Electronic Supplementary Information

Exploring Unsymmetrical Diboranes(4) as Boryl Ligand Precursors: Platinum(II) *bis*-Boryl Complexes

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1. ^{1}H-^{1}H NOESY Spectra of Platinum Boryl Complexes

1.a. [Pt(PPh$_3$)$_2$(Bpin)(Bcat)] (**3ab**)

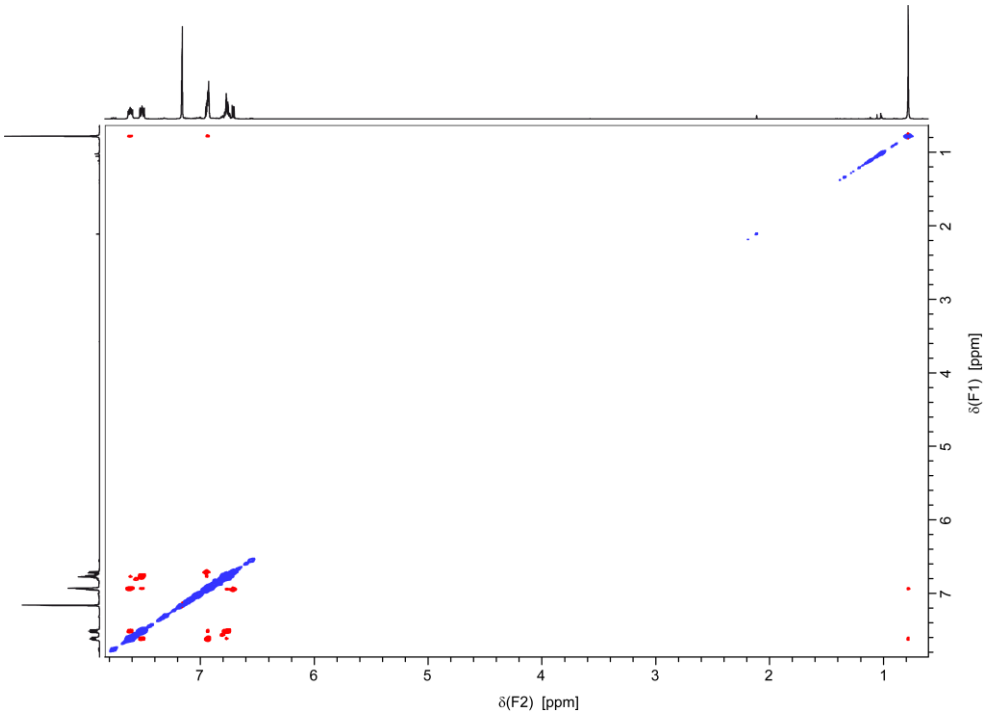

Figure S1a. ^{1}H-^{1}H NOESY NMR Spectrum of **3ab** (500 MHz, C_6D_6).

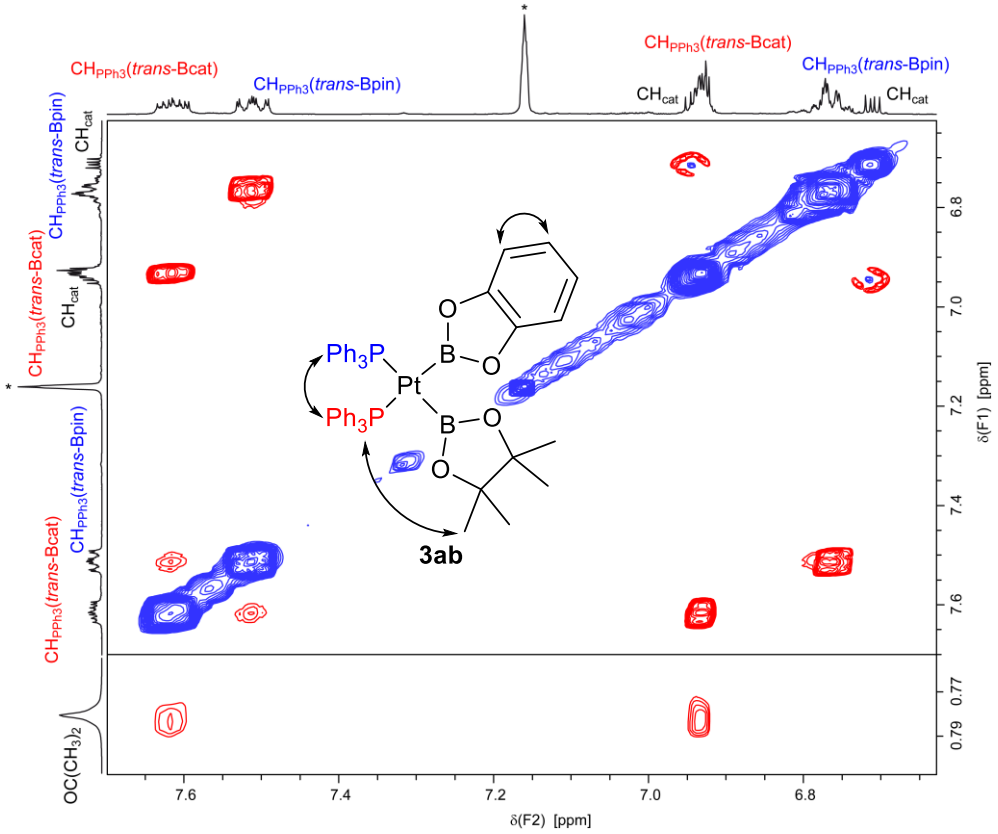

Figure S1b. Details of the ^{1}H-^{1}H NOESY NMR spectrum of **3ab**. NOESY contacts relevant to establish the solution structure are assigned (500 MHz, C_6D_6).

1.b. [Pt(PPh$_3$)$_2$(Bpin)(Bneop)] (**3ac**)

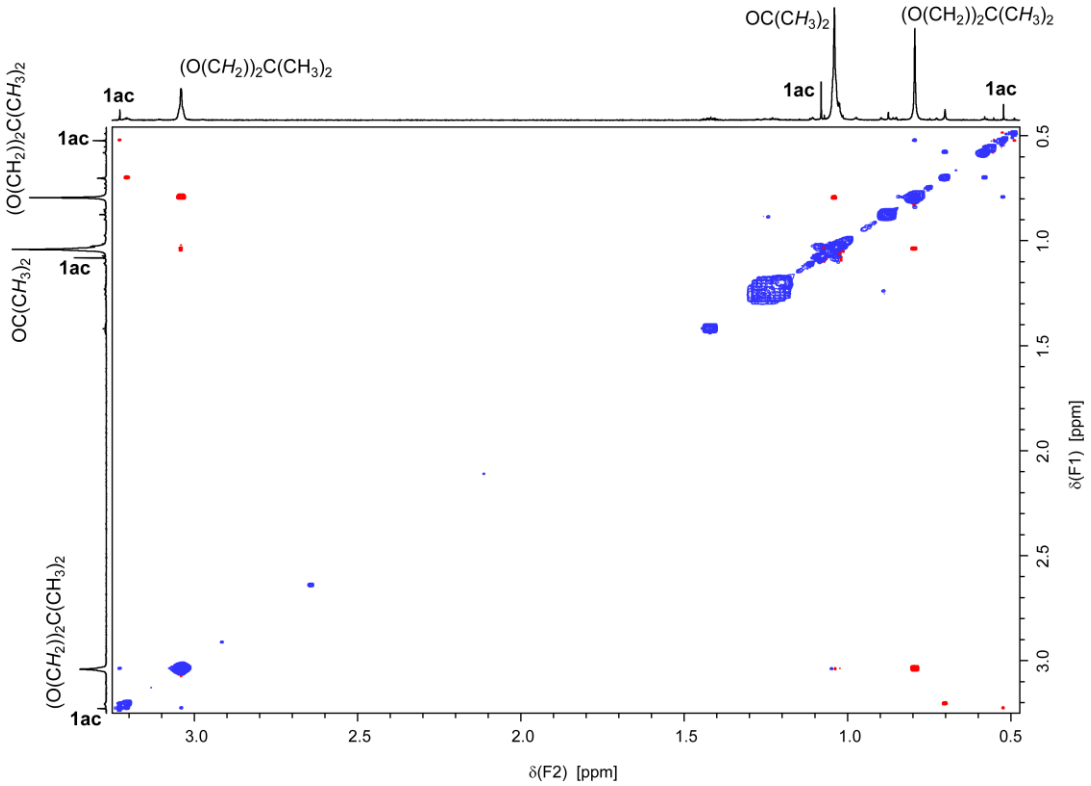

Figure S2a. Detail of the ^{1}H-^{1}H NOESY NMR spectrum of **3ac** (500 MHz, C_6D_6); Signals of **1ac** are assigned.

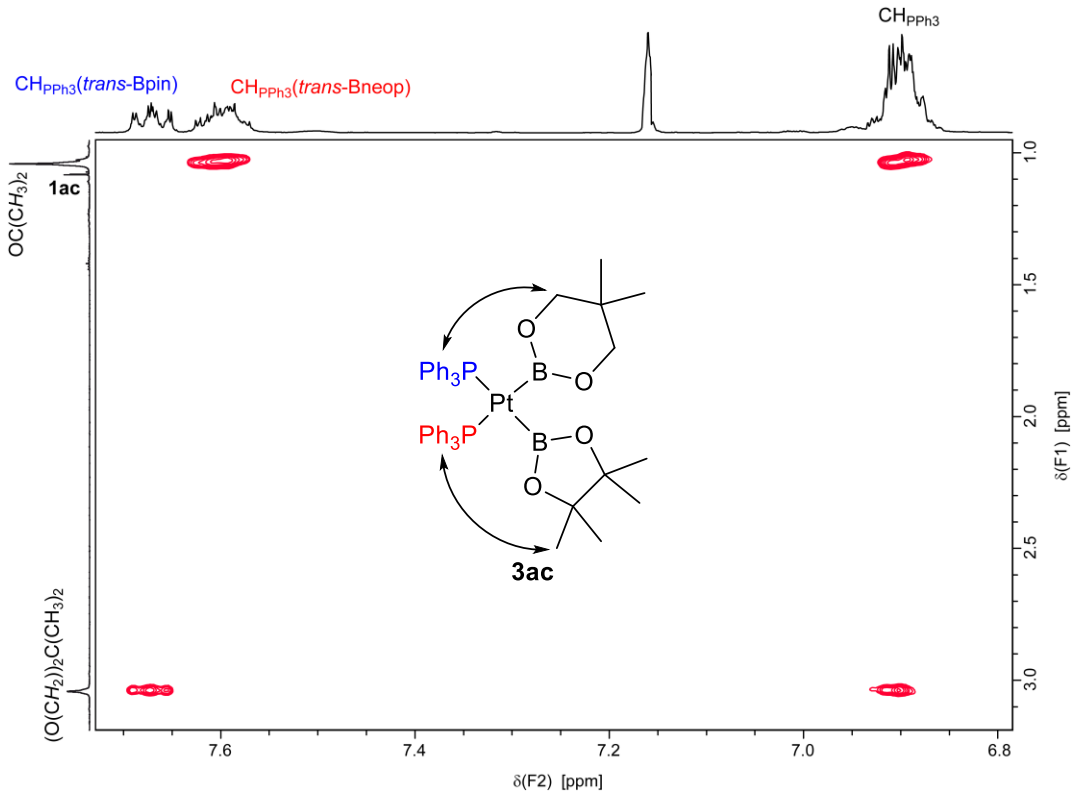

Figure S2b. Detail of the ^{1}H-^{1}H NOESY NMR spectrum of **3ac** (500 MHz, C_6D_6). NOESY contacts relevant to establish the solution structure are assigned; Signals of **1ac** are assigned.

1.c. [Pt(PPh$_3$)$_2$(Bpin)(BMeEn)] (**3ae**)

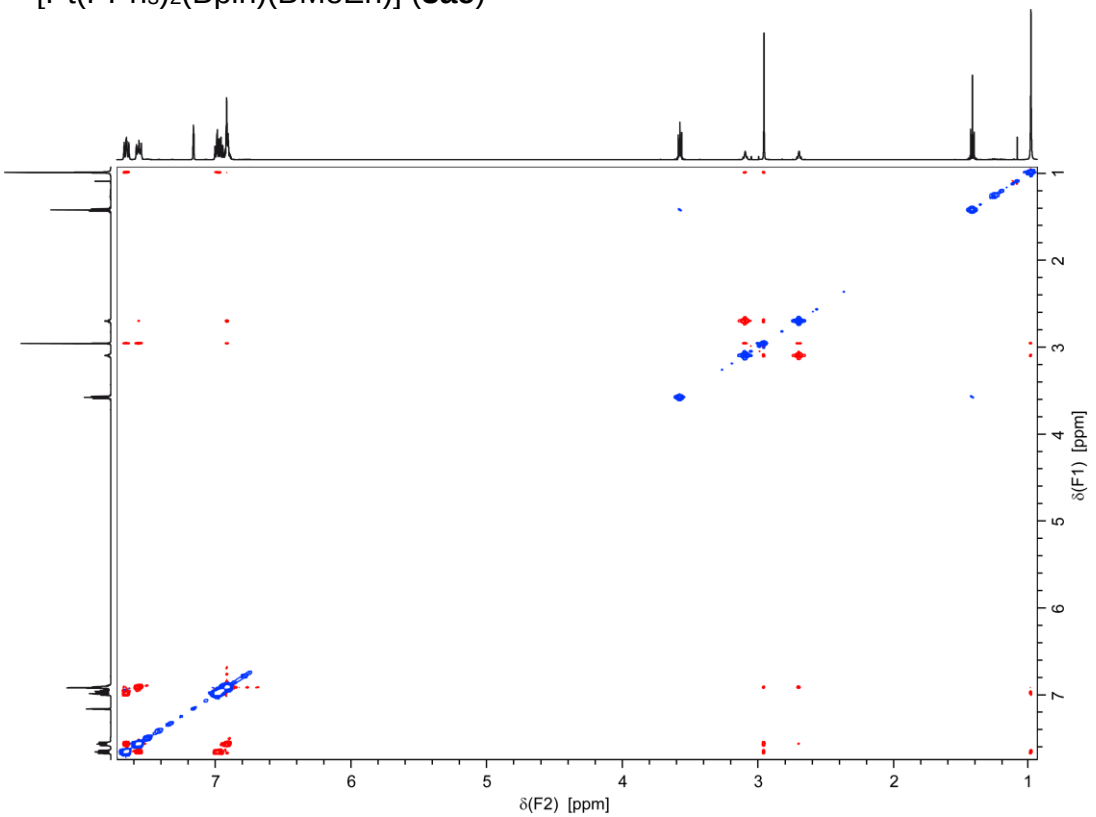

Figure S3a. ^{1}H-^{1}H NOESY NMR spectrum of **3ae** (500 MHz, C_6D_6).

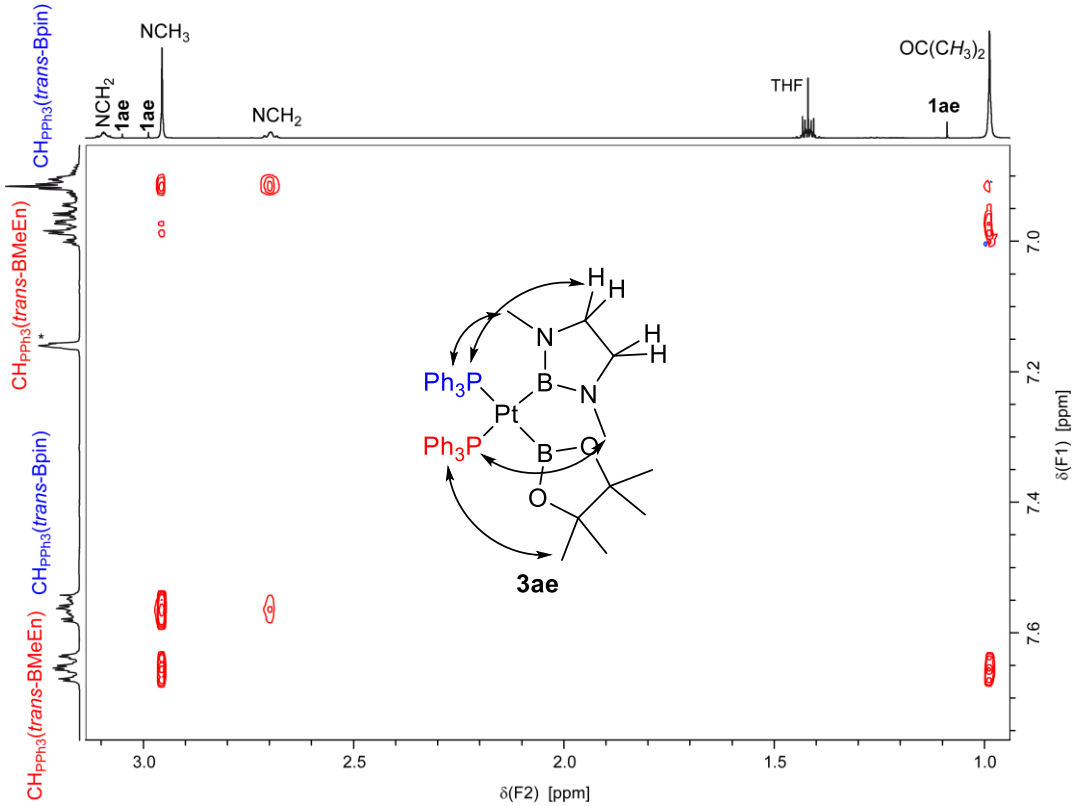

Figure S3b. Detail of the ^{1}H-^{1}H NOESY NMR spectrum of **3ae** (500 MHz, C_6D_6). NOESY contacts relevant to establish the solution structure are assigned; Signals of **1ae** are assigned.

1.d. [Pt(PPh$_3$)$_2$(Bcat)(Bdmab)] (**3bd**)

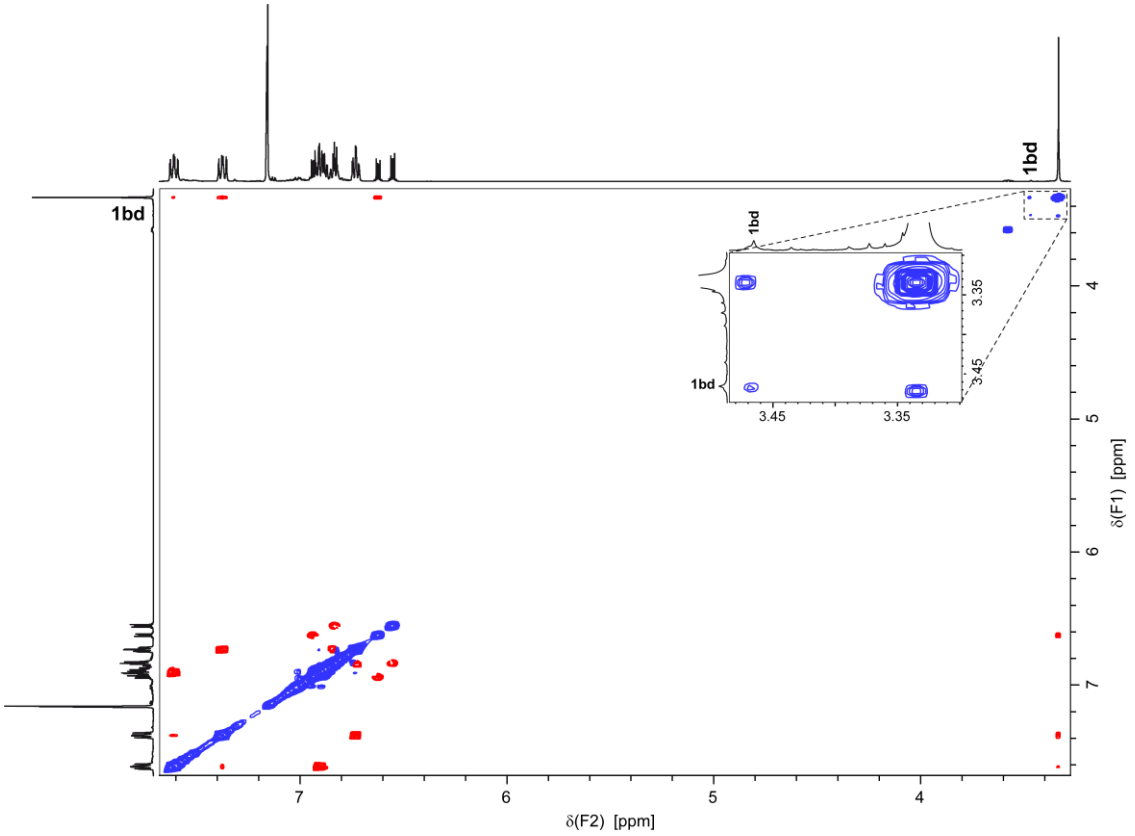

Figure S4a. ^{1}H-^{1}H NOESY NMR spectrum of **3bd** (500 MHz, C_6D_6). Selected signals of **1bd** are assigned.

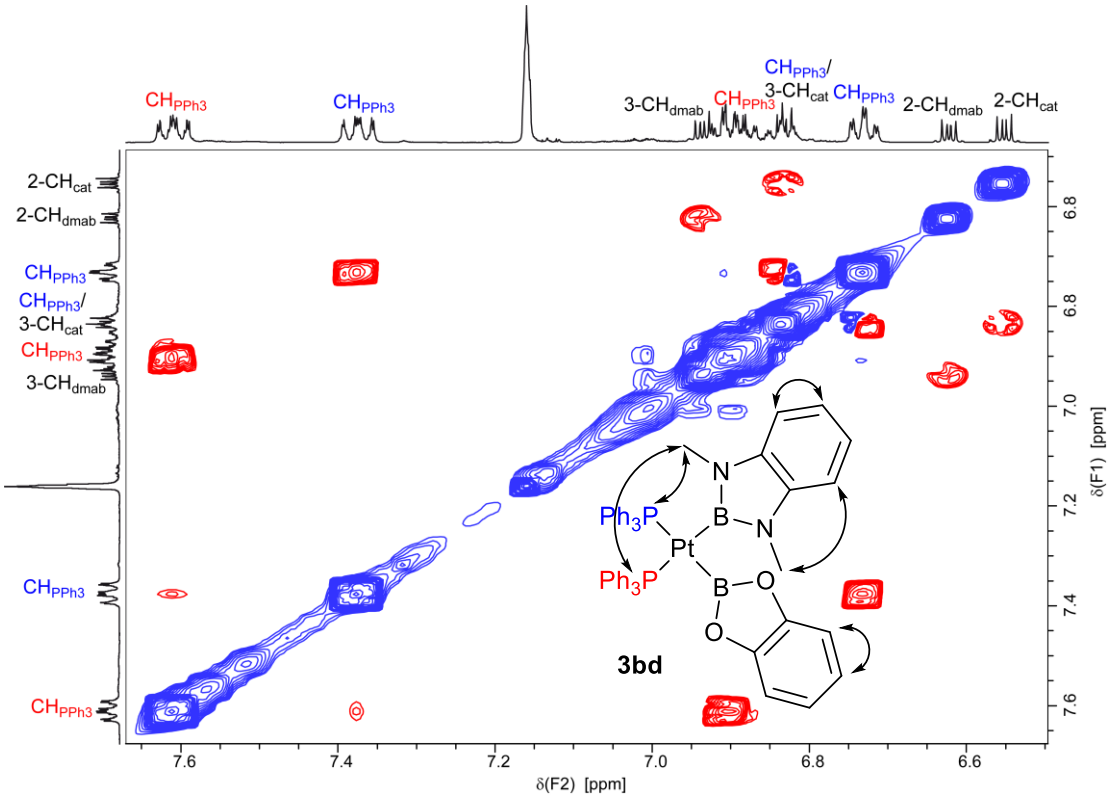

Figure S4b. Detail of the ^{1}H-^{1}H NOESY NMR spectrum of **3bd** (500 MHz, C_6D_6). NOESY contacts relevant to establish the solution structure are assigned.

1.e. [Pt(PPh$_3$)$_2$(Bcat)(BMeEn)] (**3be**)

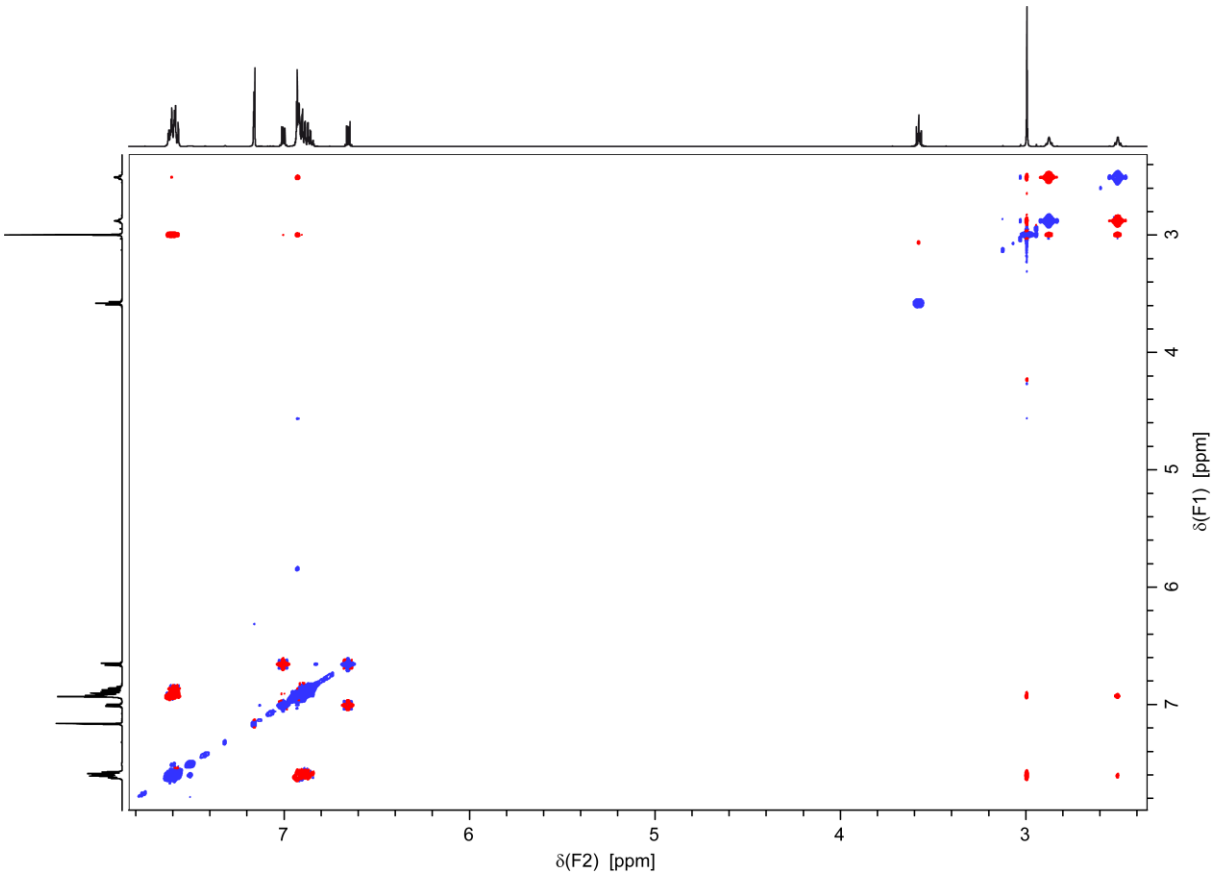

Figure S5. ^{1}H-^{1}H NOESY NMR spectrum of **3be** (500 MHz, C_6D_6).

2. ADDITIONAL EXPERIMENTAL DATA

2.a. Synthesis of B_2map_2 (**1hh**)

In an atmosphere of dry nitrogen *N*-methyl-2-aminophenol (500 mg, 4.06 mmol, 2.0 eq) and tetrakis(dimethylamino)diboron(4) (422 mg, 2.13 mmol, 1.05 eq) were combined in dry CH_2Cl_2 (10 mL). To this suspension HCl was added (2 M in Et_2O; 0.1 mL, 0.2 mmol, 0.1 eq). After 40 h at ambient temperature all volatiles were removed *in vacuo* and the residue extracted with hot *n*-hexane (2 × 10 mL). The product crystallises upon concentration of the extract *in vacuo* and was obtained after drying in vacuo as a beige solid (184 mg, 0.7 mmol, 34%).

mp 161–165 °C.

Found: C, 63.7; H, 5.35; N, 10.6%. Calc. for $C_{14}H_{14}B_2N_2O_2$ (**1hh**): C, 63.4; H, 5.3; N, 10.5%.

δ_{1H} (300 MHz, C_6D_6, rt): 3.26 (6 H, s, NCH_3), 6.78 (2 H, dd, J = 7.6, 1.4 Hz, CH_{map}), 6.98 (2 H, td, J = 7.6, 1.5 Hz, CH_{map}), 7.07 (2 H, td, J = 7.6, 1.2 Hz, CH_{map}), 7.37 (2 H, ddd, J = 7.7, 1.3, 0.6 Hz, CH_{map}).

$\delta_{13C\{1H\}}$ (75 MHz, C_6D_6, rt): 29.5 (NCH_3), 109.6 (CH_{map}), 112.6 (CH_{map}), 120.7 (CH_{map}), 122.2 (CH_{map}), 138.7 (C_{map}), 151.5 (C_{map}).

$\delta_{11B\{1H\}}$ (96 MHz, C_6D_6, rt): 31.0 (s, $\Delta w_{½}$ = 343 Hz).

m/z (GC/MS, 70 eV): 264 $[M]^+$, 235 $[M–NMe]^+$, 132 $[C_7H_7BNO]^+$, 77 $[C_6H_5]^+$.

2.b. Attempted Synthesis of [Pt(PPh$_3$)$_2$(Bpin)(B*i*PrEn)] (**3af**)

Attempted Synthesis: [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] (**2**) (50 mg, 67 μmol, 1.0 eq) and pinB–B*i*PrEn (**1af**) (18.7 mg, 67 μmol, 1.0 eq) were mixed in toluene (5 mL). The redish solution was stirred at room temperature for 8 h whilst flask was evacuated for a few seconds every 60 min. The solvent was removed under reduced pressure to give a brownish-red solid that was analysed by NMR spectroscopy.

NMR experiment: [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] (**2**) (15 mg, 20 μmol, 1.0 eq) and pinB–B*i*PrEn (**1af**) (5.6 mg, 20 μmol, 1.0 eq) were combined in C$_6$D$_6$ (0.7 mL). After 1 h NMR spectra were recorded and the mixture was transferred under inert atmosphere to a Schlenk flask and the volatiles were removed *in vacuo* until approx. 0.1 mL of solution was left. To the residue C$_6$D$_6$ was added (until 0.6 – 0.7 mL overall volume) and NMR spectra were recorded. This evacuation/measurement cycle was repeated in the given intervals (Figure S6).

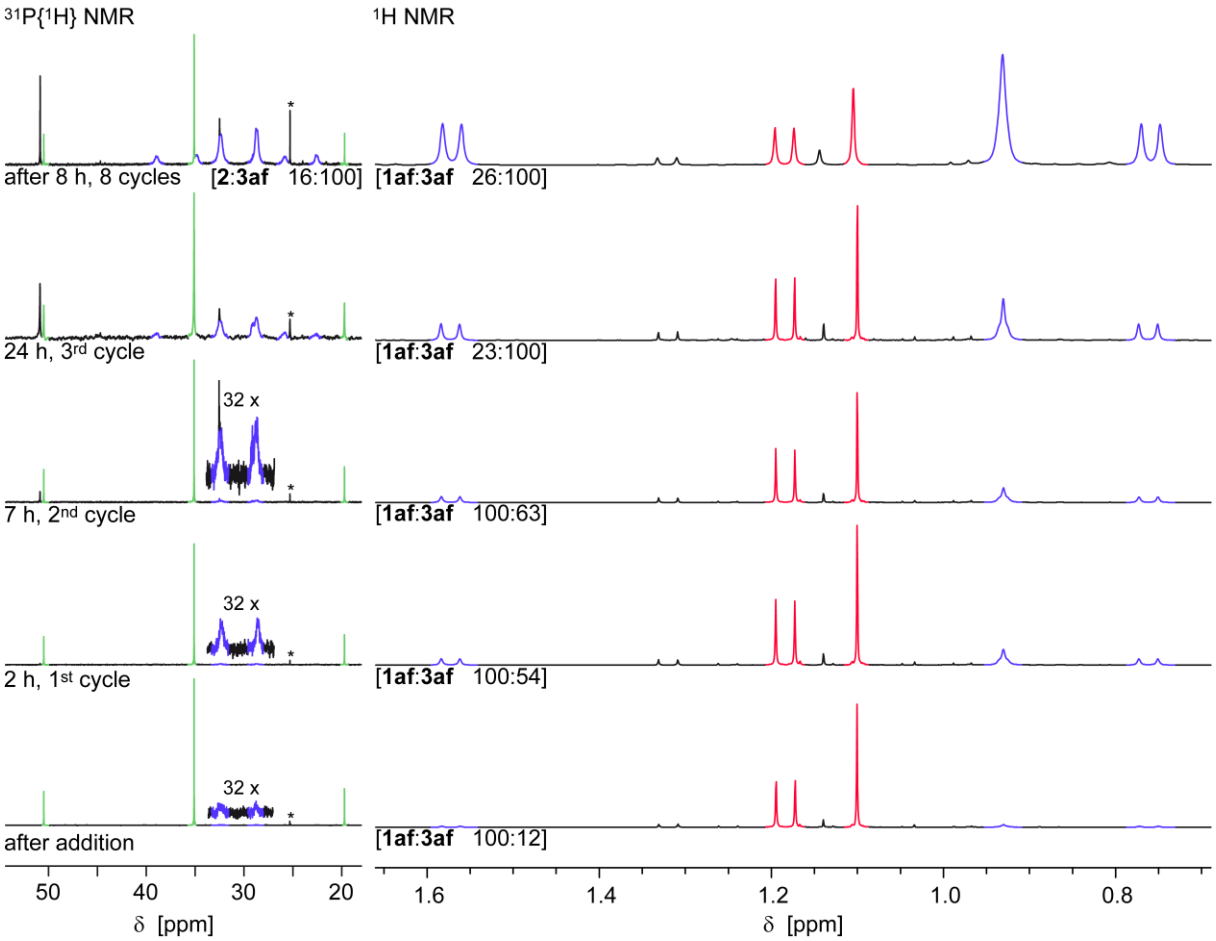

Figure S6. NMR spectra of the reactions of **2** with **1af**. Top: **1af** + **2**, isolated material after eight cycles of evacuation (8 h). Row 1–4: *In situ* NMR spectra of **1af** + **2**. 300/122 MHz, rt, C$_6$D$_6$, *: impurity of OPPh$_3$.

NMR data of **3af** obtained from spectra of mixtures of **1af**, **2** and **3af** (see above).

δ_H (300 MHz, C_6D_6, rt): δ 0.76 (6 H, d, J_{H-P} = 6.6 Hz, NCH(CH_3)$_2$), 0.94 (12 H, s, OC(CH_3)$_2$), 1.57 (6 H, d, J_{H-P} = 6.6 Hz, NCH(CH_3)$_2$), 3.11 (2 H, br. virt. t, J = 7.4 Hz, NCH_2), 3.32 (2 H, br. virt. t, J = 6.9 Hz, NCH_2), 4.50 (2 H, sept., J_{H-P} = 6.6 Hz, J_{H-Pt} = 8.2 Hz (satellites), NCH(CH_3)$_2$), 6.83 – 7.02 (9 H, m, CH_{PPh3}), 7.45 – 7.69 (6 H, m, CH_{PPh3}).

$\delta_{31P\{1H\}}$ (122 MHz, C_6D_6, rt): 28.7 (J_{P-Pt} = 1495 Hz (satellites), P_{PPh3}), 32.4 (J_{P-Pt} = 1600 Hz (satellites), P_{PPh3}).

$\delta_{11B\{1H\}}$ (96 MHz, C_6D_6, rt): 45 (br. s, $\Delta w_{½}$ = 1200 Hz).

2.c. [Pt(PPh$_3$)$_2$(Bpin)(B*t*BuEn)] (**3ag**) (*in situ* NMR experiment)

[Pt(PPh$_3$)$_2$(C$_2$H$_4$)] (**2**) (15 mg, 20 μmol, 1.0 eq) and pinB–B*t*BuEn (**1af**) (6.2 mg, 20 μmol, 1.0 eq) were combined in C$_6$D$_6$ (0.7 mL). After 1 h NMR spectra were recorded and the mixture was transferred under inert atmosphere to a Schlenk flask and the volatiles were removed *in vacuo* until approx. 0.1 mL solution was left. To the residue C$_6$D$_6$ was added (until 0.6 – 0.7 mL over all volume) and NMR spectra were recorded. This evacuation/measurement cycle was repeated in the given intervals.

2.d. Decomposition of $[Pt(PPh_3)_2(Bneop)_2]$ (**3cc**) (*in situ* NMR experiment)

$[Pt(PPh_3)_2(Bneop)_2]$ (**3cc**) (20 mg) was dissolved in C_6D_6 (0.65 mL) and transferred to a screw-cap NMR tube; NMR spectra were recorded in the given intervals.

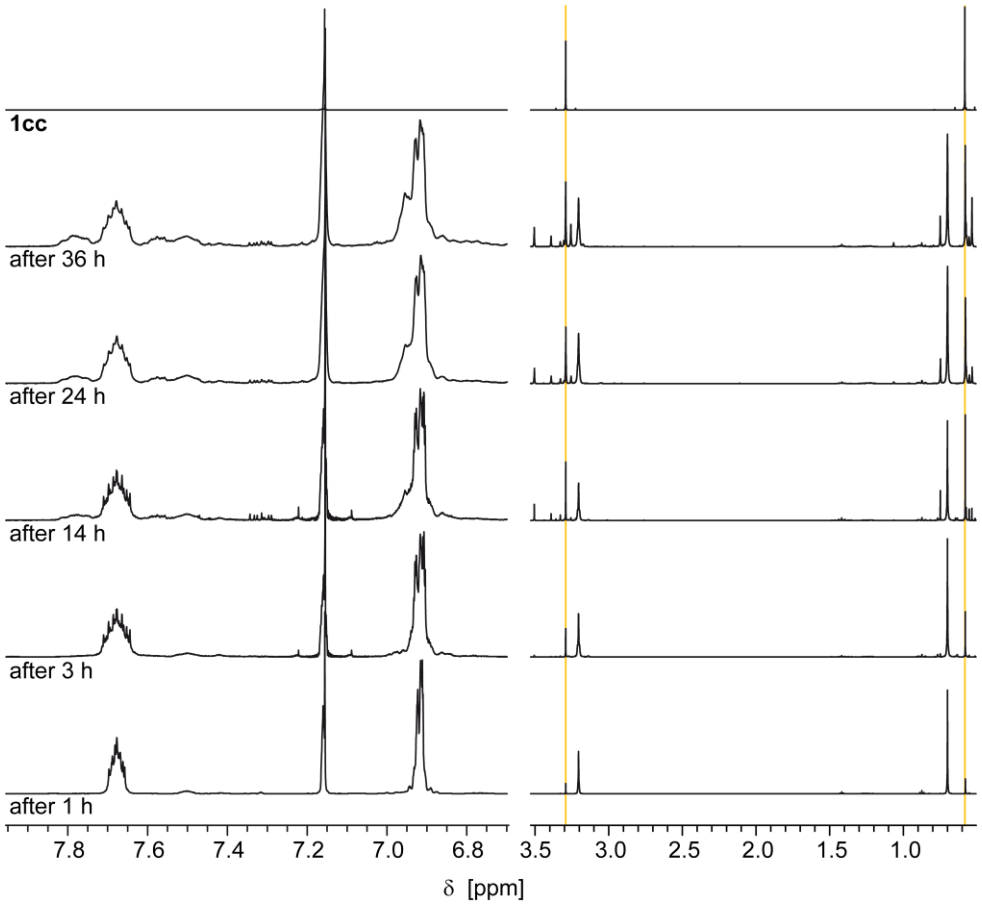

Figure S7a. Details of ^1H NMR spectra of **3cc** in C_6D_6 after different time intervals at room temperature and **1cc** for comparison (after 1 h: 500 MHz, all other 300 MHz).

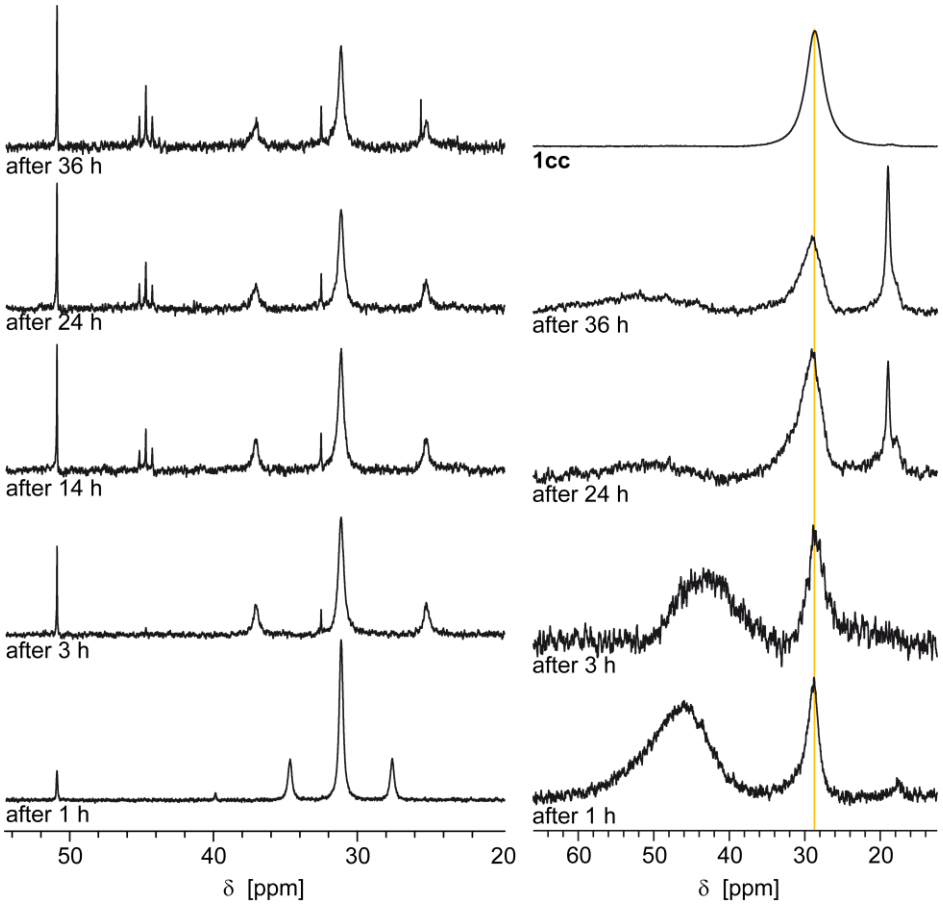

Figure S7b. Details of $^{31}P\{^{1}H\}$ NMR (left) and $^{11}B\{^{1}H\}$ NMR (right) spectra of **3cc** in C_6D_6 after different time intervals at room temperature and **1cc** for comparison (after 1 h: 202/160 MHz, all other 121/96 MHz).

3. ADDITIONAL CRYSTALLOGRAPHIC DATA

Table S1. Crystallographic data collection parameter of **1hh**, [((Ph$_3$P)Pt-μ-PPh$_2$)$_2$](C$_4$H$_8$O), (Ph$_3$P)$_2$Pt$_3$(μ-PPh$_2$)$_3$Ph](C$_4$H$_8$O)$_2$ and (dmabB)(Ph)C=C(Ph)(Bpin) (**4ad**).

Compound	**1hh**	**[((Ph$_3$P)Pt (μ-PPh$_2$)$_2$](C$_4$H$_8$O)**	**[(Ph$_3$P)$_2$Pt$_3$ (μ-PPh$_2$)$_3$Ph](C$_4$H$_8$O)$_2$**	**4ad**
Formula	$C_{14}H_{14}B_2N_2O_2$	$C_{60}H_{50}P_4Pt_2$, C_4H_8O	$C_{78}H_{65}P_5Pt_3$, 2 C_4H_8O	$C_{28}H_{32}B_2N_2O_2$
M_r/(g mol^{-1})	263.89	1357.16	1886.62	450.17
crystal shape	needle	fragment	needle	fragment
crystal colour	clear colourless	intense orange	intense orange	clear colourless
cryst. dim. /mm^3	0.22 × 0.05 × 0.06	0.28 × 0.16 × 0.09	0.25 × 0.03 × 0.02	0.36 × 0.32 × 0.06
crystal system	monoclinic	monoclinic	orthorhombic	triclinic
space group (no.)	$P2_1/n$ (14)	$P2_1/n$ (14)	$Pbcn$ (60)	$P\bar{1}$ (2)
a /Å	8.4528(9)	15.4162(4)	22.117(1)	8.3489(5)
b /Å	5.4962(9)	16.3872(6)	17.9826(8)	10.4195(6)
c /Å	14.461(2)	21.6032(6)	17.998(1)	15.5364(8)
α	90°	90°	90°	99.516(5)°
β	99.64(1)°	96.815(3)°	90°	101.387(5)°
γ	90°	90°	90°	101.387(5)°
V /Å^3	662.4(2)	5419.0(3)	7158.0(6)	1272.7(1)
Z, Z'	2, ½	4, 1	4, ½	2, 1
$D_{calcd.}$ /(g cm^{-3})	1.323	1.663	1.751	1.175
μ /mm^{-1} (λ /Å)	0.696 (1.54184)	5.318 (0.71073)	6.011 (0.71073)	0.072 (0.71073)
Absorption corr.	multi-scan	analytical	analytical	multi-scan
2θ range (compl.)	11.37–139.9° (100%)	4.25–49.99° (99.9%)	4.52–51.99° (100%)	5.09–54.00° (99.3%)
refl. measured	15928	29267	182179	18499
unique (R_{int})	1257 (0.0744)	29267 (n/a)	7040 (0.2267)	5526 (0.0426)
observed[a]	1090	9689	4635	3964
param. / restr.	92 / 0	642 / 12	435 / 0	313 / 0
R_1 (obs. rflns.)[a]	0.0494	0.0432	0.0441	0.0523
wR_2 (all rflns.)	0.1474	0.0709	0.1045	0.1244
GooF on F^2	1.081	0.622	1.006	1.023
max./min. ρ /(e Å^{-3})	0.423 / –0.294	1.958 / –2.104	2.160 / –1.228	0.400 / –0.259
CCDC No.	1881533	1881532	1881535	1881539

[a] Observation criterion: $I > 2\sigma(I)$.

3.a. **3ae**(C_4H_8O)$_{1.5}$

The crystal is weakly non-merohedrally twinned by 177.19° rotation about the b axis. The structure was refined as a 2-component twin. The twin ratio refined to 0.0571(7). Only reflections belonging to the major component was used in the refinement.

The structure contains 1.5 molecules of THF in the asymmetric unit. The half-occupied molecule is disordered around a centre of inversion. The latter molecule was refined employing geometry restraints (SAME); the DSR programme was used in the refinement.[S1]

3.b. **3cc**(C_4H_8O)

The crystal is a three-component twin. The structure was solved on the basis of the reflection of the main component (R_{int} = 0.074); for refinement data of all three components were used. The twin factors refined to 0.2930(7) and 0.1163(8). The high additional residual electron density may be associated with further not included twin components.

Twin law:

Component 2 rotated by 180° around [0 1 0] (reciprocal) or [0.15 0.92 -0.37] (direct)

Component 3 rotated by 180° around [0.03 1.00 0.02] (reciprocal) or [0.17 0.92 -0.36] (direct)

3.c. [((Ph$_3$P)Pt-μ-PPh$_2$)$_2$](C$_4$H$_8$O)

The crystal is non-merohedrally twinned by rotation about [0.01 0.83 -0.56] (reciprocal), [-0.05 0.93 -0.37] (direct) axis, respectively, and was refined as two component twin. The twin factor refined to 0.07024.

The atoms O1 and C61 within the THF molecule were restraint to approximate isotropic behaviour (ISOR).

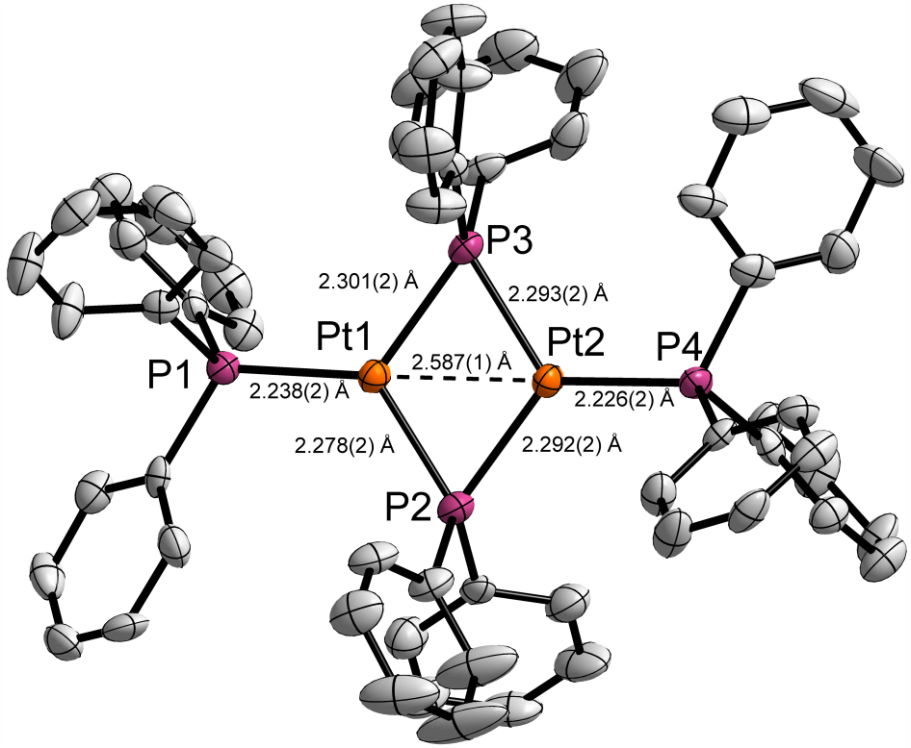

Figure S8. Molecular structure of [((Ph$_3$P)Pt-μ-PPh$_2$)$_2$] in the crystal structure of [((Ph$_3$P)Pt-μ-PPh$_2$)$_2$](C$_4$H$_8$O) with selected distances.

3.d. $[(Ph_3P)_2Pt_3(\mu\text{-}PPh_2)_3Ph](C_4H_8O)_2$

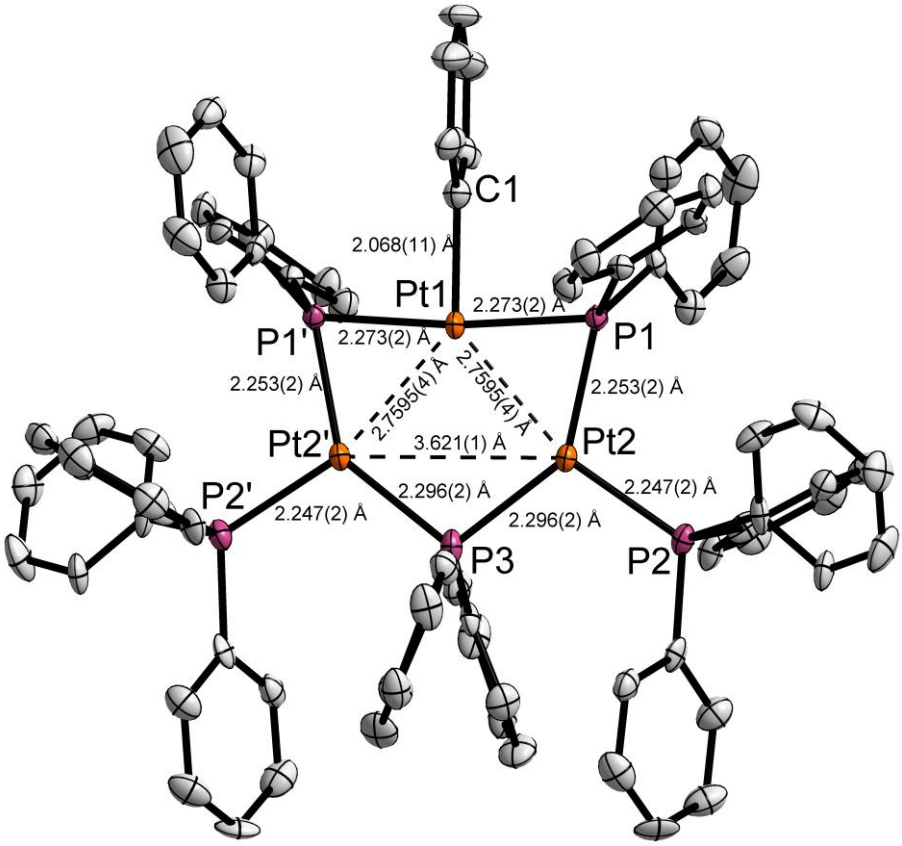

Figure S9. Molecular structure of $[(Ph_3P)_2Pt_3(\mu\text{-}PPh_2)_3Ph]$ in the crystal structure of $[(Ph_3P)_2Pt_3(\mu\text{-}PPh_2)_3Ph](C_4H_8O)$ with selected distances.

3.e. B_2map_2 (**1hh**)

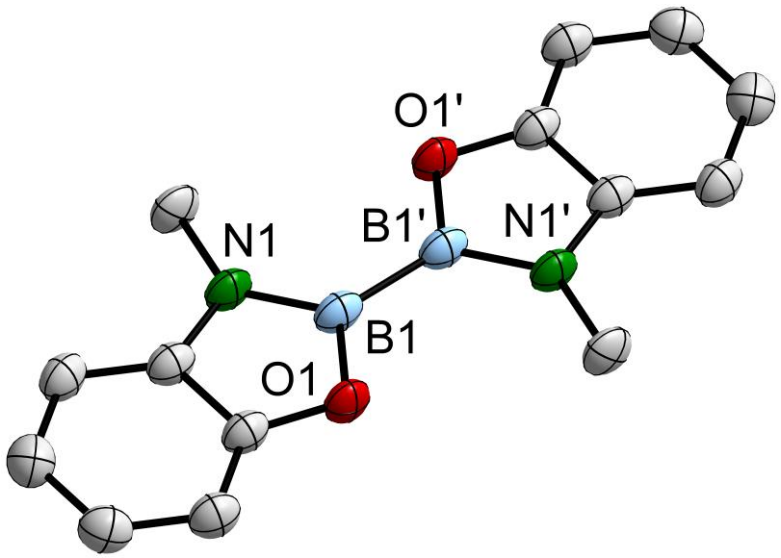

Figure S10. Molecular structure of B_2map_2 (**1hh**) situated on a centre of inversion (at (½, 0, 0)). Selected distances (Å) and angles [°]: B1–B1' 1.678(4), B1–O1 1.417(2), B1–N1 1.420(2), O1–B1–N1 107.4(2), B1'–B1–O1 123.89(2), B1'–B1–N1 128.8(2).

3.f. (dmabB)(Ph)C=C(Ph)(Bpin) (**4ad**)

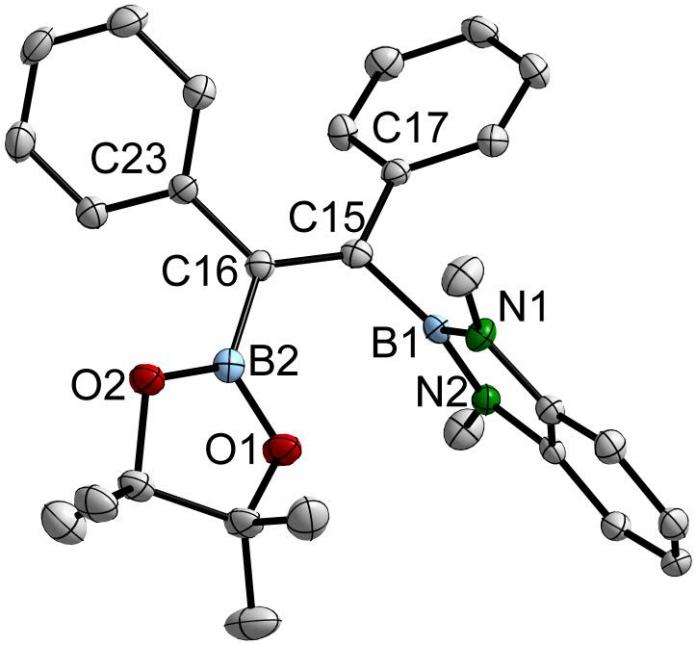

Figure S11. Molecular structure of (dmabB)(Ph)C=C(Ph)(Bpin) (**4ad**).
Selected distances (Å): B1–C15 1.571(3), B1–N1 1.433(2), B1–N2 1.423(2), B2–C16 1.565(2), B2–O1 1.368(2), B2–O2 1.367(2), C15–C16 1.362(2), C15–C17 1.495(2), C16–C23 1.490(2).

4. REFERENCES

[S1] D. Kratzert, J. J. Holstein, I. Krossing, *J. Appl. Cryst.*, 2015, **48**, 933-938.