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Influence of Lewis Acid and Solvent in the Hydrosilylation of Aldehydes and Ketones with Et_3SiH; Tris(pentafluorophenyl)borane $B(C_6F_5)_3$ versus Metal Triflates [$M(OTf)_3$; M = Sc, Bi, Ga, and Al] – Mechanistic Implications

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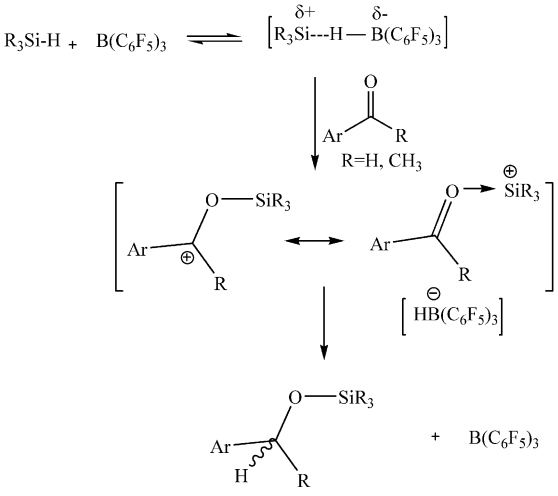
The scope of the $B(C_6F_5)_3$-catalyzed hydrosilylation of (X)Ph–CH=O and (X)Ph–C(R)=O was expanded to include a large set of substitutents (X = H, *p*-Me, *o*-Me, *p*-F, *o*-F, *p*-Cl, *p*-Br, *p*-NO_2, *m*-NO_2, *p*-Et; R = Me or CF_3). Reactions proceed at room temperature with high chemoselectivity in a host of solvents (toluene, benzene, CCl_4, 1,2-dichloroethane, and methylcyclohexane), or under solventless conditions, with hydrosilylation yields ranging from 85 to 95 % (for aldehydes) and 71 to 100 % (for ketones) and no noticeable solvent dependency of hydrosilylation yields. Replacing $B(C_6F_5)_3$ for $M(OTf)_3$ (M = Bi, Al, Ga, Sc) causes a dramatic change in chemoselectivity, forming dibenzyl ether and benzylated solvent (with toluene and benzene), with hydrosilylation products becoming negligible in most cases. The $M(OTf)_3$-catalyzed reactions thus represent a practical method for the synthesis of dibenzyl ethers. Remarkably, substantial amounts of dibenzyl ether was formed in the $B(C_6F_5)_3$-catalyzed reactions, when MeCN was used as solvent. Mechanistic implications of these Lewis acid catalyzed reactions are discussed.

Introduction

The mechanism of $B(C_6F_5)_3$-catalyzed hydrosilylation of carbonyl compounds was examined by Parks and Piers[1,2] through kinetic studies, competitive experiments, kinetic isotope effect measurement, isotope labeling, and crossover experiments. It was shown that whereas the most basic substrates were reduced selectively in competitive experiments, the least basic substrates were hydrosilylated more rapidly. Furthermore, increased concentrations of substrate had a rate-lowering effect. On the basis of these and other controls, the mechanism outline in Scheme 1 was postulated.

The key role of $B(C_6F_5)_3$ is to polarize the Si–H bond to form an incipient silylium/hydridoborate ion-pair species, which is attacked by the carbonyl oxygen atom to form a resonance-stabilized silylcarboxonium ion, which is then selectively reduced by $[HB(C_6F_5)_3]^-$. Similar mechanisms involving the $B(C_6F_5)_3$/silane reagent were proposed by Piers et al. for the conversion of imines to amines[3] via a silyliminium ion, and for the hydrosilylation of silyl enol ethers,[4] and by Gevorgyan et al.[5] for the hydrosilylation of olefins via a β-silyl-stabilized carbocation, to which hydride is delivered by $[HB(C_6F_5)_3]^-$.



Scheme 1. Mechanism of the $B(C_6F_5)_3$-catalyzed hydrosilylation.

An interesting feature of carbonyl hydrosilylation studies of Parks and Piers[1,2] is that, although the reactions are run in toluene (or in benzene), products arising from capture of the silylcarboxonium ion by the solvent are not formed.

By employing a silane with a stereogenic silicon center as a mechanistic probe, Rendler and Oestreich[6] recently proposed a more refined mechanistic picture for the $B(C_6F_5)_3$-catalyzed hydrosilylation of carbonyl groups involving a concerted S_N2-Si mechanism via a four-centered cyclic transition state, thus excluding the formation of a free silylium ion.

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Metal(III) triflates, in particular $Sc(OTf)_3$, $Bi(OTf)_3$, $Ga(OTf)_3$ and $Al(OTf)_3$ have been extensively employed in recent years in a variety of organic transformations, in particular for electrophilic/carbocationic chemistry, not only in conventional molecular solvents but also in green media.[7–14]

The aim of the present study was to examine the utility of $M(OTf)_3/Et_3SiH$ systems for carbonyl activation/reduction, for parallel comparison with the results obtained with $B(C_6F_5)_3/R_3SiH$.

Results and Discussion

We began our studies by extending the scope of aldehyde and ketone substrates in the hydrosilylation by the $B(C_6F_5)_3/Et_3SiH$ system. Thus, benzaldehydes and acetophenones bearing a diverse set of isomeric electron-donating and electron-withdrawing substituents were efficiently hydrosilylated at room temperature by employing 2 mol-% of $B(C_6F_5)_3$ and with a substrate/silane ratio of 1:1. Reactions proceeded quickly (GC monitoring), but were typically allowed to continue overnight. The results are summarized in Tables 1 and 2. Hexaethyldisiloxane was present in all reaction mixtures in variable amounts, due to the presence of adventitious water,[15] but this had no noticeable effect on the hydrosilylation efficiency. The hydrosilylation of *p*-fluoroacetophenone was studied in toluene and in CCl_4 with nearly equal outcomes. The hydrosilylation of (trifluoromethyl)acetophenone took place quantitatively (GC). As an extension, the hydrosilylation of *p*-fluorobenzaldehyde was examined under solventless conditions and found to work equally well.

Table 1. Scope of hydrosilylation of benzaldehydes with Et_3SiH and $B(C_6F_5)_3$ in toluene.

Benzaldehyde	Hydrosilylation product	Unreacted starting material	Trace unknown
X = H	87%	6%	4%, 1%, 2%
X = *p*-Me	87%	13%	–
X = *o*-Me	75%	5%	7%, 2%, 5%, 6%
X = *p*-F	95%	3%	2%
Neat	91%	8%	1%
X = *o*-F	86%	10%	3%, 1%
X = *p*-Cl	94%	6%	–
X = *p*-Br	93%	7%	–
X = *p*-NO_2	92%	3%	5%
X = *m*-NO_2	95%	4%	1%
X = *p*-Et	85%	9%	6%

Table 2. Scope of hydrosilylation of aromatic ketones with Et_3SiH and $B(C_6F_5)_3$ in toluene or CCl_4 at room temperature.

ArC(O)R	Hydrosilylation product	Unreacted starting material	Trace unknown
X = H	88%	12%	–
X = *p*-Me	85%	13%	2%
X = *o*-Me	92%	5%	3%
X = *p*-F		–	3%
in toluene	97%	2%	–
in CCl_4	98%		
X = *o*-F	91%	5%	4%
X = *p*-Cl	96%	1%	2%, 1%
X = *p*-Br	96%	2%	2%
X = *p*-NO_2	89%	8%	3%
X = H and R = CF_3	100%	–	–
X = *p*-Et	71%	24%	2%, 1%, 1%, 1%

By using *p*-fluorobenzaldehyde as a test substrate, the hydrosilylation reactions were performed in several other solvents. The results (Table 3) clearly show that the nature of the solvent has little or no effect on the overall efficiency, underscoring the highly robust nature of the $B(C_6F_5)_3/R_3SiH$ system for carbonyl reduction.

Focusing on $M(OTf)_3/Et_3SiH$ systems, reactions were set up analogously to those with $B(C_6F_5)_3/Et_3SiH$, typically with 2 mol-% of the metal triflate, with substrate/silane ratios of 1:1, in toluene or in benzene as solvent. Reactions (assisted by initial sonication) were performed at room temperature or at 65 °C. The results are summarized in Table 4.

It can be seen that the main products of these reactions were the corresponding dibenzyl ethers and benzylated solvent (3 isomers with toluene in each case, with near equal *ortho*/*para* ratios and with the *meta*-tolyl isomer typically in <5%), with little or no hydrosilylation products being detected in the mixture, depending on the Lewis acid and the substrate. Table 5 gives a survey of the reactions of the $M(OTf)_3/Et_3SiH$ systems with representative benzaldehydes under solventless conditions and sonication at room temperature. In all cases, dibenzyl ethers were formed in respectable yields.

Reactions with the ketones were carried out in a similar fashion at room temperature or at 65 °C in toluene or in DCE as solvent, or were run neat. The results are summarized in Table 6. The acetophenone reactions were overall less efficient, with more substrates remaining unreacted. GC analysis of the reaction mixtures showed that dibenzyl ethers were the primary products in DCE, whereas in toluene more benzylated solvent was formed and no hydrosilylation products were detected. Among the metal triflates

Table 3. Reaction of *p*-fluorobenzaldehyde with Et_3SiH and with $B(C_6F_5)_3$ in selected solvents.

	Toluene	Benzene	CCl_4	Dichloroethane	Methylcyclohexane
Hydrosilylation product	95%	98%	98%	91%	100%
Unreacted substrate	3%	–	2%	8%	–
Trace unknown	2%	2%	–	1%	–

Table 4. Reaction of benzaldehydes with Et_3SiH and $M(OTf)_3$ in toluene (or benzene) at 65 °C (or at room temperature).

Substituent	Lewis acid $M(OTf)_3$ M	Hydrosilylation product	Benzylated solvent	Benzyl ether	Unreacted substrate	Trace unknown
p-H	Bi[a,b]	–	2%	85%	12%	1%
	Al	–	9%	91%	–	–
	Ga	1%	30%	69%	–	–
p-CH_3	Bi[a,b]	–	22%	78%	–	–
	Al	–	77%	16%	5%	2%
	Ga[b]	2%	11%	55%	32%	
	Ga	1%	13%	69%	17%	–
	Sc[b]	3%	6%	53%	38%	–
p-F	Bi[a]	–	87%	12%	1%	–
	Bi[b]	–	12%	73%	14%	–
	Bi[c]	–	54%	–	38%	1%
	Al	–	39%	55%	5%	1%
	Ga[b]	–	–	54%	45%	1%
	Sc	–	22%	49%	27%	1%, 1%
p-Cl	Bi[a,b]	3%	1%	77%	15%	4%
	Al	5%	11%	68%	14%	2%
	Ga	2%	9%	70%	5%	7%, 1%, 4%, 2%
	Sc	21%	–	51%	28%	–
p-Br	Bi[a,b]	–	5%	90%	4%	1%

[a] $Bi(OTf)_3$-catalyzed reactions run in toluene had 2 mol-% catalyst. All others used 4 mol-%. [b] At room temperature. [c] In benzene.

Table 5. Solventless reactions of benzaldehydes with Et_3SiH and $M(OTf)_3$ at room temperature.

Substituent	$M(OTf)_3$ M	Hydrosilylation product	Benzyl ether	Unreacted substrate	Trace unknown
p-H	Bi	–	93%	–	1%, 2%, 4%
	Al	–	100%	–	–
	Ga	1%	99%	–	–
	Sc	–	94%	–	6%
p-CH_3	Bi	–	53%	14%	6%, 7%, 6%, 3%, 11%
	Al	–	100%	–	–
	Ga	–	88%	12%	–
	Sc	–	91%	9%	–
p-F	Bi	–	94%	–	–
	Al	–	97%	3%	–
	Ga	–	100%	–	–
	Sc	–	93%	2%	5%

Table 6. Reaction of acetophenones with $M(OTf)_3/Et_3SiH$ in toluene (DCE or neat if stated) at 65 °C (unless otherwise stated).

Substituent	$M(OTf)_3$ M	Hydrosilylation product	Benzylated solvent	Benzyl ether	Unreacted substrate	Unknown impurities and/or by-products
p-H	Bi	–	51%	14%	35%	–
p-F	Bi DCE	–	–	57%	36%	3%, 4%
	neat, room temp.	–	–	9%	42%	22%, 6%, 2%, 4%, 3%, 9%, 3%
p-Cl	Bi	–	56%	6%	28%	1%, 8%, 1%
	neat, room temp.	–	–	61%	16%	5%, 4%, 1%, 13%
	Ga, neat, room temp.	–	–	33%	65%	2%
	Sc, neat, room temp.	–	–	8%	92%	–
p-Br	Bi	–	49%	–	38%	1%, 7%, 3%, 2%

tested, $Sc(OTf)_3$ was the least effective, showing no conversion with *p*-fluoroacetophenone in toluene or in CCl_4.

To further examine the influence of solvent on the conversions and chemoselectivity with $M(OTf)_3/Et_3SiH$ systems, representative benzaldehydes were allowed to react in DCE or in CCl_4 at 65 °C or at room temperature. In all cases, the dibenzyl ethers were formed in respectable yields (Table 7). It is noteworthy that hexaethyldisiloxane was consistently formed as byproduct in the reactions of $M(OTf)_3/Et_3SiH$ systems with both aldehydes and ketones.

Collectively, the results obtained with $M(OTf)_3/Et_3SiH$ systems versus the $B(C_6F_5)_3/Et_3SiH$ system point to a fundamental difference in the mechanism of these transformations, with the former system producing dibenzyl ethers and benzylated solvent (with toluene and benzene), and the latter being highly selective to hydrosilylation.

In a much earlier study, Olah et al.[16] had reported on a general ether synthesis method by employing TMSOTf or TMSI with Et_3SiH. A condensation reaction between a silylcarboxonium ion and the hydrosilylation product was

Table 7. Reaction of benzaldehyes with $M(OTf)_3/Et_3SiH$ in DCE (or CCl_4) at room temperature (or at 65 °C).

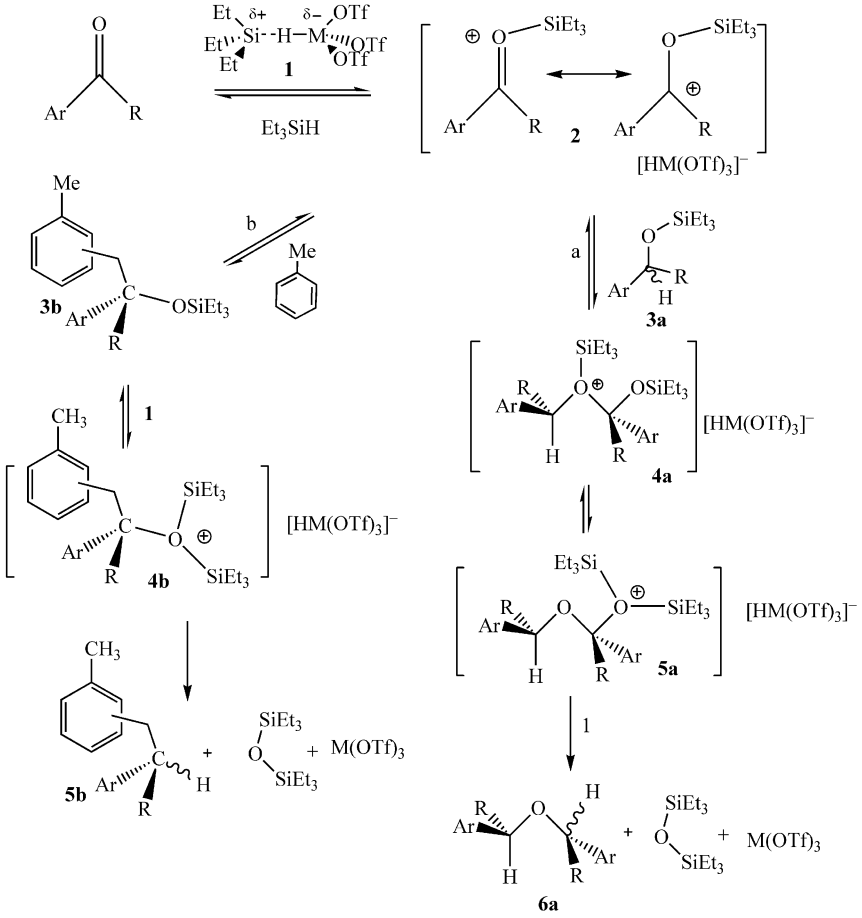
Substituent	$M(OTf)_3$ M	Hydrosilylation product	Benzyl ether	Unreacted substrate	Trace unknown
p-H	Ga	–	100%	–	–
p-CH_3	Al	–	89%	11%	–
p-F	Bi	–	89%	10%	1%
	Al	–	92%	8%	–
	Ga	–	97%	3%	–
	Sc, CCl_4, 65 °C	–	95%	–	1%, 1%, 3%
p-Cl	Bi, CCl_4	3%	95%	2%	–
	Al	–	81%	19%	–
	Sc	5%	85%	11%	–

suggested to account for the formation of ethers in those reactions.

The results obtained in the present study with $M(OTf)_3/Et_3SiH$ systems can be explained by modifications of Piers' and Olah's mechanisms, as outlined in Scheme 2. A condensation reaction between the incipient silylcarboxonium ion **2** and the hydrosilylation product **3a** leads to the silyloxonium ion **4a**. A silyl shift followed by loss of hexaethyldisiloxane and hydride quenching furnishes the observed dibenzyl ether **6a**. When aromatic solvents are employed, path b becomes operative, which leads to the observed benzylated toluene isomers **5b** (or $ArCH_2Ph$ in the case of benzene). Formation of solvent-capture products become more pronounced in reactions carried out at 65 °C as compared to room temperature (see Table 4).

The key difference between the mechanistic outcomes outlined in Scheme 2, appears to be related to the difference in the lifetime of the incipient silylcarboxonium ion, enabling a condensation between **2** and **3a** in the case of $M(OTf)_3/Et_3SiH$ systems.

Several control experiments were performed (see Experimental Section) to determine if **6a** (Scheme 2) might originate from in situ reaction of **3a** under the influence of $M(OTf)_3$, without the carbonyl compound. These proved



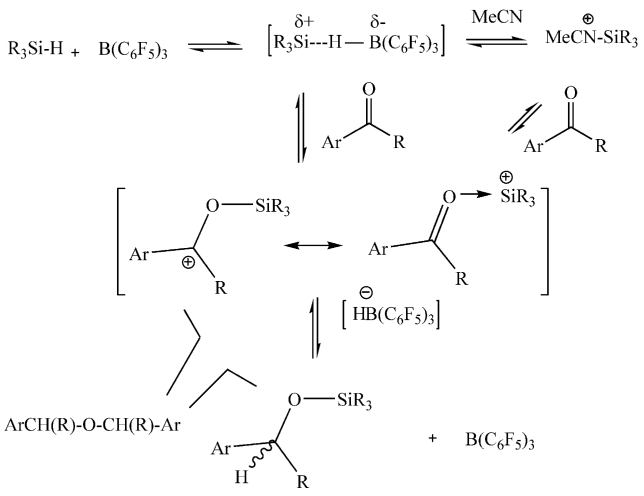
Scheme 2. Suggested mechanism for the reaction of aldehydes or ketones with $M(OTf)_3/R_3SiH$ systems.

negative. Another control experiment indicated that **6a** and **5b** are not formed via the ternary system aldehyde/$M(OTf)_3$/toluene in the absence of silane.

To gain further insight into the mechanism, in selected cases the reaction of benzaldehydes with the $B(C_6F_5)_3/Et_3SiH$ system was studied in MeCN as solvent (Table 8). Remarkably, this caused a change in chemoselectivity, forming dibenzyl ether along with the usual hydrosilylation product. This outcome can be accommodated by equilibrium formation of silylnitrilium ion as outlined in Scheme 3. The net result of this partitioning effect is to slow down the hydride transfer and quenching of the silylcarboxonium ion, thus allowing for intermolecular reaction of the two species forming dibenzyl ether. It is also noteworthy that representative acetophenones (with X = H, F, and Cl) did not react with $M(OTf)_3/Et_3SiH$ in MeCN as solvent.

Table 8. Reactions of benzaldehydes with $B(C_6F_5)_3$ in acetonitrile at room temperature.

Substituent	Hydrosilylation	Dibenzyl ether	Unreacted substrate
p-CH_3	13%	73%	14%
p-F	4%	46%	50%
p-Cl	44%	17%	39%



Scheme 3. Modified Piers mechanism for the $B(C_6F_5)_3/R_3SiH$ system in MeCN solvent.

Conclusion

The present study examines the efficacy of $M(OTf)_3/Et_3SiH$ systems for carbonyl activation/reduction and provides a parallel comparison with the $B(C_6F_5)_3/R_3SiH$ system.

Whereas both systems are quite effective in carbonyl activation/reduction, they exhibit markedly different chemoselectivities. The $B(C_6F_5)_3/R_3SiH$ reagent is highly efficient for hydrosilylation of a wide variety of aromatic aldehydes and ketones in a wide range of solvents or without solvent. The $M(OTf)_3/Et_3SiH$ system, on the other hand, is highly selective to the formation of dibenzyl ethers. The reactions can be carried out in aromatic solvents, in which case the formation of benzylated solvent competes. This can be avoided by performing the reaction in nonaromatic solvents such as DCE or CCl_4 or under solventless conditions. The ready availability of $M(OTf)_3$ (M = Bi, Sc, Al, Ga), use of only 2–4 mol-% of the Lewis acid and a simple setup requiring no special precautions make the $M(OTf)_3/Et_3SiH$ system synthetically attractive for the preparation of dibenzyl ethers from aldehydes and ketones. From a mechanistic standpoint, taking into account the mechanisms outlined in Scheme 2, the key difference between the two systems lies in the lifetime of the incipient silylcarboxonium ion, which permits its reaction with the hydrosilylation product, thus leading to ethers. Remarkably, the $B(C_6F_5)_3/R_3SiH$ system produces dibenzyl ether, when MeCN is used as solvent. It is suggested that this stems from equilibrium formation of silylnitrilium ion (Scheme 3).

Experimental Section

General: The Lewis acids $B(C_6F_5)_3$, $Bi(OTf)_3$, $Al(OTf)_3$, $Sc(OTf)_3$ were high-purity commercial samples and were used without further purification. $Ga(OTf)_3$ was synthesized and dried according to the procedure reported by Prakash et al.[13] The Et_3SiH samples were freshly opened commercial products which were used as received. The solvents employed (toluene, benzene, 1,2-dichloroethane, CCl_4, MeCN, and methylcyclohexane) were of high purity (HPLC grade or anhydrous) and were used without additional purification. The aldehyde and ketone substrates were either available from earlier studies in our laboratory or were purchased from commercial sources. Their purities were checked by GC prior to use and determined to be >98%.

General Synthetic Procedures with $B(C_6F_5)_3/Et_3SiH$: The hydrosilylation procedures were analogous to those reported by Piers et al.[1,2] The reactions employed 2 mol-% Lewis acid and a 1:0 to 1:0 stoichiometry of substrate/silane. They were carried out in small Schlenk tubes under a blanket of nitrogen. In selected cases, the reaction progress was periodically monitored by GC. The reactions were allowed to continue overnight whilst stirring, and the mixtures were subsequently analyzed by GC, GC-MS and/or by coinjection with authentic silyl ethers (see further). GC analysis in all cases showed the hydrosilylation products as the major component, along with some unreacted starting material, and traces of impurities/unknowns. Hexaethyldisiloxane was present in variable amounts in all reaction mixtures. The reported yields are GC yields and are not corrected for response factor (hexaethyldisiloxane was not included in determining GC conversions). To demonstrate the feasibility, the hydrosilylation of *p*-fluorobenzaldehyde was run with no solvent. In this case, a short 5-mm NMR tube was used as reaction vessel, and instead of magnetic stirring the tube was immersed in an ultrasonic bath for 3 h, and the reaction mixture was analyzed by GC afterwards.

General Synthetic Procedure with $M(OTf)_3/Et_3SiH$ Systems: Triethylsilane (0.96 mmol, 111.6 mg) was added to a mixture of 2.5 mL of solvent, 2 mol-% of the Lewis acid (4 mol-% for the noted reactions with bismuth triflate), and 1 equiv. of the substrate. Addition of metal triflates to the aldehydes led to notable color changes even at room temp., whereas no such color changes were observed with the ketones. The reactions were carried out in small Schlenk tubes with magnetic stirring under nitrogen. To increase the contact between the liquid phase and the metal triflates, the reaction mixtures

were first sonicated at room temp. for 1 h, then stirred at room temp. or at 65 °C in an oil bath (see tables). For the solventless reactions, the silane/substrate/Lewis acid ratios were the same, but no solvent was employed. The reactions were performed in short 5-mm NMR tubes as described for the $B(C_6F_5)_3/Et_3SiH$ system.

Synthesis of Authentic Silyl Ethers: In several cases authentic samples of the silyl ethers (the hydrosilylation products) were independently synthesized by treating the corresponding benzyl alcohols (parent, *p*-CH_3, *p*-F, and *m*-NO_2) and α-methylbenzyl alcohols (parent and *p*-F) (all commercial samples) with Et_3SiCl/imidazole in CH_2Cl_2 as solvent. Typically, a mixture of chlorotriethylsilane (2 mmol, 301.4 mg) in CH_2Cl_2 (5 mL) was added dropwise to a mixture of a given benzyl alcohol (1 equiv.) and imidazole (2 mmol, 136.2 mg) in CH_2Cl_2 (20 mL) at room temp., whereupon the imidazolium chloride rapidly precipitated out of solution. After 1 h of stirring at room temperature, the salt was filtered. The protected alcohols were analyzed by GC and subsequently used for co-injection with the hydrosilylation reaction mixtures.

Synthesis of Authentic Solvent Benzylation Products (Diarylmethanes) and Dibenzyl Ethers: The cation exchange resin catalyzed benzylation of aromatics reported by Latcher et al.[17] was adopted as a method to prepare the corresponding diarylmethanes and the dibenzyl ethers together for GC and GC-MS comparisons with the corresponding products formed in the $M(OTf)_3/Et_3SiH$ reactions. The following alcohols were used for authentic sample synthesis: benzyl alcohols (with *p*-CH_3, *p*-F, and *m*-NO_2) and α-methylbenzyl alcohols (parent and *p*-F) (all commercial samples). Typically, the benzyl alcohol (8 mmol) was added to a mixture of toluene (12 mmol, 115.7 mg) and Amberlyst-15 (400 mg). The reaction mixture was heated at 75 °C for 2–4 h, then the resin was filtered and the reaction mixture analyzed by GC and GC-MS.

Control Experiments. (A) An authentic sample of *p*-$MeC_6H_4CH_2OSiEt_3$ (150 mg, 0.635 mmol) was added to $Sc(OTf)_3$ (6.3 mg, 0.0127 mmol) and 1.6 mL of toluene, in the absence of *p*-tolualdehyde, and the reaction mixture was stirred at room temperature overnight. GC analysis showed no reaction. **(B)** In an effort to recreate conditions where only a small concentration of the hydrosilylation product would be present in the reaction mixture at any given time, authentic *p*-$MeC_6H_4CH_2OSiEt_3$ (100.9 μL) was added dropwise to a mixture of toluene and $Sc(OTf)_3$ (9.50 mg, 0.0193 mmol) with efficient stirring at room temperature over 2 h. Again, no reaction occurred. **(C)** *p*-Tolualdehyde (115.3 mg, 0.96 mmol) was added to a mixture of 2.5 mL of toluene and $Sc(OTf)_3$ (9.50 mg, 0.0193 mmol), and the reaction mixture was sonicated for 1 h and then stirred at room temperature overnight. The reaction mixture became orange. After standard workup, the organic layer (in CH_2Cl_2) was analyzed by GC, showing again no reaction.

Acknowledgments

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