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Iridium-PPh$_3$ Catalysts for Conversion of Amides to Enamines

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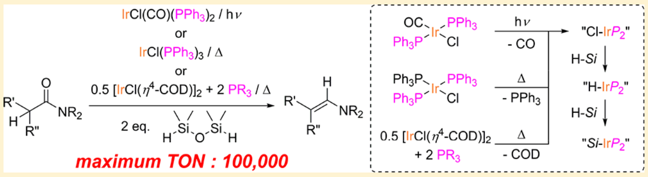
Supporting Information



ABSTRACT: Studies on the deactivation mechanism of the reaction of *N,N*-dialkylamides with TMDS catalyzed by Vaska's complex, IrCl(CO)(PPh$_3$)$_2$ (**1a**), triggered the discovery of highly active Ir-PPh$_3$ catalysts: photochemically activated **1a** and thermally activated IrCl(PPh$_3$)$_3$ (**8**). Both catalysts showed excellent activity toward the selective conversion of a variety of *N,N*-dialkyl-, *N*-alkyl-*N*-aryl-, and *N,N*-diarylamides to the corresponding enamines with low catalyst loadings. The 14-electron species "ClIr(PPh$_3$)$_2$", which is stabilized by solvents or reactants in the actual catalytic reactions, could be involved in the catalysis, which produces "HIr(PPh$_3$)$_2$" and "*Si*Ir(PPh$_3$)$_2$" (*Si* = Me$_2$HSiOMe$_2$Si−) species in the catalytic cycle. An in situ generation method for the "ClIrL$_2$" species was established by simply mixing [IrCl(η^4-COD)]$_2$ with PPh$_3$ or other phosphorus ligands, which realized the facile large-scale syntheses of enamines.

■ INTRODUCTION

Hydrosilanes are stable metal hydrides that are useful for carbonyl reduction in the presence of Brønsted acids, Lewis acids, fluoride anion, and transition-metal catalysts.[1] Recent progress in catalyst design to achieve high catalytic efficiency has led to the discovery of new catalysts containing not only conventional precious metals but also base metals, attracting the attention of scientists due to their environmentally benign nature.[2] While the initial stage of studies on metal-catalyzed reduction with hydrosilanes was limited to the hydrosilylation of aldehydes and ketones, recent studies have focused on hydrosilane reduction of carboxylic acids or esters to silyl ethers as well as amides to amines.[3] It is known that the reduction of carboxylic acid derivatives is more difficult than that of aldehydes and ketones with conventional alumino- and borohydrides.[1,2]

One of the keys to achieving the efficient hydrosilane reduction of carboxylic acid derivatives is the contribution of hydrosilane structures to increase the reduction rates. As summarized by our accounts and perspective,[4] we have investigated the high reactivity of bifunctional hydrosilanes, in which two Si−H groups are located in close proximity. Bifunctional hydrosilanes such as Me$_2$HSi(CH$_2$)$_2$SiHMe$_2$ (BDMSE), Me$_2$HSiOSiHMe$_2$ (TMDS), Me$_3$Si(OSiHMe)$_n$OSiMe$_3$ (PMHS), and 1,2-dimethylsilylbenzene (BDSB) are capable of forming disilametallacyclic intermediates by a reaction with metal complexes and take part in the efficient reduction of carboxylic acid derivatives: in particular, the conversion of amides to amines. A combination of these bifunctional hydrosilanes with ruthenium,[5] platinum,[6] and iron[7] catalysts realized the reduction of secondary and tertiary amides to the corresponding secondary and tertiary amines, respectively. These bifunctional hydrosilanes are commercially available, storable under aerobic conditions, and easy to handle. Among them, TMDS is especially useful and is inexpensive enough to be applied to industrial reduction processes.[8]

Among the metal-catalyzed hydrosilane reductions of amides, those catalyzed by Vaska-type iridium complexes, IrCl(CO)L$_2$, where L is a phosphorus ligand, are unique in not affording amines but selectively providing enamines through silylhemiaminal intermediates.[9a] Among hydrosilanes including the bifunctional hydrosilanes described above, only TMDS and PMHS successfully promoted the conversion of amides to enamines. No reaction occurred with other bifunctional hydrosilanes such as BDSE and BDMSE or monofunctional primary, secondary, and tertiary hydrosilanes such as PhSiH$_3$, Ph$_2$SiH$_2$, and PhMe$_2$SiH.

Vaska-type iridium complexes are surprisingly efficient for the conversion of amides to enamines with TMDS. As shown in the upper equation in Scheme 1, *N,N*-dialkylamides **2** underwent the reaction with TMDS by catalysis of IrCl(CO)(PPh$_3$)$_2$ (**1a**) at room temperature. The corresponding enamines **3** were formed as a single product in quantitative yields within 1 h. In an extreme case, the TON and TOF (h^{-1}) reached 8000 and 16000, respectively. The reaction is considered to proceed through a silylhemiaminal intermediate, which is not detectable in the reaction of **2**. π-Conjugated enamines are attractive donor molecules in materials science.[10] The preparation of a series of π-conjugated enamines from *N,N*-diaryl-2-arylacetamides **4** and TMDS has not been very successful by catalysis of **1a**. However, they were efficiently hydrosilylated to the corresponding silylhemiaminals **5** by the

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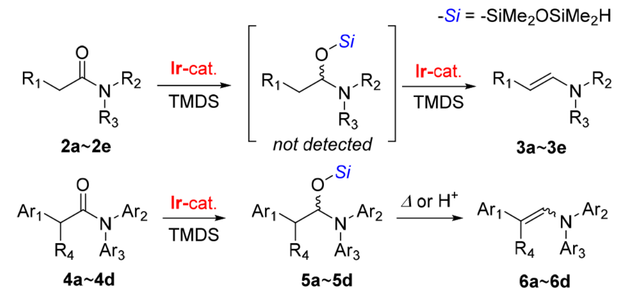
Organometallics XXXX, XXX, XXX−XXX

Scheme 1. Iridium-Catalyzed Hydrosilane Reduction of Amides, Leading to Efficient Synthesis of Aldenamines



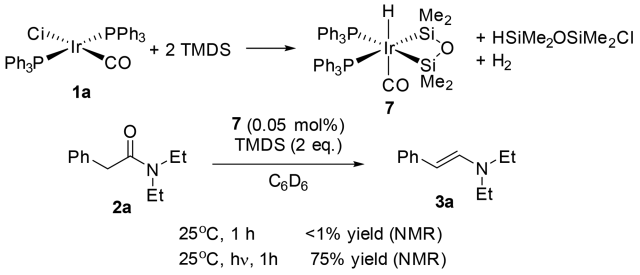
catalysis of $IrCl(CO)[P(OC_6F_5)_3]_2$ (**1b**).[9b] The silylhemiaminals **5** were converted to π-conjugated enamines **6** either by thermal treatment or by the action of acid. The catalytic activity of the iridium complex **1b** was higher than that of **1a**, when **1b** was applied to the conversion of **2** to **3**, for which the TON exceeded 10^5 at room temperature within a few hours.

The high efficiency of **1a**,**b** for the hydrosilane reduction of amides to enamines or silylhemiaminal intermediates is satisfactory as a convenient synthesis of enamines in organic synthesis. However, we suspected that the catalytic performance of Vaska's complex **1a** could potentially be better than that actually attained. We observed in experiments with low catalyst loadings that catalyst deactivation occurred at the later stage of the reaction. We analyzed the deactivated iridium species and found that Curtis' complex **7**[11] was formed. Interestingly, **7** was reactivated by photolysis. This prompted us to search for a series of PPh_3-based iridium complexes as catalysts for the conversion of amides to enamines via silylhemiaminals under thermal or photochemical conditions. These studies have brought about highly efficient catalysis, achieving TON $>10^5$ in extreme cases, by **1a** under photolysis or by $IrCl(PPh_3)_3$ at 60 °C. Consideration of the net catalytically active species yielded the hypothesis that a "$Z\text{-}Ir(PPh_3)_2$" species, where Z is H, Cl, or $-SiMe_2OSiMe_2H$, is possibly involved. This hypothesis provided a convenient method to access the catalytically active species by simply mixing $[IrCl(\eta^4\text{-COD})]_2$ with PPh_3 or other phosphorus ligands.

■ RESULTS AND DISCUSSION

Formation and Reactivation of Curtis' Complex 7. The reaction of **1a** with TMDS was reported by Curtis and coworkers in 1977.[11] The product was the disilametallacyclic iridium hydride **7**, as shown in Scheme 2. Two moles of TMDS was involved in the formation of **7**; one molecule of TMDS contributed to the exchange of a chloride ligand in **1a** by a hydride, and double oxidative addition of another molecule of TMDS to the resulting $IrH(CO)(PPh_3)_2$ was followed by elimination of H_2 to form **7**. The ^1H NMR spectrum of **7** showed a characteristic triplet at δ −7.66 in C_6D_6 due to Ir−H. The Ir−H signal was coupled with two ^{31}P nuclei at the cis position with J_{P-H} = 16.5 Hz. A $^{31}P\{^1H\}$ resonance appeared as a singlet at 1.95 ppm.

Scheme 2. Catalytic Activity of Curtis's Complex 7



When the reaction of $PhCH_2CONEt_2$ (**2a**) with TMDS was carried out in toluene at room temperature in the presence of 0.05 mol % of **1a**, the reaction was complete in 1 h to give $PhCH{=}CHNEt_2$ (**3a**) quantitatively (entry 1, Table 1). The reaction performed with lower catalyst loading (0.001 mol %; entry 2) was terminated at 25% conversion of **2a**, as seen in the reaction profile in Figure 1. Analysis of the iridium species in solution after the reaction revealed the existence of **7** as a single iridium species. ^1H and ^{31}P resonances due to **7** were observed in the reaction mixture, while the $^{31}P\{^1H\}$ signal (δ 24.73, s) due to **1a** disappeared. An important discovery was obtained when we photolyzed the reaction mixture by a high-pressure Hg lamp at room temperature, after the enamine formation was terminated. As shown in the reaction profile in Figure 1, after 2 h, the photolysis restarted the catalytic reaction, though the reaction was much slower than the initial rate catalyzed by **1a**. We also attempted to reactivate the catalytically active species by heating the reaction mixture after the catalyst deactivation at 60 °C, which did not restart the reaction (section 1-1 in the Supporting Information).

We confirmed the catalytic activity of **7**, which was isolated and well-characterized, for the reaction of **2a** with TMDS (Scheme 2). The reaction was slow when the catalyst loading was 0.001 mol % under photoirradiation conditions. However, the photochemical treatment of **2a** with TMDS in the presence of 0.05 mol % of **7** in toluene at 25 °C resulted in a 75% yield of **3a** after 1 h. No reaction occurred without photolysis at 25 °C (sections 1-2 and 1-3 in the Supporting Information).

Catalyst Screening for Photochemical and Thermal Conversion of 2a to 3a. The above results clearly indicate that formation of **7** is the origin of the catalyst deactivation of the **1a**-catalyzed conversion of amides to enamines with TMDS, while photolysis of **7** generates a catalytically active species. Since the photoirradiation of metal carbonyls is known to result in the dissociation of CO ligands from the metal center,[12] it is likely that regeneration of the catalytically active species from **7** was promoted by photoassisted dissociation of CO. These considerations suggested that continuous photoirradiation of the reaction of **2a** to **3a** in the presence of Vaska's complex **1a** could improve the catalytic efficiency in comparison with that under dark conditions.

Table 1, entries 2−4, shows the reaction of **2a** with TMDS catalyzed by 0.001 mol % of **1a** in toluene. At room temperature, the reaction was terminated at 25% conversion of **2a**, and no significant improvement of the conversion was observed at 60 °C (entries 2 and 3). In sharp contrast, photoirradiation of the reaction solution at room temperature resulted in efficient production of **3a**, for which both the TON and TOF (h^{-1}) reached 10^5 (entry 4). Toluene was a better solvent than dichloromethane and THF (entries 5 and 6).

We considered two possibilities to explain the experimental results described above: (1) the reaction of **1a** with TMDS during the catalysis is accompanied by formation of inactive **7**, but continuous photolysis can regenerate the catalytic activity by CO dissociation from **7** (possibility 1); (2) photolysis of Vaska's complex **1a** results in dissociation of CO to form a "$ClIr(PPh_3)_2$"[13] species,[12b] which may be more catalytically

Table 1. Hydrosilane Reduction of $PhCH_2CONEt_2$ (2a) To Form $PhCH{=}CHNEt_2$ (3a) Catalyzed by 1a and 8 under Thermal and Photochemical Conditions[a]

entry	catalyst	mol %	Δ or $h\nu$	temp (°C)	solvent	conversn of **2a** (%)[b]	yield of **3a** (%)[b]
1	$IrCl(CO)(PPh_3)_2$ (**1a**)	0.05	Δ	25	toluene	99	99
2	**1a**	0.001	Δ	25	toluene	25	25
3	**1a**	0.001	Δ	60	toluene	30	30
4	**1a**	0.001	$h\nu$	25	toluene	99	99
5	**1a**	0.001	$h\nu$	25	CH_2Cl_2	82	81
6	**1a**	0.001	$h\nu$	25	THF	48	48
7	$IrCl(PPh_3)_3$ (**8**)	0.05	Δ	25	toluene	99	99
8	**8**	0.001	Δ	25	toluene	14	14
9	**8**	0.001	Δ	60	toluene	81	81
10	**8**	0.001	Δ	60	CH_2Cl_2	41	41
11	**8**	0.001	Δ	60	THF	20	20
12	**8**	0.001	$h\nu$	25	toluene	34	34

[a] All reactions were carried out by using amide **2a** (1.00 mmol), TMDS (2.0 mmol), and the solvent given above (0.5 mL total) in the presence of **1a** or **8** (0.05 mol % or 0.001 mol %) under an inert gas atmosphere for 1 h. [b] Determined by ^1H NMR in the presence of anisole as the internal standard.

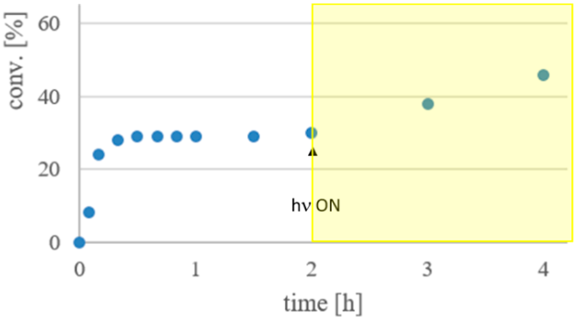


Figure 1. Reaction profile for the reaction of $PhCH_2CONEt_2$ (**2a**) with TMDS in the presence of 0.001 mol % of $IrCl(CO)(PPh_3)_2$ (**1a**).

active than **1a** itself or the species photochemically generated from 7 (possibility 2). As described above, the catalytically active species generated by photolysis of 7 was much less efficient than that from **1a** in the dark. Since the catalytic activity of **1a** under photolysis in toluene (entry 4) was higher than we expected from this, we assumed possibility 2 to be more reasonable.

We were interested in an alternative generation method of "$ClIr(PPh_3)_2$", which is formed by photoirradiation of $IrCl(CO)(PPh_3)_2$, and thought that thermal dissociation of PPh_3 from $IrCl(PPh_3)_3$ (**8**)[14] could be useful. As shown in Table 1, entry 7, the catalytic activity of **8** was as high as that of **1a** at room temperature, when 0.05 mol % of **8** was used as the catalyst. While the reaction with 0.001 mol % of **8** resulted in low conversion of **2a** to **3a** (14%) at room temperature for 1 h (entry 8), heating at 60 °C increased the conversion of **2a** (entry 9) 6 times as much as that at 25 °C; the catalyst efficiency is high enough to be comparable to that of **1a**/$h\nu$ shown in entry 4. Among three solvents examined, toluene was better than CH_2Cl_2 and THF (entries 10 and 11). It was confirmed that photoirradiation of the reaction mixture at room temperature did not contribute to increase the efficiency (entry 12). In the cases of both **1a** and **8**, TMDS was the best hydrosilane in comparison with PMDS, BDSB, and $PhMe_2SiH$ (sections 1-6 and 1-7 in the Supporting Information).

This discovery of the highly active Ir-PPh_3-based catalyst systems, photochemically activated **1a** and thermally activated **8**, prompted us to screen additional iridium complexes for catalysts to convert **2a** to **3a**. The list of the Ir-PPh_3 catalysts contains $IrH(CO)(PPh_3)_3$ (**9**),[15] $IrH(\eta^4\text{-COD})(PPh_3)_2$ (**10**),[16] $IrH_5(PPh_3)_2$ (**11**),[17] $IrH_3(PPh_3)_3$ (**12**),[18] and a disilyltrihydride iridium(V) compound (**13**),[19] which has a disilametallacyclic skeleton derived from BDSB. Corriu and coworkers briefly reported the reaction of **2a** with BDSB to form **3a** by catalysis of $RhCl(PPh_3)_3$ (**14**), in which the catalytic activity of **14** was much lower than that of **8**.[20] We examined the catalytic activity of $RhCl(CO)(PPh_3)_2$ (**15**),[21] $RhH(CO)(PPh_3)_3$ (**16**),[22] and $RhH(PPh_3)_4$ (**17**)[22] in addition to **14**. The results are summarized in Chart 1, and the details are described in sections 1-2 through 1-5 in the Supporting Information. **9**−**17** all showed some catalytic activity, but none of them exhibited higher activity in comparison to photochemically activated **1a** and thermally activated **8**. However, four of them promoted the reaction with 0.5−0.05 mol % of

Chart 1. Catalytic Activity of a Series of Ir/Rh Catalysts for Hydrosilane Reduction of 2a with TMDS

(a) Highly active catalysts that promoted the reaction with 0.001 mol% catalyst loadings.

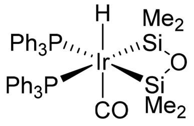
$IrCl(CO)(PPh_3)_2$ (**1a**) / hν $IrCl(PPh_3)_3$ (**8**) / Δ

(b) Catalysts showing moderate activity that promoted the reaction with 0.5 - 0.05 mol% catalyst loadings.

$IrH(CO)(PPh_3)_3$ (**9**) / Δ

$IrH(\eta^4\text{-COD})(PPh_3)_2$ (**10**) / Δ and hν

$IrH_5(PPh_3)_2$ (**11**) / Δ and hν



7 / Δ and hν

(c) Catalysts showing lower activity that promoted the reaction with 1 - 0.5 mol% catalyst loadings.

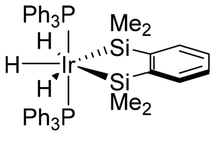
$IrH_3(PPh_3)_3$ (**12**) / Δ and hν

$RhCl(PPh_3)_3$ (**14**) / Δ and hν

$RhCl(CO)(PPh_3)_2$ (**15**) / Δ and hν

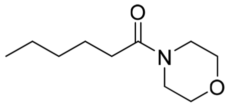
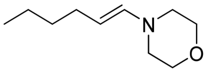
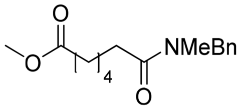
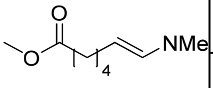
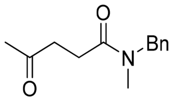
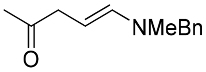
$RhH(CO)(PPh_3)_3$ (**16**) / Δ and hν

$RhH(PPh_3)_4$ (**17**) / Δ and hν



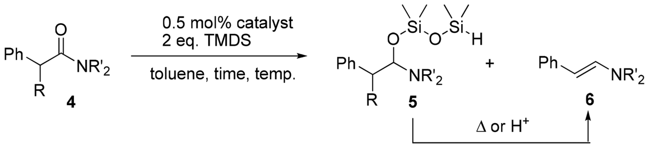
13 / Δ and hν

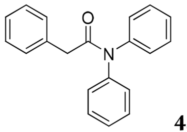
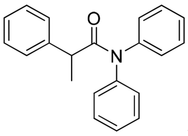
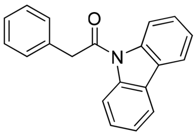
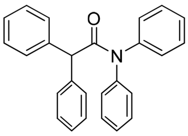
Table 2. Hydrosilane Reduction of *N*,*N*-Dialkyl- or *N*-Alkyl-*N*-arylamides Catalyzed by Photochemically Activated **1a** or Thermally Activated **8** with 0.001 mol % Catalyst Loading[a]

Entry	Amide	Cat.	Temp. (°C)	Time (h)	Enamine	Conv. (%)[b]	Yield (%) (NMR)[b]	Yield (%) (Isolated)
1	$PhCH_2CONEt_2$ (**2a**)	**1a** / hν	25	1	$PhCH{=}CHNEt_2$ (**3a**)	99	99	96
2		**8**	60	2		99	99	93
3	$PhCH_2CONMePh$ (**2b**)	**1a** / hν	25	3	$PhCH{=}CHNPMePh$ (**3b**)	99	99	94
4		**8**	60	8		99	99	93
5	 **2c**	**1a** / hν	25	2	 **3c**	99	96	--
6		**8**	60	2		99	96	--
7	 **2d**	**1a** / hν	25	6	 **3d**	99	99	--
8		**8**	60	6		99	99	86
9	 **2e**	**1a** / hν	25	4	 **3e**	99	99	--
10		**8**	60	4		99	99	--

[a] All reactions were carried out by using amides **2** (1.00 mmol), TMDS (2.0 mmol), toluene (0.5 mL total) in the presence of **1a** or **8** (0.001 mol %) under inert gas atmosphere. [b] Determined by ^1H NMR in the presence of anisole as the internal standard.

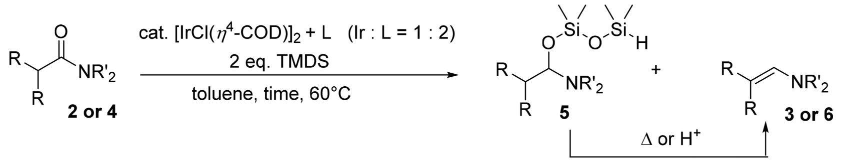
Table 3. Hydrosilane Reduction of *N*,*N*-Diarylamides Catalyzed by Photochemically Activated **1a** or Thermally Activated **8** with 0.5 mol % Catalyst Loading[a]



Entry	Amide	Cat. (mol%)	Temp. (°C)	Time (h)	Conv. of **4** (%)	NMR Yield (%)		Isolated Yield of **6** (%)
						5	**6**	
1	 **4a**	**1a** / hν	25	2	99	99	0	90
2		**8**	60	2	99	0	99	88
3	 **4b**	**1a** / hν	25	6	99	99	0	91
4		**8**	60	3	97	83	15	93
5	 **4c**	**1a** / hν	25	24	47	43	0	--
6		**8**	60	24	76	74	0	--
7	 **4d**	**1a** / hν	25	24	25	25	0	--
8		**8**	60	24	50	13	30	--

[a] All reactions were carried out by using amides **4** (1.00 mmol), TMDS (2.0 mmol), toluene (0.5 mL total) in the presence of **1a** or **8** (0.5 mol %) under inert gas atmosphere. [b] Determined by ^1H NMR in the presence of anisole as the internal standard.

Table 4. Hydrosilane Reduction of Various Amides 2 and 4 To Form Enamines 3 and 6 by in Situ Generation of the Catalytically Active Species from $[IrCl(\eta^4\text{-COD})Cl]_2$ and PPh_3 or $P(OC_6F_5)_3$[a]



entry	amide	cat. (mol % per Ir atom)	L	time (h)	conversn of **5** (%)[b]	product [NMR yield (%)][b] **5**	product [NMR yield (%)][b] **3** or **6**	isolated yield of **6** (%)
1	**2a**	0.001	PPh_3	2	99		**3a** [99]	96 (99)[c]
2	**2d**	0.001	PPh_3	2	99		**3d** [99]	
3	**2e**	0.001	PPh_3	6	99		**3e** [99]	
4	**4a**	0.5	PPh_3	4	99	**5a** [0]	**6a** [99]	92
5	**4c**	0.5	PPh_3	24	0	**5c** [0]	**6c** [0]	0
6		0.5	$P(OC_6F_5)_3$	2	99	**5c** [99]	**6c** [0]	84 (86)[d]

[a] All reactions were carried out by using amides **2** (1.00 mmol), TMDS (2.0 mmol), and toluene (0.5 mL total) in the presence of $[IrCl(\eta^4\text{-COD})Cl]_2$ (0.0005 mol % or 0.25 mol %) and PPh_3 (0.002 mol % or 1.0 mol %) under an inert gas atmosphere. [b] Determined by ^1H NMR in the presence of anisole as the internal standard. [c] Isolated yield when the reaction was performed with 0.1 mol of **2a**. [d] Isolated yield when the reaction was performed with 10 mmol of **4c**.

catalyst loading both thermally and photochemically. Lower catalytic activity was observed for the iridium complex **12** and all of the rhodium complexes. Although the catalyst screening did not yield any catalysts more efficient than **1a**/*hν* or **8a** at 60 °C, the results are helpful for the mechanistic considerations described later.

Scope of the Substrates for the Reactions Catalyzed by 1a/*hν* or 8 at 60 °C. The catalysis of photoactivated **1a** and thermally activated **8** provided excellent results in the conversion of a variety of tertiary amides to the corresponding enamines. Table 2 shows the results for the reactions of five *N,N*-dialkyl- and *N*-alkyl-*N*-arylamides **2a**−**e** with TMDS. All of the reactions were carried out with 0.001 mol % catalyst loading. Both the conversion of the amide and the yield of the product were determined by ^1H NMR spectroscopy, and isolated yields are reported in the table. With either **1a** at 25 °C under photolysis or **8** at 60 °C, two phenylacetamide derivatives, **2a**,**b**, underwent the hydrosilane reduction and subsequent elimination of silanol to form **3a**,**b**, respectively, in quantitative yields. As described previously, a phenyl group on the amide nitrogen led to lowered activity of amides toward the iridium-catalyzed hydrosilane reduction.[9b] For this reason, the reaction with **2b** needed a somewhat longer reaction time to complete the reaction than did **2a**. The aliphatic amide **3c** was also smoothly converted to the corresponding enamine, as shown in entries 5 and 6.

A characteristic feature of these iridium-catalyzed hydrosilane reductions of amides to enamines is the high functional group compatibility. Table 2, entries 7−10, show the reactions of amides including another reducible functional group such as a carbonyl group in the molecule. Amide ester **2d** was converted to the corresponding enamino ester **3d** catalyzed by either **1a** under photolysis or **8** at 60 °C. After 6 h, the crude product was unstable, but it could be isolated by passage through Celite followed by washing with cold pentane. The experiment shown in entry 8 afforded **3d** in 86% yield. Keto amide **2e** was also subjected to the catalysis of photochemically activated **1a** or thermally activated **8** for 4 h. In both cases, NMR spectra of the crude sample showed quantitative formation of **3e**, as shown in the Supporting Information. However, the attempted isolation of **3e** was not successful, giving a complicated mixture of products.

As reported previously, *N,N*-diarylamides **4** are precursors of *π*-conjugated enamines **6**. Electrons on the amide groups are delocalized over the aryl groups on the nitrogen atom, which makes the reaction with TMDS by catalysis of $IrCl(CO)(PPh_3)_2$ difficult. The reactivity of **2a** and four *N,N*-diarylamides decreased in the order **2a** ≫ **4a** > **4b** > **4c**, **4d**.[9b]

Under the conditions generally used for the reactions of the usual amides **2** (0.5 mol % of **1a**, at room temperature for 2 h), the reactions of **4b**−**d** did not occur, but they did take place by using **1b** as the catalyst (0.5 mol %, at room temperature for 2 h).[9b] The primary product of the reaction of **4** was not the enamine **6** but the silylhemiaminal **5**, which was converted to **6** under acidic conditions or by heat. Table 3 shows the reactions of the four amides **4a**−**d** with TMDS catalyzed by photoactivated **1a** at room temperature or **8** at 60 °C. With 0.5 mol % catalyst loading, the reactions of **4a** were over within 2 h using both systems, but the products were different. The silylhemiaminal **5a** was formed as a single product with the **1a**/*hν* system, which was then converted to enamine **6a** by thermal treatment at 100 °C. In contrast, when **8** was used as the catalyst at 60 °C, **5a** was not observed at the end of the reaction but **6a** was formed selectively. The reaction of amide **4b** with TMDS by catalysis of the **1a**/*hν* system also gave the corresponding silylhemiaminal **5b** selectively, whereas the reaction with **8** at 60 °C gave a mixture of **5b** and **6b**. In both cases, conversion of **4b** reached over 97% after several hours, and thermal treatment of the obtained crude product gave the enamine **6b** in good yields. The reactions of **4c**,**d** with TMDS also occurred with the **1a**/*hν* system at 25 °C and **8** at 60 °C. This is in sharp contrast to the previous results in which no reaction with $IrCl(CO)(PPh_3)_2$ occurred at 25−80 °C. However, the reactions were terminated after 25−76% of the starting material was consumed, and attempts to complete the reaction have so far been unsuccessful. Use of $IrCl(CO)[P(OC_6F_5)_3]_2$ (**1b**) as the catalyst for the reactions of **4c**,**d** was more efficient than those using the **1a**/*hν* system at 25 °C or **8** at 60 °C as the catalyst.[9b]

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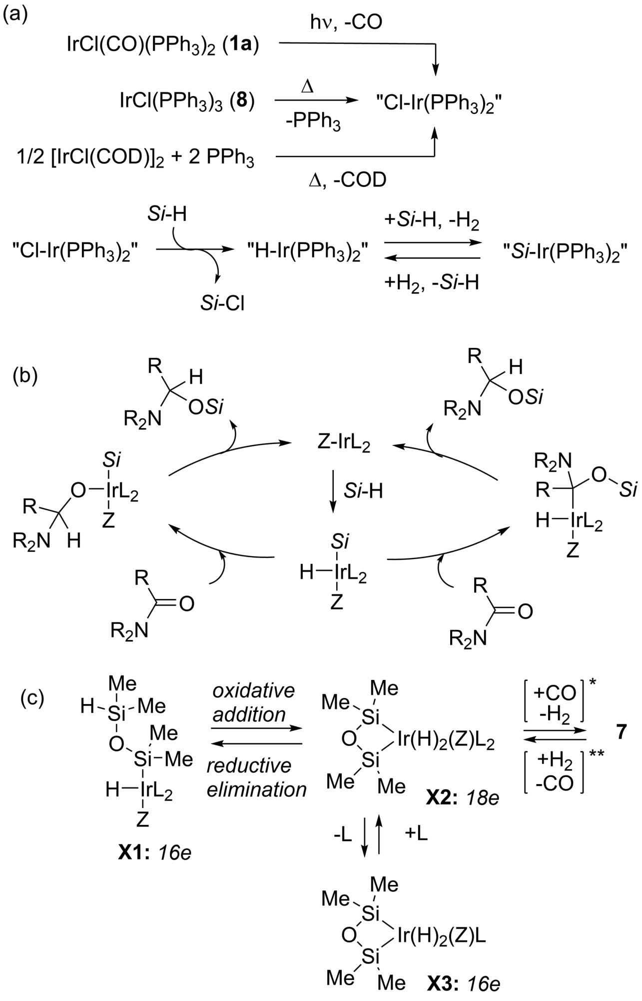
In Situ Generation of Catalytically Active Species. It is known that $IrCl(PPh_3)_3$ (**8**) was prepared by treatment of $[IrCl(\eta^4\text{-COD})]_2$ with PPh_3.[14] As described above, enamines were formed from amides by using **8** as the catalyst, and the active species "$ClIr(PPh_3)_2$" was formed by thermal dissociation of PPh_3 from **8**. We believed that these catalytically active species could be conveniently generated in situ from a mixture of $[IrCl(\eta^4\text{-COD})]_2$ with PPh_3. One advantage of this in situ generation method is the possible use of various phosphorus ligands instead of PPh_3. Table 4 clearly demonstrates that our idea provided fruitful outcomes. The results shown in entries 1−4 using a mixture of $[IrCl(\eta^4\text{-COD})]_2$ with PPh_3 (Ir:P = 1:2) correspond to the experiments reported as entries 2, 8, and 10 in Table 2 and entry 2 in Table 3 using $IrCl(PPh_3)_3$ (**8**). It is clear that a mixture of $[IrCl(\eta^4\text{-COD})]_2$ with PPh_3 (Ir:P = 1:2) behaved as a good catalyst comparable to **8**. As shown in entry 6 in Table 3, the reaction of the amide **4c** was not complete with **8** at 60 °C for 24 h. The in situ generated catalyst from $[IrCl(\eta^4\text{-COD})]_2$ with PPh_3 was even less active than **8**, affording no conversion of **4c** at 60 °C for 24 h. In contrast, full conversion of **4c** and quantitative formation of **5c** were achieved with a mixture of $[IrCl(\eta^4\text{-COD})]_2$ with $P(OC_6F_5)_3$ (Ir:P = 1:2).

The synthetic utility of this in situ generation method was demonstrated by the large-scale production of two enamines. The first is an example of *N,N*-dialkylenamine synthesis on a 0.1 mol scale; the amide **2a** (19.1 g) and TMDS (26.8 g) were subjected to catalysis with a mixture of $[IrCl(\eta^4\text{-COD})]_2$ and PPh_3 (Ir:P = 1:2, 0.001 mol % per Ir atom) at 60 °C for 19 h to give **3a** (17.4 g, 99.2 mmol) in 99% isolated yield. The second is the preparation of a *N,N*-diarylenamine on a 1 g scale; treatment of **4c** (1.43 g) with TMDS (1.34 g) in the presence of a mixture of $[IrCl(\eta^4\text{-COD})]_2$ and $P(OC_6F_5)_3$ (Ir:P = 1:2, 0.5 mol % per Ir atom) at 60 °C for 2 h gave **3a** (1.16 g) in 86% isolated yield.

Considerations of the Active Species Generated from "$ClIr(PPh_3)_2$" and TMDS. As described above, the catalytic conversion of amides to enamines occurs stepwise, and the iridium catalysis only takes part in the first step: i.e., the hydrosilylation of amides to silylhemiaminals. The results described in this paper are in good agreement with the hypothesis that the 14-electron species "$ClIr(PPh_3)_2$", which is stabilized by solvents or reactants in the actual catalytic reactions,[13] is generated from the catalyst precursors, contributing to the catalytic hydrosilylation reaction. In fact, it is known that "$ClIr(PPh_3)_2$" is generated by photolysis of $IrCl(CO)(PPh_3)_2$ (**1a**).[12b] From analogy to $RhCl(PPh_3)_3$, "$ClIr(PPh_3)_2$" can be generated by thermal dissociation of PPh_3 from $IrCl(PPh_3)_3$ (**8**).[23] The results whereby a mixture of $[IrCl(\eta^4\text{-COD})]_2$ with PPh_3 (Ir:P = 1:2) behaved as a good catalyst comparable to **8** support the involvement of "$ClIr(PPh_3)_2$" at any step in the catalytic reaction (Scheme 3a).

Scheme 3. Possible Catalytic Cycles[a]



[a]Legend: (*) deactivation process when **1a** is used as the catalyst; (**) reactivation process from **7** under photoirradiation.

In contrast, the following discussion indicates that the Cl−Ir bond is not necessarily important for the catalytically active species. It is known that a metal−Cl bond of a transition-metal complex is converted to a metal hydride and a metal silyl species by the action of a hydrosilane.[24] As shown in Scheme 3a, treatment of "$ClIr(PPh_3)_2$" with a *Si*−H moiety affords "$HIr(PPh_3)_2$".[13] The reaction of "$HIr(PPh_3)_2$" with a Si−H bond is reversible with that of "*Si*$Ir(PPh_3)_2$"[13] with H_2 by way of a "*Si*$IrH_2(PPh_3)_2$" intermediate. Supporting evidence for Scheme 3a is seen in the formation mechanism of Curtis' complex **7**. The Cl/H exchange is involved in the reaction of **1a** with TMDS to form "$HIr(PPh_3)_2$" and $ClMe_2SiOSiMe_2H$, which proceeds through the oxidative addition of a Si−H bond in TMDS to "$ClIr(PPh_3)_2$" and subsequent reductive elimination of a Si−Cl bond.[11] The H/Si exchange is seen in further reaction of the resulting "$HIr(PPh_3)_2$" species with TMDS. This forms a "*Si*$IrH_2(PPh_3)_2$" intermediate, from which reductive elimination of H_2 forms the "*Si*$Ir(PPh_3)_2$" species, where *Si* = $Me_2HSiOMe_2HSi$−. The formation of **7** is accomplished by intramolecular oxidative addition of the Si−H moiety in "$Me_2HSiOMe_2Si{-}Ir(PPh_3)_2$". In other words, in addition to "$ClIr(PPh_3)_2$", "$HIr(PPh_3)_2$" and "*Si*$Ir(PPh_3)_2$" species could be involved in the reaction mechanism. The involvement of iridium hydride or iridium silyl species as the catalytically active species is supported by the experimental results obtained from the catalyst screening. As described in the sections 1-2 through 1-5 in the Supporting Information in detail, we studied several iridium hydride and silyl iridium complexes, $IrH_5(PPh_3)_2$ (**10**), $IrH_3(PPh_3)_3$ (**12**), $IrH(\eta^4\text{-COD})(PPh_3)_2$ (**9**), and one disilyl trihydride iridium(V) compound, **13**, having a disilametallacyclic skeleton derived from BDSB as candidates for alternative efficient catalysts. All of these compounds more or less showed catalytic activity toward the reaction of **2a** with TMDS to form **3a** as a single product, though none of them were as efficient as **1a** under photolysis or **8** at 60 °C. Two chloro complexes, $RhCl(PPh_3)_3$ (**14**) and $RhCl(CO)(PPh_3)_2$ (**15**), showed some activity, but the rhodium hydride catalysts $RhH(CO)(PPh_3)_3$ (**16**) and $RhH(PPh_3)_4$ (**17**) also behaved as catalysts. It is known that the Rh−Cl bond is converted to a Rh−H bond by the action of a hydrosilane.[24] From these results, we consider that "$ClIr(PPh_3)_2$" is generated from **1a**, **8**, and a mixture of $[IrCl(\eta^4\text{-COD})]_2$ with PPh_3 (Ir:P = 1:2) and exists in the reaction medium. However, it does not participate directly in the catalytic cycle but rather acts as an intermediary species to generate "$HIr(PPh_3)_2$" and "*Si*$Ir(PPh_3)_2$" species.

Scheme 3b illustrates a simplified catalytic cycle for the hydrosilylation of amides. Mechanisms of hydrosilylation of alkenes were investigated by Sakaki and co-workers, who proposed the involvement of oxidative addition of a Si−H bond to either $Pt(PH_3)_2$ or $RhCl(PH_3)_2$ at the initial step of the catalytic cycle.[25c,26c,d] In a similar fashion, oxidative addition of a Si−H bond to Z-$Ir(PPh_3)_2$, where Z = Cl, H, *Si*, would initiate the iridium-catalyzed hydrosilylation of amides, which forms an Ir(III) silyl hydride species, Z-$Ir(H)Si(PPh_3)_2$. Insertion of a C═O bond in the amide between the Ir−H bond or between the Ir−Si bond initiates the Chalk−Harrod[25] and modified Chalk−Harrod[26] cycles, respectively. The resulting insertion products undergo the reductive elimination of a silylhemiaminal to regenerate Z-$Ir(PPh_3)_2$.[27−29]

Chalk−Harrod and modified Chalk−Harrod cycles mediated by Z-$Ir(PPh_3)_2$ are general schemes for hydrosilylation; however, they cannot explain two characteristic features in the catalytic hydrosilane reduction catalyzed by iridium phosphine or iridium phosphite catalysts. The first is the extremely high catalyst efficiency, which is achieved only with TMDS. The second is the selective formation of enamines from amides by way of silylhemiaminal intermediates.

Regarding the high catalytic activity, we have published a series of papers in which unusual rate enhancement by two closely located Si−H groups in bifunctional hydrosilanes was generally observed in hydrosilylation of ketones and aldehydes to the corresponding silyl ethers or the hydrosilane reduction of amides to amines.[4,30] We carried out mechanistic studies on this proximity effect of the two Si−H groups in the platinum-catalyzed hydrosilane reduction of amides with BDSB and isolated several disilaplatina(IV)cycles, which were formed by double oxidative addition of two Si−H groups in BDSB to the Pt(0) precursor and showed catalytic activity toward hydrosilane reduction of amides to amines.[6] Nakatani and co-workers performed DFT calculations based on these experimental results and proposed that the $H_2Pt^{IV}\mathit{Si}_2$ species is responsible for the high catalytic activity and selective formation of amines.[31] Experimental studies to isolate dormant species were performed for the $RhCl(PPh_3)_3$-catalyzed hydrosilylation of acetone, which suggest that double oxidative addition of two Si−H groups in BDSB to the rhodium center is involved in the catalytic hydrosilylation of acetone to the corresponding isopropoxysilane. A H_3RhSi_2 species was identified by NMR spectroscopy, suggesting that the Rh−Cl bond in the rhodium species is replaced by a hydride.[24]

In this context, the scheme shown in Scheme 3c should be considered as the key to understanding the high reactivity of the iridium-catalyzed hydrosilylation of amides to silylhemiaminals. Oxidative addition of one of the Si−H bonds in TMDS gives a 16e species, $(Me_2HSiOMe_2Si)Ir(H)(Z)L_2$ (**X1**; Ir(III), L = PPh_3). Intramolecular oxidative addition of the Si−H bond in this species forms the 18e Ir(V) disilametallacyclic species **X2**. If **X1** is the active species, **X2** is a dormant species reversibly generating **X1**. **X2** is also the source of the deactivated species **7**, which can be formed by reductive elimination of H_2 from **X2** followed by coordination of CO. As described above, regeneration of the active species from **7** is achieved by photoirradiation. These deactivation/reactivation steps would be involved in the reactions using **1a**/*hν*.[32] It is worthwhile to point out that the Ir(V) species **X3** is possibly generated from **X2** by dissociation of PPh_3, which may be another candidate for the catalytic intermediate.

Regarding the selectivity of the product, this is in sharp contrast to the results that ruthenium-, platinum-, and iron-catalyzed hydrosilane reductions of amides result in selective formation of amines.[5−7] Nakatani's calculation suggested the involvement of $H_2Pt^{IV}\mathit{Si}_2$, of which one of the two hydrides and one of the two silyl species take part in rapid hydrosilylation of an amide to a silylhemiaminal. The resulting $HPt^{II}\mathit{Si}$ species contributes to conversion of the silylhemiaminal to a mixture of a disiloxane and an amine.[31] In the case of the present Ir-catalyzed reactions of amides with TMDS, the formation of silylhemiaminals is rapid but further conversion of the silylhemiaminals to the amines and the disiloxanes is somehow suppressed.

Detailed studies on the catalytically active species, possible reaction pathways, and explanation of unusually high hidrosilylation activity and selective formation of silylhemiamals from amides require further investigation and are now underway by using DFT calculations in collaboration with Dr. Nakatani.[33]

CONCLUSION

Two new methods for the efficient conversion of tertiary amides to enamines were established by the discovery of photochemically activated $IrCl(CO)(PPh_3)_2$ (**1a**) and thermally activated $IrCl(PPh_3)_3$ (**8**) as species with extremely high catalytic activity. In extreme cases, the TON and TOF (h^{-1}) reached 10^5 with full conversion of the starting amide.[34] These new catalysts contribute to the successful synthesis of a variety of enamines in high yields with low catalyst loadings. Unique functional group compatibility leads to the selective reaction of amides with coexisting ester or ketone groups remaining intact. Mechanistic studies indicate that the 14-electron species "$ClIr(PPh_3)_2$" is generated from **1a**/*hν* or **8**, which is a precursor of "$HIr(PPh_3)_2$" and "*Si*$IrCl(PPh_3)_2$" species involved in the catalytic cycle. An alternative source of "$ClIr(PPh_3)_2$" is a mixture of commercially available $[IrCl(\eta^4\text{-COD})]_2$ and PPh_3, which generate in situ a highly catalytically active species useful for conversion of *N,N*-dialkylamides to enamines. A mixture of $[IrCl(\eta^4\text{-COD})]_2$ and $P(OC_6F_5)_3$ generates "$ClIr[P(OC_6F_5)_3]_2$", which contributes to the facile synthesis of *π*-conjugated enamines from *N,N*-diarylamides. The synthetic utility was demonstrated by large-scale (10 mmol ~0.1 mol) syntheses of two enamines.

The present method is useful for practical syntheses of enamines from easily available iridium complexes. The new catalysts including in situ generation of active species showed distinguished catalytic activity and interesting functional group compatibility. The $IrCl(CO)(PPh_3)_2$-catalyzed reactions of tertiary amides with TMDS are now utilized by Chida, Dixon, and other chemists as in situ generation of silylhemiaminals, which reacted with nucleophiles to synthesize functionalized amino derivatives including natural products. The present results contribute to the progress of this research field.[35] In addition to the synthetic utility, mechanistic considerations provide fresh insights that include the involvement of “HIr(PPh_3)$_2$” and “*Si*IrCl(PPh_3)$_2$” species in the catalytic cycle. Elucidation of detailed mechanisms by DFT calculations is now in progress.

■ EXPERIMENTAL SECTION

General Procedure. All reactions were carried out under an argon atmosphere using standard Schlenk techniques or performed in a N_2-filled glovebox. ^{1}H, ^{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 ^{1}H and ^{13}C are given in parts per million relative to the solvent signal. Chemical shifts for ^{31}P are given in parts per million downfield from phosphoric acid (δ_P 0) as an external standard. IR spectra were measured on a JASCO FT/IR 4200 spectrometer. HR-MS analyses were performed at the Analytical Center at the Institute for Materials Chemistry and Engineering, Kyushu University. Photoirradiation was carried out by an Ushio UM-453B-A high-pressure mercury lamp (450 W) according to the procedure below; a reaction mixture was placed in a VIDTEC 30 mL quartz round-shaped flask equipped with a three-way stopcock. The flask was set at a position of 15 cm away from the lamp. A quartz dewar condenser was also set around the lamp to avoid thermal effects. Then the solution was stirred under photoirradiation for the time described in Tables 1−3. For the reaction on an NMR scale (see sections 1-1, 1-3, and 1-5 in the Supporting Information), a Pyrex NMR tube equipped with a J. Young valve was used as a reaction vessel. Deuterated solvents (C_6D_6, $CDCl_3$) were purchased from Wako Pure Chemical Industries Ltd. and used after dehydration by using Na/Ph_2CO (for C_6D_6) or activated MS4A (for $CDCl_3$). Hydrosilane reagents, 1,1,3,3-tetramethyldisiloxane (TMDS), 1,1,3,3,3-pentamethyldisiloxane (PMDS), and $PhMe_2SiH$ were purchased from Wako Pure Chemical Industries, AZmax Co. Ltd., respectively, and distilled before using. Dehydrated solvents (*n*-pentane, toluene, THF, ethyl acetate, CH_2Cl_2), PPh_3, and anisole were purchased from Kanto Chemical Co. Ltd. and used as received. Iridium complexes **1a**,[36] **7**,[11] **8**,[14] **9**,[15] **10**,[16] **11**,[17] **12**,[18] **13**,[19] and [IrCl(η^4-COD)]$_2$,[37] rhodium derivatives **14**,[20] **15**,[21] **16**,[22] and **17**,[22] the phosphite reagent P(OC_6F_5)$_3$,[38] amides **2a−e**,[9a] **4a**,[39] and **4b−d**,[9b] and the hydrosilane reagent 1,2-bis(dimethylsilyl)benzene[24] were prepared according to the literature.

Hydrosilane Reduction of $PhCH_2CONEt_2$ (2a) To Form PhCH=CHNEt$_2$ (3a) Catalyzed by 1a and 8 under Thermal and Photochemical Conditions (Table 1). For entries 1 and 7, a stock solution of the catalyst was prepared by dissolving complex **1a** (7.8 mg, 1.0 × 10^{-2} mmol) or **8** (10.1 mg, 1.0 × 10^{-2} mmol) in toluene (2 mL). For entries 2−6 and 8−12, a stock solution of the catalyst was prepared by dissolving complex **1a** (7.8 mg, 1.0 × 10^{-2} mmol) or **8** (10.1 mg, 1.0 × 10^{-2} mmol) in toluene, THF, or CH_2Cl_2 (10 mL), followed by the dilution of 0.1 mL of the solution with 0.9 mL of the solvent. A 0.1 mL portion of the stock solution of **1a** or **8** (0.05 mol % for entries 1 and 7, 0.001 mol % for entries 2−6 and 8−12) was placed in a two-necked 20 mL round flask, and then solvent (0.4 mL), substrate **2a** (191.2 mg, 1.0 mmol), anisole (108.1 mg, 1.0 mmol, as an internal standard), and TMDS (268.7 mg, 2.0 mmol) were added. The mixture was stirred at 25 °C (entries 1, 2, 7, and 8), or 60 °C (entries 3 and 9−11) or irradiated with a high-pressure mercury lamp (entries 4−6 and 12) for 1 h. The conversion of **2a** and the yield of **3a** were determined by ^{1}H NMR spectroscopy.

Hydrosilane Reduction of *N,N*-Dialkylamides 2 To Form the Corresponding Aldenamines 3 Catalyzed by Photochemically Activated 1a or Thermally Activated 8 (Table 2). A stock solution of the catalyst was prepared by dissolving complex **1a** (7.8 mg, 1.0 × 10^{-2} mmol) or **8** (10.1 mg, 1.0 × 10^{-2} mmol) in toluene (10 mL), followed by the dilution of 0.1 mL of the solution with 0.9 mL of the solvent. A 0.1 mL portion of the stock solution of **1a** or **8** (0.001 mol %) was placed in a two-necked 20 mL round flask, and then toluene (0.4 mL), the substrate **2a−e** (1.0 mmol), anisole (108.1 mg, 1.0 mmol, as an internal standard), and TMDS (268.7 mg, 2.0 mmol) were added. The mixture was irradiated with a high-pressure mercury lamp (entries 1, 3, 5, 7, and 9) or heated at 60 °C (entries 2, 4, 6, 8, and 10) for the time described in the table. The conversion of **2** and the yield of **3** were determined by ^{1}H NMR spectroscopy. For **2a,b**, the reaction mixture was filtered through a pad of Celite and the resulting silane residue including unreacted TMDS and the solvent were removed in vacuo to obtain enamines **3a,c** as colorless oils. For **2d**, after the same treatment as that of **2a−c**, the resulting sample was cooled and washed with cold hexane (−30 °C) followed by evacuation to obtain **3d**. For **2c,e**, the corresponding enamines **3c,e** were too unstable due to the strong density to be isolated; therefore, only the NMR yield was determined.

Hydrosilane Reduction of *N,N*-Diarylamides 4 To Form the Corresponding *π*-Conjugated Aldenamines 6 Catalyzed by Photochemically Activated 1a or Thermally Activated 8 (Table 3). In a two-necked 20 mL round flask were placed complex **1a** (3.9 mg, 5.0 × 10^{-3} mmol) or **8** (4.5 mg, 5.0 × 10^{-3} mmol), toluene (0.5 mL), a substrate **4a−4d** (1.0 mmol), anisole (108.1 mg, 1.0 mmol, as an internal standard), and TMDS (268.7 mg, 2.0 mmol). The mixture was irradiated with a high-pressure mercury lamp (entries 1, 3, 5 ,and 7) or heated at 60 °C (entries 2, 4, 6, and 8) for the time described in the table. The conversion of **4** and the yield of **5** or **6** were determined by ^{1}H NMR spectroscopy. For **4a,b**, the reaction mixture was filtered through a pad of Celite and the resulting silane residue including unreacted TMDS and the solvent were removed in vacuo. The obtained viscous solid was again dissolved in toluene (10 mL) and heated at 80 °C for 2 h to convert **5** to **6** according to a previous report.[9b] The solution was concentrated under reduced pressure. Purification by silica gel column chromatography (hexane/toluene) gave **6a,b**.

Hydrosilane Reduction of 4 To Form 6 by in Situ Generation of the Catalytically Active Species from [IrCl(η^4-COD)]$_2$ and PPh_3 or P(OC_6F_5)$_3$ (Table 4). A stock solution of the catalyst was prepared by dissolving [IrCl(η^4-COD)]$_2$ (3.4 mg, 5.0 × 10^{-3} mmol) and PPh_3 (5.2 mg, 2.0 × 10^{-2} mmol) or P(OC_6F_5)$_3$ (12.8 mg, 2.0 × 10^{-2} mmol) in toluene (10 mL) and stirring for 10 min, followed by the dilution of 0.1 mL of the solution with 0.9 mL of toluene. A 0.1 mL portion of the stock solution (0.001 mol % per Ir atom) was placed in a two-necked 20 mL round flask, and then toluene (0.4 mL), one of the substrates **2d,e** and **4a,c** (1.0 mmol), anisole (108.1 mg, 1.0 mmol, as an internal standard), and TMDS (268.7 mg, 2.0 mmol) were added. The mixture was stirred at 60 °C for the time described in the table. The conversion of amides and the yield of enamines or silylhemiaminals were determined by ^{1}H NMR spectroscopy. For **4a**, the reaction mixture was filtered through a pad of Celite and the resulting silane residue including unreacted TMDS and the solvent were removed in vacuo. Purification by silica gel column chromatography (hexane/toluene) gave **6a**. For **4c**, after the same treatment as that of **4a**, toluene (10 mL) and P_2O_5 (30 mg) were added to the resulting mixture and stirred at 25 °C for 0.5 h to convert **5c** to **6c** according to a previous report.[9b] The solution was concentrated under reduced pressure. Purification by silica gel column chromatography (hexane/toluene) gave **6c**.

The 0.1 mol Scale Reaction of 2a with TMDS Catalyzed by in Situ Generated Catalyst Species from [IrCl(η^4-COD)]$_2$ and PPh_3 (Entry 1 in Parentheses, Table 4). A stock solution of the catalyst was prepared by dissolving [IrCl(η^4-COD)]$_2$ (3.4 mg, 0.5 × 10^{-2} mmol) and PPh_3 (5.2 mg, 2.0 × 10^{-2} mmol) in toluene (10 mL) After the mixture was stirred for 10 min, 1.0 mL of the stock solution (0.001 mol % per Ir atom) was placed in a two-necked 100 mL round flask that contained amide **2a** (19.1 g, 100.0 mmol) and toluene (9 mL). TMDS (26.8 g, 200.0 mmol) was then placed slowly into the flask. The mixture was stirred at 60 °C for 19 h. Complete consumption of the substrate was confirmed by ^{1}H NMR spectroscopy. After removal of the volatiles, the product **3a** was obtained by distillation under reduced pressure (8 Pa, 100 °C) as a colorless oil (17.4 g, 99.2 mmol, 99%).

Reaction of 4c with TMDS (10 mmol Scale) Catalyzed by in Situ Generated Catalyst Species from [IrCl(η^4-COD)]$_2$ and P(OC_6F_5)$_3$ (Entry 6 in Parentheses, Table 4). In a two-necked 50 mL round flask were placed $[IrCl(\eta^4\text{-COD})]_2$ (8.5 mg, 1.25×10^{-2} mmol), $P(OC_6F_5)_3$ (29.0 mg, 5.00×10^{-2} mmol), toluene (2.5 mL), and amide **4c** (1.43 g, 5.0 mmol). TMDS (1.34 g, 10.0 mmol) was then placed slowly into the flask. The mixture was heated at 60 °C for 2 h. The reaction mixture was filtered through a pad of Celite, and the resulting silane residue including unreacted TMDS and the solvent were removed in vacuo. The resulting mixture was dissolved in toluene (50 mL), and P_2O_5 (150 mg) was added to the solution at −78 °C and stirred at 25 °C for 1 h to convert **5c** to **6c**. The solution was concentrated under reduced pressure.[9b] Purification by silica gel column chromatography (hexane/toluene) gave **6c** (1.16 g, 4.3 mmol, 86%).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00835.

> Experimental details, spectral data for complexes and compounds, and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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(32) When **1a** was used as the catalyst, dissociation of CO generated catalytically active species. In the catalytic reaction, the active species

reacted with TMDS and amide existing in the solution. Coordination of CO to form **7** is competitive with that of the amide and does not occur as long as large amounts of amides exist in the reaction medium. In other words, progress of the catalytic reaction results in lowering the amide concentration, which triggers the reaction of CO with the active species to form **7**.

(33) Curtis's complex **7** as the deactivated species was observed in the catalysis of $IrCl(CO)(PPh_3)_2$. The CO ligand required for the conversion of **X2** to **7** originates from the CO ligand in $IrCl(CO)(PPh_3)_2$. Photoassisted dissociation of the CO ligand in **7** caused it to react with H_2 to form **X2**, which initiates the catalytic hydrosilylation. It is known that a small amount of H_2 is often formed by the catalytic reaction of hydrosilanes with moisture, which is a source of H_2 to form **X2** from **7**.

(34) One of the reviewers requested experiments to suggest the robustness of catalytically active species. As described in section 1-8-1, page S-8, in the Supporting Information, we carried out the reaction of **2a** with **3a** catalyzed by **8** and attempted isolation of the product by distillation and subsequent catalyst recovery from the residue; however, the recycling experiment was hampered due to decomposition of a part of the catalytically active species during the recovery process. As a supporting experiment, we carried out five successive runs of the reaction, in which volatiles were removed in vacuo after the reaction of each run, **2a** and TMDS were added, and performed the next run was performed (section 1-8-2, page S-8, in the Supporting Information). The yield of the product at each run was 73−97% (TON = 73000−97000), suggesting that the catalytic activity of each run was not very different, and no substantial decomposition of the catalytically active species occurred. The total reached TON = 475000.

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