Computed thermodynamic stabilities of silylium Lewis base adducts

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We report a computational study of the transfer of silylium from phosphine to hetero-atom containing Lewis bases including ethers, phosphines, and amines. The relative free energy of these compounds are compared to develop a thermodynamic scale of stabilites that can help interpret the chemoselectivity observed with complex natural products and bio-mass derived sugars. Both the choice of silane and the phosphine Lewis base impact the thermodynamics of this transfer.

Introduction

The use of silylium ions ("R_3Si^+") to activate Lewis bases for catalysis has proven to be of great importance in many synthetic applications.[1] The pronounced electrophilicity of the silylium ion requires stabilization by a Lewis base or solvent molecule as outside of situations with extreme steric congestion, the free ion is too high in energy.[2,3] The high Lewis acidity of the silylium ion can be attributed to the combination of an empty p-orbital on silicon, as well as an inefficient hyperconjugative stabilization of the electron deficient silicon cation.

While there are several methodologies for generating silylium ions *in situ*,[4] a common and mild method is through the activation of a hydrosilane with the perfluoroaryl borane catalyst $B(C_6F_5)_3$ (BCF). The BCF catalyst heterolytically activates the silane by adding a Lewis base to a transiently formed BCF-silane adduct.[5,6] The resulting stabilized silylium and borohydride ion pair can then act together to activate substrates for reduction (e.g. see Figure 1 for the phosphine variant[7] on ethers). The combination of BCF and silane is effective in a number of reductions,[8,9] including the reduction of bio-mass derived sugars,[10–13] ethers,[14] and imines.[15–17] Okuda has shown that Ph_3B can also activate silanes for amide reductions, though this appears to proceed by a different mechanism.[18]

Most recently, our group demonstrated that this methodology could also provide highly chemoselective transformations on complex natural products.[19] Through careful selection of Lewis acid catalyst and silane, the selective modification of diverse, densely functionalized molecules could be achieved. Important for sensitive compounds was the realization that the addition of a phosphine Lewis base attenuates the reactivity of the system (through the formation of a silyl-phosphonium ion), and seemingly acts as a silylium ion carrier that delivers silylium to the various Lewis basic sites in the molecule. This report was followed by an experimental and theoretical study on the role of silyl phosphonium ions as a silylium ion carrier and thermodynamic driver for catalyst speciation into the $[R_3Si–PR_3^+][H–BCF^-]$ ion pair (Figure 1).[7] With these studies in mind, we aimed to compute the "silaphilicty" of various Lewis bases, including phosphines, amines and oxygenated groups as a way to further understand how inherent Lewis base preferences might correlate with chemoselectivity in complex molecules.

Herein we report a computational investigation on the thermodynamic stability of Lewis base silylium adducts as a function of silane and Lewis base. These studies delineate optimum coordination geometries in addition to revealing comparative strengths of the Lewis bases that would be competing to coordinate a silylium ion in a complex molecule.

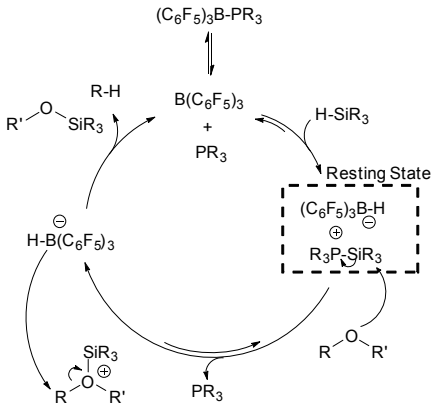

Figure 1. Phosphine-modified catalytic cycle for the BCF-catalyzed reduction of ethers.

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Electronic Supplementary Information (ESI) available: rationale for basis set choice, computational procedures, full Gaussian reference and optimized coordinates and energies. See DOI: 10.1039/x0xx00000x

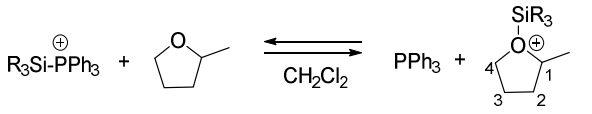
Computational Methods

All calculations were performed using the Gaussian 09[20] software package, revision E.01. The ωB97X-D[21] functional was used in conjunction with the 6-31G+**[22] basis set (see the Supporting Information for basis set rationale). Geometry optimizations were performed using standard gradient methods. Final geometry optimizations and frequency calculations were performed without symmetry constraints. The conductor-like polarizable continuum (CPCM)[23] solvation model was used with solvent parameters for dichloromethane. All free energy calculations were obtained by taking into account vibrational zero-point energies, thermal motions, and entropy contributions at standard conditions (298 K, 1 M).

Results and discussion

The reactivity and selectivity in the reduction of ethers and biomass-derived sugars is sensitive to the reducing silane. While steric bulk in the substrate can play a role in determining regioselectivity, it is the steric and electronic properties of the silane that impart the largest impact over chemoselectivity. We therefore began our study by computing ΔG for silylium exchange between triphenylphosphine and 2-methyltetrahydrofuran (2-Me-THF) as a function of silane (Table 1).

Table 1. Effect of substituents on free energy of transfer to 2-Me-THF.



R_3Si^+	ΔG[a]	ΔG_{ref}[a,b]	Si–P bond length[c]	Si–O bond length[c]	Δ C–O[c,d]
Me_3Si^+	3.1	0.0	2.333	1.818	0.031
Me_2EtSi^+	4.6	1.5	2.331	1.821	0.031
Et_3Si^+	2.5	-0.6	2.343	1.828	0.031
Me_2PhSi^+	4.1	1.0	2.333	1.819	0.028
Ph_3Si^+	8.5	5.4	2.337	1.808	0.036

[a]Free energy reported in kcal/mol. [b]ΔG_{ref} normalized to the free energy of Me_3SiH. [c]Bond lengths reported in Ångströms. [d]ΔC–O reflects the change in bond length between C1–O and C4–O of the silyloxonium. ΔC–O for the free 2-Me-THF is 0.006 Å.

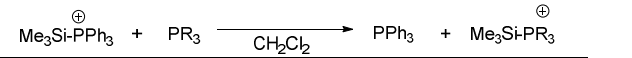
The results follow the trend that silylium-transfer from PPh_3 to 2-Me-THF becomes increasingly less favorable as the size of the R_3Si increases, presumably due to the short Si–O in the products (c.f. Si–P). The Et_3Si^+ group exhibits the lowest Gibbs free energy for transfer to 2-Me-THF at +2.5 kcal/mol, followed by Me_3Si^+ at 3.1 kcal/mol. While it is somewhat unexpected that the free energy of Et_3Si^+ is lower than that of Me_3Si^+, the calculated Si–P and Si–O bond lengths are longer (by 0.01 Å), which would alleviate steric congestion in the 2-Me-THF adduct (especially). The free energies for Me_2EtSi^+ and Me_2PhSi^+ transfer were calculated to be +4.6 and +4.1 kcal/mol, respectively. Of the five R_3Si's calculated, Ph_3Si^+ is the least favorable at +8.5 kcal/mol. Experimentally, bulkier silanes are less prone to ionization upon reacting with a combination of phosphine and BCF.[7] Those same studies demonstrated that triphenylsilane is only partially speciated by the combination of BCF and a triarylphosphine, while even bulkier silanes such as tri-*iso*-propylsilane are completely unreactive. To simplify the model and reduce computational costs, the following calculations were done using "Me_3Si^+".

We next aimed to study how the phosphine basicity and steric profile affects the thermodynamics of silylium transfer; experimentally both features play a crucial role in ionizing the silane with BCF. Phosphines such as PPh_3 make a stable and insoluble adduct with BCF, which provides little free BCF and phosphine to allow for silylium ion generation. Bulkier phosphines such as tri(*o*-tolyl)phosphine don't ionize bulkier silanes such as Et_3SiH, though the smaller Me_2EtSiH does efficiently heterolyze to give the silylphosphonium/ borohydride ion pair.[7]

The propensity to transfer Me_3Si^+ from triphenylphosphine to a broad array of phosphine Lewis bases is collected in Table 2. These calculations reveal the general trend that smaller, electron-rich phosphines are better able to stabilize a silylium ion relative to larger, electron deficient phosphines. The balance of steric and electronic factors is rather nuanced as demonstrated by trimesitylphosphine and di-*tert*-butyl(*o*-biphenyl)phosphine forming poor silyl-phosphoniums, while P^tBu_3 and PCy_3 are actually more stabilizing than PPh_3.

These computational studies correlate well to experimental results previously reported using triethylsilane.[7] For example, when [Et_3Si–PPh_2(*o*-biphenyl$^+$][H–BCF$^-$] (in the presence of 5 equivalents of free PPh_2(*o*-biphenyl)) is treated with 5 equivalents of PPh_2(*p*-tol), silylium transfer to the less sterically hindered phosphine occurs quantitatively. Computationally, the transfer of Me_3Si^+ from PPh_2(*o*-biphenyl) to PPh_2(*p*-tol) is thermodynamically favorable by 3 kcal/mol.

Table 2. Steric and electronic perturbations of phosphine Lewis base acceptor.

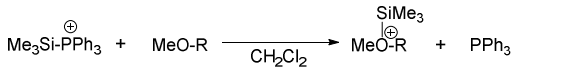


Phosphine	ΔG (kcal/mol)	Si–P bond length (Å)[a]	Δ Si–P (Å)[b]
P^tBu_3	-6.0	2.357	0.024
P(*p*-tol)$_3$	-3.9	2.330	0.003
PCy_3	-3.3	2.351	0.018
P(*o*-tol)$_3$	-2.2	2.367	0.035
PPh_2(*p*-tol)	-1.7	2.332	-0.001
PPh_2*i*Pr	-1.3	2.329	-0.004
PPh_2(*o*-biphenyl)	1.4	2.346	0.013
P(*p*-F-Ph)$_3$	2.3	2.336	0.003
P(1-naphthyl)$_3$	3.3	2.380	0.047
$PPh_2(C_6F_5)$	6.1	2.359	0.026
P(*p*-CF_3-Ph)$_3$	6.2	2.344	0.011
P(^{t}Bu)$_2$(*o*-biphenyl)	10.8	2.400	0.067
P(mesityl)$_3$	11.1	2.412	0.079

[a]The calculated Si–P bond length of Me_3Si–PPh_3^+ is 2.333 Å. [b]Δ Si–P measures the difference in bond length between the silyl-phosphonium and Me_3Si–PPh_3^+.

To begin comparing heteroatom-stabilizers of silylium, the thermodynamics of silylium transfer from $Me_3Si–PPh_3^+$ to simple ethers was studied. These calculations were designed to reveal how sterics affected the ether's ability to stabilize a silylium ion (Table 3). The transfer of silylium from the reference $Me_3Si–PPh_3^+$ to the simplest ether, dimethylether, is disfavored by +7.5 kcal/mol. The corresponding ethyl ether increases slightly (0.2 kcal/mol), while bulkier groups are even more destabilizing (+1.5 and +4.7 kcal/mol for ^{i}Pr and ^{t}Bu, respectively). Dimethoxyethane reports on how inductive deactivation of a β-OMe group lowers O-basicity (+9.9 vs. MeOEt at +7.7 kcal/mol). Despite increasing charge delocalization to the more substituted carbons (as reflected by ΔC–O), it is clear that sterics dominate the thermodynamics, and this would be enhanced for larger R_3Si^+ groups.

Table 3. Effect of substitution on methyl ether silylium acceptors.

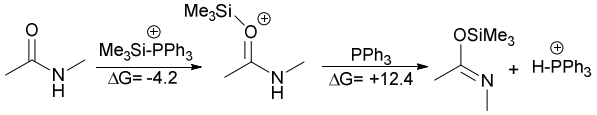


Ether	ΔG[a]	ΔΔG$_{ref}$[a,b]	Δ C–O[c,d]	ΔSi–O[c,e]
Me_2O	7.5	–	0.000	0.000
MeOEt	7.7	0.2	0.021	-0.011
MeO*i*Pr	9.0	1.5	0.050	-0.012
MeO*t*Bu	12.2	4.7	0.079	-0.001
$(MeOCH_2)_2$	9.9	2.4	0.002	-0.005

[a]Free energy reported in kcal/mol. [b]ΔG$_{ref}$ normalized to the free energy of Me_2O. [c]Bond lengths reported in Ångströms. [d]ΔC–O reflects the change in bond length between R–O and H_3C–O of the silyloxonium. [e]ΔSi–O reflects the change in bond length between O–Si of the silyl oxonium and O–Si of Me_2O–$SiMe_3^+$.

The stability of a collection of Lewis bases/functional groups commonly encountered in complex structures was assessed relative to PPh_3, the Lewis base added to inhibit decomposition in our work on Natamycin (vide infra). The tested groups include amines, ethers, epoxides, and carbonyls (Figure 2). Thermodynamic data on where silylium preferentially rests could provide insights into the chemoselectivity that is observed when reactive groups compete in complex natural products, sugars and other simpler substrates.

A limited number of substrates were more stabilizing than PPh_3, including aliphatic amines and amides, as well as triphenylarsine. DABCO has the most negative ΔG (-9.5 kcal/mol) and benefits from a reduced steric profile and the high basicity of the pre-pyramidalized nitrogen. Tertiary amides, including N,N-dimethylacetamide and N-acetylpyrrolidine, are more stabilizing than a secondary amide. We considered the possibility that the O-silylium adduct of a secondary amide might also be deprotonated by the PPh_3, however this reaction is computed to be disfavored by 12.4 kcal/mol in CH_2Cl_2 (Scheme 1).



Scheme 1. Potential reactivity pathway for N-methylacetamide.

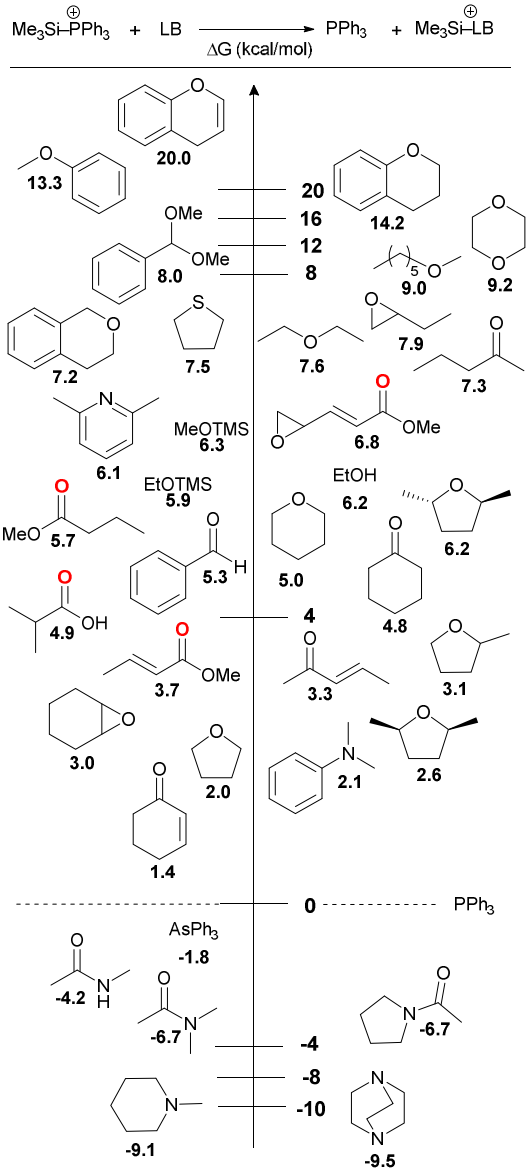


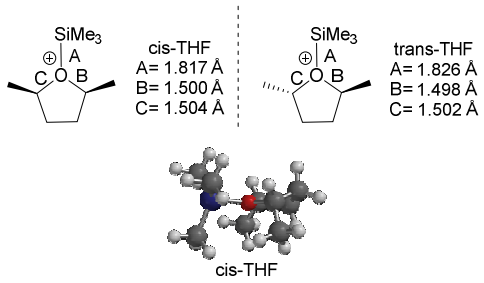
Figure 2. Thermodynamic Lewis basic stabilities of various substrates. The numbers in bold indicate the Gibbs free energy (in kcal/mol) for the transfer of Me_3Si^+ from $Me_3Si–PPh_3^+$ to the Lewis base. The heterolysis of $Me_3Si–PPh_3^+$ to PPh_3 and Lewis base free Me_3Si^+ is endergonic by 24.0 kcal/mol.

The majority of the calculated functional groups were less stabilizing than PPh_3. Cyclic and acyclic ketones follow the trend that the enones are lower in energy than their saturated counterparts—2-cyclohexenone is 3.4 kcal/mol more stabilizing than cyclohexanone, 3-penten-2-one is 4 kcal/mol lower than 2-pentanone, and methyl crotonate is 2 kcal/mol more stabilizing than methyl butyrate. The conjugate alkene thus provides 2-4 kcal/mol of extra stabilization. When an inductive electron withdrawing group is near the enoate, a

predictable reduction in stabilization is observed (3.1 kcal/mol). This array is present in Natamycin (vide infra). Recent reactivity initiated by Me_3Si^+ transfer to acetal ethers is also included in the above ranking.[4]

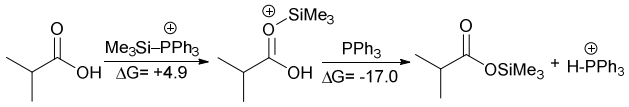
A comparison of the cyclic ethers was also informative. THF is 1.1 kcal/mol lower in energy than the 2-Me-THF, and it is 5.5 kcal/mol more stable than tetrahydrothiophene.[24] Tetrahydropyran (THP) is 4.2 kcal/mol lower in energy than 1,4-dioxane and is also lower in energy than isochroman, chromane, and 4H-chromene (2.2, 9.2 and 15.0 kcal/mol, respectively). Each of these latter cases reduces O-basicity through conjugation or inductive effects.

While most substrates followed reasonable trends, several cases stood out. The cis and trans 2,5-Me_2-THF optimizations revealed that silylium transfer to the cis-Me_2-THF is more favorable than the trans-Me_2-THF (by 3.7 kcal/mol). In the optimized geometries, the methyl groups of the cis-THF allow Me_3Si^+ to occupy a position more distal from the methyl groups while in the trans case it is forced to reside between them causing the Si–O bond length to lengthen (Scheme 2).



Scheme 2. Bond lengths for the cis and trans 2,5-Me_2-THF silylium ions.

For carboxylic acids, the product of O-silylation is expected to be quite acidic. The viability of PPh_3, a weak base, to deprotonate the intermediate is supported by the large negative free energy change for the follow-up deprotonation (Scheme 3). An exogenous Lewis base could therefore also function as a Brønsted base under catalytic conditions.



Scheme 3. Potential reactivity pathway for isobutyric acid.

A number of biomass-derived sugar molecules were also examined. To best mimic experiments demonstrating selective deoxygenation of these structures, the free alcohols on the sugar were protected with Me_3Si groups (Figure 3). In the case of isosorbide, there are two diastereomeric ethereal sites, with transfer of Me_3Si^+ to O-2 being more favorable by 2.0 kcal/mol. Transfer to isomannide (+3.2 kcal/mol), a diastereomer of isosorbide, is more favorable than both isomers of isosorbide. Experimentally, the reductive pathways of isosorbide and isomannide are highly dependent on the sterics of the reducing silane.[11]

The stability of the alpha- and beta- anomers of per-silyl protected methylglucose were also studied. To begin, the belt of Me_3Si-protecting groups is geared and well-organized around the sugar, and the α-anomer is 3.7 kcal/mol more stable than the β-form (Figure 4).

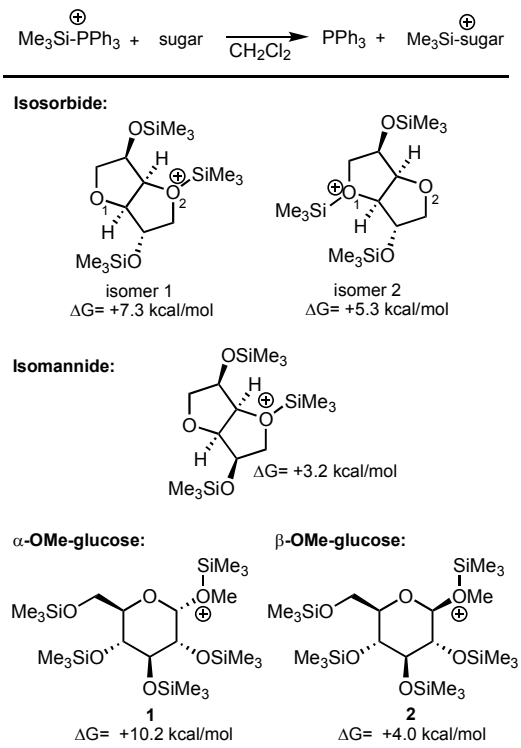


Figure 3. Silylium Lewis base adducts of bio-mass derived sugar substrates.

These stabilities, however, are inverted in the silyloxonium ion, where the β-anomer is now 2.4 kcal/mol more stable than the α (Figure 3). This is in agreement with experimental observations as β-OMe-glucose is considerably more reactive than α-OMe-glucose.[25] The mechanism of demethoxylation has been proposed to occur via a common oxocarbenium intermediate.[25,26] As shown in Figure 4, generation of this species is calculated to be downhill (-0.6 kcal/mol) for the α-silyloxonium, and slightly uphill by 1.8 kcal/mol for the β-silyloxonium ion. In hindered gluco-disaccharides the α-linkage is more reactive than the β-disaccharide.[13]

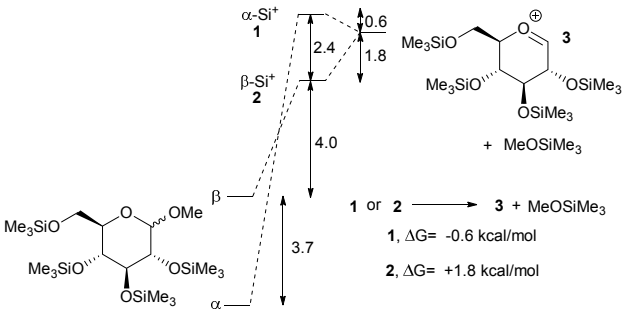


Figure 4. Free energy diagram for the demethoxylation of α- and β-OMe-glucose. Each horizontal line represents the energy of the most stable energy minimized conformer.

Our small molecule model systems can be used to begin rationalizing the reactivity observed with the complex natural product natamycin. A rank ordering of the reactivity of the functional groups in Natamycin was experimentally determined via the stepwise addition of one equivalent of silane in combination with catalytic amounts of fluoroarylborane and triphenylphosphine (Figure 5).[19] The reaction was monitored by *in situ* NMR spectroscopy. The most reactive site is the carboxylic acid, which undergoes dehydrosilation to form the silyl ester (↑H_2). While the initial silylium transfer to model isobutyric acid is uphill by +4.9 kcal/mol, the subsequent acid-base chemistry to form silyl ester and H–PPh_3^+ is favored by -12.1 kcal/mol.

Thus, while the amide in Natamycin is likely more basic, a rapid and favorable deprotonation apparently enhances acid silylation reactivity. The resulting phosphonium acid/borohydride would recombine to form H_2 (observed), though it is also conceivable that the acid directly reacts with borohydride to give H_2 without the intervention of PPh_3. Traces of H–PPh_3^+ is observed by ^{31}P NMR, though its kinetic role is difficult to ascertain.

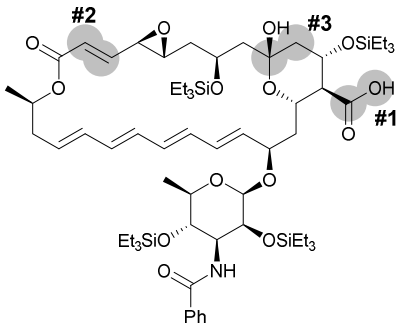


Figure 5. Reactivity hierarchy observed experimentally with natamycin (using B(3,5-$(CF_3)_2C_6H_3)_3$ and Me_2EtSiH).

The second most reactive site in natamycin under these conditions was the enoate, which is conjugatively reduced to a silyl ketene acetal (hydrolyzed upon workup). Computationally, an electronically deactivated enoate should be comparable to cyclic ethers, though the experimental data clearly show that the latter sp^3-electrophiles are kinetically disadvantaged. While these thermodynamic measures of silylium activation suggest that $SiMe_3^+$ should predominantly bind to the amide, the reducing agent generated in situ (H–BAr_{F3}^-) is apparently insufficiently nucleophilic to reduce the activated amide. In contrast, the less electrophilic mixed fluoroaryl/alkyl Lewis acids (BAr_{F2}(R)) are likely more nucleophilic and are capable of amide reductions, i.e. H–BAr_{F2}(R)$^-$ vs H–BAr_{F3}^-. Continuing this trend to Ph_3B, Okuda has shown that this much less Lewis acidic borane can reduce amides with silane.[18] Based on the calculations of Heiden, Ph_3B–H$^-$ should be 19 kcal/mol more hydridic than $(C_6F_5)_2BR$–H$^-$, which in turn is 10 kcal/mol more hydridic than BCF–H$^-$.[27] These calculations therefore imply that chemoselectivity is a consequence of both silylium ion Lewis base preference and the nucleophilicity of the ion-pair reductant. The lactol is the third most reactive site, resulting in elimination at ambient temperatures and reduction at reduced temperatures (0°C).

Monitoring of catalytic reductions by ^{19}F NMR spectroscopy clearly shows that the BAr_{F3} catalyst rests as the borohydride ion, whose ion pair is presumably a silylium–Lewis base adduct. The location of the $SiMe_2Et^+$ group under these conditions is murky as broad signals are observed in both the ^{31}P and ^{1}H NMR spectra. Our working hypothesis is that the silylium ion exchanges between multiple Lewis basic functional groups, but that it predominantly exists on PPh_3 and the amide, both of which are unreactive under the reaction conditions. The PPh_3 can thus be considered a carrier of SiR_3^+ and is able to transfer this activating group to multiple positions, some of which are more reactive to reduction than others. A second role for the PPh_3 in these experiments is to ensure that the concentration of BCF remains low by driving the formation of H–BCF$^-$-containing ion pairs. In this form the fluoroaryl borane is not electrophilic and does not decompose the sensitive natural product.

Conclusions

In summary, we have compared the relative thermodynamic stabilities of several Lewis bases relevant to catalysis. Through these calculations we are able to understand the balance between sterics and basicity in the transfer of silylium to various Lewis basic sites to both simple and more complex substrates. These calculations will help rationalize and guide future experiments.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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