Activation of Acetonitrile in $[Cp^*Ir(\eta^3\text{-}CH_2CHCHPh)(NCMe)]^+$: Crystal Structures of Iridium−Amidine, Imino−Ether, Amido, and Amide Complexes

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Reactions of $[Cp^*Ir(\eta^3\text{-}CH_2CHCHPh)(NCMe)]OTf$ (**1**) with protic amines, alcohols, and water produce amidine complexes $[Cp^*Ir(\eta^3\text{-}CH_2CHCHPh)(NH{=}C(NR_2)Me)]OTf$ (**2**) (R_2 = $(Me)_2$ (**a**), (Me)(H) (**b**), (*i*-Pr)(H) (**c**), ($-CH_2(CH_2)_3CH_2-$) (**d**)), imino−ether complexes $[Cp^*Ir(\eta^3\text{-}CH_2CHCHPh)(NH{=}C(OR')Me)]OTf$ (**4**) (R′ = Me (**a**), Et (**b**), *i*-Pr (**c**)), and amido complex $Cp^*Ir(\eta^3\text{-}CH_2CHCHPh)(NHC(=O)Me)$ (**5-K**), respectively. The keto form amido complex **5-K** undergoes tautomerization to give the enol form complex $Cp^*Ir(\eta^3\text{-}CH_2CHCHPh)(N{=}C(OH)Me)$ (**5-E**) in polar solvents. Tertiary amines (NMe_3, NEt_3) react with **1** in chlorinated solvents (XCl) to give the chloro complex $Cp^*IrCl(\eta^3\text{-}CH_2CHCHPh)$ (**3**) and quaternary ammonium salts $[R_3NX]OTf$ (R = Me, Et and X = CH_2Cl, CH_3, $CHCl_2$, CCl_3, $PhCH_2$). Crystal structures of **2a**, **4a**, **5-K**, and $[Cp^*Ir(NH{=}C(OH)Me)(OH_2)(PPh_3)]OTf_2$ (**6**) have been determined by single-crystal X-ray diffraction analysis, which lead us to suggest hybrid structures, $Ir-{}^-NH-C(=N^+Me_2)Me$ (**2a′**) for **2a** and $Ir-{}^-NH-C(=O^+Me)Me$ (**4a′**) for **4a** to some extent. Complexes **2** and **4** react with PPh_3 to give an iridium(III) complex $[Cp^*Ir(\eta^3\text{-}CH_2CHCHPh)(PPh_3)]OTf$ (**7**) and the free amidines $NH{=}C(NR_2)Me$ (**8**) and imino−ethers $NH{=}C(OR')Me$ (**9**), respectively. Nitrile complexes **1** and $[Cp^*Ir(\eta^3\text{-}CH_2CHCHPh)(NCCH{=}CHMe)]OTf$ (**10**) catalyze the hydration of the nitriles in the presence of Na_2CO_3 to produce amides, and the benzonitrile complex $[Cp^*Ir(\eta^3\text{-}CH_2CHCHPh)(NCPh)]OTf$ (**11**) catalyzes the methanolysis of benzonitrile in the presence of Na_2CO_3 to produce $NH{=}C(OMe)Ph$. Plausible mechanisms for these catalytic reactions are suggested with the amido and imino−ether complexes such as **4** and **5** being involved.

Introduction

While metal-coordinated nitriles (M−N≡CR) in general are so labile that they are readily replaced by many other organic molecules, they also show higher reactivity than free ones.[1] Reactions between free nitriles and nucleophiles such as amines, alcohols, and water usually proceed in the presence of acid or base,[2] whereas coordinated nitriles react with those nucleophiles without the help of an acid or base.[3]

Metal−amidine (M−NH=CR(NR_2)), metal−imino−ether (M−NH=CR(OR)), metal−amido (M−NHC(=O)R), and metal−imine (M−NH=CHR) complexes have been prepared from the reactions of M−N≡CR with HNR_2,[4] ROH,[5] H_2O,[6] and $LiEt_3BH$,[7] respectively. Catalytic hydration of nitriles to produce amides has been extensively studied with homogeneous catalysts[8−12] and heterogeneous catalysts.[13−15] On the other hand, alcoholysis and aminolysis of nitriles catalyzed by metal compounds have not been previously reported.

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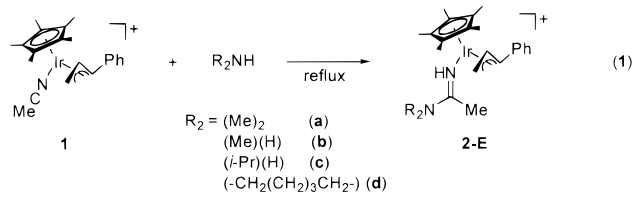
During the investigation on the catalytic activity of the iridium(III) complex [Cp*Ir(η^3-$CH_2CHCHPh$)(NCMe)]-OTf (**1**) (Cp* = $C_5Me_5^-$ and OTf = $^-OSO_2CF_3$),[16] we found that nucleophiles such as amines, alcohols, and water are added to the coordinated MeCN of **1** to give stable Ir−amidine, Ir−imino−ether, and Ir−amido complexes. Organic molecules containing imino−ether and amidine moieties are important as pharmaceutical materials as well as intermediates in organic syntheses.[17] The hydration of nitrile groups can lead to the preparation of useful monomers; for example, the hydrolysis of acrylonitrile affords acrylamide, of which polymers are very important materials in paper production and wastewater treatment.[18]

Results and Discussion

Addition of Protic Amines to MeCN in 1: Amidine Complex [Cp*Ir(η^3-$CH_2CHCHPh$)(NH=C(NR_2)-Me]OTf (2). Compound **1** reacts with protic amines under refluxing condition to give stable amidine complexes **2a**−**d** (eq 1). The amine addition is much faster in the presence of Na_2CO_3 than in the absence of Na_2CO_3.



The amidine complexes have been characterized by spectral (^{1}H, ^{13}C NMR, and IR) data and by crystal structure determination for [Cp*Ir(η^3-$CH_2CHCHPh$)-(NH=C(NMe_2)Me]OTf (**2a**). The crystal structure analysis for **2a** reveals that the stable form is **2a-E**, where the NMe_2 group is *trans* to Ir (Figure 1).

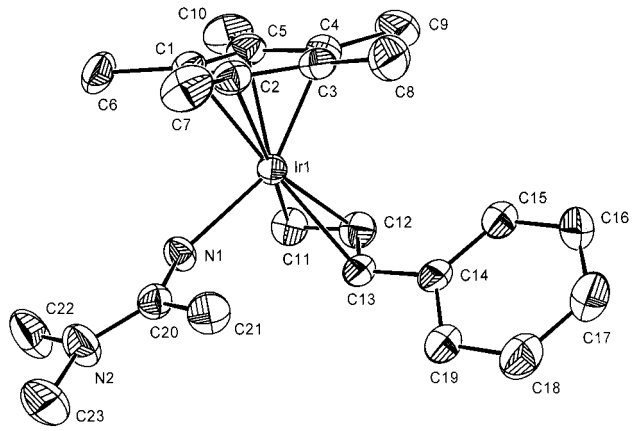


Figure 1. ORTEP drawing of [Cp*Ir(η^3-$CH_2CHCHPh$)-(NH=C(NMe_2)Me)]OTf (**2a-E**) with 30% thermal ellipsoids probability. Selected bond distances (Å): Ir_1-N_1 = 2.090(4); Ir_1-C_{11} = 2.144(6); Ir_1-C_{12} = 2.123(6); Ir_1-C_{13} = 2.233(5); $C_{11}-C_{12}$ = 1.393(8); $C_{12}-C_{13}$ = 1.431(8); N_1-C_{20} = 1.298(6); $C_{20}-N_2$ = 1.347(6); N_2-C_{22} = 1.446(8); N_2-C_{23} = 1.463(7); $C_{20}-C_{21}$ = 1.500(7). Selected bond angles (deg): $Ir_1N_1C_{20}$ = 133.1(4); $N_1C_{20}C_{21}$ = 120.4(5); $N_1C_{20}N_2$ = 121.8(5); $C_{21}C_{20}N_2$ = 117.8(4); $C_{20}N_2C_{22}$ = 120.8(5); $C_{20}N_2C_{23}$ = 122.4(5). Counteranion (OTf) and hydrogen atoms are omitted for clarity.

The bond distance of N(2)−C(20) (1.347(6) Å) of **2a** is somewhat shorter than the average value of N−C(sp^2) (1.38 Å)[19] and significantly shorter than those of N(2)−C(22) (1.446(8) Å), N(2)−C(23) (1.463(7) Å), and the average value of N−C(sp^3) (1.47 Å)[19] (see Figure 1). The bond distance of N(1)−C(20) (1.298(6) Å) on the other hand is somewhat longer than the average value of N=C(sp^2) (1.28 Å).[19] The amidine moiety (NH=C(NMe_2)-Me) of **2a** seems to be planar (planarity data of 6 atoms are −0.004(4) Å for N(1), 0.001(5) Å for C(20), −0.007(4) Å for C(21), 0.038(5) Å for N(2), −0.016(4) Å for C(22), and −0.012(4) Å for C(23)) with all the relevant bond angles being close to 120°: N(1)−C(20)−C(21), 120.4(5)°; N(1)−C(20)−N(2), 121.8(5)°; N(2)−C(20)−C(21), 117.8(4)°; C(20)−N(2)−C(22), 120.8(5)°; C(20)−N(2)−C(23), 122.4(5)°; C(22)−N(2)−C(23), 116.4(5)°.

These observations may be understood in terms of the hybrid structures between the two species as shown in eq 2. The same type of resonance structure has been suggested for Pt complexes based on spectral and crystallographic data.[4d,f] The isomerization of **2a-E** to **2a-Z** has not been observed even under reflux conditions in CH_2Cl_2. All other amidine complexes (**2b**−**d**) were prepared in refluxing CH_2Cl_2, and no Z isomers have been observed.

Reactions of 1 with Tertiary Amines (R_3N) in Chlorinated Solvents: Cp*IrCl(η^3-$CH_2CHCHPh$) (3) and Quaternary Ammonium Salts ([R_3NX]OTf). While no reaction has been observed between compound **1** and tertiary amines (NMe_3, NEt_3) in THF, compound **1** reacts with tertiary amines in chlorinated solvents to give chlorine-substituted complex Cp*IrCl(η^3-CH_2CH-

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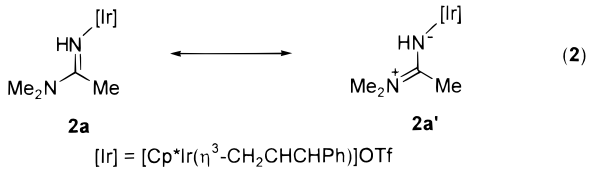
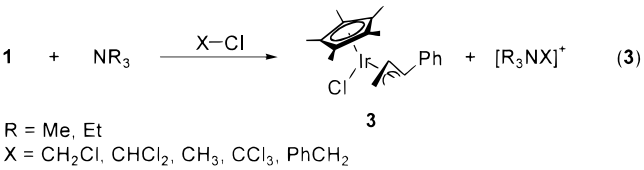


(2)

CHPh) (**3**) and related quaternary ammonium salts $[R_3NX]OTf$ (R = Me, Et and X = CH_2Cl, $CHCl_2$, CH_3, CCl_3, $PhCH_2$) (eq 3).



(3)

Identification of **3** is straightforward by comparison with the analogous spectral data for the (methylallyl)-chloro complex $Cp^*IrCl(\eta^3\text{-}CH_2CHCHMe)$[20] previously reported (see Experimental Section for spectral data). Dichloromethane was known to act as an alkylating agent toward NEt_3.[21] Sulfur alkylation was also reported in the reactions of $[PtS(PPh_3)_2]_2$ with CH_2Cl_2 (or $CHCl_3$) and of $[PtCl_2(PR_3)_2]$ with NaSH in CH_2Cl_2 to produce $[Pt_2(-S)(-SR)(PPh_3)_4]^+$ (R = CH_2Cl, $CHCl_2$)[22] and $[Pt(S_2-CH_2)(PR_3)_2]$,[23] respectively. Other chlorinated solvents, $CHCl_3$, CH_3Cl, CCl_4, and $PhCH_2Cl$, are also known to coordinate Cl^- to transition metals.[24] Coordination of CH_2Cl_2 to a transition metal is known to occur through Cl.[25] The C−Cl bond cleavage probably occurs through the coordination of XCl *via* Cl atoms to the metal followed by attack of the tertiary amine on X.

It should be mentioned here the amine-substituted complexes $[Cp^*Ir(\eta^3\text{-}CH_2CHCHPh)(L)]^+$ (L = H_2NPh, C_5H_5N) are obtained from the reactions of **1** with aniline and pyridine in $CHCl_3$ or benzene.

Addition of Alcohols to MeCN in 1: Imino−Ether Complex $[Cp^*Ir(\eta^3\text{-}CH_2CHCHPh)(NH{=}C(OR)Me]OTf$ (4). Compound **1** also reacts with alcohols under refluxing conditions to produce imino−ether iridium(III) complexes **4a**−**c** in the presence of Na_2CO_3 (eq 4). The base CO_3^{2-} seems to facilitate the cleavage of the RO−H bond.

The imino−ether complexes **4a**−**c** have been unambiguously characterized by spectral data (^1H and ^{13}C NMR and IR) and by crystal structure determination for **4a** by X-ray diffraction data analysis (Experimental Section and Figure 2). The crystal structure reveals the *OMe* group being *cis* to the Ir.

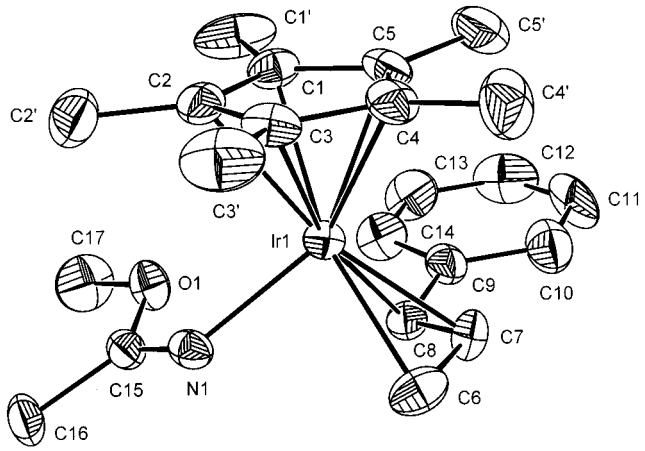
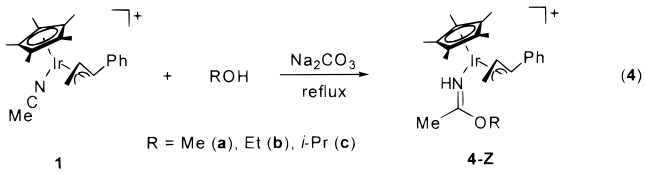
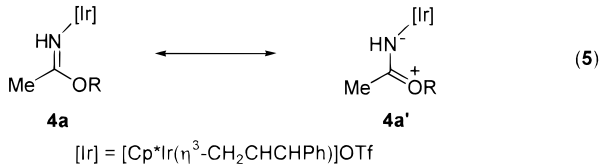


Figure 2. ORTEP drawing of $[Cp^*Ir(\eta^3\text{-}CH_2CHCHPh)(NH{=}C(OMe)Me)]OTf$ (**4a-Z**) with 30% thermal ellipsoids probability. Selected bond distances (Å): Ir_1-N_1 = 2.094(5); Ir_1-C_6 = 2.164(7); Ir_1-C_7 = 2.150(9); Ir_1-C_8 = 2.225(10); C_6-C_7 = 1.42(2); C_7-C_8 = 1.417(11); N_1-C_{15} = 1.276(8); $C_{15}-O_1$ = 1.300(12); O_1-C_{17} = 1.434(8); $C_{15}-C_{16}$ = 1.500(12). Selected bond angles (deg): $Ir_1N_1C_{15}$ = 130.5(6); $N_1C_{15}C_{16}$ = 121.0(9); $N_1C_{15}O_1$ = 116.8(7); $C_{16}C_{15}O_1$ = 122.1(7); $C_{15}O_1C_{17}$ = 118.8(7); $C_6C_7C_8$ = 118.3(9). Counteranion (OTf) and hydrogen atoms are omitted for clarity.



(4)

The short bond distance of N(1)−C(15) (1.276(8) Å) of **4a-Z** shows a typical double-bond character (Figure 2). It is noticed that the C(15)−O(1) distance (1.300(12) Å) is somewhat shorter than the average $C(sp^2)-O$ (1.34 Å),[19] while it is much longer than $C(sp^2){=}O$ (1.21 Å).[19] It is also noticed that the angle C(15)−O(1)−C(17) (118.8(7)°) is close to 120°. These observations may be understood in terms of a resonance between the two species, as shown in eq 5.



(5)

The reaction of **1** with MeOH at room temperature produces a mixture of **4a-Z** (OMe group *cis* to Ir) and **4a-E** (OMe group *trans* to Ir). As the crystal structure of **4a-Z** has been determined by X-ray diffraction data analysis (Figure 2), assignments of the ^1H NMR signals measured for the mixture of **4a-Z** and **4a-E** to each **4a-Z** and **4a-E** are rather straightforward. Z and E isomers of imino−ether metal complexes have been reported with a suggested mechanism for the isomerization between E and Z isomers.[5a] The isomer **4a-E** slowly undergoes isomerization to give **4a-Z** in the presence of MeOH and Na_2CO_3, which can be measured by ^1H NMR spectral changes (see Experimental Section). The reaction of **1** with EtOH also produces both isomers **4b-E** and **-Z** at room temperature, and **4b-E** undergoes

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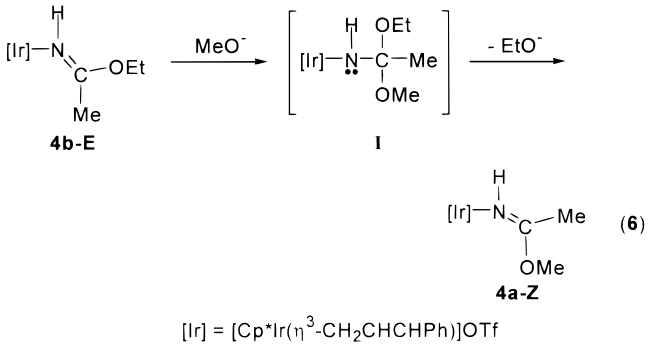
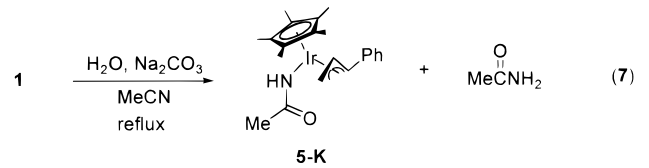
isomerization to give **4b-Z** in the presence of EtOH and Na_2CO_3. Only the Z isomer, **4c-Z**, has been observed from the reaction of **1** with *i*-PrOH and does not undergo isomerization to give **4c-E** even in the presence of *i*-PrOH and Na_2CO_3.

To obtain more information on the reaction pathways for the isomerization of **4-E** to **4-Z**, the ethanol adduct (mixture of **4b-Z** and **-E**) was stirred in MeOH solution in the presence of Na_2CO_3 for 24 h at room temperature to obtain **4a-Z** in high purity. This observation suggests that the isomerization is initiated by the attack of a methoxy group on the imino carbon of **4b-E** to give the amido−ketal complex **I**, which then undergoes the elimination of an ethoxy group to produce **4a-Z** (eq 6). The same type of mechanism has been suggested for the isomerization of imino−ether Pt complexes.[5a]



The isomerization (**4a-E** to **4a-Z**) does not occur in the absence of MeOH and Na_2CO_3.

Reaction of 1 with H_2O in the Presence of Na_2CO_3: Amido Complex Cp*Ir(η^3-$CH_2CHCHPh$)(NHC(=O)Me) (5-K). The MeCN of compound **1** is also activated by H_2O in the presence of Na_2CO_3 in refluxing MeCN to produce the amido complex Cp*Ir(η^3-CH_2-CHCHPh)(NHC(=O)Me) (**5-K**) with a significant amount of acetamide (eq 7). The amido complex **5-K** is also obtained from the reactions of **1** with KOH or NaOH solution of H_2O/MeCN in the absence of Na_2CO_3.



The amido complex **5-K** has been unequivocally characterized by spectral and elemental analysis data and also by crystal structure determination by X-ray diffraction data analysis (Figure 3). Formation of **5-K** seems to be initiated by the attack of nucleophile $^-$OH on the nitrile carbon atom of **1** followed by a proton transfer from the oxygen to the nitrogen atom. A similar reaction mechanism has been proposed for the hydration of the coordinated nitrile.[11] It is well-established that the base hydrolysis of coordinated nitriles produces a keto form of amido complexes which have been identified by spectral[6b−d,f,g,8a,b,e,11] and crystal structural data.[4f]

The amido moiety of **5-K** in the solid state is best described as the keto form, Ir−NHC(=O)Me, by a much shorter distance of C(9)−O than that of C(9)−N. The C(9)−O distance (1.237(8) Å) is much shorter than the average C(sp^2)−O distance (1.34 Å)[19] but somewhat

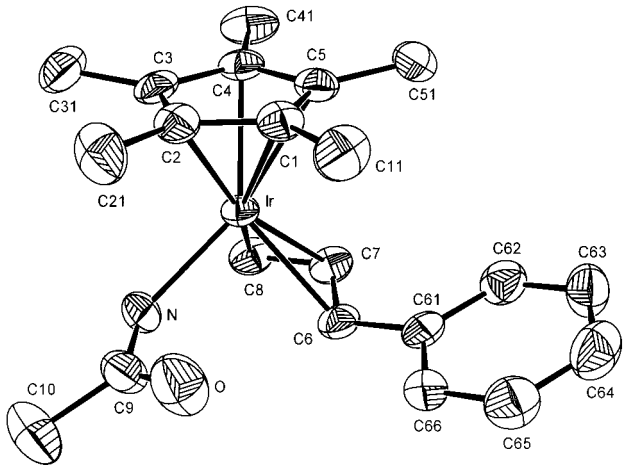
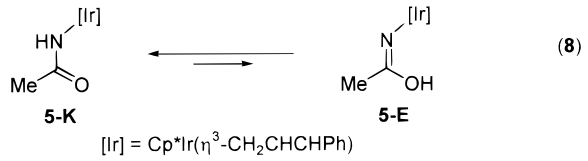


Figure 3. ORTEP drawing of Cp*Ir(η^3-$CH_2CHCHPh$)-(NHC(=O)Me) (**5-K**) with 50% thermal ellipsoids probability. Selected bond distances (Å): Ir−N = 2.078(5); Ir−C_6 = 2.219(6); Ir_1−C_7 = 2.118(6); Ir_1−C_8 = 2.153(6); C_6−C_7 = 1.422(9); C_7−C_8 = 1.413(9); N−C_9 = 1.325(8); C_9−O = 1.237(8); C_9−C_{10} = 1.505(10). Selected bond angles (deg): $IrNC_9$ = 128.0(4); NC_9C_{10} = 117.5(7); NC_9O = 124.2-(6); $C_{10}C_9O$ = 118.2(7); $C_6C_7C_8$ = 118.9(6).

longer than the average C(sp^2)=O distance (1.21 Å),[19] while C(9)−N (1.325(8) Å) is somewhat shorter than the average C(sp^2)−N (1.38 Å)[19] but significantly longer than the average C(sp^2)=N (1.28 Å).[19] These observations may be understood in terms of the resonance structure, Ir−NHC(=O)Me ↔ Ir−$^+$NH=C(O$^-$)Me.



The ^{1}H NMR spectral measurements suggest two isomers (**5-K** and **5-E**) present in polar solvents such as $CDCl_3$ and CD_2Cl_2 (eq 8). Figure 4 clearly shows two sets of signals in $CDCl_3$ and CD_2Cl_2 and only one set of signals in C_6D_6 and CD_3COCD_3. The signals in CD_3-$COCD_3$ may be assigned to **5-E** rather than **5-K** taking into account of the polarity of acetone.

There have been reports on the enol form of amide (M−NH=C(OH)R) complexes,[6b,c] whereas no enol form of the amido (M−$^-$N=C(OH)R) complex has been identified, although it has been suggested as the initial products in the hydrolysis of coordinated nitriles.[8e,9a]

It may be conceivable to assign those signals (denoted by a′ and b′) that are growing with increasing amount of $CDCl_3$ in Figure 5 to the enol form **5-E** (see Experimental Section).

Exactly the same spectrum in C_6D_6 (Figure 4 (i)) is regenerated when the solvent is removed from the solution of **5-E** and **5-K** in $CDCl_3$, CD_2Cl_2, or CD_3COCD_3 and the resulting solid is redissolved in C_6D_6.

It should be mentioned here that infrared spectral measurements both in Nujol and KBr suggest the keto form complex **5-K** being the dominant species in the solid state. No differences have been found between the spectra for all isolated solids from C_6H_6, CH_3COCH_3, $CHCl_3$, and CH_2Cl_2. The unusually low frequency (1600 cm^{-1}) is observed for ν(CO) in **5-K** with somewhat

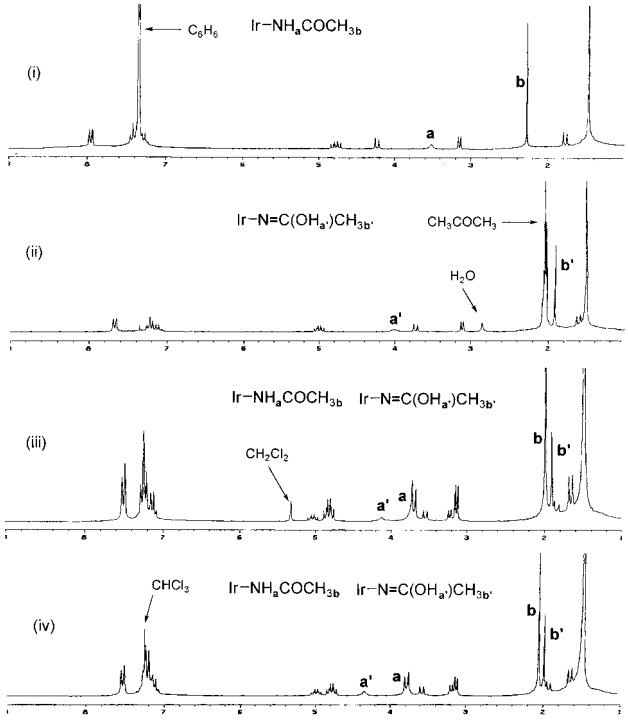


Figure 4. ^{1}H NMR spectra of Cp*Ir(η^3-$CH_2CHCHPh$)(NHC(=O)Me) (**5-K**) and Cp*Ir(η^3-$CH_2CHCHPh$)(N=C(OH)Me) (**5-E**) in different deuterated solvents: (i) pure C_6D_6, (ii) pure CD_3COCD_3, (iii) pure CD_2Cl_2, and (iv) pure $CDCl_3$ at 300 MHz.

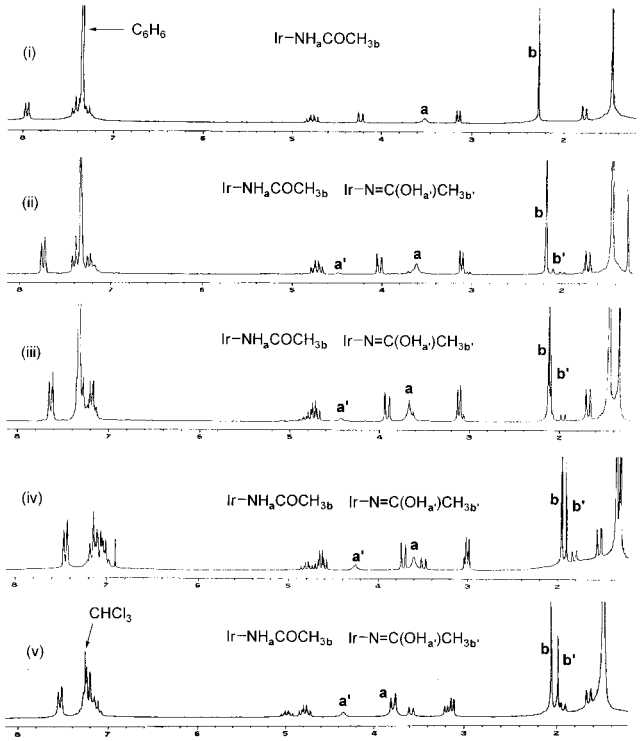
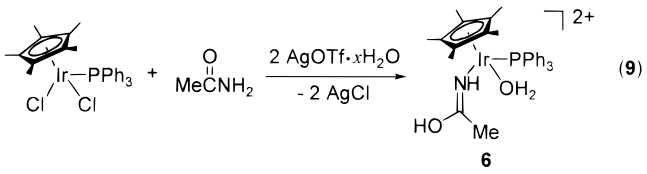


Figure 5. ^{1}H NMR spectral change of Cp*Ir(η^3-CH_2-CHCHPh)(NHC(=O)Me) (**5-K**) and Cp*Ir(η^3-$CH_2CHCHPh$)(N=C(OH)Me) (**5-E**) in different volume ratio of C_6D_6/$CDCl_3$ solution: (i) pure C_6D_6, (ii) $C_6D_6/CDCl_3$ = 8/2, (iii) $C_6D_6/CDCl_3$ = 5/5, (iv) $C_6D_6/CDCl_3$ = 2/8, and (v) pure $CDCl_3$ at 300 MHz.

higher frequency (1618 cm^{-1}) for ρ(N−H), which is confirmed by an H/D exchange experiment. It is seen that the absorption bands at 1618 and 3374 (ν(N−H)) decrease significantly in intensity and a new absorption band (ν(N−D)) appears at 2504 cm^{-1} in the infrared spectrum of the deuterated amido complex **5-K-*d*$_1$** isolated from the C_6D_6/D_2O solution.

Amido complex **5** reacts with HCl to give the chloro−Cp*Ir(III) complex **3** and free acetamide, but no coordinated acetamide complex has been observed. It is well-established that amido complexes M−*N*HC(=O)R (M = Pt,[6c] Co,[6j] Ru[6h]) are acidified to give amide complexes M−*N*H_2C(=O)R (M = Pt,[6b,c] Ni,[6a,i] Pd[6i]). It is also known that N-bonded amide complexes show a keto−enol equilibrium between M−NH_2C(=O)R and M−NH=C(OH)R and also show linkage isomerization to *O*-coordinated amide complexes M−*O*=C(NH_2)R (M = Co,[11] Pt,[6c] Ru[6h]). Amide complexes are also obtained from the direct reactions of metals and amides.[6c]

Synthesis of the Enol Form of Amide (Iminol) Complex [Cp*Ir(NH=C(OH)Me)(PPh_3)(OH_2)](OTf)$_2$ (6). In this study, attempts to prepare the acetamide complex [Cp*Ir(η^3-$CH_2CHCHPh$)(NH_2C(=O)Me)]$^+$ have been unsuccessful, while one acetamide complex **6** was prepared from the reaction of Cp*$IrCl_2(PPh_3)$[26] with acetamide and AgOTf·*x*H_2O in CH_2Cl_2 (eq 9). The iminol complex **6** has been characterized by spectral data and also by crystal structure determination by X-ray diffraction data analysis.



The binding mode of acetamide, that is, whether N- or O-binding, was determined by the comparison of the final *R* value, which is lower for the N-bonded form than for the O-bonded one. The N-bonded Ir−NH=C(OH)-Me moiety for **6** is also supported by a comparison between the bond lengths Ir−N, C−N, and C−O of **6** and **4a-Z** with Ir−NH=C(OMe)Me: bond lengths in Å, Ir−N (2.048(16)), C−N (1.25(3)), and C−O (1.35(2)), of **6** are close to those (2.094(5), 1.276(8), and 1.300(12)) of **4a-Z**.

The iminol moiety of **6** in the solid state is best described by iminol ligand (Ir−NH=C(OH)Me) since the distance of C(1)−N(1) is much shorter than the C(1)−O(2) distance (Figure 6). The short bond length of C(1)−N(1) (1.25(3) Å) is close to the average C(sp^2)=N length (1.28 Å)[19] and much shorter than the average length of C(sp^2)−N (1.38 Å),[19] while C(1)−O(2) (1.35(2) Å) is very close to the average C(sp^2)−O distance (1.34 Å)[19] and much longer than the average C(sp^2)=O (1.21 Å).[19]

^{1}H, ^{13}C, and ^{31}P NMR spectra of **6** show no evidence for the other isomer of **6** in $CDCl_3$. ^{1}H NMR resonances at 12.8 ppm (1H), 5.79 ppm (1H), and 1.88 ppm (3H) are assigned to O*H*, N*H*, and *Me* of Ir−NH=C(OH)Me (**6**), respectively. These observed chemical shifts in the ^{1}H NMR spectrum of **6** are very close to those of the well-known iminol complexes such as [dienPt(NH=C(OH)Me)]$^{2+}$ and [$(NH_3)_5$Co(NH=C(OH)Me)]$^{3+}$.[6d,k]

To the best of our knowledge, there have been only two reports on the crystal structures of metal complexes with N-bonded iminol.[6a,b]

(26) Glueck, D. S.; Winslow, L. J. N.; Bergman, R. G. *Organometallics* **1991**, *10*, 1462, and references therein.

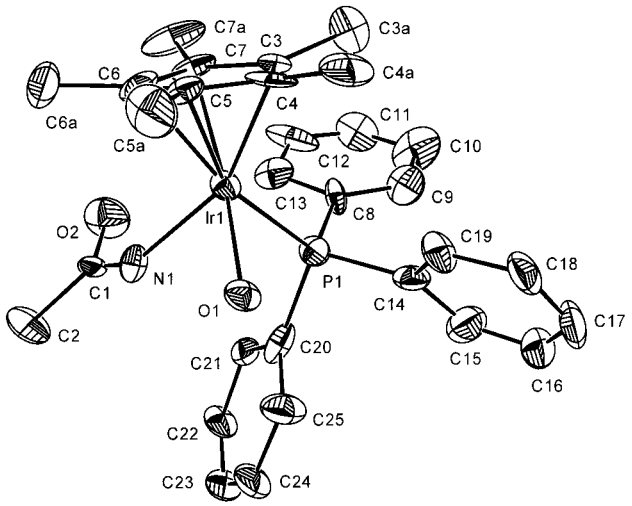
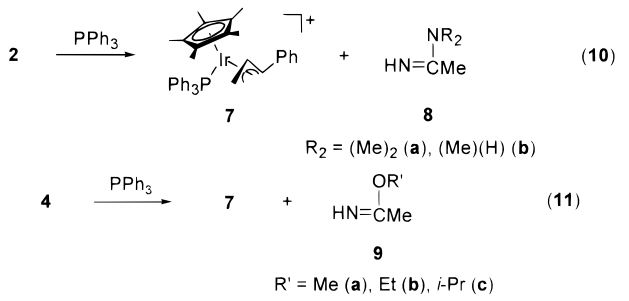


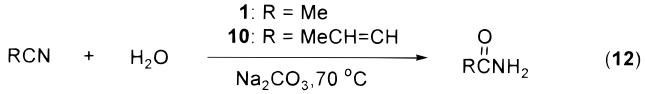
Figure 6. ORTEP drawing of [Cp*Ir(NH=C(OH)Me)-$(OH_2)(PPh_3)$]OTf_2 (**6**) with 30% thermal ellipsoids probability. Selected bond distances (Å): Ir_1-N_1 = 2.048(16); Ir_1-P_1 = 2.332(5); Ir_1-O_1 = 2.245(11); N_1-C_1 = 1.25(3); C_1-O_2 = 1.35(2); C_1-C_2 = 1.49(3). Selected bond angles (deg): $Ir_1P_1C_{14}$ = 114.8(6); $Ir_1P_1C_8$ = 115.1(6); $Ir_1P_1C_{20}$ = 113.9(6); $P_1Ir_1O_1$ = 87.7(4); $O_1Ir_1N_1$ = 78.4(5); $Ir_1N_1C_1$ = 134.6(13); $N_1C_1O_2$ = 121.0(18); $N_1C_1C_2$ = 126(2). Two counteranions (OTf) and hydrogen atoms are omitted for clarity.

Dissociation of Amidines and Imino−Ethers from 2 and 4. Should amidines and imino−ethers in **2** and **4**, respectively, be replaced by acetonitrile, one may expect catalytic production of these organic compounds from the reactions of acetonitrile with amines and alcohols in the presence of **1**. Amidines and imino−ethers in **2** and **4** are not replaced by acetonitrile even under refluxing conditions.

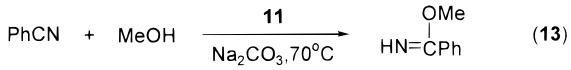
They are, however, readily replaced with triphenylphosphine (PPh_3) (eqs 10 and 11). Imino−ethers are known to undergo hydrolysis in the presence of acid and water to give corresponding esters, while amidines are relatively stable under similar conditions.[27] Amidines (**8**) and imino−ethers (**9**) have been unequivocally identified by ^{1}H and ^{13}C NMR measurements for the reaction mixtures of **2** and **4** with PPh_3, respectively, in dried deuterated solvents (see Experimental Section).



Catalytic Hydration and Methanolysis of Nitriles with [Cp*Ir(η^3-$CH_2CHCHPh$)(NCR)]OTf (R = Me (1), MeCH=CH (10), Ph (11)). The hydration of acetonitrile is catalyzed by compound **1** at 70 °C to produce acetamide (eq 12), which most likely proceeds through the amido complex **5**. The hydration of MeCN is fairly rapid ($MeC(=O)NH_2$/Ir/h = 8.3 and total conversion = 4.1%) in the presence of **1** and Na_2CO_3, while it is very slow in the absence of **1**. Very small amounts of $MeC(=O)NH_2$ are obtained in the presence of Na_2CO_3 (<0.01/h) and NaOH (0.4/h), respectively. The hydration of crotononitrile (MeCH=CHCN) (eq 12) is faster ($MeCH=CHC(=O)NH_2$/Ir/h = 13.3 and total conversion = 6.1%) than that of acetonitrile, while the hydration of acrylonitrile (CH_2=CHCN) is too slow ($CH_2=CHC(=O)NH_2$/Ir/h < 0.1) to measure under the same experimental conditions.



The hydration of benzonitrile is very slow ($PhC(=O)NH_2$/Ir/h < 0.1) in the presence of the benzonitrile complex [Cp*Ir(η^3-$CH_2CHCHPh$)(NCPh)]$^+$ (**11**).[28] On the other hand, the methanolysis of benzonitrile proceeds rapidly (NH=C(OMe)Ph/Ir/h = 6.2 and total conversion = 3.2%) to produce the imino−ether in the presence of **11** and Na_2CO_3 (eq 13).



These two catalytic reactions (eqs 12 and 13) may be represented by those cycles in Scheme 1 since the amido complex **5** and imino−ether complex **4** have been identified in the reactions of **1** with H_2O and MeOH, respectively.

Experimental Section

General Information. A standard vacuum system and Schlenk type glassware were used in handling metal complexes, although most of metal complexes investigated in this study seemed to be stable enough to be handled without much precautions against air and moisture.

The NMR spectra were obtained on a Varian Gemini 200, 300, or 500 MHz spectrometer for ^{1}H and 50, 75, or 125 MHz for ^{13}C, and 121.3 MHz for ^{31}P. Infrared spectra were obtained on a Nicolet 205 or Shimadzu IR-440 spectrophotometer. Gas chromatography/mass spectra were measured by Hewlett-Packard HP 5890A and VG-trio 2000 instruments. Elemental analysis was performed with a Carlo Erba EA1108 at the Organic Chemistry Research Center, Sogang University, Korea.

[Cp*Ir(η^3-$CH_2CHCHPh$)(NCMe)]OTf (**1**)[16] and Cp*$IrCl_2$-(PPh_3)[26] were prepared by the literature methods.

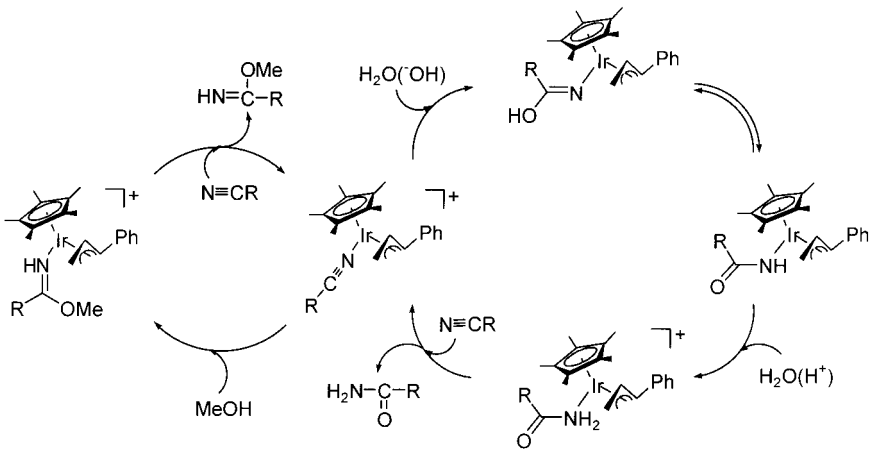
Synthesis of [Cp*Ir(η^3-$CH_2CHCHPh$)(NH=C(NMe_2)-Me)]OTf (2a). Method I. Compound **1** (0.10 g, 0.16 mmol) was dissolved in CH_2Cl_2 (20 mL), and a 0.50 mL portion of a 50% aqueous solution of Me_2NH was added drop by drop at room temperature. The resulting mixture was refluxed for 6 h. The deep yellow solution was dehydrated by treatment of $MgSO_4$ and evaporated completely to remove the remaining dimethylamine. The yellow residue was washed with cold Et_2O (10 mL) and recrystallized in CH_2Cl_2/Et_2O to obtain pale yellow microcrystals of [Cp*Ir(η^3-$CH_2CHCHPh$)(NH=C(NMe_2)Me)]-OTf (**2a**, 0.095 g, 87%).

Method II. Compound **1** (0.10 g, 0.16 mmol) in CH_2Cl_2 (10 mL) was added into a CH_2Cl_2 (10 mL) solution of Me_2NH

(27) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley-Interscience: New York, 1992; p 892.

(28) Complex **10** and **11** have been prepared from the reactions of **3** with the corresponding nitriles in the presence of AgOTf. See Experimental Section for experimental details and spectral data.

Scheme 1. Possible Reaction Pathways for the Catalytic Hydration (R = Me, MeCH=CH) and Methanolysis (R = Ph) of Nitriles



(extracted from a 50% aqueous solution of Me_2NH in water). The mixture was refluxed in the presence of Na_2CO_3 for 3 h. Na_2CO_3 was removed on a Celite-packed filter, and the resulting yellow filtrate was distilled under vacuum to obtain a beige solid, which was washed with H_2O (5.0 mL) to remove unreacted Me_2NH. The beige solid was recrystallized in CH_2Cl_2/Et_2O to obtain pale yellow microcrystals of **2a** (0.10 g, 93%). ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.42 (s, 15H, CH_3 of Cp*), 1.72 (d, 1H, J(HH) = 9.4 Hz, C*H*HCHCHPh), 2.07 (s, 3H, NH=C(NMe$_2$)CH_3), 2.93 (s, 6H, NH=C(N(CH_3)$_2$)Me), 3.20 (d, 1H, J(HH) = 6.0 Hz, CH*H*CHCHPh), 3.26 (d, 1H, J(HH) = 9.0 Hz, CH$_2$CHC*H*Ph), 4.89 (m, 1H, CH$_2$C*H*CHPh), 5.42 (br s, 1H, N*H*=C), 6.90−7.17 (m, 5H, C$_6H_5$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 8.0 and 93.0 (Cp*), 22.1 (NH=C(NMe$_2$)*C*H$_3$), 39.1 and 40.1 (NH=C(N(*C*H$_3$)$_2$)Me), 44.4 (*C*H$_2$CHCHPh), 63.1 (CH$_2$CH*C*HPh), 77.7 (CH$_2$*C*HCHPh), 125.9, 126.3, 129.1 and 139.0 (*C*$_6$H$_5$), 167.3 (NH=*C*). IR (Nujol, cm^{-1}): 1590 (s, $\nu_{C=N}$), 1032, 1146 and 1271 (br s, OTf). Anal. Calcd for $C_{24}H_{34}O_3N_2SF_3Ir$: C, 42.40; H, 5.04; N, 4.12. Found: C, 42.35; H, 4.90; N, 4.11.

Synthesis of [Cp*Ir(η^3-CH$_2$CHCHPh)(NH=C(NHMe)Me)]OTf (2b). Method I. A 0.50 mL portion of 40% aqueous solution of $MeNH_2$ was added into a CH_2Cl_2 solution of **1** (0.10 g, 0.16 mmol) at room temperature in a bomb reactor (Parr 1341, 360 mL), which was placed on an oil bath maintained at 50 °C for 12 h with stirring. The pale yellow microcrystals of [Cp*Ir(η^3-CH$_2$CHCHPh)(NH=C(NHMe)Me)]OTf (**2b**, 0.082 g, 77%) were obtained after treatment of the reaction mixture in the same manner as described for **2a** above.

Method II. To 0.10 g (0.16 mmol) of **1** in CH_2Cl_2 (10 mL) was added a CH_2Cl_2 (10 mL) solution of $MeNH_2$ (extracted from a 40% aqueous solution of $MeNH_2$ in water). The mixture was refluxed for 12 h before a 10 mL portion of water was added to the reaction mixture. Excess $MeNH_2$ in the aqueous layer was separated from **2b** in the CH_2Cl_2 layer, which was concentrated to 2.0 mL. Addition of Et_2O (20 mL) to the CH_2Cl_2 solution resulted in precipitation of pale yellow microcrystals of [Cp*Ir(η^3-CH$_2$CHCHPh)(NH=C(NHMe)Me)]OTf (**2b**, 0.096 g, 90%). ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.60 (s, 15H, CH_3 of Cp*), 1.88 (d, 1H, J(HH) = 9.4 Hz, C*H*HCHCHPh), 2.43 (s, 3H, NH=C(NHMe)CH_3), 3.06 (s, 3H, NHCH_3), 3.45 (d, 1H, J(HH) = 6.0 Hz, CH*H*CHCHPh), 3.49 (d, 1H, J(HH) = 9.0 Hz, CH$_2$CHC*H*Ph), 4.96 (m, 1H, CH$_2$C*H*CHPh), 5.58 (br s, 1H, N*H*Me), 7.25 (br s, 1H, N*H*=C), 7.33−7.64 (m, 5H, C$_6H_5$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 8.34 and 93.2 (Cp*), 19.2 (NH=C(NHMe)*C*H$_3$), 30.4 (*C*H$_2$CHCHPh), 40.9 (NH=C(NH*C*H$_3$)Me), 63.4 (CH$_2$CH*C*HPh), 75.9 (CH$_2$*C*HCHPh), 126.1, 126.4, 129.0 and 138.8 (*C*$_6$H$_5$), 168.2 (NH=*C*). IR (Nujol, cm^{-1}): 1624 (br s, $\nu_{C=N}$), 1032, 1146 and 1271 (br s, OTf). Anal. Calcd for $C_{23}H_{32}O_3N_2SF_3Ir$: C, 41.49; H, 4.84; N, 4.21. Found: C, 41.48; H, 4.74; N, 4.17.

Synthesis of [Cp*Ir(η^3-CH$_2$CHCHPh)(NH=C(NH(*i*-Pr))Me)]OTf (2c). Isopropylamine (0.035 mL, 0.41 mmol) was added to a CH_2Cl_2 (20 mL) solution of **1** (0.10 g, 0.16 mmol), and the reaction mixture was refluxed for 1.5 h. The reaction mixture was cooled to room temperature and distilled under vacuum to obtain a yellow residue, which was washed with H_2O (2.0 mL) and Et_2O (10 mL) and recrystallized in CH_2Cl_2/*n*-pentane to obtain beige-white microcrystals of [Cp*Ir(η^3-CH$_2$CHCHPh)(NH=C(NH(*i*-Pr))Me)]OTf (**2c**, 0.096 g, 86%). ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.23 and 1.31 (d, 6H, J(HH) = 6.0 Hz, NH=C(NHCH(CH_3)$_2$)Me), 1.64 (s, 15H, CH_3 of Cp*), 2.46 (s, 3H, NH=C(NH(*i*-Pr))CH_3), 3.31 (d, 1H, J(HH) = 9.4 Hz, C*H*HCHCHPh), 3.56 (m, 1H, NHC*H*(Me)$_2$), 3.74 (m, 2H, CH$_2$CHC*H*Ph and CH*H*CHCHPh), 4.90 (m, 1H, CH$_2$C*H*CHPh), 5.45 (br s, 1H, N*H*(*i*-Pr)), 7.48 (br s, 1H, N*H*=C), 7.12−7.37 (m, 5H, C$_6H_5$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 8.14 and 92.8 (Cp*), 22.7 (NH=C(NH(*i*-Pr))*C*H$_3$), 23.9 (NHCH(*C*H$_3$)$_2$), 43.0 (*C*H$_2$CHCHPh), 45.3 (NH*C*H(Me)$_2$), 63.9 (CH$_2$CH*C*HPh), 77.0 (CH$_2$*C*HCHPh), 126.4, 126.6, 128.7 and 138.4 (*C*$_6$H$_5$), 174.1 (NH=*C*). IR (Nujol, cm^{-1}): 1621 (s, $\nu_{C=N}$), 1030, 1163 and 1257 (br s, OTf). Anal. Calcd for $C_{25}H_{36}O_3N_2SF_3Ir$: C, 43.28; H, 5.23; N, 4.04. Found: C, 43.25; H, 5.09; N, 4.00.

Synthesis of [Cp*Ir(η^3-CH$_2$CHCHPh)(NH=C(NCH$_2$(CH$_2$)$_3$CH$_2$)Me)]OTf (2d). This compound was prepared in the same manner as described for the reaction of **2c** using **1** (0.10 g, 0.16 mmol) and piperidine (0.035 g, 0.41 mmol). Beige-white microcrystals of [Cp*Ir(η^3-CH$_2$CHCHPh)(NH=C(NCH$_2$(CH$_2$)$_3$CH$_2$)Me)]OTf (**2d**, 0.11 g, 97%) were obtained. ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.62 (s, 15H, CH_3 of Cp*), 2.05 (d, 1H, J(HH) = 10.0 Hz, C*H*HCHCHPh), 2.33 (s, 3H, NH=C(NCH$_2$(CH$_2$)$_3$CH$_2$)CH_3), 3.41 (d, 1H, J(HH) = 7.0 Hz, CH*H*CHCHPh), 3.62 and 1.67 (m, 10H, NH=C(NC*H*$_2$(C*H*$_2$)$_3$C*H*$_2$)Me), 3.71 (d, 1H, J(HH) = 9.8 Hz, CH$_2$CHC*H*Ph), 5.1 (m, 1H, CH$_2$C*H*CHPh), 6.07 (br s, 1H, N*H*=C), 7.1−7.3 (m, 5H, C$_6H_5$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 8.29 and 93.0 (Cp*), 22.7, 23.7 and 47.8 (NH=C(N*C*H$_2$(*C*H$_2$)$_3$*C*H$_2$)Me), 25.6 (NH=C(NCH$_2$(CH$_2$)$_3$CH$_2$)-*C*H$_3$), 45.0 (*C*H$_2$CHCHPh), 63.1 (CH$_2$CH*C*HPh), 77.8 (CH$_2$*C*HCHPh), 125.9, 126.1, 129.0 and 138.8 (*C*$_6$H$_5$), 166.6 (NH=*C*). IR (Nujol, cm^{-1}): 1605 (s, $\nu_{C=N}$), 1028, 1125 and 1250 (br s, OTf). Anal. Calcd for $C_{27}H_{38}O_3N_2SF_3Ir$: C, 45.05; H, 5.32; N, 3.89. Found: C, 45.01; H, 5.28; N, 3.88.

Reaction of 1 with NEt$_3$ in CH$_2$Cl$_2$. A 10 mL portion of NEt_3 was added to a CH_2Cl_2 solution of **1** (0.10 g, 0.16 mmol), and the reaction mixture was refluxed for 2.5 h, during which time the reaction mixture turned more yellowish. After solvents and excess reacted Et_3N were removed by vacuum distillation, *n*-pentane (20 mL) was added to dissolve **3** (Cp*Ir-

(η^3-$CH_2CHCHPh$)Cl), and the reaction mixture was filtered to separate the insoluble white ammonium salt, [Et_3NCH_2Cl]OTf. The filtrate was distilled under vacuum to obtain a yellow solid, which was recrystallized in *n*-pentane/MeOH at −20 °C to obtain yellow microcrystals of Cp*IrCl(η^3-$CH_2CHCHPh$) (**3**, 0.073 g, 95%). ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.51 (s, 15H, CH_3 of Cp*), 2.74 (d, 1H, J(HH) = 10.0 Hz, CHHCHCHPh), 3.30 (d, 1H, J(HH) = 6.0 Hz, CHHCHCHPh), 4.50 (d, 1H, J(HH) = 10.0 Hz, CH_2CHCHPh), 5.04 (m, 1H, CH_2CHCHPh), 7.14−7.33 (m, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$, 25 °C): δ 8.6 and 92.6 (Cp*), 44.3 (CH_2CHCHPh), 64.6 (CH_2CHCHPh), 77.2 (CH_2CHCHPh), 125.8, 126.1, 129 and 141.0 (C_6H_5). Anal. Calcd for $C_{19}H_{24}ClIr$: C, 47.54; H, 5.04. Found: C, 47.52; H, 5.00.

Data for [Et_3NCH_2Cl]OTf (0.048 g, 95%) are as follows. ^{1}H NMR (D_2O, 25 °C): δ 1.36 (t, 9H, J(HH) = 7.3 Hz, CH_2CH_3), 3.38 (q, 6H, J(HH) = 7.3 Hz, CH_2CH_3), 5.09 (s, 2H, CH_2Cl). ^{13}C NMR (D_2O, 25 °C): δ 6.46 (CH_2CH_3), 52.3 (CH_2CH_3), 62.2 (CH_2Cl). IR (KBr, cm^{-1}): 1032, 1165 and 1249 (br s, OTf).

All Other Reactions of 1 with NR_3 (R = Me, Et) in $CHCl_3$, CH_2Cl_2, MeCl, $PhCH_2Cl$, and CCl_4. These reactions were carried out in the same manner described above for the reaction of **1** with NEt_3 in CH_2Cl_2. Yields of [R_3NX]OTf and their spectral data are summarized below.

Data for [Me_3NCH_2Cl]OTf (95%) are as follows. ^{1}H NMR (CD_3CN, 25 °C): δ 3.28 (s, 9H, N(CH_3)$_3$), 5.44 (s, 2H, CH_2). ^{13}C NMR (CD_3CN, 25 °C): δ 51.5 (CH_3), 70.6 (CH_2). IR (KBr, cm^{-1}): 1024, 1138 and 1247 (br s, OTf).

Data for [Et_3NMe]OTf (95%) are as follows. ^{1}H NMR (D_2O, 25 °C): δ 1.31 (t, 9H, J(HH) = 7.4 Hz, CH_2CH_3), 3.33 (q, 6H, J(HH) = 7.4 Hz, CH_2CH_3), 2.94 (s, 3H, NCH_3). ^{13}C NMR (D_2O, 25 °C): δ 6.7 (CH_2CH_3), 55.6 (CH_2CH_3), 46.2 (NCH_3). IR (KBr, cm^{-1}): 1024, 1140 and 1256 (br s, OTf).

Data for [Me_4N]OTf (96.5%) are as follows. ^{1}H NMR (D_2O, 25 °C): δ 3.17 (s, 12H, CH_3). ^{13}C NMR (D_2O, 25 °C): δ 55.1 (CH_3). IR (KBr, cm^{-1}): 1028, 1148 and 1252 (br s, OTf).

Data for [Et_3NCHCl_2]OTf (95%) are as follows. ^{1}H NMR (D_2O, 25 °C): δ 1.28 (t, 9H, J(HH) = 7.3 Hz, CH_2CH_3), 3.21 (q, 6H, J(HH) = 7.3 Hz, CH_2CH_3), 7.58 (s, 1H, $CHCl_2$). ^{13}C NMR (D_2O, 25 °C): δ 8.04 (CH_2CH_3), 46.6 (CH_2CH_3), 57.4 ($CHCl_2$). IR (KBr, cm^{-1}): 1026, 1155 and 1242 (br s, OTf).

Data for [Me_3NCHCl_2]OTf (90%) are as follows. ^{1}H NMR (D_2O, 25 °C): δ 3.14 (s, 9H, CH_3), 7.78 (s, 1H, CHCl$_2$). ^{13}C NMR (D_2O, 25 °C): δ 47.58 (CH_3), 58.0 ($CHCl_2$). IR (KBr, cm^{-1}): 1026, 1140 and 1248 (br s, OTf).

Data for [Et_3NCH_2Ph]OTf (98%) are as follows. ^{1}H NMR (D_2O, 25 °C): δ 1.28 (t, 9H, J(HH) = 7.3 Hz, CH_2CH_3), 3.24 (q, 6H, J(HH) = 7.3 Hz, CH_2CH_3), 4.42 (s, 2H, CH_2Ph), 7.55 (br s, 5H, C_6H_5). ^{13}C NMR (D_2O, 25 °C): δ 6.77 (CH_2CH_3), 52.1 (CH_2CH_3), 59.77 (CH_2Ph), 127.36, 129.5, 130.8 and 132.6 (C_6H_5). IR (KBr, cm^{-1}): 1000, 1146 and 1208 (br s, OTf).

Data for [Me_3NCH_2Ph]OTf (97%) are as follows. ^{1}H NMR (D_2O, 25 °C): δ 3.06 (s, 9H, CH_3), 4.46 (s, 2H, CH_2Ph), 7.53 (br s, 5H, C_6H_5). ^{13}C NMR (D_2O, 25 °C): δ 52.7 (CH_3), 68.9 (CH_2Ph), 133.1, 130.7, 129.1 and 127.8 (C_6H_5). IR (KBr, cm^{-1}): 1026, 1146 and 1247 (br s, OTf).

Data for [Et_3NCCl_3]OTf (95%) are as follows. ^{1}H NMR (D_2O, 25 °C): δ 1.27 (t, 9H, J(HH) = 7.4 Hz, CH_2CH_3), 3.19 (q, 6H, J(HH) = 7.4 Hz, CH_2CH_3). ^{13}C NMR (D_2O, 25 °C): δ 8.63 (CH_2CH_3), 46.0 (CH_2CH_3). IR (KBr, cm^{-1}): 1022, 1159 and 1231 (br s, OTf).

Data for [Me_3NCCl_3]OTf (98%) are as follows. ^{1}H NMR (D_2O, 25 °C): δ 2.87(s, 9H, CH_3). ^{13}C NMR (D_2O, 25 °C): δ 44.68 (CH_3). IR (KBr, cm^{-1}): 1025, 1149 and 1248 (br s, OTf).

Synthesis of [Cp*Ir(η^3-$CH_2CHCHPh$)(NH=C(OMe)Me)]OTf (4a-Z). A methanol (20 mL) solution of **1** (0.10 g, 0.16 mmol) was refluxed in the presence of Na_2CO_3 (0.055 g, 0.52 mmol) for 6 h. Na_2CO_3 was removed on a Celite-packed filter, and the resulting filtrate was distilled under vacuum to obtain a beige solid, which was recrystallized in cold $CHCl_3$/Et_2O to obtain beige-white microcrystals of [Cp*Ir(η^3-$CH_2CHCHPh$)(NH=C(OMe)Me)]OTf (**4a-Z**, 0.095 g, 89%).^{1}H NMR ($CDCl_3$, 25 °C): δ 1.51 (s, 15H, CH_3 of Cp*), 2.07 (d, 1H, J(HH) = 10.0 Hz, CHHCHCHPh), 2.62 (s, 3H, NH=C(OMe)CH_3), 3.38 (d, 1H, J(HH) = 6.0 Hz, CHHCHCHPh), 3.65 (d, 1H, J(HH) = 10.0 Hz, CH_2CHCHPh), 4.01 (s, 3H, OCH_3), 4.87 (m, 1H, CH_2CHCHPh), 7.15−7.33 (m, 5H, C_6H_5), 9.35 (br s, 1H, NH). ^{13}C NMR ($CDCl_3$, 25 °C): δ 8.03 and 92.6 (Cp*), 19.1 (NH=C(OMe)CH_3), 42.5 (CH_2CHCHPh), 57.1 (OCH_3), 62.0 (CH_2CHCHPh), 76.0 (CH_2CHCHPh), 126.2, 126.5, 128.7 and 139.5 (C_6H_5), 177.6 (NH=C). IR (KBr, cm^{-1}): 1629 (s, $\nu_{C=N}$), 1027, 1143 and 1254 (br s, OTf). Anal. Calcd for $C_{23}H_{31}O_4NSF_3Ir$: C, 41.43; H, 4.69; N, 2.10. Found: C, 41.42; H, 4.66; N, 2.00.

Synthesis of [Cp*Ir(η^3-$CH_2CHCHPh$)(NH=C(OMe)Me)]OTf (mixture of 4a-Z/4a-E) and Isomerization of 4a-E to 4a-Z. A methanol (20 mL) solution of **1** (0.10 g, 0.16 mmol) was stirred in the presence of Na_2CO_3 (0.055 g, 0.52 mmol) at room temperature for 6 h. Na_2CO_3 was removed on a Celite-packed filter, and the resulting filtrate was distilled under vacuum to obtain a beige solid, which was recrystallized in cold $CHCl_3$/Et_2O to obtain beige-white microcrystals of [Cp*Ir(η^3-$CH_2CHCHPh$)(NH=C(OMe)Me)]OTf (0.097 g, 91%, **4a-Z/E** = 4/1 measured by ^{1}H NMR). Data for **4a-E** are as follows. ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.55 (s, 15H, CH_3 of Cp*), 2.07 (d, 1H, J(HH) = 10.0 Hz, CHHCHCHPh), 2.32 (s, 3H, CH_3), 3.27 (d, 1H, J(HH) = 6.0 Hz, CHHCHCHPh), 3.64 (d, 1H, J(HH) = 10.0 Hz, CH_2CHCHPh), 4.02 (s, 3H, OCH_3), 5.03 (m, 1H, CH_2CHCHPh), 7.15−7.33 (m, 5H, C_6H_5), 8.37 (br s, 1H, NH=C). The **4a-E** was converted to **4a-Z** when the mixture was refluxed for 6 h or stirred for 24 h at room temperature in MeOH solution in the presence of Na_2CO_3. The isomerization (**4a-E** to **4a-Z**) was not observed under refluxing conditions in $CHCl_3$ for 6 h in the absence of MeOH and/or Na_2CO_3.

Synthesis of [Cp*Ir(η^3-$CH_2CHCHPh$)(NH=C(OEt)Me)]OTf (4b-Z). This compound was prepared by the same method as described above for the synthesis of **4a-Z** using 0.10 g of **1** in ethanol. The yield was 0.10 g (91%) based on [Cp*Ir(η^3-CH_2-CHCHPh)(NH=C(OEt)Me)]OTf (**4b-Z**). ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.45 (t, 3H, J(HH) = 10.0 Hz, OCH_2CH_3), 1.52 (s, 15H, CH_3 of Cp*), 2.04 (d, 1H, J(HH) = 10.0 Hz, CHHCHCHPh), 2.62 (s, 3H, NH=C(OEt)CH_3), 3.36 (d, 1H, J(HH) = 6.0 Hz, CHHCHCHPh), 3.66 (d, 1H, J(HH) = 10.0 Hz, CH_2CHCHPh), 4.27 (q, 2H, J(HH) = 10.0 Hz, OCH_2CH$_3$), 4.88 (m, 1H, CH_2CHCHPh), 7.15−7.50 (m, 5H, C_6H_5), 9.13 (br s, 1H, NH=C). ^{13}C NMR ($CDCl_3$, 25 °C): δ 8.06 and 92.6 (Cp*), 14.8 (OCH_2CH_3), 19.7 (NH=C(OEt)CH_3), 42.4 (CH_2CHCHPh), 62.2 (OCH_2CH$_3$), 66.4 (CH_2CHCHPh), 75.9 (CH_2CHCHPh), 126.1, 126.5, 126.7 and 139.4 (C_6H_5), 177.3 (NH=C). IR (Nujol, cm^{-1}): 1641 (s, $\nu_{C=N}$), 1030, 1163 and 1257 (br s, OTf). Anal. Calcd for $C_{24}H_{33}O_4NSF_3Ir$: C, 42.34; H, 4.89; N, 2.06. Found: C, 42.33; H, 4.85; N, 2.04.

Synthesis of [Cp*Ir(η^3-$CH_2CHCHPh$)(NH=C(OEt)Me)]OTf (mixture of 4b-Z/4b-E). This compound was prepared by the same method as described above for the synthesis of the mixture of **4a-Z/E** using 0.10 g of **1** in ethanol. The yield was 0.097 g (89%) based on [Cp*Ir(η^3-$CH_2CHCHPh$)(NH=C(OEt)Me)]OTf (**4b-Z/E** = 5/1). Data for **4b-E** are as follows. ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.36 (t, 3H, J(HH) = 10.0 Hz, OCH_2CH_3), 1.55 (s, 15H, CH_3 of Cp*), 2.09 (d, 1H, J(HH) = 10.0 Hz, CHHCHCHPh), 2.31 (s, 3H, NH=C(OEt)CH_3), 3.03 (d, 1H, J(HH) = 6.0 Hz, CHHCHCHPh), 3.55 (d, 1H, J(HH) = 10.0 Hz, CH_2CHCHPh), 4.31 (q, 2H, J(HH) = 10.0 Hz, OCH_2-CH$_3$), 5.07 (m, 1H, CH_2CHCHPh), 7.15−7.50 (m, 5H, C_6H_5), 8.16 (br s, 1H, NH=C). The **4b-E** was converted to **4b-Z** when the mixture was refluxed for 6 h or stirred for 24 h at room temperature in EtOH solution in the presence of Na_2CO_3. The isomerization (**4b-E** to **4b-Z**) was not observed under refluxing conditions in $CHCl_3$ for 6 h in the absence of EtOH and/or Na_2-CO_3.

Isomerization and Substitution of 4b-Z/E for 4a-Z. The mixture of **4b-Z/E** (0.088 g, 0.13 mmol) was stirred for 24 h at room temperature in MeOH (20 mL) solution in the presence of Na_2CO_3 (0.051 g, 0.52 mmol). Excess Na_2CO_3 was removed

by filtration on a Celite-packed filter, and the resulting filtrate was distilled under vacuum to obtain a beige solid. The ^{1}H NMR spectrum of this beige solid shows only the signals due to **4a-Z**.

Synthesis of [Cp*Ir(η^3-CH$_2$CHCHPh)(NH=C(O-*i*-Pr)-Me)]OTf (4c-Z). This compound was prepared in the same manner as described above for the synthesis of **4a** using 0.10 g of **1** in 2-propanol. The yield was 0.10 g (90%) based on [Cp*Ir(η^3-CH$_2$CHCHPh)(NH=C(O-*i*-Pr)Me)]OTf (**4c-Z**). ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.29 and 1.39 (d, 6H, J(HH) = 6.0 Hz, OCH(CH_3)$_2$), 1.54 (s, 15H, CH_3 of Cp*), 1.93 (d, 1H, J(HH) = 9.0 Hz, CHHCHCHPh), 2.64 (s, 3H, NH=CCH_3), 3.36 (d, 1H, J(HH) = 5.0 Hz, CHHCHCHPh), 3.43 (d, 1H, J(HH) = 10.0 Hz, CH$_2$CHCHPh), 4.71 (m, 1H, OCH(Me)$_2$), 4.83 (m, 1H, CH$_2$CHCHPh), 7.23−7.38 (m, 5H, C$_6H_5$), 9.26 (br s, 1H, NH). ^{13}C NMR ($CDCl_3$, 25 °C): δ 8.01 and 92.6 (Cp*), 19.6 (NH=CCH_3), 22.7 (OCH(CH_3)$_2$), 41.9 (CH_2CHCHPh), 62.2 (CH$_2$-CHCHPh), 74.2 (OCHMe$_2$), 75.8 (CH$_2$$C$HCHPh), 126.8, 127, 128.6 and 139.4 (C_6H_5), 176.4 (NH=C). IR (KBr, cm^{-1}): 1629 (s, $\nu_{C=N}$), 1024, 1146 and 1252 (br s, OTf). Anal. Calcd for $C_{25}H_{35}O_4NSF_3Ir$: C, 43.22; H, 5.08; N, 2.01. Found: C, 42.45; H, 4.77; N, 1.89.

Synthesis of Cp*Ir(η^3-CH$_2$CHCHPh)(NHC(=O)Me) (5-K) and Characterization of Cp*Ir(η^3-CH$_2$CHCHPh)(N=C(OH)Me) (5-E) in Polar Solvents. A 0.5 mL portion of distilled water and 0.5 g (4.7 mmol) of Na_2CO_3 were added to MeCN (10 mL) solution of **1** (0.20 g, 0.32 mmol) under N_2, and the solution was refluxed for 3 h and cooled to room temperature. Na_2CO_3 was removed on a Celite-packed filter, and the resulting filtrate was distilled under vacuum to obtain yellow powders, which were recrystallized in cold CH_2Cl_2/*n*-pentane to obtain yellow microcrystals of Cp*Ir(η^3-CH$_2$CHCHPh)(NHC(=O)Me) (**5-K**, 0.15 g, 93%). ^{1}H NMR (C_6D_6, 25 °C): δ 1.43 (s, 15H, CH_3 of Cp*), 1.75 (d, 1H, J(HH) = 10.0 Hz, CHHCHCHPh), 2.21 (s, 3H, NHC(=O)CH_3), 3.11 (d, 1H, J(HH) = 6.0 Hz, CHHCHCHPh), 3.51 (br s, NHC(=O)Me), 4.15 (d, 1H, J(HH) = 10.0 Hz, CH$_2$CHCHPh), 4.73 (m, 1H, CH$_2$CHCHPh), 7.25−7.87 (m, 5H, C$_6H_5$). ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.51 (s, 15H, CH_3 of Cp*), 1.68 (d, 1H, J(HH) = 10.0 Hz, CHHCHCHPh), 2.01 (s, 3H, NHC(=O)CH_3), 3.15 (d, 1H, J(HH) = 6.0 Hz, CHHCHCHPh), 3.79 (br s, 1H, NHC(=O)Me), 3.81 (d, 1H, J(HH) = 10.0 Hz, CH$_2$CHCHPh), 4.80 (m, 1H, CH$_2$CHCHPh), 7.05−7.60 (m, 5H, C$_6H_5$). ^{1}H NMR (CD_2Cl_2, 25 °C): δ 1.50 (s, 15H, CH_3 of Cp*), 1.67 (d, 1H, J(HH) = 10.0 Hz, CHHCHCHPh), 2.00 (s, 3H, NHC(=O)CH_3), 3.14 (d, 1H, J(HH) = 6.0 Hz, CHHCHCHPh), 3.70 (d, 1H, J(HH) = 10.0 Hz, CH$_2$-CHCHPh), 3.75 (br s, 1H, NHC(=O)Me), 4.83 (m, 1H, CH$_2$CHCHPh), 7.05−7.60 (m, 5H, C$_6H_5$). ^{13}C NMR (C_6D_6, 25 °C): δ 8.98 and 92.4 (Cp*), 27.5 (CH_3), 41.2 (CH_2CHCHPh), 63.0 (CH$_2$CHCHPh), 74.0 (CH$_2$$C$HCHPh), 174.5 (NH$C$(=O)-Me). ^{13}C NMR ($CDCl_3$, 25 °C): δ 8.02 and 92.4 (Cp*), 29.5 (CH_3), 43.7 (CH_2CHCHPh), 64.1 (CH$_2$CHCHPh), 76.8 (CH$_2$-CHCHPh), 125.5, 125.8, 127.2 and 140.4 (C_6H_5), 179.1 (NHC(=O)Me). IR (KBr, cm^{-1}): 1600 (s, $\nu_{C=O}$), 3374 (w, ν_{N-H}), 1618 (s, ρ_{N-H}). Anal. Calcd for $C_{21}H_{28}ONIr$: C, 50.18; H, 5.61; N, 2.79. Found: C, 50.21; H, 5.59; N, 2.75. The enol form of the amido complex Cp*Ir(η^3-CH$_2$CHCHPh)(N=C(OH)Me) (**5-E**) was measured by ^{1}H and ^{13}C NMR in polar solvents such as CD_3COCD_3 (**5-E**), $CDCl_3$ (**5-E/K** = ca. 1:2), and CD_2Cl_2 (**5-E/K** = ca. 1:3) (see Figure 4). Spectral data for **5-E** are as follows. ^{1}H NMR (CD_3COCD_3, 25 °C): δ 1.52 (s, 15H, CH_3 of Cp*), 1.67 (d, 1H, J(HH) = 9.2 Hz, CHHCHCHPh), 1.93 (s, 3H, N=C(OH)CH_3), 3.11 (d, 1H, J(HH) = 6.2 Hz, CHHCHCHPh), 3.72 (d, 1H, J(HH) = 9.6 Hz, CH$_2$CHCHPh), 4.00 (br s, N=C(OH)Me), 5.00 (m, 1H, CH$_2$CHCHPh), 7.25−7.72 (m, 5H, C$_6H_5$). ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.51 (s, 15H, CH_3 of Cp*), 1.95 (d, 1H, J(HH) = 10.0 Hz, CHHCHCHPh), 2.00 (s, 3H, N=C(OH)CH_3), 3.21 (d, 1H, J(HH) = 6.0 Hz, CHHCHCHPh), 3.60 (d, 1H, J(HH) = 10.0 Hz, CH$_2$CHCHPh), 4.34 (br s, N=C(OH)Me), 5.00 (m, 1H, CH$_2$CHCHPh), 7.05−7.60 (m, 5H, C$_6H_5$). ^{1}H NMR (CD_2Cl_2, 25 °C): δ 1.50 (s, 15H, CH_3 of Cp*), 1.86 (d, 1H, J(HH) = 10.0 Hz, CHHCHCHPh), 1.92 (s, 3H, N=C(OH)CH_3), 3.23 (d, 1H, J(HH) = 6.0 Hz, CHHCHCHPh), 3.55 (d, 1H, J(HH) = 10.0 Hz, CH$_2$CHCHPh), 4.13 (br s, N=C(OH)Me), 5.04 (m, 1H, CH$_2$CHCHPh), 7.20−7.60 (m, 5H, C$_6H_5$). ^{13}C NMR (CD_3COCD_3, 25 °C): δ 9.08 and 92.9 (Cp*), 27.0 (N=C(OH)-CH$_3$), 41.3 (CH_2CHCHPh), 62.1 (CH$_2$CHCHPh), 74.2 (CH$_2$CHCHPh), 125.8, 128.6, 129.0 and 142.9 (C_6H_5), 173.6 (N=C(OH)CH_3). ^{13}C NMR ($CDCl_3$, 25 °C): δ 8.08 and 91.8 (Cp*), 26.8 (N=C(OH)CH$_3$), 40.5 (CH_2CHCHPh), 61.1 (CH$_2$CHCHPh), 73.3 (CH$_2$$C$HCHPh), 125.1, 125.7, 128.2 and 141.3 (C_6H_5), 175.0 (N=C(OH)Me).

Synthesis of Cp*Ir(η^3-CH$_2$CHCHPh)(NDC(=O)Me) (5-K-d_1): H/D Exchange Reaction of 5-K in D_2O. A 0.05 mL portion of D_2O was added to a yellow C_6D_6 (0.50 mL) solution of **5-K** (0.056 mmol) in an absolutely dried NMR tube, which was maintained at room temperature for 5 h. The deuterated amido complex **5-K-d_1** was isolated by vacuum distillation of all solvents. The complex **5-K-d_1** was characterized by comparison of its ^{1}H NMR and IR spectral data to those assigned by **5-K**. The ^{1}H NMR resonance at δ 3.51 (Ir−NHC(=O)Me) and IR absorption band at 3374 cm^{-1} (ν(N−H)) of **5-K** were decreased in intensity (ca. 50%), and a new absorption band (ν(N−D)) appeared at 2504 cm^{-1} in the infrared spectrum of **5-K-d_1**. IR (KBr, cm^{-1}): 2504 (w, ν_{N-D}).

Reaction of 5 with HCl. HCl (0.21 mmol, 0.20 mL of a 32 wt % solution in H_2O) was added to a solution of **5** (0.10 g, 0.20 mmol) in $CHCl_3$ (15 mL) at room temperature, and the reaction mixture was stirred for 3 h. After the yellow solution was dehydrated by treatment with $MgSO_4$ and vacuum distilled to remove the solvents and unreacted HCl, *n*-pentane (20 mL) was added to dissolved chloro−metal complex **3**, and the reaction mixture was filtered to obtain less soluble MeC(=O)NH_2, which was identified by ^{1}H NMR spectroscopy and also by GC.

Synthesis of [Cp*Ir(NH=C(OH)Me)(PPh$_3$)(OH$_2$)](OTf)$_2$ (6). A 0.015 g (0.25 mmol) sample of acetamide and 0.13 g (ca. 0.50 mmol) of AgOTf·xH$_2$O were added to a 10 mL CH_2Cl_2 solution of Cp*IrCl_2(PPh_3) (0.15 g, 0.23 mmol), and the reaction mixture was stirred at room temperature for 1 h. AgCl was removed by filtration, and the filtrate was vacuum distilled to obtain a yellow solid, which was recrystallized in CH_2Cl_2/Et_2O to obtain yellow microcrystals of [Cp*Ir(NH=C(OH)Me)(PPh_3)(OH_2)](OTf)$_2$ (**6**, 0.21 g, 95%). ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.49 (s, 15H, CH_3 of Cp*), 1.88 (s, 3H, NH=C(OH)-CH_3), 5.79 (br s, 1H, NH=C(OH)Me), 7.2−7.6 (m, 15H, P(C$_6H_5$)$_3$), 12.8 (br s, 1H, NH=C(OH)Me). ^{31}P NMR ($CDCl_3$, 25 °C): δ 19.6 (PPh$_3$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 9.4 and 94.0 (Cp*), 22.1 (NH=C(OH)CH$_3$), 129.0, 131.8, 134.5 and 141.9 (P(C_6H_5)$_3$), 175.8 (NH=C(OH)Me). IR (KBr, cm^{-1}): 1669.7 (m, $\nu_{C=N}$), 1035, 1179 and 1266 (br s, OTf). Anal. Calcd for $C_{32}H_{37}O_8NPS_2F_6Ir$: C, 39.10; H, 3.79; N, 1.43. Found: C, 39.06; H, 3.78; N, 1.35.

Dissociation of Imino−Ethers and Amidines from Iridium(III) Compounds: Reaction of 2a with PPh$_3$. A 0.041 g (0.16 mmol) of PPh_3 was added to a THF-d_8 (1.0 mL) (or CD_2Cl_2) solution of **2a** (0.052 mmol), and the reaction mixture was refluxed for 12 h and cooled to room temperature. Both THF-d_8 and NH=C(NMe_2)Me (**8a**) were collected in the cold trap of a dry ice/*i*-PrOH bath, and the residue was washed with Et_2O (10 mL) to obtain [Cp*Ir(η^3-CH$_2$CHCHPh)(PPh_3)]-OTf (**7**) in high yield (90%, 0.040 g).

Data for **8a** (0.044 mmol, 85% based on NH=C(NMe_2)Me measured by ^{1}H NMR) are as follows. ^{1}H NMR (THF-d_8, 25 °C): δ 2.15 (s, 3H, NH=C(NMe_2)CH_3), 3.01 (s, 6H, NH=C(N(CH_3)$_2$)Me). ^{1}H NMR (CD_2Cl_2, 25 °C): δ 2.18 (s, 3H, NH=C(NMe_2)CH_3), 2.90 (s, 6H, NH=C(N(CH_3)$_2$)Me).

Data for **7** are as follows. ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.32 (d, 15H, J(HP) = 2.1 Hz, CH_3 of Cp*), 1.92 (dd, 1H, J(HH) = 12.0 Hz, J(HP) = 14.0 Hz, CHHCHCHPh), 3.17 (d, 1H, J(HH) = 7.0 Hz, CHHCHCHPh), 3.73 (dd, 1H, J(HH) = 10.0 Hz, J(HP) = 14.0 Hz, CH$_2$CHCHPh), 4.71 (m, 1H, CH$_2$CHCHPh),

Table 1. Details of Crystallographic Data Collection of the Complexes 2a-E, 4a-Z, 5-K, and 6

	2a-E	4a-Z	5-K	6
chemical formula	$C_{24}H_{34}O_3N_2F_3SIr$	$C_{23}H_{31}O_4NF_3SIr$	$C_{21}H_{28}ONIr$	$C_{32}H_{37}O_8NPS_2F_6Ir$
fw	679.79	666.75	502.64	982.93
temp, K	296(2)	293	293(2)	293(2)
cryst dimens, mm	0.3 × 0.4 × 0.5	0.2 × 0.3 × 0.3	0.75 × 0.3 × 0.2	0.3 × 0.1 × 0.2
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P112_1/n$	$P2_1/n$	$P2_1/n$
a, Å	15.091(6)	8.4789(13)	7.475(10)	20.2001(10)
b, Å	11.4200(10)	13.491(3)	14.460(3)	9.0054(10)
c, Å	15.603(2)	22.245(6)	17.647(3)	20.8287(10)
α, deg	90.00	90.00	90.00	90.00(5)
β, deg	101.08(2)	92.68(2)	99.380(10)	90.57(5)
γ, deg	90.00	90.00	90.00	90.00(5)
V, Å^3	2237.7(6)	2541.8(9)	1881.9(6)	3788.8(5)
Z	4	4	4	4
$\rho_{(calc)}$, g cm^{-1}	1.711	1.742	1.774	1.723
μ, mm^{-1}	5.187	5.385	7.101	3.757
F(000)	1344	1312	984	1952
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
wavelength	0.7107	0.7107	0.7107	0.7107
2θ max, deg	50	50	25	46.05
hkl range	$-17 \le h \le 17$	$0 \le h \le 10$	$0 \le h \le 8$	$0 \le h \le 22$
	$0 \le k \le 13$	$0 \le k \le 16$	$0 \le k \le 17$	$0 \le k \le 9$
	$0 \le l \le 18$	$-26 \le l \le 26$	$-20 \le l \le 20$	$-22 \le l \le 22$
no. of reflcns	4399	4450	3606	5550
no. of unique data	4319	2358	3300	5279
no. of obs ($\|F_o\| > 2\sigma F_o$) data	4019	2058	2694	2936
no. of params	323	314	329	469
scan type	$\omega/2\theta$ scan	ω scan	$\omega/2\theta$ scan	$\omega/2\theta$ scan
R_1	0.031	0.024	0.024	0.067
wR_2	0.077	0.054	0.058	0.1701
GOF	1.080	1.091	1.142	1.099

7.13−7.41 (m, 5H, C_6H_5), 7.63 (br s, 15H of PPh_3). ^{31}P NMR ($CDCl_3$, 25 °C): δ 11.2 (s, PPh$_3$). ^{13}C NMR ($CDCl_3$, 25 °C): δ 8.28 (d, J(CP) = 0.6 Hz, $C_5(CH_3)_5$), 97.9 (d, J(CP) = 2.0 Hz, C_5(Me)$_5$), 37.0 (CH_2CHCHPh), 58.2 (CH_2CH*C*HPh), 73.9 (CH_2*C*HCHPh), 126.5, 127.4, 128.8, 129.0 (d, J(CP) = 10.0 Hz), 128.9, 131.8, 134.9 (d, J(CP) = 9.5 Hz) and 136.9 (CH_2-CHCH*Ph* and P*Ph*$_3$). IR (KBr, cm^{-1}): 1031, 1149 and 1272 (s, OTf). Anal. Calcd for $C_{38}H_{39}O_3PSF_3Ir$: C, 53.32; H, 4.59. Found: C, 52.94; H, 4.14.

Reaction of 2b and 4a−c with PPh$_3$. These reactions were carried out in the same manner as described above for the reaction of **2a** with PPh$_3$.

Data for NH=C(NHMe)Me (**8b**, 0.045 mmol, 86%) are as follows. ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.99 (s, 3H, NH=C(NHMe)-C*H*$_3$), 2.64 (s, 3H, NH=C(NHC*H*$_3$)Me), 3.64 (br s, 1H, NH=C(N*H*Me)Me), 6.95 (br s, 1H, N*H*=C(NHMe)Me).

Data for NH=C(OMe)Me (**9a**, 0.043 mmol, 82%) are as follows. ^{1}H NMR ($CDCl_3$, 25 °C): δ 2.01 (s, 3H, NH=C(OMe)-C*H*$_3$), 3.69 (s, 3H, NH=C(OC*H*$_3$)Me), 6.92 (br s, 1H, N*H*=C(OC*H*$_3$)Me). ^{13}C NMR ($CDCl_3$, 25 °C, 125 MHz); δ 22.3 (NH=C(OMe)*C*H$_3$), 53.0 (NH=C(O*C*H$_3$)Me).

Data for NH=C(OEt)Me (**9b**, 0.042 mmol, 80%) are as follows. ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.29 (t, 3H, J(HH) = 7.0 Hz, NH=C(OCH$_2$C*H*$_3$)Me), 2.01 (s, 3H, NH=C(OEt)C*H*$_3$), 4.10 (q, 2H, J(HH) = 7.0 Hz, NH=C(OC*H*$_2$CH$_3$)Me). ^{1}H NMR (THF-d_8, 25 °C): δ 1.37 (t, 3H, J(HH) = 7.0 Hz, NH=C(OCH$_2$C*H*$_3$)-Me), 2.05 (s, 3H, NH=C(OEt)C*H*$_3$), 4.21 (q, 2H, J(HH) = 7.0 Hz, NH=C(OC*H*$_2$CH$_3$)Me), 7.45 (br s, 1H, N*H*=C(OEt)Me). ^{13}C NMR ($CDCl_3$, 25 °C): δ 13.9 (NH=C(OCH$_2$*C*H$_3$)Me), 22.5 (NH=C(OEt)*C*H$_3$), 61.2 (NH=C(O*C*H$_2$CH$_3$)Me), 170.2 (NH=*C*(OEt)Me).

Data for NH=C(O-*i*-Pr)Me (**9c**, 0.042 mmol, 80%) are as follows. ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.25 (d, 6H, NH=C(OCH-(C*H*$_3$)$_2$)Me), 1.98 (s, 3H, NH=C(O-*i*-Pr)C*H*$_3$), 5.00 (m, 1H, NH=C(OC*H*(Me)$_2$)Me), 6.82 (br s, 1H, N*H*=C(O-*i*-Pr)Me).

Synthesis of [Cp*Ir(η^3-$CH_2CHCHPh$)(NCCH=CHMe)]-OTf (10). A 0.060 g (0.23 mmol) of AgOTf was added to a MeCH=CHCN (1.0 mL: *cis*/*trans* = 2/1)/CH_2Cl_2 (v/v = 1/9) solution of **3** (0.10 g, 0.21 mmol), and the reaction mixture was stirred for 1 h at room temperature. AgCl was removed by filtration, and the filtrate was vacuum distilled to obtain a pale yellow solid, which was recrystallized in $CHCl_3$/Et_2O to obtain pale yellow microcrystals of [Cp*Ir(η^3-$CH_2CHCHPh$)-(NCCH=CHMe)]OTf (**10**, 0.13 g, 94%). ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.58 and 1.61 (s, 15H, C*H*$_3$ of Cp*), 2.1−2.2 (m, 3H, NCCH=CHC*H*$_3$), 2.47 (d, 1H, J(HH) = 9.5 Hz, C*H*HCHCHPh), 3.40 and 3.45 (d, 1H, J(HH) = 6.7 Hz, CH*H*CHCHPh), 4.16 (d, 1H, J(HH) = 10.6 Hz, CH$_2$CHC*H*Ph), 5.0 (m, 1H, CH$_2$C*H*-CHPh), 6.8−7.0 and 7.0−7.2 (m, 1H, NCC*H*=CHMe), 6.1−6.2 (m, 1H, NCCH=C*H*Me), 7.2−7.4 (m, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$, 25 °C): δ 18.0 and 19.3 (NCCH=CHC*H*$_3$), 7.80, 7.94, 94.7 and 94.8 (Cp*), 43.4 and 43.6 (*C*H$_2$CHCHPh), 65.7 and 65.9 (CH$_2$CH*C*HPh), 79.3 and 79.4 (CH$_2$*C*HCHPh), 99.5 and 99.6 (NCCH=*C*HMe), 121 and 123 (N≡*C*), 157.5 and 159.8 (NC*C*H=CHMe), 109.3, 126.7, 127.7, 129.6, 130.3, 134.1, 135.8 and 137.5 (C_6H_5). IR (KBr, cm^{-1}): 1023, 1151 and 1260 (br s, OTf). Anal. Calcd for $C_{24}H_{29}O_3NSF_3Ir$: C, 43.63; H, 4.42; N, 2.12. Found: C, 43.60; H, 4.38; N, 2.10.

Synthesis of [Cp*Ir(η^3-$CH_2CHCHPh$)(NCPh)]OTf (11). This compound was prepared in the same manner as described for the synthesis of **10** using 0.10 g of **3** (0.21 mmol) in PhCN/CH_2Cl_2 (v/v = 3/10) solution. The yield was 0.12 g (82%) based on [Cp*Ir(η^3-$CH_2CHCHPh$)(NCPh)]OTf (**11**). ^{1}H NMR ($CDCl_3$, 25 °C): δ 1.60 (s, 15H, C*H*$_3$ of Cp*), 2.52 (d, 1H, J(HH) = 10.0 Hz, C*H*HCHCHPh), 3.50 (d, 1H, J(HH) = 7.0 Hz, CH*H*CH-CHPh), 4.20 (d, 1H, J(HH) = 11.0 Hz, CH$_2$CHC*H*Ph), 5.10 (m, 1H, CH$_2$C*H*CHPh), 7.20−7.84 (m, 10H, CH$_2$CHCHC$_6$*H*$_5$ and C$_6$*H*$_5$CN). ^{13}C NMR ($CDCl_3$, 25 °C): δ 9.0 and 95.4 (Cp*), 44.4 (*C*H$_2$CHCHPh), 66.3 (CH$_2$CH*C*HPh), 80.1 (CH$_2$*C*HCHPh), 122.5 (N≡*C*Ph), 109.3, 126.7, 127.7, 129.6, 130.3, 134.1, 135.8 and 137.5 (CH$_2$CHC*C*$_6$H$_5$ and *C*$_6$H$_5$CN). IR (KBr, cm^{-1}): 1023, 1151 and 1260 (br s, OTf). Anal. Calcd for $C_{27}H_{29}O_3NSF_3$-Ir: C, 46.54; H, 4.20; N, 2.01. Found: C, 46.52; H, 4.09; N, 1.99.

Catalytic Hydration of Nitriles (RCN) with [Cp*Ir(η^3-$CH_2CHCHPh$)(NCR)]OTf (R = Me (1), MeCH=CH (10)). The reaction mixture of RCN (16 mmol), H_2O (100 mmol), Na_2-CO_3 (100 mmol), and 0.08 mmol of iridium compound was

heated at 70 °C in a 25 mL bomb type reactor under N_2 for 1 h before it was cooled to room temperature. Organic compounds in the reaction mixture were extracted with $CDCl_3$ (5 mL), and the organic layer was dried with $MgSO_4$. ^1H NMR spectroscopy and GC were used to analyze the product, RC(=O)NH_2. The yields of MeC(=O)NH_2 and MeCH=CHC(=O)NH_2 were 4.1 (0.66 mmol) and 6.6% (1.05 mmol), respectively.

Catalytic Hydration of Acetonitrile (MeCN) with Na_2CO_3 in the Absence of Compound 1. The reaction was carried out in the same manner as described above for the reaction of MeCN with H_2O in the presence of **1** and Na_2CO_3 except that compound **1** was not used. The ^1H NMR spectrum of the $CDCl_3$ solution showed a very small signal due to CH_3CONH_2 (δ 2.06 ppm).

Catalytic Methanolysis of Benzonitrile (PhCN) with [Cp*Ir(η^3-$CH_2CHCHPh$)(NCPh)]OTf (11). The reaction mixture of PhCN (16 mmol), MeOH (100 mmol), Na_2CO_3 (100 mmol), and 0.08 mmol of iridium compound was heated at 70 °C in a 25 mL bomb type reactor under N_2 for 1 h before it was cooled to room temperature. Organic compounds in the reaction mixture were extracted with $CDCl_3$ (5 mL). ^1H NMR, GC, and mass (M^+ at m/z 135) spectra were used to analyze the product, HN=C(OMe)Ph. The yield of HN=C(OMe)Ph was 3.2% (0.51 mmol).

X-ray Structural Determination of [Cp*Ir(η^3-$CH_2CHCHPh$)(NH=C(NMe_2)Me)]OTf (2a-E), [Cp*Ir(η^3-$CH_2CHCHPh$)(NH=C(OMe)Me)]OTf (4a-Z), Cp*Ir(η^3-$CH_2CHCHPh$)(NHC(=O)Me) (5-K), and [Cp*Ir(NH=C(OH)Me)(OH_2)(PPh_3)]($OTf)_2$ (6). Crystals were grown from $CHCl_3$ (**2a-E**, **4a-Z**, **6**) and benzene (**5-K**). Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation at room temperature. Accurate cell parameters were determined from the least-squares fit of 24 accurately centered reflections in each selected range. All data were collected with the $\omega/2\theta$ (for **2a-E**, **5-K**, and **6**) and ω (for **4a-Z**) scan modes, respectively, and corrected for Lp effects and absorption. The structures of these compounds were solved by Patterson's heavy atom methods (SHELXS-86 for **2a-E**, **4a-Z** and SHELXS-97 for **5-K**, **6**). Details of crystallographic data collection are listed in Table 1. Bond distances and angles, positional and thermal parameters, and anisotropic thermal parameters have been included in the tables of Supporting Information. Non-hydrogen atoms were refined by full-matrix least-squares techniques (SHELXL-93 for **2a-E**, **4a-Z** and SHELXL-97 for **5-K**, **6**). All hydrogen atoms were placed at their geometrically calculated positions (d(CH) = 0.960 Å for methyl and 0.930 Å for aromatic) and refined riding on the corresponding carbon atoms with isotropic thermal parameters. The final R_1 and wR_2 ($R_1 = [\sum|F_o| - |F_c|/|F_o|$ and $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{0.5}$) values were 0.031 and 0.077 for **2a-E**, 0.024 and 0.054 for **4a-Z**, 0.024 and 0.058 for **5-K**, and 0.067 and 0.17 for **6**, respectively.

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Supporting Information Available: Tables of bond distances and angles, positional and thermal parameters, and anisotropic thermal parameters for complexes **2a-E**, **4a-Z**, **5-K**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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