CHAPTER 4

SYNTHESIS, CHARACTERIZATION AND SOLID STATE REACTIONS OF RUTHENIUM COMPLEXES

4.0 Introduction

Solid phase reactions of some ruthenium (II) complexes, $Ru(Cl)_2(CO)_x(PR_3)_{3-x}$, ($PR_3$ = $PMePh_2$, PMe_2Ph, PMe_3, $P(CH_2C_6H_5)_3$, x = 1, 2) have been reported in the literature and the studies revealed ligand isomerisation reactions in the temperature range 140 – 180 °C [1, 2] (See figure 4.1)

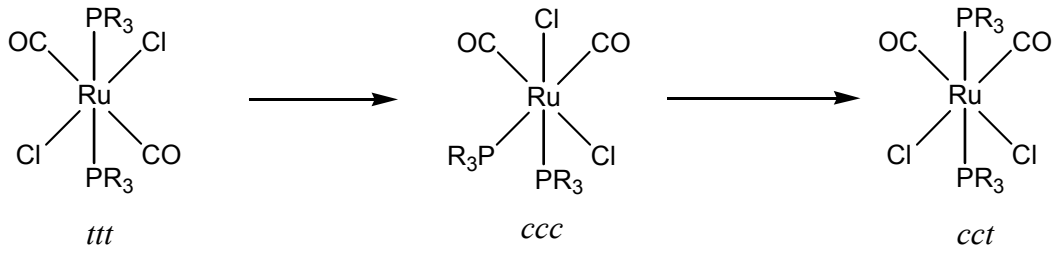


Figure 4.1: Solid state isomerisation of *ttt*-$RuCl_2(CO)_2(PR_3)_2$ complexes.

DSC and TGA analysis showed that no mass loss occurred at the phase change (exothermic) which corresponded to the isomerisation reaction. Results showed no clear correlation between heats of isomerisation (H_i) and heats of formation (H_f) with

properties of the phosphine ligand and no clear trends were observed. Furthermore, in most instances the *trans* to *cis* isomerisation reaction (from the *ttt* to the *cct* isomer) entailed movement of small groups with exchange of a CO and Cl group (see Figure 4.1 above). In general the reaction did not entail movement of a large phosphine ligand. By contrast, formation of the *ccc*-isomer was found in solution. An exception was *ccc*-$RuCl_2(CO)_2(PPh_2Me)_2$ which isomerised in the solid state to the *cct*-isomer, thus involving movement of the bulky phosphine group. However 'considerable compression' of the sample was noted and it is possible that the reaction took place in the melt [2]. This study made no comment on the solid state reaction mechanism of the complexes, although previous work on these complexes in solution revealed an isomerisation reaction which is consistent with a ligand dissociative process. The isomerisation rates decreased with increasing phosphine basicity and decreasing phosphine steric bulk [2].

A later study of related complexes of $RuCl_2(RNC)_{4-x}(PR^*_3)_x$ (R = xyl, 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 (Figure 4.2) [3].

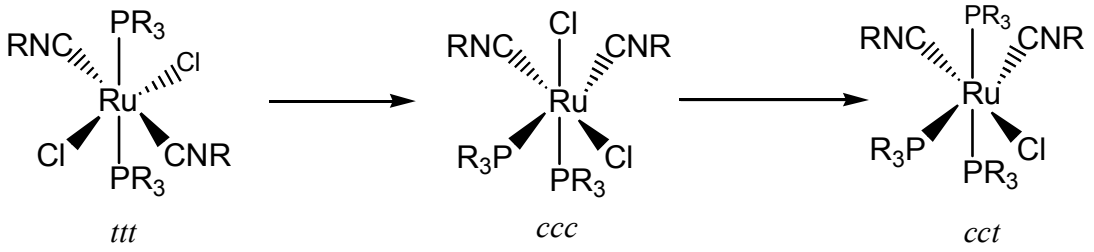


Figure 4.2: Solid state isomerisation of *ttt*-$RuCl_2(RNC)_{4-x}(PR^*_3)_x$ complexes

The study revealed that even complexes that contained bulky phosphine and bulky isonitrile ligands underwent an isomerisation reaction. No comment was made about the mechanism of the reaction.

From the above studies it is clear that interesting solvent free reactions had been detected. The use of alternative techniques to those used in initial studies could provide further information on these reactions of ruthenium. In particular the use of optical microscopy provides a means of observing the possible changes that occur during a solvent free reaction. Furthermore the use of new CCD detectors has made data collection of crystals by X-ray crystallography a facile process and opens up the possibility of monitoring reactions in single crystals.

It was thus decided to synthesise and study a range of ruthenium complexes related to those reported earlier. In this chapter we report on the synthesis of these complexes. Synthesis of the *ttt*-$RuCl_2(RNC)_2(PPh_3)_2$ complexes was therefore undertaken to study the kinetics and determine the mechanism of the isomerisation process of these ruthenium complexes.

4.1 Experimental

The RNC ligands (R = ^{t}Bu, 2,6-xylyl, benzyl, and ^{i}Pr) were obtained from Strem Chemicals. 2-MeO-4-Cl-C_6H_4NC (OMeClPhNC) was obtained as a gift from Dr M Layh of the School of Chemistry. $RuCl_2(PPh_3)_3$ was prepared by known procedures [4] The dichloromethane and diethyl ether were distilled over $LiAlH_4$ and Na/benzophenone respectively. The known complexes *ttt*-$RuX_2(RNC)_2(PPh_3)_2$ (X = Cl or Br; R = ^{t}Bu, 2,6-xylyl) were prepared by modification of the literature method [5]. The corresponding *cct*-isomers were prepared by heating the *ttt*-isomers at high temperature in the solid-state.
Thermal analysis was carried out on ~10 mg samples under flowing nitrogen at a constant heating rate of 10 ^{o}C/min with a Du Pont Instruments 910 Differential Scanning Calorimeter for monitoring phase changes. Solution IR spectra were measured in CH_2Cl_2 on a Brucker VECTOR 22 FTIR spectrometer. The ^{1}HNMR spectra were measured on a Brucker AVANCE 300 NMR spectrometer in $CDCl_3$ with TMS as the reference.

4.1.1 Solution Synthesis of $RuCl_2(RNC)_2(PPh_3)_2$

A mixture of $RuCl_2(PPh_3)_3$ (1.0 g, 1.04 mmol) and ^tBuNC (0.189 g, 2.28 mmol) was dissolved in 30 ml freshly distilled CH_2Cl_2. The mixture was stirred for 1 hour. The solvent was removed in vacuo and the orange residue was washed with 3 x 25 ml portions of diethyl ether. The solid was dried under vacuum overnight. Yield = 0.716 g (80 %). An analogous procedure was followed for the synthesis of *ttt*-$RuCl_2$(2,6-xylylNC)$_2(PPh_3)_2$ 0.848 g (85 %), *ttt*-$RuCl_2$(benzylNC)$_2(PPh_3)_2$ 0.642 g (67 %), *ttt*-$RuCl_2$(MeClPhNC)$_2(PPh_3)_2$ 0.213 g (20 %) and *ttt*-$RuCl_2(^iPrNC)_2(PPh_3)_2$ 0.671 g (78 %). IR and NMR data for the complexes are recorded in Tables 4.1 and 4.2 respectively and the DSC data in Table 4.3. Elemental analysis data (for the new complexes): $RuCl_2(MeClPhNC)_2(PPh_3)_2$ *Anal. found*: C, 59.93; N, 2.99; H, 3.99; calcd: C, 60.53; N, 2.72; H, 4.10. *ttt*-$RuCl_2(^iPrNC)_2(PPh_3)_2$ *Anal. found*: C, 63.12; N, 3.33; H, 5.34; calcd: C, 63.31; N, 3.36; H, 5.31.

4.1.2 Purification of $RuCl_2(^tBuNC)_2(PPh_3)_2$

The compound was prepared as in Section 4.1.1. The compound was columned on silica gel 60 and eluted with a 1:9 hexane:CH_2Cl_2 mixture. A yellow band was collected. Solvent was removed by means of a rotary evaporator leaving behind an orange solid. Yield (0.070 g, 7.82 %).

Table 4.1: IR spectra of *ttt*- and *cct*-$RuCl_2(RNC)_2(PPh_3)_2$ complexes.(υCN bands)[a]

R	ttt–isomer /cm $^{-1}$	cct–isomer /cm^{-1}
^{t}Bu	2126 [b] (2130)[b] [ref 5]	2112, 2154 (2116, 2150) [ref 3]
Xylyl	2095 (2090) [ref 5]	2094, 2141 (2096, 2142) [ref 3]
Benzyl	2134	2131, 2176
^{i}Propyl	2131	2119, 2166
MeClPhNC[c]	2082, 2105	2082, 2144, 2105(sh)

[a] values recorded in CH_2Cl_2, [b]values in brackets are literature values in nujol mull [c] extra peaks may be associated with restricted rotation of the RNC ligand.

Table 4.2: ^{1}H NMR data for the *ttt*- and *cct*-$RuCl_2(RNC)_2(PPh_3)_2$ complexes. [a]

Isomer	R	CH_x region/ppm	Phenyl region/ppm
ttt	^{t}Bu	1.0 (s) (1.0) [ref 5]	7.26 – 7.33(m), 7.80 – 7.87 (m), (7.2 - 8.2)
cct	^{t}Bu	0.72 (s)	7.31 – 7.34(m), 7.86 – 7.90 (m)
ttt	2,6-Xylyl	2.05 (s) (2.0) [ref 5]	6.91(d), 6.94 (t), 7.10 – 7.14 (m), 7.78 – 7.85 (m) (7.2 – 8.2)
cct	2,6-Xylyl	1.81(s)	6.81(d), 6.92 (t),7.05 – 7.09 (m), 7.88 – 7.94 (m),
ttt	Benzyl	4.32 (s)	6.92 - 7.02(m), 7.13 – 7.28 (m), 7.71- 7.80(m)
cct	Benzyl-	3.76 (s)	6.60 – 6.63(m), 7.13 – 7.30(m), 7.90 – 8.00(m)
ttt	^{i}Pr	0.92 - 0.95 (CH_3 d), 3.4-3.5 (CH, m)	7. 30 -7.32(m), 7.79 – 7.82 (m)
cct	^{i}Pr	0.59-0.62 (CH_3 d), 3.4-3.6 (CH, m)	7.26 – 7.34(m), 7.90 - 8.00(m),
ttt	MeClPh	3.49 (s)	6.31-6.32 (d), 6.66 –6.69(d); 7.10 – 7.14 9(dd), 7.24 – 7.26 (m), 7.84–7.9(m)
cct	MeClPh	3.48 (d)	6.28,6.29(d); 6.56, 6.60(d); 7.02, 7.03(d); 7.05, 7.06(d); 7.13 – 7.32 (m), 7.97 -8.03 (m)

[a] recorded in $CDCl_3$, values inside brackets are literature values.

Table 4. 3: DSC data for the *ttt*-and *cct*-$RuCl_2(RNC)_2(PPh_3)_2$ complexes.

Isomer	R	Exothermic Peak/ ^oC	Endothermic Peak/ ^oC
ttt	^{t}Bu	210	253
cct	^{t}Bu	-	254
ttt	xylyl	230	317
cct	xylyl	-	318
ttt	Benzyl	211	258-266
cct	Benzyl	-	254
ttt	^{i}Propyl	228	288
cct	^{i}Propyl	-	290
ttt	MeClPhNC	208	240, 257[a]
cct	MeClPhNC	-	240, 261[a]

[a] Peak associated with decomposition; confirmed by TGA analysis.

4.1.3 Solid state (solvent free) synthesis of *ttt*-$RuCl_2(RNC)_2(PPh_3)_2$ (R = R = ^{t}Bu, 2,6-xylyl, benzyl, and ^{i}Pr, MeClPhNC)

$RuCl_2(PPh_3)_3$(0.093 g, 0.093 mmol) and 2,6-XylylNC (0.028 g, 0.21 mmol) were mixed uniformly with a spatula and placed in an NMR tube. This tube was evacuated, purged with nitrogen and sealed. The mixture was then heated at 100 ^oC. In less than one minute the grayish brown mixture completely changed to a yellow colour. Some white deposit assumed to be the displaced triphenylphosphine ligand was noted. The yellow solid was washed with diethylether leaving behind a bright yellow solid. Yield (0.08 g, 90 %).

A similar synthetic route was followed to make *ttt*-$RuCl_2(^tBuNC)_2(PPh_3)_2$ (96 %), and *ttt*-$RuCl_2(^iPrNC)_2(PPh_3)_2$(93 %) and *ttt*-$RuCl_2(OMeClPhNC)_2(PPh_3)_2$ (75 %)

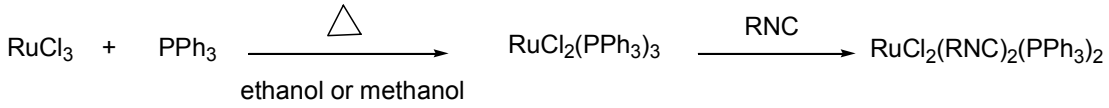
4.1.4 Synthesis of *ttt* and *cct*-$RuCl_2(CO)_2(PMePh_2)_2$

The complexes were prepared according to the literature method [1]
ttt-isomer: CO was bubbled for 5 h through a refluxing solution of $RuCl_3.3H_2O$ (2.43 g, 9.30 mmol) in 50 ml of absolute ethanol. The resulting deep red solution was cooled to 0 °C and stirred magnetically while a solution containing 3.83 g (19.1 mmol) of $PMePh_2$ in 30 ml of freshly distilled chloroform was added dropwise. With CO still passing through the red solution, stirring was continued until the solution turned yellow and a precipitate formed (about 15 min). The precipitate was isolated by filtration, washed with absolute ethanol and anhydrous diethyl ether, and vacuum-dried overnight. Yield (63%).
cct-isomer: A saturated solution containing 4.76 g of the *ttt*-isomer in 20 ml of chloroform was refluxed for 27 h. The yellow $[RuCl_2(CO)(PMePh_2)_2]_2$ (2.16 g) that precipitated was isolated by filtration and washed with anhydrous diethyl ether. Absolute ethanol (20 ml) was added to the original orange filtrate, and this solution was left standing at room temperature overnight. The white needles that formed were isolated by filtration and recrystallised from chloroform/ethanol. Yield (5%). The *cct*-isomer may also be obtained by solid-state conversion of the *ttt*-isomer [2].

4.2 Results and Discussion

4.2.1 Synthesis and Characterisation of $RuCl_2(RNC)_2(PPh_3)_2$

$RuCl_2(PPh_3)_3$ and an appropriate amount of RNC were stirred together in CH_2Cl_2 at room temperature to give the yellow complexes of *ttt*-$RuCl_2(RNC)_2(PPh_3)_2$ (reaction scheme 11) with yields between 67 % and 85 %. Attempts to prepare these complexes in refluxing solvent, as described in the literature [5], only yielded a mixture of a black and yellow solid. Separation of the mixture by column chromatography led to the disappearance of much of the yellow complex on the column resulting in a very low yield of the product. The Ru complexes are soluble in most polar organic solvents and insoluble in non-polar solvents.



Scheme 12

Heating a mixture of $RuCl_2(PPh_3)_3$ and 2,6-xylylisocyanide in the *solid state* between room temperature and 60 ^{0}C did not reveal any visual reaction (10 min) but at 100 ^{o}C rapid formation of a yellow complex occurred (< 1 min) . A white deposit also formed on the complex that was assumed to be the triphenylphosphine ligand. Washing the solid with diethylether left behind a bright yellow solid. Since the melting point of the isonitrile is ca. 175 ^{0}C this suggests that the reaction occurred in the solid phase or between a solid and a vapour (xylylisonitrile has a high vapour pressure at room temperature). Either way, the Ru complex remained in the solid state throughout the reaction. A similar result was obtained with *solid* 2-OMe-4-ClphenylNC, showing the generality of the reaction. In a related study, a thermomicroscopic investigation has revealed that a reaction between solid $Mn(CO)_4Br$ and solid triarylphosphine showed that one of the reagents melted in the reaction even though the reaction appeared to occur in the solid state [6]. It is possible that a similar melt reaction, not detected, occurred here.

Reaction between $RuCl_2(PPh_3)_3$ and the liquid isonitriles occurred without the addition of solvent at room temperature to slowly (or more rapidly at 50 ^{0}C) give the required complexes in greater than 85% yield. Thus very clean reactions are possible in the absence of solvent [7, 8]. The reaction proceeds well within a very short time with a stoichiometric amount of reactants. Their chemical structures were secured by IR and ^{1}H NMR spectral data and by comparison of their melting points with literature values [5]. This clearly shows that the solid state/solvent free synthesis of *ttt*-$RuCl_2(RNC)_2(PPh_3)_2$ is vastly superior to solution synthesis which often require separation by column chromatography to produce pure products. Only PPh_3 is produced as a by-product but the cost of washing it off easily with diethylether is less strenuous and less costly than working up crude *ttt*-$RuCl_2(RNC)_2(PPh_3)_2$ by column chromatography. The PPh_3 can also

be sublimed off as it evaporates far below the isomerisation temperatures of the complexes

Characterisation of the isonitrile complexes by ^{1}H NMR and IR spectroscopy gave data consistent with the structure of *ttt*-$RuCl_2(RNC)_2(PPh_3)_2$. When *ttt*-$RuCl_2(RNC)_2(PPh_3)_2$ was heated in the solid state pale yellow to near white complexes of *cct*-$RuCl_2(RNC)_2(PPh_3)_2$ (R = ^{t}Bu, 2,6-xylyl, ^{i}Pr, benzyl, MeClPh) were produced in quantitative yield (near 100%). The complexes with R = ^{t}Bu , benzyl and 2,6-xylyl have been prepared before only by solution procedures while the other complexes with R = ^{i}Pr, benzyl and- MeClPh are new. The solid-state isomerisation reaction of the complexes $RuCl_2(RNC)_2(PPh_3)_2$ was monitored by IR, DSC, ^{1}H NMR and XRD techniques.

4.2.2 IR studies

Solution IR spectra of the *ttt*–isomers display one strong ν(CN) band. Two bands were noted for the MeClPh complex; this could arise from two different arrangements of the bulky OMe groups attached to the ligand. Analogous *ttt*-$RuX_2(RNC)_2(EPh_3)_2$ (where E = P, As or Sb and X = Cl or Br) complexes were also reported to show one absorption band, both in the solid state and in solution [9]. The ν(CN) band position increases in the order 2,6-xylyl< MeClPh < ^{t}Bu < ^{i}Pr ≤ benzyl, suggestive of a correlation with the electron donating capacity of the RNC ligand.

When the complexes *ttt*–$RuCl_2(RNC)_2(PPh_3)_2$ are heated in the solid state two ν(CN) IR bands, with positions different from that of the original samples, were detected. These are associated with the *cis* arrangement of the isonitrile ligands and the band positions again vary with the electron donating capacity of the RNC ligand, in a predictable manner.

4.2.3 Characterization by ^{1}H NMR spectroscopy

^{1}H NMR spectral data for the samples are given in Table 4.2. The NMR data are consistent with the proposed molecular structures.

The *ttt*-$RuCl_2(^t BuNC)_2(PPh_3)_2$ isomer undergoes 100 % conversion to the *cct* complex on heating. Similar results were found for the other complexes. The CH_3/CH_2 resonance of

the RNC ligand of the *ttt* isomer always shifted downfield as the *cct* isomer formed. These NMR absorptions were thus chosen to monitor the extent of the isomerisation reaction as a function of time (see Section 5.3.1).

4.2.4 DSC studies

The results of a DSC study for the different RNC complexes are shown in Table 4.3. The DSC profiles of all the *ttt* complexes exhibit the same pattern, with an exotherm appearing before the endotherm. The endotherm corresponds to the melting point of the *cct*-isomer and ranges between 250 and 320 ^{o}C. The exothermic peaks range between 210 to 230 ^{o}C. The exotherm is associated with the isomerisation process i.e. conversion of *ttt*- to *cct*-isomer. A DSC profile for a typical isomer pair viz. *ttt*- and *cct*-$RuCl_2(^{i}PrNC)_2(PPh_3)_2$ is shown in figure 4.3.

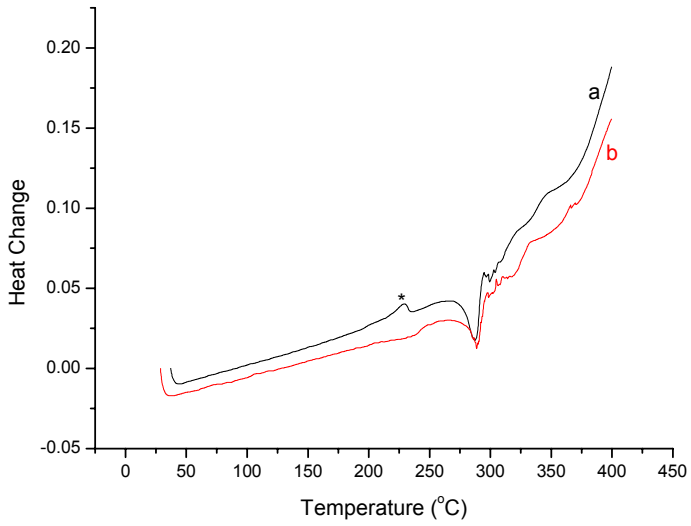


Figure 4.3: DSC profile of (a) *ttt*- and (b) *cct*-$RuCl_2(^{i}PrNC)_2(PPh_3)_2$ recorded at a scan rate of 10 ^{o}C/min (* = isomerisation process).

It will be noted that the profiles for the two isomers differ. Both isomers exhibit the same endotherm (melting peak; 288 ^{o}C) but only the *ttt* isomer exhibits an exotherm (isomerisation peak; 228 ^{o}C) (Figure 4.3). The DSC profiles reveal that the isomerisation

of the *ttt* complexes takes place in the solid state. This was confirmed by heating the *ttt* isomer to above the exotherm and then cooling the sample. Part of the sample was then used to record a NMR spectrum that revealed only the *cct* isomer while the second part was used to re-record the DSC that indicated no exotherm in the rerun.

The DSC profiles of R = 2,6-xylyl, and ^{t}Bu have been reported previously [3] and minor changes in the positions of the endothermic/exothermic peaks between data obtained in this experiment and the literature data were noted. The differences are associated with different operating conditions and the different instruments used.

The DSC studies on the *ttt* complexes show that the complexes undergo similar rearrangement processes irrespective of the RNC ligand used. It has been noted that isomerisation reactions can take place at 10 to 20 ^{o}C below the isomerisation temperatures and kinetic studies were normally done at these temperatures (see Chapter 5).

4.3 References

1. D. W. Krassowski, J. H. Nelson, K. R. Brower, D. Hauenstein, R. A. Jacobson, *Inorg. Chem*. **27** (1988) 4294.
2. D. W. Krassowski, K. Reimer, H. E. LeMay Jr., J. H. Nelson, *Inorg. Chem*. **27** (1988) 4307.
3. K. Katsuki, Y. Ooyama, M. Okamoto, Y. Yamamoto, *Inorg. Chim. Acta* **217** (1994)181.
4. P. S. Hallman, T. A. Stephenson, and G. Wilkingon, *Inorg. Synth.* **12** (1972) 237.
5. Y. Yamamoto, T. Tanase, T. Date, Y. Koide, *J. Organomet. Chem.* **386** (1990) 365.
6. S. S. Manzini, N. J. Coville, *Inorg. Chem. Comm*. **7** (2004) 476.
7. K. Tanaka, F. Toda, *Chem. Rev.* **100** (2000) 1025.
8. D. Bradley, *Chem. Ber.* **42** (2002).
9. B. E. Prater, *J. Organomet Chem*. **34** (1972) 379.