## **Electronic Supplementary Information**

## Classical and non-classical phosphine-Ru(II)-hyidrides in aqueous solution: Many, various, and useful.

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Figure S1: Effect of increasing NaCl concentration on the <sup>1</sup>H NMR spectra of  $[RuHCl(mtppms)_3]$  (1).

[Ru] = 0.051M; [*m*tppms] = 0.202M; 0.6mL 0.1M phosphoric acid/10% CD<sub>3</sub>OD; *P*(H<sub>2</sub>)=1bar



Figure S2: <sup>1</sup>H NMR spectra of [RuHCl(*m*tppms)<sub>3</sub>] (1), [{RuHCl(*m*tppms)<sub>2</sub>}] (3), [RuHBr(*m*tppms)<sub>3</sub>] (9) and [RuHI(*m*tppms)<sub>3</sub>] (10).

[Ru] = 0.051M; [*m*tppms] = 0.202M; 0.6mL 0.1M phosphoric acid/10% CD<sub>3</sub>OD; *P*(H<sub>2</sub>)=1bar



Figure S3: Determination of  $T_{1(\min)}$  for *trans*-[RuH<sub>2</sub>(*m*tppms)<sub>4</sub>] (11).

[Ru] = 0.042M; [*m*tppms] = 0.17M; 0.6mL 0.2M phosphate buffer pH=3.01/10% CD<sub>3</sub>OD; *P*(H<sub>2</sub>)>5bar

<sup>31</sup>P-NMR



Figure S4: Determination of the composition of *cis-fac*-[RuH<sub>2</sub>(H<sub>2</sub>O)(*m*tppms)<sub>3</sub>] (**12**) from integrated intensities of <sup>31</sup>P-NMR signals in the presence of added *m*tppms.

[Ru] = 0.042M; [mtppms] = 0.126M, 0.168M, 0.21M; 0.6mL 0.2M phosphate buffer pH=10.0/10% CD<sub>3</sub>OD; P(H<sub>2</sub>)=1bar



Figure S5: Determination of  $T_{1(\min)}$  for  $[\operatorname{RuH}_2(\eta^2-\operatorname{H}_2)(m\operatorname{tppms})_3]$  (13).

[Ru] = 0.042M; [*m*tppms] = 0.17M; 0.6mL 0.2M phosphate buffer pH=10.0/10% CD<sub>3</sub>OD; *P*(H<sub>2</sub>)>5bar



Figure S6: <sup>31</sup>P-<sup>31</sup>P COSY spectrum for *trans*-[RuH<sub>2</sub>(HCOO)(*m*tppms)<sub>3</sub>)]<sup>-</sup> (**14**).

 $[Ru] = 0.042 \text{ M}, [mtppms] = 0.17 \text{ M}, [HCOONa] = 0.84 \text{ M}; 0.6mL H_2O/D_2O \text{ in capillary}$ 



Figure S7: Distinguishing *trans*-[RuH<sub>2</sub>(HCOO)(mtppms)<sub>3</sub>)]<sup>-</sup> (14) and *trans*-[RuH<sub>2</sub>(H<sub>2</sub>O)(*m*tppms)<sub>3</sub>] (15) by selective phosphorus decoupling experiments  ${}^{1}$ H{P}-NMR [Ru] = 0.042 M, [*m*tppms] = 0.17 M, [HCOONa] = 0.84 M; 0,6mL H<sub>2</sub>O/D<sub>2</sub>O in capillary