

**Supplementary data. Calculated coordinates for 1a and 5a and pictures of 160 MHz  $^{11}\text{B}$  and  $^{11}\text{B}\{-^1\text{H}\}$  NMR spectra for species 1a, 3 and 5.**

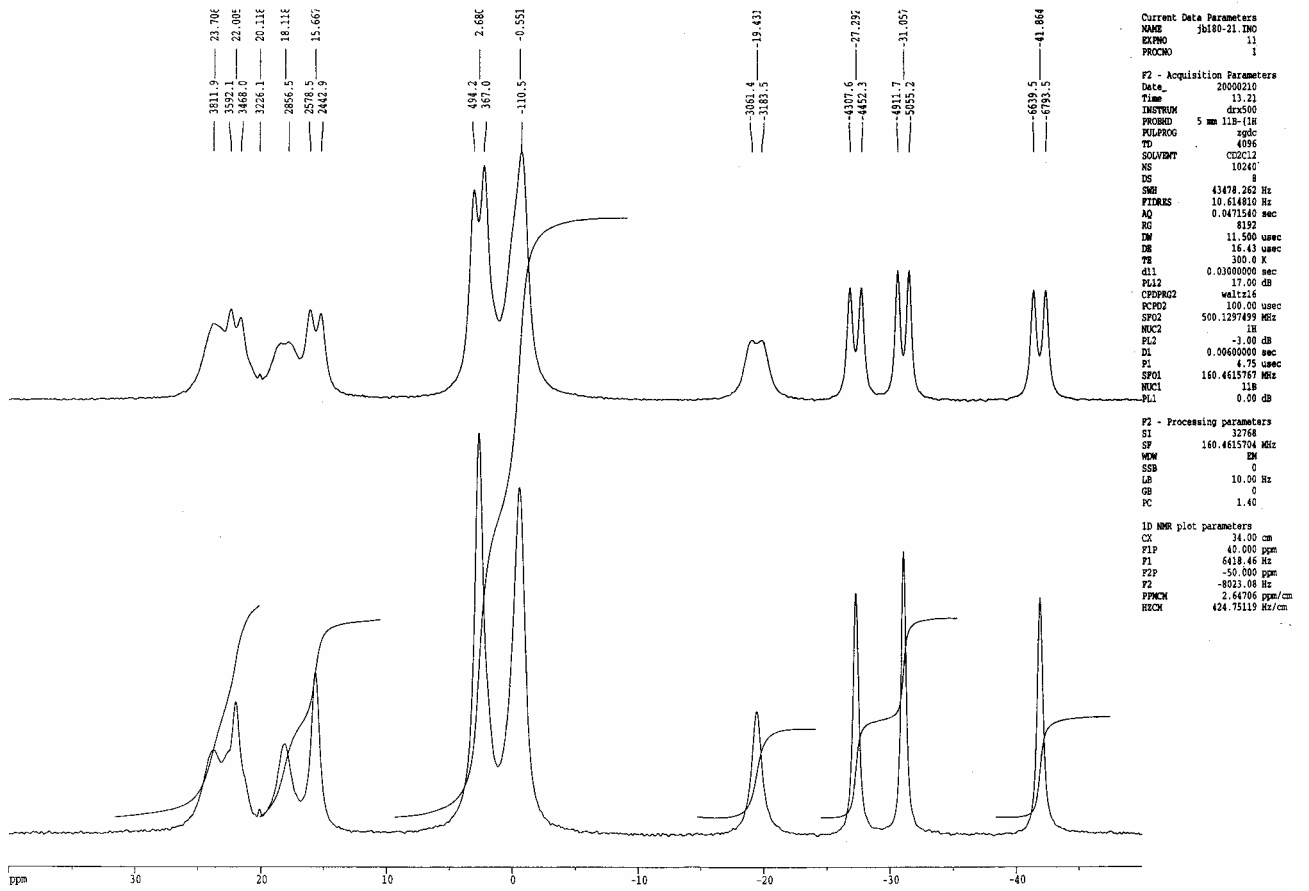
**Calculated coordinates [ DFT; B3LYP / 6-31G\* ] for the  $[\text{B}_{16}\text{H}_{19}]^-$  monoanion 1a**

B,0,1.2334640778,-0.7724246898,1.2691607424  
H,0,1.2139084951,-1.4512399459,2.2504908336  
B,0,0.2933431831,0.7347591134,1.1833411711  
B,0,2.0443693619,0.825346687,1.1150972956  
B,0,2.8339617284,-0.6346731439,0.4300122036  
B,0,-0.1348270145,-0.7097411758,0.2055482951  
B,0,1.4883592456,-1.5736013239,-0.286392005  
H,0,-0.2840765037,1.1241816249,2.1546821021  
H,0,2.6151463922,1.431491017,1.9712545633  
H,0,3.8066532223,-1.0876679723,0.9501392201  
B,0,-0.4030421983,0.8858997992,-0.4092127353  
B,0,1.0843167606,1.8027138903,-0.0091861293  
B,0,2.8113735104,0.9153457747,-0.4570920002  
B,0,2.6777229298,-0.6747330681,-1.2750849861  
H,0,1.4576217313,-1.0858581099,-1.5303656357  
H,0,1.4611673985,-2.7566960028,-0.4272186658  
B,0,-1.1676048285,-0.5071081381,-1.1785387806  
B,0,-1.7480318639,-1.4605625322,0.2710114502  
H,0,0.5762185231,1.4544370696,-1.147809989  
H,0,1.106024427,2.9940746684,0.0063923333  
H,0,3.7585497655,1.6038561393,-0.6773481855  
H,0,2.3647922817,0.5559460386,-1.6582856903  
H,0,3.4349621128,-1.1293748267,-2.0726688956  
H,0,-0.8418689359,-1.0554943644,-2.1907415839  
B,0,-2.8817420019,-0.4399136045,-0.7382254424  
B,0,-1.9587446846,1.1018732914,-1.0816776989  
B,0,-3.1065843761,-0.4472841571,0.9828911562  
H,0,-1.9299174627,-0.9582223554,1.4533714785  
H,0,-1.8891564432,-2.6454867152,0.3214152143  
H,0,-3.705795889,-0.9139390005,-1.4637176365  
H,0,-2.1402857251,1.7203191798,-2.0946341565  
B,0,-3.1135501911,1.0669268193,0.1414487239  
H,0,-2.7187873994,0.7412984326,1.4020253515  
H,0,-3.9838951677,-0.8836966926,1.6615071982  
H,0,-4.0651790161,1.7779541071,0.2760058418

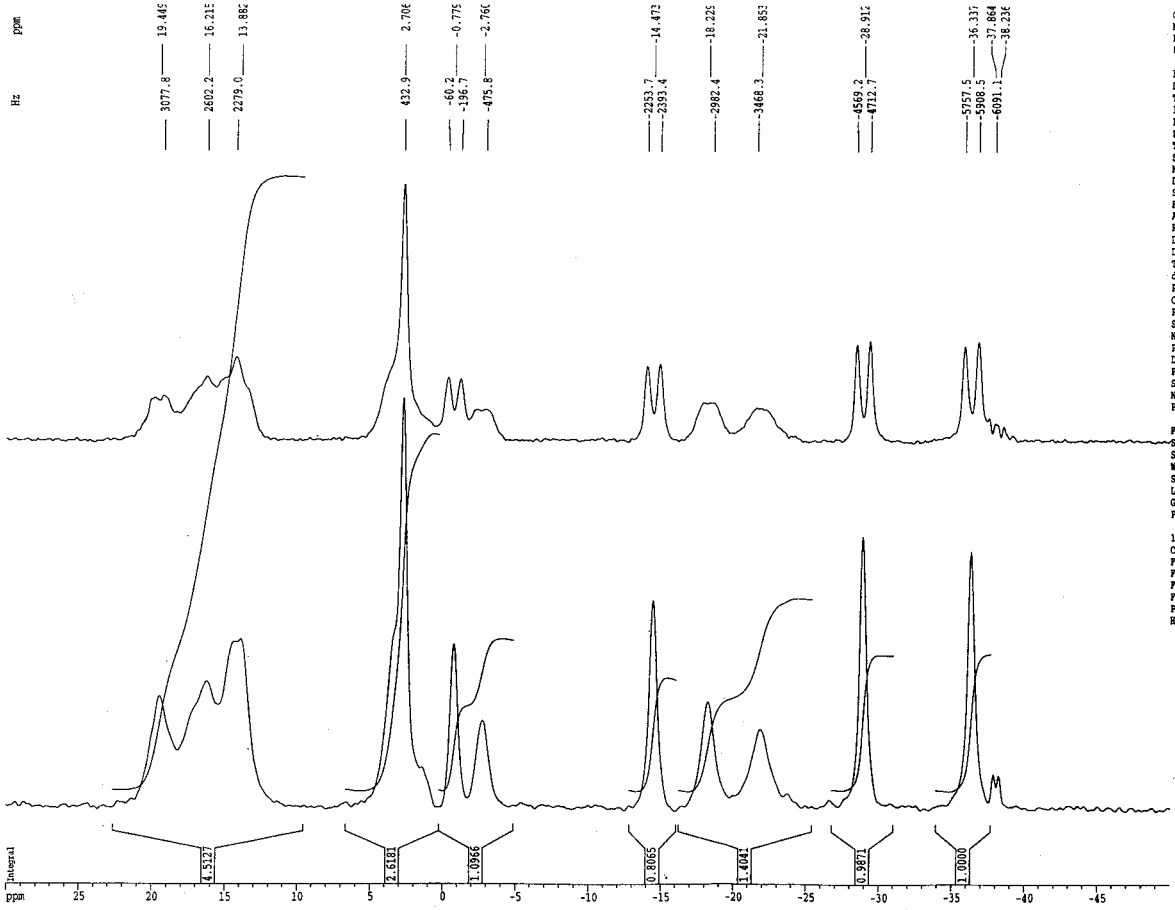
**Calculated coordinates [DFT; B3LYP / 6-31G\* / LANL2DZ ] for [(PH<sub>3</sub>)<sub>2</sub>PtB<sub>14</sub>H<sub>16</sub>] (species 5a)**

H,0,-2.5795015563,2.802980021,-2.5658468398  
B,0,-2.5795645839,2.8029790123,-1.1668702811  
B,0,-1.2889537511,2.8029969513,-2.4148813385  
B,0,-0.5086340088,1.1644436918,-2.2145949894  
B,0,-1.0045128409,2.1758127255,-0.8122423701  
H,0,-3.1339297469,3.807238663,-0.8650850917  
B,0,-2.4892481166,1.3591644361,-0.2270247962  
H,0,-3.3595130373,1.6947298429,-1.1743044492  
H,0,-1.1312989009,1.836087136,-3.240689844  
H,0,-0.8167627384,3.7941214975,-2.8627235866  
B,0,-1.2302559361,-0.4615229203,-2.3964961064  
B,0,0.3035411255,-0.0170935132,-3.2212201195  
B,0,-1.3438479793,0.3390419275,-0.8385634406  
B,0,1.3836260843,0.9860659261,-2.2560569248  
H,0,-0.2280568447,2.716067574,-0.0898250096  
H,0,-3.0191333549,1.4530569569,0.8370229442  
Pt,0,0.2664711036,-0.387768912,0.7548561538  
B,0,0.11196440456,-1.6123712192,-2.4649872256  
H,0,-2.2332201338,-0.6399701201,-3.0159772114  
B,0,-0.7994783388,-1.398386351,-0.955736196  
B,0,1.6902619293,-0.7699336781,-2.4020260493  
H,0,0.3198315604,0.2064336497,-4.3910513635  
B,0,1.922128391,-0.0261848806,-0.8288219207  
H,0,1.4253318984,1.1957073142,-0.9664891377  
H,0,2.0575286237,1.8420533902,-2.7345221561  
P,0,2.0624419688,-0.0651988632,2.2711392996  
P,0,-1.5067446997,-0.5299303205,2.3462499885  
H,0,-0.0158667378,-2.6132876341,-3.0959813459  
H,0,-1.5211079793,-2.2553343804,-0.5437156756  
B,0,1.0460100993,-1.5981082551,-0.9780784721  
H,0,2.6294955751,-1.1797697857,-3.0075079315  
H,0,3.0142439125,0.1208996122,-0.3682163777  
H,0,3.1448572782,-0.9540238455,2.1184465314  
H,0,2.7559712735,1.1583560333,2.1809066869  
H,0,-1.2782741716,-1.3697050498,3.4610689343  
H,0,-2.7147017709,-1.0807689394,1.8830171848  
H,0,-2.0051929846,0.5975094798,3.0327271229  
H,0,1.5809616148,-2.5631805351,-0.5213712493  
H,0,1.922952504,-0.1308072507,3.6784996985

160 MHz  $^{11}\text{B}$  (upper trace) and  $^{11}\text{B}\{-^1\text{H}\}$  (lower trace) spectra for  $[(\text{PMe}_2\text{Ph})_2\text{PtB}_{14}\text{H}_{16}]$  (compound 5)



160 MHz <sup>11</sup>B (upper trace) and <sup>11</sup>B-{<sup>1</sup>H} (lower trace) spectra for [(PMe<sub>2</sub>Ph)<sub>2</sub>PtB<sub>16</sub>H<sub>17</sub>Me] (compound 3)  
(line narrowed)



Current Data Parameters  
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 PROCNO 1

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 SOLVENT CDCl3  
 NS 32768  
 DS 8  
 SSB 43478.262 Hz  
 P1DRMS 10.614810 Hz  
 AQ 0.0471540 sec  
 RG 574.7  
 DM 11.500 usec  
 DE 16.43 usec  
 TS 300.0 K  
 d11 0.03000000 sec  
 PL12 21.00 dB  
 CPOPRG2 waltz16  
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 SFO2 500.1297499 MHz  
 NUC2 1H  
 PL2 0.00 dB  
 IH 0.0000000 sec  
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 SFO1 160.4615767 MHz  
 NUC1 11B  
 PL1 0.00 dB

F2 - Processing parameters  
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 LB -30.00 Hz  
 GB 0.15  
 PC 1.40

ID NMR plot parameters  
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 PIP 30.000 ppm  
 PI 4813.85 Hz  
 PIZ -50.000 ppm  
 FZ -8023.08 Hz  
 PPRCM 2.35294 ppm/cm  
 BSCM 377.55661 Hz/cm

160 MHz  $^{11}\text{B}$  (upper trace) and  $^{11}\text{B}\{-^1\text{H}\}$  (lower trace) spectra for the  $[\text{B}_{16}\text{H}_{19}]^-$  anion (species 1a) as its  $[\text{C}_{10}\text{H}_{16}(\text{NMe}_2)_2\text{H}]^+$  salt 1b

