

## Comparative properties of coordinated H<sub>2</sub> and H<sub>2</sub>S at a ruthenium(II) centre

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### SUPPLEMENTARY MATERIAL

**Table S1.** <sup>1</sup>H NMR integration values ( $\alpha$ ,  $\beta$ ,  $\omega$ ) and equilibrium concentrations for determination of  $K$

**Figure S1.** van't Hoff plot for the equilibrium ( $1\mathbf{a} + \text{H}_2 \rightleftharpoons 2\mathbf{a}$ )

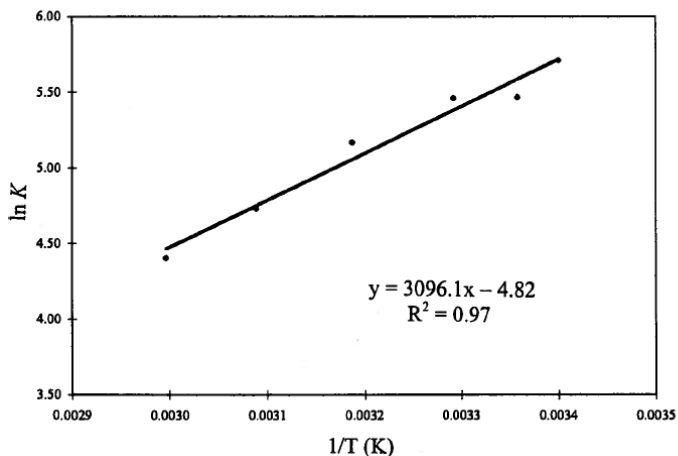
**Figure S2.** DSC curve for *cis*-RuCl<sub>2</sub>(P-N)(PPh<sub>3</sub>)( $\eta^2$ -H<sub>2</sub>) ( $2\mathbf{a}$ ). The sample is heated in a N<sub>2</sub> atmosphere (flow rate = 40 cc/min) at a rate of 5 °C/min to 200°C.

**Appendix 1.** Calculation of  $K_{\text{eq}}$  for the equilibrium  $4\mathbf{a} + \text{PS} \rightleftharpoons 5\mathbf{a} + \text{PSH}^+\text{Cl}^-$

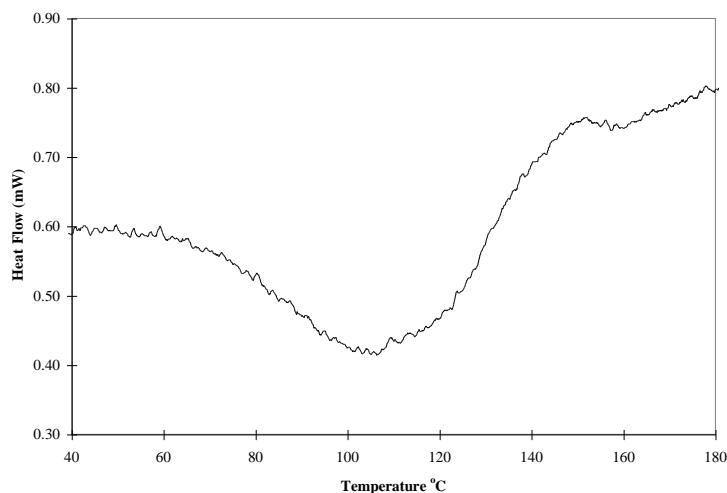
**Table S1.** <sup>1</sup>H NMR integration values ( $\alpha$ ,  $\beta$ ,  $\omega$ ) and equilibrium concentrations for determination of  $K$

T(°C)	1/T(K)	$\alpha$	$\beta$	$\omega$	x	y	[1](M)	[2](M)	[H <sub>2</sub> ](M) <sup>a</sup>	$K$	ln $K$
20.9	0.00340	2.30	8.05	0.49	0.57	3.13	0.0104	0.0059	0.0019	302	5.71
24.6	0.00336	2.20	8.00	0.59	0.55	2.49	0.0105	0.0058	0.0023	236	5.47
30.6	0.00329	1.81	7.35	0.47	0.49	2.57	0.0109	0.0054	0.0021	235	5.46
40.6	0.00319	1.51	7.15	0.50	0.42	2.01	0.0115	0.0048	0.0024	176	5.17
50.6	0.00309	1.10	7.06	0.52	0.31	1.41	0.0124	0.0039	0.0027	113	4.73
60.6	0.00300	1.07	7.40	0.69	0.29	1.03	0.0126	0.0037	0.0035	82	4.40

<sup>a</sup> The values for the [H<sub>2</sub>] are compatible with solubility data for H<sub>2</sub> in benzene (S. Kruyer and A.P.P. Nobel, *Recl. Trav. Chim. Pay – BA*, **1961**, 80, 1145; E. Brunner, *J. Chem. Eng. Data*, **1985**, 30, 269).



**Figure S1.** van't Hoff plot for the equilibrium ( $1a + H_2 \rightleftharpoons 2a$ ).



**Figure S2.** DSC curve for *cis*- $RuCl_2(P-N)(PPh_3)(\eta^2-H_2)$  (**2a**). The sample is heated in a  $N_2$  atmosphere (flow rate = 40 cc/min) at a rate of 5 °C/min. to 200°C.

### Appendix 1

Calculation of  $K_{eq}$  for the equilibrium  $4a + PS \rightleftharpoons 5a + PSH^+Cl^-$  from  $^{31}P\{^1H\}$ -NMR spectra shown in Fig.6c (-25 °C) and 6d (-60 °C); initial  $[4a] = 0.015M$ , and initial  $[PS] = 0.045 M$

Fig. 6c.  $[5a]/[4a] \sim 0.2$ , thus  $[PSH^+Cl^-]/[PS] \sim 0.062$ , and  $K_{eq} \sim 0.012$  ( $pK_{eq} \sim 1.9$ )

Fig. 6d.  $[5a]/[4a] \sim 0.5$ , thus  $[PSH^+Cl^-]/[PS] \sim 0.125$ , and  $K_{eq} \sim 0.06$  ( $pK_{eq} \sim 1.2$ )  
 $pK_a$  of coordinated  $H_2S$  ( $= pK_{eq} + pK_{PSH^+}$ )

$pK_a$  of coordinated  $H_2S$  ( $= pK_{eq} + pK_{PSH^+}$ ) ( $= pK_{eq} + 12.3$ ) =  $\sim 13.5$  to 14.2