COMMUNICATION

Recycling Organoiridium Waste to $[(1,5\text{-Cyclooctadiene})IrCl]_2$

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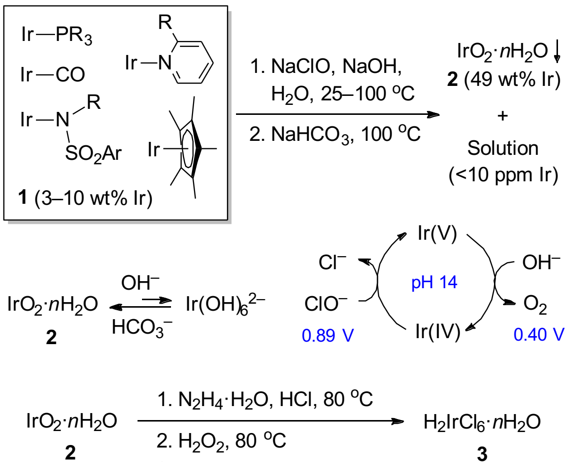
We report the first process for iridium element recovery from organoiridium waste that is quantitative, pyrolysis-free, and generates no iridium(0) metal. The key step is oxidative degradation of the waste by bleach to crude iridium(IV) hydroxide. Its treatment with hydrazine and then hydrogen peroxide gives synthetically important hexachloroiridic acid, which is converted to $[(1,5\text{-cyclooctadiene})IrCl]_2$ 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 (Figure 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

Scheme 1 Processing Organoiridium Waste



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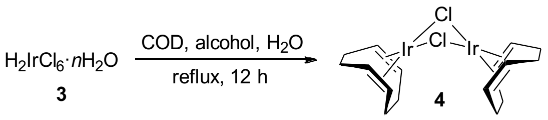
Electronic Supplementary Information (ESI) available: Experimental procedures and characterization data (PDF). See DOI: 10.1039/x0xx00000x was not a practical approach on our hands: these conditions give persistent organic derivatives of Ir(IV) rather than converging the system to the desired $IrCl_6^{2-}$. By 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 also catalytically involved 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 (Figure S1-C), a colorless supernatant contains less than 10 ppm iridium, as determined by atomic emission spectroscopy (ICP-OES, Figure S7). Sometimes, **2** may form intensely colored colloid solutions because of a slow and incomplete hydrolysis of $Ir(OH)_6^{2-}$ (Figure 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.

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 $Cs_2[IrCl_6]$.

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, Figure 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 $IrCl_6^{2-}$ (Figure S3-B). Its formation was confirmed by UV-Vis spectroscopy: the characteristic bands were observed at 412, 428, and 486 nm (Figure S8).[27] Subsequent careful evaporation gives a brown-black crystalline hexachloroiridic acid, $H_2IrCl_6 \cdot nH_2O$ (**3**, Figure 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 $[(1,5\text{-cyclooctadiene})IrCl]_2$ (**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 (Figure S4-C). Finally, the identity of **4** was confirmed by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy (Figures 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 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.

Acknowledgments

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Supporting Information

Recycling Organoiridium Waste to [(1,5-Cyclooctadiene)IrCl]$_2$

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Materials and Methods

Hexane and CH_2Cl_2 were dried using a JC Meyer solvent purification system. All other reagents and solvents were purchased from commercial sources as cited and used without purification. Deionized water was sourced from VWR Chemicals.

All manipulations with $[(1,5\text{-cyclooctadiene})IrCl]_2$ were performed under nitrogen using Schlenk technique or in a Vacuum Atmospheres glovebox (0−10 ppm O_2). ^1H and ^{13}C NMR spectra were recorded in 8″ J. Young tubes with Teflon valves on Varian Mercury 400 and VNMRS-500 spectrometers and processed with MestReNova 12.0.1. All chemical shifts are reported in ppm and referenced to solvent peaks. Elemental analyses were conducted on Flash 2000 CHNS Elemental Analyzer. Electronic absorption spectra were acquired on Perkin-Elmer UV-vis-NIR spectrometer. Analyses of residual iridium were performed on Thermo ICP-OES 7000 Spectrometer. X-ray powder diffraction test was done on Rigaku Miniflex powder diffractometer.

Oxidation of Organoiridium Waste to $IrO_2{\cdot}nH_2O$

$$2IrX_3 + ClO^- + 10OH^- + H_2O = 2Ir(OH)_6^{2-} + Cl^- + 6X^-$$

$$Ir(OH)_6^{2-} + 2HCO_3^- + (n-4)H_2O = IrO_2{\cdot}nH_2O + 2CO_3^{2-}$$

A solution of organoiridium waste in a mixture of solvents (CH_2Cl_2, ether, acetone, hexane, toluene, etc.) was evaporated under reduced pressure to give a brown paste (**1**, 13.4 g, 10 wt% Ir)[1], which was first emulsified with NaOH solution (Macron Fine Chemicals, 5 M, 100 mL, Figure S1-A) and then treated with a household solution of NaClO ("Germicidal Bleach", First Street, 7.5 wt%, 100 mL). During the hypochlorite addition the emulsion turns black due to formation of $IrO_2{\cdot}nH_2O$ (**2**, Figure S1-B). The resulting mixture was stirred at 25 °C for one hour and then extra 100 mL of NaClO was added. The next day, the mixture was heated to 90–100 °C and extra NaClO (100 mL) was added in small portions at stirring.[2] When O_2 evolution stopped, pH was brought to 7–8 by adding solid $NaHCO_3$ (Macron Fine Chemicals).[3] After stirring the mixture at 95–100 °C for 5 min it was allowed to cool. The next day, fully-settled black precipitate (Figure S1-C)[4] was filtered on a Buchner funnel, washed thoroughly with deionized water, then with acetone, and air-dried on the filter. Finally, a bluish-black powder of crude **2** was dried in a vacuum desiccator over KOH (VWR Chemicals) for 3 days. Yield: 2.80 g.

Anal. calcd. for $Ir(OH)_4$: Ir, 73.86; C, 0.00; H, 1.55. Found: Ir, 48.96; C, 2.90; H, 1.82.

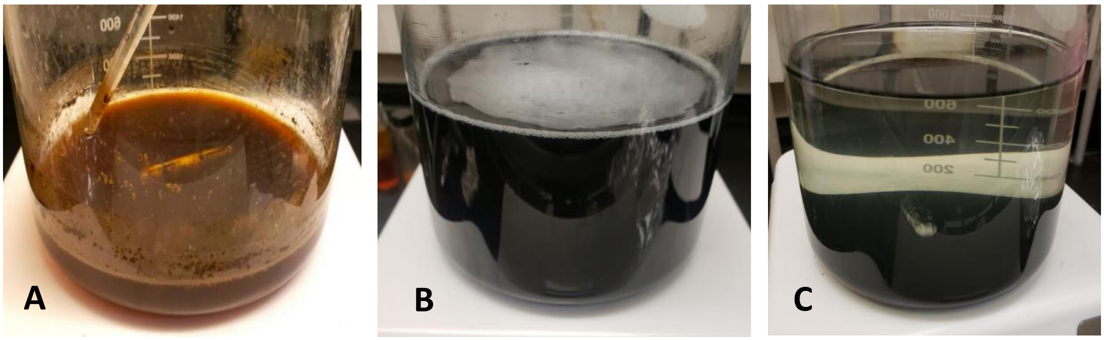

Figure S1. Oxidation of organoiridium waste: emulsion of the waste (A), oxidation in progress (B), full precipitation of **2** (C).

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[1] If the residue is solid, it is redissolved in minimum amount of CH_2Cl_2 to ensure good mass transfer and full oxidation.

[2] Caution: active evolution of O_2! Hypochlorite degradation ($2ClO^- = O_2 + 2Cl^-$) catalyzed by **2** and $Ir(OH)_6^{2-}$ is slow at 25 °C and fast at heating. It indicates full consumption of easily oxidized components in the solution.

[3] The full hydrolysis of $Ir(OH)_6^{2-}$ to **2** was monitored using universal pH paper.

[4] Sometimes colored colloid solutions of **2** (Figure S2, A-C) are formed due to incomplete hydrolysis of $Ir(OH)_6^{2-}$. In this case, the colloid is converted to $Ir(OH)_6^{2-}$ (Figure S2-D) with NaClO (pH 14, 90 °C) and then buffered with $NaHCO_3$ (pH 8, 90 °C) to precipitate **2**.

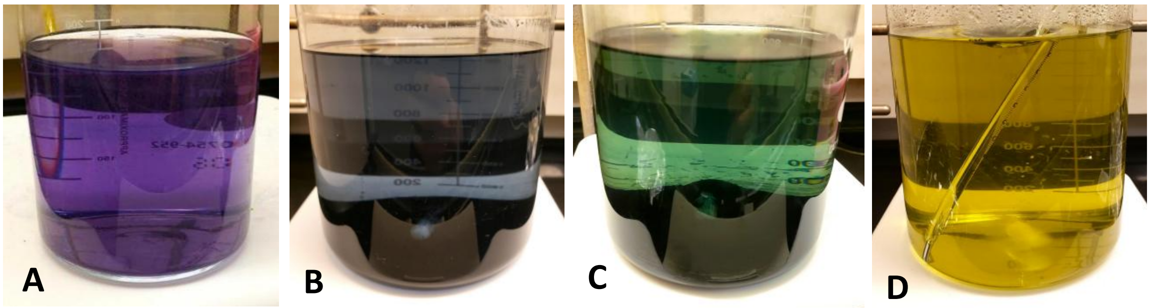

Figure S2. Examples of colloid solutions of **2** (A–C) and a solution of $Ir(OH)_6^{2-}$ (D).

Safety Note

Combination of bleach with CH_2Cl_2 could potentially generate phosgene, Cl_2CO. Under our alkaline conditions, this would rapidly hydrolyze to carbonate and chloride; still, this operation should be conducted in a fume hood or with appropriate ventilation. Bleach should not be combined with CH_2Cl_2 under acidic or aprotic conditions.

Conversion of $IrO_2\cdot nH_2O$ to $H_2IrCl_6\cdot nH_2O$

$$4IrO_2\cdot nH_2O + N_2H_5^+ + 12HCl = 4\text{”}IrCl_3\text{“} + N_2 + (4n+8)H_2O + H^+$$

$$(N_2H_5^+ + 2H_2O_2 = N_2 + 4H_2O + H^+)$$

$$2\text{”}IrCl_3\text{“} + 6HCl + H_2O_2 = 2H_2IrCl_6 + 2H_2O$$

$$(2HCl + H_2O_2 = Cl_2 + 2H_2O)$$

$$(2H_2O_2 = O_2 + 2H_2O)$$

The following synthesis was conducted in a well-ventilated fume hood. A solution of hydrazine monohydrate (Oakwood Chemical, 0.386 g) in water (2 mL) was added to a suspension of **2** (1.500 g, 49 wt% Ir) in aqueous HCl (EMD Millipore, 6 M, 40 mL) in an Erlenmeyer flask. The mixture was stirred on a hot plate at 80 °C for 10 min, during which the black hydroxide dissolved, and the solution turned orange-brown due to formation of Ir(III) chloride complexes (Figure S3-A). Then, hydrogen peroxide solution (EMD Millipore, 30 wt%, 3 mL) was added dropwise to the stirred hot mixture (*Caution: active evolution of* N_2). A sudden blackening indicates a full oxidation of hydrazine and initial oxidation of Ir(III) to Ir(IV). After adding all peroxide, the heating was continued until the gas evolution stopped (80 °C, 10 min). The solution of H_2IrCl_6 (Figure S3-B) was cooled to room temperature, filtered if necessary, and transferred to a beaker. Then, it was evaporated to dryness on a hot plate or a water bath. To remove traces of HCl, the residue was redissolved in water and evaporated again. The resulting dark-brown crystalline $H_2IrCl_6\cdot nH_2O$ (**3**, Figure S3-C) was used without purification.

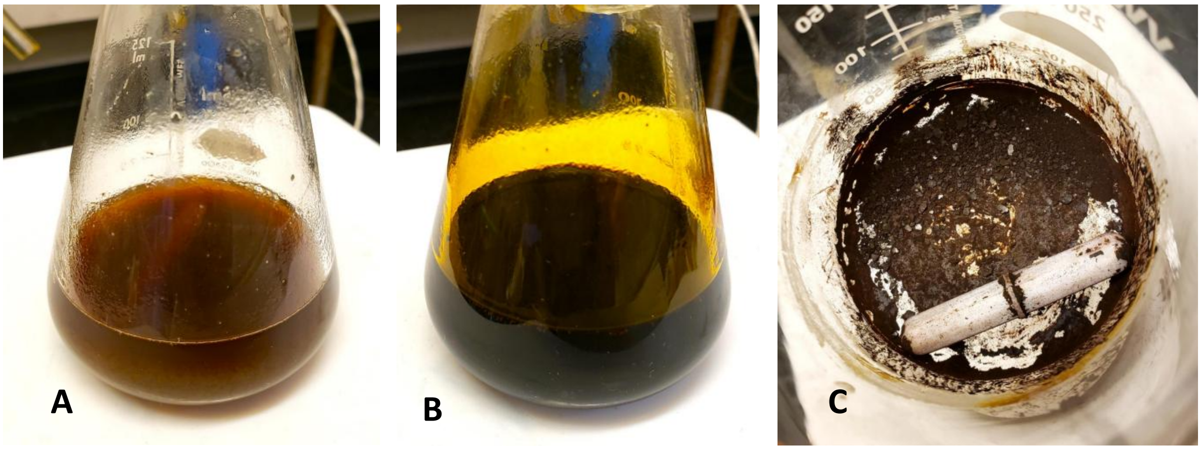

Figure S3. Synthesis of **3**: solution of Ir(III) (A), solution of H_2IrCl_6 (B), and solid **3** (C).

Synthesis of [(1,5-Cyclooctadiene)IrCl]$_2$

$$2H_2IrCl_6 + 3(CH_3)_2CHOH + 2COD = Ir_2Cl_2(COD)_2 + 3(CH_3)_2CO + 10HCl$$

A 100 mL Schlenk flask was charged with **3** (prepared from 1.500 g of **2**), 1,5-cyclooctadiene (Aldrich Chemical Co., 6 mL, 49 mmol), 2-propanol (VWR Chemicals, 10 mL), and DI water (10 mL). The mixture was heated at reflux under nitrogen for 12 hours resulting in bright-red and orange phases (Figure S4-A). The following steps were performed in a glovebox, since the solutions of [(1,5-cyclooctadiene)IrCl]$_2$ (**4**) readily react with oxygen. The reaction mixture was concentrated in vacuum to ca. 10 mL, and then the organics were extracted with CH_2Cl_2. The extract was dried over Na_2SO_4, then filtered, and evaporated to give a solid mixture of yellow and red polymorphs of the product. The solid was triturated with hexane (10 mL), then filtered on a Buchner funnel, washed with hexane, and dried on the filter (932 mg). More product (175 mg) was collected from the filtrate after its evaporation and washing away oily impurities with hexane (3 × 1 mL). Compound **4** was obtained as an orange crystalline solid (Figure S4-B). Yield: 1.107 g (87%). Analytically pure product was slowly crystallized from CH_2Cl_2/hexane solution (Figure S4-C).

The remaining iridium in the synthesis (13%) was recovered as $Cs_2[IrCl_6]$ (322 mg) after treating all iridium-containing leftover materials (in the solid form) with hot aqua regia and CsCl in a minimum amount of water.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.32–4.14 (m, 4H, CH), 2.34–2.15 (m, 4H, CH_2), 1.62–1.44 (m, 4H, CH_2).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 62.36 (s, CH), 31.94 (s, CH_2).

Anal. calcd. for $IrClC_8H_{12}$: C, 28.61; H, 3.60. Found: C, 28.63; H, 3.19.

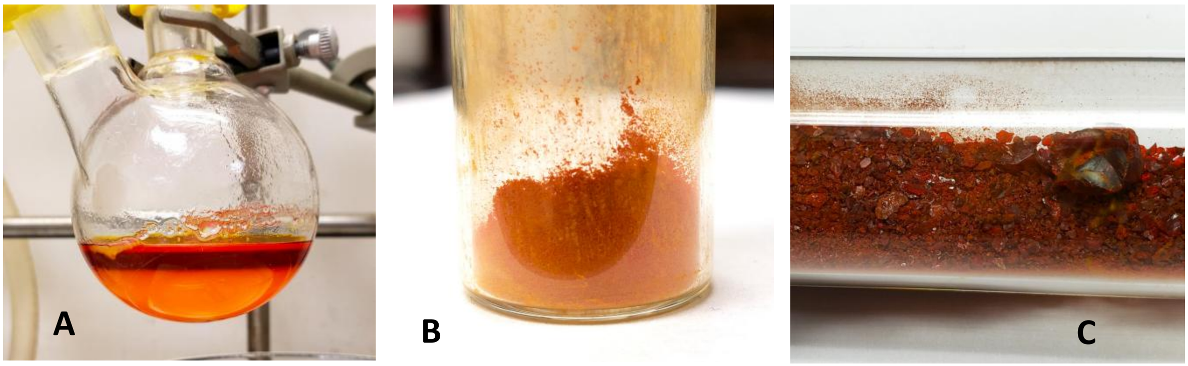

Figure S4. Synthesis of complex **4**: reaction mixture (A), isolated product (B), and recrystallized product (C).

NMR Spectroscopy

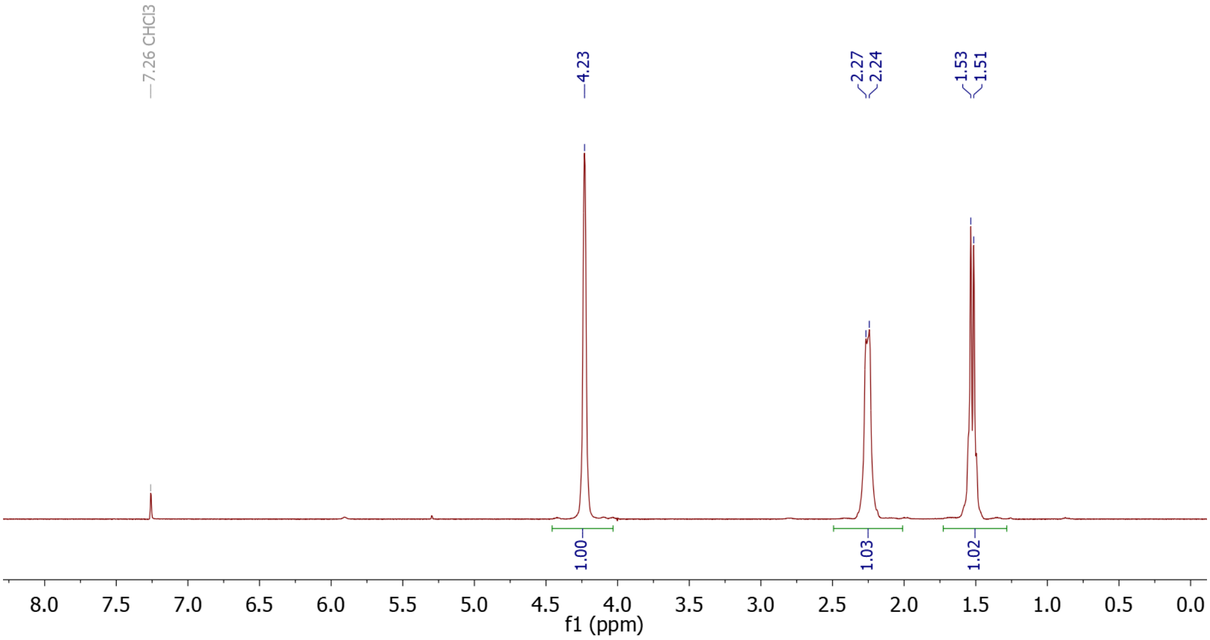

Figure S5. ^{1}H NMR spectrum of complex **4** in $CDCl_3$.

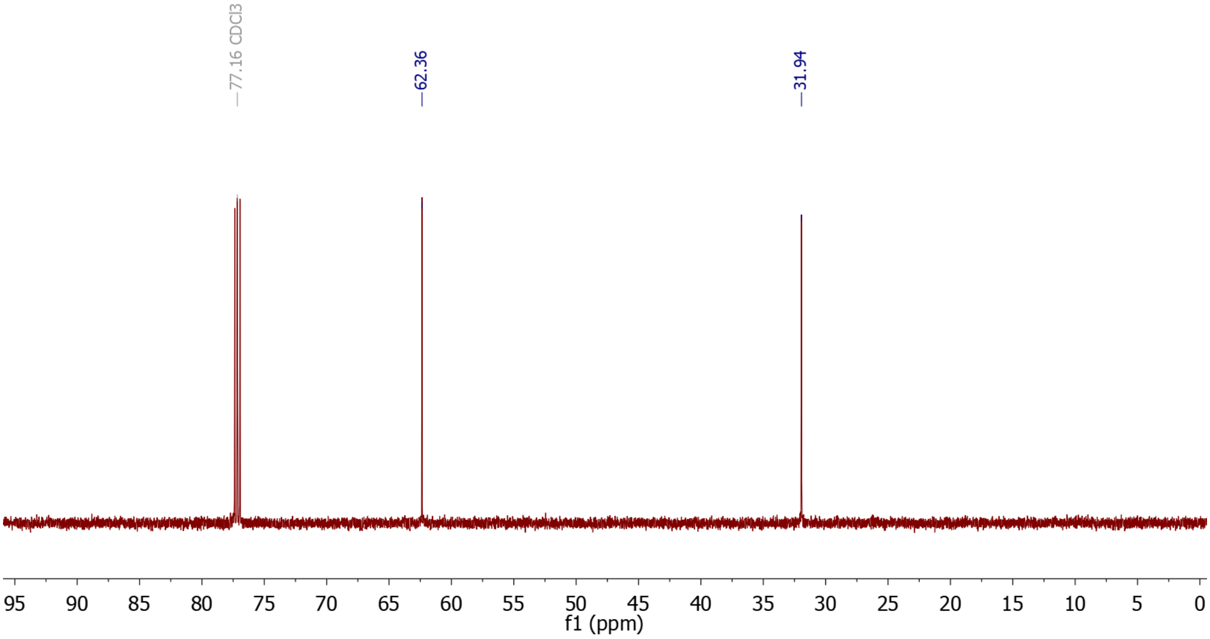

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of complex **4** in $CDCl_3$.

Determination of Residual Iridium by ICP-OES

The filtrates obtained after separating **2** were analyzed by ICP-OES to determine the residual concentration of iridium (Table S1, entries 7–9). The analysis was conducted at the iridium emission wavelengths of 224.268 and 212.681 nm. The concentration of iridium varies within the range (1.52–3.75)×10^{-5} M.

Table S1. ICP-OES data

Entry	Concentration of iridium			224.268 nm, cps	212.681 nm, cps
	mol/L	g/L	ppm		
Standards:					
1	5.20×10^{-4}	1.00×10^{-1}	97.8	4,066	3,686
2	2.60×10^{-4}	5.00×10^{-2}	48.9	2,055	1,856
3	1.04×10^{-4}	2.00×10^{-2}	19.6	903	816
4	5.20×10^{-5}	1.00×10^{-2}	9.78	460	412
5	2.60×10^{-5}	5.00×10^{-3}	4.89	227	204
6	5.20×10^{-6}	1.00×10^{-3}	0.978	46	41
Samples:					
7	3.75×10^{-5}	7.22×10^{-3}	7.06	334	301
8	1.52×10^{-5}	2.92×10^{-3}	2.86	161	146
9	2.68×10^{-5}	5.16×10^{-3}	5.05	251	229

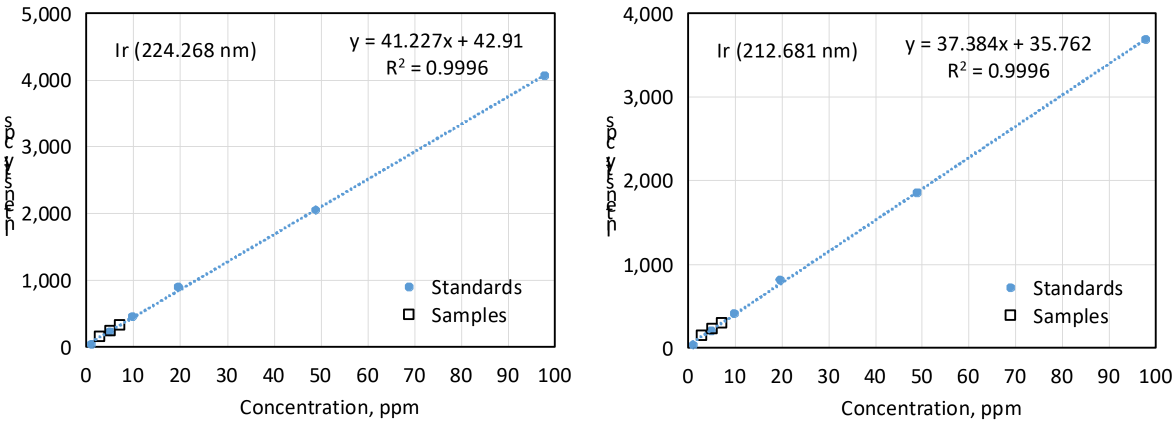

Figure S7. ICP-OES data plots

UV-Vis Spectroscopy

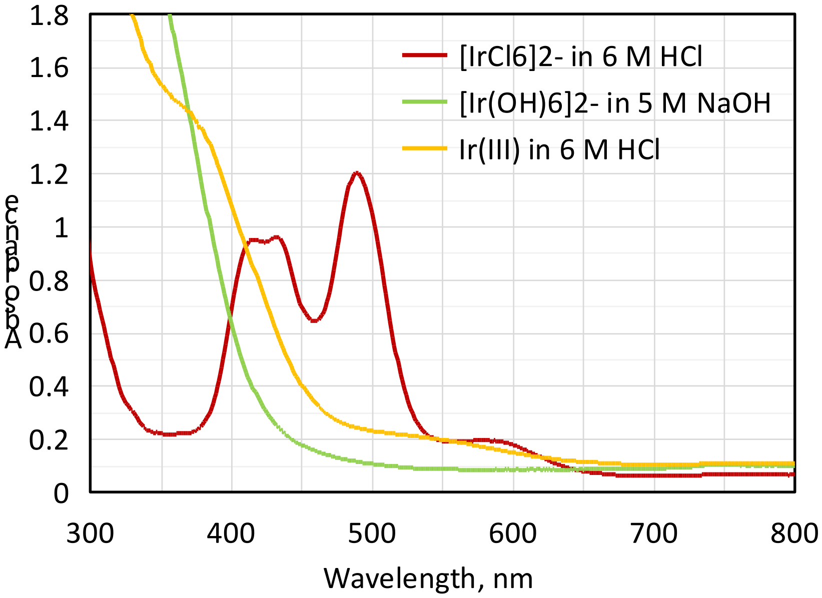

Figure S8. UV-Vis spectra of iridium-containing aqueous solutions generated during waste processing (concentration of Ir is arbitrary). The absorption bands of $IrCl_6^{2-}$ are at λ_{max} = 412, 428, and 486 nm.

List of Iridium Complexes

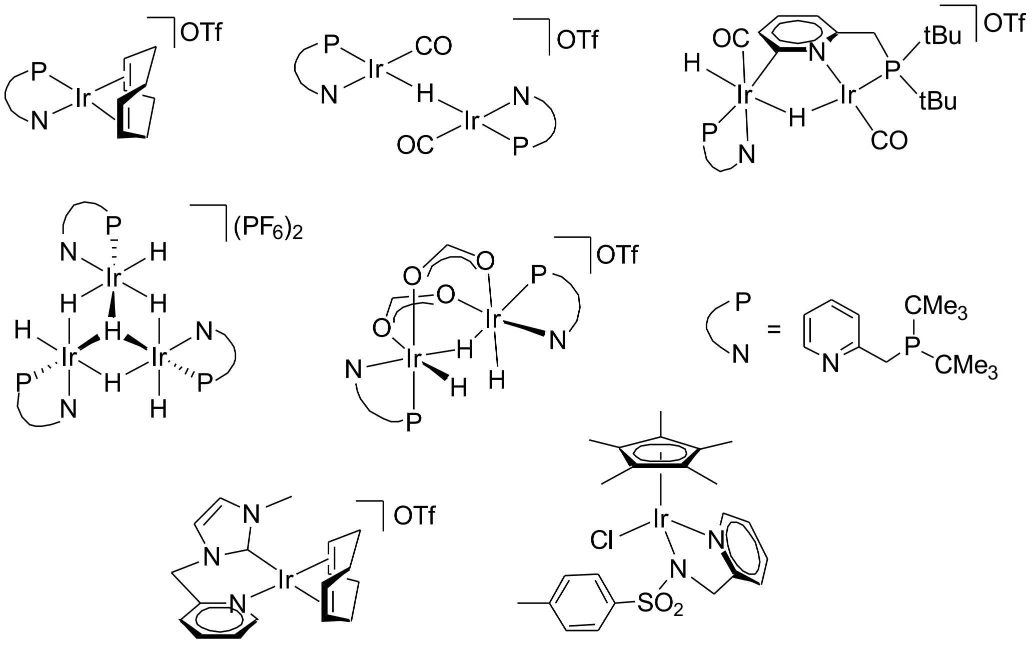

Figure S9. Parent iridium complexes that generated the organoiridium waste.