

CHAPTER TWO

SOLID STATE REACTIONS

2.0 Introduction

The discovery of ferrocene in the 1950s was a gateway to the area of organometallic chemistry and this event led to the synthesis of numerous organometallic complexes. Many of these complexes have been widely used as industrial homogeneous catalysts and also in organic synthesis where they have provided new synthetic routes to inaccessible compounds

Traditionally, most of these organometallic reactions were carried out in solution. This might have been due to the ready availability of characterisation techniques, many of which required solution media at the time. Reactions in the gas phase have also been described but here the emphasis has not been on synthetic chemistry [1]. The development of synthetic organometallic chemistry in the solid state as well as reactions on surfaces, by contrast, has been little mentioned in the literature.

Solid state organic reactions have also been studied for many years and numerous principles that provide for an understanding of the chemistry associated with this field have been developed. However, transfer of this knowledge to the field of organometallic chemistry is hardly known.

There are many reasons for this situation (i) Aristotle's famous philosophy, which says that "No reaction occurs in the absence of a solvent" [2]. This philosophy had a big influence in the development of synthetic chemistry and many reactions were performed in the presence of solvents even if there was no reason to do the reaction in solvent media; (ii) lack of contact between reactants; (iii) the delicate nature of the organometallic complexes *i.e.* they easily decompose on heating and react with oxygen and moisture to give undesirable products and (iv) lack of techniques available to study reactions in a confined environment.

Although X-ray diffractometers were available in the early studies on organometallic complexes, the use of this technique was time consuming and it was predominantly used for structural determination and the emphasis was certainly not on the study of reactions in the solid state. However the latest developments in diffractometer design as well as the availability of equipment for thermal analysis (e.g. differential scanning calorimetry, thermal gravimetric analysis), solid state NMR spectroscopy, optical microscopy (for visualizing the reaction), DRIFTS and other related techniques has in recent years made it possible to study reactions in the solid state and under inert atmospheres.

2.1 Solid State Reactivity

Reactions between or within solid reactants to yield a solid product are prototypical of solvent free reactions [3, 4]. From literature reports the concept of chemical reactivity between solids (and very often within solids) is very difficult to define [5]. Reactions which occurred in the melt were not considered as genuine solid state reactions. The same applied to reactions which occurred with crystal degradation prior to the reaction. For the purpose of this thesis, solid state reactions shall refer to all solventless processes leading from a solid reactant to a solid product. Gas solid reactions will also be regarded as solid state reactions as they can eventually produce a solid product.

The difference between solid state reactions and solution ones is that solid state reactions occur within the rigid constraining environment of the crystal lattice (reaction cavity concept [6]). Solid state reactions therefore provide an extreme case for evaluating the effect of intermolecular forces on a reaction and their influence on reaction mechanism and direction [7]. The confined environment of the reactant crystal lattice can control the kinetic features of a reaction and hence the nature of products. Such reactions are said to be topochemically controlled and illustrate the topochemical principle proposed by Cohen and Schmidt in which reactions in the solid state take place with minimum requirements of energy and atomic or molecular motion requirements [8, 9, 10]. Topochemical control of a reaction to produce a product is analogous to the kinetic control of a reaction in solution. The product is not necessarily the thermodynamically

most stable product available to the system, but is rather the one dictated by the reaction pathway available in the encapsulating surroundings of the solid [11]. Thus product selectivity in the solid state can be different from reactions in solution or gaseous media since the range of intermediates or transition state structures accessible in a confined environment are more limited [10, 12]. Regardless of whether or not topochemical control is evident in a reaction, there is often correlation at the molecular level, between the lattice of the product and that of the reactant. When this occurs the reaction is then described as being topotactic. In other instances the growth of the product phase proceeds in a less orderly manner, producing a product that is amorphous to X-rays. This situation seems to arise when the product lattice fractures and disrupts the host lattice such that long range coherence within the crystal lattice is lost [11].

Generally, solid state reactions may have the following advantages over solution phase reactions:

- (i) The atom economic nature of the solid state reactions and the limited formation of side products [13].
- (ii) No solvents are needed in the reaction and hence no waste disposal issues associated with the solvent need be considered [14]. This is of considerable importance in the rapidly emerging field of Green Chemistry which has resulted in major changes in the way synthetic chemists develop processes and products [15]. Also, products do not require extensive purification to remove traces of solvent and impurities [2].
- (iii) The constrained environment in a 'reaction cavity' can lead to novel chemical reactions, with product selectivity different from that expected in the liquid phase [8, 9, 16, 17, 18]. It is expected that the crystalline solid state may affect the product selectivity of chemical reactions, not only by rate accelerations but also by slowing down rates of competing processes. Manipulating rates and selectivities by changing activation energies in the liquid phase can be thought of as a low resolution approach to controlling chemical reactivity [19]. It is therefore possible that solid state reactions may occur with both control and

yields not achievable by any other media, indeed quantitative yields have been observed with solid state reactions. These reactions are often faster, taking just a few minutes rather than hours to complete because the reactants are in intimate contact with each other [2].

- (iv) Enantioselective reactions are feasible in a chiral cavity [20]. In such reactions the asymmetry is only determined by its physical origin without any chemical reagent - the chiral source being the chiral crystal packing [20].
- (v) Kinetic trapping of highly reactive intermediates [16, 17, 18].
- (vi) Crystal engineering using organometallic complexes is possible in the solid state [21, 22].
- (vii) Cascade reactions can be carried out quite easily and with high yields [2].

The potential of solid state chemistry for mechanistic studies, solvent free synthesis and materials applications is now fully recognised [23].

2.2 Literature survey

2.2.1 Solid State Organic Chemistry

Scientific investigations in solid state organic chemistry date back to the early 1800's but Schmidt and co-workers have been credited with the field's revival after their intensive investigation that led to the formulation of the topochemical principle, providing the 'first model' for the interpretation of chemical reactions in the solid state [24, 25, 26]. One of the classic reactions that they described was the photodimerisation of *ortho*-ethoxy-*trans*-cinnamic acid by exposure of the molecule to UV radiation, a reaction which depended on which polymorph was being irradiated (Figure 2.1)

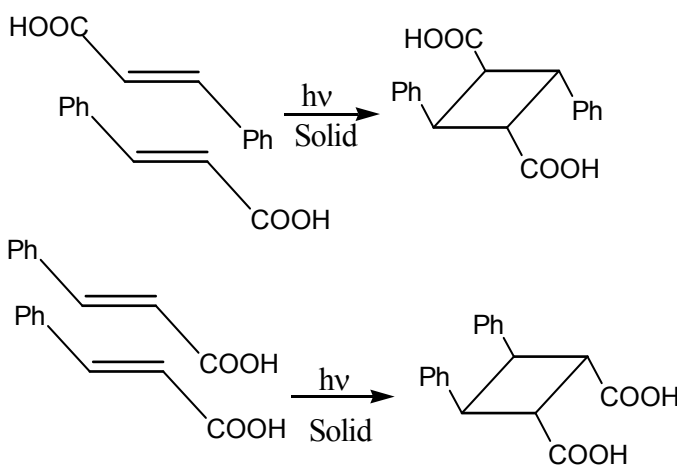


Figure 2.1: Irradiation of cinnamic acid in the solid state with products dependant on the polymorph irradiated [27].

This reaction is still under investigation and recently it has been shown that factors other than topochemical ones may be operative [27]. These other important factors that influence the course of solid state reactions include the presence of solvates, planar defects, phase transitions [27], disorder and even crystal morphology [28].

Other reaction types also occur in organic crystals. Closely related to photodimerisation is photopolymerisation and since the 1980's many of these types of organic solid state reactions have been reported. These include thermal or photochemical interconversion reactions between geometric isomers and conformers with E/Z configurations [5, 29 and 6]. Recently, Knoevenagel condensation and Michael addition reactions have also been reported to occur in the solid state [30]. The incentive for these reactions is the quantitative yield and the atom economic nature of the reactions.

To date several hundred solid-state syntheses involving numerous organic reaction types have been reported [31]. Incentives driving the rapid development are the advantages associated with "solvent free syntheses" [32], reactions that are atom economic and sustainable [30]. Other factors include the high yields [12, 33-37] associated with these reactions as well as the possibility of achieving novel or stereoselective products as a consequence of the reactions in a constrained crystalline environment [38]. For more details see the extensive data summarised in the book by Tanaka [23].

2.2.2 Solid State Coordination Chemistry

A large number of coordination compounds undergo either thermal or photochemical reactions in the solid state [39]. Most of these studies were carried out on cobalt(III) and chromium (III) complexes. Some of these reactions have been known since the time of Werner in the early 1900's and Le May has written a comprehensive review on solid state

reactions of coordination compounds [39] Since then numerous types of reactions continue to be reported and these include, ligand exchange reactions, isomerization reactions [40], redox reactions and reactions of coordinated ligands [10]. The use of solventless techniques to prepare coordination complexes is beginning to be realised [4]. One example entails the use of mechanochemical procedures (co-grinding or milling of solid reagents).

2.2.2.1 Cis/trans Isomerisation reactions

Solid state *cis-trans* isomerisation reactions of four coordinate square planar platinum complexes PtL_2X_2 (L = neutral donor ligand, X = halide) were reported as early as 1970 [41]. The isomerisation of these complexes is still under investigation. For example, it has been found that for the complexes $Pd(NH_3)_2X_2$ (X = Cl, Br, I), the solid state isomerisation also proceeds from the *cis* to *trans* isomer (see Figure 2.2) and that the isomerisation process involves the ‘breaking of Pd-X and Pd-N bonds’[42].

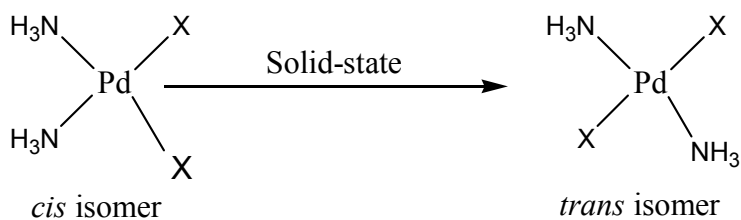


Figure 2.2: Conversion of *cis*- $Pd(NH_3)_2X_2$ (X = Cl, Br, I) to *trans*- $Pd(NH_3)_2X_2$ [42]

It was found that pure *trans*-Pt(CO)(NH₂R)Cl₂ (e.g. R = CHMePh) also directly rearranges to the *cis* isomer under thermal conditions. Fushini *et al* also found that complexes of the type PtX₂(PR₃)₂ undergo *cis-trans* isomerisation in the solid state [43]. The isomerisation reactions were studied using DTA/TGA methods.

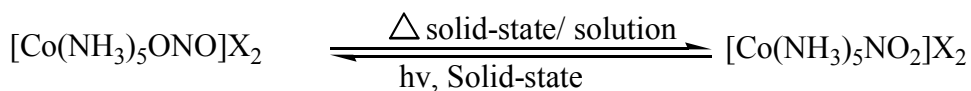
The six coordinate chromium and cobalt complexes of the type, [MX₂(a-a)₂]X, (M = Co(III), Cr(III); a-a = diammine, X = halide) were reported to undergo solid state isomerisation reactions [44 - 46]. Originally, the isomerisation of these complexes were thought to be catalysed by the presence of occluded H₂O molecules and to occur in the melt phase. A so-called “aquation-anation” isomerisation mechanism was proposed to explain the findings [45, 46]. The isomerisation of the complex *trans*-[CrBr₂(Pn)₂]Br·H₂O (Pn = propylenediamine) in the anhydrous state led to a different mechanistic proposal [47 - 49].

2.2.2.2 Linkage Isomerisation Reactions

Coordination compounds have also been observed to undergo linkage isomerisation reactions. This type of isomerism is exhibited by complexes with ambidentate ligands. An extensively studied solid-state linkage isomerisation reaction involves the nitrito-nitro linkage isomerisation of Co(II) amine complexes [50]. An example is [Co(NH₃)₅ONO]XY ↔ [Co(NH₃)₅NO₂]XY where XY = Cl₂, Br₂, I₂, (NO₃)₂ and Cl(NO₃). Transition metals other than cobalt have also been studied and much effort has been made to clarify the mechanism of this solid state isomerisation reaction.

Jorgensen synthesised both nitro (NO₂, nitrogen coordination) (Scheme 1) and nitrite

(ONO, oxygen coordination) cobalt isomers [50]. ONO isomers could be synthesized in solution reactions as well as by irradiating the corresponding NO₂ isomers in the solid state.



Scheme 1

A solid state reversible reaction was achieved by employing thermal and photochemical reaction conditions. Single-crystal to single-crystal studies on the linkage isomerisation involving NO₂-ONO interconversion in complexes of the type [Co(NH₃)₅NO₂]²⁺ has generated data on the role of heat, pressure, irradiation, cavity size, and other factors on the reaction [51].

Thermally induced nitro-nitrito(O, O) linkage isomerisation in diamine complexes of nickel(II) in the solid state is known [52]. For example, *trans*-[NiL₂(NO₂)₂] (L = N, N dipropyl 1,2-diaminoethane) transforms slowly to a nitrite (O,O) isomer, *cis*-[NiL₂(O₂N)(NO₂)] at 298 K. 100 % conversion is achieved within 5 days. The nitro complex is brown in colour and the nitrite complex is green. Single-crystal to single-crystal studies revealed that the nitrite complex also show a reversible phase transition which is associated with thermal motion of the side chains of L with variation of temperature. The isomerisation reactions have been shown to be intramolecular, with no exchange of the ligands between different complex cations [53].

2.2.2.3 Synthesis of coordination compounds by mechanochemical methods

It has been shown that a few coordination compounds can be prepared in the solid state by grinding or milling together solid reagents [4]. Balema *et al* showed that some *cis*-platinum complexes *cis*-[(PPh₃)PtCl₂] and *cis*-[(PPh₃)PtCO₃] can be prepared mechanochemically from solid reactants in the absence of solvents. *cis*-[(PPh₃)PtCl₂] was obtained in 98 % yield after ball milling of polycrystalline PtCl₂ and PPh₃, while the mechanically induced solid state reaction of *cis*-[(PPh₃)PtCl₂] with an excess of anhydrous K₂CO₃ produced *cis*-[(PPh₃)PtCO₃] in 70 % yield [54]. The same group has investigated, by means of solid state ³¹P NMR spectroscopy and powder XRD, the formation of phosphonium salts during the high energy ball-milling of triphenylphosphine with solid organic bromides [55]. In the case of 2-bromo-2-phenylacetophenone the solvent-free, mechanically induced, transformation results in the formation of the thermodynamically favorable C-phosphorylated product, which in solution is only obtained together with side products [55]. The mechanical preparation of phosphorus ylides has also been reported [56].

The complex Fe(phen)(H₂O)₃SO₄ (where phen is 1,10-phenanthroline) is reported to be produced from the solid state reaction of FeSO₄·7H₂O and 1,10-phenanthroline at 70 °C [57]. Solution reaction of the two reagents has often produced [Fe(phen)₃][SO₄]. The complex [Fe(phen)(H₂O)₃][SO₄] resulting from the solid state reaction has been found to be neutral and is an octahedral Fe(II) complex with unidentate sulfate ligand. The other five coordination sites have been observed to be occupied by water and the 1,10-phenanthroline ligand. This provided yet another facile example in which the solid state reaction produced new compounds which are not accessible in solution media. Many other solid state reactions of this type, in which a transition metal salt is reacted with a ligand are known [58 - 65]. In some cases it was shown that coordination of the ligand takes place in a stepwise manner with sequential substitution of coordinated water in hydrated salts. The water molecules in these hydrated salts have also been shown to have a significant effect on the rates of these reactions [66, 67].

In a related study, grinding of Ni(NO₃)₂ with 1,10-phenanthroline resulted in the facile preparation of [Ni(phen)₃]⁺ accompanied by a dramatic and rapid colour change [68].

Addition of the sodium salt of tetrasulfonatocalix[4]arene (tsc) gives two porous π -stacked supramolecular arrays $[\text{Ni}(\text{phen})_3]_2[\text{tsc}^{4-}] \cdot n\text{H}_2\text{O}$ [68] and the related $[\text{Na}(\text{H}_2\text{O})(\text{phen})][\text{Ni}(\text{phen})_3]_4[\text{Ni}(\text{phen})_3]_2[\text{tsc}^{4-}][\text{tsc}^{5-}] \cdot n\text{H}_2\text{O}$ depending on the stoichiometry of the reaction [68].

A reaction between $\text{M}_2\text{Cl}_2(\text{NMe}_2)_4$ ($\text{M} = \text{Mo}$ or W) and Hhpp (1,3,4,6,7,8-hexahydro-2H-pyrimido[2,2-*a*]pyrimidine (8 equiv) at 150 °C has been found to form compounds of $\text{M}_2(\text{hpp})_4\text{Cl}_2$ (hpp is the anion derived from deprotonation of Hhpp) under solventless conditions [69]. The reaction however takes place in the melt by elimination of HNMe_2 and the products are purified by sublimation followed by recrystallization in appropriate solvents.

Grinding copper(II) acetate hydrate with 1,3-di(4-pyridyl)propane (dpp) gives a gradual colour change of the Cu complex from blue to blue-green over a period of 15 minutes. The resulting material was shown by solid-state NMR spectroscopy to comprise of a 1D coordination polymer with water-filled pores. The same host structure, $[\{\text{Cu}(\text{OAc})_2\}_2(\mu\text{-dpp})]_n$ could be obtained from solution containing methanol, acetic acid or ethylene glycol as guest species [70].

Otera and co-workers have shown that the supramolecular self-assembly of a number of complexes is dramatically accelerated under solvent-free conditions leading to the formation of two- or three-dimensional structures and even double helicates [71]. For instance, reaction of $[(\text{ethylenediamine})\text{Pt}(\text{NO}_3)_2]$ with 4,4' bipyridine to form molecular squares takes more than 4 weeks at 100 °C, while the reaction is brought to completion within 10 minutes at room temperature by mixing the reactants without solvents [71]. Double-helix formation under solvent-free conditions has also been achieved by treating chiral oligo(bipyridine) copper complexes with $[(\text{CH}_3\text{CN})\text{Cu}]\text{PF}_6$. The progress of the reaction was monitored by measuring solid-state CD-spectra, which showed that after grinding for 5 minutes the desired helicate had been obtained. The results showed that solvent-free complexation can be easily achieved, even with relatively complex systems, but also reactions are much faster than in solution.

A dinuclear bridged species $[\text{Cu}_2(\text{dpp})(\text{H}_2\text{O})(\text{dmsO})\text{Cl}_4]\cdot\text{dmsO}$ is reported to undergo solid state polymerisation [72]. Upon removal of water and dmsO molecules, the complex polymerises in the solid state to a polynuclear complex of the formula $[\text{Cu}(\text{dpp})\text{Cl}_4]_n$. The complex $[\text{Cu}_2(\text{dpp})(\text{H}_2\text{O})(\text{dmsO})\text{Cl}_4]\cdot\text{dmsO}$ is antiferromagnetic, and the resulting polymer is ferromagnetic. The solid state reaction has therefore been monitored by studying the magnetic susceptibility data of the starting and product material. TGA as well as XRD have been used to study the solid state reaction. In a related study, a one dimensional polymer network, $[\{\text{Cu}(\text{O}_2\text{CMe})_2\}_2(\text{dpp})]_n$ has been prepared by simple grinding of solid copper (II) acetate dehydrate with dpp in a pestle and mortar [73, 74].

Solid state intercalation of organic compounds into the interlayer spaces of some metal complexes has been reported [75 to 79]. 4,4'-bipyridine and 1,2-di(4-pyridine)ethylene molecules has been intercalated into the interlayer of cobalt(II)-, nickel(II)- and copper(II)-montmorillonites by solid-solid reactions at room temperature. The intercalated molecules of the diimines formed $(\text{ML}_2)_n$ -type coordination polymers in the interlayer spaces of montmorillonites. Tris(8-hydroxyquinoline)aluminum(III) complexes (Alq_3), a molecule widely studied as an organic light-emitting device, has been found to form in the interlayer spaces of smectites by solid-solid reactions between Al-smectites (Al-montmorillonite and Al-synthetic saponite (Sumecton)) and 8-hydroxyquinoline (8Hq) at room temperature [80]. The intercalation of 8-hydroxyquinoline molecules into Al-smectites was demonstrated by powder XRD, FTIR, DTA, TG, TG-MS, and chemical analysis. The coordination of the ligand to the interlayer Al cations was proved by FTIR, UV-Vis, and photoluminescence spectroscopies. The solid state method of preparation was found to be better than the conventional ion exchange methods owing to the low solubility of the coordination polymers.

2.2.3 Solid state organometallic reactions

The first solid state organometallic reaction was reported in 1966 by Vaska on the reaction between $\text{IrX}(\text{CO})(\text{PPh}_3)_2$ ($\text{X} = \text{Cl}, \text{Br}$ etc) and HY ($\text{Y} = \text{Cl}, \text{Br}$ etc.) to give oxidative addition products $\text{IrX}(\text{H})(\text{Y})(\text{CO})(\text{PPh}_3)_2$ [81]. Other reactions of this nature were also reported in the 1980s.

Numerous organometallic reactions which occur in the solid state have now been reported and are notably, isomerisation, solid-gas reactions and reactions at a solid surface. Recently polymerisation reactions and formation of supramolecular complexes in the solid state have also been reported. Solid state formation of carbon nanotubes using organometallic precursors has also received attention [82]. Other reactions which are still in the early stages of development are migratory/insertion and solid state substitution reactions. The first comprehensive review on solid state organometallic reactions came out in 1998 [83], while a micro review related to this topic has also been published more recently [84]. These reviews indicate that work in this field has been little developed.

2.2.3.1 Surface organometallic synthesis

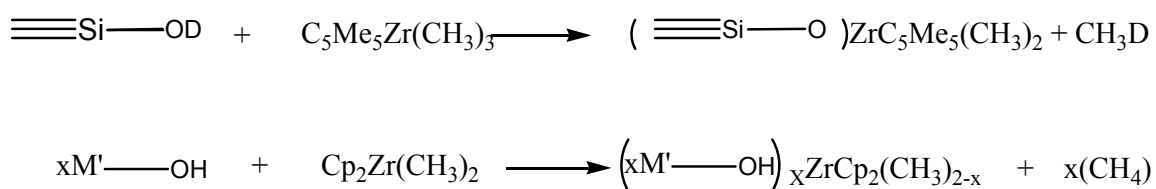
This type of reaction is dependant on the interaction between organometallic precursor compounds and inorganic oxides (silica, alumina, magnesia and zeolites) to activate bonds in organometallic complexes. In the presence of other reactants such as CO, new organometallic compounds or catalyst precursors can be formed on the surface of inorganic oxides by thermal or by photolytic irradiation procedures.

By using this methodology, many polymeric chlorocarbonyl metal complexes and their related clusters have been synthesised in high yields from the corresponding metal trichlorides supported on a silica surface by reductive carbonylation at atmospheric pressure [85]. One of the key factors in determining the direction of the reaction was

found to be the basicity of the support. This could be varied by adding different amounts of carbonate salts.

In recent applications in catalysis of surface organometallic chemistry, Basset *et al* have reported various catalytic applications of well defined surface hydrides supported on oxides [86 - 87]. The hydrides were prepared by the reaction of an alkyl metal with hydroxyl groups present on the surface of the oxides. For example, they found that the treatment of this surface complex, under hydrogen at 150 °C, led to the formation of a highly reactive metal hydride and a restructuring of the surface of the oxide

Basset and workers have also reported that it is possible for one to design, construct and fully characterise, at the surface of oxides, well defined coordination spheres around zirconium, which may be suitable for olefin polymerization in the absence of additional cocatalysts (alumoxane or an organo Lewis acid initiator) [88]. They found that the reactions of zirconium organometallic complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{Zr}(\text{CH}_3)_2]$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Zr}(\text{CH}_3)_2]$ with dehydroxylated silica, silica-alumina, and aluminium surfaces led to the formation of well defined neutral compounds [89] (Scheme 2) and the complexes could be converted to well defined neutral compounds, which were easily characterized by in-situ infrared spectroscopy, surface microanalysis, qualitative and quantitative analysis of evolved gases during surface reactions with the labeled surface solid state as well as ^1H and ^{13}C NMR spectroscopy using ^{13}C -enriched compounds and EXAFS.



Where M = Metal and $\equiv\text{Si}$ is the silicon bonds.

Scheme 2

In a related study, the reaction of $[\text{Ta}(=\text{CH}^t\text{Bu})(\text{CH}_2^t\text{Bu})_3]$ or $[\text{C}_5\text{Me}_5\text{Ta}(\text{CH}_3)_4]$ with a silica partially dehydroxylated at 700 °C has been reported to give the corresponding monosiloxy surface complexes $[(\equiv\text{SiO})\text{Ta}(=\text{CH}^t\text{Bu})(\text{CH}_2^t\text{Bu})_2]$ and $[\equiv(\text{SiO})\text{Ta}(\text{CH}_3)_3\text{C}_5\text{Me}_5]$ by eliminating a σ -bonded ligand as the corresponding alkane ($\text{H}-\text{CH}_2^t\text{Bu}$ or $\text{H}-\text{CH}_3$) [89].

The very same authors, have also reported that the reaction of AsPh_3 with $\text{Ni}/\text{Al}_2\text{O}_3$ in the 100 to 200 °C range under 6 to 30 bar of hydrogen proceeds by complete hydrogenolysis of As-Ph bonds, with formation of an NiAs alloy [90]. The mechanism of alloy formation is complex. It was found that at low coverage of the Ni surface, stepwise hydrogenolysis of As-Ph bonds led to the formation of a surface organometallic fragments such as $\text{Ni}_s[\text{AsPh}_x]_y$ [90].

Another example of reaction is the solid surface isomerisation reaction on silica of $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Re}(\text{CO})(\text{L})\text{X}_2]$ ($\text{X} = \text{Br}$; $\text{L} = \text{CO}$, phosphite) [91, 92]. This complex was found to undergo a solid state photochemical isomerisation reaction in the reverse direction to that in the solution phase. This reaction indicates the influence of the surface as a ligand in the overall reaction. It also provided a route for the facile synthesis of *cis*- $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Re}(\text{CO})(\text{L})\text{X}_2]$.

2.2.3.2 Reactions between solid particles (and within solids)

Historically it has been assumed that reactions can only occur through the intervention of solution media (Aristotle's Principle) to form molecular species [2]. The assumption has always been that this is the best approach to inducing a reaction. However in the absence of a solvent a reaction involving the physical mixing of two or more different reagents in the solid state is possible. This is a procedure commonly used in metallurgical preparations like ball milling and it entails the use of fine particles to ensure as much surface-surface interaction as possible [93 - 94]. Traditionally, the solid-solid reactions have been used primarily for the preparation of alloys or inorganic solids such as ceramics, and most of these reactions entailed the use of high temperatures. Solid state synthetic methodology has become more common for organic reactions in the last two decades [38] and recently has been used in the field of crystal engineering [95 - 96] . Comparatively, there are less reports on solventless or solid state reactions in the field of organometallic chemistry. However, in the late 90's and beginning of the new millennium, reactions in the field of organometallic chemistry in the absence of solvents, also began to be realized [83 - 85].

An example of this reaction type is the solid state mechanochemical synthesis of ferrocene [97]. Historically, ferrocene was prepared by solution methods which often involved chromatographic separations. It has been found that ferrocene can be formed in high yields by mechanical loading of iron (II) chloride with solid cyclopentadienides of either alkaline earth metals or thallium. The yield of the product is dependant on parameters such as the amount and ratio of the reactants used. The yield of ferrocene increased with the increase in the amount of cyclopentadienide salt. The increase in the amplitude of frequency used in the milling process also led to an increase in the conversion to ferrocene.

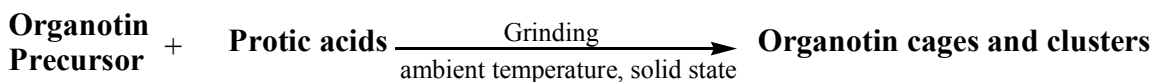
Solid state as well as solution reactions between $\text{RhX}(\text{PPh}_3)_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{W}(\text{CO})_3\text{X}]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) have been reported [98]. Both the solid and solution reactions led to exchange of CO/PPh_3 and X/Y between the two reactants. The solid state reaction gave higher yields of products than achieved from the corresponding solution reactions. Similar results have been noted for related Re and Mo complexes, suggesting a very general and facile solid state reaction type. Synthesis of the complex $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Re}(\text{CO})_2\text{I}_2]$ has been achieved by mixing solid $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Re}(\text{CO})_2\text{Br}_2]$ and solid NaI [99].

Preparations of supramolecular compounds complexes in the solid state are known [100]. Pressing solid $[\text{Co}^{\text{III}}(\eta^5\text{-C}_5\text{H}_4\text{COOH})(\eta^5\text{-C}_5\text{H}_4\text{COO})]$ with KBr to prepare samples for IR spectroscopy led to a solid state rearrangement with the formation of the supra-molecular complex $[\text{Co}^{\text{III}}(\eta^5\text{-C}_5\text{H}_4\text{COOH})(\eta^5\text{-C}_5\text{H}_4\text{COO})]_2\text{K}^+\text{Br}^-$, which could also be obtained from solution crystallization [100]. Similar solid-solid supramolecular complexation reactions have been observed with $\text{K}[\text{PF}_6]$ and $[\text{NH}_4][\text{PF}_6]$. Further examples of this kind of reaction are given in Section 2.3.3. Hybrid organic organometallic complexes have also been prepared in the solid state [101]. Grinding $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{COOH})_2]$ with solid bases **B** (**B** = 1,4 diazabicyclo[2,2,2] octane, 1,4 phenylenediamine) generates quantitatively the corresponding hydrogen bonded salts $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{COOH})(\eta^5\text{-C}_5\text{H}_4\text{COO})][\text{HB}]$. Gas-solid reactions are possible with volatile bases. No intermediate liquid phases have been observed in these solid state reactions. Sublimation of the complex yielded the starting material, $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{COOH})_2]$. In these reaction types between molecular solid reagents to form new molecular solid product, it has been observed that the covalent bonding is not affected while non-covalent van der Waals or hydrogen bonding interactions are affected.

Solid state synthesis of organometallic cluster compounds has been reported [102 - 104]. The complexes $\{\text{MS}_4[\text{Cu}(p\text{-MeOC}_6\text{H}_4)_3\text{P}]_2\} \cdot 0.5 \text{C}_6\text{H}_{12}$ ($\text{M} = \text{Mo}, \text{W}$) are prepared by heating mixtures of $(\text{NH}_4)_2\text{MS}_4$ ($\text{M} = \text{Mo}, \text{W}$), CuI and $(p\text{-MeOC}_6\text{H}_4)_3\text{P}$ at 90°C for 12 hours under nitrogen [102]. Owing to the insolubility of CuX in organic solvents and the difficulty of generating products by reaction with other materials, solid state synthesis is

the best option for the syntheses of these cluster compounds. Yields of the desired products are above 45 %. The method is better than the solution method since it does not need solvent and *thus* avoids generating undesired products. In a related study, Mo(W)-S cluster compounds have been synthesized in the solid state at low temperatures [103]. Over forty new Mo(W)-S cluster compounds were produced by this method. Mixed metal sulphur cluster anion $[\text{Cu}_{12}\text{Mo}_8\text{S}_{32}]^{4-}$ has been formed from the solid state reaction of $[\text{NH}_4][\text{MoS}_4]$, CuCN and $[\text{nBu}_4\text{N}]\text{Br}$ [104]. Temperature has been identified as the factor which influenced the solid state reaction.

Various known examples of organotin clusters and cages have been prepared by solid state synthesis [105]. The synthetic procedure involved grinding solid organotin reagents such as *n*-BuSn(O)OH, *n*-BuSn(OH)₂Cl, *n*-Bu₂SnO or (Ph₃Sn)₂O with appropriate solid protic reagents such as carboxylic acids, phosphonic acid or a sulfonic acid (Scheme 3).



Scheme 3

The yields of the solid state reactions are very high. These complexes have been traditionally prepared by the use of high boiling point solvents under reflux conditions, and involved several bond breaking and bond forming processes [106 - 108]. Some of the products appeared to form in the solid state while in other instances melting prior to solidification of the product was observed.

2.2.3.3. Solid-Gas Organometallic reactions

Gas solid reactions were among the first solventless processes to be studied. In 1884 Pellizari reported a study of the reaction of ammonia vapours with dried and pulverized phenols and carboxylic acids [108 and 109]. A systematic exploration of this field was only undertaken by Paul and Curtin in a series of elegant studies in the early 1970's [110].

One of the earliest reported reactions between an organometallic complex and a gas, was the reaction of Vaska type complexes with gaseous alkyl halides [81]. Synthesis of $\text{Ni}(\text{CO})_4$ has also been achieved by heating nickel metal and CO under high pressure [111]. Many metal carbonyl complexes have been prepared by reaction of metal salts and CO and numerous of these reactions involved reduction of metal in the absence of a solvent.

Solid-gas reactions between $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ and CO yielded $\text{Rh}(\text{PPh}_3)_3(\text{CO})\text{Cl}$ [112]. TGA analysis of the complex followed by washing with organic solvents yielded $\text{Rh}(\text{PPh}_3)_2(\text{CO})\text{Cl}$ and uncoordinated PPh_3 . This led to the conclusion that formation of $\text{Rh}(\text{PPh}_3)_2(\text{CO})\text{Cl}$ is *via* association of CO into $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ followed by dissociation of the PPh_3 ligand. In solution, the reaction gave two isomers; one in which the PPh_3 ligands are *trans* to each other but staggered and the other in which the PPh_3 ligand are *trans* but eclipsed. The solid state reaction gave only one isomer in which the PPh_3 ligands are staggered. A similar carbonylation reaction in the solid state on $\text{RuCl}_2(\text{PPh}_3)_3$ gave *cct*- $\text{RuCl}_2(\text{CO})_2(\text{PPh}_3)_2$. In this case the solid-gas reactions occurred at relatively low temperature and offered the advantage that structural elements can be preserved in the transformation from reactant to product. In this way, new structural types including metastable species, may be detected [113].

Oxidation reactions of the overcrowded distilbene with molecular oxygen was found to proceed in a single-crystal to single-crystal manner [114]. The green crystals of the complex reacted with atmospheric oxygen to give a colourless crystal of the complex

shown in Figure 2.3. The reaction is much faster in the solid state (10 hr) than in solution (30 hr).

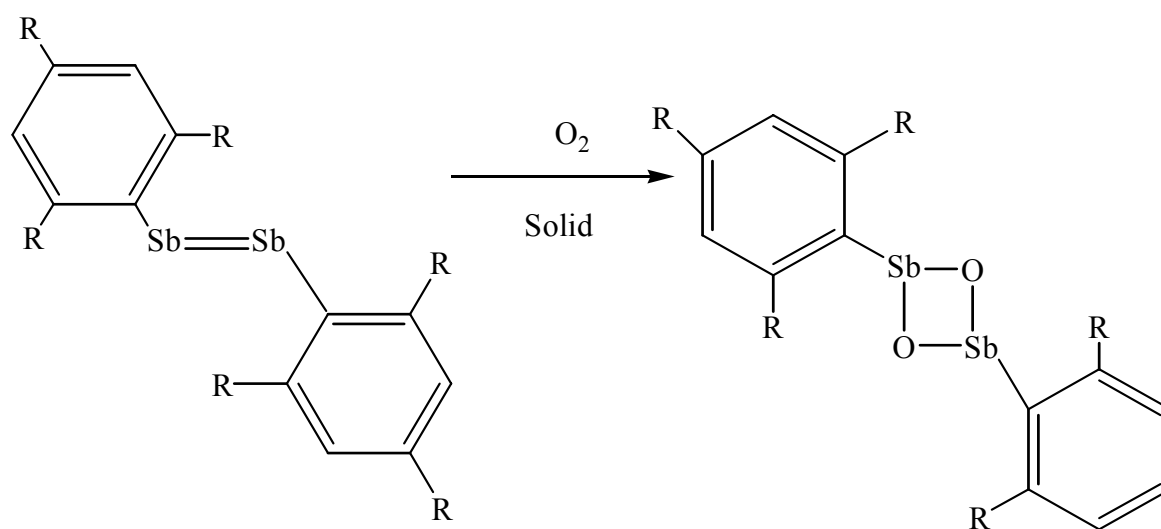
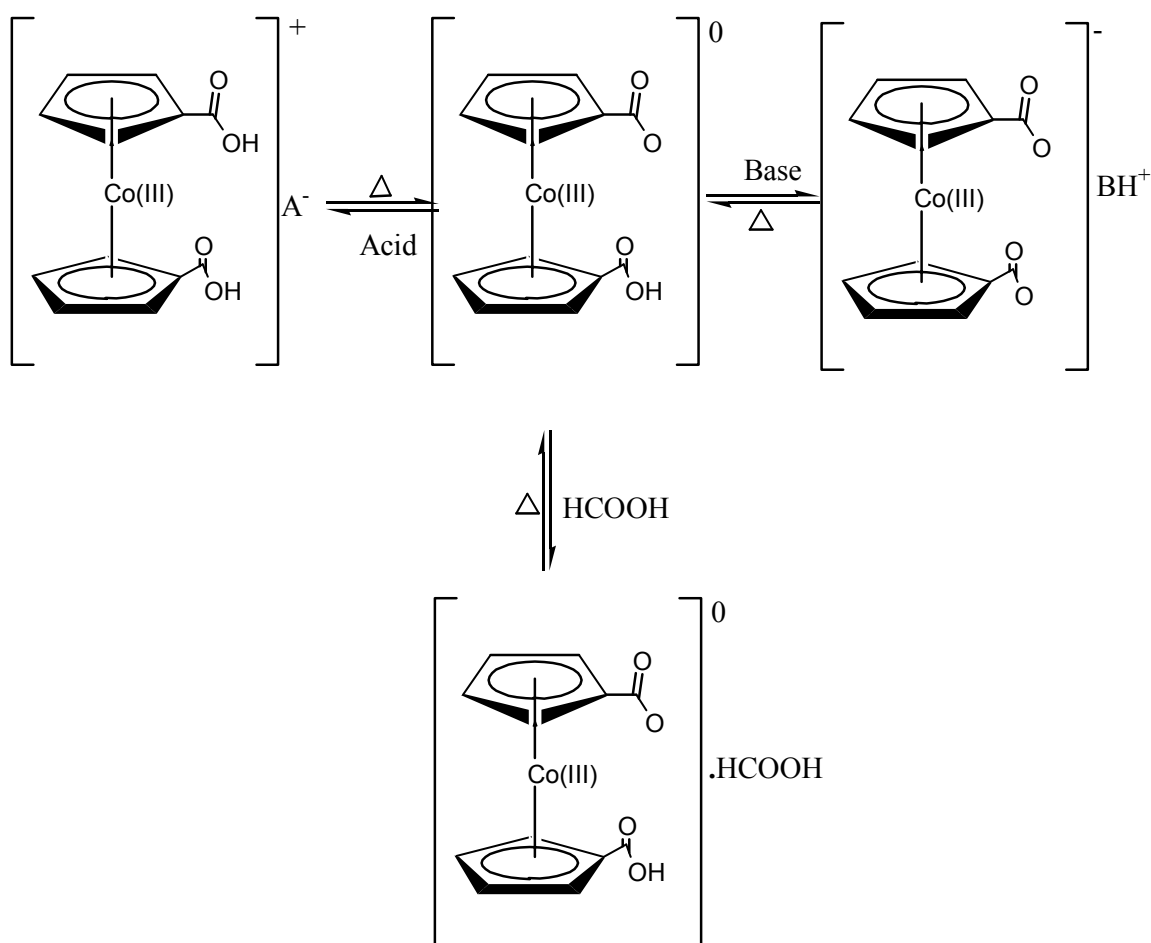


Figure 2.3: Solid state reaction of distibene in air [114]

In a related reaction, West *et al* have reported an interesting isomerisation reaction of a 1, 2-dioxadisiletane derivative of the corresponding 1,3-dioxadisiletane isomer in the crystalline state, the process of which was partially monitored by XRD techniques and solid state NMR spectroscopy [115].

Supramolecular complexes of organometallic –inorganic species have been prepared by reacting solid zwitterions, with various acid vapours [116 and 117]. Exposure of solid zwitterion $[\text{Co}^{\text{III}}(\eta^5\text{-C}_5\text{H}_4\text{COOH})(\eta^5\text{-C}_5\text{H}_4\text{COO})]$ to formic acid quantitatively produced the co-crystal $[\text{Co}^{\text{III}}(\eta^5\text{-C}_5\text{H}_4\text{COOH})(\eta^5\text{-C}_5\text{H}_4\text{COO})][\text{HCOO}]$ without proton transfer from formic acid to the deprotonated $-\text{COO}^-$ group on the zwitterion [116]. Exposure of the zwitterion to CF_3COOH and HBF_4 quantitatively yielded

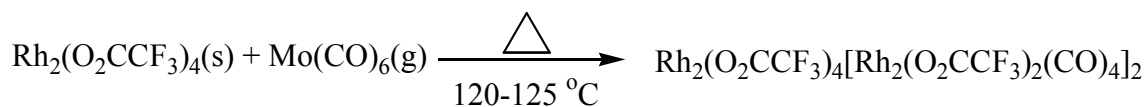
$[\text{Co}^{\text{III}}(\eta^5\text{-C}_5\text{H}_4\text{COOH})_2[\text{CF}_3\text{COO}]$ and $[\text{Co}^{\text{III}}(\eta^5\text{-C}_5\text{H}_4\text{COOH})_2[\text{BF}_4]$ respectively. In a related study, exposure of the solid zwitterion to hydrated volatile acids or bases quantitatively produced the corresponding salts [118]. All these heterogeneous reactions are fully reversible (Scheme 4) and the acid or base can be quantitatively removed by thermal treatment which generates the starting material. These reactions are important as they can be used to trap environmentally dangerous or poisonous molecules. An added advantage is that the zwitterion can be regenerated by a mild thermal treatment.



Scheme 4

Reactions of $\text{Ru}_3(\text{CO})_{12}$ with gaseous alkynes to give corresponding tri-nuclear acetylide or acetylene disubstituted clusters are known [119]. Reactions are carried out over different oxide supports and the products produced are dependent on the nature of these oxides as well as the vapour pressure of the alkynes. This work revealed the versatility of solid-gas reactions for preparative purposes under mild conditions and in the absence of solvents. This is also an example of a surface mediated organometallic reaction.

The synthesis of $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4[\text{Rh}_2(\text{O}_2\text{CCF}_3)_2(\text{CO})_4]$ has been carried out without solvent by way of the gas phase [120] (Scheme 5).



Scheme 5

The same technique has been used for studying the complexation of $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ with solid sublimable ligands [121]. The reaction of naphthalene and $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ gave a one dimensional polymer of $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4 \cdot \text{C}_{10}\text{H}_8]_\infty$. The solid state synthetic procedure offered pure products whereas solvated products were isolated with solution synthesis techniques [120 - 121].

2.2.3.4 Solid State Polymerisation reactions

The first synthesis of an organometallic polymer using the technique of solid state polymerization was reported by Rasburn *et.al* [122]. The complex investigated was Ferrocenophane $\text{Fe}(\eta\text{-C}_5\text{H}_4)_2\text{SiMePh}$. This complex was found to produce a stereoregular poly(ferrocenylmethylphenylsilane (Figure 2.4) consisting of alternating ferrocene and organosilane units. Preparation of this polymer by thermal ring opening or irradiation with γ - radiation polymerization yield an atactic polymer (**2b**) and tactic polymer respectively.

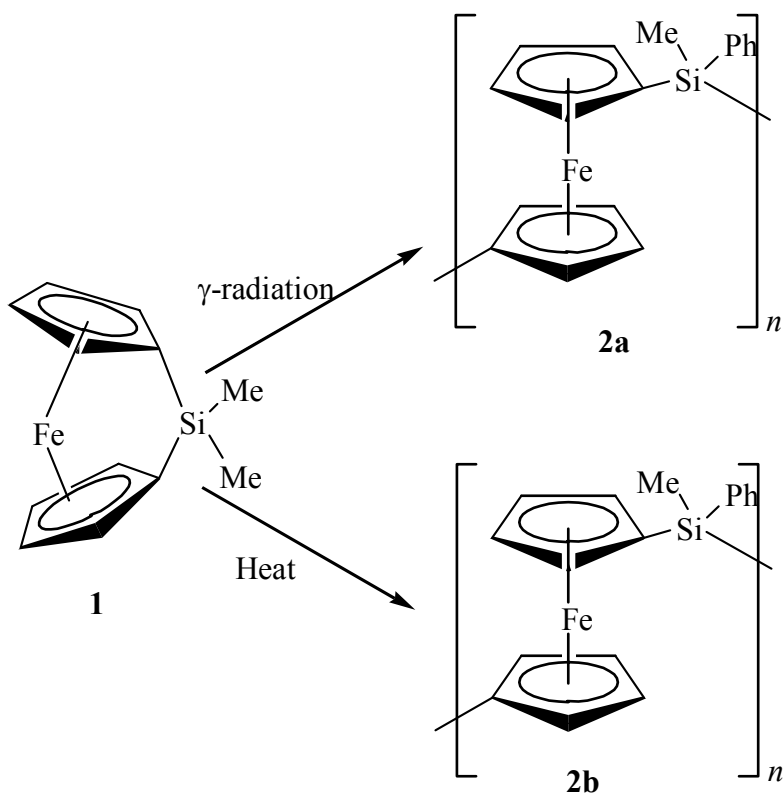


Figure 2.4: Thermal and irradiation induced polymerisation of ferrocenophane in the solid state [122].

Irradiation (^{60}Co - γ rays) of crystalline bis(but-3-enoato)zinc affords isotactic zinc poly(but-3-enoate) [123] in a solid state reaction that led to an isotactic oligomer. Solid state polymerization of alkali and alkaline acrylates and methacrylates as well as crystalline styryl monomer leads to atactic polymer. It apparently seems that topochemical effects are responsible for at least the onset of reactivity, while other factors such as crystal degradation later produce a product that is atactic

2.2.3.5 Solventless Migratory Insertion Reactions:

Migratory insertion reactions occur under solventless conditions [124]. The reaction between $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{Me}$ ($\text{M} = \text{Mo}, \text{W}$) and PPh_3 occurred below $80\text{ }^\circ\text{C}$ and gave 60-99 % yield of the product (Figure 2.5)

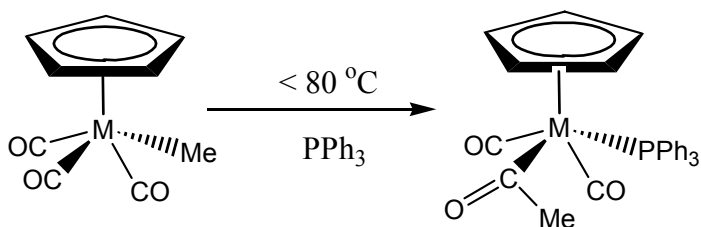
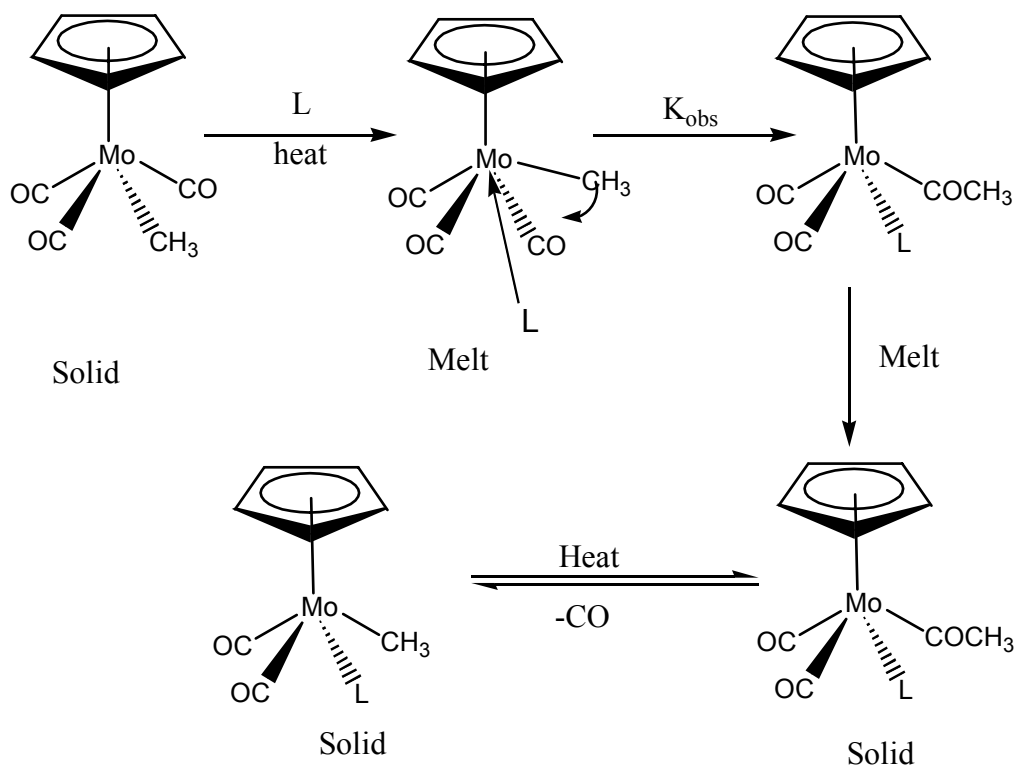


Figure 2.5: Solid state migratory/insertion reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{Me}$ ($\text{M} = \text{Mo}, \text{W}$) and PPh_3 [124].

The rate data has been observed to be consistent with a pseudo first-order process. Diffusional effects on the rate of reaction have been detected at low temperatures and low PPh_3 ratios.

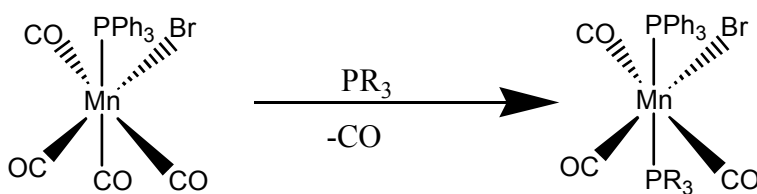
Similar reactions occurred with other triaryphosphines or phosphites. The reactions occur in the melt phase in the absence of a solvent. Trace amounts of decarbonylation product in the solid state have been observed as well. In a related study, a reaction between $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{Me}]$ and $\text{P}(p\text{-FC}_6\text{H}_4)_3$ was found to form $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2\text{P}(p\text{-FC}_6\text{H}_4)_3\text{COMe}]$ [125]. The kinetics of the reaction, which was monitored by DRIFTS, revealed a pseudo-first order reaction, while the microscopic investigation actually showed that the reaction occurred in the melt phase below the melting points of the two reagents. Melting of the phosphine was noted before the reaction could start, this suggested that the methyl migration/insertion reaction occurs in the melt by the classical mechanism that occurs in the solution phase. Diffusional effects for this reaction have been noted as well. The mechanism of the migratory insertion reaction was deduced and is shown in the Scheme 6 below [125].



Scheme 6

2.2.3.6 Solventless Substitution Reactions

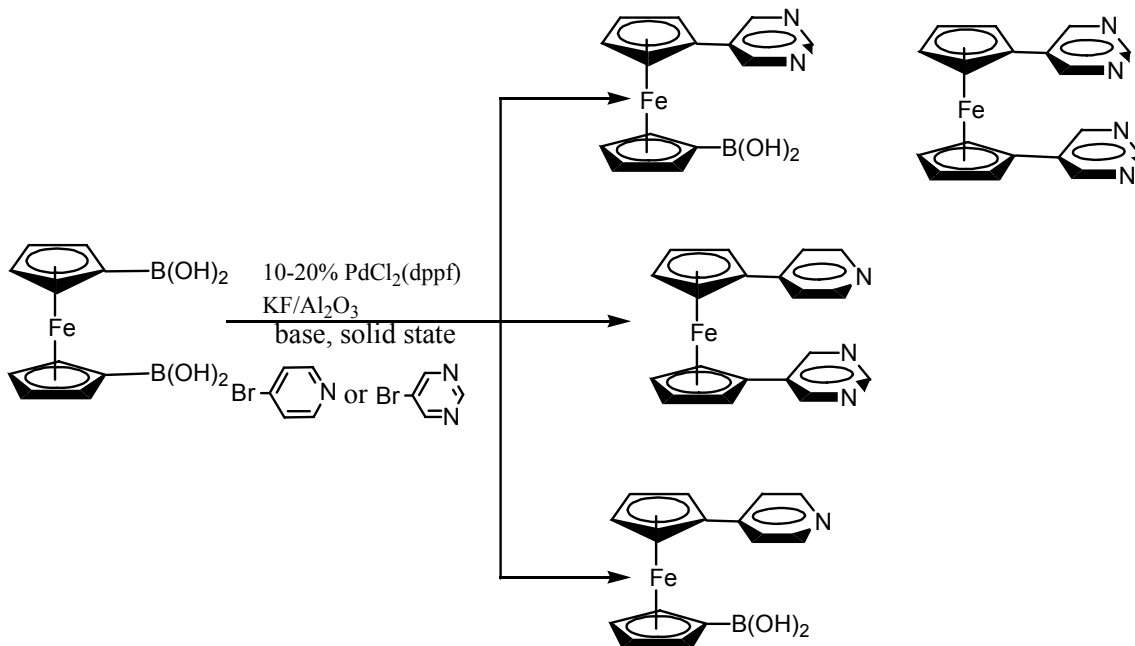
Recently, it has been found that the complex $\text{Mn}(\text{CO})_4(\text{PPh}_3)\text{Br}$ underwent CO substitution by triarylphospine ligands at temperatures below the reagents melting point and decomposition points (scheme 7) to give a *trans*- product [126].



Scheme 7

Studies on this reaction revealed first-order kinetics. The kinetic data and DSC studies showed a well behaved solid state reaction and visual inspection revealed the same. Microscopic investigation of this reaction revealed that the reaction commenced at 39 °C when the reagents melted at a temperature far below the melting point and decomposition temperature of both PPh_3 and $\text{Mn}(\text{CO})_4(\text{PPh}_3)\text{Br}$. Reaction of $\text{Mn}(\text{CO})_4(\text{PPh}_3)\text{Br}$ with $\text{P}(p\text{-OMePh})_3$ showed that the $\text{Mn}(\text{CO})_4(\text{PPh}_3)\text{Br}$ melted at 65 °C. Studies of this reaction revealed that melting of either reactant initiated the reaction with the reaction occurring in the melt, prior to crystallization. The data is also consistent with the proposal by Kaupp *et al.* [3, 30] that many reactions previously thought to be solid state reactions actually occur in the melt. Solid state substitution reaction between halogenoacetate and metal halides is known [127], but here the reaction is between a metal halide (inorganic compound) and a halogenoacetate (organic reagent) molecule.

Disubstituted pyridine/pyrimidine ferrocenyl complexes have been prepared by mechanically induced Suzuki coupling reactions in the solid state [95] (see Scheme 8 below)



Scheme 8

The reaction is much faster, and more selective than the solution synthesis. More important is the possibility of combining different synthetic steps to produce the complex in Figure 2.6

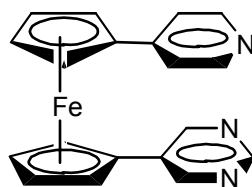


Figure 2.6: Disubstituted pyridine-pyrimidine complex [95]

2.2.4 Solid state/Solventless isomerisation reactions

Isomerisation reactions commonly occur in the solution state. Similar reactions have been found to occur in the solid state. Three types of isomerisation reactions can occur: isomerisation at the ligand, isomerisation at the metal centre and linkage isomerisation. Some examples of solid state isomerisation reactions involving organometallic complexes are shown below in Figure 2.7 and Schemes 9 - 11.

2.2.4.1 Isomerisation at the ligand

The most studied complexes are the cobaloximes that have been thoroughly investigated by Ohashi *et al.* [128]. Ohashi and his colleagues discovered that the cyanoethyl group in crystalline chiral [(**R**)-1-cyanoethyl][(**S**)-ethylbenzylamine]bisdimethylglyoximate cobalt-(III) was racemized by exposure to X-rays in a diffractometer (Figure 2.7).

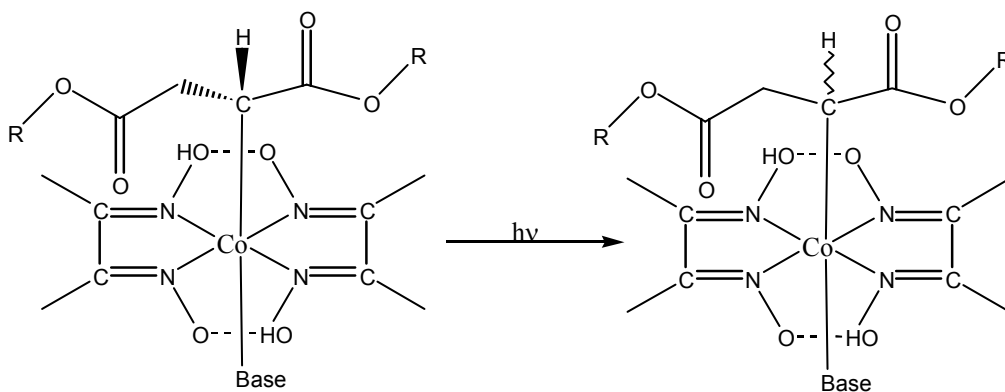
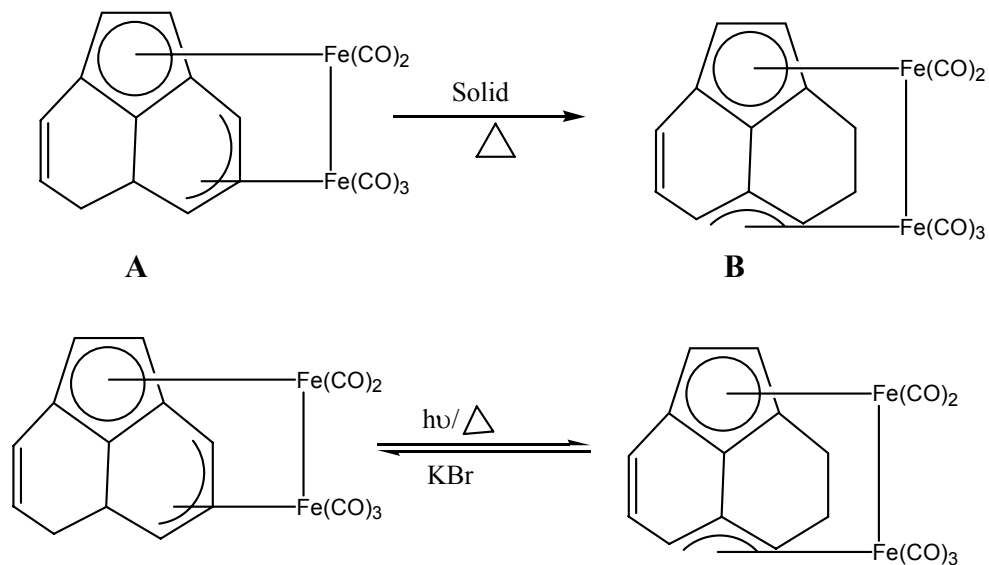


Figure 2.7: Racemisation of the CN group of a crystal of cobalt(II) complex [128]

Of importance was the observation that the reaction could occur without crystal decay and this made it possible to study the mechanism of the reaction in a single crystal. Since then an extensive study on these cobaloxime complexes was carried out and the studies revealed that

- (i) racemisation can be photo-induced [129 and 130]
- (ii) packing around the cyanoethyl group was important in determining the degree of reactivity [131]
- (iii) Irradiation of racemic mixtures by either X-ray or visible light resulted in conversion of a racemic complex to a chiral complex [132]
- (iv) Asymmetric synthesis is possible [133]

Another example of this isomerisation reaction is the rearrangement of a diiron carbonyl species on the conjugate π -ligand [134] shown in Scheme 9.



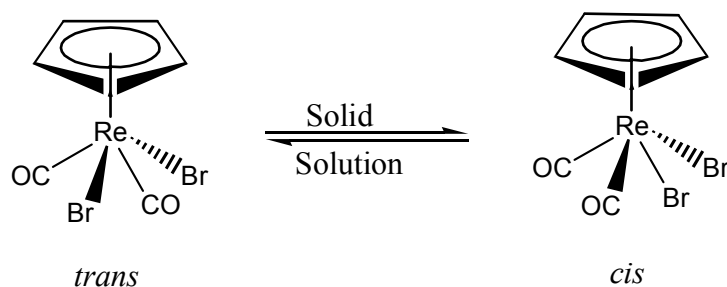
Scheme 9

A single crystal of the starting material **A** converts to a single crystal of **B** upon heating. A photolysis (5 min by a 500 W xenon lamp)/ thermal treatment (10 min at 100 °C) cycle of a KBr pellet containing either isomers has shown a reversible interconversion between the two isomers in the solid state. This reaction indicated a possible organometallic photochromism in the solid state.

2.2.4.2 Isomerisation of ligands around the metal centre

Studies have revealed that solution state fluxional behavior is a common phenomenon and that the energy barrier for rearrangement of ligands around the metal center can be quite low [135]. In addition, as the number of ligands around the central metal atom increases, the ease of ligand rearrangement around the metal also increases. Such behavior has been observed in the solid state for 4-, 5- 6- and 7-coordinate systems and to date isomerisation reactions have been detected for numerous organometallic complexes.

A range of ‘piano stool’ complexes of the type CpML₄ (M = Re, Mo, W) have been synthesised and found to undergo *trans-cis (diag-lat)* isomerisation in the solid state [91, 99, 136 - 142] (Scheme 10).

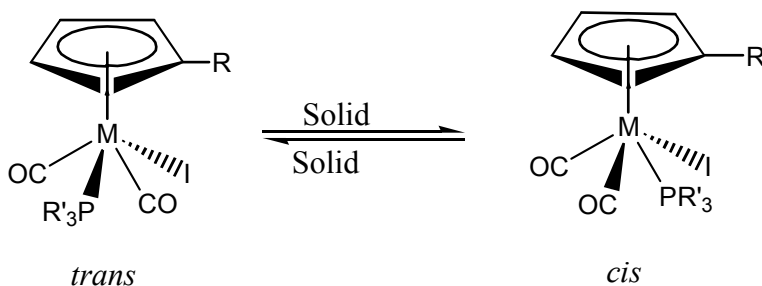


Scheme 10

The isomerisation reactions of rhenium complexes have been found to be unidirectional that is, the reaction is from the *trans* isomer to the *cis* isomer. It was observed that

solution and solid state reactions could be different [83, 84 , 143], and studies in the solid state revealed a possible alternative isomerisation pathway to those found in solution. In the studies of these complexes, it was found that one member of this series , namely, $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Re}(\text{CO})[\text{P}(\text{O}^i\text{Pr})_3]\text{Br}_2]$ [136, 144] underwent isomerisation in the solid state without cracking or any serious crystal deterioration. This therefore permitted the isomerisation process to be followed by X-ray diffraction methods [143]. The studies suggested a 2-fold rotation mechanism for the *trans* to *cis* isomerization reaction. This mechanism involved a unidirectional anticlockwise movement of CO and only one Br atom.

However, for trichlorogermyl complexes of Mo and W, bearing a cyclopentadienyl ligand, isomerisation is from the *cis* isomer to the *trans* isomer [138]. Recently, similar studies carried out on *cis*- and *trans*- $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Mo}(\text{CO})_2(\text{P}(\text{O}^i\text{Pr})_3)\text{I}]$ complexes revealed a bidirectional thermal ligand isomerization reaction. This yielded an equilibrium mixture of isomers (30:70 *cis/trans* ratio, 90°C, < 80 min) in the solid state [139]. In benzene (reflux, 2 hrs) this isomer ratio was found to be 70:30 *cis/trans*. DSC and XRD studies have shown that the reaction occurs in the solid state, even though DSC experiments did not reveal the presence of the *cis-trans* isomerisation reaction. Solid state isomerisation reactions on complexes of the type $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Mo}(\text{CO})_2(\text{PR}'_3)\text{I}$ ($\text{M} = \text{W}, \text{Mo}$; $\text{R} = \textit{t}\text{Bu}, \text{Me}$; $\text{R}' = \text{Ph}, \text{O}^i\text{Pr}_3$) revealed a bidirectional thermal solid state reaction [145] (Scheme 11)



Scheme 11

Studies investigating the effects of ring substituents, the phosphine ligands as well as the relationship between the melting points of the isomers have been done [145]. It was noted that there is no obvious relationship between the melting point and the metal, the ring substituent or the type of phosphine ligand used. However, the general trend observed was that isomerisation took place from the lower melting point isomer to the higher melting point isomer *i.e.* the favoured direction of isomerisation is related to intermolecular forces in the solid state.

2.5 Conclusion

Solid state organometallic chemistry is beginning to be realised. The work is still in its infancy and little is known about reactivity patterns of organometallic complexes in the solid-state. However the many reports on solid state organic and coordination complexes suggest that the principles that govern these reactions might well be applied to the area of organometallic chemistry.

2.6 REFERENCES

- 1 J. A. M. Simoes, J. L. Beauchamp, *Chem. Rev.* **90** (1990) 629.
- 2 D. Bradly, *Chemistry in Britain*, September 2002 p 42.
- 3 G. W. Cave, C. L. Raston, J. L. Scott, *Chem. Commun.* (2001) 2159.
- 4 G. Rothenberg, A. P. Downie, C.L Raston, J. L Scott, *J. Am. Chem. Soc.* **123** (2001) 8701
- 5 D. Braga, F.Grepioni, *Angew. Chem. Int. Ed.* **43** (2004) 4002.
- 6 T. Ohara, J. Harada, Y. Ohashi, I. Tanaka, S. Kumazawa, N. Niimura, *Acta Cryst.* **B56** (2000) 245.
- 7 T. Luty, C. J. Eckhardt, *J. Am. Chem. Soc.* **117** (1995) 2441
- 9 M. D. Cohen, G. M. Schmidt, *J. Chem. Soc.* (1964) 1996.
- 9 M. D. Cohen, *Angew. Chem. Int. Ed. Engl.* **14** (1975) 386.
- 10 Y. Ohashi, *Acc. Chem. Res.* **21** (1988) 268.
- 11 H. E. LeMay Jr., in: G. Wilkinson, R. D. Gillard, J. A. McLeverty (Eds), *Comprehensive Coordination Chemistry*, Ch. 7.5, Vol. 1, Pergamon, New York.
- 12 S. V. Evans, M. Garcia-Garibay, N. Omkaram, J. R Scheffer, J. Trotter, F. Wireko, *J. Am. Chem. Soc.* **108** (1986) 5648.
- 13 G. Kaupp, *CrystEngComm.* **23** (2003) 117.
- 14 D. C. Dittmer, *Chem. Ind.* (1997) 779.
- 15 G. W. Cave, C. L. Raston, J. L. Scott, *Chem. Commun.* (2001) 2159.
- 16 M. Sakamoto, *Chem. Eur. J.* **3** (1997) 684.
- 17 F. Toda, *Acc. Chem. Res.* **28** (1995) 480.
- 18 V. Ramamurthy, K. Venkatesan, *Chem. Rev.* **87** (1987) 433.
- 19 M. Garcia-Garibay, *Curr. Opin. Solid State Mater. Sci.* **3** (1998) 399.
- 20 Y. Ohashi, *Curr. Opin. Solid State Mater. Sci.* **1** (1996) 522.
- 21 D. Braga, G. R. Desiraju, J. S. Miller, A. G. Orpen, S. L. Price, *CrystEng. Commun.* **4** (2002) 500.
- 22 D. R. Desiraju in: *Crystal Engineering: The Design of Organic Solids*, Elsevier, New York, 1989.
- 23 K. Tanaka, *Solvent Free Organic Synthesis*, Wiley Interscience, 2003.
- 24 Cohen M.D. Schmidt G. M. , *J. Chem. Soc.* (1964), 1996.

- 25 Cohen M.D., *Angew. Chem. Int. Ed. Engl.* **14** (1975) 386.
- 26 Schmidt G. M., *Pure Appl. Chem.* **27** (1971) 647.
- 27 M. A. Fernandes, D.C Levindis, C. B. de Koning, *Cryst. Eng.* **4** (2000) 215.
- 28 H. E. Zimmerman, I. V. Alabugin, W. S.Chen, Z. N. Zhu, *J. Am. Chem. Soc.* **121** (1999) 11930.
- 29 G. Kaupp, *Curr. Opin. Solid State Mater. Sci.* **6** (2002) 131.
- 30 G. Kaupp, M. Reza, N. Jamal, J. Schmeyers, *Tetrahedron* **59** (2003) 3753.
- 31 V. Ramamurthy, K. Venkatesan, *Chem. Rev.* **87** (1987) 433.
- 32 R. Psaro, R. Recchia, *Catalysis Today* **41** (1998) 139.
- 33 F. Toda, *Acc. Chem. Res.* **28** (1995) 480.
- 34 G. Kaupp, J. Schmeyers, J. Boy, *Chemosphere* **43** (2001) 55.
- 35 J. Schmeyers, F. Toda, J. Boy, G. Kaupp, *J. Chem. Soc., Perkin Trans. 2* (1998) 989.
- 36 J. L. Scott, C. L. Raston, *Green Chemistry* **2** (2000) 245.
- 37 J. A. R. P. Sarma, A. Nagaraju, *J. Chem. Soc., Perkin Trans 2* (2000) 1113.
- 38 K. Tanaka, F. Toda, *Chem. Rev.* **100** (2000) 1025.
- 39 Le May, , H. E. Jr. In *Comprehensive Coordination Chemistry*,; G. Wilkinson, Ed., Pergamon Press, New York, 1986, Vol. **17**, p 643.
- 40 A. Werner, A. Frohlich, *Chem. Rev.* **40** (1907) 2228.
- 41 R. Ellis, T. A. Weil, M. Orchin, *J. Am. Chem. Soc.* **92** (1970) 1078
- 42 S.D. Kirik, L. A. Solovyov, A. I. Blokhin, I. S. Yakimov, *Acta Cryst.* **B56** (2000) 419.
- 43 M. Fushini, M. Suzuki, A. Uehara, *Bull. Chem. Soc. Jpn.* **61** (1988) 1809.
- 44 H. E. Le May Jr., *Inorg. Chem*, **7** (1968) 2631.
- 45 R. Tsuchiya, Y. Natsume, A. Uehara, E. Kyuno, *Bull. Chem. Soc., Jpn.* **43** (1970) 1383.
- 46 R. Tsuchiya, Y. Natsume, A. Uehara and E. Kyuno, *Thermochim. Acta* **12** (1975) 147.
- 47 R. Tsuchiya, T. Ohki, A. Uehara, E. Kyuno, *Thermochim. Acta* **12** (1975) 413.
- 48 T. Yoshikuni, R. Tsuchiya, A. Uehara, E. Kyuno, *Bull. Chem. Soc. Jpn.* **51** (1978) 113.

- 49 C. Sato, S. Hatakeyama, *Bull. Chem. Soc. Jpn.* **45** (1972) 646.
- 50 S. Jorgensen, *Z. Anorg. Chem.* **5** (1893) 168.
- 51 E. V. Boldreva in: E. V. Boldreva, V. Boldrev, (Eds), *Reactivity of Molecular Solids*, Wiley, New York, (1999) p 1.
- 52 I. R. Laskar, D. Das, G. Mostafa, T. H. Lu, T. C. Keng, J. C. Wang, A. Ghosh, N. R. Chaudhuri, *New. J. Chem* **25** (2001) 764.
- 53 I. Grenthe and E. Nordin, *Inorg. Chem.* (1979) 1869.
- 54 V. P. Balema, J. W. Wiench, M. Pruski, V. K. Pecharsky, *Chem. Commun.* (2002) 1606.
- 55 V. P. Balema, J. W. Wiench, M. Pruski, V. K. Pecharsky, *Chem. Commun.* (2002) 724.
- 56 V. P. Balema, J. W. Wiench, M. Pruski, V. K. Pecharsky, *J. Am. Chem. Soc.* **124** (2002) 6244.
- 57 L. Lei, S. Jing, R. I. Walton, X. Xin, D. O'hare, *J. Chem. Soc., Dalton Trans.* (2002) 3477.
- 58 T. Chen, B. Liang, X. Xin, *J. Phys. Chem. Solids* **58** (1997) 951.
- 59 B. Liang, Q. Dai, X. Xin, *Synth. React. Inorg. Met.-Org. Chem.* **28** (1998) 165.
- 60 X. Yao, L. Zheng, X. Xin, *J. Solid State Chem.* **117** (1995) 333.
- 61 X. R. Ye, D. Z. Jia, Q. Yu, X. Q. Xin, Z. Xue, *Adv. Mater. (Weinheim, Ger.)* **11** (1999) 941.
- 62 H.G. Zheng, D. Zheng, X.Q. Xin, W. T. Wong, *Polyhedron* **16** (1997) 3499.
- 63 L. Lei, X. Xin, *Thermochim. Acta* **273** (1996) 61.
- 64 L. Lei, X. Xin, *J. Solid State Chem.* **119** (1995) 299.
- 65 L. Lei, Z. Wang, X. Xin, *Thermochim. Acta* **297** (1997) 193.
- 66 Y. M. Zhou, X. Xin, *Wuji Huaxue Xuebao* **15** (1999) 273.
- 67 L. Lei, X. Xin, *Huaxue Tongbao*, 1997, 1.
- 68 P. J. Nicholls, C. L. Raston, J. W. Steed, *Chem. Commun.* (2001) 1062.
- 69 M. H. Chisholm, J. Gallucci, C. M. Hadad, J. C. Huffman, P. J. Wilson, *J. Am. Chem. Soc.* **125** (2003) 16040.
- 70 W. J. Belcher, C. A. Longstaff, M. R. Neckenig and W. J. Steed, *Chem. Commun.* (2002) 1602.

- 71 A. Orita, L. S. Jiang, T. Nakano, N. C. Ma, J. Otera, *Daltons* (2001) 1362.
- 72 H. Grove, J. Sletten, M. Julve, F. Lloret, *J. Chem. Soc., Daltons Trans.* (2001) 2487.
- 73 P. J. Nichols, C. L. Raston, J. W. Steed, *Chem. Commun.* (2001) 1062.
- 74 J. F. Fernandez-Bertran, *Pure Appl. Chem.* **71** (1999) 581.
- 75 N. Khaorapong, K. Kuroda, H. Hashizume, M. Ogawa, *Appl. Clay Sci.* **19** (2001) 69.
- 76 M. Ogawa, K. Kuroda, C. Kato, *Chem. Lett.* (1989) 1659
- 77 M. Ogawa, T. Handa, K. Kuroda, C. Kato *Chem. Lett.* (1990) 71.
- 78 M. Ogawa, K. Kato, K. Kuroda, C. Kato, *Clay. Sci.* **8** (1990) 31.
- 79 M. Ogawa, K. Fujii, K. Kuroda, C. Kato, *Mater. Res. Soc. Symp. Proc.* 233 (1991) 89.
- 80 T. Okada, Y. Watanabe, M. Ogawa, *J. Mater. Chem.* **15** (2005) 987.
- 81 L. Vaska, *J. Am. Chem. Soc.* **88** (1966), 5325.
- 82 M. Burghard, *Angew. Chem. Int. Ed.* **42** (2003) 5929.
- 83 N. J. Coville, L. Cheng, *J. Organomet. Chem.* **571** (1998) 149.
- 84 N.J. Coville, D. C. Leventis, *Eur. J. Inorg. Chem.* (2002) 3067.
- 85 D. Roberto, R. Psaro, R. Ugo, *Organometallics* **12** (1993) 2292.
- 86 F. Lefebvre, J.-M. Basset, *J. Mol. Catal. A* **146** (1999) 3.
- 87 C. Copéret, O. Maury, J. Thiovolle-Cazat, J.-M. Basset, *Angew. Chem. Int. Ed. Engl.* **40** (2001) 2331.
- 88 F. Lefebvre, J. Malinge, J. P. Broyer, M. Jezequel, M. J. Ruiz-Garcia, J. Evans, V. Dufaud, G. P. Nicollai, J.-M. Basset, *J. Am. Chem. Soc.* **123** (2001) 3520.
- 89 E. Le Roux, M. Chabanas, A. Baudouin, A. Mallmann, C. Copéret, E. A. Quadrelli, J.T-Cazat, J.-M. Basset, W. Lukens, A. Lesage, L. Emsley, G. J. Sunley, *J. Am. Chem. Soc.* **126** (2004) 13391.
- 90 Yu. A. Ryndin, J. P. Candy, B. Didillon, L. Salvary, J.-M. Basset, *J. Cat.* **198** (2001) 103.
- 91 L. Cheng, N. J. Coville, *Organometallics*, **16** (1997) 591.
- 92 L. Cheng, PhD Thesis, University of Witwatersrand, Johannesburg, South Africa, 1997.

- 93 D. C. Dittmer, *Chem. Ind.* (1997) 779.
- 94 H. Koshima, H. Ichimura, T. Matsuura, *Chem. Lett.* (1994) 847.
- 95 D. Braga, D. D'Addario, M. Polito, *Organometallics* **23** (2004) 2810.
- 96 G. R. Desiraju, *J. Mol. Struct.* **656** (2003) 5.
- 97 V. D. Makhaev, A. P. Borisov, L. A. Petrova, *J. Organomet. Chem.* **590** (1999) 222.
- 98 B. Eke, N. J. Coville, *Inorg. Chem. Commun.* **3** (2000) 368.
- 99 L. Cheng, N. J. Coville, *J. Organomet. Chem.* **556** (1998) 111.
- 100 D. Braga, L. Maini, M. Polito, F. Grepioni, *Chem. Commun.* (2002) 2302.
- 101 D. Braga, L. Maini, M. Polito, L. Mirolo, F. Grepioni, *Chem. Commun.* (2002) 2960.
- 102 H. G. Zheng, J. L. Zhou, W. L. Tan, Y.Y. Niu, W. Ji, X. Q. Xin, *Inorg. Chim. Acta.* **340** (2002) 29.
- 103 L. Jianping, X. Xinquan, *J. Solid State Chem.* **108** (1994) 118-127.
- 104 L. Jiguo, X. Xinquan, Z. Zhongyuan, Y. Kaibei, *Chem. Commun.* (1991) 249.
- 105 V. Chandrasekhar, V. Baskar, R. Boomishankar, K. Gopal, S. Zacchini, J. F. Bickley, A. Steiner, *Organometallics* **22** (2003) 3710.
- 106 V. Chandrasekhar, S. Nagendran, V. Baskar, *Coord. Chem. Rev.* **235** (2002) 1.
- 107 R. R. Holmes, *Acc. Chem. Res.* **22** (1989) 190.
- 108 E. R. T. Tiekink, *Appl. Organomet. Chem.* **5** (1991) 1.
- 109 G. Pellizzari, *Gazz. Chim. Ital.* **14** (1884) 362.
- 110 I. C. Paul, D. Y. Curtin, *Science* **187** (1975) 19.
- 111 L. Mond, C. Langer, F. Quimke, *J. Chem. Soc.* **57** (1890) 749.
- 112 F. Porta, S. Tollari, C. Bianchini, S. Recchia, *Inorg. Chim. Acta* **249** (1994) 79.
- 113 C. Bianchini, F. Zanobini, S. Aime, R. Gobetto, R. Psaro, L. Sordelli, *Organometallics* **12** (1993) 4757.
- 114 N. Tokitoh, Y. Arai, T. Sasamori, R. Okazaki, S. Nagase, H. Uekisa, Y. Ohashi, *J. Am. Chem. Soc.* **120** (1998) 433.
- 115 K. L. McKillop, G. R. Gillette, D. R. Powell, R. West, *J. Am. Chem. Soc.* **114** (1992) 5203.

- 116 D. Braga, L. Maini, M. Mazzotti, K. Rubini, A. Masic, R. Gobetto, F. Grepioni, *Chem. Commun.* (2002) 2296.
- 117 G. Cojazzi, D. Emiliani, L. Maini, F. Grepioni, *Organometallics* **21** (2002) 1315.
- 118 D. Braga, G. Cojazzi, D. Emiliani, L. Maini, F. Grepioni, *Chem. Commun.* (2001) 2272.
- 119 P. J. King, E. Sappa, C. Sciacca, *Inorg. Chim. Acta* **334** (2002) 131.
- 120 F. A. Cotton, E. V. Dikarev, M. A. Petrukhina, *J. Organomet. Chem.* **596** (2000) 130.
- 121 F. A. Cotton, E. V. Dikarev, M. A. Petrukhina, S. E. Stiriba, *Polyhedron* **19** (2000) 1829.
- 122 J. Rasburn, D. A. Foucher, W.F. Reynolds, I. Manners, G. J. Vasco, *Chem. Commun.* (1998) 843.
- 123 M. J. Vela, V. Buchiolz, V. Enkelmann, B. B. Snider, B. M. Foxman, *Chem. Commun.* (2000) 2225.
- 124 O. G. Adeyemi, N. J. Coville, *Organometallics* **22** (2003) 2284.
- 125 M. D. Bala, A. Budhai, N. J. Coville, *Organometallics* **23** (2004) 2048.
- 126 S. S. Manzini, N. J. Coville, *Inorg. Chem. Commun.* **7** (2004) 676.
- 127 M. Epple, R. Seifert, *J. Solid State Chem.* **121** (1996) 129.
- 128 Y. Ohashi, Y. Sasada, *Nature* (1977) **267** 142.
- 129 H. Sato, Y. Ohashi *Bull. Chem. Soc. Jpn.* **72** (1999) 367.
- 130 Y. Ohashi, Y. Sakai A. Sekine, Y. Arai, Y. Ohgo, N. Kamiya, H. Iwasaki, *Bull. Chem. Soc. Jpn.* **68** (1995) 2517.
- 131 Y. Ohashi, *Acc. Chem. Res.* **21** (1988) 268.
- 132 Y. T. Otsano, A. Uchida, Y. Ohashi, *Nature* **352** (1991) 510.
- 133 A. Sekino, H. Tatsuki, Y. Ohashi, *J. Organomet. Chem.* **536** (1997) 389.
- 134 S. Niibayashi, K. Matsubara, M-aki Haga, H. Nagashima, *Organometallics* **23** (2004) 635.
- 135 D. Braga, *Chem. Rev.* **92** (1992) 633.
- 136 L. Cheng, N. J. Coville, *Thermochim. Act* **319** (1998) 27.
- 137 L. Cheng, L. Carlton, N. J. Coville, *S. Afri. J. Chem.* **51** (1998) 127.

- 138 A. C. Filippou, J. G. Winter, M. Feist, G. K-Kohn, I. Hinz, *Polyhedron* **17** (1998) 1103.
- 139 O.G Adeyemi, M. A. Fernandes, L . Cheng, U. B. Eke, D. C. Levendis, N. J. Coville, *C. R. Chimie* **5** (2002) 387.
- 140 L. Cheng, N. J. Coville, *Organometallics* **15** (1996) 867.
- 141 A. C. Fillipou, J. G. Winter, G. K-Kohn, I. Hinz, *J. Organomet. Chem.* **542** (1997) 35.
- 142 N. Trindade, Honours Project, University of Witwatersrand, Johannesburg, South Africa. 1999
- 143 R.S. Bogadi, D. C. Levendis, N. J. Coville, *J. Am. Chem. Soc.* **124** (2002) 1104.
- 144 J. M. Smith, L. Cheng, N. J. Coville, J. Schulte, P. S. Dimpe, M. S. Addsetts, L. M. Cook, J. C. A. Boeyens, D. C. Levendis, *Organometallics* **19** (2000) 2597.
- 145 O. G. Adeyemi, U. B. Eke, L. Cheng, L. M. Cook, D. G. Billing, B. B. Mamba, D. C. Levendis, and N. J. Coville, *J. Organomet. Chem.* **689** (2004) 2207.