

## CHAPTER 7

### SYNTHESIS AND CHARACTERISATION OF *cis*-Mo(CO)<sub>4</sub>L<sub>2</sub> COMPLEXES

#### 7.0 Introduction

The chemistry of the disubstituted molybdenum tetracarbonyl complexes dates back to the 1950s [1]. Much of the early work focused on synthetic strategies [2, 3] and the reactions of these complexes *i.e.* substitution reactions and reactions with other ligands [1].

Mo(CO)<sub>4</sub>L<sub>2</sub> complexes can exist in two isomeric forms *i.e.* the *trans* and the *cis* isomers (see figure 7.1). The *cis* isomer is thought to be a kinetic product and the *trans* isomer the thermodynamic product of the reaction of Mo(CO)<sub>6</sub> with L. The *cis-trans* isomerisation process has been found to be influenced by structural factors [4, 5, 6]. Bulky ligands like PPh<sub>3</sub> tend to favour the *trans* position in order to avoid steric repulsion. Such complexes have been found to isomerise *via* a dissociative mechanism involving Mo-P bond cleavage [3, 4]. For less bulky ligands, the isomerisation process has been found to proceed *via* a non-dissociative mechanism [5]. Many of these reactions were done in solution media and there are no reported data on their reactivity in the solid state. Early solid-state studies only focused on structural analysis issues [6-12].

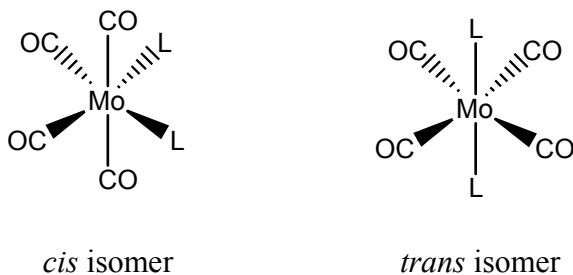


Figure 7.1: Stereoisomers of Mo(CO)<sub>4</sub>L<sub>2</sub> complexes

There is no prior mention of the reactivity of these complexes in the solid state. In this study, the synthesis of *cis*-Mo(CO)<sub>4</sub>(L<sub>2</sub>) (L = PPh<sub>3</sub>, PPh<sub>2</sub>Me, PPh<sub>2</sub>Et and P(m-tolyl)<sub>3</sub>) was done for purposes of investigating their reactions in the solid state.

## 7.1 Syntheses of Mo(CO)<sub>4</sub>L<sub>2</sub> Complexes

Mo(CO)<sub>6</sub> and piperidine were obtained commercially. Dichloromethane was distilled over LiAlH<sub>4</sub>, while toluene and methanol were distilled over sodium wire and collected under an inert atmosphere. The complexes were prepared by slightly modified procedures from those reported in the literature [3]. The prepared complexes were characterised by IR (table 7.1) and NMR (table 7.2) spectroscopy. CHN analysis was performed on the new compound. Thermal analysis was carried out by DSC and TGA techniques (table 7.3) as reported for the ruthenium complexes (see chapter 4). Some heating experiments were carried out with a DSC instrument. The DSC instrument was set to heat from room temperature to the required temperature and the heated samples were then taken for <sup>31</sup>P NMR analysis.

### 7.1.1 *cis*-Mo(CO)<sub>4</sub>(C<sub>5</sub>H<sub>10</sub>NH)<sub>2</sub>

Mo(CO)<sub>6</sub> (10.0 g, 0.0378 mol) was added to a flask previously evacuated and then purged with nitrogen. Degassed piperidine (C<sub>5</sub>H<sub>10</sub>NH) (25.0 ml, 0.253 mol) was added to Mo(CO)<sub>6</sub> and the solution was refluxed in 120 ml of dried toluene for 4 hours. The resulting yellow precipitate was filtered hot. The isolated yellow solid was washed with cold toluene and then dried under vacuum overnight and characterised by IR and NMR spectroscopy. Yield: 12.91 g (90%)

### 7.1.2 *cis*-Mo(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>

A 100 ml round bottom flask was charged with *cis*-Mo(CO)<sub>4</sub>(C<sub>5</sub>H<sub>10</sub>NH)<sub>2</sub> (2.0 g, 5.28 mmol) and triphenylphosphine (2.89 g, 11.0 mmols). This was evacuated and purged

with nitrogen. Degassed  $\text{CH}_2\text{Cl}_2$  (60 ml) was added and the reaction mixture was left to reflux under nitrogen for 30 minutes. The volume of the yellow solution was reduced and cold dry methanol was added. The solution was stored in the freezer ( $-10\text{ }^\circ\text{C}$ ) overnight. The yellow crystals that formed were filtered off and the material characterised by IR and NMR spectroscopy. Yield 2.78 g, (72 %).

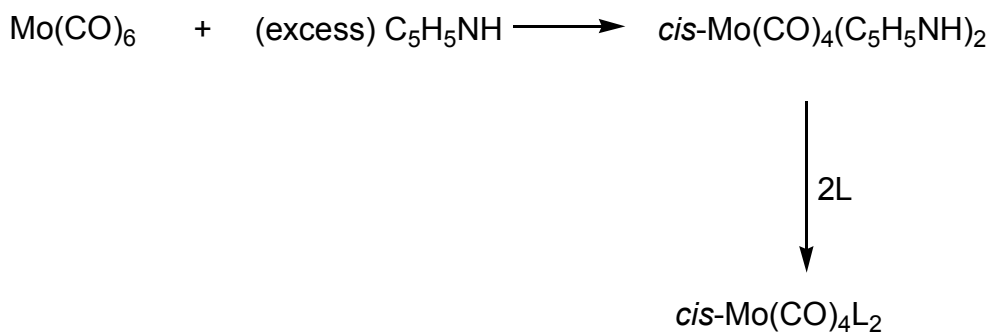
### 7.1.3 *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_2\text{Me})_2$

*cis*- $\text{Mo}(\text{CO})_4(\text{C}_5\text{H}_{10}\text{NH})_2$  (1.0 g, 2.64 mmol) and methyldiphenylphosphine (1.12 g, 0.006 mmol) were dissolved in 60 ml  $\text{CH}_2\text{Cl}_2$  and refluxed for 15 minutes. The volume of the solvent was reduced and cold methanol was added. The solution was left in the freezer for 14 days. Yellow crystals were obtained and characterised by IR and NMR spectroscopy. Yield 1.43 g (89%). The complexes *cis*- $\text{Mo}(\text{CO})_4(\text{PPh}_2\text{Et})_2$  (60%), *cis*- $\text{Mo}(\text{CO})_4\{\text{P}(\text{OEt})_3\}_2$  (60%), *cis*- $\text{Mo}(\text{CO})_4\{\text{P}(\text{C}_6\text{H}_4\text{Me})_3\}_2$  (46%) were prepared following a similar synthetic route.

## 7.2 Results and discussion

### 7.2.1. Synthesis and Spectral characterisation

The preparation of *cis*- $\text{Mo}(\text{CO})_4\text{L}_2$  by refluxing *cis*- $\text{Mo}(\text{CO})_4(\text{C}_5\text{H}_{10}\text{NH})_2$  and appropriate phosphines in dichloromethane gave the required complexes in good yields [3] (see Scheme 13)



### Scheme 13

The complexes are bright yellow in colour. Characterisation of these complexes was achieved by IR spectroscopy. Each spectrum showed four bands typical of *cis*-Mo(CO)<sub>4</sub>L<sub>2</sub> complexes (table 7.1) while the corresponding *trans* isomers are characterised by one strong band associated with the symmetrical nature of the *trans*-Mo(CO)<sub>4</sub>L<sub>2</sub> complexes.

**Table 7.1: Carbonyl stretching frequencies of *cis*-Mo(CO)<sub>4</sub>(L)<sub>2</sub> complexes in dichloromethane solutions**

L	$\nu(\text{cm}^{-1})$
PPh <sub>3</sub>	1874, 1910, 1926, 2021 (1897, 1908, 1927, 2023) [3]
PPh <sub>2</sub> Me	1872, 1905, 1923, 2019 (1891, 1902, 1925, 2020) [3]
PPh <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	1874, 1900, 1920, 2019
P(OEt) <sub>3</sub>	1849, 1895, 1917, 2021
P( <i>m</i> -tolyl)	1873, 1901, 1920, 2019

Literature values in brackets

There are no reports on synthesis of *cis*-Mo(CO)<sub>4</sub>{P(*m*-tolyl)<sub>3</sub>}<sub>2</sub> and it is reported here for the first time. All the other complexes have been prepared before [1-13]. The IR pattern for this complex is similar to the known ones. The only difference is in the position of the absorption frequencies.

The NMR data (see table 7.2) for these complexes are consistent with the literature values [3]. The <sup>31</sup>P NMR data for the *cis*-isomers show a singlet, and the resonance peaks for the *cis*-complexes are well separated from their corresponding *trans* isomers (see figure 7.2). The <sup>31</sup>P NMR spectra was chosen over <sup>1</sup>H NMR spectra for use in kinetic studies because it was observed that after prolonged heating experiments, the isomerised complexes decomposed giving oxidized phosphine. The oxidized phosphine is not easily detectable in a <sup>1</sup>H NMR spectrum as it is in a <sup>31</sup>P NMR spectrum.

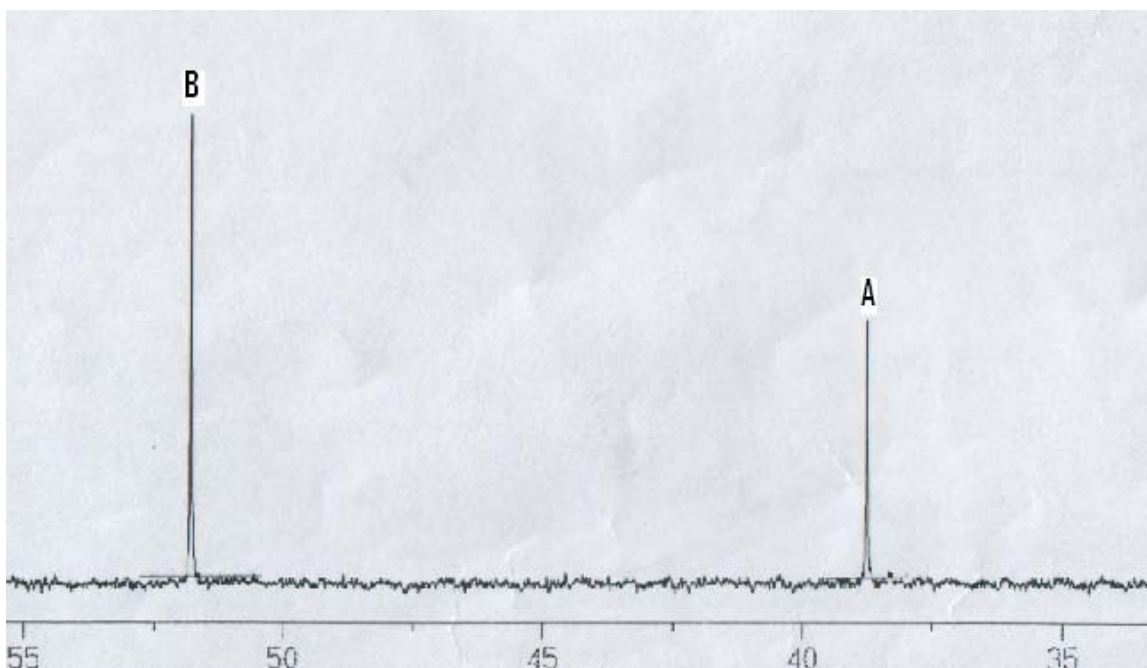


Figure 7.2: Showing peaks due to; A) *cis*- and B) *trans*-isomers of Mo(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> complex

**Table 7.2: NMR data for *cis*-Mo(CO)<sub>4</sub>(L)<sub>2</sub> Complexes in d-chloroform**

L	<sup>1</sup> H NMR (ppm)		<sup>31</sup> P NMR (ppm)
	Me Region	Phenyl region	
PPh <sub>3</sub>	-	7.04 – 7.31	38.8
PPh <sub>2</sub> Me	1.73-1.73 (t)	7.25 – 7.45	15.5
PPh <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	0.78 -0.88(m)	7.26 – 7.37	14.6 -14.8 (d)
	1.68-1.70 (d)		15.5 (s)
	1.73-1.74 (t)		30.5 – 30.7 (d)
	2.05 – 2.12 (m)		
P(OEt) <sub>3</sub>	1.27 – 1.34(m)	-	158.7
	4.02 – 4.09 (m)		
P( <i>m</i> -tolyl)	2.15 (s)	6.98-7.01(t), 7.05-	37.7
		7.11(dd), 7.17-	
		7.20(t)	

### 7.2.2 Thermal Analysis Studies

DSC studies for these complexes were performed in the range of 25 to 400 °C at a heating rate of 10 °C /minute. TGA analysis was done at 30 to 800 °C at the same heating rate and the results are shown in table 7.3. Thermal analysis of the *cis*-Mo(CO)<sub>4</sub>(L)<sub>2</sub> complexes is reported for the first time in this study.

**Table 7.3: DSC and TGA results of *cis* Mo(CO)<sub>4</sub>(L)<sub>2</sub> Complexes**

L	DSC data <sup>a</sup> (°C)	TGA data <sup>b</sup> (°C)
PPh <sub>3</sub>	171 (exo), 217 (exo), 250 (endo)	130
PPh <sub>2</sub> Me	128 (endo), 298 (endo)	235
PPh <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	102 (endo), 300 (endo)	230
P(OEt) <sub>3</sub>	93(endo), 124(small exo), 199 (endo)	
P( <i>m</i> -tolyl)	160(endo), 175 (exo), 206(endo) decomposition	130

<sup>a</sup>Temperature of reaction with endo/exothermicity indicated in brackets

<sup>b</sup>Temperature where the complex begins to decompose.

**L = PPh<sub>3</sub>**

A thermogram of the *cis*-Mo(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> complex in nitrogen shows that the mass is constant from 25 °C to about 130 °C (See figure 7.3). Between 130 °C to 300 °C there is a total loss of 75 % in mass which could be due to loss of the two PPh<sub>3</sub> ligands (theoretical value = 71.60). A small percentage loss of 2 % is noted between 180 and 200 °C. The final mass of the residue is around 25 % of the original mass. After heating, the product was dissolved in chloroform. Some undissolved tiny black particles were noted. The

colour of the solution was dark green.

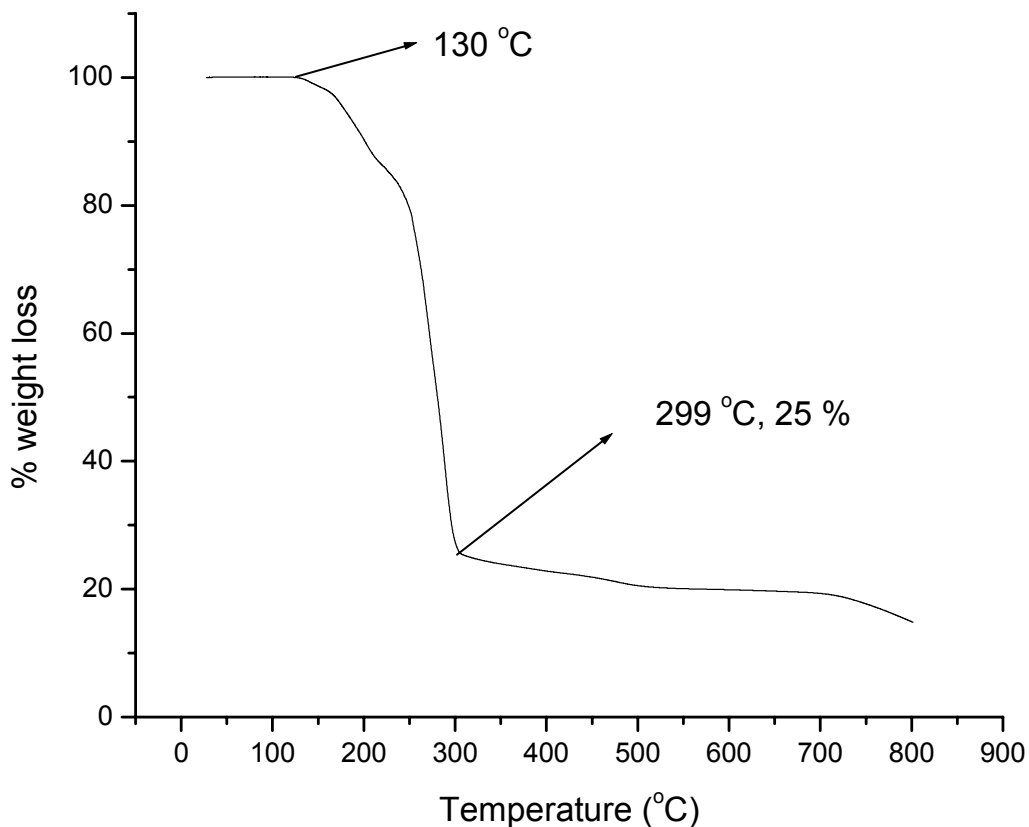


Figure 7.3 TGA scan of *cis*-Mo(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>

When heating pure *cis*-Mo(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> complex in a DSC instrument up to 180 °C, all the *cis*-complex was converted to the *trans* isomer. The 10 % loss of weight observed between 180 and 200 °C corresponds to some decomposition of the material. Heating beyond 200 °C resulted in formation of a dark brown solid. When dissolved in *d*-chloroform and taken for <sup>31</sup>P NMR spectral analysis the brown solid indicated the presence of the *trans* isomer at 51.0 ppm and a resonance peak at 29.0 ppm due to oxidized phosphine.

A DSC profile of the *cis*-Mo(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> complex is shown in Figure 7.4. It shows a small exotherm at 171 °C, followed by a very broad exotherm at 217 °C. The first

exotherm is probably related to the isomerisation of the complex to the *trans* isomer while the exotherm at 217 °C is probably due to decomposition of the *trans* isomer.

According to reports in literature [2], the melting point of the *trans* isomer ranges between 210 -220 °C. This observation does not correlate with the DSC. However there is a notable trough in between the two exotherms which could be associated with the melting of the isomer followed by decomposition. The complex immediately darkens in colour on melting which shows that the complex decomposes on melting.

The melting point of *cis*-isomer is said to be at 150 °C [2] but no endotherm was observed at this temperature.

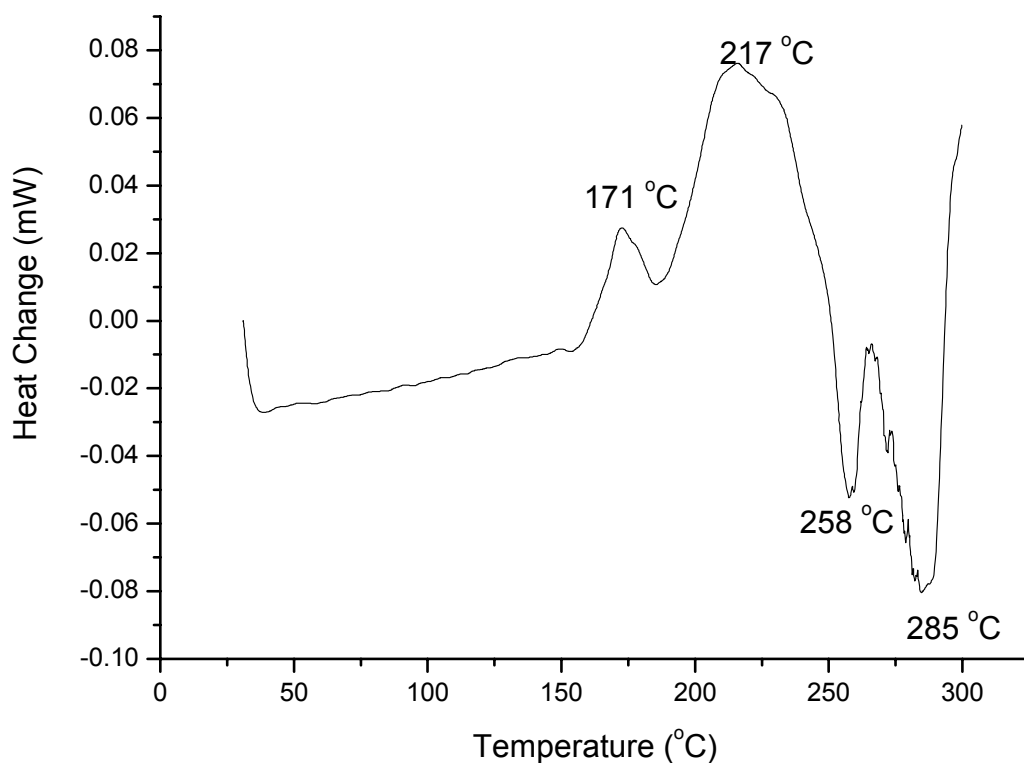


Figure 7.4: DSC profile of *cis*-Mo(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>

**L = *Pm*-tolyl<sub>3</sub>**

A TGA profile of the *cis*-Mo(CO)<sub>4</sub>(*Pm*-tolyl<sub>3</sub>)<sub>2</sub> complex (see Figure 7.5) shows some similarity with the one for the *cis*-Mo(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> complex. There is a small mass loss between 130 and 180 °C (about 3%), with the final mass of the residue being about 28 % of the original. On heating the sample in an NMR tube up to 210 °C melting of the complex is observed at 206 °C with darkening in colour upon melting. Dissolving the residue in *d*-chloroform resulted in formation of a green solution. The <sup>1</sup>H NMR as well as the <sup>31</sup>P NMR spectra of the residue did not indicate the presence of phosphine ligands. This shows that the 72 % mass loss observed in the TGA is due to loss of the two volatile phosphine ligands to form some insoluble phosphorus containing product.

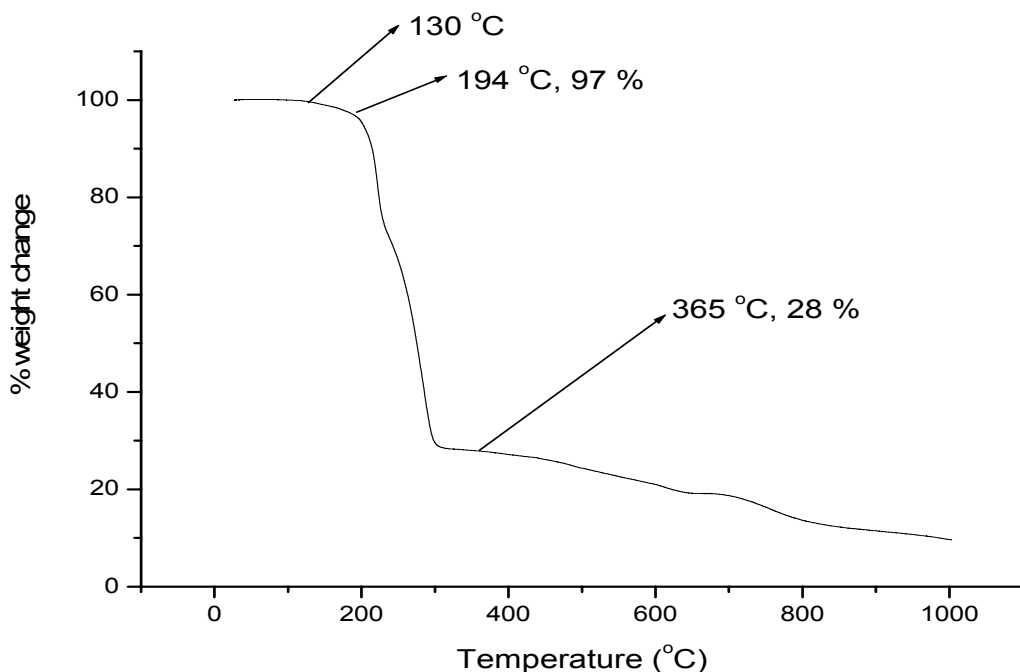


Figure 7.5: TGA profile of the *cis*-Mo(CO)<sub>4</sub>{*P*(*m*-tolyl)<sub>3</sub>}<sub>2</sub> complex

The DSC profile of the *cis*-Mo(CO)<sub>4</sub>(*Pm*-tolyl<sub>3</sub>)<sub>2</sub> complex (see figure 7.6) shows three peaks, an endotherm at 160 °C, probably due to melting of the *cis* isomer, an exotherm at

175 °C and another endotherm at 206 °C. The profile shows some similarities to that of the *cis*-Mo(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> complex except for the endotherm observed at 160 °C. Otherwise the exotherm observed at 175 °C and endotherm at 206 °C could indicate similar behaviour to that observed in the exotherm observed at 171 °C and endotherm (trough) around 200 °C in the DSC profile of the *cis*-Mo(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub> complex. Other differences could be associated with the nature of the ligand used. There was no visible melting on heating the complex in the melting point apparatus up to 180 °C. It is therefore difficult to account for the endotherm observed at 160 °C. Heating the sample to 160 °C and observing the material under an optical microscope did not give evidence of melting by the complex. Probably the melting of the complex might be preceded by the isomerisation and solidification of the isomerised complex and thus it is not easy to visualize melting of the complex. Melting is observed at around 206 °C and this is associated with the melting point of the *trans*-isomer.

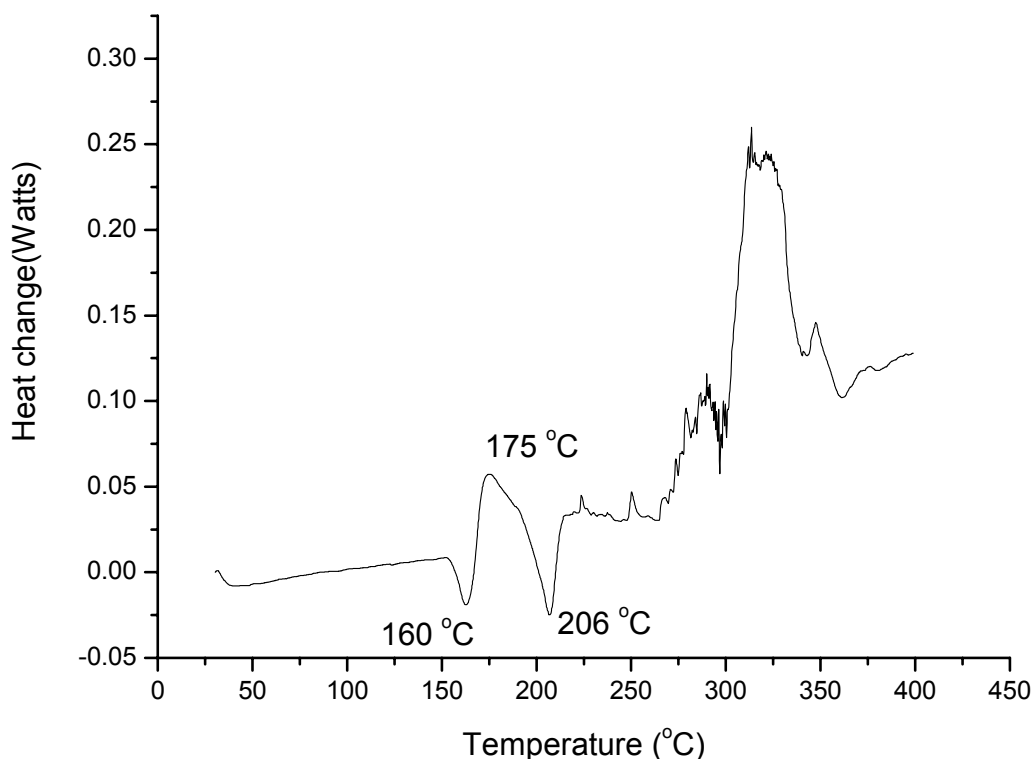


Figure 7.6: DSC profile of *cis*-Mo(CO)<sub>4</sub>{P(*m*-tolyl)<sub>3</sub>}<sub>2</sub> complex

**L = PPh<sub>2</sub>Me**

The TGA analysis of the *cis*-Mo(CO)<sub>4</sub>(PPh<sub>2</sub>Me)<sub>2</sub> complex (see Figure 7.7) shows no mass change up to 235 °C. Beyond this temperature the complex decomposes leaving a residue with 22 % of the original mass. This is also probably associated with the loss of two phosphine ligands.

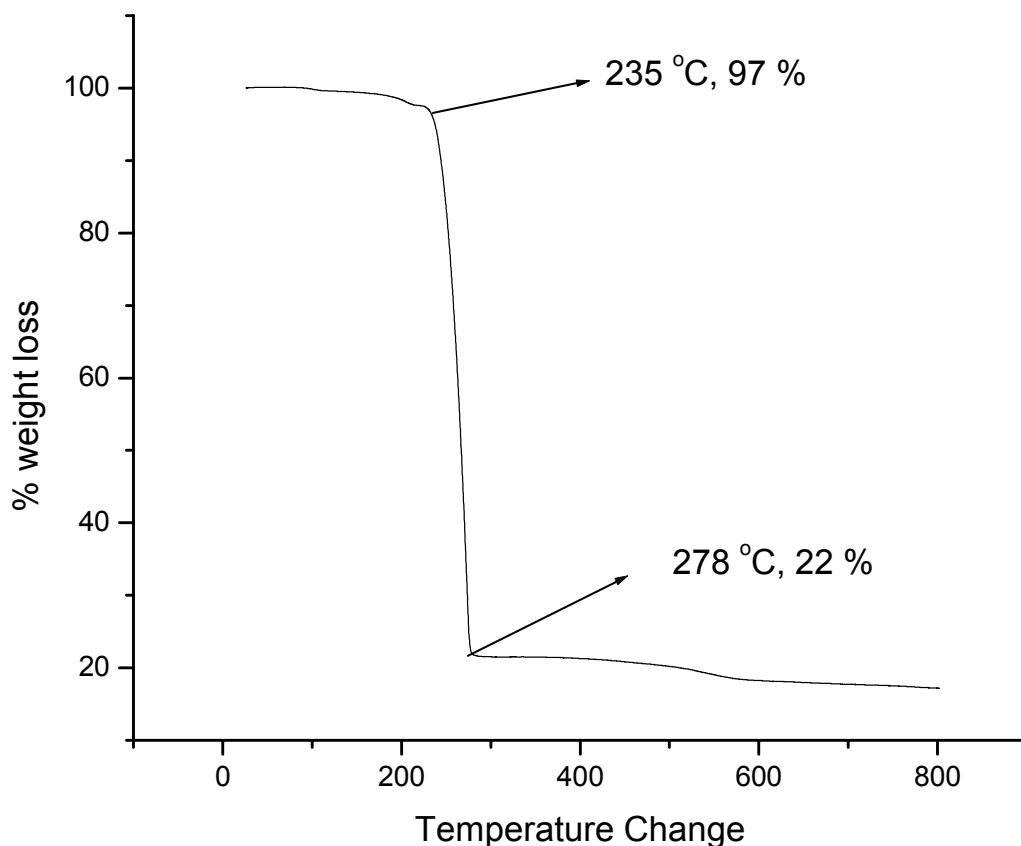


Figure 7.7: TGA profile of *cis*-Mo(CO)<sub>4</sub>(PPh<sub>2</sub>Me)<sub>2</sub> complex

The DSC profile (see fig 7.8) shows two endotherms at 128 and 298 °C corresponding to the melting points of the *cis* and *trans* (300 °C) isomers. When the complex is heated between 130 to 150 °C the spectra of the sample shows it to be a mixture of isomers (20:80 % *cis/trans* mixture) indicating that isomerisation has occurred in this temperature

range. The complex isomerizes in the melt and then quickly solidifies. There was no isomerisation observed by IR spectroscopy when the complex was heated overnight at 100 °C.

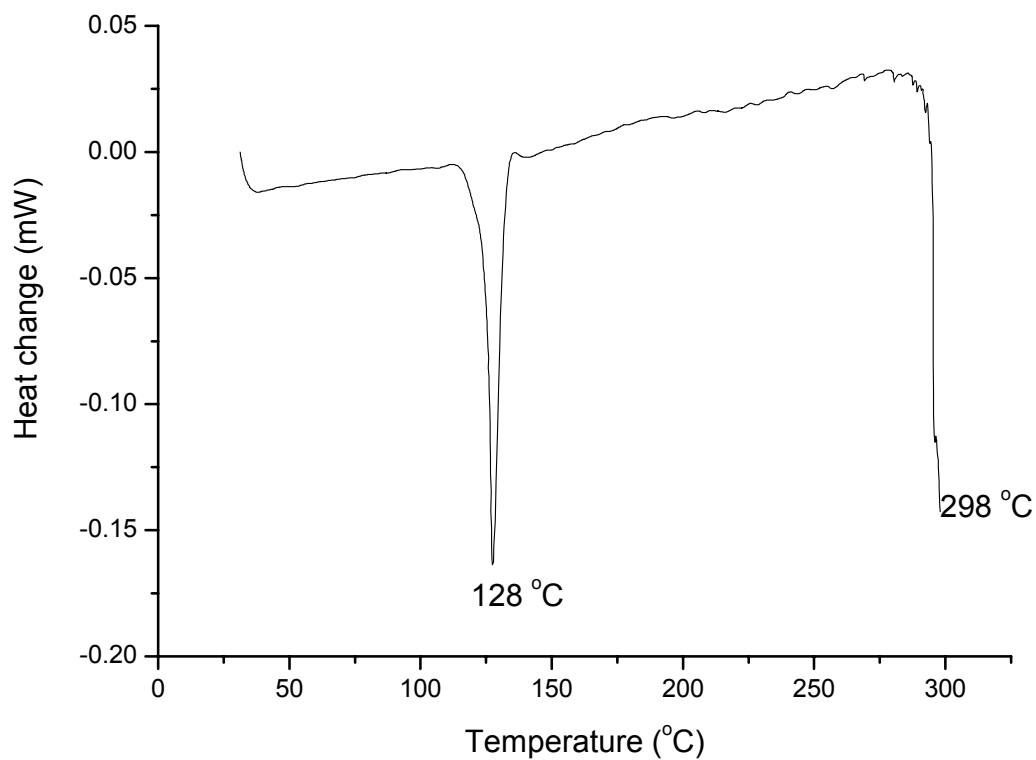


Figure 7.8: DSC scan of *cis*-Mo(CO)<sub>4</sub>(PPh<sub>2</sub>Me)<sub>2</sub> complex

**L = PPh<sub>2</sub>Et**

The TGA analysis of the *cis*-Mo(CO)<sub>4</sub>(PPh<sub>2</sub>Et)<sub>2</sub> complex (see figure 7.9) shows no mass change up to 171 °C. Beyond this temperature the complex decomposes leaving a residue with 22 % of the original mass. This also, is probably due to the loss of two phosphine ligands.

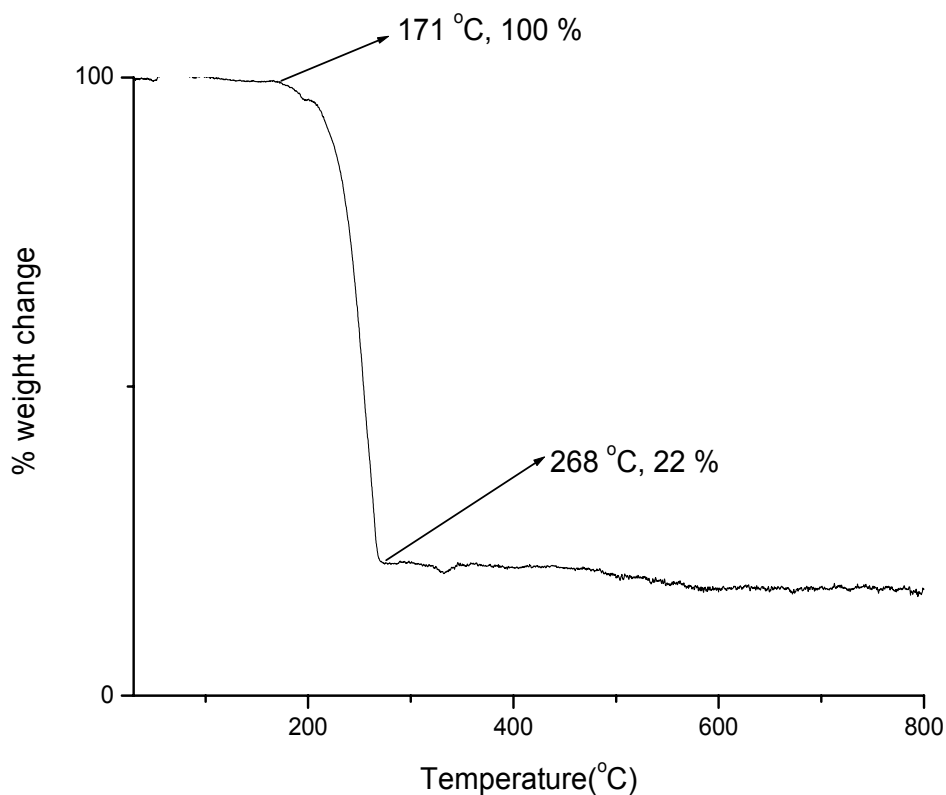


Fig 7.9: TGA profile of *cis*-Mo(CO)<sub>4</sub>(PPh<sub>2</sub>Et)<sub>2</sub> complex

The DSC of the *cis*-Mo(CO)<sub>4</sub>(PPh<sub>2</sub>Et)<sub>2</sub> shows two endotherms at 102 and 298 °C respectively (figure 7.10), similar to the *cis*-Mo(CO)<sub>4</sub>(PPh<sub>2</sub>Me)<sub>2</sub> complex. The slight differences are associated with the nature of the phosphine ligand used. The complex isomerizes in the melt when heated at 110 °C overnight. There is a small percentage *cis* isomer (19 %) left in the sample. There is only a slight conversion when the sample is

heated overnight at 100 °C. The sample also melted at this temperature. Isomerisation hence occurs in the melt as observed for the *cis*-Mo(CO)<sub>4</sub>(PPh<sub>2</sub>Me)<sub>2</sub> complex.

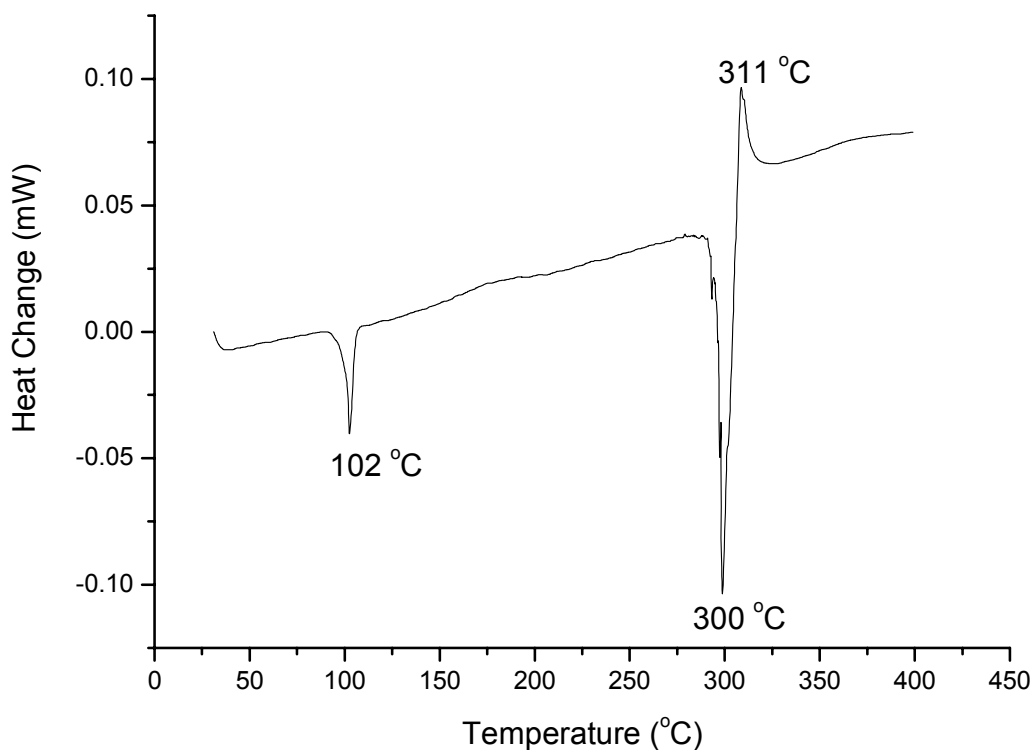


Figure 7.10: DSC profile of *cis*-Mo(CO)<sub>4</sub>(PPh<sub>2</sub>Et)<sub>2</sub>

### **L = P(OEt)<sub>3</sub>**

The DSC profile of the *cis*-Mo(CO)<sub>4</sub>[P(OEt)<sub>3</sub>]<sub>2</sub> (See figure 7.11) complex shows an endothermic peak at 93 °C, a small exothermic peak at 124 °C and another endothermic peak at 199 °C. The first endothermic peak is associated with the melting of *cis*-Mo(CO)<sub>4</sub>[P(OEt)<sub>3</sub>]<sub>2</sub>. The exothermic peak occurs because of the conversion of the *cis* isomer to the *trans* isomer. The conversion of this complex also occurs in the melt. After melting the complex solidifies and melts again at 199 °C generating the endotherm observed at this temperature.

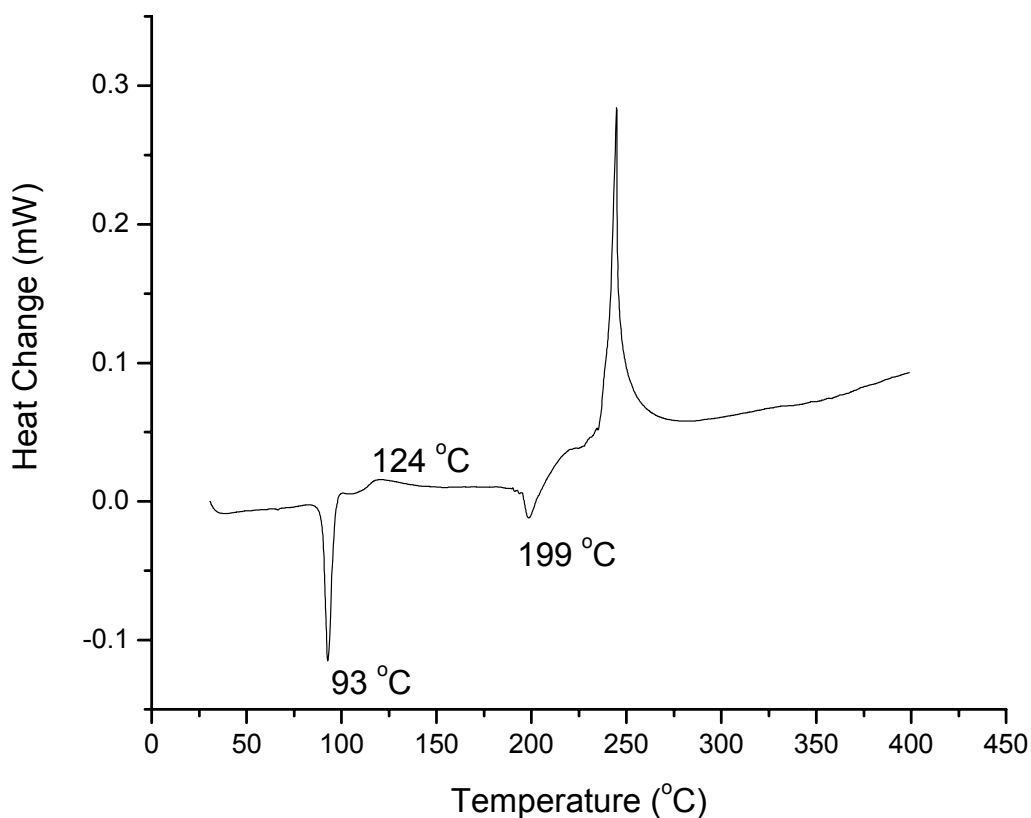


Figure 7.11: DSC of *cis*-Mo(CO)<sub>4</sub>{P(OEt)<sub>3</sub>}<sub>2</sub>

### 7.3.3 Summary

All the complexes changed colour to brownish and to a near black colour when heated for prolonged periods of time at temperatures higher than the isomerisation temperatures. There is always a phosphine oxide peak observed in the <sup>31</sup>P NMR spectrum when the complexes L = PPh<sub>3</sub> and P(*m*-tolyl)<sub>3</sub> are heated above 130 °C. Experiments done suggest that phosphine might be lost from the *trans* isomer (not the *cis*-isomer) since the peak is only observed after formation of the *trans*-isomer. The small mass loss that was observed between 180 to 200 °C for the two complexes could be due to decomposition of the *trans* isomer. This observation was not observed for L = PPh<sub>2</sub>Me and PPh<sub>2</sub>Et at these temperatures.

The  $L = PPh_3$  and  $P(m\text{-tolyl})_3$  complexes exhibit similar trends in both the DSC and TGA studies. The same is the case for  $L = PPh_2Me$  and  $PPh_2Et$  complexes. Two consecutive endotherms have been observed for these two complexes with no exotherm in between. The presence of the two endotherms could mean that the sample is a mixture of two compounds (or isomers). However, the NMR spectra of these two complexes show the presence of the *cis*-complex only. On heating at temperatures between these two endotherms, the complexes converted to their corresponding *trans*-isomers. This therefore suggest that the rearrangement reaction is not indicated by an exotherm in the DSC graph. However an exothermic peak due to the *cis* to *trans* isomerisation for the *cis*- $Mo(CO)_4\{P(OEt)_3\}_2$  has been observed. All the complexes lose the two phosphine ligands on decomposition.

#### 7.4 Conclusion

Synthesis and characterisation of  $Mo(CO)_4L_2$  ( $L = PPh_3, PPh_2Me, PPh_2Et$  and  $P(OEt)_3$ ) was carried out successfully. Thermal analysis of the complexes was done for the first time and the studies revealed that the *cis*- $Mo(CO)_4L_2$  complexes undergo a *cis* to *trans* isomerisation reaction under solventless conditions. It appears that this reaction can occur either in the solid state or melt phases. Decomposition of the material at higher temperatures appears to occur from the *trans*-isomer. The solventless isomerisation reactions are investigated in the next chapter.

## 7.5 References

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