

Review

Organometallic chemistry in the melt phase

Muhammad D. Bala, Neil J. Coville*

Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Johannesburg 2050, South Africa

Received 15 June 2006; received in revised form 13 October 2006; accepted 16 October 2006

Available online 27 October 2006

Abstract

In this review organometallic chemistry reactions in the *melt phase* are described. As will be indicated this is a viable approach to make new and known complexes. Examples from the literature highlighting procedures used to generate melts and results that have been obtained in this area of synthesis are described. Clearly there will be limitations to the use of the melt phase, and these limitations are also discussed.

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Keywords: Melt chemistry; Solventless organometallic chemistry; Solvent-free organometallic syntheses; Green chemistry

Contents

1. Introduction	710
1.1. Scope of the review	710
2. Melt reactions	712
2.1. Historical	712
2.2. The solid solution and melt phase reactions.	713
2.3. Features of melt reactions	713
2.3.1. The melt reaction	713
2.3.2. Reactions in a localized melt regime	714
2.3.3. Reactions involving a solid and a liquid.	714
2.3.4. Solid–gas reactions	714
2.4. Dispersants as rate controllers in melt reactions.	714
3. Melt phase chemistry	714
3.1. Mechanochemical induction	714
3.1.1. Mechanochemically initiated reactions.	715
3.1.2. Three dimensional (3-D) coordination networks and compounds by supramolecular self-assembly	715
3.1.3. Ferrocene and ferrocenyl compounds.	718

Abbreviations: *diag*, Diagonal; DGV, differential thermogas volumetry; DSC, differential scanning calorimetry; DTA, differential thermal analysis; DRIFTS, diffuse reflectance infrared spectroscopy; DTG, differential TG; EDXRD, energy dispersive X-ray diffraction; en, ethylenediamine; Fc, ferrocene, ferrocenyl; IR, Infra-red; *i*Pr, *iso*-propyl; *lat*, Lateral; L, Donor ligand; M, transition metal; Me, methyl; m.p., melting point; NMR, nuclear magnetic resonance; phen, phenanthroline; Ph, phenyl; PR₃, phosphine e.g. PPh₃; P(OR)₃, phosphite e.g. P(O^{*i*}Pr)₃; PXRD, powder- X-ray diffraction; R, organic group; r.t., room temperature; SCXRD, Single crystal- X-ray diffraction; STA, simultaneous thermal analysis (DTA TG DTG); TGA, thermogravimetric analysis; ^{*t*}Bu, *tert*-butyl; X, halogen.

* Corresponding author. Fax: +27 11 717 6749.

E-mail address: ncoville@aurum.wits.ac.za (N.J. Coville).

3.2.	Thermochemical induction	718
3.2.1.	Inter-solid reactions	718
3.2.2.	Intra-solid transformations	722
3.3.	Sonochemical induction	723
3.4.	Induction by microwave irradiation	724
4.	Solid–gas reactions	724
5.	Monitoring melt reactions	726
5.1.	Thermal analysis	726
5.2.	Thermomicroscopic techniques	727
5.3.	DRIFTS	727
5.4.	Other techniques	727
6.	Conclusions and prospects	727
	Acknowledgements	728
	References	728

1. Introduction

In the last decade new pressures have been exerted on synthetic chemists to not only consider the specific activity and selectivity of a reaction under study but to also consider the reagents used, the by-products formed and methods needed to purify the reaction products. Overall, this is classified as a *green chemistry* approach to synthesis and principles have been enunciated to provide a guideline to this synthetic approach [1]. Controversy about what constitutes a green approach to synthesis still arises. This relates to ‘holistic’ issues – how many and which factors need to be taken into account to determine whether a new process is greener than an older more conventional synthetic strategy. For example, ionic liquids are often touted as green reagents as their vapor pressure is negligible [2] yet environmental disposal of these liquids is a non-trivial issue. Are they really green solvents? The use of MTBE (methyl tert-butyl ether) was regarded as an excellent gasoline additive until it was noted that seepage of MTBE into ground waters posed a greater hazard than the benefits of cleaner burning fuels in automobile engines [3]. A greener reagent that was not green!

Notwithstanding these issues it is clear that factors such as atom economy and a reconsideration of the use of harmful reagents/intermediates/solvents has to be considered, where possible, in synthetic strategies. This must then lead to alternative strategies to bring about the reaction between two (or more) reagents to create new and known products.

In this review the focus will be on one approach that could prove useful in this philosophy to synthesis – the solventless approach. More particularly the review will focus on one aspect, the possibility of performing reactions in the *melt phase* with particular emphasis on reactions that have been reported in the organometallic chemistry literature. By avoiding the use of solvents the concentration of reactants will be at their maximum. In principle this should lead to faster reactions.

The idea of performing chemical syntheses in the absence of solvents (termed variously as: solvent-free, solventless, solid–solid and solid state reactions) is not new

even though chemists have historically performed syntheses using solvents. Indeed the idea that “No reaction proceeds without solvent” [4], assigned to Aristotle, has guided much laboratory synthesis both historically and to the present day. However, in recent years there has been much interest generated in academic and industrial laboratories on solventless chemistry and books and reviews on this approach in the field of organic chemistry have now appeared [5–10]. There are even reviews that have been published in the area of organometallic chemistry focusing on solventless organometallic synthetic strategies [11,12]. The focus in all these studies has, however, been limited to solid to solid reactions (and its link to crystal engineering) [13], although the possibility that many of these reactions may in fact occur in the melt has been recognized (see below). Herein we focus on melt reactions, a subgroup of solventless reactions, which may or may not produce solid products.

1.1. Scope of the review

As with any review the limits of what is to be covered needs to be delineated.

In this review the focus will be on emphasizing the importance of the melt phase in organometallic chemistry reactions. Fig. 1 presents a general schematic representation and cartoon of the reactions covered in this review.

- (i) The issue of melt chemistry is but one specific and special case of liquid–liquid chemistry. Melt chemistry, generally unexplored, is potentially pervasive since many chemical reagents that are solids at *room temperature* may be liquids at higher temperatures. The discussion to follow will cover reactions in which at *least one* of the reactants must be a solid at room temperature.
- (ii) Reagents will be considered to be *molecular in nature*. It is recognized that in many solids strong van der Waals forces may operate to assist in creating stable solids [14]. Ionic and metallic solids will only be discussed as appropriate.

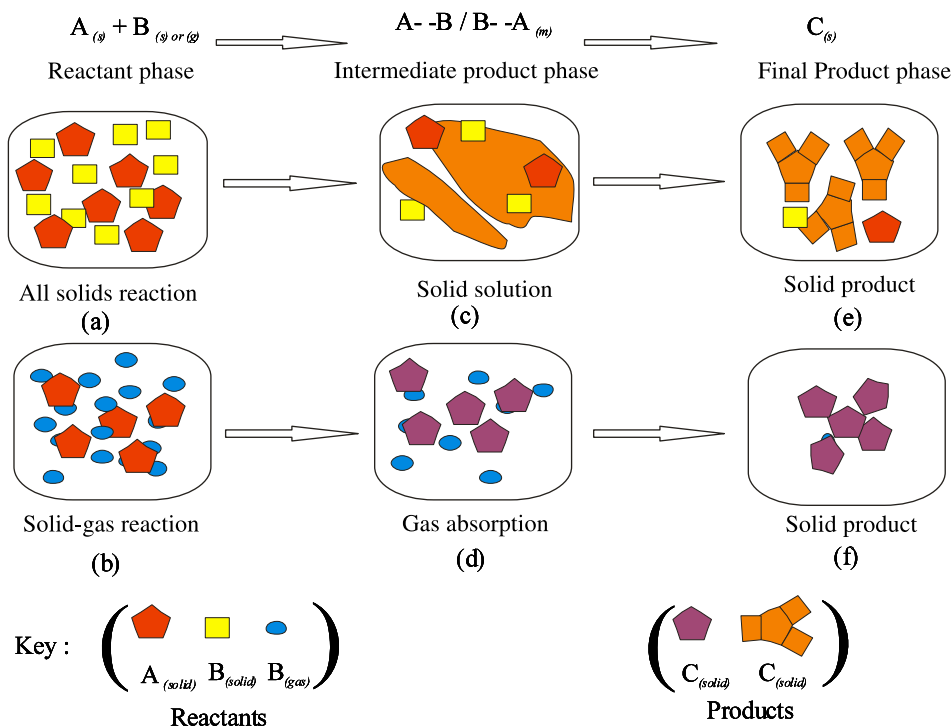


Fig. 1. Schematic representation of the reactions $A_{(s)} + B_{(s/g)} \rightarrow C_{(s)}$ covered in this paper. The route (a) → (c) → (e) denotes an all solids reaction passing through an intermediary (eutectic) melt phase, while the route (b) → (d) → (f) denotes a solid–gas reaction, in which diffusion at the solid–gas interface is important.

(iii) In reality numerous so-called solid–solid and solid state reactions involve significant movement of many molecules simultaneously and this may or may not manifest itself as a melt. This is nicely shown by the figure from a Paul and Curtin review (Fig. 2) [15].

Thus, examples where solid–solid inter-conversions occur will be discussed where necessary.

(iv) Numerous studies of the melt phase have been discussed in the organic chemistry literature and examples from appropriate studies will be described as

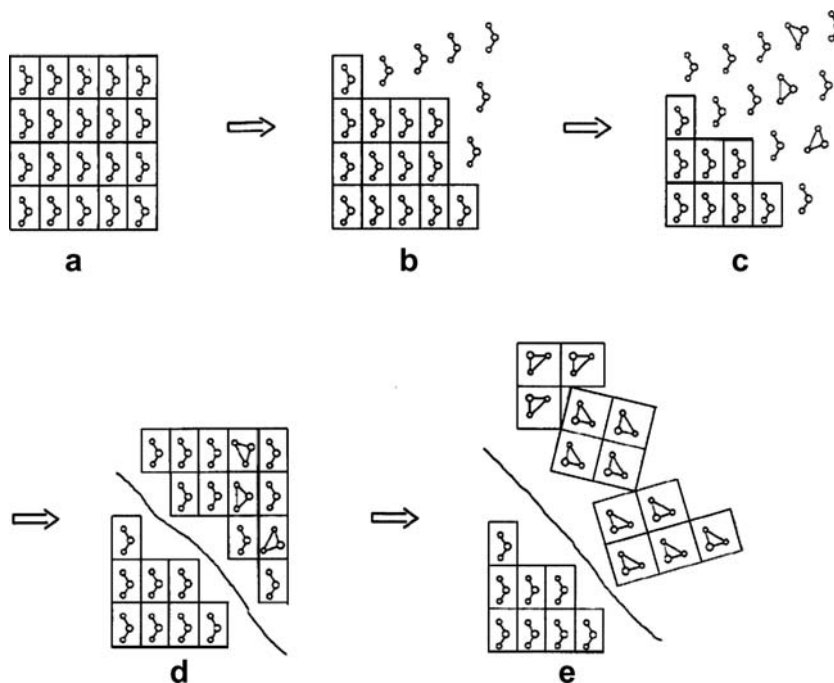


Fig. 2. Schematic representation of the stages of reaction in the solid state: (a) unreacted crystal; (b) loosening of molecules at the reaction site; (c) molecular change; (d) solid solution formation; (e) separation or product. (Reproduced from [15] with permission, copyright American Chemical Society.)

necessary. Indeed to date there are only a limited number of studies in which organometallic reactions have been studied in the melt phase.

- (v) The area of ‘mechanochemical’ synthesis is well known in metallurgy [16] and has more recently been exploited in organic [17] and organometallic [18] synthesis. Reactions involving ball milling, kneading, etc. could, and often does, involve localized melting at a particle-particle interface. The review will include comments on this synthetic approach. Sonochemical and microwave induced approaches to solventless chemistry are also mentioned.
- (vi) Where possible, links between solid-state and melt reactions will be indicated. This will entail discussion of some solventless reactions that currently are believed to go in the solid state but may have occurred in a melt phase but were not detected as such. In this category will be included intramolecular isomerization reactions and solid–gas reactions.

Finally it should be mentioned that the issue of reactions associated with the melt phase is a broad topic with input possible from a wide range of areas. Some recent examples where melts have been implicated include:

- (1) A common approach to the synthesis of carbon nanotubes involves passing a carbon source (e.g. methane, toluene, etc.) over a supported metal at high temperature. Studies have shown that the metal often (always?) is in the melt when carbon nanotubes are formed [19]. An interaction thus occurs between a melt phase and gas molecules.
- (2) The process of sintering (coalescence) in heterogeneous catalysis has been well studied. The mobility of metals (e.g. Au) is high at surprisingly low temperatures and again the issue of the melt phase needs to sometimes be considered when rationalizing catalytic data [20].
- (3) The issue of melting can apply to the synthesis of heterogeneous catalysts where reagents like $\text{Co}(\text{NO}_3)_2$, used to make Co-supported catalysts, melt at temperature circa 120 °C thus resulting in difficulties of dispersing a catalyst on a support.

2. Melt reactions

2.1. Historical

Water was the solvent medium for much chemistry reported prior to 1900. This solvent plus reactions entailing no solvents dominated early synthesis approaches in chemistry. However, access to cheap, large volume organic solvents, especially in the 19th and 20th centuries, brought about a transformation in the ability of chemists to tailor reactions by use of solvent effects. For example, enhanced solubility of solid reagents in solvents leads to enhanced

mobility of the reagents, and better interaction between the starting solids, resulting in more rapid reactions. One of the key issues when using solvents is the reagent diffusion issue; consequently reactions have “become reliant on solvents” [4]. Indeed this diffusion issue is an important one and reagent diffusion certainly can create a potential bottleneck for reactions in viscous solvents.

What about molecular solid–solid interactions that take place without the intervention of solvents? Intuitively this appears to be a diffusion limited reaction with only surface atoms that touch each other interacting! However, as will be described below, solids can be made to interact with each other and (i) provide more rapid reactions than observed in solvents and (ii) provide products different to those synthesized in conventional solvents. The ability to achieve *inter-solid reactions of molecular materials* can be driven by melt chemistry. In contrast, intermolecular reactions of either ionic or metallic solids in the solid state, at temperatures lower than their melting temperatures, are dominated by diffusion of one reactant into another. This is a well known and studied phenomenon in materials science.

One of the earliest comprehensive investigations of melt chemistry appears to be that reported by Rastogi and coworkers. They addressed fundamental issues associated with reactions of solids, such as reactant mobility across an interface [21], and laid down the foundations for understanding the kinetics [21] and mechanisms [22] of solid [23] and eutectic melt reactions [24].

The upsurge of interest in crystal engineering initiated by Desiraju [13] and others has led to an investigation of many intra-solid reactions [12]. The possibility of using solvent free procedures to synthesize organic compounds has been comprehensively detailed by Toda [10], Tanaka [5], Kaupp et al. [7], Raston and coworkers [6] and others. Initially much of the solvent free work was described as occurring in the solid state. However, as pointed out by Curtin and Paul [15], most inter-solid reactions involving molecular solids can be expected to occur in the melt phase. Indeed, this has now been recognized and numerous organic reactions previously described as solid–solid reactions have been shown to be melt reactions [25].

In a similar vein early studies on organometallic complexes carried out in our own laboratories on solid state isomerization reactions [26], many occurring in the solid state, influenced our decision to investigate inter-solid reactions. Our studies on inter-solid reactions revealed that indeed these inter-solid reactions occurred in the melt phase [26e].

However, to date it is clear that few *systematic* studies have been described in the organometallic chemistry literature (or the general synthetic literature of *molecules*) on the use and possible role of the melt phase in synthesis.

A requirement for reactions to occur in the melt is that the reactant molecular solids do not decompose on being heated at and beyond their melting temperature. At the very least the reagents should not decompose in the eutectic

mixture formed from two or more reagents. Once the melt has formed there is no guarantee that a chemical reaction will occur – all that has happened is that the diffusional constraint on the reaction (molecules reaching each other) has been lifted. Thereafter, well described factors that influence the reaction (reagent concentrations, kinetic barriers, temperature, etc.) determine the reaction rate and pathway.

A complicating issue is that the melt provides a little understood solvent mixture (typically made up of at least the two reactants) for the reaction. This ‘solvent mixture’ will impact on both molecular and thermal diffusion issues related to the formation of products. Thermal diffusion can be detrimental to a melt reaction. The limited amount of melt material in a reaction mixture can lead to possible ‘hot spots’ and dissipation of this heat in a melt reaction is needed. This can be achieved using classical chemical engineering principles in terms of reactor design taking effective heat transfer issues into consideration.

2.2. The solid solution and melt phase reactions

A solid solution is a homogeneous and stable solution of one solid substance in another. The term is often used in metallurgy to describe an alloy formed from two or more component materials to give a single phase over a range of chemical compositions. Some mixtures will readily form solid solutions over a range of concentrations and are said to be *mutually soluble*, while other mixtures (*mutually insoluble*) will not form solid solutions at all. The tendency for any two substances to form a solid solution is a strong function of temperature and the chemical properties (intra- and inter-molecular, crystallographic, etc.) associated with the two components.

The use of phase diagrams to explain inter-solid interactions is well established in metallurgy and mining [27,28] and recently Scott and coworkers [25] have elegantly used binary phase diagrams to explain why many so called solid–solid reactions in organic chemistry are indeed melt reactions. Earlier, Rastogi and Bassi [24] laid down the fundamental principles governing eutectic formation and crystallization of organic compounds.

A traditional binary phase diagram is shown in Fig. 3 which may be used to illustrate the relationship between the various factors that affect a simple solventless reaction involving macroscopic solid reactants as described by the reaction $A_{(s)} + B_{(s)} \rightarrow C_{(s)}$. The following are discernable from the figure and are relevant in visualizing the concept of solids reacting in the absence of a mediating solvent.

- Upon mixing of two reagents at low temperature ($<T_e$, the eutectic temperature) the phase diagram is that of two discrete solids A and B (i.e. the area below the dotted red line). No reaction is expected between A and B in this region.
- The easiest way to initiate any reaction between A and B is to increase intermolecular interactions between the two reagents (A–B).

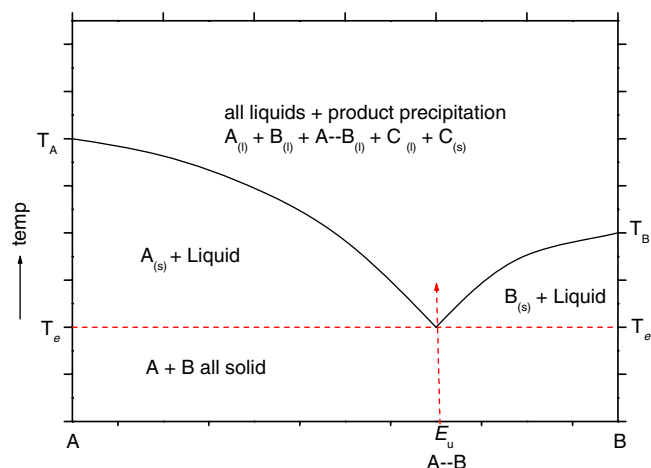


Fig. 3. Typical binary phase diagram for the A + B bicomponent eutectic system. T_A and T_B are the melting temperatures of the pure components; T_e is the eutectic melting point.

- This can be achieved by increasing the temperature of the system (thermal activation) and generating a partial or complete melt phase (or solid solution) of the A/B mixture. Similar effects can be achieved by milling and grinding (mechanochemical activation). It is possible that one reagent may melt before the other. Eventually both A and B could melt. The temperature at which the reaction occurs will relate to the composition of the mixture.
- The lowest temperature at which reaction will occur is the eutectic temperature, T_e (at molar composition E_u).
- A reaction can occur above this temperature and with time the melt phase becomes enriched in C. As saturation occurs, C could start to crystallize out of the melt (dependent on its melting point relative to the temperature of the reaction).
- The crystallization of C may retard the rate of reaction of A and B which then becomes diffusion controlled but further reaction may be sustained by increasing the reaction temperature. Such systems require a molar excess of one reactant (often the lower melting reactant) for this to occur.

2.3. Features of melt reactions

2.3.1. The melt reaction

When solid reagents are heated above the melting point of both reagents they can form a liquid medium (the melt). The reagents thus act as co-solvents in the reaction and the product forms in this ‘solvent’ mixture (the all liquid regime in Fig. 3).

Three scenarios are then possible. The product can precipitate out at the reaction temperature, the product can precipitate out as the melt cools to room temperature or the product could be a liquid. To date, it appears that most reactions reported entail product precipitation/solidification from the melt and not formation of a room temperature liquid product.

As discussed above, many systems form a eutectic melt that allows for the formation of products from reactions that are conducted at conditions well below the melting points of the individual reactants.

2.3.2. Reactions in a localized melt regime

A number of examples are known in which a chemical reaction occurs in a crystal lattice of a single reactant i.e. by a solvent free solid to solid transformation. As will be discussed, this reaction could occur in a localized regime (a cavity) or it could occur at a reaction front. In the latter case this could be imagined as a reaction occurring in a region of localized melting, followed by product precipitation.

Inter-solid reactions between molecular reactants involve the reaction between two or more *macroscopic solids*. A melt may not be observed and the reaction will appear to occur only on the surface of the macroscopic particles. The reaction can be initiated by a variety of strategies as discussed below.

2.3.3. Reactions involving a solid and a liquid

It is possible to mix two reagents together, one solid and the other liquid, to yield a heterogeneous mixture. At low temperatures, little if any reaction need occur. However, at higher temperatures the solid reagent could melt (or even dissolve in the other reagent) to give a homogeneous mixture. This mixture will then react at an appropriate temperature to give a product which may or may not precipitate from the melt (liquid) phase. A variant of this is when two solids are mixed and only one reagent initially melts on heating. This will provide a fluid phase for the reaction [29]. An example of this is the rhodium catalyzed hydroformylation reaction performed in a PPh_3 melt phase [30].

2.3.4. Solid–gas reactions

In this reaction type, gas molecules can interact with a solid (surface reaction or diffusion through channels into the bulk) to yield a new product. Gas–solid reactions can bear a close relationship to certain types of solid–solid reactions. This will occur when the vapor phase reacts with the solid and reaction occurs at a mobile gas/solid front [31].

2.4. Dispersants as rate controllers in melt reactions

Addition of a high melting point inert solid to a melt can be used to control the rate of a solvent-free reaction just as the rates of some reactions are controlled by solvents. The role of the nature of the solid dispersant or diluent has been investigated in solventless reactions [32]. A range of dispersants (KBr , Al_2O_3 , Na_2SO_4 , NaNO_2 , SiO_2 , Na_2CO_3 , $\text{NaC}_2\text{H}_3\text{O}_2$, NaNO_3 , sucrose and TiO_2), ground and filtered, to provide a comparable particle size, were investigated in the solventless substitution reaction of $\text{Mn}(\text{CO})_4(\text{PPh}_3)\text{Br}$ with PPh_3 which was monitored by in situ DRIFTS. The result of the study showed that the

chemical nature of the diluent matrix influenced the rate of the solventless reaction. Hence, when the reaction was carried out in sucrose and SiO_2 , the rate of the reaction was fastest ($1.71 \times 10^{-2} \text{ s}^{-1}$ and $2.02 \times 10^{-2} \text{ s}^{-1}$ respectively), and conversely it was slowest when ionic solids, KBr , Na_2SO_4 , NaNO_2 , Na_2CO_3 , $\text{NaC}_2\text{H}_3\text{O}_2$ and NaNO_3 were used. When Al_2O_3 and TiO_2 were used, the reaction was slower ($8.26 \times 10^{-3} \text{ s}^{-1}$ for Al_2O_3 and $6.81 \times 10^{-3} \text{ s}^{-1}$ for TiO_2). Therefore, inorganic dispersants that are insoluble in the melt may be appropriately chosen as additives to control the rate of such reactions.

3. Melt phase chemistry

Melt formation is an often overlooked process on the route to product formation in many solvent-free reactions [25]. The activation of solid reactants in the absence of solvents has been achieved via a variety of procedures with the most common being the mechanochemical and thermochemical techniques.

3.1. Mechanochemical induction

A detailed analysis of the equipment and techniques used for mechanochemical activation has been presented by Baláz [33].

The term mechanochemistry was introduced at the beginning of the 20th century by Ostwald [34] to describe the process of mechanical action on a chemical reaction. These types of reactions are important in industry [16]. A comprehensive review which details examples of the enhancement of chemical reactions by mechanochemical activation has recently been published [35].

In general when two solids are ground together, the heat generated in the grinding process may be sufficient to either create a melt at the surface or completely melt the solid reagents. This could arise from the generation of a ‘hot spot’ (an exotherm) that could lead to a self-sustaining reaction. Clearly control of this type of reaction can be problematic and could lead to run away reactions [6,36].

The grinding can be controlled by use of a ball mill. The role and chemical nature of the balls needs to be considered in these reactions; contamination of the products by the ball material is a well known phenomenon.

In ball milling it is assumed that solid surfaces are constantly being brought together where reaction takes place. Localized melting (eutectic formation?) becomes possible and once a product is formed it gets eroded from the reaction surface to regenerate fresh reactant molecules. The possibility of enhanced diffusion of the molecules of one material *into* the lattice of another molecular material (as occurs in many ionic materials), has also been reported [37].

A variant of this approach is kneading, in which a trace amount of solvent is added to the reagents during or prior to milling. It is presumed that the solvent is added to provide better contact between the solids, possibly by dissolving small amounts of reactants. Kneading is an industrially

useful process that is mostly applied in the pharmaceutical industry for tableting powdered products, although it has also found use in several laboratories for preparative purposes [18].

The versatility of mechanochemistry as a means of initiating chemical reactions is illustrated by the variety of reactions and compounds obtainable via the technique. It is sometimes a cheaper alternative when compared to traditional methods of chemical synthesis. It hence finds wide application in the materials industry for alloying of metals with ceramics and in the pharmaceutical and chemical industry for the preparation of powdered compounds and reagents. Since few organometallic complexes have been prepared via mechanochemical activation, examples to illustrate the wide applicability of the procedure, listed below, will of necessity include coordination compounds.

3.1.1. Mechanochemically initiated reactions

In the mechanochemical preparation of $[\text{Ni}(\text{Hdmg})_2]$ and $[\text{Ni}(\text{H}_2\text{dmg})_2]\text{Y}_2$ ($\text{Y} = \text{CH}_3\text{COO}$, OH , CO_3) from nickel halides and dimethylglyoxime (H_2dmg) the authors isolated the powdered metal complexes in high-purity without recourse to any solvent processing [38] (Table 1 – 1).

The four coordinate compounds *cis*- $[\text{Pd}(\text{NH}_3)_2\text{X}_2]$ have been prepared by a mechanochemical route from $[\text{Pd}(\text{NH}_3)_2\text{C}_2\text{O}_4]$ and HX ($\text{X} = \text{Br}$, I) (Table 1 – 2) [39]. Mechanochemistry has also been used to activate complexes. For example, the simple mechanical treatment of solid K_2PtX_6 ($\text{X} = \text{Cl}$, Br) salts under air or argon led to the formation of paramagnetic platinum (III) complexes via homolytic cleavage of $\text{Pt}-\text{X}$ bonds, which are metastable intermediates often proposed in catalytic reactions. The reactive species were detected by ESR measurements (Table 1 – 3) [40].

The use of diluents to control the rate of a solventless reaction (see above Section 2.4 for details) is illustrated by the synthesis of some zirconium carboxylate complexes [32]. The products were obtained from the 1:1 mechanochemical reaction of zirconocene dichloride with sodium aryl carboxylates. In the absence of a diluent, the reaction occurred instantaneously with a high exotherm. When however a diluent such as sodium chloride was added, the rate of the reaction could be slowed down (Table 1 – 4).

The mechanochemical treatment of solid polycrystalline PtCl_2 with PPh_3 for 2 h yielded *cis*- $\text{Pt}(\text{PPh}_3)_2\text{Cl}_2$ in 98% yield, that further reacted with an excess of anhydrous K_2CO_3 to produce *cis*- $\text{Pt}(\text{PPh}_3)_2\text{CO}_3$ in 70% yield (Table 1 – 5). The formation of the transition metal complexes initiated by ball milling has been confirmed by means of solid-state ^{31}P MAS NMR spectroscopy, PXRD and DTA. The authors [41] considered the possibility of melt formation as one of the explanations for the facile nature of the reaction. It was thought that the melt was formed locally and momentarily from a fraction of the reactants that were trapped in the areas where the balls collide with the walls of the reaction chamber and with one another.

The successful engineering of extended π -stacked arrays based on charge assisted interactions between *p*-sulfonatocalix[4]arene anions and 1,10-phenanthroline Ni cations has been reported by Nichols et al. [42]. The compound was obtained from the grinding of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with 1,10-phenanthroline followed by grinding with the *p*-sulfonatocalix[4]arene penta-anion. The product has a crystal structure composed of large porous arrays of $[\text{Ni}(\text{phen})_3]^{2+}$ cations included within the cavities of the *p*-sulfonatocalix[4]arene(4-) anion (Table 1 – 6; Fig. 4). Thus, mechanochemistry can be a means (in some cases the only means) to induce intermolecular interactions between organic ligands and metal salts leading to stacked and networked structures (see below Section 3.1.2 for more details).

The grinding of thallium salts of tris(pyrazolylborate), Tp, with Mn(II), Co(II) and Ni(II) salts in an agate mortar has been reported to yield Mn, Co and Ni tris(pyrazolylborate) metal complexes of the type TpMCl [43] via a substitution type of reaction. The X-ray structure of the Co compound and the electronic spectra of the coordination compounds were presented (Table 1 – 7).

3.1.2. Three dimensional (3-D) coordination networks and compounds by supramolecular self-assembly

The ingenuity of the synthetic chemist has ensured that solventless techniques are not limited to the preparation of linear organic and organometallic compounds by the simple making and breaking of covalent bonds. Complex 3-D networks can also be made more efficiently in the absence of solvents by inducing concerted metal–ligand interactions. Both hydrogen-bonding and supramolecular self-assembly procedures are responsible for generating the new materials.

Orita et al. [44] reported that grinding a 1:1 ratio of a powdered mixture of $\text{M}(\text{en})(\text{NO}_3)_2$ ($\text{en} = \text{ethylenediamine}$) ($\text{M} = \text{Pd}$, Pt), and bidentate 4,4'-bipyridine at room temperature afforded molecular squares (Table 1 – 8) within 10 min. The reaction mixture became gummy on grinding, clearly indicating melt formation. The authors noted that in D_2O as a solvent the reaction of the platinum complex took more than 4 weeks at 100 °C to yield 80% of the same product. Using the same procedure the authors were also able to prepare other compounds with ligand-metal connectivity, such as 3-D bowl-shaped compounds and compounds with double helicate topology. For example, increasing the ligand dentation by use of a triazine-based tridentate ligand afforded a 3-D bowl shaped Pd compound (Table 1 – 9).

Using a similar approach, and utilizing the H-bonding ability of bis-amine ligands, Braga et al. [45–47] have prepared coordination polymers of Ag, Zn and Cu by co-grinding the ligands 1,4-diaminocyclohexane and 1,4-diazabicyclooctane with the corresponding metal salts (Table 1 – 10, 11). The structural features of the compounds have been confirmed by X-ray diffraction and the materials were characterized by the ability to reversibly

Table 1
Mechanochemically induced inter-solid reactions

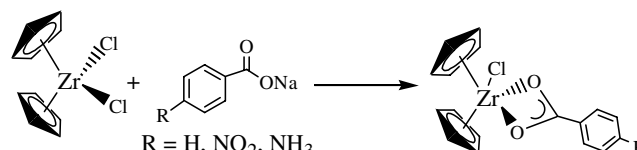
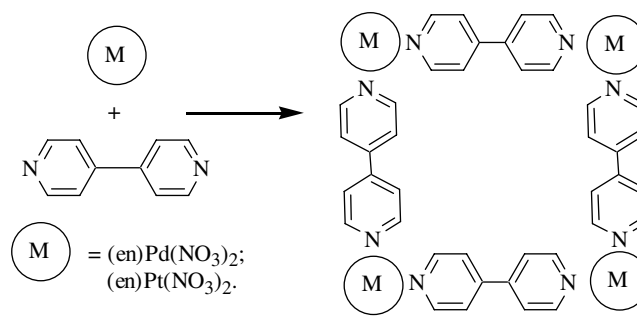
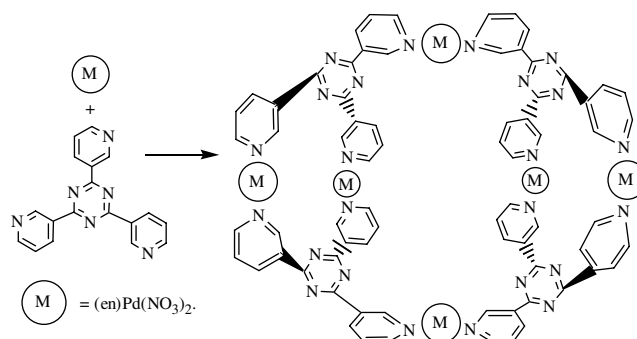
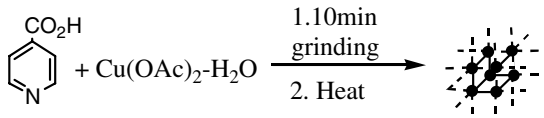
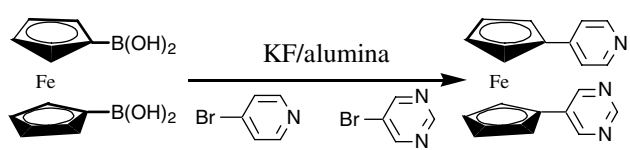
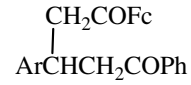
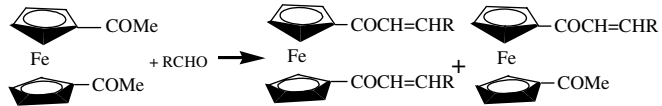
No.	Reaction	Comments	Reference
1	$\text{NiX}_2 + \text{H}_2\text{dmg} \rightarrow [\text{Ni}(\text{Hdmg})_2]$ $\text{NiY}_2 + \text{H}_2\text{dmg} \rightarrow [\text{Ni}(\text{H}_2\text{dmg})_2]\text{Y}_2$ $\text{X} = \text{Cl}, \text{NO}_3; \text{Y} = \text{CH}_3\text{COO}, \text{OH}, \text{CO}_3$ $\text{H}_2\text{dmg} = \text{dimethylglyoxime}$	$[\text{Ni}(\text{Hdmg})_2]$ was obtained for nickel salts of a weak acid $[\text{Ni}(\text{H}_2\text{dmg})_2]\text{Y}_2$ for salts of a strong acid	[38]
2	$[\text{Pd}(\text{NH}_3)_2\text{C}_2\text{O}_4] \xrightarrow[\text{X} = \text{Br}, \text{I}]{\text{HX}} \begin{array}{c} \text{H}_3\text{N} \diagup \\ \text{Pd} \\ \text{NH}_3 \diagdown \\ \text{X} \quad \text{X} \end{array}$	NMR, IR	[39]
3	$\text{K}_2\text{PtX}_4 \rightarrow [\text{PtX}_3]^- + \text{X}^+$ $\text{K}_2\text{PtX}_6 \rightarrow [\text{PtX}_5]^- + \text{X}^+$	ESR	[40]
4	 $\text{R} = \text{H}, \text{NO}_2, \text{NH}_3$	NMR SCXRD	[32]
5	$\text{PtCl}_2 + \text{PPh}_3 \xrightarrow{\text{milling}} \text{cis-PtCl}_2[\text{PPh}_3]_2 \xrightarrow{\text{K}_2\text{CO}_3} \text{cis-PtCO}_3[\text{PPh}_3]_2$ Yields of 98% and 70% were recorded respectively	Solid-state ^{31}P MAS NMR, PXRD, DTA	[41]
6	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + 1,10\text{-phen} \rightarrow \text{Ni}(\text{phen})_3(\text{NO}_3)_2 \cdot x\text{H}_2\text{O} + p\text{-sulfonatocalix[4]arene(5-)} \rightarrow [\text{Ni}(\text{phen})_3]^{2+} \cap p\text{-sulfonatocalix[4]arene(5-)}$ $\cap = \text{cavity inclusion}$	Charge assisted π -stacking interactions SCXRD, ES, IR	[42]
7	$\text{MCl}_2 + \text{Tp}^x\text{Ti} \rightarrow \text{Tp}^x\text{MCl}$ $\text{M} = \text{Mn}, \text{Co}, \text{Ni}$ $\text{Tp} = \text{tris(pyrazolylborate) moiety}$ $x = \text{H}, \text{alkyl}, \text{aryl}, \text{alkoyl ligands}$	Three complexes each of tris(pyrazolylborate) Co, Ni and Mn prepared in yields of up to 80%	[43]
8	 $\text{M} = (\text{en})\text{Pd}(\text{NO}_3)_2; (\text{en})\text{Pt}(\text{NO}_3)_2$	NMR Self-assembly produced the square shaped complex	[44]
9	 $\text{M} = (\text{en})\text{Pd}(\text{NO}_3)_2$	NMR Self-assembly produced the bowl shaped complex	[44]
10	$\text{AgCH}_3\text{COO} + \text{N-X} \cdot \text{Y-N} \rightarrow \text{Ag}[\text{N-X} \cdot \text{Y-N}] [\text{CH}_3\text{COO}] \cdot n\text{H}_2\text{O}$ $\text{N-X} \cdot \text{Y-N} = [\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}]; [\text{H}_2\text{NC}_6\text{H}_{10}\text{NH}_2]$	XRD	[45]
11	$\text{MCl}_2 + \text{N-X} \cdot \text{Y-N} \rightarrow \text{MCl}_2[\text{N-X} \cdot \text{Y-N}] \cdot n\text{H}_2\text{O}$ $\text{M} = \text{Zn}, \text{Cu}$	XRD	[45]

Table 1 (continued)

No.	Reaction	Comments	Reference
12 ^a		PXRD The product has an empty microporous 3-D network	[48]
13 ^a	organotin Precursors + Protic acids → Organotin cages & clusters <div style="display: flex; justify-content: space-around; font-size: small;"> <div style="border: 1px solid black; padding: 2px;"> eg. n-BuSn(O)OH n-BuSn(OH)₂Cl n-Bu₂SnO (SnPh₃)₂O </div> <div style="border: 1px solid black; padding: 2px;"> eg. RCOOH R₂POOH RⁱP(O)(OH)₂ RSO₃H </div> <div style="border: 1px solid black; padding: 2px;"> drum, O-capped extended tetranuclear tetranuclear oxo cage supra and discrete molecules </div> </div>	12 organotin complexes were synthesized by grinding at ambient temperature	[49]
14	2CpTl + FeCl ₂ → Cp ₂ Fe + 2TlCl	IR, DTA and PXRD	[50]
15		[51] [52]	
16	FcCHO + H ₂ NC ₆ H ₅ X → FcCH=NC ₆ H ₅ X 11 ferrocenylimine complexes have been prepared in isolated yields of over 90%	IR, NMR, DSC, MS	[53]
17	FcCHO + RCH ₂ PPh ₃ X $\xrightarrow{\text{NaOH}}$ FcCH=CHR R = H, Aryl halides, Ferrocene	IR, NMR DSC, MS	[54]
18	ArCH=CHCOFc + PhCOMe $\xrightarrow{\text{NaOH}}$ 	IR, NMR	[55]
19		IR, NMR	[56]

^a No apparent melting was observed.

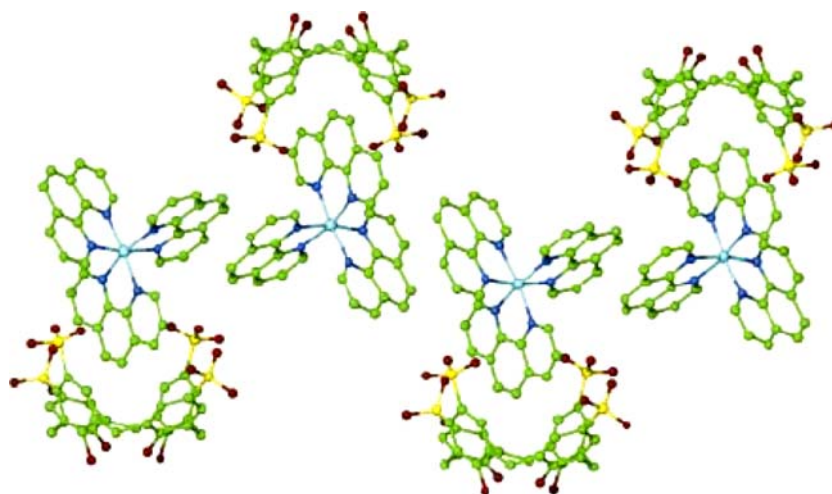


Fig. 4. Mechanochemically induced infinite π -stacked chain showing the inclusion of $[\text{Ni}(\text{phen})_3]^{2+}$ cations within the cavity of a *p*-sulfonatocalix[4]arene(4⁻) anion, in a C_{2v} symmetric conformation. (Reproduced from [42] with permission, copyright Royal Society of Chemistry).

accommodate varying quantities of other donor ligands within their coordination spheres.

In a few cases, an intervening melt phase reaction pathway has been specifically excluded by authors. In such cases, it is

assumed that the process of grinding induces a mechanical stress that disrupts the passivating surface layer of product on the consumed reactants, thereby exposing fresh reagent for the continuation of the reactions. The first solvent-free mechanochemical synthesis of a microporous metal–organic framework complex $[\text{Cu}(\text{NC}_6\text{H}_4\text{COO})_2]$ which was recently reported by James and coworkers [48] falls into this category. The compound has been obtained quantitatively by grinding copper acetate and isonicotinic acid together for 10 min (Table 1 – 12). The product has a robust 3-dimensional connectivity. Similarly, the organotin clusters and cages quantitatively synthesized by Chandrasekhar et al. [49] via the ambient temperature grinding of organotin precursors with protic acids have been obtained without the observation of a melt phase. Using this method the authors prepared a variety of structural forms, including the drum, O-capped cluster and tetranuclear oxo cages. Discrete as well as polymeric compounds (Table 1 – 13) were also formed. These reactions have been monitored by PXRD, and the observance of crystalline phases throughout the course of the reaction prompted the authors' conclusions.

3.1.3. Ferrocene and ferrocenyl compounds

The solvent-free synthesis of ferrocene by the mechanical milling of iron (II) chloride with (alkaline metals or thallium) cyclopentadienides (Table 1 – 14) [50], and the synthesis of various ferrocenyl derivatives has been the focus of several research initiatives.

It has been shown that the use of KF/alumina as a solid-phase support for a solventless Suzuki synthesis (Table 1 – 15) offers a convenient and environmentally friendly route that is a faster, more selective alternative, to the preparation of disubstituted pyridine/pyrimidine ferrocenyl complexes in solution [51,52]. The solventless mixing of equimolar quantities of ferrocenylaldehydes and aromatic amines provided excellent yields of ferrocenylimines via melt formation (Table 1 – 16) [53].

Ma and coworkers [54–56] have reported on the efficient solvent-free synthesis of a variety of ferrocenyl compounds. The Wittig reaction of formylferrocene with ylides yielded ferrocenylethene derivatives (Table 1 – 17) which were proposed to serve as monomers for ferrocene containing polymers [54]. Michael reaction was used to prepare 1,5-diketone compounds containing the ferrocene backbone (Table 1 – 18) [55]. The authors also reported on a selective synthesis of 1-acetyl-1'-enonylferrocenes and 1,1'-dienonylferrocenes by using a powdered NaOH catalyzed Aldol condensation of diacetylferrocene with aromatic aldehydes (Table 1 – 19). Several new compounds have thus been isolated and fully characterized using the solventless (melt) chemistry approaches.

3.2. Thermochemical induction

The initiation and sustenance of chemical reactions due to a rise in temperature which results from the direct application of heating or the conversion of other forms of

energy (mechano-, sono-, photo-, etc.) into thermal energy is central to the theme of this review. Thermochemical induction can thus be regarded as the simplest method to generate a melt from a solid or solids. The energy input manifests itself in the form of melt formation and/or vaporization of volatile components, which permits reaction to occur. To date, thermochemical initiation has been utilized largely by us [11,57] and others [58,59] to study a variety of solvent-free inter-solid reactions and intra-solid organometallic transformations (see Tables 2 and 3 for details).

3.2.1. Inter-solid reactions

An inter-solid reaction involves the interaction of two (or more) macroscopic solids to produce a solid product. The application of thermal energy results in the formation of a eutectic melt beginning at the interface where the two reactants are in contact. This is highlighted in Fig. 5 by the reaction $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Ru}(\text{CO})_2\text{I} + \text{PPh}_3 \rightarrow [(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{-Ru}(\text{CO})_2\text{PPh}_3]\text{I}$. It can be seen that reactants that do not touch did not form a eutectic melt (Fig. 5(b) and (c)). Spectroscopic analysis of the melt indicated addition of PPh_3 to Ru and formation of the product $[(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{-Ru}(\text{CO})_2\text{PPh}_3]\text{I}$. When the added energy is sufficient the reactants melt, and this melt will act as a 'solvent' for the reaction.

3.2.1.1. Ligand exchange reactions. A series of 'ligand exchange reactions' in which ligands are exchanged between solid organometallic complexes have been reported. For example, the reaction between $\text{RhX}(\text{PPh}_3)_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{W}(\text{CO})_3\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) resulted in the exchange of CO/PPh_3 and X/Y between the two reactants with the same product yields and distributions as found for the corresponding solution state reactions (Table 2 – 20) [60]. Similarly, exchange of halogen ligands have been observed on the heating of a mixture of piano-stool Mo, W and Re complexes (Table 2 – 21) [61]. For example, a mixture of $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{W}(\text{CO})_2\text{Br}_2$ and $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{W}(\text{CO})_2\text{I}_2$ yielded a mixed halide $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{W}(\text{CO})_2\text{BrI}$ product. Heating the pure mixed halide product reconverted it back to the pure starting compounds (very low yield) demonstrating the reversibility of the exchange reaction $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{W}(\text{CO})_2\text{Br}_2 + \text{C}_5\text{H}_4\text{-Me})\text{W}(\text{CO})_2\text{I}_2 \leftrightarrow (\eta^5\text{-C}_5\text{H}_4\text{Me})\text{W}(\text{CO})_2\text{BrI}$ (Table 2 – 22) [61]. A facile solvent-free inter-halogen exchange reaction has been reported with isolation of 81% of the iodo product $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Re}(\text{CO})_2\text{I}_2$ from its brominated precursor $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Re}(\text{CO})_2\text{Br}_2$ by mixing with NaI (Table 2 – 23). The detection of a melt was not reported, but the reaction certainly, in retrospect, occurs in the melt phase.

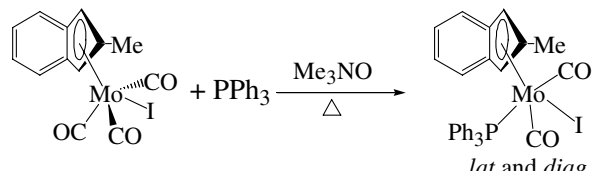
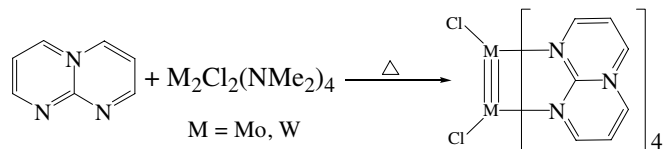
3.2.1.2. Migratory-insertion/addition reactions. The reaction of $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_x\text{Me}$ ($\text{M} = \text{Mo}, \text{W}, x = 3$; $\text{M} = \text{Fe}, x = 2$) with nucleophilic ligands, L, to give $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_{x-1}\text{L}(\text{COMe})$ represents one of the earliest reactions reported in organometallic chemistry [62]. Most

Table 2
Thermochemically induced inter-solid reactions

No	Reaction	Comments	Reference
20	<p>Reactants</p> <p>Products</p> <p>$L = PPh_3$ $X; Y = Cl, Br, I$</p>	NMR; IR; DSC Both CO/ PPh_3 and X/Y were exchanged between the two reactants	[60]
21	<p>Reactants</p> <p>Products</p> <p>$R \equiv R_1$ Me, tBu $M \equiv M_1$ Mo, W, Re $X \equiv Y$ Cl, Br, I</p>	Exchange reactions have been recorded, at low yields due to decomposition of material	[61]
22	<p>$lat = 25\%; diag = 29\%$</p>		[61]
23	<p>+ NaI</p>	The product was isolated in 81% yield	[61]
24	<p>+ L</p> <p>$M = Mo, W; L = PR_3; P(OR)_3$ $R = H, Me, COMe, CHO$</p>	NMR, DRIFTS Thermomicroscopy	[63] [64]
25	<p>$X = Cl, Br, I$ $L, L' = PR_3; P(OR)_3$</p>	NMR, IR, DRIFTS Thermomicroscopy	[26e] [32]
26	<p>+ L</p> <p>Catalysed</p> <p>$R = H, Me$ $L = PR_3, P(OR)_3$</p>	NMR IR	[66]

(continued on next page)

Table 2 (continued)

No	Reaction	Comments	Reference
27		NMR	[67]
28		SCXRD ESR	[68]
29	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O} + 1,10\text{-phen} \rightarrow \text{Fe}(\text{phen})_3\text{SO}_4 \cdot x\text{H}_2\text{O}$	In situ EDXRD; DSC; TG/DTA; Mössbauer; IR	[69]

of the pioneering studies, as expected, were conducted in solvents and it was from these studies that the mechanism of these reactions was shown to involve methyl migration, resulting in the process being referred to as a migratory-insertion reaction. Recently, a systematic investigation of similar reactions in the absence of solvents was initiated [63,64] and it was found that the thermochemically induced solventless migratory-insertion reaction of similar Mo, W and Fe piano-stool complexes with a series of solid phosphines and phosphites occurred in the melt phase (Table 2 – 24) [64]. The kinetics of the melt reaction has been studied by employing simple techniques such as in situ DRIFTS. In all the reactions studied the kinetic data fitted a pseudo-first order reaction model, consistent with melt phase chemistry.

Heating a mixture of $\text{RuCl}_2(\text{PPh}_3)_2$ and 2,6-xylylisocyanide (XylNC) at 100 °C gave rapid formation of a yellow complex. A white deposit also formed on the complex that was identified as the triphenylphosphine ligand. Washing the solid with diethyl ether left behind a bright yellow solid of the required product, $\text{RuCl}_2(\text{PPh}_3)_2(\text{XylNC})_2$. Since the melting point of the isonitrile is ca. 175 °C this suggests that the reaction occurred in the solid phase or between a solid and a vapor (xylylisocyanide has a high vapor 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 [65]. Reaction between $\text{RuCl}_2(\text{PPh}_3)_2$ and liquid isocyanides also occurred without the addition of solvent at room temperature to slowly (or more rapidly at 50 °C) give the required complexes in ca. 85% yield. Thus very clean reactions are possible in the absence of an added solvent.

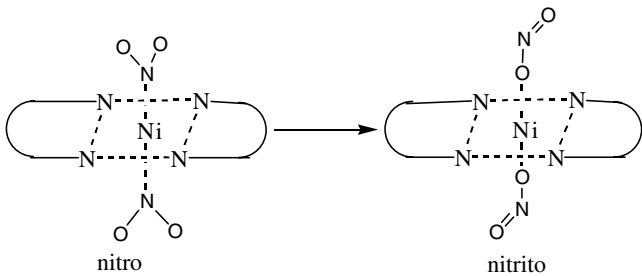
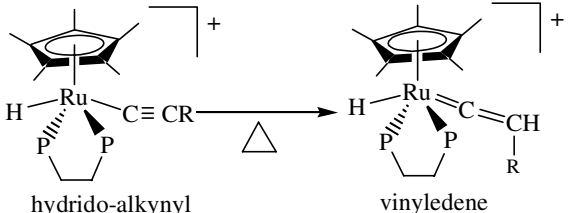
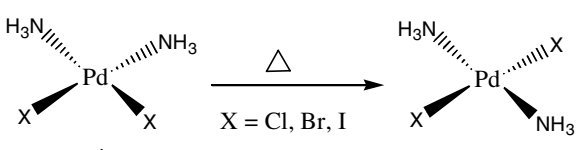
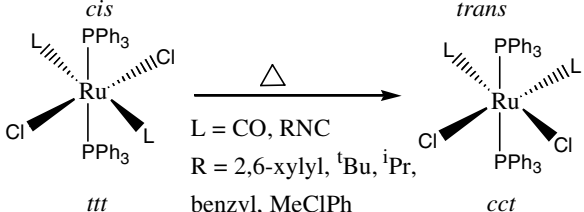
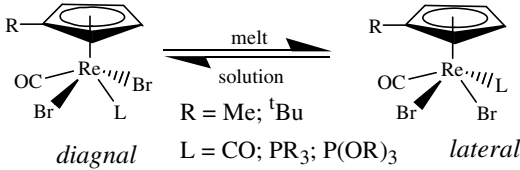
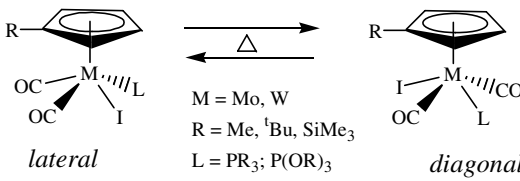
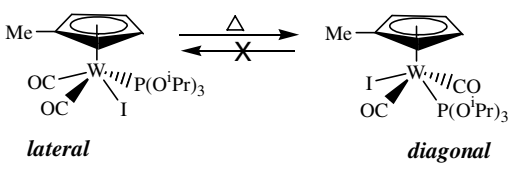
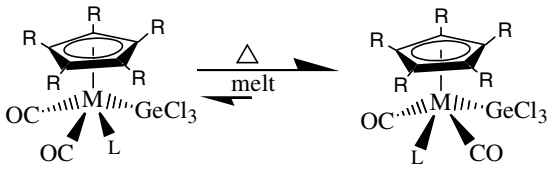
3.2.1.3. Ligand substitution reactions. The solvent-free reaction between $\text{Mn}(\text{CO})_4(\text{PPh}_3)\text{Br}$ and PPh_3 [26e] was the first organometallic melt reaction monitored by thermomicroscopy (Table 2 – 25). The reaction provided substantive data on the mechanism of the ‘solid–solid’ CO substitution reaction underpinning the relevance of a eutec-

tic melt in such ‘solid–solid’ reactions. It was realized that interface melting (which only occurred for reactants in contact with each other) was the key step in the thermally driven reaction. An example depicting melt formation is shown in Fig. 5. The observation has since led to many studies on related systems. While interface melting is important in the initiation and/or sustenance of melt-phase solvent-free reactions, reactions where interface melting occurred and *did not* lead to the initiation of a reaction were also found [66].

Solvent-free CO substitution reactions of piano-stool iron (Table 2 – 26) and molybdenum (Table 2 – 27) complexes by PR_3 and $\text{P}(\text{OR})_3$ donor ligands were also noted [66,67] to occur in the melt. In the reaction of $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Fe}(\text{CO})_2\text{I}$ with phosphine ligands (L), ionic products $[(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Fe}(\text{CO})_2\text{L}]^+\text{I}^-$ were predominantly isolated. This is in contrast to the CO substitution products $(\eta^5\text{-C}_5\text{H}_4\text{R})\text{Fe}(\text{CO})(\text{L})\text{I}$ obtained from the same reaction in benzene as a solvent [66b]. Mechanistic studies have indicated that the melt phase reaction proceeds via an associative 19 electron transition state/intermediate while the reaction in a solvent occurs via a 17 electron transition state/intermediate [66a].

Even more complicated structures such as inorganic and organometallic polymers and oligomers have been obtained via substitution reactions in the melt phase. In this respect, Chisholm et al. [68] have reported the synthesis of the M–M quadruply bonded oligomeric compounds $\text{M}_2(\text{hpp})_4\text{Cl}_2$ (M = Mo, W) by the reaction of $\text{M}_2\text{Cl}_2(\text{NMe}_2)_4$, with 8 equiv. of Hhpp (hpp is the anion derived from deprotonation of 1,3,4,6,7,8-hexahydro-2H-pyrimido-[1,2-a]pyrimidine, Hhpp) (Table 2 – 28) in a solvent-free melt reaction at 150 °C (see Fig. 6 for a crystal structure of the Mo oligomer). The solvent-free coordination of the bidentate 1,10-phenanthroline ligand to transition metal centers has been studied by Nichols et al. [42] and O’Hare and coworkers [69]. A 1:1 reaction of the ligand with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ took place rapidly at around 70 °C initially producing an intermediate crystalline phase, $\text{Fe}(\text{phen})_3\text{SO}_4 \cdot 5\text{H}_2\text{O}$ which cleanly self-assembled to the

Table 3
Thermochemically induced intra-solid reactions

No	Reaction	Comments	Reference
30	 <p style="text-align: center;">nitro nitrito</p>	ESR DRIFTS	[79]
31	 <p style="text-align: center;">hydrido-alkynyl vinylidene</p>	IR	[80]
32	 <p style="text-align: center;">X = Cl, Br, I</p>	PXRD	[39]
33	 <p style="text-align: center;"><i>cis</i> <i>trans</i></p> <p style="text-align: center;">L = CO, RNC R = 2,6-xylyl, ^tBu, ⁱPr, benzyl, MeCIPh</p> <p style="text-align: center;"><i>ttt</i> <i>cct</i></p>	PXRD IR, NMR	[81]
34	 <p style="text-align: center;">melt solution</p> <p style="text-align: center;">R = Me, ^tBu L = CO; PR₃; P(OR)₃</p> <p style="text-align: center;"><i>diagonal</i> <i>lateral</i></p>	Thermomicroscopy DSC SC- and PXRD phase analyses DSC	[82] [83] [84]
35	 <p style="text-align: center;">Δ</p> <p style="text-align: center;">M = Mo, W R = Me, ^tBu, SiMe₃ L = PR₃; P(OR)₃</p> <p style="text-align: center;"><i>lateral</i> <i>diagonal</i></p>	Thermomicroscopy NMR TGA	[85] [86]
36	 <p style="text-align: center;">Δ X</p> <p style="text-align: center;"><i>lateral</i> <i>diagonal</i></p>	DSC PXRD NMR PXRD	[87]
37	 <p style="text-align: center;">Δ melt</p> <p style="text-align: center;">M = Mo, W; R = H, Me; L = CHNEt₂, CNEt, PMe₃</p>	Simultaneous thermal analysis STA (T, DTA, TG, DTG) IR NMR	[58] [59]

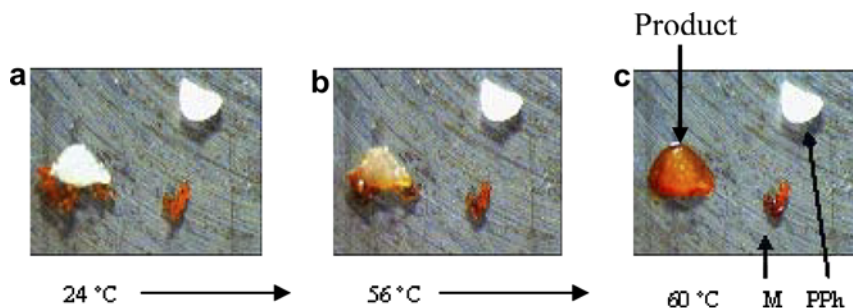


Fig. 5. The thermochemical reaction of $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Ru}(\text{CO})_2\text{I} + \text{PPh}_3 \rightarrow [(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Ru}(\text{CO})_2\text{PPh}_3]\text{I}$ as a function of temperature: (a) solid reactants at r.t., (b) eutectic melting at the solids interface for reactants in contact, (c) melt phase; below the melting point of the pure reagents.

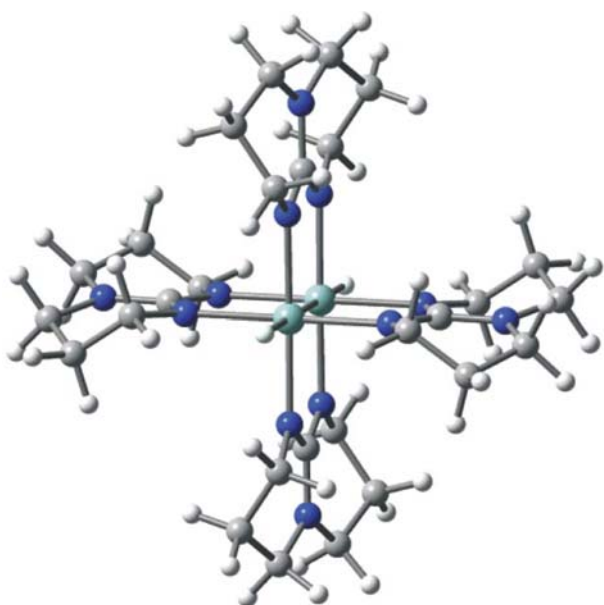


Fig. 6. Oligomeric Mo–Mo quadruple bond containing complex prepared via melt-phase thermochemical reaction. (Reproduced from [67] with permission, copyright American Chemical Society.)

octahedral six-coordinate Fe(II) complex $\text{Fe}(\text{phen})\text{-(H}_2\text{O)}_3\text{SO}_4$ (Table 2 – 29) [69]. This has been investigated by time-resolved in situ EDXRD, DSC, TG/DTA, Mössbauer and IR spectroscopy. This was noted to be another example where the solvent-free technique yielded a product different from the same reaction conducted in aqueous solution, that yielded $\text{Fe}(\text{phen})_3\text{SO}_4$.

3.2.2. Intra-solid transformations

Intra-solid transformations occur within the molecular lattice of a single compound, and gives rise to a high chance of topotactic control of product geometry. The change from reactant to product may occur without a change in phase as is observed in single-to-single crystal transformations.

Examples of transformations that have been reported to occur with the retention of crystallinity include the *diag-to-lat* thermal isomerization of $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{Re}(\text{CO})\text{-[P(OPh)}_3\text{]Br}_2$ [70], the photo-induced coordination-driven [2+2] self-assembly of dinuclear Zn complexes [71], the racemisation of cobaloximes [72], the thermal dimerisation of

cyclopentadienyl(*o*-dithiobenzene)cobalt, [73] and the X-ray-, thermal-, and pressure-induced ONO to NO_2 linkage isomerization reaction of a series of cobalt [74] complexes. Transformations of this type are rare and have provided information for the interpretation of solid state and solvent-free organometallic reaction mechanisms [70]. A detailed treatment of single-to-single crystal transformations falls outside the scope of this review.

However, many intra-solid transformations do involve a change in phase as reactants convert to products and this is accompanied by a disruption of the 3-D crystallinity of the reactant. This could involve a localized cycle of melting/reaction/resolidification of crystallites in a solid material. Reactions in which a melt phase was observed are discussed below.

3.2.2.1. Isomerization reactions. Isomerization reactions are amongst the most studied solvent-free intra-molecular transformations of organometallic compounds as evidenced by the frequent discussion of the subject in reviews dealing with solvent-free reactions [11,57,75–78]. Most of the reactions described have been shown to occur in the solid state, but future studies may reveal the possibility of the reaction occurring in a melt phase for related complexes. These types of reactions have potential practical importance as highlighted by the example given below.

Coordination compounds in which an ambidentate ligand (e.g., NO_2^-) binds to the metal center through either the N (nitro form) or O (nitrito form) donor atoms have been well studied [11]. In a recent study by Fabrizzi and coworkers [79] of a nickel(II) bis(diamine) complex having a pink-red nitro isomer and a blue colored nitrito isomer, the possibility of utilizing the reversible thermally induced nitro–nitrito interconversion for the design of thermochromic devices for use as visual and prompt monitoring of temperature changes was studied. The key to the study was the facile thermochromic interconversion between the two isomers (Table 3 – 30). The electronic changes and kinetics of the isomerization reaction were monitored by ESR and in situ DRIFTS.

One example of a reaction that may occur in the melt phase has been reported. The kinetics of the solvent-free tautomerization of the hydrido-alkynyl ruthenium complexes to their vinylidene isomers has been monitored by

IR spectroscopy (Table 3 – 31) [80]. The rate of disappearance of the $\nu(\text{C}\equiv\text{C})$ vibration at ca. 2000 cm^{-1} with time was analyzed using the Avrami-Erofeev equation and some new insight into the mechanism of the transformation, which was different from that observed in similar solution studies, has been given by the authors.

3.2.2.2. *cis–trans Isomerization reactions.* Isomerization studies on 4- and 6-coordinate inorganic compounds have been published in the literature and much of the early work on the study of the solid state reactions of these classical coordination complexes has been summarized by LeMay [76].

The four coordinate compounds *cis*-[Pd(NH₃)₂X₂] that have earlier been prepared by a mechanochemical route from [Pd(NH₃)₂C₂O₄] and halogens (Table 1 – 2) were subjected to thermochemical isomerization transformation. The thermally induced *cis* → *trans* transformation of the isolated compounds was monitored at 400 K by high temperature PXRD. The reaction was observed to occur through *cis* → *trans* → β -*trans* structures. The authors concluded that the *cis* → *trans* transformation was not just a transition between the phases but occurred through the breaking of Pd-N or Pd-X bonds to finally yield the thermodynamic products (Table 3 – 32) [39].

The thermal, unidirectional isomerization of the *trans*, *trans*, *trans* (*ttt*) isomer to the thermodynamic *cis*, *cis*, *trans* (*cct*) isomer of six coordinate ruthenium complexes, RuCl₂(L)₂(PR₃)₂ (L = CO, RNC) (Table 3 – 33), was investigated by PXRD and thermomicroscopy techniques [81]. The solvent-free conversion of the *ttt* to the *cct* is unidirectional, and no *ccc* isomer was detected. In formulating the mechanism of the isomerization reaction it was assumed that only one pair of ligands (Cl, RNC) exchanged to bring about the isomerization reaction in an intramolecular process involving no loss of ligands from the Ru during the ligand exchange. PXRD and NMR [65] techniques were used to study the reaction and results obtained were consistent with first-order kinetics with $E_a \sim 219 (\pm 26)\text{ kJ mol}^{-1}$ indicating a high-energy process, consistent with the two ligand movement.

The example of the isomerization reaction above is indicative of the close relationship between solid state and melt reactions. When high-temperature studies of *ttt*-RuCl₂(CO)₂(PMePh₂)₂ single crystals were undertaken, two competing processes were noted. Either the thermal energy broke intermolecular bonds (melting), or the added thermal energy induced an intramolecular process (solid state isomerization reaction). It was shown that only limited (i.e. surface or bulk-initiated) isomerization took place in the solid state before melting ensued. Furthermore, it was noted that the isomerization reaction continued in the molten state.

3.2.2.3. *Diagonal–lateral isomerization reactions.* A range of piano stool complexes of the type RCpML₄ (M = Re, Mo, W) have been synthesized in our laboratories and

shown to undergo solventless *diag* to *lat* isomerization [82–86]. Variation of the Cp ring substituent R, the metal M and the ligands L, have yielded tens of compounds and provided a wide range of variables for systematic studies (Table 3 – 34–36). These studies have involved the use of several techniques from the more traditional ones like IR, DSC and NMR to less common ones such as thermomicroscopy, in situ DRIFTS and PXRD [11,57] to monitor the reactions. Important conclusions from the studies include:

1. In some cases the melt process is the only route for the synthesis of pure isomers in high yield, and can provide a very simple alternative to often tedious solution techniques.
2. Based only on a theoretical analysis of intra- and intermolecular properties it is not possible to predict as to whether a compound will or will not undergo isomerization in the melt (or solid) phase.
3. Isomerization reactions in the melt phase may or may not occur in the same direction as when conducted in solution.
4. In all the cases thus far studied, the isomerization reaction *always* goes from the low melting isomer to that with a higher melting point.

The complexes studied isomerize in either a bidirectional (i.e. isomerization takes place starting from either isomer) or unidirectional *diag* to *lat* direction. Combined IR, NMR, powder and single crystal XRD and thermomicroscopy studies were used to follow the kinetics of the isomerization process. The tungsten complex (η^5 -C₅H₄Me)W(CO)₂P(OⁱPr)₃I (Table 3 – 36) represented a special case because it was the only one in which a unidirectional *lat* to *diag* transformation occurs in the melt [87]. Fig. 7 shows a thermomicroscopic study on a single crystal of *lat*-(η^5 -C₅H₄Me)W(CO)₂P(OⁱPr)₃I. The isomerization is characterized by a heterogeneous localized melting process (b). As the crystal is heated, crystallinity is gradually lost as it becomes rougher (c), but the overall morphology of the crystal is retained in forming the product *diag*-(η^5 -C₅H₄Me)W(CO)₂P(OⁱPr)₃I (d) which was confirmed by IR and NMR analyses. The data has been interpreted as involving localized melting occurring at defect sites that permit the reaction to occur in the heterogeneous manner observed. Fillippou and coworkers [58,59] have prepared similar complexes via a melt phase isomerization reaction characterized by a tungsten-germyl moiety [(η^5 -C₅Me₅)W(CO)₂L(GeCl₃), L = CNEt, PMe₃] (Table 3 – 37).

3.3. Sonochemical induction

The application of sonochemistry procedures to synthetic organometallic chemistry has been promoted through the works of Suslick [88] and Luche [89]. Suslick and coworkers have shown that variation of acoustic cavitation conditions can be used to produce organometallic

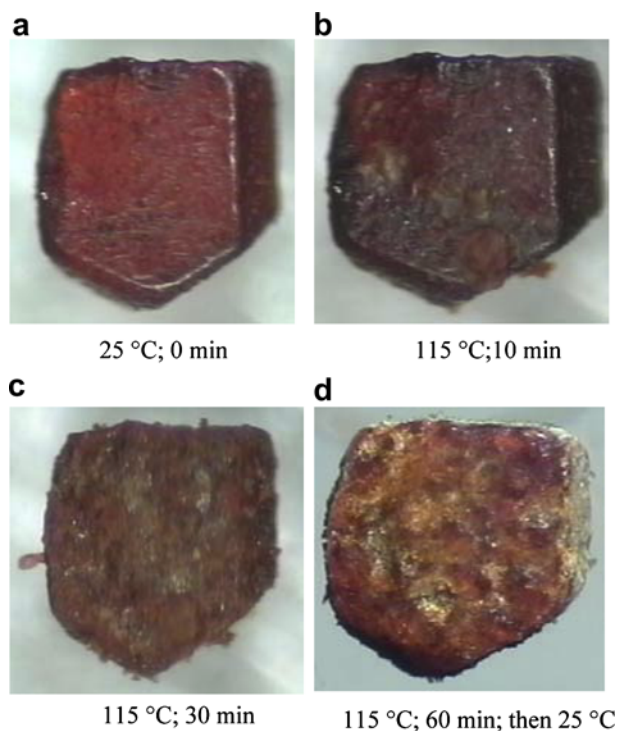


Fig. 7. The thermally induced intramolecular isomerization of *lat-to-dia*-(η^5 -C₅H₄Me)W(CO)₂P(OⁱPr)₃I: (a) initial crystal, (b) the beginning of the heterogeneous melt/solidification process, (c) as the crystal isomerizes it becomes rougher and (d) loss of crystallinity. The overall morphology of the crystal is retained even after the isomerization. (Reproduced from [87] with permission, copyright Elsevier B.V.)

complexes. For example, the ultrasonic irradiation of Fe(CO)₅ produced a variety of products inaccessible by conventional techniques [90]. Ultrasound has also been found to increase surface disruption leading to increased activity in the preparation of a CuBr₂/alumina catalyst [91]. This has been attributed to the high velocity convective currents generated by sonication which leads to reduction in diffusion layer thickness, thereby enhancing reactions that are under mass transport control [92]. The direct application of sonochemistry to melt processes, to our knowledge, has not as yet been documented. The advantages of cavitation produced from ultrasonic irradiation of reactions performed in solution should apply to melt reactions. Thus, improvement of nucleation and growth processes and the production of localized ‘hot-spots’ that initiate chemical reactions [90], are conditions that could improve melt reactions normally initiated by others means (grinding or milling). It therefore seems that the application of ultrasound to solvent-free reactions in conjunction with or without other means of initiation will have a beneficial effect on reactions that pass through a melt phase.

3.4. Induction by microwave irradiation

Microwave assisted synthesis has been widely applied to the preparation of organic [93] and inorganic compounds [94]. It has been noted that the wide application of micro-

wave initiation to organometallic chemistry is hampered by some limitations of the technique [95]. These include real-time reaction monitoring using standard techniques (IR, NMR) and the optimization of reaction conditions such as time and temperature. Available examples of application of microwave initiation in suitable solvents to organometallic compounds include the rapid synthesis of arene-metal complexes [96], the substitution reaction of metal carbonyls [97] and the synthesis of coordination compounds [98].

The application of microwave initiation to solvent-free organometallic reactions will offer certain unique advantages. This includes the significant improvements in temperature homogeneity and heating rates, leading to a significant decrease in reaction time and less degradation of reactants and final products when compared to classical heating. This approach could lead to a clean reaction with higher yields than obtained by conventional heating techniques.

The microwave technique has also been shown to provide synergy with solvent-free conditions [99]. This is most applicable when at least one of the solid reactants in a mixture absorbs microwaves and this process can then be used to supply the energy required to drive the reaction. Loupy [100] has recently surveyed the utilization of solvent-free microwave organic synthesis as an efficient procedure for green chemistry.

An example of the application of microwave assistance to the solvent-free synthesis of organometallic compounds has been performed by Imrie and coworkers [101]. They prepared ferrocenyl esters in moderate to high yields from the microwave-promoted solvent-free reactions of ferrocenyl fluoride and substituted phenols. The reaction which combined mechanochemistry and subsequent microwave irradiation for 1 min resulted in melt formation.

4. Solid–gas reactions

Solid–gas reactions involve the interaction of molecular solids with gaseous reactants to yield molecular solid products (Fig. 1). The reaction ‘front’ in this case is the solid/gas interface. This is a mobile phase, controlled by the ability of the gas to diffuse into the lattice of the solid. Significant motion of this ‘front’ leading to molecular loosening is necessary for a reaction to occur. This molecular loosening may or may not manifest itself as physical melting. It is the recognition of this mobile reaction ‘front’ that relates chemical interactions between solid and gaseous reactants with main stream solid–solid melt reactions that occur at the physical interface between the solids, as already discussed.

Following are examples of solventless solid–gas reactions, mainly occurring in the solid state, that highlight this area of chemistry. Reactions between molecular solids and small gaseous molecules were amongst the first solventless organometallic reactions to be studied. In the 1960s Vaska performed a series of reactions involving Ir(CO)Cl(PPh₃)₂

with small two electron donor gaseous molecules [102]. This was followed in the 1970s by a series of elegant studies involving organic compounds and vapors, such as NH_3 , HCl and SO_2 by Paul and Curtin [103].

In more recent times, several research groups have focused attention on solid–gas reactions with a view towards developing carriers, sensors and traps for gases. The ease of sorption and desorption of the gases is required for practical application. In particular a compound should be capable of withstanding repeated cycles of sorption and desorption under moderately mild conditions. In addition, since the early days of organometallic chemistry the instability of many organometallic complexes to atmospheric exposure has been well recognized. Some of the reactions are known to involve oxidation and/or ligand substitution by gaseous molecules (oxygen, moisture) in the atmosphere. Hence, the study and clear understanding of solid–gas interactions is important in organometallic chemistry. It is therefore interesting to note that the first example of an intermolecular single-to-single crystal chemical reaction with an external reagent was with molecular oxygen [104].

Recently, Braga et al. [105–107] have shown that the powdered form of the organometallic zwitterion $[\text{Co}^{\text{III}}(\eta^5\text{-C}_5\text{H}_4\text{COOH})(\eta^5\text{-C}_5\text{H}_4\text{COO})]$ reacts in the solid state with hydrated vapors of volatile acids (HCl , $\text{CF}_3\text{CO}_2\text{H}$, HBF_4) or bases (NH_3 , NMe_3 , NH_2Me) to

quantitatively produce the corresponding salts of the cation $[\text{Co}^{\text{III}}(\eta^5\text{-C}_5\text{H}_4\text{COOH})_2]^+\text{A}^-$ or anion $[\text{Co}^{\text{III}}(\eta^5\text{-C}_5\text{H}_4\text{COOH})_2]^- \text{BH}^+$ respectively. This behavior of the Co compound is due to the zwitterionic nature of the $-\text{COOH}$ group (Table 4 – 38). The heterogeneous reactions are fully reversible, as the acid or base molecules can be removed by thermal treatment, regenerating the starting material as observed from the loss of the cation or anion in TG experiments. The authors have proposed the compound as a candidate for diverse applications. These include their use as solid-state sensors, reservoirs, filters and sieves for detecting or trapping small gaseous molecules.

Similarly, Albrecht et al. [108] have observed that when colorless crystalline $[\text{PtCl}(\text{NCN}-\text{OH})]$ is subjected to an atmosphere containing gaseous SO_2 (1 atm), a fast reaction took place affording the corresponding bright orange adduct $[\text{PtCl}(\text{NCN}-\text{OH})(\text{SO}_2)]$. The reaction was monitored by PXRD, and a completely new powder pattern in the X-ray diffractogram of the product corresponding to the known pattern of the pure SO_2 adduct $[\text{PtCl}(\text{NCN}-\text{OH})(\text{SO}_2)]$ was observed. All peaks originating from $[\text{PtCl}(\text{NCN}-\text{OH})]$ were absent. Exposure of a sample of the adduct to air completely reversed the process of this selective inclusion of SO_2 into these arylplatinum structures which involved successive making and breaking of $\text{Pt}-\text{SO}_2-\text{Cl}$ interactions (Table 4 – 39). Because the process of SO_2

Table 4
Solid–gas reactions

No	Reaction	Comments	Reference
38		NMR, XRD, AFM Hydrated vapors of volatile acids (A) and bases (BH) are reversibly absorbed	[105] [106] [107]
39		IR, PXRD Reaction is fully reversible and easily monitored	[108]
40		IR, NMR, XRD, EA	[109]
41		L = diiodine, octa-sulfur; ethylene, benzene; polycyclic aromatic hydrocarbons and corannulene	[110]

gas absorption/desorption is fully reversible over many ‘on/off’ cycles without any material deterioration, and is accompanied by a distinct color change the authors have proposed its application as a ‘molecular switch’ for SO₂ sensing.

Other researchers have reported on the importance of solid–gas reactions as a component of solvent-free chemistry. The reaction of CO with aryloxide rhodium (I) complexes, Rh(OAr)(PR₃)₃ has been conducted by Osakada and Ishii [109] with and without a solvent. The products of the solvent-free methodology were found to be ionic complexes formulated as [Rh(CO)(PR₃)₃]⁺OAr[−]. These products differ from those obtained in toluene, in which Vaska-type complexes *trans*-Rh(OAr)(CO)(PR₃)₂ were obtained via a carbonylation reaction (Table 4 – 40). It is interesting to note that the catalyzed melt phase substitution reaction of (η⁵-C₅H₄R)Fe(CO)₂I with a series of phosphines also resulted in the formation of a salt product [(η⁵-C₅H₄R)Fe(CO)₂PR₃]⁺I[−], instead of the substitution product [(η⁵-C₅H₄R)Fe(CO)(PR₃)I] usually obtained in solution [66].

Examples in which gas uptake occurred in a melt reaction have been reported. Thus the insertion reaction of CO into (η⁵-C₅H₅)Fe(CO)₂Me and (η⁵-C₅H₅)Mo(CO)₃Me has generated the expected insertion product [63].

Sublimation–condensation is a solvent-free technique that involves the direct vaporization of solid reactants and subsequent reaction in the vapor phase followed by the deposition of solid products. The technique was developed for the coordination of a variety of ligands to the tetrakis(trifluoroacetate) dirhodium(II) molecule

[Rh₂(O₂CCF₃)₄] by Cotton and coworkers [110] to prepare several compounds unobtainable by conventional solution techniques (Table 4 – 41). It is possible that some of these reactions may occur in the melt phase.

5. Monitoring melt reactions

A variety of techniques are available to both study reactions in the melt and to detect the melt phase.

5.1. Thermal analysis

DSC measurements of solid mixtures permits the evaluation of eutectic formation. By comparing the melting points of pure samples and sample mixtures an estimate can be made as to the temperature to use in a melt reaction. An example of this is shown in Fig. 8. Here the migratory insertion and the subsequent decarbonylation (Section 3.2.2.2) reactions [(η⁵-C₅H₅)M(CO)₃Me + PPh₃ → (η⁵-C₅H₅)M(CO)₂PPh₃(COMe) → (η⁵-C₅H₅)M(CO)₂(PPh₃)Me + CO] were monitored by DSC. The curves represent (a) pure PPh₃ ligand, m.p. = 81 °C, (b) pure molybdenum complex (η⁵-C₅H₅)Mo(CO)₃Me, m.p. = 100 °C (plus peaks relating to secondary reactions), (c) 1:1 mixture of ligand and molybdenum complex, eutectic m.p. = 64 °C (plus peaks relating to carbonylation/decarbonylation reactions), (d) pure tungsten complex (η⁵-C₅H₅)W(CO)₃Me, m.p. = 116 °C, and (e) 1:1 mixture of ligand and tungsten complex, eutectic m.p. = 68 °C with no product formation. It can be seen that both metal complexes formed a eutectic mixture with

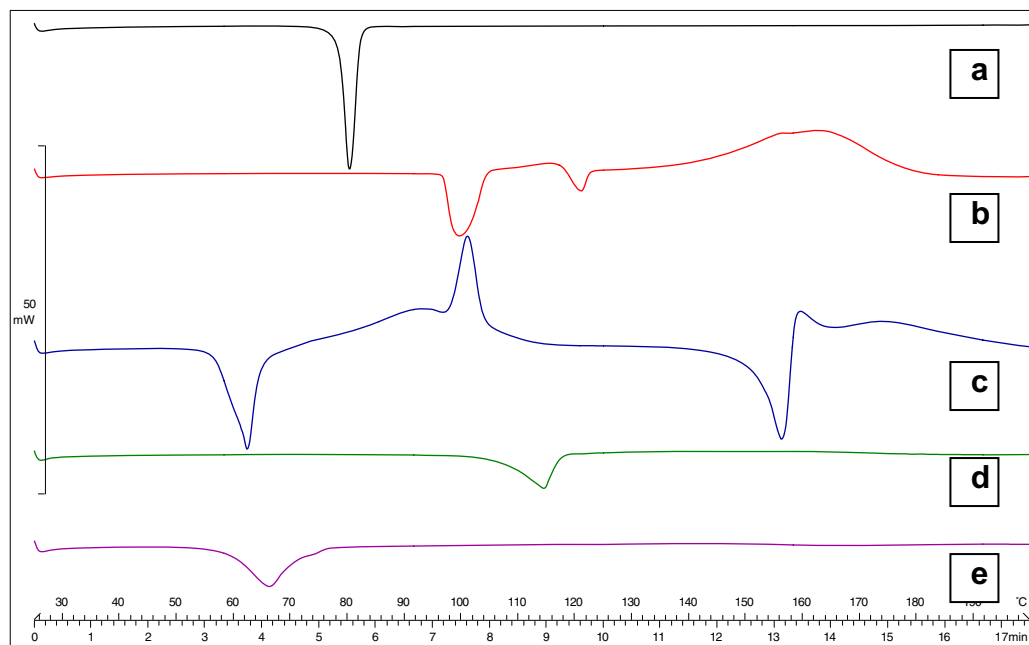


Fig. 8. DSC curves of (a) PPh₃, (b) (η⁵-C₅H₅)Mo(CO)₃Me, (c) 1:1 mixture of PPh₃ + (η⁵-C₅H₅)Mo(CO)₃Me, (d) (η⁵-C₅H₅)W(CO)₃Me, (e) 1:1 mixture of PPh₃ + (η⁵-C₅H₅)W(CO)₃Me. Both metal complexes formed a eutectic mixture with PPh₃ (at about 15–20 °C lower than the m.p. of PPh₃), but only the Mo complex formed an insertion product which decarbonylated and finally melted at 158 °C.

the ligand (about 15–20 °C lower than the m.p. of the ligand). However only the Mo complex formed an insertion product (endotherm at 98 °C) which decarbonylated (exotherm at 102 °C) and the decarbonylated product melted at 158 °C (Fig. 8c). This example illustrates that even though melt formation is required for inter-solid reactions the mere formation of a melt is insufficient to result in product formation.

5.2. Thermomicroscopic techniques

The most obvious approach to monitor a reaction is to follow the reaction as a function of temperature under a microscope. The progress of the reaction can be captured by a camera and digitally stored on a computer. An example of an experimental set-up to achieve this is shown in Fig. 9. The apparatus consists of a bifocal Olympus polarizing microscope, a heating stage to permit reactions to be monitored under an inert atmosphere and a camera. Examples of reactions monitored by this procedure are shown in Figs. 5 [66] and 7 [87].

5.3. DRIFTS

Diffuse reflectance Fourier transform IR spectroscopy (DRIFTS) allows a melt reaction to be monitored directly. Mixed solid samples are placed in the DRIFTS reactor. Inert gases can be used to ensure no reaction of the solids or melt with air. The reaction is carried out at a set temperature and the reaction progress monitored as a function of

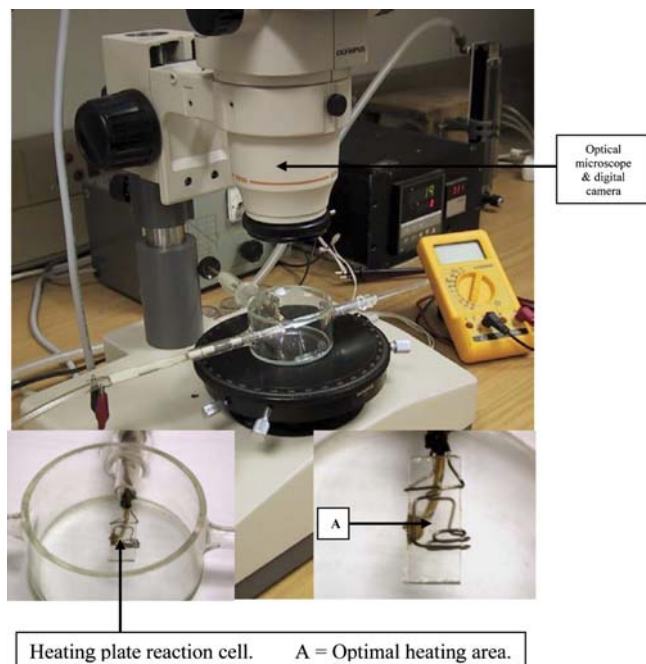


Fig. 9. Experimental set-up for thermomicroscopic studies. The reactants (powder or single crystals) are placed in the heating area. Heating is commenced and the physical changes occurring are monitored with time using the polarizing optical camera. All data presented in this report are obtained at (40–60×) magnification.

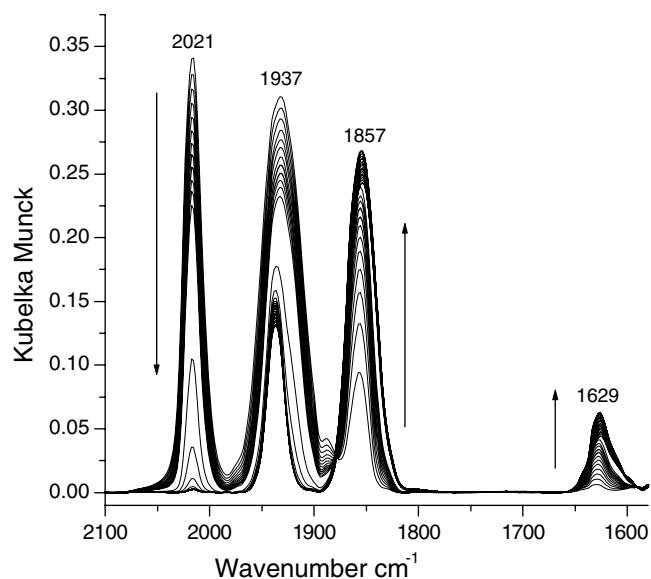


Fig. 10. In situ DRIFTS study of the kinetics of the migratory-insertion reaction $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{Me} + \text{P}(p\text{-FC}_6\text{H}_4)_3 \rightarrow (\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2\text{P}(p\text{-FC}_6\text{H}_4)_3(\text{COMe})$ (60 °C; metal:phosphine ratio 1:10 mol/mol). The rate of disappearance of the carbonyl peak at 2021 cm^{-1} was monitored over time. (Reproduced from [64] with permission, copyright American Chemical Society.)

time. Typically a diluent is added to the solid mixture. The influence of various diluents on the reaction kinetics has been discussed (see Section 2.4 above). An example of data collected from a DRIFTS monitored migratory-insertion reaction $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_3\text{Me} + \text{P}(p\text{-FC}_6\text{H}_4)_3 \rightarrow (\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CO})_2\text{P}(p\text{-FC}_6\text{H}_4)_3(\text{COMe})$ in the melt is shown in Fig. 10. The rate of disappearance of the carbonyl peak due to the reactant at 2021 cm^{-1} or appearance of the carbonyl peaks due to the product (1857, 1629 cm^{-1}) were monitored over time. The kinetic data were obtained by fitting the DRIFTS data to a pseudo-first order rate equation [64].

5.4. Other techniques

Post-reaction monitoring of products can be performed by conventional IR and NMR spectroscopic techniques. Reactions can also be carried out in NMR tubes (at appropriate temperatures) or monitored by PXRD (loss of crystallinity with time, temperature).

6. Conclusions and prospects

In this review the role of the melt phase as a possible reaction phase has been described. Examples from the organometallic chemistry literature have been given to indicate studies that have been carried out to date. Attempts have been made to be comprehensive but some examples (unintentionally) may not have been discussed in this review.

Key issues relating to the use of a melt relate to (i) high reactant concentrations, (ii) heat and mass diffusion issues and (iii) the properties of the melt derived from the reactants. This review reveals that very few *systematic* studies

have been performed in organometallic chemistry in this phase. However, the review has revealed the promise associated with reactions in the melt phase:

- (1) faster reaction kinetics;
- (2) reactions with products different to those obtained in solvents;
- (3) control of reaction kinetics via use of solid diluents;
- (4) a greener approach to chemistry.

That these reactions have industrial importance is shown by the hydroformylation studies carried out with $\text{RhCl}(\text{PR}_3)_3$ as catalyst in a PPh_3 melt [30]. Clearly, many more studies need to be performed to evaluate the role of the diffusion (heat, mass) in the melt and also how the properties of the melt materials influence the reaction.

Acknowledgements

We wish to thank the NRF and the University of the Witwatersrand for financial assistance. We would also like to acknowledge the many students who over the years may have played a key role in developing the procedures and much of the data that have been generated in our own studies of the melt phase – these in particular include Drs. S. S. Manzini, L. Cheng, O. G. Adeyemi, T. Malefetse, B. Mamba, F. Nareetsile and Mr. O. Horwood, Mr. A. Munyaneza and Ms. A. Budhai.

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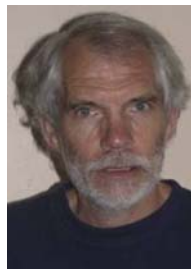
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M.D. Bala is currently a lecturer of inorganic chemistry at the University of KwaZulu-Natal.

Muhammad D. Bala received his B.Sc. (Hons.) degree from Ahmadu Bello University (Zaria, Nigeria) in 1991. He obtained his Ph.D. in 2002 from East China University of Science and Technology (Shanghai, China) under the supervision of the late Y. Qian. During this period he worked on the synthesis of novel organolanthanide compounds and their application in homogeneous catalysis. Since April 2003 he has been a Post-doctoral Fellow working on solvent-free organometallic chemistry in the group of N. J. Coville.



He holds the Chair of Inorganic Chemistry in the School of Chemistry. His current research interests include Fischer–Tropsch catalysis, synthetic routes to shaped materials (carbon titania, silica, etc.), and solventless organometallic chemistry.

Neil J. Coville obtained his B.Sc. (Hons.) and M.Sc. degrees at the University of the Witwatersrand ('Wits') before proceeding to McGill University, Montreal where he obtained his Ph.D. (1973) under the supervision of Ian Butler. After post-doctoral work at Harvard University with (the late) John Osborn he returned to 'Wits' in 1976 where he has remained. He is currently a focus area leader in the DST/NRF Centre of Excellence in Strong Materials and a member of the DST/NRF Centre of Excellence in Catalysis.