Electronic Supplementary Information

for the article

The Half-sandwich 18- and 16-electron Arene Ruthenium Iminophosphonamide Complexes

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1. Complete crystallographic data for the complexes [(η^6-C_6Me_6)RuCl{(*p*-TolN)$_2$PPh$_2$}] (**3a**), [(η^6-C_6Me_6)RuCl{(*p*-TolN)$_2$PEt$_2$}] (**3b**), [(η^6-C_6Me_6)RuCl{(MeN)$_2$PPh$_2$}] (**3c**), [(η^6-C_6Me_6)Ru{(*p*-TolN)$_2$PPh$_2$}]$^+$(PF_6^-) (**4a**), [(η^6-C_6Me_6)Ru{(*p*-TolN)$_2$PPh$_2$}]$^+$(BF_4^-) (**4b**) and [(η^6-C_6Me_6)Ru{(MeN)$_2$PPh$_2$}]$^+$($BAr^F{}_4^-$) (**4c**) are collected in a separate file all_cifs.cif.

2. The exchange rate constant k_{ex} and the corresponding free energy of activation $\Delta G^{\neq}$ at the coalescence temperature T_c were calculated for the complex **3b** in dichloromethane-d_2 according to the [a) A.D. Bain, *Prog. Nucl. Magn. Reson. Spectrosc.,* 2003, **43**, 63-103. b) J. Sandström, "Dynamic NMR Spectroscopy", Academic Press, 1984]:

At the coalescence temperature, the $k_{ex} = \frac{\pi(\Delta\nu)}{\sqrt{2}}$, $\Delta\nu = 600MHz \bullet 1.029\,ppm = 617Hz$,

hence the $k_{ex} = 1370s^{-1}$ at the T_c = 238K.

The free energy of activation $\Delta G^{\neq} = -RT_c \ln(\frac{k_{ex} * h}{k_B * T_c})$, where k_B and h are the Boltzmann and the Planck constants, correspondingly. At the T_c = 238K, the $\Delta G^{\neq} = 43.5kJ/mol$.

3. The VT NMR of the complex **3b** in toluene-d_8 at 273 – 353K.