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A Photo Lewis Acid Generator (PhLAG): Controlled Photorelease of $B(C_6F_5)_3$

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Supporting Information

ABSTRACT: A molecule that releases the strong organometallic Lewis acid $B(C_6F_5)_3$ upon irradiation with 254 nm light has been developed. This photo Lewis acid generator (PhLAG) now enables the photocontrolled initiation of several reactions catalyzed by this important Lewis acid. Herein is described the synthesis of the triphenylsulfonium salt of a carbamato borate based on a carbazole function, its establishment as a PhLAG, and the application of the photorelease of $B(C_6F_5)_3$ to the fabrication of thin films of a polysiloxane material.

In homogeneous catalysis, reactions typically commence when catalyst precursors are physically introduced to the reagents. This limits the conditions under which reactions can be initiated. The ability to induce reactions with the imposition of an external stimulus, such as heat,[1] mechanical force,[2] or light,[3] allows for exquisite temporal control over the initiation of catalytic reactions. This is particularly important for certain materials chemistry applictions, where premature initiation of polymerization, depolymerization, or cross-linking reactions can be detrimental to pattern formation or device manufacture. For example, in the photolithography arena, photoacid generators (PAGs) are utilized to eject protons upon irradiation at a defined wavelength, which triggers the catalyzed ester deprotection of resist polymers in the region of exposure, allowing for patterning to sub-20 nm resolution. Typical commercially available and industrially relevant PAGs consist of triphenylsulfonium salts[4] that release protons upon irradiation with 254 nm wavelength light. Despite the advanced practice of this chemistry, the reactions that protons can amplify are limited, and so the ability to photochemically liberate functionally distinct and potentially more versatile Lewis acid catalysts is highly desirable.

One important class of Lewis acids are the perfluoroarylboranes,[5] typified by the simplest member, tris(pentafluorophenyl)borane, $B(C_6F_5)_3$. First prepared almost 50 years ago,[6] $B(C_6F_5)_3$ exhibits strong Lewis acidity, high thermal stability, and air and water tolerance. In the 1990s this borane emerged as an important cocatalyst for olefin polymerizations mediated by single site catalysts.[7] As a consequence, it became widely available, and new reactions mediated by this versatile Lewis acid were discovered, most notably its use in the transition-metal free hydrosilylation[8−10] of a variety of substrates and hydrogenation of imines.[11,12] It is also effective for the clean and rapid construction of siloxane and polysiloxane scaffolds via the Piers−Rubinsztajn reaction, eq 1,[13,14] a process for which controlled photogeneration of $B(C_6F_5)_3$ would be particularly attractive in thin film synthesis and patterning processes since siloxane-based films find many uses in the semiconductor industry.[15]

$$R_3SiOR' + HSiR_3'' \xrightarrow[(1\%)]{B(C_6F_5)_3} R_3SiOSiR_3'' + HR' \qquad (1)$$

While photochemical unmasking of Lewis acidic coordination sites in transition-metal complexes is well-known, an efficient photo Lewis acid generator (PhLAG), in which a well-defined main group Lewis acid is released photochemically from a thermally stable and easily handled precursor, is a less well developed concept. A few reports in the early 1970s described the photopolymerization of epoxides upon irradiation of aryl diazonium salts of general formula $[ArN_2]^+[EF_n]^-$ ($E = P$, $n = 6$; $E = B$, $n = 4$); the reaction was proposed to be catalyzed by EF_{n-1} Lewis acids formed upon photodecomposition of the salt.[16,17] While reasonably effective, the sensitivity of these Lewis acids to water raises questions as to the true nature of the catalyst and the reproducibility of the catalyzed transformations. With this in mind, we sought a protecting group for $B(C_6F_5)_3$ whose removal could be induced with a photon, releasing the water stable borane. Essentially, the photochemical activation must convert the strongly Lewis basic protecting group into one or more weaker Lewis bases whose presence does not preclude the desired catalysis.

We have previously observed that the "frustrated Lewis pair"[18] combination of 2,2,6,6-tetramethylpiperidine (TMP) and $B(C_6F_5)_3$ takes up CO_2 to form the ammonium carbamato borate ion pair **1-TMPH** (Scheme 1).[19] This process is reversible as evidence by incorporation of ^{13}C label into **1-TMPH** upon exposure to $^{13}CO_2$. Based on the X-ray structure, which shows a hydrogen bond between the ammonium cation and the carbamato carbonyl oxygen, we hypothesized that the reverse process is aided by protonation of the carbamato carbonyl oxygen. We thus set out to prepare compounds similar to **1-TMPH** but with a triaryl sulfonium countercation; to reduce the basicity of the nitrogen center, we targeted the carbazole-based system **2-Ph$_3$S**[20] (Scheme 2). We anticipated that irradiation of **2-Ph$_3$S** at 254 nm would cause the $[Ph_3S]^+$ cation to eject a proton (along with several other photoproducts derived from this cation)[4] and trigger the release of CO_2 and $B(C_6F_5)_3$ from the anion.

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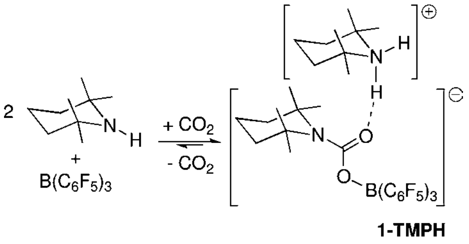
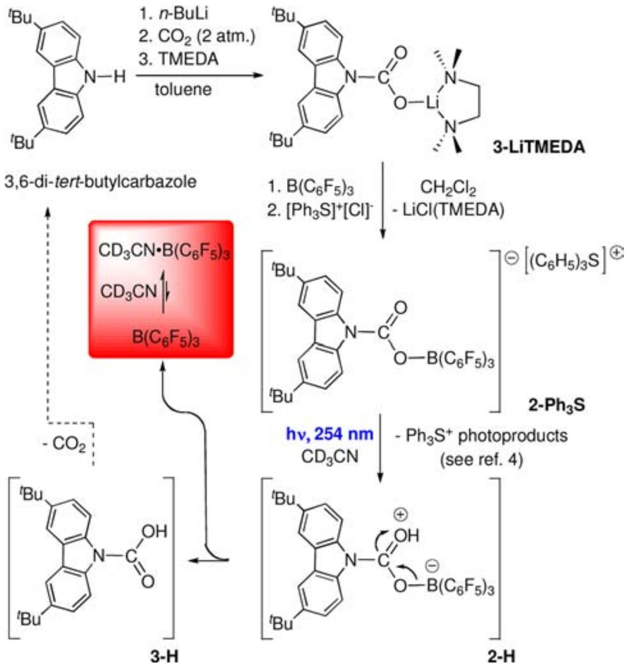
Scheme 1



Scheme 2



In a series of sequential steps, the TMEDA stabilized lithium salt of the carbamic acid derived from 3,6-di-*tert*-butylcarbazole (**3-LiTMEDA**) was synthesized and isolated. Reaction of **3-LiTMEDA** with $B(C_6F_5)_3$ formed a lithium carbamato borate, which was converted to the triphenylsulfonium salt **2-Ph$_3$S** via ion exchange with $[Ph_3S]^+[Cl]^-$ in excellent yield. This salt is a thermally robust, air and moisture stable microcrystalline white solid that was fully characterized by multinuclear NMR, IR and absorption spectroscopic techniques as well as X-ray crystallography. Key spectroscopic data include characteristic resonances in the aromatic region of the proton NMR spectrum at 7.42, 7.65, and 7.77 ppm for the phenyl group protons of the cation, an IR band at 1700 cm^{-1} for the stretching frequency of the carbonyl group in the anion, and a resonance at −4.1 ppm in the ^{11}B NMR spectrum for the boron nucleus of the carbamato borate moiety. Figure 1 depicts the molecular structure of the ion pair along with selected metrical data. The B1−O1 distance of 1.521(3) Å in **2-Ph$_3$S** is shorter than those found in carbonyl function adducts of $B(C_6F_5)_3$[21] and similar to that observed for the formatoborate complex $[TMPH][HCO_2B(C_6F_5)_3]$,[22] consistent with its formulation as a carbamato borate anion. The triphenyl sulfonium countercation sits above the five-membered C_4N core of the carbamato function, with nonbonding distances between S1 and these atoms of ≈3.5 Å.

Ion pair **2-Ph$_3$S** is a true PhLAG on the basis of the following observations. Exposure of the compound to an atmosphere of $^{13}CO_2$ under ambient conditions for several hours results in no incorporation of the isotopic label into the carbamato carbon. Furthermore, thermogravimetric analysis (TGA) shows that it is thermally stable up to its melting point of 185 °C at which time it loses mass at a steady rate presumably due to decomposition (Figure S1, Supporting Information (SI)). It is stable also in refluxing acetonitrile or tetrahydrofuran solution under ambient light. However, upon irradiation with 254 nm light in CD_2Cl_2 solution (2.1×10^{-3} M) in the presence of 1 equiv of acetonitrile, it efficiently releases $B(C_6F_5)_3$, which is trapped as its acetonitrile adduct, $CH_3CN{\cdot}B(C_6F_5)_3$[23,24] (Figure 2; Figures S5−7, SI); at this concentration the photoreaction proceeds to >99% within 12 min with an apparent rate constant of $\approx 3.3 \times 10^{-3}$ s^{-1}. The generation of $CH_3CN{\cdot}B(C_6F_5)_3$ only proceeds when the light source is on; turning the lamp off stops the photorelease of borane immediately. We propose that the release of borane proceeds, as shown in Scheme 2, via protonation of the carbonyl group; the resulting salt **2-H** spontaneously ejects borane and the carbamic acid **3-H**, which undergoes decomposition to 3,6-di-*tert*-butyl carbazole and CO_2. This notion is supported by the observation of a transient signal at

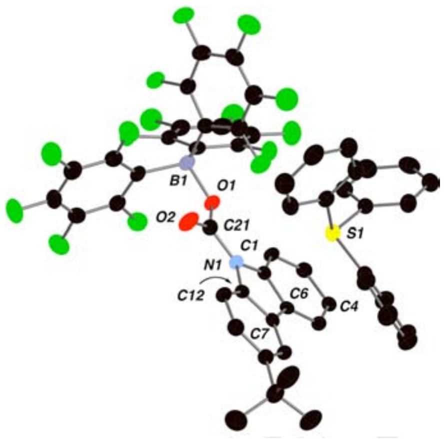


Figure 1. X-ray structure of **2-Ph$_3$S** (thermal ellipsoids drawn to 50% probability level). The *tert*-butyl group on C4 has been removed for clarity. Selected bond distances (Å): B1−O1, 1.521(3); C21−O1, 1.310(3); C21−O2, 1.205(3); C21−N1, 1.393(3). Selected nonbonded distances (Å): S1−C1, 3.54; S1−C6, 3.49; S1−C7, 3.47; S1−C12, 3.47; S1−N1, 3.52. Selected bond angle (°): B1−O1−C21, 121.9(2).

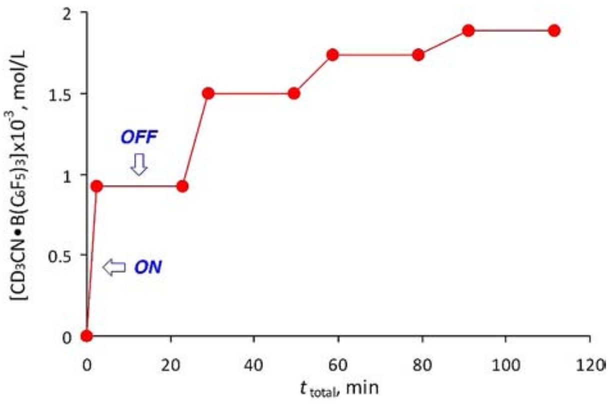


Figure 2. Plot of the appearance of $CH_3CN{\cdot}B(C_6F_5)_3$ vs time as a function of intermittent irradiation (254 nm) of **2-Ph$_3$S** (2.1×10^{-3} M in CD_2Cl_2) in the presence of 1 equiv of CH_3CN.

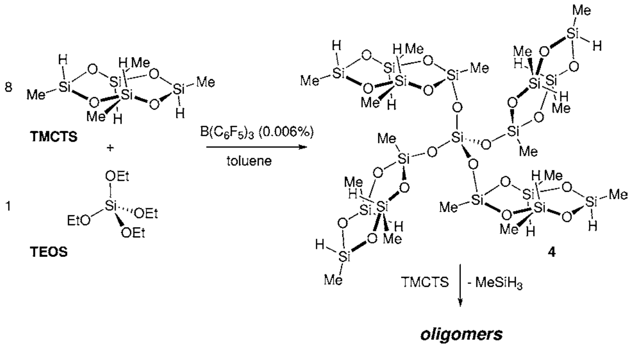
153.4 ppm (assigned to **3-H**) and $^{13}CO_2$ (126.2 ppm) in the ^{13}C NMR spectrum of the photoproducts of irradiated solutions of **2-Ph$_3$S** selectively ^{13}C labeled in the carbamate carbon (Figure S6, SI). Furthermore, strong Bronsted acids, like triflic acid, react rapidly with **2-Ph$_3$S** to release $B(C_6F_5)_3$, CO_2, and carbazole, along with $[Ph_3S]^+[OTf]^-$. The carbazole is a weak Lewis base that, shown in separate experiments, does not bind $B(C_6F_5)_3$ strongly (Figures S8–10, SI) nor interfere with catalytic reactions mediated by $B(C_6F_5)_3$.

The efficacy of **2-Ph$_3$S** as a PhLAG was further demonstrated by the photoinitiated hydrosilylation of carbonyl functions[25] and silation of alcohols and ethers,[8] well established reactions catalyzed by $B(C_6F_5)_3$. Solutions of substrate, 1 equiv of Et_3SiH and 1 mol % of **2-Ph$_3$S** were prepared; no reaction was observed. Upon irradiation of these solutions at 254 nm for 15 min, silation reactions ensued and were complete in reaction times consistent with the reactions catalyzed by $B(C_6F_5)_3$ itself.[8,25] The results of these experiments are summarized in Table S2, SI.

While these results point to photogeneration of $B(C_6F_5)_3$, the ability to trigger these sorts of reactions photochemically provides minimal advantage. Conversely, the ability to photoinitiate the $B(C_6F_5)_3$ catalyzed formation of siloxane structures, i.e., the Piers–Rubinsztajn reaction shown in eq 1, offers an opportunity to control the formation of thin films of these materials. Such films have potential application as low *k* dielectric materials, and the ability to create photodefined dielectric films on wafer is of considerable interest.[15] Furthermore, siloxane film formation catalyzed by $B(C_6F_5)_3$ can be achieved at significantly lower temperatures than other avenues. Model reactions using silanes and silanols, R_3SiOH, or silyl ethers, $RSi(OR)_3$, demonstrate the efficacy of photoinduced Si–O bond formation (and O–R bond cleavage) using **2-Ph$_3$S** as a PhLAG, producing essentially identical results as those obtained by physical introduction of $B(C_6F_5)_3$ to solutions of these reactants. Table S3, SI, shows the results of these model studies and suggests that **2-Ph$_3$S** can be used for photoinduced cross-linking of suitable precursors in the formation of siloxane-based thin films.

A suitable soluble precursor to siloxane thin films containing Si–H functions to use in photoinitiated cross-linking reactions was synthesized from tetraethoxysilane (TEOS) and 2,4,6,8-tetramethylcyclotetrasiloxane (TMCTS). Simply spin-coating a silicon wafer with a mixture of TMCTS and TEOS in the presence of 1% **2-Ph$_3$S** did not produce a stable, high-quality thin film, so solutions of TMCTS:TEOS (8:1, 0.06 M TEOS) in toluene were aged with 0.006 mol % loading of $B(C_6F_5)_3$. When such solutions were monitored by ^1H NMR spectroscopy, evolved ethane was observed, and all Si-OEt groups were consumed, suggesting that the major product is the TMCTS "tetramer" **4** (Scheme 3). However, significant quantities of methylsilane, $MeSiH_3$, were also produced, and the ratio of remaining Si–Me groups to Si–H groups in the final solution after three days (when no further spectral changes were observed and ^{19}F NMR spectroscopy showed complete decompostion of $B(C_6F_5)_3$) was approximately 2.7:1 rather than the 4:1 ratio expected for **4**. Control experiments (Figures S11–16, SI) in which TMCTS was treated with low loadings of $B(C_6F_5)_3$ also show the presence of $MeSiH_3$ and suggest that ring opening of the TMCTS ring precedes elimination of $MeSiH_3$. Indeed, while this manuscript was in preparation, Chojnowski et al. published a thorough study concerning the "hydride transfer ring-opening polymerization" of TMCTS in the absence of TEOS and characterized a soluble polymer consisting of macrocyclic rings of various sizes due to the partial ring opening of the cyclic monomer.[26] In the present system, while $B(C_6F_5)_3$ catalyzes ring-opening reactions of TMCTS, these reactions are minimized through use of very low $B(C_6F_5)_3$ loadings, which also ensures eventual degradation of the active borane catalyst as the solution ages. Furthermore, the use of eight equivalents of TMCTS controls the MW of these products and helps to maintain solubility in toluene reaction solvent and suitability for thin film formation via spin-coating techniques. The use of TEOS aids the curing of these films by providing polymer networks with more extensive cross-linking, although the ^{29}Si NMR spectra of the TMCTS/TEOS polymers are very similar to those reported by Chojnowski and co-workers for the polymer prepared exclusively from TMCTS.[26]

Scheme 3



Toluene solutions of oligomerized **4** prepared as described above and then diluted 2× with additional toluene were charged with PhLAG **2-SPh$_3$** (≈1 wt %) and used to form high-quality thin films which can be subsequently rendered insoluble in 2-heptanone via a combination of UV exposure (254 nm, 150 mJ/cm^2) and baking (105 °C, 1 min, air). Control studies have shown that both UV activation and subsequent heating are required to render the films insoluble (Figure S17, SI); either UV activation or thermal activation alone does not generate insoluble films. IR analysis of the films show that those formed via UV exposure and bake exhibit a distinct decrease in intensity of the bands due to the Si–H stretching (2170 cm^{-1}) and bending (905 cm^{-1}) modes, while the collection of bands centered around 1070 cm^{-1} assignable to various Si–O–Si modes increases in intensity relative to the film as deposited prior to irradiation/bake (Figures S18–23, SI). Again, samples that were only irradiated, or only baked, show minimal change from the soluble "as deposited" films.

Although more detailed studies are required to fully elucidate the cross-linking mechanism occurring on the wafer, these results show that photoreleased $B(C_6F_5)_3$ utilize Si–H groups in soluble **4** to form a cross-linked film with more Si–O–Si bonds. We believe that cross-linking results from either of two processes: First, $B(C_6F_5)_3$ can catalyze the dehydrogenative silation of water absorbed into the film from atmosphere with Si–H functions from two distinct oligomers.[8,27] Alternatively, in the absence of water, $B(C_6F_5)_3$ could also catalyze the ring-opening condensation reaction between two oligomers with expulsion of $MeSiH_3$ as observed in the solution chemistry control experiments.[26] In both cases, higher MW species will be formed on the wafer, ultimately leading to films that are no longer soluble in developing solvent, such as 2-heptanone.

Likely, the baking step is required to ensure mobility of the $B(C_6F_5)_3$ within the film once it is photogenerated.

In summary, we have developed a molecule capable of efficiently releasing the strong organometallic Lewis acid $B(C_6F_5)_3$ upon irradiation with UV light. Thus several of the many reactions catalyzed by this borane[5] can now be photoinitiated. From a materials perspective, perhaps the most versatile is the dehydrocarbon polycondensation reaction between silanes and alkoxy silanes,[28] the Piers–Rubinsztajn reaction.[13] We have employed this chemistry to develop a method for photocuring thin films of a siloxane polymer on silicon surfaces; optimization of the conditions for this process and the potential of this method for fashioning patterned structures of this material are currently under investigation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full experimental details for the synthesis of **2-Ph$_3$S**, its verification as a PhLAG, and its application toward formation of siloxane-based thin films. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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