

Solventless isomerisation reactions: A crystallographic and thermomicroscopic investigation of some six coordinate $\text{RuCl}_2\text{L}_2\text{L}'_2$ complexes

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The thermal, unidirectional *ttt* to *cct* ligand isomerisation of six coordinate ruthenium complexes, $\text{RuCl}_2(\text{RNC})_2(\text{PPh}_3)_2$ ($\text{R} = \text{Bu}^t$, 2,6-Xyl, PhCH_2) and $\text{RuCl}_2(\text{CO})_2(\text{PMePh}_2)_2$, was investigated in the solid state by powder X-ray diffraction and thermomicroscopy techniques. Temperature studies (under a microscope) on single crystals of *ttt*- $\text{RuCl}_2(\text{RNC})_2(\text{PPh}_3)_2$ and *ttt*- $\text{RuCl}_2(\text{CO})_2(\text{PMePh}_2)_2$, revealed the reaction took place heterogeneously, *via* a nuclear formation and growth process commencing at the crystal surface and/or at defects within the crystal. The reaction proceeded without retention of crystallinity. A powder diffraction study was used to follow the isomerisation reaction of *ttt*- $\text{RuCl}_2(\text{Bu}^t\text{NC})_2(\text{PPh}_3)_2$ and the reaction was found to follow first-order kinetics with $E_a = 219 (\pm 26) \text{ kJ mol}^{-1}$.

1. Introduction

Environmental issues have resulted in a reconsideration of approaches to synthetic chemistry.^{1,2} One simple methodology is to carry out reactions in the absence of solvents, but because of issues of heat and mass transfer direct correlations between solvent and solventless reactions are not straightforward.³ Further, issues relate to whether reactions in the absence of solvents occur in the solid state or in the melt.

To further explore the issue of solventless reactions, and in particular solid-state *versus* melt reactions, we have investigated the isomerisation reactions of a series of $\text{RuCl}_2(\text{L})_2(\text{PR}_3)_2$ ($\text{L} = \text{CO}, \text{RNC}$) complexes.

A study by Nelson and co-workers,⁴ in which they investigated the solid-state reactions of a series of ruthenium(II) complexes $\text{RuCl}_2(\text{PR}_3)_{3-x}(\text{CO})_x$, ($\text{PR}_3 = \text{PMePh}_2, \text{PMe}_2\text{Ph}, \text{PMe}_3, \text{P}(\text{CH}_2\text{C}_6\text{H}_5)_3$; $x = 1, 2$) provides the starting point for this study. In the Nelson study a thermal *trans* to *cis* ligand isomerisation reaction (Fig. 1) was found to occur in the temperature range 140–180 °C both in the presence and absence of solvents.⁵ We have also recently reported a synthetic/mechanistic study of similar complexes in the absence of solvent.⁶ A study by Yamamoto and co-workers⁷ also found similar *trans* to *cis* ligand isomerisation reactions in the solid state for some related ruthenium isonitrile complexes, $\text{RuCl}_2(\text{RNC})_{4-x}(\text{PR}'_3)_x$ ($\text{R} = \text{Xyl}, \text{Mes}, \text{etc.}$, $\text{PR}'_3 = \text{PPh}_3, \text{P}(4\text{-MeC}_6\text{H}_5)_3$; $x = 0, 2$).

While the solution data reported by Nelson are consistent with ligand dissociative processes and rates that decreased with increasing phosphine basicity and decreasing phosphine steric

bulk,⁵ the solid-state reaction mechanism is unknown. Mechanistic information on similar six coordinate ruthenium dihydride complexes has been reported, from data generated from NMR studies on the intramolecular isomerisation and fluxionality, on $\text{Ru}(\text{CO})_2(\text{H})_2\text{L}_2$ complexes.⁸ The use of molecular orbital calculations at the *ab initio* level to study intramolecular rearrangements in $\text{Ru}(\text{H})_2(\text{PH}_3)_4$ and $\text{Fe}(\text{H})_2(\text{CO})_4$ compounds has also been described.⁹

Herein we report on attempts to use powder X-ray crystallography and single-crystal thermomicroscopy to investigate the solventless isomerisation reaction of *ttt*- $\text{RuCl}_2(\text{Bu}^t\text{NC})_2(\text{PPh}_3)_2$, *ttt*- $\text{RuCl}_2(2,6\text{-XylNC})_2(\text{PPh}_3)_2$, *ttt*- $\text{RuCl}_2(2,6\text{-PhCH}_2\text{NC})_2(\text{PPh}_3)_2$ and *ttt*- $\text{RuCl}_2(\text{CO})_2(\text{PMePh}_2)_2$ to their respective *cct* isomers and to more fully explore the solid-state reaction behaviour of these types of complexes.

2. Experimental

The six coordinate ruthenium(II) complexes studied in this work were prepared as described previously.^{5,10} They were characterised by IR and NMR spectroscopy and the solids showed a solid-state unidirectional isomerisation reaction proceeding from the *trans, trans, trans* (*ttt*) isomer to the thermodynamically preferred *cis, cis, trans* (*cct*) isomer (Fig. 1) with time.^{4,7}

XRD powder analysis

Samples were ground to a fine homogenous powder using an agate pestle and mortar. A small portion of sample was subsequently withdrawn and submitted for NMR analysis—this was undertaken to confirm sample purity and identity. For characterisation work, powdered samples were mounted on silicon wafers by evenly distributing the powder over the wafer and using silicon grease for attachment.

For solid-state kinetic studies, a powdered sample of starting material was divided into a number of sub-samples. Each sub-sample was placed into its own, shortened NMR tube. The

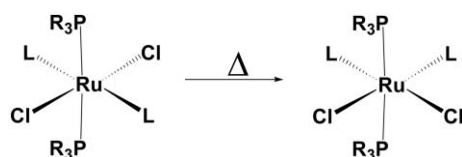


Fig. 1 *ttt* to *cct* isomerisation of $\text{RuCl}_2\text{L}_2(\text{PR}_3)_2$ ($\text{L} = \text{CO}, \text{RNC}$).

NMR tubes were evacuated and then flushed with nitrogen gas and the tube sealed, prior to heating. Heating was accomplished by immersing the tubes in an oil bath, set at the temperature of the reaction experiment. The NMR tubes were withdrawn from the oil bath at regular time intervals and allowed to cool to room temperature. Due to the small amounts of powder studied, 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 silicon grease at the tips.

The powder diffractometer used for data collection consisted of a Philips PW 1710 generator fitted with a Philips PW 1820 vertical goniometer (with secondary beam monochromator). Cu K α radiation was used, with generator tension and current being 40 kV and 20 mA, respectively. All samples were spun during data collection to ensure more homogeneous (*i.e.*, isotropic) diffraction patterns. Data collection was at room temperature. Diffraction patterns were recorded in step-scan mode with a step size of (2θ) 0.02° . Characterisation patterns were typically from (2θ) 3° to 70° (25 s per step), while those for kinetic work were typically from (2θ) 4° to 40° (15 s per step). Partial recollection of data after each scan was undertaken to confirm sample integrity—samples showed no significant evidence of degradation within the X-ray beam. For every powder pattern obtained, the background pattern of an unfilled Lindemann tube was subtracted, followed by K α_2 stripping and smoothing of the data.

The software packages POWDER-X¹¹ and DIFFRAC-PLUS¹² were used for the processing and presentation of the experimental powder X-ray diffraction data collected. The peak areas used in the kinetic study were evaluated from the powder diffraction data after application of DIFFRAC-PLUS to the raw data.

Thermomicroscopy

Optical microscopy experiments were carried out as described previously.^{13–15} Single crystals up to 0.5 mm in dimension were used and reactions were performed in an inert atmosphere in

the specially constructed cell. Reactions were routinely performed in the range 140–230 °C.

A CCD camera attachment, fitted to an Olympus polarising microscope, was used to take micrographs of the solid-state isomerisation reaction. The microscope was adjusted for optimum light transmission through an unreacted crystal.

Calibration of the equipment was performed with samples of known melting point.

3. Results and discussion

3.1 Single-crystal studies of the solid-state isomerisation of six coordinate ruthenium(II) complexes

Heating of *ttt*-RuCl₂(Bu^tNC)₂(PPh₃)₂ crystals. The results of the various high-temperature studies of *ttt*-RuCl₂(Bu^tNC)₂(PPh₃)₂ single crystals are given in Table 1. Crystals were reacted at different temperatures, and for different periods of time, in the heating cell. Prior to use of the heating cell, crystals were reacted under nitrogen in a modified NMR tube immersed in an oil bath. As far as possible, the samples investigated (experiments 1–7, Table 1) consisted of crystals of similar dimensions to control for the potential dependence of isomerisation reaction rate on particle size.¹⁶ As anticipated, observations were found to be consistent across all crystals in a particular sample (Fig. 2).

With reference to Table 1, the thermal solid-state isomerisation reaction of *ttt*-RuCl₂(Bu^tNC)₂(PPh₃)₂ is characterised by the following points:

(i) Under the microscope, crystal darkening from yellow to black indicated an isomerisation reaction. This is confirmed by experiments 1–4: darkening at 179–180 °C agrees with previous DSC data^{6,7} that reveals isomerisation (exothermic peak) between 184 and 231 °C. The only other DSC event (an endothermic peak) relates to melting of the product isomer at 250 °C. Furthermore, NMR analysis of partially darkened crystals (experiments 1 and 7) indicated the presence of both reactant (*ttt*) and product (*cct*) isomers (no other species detected).

(ii) The isomerisation reaction takes place without any crystal cracking or other serious deterioration of crystal

Table 1 Heating experiments of *ttt*-RuCl₂(Bu^tNC)₂(PPh₃)₂ single crystals

Exp. No.	Temperature/°C	Duration	Observations
1 ^a	162 ^c	10 min	At 146 °C the initially yellow crystals started to darken (blacken) rapidly. At 149–150 °C significant crystal melting occurred. At 152–154 °C crystal morphology degraded due to melting. At 160–161 °C crystals completely melted.
	followed by decline to 150	0.15 °C min ^{−1}	Molten material solidified to form a yellow globule, in each case. No recrystallisation took place.
	followed by decline to room temp.	10 °C min ^{−1}	Globules unchanged.
2 ^b	145 ^c	2–3 min	Globules extinguished plane-polarised light uniformly. XRD ^d : globules amorphous (no diffraction pattern).
3 ^a	140 ^c	1 h	At 144–145 °C crystals started to melt, and darken somewhat. At expt. end: partial distortion of crystal morphology due to melting. XRD ^d : microcrystalline powder rings.
4 ^a	140 ^c	30 min	Crystals started to darken slowly. During expt., no melting noticed. At expt. end: crystals had a few darkened surface regions. Crystal morphology unchanged. XRD ^d : Crystal structure of <i>ttt</i> -isomer (starting material) solved.
5 ^a	130 ^c	1 hr	Some of the crystals from expt. 3 heated further. Slight melting preceded complete crystal darkening. At expt. end: crystals totally darkened. Crystal morphology essentially unchanged. XRD ^d : microcrystalline powder rings.
			NMR ^e : <i>cct</i> -isomer only.
			Remainder of the crystals from expt. 3 heated at lower temperature. During expt., no melting noticed. At expt. end: crystals almost completely darkened. Crystal morphology unchanged.
			XRD ^d : microcrystalline powder rings.
			NMR ^e : <i>cct</i> -isomer only.

^a Heating plate cell used. ^b Heated gas stream cell used. ^c Heating rate to experimental temperature: 2.5 °C min^{−1}. ^d XRD behaviour of selected crystals (or globules in expt. 1) tested on single-crystal diffractometer. ^e Combined sample of crystals from expt. 4 and 5. Minimum of 3–4 crystals dissolved in CDCl₃, 400 MHz spectrometer, *cct*-isomer identified from ³¹P NMR resonance (refs 6,13).

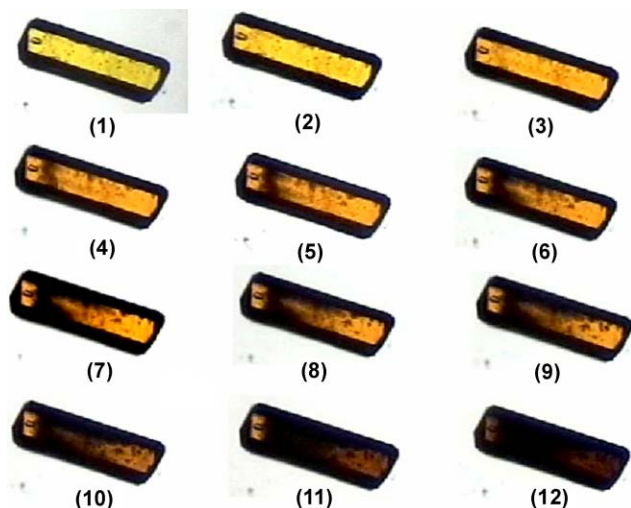


Fig. 2 Isomerisation of $ttt\text{-RuCl}_2(\text{Bu}^t\text{NC})_2(\text{PPh}_3)_2$ at 180°C (1: no heating; 2,3: at $165\text{--}170^\circ\text{C}$ at 5 min intervals; 4–12: at 180°C at 5 min intervals; 12: after 60 min)

morphology (experiments 1–7). However, internal crystallinity is not retained (see below), with progressive lattice disruption occurring as the reaction proceeds, as indicated by single-crystal XRD analysis.

(iii) Following an induction period (see below), the isomerisation reaction initially proceeds quickly (acceleratory stage), then far more slowly (deceleratory stage). This is confirmed by experiments 1–4. For example, after 4–5 min reaction at the isomerisation temperature (180°C), NMR analysis indicated approximately 35% isomer conversion (experiment 1). However, after 11 h reaction at this temperature, there is only *ca.* 44% isomer conversion (experiment 2). Crystals were also observed to darken rapidly, then gradually, at the isomerisation temperature.

(iv) The isomerisation reaction (experiments 5–7) also occurs $20\text{--}30^\circ\text{C}$ below the isomerisation temperature ($179\text{--}180^\circ\text{C}$) described above. However, the reaction takes place much more slowly, confirming the dependence of the process on thermal activation. For example, heating at 155°C for 4 h (experiment 7) resulted in almost the same level of isomer conversion as heating at 180°C for 4–5 min (experiment 1), *i.e.* 33% *versus* 35% conversion, respectively.

(v) In some instances (experiments 4 and 6), the yellow *ttt*-isomer crystals turned darker in colour (to light orange), before significant darkening (black) occurred. The yellow–orange colour change appears to signify the onset of an initial isomerisation reaction, as small (grey) nucleation sites subsequently start to form (see below). In addition, this colour change is observed to be predominantly a surface phenomenon, and is thus associated with surface-initiated reaction. Indeed, it is possible that the yellow–orange colour change indicates transition to a high-temperature intermediate phase (beginning at the crystal surface).

Optical micrographs of the solid-state isomerisation of $ttt\text{-RuCl}_2(\text{Bu}^t\text{NC})_2(\text{PPh}_3)_2$ are shown in Fig. 2. A largely surface-initiated, heterogeneous reaction is possible. Small nucleation sites are observed to randomly appear on the surface of the crystal, becoming larger as the reaction proceeds. This is a classical process well described in the literature.^{17,18} However, the nucleation sites grow anisotropically. Significant isomerisation (darkening) is initially localised (pictures 4 and 5), followed by anisotropic interface advance (mainly along crystal edges, pictures 6–9) that combines with nucleation sites that have hitherto experienced only limited growth. Eventually, the entire crystal surface turns dark under the microscope (pictures 10–12). The yellow to light orange colour change mentioned previously is seen in pictures 2 and 3.

While the above explanation assumes a surface initiated reaction the possibility of the reaction being initiated in the bulk and creating the observed anisotropic surface features cannot be discounted.

The figures show that the solid-state isomerisation of $ttt\text{-RuCl}_2(\text{Bu}^t\text{NC})_2(\text{PPh}_3)_2$ does not lead to disintegration, fracturing or degradation at crystal surfaces or edges.

Although crystal morphology remains largely unchanged, the solid-state isomerisation reaction of $ttt\text{-RuCl}_2(\text{Bu}^t\text{NC})_2(\text{PPh}_3)_2$ is not a single-crystal to single-crystal transformation. Destruction of the crystal lattice is observed as the reaction proceeds. X-ray rotation photos indicative of this process are shown in Fig. 3. Frame 1 shows the well-defined layer lines of an unreacted (*ttt*-isomer) crystal, while change in the diffraction pattern after 5 min reaction at 180°C is indicated by frame 2. Reflections begin to follow the paths of rings about the diffraction centre. The isomerisation reaction appears to degrade the single crystal to a polycrystalline solid (frame 3), before ultimately continuing to a microcrystalline powder (frame 4: after more than 45 min reaction). This breakdown of internal 3-D order precludes detailed evaluation of the reaction mechanism, as single-crystal structures at intermediate and final stages of reaction are consequently not available. Solid-state reactions are known to commonly result in a loss of crystallinity.¹⁹

The results shown in Table 1 indicate that even with up to 33–35% isomer conversion (experiments 1 and 7), crystallinity is still sufficiently preserved to yield a structural solution of the *ttt*-isomer. The *ttt*-isomer structures of crystals that reacted under different conditions (experiments 1, 5 and 7) were found not to be significantly different from the unreacted *ttt*-isomer structure (*viz.* lattice parameters, molecular geometry, *etc.*). However, between 35 and 44% isomer conversion (experiments 1 and 2), X-ray structure determination no longer becomes possible due to the substantial deterioration in internal crystal quality. The isomerisation reaction therefore takes place inhomogeneously, with lattice-degraded (*i.e.* reacted) regions growing at the expense of crystalline (*i.e.* unreacted *ttt*-isomer) regions. This is consistent with the optical micrograph results discussed above. As the solid-state isomerisation of $ttt\text{-RuCl}_2(\text{Bu}^t\text{NC})_2(\text{PPh}_3)_2$ is a unidirectional reaction proceeding

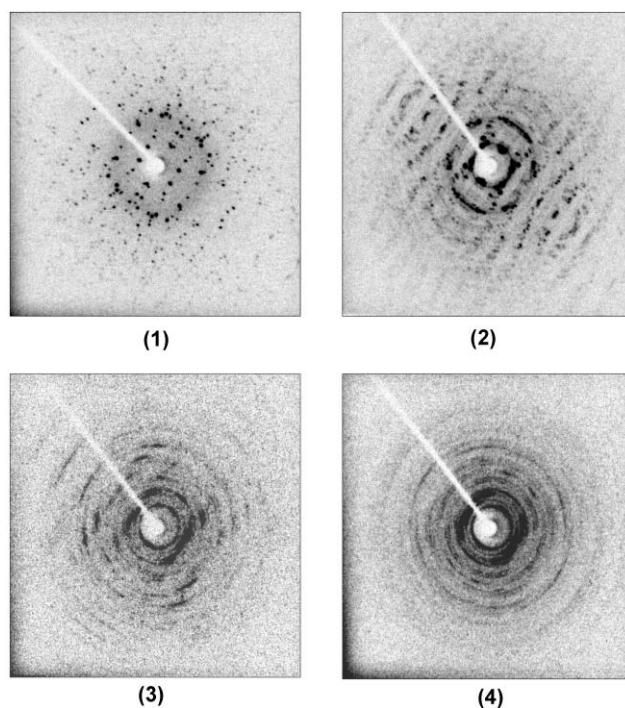


Fig. 3 Progressive loss of crystallinity due to the isomerisation of $ttt\text{-RuCl}_2(\text{Bu}^t\text{NC})_2(\text{PPh}_3)_2$ (1–4: described in text).

to completion,⁷ it is expected that, nearer to complete isomer conversion, external crystal form would also eventually be reduced to microcrystalline powder.

Previous work⁶ with powdered samples of *ttt*-RuCl₂-(Bu¹NC)₂(PPh₃)₂ has shown over 90% isomer conversion to occur after a 12 h reaction, at a temperature close to 180 °C. This information was taken into account when crystal samples of *ttt*-RuCl₂(Bu¹NC)₂(PPh₃)₂ were heated for long time intervals, in order to reach high isomer conversion levels (experiment 2: 11 h reaction at 180 °C; experiment 3: 30 h reaction at 180 °C; Table 1). However, results from these experiments (only 44% product isomer in experiment 2; crystal morphology not reduced to microcrystalline powder in experiments 2 and 3) indicate that high isomer conversion levels are reached more slowly in the crystalline state.

Heating of *ttt*-RuCl₂(2,6-XylNC)₂(PPh₃)₂ crystals. An extensive high-temperature study of crystals of *ttt*-RuCl₂(2,6-XylNC)₂(PPh₃)₂ was not pursued. A preliminary microscopy investigation (190 °C, 30 min) revealed that crystals also underwent a slow surface darkening with time. Darkening took place anisotropically as described above. At the end of the experiment, crystals had unreacted (pale-yellow) and reacted (blackened) regions. Crystal morphology was unchanged. Faint microcrystalline powder rings were detected when selected crystals were tested on the single-crystal diffractometer. It is believed that the above-mentioned crystal darkening indicates solid-state isomerisation reaction of *ttt*-RuCl₂(2,6-XylNC)₂(PPh₃)₂, as previous DSC data^{6,7} reveal isomerisation (exothermic peak) between 204 and 244 °C. The observations suggest that the isomerisation reactions of *ttt*-RuCl₂(2,6-XylNC)₂(PPh₃)₂ and *ttt*-RuCl₂(*t*-BuNC)₂(PPh₃)₂ show similar crystal effects on heating.

Heating of *ttt*-RuCl₂(PhCH₂NC)₂(PPh₃)₂ crystals. Crystals of *ttt*-RuCl₂(PhCH₂NC)₂(PPh₃)₂ that were found to contain dichloromethane solvent of crystallisation¹⁴ were studied for

comparison purposes. While stable under ambient temperature and atmosphere conditions, the crystals rapidly deteriorated upon heating. Between 45 and 55 °C, extreme puckering of crystal faces was observed, followed by complete crystal disintegration. As this temperature interval is close to, but above, the boiling point of dichloromethane (40 °C²⁰), structural collapse was clearly due to the liberation of the lattice solvent. Coating some crystals with epoxy glue was observed to delay crystal degradation up to *ca.* 80 °C. Crystal efflorescence therefore prevented investigation of the solid-state isomerisation reaction of *ttt*-RuCl₂(BzlNC)₂(PPh₃)₂ by single crystal XRD analysis.

Heating of *ttt*-RuCl₂(CO)₂(PMePh₂)₂ crystals. Various high-temperature studies of *ttt*-RuCl₂(CO)₂(PMePh₂)₂ single crystals were undertaken and the results are given in Table 2. Two competing processes can take place when heat is supplied to these crystals. Either the heat breaks intermolecular bonds (melting), or the heat induces an intramolecular process (solid-state isomerisation reaction). This agrees with DSC data reported for *ttt*-RuCl₂(CO)₂(PMePh₂)₂^{4,6} that reveal a small endothermic peak (slight melting) between 150 and 155 °C, closely followed by an exothermic peak (isomerisation) near 161 °C.

In experiment 1 (Table 2), substantial *crystal melting* was observed from 149 °C onwards. This agrees with the above-mentioned DSC result for melting of the *ttt*-isomer (150–155 °C), but differs in that melting was observed to proceed to completion in the crystals, yielding a liquid phase. Interestingly, the initially pale-yellow crystals started to darken (blacken) under the microscope at 146 °C (indicative of the onset of isomerisation reaction), but were not totally darkened when melting began. It therefore appears that only limited (*i.e.* surface or bulk-initiated) isomerisation took place in the solid-state, before melting ensued. Furthermore, it is believed that the isomerisation reaction continued in the molten state (but not to completion). On gradual cooling of the molten samples

Table 2 Heating experiments of *ttt*-RuCl₂(CO)₂(PMePh₂)₂ single crystals

Exp. No.	Temperature/°C	Duration	Observations
1 ^a	180 ^d	4–5 min	At 179–180 °C crystals started to darken rapidly. At expt. end: crystals had clear (yellow) and dark (black) regions. Crystal morphology unchanged. XRD ^f : Crystal structure of <i>ttt</i> -isomer (starting material) solved. NMR ^g : 65% <i>ttt</i> -isomer, 35% <i>cct</i> -isomer.
2 ^b	180 ^e	11 h	At expt. end: crystals totally darkened. Crystal morphology unchanged. XRD ^f : microcrystalline powder rings. NMR ^g : 56% <i>ttt</i> -isomer, 44% <i>cct</i> -isomer.
3 ^b	180 ^e	30 h	At expt. end: crystals totally darkened. Crystal morphology unchanged. XRD ^f : microcrystalline powder rings.
4 ^a	180 ^d	48 min	At 165–170 °C the initially yellow crystals turned light orange in colour. At 180 °C crystals started to darken rapidly, then more slowly. At expt. end: crystals almost completely darkened. Crystal morphology unchanged. XRD ^f : microcrystalline powder rings.
5 ^a	165 ^d	1 h	At expt. end: crystals not darkened (remained yellow). Crystal morphology unchanged. XRD ^f : Crystal structure of <i>ttt</i> -isomer (starting material) solved.
6 ^c	165 ^d	5 h	At 155 °C the initially yellow crystals turned light orange in colour. At 160 °C crystals started to darken slowly. At expt. end: crystals totally darkened. Crystal morphology unchanged. XRD ^f : microcrystalline powder rings
7 ^c	155 ^d	4 h	After 20 min crystals started to darken slowly. At expt. end: crystals had clear (yellow) and dark (black) regions. Crystal morphology unchanged. XRD ^f : Faint powder rings detected. Crystal structure of <i>ttt</i> -isomer (starting material) solved. NMR ^g : 67% <i>ttt</i> -isomer, 33% <i>cct</i> -isomer.

^a Heating plate cell used. ^b Shortened NMR tube used, flushed with N₂ gas, immersed in oil bath. ^c Heated gas stream cell used. ^d Heating rate to experiment temperature: 2.5 °C min⁻¹. ^e Heating rate to experiment temperature: 10 °C min⁻¹. ^f XRD behaviour of selected crystals tested on single-crystal diffractometer. ^g Minimum of 3–4 crystals dissolved in CDCl₃, 400 MHz spectrometer, *ttt* and *cct*-isomer Me resonance (¹H NMR data, refs 6,13) compared.

no recrystallisation of (predominantly) *ttt*-isomer crystals, or crystallisation of product-isomer crystals was observed. Cooling resulted in the solidification of the molten samples, forming globules that showed no lattice structure (amorphous to X-rays), and therefore likely represented a solid-state mixture of both *ttt* and *cct*-isomers.

Subsequent experiments, at lower temperatures, were more successful in separating the two processes of isomerisation and melting. In experiment 2, only partial crystal melting took place at 144–145 °C, with some crystal darkening (isomerisation reaction) observed at this temperature as well. Apart from disruption due to melting, the lattice structure was also found to degrade in the isomerisation reaction, as crystals from this experiment were not amorphous to X-rays, and gave diffraction patterns indicating microcrystalline powder rings. In experiment 3 (140 °C, 1 h) no melting was noticed, however isomerisation reaction did occur slowly, as revealed by the partially darkened crystal surfaces. Crystal morphology remained unchanged. As a consequence of the predominantly surface isomerisation in this experiment (*i.e.*, low isomer conversion), crystallinity was still sufficiently preserved to yield a structural solution of the *ttt*-isomer. The *ttt*-isomer structure was found not to be significantly different from the unreacted *ttt*-isomer structure described above (*viz.* lattice parameters, molecular geometry, *etc.*). The crystals used in experiment 3 were heated further in experiments 4 (140 °C, 30 min) and 5 (130 °C, 1 h).

In experiment 4, only slight melting took place, while in experiment 5 (recorded at a lower temperature) no melting was observed. These experiments therefore provided further information on the solid-state isomerisation reaction of *ttt*-RuCl₂(CO)₂(PMePh₂)₂. NMR analysis of the completely darkened crystals from both experiments showed only the product (*cct*) isomer to be present (with no other species), thus confirming that crystal darkening was indeed indicative of an isomerisation reaction. Furthermore, although the isomerisation reaction did not cause any crystal cracking or other serious deterioration of crystal morphology, the reaction did result in progressive loss of crystallinity. X-ray rotation photos of the totally darkened crystals showed microcrystalline powder rings indicating significant lattice destruction near complete isomer conversion. The reaction was therefore found not to be a single-crystal to single-crystal transformation.

The experiments performed therefore establish that heating 20–30 °C below the reported DSC isomerisation temperature is sufficient to induce isomerisation in *ttt*-RuCl₂(CO)₂(PMePh₂)₂ crystals, *without apparent melting*. Furthermore, the solid-state isomerisation reaction of *ttt*-RuCl₂(CO)₂(PMePh₂)₂ takes place in a heterogeneous manner, as detected by the inhomogeneous surface darkening of crystals. The results shown in Table 2, as well as the findings discussed above, confirm the characteristically similar solid-state reaction behaviour of the complexes studied.

3.2 Powder diffraction studies of the solid-state isomerisation reaction of *ttt*-RuCl₂(Bu^tNC)₂(PPh₃)₂

Diffraction patterns for RuCl₂(Bu^tNC)₂(PPh₃)₂ are shown in Fig. 4. Fig. 4A 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 Fig. 4B. Isomer conversion was confirmed by NMR analysis. It is seen that the two isomers have distinctive XRD patterns.

The *cct*-isomer was also recrystallised from dichloromethane solution and the powder pattern recorded (Fig. 4C). The patterns of the two *cct*-samples are quite different, 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

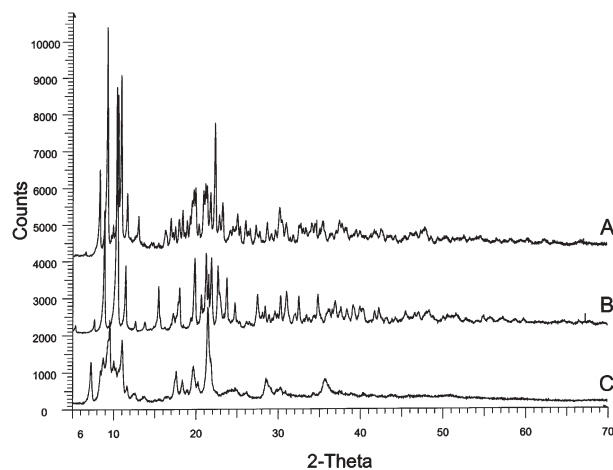


Fig. 4 Characterisation powder diffraction patterns of RuCl₂(Bu^tNC)₂(PPh₃)₂. (A) *ttt*-isomer, (B) *cct*-isomer (after complete solid-state conversion from the *ttt*-isomer), (C) *cct*-isomer (after recrystallisation from dichloromethane solution).

of the nitrito isomers of a series of six coordinate cobalt complexes.²¹

Kinetic studies of the solid-state isomerisation reaction of RuCl₂(Bu^tNC)₂(PPh₃)₂ were performed at three different temperatures (175, 180 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. The decrease in intensity as a function of time of the *ttt*-isomer reflection at (2θ) 9.1–9.5° (Fig. 5) 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:

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

where $I_{(ttt)}$ is the intensity of the *ttt*-isomer at time *t*, and $I_{0(tt)}$ 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 (Fig. 6), with the corresponding plots of $\ln \alpha$ versus *t* yielding straight lines as expected (Fig. 7). From the $\ln \alpha$ versus *t* plots, the following rate constants for the

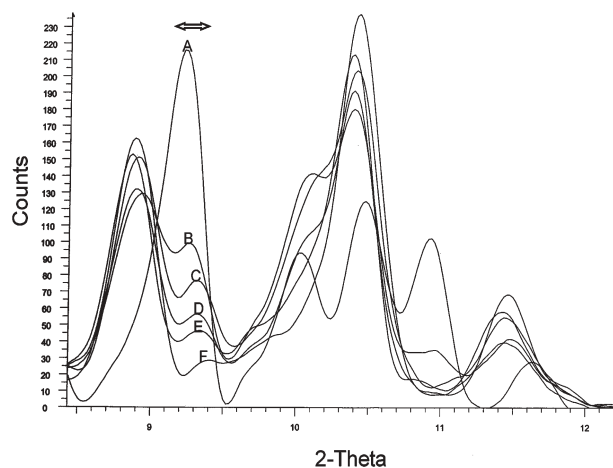


Fig. 5 Change in the powder pattern of RuCl₂(Bu^tNC)₂(PPh₃)₂ during solid-state isomerisation reaction at 185 °C; the diminishing *ttt*-isomer reflection indicated was monitored (A–F: Lindemann tube samples after 0, 35, 70, 105, 140, 1080 min reaction, respectively).

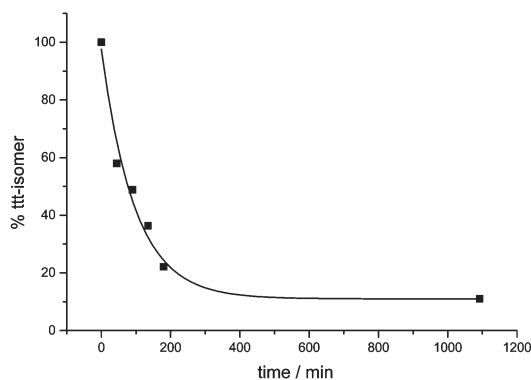


Fig. 6 Typical α versus time curve for the solid-state isomerisation of $\text{RuCl}_2(\text{Bu}^1\text{NC})_2(\text{PPh}_3)_2$ (175 °C).

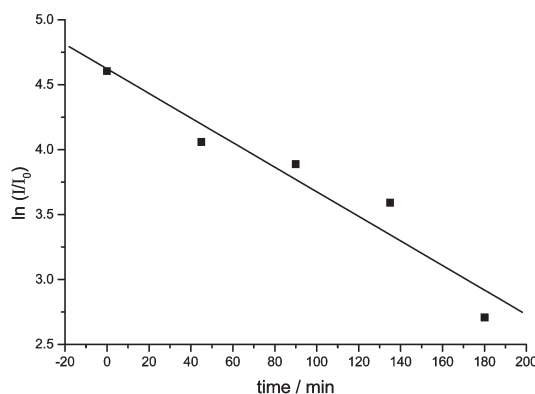


Fig. 7 Typical $\ln \alpha$ versus time plot for the solid-state isomerisation of $\text{RuCl}_2(\text{Bu}^1\text{NC})_2(\text{PPh}_3)_2$ (175 °C).

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 $\ln k$ versus $1/T$ plot (Fig. 8) was found to be $219 (\pm 26) \text{ kJ mol}^{-1}$.

Previous kinetic studies of the solid-state isomerisation of $\text{RuCl}_2(\text{Bu}^1\text{NC})_2(\text{PPh}_3)_2$ followed the reaction by heating powdered samples for periods of time, then dissolving the material and evaluating the extent of reaction by ^1H NMR spectroscopy. These studies revealed an activation energy of 210 kJ mol^{-1} for the process.⁶ Thus, the favourable agreement between results suggests the powder diffraction method used in

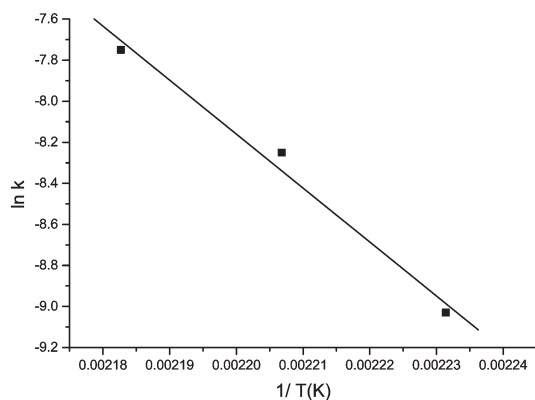


Fig. 8 Arrhenius plot for the solid-state isomerisation of $\text{RuCl}_2(\text{Bu}^1\text{NC})_2(\text{PPh}_3)_2$.

this work to be a suitable method for further high-temperature, solid-state kinetic analysis.

4. Conclusions

The data above suggest that solid state isomerisation reactions of six coordinate materials of the type $\text{Ru}(\text{Cl})_2\text{L}_2\text{L}'_2$ readily occur in the solid state and can be monitored by classical techniques. Careful analysis of the complexes reveals that the reaction does not occur in the melt but that crystallinity is lost due to molecule–molecule rearrangements in the solid as the reaction proceeds. This suggests gross atom movements in the process, consistent with a phase rebuilding mechanism, as described by Kaupp and co-workers.^{1,2} Unfortunately, at this stage, details of the isomerisation reaction at the atomic level are not available. The high activation energies are, however, consistent with mechanisms proposed for the isomerisation reaction in the solvent phase.²²

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