Addition of OH^- and Alcohols or Amines to $-C{\equiv}N$ and $-CH{=}CH_2$ Groups of $CH_2{=}CHCN$ Coordinated to Cp*Ir(η^3-$CH_2CHCHPh$)

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Hydroxide ion and alcohols or amines are added regioselectively to the $-C{\equiv}N$ and $-CH{=}CH_2$ groups of $CH_2{=}CHCN$ in [Cp*Ir(η^3-$CH_2CHCHPh$)($NCCH{=}CH_2$)]$^+$ (**1a**). The unsaturated amido complex Cp*Ir(η^3-$CH_2CHCHPh$)($NHCOCH{=}CH_2$) (**2a**), alkoxo amido complexes Cp*Ir(η^3-$CH_2CHCHPh$)($NHCOCH_2CH_2OR$) (**4**, R = Me (**a**), Et (**b**)), amino amido complexes Cp*Ir(η^3-$CH_2CHCHPh$)($NHCOCH_2CH_2NR_2$) (**6**, R_2 = Me_2 (**a**), (Me)(H) (**b**)), and an amino imino−ether complex [Cp*Ir(η^3-$CH_2CHCHPh$)($NH{=}C(OMe)CH_2CH_2NMe_2$)]$^+$ (**8**) have been prepared from the reactions of **1a** with OH^-, OH^-/ROH (R = Me, Et), OH^-/HNR_2 (R_2 = Me_2, (Me)(H)), and MeOH/$NHMe_2$, respectively. Reactions of **2**, **4**, **6**, and **8** with aqueous HCl yield Cp*IrCl(η^3-$CH_2CHCHPh$) and quantitative amounts of $H_2NCOCH{=}CH_2$, $H_2NCOCH_2CH_2OR$, $H_2NCOCH_2CH_2NR_2$, and $MeOCOCH_2CH_2NMe_2$, respectively. Crystal structures of **1a** and **4a** have been determined by X-ray diffraction data analysis.

Introduction

Nitriles coordinated to transition metals show reactivity toward nucleophiles different from that of free nitriles probably because the coordination through the nitrogen atom increases the nucleophilicity of the carbon of the nitrile ($N{\equiv}C{-}R$).[1] Reactions of nitriles such as hydrolysis[2,3] and alcoholysis[3] are known to be catalyzed by metal complexes. Hydrolysis of unsaturated nitriles such as $H_2C{=}CHCN$ produces unsaturated amides, which are polymerized to produce chemicals that are used in paper industry and wastewater treatment.[4] We recently reported the addition of OH^-, alcohols, and amines to CH_3CN coordinated to iridium to produce amido ($Ir{-}NHCOCH_3$), imino−ether ($Ir{-}NH{=}C(OR){-}CH_3$), and amidine complexes ($Ir{-}NH{=}C(NR_2)CH_3$) and catalytic production of amides by these iridium complexes.[3] We now wish to report the simultaneous addition of OH^-, ROH, and HNR_2 to both the nitrile ($N{\equiv}C{-}$) and olefinic ($-CH{=}CH_2$) groups of $CH_2{=}CHCN$ coordinated to iridium. To the best of our knowledge, there has been no report made on the addition of nucleophiles to both the nitrile and olefinic groups of unsaturated nitriles coordinated to metals.

Results and Discussion

Iridium complexes of unsaturated nitriles, [Cp*Ir(η^3-$CH_2CHCHPh$)($NCCR{=}CH_2$)]$^+$ (**1**, R = H (**a**), CH_3 (**b**)) and [Cp*Ir(η^3-$CH_2CHCHPh$)($NCCH_2CH_2OCH_3$)]$^+$ (**1c**) have been prepared by the known method for complexes of saturated nitriles (see Experimental Section).[3,5]

Properties of $CH_2{=}CHCN$ in [Cp*Ir(η^3-$CH_2CHCHPh$)($NCCH{=}CH_2$)]$^+$ (1a). The crystal structure of **1a** (Figure 1) reveals somewhat interesting results that the bond distance of $C{\equiv}N$ (1.141(14) Å) of $CH_2{=}CHCN$ is decreased upon coordination to Cp*Ir(η^3-$CH_2CHCHPh$) from that (1.163(1) Å) of free $CH_2{=}CHCN$, while the $C{=}C$ distance (1.353(2) Å) is increased from that (1.339(1) Å) of free $CH_2{=}CHCN$. These results are different from the data previously reported for $Ni{-}NC{-}CH{=}CH_2$ and $Cu{-}NC{-}CH{=}CH_2$, where the $C{=}C$ distances are shorter than that of free $CH_2{=}CHCN$.[1c] This lengthening of the $C{=}C$ distance of $CH_2{=}CHCN$ in **1a** led us to expect an increase in reactivity of the $C{=}C$ group.

Reaction of [Cp*Ir(η^3-$CH_2CHCHPh$)($NCCR{=}CH_2$)]$^+$ (1) with OH^-. Unsaturated nitriles, $CH_2{=}CRC{\equiv}N$ (R = H (**a**), CH_3 (**b**)), in [$L_n{-}Ir{-}N{\equiv}CCR{=}CH_2$]$^+$ (**1**, L_n = Cp*(η^3-$CH_2CHCHPh$)) react with OH^- to give amido complexes **2**, leaving the olefinic group intact (eq 1). Comparing the detailed spectral (^{1}H and ^{13}C NMR, IR) data for **2** with extensive data for related

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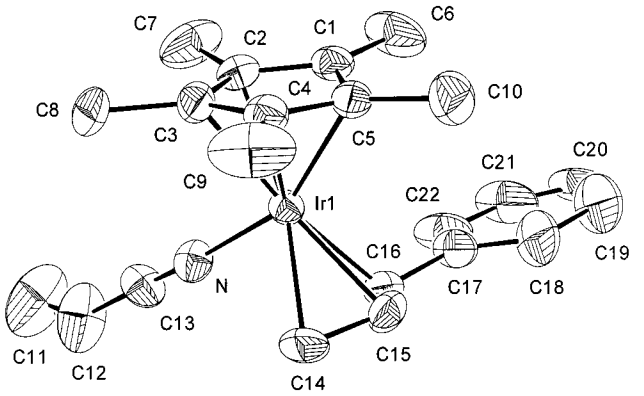
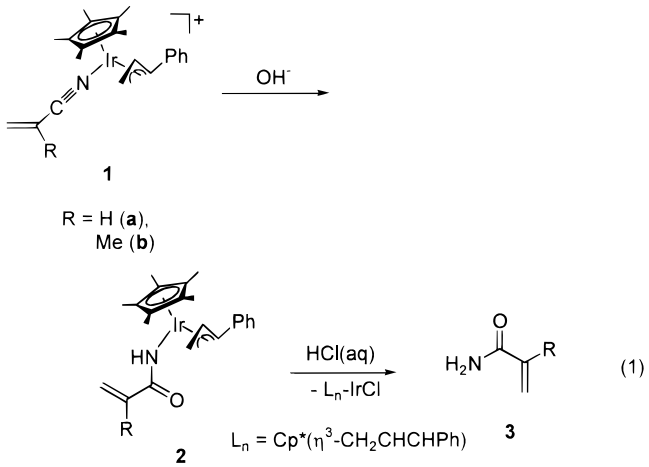


Figure 1. ORTEP drawing of [Cp*Ir(η^3-CHPhCHCH$_2$)(N≡CCH=CH$_2$)]OTf (**1a**) with 30% thermal ellipsoids probability. Selected bond distances (Å): Ir$_1$−N = 2.038(10); Ir$_1$−C$_{14}$ = 2.182(11); Ir$_1$−C$_{15}$ = 2.148(11); Ir$_1$−C$_{16}$ = 2.223(12); C$_{14}$−C$_{15}$ = 1.401(17); C$_{15}$−C$_{16}$ = 1.463(16); N−C$_{13}$ = 1.141(14); C$_{13}$−C$_{12}$ = 1.40(2); C$_{12}$−C$_{11}$ = 1.353(2). Selected bond angles (deg): Ir$_1$NC$_{13}$ = 176.6(11); NC$_{13}$C$_{12}$ = 175.8(16); C$_{13}$C$_{12}$C$_{11}$ = 138(3). Counteranion (OTf) and hydrogen atoms are omitted for clarity.

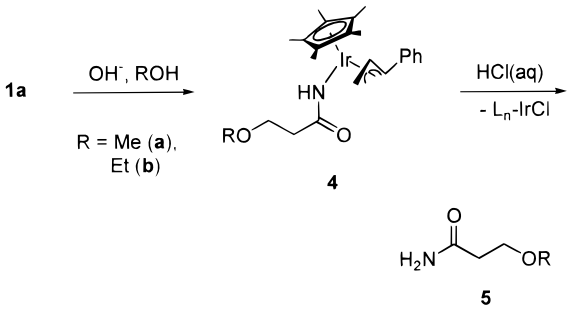
amido complexes[2a,b,e,3,6] unambiguously characterizes the unsaturated amido−iridium complexes **2** as shown in eq 1.



(1)

The ^{1}H NMR spectra of **2** in C$_6$D$_6$ clearly show the signals due to every proton of C*HH*C*H*C*H*Ph and N*H*−CO−C*R*=C*HH* (*R* = *H*, C*H*$_3$). The signals at δ 170.7 (**2a**) and 174.6 (**2b**) in the ^{13}C NMR spectra and strong IR absorptions at 1595 (**2a**) and 1588 cm^{-1} (**2b**) also suggest the carbonyl moiety, Ir−NH−*C**O***−CR=CH$_2$, in **2** as observed previously for L$_n$−Ir(−NH−CO−CH$_3$), whose crystal structure was also determined by X-ray diffraction data analysis.[3] There seems to be an isomerization between two isomers L$_n$−Ir(−NH−COCH=CH$_2$) (**2a**) and L$_n$−Ir(−N=C(OH)CH=CH$_2$) (**2aE**) in chloroform since two sets of all the ^{1}H and ^{13}C NMR signals are measured in CDCl$_3$ (see Supporting Information for the spectra of ^{1}H and ^{13}C NMR in CDCl$_3$) as observed for L$_n$−Ir(−NHCOCH$_3$) (keto form in 100% in C$_6$D$_6$) and Ir(−N=C(OH)CH$_3$) (enol form as the minor product in CDCl$_3$).[3] It may be also mentioned that exactly the same ^{1}H and ^{13}C NMR spectra in C$_6$D$_6$ are regenerated when CDCl$_3$ is removed from the solution of **2a** and **2aE** in CDCl$_3$ and the resulting solid is redissolved in C$_6$D$_6$. The unsaturated amido moiety in **2** is also supported by production of the unsaturated amides H$_2$NCOCR=CH$_2$ (**3**, identified by ^{1}H NMR and mass spectra) from the reactions of **2** with HCl (eq 1).

Reactions of [Cp*Ir(η^3-CH$_2$CHCHPh)(NCCH=CH$_2$)]$^+$ (1a) with Alcohols in the Presence of OH$^-$. Reactions of **1a** with alcohols (ROH) in the presence of OH$^-$ readily give the alkoxo amido complexes L$_n$−Ir−NHCOCH$_2$CH$_2$OR (**4**) (eq 2), which have been unambiguously characterized by detailed spectral and elemental analysis data (see below) and also by crystal structure determination for **4a** by X-ray diffraction data analysis.



(2)

It is noticed that distances of C(21)−C(22) (1.45(2) Å) and C(20)−N (1.309(16) Å) in **4a** are somewhat shorter than the average values of C(sp^3)−C(sp^3) (1.53 Å) and C(sp^2)−N (1.38 Å),[7] respectively, while those of C(20)−O(1) (1.236(16) Å) and C(20)−C(21) (1.491(18) Å) are close to the average values of C(sp^2)=O (1.21 Å) and C(sp^2)−C(sp^3) (1.51 Å),[7] respectively (Figure 2).

The reaction of **1b** with CH$_3$OH is so slow that most of **1b** was recovered after 18 h of the reaction at room temperature. ^{1}H NMR measurements show several weak and broad signals, which are not fully assigned. Under the refluxing conditions in CHCl$_3$, however, the reaction of **1b** with CH$_3$OH gives unidentified compound(s).

The ^{1}H NMR spectrum of **4a** in C$_6$D$_6$ clearly shows all the signals due to η^3-C*HH*C*H*C*H*Ph and −COC*H*$_2$C*HH*OC*H*$_3$. Deuterium labeling experiments also confirm the assignments of the signals due to the methylene protons, Ir−NHCOC*H*$_2$C*HH*OCH$_3$. The triplet at δ 2.56 for **4a** completely disappears in the ^{1}H NMR spectrum (see Supporting Information) of the Ir complex obtained from the reaction of **1a** with NaOD and CH$_3$OD. This observation suggests that the triplet at δ 2.56 is due to L$_n$−Ir−NHCOC*H*$_2$CH$_2$OCH$_3$ of **4a**, and the ***d*$_2$** isotopomer L$_n$−Ir−NHCOCD$_2$CH$_2$OCH$_3$ (**4a-*d*$_2$**)[8] is obtained from the reaction of **1a** with NaOD and CH$_3$OD (see below).

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(8) Nondeutrated H$_2$O was used in the isolation of **4a-*d*$_2$** (see Experimental Section for detailed procedure), which may explain how the isolated **4a-*d*$_2$** has the hydrogen (rather than deuterium) bound to the nitrogen in L−Ir−N*H*COCD$_2$CH$_2$OCH$_3$ (**4a-*d*$_2$**).

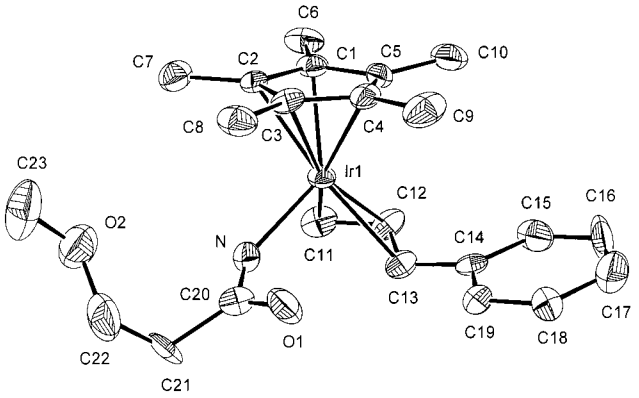


Figure 2. ORTEP drawing of Cp*Ir(η^3-$CH_2CHCHPh$)(NHC(=O)CH_2CH_2OMe) (**4a**) with 30% thermal ellipsoids probability. Selected bond distances (Å): Ir_1-N = 2.073(11); Ir_1-C_{11} = 2.144(6); Ir_1-C_{12} = 2.110(11); Ir_1-C_{13} = 2.221(12); $C_{11}-C_{12}$ = 1.429(18); $C_{12}-C_{13}$ = 1.418(18); $N-C_{20}$ = 1.309(16); O_1-C_{20} = 1.236(16); O_2-C_{22} = 1.391(18); O_2-C_{23} = 1.407(19); $C_{20}-C_{21}$ = 1.491(18); $C_{21}-C_{22}$ = 1.45(2). Selected bond angles (deg): Ir_1NC_{20} = 132.9(10); $NC_{20}C_{21}$ = 119.9(15); $NC_{20}O_1$ = 121.4(13); $O_1C_{20}C_{21}$ = 118.7(14); $C_{20}C_{21}C_{22}$ = 113.6(13); $C_{21}C_{22}O_2$ = 112.7(14); $C_{22}O_2C_{23}$ = 110.8(14).

The assignments above are also unambiguously supported by ^{1}H, ^{1}H-2D COSY, and ^{1}H, ^{13}C-2D HETCOR spectra for **4a** (see Supporting Information). Methoxo amide $H_2NCOCH_2CH_2OCH_3$ (**5a**) is quantitatively obtained from the reaction of **4a** with aqueous HCl (eq 2).

The ^{1}H NMR spectrum of **4a** in $CDCl_3$ (Figure 3b and Supporting Information) shows a set of small signals (less than 15% of the corresponding signals of the major compound, **4a**) which are assigned to those of the enol form isomer $L_n-Ir-N=C(OH)CH_2CH_2OCH_3$ (**4aE**) as discussed above for **2a** in C_6D_6 and **2aE** (in small amount) in $CDCl_3$.

It is noticed that the ^{1}H NMR spectrum of **4a** in C_6D_6 shows one signal for the two protons of the keto form, $L_n-Ir-NHCOCH_2CH_\alpha H_{\alpha'}OCH_3$, while the spectrum in CD_3COCD_3 shows two signals for the two protons of the enol form, $L_n-Ir-N=C(OH)CH_\beta H_{\beta'}CH_\alpha H_{\alpha'}OCH_3$ (**4aE**)[9] (Figure 3c,d and Supporting Information). A similar observation was previously reported for $(PMe_3)Cp^*Ir-CH_\alpha H_{\alpha'}CH_\beta H_{\beta'}-t$-Bu that shows four signals in C_6D_6.[10]

Separate experiments have been carried out to understand the nature of the formation of di-deuterio complex **4a-d_2** from the reaction of **1a** with NaOD and CH_3OD. It has been found that the α-proton of $CH_2=CHCN$ in **1a** is completely replaced by deuterium to give $L_n-Ir-NCCD=CH_2$ (**1a-d_1**) when the slurry of **1a** was stirred in D_2O. It has been found that the H/D exchange does not occur between OD^-/CH_3OD and $Ir-NHCOCH_2CH_2OCH_3$ (**4a**). It is, therefore, likely that **1a-d_1** ($L_n-Ir-NCCD=CH_2$) is formed by the H/D exchange between **1a** and OD^-/CH_3OD before the addition of OD^- and CH_3OD to $CH_2=CHCN$ of **1a** in the presence of NaOD and CH_3OD. It has been known that deprotonation of the α-carbon of $CH_2=CHCN$ is facilitated by coordination to a metal.[1c]

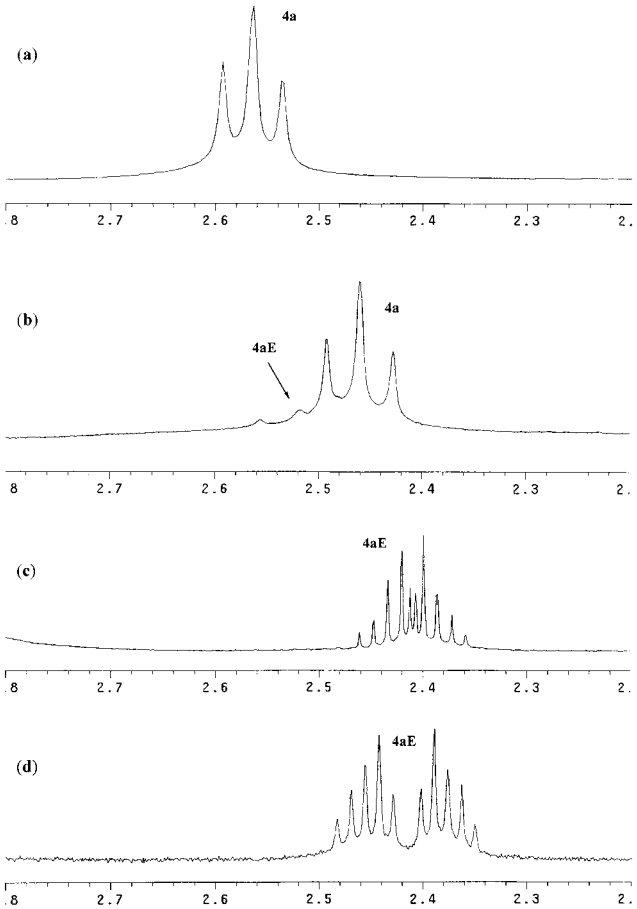


Figure 3. ^{1}H NMR spectra of Cp*Ir(η^3-$CH_2CHCHPh$)(NHC(=O)CH_2CH_2OMe) (**4a**) and Cp*Ir(η^3-$CH_2CHCHPh$)(N=C(OH)CH_2CH_2OMe) (**4aE**) in different deutrated solvents, (a) C_6D_6, (b) $CDCl_3$, (c) CD_3COCD_3 (25 °C), and (d) CD_3COCD_3 (−30 °C) at 500 MHz.

A relevant and interesting observation has been made during this investigation. The protons of CH_3CN in $[L_n-Ir(NCCH_3)]^+$ (**A**)[3] are also readily replaced by deuterium in the reactions of **A** with D_2O and CH_3OD to give $[L_n-Ir(NCCD_3)]^+$ (**A-d_3**) and $[L_n-Ir-ND=C(OCH_3)CD_3]^+$ (**B-d_4**), respectively (Scheme 1). The H/D exchange, however, does not occur between CH_3OD and CH_3 of $[L_n-Ir-NH=C(OCH_3)CH_3]^+$ (**B**)[3] (which is obtained from the reaction of **A** with CH_3OH) and between CH_3OH and CD_3 of $[L_n-Ir-ND=C(OCH_3)CD_3]^+$ (**B-d_4**) (which is obtained from the reaction of **A** with CH_3OD) (see Scheme 1).

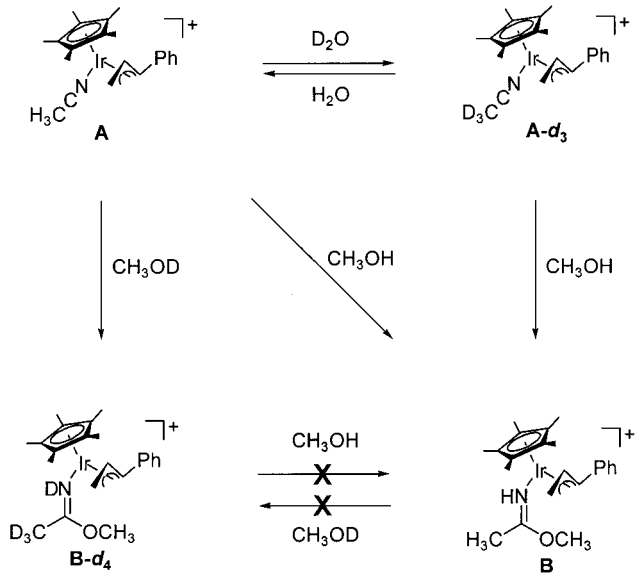
The compound **4b** has been also unequivocally characterized by detailed spectral (^{1}H, ^{13}C NMR, ^{1}H, ^{1}H-2D COSY, ^{1}H, ^{13}C-2D HETCOR, IR) and elemental analysis data (see Supporting Information). Production of the ethoxo amide $H_2NCOCH_2CH_2OCH_2CH_3$ (**5b**) from the reaction of **4b** with aqueous HCl (eq 2) also supports the ethoxo amido moiety, $Ir-NHCOCH_2CH_2OCH_2CH_3$ in **4b**.

It is interesting to find that OH^- always selectively attacks the nitrile group (N≡C−) of **1a**, while ROH selectively attacks the olefinic ($-CH=CH_2$) group. No experimental evidence has been obtained for the addition of CH_3OH to the −C≡N group of **1a** to give imino−ether complexes ($[L_n-Ir-NH=C(OCH_3)CH=CH_2]^+$ or

(9) It has been suggested that amido complexes exist mainly as the enol form isomers, M−N=C(OH)R, in a polar solvent such as acetone, while the keto form isomer, M−NHCOR, is the predominant species in a nonpolar solvent such as benzene. See refs 3 and 6c.

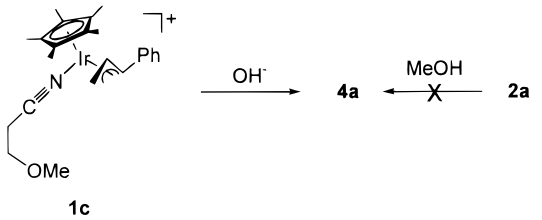
(10) Bergman, R. G.; Golden, J. T.; Peterson, T. H. *Organometallics* **1999**, *18*, 2005, and see references therein for related NMR spectral data.

Scheme 1



$[L_n{-}Ir{-}NH{=}C(OCH_3)CH_2CH_2OCH_3]^+$) in the presence of OH^-. In the absence of OH^-, however, CH_3OH seems to attack both the $-C{\equiv}N$ and $-CH{=}CH_2$ groups of **1a** in the presence of Na_2CO_3 to give unknown Ir complex(es).

Complex **4a** is also obtained from the reaction of the 3-methoxo propionitrile complex $[L_n{-}Ir{-}N{\equiv}CCH_2CH_2OCH_3]^+$ (**1c**) with OH^- but not from the reaction of **2a** with CH_3OH in the presence of OH^- (eq 3). It is, therefore, likely that the addition of CH_3OH to the olefinic group of $CH_2{=}CHCN$ in **1a** is followed by the OH^- addition to the nitrile group in the formation of **4a** (eq 2).

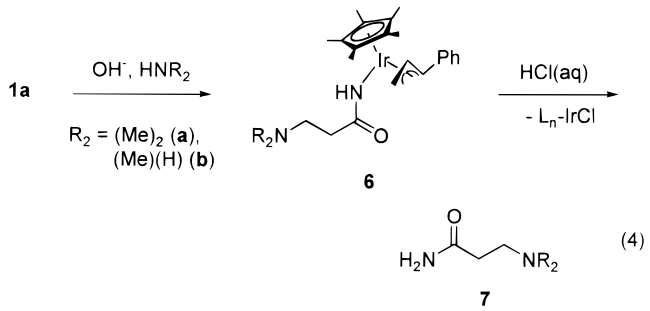


(3)

It should be mentioned that addition of alcohols to the olefinic group of **1b** has not been observed in the reaction of **1b** with alcohols (CH_3OH, C_2H_5OH) in the presence of OH^- at room temperature.

Reactions of [Cp*Ir(η^3-$CH_2CHCHPh$)(NCCH=CH_2)]$^+$ (1a) with Protic Amines in the Presence of OH^-. Amino amido complexes $L_n{-}Ir{-}NHCOCH_2CH_2NR_2$ (**6**, $R_2 = (CH_3)_2$ (**a**), $(CH_3)(H)$ (**b**)) have been obtained from the reactions of **1a** with HNR_2 in the presence of OH^- (eq 4) and unambiguously characterized by spectral and elemental analysis data.

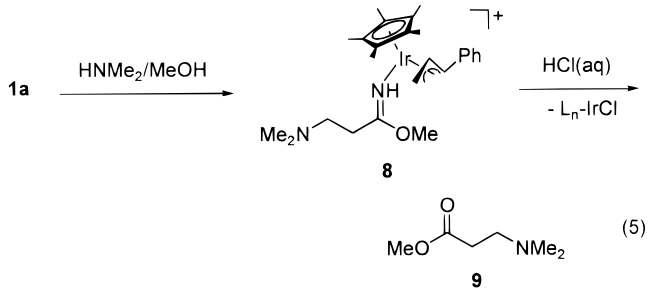
For example, the ^1H NMR spectrum of **6a** in C_6D_6 clearly shows all the signals due to the protons of η^3-C*HH*C*H*CH*H*Ph and CH_2CH_2N(CH_3)$_2$. The signal at δ 175.7 in the ^{13}C NMR spectrum and strong IR absorption at 1599 cm^{-1} are assigned to *C*=O and $\nu_{C=O}$, respectively. Acidification of **6** with aqueous HCl produces quantitative amounts of the amino amides $H_2NCOCH_2CH_2NR_2$ (**7**), which supports the identification of the amino amido complexes, **6**. As observed and discussed above for complex **2a** and **4a**, it is also possible



(4)

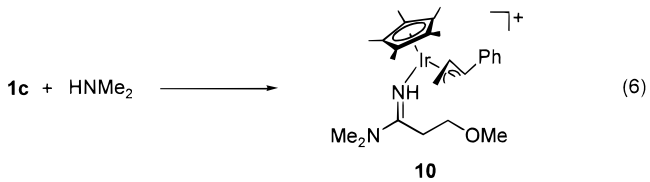
for **6** to isomerize to the enol form $L_n{-}Ir{-}N{=}C(OH)CH_2CH_2NR_2$ (**6E**) in polar solvents. In fact, a set of small signals are seen in the ^1H NMR spectrum of **6a** in $CDCl_3$ and assigned to those of the enol form (**6aE**) of **6a**.

Reaction of [Cp*Ir(η^3-$CH_2CHCHPh$)(NCCH=CH_2)]$^+$ (1a) with $HN(CH_3)_2$ and CH_3OH. The reaction of **1a** with $HN(CH_3)_2$ and CH_3OH yields the amino imino−ether complex $[L_n{-}Ir{-}NH{=}C(OCH_3)CH_2CH_2N(CH_3)_2]OTf$ (**8**) (eq 5). The ^1H NMR spectrum of **8** shows three singlets at δ 1.51 (15H), 2.29 (6H), and 4.09 (3H) that are unequivocally assigned to the methyl protons of Cp* ($C_5(CH_3)_5$), $N(CH_3)_2$, and $C(OCH_3)$, respectively. The signal due to N=*C* at δ 179.7 in the ^{13}C NMR spectrum and medium IR absorption at 1637 cm^{-1} due to $\nu_{N=C}$ (and the absence of a strong absorption due to $\nu_{C=O}$ at ~1600 cm^{-1}) support the imino moiety in **8**. The $Ir{-}NH{=}C(OCH_3)CH_2CH_2N(CH_3)_2$ unit in **8** is also supported by the quantitative production of the ester $CH_3OCOCH_2CH_2N(CH_3)_2$ (**9**) from the hydrolysis of **8** (eq 5).



(5)

The addition of $HN(CH_3)_2$ to the nitrile group of **1a** has not been observed in the presence of both CH_3OH and $HN(CH_3)_2$. On the other hand, $HN(CH_3)_2$ is readily added to the nitrile of **1c** to give the methoxo amidine complex $[L_n{-}Ir{-}NH{=}C(N(CH_3)_2)CH_2CH_2OCH_3)]OTf$ (**10**) (eq 6). It is well established that amines are added to saturated nitriles coordinated to metal to give amidine complexes.[3] Complex **10** has been unambiguously characterized by detailed NMR spectral and elemental analysis data (see Supporting Information) compared with those of well-identified amidine complexes.[3]



(6)

In summary, it is noteworthy that the addition of OH^- and alcohols or protic amines to the $N{\equiv}C-$ and $-CH{=}CH_2$ groups in **1a** is evidently regioselective. Hydroxide

ion has a priority of attacking the N≡C− group over CH_3OH and $HN(CH_3)_2$, whereas $HN(CH_3)_2$ has priority of attackingthe −CH=CH_2 group over OH^- and CH_3-OH. It may be mentioned that *no report, to the best of our knowledge, has been made for an addition of OH^- and ROH or HNR_2, and CH_3OH and $HN(CH_3)_2$, respectively, to both nitrile (N≡C−) and olefinic (−CH=CH−) groups of coordinated unsaturated nitriles.*

Catalytic Activity of 1a for the Production of Amides. That the metal complexes **2**, **4**, **6**, and **8** dissociate the amides (**3**, **5**, **7**) and ester (**9**) in the presence of H^+ has led us to investigate the catalytic activity of **1a** for the production of the amides and imino−ether. Unsaturated amide CH_2=$CHCONH_2$ is slowly (>0.1 mol/Ir/h at 70 °C) produced from the reaction of CH_2=CHCN with H_2O in the presence of **1a** and Na_2CO_3. Larger amounts of an ether (($NCCH_2CH_2)_2O$/Ir/h = 0.9 at 70 °C) and alcohol ($NCCH_2CH_2OH$/Ir/h = 2.3 at 70 °C) were also found in the reaction mixture (see Experimental Section for detailed data). All of these products (CH_2=$CHCONH_2$, $(NCCH_2CH_2)_2O$, $NCCH_2CH_2OH$) have been reported as the products of the catalytic hydration of CH_2=CHCN in the presence of $Pt(PEt_3)_3$.[2c] Methoxo amide is also slowly (($CH_3OCH_2CH_2CONH_2$)/Ir/h = 0.8 at 70 °C) produced from the reaction of CH_2=CHCN with CH_3OH and H_2O in the presence of Na_2CO_3. A much larger amount of the methoxo nitrile (($CH_3OCH_2CH_2CN$)/Ir/h = 39 at 70 °C) was also found in the reaction mixture (see Experimental Section for detailed data). Neither the amino amide ($H_2NCOCH_2CH_2N(CH_3)_2$) nor the amino imino−ether (NH=$C(OCH_3)CH_2CH_2N(CH_3)_2$) has been obtained from the reactions of excess CH_2=CHCN with $HN(CH_3)_2$ and **1a** in the presence of H_2O and CH_3OH, respectively.

Experimental Section

General Information. A standard vacuum system and Schlenk type glassware were used in most of the experimental procedures in handling metal compounds, although most of compounds seem to be stable enough to be handled without much precautions in air. NMR spectra were recorded on a Varian Gemini 200, 300, or 500 spectrometer (^{1}H, 200, 300, or 500 MHz; ^{13}C, 50, 75, or 125 MHz). IR spectra were measured on a Nicholet 205 spectrophotometer. Gas chromatography and mass spectra were obtained with Hewlett-Packard HP 5890A and VG-trio 2000 instruments. Elemental analyses were carried out with a Carlo Erba EA 1108.

Synthesis of [Cp*Ir(η^3-$CH_2CHCHPh$)(N≡CCH=CH_2)]OTf (1a). A 0.09 g (0.33 mmol) sample of AgOTf and two drops of CH_2=CHCN (ca. 20 mmol) were added to a $CHCl_3$ (20 mL) solution of Cp*IrCl(η^3-$CH_2CHCHPh$)[3,5] (0.15 g, 0.3 mmol), and the resulting solution was stirred at room temperature for 1 h before AgCl was removed by filtration. A beige solid was obtained by distillation of the filtrate solution under vacuum and recrystallized in cold $CHCl_3/(C_2H_5)_2O$ to isolate beige microcrystals of **1a**. The yield was 0.16 g and 90% based on [Cp*Ir(η^3-$CH_2CHCHPh$)(N≡CCH=CH_2)]OTf. ^{1}H NMR ($CDCl_3$): δ 1.60 (s, 15H, CH_3 of Cp*), 2.55 (dd, 1H, J = 2.0, 10.0 Hz, CHHCHCHPh), 3.42 (dd, 1H, J = 2.0, 7.0 Hz, CHHCHCHPh), 4.52 (d, 1H, J = 10.0 Hz, $CH_2CHCHPh$), 4.99 (dt, 1H, J = 7.0, 10.0 Hz, $CH_2CHCHPh$), 6.35−6.56 (m, 3H, NCCH=CH_2), 7.22−7.43 (m, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$): δ 8.0 (*C*H_3 of Cp*), 43.6 (*C*H_2CHCHPh), 65.5 ($CH_2CHCHPh$), 79.4 ($CH_2CHCHPh$), 94.7 (ring *C* of Cp*), 106.2 (NC*C*H=CH_2), 120.4 (N≡*C*), 126.1, 126.9, 128.9, 137.1 (*C*$_6$H$_5$), 143.4 (NCCH=*C*H_2). IR (KBr, cm^{-1}): 2259 (w, $\nu_{C\equiv N}$). Anal. Calcd for $C_{23}H_{27}O_3NSF_3Ir$: C, 42.71; H, 4.21; N, 2.17. Found: C, 42.91; H, 4. 26; N, 2.17.

Synthesis of [Cp*Ir(η^3-$CH_2CHCHPh$)(N≡CC(CH_3)=CH_2)]OTf (1b). This compound was prepared in the same manner as described above for **1a** using the same amounts of reactants. The yield was 90% based on Cp*Ir(η^3-$CH_2CHCHPh$)(N≡CC(CH_3)=CH_2)]OTf. ^{1}H NMR ($CDCl_3$): δ 1.57 (s, 15H, CH_3 of Cp*), 2.10 (s, 3H, C(CH_3)=CH_2), 2.44 (d, 1H, J = 10.0 Hz, CHHCHCHPh), 3.45 (d, 1H, J = 6.5 Hz, CHHCHCHPh), 4.11 (d, 1H, J = 10.0 Hz, $CH_2CHCHPh$), 5.05 (dt, 1H, J = 6.5, 10.0 Hz, $CH_2CHCHPh$), 6.09 (d, 1H, J = 1.0 Hz, C(CH_3)=CHH), 6.16 (d, 1H, J = 1.0 Hz, C(CH_3)=CHH), 7.18−7.37 (m, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$): δ 8.0 (*C*H_3 of Cp*), 20.3 (C(*C*H_3)=CH_2), 43.6 (*C*H_2CHCHPh), 65.4 ($CH_2CHCHPh$), 79.4 (CH_2-*C*HCHPh), 94.6 (ring *C* of Cp*), 115.2 (*C*(CH_3)=CH_2), 122.2, 126.0, 126.8, 128.9, 136.9, 137.9 (N≡*C*, *C*$_6$H$_5$, C(CH_3)=*C*H_2). IR (KBr, cm^{-1}): 2296 (w, $\nu_{C\equiv N}$). Anal. Calcd for $C_{24}H_{29}O_3NSF_3$-Ir: C, 43.63; H, 4.41; N, 2.12. Found: C, 43.91; H, 4.51; N, 2.04.

Synthesis of [Cp*Ir(η^3-$CH_2CHCHPh$)(N≡CCH_2CH_2O-CH_3)]OTf (1c). This compound was prepared in the same manner as described above for **1a** using same amounts of reactants. The yield was 91% based on [Cp*Ir(η^3-$CH_2CHCHPh$)-(N≡C$CH_2CH_2OCH_3$)]OTf. ^{1}H NMR ($CDCl_3$): δ 1.59 (s, 15H, CH_3 of Cp*), 2.53 (dd, 1H, J = 1.8, 10.5 Hz, CHHCHCHPh), 3.37 (dd, 1H, J = 1.8, 7.0 Hz, CHHCHCHPh), 3.43 (s, 3H, OCH_3), 3.46 (t, 2H, J = 6.0 Hz, C$H_2CH_2OCH_3$), 3.73 (t, 2H, J = 6.0 Hz, $CH_2CH_2OCH_3$), 4.23 (d, 1H, J = 10.5 Hz, CH_2-CHCHPh), 4.99 (dt, 1H, J = 7.0, 10.5 Hz, $CH_2CHCHPh$), 7.2−7.4 (m, 5H, C_6H_5). ^{13}C NMR ($CDCl_3$): δ 7.8 (*C*H_3 of Cp*), 20.6 (*C*$H_2CH_2OCH_3$), 43.0 (*C*H_2CHCHPh), 58.3 ($CH_2CH_2OCH_3$), 64.9 ($CH_2CHCHPh$), 66.4 ($CH_2CH_2OCH_3$), 78.9 ($CH_2CHCHPh$), 94.1 (ring *C* of Cp*), 122.6, 125.8, 126.5, 128.7, 137.3 (N≡*C*, *C*$_6$H$_5$). IR (KBr, cm^{-1}): 2298 (w, $\nu_{C\equiv N}$). Anal. Calcd for $C_{24}H_{31}O_4$-NSF_3Ir: C, 42.47; H, 4.60, N, 2.09. Found: C, 42.65; H, 4.54; N, 2.01.

Synthesis of Cp*Ir(η^3-$CH_2CHCHPh$)(NHCOCH=CH_2) (2a). A reaction mixture of **1a** (0.10 g, 0.15 mmol) in THF (10.0 mL) and NaOH (3.0 mL of 0.1 M solution in H_2O, 0.3 mmol) was stirred for 20 min at room temperature before CH_2Cl_2 (20 mL) was added to dissolve the product **2a** precipitated during the reaction. Excess NaOH and NaOTf were removed by extraction with H_2O (2 × 20 mL), and a pale yellow solid was obtained by vacuum distillation of the organic layer and recrystallized with $CHCl_3$/*n*-pentane. The yield was 0.095 g and 94% based on Cp*Ir(η^3-$CH_2CHCHPh$)(NHCOCH=CH_2). ^{1}H NMR (C_6D_6): δ 1.24 (s, 15H, CH_3 of Cp*), 1.54 (d, 1H, J = 9.5 Hz, CHHCHCHPh), 2.90 (d, 1H, J = 6.5 Hz, CHHCH-CHPh), 3.65 (br, 1H, NH), 4.05 (d, 1H, J = 9.5 Hz, CH_2-CHCHPh), 4.53 (dt, 1H, J = 6.5, 9.5 Hz, $CH_2CHCHPh$), 5.16 (dd, 1H, J = 3.0, 9.5 Hz, CH=CHH), 6.23 (dd, 1H, J = 9.5, 16.5 Hz, CH=CH_2), 6.36 (dd, 1H, J = 3.0, 16.5 Hz, CH=CHH). ^{13}C NMR (C_6D_6): δ 8.3 (*C*H_3 of Cp*), 40.6 (*C*H_2CHCHPh), 62.5 ($CH_2CHCHPh$), 73.6 ($CH_2CHCHPh$), 91.9 (ring *C* of Cp*), 119.9 (*C*H=CH_2), 136.8 (CH=*C*H_2), 170.7 (*C*=O). IR (KBr, cm^{-1}): 3309 (m, ν_{NH}), 1595 (s, $\nu_{C=O}$). Anal. Calcd for $C_{22}H_{28}$-ONIr: C, 51.34; H; 5.48, N, 2.72. Found: C, 51.33; H, 5. 48; N, 2.71.

^{1}H NMR (**2a**, $CDCl_3$): δ 1.51 (s, 15H, CH_3 of Cp*), 1.69 (d, 1H, J = 9.6 Hz, CHHCHCHPh), 3.15 (d, 1H, J = 6.6 Hz, CHHCHCHPh), 3.83 (d, 1H, J = 9.6 Hz, $CH_2CHCHPh$), 4.09 (br, 1H, NH), 4.81 (dt, 1H, J = 6.6, 9.6 Hz, $CH_2CHCHPh$), 5.20 (dd, 1H, J = 2.1, 10.0 Hz, CH=CHH), 5.93 (dd, 1H, J = 2.1, 17.0 Hz, CH=CHH), 6.27 (dd, 1H, J = 10.0, 17.0 Hz, CH=CH_2), 7.04−7.59 (m, 5H, C_6H_5). ^{13}C NMR (**2a**, $CDCl_3$): δ 7.90 (*C*H_3 of Cp*), 40.5 (*C*H_2CHCHPh), 60.6 ($CH_2CHCHPh$), 73.1 ($CH_2CHCHPh$), 91.4 (ring *C* of Cp*), 119.1 (*C*H=CH_2), 124.4 126.6, 127.6 and 140.4 (*C*$_6$H$_5$), 135.9 (CH=*C*H_2), 170.5(*C*=O).^{1}H NMR (**2aE**, $CDCl_3$): δ 1.49 (s, 15H, CH_3 of Cp*), 1.91 (d, 1H, J = 9.6 Hz, CHHCHCHPh), 3.20 (d, 1H, J = 6.3 Hz,

CH*H*CHCHPh), 3.55 (d, 1H, J = 9.6 Hz, $CH_2CHCHPh$), 4.62 (br, 1H, O*H*), 5.02 (dt, 1H, J = 6.3, 9.6 Hz, $CH_2CHCHPh$), 5.45 (dd, 1H, J = 2.4, 10.0 Hz, CH=C*H*H), 6.26 (dd, 1H, J = 2.4, 17.4 Hz, CH=CH*H*), 6.53 (dd, 1H, J = 10.0, 17.4 Hz, C*H*=CH_2).^{13}C NMR (**2aE**, $CDCl_3$): δ 7.81 (*C*H_3 of Cp*), 41.5 (CH_2-CHCHPh), 61.9 ($CH_2CHCHPh$), 75.1 ($CH_2CHCHPh$), 92.0 (ring *C* of Cp*), 123.2 (*C*H=CH_2), 125.0, 127.0, 128.2 and 139.5 (C_6H_5), 133.8 (CH=*C*H_2), 171.3 (*C*=N).^{1}H NMR (**2aE**, CD_3-$COCD_3$): δ 1.54 (s, 15H, C*H*$_3$ of Cp*), 1.67 (d, 1H, J = 9.5 Hz, C*H*HCHCHPh), 3.15 (d, 1H, J = 6.5 Hz, CH*H*CHCHPh), 4.45 (br, 1H, O*H*), 3.76 (d, 1H, J = 10.0 Hz, $CH_2CHCHPh$), 5.02 (dt, 1H, J = 6.5, 10.0 Hz, $CH_2CHCHPh$), 5.07 (dd, 1H, J = 3.0, 10.0 Hz, CH=C*H*H), 5.83 (dd, 1H, J = 3.0, 17.0 Hz, CH=CH*H*), 6.37 (dd, 1H, J = 10.0, 17.0 Hz, C*H*=CH_2).^{13}C NMR (**2aE**, CD_3COCD_3): δ 3.1 (*C*H_3 of Cp*), 35.7 ($CH_2CHCHPh$), 56.5 ($CH_2CHCHPh$), 68.7 ($CH_2CHCHPh$), 87.3 (ring *C* of Cp*), 113.5 (*C*H=CH_2), 120.2, 122.9, 123.3, 137.0 (C_6H_5), 132.5 (CH=*C*H_2), 165.3 (*C*=N).

Synthesis of Cp*Ir(η^3-$CH_2CHCHPh$)($NHCOC(CH_3)$=CH_2) (2b). This compound was prepared in the same manner as described above for **2a** using the same amounts of reactants. The yield was 93% based on Cp*Ir(η^3-$CH_2CHCHPh$)($NHCOC$-(CH_3)=CH_2). ^{1}H NMR (C_6D_6): δ 1.50 (s, 15H, C*H*$_3$ of Cp*), 1.66 (d, 1H, J = 9.5 Hz, C*H*HCHCHPh), 1.92 (s, 3H, C(C*H*$_3$)=CH_2), 3.15 (d, 1H, J = 6.5 Hz, CH*H*CHCHPh), 3.77 (d, 1H, J = 9.5 Hz, $CH_2CHCHPh$), 4.27 (br, 1H, N*H*), 4.80 (dt, 1H, J = 6.5, 9.5 Hz, $CH_2CHCHPh$), 4.94 (d, 1H, J = 1.0 Hz, C(CH_3)=C*H*H), 5.34 (d, 1H, J = 1.0 Hz, C(CH_3)=CH*H*). ^{13}C NMR (C_6D_6): δ 8.3 (*C*H_3 of Cp*), 20.1 (C(*C*H_3)=CH_2), 40.9 ($CH_2CHCHPh$), 61.3 ($CH_2CHCHPh$), 73.5 ($CH_2CHCHPh$), 91.8 (ring *C* of Cp*), 114.2 (*C*(CH_3)=CH_2), 145.7 (C(CH_3)=*C*H_2), 174.6 (*C*=O). IR (KBr, cm^{-1}): 3407 (w, ν_{NH}), 1588 (s, $\nu_{C=O}$). Anal. Calcd for $C_{23}H_{30}ONIr$: C, 52.25; H, 5.72; N, 2.65. Found: C, 52.23; H, 5. 68; N, 2.61.

Synthesis of Cp*Ir(η^3-$CH_2CHCHPh$)($NHCOCH_2CH_2$-OCH_3) (4a). A reaction mixture of **1a** (0.1 g, 0.15 mmol) in CH_3OH (10.0 mL) and NaOH (3.0 mL of 0.1 M solution in H_2O, ca. 0.3 mmol) was stirred for 20 min at room temperature before CH_2Cl_2 (20 mL) was added to dissolve the product **4a** precipitated during the reaction. Excess NaOH and NaOTf were removed by extraction with H_2O, and a pale yellow solid was obtained by distillation of the organic layer under vacuum and recrystallized with $CHCl_3$/*n*-pentane. The yield was 0.076 g and 93% based on Cp*Ir(η^3-$CH_2CHCHPh$)($NHCOCH_2CH_2$-OCH_3). ^{1}H NMR (C_6D_6): δ 1.32 (s, 15H, C*H*$_3$ of Cp*), 1.65 (d, 1H, J = 9.0 Hz, C*H*HCHCHPh), 2.56 (t, 2H, J = 6.3 Hz, CH_2-CH_2OCH_3), 2.96 (d, 1H, J = 6.5 Hz, CH*H*CHCHPh), 3.17 (s, 3H, $CH_2CH_2OCH_3$), 3.67 (m, 1H, $CH_2CHHOCH_3$), 3.79 (m, 1H, $CH_2CHHOCH_3$), 4.08 (d, 1H, J = 9.0 Hz, $CH_2CHCHPh$), 4.61 (dt, 1H, J = 9.0, 6.3 Hz, $CH_2CHCHPh$). ^{13}C NMR (C_6D_6): δ 8.3 (*C*H_3 of Cp*), 40.6 ($CH_2CH_2OCH_3$), 40.9 ($CH_2CHCHPh$), 58.2 ($CH_2CH_2OCH_3$), 62.3 (CH_2CH_2CHPh), 71.5 (CH_2CH_2-OCH_3), 73.4 ($CH_2CHCHPh$), 91.8 (ring *C* of Cp*), 174.4 (*C*=O). IR (KBr, cm^{-1}): 3380 (w, ν_{N-H}), 1612 (s, $\nu_{C=O}$). Anal. Calcd for $C_{23}H_{32}O_2NIr$: C, 50.53; H, 5.90, N, 2.56. Found: C, 50.32; H, 5. 81; N, 2.49.

^{1}H NMR (**4a**, $CDCl_3$): δ 1.49 (s, 15H, C*H*$_3$ of Cp*), 1.67 (d, 1H, J = 9.5 Hz, C*H*HCHCHPh), 2.46 (t, 2H, J = 6.0 Hz, CH_2-CH_2OCH_3), 3.14 (d, 1H, J = 6.5 Hz, CH*H*CHCHPh), 3.35 (s, 3H, $CH_2CH_2OCH_3$), 3.65 (m, 2H, $CH_2CH_2OCH_3$), 3.78 (d, 1H, J = 9.5 Hz, $CH_2CHCHPh$), 4.03 (br, 1H, N*H*), 4.80 (dt, 1H, J = 6.5, 9.5 Hz, $CH_2CHCHPh$), 7.00−7.45 (m, 5H, C_6H_5). ^{13}C NMR (**4a**, $CDCl_3$): δ 8.02 (*C*H_3 of Cp*), 40.3 ($CH_2CH_2OCH_3$), 40.5($CH_2CHCHPh$), 58.1 ($CH_2CH_2OCH_3$), 60.8 ($CH_2CHCHPh$), 70.6 ($CH_2CH_2OCH_3$), 73.0 ($CH_2CHCHPh$), 91.5 (ring *C* of Cp*), 124.5, 126.6, 127.8 and 140.8 (C_6H_5), 174.7 (*C*=O). ^{1}H NMR (**4aE**, $CDCl_3$): δ 1.42 (s, 15H, C*H*$_3$ of Cp*), 1.84 (d, 1H, J = 9.5 Hz, C*H*HCHCHPh), 2.55 (t, 2H, J = 6.0 Hz, $CH_2CH_2OCH_3$), 3.25 (d, 1H, J = 6.5 Hz, CH*H*CHCHPh), 3.38 (s, 3H, CH_2CH_2-OCH_3), 3.65 (m, 2H, $CH_2CH_2OCH_3$), 4.49 (br, 1H, O*H*), 4.98 (dt, 1H, J = 6.5, 9.5 Hz, $CH_2CHCHPh$), 7.00−7.45 (m, 5H, C_6H_5). ^{1}H NMR (**4aE**, CD_3COCD_3): δ 1.58 (s, 15H, C*H*$_3$ of Cp*), 1.67 (d, 1H, J = 9.5 Hz, C*H*HCHCHPh), 2.41 (t, 2H, J = 6.0 Hz, $CH_2CH_2OCH_3$), 3.16 (d, 1H, J = 6.5 Hz, CH*H*CHCHPh), 3.28 (s, 3H, $CH_2CH_2OCH_3$), 3.58 (m, 2H, $CH_2CH_2OCH_3$), 3.77 (d, 1H, J = 9.5 Hz, $CH_2CHCHPh$), 4.16 (br, 1H, O*H*), 5.03 (dt, 1H, J = 6.5, 9.5 Hz, $CH_2CHCHPh$), 7.00−7.45 (m, 5H, C_6H_5). ^{13}C NMR (**4aE**, CD_3COCD_3): δ 8.05 (*C*H_3 of Cp*), 41.6 (CH_2-CH_2OCH_3), 41.8 ($CH_2CHCHPh$), 58.8 ($CH_2CH_2OCH_3$), 62.3 ($CH_2CHCHPh$), 72.2 ($CH_2CH_2OCH_3$), 74.5 ($CH_2CHCHPh$), 92.8 (ring *C* of Cp*), 125.1, 127.0, 128.2 and 139.5 (C_6H_5), 170.3(*C*=N). HETCOR (**4a**, ^{1}H (500 MHz) → ^{13}C (126 MHz), $CDCl_3$): δ 2.46 → 40.3; δ 3.35 → 58.1; δ 3.65 → 70.6 (Supporting Information).

Synthesis of Cp*Ir(η^3-$CH_2CHCHPh$)($NHCOCD_2CH_2$-OCH_3) (4a-d_2). This compound was prepared in the same manner as described above for **4a** using **1a** (0.15 mmol), CH_3-OD (10 mL), and NaOD (3.0 mL of 0.1 M solution in D_2O, ca. 0.3 mmol). Excess NaOD and NaOTf were removed by dissolving in H_2O, which presumably replaced the deuterium bound to the nitrogen (Ir−N*D*$COCD_2CH_2OCH_3$) with hydrogen.

Reaction of [Cp*Ir(η^3-$CH_2CHCHPh$)(N≡CCH=CH_2)]-OTf (1a) with D_2O to Produce [Cp*Ir(η^3-$CH_2CHCHPh$)-(N≡CCD=CH_2)]OTf (1a-d_1). A slurry of **1a** (0.05 g) in D_2O (3 mL) was stirred at 50 °C for 15 h and cooled to room temperature. Pale yellow solid was obtained by filtration and dried under vacuum. ^{1}H NMR spectrum clearly showed a significant decrease (by one-third) in the integration of those signals due to NCC*H*=C*H*$_2$ in δ 6.35−6.56 compared with those of **1a** (see Supporting Information). The ^{13}C NMR spectrum (^{1}H decoupled) of **1a-d_1** also showed that the signal due to the α-carbon of the nitrile (Ir−NC*C*D=CH_2) at δ 106.2 ppm is broadened due to the coupling with deuterium (Supporting Information).

Deutration of CH_3CN in [Cp*Ir(η^3-$CH_2CHCHPh$)(NC-CH_3)]$^+$ (A) and Related Reactions in Scheme 1. Compound **A** and its methanol adduct [Cp*Ir(η^3-$CH_2CHCHPh$)(NH=$C(OCH_3)CH_3$)]$^+$ (**B**) were prepared by the literature methods.[3] Deuterium-containing compounds **A-d_3** and **B-d_4** were prepared by the same manner as described in the literature[3] for **A** using CH_3OD and for **1a-d_1** (see above), respectively, and identified by ^{1}H NMR spectral measurements.

Synthesis of Cp*Ir(η^3-$CH_2CHCHPh$)($NHCOCH_2CH_2O$-CH_2CH_3) (4b). This compound was prepared in the same manner as described above for **4a** using the same amounts of reactants. The yield was 85% based on Cp*Ir(η^3-$CH_2CHCHPh$)-($NHCOCH_2CH_2OCH_2CH_3$). ^{1}H NMR (C_6D_6): δ 1.12 (t, 3H, J = 7.0 Hz, OCH_2CH_3), 1.33 (s, 15H, C*H*$_3$ of Cp*), 1.66 (d, 1H, J = 9.0 Hz, C*H*HCHCHPh), 2.58 (t, 2H, J = 6.3 Hz, CH_2CH_2-OCH_2CH_3), 2.97 (d, 1H, J = 6.9 Hz, CH*H*CHCHPh), 3.35 (q, 2H, J = 7.0 Hz, OCH_2CH_3), 3.67 (br, 1H, N*H*), 3.73 (m, 1H, $CH_2CHHOCH_2CH_3$), 3.85 (m, 1H, $CH_2CHHOCH_2CH_3$), 4.09 (d, 1H, J = 9.0 Hz, $CH_2CHCHPh$), 4.62 (dt, 1H, J = 9.0, 6.9 Hz, $CH_2CHCHPh$). ^{13}C NMR (C_6D_6): δ 8.4 (*C*H_3 of Cp*), 15.6 (OCH_2CH_3), 40.5, 41.0 ($CH_2CH_2OCH_2CH_3$, $CH_2CHCHPh$), 62.2 ($CH_2CHCHPh$), 66.1 (OCH_2CH_3), 69.4 ($CH_2CH_2OCH_2CH_3$), 73.3 ($CH_2CHCHPh$), 91.8 (ring *C* of Cp*), 174.9 (*C*=O). IR (KBr, cm^{-1}): 3281 (w, ν_{N-H}), 1610 (s, $\nu_{C=O}$). Anal. Calcd for $C_{24}H_{34}O_2NIr$: C, 51.41; H, 6.11; N, 2.50. Found: C, 51.33; H, 6.08; N, 2.61.

^{1}H NMR (**4b**, $CDCl_3$): δ 1.06 (t, 3H, J = 7.0 Hz, OCH_2CH_3), 1.38 (s, 15H, C*H*$_3$ of Cp*), 1.54 (d, 1H, J = 10.0 Hz, C*H*HCH-CHPh), 2.36 (t, 2H, J = 6.5 Hz, CH_2CH_2O CH_2CH_3), 3.00 (d, 1H, J = 6.5 Hz, CH*H*CHCHPh), 3.36 (q, 2H, J = 7.0 Hz, OCH_2-CH_3), 3.56 (m, 2H, $CH_2CH_2OCH_2CH_3$), 3.64 (d, 1H, J = 10.0 Hz, $CH_2CHCHPh$), 3.96 (br, 1H, N*H*), 4.66 (dt, 1H, J = 6.5, 10.0 Hz, $CH_2CHCHPh$), 6.96−7.40 (m, 5H, C_6H_5). ^{13}C NMR (**4b**, $CDCl_3$): δ 8.00 (*C*H_3 of Cp*), 14.9 (OCH_2CH_3), 40.4 (CH_2-$CH_2OCH_2CH_3$), 40.5 ($CH_2CHCHPh$), 60.7 ($CH_2CHCHPh$), 65.6 (OCH_2CH_3), 68.4 ($CH_2CH_2OCH_2CH_3$), 73.0 ($CH_2CHCHPh$), 91.4 (ring *C* of Cp*), 124.4, 126.6, 127.7 and 140.8 (C_6H_5), 174.9

(*C*=O). HETCOR (**4b**, ^{1}H (500 MHz) → ^{13}C (126 MHz), $CDCl_3$): δ 1.06 → 14.9; δ 2.36 → 40.4; δ 3.36 → 65.6; δ 3.56 → 68.4 (Supporting Information).

Synthesis of Cp*Ir(η^3-$CH_2CHCHPh$)($NHCOCH_2CH_2N(CH_3)_2$) (6a). This compound was prepared in the same manner as described above for **4a** using 0.15 mmol of **1a**, $HN(CH_3)_2$ (1.0 mL of 40 wt % solution in H_2O), and NaOH (3.0 mL of 0.1 M in H_2O, 0.32 mmol). The yield was 87% based on Cp*Ir(η^3-$CH_2CHCHPh$)($NHCOCH_2CH_2N(CH_3)_2$).^{1}H NMR (C_6D_6): δ 1.39 (s, 15H, CH_3 of Cp*), 1.76 (d, 1H, J = 9.5 Hz, C*H*HCHCHPh), 2.16 (s, 6H, N(CH_3)$_2$), 2.54 (t, 2H, J = 7.0 Hz, CH_2CH$_2$N(CH$_3$)$_2$), 2.69 (m, 2H, CH$_2$CH_2N(CH$_3$)$_2$), 3.06 (d, 1H, J = 6.5 Hz, CH*H*CHCHPh), 4.16 (d, 1H, J = 9.5 Hz, CH$_2$CHC*H*Ph,), 4.17 (br, 1H, N*H*), 4.68 (dt, 1H, J = 9.5, 6.5 Hz, CH$_2$C*H*CHPh). ^{13}C NMR (C_6D_6): δ 8.3 (*C*H$_3$ of Cp*), 38.1 (*C*H$_2$CH$_2$N(CH$_3$)$_2$), 40.5 (*C*H$_2$CHCHPh), 45.3 (CH$_2$CH$_2$N(*C*H$_3$)$_2$), 58.0 (CH$_2$*C*H$_2$N(CH$_3$)$_2$), 62.3 (CH$_2$CH*C*HPh), 73.3 (CH$_2$*C*HCHPh), 91.7 (ring *C* of Cp*), 175.7 (*C*=O). IR (KBr, cm^{-1}): 3381 (w, ν_{NH}), 1599 (s, $\nu_{C=O}$). Anal. Calcd for $C_{24}H_{35}ON_2Ir$: C, 51.50; H, 6.30; N, 5.00. Found: C; 51.41; H, 6.31; N, 4.99.

Synthesis of Cp*Ir(η^3-$CH_2CHCHPh$)($NHCOCH_2CH_2NHCH_3$) (6b). This compound was prepared in the same manner as described above for **4a** using 0.15 mmol of **1a**, H_2NCH_3 (1.0 mL of 40 wt % solution in H_2O), and NaOH (3.0 mL of 0.1 M in H_2O, ca. 0.32 mmol). The yield was 84% based on Cp*Ir(η^3-$CH_2CHCHPh$)($NHCOCH_2CH_2NHCH_3$). ^{1}H NMR (C_6D_6): δ 1.45 (s, 15H, CH_3 of Cp*), 1.77 (d, 1H, J = 9.5 Hz, C*H*HCHCHPh), 2.51 (s, 3H, NHCH_3), 2.60 (t, 2H, J = 6.5 Hz, CH_2CH$_2$NHCH$_3$), 3.02 (m, 2H, CH$_2$CH_2NHCH$_3$), 3.11 (d, 1H, J = 6.5 Hz, CH*H*CHCHPh), 3.87 (br, 1H, N*H*), 4.19 (d, 1H, J = 9.5 Hz, CH$_2$CHC*H*Ph), 4.74 (dt, 1H, J = 9.5, 6.5 Hz, CH$_2$C*H*CHPh). ^{13}C NMR (C_6D_6): δ 8.5 (*C*H$_3$ of Cp*), 36.6 (*C*H$_2$CH$_2$NHCH$_3$), 40.1 (CH$_2$CH$_2$NH*C*H$_3$), 41.5 (*C*H$_2$CHCHPh), 49.9 (CH$_2$*C*H$_2$NHCH$_3$), 61.3 (CH$_2$CH*C*HPh), 73.5 (CH$_2$*C*HCHPh), 91.9 (ring *C* of Cp*), 176.1 (*C*=O). IR (KBr, cm^{-1}): 3381 (w, ν_{NH}), 1599 (s, $\nu_{C=O}$). Anal. Calcd for $C_{23}H_{33}ON_2Ir$: C, 50.62; H, 6.09; N, 5.13. Found: C; 50.49, H, 6.01; N, 4.99.

Synthesis of [Cp*Ir(η^3-$CH_2CHCHPh$)($NH=C(OCH_3)CH_2CH_2N(CH_3)_2$)]OTf (8). A reaction mixture of **1a** (0.10 g, 0.15 mmol) and $HN(CH_3)_2$ (5 mL of 2.0 M in CH_3OH) was stirred at 0 °C for 1 h and distilled under vacuum to obtain yellow solid, which was recrystallized with cold $CHCl_3$/$(C_2H_5)_2O$ to obtain pale yellow microcrystals of **8**. The yield was 0.097 g and 89% based on [Cp*Ir(η^3-$CH_2CHCHPh$)($HN=C(OCH_3)CH_2CH_2N(CH_3)_2$)]OTf. ^{1}H NMR ($CDCl_3$): δ 1.51 (s, 15H, CH_3 of Cp*), 1.83 (d, 1H, J = 10.0 Hz, C*H*HCHCHPh), 2.29 (s, 6H, N(CH_3)$_2$), 2.74 (m, 2H, CH$_2$CH_2N(CH$_3$)$_2$), 2.96 (t, 2H, J = 6.5 Hz, CH_2CH$_2$N(CH$_3$)$_2$), 3.30 (d, 1H, J = 7.0 Hz, CH*H*CHCHPh), 3.48 (d, 1H, J = 10.0 Hz, CH$_2$CHC*H*Ph), 4.09 (s, 3H, HN=C(OCH_3)CH$_2$), 4.90 (dt, 1H, J = 7.0, 10.0 Hz, CH$_2$C*H*CHPh), 10.2 (br, 1H, N*H*=C). ^{13}C NMR ($CDCl_3$): δ 8.3 (*C*H$_3$ of Cp*), 26.6 (*C*H$_2$CH$_2$N(CH$_3$)$_2$), 41.6 (*C*H$_2$CHCHPh), 44.2 (N(*C*H$_3$)$_2$), 55.2 (CH$_2$*C*H$_2$N(CH$_3$)$_2$), 57.1 (O*C*H$_3$), 62.6 (CH$_2$CH*C*HPh), 75.7 (CH$_2$*C*HCHPh), 92.8 (ring *C* of Cp*), 125.9, 126.1, 128.8, 139.3 (*C*$_6$H$_5$), 179.7 (*C*=N). IR (KBr, cm^{-1}): 1637 (s, $\nu_{C=N}$). Anal. Calcd for $C_{26}H_{38}O_4N_2F_3SIr$: C, 43.14; H, 5.29; N, 3.87. Found: C, 42.92; H, 5.50; N, 3.89.

Reactions of 2, 4, 6, and 8 with HCl (aqueous) to Produce Amides, $H_2NCOCR=CH_2$ (3, R = H (a), CH_3 (b)), $H_2NCOCH_2CH_2OR$ (5, R = CH_3 (a), C_2H_5 (b)), and $H_2NCOCH_2CH_2$ NR_2 (7, R = $(CH_3)_2$ (a), $(CH_3)(H)$ (b)), and Ester ($CH_3OCOCH_2CH_2N(CH_3)_2$ (9)), Respectively. All of these reactions were carried out in the same manner as described below for the reaction of **2a** with HCl (aqueous). A mixture of HCl solution (0.5 mL of 32 wt % HCl in H_2O) and **2a** (0.10 g, 0.19 mmol) in $CHCl_3$ (5.0 mL) was stirred at room temperature for 3 h, during which time the light yellow mixture turned darker. A 3.0 mL sample of H_2O was added to the reaction mixture to extract the water-soluble amide, and the aqueous layer was distilled under vacuum to obtain a white solid, which was washed with cold $CHCl_3$ (3 mL) to obtain relatively pure $H_2NCOCH=CH_2$ (**3a**). ^{1}H NMR ($CDCl_3$): δ 5.58 (br, 2H, NH_2), 5.73 (dd, 1H, J = 1.5, 10.2 Hz, CH=C*H*H), 6.15 (dd, 1H, J = 10.2, 17.2 Hz, C*H*=CH$_2$), 6.30 (dd, 1H, J = 1.5, 17.2 Hz, CH=CH*H*). Mass: M$^+$ at *m*/*z* 71. The iridium compound Cp*IrCl(η^3-$CH_2CHCHPh$) in the $CHCl_3$ layer was extracted by diethyl ether (10 mL), isolated by evaporation of the solvent, and identified by ^{1}H NMR measurement.[3]

Data for $H_2NCOC(CH_3)=CH_2$ (**3b**) as follows. ^{1}H NMR ($CDCl_3$): δ 1.98 (s, 3H, CH_3), 5.42 (s, 1H, C(CH$_3$)=C*H*H), 5.62 (br, 2H, NH_2), 5.77 (s, 1H, C(CH$_3$)=CH*H*). Mass: M$^+$ at *m*/*z* 85.

Data for $H_2NCOCH_2CH_2OCH_3$ (**5a**) as follows.^{1}H NMR ($CDCl_3$): δ 2.50 (t, 2H, J = 5.3 Hz, CH_2CH$_2$OCH$_3$), 3.38 (s, 3H, OCH_3), 3.64 (t, 2H, J = 5.3 Hz, CH$_2$CH_2OCH$_3$), 5.93, 6.41 (br, 2H, NH_2). Mass: M$^+$ at *m*/*z* 103.

Data for $H_2NCOCH_2CH_2OCH_2CH_3$ (**5b**) as follows.^{1}H NMR ($CDCl_3$): δ 1.23 (t, 3H, J = 7.0 Hz, OCH$_2$CH_3), 2.50 (t, 2H, J = 6.0 Hz, CH_2CH$_2$OCH$_2$CH$_3$), 3.54 (q, 2H, J = 7.0 Hz, OCH_2CH$_3$), 3.69 (t, 2H, J = 6.0 Hz, CH$_2$CH_2OCH$_2$CH$_3$), 5.33, 6.33 (br, 2H, NH_2). Mass: M$^+$ at *m*/*z* 117.

Data for $H_2NCOCH_2CH_2N(CH_3)_2$ (**7a**) as follows. ^{1}H NMR (D_2O): δ 2.70 (t, 2H, J = 6.9 Hz, CH_2CH$_2$N(CH$_3$)$_2$), 2.80 (s, 6H, N(CH_3)$_2$), 3.31 (t, 2H, CH$_2$CH_2N(CH$_3$)$_2$). Mass: M$^+$ at *m*/*z* 116.

Data for $H_2NCOCH_2CH_2NHCH_3$ (**7b**) as follows.^{1}H NMR (D_2O): δ 2.75 (t, 2H, J = 6.6 Hz, CH$_2$CH_2N(CH$_3$)$_2$), 2.77 (s, 3H, NHCH_3), 3.31 (t, 2H, J = 6.6 Hz, CH_2CH$_2$NHCH$_3$). Mass: M$^+$ at *m*/*z* 102.

Data for $CH_3OCOCH_2CH_2N(CH_3)_2$ (**9**) as follows. ^{1}H NMR ($CDCl_3$): δ 2.92 (s, 6H, N(CH_3)$_2$), 2.93 (t, 2H, J = 6.6 Hz, CH_2CH$_2$N(CH$_3$)$_2$), 3.43 (t, 2H, J = 6.6 Hz, CH$_2$CH_2N(CH$_3$)$_2$), 3.76 (s, 3H, OCH_3). Mass: M$^+$ at *m*/*z* 131.

Synthesis of [Cp*Ir(η^3-$CH_2CHCHPh$)($NH=C(N(CH_3)_2)CH_2CH_2OCH_3$)]OTf (10). This compound has been prepared in the same manner as described for the addition of amines to the saturated nitriles coordinated to [Cp*Ir(η^3-$CH_2CHCHPh$)]$^+$ in the previous report.[3] The yield was 89% based on [Cp*Ir(η^3-$CH_2CHCHPh$)($NH=C(N(CH_3)_2)CH_2CH_2OCH_3$)]OTf. ^{1}H NMR ($CDCl_3$): δ 1.48 (s, 15H, CH_3 of Cp*), 2.08 (d, 1H, J = 9.6 Hz, C*H*HCHCHPh), 3.00 (t, 2H, J = 7.0 Hz, CH_2CH$_2$OCH$_3$), 3.17 (s, 6H, HN=C(N(CH_3)$_2$)), 3.34 (s, 3H, CH$_2$CH$_2$OCH_3), 3.46 (d, 1H, J = 6.5 Hz, CH*H*CHCHPh), 3.60 (m, 2H, CH$_2$CH_2OCH$_3$), 3.81 (d, J = 9.6 Hz, CH$_2$CHC*H*Ph), 5.04 (dt, 1H, J = 9.6, 6.5 Hz, CH$_2$C*H*CHPh), 5.80 (br, 1H, N*H*), 7.19−7.37 (m, 5H, C$_6$*H*$_5$). ^{13}C NMR ($CDCl_3$): δ 8.15 (*C*H$_3$ of Cp*), 35.2 (*C*H$_2$CH$_2$OCH$_3$), 39.9 (N(*C*H$_3$)$_2$), 43.9 (*C*H$_2$CHCHPh), 58.7 (O*C*H$_3$), 62.5 (CH$_2$CH*C*HPh), 68.4 (CH$_2$*C*H$_2$OCH$_3$), 77.7 (CH$_2$*C*HCHPh), 92.8 (ring *C* of Cp*), 125.9, 126.2, 128.8 and 138.9 (*C*$_6$H$_5$), 167.6 (N=*C*). IR (KBr, cm^{-1}): 3312 (w, ν_{NH}), 1584 (s, $\nu_{C=N}$), 1029, 1152 and 1272 (s, OTf). Anal. Calcd for $C_{26}H_{38}O_4N_2F_3SIr$: C, 43.14; H, 5.29; N, 3.87. Found: C, 43.06; H, 5.12; N, 3.81.

Catalytic Reactions of CH_2=CHCN with H_2O, CH_3OH, or $NH(CH_3)_2$ in the Presence of 1a. All these reactions have been carried out in the same manner as described below for the reaction of CH_2=CHCN with H_2O in the presence of **1a** and Na_2CO_3. A 0.05 mmol sample of **1a**, 10.0 mmol of CH_2=CHCN, and 50 mmols each of H_2O, Na_2CO_3, CH_3OH, and $NH(CH_3)_2$ were used for all catalytic reactions. The reaction mixture of **1a**, CH_2=CHCN, H_2O, and Na_2CO_3 was stirred at 70 °C for 5 h in a bomb reactor under N_2 before it was cooled on an ice bath. A portion of the reaction mixture was analyzed by GC/mass data. Reaction of NCCH=CH_2 with H_2O: NCCH=CH_2 (89%, 8.9 mmol), $H_2NCOCH=CH_2$ (0.2%, 0.02 mmol), $(NCCH_2CH_2)_2O$ (2%, 0.2 mmol), $NCCH_2CH_2OH$ (6%, 0.6 mmol). Reaction of NCCH=CH_2 with CH_3OH: NCCH=CH_2 (2%, 0.2 mmol), $NCCH_2CH_2OCH_3$ (98%, 9.8 mmol).

X-ray Structural Determination of [Cp*Ir(η^3-$CH_2CHCHPh$)($N\equiv CCH=CH_2$]OTf (1a) and Cp*Ir(η^3-$CH_2CHCHPh$)($NHC(=O)CH_2CH_2OMe$) (4a). Crystals were grown

Table 1. Details of Crystallographic Data Collection of the Complexes 1a and 4a[a]

	1a	**4a**
chemical formula	$C_{23}H_{27}NO_3SF_3Ir$	$C_{23}H_{32}O_2NIr$
fw	646.72	546.70
temp, K	293(2)	293(2)
cryst dimen, mm	0.4 × 0.5 × 0.5	0.3 × 0.1 × 0.6
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a, Å	13.668(4)	7.269(6)
b, Å	12.011(2)	15.060(5)
c, Å	16.133(8)	19.619(9)
α, deg.	90.00	90.00
β, deg.	111.85(3)	92.61(6)
γ, deg.	90.00	90.00
V, Å^3	2548.2(15)	2145(2)
Z	4	4
$\rho_{(calc)}$, g cm^{-1}	1.747	1.693
μ, mm^{-1}	5.563	6.240
$F(000)$	1264	1080
radiation	Mo Kα	Mo Kα
wavelength	0.7107	0.7107
2θ max, deg	50	50
hkl range	$0 \le h \le 16$	$-6 \le h \le 6$
	$0 \le k \le 14$	$0 \le k \le 14$
	$-19 \le l \le 17$	$-3 \le l \le 18$
no. of reflns	4545	2018
no. of unique data	4317	1989
no. of obs data ($\|F_o\| \delta 4\sigma F_o$)	2763	1655
no. of params	307	244
scan type	$\omega/2\theta$	$\omega/2\theta$
R_1	0.043	0.031
wR_2	0.1143	0.079
GOF	1.063	1.193

[a] $R_1 = [\sum|F_o| - |F_c|/|F_o|]$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{0.5}$.

from $CHCl_3$ (**1a**) and benzene (**4a**). 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 $\omega/2\theta$ scan modes and corrected Lp effects and absorption. The structures of these compounds were solved by Patterson's heavy atom methods (SHELXS-97). 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 atom were refined by full-matrix least-squares techniques (SHELXL-97). All hydrogen atoms were placed at their geometrically calculated positions (dCH = 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 0.043 and 0.1143 for **1a** and 0.031 and 0.079 for **4a**, respectively.

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Supporting Information Available: Tables of bond distances and angles, positional and thermal parameters, and anisotropic thermal parameters for complexes **1a** and **4a**. ^{1}H (for **1a**, **1a-*d*$_1$**, **2a**, **2aE**, **4a**, **4aE**, **10** in $CDCl_3$, **4a**, **4a-*d*$_2$** in C_6D_6, and **4aE** in CD_3COCD_3), ^{13}C (for **1a**, **1a-*d*$_1$**, **2a**, **2aE** in $CDCl_3$,), ^{1}H, ^{1}H-2D COSY (for **4a**, **4b**), and ^{1}H, ^{13}C-2D HETCOR (for **4a**, **4b**). This material is available free of charge via the Internet at http://pubs.acs.org.

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