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One-Pot, One-Step Precatalysts through Mechanochemistry

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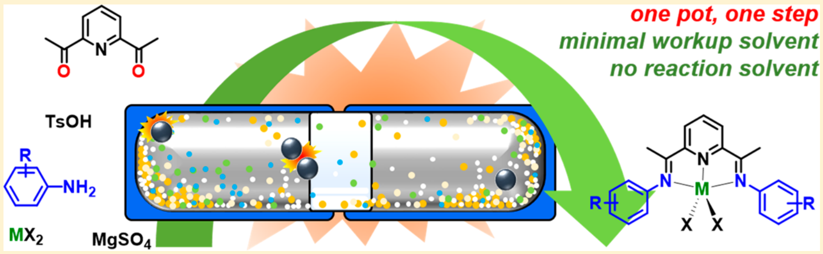
Supporting Information



ABSTRACT: The development and implementation of transition-metal-based precatalysts have played crucial roles in modern organic synthesis. However, while the use of such species greatly improves sustainability, their preparative routes often rely on multiple time-, energy-, and solvent-intensive steps. By leveraging solvent-free mechanochemical synthesis through vibratory ball milling, we report the one-pot, one-step synthesis of a range of first-row transition-metal bis(imino)pyridine complexes, where both the ligand and coordination complex are assembled in situ. Bis(imino)pyridine complexes of the first-row transition metals have an extensive history of application as precatalysts for numerous bond-forming transformations. The method reported herein facilitates access to such species in a time-, solvent-, and space-saving manner which can easily be adapted to any laboratory setting regardless of prior experience with coordination complex synthesis.

The application of organometallic and inorganic coordination compounds as precatalysts for bond transformations is a cornerstone of modern molecular and macromolecular chemical synthesis. Their implementation lowers energy input, reduces reaction time, and often increases selectivity, thus contributing to enhanced overall sustainability in comparison to noncatalytic synthetic protocols. While utilization of such precatalysts has a profound influence on sustainability, their traditional preparative routes rarely follow "green" principles.[1] In contrast, heterogeneous catalyst development has long focused on increased sustainability by utilizing recycled or biosourced materials as either the catalyst or support.[2] Although identical efforts for precatalyst preparation are not feasible, synthetic approaches requiring fewer steps and less solvent are imperative for enhancing overall sustainability in homogeneous catalysis.

In recent years, mechanochemistry, conducted by milling or grinding, has emerged as a powerful tool for the synthesis of both organic and inorganic molecules and materials.[3] This has enabled the development of numerous facile and sustainable synthetic methodologies.[4] Conversely, the development of mechanochemical routes toward coordination complexes and related supporting ligand frameworks is relatively nascent. Nonetheless, the past few years have ushered in seminal works in this promising area of research.[5] However, mechanochemical routes where both the ligand and metal complex are assembled in situ (one pot) are rare.[6]

Our studies focus on the bis(imino)pyridine ligand class, a ubiquitous supporting architecture which has enabled countless discoveries in olefin polymerization,[7] alkene hydrogenation,[8] single-molecule magnets,[9] and synthesis of broad families of coordination complexes spanning the periodic table, to name a few.[10] The majority of the applications are as precatalysts for chemical transformations, an inherently "green" process. However, while their downstream application may be sustainable, the conventional preparation of bis(imino)pyridine species is not. In a typical process, ligand synthesis involves prolonged reflux in toluene or ethanol (24−48 h) with subsequent solution-based workup.[10] Successive ligation to the metal requires a second solution-based process, with further purification. The combination thereof necessitates significant amounts of both solvent and time. Previously, our group reported an efficient mechanochemical route to acetyl- and bis(imino)pyridine ligands and the one-pot, one-step synthesis of an acetyl(imino)pyridine-CoCl$_2$ species with excellent global yield.[6c] With several parametric modifications to our original protocol, and by running three reactions in tandem (Figure 1), we now report a facile, on-demand, one-pot, one-step mechanochemical synthesis of bis(imino)pyridine-MX$_2$ (M = Mn, Fe, Co, Ni, Cu, Zn; X = Cl, Br).

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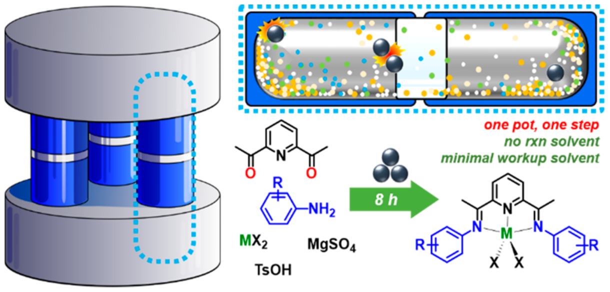


Figure 1. (left) Holder/assembly for 3 × 5 mL stainless steel (ss) grinding jars used in this study, (top right) illustrated cross-section of the grinding jar with reagents, and (bottom right) general reaction scheme for the one-pot, one-step synthesis of bis(imino)pyridine-based transition-metal complexes.

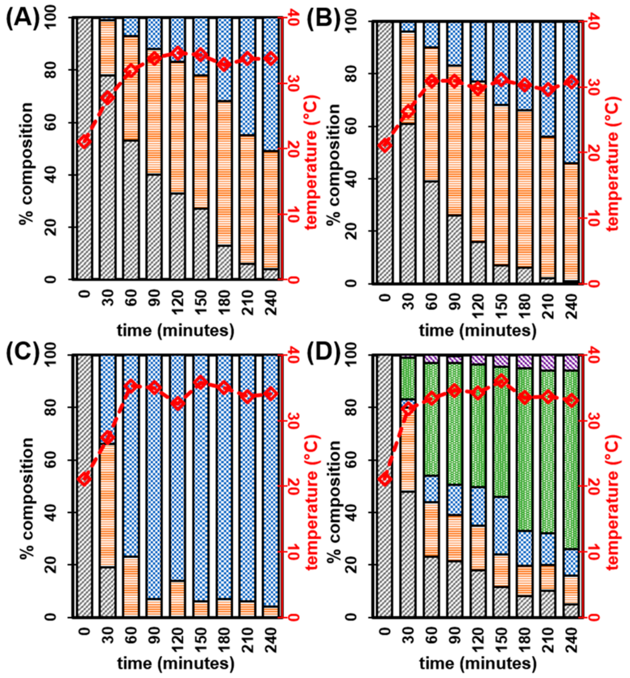


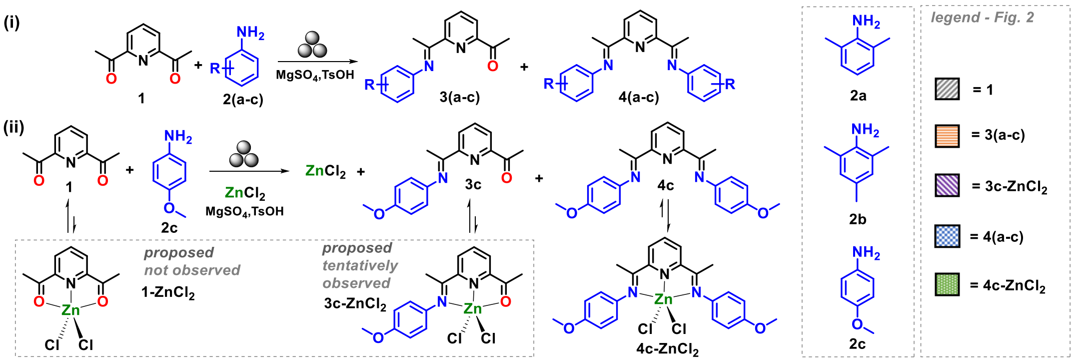
Figure 2. Percent composition by ^{1}H NMR for the reaction of **1** and **2a** (A), **2b** (B), **2c** (C), and **2c** + ZnCl$_2$ (D) sampled from individual reaction mixtures at 30 min intervals. See Scheme 1 for the legend.

Our group has previously optimized the mechanochemical reaction conditions for small-scale bis(imino)pyridine ligand synthesis: 2,6-diacetylpyridine (**1**; 1.2 mmol), aniline (**2**, 3.8 mmol; **2a**, 2,6-dimethylaniline, **2b**, 2,4,6-trimethylaniline, **2c**, *p*-anisidine), MgSO$_4$ (200 mg, 1.7 mmol), *p*-toluenesulfonic acid (TsOH; 7−10 mg), and 3.175 mm ss (440c) balls.[3f,6c] It was found that reactions proceeded cleanly via acetyl(imino)-pyridine (Scheme 1), with the reactivity being largely governed by steric encumbrance at the aniline 2- and 6-positions. The ball to reagent ratio played a secondary but important role, with higher molar masses of anilines leading to lower conversion rates. The prior study was conducted in a 316 ss vessel with an internal volume of 4.6 cm^3 on a SPEX 5100 Mixer/Mill (50 Hz).[3e] In this study, we utilize the higher capacity, more robust SPEX 8000 M mill (18 Hz) and 5 cm^3 ss Smartsnap grinding jars from Form-Tech Scientific. To take advantage of the expanded capacity and expedite our process development, we implemented a home-built aluminum holder (Figure 1) which allowed us to perform three trials in parallel.

By use of this protocol, the reaction progress and bulk material temperature (measured in the vessel immediately after removal from the mill) as a function of time were monitored over 4 h; each time point is an individual reaction carried out with continuous milling. When the reaction was complete, an aliquot of the slurry or powder was analyzed by ^{1}H NMR spectroscopy, and the percent composition was determined by the integration of peaks in the aromatic region (Figure 2A−C, Figures S1−S3). The reactions proceed stepwise with initial formation of **3**, followed by the consumption of **3** to form **4**, with no observable byproducts (Scheme 1 and Figures S1−S3). As **2c** facilitated the most complete conversion, we repeated the process with additional diamagnetic d^{10} metal halide ZnCl$_2$ (0.75:1 equiv with respect to to **1**) to monitor the one-pot formation of both the ligand and the related coordination complex (Scheme 1, Figure 2D, and Figure S4; vide infra). Moreover, although the recorded temperatures are not fully representative of in situ reaction conditions, they reveal that the temperature of the bulk material remains low (<37 °C).[11] This likely aids in negating byproduct formation or reversibly hydrolyzing the imine.

To compare relative reaction rates for **2a−c**, we monitor consumption of **1** (moles) per volume of free space in the reaction vessel.[3d,4c,6c] The consumption of **1** appears to follow a first-order process with comparable rates of 0.013 and 0.019 min^{-1} for **2a** and **2b**, respectively. For **2c**, the rate is dramatically enhanced to 0.06 min^{-1}. Formation of the final products **4a−c** can be approximated as a pseudo-zeroth-order process, which is dependent on the availability of the faster-forming **3a−c** (Figure S6). Addition of ZnCl$_2$ complicates the process; occupied 3d orbitals of Zn necessitate ligand

Scheme 1. Formula for the Mechanochemical Synthesis of (i) 3a−c and 4a−c and (ii) 3c, 4c, and 4c-ZnCl$_2$



interaction with available 4s and 4p orbitals. The resulting weaker bonds in comparison to metals with d orbital vacancy may invariably lead to reversible metal−ligand binding (Scheme 1).[12,13] Additionally, there are numerous species capable of H-bonding interactions in the system, resulting in significant shifting of ^{1}H signals from sample to sample (Figure S4). Nonetheless, we tentatively approximate the percent composition to Figure 2D (Figure S5). The reaction appears to proceed by rapid formation of both **3c** and **4c**, the latter of which readily binds $ZnCl_2$, forming **4c-ZnCl$_2$**. This pattern is observed through the 240 min monitored, with free **4c** appearing as a minor component vs **4c-ZnCl$_2$**. The concentration of **3c** remains nearly similar to that in the ligand-only system (Figure 2C), with only a minor component tentatively ascribed to **3c-ZnCl$_2$** being observed (Scheme 1 and the Supporting Information). This is likely due to weaker ligand−metal binding interactions for **3c-ZnCl$_2$**. Notably, consumption of **1** follows a slower (vs **2c**/no $ZnCl_2$) first-order process (0.025 min^{-1}, Figure S6) over 90 min, after which point there are too many components to accurately determine a rate. Moreover, in stark contrast to **2c**/no $ZnCl_2$ (Figure 2C), **1** is not fully consumed throughout the time monitored. We tentatively attribute this to a solid-state interaction between **1** and $ZnCl_2$ (Scheme 1) which was not observable in solution but likely sufficient to slow conversion of **1** in the solid state.

As the ligand component of the mixture was in excess, the maximum attainable composition of **4c-ZnCl$_2$** is ca. 75%. Thus, the observed combination of 68% **4c-ZnCl$_2$** and 6% **3c-ZnCl$_2$** accounts for the consumption of $ZnCl_2$ and corresponds to an NMR yield of 91% for **4c-ZnCl$_2$**. The product was cleanly isolated in 76% yield, and the structure was confirmed by a single-crystal X-ray structure determination (Figure 3A).

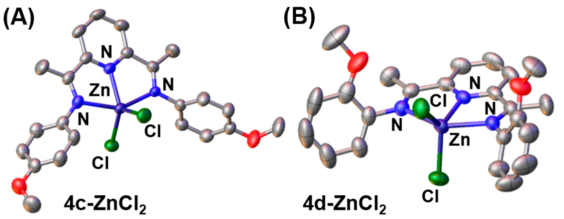
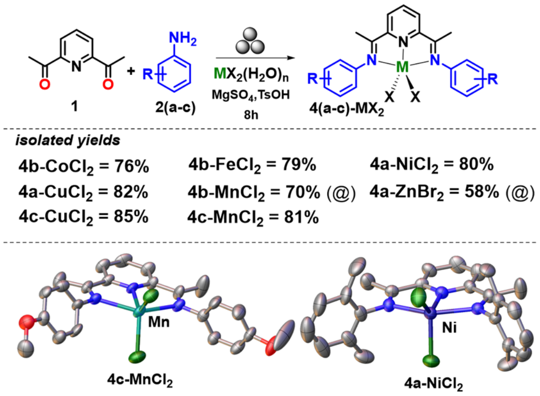


Figure 3. Structural representations of compounds **4c-ZnCl$_2$** (A) and **4d-ZnCl$_2$** (B) with hydrogen atoms and solvents of crystallization omitted for clarity. Thermal ellipsoids are drawn at the 50% level. For bond lengths and angles see the Supporting Information.

The reaction was scaled up 5-fold utilizing 12.7 mm ss balls, in a 65 mL SPEX 8007 ss grinding jar (440c), and the reactants were milled for 4 h continuously on a SPEX 8000 M mill (18 Hz). The isolated yield over one single crop was 78% (1.87 g), thus validating the scalability of the process. In a second smaller scale reaction, as noted previously, **2c** was replaced with *o*-anisidine (**2d**), and the reaction was conducted under identical protocols (vide supra). Similarly, the reaction led to the isolation of **4d-ZnCl$_2$** in 73% yield. The structure was confirmed by single-crystal X-ray crystallography (Figure 3B).

Encouraged by our findings with $ZnCl_2$, we turned to other **4-MX$_2$** target compounds (M = Mn, Fe, Co, Ni, Cu, Zn, X = Cl, Br). To avoid isolation of a predominantly acetyl(imino)pyridine complex (**3-MX$_2$**) as observed previously by our group with $CoCl_2$,[6c] the reaction time was extended to 8 h (Scheme 2). Unless otherwise noted (see the Supporting Information), reactions were conducted under a similar small-scale, parallel reaction protocol (vide supra). Upon reaction completion, powders were rinsed with minimal toluene to remove excess organic components, and then the metal complexes were dissolved in minimal dichloromethane to remove the product from $MgSO_4$. The solutions were then concentrated, allowed to recrystallize at −25 °C overnight, and dried under vacuum. Reaction products that did not crystallize readily were rapidly precipitated with a small amount of hexanes. Products were authenticated by ESI-MS, elemental analysis (C,H,N), and in the case of **4a-NiCl$_2$** and **4c-MnCl$_2$** single-crystal X-ray measurements (Scheme 2). The connectivity of **4a-ZnBr$_2$** and **4b-MnCl$_2$** was confirmed by single-crystal X-ray determinations; unfortunately, crystals of the latter were not of adequate quality for a full structure solution (SI). Nonetheless, all complexes were readily isolated with reasonable purity and in good to excellent yields (58−85%, Scheme 2). Complexes **4a-CuCl$_2$**,[14] **4c-MnCl$_2$**,[15] **4b-CoCl$_2$**,[7b] **4a-FeCl$_2$**,[7b] **4a-NiCl$_2$**,[16] and **4a-ZnBr$_2$**,[17] have been previously reported, and their properties and applications, in most cases, have been well established.

Scheme 2. Mechanochemical Synthesis of 4a−c-MX$_2$[a]



isolated yields

4b-$CoCl_2$ = 76%
4a-$CuCl_2$ = 82%
4c-$CuCl_2$ = 85%
4b-$FeCl_2$ = 79%
4b-$MnCl_2$ = 70% (@)
4c-$MnCl_2$ = 81%
4a-$NiCl_2$ = 80%
4a-$ZnBr_2$ = 58% (@)

[a]Reaction conditions: $MX_2(H_2O)_n$ 300 mg, **1** 1.2 mol equiv, **2a−c** 3 mol equiv, $MgSO_4$ 200 mg, TsOH 10 mg, 3.175 mm ss balls, ss jar, SPEX 8000 mill. The $^@$ symbol denotes that the connectivity was confirmed by single-crystal X-ray determinations (Supporting Information).

In summary, we report a facile and expedient protocol for the synthesis of bis(imino)pyridine complexes of first-row transition-metal halides Mn−Zn, complexes broadly relevant to catalysis.[8−11] While some amount of solvent is still required for final purification, the one-pot nature of the synthetic process eschews any solvent as part of the reaction step and all solvents which would be necessary for the isolation and further reaction of intermediates. Furthermore, a previously multiday process can now be completed in 1 day, saving not only solvent but also valuable laboratory resources, such as bench and fumehood space, and researcher time. Our ongoing efforts focus on increasing the complexity of the one-pot mechanochemical process to include precatalysts with asymmetric ligand frameworks.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.9b00575.

Detailed synthetic protocol, NMR data and spectra, and details of X-ray studies for all relevant compounds (PDF)

Accession Codes

CCDC 1948354−1948358 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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