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Oxidative mechanochemistry for direct, room-temperature, solvent-free conversion of palladium and gold metals into soluble salts and coordination complexes**

Jean-Louis Do, Davin Tan, and Tomislav Friščić*

Abstract: Noble metals are valued critical elements whose chemical activation or recycling is challenging, traditionally requiring high temperatures, strong acids or bases, or aggressive complexation agents. Using elementary palladium and gold, we demonstrate mechanochemistry for noble metal activation and recycling *via* mild, clean, solvent-free and room-temperature chemistry, leading to direct, efficient, one-pot conversion of the metals, including spent catalysts, to simple water-soluble salts, or to metal-organic catalysts.

Noble metals are valued for outstanding chemical, catalytic, thermal, electrical and other properties,^[1-9] and many are considered critical due to limited production and specific uses. They are resistant to chemical attack, needing harsh conditions to form soluble derivatives needed for transformations and processing. Examples include *aqua regia*, a 1:3 mixture of concentrated HNO₃ and HCl used as a solvent for activation and dissolution of noble metals, and a variety of methodologies based on harsh and hazardous conditions, from molten salts to cyanide complexation (Figure 1a, top).^[1-3] Thus, the development of effective, milder and environmentally-friendly technologies for activation, processing and recycling of noble metals is an important challenge.^[10] Recent innovations in that context include new organic systems^[3] for dissolving noble metals, and precipitation of KAuBr₄ from aqueous solutions with α -cyclodextrin.^[4]

Mechanochemistry, *i.e.* reactivity induced or conducted by mechanical force, such as ball milling, offers a cleaner, solvent-free alternative to solution reactivity.^[11-16] Metallurgical uses of ball milling for alloying and metal leaching are known,^[17,18] and mechanochemistry was recently used for conversion of base metals (Zn, Mn or Cu) and the critical element germanium into coordination complexes and polymers.^[19,20]

We now demonstrate mechanochemistry for direct, room-temperature, solvent-free conversion of noble metals into water-soluble halide complexes or, by orthogonal oxidative and coordination chemistry, into metal-organic catalysts (Figure 1a, bottom).

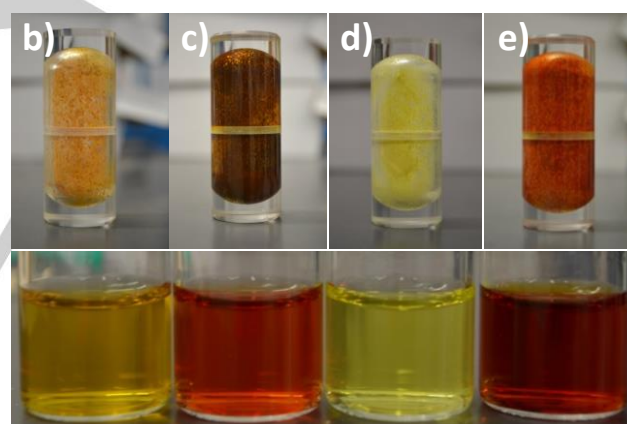
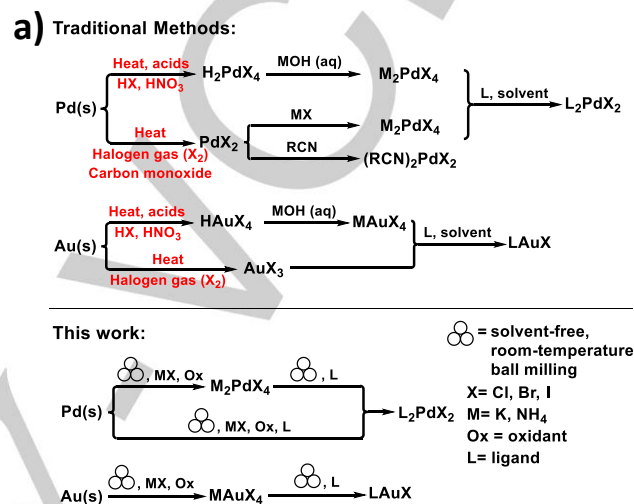


Figure 1. (a) Comparison of routes for Pd and Au oxidation to herein reported method. Symbol for mechanochemical reactivity is adapted from reference 11. Products of mechanochemical Pd and Au oxidation shown in transparent milling jars (middle) and dissolved in H₂O (bottom): (b) (NH₄)₂PdCl₄; (c) (NH₄)₂PdBr₄; (d) NH₄AuCl₄; (e) NH₄AuBr₄.

Focusing on Pd and Au, this study establishes the combination of the mild oxidant Oxone® and halide salts^[21,22] as a reagent for activation of noble metal powder, pellets, or wire, without aggressive solvents or reagents. The procedure is significantly simpler, cleaner and safer than conventional routes for converting the metals into water-soluble or metal-organic complexes (Figure 1b-e).

Oxidative conversion of Pd metal to water-soluble tetrachloropalladate(II) (PdCl₄²⁻) salts was explored by milling with readily available solid oxidants and 4 equivalents of KCl or NH₄Cl as halide sources. Comparing potassium peroxymonosulfate (2KHSO₅·KHSO₄·K₂SO₄, Oxone®), calcium hypochlorite

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(CaCl(OCl)), potassium persulfate ($K_2S_2O_8$), sodium percarbonate ($Na_2CO_3 \cdot 3/2 H_2O$), and sodium perborate ($NaBO_3 \cdot 4H_2O$) demonstrated Oxone® as the most effective, generally applicable oxidant (Table 1, also ESI). CaCl(OCl) and $K_2S_2O_8$ were effective only in presence of NH_4Cl by neat and liquid-assisted grinding (LAG),^[23] respectively, while sodium percarbonate and perborate were not effective. Similarly non-effective were other hydrogen peroxide-based oxidants, e.g. 50% aqueous H_2O_2 and solid urea- H_2O_2 complex. Products were characterized by powder (PXRD) and single crystal X-ray diffraction, 1H - and ^{31}P nuclear magnetic resonance (NMR) and high-resolution mass spectrometry (HR-MS).

Table 1. Results of exploring chloride and oxidant combinations for mechanochemical oxidation of Pd metal.^[a] Each reaction was repeated 10 or more times.

Entry	oxidant	halide salt	liquid additive ^[b]	conversion ^[c]
1	Oxone®	KCl	-	≥95(3)% ^[d]
2	Oxone®	NH_4Cl	-	≥95(1)% ^[d]
3	CaCl(OCl)	KCl	-	-
4	CaCl(OCl)	KCl	-	-
5	CaCl(OCl)	KCl	H_2O	-
6	CaCl(OCl)	KCl	AcOH	0-32%
7 ^[e]	CaCl(OCl)	NH_4Cl	-	15-71%
9 ^[e]	CaCl(OCl)	NH_4Cl	H_2O	43-72%
10 ^[e]	CaCl(OCl)	NH_4Cl	-	≥95(4)%
11	$K_2S_2O_8$	KCl	-	-
12	$K_2S_2O_8$	KCl	H_2O	-
13	$K_2S_2O_8$	KCl	AcOH	-
14	$K_2S_2O_8$	NH_4Cl	-	0-34%
15	$K_2S_2O_8$	NH_4Cl	H_2O	≥95(3)%
16	$K_2S_2O_8$	NH_4Cl	AcOH	-

[a] done using 0.2 mmol Pd, 4 equivalents KCl or NH_4Cl and 1-4 equivalents of oxidant (see ESI); [b] LAG with 25 μL liquid additive; [c] conversion based on gravimetric determination of Pd precipitated with dimethylglyoxime; [d] identical conversions obtained using either 1 or 2 equivalents of Oxone®; [e] reactions by neat milling or LAG (entries 7 and 8) were difficult to reproduce due to poor mixing, resolved by adding 250 wt. % Na_2SO_4 grinding auxiliary (entry 9).

Milling Pd with a mixture of 4 equivalents of KCl and either 1, 1.5 or 2 equivalents of Oxone® (Table 1, also ESI) yielded a product amorphous to PXRD analysis and fully soluble in water. Crystallization from water gave crystals of K_2PdCl_4 , identified by comparison of measured crystallographic unit cell to the published one (see ESI). Milder milling using Teflon jars^[24] enabled the observation of X-ray reflections of K_2PdCl_4 in the diffraction pattern of crude product. Similar results were obtained with NH_4Cl as the halide source, and subsequent solution ^{15}N NMR analysis revealed a single nitrogen environment, consistent with NH_4^+ ions and absence of ammine complexes (see ESI). $PdCl_4^{2-}$ formation was confirmed by XPS bands centered at 338.5-339.4 eV and 343.9-344.4 eV, consistent with Pd $3d_{5/2}$ and $3d_{3/2}$ bands (see ESI). Conversion was quantified gravimetrically via the dimethylglyoxime complex.^[25]

Mechanochemical conversion of Pd to $PdCl_4^{2-}$ was applicable to pellets, wire, powder and even palladium on carbon. The procedure also allowed recovery of "spent" palladium black

catalyst,^[26] which is seldom recycled in the laboratory due to aggressive methods needed. Mechanochemistry enabled the recycling of up to 89% of Pd from palladium black waste which was isolated from a Suzuki coupling reaction, dried and used in the mechanochemical procedure just as bulk palladium.

Mechanochemistry was also applicable to bromides and iodides. Formation of $PdBr_4^{2-}$ with NH_4Br and KBr was verified by PXRD and XPS (see ESI), and the formation of iodide and bromide palladium complexes was also confirmed indirectly by subsequent synthesis of metal-organic complexes characterized by PXRD, HR-MS, ^{31}P -NMR and determination of crystallographic unit cells after recrystallization (see ESI). Efficiency of metal activation using bromides was comparable to that with chlorides, while NH_4I and KI were less effective, yielding the byproduct I_2 (Table 2).

Having identified a reliable mechanochemical route to convert palladium to PdX_4^{2-} salts ($X=Cl, Br, I$), we explored their further conversion into metal-organic catalysts in one-pot manner, without prior isolation or purification. We focused on complexes of bidentate 1,1'-bis(diphenylphosphino)ferrocene (DPPF) and monodentate triphenylphosphine (PPh₃), tricyclohexylphosphine (PCy₃) and tris(pentafluorophenyl)phosphine (PPFP₃) ligands (Scheme 1a). In all cases, adding a slight excess of the ligand to the reaction jar after mechanochemical conversion of Pd to $PdCl_4^{2-}$, followed by another 30 minutes milling, gave the expected **1a-d** (Scheme 1d).

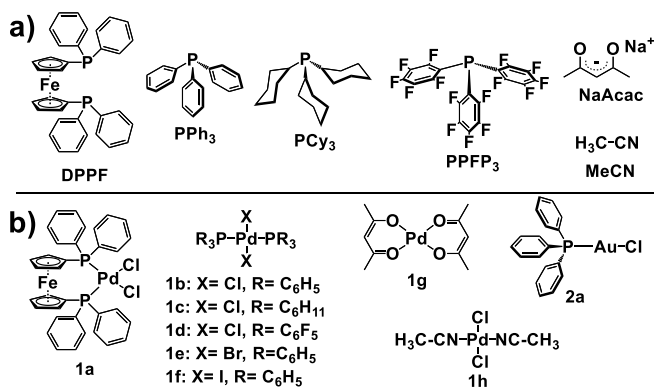
Table 2. Comparison of halide-Oxone® combinations for the oxidation of metallic Pd and Au by 30 minutes milling with 4 equivalents of a halide salt.^[a] Each reaction was repeated 10 or more times.

Entry	metal	metal:Oxone® ratio	halide salt	conversion (%) ^[b]
1	Pd	1:2	KCl	≥95(3)%
2	Pd	1:2	NH_4Cl	≥95(1)%
3	Pd	1:2	KBr	≥95(1)%
4	Pd	1:2	NH_4Br ^[c]	35-78%
5	Pd	1:2	NH_4Br ^[d]	≥95(4)%
6	Pd	1:2	KI	90(3)%
7	Pd	1:2	NH_4I ^[e]	86(5)%
8	Au	1:3	KCl	≥95(3)%
9	Au	1:3	NH_4Cl	≥95(2)%
10	Au	1:3	KBr	≥ 93(2)%
11	Au	1:3	NH_4Br	≥95(4)%

[a] done using 0.2 mmol Pd or 0.1 mmol Au, by milling at 30 Hz; [b] conversion based on gravimetric determination of Pd dimethylglyoxime complex, and Au metal; [c] used as received; [d] dried prior to use.

Formation of these complexes represents the first example of a telescoping^[27] mechanochemical process starting from an elementary metal. Complexes were soluble in acetone, THF, CH_2Cl_2 or $CHCl_3$, enabling simple, high-yielding separation from ionic byproducts ($KHSO_4$, K_2SO_4) of Oxone® reduction by dissolution and filtration. Formation of **1a-d** was confirmed by HR-MS and solution ^{31}P NMR spectra of dissolved crude material (see ESI).

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Scheme 1. a) Ligands and b) prepared coordination complexes.

Complexes **1a-d** were also characterized by PXRD and analysis of crystallographic unitcell parameters by single crystal X-ray diffraction after recrystallization (see ESI), revealing a previously not known trigonal polymorph of **1d** (Figure 2).^[28] The bromide and iodide complexes Pd(PPh₃)₂Br₂ (**1e**) and Pd(PPh₃)₂I₂ (**1f**) were also obtained in 90% and 72% isolated yields by using bromide and iodide salts in the first mechanochemical step.

The telescoping procedure was also applicable to making palladium(II) acetylacetonate (**1g**), a popular precursor in palladium chemistry, in 90% isolated yield, by replacing phosphines with sodium acetylacetonate (NaAcac). Stability of NaAcac to oxidation enabled a high-yielding (up to 91%) synthesis of **1g** in a single step, by milling the halide salt, Pd metal, Oxone® and NaAcac. Similarly, the complex Pd(MeCN)₂Cl₂ (**1h**) was prepared in 91% yield in a one pot, one-step process by milling palladium, Oxone®, and a chloride salt with acetonitrile (MeCN). Both **1g** and **1h** were characterized by MS, PXRD, and solution ¹H- and ¹³C-NMR analysis.

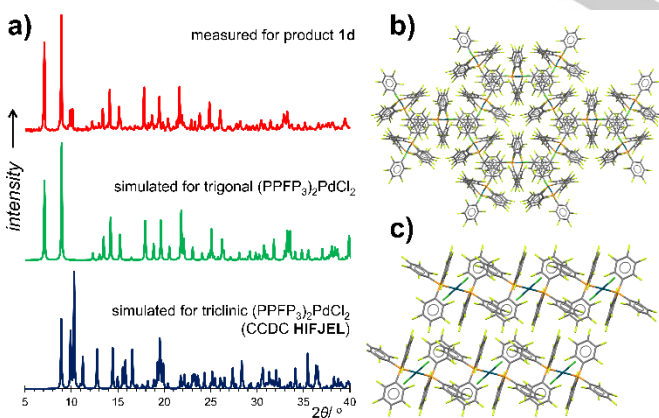
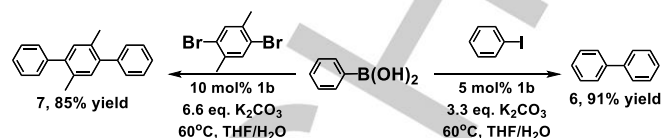


Figure 2. Comparison of trigonal **1d** to the monoclinic form (CCDC HIFJEL): (a) experimental (top) and simulated PXRD data (middle, bottom). Structures of: b) trigonal and c) monoclinic polymorphs of **1d** viewed along the crystallographic c-axis.

To demonstrate catalytic activity of mechanochemically made complexes, **1b** was separated from the reaction mixture by

dissolving in THF followed by filtration, and immediately used as a catalyst for Suzuki coupling reactions to form biphenyl and terphenyl products **6** and **7**, respectively (Scheme 2). Yields were comparable to the literature ones.^[29]



Scheme 2. Suzuki coupling reactions used for investigating catalytic activity of as-synthesized **1b**.

Milling Au with a mixture of Oxone® and KCl or NH₄Cl gave fully water-soluble products (Figures 1b-e, 3a). Characterization of the freshly prepared crude reaction mixtures by PXRD revealed Bragg reflections consistent with KAuCl₄ and NH₄AuCl₄ (see ESI). The analysis of crude mechanochemical reaction products by XPS revealed the formation of Au(III) species with NH₄Cl, KCl, NH₄Br or KBr, evidenced by 4f_{7/2} and 4f_{5/2} bands centered at 87.0-87.9 eV and 90.7-91.5 eV (see ESI).^[30] Variable amounts of Au(I) were also detected, due to degradation upon storage before XPS analysis, identified by the 4f_{7/2} and 4f_{5/2} bands centered at 85.0-85.5 eV and 88.9-89.9 eV, respectively. Conversion was evaluated by reduction to the metal and gravimetric analysis.^[31]

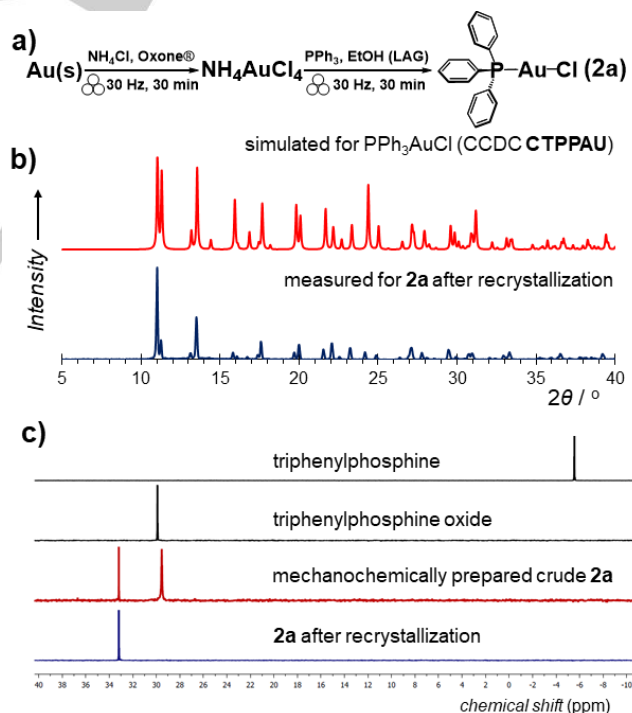


Figure 3. a) One-pot synthesis of **2a** from Au metal and corresponding b) PXRD and c) solution ³¹P-NMR data.

The mechanochemical oxidative activation of Au was coupled with a second mechanochemical step to yield a well-defined

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complex (Figure 3a). This was done by adding excess **PPh₃**, followed by further 30 minutes milling with ethanol. The **PPh₃** acted as both a reducing and a complexation agent, yielding the complex Au(**PPh₃**)Cl (**2a**) and triphenylphosphine oxide. Reduction of Au(III) to Au(I) was evident by change of the reaction mixture color to white, and formation of **2a** was verified by HR-MS of the crude reaction mixture. The complexation of **PPh₃** and formation of triphenylphosphine oxide were evident by ³¹P-NMR spectroscopy in CDCl₃ (Figure 3). Compound **2a** was separated by washing with diethylether and recrystallization from CHCl₃ (Figure 3), or by washing with water to remove Oxone® byproducts.

Due to the cost of palladium and gold, all reactions were done at 0.2 mmol scale. We have also demonstrated scale-up to at least 2 mmol for palladium metal: purified **1d-f** were obtained in 87% (1.42 g of (PPh₃)PdCl₂·CHCl₃), 81% (1.47 g of (PPh₃)PdBr₂·CHCl₃) and 69% (1.38 g of (PPh₃)PdI₂·CHCl₃) yields, respectively (see ESI).

Preliminary results also reveal 56% conversion of platinum into (NH₄)₂PtCl₆ with Oxone® and NH₄Cl (see ESI), as well as potential for metal separation: milling three-component mixtures of Pd, Pt and Au in approximate 1:2:1 molar ratios with limited Oxone® and NH₄Cl led to selective dissolution of only Pd and Au. Depending on the milling conditions, activation of Au is preferred by 2 or 3 times to Pd (see ESI).

In summary, we demonstrated mechanochemistry for simple, rapid and safe conversion of palladium and gold into water-soluble, well-defined salts. A second mechanochemical step enables one-pot transformation of noble metals into well-defined, catalytically active complexes. To the best of our knowledge, this is the first strategy for noble metal activation and recycling that is solvent-free, avoids harsh oxidative or complexation reagents, and proceeds at room temperature. The halides used for this mechanochemical process are readily available (NH₄Cl, KCl) and inexpensive, particularly compared to the end product,^[32] and the oxidant is stable on storage, chemically similar to those already used in solution.^[33] Although the solid-state procedure generates sulfate byproducts of Oxone® reduction, it offers promise for replacement of aggressive HNO₃, *aqua regia*, molten salts or cyanides. Further work on generality, scalability and selectivity is ongoing.

Experimental Section

Details of all experiments, diffraction, and spectroscopic data are given in the Electronic Supplementary Information (ESI). In a general procedure, mechanochemical reactions were done on a Retsch MM400 mill operating at 30 Hz, using a ZrO₂ grinding assembly (10 mL jar, one 10 mm diameter ball of 3.5 g). Palladium or gold metal, a halide salt, an oxidant, and an optional liquid additive were milled for 30 minutes. For two-step, one-pot reactions, the ligand and a liquid additive were then added, and the reaction milled for 30 minutes more. The products were purified by standard recrystallization and chromatographic techniques. Crystallographic data for trigonal **1d** were deposited with the Cambridge Crystallographic Data Centre, deposition code CCDC 1564633.

Keywords: mechanochemistry • noble metals • green chemistry • sustainability • coordination chemistry

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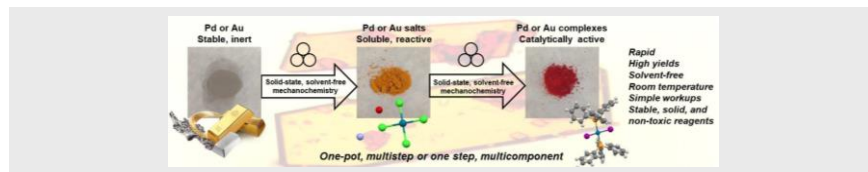
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Oxidative mechanochemistry for direct, room-temperature, solvent-free conversion of palladium and gold metals into soluble salts and coordination complexes

Solvent-free mechanochemistry enables the rapid, direct, room-temperature transformation or recycling of noble metals gold and platinum into water-soluble salts or catalytic complexes, without need for aqua regia or aggressive complexation agents.