ChemComm

COMMUNICATION

View Article Online
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Cite this: *Chem. Commun.*, 2018, 54, 7243

Received 9th May 2018,
Accepted 6th June 2018

DOI: 10.1039/c8cc03741h

rsc.li/chemcomm

Piers' borane-mediated hydrosilylation of epoxides and cyclic ethers†

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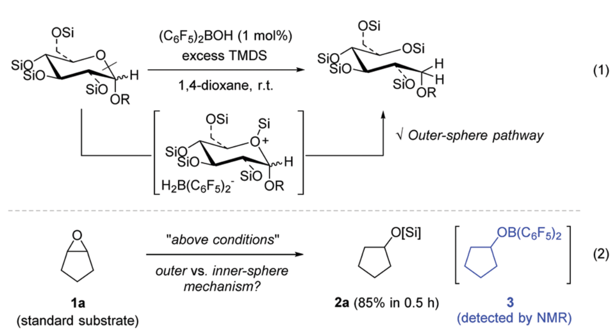
We report the first diarylborane-catalysed hydrosilylation of epoxides and cyclic ethers. Mechanistic studies on the *in situ* generated Piers' borane $(C_6F_5)_2BH$ with hydrosilanes in the presence of an epoxide revealed that an alkyloxy(diaryl)borane $(C_6F_5)_2BOR$ is readily formed as a catalytically competent species for the outer-sphere hydrosilylation of epoxides and cyclic ethers.

Epoxides are a highly useful synthetic building unit frequently employed for the construction of multi-functionalized and/or complex molecules in organic synthesis[1] and polymer chemistry.[2] Among various transformations, selective reduction of unsymmetrical epoxides has drawn special attention since it could selectively afford one of the two isomeric alcohol products. For instance, heterogeneous hydrogenolysis of epoxides by a Pd-based catalyst system has been well studied.[3,4] Although this procedure offers a straightforward synthetic route to alcohols from epoxides, it often suffers from low selectivity and a narrow substrate scope.[5] In this regard, the hydrosilylation of epoxides using well-defined homogeneous catalysts could be a competent alternative to the hydrogenolysis. In fact, a number of homogeneous catalysts have been developed for the epoxide hydrosilylation by several research groups (Scheme 1a).[6] The working mode of these catalysts can be divided into four types: (i) a silylium ion-mediated outer-sphere pathway; (ii) an inner-sphere path involving an epoxide C–O bond insertion into a metal hydride; (iii) a radical process involving a metal-centered radical species; and (iv) a route *via* a base-initiated outer-sphere hydride transfer.

On the other hand, a highly electron-deficient arylborane $B(C_6F_5)_3$ is known to be an efficient catalyst for the conversion of ethers and alcohols with hydrosilanes to provide a range of silyl ethers.[7] One critical limitation in this procedure is an exhaustive reduction giving rise to alkanes. Such a deoxygenative path is mainly driven by intrinsically high Lewis acidity of $B(C_6F_5)_3$ (Scheme 1b).[7c–f] The $B(C_6F_5)_3$-catalysed hydrosilylative transformation has been postulated to proceed *via* a silyloxonium ion bearing a borohydride anion $[HB(C_6F_5)_3^-]$, where the borohydride attacks the α-carbon of oxonium leading to the C–O bond cleavage. In this context, we hypothesized that a less Lewis acidic Piers' borane $(C_6F_5)_2BH$ that is readily generated *in situ* from the reaction of $(C_6F_5)_2BOH$ with hydrosilanes can mediate the hydrosilylation of epoxides and cyclic ethers without the exhaustive deoxygenation.

Here, we report the hydrosilylation of epoxides mediated by *in situ* generated Piers' borane $(C_6F_5)_2BH$ with an emphasis on the catalytic pathway (Scheme 1c).[8] Mechanistic investigations revealed that an alkyloxy(diaryl)borane $(C_6F_5)_2BOR$ is formed upon the reaction of *in situ* generated Piers' borane with epoxides, and that it acts as a competent catalyst for the outer-sphere hydrosilylation of epoxides. Stoichiometric studies suggested that the generation of Piers' borane from the alkyloxyborane is slower relative to the alkyloxyborane-mediated hydrosilylation process. Most significantly, it was found that the selectivity for the ring-opening of epoxides is reversed between the Piers' borane and the $B(C_6F_5)_3$ catalyst.



Previously, we reported a selective C–O bond cleavage of sugars *via* hydrosilylation catalysed by Piers' borane $(C_6F_5)_2BH$ generated *in situ* [eqn (1)].[9] This reductive transformation of sugars was proposed to proceed *via* an outer-sphere ionic

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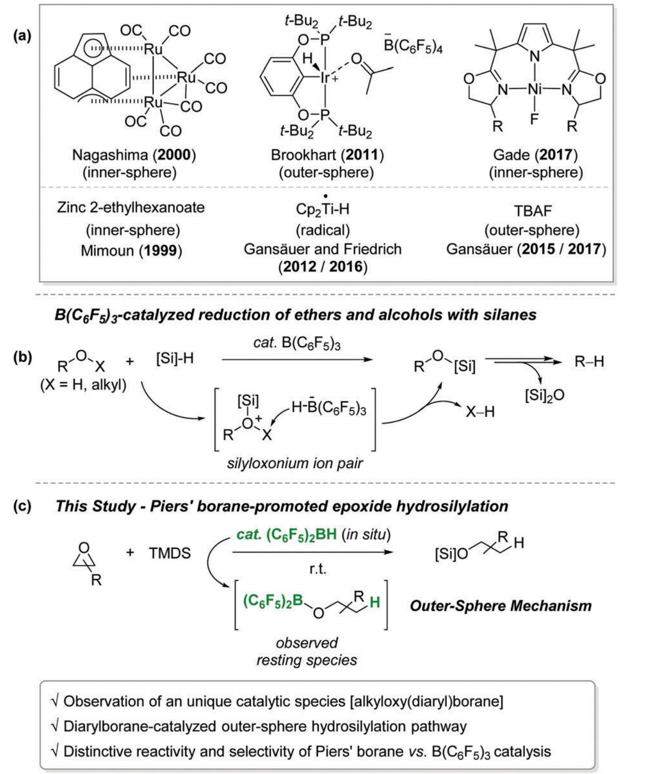
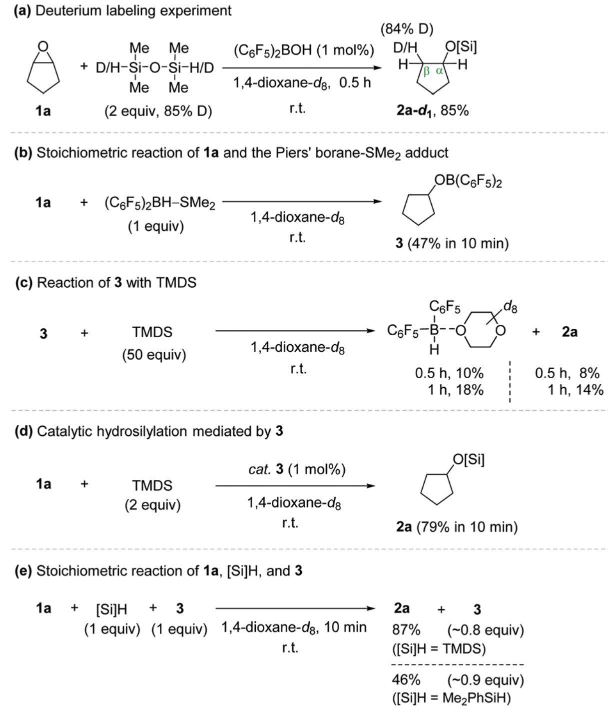
† Electronic supplementary information (ESI) available: Detailed experimental procedures and characterization data. See DOI: 10.1039/c8cc03741h



Scheme 1 (a) Homogeneous catalysts for epoxide hydrosilylation. (b) $B(C_6F_5)_3$-catalysed C–O bond cleavage of alkylethers with hydrosilanes. (c) Bis(pentafluorophenyl)borane-promoted hydrosilylation of epoxides (this work). TBAF = tetrabutylammonium fluoride, TMDS = 1,1,3,3-tetramethyldisiloxane.



Scheme 2 Preliminary mechanistic experiments.

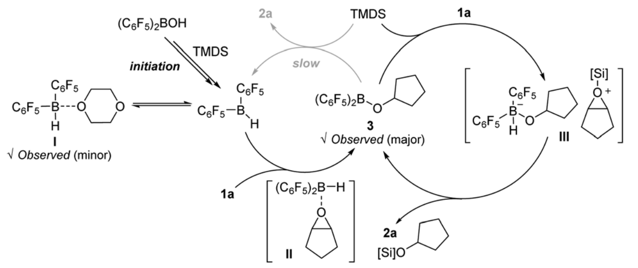
pathway involving a cyclic silyloxonium ion bearing a borohydride $[H_2B(C_6F_5)_2^-]$, selectively providing a range of linear polyols. Based on this precedent, we were encouraged to apply the procedure for the hydrosilylation of cyclopentene oxide **1a**, which was chosen as a representative substrate for preliminary mechanistic studies in an effort to elucidate the reaction pathway. As envisaged, the reaction of **1a** with 1,1,3,3-tetramethyldisiloxane (TMDS) took place in the presence of $(C_6F_5)_2BOH$ (1 mol%) to furnish the corresponding cyclopentyloxysilane **2a** in 85% yield in 0.5 h [eqn (2)]. Interestingly, ^{19}F NMR spectroscopy of the reaction mixture exhibited a set of major signals due to cyclopentyloxy-[bis(pentafluorophenyl)]borane **3**[10] at δ −133.5, −150.9, and −162.8, in addition to a dioxane adduct with Piers' borane, $(C_6F_5)_2BH$-dioxane, as a minor species (see details in the ESI†).

To shed light on the plausible working mode, a series of catalytic and stoichiometric reactions were conducted (Scheme 2). A hydrosilylation reaction of cyclopentene oxide (**1a**) using TMDS-d_2 as a reductant gave cyclopentyloxysilane **2a-*d*₁** in 85% yield in 0.5 h at room temperature (Scheme 2a). This product was found to contain a deuterium incorporated exclusively at the β-position relative to the oxygen atom of the product. On the other hand, a stoichiometric treatment of cyclopentene oxide with $(C_6F_5)_2BH–SMe_2$ in the absence of hydrosilane afforded cyclopentyloxyborane **3** in 47% yield in 10 min at room temperature,[11] whereas a reaction of cyclopentyloxyborane **3** with excess TMDS (50 equiv.) led to the formation of Piers' borane at a relatively slower rate (10% in 0.5 h) (Scheme 2b and c).

Notably, cyclopentyloxyborane **3** was shown to catalyse the hydrosilylation of epoxide **1a** by using TMDS to furnish **2a** in 79% yield in 10 min, implying that an outer-sphere ionic path is operative in this process (Scheme 2d). To obtain additional insights, a stoichiometric reaction of **1a**, hydrosilanes, and **3** (1 : 1 : 1) was performed in 1,4-dioxane (Scheme 2e). Cyclopentene oxide **1a** was gradually converted to **2a**, and its progress was found to be dependent on the hydrosilanes employed (87% with TMDS; 46% with Me_2PhSiH in 10 min). ^1H and ^{19}F NMR spectroscopy of the reaction mixtures displayed a set of major signals for **3** and minor signals for $(C_6F_5)_2BH$–dioxane (see details in the ESI†).

Based on the observation that the isolated alkoxy(bisaryl)-borane (**3**) efficiently mediates both catalytic and stoichiometric hydrosilylation of epoxide **1a** to give **2a** and that the conversion of **3** to $(C_6F_5)_2BH$ with TMDS is rather slow, the species **3** generated *in situ* under the employed catalytic conditions is proposed to be a competent catalyst for the present outer-sphere ionic hydrosilylation involving a silylium ion transfer.[12]

Given the above experimental results, a catalytic cycle of the borane-mediated hydrosilylation of cyclopentene oxide (**1a**) is depicted in Scheme 3. Initially, the Piers' borane $(C_6F_5)_2BH$ is assumed to be generated upon the reaction of $(C_6F_5)_2BOH$ with TMDS in dioxane. The *in situ* generated Piers' borane would be in equilibrium with its dioxane adduct **I**. An epoxide substrate coordinates to the boron center of $(C_6F_5)_2BH$ to form an epoxide adduct **II**, which induces a hydroborative ring-opening of the epoxide[13] to afford an alkoxy(bisaryl)borane **3**. The species **3** is proposed to catalyse the outer-sphere hydrosilylation of the epoxide *via* a silyloxonium ion intermediacy (**III**), where a nucleophilic hydride transfer is highly facile to occur, releasing an *O*-silyl ether product **2a**. An intuitive path proceeding *via* a direct release of



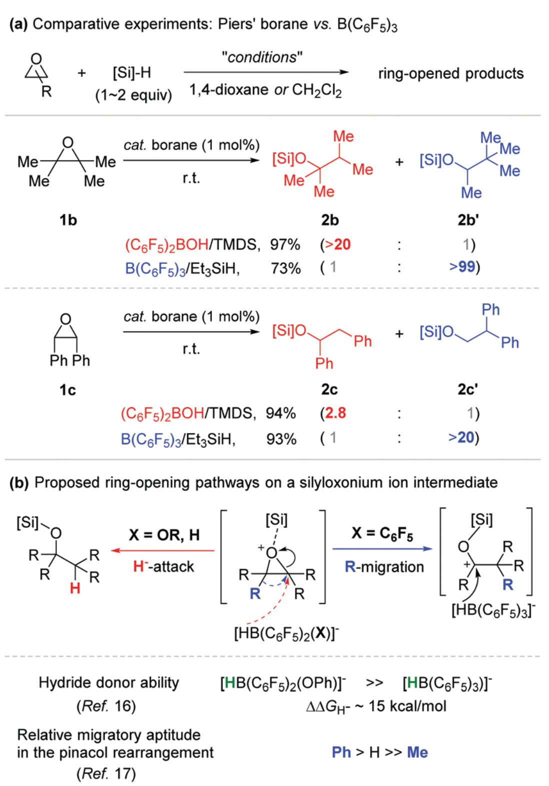
Scheme 3 Proposed reaction pathway.

product **2a** from **3** with the regeneration of Piers' borane is assumed to be kinetically less favoured.[14]

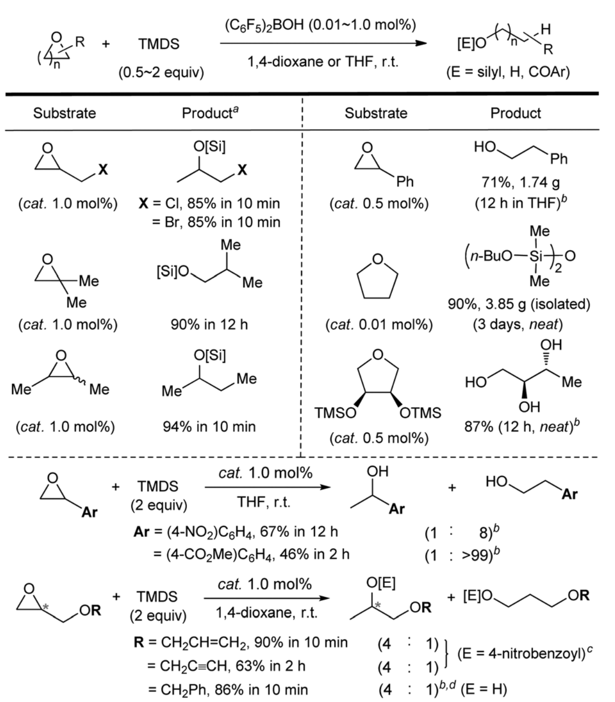
Next, our proposal involving an alkoxy(bisaryl)borane as a catalytically active species (Scheme 3) led us to investigate comparative catalytic reactivity between Piers' borane and $B(C_6F_5)_3$ with regard to hydrosilylation of certain epoxides (Scheme 4a). When 2,2,3,3-tetramethyloxirane (**1b**) was applied as a substrate, two isomeric products were obtained depending on the borane catalysts used. With Piers' borane generated *in situ* (TMDS), 2,3-dimethylbutan-2-silyl ether (**2b**) was formed in 97% yield, while 3,3-dimethylbutan-2-silyl ether (**2b′**) was obtained exclusively by using the $B(C_6F_5)_3$ catalyst in combination with Et_3SiH.[15] This isomeric product (**2b′**) is assumed to be formed *via* a migratory ring-opening process. Although there is no compelling evidence to account for the selectivity reversal between the two borane catalysts applied, this outcome can be rationalized by the difference in hydride donor ability between the individually presupposed borohydride species, $HB(C_6F_5)_2(X)^-$ (X = alkoxy and H) and $HB(C_6F_5)_3^-$ (*e.g.* $\Delta\Delta G_{H^-}$ = *ca.* 15 kcal mol^{-1}, when X = OPh).[16] For example, a silyloxonium intermediate formed upon a silylium ion transfer undergoes a nucleophilic attack by $HB(C_6F_5)_2(X)^-$ (X = alkoxy and H) prior to a methyl migration, whereas the same intermediate is first ring-opened and a methyl group is migrated before hydride reduction by the relatively less hydridic borohydride species $HB(C_6F_5)_3^-$ (Scheme 4b). A similar trend of selectivity was also observed in the hydrosilylation of *cis*-stilbene oxide mediated by the same borane (pre)catalysts.[17]

Finally, the substrate scope was investigated (Scheme 5).[18] A range of mono- and di-substituted epoxides and cyclic ethers was efficiently hydrosilylated at room temperature in the presence of catalytic $(C_6F_5)_2BOH$ (0.01–1.0 mol%). The present system proved to be compatible with functional groups such as halides, nitro, alkenyl, or alkynyl, while the product yield of an ester-containing epoxide was slightly lower. Significantly, the present system was readily amenable to gram-scale reactions: styrene oxide and tetrahydrofuran (in neat) were transformed to the corresponding products in 71% (1.74 g) and 90% (3.85 g, 9000 TON) yields, respectively (see details in the ESI†). When a chiral epoxide (98% ee) was subjected to the present conditions, an enantioenriched alcohol product was obtained (>98% ee).

In summary, for the first time, we have developed the Piers' borane-catalysed hydrosilylation of epoxides and cyclic ethers. Mechanistic studies indicated that an alkyloxy(diaryl)borane is



Scheme 4 (a) Comparative experiments using *in situ* generated Piers' borane *vs.* $B(C_6F_5)_3$ (pre)catalysts. (b) Plausible pathways of epoxide ring-opening on the presupposed silyloxonium ion intermediate.



Scheme 5 Substrate scope of the Piers' borane-catalysed hydrosilylation. [a] Yields were determined using ^1H NMR. [b] The desired alcohol products were isolated upon hydrolysis with saturated K_2CO_3 in MeOH. [c] The crude products were *O*-benzoylated *in situ* through the reaction with 4-nitrobenzoyl chloride. [d] (*S*)-1-(Benzyloxy)propan-2-ol was obtained as a major product with >98% ee.

a competent catalytic species, while the reaction proceeds *via* an outer-sphere ionic pathway. Significantly, a selectivity reversal between Piers' borane and $B(C_6F_5)_3$ catalyst systems was observed, which could be in turn rationalized by the difference in hydride donor ability of the presupposed borohydride species. The present catalyst system is convenient to perform under mild conditions and compatible with functional groups, thus enabling applications in synthetic organic chemistry plausible.

This research was supported by the Institute for Basic Science (IBS-R010-D1), South Korea.

Conflicts of interest

There are no conflicts to declare.

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