Supporting Information

Ligand-Promoted Dehydrogenation of Alcohols Catalyzed by Cp*Ir Complexes. A New Catalytic System for Oxidant-Free Oxidation of Alcohols

Ken-ichi Fujita,^{*,a,b} Nobuhide Tanino,^a and Ryohei Yamaguchi^{*,a}

^a*Graduate School of Human and Environmental Studies, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan*

^b*Graduate School of Global Environmental Studies, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan*

Experimental Section:

General: All reactions and manipulations were carried out under an atmosphere of argon by means of standard Schlenk techniques. ¹H- and ¹³C-NMR spectra were recorded on JEOL A-500 and EX-270 spectrometers. Gas chromatography (GC) analyses were performed on a Shimadzu GC-14A or a GL-Sciences GC353B gas chromatograph with a capillary column (GL-Sciences TC-17). Column chromatography was carried out by using Wako-gel C-200. Elemental analyses were carried out at the Microanalysis Center of Kyoto University. Solvents were dried by standard procedures and distilled prior to use. The catalysts [Cp*IrCl₂]₂ (Cp* = pentamethylcyclopentadienyl) and Cp*Ir(pyridine)Cl₂ were prepared according to the literature method.¹ 1-(4-Methoxyphenyl)ethanol, 1-(4-bromophenyl)ethanol, 1-(4-nitrophenyl)ethanol, 1-(2-methylphenyl)ethanol, 1-(3-methylphenyl)ethanol, and 1-(2-furyl)ethanol were prepared by reduction of corresponding ketones with small excess (1.1 - 2.0 equiv) NaBH₄. All other reagents are commercially available and were used as received.

Preparation of the catalyst Cp*Ir(2-hydroxypyridine)Cl₂ (1a). Under an atmosphere of argon, [Cp*IrCl₂]₂ (1.01 g, 1.27 mmol) was placed in a flask. Dichloromethane (25 mL) and 2-hydroxypyridine (0.250 g, 2.63 mmol) were added, and the mixture was stirred for 30 min at room temperature. The solution was filtered, and the solvent was removed in vacuum.

Recrystallization from dichloromethane-hexane gave orange crystals of **1a** (0.938 g, 1.90 mmol, 75%).

^1H NMR (500 MHz, CDCl_3) δ 10.57 (br, 1H, OH), 8.54 (d, J = 5 Hz, 1H, aromatic), 7.63 (t, J = 7 Hz, 1H, aromatic), 6.92-6.87 (m, 2H, aromatic), 1.54 (s, 15H, C_5Me_5).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.65 MHz, CDCl_3) δ 165.7, 151.1, 141.3, 117.5, 113.2, 86.5, 8.6.

Anal. Calcd for $\text{C}_{15}\text{H}_{20}\text{Cl}_2\text{NOIr}$: C, 36.51; H, 4.09; N, 2.84. Found: C, 36.38; H, 3.94; N, 2.80.

Preparation of the catalyst $\text{Cp}^*\text{Ir}(\text{3-hydroxypyridine})\text{Cl}_2$ (1b**).** Under an atmosphere of argon, $[\text{Cp}^*\text{IrCl}_2]_2$ (0.200 g, 0.250 mmol) was placed in a flask. Dichloromethane (5 mL) and 3-hydroxypyridine (0.0436 g, 0.458 mmol) were added, and the mixture was stirred for 30 min at room temperature. After evaporation of the solvent, the residue was washed with dichloromethane (15 mL). Drying in vacuum gave a yellow solid of **1b** (0.215 g, 0.437 mmol, 95%).

^1H NMR (270 MHz, $\text{DMSO}-d_6$) δ 9.84 (s, 1H, OH), 8.12 (d, J = 3 Hz, 1H, aromatic), 8.01 (d, J = 3 Hz, 1H, aromatic), 7.22-7.11 (m, 2H, aromatic), 1.63 (s, 15H, C_5Me_5).

Anal. Calcd for $\text{C}_{15}\text{H}_{20}\text{Cl}_2\text{NOIr}$: C, 36.51; H, 4.09; N, 2.84. Found: C, 36.27; H, 4.04; N, 2.83.

Preparation of the catalyst $\text{Cp}^*\text{Ir}(\text{4-hydroxypyridine})\text{Cl}_2$ (1c**).** Under an atmosphere of argon, $[\text{Cp}^*\text{IrCl}_2]_2$ (0.201 g, 0.253 mmol) was placed in a flask. Dichloromethane (5 mL) and 4-hydroxypyridine (0.0465 g, 0.489 mmol) were added, and the mixture was stirred for 30 min at room temperature. After evaporation of the solvent, the residue was washed with dichloromethane (15 mL). Drying in vacuum gave a yellow solid of **1c** (0.206 g, 0.417 mmol, 85%).

^1H NMR (270 MHz, $\text{acetone}-d_6$) δ 8.62 (d, J = 7 Hz, 2H, aromatic), 6.91 (d, J = 7 Hz, 2H, aromatic), 1.49 (s, 15H, C_5Me_5).

Anal. Calcd for $\text{C}_{15}\text{H}_{20}\text{Cl}_2\text{NOIr}$: C, 36.51; H, 4.09; N, 2.84. Found: C, 36.06; H, 4.02; N, 2.90.

Preparation of the 2-hydroxypyridinate chelated Cp^*Ir complex **2.** Under an atmosphere of argon, $[\text{Cp}^*\text{IrCl}_2]_2$ (0.399 g, 0.501 mmol) was suspended in benzene (10 mL). To this suspension was added sodium 2-hydroxypyridinate (0.117 g, 0.998 mmol), and the mixture was stirred for 2 h at room temperature. After evaporation of the solvent, the residue was extracted with benzene (30 mL) and filtered. Evaporation of the filtrate gave a yellow solid of **2** (0.447 g, 0.978 mmol, 98%).

^1H NMR (500 MHz, CDCl_3) δ 7.80 (d, J = 5 Hz, 1H, aromatic), 7.38 (t, J = 8 Hz, 1H, aromatic), 6.51 (t, J = 6 Hz, 1H, aromatic), 6.15 (d, J = 9 Hz, 1H, aromatic), 1.76 (s, 15H, C_5Me_5).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.65 MHz, CDCl_3) δ 176.9, 141.5, 138.6, 113.8, 111.2, 83.6, 9.4.

Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{ClINOIr}$: C, 39.42; H, 4.19; N, 3.07. Found: C, 39.43; H, 4.05; N, 3.09.

General procedure for the oxidant-free oxidation of 1-phenylethanol under various conditions shown in Table 1. Under an atmosphere of argon, 1-phenylethanol (20 mmol), catalyst (0.10 mol%Ir), additive (0.10 mol%), and toluene (6 mL) were placed in a flask. The mixture was magnetically stirred for 20 h under reflux (oil bath temperature was 130 °C). The yield of acetophenone was determined by GC analysis using undecane as an internal standard.

General procedure for the oxidant-free oxidation of various secondary alcohols shown in Table 2: Under an atmosphere of argon, secondary alcohol (1.0 - 5.0 mmol), catalyst **1a** (0.20 - 1.0 mol%Ir), and toluene (2 - 6 mL) were placed in a flask. The mixture was magnetically stirred for 20 or 50 h under reflux (oil bath temperature was 130 °C). After evaporation of the solvent, the products were isolated by silica-gel column chromatography (eluent: hexane/ethyl acetate).

Spectroscopic data of the products.

acetophenone:² ¹H NMR (270 MHz, CDCl₃) δ 7.95-7.40 (m, 5H, aromatic), 2.57 (s, 3H, Me). ¹³C{¹H} NMR (67.8 MHz, CDCl₃) δ 197.6, 136.8, 132.8, 128.2, 128.0, 26.4.

4'-methylacetophenone:³ ¹H NMR (270 MHz, CDCl₃) δ 7.84 (d, *J* = 8 Hz, 2H, aromatic), 7.24 (d, *J* = 8 Hz, 2H, aromatic), 2.56 (s, 3H, Me), 2.39 (s, 3H, Me). ¹³C{¹H} NMR (67.8 MHz, CDCl₃) δ 197.4, 143.6, 134.4, 129.0, 128.2, 26.5, 21.6.

4'-methoxyacetophenone:⁴ ¹H NMR (270 MHz, CDCl₃) δ 7.93 (d, *J* = 9 Hz, 2H, aromatic), 6.93 (d, *J* = 9 Hz, 2H, aromatic), 3.86 (s, 3H, OMe), 2.55 (s, 3H, Me). ¹³C{¹H} NMR (67.8 MHz, CDCl₃) δ 196.4, 163.3, 130.4, 130.2, 113.5, 55.4, 26.3.

4'-chloroacetophenone:⁵ ¹H NMR (270 MHz, CDCl₃) δ 7.86 (d, *J* = 8 Hz, 2H, aromatic), 7.40 (d, *J* = 9 Hz, 2H, aromatic), 2.57 (s, 3H, Me). ¹³C{¹H} NMR (67.8 MHz, CDCl₃) δ 196.2, 139.1, 135.1, 129.4, 128.5, 26.3.

4'-bromoacetophenone:⁶ ¹H NMR (270 MHz, CDCl₃) δ 7.65 (d, *J* = 9 Hz, 2H, aromatic), 7.42 (d, *J* = 8 Hz, 2H, aromatic), 2.43 (s, 3H, Me). ¹³C{¹H} NMR (67.8 MHz, CDCl₃) δ 196.2, 135.4, 131.4, 129.4, 127.8, 26.3.

4'-nitroacetophenone:⁵ ¹H NMR (270 MHz, CDCl₃) δ 8.32 (d, *J* = 9 Hz, 2H, aromatic), 8.12 (d, *J* = 9 Hz, 2H, aromatic), 2.69 (s, 3H, Me). ¹³C{¹H} NMR (67.8 MHz, CDCl₃) δ 196.1, 150.2, 141.2, 129.2, 123.8, 27.1.

2'-methylacetophenone:⁷ ¹H NMR (270 MHz, CDCl₃) δ 7.67-7.18 (m, 4H, aromatic), 2.53 (s, 3H, Me), 2.51 (s, 3H, Me). ¹³C{¹H} NMR (67.8 MHz, CDCl₃) δ 200.9, 138.0, 137.1, 131.6, 131.1, 129.0, 125.3, 29.2, 21.4.

3'-methylacetophenone:⁸ ¹H NMR (270 MHz, CDCl₃) δ 7.74-7.28 (m, 4H, aromatic), 2.55 (s, 3H, Me), 2.38 (s, 3H, Me). ¹³C{¹H} NMR (67.8 MHz, CDCl₃) δ 197.8, 138.0, 136.8, 133.5, 128.4, 128.1, 125.2, 26.5, 21.2.

propiophenone:⁹ ¹H NMR (270 MHz, CDCl₃) δ 7.97-7.41 (m, 5H, aromatic), 2.99 (q, *J* = 7 Hz, 2H,

CO-CH₂-CH₃), 1.22 (t, *J* = 7 Hz, 3H, C-CH₂-CH₃). ¹³C{¹H} NMR (67.8 MHz, CDCl₃) δ 200.5, 136.7, 132.7, 128.4, 127.8, 31.8, 8.3.

1-indanone:¹⁰ ¹H NMR (270 MHz, CDCl₃) δ 7.72-7.30 (m, 4H, aromatic), 3.10 (t, *J* = 6 Hz, 2H, CO-CH₂-CH₂-Ar), 2.63 (t, *J* = 6 Hz, 2H, CO-CH₂-CH₂-Ar). ¹³C{¹H} NMR (67.8 MHz, CDCl₃) δ 206.4, 154.7, 136.6, 134.1, 126.8, 126.3, 123.1, 35.9, 25.6.

1-tetralone:¹¹ ¹H NMR (270 MHz, CDCl₃) δ 8.04-7.23 (m, 4H, aromatic), 2.96 (t, *J* = 6 Hz, 2H, CO-CH₂-CH₂-CH₂-Ar), 2.65 (t, *J* = 6 Hz, 2H, CO-CH₂-CH₂-CH₂-Ar), 2.13 (m, 2H, CO-CH₂-CH₂-CH₂-Ar). ¹³C{¹H} NMR (67.8 MHz, CDCl₃) δ 198.1, 144.3, 133.2, 132.4, 128.6, 127.0, 126.4, 39.2, 29.7, 23.3.

References

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9. The Aldrich Library of ¹³C and ¹H FT NMR Spectra 2, 802 B.
10. The Aldrich Library of ¹³C and ¹H FT NMR Spectra 2, 808 C.
11. The Aldrich Library of ¹³C and ¹H FT NMR Spectra 2, 810 C.

Figure S1. ORTEP drawing of **1b** with 50 % thermal probability ellipsoids. Hydrogen atoms are omitted for clarity.

Figure S2. ORTEP drawing of **1c** with 50 % thermal probability ellipsoids. Hydrogen atoms are omitted for clarity.