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Effect of a Substituent in Cyclopentadienyl Ligand on Iridium-Catalyzed Acceptorless Dehydrogenation of Alcohols and 2-Methyl-1,2,3,4-tetrahydroquinoline

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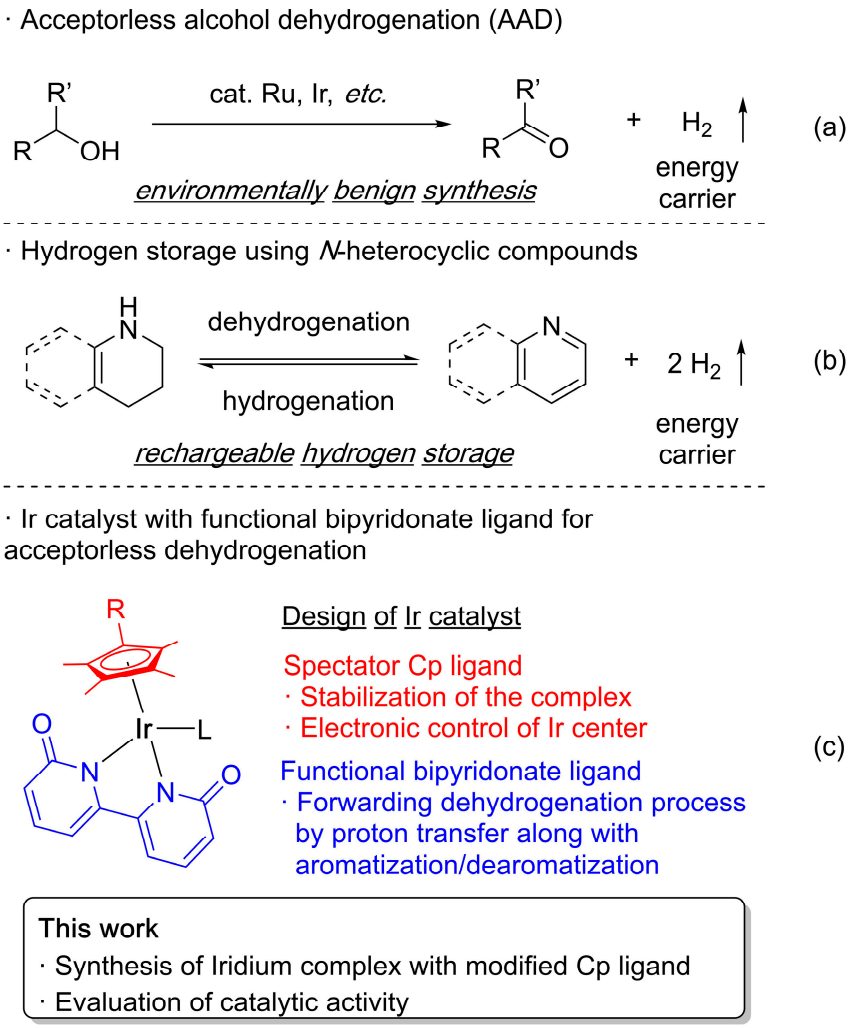
Abstract: New iridium(III)-bipyridonate complexes having cyclopentadienyl ligands with a series of alkyl substituents were synthesized for the purpose of tuning the catalytic activity for acceptorless dehydrogenation reactions. A comparison of the catalytic activity was performed for the reaction of alcoholic substrates such as 1-phenylethanol, 2-octanol, and benzyl alcohol. The 1-*t*-butyl-2,3,4,5-tetramethylcyclopentadienyl iridium complex exhibited the best performance, which surpassed that of the 1,2,3,4,5-pentamethylcyclopentadienyl (Cp*) iridium catalyst in the dehydrogenation reaction of alcohols. The catalytic activity in the dehydrogenation of 2-methyl-1,2,3,4-tetrahydroquinoline was also examined. The highest efficiency was obtained in the reaction catalyzed by the same *t*-butyl-substituted cyclopentadienyl iridium complex.

Keywords: iridium complex; cyclopentadienyl ligand; functional ligand; catalytic dehydrogenation; alcohol; *N*-heterocycle

1. Introduction

Dehydrogenation of small organic molecules without using external oxidants (i.e., acceptorless dehydrogenation) is an attractive transformation reaction from the viewpoint of excellent atomic efficiency [1–4]. Avoidance of the use of harmful oxidants without generating stoichiometric amounts of waste (other than hydrogen gas) meets the requirements of green chemistry. Moreover, the resulting hydrogen gas can be used as a promising energy carrier owing to its high weight energy density and carbon neutrality. These characteristics make the significance of acceptorless dehydrogenation much greater in the field of organic synthesis as well as energy science [4–9]. Owing to the catalytic activity of ruthenium complexes in dehydrogenation reactions of alcohols [10,11], considerable efforts have been made to improve catalytic systems with the development of complexes such as pincer-type ruthenium or iridium complexes with non-innocent behavior of the pincer ligands (Scheme 1a) [12–22]. Recently, a catalytic system has been applied to the dehydrogenation reaction of *N*-heterocyclic compounds for use in hydrogen storage (Scheme 1b) [23–30]. The search for a highly efficient catalytic dehydrogenation system remains a challenging task. Our research group has consistently studied the catalytic activity of pentamethylcyclopentadienyl (Cp*) iridium complexes for the hydrogen transfer process of alcoholic substrates [31–35]. By combining hydroxypyridine or dihydroxybipyridine derivatives as non-innocent ligands, the Cp* iridium complex shows an extremely high catalytic activity in acceptorless dehydrogenation reactions of alcoholic substrates and *N*-heterocyclic compounds (Scheme 1c) [36–47]. Theoretical studies suggest that the spectator Cp* ligand contributes to the stabilization of catalytically active species and to the milder electron-population change on the iridium center during the reaction, which decreases the overall reaction barrier [48].

In general, a cyclopentadienyl (Cp) ligand donates six electrons to a metal center with tridentate coordination mode, which results in stable complexes that are widely used as catalysts. The incorporation of substituents on the Cp ring allows both electronic and steric perturbation on the Cp metal complexes [49–51]. Well-modified Cp ligands have been used to improve the potential catalytic activity and reaction selectivity of transition metal complexes [52–61]. Thus, a systematic study of the modified Cp-ligated iridium complex should provide significant insight for the development of a more active catalytic system for acceptorless dehydrogenation reactions. Herein, we synthesized a series of bipyridonate-coordinated iridium(III) complexes bearing Cp ligands with various alkyl substituents to reveal the trend of catalytic activity in the dehydrogenation of alcohols and 2-methyl-1,2,3,4-tetrahydroquinoline (Scheme 1c). The 1-*tert*-butyl-2,3,4,5-tetramethylcyclopentadienyl iridium complex exhibited higher activity.

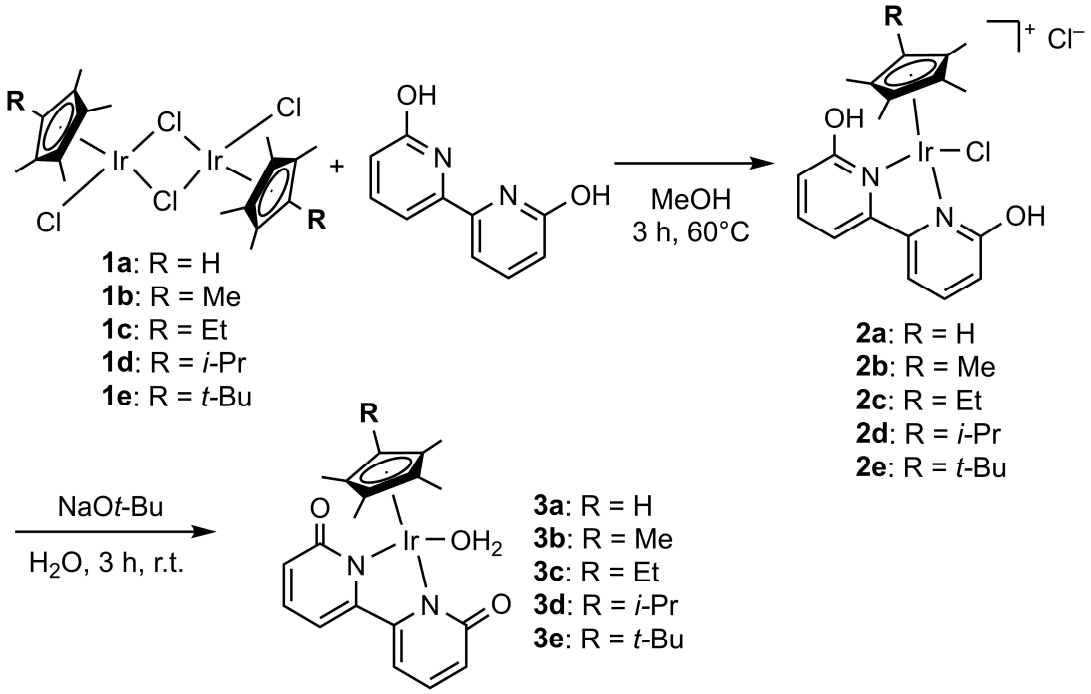


Scheme 1. Acceptorless dehydrogenation of alcohols (**a**) and *N*-heterocyclic compounds (**b**) and design of the iridium catalyst bearing Cp and bipyridonate ligand (**c**).

2. Results

On the basis of our previous studies, in which Cp* iridium complexes exhibited excellent catalytic activity [36–47], we attempted to modify one methyl group in the Cp* ligand to hydrogen, ethyl, isopropyl, and *t*-butyl groups in order to improve the catalytic properties (Scheme 2). A series of cyclopentadienyl-ligated iridium dichloride dimers **1a–1e** were synthesized by the reaction of iridium trichloride with parent cyclopentadiene derivatives [62–64]. The structure of novel complex **1e** was successfully identified by X-ray crystallographic analysis. The coordination reactions of **1a–1e** with

6,6′-dihydroxy-2,2′-bipyridine in methanol at 60 °C gave cationic complexes **2a**–**2e**, which were converted into neutral aquo complexes **3a**–**3e** by treatment with NaO*t*Bu in water. The structures of cationic bipyridine complexes **2** and neutral bipyridonate complexes **3** were fully characterized by ^{1}H and ^{13}C NMR and elemental analysis. X-ray crystallographic analysis could be performed for **2a** and **2e** to provide unambiguous structural information (Figure 1, details are indicated in the Supplementary Materials). The *t*-butyl group of **2e** is located at the trans position to the chloro ligand probably owing to its steric demand. Complexes **2a** and **2e** showed similar structural parameters around the iridium center.



Scheme 2. Synthesis of bipyridonate iridium complexes with a Cp ligand bearing a series of alkyl groups.

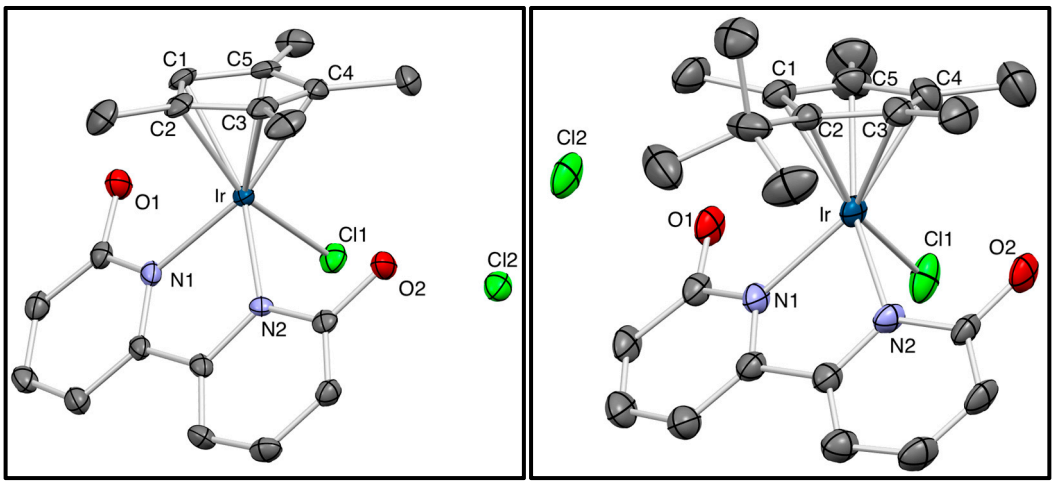
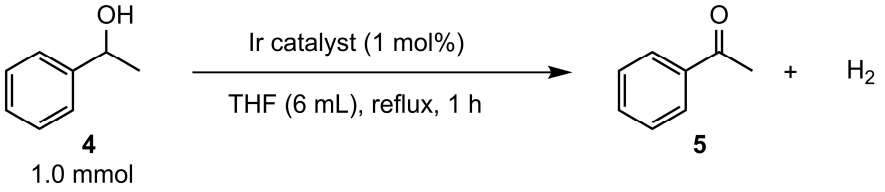


Figure 1. ORTEP illustrations of complexes **2a** (left) and **2e** (right) at the 50% probability level: Solvent molecules and hydrogen atoms are omitted for clarity.

After obtaining a series of iridium catalysts (**3**), their catalytic activities in the dehydrogenation of 1-phenylethanol (**4**), which is a model substrate that we previously studied in detail, were investigated (Table 1). To ensure full solubility of iridium complexes, reactions were performed in THF under reflux conditions. The yield of the dehydrogenated product acetophenone (**5**) after

1 h was determined by gas chromatography (GC) analysis to evaluate initial catalytic activity. In the presence of tetramethylcyclopentadienyl complex **3a**, the dehydrogenation reaction proceeded to give acetophenone in 35% yield (Table 1, entry 1). Cp* complex **3b**, ethyltetramethylcyclopentadienyl complex **3c**, and isopropyltetramethylcyclopentadienyl complex **3d** exhibited higher catalytic activities than **3a** to produce **5** in similar yields (Table 1, entries 2–4). The *t*-butyltetramethylcyclopentadienyl complex **3e** exhibited the highest catalytic activity (Table 1, entry 5). Although the differences in catalytic activity between **3b**–**3d** were not large, the observed trend indicated that a stronger electron-donating cyclopentadienyl ligand leads up to higher catalytic activity. This conclusion is based on the observation that **3a** was least active while **3e** showed the highest catalytic activity. After 24 h, the complete conversion of the starting alcohol was achieved, which suggests that the obtained results originated only from the catalytic activity and not from the deactivation of catalysts.

Table 1. Catalytic activity of iridium complexes (**3**) in the dehydrogenation of **4**.

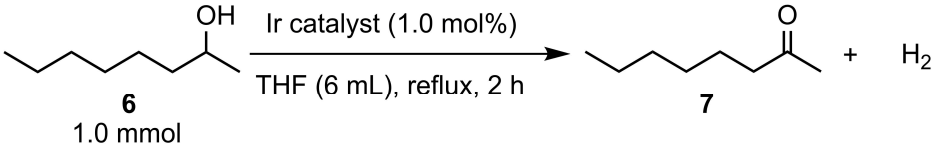


entry	catalyst	conv. (%) [a, b]	yield (%) [a, b]
1	**3a**	35	35
2	**3b**	57	57
3	**3c**	53	53
4	**3d**	55	55
5	**3e**	64	64

[a] Conversion and yields were determined by GC using undecane as internal standard. [b] Average of three runs.

The catalytic abilities of iridium complexes (**3**) were also examined in the dehydrogenation reaction of 2-octanol (**6**) as an aliphatic alcohol in refluxing THF (Table 2). Catalyst **3a** exhibited the lowest catalytic activity to give 2-octanone (**7**) with an 18% yield after 2 h (Table 2, entry 1). Catalyst **3b** exhibited moderate performance and produced a dehydrogenated product with a 49% yield (Table 2, entry 2). The highest catalytic ability was achieved by **3e**, which produced **7** with a 57% yield (Table 2, entry 3). The trend of catalytic ability is consistent with that of the dehydrogenation reaction of 1-phenylethanol (**4**), which is shown in Table 1.

Table 2. Catalytic activity of iridium complexes (**3**) in the dehydrogenation of **6**.



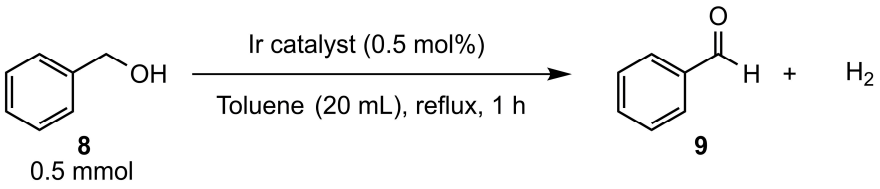
entry	catalyst	conv. (%) [a]	yield (%) [a]
1	**3a**	19	18
2	**3b**	49	49
3	**3e**	57	57

[a] Conversion and yields were determined by GC using biphenyl as internal standard.

However, compared with the dehydrogenation of secondary alcohols, no significant difference in catalytic activity was observed for the primary alcohol (Table 3). The reactions were performed under more diluted conditions than those for secondary alcohols to suppress undesired side reactions, such as self-condensation, leading to ester product. Dehydrogenation reaction of benzyl alcohol (**8**) in refluxing

toluene was carried out in the presence of 0.5 mol% of iridium catalyst to produce benzaldehyde (**9**). Catalyst **3a** exhibited a slightly lower performance compared with catalyst **3b** and **3e** (Table 3, entries 1–3). Catalysts **3b** and **3e** showed similar catalytic activities.

Table 3. Catalytic activity of iridium complexes **3a**, **3b**, and **3e** in the dehydrogenation of **8**.

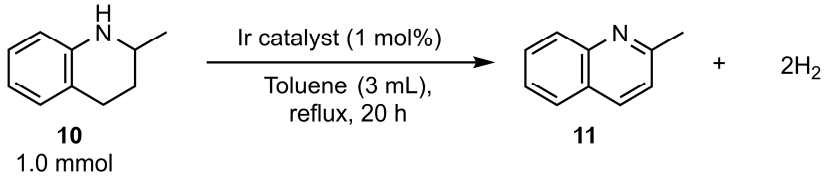


entry	catalyst	yield (%) [a]
1	**3a**	41
2	**3b**	46
3	**3e**	48

[a] Conversion and yields were determined by GC using biphenyl as internal standard.

We have previously reported that the dehydrogenation of a cyclic amine, which leads to aromatized *N*-heterocycles, is also catalyzed by the same iridium complex used for the dehydrogenation of alcoholic substrates [45–47]. Hence, we also examined the catalytic activity of a series of iridium complexes (**3**) in the dehydrogenation of 2-methyl-1,2,3,4-tetrahydroquinoline (**10**) as a model substrate (Table 4). Considering the relatively slower reaction rate for the dehydrogenation of cyclic amines than that of alcohols, the reactions were performed under toluene reflux conditions for 20 h. Catalyst **3a** exhibited moderate catalytic activity to produce the dehydrogenated product 2-methylquinoline (**11**) with a 55% yield (Table 4, entry 1). Catalyst **3b** exhibited high performance with a 91% yield (Table 4, entry 2). The reactions in the presence of catalysts **3c** and **3d** were somehow significantly less effective than the reaction catalyzed by **3b** (Table 4, entries 3 and 4). Similar to the dehydrogenation of alcoholic substrates, the highest catalytic ability was achieved by catalyst **3e** (Table 4, entry 5).

Table 4. Catalytic activity of iridium complexes (**3**) in the dehydrogenation of **10**.



entry	catalyst	conv. (%) [a]	yield (%) [a]
1	3a	55	55
2	3b	91	91
3	3c	83	83
4	3d	62	62
5	3e	99	99

[a] Conversion and yields were determined by GC using undecane as internal standard.

3. Materials and Methods

3.1. General

^{1}H and ^{13}C NMR spectra were recorded on JEOL ECX-500 (500 MHz) and ECS-400 (400 MHz) spectrometers (JEOL, Tokyo, Japan). ^{1}H and ^{13}C NMR spectra of each isolated products are shown in Supplementary Materials. Gas chromatography (GC) analyses were performed on a GC-4000Plus (GL-Science, Tokyo, Japan) with a capillary column (InertCap for Amines and InertCap Pure WAX).

Elemental analyses were carried out at the Microanalysis Center of Kyoto University. Melting points were measured by a Yanaco MP-500D (Yanaco Group, Kyoto, Japan) in air. Dehydrated solvent was used in the reaction. HCp^{*Ethyl}(5-ethyl-1,2,3,4-tetramethylcyclopentadiene) [65], HCp^{*iPr}(5-isopropyl-1,2,3,4-tetramethylcyclopentadiene) [64,65], HCp^{*tBu}(5-tert-butyl-1,2,3,4-tetramethylcyclopentadiene) [66], (Cp*Ir(6,6′-dihydroxy-2,2′-bipyridine)Cl)Cl (**2b**) [67], Cp*Ir(2.2′-bipyridine-6,6′-dionato)H_2O (**3b**) [40], and 6,6′-dihydroxy-2,2′-bipyridine [68] were prepared according to the literature method. All other reagents are commercially available and were used as received (FUJIFILM Wako Pure Chemical Corp., Osaka, Japan); (Nacalai Tesque, Kyoto, Japan); (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan).

3.2. Procedures for the Synthesis of $(Cp^RIrCl_2)_2$

3.2.1. $(\eta^5\text{-}C_5Me_4H)IrCl_2)_2$ (CAS: 835614-43-2) (**1a**)

Under an atmosphere of argon, $IrCl_3{\cdot}5H_2O$ (998.2 mg, 2.57 mmol) was placed in a 50-mL two-neck flask equipped with a Dimroth condenser and three-way cock. Methanol (19.7 mL) and 1,2,3,4-tetramethylcyclopentadiene (1271.3 mg, 10.37 mmol) [69] were added, and the mixture was stirred for 48 h at 90 °C. After cooling to r.t., orange precipitate was filtered with a glass filter, washed with Et_2O (15 mL), and then dried under vacuum to give the title compound as an orange solid (355.5 mg, 0.463 mmol, 36%). ^{1}H NMR (400 MHz, $CDCl_3$, r.t.) δ 5.24 (s, 2H, CpH), 1.66 (s, 12H, $CpCH_3$), 1.61 (s, 12H, $CpCH_3$). ^{13}C NMR (100.5 MHz, $CDCl_3$, r.t.) δ 92.1 (s, CpC), 86.4(s, CpC), 68.0 (s, CpC), 11.1 (s, $CpCH_3$), 9.4 (s, $CpCH_3$).

3.2.2. $(Cp^{*Ethyl}IrCl_2)_2$ (CAS: 2050480-26-5) (**1c**)

Under an atmosphere of argon, $IrCl_3{\cdot}5H_2O$ (645.6 mg, 1.66 mmol) was placed in a 50-mL two-neck flask equipped with a Dimroth condenser and three-way cock. Methanol (13.0 mL) and 5-ethyl-1,2,3,4-tetramethylcyclopentadiene [65] (996.3 mg, 6.63 mmol) were added, and the mixture was stirred for 72 h at 90 °C. After cooling to r.t., the solvent was slightly removed by vacuum and orange precipitate was filtered with a glass filter, washed with Et_2O (15 mL), and then dried under vacuum to give the title compound as an orange solid (458.2 mg, 0.519 mmol, 77%). ^{1}H NMR (400 MHz, $CDCl_3$, r.t.) δ 2.13 (q, 4H, J = 7.6 Hz, CH_2), 1.58 (s, 12H, $CpCH_3$), 1.56 (s, 12H, $CpCH_3$), 1.05 (t, 6H, J = 7.6 Hz, CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, r.t.) δ 89.2 (s, CpC), 86.6 (s, CpC), 86.2 (s, CpC), 17.7 (s, CH_2), 11.8 (s, CH_3), 9.4 (s, $CpCH_3$), 9.2 (s, $CpCH_3$).

3.2.3. $(Cp^{*iPr}IrCl_2)_2$ (CAS: 1621315-48-7) (**1d**)

Under an atmosphere of argon, $IrCl_3{\cdot}5H_2O$ (840.2 mg, 2.16 mmol) was placed in a 50-mL two-neck flask equipped with a Dimroth condenser and three-way cock. Methanol (16.6 mL) and 5-isopropyl-1,2,3,4-tetramethylcyclopentadiene [64,65] (1440.7 mg, 8.77 mmol) were added, and the mixture was stirred for 48 h at 90 °C. After cooling to r.t., orange precipitate was filtered with a glass filter, washed with Et_2O (20 mL), and then dried under vacuum to give the title compound as an orange solid (783.8 mg, 0.919 mmol, 85%). ^{1}H NMR (400 MHz, $CDCl_3$, r.t.) δ 2.46 (sept, 2H, J = 7.2 Hz, CH), 1.66 (s, 12H, $CpCH_3$), 1.58 (s, 12H, $CpCH_3$), 1.26 (d, 12H, J = 7.2 Hz, CH_3). ^{13}C NMR (100.5 MHz, $CDCl_3$, r.t.) δ 90.4 (s, CpC), 86.3 (s, CpC), 86.1 (s, CpC), 25.3 (s, CH), 20.7 (s, $CH(CH_3)_2$), 10.4 (s, $CpCH_3$), 9.6 (s, $CpCH_3$).

3.2.4. $(Cp^{*tBu}IrCl_2)_2$ (**1e**)

Under an atmosphere of argon, $IrCl_3{\cdot}5H_2O$ (546.5 mg, 1.41 mmol) was placed in a 50-mL two-neck flask equipped with a Dimroth condenser and three-way cock. Methanol (11.1 mL) and 5-*tert*-butyl-1,2,3,4-tetramethylcyclopentadiene [66] (1010.0 mg, 5.66 mmol) were added, and the mixture was stirred for 144 h at 90 °C. After cooling to r.t., orange precipitate was filtered with a glass filter, washed with Et_2O (10 mL), and then dried under vacuum to give an orange solid (276.8 mg,

0.314 mmol, 45%). M.P. (decomp.) > 277.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$, r.t.) δ 1.79 (s, 12H, $CpCH_3$), 1.61 (s, 12H, $CpCH_3$), 1.37 (s, 18H, $C(CH_3)_3$). ^{13}C NMR (100.5 MHz, $CDCl_3$, r.t.) δ 92.1 (s, CpC), 87.4 (s, CpC), 84.8 (s, CpC), 33.8 (s, CMe_3), 30.9 (s, $C(CH_3)_3$), 13.3 (s, $CpCH_3$), 10.1 (s, $CpCH_3$). Anal. Calcd for $C_{26}H_{42}Cl_4Ir_2$: C, 35.45; H, 4.81. Found: C, 35.05; H, 4.69.

3.3. Procedures for the Synthesis of (Cp^RIr(6,6′-dihydroxy-2,2′-bipyridine)Cl)Cl

3.3.1. ((η^5-C_5Me_4H)Ir(6,6′-dihydroxy-2,2′-bipyridine)Cl)Cl (**2a**)

Under an atmosphere of argon, ((η^5-C_5Me_4H)$IrCl_2$)$_2$ (**1a**) (49.8 mg, 0.065 mmol), 6,6′-dihydroxy-2,2′-bipyridine (24.4 mg, 0.130 mmol), and methanol (1.1 mL) were placed in a 10-mL two-neck test tube flask equipped with a Dimroth condenser and three-way cock. The mixture was stirred for 3 h at 60 °C. After cooling to r.t., the solvent was removed under reduced pressure and the residue was dried under vacuum to give the title compound as a yellow solid (59.3 mg, 0.1036 mmol, 80%). M.P. (decomp.) > 344.9 °C. ^{1}H NMR (500 MHz, CD_3OD, r.t.) δ 7.99 (t, 2H, *J* = 7.5 Hz, aromatic), 7.93 (d, 2H, *J* = 7.5 Hz, aromatic), 7.12 (d, 2H, *J* = 8.0 Hz, aromatic), 5.87 (s, CpH), 1.73 (s, $Cp(CH)_3$), 1.68 (s, $Cp(CH)_3$). ^{13}C NMR (100.5 MHz, CD_3OD, r.t.) δ 165.4 (s, aromatic), 156.1 (s, aromatic), 143.3 (s, aromatic), 116.4 (s, aromatic), 113.9 (s, aromatic), 92.3 (s, CpC), 91.9 (s, CpC), 77.3 (s, CpC), 10.7 (s, CH_3), 10.0 (s, CH_3). Anal. Calcd for $C_{19}H_{21}Cl_2IrN_2O_2$: C, 39.86; H, 3.70; N, 4.89. Found: C, 39.69; H, 3.68; N, 4.77.

3.3.2. (Cp^{*Ethyl}Ir(6,6′-dihydroxy-2,2′-bipyridine)Cl)Cl (**2c**)

Under an atmosphere of argon, ($Cp^{*Ethyl}IrCl_2$)$_2$ (**1c**) (106.1 mg, 0.13 mmol), 6,6′-dihydroxy-2,2′-bipyridine (48.7 mg, 0.26 mmol), and methanol (2.0 mL) were placed in a 10-mL two-neck test tube flask equipped with a Dimroth condenser and three-way cock. The mixture was stirred for 3 h at 60 °C. After cooling to r.t., the solvent was removed under reduced pressure and the residue was dried under vacuum to give the title compound as a yellow solid (121 mg, 0.201 mmol, 78%). M.P. (decomp.) > 344.7 °C. ^{1}H NMR (400 MHz, CD_3OD, r.t.) δ 7.97 (t, 2H, *J* = 8.0 Hz, aromatic), 7.89 (d, 2H, *J* = 7.8 Hz, aromatic), 7.07 (d, 2H, *J* = 8.2 Hz, aromatic), 2.12 (q, 2H, *J* = 7.6 Hz, CH_2), 1.67 (s, 6H, $Cp(CH)_3$), 1.66 (s, 6H, $Cp(CH)_3$), 1.05 (t, 3H, *J* = 8.0 Hz, CH_3). ^{13}C NMR (100.5 MHz, CD_3OD, r.t.) δ 164.1 (s, aromatic), 154.5 (s, aromatic), 142.0 (s, aromatic), 114.8 (s, aromatic), 112.7 (s, aromatic), 91.2 (s, CpC), 89.6 (s, CpC), 88.9 (s, CpC), 17.3 (s, CH_2), 11.0 (s, CH_3), 8.4 (s, $CpCH_3$), 8.3 (s, $CpCH_3$). Anal. Calcd for $C_{21}H_{25}Cl_2IrN_2O_2$: C, 42.00; H, 4.20; N, 4.66. Found: C, 41.90; H, 4.38; N, 4.53.

3.3.3. (Cp^{*iPr}Ir(6,6′-dihydroxy-2,2′-bipyridine)Cl)Cl (**2d**)

Under an atmosphere of argon, ($Cp^{*iPr}IrCl_2$)$_2$ (**1d**) (101.6 mg, 0.12 mmol), 6,6′-dihydroxy-2,2′-bipyridine (44.8 mg, 0.24 mmol), and methanol (2.0 mL) were placed in a 10-mL two-neck test tube flask equipped with a Dimroth condenser and three-way cock. The mixture was stirred for 3 h at 60 °C. After cooling to r.t., the solvent was removed under reduced pressure and the residue was dried under vacuum to give the title compound as a yellow solid (121.3 mg, 0.197 mmol, 83%). M.P. (decomp.) > 342.3 °C. ^{1}H NMR (400 MHz, CD_3OD, r.t.) δ 7.97 (t, 2H, *J* = 7.6 Hz, aromatic), 7.90 (d, 2H, *J* = 7.8 Hz, aromatic), 7.08 (d, 2H, *J* = 8.2 Hz, aromatic), 2.38 (sept, 1H, *J* = 7.6 Hz, CH), 1.79 (s, 6H, $CpCH_3$), 1.73 (s, 6H, $CpCH_3$), 0.99 (d, 6H, *J* = 7.2 Hz, CH_3). ^{13}C NMR (100.5 MHz, CD_3OD, r.t.) δ 165.5 (s, aromatic), 156.1 (s, aromatic), 143.4 (s, aromatic), 116.1 (s, aromatic), 114.1 (s, aromatic), 98.2 (s, CpC), 88.3 (s, CpC), 86.9 (s, CpC), 26.8 (s, CH), 20.5 (s, CH_3), 11.6 (s, $CpCH_3$), 9.4 (s, $CpCH_3$). Anal. Calcd for $C_{22}H_{27}Cl_2IrN_2O_2$: C, 43.00; H, 4.43; N, 4.56. Found: C, 42.60; H, 4.74; N, 4.42.

3.3.4. (Cp^{*tBu}Ir(6,6′-dihydroxy-2,2′-bipyridine)Cl)Cl (**2e**)

Under an atmosphere of argon, ($Cp^{*tBu}IrCl_2$)$_2$ (**1e**) (36.3 mg, 0.04 mmol), 6,6′-dihydroxy-2,2′-bipyridine (15.7 mg, 0.08 mmol), and methanol (0.7 mL) were placed in a 10-mL two-neck test tube flask equipped with a Dimroth condenser and three-way cock. The mixture was stirred for 3 h at 60 °C.

After cooling to r.t., the solvent was removed under reduced pressure and the residue was dried under vacuum to give the title compound as a yellow solid (44.2 mg, 0.0703 mmol, 86%). M.P. (decomp.) > 344.6 °C. ^{1}H NMR (400 MHz, CD_3OD, r.t.) δ 7.99 (t, 2H, *J* = 7.6 Hz, aromatic), 7.94 (d, 2H, *J* = 8.0 Hz, aromatic), 7.08 (d, 2H, *J* = 8.0 Hz, aromatic), 1.88 (s, 6H, $CpCH_3$), 1.82 (s, 6H, $CpCH_3$), 0.93 (s, 9H, CH_3). ^{13}C NMR (100.5 MHz, CD_3OD, r.t.) δ 165.4 (s, aromatic), 156.2 (s, aromatic), 143.5 (s, aromatic), 116.1 (s, aromatic), 114.2 (s, aromatic), 101.8 (s, CpC), 88.9 (s, CpC), 84.4 (s, CpC), 34.3 (s, CMe_3), 30.3 (s, CH_3), 15.0 (s, $CpCH_3$), 9.6 (s, $CpCH_3$).

3.4. Procedures for the Synthesis of Cp^RIr(2.2′-bipyridine-6,6′-dionato)H_2O

3.4.1. (η^5-C_5Me_4H)Ir(2,2′-bipyridine-6,6′-dionato)H_2O (**3a**)

Under an atmosphere of argon, ((η^5-C_5Me_4H)$IrCl_2$)$_2$ (**1a**) (203.8 mg, 0.27 mmol), 6,6′-dihydroxy-2,2′-bipyridine (99.8 mg, 0.53 mmol), and methanol (6.4 mL) were placed in a 30-mL two-neck round flask equipped with a Dimroth condenser and three-way cock. The mixture was stirred for 3 h at 60 °C. After cooling to r.t., the solvent was removed under reduced pressure and the residue was dried under vacuum overnight to give a yellow solid. Sodium tert-butoxide (102.6 mg, 1.07 mmol) and degassed H_2O (9.3 mL) were added to the same flask and stirred for 3 h at r.t. After the reaction, the precipitate was filtered by cannulation through glass filter under argon atmosphere and dried under vacuum. CH_2Cl_2 (35 mL) was added to dissolve the solid. Solution was collected in flask, and the solvent was evaporated. CH_2Cl_2 (1 mL) was added, followed by the addition of hexane (15 mL) for reprecipitation. The resulting solid was filtered with glass filter and washed with H_2O (10 mL), affording the title compound as a green yellow solid (158.3 mg, 0.306 mmol, 57%) after drying under vacuum. M.P. (decomp.) > 288.9 °C. ^{1}H NMR (400 MHz, CD_3OD, r.t.) δ 7.45 (br t, 2H, *J* = 8.0 Hz, aromatic), 6.71 (br d, 2H, *J* = 7.2 Hz, aromatic), 6.51 (br d, 2H, *J* = 6.8 Hz aromatic), 5.85 (br s, 1H, CpH), 1.72 (br s, 6H, $CpCH_3$), 1.52 (br s, 6H, $CpCH_3$). ^{1}H NMR (500 MHz, CD_3OD, 60 °C) δ 7.23 (t, 2H, , *J* = 12 Hz, aromatic), 6.92 (d, 2H, *J* = 9.0 Hz, aromatic), 6.64 (br, 2H, aromatic), 5.60 (br, 1H, CpH), 1.59 (s, 6H, $CpCH_3$), 1.43 (s, 6H, $CpCH_3$). ^{13}C NMR (100.5 MHz, CD_3OD, 60 °C) δ 171.4 (s, aromatic), 157.7 (s, aromatic), 139.7 (s, aromatic), 118.5 (s, aromatic), 107.5 (s, aromatic), 92.0 (s, CpC), 88.7 (s, CpC), 74.4 (s, CpC), 10.7 (s, $CpCH_3$), 9.9 (s, $CpCH_3$). Anal. Calcd for $C_{19}H_{21}IrN_2O_3$: C, 44.09; H, 4.09; N, 5.41. Found: C, 43.84; H, 3.96; N, 5.39.

3.4.2. Cp^{*Ethyl}Ir(2,2′-bipyridine-6,6′-dionato)H_2O (**3c**)

Under an atmosphere of argon, ($Cp^{*Ethyl}IrCl_2$)$_2$ (**1c**) (198.2 mg, 0.24 mmol), 6,6′-dihydroxy-2,2′-bipyridine (90.4 mg, 0.48 mmol), and methanol (5.8 mL) were placed in a 30-mL two-neck round flask equipped with a Dimroth condenser and three-way cock. The mixture was stirred for 3 h at 60 °C. After cooling to r.t., the solvent was removed under reduced pressure and the residue was dried under vacuum overnight to give a yellow solid. Sodium tert-butoxide (92.3 mg, 0.96 mmol) and degassed H_2O (8.4 mL) were added to the same flask and stirred for 3 h at r.t. After the reaction, the precipitate was filtered by cannulation through glass filter under argon atmosphere and dried under vacuum. CH_2Cl_2 (35 mL) was added to dissolve the solid. Solution was collected in flask, and the solvent was evaporated. CH_2Cl_2 (1 mL) was added, followed by the addition of hexane (15 mL) for reprecipitation. The resulting solid was filtered with glass filter and washed with H_2O (8 mL). The title compound was obtained as a green yellow solid (141.3 mg, 0.259 mmol, 57%) after drying under vacuum. M.P. (decomp.) > 272.3 °C. ^{1}H NMR (400 MHz, CD_3OD, 60 °C) δ 7.42 (t, 2H, *J* = 6.5 Hz, aromatic), 6.90 (d, 2H, *J* = 6.5 Hz, aromatic), 6.52 (br s, 2H, aromatic), 1.95 (br s, 2H, CH_2), 1.47 (s, 12H, $CpCH_3$), 0.93 (br s, 3H, CH_3). ^{13}C NMR (100.5 MHz, CD_3OD, 60 °C) δ 171.3 (s, aromatic), 157.2 (s, aromatic), 139.5 (s, aromatic), 118.3 (s, aromatic), 106.7 (s, aromatic), 90.0 (s, CpC), 88.2 (s, CpC, two peaks may be overlapped), 18.7 (s, CH), 11.9 (s, CH_3), 9.7 (s, $CpCH_3$, two peaks may be overlapped). Anal. Calcd for $C_{21}H_{25}IrN_2O_3$: C, 46.23; H, 4.62; N, 5.13. Found: C, 46.13; H, 4.56; N, 5.11.

3.4.3. $Cp^{*iPr}Ir(2,2'\text{-bipyridine-}6,6'\text{-dionato})H_2O$ (**3d**)

Under an atmosphere of argon, $(Cp^{*iPr}IrCl_2)_2$ (**1d**) (159.3 mg, 0.19 mmol), 6,6′-dihydroxy-2,2′-bipyridine (70.8 mg, 0.38 mmol), and methanol (4.4 mL) were placed in a 30-mL two-neck round flask equipped with a Dimroth condenser and three-way cock. The mixture was stirred for 3 h at 60 °C. After cooling to r.t., the solvent was removed under reduced pressure and the residue was dried with vacuum overnight to give a yellow solid. Sodium tert-butoxide (71.8 mg, 0.75 mmol) and degassed H_2O (6.6 mL) were added to the same flask and stirred for 3 h at r.t. After the reaction, the precipitate was filtered by cannulation through glass filter under argon atmosphere and dried under vacuum. $CHCl_3$ (35 mL) was added to dissolve the solid. The solution was collected in flask, and solvent was evaporated. $CHCl_3$ (1 mL) was added, followed by the addition of hexane (10 mL) for reprecipitation. The resulting solid was filtered with glass filter and washed with H_2O (8 mL). Title compound was obtained as a green yellow solid (87 mg, 0.155 mmol, 42%) after drying under reduced pressure. M.P. (decomp.) > 274.7 °C. ^{1}H NMR (400 MHz, CD_3OD, r.t.) δ 7.43 (t, 2H, *J* = 7.6 Hz, aromatic), 6.93 (d, 2H, *J* = 6.0 Hz, aromatic), 6.42 (d, 2H, *J* = 7.2 Hz, aromatic), 2.16 (br sept, 1H, *J* = 3.6 Hz CH), 1.83 (br s, 6H, $CpCH_3$), 1.71 (br s, 6H, $CpCH_3$), 0.94 (br d, 6H, *J* = 6.4 Hz, CH_3). ^{1}H NMR (400 MHz, CD_3OD, 60 °C) δ 7.40 (t, 2H, *J* = 10.5 Hz, aromatic), 6.88 (d, 2H, *J* = 9.0 Hz, aromatic), 6.43 (br s, 2H, *J* = 11.0 Hz, aromatic), 2.22 (sept, 1H, *J* = 9.0 Hz, CH), 1.77 (s, 6H, $CpCH_3$), 1.70 (s, 6H, $CpCH_3$), 0.97 (d, 6H, *J* = 9.0 Hz, CH_3). ^{13}C NMR (100.5 MHz, CD_3OD, 60 °C) δ 171.2 (s, aromatic), 157.6 (s, aromatic), 139.6 (s, aromatic), 118.2 (s, aromatic), 106.4 (s, aromatic), 94.5 (s, CpC), 89.0 (s, CpC), 81.5 (s, CpC), 26.8 (s, CH), 20.1 (s, CH_3), 11.2 (s, $CpCH_3$), 9.7 (s, $CpCH_3$). Anal. Calcd for $C_{22}H_{27}IrN_2O_3$: C, 47.21; H, 4.86; N, 5.01. Found: C, 47.41; H, 4.98; N, 4.90.

3.4.4. $Cp^{*tBu}Ir(2,2'\text{-bipyridine-}6,6'\text{-dionato})H_2O$ (**3e**)

Under an atmosphere of argon, $(Cp^{tBu}IrCl_2)_2$ (**1e**) (146.5 mg, 0.17 mmol), 6,6′-dihydroxy-2,2′-bipyridine (63.2 mg, 0.34 mmol), and methanol (4.0 mL) were placed in a 30-mL two-neck round flask equipped with a Dimroth condenser and three-way cock. The mixture was stirred for 3 h at 60 °C. After cooling to r.t., the solvent was removed under reduced pressure and dried under vacuum overnight to give a yellow solid. Sodium tert-butoxide (65.5 mg, 0.68 mmol) and degassed H_2O (6.6 mL) were added to the same flask and stirred for 3 h at r.t. After the reaction, the precipitate was filtered by cannulation through glass filter under argon atmosphere and dried under vacuum. $CHCl_3$ (55 mL) was added to dissolve the solid. The solution was collected in flask, and solvent was evaporated. $CHCl_3$ (1 mL) was added, followed by the addition of hexane (15 mL) for reprecipitation. The resulting solid was filtered with glass filter and washed with H_2O (10 mL). The title compound was obtained as a green yellow solid (121.1 mg, 0.211 mmol, 63.6%) after drying under vacuum. M.P. (decomp.) > 280.2 °C. ^{1}H NMR (400 MHz, CD_3OD, r.t.) δ 7.43 (t, 2H, *J* = 7.6 Hz, aromatic), 6.96 (d, 2H, *J* = 6.8 Hz, aromatic), 6.43 (br d, 2H, *J* = 4.8 Hz), 1.93 (s, $CpCH_3$), 1.80 (s, $CpCH_3$), 0,90 (s, CH_3), ^{13}C NMR (100.5 MHz, CD_3OD, r.t.) δ 170.7 (s, aromatic), 157.8 (s, aromatic), 140.0 (s, aromatic), 118.1 (s, aromatic), 106.8 (s, aromatic), 100.2 (s, CpC), 90.6 (s, CpC), 74.5 (s, CpC), 33.7 (s, CH), 29.8 (s, CH_3), 14.8 (s, $CpCH_3$), 10.1 (s, $CpCH_3$), Anal. Calcd for $C_{23}H_{29}IrN_2O_3$: C, 48.15; H, 5.10; N, 4.88. Found: C, 48.36; H, 5.15; N, 4.90.

*3.5. Investigation of Catalytic Activity in Dehydrogenation of 1-Phenylethanol (**4**)*

Under an atmosphere of argon, Ir catalyst (1.0 mol%), THF (6.0 mL), and 1-phenylethanol (**4**) (1.0 mmol) were placed in a 50-mL two-neck round flask equipped with a Dimroth condenser and three-way cock. It was stirred for 1 h at 106 °C (oil bath temperature) under reflux. After the reaction, THF (24 mL) and undecane (internal standard) were added and stirred. Conversion and yield were determined by GC. Average of three runs is shown.

*3.6. Investigation of Catalytic Activity in Dehydrogenation of Benzyl alcohol (**6**)*

Under an atmosphere of argon, Ir catalyst (0.5 mol%), toluene (20 mL), and benzylalcohol (**6**) (0.5 mmol) were placed in a 50-mL two-neck round flask equipped with a Dimroth condenser and three-way cock. It was stirred for 1 h at 131 °C (oil bath temperature) under reflux. After the reaction, toluene (10 mL) and biphenyl (internal standard) were added and stirred. Conversion and yield were determined by GC.

*3.7. Investigation of Catalytic Activity in Dehydrogenation of 2-Octanol (**8**)*

Under an atmosphere of argon, Ir catalyst (1.0 mol%), THF (6 mL), and 2-octanol (**8**) (1.0 mmol) were placed in a 30-mL two-neck round flask equipped with a Dimroth condenser and three-way cock. It was stirred at 131 °C (oil bath temperature) under reflux. After the reaction, toluene (14 mL) and biphenyl (internal standard) were added and stirred. Conversion and yield were determined by GC.

*3.8. Investigation of Catalytic Activity in Dehydrogenation of 2-MeTHQ (**10**)*

Under an atmosphere of argon, Ir catalyst (1.0 mol%), toluene (3 mL), and 2-methyl-1,2,3,4-tetrahydroquinoline (**10**) (1.0 mmol) were placed in a 30-mL two-neck round flask equipped with a Dimroth condenser and three-way cock. It was stirred for 20 h at 131 °C (oil bath temperature) under reflux. After the reaction, toluene (14 mL) and undecane (internal standard) were added and stirred. Conversion and yield were determined by GC.

3.9. X-ray Crystallographic Analyses

Crystallographic data of **1e** was collected on a Rigaku/R Axis Rapid diffractometer with CrystalClear (Rigaku, Tokyo, Japan). Crystallographic data of **2a** and **2e** were collected on a Rigaku/Saturn 70 CCD diffractometer and processed with CrystalClear (Rigaku, Tokyo, Japan). Calculations for **1e** were performed with the CrystalStructure software package (Rigaku, Tokyo, Japan). Calculations for **2a** and **2e** were performed with the Olex2 software package (Ver. 1.2.10, OlexSys Ltd., Durham, UK). Details are indicated in the Supplementary Materials.

4. Conclusions

In conclusion, we successfully synthesized new iridium complexes (**1–3**) having cyclopentadienyl ligands with various alkyl substituents. The *t*-butyl-substituted cyclopentadienyl complex **3e** exhibited a slightly higher catalytic activity than other complexes in the dehydrogenation of alcohols and 2-methyl-1,2,3,4-tetrahydroquinoline. This study provides systematic information on the effect of substituents on the cyclopentadienyl ligand in a catalytic dehydrogenation reaction. However, the reason for the better catalytic performance of **3e** is unclear. Computational studies on the relationship between the effect of the cyclopentadienyl ligand on iridium complexes and their catalytic activity are ongoing.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/9/10/846/s1, detailed description of experimental procedures, ^{1}H and ^{13}C NMR data of the isolated products with spectral charts; the cif and checkcif output files for **1e**, **2a**, and **2e**.

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