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Catalyst Design of Vaska-Type Iridium Complexes for Highly Efficient Synthesis of π-Conjugated Enamines

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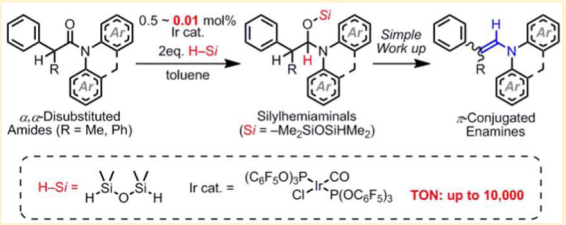
Supporting Information

ABSTRACT: The appropriate design of a ligand (L) in $IrCl(CO)(L)_2$ (**4**) realized the efficient synthesis of π-conjugated enamines possessing hole-transport properties. The iridium complex with electron-withdrawing phosphorus ligands catalyzed the hydrosilylation of amides to the corresponding silylhemiaminals, which were transformed to the enamines by heat or by treatment with acids. High catalytic efficiency (TON > 10,000) was achieved, which made it possible for the residual iridium in the enamine product to be below 20 ppb.



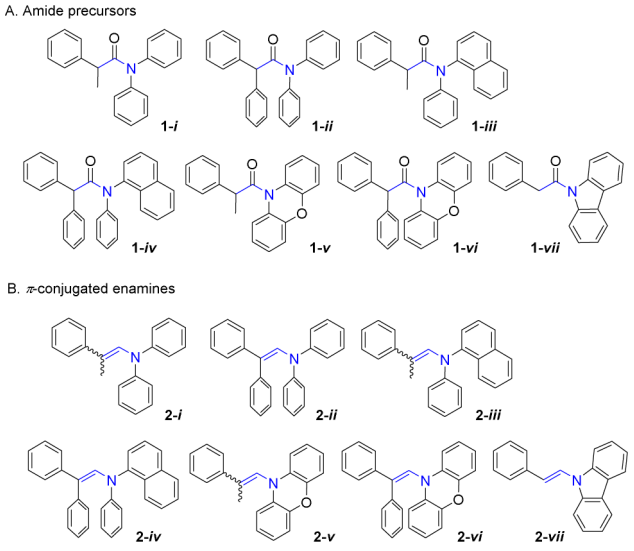
INTRODUCTION

Enamines have been useful synthetic intermediates as "enolate equivalents" in organic synthesis since their discovery by Stork and co-workers.[1] Except for enamines conjugated to carbonyl groups such as β-ketoenamines,[2] enamines are generally unstable to moisture and easily undergo hydrolysis to afford aldehydes and amines. Thus, most enamines have been either isolated by careful experiments under anhydrous conditions to avoid hydrolysis or prepared in situ and used for further organic reactions without isolation.[3] Although good reactivity of enamines toward electrophiles suggests the potential of enamines as excellent electron donors, their application to materials did not receive much attention until a report by Borsenberger and co-workers in 1997.[4] They investigated hole-transport properties of several aldenamines conjugated to delocalized aromatic rings, and found that these weakly polar aldenamines were stable enough to prepare vapor-deposited enamine glasses and enamine-doped polymers,[4a] which showed good room-temperature mobilities.[2] These interesting properties of enamines were later supported by further studies by Jankauskas and co-workers on the hole-transport properties of certain π-conjugated enamines[4b−f] and actual applications of π-conjugated enamines to electrophotographic photoreceptors.[5,6] The π-conjugated enamines, typical examples of which are shown in Chart 1, were synthesized by conventional preparative methods using the condensation of aldehydes or ketones with secondary amines.[1,4b−f] However, the reaction was essentially reversible, and effective removal of water was necessary for isolation of the product at high temperatures. Yields of the products were low to moderate.[1,7]

We are interested in the development of new and efficient synthetic methods for π-conjugated aldenamines. The synthesis of enamines by virtue of transition-metal catalysts has recently attracted attention and includes cross-coupling of vinyl halides with secondary amines,[8] dehydrogenation of amines,[9] hydroamination of alkynes,[10] and cross-coupling of ynamides and boronic acids.[11]

Among these methods, catalytic hydrosilane reduction of tertiary amides provides unique access to aldenamines from easily available amides.[12−15] Although reduction of amides to amines has recently attracted attention from organic and

Chart 1. π-Conjugated Enamines 2-*i*−*vii* Possessing Hole-Transport Properties and Their Amide Precursors 1-*i*−*vii*



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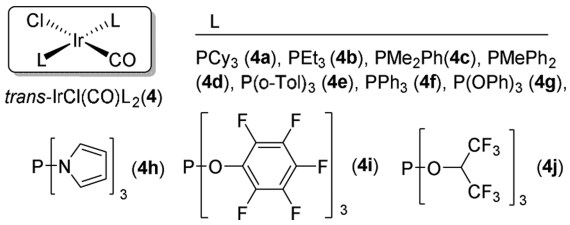
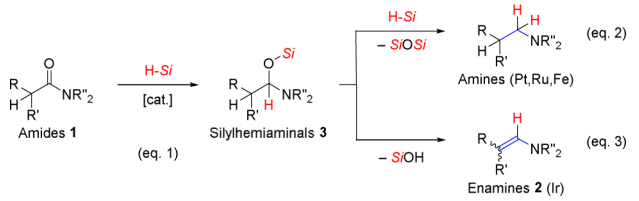
organometallic chemists,[16−18] relatively little has been investigated for the preparation of enamines from amides. The first report of this transformation was from Corriu and co-workers in 1984, in which $RhCl(PPh_3)_3$ catalyzed the reaction of $PhCH_2CONEt_2$ (**1-*viii***) with $Me_2HSi(CH_2)_2SiHMe_2$ (BDMSE) or 1,2-$(Me_2HSi)_2C_6H_4$ (BDSB) to give $PhCH{=}CHNEt_2$ (**2-*viii***) in moderate yields.[12a] Our discovery in 2009 of a highly efficient reaction of a series of aliphatic tertiary amides to aldenamines was achieved by using a catalytic amount of $IrCl(CO)(PPh_3)_2$ (Vaska's complex **4f**, shown in Chart 2) and certain hydrosilanes, $Me_2HSiOSiHMe_2$ (TMDS)

Chart 2. Vaska-Type Complexes 4a−j



and $Me_3Si[OSiHMe]_n$-$OSiMe_3$ (PMHS).[13] This $IrCl(CO)(PPh_3)_2$-catalyzed reaction has several potential advantages for the synthesis of π-conjugated enamines for applications as materials. The first advantage is the selectivity of the reaction to form aldenamines. As shown in Scheme 1, transition-metal-

Scheme 1. Hydrosilane Reduction of Tertiary Amides



catalyzed reactions of tertiary amides with hydrosilanes generally afford the corresponding tertiary amines. The reaction proceeds through a silylhemiaminal as an intermediate, which is formed by addition of a Si−H bond of the hydrosilane across a C=O bond in the tertiary amide (hydrosilylation of the amide, eq 1). Further reduction of the silylhemiaminal by hydrosilanes results in the formation of tertiary amines (deoxygenative reduction, eq 2), whereas formal elimination of silanol gives the enamine (eq 3). In fact, we have investigated hydrosilane reduction reactions of tertiary amides catalyzed by ruthenium, platinum, and iron complexes, which generally afford tertiary amines as a single product, though aldenamines are sometimes detected as a byproduct under special reaction conditions such as when the catalyst loadings are low.[16] Recently, Brookhart and co-workers reported the reduction of tertiary amides with hydrosilanes catalyzed by pincer-type iridium complexes, in which a mixture of the corresponding aldenamine and the tertiary amine was obtained.[14] It is a notable feature of the $IrCl(CO)(PPh_3)_2$-catalyzed hydrosilane reduction that aldenamines were obtained as a single product without the formation of tertiary amines.[13] The second advantage is that amides, which are easily available from the corresponding carboxylic acids and amines, can be used as the starting materials for π-conjugated aldenamines. The third advantage is the high catalytic efficiency of TOF > 10^4 (TON > 5000) observed in the hydrosilane reduction of $PhCH_2CONEt_2$, which was achieved at room temperature in 30 min. The use of extremely low catalyst loadings is important for the preparation of chemicals for applications to materials whose properties are affected by contamination by metals. Highly efficient catalytic reactions achievable by a very small amount of metal compounds lead to facile removal of the metal residues from the catalyst component.[16h]

These excellent features of $IrCl(CO)(PPh_3)_2$-catalyzed aldenamine synthesis suggested that it should be useful for the preparation of the π-conjugated enamines shown in Chart 1. However, we were disappointed to see that Vaska's complex **4f** showed no catalytic activity for the reaction of π-conjugated enamine precursors with TMDS even at high temperature. We pursued a solution to this problem by the appropriate ligand design of $IrCl(CO)(L)_2$ (**4**) on the basis of Tolman's χ values[19] and succeeded in discovering that $IrCl(CO)(L)_2$ with electron-withdrawing phosphorus ligands provided highly efficient selective preparation of π-conjugated enamines.

RESULTS AND DISCUSSION

Synthesis of $IrCl(CO)(L)_2$ (4). To improve the catalytic activity toward the reaction of π-conjugated aldenamine precursors, we prepared the series of Vaska-type complexes shown in Chart 2 by changing the phosphorus ligands L. For the complexes bearing electron-donating phosphorus ligands, six phosphine and one phosphite complexes **4a−g** were synthesized according to the procedure in the literature.[20] Among the ligands in these complexes, $P(OPh)_3$ was the most electron withdrawing. To investigate the effect of more electron withdrawing ligands, we prepared three new Vaska-type complexes, where L = $P(NC_4H_4)_3$, $P(OC_6F_5)_3$, $P\{OCH(CF_3)_2\}_3$. The unique electron-withdrawing effects of $P(NC_4H_4)_3$ were investigated by several rhodium complexes,[21a] for which rhodium compounds bearing $P\{OCH(CF_3)_2\}_3$ showed significant reactivity in several catalytic reactions.[21b,c] A platinum complex of $P(OC_6F_5)_3$ was prepared, but no detailed studies in reactivity were undertaken.[21d]

The synthesis of three new complexes, **4h−j**, was performed by the treatment of $\{Ir(COD)Cl\}_2$ with the corresponding phosphorus ligand under a CO atmosphere.[20] All of the synthesized complexes **4h−j** were characterized by NMR and IR spectroscopy and elemental analyses, and their structures were determined by X-ray diffraction studies. The molecular structures of **4h−j** are similar to that of the Vaska complex **4f**, which has a square-planar geometry with the iridium atom bound to two mutually trans PPh_3 ligands, a CO group, and a chlorine atom. A representative ORTEP drawing of **4i** is shown in Figure 1. The Ir−P(1), Ir−P(2), Ir−C(1), and Ir−Cl(1) bond distances indicated in the figure caption are comparable to those found in **4f**. The molecular structures of **4h,j** are summarized in the Supporting Information. NMR and IR spectra of **4h−j** were consistent with those expected from the molecular structure of each complex, showing that the structure in the solid state is maintained in solution. A single ^{31}P resonance was observed at δ 79.5 (**4h**), 108.0 (**4i**), and 113.2 (**4j**), indicating that the two PR_3 ligands are in the trans configuration. A ^{13}C signal due to the CO ligand was observed at δ 166.4 (**4h**), 165.1 (**4i**), and 162.6 (**4j**). IR absorption bands (ν_{CO}) were visible at 2011 cm^{-1} (**4h**), 2052 cm^{-1} (**4i**), and 2059 cm^{-1} (**4j**). ^{31}P signals of **4h−j** showed significant upfield shifts in comparison with that of Vaska's complex **4f** (δ_P 24.7).

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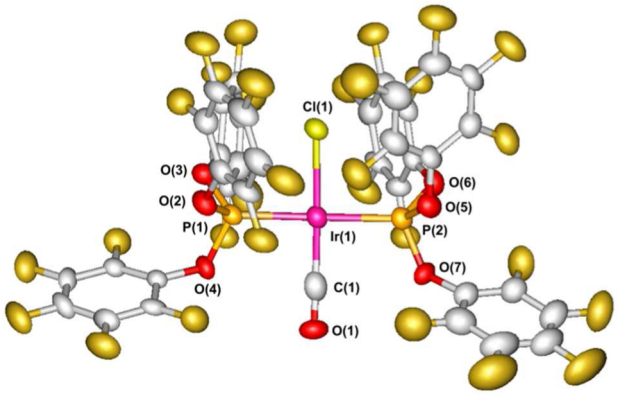


Figure 1. Molecular structure of **4i** (thermal ellipsoids with 50% probability). One THF molecule exists in the unit cell as a crystallization solvent, which is omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir–P(1) = 2.249(2), Ir–P(2) = 2.257(2), Ir–Cl(1) = 2.343(2), Ir–C(1) = 1.838(10), C(1)–O(1) = 1.149(12); P(1)–Ir–P(2) = 174.98(9), P(1)–Ir–Cl(1) = 87.85(8), P(2)–Ir–Cl(1) = 90.97(8), Cl(1)–Ir–C(1) = 178.3(3), P(1)–Ir–C(1) = 90.5(3), P(2)–Ir–C(1) = 90.6(3).

In contrast, ν_{CO} of **4f** was observed at 1967 cm^{-1}, which was markedly lower than those of **4h–j**.

It is important for appropriate catalyst design to understand the steric as well as electronic effects of ligands. Although detailed computational studies[22] have recently been performed for possible prediction of phosphorus ligand properties, Tolman's cone angles and χ values are still convenient to consider the ligand effect.[19] Table 1 shows the CO stretching

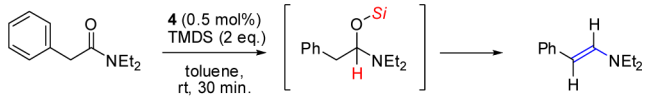
Table 1. ν_{CO} Value of 4 vs χ Value and Cone Angle of L

entry	complex	L	ν_{CO} of **4** (cm^{-1})	χ value of L[19]	cone angle of L (deg)[19]
1	**4a**	PCy_3	1932	0.3	170
2	**4b**	PEt_3	1942	5.6	132
3	**4c**	PMe_2Ph	1955	9.2	122
4	**4d**	$PMePh_2$	1959	10.9	136
5	**4e**	$P(o\text{-Tol})_3$	1961	10.5	194
6	**4f**	PPh_3	1967	12.8	145
7	**4g**	$P(OPh)_3$	2003	29.2	128
8	**4h**	$P(Pyrrolyl)_3$	2011		137
9	**4i**	$P(OC_6F_5)_3$	2052		137
10	**4j**	$P\{OCH(CF_3)_2\}_3$	2059	51.3	130

frequency for the iridium complexes (ν_{CO}(Ir)) with the cone angle and χ values of the corresponding phosphines and phosphites. These indicate the electronic properties of the iridium center bonded with the phosphorus ligands and contribute to achieving a better understanding of the ligand effect, as described in Catalyst Screening.

Catalyst Screening. We selected three tertiary amides for screening of the iridium catalysts **4**. One was *N,N*-dialkylamide **1-*viii*** for comparison with our previous results, and the other two were the amide precursors of π-conjugated enamines **1-*i*** and **1-*ii***. Scheme 2 and Table 2 show the reaction of **1-*viii*** with TMDS (2 equiv), which gave **2-*viii*** by catalysis of 0.5 mol % of the iridium complex at room temperature. Although the reaction proceeded through the silylhemiaminal intermediate **3-*viii***, only **2-*viii*** was visible in the NMR spectrum in all cases shown in the table, even in the initial stage of the reaction (Scheme 2). It is clear from Table 2 that the four complexes

Scheme 2. Conversion of 1-*viii* to 2-*viii*



TMDS = $Me_2HSiOSiHMe_2$, –*Si* = $–Me_2SiOSiHMe_2$

Table 2. Catalyst Screening for the Reaction of 1-*viii*[a]

entry	complex	yield of **2-*viii***[b] (%)	entry	complex	yield of **2-*viii***[b] (%)
1	**4a**	11	6	**4f**	>99
2	**4b**	0	7	**4g**	>99
3	**4c**	23	8	**4h**	>99
4	**4d**	45	9	**4i**	>99
5	**4e**	3	10[c]	**4j**	45

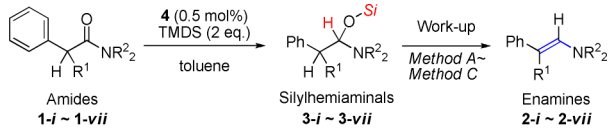
[a]All reactions were carried out with amide **1-*viii*** (1.0 mmol) in the presence of 0.5 mol % of **4** and 1,1,3,3-tetramethyldisiloxane (2.0 mmol) in C_6D_6 (0.5 mL) at room temperature for 30 min. [b]Yields were determined by ^1H NMR with hexamethylbenzene (0.05 mmol) as an internal standard. [c]A mixture of the enamine **2-*viii*** and the corresponding amine $PhCH_2CH_2NEt_2$ was obtained in a ratio of 45:55.

bearing electron-donating ligands in the left column were less reactive than those having electron-withdrawing ligands in the right column. In addition to Vaska's complex **4f** reported previously, the analogous Vaska-type complexes **4g–j** bearing electron-withdrawing phosphorus ligands (χ value of L >12.8, ν_{CO} of **4** >1967 cm^{-1}) showed high catalytic activity and brought the reaction to completion within 30 min. The complexes shown in entries 3–5 have χ and ν_{CO} values similar to those of **4**.

The low catalytic activity of **4e** may indicate that less sterically bulky ligands are more appropriate for efficient conversion of **1-*viii*** to **2-*viii***, when the χ values of L and ν_{CO} values of **4** are similar.

The reactions of π-conjugated aldenamine precursors **1-*i,ii*** were different from those of **1-*viii*** and did not directly afford the enamines **2-*i,ii***, respectively. NMR spectra indicated formation of a single products, which were assignable as the silylheminals **3-*i,ii***, as shown in Scheme 3. Quantitative

Scheme 3. Conversion of 1-*i–vii* to 2-*i–vii*



TMDS = $Me_2HSiOSiHMe_2$, –*Si* = $–Me_2SiOSiHMe_2$

formation of **3-*i,ii*** from **1-*i,ii*** was suggested by comparison of the integral value of the signals of **3-*i,ii*** with that from the added internal standard. Since **3-*i,ii*** were sensitive to moisture, attempted chromatographic purification gave a mixture of products, including the corresponding aldehyde. However, the crude silylheminals were quantitatively converted to the corresponding π-conjugated enamines **2-*i,ii*** by thermal treatment (method A) or reaction with HCl in Et_2O (method B).

Table 3 shows the reactions of **1-*i,ii*** with TMDS catalyzed by five selected Vaska-type complexes, **4f–j**, which showed excellent catalytic activity in the conversion of **1-*viii*** to **2-*viii***. For the conversion of **1-*i*** to **3-*i***, the reaction was performed at room temperature for 0.5 h in the presence of 0.5 mol % of the

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Table 3. Catalyst Screening for the Hydrosilylation of 1-*i*,*ii* by the Iridium Catalysts 4f–j[a]

entry	amide	catalyst	temp (°C)	time (h)	yield of 3 (%)[b]	method	yield of 2 (%)[b]
1	**1-*i***	**4f**	room temp	0.5	0		
2	**1-*i***	**4g**	60	21	>99	A	90
3	**1-*i***	**4h**	room temp	0.5	>99	A	92
4	**1-*i***	**4i**	room temp	0.5	>99	A	94
5	**1-*i***	**4j**	room temp	0.5	>99	A	93
6	**1-*ii***	**4f**	room temp	2	0		
7	**1-*ii***	**4g**	room temp	2	0		
8	**1-*ii***	**4h**	room temp	21	>99	B	> 99
9	**1-*ii***	**4i**	room temp	2	>99	B	> 99
10	**1-*ii***	**4j**	room temp	2	>99	B	> 99

[a]All reactions were carried out with amide **1-*i*** (1.0 mmol) or **1-*ii*** (1.0 mmol) in the presence of 0.5 mol % of **4f** ∼ **4j** and 1,1,3,3-tetramethyldisiloxane (2.0 mmol) in toluene (4.0 mL). [b]Yields were determined by ^{1}H NMR with anisole (1.0 mmol) as an internal standard. Method A: heating at 100 °C for 6 h. Method B: addition of HCl in Et_2O and stirring at room temperature for 0.5 h.

Table 4. Isolation of 2-*i*–*vii* via the Silylhemiaminal Intermediates 3-*i*–*vii* by the Iridium Catalyst 4i[a]

entry	amide	time (h)	NMR yield of 3 (%)[b]	diastereomer ratio of 3	method	isolated yield of 2 (%)[c]	*E*:*Z* ratio of 2
1	**1-*i***	0.5	>99	96:4	A	91	90:10
2	**1-*ii***	2	>99		B	86	
3	**1-*iii***	2	98	95:5	A	90	98:2
4	**1-*iv***	16	>99		B	96	
5	**1-*v***	2	95	87:13	A	93	21:79
6	**1-*vi***	30	95		A	92	
7	**1-*vii***	2	>99		C	77	100:0

[a]All reactions were carried out with amides **1-*i*–*vii*** (1.0 mmol) in the presence of 0.5 mol % of **4i** and 1,1,3,3-tetramethyldisiloxane (2.0 mmol) in toluene (4.0 mL) at room temperature. [b]Yields were determined by ^{1}H NMR with anisole (1.0 mmol) as an internal standard. [c]Isolated yield. Method A: heating at 80–100 °C for 6 h. Method B: addition of HCl in Et_2O and stirring at room temperature for 0.5 h. Method C: addition of P_2O_5 and stirring at room temperature for 0.5 h.

catalyst (entries 1–5). No reaction took place when **4f**,**g** were used as the catalysts. The reaction did not occur with **4f** even at elevated temperatures and prolonged reaction times, while **4g** catalyzed the reaction at 60 °C, and the silylhemiaminal **3-*i*** was formed quantitatively after 21 h. In sharp contrast to these two catalysts, the reactions catalyzed by **4h–j** were complete at room temperature in 0.5 h to give **3-*i*** quantitatively. In these reactions, the best yield of **3-*i*** was obtained when 2 equiv of TMDS was used with respect to **1-*i***. For instance, the yield of **3-*i*** was decreased in the reaction catalyzed by **4i** with lower amounts of TMDS (>99% (2 equiv of TMDS) > 83% (1 equiv) > 41% (0.5 equiv)).

Since **1-*ii*** was less reactive than **1-*i***, we set the standard conditions at room temperature for 2 h in the presence of 0.5 mol % of **4**. As shown in entries 6–10, no reaction took place with **4f**,**g**, whereas the reaction was slow but complete after 21 h with **4h**. It is notable that **4i**,**j** both resulted in complete conversion of **1-*ii*** to **3-*ii*** within 0.5 h. The results shown in Table 3 clearly demonstrate that Vaska-type complexes bearing electron-withdrawing fluorinated phosphites are active catalysts for the conversion of π-conjugated enamine precursors to the corresponding silylhemiaminals, which can be transformed to the desired enamines by further treatment as in methods A and B.

Isolation of π-Conjugated Enamines 2-*i*–*vii*. Experiments aimed at the isolation of **2-*i*–*vii*** were performed using **4i** as the catalyst. The results are summarized in Table 4. All reactions were carried out at room temperature in the presence of 0.5 mol % of **4i**. The reactions were complete after 0.5–30 h. The complete conversion of the amide to the silylhemiaminal was confirmed by ^{1}H NMR, and the crude product was subjected to a reaction to eliminate a silanol to form the desired aldenamine. Three procedures were used for the reaction of **3** to **2**,:the aforementioned methods A and B and treatment with P_2O_5 (method C) reported previously. The seven π-conjugated enamines **2-*i*–*vii*** were obtained in good to high yields. In four cases, shown in entries 1, 3, 5, and 7, the enamine formed had geometrical isomers. Only one isomer of **2-*vii*** was detected in the reaction of **1-*vii***, and the coupling constant between the two olefinic protons of **2-*vii*** in the ^{1}H NMR spectrum indicated the isomer to be exclusively trans ($^3J_{H-H}$ = 14.4 Hz). A mixture of *E* and *Z* isomers was obtained in the reactions of **1-*i*,*iii*,*v***, in ratios of 90:10, 98:2, and 21:79, respectively. The stereochemistry of the isomers was determined by NOESY spectra, as summarized in the Supporting Information. The major isomer of **2-*i*,*iii*** was *E*, whereas that of **2-*v*** was *Z*. It was curious that the major isomer was different between **2-*i*** (and **2-*iii***) and **2-*v***, even though the structures of these enamines were similar. To investigate the stereospecificity of the elimination of silanol from the silylhemiaminal, stereochemical analysis of **3-*i*,*iii*,*v*** by ^{1}H NMR was undertaken, and the results are summarized in Preparation of Enamines with Low Catalyst Loadings.

Preparation of Enamines with Low Catalyst Loadings. As noted in the Introduction, our previous paper demonstrated the high catalytic activity of **4f**, which was proved by the reaction of **1-*viii*** with TMDS with low catalyst loadings. In the extreme case, the reaction was complete within 0.5 h at room temperature, and the TOF exceeded 10^4. We attempted further improvement of the catalyst efficiency in this reaction by using the new catalyst **4i** and found that selective synthesis of **2-*viii*** was achieved by catalysis of 0.001 mol % of **4i** at room temperature within 30 min (TOF = 2×10^5 h^{-1}, TON = 10^5). Similarly, the preparation of **2-*iii*** in gram quantities was

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examined with a minimum concentration of the catalyst **4i**. Hydrosilylation of **1-*iii*** to **3-*iii*** proceeded smoothly with 0.01 mol % of catalyst loading (40 °C, 24 h, 98% yield), and the TON reached 10000. The crude **3-*iii*** was subjected to elimination of silanol by method A to give **2-*iii*** in 93% yield. In this case, iridium catalyst and silane wastes were easily separable from the products by a short silica gel column, and there was no detectable Ir species in the enamine product by ICP-MS analysis (<20 ppb; see the Supporting Information).

NMR Analysis of Silylhemiaminal Intermediates 3-*i*–*vii*. The silylhemiaminals **3-*i*–*vii*** are intermediates in the synthesis of π-conjugated enamines as described above. Most of them are unstable to moisture or the reagent that cleaves the O–Si bond. For example, signals due to the silylhemiaminal were clearly observed by ^{1}H NMR from C_6D_6, whereas peaks due to the corresponding aldehyde were observed rather than those from the hemiaminal in $CDCl_3$. Among the seven hemiaminals, **3-*vii*** was relatively stable and isolable. Treatment of **1-*vii*** with 2 equiv of TMDS in the presence of **4i** (0.5 mol %) was followed by removal of TMDS under vacuum. The yield was determined by quantitative ^{1}H NMR spectroscopy in the presence of an internal standard (hexamethylbenzene). The ^{1}H NMR spectrum of crude **3-*vii*** showed well-resolved signals without any peaks derived from impurities. The spectrum measured at room temperature consisted of four signals due to the diastereotopic $SiMe_2$ groups (O–$SiMe_2$–O–$SiHMe_2$, δ–0.26 (s, 3H), − 0.11 (d, $^3J_{H-H}$ = 2.8 Hz, 3H), − 0.10 (d, $^3J_{H-H}$ = 2.8 Hz, 3H), − 0.09 (s, 3H)), those showing an ABX pattern due to $CH_2CH(OSi)(NR_2)$ (δ 3.28 (dd, $^3J_{H-H}$ = 6.9 Hz, $^2J_{H-H}$ = 13.7 Hz, 1H), 3.50 (dd, $^3J_{H-H}$ = 6.9 Hz, $^2J_{H-H}$ = 13.7 Hz, 1H) and δ 6.41 (dd, $^3J_{H-H}$ = 6.9, 6.9 Hz, 1H)), and signals due to a Si–H group (4.72 (sept, $^3J_{H-H}$ = 2.8 Hz, 1H)) and the aromatic moieties. Sixteen resonances were visible in the ^{13}C NMR spectrum, whereas two resonances appeared in the ^{29}Si NMR spectrum. The high-resolution mass spectrum (EI) showed the $[M]^+$ signal. These spectral data are consistent with **3-*vii***.

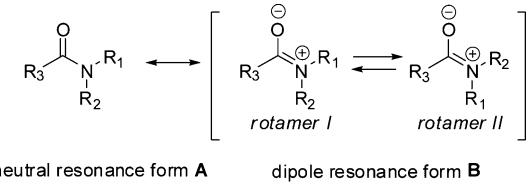
Isolation of the other six silylhemiaminals was unsuccessful due to contamination by a small amount of silicon products derived from TMDS, which were not removed under vacuum. Attempted chromatographic purification led to decomposition of the silylhemiaminal. Nevertheless, these species provided characteristic ^{1}H signals due to one methyl and two vicinal methine protons in Ph(Me)$CHCH$(OSi)(NR_2) of **3-*i*,*iii*,*v*** and those due to two vicinal methine protons in Ph_2CHCH(OSi)-(NR_2) of **3-*ii*,*iv*,*vi*** (see the Experimental Section and the Supporting Information). The α-methyl-α-phenyl derivatives **3-*i*,*iii*,*v*** exist as a mixture of diastereomers in ratios of 96:4, 95:5, and 85:15, respectively. The signal due to the α-methyl group of the major isomer for **3-*i*,*iii*,*v*** appeared as a doublet at δ 1.22, which was a chemical shift higher than that for the minor isomer. Similarly, the signal due to −SiOC*H*− was always observed in the downfield region (δ 5.55, 5.74, and 5.31, respectively). These results suggest that all of the three major isomers possess the same relative stereochemistry. As described above, the major isomer of **2-*i*,*iii*** was *E*; this is different from the major isomer of **2-*v*** (*Z*). They were formed from the major diastereomer of **3-*i*,*iii*,*v*** having the same configuration. A reasonable explanation for this is elimination of silanol, which did not proceed stereospecifically. It is also important that the *E*:*Z* ratio changed in the progress of the reaction, suggesting that it was controlled thermodynamically. For example, the ratio of (*E*)-**2-*i*** to (*Z*)-**2-*i*** was lower at the initial stage of the reaction (67:33 (after 30 min, conversion of **3-*i*** 20%), 84:16, (after 1 h, conversion of **3-*i*** 54%)) and came close to 90:10 after 4 h (conversion >99%). Although the mechanism is unclear at present, *E*/*Z* isomerization took place under the reaction conditions.

Mechanistic Considerations. As described above, marked differences in reactivity were present between *N*,*N*-dialkylamides such as **1-*viii*** and *N*,*N*-diarylamides **1-*i*–*vii***. The iridium complexes **4a–j** all showed some catalytic activity for the reaction of the former with TMDS, but only a limited number of iridium complexes exhibited activity for the reaction of the latter. It is also interesting that the products of the reactions of *N*,*N*-diarylamides **1-*i*–*vii*** were the corresponding silylhemiaminals **3-*i*–*vii***, whereas the reaction of **1-*viii*** gave the enamine **2-*viii*** and the silylheminal intermediate **3-*viii*** was never observed. A primary clue for understanding these results is the electronic nature of both the iridium catalysts and the amide precursors.

The electronic nature of the iridium centers of **4a–j** was estimated from ν_{CO}(Ir). Since **4a–j** have similar square-planar geometries and two phosphorus ligands are in the trans orientation, ν_{CO}(Ir) is strongly correlated with Tolman's value (Table 1). The complexes **4a–e**, where L is electron donating (χ = 0.3–10.9; ν_{CO}(Ir) 1932–1961 cm^{-1}) showed catalytic activity lower than that of Vaska's complex **4f** (χ = 12.8; ν_{CO} of **4f** 1967 cm^{-1}) in the reaction of *N*,*N*-diethylamide **1-*viii*** with TMDS to give the corresponding enamine **2-*viii***. In sharp contrast, the iridium complexes bearing electron-withdrawing phosphorus ligands (χ = 29.2–51.3; ν_{CO}(Ir) 2003–2059 cm^{-1}) exhibit high catalytic activity toward the hydrosilylation of **1-*i*–*vii*** to **3-*i*–*vii***, whereas no reaction occurred with **4f**. The results shown in Table 3 indicate the order of increasing catalytic activity as **4j** ≈ **4i** > **4h** > **4g**, which is consistent with the order of ν_{CO}(Ir): 2059 ≈ 2052 > 2011 > 2003 cm^{-1}. The results clearly showed that an iridium complex having an electron-deficient iridium center is a better catalyst for the hydrosilylation of the amides **1-*i*–*vii***.

The IR spectra of amides (ν_{CO}(amide)) **1-*i*–*viii*** also correlated with the reactivity. The ν_{CO}(amide) value was in the range 1632–1697 cm^{-1} and increased in the order **1-*viii*** (1632 cm^{-1}) < **1-*i*** (1659 cm^{-1}) < **1-*ii*–*iv*** (1667–1672 cm^{-1}) < **1-*v*,*vi*** (1680–1684 cm^{-1}) < **1-*vii*** (1697 cm^{-1}). Amides have the two resonance forms **A** and **B**, as shown in Chart 3, and the

Chart 3. Resonance Forms of Amides and Amide Rotation



lower ν_{CO} stretching is due to a higher contribution of the dipole resonance form **B**. Since **B** has two rotamers, the energy barrier of interconversion between the two rotamers can predict the reactivity of the amides. A higher energy barrier suggests a higher contribution of **B** in comparison to that of **A**.

Solution dynamics allow qualitative comparison of the energy barrier. NMR analysis of **1-*i*–*viii*** clearly showed that the amides were divided into three groups. The first group is **1-*viii***, which gave well-resolved ^{1}H and ^{13}C NMR spectra assignable to the dipole resonance form **B** at room temperature. In

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contrast, **1-*v*–*vii*** are in a second group, which afforded ^{1}H and ^{13}C resonances corresponding to the neutral resonance form **A** above room temperature. The remaining four amides, **1-*i*–*iv***, belong to a third group that exhibited ^{1}H and ^{13}C NMR spectra with extensive broadening of signals due to the NAr_2 group at room temperature. The spectra changed by cooling or heating, as shown in Figure S-1(a) in the Supporting Information as a typical example. Variable-temperature ^{1}H NMR of **1-*i*** in THF-d_8 showed two sets of signals at −40 °C due to the NPh_2 group, which correspond to the dipole resonance form **B**. The peaks began to broaden at −20 °C and coalesced at 25 °C. Broad signals assignable to the neutral resonance form **A** were observed at 40 °C and became sharp at 65 °C. Similar temperature-dependent phenomena were seen in the ^{13}C NMR spectra of **1-*i*** (Figure S-1(b)). These clearly demonstrate that the rotational barrier of the C(O)–N bond decreased in the order **1-*viii*** > **1-*i*–*iv*** > **1-*v*–*vii***. This is consistent with the order of ν_{CO} described above, suggesting that the contribution of the two rotamers was dependent on the substituents on the amide nitrogen atom.

The relationship of the reactivity of the amides to the catalytic activity of the iridium complexes is primarily correlated to that of the ν_{CO}(Ir) and ν_{CO}(amide) stretches, as shown in Figure 2. A higher ν_{CO}(Ir) value corresponds to a lower

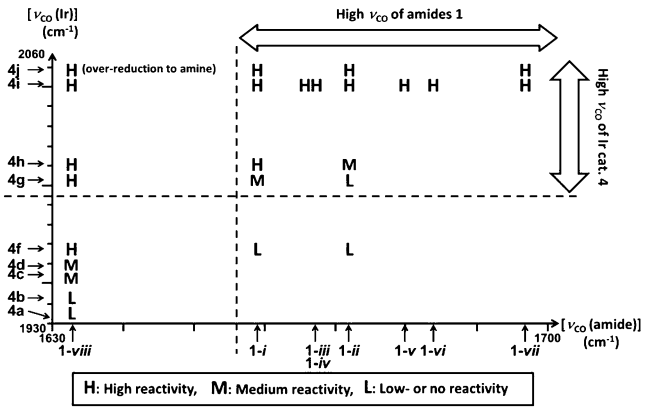

Figure 2. Catalytic activity of **4**: correlation with ν_{CO}(amide) and barrier of amide rotation vs ν_{CO}(Ir).

electron density of the iridium center. In contrast, a higher ν_{CO}(amide) value results from a lower contribution of dipole resonance form **B**. The results revealed that the amides with a lower contribution of dipole resonance form **B** (ν_{CO}(amide) >1650 cm^{-1}) were more difficult to hydrosilylate, but the reaction was achieved by a catalyst a more electron deficient iridium center (ν_{CO}(Ir) >2000 cm^{-1}), which showed higher activity for the amide having a lower contribution of the resonance form **B** (ν_{CO}(amide) >1650 cm^{-1}). A typical example is the reaction of **1-*vii*** (ν_{CO}(amide) 1697 cm^{-1}) catalyzed by **4i** (ν_{CO}(Ir) 2052 cm^{-1}), which is in sharp contrast to the facile hydrosilylation of **1-*viii*** (ν_{CO}(amide) 1632 cm^{-1}) by **4f** (ν_{CO}(Ir) 1967 cm^{-1}). It should also be noted that steric hindrance around the carbonyl group of the amides is an additional factor in the reactivity of the amides. For example, longer reaction times were needed to perform the hydrosilylation of *α*,*α*-diphenylacetamides **1-*ii*,*iv*,*vi*** in comparison with that of *α*-methyl-*α*-phenylacetamides **1-*i*,*iii*,*v***, respectively, having the same *N*-aryl group. The reaction of **1-*vii*** having one *α*-phenyl substituent was achieved by **4i**. However, no reaction took place for the *α*,*α*-diphenyl analogue under the same conditions.

It is necessary to gain additional mechanistic insight into the catalytic cycles proposed for the hydrosilylation of carbonyl compounds.[23] The Chalk–Harrod mechanism was proposed for the platinum-catalyzed hydrosilylation of alkenes in the earlier stages of the hydrosilylation studies, and later a modified Chalk–Harrod cycle was discussed both experimentally and theoretically.[24] The hydrosilylation of carbonyl compounds has been considered to proceed through the modified Chalk–Harrod cycle as proposed by Ojima and Kogure in 1975.[25] In a recent review on the rhodium-catalyzed hydrosilylation of ketones, several other possible mechanisms were described for the reaction with di- or trihydrosilanes;[23a] however, these are not suitable for the present hydrosilylation with TMDS, in which the silicon center is trisubstituted. When Ojima's mechanism shown in Scheme 4a is adapted to the iridium-catalyzed hydrosilylation of amides to silylhemiaminals, the initial step is oxidative addition of a Si–H bond to a transition-metal center to form the H–Ir–Si moiety **X**, as shown in Scheme 4b. A C═O bond in the amide is inserted in the resulting M–Si bond to give the intermediate **Y**. Reductive elimination of a silyl ether from **Y** gives the silylhemiaminal. It is important that the Si–Ir bond of **X** is polarized as $Ir^{\delta-}$ and $Si^{\delta+}$ due to the difference in electronegativity between Si and Ir. In an extreme case, the R_3Si–Ir–H species is dissociated to form R_3Si^+ and $[Ir–H]^-$. The negative charge of the $[Ir–H]^-$ species is mitigated by electron-withdrawing ligands such as $P(NC_4H_4)_3$, $P(OC_6F_5)_3$, and $P\{O(CHCF_3)_2\}_3$, which are bound to the iridium phosphorus center. This increases the thermodynamic stability of $[Ir–H]^-$ and enhances the electrophilicity of R_3Si^+.

On the other hand, in the reaction of the two resonance forms **A** and **B** of amides with the intermediate **X**, the dipole resonance form **B**, having a negative charge on the oxygen atom, should react with the highly electrophilic silicon atom in the R_3Si–Ir–H species **X** with ease. This explains the higher reactivity of *N*,*N*-dialkylamides such as **1-*viii*** in the present iridium-catalyzed reactions; the reaction was achieved even with Vaska's complex **4f**. In contrast, the contribution of **B** is smaller in the amides **1-*i*–*vii***; this made the reaction catalyzed by **4f** difficult. In sharp contrast, when the electrophilicity of the silicon atom in **X** is enhanced by the electron-drawing phosphorus ligands, the less reactive neutral resonance form **A** of **1-*i*–*vii*** is able to react with R_3Si–Ir–H.

The higher contribution of neutral resonance form **A** in comparison to that of dipole resonance form **B** in **1-*i*–*vii*** is due to delocalization of lone-pair electrons of the nitrogen atom over conjugated *π* systems in the adjacent *N*-aryl substituents. This also explains why the reaction of **1-*viii*** directly afforded **2-*viii*** but those of **1-*i*–*vii*** were terminated after the silylhemiaminals **3-*i*–*vii*** were formed. As shown in Scheme 4, elimination of a silanol anion assisted by heat or acid from the silylhemiaminal **3** forms iminium cation **Z**. Deprotonation of **Z** takes place with ease to form the enamine **2**. In other words, the E1 elimination of silanol is preferable to the E2 process. Elimination of silanol by the E1 process does not occur in a stereospecific manner; this explains the formation of both *E* and *Z* isomers of **2** from the same diastereomeric configuration of **3**.

■ CONCLUSION

As reported previously, transformation of *N*,*N*-dialkylamides to aldenamines by treatment with TMDS is efficiently catalyzed by

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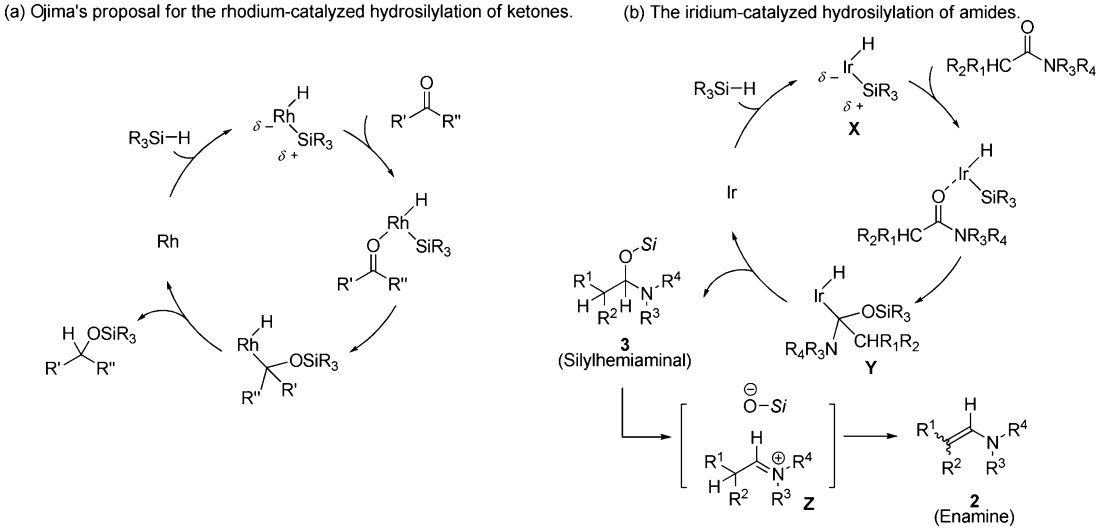
Scheme 4. Modified Chalk−Harrod Cycle[25] Proposed by Ojima and a Possible Mechanism for the Hydrosilylation of Amides and Conversion of Silylhemiaminals to Enamines



Vaska's complex **4f**. However, *N,N*-diarylamides **1-*i*−*vii***, which are precursors of the π-conjugated enamines **2-*i*−*vii***, hardly reacted with TMDS under the same conditions. A new discovery presented in this paper is that $IrCl(CO)L_2$ complexes bearing electron-withdrawing fluorinated phosphites as L such as **4i,j** are effective catalysts for the preparation of **2-*i*−*vii***. In contrast to *N,N*-dialkylamides such as **1-*viii*** that directly afford the corresponding aldenamines, the reaction of *N,N*-diarylamides with TMDS gives silylhemiaminals **3** as the primary products, which are converted to π-conjugated enamines by subsequent treatment with heat or acid. The new catalyst **4i** showed extremely high catalytic activity for both the one-step conversion of *N,N*-dialkylamides **1-*viii*** to **2-*viii*** and the two-step procedure to form **2-*iii*** from *N,N*-diarylamide **1-*iii***. The TON of the formation of **2-*viii*** exceeded 10^5, which was accomplished at room temperature within 30 min. A TON of 10^4 was achieved at 40 °C when **1-*iii*** was the substrate. In both cases, the level of residual iridium in the product was below the detection limit (20 ppb) of ICP-MS analysis. The remarkable catalytic activity of **4i,j** is ascribed to the generation of an electron-deficient iridium center in the catalytic cycle, which was achieved by the ligand effect of electron-withdrawing fluorinated phosphites. The electron-deficient iridium species activates a Si−H bond to form the oxidative adduct including an electrophilic silicon atom, which is capable of reacting with the neutral resonance form of the *N,N*-diarylamides. Since the residual metal has to be minimized when transition-metal-catalyzed reactions are applied to the preparation of electronic materials, the present method will be useful for synthesis of π-conjugated enamines as hole-transport materials. Good donor properties of metal-free π-conjugated enamines could open further applications of these compounds to control photo and electron functionality.

Elucidation of the mechanism awaits further investigation. One of the questions that has remained unsolved is why only TMDS is useful for the conversion from an amide to a silylhemiaminal, while no reaction took place with other hydrosilanes such as $Me_3SiOSiHMe_2$, $PhMe_2SiH$, Ph_2SiH_2, and $PhSiH_3$. Similar results where use of hydrosilanes bearing two closely located Si−H groups is crucially important are seen in several metal-catalyzed hydrosilylation, as summarized in our recent account.[16h] It is also important to investigate further insights into the catalytic intermediates and transition states involved in the catalytic cycle. We referred to discussion of the Chalk−Harrod and modified Chalk−Harrod mechanisms in a previous section. Other than these, an alternative outer-sphere route where the amide directly attacks the silicon atom of the oxidative adduct, H−M−Si, was proposed in the rhodium-catalyzed hydrosilylation of ketones with Ph_2SiH_2.[23a] The recent development of hydrosilylation catalyzed by cationic iridium or ruthenium complexes suggested ionic outer-sphere mechanisms,[26] which were also summarized as a recent review.[23b] The iridium complexes used in this study are neutral and not cationic; however, the possible involvement of these outer-sphere mechanisms should not be excluded in further detailed studies. We are currently investigating these mechanistic aspects by isolation of the catalytic intermediates and DFT calculations.

EXPERIMENTAL SECTION

General Procedure. All reactions were carried out under an argon atmosphere using standard Schlenk techniques or were performed in a N_2-filled glovebox. ^1H, ^{13}C, ^{19}F, ^{29}Si, and ^{31}P NMR spectra were measured on JEOL ECA 400 (396 MHz) and ECA600 (600 MHz) spectrometers. Chemical shifts for ^1H and ^{13}C were given in parts per million relative to the solvent signal. Chemical shifts for ^{19}F, ^{31}P, and ^{29}Si are given in parts per million downfield from hexafluorobenzene (δ_F −163.6), phosphoric acid (δ_P 0), and tetramethylsilane (δ_{Si} 0) as external standards, respectively. IR spectra were measured on a JASCO FT/IR 4200 spectrometer. Elemental analyses were measured on a PerkinElmer 2400II/CHN analyzer. HR-MS analyses, ICP-MS analyses, and X-ray diffraction analyses were performed at the Analytical Center of the Institute for Materials Chemistry and Engineering, Kyushu University. Dehydrated solvents (toluene, 1,4-dioxane, THF, Et_2O, *n*-pentane) were purchased from Kanto Chemical Co. Ltd. and used as received. *N,N*-Diethyl-2-phenylacetylamide (**1-*viii***), 1,1,3,3- tetramethyldisiloxane (TMDS), and P_2O_5 were purchased from Wako Pure Chemical Industries, AZmax Co. Ltd., and Merck, respectively. The phosphorus ligands PCy_3, PEt_3, PMe_2Ph, $PMePh_2$, P(*o*-tolyl)$_3$, PPh_3, and P(OPh)$_3$ were purchased from Kanto Chemical Co. Ltd. The syntheses of the three phosphorus compounds tris(*N*-pyrrolyl)phosphine ($P(NC_4H_4)_3$),[21a] tris(1,1,1,3,3,3-hexafluoro-2-propyl) phosphite ($P\{OCH(CF_3)_2\}_3$),[21b,c] and tris(2,3,4,5,6-pentafluorophenyl) phosphite ($P(OC_6F_5)_3$)[21d] have been reported in the

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literature. $Ir(COD)Cl\}_2$[27] and **4a−g** were prepared according to known methods.[20,28]

Preparation of Ir{P(NC$_4$H$_4$)$_3$}$_2$(CO)Cl (4h), Ir{P(OC$_6$F$_5$)$_3$}$_2$(CO)Cl (4i), and Ir[P{CH(CF$_3$)$_2$}$_3$]$_2$(CO)Cl (4j). These iridium complexes were synthesized from $\{Ir(COD)Cl\}_2$ and the corresponding phosphorus ligands. In a typical example, $\{Ir(COD)Cl\}_2$ (133.5 mg, 0.20 mmol), tris(*N*-pyrrolyl)phosphine (192.0 mg, 0.64 mmol), and THF (5 mL) were placed in a 50 mL Schlenk flask at −78 °C, the solution was degassed by three freeze−pump−thaw cycles, and the atmosphere was replaced by carbon monoxide. The solution was stirred for 1 h at −78 °C and for an additional 12 h at ambient temperature. The solution turned from orange to light yellow. The solution was filtered through a short pad of Celite, and the solvent was then removed under reduced pressure. The desired complex **4h** was obtained as a yellow solid (307 mg, 0.39 mmol, 96%). ^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 6.42 (br, 12H, NC$_4$*H*$_4$), 7.05 (br, 12H, NC$_4$*H*$_4$). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, room temperature): δ 114.1 (NC$_4$H$_4$), 124.5 (NC$_4$H$_4$), 166.4 (*C*O). $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$, room temperature): δ 79.5 (*P*(NC$_4$H$_4$)$_3$). IR (KBr, cm^{-1}): 2011 (ν_{CO}). Dec pt: 152 °C. Anal. Calcd for $C_{25}H_{24}N_6OP_2ClIr$: C, 42.05, H, 3.39, N, 11.77. Found: C, 42.15, H, 3.41, N, 11.58.

In a similar fashion, **4i** was synthesized from $\{Ir(COD)Cl\}_2$ (100.0 mg, 0.15 mmol) and tris(2,3,4,5,6-pentafluorophenyl) phosphite (345.0 mg, 0.60 mmol). The crude compound was recrystallized from THF and pentane to afford **4i** as a yellow solid (64.0 mg, 0.05 mmol, 30%). $^{13}C\{^{19}F\}$ NMR (151 MHz, $CDCl_3$, room temperature): δ 125.0 (*ipso*-C_6F_5), 138.1 (*m*-C_6F_5), 140.0 (*p*-C_6F_5), 141.0 (*o*-C_6F_5), 165.1 (CO). ^{19}F NMR (565 MHz, $CDCl_3$, room temperature): δ − 161.7 (dd, $^3J_{F-F}$ = 20.7 Hz, *m*-C_6F_5), − 156.7 (t, $^3J_{F-F}$ = 20.7 Hz, *p*-C_6F_5), − 151.8 (d, $^3J_{F-F}$ = 20.7 Hz, *o*-C_6F_5). $^{31}P\{^{19}F\}$ NMR (243 MHz, $CDCl_3$, room temperature): δ 108.0 (*P*(OC$_6$F$_5$)$_3$). IR (KBr, cm^{-1}): 2052 (ν_{CO}). Dec pt: 176 °C. Anal. Calcd for $C_{37}O_7F_{30}P_2ClIr$: C, 31.39, H, 0.00. Found: C, 31.56, H, 0.12.

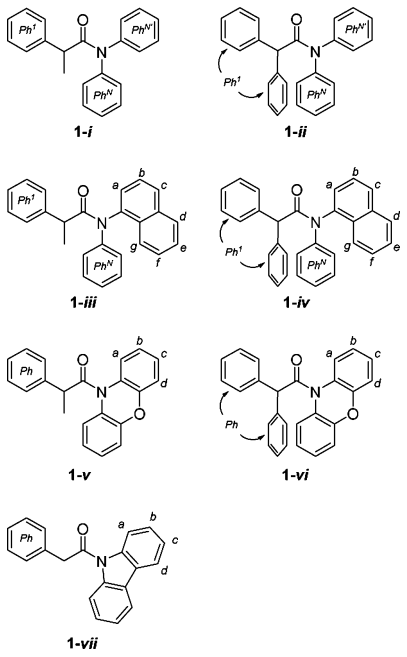
The preparation of **4j** was performed by treatment of $\{Ir(COD)Cl\}_2$ (100.0 mg, 0.15 mmol) and tris(1,1,1,3,3,3-hexafluoro-2-propyl) phosphite (317.0 mg, 0.60 mmol) in a manner similar to that above. The crude product was recrystallized from THF and pentane to afford **4j** as a yellow solid (31.0 mg, 0.02 mmol, 16%). ^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 5.64 (br, 6H, −C*H*(CF$_3$)$_2$). $^{13}C\{^{19}F\}$ NMR (151 MHz, $CDCl_3$, room temperature): δ 71.7 (d, $^1J_{C-H}$ = 151 Hz, −CH(CF$_3$)$_2$), 119.6 (s, −CH(*C*F$_3$)$_2$), 162.6 (s, *C*O). ^{19}F NMR (565 MHz, $CDCl_3$, room temperature): δ − 73.38 (s, −CH(C*F*$_3$)$_2$). $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$, room temperature): δ 113.20 (*P*{OCH(CF$_3$)$_2$}$_3$). IR (KBr, cm^{-1}): 2059 (ν_{CO}). Dec pt: 184 °C. Anal. Calcd for $C_{19}H_6O_7F_{36}P_2ClIr$: C, 17.29, H, 0.46. Found: C, 17.55 H, 0.39.

Preparation and Characterization of Carboxamides. The following procedure, reported for the preparation of ***1-viii***,[13] was adopted to synthesize the five carboxamides ***1-i,ii,iv−vi***. In a 500 mL of three-necked flask, amine (13 mmol) and pyridine (26 mmol) were dissolved in CH_2Cl_2 (10 mL). A solution of acyl chloride (10 mmol) in CH_2Cl_2 (10 mL) was then added dropwise at −78 °C. The solution was then stirred at ambient temperature for 8 h. The reaction was quenched with 1 M aqueous HCl, and the organic layer was separated, washed with saturated aqueous $NaHCO_3$, and dried over $MgSO_4$. After filtration, the solution was concentrated in vacuo. The residue was purified by chromatography on silica gel (hexane/EtOAc 10/1). Further purification by recrystallization from ethanol afforded the desired amide.

The amide ***1-iii*** was prepared by a procedure similar to that reported for the preparation of $PhCH_2(C{=}O)NPh_2$.[29a] To a solution of 1-naphthylamine (1.75 g, 8.0 mmol) in 1,4-dioxane (20 mL) was added a solution of 2-phenylpropyonyl chloride (1.68 g, 10.0 mmol) in 1,4-dioxane (10 mL) dropwise at ambient temperature in a 300 mL three-necked flask. The solution was then heated under reflux for 8 h. The reaction mixture was cooled and poured into cool water. The white precipitates that formed were collected, washed with hexane (5 mL × 5), and dried under vacuum to afford ***1-iii*** (1.56 g, 4.43 mmol, 44%) as a white solid. The residue was purified by chromatography on silica gel (hexane/EtOAc 10/1). Further purification by recrystallization from ethanol afforded the desired amide. The preparation of ***1-vii*** was performed according to the literature method.[29b] From carbazole (2.17 g, 13.0 mmol) and phenylacetyl chloride (1.54 g, 10 mmol), ***1-vii*** was obtained as a white solid (2.35 g, 8.24 mmol, 82%).

Although amides ***1-i,vii*** are known compounds, NMR data reported in the literature were ambiguous due to the amide rotation on the NMR time scale or contamination by impurities.[30,31] We performed variable-temperature NMR studies for ***1-i−vi*** in several different solvents. Assignments of NMR data were performed with the aid of ^{1}H−^{1}H COSY experiments (protons are labeled as shown in Chart 4).

Chart 4. Labels for Identification of Amide 1



In this Experimental Section, the data measured at the temperature whiched afford the best-resolved resonances are described, and other data are summarized in the Supporting Information.

N,N-Diphenyl-2-phenylpropionamide (1-i).[30] From diphenylamine (2.20 g, 13.0 mmol) and 2-phenylpropyonyl chloride (1.68 g, 10.0 mmol), ***1-i*** was obtained as a white solid (2.02 g, 6.72 mmol, 67%). Measurement at −40 °C provided spectra due to the dipole resonance form **B**. ^{1}H NMR (600 MHz, THF-d_8, −40 °C): δ 1.37 (d, $^3J_{H-H}$ = 6.8 Hz, 3H, −CH*Me*Ph), 3.83 (q, $^3J_{H-H}$ = 6.8 Hz, 1H, −C*H*MePh), 7.02 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, *o*-*Ph*^{1}), 7.08 (t, $^3J_{H-H}$ = 7.2 Hz, 1H, *p*-*Ph*^{N}), 7.16 (d, $^3J_{H-H}$ = 7.6 Hz, 2H, *o*-*Ph*^{N}), 7.17 (t, $^3J_{H-H}$ = 7.2 Hz, 1H, *p*-*Ph*^{1}), 7.21 (dd, $^3J_{H-H}$ = 7.6, 7.6 Hz, 2H, *m*-*Ph*^{1}), 7.23 (dd, $^3J_{H-H}$ = 7.2 Hz, 2H, *m*-*Ph*^{N}), 7.33 (br-dd, 1H, *p*-*Ph*$^{N\prime}$); 7.35 (br, 2H, *m*-*Ph*$^{N\prime}$); 6.7−7.8 (br, 2H, *o*-*Ph*$^{N\prime}$). $^{13}C\{^1H\}$ NMR (151 MHz, THF-d_8, −40 °C): δ 20.9, 44.8, 126.0, 127.2, 127.3, 128.2, 128.4, 129.0, 129.1, 130.2, 130.3, 142.9, 143.7, 144.3, 173.2. Measurement at +65 °C provided spectra due to the neutral resonance form **A**. ^{1}H NMR (600 MHz, THF-d_8, 65 °C): δ 1.38 (d, $^3J_{H-H}$ = 6.8 Hz, 3H, −CH*Me*Ph), 3.81 (q, $^3J_{H-H}$ = 6.8 Hz, 1H, −C*H*MePh), 7.04 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, *o*-*Ph*^{1}), 7.11 (d, $^3J_{H-H}$ = 7.2 Hz, 4H, *o*-*NPh*$_2$), 7.14 (t, $^3J_{H-H}$ = 7.2 Hz, 1H, *p*-*Ph*^{1}), 7.27 (dd, $^3J_{H-H}$ = 7.2 Hz, 2H, *m*-*Ph*^{1}), 7.28 (t, $^3J_{H-H}$ = 7.2 Hz, 2H, *p*-*NPh*$_2$), 7.35 (dd, $^3J_{H-H}$ = 7.2 Hz, 4H, *m*-*NPh*$_2$). $^{13}C\{^1H\}$ NMR (151 MHz, THF-d_8, 65 °C): δ 20.7, 45.1, 127.0 (br), 127.1, 128.3, 128.7 (br), 128.9, 129.5 (br), 143.2, 144.4, 173.5. IR (ATR, cm^{-1}): 1659 (ν_{CO}). Mp: 118−119 °C. HRMS-EI(+) (*m*/*z*): $[M]^+$ calcd for $C_{21}H_{19}NO$, 301.1467; found, 301.1468. Anal. Calcd for $C_{21}H_{19}NO$: C, 83.69, H, 6.35, N, 4.65. Found: C, 83.51, H, 6.38, N, 4.46.

N,N-Diphenyl-2,2-diphenylacetamide (1-ii). From diphenylamine (2.20 g, 13.0 mmol) and diphenylacetyl chloride (2.31 g, 10.0 mmol), ***1-ii*** was obtained as a white solid (2.28 g, 6.28 mmol, 63%). The ^{1}H

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NMR spectrum at 70 °C gave well-resolved signals due to the neutral resonance form **A**. ^{1}H NMR (600 MHz, CD_3CN, 70 °C): δ 5.20 (s, 1H, $-CHPh_2$), 7.23 (d, $^3J_{H-H}$ = 7.2 Hz, 4H, *o*-Ph^1), 7.24 (d, $^3J_{H-H}$ = 7.2 Hz, 4H, *o*-NPh_2), 7.27 (t, $^3J_{H-H}$ = 7.2 Hz, 2H, *p*-NPh_2), 7.31 (t, $^3J_{H-H}$ = 7.2 Hz, 2H, *p*-Ph^1), 7.31 (dd, $^3J_{H-H}$ = 7.2, 7.2 Hz, 4H, *m*-Ph^1), 7.37 (dd, $^3J_{H-H}$ = 7.2, 7.2 Hz, 4H, *m*-NPh_2). $^{13}C\{^1H\}$ NMR (151 MHz, THF-d_8, −40 °C): 55.7, 126.3, 127.3, 127.5, 128.8, 128.9, 129.1, 129.7, 130.1, 130.5, 140.9, 143.96, 144.02, 171.2. IR (ATR, cm^{-1}): 1672 (ν_{CO}). Mp: 83−84 °C. HRMS-EI(+) (m/z): $[M]^+$ calcd for $C_{26}H_{21}NO$, 363.1623; found, 363.1620. Anal. Calcd for $C_{26}H_{21}NO$: C, 85.92, H, 5.82, N, 3.85. Found: C, 86.10, H, 5.93, N, 3.86.

*N-(1-Naphthyl)-N-phenyl-2-phenylpropionamide (**1-iii**).* Measurement at −20 °C provided spectra due to the dipole resonance form **B**. A mixture of four rotamers was observed in a ratio of 54:26:13:7. ^{1}H NMR (600 MHz, $CDCl_3$, −20 °C): δ 1.38, 1.47, 1.55, and 1.59 (54:26:13:7, d each, $^3J_{H-H}$ = 6.8 Hz, 3H in total, $-CHMePh$), 3.38, 3.72, 4.21, and 4.08 (54:26:13:7, q each, $^3J_{H-H}$ = 6.8 Hz, 1H in total, $-CHMePh$), 6.74−7.54 (a mixture of signals, 15H in total, Ph^1, Ph^N and *Naphthyl*), 7.98, 7.84, 7.75, and 7.78 (54:26:13:7, d each, $^3J_{H-H}$ = 7.6 Hz, 1H in total, H^d), 8.14, 7.95, 7.82, and 8.10 (54:26:13:7, d each, $^3J_{H-H}$ = 7.6 Hz, 1H in total, H^g). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, −20 °C): 20.9, 20.2, 19.4, and 21.7 (54:26:13:7, $-CHMePh$), 45.0, 44.4, 43.6, and 43.7 (54:26:13:7, -CHMePh), 125.3−143.2 (^{13}C resonances due to Ph^1, Ph^N and *Naphthyl*), 174.7, 175.1, 174.6, and 174.9 (54:26:13:7, C═O). IR (ATR, cm^{-1}): 1667 (ν_{CO}). Mp: 95−96 °C. HRMS−EI(+) (m/z): $[M]^+$ calcd for $C_{25}H_{21}NO$, 351.1623; found, 351.1618.

*N-(1-Naphthyl)-N-phenyl-2,2-diphenylacetamide (**1-iv**).* From 1-naphthylphenylamine (2.85 g, 13.0 mmol) and diphenylacetyl chloride (2.31 g, 10.0 mmol), **1-*iv*** was obtained as a white solid (2.88 g, 6.96 mmol, 70%). Measurement at −20 °C provided spectra due to the dipole resonance form **B**. A mixture of two rotamers was observed in a ratio of 86:14 at −20 °C. Data for the major rotamer are as follows. ^{1}H NMR (600 MHz, $CDCl_3$, −20 °C): δ 4.76 (s, 1H, $-CHPh_2$), 7.03 (t, $^3J_{H-H}$ = 7.2 Hz, 2H, Ph^1 *or* Ph^N), 7.08 (d, $^3J_{H-H}$ = 7.6 Hz, 1H, H^a), 7.12 (t, $^3J_{H-H}$ = 7.2 Hz, 1H, Ph^1 *or* Ph^N), 7.14−7.22 (a mixture of signals, 5H in total, Ph^1 *or* Ph^N), 7.24−7.42 (a mixture of signals, 10H in total, Ph^1 *or* Ph^N), 7.39 (dd, $^3J_{H-H}$ = 7.6 Hz, 1H, H^b), 7.53 (dd, $^3J_{H-H}$ = 7.6, 7.6 Hz, 1H, H^f), 7.57 (d, $^3J_{H-H}$ = 7.6, 7.6 Hz, 1H, H^e), 7.93 (d, $^3J_{H-H}$ = 7.6 Hz, 1H, H^c), 7.96 (d, $^3J_{H-H}$ = 7.6 Hz, 1H, H^d), 8.02 (d, $^3J_{H-H}$ = 7.6 Hz, 1H, H^g). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, −20 °C): 56.2, 122.9, 125.2, 125.6, 125.9, 126.9, 127.0, 127.2, 127.8, 128.2, 128.3, 128.6, 128.6, 128.7, 128.7, 129.0, 129.4, 130.9, 134.7, 137.7, 139.0, 139.5, 142.0, 172.6. ^{1}H and ^{13}C signals due to the minor rotamer were visible in the same spectra. ^{1}H NMR of minor rotamer (600 MHz, $CDCl_3$, −20 °C): δ 5.42 (s, 1H, $-CHPh_2$), 7.00−7.60 (a mixture of signals, 19H in total, Ph^1, Ph^N and *Naphthyl*), 7.71 (d, $^3J_{H-H}$ = 7.6 Hz, 1H, H^c), 7.78 (d, $^3J_{H-H}$ = 7.6 Hz, 1H, H^d), 7.85 (d, $^3J_{H-H}$ = 7.6 Hz, 1H, H^g). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, −20 °C): 54.6, 122.7, 125.8, 126.0, 126.3, 127.1, 127.2, 127.4, 127.7, 128.1, 128.6, 128.8, 128.9, 129.1, 129.8, 129.9, 134.4, 139.4, 139.5, 139.6, 143.2, 172.4. The other two peaks were unable to be observed due to overlap with the major rotamer. IR (ATR, cm^{-1}): 1667 (ν_{CO}). Mp: 124−125 °C. HRMS-EI(+) (m/z): $[M]^+$ calcd for $C_{30}H_{23}NO$, 413.1780; found, 413.1778.

*N-Phenoxazinyl-2-phenylpropionamide (**1-v**).* From phenoxazine (2.38 g, 13.0 mmol) and 2-phenylpropyonyl chloride (1.68 g, 10.0 mmol), **1-*v*** was obtained as a dark green solid (1.74 g, 5.51 mmol, 55%). Measurement at 50 °C provided spectra due to the neutral resonance form **A**. ^{1}H NMR (600 MHz, CD_3CN, 50 °C): δ 1.42 (d, $^3J_{H-H}$ = 6.8 Hz, 3H, $-CHMePh$), 4.48 (q, $^3J_{H-H}$ = 6.8 Hz, 1H, $-CHMePh$), 6.97 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, *o-Ph*), 7.02 (d, $^3J_{H-H}$ = 7.6 Hz, 2H, H^d), 7.17 (dd, $^3J_{H-H}$ = 7.6 Hz, 2H, H^b), 7.18 (dd, $^3J_{H-H}$ = 7.2 Hz, 2H, *m-Ph*), 7.19 (t, $^3J_{H-H}$ = 6.8 Hz, 1H, *p-Ph*), 7.21 (dd, $^3J_{H-H}$ = 8.2, 7.6 Hz, 2H, H^c), 7.54 (d, $^3J_{H-H}$ = 8.2 Hz, 2H, H^a). $^{13}C\{^1H\}$ NMR (151 MHz, CD_3CN, 50 °C): δ 20.6, 43.8, 117.7, 124.7, 126.8, 127.9, 128.3, 128.3, 129.7, 130.9, 142.3, 152.6, 174.7. IR (ATR, cm^{-1}): 1680 (ν_{CO}). Mp: 139−140 °C. HRMS-EI(+) (m/z): $[M]^+$ calcd for $C_{21}H_{17}NO_2$, 315.1259; found, 315.1273. Anal. Calcd for $C_{21}H_{17}NO_2$: C, 79.98, H, 5.43, N, 4.44. Found: C, 79.72, H, 5.54, N, 4.52.

*N-Phenoxazinyl-2,2-diphenylacetamide (**1-vi**).* From phenoxazine (2.38 g, 13.0 mmol) and diphenylacetyl chloride (2.31 g, 10.0 mmol), **1-*vi*** was obtained as a dark green solid (3.01 g, 7.98 mmol, 80%). Measurement from room temperature to +70 °C provided spectra due to the neutral resonance form **A**. ^{1}H NMR (600 MHz, CD_3CN, 70 °C): δ 5.80 (s, 1H, $-CHPh_2$), 7.07 (d, $^3J_{H-H}$ = 8.2 Hz, 2H, H^d), 7.17 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, *o-Ph*), 7.19 (dd, $^3J_{H-H}$ = 7.2, 7.2 Hz, 2H, H^b), 7.24 (dd, $^3J_{H-H}$ = 8.2, 7.2 Hz, 2H, H^c), 7.25 (t, $^3J_{H-H}$ = 6.8 Hz, 2H, *p-Ph*), 7.28 (dd, $^3J_{H-H}$ = 6.8 Hz, 4H, *m-Ph*), 7.59 (d, $^3J_{H-H}$ = 8.2 Hz, 2H, H^a). $^{13}C\{^1H\}$ NMR (151 MHz, CD_3CN, 70 °C): δ 55.5, 118.0, 124.9, 126.9, 128.4, 128.7, 129.7, 130.2, 131.1, 140.6, 152.9, 172.9. IR (ATR, cm^{-1}): 1684 (ν_{CO}). Mp: 125−127 °C. HRMS-EI(+) (m/z): $[M]^+$ calcd for $C_{26}H_{19}NO_2$, 377.1416; found, 377.1409. Anal. Calcd for $C_{26}H_{19}NO_2$: C, 82.74, H, 5.07, N, 3.71. Found: C, 82.86, H, 4.98, N, 3.63.

*N-Carbazolyl-2-phenylacetamide (**1-vii**).*[31] Measurement at room temperature provided spectra due to the neutral resonance form **A**. ^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 4.51 (s, 2H, $-CH_2Ph$), 7.34 (t, $^3J_{H-H}$ = 6.8 Hz, 1H, *p-Ph*), 7.36 (d, $^3J_{H-H}$ = 7.6 Hz, 2H, *o-Ph*), 7.41 (dd, $^3J_{H-H}$ = 6.8,7.6 Hz, 2H, *m-Ph*), 7.42 (dd, $^3J_{H-H}$ = 8.2, 7.6 Hz, 2H, H^c), 7.48 (dd, $^3J_{H-H}$ = 8.9, 7.6 Hz, 2H, H^b), 8.02 (d, $^3J_{H-H}$ = 8.2 Hz, 2H, H^d), 8.26 (d, $^3J_{H-H}$ = 8.9 Hz, 2H, H^a). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, room temperature): δ 45.5, 116.7, 120.0, 124.0, 126.7, 127.5, 127.6, 129.0, 129.7, 133.7, 138.7, 171.3. IR (ATR, cm^{-1}): 1697 (ν_{CO}); Mp: 113−114 °C (lit. mp 123−124 °C). HRMS-EI(+) (m/z): $[M]^+$ calcd for $C_{20}H_{15}NO$, 285.1154; found 285.1150. Anal. Calcd for $C_{20}H_{15}NO$: C, 84.19, H, 5.30, N, 4.91. Found: C, 84.21, H, 5.31, N, 4.80.

Screening of Iridium Catalysts for the Reduction of 1-*viii* with TMDS (Table 2). In an NMR tube equipped with a J. Young valve were placed *N*,*N*-diethyl-2-phenylacetamide (**1-*viii***; 190 μL, 1.00 mmol) and an iridium catalyst selected from **4a−j** (0.005 mmol, 0.5 mol %). Hexamethylbenzene was also added (0.05 mmol) as an internal standard. Then 1,1,3,3-tetramethyldisiloxane (2.00 mmol) and C_6D_6 (0.2 mL) were added, and the reaction was monitored by ^{1}H NMR spectroscopy. During the reaction, generation of H_2 gas was observed. The conversion of **1-*viii*** and yield of **2-*viii*** were calculated by integral ratios on the basis of the internal standard. The results are summarized in Table 2. Since no byproduct was formed, the conversion of **1-*viii*** matched the yield of **2-*viii***. The exception was the reaction with **4j**, giving a mixture of **2-*viii*** (45%) and an amine, $PhCH_2CH_2NEt_2$ (55%). Only the trans isomer was formed for **2-*viii***.

Screening of Iridium Catalysts for the Reduction of 1-*i* and 1-*ii* with TMDS Catalyzed by Selected Iridium Complexes 4f−j (Table 3). In a 50 mL two-necked flask were placed *N*,*N*-diphenyl-2-phenylpropionamide (**1-*i***; 301 mg, 1.00 mmol) and one of the iridium catalysts (0.005 mmol, 0.5 mol %) selected from **4f−j**. Then 1,1,3,3-tetramethyldisiloxane (2.00 mmol) and toluene (4.0 mL) were added, and the mixture was stirred at ambient temperature for 30 min. After the reaction, anisole (1.00 mmol) was added as an internal standard. The sample was subjected to ^{1}H NMR analysis, and the conversion of **1-*i*** and yield of silylhemiaminal **3-*i*** were determined by comparison of the integral ratios relative to that of the internal standard, as shown in Table 3. The silylhemiaminal **3-*i*** was obtained as a mixture of two diastereomers (vide infra). The solvent and unreacted TMDS in the solution were removed under reduced pressure, and the residue was dissolved in toluene (15 mL). Conversion of **3-*i*** to **2-*i*** was performed by method A. The resulting solution of **3-*i*** was heated to 100 °C for 6 h. The solvent was then removed under reduced pressure, and anisole (1.00 mmol) was again added as an internal standard. The sample was subjected to ^{1}H NMR analysis, and the yield of enamine **2-*i*** were determined by comparison of the integral ratios relative to that of the internal standard, as shown in Table 3.

In a similar fashion, screening of the iridium catalyst was performed for the reaction of **1-*ii*** with TMDS. After the conversion of **1-*ii*** and the yield of silylhemiaminal **3-*ii*** were determined by ^{1}H NMR, volatiles were removed under reduced pressure. Conversion of **3-*ii*** to **2-*ii*** was performed by method B; toluene (10 mL) and 1 M HCl in

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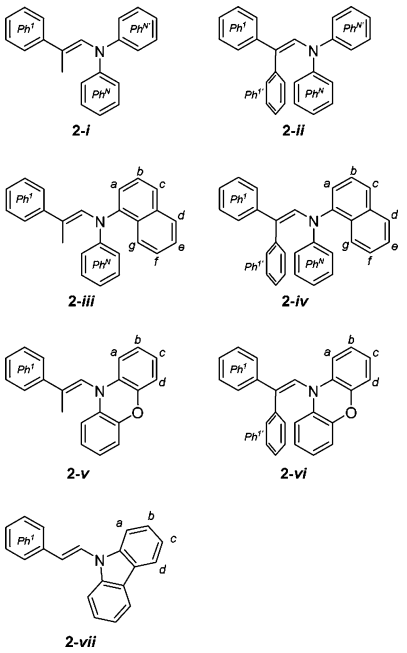
Et_2O (5 mL) were placed in the flask. The solution was stirred for 30 min at ambient temperature. The solvent was then removed under reduced pressure, and anisole (1.00 mmol) was again added as an internal standard. The sample was subjected to ^1H NMR analysis, and the yield of enamine **2-*ii*** was determined by comparison of the integral ratio relative to that of the internal standard, as shown in Table 3.

Isolation of 2-*i*–*vii* by Reactions Catalyzed by 4i. The general procedure is as follows: in a 20 mL two-necked found flask were placed carboxamides **1-*i*–*vii*** (1.00 mmol) and the iridium catalyst **4i** (7.1 mg, 0.005 mmol, 0.5 mol %). Then 1,1,3,3-tetramethyldisiloxane (2.00 mmol) and toluene (4.0 mL) were added, and the mixture was stirred at ambient temperature for 2 h. The reaction of **1-*iii*** required 16 h to complete, whereas that of **1-*v*** needed 21 h. After the reaction was complete, the ^1H NMR spectrum of the crude sample was measured in the presence of 1.00 mmol of anisole as an internal standard. The conversions of **1-*i*–*vii*** and the yields of **3-*i*–*vii*** were estimated as shown in Table 4. Some silylhemiaminals, **3-*i,iii,v***, were obtained as mixtures of two diastereomers (**3-*i***, 96:4; **3-*iii***, 95:5; **3-*v***, 87:13). The resulting silylhemiaminals **3-*i*–*vii*** were converted to the enamines **2-*i*–*vii*** by the method indicated in Table 4. The solvent was removed under a reduced pressure, and the resulting residue was purified by chromatography on silica gel (eluents hexane and toluene) to afford the corresponding enamines **2-*i*–*vii***. Assignments of NMR data were performed with the aid of ^1H–^1H COSY experiments (protons are labeled as shown in Chart 5). Although **2-*i*–*vii*** have all been reported in the literature,[4c,32–34] some of the spectroscopic data were not described. In the cases of **2-*i,iii,v***, analyses of the stereoisomers were not performed. In this context, ^1H and ^{13}C NMR, IR, and HRMS data are reported below.

Chart 5. Labels for Identification of Enamine 2



*N-(2-Phenyl-2-methylvinyl)-N,N-diphenylamine (**2-*i*)*.[32] From **1-*i*** (301.2 mg, 1.00 mmol), **2-*i*** was obtained as a 90:10 mixture of *E* and *Z* isomers (259.5 mg, 0.91 mmol, 91%). Conversion of **3-*i*** to **2-*i*** was achieved by thermal treatment of **3-*i*** in toluene at 100 °C for 6h (method A). ^1H NMR of (***E***)-**2-*i*** (600 MHz, $CDCl_3$, room temperature): δ 1.74 (d, $^3J_{H-H}$ = 1.4 Hz, 3H, −CH═C*Me*Ph), 6.59 (q, $^3J_{H-H}$ = 1.4 Hz, 1H, −C*H*═CMePh), 7.04 (t, $^3J_{H-H}$ = 7.6 Hz, 2H, *p*-Ph^N), 7.17 (d, $^3J_{H-H}$ = 7.6 Hz, 4H, *o*-Ph^N), 7.27 (t, $^3J_{H-H}$ = 7.6 Hz, 1H, *p*-Ph^1), 7.31 (dd, $^3J_{H-H}$ = 7.6 Hz, 4H, *m*-Ph^N), 7.37 (t, $^3J_{H-H}$ = 7.6 Hz, 2H, *m*-Ph^1), 7.49 (d, $^3J_{H-H}$ = 7.6 Hz, 2H, *o*-Ph^1). $^{13}C\{^1H\}$ NMR of (***E***)-**2-*i*** (151 MHz, $CDCl_3$, room temperature): δ 16.3, 122.0, 122.5, 125.7, 126.5, 126.7, 128.5, 129.3, 130.8, 142.0, 146.7. ^1H NMR of (***Z***)-**2-*i*** (600 MHz, $CDCl_3$, rt): δ 2.14 (s, 3H, −CH═C*Me*Ph), 6.30 (s, 1H, −C*H*═CMePh), 6.87 (t, $^3J_{H-H}$ = 7.6 Hz, 2H, *p*-Ph^N), 7.01 (d, $^3J_{H-H}$ = 7.6 Hz, 4H, *o*-Ph^N), 7.11 (t, $^3J_{H-H}$ = 7.6 Hz, 1H, *p*-Ph^1), 7.13 (dd, $^3J_{H-H}$ = 7.6 Hz, 4H, *m*-Ph^N). The other signals overlapped with those of the major *E* isomer. IR (ATR, cm^{-1}): 1627, 1583 ($\nu_{C=CN}$). Mp: 92–93 °C. HRMS-EI(+) (*m*/*z*): $[M]^+$ calcd for $C_{21}H_{19}N$, 285.1517; found, 285.1511.

*N-(2,2-Diphenylvinyl)-N,N-diphenylamine (**2-*ii*)*.[33] From **1-*ii*** (363.2 mg, 1.00 mmol), **2-*ii*** was obtained as a white solid (298.6 mg, 0.86 mmol, 86%), though **2-*ii*** was reported as a yellow oil in the literature.[32] Conversion of **3-*ii*** to **2-*ii*** was achieved by treatment of a toluene solution of **3-*ii*** with 1 M HCl in Et_2O (5 mL) at ambient temperature for 30 min (method B). ^1H NMR (600 MHz, $CDCl_3$, room temperature): δ 6.72 (s, 1H, −C*H*═CPh_2), 6.87 (t, $^3J_{H-H}$ = 7.2 Hz, 2H, *p*-Ph^N), 6.92–6.96 (a mixture of signals, 6H, Ph^1 or $Ph^{1\prime}$, overlapped with *o*-Ph^N), 6.97 (d, $^3J_{H-H}$ = 7.2 Hz, 4H, *o*-Ph^N), 7.08 (dd, $^3J_{H-H}$ = 7.2, 7.2 Hz, 4H, *m*-Ph^N), 7.20–7.28 (a mixture of signals, 4H, Ph^1 or $Ph^{1\prime}$, overlapped with a residual proton of $CDCl_3$). The signals were assigned by ^1H–^1H COSY. $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, room temperature): δ 122.6, 122.8, 126.4, 126.8, 127.6, 127.7, 128.3, 128.9, 130.2, 130.5, 131.4, 139.1, 142.2, 145.9. IR (ATR, cm^{-1}): 1611, 1584, 1566 ($\nu_{C=CN}$). Mp: 153 °C. HRMS-FAB(+) (*m*/*z*): $[M]^+$ calcd for $C_{26}H_{21}N$, 347.1677; found, 347.1672.

*N-(2-Phenyl-2-methylvinyl)-N-phenyl-N-(1-naphthyl) amine (**2-*iii*)*.[4c] From **1-*iii*** (351.2 mg, 1.00 mmol), **2-*iii*** was obtained as a 98:2 mixture of *E* and *Z* isomers (320.0 mg, 0.90 mmol, 90%). Conversion of **3-*iii*** to **2-*iii*** was achieved by thermal treatment of **3-*iii*** in toluene at 80 °C for 6 h (method A). ^1H NMR of (*E*)-**2-*iii*** (600 MHz, $CDCl_3$, room temperature): δ 1.59 (d, $^3J_{H-H}$ = 1.4 Hz, 3H, −CH═C*Me*Ph), 6.80 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, *o*-Ph^N), 6.89 (q, $^3J_{H-H}$ = 1.4 Hz, 1H, −C*H*═CMePh), 6.92 (t, $^3J_{H-H}$ = 7.2 Hz, 1H, *p*-Ph^N), 7.20 (dd, $^3J_{H-H}$ = 7.2 Hz, 2H, *m*-Ph^N), 7.24 (t, $^3J_{H-H}$ = 7.2 Hz, 1H, *p*-Ph^1), 7.34 (dd, $^3J_{H-H}$ = 7.2 Hz, 2H, *m*-Ph^1), 7.39 (dd, $^3J_{H-H}$ = 7.2 Hz, 1H, H^e), 7.45 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, *o*-Ph^1, overlapped with H^a), 7.45 (d, $^3J_{H-H}$ = 7.2 Hz, 1H, H^a), 7.48 (dd, $^3J_{H-H}$ = 7.2 Hz, 1H, H^f), 7.51 (dd, $^3J_{H-H}$ = 7.2 Hz, 1H, H^b), 7.76 (d, $^3J_{H-H}$ = 7.2 Hz, 1H, H^c), 7.89 (d, $^3J_{H-H}$ = 7.2 Hz, 1H, H^d), 7.91 (d, $^3J_{H-H}$ = 7.2 Hz, 1H, H^g). $^{13}C\{^1H\}$ NMR of **2-*iii*** (151 MHz, $CDCl_3$, room temperature): δ 16.0, 118.3, 120.9, 124.6, 124.7, 125.3, 125.7, 126.19, 126.24, 126.3, 126.4, 126.5, 128.5, 128.7, 129.1, 130.4, 132.9, 135.1, 142.3, 142.4, 148.9; ^1H NMR of (***Z***)-**2-*iii*** (600 MHz, $CDCl_3$, room temperature): δ 2.09 (s, 3H, −CH═C*Me*Ph), 6.44 (s, 1H, −C*H*═CMePh). The other signals were overlapped with those of the major *E* isomer; IR (ATR, cm^{-1}): 1627, 1589 ($\nu_{C=CN}$). Mp: 135 °C (lit. mp 135 °C determined by DSC). HRMS-EI(+) (*m*/*z*): $[M]^+$ calcd for $C_{25}H_{21}N$, 355.1674; found, 355.1675.

*N-(2,2-Diphenylvinyl)-N-phenyl-N-(1-naphthyl)amine (**2-*iv*)*.[4c] From **1-*iv*** (413.2 mg, 1.00 mmol), **2-*iv*** was obtained as a white solid (381.3 mg, 0.96 mmol, 96%). Conversion of **3-*iv*** to **2-*iv*** was achieved by treatment of a toluene solution of **3-*iv*** with 1 M HCl in Et_2O (5 mL) at ambient temperature for 30 min (method B). ^1H NMR (600 MHz, $CDCl_3$, room temperature): δ 6.64–6.70 (a mixture of signals, 4H, Ph^1 or $Ph^{1\prime}$), 6.65 (s, 1H, −C*H*═CPh_2, overlapped with *Ph*), 6.86 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, *o*-Ph^N), 6.92 (t, $^3J_{H-H}$ = 7.2 Hz, 2H, *p*-Ph^N), 7.12 (d, $^3J_{H-H}$ = 3.4 Hz, 3H, Ph^1 or $Ph^{1\prime}$) 7.17 (dd, $^3J_{H-H}$ = 7.2 Hz, 2H, *m*-Ph^N), 6.64–6.70 (a mixture of signals, 5H, Ph^1, $Ph^{1\prime}$, and *Naphthyl*), 7.27 (dd, $^3J_{H-H}$ = 7.2 Hz, 1H, H^f), 7.33 (dd, $^3J_{H-H}$ = 7.2 Hz, 1H, H^e), 7.43 (quint, $^3J_{H-H}$ = 3.4 Hz, 1H, Ph^1 or $Ph^{1\prime}$), 7.65 (d, $^3J_{H-H}$ = 8.3 Hz, 1H, H^d), 7.68 (d, $^3J_{H-H}$ = 8.3 Hz, 1H, H^g). The signals were assigned by ^1H–^1H COSY. $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, room temperature): δ 118.6, 121.5, 124.6, 125.6$_0$, 125.6$_6$, 125.7, 125.8, 126.1, 126.4, 126.5, 127.1, 127.2, 127.9, 128.2$_5$, 128.2$_7$, 129.1, 129.8, 130.1, 132.8, 134.8, 138.7, 140.8, 142.5, 148.5. IR (ATR, cm^{-1}): 1613, 1588, 1572 ($\nu_{C=CN}$). Mp: 142 °C (lit. mp 131 °C determined by DSC[4c]). HRMS-EI(+) (*m*/*z*): $[M]^+$ calcd for $C_{30}H_{23}N$, 397.1830; found, 397.1830.

*N-(2-Phenyl-2-methylvinyl)phenoxazine (**2-*v*)*.[4c] From **1-*v*** (315.1 mg, 1.00 mmol), **2-*v*** was obtained as a 21:79 mixture of *E* and *Z* isomers (245.3 mg, 0.82 mmol, 82%). Conversion of **3-*v*** to **2-*v*** was achieved by thermal treatment of **3-*v*** in toluene at 100 °C for 6h

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(method A). ^{1}H NMR of (*Z*)-**2-*v*** (600 MHz, $CDCl_3$, room temperature): δ 2.28 (s, 3H, −CH═C*Me*Ph), 5.77 (s, 1H, −C*H*═CMePh), 6.55 (d, $^3J_{H-H}$ = 8.3 Hz, 2H, H^d), 6.61 (d, $^3J_{H-H}$ = 8.3 Hz, 2H, H^a), 6.64 (dd, $^3J_{H-H}$ = 8.3 Hz, 2H, H^c), 6.69 (dd, $^3J_{H-H}$ = 8.3 Hz, 2H, H^b), 7.19 (t, $^3J_{H-H}$ = 7.2 Hz, 1H, *p*-*Ph*^{1}), 7.25 (dd, $^3J_{H-H}$ = 7.2 Hz, 2H, *m*-*Ph*^{1}), 7.39 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, *o*-*Ph*^{1}). The signals were assigned by ^{1}H−^{1}H COSY. ^{13}C{^{1}H} NMR of (*Z*)-**2-*v*** (151 MHz, $CDCl_3$, room temperature): δ 21.5, 113.6, 115.5, 120.4, 121.1, 121.7, 123.5, 126.9, 28.1, 128.5, 138.3, 141.1, 144.2. ^{1}H NMR of (*E*)-**2-*v*** (600 MHz, $CDCl_3$, room temperature): δ 2.07 (s, 3H, −CH═C*Me*Ph), 6.13 (s, 1H, −C*H*═CMePh), 6.51 (d, $^3J_{H-H}$ = 8.3 Hz, 2H, H^d), 6.61 (d, $^3J_{H-H}$ = 8.3 Hz, 2H, H^a), 6.64 (dd, $^3J_{H-H}$ = 8.3 Hz, 2H, H^c), 6.75 (a mixture of signals, 4H, H^b and H^c), 7.31 (t, $^3J_{H-H}$ = 7.2 Hz, 1H, *p*-*Ph*^{1}), 7.43 (dd, $^3J_{H-H}$ = 7.2 Hz, 2H, *m*-*Ph*^{1}), 7.57 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, *o*-*Ph*^{1}). The other signals derived from H^a could not be observed due to the signals for the major *Z* isomer. ^{13}C{^{1}H} NMR of (*E*)-**2-*v*** (151 MHz, $CDCl_3$, room temperature): δ 16.0, 113.2, 115.8, 121.4, 121.9, 123.7, 126.2, 128.4, 128.8, 132.7, 139.8, 141.9, 144.3. IR (ATR, cm^{-1}): 1622, 1588 ($\nu_{C=CN}$). Mp: 153 °C (lit. mp 100 °C determined by DSC). HRMS-EI(+) (*m*/*z*): [M]$^+$ calcd for $C_{21}H_{17}NO$, 299.1310; found, 299.1304.

N-(2,2-Diphenylvinyl)phenoxazine (**2-*vi***).[4c] From **1-*vi*** (377.2 mg, 1.00 mmol), **2-*vi*** was obtained as a yellow solid (332.3 mg, 0.92 mmol, 92%). Conversion of **3-*vi*** to **2-*vi*** was achieved by thermal treatment of **3-*vi*** in toluene at 100 °C for 6 h (method A). ^{1}H NMR (600 MHz, C_6D_6, room temperature): δ 5.93 (s, 1H, −C*H*═CPh$_2$), 6.48 (ddd, $^3J_{H-H}$ = 8.3, 8.3 Hz, $^4J_{H-H}$ = 1.4 Hz, 2H, H^b), 6.53 (a mixture of signals, 4H, Ph$^{1\prime}$), 6.67 (d, $^3J_{H-H}$ = 7.6 Hz, 2H, H^d), 6.85 (t, $^3J_{H-H}$ = 7.6 Hz, 1H, *p*-*Ph*^{1}), 6.91 (dd, $^3J_{H-H}$ = 7.6 Hz, 2H, H^c), 7.13 (1H, *p*-*Ph*$^{1\prime}$, overlapped with *m*-*Ph*^{1}), 7.13 (d, $^3J_{H-H}$ = 7.6 Hz, 2H, *m*-*Ph*^{1}), 7.25 (dd, $^3J_{H-H}$ = 8.3 Hz, $^4J_{H-H}$ = 1.4 Hz, 2H, H^a), 6.67 (d, $^3J_{H-H}$ = 7.6 Hz, 2H, *o*-*Ph*^{1}). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, room temperature): δ 113.8, 116.0, 121.8, 122.3, 123.6, 128.4, 128.5, 128.57, 128.60, 128.8, 129.2, 132.1, 138.1, 140.5, 144.7, 144.8. IR (ATR, cm^{-1}): 1592.0 ($\nu_{C=CN}$). Mp: 189 °C (lit. mp 195 °C determined by DSC). HRMS−EI(+) (*m*/*z*): [M]$^+$ calcd for $C_{26}H_{19}NO$, 361.1467; found, 361.1460.

trans-N-(2,2-Diphenylvinyl)carbazole (**2-*vii***).[34] From **1-*vii*** (285.1 mg, 1.00 mmol), **2-*vii*** was obtained as a white solid (219.5 mg, 0.77 mmol, 77%). Conversion of **3-*vii*** to **2-*vii*** was achieved by treatment of a toluene solution of **3-*vii*** with P_2O_5 (30 mg) at ambient temperature for 30 min (method C). ^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 7.08 (d, $^3J_{H-H}$ = 14.4 Hz, 1H, −CH═C*H*Ph), 7.33 (t, $^3J_{H-H}$ = 7.2 Hz, 1H, *p*-*Ph*), 7.34 (dd, $^3J_{H-H}$ = 7.2 Hz, 2H, H^b), 7.44 (dd, $^3J_{H-H}$ = 7.2 Hz, 2H, *m*-*Ph*), 7.52 (dd, $^3J_{H-H}$ = 7.2 Hz, 2H, H^c), 7.56 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, *o*-*Ph*), 7.72 (d, $^3J_{H-H}$ = 14.4 Hz, 1H, −C*H*═CHPh, overlapped with H^d), 7.74 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, H^d), 8.12 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, H^a). The signals were assigned by ^{1}H−^{1}H COSY. ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, room temperature): δ 110.72, 120.0, 120.5, 120.9, 123.5, 124.3, 126.0, 126.4, 127.4, 129.0, 136.5, 139.7. IR (ATR, cm^{-1}): 1651, 1620, 1597 ($\nu_{C=CN}$). Mp: 104.1 °C (lit. mp 116−120 °C). HRMS−FAB(+) (*m*/*z*): [M]$^+$ calcd for $C_{20}H_{15}N$, 269.1205; found, 269.1203.

Preparation of Enamines with Low Catalyst Loadings. *Preparation of* **2-*iii***. In a 20 mL two-necked found flask equipped with a Dimroth condenser were placed carboxamide **1-*iii*** (1.08 g, 2.85 mmol) and a 2.83 M solution of iridium complex **4i** in toluene (0.1 mL, 2.83 × 10^{-4} mmol). Then 1,1,3,3-tetramethyldisiloxane (2.0 equiv with respect to amide **1-*iii***) and toluene (3 mL) were added, and the mixture was stirred at 40 °C for 24 h. After the reaction was over, the ^{1}H NMR spectrum was measured in the presence of anisole as an internal standard. The conversion of **1-*iii*** was estimated as >99% from the integral ratios of the signals of the starting materials to the internal standard. The solvent and unreacted TMDS in the solution of **3-*iii*** were removed under reduced pressure, and again toluene (20 mL) was placed in the flask. Thermolysis of a solution of **3-*iii*** in toluene at 80 °C for 6 h gave the enamine **2-*iii*** in 93% ^{1}H NMR yield, which was a 90:10 mixture of *E* and *Z* isomers. The solvent was removed under reduced pressure, and the resulting residue was purified by short column chromatography on silica gel (eluent hexane) to afford the enamine **2-*iii*** as a white powder (0.84 g, 2.51 mmol, 88% in isolated yield). The amount of the residual metal in the enamine **2-*iii*** isolated was determined by ICP-MS, which clearly showed that there were no detectable iridium species in the enamine **2-*iii*** (<20 ppb).

Preparation of **2-*viii***. In a 50 mL two-necked found flask equipped with a Dimroth condenser were placed carboxamide **1-*viii*** (2.0 g, 10.5 mmol) and the iridium complex **4i** (0.15 mg, 1.0 × 10^{-5} mmol). Then 1,1,3,3-tetramethyldisiloxane (2.0 equiv with respect to amide **1-*viii***) was added, and the mixture was stirred without any solvent at 100 °C for 30 min. During the reaction, generation of H_2 gas was observed. After the reaction was over, the ^{1}H NMR spectrum was measured in the presence of anisole as an internal standard. The conversion of **1-*viii***, the same as the yield of **2-*viii***, was estimated as >99% from the integral ratios of the signals of the starting materials to those of the internal standard. The solvent and unreacted TMDS were removed under reduced pressure, and the resulting residue was purified by short column chromatography on silica gel (eluent hexane) to afford the enamine **2-*viii*** as a colorless oil (1.53 g, 8.71 mmol, 83% in isolated yield). The amount of the residual metal in the isolated enamine **2-*viii*** was determined by ICP-MS, which clearly showed that there were no detectable iridium species in the enamine **2-*viii*** (<20 ppb).

^{1}H NMR Analysis of the Silylhemiaminals 3-*i*−*vii*. In an NMR tube equipped with a J. Young valve were placed carboxamides **1-*i*−*vii*** (0.1 mmol), the iridium catalyst **4k** (0.7 mg, 0.5 μmol, 0.5 mol %), and C_6D_6 (0.4 mL). Hexamethylbenzene (C_6Me_6) was also added as an internal standard. After the integral ratio between amides **1** and C_6Me_6 was confirmed by ^{1}H NMR, 1,1,3,3-tetramethyldisiloxane (0.2 mmol) was added and the reaction was monitored by ^{1}H NMR. The conversions of **1-*i*−*vii*** and the yields of **3-*i*−*vii*** were estimated from the integral ratio relative to the internal standard. Since **3-*i*−*vii*** were unstable toward moisture, those other than **3-*vii*** were characterized by specific signals of the ^{1}H NMR spectrum of the crude mixture which was obtained by an experiment in the absence of C_6Me_6. Three enamines, **3-*i*,*iii*,*v***, were obtained as mixtures of two diastereomers in ratios of 96:4, 95:5, and 85:15, respectively. Details of these are described in the Supporting Information.

Spectroscopic Identification of the Silylhemiaminal Intermediate 3-*vii*. The silylhemiaminal **3-*vii*** was relatively stable enough to allow removal of excess TMDS to give NMR spectra without impurities. Treatment of **1-*vii*** (28.5 mg, 0.1 mmol) with TMDS at ambient temperature for 21 h gave **3-*vii***. The conversion of **1-*vii*** and the yield of **3-*vii*** were estimated by ^{1}H NMR to be >99%. ^{1}H NMR (600 MHz, C_6D_6, 70 °C): δ −0.23 (s, 3H, -Si*Me*$_2$), −0.09 (d, $^3J_{H-H}$ = 2.8 Hz, 3H, -Si*Me*$_2$H), −0.09 (d, $^3J_{H-H}$ = 2.8 Hz, 3H, −Si*Me*$_2$H), −0.08 (s, 3H, −Si*Me*$_2$), 3.31 (dd, $^3J_{H-H}$ = 6.9 Hz, $^2J_{H-H}$ = 13.7 Hz, 1H, −C*H*$_2$Ph), 3.50 (dd, $^3J_{H-H}$ = 6.9 Hz, $^2J_{H-H}$ = 13.7 Hz, 1H, −C*H*$_2$Ph), 4.69 (sept, $^3J_{H-H}$ = 2.8 Hz, 1H, −SiMe$_2$*H*), 6.43 (dd, $^3J_{H-H}$ = 6.9 Hz, 1H, −SiOC*H*−), 6.88−6.98 (a mixture of signals, 5H, *Ph*), 7.17 (dd, $^3J_{H-H}$ = 8.2 Hz, 2H, H^b), 7.34 (dd, $^3J_{H-H}$ = 8.2 Hz, 2H, H^c), 7.60 (br, 2H, H^a), 7.98 (d, $^3J_{H-H}$ = 8.2 Hz, 2H, H^d). ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, room temperature): δ −1.3, −1.2, 0.37, 0.40, 43.0, 81.2, 119.8, 120.6, 124.0 (br), 125.9, 126.9, 128.3, 128.5, 129.7, 137.1, 139.5 (br). ^{29}Si NMR (119 MHz, C_6D_6, room temperature): δ −8.72 (*Si*Me), −4.64 (*Si*Me). HRMS-EI(+) (*m*/*z*): [M]$^+$ calcd for $C_{24}H_{29}NO_2Si_2$, 419.1737; found, 419.1736.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00636.

Detailed experimental details, molecular structures of **4h−j**, details of crystallographic studies (**4h−j**), and spectral data for all new and some reported compounds (PDF)

Crystallographic data for **4h−j** (CIF)

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Notes

The authors declare no competing financial interest.

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