

# Solvent-free synthesis of metal complexes

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Avoiding the use of solvents in synthesis can reduce environmental contamination and even be more convenient than using solvent-based synthesis. In this *tutorial review* we focus on recent research into the use of mechanochemistry (grinding) to synthesise metal complexes in the absence of solvent. We include synthesis of mononuclear complexes, coordination clusters, spacious coordination cages, and 1-, 2- and 3-dimensional coordination polymers (metal organic frameworks) which can even exhibit microporosity. Remarkably, in many cases, mechanochemical synthesis is actually faster and more convenient than the original solvent-based methods. Examples of solvent-free methods other than grinding are also briefly discussed, and the positive outlook for this growing topic is emphasised.

## Introduction

As a society we are increasingly aware of the environmental impact of human activity, and consequently of the need to develop cleaner and more energy-efficient technologies. It has long been recognised that the large-scale use of volatile organic solvents has important implications for environmental contamination.<sup>1,2</sup> Approaches to the problems presented by organic solvents include the use of more benign solvents (especially water and supercritical CO<sub>2</sub>), or solvents with negligible vapour pressures (ionic liquids).<sup>2</sup> It has also been said that ‘the best solvent is no solvent’.<sup>2</sup> Despite the power of this statement, our use and understanding of solvent-free synthesis, especially where solid starting materials are concerned, has remained undeveloped in comparison to solvent-based methods. The question normally asked when planning synthesis is still ‘which solvent should I use?’, and not ‘do I need to use a solvent?’ As solvent-free synthesis becomes more

widely investigated many people are likely to be impressed at the range of reactions, even between solid starting materials,



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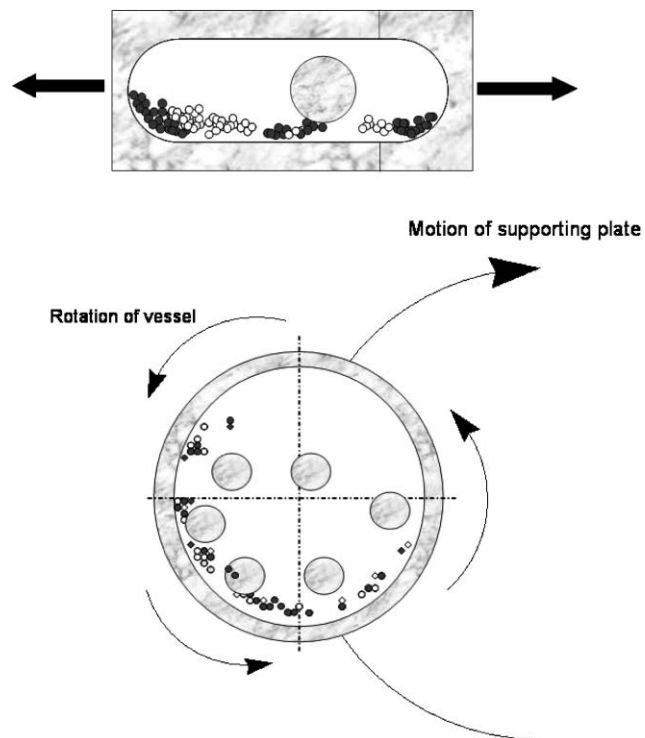
that do not need solvents, and how many are actually more conveniently performed without them.

This review highlights recent advances in solvent-free synthesis, in particular reactions between metal salts and organic ligands to give coordination complexes. It concentrates on the use of grinding to promote reactions between solid reactants. This approach is known as *mechanochemistry* and whilst its usefulness appears to have been recognised for a long time,<sup>3,4</sup> it has become neglected in comparison to solvent-based methods. A concise introduction to the topic has been provided by Fernández-Bertran.<sup>4</sup> Since the 1980s, increasing interest has been shown in organic synthesis by mechanochemical methods,<sup>5–8</sup> including the synthesis of co-crystals<sup>9</sup> (as well as non-mechanochemical solid state topochemical reactions within crystals<sup>10</sup>). An impressive range of reactions has been demonstrated to be efficiently and conveniently performed, even between solid reactants, and some mechanistic insights have been obtained. Recent reports have shown that mechanochemistry is also effective for the efficient, rapid synthesis of a wide range of metal complexes, which vary from straightforward mononuclear complexes to spacious coordination cages and even porous infinite frameworks. After a brief description of grinding effects and mechanistic aspects, the following sections deal with each of these types of structure in turn.

## Grinding<sup>11</sup>

Mechanochemistry can be as simple as grinding two reactants in a pestle and mortar, and this technique has been employed by several groups to demonstrate solvent-free synthesis of metal complexes (see examples below). Ball mills, however, have the advantage of requiring no physical effort, supplying greater power and being programmable, allowing more systematic studies of the process. They are readily available commercially and two types appropriate for laboratory-scale synthesis are the shaker and planetary mills (Fig. 1). In shaker mills (also called ‘mixer’, ‘vibrant’, or ‘SPEX’ mills), a rapid (*e.g.* 10–50 Hz) side-to-side motion of the reaction vessel causes a ball bearing inside to impact against the sides of the vessel and its contents. The motion can also be more complex, *e.g.* figure of eight. In planetary mills the reaction vessel describes a circular path whilst simultaneously spinning in the reverse direction, *i.e.* mimicking the motion of planets around the sun. Depending on the relative speeds of these two rotations this motion causes the ball bearings to move around the surfaces of the walls (friction mode) or jump across the vessel and impact against the sides (impact mode). Planetary mills on the laboratory scale often have larger capacities than shaker mills, but generally have a lower impact frequency and so are sometimes referred to as being lower energy than shaker mills.

Various process parameters are associated with ball milling.<sup>11</sup> The grinding speed and duration affect the kinetics in generally intuitive ways, *e.g.* the faster the milling speed the higher energy input, and generally the faster the reaction. However, high speeds can also lead to higher temperatures, which may be undesirable if this causes side reactions. The charge ratio (or ball-to-powder ratio, *i.e.* mass of balls over mass of reactants) has also been found to be a useful parameter



**Fig. 1** Schematic diagram of shaker mills (above) and planetary mills (below)

to correlate with kinetics. These and several other parameters are discussed in reference 11.

### How does grinding induce reactions?

The kinetic energy supplied during grinding can have several effects on a crystalline solid<sup>4,11</sup> including: heating, reduction of particle size (with concomitant increase in surface area and the generation of fresh surfaces), formation of defects and dislocations in crystal lattices, local melting and even phase changes to alternative polymorphs. Collisions between crystals during grinding can also lead to local deformations and potentially melting. Importantly, grinding also provides mass transfer, *i.e.* it is a sort of ‘stirring’.

## Solvent free synthesis *via* mechanochemistry

### Mechanistic aspects

As mentioned above, organic reactions have been investigated, so far, in more detail than reactions between metal compounds and organics.<sup>5–9</sup> There has correspondingly been greater consideration of mechanistic aspects in the context of organic intra- and inter-crystal reactions. Kaupp has put forward a general mechanism involving three stages.<sup>5</sup> For an inter-crystalline reaction, between crystals of A and B to give product C, this process may be described as follows. The first stage is phase rebuilding, during which there are directional long-range migrations of molecules of reactant A into cleavage planes or channels in crystalline B (and *vice versa*). This is driven by the internal pressure which comes from formation of the product C at the interface between the reactants. It distorts

the original crystal structures and results in a mixed A–B–C phase. It can also give rise to features on the surfaces of reacting crystals such as hills and troughs, which can be observed by atomic force microscopy (AFM). The second step is phase transformation in which crystals of product C grow from the distorted mixed A–B–C phase. During this second step, the growing crystals of C remain spatially discontinuous on the A and B particles. Finally, the chemical and geometrical mismatch between the starting (A and B) phases and the product (C) phase causes disintegration of the particles. This in turn reveals fresh surfaces of the reactants, and continued grinding then serves to bring these fresh surfaces into contact for further reaction.

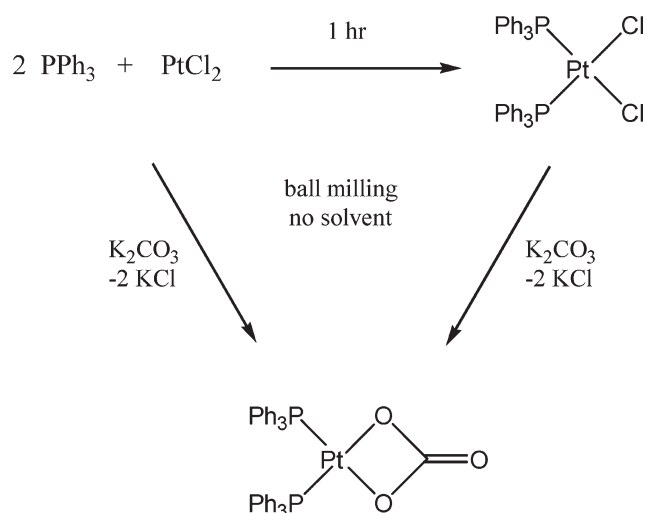
Scott and co-workers have highlighted the important fact that in some cases, solvent-free reactions between solid reactants actually proceed through bulk liquid phases. Such liquid phases are possible due to the formation of eutectics between the reactants and product(s) and any evolution of heat.<sup>12</sup> Also, Jones has shown that addition of very small amounts of solvent can accelerate the formation of co-crystals by grinding.<sup>13</sup>

### Solvent-free synthesis of metal complexes

There are some metal complexes which undergo phase changes upon grinding (providing an example of the grinding effects described above), in particular the vanadyl salen compounds investigated by Tsuchimoto and coworkers.<sup>14</sup> As solids they exist in green, monomeric, or orange, polymeric forms, the latter connected through V=O...V=O contacts into infinite chains. The orange form converts to the green form on grinding due to the break up of the polymer chains.

Salts of labile metal ions will react rapidly under mechanochemical conditions with good chelating ligands. In particular Raston and Steed described that simple, manual grinding of divalent first-row metal halides or nitrates with phenanthroline resulted in clear colour changes indicative of the [M(phen)<sub>3</sub>]<sup>2+</sup> dications such as the red [Ni(phen)<sub>3</sub>]<sup>2+</sup> within two minutes (eqn (1)).<sup>15</sup>

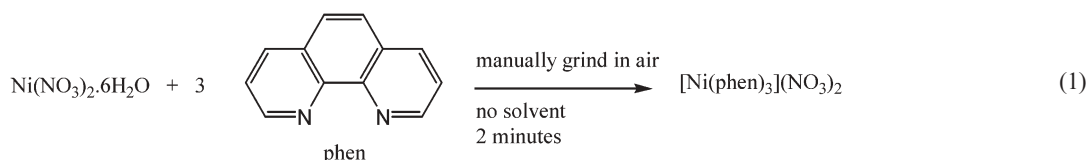
Substitution at platinum(II) is generally far slower than at divalent first row metals. Despite this, solid phosphines also react effectively with polymeric PtCl<sub>2</sub>, in a ball mill, to produce *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>], which can subsequently react with solid K<sub>2</sub>CO<sub>3</sub> to give [Pt(CO<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (Scheme 1).<sup>16</sup> These reactions, studied by Balema, Pecharsky and co-workers, were followed by solid state <sup>31</sup>P MAS NMR, X-ray powder diffraction (XRPD) and differential thermal analysis (DTA). *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] was obtained in 98% yield by grinding PtCl<sub>2</sub> and PPh<sub>3</sub> together in a ball mill for one hour (Scheme 1), although dissolution of the product in dichloromethane, filtration and evaporation were required to remove some insoluble impurities. Whilst XRPD showed the product to be amorphous, solid state <sup>31</sup>P MAS NMR spectroscopy confirmed

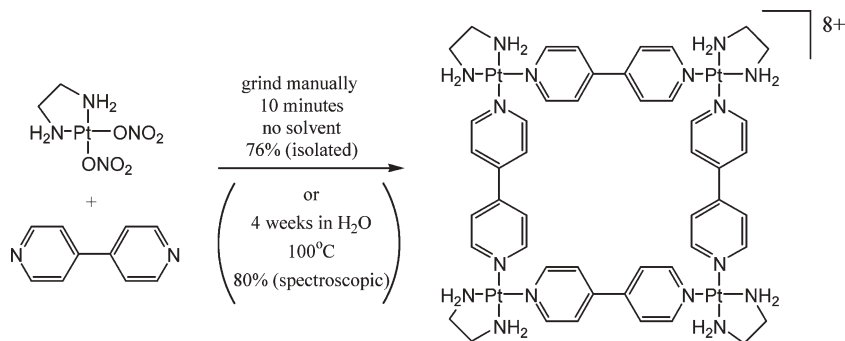


**Scheme 1** Solvent-free synthesis of platinum–phosphine complexes

its identity prior to the work-up. DTA of the product revealed thermal anomalies between 100 and 180 °C consistent with transformation from an amorphous to a crystalline phase. In fact, ball-milling of crystalline *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] also led to a material with the same thermal anomalies, as well as a broader solid-state <sup>31</sup>P MAS NMR spectrum, which provides an example of ball-milling reducing crystallinity. The chloride ligands in *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] were exchanged for carbonate by milling with K<sub>2</sub>CO<sub>3</sub>, although this also gave some phosphine oxide by-product. The authors considered the way in which mechanochemical energy allowed reactions between the metals and ligands to occur. They had previously estimated that local transient temperatures induced by impact of the ball should not exceed 110 °C. This suggests that local melting could not account for the reaction between *cis*-[PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (mp 193 °C) and K<sub>2</sub>CO<sub>3</sub> (mp 891 °C), but could possibly account for the reaction between PPh<sub>3</sub> (mp 79–82 °C) and PtCl<sub>2</sub>. However, interestingly, reaction between molten PPh<sub>3</sub> and PtCl<sub>2</sub> can produce a mixture of *cis* and *trans* isomers.<sup>17</sup> Since only the *cis* isomer was obtained in the mechanochemical reaction, the authors considered that local melting of PPh<sub>3</sub> as pathway to the product was therefore not significant. They concluded that these reactions were genuinely ‘solid state’ in nature, the effect of the ball milling being to disrupt the crystallinity of the reactants and provide the necessary mass-transfer.

More elaborate polynuclear structures can also be prepared rapidly in high yields. Sokolov and coworkers<sup>18</sup> have reported that the infinite polymeric species [M<sub>3</sub>Q<sub>7</sub>Br<sub>4</sub>] (M = Mo, W; Q = S, Se) are broken down by grinding with potassium oxalate K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> to give discrete trinuclear oxalate cluster complexes [M<sub>3</sub>(μ<sup>3</sup>-Q)(μ<sup>2</sup>-Q)<sub>3</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>2-</sup> and [Mo(μ<sup>3</sup>-Q)(μ<sup>2</sup>-Q)<sub>3</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>]<sup>2-</sup>. The initial products of the grinding reactions were characterised as [M<sub>3</sub>Q<sub>7</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]<sup>2-</sup> and then recrystallised from



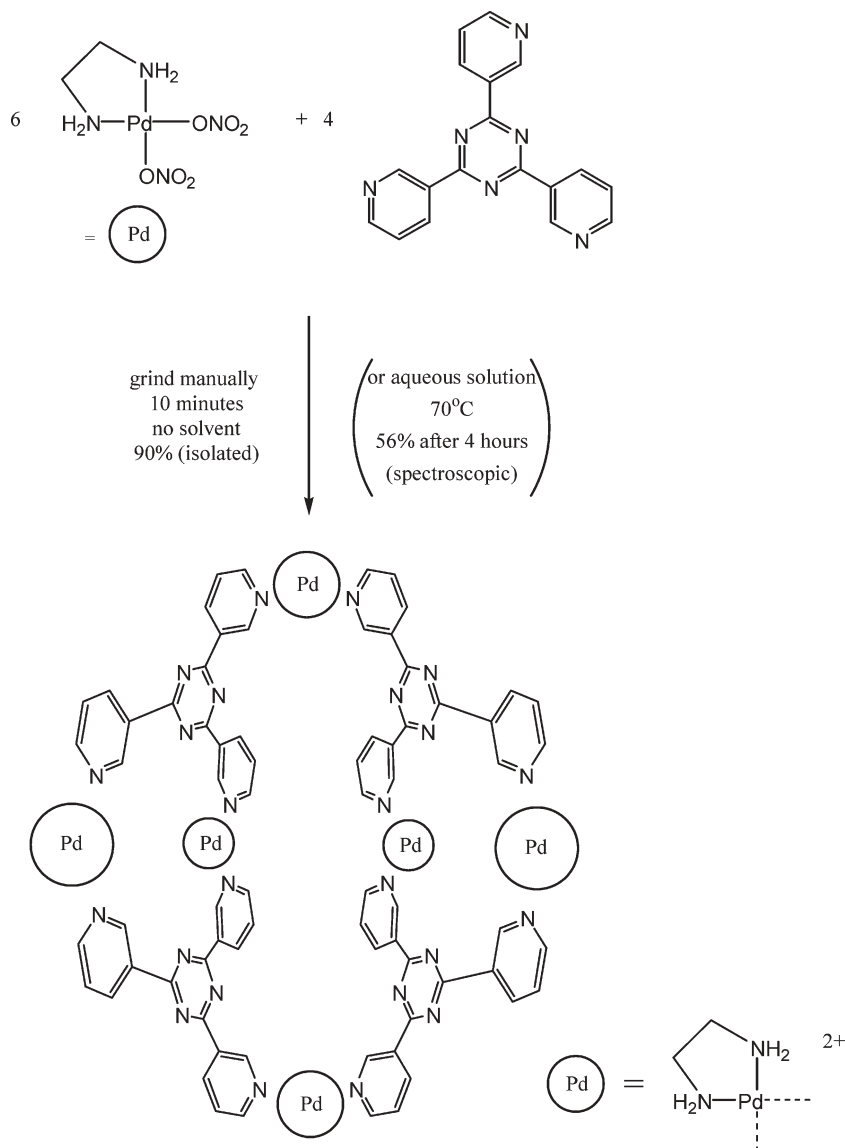


**Scheme 2** Solvent-free synthesis of a molecular square

water to give a range of clusters which were structurally characterised by single crystal X-ray diffraction.

Otera and coworkers<sup>19</sup> investigated solvent-free preparation of spacious multimetallic rings and cages, by simply grinding manually with a pestle and mortar. Remarkably, the

solvent-free reaction between 4,4'-bipyridyl and [Pt(NO<sub>3</sub>)<sub>2</sub>(en)] (en = ethylenediamine) gave the corresponding tetraplatinum square in only 10 minutes, and with only a few percent of by-products visible in the <sup>1</sup>H NMR spectrum of the product. After work-up it was isolated in 76% yield (Scheme 2). Whilst the



**Scheme 3** Solvent-free synthesis of a large, hexapalladium coordination bowl

progress of the solvent-free reaction was monitored by dissolving the reaction mixture in  $D_2O$  to obtain  $^1H$  NMR spectra, and it could be argued that the reaction is likely to continue in solution, the reaction during grinding was clearly much faster than in aqueous solution, in which it took four weeks to go to completion.

Using the same procedure a still more elaborate assembly, a hexapalladium bowl-shaped cluster based on a tripodal tripyridine ligand, was also obtained quantitatively in only ten minutes (Scheme 3). Again, the reaction was apparently faster under solvent-free conditions than in solution in  $D_2O$ .

It was also found that a series of Cu(I) helicates based on bipyridine-containing ligand strands could be efficiently prepared by grinding.

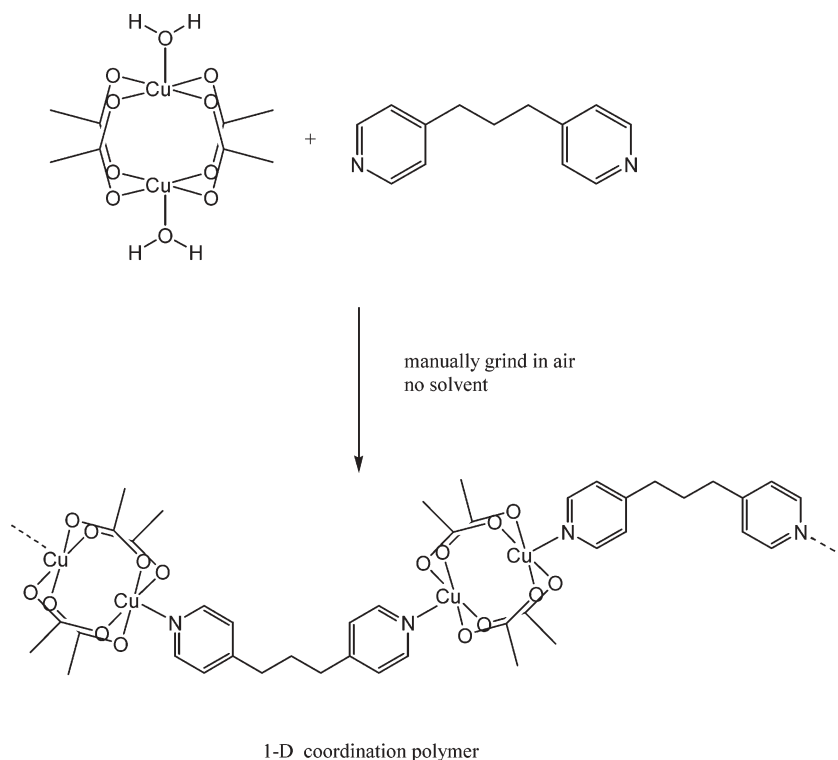
A different kind of polymetallic cluster, specifically multi-tin species with bridging ligands such as  $O^{2-}$ ,  $OH^-$  and  $CH_3CO_2^-$  have also been synthesised by grinding solid  $n-BuSn(O)OH$  with various solid acids for 30–120 minutes.<sup>20</sup> Grinding results in the reaction mixture becoming progressively more soluble, indicating the progress of the reaction. The products were characterised indirectly after dissolution, filtration and crystallisation to give a range of cluster topologies and a one-dimensional coordination polymer.

Coordination polymers (or metal organic frameworks) can also be synthesised from metal precursors and bridging ligands. Steed and co-workers crystallised from methanol–water solution a one-dimensional coordination polymer based on the dicopper tetraacetate ‘paddle wheel’ and 1,3-di-4-pyridylpropane connectors. Simply grinding together copper acetate with the di-pyridine ligand produced a similar colour change to the solvent-based reaction (Scheme 4).<sup>21</sup>

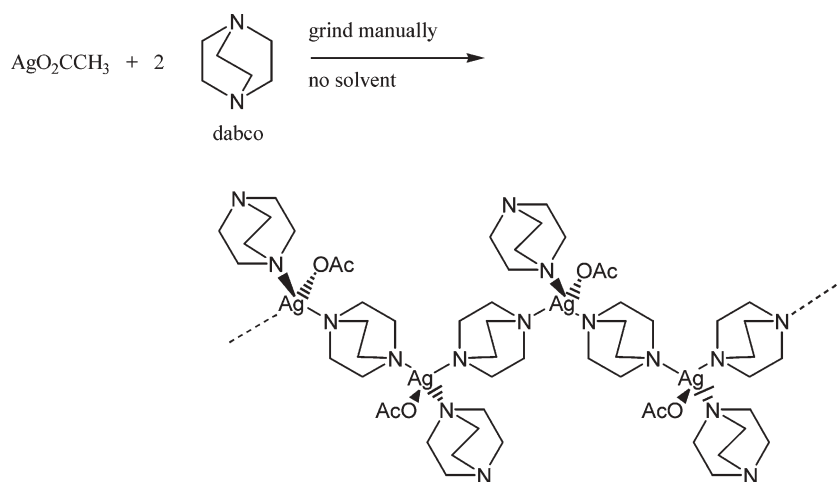
Although the crystallinity of the grinding product was not ascertained, it is likely that coordination occurred in a similar manner to that of the crystallographically characterised product. Braga, Polito, Grepioni and co-workers have reported the mechanochemical syntheses of several one-dimensional coordination polymers, and confirmed that these are indeed crystalline products by X-ray powder diffraction (XRPD).<sup>22–24</sup> Their crystal structures were not solved from the XRPD data, but comparison of their XRPD patterns with those simulated from single-crystal structure determinations allowed them to be structurally identified.

A series of polymers based on bridging diamine ligands was investigated, in particular based on  $N(CH_2CH_2)_3N$ , ‘dabco’ and *trans*-1,4-diaminocyclohexane,  $NH_2C_6H_{10}NH_2$ , ‘dace’. Grinding a 2 : 1 mixture of dabco with silver acetate in air gave the 1-dimensional coordination polymer  $[Ag\{N(CH_2CH_2)_3N\}_2]CH_3CO_2 \cdot 5H_2O$  (Scheme 5).

Its structure was ascertained by comparing its XRPD pattern with that simulated from the single crystal data of a sample crystallised from a water–methanol solution. As shown in Scheme 5 it is a 1-dimensional polymer with distorted tetrahedral  $Ag^+$  centres coordinated to two bidentate chain-propagating dabco units, one monodentate terminal dabco ligand and one aquo ligand. The acetate anions, aquo ligands and the free end of the terminal dabco unit also formed a hydrogen-bonded network. Grinding  $ZnCl_2$  and dabco gave, initially, a phase whose XRPD pattern could not be matched with that from any available single crystal data. However, on prolonged grinding this intermediate phase was transformed into a product whose XRPD pattern allowed it to be characterised as a zig-zag coordination polymer with alternating



**Scheme 4** Solvent-free synthesis of a 1-dimensional Cu(II) coordination polymer



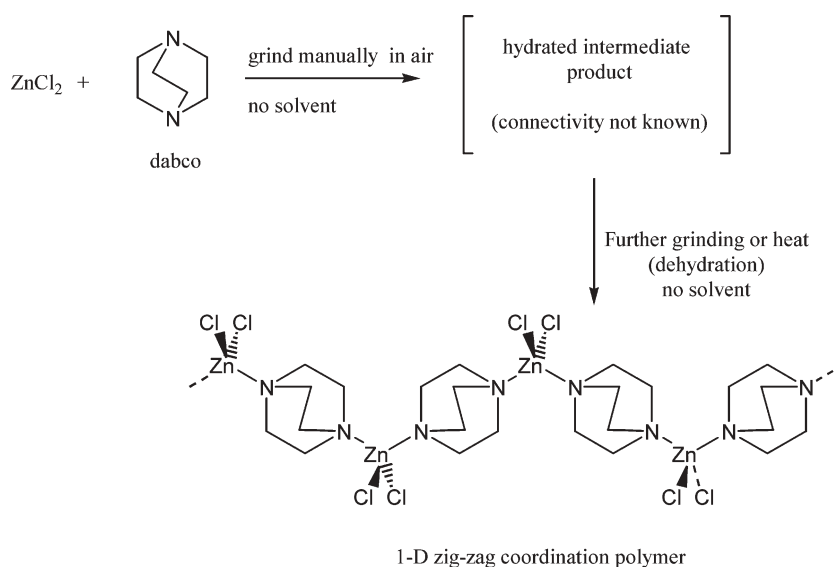
1-D zig-zag coordination polymer with bridging and terminal ligands

**Scheme 5** Solvent-free synthesis of a 1-dimensional Ag(I) coordination polymer

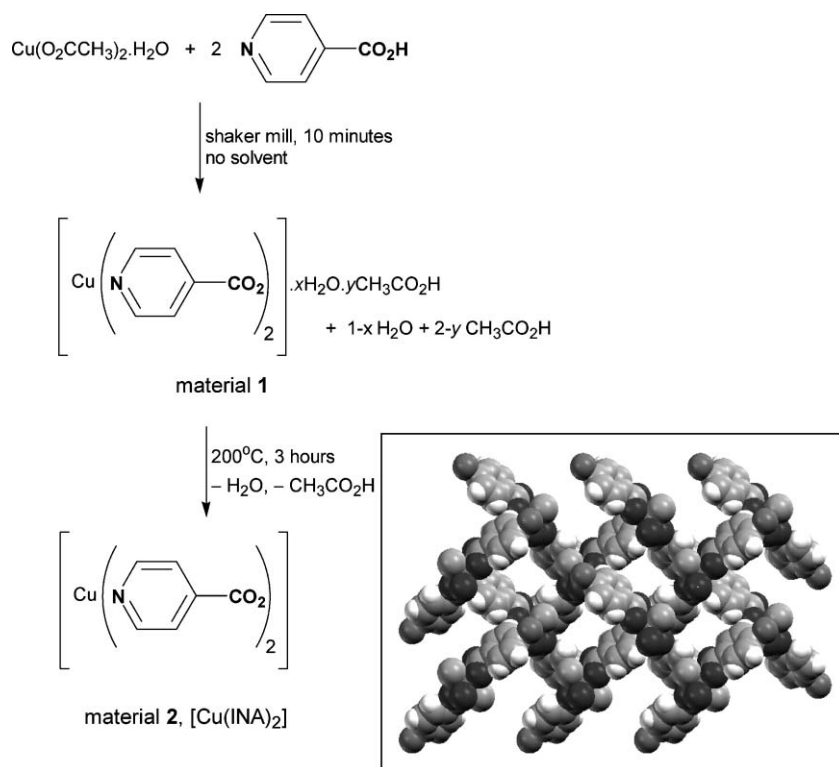
dabco and tetrahedral Zn(II) centres (Scheme 6). The intermediate phase was a hydrated form of the material, from which water was lost by prolonged grinding, or heating. A further material, thought to be a linear coordination polymer was prepared by grinding  $\text{CuCl}_2$  and dace. The product was crystalline, but its XRPD pattern could not be perfectly matched with any single-crystal structure determination. However, when the grinding was conducted in the presence of DMSO, a structurally-identifiable DMSO adduct was formed, which consisted of 1-dimensional chains of alternating dace and square-planar  $\text{CuCl}_2$  units with *trans* geometry. DMSO molecules were included between the chains as revealed by the single-crystal X-ray structure of the compound (crystallised from DMSO). Heating removed the included solvent and generated the same product as from grinding dace with  $\text{CuCl}_2$ . It was proposed that this non-solvated phase

consisted of the same 1-dimensional chains but more closely packed. The desolvated phase could uptake a variety of small solvent molecules (methanol, acetone, water) on suspension in the appropriate liquid. In other work, this group has also demonstrated the value of using microcrystalline grinding products as seed crystals for the growth of large single crystals for X-ray analysis.<sup>25</sup>

It is even possible to prepare 3-dimensional polymers, *i.e.* framework materials, by grinding together metal salts and organic ligands.<sup>26</sup> This is significant because 2- or 3-dimensional connectivity is generally required for a metal-organic framework to be sufficiently robust to support empty, open cavities, *i.e.* to be genuinely porous. A series of 3-dimensional frameworks based on divalent cobalt, iron, manganese or copper ions and the hybrid ligand isonicotinate ( $\text{NC}_5\text{H}_4\text{-4-CO}_2^-$ , INA) is known, some of which have been shown to be

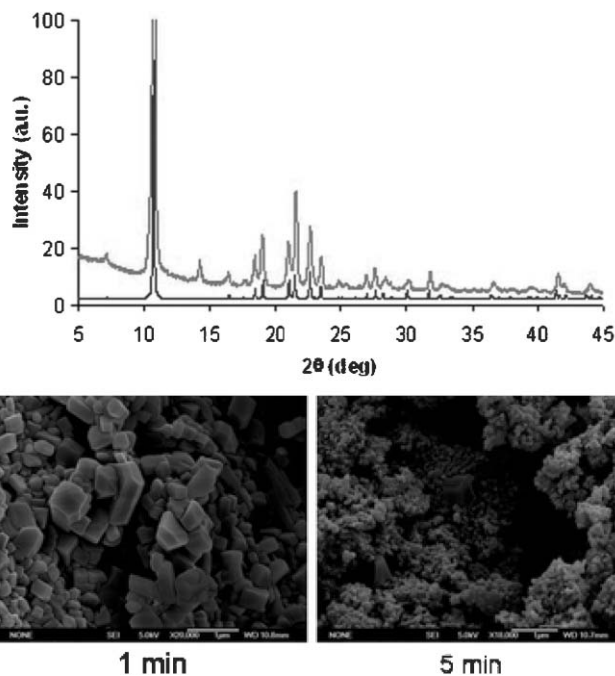


**Scheme 6** Solvent-free synthesis of a 1-dimensional Zn(II) coordination polymer

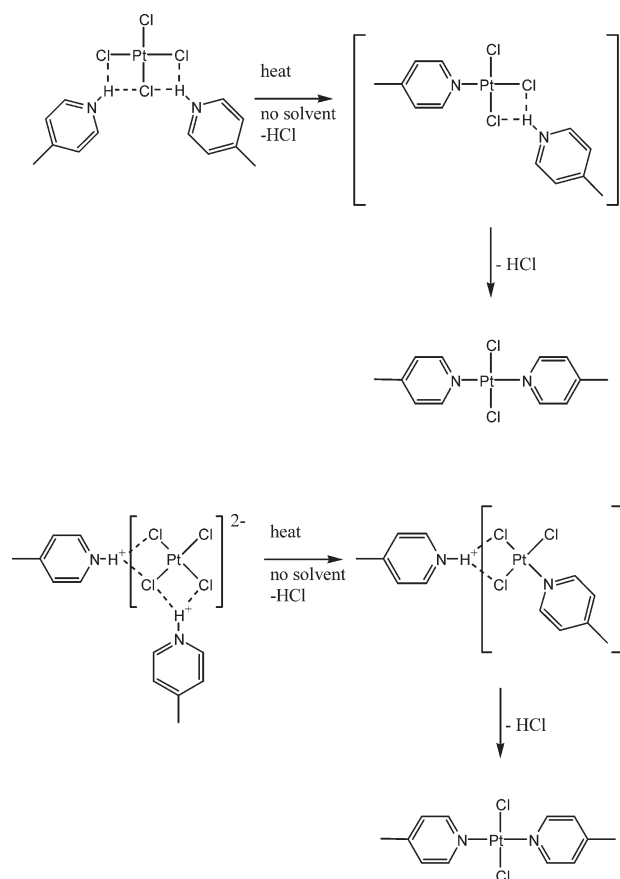


**Scheme 7** Solvent-free synthesis of a microporous 3-dimensional Cu(II) coordination framework. Adapted with permission from ref. 25.

capable of supporting open porosity.<sup>27,28</sup> Cu(INA)<sub>2</sub> has been synthesised solvothermally, *i.e.* at high temperatures with solvent in a sealed autoclave, over several hours or days.<sup>28</sup> However, on simply grinding together copper acetate and solid INAH (isonicotinic acid, NC<sub>5</sub>H<sub>4</sub>-4-CO<sub>2</sub>H) for 10 minutes in a shaker mill, crystalline Cu(INA)<sub>2</sub> was also obtained in quantitative yield (Scheme 7).<sup>25</sup> After heating to remove the water and acetic acid by-products, the XRPD pattern of the product was identical to that simulated from the single crystal data for the empty microporous phase Cu(INA)<sub>2</sub>. The connectivity of Cu(INA)<sub>2</sub> consists of 5-coordinate Cu(II) centres, linked by bridging carboxylate groups to form chains. These chains then cross-link into a 3-D framework through N–Cu coordination. Square channels are formed which, at their narrowest are *ca.* 3.8 Å, but are still able to accommodate and exchange molecules such as water, methanol and ethanol. The material shows size- and chemo selective inclusion. The available volume has been estimated at *ca.* 20%.<sup>28a</sup> Interestingly, it was found that grinding for only 1 minute was enough to initiate the formation of Cu(INA)<sub>2</sub>, after which the reaction was self-propagating (then taking 6 hours to go to completion). The fact that the impacting of the ball (sometimes thought to be important in causing transient local melting), is *not* essential to the propagation of this reaction is striking. The reaction could be self-sustaining because it releases acetic acid and water as by-products, which might aid local dissolution/melting and enable mass transfer, even though no bulk liquid phases were observed. SEM revealed that the product formed by the relatively soft ‘initiation’ method consisted of larger crystals (Fig. 2), and its XRPD pattern had more intense peaks at larger 2-theta.



**Fig. 2** Comparison of XRPD pattern of [Cu(INA)<sub>2</sub>] synthesised under solvent-free conditions and the XRPD pattern simulated from the single-crystal structure (above); SEM images of the product obtained by the ‘soft’ method (grinding for only 1 minute to initiate the reaction, lower left), then leaving for several hours), and the ‘hard’ method (grinding for 5 minutes, after which the reaction is virtually complete, lower right). Adapted with permission from ref. 26.



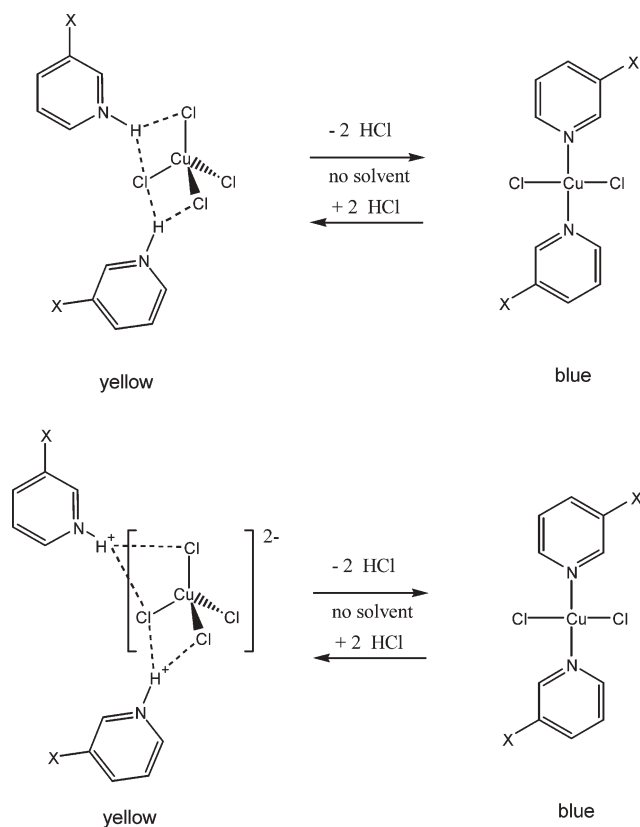
**Scheme 8** Formation of coordination complexes by heating hydrogen-bonded salts to eliminate HCl.

## Non-mechanochemical solvent-free synthesis

### From H-bonded precursors

Other workers have shown that coordination complexes can be obtained by simply heating hydrogen-bonded precursors. In particular, Orpen and co-workers investigated tetrachlorometallate-4-picolinium salts (metal = Pt or Pd) shown in Scheme 8, which are obtained by co-crystallisation of picolinium and halometallate ions.<sup>29</sup> Single-crystal X-ray analysis shows that these salts are organised in the crystal through bifurcated  $\text{H}\cdots\text{Cl}_2\text{M}$  hydrogen bonds. They were found to eliminate hydrogen chloride on heating to produce the corresponding picoline complexes  $\text{trans}[\text{MCl}_2(\text{NC}_5\text{H}_4\text{-4-CH}_3)_2]$  quantitatively. For the platinum complex, the mono-substituted complex  $[\text{HNC}_5\text{H}_4\text{-4-CH}_3][\text{PtCl}_3(\text{NC}_5\text{H}_4\text{-4-CH}_3)]$  was observed as an intermediate by XRPD.

Brammer and co-workers extended this idea using copper(II) complexes, specifically  $[\text{3-halopyridinium}][\text{CuCl}_4]$  (Scheme 9).<sup>30</sup> On standing after manual grinding, these salts, which have tetrahedral  $[\text{CuCl}_4]^{2-}$  ions and bifurcated  $\text{CuCl}_2\cdots\text{H-N}$  hydrogen bonds, were found to eliminate HCl, with concomitant coordination of the halopyridine ligand. The product complexes  $[\text{CuCl}_2(\text{3-halopyridine})_2]$  are square-planar, and the elimination causes a change in colour from yellow blue. Remarkably, the elimination and structural transformation was found to be fully reversible, so that



**Scheme 9** Reversible formation of coordination bonds by elimination of HCl from a hydrogen-bonded precursor and addition of HCl to the complex.

exposure to the vapour from concentrated HCl solution regenerated the H-bonded precursor.

Clearly, these observations have implications for solvent-free reactions between protic ligands and metallate salts under mechanochemical conditions, *i.e.* H-bonded co-crystals might form as intermediates prior to ligation.

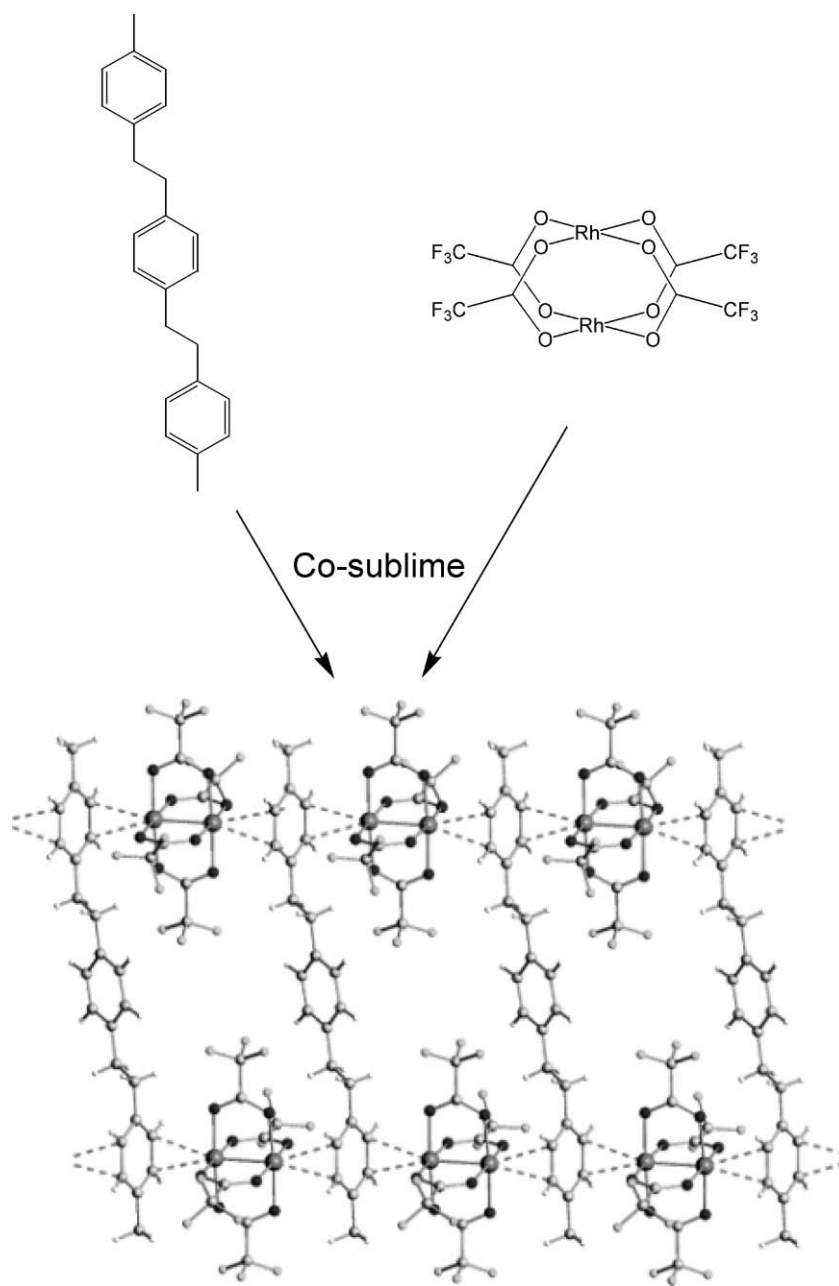
### Gas-solid reactions

An example of a gas reacting at the metal centre of a solid metal complex was reported by van Koten, Albrecht and co-workers, who showed that sulfur dioxide gas reacted quantitatively with the crystalline platinum pincer complex  $[\text{PtCl}\{\text{OH-4-C}_6\text{H}_2\text{-2,6-(CH}_2\text{NMe}_2)_2\}]$  to give the corresponding Pt-SO<sub>2</sub> adduct.<sup>31</sup> Remarkably, this occurred with retention of crystallinity. Doubtless there are many other isolated examples of gas-solid reactions at metal centres, *e.g.* reactions with molecular oxygen *etc.*, even if these have not been collected into a single topic and systematically considered and investigated in terms of practical synthesis. Given the high efficiency of gas-solid reactions in organic synthesis<sup>5</sup> and at the organic peripheries of metal complexes<sup>32</sup> it seems likely that many other solid complexes will react at their metal centres with other gases such as H<sub>2</sub>, CO, HX *etc.*

### Co-sublimation

Other workers have recently developed solvent-free synthesis of coordination complexes by exploiting the volatility of





**Scheme 10** Solvent-free formation of a crystalline organometallic coordination polymer by co-sublimation. Reproduced with permission from ref. 34.

certain metal complexes and ligands.<sup>33,34</sup> Dirhodium tetra(trifluoroacetate),  $[\text{Rh}_2(\text{CF}_3\text{CO}_2)_4]$ , is a strong Lewis acid which can be readily sublimed together with a variety of arenes to form crystalline coordination polymers. The arenes bond in  $\eta^2$  fashion. The potential complications of solvation were thus avoided, and the structures obtained correlated well with those predicted by DFT calculations.<sup>33</sup> Another attractive aspect of this method is that it leads directly to large single crystals which facilitates structural characterisation. A number of discrete complexes, as well as polymeric chains and sheets were prepared using cyclophanes as bridging ligands and a ladder structure was obtained with 1,4-bis(*p*-tolylethyl)benzene as shown Scheme 10.<sup>34</sup>

This approach is related to metal atom vapour synthesis, in which pure metals are evaporated onto organic ligands to form low-valent complexes.<sup>35</sup>

## Outlook

There are compelling reasons why the solvent-free synthesis of coordination complexes is likely to become increasingly investigated in the near future. Firstly, there is the escalating need to develop greener preparative methods, bearing in mind the diverse applications of metal complexes,<sup>36</sup> and that ball-milling is a technique which can be scaled up and even applied on a commercial level.<sup>11,37</sup> Secondly, to obtain a full

mechanistic understanding of chemistry under these conditions provides worthwhile academic challenges. Thirdly, important developments are occurring in the characterisation of complex structures by X-ray diffraction of powders. For example, it has been possible to use XRPD data to determine directly the crystal structures of coordination polymers<sup>38</sup> as well as products of grinding reactions.<sup>39</sup> Fourthly, as can be seen from the examples given in this article, a wide range of complexes can be accessed using solvent-free techniques, featuring diverse structures, metal ions, ligand types and dimensionalities. One, so far, even exhibits open porosity. Therefore the approach seems to be remarkably broadly applicable. Lastly, and possibly most importantly when it comes to adopting these methods in the laboratory, it is sometimes actually *easier* and *faster* to make metal complexes by avoiding the use of solvents.

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