Synthesis of New Iridium N-Heterocyclic Carbene Complexes Bearing a Functionalized Cp* Ligand and Their High Catalytic Activities in the Oppenauer-Type Oxidation of Alcohol

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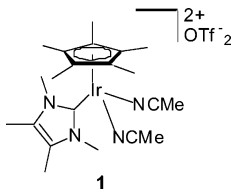
The new iridium N-heterocyclic carbene complexes $Cp^{*N}Ir(IMeMe)Cl_2$ and $Cp^{*N}Ir(IMe)Cl_2$ (Cp^{*N} = η^5-1-[2-(dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl; IMeMe = 1,3,4,5-tetramethylimidazol-2-ylidene; IMe = 1,3-dimethylimidazol-2-ylidene) have been synthesized by reaction of η^5:η^1-$Cp^{*N}IrCl_2$ with silver(I) carbene complexes or a free carbene. The catalytic systems using new iridium carbene complexes as a catalyst precursor and AgOTf showed high catalytic activities in Oppenauer-type oxidation of alcohol and were applicable to oxidations of acid-sensitive alcohols that had been hard to oxidize by using $[Cp^*Ir(IMeMe)(MeCN)_2][OTf]_2$.

Introduction

Cp (Cp = η^5-cyclopentadienyl) and Cp* (Cp* = η^5-pentamethylcyclopentadienyl) ligands are not susceptible to chemical transformation and have been used as effective anchors because they form stable coordination bonds with a metal center in a tridentate coordination fashion. Thus, Cp or Cp* ligands bearing a donor functional group have been employed for the purpose of improving stabilities and hemilabilities of catalytically active species.[1] Recently, N-heterocyclic carbenes (NHCs) have been used as important ligands that can tune properties of a metal center in terms of electron-donating ability and steric hindrance.[2,3] Although the transition metal complexes bearing both functionalized Cp and NHC ligands have been synthesized,[4] to the best of our knowledge, there has been no report on a complex bearing both *functionalized Cp** and NHC ligands to date.

We have reported the synthesis and structure of dicationic Cp*Ir NHC complex **1** and disclosed extremely high catalytic activity (TON up to = 6640) of **1** toward the Oppenauer-type oxidation of primary and secondary alcohols (Chart 1).[5] While complex **1** showed higher catalytic activity than those of some Ru complexes,[6] the oxidation reaction system employing catalyst **1** needs an appropriate base (K_2CO_3 or NEt_3) for selective oxidation of alcohols. However, oxidation of acid-sensitive alcohols by using **1** causes decomposition of starting materials and/or side reactions probably due to the cationic nature of **1**. Furthermore, it has been found that deactivation of **1** occurs by dimerization reaction of the iridium monohydride intermediate. To make an addition of base unnecessary and to decrease the possible deactivation path of **1**, it has been thought that introduction of a 2-(dimethylamino)ethyl group possessing both basicity and coordinating ability into the tetramethylcyclopentadienyl moiety (C_5Me_4) could be effective. Thus, we have synthesized new $Cp^{*N}Ir(NHC)Cl_2$ {Cp^{*N} = η^5-1-[2-(dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl} bearing a η^5-C_5Me_4 ligand functionalized by a 2-(dimethylamino)ethyl substituent.[7] Because the catalytic system using $Cp^{*N}Ir(NHC)Cl_2$ might be kept approximately neutral by the effective intramolecular deprotonation with the dimethylamino group, it is expected that a dicationic complex generated from $Cp^{*N}Ir(NHC)Cl_2$ could exhibit activity in the oxidation of acid-sensitive alcohols with minimal decomposition.

Chart 1



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In this paper, we report the synthesis and structure of new $Cp^{*N}Ir(NHC)Cl_2$. In addition, it is described that the catalytic system employing $Cp^{*N}Ir(NHC)Cl_2$ is applicable to the oxidation of acid-sensitive alcohols and has shown higher catalytic activity than that of **1**.

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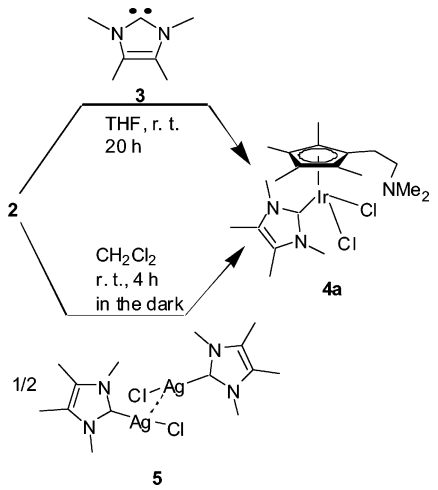
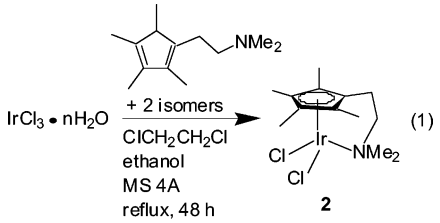
Publication on Web 08/05/2006

Scheme 1. Synthesis of Cp*^{N}Ir(NHC)Cl$_2$ (4a)



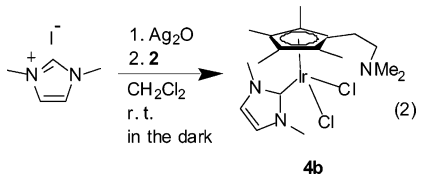
Results and Discussion

Synthesis of Tethered η^5:η^1-Cp*^{N}IrCl$_2$ (2). Reaction of $IrCl_3 \cdot nH_2O$ with isomers of (2-(dimethylamino)ethyl)tetramethylcyclopentadiene in the presence of 4 Å molecular sieves gave tethered η^5:η^1-Cp*^{N}IrCl$_2$ (**2**) in 46% yield (eq 1).[8] The ^{1}H NMR spectrum of **2** in $CDCl_3$ was similar to that of the tethered η^5:η^1-Cp*^{N}IrI$_2$ reported by Jutzi and co-workers.[7] A signal due to the dimethylamino group coordinated to the iridium center was observed at δ 2.73 ppm, and two triplet signals due to methylene protons of the (dimethylamino)ethyl group were observed at δ 3.64 and 2.35 ppm. Two signals assigned to the η^5-C_5Me_4 ligand were also observed at δ 1.78 and 1.60 ppm. In the $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$) of **2**, three signals due to a methyl carbon and methylene carbons of the (dimethylamino)ethyl group were observed at δ 51.7, 79.1, and 22.7 ppm, respectively. Two signals assigned to methyl carbons of the η^5-C_5Me_4 ligand were also observed at δ 9.0 and 8.1 ppm.



Synthesis of Cp*^{N}Ir(NHC)Cl$_2$ (4). Reaction of **2** with 1,3,4,5-tetramethylimidazol-2-ylidene (**3**) afforded Cp*^{N}Ir(L)Cl$_2$ (**4a**; L = **3**) in 37% yield, although 2 equiv of **3** was used for complete conversion of **2** (Scheme 1). The ^{1}H NMR spectrum of **4a** in $CDCl_3$ showed two singlet signals due to methyl protons of the carbene ligand at δ 3.81 and 2.15 ppm with two signals due to the C_5Me_4 ligand (δ 1.66, 1.65 ppm). The multiplet signal due to the methylene proton adjacent to nitrogen of the (dimethylamino)ethyl group and the singlet signal due to the methyl proton of the dimethylamino group were observed at δ 2.4−2.3 and 2.25 ppm, respectively. These signals showed a high-field shift as compared with corresponding signals (δ 3.64, 2.73 ppm) of **2**, indicating that the dimethylamino group is dissociated from the iridium center by coordination of the carbene **3a**.[7] In the $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$) of **4a**, the carbene carbon was observed at δ 153.2 ppm. Signals due to the methylene carbon and methyl carbon adjacent to nitrogen of the (dimethylamino)ethyl group were observed at δ 57.7 and 45.3 ppm, respectively, indicating a high-field shift as compared with corresponding signals (δ 79.1, 51.7 ppm) of **2**.

To improve the yield of **4a**, we examined the preparation of **4a** by means of the synthetic method employing a silver(I) carbene complex as a carbene transfer reagent.[9,10] Reaction of **2** with silver carbene complex **5**[11] gave **4a** in 90% yield (Scheme 1). Similarly a Cp*^{N} iridium complex bearing 1,3-dimethylimidazol-2-ylidene without methyl groups at the C4,5 positions, an analogue of **4a**, was synthesized by using a carbene transfer reagent. Reaction of **2** with a silver(I) carbene complex[9] obtained by treatment of 1,3-dimethylimidazolium iodide with Ag_2O gave Cp*^{N}Ir(L)Cl$_2$ (**4b**; L = 1,3-dimethylimidazol-2-ylidene) in 64% yield (eq 2). The ^{1}H NMR spectrum of **4b** in $CDCl_3$ showed a signal due to the C4, C5 protons of the carbene ligand at δ 6.94 ppm, and a signal due to methyl protons of the carbene ligand was also observed at δ 3.96 ppm. The multiplet signal of the methylene proton adjacent to nitrogen of the (dimethylamino)ethyl group and the singlet signal of the methyl proton of the dimethylamino group were observed at δ 2.3 and 2.24 ppm, respectively, indicating the dissociation of the dimethylamino group from the iridium center. Signals due to the methylene carbon and methyl carbon adjacent to nitrogen of the (dimethylamino)ethyl group were observed at δ 57.7 and 45.3 ppm, respectively, with a signal due to the carbene carbon (δ 155.5 ppm).



Crystal Structure of 4a. The structure of **4a** was confirmed by X-ray crystallographic analysis. The ORTEP drawing of **4a** is illustrated in Figure 1. In the unit cell of **4a**, there are two independent molecules, a and b, but they are isomers formed by rotation of the Cp*^{N} ligand. The carbene carbon (C(1)) of **4a** is attached to the iridium center (Ir(1)) with a bond length of 2.062(8), 2.040(8) Å. Furthermore, the X-ray crystallographic analyses disclosed that the dimethylamino group of the Cp*^{N} ligand dissociates from the iridium center, as the NMR data of **4a** and **4b** indicated the dissociation of a dimethylamino group.

Catalytic Activities of New Cp*^{N}Ir(NHC)Cl$_2$ (4). Because dicationic complexes produced by reaction of **4** with 2 equiv of AgOTf were very unstable, we have chosen to generate the dicationic complexes in situ in the catalytic system. Thus, the Oppenauer-type oxidation of 1-phenylethanol to acetophenone was examined in the presence of the catalyst precursor **4** (0.10 mol %) and AgOTf (0.20 mol %). The results are summarized in Table 1.

Although the previous dicationic Cp*Ir NHC complex **1** showed moderate catalytic activity without base (entry 4), the catalytic systems employing **4** and AgOTf showed high catatytic activities (entries 1, 3). In contrast with these results, the yield

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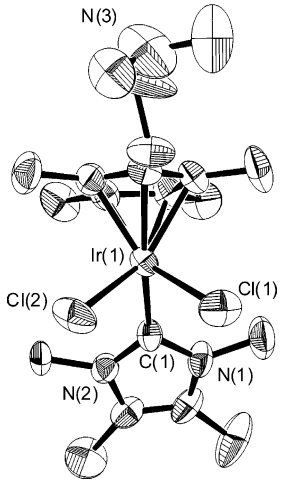
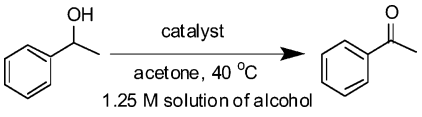


Figure 1. ORTEP drawing (ellipsoids at 50% probability) of **4a**. Hydrogen atoms are omitted for clarity. One of the two independent molecules is represented. Selected bond lengths (Å) and angles (deg): Ir(1)−C(1), 2.062(8), 2.040(8); Ir(1)−Cl(1), 2.423(3), 2.420(2); Ir(1)−Cl(2), 2.419(3), 2.412(2); Cl(1)−Ir(1)−Cl(2), 84.45(9), 86.09(7).

Table 1. Oxidations of 1-Phenylethanol to Acetophenone Catalyzed by 4/AgOTf or 1



entry	catalyst (mol %)	AgOTf (mol %)	time (h)	K_2CO_3 (mol %)	conversion (%)[a]	yield (%)[a]
1	**4a**(0.10)	0.20	4	none	95	95
2	**4a**(0.10)	0.20	4	0.10	63	60
3	**4b**(0.10)	0.20	4	none	97	96
4	**1**(0.10)	none	4	none	60	41
5	**1**(0.025)	none	8	0.025	81	80[b]
6	**4a**(0.026)	0.05	6	none	94	90
7	**4b**(0.026)	0.05	8	none	69	69
8	**4a**(0.10)	none	4	none	1	1
9	**4b**(0.10)	none	4	none	4	1
10	none	0.20	4	none	1	1

[a] The conversion and yield were determined by GC. [b] Ref 5a.

of acetophenone was decreased by addition of K_2CO_3, which was necessary in the oxidation reaction catalyzed by **1**, into the present catalytic system (entry 2). When the amount of the catalyst was reduced to 0.026 mol %, the catalytic system using **4a** showed higher TON than that of the system using **4b** or **1** (entries 5−7). Almost no reaction proceeded without AgOTf or catalyst precursor **4** (entries 8−10).

Time-resolved reaction profiles for the oxidations of 1-phenylethanol to acetophenone catalyzed by catalytic systems of **1**/NEt_3 and **4a**/AgOTf are shown in Figure 2. In the case of the catalytic system of **4a**/AgOTf, the TON in the first 30 min was 880, although the TON of oxidation catalyzed by **1**/NEt_3 was 670 in the first 60 min.[5b] These results indicated that the internal basic (dimethylamino)ethyl group attached to η^5-C_5Me_4 of the catalyst precursor **4a** played a more effective role in trapping of a proton than that of the external base in the catalytic system **1**/NEt_3.

Because the synthesis of **4b** is easier than that of **4a**, we have next undertaken the oxidation reactions of secondary alcohols using **4b** as a main catalyst precursor, and the results are shown in Table 2. In the oxidation of 1-(4-methylphenyl)ethanol, 4-methylacetophenone was obtained in 95% yield, whereas oxidation of 1-(4-chlorophenyl)ethanol substituted by an electron-withdrawing group deceased the yield of the corresponding ketone to 73% (entries 1, 2). When the catalyst **1** was employed in the oxidation of 1-(4-methoxyphenyl)ethanol, 4-methoxyacetophenone was obtained as a minor product probably due to some acid-catalyzed side reaction. In the case of the present catalytic system of **4a**/AgOTf, 4-methoxyacetophenone was obtained in 54% yield (entry 3). Oxidations of cyclopentanol and cycloheptanol gave corresponding ketones in good yield, but oxidation of cyclohexanol afforded cyclohexanone in moderate yield (entries 4−6), showing the similar tendency to that observed in the reactions catalyzed by **1**[5] and other complexes.[6a,b,12]

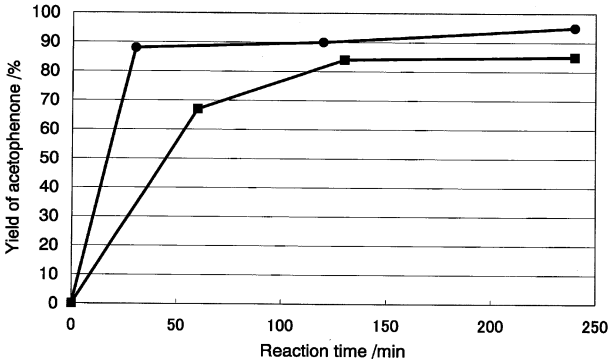
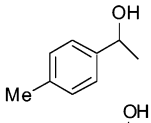
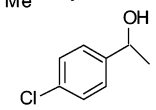
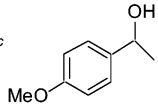
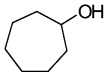


Figure 2. Time-resolved reaction profiles observed for the oxidation of 1-phenylethanol catalyzed by **4a**/AgOTf (●) and **1**/NEt_3 (■). The reaction was carried out at 40 °C with 1-phenylethanol (20 mmol), **4a** or **1** (0.10 mol %), and the additive [AgOTf (0.20 mol %) or NEt_3 (0.10 mol %)] in acetone (16 mL).

Table 2. Oxidations of Secondary Alcohols Catalyzed by 4/AgOTf[a]

entry	alcohol	time (h)	conversion (%)[b]	yield (%)[b]
1		4	97	95
2		4	73	73
3[c]		4	100	54[d]
4		4.5	96	96
5		4	57	57
6		8.5	85	84

[a] The oxidation of a secondary alcohol was carried out at 40 °C with a secondary alcohol (20.0 mmol), **4b** (0.10 mol %), and AgOTf (0.20 mol %) in acetone (16 mL). [b] The conversion and yield were determined by GC. [c] The alcohol (10.0 mmol), **4a** (0.10 mol %), and AgOTf (0.20 mol %) in acetone (8 mL) were used. [d] Unidentified compounds were produced.

The results for oxidation reactions of primary alcohols are shown in Table 3. In the oxidation of primary alcohol, the catalytic system employing **4** as a catalyst precursor showed

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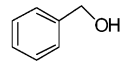
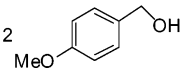
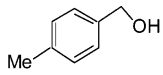
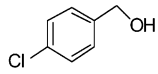
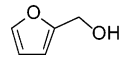
Table 3. Oxidations of Primary Alcohols Catalyzed by 4/AgOTf[a]

entry	alcohol	S/C	time (h)	conversion (%)[b]	yield (%)[b]
1		200	4	100	100
		500	4	91	91
		1000	19	76	76
2		500	6	77	77
3		500	6	77	73
4		500	6	65	63
5[c]		100	6.5	64	56

[a] The oxidation of a primary alcohol was carried out at 40 °C with a primary alcohol (5.0 mmol), **4b** (0.20 mol %), and AgOTf (0.4 mol %) in acetone (60 mL). [b] The conversion and yield were determined by GC. [c] **4a** was used instead of **4b**.

higher catalytic activity than that of the previous catalyst **1**. Although benzaldehyde was obtained in 86% yield in the oxidation of benzyl alcohol catalyzed by **1** (0.50 mol %), in the case of catalytic system **4b**/AgOTf, benzaldehyde was obtained in almost quantitative yield (entry 1). When the amount of **4b** was reduced to 0.20 mol %, a good yield (91%) was still obtained in 4 h. By using even a small amount of **4b** (0.10 mol %), benzaldehyde was obtained in 76% yield, and the TON reached 760 in 19 h. Oxidations of 4-methoxy, 4-methyl, and 4-chlorobenzyl alcohols by the catalytic system **4b** (0.20 mol %)/AgOTf gave corresponding aldehydes in 77, 73, and 63% yield, respectively (entries 2−4). It should be noted that furfuryl alcohol, which decomposed in the oxidation catalyzed by **1**, can be oxidized to afford furfural in 56% yield without a detectable amount of degradation products by the present catalytic system of **4a**/AgOTf (entry 5).

In the present catalytic system, the initial step of the catalytic cycle would involve coordination of an alcohol to the dicationic iridium center produced by treatment of **4** with AgOTf and the subsequent prompt intramolecular deprotonation with the basic (dimethylamino)ethyl group to afford an alkoxo Ir(III) complex.[5a] Because of the existence of a (dimethylamino)ethyl substituent, which would undergo effective intramolecular deprotonation, the oxidation of acid-sensitive alcohols might also proceed successfully.

Conclusion

We have accomplished the synthesis and structure determination of new Cp*^{N}Ir(NHC)Cl$_2$ (**4**) bearing both functionalized Cp* and NHC ligands, on which, to the best of our knowledge, there has been no report to date. The catalytically active species generated by reaction of **4** with AgOTf showed higher catalytic activity than that of **1** in Oppenauer-type oxidation of an alcohol. The present catalytic system makes the addition of base unnecessary and is applicable to oxidation of acid-sensitive alcohols in Oppenauer-type oxidation.

Experimental Section

General Procedures. All the reactions and manipulations were carried out under an atmosphere of argon by means of Schlenk techniques. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on JEOL A-500 and EX-270 spectrometers. Gas chromatography analyses were performed on a GL-Sciences GC353B gas chromatograph with a capillary column (GL-Sciences TC-17). Melting points were determined on a Yanagimoto micro melting point apparatus. Elemental analyses were carried out at the Microanalysis Center of Kyoto University.

Materials. Solvents were dried by using standard procedures and distilled prior to use. THF was distilled from sodium benzophenone ketyl and stored in the presence of metallic potassium. The isomers of (2-(dimethylamino)ethyl)tetramethylcyclopentadiene,[13] 1,3,4,5-tetramethylimidazol-2-ylidene (**3**),[14] silver carbene complex **5**,[11] and 1,3-dimethylimidazolium iodide[15] were prepared by the literature methods. Other reagents were used as obtained from commercial sources.

η^5:η^1-Cp*^{N}IrCl$_2$ (2).[8] IrCl$_3$·*n*H$_2$O (2.442 g, 6.72 mmol), 4 Å molecular sieves (42.286 g), 1,2-dichloroethane (85 mL), and ethanol (20 mL) were placed into a 300 mL flask. The resulting suspension was stirred for 30 min, and isomers of (2-(dimethylamino)ethyl)tetramethylcyclopentadiene (1.396 g, 7.22 mmol) in 1,2-dichloroethane (15 mL) were added into the reaction mixture at room temperature. The mixture was stirred at 90 °C for 48 h and was cooled to room temperature. The suspension was filtered through a pad of Celite, and the solvent was removed to give a crude solid of **2**. The resulting solid was purified by chromatography using a mixed solvent consisting of CH_2Cl_2 (99%) and MeOH (1%) as an eluent. The removal of the solvent gave a brown solid, **2** (3.12 mmol, 46%). Mp: 213.5−215.9 °C. ^{1}H NMR ($CDCl_3$): δ 3.64 (t, J = 7 Hz, 2H, CH_2NMe$_2$), 2.73 (s, 6H, NMe$_2$), 2.35 (t, J = 7 Hz, 2H, Me$_4$C$_5$CH_2), 1.78 (s, 6H, C$_5$Me$_4$), 1.60 (s, 6H, C$_5$Me$_4$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 96.4 (s, *C*$_5$Me$_4$), 89.0 (s, *C*$_5$Me$_4$), 79.1 (s, *C*H$_2$NMe$_2$), 75.6 (s, *C*$_5$Me$_4$), 51.7 (s, NMe$_2$), 22.7 (s, Me$_4$C$_5$*C*H$_2$), 9.0 (s, C$_5$*Me*$_4$), 8.1 (s, C$_5$*Me*$_4$). Anal. Calad for C$_{13}$H$_{22}$NCl$_2$Ir: C, 34.28; H, 4.88; N, 3.08. Found: C, 34.19; H, 4.61; N, 2.92.

Cp*^{N}Ir(IMeMe)Cl$_2$ (4a). 1,3,4,5-Tetramethylimidazole-2(3*H*)-thione (0.207 g, 1.32 mmol) was stirred in THF (4.0 mL) at 0 °C, and metallic potassium (0.511 g, 13.1 mmol) was added. After 15 min, the resulting mixture was heated at reflux for 4 h. The resulting mixture was cooled to room temperature and filtered through a glass filter. The filtrate was dropped through a cannula into a solution of **2** (0.302 g, 0.664 mmol) in THF (4.0 mL) at room temperature. The reaction mixture was stirred for 20 h, and the solvent was removed in vacuo to give a crude solid of **4a**. The resulting solid was purified by chromatography using a mixed solvent consisting of CH_2Cl_2 (97%) and NEt$_3$ (3%) as an eluent. After the solvent was removed, the residue was washed with ether to give a yellow-brown solid, **4a** (0.248 mmol, 37%). Crystals suitable for an X-ray diffraction study were grown from the slow diffusion of hexane into the toluene solution of **4a**. Mp: 148.9−150.3 °C. ^{1}H NMR ($CDCl_3$): δ 3.81 (s, 6H, NMe), 2.3−2.4 (m, 2H, CH_2NMe$_2$), 2.25 (s, 6H, NMe$_2$), 2.1−2.2 (m, 2H, Me$_4$C$_5$CH_2), 2.15 (s, 6H, C═CMe), 1.66 (s, 6H, C$_5$Me$_4$), 1.65 (s, 6H, C$_5$Me$_4$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 153.2 (s, Ir−C), 125.8 (s, C═C), 89.7 (s, *C*$_5$Me$_4$), 88.7 (s, *C*$_5$Me$_4$), 85.8 (s, *C*$_5$Me$_4$), 57.7 (s, *C*H$_2$NMe$_2$), 45.3 (s, NMe$_2$), 35.7 (s, NMe), 23.2 (s, Me$_4$C$_5$*C*H$_2$), 9.5 (s, C═C*Me*), 9.1 (s, C$_5$*Me*$_4$), 8.9 (s, C$_5$*Me*$_4$). Anal. Calcd for C$_{20}$H$_{34}$N$_3$Cl$_2$Ir: C, 41.44; H, 5.92; N, 7.25. Found: C, 41.42; H, 5.78; N, 7.26.

A 50 mL flask was charged with **2** (0.399 g, 0.877 mmol) and CH_2Cl_2 (18 mL). To the resulting solution was added silver(I) carbene complex **5** (0.244 g, 0.911 mmol), and the reaction mixture was stirred for 4 h in the dark at room temperature. After removal of the solvent in vacuo, the residue was extracted with CH_2Cl_2,

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and the solution was filtered through a pad of Celite. After the solvent was removed, the residue was extracted with toluene. The residue formed by the removal of toluene was dissolved in CH_2Cl_2, and then hexane was added into the solution of the crude product to give a yellow-brown precipitate, **4a** (0.785 g, 90%).

Cp*^{N}Ir(IMe)Cl$_2$ (4b). A 50 mL flask was charged with 1,3-dimethylimidazole iodide (1.421 g, 6.34 mmol) and CH_2Cl_2 (25 mL). To the resulting solution was added Ag_2O (1.124 g, 4.85 mmol), and the reaction mixture was stirred for 1.5 h in the dark. The mixture was filtered though a glass filter, and the filtrate was poured into the 50 mL flask, which was charged with **2** (0.364 g, 0.799 mmol) at room temperature. The mixture was stirred for 8 h in the dark, and the suspension was filtered through a pad of Celite. After the solvent was removed, the residue was extracted with CH_2Cl_2, and the solution was filtered through a pad of Celite. After the solvent was removed, the residue was extracted with toluene. The residue formed by the removal of toluene was dissolved in CH_2Cl_2, and recrystallization using CH_2Cl_2 solution and hexane gave orange crystals of **4b** (0.513 mmol, 64%). Mp: 169.3−171.3 °C. ^{1}H NMR ($CDCl_3$): δ 6.94 (s, 2H, NCH=CHN), 3.96 (s, 6H, NMe), 2.3 (m, 2H, C*H*$_2$NMe$_2$), 2.24 (s, 6H, NMe$_2$), 2.2 (m, 2H, Me$_4$C$_5$C*H*$_2$), 1.67 (s, 6H, C$_5$Me$_4$), 1.65 (s, 6H, C$_5$Me$_4$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 155.5 (s, Ir−C), 123.2 (s, C=C), 89.9 (s, *C*$_5$Me$_4$), 89.0 (s, *C*$_5$Me$_4$), 86.3 (s, *C*$_5$Me$_4$), 57.7 (s, *C*H$_2$NMe$_2$), 45.3 (s, NMe$_2$), 38.5 (s, NMe), 23.1 (s, Me$_4$C$_5$*C*H$_2$), 9.1 (s, C$_5$*Me*$_4$), 8.9 (s, C$_5$*Me*$_4$). Anal. Calad for $C_{18}H_{30}N_3Cl_2Ir$: C, 39.19; H, 5.49; N, 7.62; Cl, 12.85. Found: C, 39.10; H, 5.29; N, 7.68; Cl, 12.59.

Typical Procedure for the Oppenaure-Type Oxidation of 1-Phenylethanol Using the Catalyst Precursor 4 (Table 1). The catalyst precursor **4** (20 μmol) and acetone (8 mL) were placed into a 50 mL flask, while another flask was charged with 1-phenylethanol (20 mmol) and acetone (8 mL). Then the solution of 1-phenylethanol was added into the solution containing **4**, and AgOTf (40 μmol) was added into the mixture. The reaction mixture was stirred at 40 °C for 4 h. Conversion of 1-phenylethanol and yield of acetophenone were determined by GC analysis using undecane as an internal standard. The product was characterized by comparing with authentic samples.

Oxidations of Secondary Alcohols Using the Catalyst Precursor 4 (Table 2). The oxidations of secondary alcohols were carried out by procedures similar to the above. The products were characterized by comparing with authentic samples.

4-Methylacetophenone (entry 1). 4-Methylacetophenone (95% yield) was obtained in the oxidation of 1-(4-methylphenyl)ethanol (2.729 g, 20.0 mmol) using **4b** (11.2 mg, 20.3 μmol) and AgOTf (10.5 mg, 40.9 μmol) in acetone (16 mL) for 4 h.

4-Chloroacetophenone (entry 2). 4-Chloroacetophenone (73% yield) was obtained in the oxidation of 1-(4-chlorophenyl)ethanol (3.134 g, 20.0 mmol) using **4b** (11.1 mg, 20.1 μmol) and AgOTf (10.3 mg, 40.1 μmol) in acetone (16 mL) for 4 h.

4-Methoxyacetophenone (entry 3). 4-Methoxyacetophenone (54% yield) was obtained in the oxidation of 1-(4-methoxyphenyl)-ethanol (1.527 g, 10.0 mmol) using **4a** (6.0 mg, 10.4 μmol) and AgOTf (5.2 mg, 20.2 μmol) in acetone (8 mL) for 4 h.

Cyclopentanone (entry 4). Cyclopentanone (96% yield) was obtained in the oxidation of cyclopentanol (1.728 g, 20.1 mmol) using **4b** (11.1 mg, 20.1 μmol) and AgOTf (10.7 mg, 41.6 μmol) in acetone (16 mL) for 4.5 h.

Cyclohexanone (entry 5). Cyclohexanone (57% yield) was obtained in the oxidation of cyclohexanol (2.008 g, 20.0 mmol) using **4b** (11.3 mg, 20.5 μmol) and AgOTf (10.9 mg, 42.4 μmol) in acetone (16 mL) for 4 h.

Cycloheptanone (entry 6). Cycloheptanone (84% yield) was obtained in the oxidation of cycloheptanol (2.286 g, 20.0 mmol) using **4b** (11.0 mg, 19.9 μmol) and AgOTf (10.6 mg, 41.2 μmol) in acetone (16 mL) for 8.5 h.

Oxidations of Primary Alcohols Using the Catalyst Precursor 4 (Table 3). The oxidations were carried out by procedures similar to the oxidation of secondary alcohols. The products were characterized by comparing with authentic samples.

Benzaldehyde (entry 1). Benzaldehyde (91% yield) was obtained in the oxidation of benzyl alcohol (0.541 g, 5.00 mmol) using **4b** (5.7 mg, 10.3 μmol) and AgOTf (5.5 mg, 21.4 μmol) in acetone (60 mL) for 4 h.

4-Methoxybenzaldehyde (entry 2). 4-Methoxybenzaldehyde (77% yield) was obtained in the oxidation of 4-methoxybenzyl alcohol (0.694 g, 5.02 mmol) using **4b** (5.5 mg, 9.97 μmol) and AgOTf (5.5 mg, 21.4 μmol) in acetone (60 mL) for 6 h.

4-Methylbenzaldehyde (entry 3). 4-Methylbenzaldehyde (73% yield) was obtained in the oxidation of 4-methylbenzyl alcohol (0.612 g, 5.01 mmol) using **4b** (5.5 mg, 9.97 μmol) and AgOTf (5.3 mg, 20.6 μmol) in acetone (60 mL) for 6 h.

4-Chlorobenzaldehyde (entry 4). 4-Chlorobenzaldehyde (63% yield) was obtained in the oxidation of 4-chlorobenzyl alcohol (0.713 g, 5.00 mmol) using **4b** (5.6 mg, 10.2 μmol) and AgOTf (5.7 mg, 22.2 μmol) in acetone (60 mL) for 6 h.

Furfural (entry 5). Furfural (56% yield) was obtained in the oxidation of furfuryl alcohol (98.4 mg, 1.00 mmol) using **4a** (5.9 mg, 10.1 μmol) and AgOTf (5.2 mg, 20.2 μmol) in acetone (60 mL) for 6.5 h.

X-ray Structure Analysis of 4a. The crystal data and experimental details for **4a** are summarized in Table S1 (see the Supporting Information). Diffraction data for **4a** were obtained with a Rigaku AFC-5S instrument. The reflection intensities were monitored by three standard reflections every 150 measurements. Reflection data for **4a** were corrected for Lorentz and polarization effects. An absorption correction was empirically applied. The structure of **4a** was solved by the heavy-atom Patterson method[16,17] and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculation. Four carbon atoms were located on a Fourier difference map because of the presence of the corresponding electron densities, although elemental analysis of **4a** showed the absence of the toluene molecules in the crystal. Atomic scattering factors and anomalous dispersion terms were taken from the literature.[18] The hydrogen atoms were located on idealized positions. The calculations were performed using the program system CrystalStructure.[19]

Supporting Information Available: A crystallographic information file (CIF) and Table S1 giving crystallographic data for **4a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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