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INVESTIGATION OF THE SOLVENT FREE ISOMERISATION OF *cis*-$Mo(CO)_4L_2$ [L = PPh_2Et, PPh_3, PPh_2Me, AND $P(m\text{-tolyl})_3$] BY DIFFUSE REFLECTANCE INFRARED FOURIER TRANSFORM SPECTROSCOPY AND THERMAL METHODS

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ABSTRACT. Thermal analysis of *cis*-$Mo(CO)_4L_2$ [L = PPh_2Et, PPh_3, PPh_2Me and $P(m\text{-tolyl})_3$] revealed that they undergo *cis* to *trans* isomerisation under solventless conditions. For L = PPh_3 and $P(m\text{-tolyl})_3$, the reaction occurred in the solid state. For L = PPh_2Et and PPh_2Me the reaction occurred in the melt and was followed by *trans* isomer solidification. The rate of the solid state isomerisation of *cis*-$Mo(CO)_4(PPh_3)_2$ was investigated by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and the results showed that the reaction was first order. A thermomicroscopic investigation of *cis*-$Mo(CO)_4[P(m\text{-tolyl})_3]_2$ revealed that the isomerisation was surface-initiated.

KEY WORDS: Solventless reactions, Molybdenum, Isomerisation, Thermal analysis

INTRODUCTION

Solventless reactions are becoming increasingly important and are promising to be an excellent synthetic tool in the emerging field of green chemistry [1], in the fields of organic [2] and coordination chemistry [3] as well as in the area of materials science [4]. However, few solventless reactions are known in the field of organometallic chemistry [5]. Some years ago, Nelson and co-workers investigated the solid state and melt reactions of six-coordinate ruthenium complexes, viz $RuCl_2(CO)_x(PR_3)_{4-x}$, (PR_3 = $PMePh_2$, PMe_2Ph, PMe_3, $P(CH_2C_6H_5)_3$, x = 1, 2) and the studies revealed ligand isomerisations in the temperature range 140–180 °C [6, 7]. A later study of related complexes $RuCl_2(RNC)_{4-x}(PR^*_3)_x$ (R = xylyl, Mes, etc; PR^*_3 = PPh_3, $P(4\text{-MeC}_6H_5)_3$; x = 0, 1, 2), i.e. involving isonitrile ligands, also revealed *cis-trans* isomerisation in the solid state [8]. Mechanistic studies [6, 9] and a thermomicroscopic investigation [10] of these complexes under solventless conditions have been reported. The studies revealed that the isomerisation in the solid state is surface-initiated [10] and follows first order kinetics [9]. The question then becomes: can solid-state (or more particularly solvent-free) reactions of six-coordinate ruthenium complexes be generalised to other 6-coordinate complexes? Indeed, simpler systems could provide more fundamental information on the complex isomerisation and decomposition reaction of 6-coordinate complexes, especially of more classical organometallic complexes. Consequently, solid-state studies of some six-coordinate molybdenum complexes of the type $Mo(CO)_4L_2$ have been undertaken.

The chemistry of the disubstituted molybdenum tetracarbonyl complexes, $Mo(CO)_4L_2$, dates back to the 1950s [11]. Much of the early work focused on synthetic strategies [12, 13] and substitution reactions [11]. The $Mo(CO)_4L_2$ (L = phosphine or phosphite) complexes can exist in two isomeric forms, i.e. *trans* and *cis* (Figure 1). The *cis*-isomer is believed to be a kinetic and the *trans*-isomer the thermodynamic product of the reaction of $Mo(CO)_6$ with L.

The *cis-trans* isomerisation in solution is influenced by steric factors associated with L [14-16]. Bulky ligands like PPh_3 favour the *trans* isomer in order to reduce steric repulsion between two PPh_3 ligands. Such complexes isomerise *via* a dissociative mechanism involving Mo-P

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*Corresponding author. E-mail: neil.coville@wits.ac.za; nareetsilef@mopipi.ub.bw bond cleavage [13, 14]. For less bulky ligands, the isomerisation proceeds via a non-dissociative mechanism [15]. All the above reports relate to solution studies and there are no reported data on reactions of the $Mo(CO)_4L_2$ complexes in the solid state [16-18]. Early solid-state studies focused on structural features of the products [19-25].

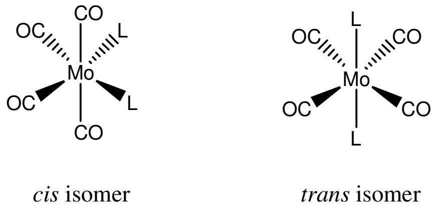

Figure 1. Isomers of $Mo(CO)_4L_2$ complexes.

In this study, we report on the solid state reactivity of the *cis*-$Mo(CO)_4L_2$ [L = PPh_2Et, PPh_3, PPh_2Me, and P(*m*-tolyl)$_3$] as monitored by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). This paper also describes rate studies of the solid state isomerisation of *cis*-$Mo(CO)_4(PPh_3)_2$ monitored by diffuse reflectance infrared spectroscopy (DRIFTS) and that of *cis*-$Mo(CO)_4$[P(m-tolyl$_3$)]$_2$ by thermomicroscopy. DRIFTS is an analytical tool that can be used to investigate solventless reactions [26, 27]. Related work includes a study of the formation of chromogenic calyx[4]arene derivatives [28], an investigation of supported and unsupported allyl-lanthanide complexes [29], and work on the reaction of molybdenum hexacarbonyl with benzene after thermal activation [30]. A limited number of DRIFTS studies of solventless organometallic complexes have been reported [26, 27, 31].

EXPERIMENTAL

$Mo(CO)_6$ and piperidine were obtained commercially from Strem Chemicals (USA) and Merck (SA), respectively. Dichloromethane was distilled over $LiAlH_4$, and toluene and methanol were distilled over sodium wire and collected under an inert atmosphere. The *cis*-$Mo(CO)_4L_2$ complexes were prepared according to literature procedures [13] and characterised by IR (Table 1) and NMR (Table 2) spectroscopy. Thermal analysis was carried out on ~10 mg samples under flowing nitrogen at a constant heating rate of 10 °C/min with a Du Pont Instruments 910 Differential Scanning Calorimeter (USA). Solution IR spectra were measured in CH_2Cl_2 on a Bruker VECTOR 22 FTIR spectrometer (Germany). The ^{31}P NMR spectra were measured on a Bruker AVANCE 300 NMR spectrometer (Germany) in $CDCl_3$ with TMS as reference.

Synthesis

cis-Mo(CO)$_4$(C$_5$H$_{10}$NH)$_2$ [13]. $Mo(CO)_6$ (10.0 g, 0.0378 mol) was added to a flask previously evacuated and purged with nitrogen. Degassed piperidine ($C_5H_{10}NH$) (25.0 mL, 0.253 mol) was added to the $Mo(CO)_6$ and the solution was refluxed in 120 mL of dried toluene for 4 h. The solution was filtered hot and the filtrate was concentrated and cooled in a refrigerator to give yellow crystals that were filtered off and washed with cold toluene. They were dried under vacuum overnight and characterised by IR and NMR spectroscopy. Yield: 12.9 g (90%).

cis-Mo(CO)$_4$(PPh$_3$)$_2$ [13]. A 100 mL round-bottomed flask was charged under nitrogen with *cis*-$Mo(CO)_4(C_5H_{10}NH)_2$ (2.0 g, 5.28 mmol) and triphenylphosphine (2.89 g, 11.0 mmol). Degassed CH_2Cl_2 (60 mL) was added and the reaction mixture was left to reflux under nitrogen for 30 min. The volume of the yellow solution was reduced and cold dry methanol was added. The solution was stored in the freezer (−10 °C) overnight. The yellow crystals were filtered off and characterised by IR and NMR spectroscopy. Yield 2.78 g (72 %).

cis-Mo(CO)$_4$(PPh$_2$Me)$_2$ [13]. *cis*-Mo(CO)$_4$($C_5H_{10}NH$)$_2$ (1.0 g, 2.64 mmol) and methyldiphenylphosphine (1.12 g, 5.6 mmol) were dissolved in 60 mL CH_2Cl_2 and refluxed for 15 min. The volume of the solvent was reduced and cold methanol was added. The solution was left in a freezer for 14 days. Yellow crystals were characterised by IR and NMR spectroscopy. Yield 1.43 g (89%).

The complexes *cis*-Mo(CO)$_4$(PPh$_2$Et)$_2$ (60%), and *cis*-Mo(CO)$_4$[P(*m*-tolyl)$_3$]$_2$ (yield 46%; melting point 206 °C; $MoP_2C_{18}H_{15}O_4$ calcd (%) C = 47.70, H = 3.34, found (%) C = 47.01, H 3.02) were prepared similarly.

Rate studies monitored by DRIFTS

DRIFTS measurements were made with a Bruker Tensor 27 DRIFTS spectrometer which housed the light source and the detector and a DRIFTS cell which contained a sample compartment. Samples were prepared by mechanical grinding of the complex, with previously dried KBr, to a very fine powder using a pestle and mortar until a homogeneous mixture was obtained. Finely ground KBr powder was first loaded into a DRIFTS cell and measured as background. The homogeneous mixture of the complex in KBr (1-2%) was then loaded into the DRIFTS cell equipped with heating device and air and water inlet/outlets and wirings. The initial IR spectrum was recorded. The heating control was then adjusted to the required temperature. The rate of disappearance of the peaks associated with the *cis*-isomer was measured by disappearance of the CO absorption peak at 2024 cm^{-1} until an appreciable amount of conversion to the *trans* isomer was achieved. A rate plot of the *cis*-isomer conversion was measured in terms of Kubelka Munk [32] units. The Kubelka Munk theory provides a correlation between reflectance and concentration. The concentration of an absorbing species can be determined using the Kubelka Munk formula viz. $F(R) = (1-R)^2/2R = k/s = AC/s$ where R = reflectance, k = absorption coefficient, s = scattering coefficient, c = concentration of the absorbing species and A = absorbance.

A plot of F(R) *versus* time was used to obtain a measure of the reaction kinetics. Assuming that the reaction was first order, the Arrhenius plot for each individual isomerisation reaction was constructed. Samples were run under nitrogen.

Thermomicroscopic studies of cis-Mo(CO)$_4$[P(m-tolyl)$_3$]$_2$

Optical microscopy experiments were carried out by a slightly modified procedure to that reported previously [10, 33]. Single crystals up to 0.5 mm in dimension were used and reactions were followed at 130–150 °C in an inert atmosphere in a specially constructed cell made out of an aluminium block connected to a thermostat. A CCD camera attachment, fitted to an Olympus polarising microscope, was used to take micrographs. The microscope was adjusted for optimum light transmission through an unreacted crystal. The equipment was calibrated with samples of known melting points.

RESULTS AND DISCUSSION

Synthesis and spectral characterisation

The preparation of *cis*-Mo(CO)$_4$L$_2$ by heating *cis*-Mo(CO)$_4$($C_5H_{10}NH$)$_2$ with appropriate phosphines in dichloromethane gave bright yellow complexes in good yields [13]. The IR spectra showed four bands in the carbonyl stretching frequency region typical of *cis*-$Mo(CO)_4L_2$ (Table 1). The corresponding *trans* isomers showed one strong band. All the other complexes have been prepared previously except for *cis*-$Mo(CO)_4[P(m\text{-tolyl})_3]_2$ [11-22].

Table 1. Carbonyl stretching frequencies of *cis*-$Mo(CO)_4L_2$[a].

L	ν (cm^{-1})
PPh_3	1874, 1910, 1926, 2021 (1897, 1908, 1927, 2023) [3]
PPh_2CH_3	1872, 1905, 1923, 2019 (1891, 1902, 1925, 2020) [3]
$PPh_2CH_2CH_3$	1874, 1900, 1920, 2019
$P(m\text{-tolyl})_3$	1873, 1901, 1920, 2019

[a] CD_2Cl_2.

The NMR data (Table 2) for these complexes are consistent with literature values [13]. The ^{31}P NMR spectra for the *cis*-isomers all show singlets. The NMR data for the *trans* complexes were also recorded. Peaks for *cis*-complexes were well separated from those of the *trans* isomers.

The solventlesss *cis/trans* isomerisation reactions were monitored by dissolving the reaction mixture in $CDCl_3$ (in an NMR tube) and the ^{31}P NMR spectra of the mixture were recorded as a function of time. After prolonged heating it was noted that the reaction solutions contained free phosphine that could readily be identified in the ^{31}P NMR spectra.

Table 2. NMR data for *cis*-$Mo(CO)_4L_2$[a].

L	^1H NMR (ppm)		^{31}P NMR (ppm)
	Me region	Phenyl region	
PPh_3	-	7.04 – 7.31	38.8
PPh_2Me	1.73-1.73 (t)	7.25 – 7.45	15.5
$PPh_2CH_2CH_3$	0.78 -0.88(m), 1.68-1.70 (d) 1.73-1.74 (t), 2.05 – 2.12 (m)	7.26 – 7.37	15.5[b]
P(*m*-tolyl)	2.15 (s)	6.98-7.01(t), 7.05-7.11 (dd), 7.17-7.20(t)	37.7

[a] $CDCl_3$. [b] Extra peaks seen at 14.6 -14.8 (d), 30.5 – 30.7 (d).

Thermal analysis

DSC data were obtained in the range of 25 to 400 °C at a heating rate of 10 °C/min. TGA analysis was in the temperature range 30 to 800 °C at the same heating rate. DSC and TGA results are shown in Table 3.

Table 3. DSC and TGA results of *cis* $Mo(CO)_4L_2$ complexes.

L	DSC data [a](°C)	TGA data [b](°C)
PPh_3	171 (exo), 217 (exo), 250 (endo)	130
PPh_2Me	128 (endo), 298 (endo)	235
$PPh_2CH_2CH_3$	102 (endo), 300 (endo)	230
P(*m*-tolyl)	160(endo), 175 (exo), 206(endo) decomposition	130

[a] Temperature of reaction with endo/exothermicity indicated in brackes. [b] Temperature at which the complex begins to decompose.

$Mo(CO)_4(PPh_3)_2$. A TGA trace for *cis*-$Mo(CO)_4(PPh_3)_2$, recorded under nitrogen, shows that the mass is constant from 25 °C to about 130 °C (Figure 2). Between 130 °C and 300 °C there is a total loss of 75 % mass, which is assumed to be due to loss of the two PPh_3 ligands (theoretical loss = 71.6 %). After heating to 400 °C, the product was added to chloroform to give a dark green solution containing some undissolved tiny black particles. No absorptions were observed in the ^{31}P NMR spectrum.

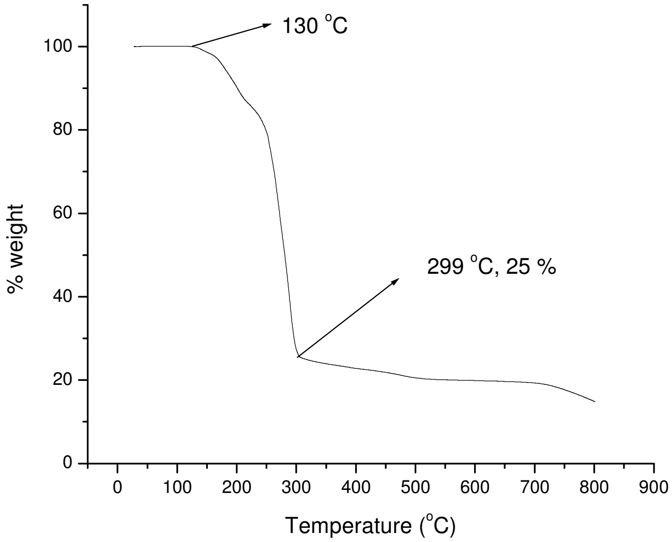

Figure 2. TGA profile of *cis*-$Mo(CO)_4(PPh_3)_2$.

A DSC profile of *cis*-$Mo(CO)_4(PPh_3)_2$ is shown in Figure 3. A small exotherm at 171 °C, is followed by a very broad exotherm at 217 °C. The complex immediately darkened on melting (T > 220 °C) indicating that the complex decomposed. The peaks above 220 °C relate to decomposition peaks.

In a separate experiment, *cis*-$Mo(CO)_4(PPh_3)_2$ was heated in the DSC instrument up to 180 °C. The material was then transferred to an NMR tube and the ^{31}P spectrum revealed that complete conversion of the *cis* to the *trans* isomer had occurred. Heating to 210 °C resulted in formation of a dark brown solid. According to literature reports [2], the melting point of the *trans* isomer ranges between 210-220 °C. A solution in $CDCl_3$ was shown by ^{31}P NMR spectroscopy to contain *trans* isomer (51.0 ppm) and Ph_3PO (i.e. oxidised phosphine ligand (29.0 ppm).

A consideration of the TGA, and NMR data permits an interpretation of the DSC results. The first exotherm reflects the isomerisation of the *cis* to the *trans* isomer and that at 217 °C to melting and decomposition of the *trans* isomer. It is to be noted that the melting point of the *cis*-isomer is reported as 150 °C [2] but no melting was detected by DSC (Figure 5) nor observed visually. This suggests that either *cis-trans* isomerisation occurs *in the solid state* or that *after melting* there is rapid isomerisation and crystallisation of the new isomer.

$Mo(CO)_4[P(m\text{-}tolyl)_3]_2$. A TGA profile of *cis*-$Mo(CO)_4[P(m\text{-}tolyl)_3]_2$ showed a small mass loss between 130 and 180 °C (about 3%), with the final mass loss being about 72% of the original (theoretical loss = 74.7% after loss of the P(*m*-tolyl)$_3$ ligands).

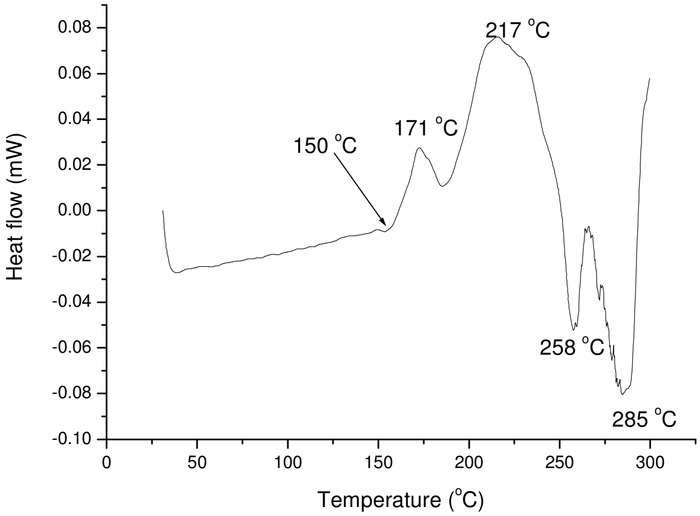

Figure 3. DSC profile of *cis*-$Mo(CO)_4(PPh_3)_2$.

A portion of the solid sample was heated in an NMR tube and the complex was observed to melt at 206 °C with darkening at higher temperatures. An NMR spectrum of the sample after it had been heated to 220 °C in the TGA was recorded in $CDCl_3$. The ^1H NMR spectrum as well as the ^{31}P NMR spectrum of the residue (a green solution) did not indicate the presence of phosphine ligands.

The DSC profile of *cis*-$Mo(CO)_4[P(m\text{-tolyl})_3]_2$ showed three peaks; an endotherm at 160 °C, an exotherm at 175 °C and another endotherm at 206 °C. The profile is similar to that of *cis*-$Mo(CO)_4(PPh_3)_2$. There was no visible sign of melting on heating the complex in a melting point apparatus up to 180 °C. The sample was also heated to 160 °C under an optical microscope; again no evidence of melting was noted (see below). It therefore appears that if melting does occur (as suggested by the exotherm at 160 °C) there is immediate isomerisation leading to solid *trans* isomer, which melts at around 206 °C. Decomposition follows melting (for the PPh_3 complex these events occurred simultaneously as shown by DSC profiles).

$Mo(CO)_4(PPh_2Me)_2$. TGA of *cis*-$Mo(CO)_4(PPh_2Me)_2$ (Figure 4) shows no mass change up to 235 °C. Beyond this temperature the complex decomposes leaving a residue with 22% of the original mass (theoretical = 76.40% loss for two PPh_2Me ligands).

The DSC profile (Figure 5) shows two endotherms at 128 and 298 °C corresponding to the melting points of the *cis* and *trans* isomers. A broad (weak) exotherm is also noted, at ca. 200 °C. To interpret the data the sample was heated overnight at 100 °C but no isomerisation was observed by IR spectroscopy. Above 100 °C, melting was seen by visual inspection (mp 127-129 °C). When the complex was heated to 150 °C and then cooled, the ^{31}P NMR spectrum revealed that a mixture of isomers (20:80% *cis/trans* mixture) had formed, indicating that isomerisation had occurred in this temperature range and that melting preceeded isomerisation.

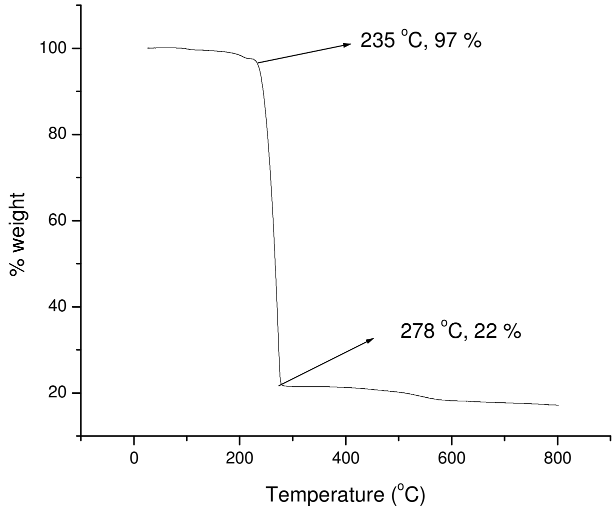

Figure 4. TGA profile of *cis*-Mo(CO)$_4$(PPh$_2$Me)$_2$.

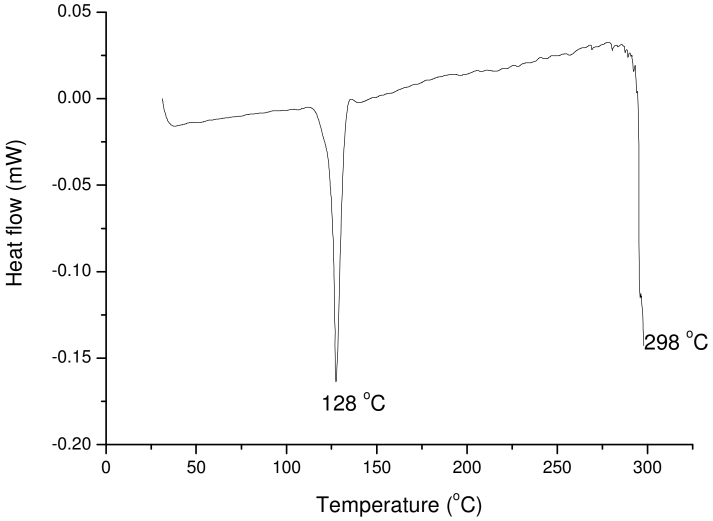

Figure 5. DSC profile of *cis*-Mo(CO)$_4$(PPh$_2$Me)$_2$.

Mo(CO)$_4$(PPh$_2$Et)$_2$. TGA of *cis*-Mo(CO)$_4$(PPh$_2$Et)$_2$ showed no mass change up to 171 °C. Beyond this temperature the complex decomposed leaving a residue with 22 % of the original mass, corresponding to the loss of two phosphine ligands.

The DSC profile of *cis*-Mo(CO)$_4$(PPh$_2$Et)$_2$ showed two endotherms at 102 and 298 °C respectively and a broad weak exotherm at ca. 200°C, similar to that for *cis*-Mo(CO)$_4$(PPh$_2$Me)$_2$. There is only modest isomerisation (<5%) when the sample is heated overnight at 100 °C. On raising the temperature to 110 °C, the complex isomerizes in the melt as NMR analysis reveals a 19:81 *cis-trans* isomer ratio.

DRIFTS studies on cis-Mo(CO)$_4$(PPh$_3$)$_2$

Data for the solid state isomerisation at various temperatures are shown in Figure 6. Data were also recorded at 140 and 160 °C.

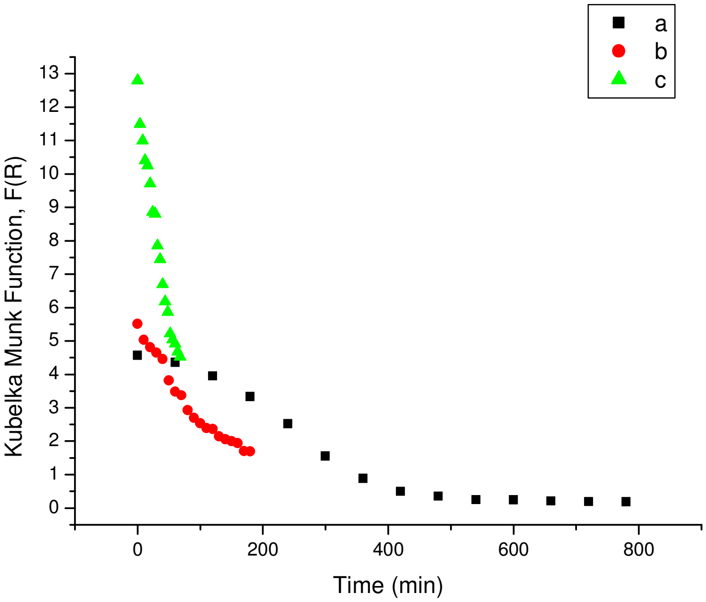

Figure 6. Rate plot of *cis*-Mo(CO)$_4$(PPh$_3$)$_2$ at a) 120 °C (data points collected after 60 min intervals); b) at 130 °C (data points collected after 5 min intervals); c) at 150 °C (data points collected after 4 min intervals).

At 120 °C isomerisation occurs in three steps. During the first 100 min there is a slow reaction attributed to initiation on the surface. This is followed by a rapid reaction between 100 and 300 min (propagation step), and a final slow reaction at 300 minutes and beyond (reaction approaching completion). The rate data collected at 130, 140, 150 and 160 °C show what appears to be simpler behaviour. Isomerisation occurs more rapidly with a minimal activation step at these higher temperatures. Assuming first order behaviour, rate constants were obtained from the temperature studies and the data are shown in Table 4. An Arrhenius plot (Figure 7) for the isomerisation of *cis*-Mo(CO)$_4$(PPh$_3$)$_2$ was constructed from the k values (Table 4) to give an activation energy of 89 ± 8 kJ mol^{-1}. This is to be compared to solution studies in which the activation energy is >100 kJ mol^{-1} [14, 15].

Table 4. Rate constants for the isomerisation of *cis*-Mo(CO)$_4$(PPh$_3$)$_2$ at various temperatures.

Temperature (°C)	Rate constant, k (s^{-1})
130	$5.37 \pm 0.06 \times 10^{-3}$
140	$1.10 \pm 0.03 \times 10^{-2}$
150	$1.60 \pm 0.04 \times 10^{-2}$
160	$3.64 \pm 0.2 \times 10^{-2}$

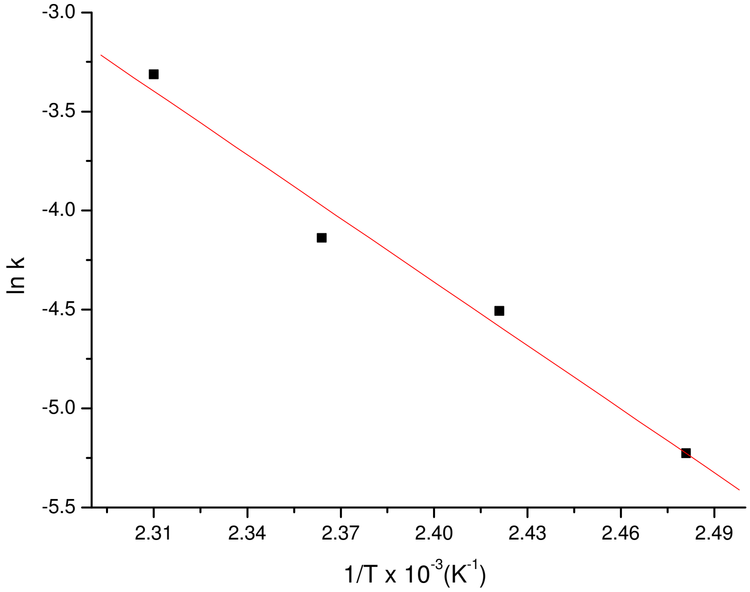

Figure 7. Arrhenius plot for *cis*-Mo(CO)$_2$(PPh$_3$)$_2$.

Thermomicroscopic studies of cis-Mo(CO)$_4${P(m-tolyl)$_3$]$_2$

Thermomicroscopic studies on selected *crystals* of *cis*-Mo(CO)$_4$[P(*m*-tolyl)$_3$]$_2$ at 130, 140 and 150 °C showed similar behavior at all three temperatures. On heating crystals of the reactant at 130 °C, the colour gradually changed from bright to dull yellow. After the sample was heated for 2 h, NMR analysis revealed less than 5% conversion. Isomerisation occurred during the heating process without any apparent crystal degradation. However, analysis by single-crystal X-ray diffraction showed that the crystallinity had been lost. Figure 8 shows data collected for the reaction at 140 °C. On heating the crystals, the surface gradually changed from yellow to orange and then darkened. When a crystal was cut in half, it shattered and the inner surface was observed to be yellow and only the outer surface dark. Similar colour changes were observed when samples were heated in an NMR tube. When the heated crystals (2 h) were dissolved in CDCl$_3$ the ^{31}P NMR spectrum showed about 10 % conversion to the *trans* isomer (with no other P-containing species present). The data thus show that the isomerisation is surface-initiated. The onset of opacity is attributed to isomerisation. The orange colour observed during the heating could possibly indicate formation of an intermediate phase on the crystal surface.

Mechanism for the solid state reaction

Detailed studies have been undertaken on the *cis→trans* isomerisations of Mo(CO)$_4$L$_2$ (L = PPh$_3$, PEt$_3$, P(^{n}Bu)$_3$ and PMe$_3$) in solution. The solution data, as mentioned in the introduction, indicated that the isomerisation can occur via a *dissociative* rearrangement or an *intramolecula*r reaction in which a trigonal prism species is an intermediate [33]. The data indicated a dissociative process when L is large, e.g. PPh$_3$. The activation energies for the dissociation process and intramolecular process were reported to be ~124 kJ/mol [15] and 100 kJ/mol [14] respectively. In comparison, activation energies between 114 and 420 kJ mol^{-1} have been reported in the literature [34, 35] for the thermal solid-state isomerisations of related chromium complexes.

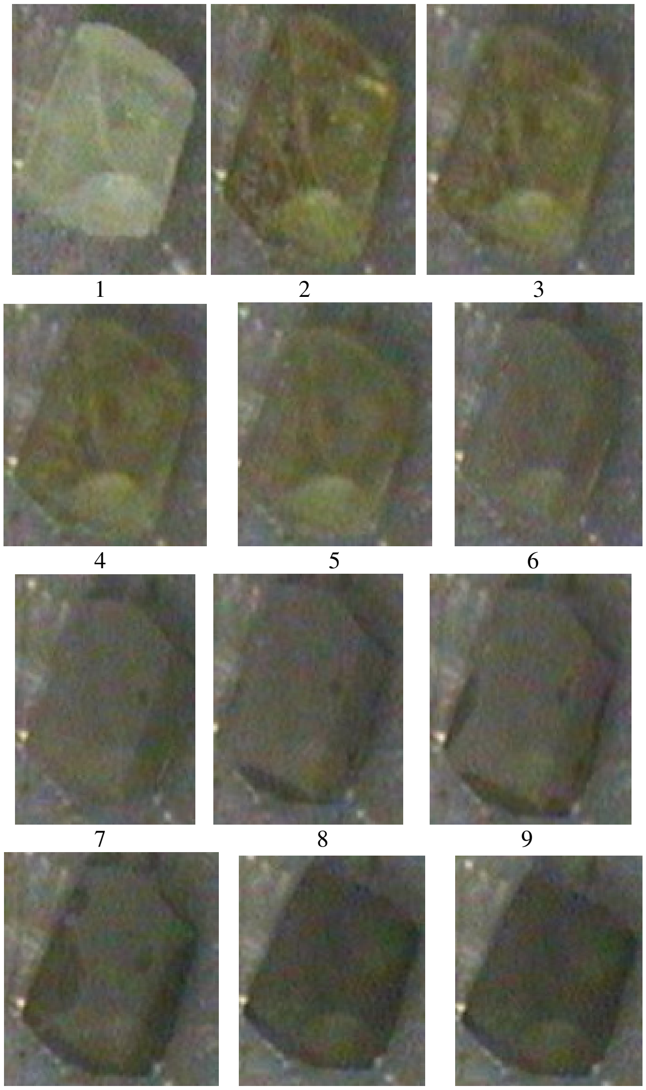

Figure 8. *cis*-$Mo(CO)_4\{P(m\text{-tolyl})_3\}_2$ heated for 2 hours at 140 °C (pictures taken at 10 min interval).

Reactions performed *in the absence of a solvent,* described here, show the following.

(i) *Cis* to *trans* isomerism occurs in the absence of solvent.
(ii) Once formed, *trans* isomers can decompose at high temperatures.
(iii) The reaction is first order in complex. The energy barrier for the isomerisation is lower than that in solution.

(iv) In some instances the reaction occurs in the melt (L = PPh$_2$Et and PPh$_2$Me) and in others in the solid phase (L = PPh$_3$ and P(*m*-tolyl)$_3$). The different reaction types can be detected by DSC. Sharp melting points for *cis* isomers are associated with melt reactions.

(v) Optical microscopic studies show that the reactions are surface-initiated.

The reaction involves movement of a ligand from a *cis* to a *trans* position. Thus, a key issue is the degree to which rotation occurs without any bond-breaking. A mechanism involving a trigonal prismatic intermediate is shown in Figure 9. If the L group that interchanges with a CO ligand is large (L = PPh$_3$ or P(*m*-tolyl)$_3$) dissociation may occur, but when L is small an intermolecular process is more likely. In this study the TGA data suggest a solventless reaction with no dissociation or decomposition when L is small, but not when L is large. When L is small a mechanism in the melt similar to that in solution is possible. When L is large reactions in the melt and in solution are similar to those in the solid state and probably proceed by a dissociative mechanism involving a 5 coordinate intermediate.

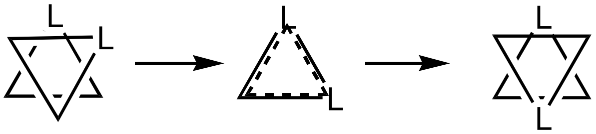

Figure 9. Isomerisation mechanism; L = PPh$_3$.

In solution, dissociation of a ligand, e.g. PPh$_3$ would be facile but in the solid state the PPh$_3$ would be constrained by the other reactant molecules so it is more likely that the reactions occurs at the surface. Once isomerisation occurs, crystallinity is lost, and isomerisation is propagated through the bulk. This propagation may be facilitated by the amorphous structure of the less well-packed product.

CONCLUSIONS

Isomerisation of a series of *cis*-Mo(CO)$_4$L$_2$ [L = PPh$_3$, PPh$_2$Me, PPh$_2$Et and P(*m*-tolyl)$_3$] complexes to their corresponding *trans* isomers has been studied under solventless conditions. Thermal analysis of the complexes revealed that *cis*-Mo(CO)$_4$L$_2$ complexes undergo *cis* to *trans* isomerisations in both the solid and melt phases, and that the reaction is dependent on the ligand. Decomposition of the *trans*-isomer occurs at higher temperatures. DRIFTS rate data for *cis*-Mo(CO)$_4$(PPh$_3$)$_2$ revealed a first order reaction with an activation energy less than 100 kJ mol^{-1}. A thermomicroscopic investigation revealed that the isomerisation is a surface reaction as observed for that of similar six-coordinate RuCl$_2$(RNC)$_2$(PPh$_3$)$_2$ [10] complexes that proceed with loss of crystallinity.

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