

Coordination of Aniline to an (η^1 -Allenyl)iridium Complex Leading to Hydroanilination[†]

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Formation of the N-arylated η^3 -aza-TMM complexes of iridium from regioselective hydroanilination of an octahedral (η^1 -allenyl)iridium complex has been studied. (*OC*-6-42)-Ir(Cl)(PPh₃)₂(OTf)(CO)(η^1 -CHCCH₂) (**2**) undergoes the substitution of L (L = NH₃, NH₂NH₂, MeNH₂, EtNH₂, ⁱPrNH₂, PhCH₂NH₂) for the triflate ligand to yield {(OC-6-42)-Ir(Cl)(PPh₃)₂(L)(CO)(η^1 -CHCCH₂)}(OTf) (**3d–i**). In contrast, the reactions of **2** with XC₆H₄NH₂ (X = F, NO₂, MeO, H, Me), Ph₂NH, and Ph(Me)NH result in regioselective addition at the allenyl ligand, thereby generating the N-arylated η^3 -aza-TMM complexes **5a–g**. The mechanistic studies confirm that the hydroanilination is preceded by the formation of an aniline-ligated intermediate.

Introduction

Organometallic transformations of transition-metal allenyl species are useful in organic synthesis.¹ Recent development of metal allenyl chemistry allows for adding a vast variety of nucleophiles to the allenyl moiety.² The involvement of metal in the addition reactions may contribute to at least two aspects. First, the bonding between the metal and the allenyl ligand profoundly affects the chemical reactivity.³ Second, the coordination of the nucleophile provides the metal with the opportunity of applying chemical selectivity.⁴

We previously discovered that adding nucleophiles such as water, alcohol, thiol, selenol, ammonia, amine, etc. either to the four-coordinate neutral η^1 -allenyl complexes *trans*-Pt(X)(PPh₃)₂(η^1 -CHCCH₂) (X = halide)

or to the cationic η^3 -propargyl/allenyl complex [Pt-(PPh₃)₂(η^3 -C₃H₃)](BF₄) led to the formation of the central-carbon-substituted η^3 -allyl or N-protonated or alkylated η^3 -aza-TMM⁵ complexes {Pt(PPh₃)₂[η^3 -CH₂C(Nu)CH₂]}(X) (Nu = OH, OR, SR, SeR, NRR'; X = halide, OTf, BF₄).^{2b,6} However, the octahedral neutral (η^1 -allenyl)-haloiridium complexes Ir(X)(X')(PPh₃)₂(CO)(η^1 -CHCCH₂) (**1**; X, X' = halide) are inert to nucleophilic addition. We have thus prepared the labile (η^1 -allenyl)(triflate)-iridium species (*OC*-6-42)-Ir(Cl)(PPh₃)₂(OTf)(CO)(η^1 -CHCCH₂) (**2**),⁷ which can react with water and alcohol to result in regioselective hydroxylation and alkoxylation. The iridium complexes with the central-carbon-substituted η^3 -allyl ligand are thereby generated.⁸

To our surprise, the reaction of **2** with ammonia leads to a product of substitution, {(OC-6-42)-Ir(Cl)(PPh₃)₂(NH₃)(CO)(η^1 -CHCCH₂)}(OTf). The expected product of hydroamination is never observed in such a reaction. Our successive studies show that complex **2** can react with aniline and its relatives to produce the N-arylated η^3 -aza-TMM complexes. Such distinct reactivities have spurred us to further investigate the reactions of **2** with various amine and aniline derivatives as well as the reaction mechanism. The mechanistic studies confirm that the hydroanilination is preceded by the formation of an aniline-ligated intermediate.

Results and Discussion

Substitution of a Labile Octahedral (η^1 -Allenyl)-iridium Complex. Because the octahedral (η^1 -allenyl)-haloiridium complexes (*OC*-6-43)-Ir(X)₂(PPh₃)₂(CO)(η^1 -CHCCH₂) (X = Cl (**1a**), Br (**1b**)) and (*OC*-6-54)-

[†] Based on the M.S. thesis of Y.-K.C., National Taiwan University, 1995.

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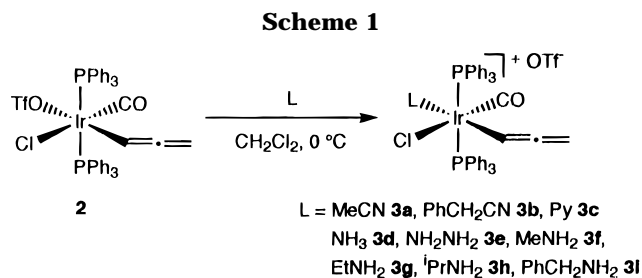
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(5) The η^3 -azatrimethylenemethane species M[η^3 -CH₂C(NR)CH₂](R = hydrocarbyl) is abbreviated as η^3 -aza-TMM. Accordingly, the nomenclature for M[η^3 -CH₂C(NH₂)CH₂] is N-protonated η^3 -azatrimethylenemethane and for M[η^3 -CH₂C(NRR')CH₂](R = alkyl, aryl) is N-alkylated (or N-arylated) η^3 -azatrimethylenemethane.

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Ir(Br)(Cl)(PPh₃)₂(CO)(η¹-CHCCH₂) (**1c**) are found to be inert to ammonia and amine, we prepared the labile allenyliridium complex (OC-6-42)-Ir(Cl)(PPh₃)₂(OTf)(CO)(η¹-CHCCH₂) (**2**). Complex **2** is air-sensitive and is subject to thermal decomposition in the solution. In the presence of coordinating compounds such as acetonitrile, benzonitrile, and pyridine, the transformation of **2** into {(OC-6-52)-Ir(Cl)(PPh₃)₂(L)(CO)(η¹-CHCCH₂)}(OTf) (L = MeCN (**3a**), PhCH₂CN (**3b**), C₆H₅N (**3c**), respectively) readily takes place.

Similarly, complex **2** can react with equimolar amounts of ammonia, hydrazine, and various amines at 0 °C to form {(OC-6-52)-Ir(Cl)(PPh₃)₂(L)(CO)(η¹-CHCCH₂)}(OTf) (L = NH₃ (**3d**), NH₂NH₂ (**3e**), MeNH₂ (**3f**), EtNH₂ (**3g**), ⁱPrNH₂ (**3h**), PhCH₂NH₂ (**3i**)) (Scheme 1). The complexes **2** and **3a–i** decompose in solution at 25 °C, presumably due to the high lability of the nitrogen-donor ligands on iridium. Complexes **3d,g,i** were isolated by crystallization below 0 °C. Others were primarily characterized by NMR spectroscopy. In the typical case of formation of **3i**, the sole signal of a singlet at δ -9.5 in the ³¹P NMR spectrum indicates that the reaction is exclusive and the two phosphines are in trans positions. In the ¹H NMR spectrum of **3i**, two resonance signals in a 2:1 ratio due to the allenyl ligand were observed at δ 5.93 and 3.50. We assign a broad resonance at δ 3.60 to the amino hydrogen and a multiplet at δ 3.18 to the benzyl methylene hydrogen. The carbonyl ligand is evidenced by IR spectroscopy, showing a stretching band at 2062 cm⁻¹. In addition, the weak stretching of the linear allenyl group is at 1925 cm⁻¹ and the NH peak at 3500 cm⁻¹. The ¹³C NMR data further support the assigned structure.

The reaction of **2** with diethylamine results in complicated products. It is assumed that diethylamine probably could displace other ligands besides the triflate ion. *tert*-Butylamine and NH₂SO₂Ph do not react with **2** under similar conditions. The former is considered to be too bulky and the latter fails due to its weak electron-donating ability; therefore, neither undergoes substitution. Benzenesulfonamide is a strong nucleophile and is able to replace the triflate ion of **2** to yield (OC-6-42)-Ir(Cl)(PPh₃)₂(NHSO₂Ph)(CO)(η¹-CHCCH₂) (**4**). Complex **4** is stable in solution, and single crystals can be grown from CHCl₃/Et₂O cosolvent. X-ray crystallography affords the ORTEP drawing of **4** (Figure 1). It displays an octahedral configuration in which the amido ligand is trans to the η¹-allenyl group. The allenyl ligand is in a linear array with ∠C2–C3–C4 = 178(1)°, D(C2–C3) = 1.27(1) Å, and D(C3–C4) = 1.32(1) Å.^{3e} The single-bond distance of Ir–N and ∠Ir–N–S = 120.0(3) confirm the amide feature.⁹ The NMR studies show that protonation of **4** by HBF₄ or CF₃CO₂H instantaneously gives the amine derivative {(OC-6-42)-Ir(Cl)(PPh₃)₂(NH₂SO₂Ph)(CO)(η¹-CHCCH₂)}(BF₄) (**3j**).

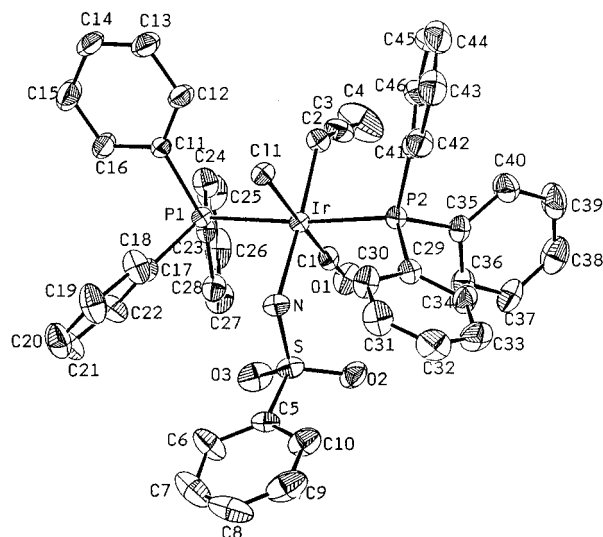
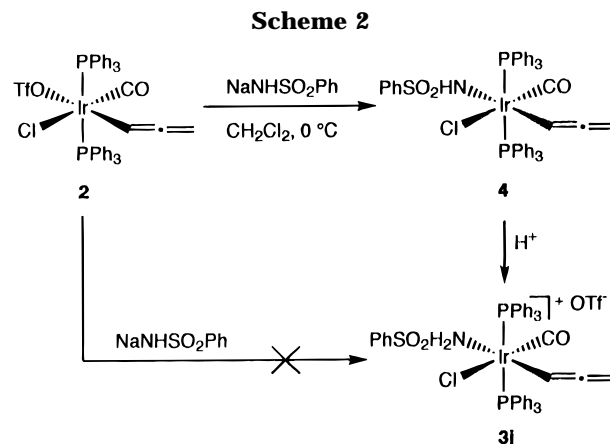


Figure 1. ORTEP drawing of (OC-6-42)Ir(Cl)(PPh₃)₂(NHSO₂Ph)(CO)(η¹-CHCCH₂) (**4**). All hydrogen atoms are omitted for clarity.

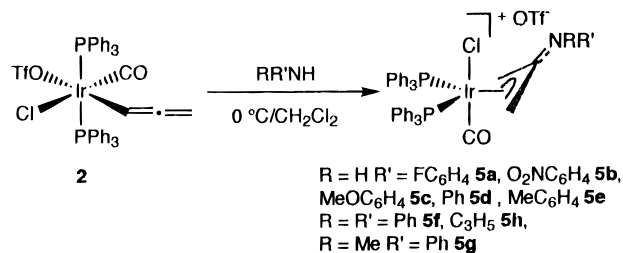


This formation of **3j** proves that the reaction of **2** with NH₂SO₂Ph is kinetically difficult. Weaker acids such as CH₃CO₂H and PhCO₂H take a couple of days to accomplish the protonation under the same conditions. Such experiments also confirm the amido character of **4** (Scheme 2).

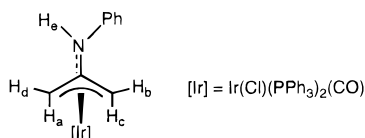
Reaction of Complex 2 with Aniline. Unlike the aforementioned reactions of **2** with ammonia or amine, when **2** reacts with aniline at 0 °C for 1 h, a light green compound designated as **5d** is produced in good yields. The tetrafluoroborate salt of **5d** can be obtained by first reacting **1c** and AgBF₄ in situ, followed by adding aniline. Complex **5d** is stable in air and in solution. Its ³¹P NMR spectrum shows two doublets at δ -11.2 and 10.1 with J_{p-p} = 3.1 Hz. In the ¹H spectrum of **5d**, the allenyl signals disappear. Instead, resonances at δ 2.43 (H_a), 2.80 (H_b), 3.16 (H_c), 3.62 (H_d) and 10.14 (H_e) with one-hydrogen integration for each are detected. The 2D H–H COSY spectrum exhibits H_a–H_d and H_b–H_c couplings, and the 1D NOE shows that the H_d signal gains 4.07% enhancement upon saturating H_e. Accordingly, **5d** is identified as the N-phenylated η³-

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Scheme 3



azatrimethylenemethane complex $\{\text{Ir}(\text{Cl})(\text{PPh}_3)_2(\text{CO})[\eta^3\text{-CH}_2\text{C}(\text{NHPh})\text{CH}_2]\}(\text{OTf})$. The singlet at δ 10.14 is assigned to the amino hydrogen H_e . The H_d and H_b signals, which displays similar patterns, are ascribed to the two syn hydrogen atoms and H_a and H_c to the anti hydrogens.



The ^{13}C NMR data at δ 169.6 and at δ 31.7, 39.5 correspond to the quaternary and secondary carbon atoms. These data are consistent with those of the known N-alkylated η^3 -aza-TMM iridium complexes.⁶ The C–H COSY spectrum indicates that the signal at δ 31.7 correlates with H_a and H_d and that at δ 39.5 correlates with H_b and H_c . The diastereotopic data of syn and anti hydrogens support the existence of the C=N double bond. The exchange between syn and anti hydrogens of **5d** is not observed even at 60 °C. In addition, the substituted aniline derivatives $\text{XC}_6\text{H}_4\text{NH}_2$ ($\text{X} = \text{F}$, NO_2 , OMe , Me) and other related compounds such as Ph_2NH and $\text{PhNH}(\text{Me})$ are also found to react with **2** to yield the N-arylated η^3 -aza-TMM complexes **5a–c, e–g**, respectively (Scheme 3). The reaction of **2** with diallylamine unexpectedly gives $\{\text{Ir}(\text{Cl})(\text{PPh}_3)_2(\text{CO})[\eta^3\text{-CH}_2\text{C}(\text{N}(\text{C}_3\text{H}_5)_2)\text{CH}_2]\}(\text{OTf})$ (**5h**).

The molecular structures of **5f** and **5g** determined by X-ray diffraction confirm our structural assignment for **5d**. The ORTEP drawing of **5g** is shown in Figure 2 as an example. Complex **5g** is in a distorted-trigonal-bipyramidal geometry with the chloride and the carbonyl at the axial sites, forming $\angle\text{Cl–Ir–C1} = 178.5(4)^\circ$. The two phosphines on the equatorial plane have $\angle\text{P1–Ir–P2} = 109.2(1)^\circ$. The organic ligand, which also sits on the equatorial plane, is bonded to the metal center in a η^3 mode. The dihedral angle between the C2–C3–C4 and C2–Ir–C4 planes is 47° . As a result, the central carbon is more distant from the metal than the terminal carbons with $D(\text{Ir–C2}) = 2.19(1)$ Å, $D(\text{Ir–C3}) = 2.50(1)$ Å, and $D(\text{Ir–C4}) = 2.21(1)$ Å. The amino group is attached to the central carbon C3 and approaches to the chloride end. This finding is in contrast to the structures of the N-protonated η^3 -aza-TMM iridium complexes, in which the amino substituent approaches the carbonyl end. The N–C3 bond is substantially a double bond. Besides, the rather planar relationship among the six atoms of C2–6 and N, as well as the small distortion angles of C5–N–C3–C4 ($4.6(9)^\circ$) and C5–N–C3–C2 ($-4.2(8)^\circ$) reveal the good $p\pi\text{–}p\pi$ interaction in the $\text{N}=\text{C3}$ bond. The C3–C4 and C3–C2 bonds are 1.40(2) and 1.45(2) Å, respectively. Other data are

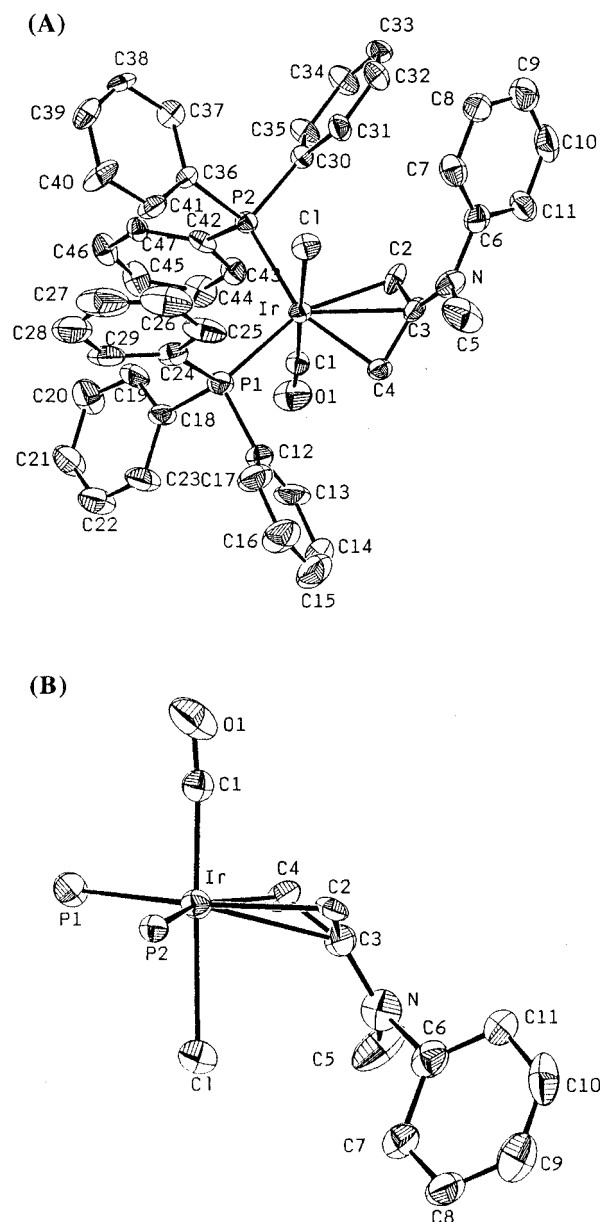
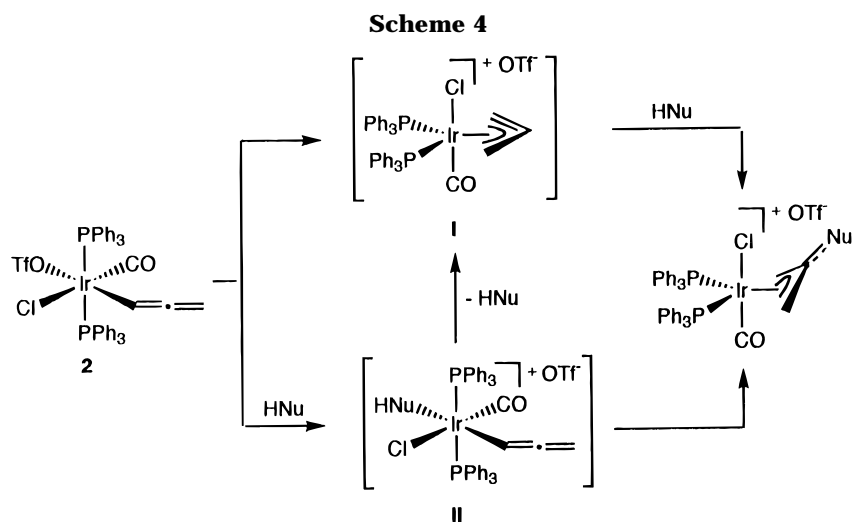


Figure 2. ORTEP drawing of $\{\text{Ir}(\text{Cl})(\text{PPh}_3)_2(\text{CO})[\eta^3\text{-CH}_2\text{C}(\text{NMePh})\text{CH}_2]\}(\text{OTf})$ (**5g**): (A) top view (all hydrogen atoms are omitted for clarity); (B) side view (all hydrogen atoms and the phosphino phenyls are omitted for clarity).

comparable with the structurally characterized N-protonated or N-alkylated η^3 -aza-TMM iridium complexes.

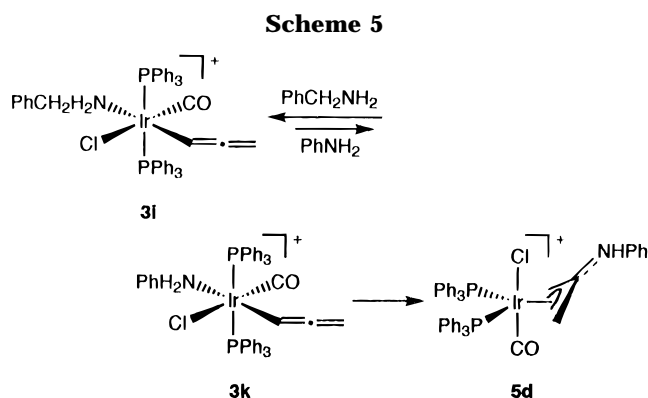
Mechanistic Studies of Hydroamination of Complex 2. The difference in the reactivity toward nucleophilic addition between **2** and **1a–c** is attributed to the replacement of a labile triflate ligand for the inert halide. The linear η^1 -allenyl ligand appears to be stable to external nucleophilic attack. A general mechanism for the nucleophilic addition of $(\eta^1\text{-allenyl})\text{iridium}$ is proposed in Scheme 4. In the first pathway, the dissociation of the triflate anion from **2** leads to the cationic η^3 -propargyl/allenyl species **I**, which is known to be subject to nucleophilic addition at the central carbon.⁴ In another pathway, the labile triflate ligand in **2** may be first replaced by aniline to form the nucleophile-ligated **II**. Complex **II** may form a product of addition either via an intramolecular process or through **I**.



The NMR measurements with temperature variation have supplied solid evidence for the occurrence of substitution. At 220 K, 35 mg of **2** and equimolar aniline was allowed to react in predried CDCl_3 . A metastable species designated as **3k** which showed a ^{31}P NMR peak at $\delta -15.7$ was first formed. The transformation was complete at 243 K. In comparison with the data for **2** and **3**, an η^1 -allenyl group and a carbonyl group in **3k** are evidenced by the ^1H and ^{13}C NMR spectra. A relatively broad signal at $\delta 5.3$ with two-hydrogen integration is ascribed to the amino hydrogens. The labeling experiments also shed light on the structural assignment for **3k**. The reaction of **2** and equimolar $^{13}\text{C}_6\text{H}_5\text{NH}_2$ gave the intermediate $^{13}\text{C}_6$ -**3k**. The ^{13}C signals of $^{13}\text{C}_6$ -**3k** were at $\delta 141.3$ for the *ipso*, $\delta 120.2$ for the *ortho*, $\delta 126.5$ for the *para*, and $\delta 129.5$ for the *meta* carbons. Accordingly, **3k** is identified as the aniline-ligated η^1 -allenyl complex $\{(OC-6-42)\text{-Ir}(\text{Cl})(\text{PPh}_3)_2(\text{NH}_2\text{Ph})(\text{CO})(\eta^1\text{-CHCCH}_2)\}(\text{OTf})$.

Coordinating the nucleophile to a metal allows us to facilitate addition to the allenyl ligand. Furthermore, the metal mediator in such a nucleophile addition of the coordinated allenyl group provides the implementation of selectivity into the chemical transformation. Adding 1 equiv of benzylamine to **3k** at 243 K followed by raising the reaction temperature to 273 K resulted in a mixture of the benzylamine-coordinated product **3i** and the N-phenylated η^3 -aza-TMM complex **5d** in 1:1.3 relative yields. Complex **3i** did not transform into the N-alkylated η^3 -aza-TMM complex but slowly decomposed in the reaction solution. We also allowed equimolar amounts of aniline and **3i** to mix at 25 °C. The reaction was monitored by ^1H NMR spectroscopy. After 3.5 h, **5d** appeared at the expense of **3i**, and the conversion was 46%. After 7 h, **5d** accounted for 96% stoichiometric molarity of iridium. We conclude that there is reversible ligand exchange between complexes **3i** and **3k**. The equilibrium favors the former species (Scheme 5). This is ascribed to the fact that the more electron-donating benzylamine is a stronger ligand than aniline.

The reaction course from **3k** to **5d** is not so explicit. Since **3i** and **3k** show distinct reactivities toward addition, one would suspect the presence of a η^3 -propargyl/allenyl intermediate which ought to be too reactive to discern the addition of aniline from benzylamine. Since the η^1 -allenyl ligand does not appeal to



direct external nucleophilic attack, **3k** likely transforms into **5d** via an intramolecular process. Scheme 6 depicts two possible mechanisms. The nucleophile-ligated allenyliridium complex **II** may proceed either via the metallacyclobutene **III** or via the π -allene complex **IV** to accomplish the hydroamination. In a general sense, a step of hydrogen transfer and a step of nucleophilic addition are involved in both paths, but with opposite orders. Such a mechanism is attractive for the following reasons. First, the formation of metallacyclobutene by nucleophilic addition,⁴ insertion into the coordinated allene,⁹ and the addition of anilide ligand to olefin are all documented.¹⁰⁻¹² Second, the relatively low basicity of water, alcohol, or aniline may facilitate the hydrogen transfer. With regard to ammonia, amide, and amine, their higher basicity perhaps hinders the N-H activation and thus retards the addition. We find that adding HBF_4 to the reaction solution does not cause any noticeable change of reactivity in such reactions, in accord with the intramolecular hydrogen transfer. It is difficult for us to explain why the reactions of **2** with methylphenylamine or diallylamine of high basicity still result in hydroamination.

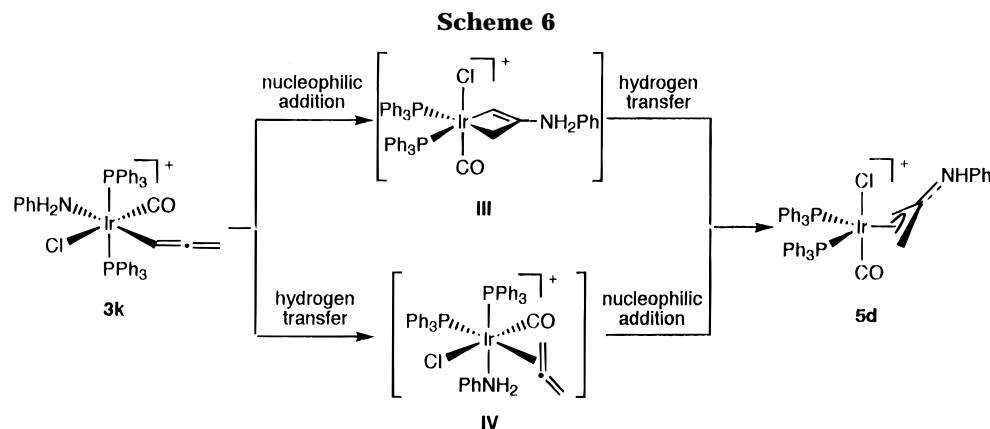
Concluding Remarks

Adding aniline or its relatives to a labile octahedral (η^1 -allenyl)iridium complex, $(OC-6-42)\text{-Ir}(\text{Cl})(\text{PPh}_3)_2(\text{OTf})(\text{CO})(\eta^1\text{-CHCCH}_2)$, at its central allenyl carbon

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leads to the formation of N-arylated iridium η^3 -azatri-methylenemethane species. In contrast, this (η^1 -allen-yl)iridium complex does not undergo addition with a stronger nucleophile such as ammonia or amine but suffers ligand substitution. A mechanistic study indicates that precoordination of the added nucleophile takes place first in these reactions. The coordinating nucleophile thereby allows the metal to play a prominent role in facilitating the addition process that comprises the activation of the N–H bond and the formation of the C=N bond, as well as to provide the implementation of selectivity into the chemical transformation.

Experimental Section

General Considerations. Commercially available reagents were purchased and used without purification. Solvents were dried by means of standard procedures. The IR spectra were recorded on a Bio-Rad FTS-40 spectrophotometer. The NMR spectra were routinely measured on Bruker ACE-200 and ACE-300 spectrometers. For the ^{31}P NMR spectra, the spectrometer frequency 81.015 or 121.49 MHz was employed, respectively, and the chemical shifts are given in ppm (δ) relative to 85% H_3PO_4 in CDCl_3 . The corresponding frequencies for ^{13}C NMR spectra were at 50.32, 75.47, or 125.76 MHz for the various spectrometers.

Synthesis and Characterization. (OC-6-42)-[Ir(Cl)-(PPh₃)₂(NCMe)(CO)(η^1 -CHCCH₂)]-(OTf) (3a). To a CDCl_3 solution containing **2** (30 mg) was added 1 equiv of acetonitrile, and the product was monitored by NMR. ^{31}P NMR (CDCl_3): δ -12.6. ^1H NMR (CDCl_3): δ 1.81 (3H, s, CH_3), 3.68 (2H, dt, $J_{\text{H-H}} = 6$ Hz, $J_{\text{P-H}} = 2.9$ Hz, CH_2), 5.72 (1H, tt, $J_{\text{H-H}} = 6$ Hz, $J_{\text{P-H}} = 3.1$ Hz, CH), 6.7–7.8 (30H, m, phenyl H). ^{13}C NMR (CDCl_3): δ 2.96 (s, CH_3), 57.7 (s, CH), 70.7 (s, CH_2), 116.9 (s, CN), 123–134 (phenyl C), 156.7 (s, CO), 207.1 (t, $J_{\text{P-C}} = 2.8$ Hz, C_β).

(OC-6-42)-[Ir(Cl)(PPh₃)₂(NCCH₂Ph)(CO)(η^1 -CHCCH₂)]-(OTf) (3b). To a mixture that contains **1c** (250 mg, 0.28 mmol) and AgOTf (1.1 equiv) was added 15 mL of N_2 -degassed dry CH_2Cl_2 at -30 °C followed by benzylnitrile (32 μL , 1 equiv). The reaction solution was stirred at 0 °C for 1 h. After removal of AgBr, the reaction solution was concentrated. The addition of dry Et_2O to the solution resulted in a yellow solid product. The isolated yield of **3b** was 57% (173 mg) after recrystallization. IR (KBr pellet): $\nu_{\text{C=C}} = 1926$ cm^{-1} , $\nu_{\text{CO}} = 2073$ cm^{-1} . ^{31}P NMR (CDCl_3): δ -11.4. ^1H NMR (CDCl_3): δ 3.67 (2H, m, CCH_2), 3.68 (2H, s, PhCH_2), 5.70 (1H, tt, $J_{\text{H-H}} = 6.2$ Hz, $J_{\text{P-H}} = 2.7$ Hz, CHC), 6.82–7.71 (35H, m, phenyl H). ^{13}C NMR (CDCl_3): δ 58.4 (s, CH), 65.9 (s, CH_2), 123–134 (phenyl C), 156.6 (t, $J_{\text{P-C}} = 5.5$ Hz, CO), 206.9 (s, C_β). FAB MS (m/z): 819.4 ($\text{M}^+ - 117$). Anal. Calcd for $\text{IrC}_{49}\text{H}_{40}\text{O}_4\text{ClNP}_2\text{SF}_3$: C, 54.19; H, 3.71; N, 1.29. Found: C, 54.38; H, 3.86; N, 1.14.

(OC-6-42)-[Ir(Cl)(PPh₃)₂(NC₆H₅)(CO)(η^1 -CHCCH₂)]-(OTf) (3c). Refer to the procedure for **3b**. The isolated yield of light green **3c** was 61% (210 mg) after recrystallization. IR (KBr pellet): $\nu_{\text{C=C}} = 1923$ cm^{-1} , $\nu_{\text{CO}} = 2055$ cm^{-1} . ^{31}P NMR (CDCl_3): δ -11.4. ^1H NMR (CDCl_3): δ 3.77 (2H, dt, $J_{\text{H-H}} = 6.3$ Hz, $J_{\text{P-H}} = 3.6$ Hz, CH_2), 6.1 (1H, tt, $J_{\text{H-H}} = 6.3$ Hz, $J_{\text{P-H}} = 3.2$ Hz, CH), 6.7–8.5 (35H, m, phenyl H). ^{13}C NMR (CDCl_3): δ 55.7 (s, CH), 69.8 (s, CH_2), 118–155 (phenyl C), 159.7 (s, CO), 208.3 (t, $J_{\text{P-C}} = 3.5$ Hz, C_β). FAB MS (m/z): 898.5 (M^+).

(OC-6-42)-[Ir(Cl)(PPh₃)₂(NH₂NH₂)(CO)(η^1 -CHCCH₂)]-(OTf) (3e). Refer to the procedure for **3b**. The isolated yield of **3e** was 69% (138 mg) after recrystallization. IR (KBr pellet): $\nu_{\text{C=C}} = 1925$ cm^{-1} , $\nu_{\text{CO}} = 2067$ cm^{-1} . ^{31}P NMR (CDCl_3): δ -11.2. ^1H NMR (CDCl_3): δ 3.44 (2H, br, NH), 3.60 (2H, dt, $J_{\text{H-H}} = 6.4$ Hz, $J_{\text{P-H}} = 3.7$ Hz, CH_2), 4.95 (2H, br, NH), 5.89 (1H, tt, $J_{\text{H-H}} = 6.4$ Hz, $J_{\text{P-H}} = 3.0$ Hz, CH), 7.2–7.9 (30H, m, phenyl H). ^{13}C NMR (CDCl_3): δ 56.7 (t, $J_{\text{P-C}} = 8$ CH), 69.2 (s, CH_2), 122–135 (phenyl C), 158.4 (t, $J_{\text{P-C}} = 7.8$ Hz, CO), 208.0 (s, C_β).

(OC-6-42)-[Ir(Cl)(PPh₃)₂(NH₂Me)(CO)(η^1 -CHCCH₂)]-(OTf) (3f). The reaction of **2** (30 mg) and MeNH_2 (1 equiv of aqueous solution) was carried out in CDCl_3 (0.5 mL) in an NMR tube, and the complex **3f** was characterized only by NMR techniques. ^{31}P NMR (CDCl_3): δ -12.9. ^1H NMR (CDCl_3): δ 3.16 (2H, br, NH), 3.18 (3H, t, $J_{\text{H-H}} = 6.2$ Hz, CH_3), 3.61 (2H, dt, $J_{\text{H-H}} = 6.2$ Hz, $J_{\text{P-H}} = 3.6$ Hz, CH_2), 5.97 (1H, tt, $J_{\text{H-H}} = 6.2$ Hz, $J_{\text{P-H}} = 3.2$ Hz, CH), 7.2–7.9 (30H, m, phenyl H). ^{13}C NMR (CDCl_3): δ 32.2 (s, CH_3), 55.1 (t, $J_{\text{P-C}} = 7.5$, CH), 69.2 (s, CH_2), 118–135 (phenyl C), 158.4 (t, $J_{\text{P-C}} = 6.9$ Hz, CO), 207.6 (s, C_β).

(OC-6-42)-[Ir(Cl)(PPh₃)₂(NH₂Et)(CO)(η^1 -CHCCH₂)]-(OTf) (3g). Refer to the procedure for **3b**. The isolated yield of **3g** was 53% (182 mg) after recrystallization. IR (KBr pellet): $\nu_{\text{C=C}} = 1923$ cm^{-1} , $\nu_{\text{CO}} = 2059$ cm^{-1} . ^{31}P NMR (CDCl_3): δ -12.1. ^1H NMR (CDCl_3): δ 0.30 (3H, t, $J_{\text{H-H}} = 6.9$ Hz, CH_3), 2.03 (2H, q, $J_{\text{H-H}} = 6.9$ Hz, CH_2), 2.87 (2H, br, NH), 3.59 (2H, dt, $J_{\text{H-H}} = 6.4$ Hz, $J_{\text{P-H}} = 3.6$ Hz, CH_2), 6.00 (1H, tt, $J_{\text{H-H}} = 6.4$ Hz, $J_{\text{P-H}} = 3.2$ Hz, CH), 6.7–8.0 (30H, m, phenyl H). ^{13}C NMR (CDCl_3): δ 17.4 (s, CH_3), 42.0 (s, CH_2), 55.1 (t, $J_{\text{P-C}} = 8$ Hz, CH), 69.4 (s, CH_2), 117–135 (phenyl C), 158.6 (s, CO), 208.4 (t, $J_{\text{P-C}} = 3.5$ Hz, C_β). FAB MS (m/z): 864.4 (M^+). Anal. Calcd for $\text{IrC}_{43}\text{H}_{40}\text{O}_4\text{ClNP}_2\text{SF}_3$: C, 50.93; H, 3.98; N, 1.38. Found: C, 50.90; H, 3.98; N, 1.43.

(OC-6-42)-[Ir(Cl)(PPh₃)₂(NH₂ⁱPr)(CO)(η^1 -CHCCH₂)]-(OTf) (3h). Refer to the procedure for **3f**. ^{31}P NMR (CDCl_3): δ -14.8. ^1H NMR (CDCl_3): δ 0.43 (6H, d, $J_{\text{H-H}} = 6.1$ Hz, CH_3), 2.54 (1H, m, $J_{\text{H-H}} = 6.1$ Hz, CHMe_2), 3.00 (2H, br, NH_2), 3.44 (2H, m, CH_2), 6.11 (1H, tt, $J_{\text{H-H}} = 6.1$ Hz, $J_{\text{P-H}} = 3.2$ Hz, CH), 7.2–7.9 (30H, m, phenyl H). ^{13}C NMR (CDCl_3): δ 23.4 (s, CH_3), 51.4 (s, CHMe_2), 53.7 (t, $J_{\text{P-C}} = 8.6$ Hz, CH), 69.5 (s, CH_2), 125–135 (phenyl C), 159.6 (t, $J_{\text{P-C}} = 7.1$ Hz, CO), 207.3 (t, $J_{\text{P-C}} = 2.6$ Hz, C_β).

(OC-6-42)-[Ir(Cl)(PPh₃)₂(NH₂CH₂Ph)(CO)(η^1 -CHCCH₂)]-(OTf) (3i). Refer to the procedure for **3b**. The isolated yield

Table 1. X-ray Crystal Parameters and Data Collection

	4	5f	5g
formula	IrClSP ₂ O ₃ NC ₄₆ H ₃₉ ·2CH ₂ Cl ₂	IrClSP ₂ F ₃ O ₄ NC ₅₃ H ₄₄	IrClSP ₂ F ₃ O ₄ NC ₄₈ H ₄₁ ·0.5CH ₂ Cl ₂
fw	1145.36	1137.60	1116.99
cryst dimens, mm	0.04 × 0.40 × 0.45	0.04 × 0.08 × 0.15	0.20 × 0.30 × 0.50
space group	<i>P2₁/n</i>	<i>P2₁/c</i>	<i>Pbcn</i>
<i>a</i> , Å	10.210(2)	12.216(1)	37.838(9)
<i>b</i> , Å	20.265(3)	35.803(6)	10.728(3)
<i>c</i> , Å	23.677(6)	11.287(2)	23.661(6)
α, deg	90	90	90
β, deg	101.02(2)	98.07(1)	90
γ, deg	90	90	90
<i>V</i> , Å ³	4809(2)	4888(1)	9605(4)
<i>Z</i>	4	4	8
ρ(calcd), Mg m ⁻³	1.582	1.546	1.545
<i>F</i> (000)	2278	2268	4441
radiation; λ, Å	Mo Kα; 0.7107	Mo Kα; 0.7107	Mo Kα; 0.7107
<i>T</i> , K	298	298	298
μ, mm ⁻¹	2.96	2.94	2.99
transmission	0.58–1.0	0.92–1.0	0.86–1.0
max 2θ, deg	50	45	45
<i>hkl</i>	±12,24,28	±13,38,12	40,11,25
no. of rflns measd	8440	6358	6253
no. of rflns obsd	5091 (>2.0σ)	2950 (>2.0σ)	3594 (>2.0σ)
no. of variables	551	595	550
<i>R</i> (<i>F</i>)	0.037	0.073	0.052
<i>R_w</i> (<i>F</i>)	0.037	0.074	0.051
<i>S</i>	1.30	2.25	1.93
(Δ/ <i>σ</i>) _{max}	0.0137	0.1350	0.0308

Table 2. Selected Bond Distances (Å) and Angles (deg)

<i>(OC-6-42)-Ir(Cl)(PPh₃)₂(NH₂SO₂Ph)(CO)(η¹-CHCCH₂) (4)</i>							
Ir–Cl(1)	2.407(2)	Ir–C1	1.829(8)	C3–C4	1.32(1)	S–O2	1.435(6)
Ir–P1	2.402(2)	Ir–C2	2.079(7)	S–N	1.580(6)	S–O3	1.453(6)
Pt–P2	2.410(2)	C1–O1	1.145(9)	S–C5	1.772(8)		
Ir–N	2.158(6)	C2–C3	1.27(1)				
Cl1–Ir–P1	90.62(7)	P1–Ir–C2	87.9(2)	Cl–Ir–C2	87.5(3)	Ir–N–S	120.0(3)
Cl1–Ir–P2	85.75(7)	P1–Ir–N	90.8(2)	N–S–C5	104.3(3)	Ir–C1–O1	177.5(6)
Cl1–Ir–C2	178.9(2)	P2–Ir–C1	93.3(2)	N–S–O2	110.4(4)	Ir–C2–C3	128.4(6)
Cl1–Ir–C2	91.9(2)	P2–Ir–C2	88.2(2)	N–S–O3	112.2(3)	C2–C3–C4	178(1)
Cl1–Ir–N	85.0(2)	P2–Ir–N	92.8(2)	C5–S–O2	108.2(4)	S–C5–C6	120.4(7)
P1–Ir–P2	174.58(7)	C1–Ir–N	95.6(3)	C5–S–O3	106.6(4)	S–C5–C10	119.1(7)
P1–Ir–C1	90.3(2)	C2–Ir–N	176.7(3)	O3–S–O2	114.5(4)		
<i>{Ir(Cl)(PPh₃)₂(CO)[η³-CH₂C(NPh₂)CH₂]}(OTf) (5f)</i>							
Ir–Cl	2.376(9)	Ir–C2	2.18(3)	C5–N	1.46(3)	C2–C3	1.41(4)
Ir–P1	2.422(8)	Ir–C3	2.54(3)	C11–N	1.44(4)	C3–C4	1.54(4)
Ir–P2	2.403(8)	Ir–C4	2.15(3)	C1–O1	1.05(4)		
Ir–C1	1.86(3)	C3–N	1.31(3)				
Cl–Ir–P1	89.4(3)	P1–Ir–C4	91.5(7)	C2–Ir–C4	66(1)	Ir–C4–C3	85(2)
Cl–Ir–P2	91.8(3)	P2–Ir–Cl	93(1)	C3–Ir–C4	37.3(9)	Ir–C3–N	136(2)
Cl–Ir–Cl	174(1)	P2–Ir–C2	94.0(7)	C3–N–C5	118(2)	C2–C3–C4	105(2)
Cl–Ir–C2	88.5(8)	P2–Ir–C3	125.4(6)	C3–N–C11	118(2)	C2–C3–N	125(3)
Cl–Ir–C3	76.7(7)	P2–Ir–C4	158.6(7)	C5–N–C11	124(2)	C4–C3–N	128(2)
Cl–Ir–C4	93.9(8)	C1–Ir–C2	87(1)	Ir–C1–O1	158(3)	N–C5–C6	120(3)
P1–Ir–P2	109.2(3)	C1–Ir–C3	97(1)	Ir–C2–C3	87(2)	N–C5–C10	123(3)
P1–Ir–C1	92.7(9)	C1–Ir–C4	80(1)	Ir–C3–C4	61.4(1)	N–C11–C12	114(2)
P1–Ir–C2	156.8(7)	C2–Ir–C3	33.9(9)	Ir–C3–C2	59(2)	N–C11–C16	117(3)
P1–Ir–C3	123.5(6)						
<i>{Ir(Cl)(PPh₃)₂(CO)[η³-CH₂C(NMePh)CH₂]}(OTf) (5g)</i>							
Ir–Cl	2.390(4)	Ir–C2	2.19(1)	C5–N	1.46(2)	C2–C3	1.40(2)
Ir–P1	2.429(4)	Ir–C3	2.50(1)	C6–N	1.47(2)	C3–C4	1.45(2)
Ir–P2	2.416(3)	Ir–C4	2.21(1)	C1–O1	1.05(2)		
Ir–C1	1.86(1)	C3–N	1.32(2)				
Cl–Ir–P1	92.9(1)	P1–Ir–C3	124.9(3)	C2–Ir–C3	33.8(4)	Ir–C3–C2	61.0(7)
Cl–Ir–P2	86.3(1)	P1–Ir–C4	92.9(3)	C2–Ir–C4	63.8(5)	Ir–C4–C3	83.4(7)
Cl–Ir–C1	178.5(4)	P2–Ir–Cl	94.4(4)	C3–Ir–C4	35.2(4)	Ir–C3–N	137(1)
Cl–Ir–C2	88.7(3)	P2–Ir–C2	94.1(3)	C3–N–C5	123(1)	C2–C3–C4	110(1)
Cl–Ir–C3	74.6(3)	P2–Ir–C3	122.7(3)	C3–N–C6	120(1)	C2–C3–N	126(1)
Cl–Ir–C4	88.8(4)	P2–Ir–C4	157.5(3)	C5–N–C6	116(1)	C4–C3–N	123(1)
P1–Ir–P2	109.2(1)	C1–Ir–C2	89.9(5)	Ir–C1–O1	173(1)	N–C6–C7	118(1)
P1–Ir–C1	88.2(4)	C1–Ir–C3	103.9(5)	Ir–C2–C3	85.1(8)	N–C6–C11	121(1)
P1–Ir–C2	156.7(4)	C1–Ir–C4	90.1(5)	Ir–C3–C4	61.4(6)		

X-ray Crystallographic Analysis. Diffraction data were measured at 298 K on a Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. Cell parameters

were determined by a least-squares fit on 25 reflections. Intensity data were corrected for absorption on the basis of an experimental ψ rotation curve. The refinement procedure

was by a full-matrix least-squares method including all the non-hydrogen atoms anisotropically. Hydrogen atoms were fixed at the ideal geometry and the C–H distance of 1.0 Å; their isotopic thermal parameters were fixed to the values of the attached carbon atoms at the convergence of the isotropic refinement. Atomic scattering factors were taken from ref 13. Computing programs are from the NRCC SDP VAX package.¹⁴ Crystallographic data and selected bond parameters for **4**, **5f**,

and **5g** are collected in Tables 1 and 2. Other detailed data are supplied in the Supporting Information.

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Supporting Information Available: Complete listings of crystal data, bond lengths and angles, atomic coordinates, and thermal parameters and figures giving fully labeled ORTEP drawings for **4**, **5f**, and **5g** (32 pages). Ordering information is given on any current masthead page.

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