Supporting Information

[1,1-(dppe)-3-(NC_5H_5)-*closo*-1,2-$RhSB_9H_8$]: conformational lability and reactivity with H_2 upon protonation

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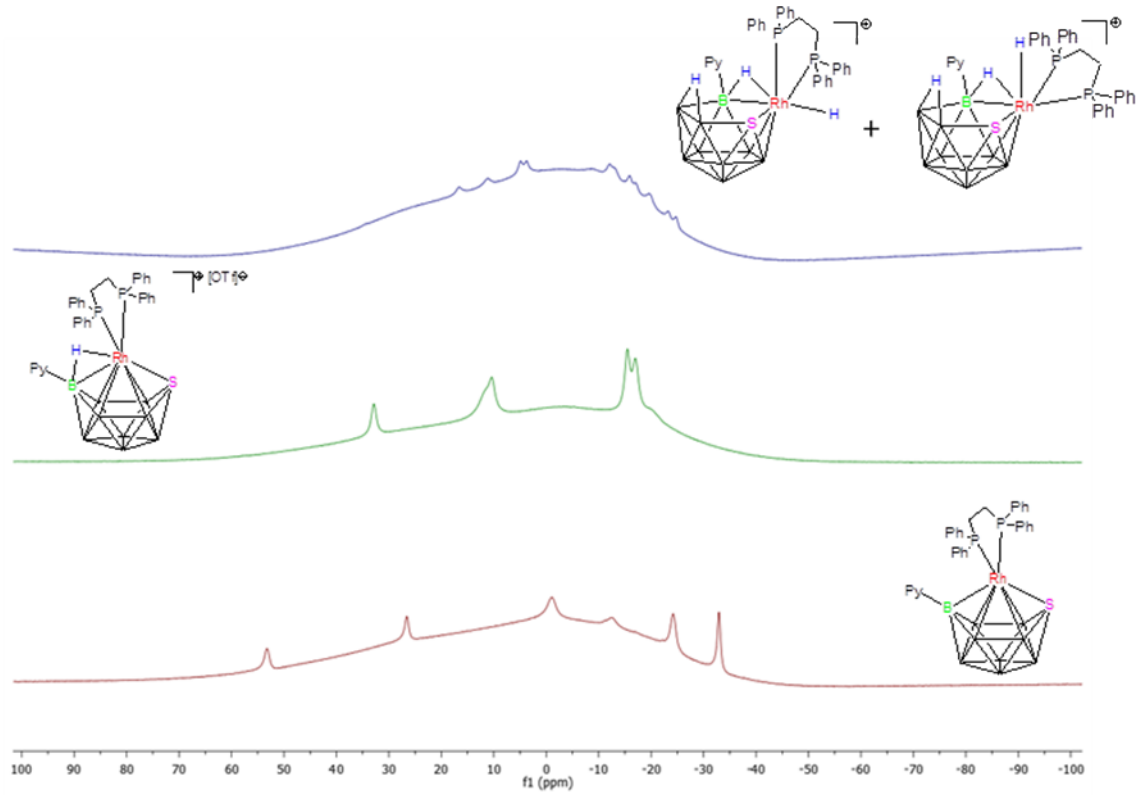

Figure S1 ^{11}B-{^{1}H} NMR spectra for **2** (bottom), **3** (middle) and the mixture of isomers **4** (top).

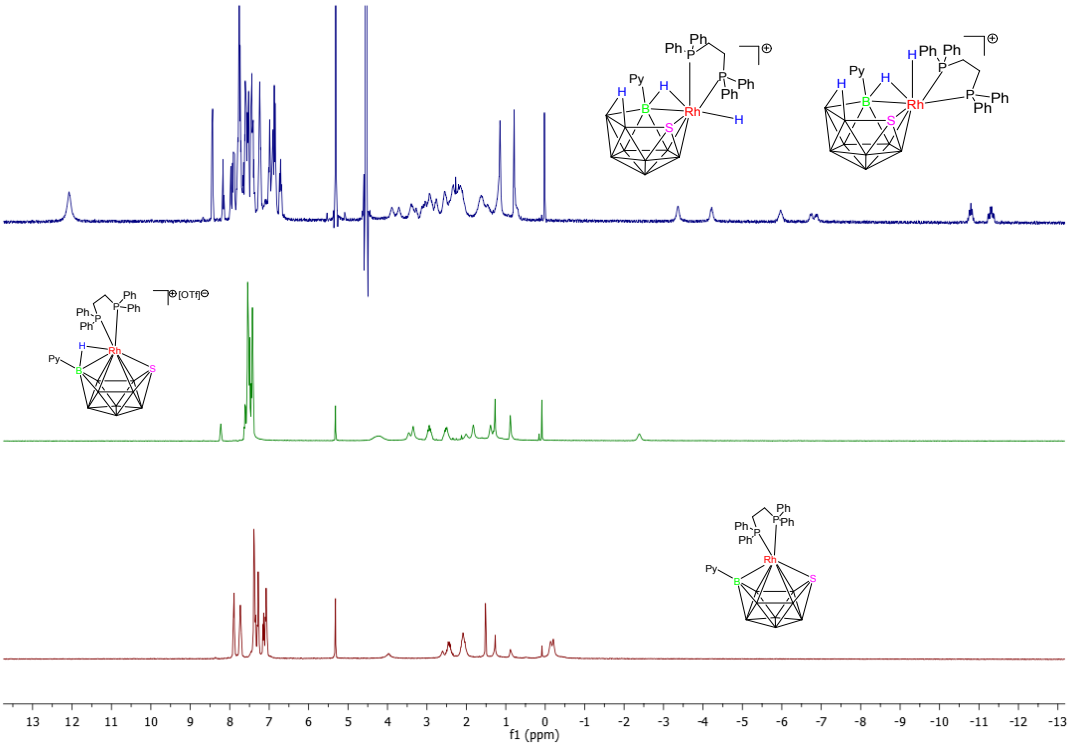

Figure S2 ^{1}H-{^{11}B} NMR spectra for **2** (bottom), **3** (middle) and the mixture of isomers **4** (top).

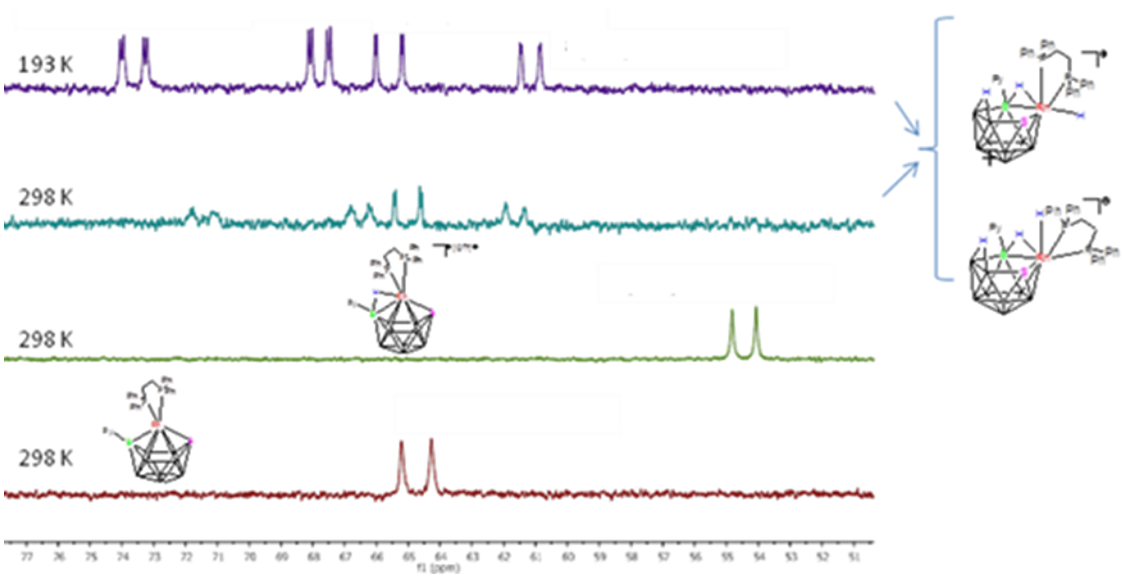

Figure S3 ^{31}P-{^{1}H}NMR spectra for **2** (1st from bottom), **3** (2nd) and the mixture of isomers **4** (3rd and 4th top).

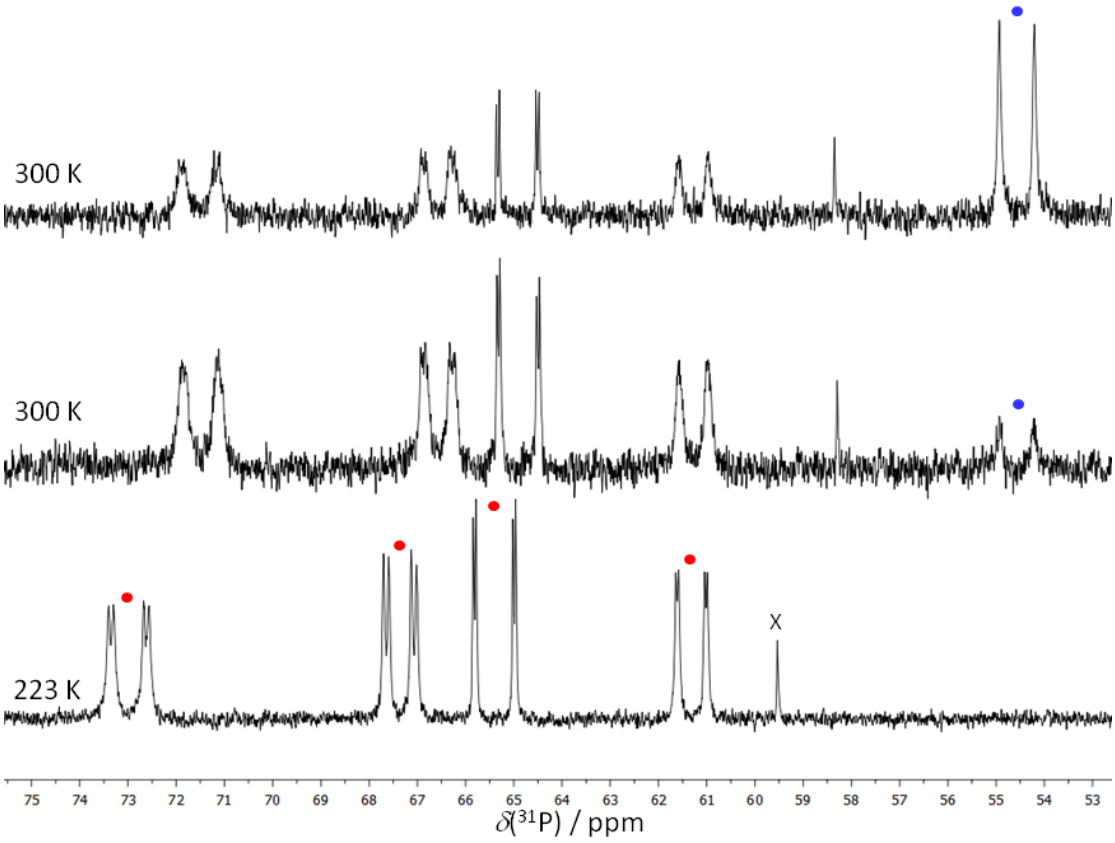

Figure S4 ^{31}P-{^{1}H}NMR spectra for the mixture of isomers, **4a** and **4b** (red ellipsoids), under an atmosphere of 10 bar of H_2 (bottom and middle spectra); the spectrum at the top results after releasing some dihydrogen from the quick pressure valve NMR tube. The doublet marked with a blue ellipsoid corresponds to **3**, and the singlet marked with an X is an impurity.

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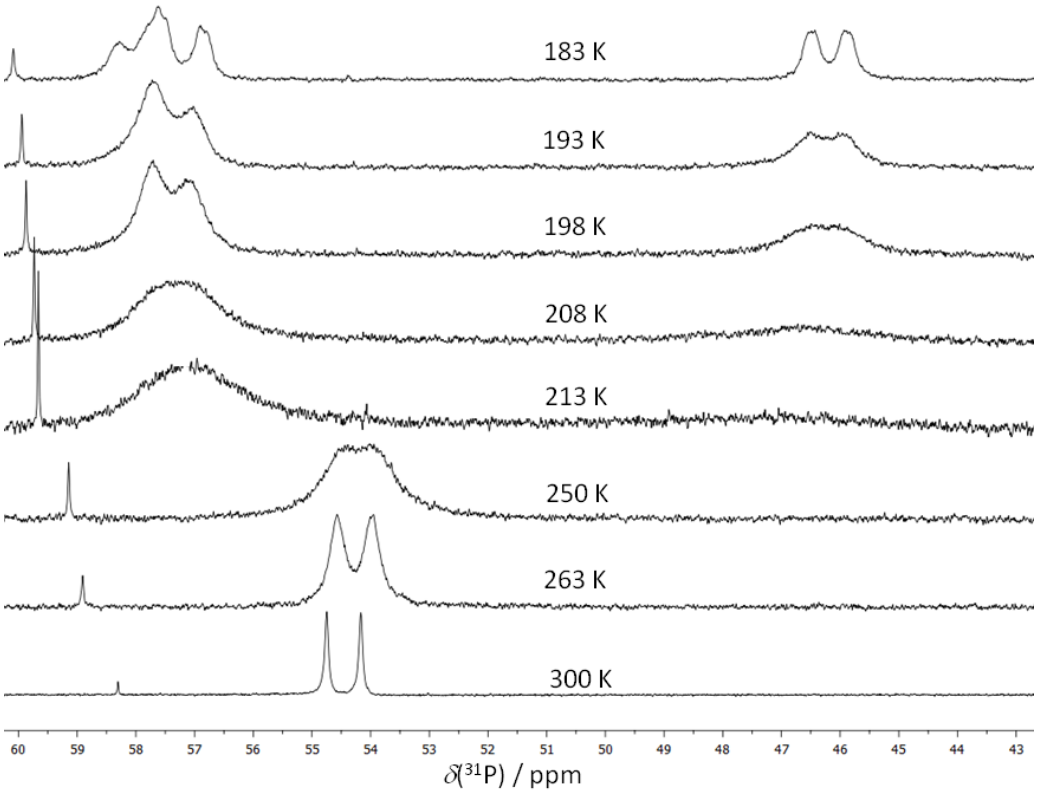

Figure S5 VT ^{31}P-{^{1}H} NMR spectra of compound **3** in CD_2Cl_2.

Calculation of free energy of activation by the coalescence temperature

$\Delta G^{\ddagger} = -RT_C[\ln(\pi\delta\upsilon h/2^{1/2}\kappa_B T_C)] = RT_c[22.8 + \ln(T_C/\delta\upsilon)] = 36.1$ kJ/mol = 8.6 kcal /mol

$T_c = 213$ K, $\delta\upsilon = 2388$ Hz in a magnetic field of 202 MHz.

R = 8.3145 J/K mol

h = $6.626 \cdot 10^{-34}$ J s

$\kappa_B = 1.381 \bullet 10^{-23}$ J/K

Fluxionalities that cannot be stopped on the NMR time-scale down to about -100 °C imply values of $\Delta G^{\ddagger} <$ *ca*. 7 kcal/mol.

[8,8-dppe-*nido*-$RhSB_9H_{10}$]

The synthesis and characterization of this 11-vertex dppe-ligated rhodathiaborane was reported first by Welch and co-workers in *J. Organomet. Chem.* **1998**, *550*, 315. The compound was latter prepared, following a different route, by Barton and Macías (*Organometallics, 18, 1999,* 3639). However, these works do not report the fluxional

behavior of this cluster. Now, we have carried out a VT NMR study that has provided new spectroscopic data as well as the measurement of the free activation energy for the fluxional process of this compound. These data are gathered bellow.

NMR data. $^{11}B–\{^{1}H\}$ (128 MHz) and $^{1}H-\{^{11}B\}$ NMR (400 MHz) in CD_2Cl_2 at 323 K) {cluster resonances ordered as: assignment $\delta(^{11}B)$/ppm [$\delta(^{1}H)$/ppm for directly attached exo-hydrogen]}: 1BH +10.7 [+2.35], 2BH +8.9 [+3.26], 1BH –7.5 [+1.83], 2BH –11.7 [+2.17], 2BH –13.2 [+1.59], 1BH –26.8 [+1.65]. Additional ^{1}H NMR data are: δ = +7.81 to +7.39 (20H, dppe, C_6H_5), +2.89 (m, 2H; CH_2), +2.43 (m, 2H; CH_2), –2.10 (s, 1H, B–H–B). $^{31}P-\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2, 323 K): δ = +58.07 (d, J_{RhP}= 150.2 Hz).

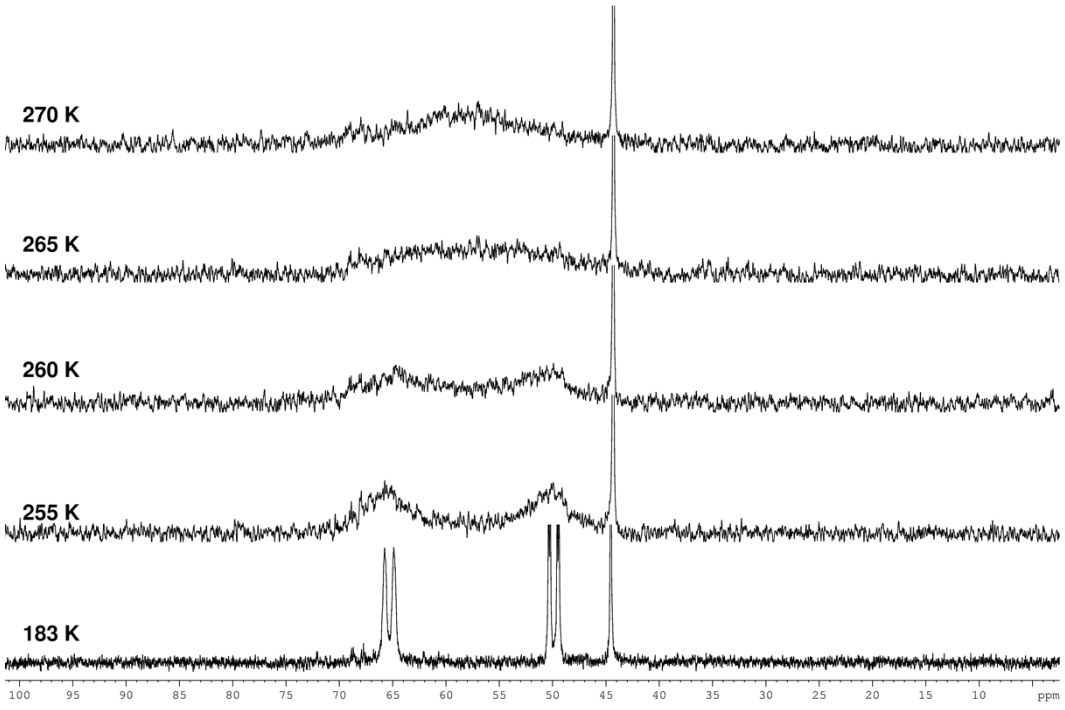

Figure S6 VT $^{31}P-\{^{1}H\}$ NMR spectra (162 MHz) of compound [8,8-(dppe)-*nido*-8,7-$RhSB_9H_{10}$] in CD_2Cl_2.

1. *Free energy calculated from the ^{31}P NMR spectra*

$\Delta G^{\ddagger} = -RT_C[\ln(\pi\delta\upsilon h/2^{1/2}\kappa_B T_C)] = RT_c[22.8 + \ln(T_C/\delta\upsilon)] = 45.3$ kJ/mol = 10.8 kcal /mol

T_c = 265 K, $\delta\upsilon$ = 2508 Hz in a magnetic field of 162 MHz.

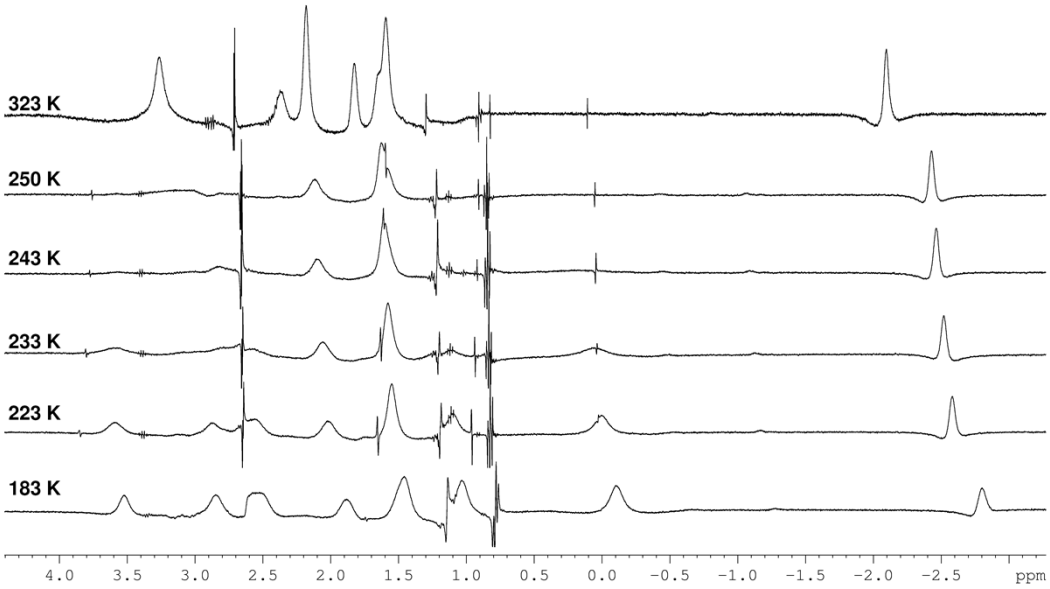

Figure S7 VT ^{1}H-{^{1}B} NMR spectra (400 MHz) of compound [8,8-(dppe)-*nido*-8,7-$RhSB_9H_{10}$] in CD_2Cl_2.

2. *Free energy calculated from the ^{1}H NMR spectra*

The proton resonances at +3.52 and +2.85 ppm that exhibit a δυ of 273 Hz in the spectrum at 183K, coalesce at 250 K in a magnetic field of 400 MHz.

$\Delta G^{\ddagger} = -RT_C[\ln(\pi\delta\upsilon h/2^{1/2}\kappa_B T_C)] = RT_c[22.8 + \ln(T_C/\delta\upsilon)] = 47.2$ kJ/mol = 11.3 kcal /mol