Supplementary information for:

Unprecedented Borane, Diborane(3), Diborene and Borylene Ligands via Pt-Mediated Borane Dehydrogenation

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Experimental methods

Physical Methods: NMR spectra were recorded on a Bruker Avance 400 spectrometer at 296 K. Chemical shifts (δ) are given in ppm, and are referenced against external Me_4Si (^1H, ^{13}C), 85% H_3PO_4 (^{31}P); $Na_2[PtCl_6]$ in D_2O (^{195}Pt), or $BF_3{\cdot}Et_2O$ (^{11}B). Elemental analyses for C, H, and N were obtained on either a LecoCHNS-932 or a Carlo Erba Model 1106 instrument.

Materials: The precursors $[Pt(PCy_3)_2]$,[1] $[Pt(nbe)_2(PCy_3)]$,[2] and H_2BDur,[3] were prepared by established methods. All manipulations were performed in dried glassware under a dry argon atmosphere using glovebox or standard Schlenk-line techniques. Pentane and tetrahydrofuran were dried over and distilled from alkali metals and stored under argon over molecular sieves (4 Å). C_6D_6 was degassed by three freeze-pump-thaw cycles and stored under argon over molecular sieves (4 Å).

Equimolar reaction of $DurBH_2$ and $[Pt(PCy_3)_2]$: Dihydrodurylborane (19.4 mg, 0.132 mmol) was dissolved in THF (12 mL) and added dropwise over a period of 60 minutes to a 70 °C solution of $[Pt(PCy_3)_2]$ (100 mg, 0.132 mmol) in THF (15 mL). The colorless reaction mixture turned dark red during stirring over a period of 30 minutes. The $^{31}P\{^1H\}$ NMR showed the formation of *trans*-$[PtH_2(PCy_3)_2]$ (**1**) and $Cy_3P{\rightarrow}BH_2Dur$ (**2**). The solvent was removed in vacuum and the most of the side products were separated by washing the solid with cold pentane (–78 °C). By fractional crystallisation at –35 °C in pentane a dark red crystal was obtained, suitable for diffraction, of the trinuclear π-diborene Pt complex **3** and a twinned crystal of poor quality of the tetranuclear tris(bridging borylene) Pt complex **4**. Due to the very low yield of complexes **3** and **4**, their instability in solution over a longer period and their high molar masses it was not possible to fully characterize them. A signal of higher order was observed (52.1-11.7 ppm) in the $^{31}P\{^1H\}$ NMR spectrum of **4**, while in the ^1H NMR the signals for the aryl protons of the duryl moieties also fit well (6.96, 1H, C*H*, bridging Dur; 6.81, 2H, C*H*, borylene moieties). However, we

were able to obtain fitting elemental analyses for both **3** and **4**. **Elemental analysis** (%) calcd. for $C_{74}H_{125}B_2P_3Pt_3$ (**3**) (1714.56 g·mol^{-1}): C 51.84, H 7.35; found: C 51.41, H 7.40. **Elemental analysis** (%) calcd. for $C_{102}H_{167}B_3P_4Pt_4$ (**4**) (2330.12 g·mol^{-1}): C 52.58, H 7.22; found: C 52.96, H 7.69.

$Cy_3P{\rightarrow}BH_2Dur$ (2): The phosphine–borane adduct **2** is the side product of the syntheses of **1, 3**-6. Adduct **2** was independently synthesized without side-products by mixing equimolar amounts of PCy_3 (60.0 mg, 0.214 mmol) and BH_2Dur (31.3 mg, 0.214 mmol) in toluene. After removing the solvent under vacuum, **2** was isolated as a colorless solid (yield 85.8 mg, 94%). **^{1}H NMR** (400.13 MHz, C_6D_6, 24 °C): δ = 6.97 (s, 1H, C*H*, H_2BDur), 3.21-2.40 (vbr s, 2H, *H*$_2$BDur), 2.73 (s, 6H, C*H*$_3^{ortho}$, BDur), 2.36 (s, 6H, C*H*$_3^{meta}$, BH_2Dur), 1.99-1.88 (m, 3H, Cy), 1.83-1.48 (m, 15H, Cy), 1.40-1.26 (m, 6H, Cy), 1.12-0.97 (m, 9H, Cy); **^{13}C{^{1}H} NMR** (100.61 MHz, C_6D_6, 24 °C): δ = 139.2 (s, C^q, Dur), 132.4 (s, C^q, Dur), 129.4 (s, C^q, Dur), 129.3 (br s, *C*H, Dur), 33.5 (m, C^{3,5}, Cy), 28.3 (m, C^1, Cy), 27.9 (m, C, Cy), 26.6 (m, C^4, Cy), 21.7 (br s, CH_3^{ortho}, BH_2Dur), 21.4 (br s, CH_3^{meta}, BH_2Dur); **^{11}B{^{1}H} NMR** (128.38 MHz, C_6D_6, 24 °C): δ = –29.9 (br s, *B*H_2Dur); **^{31}P{^{1}H} NMR** (161.98 MHz, C_6D_6, 24 °C): δ = 13.6 (s, *P*Cy_3). **Elemental analysis** (%) calcd for $C_{28}H_{48}BP$ (426.48 g·mol^{-1}): C 78.86, H 11.35; found: C 78.76, H 11.23.

[{(Cy_3P)HPt}$_2$(μ-H){μ:η^2-B_2Dur_2(μ-H)}] (5): [Pt(PCy_3)$_2$] (100 mg, 0.132 mmol) and BH_2Dur (38.7 mg, 0.265 mmol) were dissolved in THF (24 mL) in a Schlenk flask and stirred for 6 min at 68 °C under continuous stirring, whereby the color changed from light yellow to light brown. The solvent was removed under reduced pressure and the solid was extracted with pentane (2 mL) at –78 °C. The side product $Cy_3P{\rightarrow}BH_2Dur$ is poorly soluble at low temperatures. The solvent was evaporated under reduced pressure. **5** was crystallized and isolated from fluorobenzene at –30 °C as a yellow solid (yield 67.5 mg, 41%). **^{1}H NMR** (400.13 MHz, C_6D_6, 24 °C): δ = 6.94 (s, 1H, C*H*, BDur), 3.79-3.39 (m, 1H, $(DurB)_2$(μ-*H*)), 2.83 (s, 12H, C*H*$_3^{ortho}$, BDur), 2.22 (s, 12H, C*H*$_3^{meta}$, BH_2Dur), 2.15-2.06 (m, 6H, Cy), 2.04-1.95 (m, 12H, Cy), 1.77-1.59 (m, 18H, Cy), 1.50-1.36 (m, 12H, Cy), 1.30-1.08 (m, 18H, Cy), –4.38 (m, 1H,

[$(Cy_3P)HPt]_2${μ-*H*}), –4.68 (m, 2H, [$(PCy_3)(*H*)Pt]_2${μ-H}); **$^{13}C\{^1H\}$ NMR** (100.61 MHz, C_6D_6, 24 °C): δ = 139.1 (br s, C^q, Dur), 132.9 (s, C^q, Dur), 131.2 (s, *C*H, Dur), 37.0 (m, C^1, Cy), 30.8 (m, $C^{3,5}$, Cy), 28.0 (m, $C^{2,6}$, Cy), 26.7 (m, C^4, Cy), 20.7 (br s, CH_3^{ortho}, BDur), 21.1 (s, CH_3^{meta}, BDur); **$^{11}B\{^1H\}$ NMR** (128.38 MHz, C_6D_6, 24 °C): δ = 11.7 (br s, *B*Dur); **$^{31}P\{^1H\}$ NMR** (161.98 MHz, C_6D_6, 24 °C): δ = 46.7 (s + d, $^1J_{PPt}$ = 2661 Hz). **Elemental analysis** (%) calcd. for $C_{56}H_{96}B_2P_2Pt_2$ (1243.12 g·mol^{-1}): C 54.11, H 7.78; found: C 54.71, H 8.13.

[{$(Cy_3P)Pt}_2$(μ-BDur)(η^2:μ-HBHDur)] (6): [$Pt(PCy_3)_2$] (100 mg, 0.132 mmol) and BH_2Dur (38.7 mg, 0.265 mmol) were dissolved in THF (24 mL) in a Schlenk flask and stirred for 170 min at 68 °C under continuous stirring, whereby the color changed from light yellow to brown. The solvent was removed under reduced pressure and the solid was extracted with pentane (2 mL) at –78°C. The side product $Cy_3P{\rightarrow}BH_2Dur$ is poorly soluble at low temperatures. The solvent was evaporated under reduced pressure. **6** was crystallized and isolated from fluorobenzene at –30 °C as a yellow solid (yield 60.8 mg, 37%). **^{1}H NMR** (400.13 MHz, C_6D_6, 24 °C): δ = 7.06 (s, 1H, C*H*, BDur), 6.92 (s, 1H, C*H*, BH_2Dur), 4.98 (vbr s, 2H, B*H*$_2$Dur), 2.78 (s, 6H, C*H*$_3^{ortho}$, BDur), 2.55 (s, 6H, C*H*$_3^{ortho}$, BH_2Dur), 2.35 (s, 6H, C*H*$_3^{meta}$, BDur), 2.21 (s, 6H, C*H*$_3^{meta}$, BH_2Dur), 1.19-1.16 (m, 30H, Cy), 1.60-1.53 (m, 6H, Cy), 1.42-1.30 (m, 12H, Cy), 1.12-0.93 (m, 18H, Cy); **$^1H\{^{11}B\}$ NMR** (400.13 MHz, C_6D_6, 24 °C): δ = 4.98 (m, 2H, B*H*$_2$Dur); all other signal as in previous spectrum. **$^{13}C\{^1H\}$ NMR** (100.61 MHz, C_6D_6, 24 °C): δ = 146.8 (s, C^q, Dur), 134.4 (br s, *C*H, BDur), 133.8 (s, C^q, Dur), 132.2 (s, C^q, Dur), 131.3 (s, C^q, Dur), 130.4 (br s, *C*H, BH_2Dur), 36.2 (m, C^1, Cy), 30.6 (m, $C^{3,5}$, Cy), 27.8 (m, $C^{2,6}$, Cy), 26.7 (m, C^4, Cy), 22.4 (br s, CH_3^{ortho}, BDur), 21.6 (br s, CH_3^{meta}, BDur), 19.3 (br s, CH_3^{ortho}, BH_2Dur), 19.2 (br s, CH_3^{meta}, BH_2Dur); **$^{11}B\{^1H\}$ NMR** (128.38 MHz, C_6D_6, 24 °C): δ = 101.3 (br s, *B*Dur), 32.8 (br s, H_2*B*Dur); **$^{31}P\{^1H\}$ NMR** (161.98 MHz, C_6D_6, 24 °C): δ = 58.6 (s + AA'XX' spin system). **Elemental analysis** (%) calcd. for $C_{56}H_{94}B_2P_2Pt_2$ (1241.10 g·mol^{-1}): C 54.19, H 7.63; found: C 54.53, H 7.63.

Syntheses of 5 and 6 from [(Cy_3P)Pt($nbe)_2$]: A solution of BH_2Dur (33 mg, 0.226 mmol) in THF (2 mL) was added dropwise to a solution of [(Cy_3P)Pt($nbe)_2$] (50 mg, 0.075 mmol) in benzene (1 mL) in a Schlenk flask and stirred at room temperature for 20 min to obtain **5**, The solvent was removed under reduced pressure and the solid was extracted with pentane (2 mL) at –78 °C to remove the norbornene hydroboration products. The solvent was evaporated under reduced pressure, and **5** was crystallized from fluorobenzene at –30 °C as a yellow solid (yield: 27%). Alternatively, after mixing the borane and Pt complex, the reaction could be stirred overnight at 40 °C, and worked up in an identical manner to obtain **6** as a yellow solid (yield: 26%).

Synthesis of 6 from 5: Redissolving **5** in thf or benzene leads quantitatively to **6** after 5 days in solution at room temperature or after one hour at 68 °C.

Crystallographic Details

The crystal data of **2** were collected on a BRUKER D8 QUEST diffractometer with a CMOS area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using the intrinsic phasing method (SHELXT), refined with the SHELXLprogram[4] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealized geometric positions. The unit cell contains a solvent molecule which has been treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON. Crystal data for **2**: $C_{28}H_{48}BP$, $M_r = 426.44$, colorless block, 0.126×0.061×0.059 mm^3, monoclinic space group $P21/c$, $a = 18.5671(8)$ Å, $b = 9.4261(4)$ Å, $c = 16.3054(7)$ Å, $\beta = 95.198(2)°$, $V = 2842.0(2)$ $Å^3$, $Z = 4$, $\rho_{calcd} = 0.997$ $g \cdot cm^{-3}$, $\mu = 0.108$ mm^{-1}, $F(000) = 944$, $T = 100(2)$ K, $R_1 = 0.0694$, $wR^2 = 0.1084$, 6071 independent reflections [$2\theta \leq 53.634°$] and 283 parameters.

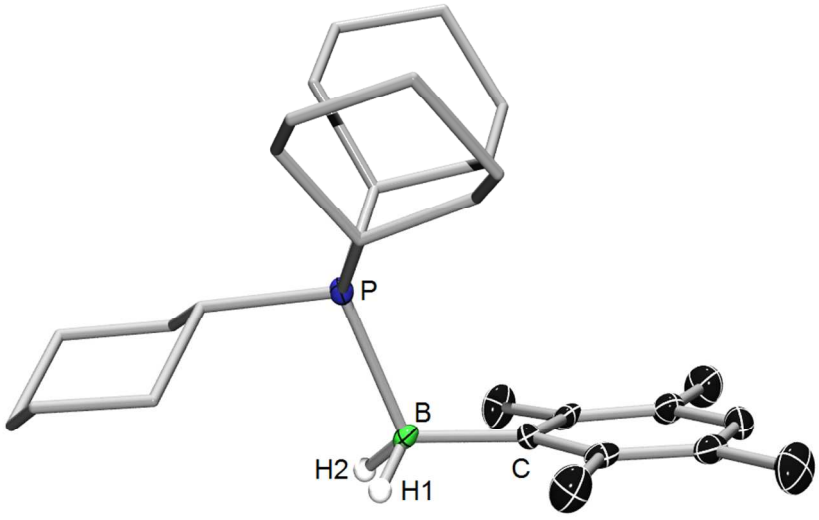


Figure S1. Crystallographically derived structure of **2**. Thermal ellipsoids drawn at the 50% probability level. Some ellipsoids have been omitted for clarity. The displayed hydrogen atoms of **2** were

crystallographically located. Selected bond lengths [Å] and angles [°]: B–P 1.973(2), B–H1 1.15(2), B–H2 1.12(2), B–C1 1.615(2); P–B–C 116.2(1).

The crystal data of **3** were collected on a BRUKER X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using the intrinsic phasing method (SHELXT), refined with the SHELXLprogram[4] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealized geometric positions. The atoms C27 to C32a and C52 to C57a reported least-squares restraints as shown by _refine_ls_number_restraints key are attributed to DELU keyword in ShelXL input ('rigid bond' restraint for all bonds in the connectivity list; standard values of 0.01 for both parameters s1 and s2 were used). The displacement parameters of atoms C27 to C32a and C52 to C57a of two cyclohexyl groups were restrained to the same value with the similarity restraint SIMU. The Uii displacement parameters of atoms C11 to C20 and C52 to C57a were restrained with the ISOR keyword to approximate isotropic behavior. Crystal data for **3**: $C_{79}H_{136}B_2P_3Pt_3$, $M_r = 1785.67$, red block, $0.20\times0.15\times0.08$ mm^3, monoclinic space group $P21/n$, $a = 12.093(4)$ Å, $b = 28.983(9)$ Å, $c = 23.083(9)$ Å, $\beta = 104.494(16)°$, $V = 7833(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.514$ g·cm^{-3}, $\mu = 5.446$ mm^{-1}, $F(000) = 3596$, $T = 100(2)$ K, $R_1 = 0.0283$, $wR^2 = 0.0520$, 15432 independent reflections [$2\theta\leq52.044°$] and 903 parameters.

The crystal data of **4** were collected on a Bruker D8 Quest diffractometer with a CMOS area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using intrinsic phasing method (ShelXT), refined with the ShelXLprogram[4] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factors calculations. All hydrogen atoms were assigned to idealised geometric positions. Crystal data for **4**: $C_{87}H_{107}B_2P_4Pt_4$, $M_r = 2078.58$, red needle, $0.164\times0.028\times0.024$ mm^3, monoclinic space group $C2/c$,

a = 32.313(13) Å, b = 23.810(10) Å, c = 32.076(17) Å, β = 98.809(18)°, V = 24388(19) Å^3, Z = 12, ρ_{calcd} = 1.698 g·cm^{-3}, μ = 6.983 mm^{-1}, F(000) = 12132, T = 100(2) K, R_1 = 0.1426, wR^2 = 0.2161, 19897 independent reflections [2θ≤53.014°] and 537 parameters.

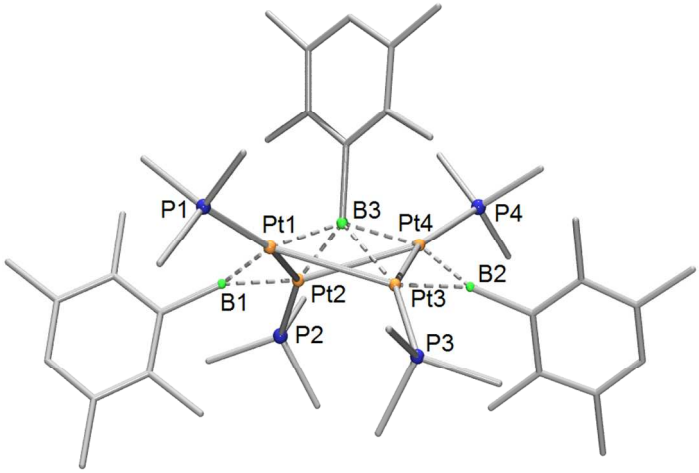


Figure S2. Crystallographically derived structure of **4**. Thermal ellipsoids drawn at the 50% probability level. Some atoms and ellipsoids have been omitted for clarity.

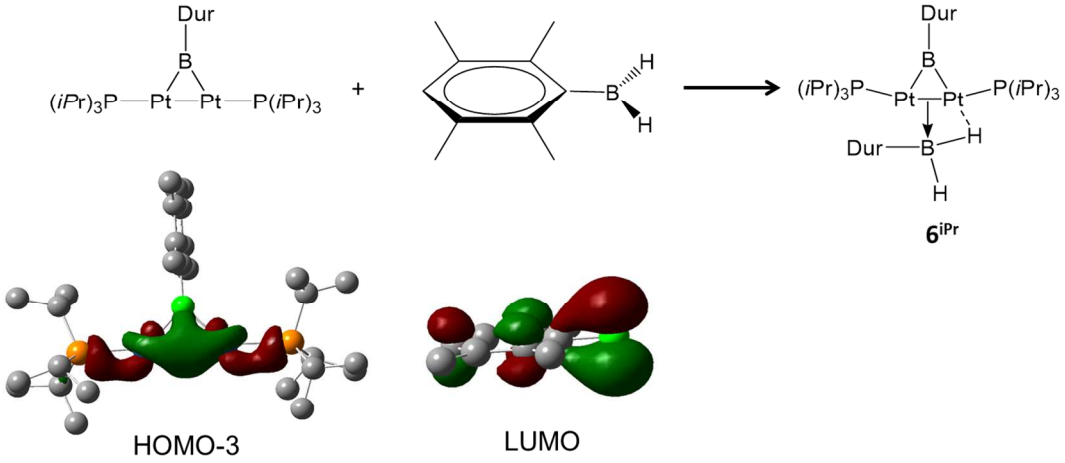
The crystal data of **5** were collected on a BRUKER D8 QUEST diffractometer with a CMOS area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using the intrinsic phasing method (SHELXT), refined with the SHELXLprogram[4] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealized geometric positions. The Uii displacement parameters of atoms C41 to C46 were restrained with the ISOR keyword to approximate isotropic behavior. Crystal data for **5**: $C_{56}H_{96}B_2P_2Pt_2$, M_r = 1243.06, yellow block, 0.112×0.088×0.058 mm^3, orthorhombic space group *Pbca*, a = 17.7835(6) Å, b = 23.3497(8) Å, c = 26.3882(10) Å, V = 10957.4(7) Å^3, Z = 8, ρ_{calcd} = 1.507 g·cm^{-3}, μ = 5.194 mm^{-1}, F(000) = 5024, T = 100(2) K, R_1 = 0.0759, wR^2 = 0.0647, 11674 independent reflections [2θ≤53.604°] and 583 parameters.

The crystal data of **6** were collected on a BRUKER D8 QUEST diffractometer with a CMOS area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using the intrinsic phasing method (SHELXT), refined with the SHELXLprogram[4] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealized geometric positions. Crystal data for **6**: $C_{56}H_{94}B_2P_2Pt_2$, $M_r = 1241.05$, orange block, $0.217\times0.19\times0.093$ mm^3, triclinic space group P-1, $a = 11.7378(5)$ Å, $b = 13.3757(6)$ Å, $c = 18.8912(9)$ Å, $\alpha = 73.2040(15)°$, $\beta = 88.2731(15)°$, $\gamma = 68.6040(15)°$, $V = 2634.3(2)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.565$ g·cm^{-3}, $\mu = 5.401$ mm^{-1}, $F(000) = 1252$, $T = 100(2)$ K, $R_1 = 0.0239$, $wR^2 = 0.0456$, 11173 independent reflections [$2\theta\leq53.608°$] and 575 parameters.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-1422418 (**2**), -1422419 (**3**), -1422420 (**5**), -1422421 (**6**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

Computational Details

All calculations were carried out in the Gaussian 09 software suite.[5] For computational efficiency, the ligands on compounds **5** and **6** were simplified as described below. The methods and basis sets employed are individually given in each instance in the figures below. Frequency analyses on all computationally minimized structures presented in the manuscript were shown to be true minima with no imaginary frequencies.



	E	G
$(PiPr_3)_2Pt_2(B[Dur])$	-2045.666969	-2045.753236
$H_2B(Dur)$	-414.810984	-414.847397
6^{iPr}	-2460.510644	-2460.607028

ΔE_{rxn} = –20.5 kcal/mol
ΔG_{rxn} = –4.0 kcal/mol

Figure S3. Calculated bond energy for the dative bond in $\mathbf{6^{iPr}}$, a simplified analogue of **6** wherein the PCy_3 groups have been replaced by $PiPr_3$ ligands, along with the relevant donor/acceptor orbitals present in the optimized fragments. Calculations were carried out at the B3LYP/6-311+G(d) level for all small atoms and with the LANL2DZ pseudopotential for Pt. The tabulated energies are in Hartrees.

Table S1. Optimized coordinates for the structures in Figure S3.

[($iPr_3P)_3Pt_2$(BDur)]

Pt	-1.34764200	-0.70672500	0.00716800

Pt	1.34772500	-0.70669700	-0.00709100
P	3.70943000	-0.76990900	-0.02314300
P	-3.70938400	-0.77005600	0.02303900
B	0.00000900	0.73917000	-0.00003200
C	-0.00008500	2.29420600	-0.00004400
C	0.12326500	2.99869500	-1.21976400
C	-0.12349600	2.99868800	1.21967400
C	0.11752100	4.40299300	-1.21801800
C	-0.11796000	4.40298400	1.21791300
C	-0.00027500	5.07398100	-0.00005500
H	-0.00034400	6.16195400	-0.00005700
C	-4.40295900	-1.82718700	-1.37996400
C	-3.93745400	-3.28405400	-1.22216000
C	-5.89937300	-1.75727700	-1.71744600
H	-3.85272700	-1.40966800	-2.23131700
H	-4.44963300	-3.79072600	-0.39962000
H	-2.86157700	-3.34998900	-1.04274200
H	-6.52774600	-2.16921500	-0.92711200
H	-6.23627100	-0.73983800	-1.91914900
C	-4.32269800	0.99628000	-0.23394600
C	-4.01692000	1.46724000	-1.66369500
C	-5.76088100	1.33579900	0.18087700
H	-3.64981300	1.54586700	0.43336800
H	-4.67091400	0.99383500	-2.40186400
H	-2.98120600	1.25715700	-1.93825700
H	-6.51065300	0.82035200	-0.42239000
H	-5.95653500	1.10690300	1.23016500
C	-4.43816700	-1.30370600	1.68603400
C	-5.89258600	-1.79672600	1.71751000
C	-3.51749800	-2.31995800	2.38333200
H	-4.37974400	-0.37029200	2.26085700
H	-5.99364100	-2.77096300	1.23378000
H	-6.59412200	-1.11139200	1.24230100
H	-3.51919300	-3.28649000	1.87155300
H	-2.48531500	-1.96667700	2.42144300
C	4.32265600	0.99635600	0.23441100
C	4.01651600	1.46693100	1.66421400
C	5.76091800	1.33606100	-0.17996500
H	3.64990800	1.54610000	-0.43292000
H	4.67044900	0.99346000	2.40239400
H	2.98078600	1.25657500	1.93852400
H	6.51056200	0.82045100	0.42332500
H	5.95683200	1.10751600	-1.22928000
C	4.40298600	-1.82735000	1.37967700
C	3.93765200	-3.28423100	1.22151000
C	5.89938300	-1.75739900	1.71727200
H	3.85268300	-1.41002800	2.23107700
H	4.44983800	-3.79058500	0.39877900
H	2.86177100	-3.35028600	1.04216500
H	6.52784700	-2.16925200	0.92696200
H	6.23622000	-0.73995000	1.91905200
C	4.43836300	-1.30308000	-1.68621500
C	5.89279500	-1.79605000	-1.71769100
C	3.51776700	-2.31913500	-2.38389400

H	4.38000000	-0.36949500	-2.26076800
H	5.99380000	-2.77050900	-1.23439400
H	6.59423000	-1.11091000	-1.24205800
H	3.51958700	-3.28586900	-1.87249400
H	2.48554100	-1.96596600	-2.42180400
C	-0.25286600	2.25580900	2.53080000
H	-1.15279000	2.55783600	3.07826400
H	-0.30472700	1.17613600	2.38422600
H	0.59597500	2.46010200	3.19403000
C	-0.23618400	5.18853700	2.50242700
H	-1.18047300	4.98868300	3.02100800
H	0.56328100	4.94090400	3.20902200
H	-0.18736700	6.26311500	2.31270700
C	0.23566100	5.18855700	-2.50253100
H	0.18688500	6.26313400	-2.31279600
H	1.17989900	4.98868500	-3.02119500
H	-0.56387300	4.94095700	-3.20906300
C	0.25282900	2.25581400	-2.53086500
H	1.15277400	2.55792700	-3.07824600
H	0.30480300	1.17614900	-2.38426700
H	-0.59597100	2.46000300	-3.19418100
H	4.17019700	2.54785400	1.74056600
H	5.92789600	2.41094400	-0.05069900
H	-4.17078500	2.54815900	-1.73975900
H	-5.92793700	2.41071500	0.05198500
H	-6.09402100	-2.34371400	-2.62256200
H	-4.15694400	-3.84794600	-2.13468100
H	-6.21331400	-1.92492300	2.75725700
H	-3.86148000	-2.49411000	3.40887300
H	3.86172500	-2.49285700	-3.40951500
H	6.21367300	-1.92376000	-2.75745200
H	6.09399500	-2.34387900	2.62236800
H	4.15730300	-3.84833600	2.13386200

H_2BDur

C	-0.00002100	-1.58653900	-0.00000400
C	-1.23046300	-0.92795400	0.00001200
C	-1.23471800	0.47549700	0.00004400
C	0.00001900	1.19215600	0.00000100
C	1.23473000	0.47546400	-0.00004700
C	1.23044100	-0.92798900	-0.00001800
H	-0.00003600	-2.67418700	-0.00000300
B	0.00007100	2.73147300	0.00001000
H	-1.01255300	3.36082500	0.00015300
H	1.01275000	3.36074400	-0.00012000
C	-2.55893400	1.21425000	0.00010900
H	-2.66131800	1.85926200	0.87577400
H	-2.66154500	1.85900700	-0.87572200
H	-3.40581600	0.53041400	0.00031500
C	-2.49733900	-1.75664000	0.00000700
H	-3.11841700	-1.56287800	0.87991300

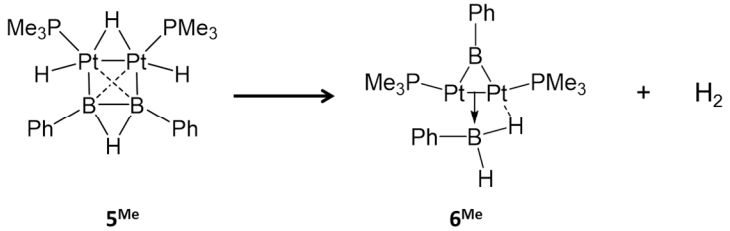
H	-3.11850000	-1.56273300	-0.87980800
H	-2.26001000	-2.82252100	-0.00009000
C	2.55893900	1.21422400	-0.00010900
H	2.66130700	1.85925100	-0.87576400
H	2.66154200	1.85897500	0.87572900
H	3.40583200	0.53040300	-0.00032600
C	2.49728800	-1.75672000	-0.00000900
H	3.11837500	-1.56298700	-0.87991600
H	3.11845500	-1.56283600	0.87980600
H	2.25992000	-2.82259300	0.00009000

6$^{i\mathrm{Pr}}$

Pt	1.22946700	-1.05690300	-0.31034600
P	3.52751000	-1.59240500	-0.20656200
C	-4.07186200	1.83751300	-1.30068100
H	-4.55312700	0.85734600	-1.22567800
Pt	-1.10533400	0.24199300	-0.18421200
P	-2.87994700	1.79393800	0.16646300
C	-3.99165800	1.33940000	1.63844000
H	-4.44118500	2.28126600	1.97703200
C	-3.15899200	0.74672800	2.78807700
H	-2.74574700	-0.22202300	2.50055400
H	-2.32342700	1.37805800	3.08954100
H	0.19573600	-2.78282200	-0.43728100
C	-5.12300900	0.36284500	1.28525000
H	-4.74150500	-0.56629900	0.85607600
H	-5.85464600	0.78485700	0.59433900
C	-2.15447300	-2.39588500	-0.34844600
C	-2.31198000	-2.85138200	0.99661500
C	-3.53183400	-3.39143900	1.43314700
C	-4.60222200	-3.44957800	0.54018300
H	-5.54366700	-3.87788400	0.87764300
C	-4.51021600	-2.97694000	-0.76609000
B	-0.71221000	-2.04271800	-0.93285300
C	-3.28939000	-2.43604500	-1.21348900
C	-3.22552600	-1.97053200	-2.65347200
H	-4.12413400	-1.41313700	-2.93267000
H	-3.16336300	-2.82370500	-3.34106000
H	-2.36394600	-1.34155100	-2.85054900
C	-5.71587600	-3.08153900	-1.67266800
H	-5.49101200	-3.62600200	-2.59542800
H	-6.09477000	-2.09894500	-1.97628600
H	-6.53424600	-3.60488300	-1.17303800
C	-3.71379600	-3.93344600	2.83350400
H	-4.70064700	-4.38766700	2.94896600
H	-3.62349000	-3.15213300	3.59643800
H	-2.96929000	-4.69744100	3.07896100
C	-1.15671300	-2.81378800	1.97190200
H	-1.49743200	-2.63536500	2.99451300
H	-0.43770400	-2.03758300	1.71675600
H	-0.61508600	-3.76873900	1.98199200
C	4.61195500	-0.79509200	-1.52044900
H	5.59094900	-1.28235600	-1.46911600

C	4.81769300	0.70576300	-1.27911000
H	5.37967900	0.90976100	-0.36517600
H	3.87004800	1.24190000	-1.21388800
C	4.01160100	-1.04797600	-2.91161400
H	3.01071300	-0.61570000	-2.98794000
H	3.92969800	-2.11166000	-3.14807900
B	0.79968200	0.86083700	-0.05257700
C	1.50947400	2.23325500	0.16301300
C	1.88356800	2.64514400	1.46185800
C	4.35378400	-1.11036900	1.41655500
H	4.28267100	-0.01828100	1.36652900
C	1.81998900	3.04156700	-0.95497800
C	2.50585500	4.25374400	-0.77155200
C	2.86740000	4.63496100	0.52110400
H	3.40085200	5.57258400	0.66097500
C	2.56982700	3.85744100	1.64100200
C	1.43130100	2.61336000	-2.35327600
H	0.77607500	3.34880800	-2.83337200
H	0.90626500	1.65730500	-2.36101400
H	2.30875100	2.51309100	-3.00198000
C	2.85750200	5.13864800	-1.94350900
H	3.38651500	6.03578000	-1.61479000
H	1.96768700	5.46332700	-2.49371700
H	3.49861700	4.62387000	-2.66734900
C	2.98702800	4.32471700	3.01513100
H	3.51091600	5.28154800	2.96376500
H	3.65543200	3.60902600	3.50610800
H	2.12814300	4.45442400	3.68257000
C	1.55500100	1.79177200	2.66659700
H	2.45987800	1.47157800	3.19477800
H	1.00086400	0.89323800	2.39146900
H	0.95091500	2.33943000	3.39864300
C	3.77060600	-3.44639200	-0.53622700
H	3.12762800	-3.58316300	-1.41330500
C	-2.51633400	3.61054600	0.53030200
H	-3.50465400	4.07882900	0.61271700
C	-1.74405500	4.30001000	-0.60083300
H	-2.28508700	4.29181000	-1.54718800
H	-0.77057600	3.83445500	-0.75843300
C	-1.78793000	3.81184400	1.86574800
H	-0.83730500	3.27699200	1.88457800
H	-2.38440000	3.49377700	2.72172600
H	-0.60510800	-1.97940400	-2.12708300
C	-3.34958100	1.86521000	-2.65726900
H	-2.91462100	2.84186500	-2.87683000
H	-2.54599300	1.12870900	-2.69948800
H	-5.66453400	0.09394900	2.19812300
H	-3.79752200	0.59709700	3.66568100
H	-1.56877900	4.87577800	2.00228000
H	-1.56864900	5.34801900	-0.33640600
H	4.64127100	-0.58998000	-3.68151700
H	5.38905000	1.13521900	-2.10884000
C	3.54272900	-1.54944000	2.64557400
H	3.63083900	-2.62080000	2.83410700

H	3.91444900	-1.03341800	3.53727100
H	2.48312200	-1.31379600	2.53439900
C	5.83499500	-1.48192600	1.57142900
H	5.96812500	-2.55538900	1.72405800
H	6.44200000	-1.18717800	0.71237100
H	6.25265900	-0.98078700	2.45142300
C	5.17963000	-3.92814300	-0.91351100
H	5.14265300	-4.99511800	-1.15875500
H	5.58499700	-3.41546500	-1.78742800
H	5.89313000	-3.81204600	-0.09571600
C	3.18344100	-4.31903600	0.58382000
H	3.83491500	-4.34285000	1.46109300
H	2.19531500	-3.97851200	0.89912200
H	3.08023700	-5.35051900	0.23244300
C	-5.16184300	2.91610700	-1.22770300
H	-4.75303600	3.91765000	-1.38367500
H	-5.90515200	2.74989300	-2.01484400
H	-5.69561200	2.92077000	-0.27430400
H	-4.06101200	1.64026900	-3.45892600



5^{Me} **6**^{Me}

	E	G
H_2	-1.155090	-1.166557
5^{Me}	-1657.423139	-1657.494656
6^{Me}	-1674.272551	-1674.339179

ΔE_{rxn} = −2.8 kcal/mol
ΔG_{rxn} = −7.0 kcal/mol

Figure S4. Energetics of a conversion calculated to model the spontaneous transformation of **5** to **6**. For computational simplicity the duryl groups have been modeled as phenyl groups, and the PCy_3 ligands have been modeled as PMe_3 ligands. Calculations were performed at the M05-2X/6-311G(d) level for all small atoms and employed the LANL2DZ pseudopotential for Pt. The tabulated energies are in Hartrees.

Table S2: Optimized coordinates for the minimized structures in Figure S4.

H_2

H	0.00000000	0.00000000	0.36746300
H	0.00000000	0.00000000	-0.36746300

5^{Me}

Pt	1.39460100	0.24870300	-0.03668800
C	0.43924900	-2.34563900	1.69604100
P	2.87445300	0.60844600	-1.83754900
B	0.16393800	-0.85712500	1.32354300
B	-0.14281700	0.71776800	1.38093800
Pt	-1.38132500	-0.28085300	-0.04930500
C	1.74723700	-2.82520100	1.82541600
P	-2.90154800	-0.39998200	-1.84768100
H	-2.56010300	-0.53147900	0.99596100
H	2.57611600	0.44055700	1.01648800
H	0.00458200	0.01448800	-1.22143800
H	0.01250500	-0.10746900	2.41331500
C	-0.61721400	-3.24241000	1.88977700
C	-0.37578400	-4.57106100	2.21480700
C	0.93001500	-5.02949000	2.34605600
H	1.11952400	-6.06461400	2.59856400
C	1.99138600	-4.15362000	2.15039700
C	-0.42105600	2.17712100	1.85498200
C	0.63157400	3.05809400	2.12613000
C	-0.92392000	4.81043000	2.68035600
H	-1.11779600	5.82564800	3.00083100
C	0.38401200	4.36139300	2.53804500
C	-1.98142500	3.95037100	2.40878500
C	-1.73113300	2.64731700	1.99730000
C	3.86721100	2.14154800	-1.69652900
H	4.41045800	2.11903800	-0.75418700
H	4.57032700	2.23835400	-2.52403700
H	3.20170900	3.00250700	-1.68280600
C	2.20367900	0.71505600	-3.54094800
H	1.49278200	1.53796000	-3.58892800
H	2.99132500	0.87159400	-4.27850700
H	1.66990400	-0.20602400	-3.76724100
C	4.15512400	-0.69353500	-1.98387500
H	4.84728700	-0.48063400	-2.79880900
H	4.70177400	-0.75255800	-1.04500000
H	3.67403900	-1.65414300	-2.15651000
C	-2.28442900	-0.27738600	-3.57010100
H	-1.74353200	0.66049900	-3.68229900
H	-1.58814000	-1.09309800	-3.75590600
H	-3.09646100	-0.31966600	-4.29645900
C	-4.15482000	0.93402300	-1.76592100
H	-4.66878900	0.86854900	-0.80921000
H	-3.65524000	1.89947500	-1.81634700

H	-4.87818900	0.85469900	-2.57779300
C	-3.92323000	-1.91997100	-1.88510600
H	-4.43010900	-2.02137200	-0.92779200
H	-4.65881200	-1.88711100	-2.68909400
H	-3.27784400	-2.78575000	-2.01984300
H	-1.63260500	-2.88504600	1.78041800
H	-1.20512900	-5.24984700	2.36512400
H	3.00944200	-4.50677000	2.25078700
H	2.57141200	-2.14221000	1.66716100
H	1.21059900	5.02781500	2.74750500
H	1.64885200	2.70917300	2.00766900
H	-2.55226300	1.97684600	1.78031300
H	-3.00120800	4.29587900	2.51785900

6^{Me}

Pt	1.20118700	-1.25557100	-0.17362000
P	3.45517400	-1.15740700	0.11314300
Pt	-1.14188800	0.03153500	-0.31568600
P	-2.41398000	1.91153000	-0.19732800
H	0.12795800	-2.99212900	-0.02657500
C	-2.13254300	-2.15396100	0.00685700
C	-2.33638800	-2.30130600	1.40007200
C	-3.56532900	-2.07512100	1.98527300
C	-4.65611700	-1.66434000	1.20767300
H	-5.62160800	-1.50182700	1.66886100
C	-4.48795500	-1.46929700	-0.14911700
B	-0.71076100	-2.27640200	-0.67007600
C	-3.23797400	-1.69987900	-0.74228300
B	0.70843000	0.63700600	-0.13016500
C	1.42670600	1.99182700	0.13938800
C	1.53321700	2.47803200	1.44768400
C	1.94657100	2.76761800	-0.90121500
C	2.54908400	3.99343600	-0.64402700
C	2.64416500	4.46443300	0.66068700
H	3.11212900	5.41895200	0.86038500
C	2.13705800	3.70215800	1.70786300
H	-0.69859300	-2.44659800	-1.86488500
C	-3.41195800	2.02593900	1.33483700
H	-4.01610300	1.12363000	1.42032600
H	-2.74231700	2.06833900	2.19174700
H	-4.05650500	2.90565200	1.33127600
C	-3.68475300	2.07960700	-1.51072700
H	-3.19938200	2.08070100	-2.48469400
H	-4.35705000	1.22554700	-1.46173600
H	-4.25674700	3.00011000	-1.38996400
C	4.39412700	-2.73761300	0.13551000
H	4.23654800	-3.26338600	-0.80437400
H	5.46143300	-2.56371400	0.27709000
H	4.02061000	-3.36611900	0.94169700
C	4.01443700	-0.35720800	1.66404800
H	3.60695200	-0.89758100	2.51619600
H	5.10297500	-0.34370100	1.72823000

H	3.63763700	0.66353700	1.68961600
C	4.35666700	-0.19663000	-1.16110800
H	4.16076200	-0.62661700	-2.14142800
H	3.98684900	0.82706200	-1.15288300
H	5.43056400	-0.19581100	-0.97174900
H	2.94301900	4.58346600	-1.46107800
H	2.21036900	4.06386100	2.72512300
H	1.13186800	1.89151900	2.26612700
H	1.87004900	2.41093000	-1.92165000
H	-3.13132700	-1.60447600	-1.81668400
H	-5.32506100	-1.15959000	-0.76267000
H	-3.69114900	-2.21942700	3.05072000
H	-1.49429300	-2.60805600	2.00820200
C	-1.57312700	3.53632100	-0.26880200
H	-1.02461700	3.61695900	-1.20529800
H	-2.29839100	4.34755300	-0.19885500
H	-0.85345000	3.61708500	0.54315200

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