

## Supplementary Data — X-Ray Crystallography

**Manuscript:** The First Rhodaboratrane:  $[\text{RhCl}(\text{PPh}_3)\{\text{B}(\text{mt})_3\}](\text{Rh} \rightarrow \text{B})$  (mt = methimazolyl)

**Authors:** Ian R. Crossley, Mark R. St.-J. Foreman, Anthony F. Hill,  
Andrew J.P. White and David J. Williams

**Table 1.** Comparative selected bond lengths (Å) and angles (°) for the two independent molecules (**A** and **B**) present in the crystals of **4**.

	<b>Mol. A</b>	<b>Mol. B</b>		<b>Mol. A</b>	<b>Mol. B</b>
Rh–Cl	2.6440(14)	2.6246(13)	Rh–S(1)	2.3704(16)	2.3674(16)
Rh–S(2)	2.3692(17)	2.3640(16)	Rh–S(3)	2.3867(15)	2.3898(15)
Rh–P	2.3148(13)	2.3264(14)	Rh–B	2.132(6)	2.122(7)
B–N(2)	1.550(8)	1.533(8)	B–N(8)	1.541(7)	1.568(7)
B–N(14)	1.566(7)	1.549(8)			
Cl–Rh–S(1)	90.26(5)	91.04(5)	Cl–Rh–S(2)	101.20(6)	100.65(5)
Cl–Rh–S(3)	80.14(5)	81.01(5)	Cl–Rh–P	94.90(5)	94.31(5)
Cl–Rh–B	165.91(16)	165.81(17)	S(1)–Rh–S(2)	168.54(5)	168.22(5)
S(1)–Rh–S(3)	91.49(6)	92.55(6)	S(1)–Rh–P	92.44(5)	91.54(5)
S(1)–Rh–B	84.23(17)	83.52(18)	S(2)–Rh–S(3)	90.78(6)	90.69(6)
S(2)–Rh–P	86.34(5)	86.22(5)	S(2)–Rh–B	84.67(17)	85.41(18)
S(3)–Rh–P	173.69(5)	173.83(6)	S(3)–Rh–B	87.04(16)	86.13(17)
P–Rh–B	98.27(16)	98.92(17)	Rh–B–N(2)	109.4(4)	110.5(4)
Rh–B–N(8)	110.0(4)	109.3(4)	Rh–B–N(14)	108.7(4)	109.8(4)
N(2)–B–N(8)	115.4(4)	114.6(5)	N(2)–B–N(14)	107.1(4)	107.6(5)
N(8)–B–N(14)	106.1(4)	104.8(5)			

**Fig. S1** The molecular structure of one (**B**) of the two independent molecules present in the crystals of **4**.

**Fig. S2** Overlay of the two independent molecules (**A** and **B**) present in the crystals of **4**. The r.m.s. fit of all the non-hydrogen atoms is *ca.* 0.14 Å.

**Fig. S3** The molecular structure of one (A) of the two independent molecules present in the crystals of **4** (30% probability ellipsoids).

**Fig. S4** The molecular structure of one (B) of the two independent molecules present in the crystals of **4** (30% probability ellipsoids).

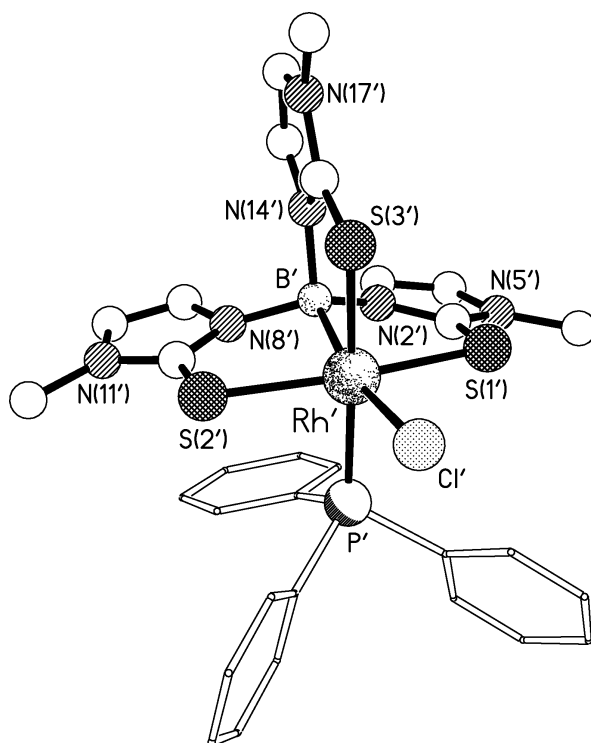


Fig. S1

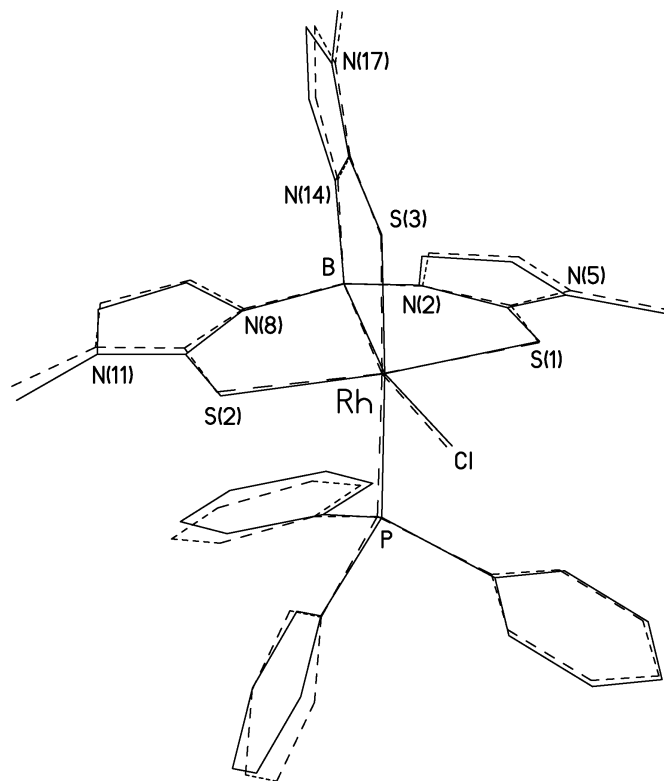


Fig. S2

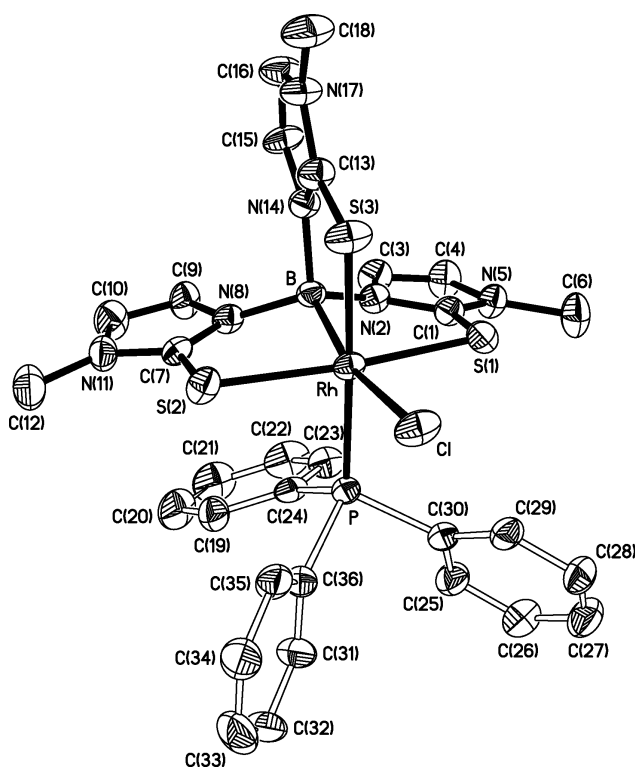


Fig. S3

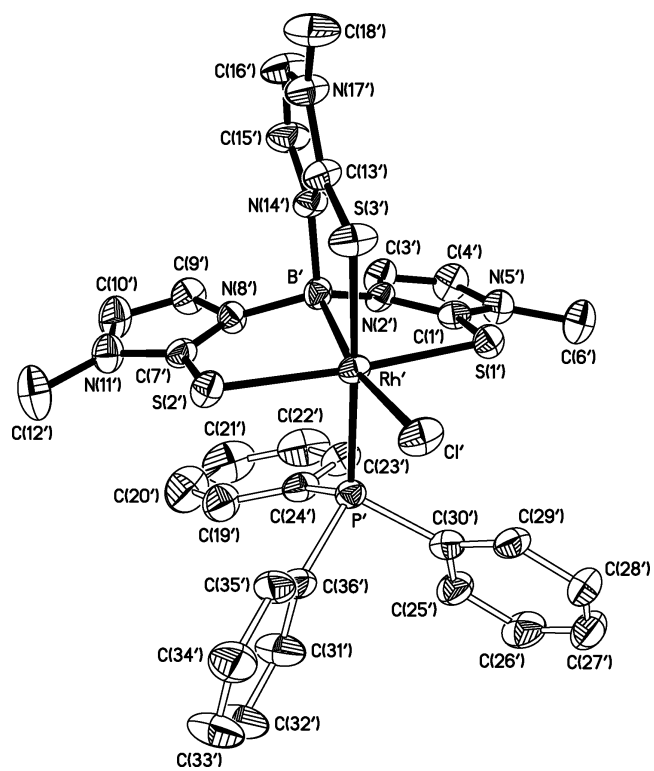


Fig. S4