

The contrarotational fluxionality of [3,3-(PMe₂Ph)₂-*closo*-3,1,2-PtC₂B₉H₁₁] and related species
Supplementary information

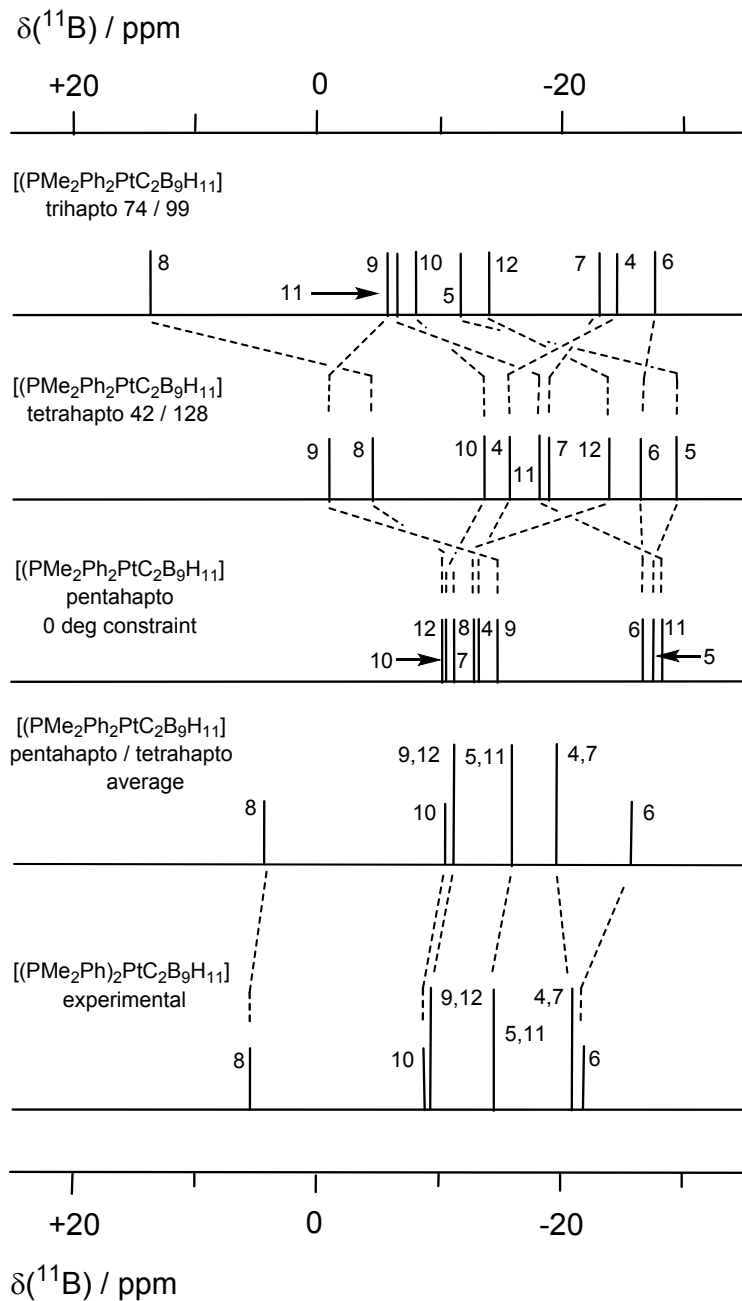
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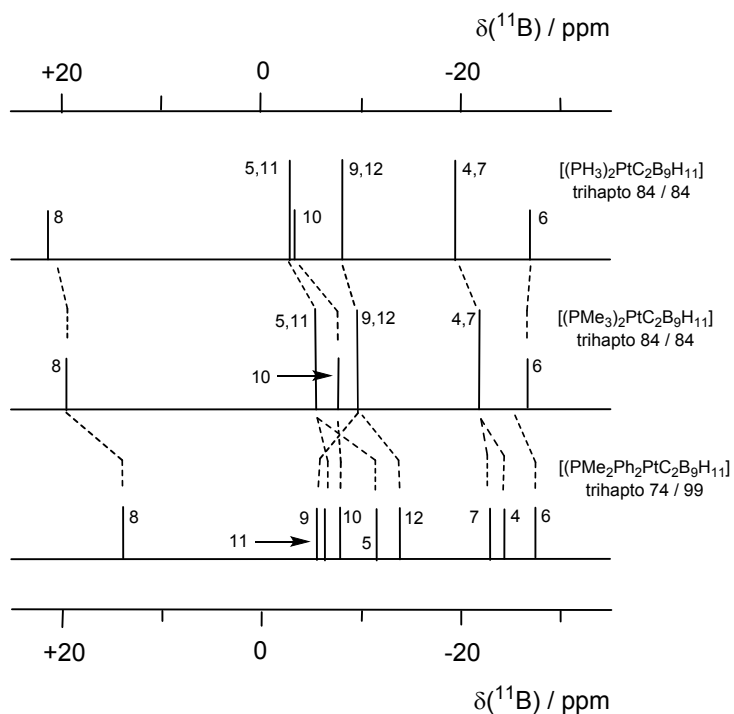
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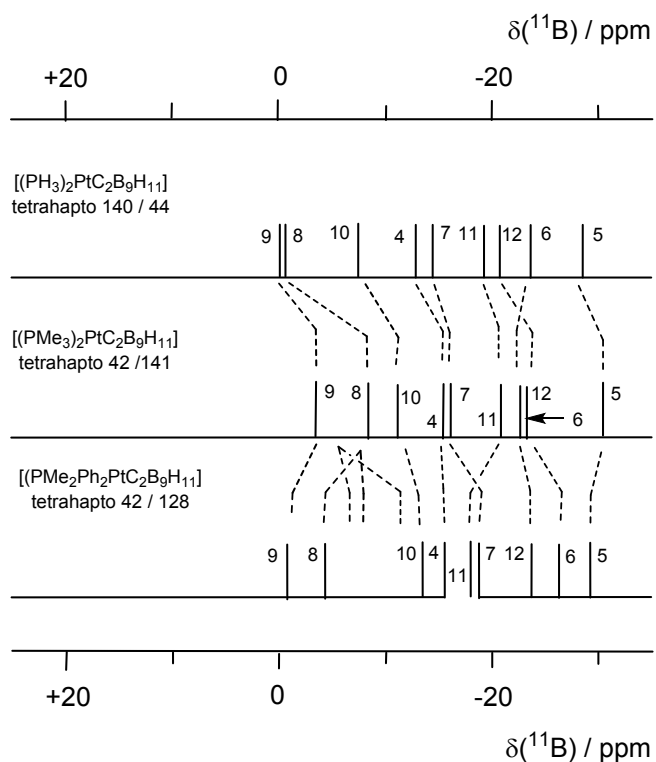
Supplementary plot S1. Representations of the boron nuclear magnetic shieldings, expressed as ^{11}B NMR chemical shifts $\delta(^{11}\text{B})$, and relative intensities, as calculated for the *trihapto*, *tetrahapto* and *pentahapto* conformations of $[(\text{PMe}_2\text{Ph})_2\text{PtC}_2\text{B}_9\text{H}_{11}]$ (upper three diagrams), the mean of the *trihapto* and *tetrahapto* values (fourth diagram), and the experimentally determined ^{11}B NMR chemical shift values $\delta(^{11}\text{B})$ for $[(\text{PMe}_2\text{Ph})_2\text{PtC}_2\text{B}_9\text{H}_{11}]$ (bottom diagram; data from reference 15).



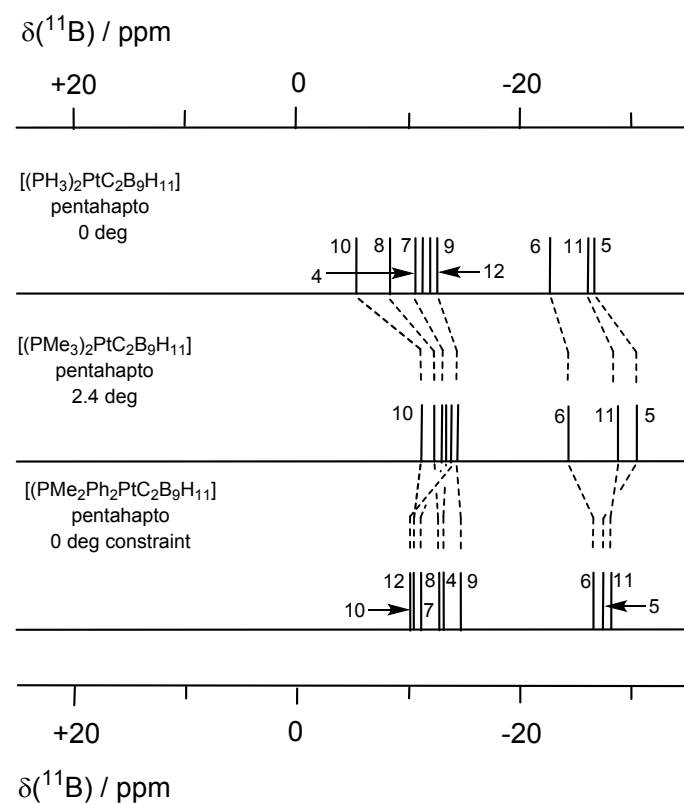
Supplementary plot S2. Representations of the boron nuclear magnetic shieldings, expressed as ^{11}B NMR chemical shifts $\delta(^{11}\text{B})$, and relative intensities, as calculated for the *trihapto* conformations of $[(\text{PH}_3)_2\text{PtC}_2\text{B}_9\text{H}_{11}]$ (top diagram) $[(\text{PMe}_3)_2\text{PtC}_2\text{B}_9\text{H}_{11}]$ (middle diagram) and $[(\text{PMe}_2\text{Ph})_2\text{PtC}_2\text{B}_9\text{H}_{11}]$ (lower diagram). Figure 6 in the text displays the same data, but with each of the (4,7), (5,11) and (9,12) pairs averaged and combined to reflect that they will be exchanging positions by libration across the notional $\text{Pt}(3)\text{B}(6)\text{B}(8)\text{B}(10)$ plane.



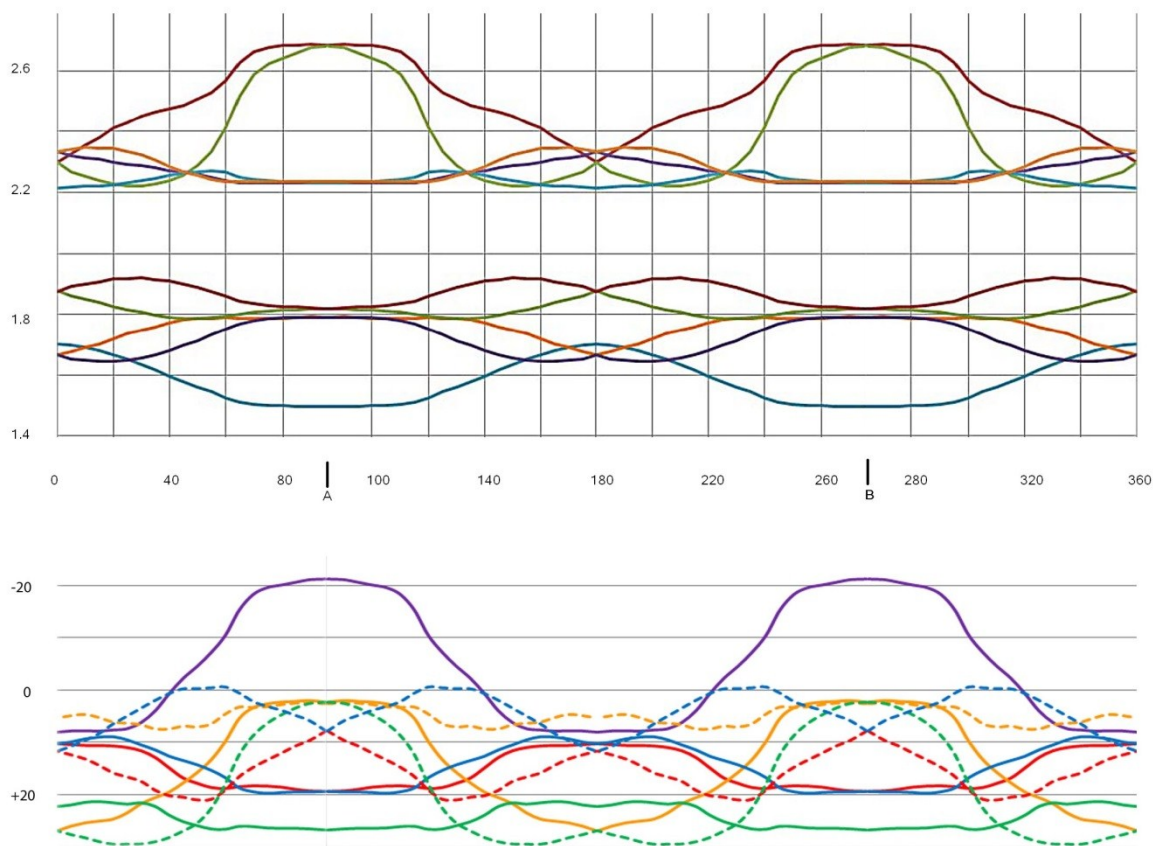
Supplementary plot S3. Representations of the boron nuclear magnetic shieldings, expressed as ^{11}B NMR chemical shifts $\delta(^{11}\text{B})$, and relative intensities, as calculated for the *tetrahapto* conformations of $[(\text{PH}_3)_2\text{PtC}_2\text{B}_9\text{H}_{11}]$ (top diagram) $[(\text{PMe}_3)_2\text{PtC}_2\text{B}_9\text{H}_{11}]$ (middle diagram) and $[(\text{PMe}_2\text{Ph})_2\text{PtC}_2\text{B}_9\text{H}_{11}]$ (lower diagram)



Supplementary plot S4. Representations of the boron nuclear magnetic shieldings, expressed as ^{11}B NMR chemical shifts $\delta(^{11}\text{B})$, and relative intensities, as calculated for the *pentahapto* conformations of $[(\text{PH}_3)_2\text{PtC}_2\text{B}_9\text{H}_{11}]$ (top diagram) $[(\text{PMe}_3)_2\text{PtC}_2\text{B}_9\text{H}_{11}]$ (middle diagram) and $[(\text{PMe}_2\text{Ph})_2\text{PtC}_2\text{B}_9\text{H}_{11}]$ (lower diagram)



Supplementary Figure S5. A representation to illustrate the general overall 360° rotational behaviour of calculated parameters for the model compound [3,3-(PH₃)₂-*clos*o-3,1,2-PtC₂B₉H₁₁]. Upper diagram: interatomic distances in Å. Lower diagram: boron nuclear shieldings as $\delta(^{11}\text{B})/\text{ppm}$. The curves are derived from combinations of the diagrams in Figure 5 and Figure 8 in the main text and their mirrorings. There are C1/C2, B4/B7, B5/B12 and B9/B11 coincidences at the 0° and 180° points, and at the notional 90° and 120° points **A** and **B**. Because of the nature of the calculational incrementation based on the dihedral angle, and because there is cluster flexing, and in addition the dihedral angle does not map directly onto the simplistic projection angle θ of schematic structure **XI**, the defining quarter-rotation occurs over 84°. In this particular representation, therefore, there is an effective 12° ‘compression’ around the notional 90° and 270° points **A** and **B**.



Supplementary Table 1. Comparisons of calculated structures of [Pt(C₂B₉H₁₁)(PH₃)₂] (global minimum), [Pt(C₂B₉H₁₁)(PMe₃)₂] (global minimum), and [Pt(C₂B₉H₁₁)(PPhMe₂)₂] (global minimum) with the crystal structures of [Pt(C₂B₉H₁₁)(PEt₃)₂] and [Pt(C₂B₉H₁₁)(PPhMe₂)₂] (75° conformer). Distances (Å), angles (deg) and torsions (deg).

	Calc 84/84 (PH ₃) ₂	Calc 84/84 (PMe ₃) ₂	Calc 74/99 (PPhMe ₂) ₂	JDK 75/99 (PPhMe ₂) ₂	Mogos 67/96 (PEt ₃) ₂
Dihedral 1	84.102	84.469	73.786	74.90(47)	66.89(2)
Dihedral 2	84.053	84.393	98.788	98.95(45)	95.66(2)
Pt(3)–C(1)	2.684	2.705	2.612	2.529(7)	2.529(16)
Pt(3)–C(2)	2.684	2.705	2.674	2.574(7)	2.612(52)
Pt(3)–B(4)	2.235	2.265	2.254	2.266(8)	2.282(30)
Pt(3)–B(7)	2.235	2.265	2.268	2.260(7)	2.278(40)
Pt(3)–B(8)	2.232	2.235	2.249	2.269(49)	2.264(15)
C(1)–C(2)	1.496	1.499	1.506	1.495(10)	1.529(30)
C(2)–B(7)	1.791	1.764	1.754	1.712(11)	1.742(2)
B(7)–B(8)	1.819	1.812	1.818	1.804(12)	1.809(24)
B(8)–B(4)	1.819	1.812	1.803	1.783(12)	1.803(20)
B(4)–C(1)	1.791	1.764	1.769	1.746(17)	1.755(2)
Pt(3)–P(A)	2.277	2.294	2.310	2.260(2)	2.284(27)
Pt(3)–P(B)	2.277	2.294	2.286	2.271(2)	2.275(46)
P–Pt–P	100.799	104.493	95.261	92.33(6)	98.36(1)

Supplementary Table 2. Comparisons of calculated structures of [Pt(C₂B₉H₁₁)(PH₃)₂] (dihedral constrained to 42.5°), [Pt(C₂B₉H₁₁)(PH₃)₂] (dihedral constrained to 130° [mirror imaged for comparison]), [Pt(C₂B₉H₁₁)(PMe₃)₂] (secondary minimum, no constraints) [Pt(C₂B₉H₁₁)(PPhMe₂)₂] (41° constrained from crystal structure) with the crystal structure of [Pt(C₂B₉H₁₁)(PPhMe₂)₂] (41° conformer). Distances (Å), angles (deg) and torsions (deg).

	Calc 43/127 (PH ₃) ₂	Calc 130/55 (PH ₃) ₂ mirror	Calc 42/141 (PMe ₃) ₂	Calc 52/124 (PPhMe ₂) ₂	Calc 42/128 (PPhMe ₂) ₂	exp JDK 41/129 (PPhMe ₂) ₂
Dihedral 1	42.5	54.593	42.006	51.889	41.647	41.65(52)
Dihedral 2	126.518	130.00	141.266	124.061	127.622	129.38(43)
Pt(3)–C(1)	2.292	2.289	2.274	2.331	2.327	2.303(7)
Pt(3)–C(2)	2.520	2.507	2.532	2.551	2.553	2.515(7)
Pt(3)–B(4)	2.259	2.259	2.275	2.269	2.278	2.283(9)
Pt(3)–B(7)	2.269	2.255	2.326	2.282	2.294	2.307(7)
Pt(3)–B(8)	2.257	2.268	2.257	2.265	2.258	2.265(7)
C(1)–C(2)	1.564	1.561	1.586	1.553	1.563	1.570(10)
C(2)–B(7)	1.704	1.712	1.664	1.696	1.689	1.668(11)
B(7)–B(8)	1.892	1.890	1.890	1.871	1.876	1.826(10)
B(8)–B(4)	1.789	1.785	1.798	1.792	1.790	1.788(12)
B(4)–C(1)	1.780	1.787	1.750	1.758	1.750	1.737(12)
Pt(3)–P(A)	2.297	2.294	2.310	2.313	2.317	2.288(2)
Pt(3)–P(B)	2.243	2.243	2.261	2.267	2.264	2.235(2)
P–Pt–P	96.809	96.912	97.799	95.964	95.111	93.11(6)

Supplementary Table 3. NMR chemical shifts for [Pt(C₂B₉H₁₁)(PH₃)₂], [Pt(C₂B₉H₁₁)(PMe₃)₂] and [Pt(C₂B₉H₁₁)(PPhMe₂)₂]. The shifts are presented relative to *D*_{2h} B₂H₆ [PBE1PBE 6-311+G(2d,p), optimized at the PBE1PBE/6-31G(d) level] which has a calculated shielding tensor of 86.5889, converted to 16.6 ppm vs BF₃·OEt₂. The values in the (PH₃)₂ column were obtained from a mirror-image of the original calculation for comparative purposes *i.e.* the dihedral was constrained to 140°. Catch my drift?

	(PH ₃) ₂ 84/84	(PMe ₃) ₂ 84/84	(PPhMe ₂) ₂ 74/99	(PH ₃) ₂ 140/44	(PMe ₃) ₂ 42/141	(PPhMe ₂) ₂ 42/128	experimental NMR data
C(1)	67.8171	62.8406	61.3264	42.6277	39.0519	46.0702	
C(2)	67.8403	62.8605	55.6402	40.1228	35.9277	37.6189	
B(4)	-19.3326	-22.8671	-23.5011	-12.6254	-15.3748	-15.8695	
B(5)	-2.3080	-5.2104	-11.5289	-28.1213	-30.5719	-28.7001	
B(6)	-26.6930	-26.9458	-27.5828	-23.8858	-22.5786	-23.8244	
B(7)	-19.3232	-22.8744	-21.6836	-14.8701	-16.4550	-18.3725	
B(8)	21.1992	19.1140	14.3727	-0.6672	-8.4806	-4.1542	
B(9)	-7.8053	-9.7095	-5.1479	-0.6514	-3.6759	-0.6842	
B(10)	-2.5705	-7.8423	-7.7864	-7.4206	-11.5733	-13.0359	
B(11)	-2.3078	-5.2182	-5.4953	-19.4407	-20.3478	-18.1216	
B(12)	-7.7813	-9.6772	-14.6894	-20.172	-22.6017	-23.8976	

Supplementary Table 4. NMR chemical shifts for [Pt(C₂B₉H₁₁)(PH₃)₂], [Pt(C₂B₉H₁₁)(PMe₃)₂] and [Pt(C₂B₉H₁₁)(PPhMe₂)₂]. The shifts are presented relative to *D*_{2h} B₂H₆ [PBE1PBE 6-311+G(2d,p), optimized at the PBE1PBE/6-31G(d) level] which has a calculated shielding tensor of 86.5889, converted to 16.6 ppm vs BF₃·OEt₂. “TS” for the last column is not a verified TS but a constrained ‘perpendicular’ optimization (0 deg)

	(PH ₃) ₂ TS	(PMe ₃) ₂ TS	(PPhMe ₂) ₂ “TS”
C(1)	43.0148	35.785	37.8550
C(2)	43.0025	35.9483	35.4377
B(4)	-10.2653	-12.4723	-13.7168
B(5)	-26.8662	-28.6766	-27.3464
B(6)	-22.2061	-24.32	-23.7567
B(7)	-10.2618	-12.8585	-11.5123
B(8)	-8.0174	-11.9065	-13.0364
B(9)	-11.6435	-13.2254	-14.7923
B(10)	-5.3207	-10.7927	-10.5579
B(11)	-26.8602	-28.0336	-28.0498
B(12)	-11.6435	-13.6861	-10.2064

Supplementary Table 5. [(PMe₃)₂PtC₂B₉H₁₁] nuclear magnetic shielding calculations

opt/freq/minimum at 84.47 deg

		ref	corr	final
C1	124.4908	187.3314	0	62.8406
C2	124.4709	187.3314	0	62.8605
Pt3	94.2083			
B4	126.056	86.5889	16.6	-22.8671

B5	108.3993	86.5889	16.6	-5.2104
B6	130.1347	86.5889	16.6	-26.9458
B7	126.0633	86.5889	16.6	-22.8744
B8	84.0749	86.5889	16.6	19.114
B9	112.8984	86.5889	16.6	-9.7095
B10	111.0312	86.5889	16.6	-7.8423
B11	108.4071	86.5889	16.6	-5.2182
B12	112.8661	86.5889	16.6	-9.6772
P25	317.4401	582.563	-266	-0.8771
P24	317.4015	582.563	-266	-0.8385

Higher minimum at 42.01 deg

		ref	corr	final
C1	148.2795	187.3314	0	39.0519
C2	151.4037	187.3314	0	35.9277
Pt3	88.3219			
B4	118.5637	86.5889	16.6	-15.3748
B5	133.7608	86.5889	16.6	-30.5719
B6	125.7675	86.5889	16.6	-22.5786
B7	119.6439	86.5889	16.6	-16.455
B8	111.6695	86.5889	16.6	-8.4806
B9	106.8648	86.5889	16.6	-3.6759
B10	114.7622	86.5889	16.6	-11.5733
B11	123.5367	86.5889	16.6	-20.3478
B12	125.7906	86.5889	16.6	-22.6017
P25	293.7617	582.563	-266	22.8013
P24	339.7368	582.563	-266	-23.1738

Transition state at 2.4 deg

		ref	corr	final
C1	151.5464	187.3314	0	35.785
C2	151.3831	187.3314	0	35.9483
Pt3	91.7402			
B4	115.6612	86.5889	16.6	-12.4723
B5	131.8655	86.5889	16.6	-28.6766
B6	127.5089	86.5889	16.6	-24.32
B7	116.0474	86.5889	16.6	-12.8585
B8	115.0954	86.5889	16.6	-11.9065
B9	116.4143	86.5889	16.6	-13.2254
B10	113.9816	86.5889	16.6	-10.7927
B11	131.2225	86.5889	16.6	-28.0336
B12	116.875	86.5889	16.6	-13.6861
P13	340.4051	582.563	-266	-23.8421
P14	279.7969	582.563	-266	36.7661

Supplementary Table 6. [(PMe₂Ph)₂PtC₂B₉H₁₁] nuclear magnetic shielding calculations

full optimization starting from X-ray result: 'parallel' conformation

		ref	corr	final
C1	126.0050	187.3314	0.0000	+61.3264
C2	131.6912	187.3314	0.0000	+55.6402
Pt3	96.6839			
B4	126.6900	86.5889	16.6000	-23.5011
B5	114.7178	86.5889	16.6000	-11.5289
B6	130.7717	86.5889	16.6000	-27.5828
B7	124.8725	86.5889	16.6000	-21.6836
B8	88.8162	86.5889	16.6000	+14.3727

B9	108.3368	86.5889	16.6000	-5.1479
B10	110.9753	86.5889	16.6000	-7.7864
B11	108.6842	86.5889	16.6000	-5.4953
B12	117.8783	86.5889	16.6000	-14.6894
P13	302.8393	582.5630	-266.0000	+13.7237
P14	313.0859	582.5630	-266.0000	+3.4771

PM₂Ph starting from X-ray result, one angle constr. 41.647 deg: ‘diagonal’ conformation

		ref	corr	final
C1	141.2611	187.3314	0.0000	+46.0703
C2	149.7125	187.3314	0.0000	+37.6189
Pt3	94.1103			
B4	119.0584	86.5889	16.6000	-15.8695
B5	131.8890	86.5889	16.6000	-28.7001
B6	127.0133	86.5889	16.6000	-23.8244
B7	121.5614	86.5889	16.6000	-18.3725
B8	107.3431	86.5889	16.6000	-4.1542
B9	103.8731	86.5889	16.6000	-0.6842
B10	116.2248	86.5889	16.6000	-13.0359
B11	121.3105	86.5889	16.6000	-18.1216
B12	127.0865	86.5889	16.6000	-23.8976
P1	323.6159	582.5630	-266.0000	-7.0529
P2	280.0446	582.5630	-266.0000	+36.5184

angle constrained to 0 deg; ‘perpendicular’ conformation

		ref	corr	final
C1	149.4764	187.3314	0.0000	+37.8550
C2	151.8937	187.3314	0.0000	+35.4377
Pt3	96.5043			
B4	116.9057	86.5889	16.6000	-13.7168
B5	130.5353	86.5889	16.6000	-27.3464
B6	126.9456	86.5889	16.6000	-23.7567
B7	114.7012	86.5889	16.6000	-11.5123
B8	116.2253	86.5889	16.6000	-13.0364
B9	117.9812	86.5889	16.6000	-14.7923
B10	113.7468	86.5889	16.6000	-10.5579
B11	131.2387	86.5889	16.6000	-28.0498
B12	113.3953	86.5889	16.6000	-10.2064
P1	329.5430	582.5630	-266.0000	-12.9800
P2	269.0471	582.5630	-266.0000	+47.5159

Supplementary citation information (reference XX)

Gaussian 03, Revision B.04, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi,

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