Supporting Information

Title: Bis(phosphine)boronium salts. Synthesis, Structures and Co-ordination Chemistry

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1. General NMR experimental details.

NMR spectra were recorded on Bruker AVD 500 MHz spectrometer at room temperature unless otherwise stated. ^{1}H NMR spectra were recorded at 500 MHz, ^{31}P NMR at 202 MHz and ^{11}B NMR at 160 MHz. Residual protio solvent (e.g. CD_2Cl_2: δ = 5.32 ppm) was used as a reference for ^{1}H NMR spectroscopy**.** ^{31}P and ^{11}B NMR spectra were referenced against 85% H_3PO_4 (external) and $BF_3.OEt_2$ (external) respectively. The spectrometer was pre-locked and pre-shimmed using a C_6D_6 (0.1 mL) and 1,2-$C_6H_4F_2$ (0.3 mL) sample. Chemical shifts are quoted in ppm and coupling constants in Hz.

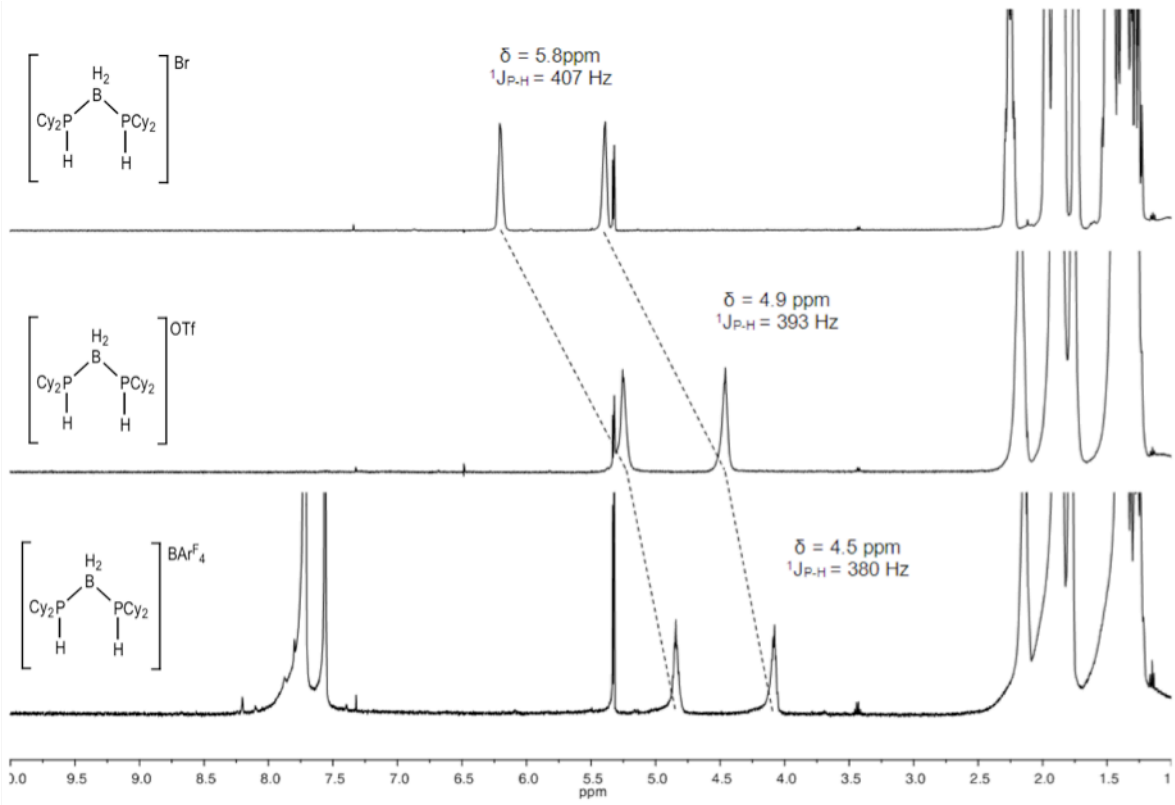


Figure 2. ^{1}H NMR (CD_2Cl_2) spectra of **2a**, **2b** and **2c.**

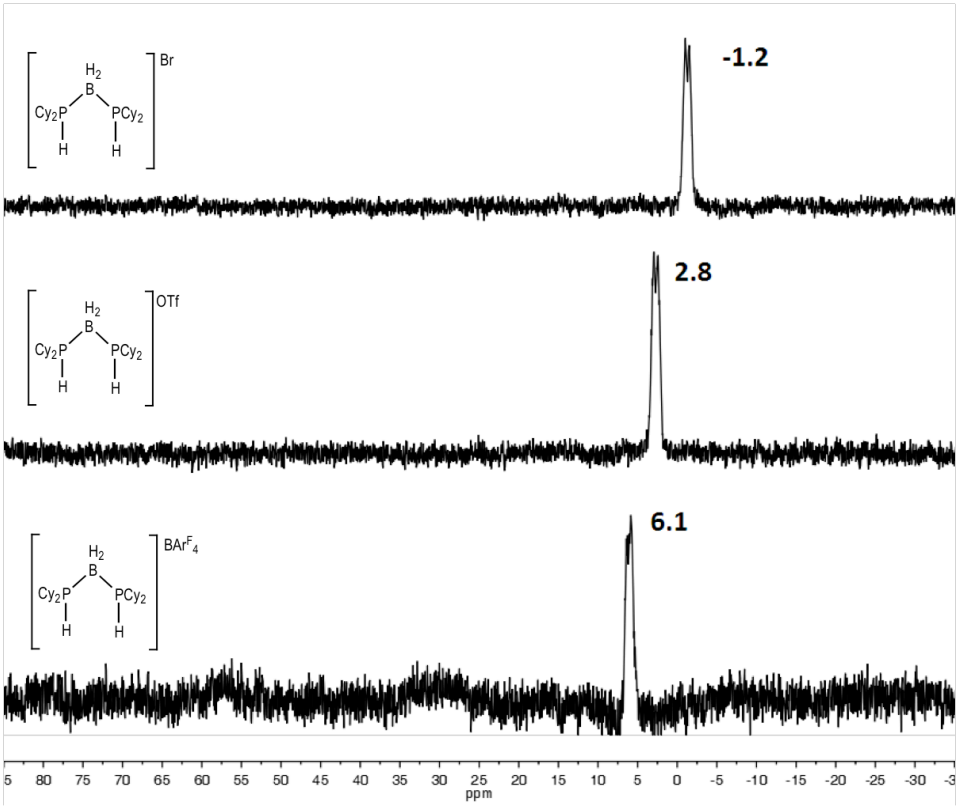


Figure 3. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2) spectra of **2a**, **2b** and **2c**.

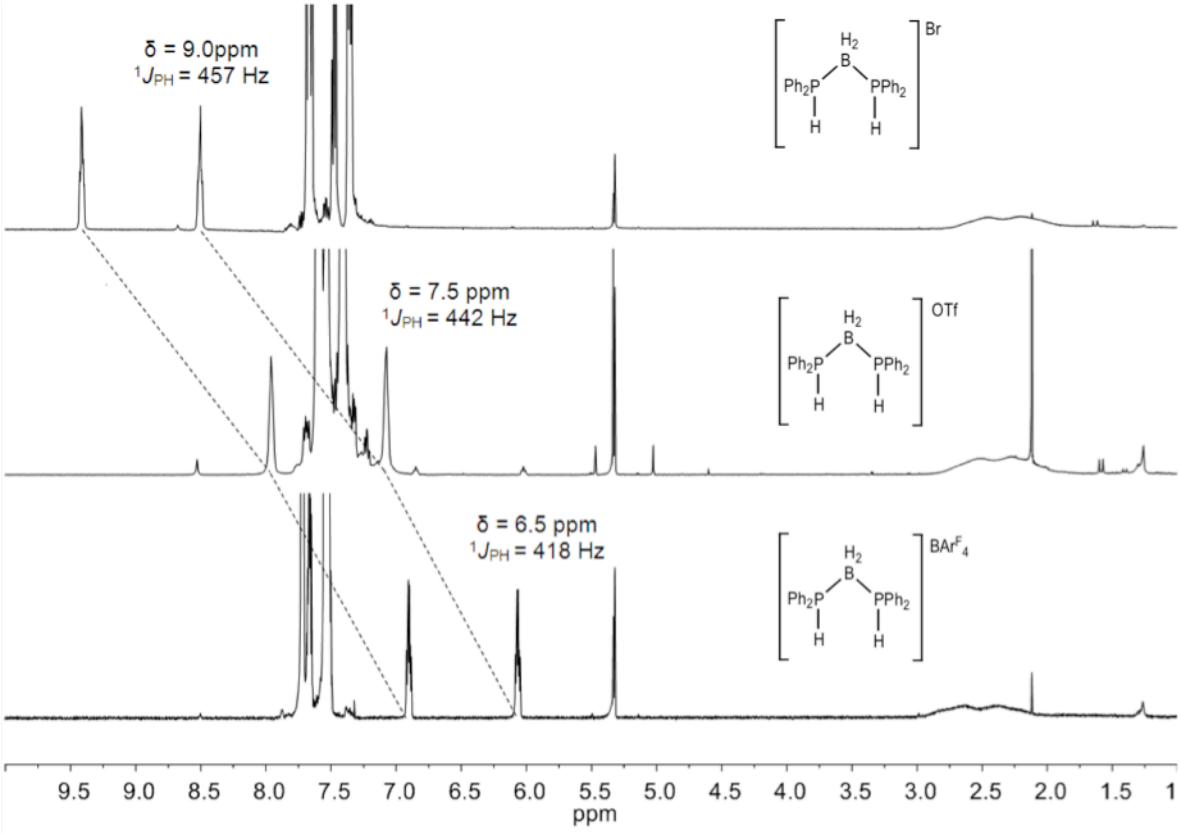


Figure 4. ^{1}H NMR (CD_2Cl_2) spectra of **3a**, **3b** and **3c**.

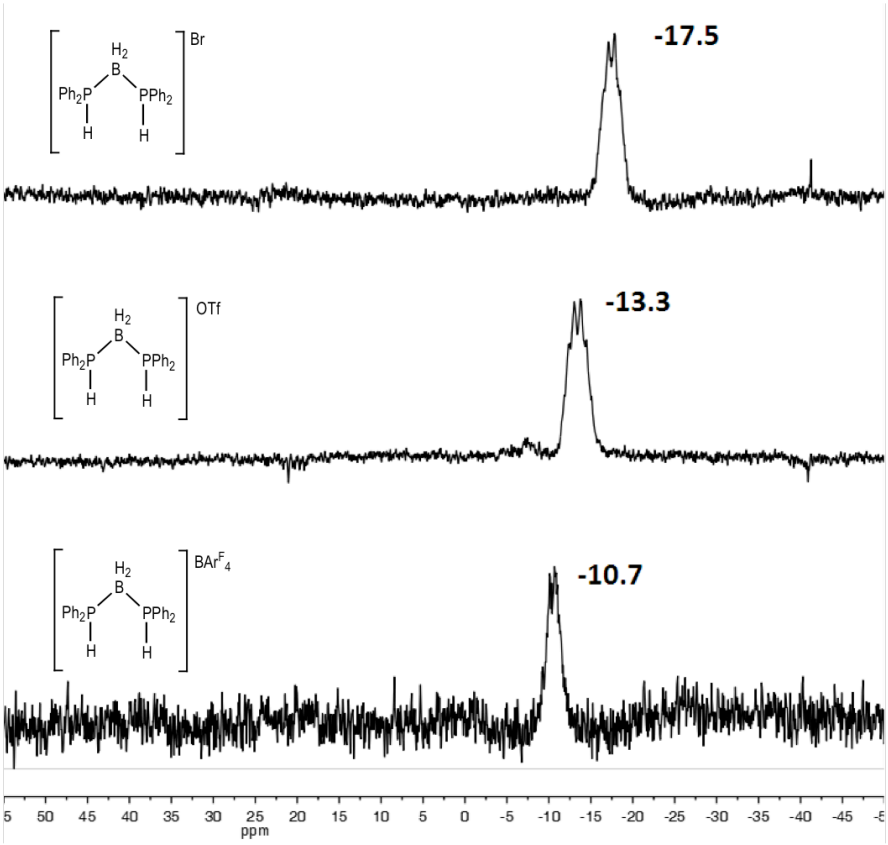


Figure 5. ^{31}P{^{1}H} NMR (CD_2Cl_2) spectra of **3a**, **3b** and **3c**.

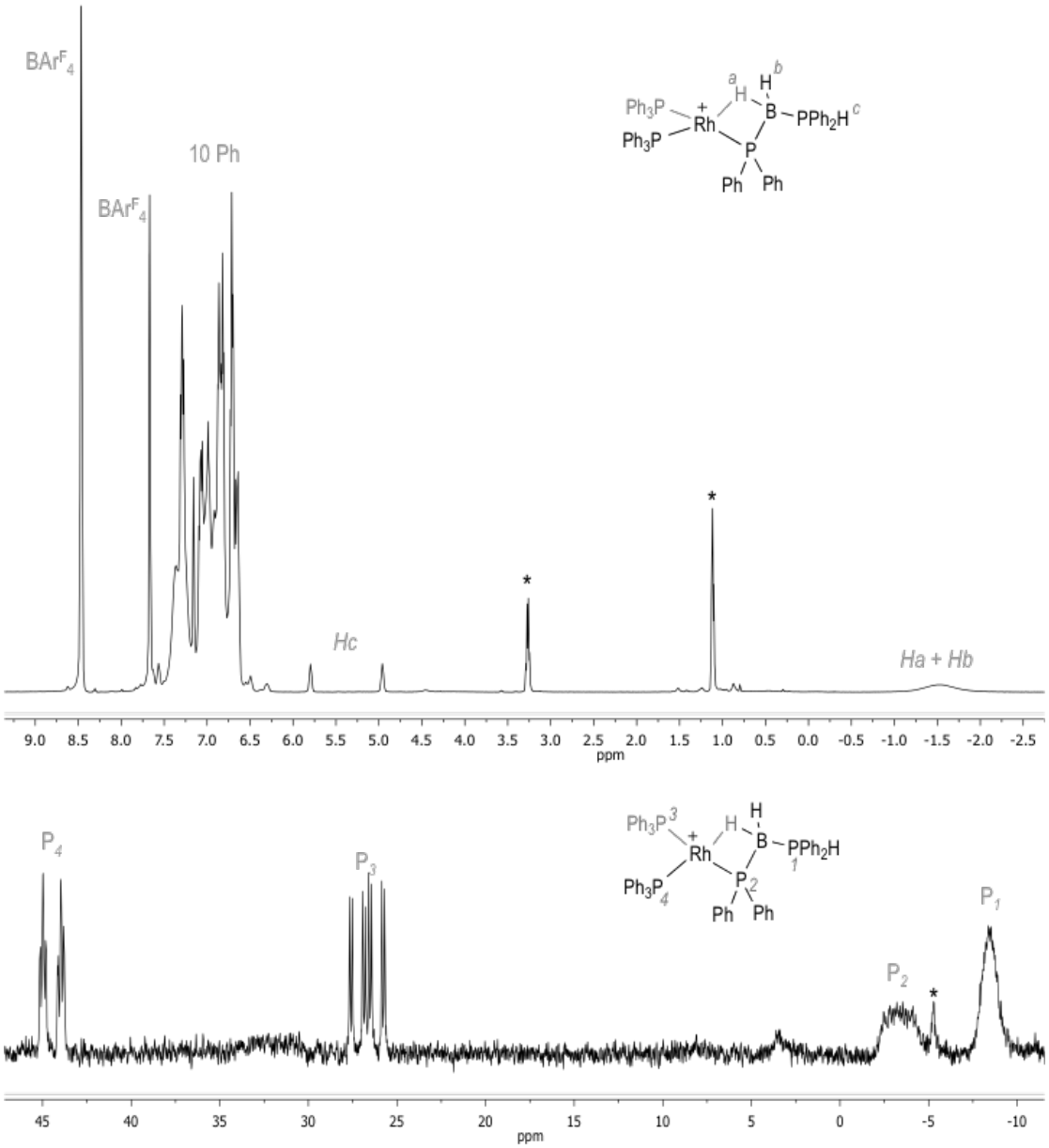


Figure 6. ^{1}H NMR (C_6D_6) spectrum of **5**, (*) = Et_2O (crystallizes with **4**) top; $^{31}P\{^{1}H\}$ NMR (C_6D_6) spectrum of **5**, (*) = PPh_3 bottom.

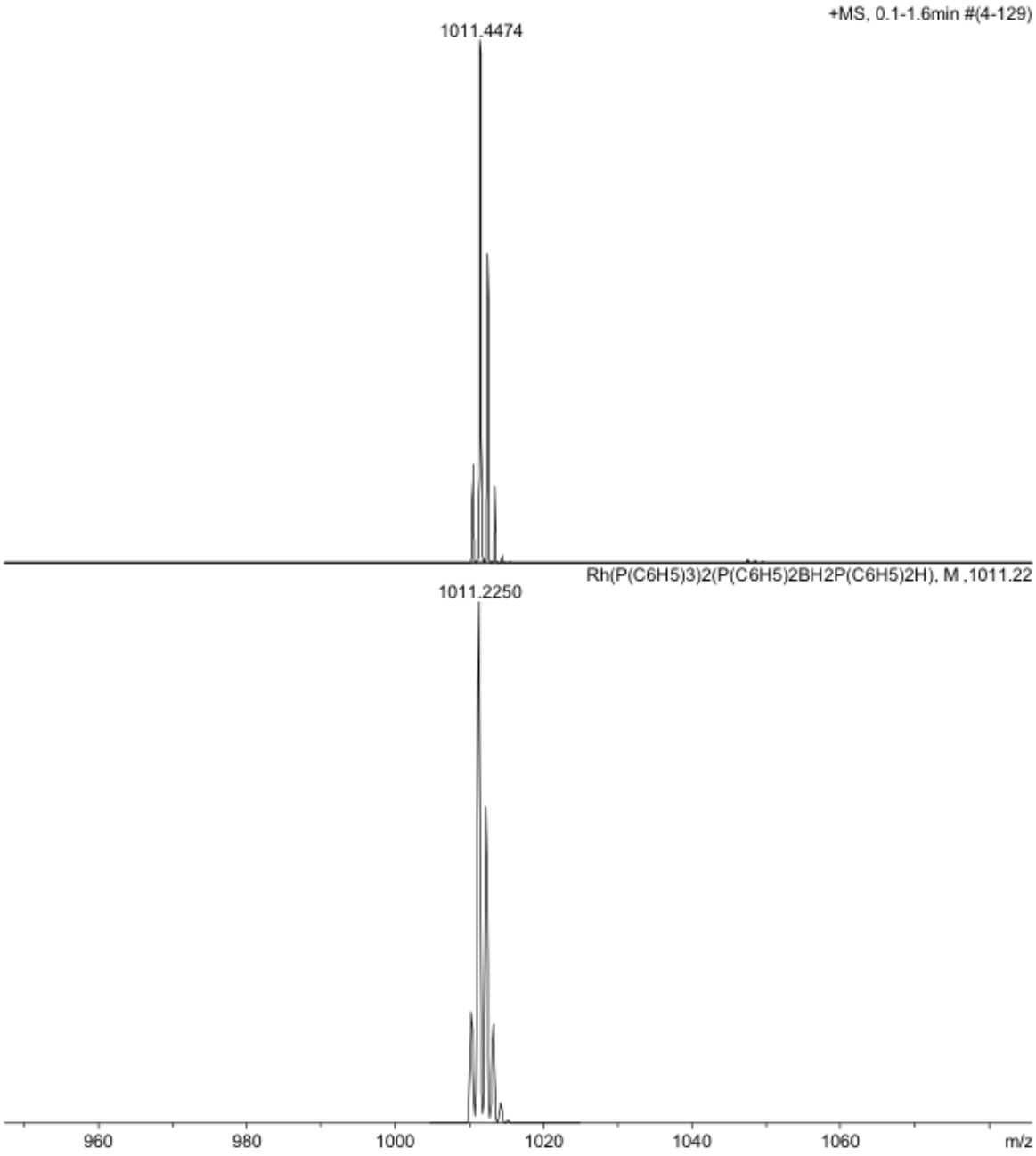


Figure 7. ESI-MS for **5**, experimental (top); simulated (bottom).

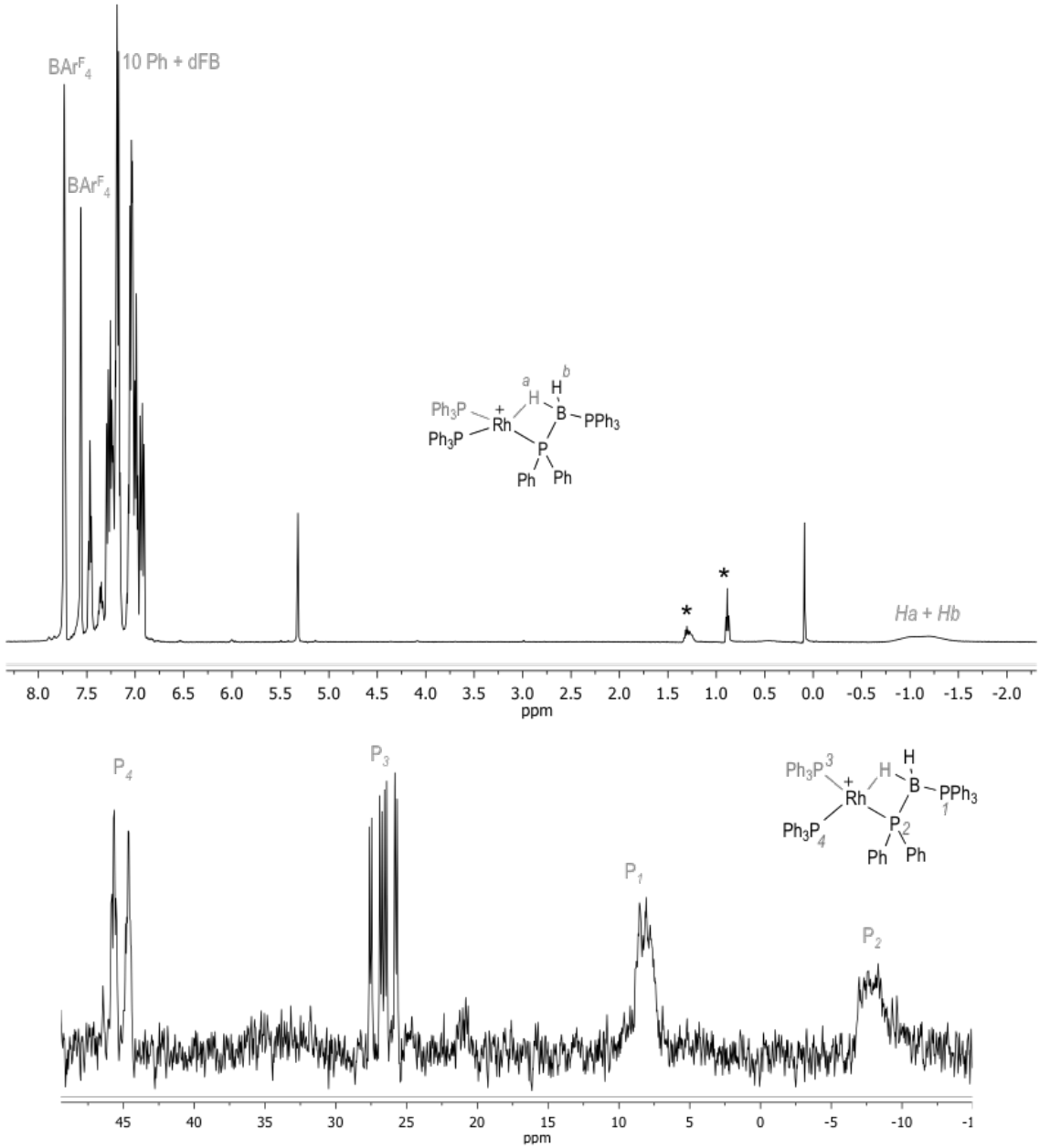


Figure 8. ^{1}H NMR (CD_2Cl_2) spectrum of **6** (top); $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2) spectrum of **6** (bottom) (* = pentane).

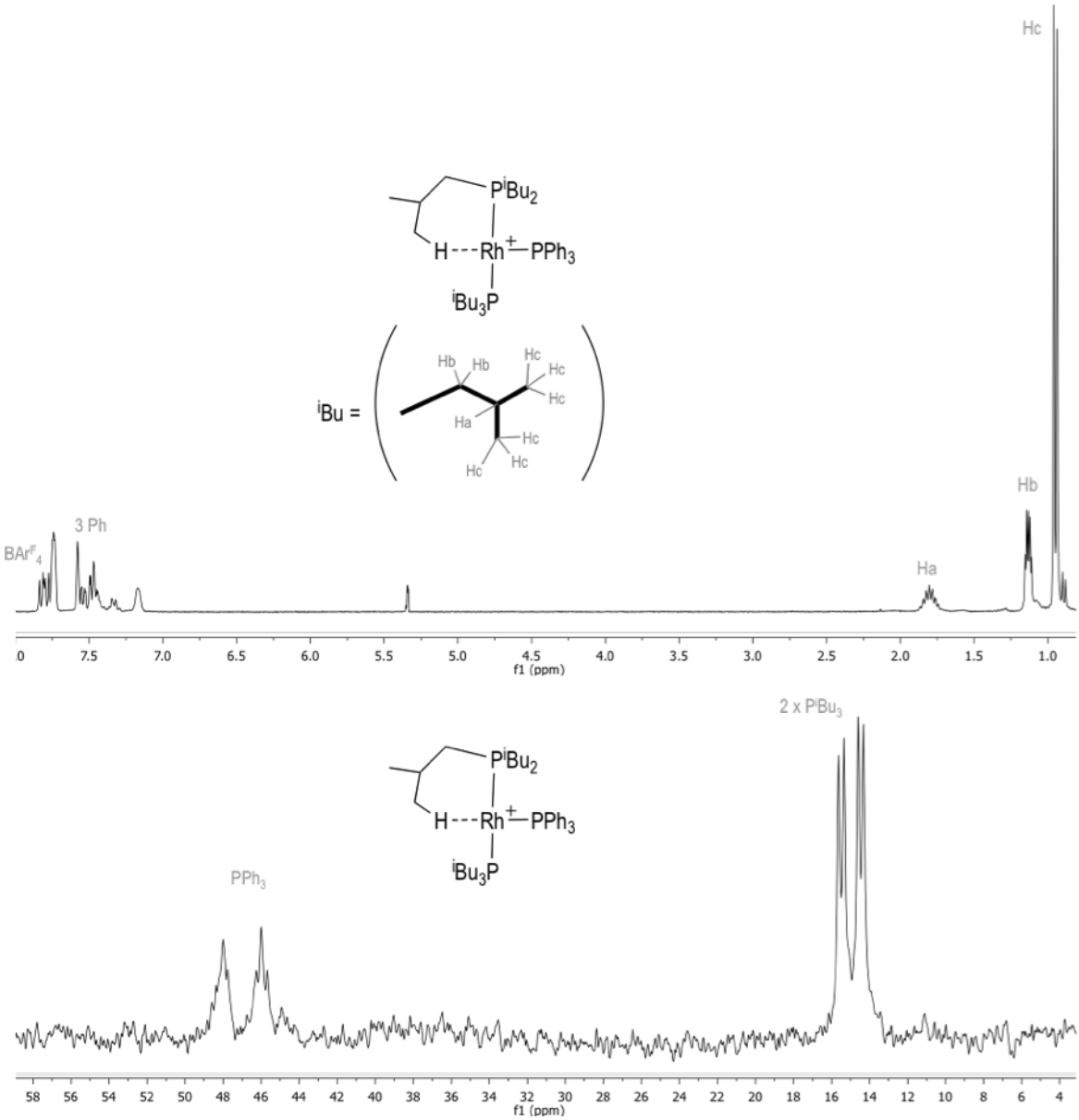


Figure 9. ^{1}H NMR (CD_2Cl_2) spectrum of **7** (top); $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2) spectrum of **7** (bottom).

2. Low Temperature ^{1}H NMR experiment for 5 and 6

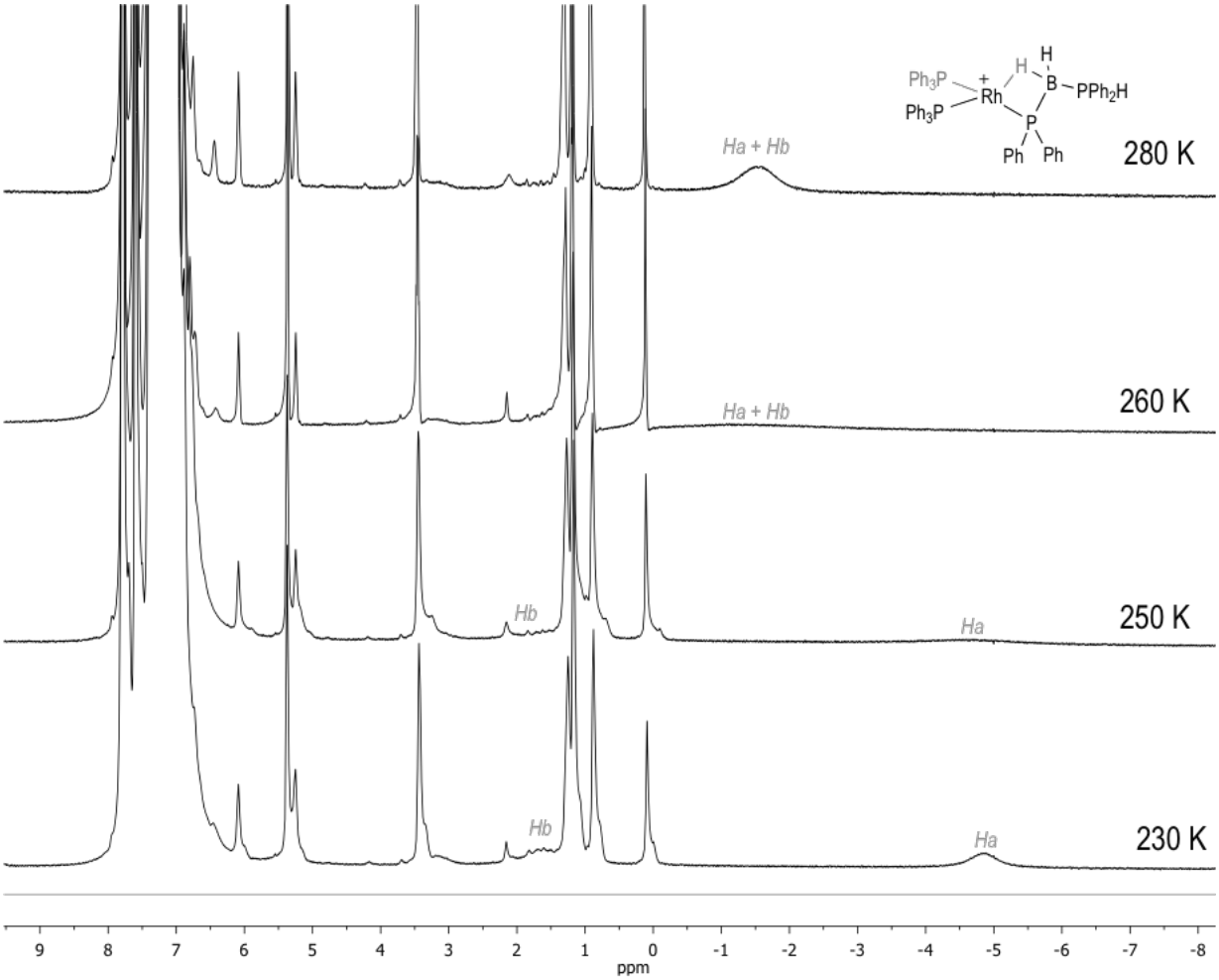


Figure 10. ^{1}H NMR (CD_2Cl_2) spectra of **5** at different temperatures. Pentane and Et_2O present in all spectra.

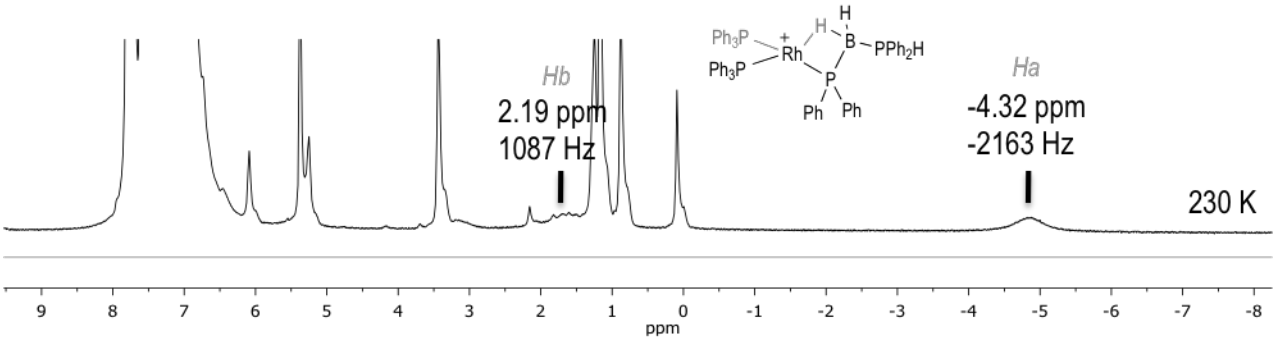


Figure 11. ^{1}H NMR (CD_2Cl_2) spectra of **5** at 230 K. Pentane and Et_2O present in the spectrum.

Low temperature ^{1}H NMR experiment is useful for calculate the coalescence rate (k_C) and the Energy for the dynamic process ($\Delta G^{\ddagger}_C$).

k_C = 7215 s^{-1} $\Delta G^{\ddagger}_C$ = 44 ± 1 kJ mol^{-1}.

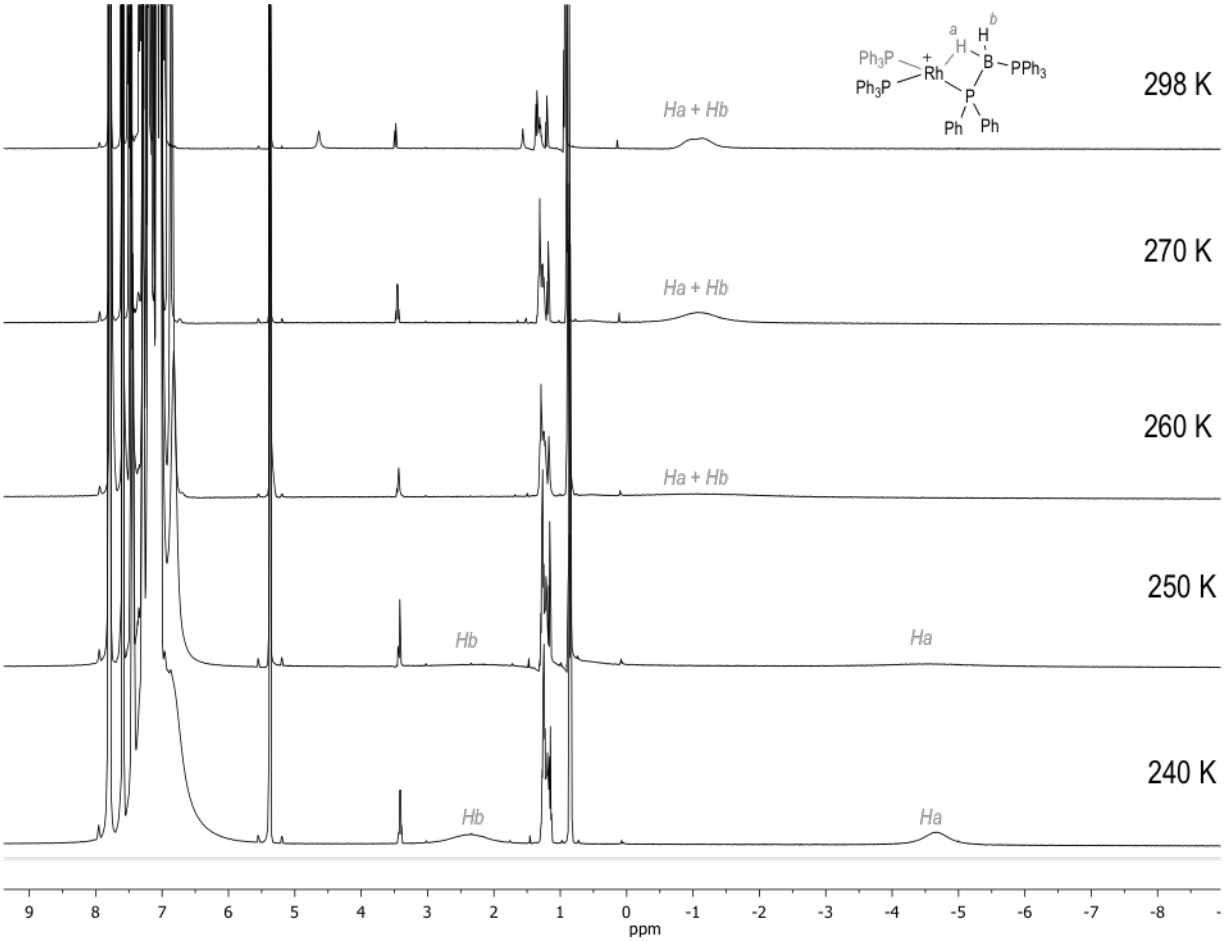


Figure 12. ^{1}H NMR (CD_2Cl_2) spectra of **6** at different temperatures. Pentane is present in all spectra.

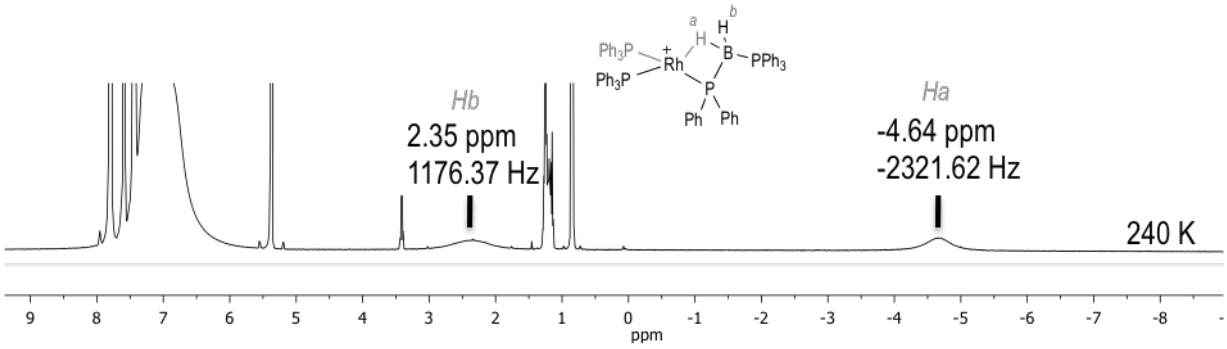


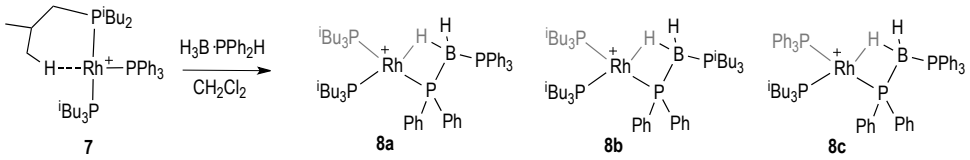
Figure 13. ^{1}H NMR (CD_2Cl_2) spectra of **6** at 240 K. Pentane is present in the spectrum.

Low temperature ^{1}H NMR experiment is useful to calculate the coalescence rate (k_C) and the energy for the dynamic process ($\Delta G^{\ddagger}_C$).

k_C = 7765 s^{-1} $\Delta G^{\ddagger}_C$ = 44 ± 1 kJ mol^{-1}.

3. Reactivity of 7 with $H_3B{\cdot}PPh_2H$.

Reaction of $[Rh(P^iBu_3)_2(PPh_3)][BAr^F_4]$ (**7**) with one equivalent of $Ph_2HP{\cdot}BH_3$ led to the formation of a mixture of **8a**, **8b** and **8c** as products(Scheme 1). The major product is the expected **8a**, while **8b** and **8c** are the result of the interchange of phosphines due to the inherent weakness of the phosphine-borane P-B bond.



Scheme 1. Reactivity of **7** with $H_3B{\cdot}PPh_2H$.

The reaction was followed by $^{31}P\ \{^1H\}$ NMR, however the signals have similar environments, making it difficult to follow this reaction by NMR spectroscopy. ESI-MS of the mixture of reaction shows clearly the formation of the three products. (Figure 11).

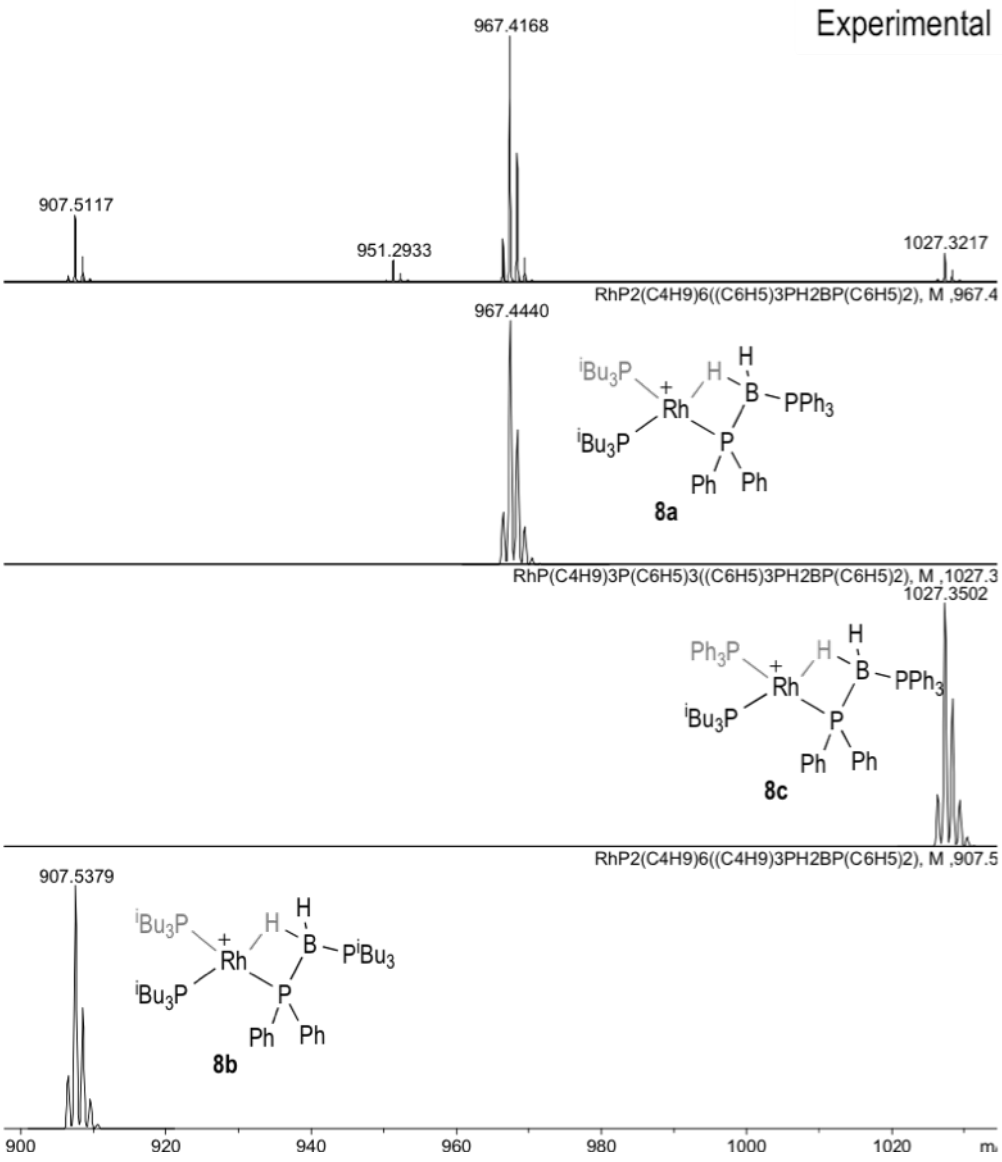


Figure 14. ESI-MS for **8a**, **8b** and **8c**.

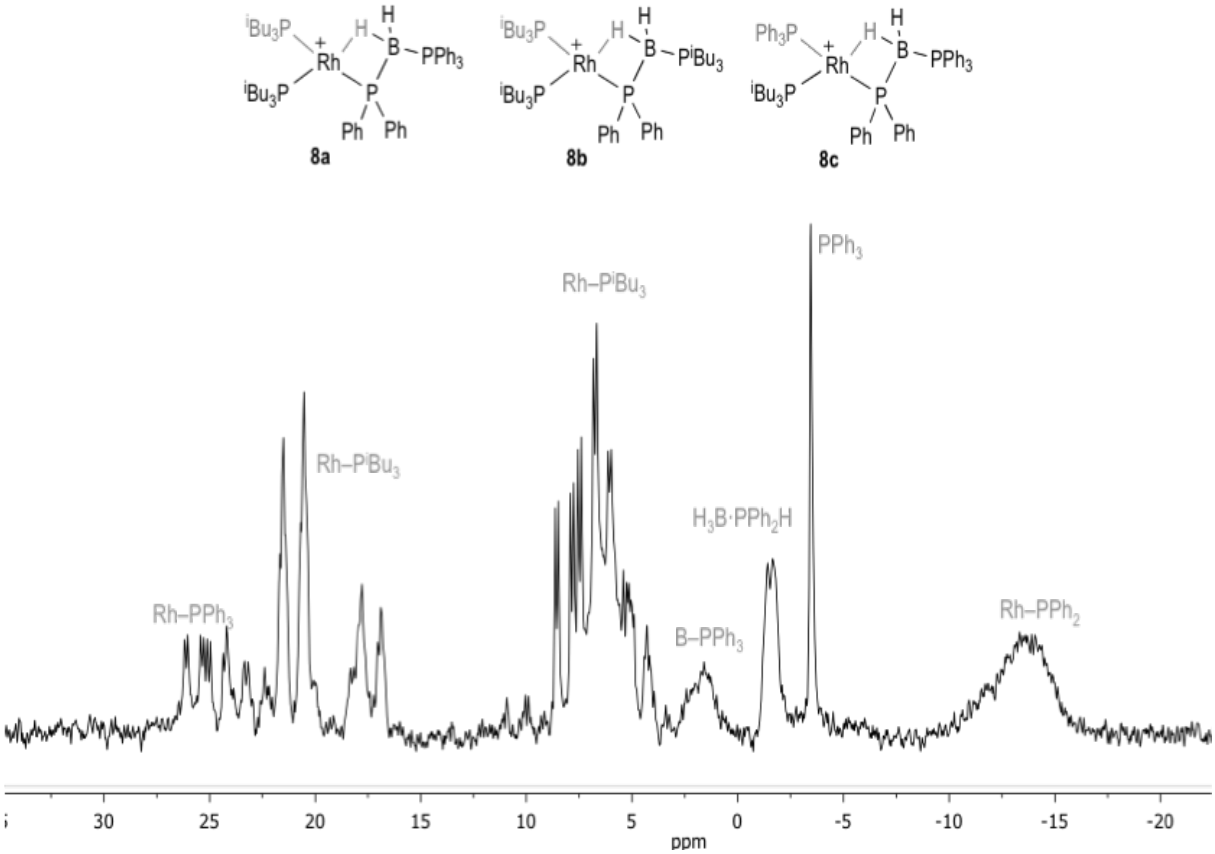


Figure 15. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2) spectra of the **8a**, **8b** and **8c** mixture.

4. Crystalography

Relevant details about structure refinement are given in Table 1. Data of **1a**, **1b**, **1c** and **7** were collected on a Enraf Nonious Kappa CCD difractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) and a low temperature device;[1] data were collected using COLLECT, reduction and cell refinement was performed using DENZO/SCALEPACK.[2] The structures were solved by direct methods using SIR92[3] and refined full-matrix least squares on F^2 using SHELX-97.[4] Data for **6** were collected on an Oxford Diffraction (Agilent Technologies) SuperNova A diffractometer using Cu Kα radiation (λ = 1.54184 Å) and an open flow N_2 cooling device [150(2) K]. Data were collected and processed using CrysAlisPro[5] including cell refinement and interframe scaling. The structure was solved using SIR92 and refined using SHELXL-97. All non-hydrogen atoms were refined with anisotropic displacement parameters. H1, H2, H3 and H4 for the structures **1a**, **1b** and **1c** and H1A and H1B for **6** were located on the Fourier difference map and were freely refined without restraints. In case of **6**, caution should always be exercised with considering the location of the H atoms near a heavy atom such as rhodium. All other hydrogen atoms were placed in calculated positions using the riding model. Rotational disorder of the CF_3 groups of the anions of **1c**, **6** and **7** were treated by modelling the fluorine atoms over two sites or the entire CF_3 group and restraining their geometry.

	1a	**1b**	**1c**	**6**	**7**
CCDC number	912134	912135	912136	926700	926701
Formula	$C_{16}H_{40}BBrP_2$	$C_{17}H_{40}BF_3O_3P_2S$	$C_{50.50}H_{58}B_2F_{24}P_2$	$C_{99}H_{71}B_2Cl_2F_{24}P_4Rh$	$C_{74}H_{81}BF_{24}P_3Rh$
M	385.14	454.30	1204.53	2035.87	1633.02
Crystal System	orthorhombic	monoclinic	monoclinic	triclinic	monoclinic
Space group	*P 21 21 21*	*P 21/n*	*P 21/c*	*P -1*	*P 21/n*
T [K]	150	150	150	150	150
a [Å]	10.6330(3)	8.84740(10)	15.97400(10)	12.9043(5)	16.3321(1)
b [Å]	11.8889(3)	11.19090(20)	18.19600(10)	17.2619(8)	25.1406(2)
c [Å]	17.0844(7)	25.10740(40)	20.96500(20)	21.6182(10)	18.8993(2)
α [deg]	90	90	90	99.497(2)	90
β [deg]	90	2.6590(10)	111.8041(3)	91.413(2)	94.56(1)
γ [deg]	90	90	90	99.906(1)	90
V [Å^3]	2159.72(12)	2483.22(7)	5657.79(7)	4671.7(4)	7735.5(1)
Z	4	4	4	2	4
Density [gcm^{-3}]	1.184	1.215	1.414	1.450	1.402
μ [mm^{-1}]	2.044	0.295	0.190	3.487	0.381
θ range [deg]	5.14 to 27.49	5.10 to 27.51	5.11 to 27.48	3.480 to 74.296	5.10 to 27.48
Reflns collected	2684	9241	25113	34348	34222
R_{int}	0.0487	0.0303	0.0214	0.050	0.0485
Completeness	98 %	99.1 %	99.1 %	98.6%	99.2%
Data/restr/param	4859 / 0 / 197	5676 / 0 / 260	12867 / 816 / 854	18321 / 1372 / 1396	15712 / 2298 / 1315
R_1 [I > 2σ(I)]	0.0489	0.0438	0.0561	0.0680	0.0484
wR_2 [all data]	0.0762	0.1176	0.1502	0.1771	0.1124
GoF	0.993	0.881	1.054	1.028	1.081
Largest diff. pk and hole [eÅ^{-3}]	0.360 and -0.580	0.352 and -0.295	0.673 and -0.452	1.74 and -1.57	0.659 and -0.811

Table 1: Crystallographic data for **1a**, **1b**, **1c**, **6** and **7**.

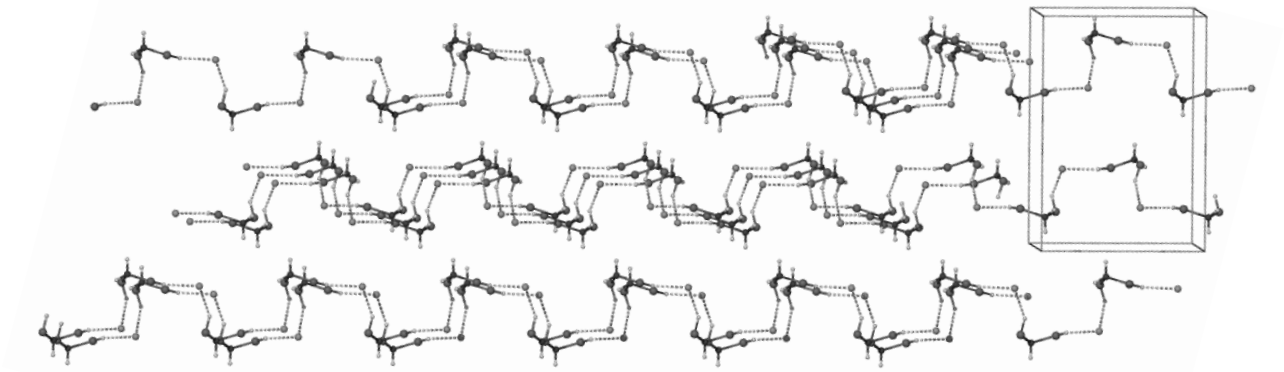


Figure 16. Extended packing diagram of compound **1a**

3.References

1. J. Cosier and M. A. Glazer, *J. Appl. Cryst.*, **1986**, *19*, 105.
2. Z. Otwinowski, Z. Minor, Processing of X-ray Diffraction Data Collected in Oscillation Mode, Methods Enzymol. **1997**, 276, Eds C. W. Carter, R. M. Sweet, Academic Press.
3. A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camali. *J. Appl. Cryst.*, **1994**, *27*, 435.
4. G. M. Sheldrick, *Acta Cryst.*, **2008**, *A64*, 112.
5. CrysAlisPro. Oxford Diffraction (AgilentTechnologies).