Electronic Supplementary Material (ESI) for ChemComm.

C,C'-Ru to C,B'-Ru Isomerisation in Bis(phosphine)Ru Complexes of [1,1′-Bis(*ortho*-carborane)]

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Supplementary Information

A. Synthesis and Characterisation

*1. Initial synthesis: [Ru(κ^3-2,2′,3′-{1-(1′-closo-1′,2′-$C_2B_{10}H_{10}$)-closo-1,2-$C_2B_{10}H_{10}$}($PMePh_2$)$_2$] (**1**) and [Ru(κ^3-2,3′,6-{1-(1′-closo-1′,2′-$C_2B_{10}H_{10}$)-closo-1,2-$C_2B_{10}H_{10}$}($PMePh_2$)$_2$] (**2**).*

To a solution of **I** (0.050 g, 0.0962 mmol) in THF (10 mL), was added $PMePh_2$ (0.09 mL, 0.481 mmol, 5 eq) and the mixture stirred at room temperature until the solution turned deep red (ca. 30 mins) following which time the solvent was removed *in vacuo*. The crude mixture was purified by preparative TLC [DCM:40-60 petroleum ether (petrol), 2:3] to afford yellow (R_f 0.58) and red (R_f 0.46) bands. Repeated TLC of the red band always produced some of the yellow product. The yellow band was subsequently identified as [Ru(κ^3-2,3′,6-{1-(1′-*closo*-1′,2′-$C_2B_{10}H_{10}$)-*closo*-1,2-$C_2B_{10}H_{10}$}($PMePh_2$)$_2$], **2**, and the red band as [Ru(κ^3-2,2′,3′-{1-(1′-*closo*-1′,2′-$C_2B_{10}H_{10}$)-*closo*-1,2-$C_2B_{10}H_{10}$}($PmePh_2$)$_2$], **1**. See below for detailed separate syntheses and spectroscopic characterisation of the two components.

*2. Synthesis of [Ru(κ^3-2,2′,3′-{1-(1′-closo-1′,2′-$C_2B_{10}H_{10}$)-closo-1,2-$C_2B_{10}H_{10}$}($PMePh_2$)$_2$] (**1**)*

To a cooled (0 °C) solution of **I** (0.050 g, 0.096 mmol) in THF (10 mL), was added $PMePh_2$ (0.09 mL, 0.481 mmol, 5 eq) and the mixture left to stir at 0 °C until the solution turned deep red (ca. 30 mins). The solvent was removed *in vacuo*. The product was dissolved in the minimum amount of DCM and then carefully layered with 5 times the volume petrol and set aside at -20 °C. Compound **1** was isolated as red crystals (0.0603 g, 80%).

NMR (CD_2Cl_2, -50 °C): $^{11}B\{^1H\}$; δ 14 to -22 overlapping resonances with prominent maxima at -3.7, -7.9 (assume 20B). ^1H; δ 7.51-7.45 [m, 2H, $PCH_3(C_6H_5)_2$], 7.44-7.38 [m, 1H, $PCH_3(C_6H_5)_2$], 7.36-7.23 [m, 7H, $PCH_3(C_6H_5)_2$], 7.21-7.09 [m, 6H, $PCH_3(C_6H_5)_2$], 7.06-6.99 [m, 2H, $PCH_3(C_6H_5)_2$], 6.96-6.89 [m, 2H, $PCH_3(C_6H_5)_2$], 2.35, [d, J_{HP} = 7.9 Hz, 3H, $PCH_3(C_6H_5)_2$], 2.16 [d, J_{HP} = 10.0 Hz, 3H, $PCH_3(C_6H_5)_2$]. $^1H\{^{11}B\}$ as for ^1H plus δ 2.67 to 2.08 considerable overlap of BH and CH_3 resonances (total integral 9BH + 6CH) with prominent BH maxima at 2.61, 2,46 and 2.24, 1.89 (4H), 1.75 to 1.47 overlapping resonances with prominent maxima at 1.70, 1.67, 1.60 and 1.55 (total integral 5H, BH), 0.95 (1H, BH), -3.27 (d, J_{HP} = 31.0 Hz, 1H, BHRu). $^{31}P\{^1H\}$; δ 34.3 (d, J_{PP} = 28.3 Hz, 1P), 22.6 (d, J_{PP} = 28.3 Hz, 1P).

EIMS: envelope centred on *m/z* 786.3 (M^+).

*3. Synthesis of [Ru(κ^3-2,3′,6-{1-(1′-closo-1′,2′-$C_2B_{10}H_{10}$)-closo-1,2-$C_2B_{10}H_{10}$}($PMePh_2$)$_2$] (**2**)*

To a solution of **I** (0.100 g, 0.192 mmol) in THF (10 mL) at room temperature, was added, dropwise, $PMePh_2$ (0.09 mL, 0.481 mmol, 2.5 eq). An immediate colour change from orange to red was observed. The solution was stirred at 40 °C until the solution turned yellow (ca. 2 hrs) following which THF was removed *in vacuo.* Compound **2** was isolated by column chromatography using an eluent system of DCM and petrol in the ratio of 2:3 as a yellow band (R_f 0.58, 0.097 g, 64%).

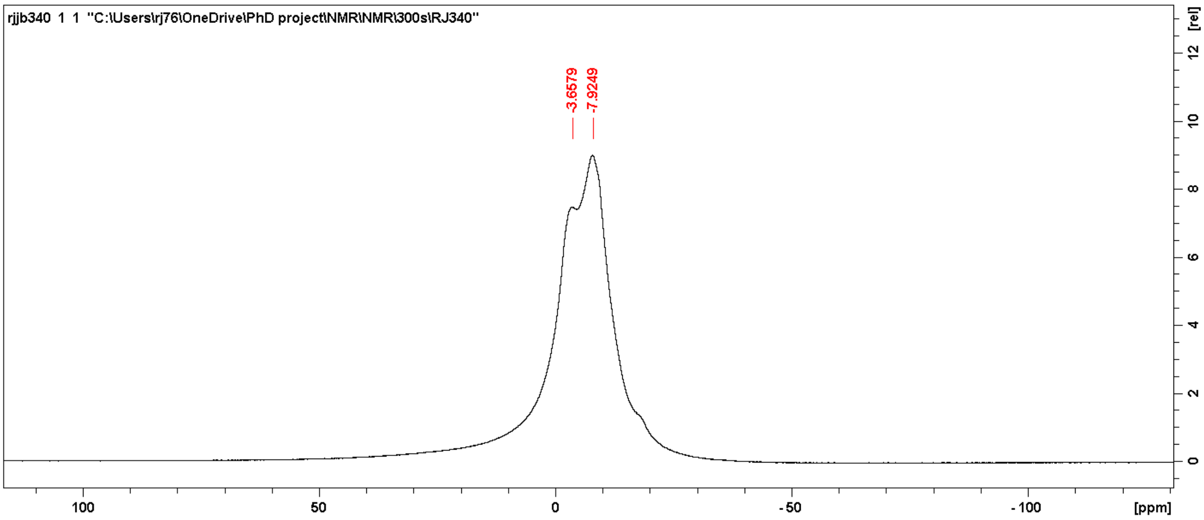
NMR (CD_2Cl_2, room temperature): $^{11}B\{^1H\}$; δ 0.2 (2B), -1.9 to -15.9 (overlapping resonances with maxima at -4.6, -8.7, and -14.6, total integral 17B), -17.0 (1B). ^1H; δ 7.60-7.55 [m, 2H, $PCH_3(C_6H_5)_2$], 7.43-7.20 [m, 18H, $PCH_3(C_6H_5)_2$], 2.34 [d, J_{PH} = 7.9 Hz, 3H, $PCH_3(C_6H_5)_2$], 1.85 (s, 1H, $C_{cage}H$) overlapping with 1.84 [d, J_{PH} = 9.5 Hz, 3H, $PCH_3(C_6H_5)_2$]. $^1H\{^{11}B\}$; as for ^1H plus δ 2.53 (2H, BH), 2.50

(1H, BH), 2.38 (1H, BH), 2.26 (3H, BH), 2.19 (1H, BH), 2.17 (2H, BH), 2.10 (2H, BH), 2.00 (1H, BH), 1.96 (1H, BH), 1.76 (1H, BH), 1.58 (3H), BH), -3.99 (d, J_{HP} = 27.6 Hz, 1H, BHRu). ^{13}C; δ 132.4 (d, J_{CP} = 11.3 Hz, $C_{arom.}$H), 132.1 (d, J_{CP} = 10.5 Hz, $C_{arom.}$H), 131.8 (d, J_{CP} = 11.2 Hz, $C_{arom.}$H), 131.5 (d, J_{CP} = 9.7 Hz, $C_{arom.}$H), 130.8 (d, J_{CP} = 2.2 Hz, $C_{arom.}$H), 130.4 (d, J_{CP} = 2.0 Hz, $C_{arom.}$H), 130.3 (d, J_{CP} = 2.5 Hz, $C_{arom.}$H), 130.2 (d, J_{CP} = 1.9 Hz, $C_{arom.}$H), 129.3 (d, J_{CP} = 9.7 Hz, $C_{arom.}$H), 129.1 (d, J_{CP} = 9.3 Hz, $C_{arom.}$H), 128.9 (d, J_{CP} = 9.3 Hz, $C_{arom.}$H), 128.7 (d, J_{CP} = 9.6 Hz, $C_{arom.}$H), 91.8 (C), 77.8 (C), 67.5 (C_{cage}H), 18.8 (d, J_{CP} = 28.2 Hz, CH_3), 14.2 (d, J_{CP} = 34.6 Hz, CH_3). ^{31}P{^{1}H}; δ 41.5 (d, J_{PP} = 28.0 Hz, 1P), 28.0 (d, J_{PP} = 28.0 Hz, 1P).

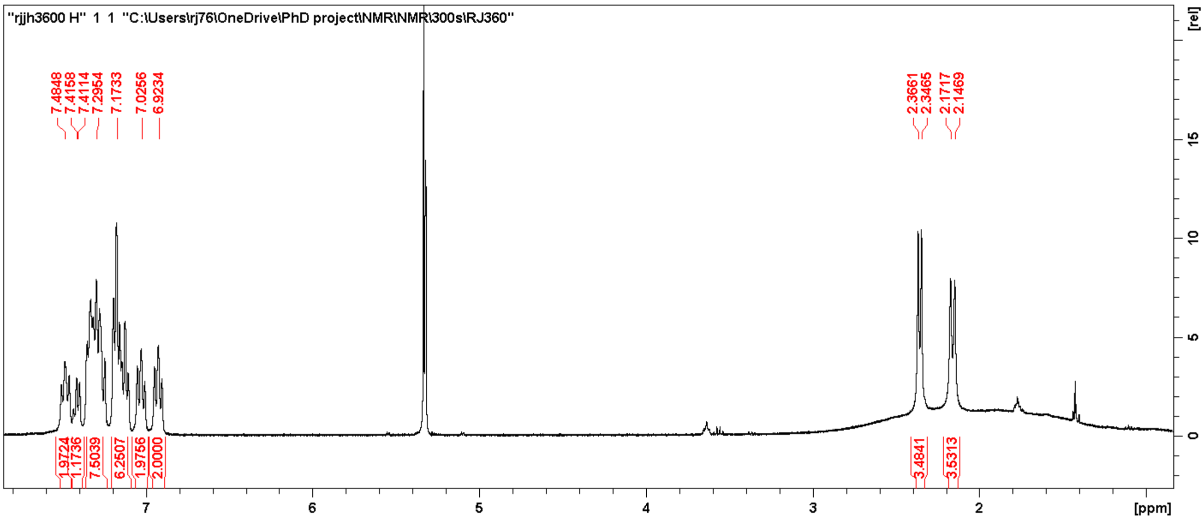
EIMS: envelope centred on *m/z* 786.3 (M^+), 586.2 (M^+ - $PMePh_2$).

NMR Spectra of **1** (CD_2Cl_2, -50 °C)

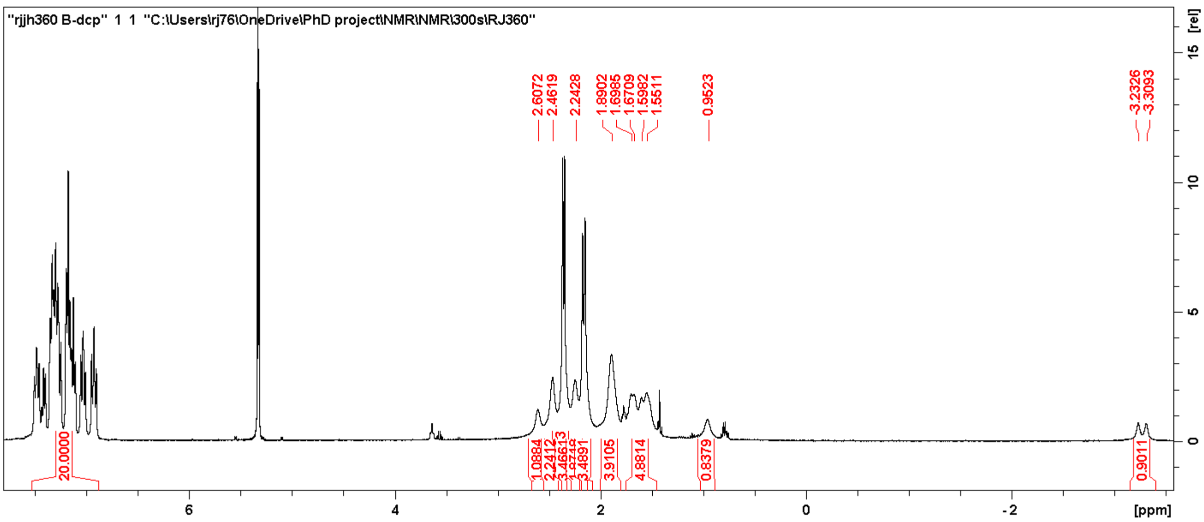
$^{11}B\{^{1}H\}$



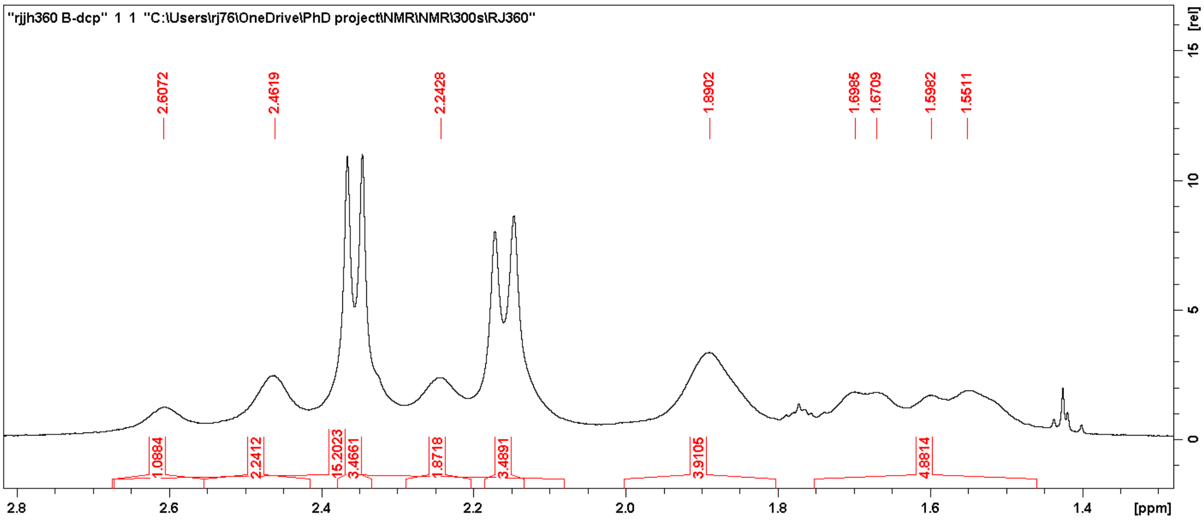
^{1}H



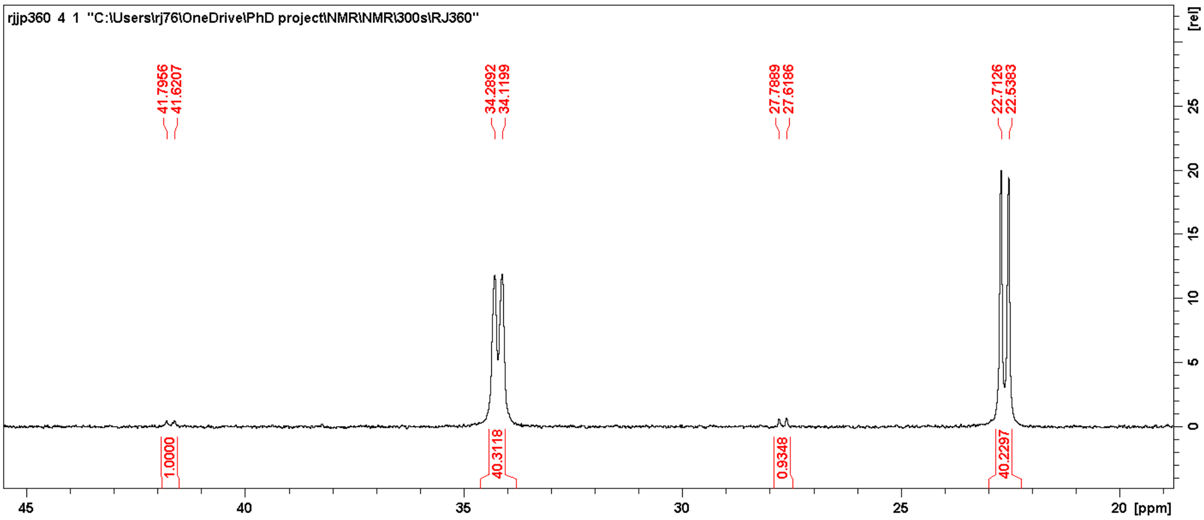
$^{1}H\{^{11}B\}$



$^{1}H\{^{11}B\}$ detail

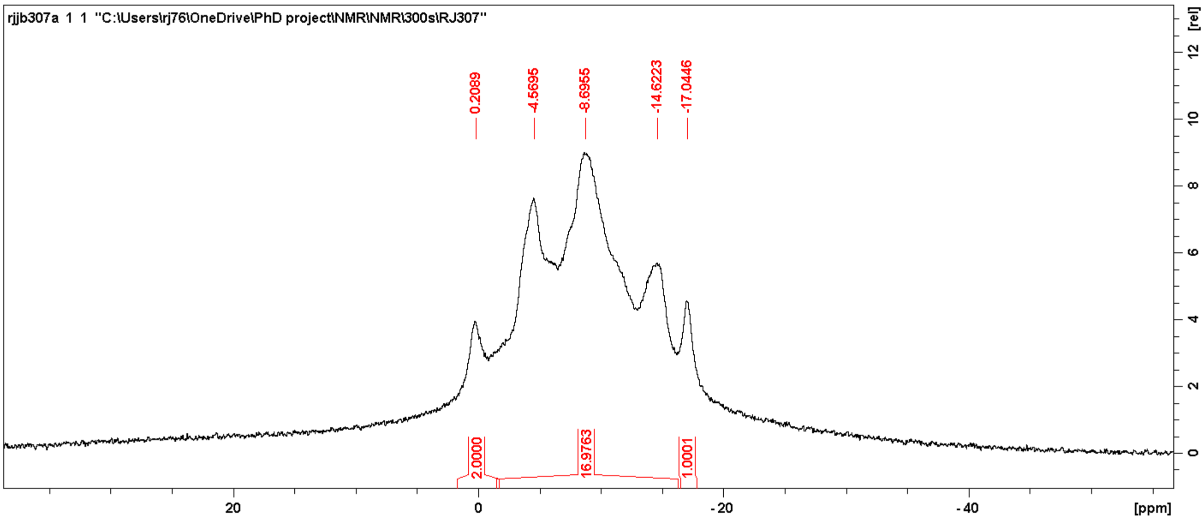


$^{31}P\{^{1}H\}$ (the small doublets at ca. 42 and 28 ppm are due to a trace of compound **2**)

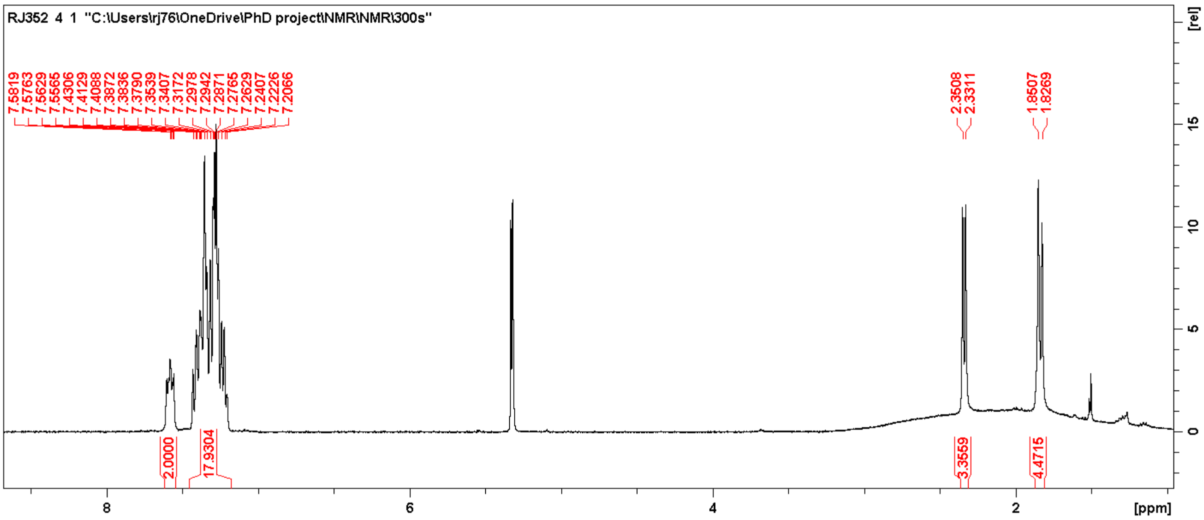


NMR Spectra of **2** (CD_2Cl_2, room temperature)

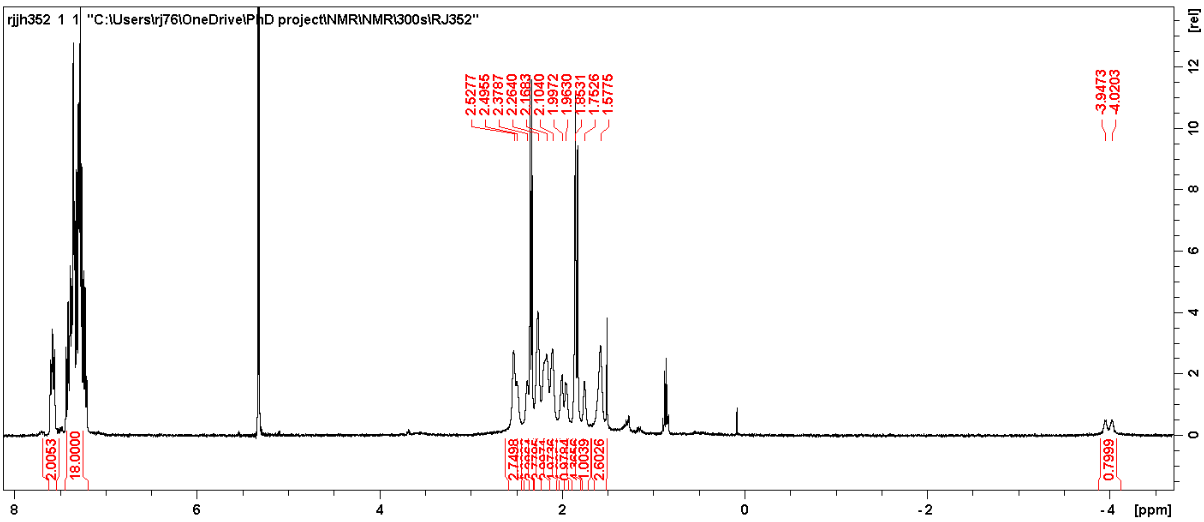
$^{11}B\{^1H\}$



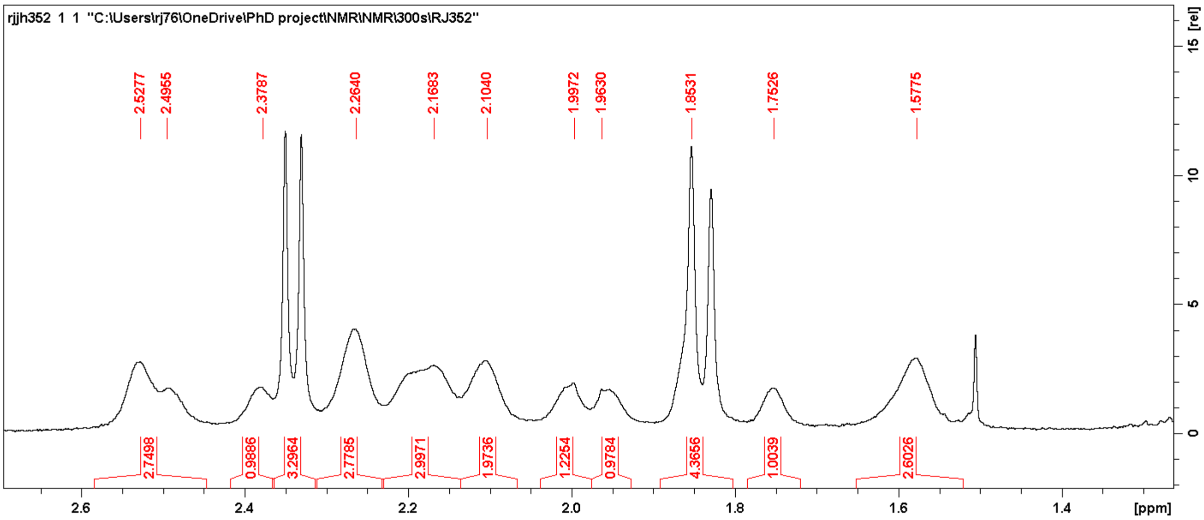
^1H



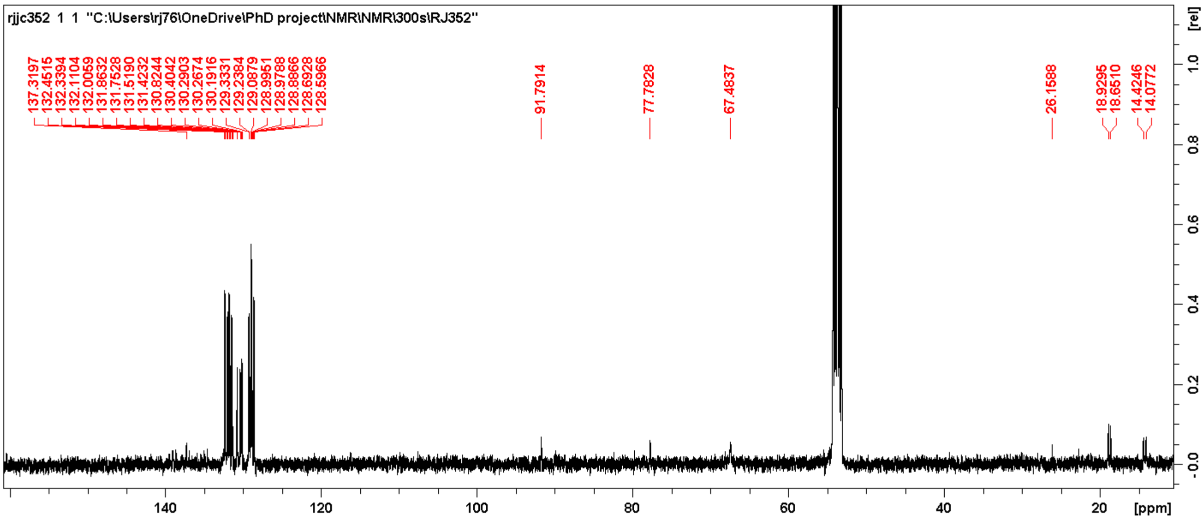
$^1H\{^{11}B\}$



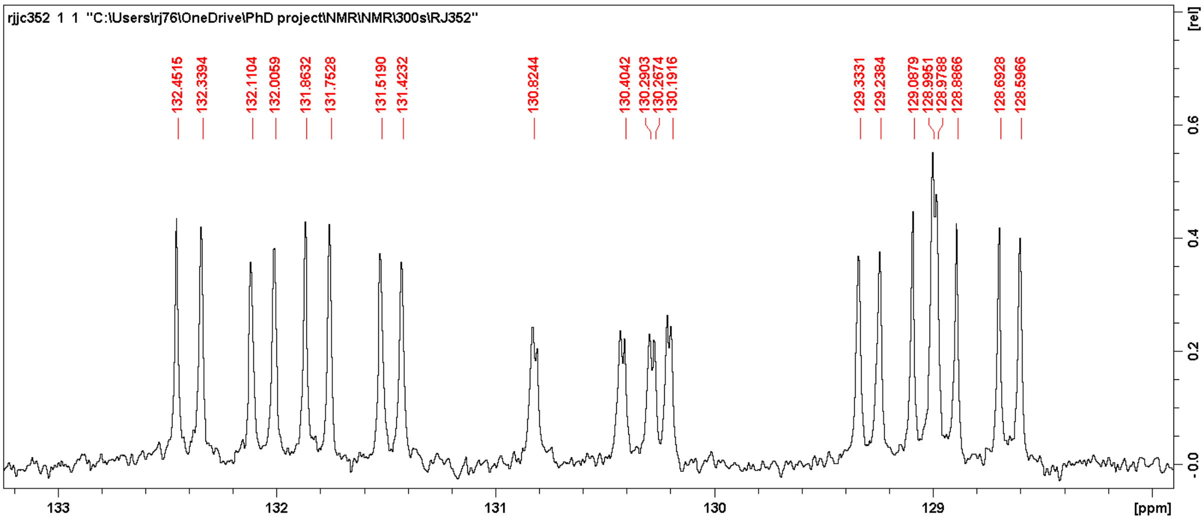
$^{1}H\{^{11}B\}$ detail



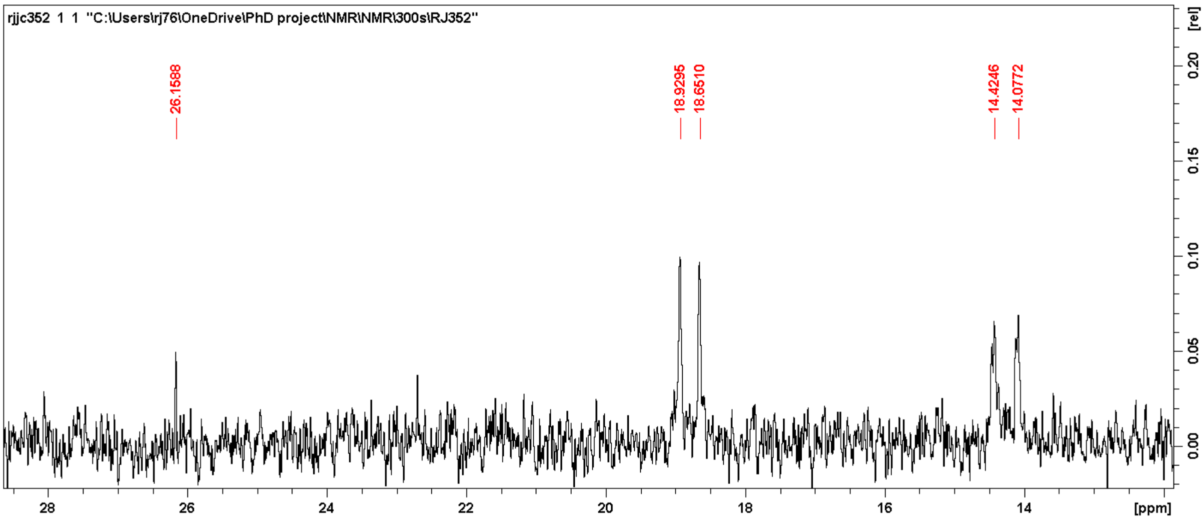
^{13}C



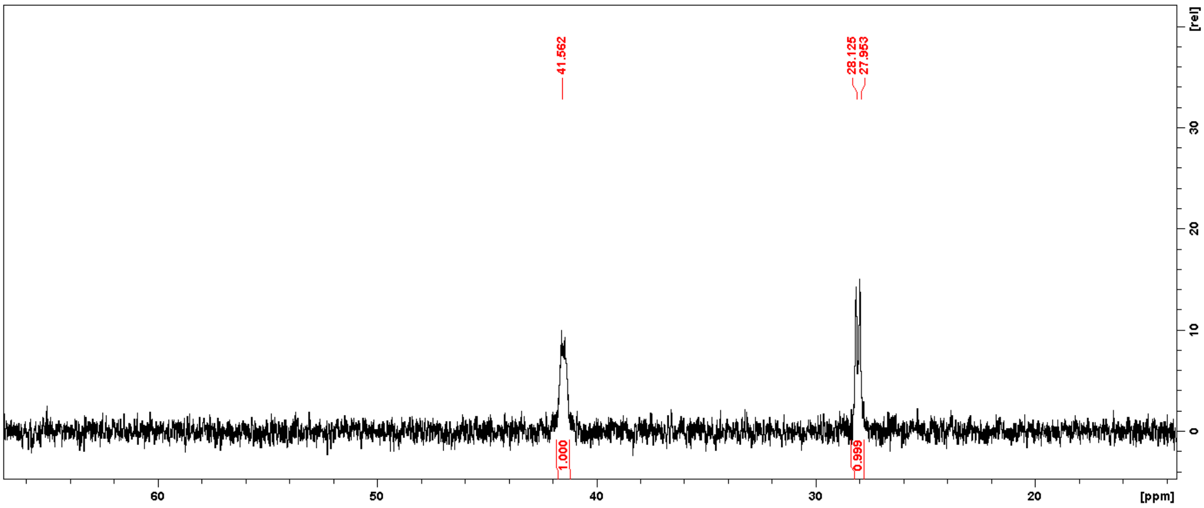
^{13}C detail (high frequency)



^{13}C detail (low frequency)



$^{31}P\{^{1}H\}$



B. Crystallographic Studies

Single crystals of **1**·0.5CH_2Cl_2 and **2**·0.5CH_2Cl_2 were grown by diffusion of a DCM solution of the appropriate compound and petrol at -20 °C. Diffraction data were collected on a Bruker D8 Venture diffractometer equipped with Cu-K_α radiation at 100 K. Using OLEX2[1] structures were solved by direct methods using the SHELXS[2] or SHELXT[3] programme, and refined by full-matrix least-squares using *SHELXL*.[4] Crystals of **1**·0.5CH_2Cl_2 and **2**·0.5CH_2Cl_2 are isomorphous. Both contain DCM of solvation and the solvate molecules were located albeit that they are only fractionally occupied and are disordered. There is also some disorder in two of the Ph rings in the structure of **1**. In both cases application of the *Vertex-Centroid Distance* (VCD) and *Boron-Hydrogen Distance* (BHD) methods[5] allowed cage C atoms and cage B atoms to be distinguished, confirming that in **1** the bis(carborane) is *C,C´*-bound to Ru (vertices 2 and 2′) whereas in **2** it is *C,B´*-bound (vertices 2 and 3′). See Table S1. In both cases cage H atoms were allowed positional refinement. All other H atoms were treated as riding, with C_{phenyl}–H 0.95 Å, $C_{primary}$–H 0.98 Å and $C_{secondary}$–H 0.99 Å. H atom displacement parameters were constrained to 1.2 × U_{eq} (bound B or C) except for Me H atoms [1.5 × U_{eq} (C_{methyl})]. Table S2 contains unit cell data and further experimental details.

Table S1

Vertex	VCD/Å	BHD/Å		Vertex	VCD/Å	BHD/Å
Compound **1**						
1	1.570(2)	-		1′	1.575(2)	-
2	1.661(2)	-		2′	1.611(2)	-
3	1.682(2)	1.08(2)		3′	1.641(3)	1.15(2)†
4	1.702(3)	1.03(2)		4′	1.711(2)	1.09(3)
5	1.699(3)	1.09(2)		5′	1.699(2)	1.11(2)
6	1.688(2)	1.06(3)		6′	1.707(2)	1.07(2)
7	1.682(3)	1.11(3)		7′	1.680(3)	1.08(2)
8	1.689(2)	1.14(3)		8′	1.703(2)	1.02(3)
9	1.690(3)	1.11(3)		9′	1.668(3)	1.03(3)
10	1.684(2)	1.10(3)		10′	1.672(3)	1.07(2)
11	1.687(3)	1.10(3)		11′	1.690(2)	1.09(2)
12	1.667(3)	1.07(3)		12′	1.685(3)	1.05(3)
Compound **2**						
1	1.586(2)	-		1′	1.563(2)	-
2	1.616(2)	-		2′	1.526(2)	0.42(3)
3	1.706(2)	1.06(2)		3′	1.834(2)	-
4	1.702(2)	1.09(2)		4′	1.676(2)	1.08(2)
5	1.708(2)	1.11(2)		5′	1.701(3)	1.11(2)
6	1.648(2)	1.10(2)†		6′	1.733(3)	1.03(2)
7	1.687(2)	1.09(2)		7′	1.680(2)	1.11(2)
8	1.677(3)	1.06(2)		8′	1.688(3)	1.05(2)
9	1.674(2)	1.07(2)		9′	1.669(2)	1.11(2)
10	1.700(2)	1.07(2)		10′	1.708(2)	1.05(3)
11	1.685(2)	1.05(2)		11′	1.697(2)	1.10(3)
12	1.683(2)	1.10(2)		12′	1.668(2)	1.06(3)

† Bridging H atom

Table S2

	1·$0.5CH_2Cl_2$	**2**·$0.5CH_2Cl_2$
CCDC	2117898	2117899
Formula	$C_{30.5}H_{47}B_{20}ClP_2Ru$	$C_{30.5}H_{47}B_{20}ClP_2Ru$
M	828.34	828.34
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*
a/Å	38.4205(9)	38.0931(9)
b/Å	10.5927(2)	10.6717(3)
c/Å	21.1877(5)	21.3413(5)
α/°	90	90
β/°	111.3870(10)	111.8580(10)
γ/°	90	90
V/Å^3	8029.1(3)	8051.9(4)
Z, *Z*′	8, 1	8, 1
F(000)/e	3368.0	3368.0
D_{calc}/Mg m^{-3}	1.371	1.367
X-radiation	Cu-K_α	Cu-K_α
λ/Å	1.54178	1.54178
μ/mm^{-1}	4.693	4.680
θ_{max}/°	74.78	74.73
Data measured	54551	64154
Unique data	8168	8221
R_{int}	0.0220	0.0283
R, wR_2 (obs. data)	0.0213, 0.0529	0.0208, 0.0512
S	1.050	1.065
Variables	632	586
E_{max}, E_{min}/e Å^{-3}	0.56, -0.61	0.36, -0.54

1 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.,* 2009, **42**, 339-341.

2 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.,* 2008, **64**, 112-122.

3 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.,* 2015, **71**, 3-8.

4 G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.,* 2015, **71**, 3-8.

5 (a) A. McAnaw, G. Scott, L. Elrick, G. M. Rosair and A. J. Welch, *Dalton Trans.,* 2013, **42**, 645-664; (b) A. McAnaw, M. E. Lopez, D. Ellis, G. M. Rosair and A. J. Welch, *Dalton Trans.,* 2014, **43**, 5095-5105; (c) A. J. Welch, *Crystals,* 2017, **7**, 234.