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Mechanochemical tools in the synthesis of organometallic compounds

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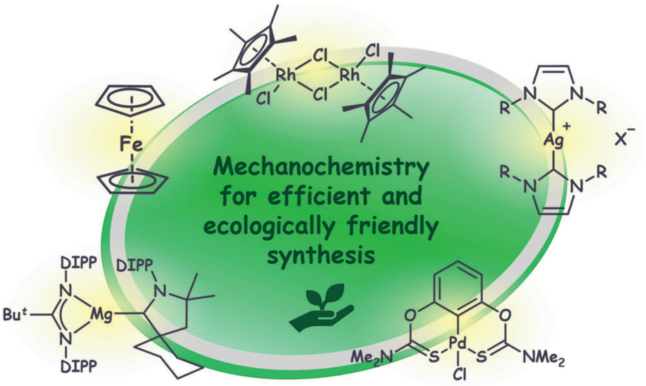
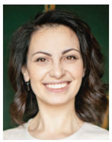
In response to rising environmental concerns, chemistry is experiencing a considerable change in both concepts and practices to adopt more efficient and sustainable technologies. One of the alternative technologies that offer many advantages over the conventional solution-based techniques is mechanochemistry which utilizes mechanical energy to induce chemical reactions. Despite the fact that mechanochemistry has reached high significance in the creation of advanced materials, such as alloys, ceramics, electrode materials, and nanocomposites, in the field of small molecule synthesis its potential remains largely untapped. This review highlights the opportunities and prospects of different mechanochemical tools in the synthesis of organometallic compounds, including transition metal complexes with N-heterocyclic carbene, arene, and cyclopentadienyl ligands, monometallacyclic and pincer derivatives, as well as main group metal compounds (*e.g.*, allyl complexes and the Grignard reagents). Many important organometallic transformations such as C–H bond metalation, transmetalation, and oxidative addition can be successfully implemented under mechanochemical conditions in a highly productive and energy-saving manner. Furthermore, the postmodification of metal-containing species upon grinding or milling is shown to be a powerful route to both new discrete metal complexes and different supramolecular architectures (metal-containing organic cages, macrocylces, networks).



Keywords: mechanochemistry, organometallic compounds, solid-state synthesis, solvent-free reactions, ball milling, grinding, green chemistry.

1. Introduction

Mechanochemistry has been extensively exploited by mankind from the early stages of the development. Its unintentional application gradually extended from the preparation of food to the processing of different materials, and, after the first systematic studies at the end of the 19th century, mechanochemistry has emerged as a separate subdiscipline.[1] Curiously, in 2019 IUPAC recognized it as one of the top ten innovative chemical technologies that can make a major contribution to the world's sustainable development.[2] As the saying goes, everything new is



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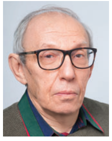


Vladimir A. Kozlov studied chemistry at Moscow State University and received his PhD (1977) and Dr. Sci. (1992) degrees from Chemical Plant Protection Institute. In 2003 he joined the Group of Organothiophosphorus Compounds at INEOS RAS (now the Laboratory of Organophosphorus Compounds) where he is still working today as a leading researcher. For a long academic career, his research has been focused on different aspects of organophosphorus chemistry. The current interests are mainly associated with transition metal chemistry, ligand design, solvent-free reactions, and medicinal chemistry.

well forgotten old. However, there is no discrepancy. The widespread integration of mechanochemical tools is an imminent advance called to address the growing environmental concerns and provide new, safer, more efficient and low-cost chemical technologies. While mechanical alloying and high-energy mechanochemical processing of metals and composites are the well-established techniques, the synthesis of small molecules under the action of mechanical energy (*e.g.*, upon grinding or milling) is still a relatively unexplored research area.

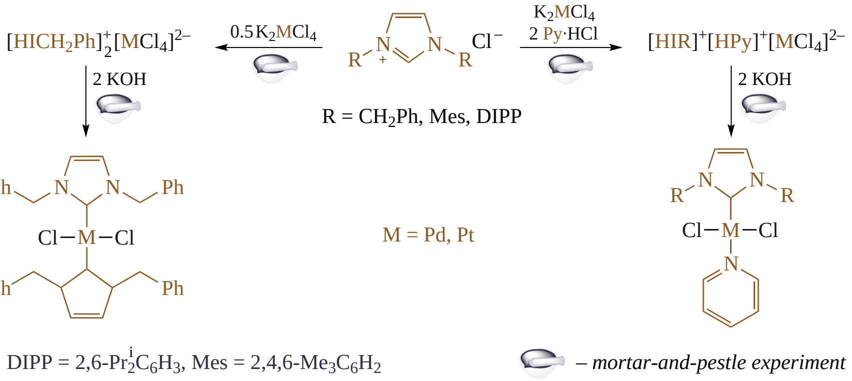
Organometallic compounds have remained in the shadows of their organic and inorganic counterparts for a long time until several landmark works demonstrated the feasibility of their successful synthesis under mechanochemical conditions (consider, for example, the ball-milling synthesis of ferrocene[3]). In recent years, a powerful impetus has been provided by the rapid development of solvent-free organic transformations catalyzed or mediated by transition metal complexes.[4–7] An obvious benefit of mechanochemically driven processes is the complete absence or significantly reduced amount of bulk solvents at least at the synthesis step, which is fully consistent with the modern concept of green chemistry. Furthermore, for a great variety of chemical reactions, the mechanochemical approaches offer such important advantages as considerable yield and rate enhancement. In combination with simplified product recovery (isolation and purification), this improves the overall process efficiency and lowers the energy consumption. The higher selectivity of reactions under grinding conditions makes them especially attractive from the viewpoint of atom economy. In the case of organometallic species, mechanochemistry can additionally be useful in addressing solubility and stability issues often observed for many types of metal complexes in solution. And last but not least, the mechanical activation can lead to new reactivity patterns unavailable under the conventional solution-state conditions.

A few early reviews cover the major achievements of solid-phase organometallic chemistry.[8,9] The primary generalizations in the field of mechanochemical synthesis of organometallic compounds, including those relating to the important technical aspects (equipment) and main outcomes and challenges, were made by Rightmire and Hanusa in 2016.[10] Bantreil, Métro, Lamaty, and colleagues[11] presented an overview of the most prominent reports on mechanosynthesis of both organometallic and metal-organic derivatives of different metals (performed mostly through mortar-and-pestle experiments) in the broader context of enabling technologies (photochemistry, microwave and ultrasonic activation, as well as continuous flow chemistry). Fiss *et al.*[12] highlighted some important examples of mechanochemical ion metathesis and electron reduction reactions that lead to organometallic compounds. A recent chapter by Leon and Garcia[13] shows how the mechanochemical methods have expanded to the chemistry of metal complexes, with a particular emphasis on catalytic applications. However, neither of these reviews provides a comprehensive analysis of the possibilities of mechanochemistry with respect to particular classes of organometallic compounds. To fill this gap, the following sections summarize the advances in the field of mechanochemical synthesis and (post)modification of different types of main group and transition metal complexes. Both the achieved breakthroughs and untapped potential of grinding and milling techniques are highlighted to demonstrate great prospects of mechanochemistry in the synthesis of organometallic compounds.

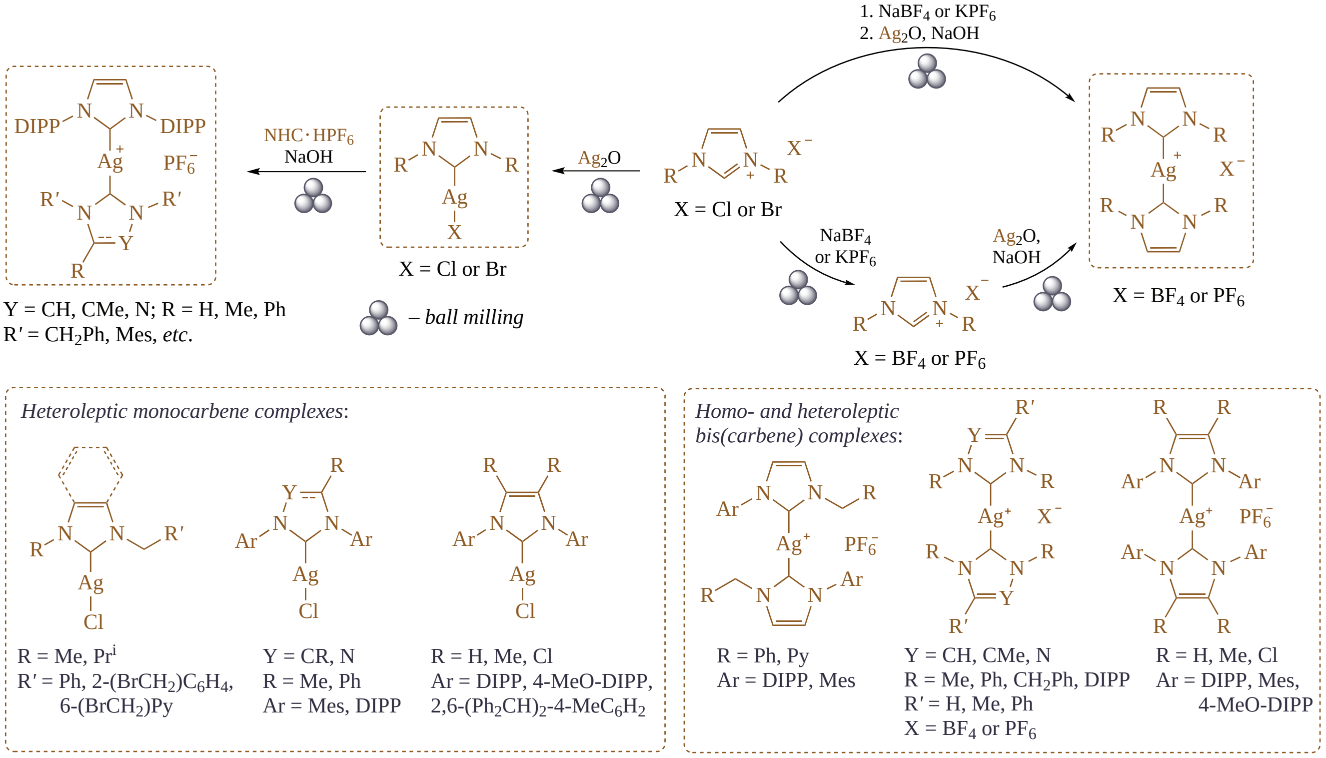
2. Transition metal–N-heterocyclic carbene complexes

To date, the enormous potential of mechanochemistry for the synthesis of discrete organometallic compounds has been realized to the fullest extent for transition metal complexes of N-heterocyclic carbenes (NHCs). Research into this field was galvanized by the pioneering work of Nolan *et al.*[14] who demonstrated the possibility of substituting a chloride ligand in [Au(IPr)Cl] [IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] for different phenolates, carboxylates, and other residues simply by grinding with organic substrates in the presence of KOH for several minutes. The mechanochemical methodology saved hours of reaction time which are typically required for these transformations in solution. Later Lusi, Orpen, and colleagues presented the mechanochemical synthesis of heteroleptic carbene–pyridine[15] and homoleptic bis(carbene)[16] Pd^{II} and Pt^{II} complexes. A two-step strategy utilized simple organic and inorganic salt predecessors and involved the intermediate formation of metallate species. Owing to the charge-assisted hydrogen bonding between anions and cations in these salts, the following dehydrochlorination was readily accomplished upon grinding with KOH (Scheme 1). It is noteworthy that solid-state synthesis of the bis(carbene) derivatives proceeded under topochemical conditions and afforded isomerically and polymorphically pure products, while the conventional solution-based protocols often produce mixed outcome. Note that the PEPPSI-type (pyridine-enhanced precatalyst preparation stabilization and initiation) complexes comprise a commercially available class of organometallic compounds that find extensive use in catalysis (for some recent examples, see refs. 17–21).

Bantreil, Métro, Lamaty, and coworkers laid the foundation for mechanochemical realization of one of the most popular synthetic approaches to metal–NHC complexes, namely, a built-in base route (Scheme 2). In their seminal report, the first mechanosynthesis of *N*,*N*′-dialkyl-substituted NHC precursors and their corresponding Ag^{I} complexes was presented.[22] The silver complexes were obtained either from preformed imidazolium salts or directly from imidazole and alkyl halides in a highly efficient one-pot two-step procedure. Furthermore, the possibility of their transmetalation to [Au(NHC)Cl] species was



Scheme 1 Mechanosynthesis of homo- and heteroleptic Pd^{II}, Pt^{II} carbene complexes through intermediate formation of metallate species.

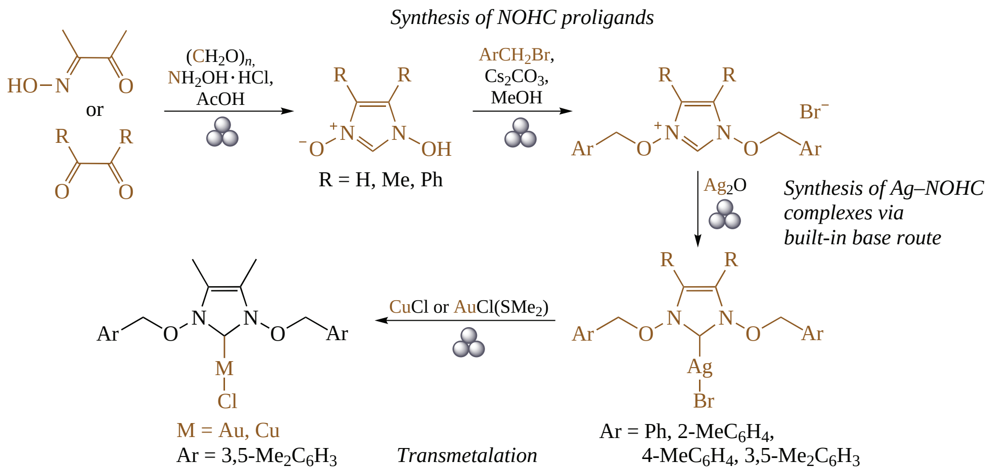


Scheme 2 Preparation of various homo- and heteroleptic Ag–NHC complexes in a ball mill (built-in base route).

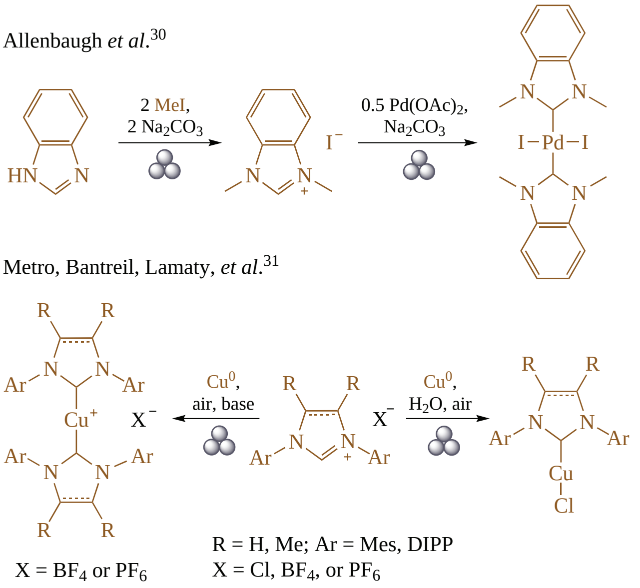
also demonstrated (*vide infra*). More importantly, the ball-milling synthesis of the gold(I) derivatives was confined to a one-pot three-step procedure that includes the alkylation of imidazole, metalation with Ag^I, and transmetalation with Au^I and avoids the use of solvents for isolating the intermediates.

This method was successfully extended to a wide range of other neutral monocarbene[23–25] as well as cationic homo- and heteroleptic bis(carbene) Ag^I complexes[23,26] (see Scheme 2). The scope of NHC proligands included *N*,*N′*-dialkyl-, diaryl-, and alkyl/aryl-substituted imidazolium, imidazolinium and triazolium salts, including highly encumbered and poorly soluble compounds application of which under conventional solution conditions is problematic. In some cases, the addition of an external base (*e.g.*, NaOH) was required to ensure higher yields of the target products. The preceding anion metathesis of Cl to BF_4 or PF_6 upon grinding in a ball mill allowed for additional time and reagent savings.[23,26] More recently, the synthesis of silver(I) *N*-oxy-heterocyclic carbene (NOHC) complexes was accomplished under analogous solvent-free conditions (Scheme 3).[27] It is important to note that since milling jars are not transparent, there is no need to provide additional light protection for the production of light-sensitive silver complexes. Some of the resulting Ag^I–NHC complexes displayed remarkable cytotoxic properties on HCT116 human colon cancer cell line, being active even in the nanomolar range.[23,25,27] The compounds bearing additional thioglycoside residues in lateral aromatic substituents demonstrated both anticancer potential and high catalytic activity in the oxidation of benzaldehyde in aqueous media.[25]

An important achievement in the field of mechanochemistry of metal–NHC complexes is the possibility of mechanochemical synthesis of the starting imidazolium salts. In the simplest case, this is the above-mentioned alkylation of imidazoles with alkyl halides.[22] Furthermore, the mechanochemical approach appeared to be particularly efficient for the selective methylation of tripodal tris[4-(1-aryl-1,2,3-triazol-5-yl)methyl]amines without affecting the central amine unit.[28] More significantly, the condensation of various amines with glyoxal or butane-2,3-dione followed by the cyclization of *in situ* generated diazabutadienes upon addition of an appropriate carbon source



Scheme 3 Synthesis, metalation, and transmetalation of NOHC derivatives upon grinding.



Scheme 4 Pd^{II} and Cu^{II}–NHC complexes obtained by the built-in base route in a mill.

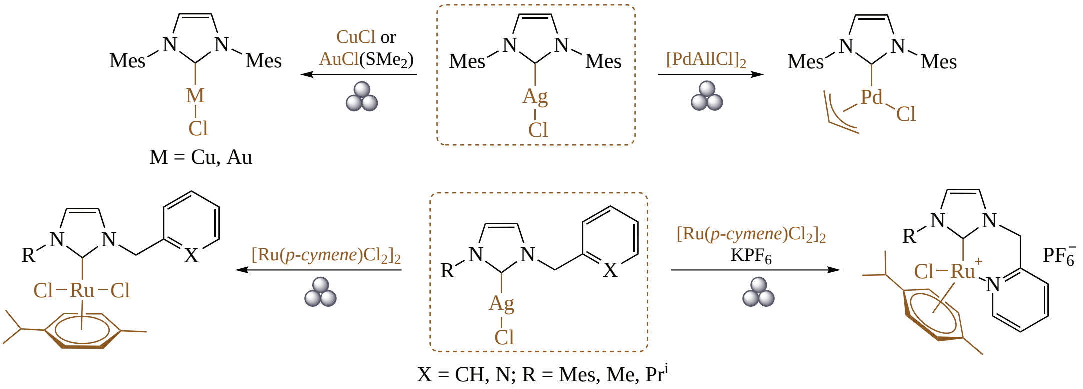
and activating agent was smoothly accomplished in a ball mill.[29] It is noteworthy that the *E*-factor and ecoscale score for this one-pot two-step milling procedure were considerably better than those for the solvent-based methodology. It also allowed for obviating the problem of solvent incompatibility between the two synthetic stages. A slightly modified strategy was used to produce NOHC proligands, starting from diketones or α-(hydroxyimino)ketone, hydroxylamine hydrochloride, paraformaldehyde, and AcOH and isolating the intermediate *N*-oxides for the following alkylation with a variety of benzyl bromides (see Scheme 3).[27] These examples in combination with the above-mentioned metalation reactions show the possibility of complete mechanochemical synthesis of metal–NHC complexes.

The built-in base route was also applied to the mechanochemical synthesis of palladium(II)[30] and copper(II)[31] complexes (Scheme 4). In the latter case, both heteroleptic monocarbene and homoleptic bis(carbene) complexes were readily obtained by reacting *N,N'*-diarylimidazolium salts, metallic copper, and atmospheric O_2 in the presence of a small amount of water used as a liquid assistant [the so-called liquid-assisted grinding (LAG) conditions] or a base additive (NaOH or KHMDS). Although the starting materials featured high physical state heterogeneity (gas, solid, and soft), the reaction mixtures were homogeneous at the macroscopic level. The process rate was much higher than that under traditional solvent-based conditions. Allenbaugh *et al.*[30] accomplished the mechanosynthesis of both a benzimidazolium salt and ensuing Pd^{II} complex and presented the results of the first kinetic analysis of these transformations, which revealed the applicability of different models for these systems.

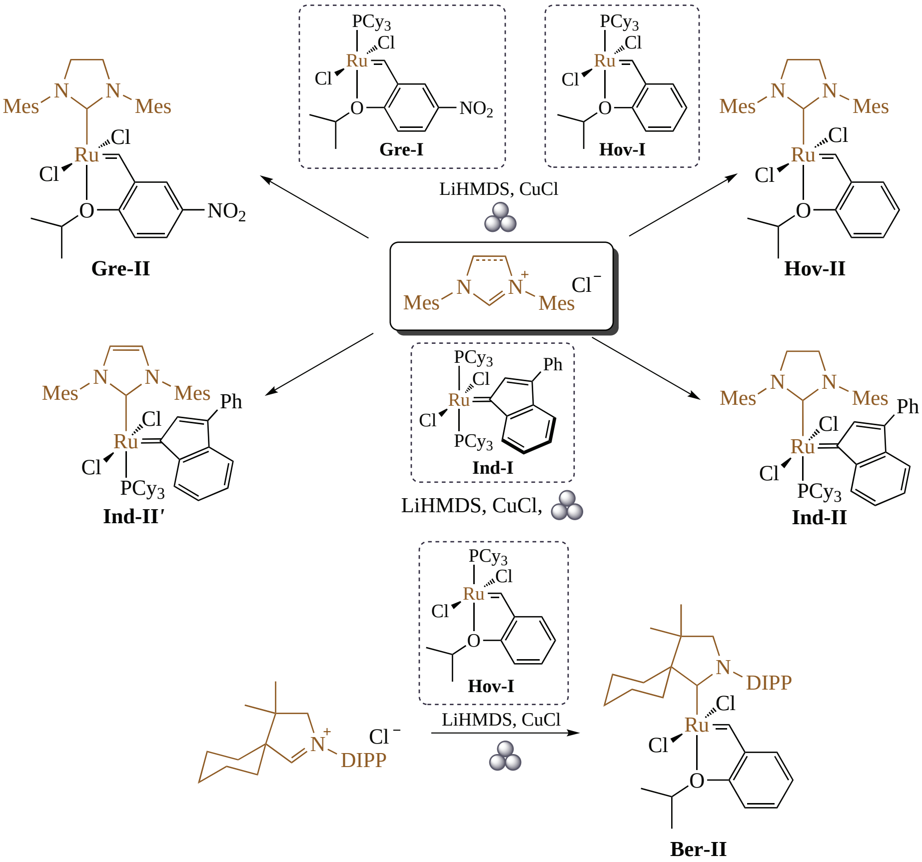
A powerful synthetic route to transition metal–NHC complexes is transmetalation of silver(I) precursors, which has also been successfully implemented under milling conditions. Besides the above-mentioned facile one-pot synthesis of Au^{I} complexes[22] and analogous reactions with other NHC derivatives including the oxy-substituted counterparts that opened the way to new Au^{I}, Cu^{I}, and Pd^{II} complexes (see, for example, Schemes 3 and 5),[24,27] mechanochemically driven transmetalation was used to obtain Noels-type Ru^{II}–NHC complexes in high yields over short reaction times (Scheme 5).[32] The latter were tested in the ring-opening metathesis polymerization of norbornene and one of the resulting complexes was found to be competitive with *in situ* generated Noels catalyst.

Highly demanded ruthenium olefin metathesis catalysts can also be obtained in the solid state through a free carbene route. Thus, Grela *et al.*[33] demonstrated that treatment of 1,3-dimesitylimidazolinium chloride with LiHMDS upon grinding in a ball mill results in free SIMes carbene which in the presence of the first generation Hoveyda catalyst and CuCl used as a phosphine scavenger smoothly affords Hoveyda–Grubbs catalyst **Hov-II** (Scheme 6). Delightfully, the reaction was readily repeated in 0.5 g scale. The developed approach was further applied to the synthesis of other advanced second-generation catalysts, including the ex-Evonik Catmetium® RF catalyst **Ind-II′** and its saturated analog **Ind-II**, Bertrand–Grubbs complex **Ber-II** bearing a cyclic (alkyl)(amino)carbene ligand, and even challenging nitro-activated catalyst **Gre-II** which cannot be obtained in solution due to low stability of the first-generation precursor under strongly basic conditions required for the generation of a free carbene (see Scheme 6). Although the mechanochemical synthesis must be carried out in a dry setup under an inert atmosphere, it partially alleviates the operational burden of the free carbene route under solution conditions and is fairly advantageous in terms of green chemistry metrics.

In contrast to the above methodology that utilizes strong bases, a weak base approach, recently disclosed as a remarkable advance in the synthetic access to metal–NHC complexes, involves the treatment of metallate species with inexpensive weak bases (*e.g.*, K_2CO_3) and can be implemented under aerobic conditions. The metallate intermediates result from the interaction of metal precursors with azolium salts. In 2020, Udvardy, Czégéni, and colleagues[34] realized this methodology in a ball mill to obtain binuclear Rh^{I}–NHC complexes (Scheme 7). Concomitantly, Pisanò and Cazin[35] reported the mechanosynthesis of Cu^{I}–NHC complexes mediated by the formation of cuprates and demonstrated its scalability (see Scheme 7). Shortly afterwards they confirmed the applicability of the weak base route under solvent-free conditions to a number of other



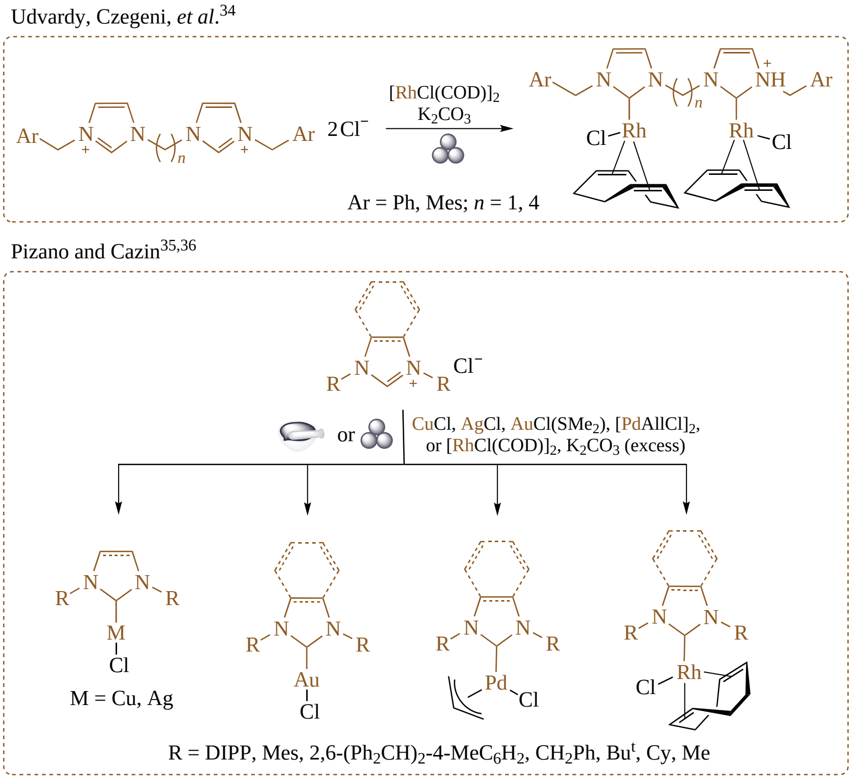
Scheme 5 Synthesis of metal–NHC complexes *via* transmetalation of Ag^{I} precursors under milling conditions.



Scheme 6 Mechanosynthesis of popular Ru metathesis catalysts *via* the free carbene route.

transition metals, including Ag, Au, and Pd (see Scheme 7).[36] Zhao, Liu, and coauthors[37] extended this methodology to Cu^I complexes bearing cyclic (alkyl)(amino)carbene ligands, some of which exhibited high catalytic performance in CO_2 hydrogenation to formate. Note that the mechanochemical version of the weak base approach significantly reduces the reaction time and environmental footprint compared to the conventional solution-based methodology and provides even sterically hindered derivatives.

In addition to a considerable progress in the mechanochemical synthesis of transition metal–NHC complexes, recent years have been marked with emerging interest in their modification under



Scheme 7 Transition metal–NHC complexes obtained mechanochemically by the weak base approach.

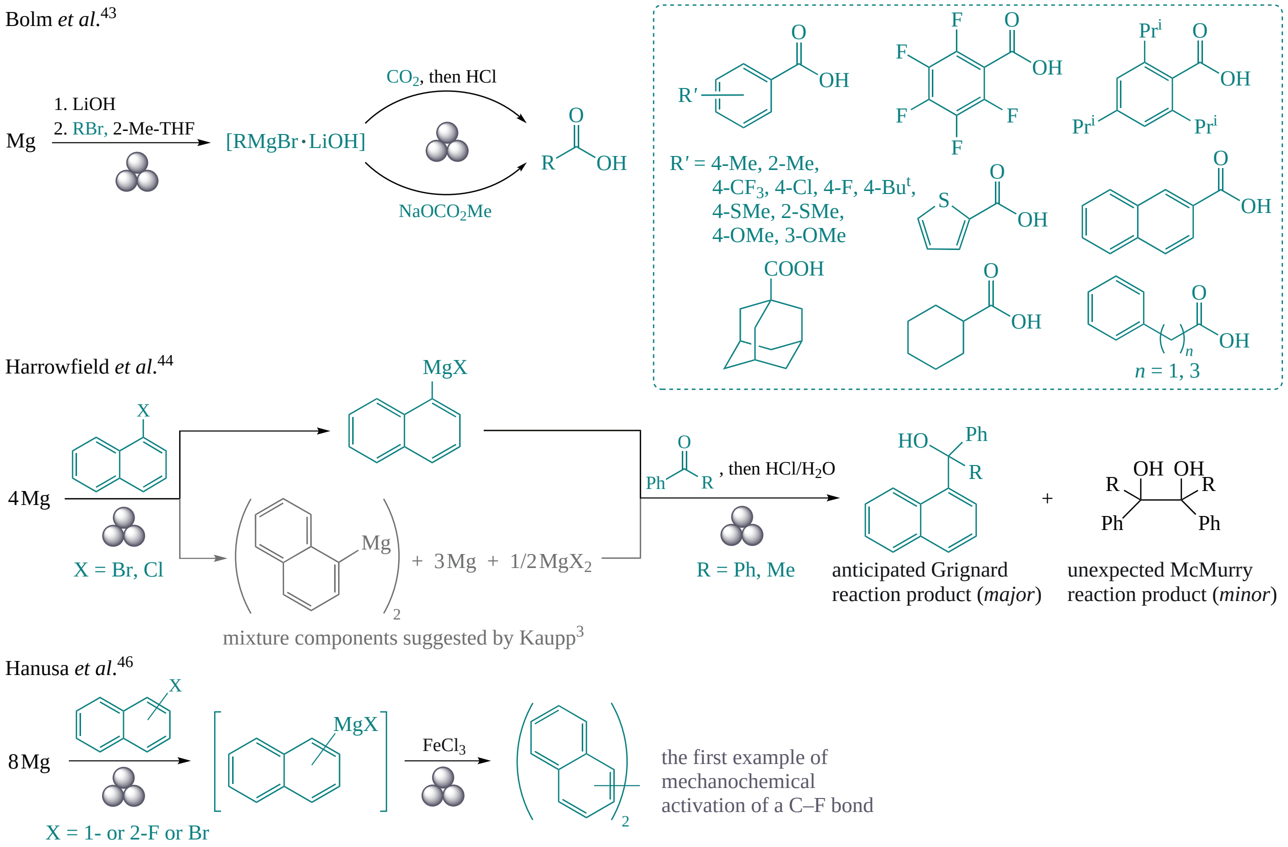
solvent-free conditions. Chernyshev *et al.*[38] reported the first example of mechanochemical oxidation of Pt^{II} PEPPSI-type complexes upon grinding with $PhICl_2$ or $PyHBr_3$ in a mortar, which smoothly yielded the corresponding Pt^{IV} derivatives. Nolan, Cazin, and coauthors[39] presented an expedient method for the synthesis of gold and copper–NHC diketonates, starting from the corresponding chloride precursors. Analogously, the reactions of dibromide Au^{I} precursors having bridging dicarbene ligands with phenylacetylene and KOH upon grinding smoothly afforded the corresponding alkynyl complexes featuring luminescence properties.[40] The alkylidene and phosphine ligand exchange processes in Ru metathesis catalysts (for example, some of those depicted in Scheme 6) under mechanochemical activation provided easy access to other valuable second- and third-generation catalysts.[33] Furthermore, the possibility of stepwise synthesis and following application in C–S cross-coupling of nickel and copper complexes of pyridine-functionalized N-heterocyclic carbenes has been recently highlighted.[41,42] Undoubtedly, these encouraging results will facilitate further integration of mechanochemical tools into the chemistry of transition metal–NHC complexes.

3. Main group metal organometallic compounds

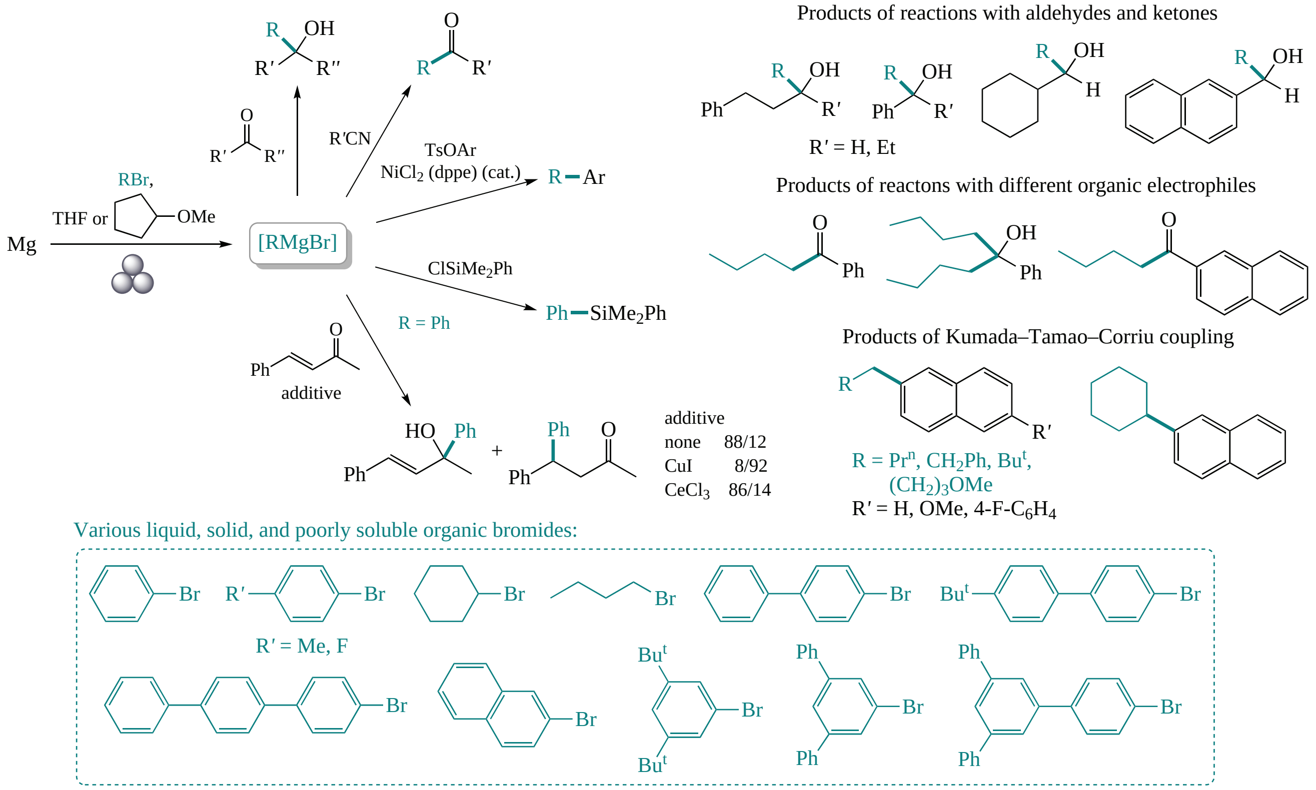
The utility of mechanochemistry is not restricted to the realm of transition metal complexes; it can also serve as a powerful tool for the synthesis of main group organometallic compounds. A very recent report from the group of C. Bolm[43] demonstrates the possibility of one-pot synthesis of the Grignard reagents from a broad range of organic bromides and their conversion to the corresponding carboxylic acids upon treatment with gaseous carbon dioxide or sodium methyl carbonate (Scheme 8). The process efficiency was maximized by the preliminary activation of Mg with LiOH upon grinding in a planetary ball mill and the addition of 2-Me-THF at the main synthetic step to promote the formation of the Grignard reagents under LAG conditions. Although sodium methyl carbonate demonstrated lower performance than CO_2, the use of this solid reagent as an $HCOO^+$ synthon can be justified not only by simplicity in handling (no need to use an inert atmosphere and special equipment) and reduction of the number of steps but also by significant acceleration of the process.

Note that an early attempt to extend the mechanochemical tools to organomagnesium chemistry was mainly focused on obtaining the Grignard reagents in a storable form.[44] Despite certain achievements, including the stability of the resulting samples in an inert atmosphere for at least 10 weeks, the presence of an excess of highly active metallic magnesium, which was required to provide an isolable powder after milling, negatively affected the reactivity of these solid analogs of the Grignard reagents. For example, their interaction with different ketones was complicated by the concomitant McMurry reaction (see Scheme 8). Later Kaupp[45] assumed that diarylmagnesium species were operative in these systems rather than RMgX (see Scheme 8). However, the work by Harrowfield *et al.*[44] did not remain unclaimed. Recently, Speight and Hanusa[46] used a similar approach to show a principal possibility of the mechanochemical activation of strong C–F bonds, which is almost impossible through the conventional solution-based protocols (see Scheme 8).

Kubota, Ito, and coauthors[47] developed a general and robust approach to the Grignard reagents in a paste form and demonstrated their successful application to a number of one-pot organic transformations under mechanochemical conditions (Scheme 9). Unlike the methodology suggested by Bolm *et al.*,[43] small amounts of liquid ethers were used to promote both the formation of organomagnesium nucleophiles and their addition to various electrophiles. The latter included aldehydes, ketones, carbon dioxide, amides, esters, nitriles, and conjugated enones, which afforded C–C bond coupling products (see Scheme 9). The reaction with chloro(dimethyl)phenylsilane in the presence



Scheme 8 Synthesis and conversion of the Grignard reagents upon ball milling.



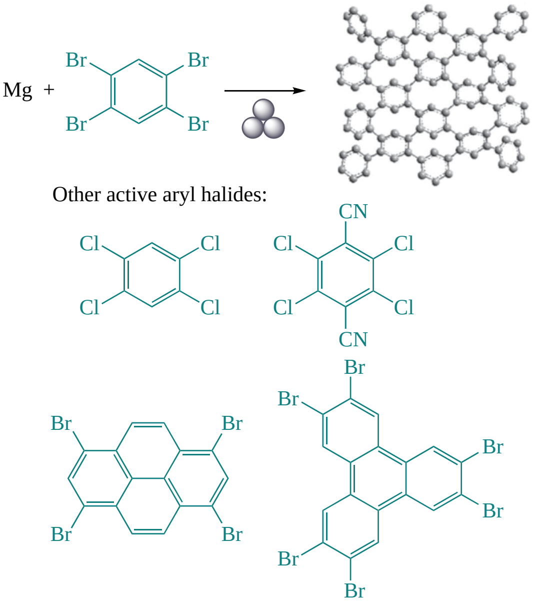
Scheme 9 Generation of the Grignard reagents in a paste form and their one-pot organic transformations under mechanochemical conditions.

of a catalytic amount of copper iodide led to the formation of a C–Si bond. Using a range of aryl tosylates, the Kumada–Tamao–Corriu cross-coupling was realized for the first time under mechanochemical conditions. In turn, a wide range of organic halides, including those poorly soluble in common organic solvents and therefore incompatible with the conventional solution-based techniques, readily underwent insertion of Mg into the C–X (X = Cl, Br, I) bond upon mechanical agitation in a ball mill. The generation of the magnesium-based carbon nucleophiles was confirmed by near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. An important advance of this comprehensive study is that all the stages were performed without the use of dry organic solvents and an inert gas, although the authors caution that the time for manipulations with an open jar should be shortened to a minimum. Earlier Mack *et al.*[48] explained the lower sensitivity of mechanochemical reactions to ambient moisture and oxygen by their low levels in a closed vessel and reduced reactivity of gaseous components since they are continually displaced from the pathway of milling balls during the reaction course.

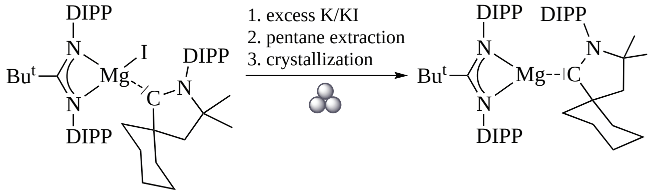
Mechanochemistry can also provide access to the calcium-based heavy Grignard reagents.[49] The reactions of aryl halides with calcium metal were found to proceed under mild conditions upon ball milling in the presence of THF or tetrahydropyran as a liquid additive and did not require any preactivation procedure or the use of an inert gas atmosphere. Furthermore, the *in situ* generated organocalcium nucleophiles readily underwent nucleophilic substitution with a range of alkyl halides upon mechanical agitation to form the cross-electrophile coupling products. These findings open up new horizons for both mechanochemical methods in organometallic chemistry and organocalcium compounds in organic synthesis.

An interesting line of research is the reductive dehalogenation of toxic chlorinated organic compounds upon treatment with Mg in a ball mill (either with an additional hydrogen donor or not), which was suggested to proceed through the intermediate formation of the Grignard reagents.[50,51] This is highly efficient non-thermal and non-combustion method to destruct organic pollutants that does not afford toxic by-products. Dehalogenation of aryl halides in the presence of Mg by the Ullmann-type reductive homocoupling (Scheme 10), also involving the formation of the Grignard reagent intermediates, can serve as a powerful tool for aromatic ring knitting which results in conjugated porous networks that find application as catalysts as well as materials for gas separation and energy storage.[52]

Quite recently, Harder *et al.*[53,54] disclosed the potential of mechanochemistry for low-valent magnesium compounds. The reduction of a Mg^{II} complex featuring amidinate and cyclic (alkyl)(amino)carbene ligands with K/KI under ball-milling



Scheme 10 Dehalogenation of aryl halides by the mechanochemical Ullmann-type reductive coupling resulting in conjugated porous networks. The product structure is reproduced with permission from ref. 52. © 2021 Wiley-VCH GmbH.



Scheme 11 Mechanochemical preparation of a stable Mg^I radical.

conditions followed by extraction with pentane and crystallization afforded an unusual mononuclear Mg^I radical which is stable only in the solid state and cannot be obtained by the conventional solution-based technique due to rapid decomposition (Scheme 11).[53] Furthermore, a binuclear β-diketiminate Mg^{II} complex with a bridging $Ph_3C_6H_3$ dianion, readily accessible by the mechanochemical approach, gradually loses triphenylbenzene upon dissolution, providing a clean synthetic method for the low-valent Mg^I species.[54]

Of note is also a recent report on the highly robust and effective strategy for the C–H functionalization of pyrimidines, which is based on the mechanochemical Minisci reaction with a broad range of primary, secondary and tertiary alkyl bromides and even alkyl chlorides in the presence of Mg chips and TMEDA.[55] The process was readily accomplished in a ball mill without the use of an inert atmosphere. Although the results of mechanistic studies suggested the formation of alkyl radicals, discarding the *in situ* generation of the Grignard compounds, this example demonstrates the huge potential of metal-mediated mechanochemical reactions, which is yet to be fully disclosed.

Continuous efforts of Hanusa and coworkers[56–62] laid the foundation for mechanochemical synthesis of another class of main group organometallic compounds, namely, allyl complexes, which have been long overshadowed by transition metal counterparts but now are gaining increasing importance, particularly, in polymerization catalysis.[63] Grinding AlX_3 (X = I, Br) with K[1,3-$(SiMe_3)_2C_3H_3$] in a tube disperser or planetary ball mill afforded the first example of unsolvated tris(allyl) complex of aluminum.[56] The latter contains σ-bound allyl ligands in the solid state and displays the reactivity expected for allyl complexes. Depending on the milling duration and ratio of the reagents, an analogous reaction of the bulky allyl precursor with $SnCl_2$ led to either tris(allyl)stannate, which forms a coordination polymer in the solid phase, or tetraallyltin derivatives in chiral and meso forms, which result from disproportionation.[57] None of these products can be derived from the synthesis in solution. In turn, trimethylsilylated allyl complexes of arsenic, antimony, and bismuth can be obtained both by the conventional solution-based technique and by the mechanochemical approach; however, the latter provides stereoselectivity that is correlated with the asymmetric environment of group 15 trihalides in the solid state.[58] An attempt to accomplish the halide metathesis between K[1,3-$(SiMe_3)_2C_3H_3$] and $BeCl_2$ in a planetary ball mill afforded the kinetic product, namely, potassium tris(allyl)beryllate as the only isolable compound regardless of the ratio of the reagents in use.[59] Analogously, the reaction of CaI_2 with the same potassium precursor under milling conditions, which are often far from equilibrium, gave rise to the potassium calciate instead of a neutral adduct.[60] Interestingly, the originally produced complex with one or more σ-bound allyl ligands rearranges into the more thermodynamically stable form featuring only π-coordinated allyl units even in the solid state. The latter was found to serve as an efficient initiator for anionic polymerization of isoprene under mild conditions, where the lack of THF in the catalyst ensured by the solvent-free synthesis appeared to be crucial for its activity. The intra-alkali ligand exchange furnished mixed complex {KCs[1,3-$(SiMe_3)_2C_3H_3]_2$}, showing that otherwise unfavorable halide metathesis can proceed with mechanochemical assistance.[61] Finally, mechanochemistry opened the way to heterometallic complex {K_2Mg[1,3-$(SiMe_3)_2C_3H_3$]} whose unsolvated crystals from hexanes consist of 2D coordination polymers where each magnesium atom is surrounded by three allyl ligands, one being coordinated in a η^3-fashion.[62] This is an unprecedented coordination mode for an allyl ligand bound to Mg. The resulting complex demonstrated moderate activity in the polymerization of methyl methacrylate, comparable to that of the starting potassium allyl complex but markedly higher than that of the homometallic neutral bis(allyl) magnesium derivative. This renders further mechanochemical synthesis of the related -ate complexes as potential initiators for anionic polymerization very promising.

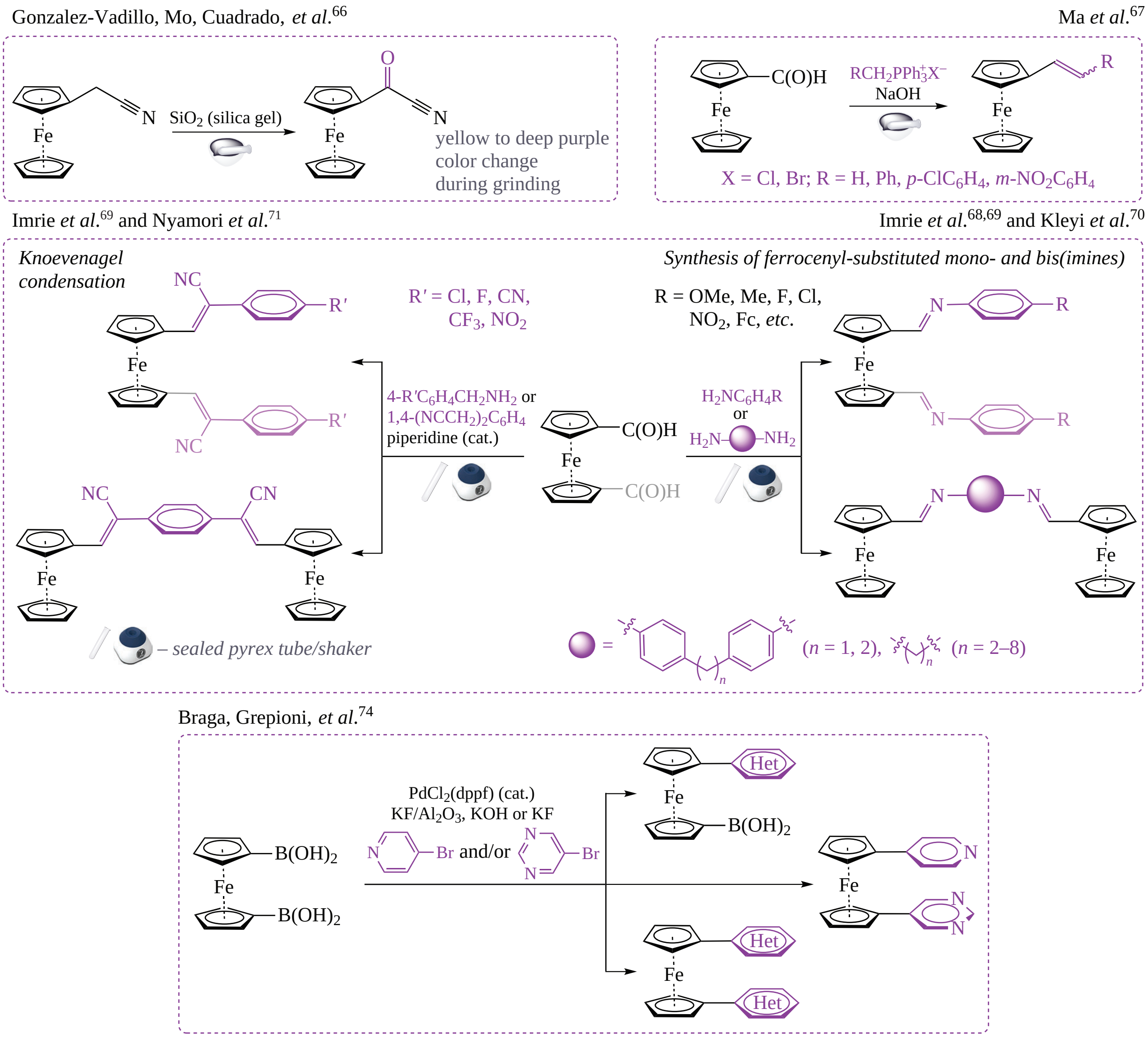
Ball milling enabled the synthesis of the first examples of beryllium indenyl complexes.[64] Thus, the reaction of potassium indenide with $BeBr_2$ afforded a slip-sandwich bis(indenyl) derivative that features mixed hapticity (η^1/η^5) of the ligands, while the application of the more sterically bulky precursor, K[1,3-$(Me_3Si)_2$Ind], afforded a monosubstitution product with the Be atom bound in an η^5-manner to the five-membered ring of the indenyl unit. It should be emphasized that in both cases the standard halide metathesis in solution led only to intractable mixtures. Peters and Blair[65] reported the mechanochemical synthesis of another representative of main group metal π-complexes, namely, bis(*n*-propyltetramethylcyclopentadienyl)-strontium which is a promising CVD precursor. Grinding the potassium cyclopentadienide with SrI_2 in a glass reactor designed for traditional solvent-based chemistry in the presence of diethyl ether smoothly afforded the target product. The mechanochemical synthesis was six times faster than the synthesis in solution. More importantly, it can be readily scaled up and provides high yields even on the pre-pilot plant scale (500 g). The potential of mechanochemistry in the synthesis of transition metal π-complexes, as will be shown below, is even more impressive.

4. Transition metal cyclopentadienyl, arene, and related π-complexes

One of the prominent examples of the synthesis of organometallic compounds through mechanochemically driven reactions is the production of ferrocene from $FeCl_2$ and CpM (M = Na, K, Tl) upon grinding in a ball mill, presented by Makhaev *et al*. as early as in 1999.[3] CpTl appeared to be an efficient alternative to the moisture- and air-sensitive alkali metal cyclopentadienides and ensured a high yield of ferrocene at the lower excess relative to the iron(II) salt. Furthermore, an analogous reaction of $NiCl_2$ smoothly furnished nickelocene.[3]

The robustness of a ferrocene core allows for its multidirectional modification under mechanochemical conditions, giving access to both simple ferrocenyl derivatives and complex supramolecular organometallic structures.[66–81] For example, manual grinding of caynomethylferrocene and silica gel provided a facile synthetic route to highly electron-poor 1-cyanocarbonylferrocene (Scheme 12).[66] The process efficiency was ensured by the presence of a redox-active organometallic moiety and the ability of silica gel to mediate one-electron oxidation of the Fe^{II} atom. The formation of 1-cyanocarbonylferrocene in the solid state is quite a striking result since the preparation of acyl cyanide derivatives in solution usually requires multistep procedures.

The Wittig reaction of ferrocenecarboxaldehyde with a range of phosphonium halides in the presence of NaOH, also accomplished by simple grinding of the reactants in a mortar, afforded various ferrocenylethene derivatives, preferentially in the form of *E*-isomers (see Scheme 12).[67]



Scheme 12 Mechanochemical modification of the ferrocene core to generate new ferrocenyl derivatives.

Imrie *et al.*[68,69] and Kleyi *et al.*[70] described the high-yield synthesis of ferrocenylimines and 1,1′-ferrocenyldiimines by shaking the ferrocenyl-substituted aldehyde precursors with mono- or bifunctional amines in a sealed tube (see Scheme 12). This solvent-free method was also successfully applied to the production of ferrocenylacrylonitriles and diacrylonitriles by the Knoevenagel condensation of ferrocene(di)carboxaldehyde with phenylacetonitrile or its substituted analogs bearing electron-withdrawing groups at the *para*-position of the phenyl ring in the presence of a catalytic amount of piperidine (see Scheme 12).[69,71] Of note are also the mechanochemically induced reactions of ferrocenylcarbinols with *N*,*N*′-thiocarbonyldiimidazole which furnish different types of products depending on the structure of the alcohol reactant.[72]

The condensation of ferrocenyl-substituted aldehydes with a range of di- and triamines in the solid state afforded ferrocene-containing organic cages (Figure 1).[73] This report is a rare example of the successful realization of dynamic covalent chemistry strategy towards cage compounds under mechanochemical conditions. It is noteworthy that most of the reactions were accomplished by grinding using simple glassware in 10–30 min, while ball-milling gave access to otherwise unavailable structures. In all cases, the mechanochemical approach significantly accelerated the synthetic procedure, thus providing a valuable alternative to the conventional solution-based protocol.

The Suzuki cross-coupling between ferrocene-1,1′-diboronic acid and 4-bromopyridine or 5-bromopyrimidine afforded disubstituted ferrocenyl derivatives (see Scheme 12).[74] Owing to the presence of N-heterocyclic units with coordination-active sites, the latter were used to construct different supramolecular

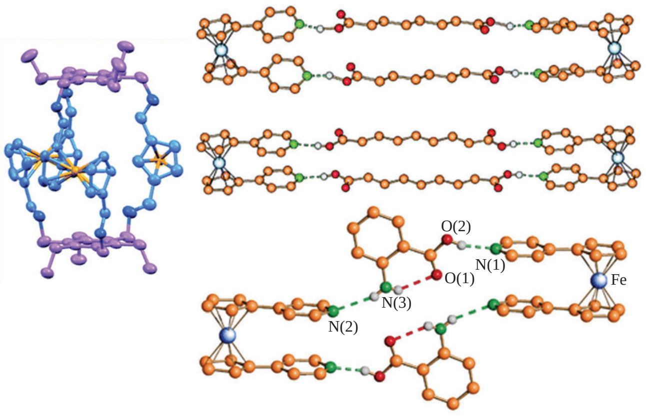
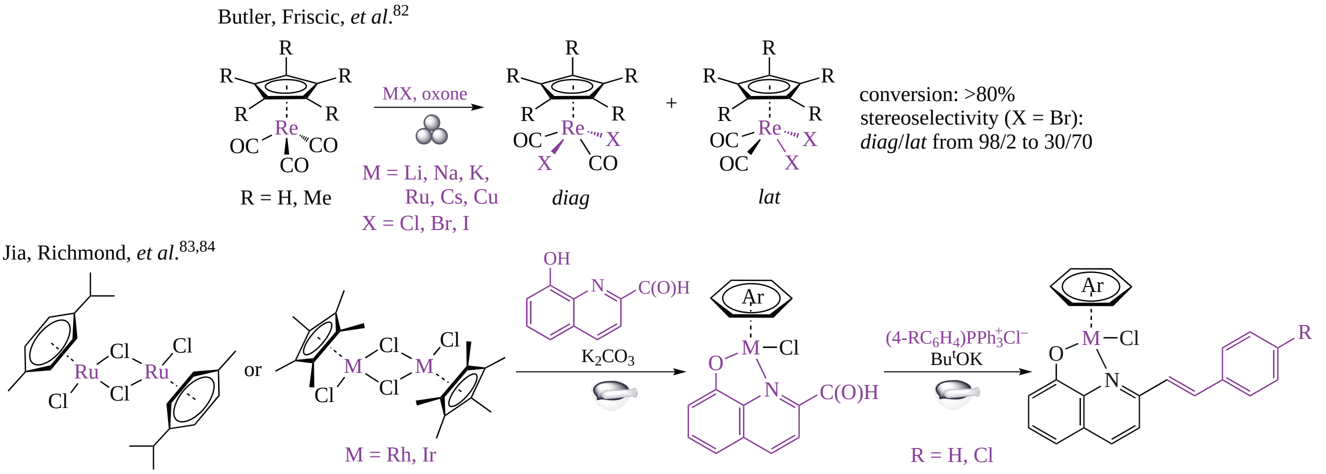


Figure 1 Ferrocene-containing organic cages and supramolecular structures obtained by mechanochemical methods. The left figure was reproduced from ref. 73. The upper right figure was used with permission of Royal Society of Chemistry, from ref. 75; permission conveyed through Copyright Clearance Center, Inc. The lower right figure was used with permission of Royal Society of Chemistry, from ref. 77; permission conveyed through Copyright Clearance Center, Inc.



Scheme 13 Postsynthetic modification of Re, Ru, Rh, and Ir half-sandwich complexes *via* mechanochemically induced oxidative addition or ligand exchange processes.

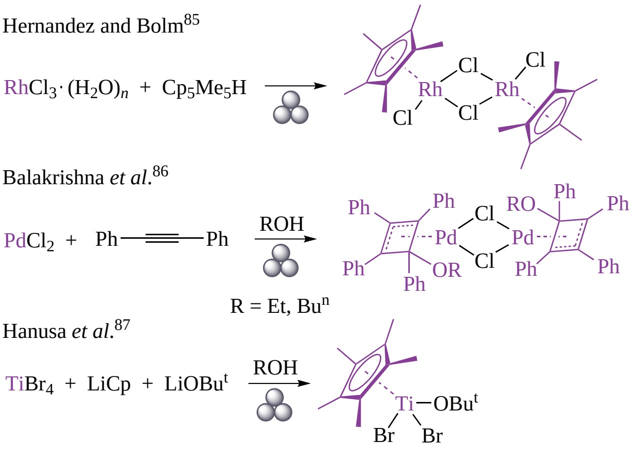
architectures, including hydrogen-bonded organic–organometallic macrocycles and networks (see Figure 1).[75–79] Analogously, the reactions of 1,1′-ferrocenedicarboxylic acid with a variety of solid bases afforded hybrid materials with either neutral or charge-assisted hydrogen bonding interactions.[76,79–81]

The past decade has witnessed nascent efforts to adopt mechanochemical methods for the synthesis and modification of half-sandwich complexes. Butler, Friščič, and colleagues[82] reported a simple and high-yielding procedure for the oxidative halogenation of cyclopentadienylrhenium(I) tricarbonyl and its pentamethyl-substituted analog to form $CpRe(CO)_2X_2$ (X = Cl, Br, I) complexes under milling conditions (Scheme 13). A combination of metal halides with oxone provided high conversion of the starting Re^I compounds. In the case of bromination, the variation of reaction conditions (mainly, the bromide source) enabled the stereoselective formation of either lateral or diagonal isomer. The mechanical load was shown to be crucial for the reaction efficiency. Another important finding is that the individual stereoisomers undergo system equilibration upon grinding. This proof-of-principle study appeared to be the first example of the use of mechanochemistry to conduct a fundamental organometallic transformation of oxidative addition.

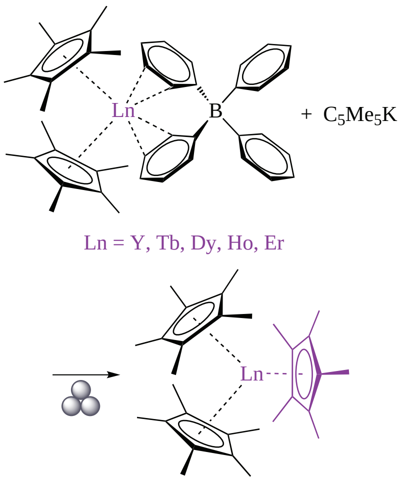
Jia, Lee, *et al.*[83,84] demonstrated the possibility of solvent-free ligand exchange using dimeric half-sandwich Ru, Rh, and Ir complexes and 8-hydroxyquinoline-2-carbaldehyde as the starting materials (see Scheme 13). The reactions were smoothly accomplished by grinding in a mortar for 20 min – much faster than in solution. Moreover, the presence of the anchor aldehyde function was further used to perform the mechanochemical Wittig reaction with benzyltriphenylphosphonium chloride or its *p*-Cl-substituted analog under LAG conditions (upon addition of several drops of CH_2Cl_2). Such a postsynthetic modification turned out to be a highly efficient and green alternative to the conventional solvent-based methodology. The resulting Ru complexes exhibited high catalytic activity in the transfer hydrogenation of ketones with a broad range of substrates, furnishing a library of synthetically valuable alcohols.[83] Their rhodium counterparts efficiently promoted the synthesis of amides from aliphatic, aromatic, or (hetero)aromatic aldehydes and hydroxylamine hydrochloride with good functional group tolerance.[84]

As for the Rh half-sandwich complex used as a precursor for the hydroxyquinoline-based derivatives,[83] its mechanosynthesis was readily achieved by grinding $RhCl_3$ hydrate with pentamethylcyclopentadiene in a planetary ball mill (Scheme 14).[85] Analogously, the reaction of $PdCl_2$ with diphenylacetylene upon milling in the presence of a small amount of EtOH or Bu^nOH afforded the dimeric half-sandwich complexes with the coordinated tetraphenylcyclobutenyl ligands, which resulted from the [2 + 2] cycloaddition of the alkyne (see Scheme 14).[86] Although the complex formation was accompanied by partial cyclotrimerization of diphenylacetylene, which was catalyzed by the palladium species, the yield of hexaphenylbenzene under optimized conditions did not exceed 10%. Studying the feasibility of preparation of Ti, Zr, and Hf mixed cyclopentadienyl/alkoxide complexes in the solid state, Hanusa *et al.*[87,88] developed, in particular, an elegant synthetic route to the titanium complexes based on the multicomponent reactions between $TiBr_4$, LiCp, and $LiOBu^t$ (see Scheme 14). The formation of mono- or bis(cyclopentadienyl) derivatives depended on the ratio of the reagents. Although the mechanochemical synthesis was associated with certain obstacles (*e.g.*, ring lability), further development of a reliable and ecologically friendly alternative to the conventional solution-based protocols is highly desirable, especially in view of considerable potential of this type of complexes in catalysis.

An important achievement of mechanochemistry in the field of cyclopentadienyl complexes is the synthesis of highly reactive air-sensitive lanthanide derivatives that cannot be obtained by the conventional solution-based techniques. For example, sterically crowded compounds $(C_5Me_5)_3Ln$ exhibit alkyl-complex reactivity or single-electron reducing ability towards aromatic solvents (benzene or toluene) and therefore cannot be isolated. At the same time, grinding cationic metallocenes, namely, $(C_5Me_5)M(\mu\text{-}Ph)_2BPh_2$ with C_5Me_5K in a disperser tube afforded tris(cyclopentadienyl) complexes of late lanthanides



Scheme 14 Half-sandwich complexes synthesized by ball milling.



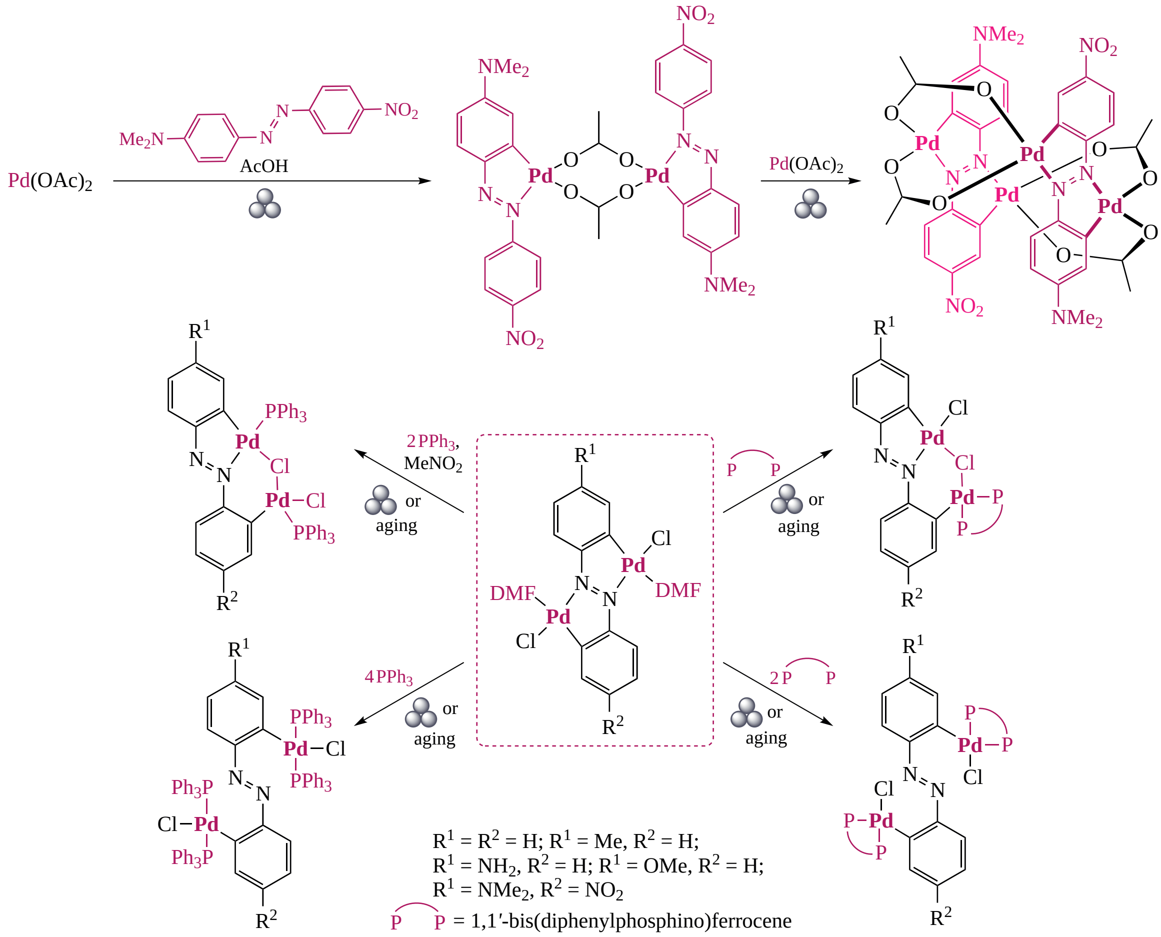
Scheme 15 Mechanosynthesis of Y and late lanthanide tris(cyclopentadienyl) complexes.

Tb, Dy, Ho, and Er as well as Y (Scheme 15).[89] Interestingly, an attempt to perform analogous metathesis reactions with the derivatives of the smallest lanthanide metals (Ln = Tm, Lu) led to the formation of tuckover hydride complexes, albeit in low yields, which result from the C–H bond activation of one of the methyl substituents in the Cp ligand.[90]

5. Monometallacycles and pincer-type complexes

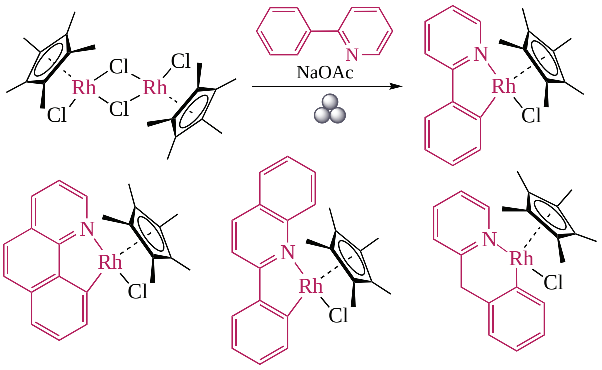
A huge contribution of metallacycles to the development of many sustainable chemical processes promotes continuous interest of researchers in the design and synthesis of new representatives of these valuable organometallic compounds. Direct cyclometalation, which involves the preliminary coordination of a metal center with a donor moiety followed by the C–H bond activation, is the most versatile and popular method that gives simple and straightforward access to different metallacyclic species. Unlike the above-described cases, the alternative technologies that use mechanical force to drive reactions have barely entered into this field; however, the results available today offer good prospects, as will be shown below.

Ćurić *et al.*[91] reported the first example of solvent-free cyclopalladation which was quantitatively accomplished in an unsymmetrically substituted azobenzene (Scheme 16). For the monocyclometalated product, the mechanochemical synthesis under LAG conditions appeared to be a rapid and regioselective alternative to the conventional solution-based technique. More importantly, the doubly cyclometalated product was not observed in solution and can be obtained only upon milling. The reaction course was monitored by *in situ* Raman spectroscopy which in combination with quantum-chemical calculations gave some valuable mechanistic insights. Later, the same research group presented a comprehensive study on the kinetics and mechanism of solvent-free cyclopalladation in the related azobenzene ligand under the action of different Pd^{II} precursors and in the presence of various liquid and ionic additives.[92] The comparative investigations by *in situ* Raman spectroscopy supplemented with the detailed analysis using *ex situ* IR and NMR spectroscopy as well as powder X-ray diffraction enabled the full elucidation of key stages in the stepwise double cyclometalation and identification of intermediates. Interestingly, the cyclopalladated azobenzene derivatives can be produced under conditions of vapor-induced solid-state C–H bond activation also referred to as accelerated aging.[93] This strategy afforded a selective chromogenic biothiol sensor based on the dicyclopalladated



$R^1 = R^2 = H$; $R^1 = Me$, $R^2 = H$;
$R^1 = NH_2$, $R^2 = H$; $R^1 = OMe$, $R^2 = H$;
$R^1 = NMe_2$, $R^2 = NO_2$
P P = 1,1′-bis(diphenylphosphino)ferrocene

Scheme 16 Synthesis and modification of azobenzene-based monopalladacycles under solvent-free conditions.



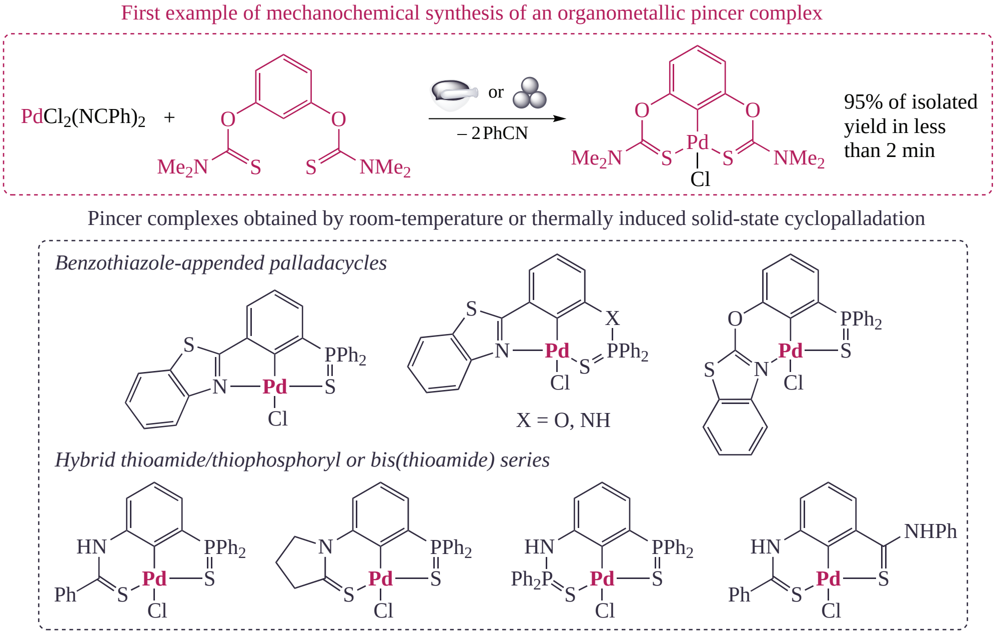
Scheme 17 First rhodium cyclometalated complex obtained upon ball milling and the examples of other mechanochemically produced five- and six-membered monorhodacycles.

derivative of methyl orange, which is active at physiologically relevant biothiol levels. Recently, the monopalladacyclic species have been found to play a key role during catalytic halogenation of substituted and unsubstituted azobenzenes.[94,95]

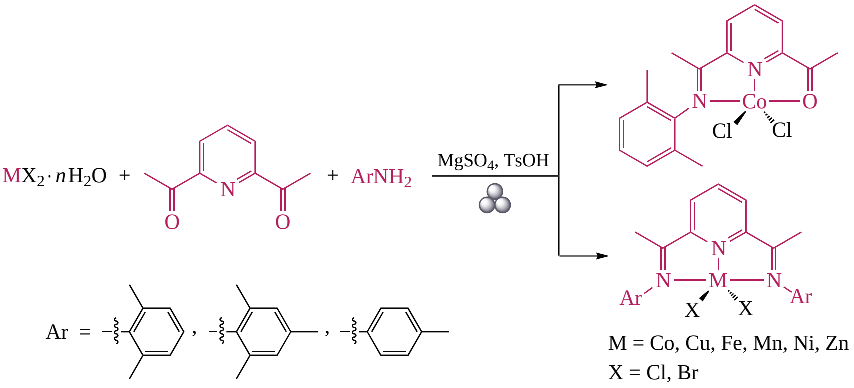
Both milling and aging techniques were shown to be powerful tools for further modification of the resulting azobenzene-based palladacycles.[96–98] Thus, the reactions of dicyclometalated derivatives bearing labile DMF ligands with PPh_3 upon grinding in a ball mill led to unexpected bridged species (Scheme 17).[96] It should be noted that the formation of the latter is not reduced to a simple ligand exchange and implies the realization of a series of bond breaking/making and isomerization processes, which indicates the feasibility of complex structural modifications in the solid state. The subsequent variation of the nature of both azobenzene and auxiliary phosphine ligands as well as the ratio of reactants allowed for obtaining heteroleptic complexes with diverse structures, some of which displayed remarkable fluorescence properties at room temperature and can be used in photoactive units of optical devices.[97] The ball milling also enabled the interconversion of anionic ligands (chloride, acetate, and acetyl acetonate) in mono- and dicyclopalladated azobenzenes, offering a convenient synthetic route to different complexes and, in some cases, opening the way to the products that are unavailable by the conventional solution-based techniques.[98]

Hernández and Bolm[85] reported the mechanosynthesis of a five-membered *C*,*N*-rhodacycle which was proven to serve as an intermediate in halogenation of 2-phenylpyridine (see Scheme 17). Subsequently, the formation of rhodacyclic species as key intermediates was postulated and confirmed for a number of other mechanochemical C–H bond functionalizations, including amidation of arenes,[99,100] alkynylation of indoles,[101] and methylation of (hetero)arenes.[102] Recently, Hernández *et al*.[103] demonstrated the possibility of realization of acetate-assisted C–H bond activation in a range of pyridine- and quinoline-containing substrates under the action of $[Cp^*RhCl_2]_2$ upon mechanical treatment. The reactions readily afforded not only five-membered derivatives but also their more elusive six-membered counterparts (see Scheme 17). It was revealed that, unlike the conventional solution-based synthesis, the solid-state processes occur through preliminary formation of cocrystals between the substrate and dimeric Rh^{III} precursor, which may be the key to their higher efficiency compared to the cyclometalation in solution.

In 2017, our research group introduced a facile mechanochemical approach to the so-called pincer-type complexes.[104] The latter represent bis(metallacyclic) derivatives with a highly tunable tridentate monoanionic ligand framework which has made them one of the most attractive metal-containing objects for intensive studies in catalysis, materials science, and medicinal chemistry over the last several decades.[105–111] The mechanochemical synthesis of a symmetrical Pd^{II} pincer complex was readily accomplished by grinding a bis(thiocarbamate) ligand and $PdCl_2(NCPh)_2$ without recourse to any additive (neat grinding) (Scheme 18). The preliminary mortar-and-pestle experiment was successfully transferred to a vibration ball mill and was extended to gram scale. The target palladacycle was isolated in 95% yield just in 2 min of mechanochemical milling and a simple workup procedure (rinsing with hexane to remove residual benzonitrile). This discovery was preceded by a few original works devoted to the solid-state cyclopalladation in the related pincer systems bearing nitrogen and/or sulfur donors achieved, as a rule, under thermal induction (see Scheme 18).[112,113] The simple homogenization of a ligand and appropriate Pd^{II} precursor by manual grinding in a mortar followed by heating of the resulting mixture at the specific temperature in the absence of an added solvent appeared to be an



Scheme 18 Pd^{II} pincer complexes produced under solvent-free conditions.



Scheme 19 Mechanosynthesis of the first-row transition metal pincer complexes.

efficient and green alternative to the traditional synthesis of these complex organometallic systems in solution. Furthermore, grinding some functionalized carboxamides with $PdCl_2(NCPh)_2$ in a mortar or vibration ball mill resulted in the palladation of a central amide unit with concomitant coordination of ancillary donor groups, affording non-classical pincer complexes with a covalent Pd–N bond.[114,115] The developed mechanochemical approach offers such advantages as the absence of any auxiliary and significant rate and yield enhancement, especially for the challenging ligands. Obviously, a proper choice of ancillary donor groups and/or switching to higher energy milling can extend the mechanochemical tools to wider metal-organic and organometallic pincer chemistry, which we are currently developing. A good proof of this has been afforded by Jurca and colleagues.[116,117] The mechanical agitation of 2,6-diacetylpyridine, 2,6-xylidine, $CoCl_2·6H_2O$, and several auxiliaries in a planetary ball mill led to an unsymmetrical Co^{II} pincer complex (Scheme 19).[116] Although the described procedure required much longer reaction time than our solvent-free cyclometalation protocol (4 h *vs.* ~2 min), it appeared to be the first synthesis of both pincer-type ligand and its complex under mechanochemical conditions, which was accomplished, in addition, in a one-pot manner. This methodology was successfully adapted for the solvent-free synthesis of a range of first-row transition metal bis(imino)pyridine complexes (see Scheme 19).[116]

Taking into account the paramount importance of cyclometalation as one of the basic reactions in organometallic chemistry, a prominent key role of metallacyclic species in different catalytic C–H bond functionalization processes, and the described encouraging results, we are confident that mechanochemical synthesis of monometallacycles and pincer-type complexes will become a prolific research topic in the nearest future.

6. Miscellaneous examples, conclusions, and future outlook

There are also several other prominent examples of the synthesis and modification of organometallic compounds under the action of mechanical force that do not fall under the above sections but deserve a special mention. These include the multistep and multicomponent mechanosynthesis of Re^I tricarbonyl complexes[118] and highly selective ball-milling preparation of the Lewis acid–base adducts in the reaction system involving bis(pentafluorophenyl)zinc and 2,2,6,6-tetramethylpiperidinyl oxide.[119] The latter was shown to be advantageous over other techniques, namely, solid-state slow chemistry and synthesis in melt and, especially, compared to the conventional solution-based methodology. Mechanochemistry appeared to be highly useful for the synthesis of (hetero)aryl Au^I complexes by direct C–H bond activation in different halo- and heteroarenes.[120] It also smoothly provided Buchwald-type phosphine-ligated Pd^{II} complexes by stoichiometric oxidative addition of oxygen-sensitive Pd^0 species to aryl halides in the absence of customary precautions to exclude air, which are required for the synthesis in solution.[121]

To summarize, grinding and milling are viable routes for the improved synthesis of the known and highly demanded metal complexes as well as for the preparation of novel organometallic compounds. The inherent merits of mechanochemical processes such as operational simplicity, reduced wastes, and high reaction rates make them attractive alternatives to the conventional solution-based versions for a great variety of metal-containing compounds. In the field of organometallic chemistry, mechanochemical approaches can be additionally useful from the viewpoint of solubility and stability of reactants, intermediates, and products. All this promises great future for mechanochemical tools in the synthesis of organometallic compounds. The reactivity studies under solvent-free conditions, including different isomerization, ligand exchange and rearrangement processes, will inevitably evolve to encompass wider range of compound types. Finally, further expansion of mechanochemical strategies to organic transformations mediated or catalyzed by metal complexes will also be facilitated in the forthcoming years, with a particular focus on different C–H bond functionalization processes.

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