599(3)	0.017(1)
I(2)	0.0000	0.69270(2)	0.2500	0.025(1)
Pd(2)	−0.00594(4)	0.47853(3)	0.23895(3)	0.014(1)
P(2)	0.36354(3)	0.59939(6)	0.51720(3)	0.018(1)
P(3)	−0.06005(3)	0.45376(6)	0.29734(4)	0.024(1)
C(3)	−0.01539(19)	0.3167(4)	0.2178(2)	0.016(1)
C(11)	0.37607(10)	0.2939(2)	0.47133(13)	0.020(1)
C(12)	0.34020(10)	0.2541(2)	0.42041(13)	0.019(1)
C(13)	0.32637(10)	0.1472(2)	0.41872(14)	0.022(1)
C(14)	0.34504(11)	0.0804(2)	0.46918(15)	0.027(1)
C(15)	0.37763(11)	0.1208(2)	0.52116(15)	0.026(1)
C(16)	0.39344(10)	0.2258(2)	0.52215(14)	0.023(1)
C(21)	0.43089(10)	0.4491(2)	0.52306(13)	0.022(1)
C(22)	0.42107(10)	0.5405(2)	0.55357(13)	0.021(1)
C(23)	0.45474(11)	0.5803(3)	0.60619(14)	0.027(1)
C(24)	0.49820(11)	0.5299(3)	0.62705(15)	0.032(1)
C(25)	0.50869(11)	0.4411(3)	0.59638(16)	0.033(1)
C(26)	0.47551(11)	0.4011(3)	0.54443(15)	0.028(1)
C(31)	0.32089(11)	0.3272(2)	0.28938(14)	0.024(1)
C(32)	0.24592(10)	0.3413(2)	0.35603(13)	0.021(1)
C(36)	0.22246(11)	0.2461(3)	0.31670(14)	0.028(1)
C(35)	0.23516(11)	0.3420(3)	0.41967(14)	0.029(1)
C(34)	0.29222(11)	0.4026(3)	0.23943(14)	0.028(1)
C(33)	0.37407(12)	0.3354(3)	0.29457(16)	0.033(1)
C(43)	0.40940(14)	0.7730(3)	0.48481(17)	0.041(1)
C(42)	0.32747(11)	0.5722(2)	0.57239(13)	0.025(1)
C(41)	0.36929(12)	0.7455(2)	0.51405(14)	0.027(1)
C(44)	0.37399(14)	0.8065(3)	0.57491(15)	0.038(1)
C(45)	0.32662(12)	0.4521(3)	0.58528(15)	0.031(1)
C(46)	0.27719(12)	0.6163(3)	0.54834(16)	0.035(1)
C(51)	−0.11538(11)	0.5207(2)	0.25533(13)	0.024(1)

Continued on next page

Table S52. – continued from previous page

atom	x	y	x	U(eq)
C(52)	−0.05156(12)	0.4810(3)	0.38051(15)	0.033(1)
C(53)	−0.15841(11)	0.5008(3)	0.28087(15)	0.031(1)
C(54)	−0.12646(15)	0.4913(3)	0.18617(15)	0.043(1)
C(55)	−0.04938(15)	0.6002(3)	0.39489(19)	0.051(1)
C(56)	−0.00661(14)	0.4238(3)	0.41657(19)	0.051(1)
C(61)	−0.07152(11)	0.3109(2)	0.28764(15)	0.027(1)
C(62)	−0.10734(11)	0.2546(2)	0.30357(15)	0.027(1)
C(63)	−0.11705(11)	0.1501(2)	0.28348(14)	0.027(1)
H(69)	−0.0215	0.1262	0.2250	0.033
H(70)	−0.0547	0.1225	0.1894	0.033
H(64)	−0.0951	0.0292	0.2382	0.033
H(1)	0.4121	0.3998	0.4334	0.023
H(3)	−0.0267	0.3173	0.1739	0.019
H(13)	0.3041	0.1199	0.3829	0.026
H(14)	0.3355	0.0077	0.4680	0.032
H(15)	0.3893	0.0763	0.5565	0.031
H(16)	0.4164	0.2516	0.5579	0.028
H(23)	0.4476	0.6415	0.6273	0.033
H(24)	0.5210	0.5566	0.6627	0.038
H(25)	0.5387	0.4072	0.6108	0.040
H(26)	0.4832	0.3405	0.5233	0.034
H(31)	0.3103	0.2523	0.2777	0.029
H(32)	0.2305	0.4067	0.3337	0.026
H(36A)	0.1881	0.2484	0.3116	0.043
H(36B)	0.2354	0.1795	0.3376	0.043
H(36C)	0.2289	0.2494	0.2757	0.043
H(35A)	0.2007	0.3391	0.4139	0.044
H(35B)	0.2478	0.4076	0.4420	0.044
H(35C)	0.2501	0.2798	0.4438	0.044
H(34A)	0.3003	0.3896	0.2000	0.042
H(34B)	0.2998	0.4768	0.2524	0.042
H(34C)	0.2582	0.3899	0.2338	0.042
H(33A)	0.3800	0.3161	0.2546	0.049
H(33B)	0.3915	0.2865	0.3270	0.049
H(33C)	0.3848	0.4088	0.3055	0.049
H(43A)	0.4053	0.7328	0.4459	0.062
H(43B)	0.4399	0.7541	0.5137	0.062
H(43C)	0.4088	0.8497	0.4759	0.062
H(42)	0.3428	0.6090	0.6126	0.030
H(41)	0.3394	0.7717	0.4844	0.033
H(44A)	0.3739	0.8835	0.5668	0.057
H(44B)	0.4038	0.7866	0.6050	0.057

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Table S52. – continued from previous page

atom	x	y	x	U(eq)
H(44C)	0.3472	0.7886	0.5919	0.057
H(45A)	0.3111	0.4145	0.5466	0.047
H(45B)	0.3089	0.4391	0.6164	0.047
H(45C)	0.3592	0.4259	0.6011	0.047
H(46A)	0.2787	0.6935	0.5416	0.052
H(46B)	0.2592	0.6026	0.5791	0.052
H(46C)	0.2614	0.5813	0.5089	0.052
H(51)	−0.1090	0.5993	0.2584	0.028
H(52)	−0.0791	0.4500	0.3934	0.040
H(53A)	−0.1846	0.5474	0.2594	0.047
H(53B)	−0.1499	0.5163	0.3256	0.047
H(53C)	−0.1683	0.4260	0.2740	0.047
H(54A)	−0.1547	0.5304	0.1630	0.064
H(54B)	−0.1324	0.4143	0.1812	0.064
H(54C)	−0.0994	0.5104	0.1700	0.064
H(55A)	−0.0231	0.6325	0.3815	0.077
H(55B)	−0.0442	0.6107	0.4398	0.077
H(55C)	−0.0794	0.6339	0.3726	0.077
H(56A)	−0.0084	0.3483	0.4046	0.077
H(56B)	−0.0036	0.4297	0.4614	0.077
H(56C)	0.0211	0.4568	0.4070	0.077
H(62)	−0.1254	0.2876	0.3283	0.033
H(63)	−0.1409	0.1106	0.2957	0.033

Table S53. Anisotropic displacement parameters ($\text{\AA}^2$) for [PC(sp³)HP]PdI (**11**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$.

atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C(67)	0.0314(8)	0.0218(7)	0.0286(8)	0.0054(6)	0.0073(6)	0.0044(6)
C(69)	0.0314(8)	0.0218(7)	0.0286(8)	0.0054(6)	0.0073(6)	0.0044(6)
C(66)	0.0314(8)	0.0218(7)	0.0286(8)	0.0054(6)	0.0073(6)	0.0044(6)
C(70)	0.0314(8)	0.0218(7)	0.0286(8)	0.0054(6)	0.0073(6)	0.0044(6)
C(64)	0.0314(8)	0.0218(7)	0.0286(8)	0.0054(6)	0.0073(6)	0.0044(6)
I(1)	0.0250(1)	0.0224(1)	0.0209(1)	0.0013(1)	0.0012(1)	0.0077(1)
C(1)	0.0168(13)	0.0186(14)	0.0219(14)	0.0010(11)	0.0033(11)	0.0022(11)
Pd(1)	0.0169(1)	0.0147(1)	0.0151(1)	-0.0004(1)	0.0010(1)	0.0012(1)
P(1)	0.0174(3)	0.0165(3)	0.0172(3)	-0.0013(3)	0.0038(3)	-0.0015(3)
I(2)	0.0290(2)	0.0151(1)	0.0313(2)	0.000	0.0087(1)	0.000
Pd(2)	0.0151(5)	0.0137(2)	0.0144(6)	-0.0003(2)	0.0039(4)	-0.0009(2)
P(2)	0.0227(4)	0.0170(4)	0.0142(3)	0.0005(3)	0.0030(3)	-0.0006(3)
P(3)	0.0224(4)	0.0174(4)	0.0386(5)	0.0059(3)	0.0173(3)	0.0053(3)
C(3)	0.019(3)	0.012(3)	0.015(3)	-0.001(2)	0.003(2)	0.000(2)
C(11)	0.0200(14)	0.0182(14)	0.0221(14)	-0.0006(11)	0.0082(12)	0.0031(11)
C(12)	0.0202(14)	0.0187(14)	0.0194(14)	0.0006(11)	0.0085(11)	0.0017(11)
C(13)	0.0210(14)	0.0192(14)	0.0259(15)	-0.0044(12)	0.0080(12)	-0.0020(12)
C(14)	0.0257(15)	0.0167(14)	0.0402(18)	0.0022(13)	0.0138(14)	-0.0005(12)
C(15)	0.0258(16)	0.0245(16)	0.0295(16)	0.0080(13)	0.0098(13)	0.0048(13)
C(16)	0.0209(14)	0.0237(15)	0.0247(15)	0.0007(12)	0.0038(12)	0.0036(12)
C(21)	0.0219(14)	0.0200(15)	0.0221(15)	0.0044(12)	0.0006(12)	-0.0035(12)
C(22)	0.0223(15)	0.0191(14)	0.0198(14)	0.0039(12)	0.0004(12)	-0.0041(12)
C(23)	0.0312(17)	0.0255(16)	0.0211(15)	0.0004(13)	0.0004(13)	-0.0066(13)
C(24)	0.0263(16)	0.0344(18)	0.0266(16)	0.0044(14)	-0.0077(13)	-0.0099(14)
C(25)	0.0227(16)	0.0343(18)	0.0356(18)	0.0100(15)	-0.0049(14)	-0.0003(14)
C(26)	0.0240(16)	0.0258(16)	0.0327(17)	0.0037(13)	0.0026(13)	0.0015(13)
C(31)	0.0338(17)	0.0190(15)	0.0228(15)	-0.0023(12)	0.0130(13)	-0.0039(13)
C(32)	0.0182(14)	0.0252(15)	0.0190(14)	0.0011(12)	0.0025(11)	-0.0017(12)
C(36)	0.0251(16)	0.0326(17)	0.0253(16)	-0.0001(13)	0.0027(13)	-0.0116(13)
C(35)	0.0221(15)	0.0432(19)	0.0239(16)	0.0001(14)	0.0085(12)	0.0001(14)
C(34)	0.0326(17)	0.0327(17)	0.0199(15)	0.0000(13)	0.0082(13)	-0.0071(14)
C(33)	0.0361(18)	0.0329(18)	0.0364(18)	0.0045(15)	0.0221(15)	0.0063(15)
C(43)	0.063(2)	0.0269(18)	0.0349(19)	0.0042(15)	0.0153(18)	-0.0096(17)
C(42)	0.0326(17)	0.0272(16)	0.0161(14)	-0.0020(12)	0.0079(12)	-0.0010(13)
C(41)	0.0416(18)	0.0155(14)	0.0217(15)	-0.0001(12)	0.0030(13)	-0.0004(13)
C(44)	0.064(2)	0.0196(16)	0.0281(17)	-0.0039(14)	0.0084(16)	-0.0028(16)
C(45)	0.0361(18)	0.0337(18)	0.0255(16)	0.0065(14)	0.0117(14)	-0.0040(14)
C(46)	0.0369(19)	0.040(2)	0.0322(18)	-0.0024(15)	0.0166(15)	0.0060(16)
C(51)	0.0300(16)	0.0200(15)	0.0185(14)	0.0022(12)	0.0018(12)	0.0046(12)
C(52)	0.0280(17)	0.0357(19)	0.0297(17)	0.0130(14)	-0.0021(13)	-0.0003(14)

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Table S53. – continued from previous page

atom	U₁₁	U₂₂	U₃₃	U₂₃	U₁₃	U₁₂
C(53)	0.0219(15)	0.0398(19)	0.0288(17)	−0.0050(14)	0.0018(13)	0.0120(14)
C(54)	0.063(2)	0.043(2)	0.0216(17)	−0.0002(15)	0.0094(16)	−0.0166(19)
C(55)	0.0472(16)	0.0444(16)	0.0484(17)	0.0065(13)	−0.0123(13)	0.0077(13)
C(56)	0.0472(16)	0.0444(16)	0.0484(17)	0.0065(13)	−0.0123(13)	0.0077(13)
C(61)	0.0314(8)	0.0218(7)	0.0286(8)	0.0054(6)	0.0073(6)	0.0044(6)
C(62)	0.0314(8)	0.0218(7)	0.0286(8)	0.0054(6)	0.0073(6)	0.0044(6)
C(63)	0.0314(8)	0.0218(7)	0.0286(8)	0.0054(6)	0.0073(6)	0.0044(6)

Table S54. Distances [Å] for [PC(sp³)HP]PdI (**11**).

atom – atom	distance	atom – atom	distance
C(67) – C(69)	1.391(9)	C(67) – C(61)	1.427(7)
C(67) – C(3)#1	1.525(8)	C(67) – C(3)	1.572(8)
C(69) – C(64)	1.602(7)	C(69) – H(69)	0.9500
C(66) – C(70)	1.406(9)	C(66) – C(61)	1.446(7)
C(66) – C(3)	1.508(8)	C(70) – C(64)	1.211(7)
C(70) – H(70)	0.9500	C(64) – C(63)	1.379(4)
C(64) – H(64)	0.9500	I(1) – Pd(1)	2.6887(4)
C(1) – C(11)	1.515(4)	C(1) – C(21)	1.524(4)
C(1) – Pd(1)	2.080(3)	C(1) – H(1)	1.0000
Pd(1) – P(2)	2.2744(8)	Pd(1) – P(1)	2.3144(8)
P(1) – C(12)	1.827(3)	P(1) – C(31)	1.847(3)
P(1) – C(32)	1.851(3)	I(2) – Pd(2)	2.6930(6)
I(2) – Pd(2)#1	2.6930(6)	Pd(2) – Pd(2)#1	0.5212(9)
Pd(2) – C(3)	2.082(5)	Pd(2) – C(3)#1	2.259(5)
Pd(2) – P(3)#1	2.2968(15)	Pd(2) – P(3)	2.3151(15)
P(2) – C(22)	1.816(3)	P(2) – C(41)	1.839(3)
P(2) – C(42)	1.848(3)	P(3) – C(61)	1.821(3)
P(3) – C(52)	1.833(4)	P(3) – C(51)	1.840(3)
P(3) – Pd(2)#1	2.2968(15)	C(3) – C(3)#1	1.478(10)
C(3) – C(67)#1	1.525(8)	C(3) – Pd(2)#1	2.259(5)
C(3) – H(3)	0.9440	C(11) – C(16)	1.400(4)
C(11) – C(12)	1.414(4)	C(12) – C(13)	1.395(4)
C(13) – C(14)	1.390(4)	C(13) – H(13)	0.9500
C(14) – C(15)	1.384(5)	C(14) – H(14)	0.9500
C(15) – C(16)	1.391(4)	C(15) – H(15)	0.9500
C(16) – H(16)	0.9500	C(21) – C(22)	1.398(4)
C(21) – C(26)	1.398(4)	C(22) – C(23)	1.406(4)
C(23) – C(24)	1.382(5)	C(23) – H(23)	0.9500
C(24) – C(25)	1.380(5)	C(24) – H(24)	0.9500
C(25) – C(26)	1.390(4)	C(25) – H(25)	0.9500
C(26) – H(26)	0.9500	C(31) – C(34)	1.528(4)
C(31) – C(33)	1.529(4)	C(31) – H(31)	1.0000
C(32) – C(35)	1.529(4)	C(32) – C(36)	1.529(4)
C(32) – H(32)	1.0000	C(36) – H(36A)	0.9800
C(36) – H(36B)	0.9800	C(36) – H(36C)	0.9800
C(35) – H(35A)	0.9800	C(35) – H(35B)	0.9800
C(35) – H(35C)	0.9800	C(34) – H(34A)	0.9800
C(34) – H(34B)	0.9800	C(34) – H(34C)	0.9800
C(33) – H(33A)	0.9800	C(33) – H(33B)	0.9800
C(33) – H(33C)	0.9800	C(43) – C(41)	1.521(5)

Symmetry transformations used to generate equivalent atoms: #1 $-x, y, -z + \frac{1}{2}$

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Table S54. – continued from previous page

atom – atom	distance	atom – atom	distance
C(43) – H(43A)	0.9800	C(43) – H(43B)	0.9800
C(43) – H(43C)	0.9800	C(42) – C(46)	1.526(4)
C(42) – C(45)	1.532(4)	C(42) – H(42)	1.0000
C(41) – C(44)	1.529(4)	C(41) – H(41)	1.0000
C(44) – H(44A)	0.9800	C(44) – H(44B)	0.9800
C(44) – H(44C)	0.9800	C(45) – H(45A)	0.9800
C(45) – H(45B)	0.9800	C(45) – H(45C)	0.9800
C(46) – H(46A)	0.9800	C(46) – H(46B)	0.9800
C(46) – H(46C)	0.9800	C(51) – C(53)	1.529(4)
C(51) – C(54)	1.531(4)	C(51) – H(51)	1.0000
C(52) – C(55)	1.523(5)	C(52) – C(56)	1.523(5)
C(52) – H(52)	1.0000	C(53) – H(53A)	0.9800
C(53) – H(53B)	0.9800	C(53) – H(53C)	0.9800
C(54) – H(54A)	0.9800	C(54) – H(54B)	0.9800
C(54) – H(54C)	0.9800	C(55) – H(55A)	0.9800
C(55) – H(55B)	0.9800	C(55) – H(55C)	0.9800
C(56) – H(56A)	0.9800	C(56) – H(56B)	0.9800
C(56) – H(56C)	0.9800	C(61) – C(62)	1.382(4)
C(62) – C(63)	1.387(4)	C(62) – H(62)	0.9500
C(63) – H(63)	0.9500		
Symmetry transformations used to generate equivalent atoms: #1 $-x,y,-z+\frac{1}{2}$			

Table S55. Angles [°] for [PC(sp³)HP]PdI (**11**).

atom – atom – atom	angle	atom – atom – atom	angle
C(69) – C(67) – C(61)	114.1(6)	C(69) – C(67) – C(3)#1	124.8(6)
C(61) – C(67) – C(3)#1	121.1(5)	C(69) – C(67) – C(3)	98.6(5)
C(61) – C(67) – C(3)	115.6(5)	C(3)#1 – C(67) – C(3)	57.0(4)
C(67) – C(69) – C(64)	119.0(5)	C(67) – C(69) – H(69)	120.5
C(64) – C(69) – H(69)	120.5	C(70) – C(66) – C(61)	120.9(5)
C(70) – C(66) – C(3)	120.4(6)	C(61) – C(66) – C(3)	118.5(5)
C(64) – C(70) – C(66)	120.1(6)	C(64) – C(70) – H(70)	120.0
C(66) – C(70) – H(70)	120.0	C(70) – C(64) – C(63)	123.1(4)
C(63) – C(64) – C(69)	116.5(3)	C(70) – C(64) – H(64)	118.4
C(63) – C(64) – H(64)	118.4	C(69) – C(64) – H(64)	118.6
C(11) – C(1) – C(21)	116.6(2)	C(11) – C(1) – Pd(1)	109.52(18)
C(21) – C(1) – Pd(1)	116.03(19)	C(11) – C(1) – H(1)	104.4
C(21) – C(1) – H(1)	104.4	Pd(1) – C(1) – H(1)	104.4
C(1) – Pd(1) – P(2)	84.02(8)	C(1) – Pd(1) – P(1)	82.51(8)
P(2) – Pd(1) – P(1)	155.68(3)	C(1) – Pd(1) – I(1)	171.75(8)
P(2) – Pd(1) – I(1)	98.17(2)	P(1) – Pd(1) – I(1)	98.05(2)
C(12) – P(1) – C(31)	107.58(13)	C(12) – P(1) – C(32)	106.93(13)
C(31) – P(1) – C(32)	106.07(13)	C(12) – P(1) – Pd(1)	98.88(9)
C(31) – P(1) – Pd(1)	126.19(10)	C(32) – P(1) – Pd(1)	109.73(10)
Pd(2)#1 – Pd(2) – C(3)	103.23(14)	Pd(2)#1 – Pd(2) – C(3)#1	63.79(13)
C(3) – Pd(2) – C(3)#1	39.5(3)	Pd(2)#1 – Pd(2) – P(3)#1	85.5(3)
C(3) – Pd(2) – P(3)#1	82.08(15)	C(3)#1 – Pd(2) – P(3)#1	82.34(14)
Pd(2)#1 – Pd(2) – P(3)	81.5(3)	C(3) – Pd(2) – P(3)	85.84(15)
C(3)#1 – Pd(2) – P(3)	78.03(14)	P(3)#1 – Pd(2) – P(3)	159.77(4)
Pd(2)#1 – Pd(2) – I(2)	84.447(10)	C(3) – Pd(2) – I(2)	172.19(14)
C(3)#1 – Pd(2) – I(2)	148.20(13)	P(3)#1 – Pd(2) – I(2)	97.28(4)
P(3) – Pd(2) – I(2)	96.84(4)	C(22) – P(2) – C(41)	109.72(14)
C(22) – P(2) – C(42)	104.53(14)	C(41) – P(2) – C(42)	106.38(14)
C(22) – P(2) – Pd(1)	103.82(10)	C(41) – P(2) – Pd(1)	119.19(10)
C(42) – P(2) – Pd(1)	112.27(10)	C(61) – P(3) – C(52)	105.90(15)
C(61) – P(3) – C(51)	106.11(14)	C(52) – P(3) – C(51)	107.14(14)
C(61) – P(3) – Pd(2)#1	103.64(11)	C(52) – P(3) – Pd(2)#1	115.31(11)
C(51) – P(3) – Pd(2)#1	117.68(10)	C(61) – P(3) – Pd(2)	101.32(11)
C(52) – P(3) – Pd(2)	127.68(11)	C(51) – P(3) – Pd(2)	106.91(10)
C(3)#1 – C(3) – C(66)	88.5(5)	C(3)#1 – C(3) – C(67)#1	63.1(4)
C(66) – C(3) – C(67)#1	116.1(5)	C(3)#1 – C(3) – C(67)	59.9(4)
C(67)#1 – C(3) – C(67)	97.9(5)	C(3)#1 – C(3) – Pd(2)	76.70(14)
C(66) – C(3) – Pd(2)	116.9(4)	C(67)#1 – C(3) – Pd(2)	110.4(4)
C(67) – C(3) – Pd(2)	108.1(4)	C(3)#1 – C(3) – Pd(2)#1	63.76(13)
C(66) – C(3) – Pd(2)#1	115.1(4)	C(67)#1 – C(3) – Pd(2)#1	101.8(4)

Symmetry transformations used to generate equivalent atoms: #1 –x,y,-z+ $\frac{1}{2}$

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Table S55. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(67) – C(3) – Pd(2)#1	100.5(3)	C(3)#1 – C(3) – H(3)	163.8
C(66) – C(3) – H(3)	105.9	C(67)#1 – C(3) – H(3)	103.0
C(67) – C(3) – H(3)	133.8	Pd(2) – C(3) – H(3)	102.4
Pd(2)#1 – C(3) – H(3)	114.5	C(16) – C(11) – C(12)	117.8(3)
C(16) – C(11) – C(1)	124.5(3)	C(12) – C(11) – C(1)	117.7(2)
C(13) – C(12) – C(11)	120.5(3)	C(13) – C(12) – P(1)	125.4(2)
C(11) – C(12) – P(1)	113.7(2)	C(14) – C(13) – C(12)	120.4(3)
C(14) – C(13) – H(13)	119.8	C(12) – C(13) – H(13)	119.8
C(15) – C(14) – C(13)	119.4(3)	C(15) – C(14) – H(14)	120.3
C(13) – C(14) – H(14)	120.3	C(14) – C(15) – C(16)	120.7(3)
C(14) – C(15) – H(15)	119.7	C(16) – C(15) – H(15)	119.7
C(15) – C(16) – C(11)	121.0(3)	C(15) – C(16) – H(16)	119.5
C(11) – C(16) – H(16)	119.5	C(22) – C(21) – C(26)	118.6(3)
C(22) – C(21) – C(1)	120.5(3)	C(26) – C(21) – C(1)	120.9(3)
C(21) – C(22) – C(23)	120.4(3)	C(21) – C(22) – P(2)	113.6(2)
C(23) – C(22) – P(2)	126.0(2)	C(24) – C(23) – C(22)	119.7(3)
C(24) – C(23) – H(23)	120.1	C(22) – C(23) – H(23)	120.1
C(25) – C(24) – C(23)	120.3(3)	C(25) – C(24) – H(24)	119.8
C(23) – C(24) – H(24)	119.8	C(24) – C(25) – C(26)	120.3(3)
C(24) – C(25) – H(25)	119.8	C(26) – C(25) – H(25)	119.8
C(25) – C(26) – C(21)	120.6(3)	C(25) – C(26) – H(26)	119.7
C(21) – C(26) – H(26)	119.7	C(34) – C(31) – C(33)	111.3(2)
C(34) – C(31) – P(1)	110.7(2)	C(33) – C(31) – P(1)	109.1(2)
C(34) – C(31) – H(31)	108.6	C(33) – C(31) – H(31)	108.6
P(1) – C(31) – H(31)	108.6	C(35) – C(32) – C(36)	111.3(3)
C(35) – C(32) – P(1)	109.90(19)	C(36) – C(32) – P(1)	116.2(2)
C(35) – C(32) – H(32)	106.2	C(36) – C(32) – H(32)	106.2
P(1) – C(32) – H(32)	106.2	C(32) – C(36) – H(36A)	109.5
C(32) – C(36) – H(36B)	109.5	H(36A) – C(36) – H(36B)	109.5
C(32) – C(36) – H(36C)	109.5	H(36A) – C(36) – H(36C)	109.5
H(36B) – C(36) – H(36C)	109.5	C(32) – C(35) – H(35A)	109.5
C(32) – C(35) – H(35B)	109.5	H(35A) – C(35) – H(35B)	109.5
C(32) – C(35) – H(35C)	109.5	H(35A) – C(35) – H(35C)	109.5
H(35B) – C(35) – H(35C)	109.5	C(31) – C(34) – H(34A)	109.5
C(31) – C(34) – H(34B)	109.5	H(34A) – C(34) – H(34B)	109.5
C(31) – C(34) – H(34C)	109.5	H(34A) – C(34) – H(34C)	109.5
H(34B) – C(34) – H(34C)	109.5	C(31) – C(33) – H(33A)	109.5
C(31) – C(33) – H(33B)	109.5	H(33A) – C(33) – H(33B)	109.5
C(31) – C(33) – H(33C)	109.5	H(33A) – C(33) – H(33C)	109.5
H(33B) – C(33) – H(33C)	109.5	C(41) – C(43) – H(43A)	109.5

Symmetry transformations used to generate equivalent atoms: #1 $-x, y, -z + \frac{1}{2}$

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Table S55. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
C(41) – C(43) – H(43B)	109.5	H(43A) – C(43) – H(43B)	109.5
C(41) – C(43) – H(43C)	109.5	H(43A) – C(43) – H(43C)	109.5
H(43B) – C(43) – H(43C)	109.5	C(46) – C(42) – C(45)	111.0(3)
C(46) – C(42) – P(2)	111.3(2)	C(45) – C(42) – P(2)	110.2(2)
C(46) – C(42) – H(42)	108.0	C(45) – C(42) – H(42)	108.0
P(2) – C(42) – H(42)	108.0	C(43) – C(41) – C(44)	111.5(3)
C(43) – C(41) – P(2)	109.2(2)	C(44) – C(41) – P(2)	116.8(2)
C(43) – C(41) – H(41)	106.2	C(44) – C(41) – H(41)	106.2
P(2) – C(41) – H(41)	106.2	C(41) – C(44) – H(44A)	109.5
C(41) – C(44) – H(44B)	109.5	H(44A) – C(44) – H(44B)	109.5
C(41) – C(44) – H(44C)	109.5	H(44A) – C(44) – H(44C)	109.5
H(44B) – C(44) – H(44C)	109.5	C(42) – C(45) – H(45A)	109.5
C(42) – C(45) – H(45B)	109.5	H(45A) – C(45) – H(45B)	109.5
C(42) – C(45) – H(45C)	109.5	H(45A) – C(45) – H(45C)	109.5
H(45B) – C(45) – H(45C)	109.5	C(42) – C(46) – H(46A)	109.5
C(42) – C(46) – H(46B)	109.5	H(46A) – C(46) – H(46B)	109.5
C(42) – C(46) – H(46C)	109.5	H(46A) – C(46) – H(46C)	109.5
H(46B) – C(46) – H(46C)	109.5	C(53) – C(51) – C(54)	111.0(3)
C(53) – C(51) – P(3)	115.7(2)	C(54) – C(51) – P(3)	109.0(2)
C(53) – C(51) – H(51)	106.9	C(54) – C(51) – H(51)	106.9
P(3) – C(51) – H(51)	106.9	C(55) – C(52) – C(56)	111.5(3)
C(55) – C(52) – P(3)	112.4(2)	C(56) – C(52) – P(3)	108.2(3)
C(55) – C(52) – H(52)	108.2	C(56) – C(52) – H(52)	108.2
P(3) – C(52) – H(52)	108.2	C(51) – C(53) – H(53A)	109.5
C(51) – C(53) – H(53B)	109.5	H(53A) – C(53) – H(53B)	109.5
C(51) – C(53) – H(53C)	109.5	H(53A) – C(53) – H(53C)	109.5
H(53B) – C(53) – H(53C)	109.5	C(51) – C(54) – H(54A)	109.5
C(51) – C(54) – H(54B)	109.5	H(54A) – C(54) – H(54B)	109.5
C(51) – C(54) – H(54C)	109.5	H(54A) – C(54) – H(54C)	109.5
H(54B) – C(54) – H(54C)	109.5	C(52) – C(55) – H(55A)	109.5
C(52) – C(55) – H(55B)	109.5	H(55A) – C(55) – H(55B)	109.5
C(52) – C(55) – H(55C)	109.5	H(55A) – C(55) – H(55C)	109.5
H(55B) – C(55) – H(55C)	109.5	C(52) – C(56) – H(56A)	109.5
C(52) – C(56) – H(56B)	109.5	H(56A) – C(56) – H(56B)	109.5
C(52) – C(56) – H(56C)	109.5	H(56A) – C(56) – H(56C)	109.5
H(56B) – C(56) – H(56C)	109.5	C(62) – C(61) – C(67)	123.3(4)
C(62) – C(61) – C(66)	114.2(4)	C(62) – C(61) – P(3)	126.7(2)
C(67) – C(61) – P(3)	109.1(3)	C(66) – C(61) – P(3)	115.6(3)
C(61) – C(62) – C(63)	120.1(3)	C(61) – C(62) – H(62)	119.9
C(64) – C(63) – H(63)	120.1	C(62) – C(63) – H(63)	120.1

Symmetry transformations used to generate equivalent atoms: #1 $-x, y, -z + \frac{1}{2}$

8.9 Crystal data for $[\text{PC}(\text{sp}^3)\text{H}_2\text{P}]\text{PdBr}_2 \cdot \text{CH}_2\text{Cl}_2$ ($12 \cdot \text{CH}_2\text{Cl}_2$)

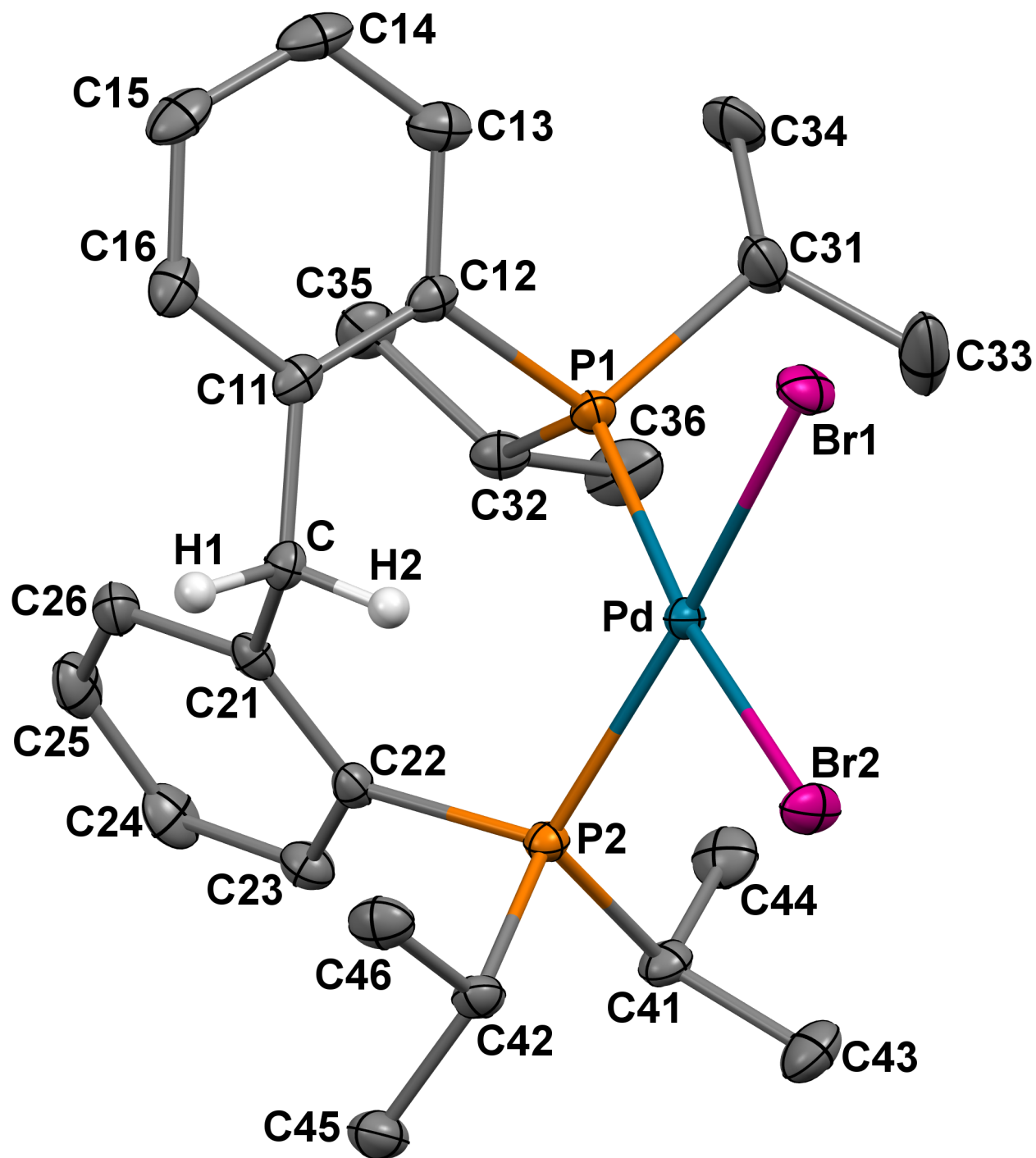


Figure S81. Thermal-ellipsoid representation of $[\text{PC}(\text{sp}^3)\text{H}_2\text{P}]\text{PdBr}_2 \cdot \text{CH}_2\text{Cl}_2$ ($12 \cdot \text{CH}_2\text{Cl}_2$) at 50% probability. Most hydrogen atoms and the solvent were omitted for clarity.

Table S56. Crystal data and structure refinement for [PC(sp³)H₂P]PdBr₂·CH₂Cl₂ (**12**·CH₂Cl₂).

Identification code:	cc298	
Empirical formula:	C ₅₁ H ₇₈ Br ₄ Cl ₂ P ₄ Pd ₂	
Formula weight:	1418.35	
Temperature:	120(2) K	
Wavelength:	0.71073 Å	
Crystal system:	Monoclinic	
Space group:	<i>P</i> 2 ₁ / <i>n</i>	
Unit cell dimensions:	<i>a</i> = 10.3876(9) Å	$\alpha = 90^\circ$
	<i>b</i> = 16.2993(14) Å	$\beta = 103.4770(14)^\circ$
	<i>c</i> = 17.0895(15) Å	$\gamma = 90^\circ$
Volume:	2813.8(4) Å ³	
Z:	2	
Density (calculated):	1.674 g·cm ⁻³	
Absorption coefficient (μ):	3.721 mm ⁻¹	
F(000):	1420	
Crystal size:	0.12 × 0.10 × 0.09 mm ³	
θ range for data collection:	1.75 to 25.00°	
Index ranges:	-12 ≤ <i>h</i> ≤ 12, -19 ≤ <i>k</i> ≤ 19, -20 ≤ <i>l</i> ≤ 20	
Reflections collected:	50587	
Independent reflections:	4956 [<i>R</i> _{int} = 0.0399]	
Completeness to $\theta = 25.00^\circ$:	100.0 %	
Absorption correction:	Semi-empirical from equivalents	
Max. and min. transmission:	0.7458 and 0.5977	
Refinement method:	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters:	4956 / 0 / 307	
Goodness-of-fit on <i>F</i> ² :	1.031	
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]:	<i>R</i> ₁ = 0.0185, <i>wR</i> ₂ = 0.0423	
<i>R</i> indices (all data):	<i>R</i> ₁ = 0.0239, <i>wR</i> ₂ = 0.0435	
Largest diff. peak and hole:	0.371 and -0.325 e ⁻ ·Å ⁻³	

Table S57. Atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$) for [PC(sp³)H₂P]PdBr₂·CH₂Cl₂ (**12**·CH₂Cl₂). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

atom	x	y	z	U(eq)
Pd	0.39516(2)	0.40354(1)	0.72121(1)	0.012(1)
Br(1)	0.49003(2)	0.54512(1)	0.73904(2)	0.022(1)
P(1)	0.61024(5)	0.35928(3)	0.72070(3)	0.015(1)
P(2)	0.27881(5)	0.28512(3)	0.68228(3)	0.013(1)
Br(2)	0.18270(2)	0.46667(1)	0.73201(2)	0.023(1)
C	0.4226(2)	0.34341(13)	0.54284(13)	0.015(1)
C(11)	0.5573(2)	0.38260(13)	0.55160(13)	0.016(1)
C(12)	0.6446(2)	0.39761(13)	0.62652(13)	0.016(1)
C(13)	0.7599(2)	0.44243(14)	0.62756(15)	0.022(1)
C(14)	0.7928(2)	0.46752(14)	0.55758(16)	0.026(1)
C(15)	0.7099(2)	0.44941(14)	0.48379(15)	0.024(1)
C(16)	0.5924(2)	0.40860(13)	0.48176(14)	0.020(1)
C(21)	0.4219(2)	0.25286(13)	0.56285(12)	0.014(1)
C(22)	0.3565(2)	0.21949(13)	0.61934(12)	0.014(1)
C(23)	0.3576(2)	0.13442(13)	0.63028(13)	0.019(1)
C(24)	0.4260(2)	0.08330(14)	0.58972(14)	0.023(1)
C(25)	0.4951(2)	0.11613(14)	0.53724(14)	0.024(1)
C(26)	0.4905(2)	0.19980(14)	0.52280(13)	0.020(1)
C(31)	0.7298(2)	0.41123(16)	0.80335(14)	0.026(1)
C(32)	0.6620(2)	0.24818(14)	0.72453(13)	0.019(1)
C(33)	0.6844(3)	0.4066(2)	0.88244(16)	0.042(1)
C(5)	0.4278(15)	0.5135(6)	0.9606(9)	0.043(3)
Cl(52)	0.34493(16)	0.41964(9)	0.96465(9)	0.045(1)
Cl(51)	0.5775(3)	0.51970(16)	1.0320(2)	0.045(1)
C(34)	0.8769(2)	0.38661(17)	0.81821(16)	0.031(1)
C(35)	0.7672(2)	0.23084(14)	0.67644(14)	0.023(1)
C(36)	0.7074(2)	0.21172(17)	0.80940(15)	0.032(1)
C(41)	0.2548(2)	0.22043(13)	0.76663(13)	0.018(1)
C(42)	0.1085(2)	0.29878(13)	0.61879(13)	0.017(1)
C(43)	0.1622(2)	0.26151(15)	0.81267(15)	0.027(1)
C(44)	0.3858(2)	0.19839(15)	0.82388(14)	0.026(1)
C(45)	0.0426(2)	0.21639(14)	0.59144(15)	0.024(1)
C(46)	0.1027(2)	0.35380(15)	0.54563(14)	0.023(1)
H(1)	0.3720	0.3511	0.4866	0.018
H(2)	0.3751	0.3733	0.5780	0.018
H(13)	0.8172	0.4560	0.6778	0.027
H(14)	0.8724	0.4972	0.5601	0.032
H(15)	0.7332	0.4648	0.4353	0.029
H(16)	0.5338	0.3980	0.4312	0.024

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Table S57. – continued from previous page

atom	x	y	x	U(eq)
H(23)	0.3104	0.1113	0.6663	0.022
H(24)	0.4255	0.0257	0.5979	0.028
H(25)	0.5456	0.0815	0.5111	0.029
H(26)	0.5351	0.2216	0.4848	0.024
H(31)	0.7263	0.4707	0.7885	0.031
H(32)	0.5815	0.2165	0.6974	0.022
H(33A)	0.5899	0.4198	0.8722	0.064
H(33B)	0.7349	0.4460	0.9210	0.064
H(33C)	0.6994	0.3511	0.9047	0.064
H(5A)	0.4447	0.5201	0.9063	0.052
H(5B)	0.3698	0.5591	0.9693	0.052
H(34A)	0.9029	0.3840	0.7667	0.046
H(34B)	0.8898	0.3327	0.8443	0.046
H(34C)	0.9314	0.4274	0.8530	0.046
H(35A)	0.7329	0.2471	0.6202	0.034
H(35B)	0.7881	0.1721	0.6790	0.034
H(35C)	0.8475	0.2623	0.6995	0.034
H(36A)	0.7010	0.1518	0.8063	0.049
H(36B)	0.6507	0.2325	0.8435	0.049
H(36C)	0.7994	0.2276	0.8325	0.049
H(41)	0.2120	0.1682	0.7433	0.021
H(42)	0.0548	0.3260	0.6529	0.021
H(43A)	0.0750	0.2697	0.7764	0.041
H(43B)	0.1991	0.3147	0.8334	0.041
H(43C)	0.1533	0.2264	0.8577	0.041
H(44A)	0.4423	0.1697	0.7942	0.038
H(44B)	0.3692	0.1627	0.8666	0.038
H(44C)	0.4302	0.2486	0.8477	0.038
H(45A)	-0.0495	0.2256	0.5627	0.036
H(45B)	0.0449	0.1816	0.6385	0.036
H(45C)	0.0903	0.1892	0.5555	0.036
H(46A)	0.1493	0.3271	0.5088	0.035
H(46B)	0.1450	0.4065	0.5633	0.035
H(46C)	0.0101	0.3631	0.5179	0.035

Table S58. Anisotropic displacement parameters ($\text{\AA}^2$) for $[\text{PC}(\text{sp}^3)\text{H}_2\text{P}]\text{PdBr}_2\cdot\text{CH}_2\text{Cl}_2$ (**12-CH₂Cl₂**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\text{h}^2\text{a}^{*2}\text{U}_{11} + \dots + 2\text{hka}^*\text{b}^*\text{U}_{12}]$.

atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Pd	0.0121(1)	0.0110(1)	0.0149(1)	-0.0023(1)	0.0049(1)	-0.0004(1)
Br(1)	0.0212(1)	0.0135(1)	0.0330(1)	-0.0074(1)	0.0082(1)	-0.0041(1)
P(1)	0.0120(3)	0.0182(3)	0.0146(3)	-0.0019(2)	0.0034(2)	0.0003(2)
P(2)	0.0133(3)	0.0115(3)	0.0153(3)	0.0000(2)	0.0050(2)	-0.0009(2)
Br(2)	0.0177(1)	0.0164(1)	0.0373(1)	-0.0073(1)	0.0125(1)	0.0012(1)
C	0.0165(11)	0.0164(11)	0.0120(11)	0.0004(9)	0.0039(9)	0.0005(9)
C(11)	0.0182(11)	0.0102(11)	0.0216(12)	0.0010(9)	0.0092(9)	0.0032(9)
C(12)	0.0158(11)	0.0131(11)	0.0214(12)	0.0000(9)	0.0081(9)	0.0020(9)
C(13)	0.0180(12)	0.0180(12)	0.0315(14)	-0.0004(10)	0.0065(10)	-0.0012(9)
C(14)	0.0216(13)	0.0198(13)	0.0425(16)	0.0060(11)	0.0162(12)	-0.0012(10)
C(15)	0.0297(14)	0.0176(12)	0.0312(14)	0.0073(10)	0.0179(12)	0.0015(10)
C(16)	0.0282(13)	0.0145(12)	0.0207(12)	0.0014(9)	0.0105(10)	0.0028(10)
C(21)	0.0128(11)	0.0150(11)	0.0131(11)	-0.0011(9)	-0.0011(9)	0.0000(9)
C(22)	0.0123(11)	0.0147(11)	0.0145(11)	-0.0028(9)	0.0013(9)	0.0007(9)
C(23)	0.0189(12)	0.0152(11)	0.0205(12)	0.0001(9)	0.0029(9)	-0.0023(9)
C(24)	0.0265(13)	0.0114(12)	0.0292(13)	-0.0045(10)	0.0022(11)	0.0036(10)
C(25)	0.0247(13)	0.0205(13)	0.0268(13)	-0.0101(10)	0.0052(11)	0.0043(10)
C(26)	0.0196(12)	0.0221(13)	0.0177(12)	-0.0050(9)	0.0046(10)	-0.0012(10)
C(31)	0.0177(12)	0.0353(15)	0.0236(13)	-0.0129(11)	0.0015(10)	-0.0005(10)
C(32)	0.0143(11)	0.0185(12)	0.0221(12)	0.0030(9)	0.0028(9)	0.0013(9)
C(33)	0.0228(14)	0.079(2)	0.0232(14)	-0.0211(14)	0.0000(11)	0.0099(14)
C(5)	0.054(5)	0.037(6)	0.044(5)	-0.004(6)	0.024(4)	0.007(6)
Cl(52)	0.0599(10)	0.0248(7)	0.0433(9)	0.0039(6)	-0.0011(7)	0.0090(7)
Cl(51)	0.0369(11)	0.0539(19)	0.0465(13)	-0.0100(15)	0.0167(8)	0.0107(15)
C(34)	0.0150(12)	0.0429(16)	0.0318(15)	-0.0126(12)	-0.0010(11)	-0.0035(11)
C(35)	0.0175(12)	0.0220(13)	0.0285(13)	-0.0015(10)	0.0053(10)	0.0060(10)
C(36)	0.0240(14)	0.0418(16)	0.0308(15)	0.0137(12)	0.0045(11)	0.0064(12)
C(41)	0.0195(12)	0.0159(12)	0.0201(12)	0.0024(9)	0.0084(10)	-0.0025(9)
C(42)	0.0119(11)	0.0199(12)	0.0209(12)	-0.0014(9)	0.0045(9)	-0.0006(9)
C(43)	0.0311(14)	0.0290(14)	0.0263(14)	0.0047(11)	0.0162(11)	-0.0003(11)
C(44)	0.0278(13)	0.0264(14)	0.0225(13)	0.0087(10)	0.0053(11)	0.0002(10)
C(45)	0.0180(12)	0.0237(13)	0.0291(13)	-0.0036(10)	0.0050(10)	-0.0046(10)
C(46)	0.0164(12)	0.0265(13)	0.0247(13)	0.0046(10)	0.0010(10)	0.0002(10)

Table S59. Distances [Å] for [PC(sp³)H₂P]PdBr₂·CH₂Cl₂ (**12**·CH₂Cl₂).

atom – atom	distance	atom – atom	distance
Pd – P(2)	2.2922(6)	Pd – P(1)	2.3497(6)
Pd – Br(2)	2.4806(3)	Pd – Br(1)	2.4999(3)
P(1) – C(12)	1.837(2)	P(1) – C(31)	1.854(2)
P(1) – C(32)	1.886(2)	P(2) – C(22)	1.832(2)
P(2) – C(41)	1.849(2)	P(2) – C(42)	1.861(2)
C – C(11)	1.513(3)	C – C(21)	1.515(3)
C – H(1)	0.9900	C – H(2)	0.9900
C(11) – C(16)	1.392(3)	C(11) – C(12)	1.407(3)
C(12) – C(13)	1.400(3)	C(13) – C(14)	1.380(3)
C(13) – H(13)	0.9500	C(14) – C(15)	1.383(4)
C(14) – H(14)	0.9500	C(15) – C(16)	1.383(3)
C(15) – H(15)	0.9500	C(16) – H(16)	0.9500
C(21) – C(26)	1.397(3)	C(21) – C(22)	1.412(3)
C(22) – C(23)	1.399(3)	C(23) – C(24)	1.382(3)
C(23) – H(23)	0.9500	C(24) – C(25)	1.380(3)
C(24) – H(24)	0.9500	C(25) – C(26)	1.385(3)
C(25) – H(25)	0.9500	C(26) – H(26)	0.9500
C(31) – C(33)	1.534(3)	C(31) – C(34)	1.542(3)
C(31) – H(31)	1.0000	C(32) – C(36)	1.536(3)
C(32) – C(35)	1.539(3)	C(32) – H(32)	1.0000
C(33) – H(33A)	0.9800	C(33) – H(33B)	0.9800
C(33) – H(33C)	0.9800	C(5) – Cl(51)	1.741(12)
C(5) – Cl(52)	1.764(11)	C(5) – H(5A)	0.9900
C(5) – H(5B)	0.9900	C(34) – H(34A)	0.9800
C(34) – H(34B)	0.9800	C(34) – H(34C)	0.9800
C(35) – H(35A)	0.9800	C(35) – H(35B)	0.9800
C(35) – H(35C)	0.9800	C(36) – H(36A)	0.9800
C(36) – H(36B)	0.9800	C(36) – H(36C)	0.9800
C(41) – C(44)	1.522(3)	C(41) – C(43)	1.532(3)
C(41) – H(41)	1.0000	C(42) – C(46)	1.528(3)
C(42) – C(45)	1.530(3)	C(42) – H(42)	1.0000
C(43) – H(43A)	0.9800	C(43) – H(43B)	0.9800
C(43) – H(43C)	0.9800	C(44) – H(44A)	0.9800
C(44) – H(44B)	0.9800	C(44) – H(44C)	0.9800
C(45) – H(45A)	0.9800	C(45) – H(45B)	0.9800
C(45) – H(45C)	0.9800	C(46) – H(46A)	0.9800
C(46) – H(46B)	0.9800	C(46) – H(46C)	0.9800

Table S60. Angles [°] for [PC(sp³)H₂P]PdBr₂·CH₂Cl₂ (**12**·CH₂Cl₂).

atom – atom – atom	angle	atom – atom – atom	angle
P(2) – Pd – P(1)	100.25(2)	P(2) – Pd – Br(2)	87.297(16)
P(1) – Pd – Br(2)	172.235(16)	P(2) – Pd – Br(1)	168.212(17)
P(1) – Pd – Br(1)	86.311(16)	Br(2) – Pd – Br(1)	86.579(10)
C(12) – P(1) – C(31)	106.23(11)	C(12) – P(1) – C(32)	104.17(10)
C(31) – P(1) – C(32)	106.08(11)	C(12) – P(1) – Pd	106.13(7)
C(31) – P(1) – Pd	109.02(8)	C(32) – P(1) – Pd	123.94(7)
C(22) – P(2) – C(41)	106.41(10)	C(22) – P(2) – C(42)	102.51(10)
C(41) – P(2) – C(42)	103.89(10)	C(22) – P(2) – Pd	112.80(7)
C(41) – P(2) – Pd	114.31(8)	C(42) – P(2) – Pd	115.71(7)
C(11) – C – C(21)	116.24(17)	C(11) – C – H(1)	108.2
C(21) – C – H(1)	108.2	C(11) – C – H(2)	108.2
C(21) – C – H(2)	108.2	H(1) – C – H(2)	107.4
C(16) – C(11) – C(12)	119.0(2)	C(16) – C(11) – C	117.6(2)
C(12) – C(11) – C	123.24(19)	C(13) – C(12) – C(11)	118.1(2)
C(13) – C(12) – P(1)	120.45(17)	C(11) – C(12) – P(1)	121.49(16)
C(14) – C(13) – C(12)	121.8(2)	C(14) – C(13) – H(13)	119.1
C(12) – C(13) – H(13)	119.1	C(13) – C(14) – C(15)	120.0(2)
C(13) – C(14) – H(14)	120.0	C(15) – C(14) – H(14)	120.0
C(16) – C(15) – C(14)	118.9(2)	C(16) – C(15) – H(15)	120.5
C(14) – C(15) – H(15)	120.5	C(15) – C(16) – C(11)	122.0(2)
C(15) – C(16) – H(16)	119.0	C(11) – C(16) – H(16)	119.0
C(26) – C(21) – C(22)	118.56(19)	C(26) – C(21) – C	117.52(19)
C(22) – C(21) – C	123.92(18)	C(23) – C(22) – C(21)	118.86(19)
C(23) – C(22) – P(2)	119.44(16)	C(21) – C(22) – P(2)	121.61(16)
C(24) – C(23) – C(22)	121.3(2)	C(24) – C(23) – H(23)	119.3
C(22) – C(23) – H(23)	119.3	C(25) – C(24) – C(23)	119.9(2)
C(25) – C(24) – H(24)	120.1	C(23) – C(24) – H(24)	120.1
C(24) – C(25) – C(26)	119.8(2)	C(24) – C(25) – H(25)	120.1
C(26) – C(25) – H(25)	120.1	C(25) – C(26) – C(21)	121.5(2)
C(25) – C(26) – H(26)	119.3	C(21) – C(26) – H(26)	119.3
C(33) – C(31) – C(34)	109.8(2)	C(33) – C(31) – P(1)	111.08(17)
C(34) – C(31) – P(1)	117.95(17)	C(33) – C(31) – H(31)	105.7
C(34) – C(31) – H(31)	105.7	P(1) – C(31) – H(31)	105.7
C(36) – C(32) – C(35)	109.48(19)	C(36) – C(32) – P(1)	115.25(17)
C(35) – C(32) – P(1)	112.96(15)	C(36) – C(32) – H(32)	106.2
C(35) – C(32) – H(32)	106.2	P(1) – C(32) – H(32)	106.2
C(31) – C(33) – H(33A)	109.5	C(31) – C(33) – H(33B)	109.5
H(33A) – C(33) – H(33B)	109.5	C(31) – C(33) – H(33C)	109.5
H(33A) – C(33) – H(33C)	109.5	H(33B) – C(33) – H(33C)	109.5
Cl(51) – C(5) – Cl(52)	112.8(6)	Cl(51) – C(5) – H(5A)	109.0
Cl(52) – C(5) – H(5A)	109.0	Cl(51) – C(5) – H(5B)	109.0

Continued on next page

Table S60. – continued from previous page

atom – atom – atom	angle	atom – atom – atom	angle
Cl(52) – C(5) – H(5B)	109.0	H(5A) – C(5) – H(5B)	107.8
C(31) – C(34) – H(34A)	109.5	C(31) – C(34) – H(34B)	109.5
H(34A) – C(34) – H(34B)	109.5	C(31) – C(34) – H(34C)	109.5
H(34A) – C(34) – H(34C)	109.5	H(34B) – C(34) – H(34C)	109.5
C(32) – C(35) – H(35A)	109.5	C(32) – C(35) – H(35B)	109.5
H(35A) – C(35) – H(35B)	109.5	C(32) – C(35) – H(35C)	109.5
H(35A) – C(35) – H(35C)	109.5	H(35B) – C(35) – H(35C)	109.5
C(32) – C(36) – H(36A)	109.5	C(32) – C(36) – H(36B)	109.5
H(36A) – C(36) – H(36B)	109.5	C(32) – C(36) – H(36C)	109.5
H(36A) – C(36) – H(36C)	109.5	H(36B) – C(36) – H(36C)	109.5
C(44) – C(41) – C(43)	110.33(19)	C(44) – C(41) – P(2)	111.89(15)
C(43) – C(41) – P(2)	111.48(15)	C(44) – C(41) – H(41)	107.6
C(43) – C(41) – H(41)	107.6	P(2) – C(41) – H(41)	107.6
C(46) – C(42) – C(45)	109.61(19)	C(46) – C(42) – P(2)	113.44(15)
C(45) – C(42) – P(2)	111.70(15)	C(46) – C(42) – H(42)	107.3
C(45) – C(42) – H(42)	107.3	P(2) – C(42) – H(42)	107.3
C(41) – C(43) – H(43A)	109.5	C(41) – C(43) – H(43B)	109.5
H(43A) – C(43) – H(43B)	109.5	C(41) – C(43) – H(43C)	109.5
H(43A) – C(43) – H(43C)	109.5	H(43B) – C(43) – H(43C)	109.5
C(41) – C(44) – H(44A)	109.5	C(41) – C(44) – H(44B)	109.5
H(44A) – C(44) – H(44B)	109.5	C(41) – C(44) – H(44C)	109.5
H(44A) – C(44) – H(44C)	109.5	H(44B) – C(44) – H(44C)	109.5
C(42) – C(45) – H(45A)	109.5	C(42) – C(45) – H(45B)	109.5
H(45A) – C(45) – H(45B)	109.5	C(42) – C(45) – H(45C)	109.5
H(45A) – C(45) – H(45C)	109.5	H(45B) – C(45) – H(45C)	109.5
C(42) – C(46) – H(46A)	109.5	C(42) – C(46) – H(46B)	109.5
H(46A) – C(46) – H(46B)	109.5	C(42) – C(46) – H(46C)	109.5
H(46A) – C(46) – H(46C)	109.5	H(46B) – C(46) – H(46C)	109.5