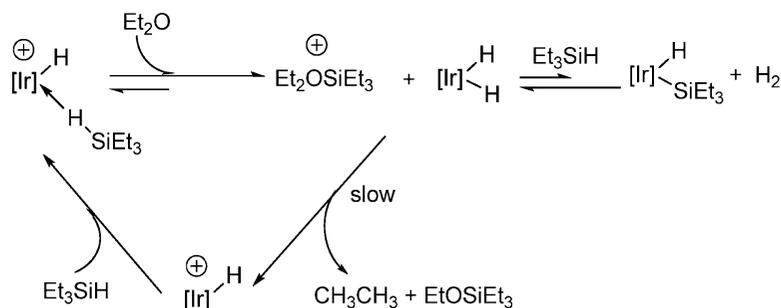


## Scope and Mechanism of the Iridium-Catalyzed Cleavage of Alkyl Ethers with Triethylsilane

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## Scope and Mechanism of the Iridium-Catalyzed Cleavage of Alkyl Ethers with Triethylsilane

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**Abstract:** The cationic iridium pincer complex  $[(\text{POCOP})\text{Ir}(\text{H})(\text{acetone})]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  (**1**, POCOP = 2,6-[OP(*t*Bu)<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) was found to be a highly active catalyst for the room-temperature cleavage and reduction of a wide variety of unactivated alkyl ethers including primary, secondary, and tertiary alkyl ethers as well as aryl alkyl ethers by triethylsilane. Mechanistic studies have revealed the full details of the catalytic cycle with the catalyst resting state(s) depending on the basicity of the alkyl ether. During the catalytic reduction of diethyl ether, cationic iridium silane complex,  $[(\text{POCOP})\text{Ir}(\text{H})(\eta^1\text{-Et}_3\text{SiH})]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  (**3**), and Et<sub>2</sub>O are in rapid equilibrium with neutral dihydride, (POCOP)Ir(H)<sub>2</sub> (**5**) and diethyl(triethylsilyl)oxonium ion,  $[\text{Et}_3\text{SiOEt}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  (**7**), with **5** + **7** strongly favored. Species **7** has been isolated from the reaction mixture and fully characterized. The turnover-limiting step in this cycle is the reduction of **7** by the neutral dihydride **5**. The relative rates of reduction of **7** by dihydride **5** and Et<sub>3</sub>SiH were determined to be ~30,000:1. In the cleavage of the less basic ethers anisole and EtOSiEt<sub>3</sub>, the cationic iridium silane complex, **3**, was found to be the catalyst resting state. The hydride reduction of the intermediate oxonium ion EtO(SiEt<sub>3</sub>)<sub>2</sub><sup>+</sup>, **9**, occurs via attack by Et<sub>3</sub>SiH. In the case of anisole, the intermediate PhMeOSiEt<sub>3</sub><sup>+</sup>, **10**, is reduced by **5** and/or Et<sub>3</sub>SiH.

### 1. Introduction

Heterolytic activation of H<sub>2</sub><sup>1</sup> by several classes of organo-metallic systems has resulted in catalysts which can perform ionic hydrogenations of aldehydes and ketones.<sup>2</sup> The basic catalytic mechanism, termed ionic hydrogenation, involves transfer of H<sup>+</sup> and H<sup>-</sup> equivalents from the catalyst to the carbonyl group to generate the product alcohol followed by reaction of H<sub>2</sub> with the metal complex to regenerate the active catalyst and close the cycle.<sup>2</sup> Similar chemistry has been reported for reduction of iminium ions to amines.<sup>3</sup> Stephan has recently described phosphinoboranes (termed “frustrated” Lewis pairs, FLPs) which heterolytically activate hydrogen to produce phosphonium borate species which perform ionic hydrogenation of imines.<sup>4</sup>

Related hydrosilation chemistry has been reported.<sup>5,6</sup> Mechanistic studies by Piers<sup>5b</sup> have shown that hydrosilation of carbonyl functionalities catalyzed by (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>B<sup>5a</sup> proceeds by activation of the silane by (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>B and transfer of R<sub>3</sub>Si<sup>+</sup> to oxygen to produce R<sub>2</sub>C=OSiR<sub>3</sub><sup>+</sup> and H(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>B<sup>-</sup>. The catalytic cycle is closed by hydride reduction of R<sub>2</sub>C=OSiR<sub>3</sub><sup>+</sup>. Hydrosi-

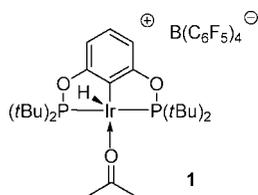
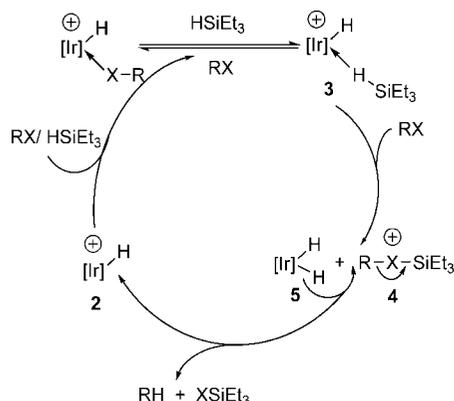
lation of imines,<sup>5d</sup> enones, and silyl enol ethers<sup>5e</sup> and olefins<sup>5f</sup> is reported to occur by a similar mechanism.

The reduction of C–O single bonds<sup>7</sup> has also been achieved catalytically using the (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>B/silane system. Gevorgyan and Yamamoto reported that using Et<sub>3</sub>SiH as reductant certain alcohols could be converted to alkanes via initial formation and reduction of triethylsilyl alkyl ethers.<sup>8</sup> Furthermore, alkyl ethers could be reduced to silyl alkyl ethers. Extending this work, McRae demonstrated reduction of ketones and aldehydes as well as primary, secondary, and tertiary alcohols to alkanes using either diethylsilane or butylsilane in combination with (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>B.<sup>9</sup> Mechanistic studies of the reduction of alkyl silyl ethers by Ph<sub>2</sub>MeSiH/(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>B have been reported.<sup>10</sup>

- (1) (a) Kubas, G. J. *Metal Dihydrogen and σ-Bond Complexes*; Kluwer Academic/Plenum Publishers: New York, 2001. (b) Kubas, G. J. *Adv. Inorg. Chem.* **2004**, *56*, 127. (c) Kubas, G. J. *Chem. Rev.* **2007**, *107*, 4152.
- (2) (a) Bullock, R. M. *Chem. Eur. J.* **2004**, *10*, 2366. (b) Bullock, R. M. In *Handbook of Homogeneous Hydrogenation* de Vries, J. G., Elsevier, C. J., Eds.; Wiley-VCH: Weinheim, 2007; Chapter 7.
- (3) (a) Guan, H.; Iimura, M.; Magee, M. P.; Norton, J. R.; Zhu, G. *J. Am. Chem. Soc.* **2005**, *127*, 7805. (b) Magee, M. P.; Norton, J. R. *J. Am. Chem. Soc.* **2001**, *123*, 1778. (c) Guan, H.; Saddington, S. A.; Shaw, A. P.; Norton, J. R. *Organometallics* **2005**, *24*, 6358. (d) Guan, H.; Iimura, M.; Magee, M. P.; Norton, J. R.; Janak, K. E. *Organometallics* **2003**, *22*, 4084.

- (4) (a) Stephan, D. W. *Org. Biomol. Chem.* **2008**, *6*, 1535. (b) Kenward, A. L.; Piers, W. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 38. (c) Welch, G. C.; Stephan, D. W. *J. Am. Chem. Soc.* **2007**, *129*, 1880. (d) Spies, P.; Erker, G.; Kehr, G.; Bergander, K.; Fröhlich, R.; Grimme, S.; Stephan, D. W. *Chem. Commun.* **2007**, 5072. (e) Chase, P. A.; Welch, G. C.; Jurca, T.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2007**, *49*, 8050. (f) Chase, P. A.; Jurca, T.; Stephan, D. W. *Chem. Commun.* **2008**, 1701. (g) Welch, G. C.; Cabrera, L.; Chase, P. A.; Hollink, E.; Masuda, J. D.; Wei, P.; Stephan, D. W. *Dalton Trans.* **2007**, 3407. (h) Welch, G. C.; Juan, R. R. S.; Masuda, J. D.; Stephan, D. W. *Science* **2006**, *314*, 1124.
- (5) (a) Piers, W. E. *Adv. Organomet. Chem.* **2005**, *52*, 1. (b) Parks, D. J.; Blackwell, J. M.; Piers, W. E. *J. Org. Chem.* **2000**, *65*, 3090. (c) Parks, D. J.; Piers, W. E. *J. Am. Chem. Soc.* **1996**, *118*, 9440. (d) Blackwell, J. M.; Sonmor, E. R.; Scoccitti, T.; Piers, W. E. *Org. Lett.* **2000**, *2*, 3921. (e) Blackwell, J. M.; Morrison, D. J.; Piers, W. E. *Tetrahedron* **2002**, *58*, 8247. (f) Rubin, M.; Schwier, T.; Gevorgyan, V. *J. Org. Chem.* **2002**, *67*, 1936.
- (6) (a) Du, G.; Fanwick, P. E.; Abu-Omar, M. M. *J. Am. Chem. Soc.* **2007**, *129*, 5180. (b) Dioumaev, V. K.; Bullock, R. M. *Nature* **2003**, *424*, 530.

## Chart 1. Cationic Iridium Pincer Catalyst 1

Scheme 1. Proposed Catalytic Cycle for Iridium-Catalyzed Reduction of Alkyl Halides by Triethylsilane<sup>11</sup>

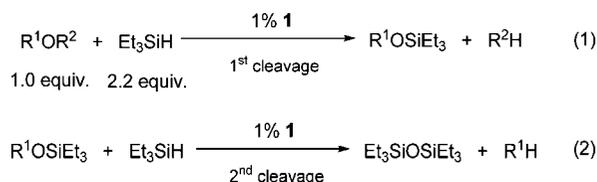
We have discovered that the highly active cationic iridium pincer complex **1** (Chart 1) catalyzes the reduction by triethylsilane of primary, secondary, and tertiary chlorides, bromides, and iodides as well as certain fluorides.<sup>11</sup> In-depth mechanistic studies have been carried out which have revealed a unique catalytic cycle (Scheme 1). The electrophilic iridium hydride complex **2** binds and activates the silane to form **3**. This complex transfers  $\text{Et}_3\text{Si}^+$  to the halide, forming a bridged halonium ion **4** which is rapidly reduced by the iridium dihydride **5** which remains following the silyl transfer. This step regenerates the

cationic iridium hydride complex and closes the catalytic cycle. The key Ir(silane) intermediate **3** has been isolated and fully characterized by NMR spectroscopy and X-ray crystallography, which shows it to be an unprecedented cationic transition metal  $\eta^1$ -silane complex.<sup>12</sup>

In considering application of this chemistry to other organic functional groups, we have been particularly drawn to the cleavage and reduction of alkyl ethers due to the potential synthetic applications of this reaction. Herein we report the use of cationic iridium pincer catalysts for the room-temperature cleavage and reduction of a broad range of alkyl ethers with triethylsilane, as well as mechanistic details of these novel catalytic transformations including identification of catalyst resting states and *isolation* and spectroscopic and structural characterization of a key intermediate, the diethyl(triethylsilyl)-oxonium ion, in the reduction of diethyl ether.

## 2. Results and Discussion

**2.1. Cleavage of Alkyl Ethers with  $\text{Et}_3\text{SiH}$  Catalyzed by Iridium Complex 1.** Alkyl ethers are readily cleaved with  $\text{Et}_3\text{SiH}$  in the presence of 1 mol % of iridium complex **1** at room temperature to yield alkyl triethylsilyl ethers and alkane (eq 1). In some cases cleavage of the silyl ether can be achieved to yield hexaethyldisiloxane and a second equivalent of alkane (eq 2).



Dichlorobenzene is generally used as solvent; however, reactions in chlorobenzene, fluorobenzene, or neat alkyl ether<sup>13</sup> also proved successful. Results of typical reactions are illustrated in Table 1. Conversions are determined by NMR spectroscopy.

Entry 1 shows that rapid cleavage of diethyl ether and formation of ethane and ethoxytriethylsilane (first cleavage) is accomplished in 3 h at 23 °C with 1% catalyst loading, while ~23 h is required for reduction of the formed ethoxytriethylsilane to a second equivalent of ethane and hexaethyldisiloxane (second cleavage). Under similar conditions cleavage of secondary alkyl ethers is slow. For example, as shown in entry 2, diisopropyl ether requires ~44 h for 95% conversion to propane and isopropyl triethylsilyl ether and resists further reduction to hexaethyldisiloxane (2nd cleavage). Even at longer reaction times (8 days) or elevated reaction temperatures (65 °C, 5 h) only negligible amounts of hexaethyldisiloxane were observed. Similarly, efficient cleavage of alkyl aryl ethers to aryl silyl ethers can be achieved readily. Thus, anisole can be cleaved in 3 h with 1% **1** at 23 °C (entry 3). At 0.1% loading, complete cleavage of anisole is accomplished in 18.5 h at 65 °C (entry 4). Cleavage reactions can also be carried out in neat anisole and 400 TOs can be readily achieved at 23 °C (entry 5). The bulkier alkyl aryl ether, 2,6-dimethylanisole, is also cleaved efficiently at 23 °C with a slight excess of  $\text{Et}_3\text{SiH}$  (1.1 equiv)

(12) Yang, J.; White, P. S.; Schauer, C. K.; Brookhart, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 4141.

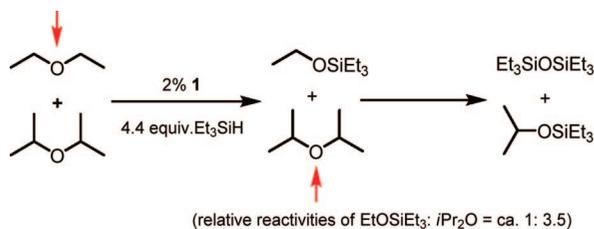
(13) Active catalyst species were not very soluble in neat diethyl ether and triethylsilane; therefore, the solvent-free reduction of diethyl ether was carried out at an elevated reaction temperature (65 °C); see Experimental Section for details.

- (7) It is known that hydrosilanes are able to reduce alkyl ethers in the presence of stoichiometric (or excess) amounts of Lewis acids: (a) Adlington, M. G.; Orfanopoulos, M.; Fry, J. L. *Tetrahedron Lett.* **1976**, 2955. (b) Fry, J. L.; Orfanopoulos, M.; Adlington, M. G.; Dittman, W. R.; Silverman, S. B. *J. Org. Chem.* **1978**, *43*, 374. (c) Orfanopoulos, M.; Smonou, I. *Synth. Commun.* **1988**, *18*, 833. (d) Larsen, J. W.; Chang, L. W. *J. Org. Chem.* **1979**, *44*, 1168. (e) Yato, M.; Ishida, A. *Heterocycles* **1995**, *41*, 17. (f) Smonou, I. *Synth. Commun.* **1994**, *24*, 1999. A catalytic system using 5%  $\text{InCl}_3$  in combination with  $\text{Ph}_2\text{SiHCl}$  shows high selectivities for reduction of benzyl, secondary, and tertiary alcohols to alkanes but not for reduction of primary alcohol: (g) Yasuda, M.; Onishi, Y.; Ueba, M.; Miyai, T.; Baba, A. *J. Org. Chem.* **2001**, *66*, 7741. Bi(OTf)<sub>3</sub>-catalyzed reduction of *p*-methoxybenzyl alcohols with  $\text{Et}_3\text{SiH}$ : (h) Rubenbauer, P.; Bach, T. *Tetrahedron Lett.* **2008**, *49*, 1305.
- (8) (a) Gevorgyan, V.; Rubin, M.; Benson, S.; Liu, J.-X.; Yamamoto, Y. *J. Org. Chem.* **2000**, *65*, 6179. (b) Gevorgyan, V.; Liu, J.-X.; Rubin, M.; Benson, S.; Yamamoto, Y. *Tetrahedron Lett.* **1999**, *40*, 8919. Also see: (c) Blackwell, J. M.; Foster, K. L.; Beck, V. H.; Piers, W. E. *J. Org. Chem.* **1999**, *64*, 4887. High loadings of Pd(II) salts have been shown to induce  $\text{Et}_3\text{SiH}$  reduction of certain classes of primary and secondary alcohols: (d) Ferreri, C.; Costantino, C.; Chatgililoglu, C.; Boukherroub, R.; Manuel, G. *J. Organomet. Chem.* **1998**, *554*, 135.
- (9) (a) Nimmagadda, R. D.; McRae, C. *Tetrahedron Lett.* **2006**, *47*, 5755. For  $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed reductions of carbonyl functions to the corresponding alkyl functions with  $\text{Et}_3\text{SiH}$ : (b) Gevorgyan, V.; Rubin, M.; Liu, J.-X.; Yamamoto, Y. *J. Org. Chem.* **2001**, *66*, 1672. (c) Bajracharya, G. B.; Nogami, T.; Jin, T.; Matsuda, K.; Gevorgyan, V.; Yamamoto, Y. *Synthesis* **2004**, 308. With polymethylhydrosiloxane as reductant: (d) Chandrasekhar, S.; Reddy, C. R.; Babu, B. N. *J. Org. Chem.* **2002**, *67*, 9080.
- (10) Chojnowski, J.; Rubinsztajn, S.; Cella, J. A.; Fortuniak, W.; Cypryk, M.; Kurjata, J.; Kazmierski, K. *Organometallics* **2005**, *24*, 6077.
- (11) Yang, J.; Brookhart, M. *J. Am. Chem. Soc.* **2007**, *129*, 12656.

**Table 1.** Cleavage of Alkyl Ethers with Et<sub>3</sub>SiH Catalyzed by **1**<sup>a</sup>

entry	cat. [mol %]	ether	time (h)	conversion <sup>f</sup> (%)	product
1	1.0	diethyl ether	3	>99	EtOSiEt <sub>3</sub>
		second cleavage	23	98	Et <sub>3</sub> SiOSiEt <sub>3</sub>
2	1.0	diisopropyl ether	43.5	95	<i>i</i> -PrOSiEt <sub>3</sub>
3	1.0	anisole	3	>99	PhOSiEt <sub>3</sub>
4 <sup>b</sup>	0.1	anisole	18.5	>99	PhOSiEt <sub>3</sub>
5 <sup>c</sup>	0.25	anisole	23.2	>99	PhOSiEt <sub>3</sub>
6 <sup>d</sup>	0.5	2,6-dimethylanisole	10	>99	ArOSiEt <sub>3</sub>
7 <sup>e</sup>	1.0	benzyl methyl ether	0.3	>99	MeOSiEt <sub>3</sub> <sup>g</sup>
		second cleavage	5.5	>99	Et <sub>3</sub> SiOSiEt <sub>3</sub>
8 <sup>e</sup>	1.0	<i>tert</i> -butyl methyl ether	8	>99	Et <sub>3</sub> SiOSiEt <sub>3</sub> <sup>h</sup>
9	1.0	<i>n</i> -butyl methyl ether	0.3	>99	<i>n</i> -BuOSiEt <sub>3</sub>
		second cleavage	69	92	Et <sub>3</sub> SiOSiEt <sub>3</sub>

<sup>a</sup> General reaction conditions: 1 mol % of **1**, 2.2 equiv of Et<sub>3</sub>SiH, C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub>, 23 °C. <sup>b</sup> Reaction was carried out at 65 °C. <sup>c</sup> In neat anisole. <sup>d</sup> 1.1 equiv of Et<sub>3</sub>SiH was used. <sup>e</sup> 6 equiv of Et<sub>3</sub>SiH was used. <sup>f</sup> Determined by loss of reactant ethers by <sup>1</sup>H NMR spectroscopy. <sup>g</sup> In addition to toluene, some alkylation products were observed. <sup>h</sup> In addition to isobutane, isobutene and H<sub>2</sub> were observed.

**Scheme 2.** Competition Experiments to Determine Relative Reactivities of Et<sub>2</sub>O and *i*Pr<sub>2</sub>O with **1**/Et<sub>3</sub>SiH System

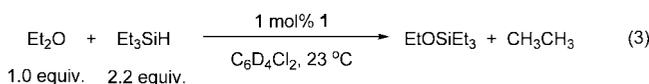
and 0.5% loading of **1** (entry 6). In the case of aromatic ethers no C(sp<sup>2</sup>)–O cleavage is ever observed.

Results of the cleavage of mixed alkyl ethers (R<sup>1</sup>OR<sup>2</sup>) are shown in entries 7–9. Benzyl methyl ether is cleaved to methyl triethylsilyl ether (first cleavage) in less than 20 min with 1% catalyst loading and the formed methyl triethylsilyl ether is further reduced to methane and hexaethyldisiloxane (second cleavage) within another 5.5 h. Similarly, *tert*-butyl methyl ether is rapidly cleaved to methyl triethylsilyl ether and a mixture of isobutene, H<sub>2</sub>, and isobutane. At longer reaction times, methyl triethylsilyl ether is further reduced to methane and hexaethyldisiloxane, while isobutene is hydrogenated to isobutane. The methyl group of *n*-butyl methyl ether is selectively (>95%) and rapidly cleaved to yield *n*-butyl triethylsilyl ether and methane. At longer reaction times, the formed *n*-butyl triethylsilyl ether can be further reduced to *n*-butane and hexaethyldisiloxane.

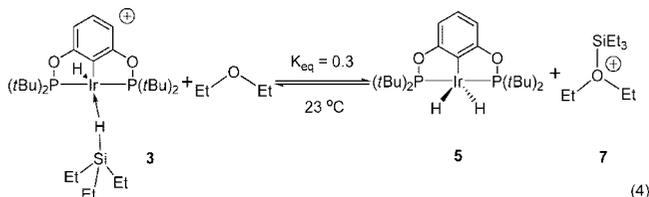
In a competition experiment, a mixture of diethyl ether (1 equiv) and diisopropyl ether (1 equiv) was treated with Et<sub>3</sub>SiH (4.4 equiv) and 2% **1** (Scheme 2). Rapid, selective (>90%) cleavage of diethyl ether resulted in formation of a mixture of ethoxytriethylsilane and unreacted diisopropyl ether. At longer reaction times, reduction of diisopropyl ether occurs faster than reduction of ethoxytriethylsilane. These results indicate that highly chemoselective cleavage of alkyl ethers can be achieved with the **1**/Et<sub>3</sub>SiH system.

This C–O cleavage chemistry has also been applied to catalytic fragmentation of poly(ethylene glycol) by triethylsilane. Thus, in the presence of a catalytic amount of **1**, poly(ethylene glycol) was readily degraded to Et<sub>3</sub>SiOCH<sub>2</sub>CH<sub>2</sub>OSiEt<sub>3</sub> and ethane at 65 °C (Scheme 3) (some H<sub>2</sub> is also likely generated from the terminal OH group).

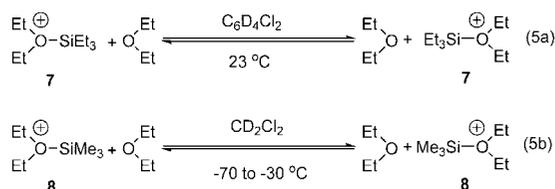
**2.2. In Situ <sup>31</sup>P and <sup>1</sup>H NMR Spectroscopic Monitoring of the Working Catalyst System for Et<sub>2</sub>O Reduction: Identification of the Catalytic Resting State and Key Intermediates.** To identify catalyst resting state(s) and key intermediates for this catalytic process, the cleavage of diethyl ether was performed under standard catalytic conditions and monitored by <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. From earlier studies<sup>11</sup> we know that complex **1** is rapidly converted to the cationic monohydride complex, **2**, which binds triethylsilane to form **3**. Following the in situ cleavage of Et<sub>2</sub>O at 23 °C with 1 mol % catalyst loading (eq 3), the only iridium species observable initially are the *neutral* iridium dihydride complex,<sup>14</sup> **5** (~80%), and the neutral silyl hydride complex (POCOP)Ir(H)(SiEt<sub>3</sub>)<sup>11</sup> {POCOP = 2,6-[OP(*t*Bu)<sub>2</sub>]<sub>2</sub>C<sub>6</sub>H<sub>3</sub>}, **6** (~20%). (This complex is formed by reaction of **5** with triethylsilane, see below.) As the reduction proceeds, Et<sub>2</sub>O, **5**, and **6** decrease in concentration, while the cationic iridium silane complex, **3**, appears and grows in concentration equivalent to the loss of **5** and **6**.



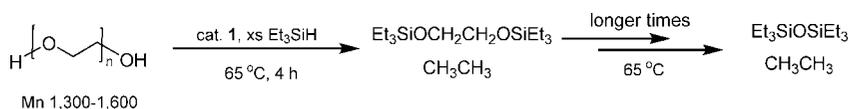
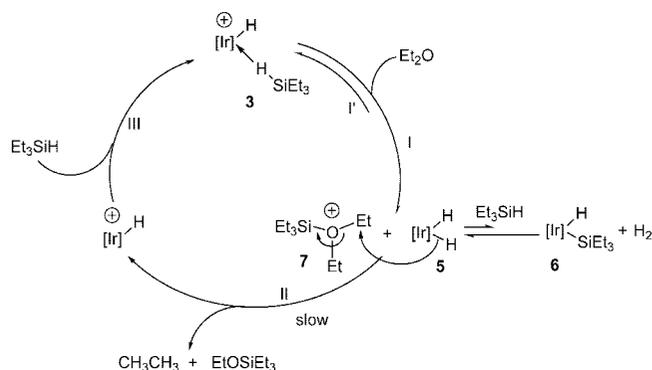
This observation suggests that the iridium silane complex **3** is in equilibrium with the iridium dihydride **5** and diethyl(triethylsilyl)oxonium ion **7** as shown in eq 4 and that this equilibrium is established rapidly relative to the rate of reduction. Once the concentration of **3** is sufficient to be measured relative to **5** and Et<sub>2</sub>O, the equilibrium constant can be determined by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. At several stages of conversion *K*<sub>eq</sub> was determined to be 0.3, consistent with the proposition that equilibrium is maintained between **3** and **5** throughout the catalytic reduction.



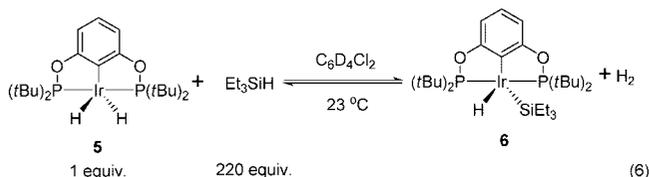
Species **7** cannot be spectroscopically observed at 23 °C. Significant line broadening of the ethyl groups of diethyl ether is observed in both the <sup>1</sup>H and <sup>13</sup>C NMR spectra which we propose indicates rapid dynamic exchange between **7** and Et<sub>2</sub>O (eq 5a). Observations by Kira, Sakurai, and co-workers<sup>15a</sup> support this hypothesis. They showed that in situ generation of [Et<sub>2</sub>OSiMe<sub>3</sub>]<sup>+</sup>[B(Ar<sub>F</sub>)<sub>4</sub>]<sup>-</sup> [Ar<sub>F</sub> = 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>] in the presence of excess Et<sub>2</sub>O at -70 °C resulted in a dynamic system described by eq 5b as shown by line broadening in the <sup>1</sup>H and <sup>13</sup>C NMR spectrum.<sup>15a</sup>



As noted above, a small quantity (~20% by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy) of an iridium species assigned as the silyl hydride **6** was observed in the working catalytic system. This complex was independently generated by treatment of (POCOP)Ir(H)(Cl) with NaO*t*Bu in presence of excess Et<sub>3</sub>SiH in C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub> and

**Scheme 3.** Fragmentation of Poly(ethylene glycol) with 1/Et<sub>3</sub>SiH System**Scheme 4.** Proposed Catalytic Cycle for Cleavage of Et<sub>2</sub>O with 1/Et<sub>3</sub>SiH

characterized by NMR spectroscopy.<sup>11</sup> It can also be generated by treatment of dihydride **5** with a very large excess of Et<sub>3</sub>SiH in C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub> in the absence of diethyl ether (eq 6). The *K*<sub>eq</sub> is not available due to the difficulty of accurately measuring the concentration of H<sub>2</sub> in C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub> solution.

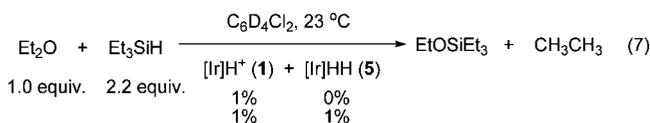


In the working catalyst system for diethyl ether cleavage (eq 3), the ratio of **6** to **5** increases with an increase of the initial Et<sub>3</sub>SiH:Ir ratio. Thus, it is instructive to note that increasing the Et<sub>3</sub>SiH concentration while holding the loading of **1** at 1 mol % (relative to Et<sub>2</sub>O) results in a *decrease* in the rate of the first cleavage. This suggests that dihydride **5** is a much more effective hydride donor for reducing **7** than silyl hydride, **6**.

The above results support the proposed catalytic cycle shown in Scheme 4. At high Et<sub>2</sub>O concentrations in the initial stages of catalysis equilibrium between **3** + Et<sub>2</sub>O and **5** + **7** strongly favors **5** + **7**. The dihydride, **5**, reacts with silane to generate small quantities of silyl hydride, **6**. The dihydride reduces **7** to yield product EtOSiEt<sub>3</sub> and cationic monohydride **2**, which, upon reaction with silane, forms **3** and closes the catalytic cycle. The silyl hydride does not effectively compete with dihydride as a hydride donor. As catalysis proceeds and ether is depleted, the concentration of the silane complex, **3**, increases and becomes observable by NMR spectroscopy. The turnover-limiting step in the cycle is reduction of Et<sub>3</sub>SiOEt<sub>2</sub><sup>+</sup> by the neutral dihydride complex. Two additional experiments were carried out to confirm this catalytic cycle as described in sections 2.2.1. and 2.2.2. below.

**2.2.1. Effect of Adding Additional Iridium Dihydride, 5.** If the turnover-limiting step is reaction of dihydride, **5**, with the oxonium species, **7**, (and dihydride, **5**, is the catalyst resting state), then addition of **5** to the reaction should result in a proportionate increase in turnover frequency. Addition of 1.0 mol % of iridium dihydride **5** to the catalytic system initiated with 1% Ir (eq 7) was found to increase the initial turnover

frequency by a factor of 1.8 as can be seen from the data shown in Figure 1. The value of 1.8 is within experimental error of the expected factor of 2.0 and in fact matches the NMR measured increase in the concentration of **5** relative to that of **7**. These results further support the mechanistic proposal in Scheme 4.



### 2.2.2. Generation, Spectroscopic and Structural Characterization, and Dynamic Behavior of Diethyl(triethylsilyl)oxonium ion (7) and Its Reaction with Dihydride (5).

The proposed catalytic intermediate diethyl(triethylsilyl)oxonium ion, Et<sub>3</sub>SiOEt<sub>2</sub><sup>+</sup>, **7**, can be independently generated using Lambert methodology<sup>16,5b</sup> by treating the in situ formed C<sub>6</sub>D<sub>6</sub>-stabilized triethylsilyl cation [Et<sub>3</sub>Si(C<sub>6</sub>D<sub>6</sub>)]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup> with diethyl ether in C<sub>6</sub>D<sub>5</sub>Cl at -40 °C. The <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>29</sup>Si{<sup>1</sup>H} NMR spectra confirm clean formation of cation **7**. The <sup>1</sup>H spectrum shows triethylsilyl group resonances at δ 0.58 (CH<sub>3</sub>) and 0.30 (CH<sub>2</sub>), and the methyl and methylene protons adjacent to the oxygen at δ 0.82 and 3.53, respectively. The <sup>13</sup>C{<sup>1</sup>H} shows, in addition to the B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> counteranion and excess free Et<sub>2</sub>O (δ 66.2 and 15.8) and traces of excess Et<sub>3</sub>SiH, only four signals corresponding to the methyl and methylene carbons of the EtO- group at δ 75.1 and 12.8, and the triethylsilyl group at δ 3.1 and 5.5. Slight line broadening of the ethyl groups of **7** is seen in the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectrum, which indicates rapid dynamic exchange with free Et<sub>2</sub>O even at -40 °C. The <sup>29</sup>Si{<sup>1</sup>H} resonance of **7** appeared as a singlet at δ 68.9. This is downfield compared to free Et<sub>3</sub>SiH (δ 0.2) and the iridium η<sup>1</sup>-Et<sub>3</sub>SiH complex **3** (δ 30.2),<sup>12</sup> but still upfield of that for the C<sub>6</sub>D<sub>6</sub>-stabilized triethylsilyl cation [Et<sub>3</sub>Si(C<sub>6</sub>D<sub>6</sub>)]<sup>+</sup> (δ 92.3).<sup>16</sup>

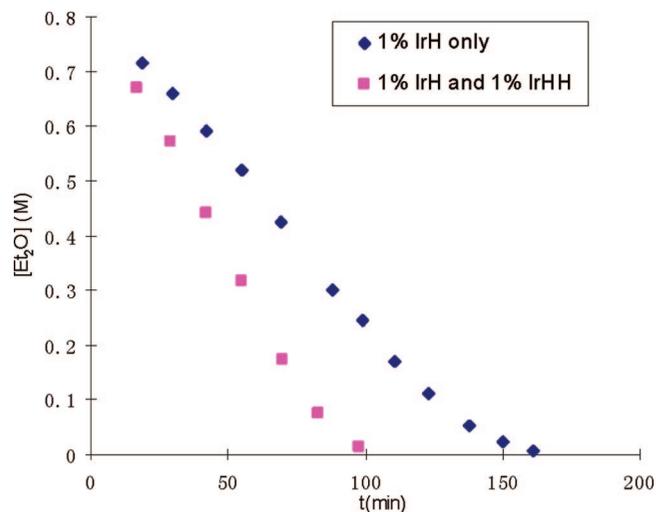
Upon warming, the <sup>1</sup>H and <sup>13</sup>C resonances corresponding to **7** and free Et<sub>2</sub>O broaden and coalesce. At 20 °C the <sup>1</sup>H NMR spectrum shows broad bands at δ 3.4 and 1.0, respectively, for the methylene and methyl protons of the -OCH<sub>2</sub>CH<sub>3</sub> group. The methyl and methylene <sup>13</sup>C signals of the EtO- group, however, are too broad to be observed in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum due to exchange.

An X-ray-quality crystal<sup>17a</sup> of **7** was obtained by slow diffusion of pentane into a C<sub>6</sub>D<sub>5</sub>Cl solution of **7** at -35 °C under Ar. Complex **7** can also be isolated by crystallization from the catalytic reaction mixture at -35 °C, which further indicates

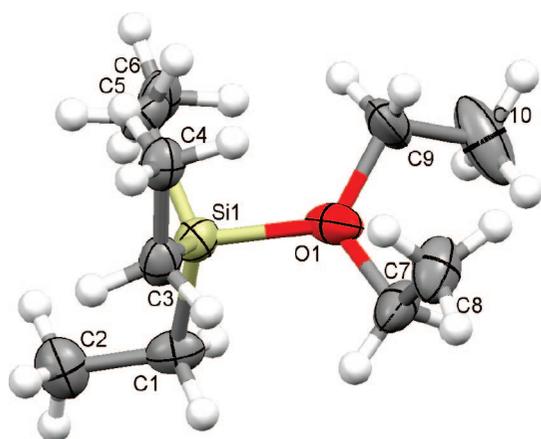
(14) Goettker-Schnetmann, I.; White, P.; Brookhart, M. *Organometallics* **2004**, *23*, 1766.

(15) (a) Kira, M.; Hino, T.; Sakurai, H. *J. Am. Chem. Soc.* **1992**, *114*, 6697. (b) Scharrer, E.; Chang, S.; Brookhart, M. *Organometallics* **1995**, *14*, 5686.

(16) (a) Lambert, J. B.; Zhao, Y.; Wu, H. *J. Org. Chem.* **1999**, *64*, 2729. (b) Lambert, J. B.; Zhang, S.; Ciro, S. M. *Organometallics* **1994**, *13*, 2430. (c) Lambert, J. B.; Kania, L.; Zhang, S. *Chem. Rev.* **1995**, *95*, 1191. (d) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 325. (e) Lambert, J. B.; Zhang, S.; Stern, C. L.; Huffman, J. C. *Science* **1993**, *260*, 1917. (f) Corey, J. Y. *J. Am. Chem. Soc.* **1975**, *97*, 3237. (g) Müller, T. *Adv. Organomet. Chem.* **2005**, *53*, 155.



**Figure 1.** Plot of Et<sub>2</sub>O concentration vs time for the cleavage of Et<sub>2</sub>O with and without adding additional **5**.



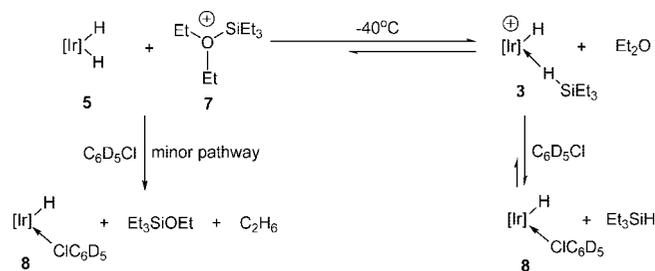
**Figure 2.** ORTEP diagram of the cation in **7**. Key bond distances (Å) and bond angles (deg): Si(1)–O(1) = 1.788(3), Si(1)–C(1) = 1.855(4), Si(1)–C(3) = 1.859(4), Si(1)–C(5) = 1.862(4), O(1)–C(7) = 1.507(5), O(1)–C(9) = 1.494(5), C(1)–C(2) = 1.537(6), C(3)–C(4) = 1.549(6), C(5)–C(6) = 1.532(7), C(7)–C(8) = 1.487(6), C(9)–C(10) = 1.478(7), O(1)–Si(1)–C(1) = 103.61(16), O(1)–Si(1)–C(3) = 105.09(16), O(1)–Si(1)–C(5) = 105.15(16), C(1)–Si(1)–C(3) = 115.56(17), C(1)–Si(1)–C(5) = 112.62(17), C(3)–Si(1)–C(5) = 113.39(17), C(7)–O(1)–C(9) = 115.0(3), C(7)–O(1)–Si(1) = 118.4(2), C(9)–O(1)–Si(1) = 124.5(2).

its intermediacy as a resting state in the working catalyst system. The ORTEP diagram of **7** is shown in Figure 2.

Addition of iridium dihydride **5** in C<sub>6</sub>D<sub>5</sub>Cl solution at –40 °C to in situ generated diethyl(triethylsilyl)oxonium ion **7** at –40 °C, initially results in formation of free Et<sub>3</sub>SiH and cationic iridium chlorobenzene-*d*<sub>5</sub> complex **8** with little formation of cleavage products EtOSiEt<sub>3</sub> and C<sub>2</sub>H<sub>6</sub> (Scheme 5). This result is consistent with the mechanistic proposal shown in Scheme 4 in which there is a rapid pre-equilibrium between **5** and **3** prior to product formation. If nucleophilic attack of **5** on **7** to yield EtOSiEt<sub>3</sub> is turnover-limiting, then reaction of **5** with **7** should initially yield predominantly **3** and Et<sub>2</sub>O as observed. (Under these conditions with only one equivalent of silane present per Ir center, we have previously established that silane will be displaced from **3** by solvent to yield the chlorobenzene adduct, **8**.)

**2.3. Mechanistic Analysis of the Reduction of EtOSiEt<sub>3</sub>.** A very different mechanistic profile was observed in the second step of the cleavage of diethyl ether, conversion of EtOSiEt<sub>3</sub> to

**Scheme 5.** Reaction of **7** with **5** at –40 °C

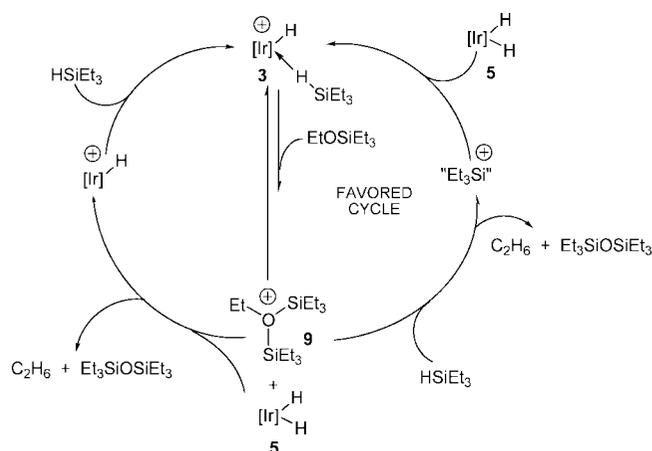


Et<sub>3</sub>SiOSiEt<sub>3</sub> and ethane (eq 2). After complete conversion of Et<sub>2</sub>O to EtOSiEt<sub>3</sub>, the dihydride complex **5** vanishes and is replaced by the cationic iridium silane complex, **3**, as the catalyst resting state. The less basic and more hindered EtOSiEt<sub>3</sub> (relative to Et<sub>2</sub>O) must result in disfavoring Et<sub>3</sub>Si<sup>+</sup> transfer from **3** to EtOSiEt<sub>3</sub> to form the (high-energy) oxonium species EtO–(SiEt<sub>3</sub>)<sub>2</sub><sup>+</sup>, **9**. Under standard conditions where 120 equiv of Et<sub>3</sub>SiH is used relative to iridium complex, the half-life of conversion of EtOSiEt<sub>3</sub> to Et<sub>3</sub>SiOSiEt<sub>3</sub> is ~10 h. Interestingly, when the same reaction is carried out with addition of 1 equiv of dihydride **5** relative to **1**, the reduction of EtOSiEt<sub>3</sub> is dramatically retarded, with the half-life now being ~100 h (~94% conversion after 353 h). (Recall in the case of the reduction of Et<sub>2</sub>O where the dihydride was the resting state and the oxonium species Et<sub>2</sub>OSiEt<sub>3</sub><sup>+</sup>, **7**, prevailed, addition of dihydride **5** accelerated the reduction.) The equilibrium **3** + EtOSiEt<sub>3</sub> ⇌ **5** + **9** is driven to the left by addition of **5**; however, if **5** were the sole hydride donor to **9**, then the shift in equilibrium would be balanced by increase in [5], and no effect on the rate of reduction of EtOSiEt<sub>3</sub> should be observed. This result implies that Et<sub>3</sub>SiH is the major if not the sole hydride donor to EtO(SiEt<sub>3</sub>)<sub>2</sub><sup>+</sup>, **9**. In support of this contention, the rate of cleavage of EtOSiEt<sub>3</sub> is accelerated as the concentration of Et<sub>3</sub>SiH is increased. For example, using 300 vs 120 equiv of Et<sub>3</sub>SiH results in a ~3-fold rate increase in turnover frequency.<sup>18</sup>

The fact that Et<sub>3</sub>SiH (not dihydride **5**) is the sole or at least major hydride donor is likely a result of two factors. First, since the cationic silane complex **3** is the resting state, the concentration of **5** is quite low relative to Et<sub>3</sub>SiH. Second, the pincer dihydride **5** is certainly a more hindered hydride donor than Et<sub>3</sub>SiH and EtO(SiEt<sub>3</sub>)<sub>2</sub><sup>+</sup> is a more hindered substrate than Et<sub>2</sub>OSiEt<sub>3</sub><sup>+</sup>, so steric factors favor reduction of EtO(SiEt<sub>3</sub>)<sub>2</sub><sup>+</sup> by Et<sub>3</sub>SiH. The overall catalytic process for reduction of EtOSiEt<sub>3</sub> is summarized in Scheme 6 with the right side of the cycle the sole or at least major pathway for reduction.

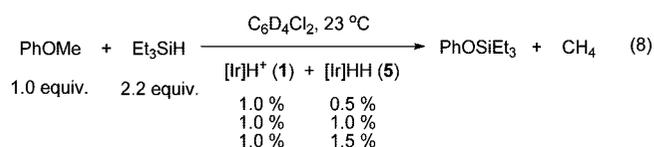
**2.4. Mechanistic Investigation of the Catalytic Cleavage of PhOCH<sub>3</sub> with Et<sub>3</sub>SiH.** Following the in situ NMR monitoring and mechanistic analysis of the diethyl ether cleavage reactions, we turned to investigate a much less basic alkyl aryl ether, anisole. The catalytic cleavage reaction with PhOCH<sub>3</sub> was also monitored by both <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. The only Ir species present throughout the entire catalytic reaction is the cationic iridium silane complex, **3**. This could be due to (1) the low basicity of anisole, which results in very low equilibrium

(17) The crystal structure of the trimethyl silyl analogue of **7**, [Me<sub>3</sub>SiOEt<sub>2</sub>]<sup>+</sup>–[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>–</sup>, has been reported as reaction byproduct in the synthesis of E(SiMe<sub>3</sub>)<sub>4</sub><sup>+</sup> ions (E = P, As) and also by independent synthesis: (a) Driess, M.; Barmeyer, R.; Monsé, C.; Merz, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 2308. (b) Crystal structure of *t*Bu<sub>3</sub>SiOH<sub>2</sub><sup>+</sup> ion: Xie, Z.; Bau, R.; Reed, C. A. *Chem. Commun.* **1994**, 2519. (c) Olah, G. A.; Li, X.-Y.; Wang, Q.; Rasul, G.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1995**, *117*, 8962.

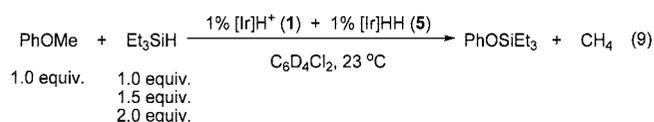
**Scheme 6.** Proposed Catalytic Cycle for Reduction of EtOSiEt<sub>3</sub>

concentrations (beyond NMR detection limit) of neutral iridium dihydride, **5**, and methylphenyl(triethylsilyl)oxonium ion, **10** (Scheme 7A), or (2) the result of slow transfer of Et<sub>3</sub>Si<sup>+</sup> from **3** to anisole followed by fast reaction of **5** with oxonium species **10** (Scheme 7B). However, in either of these two cases, no dependence of the turnover frequency on the concentration of **5** would be expected.

Thus, addition of 0.5 mol % to 1.5 mol % iridium dihydride **5** to the catalytic reaction mixture (eq 8) was found to have no effect on the reaction rate (Figure 3).



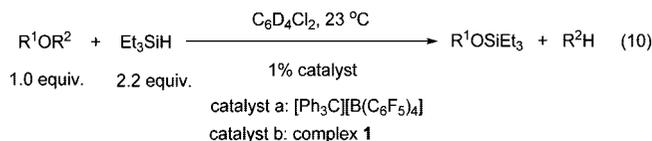
Varying the Et<sub>3</sub>SiH concentration under these reaction conditions as shown in eq 9 (1% **1** + 1% **5**) shows the turnover frequency is zero-order in the concentration of Et<sub>3</sub>SiH (Figure 4) and implies that Et<sub>3</sub>SiH does not compete with dihydride **5** as the hydride donor.



Under conditions where no additional iridium dihydride **5** is added, the concentration of **5** and PhMeOSiEt<sub>3</sub><sup>+</sup> **10** are quite low since **3** is the resting state. Triethylsilane is present in much higher concentration than **5** and thus may compete with **5** for the reduction of **10**. Indeed, we observe an increase in the turnover frequency of reduction with increased silane concentrations (e.g., 220 to 600 equiv), but due to the formation of varying small amounts of silyl hydride, **6**, quantitative kinetic analysis is not possible. Nevertheless, these results suggest Et<sub>3</sub>SiH can compete with **5** as the hydride donor under these conditions.

**2.5. Comparison of (POCOP)IrH<sup>+</sup>/Et<sub>3</sub>SiH with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]/Et<sub>3</sub>SiH for Alkyl Ether Cleavage.** The combination of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]/Et<sub>3</sub>SiH was reported by Lambert<sup>16a</sup> for catalytic hydrosilylation of diphenylethene and has also been demonstrated recently by Ozerov<sup>19</sup> to be capable of catalytic hydrodefluorination of C(sp<sup>3</sup>)-F bonds presumably via a mechanism involving a carbenium ion intermediate. To gain further mechanistic insight into the system, we have examined the capability of the [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]/Et<sub>3</sub>SiH system for alkyl ether cleavage reac-

tions and compared it with the **1**/Et<sub>3</sub>SiH system (eq 10). In the catalytic cleavage of anisole, as shown in Figure 5, iridium complex **1** is less reactive than [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (*t*<sub>1/2</sub> (23 °C) = 80 min for **1**; *t*<sub>1/2</sub> (23 °C) = 10 min for [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]). However, for catalytic reactions with the more basic alkyl ether Et<sub>2</sub>O (Figure 6), iridium complex **1** is much more reactive than the [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]/Et<sub>3</sub>SiH system under same reaction conditions (*t*<sub>1/2</sub> (23 °C) = 80 min for **1**; *t*<sub>1/2</sub> (23 °C) = 120 h for [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]).



When the catalytic cleavage of Et<sub>2</sub>O with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] was followed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, similar to the iridium catalytic system, line broadening of the ethyl groups of diethyl ether was observed in both <sup>1</sup>H and <sup>13</sup>C NMR spectra. This indicates that Et<sub>3</sub>SiOEt<sub>2</sub><sup>+</sup>, **7**, is the resting state in the Et<sub>2</sub>O cleavage reaction catalyzed by [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (Scheme 8). Indeed **7** can be isolated from this catalytic reaction mixture as well. Although lower in concentration ([**5**]/[Et<sub>3</sub>SiH] = 1/250 in Et<sub>2</sub>O reduction), iridium dihydride **5** is more nucleophilic than Et<sub>3</sub>SiH and potentially a much better hydride donor; therefore, the turnover-limiting hydride transfer step is much faster for iridium catalysis compared with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] catalysis in diethyl ether cleavage. Relative rates of hydride reduction of **7** by **5** versus Et<sub>3</sub>SiH can be estimated as ~30,000:1 from the ratio of initial reduction rates (*V*<sub>i</sub>(Ir):*V*<sub>i</sub>(Ph<sub>3</sub>C<sup>+</sup>) = 105:1) and the relative initial concentration ratio ([**5**]:[Et<sub>3</sub>SiH] = 1:270).

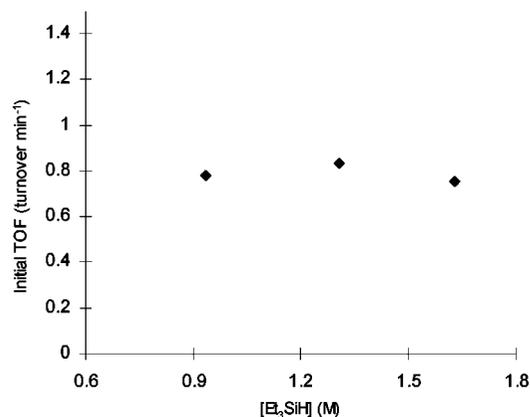
In the catalytic cleavage of PhOCH<sub>3</sub> with the **1**/Et<sub>3</sub>SiH system, as noted earlier, cationic iridium silane complex, **3**, is the catalyst resting state, and there is very little iridium dihydride, **5**, and PhMeOSiEt<sub>3</sub><sup>+</sup>, **10**, present in the working catalyst system. Triethylsilane thus competes with low concentrations of **5** as the hydride donor to **10**. The very low equilibrium concentration of PhMeOSiEt<sub>3</sub><sup>+</sup>, **10**, results in slower overall hydride reduction (by **5** and Et<sub>3</sub>SiH) rate as compared to the [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]/Et<sub>3</sub>SiH system. In the latter system **10** is presumably the catalyst resting state<sup>20</sup> (and thus exists in much higher concentration than in the **1**/Et<sub>3</sub>SiH system) and results in faster overall reduction by Et<sub>3</sub>SiH.

### 3. Summary

We have shown that cationic iridium pincer catalyst **1** in combination with Et<sub>3</sub>SiH reduces a wide variety of unactivated

- (18) Quantitative analysis of these kinetics is complicated by formation of silyl hydride **6**. As the Et<sub>3</sub>SiH concentration increases, we note that the neutral silyl hydride species **6** begins to appear in the working catalyst system as noted by the <sup>31</sup>P signal at 189.2 ppm. This must arise as noted above by reaction of silane with dihydride **5**. The silyl hydride apparently will not react with EtO(SiEt<sub>3</sub>)<sub>2</sub><sup>+</sup>, **9**, so that we assume the appearance of silyl hydride is also accompanied by formation of **9**, but we have no good spectroscopic method to detect small quantities of **9** which may be rapidly exchanging with Et<sub>3</sub>SiOEt.
- (19) (a) Scott, V. J.; Çelenligil-Çetin, R.; Ozerov, O. V. *J. Am. Chem. Soc.* **2005**, *127*, 2852. (b) Douvris, C.; Ozerov, O. V. *Science* **2008**, *321*, 1188 reported efficient catalytic reduction of C-F bonds using [Ph<sub>3</sub>C][HCB<sub>11</sub>H<sub>5</sub>Cl<sub>6</sub>]/Et<sub>3</sub>SiH.
- (20) PhMeOSiEt<sub>3</sub><sup>+</sup>, **10**, has been independently generated in C<sub>6</sub>D<sub>5</sub>Cl according to procedures analogous to that for **7**; see Experimental Section for details.





**Figure 4.** Plot of the initial turnover frequency (TOF) vs Et<sub>3</sub>SiH concentration for the cleavage of anisole catalyzed by **1** and **5**.

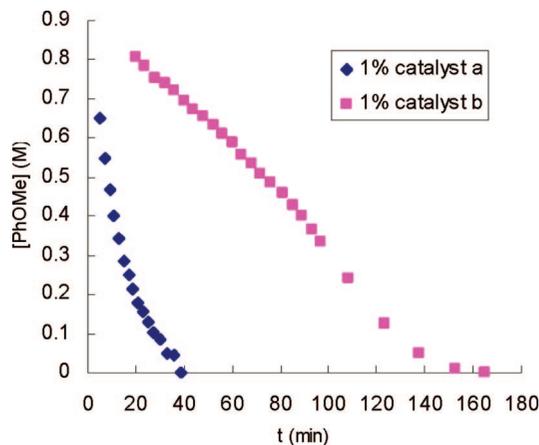
ensure complete mixing. The reactions were allowed to stand at room temperature, and the progress was monitored by NMR spectroscopy. Reduction products (PhOSiEt<sub>3</sub> and CH<sub>4</sub>) were identified using <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR data in comparison to literature data.

**4.4. Cleavage of Et<sub>2</sub>O with Et<sub>3</sub>SiH Catalyzed by **1** without Solvent.** Triethylsilane (352 μL, 2.2 mmol, 2.2 equiv) was added to a medium-walled J. Young NMR tube with **1** (2 mg, 0.0015 mmol, 0.15 mol %) and a sealed capillary tube with C<sub>6</sub>D<sub>6</sub> as internal standard. To this suspension was then added Et<sub>2</sub>O (105 μL, 1.0 mmol, 1 equiv), and the tube was quickly inverted to ensure complete mixing. Active catalyst species were not very soluble in neat diethyl ether and triethylsilane; therefore, the reaction was carried out at 65 °C in an oil bath. The progress was monitored by NMR spectroscopy. Reduction products (EtOSiEt<sub>3</sub>, Et<sub>3</sub>SiOSiEt<sub>3</sub>, and C<sub>2</sub>H<sub>6</sub>) were identified using <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR data in comparison to literature data. About 370 TOs were achieved after 44 h., while at 112 h 590 TOs were obtained. Complete conversion of Et<sub>2</sub>O to EtOSiEt<sub>3</sub> was achieved at longer reaction times (159 h) at the expense of losing selectivity at 65 °C since some of the EtOSiEt<sub>3</sub> was converted to Et<sub>3</sub>SiOSiEt<sub>3</sub>.

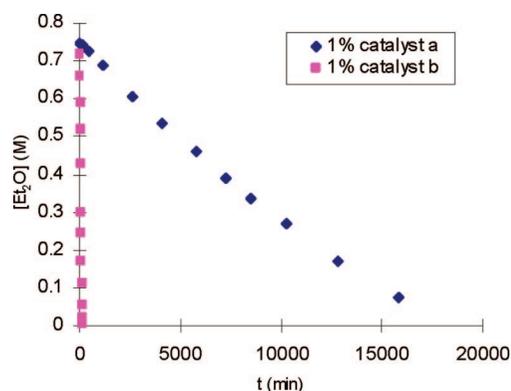
**4.5. Competition Experiments to Determine Relative Reactivities of Et<sub>2</sub>O and *i*Pr<sub>2</sub>O with **1**/Et<sub>3</sub>SiH System.** Triethylsilane (175 μL, 1.1 mmol, 4.4 equiv) was added to a solution of **1** (6.7 mg, 0.005 mmol, 2 mol %) in C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub> (0.3 mL) in a medium-walled J. Young NMR tube, and the contents were well shaken. Diethyl ether (0.25 mmol, 26 μL, 1 equiv) and diisopropyl ether (0.25 mmol, 35 μL, 1 equiv) were then added, the reactions were allowed to stand at room temperature, and the progress was followed by NMR spectroscopy. Reduction products were identified using <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR in comparison to literature data. After about 2.5 h, Et<sub>2</sub>O was quantitatively converted to EtOSiEt<sub>3</sub>, while 93% of the *i*Pr<sub>2</sub>O remained unreacted. At longer reaction times, reduction of *i*Pr<sub>2</sub>O occurs faster than reduction of EtOSiEt<sub>3</sub> with an initial rate ratio of ~3.5:1 as determined by the substrate ether loss.

**4.6. Fragmentation of Poly(ethylene glycol) with Et<sub>3</sub>SiH catalyzed by **1**.** Catalyst **1** (3.3 mg, 0.0025 mmol) and poly(ethylene glycol) (22 mg, Sigma-Aldrich, average M<sub>n</sub> = 1300–1600) were dissolved in C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub> (0.3 mL) in a J. Young NMR tube. Triethylsilane (240 μL, 1.5 mmol) was added to this solution, and the reaction was heated in a 65 °C oil bath for 4 h. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra show the disappearance of the poly(ethylene glycol) and formation of Et<sub>3</sub>SiOCH<sub>2</sub>CH<sub>2</sub>OSiEt<sub>3</sub> and ethane. Et<sub>3</sub>SiOCH<sub>2</sub>CH<sub>2</sub>OSiEt<sub>3</sub>: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub>, 400 MHz, 23 °C): δ 3.60 (s, 4H), 0.9 (m, 9H), 0.5 (m, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub>, 100.6 MHz, 23 °C): δ 64.3 (s), 6.5 (s), 4.5 (s). At longer reaction times Et<sub>3</sub>SiOCH<sub>2</sub>CH<sub>2</sub>OSiEt<sub>3</sub> was converted to Et<sub>3</sub>SiOSiEt<sub>3</sub>.

**4.7. Determination of the Equilibrium Constants for Silyl Transfer between **3** and **7** during Diethyl Ether Cleavage.** The cleavage of Et<sub>2</sub>O was performed under standard catalytic

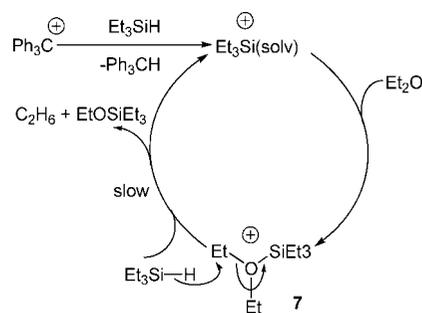


**Figure 5.** Plot of PhOMe concentration vs time for anisole cleavage reactions catalyzed by catalyst a: [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and by catalyst b: complex **1**.

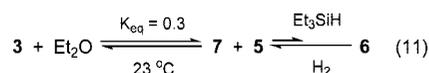


**Figure 6.** Plot of Et<sub>2</sub>O concentration vs time for Et<sub>2</sub>O cleavage reactions catalyzed by catalyst a: [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and by catalyst b: complex **1**.

**Scheme 8.** Proposed Catalytic Cycle for Et<sub>2</sub>O Cleavage with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]/Et<sub>3</sub>SiH

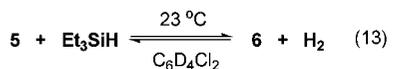


conditions and monitored by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. As discussed in the text, a small quantity of **6** was formed by reaction of **5** with triethylsilane (eq 11). Thus, the concentration of **7** was calculated from the sum of the concentrations of **5** and **6**. Once the concentration of **3** was sufficient to be measured relative to that of **5** and Et<sub>2</sub>O, the equilibrium constant was determined by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy following the formula shown in eq 12. At several stages of conversion K<sub>eq</sub> was determined to be 0.3.



$$K_{\text{eq}} = \frac{[\mathbf{7}][\mathbf{5}]}{[\mathbf{3}][\text{Et}_2\text{O}]} = \frac{([\mathbf{5}] + [\mathbf{6}])[\mathbf{5}]}{[\mathbf{3}][\text{Et}_2\text{O}]} \quad (12)$$

**4.8. Reaction of Iridium Dihydride Complex, 5, with Et<sub>3</sub>SiH.** The iridium silyl hydride, **6**, has been previously generated and characterized by treatment of (POCOP)Ir(H)(Cl) with NaOtBu in presence of excess Et<sub>3</sub>SiH in C<sub>7</sub>D<sub>8</sub>.<sup>11</sup> In experiments carried out in this work, triethylsilane (175 μL, 1.1 mmol, 220 equiv) was added to a solution of **5** (3.0 mg, 0.005 mmol, 1 equiv) in C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub> (0.4 mL) in a J. Young NMR tube (eq 13, see below). The reaction was allowed to stand at room temperature and the establishment of equilibrium was followed by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub>, 400 MHz, 23 °C): **6**, δ -15.9 (t, 1H, IrH); **5**, δ -17.0 (b, 2H, IrH). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub>, 162 MHz, 23 °C): **6**, δ 189.2; **5**, δ 204.5.



t(min)	<b>6</b> : <b>5</b> (by <sup>31</sup> P NMR)
22	0.69:1.00
36	0.75:1.00
46	0.79:1.00
56	0.83:1.00
86	0.81:1.00
106	0.81:1.00
126	0.86:1.00
1016	0.80:1.00
6788	0.81:1.00

#### 4.9. Cleavage of Et<sub>2</sub>O with Et<sub>3</sub>SiH Catalyzed by the Mixture of Cationic Complex, 1 and Dihydride Complex, 5.

Triethylsilane (175 μL, 1.1 mmol, 2.2 equiv) and Et<sub>2</sub>O (52 μL, 0.5 mmol, 1 equiv) were added to a solution of **1** (6.7 mg, 0.005 mmol, 1 mol %) and **5** (3.0 mg, 0.005 mmol, 1 mol %) in C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub> (0.3 mL) in a medium-walled J. Young NMR tube. The contents were well shaken, and the reaction progress was monitored by decrease of Et<sub>2</sub>O resonances relative to the signal of the CH<sub>3</sub>CH<sub>2</sub>- groups of the silanes [sum of (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>SiH and (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>SiOEt] with respect to time by <sup>1</sup>H NMR spectroscopy. Data is plotted in Figure 1.

#### 4.10. In Situ Generation and Variable-Temperature NMR Spectroscopic Characterization of Diethyl(triethylsilyl)oxonium Ion, 7.

Dry C<sub>6</sub>D<sub>6</sub> (0.5 mL) was added to a screw-cap NMR tube with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (92 mg, 0.1 mmol, 1.0 equiv) in a drybox. To this suspension was then added triethylsilane (18 μL, 0.113 mmol, 1.13 equiv), and the tube was quickly inverted to ensure complete mixing. A light brown oil was produced. The clear top phase was removed by syringe, and the oil was washed with C<sub>6</sub>D<sub>6</sub> (0.1 mL × 2). The oil (~0.1 mL) was dissolved in C<sub>6</sub>D<sub>5</sub>Cl (0.6 mL) at room temperature, and the solution was cooled to -40 °C. Diethyl ether (20–100 μL, 0.19–0.95 mmol, 1.9–9.5 equiv) was added by syringe, and the NMR tube was then placed in the precooled NMR probe at -40 °C. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>5</sub>Cl, 400 MHz, -40 °C): δ 3.53 (br, 4H), 0.82 (s, 6H), 0.58 (m, 9H), 0.30 (m, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>5</sub>Cl, 100.6 MHz, -40 °C): δ 148.8 (d, <sup>1</sup>J<sub>C-F</sub> = 244.5 Hz), 138.7 (d, <sup>1</sup>J<sub>C-F</sub> = 246.7 Hz), 136.9 (d, <sup>1</sup>J<sub>C-F</sub> = 248.6 Hz), 124.5 (br), 75.1 (br), 12.8 (br), 5.5 (s), 3.1 (s). <sup>29</sup>Si{<sup>1</sup>H} DEPT 45 (C<sub>6</sub>D<sub>5</sub>Cl, 79 MHz, -40 °C) δ 68.9. The variable-temperature (-40 to 20 °C) <sup>1</sup>H NMR dynamic behavior of **7** is discussed in the text.

**4.11. Isolation and X-ray Structure of 7.** *Method A:* colorless crystals of **7** can be obtained by slow diffusion of dry pentane into the above-described solution in C<sub>6</sub>D<sub>5</sub>Cl at -35 °C. *Method B:* **7** can also be isolated by crystallization from the iridium-catalyzed reaction mixture. Triethylsilane (240 μL, 1.5 mmol, 2.0 equiv) was added to a solution of **1** (20 mg, 0.015 mmol, 2 mol %) in C<sub>6</sub>D<sub>5</sub>Cl (0.6 mL) in a J. Young NMR tube. Diethyl ether (78.8 μL, 0.75 mmol, 1.0 equiv) was then added, and the tube was quickly inverted

**Table 2.** X-ray Crystal Structure Data for Complex **7**

empirical formula	C <sub>34</sub> H <sub>25</sub> BF <sub>20</sub> OSi
formula weight	868.44
crystal system	orthorhombic
space group	<i>Pbca</i>
unit cell dimensions	<i>a</i> = 19.5991(9) Å, α = 90° <i>b</i> = 17.4575(9) Å, β = 90° <i>c</i> = 21.7621(12) Å, γ = 90°
volume	7445.9(7) Å <sup>3</sup>
Z	8
absorption coefficient	0.192 mm <sup>-1</sup>
density (calculated)	1.549 mg/m <sup>3</sup>
crystal size	0.30 × 0.30 × 0.10 mm <sup>3</sup>
data/restraints/parameters	7075/38/578
final R indices [ <i>I</i> > 2σ( <i>I</i> )]	R1 = 0.0522, wR2 = 0.1414

to ensure complete mixing. Oxonium ion **7** crystallized from this reaction mixture at -35 °C. *Method C:* Oxonium ion **7** can also be obtained in crystalline form from the [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]-catalyzed reaction mixture as well. Triethylsilane (110 μL, 0.69 mmol, 0.97 equiv) and diethyl ether (75 μL, 0.71 mmol, 1.0 equiv) were added to a solution of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (16 mg, 0.0174 mmol, 2.5 mol %) in C<sub>6</sub>D<sub>5</sub>Cl (0.6 mL) in a J. Young NMR tube. The tube was quickly inverted to ensure complete mixing. The solution was layered with pentane (1–2 mL) and left at room temperature overnight and then at -35 °C for a few days to give **7**.

Crystallographic data for **7** were collected on a Bruker SMART APEX-2 using Cu Kα radiation. Final agreement indices were R1 (all) = 6.87% and R2 (all) = 14.98%. All atoms were refined anisotropically. Selected crystallographic data appear in Table 2.

**4.12. Reaction of 7 with 5 at Low Temperature.** A stock solution of **5** (0.25 M) was prepared in C<sub>6</sub>D<sub>5</sub>Cl in a glovebox at room temperature. Upon generating **7** in C<sub>6</sub>D<sub>5</sub>Cl (0.1 mmol, 1.0 equiv) in a screw-cap NMR tube, an aliquot of the stock solution of **5** (400 μL, 0.1 mmol, 1.0 equiv) was added by syringe at -40 °C. The NMR tube was then placed in the precooled NMR probe at -40 °C. The progress was monitored by <sup>1</sup>H, <sup>31</sup>P{<sup>1</sup>H}, and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy. Observations are summarized in the text.

**4.13. Typical Procedures for Cleavage of PhOMe Catalyzed by the Mixture of Cationic Complex, 1, and Dihydride Complex, 5.** A stock solution (**A**) of **1** (33.3 mM) and a stock solution of **5** (50 mM) (**B**) were respectively prepared in C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub> in a glovebox. An aliquot (50–150 μL, 0.5–1.5 mol % **5**) of stock solution **B** was added by syringe to an aliquot (150 μL, 1 mol % **1**) of stock solution **A** in a J. Young NMR tube. C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub> (100–0 μL) was added to keep the total amount of C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub> at 300 μL. Triethylsilane (175 μL, 1.1 mmol, 2.2 equiv) and anisole (54 μL, 0.5 mmol, 1 equiv) were then added to the solution, and the contents were well shaken. The reaction was monitored by anisole loss relative to the CH<sub>3</sub>CH<sub>2</sub>- groups of the silanes [sum of (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>SiH and (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>SiOPh] with respect to time by <sup>1</sup>H NMR spectroscopy. The data were analyzed using the method of initial rates.

**4.14. Kinetic Studies of Cleavage of PhOMe with Various Amounts of Et<sub>3</sub>SiH Catalyzed by 1 and 5.** A stock solution of the mixture of **1** (12.5 mM) and **5** (12.5 mM) was prepared in C<sub>6</sub>D<sub>4</sub>Cl<sub>2</sub> in a glovebox. Triethylsilane (80–160 μL, 0.5–1.0 mmol, 1–2 equiv) and anisole (54 μL, 0.5 mmol, 1 equiv) were added by syringe to an aliquot (400 μL) of this stock solution in a J. Young NMR tube, and the contents were well shaken. The reaction was monitored by anisole loss relative to the CH<sub>3</sub>CH<sub>2</sub>- groups of the

- (21) (a) Ishihara, K. In *Lewis Acids in Organic Synthesis*; Yamamoto, H., Ed.; Wiley-VCH: Weinheim, 2000; Vol. 1, p 91. (b) Kocienski, P. J. *Protecting Groups*; Thieme: Stuttgart, New York, 1994; p 42.  
(22) (a) Alaimo, P. J.; Peters, D. W.; Arnold, J.; Bergman, R. G. *J. Chem. Educ.* **2001**, *78*, 64. (b) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

silanes [sum of  $(\text{CH}_3\text{CH}_2)_3\text{SiH}$  and  $(\text{CH}_3\text{CH}_2)_3\text{SiOPh}$ ] with respect to time by  $^1\text{H}$  NMR spectroscopy. The data were analyzed using the method of initial rates.

**4.15. Cleavage of PhOMe with  $\text{Et}_3\text{SiH}$  Catalyzed by  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ .** Anisole ( $54 \mu\text{L}$ , 0.5 mmol, 1 equiv) was added to a solution of  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  (4.6 mg, 0.005 mmol, 1 mol %) in  $\text{C}_6\text{D}_4\text{Cl}_2$  (0.3 mL) in a medium-walled J. Young NMR tube. Triethylsilane ( $175 \mu\text{L}$ , 1.1 mmol, 2.2 equiv) was then added, and the reaction was allowed to stand at room temperature and was monitored by anisole loss relative to the  $\text{CH}_3\text{CH}_2-$  groups of silanes [sum of  $(\text{CH}_3\text{CH}_2)_3\text{SiH}$  and  $(\text{CH}_3\text{CH}_2)_3\text{SiOPh}$ ] with respect to time by  $^1\text{H}$  NMR spectroscopy.

**4.16. Cleavage of  $\text{Et}_2\text{O}$  with  $\text{Et}_3\text{SiH}$  Catalyzed by  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ .** Triethylsilane ( $175 \mu\text{L}$ , 1.10 mmol, 2.2 equiv) was added to a solution of  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  (4.6 mg, 0.005 mmol, 1 mol %) in  $\text{C}_6\text{D}_4\text{Cl}_2$  (0.3 mL) in a medium-walled J. Young NMR tube. Diethyl ether ( $52 \mu\text{L}$ , 0.5 mmol, 1 equiv) was then added, and the reaction was allowed to stand at room temperature and was monitored by  $\text{Et}_2\text{O}$  loss relative to the  $\text{CH}_3\text{CH}_2-$  groups of the silanes [sum of  $(\text{CH}_3\text{CH}_2)_3\text{SiH}$  and  $(\text{CH}_3\text{CH}_2)_3\text{SiOEt}$ ] with respect to time by  $^1\text{H}$  NMR spectroscopy.

**4.17. In Situ Generation and NMR Spectroscopic Characterization of Methylphenyl(triethylsilyl)oxonium Ion, **10**.** Dry  $\text{C}_6\text{D}_6$  (0.4 mL) was added to a screw-cap NMR tube with  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  (46 mg, 0.05 mmol, 1.0 equiv) in a drybox. To this suspension was then added triethylsilane ( $9 \mu\text{L}$ , 0.056 mmol, 1.13 equiv), and the tube was quickly inverted to ensure complete mixing. Light-brown oil was produced. The clear top phase was removed by syringe, and the oil was washed with  $\text{C}_6\text{D}_6$  (0.1 mL  $\times$

2). The oil was dissolved in  $\text{C}_6\text{D}_5\text{Cl}$  (0.6 mL), and the solution was cooled down to  $-40^\circ\text{C}$ . Anisole ( $20 \mu\text{L}$ , 0.19 mmol, 3.7 equiv) was added by syringe, and the NMR tube was then placed in the precooled NMR probe at  $-40^\circ\text{C}$ . Oxonium ion **10** and free anisole coalesce under these conditions due to rapid exchange on the NMR time scale. The  $^1\text{H}$  spectrum shows the triethylsilyl group resonances at  $\delta$  0.54 ( $\text{CH}_3$ ) and 0.32 ( $\text{CH}_2$ ), and broad bands at  $\delta$  3.42 for the methyl protons of the  $-\text{OCH}_3$  group. The  $^{13}\text{C}\{^1\text{H}\}$  shows, in addition to the  $\text{B}(\text{C}_6\text{F}_5)_4^-$  counteranion [ $\delta$  148.8 (d), 138.8 (d), 136.9 (d), 124.5 (br)] and free PhOMe [line broadenings observed,  $\delta$  159.7 (br), 130 (br, overlapped with  $\text{C}_6\text{D}_5\text{Cl}$ ), 121.0 (br), 114.1 (br)], two major signals corresponding to the triethylsilyl group at  $\delta$  3.6 and 5.4.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_5\text{Cl}$ , 500.13 MHz,  $-40^\circ\text{C}$ ):  $\delta$  7.16 (br), 6.96 (br), 6.75 (br), 3.42 (br), 0.54 (m), 0.32 (m).  $^{29}\text{Si}\{^1\text{H}\}$  DEPT 45 ( $\text{C}_6\text{D}_5\text{Cl}$ , 99.35 MHz,  $-40^\circ\text{C}$ )  $\delta$  77.2. The  $^{29}\text{Si}$  shift of  $\delta$  77.2 clearly indicates formation of  $\text{Et}_3\text{SiOMePh}^+$  (**10**) as exchange of PhOMe with silicon-bound PhOMe will not affect the  $^{29}\text{Si}$  resonance.

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**Supporting Information Available:** CIF file containing X-ray crystallographic data for **7**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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