Thermal solid-state diag–lat isomerisation studies of $(\eta^5\text{-}C_5H_4R)Re(CO)(L)Br_2$: DSC and thermomicroscopy studies

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Abstract

The thermal solid-state *diag–lat* isomerisation of $(\eta^5\text{-}C_5H_4R)Re(CO)(L)Br_2$ (R=Me, *t*Bu and SiMe$_3$; L=CO, CNC$_6$H$_3$Me$_2$, P(OMe)$_3$ and P(OPh)$_3$) has been studied by DSC, and thermomicroscopy. In all instances, where isomerisation of $(\eta^5\text{-}C_5H_4R)Re(CO)(L)Br_2$ (**1**) was observed, the diagonal (*trans*) isomer converted to the lateral (*cis*) isomer in an exothermic reaction. The effects of heating rate and crystal size on the isomerisation reaction involving (**1**) (R=Me, L=CO) has been studied. Microscopic studies on **1**, (R=Me, L=CO and P(OPh)$_3$; R=*t*Bu, L=CNC$_6$H$_3$Me$_2$) showed that the solid-state isomerisation reactions proceeded via a nuclear formation and growth mechanism.. Interestingly, no crystal cracking was observed when (**1**) (R=Me, L=P(OPh)$_3$) underwent a thermal solid-state isomerisation reaction. © 1998 Elsevier Science B.V.

Keywords: DSC; Microscopy; Isomerisation; Rhenium complexes; Cyclopentadienyl

1. Introduction

Thermal solid-state reactions of coordination compounds have been under investigation since the original syntheses of these types of complexes over 100 years ago. A sub-class of these reactions are the solid-state isomerisation reactions which include the metal coordinated NO$_2$–ONO linkage isomerisation reaction, a reaction still under investigation today [1]. Solid-state *cis–trans* isomerisation reactions of classical coordination complexes have also been extensively studied since the early part of this century [2].

By contrast, solid-state isomerisation reactions involving organometallic complexes [3,4], and even solid-state organometallic reactions in general [5–9], have been studied very little until recently.

A few years ago we discovered that the complex $(\eta^5\text{-}C_5H_4Me)Re(CO)_2Br_2$ underwent *trans–cis (diag–lat)* isomerisation in the solid state [10] (Fig. 1). The solid-state isomerisation reaction appeared to be limited to this specific complex, as isomerisation was not observed for the related complexes in which the methyl ring substituent was replaced by ethyl, *t*-butyl or trimethylsilyl groups [10]. In a recent study we have reported the synthesis of a range of CO substituted derivatives of the type $(\eta^5\text{-}C_5H_4R)Re(CO)(L)X_2$ (R=Me, *t*Bu and SiMe$_3$; L=isocyanides, phosphites

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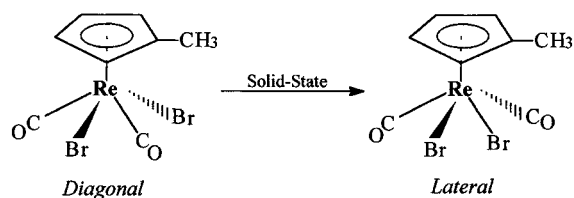
Fig. 1. Solid-state *diag*-to-*lat* isomerisation of $(\eta^5\text{-}C_5H_4Me)Re\text{-}(CO)_2Br_2$.

and PPh_3; X= Br and I) [11]. The new complexes have been prepared via solution reactions and in every instance the diagonal isomer of $(\eta^5\text{-}C_5H_4R)Re\text{-}(CO)(L)X_2$ has been prepared in high yield. More importantly, preliminary studies showed that the new complexes all isomerised into the corresponding lateral isomers when heated in the solid-state [11]. In this publication, we wish to report our DSC and thermomicroscopy results on these new thermal solid-state organometallic isomerisation reactions.

2. Experimental

The diagonal and lateral $(\eta^5\text{-}C_5H_4R)Re(CO)(L)Br_2$ (R=Me, *t*Bu and $SiMe_3$; L=CO, $CNC_6H_3Me_2$ and $P(OMe)_3$, $P(OPh)_3$) complexes were synthesized by the literature methods [10,11]. Pertinent data for the new complexes are shown in Table 1. Differential scanning calorimetry (DSC) was performed on 5–10 mg micro-crystal samples under flowing nitrogen

on a Du Pont 910 DSC instrument. Data were recorded at a heating rate of 2.0°C/min (unless otherwise stated). Micrographs were obtained on single crystal samples from a standard Zeiss microscope fitted with a MC 63 photomicrographic camera (64×magnification) at room temperature. Samples were also isomerised by heating single crystal samples of *diag*-$(\eta^5\text{-}C_5H_4R)Re(CO)(L)Br_2$ in a flat-bottom flask in an oil bath under nitrogen for different periods of time. The crystals were monitored under the microscope (after cooling the samples to room temperature) during the course of the reaction and photographs were taken after appropriate time intervals until the isomerisation processes was complete.

3. Results and discussion

3.1. DSC

DSC measurements on *diag*-$(\eta^5\text{-}C_5H_4Me)Re\text{-}(CO)_2Br_2$ were carried out at different heating rates (1.0, 2.0, 5.0, 10.0 and 20.0°C/min) and the data are shown in Fig. 2. Two peaks were observed in the spectra at all the heating rates. The higher temperature peak, an endotherm (≈170°C), corresponds to the melting point of the lateral isomer product. It had variable shape and this was found to relate to the crystallinity of the material (see below).

The lower temperature peak corresponded to both the melting point of the diagonal isomer and the

Table 1
Properties of *diag*- and *lat*-$(\eta^5\text{-}C_5H_4R)Re(CO)(L)Br_2$

Complex	Colour	m.p. (°C)	Expt.[a]
$(\eta^5\text{-}C_5H_4Me)Re(CO)_2Br_2$	*diag*: maroon	*diag*: 116–118	D/T
	lat: brown	*lat*: 158–160	
$(\eta^5\text{-}C_5H_4Me)Re(CO)(CNC_6H_3Me_2)Br_2$	*diag*: yellow-red	*diag*: 154–156	D/T
	lat: brown	*lat*: 192–194	
$(\eta^5\text{-}C_5H_4Me)Re(CO)[P(OPh)_3]Br_2$	*diag*: red	*diag*: 164–169	D/T
	lat: brown	*lat*: 183–185	
$(\eta^5\text{-}C_5H_4tBu)Re(CO)[P(OMe)_3]Br_2$	*diag*: red	*diag*: 123–125	D
	lat: brown	*lat*: 154–156	
$(\eta^5\text{-}C_5H_4tBu)Re(CO)(CNC_6H_3Me_2)Br_2$	*diag*: yellow-red	*diag*: 142–144	D
	lat: brown	*lat*: 194–196	
$(\eta^5\text{-}C_5H_4SiMe_3)Re(CO)(CNC_6H_3Me_2)Br_2$	*diag*: yellow-red	*diag*: 144–146	D
	lat: brown	*diag*: 179–181	

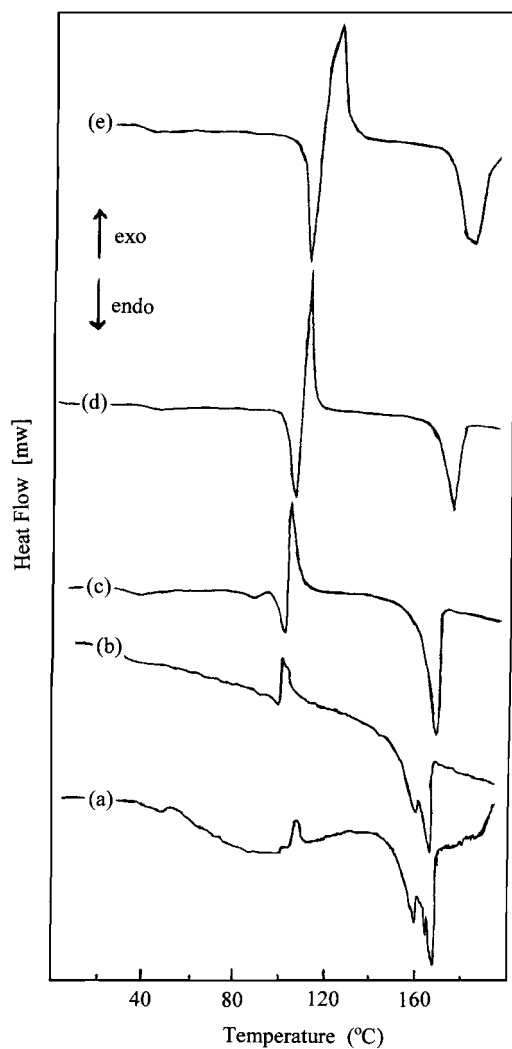[a] D: DSC measurements; T: thermomicroscopic studies.

Fig. 2. DSC curves for *diag*-(η^5-C_5H_4Me)Re(CO)$_2$Br$_2$ at different heating rates. (a) 1.0, $\Delta H_i = -3$ kJ/mole, (b) 2.0, (c) 5.0, (d) 10.0 and (e) 20.0 °C/min.

Fig. 3. DSC curves for *diag*-(η^5-C_5H_4Me)Re(CO)$_2$Br$_2$. (a) large crystals, $\Delta H_i = -4.6$ kJ/mole, (b) microcrystals, $\Delta H_i = -10.0$ kJ/mole and (c) fine powder, $\Delta H_i = -3.7$ kJ/mole.

exothermic reaction associated with the *diag–lat* reaction. This peak at ≈ 115°C showed variable intensity and shape as the heating rate was varied. At the lowest heating rate shown (Fig. 2(a)) only an exotherm is noted. This corresponds to the diagonal to lateral isomerisation reaction of the complex (see below). As the heating rate was increased (Fig. 2(b)–(e))) this peak became larger and revealed exothermic behaviour. Indeed, observation of the crystalline material under a microscope at high heating rates indicated
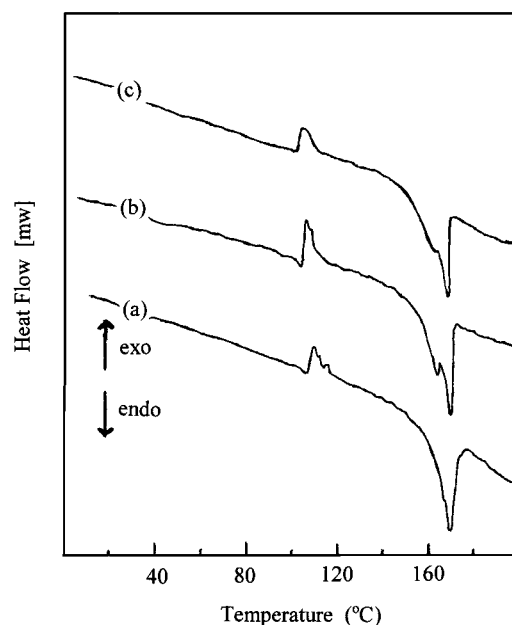
melting to give a liquid phase followed by solidification. In this instance the isomerisation reaction occurred in the molten state. It is thus apparent that when heat is supplied to crystals of (η^5-C_5H_4Me)Re(CO)$_2$Br$_2$, two competing processes can take place. Either the heat can break the intermolecular bonds (melting results) or the heat supplied can be used to induce an intramolecular process (the isomerisation reaction). The lower energy process is the isomerisation reaction.

A DSC study was also carried out on different size crystals of (η^5-C_5H_4Me)Re(CO)$_2$Br$_2$ to assess the effect of this variable on the DSC spectrum (Fig. 3). The three samples, large crystals ($\approx 3 \times 2$ mm), small crystals ($\approx 1 \times 0.1$ mm) and fine powder all gave similar spectra. However, some significant differences were observed.

More complex features are observed for the lower temperature exotherm for the large crystals. This suggests that the isomerisation reaction does not occur in a homogeneous manner but rather heterogeneously, e.g., at defects, and then spreads through the crystal framework. This would not necessarily be detected in smaller crystals.
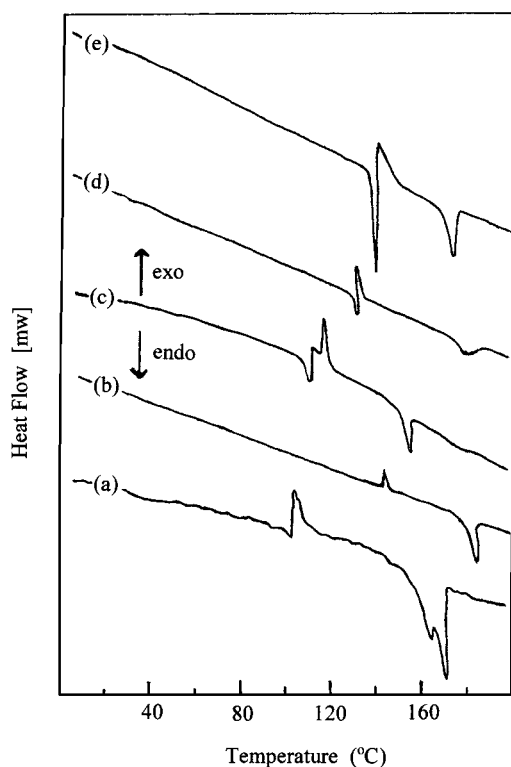
Fig. 4. DSC curves of (a) *diag*-(η^5-C$_5$H$_4$Me)Re(CO)$_2$Br$_2$, (b) *diag*-(η^5-C$_5$H$_4$Me)Re(CO)(CNC$_6$H$_3$Me$_2$)Br$_2$, ΔH_i=−3.5 kJ/mole, (c) *diag*-(η^5-C$_5$H$_4$*t*Bu)Re(CO)[P(OMe)$_3$]Br$_2$, (d) *diag*-(η^5-C$_5$H$_4$*t*Bu)Re(CO)(CNC$_6$H$_3$Me$_2$)Br$_2$ and (e) *diag*-(η^5-C$_5$H$_4$SiMe$_3$)Re(CO)(CNC$_6$H$_3$Me$_2$)Br$_2$.

The higher temperature (endothermic) peak also reveals a 'doublet' peak which is most clearly observed in Fig. 3(b). This relates to the crystallinity of the product and will be discussed further below.

The DSC curves of four typical complexes, *diag*-(η^5-C$_5$H$_4$Me)Re(CO)(CNC$_6$H$_3$Me$_2$)Br$_2$, *diag*-(η^5-C$_5$H$_4$*t*Bu)Re(CO)[P(OMe)$_3$]Br$_2$, *diag*-(η^5-C$_5$H$_4$*t*Bu)-Re(CO)(CNC$_6$H$_3$Me$_2$)Br$_2$ and *diag*-(η^5-C$_5$H$_4$SiMe$_3$)-Re(CO)(CNC$_6$H$_3$Me$_2$)Br$_2$, as well as *diag*-(η^5-C$_5$H$_4$Me)Re(CO)$_2$Br$_2$, are shown in Fig. 4. All data were measured at a heating rate 2.0°C/min. In all cases, an exotherm and an endotherm were observed.

It is apparent that the same phenomena occurs for all the complexes. Thus, the low temperature exotherm/endotherm peak corresponds to the processes of melting and isomerisation while the high temperature peak corresponds to the melting point of the lateral isomer. It is clear that the heating rate

chosen determines the degree to which the two processes can be separated. Heating of the diagonal isomers at about 20°C below the melting point of the isomer has been found to be sufficient to induce the isomerisation reaction to occur in the solid state without apparent liquid formation.

In all instances IR and NMR spectra were recorded on the materials both before and after the heating process. Spectra were also recorded on samples which had only been heated to a temperature beyond the first absorption in the DSC spectrum (i.e., prior to reaching the second thermal process). This data confirmed the composition of the materials [10,11]. DSC spectra were also recorded on pure lateral isomers to confirm the position of the melting points assigned above.

The above data suggest that the thermodynamic product in the isomerisation reaction is the isomer with the highest melting point. Clearly this 'thermodynamic product' is different from that found in the solution state [10]. As no gas phase data are available on the respective isomers it is not clear what the thermodynamic product will be in the absence of the nearest neighbours (solvent, melt and crystal environment).

An attempt was made to determine the reversibility of the isomerisation reaction in the solid-state by heating (η^5-C$_5$H$_4$Me)Re(CO)$_2$Br$_2$ slowly to 125°C and then cooling the sample to 70°C. No absorption peak was noted in the cooling process, or in the subsequent re-heating process through this temperature range. It is thus clear that the isomerisation reaction is irreversible in the solid state.

DSC spectra were also recorded on samples (e.g. (η^5-C$_5$H$_4$*t*Bu)Re(CO)$_2$Br$_2$ and (η^5-C$_5$H$_4$SiMe$_3$)Re-(CO)$_2$Br$_2$) which did not undergo isomerisation in the solid-state. In these samples only endotherms corresponding to the respective melting points were detected for both the lateral and diagonal isomers.

The isomerisation enthalpy change, ΔH_i, measured from the DSC spectra, (<5 kJ/mole) was generally lower than the values reported for *cis–trans* isomerisation reactions of square planar complexes which are usually in the range of 5–50 kJ/mole [3,4]. Further, molecular mechanics calculations carried out on (**1**) (R= Me, L=CO) indicate a very small difference in the crystal energies between the diagonal and lateral isomers. It is hence noted that the *diag–lat* isomerisation reactions of cyclopentadineyl four-legged piano
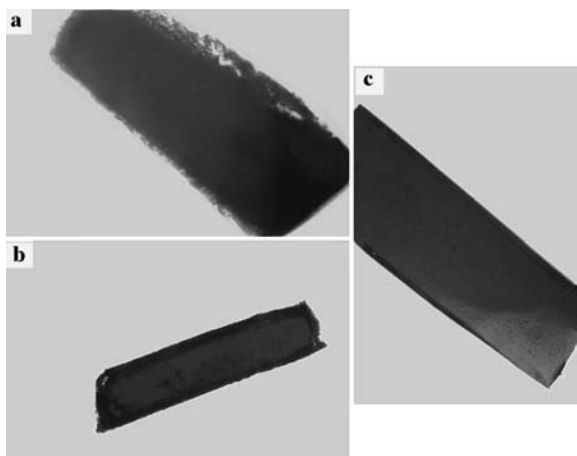
Fig. 5. Micrographs of (a) *diag*-(η^5-C_5H_4Me)Re(CO)$_2$Br$_2$, (b) *diag*-(η^5-C_5H_4Me)Re(CO)(CNC$_6$H$_3$Me$_2$)Br$_2$ and (c) *diag*-(η^5-C_5H_4Me)Re(CO)[P(OPh)$_3$]Br$_2$. The pictures were taken after near complete thermal isomerisation of the reactant.

stool transition metal complexes is a low energy processes.

3.2. Thermomicroscopy studies

The thermal solid-state isomerisation reactions of *diag*-(η^5-C_5H_4Me)Re(CO)$_2$Br$_2$, *diag*-(η^5-C_5H_4Me)-Re(CO)(CNC$_6$H$_3$Me$_2$)Br$_2$ and *diag*-(η^5-C_5H_4Me)-Re(CO)[(P(OPh)$_3$]Br$_2$ have been studied by thermomicroscopy. Pictures indicating the changes that occurred towards the end of the heating process are shown in Fig. 5.

3.2.1. *Diag*-(η^5-C_5H_4Me)Re(Co)$_2$Br$_2$ (Fig. 5(a))

It can be seen that the isomerisation reaction started at the crystal edge and/or at surface imperfections in the single crystal and then moved isotropically through the entire crystal. This process is easy to monitor as the two different isomers have different colours (*diag*: red, *lat*: brown). The interface advance was accompanied by cracking. At the end of the reaction small micro-crystals could be observed at the edges of the dominant crystal. Indeed it is thought that this behaviour is responsible for the complex pattern noted for the endotherm shown in Fig. 2((a)-(b)). Because the material consists of crystals of two (dominant) different sizes a broadened 'doublet' melting point was observed.

3.2.2. *Diag*-(η^5-C_5H_4Me)Re(Co)(CnC$_6$H$_3$Me$_2$)Br$_2$ (Fig. 5(b))

Similar observations as observed for *diag*-(η^5-C_5H_4Me)Re(CO)$_2$Br$_2$ (Fig. 5(a)) were noted. The brown isomerisation product was first formed at the edges and at surface defects of the red starting crystals. When the reaction was complete the whole crystal had changed into a dark brown cracked crystal.

3.2.3. *Diag*-(η^5-C_5H_4Me)Re(CO)[P(OPh)$_3$]Br$_2$ (Fig. 5(c))

The crystal of this isomer did not disintegrate on heating but the crystal did change colour during the heating process. The colour change occurred at small nucleation points on the surface of the crystal and these nucleation sites became larger as the reaction progressed. This is a classical process well described in the literature [12,13].

3.3. Mechanism

A consideration of the specific complexes investigated reveals the following

The electronic or steric effects associated with the cyclopentadienyl ligand of individual molecules do not correlate with the isomerisation reaction. Thus, changing the methyl substituent for a *t*-butyl substituent in (**1**) yields complexes that undergo isomerisation (L=CNC$_6$H$_3$Me$_2$) and do not undergo isomerisation (L=CO) in the solid state.

It appears that, to date, all complexes that contain a bulky ligand do undergo the isomerisation reaction. It may be that these groups both provide more 'space' [7] in the crystal and possibly a pivot (see below) for the isomerisation reaction to occur.

The exothermic reaction always proceeds from the isomer of the lowest melting point, suggesting that the reaction is controlled by thermodynamic factors.

As mentioned above, during the isomerisation reaction, crystal disintegration generally was observed to occur. This implies that volume or phase changes (or both) are occurring in the process. If one assumes that the isomerisation reaction occurs and is *then* followed by the phase change, two current, competing, theories are available to interpret the results of the above study: the topochemical principle [14,15] and the phase

rebuilding principle [16,17]. The possibility that a phase change *drives* the isomerisation reaction can however, not be ruled out [18] and further studies will be needed to resolve this issue.

In a previous publication we suggested that the *diag–lat* isomerisation reaction of $(\eta^5$-$C_5H_4Me)Re(CO)_2Br_2$ occurred via a Berry–Turnstile combined mechanism. This proposal was based on a structure correlation analysis [19]. In this process two of the ligands act as pivots for the turnstile process. The studies described above are consistent with the proposal and would suggest that both the large cyclopentadienyl ligand and the L group are the pivots. However, more information will be needed before further proposals can be made to determine more specifically the mechanism of the above reaction.

Notwithstanding the above, this study provides the first investigation of the thermal solid-state isomerisation behaviour of classical organometallic complexes. The synthetic strategies to produce complexes of the type described above are trivial and thus a convenient series of organometallic complexes are now available for further study.

4. Conclusions

The thermal solid-state *diag–lat* isomerisation reactions of cyclopentadienyl four-legged piano stool rhenium complexes *diag*-$(\eta^5$-$C_5H_4R)Re(CO)(L)Br_2$ (R=Me, *t*Bu and SiMe$_3$; L=CO, CNC$_6$H$_3$Me$_2$ P(OMe)$_3$ and P(OPh)$_3$) have been studied by DSC and thermomicroscopy investigations. In all the reactions investigated the diagonal isomers convert to the lateral isomers via an exothermic reaction. The thermomicroscopy reactions suggest that the isomerisation reaction occurs via a nuclear formation and growth mechanism, similar to what has been observed for related compounds in other areas of chemistry.

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