Journal Name

ARTICLE

Photo Lewis acid generators: photorelease of $B(C_6F_5)_3$ and applications to catalysis†

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

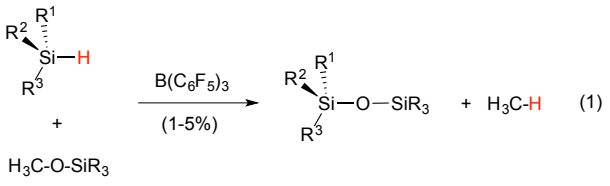
Andrey Y. Khalimon,*[a,b] Bryan K. Shaw,[a] Adam J. V. Marwitz,[a] Warren E. Piers,*[a] James M. Blackwell[c] and Masood Parvez[a]

A series of molecules capable of releasing of the strong organometallic Lewis acid $B(C_6F_5)_3$ upon exposure to 254 nm light have been developed. These photo Lewis acid generators (PhLAGs) can now serve as photoinitiators for several important $B(C_6F_5)_3$-catalyzed reactions. Herein is described the synthesis of the triphenylsulfonium and diphenyliodonium salts of carbamato- and hydridoborates, their establishment as PhLAGs, and studies aimed at defining the mechanism of borane release. Factors affecting these photolytic reactions and the application of this concept to photoinduced hydrosilylation reactions and construction of siloxane scaffolds are also discussed.

Introduction

Tris-(pentafluorophenyl)borane, $B(C_6F_5)_3$, is a widely employed borane Lewis acid for a host of catalytic applications.[1, 2] Its appeal stems from the fact that its properties of air and moisture tolerance[3, 4] (unusual for an organoborane) and very strong Lewis acidity[2, 5] (close to that of BF_3) make for a catalyst that is both easy to use *and* effective. Furthermore, after it found initial application as a co-catalyst for olefin polymerization catalysis,[6] it became widely available from several commercial sources, increasing its attractiveness. Organic chemists began to explore its use as a Lewis acid catalyst for organic transformations,[7] and subsequent seminal discoveries that it is capable of mediating Si-H[8] and H-H[9] bond activations that can be incorporated into hydrosilation[10-13] and hydrogenation[14, 15] catalytic cycles spawned a worldwide effort in so-called "frustrated Lewis pair" chemistry.[16, 17]

The ability of $B(C_6F_5)_3$ to activate Si-H bonds has lead not only to the development of a number of hydrosilation



applications, but a method for preparing complex, monodisperse silicone structures that would be difficult if not impossible to prepare using conventional methods.[18, 19] These applications rely on the "Piers-Rubinsztajn reaction",[20] a dealkylative siloxane synthesis generally depicted in equation 1. This versatile reaction can also be used to form polymeric structures,[21, 22] or as a vector for crosslinking macromolecules and changing the physical properties of polysiloxane materials.[23]

In this context, we became interested in devising a way in which the reaction could be triggered by an external stimulus, rather than simply upon introduction of the catalyst to the precursor mixture. Inducing a catalytic reaction by the some external stimulus has many benefits in materials research since one can, in principle, control the precise timing of the onset of a catalytic reaction. Examples of external stimuli include heat,[24] mechanical force[25] or, more commonly, irradiation with a specific wavelength of light.[26-28]

Light-induced catalysis is of particular importance in the area of photolithography, where photoacid generators (PAGs) eject protons upon irradiation,[29, 30] which mediate the deprotection of photoresist polymers and allow for patterning to sub-20 nm resolution. Given the importance of $B(C_6F_5)_3$ and other perfluoroaryl boranes as Lewis acid catalysts for siloxane synthesis and modification, we became interested in devising molecules that, when irradiated, would liberate this borane. In other words, we sought photo Lewis acid generators, or "PhLAGs". While the generation of vacant coordination sites in transition metal complexes via photodissociation of, for example, carbonyl ligands is well known, controlled photorelease of main group element-based Lewis acids has far less literature precedent. Photopolymerization of epoxides with the use of aryl diazonium salts $[ArN_2][EX_n]$ (E = P, n = 6; E = B, n = 4) has been demonstrated in 1970s[31, 32] and the reactions are believed to be initiated by Lewis acidic EX_{n-1}

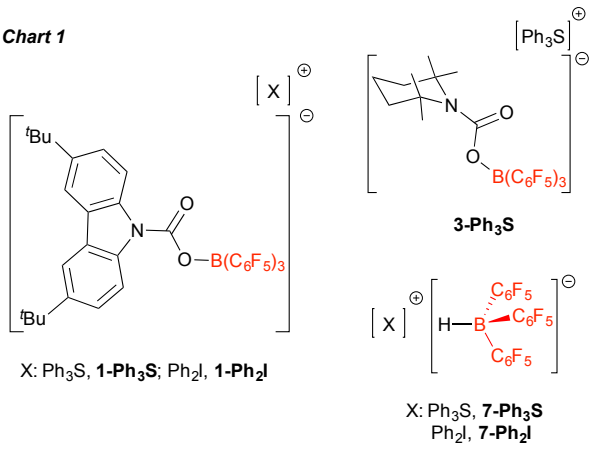
[a] Department of Chemistry, University of Calgary, 2500 University Drive Northwest, Calgary, Alberta, T2N 1N4, Canada. E-mail: wpiers@ucalgary.ca
[b] Department of Chemistry, School of Science and Technology, Nazarbayev University, 53 Kabanbay Batyr Avenue, Astana 010000, Kazakhstan. E-mail: andrey.khalimon@nu.edu.kz
[c] Intel Corporation, Components Research, 2511 NW 229th Avenue, Hillsboro, OR, 97214.

† Electronic Supplementary Information (ESI) available: Additional experimental and spectroscopic details and crystallographic data for **3-Ph$_3$S**, and **7-Ph$_2$I** (CCDC 1415835-1415836). See DOI: 10.1039/x0xx00000x

species, which are generated along with dinitrogen and aryl halides from diazonium salts upon exposure to UV light. However, Lewis acids generated in both these cases are air and moisture sensitive, which raises the question regarding the true nature of the catalytic species. Furthermore, aryl diazonium salts are often found to be thermally unstable and decompose under ambient conditions.[33] Therefore, PhLAG molecules that are thermally robust and produce a well-defined Lewis acid efficiently are of potential value in materials synthesis.

In a preliminary communication,[34] we reported preparation of the first PhLAG molecule capable of the photorelease of $B(C_6F_5)_3$ and applications of this design to photoinduced hydrosilylation and Piers-Rubinsztajn catalysis. The compound was a triphenylsulfonium-carbamatoborate ion pair, **1-Ph$_3$S** (Chart 1), which decomposes under irradiation with 254 nm light to release one equivalent of $B(C_6F_5)_3$, along with other products that were innocuous in terms of desired hydrosilation catalysis.

Chart 1



X: Ph_3S, **1-Ph$_3$S**; Ph_2I, **1-Ph$_2$I**

X: Ph_3S, **7-Ph$_3$S**
Ph_2I, **7-Ph$_2$I**

Here we report the full account of this research, including preparation of a series of next generation triphenylsulfonium and diphenyliodonium PhLAGs (Chart 1), their applications, as well as a detailed study of the mechanisms of $B(C_6F_5)_3$ photorelease and the factors affecting these photolytic reactions.

Results and discussion

Carbamato-derived PhLAGs

The synthesis of the triphenylsulfonium carbamatoborate **1-Ph$_3$S**[34] is summarized in Scheme 1A. In a series of sequential steps we prepared a TMEDA stabilized lithium salt of carbamic acid, **2-LiTMEDA**, derived from 3,6-di-*tert*-butylcarbazole (^{t}Bu$_2$C$_{12}$H$_6$NH). Treatment of **2-LiTMEDA** with $B(C_6F_5)_3$ gives a TMEDA stabilized lithium carbamatoborate [Li(TMEDA)][(^{t}Bu$_2$C$_{12}$H$_6$N)CO$_2$B(C$_6$F$_5$)$_3$], which can be converted to triphenylsulfonium salt **1-Ph$_3$S** *via* an ion exchange reaction with commercially available [Ph_3S][Cl].[34] In the absence of TMEDA, treatment of **2-Li** with $B(C_6F_5)_3$ gives a lithium carbamatoborate **1-Li** in a mixture with the starting materials suggesting an equilibrium, which is most likely induced by the interaction of Lewis acidic Li^+ with the carbonyl oxygen of the anion. Analogously to **1-Ph$_3$S**, treatment of **2-LiTMEDA** with [Ph_2I][Cl] gives a diphenyliodonium derivative **1-Ph$_2$I**; however, the reaction is less clean and requires more rigorous purification protocols. This significantly reduces the yield of **1-Ph$_2$I** (40%) in comparison with **1-Ph$_3$S** (79%). In a similar manner, the 2,2,6,6-tetramethylpiperidine (TMP, Me_4C_5NH) derivative **2-Ph$_3$S** can be prepared by the ion exchange reaction between [Ph_3S][Cl] and the corresponding lithium borate [Li][(Me_4C_5N)CO$_2$B(C$_6$F$_5$)$_3$] (**3-Li**) derived from lithium carbamate (Me_4C_5N)CO$_2$Li (**4**; Scheme 1**B**). Borate **3-Li** exhibits greater stability compared to **2-Li** and does not require additional stabilization with TMEDA. This phenomenon can most likely be explained by a higher basicity of the carbamato nitrogen centre in **3-Li** *vs.* **2-Li**, which allows for additional stabilization of the lithium cation preventing its interaction with the carbonyl oxygen of the anion and thus, inhibiting dissociation of **3-Li** to **4** and free $B(C_6F_5)_3$.

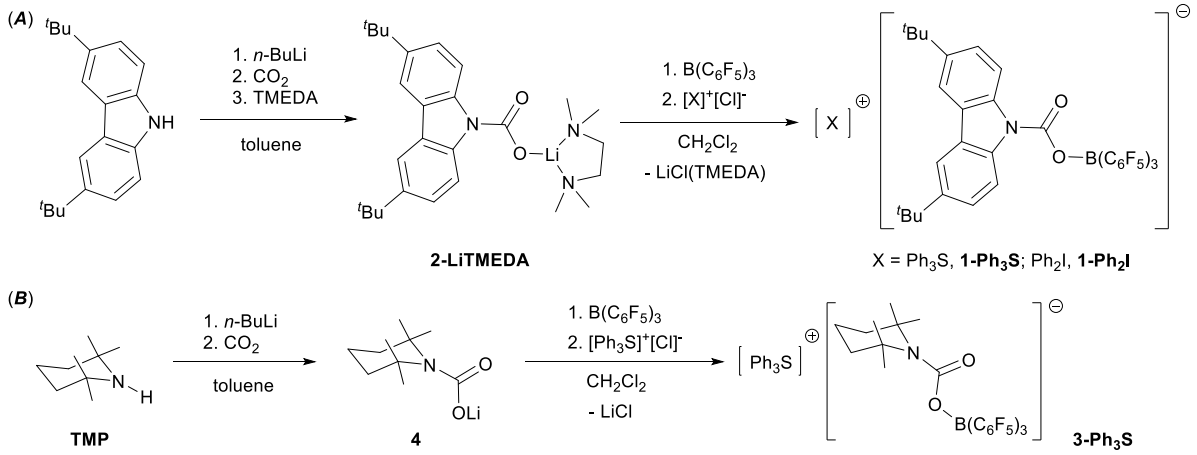
Borates **1-Ph$_3$S**, **1-Ph$_2$I**, and **3-Ph$_3$S** were fully characterized by multinuclear NMR, IR, absorption spectroscopic techniques and X-ray diffraction analysis for triphenylsulfonium salts **1-Ph$_3$S** and **3-Ph$_3$S**. The signals for the cations appear in the ^{1}H NMR spectra at δ 7.42, 7.65 and 7.77 ppm for **1-Ph$_3$S**, δ 7.39, 7.57 and 7.73 ppm for **1-Ph$_2$I**, and δ 7.55, 7.73 and 7.85 ppm for **3-Ph$_3$S**. Other characteristic spectroscopic data for borates **1-Ph$_3$S**, **1-Ph$_2$I** and **3-Ph$_3$S** include the respective boron resonances at δ -4.1, -3.8 and -5.4 ppm in the ^{11}B NMR spectra and the respective bands in the IR spectra at 1700, 1676 and 1653 cm^{-1} for the stretches of the carbonyl groups of the anions.

The molecular structure of **1-Ph$_3$S** has been described[34] and is consistent with its formulation as a triphenylsulfonium carbamatoborate anion pair. Figure 1**A** shows the molecular structure of the TMP derived salt **3-Ph$_3$S** with selected metrical data. The B1-O1 distance of 1.509(3) Å in **3-Ph$_3$S** is shorter than those typically found in the adducts between carbonyl compounds and $B(C_6F_5)_3$[35] and is close to those observed for the carbamatoborate **1-Ph$_3$S** (1.521(3) Å)[34] and previously reported [TMPH][$HCO_2B(C_6F_5)_3$] (1.546(3) Å)[36] and [TMPH][(Me_4C_5N)CO$_2$B(C$_6$F$_5$)$_3$] (1.496(2) Å).[37] The triphenylsulfonium cation of **3-Ph$_3$S** is pointing away from the anion showing interaction (3.025(2) Å) with the carbonyl oxygen of the neighbouring molecule in the unit cell (Figure 1**B**). However, this is likely attributed to the molecular packing effects of **3-Ph$_3$S**.

To probe whether or not borane release from ion pairs **1-Ph$_3$S**, **1-Ph$_2$I** and **3-Ph$_3$S** was truly induced by absorption of a photon, we performed several control experiments. First, exposure of **1-Ph$_3$S**, **1-Ph$_2$I** and **3-Ph$_3$S** to an atmosphere of $^{13}CO_2$ under ambient conditions for several hours resulted in no incorporation of the isotopic label into the carbamato carbon. This indicates that they are stable to loss of CO_2 under ambient conditions. Furthermore, each ion pair is thermally robust up to moderate temperatures as indicated by thermogravimetric (TGA) analysis, showing no decomposition of **1-Ph$_3$S**, **1-Ph$_2$I** and **3-Ph$_3$S** up to 185 °C, 158 °C and 214 °C,

Journal Name

ARTICLE



Scheme 1 Synthesis of carbamatoborates **1-Ph$_3$S**, **1-Ph$_2$I** and **3-Ph$_3$S**.

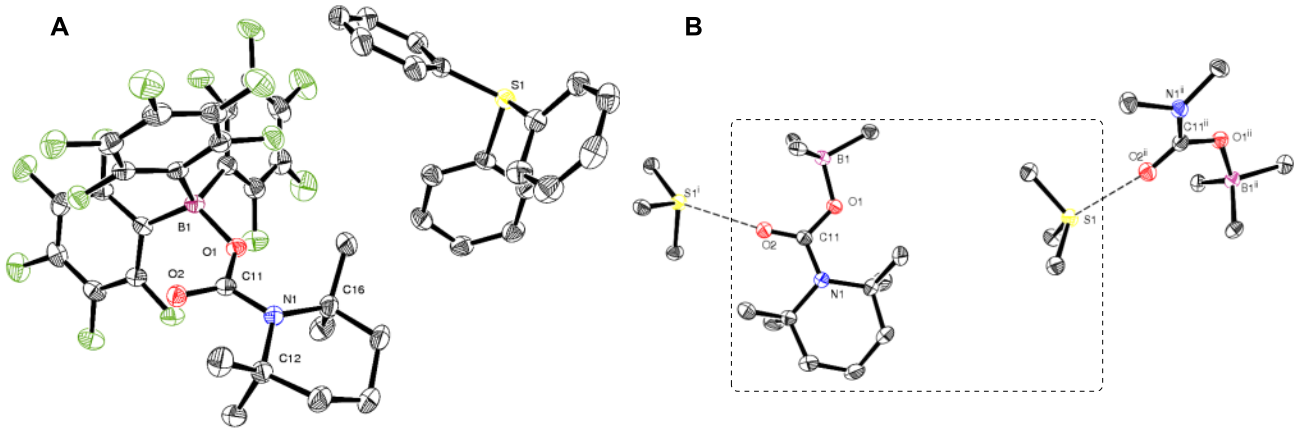
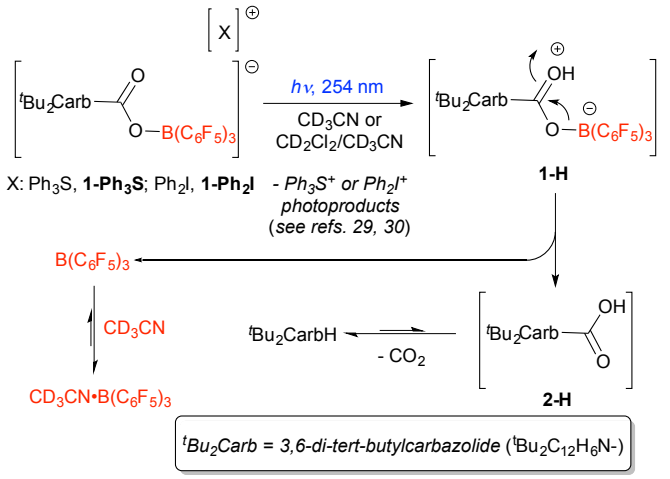


Fig. 1 (**A**) X-ray structure of **3-Ph$_3$S** (thermal ellipsoids drawn to 50% probability level). Hydrogen atoms are omitted for clarity. Selected bond distances (Å): B1-O1, 1.509(3); C11-O1, 1.328(3); C11-O2, 1.226(3); C11-N1, 1.386(3). Selected bond angles (°): B1-O1-C11, 120.96(19). (**B**) View showing C=O···S bonding motif in the unit cell of **3-Ph$_3$S**: S1^{i}···O2 = S1···O2^{ii}, 3.025(2) Å.

respectively (Figures S1-S3 in ESI). Sulfonuim ion pairs **1-Ph$_3$S** and **3-Ph$_3$S** were also found to be stable in refluxing CH_2Cl_2 and THF, whereas the iodonium derivative **1-Ph$_2$I** exhibits lower stability in solution; slow decomposition of **1-Ph$_2$I** (approx. 30% by NMR) in CD_2Cl_2 (ca. 9.0×10^{-3} M) was observed overnight at room temperature in the absence of light. Based on the IR spectra, which showed a significant shift of the C=O band for **1-Ph$_2$I** (1676 cm^{-1}) compared to **1-Ph$_3$S** (1700 cm^{-1}), we hypothesize that instability of **1-Ph$_2$I** in solution could be a result of a stronger interaction between Ph_2I^+ cation and the carbonyl group of the anion but this could not be confirmed crystallographically. An interaction between the triphenylsulfonium cation and the carbonyl moiety in the borate is not present in the structure of **1-Ph$_3$S**[34] but a weak contact is seen in **3-Ph$_3$S** (Figure 1B).

Irradiation of **1-Ph$_3$S**,[38] **1-Ph$_2$I** and **3-Ph$_3$S** with 254 nm light in either CD_3CN or a mixture of CD_2Cl_2 and CD_3CN (8.7:1, respectively) (2.1×10^{-3} M) results in the efficient release of $B(C_6F_5)_3$, which is effectively trapped as its acetonitrile adduct $CD_3CN{\cdot}B(C_6F_5)_3$.[3, 39] Qualitatively, the rate of borane photorelease from **1-Ph$_3$S**, **1-Ph$_2$I** and **3-Ph$_3$S** depends on the solvent system used (Table S1 and Figure S6 in ESI). Thus, the photolysis of **1-Ph$_3$S** and **1-Ph$_2$I** ion pairs in CD_2Cl_2/CD_3CN (8.7:1; 2.1×10^{-3} M) proceeds to >99% within 12 min, whereas less efficient borane release (58% and 46% conversion for **1-Ph$_3$S** and **3-Ph$_3$S**, respectively) observed in pure CD_3CN under the same conditions. Furthermore, we have previously

demonstrated for **1-Ph$_3$S** that the generation of $CD_3CN{\cdot}B(C_6F_5)_3$ only proceeds when the light source is on; turning the lamp off stops the photorelease of borane immediately.[34] Similar behaviour was also observed for **3-Ph$_3$S** and control experiments with **1-Ph$_3$S** and **3-Ph$_3$S** showed no borane photorelease within several days under ambient light. In contrast, exposure of a solution of **1-Ph$_2$I** in CD_2Cl_2/CD_3CN (8.7:1) to ambient light leads to a slow (≈ 40% in 18 h) formation of $CD_3CN{\cdot}B(C_6F_5)_3$ indicating the increased light sensitivity of diphenyliodonium cation *vs.* triphenylsulfonium cation.[40] In the absence of acetonitrile as trapping reagent, photolysis of CD_2Cl_2 solutions of **1-Ph$_3$S** and **1-Ph$_2$I** gives $B(C_6F_5)_3$; however, the reactions were found to be less clean due to slow photodecomposition of borane, shown in separate experiments.

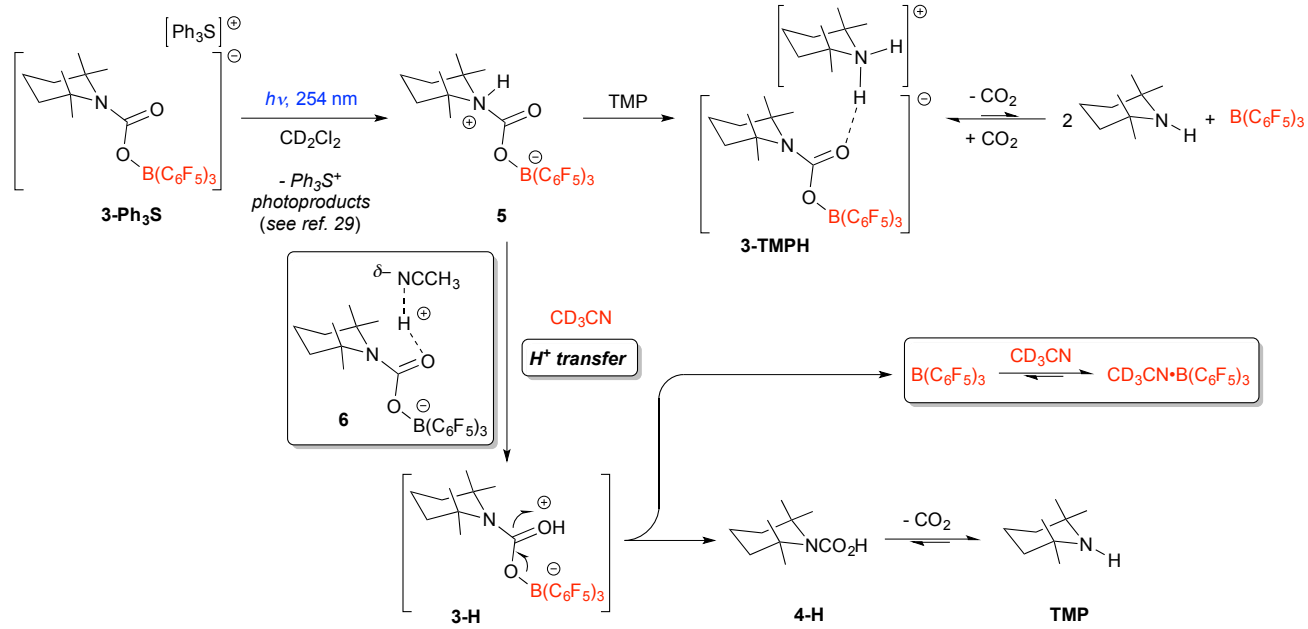


Scheme 2 Suggested mechanism for photorelease of $B(C_6F_5)_3$ from **1-Ph$_3$S**.

We have previously suggested the mechanism of borane photorelease from **1-Ph$_3$S**.[34] An analogous mechanism can be envisioned for the ion par **1-Ph$_2$I** with diphenyliodonium cation being the source of protons[30] instead of triphenylsulfonium cation[29] (Scheme 2). Taking into account the negligible basicity of the carbazolide nitrogen centre due to the conjugation of its lone pair with the aromatic system (the pK_a of the conjugated acid of carbazole is -4.9),[41] we proposed that the reaction starts with the photoinduced protonation of the carbonyl group of the anion, which results in the formation of a zwitterionic intermediate **1-H**. The latter species spontaneously ejects borane and the carbamic acid **2-H**, which undergoes decomposition to 3,6-di-*tert*-butylcarbazole and CO_2.[42] This is supported by the observation of resonances at δ 153.4 ppm (assigned to **2-H**) and 126.2 ppm (assigned to $^{13}CO_2$) in the ^{13}C NMR spectrum of the photoproducts of irradiated solutions of **1-Ph$_3$S** selectively labelled with ^{13}C in the carbamate carbon position (Figure S7, ESI). Furthermore, GS-MS analysis of the reaction mixture after photolysis of **1-Ph$_3$S** in CH_2Cl_2 revealed the presence of 3,6-di-*tert*-butylcarbazole (51%)[43] along with a mixture of Ph_3S^+ photoproducts:[29] *o*-, *m*- and *p*-(phenylthio)biphenyls (11.3%), Ph_2S (28.8%) and biphenyl (2.2%).

A slightly different pathway for the release of $B(C_6F_5)_3$ is proposed for the ion pair **3-Ph$_3$S** on the basis of the following observations. First, photolysis of **3-Ph$_3$S** in CD_2Cl_2 in the absence of acetonitrile does not give $B(C_6F_5)_3$. Instead, NMR analysis revealed the formation of a new borate product with a ^{11}B NMR signal at δ -3.6 ppm, characteristic of a four-coordinate borate species. In the ^1H NMR spectrum, this product shows a broad downfield NH resonance at δ 6.93 ppm, coupled in the ^1H-^{15}N HMQC NMR spectrum with the ^{15}N NMR signal at δ 85.0 ppm with ^1J(N-H) ≈ 70 Hz (found from ^1H-^{15}N JC HMQC NMR) (Figures S8 and S9 in ESI). Taking into account the higher basicity of the amide moiety in **3-Ph$_3$S** (pK_a of the conjugated acid of TMP is 11.1)[44] *vs.* **1-Ph$_3$S**, these spectroscopic features are consistent with the formation of a zwitterionic species $[(Me_4C_5NH)CO_2B(C_6F_5)_3]$ (**5**, Scheme 3), produced *via* protonation of the nitrogen atom of the anion in **3-Ph$_3$S**. Although compound **5** formally represents the product of CO_2 activation by the "frustrated Lewis pair" (FLP) combination of 2,2,6,6-tetramethylpiperidine and $B(C_6F_5)_3$,[45] our previous studies on the reactivity of this FLP with carbon dioxide revealed the reversible formation of an ammonium carbamatoborate [TMPH][$(Me_4C_5N)CO_2B(C_6F_5)_3$] (**3-TMPH**)[37] instead of **5**. Borate **3-TMPH** can be also viewed as a result of deprotonation of **5** with tetramethylpiperidine, and, in fact, treatment of **5** with one equivalent of TMP immediately gives **3-TMPH** (Scheme 3). We have previously demonstrated that formation of **3-TMPH** from $B(C_6F_5)_3$, TMP and CO_2 is reversible as evidenced by incorporation of ^{13}C label into **3-TMPH** upon exposure to $^{13}CO_2$.[37] Based on the X-ray analysis of **3-TMPH**, which shows a hydrogen bond between the ammonium cation and the carbamato carbonyl oxygen,[37] we hypothesized that the reverse process is aided by protonation of the carbamato carbonyl oxygen. In contrast, zwitterion **5**, formed in the *absence* of excess base, was found to be stable under ambient conditions and shows no exchange with either $^{13}CO_2$ or a different borane, $B(p\text{-}H\text{-}C_6F_4)_3$.[46, 47] However, addition of a base, in the form of acetonitrile, to a solution of **5** in CD_2Cl_2 immediately leads to the release of CO_2 and formation of $CH_3CN{\cdot}B(C_6F_5)_3$ and free TMP. This observation is consistent with the facile formation of $CD_3CN{\cdot}B(C_6F_5)_3$ upon photolysis of CD_3CN solutions of **3-Ph$_3$S** ($2.1{\cdot}10^{-3}$ mol/L) and suggests that the reaction starts with the protonation of the nitrogen centre of the anion (Scheme 3), followed by CD_3CN-assisted proton transfer to the carbonyl oxygen (as illustrated in **6**) and formation of the zwitterion **3-H**. The latter salt spontaneously ejects $B(C_6F_5)_3$ and the carbamic acid **4-H**, which decomposed to TMP and CO_2. Thus, PhLAGs of the type represented by compounds **1** and **3** release borane via slightly different paths depending on the basicity of the nitrogen center in the carbamato unit in the anion.

We have previously demonstrated the efficacy of **1-Ph$_3$S** as a PhLAG in photoinduced catalytic hydrosilylation of carbonyl compounds, silation of alcohols, silanols and ethers as well as siloxane forming Piers-Rubinsztajn reactions,[34] all well established transformations catalysed by $B(C_6F_5)_3$. In the absence of the UV light, no reactions were observed upon addition of 1 mol % of **1-Ph$_3$S** to substrate/hydrosilane



Scheme 3 Generation of **5** from **3-Ph$_3$S** under 254 nm light and suggested mechanism for photorelease of $B(C_6F_5)_3$ from **3-Ph$_3$S** in the presence of acetonitrile.

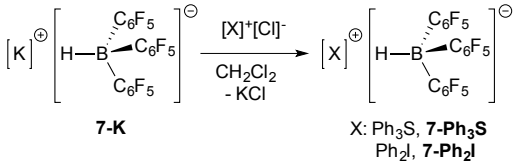
mixtures; however, irradiation of these mixtures at 254 nm for 15 min results in the initiation of the catalytic reactions which were complete in time consistent with the reactions catalysed by $B(C_6F_5)_3$ itself. In contrast, instability of the iodonium derivative **1-Ph$_2$I** in solution under ambient conditions hamper its applications as a latent catalyst and this compound was not as effective in catalytic trials. For **3-Ph$_3$S**, however, despite its stability under ambient conditions and its demonstrated ability to release $B(C_6F_5)_3$ upon irradiation, no catalytic hydrosilylation and Piers-Rubinsztajn reactions were observed even upon longer exposure to UV light. We believe the lack of catalytic reactivity observed for **3-Ph$_3$S** *vs.* **1-Ph$_3$S** is associated with the difference in the mechanism of borane release and, in particular, with the formation of the zwitterionic intermediate **5** and the necessity for base mediated conversion of this salt into $B(C_6F_5)_3$ and the carbamic acid **4-H** (see Scheme 3). However, attempts to elucidate the species that form from **3-Ph$_3$S** upon exposure to 254 nm light under catalytic conditions were unsuccessful and so the reasons for a lack of efficacy for this PhLAG remain ill defined.

Hydridoborate-derived PhLAGs

Although all three ion pairs **1-Ph$_3$S**, **1-Ph$_2$I** and **3-Ph$_3$S** are capable of photorelease of $B(C_6F_5)_3$, the instability of the iodonium salt **1-Ph$_2$I** and a lack of catalytic reactivity of **3-Ph$_3$S** hamper application of these two borates as latent catalysts. It appears that the basicity of the nitrogen centre and the presence of the carbonyl group in the carbamato substituent play the crucial role in the stability and reactivity of carbamatoborate PhLAGs. Therefore, we sought PhLAG molecules with a borane protecting group was simpler and less prone to chemistry that complicated the smooth release of $B(C_6F_5)_3$. We hypothesized that the hydridoborates $[X][HB(C_6F_5)_3]$ (X = Ph_3S, **7-Ph$_3$S**; Ph_2I, **7-Ph$_2$I**; Chart 1) would be ideal targets because photolysis of these salts should result in liberation of more inert by-products than the basic amines of the first generation PhLAGs described above.

Compounds **7-Ph$_3$S** and **7-Ph$_2$I** were prepared in good yield *via* ion exchange reactions between the potassium salt $[K][HB(C_6F_5)_3]$ (**7-K**)[48] and either $[Ph_3S][Cl]$ or $[Ph_2I][Cl]$ (Scheme 4). Both hydridoborates **7-Ph$_3$S** and **7-Ph$_2$I** are air and moisture stable, thermally robust solids (T_{decomp} = 245 °C and 130 °C, respectively, as determined by TGA; Figures S4 and S5 in ESI) and have been characterized by multinuclear NMR, IR and UV absorption spectroscopy and X-ray diffraction analysis for **7-Ph$_2$I**.

The ^{1}H NMR spectra of **7-Ph$_3$S** and **7-Ph$_2$I** show the expected peaks for the Ph_3S^+ cation (δ 7.85, 7.74 and 7.66 ppm) and Ph_2I^+ cation (δ 8.07, 7.72 and 7.54 ppm), respectively, in addition to a broad quartet centered at δ 3.61 ppm for the hydride signal. A complementary doublet is located in the ^{11}B NMR spectra of **7-Ph$_3$S** and **7-Ph$_2$I** pairs at δ -25.3 ppm and δ -25.1 ppm, respectively, for the B-H moiety with ^1J(B-H) ≈ 90 Hz. Moreover, the chemical shift difference ($\Delta_{m,p}$) between the *meta* and *para* F atoms of the C_6F_5 unit in each species is consistent with a four coordinate borate as



Scheme 4 Synthesis of hydridoborates **7-Ph$_3$S** and **7-Ph$_2$I**.

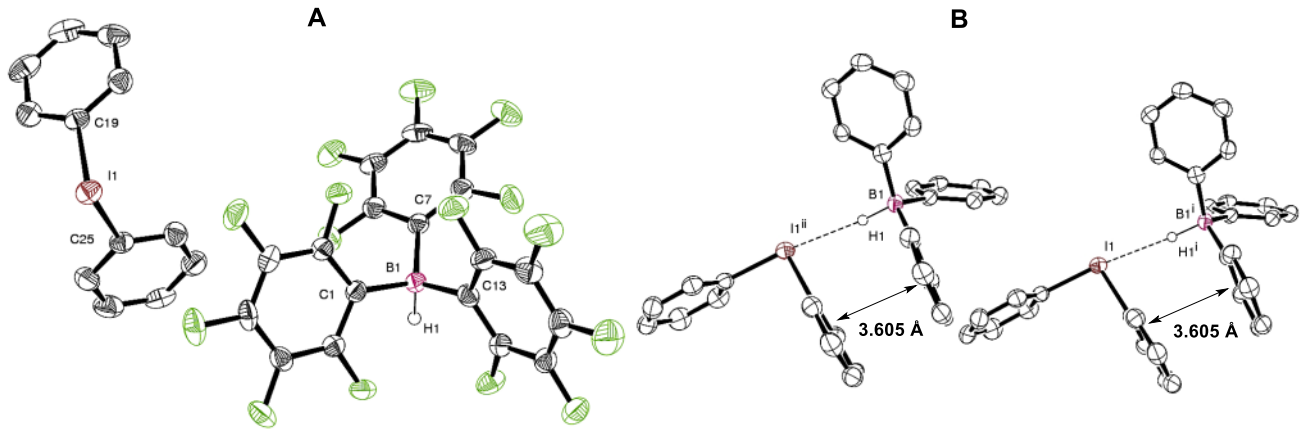
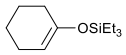


Fig. 2 (**A**) X-ray structure of **7-Ph$_2$I** (thermal ellipsoids drawn to 50% probability level). Hydrogen atoms except B-*H* hydride are omitted for clarity. Selected bond distances (Å): B1-H1, 1.24(4); B1-C1, 1.632(5); B1-C7, 1.629(5); B1-C13, 1.636(5); I1-C19, 2.100(4); I1-C25, 2.102(4). Selected bond angles (°):C1-B1-H1, 103.3(19); C1-B1-C7, 112.8(3); C1-B1-C13, 107.9(3); C19-I1-C25, 96.29(14). (**B**) View showing B-H···I interactions (I1···H1^{i} = H1···I1^{ii}, 2.57(4) Å) and a π-π contact between the benzene ring and C_6F_5 group (*centroid-centroid* distance = 3.605(6) Å) in the unit cell of **7-Ph$_2$I**.

expected.[11] The structure of **7-Ph$_2$I** was confirmed by X-ray crystallography (Figure 2). The B1-H1 bond distance of 1.24(4) Å is within the range of $[HB(C_6F_5)_3]^-$ for other reported structurally characterized hydridoborate ion pairs.[49-51] Although the iodonium ion is pointing away from the hydridoborate unit, a look at the crystal packing shows the iodonium centre is oriented towards another borate anion in the unit cell with non-bonding I•••H distance of 2.57(4) Å. A short π-π contact (3.605(6) Å) was also observed between one of the phenyl substituents of iodonium ion and C_6F_5 group of the anion of another molecule (Figure 2).

The ability of **7-Ph$_3$S** and **7-Ph$_2$I** to behave as PhLAGs was demonstrated by irradiation of acetonitrile solutions (2.1×10^{-3} M) at 254 nm and monitoring the amount of borane release through formation of $CD_3CN{\cdot}B(C_6F_5)_3$[3, 39] by NMR spectroscopy (Table S1 and Figure S6 in ESI). The diphenyliodonium salt **7-Ph$_2$I** was found to be the most efficient in releasing the borane with essentially full conversion to the acetonitrile adduct after 12 min of irradiation, whereas **7-Ph$_3$S** shows 81% conversion to $CD_3CN{\cdot}B(C_6F_5)_3$ during the same exposure time. Similar to the carbamatoborate **1-Ph$_2$I**, ion pair **7-Ph$_2$I** shows increased sensitivity to the ambient light when compared to its triphenylsulfonium analogue, showing complete conversion to $CD_3CN{\cdot}B(C_6F_5)_3$ after 96 h in CD_3CN, whereas only 14% adduct

Table 1 Photoinduced catalytic hydrosilylation[a] and Piers-Rubinsztajn reactions[b] with hydridoborates **7-Ph$_3$S and 7-Ph$_2$I**.

#	Substrate/Silane	PhLAG	Irradiation time, min	Conversion, %[c]	Products
1	PhMeC(O) / Et_3SiH	**7-Ph$_3$S**	15	>99	PhMeCH($OSiEt_3$)
2		**7-Ph$_2$I**	10	>99	
3	PhHC(O) / Et_3SiH	**7-Ph$_3$S**	15	90	$PhCH_2(OSiEt_3)$
4		**7-Ph$_2$I**	10	>99	
5	Cyclohex-2-enone / Et_3SiH	**7-Ph$_3$S**	10	>99	
6		**7-Ph$_2$I**	5	>99	
7	PhOH / Et_3SiH	**7-Ph$_3$S**	5	>99	$PhOSiEt_3$
8		**7-Ph$_2$I**	5	>99	
9	Et_2O / Et_3SiH	**7-Ph$_3$S**	10[d]	98[e]	Et_3SiOEt (86%), $(Et_3Si)_2O$ (12%)
10		**7-Ph$_2$I**	10[d]	>99[e]	Et_3SiOEt (91%), $(Et_3Si)_2O$ (9%)
11	Me_3SiOH / Et_3SiH	**7-Ph$_3$S**	15[f]	>99	$Me_3Si(OSiEt_3)$
12		**7-Ph$_2$I**	15[f]	>99	
13	Me_3SiOEt / PMHS[g]	**7-Ph$_3$S**	15	>99	$(MeHSiO)_x(MeSi(OSiMe_3)O_y$
14		**7-Ph$_2$I**	15	>99	
15	$Si(OMe)_4$ / TMCTS[h]	**7-Ph$_3$S**	15	>99	tetra(trimethoxysiloxy)TMCTS
16		**7-Ph$_2$I**	15	>99	

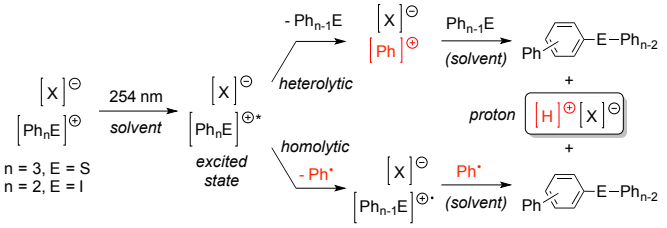
[a] *Conditions:* $C_{substrate}$ = 0.25 M, 1.0 mol % of PhLAG, substrate : Et_3SiH = 1:1 unless stated otherwise, CD_2Cl_2 (solvent), 254 nm. [b] *Conditions:* $C_{substrate}$ = 0.25 M, 1.0 mol % of PhLAG, CD_2Cl_2 (solvent), substrate : hydrosilane = 1:1 unless stated otherwise, 254 nm. [c] Conversion of organic substrate (determined by ^{1}H NMR). [d] After irradiation, the sample was left for 2 h at RT in dark. [e] Conversion and ratio of products determined by GC-MS. [f] After irradiation, the mixture was left for 2 h at RT in dark. [g] PMHS – poly(methylhydrosiloxane). [h] TMCTS - 2,4,6,8-tetramethylcyclotetrasiloxane, $Si(OMe)_4$: TMCTS = 4:1.

Journal Name

ARTICLE

formation was observed for **7-Ph$_3$S** under these conditions. To further investigate the potential of the hydridoborate species **7-Ph$_3$S** and **7-Ph$_2$I** as PhLAGs, each was tested as a latent catalyst in the photoinduced hydrosilylation of carbonyl compounds, silation of alcohols, silanols and ethers and Piers-Rubinsztajn reactions. Over the entire substrate scope (Table 1; Tables S2 and S3 in ESI) both compounds displayed high product yields, consistent with the thermal B(C_6F_5)$_3$-catalyzed reactions with the only difference being that shorter exposure times can be utilized with the diphenyliodonium salt **7-Ph$_2$I** owing to its increased photo-sensitivity. These data indicate that hydridoborates **7** release borane with high efficiency; generally, shorter irradiation times are required for these PhLAGs compared to the first generation PhLAG **1-Ph$_3$S** described above.[34]

Clearly, ion pairs **7** efficiently release B(C_6F_5)$_3$ upon irradiation and we were interested in determining the dominant pathway for borane release in these PhLAG systems. The photodegradation of the Ph_3S^+ and Ph_2I^+ cations has been studied in some detail and most of the products we observe can be rationalized on the basis of these earlier studies.[29, 30] Essentially, excitation of the $[Ph_3S]^+$ and $[Ph_2I]^+$ leads to either homolytic or heterolytic cleavage of an S-C or I-C bond, producing Ph• or Ph^+, respectively (Scheme 5).[52] These highly



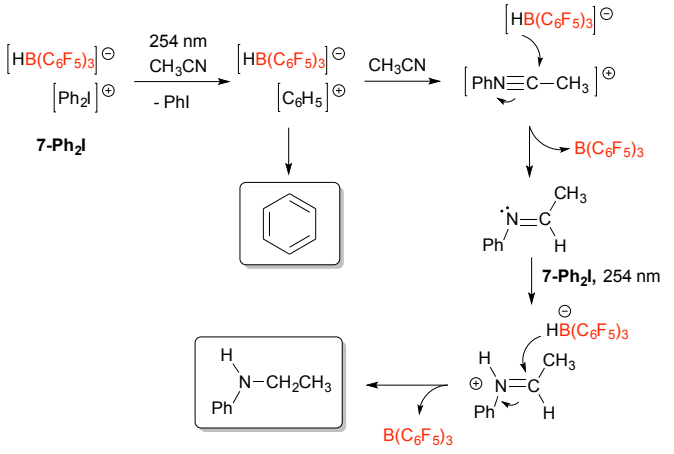
Scheme 5 Proton generation from photolysis of Ph_nE cations

reactive species then rapidly react with the sulphur or iodine containing products of bond cleavage or solvent in reactions that eject protons. When the counter anion is $[HB(C_6F_5)_3]^-$, the consequence of this sequence would presumably be protonation of the anion, loss of H_2 and liberation of B(C_6F_5)$_3$. An analysis of the other photoproducts reveals that the path to borane liberation is somewhat more complex than this and dependant on the nature of the cation and the solvent in which the photochemistry is conducted.

When photolysis (254 nm) of **7-Ph$_3$S** and **7-Ph$_2$I** was carried out in CD_2Cl_2 a resonance consistent with H_2 production was observed in the ^{1}H NMR spectra for both PhLAGs, with no detectable amount of HD. This indicates that, under these conditions, the proton that liberates borane (formed cleanly) stems from the Ph_nE cation; this was confirmed when CD_2Cl_2 solutions of d^1-**7-Ph$_3$S** and d^1-**7-Ph$_2$I** (deuterated in the hydridoborate anion) were exposed to 254 nm light and cleanly formed HD (δ 4.57 ppm, $^1J_{H\text{-}D}$ = 42.6 Hz). The detection of the intramolecular recombination products (phenylthio)biphenyl and iodobiphenyl in the GC-MS (Scheme 5) is further evidence that the main proton source is the cation itself and not the solvent. Also observed in these reactions were significant quantities of benzene and d^1-benzene (δ 7.39 ppm in methylene chloride[53]), indicating that the phenyl cation can also liberate borane by abstraction of the hydride (deuteride) from the counteranion.

Photolysis of PhLAGs **7** in acetonitrile, which was used to quantify the efficiency of borane release through formation of $CD_3CN{\cdot}B(C_6F_5)_3$, was also examined. In the case of the triphenylsulfonium compound, the path to photoliberation of borane was apparently similar to that observed in methylene chloride. Here, H_2 (δ 4.57 ppm) was the main product, along with a similar distribution of diarylthioether products as determined by GC-MS analysis. Photolysis of **7-Ph$_2$I**, however, did not produce any detectable H_2. Instead, in addition to PhI and iodobiphenyl (detected by NMR spectroscopy and GCMS), a major product with a distinct singlet resonance at δ 3.42 ppm in the ^{1}H NMR spectrum was observed along with a minor amount of benzene (δ 7.37 ppm in acetonitrile[53]). Both of these products were confirmed to originate from the hydridoborate by repeating the reaction with $[Ph_2I][DB(C_6F_5)_3]$ (d^1-**7-Ph$_2$I**) in CH_3CN and observing resonances at δ 3.42 and 7.40 ppm in the ^{2}H NMR spectrum.[54]

While the origin of benzene is relatively clear, the identity and origin of the product giving rise to the signal at 3.42 ppm was shown to be a result of reaction of photoproduced phenyl



Scheme 6 Proposed path to secondary products in the photodegradation of PhLAG **7-Ph$_2$I**

cation and the acetonitrile solvent.[55] Analysis using ^{13}C APT NMR and ^{1}H-^{13}C HSQC NMR experiments showed that the resonance at 3.42 ppm could be assigned as a CH_2 group. GC-MS analysis of this product in the photolysis of **7-Ph$_2$I** in CH_3CN indicated it has an m/z of 121, which increases to 124 when changing the solvent to CD_3CN. Furthermore, photolysis of ***d*^{1}-7-Ph$_2$I** in CH_3CN gives the same product with m/z of 123 suggesting that two $[DB(C_6F_5)_3]^-$ units are involved in the reaction. Based on comparison with an authentic sample, we assign this product as *N*-ethylaniline, and suggest it is formed via the path shown in Scheme 6. This proposal has some precedence in previously observed reactivity of phenyl cations with acetonitrile[56] and is consistent with greater tendency of the $[Ph_2I]^+$ cation to release phenyl cations, compared to $[Ph_3S]^+$.[30] Although it is plausible that adduct formation between this by-product and $B(C_6F_5)_3$ could happen, we do not observe this. It is known that *N*-alkyl anilines form very weak adducts with $B(C_6F_5)_3$[57] and so acetonitrile easily displaces this base.

Conclusions

We have developed two families of photo Lewis acid generators (PhLAGs) based on tryphenylsulfonium and diphenyliodonium carbamato- and hydridoborate ion pairs designed to efficiently release the strong Lewis acid, $B(C_6F_5)_3$, upon exposure to UV light. While the carbamatoborate compounds release borane efficiently, the amine functions in both the borate ions and the photo byproducts can interfere with the catalytic function of the release borane in $B(C_6F_5)_3$ catalyzed hydrosilation and silation reactions. The hydridoborates **7**, however, are more well-behaved since their photoproducts in CH_2Cl_2 solution are largely innocuous (H_2, benzene) or very weakly Lewis basic (thioethers or aryl iodides). Compounds **7** are also significantly easier to synthesize and can be prepared on a gram scale as air stable materials. Their use as photoinitiators for several reactions, some of which are highly relevant to siloxane materials synthesis, has been demonstrated. Given the prominence of $B(C_6F_5)_3$ in modern transition metal free catalysis, applications of these PhLAGs to a variety of reactions are possible.

Experimental section

General experimental methods are described in the ESI. The preparation, properties and reactivity of **1-Ph$_3$S** were reported previously.[34] $(Me_4C_5N)CO_2Li$ (**4**)[58] and $[K][HB(C_6F_5)_3]$ (**7-K**)[48] were synthesized according to literature procedures.

Preparation of $[Ph_2I][(^tBu_2C_{12}H_6N)CO_2B(C_6F_5)_3]$ (1-Ph$_2$I)

1-Ph$_2$I was prepared analogously to **1-Ph$_3$S** from $[Li(TMEDA)][(^tBu_2C_{12}H_6N)CO_2B(C_6F_5)_3]$ (508 mg, 0.531 mmol) and $[Ph_2I][Cl]$ (168 mg, 0.531 mmol). The product was additionally recrystallized from CH_2Cl_2 : hexanes (approx. 1:1) at -30 °C. Yield: 237 mg, 40%. Borate **1-Ph$_2$I** selectively labeled with ^{13}C in the carbonyl position was prepared analogously. The ^{13}C label was introduced to the carbamato substituent using $^{13}CO_2$ (see SI for details). ^1H NMR (400 MHz; CD_2Cl_2; δ, ppm): 8.20 (d, $^3J_{H-H}$ = 8.8 Hz, 2H, Carb); 7.95 (s, 2H, Carb); 7.73 (d, $^3J_{H-H}$ = 7.6 Hz, 4H, *o*-H, IPh_2); 7.57 (t, $^3J_{H-H}$ = 7.6 Hz, 2H, *p*-H, IPh_2); 7.39 (m, 6H, *m*-H of IPh_2 (4H) and 2H from Carb); 1.42 (s, 18 H, 2 ^{t}Bu). ^1H NMR (400 MHz; CD_3CN; δ, ppm): 8.07 (d, $^3J_{H-H}$ = 8.8 Hz, 2H, Carb); 8.11 (d, $^4J_{H-H}$ = 2.0 Hz, 2H, Carb); 8.06 (d, $^3J_{H-H}$ = 7.6 Hz, 4H, *o*-H, IPh_2); 7.72 (t, $^3J_{H-H}$ = 7.6 Hz, 2H, *p*-H, IPh_2); 7.54 (t, $^3J_{H-H}$ = 7.6 Hz, 4H, *m*-H, IPh_2); 7.45 (dd, $^3J_{H-H}$ = 8.8 Hz, $^4J_{H-H}$ = 2.0 Hz, 2H, Carb); 1.42 (s, 18 H, 2 ^{t}Bu). $^{13}C\{^1H\}$ NMR (100.6 MHz; CD_2Cl_2; δ, ppm): 32.2 (s, CH_3 of ^{t}Bu); 35.2 (s, Cq, ^{t}Bu); 116.2 (s, CH, Carb); 116.3 (s, CH, Carb); 125.1 (s, CH, Carb); 125.69 (s, Cq, Carb); 125.72 (s, Cq, Carb); 133.7 (s, CH, IPh_2); 134.3 (s, CH, IPh_2); 135.3 (s, CH, IPh_2); 138.0 (s, Cq, Carb); 145.7 (s, Cq, IPh_2) 153.6 (s, Cq, CO_2, found for ^{13}C enriched analogue); carbon signals of C_6F_5 were not observed due to broadening. ^{11}B NMR (128.4 MHz, CD_2Cl_2; δ, ppm): -3.8 (br s). $^{19}F\{^1H\}$ NMR (376.5 MHz; CD_2Cl_2; δ, ppm): –136.3 (app d, $^3J_{F-F}$ = 18.8 Hz, 6F, *o*-F); –163.5 (t, $^3J_{F-F}$ = 18.8 Hz, 3F, *p*-F); –168.2 (br s, 6F, *m*-F). $^{19}F\{^1H\}$ NMR (376.5 MHz; CD_3CN; δ, ppm): –137.1 (app d, $^3J_{F-F}$ = 18.8 Hz, 6F, *o*-F); –164.7 (t, $^3J_{F-F}$ = 18.8 Hz, 3F, *p*-F); –169.7 (br s, 6F, *m*-F). UV-vis (CH_2Cl_2; $1.1\cdot10^{-5}$ M; λ, nm (ε, $M^{-1}\cdot cm^{-1}$)): 234 (88.04×10^3); 291 (20.11×10^3); 310 (7.58×10^3); 323 (6.88×10^3). IR (nujol, selected bands): 1676 cm^{-1} (C=O). ESI-MS: $\{C_{39}H_{24}BF_{15}NO_2\}^-$ 834.2 m/z. TGA (5.8 mg; N_2 (60 mL/min); T = 23 °C – 450 °C (2.0 °C/min)): T_{decomp} = 158 °C.

Preparation of $[Li][(Me_5C_5N)CO_2B(C_6F_5)_3]$ (3-Li)

A solution of $B(C_6F_5)_3$ (667 mg, 1.3 mmol) in CH_2Cl_2 (30 mL) was added in one portion at room temperature to a solid $(Me_4C_5N)CO_2Li$ (**4**) (249 mg, 1.3 mmol). The resulting solution was stirred at room temperature for 1 h. All volatiles were pumped off to leave a beige residue, which was washed with hexanes (20 mL) and dried in vacuum. The product appears as a beige powder. Yield: 838 mg, 92%. ^1H NMR (400 MHz; CD_2Cl_2; δ, ppm): 1.63 (m, 6H); 1.33 (s, 12 H). ^7Li NMR (155.5 MHz; CD_2Cl_2; δ, ppm): -0.6 (br s). $^{13}C\{^1H\}$ NMR (100.6 MHz; CD_2Cl_2; δ, ppm): 16.1 (s); 30.2 (s); 40.8 (s); 55.6 (s); 138.0 (br s); 138.9 (br s); 148.5 (br s); 149.3 (br s); ipso-carbon of C_6F_5 and carbonyl carbon were not observed due to broadening. ^{11}B NMR (128.4 MHz, CD_2Cl_2; δ, ppm): –4.9 (br s). $^{19}F\{^1H\}$ NMR (376.5 MHz; CD_2Cl_2; δ, ppm): –135.1 (br s, 6F, o-F, $B(C_6F_5)_3$); –159.3 (br s, 3F, p-F, $B(C_6F_5)_3$); –164.0 (br s, 6F, m-F, $B(C_6F_5)_3$). IR (nujol, selected bands): 1647 cm^{-1} (C=O). UV-vis (CH_2Cl_2; $1.7\cdot10^{-3}$ M; λ, nm (ε, $M^{-1}\cdot cm^{-1}$)): 232 (2280); 260 (831); 301 (112).

Preparation of $[Ph_3S][(Me_5C_5N)CO_2B(C_6F_5)_3]$ (3-Ph$_3$S)

CH_2Cl_2 (50 mL) was added via vacuum transfer to a mixture of solid $[Ph_3S][Cl]$ (143.6 mg, 0.481 mmol) and **3-Li** (338 mg, 0.481 mmol). The reaction mixture was stirred at room temperature for 1 h. During this time, formation of white precipitate was observed. The mixture was filtered through Celite. All volatiles were pumped off to leave a yellowish foamy residue which was washed with cold (-30 °C) hexanes (20 mL) and dried in vacuum. The product appears as a beige powder. Yield: 277 mg, 60%. ^1H NMR (400 MHz; CD_2Cl_2; δ, ppm): 7.85 (t, $^3J_{H-H}$ = 7.6

Hz, 3H, p-H, SPh_3); 7.73 (t, $^3J_{H-H}$ = 7.6 Hz, 6H, m-H, SPh_3); 7.55 (d, $^3J_{H-H}$ = 7.6 Hz, 6H, o-H, SPh_3); 1.53 (br m, 6H); 1.32 (s, 12 H). ^{1}H NMR (400 MHz; CD_3CN; δ, ppm): 7.84 (t, $^3J_{H-H}$ = 7.6 Hz, 3H, p-H, SPh_3); 7.74 (t, $^3J_{H-H}$ = 7.6 Hz, 6H, m-H, SPh_3); 7.67 (d, $^3J_{H-H}$ = 7.6 Hz, 6H, o-H, SPh_3); 1.54 (br m, 6H); 1.32 (s, 12 H). $^{13}C\{^1H\}$ NMR (100.6 MHz; CD_2Cl_2; δ, ppm):16.9 (s); 31.3 (s); 42.6 (s); ipso-carbon of TMP is obscured by CD_2Cl_2 signal; 124.0 (s); 131.2 (s); 132.5 (s); 135.9 (s); 169.4 (s); carbon signals of C_6F_5 were not observed due to broadening. $^{13}C\{^1H\}$ NMR (100.6 MHz; CD_3CN; δ, ppm):17.4 (s); 30.8 (s); 43.1 (s); 56.3 (s); 125.9 (s); 132.5 (s); 133.0 (s); 136.2 (s); carbon signals of C_6F_5 and carbonyl carbon were not observed. ^{11}B NMR (128.4 MHz, CD_2Cl_2; δ, ppm): -5.4 (br s). $^{19}F\{^1H\}$ NMR (376.5 MHz; CD_2Cl_2; δ, ppm): –133.5 (br s, 6F, o-F, $B(C_6F_5)_3$); –164.2 (t, $^3J_{F-F}$ = 18.8 Hz, 3F, p-F, $B(C_6F_5)_3$); –168.0 (br s, 6F, m-F, $B(C_6F_5)_3$). IR (nujol, selected bands) 1653 cm^{-1} (C=O). UV-vis (CH_2Cl_2; $1.1\cdot10^{-5}$ M; λ, nm (ε, $M^{-1}\cdot cm^{-1}$)): 228 (23656); 247 (16112); 276 (2926). ESI-MS: $[C_{28}H_{18}BF_{15}NO_2]^-$ 696.1 m/z. TGA (6.600 mg; N_2 (60 mL/min); T = 25 °C – 450 °C (2.0 °C/min)): T(decomp) = 214 °C. Elem. Anal. ($C_{46}H_{33}BF_{15}NO_2S$, M.W.: 959.6): calcd. C(57.57), H(3.47), N(1.46); found C(57.58), H(3.56), N(1.31). Single crystals of **3-Ph$_3$S** suitable for X-ray diffraction analysis were grown by slow vaporization of hexanes into a toluene solution at -30 °C.

Photogeneration of [(Me$_4$C$_5$NH)CO$_2$B(C$_6$F$_5$)$_3$] (5) from 3-Ph$_3$S

3-Ph$_3$S (15.0 mg, 0.0156 mmol) was dissolved in 3.0 mL of CH_2Cl_2 and the resulting solution was transferred into a quartz test tube which was sealed with a septum under argon atmosphere. The tube was exposed to 254 nm light for 2 hours. All volatiles were pumped off to give yellow oily material, which was dried in vacuum and washed/sonicated with 5.0 mL of pentane. After pentane was decanted the residue was dried in high vacuum for a day to yield yellow-brown foamy material of [$(Me_4C_5NH)CO_2B(C_6F_5)_3$] (**5**), which was dissolved in CD_2Cl_2 for NMR studies. Subsequent addition of 100.0 μL of CD_3CN to a solution of **5** in CD_2Cl_2 resulted in immediate disappearance of the starting material and formation of an adduct $CD_3CN\cdot B(C_6F_5)_3$. In the absence of acetonitrile (or any similar base) **5** is stable under ambient conditions (room temperature and ambient light) as well as under UV light. An analogous addition of TMP (5.0 μL, 0.03 mmol) to a CD_2Cl_2 solution of **5** leads to immediate formation of **3-TMPH**. Borate **5** does not show exchange with $^{13}CO_2$ or B(*p*-H-$C_6F_4)_3$ under ambient conditions in the absence of a base. **5** can be also generated on NMR scale via stoichiometric treatment of either **3-Li** or **3-Ph$_3$S** with HOTf in CD_2Cl_2; however, these reactions were found to be less clean than photolysis of **3-Ph$_3$S** in CD_2Cl_2.

5: ^{1}H NMR (400 MHz; CD_2Cl_2; δ, ppm): 1.49 (s, 12H, $4CH_3$, TMP); 1.67 (br m, 4H, $2CH_2$, TMP); 1.77 (br m, 2H, CH_2, TMP); 6.93 (br s, 1H, NH; $^1J_{N-H}$ ≈ 70 Hz, found by ^{1}H-^{15}N HMQC, see Figure S9 in ESI). 1.53 (br m, 6H); 1.32 (s, 12 H). ^{11}B NMR (128.4 MHz, CD_2Cl_2; δ, ppm): -3.6 (br s). $^{19}F\{^1H\}$ NMR (376.5 MHz; CD_2Cl_2; δ, ppm): –136.0 (br s, 6F, o-F, $B(C_6F_5)_3$); –160.4 (br s 3F, p-F, $B(C_6F_5)_3$); –165.6 (t, $^3J_{F-F}$ = 18.8 Hz 6F, m-F, $B(C_6F_5)_3$). $^{13}C\{^1H\}$ NMR (100.6 MHz; CD_2Cl_2; *δ*, ppm): 16.6 (s, -*C*$H_2CH_2C(CH_3)_2$N-); 28.1 (s, -CH_2CH_2C(*C*H_3)$_2$N-); 36.0 (s, -CH_2*C*$H_2C(CH_3)_2$N-); 59.1 (s, -CH_2CH_2*C*$(CH_3)_2$N-), 136.1, 138.8, 147.2, 149.6 (all s, C_6F_5); all attempts to observe carbonyl carbon were unsuccessful. All attempts to obtain **5** in analytically pure form for elemental analysis were unsuccessful.

Preparation of [Ph$_3$S][HB(C$_6$F$_5$)$_3$] (7-Ph$_3$S)

To a stirring suspension of triphenylsufonium chloride (0.250 g, 0.837 mmol) in 10 mL of CH_3CN was added [K][$HB(C_6F_5)_3$] (**7-K**) (0.462 g, 0.837 mmol) in several portions and the reaction mixture was allowed to stir at room temperature for 2 h. Over this time a cloudy white solution was formed. Filtration of the solution through an Acrodisc followed by evaporation of all volatiles gave a white, tacky solid. The tacky residue was washed/sonicated with hexane (10 mL) and dried under vacuum to give a white powder. Further purification was achieved by dissolving the product in a minimal volume of hot CH_2Cl_2 and allowing the product to precipitate at -20 ºC. Yield: 86%, 560 mg. Deuterium labeled salt *d^1*-**7-Ph$_3$S** was prepared analogously from [K][$DB(C_6F_5)_3$]. ^{1}H NMR (400 MHz; CD_3CN; δ, ppm): 7.85 (t, $^3J_{H-H}$ = 7.5 Hz, 3H, *p*-H, Ph_3S); 7.74 (t, $^3J_{H-H}$ = 8.2 Hz, 6H, *m*-H, Ph_3S); 7.66 (d, $^3J_{H-H}$ = 7.4 Hz, 6H, *o*-H, Ph_3S); 3.61 (br q, $^1J_{B-H}$ = 91 Hz, 1H, B-H). $^{19}F\{^1H\}$ NMR (376.5 MHz; CD_3CN; δ, ppm): -136.5 (d, $^3J_{F-F}$ = 18.8 Hz, 6F, *o*-F, $B(C_6F_5)_3$); -166.9 (t, $^3J_{F-F}$ = 19.5 Hz, 3F, *p*-F, $B(C_6F_5)_3$); -170.2 (m, 6F, *m*-F, $B(C_6F_5)_3$). ^{11}B NMR (128.4 MHz; CD_3CN; δ, ppm): -25.3 (br d, $^1J_{B-H}$ = 91 Hz, B-H). $^{13}C\{^1H\}$ NMR (150.9 MHz; CD_3CN; δ, ppm): 149.1 (dm, $^1J_{C-F}$ = 244.3 Hz); 138.8 (dm, $^1J_{C-F}$ = 242.7 Hz); 137.4 (dm, $^1J_{C-F}$ = 237.1 Hz); 135.7, 132.5, 132.1, 125.5. IR (nujol, selected bands) 2344 cm^{-1} (B-H). UV-vis (CH_2Cl_2; $1.1\cdot10^{-5}$ M; λ, nm (ε, $M^{-1}\cdot cm^{-1}$)): 227 (36660). TGA (8.978 mg; N_2 (60 mL/min); T = 25 °C – 450 °C (2.0 °C/min)): T_{decomp} = 245 °C. Elem. Anal. ($C_{36}H_{16}BF_{15}S$; M.W.: 776.4): calcd. C(55.69), H(2.08); found C(55.12), H(2.05).

Preparation of [Ph$_2$I][HB(C$_6$F$_5$)$_3$] (7-Ph$_2$I)

7-Ph$_2$I was prepared analogously to **7-Ph$_3$S** from **7-K** (225 mg, 0.408 mmol) using [Ph_2I][Cl] (129 mg, 0.408 mmol) in CH_2Cl instead of [Ph_3S][Cl] in CH_3CN. Yield: 300 mg, 90%. X-ray quality crystals were obtained by dissolving the solid in a 50:50 mixture of CH_2Cl_2/hexane and cooling the solution to -20 °C. Deuterium labeled salt *d^1*-**7-Ph$_2$I** was prepared analogously from [K][$DB(C_6F_5)_3$]. ^{1}H NMR (400 MHz; CD_3CN; *δ*, ppm): 8.07 (dd, $^3J_{H-H}$ = 8.4 Hz, $^4J_{H-H}$ = 0.9 Hz, 4H, *o*-H, Ph_2I); 7.72 (t, $^3J_{H-H}$ = 7.5 Hz, 2H, *p*-H, Ph_2I); 7.54 (t, $^3J_{H-H}$ = 7.9 Hz, 4H, *m*-H, Ph_2I); 3.61 (br q, $^1J_{B-H}$ = 93 Hz, 1H, B-H). $^{19}F\{^1H\}$ NMR (376.5 MHz; CD_3CN; *δ*, ppm): -136.5 (d, $^3J_{F-F}$ = 19.3 Hz, 6F, *o*-F, $B(C_6F_5)_3$); -166.8 (t, $^3J_{F-F}$ = 19.5 Hz, 3F, *p*-F, $B(C_6F_5)_3$); -170.2 (m, 6F, *m*-F, $B(C_6F_5)_3$). ^{11}B NMR (128.4 MHz; CD_3CN; *δ*, ppm): -25.1 (br d, $^1J_{B-H}$ = 93 Hz, B-H). $^{13}C\{^1H\}$ NMR (150.9 MHz; CD_3CN; *δ*, ppm): 149.1 (dm, $^1J_{C-F}$ = 229.7 Hz); 139.0 (dm, $^1J_{C-F}$ = 248.7 Hz); 137.4 (dm, $^1J_{C-F}$ = 243.9 Hz); 136.3, 134.1, 133.5, 114.7. IR (nujol, selected bands) 2285 cm^{-1} (B-H). UV-vis (CH_2Cl_2; $1.1\cdot10^{-5}$ M; λ, nm (ε, $M^{-1}\cdot cm^{-1}$)): 226 (28636). TGA (8.978 mg; N_2 (60 mL/min); T = 25 °C – 450 °C (2.0 °C/min)): T_{decomp} = 130 °C. Elem. Anal.

($C_{30}H_{11}BF_{15}I$; M.W.: 794.6): calcd. C (45.37), H (1.40); found C (45.40), H (1.47).

Photolysis of 1-Ph_2I: trapping $B(C_6F_5)_3$

CH_3CN (65.3 µL, 1.25 mmol) was added to a solution of **1-Ph_2I** (1.4 mg, $1.25\cdot10^{-3}$ mmol) in 534.7 µL of CD_2Cl_2 in a quartz NMR tube ($[\mathbf{1\text{-}Ph_2I}]_{total}$ = $2.1\cdot10^{-3}$ mol/L). No reaction was observed in the absence of UV light within 15 min at room temperature. The sample was exposed to 254 nm light and the reaction was followed by NMR spectroscopy for 12 min. During this time >99% conversion of **1-Ph_2I** to $CH_3CN\cdot B(C_6F_5)_3$ (Table S1 and Figure S6 in ESI) was observed by ^1H and ^{19}F NMR.

Photolysis of 3-Ph_3S: trapping $B(C_6F_5)_3$

0.7 mL of a solution of **3-Ph_3S** ($2.1\cdot10^{-3}$ mol/L) and $Si(SiMe_3)_4$ (1.6 mg, 0.0048 mmol) in CD_3CN was placed into a quartz NMR tube and the sample was sealed with the septum under argon atmosphere. The mixture was left at room temperature and ambient light for 1.5 hours showing no reaction by NMR spectroscopy. The mixture was exposed to 254 nm light and the reaction was monitored by NMR spectroscopy every 4 min of irradiation (the sample was exposed to UV light for 13 min in total). The conversion of **3-Ph_3S** to $CD_3CN\cdot B(C_6F_5)_3$ was calculated from integration of the ^1H NMR spectra. Total conversion of **3-Ph_3S** after 13 min at 254 nm was 46% (Table S1 and Figure S6 in ESI). The release of TMP was also observed by ^1H NMR spectroscopy.

Photolysis of 7-Ph_3S: trapping $B(C_6F_5)_3$

A solution of **7-Ph_3S** in CD_3CN ($2.1\cdot10^{-3}$ mol/L) was placed into a quartz NMR tube. No reaction was observed in the absence of UV light during 2h at room temperature. The sample was exposed to 254 nm light for 12 min and the reaction was monitored by NMR spectroscopy showing 81% conversion of **7-Ph_3S** to $CD_3CN\cdot B(C_6F_5)_3$ (Table S1 and Figure S6 in ESI).

Photolysis of 7-Ph_2I: trapping $B(C_6F_5)_3$

The reaction was done analogously to photolysis of **7-Ph_3S**. of **7-Ph_2I** in CD_3CN. Exposure of the sample of **7-Ph_2I** in CD_3CN ($2.1\cdot10^{-3}$ mol/L) to 254 nm light for 12 min results in >99% conversion of **7-Ph_2I** to $CD_3CN\cdot B(C_6F_5)_3$ (Table 1 in ESI).

General procedure for photoinduced catalytic reactions with PhLAGs

Hydrosilane was added in one portion at room temperature to a solution of a substrate (0.25 mol/L) and either **1-Ph_3S** or hydridoborates **7-Ph_3S** or **7-Ph_2I** (1 mol % to the substrate) in either CD_2Cl_2 or CH_2Cl_2. The resulting mixture was transferred to either quartz NMR or quartz test tube under argon atmosphere. No reaction was observed in the absence of UV light within 1 hour at room temperature. For hydrosilylation reactions, the samples were exposed to 254 nm light for 15 min. Conversion of organic substrates was determined by ^1H NMR spectroscopy using $Si(SiMe_3)_4$ as a standard. For silylation and Piers-Rubinsztajn reactions, the samples were exposed to 254 nm light for 15-45 min and after that left at room temperature for 10 min – 48 hours. Yields of products were determined by NMR spectroscopy and in the case of monomeric substrates were confirmed by GS-MS analysis.

Acknowledgements

Funding for this work was provided by Intel Corp. and NSERC of Canada *via* CRD Grant to W.E.P. W.E.P. also thanks the Canada Research Chair secretariat for a Tier I CRC (2013–2020).

Notes and references

1. W. E. Piers and T. Chivers, *Chem. Soc. Rev.*, 1997, **26**, 345-354.
2. W. E. Piers, *Adv. Organomet. Chem.*, 2005, **52**, 1-76.
3. C. Bergquist, B. M. Bridgewater, C. J. Harlan, J. R. Norton, R. A. Friesner and G. Parkin, *J. Am. Chem. Soc.*, 2000, **122**, 10581-10590.
4. T. Beringhelli, D. Maggioni and G. D'Alfonso, *Organometallics*, 2001, **20**, 4927-4938.
5. G. Erker, *Dalton Trans.*, 2005, 1883-1890.
6. E. Y.-X. Chen and T. J. Marks, *Chem. Rev.*, 2000, **100**, 1391-1434.
7. K. Ishihara, N. Hananki and H. Yamamoto, *Synlett*, 1993, **1993**, 577-579.
8. D. J. Parks and W. E. Piers, *J. Am. Chem. Soc.*, 1996, **118**, 9440-9441.
9. G. C. Welch and D. W. Stephan, *J. Am. Chem. Soc.*, 2007, **129**, 1880-1881.
10. D. J. Parks, J. M. Blackwell and W. E. Piers, *J. Org. Chem.*, 2000, **65**, 3090-3098.
11. J. M. Blackwell, E. R. Sonmor, T. Scoccitti and W. E. Piers, *Org. Lett.*, 2000, **2**, 3921-3923.
12. J. M. Blackwell, K. L. Foster, V. H. Beck and W. E. Piers, *J. Org. Chem.*, 1999, **64**, 4887-4892.
13. M. Rubin, T. Schwier and V. Gevorgyan, *J. Org. Chem.*, 2002, **67**, 1936-1940.
14. P. A. Chase, T. Jurca and D. W. Stephan, *Chem. Commun.*, 2008, 1701-1703.
15. V. Sumerin, F. Schulz, M. Nieger, M. Leskelä, T. Repo and B. Rieger, *Angew. Chem. Int. Ed.*, 2008, **47**, 6001-6003.
16. D. W. Stephan and G. Erker, *Angew. Chem. Int. Ed.*, 2010, **49**, 46-76.
17. D. W. Stephan and G. Erker, *Angew. Chem. Int. Ed.*, 2015, **54**, 6400-6441.
18. D. B. Thompson and M. A. Brook, *J. Am. Chem. Soc.*, 2007, **130**, 32-33.
19. J. B. Grande, F. Gonzaga and M. A. Brook, *Dalton Trans.*, 2010, **39**, 9369-9378.
20. M. A. Brook, J. B. Grande and F. Ganachaud, *Adv. Polym. Sci.*, 2010, **235**, 161-183.
21. J. Chojnowski, S. Rubinsztajn, J. A. Cella, W. Fortuniak, M. Cypryk, J. Kurjata and K. Kaźmierski, *Organometallics*, 2005, **24**, 6077-6084.
22. J. Chojnowski, J. Kurjata, W. Fortuniak, S. Rubinsztajn and B. Trzebicka, *Macromolecules*, 2012, **45**, 2654-2661.
23. J. Kurjata, W. Fortuniak, S. Rubinsztajn and J. Chojnowski, *Eur. Polym. J.*, 2009, **45**, 3372-3379.
24. R. M. Thomas, A. Fedorov, B. K. Keitz and R. H. Grubbs, *Organometallics*, 2011, **30**, 6713-6717.

25. A. Piermattei, S. Karthikeyan and R. P. Sijbesma, *Nat. Chem.*, 2009, **1**, 133-137.
26. B. K. Keitz and R. H. Grubbs, *J. Am. Chem. Soc.*, 2009, **131**, 2038-2039.
27. A. Y. Khalimon, E. M. Leitao and W. E. Piers, *Organometallics*, 2012, **31**, 5634-5637.
28. R. A. Weitekamp, H. A. Atwater and R. H. Grubbs, *J. Am. Chem. Soc.*, 2013, **135**, 16817-16820.
29. J. L. Dektar and N. P. Hacker, *J. Am. Chem. Soc.*, 1990, **112**, 6004-6015.
30. J. L. Dektar and N. P. Hacker, *J. Org. Chem.*, 1990, **55**, 639-647.
31. S. I. Schlesinger, *Photo. Sci. Eng.*, 1974, **18**, 387-393.
32. H. Pobiner, *Anal. Chim. Acta*, 1978, **96**, 153-163.
33. U. Müller, A. Utterodt, W. Mörke, B. Deubzer and C. Herzig, *J. Photochem. Photobiol A: Chem.*, 2001, **140**, 53-66.
34. A. Y. Khalimon, W. E. Piers, J. M. Blackwell, D. J. Michalak and M. Parvez, *J. Am. Chem. Soc.*, 2012, **134**, 9601-9604.
35. D. J. Parks, W. E. Piers, M. Parvez, R. Atencio and M. J. Zaworotko, *Organometallics*, 1998, **17**, 1369-1377.
36. A. E. Ashley, A. L. Thompson and D. O'Hare, *Angew. Chem. Int. Ed.*, 2009, **48**, 9839-9843.
37. A. Berkefeld, W. E. Piers and M. Parvez, *J. Am. Chem. Soc.*, 2010, **132**, 10660-10661.
38. For detailed NMR studies of photolysis of **1-Ph$_3$S**, see ref. 29.
39. H. Jacobsen, H. Berke, S. Döring, G. Kehr, G. Erker, R. Fröhlich and O. Meyer, *Organometallics*, 1999, **18**, 1724-1735.
40. See ESI for details of decomposition of **1-Ph$_2$I** under ambient conditions.
41. T. Eicher and S. Hauptmann, *The Chemistry of Heterocycles, 2nd Ed.*, Wiley-VCH, Weinheim, 2003.
42. M. Aresta, D. Ballivet-Tkatchenko, D. B. Dell'Amico, M. C. Bonnet, D. Boschi, F. Calderazzo, R. Faure, L. Labella and F. Marchetti, *Chem. Commun.*, 2000, 1099-1100.
43. The carbazole is a weak Lewis base and does not bind B($C_6F_{5)3}$ strongly nor interfere with catalytic reactions mediated by B(C_6F_5)$_3$, see ref. 34.
44. M. Morgenthaler, E. Schweizer, A. Hoffmann-Röder, F. Benini, R. E. Martin, G. Jaeschke, B. Wagner, H. Fischer, S. Bendels, D. Zimmerli, J. Schneider, F. Diederich, M. Kansy and K. Müller, *ChemMedChem*, 2007, **2**, 1100-1115.
45. T. Voss, T. Mahdi, E. Otten, R. Fröhlich, G. Kehr, D. W. Stephan and G. Erker, *Organometallics*, 2012, **31**, 2367-2378.
46. M. Ullrich, A. J. Lough and D. W. Stephan, *Organometallics*, 2010, **29**, 3647-3654.
47. M. M. Morgan, A. J. V. Marwitz, W. E. Piers and M. Parvez, *Organometallics*, 2013, **32**, 317-322.
48. W. E. Piers, A. J. V. Marwitz and L. G. Mercier, *Inorg. Chem.*, 2011, **50**, 12252-12262.
49. X. Yang, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1994, **116**, 10015-10031.
50. F.-C. Liu, J. Liu, E. A. Meyers and S. G. Shore, *J. Am. Chem. Soc.*, 2000, **122**, 6106-6107.
51. C. Jiang, O. Blacque, T. Fox and H. Berke, *Organometallics*, 2011, **30**, 2117-2124.
52. Scheme 5 depicts the major processes involved in photolysis of these cations and it is somewhat of a simplification. Minor reactions involving, for example, coupling of phenyl radicals or quenching of these reactive species through reaction with solvent, are operative but, for clarity, not depicted in this Scheme.
53. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176-2179.
54. A second minor resonance in the aromatic region was also observed in the ^{2}H NMR spectrum. The identity of this product is unclear; however, we believe it may belong to d_1-biphenyl forming in small amount by the reaction of d_1-benzene and a second equivalent of phenyl cation coming from photodecomposition of Ph_2I^+.
55. J. J. Ritter and P. P. Minieri, *J. Am. Chem. Soc.*, 1948, **70**, 4045-4048.
56. N. P. Hacker, D. V. Leff and J. L. Dektar, *J. Org. Chem.*, 1991, **56**, 2280-2282.
57. N. Millot, Catherine C. Santini, B. Fenet and Jean M. Basset, *Eur. J. of Inorg. Chem.*, 2002, **2002**, 3328-3335.
58. A. R. Kennedy, R. E. Mulvey, D. E. Oliver and S. D. Robertson, *Dalton Trans.*, 2010, **39**, 6190-6197.

1