CHAPTER 1

Introduction

Reactions in the solid state are increasingly becoming important and are promising to be an excellent synthetic tool especially in the emerging field of Green Chemistry [1]. This seems to be the case in the field of organic [2] and coordination chemistry [3] as well as in the area of materials science [4]. However, the same progress in synthetic solid state organometallic chemistry has not been forthcoming despite wide coverage of the subject in the literature.

One of the first notable descriptions of a solid state reaction in the area of organometallic chemistry literature was reported by Vaska in 1966 on the reaction between $IrX(CO)(PPh_3)_2$ (X = halide) and HY(Y = halide) to give oxidative addition reaction products, $IrX(H)(Y)(CO)(PPh_3)_2$ [5]. Very little follow up on this or related reactions was reported in the next three decades, and the reactions that were carried out in the solid state were usually 'one-off' reactions, and were not performed to study the general concept of reactions in the solid state

Some years ago, a study of isomerisation reactions of a range of organometallic complexes in the solid state was commenced in our research group [6, 7]. The reactions were focussed on pseudo seven coordinate complexes of the type $CpML_4$ (M = Re, Mo, W; L a range of ligands) [6]. The study revealed that mechanistic pathways not available in a solution phase could occur in the solid state. This led to synthetic strategies to the synthesis of isomers that were not favoured in solution studies.

The question then became – could solid-state (or more particularly solvent free) reactions of organometallic complexes be generalised to other geometries? Studies on many 4 and 6 coordinate inorganic systems have been published in the literature and much of the early work on the study of solid-state reactions of classical coordination complexes has been summarised by le May [3]. The summary reveals that in earlier work the emphasis was on the study of 6-coordinate Cr and Co complexes containing OH and H_2O ligands. The work indicated the complexities associated with the presence of the OH/H_2O ligands. Thus simpler systems are required to obtain more fundamental information on the complex isomerisation and decomposition of 6-coordinate complexes, especially on more

classical organometallic complexes. Consequently, solid-state studies of known (and some unknown) six-coordinate complexes have been undertaken in this thesis.

Thesis Structure

This study entails an investigation of the solid-state isomerisation of six coordinate complexes. A literature survey of issues related to solid state chemistry was undertaken (Chapters 2 and 3). In particular, the literature was evaluated with respect to the solid state (and melt) reactions of organometallic compounds. Not unexpectedly mention has to be made of solid state reactions in other related disciplines of chemistry, namely inorganic chemistry/coordination chemistry and where required solid state organic chemistry

Chapter 4 of this thesis investigates the solid state isomerisation reaction of a series of 6-cordinate Ru complexes of the type $RuCl_2(RNC)_2(PPh_3)_2$ (R = ^{t}Bu, 2,6-xylyl, benzyl, 2-OMe-4-Cl-C_6H_4 and ^{i}Pr). Interestingly, it was also observed that the reaction between $RuCl_2(PPh_3)_3$ and RNC to produce *ttt*-$RuCl_2(RNC)_2(PPh_3)_2$ could also be carried out in the absence of solvents (Chapter 4). Kinetic studies of the isomerisation reactions of these complexes have been performed and monitored by NMR spectroscopy as well as by powder X-ray diffraction methods. The results of the investigations are given in Chapter 5. Thermomicroscopic and structural studies on some of these complexes are reported in Chapter 6.

The results for the ruthenium complexes suggested that other six-coordinate complexes could also undergo solid state isomerisation reactions and thus the study was extended to six-coordinate molybdenum complexes of the type $M(CO)_4L_2$ (M = Mo, W). These complexes undergo *cis-trans* isomerisation reactions in solution. However there is no reported data on the equivalent solid state reactions. Synthesis, characterisation and thermal analysis (DSC and TGA) on the $M(CO)_4L_2$ complexes was investigated for the first time and the results are presented in Chapter 7. Solid state reactivity of these complexes has been monitored by both ^{31}P NMR spectroscopy and DRIFTS and the

findings are reported in Chapter 8. Structural and thermomicroscopic investigations on $Mo(CO)_4L_2$ complexes were also carried out and the results are contained in Chapter 9.

Tables, figures and reaction schemes are integrated within the text. A detailed list of references is found at the end of each chapter.

1.3 References

1 P. T. Anastas, J. C. Warner, Green Chemistry: Theory and Practice, USA, 1998.

2 K. Tanaka, Solvent Free Organic Synthesis, Wiley Interscience, 2003.

3 Le May, H. E. Jr. In Comprehensive Coordination Chemistry; G. Wilkinson, Ed., Pergamon Press, New York, 1986, Vol. **17**, p 643.

4 D. Braga, F. Grepioni, *Angew. Chem. Int. Ed. Engl*. **43** (2004) 4002.

5 L. Vaska, *J. Am. Chem. Soc.* **88 (**1966) 5325.

6 N. J. Coville, L. Cheng, *J. Organomet. Chem.* **571** (1998) 149.

7 N.J. Coville, D. C. Levendis, *Eur. J. Inorg. Chem.* (2002) 3067.