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Mechanosynthesis of ruthenium trisbipyridyl complexes and application in photoredox catalysis in a ball-mill†

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Herein, we developed the mechanosynthesis of ruthenium trisbipyridyl complexes. Such complexes can be difficult to prepare in solution, with long reaction times and average yields. With ball-milling, less than 3.5 hours of milling were sufficient to obtain the complexes in high yield. Such complexes were then evaluated as catalysts in the light-promoted mechanochemical reductive dehalogenation reaction. In addition to working under solvent-less conditions, the use of a Hantzsch amide instead of the classical ester allowed drastic simplification of the purification of the final compounds.

Introduction

Since its discovery, photochemistry, which uses light to trigger chemical reactions, has become a useful tool for the organic chemist.[1] As many chemical reactants cannot absorb directly the energy of the photons, organic or organometallic photosensitizers are sometimes required as initiators or catalysts.[2–6] Amongst the coordination complexes with useful photophysical properties, including long lifetime of the excited state and efficient metal to ligand charge transfer (MLCT), the family of polypyridyl ruthenium(II) complexes is frequently used.[7,8] These complexes, amongst other compounds which possess both oxidant and reductive properties in their excited state, were responsible for the renewal of photoredox catalysis during the last twenty years. Given our expertise in the synthesis of coordination complexes using ball-milling,[9–18] including iron complexes with photoredox properties,[13] we thought that such photoredox complexes could be mechanosynthesized efficiently. In this domain, Kubota *et al.* recently reported the rapid and efficient synthesis of photoredox tris-cyclometalated iridium complexes using ball-milling at high temperature (with a temperature-controllable heat gun).[19] In addition, organic photosensitizers such as 2,4,5,6-tetra(9*H*-carbazol-9-yl) isophthalonitrile (4-CzIPN) could also be synthesized highly efficiently under milling conditions.[20]

Mechanochemistry, which was recognized in 2019 by IUPAC as one of the ten chemical innovations that could change the world,[21] is known to promote efficiently chemical reactions under solvent-free or solventless conditions.[22–29] Such efficiency can be assigned to an excellent mixing and mass transfer of the reagents in the milling jar while shocks and shearing forces furnish sufficient energy to promote the reactions. These benefits were highlighted in numerous domains of chemistry, including organic chemistry,[30–34] coordination chemistry,[35] and catalysis.[36–42] Amongst the latest, only three examples to date report the combination of mechanochemistry and visible light activation (Scheme 1), and a single example with UV irradiation.[43] Contrary to solution chemistry where limitations can be found in light penetration in diluted mixtures, the efficiency of ball-mills, using transparent milling jars (in PMMA or glass), to mix the reaction mixture and bring the photosensitizer under light irradiation was demonstrated. Štrukil *et al.* reported the solid-state photocatalyzed oxidation of alkynes in a ball-mill, using eosin Y as an organic photosensitizer[44] and air as an oxygen source.[45] The same year, Hernández also used eosin Y in the borylation of aryldiazonium salts under ball-milling conditions.[46] More recently, Millward *et al.* designed a novel approach for light irradiation inside a milling jar to promote various photochemical reactions, some of which could be performed, contrary to solution chemistry, under aerobic conditions.[47] In addition to milling conditions, it should be noted that photochemistry under solvent-free conditions was also reported.[48,49] In this study, given our previous work in the use of ball-mills for coordination and organic chemistry, we investigated the mechanosynthesis of photoredox polypyridyl ruthenium(II) complexes, and their further use in the mechanochemical photoredox reductive dehalogenation reaction. The use of a chemically resistant and transparent material, namely epoxy

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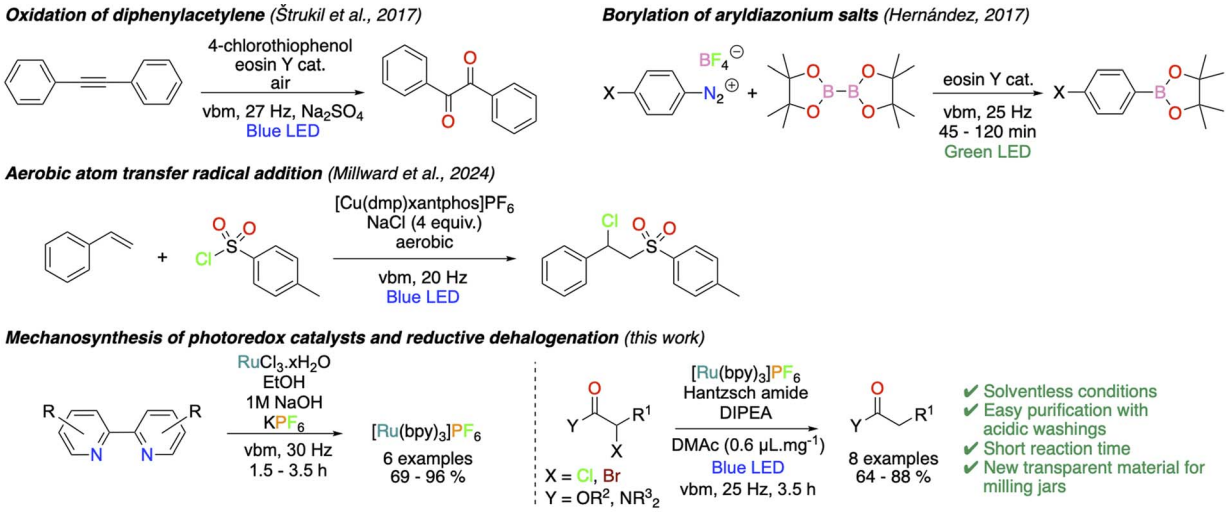
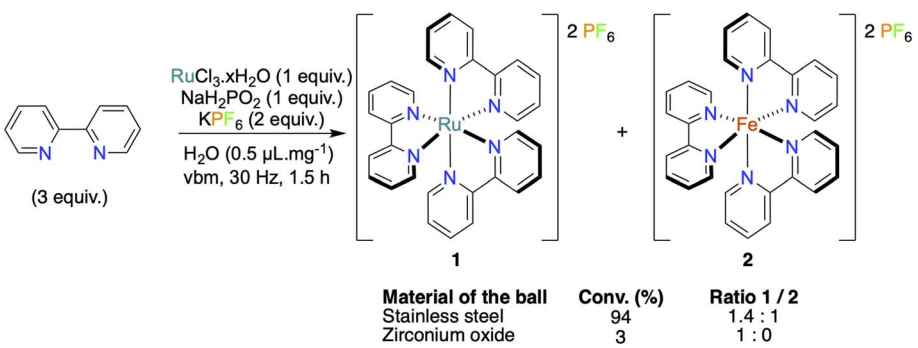


Scheme 1 Reports merging photoredox catalysis and ball-milling.

resin, for the production of novel milling jars allowed this reaction to be performed quite efficiently in a solvent-less manner. In addition, replacing the Hantzsch ester with the corresponding amide resulted in a simplified purification of the dehalogenated products.

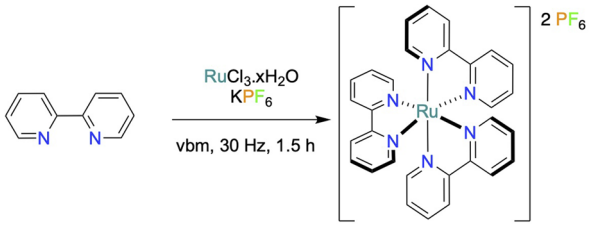
Results and discussion

As the first part of this study, we investigated the synthesis of $[Ru(bpy)_3](PF_6)_2$ complex **1** under mechanochemical conditions. Ruthenium(III) chloride was loaded in a 14 mL Teflon® jar using a 1 cm diameter stainless steel ball, together with bipyridine (3 equiv., bpy), sodium hypophosphite as a reducing agent (1 equiv.) and water as a liquid assistant, and the mixture was milled in a Retsch® MM400 mixer mill (Scheme 2). To our delight, bipyridine was converted up to 94% after 1.5 h of milling. However, careful analysis of the reaction mixture showed the formation of two complexes, namely $[Ru(bpy)_3](PF_6)_2$ **1** and $[Fe(bpy)_3](PF_6)_2$ **2** in a 1.4 : 1 ratio.[50] The same reaction performed with a ZrO_2 ball resulted in the formation of 3% of $[Ru(bpy)_3](PF_6)_2$ with no traces of $[Fe(bpy)_3](PF_6)_2$. It thus seems that the formation of $[Fe(bpy)_3](PF_6)_2$ results from the redox reaction between ruthenium(III) chloride and the iron(0) contained in the stainless steel ball and further reaction with bipyridine. Such reactivity of the milling material was in some cases willingly used for catalytic purposes.[51–54] To improve the speed of the reaction, the material of the jar and ball was changed to tungsten carbide, a harder material that provides more energetic shocks, resulting in a conversion of 20% (Table 1, entry 2). Replacing sodium hypophosphite with ethanol, which plays the role of both reagent and grinding-assistant,[55] gave a higher conversion of 40% (Table 1, entry 3). Finally, using 1 M sodium hydroxide permitted to facilitated the redox reaction, giving the desired complex in 86% conversion (Table 1, entry 4). Full conversion was obtained with a slight increase in ethanol and bipyridine quantities, yielding pure $[Ru(bpy)_3](PF_6)_2$ **1** in 96% (Table 1, entry 5). The same conditions using magnetic stirring did not give any conversion, thus showing that the ball-milling process is essential to obtain high yields. In comparison, one of the most efficient synthetic approaches so far to synthesize the $[Ru(bpy)_3](PF_6)_2$ complex involves reaction in ethylene glycol at high temperature (160 °C) for 15 min under microwave activation.[56] The optimized conditions obtained with bipyridine were then applied to a variety of symmetrical



Scheme 2 Reaction outcome depending on the material of the ball.

Table 1 Optimization of the synthesis of $[Ru(bpy)_3](PF_6)_2$[a]

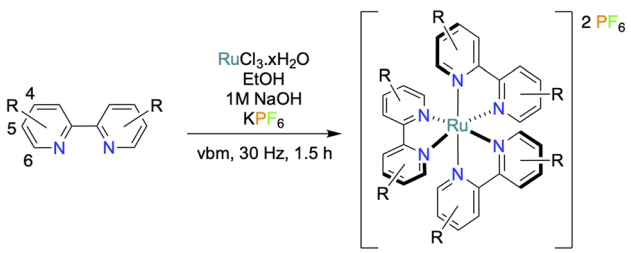


Entry	Material: Jar/ball[b]	Red. agent (equiv.)	Additive (equiv.)	Conv.[c] (%)
1	Teflon/ZrO_2	NaH_2PO_2 (1)	H_2O (0.5 μL mg^{-1})	3
2	WC/WC	NaH_2PO_2 (1)	H_2O (0.5 μL mg^{-1})	20
3	WC/WC	EtOH (9)	H_2O (0.5 μL mg^{-1})	40
4	WC/WC	EtOH (9)	1 M NaOH (0.25)	86
5[d]	WC/WC	EtOH (12)	1 M NaOH (0.25)	>99 (96)

[a] Reaction conditions: $RuCl_3 \cdot xH_2O$, bpy (3 equiv.), KPF_6 (2 equiv.), vbm (vibratory ball-mill), 30 Hz, 1.5 h. [b] WC: tungsten carbide. [c] Conv. was determined by ^1H NMR; isolated yield is given in brackets. [d] 4 equiv. of bpy were used.

ligands. Reaction with 4,4′-dimethylpyridine, featuring methyl in the para position related to the nitrogen atoms, furnished the corresponding complex **2** after 2 h in 92% (Table 2, entry 2). Having the methyl groups in the meta position did not change the outcome of the reaction and complex **3** could be isolated in 97% yield (Table 2, entry 3). However, when 6,6′-dimethylbipyridine was used, no conversion was observed, probably because of the steric hindrance of the ligand (Table 2, entry 4). It should be noted that this complex was never reported in the literature, showing the difficulty encountered to synthesize it. With methoxy groups in position 4,4′, corresponding complex **5** could be obtained in 69% yield (Table 2, entry 5). Finally, complex **6** having *t*Bu groups in position 4,4′ of the bipyridine was isolated in 85% (Table 2, entry 6). To widen the scope of complexes that could be synthesized in a ball-mill, 1,10-phenanthroline was used to furnish the corresponding complex **7** in 86% yield (Table 2, entry 7). As a comparison, the best conditions using solvent-based approaches reported in the literature are summarized in Table 2. The microwave conditions developed by Beves and coll. were found to be highly effective for the synthesis of complexes **1** and **7**.[56] However, they required the use of high boiling point and toxic ethylene glycol to obtain

Table 2 Diversification of the bipyridine ligand[a]



Entry	R	Complex	*t* (h)	Yield (%)	Conditions in lit.
1	H	**1**	1.5	96	$(CH_2OH)_2$, 160 °C, 15 min, MW, 93%[56]
2	4-Me	**2**	2	92	dmb (5 eq.), EtOH, reflux, 1 d, 80%[59]
3	5-Me	**3**	2	97	EtOH, 16 h, 55%[60]
4	6-Me	**4**	3	0	n.a.[b]
5	4-MeO	**5**	3	69	EtOH, reflux, 5 d, 40%[61] $(CH_2OH)_2$, 195 °C, 1 h, 53%[62]
6	4-*t*Bu	**6**	3.5	85	$(CH_2OH)_2$, reflux, 1 h, 69%[63]
7	1,10-Phen	**7**	2	86	$(CH_2OH)_2$, 160 °C, 15 min, MW, 94%[56]

[a] Reaction conditions: $RuCl_3 \cdot xH_2O$, substituted bpy (4 equiv.), KPF_6 (2 equiv.), EtOH (12 equiv.), 1 M NaOH (0.25 equiv.), vbm, 30 Hz, 1.5–3.5 h. [b] n.a. = not available.

high yields, similar to the ones obtained under ball-milling conditions. For the synthesis of complexes **2–6**, the mechanochemical approach was found to be highly competitive, with isolated yields higher than the ones previously reported, and more practical conditions. In addition, calculation of the *E* factor shows that synthesis under solventless conditions by mechanochemistry offers a clear advantage in terms of sustainability, with values of around 1.4–1.5 in the ball-mill, which are 25–1000 times lower than in solution.[57]

We then focused on the catalytic photoredox reductive dehalogenation of compound **8a**, which was previously described by Stephenson *et al.* as a tin-free dehalogenation method.[58] In solution, this reaction proceeds in 24 h using DMF as solvent. α-Chloroester **8a**, which was prepared using a solvent-free mechanochemical method,[57] was loaded into a transparent PMMA milling jar with a 1 cm diameter stainless steel ball, surrounded by blue LEDs. As previously shown, DIPEA (diisopropylethylamine) and Hantzsch ester were used in combination as reducing agents and proton donors. When 5 mol% of $[Ru(bpy)_3](PF_6)_2$ **1** were used, only 14% conversion was obtained after 1.5 h of milling (Table 3, entry 1). Increasing the catalyst loading to 10 mol% and reaction time to 3 h resulted in a lower conversion (Table 3, entry 2). Such an intriguing result can be explained by the formation of a hard solid sticking to the walls of the jar even at high milling frequency. A liquid assistant was thus added to furnish a homogeneous reaction mixture. Ethanol was tested for liquid-assisted grinding (LAG) with a η ratio of 0.3 μL per mg of reactants.[55] This resulted in an increased conversion of 44% (Table 3, entry 3). Having a η ratio of 0.6 μL mg^{-1} proved to be optimal since a conversion of 79% was obtained (Table 3, entry 4). Under these conditions, it was possible to reduce the catalyst loading down to 5 mol% without a dramatic loss of conversion (Table 3, entry 5).

The different complexes synthesized above were then evaluated under these mechanophotoredox reaction conditions (Table 3, entries 5–10). Catalyst **1** was found to be the most active, as it furnished ester **9a** in 76%. With a milling time of 3.5 h, different liquid additives were tested. Because PMMA is sensitive to many chemicals and can degrade quite rapidly, we designed, manufactured and used for the first time grinding jars made of epoxy resin, a transparent and chemically resistant material, to screen liquid additives. In this context, it should be noted that, in addition to commercially available materials, polymeric ones, with jars made by machining,[64] or 3D-printed,[65] have been recently evaluated for milling applications, but none of them was found to be resistant and transparent for photochemical applications. We recently reported applications of epoxy resin for heated mechanochemistry with similar milling jars, for a vertical ball-mill, doped with a dye with photothermal properties.[66] Thus, ethanol, hexane, acetonitrile and *N*,*N*-dimethylacetamide were tested as liquid additives (Table 3, entries 11–14). Gratifyingly, while the use of hexane resulted in an inhomogeneous mixture, the use of DMAc allowed reaching full conversion in 3.5 h of milling (Table 3, entry 14). Finally, control experiments in the absence of light or catalyst gave no and poor conversions (Table 3, entries 15–16). Even if the reaction conditions were found to be highly efficient, purification of the reaction mixture was tricky, especially because of the presence of Hantzsch ester and corresponding pyridine, which results from its sacrificial proton donor role. Indeed, after extraction, the crude mixture still contained both compounds in addition to the expected product (Fig. 1, upper spectrum). We thus replaced the Hantzsch ester with a Hantzsch amide developed as an NADH model for reductions,[67] and recently used in the transfer hydrogenation of enones,[68] or in a reductive Cope rearrangement.[69] The amide and corresponding pyridine, which is generated during the photoredox reaction, could be easily protonated and removed from the mixture through acidic washings. Gratifyingly, when Hantzsch amide was used under the optimized mechanochemical conditions, full conversion was again obtained, and acidic washings allowed pure compound **9a** to be obtained in 64% yield (Fig. 1, lower spectrum). We thus applied these fully optimized conditions to different α-chloro esters and amides (Scheme 3). When the phenyl group of **9a** was replaced with a methyl, corresponding dehalogenated **9b** was obtained in 66%. The same reaction using corresponding α-bromo ester **9b-Br** also proceeded efficiently and yielded **9b** in 87%. Gratifyingly, substrates **8c–d**, featuring an internal or a terminal alkyne, gave the desired dechlorinated products, in 65% and 85% yield, respectively, with no reaction on the alkyne. **8e**, featuring an ethyl ester, also reacted efficiently to give **9e** in 67%. Finally, working with amides **8f–g** also proved to be fruitful and gave corresponding **9f**

Table 3 Optimization of the photoredox reductive dehalogenation[a]

Entry	Cat. (mol%)	Additive (η in μL mg^{-1})	t (h)	Conv. (%)
1	1 (5)		1.5	14
2	1 (10)		3	7
3	1 (10)	EtOH (0.3)	3	44
4	1 (10)	EtOH (0.6)	3	79
5	1 (5)	EtOH (0.6)	3	76
6	2 (5)	EtOH (0.6)	3	30
7	3 (5)	EtOH (0.6)	3	7
8	5 (5)	EtOH (0.6)	3	71
9	6 (5)	EtOH (0.6)	3	45
10	7 (5)	EtOH (0.6)	3	16
11	1 (5)	EtOH (0.6)	3.5	81[b]
12	1 (5)	Hexane (0.6)	3.5	31[b]
13	1 (5)	CH_3CN (0.6)	3.5	35[b]
14	1 (5)	DMAc (0.6)	3.5	100[b]
15[c]	1 (5)	DMAc (0.6)	3.5	0
16	—[d]	DMAc (0.6)	3.5	10

[a] Reaction conditions: **8a** (0.27 mmol), Cat., Hantzsch ester (1.1 equiv.), DIPEA (2 equiv.), vbm, 30 Hz, N_2, blue LEDs. [b] Reaction was performed at 25 Hz in a transparent milling jar with a ZrO_2 ball for 3.5 h. [c] Reaction performed in the absence of light irradiation. [d] Reaction performed in the absence of catalyst.

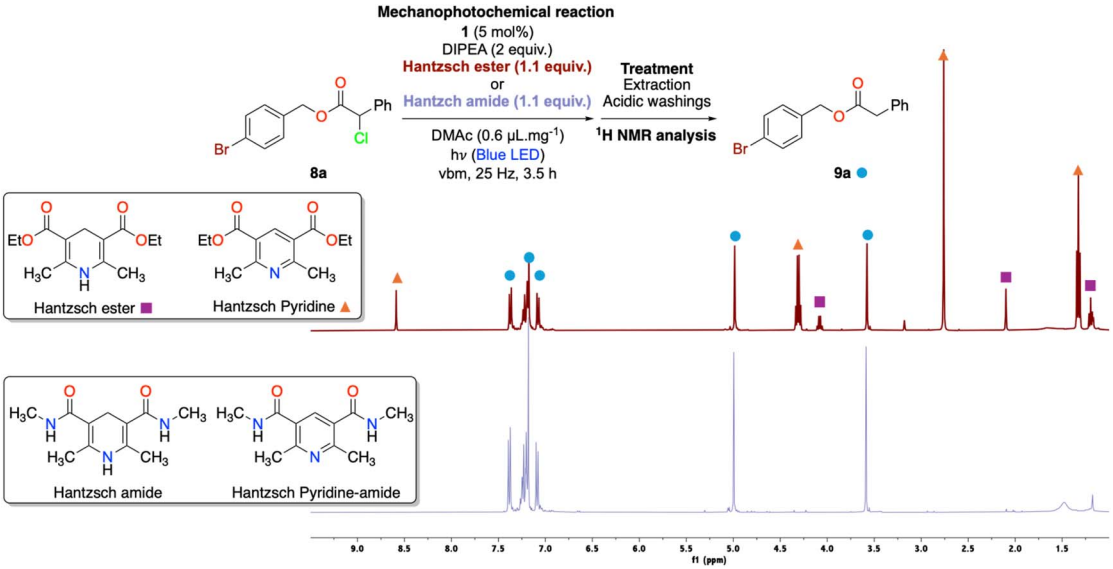


Fig. 1 ^{1}H NMR spectra of compound **9a** after extraction (acidic treatments) using Hantzsch ester (red) or Hantzsch amide (blue).

and **9g** in 81% and 88% yield, respectively. Compared to conditions in solution, this mechanochemical approach allowed drastically reducing the reaction time (from 24 h to 3.5 h) and simplifying the reaction set-up and purification thanks to the use of the Hantzsch amide.

Experimental

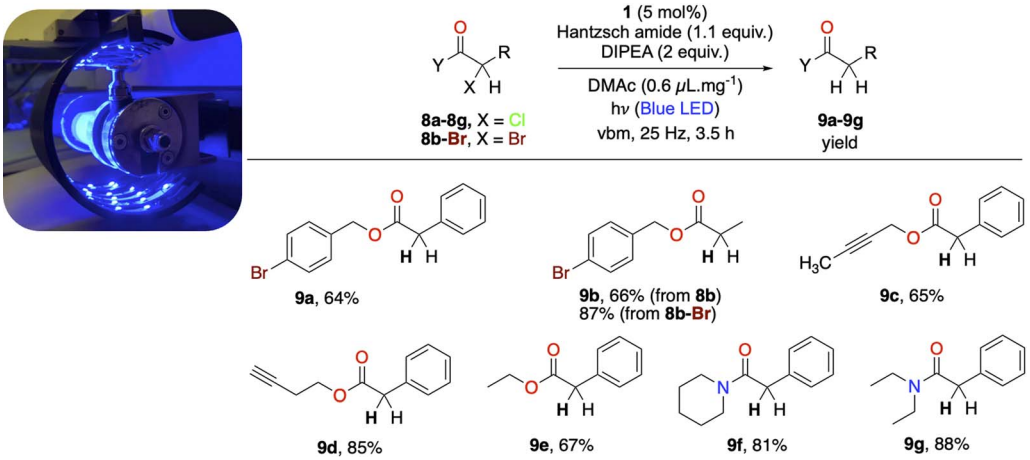
All reagents were purchased from Sigma Aldrich, Fluka, Acros or Alfa Aesar. Hantzsch amide was synthesized according to lit.[68]

Mechanophotochemistry

The milling treatments were carried out in a vibrating Retsch® Mixer Mill 400 (vbm) operating at 25–30 Hz. The milling load (ML) is defined as the ratio between the mass of the reactant over the free volume of the jar. For performing photo-mechanochemical experiments, the vbm was modified to adapt a 3D-printed $\frac{3}{4}$-cylinder (90 mm diameter) covered with LEDs (12VDC SMD3528 LED flexible strip bought from **https://lightingwill.com**; 126 LEDs, total power 10.1 W, distance to the milling jar: 35 mm).

Making epoxy milling jars

A similar protocol to the one depicted in a previous report from our group was used.[66] A mold of the two parts of a 15 mL milling PMMA jar was made using silicone 3481 and an accelerator (catalyst 81-NW) from SF-composites according to the suppliers' recommendations. Once the mold was ready for use, epoxy resin (SR8500/SD7160) was poured in the molds according to the suppliers' recommendations. After curing, the two parts of the novel milling jar were recovered. If necessary, a light sanding was carried out to obtain suitable jars for use in the vbm.



Scheme 3 Mechanochemical photoredox reductive dehalogenation reaction.

Analysis

NMR analyses were performed at the 'Laboratoire de Mesures Physiques' (IBMM, Université de Montpellier). ^{1}H NMR spectra were recorded on a Bruker AVANCE 400 MHz, a Bruker AVANCE III 500 MHz or a Bruker AVANCE III 600 MHz and are reported in ppm using deuterated solvents ($CDCl_3$ at 7.26 ppm or DMSO-d_6 at 2.50 ppm or acetone-d_6 at 2.05 ppm) as internal standards. Data are reported as s = singlet, d = doublet, t = triplet, q = quadruplet, qt = quintuplet, sept = septuplet, m = multiplet; coupling constant in Hz; integration. ^{13}C NMR spectra were recorded on a Bruker AVANCE 101 MHz, a Bruker AVANCE III 126 MHz or a Bruker AVANCE III 151 MHz and are reported in ppm using deuterated solvents ($CDCl_3$ at 77.2 ppm or DMSO-d_6 at 39.5 ppm or acetone-d_6 at 29.8 ppm) as internal standards. Mass spectra were obtained by LC-MS using a LC Waters Alliance 2695, coupled to a Waters ZQ spectrometer with an electrospray source, a single quadrupole analyzer and a Waters 2489 UV detector. HPLC conversion was measured on an Agilent technologies 1220 Infinity LC using a high-resolution Chromolith® RP-18e50-4.6 mm column and a linear gradient of 0–100% CH_3CN/0.1% TFA in H_2O/0.1% TFA over 3 min, UV lamp detection at 214 nm and a flow rate of 1 mL min^{-1}.

General procedure for the synthesis of ruthenium trisbipyridyl complexes

Reactions were performed with a ML ≈ 20–30 mg mL^{-1}, allowing 35–61 mg of final complexes to be obtained. $RuCl_3 \cdot xH_2O$ (1.0 equiv.), corresponding bipyridine (4.0 equiv.), KPF_6 (2.0 equiv.), EtOH (12.0 equiv.) and sodium hydroxide (0.25 equiv., 1 M in water) were introduced in a 5 mL WC grinding jar with one WC ball (5 mm diameter). The jar was closed, sealed with parafilm, placed in the vibratory ball-mill and subjected to grinding for 1.5–3.5 h at 30 Hz. The solid was dissolved in a minimum of dichloromethane and then filtered on Celite. Solvent was reduced to a minimum under reduced pressure, and the solid was precipitated in Et_2O, filtered and washed with Et_2O, and dried under vacuum.

General procedure for the reductive dehalogenation reaction

4-Bromobenzyl 2-chloro-2-phenylacetate **8a** (0.238 mmol, 80.8 mg, 1.0 equiv.), DIPEA (0.472 mmol, 82 μL, 2 equiv.), Hantzsch amide (0.260 mmol, 58.1 mg, 1.1 equiv.), DMAc (130 μL, 0.6 μL mg^{-1}) and catalyst **1** (0.012 mmol, 10.2 mg, 0.05 equiv.) were introduced in a 15 mL grinding jar in epoxy resin with one ZrO_2 ball (1 cm diameter). The jar was loaded, closed and put under an inert atmosphere of N_2. The milling jar was then placed in a vibratory ball-mill and subjected to grinding at 25 Hz under blue LED irradiation for 3.5 h. The mixture was recovered using EtOAc and H_2O and transferred to a separatory funnel (in some cases, toluene or DMAc was also used to recover the reaction mixture from the jar. If so, the recovered mixture was first concentrated *in vacuo* before performing the extraction). The product was extracted twice with EtOAc, and the combined organic phases were then washed with 2 M HCl_{aq} and brine. The organic phase was dried over Na_2SO_4 and concentrated *in vacuo* to afford pure **9a** in 64% yield (46.5 mg, 0.152 mmol). If necessary, flash chromatography on silica gel was performed.

Conclusions

In summary, we developed an expedient mechanosynthesis of photoredox ruthenium catalysts featuring different substituted bipyridines. Complexes $[Ru(N–N)_3](PF_6)_2$ could be obtained in high yields and short reaction times. In comparison with classical solution chemistry, this mechanochemical approach showed higher efficiency, in terms of reaction time and/or yield, with no high boiling point solvent used. The obtained complexes were then evaluated in the photoredox reductive dehalogenation reaction, which is a green alternative to tin-promoted methods, under ball-milling conditions. Photochemical reactions could be performed under solvent-less conditions in short times compared to literature conditions, with a drastic reduction of the solvent used. The use, for the first time, of a milling jar in transparent and chemically resistant epoxy resin allowed working without damaging the material, contrary to what could happen with PMMA. A key feature for a simplified treatment of the reaction mixture was the use of a Hantzsch amide instead of the classically used Hantzsch ester. Hence, acidic washings yielded analytically pure dehalogenated compounds in moderate to high yield.

Data availability

The data supporting this article have been included as part of the ESI.†

Author contributions

Florian Luttringer, Matthieu Lavayssiere, Enita Rastoder: resources (lead); writing – review and editing (equal). Nikita Salov, Tristant Gravelet, François Quintin: resources (equal). Julien Pinaud: conceptualization (equal); funding acquisition (equal). Frédéric Lamaty: conceptualization (equal); funding acquisition; writing – original draft (supporting); writing – review and editing (equal). Xavier Bantreil: conceptualization (equal); funding acquisition (lead); writing – original draft (lead); formal analysis (lead); writing – review and editing (equal).

Conflicts of interest

There are no conflicts to declare.

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