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

Jianbo Zhang, ab Sehoon Park,*ab and Sukbok Chang*ab

We report the first diarylborane-catalysed hydrosilylation of epoxides and cyclic ethers. Mechanistic studies on the in situ generated Piers’ borane \((\text{C}_6\text{F}_5)_2\text{BH}\) with hydrosilanes in the presence of an epoxide revealed that an alkyloxy(diaryl)borane \((\text{C}_6\text{F}_5)_2\text{BOR}\) 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 silyl ium 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 \(\text{B(\text{C}_6\text{F}_5)_3}\) 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 \(\text{B(\text{C}_6\text{F}_5)_3}\) (Scheme 1b).\(^7c\)\(^f\) The \(\text{B(\text{C}_6\text{F}_5)_3}\)-catalysed hydrosilylative transformation has been postulated to proceed via a silyloxonium ion bearing a borohydride anion \([\text{HB(\text{C}_6\text{F}_5)_3}]^-\), where the borohydride attacks the \(\alpha\)-carbon of oxonium leading to the C–O bond cleavage. In this context, we hypothesized that a less Lewis acidic Piers’ borane \((\text{C}_6\text{F}_5)_2\text{BH}\) that is readily generated \textit{in situ} from the reaction of \((\text{C}_6\text{F}_5)_2\text{BOH}\) with hydrosilanes can mediate the hydrosilylation of epoxides and cyclic ethers without the exhaustive deoxygenation.

Here, we report the hydrosilylation of epoxides mediated by \textit{in situ} generated Piers’ borane \((\text{C}_6\text{F}_5)_2\text{BH}\) with an emphasis on the catalytic pathway (Scheme 1c).\(^8\) Mechanistic investigations revealed that an alkyloxy(diaryl)borane \((\text{C}_6\text{F}_5)_2\text{BOR}\) is formed upon the reaction of \textit{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 \(\text{B(\text{C}_6\text{F}_5)_3}\) catalyst.

\[ (1) \]

\[ (2) \]

Previously, we reported a selective C–O bond cleavage of sugars \textit{via} hydrosilylation catalysed by Piers’ borane \((\text{C}_6\text{F}_5)_2\text{BH}\) generated \textit{in situ} [eqn (1)].\(^9\) This reductive transformation of sugars was proposed to proceed \textit{via} an outer-sphere ionic

---

\(^†\) Electronic supplementary information (ESI) available: Detailed experimental procedures and characterization data. See DOI: 10.1039/c8cc03741h
pathway involving a cyclic silyloxonium ion bearing a boro-hydride $\text{H}_2\text{B}(\text{C}_6\text{F}_5)_2$ [\text{C}_0], selectively providing a range of linear polyols. Based on this precedent, we were encouraged to apply the procedure for the hydrosilylation of cyclopentene oxide $1\text{a}$, which was chosen as a representative substrate for preliminary mechanistic studies in an effort to elucidate the reaction pathway. As envisaged, the reaction of $1\text{a}$ with 1,1,3,3-tetramethyldisiloxane (TMDS) took place in the presence of (C$_6$F$_5$)$_2$BOH (1 mol%) to furnish the corresponding cyclopentyloxysilane $2\text{a}$ 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 $3$ at $\delta/\text{C}_0$ 133.5, 150.9, and 162.8, in addition to a dioxane adduct with Piers’ borane, (C$_6$F$_5$)$_2$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 ($1\text{a}$) using TMDS-d$_2$ as a reductant gave cyclopentyloxysilane $2\text{a}$-d$_2$ in 85% yield in 0.5 h at room temperature (Scheme 2a). This product was found to contain a deuterium incorporated exclusively at the $\beta$-position relative to the oxygen atom of the product. On the other hand, a stoichiometric treatment of cyclopentene oxide with (C$_6$F$_5$)$_2$BH-SMe$_2$ in the absence of hydrosilane afforded cyclopentyloxysilane $3$ in 47% yield in 10 min at room temperature,\textsuperscript{11} whereas a reaction of cyclopentyloxysilane $3$ 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, cyclopentyloxysilane $3$ was shown to catalyse the hydrosilylation of epoxide $1\text{a}$ by using TMDS to furnish $2\text{a}$ 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 $1\text{a}$, hydrosilanes, and $3$ (1:1:1) was performed in 1,4-dioxane (Scheme 2e). Cyclopentene oxide $1\text{a}$ was gradually converted to $2\text{a}$, and its progress was found to be dependent on the hydrosilanes employed (87% with TMDS; 46% with Me$_2$PhSiH in 10 min).\textsuperscript{1}H and $^{19}$F NMR spectroscopy of the reaction mixtures displayed a set of major signals for $3$ and minor signals for (C$_6$F$_5$)$_2$BH-dioxane (see details in the ESI†).

Scheme 2

Preliminary mechanistic experiments.

Scheme 1

(a) Homogeneous catalysts for epoxide hydrosilylation. (b) B(C$_6$F$_5$)$_3$-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.
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 (2b0) was obtained exclusively by using the B(C₆F₅)₃ catalyst in combination with Et₃SiH.15 This isomeric product (2b0) 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(C₆F₅)₂(X)⁻ (X = alkoxy and H) and HB(C₆F₅)₃ (e.g. ΔΔG⧧ = ca. 15 kcal mol⁻¹, when X = OPh).16 For example, a silyloxonium intermediate formed upon a silylum ion transfer undergoes a nucleophilic attack by HB(C₆F₅)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 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 (C₆F₅)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 alkoxy(diaryl)borane is...
a competent catalytic species, while the reaction proceeds via an outer-sphere ionic pathway. Significantly, a selectivity reversal between Piers’ borane and \( \text{B}(\text{C}_6\text{F}_5)_3 \) 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.

Notes and references


10. The observed \( ^{19} \text{F} \) NMR shifts of the cyclooctenyloxyborane 3 were well matched with those of the independently synthesized borane compound. For the synthesis of alkyl(Si(aryl))boranes: (a) D. Donghi, D. Mazzoni, T. Beringhelli, G. D’Alfonso, P. Mercuri and A. Sironi, Eur. J. Inorg. Chem., 2008, 1645; (b) S. R. Longobardi, C. Tang and D. W. Stephan, Dalton Trans., 2014, 43, 15723.

11. Although the reaction led to a quantitative conversion of 1a, the reaction mixture contained intractable ring-opened side products in addition to the allyloxyborane 3. These side products are presumed to be formed upon a nucleophilic attack by \( \text{SiMe}_3^– \). See details in the ESIT.


14. The \( \text{C}(\text{SiMe}_3)_2 \)BH-mediated outer-sphere hydrosilylation could be a competitive pathway as we previously proposed it with regard to the hydrosilylative C–O bond cleavage of sugars.

15. The hydrosilylation of 1b with TMDS in the presence of the \( \text{B}(\text{C}_6\text{F}_5)_3 \) catalyst gave rise to exhaustively reduced alkanes simultaneously with disproportionation of TMDS.


17. A phenyl migration is generally known to be much faster than that of a methyl group in the acid-mediated pinacol rearrangement. This precedent could account for the differed product selectivity observed in the reactions of 2,2,3,3-tetramethyloxirane (>20:1) and cis-stilbene oxide (2.8:1): (a) H. O. House and E. J. Grubbs, J. Am. Chem. Soc., 1959, 81, 4733; (b) K. Nakamura and Y. Osumara, J. Am. Chem. Soc., 1993, 115, 9112.

18. Initially formed products were a mixture of silylated compounds having several siloxane moieties of \( \text{[Si]}_n \), which were cleanly converted to the corresponding alcoholic products upon hydrolysis.