

## Development and Mechanistic Investigation of a Highly Efficient Iridium(V) Silyl Complex for the Reduction of Tertiary Amides to Amines

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The cationic Ir(III) acetone complex (POCOP)Ir(H)<sub>2</sub>(acetone)<sup>+</sup> (POCOP = 2,6-bis(di-*tert*-butylphosphinito)phenyl) was shown to catalyze the reduction of a variety of tertiary amides to amines using diethylsilane as reductant. Mechanistic studies established that a minor species generated in the reaction, the neutral silvl trihydride Ir(V) complex (POCOP)IrH<sub>3</sub>(SiEt<sub>2</sub>H), was the catalytically active species. High concentrations of this species could be conveniently generated by treatment of readily available (POCOP)IrHCl with *tert*-butoxide in the presence of Et<sub>2</sub>SiH<sub>2</sub> under H<sub>2</sub>. Thus, using this mixture in the presence of a trialkylammonium salt, a wide array of tertiary amides, including extremely bulky substrates, are rapidly and quantitatively reduced to tertiary amines under mild conditions with low catalyst loading. A detailed mechanistic study has been carried out and intermediates identified. In brief, (POCOP)IrH<sub>3</sub>(SiEt<sub>2</sub>H) reduces the amide to the hemiaminal silvl ether that, in the presence of a trialkylammonium salt, is ionized to the iminium ion, which is then reduced to the tertiary amine by Et<sub>2</sub>SiH<sub>2</sub>. Good functional group compatibility is demonstrated, and a high catalyst stability has provided turnover numbers as high as 10 000.

## INTRODUCTION

Reduction of readily available tertiary amides is an attractive route to tertiary amines, an important class of compounds which exhibit a broad range of applications.<sup>1</sup> Alkali-metal hydrides and borohydrides are common reagents which can be used for such reductions but suffer from several disadvantages, including poor functional group tolerance, moisture and air sensitivity, and often inconvenient methods required for product isolation and purification.<sup>2</sup> Catalytic hydrogenation of primary and secondary amides to amines has been reported under conditions of high pressures and temperatures, but reductions of tertiary amides via hydrogenation have not been observed.<sup>3</sup> Over the past few years, metal-catalyzed reductions of amides employing silanes have been extensively investigated, since silanes are easily handled and environmentally attractive and product isolation procedures can be convenient.<sup>4</sup> These studies have resulted in the discovery of a variety of catalytic systems with varying levels of scope, efficiency, and functional group compatibility.<sup>4b,g,n,o</sup> In an early report Ito and co-workers showed that the rhodium complex [RhH(CO)- $(PPh_3)_3$  initiated the reduction of a variety of tertiary amides with Ph2SiH2 at room temperature to afford the corresponding tertiary amines in good to excellent yields.<sup>4b</sup> Tolerance of ester and

epoxide functionalities was demonstrated. In a series of papers, Nagashima and co-workers reported the reduction of both secondary and tertiary amides to amines using various silanes and the ruthenium cluster complex ( $\mu_3$ , $\eta^2$ : $\eta^3$ : $\eta^5$ -acenaphthylene)Ru<sub>3</sub>(CO)<sub>7</sub> as a catalyst.<sup>4e,f</sup> Using PhMe<sub>2</sub>SiH as the silane, this system selectively reduces amides in the presence of ketone or ester functionalities.<sup>4g</sup> The Nagashima group also demonstrated that using the bifunctional silane 1,1,3,3-tetramethyldisiloxane (TMDS) Pt(IV) salts served as efficient catalysts for reduction of tertiary amides to amines in good to excellent yields.<sup>4o</sup>

Iron carbonyl complexes (Fe<sub>2</sub>(CO)<sub>9</sub> or Fe<sub>3</sub>(CO)<sub>12</sub>) were shown to be efficient catalysts for reduction of amides by both Beller and Nagashima.<sup>4l,m</sup> A convenient procedure developed by Beller involved the use of polymethylhydrosiloxane (PMHS; 4–8 equiv) and 2–10 mol % Fe<sub>2</sub>(CO<sub>9</sub>) in toluene or dibutyl ether at 100 °C over 24 h. Generally good functional group tolerance was observed, and yields were good to excellent. In a further recent advance, Beller reported that  $Zn(OAc)_2$  was an effective catalyst at 10 mol % loading for the reduction of tertiary amides with (EtO)<sub>3</sub>SiH under

Received: October 11, 2011 Published: November 17, 2011 mild conditions in good to excellent yields.<sup>4n</sup> Good functional group tolerance was noted.

While a number of viable transition-metal catalysts have been discovered for silane reductions of amides, mechanistic details concerning these transformations are lacking.<sup>4e,l,n</sup> It is generally assumed that the silane is "activated" by the metal complex via oxidative addition to produce a metal silyl complex capable of transferring R<sub>3</sub>Si<sup>+</sup> to the carbonyl functionality to produce the silyl-substituted oxocarbenium ion. This species then undergoes hydride reduction to produce the silyl-substituted aminal. Amine is produced by ionization to the iminium ion followed by a second hydride reduction (Scheme 1). No intermediates in this cycle have been observed in the case of transition-metal-based systems. Beller has observed an adduct between  $Zn(OAc)_2$  and  $(EtO)_3SiH$  which is presumed to transfer  $(EtO)_3Si^+$  to the amide to form an intermediate of type A, which is then reduced by the remaining zinc hydride to form an intermediate of type **B**.<sup>4n</sup>

Recently we reported hydrosilylation of ketones (eq 1),<sup>5a</sup> aldehydes (eq 1),<sup>5a</sup> esters (eq 1),<sup>5a</sup> and epoxides (eq 4)<sup>5c</sup> as well as reduction of alkyl halides (eq 2)<sup>5d,f</sup> and ethers (eq 3)<sup>5b</sup> using the highly electrophilic  $\eta^1$ -silane complex 2<sup>5e</sup> generated in situ from the conveniently prepared acetone complex 1 in combination with Et<sub>3</sub>SiH (Scheme 2).

$$\begin{array}{c} O \\ H \\ R' \\ \hline C \\ R' \\ \hline 1 (cat.) \\ \hline 1 (cat.) \\ \hline R' \\ \hline C \\ R' \\ \hline C \\ R' \\ \hline C \\ R' \\ \hline (1) \hline \hline (1) \\ \hline (1) \\ \hline (1) \hline \hline (1) \\ \hline (1) \hline \hline (1) \\ \hline (1) \hline \hline (1) \hline \hline (1) \\ \hline (1) \hline \hline (1$$





In this paper we report applying complex 1 in combination with diethylsilane for the reduction of tertiary amides to tertiary amines. An in-depth mechanistic investigation provided surprising details of this reduction process, which contrast sharply with mechanistic processes determined for reactions described in Scheme 2. A neutral Ir(V) catalyst resting state has been identified together with characterization of intermediates during the reduction process. On the basis of these studies a highly efficient catalyst system has been developed which exhibits broad scope, high yields, and high turnover numbers (up to 10 000) under mild conditions, with significant functional group tolerance.

#### RESULTS AND DISCUSSION

Reduction of Tertiary Amides with  $Et_2SiH_2$  Catalyzed by Iridium Complex 1. Complex 1 (0.5 mol %) together with either Me<sub>2</sub>EtSiH or  $Et_2SiH_2$  (3 equiv) initiates catalytic reduction of a variety of tertiary amides, including aromatic, aliphatic, heteroaromatic, and heterocyclic amides, to produce the corresponding tertiary amines in excellent yields at 60 °C (eq 5). The bulkier silane triethylsilane, however, is nearly unreactive with tertiary amides under similar conditions. The siloxanes Me<sub>2</sub>EtSiO-SiEtMe<sub>2</sub> and HEt<sub>2</sub>SiOSiEt<sub>2</sub>H are formed as the reactions proceed, as confirmed by <sup>29</sup>Si{<sup>1</sup>H} NMR spectroscopy.

$$R \xrightarrow{O}_{R'} R' + silane \xrightarrow{1 (0.5 \text{ mol } \%)} R \xrightarrow{R'}_{R'} R' + siloxane (5)$$

$$R' \xrightarrow{R'}_{R'} R' + siloxane (5)$$

Hemiaminal ethers resulting from a single hydrosilylation event (first hydrosilylation) with  $Et_2SiH_2$  are obtained in some cases. Chlorobenzene is generally used as solvent;  $CDCl_3$  can be employed as cosolvent for less soluble amides.

Results of typical reactions are illustrated in Table 1. Entry 1 shows that N,N-dimethylisobutylamide is reduced efficiently with Et<sub>2</sub>SiH<sub>2</sub> to attain 94% conversion in 1.5 h, while reduction with Me<sub>2</sub>EtSiH proceeds more slowly (66% conversion in 22 h; entry 2). With N,N-dimethylbenzamide as substrate, Me<sub>2</sub>EtSiH exhibits a slow rate of conversion of the amide to the amine (entry 3) similar to that in entry 2; however,  $Et_2SiH_2$  leads to more rapid reduction under similar conditions (entry 4). A low catalyst loading of 0.1 mol % requires 6 h for complete conversion of the amide to the amine (entry 5). Reduction of N,Ndiisopropylbenzamide, a very bulky tertiary amide, was examined using Me<sub>2</sub>EtSiH or Et<sub>2</sub>SiH<sub>2</sub>. As expected, reduction of the amide with Me<sub>2</sub>EtSiH gives only 3% conversion in 19 h (entry 6), but using Et<sub>2</sub>SiH<sub>2</sub> enables an efficient reduction of even this bulky amide to give N,N-diisopropylbenzylamine (82% conversion in 54 h, entry 7). N,N-diphenylacetamide is quantitatively reduced to N,N-diphenylethylamine with  $Et_2SiH_2$  in 2 h (entry 8), while N,N-diphenylbenzamide converts to N,N-diphenylbenzylamine and *N*,*N*-diphenylsilylamine in a ratio of 3.5:1 in 4 h (entry 9). Observation of N,N-diphenylsilylamine and toluene in the reaction mixture indicates the further reduction of N,N-diphenylbenzylamine with the silane.

Results of the reactions of 1-acylpiperidine derivatives are shown in entries 10-12. Rapid reduction of 1-formylpiperidine with Et<sub>2</sub>SiH<sub>2</sub> occurs at 23 °C. Although 1-benzoylpiperidine is reduced with Et<sub>2</sub>SiH<sub>2</sub> to the corresponding amine as usual, the trifluoroacetyl-substituted amide exhibits a complex mixture of products suggestive of both hydrosilylation of the carbonyl functionality and C-F bond activation. In contrast, Me<sub>2</sub>EtSiH exhibits a clean single hydrosilylation of the amide even with excess Me2EtSiH to form only the corresponding hemiaminal ether. Such a preference for a single hydrosilylation is also observed in the hydrosilylation of ethyl trifluoroacetate with Me<sub>2</sub>EtSiH catalyzed by 1.<sup>5a</sup> Results of catalytic reductions of  $\gamma$ and  $\delta$ -lactams are shown in entries 13 and 14. Reduction of 1-methyl-2-pyrrolidinone with Et<sub>2</sub>SiH<sub>2</sub> at 23 °C attains 91% conversion in 27 h (reduction at 60 °C generates side products). For a similar reason (avoidance of side products) the relatively less reactive Me<sub>2</sub>EtSiH is preferred to Et<sub>2</sub>SiH<sub>2</sub> for reduction of 1-benzyl-2-piperidinone, a  $\delta$ -lactam, to the amine (entry 14, 20 h, quantitative conversion).



#### Scheme 1. General Mechanism of Metal-Catalyzed Reduction of Tertiary Amide with Hydrosilane

Scheme 2. Reduction of Carbonyl and Ether Compounds with a Cationic  $\eta^1$ -Silane Iridium(III) Complex



Results of reductions of several  $N_iN$ -dibenzylamide derivatives are shown in entries 15–19. All conversions are essentially quantitative, but in the case of  $N_iN$ -dibenzylbenzamide 7% of the hemiaminal ether is observed as well as 93% of the expected tribenzylamine. CDCl<sub>3</sub> as cosolvent in addition to chlorobenzene is needed for the reduction of the naphthoylamide, due to its poor solubility in chlorobenzene. Under these conditions, 96% conversion to the amine is achieved in 27 h. The amides bearing cyclopropyl and furanyl groups are conveniently and quantitatively reduced to the corresponding amines with no formation of side products (entries 18 and 19). The azo group on the amide is well tolerated; reduction affords only the desired amine product (entry 20).

Mechanistic Studies. Identification of Resting States by in Situ <sup>31</sup>P and <sup>1</sup>H NMR Spectroscopy. As data in Table 1 show, the reduction with  $Et_2SiH_2$  exhibits catalytic activity significantly higher than that with Me<sub>2</sub>EtSiH. To probe the potential reason for differing activities, we initially monitored both working catalyst systems by in situ <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy to identify the catalyst resting state(s).

Following the catalytic reduction of *N*,*N*-dimethylbenzamide by Me<sub>2</sub>EtSiH in the presence of **1** (0.5 mol %) (eq 6), the observable iridium species are the cationic silane complex  $(2', 69\%)^{5d}$  and the amine and/or amide complex (31%).<sup>6</sup> In sharp contrast, carrying out the same experiment using Et<sub>2</sub>SiH<sub>2</sub> (eq 7) indicates that the *neutral* iridium(III) silyl hydride complex (**3**, ca. 90%) and the *neutral* iridium(V) silyl trihydride complex (**4**, ca. 10%) are the dominant resting states throughout the reaction. Since these species are neutral,

their formation must result in production of 1 equiv of the conjugate acid of the amide and/or the product amine. (NMR spectroscopic data for intermediates are summarized in the Experimental Section.) The minor species, complex 4, is considered to be formed via reaction of 3 with a small amount of H<sub>2</sub> which evolves from hydrolysis of Et<sub>2</sub>SiH<sub>2</sub> by adventitious H<sub>2</sub>O (the facile addition of H<sub>2</sub> to the iridium center of 3 to form 4 is demonstrated below).



Complexes 3 and 4 in a ratio of 0.85:0.15 were independently prepared at 60  $^{\circ}$ C in a quantitative yield by reaction of the neutral

### Table 1. Reduction of Tertiary Amides with Silanes Catalyzed by $1^a$

entry	substrate	silane	t h	conversio %	n <sup>b</sup> prod	luct <sup>b</sup>	
1	0	Et <sub>2</sub> SiH <sub>2</sub>	1.5	94	> ^ /	+	Et <sub>2</sub> HSiOSiHEt <sub>2</sub>
2	\Ń<	 Me₂EtSiH	22	66	Ύν.	+	Me <sub>2</sub> EtSiOSiEtMe <sub>2</sub>
3	0 II	Me <sub>2</sub> EtSiH	48	90	Ph N	+	Me2EtSiOSiEtMe2
4	Ph	Et <sub>2</sub> SiH <sub>2</sub>	1	quant.	Υ.	+	Et2HSiOSiHEt2
5 <sup>c</sup>	·	Et <sub>2</sub> SiH <sub>2</sub>	6	quant.		+	Et <sub>2</sub> HSiOSiHEt <sub>2</sub>
6		Me <sub>2</sub> EtSiH	19	3			
7		Et <sub>2</sub> SiH <sub>2</sub>	54	82	$\succ$	+	Et2HSiOSiHEt2
8	O N, Ph Ph	Et <sub>2</sub> SiH <sub>2</sub>	2	quant.	N,Ph Ph	+	Et2HSiOSiHEt2
9 <sup>d</sup>	Ph N Ph Ph	Et <sub>2</sub> SiH <sub>2</sub>	4	quant.	$Ph N Ph + HEt_2$	Si~N^   Ph	- Ph + Et <sub>2</sub> HSiOSiHEt <sub>2</sub> + toluene
10 <sup>e</sup>	H N	Et <sub>2</sub> SiH <sub>2</sub>	0.5	quant.	HN	+	Et <sub>2</sub> HSiOSiHEt <sub>2</sub>
11	Ph N	Et <sub>2</sub> SiH <sub>2</sub>	1	quant.	Ph	+	Et <sub>2</sub> HSiOSiHEt <sub>2</sub>
12	F <sub>3</sub> C N	Me <sub>2</sub> EtSiH	2	quant.	F <sub>3</sub> C N		
13 <sup>ø</sup>		Et <sub>2</sub> SiH <sub>2</sub>	27	91		+	Et <sub>2</sub> HSiOSiHEt <sub>2</sub>
14 <sup>/</sup>	Ph N	Me <sub>2</sub> EtSiH	20	quant.	Ph N	+	Me <sub>2</sub> EtSiOSiEtMe <sub>2</sub>
15	Ph Ph	Et <sub>2</sub> SiH <sub>2</sub>	2	quant.	Ph N Ph	+	Et <sub>2</sub> HSiOSiHEt <sub>2</sub>
16	Ph N Ph	Et <sub>2</sub> SiH <sub>2</sub>	4	quant.	Ph N Ph	+	OSiHEtH Ph H Ph H Ph Ph
17 <sup>g</sup>	O N Ph	Et <sub>2</sub> SiH <sub>2</sub>	27	96	Ph Ph	+ +	Et <sub>2</sub> HSiOSiHEt <sub>2</sub> Et <sub>2</sub> HSiOSiHEt <sub>2</sub>
18	N Ph Ph	Et <sub>2</sub> SiH <sub>2</sub>	5	quant.	N Ph	+	Et <sub>2</sub> HSiOSiHEt <sub>2</sub>
19	N Ph O Ph	Et <sub>2</sub> SiH <sub>2</sub>	1	quant.	N Ph O Ph	+	Et2HSiOSiHEt2
20 <sup>#</sup> N Ph		Et <sub>2</sub> SiH <sub>2</sub>	1.2	quant. N= Ph		+	Et <sub>2</sub> HSiOSiHEt <sub>2</sub>

<sup>*a*</sup> Reaction conditions: 0.5 mol % 1, solvent C<sub>6</sub>D<sub>5</sub>Cl, 3 equiv of Me<sub>2</sub>EtSiH or Et<sub>2</sub>SiH<sub>2</sub>, 60 °C. <sup>*b*</sup> Determined by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR. <sup>*c*</sup> 0.1 mol % 1. <sup>*d*</sup> The ratio [PhCH<sub>2</sub>NPh<sub>2</sub>]:[HEt<sub>2</sub>SiNPh<sub>2</sub>]:[toluene] is ca. 3.5:1:1. <sup>*c*</sup> Reaction at 23 °C. <sup>*f*</sup> NMR yield 84%. <sup>*g*</sup> CDCI<sub>3</sub> is added as cosolvent. <sup>*h*</sup> 0.5 mol % (POCOP)IrH<sub>2</sub> used instead of 1 in C<sub>6</sub>D<sub>6</sub>.



iridium hydrido chloro complex 6 with NaOtBu in the presence of excess  $Et_2SiH_2$ . Complex 4 is again thought to be formed through the reaction of 3 with  $H_2$ , which evolves from the reaction of the formed HOtBu with  $Et_2SiH_2$  (eq 8).<sup>7</sup>



The <sup>1</sup>H signal due to iridium hydride 3 appears at  $\delta$  – 16.9 as a quartet (J = 6.0 Hz, equal coupling to both <sup>31</sup>P nuclei and the Si–H). This shift is very close to that for (POCOP)Ir(H)(SiEt<sub>3</sub>) (3') at  $\delta$  –15.9. Complex 4 exhibits a triplet at  $\delta$  –8.8 (J = 10.5 Hz). This shift is close to that for iridium tetrahydride complex (POCOP)IrH<sub>4</sub> (5;  $\delta$  –8.3)<sup>Sb,d,8</sup> The Ir–H signal at  $\delta$  –8.8 for 4 remains a sharp triplet at low temperatures (–70 °C), suggesting that the three hydrides are rapidly interchanging even at –70 °C. The <sup>31</sup>P signals for complexes 3 and 4 occur at  $\delta$ 190.1 and 171.2, respectively. The ratio (0.85:0.15) of 3 to 4 calculated on the basis of relative intensities of proton signals due to iridium hydrides is consistent with the ratio (0.86:0.14) based on the <sup>31</sup>P NMR data when it is assumed that complex 4 is a trihydride, thus supporting this structural assignment.

It is well established that electrophilic iridium centers can coordinate to silanes in an  $\eta^2$  fashion; therefore, an alternative to the classical Ir(V) structure shown for 4 is an Ir(III) structure (Scheme 3), in which the silane is bound in an  $\eta^2$  mode. Normally this binding mode is identified by measuring the  ${}^{1}\text{H}-{}^{29}\text{Si}$  coupling constant, which falls in the range 20–200 Hz.9 The low natural abundance of <sup>29</sup>Si (4.7%) often renders these satellites difficult to detect. In the present case the rapid scrambling of the three hydrides will reduce the observable J value by one-third and thus the expected apparent <sup>1</sup>H-<sup>29</sup>Si coupling will fall in the range 7-67 Hz.<sup>9e,f,i,j</sup> We have not been able to detect a satellite consistent with this range, but the fact that the hydride signal is a triplet and the lines are somewhat broad (coupled with the low natural abundance of <sup>29</sup>Si) does not lead to full confidence in the assignment of 4 as a classical Ir(V)trihydride, but that is the structure we currently favor.<sup>10</sup>

To probe the variation of catalyst resting states as a function of the silane, we examined the reactions of various (POCOP)Ir(H)-(silane)<sup>+</sup> (silane = HSiEt<sub>3</sub>, HSiMe<sub>2</sub>Et, H<sub>2</sub>SiEt<sub>2</sub>) complexes with NEt<sub>3</sub> as a model base for the amide and amine product. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the reaction mixture of the cationic triethylsilane complex **2** and NEt<sub>3</sub> (7 equiv) in the presence of excess Et<sub>3</sub>SiH (256 equiv) exhibits a single signal at  $\delta$  175.1 due

# Scheme 4. Generation of the Indium Silyl Hydride Complexes 3 and 4



to the amine complex (eq 9). No remaining **2** could be detected. The <sup>31</sup>P spectrum of the mixture of **2'**, Me<sub>2</sub>EtSiH, and NEt<sub>3</sub> with a ratio of 1:100:134 contains four resonances at  $\delta$  204.1, 190.4, 183.2, and 176.4, which are assignable to neutral dihydride 7 (28%), the neutral hydrido(silyl) iridium complex **3** (24%), the silane complex **2'** (40%), and the amine complex (5%), respectively. On the basis of <sup>1</sup>H and <sup>31</sup>P NMR data, the equilibrium constant  $K_{eq}$ , relating **2'** and the cationic amine complex, is calculated to be ca. 0.1 (eq 10). It is noteworthy that Me<sub>2</sub>EtSiH coordinates to the iridium center more strongly than does Et<sub>3</sub>SiH. Interestingly, the acetone complex **1** when treated with Et<sub>2</sub>SiH<sub>2</sub> (600 equiv) and NEt<sub>3</sub> (5 equiv) quantitatively converts to **3** and **4** in a ratio of 0.67:0.33 in 10 min at 23 °C, as determined by <sup>31</sup>P NMR spectroscopy (eq 11). No cationic Ir species can be observed.



The prompt conversion of 1 to monohydride 3 and trihydride 4 in the presence of  $Et_2SiH_2$  by  $Et_3N$  suggests that the silane complex  $(Ir)(H)(H_2SiEt_2)^+$  (2"), produced in situ from 1 and



Scheme 5. Reduction of N<sub>J</sub>N-Dimethyl Benzamide with Different Loadings of Ir Catalyst, Et<sub>2</sub>SiH<sub>2</sub>, and Et<sub>3</sub>NH<sup>+</sup>

 $Et_2SiH_2$ , readily undergoes a deprotonation reaction with NEt<sub>3</sub>, giving 3 and the corresponding ammonium borate salt [ $Et_3NH$ ]-[ $B(C_6F_5)_4$ ].<sup>11</sup> Subsequently, 3 can react with H<sub>2</sub> (evolved from the metal-catalyzed reduction of H<sub>2</sub>O with  $Et_2SiH_2$ ) to form 4 (see Scheme 4).

Role of the Neutral Silyl Iridium Catalysts Monohydride 3 and Trihydride 4. To test the viability of 3 and 4 for initiating catalysis, *N*,*N*-dimethylbenzamide was treated with  $Et_2SiH_2$  at 60 °C in the presence of 1 mol % 3 and 4 (0.9:0.1 ratio). Over the course of 1 h, the amide is quantitatively converted to the hemiaminal ether **B**, the first hydrosilylation product, and a trace of fully reduced *N*,*N*-dimethylbenzylamine. Extending the reaction time to 3 h results in little further conversion to the amine. This result is in sharp contrast to that when 1 initiates reduction of the amide under similar conditions where a single product, *N*, *N*-dimethylbenzylamine, is formed in 1 h. When complex 1 initiates catalysis, the neutral silane complexes 3 and 4 are formed together with 1 equiv of the conjugate acid of the amide (or



Scheme 6. Functional Group Tolerance on Reduction on *N*,*N*-Dimethylbenzamide Catalyzed by 3 and 4 with the Ammonium Borate Salt

amine as reduction proceeds); therefore, we conclude that the presence of this conjugate acid is responsible for conversion of **B** to the amine. To verify this conjecture, we treated the solution of hemiaminal **B** formed from reduction of *N*,*N*-dimethylbenzamide (eq 12a) with 1 mol %  $Et_3NH^+$  salt and observed that amine is quantitatively formed in less than 5 min (eq 12b). These experiments provide strong evidence that the catalytic reduction of amides to amines in these systems takes place in two steps. First the hydrosilylation of the amide to **B** occurs (experiments cited below indicate that the Ir(V) species is the silane complex responsible for this hydrosilylation), followed then by conversion of this ether to the amine catalyzed by the conjugate acid of the amide/amine. A likely intermediate in this second step is the iminium ion formed by acidcatalyzed cleavage of the C-O bond of **B**.



To further probe this second step, reduction of the hemiaminal ether, we have carried out experiments summarized in Scheme 5 employing *N*,*N*-dimethylbenzamide. A nearly pure

sample of hemiaminal B (92%, contaminated with 8% dimethylbenzylamine) in toluene can be prepared by reacting the amide with 3 equiv of Et<sub>2</sub>SiH<sub>2</sub> and a mixture of the iridium silane catalysts 3 + 4 (0.6 mol %) at 60 °C. Using this in situ generated hemiaminal, the second step can be probed. Treating half of this mixture with 0.1 mol % Et<sub>3</sub>NH<sup>+</sup> salt at 23 °C results in conversion of only ca. 2% of the ether to product amine after 27 min (eq 13a), while treatment of the other half with 1.0% Et<sub>3</sub>NH<sup>+</sup> salt results in ca. 54% conversion of ether to product after 24 min (eq 13b). Similarly, using 2.5 mol % 3 + 4 and 1.3 equiv of Et<sub>2</sub>SiH<sub>2</sub>, a 94:6 mixture of **B** and N,N-dimethylbenzylamine was prepared in toluene and the solution divided in half. Treatment of one half with 1.0 mol %  $Et_3NH^+$  and 7.5 equiv of  $Et_2SiH_2$  provided the amine in quantitative yield after 9 min (eq 14a). In contrast, treatment with 1.0 mol % Et<sub>3</sub>NH<sup>+</sup> and 0.8 equiv of Et<sub>2</sub>SiH<sub>2</sub> converted only 36% of the ether to the tertiary amine after 16 min (eq 14b). The results summarized in eqs 15a and 15b indicate the rate of conversion of B to the amine is independent of concentration of iridium catalyst. The qualitative results in eqs 13-15 imply that the rate of conversion of the hemiaminal ether B is dependent on ammonium ion concentration (acid) and Et<sub>2</sub>SiH<sub>2</sub> concentration, indicating that the silane, not the iridium hydride, is the hydride donor in this transformation. A mechanism consistent with these data involves the acid-induced reversible formation of the iminium ion C, followed by Et<sub>2</sub>SiH<sub>2</sub> attack on the iminium ion as summarized in eq 16. Of course, when catalysis is carried out in the presence of acid, the formation of the hemiaminal is turnover limiting and its subsequent conversion to amine is rapid.



Functional Group Tolerance of the Catalyst System Composed of Monohydride 3, Trihydride 4, and Et<sub>3</sub>NH<sup>+</sup>. Once the mixture of 3 and 4 together with [Et<sub>3</sub>NH]- $[B(C_6F_5)_4]$  was found to be effective for the reduction of amides, we employed this catalyst system for reduction of N, N-dimethylbenzamide in the presence of various functionalized molecules to investigate the functional group tolerance and chemoselectivity of the reaction (Scheme 6). The reduction of the amide with Et<sub>2</sub>SiH<sub>2</sub> proceeds smoothly in the presence of stoichiometric amounts of 1-hexene, 3-hexyne, tetrahydrofuran, and acetonitrile without any significant effect on the rate of the conversion or yield (quantitative conversion in 1.5 h at 60 °C). Acetonitrile, 1-hexene, 3-hexyne, and tetrahydrofuran are unreactive under these conditions, indicating excellent chemoselectivity with respect to these functional groups. The presence of octyl bromide appears to slightly retard the rate of reduction, but virtually all of the bromide remains following reduction. Under the reaction conditions, ketone and ester are hydrosilylated in competition with amide reduction. In the presence of 1 molar equiv of acetone or ethyl propionate, dimethylbenzamide is reduced at ca. 2 and 4 times the rate, respectively, at which acetone and ethyl propionate are hydrosilylated.

Equilibrium among 3, 4, and 7 during Catalysis. Recently we reported that the dihydride complex 7 reacts rapidly with  $Et_3SiH$  to generate an equilibrium mixture of 7 and the neutral iridium silyl hydride complex 3' at 23 °C. Under 1 atm of H<sub>2</sub>, equilibrium is established in ca. 1 h and results in a ca. 0.8:1 ratio of 3' to 7 (eq 17).<sup>Sb</sup> These results prompted examination of the reaction of 7 with  $Et_2SiH_2$  in order to explore the equilibration of 3, 4, and 7 and the role these equilibria may play in catalysis.



To gain further insights into the resting states (3 and 4) observed during catalysis, we carried out several reactions of 3, 4, and 7 with  $Et_2SiH_2$ ,  $H_2$ , and  $D_2$  at 23 °C. Addition of  $Et_2SiH_2$  (10 equiv) to a solution of 7 in  $C_6D_6$  results in complete conversion to a mixture of 3 and 4 (0.71:0.29 ratio) in 10 min at 23 °C on the basis of  ${}^{31}P{}^{1}H$  NMR (eq 18a).<sup>12</sup> After 3 h only a small change in the ratio to 0.84:0.16 occurred (eq 18b), suggesting equilibrium



**Figure 1.** <sup>31</sup>P{<sup>1</sup>H} NMR spectra of a mixture of monohydride 3 and trihydride 4 in  $C_6D_6$  at 23 °C (a), under an H<sub>2</sub> atmosphere (b), followed by purging with argon (c).

among 3,  $H_2$ , and 4 had been established (enhancement of 3 with time could be due in part to loss of  $H_2$  from solution).



Exposure of a  $C_6D_6$  solution of 3 and 4 (9:1) (Figure 1a) to 1 atm of H<sub>2</sub> at 23 °C in the presence of Et<sub>2</sub>SiH<sub>2</sub> results in the rapid conversion of 3 to 4 to reach a ratio of 2:3 after 10 min (Figure 1b). Subsequently, purging this solution with argon leads to conversion of 4 back to 3 and, after 5 min, the ratio is ca. 9:1 (Figure 1c). These results clearly indicate that the formation of 4 from 3 is proportional to the concentration of H<sub>2</sub> and that 3 and H<sub>2</sub> are in rapid equilibrium with 4 at 23 °C through addition and elimination of dihydrogen to the Ir center (eqs 19 and 20).

$$3 + 4 \xrightarrow{+ Et_2SiH_2(20 \text{ equiv})} 3 + 4 + Et_2Si(H/D)_2 (19)$$

$$\sim 91\% \sim 9\% \xrightarrow{-0.5 \text{ h, } C_6H_6 + C_7D_8} \sim 34\% \sim 66\% (3 - 7 \text{ equiv})$$



Reaction of the mixture of 3 and 4 (9:1) with  $D_2$  (1 atm) in the presence of  $Et_2SiH_2$  (20 equiv) at 23 °C affords a mixture of 3 and 4

Scheme 7.	Induction	of Formation	of 7 and 5	from a Mixt	ure of 3 and 4
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in a ratio of 0.34:0.66 in 0.5 h (eq 19). Furthermore, the <sup>2</sup>H NMR spectrum of the solution shows that deuterium has been incorporated into the free silane. Judging from the intensity of the <sup>2</sup>H signal at  $\delta$  3.84 relative to an internal standard (toluene-*d*<sub>8</sub>) ca. 3–7 equiv of deuterium (relative to Ir) was exchanged into the silane. This result strongly suggests facile reversible reductive elimination of Et<sub>2</sub>SiH<sub>2</sub> from complex 4 via formation of 7 (eq 20).

To further probe loss of  $Et_2SiH_2$  from 4, two additional experiments were carried out, as summarized in Scheme 7. A 4:6 ratio of 3 to 4 was generated in toluene- $d_8$  under 1 atm of H<sub>2</sub>. Purging of this solution with H<sub>2</sub> at 23 °C over a period of time (0.3 h) resulted in flushing all  $Et_2SiH_2$  from the solution and eventual conversion of both 3 and 4 to tetrahydride 5, no doubt through loss of silane from 4 to form the dihydride 7, followed by reaction with H<sub>2</sub> (path A).<sup>8</sup> A second experiment was carried out, in which the mixture of 3 and 4 was subjected to high vacuum. In this case, 3 was the dominant product with traces of dihydride 7, indicating that H<sub>2</sub> loss from 4 is more rapid than loss of silane (path B).

Catalytic Reduction of Tertiary Amides with  $Et_2SiH_2$  under 1 atm H<sub>2</sub>. Although 3 is the major catalyst resting state under the catalytic conditions investigated above, it seems likely that the minor iridium species present, Ir(V) complex 4, is a much more active  $Et_2SiH^+$  donor and thus the active catalyst in the first step (and the turnover-limiting step of the reduction), the hydrosilylation of the amide. Since 3 and 4 are in rapid equilibrium and the concentration of 4 can be increased under hydrogen, we have investigated the catalysis under an atmosphere of hydrogen. The general conditions we have used are summarized in eq 21. Indeed, carrying out the reaction under hydrogen substantially accelerates the reductions and supports the contention that 4 is the active catalyst.

$$R \xrightarrow{O}_{R'} (3 \text{ equiv}) \xrightarrow{C_6 D_6, 23 \, ^\circ C \text{ or } 60 \, ^\circ C} R \xrightarrow{R'}_{H_2} (21)$$

Table 2 summarizes results of catalysis under  $H_2$ . These data can be compared to data in Table 1 (argon atmosphere)

to qualitatively assess differences in rates of reduction. Reduction of N,N-dimethylisobutylamide under  $H_2$  (1 atm) is complete in only 0.4 h but gives not only the desired amine product (81%) but also a side product, N,N,2-trimethylprop-1-en-1-amine (19%) (entry 1). Entry 2 shows that N,Ndimethylbenzamide can be quantitatively reduced using 1 mol % Ir loading at 23 °C to give the corresponding amine quantitatively in only 0.3 h. This compares with the reduction in Table 1 using 0.5% catalyst loading at 60 °C, which required 1 h for quantitative reduction. A low catalyst loading of only 0.01 mol % in combination with 0.3 mol % of  $[Et_3NH][B(C_6F_5)_4]$  initiates reduction at 60 °C to attain a quantitative conversion in 4 h with formation of the hemiaminal ether and N,N-dimethylbenzylamine in a 0.12:0.88 ratio. Prolonged reaction at 60 °C for 11 h provides conversion of the hemiaminal ether to dimethylbenzylamine as a final product in 98% yield (entry 3). It is noteworthy that ca. 10 000 turnovers have been achieved in 11 h under mild conditions (60 °C, 3 equiv of Et<sub>2</sub>SiH<sub>2</sub>, H<sub>2</sub> (1 atm)). N,N-Diisopropylbenzamide, containing very bulky *i*-Pr substituents, undergoes facile reduction under H<sub>2</sub>, giving diisopropylbenzylamine in quantitative yield in 2.5 h (entry 4). This rate under a  $H_2$  atmosphere sharply contrasts with that observed in the reduction catalyzed by 1 (82% conversion in 54 h at 60 °C). In addition, the efficiency of reduction of this hindered substrate contrasts favorably with that observed in its iron carbonyl catalyzed reduction (59% yield in 24 h at 100 °C).<sup>41</sup> Reduction of N,N-diphenylacetamide is slower than that of N,N-dimethylbenzamide under the same conditions but still faster than that in the catalyst system composed of 1 and  $Et_2SiH_2$  (entry 5). Similar to the case for  $N_1N_2$ dimethylbenzamide, N,N-dibenzylamide derivatives containing benzyl or phenyl substituents on the carbonyl carbon are easily reduced to produce the amines quantitatively in 0.4 h (entries 6 and 7). The amide derivatives containing cyclopropyl and 1-furanyl groups were tested for reduction under H<sub>2</sub>. These substrates yield the amine in 0.2 h in quantitative yields (entries 8 and 9). 1-Benzoylpiperidine is also quantitatively reduced to 1-benzylpiperidine in 0.1 h with Et<sub>2</sub>SiH<sub>2</sub> under H<sub>2</sub> (entry 10). N,N-Dibenzylamide having a 1-naphthyl group on the  $\alpha$ -carbon converts to the corresponding amine

Table 2. Reduction of Tertiary Amides with  $Et_2SiH_2$  Catalyzed by a Mixture of 3 and 4 with Ammonium Borate Salt,  $Et_3NH B(C_6F_5)_{4}$ , under  $H_2$  (1 atm)<sup>*a*</sup>



<sup>*a*</sup> Reaction conditions: 1 mol % **3** + **4** and 1 mol %  $[Et_3NH][B(C_6H_5)_4]$ , 1 atm of H<sub>2</sub>, solvent  $C_6D_6$ , 3 equiv of  $Et_2SiH_2$ , 60 °C. <sup>*b*</sup> Determined by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR. <sup>*c*</sup> Gas evolution observed during the reaction. <sup>*d*</sup> Reaction at 23 °C. <sup>*e*</sup> 0.01 mol % catalyst (**3** + **4**) in combination with 0.3 mol %  $[Et_3NH][B(C_6H_5)_4]$ . <sup>*f*</sup>In a preparation-scale run (1 g), tribenzylamine was isolated as a crystalline product in 90% yield. <sup>*g*</sup> CDCl<sub>3</sub> is added as cosolvent.

to attain 95% conversion in 15 h under a  $H_2$  atmosphere (entry 11), which is more efficient than reduction employing catalyst

1 (Table 1, entry 17) or employing  $Fe_3(CO)_{12}^{41}$  with PMHS as reductant.



Scheme 8. Proposed Catalytic Cycle for the Reduction of Tertiary Amides

#### SUMMARY

Scheme 8 summarizes the proposed catalytic cycle for reduction of tertiary amides on the basis of the mechanistic results described above. The active silvlating agent is the Ir(V) trihydride complex 4. This complex is generated in situ from the cationic acetone complex 1 (see Scheme 4) or, more conveniently, from treatment of (POCOP)IrHCl with tert-butoxide in the presence of  $Et_2SiH_2$  (see eq 8). The concentration of 4 is increased under a hydrogen atmosphere by shifting the equilibrium from Ir(III) silyl hydride 3 toward silyl trihydride 4, as shown in Scheme 8 (see also eq 20). Thus, catalysis is significantly accelerated under H<sub>2</sub>. Silyl complex 4 transfers Et<sub>2</sub>SiH<sup>+</sup> to the amide to yield the oxocarbenium ion A and  $(POCOP)IrH_3^{-}$ . The oxocarbenium ion A is converted to the hemiaminal B by reaction with (POCOP)IrH<sub>3</sub><sup>-</sup>, which is converted to the dihydride 7. The dihydride reenters the catalytic cycle by reaction with Et<sub>2</sub>SiH<sub>2</sub> to regenerate 4. The hemiaminal requires a weak acid (in this case we show  $Et_3NH^+$ ) for further reduction by conversion to the iminium ion C, which is then reduced by Et<sub>2</sub>SiH<sub>2</sub> to yield the amine. The silanol produced from the ionization of the hemiaminal reacts with the (formally) generated Et<sub>2</sub>SiH<sup>+</sup> and the tertiary amine to yield the siloxane and regenerate the ammonium salt Et<sub>3</sub>NH<sup>+</sup>.

As noted, the most effective and easily generated catalyst is prepared by treatment of the (POCOP)IrHCl complex with *tert*butoxide in the presence of  $Et_2SiH_2$  and hydrogen. This system is a remarkably active and long-lived catalyst. Very highly hindered amides can be reduced readily under mild conditions using low catalyst loadings. For example, *N*,*N*-diisopropylbenzamide is quantitatively reduced in 2.5 h at 60 °C using 1 mol % catalyst loading. Catalyst loadings as low as 0.01% have provided quantitative reductions (10 000 turnovers). The catalyst system is compatible with a range of functional groups, including alkenes, internal alkynes, ethers, nitriles, and halides. Primary and secondary amines are not successfully reduced with this catalyst system.

#### EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out using standard Schlenk, high-vacuum, and glovebox techniques. Argon and nitrogen were purified by passing through columns of BASF R3-11 catalyst (Chemalog) and 4 Å molecular sieves. THF was distilled under a nitrogen atmosphere from sodium benzophenone ketyl prior to use. Methylene chloride and toluene were passed through columns of activated alumina<sup>13</sup> and degassed either by freeze-pump-thaw methods or by purging with argon. Benzene, acetone, and acetonitrile were dried with 4 Å molecular sieves and degassed by freeze-pump-thaw methods. Et<sub>3</sub>SiH, Me<sub>2</sub>EtSiH, and Et<sub>2</sub>SiH<sub>2</sub> were dried with LiAlH<sub>4</sub> and vacuum-transferred into a sealed flask. Unless otherwise stated, all of the other substrates for the preparation of amides were purchased from Sigma-Aldrich and were used without purification. Deuterated solvents (CD<sub>2</sub>Cl<sub>2</sub>, C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub>, C<sub>6</sub>D<sub>5</sub>Cl, C<sub>6</sub>D<sub>6</sub>) and pentane were dried with CaH<sub>2</sub> or 4 Å molecular sieves and vacuum-transferred into a sealed flask. NMR spectra were recorded on Bruker spectrometers (DRX-400, AVANCE-400, AMX-300, and DRX-500). <sup>1</sup>H and <sup>13</sup>C NMR spectra were referenced to residual protio solvent peaks. <sup>29</sup>Si chemical shifts were referenced to external Et<sub>3</sub>SiH. Ph<sub>3</sub>C[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>],<sup>14</sup> (POCOP)Ir(H)<sub>2</sub> (7),<sup>8</sup> and  $[(POCOP)Ir(H)(acetone)]^+[B(C_6F_5)_4]^-(1)^{5d}$  were prepared according to published procedures.

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Scheme 9. Neutral Hydrido(silyl)liridium Pincer Complexes



General Procedure for the Preparation of Amides.<sup>41</sup>. The acyl chloride (15.0 mmol) was added in one portion to a solution of the amine (16.5 mmol),  $Et_3N$  (18.75 mmol), and  $CH_2Cl_2$  (30 mL) at 23 °C (eq 22). The reaction mixture was stirred for 1 h at 23 °C and then was diluted with  $CH_2Cl_2$  (45 mL). The solution was transferred to a separatory funnel and was washed two times with 30 mL of 1 N HCl and two times with 30 mL of saturated NaCl solution. The organic layer was dried with  $Na_2SO_4$ , filtered, and concentrated under reduced pressure. All the NMR data for the synthesized amides matched those reported by Beller.<sup>41</sup>

$$R \xrightarrow{O} + R^{1}R^{2}NH \xrightarrow{Et_{3}N} \qquad O \\ CH_{2}Cl_{2}, r.t. \qquad R \xrightarrow{O} R^{1} \qquad (22)$$

For amides in entries 9 and 16 (Table 1): purified by recrystallization from ethanol and methanol, respectively.

For amides in entries 11 and 18 (Table 1): purified via silica gel column chromatography using ethyl acetate/hexane (1:10).

For amides in entries 15, 17, 19, and 20: purified by washing with hexane several times after removing solvents.

General Procedure for the Reduction of Tertiary Amides Catalyzed by Cationic Iridium Acetone Complex 1 with Hydrosilanes. The hydrosilane (1.5 mmol, 3.0 equiv) was added to a solution of 1 (3.3 mg, 0.0025 mmol, 0.5 mol %) in  $C_6D_5Cl$  (0.3 mL) in a medium-walled J. Young NMR tube, and the contents were well shaken. The substrate (0.5 mmol, 1.0 equiv) was then added, and this mixture was allowed to stand at 23 °C or was heated to 60 °C in an oil bath. The progress was followed by NMR spectroscopy. Conversions were determined by monitoring the loss of tertiary amides. Amines as reduction products were identified using <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR dada in comparison to literature data<sup>41</sup> or authentic samples.

In Situ Generation of a Mixture of (POCOP)Ir(H)(SiEt<sub>2</sub>H) (3) and (POCOP)Ir(H)<sub>3</sub>(SiEt<sub>2</sub>H) (4) from (POCOP)Ir(H)CI and NaOtBu in the Presence of Et<sub>2</sub>SiH<sub>2</sub>. Et<sub>2</sub>SiH<sub>2</sub> (26 µL, 0.2 mmol, 10 equiv) in toluene- $d_8$  (0.5 mL) was added to a mixture of (POCOP)Ir(H)(Cl) (12.6 mg, 0.02 mmol, 1 equiv) and NaOtBu (2.4 mg, 0.024 mmol, 1.2 equiv) in a medium-walled J. Young NMR tube, and this mixture was heated to 60 °C for 4 h, resulting in a mixture of 3 and 4 in a ratio of ca. 0.85:0.15. Labeling for 3 and 4 is given in Scheme 9. Data for 3 are as follows. <sup>1</sup>H NMR (toluene- $d_8$ , 400 MHz, 23 °C):  $\delta$  7.02 (t, 1H, b,  ${}^{3}J_{H-H}$  = 7.6 Hz), 6.86 (d, 2H, a,  ${}^{3}J_{H-H}$  = 7.6 Hz), 5.54 (br s, 1H, SiH), 1.39 (t, 36H, 4 × t-Bu), 1.30–1.33 (m, 10 H, SiEt, overlap with *t*Bu), -16.87 (q, 1H, Ir-H,  ${}^{2}J_{P-H} = 6.0$  Hz,  ${}^{3}J_{H-SiH} = 6.0$  Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (toluene- $d_8$ , 100.6 MHz, 23 °C):  $\delta$  13.15 (SiEt<sub>2</sub>H), 11.98 (SiEt<sub>2</sub>H). <sup>31</sup>P{<sup>1</sup>H} NMR (toluene- $d_8$ , 162 MHz, 23 °C):  $\delta$  190.3.  $^{29}\text{Si}\{^1\text{H}\}$  DEPT 45 (toluene- $d_8$ , 79 MHz, 23 °C):  $\delta$  –13.3. Data for 4 are as follows. <sup>1</sup>H NMR (toluene- $d_8$ , 400 MHz, 23 °C):  $\delta$  6.90 (t, 1H, b',  ${}^{3}J_{H-H}$  = 7.5 Hz), 6.72 (d, 2H, a',  ${}^{3}J_{H-H}$  = 7.5 Hz), 5.40 (br s, 1H, Si*H*), 1.31 (t, 36H, 4 × *t*Bu), 1.30–1.33 (m, 10 H, Si*Et*, overlap with *t*Bu), -8.90 (t, 3H, Ir-H,  ${}^{2}J_{P-H} = 10.5$  Hz).  ${}^{13}C{}^{1}H$  NMR (toluene- $d_{8}$ , 100.6 MHz, 23 °C):  $\delta$  14.03 (SiEt<sub>2</sub>H), 12.16 (SiEt<sub>2</sub>H). <sup>31</sup>P{<sup>1</sup>H} NMR (toluene- $d_{8}$ , 162 MHz, 23 °C):  $\delta$  171.4. <sup>29</sup>Si{<sup>1</sup>H} DEPT 45 (toluene- $d_{8}$ , 79 MHz, 23 °C): δ –20.62.

Determination of the Equilibrium Constant,  $K_{eqr}$  Relating Cationic Iridium Silane Complex (2 or 2') and Cationic Iridium Amine Complex (eqs 9 and 10).<sup>5d</sup>. The equilibrium constants were determined by NMR spectroscopy. The concentration ratio of 2' to the amine complex [(POCOP)Ir(H)(NEt<sub>3</sub>)]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup> was determined by <sup>31</sup>P NMR, and the concentration ratio of Me<sub>2</sub>EtSiH to Et<sub>3</sub>N was determined by <sup>1</sup>H NMR.  $K_{eq}$  was calculated to be ca. 0.1. The equilibrium constant between 2 and the cationic iridium amine complex was not obtainable by NMR spectroscopy, due to the very low equilibrium concentration of 2.

General Procedure for Reduction of *N*,*N*-Dimethylbenzamide Catalyzed by a Mixture of Monohydride 3 and Trihydride 4 with Et<sub>2</sub>SiH<sub>2</sub> in the Presence of [Et<sub>3</sub>NH][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. A stock solution of complexes 3 and 4 (33 mM, ratio ca. 9:1) was prepared in toluene- $d_8$  in a glovebox. An aliquot (75 µL, 0.5 mol % Ir) of this stock solution was then added to Et<sub>2</sub>SiH<sub>2</sub> (1.5 mmol, 0.19 mL, 3.0 equiv) in toluene- $d_8$  (0.3 mL) in a medium-walled J. Young NMR tube. The substrate (0.5 mmol, 75 mg, 1.0 equiv) was then added together with [Et<sub>3</sub>NH][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (0.005 mmol, 3.9 mg, 1.0 mol %), and the reaction mixture was heated to 60 °C for 1 h in an oil bath. The progress was followed by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy. Conversion was determined by monitoring the loss of *N*,*N*-dimethylbenzamide.

Reduction of *N*,*N*-Dimethylbenzamide with Et<sub>2</sub>SiH<sub>2</sub> Using Different Loadings of Catalyst (3 + 4), Followed by Addition of [Et<sub>3</sub>NH][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]. A stock solution of complexes 3 and 4 (100 mM, ratio ca. 9:1) was prepared in toluene- $d_8$  in a glovebox. Two aliquots (90  $\mu$ L, 3.0 mol % Ir; 10  $\mu$ L, 0.3 mol % Ir) of this stock solution were then added to Et<sub>2</sub>SiH<sub>2</sub> (0.9 mmol, 0.12 mL, 3.0 equiv) in toluene- $d_8$  (0.3 mL) in two medium-walled J. Young NMR tubes, respectively. The substrate (0.3 mmol, 45 mg, 1.0 equiv) was then added to the two NMR tubes, and the reaction mixtures were heated to 60 °C for 1–2 h in an oil bath. Following the hydrosilylation, [Et<sub>3</sub>NH][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (0.004 mmol, 3.0 mg, 2.5 mol %) was added to each NMR tube, and the two mixtures were allowed to react at 23 °C for 10 min. The progress was followed by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy. Conversion was determined by monitoring the loss of *N*,*N*-dimethylbenzamide.

Typical Competition Experiments To Determine Relative Reactivities of *N*,*N*-Dimethylbenzamide and 1-Hexene, 3-Hexyne, THF, MeCN, Acetone, or Ethyl Propionate by NMR. Et<sub>2</sub>SiH<sub>2</sub> (1.5 mmol, 0.19 mL, 3.0 equiv) was added to a solution of 3 and 4 (0.004 mmol, 0.8 mol %) in toluene- $d_8$  (0.3 mL) in a medium-walled J. Young NMR tube, and the contents were well shaken. *N*,*N*-Dimethylbenzamide (75 mg, 0.5 mmol, 1.0 equiv) and reactive compounds containing 1-hexene, 3-hexyne, THF, MeCN, acetone, or ethyl propionate (0.5 mmol, 1.0 equiv) were then added together with [Et<sub>3</sub>NH][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (0.005 mmol, 3.9 mg, 1.0 mol%) and mesitylene (14  $\mu$ L, 0.1 mmol, 25 equiv) as an internal standard. The reaction mixture was heated to 60 °C for 1.5 h in an oil bath, and the progress was followed by NMR spectroscopy.

In Situ Generation of a Mixture of (POCOP)Ir(H)(SiEt<sub>2</sub>H) (3) and (POCOP)Ir(H)<sub>3</sub>(SiEt<sub>2</sub>H) (4) from (POCOP)Ir(H)<sub>2</sub> (7) and Et<sub>2</sub>SiH<sub>2</sub>. Et<sub>2</sub>SiH<sub>2</sub> (13  $\mu$ L, 0.1 mmol, 10 equiv) in toluene- $d_8$  (0.5 mL) was added to (POCOP)Ir(H)<sub>2</sub> (5.9 mg, 0.01 mmol, 1 equiv) in a medium-walled J. Young NMR tube, and this mixture was allowed to stand at 23 °C for 10 min, resulting in a mixture of 3 and 4 in a ratio of ca. 071:0.29 with H<sub>2</sub> evolution.

In Situ Generation of a Mixture of 3 and 4 from 7 and Et<sub>2</sub>SiH<sub>2</sub>, Followed by Exposure to H<sub>2</sub>. Et<sub>2</sub>SiH<sub>2</sub> (13  $\mu$ L, 0.1 mmol, 10 equiv) in toluene- $d_8$  (0.5 mL) was added to 7 (5.9 mg, 0.01 mmol, 1 equiv) in a medium-walled J. Young NMR tube. Subsequently, this mixture was allowed to stand at 23 °C for 10 min, followed by degassing by freeze-pump-thaw methods. H<sub>2</sub> or D<sub>2</sub> (1 atm) was finally vacuum-transferred to the degassed J. Young NMR tube.

The change in the ratio of **3** to **4** was monitored by  ${}^{1}H$  and  ${}^{31}P{}^{1}H$ } NMR spectroscopy.

In Situ Generation of 5 from a Mixture of 3 and 4 (Method A). Et<sub>2</sub>SiH<sub>2</sub> (13  $\mu$ L, 0.1 mmol, 10 equiv) in toluene- $d_8$  (0.5 mL) was added to 7 (5.9 mg, 0.01 mmol, 1 equiv) in a medium-walled NMR tube with a screw cap. Subsequently, this mixture was allowed to stand at 23 °C for 10 min, followed by introducing H<sub>2</sub> via brief H<sub>2</sub> purging through the solution. The solution was stirred for 1 h at 23 °C to give a mixture of 3 and 4 in a ratio of ca. 0.4:0.6. This solution containing 3 and 4 was purged with H<sub>2</sub> for 20 min at 23 °C, during which time excess Et<sub>2</sub>SiH<sub>2</sub> was removed, to afford mainly the iridium tetrahydride complex 5 (ca. 94%).

In Situ Generation of 7 from a Mixture of Monohydride 3 and Trihydride 4 (Method B).  $Et_2SiH_2$  (13  $\mu$ L, 0.1 mmol, 10 equiv) in toluene- $d_8$  (0.5 mL) was added to 7 (5.9 mg, 0.01 mmol, 1 equiv) in a medium-walled J. Young NMR tube. Subsequently, this mixture was allowed to stand at 23 °C for 10 min, followed by degassing by freeze-pump-thaw methods.  $H_2$  (1 atm) was vacuum-transferred to the degassed J. Young NMR tube. The solution was stirred for 1 h at 23 °C to give a mixture of 3 and 4 in a ratio of ca. 0.4:0.6. This solution containing 3 and 4 was subjected to high vacuum, resulting in a mixture of 7 and 3 in a ratio of 0.06:0.91.

General Procedure for the Reduction of Tertiary Amides Catalyzed by a Mixture of Monohydride 3 and Trihydride 4 with Et<sub>2</sub>SiH<sub>2</sub> in the Presence of [Et<sub>3</sub>NH][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] under H<sub>2</sub> (1 atm). Et<sub>2</sub>SiH<sub>2</sub> (1.5 mmol, 0.19 mL, 3.0 equiv) was added to a solution of 3 and 4 (0.005 mmol, 1.0 mol %) in C<sub>6</sub>D<sub>6</sub> (0.3 mL) in a medium-walled J. Young NMR tube, and the contents were well shaken. The substrate (0.5 mmol, 1.0 equiv) was then added together with [Et<sub>3</sub>NH][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (0.005 mmol, 3.9 mg, 1.0 mol %), followed by degassing by freeze– pump–thaw methods. Finally, 1 atm of H<sub>2</sub> was vacuum-transferred to the degassed J. Young NMR tube. The reactions were then allowed to stand at 23 °C or heated to 60 °C in an oil bath. The reaction progress was followed by NMR spectroscopy. Conversions were determined by monitoring the loss of tertiary amides.

General Procedure for a Large-Scale Reduction of *N*,*N*-Dibenzylbenzamide.  $Et_2SiH_2$  (10.0 mmol, 1.30 mL, 3.0 equiv) was added to a solution of 3 and 4 (0.01 mmol, 0.2 mol %) in toluene- $d_8$  (3.0 mL) in a 25 mL flame-dried Schlenk tube containing a stir bar. The substrate (3.32 mmol, 1.0 g, 1.0 equiv) was then added together with  $Et_2OHB(C_6F_5)_4$  (0.032 mmol, 24 mg, 1.0 mol %), followed by purging  $H_2$  (1 atm) through the stirred solution for 1 min. The reaction mixture was then heated to 60 °C overnight in an oil bath. Completion of the reaction was confirmed by <sup>1</sup>H NMR spectroscopy. The volatiles were removed under reduced pressure. The residue was dissolved in pentane and washed three times with 10 mL of NaOH (1 M) solution. The organic layer was concentrated in vacuo to give a crude product. The crude product was purified by recrystallization from ethanol to yield 0.86 g of tribenzylamine as a white solid (90%).

**NMR Spectroscopic Data of Amine Products in Table 1.**<sup>41</sup> Data for *N*,*N*-dimethylisobutylamine (entry 1): <sup>1</sup>H NMR (C<sub>6</sub>D<sub>5</sub>Cl, 400 MHz, 23 °C)  $\delta$  2.30 (s, 6H), 2.11 (d, *J* = 7.6 Hz, 2H), 1.85 (septet, *J* = 6.8 Hz, 1H), 1.07 (d, *J* = 6.4 Hz, 6H); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>5</sub>Cl, 100.6 MHz, 23 °C)  $\delta$  68.41, 45.68, 26.46, 20.73.

Data for N,N,2-trimethylprop-1-en-1-amine as a side product in entry 1 (Table 2): <sup>1</sup>H NMR ( $C_6D_6$ , 400 MHz, 23 °C):  $\delta$  5.38 (s, 1H), 2.39 (s, 6H), 1.79 (s, 3H), 1.66 (s, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR ( $C_6D_6$ , 100.6 MHz, 23 °C)  $\delta$  137.3, 121.0, 45.0, 21.9, 16.9.

Data for *N*,*N*-dimethylbenzylamine (entry 4): <sup>1</sup>H NMR ( $C_6D_5Cl$ , 400 MHz, 23 °C)  $\delta$  7.49–7.35 (m, SH, overlap with solvent peaks), 3.53 (s, 2H), 2.35 (s, 6H); <sup>13</sup>C{<sup>1</sup>H} NMR ( $C_6D_5Cl$ , 100.6 MHz, 23 °C)  $\delta$  139.70, 128.82, 128.12, 126.85, 64.43, 45.22.

Data for 1-((dimethylsilyl)oxy)-*N*,*N*-dimethyl-1-phenylmethanamine as a product of first hydrosilylation: <sup>1</sup>H NMR ( $C_6D_6$ , 400 MHz, 23 °C)  $\delta$  7.57–7.28 (m, 5H, overlap with solvent peaks), 5.51 (s, 1H), 4.74 (m, 1H), 2.31 (s, 6H);  ${}^{13}C{}^{1}H$  NMR (C<sub>6</sub>D<sub>6</sub>, 100.6 MHz, 23 °C)  $\delta$  141.82, 127.6, 127.2, 126.9, 91.3, 38.8, 5.82, 5.37.

Data for *N*,*N*-diisopropylbenzylamine (entry 7): <sup>1</sup>H NMR ( $C_6D_5Cl$ , 400 MHz, 23 °C)  $\delta$  7.50–7.28 (m, 5H, overlap with solvent peaks), 3.63 (s, 2H), 3.00 (septet, *J* = 6.5 Hz, 2H), 1.11 (d, 12H, overlap with excess Et<sub>2</sub>SiH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR ( $C_6D_5Cl$ , 100.6 MHz, 23 °C)  $\delta$  139.81, 128.42, 128.22, 126.33, 49.05, 47.82, 20.72.

Data for *N*,*N*-diphenylethylamine (entry 8): <sup>1</sup>H NMR (C<sub>6</sub>D<sub>5</sub>Cl, 400 MHz, 23 °C)  $\delta$  7.50–7.10 (m, 10H, overlap with solvent peaks), 3.84 (q, *J* = 6.8 Hz, 2H), 1.31 (t, 3H, overlap with excess Et<sub>2</sub>SiH<sub>2</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>5</sub>Cl, 100.6 MHz, 23 °C)  $\delta$  147.87, 129.28, 121.14, 120.8, 46.27, 12.50.

Data for N,N-diphenylbenzylamine and N,N-diphenyldiethylsilylamine (entry 9): <sup>1</sup>H NMR (C<sub>6</sub>D<sub>5</sub>Cl, 400 MHz, 23 °C, selected data)  $\delta$  5.06 (m, 1H), 4.93 (s, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>5</sub>Cl, 100.6 MHz, 23 °C, selected data)  $\delta$  56.33, 41.57.

Data for 1-methylpiperidine (entry 10): <sup>1</sup>H NMR ( $C_6D_5Cl$ , 400 MHz, 23 °C)  $\delta$  2.41 (m, 4H), 2.32 (br s, 3H), 1.71 (m, 4H), 1.52 (br s, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR ( $C_6D_5Cl$ , 100.6 MHz, 23 °C)  $\delta$  56.61, 46.88, 26.23, 24.15.

Data for 1-benzylpiperidine (entry 11): <sup>1</sup>H NMR ( $C_6D_5Cl$ , 400 MHz, 23 °C)  $\delta$  7.50–7.31 (m, 5H, overlap with solvent peaks), 3.56 (s, 2H), 2.50 (br s, 4H), 1.71 (m, 4H), 1.58 (br s, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR ( $C_6D_5Cl$ , 100.6 MHz, 23 °C)  $\delta$  139.49, 129.26, 128.19, 126.71, 63.93, 54.66, 26.33, 24.74.

Data for 1-(1-(ethyldimethylsilyl)oxy)-2,2,2-trifluoroethyl)piperidine (entry 12): <sup>1</sup>H NMR ( $C_6D_5$ Cl, 400 MHz, 23 °C)  $\delta$  4.58 (q, *J* = 3.5 Hz, 1H), 2.89 (t, *J* = 5.2 Hz, 4H), 1.70–1.52 (m, 6H), 1.18 (m, O-SiMe<sub>2</sub>Et, overlap with excess Me<sub>2</sub>EtSiH), 0.76 (m, O-SiMe<sub>2</sub>Et, overlap with excess Me<sub>2</sub>EtSiH); <sup>13</sup>C{<sup>1</sup>H} NMR ( $C_6D_5$ Cl, 100.6 MHz, 23 °C)  $\delta$  122.84 (q, *J* = 285.7 Hz, overlap with solvent peaks), 86.39 (q, *J* = 32.1 Hz), 48.74, 26.46, 24.79, 8.49, 6.57, -2.61 (tentative).

Data for 1-methylpyrrolidine (entry 13): <sup>1</sup>H NMR ( $C_6D_5Cl$ , 400 MHz, 23 °C)  $\delta$  2.40 (br s, 4H), 2.31 (s, 3H), 1.71 (m, 4H); <sup>13</sup>C{<sup>1</sup>H} NMR ( $C_6D_5Cl$ , 100.6 MHz, 23 °C)  $\delta$  56.16, 41.86, 24.18.

Data for 1-benzylpiperidine (entry 14): <sup>1</sup>H NMR ( $C_6D_5Cl$ , 400 MHz, 23 °C)  $\delta$  7.40–7.22 (m, 5H, overlap with solvent peaks), 3.44 (s, 2H), 2.36 (m, 4H), 1.60–1.47 (m, 6H; <sup>13</sup>C{<sup>1</sup>H} NMR ( $C_6D_5Cl$ , 100.6 MHz, 23 °C)  $\delta$  139.45, 128.87, 128.13, 127.56, 63.85, 54.57, 26.25, 24.67.

Data for *N*,*N*-dibenzyl-3-phenylpropan-1-amine (entry 15): <sup>1</sup>H NMR ( $C_6D_5$ Cl, 400 MHz, 23 °C)  $\delta$  7.45–7.06 (m, 15H, overlap with solvent peaks), 3.55 (s, 4H), 2.58 (t, *J* = 7.5 Hz, 2H), 2.49 (t, *J* = 7.0 Hz, 2H), 1.82 (t, *J* = 7.0 Hz, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR ( $C_6D_5$ Cl, 100.6 MHz, 23 °C)  $\delta$  142.44, 139.96, 128.85, 128.40, 128.21, 128.14, 126.82, 125.75, 58.51, 52.95, 33.57, 29.27.

Data for tribenzylamine (entry 16): <sup>1</sup>H NMR ( $C_6D_5Cl$ , 400 MHz, 23 °C)  $\delta$  7.48–7.22 (m, 15H, overlap with solvent peaks), 3.55 (s, 6H); <sup>13</sup>C{<sup>1</sup>H} NMR ( $C_6D_5Cl$ , 100.6 MHz, 23 °C)  $\delta$  139.67, 128.89, 128.21, 126.88, 58.04.

Data for hemiaminal ether (7%) (entry 16): <sup>1</sup>H NMR ( $C_6D_5Cl$ , 400 MHz, 23 °C, selected data)  $\delta$  5.72 (s, 1H), 4.79 (m, 1H), 3.96–3.74 (m, 4H); <sup>13</sup>C{<sup>1</sup>H} NMR ( $C_6D_5Cl$ , 100.6 MHz, 23 °C, selected data)  $\delta$  86.08, 52.21.

Data for *N*,*N*-dibenzyl-1-(naphthalene-1-yl)methanamine (entry 17): <sup>1</sup>H NMR ( $C_6D_5$ Cl, 400 MHz, 23 °C)  $\delta$  8.19–7.24 (m, 17H, overlap with solvent peaks), 3.97 (s, 2H), 3.58 (s, 4H); <sup>13</sup>C{<sup>1</sup>H} NMR ( $C_6D_5$ Cl, 100.6 MHz, 23 °C, selected data)  $\delta$  58.67, 56.95.

Data for *N*,*N*-dibenzyl-1-cyclopropylmethanamine (entry 18): <sup>1</sup>H NMR (C<sub>6</sub>D<sub>5</sub>Cl, 400 MHz, 23 °C)  $\delta$  7.48–7.24 (m, 10H, overlap with solvent peaks), 3.82 (s, 4H), 2.51 (d, *J* = 6.4 Hz, 2H), 1.08 (br s, 1H), 0.61 (d, *J* = 7.2 Hz, 2H), 0.19 (br s, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>5</sub>Cl, 100.6 MHz, 23 °C)  $\delta$  140.43, 128.95, 128.01, 126.86, 58.50, 58.46, 8.72, 4.15. Data for *N*,*N*-dibenzyl-1-(furan-2-yl)methanamine (entry 19): <sup>1</sup>H NMR ( $C_6D_5Cl$ , 400 MHz, 23 °C)  $\delta$  7.64–7.39 (m, 11H, overlap with solvent peaks), 6.45 (s, 1H), 6.32 (s, 1H), 3.77 (s, 6H); <sup>13</sup>C{<sup>1</sup>H} NMR ( $C_6D_5Cl$ , 100.6 MHz, 23 °C)  $\delta$  152.94, 141.77, 139.70, 128.35, 128.25, 127.04, 110.17, 108.63, 57.79, 49.22.

Data for (*E*)-1-(4-(phenyldiazenyl)benzyl)piperidine (entry 20): <sup>1</sup>H NMR ( $C_6D_6$ , 400 MHz, 23 °C)  $\delta$  8.10–8.07 (m, 4H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.33–7.22 (m, 3H, overlap with a solvent peak), 3.39 (s, 2H), 2.35 (br s, 4H), 1.57 (q, *J* = 5.5 Hz, 4H), 1.42 (br s, 2H); <sup>13</sup>C{<sup>1</sup>H} NMR ( $C_6D_6$ , 100.6 MHz, 23 °C)  $\delta$  153.0, 152.0, 143.0, 130.6, 129.3, 128.9, 123.0, 122.9, 63.4, 54.6, 26.2, 24.5.

## ASSOCIATED CONTENT

**Supporting Information**. Figures giving variable-temperature <sup>1</sup>H NMR (hydride region) spectra of a mixture of **3** and **4** and product <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### ACKNOWLEDGMENT

We thank the National Science Foundation (No. CHE 1010170) for support of this work.

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(6) The cationic amine complex is quantitatively formed in situ within 5 min at 23 °C by reaction of 1 with Et<sub>3</sub>SiH, followed by adding NEt<sub>3</sub>. The <sup>31</sup>P shift ( $\delta$  175.2) for this complex is very close to that of the cationic iridium complex coordinated with the amide ( $\delta$  176.5) and with C<sub>6</sub>D<sub>5</sub>Cl ( $\delta$  177.0).<sup>5d</sup>

(7)  $HEt_2SiOtBu$  as a result of the reduction of HOtBu with  $Et_2SiH_2$  has been observed in the reaction mixture by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy.

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(10) Another possible structure for 4 is an Ir(III) species containing an  $\eta^2$ -H<sub>2</sub> ligand. This seems less likely in that the  $\eta^2$ -silane would be a better  $\sigma$  donor than H<sub>2</sub>. Nevertheless, we have prepared a partially deuterated isotopomer of 4 (4-d<sub>2</sub>) and find no measurable H–D coupling in the <sup>1</sup>H NMR spectrum, ruling out  $\eta^2$ -H<sub>2</sub> bonding.

(11) This salt can be synthesized by mixing  $(Et_2O)HB(C_6F_5)_4$  and  $Et_3N$  (20 equiv) in toluene at 22 °C, followed by removing volatiles in vacuo to give a white powder.

(12) The reaction of 7 with  $Et_2SiH_2$  in a ratio of 1:10 at -70 °C quantitatively yields the mixture of 3 and 4 in 10 min.

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