Synthesis of New Cationic Cp*Ir N-Heterocyclic Carbene Complexes and Their High Catalytic Activities in the Oppenauer-Type Oxidation of Primary and Secondary Alcohols

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Several new cationic Cp*Ir N-heterocyclic complexes have been synthesized and their catalytic activities in the Oppenauer-type oxidation have been investigated in order to improve the catalytic activity of $[Cp^*IrCl(\mu\text{-}Cl)]_2$. The reactions of $[Cp^*IrCl(\mu\text{-}Cl)]_2$ (**1**) with N-heterocyclic carbene ligands afforded $Cp^*Ir(L)Cl_2$ (**3a**−**d**; L = N-heterocyclic carbene ligands). The cationic complexes $[Cp^*Ir(L)(MeCN)_2]^{2+}$ (**5a**−**d**) were obtained by the treatment of **3a**−**d** with 2 equiv of AgOTf followed by addition of CH_3CN. Structures of complexes **3a**−**d** and **5a**−**d** were determined by X-ray crystallographic studies. Complex **5a** (L = 1,3,4,5-tetramethylimidazol-2-ylidene) catalyzed the Oppenauer-type oxidation of primary and secondary alcohols very selectively under mild conditions. In the oxidation of 1-phenylethanol and cyclopentanol using **5a** as a catalyst, turnover numbers reached 3200 and 6640, respectively. These results demonstrate that, to the best of our knowledge, the cationic carbene complex **5a** is the most effective catalyst in homogeneous oxidation of alcohols in terms of its high catalytic activity and wide applicability to the oxidation of primary and secondary alcohols. In this catalytic system, the stronger electron-donating ability of the N-heterocyclic carbene ligand than the phosphine ligand is more favorable for acceleration of the hydride transfer to acetone as a hydrogen acceptor. Additionally, dihydrido carbene complex $Cp^*Ir(L)(H)_2$ (**6**) and dinuclear iridium carbene complex $[Cp^*Ir(L)(\mu\text{-}H)]_2^{2+}$ (**7**) were prepared to investigate the catalytically active species and fate of the catalyst. Thus, it is highly probable that an iridium-monohydride complex is the catalytically active species and that **7**, which could be generated by dimerization of the iridium-monohydride complex in the catalytic system, is inactive.

Introduction

Cp (Cp = η^5-cyclopentadienyl) and Cp* (Cp* = η^5-pentamethylcyclopentadienyl) groups have proved to be efficient ancillary ligands in organometallic complexes. A number of Cp or Cp* transition-metal complexes were synthesized, and a great many reports on their structures and reactivity have appeared in the literature.[1] Although Cp and Cp* ligands stabilize metal centers by tridentate coordination in a facial fashion, it is rather difficult to modify the electronic and steric properties of these ligands.

Since stable N-heterocyclic carbenes (NHCs) were isolated by Arduengo and co-workers,[2] NHCs have appeared as electronically and sterically fine-tunable ligands that make stable coordinate bonds with transition metals. Accordingly, there have been considerable efforts devoted to the studies on transition-metal complexes with NHC, and their intriguing catalytic activities in organic reactions have been rapidly disclosed.[3] NHC ligands resemble tertiary phosphines in possessing strong σ-donating properties with negligible π-backbonding, whereas it has been demonstrated that NHC complexes have greater catalytic activities than those of tertiary phosphines in coupling reactions catalyzed by Pd complexes[4] and olefin metatheses catalyzed by Ru complexes.[5]

Recently, the oxidation of organic compounds in an environmentally benign fashion has received considerable attention. Thus, several transition-metal-catalyzed systems for the oxidation of alcohols using oxygen or hydrogen peroxide as an oxidant have been reported.[6] On the other hand, the Oppenauer-type oxidation of alcohols in which non-noxious acetone can be used as an oxidant is another promising method for the oxida-

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tion of alcohols. Several transition-metal-catalyzed systems for the Oppenauer-type oxidation have been reported,[7] while only a few highly effective ones have been shown. Ru(II) complexes are candidates for the highly effective catalyst in the Oppenauer-type oxidation under elevated temperatures. The turnover numbers (TONs) of $Ru(PPh_3)_3Cl_2$ and dinuclear Ru complex reached 1000 in the case of using secondary alcohols as a starting material.[7f] Additionally, the Ru(II)-diphosphine complex catalyzed the oxidative kinetic resolution of racemic alcohols with high TONs (>1000).[7h] Finally, a Rh−Ru heterobimetallic complex also catalyzed the oxidation of primary and secondary alcohols below room temperature.[7i]

We have recently reported the Oppenauer-type oxidation of alcohols catalyzed by $[Cp^*IrCl(\mu\text{-}Cl)]_2$ (**1**)[8] and found prominent catalytic activity of Cp*Ir complex.[9] However the hydrogen transfer ability of **1** is not so high, because the TON of **1** is less than 200 in the Oppenauer-type oxidation of alcohols. To improve the hydrogen transfer ability of the Cp*Ir catalyst **1**, we designed the molecular structure of the catalyst with consideration of the following points: (1) Increasing nucleophilicity of an iridium-hydride intermediate toward a hydrogen acceptor could be expected by introduction of electron-donating NHC ligands into the Cp*Ir complex. (2) A cationic unsaturated active species, which should be more active than the neutral ones, could be readily generated by dissociation of a neutral molecule (e.g., solvent) from the saturated cationic complex $[Cp^*Ir(NHC)(solvent)_2]^{2+}$. Furthermore, only three examples[10,11] of iridium complexes with both Cp* and NHC ligands have been known, in contrast to a great number of Cp*Ir phosphine complexes. Although the syntheses and reactivities of these three Cp*Ir carbene complexes were reported, their catalytic applications have not been revealed to date.

In this paper, we report the syntheses and structures of new cationic Cp*Ir NHC complexes and their high hydrogen transfer ability in the Oppenauer-type oxidation of alcohols without the formation of byproducts.[12] To the best of our knowledge, the new Cp*Ir NHC complex described here is the most effective catalyst in homogeneous catalytic systems in terms of its high catalytic activity and wide applicability to the oxidation of primary and secondary alcohols.

Results and Discussion

Synthesis of Neutral Cp*Ir NHC Complexes (3a−d). The treatment of $[Cp^*IrCl(\mu\text{-}Cl)]_2$ (**1**) with 2 equiv of the imidazol-2-ylidene (NHC) ligands (**2a**−**c**) gave $Cp^*Ir(NHC)Cl_2$ (**3a**−**c**) as air-stable crystals in 79, 49, and 73% yields, respectively. The saturated-type carbene complex $Cp^*Ir(NHC)Cl_2$ (**3d**) was also synthesized in 52% yield by the reaction of **1** with 4,5-dihydroimidazolium tetrafluoroborate in the presence of ^{t}BuOK[5b] (Scheme 1).

The ^{1}H NMR spectrum of **3a** in $CDCl_3$ showed two singlet resonances due to methyl groups on the 1,3,4,5-tetramethylimidazol-2-ylidene at δ 3.82 and 2.16 along

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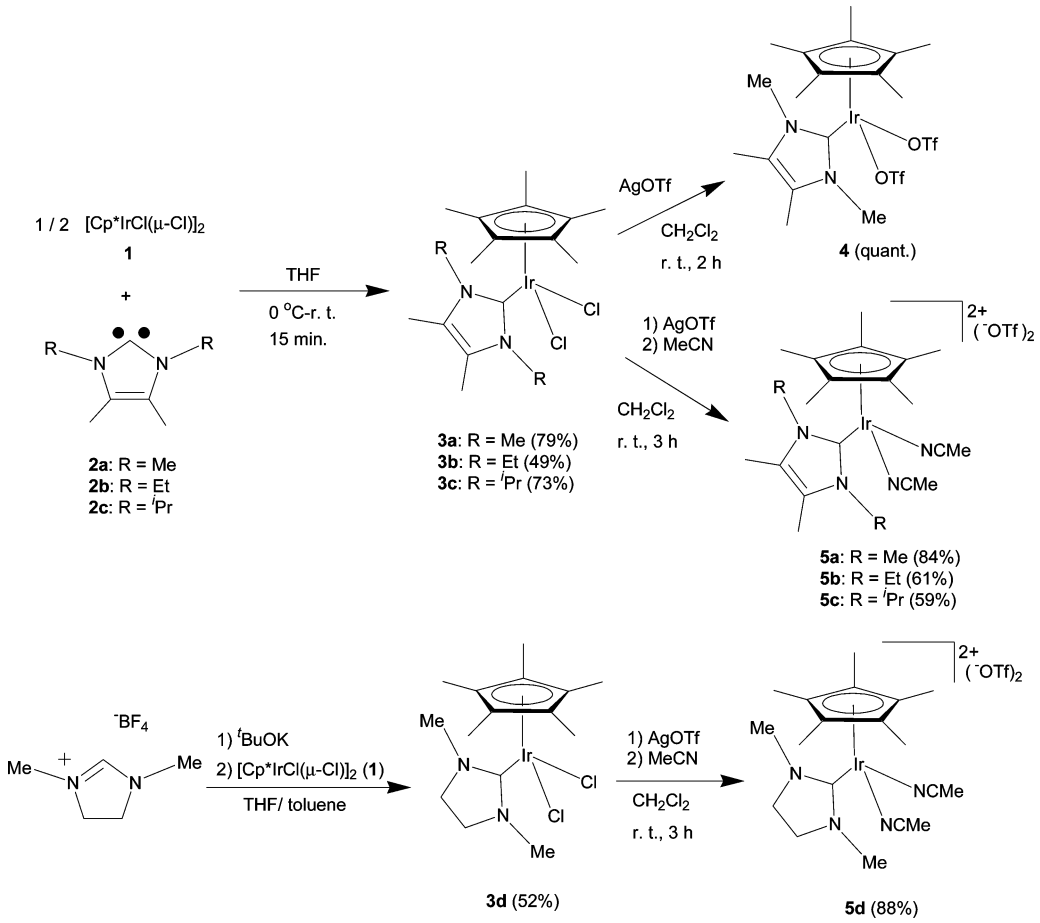
Scheme 1. Synthesis of Cp*Ir N-Heterocyclic Carbene Complexes



with a singlet resonance due to Cp* (δ 1.62). Additionally, the signal due to a carbene carbon of the NHC ligand was observed at δ 153.9 in the $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$) of **3a**. The $^{13}C\{^1H\}$ NMR spectra of **3b**−**d** in $CDCl_3$ also revealed the signals due to the carbene carbon at δ 153.2, 154.9, and 185.8, respectively. The lack of aromaticity of the 4,5-dihydroimidazol-2-ylidene ligand in **3d** was responsible for the observed downfield shift (ca. 30 ppm), indicating that the saturated 4,5-dihydroimidazol-2-ylidene ligand possesses a stronger σ-donating property than that of unsaturated imidazol-2-ylidene ligands, as is widely accepted in N-heterocyclic carbene chemistry.[3]

Crystal Structure of 3a. The structures of **3a**−**d** were elucidated by the above NMR spectral data as well as an X-ray diffraction study of **3a**. The ORTEP drawing of **3a** is illustrated in Figure 1. Selected bond lengths and angles are shown in Table 1.

The geometry around the iridium center is described as a three-legged piano stool, which is common in Cp^*Ir^{III} complexes. The iridium−carbene carbon bond distance (Ir(1)−C(1)) is 2.044(4) Å. This bond length is compatible with a typical single bond length between the iridium center and the carbene carbon reported in previous literature,[10] while the corresponding bond lengths of Fischer-type and Schrock-type carbene complexes are less than 2.00 Å.[3d]

Formation of Bis(triflate) Complex 4. With the neutral dichloro complexes **3** bearing a NHC ligand in hand, we next investigated replacement of chlorine atoms for the preparation of a cationic complex (Scheme 1). The reaction of **3a** with 2 equiv of AgOTf (OTf = trifluoromethanesulfonato) gave bis(triflate) complex $Cp^*Ir(L)(OTf)_2$ (**4**; L = **2a**), the carbene complex analogous to that which was briefly mentioned,[3d] in almost quantitative yield. Although complex **4** is relatively stable in solution under an inert atmosphere, it is very labile in isolated form. Complex **4** was characterized by IR and NMR spectroscopy. In the IR spectra of **4**, the stretching vibration of the sulfonyl group for OTf ligands coordinated to iridium showed a characteristic absorption band at 1309 cm^{-1}, although any absorption band for ionic OTf was not observed in the range 1235−1288 cm^{-1}. This result is in agreement with that of previously

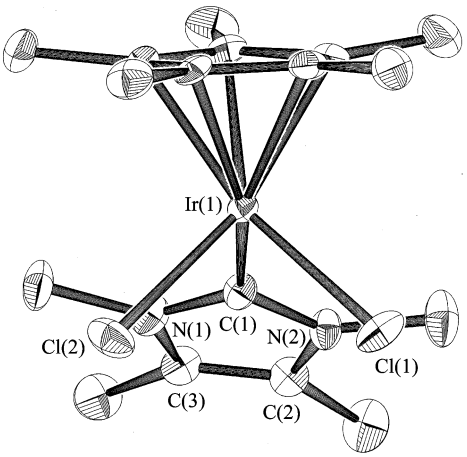


Figure 1. ORTEP drawing (ellipsoids at 50% probability) of **3a**. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for the Complexes 3a, 5a, 5d, 6, 7c, and 8b

	3a	5a	5d	6	7c	8b
			(a) Bond Distances			
Ir(1)−C(1)	2.044(4)	2.055(8)	2.06(1), 2.07(1), 2.06(1)	1.988(7)		
Ir(1a)−C(1a)					2.029(4)	
Ir(1b)−C(1b)					2.029(4)	
Ir(1)−P(1)						2.365(2)
Ir(1a)−Ir(1b)					2.7127(5)	
Ir(1)−Cl(1)	2.415(1)					
Ir(1)−Cl(2)	2.425(1)					
Ir(1)−N(3)		2.088(7)	2.08(1), 2.09(1), 2.05(1)			2.086(8)
Ir(1)−N(4)		2.060(7)	2.04(1), 2.08(1), 2.07(1)			2.066(8)
C(2)−C(3)	1.333(7)	1.34(1)	1.52(2), 1.49(2), 1.53(2)	1.327(8)		
C(2a)−C(3a)					1.336(8)	
C(2b)-C(3b)					1.336(8)	
			(b) Bond Angles			
N(1)−C(1)−N(2)	104.2(4)	103.7(6)	109(1), 110(1), 109(1)	101.9(5)		
N(1a)-C(1a)−N(2a)					105.0(4)	
N(1b)-C(1b)−N(2b)					105.0(4)	
N(3)−Ir(1)−N(4)		84.3(3)	82.3(4), 82.1(4), 83.0(3)			85.4(3)
Ir(1)−N(3)−C(18)		166.3(7)	163(1), 170(1), 174(1)			173.4(8)
Ir(1)−N(4)−C(16)		167.3(8)	174(1), 174(1), 177(1)			178(1)
N(3)−C(18)−C(19)		177.6(9)	176(1), 178(1), 179(1)			178(1)
N(4)−C(16)−C(17)		178.3(9)	177(1), 178(1), 179(1)			178(1)
Ir(1b)−Ir(1a)−C(1a)					89.5(1)	
Ir(1a)−Ir(1b)−C(1b)					89.5(1)	

reported Cp*Ir(PMe$_3$)(OTf)$_2$[13] and with other examples of the OTf ligand coordinated to metals.[14] The ^{1}H NMR spectrum of **4** in CD_2Cl_2 showed two singlet resonances due to methyl groups on the NHC ligand at δ 3.61 and 2.22 along with a singlet resonance due to Cp* (δ 1.60). In the $^{13}C\{^1H\}$ NMR spectrum (CD_2Cl_2) of **4**, signals due to the carbene carbon of the NHC ligand and CF_3 of the OTf ligand coordinated to iridium were observed at δ 156.9 (s) and 119.9 (q, J = 318 Hz), respectively.

Synthesis of Cationic Cp*Ir NHC Complexes 5a−d. The reactions of **3a−d** with 2 equiv of AgOTf followed by addition of acetonitrile gave dicationic complexes [Cp*Ir(NHC)(MeCN)$_2$]$^{2+}$ (**5a−d**) as air-stable crystals in 84, 61, 59, and 88% yields, respectively (Scheme 1). The ^{1}H NMR spectrum of **5a** in acetone-d_6 showed one singlet resonance of MeCN at δ 2.83 along with three singlet signals due to two methyl groups (δ 3.80 and 2.32) of NHC and the Cp* ligand (δ 1.89). In the $^{13}C\{^1H\}$ NMR spectrum (acetone-d_6) of **5a**, signals due to the carbene carbon of the NHC ligand, the methyl carbon of MeCN, and the nitrile carbon were observed at δ 144.9, 4.2, and 125.0, respectively. In addition, the $^{13}C\{^1H\}$ NMR spectrum of **5a** in acetone-d_6 revealed that trifluoromethanesulfonato anions ($^-$OTf) were present as counteranions because a resonance due to CF_3 of $^-$OTf is shown at δ 122.2 (q, J = 322 Hz). In the case of **5d**, the signal due to the carbene carbon of the NHC ligand was observed at δ 177.8 in the $^{13}C\{^1H\}$ NMR spectrum of an acetone-d_6 solution, indicating a downfield shift (ca. 30 ppm) similar to that of **3d**.

Crystal Structures of 5a and 5d. The structures of **5a** and **5d** were confirmed by X-ray crystallographic analyses. The ORTEP drawings of **5a** and **5d** are illustrated in Figures 2 and 3, respectively. Selected bond lengths and angles are shown in Table 1. In the unit cell of **5d**, there are three independent molecules, a, b, and c, but the structures of those are very similar to each other. The carbene carbon (C(1)) of **5a** or **5d** is attached to the iridium center (Ir(1)) with a bond length of 2.055(8) or 2.06(1), 2.07(1), and 2.06(1) Å. Furthermore, the X-ray crystallographic analyses confirmed that two MeCN molecules are coordinated to the iridium center on the nitrile nitrogen atoms.

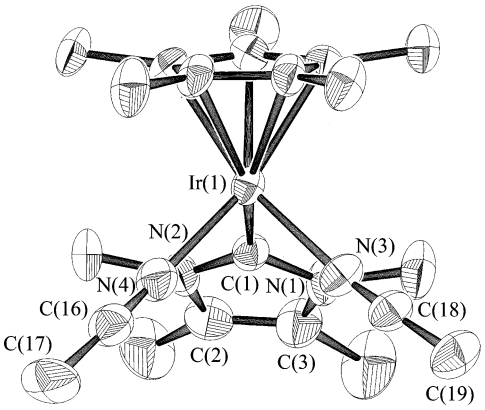


Figure 2. ORTEP drawing (ellipsoids at 50% probability) of **5a**. Hydrogen atoms are omitted for clarity.

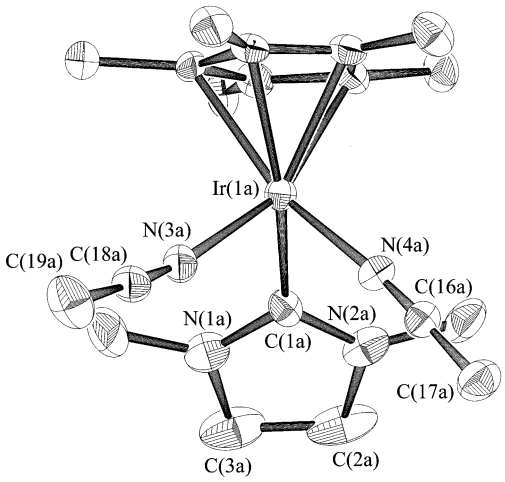


Figure 3. ORTEP drawing (ellipsoids at 30% probability) of **5d**. Hydrogen atoms are omitted for clarity. One of the three independent molecules is represented.

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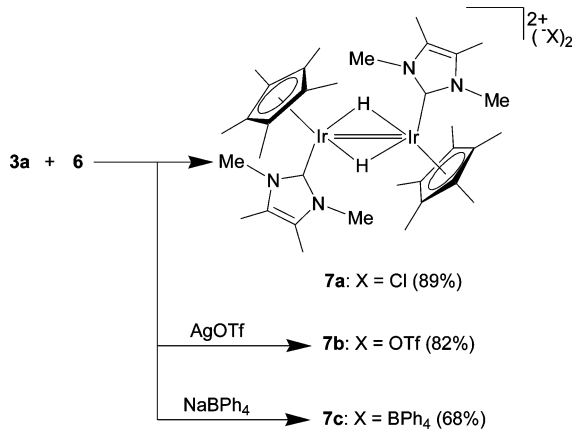
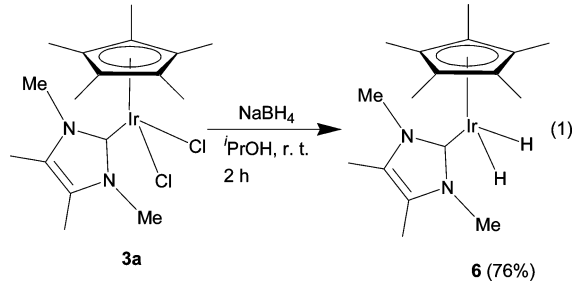
(14) Lawrance G. A. *Chem. Rev.* **1986**, *86*, 17, and references therein.

Scheme 2. Synthesis of Diiridium N-Heterocyclic Carbene Complexes



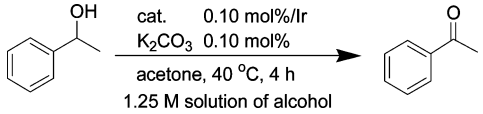
Synthesis of Dihydrido Complex 6. Complex **3a** was converted into the dihydrido complex Cp*Ir(L)$(H)_2$ (**6**; L = **2a**) in 76% yield by the reaction with excess $NaBH_4$ (eq 1). The signal due to two equivalent hydride ligands was observed at δ −16.90 along with signals due to the two methyl groups (δ 3.45 and 1.52) of NHC and a signal due to Cp* (δ 2.20) in the ^{1}H NMR spectrum (C_6D_6) of **6**. In the $^{13}C\{^1H\}$ NMR spectrum (C_6D_6), the signal due to the carbene carbon of the NHC ligand was observed at δ 161.4.



Furthermore, the structure of **6** was confirmed by X-ray diffraction analysis (see Figure S1 in the Supporting Information). Selected bond lengths and angles are shown in Table 1. Although two hydride ligands could not be located in the refinement, the geometry around the iridium center could be described as a three-legged piano stool by considering the location of the NHC, Cp*, and two equivalent hydride ligands attached to the iridium center. The iridium−carbene carbon bond distance (Ir(1)−C(1)) is 1.988(7) Å.

Synthesis of Dinuclear Iridium NHC Complexes 7. Dinuclear iridium NHC complex **7a** was prepared by the reaction of dichloro complex **3a** with dihydrido complex **6** (Scheme 2). Complexes **7b** and **7c** were also prepared by the anion exchange reactions of **7a** with 2 equiv of AgOTf and $NaBPh_4$, respectively. A signal due to the bridging hydride ligands of complex **7a** was assigned as a singlet at δ −17.50 along with signals due to two methyl groups (δ 3.67 and 2.39) of NHC and a signal due to Cp* (δ 1.45) in the ^{1}H NMR spectrum (CD_3OD) of **7a**. In the $^{13}C\{^1H\}$ NMR spectrum (CD_3OD), the carbene carbon of the NHC ligand was observed at δ 162.5. In addition, the signal patterns of ^{1}H NMR and $^{13}C\{^1H\}$ NMR spectra of complexes **7b** and **7c** are compatible with those of **7a** except for the resonances of those counteranions.

Table 2. Oxidation of 1-Phenylethanol to Acetophenone Catalyzed by Various Cp*Ir Complexes



entry	cat.	conversion (%)[a]	yield (%)[a]	TON
1	**1**	48	43	430
2	**3a**	3	1	10
3[b]	**3a**	95	92	920
4	**5a**	95	95	950
5[c]	**5a**	94	94	1880
6[d]	**5a**	81	80	3200
7	**5b**	92	91	910
8	**5c**	29	20	200
9	**5d**	87	85	850
10	**6**	4	0	0
11	**7b**	7	6	60
12	**8a**	8	1	10
13	**8b**	8	1	10

[a] The conversion and yield were determined by GC. [b] AgOTf (0.045 mmol) was added. [c] Cat. 0.050 mol %/Ir, K_2CO_3 0.050 mol %. [d] Cat. 0.025 mol %/Ir, K_2CO_3 0.025 mol %, 8 h.

The structures of complexes **7a**−**c** were elucidated by the above spectral data and X-ray diffraction analysis of **7c** (see Figure S2 in the Supporting Information). Selected bond lengths and angles of **7c** are shown in Table 1. Although two hydride ligands could not be located in the refinement, the geometry around the iridium center could be described as a three-legged piano stool except for the interaction of two iridium centers. The bond distance between dihydride-bridged iridium centers is 2.7127(5) Å, indicating a double-bond nature between them because of the 32-electron complex of **7c**. This elucidation is supported by our previous observations in dihydride-bridged diiridium complexes.[15] The carbene carbons (C(1)) are located at 2.029(4) Å with a single bond length from the iridium center (Ir(1)). Additionally, one NHC ligand is located anti to the other.

Catalytic Activities of New Cp*Ir NHC Complexes. We next examined the Oppenauer-type oxidation of 1-phenylethanol to acetophenone in the presence of a catalytic amount (0.10 mol %/Ir) of Cp*Ir NHC complexes (**3**, **5**−**7**) or other Cp*Ir complexes **1** and $[Cp^*Ir(PR_3)(MeCN)_2]^{2+}$ [R = ^{n}Bu (**8a**), Ph (**8b**)]. The results are summarized in Table 2.

The conventional Ir complex $[Cp^*IrCl(\mu\text{-}Cl)]_2$ (**1**) showed moderate catalytic activity to give acetophenone in 43% yield in 4 h (entry 1). Whereas the neutral carbene complex **3a** showed almost no catalytic activity (entry 2), addition of AgOTf to generate **4** in situ greatly improved the yield to 92% (entry 3). Finally, we have found that the well-defined dicationic carbene complex **5a** exhibited high catalytic activity: while 95% yield was obtained under standard conditions (entry 4),[16] reduction of the amount of **5a** to 0.05 mol % did not affect the yield (94%) and the turnover number (TON) was 1880 (entry 5). Furthermore, when the amount of the

(15) Fujita, K.; Nakaguma, H.; Hanasaka, F.; Yamaguchi, R. *Organometallics* **2002**, *21*, 3749.

(16) For optimization of base, a number of bases were examined in this catalytic system. Organic bases such as NEt_3 and DBU, which are stronger bases than K_2CO_3, gave lower yields. Weaker bases (pyridine and AcONa) were also less effective.

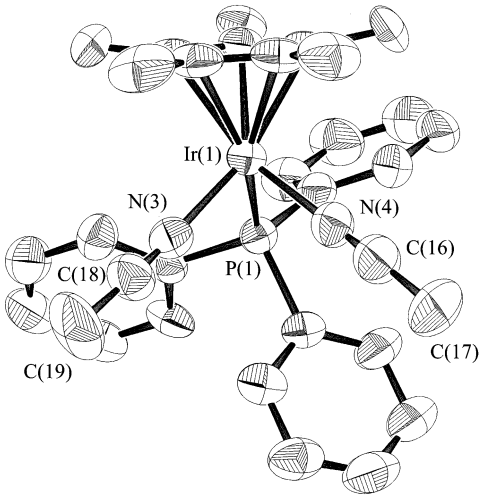


Figure 4. ORTEP drawing (ellipsoids at 50% probability) of **8b**. Hydrogen atoms are omitted for clarity.

catalyst **5a** was reduced to as little as 0.025 mol %, 80% yield was obtained and the TON reached 3200 in 8 h (entry 6). These results indicate that the new dicationic Cp* NHC complex **5a** could be the most effective catalyst in the Oppenauer-type oxidation of 1-phenylethanol.

As the steric hindrance of the alkyl groups in the NHC ligand increased, the catalytic activity decreased (entries 4, 7−8). Complex **5d** containing the 4,5-dihydroimidazol-2-ylidene ligand showed a slightly lower catalytic activity than **5a** (entry 9), indicating that the stronger σ-electron-donating ability of 4,5-dihydroimidazol-2-ylidene compared to that of imidazol-2-ylidene might cause a negative effect on its catalysis in the hydrogen transfer reaction.

In the case of the neutral dihydrido complex **6** as a catalyst, no reaction was observed (entry 10), suggesting no incorporation of dihydride species in the catalytic cycle. Since cleavage of the bridging hydride moiety of dinuclear iridium dihydrido complex **7b** might provide the iridium-monohydride species expected to have catalytic activity, **7b** was examined in the Oppenauer-type oxidation. However, little catalytic activity of **7b** was observed (entry 11), demonstrating cleavage of the bridging hydride moiety hardly proceeds in the present catalytic system.

The dicationic phosphine complexes $[Cp^*Ir(P^nBu_3)(MeCN)_2]^{2+}$ (**8a**) and $[Cp^*Ir(PPh_3)(MeCN)_2]^{2+}$ (**8b**), isoelectronic with **5**, showed almost no catalytic activity (entries 12, 13). The structure of **8b** is illustrated in Figure 4, and selected bond lengths and angles are shown in Table 1. The bond lengths (2.086(8) and 2.066(8) Å) between iridium (Ir(1)) and nitrogen of acetonitrile (N(3) and N(4)) are similar to the corresponding bond lengths (2.088(7) and 2.060(7) Å) of the NHC complex **5a**. The bond angles of N(3)−Ir(1)−N(4) of **5a** and the phosphine complex **8b** are similar to each other. These results indicate that the phosphine ligands have insufficient electron-donating ability toward the iridium center to promote the hydride transfer to acetone and that the strong σ-electron-donating ability of the NHC ligand is essential to enhance the catalytic activity.[11j,m]

To explore the hydrogen transfer ability of **5a**, we measured time-resolved reaction profiles for the oxidation of 1-phenylethanol to acetophenone catalyzed by **1** and **5a**. The results are shown in Figure 5. In the case of catalyst **5a**, the reaction was almost complete within 1 h and the TON was 910, while the yield was less than 5% and the TON was 50 in the case of **1**. Therefore, it can be said that the catalytic activity of **5a** is 18 times greater than that of **1**. While the induction period for **5a** is not detectable, ca. 80 min of the induction period was observed in the case of **1**, suggesting that the catalytically active monoiridium species could be generated during the period.

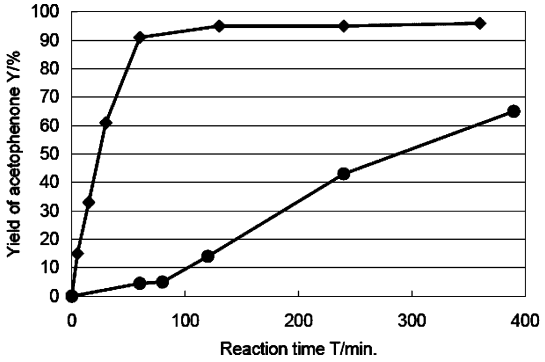


Figure 5. Time-resolved reaction profiles observed for the oxidation of 1-phenylethanol catalyzed by **5a** (♦) and **1** (●). These reactions were carried out as shown in Table 2.

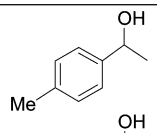
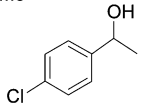
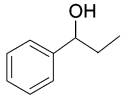
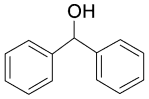
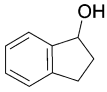
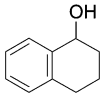
To evaluate the scope and limitations of the present catalytic system using **5a**, the oxidation reactions of several secondary and primary alcohols have been undertaken. The results for the oxidation of secondary alcohols are summarized in Table 3, and the catalyst **5a** showed high catalytic activity. The oxidations of 1-(4′-methylphenyl)ethanol, 1-(4′-chlorophenyl)ethanol, and 1-phenyl-1-propanol gave high yields comparable to that obtained in the reaction of 1-phenylethanol (entries 1−3). Sterically hindered benzhydrol was oxidized to give benzophenone in high yield (entry 4). When cyclopentanol was used as a starting material, the TON reached 6640 in 24 h, demonstrating the cationic NHC complex **5a** is the most effective catalyst in the homogeneous system (entry 5).[17] Although 1-indanol containing a five-membered cyclic alcohol was oxidized in high yield, oxidations of six-membered cyclic alcohols such as cyclohexanol and 1-tetralol resulted in moderate yields (entries 6−8). However, the yields and the conversions in the oxidations of the six-membered cyclic alcohols indicated that the ketones were produced selectively without detectable amount of byproducts. 2-Octanone was obtained in good yield when 2-octanol was used as a straight chain aliphatic alcohol (entry 9).

It has been usually difficult to oxidize primary alcohols selectively without a detectable amount of byproducts which could arise from an aldol condensation with acetone and/or Tishchenko-type reaction[18] producing esters. Therefore, it should be interesting to carry out the oxidation of primary alcohols in the present catalytic system. These results are summarized in Table 4. While larger quantities of the catalyst (0.50 mol %/Ir) and acetone were required, the oxidations of primary alcohols proceeded selectively in high to good yields. The

(17) For homogeneous oxidation systems with high TON (>1000), see refs 6n,o and 7f,h,i.

(18) Menashe, N.; Shvo, Y. *Organometallics* **1991**, *10*, 3885.

Table 3. Oxidation of Secondary Alcohols Catalyzed by 5a[a]

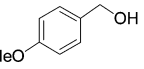
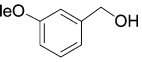
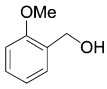
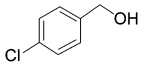
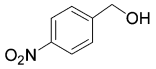
entry	alcohol	S/C	time (h)	conversion (%)[b]	yield (%)[b]	TON
1		1000	4	98	94	940
2		1000	4	90	89	890
3		1000	4	93	91	910
4		1000	6	88	83	830
5		1000	4	91	90	900
		6000	4	90	90	5400
		8000	24	85	83	6640
6[c, d]		1000	4	91	81	810
7[c]		1000	4	58	56	560
8[c, d]		1000	8	50	50	500
9		1000	7	78	76	760

[a] The oxidation of secondary alcohols was carried out at 40 °C with secondary alcohols (20.0 mmol), **5a** (0.10 mol %), and K_2CO_3 (0.10 mol %) in acetone (16 mL). [b] The conversion and yield were determined by GC. [c] NEt_3 was used instead of K_2CO_3. [d] Performed on a 10.0 mmol scale of alcohols in acetone (8 mL).

formation of byproducts was not detected. Benzyl alcohol was oxidized in high yield (entry 1). Comparing the TONs in the first 1 h, the catalytic activity of **5a** is 14 times greater than that of **1**.[19] Whereas the oxidations of 4-methoxybenzyl and 4-chlorobenzyl alcohols gave excellent and good yields, respectively, the oxidation of 4-nitrobenzyl alcohol having a strong electron-withdrawing group resulted in a poor yield (entries 2, 5, 6). These results show a tendency similar to that observed in the reactions catalyzed by **1**[8] and other complexes.[7i,9] To examine the effect of the steric hindrance of the substituent on the phenyl group, 3-methoxybenzyl and 2-methoxybenzyl alcohols were subjected to the reaction. The ortho-substituent decreased the yield, while the meta-substituent gave a slightly lower yield (entries 3, 4). In the oxidation of 1-octanol as an aliphatic alcohol, octanal was produced in moderate yield with a good selectivity (entry 7).

(19) In the first 1 h, the TON of **5a** was 168. In the case of $[Cp^*IrCl(\mu\text{-}Cl)]_2$ (**1**), the TON was 12 under the same conditions: benzyl alcohol (2.0 mmol), catalyst (0.50 mol %/Ir), and K_2CO_3 (0.50 mol %) in acetone (60 mL) at 40 °C.

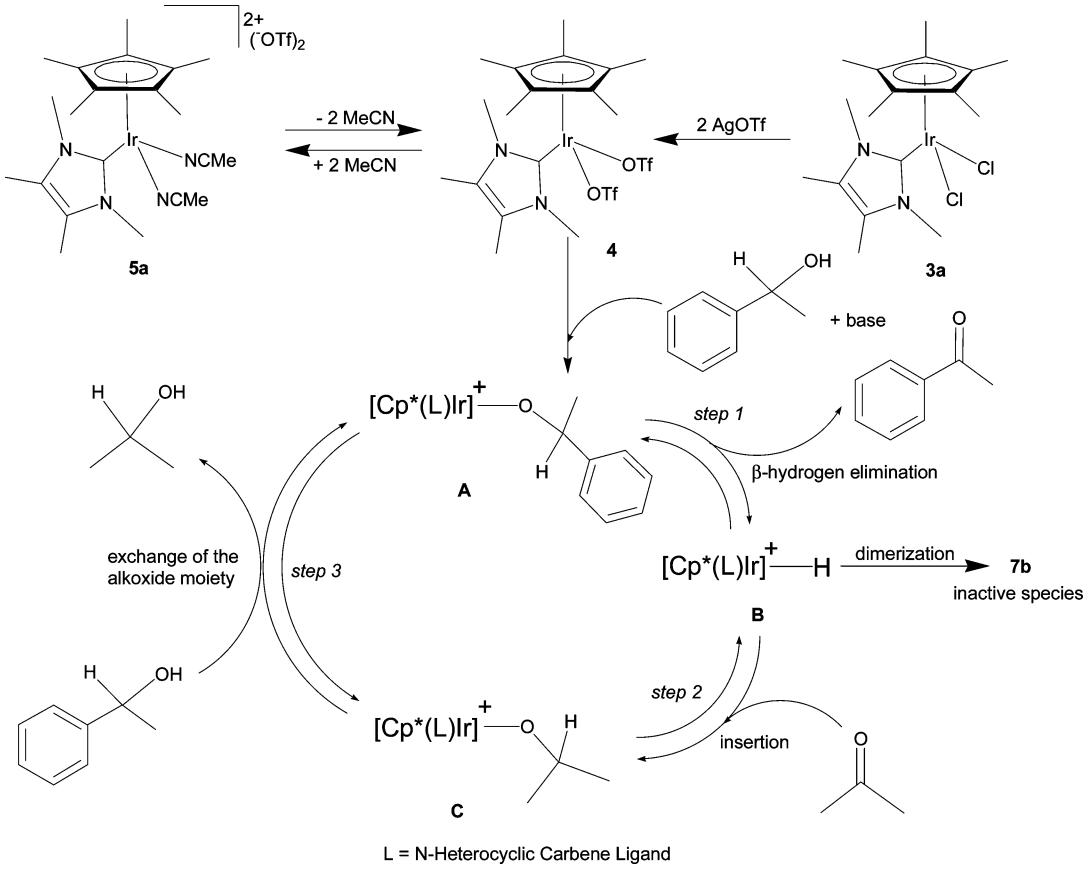
Table 4. Oxidation of Primary Alcohols Catalyzed by 5a[a]

entry	alcohol	S/C	time (h)	conversion (%)[b]	yield (%)[b]	TON
1		200	4	89	86	172
2[c]		200	2	98	98	196
3[c]		200	2	90	83	166
4[c]		200	2	75	73	146
5		200	4	76	75	150
6		200	4	31	28	56
7		200	6	57	54	108

[a] The oxidation of primary alcohols was carried out at 40 °C with primary alcohols (2.0 mmol), **5a** (0.50 mol %), and K_2CO_3 (0.50 mol %) in acetone (60 mL). [b] The conversion and yield were determined by GC. [c] NEt_3 was used instead of K_2CO_3.

A Mechanistic Consideration. A possible mechanism for the oxidation catalyzed by the Cp*Ir NHC complex is shown in Scheme 3. 1-Phenylethanol is used as a representative example. Because **4** generated in situ from **3a** and AgOTf showed almost the same catalytic activity as did **5a** (Table 2, entries 3, 4), it is likely that the first step is liberation of acetonitrile ligands from **5a** to produce **4**. It could be said that **5a** is regarded as the stabilized complex of **4**. The next step to the catalytic cycle would involve the formation of the iridium alkoxide **A** by the reaction of **4** with 1-phenylethanol in the presence of base (K_2CO_3 or NEt_3). Then, acetophenone and the iridium hydride complex **B** would be formed by the β-hydrogen elimination (step 1). Insertion of acetone into the iridium−hydride bond would lead to the formation of the iridium isopropoxide **C** (step 2). Finally, the catalytically active species **A** could be regenerated by the alkoxy exchange reaction (step 3). Step 1 should be ruled out as the rate-determining step because almost no kinetic isotope effect ($k_H/k_D = 1.1$) was observed in the reactions of 1-phenylethanol and α-deuterated 1-phenylethanol. If alkoxy exchange reaction (step 3) could be a rate-determining step, we expect that the initial rate of the reaction would be influenced by the concentration of 1-phenylethanol. Therefore, the initial rates of the oxidations in a 1.25 M solution of 1-phenylethanol and a 2.5 M solution were examined by assuming that acetone (16 mL) exists in large excess. While the initial rate was 0.536×10^{-3} M min^{-1} for 5 min in 1.25 M solution, that in 2.5 M solution increased to 0.890×10^{-3} M min^{-1}. It is likely from these results that the alkoxy exchange reaction (step 3) might be the rate-determining step. We thought that the introduction of NHC ligands into the Cp*Ir complex would increase the nucleophilicity of the iridium-hydride complex **B** due to the higher electron-donating ability of NHC ligands,

Scheme 3. Possible Mechanism for the Oppenauer-Type Oxidation Catalyzed by Cp*Ir N-Heterocyclic Carbene Complexes



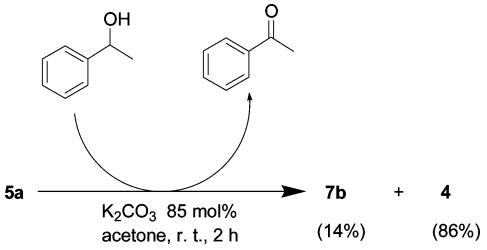
resulting in acceleration of the hydride transfer to acetone (step 2) and, eventually, the high catalytic activity of **5a**.

To obtain further information on possible reaction intermediates, the reaction was monitored by an NMR spectrum. The signal that could be assigned to the hydride of the intermediate **B** was observed at δ −13.77 along with three singlet resonances due to two methyl groups (δ 3.79 and 2.24) of NHC and the Cp* ligand (δ 1.91) in ^{1}H NMR spectrum of an acetone-d_6 solution. Although the signals corresponding to the catalyst **5a** and the complex **7b** were also observed, alkoxide species **A** and isopropoxide species **C** were not observed in the ^{1}H NMR analysis. These data implied that the reaction intermediate might be the iridium-monohydride complex **B** but not the dihydride complex, because the dihydrido complex **6** showed almost no catalytic activity (Table 2, entry 10).[20]

To investigate the fate of the catalyst **5a**, we analyzed the residual mixture of the oxidation reaction of 1-phenylethanol using 45 mol % of **5a** (Scheme 4). ^{1}H NMR spectra of an acetone-d_6 solution revealed the formation of the dinuclear NHC complex **7b** in 14% yield in addition to the catalytically active species **4** (86%). As mentioned above, an only 6% yield of acetophenone was produced by the oxidation of 1-phenylethanol using **7b** (0.1 mol %/Ir) as a catalyst (Table 2, entry 11). These results suggest that complex **7b** is an inactive species

(20) Additionally, the reaction was monitored by an IR spectrum. The spectrum did not show any characteristic absorption band of the OTf ligand coordinated to iridium, which was observed in complex **4**. This result implied that the intermediate **B** might be cationic.

Scheme 4. Oxidation of 1-Phenylethanol Using Substoichiometric Amounts of 5a



and that the dimerization of the iridium hydride complex **B** to afford **7b** should be the deactivation pathway as shown in Scheme 3.

Conclusion

We have accomplished the synthesis and structure determination of a series of new Cp*Ir N-heterocyclic carbene complexes and disclosed that the cationic complexes catalyze the Oppenauer-type oxidation of primary and secondary alcohols with very high turnover number (up to 6640). To the best of our knowledge, the new cationic N-heterocyclic carbene complex **5a** is the most effective catalyst in homogeneous oxidation of alcohols in terms of its high catalytic activity and wide applicability to the oxidation of primary and secondary alcohols. Thus, an efficient catalytic system for the Oppenauer-type oxidation of primary and secondary alcohols has been developed in an environmentally benign fashion.

Experimental Section

General Procedures. All the reactions and manipulations were carried out under an atmosphere of argon by means of Schlenk techniques. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on JEOL A-500 and EX-270 spectrometers. IR spectra were recorded on a Horiba FT-300 spectrometer. Gas chromatography analyses were performed on a Shimadzu GC-14A gas chromatograph with a capillary column (Shimadzu CBP1-M25-025) or 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 and toluene were distilled from sodium benzophenone ketyl and stored under the presence of metallic potassium. [Cp*IrCl(μ-Cl)]$_2$,[21] N-heterocyclic carbene ligands (**2a**−**c**),[22] and 1,3-dimethyl-4,5-dihydroimidazolium tetrafluoroborate[23] were prepared by literature methods. Other reagents were used as obtained from commercial sources.

Cp*Ir(IMeMe)Cl$_2$ (3a). 1,3,4,5-Tetramethylimidazole-2(3*H*)-thione (1.015 g, 6.49 mmol) was stirred in THF (30 mL) at 0 °C, and metallic potassium (4.782 g, 122.3 mmol) was added. After 15 min, the resulting mixture was heated at reflux for 4 h. The reaction mixture was cooled to room temperature and filtered through a glass filter. The filtrate was dropped by cannula to an orange suspension of [Cp*IrCl(μ-Cl)]$_2$ (2.587 g, 3.25 mmol) in THF (20 mL) at 0 °C with stirring. After 15 min, the solvent was removed in vacuo to yield a dark brown solid. The residue was dissolved in CH_2Cl_2 and acetone, and the solution was passed through a pad of activated carbon. Evaporation of the solvent gave an orange powder of **3a** (5.15 mmol, 79%). Mp: 279.9−281.4 °C (dec). ^{1}H NMR ($CDCl_3$): δ 3.82 (s, 6H, NMe), 2.16 (s, 6H, C=CMe), 1.62 (s, 15H, Cp*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 153.9 (s, Ir−C), 125.9 (s, C=C), 88.3 (s, C_5Me_5), 35.8 (s, NMe), 9.6 (s, C=C*Me*), 9.2 (s, C_5Me_5). Anal. Calcd for $C_{17}H_{27}N_2Cl_2Ir$: C, 39.07; H, 5.22; N, 5.36; Cl, 13.57. Found: C, 38.88; H, 5.11; N, 5.19; Cl, 13.05.

Cp*Ir(IEtMe)Cl$_2$ (3b). 1,3-Diethyl-4,5-dimethylimidazole-2(3*H*)-thione (0.541 g, 2.93 mmol) was stirred in THF (16 mL) at 0 °C, and metallic potassium (1.096 g, 28.0 mmol) was added. After 15 min, the resulting mixture was heated at reflux for 4 h. The reaction mixture was cooled to room temperature and filtered through a glass filter. The filtrate was dropped by cannula to an orange suspension of [Cp*IrCl(μ-Cl)]$_2$ (1.167 g, 1.46 mmol) in THF (20 mL) at 0 °C with stirring. After 15 min, the solvent was removed in vacuo to yield a dark brown solid. The residue was dissolved in CH_2Cl_2, and the solution was passed through an alumina column. Evaporation of the solvent gave an orange powder of **3b** (1.44 mmol, 49%). Mp: 246.4−247.7 °C. ^{1}H NMR ($CDCl_3$): δ 4.63 (dq, J = 14, 7 Hz, 2H, NC*H*HCH$_3$), 3.94 (dq, J = 14, 7 Hz, 2H, NCH*H*CH$_3$), 2.22 (s, 6H, C=CMe), 1.55 (s, 15H, Cp*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 153.2 (s, Ir−C), 126.1 (s, C=C), 88.4 (s, C_5Me_5), 43.9 (s, NCH_2CH_3), 17.5 (s, NCH$_2$*C*H$_3$), 9.5 (s, C=C*Me*), 9.0 (s, C_5Me_5). Anal. Calcd for $C_{19}H_{31}N_2Cl_2Ir$: C, 41.44; H, 5.69; N, 5.09; Cl, 12.88. Found: C, 41.23; H, 5.70; N, 5.07; Cl, 12.29.

Cp*Ir(I^{i}PrMe)Cl$_2$ (3c). 1,3-Diisopropyl-4,5-dimethylimidazole-2(3*H*)-thione (0.515 g, 2.42 mmol) was stirred in THF (16 mL) at 0 °C, and metallic potassium (0.655 g, 16.8 mmol) was added. After 15 min, the resulting mixture was heated at reflux for 4 h. The reaction mixture was cooled at room temperature and filtered through a glass filter. The filtrate was dropped by cannula to an orange suspension of [Cp*IrCl(μ-Cl)]$_2$ (0.965 g, 1.21 mmol) in THF (20 mL) at 0 °C with stirring. After 15 min, the solvent was removed in vacuo to yield a dark brown solid. The residue was dissolved in CH_2Cl_2, and the solution was passed through an alumina column. Evaporation of solvent gave an orange powder of **3c** (1.77 mmol, 73%). ^{1}H NMR ($CDCl_3$): δ 5.43 (sept, J = 7 Hz, 2H, NC*H*Me$_2$), 2.27 (s, 6H, C=CMe), 1.67 (d, J = 7 Hz, 6H, NCH*Me*Me), 1.61 (s, 15H, Cp*), 1.43 (d, J = 8 Hz, 6H, NCHMe*Me*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 154.9 (s, Ir−C), 126.4 (s, C=C), 88.5 (s, C_5Me_5), 52.8 (s, NC*H*Me$_2$), 23.8 (s, NCH*Me*Me), 23.6 (s, NCHMe*Me*), 10.4 (s, C=C*Me*), 9.1 (s, C_5Me_5). These data were identical with those reported by K. Lammertsma.[10b]

Cp*Ir(SIMe)Cl$_2$ (3d). A 50 mL flask was charged with 1,3-dimethyl-4,5-dihydroimidazolium tetrafluoroborate (0.403 g, 2.17 mmol) and THF (10 mL). To the resulting solution was slowly added a solution of potassium *tert*-butoxide (0.243 g, 2.17 mmol) in THF (40 mL), and the mixture was stirred for 1 h. The reaction mixture and fresh toluene (70 mL) were transferred to a 300 mL three-necked flask. Then [Cp*IrCl(μ-Cl)]$_2$ (0.858 g, 1.08 mmol) was added, and the mixture was stirred at 80 °C for 1 h. After evaporation of the solvent, the residual complex was extracted with CH_2Cl_2 (30 mL). After removal of CH_2Cl_2, the residue was washed with toluene to give an orange-yellow powder of **3d** (1.12 mmol, 52%). Mp: 285.9−287.9 °C (dec). ^{1}H NMR ($CDCl_3$): δ 3.73 (br, 4H, NCH$_2$-CH$_2$N), 3.32 (s, 6H, NMe), 1.63 (s, 15H, Cp*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 185.8 (s, Ir−C), 88.6 (s, C_5Me_5), 51.7 (s, N*C*H$_2$*C*H$_2$N), 38.4 (s, NMe), 8.8 (s, C_5Me_5). Anal. Calcd for $C_{15}H_{25}N_2Cl_2Ir$: C, 36.28; H, 5.09; N, 5.64; Cl, 14.28. Found: C, 36.08; H, 4.98; N, 5.71; Cl, 13.59.

Cp*Ir(IMeMe)(OTf)$_2$ (4).[13] A 20 mL Schlenk flask was charged with AgOTf (0.100 g, 0.390 mmol), and then it was dried under reduced pressure for 10 min. After **3a** (0.100 g, 0.192 mmol) was added, degassed CH_2Cl_2 was poured by cannula into the flask with stirring. The reaction mixture was stirred at room temperature for 2 h. The resulting reaction mixture was filtrated through a pad of Celite using a cannula, and the solvent was removed in vacuo. The very air-sensitive and labile yellow-brown solid **4** (0.146 g, 0.195 mmol) was obtained in an almost quantitative yield. IR (cm^{-1}, CH_2Cl_2): ν_{asym}(SO) 1309 m. ^{1}H NMR (CD_2Cl_2): δ 3.61 (s, 6H, NMe), 2.22 (s, 6H, C=CMe), 1.60 (s, 15H, Cp*). ^{1}H NMR (acetone-d_6): δ 3.75 (s, 6H, NMe), 2.29 (s, 6H, C=CMe), 1.72 (s, 15H, Cp*). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 156.9 (s, Ir−C), 128.0 (s, C=C), 119.9 (q, J = 318 Hz, CF_3), 89.5 (s, C_5Me_5), 35.3 (s, NMe), 10.0 (s, C_5Me_5), 9.5 (s, C=C*Me*).

[Cp*Ir(IMeMe)(MeCN)$_2$][OTf]$_2$ (5a). A 100 mL flask was charged with **3a** (1.085 g, 2.08 mmol) and CH_2Cl_2 (30 mL). To the solution was added AgOTf (1.074 g, 4.18 mmol), and the reaction mixture was stirred at room temperature for 2 h. Then acetonitrile (0.441 g, 10.7 mmol) was added, and the mixture was stirred for another 1 h. After removal of the solvent in vacuo, the residue was extracted with CH_2Cl_2, and the solution was filtrated through a pad of Celite. After evaporation of the solvent, slow diffusion of ether to the solution of the crude product in acetone gave pale yellow crystals of **5a** (1.74 mmol, 84%). Mp: 144.7−145.8 °C. IR (cm^{-1}, Nujol): ν_{CN} 2333 w, 2303 w, ν_{OTf} 1277 brs, 1223 s, 1159 s, 1026 s. ^{1}H NMR (acetone-d_6): δ 3.80 (s, 6H, NMe), 2.83 (s, 6H, MeCN), 2.32 (s, 6H, C=CMe), 1.89 (s, 15H, Cp*). ^{13}C{^{1}H} NMR (acetone-d_6): δ 144.9 (s, Ir−C), 128.8 (s, C=C), 125.0 (s, Me*C*N), 122.2 (q, J = 322 Hz, CF_3), 95.0 (s, C_5Me_5), 36.2 (s, NMe), 9.3 (s, C=C*Me*), 9.1 (s, C_5Me_5), 4.2 (s, *Me*CN). Anal. Calcd for $C_{23}H_{33}N_4F_6O_6S_2Ir$: C, 33.20; H, 4.01; N, 6.74. Found: C, 32.96; H, 3.78; N, 6.64.

[Cp*Ir(IEtMe)(MeCN)$_2$][OTf]$_2$ (5b). A 30 mL flask was charged with **3b** (0.158 g, 0.287 mmol) and CH_2Cl_2 (5 mL). To the solution was added AgOTf (0.158 g, 0.616 mmol), and the reaction mixture was stirred at room temperature for 2 h. Then acetonitrile (64.6 mg, 1.57 mmol) was added, and the mixture

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was stirred for another 1 h. After removal of the solvent in vacuo, the residue was extracted with CH_2Cl_2, and the solution was filtrated through a pad of Celite. After evaporation of the solvent, slow diffusion of ether to the solution of the crude product in acetone gave pale yellow crystals of **5b** (0.174 mmol, 61%). Mp: 132.6−134.7 °C. IR (cm^{-1}, Nujol) ν_{CN} 2306 w, 2287 w, ν_{OTf} 1261 brs, 1223 m, 1155 s, 1032 s. ^1H NMR (acetone-d_6): δ 4.31 (dq, J = 14, 7 Hz, 2H, NC*H*HCH$_3$), 4.17 (dq, J = 14, 7 Hz, 2H, NCH*H*CH$_3$), 2.90 (s, 6H, MeCN), 2.40 (s, 6H, C=CMe), 1.80 (s, 15H, Cp*), 1.43 (t, J = 7 Hz, 6H, NCH$_2$CH$_3$). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 143.8 (s, Ir−C), 129.1 (s, C=C), 125.0 (s, Me*C*N), 122.2 (q, J = 322 Hz, CF_3), 95.2 (s, C_5Me_5), 44.5 (s, N*C*H$_2$CH$_3$), 16.9 (s, NCH$_2$*C*H$_3$), 9.2 (s, C=C*Me*), 8.9 (s, C$_5$*Me*$_5$), 4.5 (s, *Me*CN). Anal. Calcd for $C_{25}H_{37}N_4F_6O_6S_2Ir$: C, 34.91; H, 4.35; N, 6.52. Found: C, 35.06; H, 4.19; N, 6.49.

[Cp*Ir(I^{i}PrMe)(MeCN)$_2$][OTf]$_2$ (5c). A 30 mL flask was charged with **3c** (0.154 g, 0.266 mmol) and CH_2Cl_2 (5 mL). To the solution was added AgOTf (0.137 g, 0.533 mmol), and the reaction mixture was stirred at room temperature for 2 h. Then acetonitrile (55.5 mg, 1.35 mmol) was added, and the mixture was stirred for another 1 h. After removal of the solvent in vacuo, the residue was extracted with CH_2Cl_2, and the solution was filtrated through a pad of Celite. After evaporation of the solvent, slow diffusion of ether to the solution of the crude product in acetone gave pale yellow crystals of **5c** (0.161 mmol, 59%). Mp: 126.2−127.7 °C. IR (cm^{-1}, Nujol): ν_{CN} 2335 w, 2303 w, ν_{OTf} 1263 brs, 1225 m, 1151 s, 1030 s. ^1H NMR (acetone-d_6): δ 4.84 (sept, J = 7 Hz, 2H, NC*H*Me$_2$), 2.86 (s, 6H, MeCN), 2.45 (s, 6H, C=CMe), 1.87 (s, 15H, Cp*), 1.66 (12H, NCH*Me*$_2$). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 146.7 (s, Ir−C), 129.3 (s, C=C), 125.1 (s, Me*C*N), 122.2 (q, J = 322 Hz, CF_3), 95.4 (s, C_5Me_5), 54.5 (s, N*C*HMe$_2$), 23.1 (s, NCH*Me*Me), 22.9 (s, NCHMe*Me*), 10.7 (s, C=C*Me*), 9.3 (s, C$_5$*Me*$_5$), 4.7 (s, *Me*CN). Anal. Calcd for $C_{27}H_{41}N_4F_6O_6S_2Ir\cdot(CH_3COCH_3)_{0.5}$: C, 37.32; H, 4.85; N, 6.11. Found: C, 37.58; H, 4.78; N, 5.86.

[Cp*Ir(SIMe)(MeCN)$_2$][OTf]$_2$ (5d). A 30 mL flask was charged with **3d** (0.199 g, 0.401 mmol) and CH_2Cl_2 (6 mL). To the solution was added AgOTf (0.206 g, 0.802 mmol), and the reaction mixture was stirred at room temperature for 2 h. Then acetonitrile (81.6 mg, 1.99 mmol) was added, and the mixture was stirred for another 1 h. After removal of the solvent in vacuo, the residue was extracted with CH_2Cl_2, and the solution was filtrated through a pad of Celite. After evaporation of the solvent, slow diffusion of ether to the solution of the crude product in acetone gave pale yellow crystal of **5d** (0.355 mmol, 88%). Mp: 136.0−137.9 °C. IR (cm^{-1}, Nujol): ν_{CN} 2332 w, 2300 w, ν_{OTf} 1261 brs, 1223 m, 1157 s, 1030 s. ^1H NMR (acetone-d_6): δ 4.00 (br, 2H, NC*H*HC*H*HN), 3.89 (br, 2H, NCH*H*-CH*H*N), 3.23 (s, NMe), 2.82 (s, 6H, MeCN), 1.89 (s, 15H, Cp*). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 177.8 (s, Ir−C), 124.9 (s, Me*C*N), 122.2 (q, J = 322 Hz, CF_3), 95.1 (s, C_5Me_5), 52.5 (s, N*C*H$_2$*C*H$_2$N), 38.3 (s, NMe), 9.1 (s, C$_5$*Me*$_5$), 4.2 (s, *Me*CN). Anal. Calcd for $C_{21}H_{31}N_4F_6O_6S_2Ir$: C, 31.30; H, 3.89; N, 6.95. Found: C, 31.32; H, 3.74; N, 6.91.

Cp*Ir(IMeMe)(H)$_2$ (6). A 100 mL flask was charged with **3a** (0.537 g, 1.03 mmol), $NaBH_4$ (0.379 g, 10.0 mmol), and 2-PrOH (40 mL). After the reaction mixture was stirred for 3 h, the solvent was evaporated in vacuo. The residual complex was extracted with toluene, and the solution was passed through a pad of Celite. After the solvent was removed, the ether solution of crude product was cooled to dry ice temperature to give colorless crystals of **6** (0.777 mmol, 76%). Mp: 148.5−149.0 °C (dec). IR (cm^{-1}, Nujol): ν_{IrH} 2081 m. ^1H NMR (C_6D_6): δ 3.45 (s, 6H, NMe), 2.20 (s, 15H, Cp*), 1.52 (s, 6H, C=CMe), −16.90 (s, 2H, Ir−H). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 161.4 (s, Ir−C), 121.9 (s, C=C), 88.5 (s, C_5Me_5), 36.6 (s, NMe), 11.8 (s, C$_5$*Me*$_5$), 9.5 (s, C=C*Me*). Anal. Calcd for $C_{17}H_{29}N_2Ir$: C, 45.00; H, 6.46; N, 6.18. Found: C, 44.96; H, 6.23; N, 6.08.

[Cp*Ir(IMeMe)(μ-H)]$_2$[Cl]$_2$ (7a). A 50 mL flask was charged with **3a** (65.8 mg, 0.126 mmol), **6** (57.1 mg, 0.126 mmol), and 2-PrOH (5.0 mL). The reaction mixture was stirred for 3 h. After the solvent was evaporated, slow diffusion of ether to the solution of the crude product in MeOH gave deep red crystals of **7a** (0.112 mmol, 89%). ^1H NMR (CD_3OD): δ 3.67 (s, 12H, NMe), 2.39 (s, 12H, C=CMe), 1.45 (s, 30H, Cp*), −17.50 (s, 2H, Ir−H−Ir). $^{13}C\{^1H\}$ NMR (CD_3OD): δ 162.5 (s, Ir−C), 129.2 (s, C=C), 97.8 (s, C_5Me_5), 36.7 (s, NMe), 10.1 (s, C_5Me_5), 9.3 (s, C=C*Me*).

[Cp*Ir(IMeMe)(μ-H)]$_2$[OTf]$_2$ (7b). A 50 mL flask was charged with **3a** (36.4 mg, 0.0697 mmol), **6** (31.8 mg, 0.0701 mmol), and 2-PrOH (3.0 mL). The reaction mixture was stirred for 2.5 h, and then AgOTf (36.7 mg, 0.143 mmol) was added to the mixture. After 2 h, the solvent was evaporated. The residual complex was extracted with acetone, and the solution was passed through a pad of Celite. After the solution was concentrated, slow diffusion of ether to the resulting solution gave deep red crystals of **7b** (0.0572 mmol, 82%). Mp: 106.7−109.4 °C (dec). ^1H NMR (CD_3OD): δ 3.68 (s, 12H, NMe), 2.39 (s, 12H, C=CMe), 1.45 (s, 30H, Cp*), −17.48 (s, 2H, Ir−H−Ir). ^1H NMR (acetone-d_6): δ 3.84 (s, 12H, NMe), 2.45 (s, 12H, C=CMe), 1.53 (s, 30H, Cp*), −17.36 (s, 2H, Ir−H−Ir). $^{13}C\{^1H\}$ NMR (CD_3OD): δ 162.5 (s, Ir−C), 129.2 (s, C=C), 121.9 (q, J = 318 Hz, CF_3), 97.9 (s, C_5Me_5), 36.7 (s, NMe), 10.1 (s, C_5Me_5), 9.2 (s, C=C*Me*). Anal. Calcd for $C_{36}H_{56}N_4F_6O_6S_2Ir_2$: C, 35.92; H, 4.70; N, 4.66. Found: C, 35.65; H, 4.40; N, 4.60.

[Cp*Ir(IMeMe)(μ-H)]$_2$[BPh$_4$]$_2$ (7c). A 50 mL flask was charged with **3a** (23.7 mg, 0.0454 mmol), **6** (20.6 mg, 0.0454 mmol), and 2-PrOH (2.0 mL). The reaction mixture was stirred for 2 h, and then a solution of $NaBPh_4$ (34.1 mg, 0.0996 mmol) in 2-PrOH was added to the mixture. After 30 min, the solution was filtrated, and the solvent was removed to give a deep red powder of **7c** (0.0311 mmol, 68%). Slow diffusion of ether to the solution of the crude product in acetone gave deep red crystals of **7c**. Mp: 138.1−140.1 °C (dec). ^1H NMR (acetone-d_6): δ 7.3 (brm, 16H, Ph$_{ortho}$), 6.91 (t, J = 7 Hz, 16H, Ph$_{meta}$), 6.77 (t, J = 7 Hz, 8H, Ph$_{para}$), 3.81 (s, 12H, NMe), 2.42 (s, 12H, C=CMe), 1.49 (s, 30H, Cp*), −17.36 (s, 2H, Ir−H−Ir). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 164.4 (q, J = 49 Hz, B−Ph$_{ipso}$), 161.4 (s, Ir−C), 136.5 (s, B−Ph$_{meta}$), 128.3 (s, B−Ph$_{para}$), 125.4 (q, J = 3 Hz, B−Ph$_{ortho}$), 121.7 (s, C=C), 96.8 (s, C_5Me_5), 36.0 (s, NMe), 9.5 (s, C_5Me_5), 8.8 (s, C=C*Me*). Anal. Calcd for $C_{82}H_{96}N_4B_2Ir_2$: C, 63.79; H, 6.28; N, 3.63. Found: C, 63.61; H, 6.37; N, 3.64.

[Cp*Ir(P^{n}Bu$_3$)(MeCN)$_2$][OTf]$_2$ (8a).[13] P^{n}Bu$_3$ (53.1 mg, 0.262 mmol) was added to an orange suspension of [Cp*IrCl-(μ-Cl)]$_2$ (0.101 g, 0.127 mmol) in THF (5.0 mL) at 0 °C. The resulting mixture was stirred for 3 h at room temperature. After the solvent was removed, the residue was dissolved in CH_2Cl_2 (5.0 mL). To the solution was added AgOTf (0.131 g, 0.510 mmol), and the reaction mixture was stirred for 2 h at room temperature. Then acetonitrile (53.0 mg, 1.29 mmol) was added and the mixture was stirred for 1 h. After removal of the solvent in vacuo, the residue was extracted with CH_2Cl_2, and the solution was filtrated through a pad of Celite. After evaporation of the solvent, slow diffusion of ether to the solution of the crude product in CH_2Cl_2 gave pale yellow crystals of **8a** (0.214 mmol, 85%). Mp: 139.0−140.9 °C. IR (cm^{-1}, Nujol) ν_{CN} 2321 w, 2299 w, ν_{OTf} 1269 brs, 1225 m, 1147 s, 1032 s. ^1H NMR (acetone-d_6): δ 2.93 (d, J = 1 Hz, 6H, MeCN), 2.22 (m, 6H), 1.96 (d, J = 2 Hz, 15H, Cp*), 1.53 (m, 12H), 0.96 (t, J = 7 Hz, 9H). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 126.4 (s, Me*C*N), 122.3 (q, J = 321 Hz, CF_3), 98.3 (s, C_5Me_5), 25.7 (d), 24.4 (d), 23.2 (d), 13.8 (s), 9.2 (s, C$_5$*Me*$_5$), 4.5 (s, *Me*CN). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ −4.3 (s). Anal. Calcd for $C_{28}H_{48}N_2F_6O_6PS_2Ir$: C, 36.95; H, 5.33; N, 3.08. Found: C, 36.75; H, 5.10; N, 2.81.

[Cp*Ir(PPh$_3$)(MeCN)$_2$][OTf]$_2$ (8b).[13] PPh$_3$ (88.7 mg, 0.338 mmol) was added to the suspension of [Cp*Ir(MeCN)$_3$][OTf]$_2$ (0.255 g, 3.41 mmol) in THF (3.0 mL) at room temperature. The resulting mixture was stirred for 5 h. After evaporation of the solvent, the residual complex was dissolved CH_2Cl_2 (1.0 mL), and the solution was filtrated. The slow diffusion of ether to a CH_2Cl_2 solution of the crude product gave pale yellow

crystals of **8b** (0.336 mmol, 99%). Mp: 161.7−163.5 °C. IR (cm^{-1}, Nujol): ν_{CN} 2332 w, 2297 w, ν_{OTf} 1273 brs, 1225 m, 1153 brm, 1032 s. ^1H NMR (acetone-d_6): δ 7.7−7.8 (m, 9 H, Ph), 7.6−7.7 (m, 6H, Ph), 2.66 (d, J = 1 Hz, 3H, MeCN), 1.69 (d, J = 2 Hz, 15H, Cp*). $^{13}C\{^1H\}$ NMR (acetone-d_6): δ 134.8 (d), 133.2 (d), 130.2 (d), 127.5 (d), 126.2 (s, Me*C*N), 99.3 (s, C_5Me_5), 8.8 (s, C_5Me_5), 4.2 (s, *Me*CN). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 8.5 (s). Anal. Calcd for $C_{34}H_{36}N_2F_6O_6PS_2Ir$: C, 42.10; H, 3.75; N, 2.89. Found: C, 42.40; H, 3.93; N, 2.63.

Typical Procedure for the Oxidation of 1-Phenylethanol in Acetone Catalyzed by Various Cp*Ir Complexes (Table 2). The catalyst (20 μmol) and K_2CO_3 (20 μmol) were placed in a flask, and acetone (8.0 mL) was added. Another flask was charged with 1-phenylethanol (20.0 mmol) and acetone (8.0 mL). Then the solution of 1-phenylethanol was added into the solution containing the catalyst and base, and the 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 products were characterized by comparing with authentic samples.

Oxidations of Secondary Alcohols Catalyzed by 5a (Table 3). The oxidations were carried out by similar procedures to the above. The products were characterized by comparing with authentic samples.

4-Methylacetophenone (entry 1). The reaction of 1-(4′-methylphenyl)ethanol (2.727 g, 20.0 mmol), **5a** (16.6 mg, 20.0 μmol), and K_2CO_3 (2.8 mg, 20.3 μmol) in acetone (16 mL) for 4 h gave 4-methylacetophenone (94% yield).

4-Chloroacetophenone (entry 2). The reaction of 1-(4′-chlorophenyl)ethanol (3.136 g, 20.0 mmol), **5a** (16.9 mg, 20.3 μmol), and K_2CO_3 (2.8 mg, 20.3 μmol) in acetone (16 mL) for 4 h gave 4-chloroacetophenone (89% yield).

Propiophenone (entry 3). The reaction of 1-phenyl-1-propanol (2.726 g, 20.0 mmol), **5a** (16.6 mg, 20.0 μmol), and K_2CO_3 (2.7 mg, 19.5 μmol) in acetone (16 mL) for 4 h gave propiophenone (91% yield).

Benzophenone (entry 4). The reaction of benzhydrol (3.687 g, 20.0 mmol), **5a** (16.5 mg, 19.8 μmol), and K_2CO_3 (2.8 mg, 20.3 μmol) in acetone (16 mL) for 6 h gave benzophenone (83% yield).

Cyclopentanone (entry 5). The reaction of cyclopentanol (13.782 g, 160 mmol), **5a** (16.7 mg, 20.1 μmol), and K_2CO_3 (2.8 mg, 20.3 μmol) in acetone (128 mL) for 24 h gave cyclopentanone (83% yield).

1-Indanone (entry 6). The reaction of 1-indanol (1.345 g, 10.0 mmol), **5a** (8.5 mg, 10.2 μmol), and NEt_3 (1.1 mg, 10.9 μmol) in acetone (8 mL) for 4 h gave 1-indanone (81% yield).

Cyclohexanone (entry 7). The reaction of cyclohexanol (2.007 g, 20.0 mmol), **5a** (16.7 mg, 20.1 μmol), and NEt_3 (2.1 mg, 20.8 μmol) in acetone (16 mL) for 4 h gave cyclohexanone (56% yield).

1-Tetralone (entry 8). The reaction of 1-tetralol (1.489 g, 10.0 mmol), **5a** (8.3 mg, 9.98 μmol), and NEt_3 (1.1 mg, 10.9 μmol) in acetone (8 mL) for 8 h gave 1-tetralone (50% yield).

2-Octanone (entry 9). The reaction of 2-octanol (2.610 g, 20.0 mmol), **5a** (16.8 mg, 20.2 μmol), and K_2CO_3 (2.9 mg, 21.0 μmol) in acetone (16 mL) for 7 h gave 2-octanone (76% yield).

Oxidations of Primary Alcohols Catalyzed by 5a (Table 4). 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). The reaction of benzyl alcohol (0.2175 g, 2.01 mmol), **5a** (8.3 mg, 9.98 μmol), and K_2CO_3 (1.4 mg, 10.1 μmol) in acetone (60 mL) for 4 h gave benzaldehyde (86% yield).

4-Methoxybenzaldehyde (entry 2). The reaction of 4-methoxybenzyl alcohol (0.2765 g, 2.00 mmol), **5a** (8.3 mg, 9.98 μmol), and NEt_3 (1.0 mg, 9.88 μmol) in acetone (60 mL) for 2 h gave 4-methoxybenzaldehyde (98% yield).

3-Methoxybenzaldehyde (entry 3). The reaction of 3-methoxybenzyl alcohol (0.2771 g, 2.01 mmol), **5a** (8.3 mg, 9.98 μmol), and NEt_3 (1.0 mg, 9.88 μmol) in acetone (60 mL) for 2 h gave 3-methoxybenzaldehyde (83% yield).

2-Methoxybenzaldehyde (entry 4). The reaction of 2-methoxybenzyl alcohol (0.2811 g, 2.03 mmol), **5a** (8.3 mg, 9.98 μmol), and NEt_3 (1.0 mg, 9.88 μmol) in acetone (60 mL) for 2 h gave 2-methoxybenzaldehyde (73% yield).

4-Chlorobenzaldehyde (entry 5). The reaction of 4-chlorobenzyl alcohol (0.2853 g, 2.00 mmol), **5a** (8.3 mg, 9.98 μmol), and K_2CO_3 (1.3 mg, 9.41 μmol) in acetone (60 mL) for 4 h gave 4-chlorobenzaldehyde (75% yield).

4-Nitrobenzaldehyde (entry 6). The reaction of 4-nitrobenzyl alcohol (0.3062 g, 2.00 mmol), **5a** (8.6 mg, 10.3 μmol), and K_2CO_3 (1.4 mg, 10.1 μmol) in acetone (60 mL) for 4 h gave 4-nitrobenzaldehyde (28% yield).

1-Octanal (entry 7). The reaction of 1-octanol (0.2656 g, 2.04 mmol), **5a** (8.3 mg, 9.98 μmol), and K_2CO_3 (1.3 mg, 9.41 μmol) in acetone (60 mL) for 6 h gave 1-octanal (54% yield).

Kinetic Isotope Effect. A mixture of 1-phenylethanol (10.0 mmol) and α-deuterated 1-phenylethanol (10.0 mmol) in acetone (8 mL) was added into a solution of **5a** (20.0 μmol) and K_2CO_3 (20.0 μmol) in acetone (8 mL). The reaction mixture was stirred at 40 °C for 30 min. Then the solvent was evaporated, and the resulting mixture was analyzed by ^1H NMR. The ratio of k_H/k_D was estimated from the amounts of each of the unreacted alcohols over three samples. The average value of the three measurements was 1.1.

Initial Rate of Oxidation in Different Concentrations of 1-Phenylethanol. The oxidations were carried out by procedures similar to the oxidation in Table 2. The catalyst **5a** (20 μmol) and K_2CO_3 (20 μmol) were placed in a flask, and acetone (8.0 mL) was added. Another flask was charged with 1-phenylethanol (20.0 or 40.0 mmol) and acetone (8.0 mL). After the solution containing the catalyst and K_2CO_3 was warmed at 40 °C, the solution of 1-phenylethanol was added into the warmed solution. The yields of acetophenone after 5 min were determined by GC analysis using undecane as an internal standard.

Monitoring of the Oxidation of 1-Phenylethanol by ^1H NMR. A NMR tube was charged with the catalyst **5a** (17.1 mg, 20.6 μmol), K_2CO_3 (2.6 mg, 18.8 μmol), and acetone-d_6 (0.5 mL). 1-Phenylethanol (23.4 mg, 0.192 mmol) was added into the resulting solution. The reaction mixture was monitored at room temperature by an NMR spectrometer.

Monitoring of the Oxidation of 1-Phenylethanol by IR. The catalyst **5a** (16.8 mg, 20.2 μmol), K_2CO_3 (2.9 mg, 21.0 μmol), and acetone (1.0 mL) were placed in a flask. After 1-phenylethanol (24.6 mg, 0.201 mmol) was added, the resulting mixture was stirred at room temperature. The reaction mixture was analyzed after 15 min by an IR spectrometer and a gas chromatograph.

Investigation of the Residues of the Reaction Mixture. To a solution of **5a** (0.020 mmol) and K_2CO_3 (0.038 mmol) in acetone (1.0 mL) was added 1-phenylethanol (0.045 mmol). The reaction mixture was stirred at room temperature. After 2 h, the solvent was evaporated, and the residual mixture was analyzed by means of ^1H NMR. The ^1H NMR spectrum showed the presence of complex **7b** (14%), **4** (86%), and acetophenone.

X-ray Structure Analyses of 3a, 5a, 5d, 6, 7c·2(H_2O), and 8b·C_3H_6O. The crystal data and experimental details for **3a**, **5a**, **5d**, **6**, **7c**·2(H_2O), and **8b**·C_3H_6O are summarized in Table S1 (see Table S1 in Supporting Information). Diffraction data were obtained with a Rigaku AFC-5S. The reflection intensities were monitored by three standard reflections every 150 measurements. Reflection data were corrected for Lorentz and polarization effects. Absorption corrections were empiri-

cally applied. The structures of **3a**, **5a**, **5d**, and **6** were solved by heavy-atom Patterson methods[24,25] and refined anisotropically for non-hydrogen atoms by full-matrix least squares calculations. The structures of **7c**·2(H_2O) and **8b**·C_3H_6O were solved by direct methods[26] and refined anisotropically for non-hydrogen atoms by full-matrix least squares calculations, except for acetone molecules in **8b**·C_3H_6O, which were not refined. In **7c**·2(H_2O), two water molecules were located on a Fourier difference map because of the presence of the corresponding electron density, although elemental analysis of **7c** showed the absence of the water molecules in crystal. Atomic scattering factors and anomalous dispersion terms were taken from the literature.[27] The hydrogen atoms were located on idealized positions except for metal hydrides in **6** and **7c**·2(H_2O). The calculations were performed using the program system teXsan[28] and CrystalStructure.[29]

Supporting Information Available: ORTEP drawings of **6** and **7c**. CIF files giving crystallographic data for **3a**, **5a**, **5d**, **6**, **7c**, and **8b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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