Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information for

Unsaturated iridium pyridinedicarboxylate pincer complexes with catalytic activity in borylation of arenes

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Kinetic parameters for pyridine exchange in compound [Ir(κ^3-pydc)(1-κ-4,5-η-C_8H_{13})(py)] (1-py).

The kinetic parameters for the pyridine exchange in compound **1-py** were determined by NMR spectroscopy.

$$\textbf{1}\text{-py} + \text{py}^* \longrightarrow \textbf{1}\text{-py}^* + \text{py}$$

First-order rate constants were determined from the decay of [**1-py**] with time under first-order conditions using linear least-square regression analysis. Typical plots of [**1-py**] and [**py**] vs *t* obtained from NMR measurements using $[\textbf{1-py}]_0$ = 3.66 *mM*, [**py***] = 0.136 M and 263.15 K are shown in Figure 1a. The ln[**1-py**] vs *t* representation provided a linear fit that is representative of a first-order kinetic transformation with the slope of the line corresponding to the observed first-order rate constant *k* (s^{-1}) (Figure 1b).

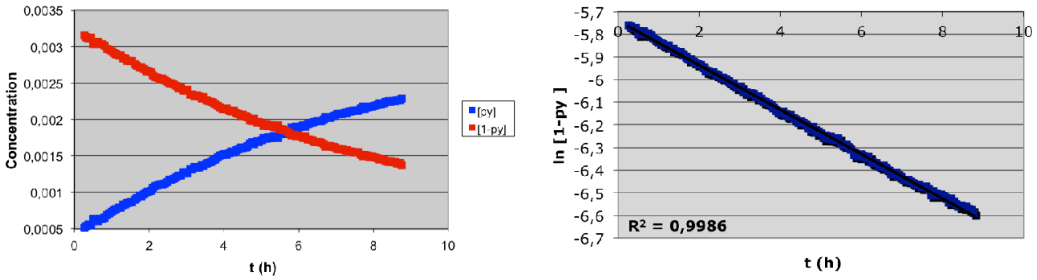


Fig. 1. a) Decay of [**1-py**] and increase of [**py**] vs *t* at $[\textbf{1-py}]_0$ = 3.66 *mM*, [py*] = 0.136 M and 263.15 K. b) First-order kinetic fit of the data: ln[**1-py**] vs *t* plot.

The influence of the [py-d^5] on the reaction rate was investigated in the concentration range 136–407 mM in CD_2Cl_2 at $[\textbf{1-py}]_0$ = 3.66 *mM* and 263.15 K (Figure 2).

Pyridine exchange: influence of [py*]

T/K	[py*]/molL^{-1}	k_{obs}/s^{-1}	R^2
263,15	0,1358	2,73 ± 0,01 E-05	0,999
263,15	0,2716	2,89 ± 0,01 E-05	0,997
263,15	0,4074	2,56 ± 0,01 E-05	0,996

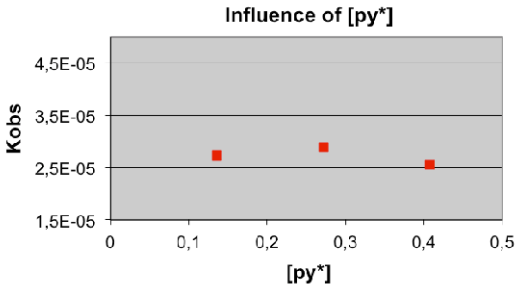


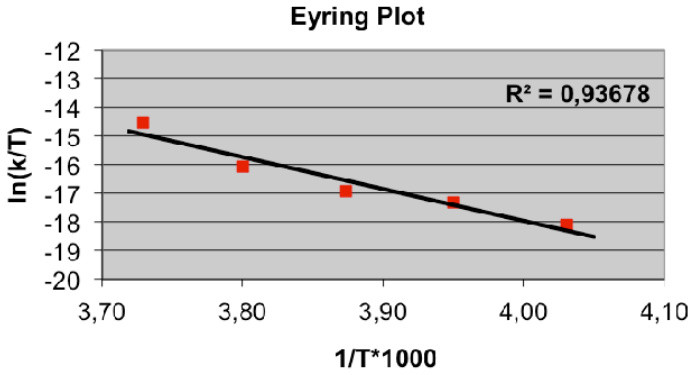
Fig. 2. Plot of k_{obs} vs [**py***] for pyridine exchange in **1-py**.

The influence of the temperature on the reaction rate was investigated in the temperature range 248.15–268.15 K in CD_2Cl_2 at [**1-py**]$_0$ = 3.66 *mM* and [**py***] = 0.136 M. The rate constant was determined at five different temperatures and the overall activation parameters, $\Delta H^{\#}$ and $\Delta S^{\#}$, were determined using the logarithmic form of the Eyring equation (Figure 3).

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{\kappa k_b}{h}\right) + \frac{\Delta S^{\neq}}{R} - \frac{\Delta H^{\neq}}{RT}$$

Pyridine exchange: influence of the temperature

T/K	[py*]/molL^{-1}	k_{obs}/s^{-1}	R^2
268,15	0,1358	1,32 ± 0,04 E-04	0,985
263,15	0,1358	2,73 ± 0,01 E-05	0,999
258,15	0,1358	1,16 ± 0,01 E-05	0,998
253,15	0,1358	7,59 ± 0,04 E-06	0,997
248,15	0,1358	3,39 ± 0,01 E-06	0,999



$\Delta H^{\#} = 93 \pm 1$ kJmol^{-1}, $\Delta S^{\#} = 24 \pm 4$ JK^{-1}mol^{-1}, $\Delta G^{\#} = 86 \pm 2$ kJmol^{-1} at 293.15 K.

Fig. 3. Eyring plot for pyridine exchange in **1-py** and derived activation parameters.