Green Chemistry

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Green Chem.*, 2024, **26**, 3146

Received 11th January 2024,
Accepted 9th February 2024

DOI: 10.1039/d4gc00151f

rsc.li/greenchem

Recycling organoiridium waste to [(1,5-cyclooctadiene)IrCl]$_2$†

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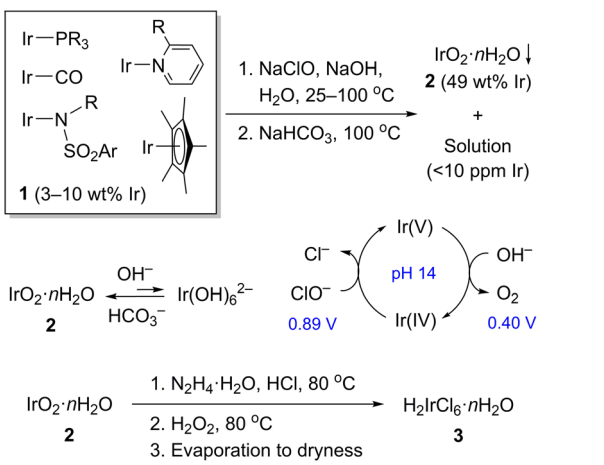
We report the first process for iridium element recovery from organoiridium waste that is quantitative, pyrolysis-free, and generates no iridium metal. The key step is oxidative degradation of the waste by bleach to crude iridium(IV) hydroxide. Its treatment with hydrazine and then hydrogen peroxide gives synthetically important hexachloroiridic acid, which is converted to [(1,5-cyclooctadiene)IrCl]$_2$ in 87% yield.

Iridium is a rare element with the estimated abundance in the Earth's crust of 1 ppb and the scale of worldwide production of only 7–8 tons a year,[1,2] yet it is in high demand for its many unique catalytic applications.[3] Since its supply is limited and demand is growing, it is crucial to have a sustainable process for its recovery from industrial and laboratory secondary sources. A few methods are known for iridium recovery,[4–6] all utilize pyrolysis and calcination of the waste materials to produce the free metal, and further processing of metallic iridium is associated with a number of problems. Particularly, iridium metal is exceptionally resistant to all known "wet" oxidants, even in the powder form.[7] Practically, this is surmounted by chlorination with Cl_2/NaCl (625 °C),[8] fusion with BaO_2 (750 °C),[9] or alkaline fusion with Na_2O_2/NaOH (600–700 °C).[10,11] These suffer from incomplete conversion, reactor corrosion, and the need for a special equipment to operate at such temperatures. R&D-scale users of iridium who develop new reactivity and processes face high metal cost and can currently satisfy our desire to conserve the metal only by returning iridium-containing waste to a large-scale recycler, but only when one can be found. In this work we address these problems with a simple protocol for iridium recycling from its waste solutions that circumvents generating the metal and is suitable for implementation using common laboratory equipment.

Over several years our research group has accumulated a substantial amount of organoiridium waste, which consisted of iridium complexes mostly with carbonyl, polydentate phosphine, pyridine, amide, NHC, and η^5-Cp* ligands dissolved in a mixture of common solvents and exposed to air. These resulted from development of reactions for lactate synthesis,[12,13] alcohol dehydrogenation,[14] H_2 generation from formic acid,[15,16] and ketone hydrogenation[17,18] among others (Fig. S9†). The waste contained considerable amounts of sodium and potassium salts (of CO_3^{2-}, HCO_2^-, $CF_3SO_3^-$, and PF_6^-) but no transition metals other than iridium. Initially, all volatile components were removed to leave a semi-solid residue (**1**) containing 3–10 wt% of iridium (Scheme 1).

As an alternative to pyrolysis, we accomplished oxidative degradation of **1** using a household solution of NaClO (7.5 wt%). This choice was justified by the facts that it is a cheap, green, and extremely powerful oxidant. Oxidation in an acidic solution was not a practical approach on our hands: these conditions give persistent organic derivatives of Ir(IV) rather than converging the system to the desired $IrCl_6^{2-}$. By



Scheme 1 Processing organoiridium waste.

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† Electronic supplementary information (ESI) available: Experimental procedures and characterization data (PDF). See DOI: https://doi.org/10.1039/d4gc00151f

contrast, **1** is successfully oxidized in 1–3 M NaOH solution to insoluble and highly stable iridium(IV) hydroxide, $IrO_2{\cdot}nH_2O$ (**2**, Scheme 1).[19,20] The waste (**1**) is processed as a semi-solid or a solution in CH_2Cl_2 to enable a good mass transfer. The reaction proceeds for one day at room temperature and then is driven to completion by heating briefly with added NaClO at 90–100 °C. Reaction completion is detected visually by two key features: (1) black hydroxide **2** is suspended in a yellow solution of $Ir(OH)_6^{2-}$. In a strongly alkaline media, iridium(IV) exists primarily as a mixture of **2** and $Ir(OH)_6^{2-}$ with the equilibrium favoring the former. Full dissolution to $Ir(OH)_6^{2-}$ requires hydrothermal conditions (20 M NaOH, 200 °C),[21] while full hydrolysis to **2** happens readily at pH 7–9. (2) Adding a fresh portion of NaClO to the completed reaction actively evolves O_2 at 70–100 °C. Once all reducing components are gone, an iridium-catalyzed decomposition of unreacted ClO^- begins.[22,23] The standard potentials of couples ClO^-/Cl^- (0.890 V) and O_2/OH^- (0.401 V *vs.* SHE)[24] are also consistent with the spontaneous reaction: $2ClO^- \rightarrow 2Cl^- + O_2$.

During the oxidation we observe reversible color changes indicative of Ir(V)/Ir(IV) redox transitions. In a control experiment, a yellow solution of $Ir(OH)_6^{2-}$ reacts with NaClO at 70 °C turning brown at first, then suddenly evolving O_2, and turning back to yellow within a few seconds. The sequence can be repeated multiple times suggesting a catalytic behavior of the brown species, apparently iridium(V) (Scheme 1). Although the existence of a transient iridium(V) species has been demonstrated in 2 M $HClO_4$,[25] nothing is known about its stability at pH 14. The transient pentavalent iridium could be involved also catalytically in degradation of organic ligands associated with the metal in mixture **1**. The oxidized organics seem to be completely water-soluble, thus facilitating the separation of **2**.

Quantitative precipitation of **2** was achieved by buffering the reaction mixture with excess of solid $NaHCO_3$ at 100 °C (Scheme 1). During this step, $Ir(OH)_6^{2-}$ is fully hydrolyzed to **2**. Once the precipitate settles (Fig. S1-C†), a colorless supernatant contains less than 10 ppm iridium, as determined by atomic emission spectroscopy (ICP-OES, Fig. S7†). Sometimes, **2** may form intensely colored colloid solutions because of a slow and incomplete hydrolysis of $Ir(OH)_6^{2-}$ (Fig. S2†). Fortunately, these colloids can be easily converted to solid **2** by the repeated oxidation (NaClO/NaOH) and buffering steps ($NaHCO_3$).

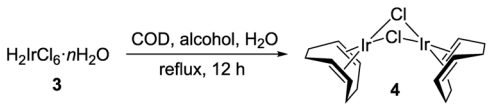
Material **2** is amorphous by powder X-ray diffraction. Its iridium content was established gravimetrically by means of $Cs_2[IrCl_6]$ as 49.0 wt%, which corresponds to net composition of $IrO_2{\cdot}9.3H_2O$. Unfortunately, the sample cannot be qualified as pure, since it contains up to 2.9 wt% of carbon revealed by the combustion analysis. The carbon content is not changed after treatment with aqueous HCl, suggesting a contamination by non-volatile organics rather than carbonate. Despite the impurity, **2** is easily used in the next steps.

Samples of **2** are resistant to mineral acids, therefore, we utilize a redox approach to convert these to a water-soluble form. A facile dissolution is possible in 6 M HCl in the presence of hydrazine (80 °C, 10 min, Fig. S3-A†). The resulting solution contains a mixture of iridium(III) aqua-chloride complexes rather than simple $IrCl_6^{3-}$, since its UV-Vis absorption bands at 415 and 356 nm were not detected.[26] Hydrogen peroxide is then added (80 °C, 10 min) to destroy the excess of hydrazine and oxidize Ir(III) to orange-black $IrCl_6^{2-}$ (Fig. S3-B†). Its formation was confirmed by UV-Vis spectroscopy: the characteristic bands were observed at 412, 428, and 486 nm (Fig. S8†).[27] Subsequent careful evaporation gives a brown-black crystalline hexachloroiridic acid, $H_2IrCl_6{\cdot}nH_2O$ (**3**, Fig. S3-C†), which was used without purification.[28] It is worth noting that excessive heating brings a partial reduction of **3** to Ir(III) chlorides, though not impactful in our case, this process might be detrimental in alternative iridium recycling schemes.

By far, compound **3** is one of the most common precursors for synthetic chemistry involving iridium. Hence, our recycling approach can be utilized to prepare a spectrum of its derivatives. To demonstrate, we synthesized [(1,5-cyclooctadiene)IrCl]$_2$ (**4**) from **3** following a modified reported procedure (Table 1).[29–31] The reaction involves reduction of **3** in a boiling alcohol solvent in the presence of 1,5-cyclooctadiene ligand. Air-sensitivity of **4** in solutions is well-known,[31] therefore, the synthesis and isolation were conducted under oxygen-free conditions. Clean **4** was obtained in 87% yield using isopropanol, while the balance of iridium (13%) was recovered as $Cs_2[IrCl_6]$ after workup (entry 3). Surprisingly, when $Cs_2[IrCl_6]$ is used as a source of iridium in this reaction, only half of it converts to **4** (Table 1, entry 4). The balance persists as beige, insoluble $Cs_3[IrCl_6]$ (calc'd 26.5%, found 28.2% Cl). An analytically pure sample of **4** was obtained after slow crystallization from CH_2Cl_2/hexane (Fig. S4-C†). Finally, the identity of **4** was confirmed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy (Fig. S5 and S6†)[32] and the combustion analysis.

In conclusion, we developed a pyrolysis-free process for quantitative iridium recovery from laboratory-generated organoiridium waste that represents the first route available to R&D-scale iridium users. This was essential to our lab, because unlike rhodium, palladium, and ruthenium, we could find no commercial vendor who would recycle our iridium waste. The crucial steps of the process are the oxidative degradation of the waste and the redox dissolution of hydroxide **2**. We show the

Table 1 Synthesis of complex **4** [a]



Entry	Ir source	Alcohol	Yield of **4**, %	Recovered Ir,[b] %
1	**2** (0.5 g) → **3**	EtOH	87	—
2	**2** (1.5 g) → **3**	EtOH	83	17
3	**2** (1.5 g) → **3**	i-PrOH	87	13
4	$Cs_2[IrCl_6]$ (3.6 g)	i-PrOH	49	50

[a] Conditions: **3** or $Cs_2[IrCl_6]$ (3.8 mmol), 1,5-cyclooctadiene (6 mL), alcohol (10 mL), and water (10 mL) were refluxed under N_2 for 12 h. [b] Solid leftover materials were treated with hot aqua regia and then with CsCl in a minimum amount of water to form insoluble $Cs_2[IrCl_6]$.

practicality of our method by recovering iridium as synthetically important complex **4**. Compounds **2**, **3**, and **4** require minimal to no purification. Because of its low cost and high simplicity, the process enables a very convenient way to reduce metal costs and protect this very precious natural resource. Overall, this route enables a very important option for sustainable use of iridium in laboratory practice and has potential to facilitate iridium recovery on industrial scale.

Author contributions

Conceptualization, data curation, formal analysis, investigation, methodology, project administration, validation, visualization, writing – original draft: V. C. Funding acquisition, resources, supervision, writing – review & editing: T. J. W.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work is sponsored by the US Department of Energy (DE-EE0008825). We thank the NSF (CHE-2018740, DBI-0821671, CHE-0840366), the NIH (S10 RR25432), and USC Research and Innovation Instrumentation Awards for analytical tools.

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