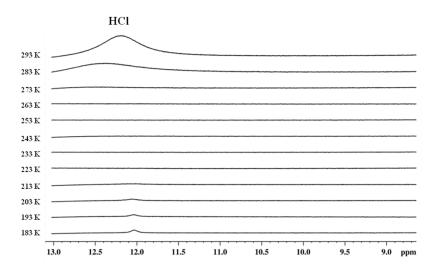
## **Electronic Supplementary Information (ESI)**

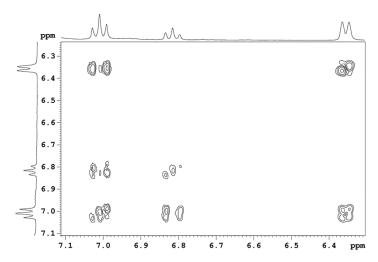
## Contrasting reactivity behaviour of [RuHCl(CO)(PNP)] complex with electrophilic reagents XOTf (X = H, CH<sub>3</sub>, Me<sub>3</sub>Si)

A. Ramaraj,<sup>a</sup> Munirathinam Nethaji<sup>a</sup> and Balaji R. Jagirdar<sup>\*a</sup>

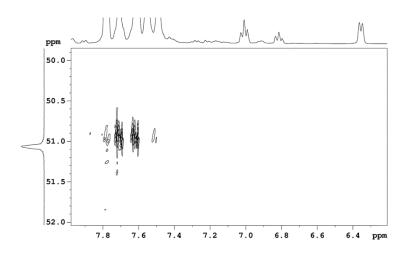
<sup>a</sup> Department of Inorganic & Physical Chemistry, Indian Institute of Science, Bangalore 560012, India



**Fig. S1.** VT <sup>1</sup>H NMR spectral stack plot of the reaction of complex **1** with HOTf in CD<sub>2</sub>Cl<sub>2</sub>. The downfield region shows the formation of HCl



**Fig. S2.** Partial <sup>1</sup>H-<sup>1</sup>H COSY NMR spectrum of complex [RuH(CO)(PNP)][BAr<sub>4</sub>f] (**5a**) in CD<sub>2</sub>Cl<sub>2</sub> at room temperature



**Fig. S3.** Partial  ${}^{1}H$ - ${}^{31}P$  HMQC NMR spectrum of complex [RuH(CO)(PNP)][BAr<sub>4</sub> ${}^{f}$ ] (**5a**) in CD<sub>2</sub>Cl<sub>2</sub> at room temperature

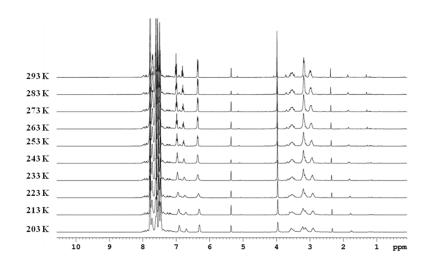


Fig. S4. Partial VT <sup>1</sup>H NMR spectrum of complex [RuH(CO)(PNP)][BAr<sub>4</sub><sup>f</sup>] (5a) in CD<sub>2</sub>Cl<sub>2</sub>

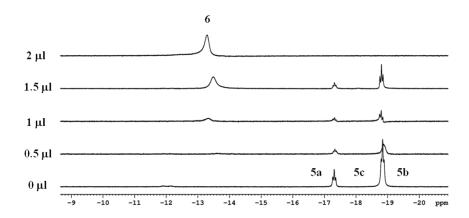


Fig S5: Partial  $^1$ H NMR stack plot of the titration of **5a**, **5b** and **5c** with CH $_3$ CN in CD $_2$ Cl $_2$ . The volume of added CH $_3$ CN is given in the left hand side of the plot. NMR spectra were recorded at 213 K.