Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for:

Variable Coordination Modes and Catalytic Dehydrogenation of *B*-Phenyl Amine-Boranes

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Crystallography

General Details

X-ray crystallography data for **1**, **2**, **η^2-3**, **5**, **7**, **10** and **11** was collected on an Agilent SuperNova diffractometer using graphite monochromated Cu Kα radiation (λ = 1.54180 Å) and a low-temperature device [150(2) K]; data were collected using SuperNova, reduction and cell refinement was performed using CrysAlis.[1] Data for **4** was collected on an Enraf Nonius Kappa CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) and a low-temperature device [150(2) K];[2] data were collected using COLLECT, reduction and cell refinement was performed using DENZO/SCALEPACK.[3] All structures were solved by direct methods (SHELXS-97) and refined by full matrix least squares using SHELXL-14.[4] Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre under **CCDC** 1445275-82. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Treatment of 10

The structure of **10** has a large R-factor due to the poor quality of the crystals and hence the data. The structure also contains a significant degree of disorder of the phosphine alkyl groups. Each Rh centre is also bound to 2 hydride ligands which were detected by NMR spectroscopy and mass spectrometry (see experimental). Due to the poor quality of the data the Rh-bound hydrogen atoms could not be reliably located and refined so they were omitted. The BH_2 hydrogen atoms were placed in calculated positions based on the geometry of the boron centre.

The i-propyl groups of the phosphine ligands contain significant disorder. The disorder has been modelled over 2 sites and the occupancies allowed to refine freely. The P-C and C-C bonds of the disordered components have been fixed to 1.84 and 1.54 Å by the DFIX command respectively. The ellipsoids of the disordered C atoms were described by the ISOR command.

Treatment of 11

The R-factor of the structure of **11** is rather high due to poor data quality resulting from a poorly diffracting crystal and disorder of the phosphine alkyl groups

The hydride H(1) was located in the difference map and the Rh-H distance fixed to 1.44 Å by the DFIX command. The presence of this hydride has also been determined by NMR spectroscopy and mass spectrometry (see experimental).

The i-propyl groups of the phosphine ligands contain significant disorder. The disorder has been modelled over 2 sites and the occupancies allowed to refine freely. The P-C and C-C bonds of the disordered components have been fixed to 1.84 and 1.54 Å by the DFIX command respectively.

Certain atoms have been fixed to the same position using the EXYZ and EADP commands. The ellipsoids of the disordered C atoms were described by the ISOR command.

Table S1: Crystallographic data

Compound	**1**	**2**	**η^2-3**
CCDC No.	1445275	1445276	1445277
Formula	$C_{59}H_{70}B_2F_{24}NP_2Rh$	$C_{56}H_{62}B_2F_{24}NP_2Rh$	$C_{65}H_{82}B_2F_{24}NP_2Rh$
M	1435.63	1391.53	1519.78
Crystal System	Monoclinic	Orthorhombic	Orthorhombic
Space group	*P* 21/c	*P b c a*	*P n a* 21
T [K]	150(2)	150(2)	150(2)
a [Å]	36.8146(6)	25.1599(2)	51.6071(4)
b [Å]	14.0680(2)	18.78740(10)	19.7098(2)
c [Å]	26.0748(4)	26.2494(2)	14.21100(10)
α [°]	90	90	90
β [°]	103.843(2)	90	90
γ [°]	90	90	90
V [Å^3]	13112.1(4)	12407.81(15)	14454.9(2)
Z	8	8	8
Density [g cm^{-3}]	1.454	1.490	1.397
μ (mm^{-1})	3.515	3.697	3.219
θ range [deg]	$3.376 \leq \theta \leq 76.415$	$3.367 \leq \theta \leq 75.020$	$3.410 \leq \theta \leq 76.478$
Reflns collected	78635	31463	166541
R_{int}	0.0295	0.0214	0.0559
Completeness	98.6%	96.9%	98.0%
No. of data/restr/param	27168/1194/1869	12403/608/1037	29727/2598/2360
R_1 [$I > 2\sigma(I)$]	0.0423	0.0393	0.0517
wR_2 [all data]	0.1206	0.1216	0.1318
GoF	0.956	0.787	0.867
Largest diff. pk and hole [eÅ^{-3}]	0.891, -0.908	0.583, -0.680	0.579, -1.076

Table S2: Crystallographic data

Compound	**4**	**5**	**7**
CCDC No.	1445278	1445279	1445280
Formula	$C_{70}H_{58}B_2F_{24}NP_2Rh$	$C_{68}H_{54}B_2F_{24}NP_2Rh$	$C_{55}H_{60}B_2F_{24}NP_2Rh$
M	1555.64	1527.59	1377.51
Crystal System	Triclinic	Triclinic	Orthorhombic
Space group	*P* -1	*P* -1	*P b c a*
T [K]	150(2)	150(2)	150(2)
a [Å]	13.050(3)	12.9920(3)	25.3462(3)
b [Å]	13.326(3)	13.1179(3)	18.3643(2)
c [Å]	20.491(4)	20.8103(6)	25.7382(3)
α [°]	104.04(3)	106.257(2)	90
β [°]	94.17(3)	93.765(2)	90
γ [°]	95.59(3)	95.408(2)	90
V [Å^3]	3423.4(13)	3373.93(15)	11980.2(2)
Z	2	2	8
Density [g cm^{-3}]	1.509	1.504	1.527
μ (mm^{-1})	0.404	3.463	3.823
θ range [deg]	$5.122 \le \theta \le 27.504$	$3.433 \le \theta \le 75.025$	$3.432 \le \theta \le 73.256$
Reflns collected	28059	24085	85542
R_{int}	0.0233	0.0188	0.0351
Completeness	99.2%	96.2%	99.5%
No. of data/restr/param	15589/648/1042	13380/792/1052	11953/243/860
R_1 [$I > 2\sigma(I)$]	0.0393	0.0278	0.0549
wR_2 [all data]	0.1061	0.0741	0.1666
GoF	0.838	1.049	0.841
Largest diff. pk and hole [eÅ^{-3}]	0.921, -0.608	0.727, -0.558	3.169, -1.150

Table S3: Crystallographic data

Compound	**10**	**11**
CCDC No.	1445281	1445282
Formula	$C_{58}H_{68}B_2F_{24}NP_2Rh$	$C_{58}H_{66}B_2F_{24}NP_2Rh$
M	1421.60	1419.58
Crystal System	Monoclinic	Triclinic
Space group	*C 2/c*	*P* -1
T [K]	150(2)	150(2)
a [Å]	39.5210(18)	12.3669(8)
b [Å]	12.9114(4)	14.4784(13)
c [Å]	53.766(2)	18.9906(11)
α [°]	90	103.872(6)
β [°]	110.023(5)	103.598(5)
γ [°]	90	91.524(6)
V [Å^3]	25776.7(19)	3196.2(4)
Z	16	2
Density [g cm^{-3}]	1.465	1.475
μ (mm^{-1})	3.571	3.600
θ range [deg]	$3.403 \leq \theta \leq 73.193$	$3.156 \leq \theta \leq 75.137$
Reflns collected	49960	23146
R_{int}	0.0874	0.0785
Completeness	96.3%	95.8%
No. of data/restr/param	24884/1008/1984	12646/553/1000
R_1 [$I > 2\sigma(I)$]	0.0890	0.0834
wR_2 [all data]	0.2482	0.2658
GoF	0.994	0.999
Largest diff. pk and hole [eÅ^{-3}]	1.666, -1.725	0.845, -1.555

Comparison of Independent Cations in 1 and η^2-3

X-ray crystal structures of compounds **1** and **η^2-3** show 2 independent cations and 2 independent anions in the asymmetric unit. The cations were overlayed (figures S1 and S2) and revealed no significant differences in amine-borane coordination geometry. Some differences in ligand conformation were observed.

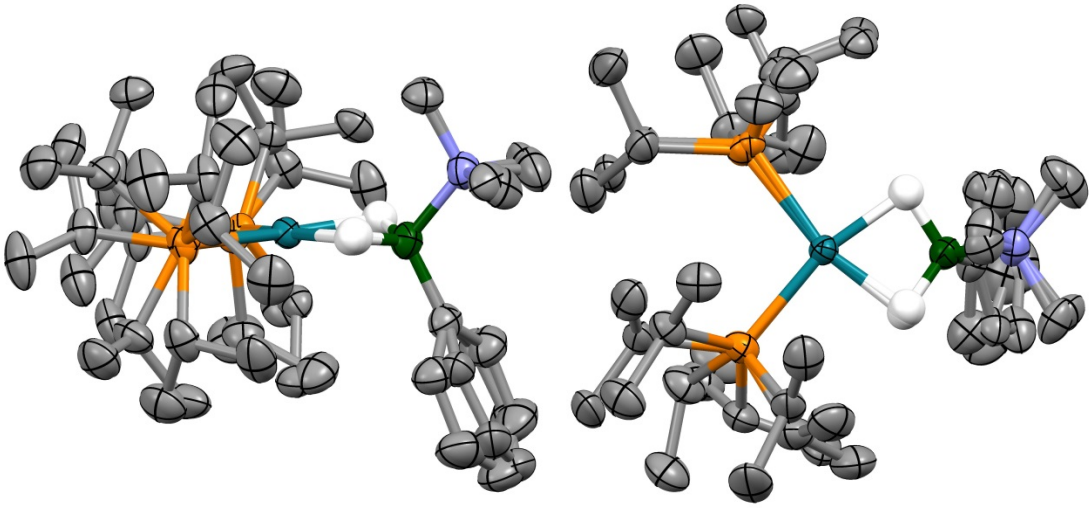

Figure S1: Overlay of the structure of the 2 independent cations in the asymmetric unit of **1**, viewed from the side (left) and top (right). Carbon – grey, hydrogen – white, rhodium – teal, phosphorus – orange, boron – green, nitrogen – blue.

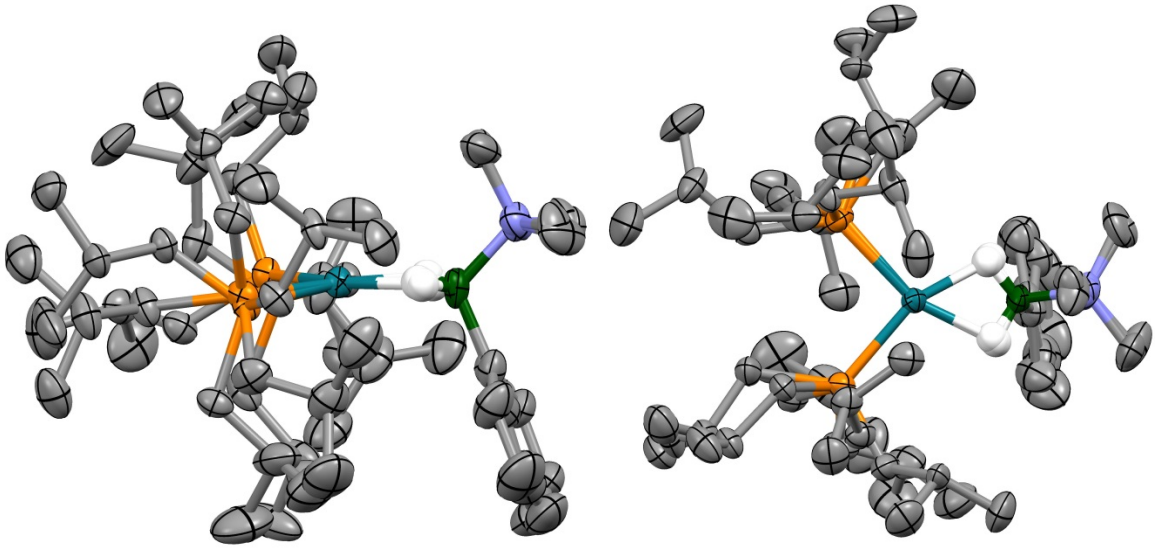

Figure S2: Overlay of the structure of the 2 independent cations in the asymmetric unit of **η^2-3**, viewed from the side (left) and top (right). Carbon – grey, hydrogen – white, rhodium – teal, phosphorus – orange, boron – green, nitrogen – blue.

Selected Spectra

Equilibrium between η^2 and η^6 binding modes of $[Rh(P^iBu_3)_2(PhH_2B{\cdot}NMe_3)][BAr^F{}_4]$ (η^2-3 and η^6-3)

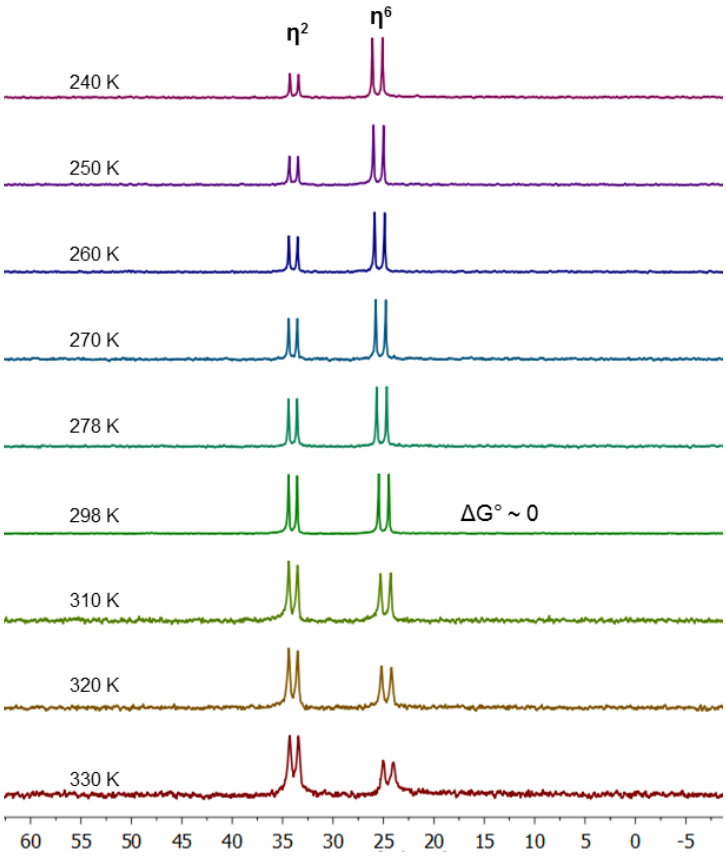

Figure S3: $^{31}P\{^1H\}$ NMR spectra of $[Rh(P^iBu_3)_2(PhH_2B{\cdot}NMe_3)][BAr^F{}_4]$ (**η^2-3** and **η^6-3**) in 1,2-$C_6H_4F_2$ at various temperatures (240-330 K).

Catalytic dehydrogenation of $PhH_2B{\cdot}NMe_2H$ (II) using $[Rh(^iPr_2P(CH_2)_3P^iPr_2)(C_6H_5F)][BAr^F_4]$ and $[Rh(P^iPr_3)_2(C_6H_5F)][BAr^F_4]$

At 298 K,

$[Rh(^iPr_2P(CH_2)_3P^iPr_2)(C_6H_5F)][BAr^F_4]$ (5 mol %): Apparent induction period of 1 h, 6% conversion in 5 h.

$[Rh(P^iPr_3)_2(C_6H_5F)][BAr^F_4]$ (5 mol %): No induction period, 15% conversion in 5 h.

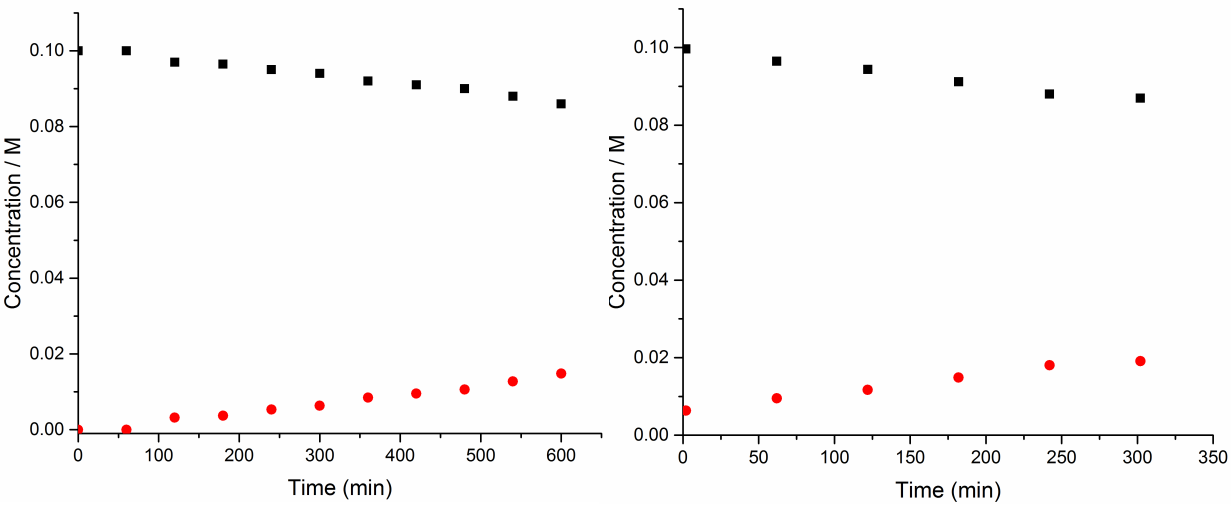

Figure S4: Plot of concentration (by ^{11}B NMR spectroscopy) against time for the catalytic dehydrogenation of $PhH_2B{\cdot}NMe_2H$ (initial concentration 0.1 M) using 5 mol % $[Rh(P^iPr_2(CH_2)_3P^iPr_2)(C_6H_5F)][BAr^F_4]$ (left) and 5 mol % $[Rh(P^iPr_3)_2(C_6H_5F)][BAr^F_4]$ (right) at 298 K, • = $PhHB{=}NMe_2$, ■ = $PhH_2B{\cdot}NMe_2H$.

At 350 K

$[Rh(^iPr_2P(CH_2)_3P^iPr_2)(C_6H_5F)][BAr^F_4]$ (5 mol %): Complete conversion in 60 minutes.

$[Rh(P^iPr_3)_2(C_6H_5F)][BAr^F_4]$ (5 mol %): Complete conversion in 30 minutes.

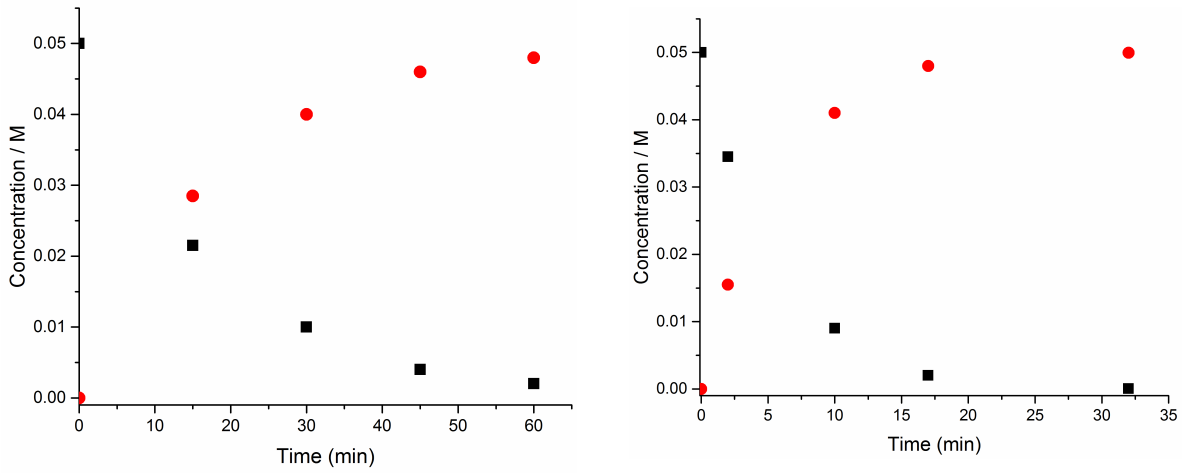

Figure S5: Plot of concentration (by ^{11}B NMR spectroscopy) against time for the catalytic dehydrogenation of $PhBH_2NHMe_2$ (initial concentration 0.05 M) using 5 mol % $[Rh(P^iPr_2(CH_2)_3P^iPr_2)(C_6H_5F)][BAr^F_4]$ (left) and 5 mol % $[Rh(P^iPr_3)_2(C_6H_5F)][BAr^F_4]$ (right) at 350 K in 1,2-$C_6H_4F_2$, • = $PhHB{=}NMe_2$, ■ = $PhH_2B{\cdot}NMe_2H$.

Dehydrogenation of $PhH_2B{\cdot}NMe_2H$ (II) Monitored In Situ by ^{11}B NMR Spectroscopy

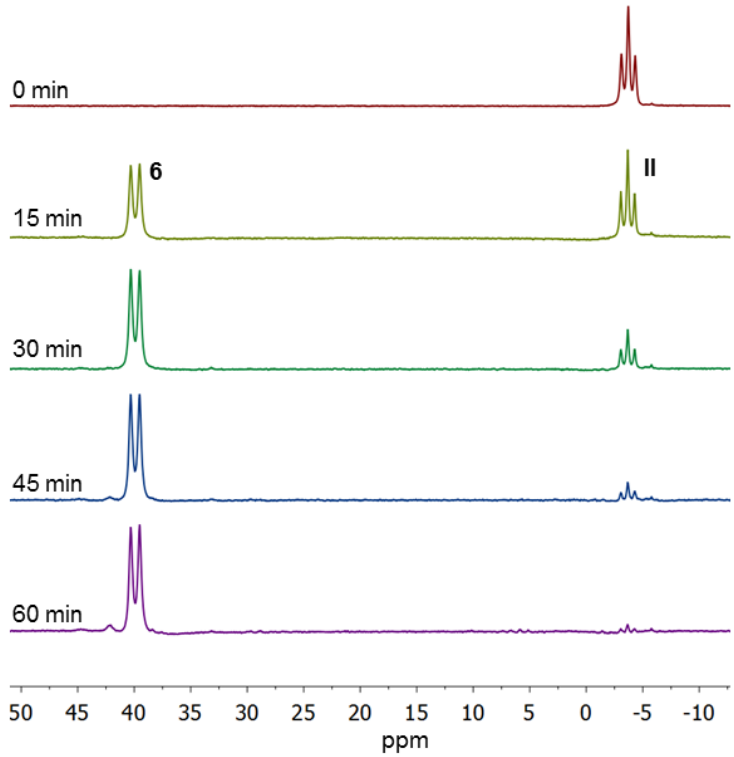

Figure S6: Representative ^{11}B NMR spectra for the catalytic dehydrogenation of $PhH_2B{\cdot}NMe_2H$ (**II**) (initial concentration 0.05 M) using 5 mol % $[Rh(^iPr_2P(CH_2)_3P^iPr_2)(C_6H_5F)][BAr^F_4]$ at 350 K in 1,2-$C_6H_4F_2$.

References

1. *Crysalis Pro.*, (2011) Oxford Diffraction Ltd, Abingdon, England.
2. J. Cosier and A. M. Glazer, *J. App. Cryst.*, 1986, **19**, 105.
3. Z. Otwinowski and W. Minor, in *Macromolecular Crystallography, Pt A*, 1997, vol. 276, pp. 307.
4. G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.