

CHAPTER 5

KINETIC STUDIES OF $\text{RuCl}_2(\text{RNC})_2(\text{PPh}_3)_2$

5.0 Introduction

Synthesis and characterisation of *ttt*- $\text{RuCl}_2(\text{RNC})_2(\text{PPh}_3)_2$ complexes has been carried out as in Chapter 4. A preliminary report on the solid state isomerisation of these complexes [1] as well as related *ttt*- $\text{RuCl}_2(\text{CO})_2(\text{PR}_3)_2$ have been previously documented. No kinetic data on these isomerisation processes have been reported previously. The kinetic investigations were followed by two methods, namely NMR spectroscopy and XRD powder diffraction methods, and the results are reported in the subsequent sections of this chapter.

5.1 Experimental

5.1.1 Kinetic studies of $\text{RuCl}_2(\text{RNC})_2(\text{PPh}_3)_2$ by NMR spectroscopy

Kinetic studies were performed at constant temperature in the range 160 – 180 °C by heating 10 mg of the solid samples in a sealed NMR tube for various time intervals. The NMR tubes containing the solid samples were evacuated and purged with nitrogen prior to heating. Heating was accomplished by immersing the tubes in an oil bath, set at the temperature of the reaction experiment. After heating, the samples were cooled to room temperature and then dissolved in CDCl_3 and taken for ^1H NMR measurement. The % *ttt* isomer versus time curves and the Arrhenius plot for each individual isomerisation process was constructed from the data (see section on results and discussion).

5.1.2 XRD data collection

Samples were ground with an agate pestle and mortar to a fine powder in preparation for powder X-ray diffraction analysis. A Philips PW 1710 diffractometer fitted with a Philips PW 1820 goniometer (with secondary beam monochromator and zero-background sample holder) was used to collect the diffractograms. Copper K-alpha radiation ($\lambda = 1.5418 \text{ \AA}$) was employed, with generator tension and current being 40 kV and 20 mA, respectively. Samples were run as powders on rotating silicon wafers using silicone grease. Diffractograms were recorded in step-scan mode, from start angle (2θ) 3.000° to end angle (2θ) 70.000° , with a step size of (2θ) 0.020° and time per step of 25 s. Diffraction data was recollected after the initial X-ray exposure and found to be essentially unchanged – hence samples showed no significant evidence of degradation within the X-ray beam. Diffractograms for $\text{RNC} = {}^t\text{BuNC}$ are presented in figure 5.5.

5.1.3 Kinetic Studies of $\text{RuCl}_2({}^t\text{BuNC})_2(\text{PPh}_3)_2$ by XRD methods:

A powdered sample of $\text{RuCl}_2({}^t\text{BuNC})_2(\text{PPh}_3)_2$ was divided into a number of sub-samples. Each sub-sample was placed into its own NMR tube. The NMR tube was evacuated and then flushed with nitrogen and the tube was sealed. Heating was achieved as described in section 5.1.1. The NMR tubes were withdrawn from the oil bath at regular time intervals and allowed to cool to room temperature. The sub-samples were then removed from the NMR tubes. Due to the small amounts of powder constituting the sub-samples, Lindemann tubes were used for powder diffraction preparation. Powdered material from a particular sub-sample was carefully tapped into a Lindemann tube, to fill approximately $\frac{2}{3}$ of the tube. The tube was subsequently cut to the required length and mounted on a silicon wafer, using minute amounts of silicon grease at the tips. Diffractograms were collected as described in section 5.1.2 and were typically recorded from (2θ) 3° to 40° (15 s per step).

5.3 Results and Discussion

5.3.1 Kinetic Studies by NMR spectroscopy

The kinetic studies of the isomerisation reactions were followed by heating solid samples for periods of time and then dissolving the material and evaluating the degree of reaction by ^1H NMR spectroscopy. The peaks that appeared in the CH_3/CH_2 region of the NMR spectrum were used to monitor these reactions. These were chosen because the CH_3/CH_2 resonances for *ttt* and *cct*-isomers in that region are well separated and thus can easily be separately integrated. For example, in the ^tBu complex, the methyl peak at 1.00 ppm gradually disappears and is replaced by the peak at 0.70 ppm corresponding to the newly formed *cct*-isomer. For the benzyl complex the peak that appeared at 4.32 ppm is gradually replaced by a peak at 3.76 ppm. (see table 4.2 and figure 5.1) By measuring the disappearance of the *ttt* complex, as a function of time, it is therefore possible to evaluate the advance of the solid state isomerisation reaction.

Kinetic studies were performed on ruthenium complexes with $\text{R} = ^t\text{Bu}$ and benzyl. It must be noted that the conversion from the *ttt*-isomer to *cct*-isomer is a solid state process, and using solution techniques might affect the outcome of the results. It was found, however, that leaving dissolved samples in solution for 24 h did not affect the ratio of isomers present.

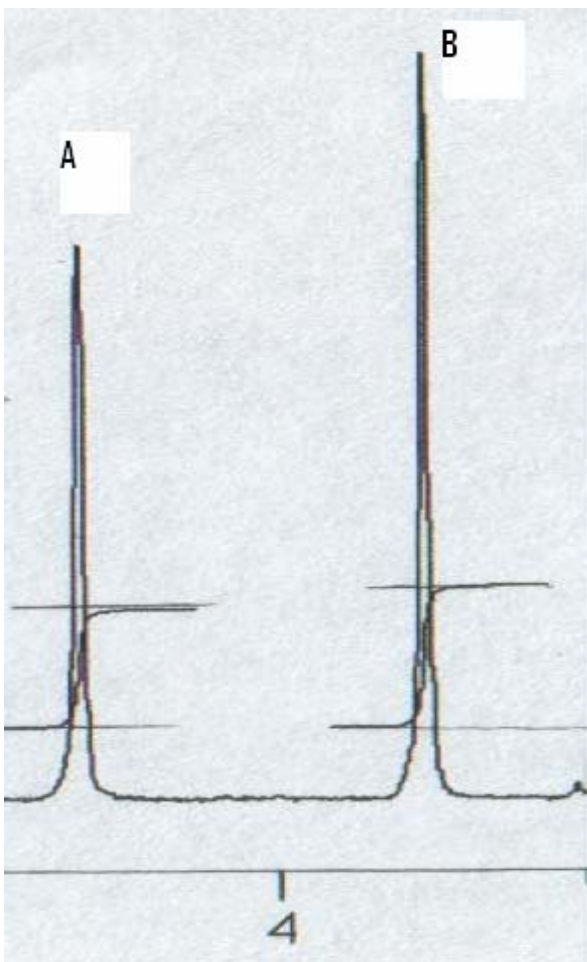


Figure 5.1: ^1H NMR spectrum showing the CH_2 resonances due to $\text{RuCl}_2(\text{benzylNC})_2(\text{PPh}_3)_2$ isomers; A) *ttt*-isomer and B) *cct*- isomer.

When complexes with $\text{R} = 2,6\text{-xylyl } ^i\text{Pr}$ and MeCIPh were used, the reaction progression was difficult to follow as the corresponding *cct*-isomers were poorly soluble in the solvents used, and hence precipitated out of CDCl_3 or C_6D_6 at high concentrations. This caused some inaccuracies in calculations of isomer ratios.

The percent conversion (α) at a given time t was calculated from the expression

$$\alpha_{(tt)} = \{I_{(tt)}/[I_{(tt)} + I_{(cct)}]\} * 100$$

where $I_{(tt)}$ is the intensity of the *ttt*-isomer and $I_{(cct)}$ is the intensity of the *cct*-isomer, the intensity data being obtained from the solution NMR spectra of the samples after reaction. The α versus time curves for the isomerisation process for the two *ttt* -

complexes show a similar sigmoid shape (see Figure 5.2). An assumption was made that the reaction would be first order. The plots of $\ln\alpha$ versus time yielded a straight line that is expected of a first order reaction (see Figure 5.3).

From these plots, the rate constant values for ^tBu complexes were found to be $0.0044 \pm 6.2 \times 10^{-4}$, $0.0025 \pm 3.2 \times 10^{-4}$, $8.58 \times 10^{-4} \pm 4.3 \times 10^{-4}$ at 185, 180 and 175 °C respectively. The activation energy, E_a , derived from the least squares analysis of the best fit from the $\ln K$ versus $1/T$ plot (see Figure 5.4) was found to be 210 kJ mol^{-1} .

For the benzyl complex the samples were heated at 160, 170 and 180 °C and the rate constants were found to be $0.0041 \pm 3 \times 10^{-4}$, $0.0057 \pm 4.0 \times 10^{-4}$ and $0.029 \pm 0.004 \text{ s}^{-1}$ respectively. The activation energy E_a was found to be 221 kJ mol^{-1} .

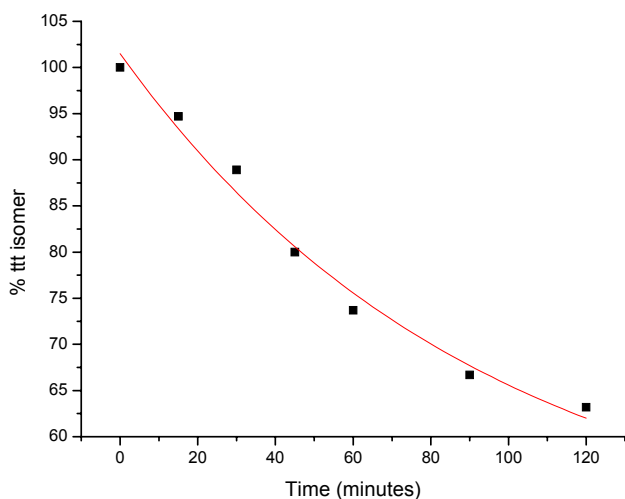


Figure 5.2: Typical % *ttt* isomer versus time curve for $\text{RuCl}_2(\text{benzylNC})_2(\text{PPh}_3)_2$ (160 °C)

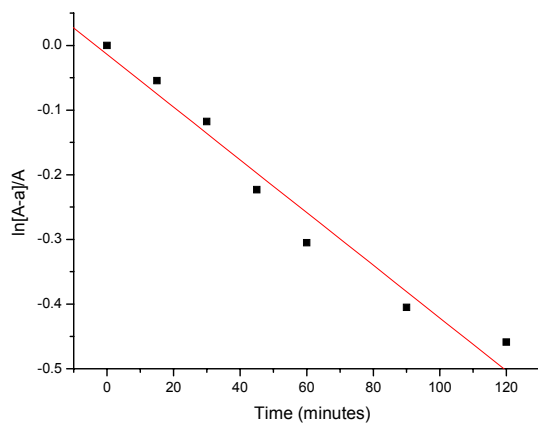


Figure 5.3: Typical plot of $\ln \alpha$ versus time for $\text{RuCl}_2(\text{benzylNC})_2(\text{PPh}_3)_2$ (160°C).

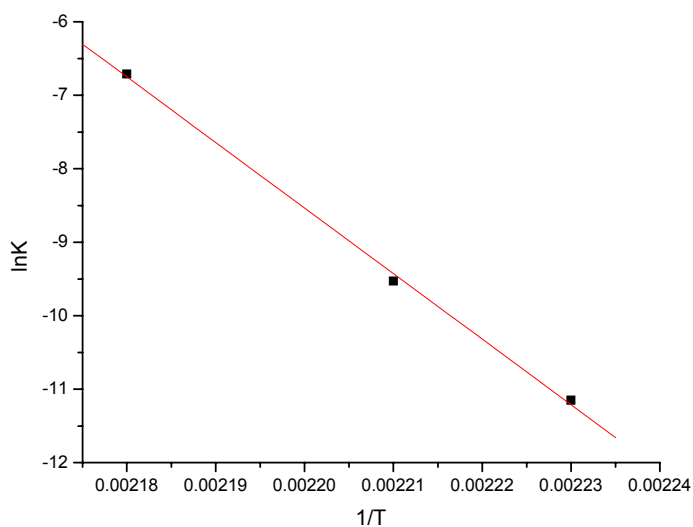


Figure 5.4: Typical Arrhenius plot for $\text{RuCl}_2(\text{t-BuNC})_2(\text{PPh}_3)_2$

5.3.2 Characterisation by XRD

Sample preparation, and powder XRD data collection, was undertaken as described in section 5.1.2. Diffractograms for $\text{RuCl}_2(\text{t-BuNC})_2(\text{PPh}_3)_2$ are shown in Figure 5.5. The figure gives the powder pattern of the starting material (i.e. *ttt*-isomer), while the powder pattern of the fully isomerised product material produced in the solid-state reaction (i.e.

cct-isomer) is shown in Figure 5.5 **B**. Isomer conversion was confirmed by NMR analysis. It is seen that the two isomers have distinctive XRD patterns.

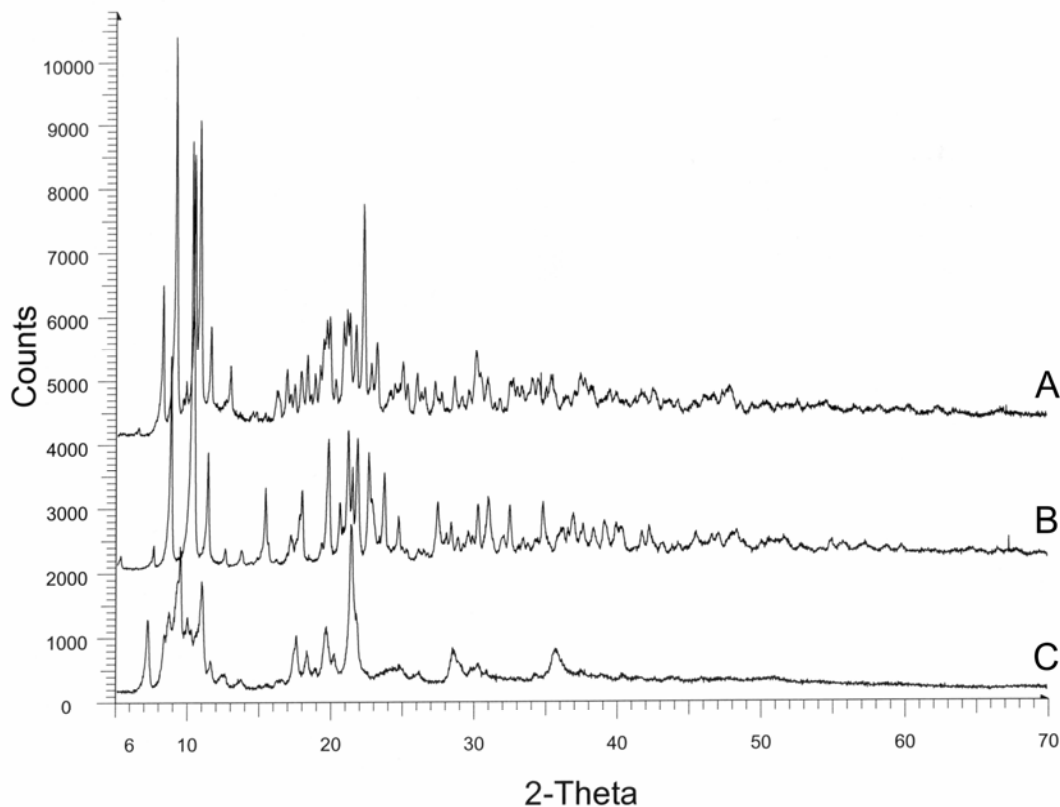


Figure 5.5: Powder pattern of the $\text{RuCl}_2(^1\text{BuNC})_2(\text{PPh}_3)_2$ (A) *ttt*-isomer, (B) *cct*-isomer (C) *cct*-isomer recrystallized from CH_2Cl_2 .

The *cct*-isomer was also recrystallised from dichloromethane solution and the powder pattern recorded (Figure 5.5 C). The patterns of the two *cct*-samples are really quite dramatic, suggesting that the *cct*-isomer can exist as a number of polymorphs. Similar findings of different powder patterns for the same isomer have been reported in the literature, e.g. the polymorphs of the nitrito isomers of a series of six coordinate cobalt complexes [3].

5.3.3. Kinetic studies by XRD analysis

Kinetic studies of the solid-state isomerisation reaction of $\text{RuCl}_2(\text{t-BuNC})_2(\text{PPh}_3)_2$ were performed at three different temperatures (175 °C, 180 °C and 185 °C). In each case, a sample of the *ttt*-isomer (starting material) was heated to the particular reaction temperature, and powder diffraction patterns of the material subsequently recorded after certain time intervals (section 5.1.2). For every powder pattern obtained, the background pattern of an unfilled Lindemann tube was subtracted, followed by $K\alpha_2$ stripping and smoothing of the data. The decrease in intensity as a function of time of the *ttt*-isomer reflection at (2θ) 9.1-9.5° (Figure 5.6) was used to evaluate the advance of the solid-state isomerisation reaction. This peak also showed the most consistent variation in intensity across the different temperature data sets collected.

The extent of reaction (α) as defined in terms of the percentage *ttt*-isomer at a given time t , was calculated from the expression:

$$\alpha_{(\text{ttt})} = (I_{(\text{ttt})} / I_{0(\text{ttt})}) \times 100$$

where $I_{(\text{ttt})}$ is the intensity of the *ttt*-isomer at time t , and $I_{0(\text{ttt})}$ the intensity at the start of the reaction – the intensity data being obtained from the powder diffraction patterns as described above. The α versus t curves were found to be well modelled by first-order kinetics, with the corresponding plots of $\ln \alpha$ versus t yielding straight lines as expected. From the $\ln \alpha$ versus t plots, the following rate constants for the isomerisation process were obtained by least-squares fitting: $4.32 (\pm 1.22) \times 10^{-4} \text{ s}^{-1}$, $2.62 (\pm 1.14) \times 10^{-4} \text{ s}^{-1}$, $1.20 \times 10^{-4} (\pm 8.61 \times 10^{-5}) \text{ s}^{-1}$ at 185, 180 and 175 °C respectively. The activation energy, derived from the best fit to the $\ln k$ versus $1/T$ plot (Fig. 4.24) was found to be $219 (\pm 26) \text{ kJmol}^{-1}$.

Kinetic studies of the solid-state isomerisation of $\text{RuCl}_2(\text{t-BuNC})_2(\text{PPh}_3)_2$ followed by heating powdered samples for periods of time, then dissolving the material and

evaluating the extent of reaction by ^1H NMR spectroscopy has revealed an activation energy of 210 kJmol^{-1} for the process (see section 5.3.1). Thus, the favourable agreement between results, suggests the powder diffraction method used in this work to be a suitable method for further high-temperature, solid-state kinetic analysis. The powder diffraction method would be particularly useful in situations where samples are not readily soluble in NMR solvents. Mechanistic conclusions relating to these findings are discussed in chapter 6.

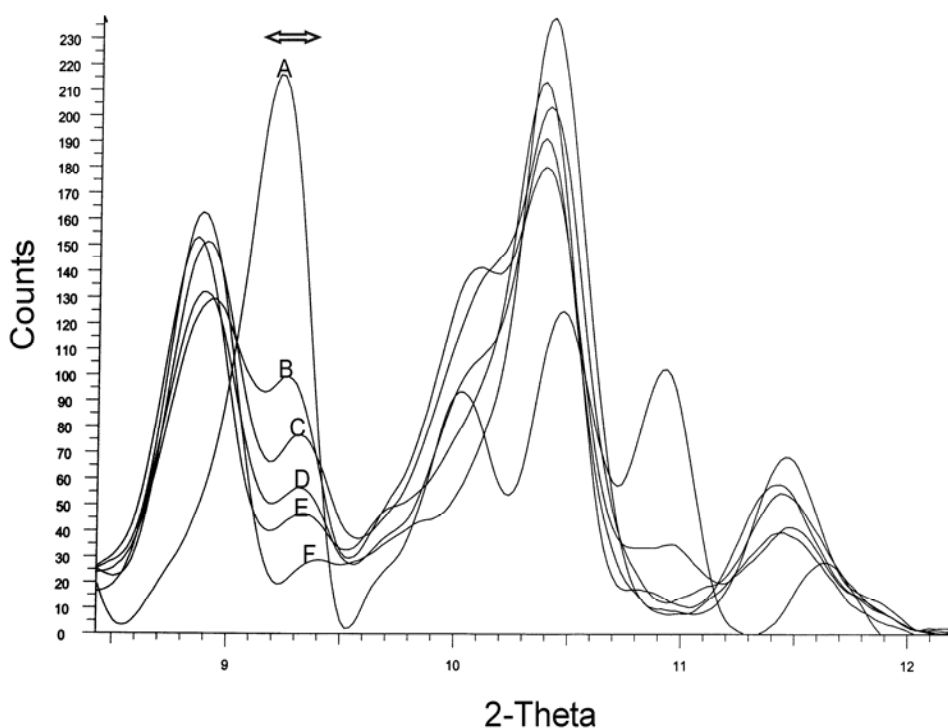


Figure 5.6: Change in the powder pattern of $\text{RuCl}_2(\text{t-BuNC})_2(\text{PPh}_3)_2$ during solid-state isomerisation reaction at $185 \text{ }^\circ\text{C}$; the diminishing *ttt*-isomer reflection indicated was monitored (A-F: Lindemann tube samples after 0, 35, 70, 105, 140, 1080 min reaction respectively).

5.4 References

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3. N. Masciocchi, A. Kolyshev, V. Dulepov, E. Boldvera, A. Sironi, *Inorg. Chem.* **33** (1994) 2579.