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Synthesis of a series of iridium complexes bearing substituted 2-pyridonates and their catalytic performance for acceptorless dehydrogenation of alcohols under neutral conditions

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ABSTRACT

A series of Cp*Ir complexes bearing 5- and 4,5-substituted 2-pyridonate ligands have been synthesized and their catalytic performance for acceptorless dehydrogenation of alcohols has been investigated under neutral conditions. Electron-withdrawing groups such as methoxycarbonyl, trifluoromethyl, cyano, and nitro groups at the 5-position promoted the acceptorless dehydrogenation of 1-phenylethanol, whereas electron-donating methyl group at the 5-position retarded the reaction. Furthermore, introduction of methyl group at the 4-position improved the catalytic performance. Thus, Cp*Ir(5-trifluoromethyl-4-methyl-2-pyridonate)Cl (**2bc**) exhibited the highest catalytic performance among the complexes examined, and also showed good catalytic performance for acceptorless dehydrogenation of primary alcohols.

1. Introduction

The oxidation of alcohols to carbonyl compounds such as aldehydes and ketones is one of the most important and fundamental reactions in organic chemistry. Recently, oxidant-free or acceptor-free oxidation based on the transition-metal catalyzed dehydrogenative transformation of alcohols accompanied by the evolution of hydrogen gas (acceptorless dehydrogenation) has attracted considerable attention from the standpoint of atom economy and environmental concerns [1–4]. Furthermore, acceptorless dehydrogenation of alcohols is important not only for the production of synthetically useful aldehydes and ketones from easily available alcohols with high atom efficiency [5–11], but also for the production of hydrogen which is one of the most promising energy carriers in future energy plans [12–15]. Thus, much effort has been devoted to develop various homogeneous catalytic systems for the acceptorless dehydrogenation of alcohols affording ketones and aldehydes.

We have previously reported several systems for acceptorless oxidation of alcohols catalysed by iridium complexes bearing functional 2-hydroxypyridine- and 2,2′-dihydroxybipyridine-based ligands (complexes **A**, **B**, and **C**, **D**), as shown in Fig. 1 [16–20], [21].

Since these catalytic systems would proceed by the activation of an alcohol with the 2-pyridonate ligand by way of either the stepwise pathway through β-hydrogen elimination of an alkoxoiridium intermediate [16] or the concreted pathway through cyclic transition state [20,22], the intramolecular reaction of hydride on iridium with protic hydrogen on the 2-hydroxypyridine-based ligand (ligand-promoted dehydrogenation) could be a critical step (Scheme 1). Thus, the 2-pyridonate ligand could act as a proton acceptor in the activation step [23] and as a proton donor in the dehydrogenation step [24,25], playing a dual role in the cooperative catalysis. Therefore, it should be indispensable to investigate the substituent effect of the 2-pyridonate ligand on the catalytic performance in order to develop the more effective catalyst. We report here the synthesis of a series of iridium complexes bearing substituted 2-pyridonates and their catalytic performance of acceptorless oxidation of alcohols.

2. Experimental

2.1. General

All reactions and manipulations were performed under

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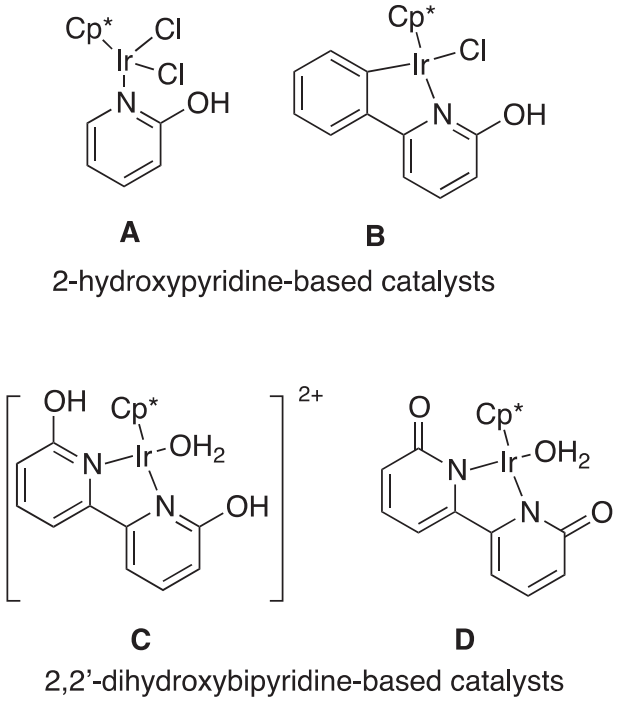
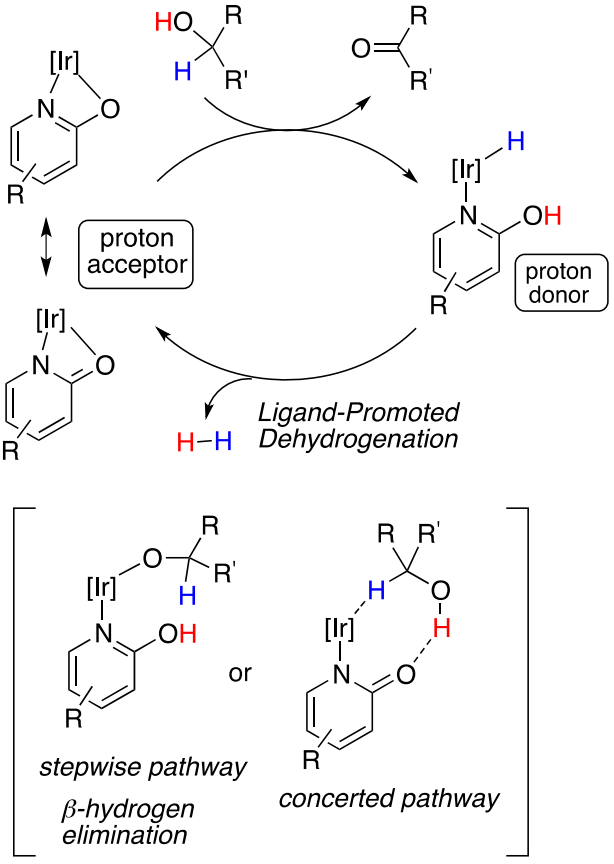


Fig. 1. Iridium complexes bearing functional 2-hydroxypyridine- and 2,2′-dihydroxybipyridine-based ligands for acceptorless oxidation of alcohols.



Scheme 1. Dual role of 2-Pyridonate Ligand in Cooperative Catalysis.

argon atmosphere using standard Schlenk techniques. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on JEOL ECX-500 and ECS-400 spectrometers. Gas chromatography (GC) analyses were performed on a GL-Sciences GC353B gas chromatograph with a capillary column (GL-Sciences InertCap 5 and InertCap Pure WAX). Elemental analyses were carried out at the Microanalysis Center of Kyoto University. Silica-gel column chromatography was carried out by using Wako-gel C-200. The compounds, $[Cp^*IrCl_2]_2$ (Cp^* = η^5-pentamethylcyclo-pentadienyl), [Cp*Ir(2-pyridonate)Cl] (**2aa**) [16], and [Cp*Ir(5-methyl-2-pyridonate)Cl] (**2ab**) [25], [Cp*Ir(5-trifuloromethyl-2-pyridonate)Cl] (**2ac**) [25] were prepared according to the literature methods. Solvents were dried by standard procedures prior to use. All other reagents are commercially available and were used as received.

2.2. Procedures for synthesis of Cp*Ir(5- and 4,5-subsutituted 2-pyridonate)Cl (**2**)

In a flask, 5- and 4,5-subsutituted 2-hydorxypyridines (0.5 mmol) and NaOEt (34 mg, 0.5 mmol) in EtOH were placed and a solution was stirred for 30 min at room temperature. After the solvent was removed under vacuo, $[Cp^*IrCl_2]_2$ (199 mg, 0.25 mmol) and CH_2Cl_2 (3 mL) were added and stirred at 5 °C. When the color of the solution changed from orange to yellowish brown, the solvent was removed under vacuo. The residue was extracted by benzene and, then, washed with a mixture of Et_2O/THF/benzene (40: 1: 1). Finally, the corresponding complex was obtained by recrystallization from CH_2Cl_2/hexane. The spectral and analytical data are summarized in Table 1.

2.2.1. [Cp*Ir(5-methoxycarbonyl-2-pyridonate)Cl] (**2ad**)

86 mg (56%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (s, 1H, Ar), 7.70 (d, 1H, J = 8.8 Hz, Ar), 6.20 (d, 1H, J = 8.8 Hz, Ar), 3.85 (s, 3H, COOMe), 1.76 (s, 15H, Cp*); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 178.8 (aromatic), 165.6 (CO), 145.8 (aromatic), 139.8 (aromatic), 114.7 (aromatic), 113.4 (aromatic), 84.3 (C_5Me_5), 52.0 (OCH_3), 9.5 ($C_5\mathit{Me}_5$). Found: C, 39.19; H, 3.98; N, 2.70. Calcd. For $C_{17}H_{21}NO_3ClIr$: C, 39.64; H, 4.11; N, 2.72.

2.2.2. [Cp*Ir(5-cyano-2-pyridonate)Cl] (**2ae**)

143 mg (56%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (s, 1H, Ar), 7.42 (d, 1H, J = 9.2 Hz, Ar), 6.13 (d, 1H, J = 9.2 Hz, Ar), 1.76 (s, 15H, Cp*); ^{13}C NMR: (100.5 MHz, $CDCl_3$): δ 172.7 (aromatic), 151.6 (aromatic), 139.8 (aromatic), 118.4 (CN), 116.0 (aromatic), 93.5 (aromatic), 85.2 (C_5Me_5), 9.5 ($C_5\mathit{Me}_5$). Found: C, 39.04; H, 3.90; N, 5.43. Calcd for $C_{16}H_{18}N_2OClIr\cdot H_2O$: C, 38.44; H, 4.03; N, 5.60.

2.2.3. [Cp*Ir(5-nitro-2-pyridonate)Cl] (**2af**)

109 mg (54%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (bs, 1H, Ar), 8.16 (d, 1H, J = 9.6 Hz, Ar), 6.24 (2a 1H, J = 9.6 Hz, Ar), 1.74 (s, 15H, Cp*); ^{13}C NMR: (100.5 MHz, $CDCl_3$): δ 173.9 (aromatic), 146.0 (aromatic), 134.4 (aromatic), 133.9 (aromatic), 114.2 (aromatic), 86.3 (C_5Me_5), 9.6 ($C_5\mathit{Me}_5$). Found: C, 34.36; H, 3.79; N, 5.47. Calcd for $C_{15}H_{18}N_2O_3ClIr\cdot H_2O$: C, 34.64; H, 3.88; N, 5.39.

2.2.4. [Cp*Ir(4-methyl-5-trifluoromethyl-2-pyridonate)Cl] (**2bc**)

104 mg (39%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (s, 1H, Ar), 6.06 (s, 1H, Ar), 2.34 (s, 3H, Me), 1.76 (s, 15H, Cp*); ^{13}C NMR: (100.5 MHz, $CDCl_3$): δ 177.9 (aromatic), 149.0 (aromatic), 124.5 (q, J = 271 Hz, CF_3), 115.8 (aromatic), 114.4 (q, J = 31 Hz, *ipso*-position of CF_3), 84.2 (C_5Me_5), 19.5 (CH_3), 9.6 ($C_5\mathit{Me}_5$). Found: C, 37.66; H, 3.73; N, 2.59.

Table 1
Spectral and analytical data of **2ad**, **2ae**, **2af**, **2bc**, **2bd**, **2be**, and **2bf**.

Complex	^{1}H NMR (400 MHz, $CDCl_3$) δ	^{13}C NMR (100.5 MHz, $CDCl_3$) δ	Elemental analysis
2ad	8.54 (s, 1H, Ar), 7.70 (d, 1H, J = 8.8 Hz, Ar), 6.20 (d, 1H, J = 8.8 Hz, Ar), 3.85 (s, 3H, COOMe), 1.76 (s, 15H, Cp*)	178.8 (Ar), 165.6 (CO), 145.8 (Ar), 139.8 (Ar), 114.7 (Ar), 113.4 (Ar), 84.3 (C_5Me_5), 52.0 (OCH_3), 9.5 ($C_5\mathit{Me}_5$)	Found: C, 39.19; H, 3.98; N, 2.70. Calcd. For $C_{17}H_{21}NO_3ClIr$: C, 39.64; H, 4.11; N, 2.72.
2ae	8.18 (s, 1H, Ar), 7.42 (d, 1H, J = 9.2 Hz, Ar), 6.13 (d, 1H, J = 9.2 Hz, Ar), 1.76 (s, 15H, Cp*)	172.7 (Ar), 151.6 (Ar), 139.8 (Ar), 118.4 (CN), 116.0 (Ar), 93.5 (Ar), 85.2 (C_5Me_5), 9.5 ($C_5\mathit{Me}_5$)	Found: C, 39.04; H, 3.90; N, 5.43. Calcd for $C_{16}H_{18}N_2OClIr\cdot H_2O$: C, 38.44; H, 4.03; N, 5.60.
2af	8.91 (bs, 1H, Ar), 8.16 (d, 1H, J = 9.6 Hz, Ar), 6.24 (2a 1H, J = 9.6 Hz, Ar), 1.74 (s, 15H, Cp*)	173.9 (Ar), 146.0 (Ar), 134.4 (Ar), 133.9 (Ar), 114.2 (Ar), 86.3 (C_5Me_5), 9.6 ($C_5\mathit{Me}_5$)	Found: C, 34.36; H, 3.79; N, 5.47. Calcd for $C_{15}H_{18}N_2O_3ClIr\cdot H_2O$: C, 34.64; H, 3.88; N, 5.39.
2bc	7.99 (s, 1H, Ar), 6.06 (s, 1H, Ar), 2.34 (s, 3H, Me), 1.76 (s, 15H, Cp*)	177.9 (Ar), 149.0 (Ar), 124.5 (q, J = 271 Hz, CF_3), 115.8 (Ar), 114.4 (q, J = 31 Hz, *ipso*-position of CF_3), 84.2 (C_5Me_5), 19.5 (CH_3), 9.6 ($C_5\mathit{Me}_5$)	Found: C, 37.66; H, 3.73; N, 2.59. Calcd. For $C_{17}H_{20}F_3NOClIr$: C, 37.88; H, 3.74; N, 2.60.
2bd	8.49 (s, 1H, Ar), 6.02 (s, 1H, Ar), 3.82 (s, 3H, COOMe), 2.51 (s, 3H, Me), 1.76 (s, 15H, Cp*)	178.2 (Ar), 166.1 (CO), 153.3 (Ar), 146.5 (Ar), 115.2 (Ar), 114.8 (Ar), 84.1 (C_5Me_5), 51.6 (OCH_3), 22.5 (CH_3), 9.6 ($C_5\mathit{Me}_5$)	Found: C, 40.17; H, 4.31; N, 2.52. Calcd for $C_{18}H_{23}NOClIr$: C, 40.86; H, 4.38; N, 2.65.
2be	8.22 (bs, 1H, Ar), 6.10 (s, 1H, Ar), 2.18(s, 3H, Me), 1.53(s, 15H, Cp*)	168.6 (Ar), 155.3 (Ar), 147.5 (Ar), 118.3 (CN), 115.6 (Ar), 94.4 (C_5Me_5), 19.0 (CH_3), 8.1 ($C_5\mathit{Me}_5$)	Found: C, 38.85; H, 4.06; N, 4.83. Calcd for $C_{17}H_{20}N_2OClIr\cdot(H_2O)_2$: C, 38.38; H, 4.55; N, 5.27.
2bf	8.82 (bs, 1H, Ar), 6.04 (s, 1H, Ar), 2.59 (s, 3H, Me), 1.76 (s, 15H, Cp*)	173.1 (Ar), 147.1 (Ar), 146.0 (Ar), 135.1 (Ar), 116.0 (Ar), 85.3 (C_5Me_5), 21.8 (CH_3), 9.6 ($C_5\mathit{Me}_5$)	Found: C, 37.07; H, 3.92; N, 5.39. Calcd for $C_{16}H_{20}ClN_2O_3Ir$: C, 37.24; H, 3.91; N, 5.43.

Calcd. For $C_{17}H_{20}F_3NOClIr$: C, 37.88; H, 3.74; N, 2.60.

*2.2.5. [Cp*Ir(5-methoxycarbonyl-4-methyl-2-pyridonate)Cl] (**2bd**)*

108 mg (68%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (s, 1H, Ar), 6.02 (s, 1H, Ar), 3.82 (s, 3H, COOMe), 2.51 (s, 3H, Me), 1.76 (s, 15H, Cp*); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 178.2 (aromatic), 166.1 (CO), 153.3 (aromatic), 146.5 (aromatic), 115.2 (aromatic), 114.8 (aromatic), 84.1 (C_5Me_5), 51.6 (OCH_3), 22.5 (CH_3), 9.6 ($C_5\mathit{Me}_5$). Found: C, 40.17; H, 4.31; N, 2.52. Calcd for $C_{18}H_{23}NOClIr$: C, 40.86; H, 4.38; N, 2.65.

*2.2.6. [Cp*Ir(5-cyano-4-methyl-2-pyridonate)Cl] (**2be**)*

78 mg (32%): ^{1}H NMR (500MHz, DMSO): δ 8.22 (bs, 1H, Ar), 6.10 (s, 1H, Ar), 2.18(s, 3H, Me), 1.53(s, 15H, Cp*); ^{13}C NMR (125.65 MHz, $CDCl_3$): δ 168.6 (aromatic), 155.3 (aromatic), 147.5 (aromatic), 118.3 (CN), 115.6 (aromatic), 94.4 (C_5Me_5), 19.0 (CH_3), 8.1 ($C_5\mathit{Me}_5$). Found: C, 38.85; H, 4.06; N, 4.83. Calcd for $C_{17}H_{20}N_2OClIr\cdot(H_2O)_2$: C, 38.38; H, 4.55; N, 5.27.

*2.2.7. [Cp*Ir(5-nitro-4-methyl-2-pyridonate)Cl] (**2bf**)*

68 mg (26%): ^{1}H NMR (400MHz, $CDCl_3$): δ 8.82 (bs, 1H, Ar), 6.04 (s, 1H, Ar), 2.59 (s, 3H, Me), 1.76 (s, 15H, Cp*); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 173.1 (aromatic), 147.1 (aromatic), 146.0 (aromatic), 135.1 (aromatic), 116.0 (aromatic), 85.3 (C_5Me_5), 21.8 (CH_3), 9.6 ($C_5\mathit{Me}_5$). Found: C, 37.07; H, 3.92; N, 5.39. Calcd for $C_{16}H_{20}ClN_2O_3Ir$: C, 37.24; H, 3.91; N, 5.43.

2.3. X-ray structure analysis of **2ad**, **2bc**, and **2bf**

Diffraction data were obtained with a Rigaku RAXIS RAPID instrument. Reflection data were corrected for Lorentz and polarization effects. Empirical absorption corrections were applied. The structure was solved by Patterson methods (DIRDIF99 PATTY) [26,27] and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. Atomic scattering factors and anomalous dispersion terms were taken from the literature [28–31]. Hydrogen atoms were located on the idealized positions, however, hydrogen atoms of the coordinated water molecule were not located. The calculations were performed using the program system Crystal Structure [32,33]. ORTEP drawings of **2ad, 2bc,** and **2bf** are shown in Fig. 2 and the bond parameters are summarized in Table 2. The crystal data and details are shown in CIF files.

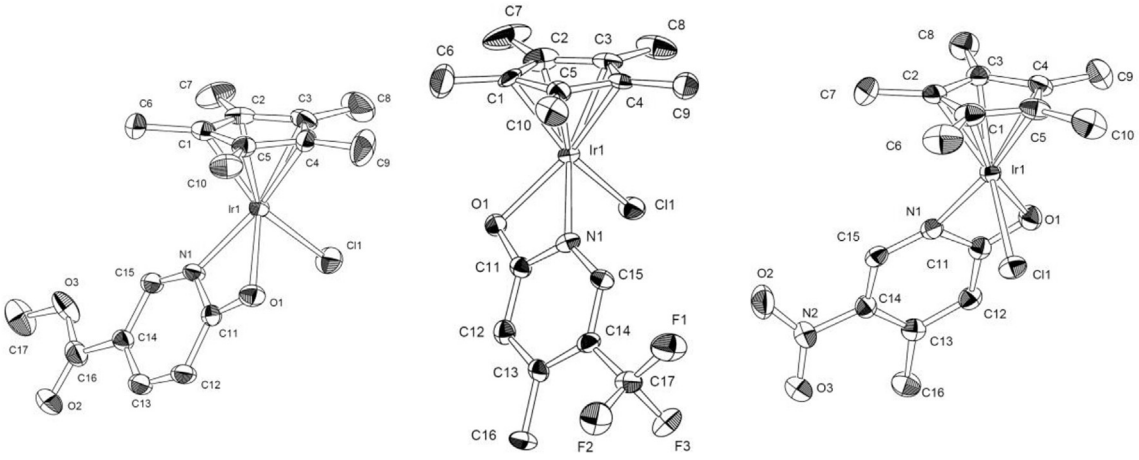


Fig. 2. ORTEP drawings of complexes **2ad** (left), **2bc** (center), and **2bf** (right).

Table 2
Bond parameters (values in Å) of **2ad**, **2bc**, **2bf,** and **2aa**.

	2ad	2bc	2bf	2aa [16]
Ir–N1	2.130(4)	2.098(6)	2.119(4)	2.118(4)
Ir–O1	2.198(4)	2.216(5)	2.192(4)	2.181(4)
Ir–Cl1	2.3899(18)	2.3834(15)	2.3998(13)	2.3818(15)
N1–C11	1.358(7)	1.348(10)	1.373(6)	1.366(8)
O1–C11	1.283(7)	1.300(8)	1.286(6)	1.276(7)

*2.4. Procedures for acceptorless dehydrogenation of 1-phenylethanol catalyzed by Cp*Ir(5- and 4,5-subsutituted 2-pyrionate)Cl (**2**) (Table 3)*

A solution of 1-phenylethanol (1.221 g, 10 mmol) and catalysts **2** (0.01 mmol) in toluene (3 mL) was refluxed for 20 h at 135 °C (oil bath temperature). After the mixture was cooled to room temperature, 1,4-diisopropylbenzene (500 mg) was added as an internal standard. The mixture was then diluted with toluene (12 mL) and analyzed by GC using authentic acetophenone. The results are shown in Table 3.

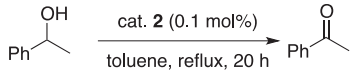
*2.5. Procedures for acceptorless dehydrogenation of 1-phenylethanol catalyzed by **2ac**, **2bc**, **2bd**, and **2be** (Table 4)*

A solution of 1-phenylethanol (2.443 g, 20 mmol) and catalysts **2** (0.01 mmol) in toluene (6 mL) was refluxed for 20 h at 135 °C (oil bath temperature). After the mixture was cooled to room temperature, 1,4-diisopropylbenzene (1.0 g) was added as an internal standard. The mixture was then diluted with toluene (24 mL) and analyzed by GC using authentic acetophenone. The results are shown in Table 4.

*2.6. Procedures for acceptorless dehydrogenation of 2-octanol catalyzed by **2bc** (eq (2))*

A solution of 2-octanol (652 mg, 20 mmol) and catalyst **2bc** (5.7 mg, 0.01 mmol) in toluene (2 mL) was refluxed for 20 h at 135 °C (oil bath temperature). After the mixture was cooled to room temperature, biphenyl (256 mg) was added as an internal standard. The mixture was then diluted with toluene (8 mL) and analyzed by GC using authentic 2-ocatnone to give 91% yield of the product.

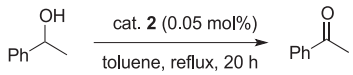
Table 3
Acceptorless dehydrogenation of 1-phenylethanol catalyzed by various Cp*Ir 2-pyridonate complexes.[a]



Entry	Catalyst	Conversion (%)[b]	Yield (%)[b]
1	**2aa**	84	84
2	**2ab**	37	35
3	**2ac**	98	97
4	**2ad**	92	91
5	**2ae**	70	70
6	**2af**	68	68
7	**2bc**	99	99
8	**2bd**	95	95
9	**2be**	97	97
10	**2bf**	87	87

[a] The reaction was carried out with 1-phenylethanol (10 mmol), catalyst (0.1 mol %) in toluene (3 mL) under reflux for 20 h.
[b] Determined by GC.

Table 4
Acceptorless dehydrogenation of 1-phenylethanol catalyzed by **2ac**, **2bc**, **2bd**, and **2be**.[a]



Entry	Catalyst	Conversion (%)[b]	Yield (%)[b]	TON[c]
1	**2ac**	78	78	1560
2	**2bc**	83	83	1660
3	**2bd**	53	52	1040
4	**2be**	59	59	1180

[a] The reaction was carried out with 1-phenylethanol (20 mmol), catalyst (0.05 mol%) in toluene (6 mL) under reflux for 20 h.
[b] Determined by GC.
[c] Turnover number.

*2.7. Procedures for acceptorless dehydrogenation of primary alcohols catalyzed by **2bc** (Table 5)*

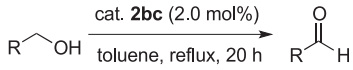
A solution of an alcohol (0.5 mmol) and catalyst **2bc** (5.7 mg, 0.01 mmol) in toluene (9 mL) was refluxed for 20 h at 135 °C (oil bath temperature). In the reaction of cyclohexylmethanol, *p*-xylene was used as the solvent and the solution was refluxed for 20 h at 160 °C (oil bath temperature). After the mixture was cooled to room temperature, biphenyl (25 mg) was added as an internal standard. The mixture was analyzed by GC using an authentic sample. The results are shown in Table 5.

3. Results and discussion

3.1. Synthesis of iridium complexes bearing substituted 2-pyridonates

We started to synthesize iridium complexes bearing various 5-susbstituted 2-pyridonates, because it is considered that the 5-position (*para*-position to the hydroxyl group) must be the most influential position for the electronic effect of the 2-pyridonate ligand. Since it is expected that an electron withdrawing group (EWG) could increase the basicity of the 2-pyridonate ligand as the proton acceptor in the activation step as well as the acidity of the 2-hydroxyl group as the proton donor in the dehydrogenation step, we have introduced several electron-withdrawing groups at the 5-position. In addition, methyl group is introduced to the 4-position (*para*-position to the nitrogen atom) as the electron-donating group (EDG) in order to increase coordination ability of the ligand

Table 5
Acceptorless dehydrogenation of primary alcohols catalyzed by **2bc**.[a]



Entry	R	Yield (%)[b]
1	Ph	94
2	4-BrC_6H_4	76
3	4-$F_3CC_6H_4$	52
4	4-$MeO_2CC_6H_4$	57
5	c-C_6H_{11}	60
6[c]	C_7H_{15}	36

[a] The reaction was carried out with an alcohol (0.5 mmol), catalyst (2.0 mol%) in toluene (9 mL) under reflux for 20 h.
[b] Determined by GC.
[c] The reaction was conducted in *p*-xylene.

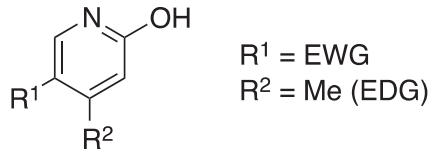
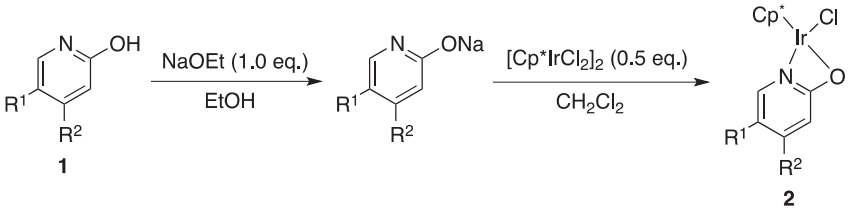


Fig. 3. Substituted 2-hydorxypyridines.

to iridium center (Fig. 3).

The synthetic route is depicted in eq. (1). Treatment of a variety of substituted 2-hydroxylpyridines (**1**) with sodium ethoxide gave sodium salts, which then reacted with $[Cp^*IrCl_2]_2$ (Cp^* = pentamethylcyclopentadienyl) to give the corresponding various Cp*Ir 2-pyridonate complexes (**2**) in 29–75% yields after recrystallization.



(1)

1aa, 2aa : R^1 = H, R^2 = H
1ab, 2ab : R^1 = Me, R^2 = H
1ac, 2ac : R^1 = CF_3, R^2 = H
1ad, 2ad : R^1 = CO_2Me, R^2 = H
1ae, 2ae : R^1 = CN, R^2 = H
1af, 2af : R^1 = NO_2, R^2 = H
1bc, 2bc : R^1 = CF_3, R^2 = Me
1bd, 2bd : R^1 = CO_2Me, R^2 = Me
1be, 2be : R^1 = CN, R^2 = Me
1bf, 2bf : R^1 = NO_2, R^2 = Me

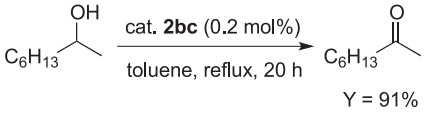
The structures of the complexes were determined by ^1H and ^{13}C NMR spectroscopy, and elemental analyses and those of complexes **2ad**, **2bc**, and **2bf** were further confirmed by X-ray analyses (Fig. 2). The bond parameters are summarized in Table 2. Bond lengths of Ir-N in complexes **2ad**, **2bc**, and **2bf** were 2.130(4), 2.098(6), 2.119(4) Å, respectively. Bond lengths of Ir-O in complexes **2ad**, **2bc**, and **2bf** were 2.198(4), 2.216(5), 2.192(4) Å, respectively. Bond lengths of Ir-N and Ir-O in complexes **2ad** and **2bf** were close to the corresponding bond lengths in complex **2aa** [Ir-N: 2.118(4) Å; Ir-O: 2.181(4) Å] [16]. On the other hand, the bond length of Ir-N in complex **2bc** was slightly shorter than that in complex **2aa**, while Ir-O in **2bc** was much longer than that in **2aa**, indicating stronger coordination of the pyridonate ligand in **2bc**.

3.2. Acceptorless dehydrogenation of 1-phenylethnol catalyzed by various Cp*Ir 2-pyridonate complexes

We next examined acceptorless dehydrogenation of 1-phenylethanol catalyzed by a series of Cp*Ir 2-pyridonate complexes (**2aa**-**2bf**) as a benchmark test to compare their catalytic performance. The reactions were conducted by using 0.1 mol% of the complexes in toluene at reflux temperature for 20 h. The results are shown in Table 3. Electron-withdrawing groups such as 5-trifluoromethyl and 5-methoxylcarobonyl groups increased the yields of acetophenone (entries 3 and 4), whereas introduction of electron-donating methyl group at the 5-position significantly retarded the reaction (entry 2). Furthermore, it is apparent that introduction of methyl group at the 4-position clearly improved the catalytic performance to give acetophenone in excellent yields (entries 3, 4, and 5 vs. entries 7, 8, and 9). These results indicate that the prediction mentioned above is valid for consideration of the catalytic performance of Cp*Ir(2-pyiridonate)Cl complexes.

In order to precisely compare the catalytic activities of complexes **2ac**, **2bc**, **2bd**, and **2be**, the reactions using a smaller amount of the catalyst (0.05 mol%) were carried out. The results are summarized in Table 4. It is obvious that complex **2bc** demonstrates the highest catalytic performance among the complexes examined, and TON reached up to 1660 in 20 h (entry 2).

It should be added that acceptorless dehydrogenation of an aliphatic secondary alcohol can also be effectively catalyzed by complex **2bc**. Thus, the reaction of 2-octanol was conducted by using 0.2 mol% of **2bc** under reflux in toluene for 20 h to give 2-octanone in 91% yield (equation (2)).



(2)

3.3. Acceptorless dehydrogenation of primary alcohols catalyzed by 2bc

We have next examined the reactions of various primary alcohols by using highly active catalyst **2bc**, because acceptorless dehydrogenations of primary alcohols are generally more difficult than those of secondary alcohols. The results are shown in Table 5. While the reactions of benzylic alcohols carried out by using 2.0 mol% of **2bc** in refluxing toluene to give the corresponding benzaldehydes in moderate to high yields (entries 1–4), the reactions of aliphatic primary alcohols gave lower yields of aliphatic aldehydes (entries 5 and 6). These results indicate that the catalytic performance of **2bc** is higher than that of catalysts **A** and **B** bearing 2-hydroxypyridine-based ligands, because **A** did not exhibit high activity [16] for the dehydrogenation of primary alcohols and **B** showed high activity only under basic conditions [17].

4. Conclusions

In summary, we have synthesized a series of Cp*Ir complexes bearing 5-substituted 2-pyridonate ligands and compared their catalytic performance for acceptorless dehydrogenation of 1-phenylethanol. Among various electron-withdrawing groups such as trifluoromethyl, methoxycarbonyl, cyano, and, nitro groups, Cp*Ir complex **2ac** bearing 5-trifluoromethyl-2-pyridonate ligand exhibited the higher catalytic activity. Furthermore, we have disclosed that introduction of methyl group at the 4-position in pyridonate ligand improved the catalytic performance. Thus, Cp*Ir complex **2bc** bearing 4-methyl-5-trifuloromethyl-2-pyridonate ligand gave the best result. Furthermore, complex **2bc** demonstrated good catalytic activity for acceptorless dehydrogenation of primary alcohols. These results may provide the valuable information for designing functional 2-hydroxypyridine-based ligands in organometallic catalysts of acceptorless dehydrogenation of alcohols under mild conditions.

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Appendix A. Supplementary data

Methods for preparations of 5- and 4,5-substitued 2-hydroxypyridines (**1ad**, **1ae**, **1bc**, **1bd**, **1be**) and CIF files for the X-ray studies.

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2017.05.018.

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