

Supporting Information

Recycling Organoiridium Waste to [(1,5-Cyclooctadiene)IrCl]₂

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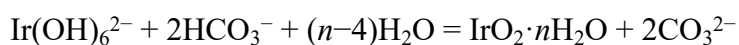
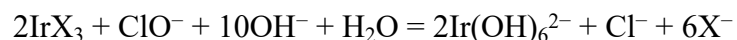
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Materials and Methods

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.

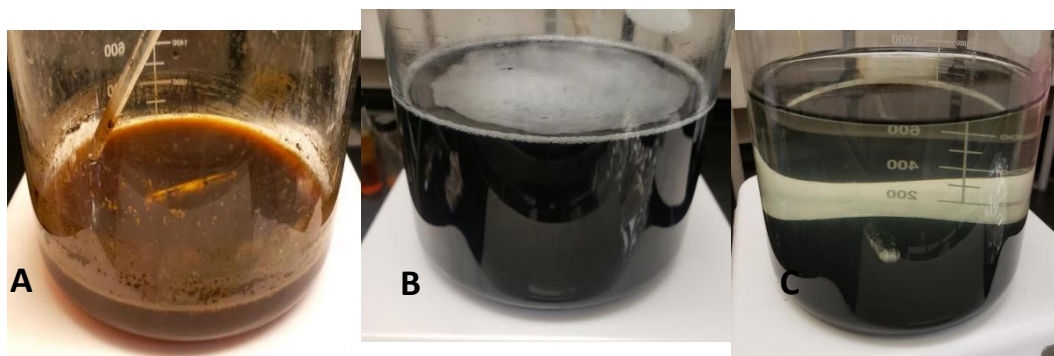
All manipulations with $[(1,5\text{-cyclooctadiene})\text{IrCl}]_2$ were performed under nitrogen using Schlenk technique or in a Vacuum Atmospheres glovebox (0–10 ppm O_2). ^1H and ^{13}C NMR spectra were recorded in 8" J. Young tubes with Teflon valves on Varian Mercury 400 and VNMRS-500 spectrometers 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 $\text{IrO}_2 \cdot n\text{H}_2\text{O}$



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 $\text{IrO}_2 \cdot n\text{H}_2\text{O}$ (**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 $\text{Ir}(\text{OH})_4$: Ir, 73.86; C, 0.00; H, 1.55. Found: Ir, 48.96; C, 2.90; H, 1.82.



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 ($2\text{ClO}^- = \text{O}_2 + 2\text{Cl}^-$) catalyzed by **2** and $\text{Ir}(\text{OH})_6^{2-}$ 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 $\text{Ir}(\text{OH})_6^{2-}$ 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 $\text{Ir}(\text{OH})_6^{2-}$. In this case, the colloid is converted to $\text{Ir}(\text{OH})_6^{2-}$ (Figure S2-D) with NaClO (pH 14, 90 °C) and then buffered with NaHCO_3 (pH 8, 90 °C) to precipitate **2**.

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

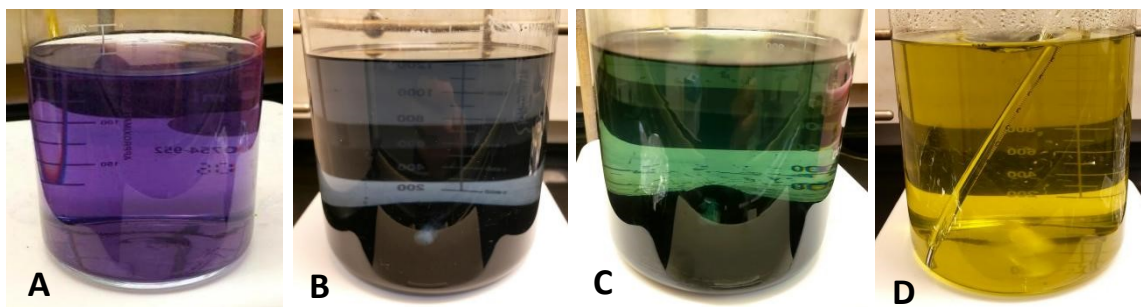
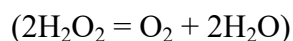
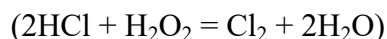
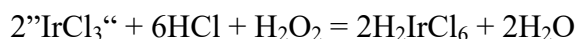
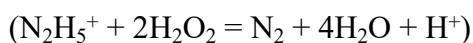
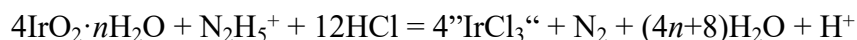


Figure S2. Examples of colloid solutions of **2** (A–C) and a solution of $\text{Ir}(\text{OH})_6^{2-}$ (D).

Safety Note

Combination of bleach with CH_2Cl_2 could potentially generate phosgene, COCl_2 . 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 $\text{IrO}_2 \cdot n\text{H}_2\text{O}$ to $\text{H}_2\text{IrCl}_6 \cdot n\text{H}_2\text{O}$



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 $\text{H}_2\text{IrCl}_6 \cdot n\text{H}_2\text{O}$ (**3**, Figure S3-C) was used without purification.

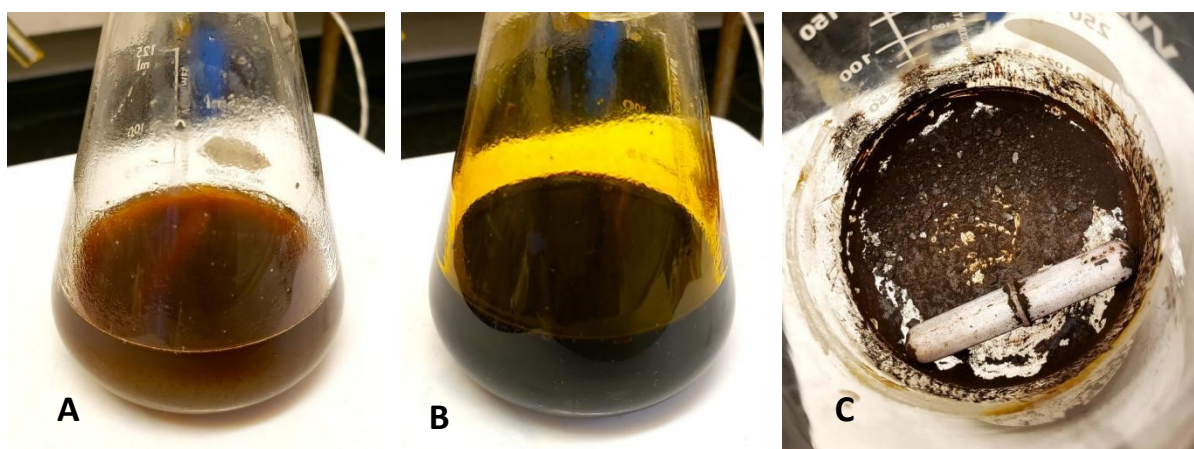
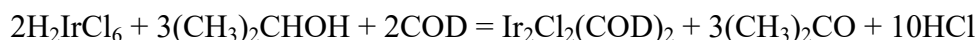


Figure S3. Synthesis of **3**: solution of Ir(III) (A), solution of H_2IrCl_6 (B), and solid **3** (C).

Synthesis of [(1,5-Cyclooctadiene)IrCl]₂



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 CH₂Cl₂. The extract was dried over Na₂SO₄, 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 CH₂Cl₂/hexane solution (Figure S4-C).

The remaining iridium in the synthesis (13%) was recovered as Cs₂[IrCl₆] (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.

¹H NMR (400 MHz, CDCl₃): δ 4.32–4.14 (m, 4H, CH), 2.34–2.15 (m, 4H, CH₂), 1.62–1.44 (m, 4H, CH₂).

¹³C {¹H} NMR (151 MHz, CDCl₃): δ 62.36 (s, CH), 31.94 (s, CH₂).

Anal. calcd. for IrClC₈H₁₂: C, 28.61; H, 3.60. Found: C, 28.63; H, 3.19.

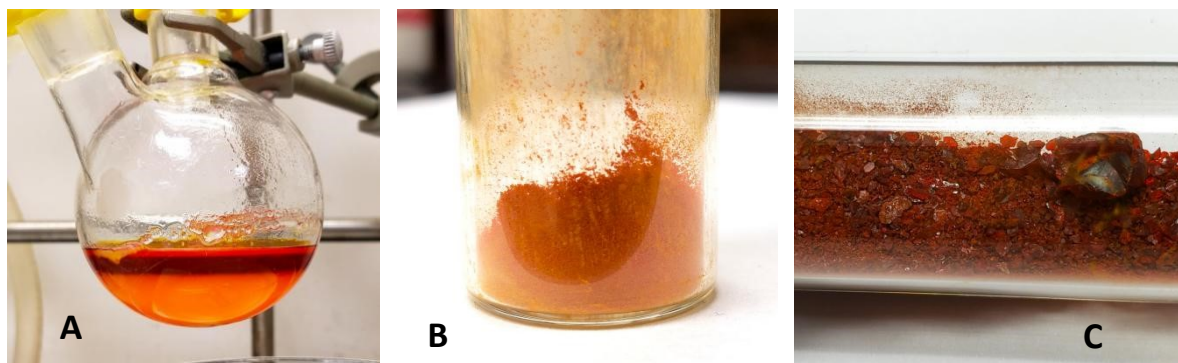


Figure S4. Synthesis of complex **4**: reaction mixture (A), isolated product (B), and recrystallized product (C).

NMR Spectroscopy

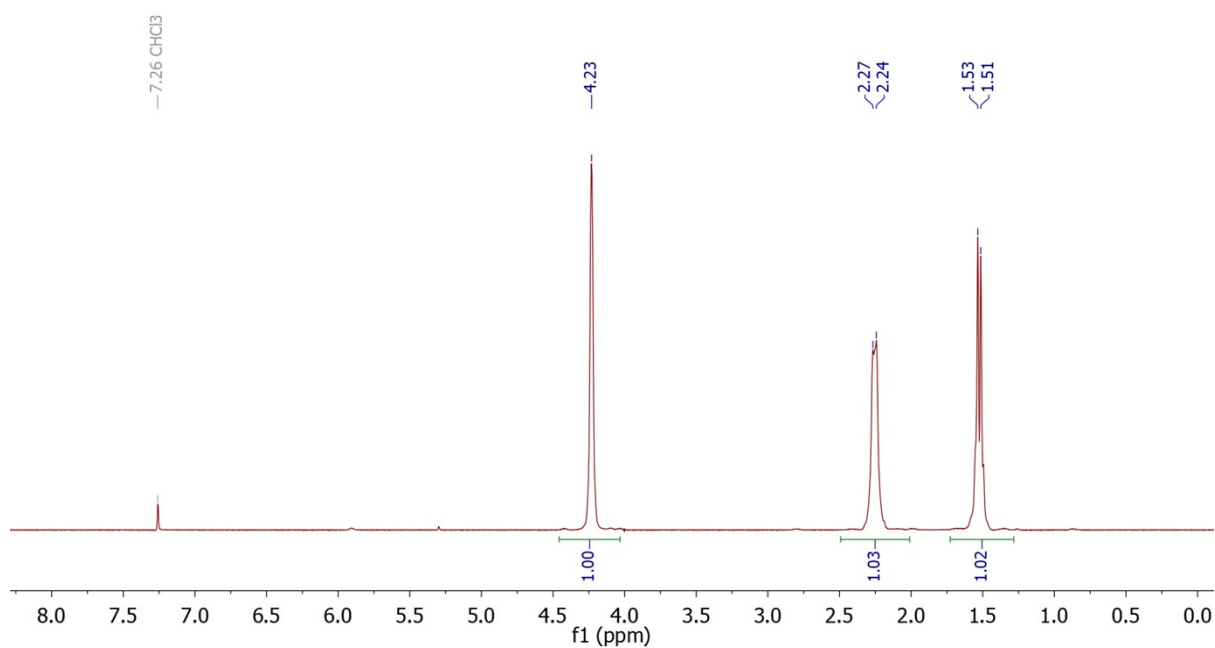


Figure S5. ^1H NMR spectrum of complex **4** in CDCl_3 .

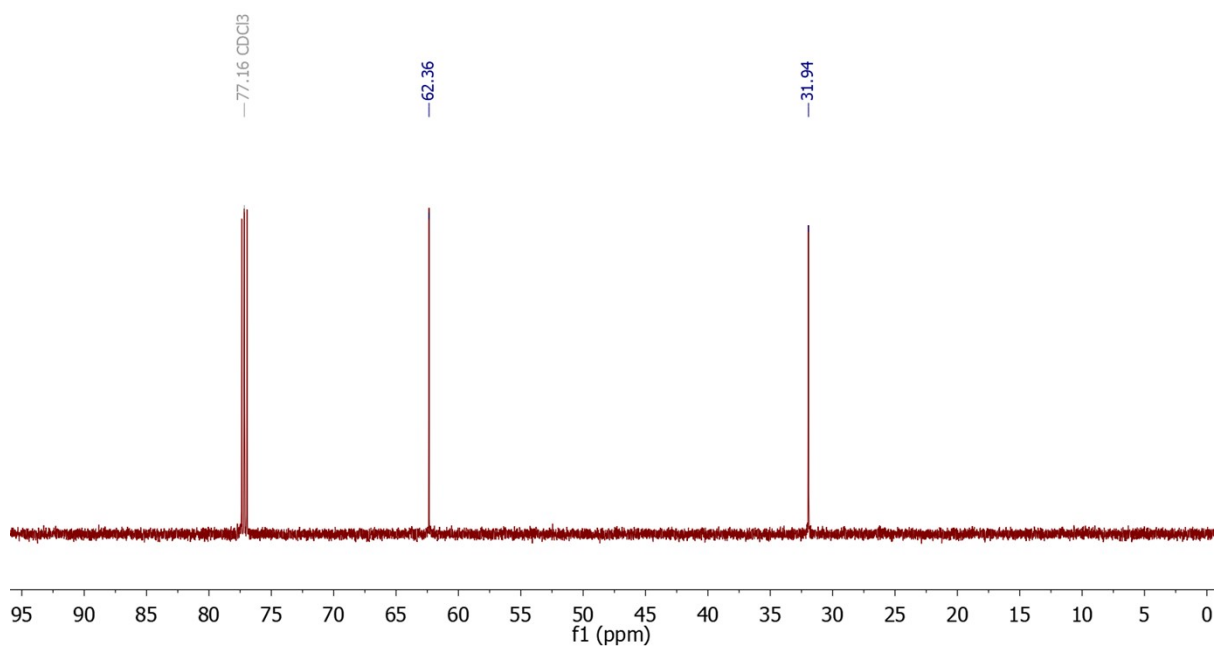


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of complex **4** in CDCl_3 .

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 $(1.52\text{--}3.75)\times 10^{-5}$ 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

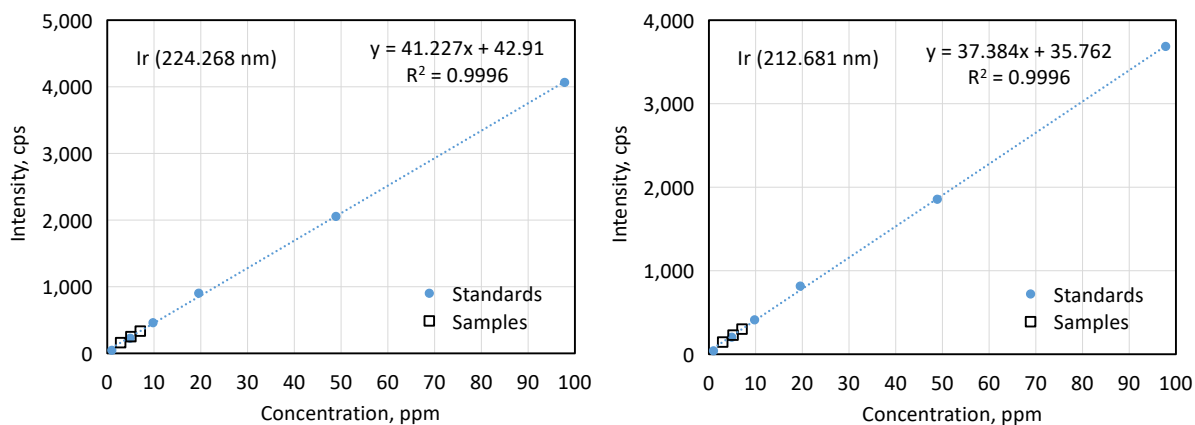


Figure S7. ICP-OES data plots

UV-Vis Spectroscopy

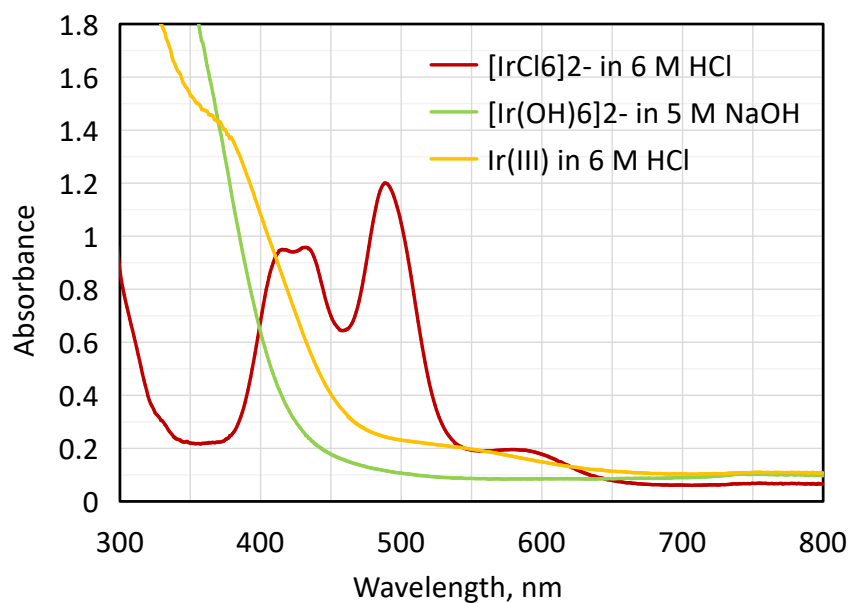


Figure S8. UV-Vis spectra of iridium-containing aqueous solutions generated during waste processing (concentration of Ir is arbitrary). The absorption bands of IrCl₆²⁻ are at $\lambda_{\text{max}} = 412, 428, \text{ and } 486 \text{ nm}$.

List of Iridium Complexes

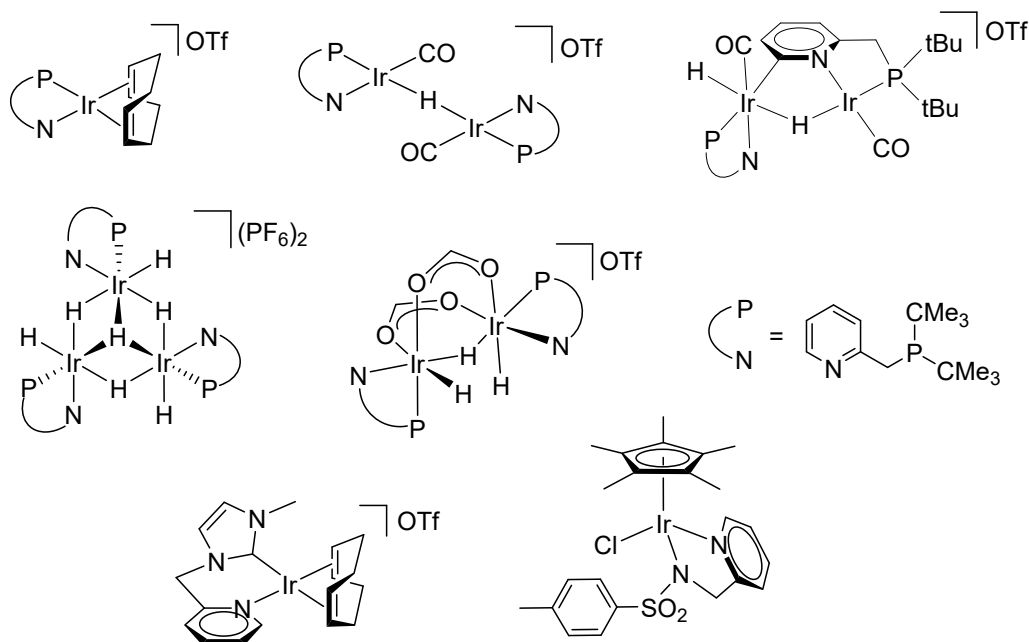


Figure S9. Parent iridium complexes that generated the organoiridium waste.