

Mechanism of Hydrogen Transfer to Imines from a Hydroxycyclopentadienyl Ruthenium Hydride. Support for a Stepwise Mechanism.

Joseph S. M. Samec, Alida H. Éll and Jan-E. Bäckvall.

Experimental

General methods. ^1H (400 MHz) and ^{13}C (100 MHz) spectra were recorded on a Varian Mercury spectrometer. Chemical shifts (δ) are reported in ppm, using residual solvent as internal standard, and coupling constants (J) are given in hertz. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. All reactions were performed under argon atmosphere in oven-dried (140 °C) glassware. Distillations were conducted in a Büchi Glass oven B-580.

[2,3,4,5-Ph₄(η^5 C₄COH)Ru(CO)₂H (2). Complex **3** (55 mg, 0.05 mmol) was charged into a Pyrex tube (2-5 mL) fitted with a screw cap with a silicone/teflon septum (Personal Chemistry AB, Uppsala, Sweden). THF (2.7 mL) was carefully syringed into the reaction vessel, washing down any complex on the glass wall. The septum was closed and the sample was cooled down to -199 °C under H₂ atmosphere. The vessel was degassed with 3 freeze-pump-thaw cycles. The vessel was allowed to reach rt and inserted into a microwave oven. The microwave irradiation was run at 90 W for 20 min (120 °C, 2 bar). When the sample had cooled down the solvent was evaporated and CD₂Cl₂ (0.5 mL) was added under argon atmosphere. The solution was transferred to an NMR tube and the conversion to hydride **2** was analyzed by ^1H NMR using ferrocene as an internal standard.

Determining the Rate Law

The first-order dependence on imine was determined by measuring the initial rates for the reaction of ruthenium hydride **2** with imine **4**. The concentration of imine was varied whereas the concentration of **2** was held constant and in excess (Table 1). Using the above-mentioned pseudo-first-order kinetics the rate expression becomes:

$$\text{rate} = k_{\text{obs}}[\text{imine}]$$

Reaction of Imine 4 with 2. Complex **2** was prepared as described above. The THF was evaporated and the CD₂Cl₂ (0.5 mL), saturated with H₂O was added. The solution was syringed into an NMR tube under argon atmosphere yielding a 0.2 M solution of **2** and cooled down to -199 °C. Freshly distilled **4** was added by syringe to the NMR tube and the mixture was warmed up to -78 °C and carefully shaken. The NMR tube was re-cooled to -199 °C and put into the spectrometer pre-cooled to -65 °C. At this temperature no reaction occurred and the sample was initially locked and shimmed and an acquisition was run to double-check the concentrations and that no reaction had taken place. The temperature was set to -58 °C, the sample was shimmed, and t_0 was set when

the temperature had reached $-58\text{ }^{\circ}\text{C}$. The time between when the temperature was initially set to $-58\text{ }^{\circ}\text{C}$ and the first acquired spectrum was $\sim 100\text{ s}$ (Reactions that had proceeded more than 25% were discarded). The reaction was followed until at least 2 half lives integrating the methoxy peaks of **4** and **5**. Complex **5** was obtained as a mixture of diastereoisomers. $^1\text{H NMR}$ (400 MHz, CD_2Cl_2 , $-54\text{ }^{\circ}\text{C}$) **5a**: δ 1.36, (d, $J = 8.25\text{ Hz}$, Me), 3.62 (s, OCH_3), 4.02-4.12 (m, CH) Aromatic signals (see below). **5b**: δ 0.86 (d, $J = 6.4\text{ Hz}$, CH_3), 3.37 (d, $J = 12\text{ Hz}$, NH), 3.55 (s, OCH_3), 4.50-4.56 (m, CH), 5.5-5.6 (m, ArH), 5.94-6.02 (m, ArH). In the early stage of the reaction diastereoisomer **5a** dominated. Towards the end of the reaction **5b** was the major diastereoisomer.

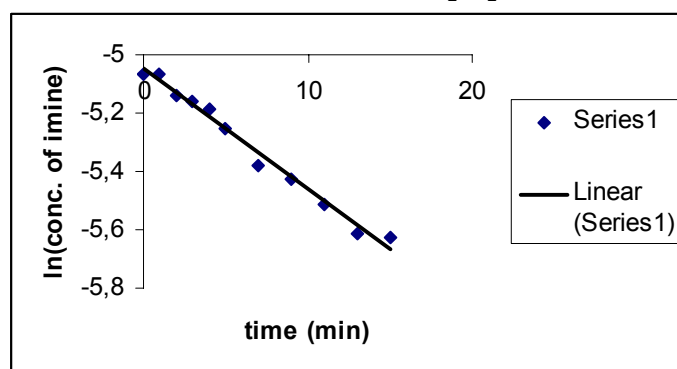
The reaction showed first order dependence in imine concentration (Table 1).

Table 1. Rates for the reaction of **2** with **4** at $-58\text{ }^{\circ}\text{C}$ in CD_2Cl_2

[imine] (mM)	k_{obs} (s^{-1}) $\times 10^{-6}$	$k_{\text{obs}}/[\text{imine}]$ ($\text{M}^{-1}\text{ s}^{-1}$)
3.7	0.9	2.9
6.6	1.8	2.8
13.7	3.8	2.8

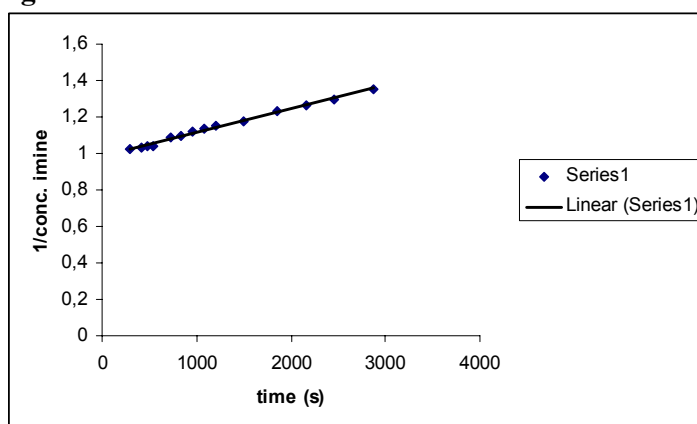
When $\ln[\text{imine}]$ was plotted against time a straight line was obtained (Figure 1)

Figure 1. First order dependence on imine for the reaction of **2** with **4** at $-58\text{ }^{\circ}\text{C}$ in CD_2Cl_2 .



The first-order dependence on **2** was difficult to measure directly due to the hydride resonance at $\delta -9.8$ and experiments at low concentrations gave unreliable results. It was demonstrated that the reaction with equimolar amounts of **2** and **4** gave second-order kinetics. When $1/[\text{imine}]$ was plotted against time a straight line was obtained establishing a second-order kinetics (Figure 2). Together with the first-order dependence on imine already determined this establishes the first-order dependence on **2**.

Figure 2. Second order kinetics in the reaction of **2** with **4**.



An NMR tube with equimolar amounts of **2** (0.6 M) and **4** (0.6 M) in CD_2Cl_2 at $-200\text{ }^\circ\text{C}$ was inserted to a precooled spectrometer ($-58\text{ }^\circ\text{C}$) and the reaction was followed until 50% conversion

These experiments show that the hydrogen transfer from **2** to **4** is an overall second-order reaction with a first-order dependence on both **2** and **4**:

$$\text{rate} = k[\mathbf{2}][\mathbf{4}]$$

Study of Kinetic Deuterium Isotope Effects

Reaction of Imine **4** with **2**. Complex **2** was prepared in either H_2 or D_2 as described above. The THF was evaporated and the CD_2Cl_2 (0.5 mL), saturated with H_2O or D_2O depending on whether H_2 or D_2 was used. The solution was syringed into an NMR tube under argon atmosphere yielding a 0.2 M solution of **2**, and cooled to $-199\text{ }^\circ\text{C}$. Freshly distilled **4** (4 μmol , 0.04 M, 0.1 mL) was added by syringe to the NMR tube and the mixture was warmed up to $-78\text{ }^\circ\text{C}$ and carefully shaken. The NMR tube was re-cooled to $-199\text{ }^\circ\text{C}$ and put into the spectrometer pre-cooled to $-65\text{ }^\circ\text{C}$. At this temperature no reaction occurred and the sample was initially locked and shimmed and an acquisition was run to double-check the concentrations and that no reaction had taken place. The temperature was set to $-54\text{ }^\circ\text{C}$, the sample was shimmed, and t_0 was set when the temperature had reached $-54\text{ }^\circ\text{C}$. The time between when the temperature was initially set to $-54\text{ }^\circ\text{C}$ and the first acquired spectrum was $\sim 140\text{ s}$ (Reactions that had proceeded more than 25% were discarded). The reaction was followed until at least 2 half lives (24 min) integrating the methoxy peaks of **4** and **5**.

From seven respectively six experiments the following data in Table 2 were acquired.

Table 2.

RuHOH	k_{obs} [s⁻¹]	RuDOD	k_{obs} [s⁻¹]
1	1.21*10 ⁻³	1	1.09*10 ⁻³
2	1.29*10 ⁻³	2	1.21*10 ⁻³
3	1.31*10 ⁻³	3	1.08*10 ⁻³
4	1.25*10 ⁻³	4	1.23*10 ⁻³
5	1.32*10 ⁻³	5	1.15*10 ⁻³
6	1.11*10 ⁻³	6	1.31*10 ⁻³
7	1.22*10 ⁻³		
mean	1.24*10⁻³ ± 7.8*10⁻⁵	mean	1.18*10⁻³ ± 8.86*10⁻⁵