Intra- and Intermolecular Hydroamination of Alkynes Catalyzed by *ortho*-Metalated Iridium Complexes

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Received October 21, 2006

Reaction of *o*-(diphenylphosphino)(*N*-benzylidene)aniline (**P**∼**N**) with $[Ir(COD)Cl]_2$ affords the substitution product [(**P**∼**N**)Ir(COD)Cl] (**1**). Treatment of **1** with $AgBF_4$ yields the cyclometalated iridium hydride complex [*P,N,C*-(**P**∼**N**)Ir(COD)H]BF_4 (**2**). On the other hand, under atmospheric pressure of CO, carrying out the substitution of $[Ir(COD)Cl]_2$ with **P**∼**N** results in the formation of [*P,N,C*-(**P**∼**N**)-Ir(CO)HCl] (**5**). Conversion of **4** into **5** can be achieved by the reaction of **4** with CO in the presence of tetraethylammonium chloride. Both **4** and **5** are characterized by spectroscopic and X-ray structural analyses. All iridium complexes are not good catalysts for hydroamination. However, the combination of **5** with $NaB[3,5\text{-}C_6H_3(CF_3)_2]_4$ (denoted as $NaBAr^F{}_4$) provides a potent catalytic system for both intra- and intermolecular hydroamination of alkynes. Intramolecular reaction of *o*-(2-phenylethynyl)anilines produces the corresponding indoles in good yields. Furthermore, intermolecular hydroamination takes place smoothly to generate the imine intermediates, which could be subsequently reduced by triethylsilane using the same catalyst, giving *N*-silylated amines. However, the *N*-silylated amines readily hydrolyze to produce secondary amines.

Introduction

Intramolecular metal-catalyzed hydroamination of alkynes, leading to *N*-heterocycles, has received considerable attention due to the important applications of these products in pharmaceutics.[1−9] For example, the cyclization of *o*-alkynylanilines is a direct approach for the synthesis of indoles.[2−5,7] Among them, however, few involve the use of iridium complexes as the catalyst.[6−9] In a recent work, Crabtree and coworkers found that iridium hydride complex **I** (Chart 1) could catalyze the cyclization of *o*-alkynylanilines efficiently to yield the desired products.[6] Messerle's group reported that cationic complex **II** possessed an excellent activity on the hydroamination of 4-pentyn-1-amine to form 2-methylpyrroline.[8] Other iridium complexes used for the hydroamination of alkynes are summarized in Chart 1.[6−9] As seen in Chart 1, despite the hydroamination reactions catalyzed by Ir(I) and Ir(III) complexes, in which various donor atoms have been employed, none of these donor systems involve the phosphine-imine bidentate.

During the past few years, we have made great efforts in the preparation of metal complexes containing *o*-(diphenylphosphino)(*N*-benzylidene)aniline (**P**∼**N**) and subsequently studying their catalytic activities.[10] We have shown that palladium complexes with the **P**∼**N** bidentate are excellent catalysts for the polymerization and/or copolymerization of olefins/CO and

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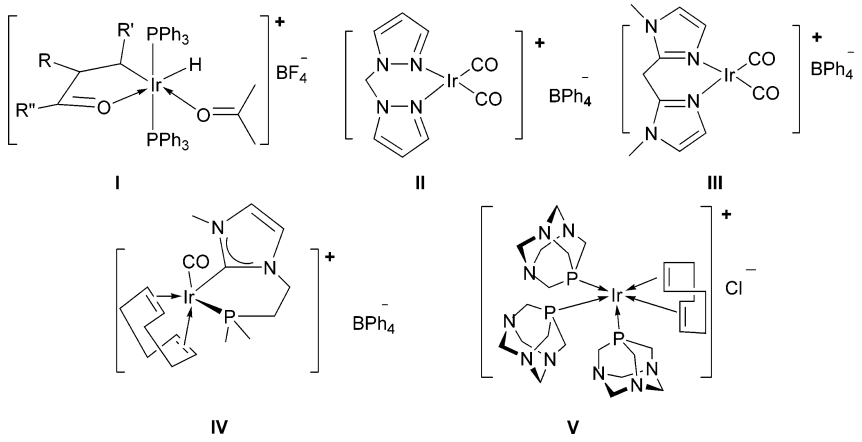
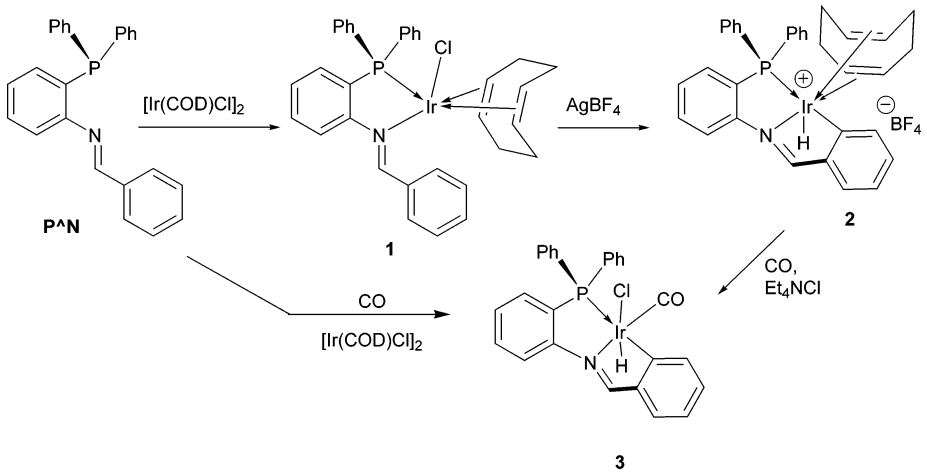
10.1021/om060965c CCC: $37.00
Publication on Web 01/12/2007

Chart 1



Scheme 1



the Heck coupling reaction due to the nature of the σ-donating phosphine and π-accepting imine-nitrogen of this bidentate.[11] As an extension of our previous investigations on the ligand effect of the catalysis, we report a comprehensive study of coordination of **P∼N** toward iridium ions and their catalytic activities on the hydroamination of alkynes.

Results and Discussion

Synthesis of Iridium Complexes. Substitution reaction of $[Ir(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) with the **P∼N** ligand in a THF solution provided the neutral iridium complex **1** in 90% yield (Scheme 1). Recrystallization from a mixture of dichloromethane and diethyl ether gave the analytically pure orange solid. Spectroscopic and elemental analyses confirm the structure of the complex (Table 1). A downfield shift (ca. 30 ppm) of the iridium complex in the ^{31}P NMR with respect to the free ligand suggests the coordination of the phosphine toward the iridium center. Although the resonance of the imine-hydrogen in **1** is slightly upfield shifted (0.03 ppm) from the **P∼N** ligand, it is believed that the nitrogen donor is coordinated to the metal center due to the chelation effect of the rigid *o*-phenylene linkage.[10] The nonconductive nature of this complex in dichloromethane by the conductivity measurement indicates that the chloride ligand is coordinated to the metal center.

Table 1. Selected Spectroscopic Data of Free Ligand and Its Iridium Complexes[a]

	^{1}H NMR (J in Hz)		^{31}P NMR
	Ir−H	−*H*C=N	
P∧N		8.34	−13.6
1		8.31	17.6
2	−12.78 (d, J_{P-H} = 17)[b]	9.76	13.0
5	−15.1 (d, J_{P-H} = 12)	9.81	15.3

[a] In acetone-d_6. [b] −70 °C.

Instead of the formation of $[(\mathbf{P}\sim\mathbf{N})Ir(COD)]BF_4$, reaction of an equal molar amount of complex **1** with silver tetrafluoroborate in THF solution afforded the cyclometalated hydride complex **2** as a green solid in 93% yield. This complex was fully characterized by ^{1}H and ^{31}P NMR spectroscopy as well as crystal structural analyses. Coordination chemical shifts of the ^{31}P NMR for the phosphine and ^{1}H NMR for the imine-hydrogen clearly reflect the coordination of both phosphorus and nitrogen donors to the metal center. The ^{1}H NMR spectrum of **2** is quite complicated, but it is clearly identified that 12 magnetically different resonances for cyclooctadiene and a resonance at δ −12.78 (assigned to the iridium hydride) are present. However, these spectroscopic data cannot easily convey the exact coordination arrangement of these donors around the metal center.

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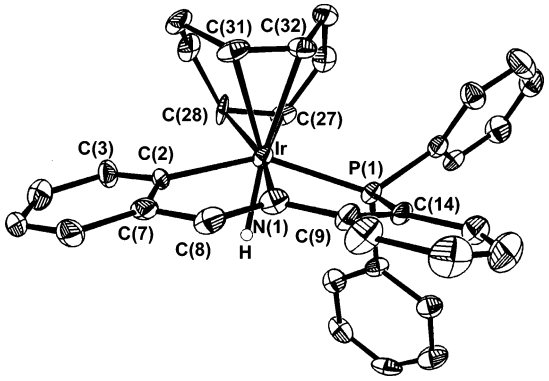

Figure 1. ORTEP plot of the cationic portion of complex **2** (drawn with 30% probability ellipsoids).

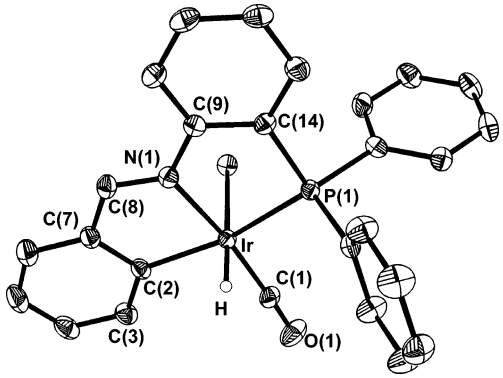

Figure 2. ORTEP plot of complex **3** (drawn with 30% probability ellipsoids).

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) of 2 and 3

	2	**3**
Ir−N(1)	2.095(9)	2.088(2)
Ir−P(1)	2.346(3)	2.3469(7)
Ir−C(2)	2.10(1)	2.069(3)
N(1)−C(8)	1.30(2)	
N(1)−C(9)	1.42(1)	1.437(4)
Ir−C(1)		1.855(3)
Ir−Cl(1)		2.4875(7)
C(1)−O(1)		1.146(4)
N(1)−Ir−C(2)	78.4(4)	79.3(1)
N(1)−Ir−P(1)	80.1(3)	82.54(7)
P(1)−Ir−C(2)	147.9(3)	160.70(9)
Ir−N(1)−C(9)	122.2(9)	121.8(2)
Ir−N(1)−C(8)	114.6(9)	115.1(2)

Single crystals of **2**•2CH_2Cl_2 suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into its dichloromethane solution. An ORTEP drawing of the cationic part of **2** is illustrated in Figure 1, and selected distances as well as bond angles are listed in Table 2. Complex **2** exists as a distorted octahedral geometry with the **P**∧**N** ligand being *P,N,C*-bonded and the remaining coordination sites containing the hydride and the C═C double bonds of the chelated cyclooctadiene. One of the double bonds lies at the apical position, *trans* to the hydride, which allows all the protons of COD to be in magnetically nonequivalent environments. The position of the hydride was calculated to be 1.59 Å below the plane defined by the organic ligand and the metal atom, which is similar to those related species.[12] The observation of the bonding of carbon C(2) to the metal center clearly indicates that the cyclometalation takes place at the *ortho* position of the phenyl ring. The dihedral angle between the two chelating planes defined by Ir−C(2)−C(7)−C(8)−N(1) and Ir−P(1)−C(14)−C(9)−N(1) is calculated to be 19.2°, which deviates from the planar arrangement. All bond distance and angles are in normal ranges.

As shown in Scheme 1, substitution of $[Ir(COD)Cl]_2$ with the **P**∼**N** ligand in the presence of carbon monoxide also provided the cyclometalated metal carbonyl complex **3**, which was isolated as a yellow solid. Alternatively, treatment of **2** with tetraethylammonium chloride in the presence of CO affords complex **3** quantitatively. Both spectroscopic and X-ray crystallographic analyses confirm the structure of the complex. Infrared absorption for the stretching band of carbonyl appears at 2019 cm^{-1}. Similar to complex **2**, the coordination shifts of the ^{31}P NMR for the phosphine and ^1H NMR for the imine-hydrogen prove that both the phosphorus and nitrogen donors are still coordinated to the iridium center. A downfield shift at δ −13 on the ^1H NMR spectrum clearly reveals the existence of a metal hydride.

X-ray-quality crystals of **3**•CH_2Cl_2 were obtained by a method similar to that described for **2**. An ORTEP diagram of **3** is shown in Figure 2. The coordination sphere of iridium is roughly octahedral for **3**. The distance of Ir−C(2) [2.069(3) Å] (Table 2) is similar to that of **2**, indicating the formation of an iridium−carbon bond via metalation. The dihedral angle between the two chelating planes defined by Ir−C(2)−C(7)−C(8)−N(1) and Ir−P(1)−C(14)−C(9)−N(1) is calculated to be 5.85°, smaller than that of **2**, suggesting that two chelating fused rings are in an approximately planar arrangement. The hydride *trans* to the chloride is located 1.76 Å below the chelating plane.

Intramolecular Hydroamination Leading to Indoles. The iridium complexes prepared in this work involving Ir(I) and Ir(III) species were subjected to the catalytic test for the intramolecular hydroamination of *o*-alkynylanilines to produce indoles. In this screen, *o*-(2-phenylethynyl)aniline was treated with 5 mol % of each complex in refluxing toluene, and the reactions were monitored by ^1H NMR spectroscopy. None of the complexes **1**−**3** is a good catalyst to promote the intramolecular cyclization effectively (entries 1−3, Table 3), but in the presence of sodium tetrakis(3,5-trifluoromethylphenyl)borate ($NaBAr^F_4$) the iridium carbonyl complex **3** becomes as an effective catalyst for the reaction (entry 4, Table 3). In the absence of $NaBAr^F_4$, no reaction occurs even at refluxing temperature for 48 h. It is known that the sodium borate salt is able to abstract the chloride from the metal center, which allows the metal complex to form the corresponding cationic species.[13] Presumably, the cationic $[P,N,C\text{-}(\mathbf{P}{\sim}\mathbf{N})IrH(CO)]^+$ is responsible for the catalysis. The catalyst efficiency is solvent dependent, and both dichloromethane and toluene are good media for the hydroamination. Nevertheless, carrying out the reaction in toluene is faster than that in CH_2Cl_2 due to the higher boiling point of the former. It is also noticed that the anions influence the effectiveness of the catalyst. The complex associated with the tetrakis(3,5-trifluoromethylphenyl)borate anion appears to be more active (entries 10, 11, Table 3) than **3** with any other anions. It is worth mentioning that the catalysis with the tetrafluoroborate salt slowly precipitates metal blacks during the reaction, but not for $BAr^F_4{}^-$, showing that the cationic

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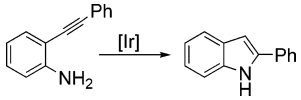
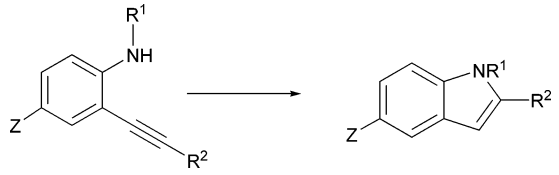
Table 3. Cyclization of *o*-(2-Phenylethynyl)aniline Catalyzed by Iridium Complexes[a]



entry	catalyst	solvent	additive	*T* (°C)	time (h)	yield
1	**1**	toluene		110	24	33%
2	**2**	toluene		110	24	41%
3	**3**	toluene		110	48	NR[b]
4	**3**	CH_2Cl_2	$NaBAr^F_4$ (5 mol %)	40	24	100%
5	**3**	THF	$NaBAr^F_4$ (5 mol %)	65	24	26%
6	**3**	EtOH	$NaBAr^F_4$ (5 mol %)	78	24	<5%
7	**3**	CH_3CN	$NaBAr^F_4$ (5 mol %)	81	24	NR
8	**3**	toluene	$NaBAr^F_4$ (1 mol %)	110	12	100%
9	**3**	CH_2Cl_2/CH_3CN	$NaBAr^F_4$ (5 mol %)	40	24	NR
10	**3**	CH_2Cl_2	$NaBF_4$ (5 mol %)	40	24	NR
11	**3**	CH_2Cl_2	$AgBF_4$ (5 mol %)	40	24	40%

[a] Reaction conditions: *o*-(2-phenylethynyl)aniline (1 mmol), iridium complex (0.05 mmol) in solvent (2 mL). [b]NR = no reaction.

Table 4. Formation of Indoles Catalyzed by 3



entry	substrate	time (h)	yield[b]	TON[d]
1	R^1 = H; R^2 = Ph; Z = H	12	95%	95
2	R^1 = H; R^2 = n-Bu; Z = H	6	96%	96
3	R^1 = H; R^2 = n-Bu; Z = CH_3	6	96%	96
4	R^1 = H; R^2 = Ph; Z = CH_3	12	96%	96
5	R^1 = CH_3CO; R^2 = n-Bu; Z = H	24	21%	21
6	R^1 = H; R^2 = Ph; Z = NO_2	24	16%	16
7	R^1 = H; R^2 = n-Bu; Z = NO_2	24	trace	
8	R^1 = H; R^2 = n-Bu; Z = Cl	24	84%	84
9	R^1 = H; R^2 = Ph; Z = Cl	24	27%	27
10[c]	R^1 = H; R^2 = H; Z = H	24	10%	10

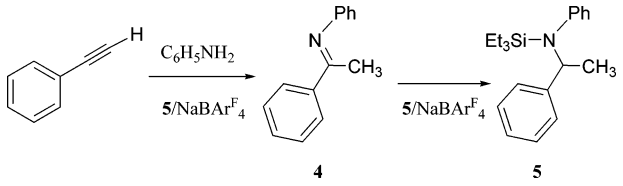
[a] Reaction conditions: substrate (1 mmol), **3** (0.01 mmol), $NaBAr^F_4$ (0.0105 mmol) in refluxing toluene (2 mL). [b]Isolated yield. [c]All of the starting materials were consumed in the catalysis. [d]TON = turnover number (mol of product/per mol of catalyst used).

iridium complex with the tetrakis(3,5-trifluoromethylphenyl)-borate anion is more stable than that with the tetrafluoroborate salt.

Intramolecular hydroaminations of other amine-alkynes were examined by using this iridium-catalyzed protocol, and the results are depicted in Table 4; a family of indoles, including methyl-, nitro-, chloro-, or acetyl-substituted indoles, can be prepared. However, the yields appear to be lower with the electron-withdrawing substituents on either the nitrogen or the aromatic ring, presumably due to the less nucleophilic nature of the amines. Cyclization of *o*-ethynylaniline, a terminal alkyne, provided a poor yield of the desired product (entry 10, Table 4), but all of the reactants were consumed. In fact, we did isolate the tri- and tetramerization products from this reaction. Unfortunately, we are not able to determine the structures of these compounds yet.

Intermolecular Hydroamination. Encouraged by the above observation, we examined the possibility of using this iridium catalytic system to achieve intermolecular hydroamination. Our experiment with the use of aniline and phenylacetylene in the presence of **3** and $NaBAr^F_4$ under refluxing toluene for 24 h yielded the corresponding imine **4** quantitatively (Scheme 2). The reaction was regioselective for the keto-imine, producing *N*-(1-phenylethylidene)aniline as the sole product of reaction. Apparently, the amine undergoes attack at the internal end (Markovnikov type), which is different from the intramolecular cyclization, as shown in the previous section.

Scheme 2



Messerle and co-workers have shown that the iridium complex [{Ir[bis(pyrazol-1-yl)methane](CO)$_2$}BPh_4] is able to catalyze the hydrosilylation of imine.[14] In addition, this iridium complex could carry out a tandem reaction, i.e., alkyne hydroamination to form an imine followed by hydrosilation.[8a] We further examined the aspect of using the iridium complex **3** to catalyze hydroamination followed by hydrosilylation, i.e., a two-step reaction in a one-pot procedure. This catalyzed hydroamination, where the N−H bond is added across the C≡C bond, provides the formation of imines, and the further hydrosilylation of the resulting imines, where the Si−H bond is added across the C═N bond, yields the corresponding *N*-silylated amine.

In the presence of **3**/$NaBAr^F_4$, the reaction of phenylacetylene with 1.2 equiv of aniline in toluene for 12 h proceeded smoothly at refluxing temperature, and the corresponding imine was obtained quantitatively via monitoring the reaction mixture with ^{1}H NMR spectroscopy. To this mixture was subsequently added 1.2 equiv of triethylsilane, giving the *N*-silylated amine **5** in 100% yield after stirring for another 2 h (Scheme 2). Due to the moisture-sensitivity of the *N*-silyl group, the corresponding secondary amine was isolated in pure form after chromatography. Table 5 summarizes the results of the iridium complex **3** catalyzing the hydroamination/silyation of phenylacetylene followed by hydrolysis. Phenylacetylene proves to be a good substrate for the hydroamination (Table 5, entries 1−4). The *para*-substituted phenylacetylene gives the desired product in poor yields (Table 5, entries 7, 8). The 2,6-disubstituted anilines show less reactivity toward nucleophilic addition, presumably due to steric reasons. However, the diphenylacetylene, an internal alkyne, does not undergo such a reaction under this catalytic condition.

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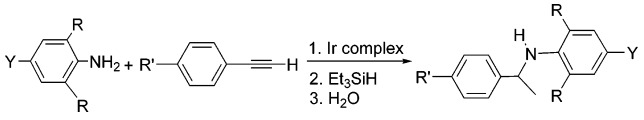
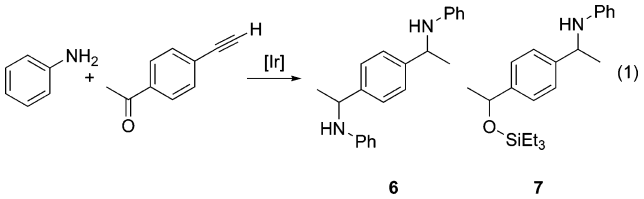
Table 5. Intermolecular Hydroamination/Hydrosilyation of Phenylacetylene Catalyzed by 3/NaBAr$^F_4$[a]



entry	aniline	time (h)	isolated yield (%)	TON[b]
1	R = H, Y = H, Rn′ = H	12	95	95
2	R = H, Y = CH_3, R′ = H	12	96	96
3	R = H, Y = CH_3O, R′ = H	12	95	95
4	R = H, Y = Br, R′ = H	20	72	72
5	R = CH_3, Y = H, R′ = H	20	12	12
6	R = CH_3, Y = CH_3, R′ = H	20	25	25
7	R = H, Y = H, R′ = CH_3O	12	14	14
8	R = H, Y = H, R′ = NC-	12	16	16

[a] Reaction conditions: acetylene (1 mmol), amine (1.2 mmol), **3** (0.01 mmol) in toluene (5 mL) under refluxing temperature. The second step: Et_3SiH (1.2 mmol) and stirred for 2 h. The reaction mixture was passed through silica gel to remove the metal complexes. [b]TON = tounover number (mol of product/per mol of catalyst used).

Reaction of *p*-ethynylacetophenone with aniline under the catalytic hydroamination and hydrosilylation conditions would give a mixture of **6** and **7** as the products (eq 1). Apparently,



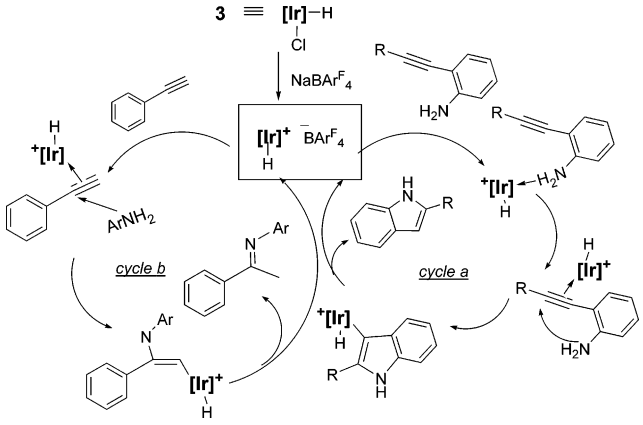
6 **7**

the hydroamination/hydrosilylation/hydrolysis of the carbon−carbon triple bond proceeds smoothly to yield the corresponding amine. In addition, the carbonyl group is partially converted into the corresponding imine, which is subsequently reduced to produce compound **6**. Meanwhile, the direct reduction of the carbonyl group followed by silylation gives compound **7**. However, the product ratio of **6**/**7** can be controlled by the amount of aniline. When the reaction is carried out with the use of equal molar amounts of both reactants, only a trace of **6** is produced. On the other hand, compound **6** is obtained in a major portion (greater than 90%) with excess aniline. This observation indicates that the catalytic hydroamination of a triple bond proceeds in a faster manner than that of imine formation under our catalytic reaction conditions.

Mechanistic Discussion

The mechanistic pathway of intra- (cycle a) and intermolecular (cycle b) hydroamination of alkyne catalyzed by **3**/NaBAr$^F_4$ is shown in Scheme 3. Basically, this pathway is quite similar to that reported by Crabtree and co-workers.[6] The catalytic pathway that leads to the hydroamination products via the iridium(III) complex involves the generation of a vacant coordination site suited for an incoming substrate, followed by the nucleophilic attack of the amino group to the coordinating alkyne, yielding the desired product. Several observations are consistent with this proposed pathway. First, for complex **3**, the lack of catalytic activity upon cyclization can be rationalized by its stortage of coordination sites for the substrate. The core iridium(III) ion is surrounded by *P*,*N*,*C*-(**P**∼**N**), hydride, chloride, and carbonyl ligands. Such a configuration is not sufficiently labile to generate a coordination site for the incoming substrates. To facilitate the reaction, the addition of

Scheme 3. Catalytic Cycles for Hydroamination of Alkynes



NaBAr$^F_4$ readily assists the dissociation of chloride. The net result not only creates a coordination site but also turns the iridium into a cationic center. Second, the activity of the cationic [*P*,*N*,*C*-(**P**∼**N**)IrH(CO)]$^+$ species appears to be better than that of **2**. As shown in the catalytic pathway, the role of iridium(III) is to act as a Lewis acid for coordinating an alkyne molecule. Thus, the coordinated carbonyl ligand, a strong π-acid, on the metal center in **3** would increase its acidity and hence the activity. Last, as shown in Tables 4 and 5, the basicity of amino groups influences the nucleophilic attack on alkynes. The less basic amino groups provide a poor yield of the cyclized product, consistent with the consequence predicted from the proposed reaction pathways.

Summary

In this work, we have successfully prepared phosphine-imine iridium complexes including iridium hydride complexes. The combination of iridium complex **3** with sodium tetrakis(3,5-trifluoromethylphenyl)borate proves to be a new class of catalyst for both intramolcular and intermolecular hydroamination of alkynes under mild reaction conditions. By adopting **3**/NaBAr$^F_4$ as a catalytic system, a series of indoles can be obtained by the cyclization of substituted alkynylanilines. Furthermore, such a catalyst catalyzes the intermolecular hydroamination of phenylacetylenes with anilines followed by hydrosilylation to yield *N*-silylated amines, which can be hydrolyzed to afford various secondary amines.

Experimental Section

General Information. All reactions and manipulations were performed under a dry nitrogen atmosphere unless otherwise noted. Tetrahydrofuran was distilled under nitrogen from a sodium/benzophenone mixture. Dichloromethane was dried over CaH_2 and distilled under nitrogen. Other solvents were used after degassing. The chemicals were purchased from commercial sources and used without further purification. The iminophosphine ligand **P**∼**N** was prepared according to the procedure reported.[10a]

Nuclear magnetic resonance spectra were recorded in $CDCl_3$ or acetone-d_6 on either a Bruker AM-300 or an AVANCE 400 spectrometer. Chemical shifts are given in parts per million relative to Me_4Si for ^1H and ^{13}C NMR and relative to 85% H_3PO_4 for ^{31}P NMR. Infrared spectra were measured on a Nicolet Magna-IR 550 spectrometer (Series-II) as KBr pellets, unless otherwise noted.

Complex 1. A mixture of **P**∼**N** ligand (108 mg, 0.30 mmol) and [Ir(COD)Cl_2] (100 mg, 0.15mmol) in THF (15 mL) was stirred at room temperature under nitrogen atmosphere for 15 min. The solvent was removed, and the orange residue was crystallized from

CH_2Cl_2/Et_2O to give **1** as an orange solid (214 mg, 90%): ^{1}H NMR (acetone-d_6) δ 8.31 (s, 1H, N=C*H*), 7.91−7.05 (m, 19H, *phenyl*), 1.92 (m, 4H, *COD*), 1.55 (m, 4H, *COD*); ^{31}P NMR δ 17.6. Anal. Calcd for $C_{33}H_{32}ClIrNP$: C, 56.62; H, 4.60; N, 2.00. Found: C, 56.39; H, 4.48; N, 1.89.

Complex 2. A mixture of **1** (200 mg, 0.25 mmol) and $AgBF_4$ (48 mg, 0.25 mmol) in THF (20 mL) was placed in a flask under nitrogen atmosphere. The solution was stirred at room temperature for 15 min. During the reaction, the solution turned yellow accompanied with the precipitation of a silver salt. After the reaction, the green solution was filtrated through Celite. The filtrate was concentrated and the residue was crystallized from CH_2Cl_2/Et_2O to give **2**, which was isolated as a green solid (174 mg, 93%): ^{1}H NMR (400 MHz, acetone-d_6) δ 9.76 (s, 1H, N=C*H*), 8.31−7.53 (m, 18H, *phenyl*), 5.09 (br, 1H, *COD*), 4.89 (br, 1H, *COD*), 4.70 (br, 1H, *COD*), 3.56 (br, 1H, *COD*), 3.01 (br, 1H, *COD*), 2.48 (br, 1H, *COD*), 2.35 (br, 1H, *COD*), 2.20 (br, 1H, *COD*), 1.82 (br, 1H, *COD*), 1.72 (br, 1H, *COD*), 1.26 (br, 1H, *COD*), 1.24 (br, 1 H COD), −12.78 (d, J_{P-H} = 17 Hz, 1H, Ir-*H*); ^{31}P NMR δ 13.0. Anal. Calcd for $C_{33}H_{32}BF_4IrNP$: C, 52.66; H, 4.29; N, 1.86. Found: C, C, 52.26; H, 3.98; N, 1.75.

Complex 3. A mixture of the **P∼N** ligand (208 mg, 0.60 mmol) and $[Ir(COD)Cl_2$ (200 mg, 0.30 mmol) was placed in a flask. The flask was evacuated and filled with CO at atmospheric pressure. THF (20 mL) was then syringed into the flask. The mixture was stirred at room temperature for 4 h, and the resulting reaction mixture was filtered and evaporated. Recrystallization of the residue from CH_2Cl_2/Et_2O gave the desired complex **3**, which was isolated as a yellow solid (294 mg, 80%): IR 2019 cm^{-1}($\nu_{C=O}$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (s, 1H, N=C*H*), 8.07−7.14 (m, 18H, *phenyl*), −13.0 (d, J_{P-H} = 12 Hz, 1H, Ir-*H*); ^{31}P NMR δ 15.9. Anal. Calcd for $C_{26}H_{20}ClIrNOP$: C, 50.28; H, 3.25; N, 2.26. Found: C, 49.97; H, 3.01; N, 1.96.

General Procedures for Intramolecular Hydroamination. Catalytic reactions were typically performed with 1 mmol of substrate, 1 mol % of complex **3**, and 0.105 mmol of $NaBAr^F_4$ in solvent (2 mL) under nitrogen. The progress of the reaction was monitored by ^{1}H NMR at regular intervals. Reactions were carried out in toluene at refluxing temperature. The reaction mixture was passed through Celite to remove metal species and salts. The filtrate was concentrated and chromatographed on silica gel with elution of dichloromethane/ethyl acetate. The desired indole product was obtained upon concentration and characterized by ^{1}H and ^{13}C NMR spectroscopy. Spectral data of all known compounds are consistent with those reported in the literature.

In the case of the solvent effect study, the yield of product was determined by integration of the product relative to the substrate peaks in the ^{1}H NMR spectrum. A 100% conversion was taken to be the time where no remaining substrate peaks (<1%) were evident in the NMR.

2-Butyl-5-methyl-1*H*-indole.[15] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (b, 1H, N-*H*), 7.45 (s, 1H, *Ar-H*), 7.19 (d, J = 8 Hz, 1H, *Ar-H*), 7.07 (d, J = 8 Hz, 1H, *Ar-H*), 6.26 (s, 1H, −C=C*H*), 2.73 (t, J = 8 Hz, 2H, −CH_2−), 2.57 (s, 3H, −*Me*), 1.75 (m, 2H, −CH_2−), 1.50 (m, 2H, −CH_2−), 1.07 (t, J = 8 Hz, −CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.1, 140.0, 129.0, 118.5, 122.2, 119.4, 110.0, 98.7, 31.2, 27.8, 22.3, 21.4, 13.8.

5-Methyl-2-phenyl-1*H*-indole.[16] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (b, 1H, N-*H*), 7.63 (m, 2H, *Ar-H*), 7.41 (m, 3H, *Ar-H*), 7.27 (m, 2H, *Ar-H*), 6.74 (d, J = 4 Hz, 1H, *Ar-H*), 6.73 (s, 1H, −C=C*H*), 2.44 (s, 3H, −*Me*). ^{13}C NMR (100 MHz, $CDCl_3$): 137.9, 135.1, 132.5, 129.5, 129.4, 129.0, 127.5, 125.0, 123.9, 120.3, 110.5, 99.5, 21.5.

2-Butyl-1*H*-indole.[17] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (b, 1H, N-*H*), 7.57 (m, 1H, *Ar-H*), 7.30 (d, J = 8 Hz, 1H, *Ar-H*), 7.13 (m, 2H, *Ar-H*), 6.27 (s, 1H, −C=C*H*), 2.76 (t, J = 8 Hz, 2H, −CH_2−), 2.57 (s, 3H, −*Me*), 1.73 (m, 2H, −CH_2−), 1.44 (m, 2H, −CH_2−), 1.09 (t, J = 7.2 Hz, −CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.0, 135.8, 128.8, 120.8, 119.7,119.5, 110.3, 99.3, 31.2, 27.9, 22.4, 13.8.

2-Phenyl-1*H*-indole.[18] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (b, 1H, N-*H*), 7.65 (m, 3H, *Ar-H*), 7.43 (m, 3H, *Ar-H*), 7.31 (m, 1H, *Ar-H*), 7.18 (m, 1H, *Ar-H*), 7.11 (m, 1H, *Ar-H*), 6.82(s, 1H, −C=C*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.9, 136.8, 132.4, 129.3, 129.1, 127.8, 125.3, 122.5, 120.8, 120.4, 110.3.

2-Butyl-5-chloro-1*H*-indole. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (b, 1H, N-*H*), 7.46 (d, J = 2 Hz, 1H, *Ar-H*), 7.16 (d, J = 8 Hz, 1H, *Ar-H*), 7.04 (d, J = 8 Hz, 2H, *Ar-H*), 6.17 (s, 1H, −C=C*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.6, 134.1, 130.0, 125.1, 121.0, 119.1, 111.1, 99.2, 31.1, 27.9, 22.3, 13.8. Anal. Calcd for $C_{12}H_{14}ClN$: C, 69.39; H, 6.79; N, 6.74. Found: C, 69.01; H, 6.34; N, 6.65.

2-Phenyl-5-chloro-1*H*-indole.[19] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (b, 1H, N-*H*), 7.63 (m, 2H, *Ar-H*), 7.57 (s, 1H, *Ar-H*), 7.43 (t, J = 7.2 Hz, 2H, *Ar-H*), 7.30 (m, 2H, *Ar-H*), 7.12 (m, 1H, *Ar-H*), 6.74(s, 1H, −C=C*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.3, 135.1, 131.8, 130.3, 129.1, 128.1, 125.8, 125.2, 122.6, 120.0, 111.8, 99.5.

2-Phenyl-5-nitro-1*H*-indole.[20] ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (b, 1H, N-*H*), 8.56 (s, 1H, *Ar-H*), 8.09 (d, J = 8 Hz, 1H, *Ar-H*), 7.67 (d, J = 8 Hz, 2H, *Ar-H*), 7.41 (m, 4H, *Ar-H*), 6.95(s, 1H, −C=C*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 141.1, 139.7, 131.0, 129.3, 128.8, 128.6, 125.4, 118.0, 117.7, 110.8, 101.6.

***N*-Acetyl-2-phenyl-1*H*-indole.**[21] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 0.8 Hz, 1H, *Ar-H*), 7.49 (m, 1H, *Ar-H*), 7.24 (m, 2H, *Ar-H*), 6.45 (s, 1H, −C=C*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3, 142.9, 136.3, 129.9, 123.4, 122.9, 123.3, 122.9, 120.1, 114.7, 108.1, 31.0, 27.6, 22.5, 14.0.

General Procedure for Intermolecular Hydroamination/Silylation. A mixture of phenylacetylene (1 mmol), aniline (1.2 mmol), **3** (0.01 mmol), and $NaBAr^F_4$(0.105 mmol) in toluene (5 mL) under nitrogen was heated to reflux for a certain period. The imine product was determined by integration of the product resonances relative to the substrate peaks in the ^{1}H NMR spectrum. After the completion of the conversion, Et_3SiH (1.2 mmol) was added and the mixture stirred for another 2 h. The reaction mixture was chromatographed on silica gel with elution of dichloromethane/ethyl acetate. The desired product was isolated and characterized by ^{1}H and ^{13}C NMR spectroscopy.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50−6.94 (m, 8H, *phenyl*), 6.83 (m, 2H, *phenyl*), 4.64 (q, J = 6.8 Hz, 1H, −C*H*), 1.54 (d, J = 6.8 Hz, 3H, −CH_3), 0.95 (t, J = 8 Hz, 9H, −CH_3), 0.70 (q, J = 8 Hz, 6H, −CH_2−).

Phenyl(1-phenylethyl)amine.[22] ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (m, 2H, *Ar-H*), 7.24 (m, 2H, *Ar-H*), 7.25 (m, 1H, *Ar-H*), 7.12 (m, 2H, *Ar-H*), 6.96(t, J = 7.2 Hz, 1H, *Ar-H*), 6.54 (d, J = 8.4 Hz, 2H, *Ar-H*), 4.51 (q, J = 6.8 Hz, 1H, −C*H*), 4.18 (b, 1H, −N*H*), 1.54 (d, J = 6.8 Hz, 3H, −CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.1, 145.0, 129.1, 128.6, 126.9, 125.8, 117.3, 113.4, 53.6, 24.9. The *N*-silylated intermediate **5**, a moisture-sensitive compound, was identified by ^{1}H NMR: δ 7.50−6.94 (m, 8H, *phenyl*), 6.83 (m, 2H, *phenyl*), 4.64 (q, J = 6.8 Hz, 1H, −C*H*),

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Table 6. Crystal Data and Structure Refinement for Complexes 2 and 3

	2	3
formula	$C_{33}H_{32}BF_4IrNP\cdot 2CH_2Cl_2$	$C_{26}H_{20}ClIrNOP\cdot CH_2Cl_2$
fw	922.43	705.98
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a, Å	11.140(3)	9.6307(4)
b, Å	13.677(1)	11.1069(4)
c, Å	23.659(2)	12.9448(5)
α, deg	90	78.296(1)
β deg	92.02(2)	74.905(1)
γ, deg	90	87.646(1)
V, Å^3; *Z*	3603(1); 4	1309.00(9); 2
d(calc), Mg/m^3	1.701	1.791
F(0,0,0)	1816	684
cryst size, mm^3	0.55 × 0.40 × 0.36	0.40 × 0.16 × 0.10
no. of rflns collected	5627	13541
no. of indep rflns	5627 (R_{int} = 0.0433)	5959 (R_{int} = 0.0271)
θ range, deg	1.72 to 23.97	1.66 to 27.48
refinement method	full-matrix least-squares on F^2	
goodness of fit on F^2	1.048	1.050
R indices [$I > 2\sigma(I)$]	R1 = 0.0633, wR2 = 0.1274	R1 = 0.0229, wR2 = 0.0559

1.54 (d, *J* = 6.8 Hz, 3H, −C*H*$_3$), 0.95 (t, *J* = 8 Hz, 9H, −C*H*$_3$), 0.70 (q, *J* = 8 Hz, 6H, −C*H*$_2$−).

(*p*-Methoxyphenyl)(1-phenylethyl)amine.[23] ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.37 (m, 4H, *Ar-H*), 7.23 (m, 1H, *Ar-H*), 6.71 (d, *J* = 8 Hz, 2H, *Ar-H*), 6.49 (d, *J* = 8 Hz, 2H, *Ar-H*), 4.43 (q, *J* = 6.8 Hz, 1H, −C*H*), 3.92 (b, 1H, −N*H*), 3.71 (s, 3H, −O*Me*), 1.52 (d, *J* = 6.4 Hz, 3H, −C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 151.3, 144.9, 141.0, 128.2, 126.4, 125.5, 114.4, 114.2, 55.8, 54.4, 25.5.

(*p*-Methylphenyl)(1-phenylethyl)amine.[22] ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.36 (m, 4H, *Ar-H*), 7.26 (m, 1H, *Ar-H*), 6.92 (d, *J* = 5.2 Hz, 2H, *Ar-H*), 6.46 (d, *J* = 5.2 Hz, 2H, *Ar-H*), 4.48 (q, *J* = 6.8 Hz, 1H, −C*H*), 3.98 (b, 1H, −N*H*), 2.23 (s, 3H, −*Me*), 1.54 (d, *J* = 6 Hz, 3H, −C*H*$_3$).

(*p*-Bromophenyl)(1-phenylethyl)amine. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.29 (m, 4H, *Ar-H*), 7.21 (m, 1H, *Ar-H*), 7.12 (d, *J* = 8 Hz, 2H, *Ar-H*), 6.35 (d, *J* = 8 Hz, 2H, *Ar-H*), 4.42 (q, *J* = 6.8 Hz, 1H, −C*H*), 4.05 (b, 1H, −N*H*), 1.50 (d, *J* = 6.8 Hz, 3H, −C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 145.7, 144.1, 131.4, 128.3, 126.7, 125.4, 114.6, 109.2, 53.7, 25.3. Anal. Calcd for $C_{14}H_{14}BrN$: C, 60.89; H, 5.11; N, 5.07. Found: C, 60.54; H, 4.92; N, 4.87.

(2,6-Dimethylphenyl)(1-phenylethyl)amine.[24] ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.14 (m, 5H, *phenyl*), 6.84 (d, *J* = 7.4 Hz, 2H, *phenyl*), 6.68 (m, 1H, *phenyl*), 4.22 (q, *J* = 6.8 Hz, 1H, −C*H*), 3.10 (b, 1H, −N*H*), 2.07 (s, 6H, −C*H*$_3$), 1.40 (d, *J* = 6.8 Hz, 3H, −C*H*$_3$).

(2,4,6-Trimethylphenyl)(1-phenylethyl)amine.[25] ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.30 (m, 4H, *phenyl*), 7.24 (m, 1H, *phenyl*), 6.79 (s, 2H, *phenyl*), 4.26 (q, *J* = 6.8 Hz, 1H, −C*H*), 3.20 (b, 1H, −N*H*), 2.22 (s, 3H, −ArC*H*$_3$), 2.15 (s, 6H, −ArC*H*$_3$), 1.52 (d, *J* = 6.8 Hz, 3H, −C*H*$_3$).

Phenyl[1-(4-methoxyphenyl)ethyl]amine. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.28 (m, 2H, *Ar-H*), 7.13 (m, 3H, *Ar-H*), 6.87 (m, 2H, *Ar-H*), 6.63 (d, 1H, *Ar-H*), 6.53 (m, 2H, *Ar-H*), 4.46 (q, *J* = 6.8 Hz, 1H, −C*H*), 4.05 (b, 1H, −N*H*), 3.77 (s, 3H, −O*Me*), 1.52 (d, *J* = 9.2 Hz, 3H, −C*H*$_3$).

Phenyl[1-(4-cyanophenyl)ethyl]amine.[26] ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.58 (d, *J* = 8.2 Hz, 2H, *phenyl*), 7.46 (d, *J* = 8.2 Hz, 2H, *phenyl*), 7.08 (m, 2H, *phenyl*), 6.66 (m, 1H, *phenyl*), 6.41 (d, *J* = 7.7 Hz, 2H, *phenyl*), 4.49 (q, *J* = 6.4 Hz, 1H, −C*H*), 3.95 (b, 1H, −N*H*), 1.53 (d, *J* = 5.6 Hz, 3H, −C*H*$_3$).

Compound 6. ^{1}H NMR (400.1 MHz, $CDCl_3$): *δ* 7.38 (s, 1H, *phenyl*), 7.18 (m,4H, *phenyl*), 6.73 (m, 2H, *phenyl*), 6.58 (m, *J* = 7.6 Hz, 4H, *phenyl*), 4.53 (q, *J* = 6.4 Hz, 2H, −C*H*), 4.05 (b, 2H, −N*H*), 1.56 (d, *J* = 6.8 Hz, 6H, −C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 147.2, 143.7, 129.0, 126.1, 117.1, 113.2, 53.0, 24.7. Anal. Calcd for $C_{22}H_{24}N_2$: C, 83.50; H, 7.64; N, 8.85. Found: C, 83.12; H, 7.24; N, 8.47.

Compound 7. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.30 (m, 4H, *phenyl*), 7.10 (m, 2H, *phenyl*), 6.66 (m, 1H, *phenyl*), 6.54 (m, 2H, *phenyl*), 6.53 (m, 2H, *phenyl*), 4.86 (q, *J* = 4.4 Hz, 1H, −C*H*), 4.49 (q, *J* = 6.8 Hz, 1H, −C*H*), 4.05 (b, 1H, −N*H*), 1.53 (d, *J* = 6.4 Hz, 3H, −C*H*$_3$), 1.45 (d, *J* = 6.4 Hz, 3H, −C*H*$_3$), 0.92 (t, *J* = 8 Hz, 9H, −CH$_2$C*H*$_3$), 0.58 (q, *J* = 4 Hz, 6H, −SiC*H*$_2$CH$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 147.3, 145.3, 143.6, 129.0, 125.6, 125.5, 117.1, 113.3, 70.3, 53.2, 26.9, 24.8, 6.8, 4.8. Anal. Calcd for $C_{22}H_{33}NOSi$: C, 74.31; H, 9.35; N, 3.94. Found: C, 74.01; H, 9.00; N, 3.77.

Crystallography. Crystals suitable for X-ray determination were obtained for **2**·2CH_2Cl_2 and **3**·CH_2Cl_2 by slow diffusion of diethyl ether into a dichloromethane solution at room temperature. Cell parameters of **2** and **3** were determined by Enraf-Norius CAD-4 and Siemens SMART CCD diffractometers, respectively. Crystal data of these complexes are listed in Table 6. Other crystallographic data are deposited as Supporting Information.

Supporting Information Available: Tables providing atomic positional parameters, bond distances and angles, anisotropic thermal parameters, and calculated hydrogen atom positions for complexes **2** and **3**. A CIF file is also available. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060965C

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