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# Platinum Complexes of a Boron-Rich Diphosphine Ligand

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**ABSTRACT:** Herein, we describe the preparation, characterization, and reactivity of two $Pt^{II}$ *bis*-hydrocarbyl complexes containing the 1,2-*bis*(di(3-dicyclohexylboraneyl)propylphosphino)ethane ($P_2B^{Cy}_4$) ligand. These scaffolds are readily accessed from four-fold hydroboration of 1,2-*bis*(diallylphosphino)ethane $Pt^{II}$ precursors. The electrophilcity of such frameworks is showcased by facile coordination of the strong Lewis base, 4-*N*,*N*-dimethylaminopyridine (DMAP). Thermolysis reactions of [$Pt(P_2B^{Cy}_4)(R)_2$] (R = $CH_3$ or Ph) show enhanced (and divergent) reactivity when compared to their "all-alkyl diphosphine" counterparts, implicating involvement of the pendant borane groups. This behaviour is attenuated by protection of these units with DMAP.

Trisubstituted boranes ($BR_3$) have been used for decades as activating agents for the labilization of M-X (M = metal, X = halide, hydride, alkyl *etc.*) bonds, providing coordinatively unsaturated compounds that feature enhanced reactivity.[1] For example, $B(C_6F_5)_3$ has found widespread applicability in olefin polymerization, enabling methyl-group abstraction from metallocenes such as [$Cp_2Zr(CH_3)_2$] (Cp = $C_5H_5^-$), providing "[$Cp_2Zr–CH_3$]$^+$", a reactive fragment that enables olefin coordination and subsequent oligomerization.[2] In the context of group 10 coordination chemistry, Tilley showed that [$Ni(dmpe)(CH_3)_2$] (dmpe = 1,2-*bis*(dimethylphosphino)ethane) undergoes intermolecular methyl group abstraction in the presence of a phosphinoborane ligand, generating a zwitterionic Ni(II) complex (**Chart 1A**).[3] Intramolecular transfers have also been achieved. Emslie showed that reaction of an ambiphilic TXPB ligand (TXPB = 2,7-*di*-*tert*-butyl-5-diphenylboryl-4-diphenylphosphino-9,9′-dimethylthioxanthene) with [$Pt(\eta^4$-COD$)(CH_3)_2$] (COD = 1,5-cyclooctadiene) yields [Pt(TXPB′)$(CH_3)$(Ph)], resulting from exchange between [Pt]–$CH_3$ and ligand [B]–Ph groups (**Chart 1A**).[4] In a reaction featuring $Pt^{IV}$, Drover and Peters showed that 0.25 equiv. [$PtMe_3I]_4$ reacts with the diphosphinoborane ligand, $(PPh_2)_2BMes$ (Mes = 2,4,6-$Me_3C_6H_3$) to give $Pt^{II}$[κ²-*P*,*P*-$(PPh_2)_2B(Mes)(CH_3)$][κ²-*P*,*P*-$(PPh_2)_2B(Mes)(I)$], which results from ethane elimination followed by iodide and methyl group abstraction (**Chart 1A**).[5]

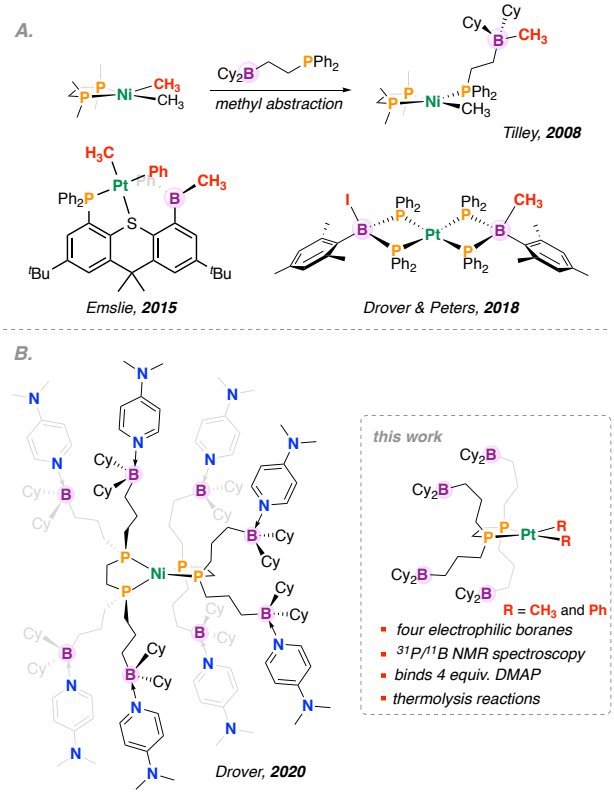


**Chart 1. A**) Group 10 coordination complexes featuring ambiphilic *P*,*B*-ligands; **B**) previous work with a $Ni(P_2B^{Cy}_4)_2$ complex[6] and *this work*: introducing $Pt^{II}$ *bis*-hydrocarbyl $P_2B^{Cy}_4$ complexes.

In designing new ambiphilic ligand candidates, we recently reported the preparation, characterization, and reactivity of a new diphosphine ligand, 1,2-*bis*(di(3-dicyclohexylboraneyl)propylphosphino)ethane ($P_2B^{Cy}_4$), a scaffold that contains four pendant boranes.[6] This ligand was installed at Ni(0), giving an octaboraneyl [$Ni(P_2B^{Cy}_4)_2$] complex that displays rich reactivity with Lewis bases (**Chart 1B**). In the case of 4,4′-bipyridine, for example, an air-sensitive coordination polymer is obtained, which contains unpaired electrons due to intramolecular Ni(0) →

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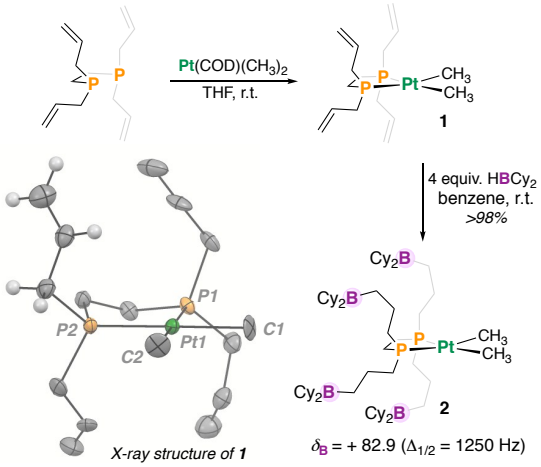
4,4′-bpyridine electron transfer.

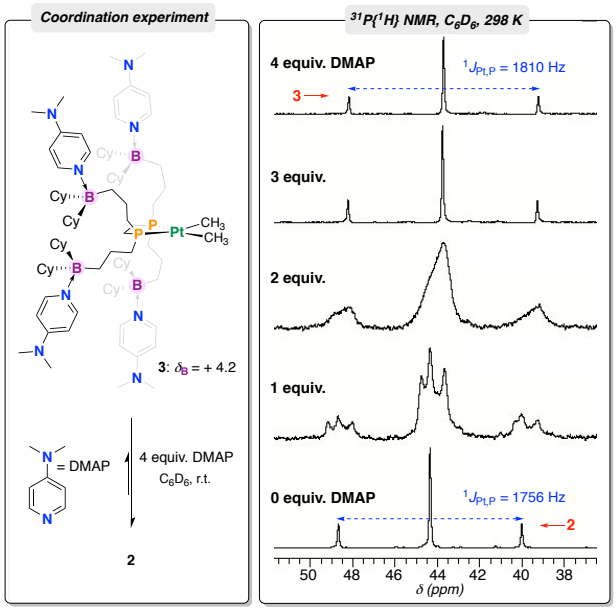
As part of our program aimed at developing the coordination chemistry of the $P_2B^{Cy}_4$ ligand, we elected to determine the influence of a boron-rich secondary coordination sphere on the the behaviour of well-defined $Pt^{II}$ precursors having hydrocarbyl groups. Herein, we present the results of these exploits and compare the behaviour of such systems to archetypical diphosphine $Pt^{II}$ compounds that are devoid of such borane functionality.

To begin, a [(diphosphine)$Pt^{II}(CH_3)_2$] precursor was targeted: reaction of 1,2-*bis*(diallylphosphino)ethane (tape)[7] with [Pt($\eta^4$-COD)$(CH_3)_2$] in THF at room temperature liberated free COD ($\delta_H$ = 5.57 and 2.22 ppm in $C_6D_6$) and afforded the diphosphino $Pt^{II}$ precursor, [Pt(tape)$(CH_3)_2$] (**1**) as a white solid in 71% yield; coordination is substantiated by $^{31}$P NMR spectroscopy, which provided a signal at $\delta_P$ = +39.7 ppm ($\Delta\delta_P$ = +68.4 ppm *cf.* free tape) with $^1J_{Pt,P}$ = 1727 Hz. Cooling a saturated solution of **1** in hexanes at –30 °C provided colorless blocks suitable for analysis by single crystal X-ray diffraction (**Scheme 1**). The structure features a square-planar $Pt^{II}$ complex with four allyl groups projecting from the equatorial plane.




**Scheme 1.** $Pt^{II}(CH_3)_2$ coordination chemistry of a boron-rich diphosphine ligand. Insert shows the Mercury depiction of the solid-state molecular structure of **1** (displacement ellipsoids are shown at 50% probability, hydrogen atoms are omitted for clarity, except for those on one alkenyl group).

With an appropriate precursor in-hand, we next sought to functionalize the alkenyl groups present in **1** by hydroboration. Reaction of $HBCy_2$ (4 equiv.) and **1** in benzene or toluene provides a clear colorless solution after 5 minutes (**Scheme 1**) with the removal of volatiles, giving [$Pt^{II}(P_2B^{Cy}_4)(CH_3)_2$] (**2**) in high yield (>98%); unlike the Ni case discussed above,[3] methyl abstraction is not observed.[8] Resulting from alkene hydroboration, the $^1$H NMR spectrum of **2** provided signals in the C($sp^3$)–H aliphatic region with 1.91 ≥ $\delta_H$ ≥ 1.08 ppm as well as a triplet at $\delta_H$ = 1.17 (t, 6H, Pt-C<u>H</u>$_3$; $^3J_{P,H}$ = 7.4 Hz, $^2J_{Pt,H}$ = 68 Hz) for the two equivalent [Pt]–$CH_3$ groups. In addition, acquisition of a $^{31}$P NMR spectrum showed consumption of the starting material and a new resonance at $\delta_P$ = +44.3 ppm ($^1J_{Pt,P}$ = 1756 Hz). The $^{11}$B NMR spectrum displayed a single broad resonance at $\delta_B$ = 82.9 ppm ($\Delta_{1/2}$ = 1250 Hz), consistent with $sp^2$–hybridized boron units that are non-interacting with the filled Pt $dz^2$ orbital.[9] The ESI(+)–MS of **2** provides a major ion signature at $m/z$ = 1217.911 (calcd. 1217.907) of the appropriate isotope pattern associated with the monocation formed by protonolysis of a methyl group and acetonitrile coordination.[10] Overall, the speed and cleanliness




**Scheme 2.** Reaction of **2** with 4 equiv. 4-*N*,*N*-dimethylaminopyridine (DMAP) and $^{31}$P{$^1$H} NMR spectra ($C_6D_6$, 203 MHz, 298 K) as a function of added DMAP.

of this reaction are notable given that **1** has undergone four successive hydroboration reactions.

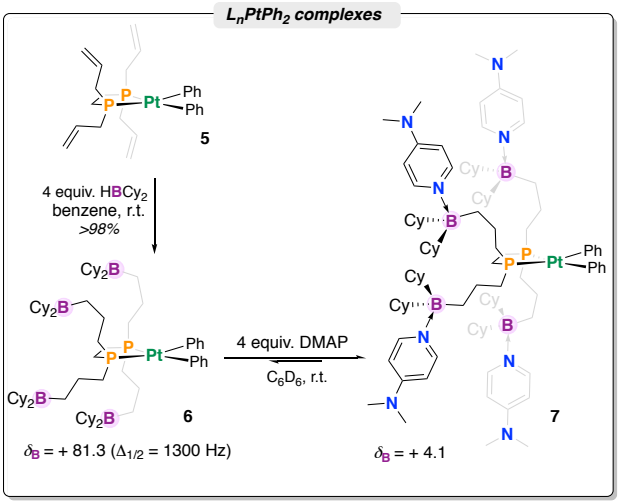
We next wished to assess the reactivity of **2** with Lewis bases. Previously, we showed that a related $Ni^0$ octaboraneyl complex, [Ni$(P_2B^{Cy}_4)_2$] binds 8 equiv. 4-*N*,*N*-dimethylaminopyridine (DMAP), providing a canopy of Lewis acid and base pairs (**Chart 1B**).[6] Toward this aim, we monitored the reaction of **2** with 1–4 equiv. DMAP in $C_6D_6$ (**Scheme 2**). Upon addition of 1 equiv., the $^{31}$P NMR spectrum broadens appreciably, indicating fluxional solution behavior or possible $^{31}$P–$^{31}$P coupling, given formation of a $C_1$–symmetric Pt complex (an AX spin system); addition of a subsequent equivalent caused the $^{31}$P NMR signal to further broaden. Two further additions provided a sharp signature at $\delta_P$ = +39.3 ppm ($^1J_{Pt,P}$ = 1810 Hz), attributable to [$Pt^{II}(P_2B^{Cy}_4)$(DMAP)$_4(CH_3)_2$] (**3**) (**Scheme 2**).[11] Intriguingly, on DMAP-binding, the value

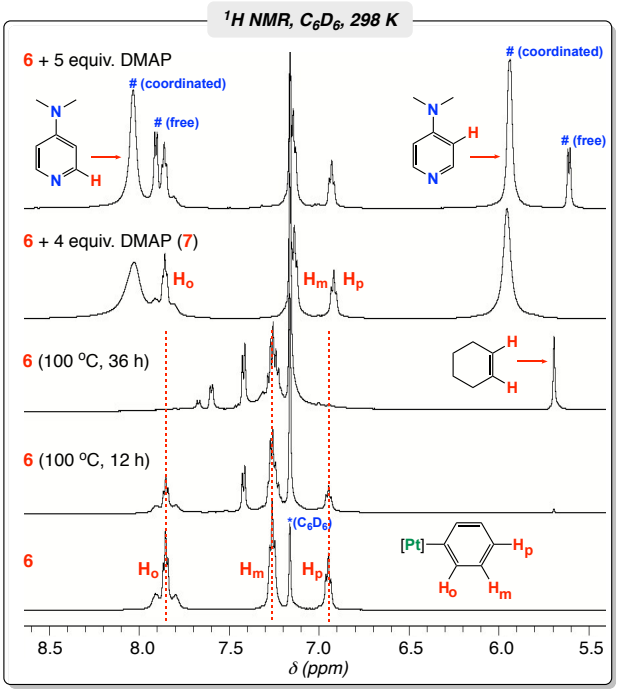
**Table 1.** Summary of $\delta_P$ and $^1J_{Pt,P}$ for Pt complexes.

| | | $\delta_P$ (ppm) | $^1J_{Pt,P}$ (Hz) |
|---|---|---|---|
| $Pt^{II}$(tape)$(CH_3)_2$ | **1** | 39.7 | 1727 |
| $Pt^{II}(P_2B^{Cy}_4)(CH_3)_2$ | **2** | 44.3 | 1756 |
| $Pt^{II}(P_2B^{Cy}_4)$(DMAP)$_4(CH_3)_2$ | **3** | 43.7 | 1810 |
| $Pt^{II}$(d*n*ppe)$(CH_3)_2$ | **4** | 44.7 | 1768 |
| $Pt^{II}$(tape)$(Ph)_2$ | **5** | 35.8 | 1646 |
| $Pt^{II}(P_2B^{Cy}_4)(Ph)_2$ | **6** | 39.4 | 1666 |
| $Pt^{II}(P_2B^{Cy}_4)$(DMAP)$_4(Ph)_2$ | **7** | 39.3 | 1730 |
| $Pt^{II}$(d*n*ppe)$(Ph)_2$ | **8** | 40.5 | 1684 |

of $^{1}J_{Pt,P}$ increased by 54 Hz (**Table 1**) - a case where binding of four Lewis bases in the secondary coordination sphere prompts an observable change in the primary coordination sphere. Of note, addition of excess DMAP (5 equiv.) shows $^{1}$H NMR signals for both free and bound donor of integration 1:4 (**Scheme 3**), indicating that owing to its boron-rich secondary coordination sphere, complex **2** binds 4 equiv. DMAP. In terms of $^{11}$B NMR spectroscopy, a new upfield-shifted signal at $\delta_B$ = 4.21 ppm ($\Delta_{1/2}$ = 200 Hz, $\Delta\delta_B$ = -78.7 ppm *cf.* **2**), is observed for **3**, consistent with formation of four DMAP → B(Cy$_2$)R units. Binding of THF or Et$_2$O by **2** is not observed.

To broaden the scope of the Pt$^{II}$ *bis*-hydrocarbyl complexes accessible using the P$_2$B$^{Cy}$$_4$ scaffold, [(diphosphine)Pt$^{II}$(Ph)$_2$] complexes were next targeted. Thus, reaction of [Pt($\eta^4$-COD)(Ph)$_2$] with tape in THF, provided [Pt(tape)(Ph)$_2$] (**5**) ($\delta_P$ = +35.8 ppm, $^{1}J_{Pt,P}$ = 1646 Hz) in 83% yield (**Scheme 3**). Compound **5** is a suitable precursor for hydrofunctionalization, undergoing B-H bond addition using 4 equiv. HBCy$_2$, providing [Pt(P$_2$B$^{Cy}$$_4$)(Ph)$_2$] (**6**) ($\delta_P$ = +39.4 ppm, $^{1}J_{Pt,P}$ = 1666 Hz) in 91% yield, following work-up. Given its electrophilic nature, and like **2**, complex **6** binds 4 equiv. DMAP to give [Pt(P$_2$B$^{Cy}$$_4$)(DMAP)$_4$(Ph)$_2$] (**7**) ($\delta_P$ = +39.3 ppm, $^{1}J_{Pt,P}$ = 1730 Hz) (**Scheme 3**). Once again, DMAP coordination prompts an increase (by 64 Hz) in the value of $^{1}J_{Pt,P}$ (**Table 1**).




**Scheme 3.** (*top*) Pt$^{II}$(Ph)$_2$ coordination chemistry of a boron-rich diphosphine ligand, (*bottom*) $^{1}$H NMR spectra (500 MHz, C$_6$D$_6$). From bottom to top: **6**, thermolysis of **6** (100 °C, 12 h), thermolysis of **6** (100 °C, 36 h), **6** + 4 equiv. DMAP (**7**), and **6** + 5 equiv. DMAP.

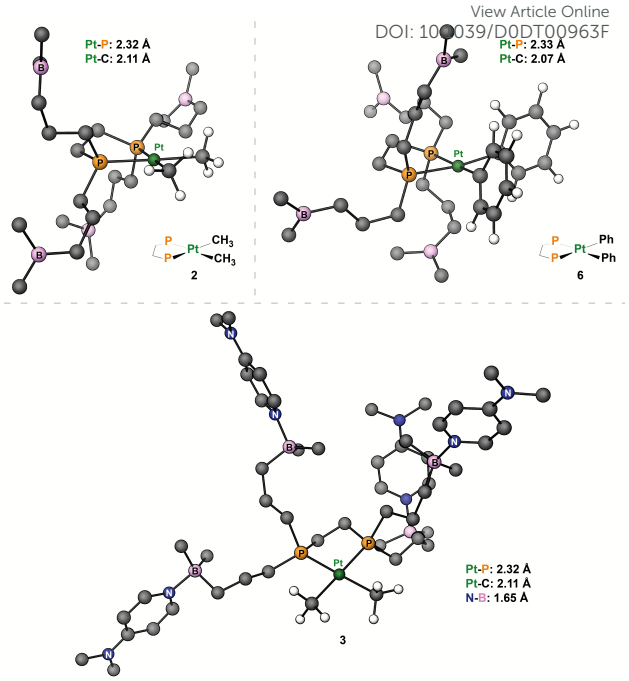



**Figure 1.** DFT-optimized structures of **2**, **3**, and **6** [BP86-D3/def2-svp] (hydrogen atoms except those on the hydrocarbyl groups, are omitted for clarity). Bond lengths are reported as averages (these differ by < 0.01 Å).

To gather structural insight into the nature of these species, DFT was performed on complexes **2**, **3**, **6**, and **7** (**Figure 1**); truncated models were used where –BCy$_2$ was modeled as –BMe$_2$.[12] All complexes are square-planar diphosphino Pt$^{II}$ complexes having two *cis*-disposed hydrocarbyl groups. Analysis of average Pt–C and Pt–P bond lengths revealed distances of *ca.* 2.11 and 2.32 Å, respectively for both **2** and **3**, indicating little change on DMAP binding; these are slightly longer than those observed in the crystal structure for **1** (Pt–C = 2.102(3) Å, Pt–P = 2.2504(7) Å). Complex **3** features four DMAP → B(Cy$_2$)R interactions in its secondary coordination sphere with an average B-N bond distance of 1.65 Å. For **6**, Pt–C and Pt–P bond lengths of *ca.* 2.07 and 2.33 Å are observed. The DFT-calculated $^{11}$B NMR chemical shifts[12] for **2**, **3**, **6**, and **7** ($\delta_B$ = +84, –8, +83, and –8 ppm) are also in good agreement with those determined experimentally ($\delta_B$ = +82.9, +4.2, +81.3, and +4.1 ).

We next sought to assess the thermal stability of complexes **2** and **6** with an eye toward determining the effect (if any) of a boron-rich secondary coordination sphere. However, in advance of delving into our findings, a brief summary of the reactivity of related Pt$^{II}$ *bis*-hydrocarbyl diphosphine complexes is warranted (**Scheme 4**). Although unreactive at 150 °C, heating a benzene solution of

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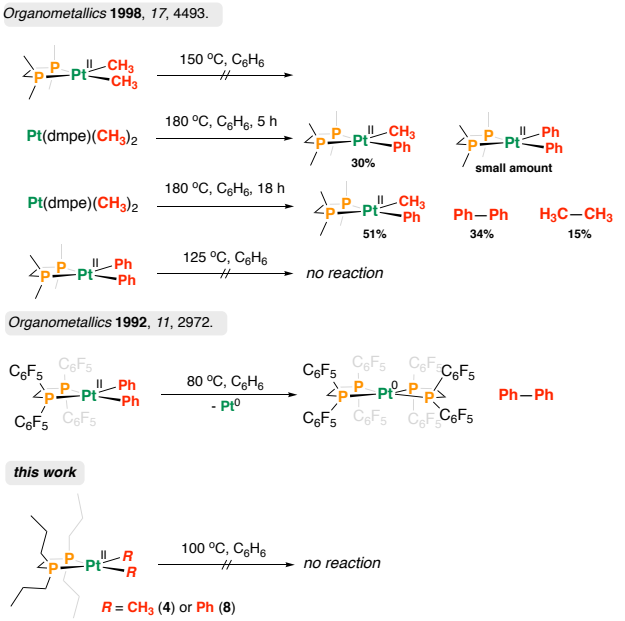


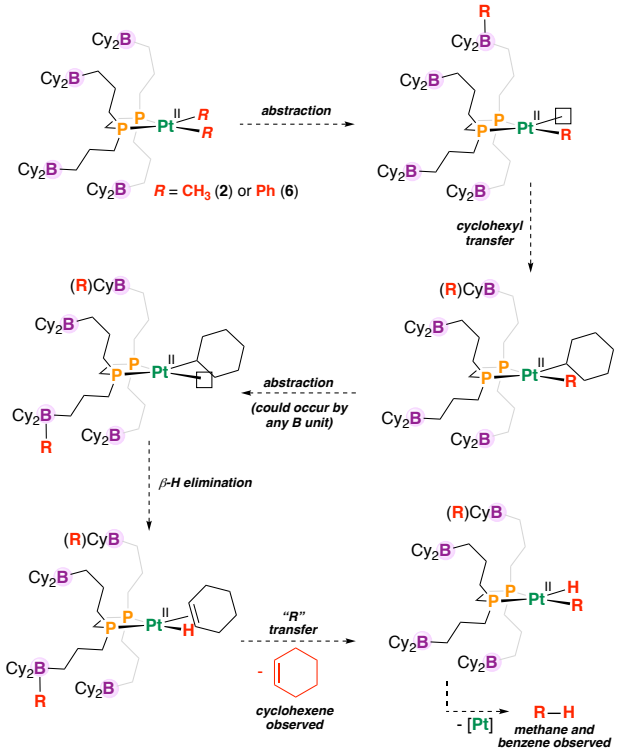

**Scheme 4.** Literature precedent for thermolysis of $Pt^{II}$ diphosphine complexes[10-12] and thermolysis of **4** and **8**.

$[Pt(dmpe)(CH_3)_2]$ (dmpe = 1,2-*bis*(dimethylphosphino)ethane) at 180 °C for 5 h provides $[Pt(dmpe)(CH_3)(Ph)]$ (30%) and a small amount of $[Pt(dmpe)(Ph)_2]$.[13] After 18 h, the major species are $[Pt(dmpe)(CH_3)(Ph)]$ (51%), biphenyl (34%) and ethane (15%). On the other hand, $[Pt(dmpe)(Ph)_2]$ is stable at 125 °C, with no evidence of benzene activation (**Scheme 4**). By contrast, thermolysis of $[Pt(dfppe)(Ph)_2]$ (dfppe = 1,2-*bis*(pentafluorophenylphosphino)ethane) at 80 °C readily gives biphenyl and $[Pt(dfppe)_2]$ (**Scheme 4**).[14] A later study employed a series of $Pt(diphosphine)(Ph)_2$ complexes using 1,2-*bis*(diphenylphosphino)ethane and seven of its fluoroaromatic analogues with the rate of biphenyl elimination increasing as a function of ligand electron-deficiency.[15]

To provide a more reasonable means for comparison in this study, two new compounds, $[Pt(dnppe)(R)_2]$ (**4**: R = $CH_3$ and **8**: R = Ph, d*n*ppe = 1,2-*bis*(di-*n*-propylphosphino)ethane) were prepared as models where *R* = $BCy_2$ has been replaced with *R* = H. These compounds are easily identifiable on the basis of $^{31}P$ NMR spectroscopy ($\delta_P$ = +44.7 ppm, $^1J_{Pt,P}$ = 1768 Hz for **4** and $\delta_P$ = +40.5 ppm, $^1J_{Pt,P}$ = 1684 Hz for **8**) (**Table 1**). Similar to $Pt(dmpe)(CH_3)_2$, benzene solutions of **4** and **8** are unreactive at 100 °C over the period of 1 week. To control for exogenous donor, benzene solutions of **4** and **8** were also heated in the presence of 4 equiv. of DMAP, which also provided no reaction at 100 °C over 1 week (**Scheme 4**).

To test which organic fragments (if any) result from the thermolysis of such borane-appended complexes, complex **2** was first heated at 100 °C for 48 h. Following the reaction by $^1H$ NMR spectroscopy showed that complex **2** is consumed and three new signals at $\delta_H$ = 5.69, 0.68, and 0.16 are observed; the latter of which is assigned to dissolved $CH_4$ (ethane is not produced).[16] The signal at $\delta_H$ = 0.68 ppm is assigned to a [B]–$CH_3$ group,[4,5] indicating methyl abstraction by boron. A $^1H$-$^{13}C$-HSQC NMR spectroscopy experiment correlates this shift to a $^{13}C$ chemical shift at $\delta_C$ = 8.39 ppm, which is broadened by the quadrupolar $^{11}B$ nucleus (*see ESI*) and a $^1H$-$^{11}B$ HMQC experiment (optimized for $^2J_{B,H}$ coupling) provides a cross-signal with a boron resonance at $\delta_B \approx 84$ ppm (consistent with an $sp^2$-hybridized boron unit). The most downfield-shifted $^1H$ NMR signal at $\delta_H$ = 5.69 ppm (which is shown by $^1H$-$^{13}C$-HSQC NMR spectroscopy to be correlated to a $^{13}C$ NMR signal at $\delta_C$ = 127.0 ppm) is attributed to cyclohexene, which results from dehydrogenation of a ligand cyclohexyl group. A plausible pathway accounting for these products is depicted in **Scheme 5**.[16] As mentioned previously, the $^{11}B$ NMR spectrum of this mixture features a resonance at $\delta_B \approx 84$ ppm and the $^{31}P$ NMR spectrum is broad, confirming the consumption of **2** and the absence of free ligand (*see ESI*).

Next, complex **6** was heated at 100 °C for 48 h, resulting in consumption to provide several new sets of Ph-derived resonances (none of these attributable to biphenyl and all of which lack $^{195}Pt$ coupling) as well as benzene ($\delta_H$ = 7.15 ppm) (**Scheme 3**). Importantly, this reactivity profile differs from that of i) $[Pt(dmpe)(Ph)_2]$, which is stable at 125 °C and ii) $[Pt(dfppe)(Ph)_2]$, which readily provides biphenyl and $[Pt(dfppe)_2]$ at 80 °C. Of the three key $^1H$ NMR signals present following the thermolysis of **2**, only one is observed from this reaction mixture: cyclohexene at $\delta_H$ = 5.69 ppm (**Scheme 3**), showing the [B]–$CH_3$ unit ($\delta_H$ = 0.68 ppm) and dissolved $CH_4$ ($\delta_H$ = 0.16 ppm) to be derived from the [Pt]–$CH_3$ groups of **2**. Once again, observation of a signal at $\delta_H$ = 5.69 ppm indicates cyclohexyl transfer and dehydrogenation (**Scheme 5**). Of note, heating complex **7** (as a protected variant of **6**) under identical conditions to **2** and **6**, showed little reactivity (<5%), im-




**Scheme 5.** Proposed scheme accounting for organic products from the thermolysis of **2** and **6**.

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plying that DMAP shields the $Pt^{II}(Ph)_2$ unit from decomposition.

While the ultimate Pt–containing product(s) from these thermolyses remains unknown,[17] the observation of $CH_4$ (from **2**), $C_6H_6$ (from **6**), and cyclohexene (from **2** and **6**) are consistent with the decomposition pathway proposed in **Scheme 5**. Taken together, it is evident that boron incorporation causes the thermolytic behaviour of **2** and **6** to differ from conventional *e.g.,* dmpe- or d*n*ppe-substituted $Pt^{II}$ *bis*-hydrocarbyl complexes (**Scheme 4**). These reactions provide valuable insight regarding the thermal stability of such $Pt^{II}$ $P_2B^{Cy}_4$ complexes; information that will be taken into account for future work with this ligand set.

We have shown that $Pt^{II}$ $P_2B^{Cy}_4$ complexes can be readily accessed from $Pt^{II}$ tetrakisallyl precursors *via* fourfold hydroboration. These compounds offer a lens into the reactivity of square-planar $Pt^{II}$ complexes having electrophilic secondary coordination spheres. In terms of reactivity, these species readily bind strong Lewis bases and when heated are more reactive (and show divergent reactivity patterns) when compared to conventional alkyl-substituted diphosphine $Pt^{II}$ complexes – such reactivity is suppressed in the presence of excess Lewis base (DMAP), implicating involvement of the peripheral borane units.

## EXPERIMENTAL

**General Considerations.** All experiments were carried out employing standard Schlenk techniques under an atmosphere of dry nitrogen employing degassed, dried solvents in a solvent purification system supplied by PPT, LLC. Non-halogenated solvents were tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran in order to confirm effective moisture removal. $d_6$-benzene was dried over molecular sieves and degassed by three freeze-pump-thaw cycles. $HBCy_2$[18], tape,[19] d*n*ppe,[20] and $Pt(\eta^4$-COD)$Ph_2$[21] were prepared according to a literature procedure. All other reagents were purchased from commercial vendors and used without further purification unless otherwise stated. Mass spectrometry was acquired using a Waters XEVO G2-XS ToF.

**Physical methods.** $^1$H NMR spectra are reported in parts per million (ppm) and are referenced to residual solvent: $^1H(C_6D_6)$: $\delta$ 7.16; $^{13}C(C_6D_6)$: 128.06; coupling constants are reported in Hz. $^{13}$C, $^{11}$B, and $^{31}$P NMR spectra were performed as proton-decoupled experiments and are reported in ppm. The multiplicities are abbreviated as follows: *s* = singlet, *d* = doublet, *dd* = doublet of doublets, *h* = heptet (septet).

**Preparation of Compounds:**

**$Pt^{II}$(tape)$(CH_3)_2$** (**1**; $C_{16}H_{30}P_2Pt$, $M_W$ = 479 g/mol): In the glovebox, Pt(COD)$(CH_3)_2$ (40 mg, 0.12 mmol) and tape (31 mg, 0.12 mmol, 1 equiv.) were combined in a 20 mL scintillation vial equipped with a stir bar. Approximately 4 mL of THF was added and the solution was allowed to stir for 4 h at room temperature. The resulting clear colorless solution was filtered through Celite® and the solvent was removed *in-vacuo*. Recrystallization from hexanes at –30 °C gave colorless crystals (41 mg, 71%). **$^1$H NMR (500 MHz, $C_6D_6$, 298 K):** $\delta$ = 5.76 (m, 4H; C<u>H</u>(allyl)), 4.90 (m, 4H; C<u>H</u>$_2$(allyl)), 4.84 (m, 4H; C<u>H</u>$_2$(allyl)), 2.44 (m, 4H; P-C<u>H</u>$_2$C<u>H</u>$_2$ linker), 2.26 (m, 4H; C<u>H</u>$_2$(allyl)), 1.27 (t, 6H, Pt-C<u>H</u>$_3$; $^3J_{P,H}$ = 7.5 Hz, $^2J_{Pt,H}$ = 70 Hz), 1.13 (m, 4H; C<u>H</u>$_2$(allyl)). **$^{13}$C{$^1$H} NMR (125.8 MHz, $C_6D_6$, 298 K):** $\delta$ = 132.33 (m), 117.34 (m), 31.05 (m), 24.45 (m), 0.14 (dd, Pt-<u>C</u>H$_3$; $^2J_{P,C}$ = 105 Hz, $^2J_{P,C}$ = 7.1 Hz, $^1J_{Pt,C}$ = 602 Hz). **$^{31}$P{$^1$H} NMR (202.5 MHz, $C_6D_6$, 298 K):** $\delta$ = + 39.7 ($^1J_{Pt,P}$ = 1727 Hz). **HRESI(+)-MS**: (*m*/*z*) calcd. 505.1501 exptl. 505.1518 for $C_{17}H_{30}NP_2Pt$ [M-CH$_3$+NCCH$_3$]$^+$.

**$Pt^{II}(P_2B^{Cy}_4)(CH_3)_2$** (**2**; $C_{64}H_{122}B_4P_2Pt$, $M_W$ = 1192 g/mol): In the glovebox, Pt(tape)$(CH_3)_2$ (24 mg, 0.05 mmol) and $HBCy_2$ (36 mg, 0.20 mmol, 4 equiv.) were added to a 20 mL scintillation vial equipped with a stir bar. Approximately 4 mL of toluene was added and the solution was allowed to stir for 30 min at room temperature. The resulting pale yellow solution was filtered through Celite® and the solvent was removed *in-vacuo* to give an off-white oil (58 mg, >98%). **$^1$H NMR (500 MHz, $C_6D_6$, 298 K):** s$\delta$ = 1.91-1.08 (multiple overlapping C($sp^3$)–H resonances), 1.17 (t, 6H, Pt-C<u>H</u>$_3$; $^3J_{P,H}$ = 7.4 Hz, $^2J_{Pt,H}$ = 68 Hz). **$^{13}$C{$^1$H} NMR (125.8 MHz, $C_6D_6$, 298 K):** $\delta$ = 36.10, 30.21, 27.99, 27.95, 27.51, 27.49, 26.98, 20.16, –0.16 (dd, Pt-<u>C</u>H$_3$; $^2J_{P,C}$ = 102 Hz, $^2J_{P,C}$ = 6.7 Hz, $^1J_{Pt,C}$ = 605 Hz). **$^{31}$P{$^1$H} NMR (202.5 MHz, $C_6D_6$, 298 K):** $\delta$ = + 44.3 ($^1J_{Pt,P}$ = 1756 Hz). **$^{11}$B{$^1$H} NMR (160.5 MHz, $C_6D_6$, 298 K):** $\delta$ = + 82.9 ($\Delta_{1/2}$ = 1250 Hz). **HRESI(+)-MS**: (*m*/*z*) calcd. 1217.9072 exptl. 1217.9111 for $C_{65}H_{122}B_4NP_2Pt$ [M-CH$_3$+NCCH$_3$]$^+$.

**$Pt^{II}(P_2B^{Cy}_4)(DMAP)_4(CH_3)_2$** (**3**; $C_{92}H_{162}B_4N_8P_2Pt$, $M_W$ = 1680 g/mol): In the glovebox, Pt($P_2B^{Cy}_4$)$(CH_3)_2$ (**2**) (25 mg, 0.02 mmol) and DMAP (10.2 mg, 0.08 mmol, 4 equiv.) were added to a 20 mL scintillation vial equipped with a stir bar. Approximately 4 mL of toluene was added and the solution was allowed to stir for 20 min at room temperature. The resulting colorless solution was filtered through Celite® and the solvent was removed *in-vacuo* to give a colorless oil (31 mg, 88%). **$^1$H NMR (500 MHz, $C_6D_6$, 298 K):** $\delta$ = 8.09 (br, 8H; DMAP|C-H$_{ortho}$), 5.99 (br, 8H; DMAP|C-H$_{meta}$), 2.19 (s, 24 H; DMAP|NMe$_2$), 2.15-0.90 (overlapping C($sp^3$)–H resonances), 1.15 (t, 6H, Pt-C<u>H</u>$_3$; $^3J_{P,H}$ = 6.6 Hz, $^2J_{Pt,H}$ = 66 Hz). **$^{13}$C{$^1$H} NMR (125.8 MHz, $C_6D_6$, 298 K):** $\delta$ = 154.14 (DMAP), 145.54 (DMAP), 106.16 (DMAP), 38.38 (DMAP), 33.96, 31.58, 31.25, 30.50, 28.99, 26.69, 25.50, 22.67, -0.16 (dd, Pt-<u>C</u>H$_3$; $^2J_{P,C}$ = 102 Hz, $^2J_{P,C}$ = 6.8 Hz, $^1J_{Pt,C}$ = 605 Hz). **$^{31}$P{$^1$H} NMR (202.5 MHz, $C_6D_6$, 298 K):** $\delta$ = + 43.7 ($^1J_{Pt,P}$ = 1810 Hz). **$^{11}$B{$^1$H} NMR (160.5 MHz, $C_6D_6$, 298 K):** $\delta$ = + 4.21 ($\Delta_{1/2}$ = 200 Hz). **ESI(+)-MS**: (*m*/*z*) 1218 for $C_{65}H_{122}B_4NP_2Pt$ [M-CH$_3$-8DMAP+NCCH$_3$]$^+$.

**$Pt^{II}$(d*n*ppe)$(CH_3)_2$** (**4**; $C_{16}H_{38}P_2Pt$, $M_W$ = 487 g/mol): In the glovebox, Pt(COD)$(CH_3)_2$ (40 mg, 0.12 mmol) and d*n*ppe (31 mg, 0.12 mmol, 1 equiv.) were combined in a 20 mL scintillation vial equipped with a stir bar. Approximately 4 mL of THF was added and the solution was allowed to stir for 4 h at room temperature. The resulting clear colorless solution was filtered through Celite® and the solvent was removed *in-vacuo*. Recrystallization from hexanes at –30 °C gave colorless crystals (56 mg, 97%). **$^1$H NMR (500 MHz, $C_6D_6$, 298 K):** $\delta$ = 1.56 (m, 8H), 1.41 (m, 4H), 1.28 (m, 4H), 1.20 (t, 6H, Pt-C<u>H</u>$_3$; $^3J_{P,H}$ = 7.5 Hz, $^2J_{Pt,H}$ = 69 Hz), 1.06 (m, 4H), 0.87 (t, 12H, $^3J_{H,H}$ = 7.1 Hz). **$^{13}$C{$^1$H} NMR (125.8 MHz, $C_6D_6$, 298 K):** $\delta$ = 28.59 (m), 26.23 (m), 18.56 (m), 16.09 (m), -0.34 (dd, Pt-<u>C</u>H$_3$; $^2J_{P,C}$ = 103 Hz, $^2J_{P,C}$ = 6.8 Hz, $^1J_{Pt,C}$ = 601 Hz). **$^{31}$P{$^1$H} NMR (202.5 MHz, $C_6D_6$, 298 K):** $\delta$ = + 44.7 ($^1J_{Pt,P}$ = 1768 Hz). **HRESI(+)-MS**: (*m*/*z*) calcd. 513.2122 exptl. 513.2122 for $C_{17}H_{38}NP_2Pt$ [M-CH$_3$+NCCH$_3$]$^+$.

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**$Pt^{II}$(tape)$(Ph)_2$** (**5**; $C_{26}H_{34}P_2Pt$, $M_W$ = 603 g/mol): In the glovebox, Pt(COD)$(Ph)_2$ (40 mg, 0.088 mmol) and tape (22 mg, 0.087 mmol, 1 equiv.) were combined in a 20 mL scintillation vial equipped with a stir bar. Approximately 4 mL of THF was added and the solution was allowed to stir for 4 h at room temperature. The resulting clear colorless solution was filtered through Celite® and the solvent was removed *in-vacuo*. Recrystallization from hexanes-layered toluene at –30 °C gave colorless crystals (44 mg, 83%). **$^1$H NMR (500 MHz, $C_6D_6$, 298 K):** $\delta$ = 7.81 (t, 4H, C$\underline{H}_{ortho}$; $^3J_{H,H}$ = 7.9 Hz, $^4J_{P,H}$ = 6.5 Hz, $^3J_{Pt,H}$ = 47 Hz), 7.28 (t, 4H, C$\underline{H}_{meta}$; $^3J_{H,H}$ = 7.5 Hz), 7.01 (t, 2H, C$\underline{H}_{para}$; $^3J_{H,H}$ = 7.4 Hz), 5.70 (m, 4H), 4.84 (m, 8H), 2.32 (m, 4H), 2.06 (m, 4H), 1.18 (m, 4H). **$^{13}$C{$^1$H} NMR (125.8 MHz, $C_6D_6$, 298 K):** $\delta$ = 163.46 (dd, Pt-$\underline{C}H_3$; $^2J_{P,C}$ = 115.7 Hz, $^2J_{P,C}$ = 9.9 Hz, $^1J_{Pt,C}$ ~ 860 Hz), 137.04, 131.76, 122.26 (m), 118.00 (m), 30.13 (m), 24.15 (m); one [Pt]-Ph resonance is obscured by $C_6D_6$. **$^{31}$P{$^1$H} NMR (202.5 MHz, $C_6D_6$, 298 K):** $\delta$ = + 35.8 ($^1J_{Pt,P}$ = 1646 Hz). **$^{195}$Pt NMR (64.3 MHz, $C_6D_6$, 298 K):** $\delta$ = - 4528 (t, $^1J_{Pt,P}$ = 1646 Hz). **HRESI(+)-MS**: (*m*/z) calcd. 567.1652 exptl. 567.1658 for $C_{22}H_{32}NP_2Pt$ [M-Ph+NCCH$_3$]$^+$.

**Pt$(P_2B^{Cy}{}_4)(Ph)_2$** (**6**; $C_{74}H_{126}B_4P_2Pt$, $M_W$ = 1316 g/mol): In the glovebox, Pt(tape)$(Ph)_2$ (**6**) (16 mg, 0.027 mmol) and $HBCy_2$ (19 mg, 0.11 mmol, 4 equiv.) were added to a 20 mL scintillation vial equipped with a stir bar. Approximately 4 mL of toluene was added and the solution was allowed to stir for 30 min at room temperature. The resulting pale yellow solution was filtered through Celite® and the solvent was removed *in-vacuo* to give an off-white oil (32 mg, 91%). **$^1$H NMR (500 MHz, $C_6D_6$, 298 K):** $\delta$ = 7.85 (t, 4H, C$\underline{H}_{ortho}$; $^3J_{H,H}$ = 7.9 Hz, $^4J_{P,H}$ = 5.2 Hz, $^3J_{Pt,H}$ = 46 Hz), 7.26 (t, 4H, C$\underline{H}_{meta}$; $^3J_{H,H}$ = 7.5 Hz), 6.95 (t, 2H, C$\underline{H}_{para}$; $^3J_{H,H}$ = 7.3 Hz), 1.93-1.18 (multiple overlapping C($sp^3$)–H resonances). **$^{13}$C{$^1$H} NMR (125.8 MHz, $C_6D_6$, 298 K):** $\delta$ = 164.08 (dd, Pt-$\underline{C}H_3$; $^2J_{P,C}$ = 112.9 Hz, $^2J_{P,C}$ = 9.6 Hz, $^1J_{Pt,C}$ ~ 842 Hz), 137.35, 122.11, 36.21, 30.53, 29.11 (m), 27.98, 27.97, 27.47, 27.21, 20.04; one [Pt]-Ph resonance is obscured by $C_6D_6$. **$^{31}$P{$^1$H} NMR (202.5 MHz, $C_6D_6$, 298 K):** $\delta$ = + 39.4 ($^1J_{Pt,P}$ = 1666 Hz). **$^{11}$B{$^1$H} NMR (160.5 MHz, $C_6D_6$, 298 K):** $\delta$ = + 81.3 ($\Delta_{1/2}$ = 1300 Hz). **$^{195}$Pt NMR (64.3 MHz, $C_6D_6$, 298 K):** $\delta$ = - 4548 (t, $^1J_{Pt,P}$ = 1666 Hz). **ESI(+)-MS**: (*m*/z) 1280 for $C_{70}H_{124}B_4NP_2Pt$ [M-Ph+NCCH$_3$]$^+$.

**$Pt^{II}(P_2B^{Cy}{}_4)(DMAP)_4(Ph)_2$** (**7**; $C_{102}H_{166}B_4N_8P_2Pt$, $M_w$ = 1804 g/mol): In the glovebox, Pt$(P_2B^{Cy}{}_4)(Ph)_2$ (**6**) (35 mg, 0.027 mmol) and DMAP (13 mg, 0.11 mmol, 4 equiv.) were added to a 20 mL scintillation vial equipped with a stir bar. Approximately 4 mL of toluene was added and the solution was allowed to stir for 20 min at room temperature. The resulting colorless solution was filtered through Celite®, the solvent was removed *in-vacuo*, and washed with hexanes (5 mL) to give a white solid (46 mg, 96%). **$^1$H NMR (500 MHz, $C_6D_6$, 298 K):** $\delta$ = 8.03 (br, 8H; DMAP|C-$H_{ortho}$), 7.86 (t, 4H, C$\underline{H}_{ortho}$; $^3J_{H,H}$ = 7.2 Hz, $^4J_{P,H}$ = 5.9 Hz, $^3J_{Pt,H}$ = 54 Hz), 7.14 (t, 4H, C$\underline{H}_{meta}$; $^3J_{H,H}$ = 7.3 Hz), 6.93 (t, 2H, C$\underline{H}_{para}$; $^3J_{H,H}$ = 7.2 Hz), 5.94 (br, 8H; DMAP|C-$H_{meta}$), 2.14 (s, 24 H; DMAP|$NMe_2$), 2.32-0.91 (overlapping C($sp^3$)–H resonances). **$^{13}$C{$^1$H} NMR (125.8 MHz, $C_6D_6$, 298 K):** $\delta$ = 166.83 (dd, Pt-$\underline{C}H_3$; $^2J_{P,C}$ = 111.4 Hz, $^2J_{P,C}$ = 9.4 Hz, $^1J_{Pt,C}$ ~ 840 Hz) 154.18 (DMAP), 145.32 (DMAP), 138.39, 127.19, 121.09, 106.15 (DMAP), 38.37 (DMAP), 33.74, 31.97, 31.39 (br), 30.52, 29.03, 25.84, 23.06. **$^{31}$P{$^1$H} NMR (202.5 MHz, $C_6D_6$, 298 K):** $\delta$ = + 39.3 ($^1J_{Pt,P}$ = 1730 Hz). **$^{11}$B{$^1$H} NMR (160.5 MHz, $C_6D_6$, 298 K):** $\delta$ = + 4.05 ($\Delta_{1/2}$ = 250 Hz). **$^{195}$Pt NMR (64.3 MHz, $C_6D_6$, 298 K):** $\delta$ = - 4545 (t, $^1J_{Pt,P}$ = 1730 Hz). **ESI(+)-MS**: (*m*/z) 1280 for $C_{70}H_{124}B_4NP_2Pt$ [M-Ph-8DMAP+NCCH$_3$]$^+$.

**$Pt^{II}$(d*n*ppe)$(Ph)_2$** (**8**; $C_{26}H_{42}P_2Pt$, $M_W$ = 611 g/mol): In the glovebox, Pt(COD)$(Ph)_2$ (40 mg, 0.088 mmol) and d*n*ppe (23 mg, 0.088 mmol, 1 equiv.) were combined in a 20 mL scintillation vial equipped with a stir bar. Approximately 4 mL of THF was added and the solution was allowed to stir for 4 h at room temperature. The resulting clear colorless solution was filtered through Celite® and the solvent was removed *in-vacuo*. Recrystallization from hexanes-layered toluene at –30 °C gave colorless crystals (52 mg, 98%). **$^1$H NMR (500 MHz, $C_6D_6$, 298 K):** $\delta$ = 7.80 (t, 4H, C$\underline{H}_{ortho}$; $^3J_{H,H}$ = 7.9 Hz, $^4J_{P,H}$ = 6.5 Hz, $^3J_{Pt,H}$ = 46 Hz), 7.26 (t, 4H, C$\underline{H}_{meta}$; $^3J_{H,H}$ = 7.5 Hz), 6.99 (t, 2H, C$\underline{H}_{para}$; $^3J_{H,H}$ = 7.3 Hz), 1.57 (m, 4H), 1.41 (m, 4H), 1.25 (m, 4H), 1.08 (m, 8H), 0.85 (t, 12H, $^3J_{H,H}$ = 7.2 Hz). **$^{13}$C{$^1$H} NMR (125.8 MHz, $C_6D_6$, 298 K):** $\delta$ = 164.44 (dd, Pt-$\underline{C}H_3$; $^2J_{P,C}$ = 113.4 Hz, $^2J_{P,C}$ = 9.8 Hz, $^1J_{Pt,C}$ ~ 850 Hz), 137.24, 127.55, 122.03, 27.49 (m), 25.68 (m), 18.51 (m), 16.12 (d, *J* = 14.2 Hz). **$^{31}$P{$^1$H} NMR (202.5 MHz, $C_6D_6$, 298 K):** $\delta$ = + 40.5 ($^1J_{Pt,P}$ = 1684 Hz). **HRESI(+)-MS**: (*m*/z) calcd. 575.2278 exptl. 575.2285 for $C_{22}H_{40}NP_2Pt$ [M-Ph+NCCH$_3$]$^+$.

**Titration experiment**: In the glovebox, $Pt^{II}(P_2B^{Cy}{}_4)(CH_3)_2$ (**2**) (30 mg, 0.025 mmol) was dissolved in *ca.* 500 µL $C_6D_6$ and DMAP (~3.1 mg, ~0.025 mmol, ~1 equiv.) was added. The mixture was transferred to a *J. Young NMR tube* and analyzed using multinuclear NMR spectroscopy. Subsequent additions (2-4 equiv. DMAP) were performed in the glovebox and sample analyzed by NMR spectroscopy as appropriate.

## ASSOCIATED CONTENT

*Supporting Information*

$^1$H, $^{13}$C{$^1$H}, $^{31}$P{$^1$H}, and $^{11}$B NMR spectra for complexes as well as crystallographic data for **1**. CCDC **1987551** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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## CONFLICTS OF INTEREST

There are no conflicts to declare.

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[12] DFT method: BP86-D3/def2-SVP for all atoms. Single point calculations were performed at the BP86-D3/def2-TZVP level of theory with solvation for calculation of NMR parameters. For full computational details see the ESI.

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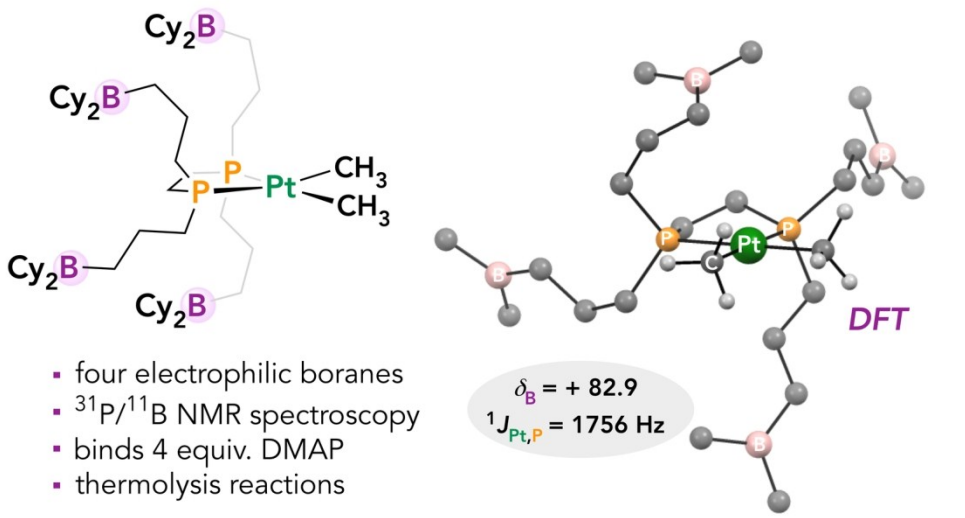


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