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Tris(pentafluorophenyl)boron-Catalyzed Hydrosilation of Aromatic Aldehydes, Ketones, and Esters

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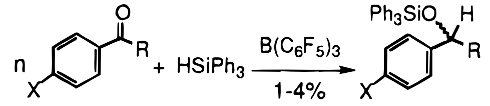
Hydrosilation of carbon−oxygen double bonds is a mild method for selective reduction of carbonyl functions. Although the reaction is exothermic, a catalyst is generally required to achieve adequate rates; consequently, many catalysts have been developed for this important reaction.[2] Nucleophilic/electrophilic hydrosilation catalysis is characterized by a synergic mechanism in which a nucleophile polarizes the Si−H bond of the silane reagent, while a Lewis acid electrophile activates the carbonyl by binding to oxygen. Among the nucleophiles that have been employed are amines[3] and halide ions,[4] and Lewis acids used include $ZnCl_2$[5] and $BF_3{\cdot}Et_2O$.[6]

Tris(pentafluorophenyl)borane[7] is a convenient, commercially available Lewis acid of comparable strength to BF_3 but without the problems associated with reactive B−F bonds. Although its primary commercial application is as a cocatalyst in metallocene mediated olefin polymerization,[8] its potential as a catalyst for organic transformations is beginning to be appreciated.[9] Herein we report its use as a catalyst for mild addition of Ph_3SiH to aromatic aldehyde, ketone, and ester carbonyl functions and the evidence we find for an unusual nucleophilic/electrophilic mechanism by which the reduction takes place.

Aromatic aldehydes, ketones, and esters were hydrosilylated at room temperature in the presence of 1−4 mol % $B(C_6F_5)_3$ and 1 equiv of Ph_3SiH; data for a selection of substrates are shown in Table 1.[10] For the aromatic substrates employed in this study, $B(C_6F_5)_3$ compares favorably with the best hydrosilation catalysts in terms of conversion rates and selectivity.[2] Limitation of the silane reagent to 1 equiv was essential for clean reactions since further reduction of the silyl ether or silyl acetal products was observed when excess silane was present. So limited, isolated yields of the silyl ethers were excellent, reflecting the >98% selectivity for product as determined by gas−liquid chromatography. Ester reductions were extremely rapid and were >90% selective for the acetal products; these could subsequently be converted to aldehydes in synthetically useful isolated yields.

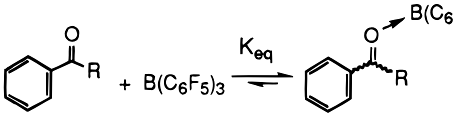
Table 1. $B(C_6F_5)_3$-Catalyzed Hydrosilation of Aromatic Aldehydes, Ketones, and Esters



E	R	X	%[a] Cat	n[b]	ton[c] (hr^{-1})	k_{obs}[d] ($s^{-1}\times10^4$)	Y[e] (%)
1a	H	H	2	1	19	6.0(1)	81
1b	H	CH_3			4	1.21(3)	82
1c	H	Cl			11	--	81
1d	H	NO_2			308	92(4)	96
2a	Me	H	2	1	45	12.4(3)	76
2b	Me	CH_3			12	3.61(7)	84
2c	Me	Cl			67	20.1(5)	80
2d	Me	NO_2			470	135(3)	91
3a	OEt	H	2	1	637[f]		80[h]
3b	OEt	CH_3			572[f]		
3c	OEt	Cl			--[g]		
3d	OEt	NO_2			--[g]		
4	H	H	1	1	18	2.75(6)	
			2		20	6.0(1)	
			3		21	9.2(2)	
			4		21	12.5(2)	
5	Me	H	2	1		12.3(2)	
				2		10.3(2)	
				4		7.7(2)	
				6		6.0(2)	
				10		4.1(2)	

[a] Mole percent of catalyst based on $[Ph_3SiH]$. [b] For $n = 1$, concentration = 0.385 M. [c] Turnover frequency. [d] First-order rate constant. [e] Isolated yield. [f] Reaction done at 0 °C. [g] Reactions too fast to follow by GC. [h] Yield of benzaldehyde.

For the unsubstituted substrates (X = H, entries 1a, 2a, and 3a, Table 1), the order of reactivity was ethyl benzoate ≫ acetophenone > benzaldehyde. Since it is generally assumed that coordination of the carbonyl oxygen to the electrophile is the means by which Lewis acids activate carbonyl substrates, this observation is surprising given that the strength of substrate binding to $B(C_6F_5)_3$ is in the opposite order. ^1H NMR experiments show that, in solution, binding of these substrates to $B(C_6F_5)_3$ is reversible and exchange between bound and free substrate is rapid;[11] the equilibria, however, strongly favor the adducts **1**. Equilibrium constants[12] for eq 1 are $2.1(1) \times 10^4$, $1.1(1) \times 10^3$, and $1.9(1) \times 10^2$ for R = H, Me, and OEt, respectively. Furthermore, competitive binding experiments revealed that the preferred order of binding is benzaldehyde > acetophenone ≫ ethyl benzoate,[13] consistent with experimentally determined binding energies of these compounds with BF_3.[14]



(1)

R = H, Me, OEt

1-H; **1-Me**; **1-OEt**

Since these equilibria favor the adduct, isolation and full spectroscopic and structural characterization[15] of the acid−base

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[10] See supporting information for further details.

[11] Rates of exchange ($k_{ex} = \pi/2\Delta\nu$) between $PhC(O)X_{bound}$ and $PhC(O)X_{free}$ as determined by VT ^1H NMR spectroscopy: X = H, 390 s^{-1}, 290 K; X = CH_3, 119 s^{-1}, 265 K; X = OEt, 811 s^{-1}, 203 K.

[12] Measured by ^1H NMR according to: Drago, R. S. *Physical Methods for Chemists*, 2nd ed.; Saunders: New York, 1992; p 257.

[13] Equilibrium constants for the competitive binding experiments: **1**-H + PhC(O)CH_3 ↔ PhC(O)H + **1**-Me, $5.45(5) \times 10^{-2}$; **1**-H + PhC(O)OEt ↔ PhC(O)H + **1**-OEt, $9.5(7) \times 10^{-3}$; **1**-Me + PhC(O)OEt ↔ PhC(O)CH_3 + **1**-OEt, $1.8(2) \times 10^{-1}$.

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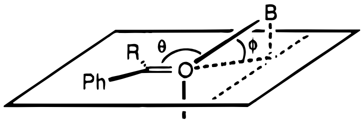
Table 2. Selected Metrical and Spectroscopic Data for Adducts **1**



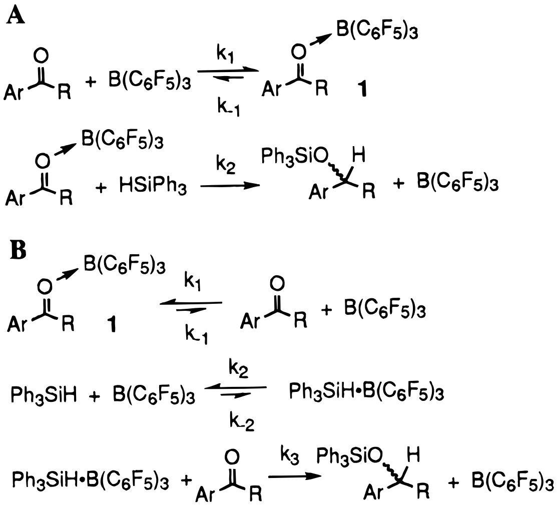
Property	1-H	1-Me	1-OEt
C=O, Å	1.241(7)	1.242(5)	1.253(5)
O-B, Å	1.610(8)	1.576(5)	1.594(5)
θ, °	126.7(5)	133.6(3)	221.8(4)
φ, °	4.6	4.2	15.6
Σ(C-B-C)	340.2	337.7	339.3
νCO, cm^{-1}	1620	1603	1669
δ^{13}CO, ppm	199.4	212.8	175.3
νCO, free	1702	1686	1718
δ^{13}CO, free	192.1	197.0	166.2

complexes **1**[16] was possible; Table 2 gives pertinent physical data for these compounds. Upon borane coordination, the chemical shifts of the carbonyl carbons shift to lower field and the ν_{CO} stretches decrease by 49 cm^{-1} for **1**-OEt and ≈80 cm^{-1} for **1**-H and **1**-Me versus that of the free substrate. **1**-OEt differs from the other two compounds in that the borane bonds to the lone pair *trans* to OEt,[17] rather than the phenyl group. Adduct **1**-OEt also has a significantly larger angle ϕ. Finally, the B–O bond distance is slightly longer in **1**-OEt than in **1**-H and **1**-Me, which are identical within experimental error. These differences support the notion that ester carbonyl binding is weaker than in **1**-H and **1**-Me but do not suggest an explanation for the much higher turnover numbers in the ester reductions.

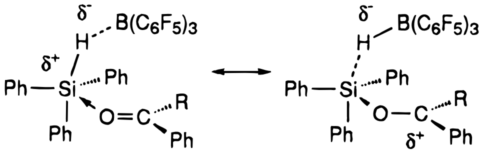
The hydrosilations were followed quantitatively by GLC ([substrate] = [Ph_3SiH] = 0.385 M). Plots of ln [Ph_3SiH] vs time were linear for several half-lives,[18] indicating that the reaction is first order in silane.[19] Other experiments (see entry 4, Table 1) indicate that k_{obs} is proportional to the amount of added Lewis acid catalyst. Within each series, the reactions were more rapid as X became more electron withdrawing.[20] Hammett plots using k_{obs} and σ^+ gave ρ values of 1.7(2) and 1.39(5) for the aldehyde and ketone series,[10] respectively; for R = OEt, the rates of hydrosilation were too fast to measure by this method for X = Cl or NO_2.

These kinetic experiments are consistent with a mechanism involving carbonyl activation through Lewis acid complexation followed by reaction with silane to give the products (Scheme 1A). For this mechanism k_{obs} is equivalent to $k_2[\mathbf{1}]$.[21] Depending on the relative magnitudes of the individual rate constants, this mechanism predicts that k_{obs} should show first order or no dependence on [substrate]. *As entry 5 of Table 1 shows, however, the magnitude of k_{obs} decreases as [acetophenone] rises in the ketone reduction.* A similar effect was observed in benzaldehyde reductions. This key observation leads to the conclusion that the role of the Lewis acid in this reaction is not to activate the carbonyl substrate and that liberation of "free" $B(C_6F_5)_3$ is required for productive reaction. A mechanism which yields a rate law[21] consistent with the observed dependence of k_{obs} on [substrate] is given in Scheme 1B. In accordance with this rate law, plots of k_{obs} vs $[B(C_6F_5)_3]_0$ and $1/k_{obs}$ vs [acetophenone] were found to be linear.[10] In this scenario, the substrate which binds the Lewis acid least effectively should be reduced the most rapidly, since more "free" borane is available. Thus, the paradoxical observation that the least basic substrates are reduced more rapidly is accommodated.[22]

Scheme 1



Scheme 2



The basicity of the substrate is, however, relevant in competitive reactions. When a 1:1 mixture of benzaldehyde and ethyl benzoate was subjected to standard hydrosilation conditions, *benzaldehyde was selectively reduced* at a turnover rate of ≈20 h^{-1}. Discriminitive reduction of the more basic substrate suggests that coordination of the carbonyl oxygen to silicon is important in the third step of mechamism B (Scheme 2). Thus, in an unusual variant of nucleophilic/electrophilic catalysis, the substrate itself serves to nucleophilically activate the Si–H bond, while hydride transfer is facilitated by the borane Lewis acid.[23] We are currently exploring the scope and synthetic utility of this unique hydrosilation reaction.

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Supporting Information Available: Listings of crystallographic data and ORTEP diagrams for **1**-H, **2**-Me, and **1**-OEt, experimental details, and representative kinetic plots (9 pages). See any current masthead page for ordering and Internet access instructions.

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(16) The structures of **1**-H, **1**-Me, **1**-OEt will be published elsewhere; spectroscopic details and ORTEP diagrams are included as supporting information.

(17) There is a well-documented electronic preference for Lewis acids to bind carbonyl lone pairs *trans* to electron donating groups. Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 256.

(18) These plots were linear for only 3–4 half-lives for ester reductions, at which point the observed rate of silane consumption declined. We believe this is due to a poisoning of the reaction due to production of small amounts of aldehydes (*vide infra*).

(19) Second order plots of 1/[Ph_3SiH] vs time were nonlinear.

(20) This may be attributed to the effect of X on the magnitude of K_{eq} for eq 1: For R = Me, K_{eq} for X = CH_3, 1.50(1) × 10^3; X = Cl, 3.40(5) × 10^2; X = NO_2, 6.0(1) × 10^1.

(21) Rate law derived for mechanism A: rate = $k_2[\mathbf{1}][\text{silane}]$. Rate law derived for mechanism B: rate = $(k_{-2}k_3/K_{eq})([\mathbf{1}][\text{silane}])/k_2 + k_3[\text{substrate}])$.

(22) A stepwise mechanism involving hydride abstraction from Ph_3SiH to form $[Ph_3Si]^+[HB(C_6F_5)_3]^-$ followed by borohydride reduction of a carbonyl–silyl cation complex is also consistent with the observed rate behavior. However, ^1H NMR spectra of $Ph_3SiH/B(C_6F_5)_3$ mixtures are *identical* to the spectrum of Ph_3SiH and observed rates of hydrosilation are *slower* in the more polar solvent CH_2Cl_2, arguing against such a stepwise process.

(23) If there is significant transfer of positive charge to the carbonyl carbon in the transition state of the third step in mechanism B, the energy will be lower for more electron releasing R, *i.e.* OEt ≫ CH_3 > H, so in addition to rate enhancements due to a decrease in K_{eq} for eq 1, transition state effects may reinforce observed reactivity trends.