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Solid-state isomerisation reactions of $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{M(CO)}_2(\text{PR}_3')\text{I}$ ($\text{M} = \text{W, Mo; R} = {}^t\text{Bu, Me; R}' = \text{Ph, O}^i\text{Pr}_3$)

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Abstract

The *cis* and *trans* monosubstituted cyclopentadienyl tungsten and molybdenum complexes $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{M(CO)}_2(\text{L})\text{I}$ (**1**) ($\text{M} = \text{W}$, $\text{R} = \text{Me}$, ${}^t\text{Bu}$, $\text{L} = \text{P(O}^i\text{Pr)}_3$, PPh_3; $\text{M} = \text{Mo}$, $\text{R} = \text{Me}$, $\text{L} = \text{PPh}_3$) have been synthesised and fully characterised by elemental analysis and IR and NMR spectroscopy. It was found that **1** underwent a thermal solid-state ligand isomerisation reaction and that the favoured direction of the isomerisation reaction is related to the melting points of the *cis* and *trans* isomers, i.e., with intermolecular forces in the solid state. No obvious relationship between the melting point and the metal, the ring-substituent or the ligand was observed. Crystal structure determinations of the *cis* and *trans* isomers of $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{W(CO)}_2(\text{PPh}_3)\text{I}$ reveal that a limited amount of isomer conversion can be accommodated in the unit cell of the *trans* isomer, prior to crystal fragmentation. The rearrangement of the molecules within the unit cell, during isomerisation, also leads to disorder in the crystal.

Keywords: Solid state; Substitution reaction; Molybdenum; Tungsten

1. Introduction

Isomerisation reactions in organometallic chemistry have a long and rich history [1]. Many systems have been studied over the last five decades and mechanisms entailing ligand rearrangements around a central metal atom have been described. Isomerisation at a ligand that is attached to a metal in an organometallic complex has also been reported [2]. In general as the number of ligands around a central metal atom increases the ease of ligand rearrangement around the metal increases, i.e., the activation energy for the rearrangement (isomerisation) reaction decreases. Consequently, isomerisation reactions of psuedo-seven coordinate complexes of the type $(\eta^5\text{-C}_5\text{H}_5)\text{ML}_4$ ($\eta^5\text{-C}_5\text{H}_5$ occupies three sites) generally require modest energy input and have been well studied. For example, early pioneering work on the separation and study of *cis* and *trans* (*lat* and *diag*) isomers of $(\eta^5\text{-C}_5\text{H}_5)\text{M(CO)}_2\text{LX}$ ($\text{M} = \text{Cr, Mo, W}$; $\text{X} = \text{halide}$) and $(\eta^5\text{-C}_5\text{H}_5)\text{Re(CO)}_2\text{Br}_2$ have provided a frame-work for many later studies [3]. With few exceptions these studies have been performed in the solution state.

Recently we have undertaken a study of the isomerisation reactions of a range of $(\eta^5\text{-C}_5\text{H}_5)\text{ML}_4$ complexes *in the solid state* [4]. Most of our earlier work focussed on Re complexes, where we observed that solution and solid-state isomerisation reactions could be different [4]. Indeed studies in the solid state revealed a possible alternative isomerisation reaction pathway to those found in solution.

We have now extended our studies to $(\eta^5\text{-C}_5\text{H}_5)\text{ML}_4$ ($\text{M} = \text{Mo, W}$) type complexes. In an earlier study we noted that $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mo(CO)}_2[\text{P(O}^i\text{Pr)}_3]\text{I}$ underwent a bidirectional *cis*/*trans* isomerisation reaction in the solid state that favoured the *trans* isomer (*trans*:*cis* = 70/30) [5]. Herein we report an extension of this earlier study to the solid-state *cis*/*trans* isomerisation reactions

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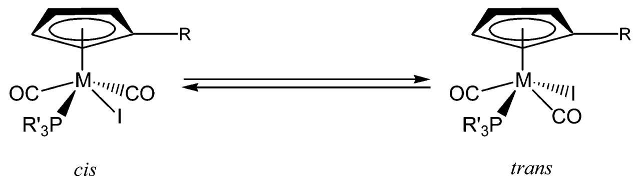

Fig. 1. The solid-state *cis–trans* isomerisation reactions of (η^5-C_5H_4R)M$(CO)_2(PR'_3)$I.

of (η^5-C_5H_4Me)M$(CO)_2(PPh_3)$I (M = Mo, W) and (η^5-C_5H_4R)W$(CO)_2[P(O^iPr)_3]$I (R = Me, ^{t}Bu) in order to evaluate the effect of ring substituents, metals and ligands on the solid-state reaction (Fig. 1). To our knowledge only two other reports on solid-state isomerisation reactions of similar Mo complexes have appeared in the literature [6,7].

2. Experimental

(η^5-C_5H_4Me)W$(CO)_3$I and (η^5-C_5H_4Me)Mo$(CO)_3$I were prepared by the standard procedures used to synthesise other ring-substituted analogues [8]. Trimethylamine N-oxide dihydrate (Aldrich) was used as received. All reactions were carried out using standard Schlenk techniques under nitrogen. Solvents were dried by conventional methods, distilled under nitrogen and used immediately. Melting points were recorded on a Kofler hot stage melting point apparatus. Infrared spectra were measured on a Midac FTIR spectrometer, usually in KBr cells (solutions). DSC profiles were measured on a Du Pont 911 DSC instrument and TGA data were measured on a Perkin–Elmer Pyris 1 thermal analyser. Powder X-ray diffraction data were collected on a Phillips PW 1710 diffractometer using a Cu tube anode. NMR spectra were measured on a Bruker AC200 spectrometer operating at 200 MHz. Microanalysis was carried out at the CSIR, Pretoria, South Africa.

2.1. *Preparation of trans- and cis-(η^5-C_5H_4Me)-M$(CO)_2(PPh_3)$I (M = W, Mo) and trans- and cis-(η^5-$C_5H_4{}^tBu$)W$(CO)_2$ (PR_3)I (R = Ph, O^iPr)*

A mixture of the *cis* and *trans* isomers were prepared in good yield (55–75%) by reaction of (η^5-C_5H_4R)M$(CO)_3$I with a 5–10-fold excess of ligand L and trimethylamine N-oxide in dichloromethane at room temperature [9]. The reaction proceeded slowly when only a stoichiometric amount of ligand or trimethylamine N-oxide was used. Isomer separation was achieved by dissolving the crude material in CH_2Cl_2 followed by mixing with a small quantity of silica gel. The yellow powder remaining after removal of CH_2Cl_2 was chromatographed on a silica gel column (2×60) with a 1:2 benzene/hexane mixture. For example (η^5-C_5H_4Me)Mo$(CO)_2(PPh_3)$I was obtained in 58% total yield (*cis* 32%, *trans* 26%). The pure isomers were characterised by mp, CHN analysis, IR and ^{1}H NMR spectroscopy (Tables 1 and 2) [10]. The complexes were stable at room temperature in the solid state and had good solubility in organic solvents, including hexane.

2.2. *Solid-state isomerisation of trans- and cis-(η^5-C_5H_4Me)M$(CO)_2(PPh_3)$I (M = Mo, W)*

About 5–10 mg of solid *cis*- or *trans*-(η^5-C_5H_4Me)-M$(CO)_2(PPh_3)$I was placed in a NMR tube under nitrogen and heated while totally immersed in an oil bath for 1–15 h at a temperature at least 15 °C below the lower melting point of the two isomers. The color and shape of the starting materials showed no visible change and no obvious decomposition during the heating process. The identification of the *cis* and *trans* products was achieved by means of TLC, and solution IR and NMR spectroscopy on the products after the reaction. The isomerisation direction in the solid state is given in Table 1.

Table 1
Solid-state isomerisation reactions of *cis* and *trans*-(η^5-C_5H_4R)M$(CO)_2(PR_3')$I complexes

Complex	m.p.[a] (°C)	Reaction temperature (°C)	Isomerisation direction[c]
cis-(η^5-C_5H_4Me)Mo$(CO)_2PPh_3$I	>141[b]	100–120	*trans* → *cis*
trans-(η^5-C_5H_4Me)Mo$(CO)_2PPh_3$I	>149[b]		
cis-(η^5-C_5H_4Me)W$(CO)_2[P(O^iPr)_3]$I	128–130	113–115	*cis* → *trans*
trans-(η^5-C_5H_4Me)W$(CO)_2[P(O^iPr)_3]$I	144–146		
cis-(η^5-C_5H_4Me)W$(CO)_2PPh_3$I	179–181	150–155	*trans* → *cis*
trans-(η^5-C_5H_4Me)W$(CO)_2PPh_3$I	177–179		
cis-(η^5-$C_5H_4{}^t$Bu)W$(CO)_2[P(O^iPr)_3]$I	135–137	100–105	*trans* → *cis*
trans-(η^5-$C_5H_4{}^t$Bu)W$(CO)_2[P(O^iPr)_3]$I	127–129		

[a] Melting point determined by melting point apparatus.
[b] Darkened.
[c] Determined by ^{1}H NMR spectroscopy.

Table 2
Spectroscopic and analytical data for (η^5-C_5H_4R)$Mo(CO)_2PR'_3I$ complexes

Compound	νCO[a] (cm^{-1})	^{1}H NMR (ppm)[b]			Analysis (%)		
		Cp	Me	Ligand		C	H
cis-(η^5-C_5H_4Me)$Mo(CO)_2PPh_3I$	1961	4.91 (m, 1H); 5.02 (t, 2H); 5.49 (m, 1H)	2.22 (s, 3H)	7.35–7.48 (m, 15H)	Calc.	50.35	3.57
	1875				Found	50.10	3.50
trans-(η^5-C_5H_4Me)$Mo(CO)_2PPh_3I$	1963	4.66(m, 2H); 4.94 (m, 2H)	2.26 (s, 3H)	7.39–7.44 (m, 15H)	Calc.	50.35	3.57
	1882				Found	50.12	3.68
cis-(η^5-C_5H_4Me)$W(CO)_2[P(O^iPr)_3]I$	1952	5.20 (m, 1H); 5.29 (m, 1H); 5.33 (m, 1H);	2.24 (s, 3H)	1.31 (m, 18H);	Calc.	31.21	4.31
	1864	5.36 (m, 1H)		4.59–4.64 (m, 3H)	Found	31.00	4.21
trans-(η^5-C_5H_4Me)$W(CO)_2[P(O^iPr)_3]I$	1956	5.12 (m, 2H); 5.20 (m, 2H)	2.32 (s, 3H)	1.32 (d, 18H);	Calc.	31.21	4.31
	1870			4.57–4.63 (m, 3H)	Found	30.96	4.15
cis-(η^5-C_5H_4Me)$W(CO)_2PPh_3I$	1950	5.04 (m, 1H); 5.16 (t, 2H); 5.64 (m, 1H)	2.31 (s, 3H)	7.28–7.73 (m, 15H)	Calc.	44.10	3.13
	1862				Found	43.50	2.91
trans-(η^5-C_5H_4Me)$W(CO)_2PPh_3I$	1953	4.75 (m, 2H); 4.97 (m, 2H)	2.36 (s, 3H)	7.36–7.73 (m, 15H)	Calc.	44.10	3.13
	1867				Found	43.80	2.84
cis-(η^5-$C_5H_4{}^tBu$)$W(CO)_2[P(O^iPr)_3]I$	1950	4.76 (m, 1H); 5.21 (m, 1H); 5.64 (m, 1H);	1.23 (s, 9H)	1.31 (m, 18H);	Calc.	34.50	4.92
	1864	5.74 (m, 1H)		4.57–4.66 (m, 3H)	Found	34.56	4.96
trans-(η^5-$C_5H_4{}^tBu$)$W(CO)_2[P(O^iPr)_3]I$	1956	5.10 (m, 2H); 5.19(m, 2H)	1.29 (s, 9H)	1.32 (d, 18H);	Calc.	34.50	4.92
	1871			4.58–4.64 (m, 3H)	Found	34.10	4.80

[a] Recorded in CH_2Cl_2.
[b] Recorded in $CDCl_3$, relative to TMS: s, singlet; m, multiplet.

2.3. Powder XRD study

The *trans* isomer (40 mg) was packed into an NMR tube and immersed completely into an oil bath (120 °C) for 80 min. Powder diffraction data were then recorded on the solid mixture. Powder diffraction data were also recorded on pure *cis* and *trans* isomers.

2.4. Single crystal XRD study of cis- and trans-(η^5-C_5H_4Me)$W(CO)_2(PPh_3)I$

The *cis* and *trans* isomers of (η^5-C_5H_4Me)-$W(CO)_2(PPh_3)I$ complexes were synthesised as described above and recrystallised from a mixture of hexane/dichloromethane under nitrogen at room temperature.

For both structures, intensity data were collected on a Bruker SMART 1K CCD area detector diffractometer with graphite monochromated Mo Kα radiation (50 kV, 30 mA). The collection method involved ω-scans of width 0.3°. Data reduction was carried out using the program SAINT+ [11] and absorption corrections were made using the program SADABS [11]. The structures were solved by standard Patterson procedures and refined by least-squares methods based on F^2. The SHELX [12] suite of programs, as incorporated into WINGX [13], were used for all crystallographic computations. In the final stages of refinement hydrogen atoms for both *cis* and *trans* isomers were placed in geometrically calculated positions and refined in riding mode with displacement parameters linked to those of their connected carbon atoms.

Numerical data pertaining to the experimental measurement and details of the structure analyses are given in Table 3.

Significant disorder was observed in the *trans* isomer. Both the cyclopentadienyl methyl group and the carbonyl/iodine positions are disordered, but not to the same extent. The cyclopentadienyl methyl group is disordered over two positions. In the refinement, the occupancy of the two sites was initially allowed to vary, converging to a site occupancy factor of ~0.49:0.51 for each site. This was fixed to 0.50 for both sites in the final cycles of the refinement. The iodine was also disordered, with about 11% of the molecules in the crystal having Iodine (I1b) occupying the position of the *trans*-carbonyl site (C(1)O(1)). The corresponding carbonyl in the I1a site (11% *cis*) could not be unambiguously identified.

The crystal data (Table 3) for both isomers are, to a very large extent, similar. Further, both structures have a monoclinic space group. The atomic numbering scheme for the *trans* isomer and the *cis* isomer are shown in the ORTEP diagrams [14] (Figs. 2 and 3). The packing diagrams (line drawings) of both isomers, viewed down the *a*-axis, are shown in Figs. 4 and 5.

Table 3
Crystal data and structure refinement for the *cis* and *trans* isomers of (η^5-C_5H_4Me)W(CO)$_2$(PPh$_3$)I

	trans isomer	*cis* isomer
Empirical formula	$C_{26}H_{22}IO_2PW$	$C_{26}H_{22}IO_2PW$
Formula weight	708.16	708.16
Temperature (K)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
Unit cell dimensions	$a = 10.4696(5)$ Å, $\alpha = 90°$ $b = 16.0379(9)$ Å, $\beta = 94.493(1)°$ $c = 14.6428(8)$ Å, $\gamma = 90°$	$a = 9.0325(5)$ Å, $\alpha = 90°$ $b = 15.0013(8)$ Å, $\beta = 99.802(1)°$ $c = 17.9727(10)$ Å, $\gamma = 90°$
Volume (Å^3)	2451.1(2)	2399.7(2)
Z, D_{calc} (mg m^{-3})	4, 1.919	4, 1.960
Absorption coefficient (mm^{-1})	6.057	6.187
$F(000)$	1344	1344
Crystal size	0.36 mm × 0.22 mm × 0.20 mm	0.70 mm × 0.40 mm × 0.18 mm
θ range for data collection (°)	1.89–28.28	1.78–28.25
Index ranges	$-10 \leqslant h \leqslant 13$, $-16 \leqslant k \leqslant 21$, $-18 \leqslant l \leqslant 19$	$-11 \leqslant h \leqslant 11$, $-19 \leqslant k \leqslant 19$, $-23 \leqslant l$ 20
Reflections collected/unique	14232/5451 [$R_{int} = 0.0434$]	14750/5438 [$R_{int} = 0.0271$]
Completeness to $2\theta = 25°$ (%)	99.3	99.6
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5451/12/290	5438/0/269
Goodness-of-fit on F^2	1.138	1.188
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0776$, $wR_2 = 0.1546$	$R_1 = 0.0281$, $wR_2 = 0.0648$
R indices (all data)	$R_1 = 0.1091$, $wR_2 = 0.1670$	$R_1 = 0.0316$, $wR_2 = 0.0665$
Largest difference peak and hole (e A^{-3})	3.222 and −2.140	0.617 and −1.309

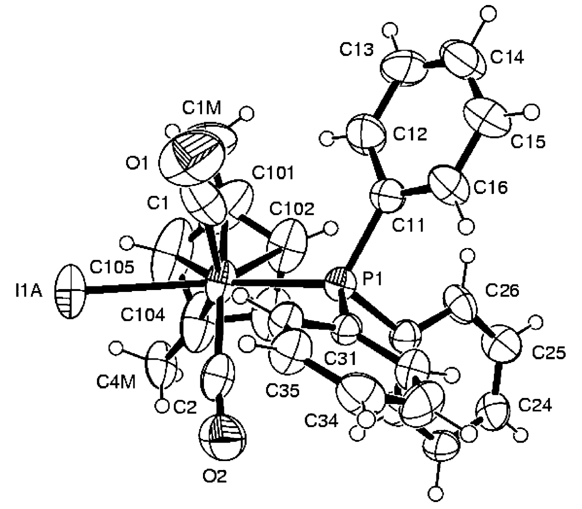

Fig. 2. An ORTEP plot of *trans*-(η^5-C_5H_4Me)W(CO)$_2$(PPh$_3$)I.

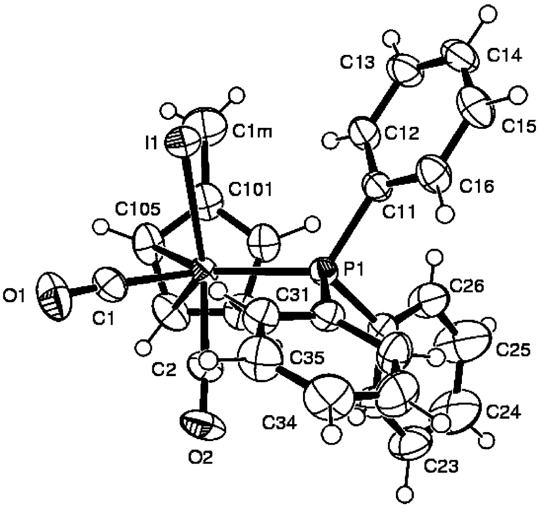

Fig. 3. An ORTEP plot of *cis*-(η^5-C_5H_4Me)W(CO)$_2$(PPh$_3$)I.

Selected bond lengths (Å) and bond angles (°) are given in Table 4.

Crystallographic data were deposited with the Cambridge Data Base (Ref. # CCDC 231709 and 231710)

3. Results and discussion

3.1. Synthesis

The synthetic strategy used to make the *cis* and *trans* Mo and W complexes followed standard procedures. The complexes were characterised by elemental analyses, and IR and NMR spectroscopy. The *cis* and *trans* isomers could readily be identified by NMR spectroscopy [3a,10] and were also characterised by single crystal X-ray crystallography which confirmed the spectroscopic results (see below).

3.2. Isomerisation direction and melting points

The isomerisation reactions for the new complexes were studied and the general trend was for the isomerisation reaction to occur from the *trans* to the *cis*

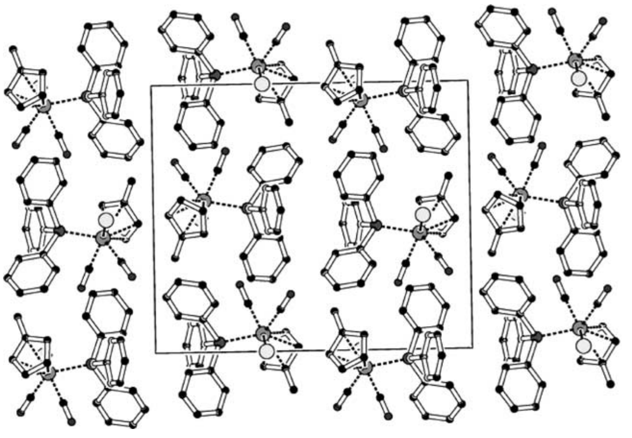

Fig. 4. A packing diagram of *cis*-(η^5-C_5H_4Me)W(CO)$_2$(PPh$_3$)I viewed down *a*-axis.

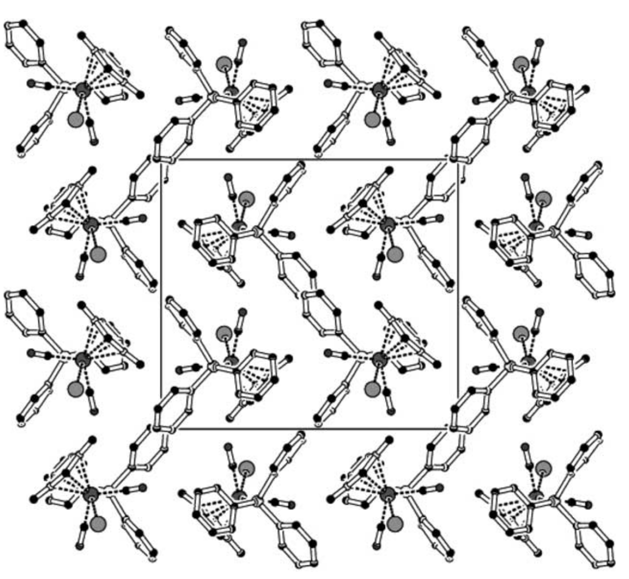

Fig. 5. A packing diagram of *trans*-(η^5-C_5H_4Me)W(CO)$_2$(PPh$_3$)I viewed down *a*-axis.

Table 4
Selected bond lengths (Å) and angles (°) for the *trans* and *cis* isomers

	trans isomer	*cis* isomer
W(1)–C(1)	1.992(1)	1.976(1)
W(1)–C(2)	1.926(11)	1.941(1)
W(1)–P(1)	2.465(3)	2.513(1)
W(1)–I(1)	2.838(1)	2.855(1)
C(2)–W(1)–C(1)	111.7(4)	72.81(1)
C(2)–W(1)–P(1)	78.7(1)	77.67(2)
C(1)–W(1)–I(1)	80.3(1)	122.40(1)
C(2)–W(1)–I(1)	78.9(1)	121.59(1)
C(1)–W(1)–I(1)	74.3(1)	74.26(1)
P(1)–W(1)–I(1)	136.7(1)	81.22(2)

isomer. However, for (η^5-C_5H_4Me)W(CO)$_2$[P(O^{i}Pr)$_3$]I, a *cis–trans* reaction was observed. This clearly indicates that the direction of the solid-state reaction is not dependent on electronic factors associated with ligand orientation effects.

3.3. Heating studies on (η^5-C_5H_4Me)Mo(CO)$_2$(PPh$_3$)I

TGA profiles for the *cis* and *trans* isomers are shown in Fig. 6. The data reveal that significant mass loss only occurs above 140 °C. ^{31}P NMR spectra recorded on the samples heated above 100 °C revealed the presence of PPh$_3$O ($\delta = 29.84$ ppm) in the samples.

The DSC profiles for *cis*-(η^5-C_5H_4Me)Mo(CO)$_2$(PPh$_3$)I at different heating rates are shown in Fig. 7. Exotherms can be seen at $T > 120$ °C. Similar profiles for *trans*-(η^5-C_5H_4Me)Mo(CO)$_2$(PPh$_3$)I, at different heating rates, are shown in Fig. 8, but here a further broad exotherm (denoted by *) is noted at about 90 °C.

In a separate study *trans* samples were heated in the DSC (heating rate = 10 °C min^{-1}) and the heating was discontinued when the temperature reached 80, 100, 120 and 130 °C, respectively. NMR spectra were then recorded on the samples. From this study a 70/30 *cis*/*trans* isomer ratio of (η^5-C_5H_4Me)Mo(CO)$_2$(PPh$_3$)I was

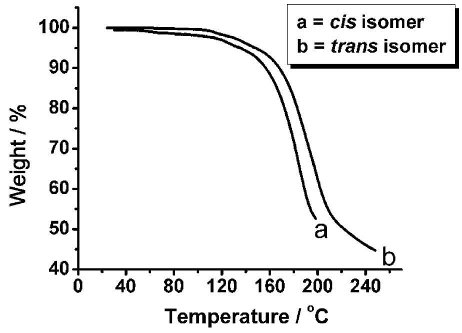

Fig. 6. TGA profiles for the *cis* and *trans* isomers of (η^5-C_5H_4R)Mo(CO)$_2$(PPh$_3$)I.

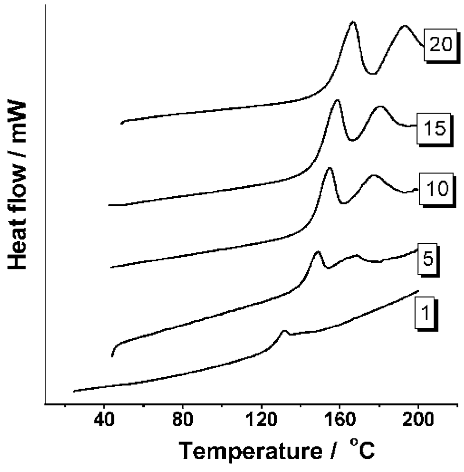

Fig. 7. DSC profile of *cis*-(η^5-C_5H_4Me)Mo(CO)$_2$(PPh$_3$)I as a function of scanning rate (°C min^{-1}).

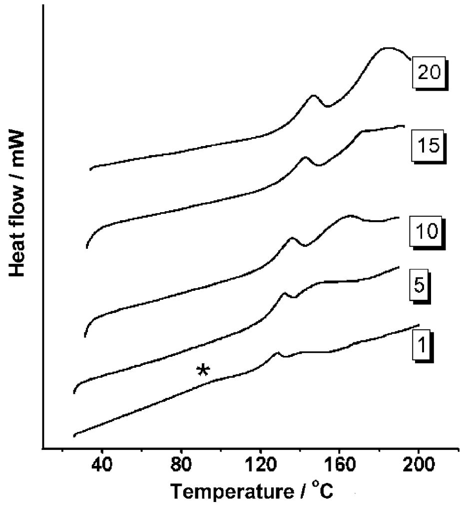

Fig. 8. DSC profile of *trans*-(η^5-C$_5$H$_4$Me)Mo(CO)$_2$(PPh$_3$)I as a function of scanning rate (°C min^{-1}).

obtained only for samples heated above 100 °C. Thus, the broad exotherm at 90 °C (Fig. 8) represents the exotherm for the *trans*/*cis* isomerisation reaction.

Although expected, no equivalent exotherm was detected in the DSC for the *cis* isomer, a finding that may relate to the low% isomer conversion (30%).

A third exotherm (shown by both *cis* and *trans* isomers) occurs above 180 °C and corresponds to the material decomposition temperature, consistent with the TGA data (see above).

3.4. Heating studies on *(η^5-C$_5$H$_4$Me)W(CO)$_2$(P(O^{i}Pr)$_3$)I*

The *solid-state* isomerisation reaction of (η^5-C$_5$H$_4$Me)W(CO)$_2$[P(O^{i}Pr)$_3$]I unexpectedly proceeds from the *cis–trans* isomer at $T < 105$ °C. This reaction was investigated further by thermomicroscopy and DSC. Under a microscope the red *cis*-(η^5-C$_5$H$_4$Me)W(CO)$_2$[P(O^{i}Pr)$_3$]I crystals, on heating, first melted at 128–130 °C, then quickly resolidified and remelted at 141–142 °C, the latter temperature being close to that of the melting point of the *trans* isomer (m.p. 144–146 °C). Silica gel TLC and IR and NMR spectroscopy confirmed that the *cis* isomer had converted to the *trans* product after the melting point process. Indeed, when *cis*-(η^5-C$_5$H$_4$Me)W(CO)$_2$[P(O^{i}Pr)$_3$]I was heated at 132 °C (in the molten state) for 15 min, 70% of the *trans* isomer was produced. Further, a DSC spectrum recorded on the material after this procedure revealed that the endothermic melting peak of *cis*-(η^5-C$_5$H$_4$R)-W(CO)$_2$[P(O^{i}Pr)$_3$]I was no longer observed (heating rate: 1.0 °C min^{-1}). The endothermic peak at 143 °C corresponding to the melting point of the *trans* isomer was still noted. Silica gel TLC, and IR and NMR spectroscopy confirmed that the *cis*-(η^5-C$_5$H$_4$Me)W(CO)$_2$[P(O^{i}Pr)$_3$]I complex isomerised into the corresponding *trans* isomer during the DSC measurement.

The data show that the isomerisation reaction (η^5-C$_5$H$_4$Me)W(CO)$_2$[P(O^{i}Pr)$_3$]I *proceeds both in the solid state and in the melt.*

3.5. Kinetic study on trans- and cis-*(η^5-C$_5$H$_4$Me)Mo(CO)$_2$(PPh$_3$)I*

The above studies suggested that a kinetic investigation of the solid-state isomerisation reaction was possible in the temperature regime 80–120 °C.

Reactions were performed on both the solid isomers of (η^5-C$_5$H$_4$Me)Mo(CO)$_2$(PPh$_3$)I in NMR tubes as described in Section 2. Because both isomers had similar red colors, the solid-state isomerisation reactions of the molybdenum (or tungsten) complexes could not be monitored visually and were only monitored after appropriate time periods by silica gel TLC, IR and NMR spectroscopy (^{1}H, ^{31}P). The kinetic data for isomerisation of the *trans* isomer (110–120 °C) are shown in Fig. 9. If the reaction temperature was lowered to 90 or 100 °C, then very long reaction times (days) are required for significant reaction. At higher temperature (>135 °C), decomposition of the reactant was observed. Analysis of the reactants revealed that the *cis* isomer is thermally unstable at high temperature and shows about 30% conversion to the *trans* isomer, triphenylphosphine oxide and an unidentified product.

The same equilibrium mixture of *cis*/*trans* isomers is reached from either isomer and the isomer ratio does not vary significantly in the temperature range studied. The data thus reveal a bi-directional isomer reaction. Rate constants for the reactions were determined, assuming opposing first-order reactions [15], and the *k* values for the reactions were used in an Arrhenius plot to give an activation energy (<160 kJ mol^{-1}) for the reaction. Some curvature was noted in the Arrhenius plot. This could have arisen from a number of sources: (i) diffu-

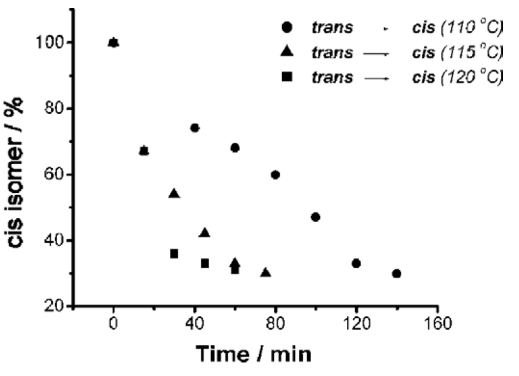

Fig. 9. The kinetic data for isomerisation of the *trans* isomer (110–120 °C).

sional effects, (ii) decomposition effects and (iii) the possibility that the reaction follows a more complex mechanism. The activation data are to be compared with the value for the solvent phase reaction (($(\eta^5$-$C_5H_5)Mo(CO)_2(PPh_3)I = 108$ kJ mol^{-1} in *o*-dichlorobenzene [10]) and for the corresponding solid-state reaction for $(C_5H_4Me)Mo(CO)_2[P(O^iPr)_3]I$ (>68 kJ mol^{-1}) [5].

3.6. Powder XRD analysis

The XRD profiles of the pure *trans*- and *cis*-(η^5-$C_5H_4Me)Mo(CO)_2(PPh_3)I$ isomers are quite distinctive and provide a possible means of monitoring the isomerisation reaction in the solid state (data not shown). The profiles show that after 80-min reaction (120 °C) the *trans* isomer had partially been converted to the *cis* isomer and confirmed the analysis of the reaction monitored by NMR spectroscopy (30/70, *trans*/*cis* ratio, similar reaction conditions). Attempts were made to obtain kinetic data from the analysis of the powder diffraction data, but quantification of the results was not achieved.

3.7. Single crystal XRD analysis

Single crystals of pairs of isomers were only obtained for *trans*- and *cis*-(η^5-$C_5H_4Me)W(CO)_2(PPh_3)I$. Single crystal analysis was thus performed on these two isomers. Relevant bond length/angle data are given in Table 4. The ORTEP plots of the *cis* and *trans* isomers of (η^5-$C_5H_4Me)W(CO)_2(PPh_3)I$ are shown in Figs. 2 and 3. The bond length/angle data for both isomers are, to a very large extent, similar. The analysis confirmed the basic structure of the isomers; no unexpected bond lengths or angles were noted.

A search of the Cambridge Data File [16] revealed that no piano-stool cyclopentadienyl tungsten complexes of the type (η^5-$C_5H_4R)W(CO)_2LI$ have previously been reported although the structure of *trans*-(η^5-C_5H_5)-$Mo(CO)_2(PPh_3)I$ [17] has been documented. Only slight differences in the Mo and W structures are expected, and were found, and these related to the slightly different sizes of the metal atoms.

Refinement of the *trans* isomer revealed that the structure was disordered. One of the CO groups and the iodine atom were interchangeable, i.e., the *trans* isomer contained 11% of the *cis*-isomer in the crystal structure after refinement. A second disorder was also observed. The methyl group attached to the cyclopentadienyl ring of the *trans* isomer refined in two separate positions (50% occupancy).

Packing diagrams for the two isomers are shown in Figs. 4 and 5. If one considers the cyclopentadienyl ring and the PPh_3 groups as “anchors”, then the geometry of the three remaining groups are almost superimposable in the two isomers. Further, the methyl groups on the cyclopentadienyl ring of the respective isomers are also seen to be in similar positions. This feature suggests that, provided a low energy barrier exists between the two isomers, the possibility of isomer interconversion should be trivial. Thus, a simple rotation of a CO and I ligand through 180 ° could relate the two structures [4c].

The cell volume of the *trans* isomer (2451.1 Å^3) is slightly larger (2% different) than that of the *cis* isomer (2399.7 Å^3). Notwithstanding the cell volume change no unusual non-bonded distances in either of the isomers were noted.

If the triphenylphosphine part of the molecule is treated as the “tail” of the molecule and the cyclopentadienyl ring as the “head”, a “tail to tail” and “head to head” packing can be observed for the *cis* isomer in Fig. 5. A centre of symmetry relates two columns of the isomer. The packing of the *trans* isomer in a unit cell shows a “head to tail” arrangement and a “tail to head” arrangement. Noteworthy is the observation that if the molecules of the *trans* isomer in the packing diagram undergo a translation by half a unit cell, then a “tail to tail” and “head to head” arrangement similar to that of the *cis* isomer would result. This could provide a means of generating the required new arrangement of molecules in the unit cell after a *trans* → *cis* isomerisation reaction of the compound on heating.

3.8. Solution state isomerisation reactions of cis and trans-(η^5-$C_5H_4R)M(CO)_2(L)I$

The *cis*- and *trans*-(η^5-$C_5H_4R)M(CO)_2(L)I$ complexes are stable in solution (e.g., $CHCl_3$, benzene) at room temperature for a period of hours. However, when refluxed in benzene they quickly isomerised to a thermodynamic equilibrium mixture. Thus, when *cis*-(η^5-$C_5H_4Me)Mo(CO)_2(PPh_3)I$ was refluxed in benzene (or $CHCl_3$) for 4 h, a [*trans*]/[*cis*] ratio, 70/30, was achieved. The corresponding *trans* isomer reached the same equilibrium ratio in 12 h in refluxing CH_2Cl_2. This result shows that the solution state isomerisation of (η^5-$C_5H_4R)M(CO)_2(L)I$ is also bidirectional. Similar equilibrium studies on (η^5-$C_5H_5)Mo(CO)_2(L)X$ ($L = PPh_3$, PBu_3; $X = Br$, I) [6] and (η^5-$C_5H_4R)M(CO)_2(L)I$ ($R = Me$, ^tBu, $SiMe_3$; L = isonitrile, phosphine, phosphite) [9b] in refluxing benzene have also been reported. It is noteworthy that, even in the solution state, PPh_3O was observed in the ^1H and ^{31}P NMR spectra.

3.9. Mechanism

Earlier work suggested that the direction of the reaction related to a *trans*–*cis* geometry preference and that this could be associated with intramolecular effects [18]. The current data suggest that not even this influence determines the isomerisation direction. Thus, the choice of the metal M, the ring-substituent R and the ligand L do not appear to be the factors that by themselves determine the direction of the reaction, nor whether the reaction will proceed or not [19]. The only property that correlates with the *direction* of the solid-state isomerisation reaction of (η^5-C_5H_4R)M(CO)$_2$(L)I (**1**) (M = W, Mo) is the melting point of the *cis* and *trans* isomers [4b]. The favoured reaction direction is *always* from the low melting point isomer to the high melting point isomer; when the differences are small, isomer mixtures are formed. This suggests that the intermolecular interactions cannot simply relate to *cis*/*trans* intermolecular polar effects in the solid state. Even this melting point information is no guarantee that a reaction will proceed [4b], which suggests that the 'shape' of the molecule and the way in which it sterically interacts with its nearest neighbours will determine the preferred solid-state isomer.

The intermolecular forces that dominate in the solid phase could thus be both steric (phase rebuilding [20], topotatic [21]) or electronic in nature. Thus, an understanding of the reaction is possible from solid state packing information [22]. However, no significant intermolecular interactions were observed between the molecules in the unit cells.

In earlier studies we determined that the *cis–trans* isomerisation reaction of Re complexes was consistent with a Turnstile type mechanism (this could involve rotation of two or three of the small ligands (CO, X)). The same could apply here. The single crystals became opaque as the isomerisation reaction proceeded, eventually disintegrating into small crystallites.

However, the structural analysis provided information via the disorder content. Part of this disorder related to the presence of *cis* isomer (11%) in the *trans* isomer. This would suggest that at low conversions, the *cis* isomer is accommodated within the unit cell of the *trans* isomer. This phenomenon of a major structural isomer determining the structure of a minor isomer has precedent in the work of Sacconi et al. [23] and has been referred to as 'structure mimicry'. Disorder in the cyclopentadienyl ring is indicative of the strain that must be built up (50% disorder) as the reaction progresses.

Further, even though both unit cells are monoclinic, the arrangement of atoms within the unit cells of the two isomers is different.

The proposed mechanism suggests that in the early stages of reaction, a *cis–trans* isomerisation reaction occurs prior to inter-molecule rearrangement. Eventually the rearrangement of molecules will result in intermolecular stresses in the unit cell and subsequent break up of the crystalline phase. Whether indeed the *cis* isomer formed in the *trans–cis* reaction is a poymorph of the *cis* isomer formed by crystallisation procedures cannot be addressed by the data at hand.

4. Conclusions

The *trans* and *cis* isomers of the tungsten and molybdenum complexes (η^5-C_5H_4R)M(CO)$_2$(L)I (M = W, R = Me, ^{t}Bu, L = P(O^{i}Pr)$_3$, PPh$_3$; M = Mo, R = Me, L = PPh$_3$) have been synthesised and fully characterised by elemental analysis and IR and NMR spectroscopy. Unlike the rhenium complexes (η^5-C_5H_4R)Re(CO)(L)X$_2$, the tungsten and molybdenum complexes (η^5-C_5H_4R)M(CO)$_2$(L)I undergo a *bidirectional* thermal solid-state isomerisation reaction. A key finding was the discovery that the direction of the reaction could not be correlated with a particular isomer. The only correlation noted is that the direction of the isomerisation reaction is determined by melting points, i.e., the reaction preferentially goes from the low melting point isomer to the high melting point isomer.

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