ChemComm



COMMUNICATION

View Article Online



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 (C₆F₅)₂BH with hydrosilanes in the presence of an epoxide revealed that an alkyloxy(diaryl)borane (C₆F₅)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 synthesis¹ 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(C₆F₅)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). The $B(C_6F_5)_3$ -catalysed hydrosilylative transformation has been postulated to proceed via a silyloxonium ion bearing a borohydride anion [HB(C₆F₅)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 (C₆F₅)₂BH that is readily generated in situ from the reaction of (C₆F₅)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 (C₆F₅)₂BH with an emphasis on the catalytic pathway (Scheme 1c).8 Mechanistic investigations revealed that an alkyloxy(diaryl)borane (C₆F₅)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 ringopening of epoxides is reversed between the Piers' borane and the $B(C_6F_5)_3$ catalyst.

$$\begin{array}{c} \text{OSi} \\ \text{SiO} \\ \text{OR} \\ \end{array} \begin{array}{c} \text{(C}_6F_5)_2\text{BOH (1 mol\%)} \\ \text{excess TMDS} \\ \text{1.4-dioxane, r.t.} \\ \end{array} \begin{array}{c} \text{SiO} \\ \text{SiO} \\ \end{array} \begin{array}{c} \text{OSi} \\ \text{SiO} \\ \text{H} \\ \end{array} \begin{array}{c} \text{OSi} \\ \text{SiO} \\ \text{H} \\ \end{array} \begin{array}{c} \text{(1)} \\ \text{SiO} \\ \text{H} \\ \text{(2)} \\ \text{(2)} \\ \end{array} \\ \begin{array}{c} \text{(2)} \\ \text{(2)} \\ \text{(3)} \\ \text{(3)} \\ \text{(4)} \\ \text{(4)} \\ \text{(4)} \\ \text{(5)} \\ \text{(5)} \\ \text{(5)} \\ \text{(1)} \\ \text{(5)} \\ \text{(1)} \\ \text{(5)} \\ \text{(5)} \\ \text{(6)} \\ \text{(5)} \\ \text{(2)} \\ \text{(5)} \\ \text{(5)} \\ \text{(1)} \\ \text{(5)} \\ \text{(6)} \\ \text{(6)} \\ \text{(7)} \\ \text{(1)} \\ \text{(1)} \\ \text{(1)} \\ \text{(1)} \\ \text{(2)} \\ \text{(2)} \\ \text{(2)} \\ \text{(2)} \\ \text{(3)} \\ \text{(4)} \\ \text{(4)} \\ \text{(5)} \\ \text{(5)} \\ \text{(5)} \\ \text{(6)} \\ \text{(6)} \\ \text{(6)} \\ \text{(7)} \\ \text{(7)} \\ \text{(8)} \\ \text{(1)} \\ \text{(8)} \\ \text{(1)} \\ \text{(1)} \\ \text{(1)} \\ \text{(1)} \\ \text{(1)} \\ \text{(2)} \\ \text{(2)} \\ \text{(2)} \\ \text{(2)} \\ \text{(3)} \\ \text{(4)} \\ \text{(4)} \\ \text{(5)} \\ \text{(5)} \\ \text{(6)} \\ \text{(6)} \\ \text{(6)} \\ \text{(7)} \\ \text{(7)} \\ \text{(8)} \\ \text{($$

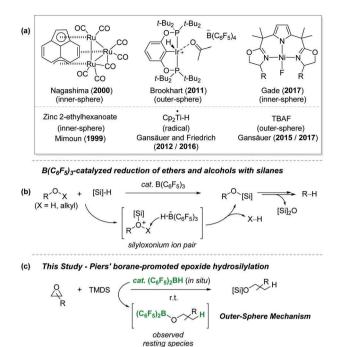
Previously, we reported a selective C-O bond cleavage of sugars via hydrosilylation catalysed by Piers' borane (C₆F₅)₂BH generated in situ [eqn (1)].9 This reductive transformation of sugars was proposed to proceed via an outer-sphere ionic

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

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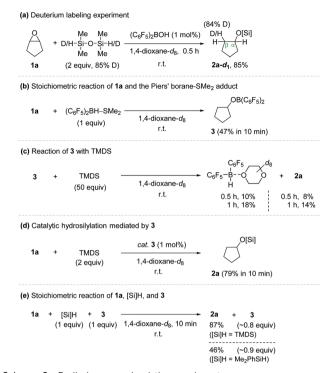


√ Observation of an unique catalytic species [alkyloxy(diaryl)borane]
√ Diarylborane-catalyzed outer-sphere hydrosilylation pathway

√ Distinctive reactivity and selectivity of Piers' borane vs. B(C₆F₅)₃ catalysis

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 $(C_6F_5)_2$ BOH (1 mol%) to furnish the corresponding cyclopentyloxysilane **2a** in 85% yield in 0.5 h [eqn (2)]. Interestingly, ¹⁹F 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, $(C_6F_5)_2$ BH-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 $2a \cdot d_1$ 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).



Scheme 2 Preliminary mechanistic experiments

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 Me₂PhSiH in 10 min). 1 H 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 outersphere 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

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$$(C_{e}F_{5})_{2}BOH$$

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(C₆F₅)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(C₆F₅)₃ catalyst in combination with Et₃SiH.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

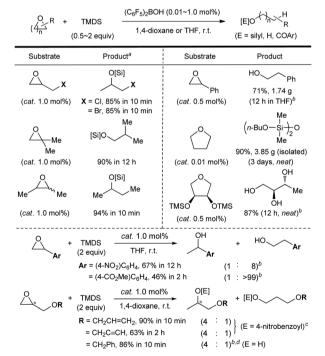
(a) Comparative experiments: Piers' borane vs. B(C₆F₅)₃ "conditions" ring-opened products 1,4-dioxane or CH₂Cl₂ (1~2 equiv) Ме 1b 2b 2b' (C₆F₅)₂BOH/TMDS, 97% 1) B(C₆F₅)₃/Et₃SiH, 73% >99) cat. borane (1 mol%) Ph Ph [Si]O r.t. 1с 2c 2c' (C₆F₅)₂BOH/TMDS, 94% (2.8 1) B(C₆F₅)₃/Et₃SiH, 93% >20) (b) Proposed ring-opening pathways on a silyloxonium ion intermediate $X = C_6F_5$ X = OR. HR-migration [HB(C₆F₅)₃] $[HB(C_6F_5)_2(X)]$ Hydride donor ability [HB(C₆F₅)₂(OPh)]>> $[HB(C_6F_5)_3)]^{-1}$ (Ref. 16) $\Delta\Delta G_{H}$ -~ 15 kcal/mol Relative migratory aptitude in the pinacol rearrangement Ph > H >> Me

Scheme 4 (a) Comparative experiments using in situ generated Piers' borane vs. B(C₆F₅)₃ (pre)catalysts. (b) Plausible pathways of epoxide ringopening on the presupposed silyloxonium ion intermediate

rationalized by the difference in hydride donor ability between the individually presupposed borohydride species, HB(C₆F₅)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(C₆F₅)₃⁻ (Scheme 4b). A similar trend of selectivity was also observed in the hydrosilylation of cisstilbene 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 5 Substrate scope of the Piers' borane-catalysed hydrosilylation. ^a Yields were determined using ¹H NMR. ^bThe desired alcohol products were isolated upon hydrolysis with saturated K₂CO₃ in MeOH. ^cThe 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.

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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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