# **Electronic Supplementary Information (ESI)**

# Surface Chemistry of Polyvinylpyrrolidone-Stabilized Iridium Nanoparticles in the Catalytic Transfer Hydrogenation of Nitrobenzene

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## **General Information**

The <sup>13</sup>C-decoupled proton NMR analysis, <sup>1</sup>H{<sup>13</sup>C}, was conducted using a Varian 400 MHz NMR spectrometer. The catalytic reactions were carried out in corrosion-resistant 22 mL Hastelloy<sup>TM</sup> high-pressure metal reactors, which were purchased from Parr Instrument Company in Moline, Illinois, USA. The maximum pressure is 1700 psi at 300 °C. Norm-Ject 1 mL disposable plastic syringes and BD PrecisionGlide needles (gauge 22 and 1 inch) were purchased from VWR International. Iridium(III) chloride trihydrate was purchased from Acros Organics (CAS number: 13569-57-8, 53–56% Ir). K-30 Polyvinylpyrrolidone (PVP, CAS number: 9003-39-8) was purchased from TCI America. Its average molecular weight is 40,000 g/mol. Reagent grade NaBH<sub>4</sub>, 88% formic acid in water, methanol, ethanol, nitrobenzene, *p*-xylene, and CDCl<sub>3</sub> (>99% purity), and deuterated 2-propanol-d8 (99.5% deuterium, CAS number: 22739-76-0) were purchased from Sigma-Aldrich or VWR International. The reagent grade (98–100% purity) 2-propanol was purchased from J-T Baker (batch number: 0000192348). Distilled water was made from Thermo Scientific Barnstead Mega-Pure<sup>TM</sup> MP-6A Glass Stills.

## Synthesis and Characterizations of PVP[Ir]

The literature procedure<sup>1, 2</sup> was used for the synthesis of  $7.0\pm1.1$  nm metallic polyvinylpyrrolidone-stabilized Ir nanoparticles (NPs), **PVP[Ir]**. The size distribution was not originally reported but was calculated using the bar chart and the formula for weighted standard deviation. Iridium(III) chloride trihydrate in 0.2786 g or  $7.9\times10^{-4}$  mol was dissolved in 25 mL of methanol, and K-30 polyvinylpyrrolidone in 0.1512 g or  $3.78\times10^{-6}$  mol was suspended in 18.4 mL of water. The polyvinylpyrrolidone was insoluble in water. The solutions were combined in a 100 mL 3-neck round-bottom flask and mixed thoroughly at 23 °C for 5 minutes using a magnetic stir bar. A 0.2 M NaOH solution in 1 mL was added dropwise to the reaction with vigorous stirring. The solution was purged with N<sub>2</sub> for 20 minutes at 23 °C, then refluxed in an oil bath at 110 °C for 1 hour. The color of the solution changed from brown to black. At the end of the reaction, solvent removal was performed under vacuum at 40 °C to obtain the product, a dark brown solid that can be re-dispersed in water or an alcohol solvent. Analyses by UV-vis, FT-IR, and PXRD confirmed the identity. The details are described in the following paragraphs. The TEM image has been reported.<sup>1</sup>

The UV-vis spectrum of **PVP[Ir]** NPs was obtained using a Cary 50 Bio spectrophotometer under wavelengths ranging from 190 to 800 nm at 23 °C. UV-vis analysis of **PVP[Ir]** was conducted on a solution suspension of 2 mg of **PVP[Ir]** in 2 mL of distilled water.

FT-IR analyses were conducted using a Mattson Galaxy Series 3000 instrument. The solid samples were analyzed via an ATR (Attenuated Total Reflectance) detector. The FT-IR spectra were collected in the range of 600-4000 cm<sup>-1</sup> with a 1 cm<sup>-1</sup> resolution. The spectrum of **PVP[Ir]** is shown below in Figure S1. The 1630 cm<sup>-1</sup> absorption was attributed to the C=O stretch of PVP.



Figure S1. FT-IR spectrum of PVP[Ir].

Elemental analysis (EA) was conducted by Galbraith Laboratories in Knoxville, Tennessee, USA. **PVP[Ir]** contained  $33.8\pm0.4\%$  Ir, measured in duplicate by inductively coupled plasma optical emission spectrometry (ICP-OES). C (21.59±1.23%), H (3.97±0.41%), and N (4.29±0.26%) were detected by combustion analyses in triplicates and attributed to the polyvinylpyrrolidone stabilizer. These elements account for  $63.66\pm2.32\%$ of the total mass. The other 36.34% of the mass was attributed to Na, O, and Cl that were detected by XPS analyses, described in the following.

High-resolution XPS and binding energy analyses were performed using a PHI-5800 spectrometer made by Physical Electronics in Chanhassen, Minnesota, USA. The instrument was equipped with a monochromatic Al K<sub>a</sub> X-ray source operated at 350.0 W power. The pass energies were 187.85 eV for the survey spectrum and 23.50 eV for the high-resolution spectrum. A take-off angle of 45° relative to the sample surface was used. Freshly made **PVP[Ir]** was stored under N<sub>2</sub> and analyzed within one week. The sample was sputtered with a <1 nm layer of gold and placed on a copper tape for analysis. Using a conductive carbon tape resulted in the apparent decomposition of the sample and the formation of a coating that has metallic luster. Therefore, a carbon tape should be avoided for the XPS analysis. XPS binding energy analyses were performed on the Ir  $4f_{7/2}$  and  $4f_{5/2}$  peaks using sputtered gold as a standard with its  $4f_{7/2}$  peak at 84.0 eV.<sup>3</sup> The binding energies were compared with the literature values of metallic Ir and Ir compounds.<sup>4</sup> The  $4f_{7/2}$  peak area for Ir(0)  $4f_{7/2}$  is 3.87%, and the area for Ir<sup>n+</sup> was 53.27%. Therefore, **PVP[Ir]** consisted of 7% Ir(0) and 93% Ir<sup>n+</sup>(n

is possibly 3 or 4). Data fitting of Ir(0) and  $Ir^{n+}$  was shown below in Figure S2. In addition to Ir, C, H, and N that were detected by EA, Na, O, and Cl were detected in an XPS survey spectrum. These additional elements were attributed to the reagents used in the synthesis of **PVP[Ir]**.



Ir 4f Binding Energy Analysis (Reference: Au 4f<sub>7/2</sub> at 83.98 eV)

Figure S2. Binding energy analysis on the Ir  $4f_{7/2}$  and  $4f_{5/2}$  peaks of PVP[Ir].

The PXRD analysis of **PVP[Ir]** was performed on a Rigaku Miniflex 600 instrument, equipped with a graphite crystal monochromator, a NaI scintillation counter detector, and a Cu K<sub> $\alpha$ </sub> X-ray source. The instrument was purchased from the Rigaku Americas Corporation in The Woodlands, Texas, USA. The Goniometer has a minimum step width of 0.005 °2 $\theta$  and an accuracy of 0.02 °2 $\theta$ . Data collection was performed under 40 kV and 15 mA (600 W) from 10 to 80 °2 $\theta$ . Data analysis was conducted using a PDXL II software suite. The PXRD spectrum of the face-centered cubic iridium metal was used as a reference.<sup>5</sup> The sample was ground into a fine powder using a mortar and pestle before analysis. **PVP[Ir]** in 10 mg was spread evenly across a 2 cm by 2 cm glass sample holder with a 0.2 mm or 0.5 mm indent, purchased from Rigaku. The sample was then pressed to a thin layer using a glass slide to form a flat surface. Only a broad, amorphous phase was observed, consistent with amorphous NPs.

#### Decarbonylation of Methanol by PVP[Ir]

**PVP[Ir]** (7.7 mg NPs, 0.013 mmol Ir) was combined with potassium hydroxide (1.43 mmol or 80 mg) in 5.0 mL of methanol. The precise Ir content of **PVP[Ir]**, measured by EA using ICP-OES, is  $33.8\pm0.4\%$ . The reaction mixture was placed in a 22 mL Hastelloy<sup>TM</sup> high-pressure metal reactor and was purged with 1 atm of N<sub>2</sub> for 20 minutes. The reactor was

closed under the constant purging with N<sub>2</sub>. Heating was then performed for one hour in a drying oven that was preheated to 160 °C. After opening the oven door and placing the reactor, the temperature of the oven briefly dropped to 155 °C and reversed to 160 °C in 10 minutes. At the end of the reaction, the reactor was cooled by opening the oven door for 20 minutes, followed by moving it onto a bench and cooling by air for 40 minutes or until it was lukewarm. No precipitates formed at the end of the reaction. The solution was transferred to a 20 mL round-bottom flask for solvent removal by a rotavap under vacuum at 40 °C.

FT-IR analysis was performed on the solid sample. The FT-IR spectra of **PVP[Ir]**, before and after the reaction, were compared in Figure S3. Before decarbonylation, no metal carbonyl stretches were detected. After decarbonylation, a new stretch appeared at 1875 cm<sup>-1</sup>, which was assigned to an Ir<sup>n+</sup>  $\mu_2$ -bridging carbonyl ligand. The lactam carbonyl peak of PVP at 1630 cm<sup>-1</sup> was split into two stretches, at 1659 and 1589 cm<sup>-1</sup>, respectively. In contrast, when **PVP[Ir]** was treated with formic acid (430  $\mu$ L in 5.0 mL methanol) and under otherwise identical conditions, the 1875 cm<sup>-1</sup> carbonyl stretch was not observed (Figure S4). A weak absorption at 1992 cm<sup>-1</sup> was observed.



Figure S3. PVP[Ir] before (grey) and after (red) the decarbonylation of methanol.



Figure S4. PVP[Ir] before (grey) and after (red) the reaction with formic acid in methanol.

#### **Catalytic Transfer Hydrogenation of Acetophenone**

Acetophenone (1.0 mmol, 120  $\mu$ L, or 124 mg) was combined with potassium hydroxide (1.43 mmol or 80 mg) and **PVP[Ir]** (7.7 mg NPs) in 5.0 mL of methanol, ethanol, or 2-propanol solvent. The precise Ir content of **PVP[Ir]**, measured by EA using ICP-OES, is 33.8±0.4%. Therefore, the catalyst loading is 1% based on iridium (0.013 mmol) and acetophenone (1.0 mmol). The reaction mixture was placed in a 22 mL Hastelloy<sup>TM</sup> high-pressure metal reactor and was purged with 1 atm of N<sub>2</sub> for 20 minutes. The reactor was closed under the constant purging with N<sub>2</sub>. Heating was then performed for one hour in a drying oven that was preheated to 160 °C. After opening the oven door and placing the reactor, the temperature of the oven briefly dropped to 155 °C and reversed to 160 °C in 10 minutes.

At the end of the reaction, the reactor was cooled by opening the oven door for 20 minutes, followed by moving it onto a bench and cooling by air for 40 minutes or until it was lukewarm. The reaction mixture was transferred to a 20 mL round-bottom flask for solvent removal by a rotavap under vacuum at 40 °C. A 400  $\mu$ L CDCl<sub>3</sub> solution containing 20 mg of an internal standard, *p*-xylene, was used to dissolve the product mixture for quantitative <sup>1</sup>H{<sup>13</sup>C} NMR analysis. The yield of the product, 1-phenylethanol, was determined using the arene chemical shift of *p*-xylene at 7.05 ppm (*s*, 4H) and the tertiary hydrogen chemical shift of 1-phenylethanol at 3.78 ppm (*q*, 1H). The proton NMR spectra of acetophenone, 1-

phenylethanol, and *p*-xylene have been reported in the Integrated Spectral Database System of Organic Compounds.<sup>6</sup> The reaction conditions and results are summarized below in Table S1.

| Entry | Solvent    | 1-Phenylethanol yield with/without PVP[Ir] |
|-------|------------|--|
| 1     | Methanol   | 0%/0%                                      |
| 2     | Ethanol    | 53%/19%                                    |
| 3     | 2-propanol | quantitative                               |
|       |            |  |

Table S1 The PVP[Ir]-catalyzed transfer hydrogenation of acetophenone to 1-phenylethanol

Reaction conditions unless otherwise specified: Acetophenone in 1.0 mmol or 0.20 M, KOH in 1.43 mmol, in an alcohol solvent in 5 mL, at 160 °C, in 1 hour, under N<sub>2</sub>, and with **PVP[Ir]** in a 1% catalyst loading, 13  $\mu$ mol. The catalyst loading is calculated by dividing the mole of Ir, obtained from EA, by the mole of acetophenone, 1.0 mmol. The yield is calculated based on the starting material, acetophenone in 1.0 mmol, using quantitative <sup>1</sup>H{<sup>13</sup>C} NMR analysis with *p*-xylene as an internal standard.

#### **Catalytic Transfer Hydrogenation of Nitrobenzene**

Nitrobenzene (1.20 mmol, 120  $\mu$ L, or 144 mg) was combined with potassium hydroxide powder (1.43 mmol or 80 mg) and **PVP[Ir]** (7.7 mg or 0.011 mmol) in 5.0 mL of ethanol, isopropanol, or formic acid-methanol (430  $\mu$ L in 5.0 mL methanol) solvent. The precise Ir content of **PVP[Ir]**, measured by EA using ICP-OES, is 33.8±0.4%. Therefore, the catalyst loading is 1% based on iridium (0.013 mmol) and nitrobenzene (1.2 mmol). The reaction mixture was placed in a 22 mL Hastelloy<sup>TM</sup> high-pressure metal reactor and was purged with 1 atm of N<sub>2</sub> for 20 minutes. The reactor was closed under the constant purging of N<sub>2</sub>. Heating was then performed for one hour in a drying oven that was preheated to 160 °C. After opening the oven door and placing the reactor, the temperature of the oven briefly dropped to 155 °C and reversed to 160 °C in 10 minutes.

At the end of the reaction, the reactor was cooled by opening the oven door for 20 minutes, followed by moving it onto a bench and cooling by air for 40 minutes or until it was lukewarm. The purification procedure depends on the solvent of the reaction. With ethanol or 2-propanol as the solvent, dark precipitates formed. Filtration was performed using a coarse sintered glass funnel packed with celite, which was then washed with 15 mL of ethyl acetate. The combined 20 mL solution was transferred to a 50 mL round-bottom flask for solvent removal by a rotavap under vacuum at 40 °C. With formic acid–methanol (430  $\mu$ L in 5.0 mL methanol) as the solvent, described in entries 7 and 8 of Table 2 of the main text, no precipitates formed, and therefore, no filtration was necessary. The reaction mixture was transferred directly to a 20 mL round-bottom flask for solvent removal by a rotavap under vacuum at 40 °C. When formic acid–methanol was used was the solvent, water was removed

under vacuum with a liquid N<sub>2</sub> trap at 23 °C. A 400  $\mu$ L CDCl<sub>3</sub> solution containing 20 mg of an internal standard, *p*-xylene, was used to dissolve the product mixture for quantitative <sup>1</sup>H{<sup>13</sup>C} NMR analysis. The yield of the aniline product, the azobenzene and azoxybenzene side products, and the recovered starting material were determined using the arene chemical shift of *p*-xylene at 7.05 ppm (*s*, 4H) and the following hydrogen chemical shifts: the *ortho*hydrogen of azobenzene at 7.92 ppm (4H), the *ortho*-hydrogen of azoxybenzene at 8.30 ppm (*d*, 2H), the *ortho*-hydrogen of aniline at 6.68 ppm (*d*, 2H), and the *para*-hydrogen of nitrobenzene at 7.69 ppm (*t*, 1H). These chemical shifts do not overlap with any peaks. The proton NMR spectra of nitrobenzene, aniline, azobenzene, azoxybenzene, and *p*-xylene have been reported in the Integrated Spectral Database System of Organic Compounds.<sup>6</sup> The structures of azobenzene and azoxybenzene are shown below, along with the proton chemical shifts used for quantitation.



#### References

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