



Cite this: *Chem. Soc. Rev.*, 2015, 44, 2202

A unified survey of Si–H and H–H bond activation catalysed by electron-deficient boranes

Martin Oestreich,* Julia Hermeke† and Jens Mohr†

The bond activation chemistry of $B(C_6F_5)_3$ and related electron-deficient boranes is currently experiencing a renaissance due to the fascinating development of frustrated Lewis pairs (FLPs). $B(C_6F_5)_3$'s ability to catalytically activate Si–H bonds through η^1 coordination opened the door to several unique reduction processes. The ground-breaking finding that the same family of fully or partially fluorinated boron Lewis acids allows for the related H–H bond activation, either alone or as a component of an FLP, brought considerable momentum into the area of transition-metal-free hydrogenation and, likewise, hydrosilylation. This review comprehensively summarises synthetic methods involving borane-catalysed Si–H and H–H bond activation. Systems corresponding to an FLP-type situation are not covered. Aside from the broad manifold of $C=X$ bond reductions and $C=X/C-X$ defunctionalisations, dehydrogenative (oxidative) Si–H couplings are also included.

Received 2nd December 2014

DOI: 10.1039/c4cs00451e

www.rsc.org/csr

1. Introduction

The potent boron Lewis acid tris(pentafluorophenyl)borane [$B(C_6F_5)_3$, Fig. 1] is one of those molecules that revealed its relevance to synthetic chemistry long after its discovery. Its preparation was described in the early 1960s¹ but, without any

obvious use, these reports laid dormant for decades with hardly any citations. The situation changed in the early 1990s when Marks and co-workers found that $B(C_6F_5)_3$ and cognate electron-deficient boranes are excellent co-catalysts in metallocene-mediated alkene polymerization.² $B(C_6F_5)_3$'s ability to act as catalyst in its own right was then discovered by Piers and co-workers in the late 1990s. These authors showed that $B(C_6F_5)_3$ catalyses $C=X$ bond hydrosilylations³ (reduction) as well as dehydrogenative Si–O couplings⁴ (oxidation) by a counterintuitive mechanism. It was proposed largely on the basis of kinetic data that $B(C_6F_5)_3$ activates the hydrosilane rather than the carbonyl group by an, at that time,

Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 115, D-10623 Berlin, Germany. E-mail: martin.oestreich@tu-berlin.de; Fax: +49 (0)30 314 28829; Tel: +49 (0)30 314 29721

† J.H. and J.M. contributed equally.



Martin Oestreich

Martin Oestreich (born in 1971 in Pforzheim/Germany) is currently Professor of Organic Chemistry at the Technische Universität Berlin. He received his diploma degree with Paul Knochel (Marburg, 1996) and his doctoral degree with Dieter Hoppe (Münster, 1999). After a two-year post-doctoral stint with Larry E. Overman (Irvine, 1999–2001), he completed his habilitation with Reinhard Brückner (Freiburg, 2001–2005) and was appointed

as Professor of Organic Chemistry at the Westfälische Wilhelms-Universität Münster (2006–2011). He also held visiting positions at Cardiff University in Wales (2005) and at The Australian National University in Canberra (2010).



Julia Hermeke

Julia Hermeke (born in 1986 in Neuruppin/Germany) studied chemistry at the Freie Universität Berlin (2006–2009) and at the University of Hong Kong (2009–2011). She spent internships with Bayer Schering Pharma AG in Berlin and with Evonik Degussa GmbH in Marl (2008). She obtained her bachelor's degree with Hans-Ulrich Reißig at the Freie Universität Berlin and her master's degree with Patrick H. Toy at the University

of Hong Kong. Her master studies were supported by a scholarship of the Studienstiftung des deutschen Volkes (2009–2011). She is currently in her final phase of her doctoral degree in the group of Martin Oestreich at the Technische Universität Berlin.



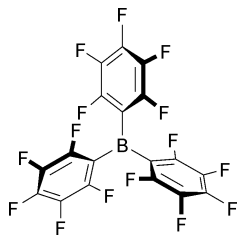
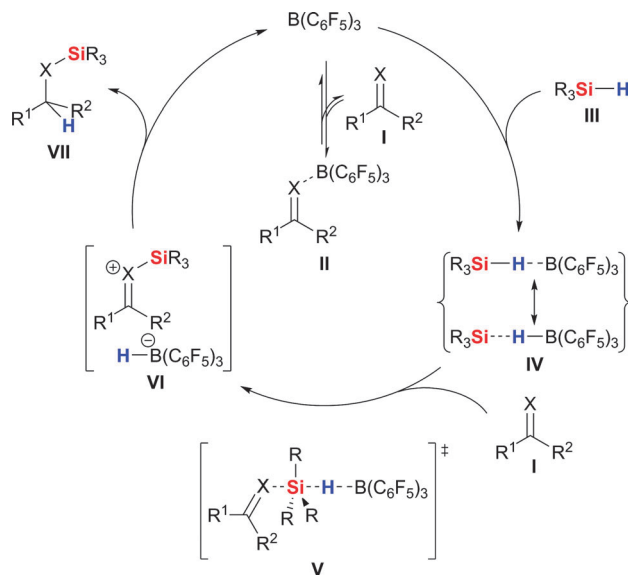


Fig. 1 Tris(pentafluorophenyl)borane $[B(C_6F_5)_3]$.

unusual η^1 coordination.⁵ Although these contributions were noticed by the community, $B(C_6F_5)_3$ catalysis still continued to develop rather slowly.⁶ The advent of frustrated Lewis pairs (FLPs) in the mid 2000s finally moved $B(C_6F_5)_3$ and related fully or partially fluorinated boranes into the limelight. Stephan's⁷ and also Erker's⁸ findings that Lewis pairs, either frustrated or formed reversibly, composed of those boron Lewis acids and a rather broad range of Lewis bases activate small molecules without the need for a transition metal were a significant advancement.^{9,10} The heterolytic splitting of dihydrogen and its application in transition-metal-free hydrogenation is particularly relevant and closely related to the Piers-type activation of the weaker Si-H bond (90 kcal mol⁻¹ for Si-H *versus* 103 kcal mol⁻¹ for H-H).¹¹ H-H bond activation is in fact not even limited to FLP-like systems, and $B(C_6F_5)_3$ alone will activate dihydrogen without the assistance of a deliberately added Lewis base.¹² The Lewis basic reactant is enough to step in. The purpose of this review is to collect synthetic methods involving borane-catalysed Si-H and H-H bond activation in a single article. We explicitly excluded clear cases of FLP-type systems as these were comprehensively covered by several reviews in recent years.^{9,10}

2. Mechanistic aspects

The fascination with $B(C_6F_5)_3$ catalysis began with the seminal discovery by Piers and co-workers that the $B(C_6F_5)_3$ -catalysed



Scheme 1 Mechanism of the $B(C_6F_5)_3$ -catalysed hydrosilylation of ketones ($X=O$) and imines ($X=NR^2$).

carbonyl hydrosilylation obeys a counterintuitive three-step mechanism ($X=O$, Scheme 1).^{3,5} A series of significant experiments established that Lewis adduct **II** composed of $B(C_6F_5)_3$ and carbonyl compound **I** is not a competent intermediate in the catalytic cycle. $B(C_6F_5)_3$ was in fact shown to be largely present in its free form. Instead, it was proposed that $B(C_6F_5)_3$ is involved in the activation of the Si-H bond of hydrosilane **III** through reversible η^1 rather than η^2 coordination, and the intermediacy of the unusual complex **IV** was suggested. The enhanced Lewis acidity of the silicon atom in **IV** would then facilitate the nucleophilic attack by the Lewis-basic oxygen atom of **I**. The hydride is transferred from the silicon to the boron atom in that step to afford ion pair **VI**, that is a borohydride along with a silylcarboxonium ion. The catalysis would come full circle by hydride transfer from the borohydride to the electrophilic carbon atom of the silylcarboxonium ion, thereby yielding silyl ether **VII** and releasing free $B(C_6F_5)_3$. That unique mechanism was in accordance with kinetic analyses, NMR spectroscopic measurements and isotopic labelling experiments. Preliminary computational investigations lent further support to the existence of the hydrosilane-borane adduct **IV**.¹¹ Later, Rendler and Oestreich verified the nature of the actual activation step for carbonyl compounds **I** with the aid of a silicon-stereogenic hydrosilane as a stereochemical probe.^{13,14} The Si-H bond activation was shown to proceed through the S_N2 -Si transition state **V** ($X=O$).

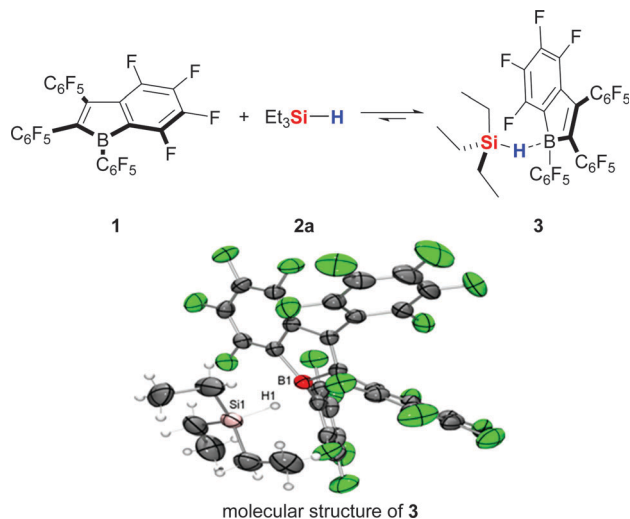
Recently, Sakata and Fujimoto further supported the experimentally observed mechanism by quantum-chemical calculations with acetone and Me_3SiH as model compounds.¹⁵ Their results are in full agreement with the Piers-Oestreich mechanism.^{5,13} That work also included a comparison of $B(C_6F_5)_3$ with BF_3 as catalyst, and it was found that conventional carbonyl activation is operative in the latter case.¹⁶ The Si-H bond is cleaved in a four-membered transition state where the carbonyl oxygen atom



Jens Mohr

Jens Mohr (born in 1987 in Otterndorf/Germany) studied chemistry at the Westfälische Wilhelms-Universität Münster (2007–2012) and spent a three-month research internship at Hoffmann-La Roche in Basel (2011). He obtained his bachelor's (2010) and master's degrees (2012) with Martin Oestreich. His master studies were supported by an Almuth Klemer fellowship from the Organisches-Chemisches Institut of the Westfälische Wilhelms-Universität Münster. He is currently pursuing graduate research in the group of Martin Oestreich at the Technische Universität Berlin.





Scheme 2 Adduct formation between Et_3SiH (**2a**) and 1,2,3-tris(pentafluorophenyl)-4,5,6,7-tetrafluoro-1-boraindene (**1**) and its molecular structure **3**.

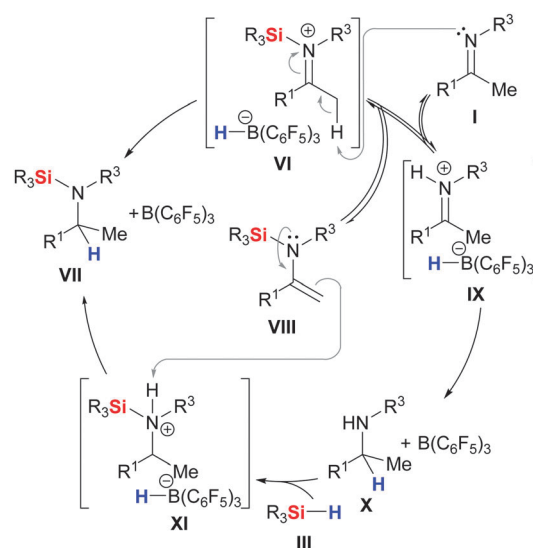
accommodates both the boron atom and the weakly Lewis acidic silicon atom. The hydride is directly transferred from the silicon atom to the highly electrophilic carbonyl carbon atom. The fundamentally different activation modes exerted by BF_3 ($\text{C}=\text{O}$ group) and $\text{B}(\text{C}_6\text{F}_5)_3$ ($\text{Si}-\text{H}$ bond) were mainly attributed to the electronic nature of their boron centres.

Just recently, Piers, Tuononen, and co-workers finally presented the long-awaited experimental evidence for the *missing link* of the catalytic cycle, that is the hydrosilane–borane adduct **IV**.¹⁷ These authors utilised antiaromatic 1,2,3-tris(pentafluorophenyl)-4,5,6,7-tetrafluoro-1-boraindene¹⁸ (**1**) as a more Lewis acidic model structure for $\text{B}(\text{C}_6\text{F}_5)_3$ and were able to isolate its adduct with Et_3SiH (**2a**) (**3**, Scheme 2). The careful study includes variable-temperature NMR spectroscopic analysis of the equilibrium of adduct formation and structural characterisation of **3** by X-ray crystallography. Quantum-chemical calculations were used to further probe the stability of **3** and to compare **3** with $\text{Et}_3\text{SiH}/\text{B}(\text{C}_6\text{F}_5)_3$ and the hypothetical adduct of Et_3SiH (**2a**) and perfluoropentaphenylborole. The adduct $\text{Et}_3\text{SiH}/\text{B}(\text{C}_6\text{F}_5)_3$ was found to be weakest, and the higher stability of **3** was rationalized by a fine balance of steric and electronic effects rather than merely being the result of the higher Lewis acidity of **3** relative to $\text{B}(\text{C}_6\text{F}_5)_3$. The molecular structure of **3** shows the anticipated $\text{Si}-\text{H}-\text{B}$ bridge with the hydrogen atom remaining at the silicon atom. The $\text{Si}-\text{H}$ distance is 1.51(2) Å and, hence, in the typical range of $\text{Si}-\text{H}$ bonds (1.48 Å); the $\text{B}-\text{H}$ distance of 1.46(2) Å is substantially longer than typical $\text{B}-\text{H}$ bonds (1.14 Å). The $\text{Si}-\text{H}-\text{B}$ bridge is not linear but significantly bent with a bond angle of 157°, a feature that it shares with related, less-bent $[\text{Si}-\text{H}-\text{Si}]^+$ hydronium ions.¹⁹

Regarding the imine hydrosilylation, the above basic mechanistic principles are still valid ($\text{X}=\text{NR}^3$, Scheme 1).²⁰ Again, $\text{B}(\text{C}_6\text{F}_5)_3$ dissociates from adduct **II** to form adduct **IV** with hydrosilane **III**. Imine **I** then acts as a nucleophile in the concerted displacement of the $\text{Si}-\text{H}$ bond (**IV** → **V** → **VI**). However, there were doubts about the involvement of the silyliminium ion in the borohydride reduction step (**VI** → **VII**). Hog and Oestreich had tried to apply the

aforementioned stereochemical probe¹³ to the hydrosilylation of imines but results were inconclusive.²¹ Initial attempts to determine the absolute configuration and the enantiomeric purity of the silicon-stereogenic hydrosilane reisolated after the hydrosilylation/ $\text{Si}-\text{N}$ cleavage sequence had failed. Also, the stereogenicity at the silicon atom had not induced any diastereoselectivity ($\text{dr} = 74:26$ in the corresponding carbonyl hydrosilylation¹³); the free amine was isolated in racemic form after hydrolysis. These findings led the authors to question the transformation of **VI** into **VII**, and to propose several alternative hydride transfer scenarios. Later, Mewald and Oestreich were able to show that the stereochemical information at the silicon atom is indeed lost in the catalytic cycle.²² It was speculated that dissociation of the silyliminium ion accounts for the racemization. However, the same authors demonstrated through matched–mismatched combinations of an axially chiral borane catalyst and a chiral hydrosilane reagent that the silyliminium ion is in fact participating in the borohydride reduction.²²

This confusion was finally solved by Oestreich and co-workers.²³ A closer look at the imine hydrosilylation by NMR spectroscopy revealed the formation of unexpected intermediates that play a major role in the catalytic cycle (Scheme 3). The existence of free amine **X** and silylated enamine **VIII** in equimolar ratio indicated that a competing reaction pathway must be added to the established mechanistic picture. These intermediates emerge from the abstraction of a proton in the α -position of the silyliminium ion in **VI** (**VI** → **VIII** and **IX**). The resulting iminium ion in **IX** is reduced to the free amine **X** (**IX** → **X**). That free amine **X** is then transformed into the silylated amine **VII** by a two-step process: FLP-like and at that time unprecedented $\text{Si}-\text{H}$ bond cleavage (**X** → **XI**)²⁴ is followed by protonation of the silylated enamine **VIII** with the kinetically stable ion pair **XI**²⁵ (**XI** → **VII**). The latter step also converts **VIII** back into the silyliminium ion **VI**. Based on these findings, the generally accepted mechanism must be expanded by another reaction pathway with another borohydride reduction step. The fact that there are



Scheme 3 Competing pathways in $\text{B}(\text{C}_6\text{F}_5)_3$ -catalysed hydrosilylation of imines.



two potentially stereoselectivity-determining steps hidden in the catalytic cycle must be considered for asymmetric variants.²³

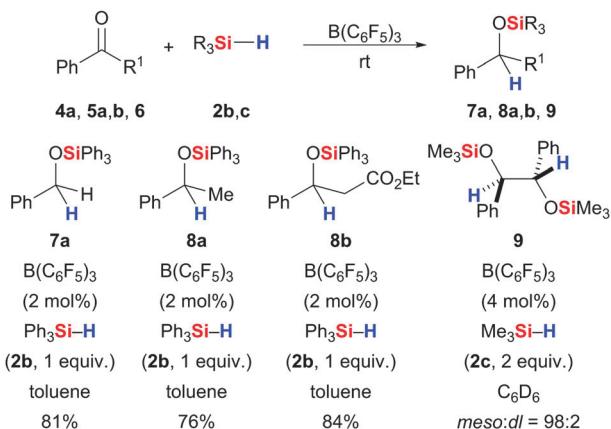
The related hydrogenation is believed to pass through similar key intermediates as the hydrosilylation (*cf.* Scheme 1). Cooperative H–H activation by the Lewis acid catalyst and the Lewis basic substrate results in an ion pair composed of an iminium ion and a borohydride.^{26,27} The subsequent hydride transfer affords an amine–borane adduct that dissociates into the amine and the free borane catalyst. It must be noted though that there is evidence of an autocatalytic pathway where the amine rather than the imine is involved in the FLP-type heterolytic H–H splitting. Initially proposed by Klankermayer,²⁸ this competing reaction was confirmed by quantum-chemical calculations by Pápai and co-workers.^{27c}

3. Hydrosilylation and hydrogenation

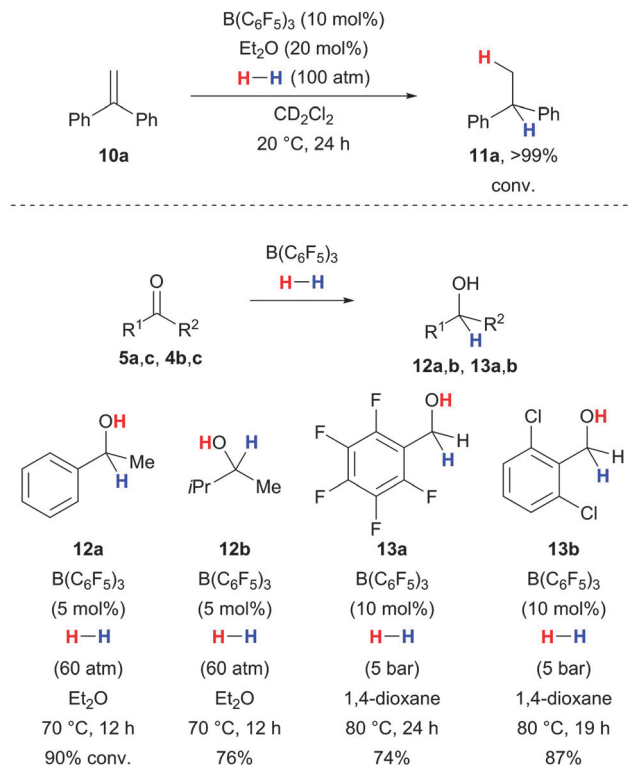
3.1 Reduction of C=X double bonds

As shown above, $B(C_6F_5)_3$ is a suitable catalyst for the activation of the Si–H bond. The focus of this section is on hydrosilylation of C=X bonds, initially introduced by Piers and co-workers.^{3,5} The ground-breaking discovery by Stephan and, independently, Klankermayer that the same catalyst also activates the H–H bond led to the development of several related hydrogenations, and these will be presented together with the hydrosilylations where appropriate. Piers and co-workers reported the $B(C_6F_5)_3$ -catalysed hydrosilylation of various aromatic and, later, aliphatic carbonyl compounds using Ph_3SiH (**2b**) (**4/5** → **7/8**, Scheme 4).^{3,5} These catalyses are generally quite efficient, and it was shown in subsequent years that other electron-deficient boranes decorated with at least one $C_6F_nH_{5-n}$ group ($n = 1–5$) are also capable of promoting these reductions.²⁹

Rosenberg and co-workers elaborated the diastereoselective hydrosilylation of α -diketones where the steric bulk of the hydrosilane determines the relative configuration (*syn/anti* or *meso/dl*) of the 1,2-diol (**6** → **9**, Scheme 4).^{29e} “Small” hydrosilanes and dihydrosilanes afforded *meso* whereas “large” hydrosilanes gave *dl* configuration.



Scheme 4 $B(C_6F_5)_3$ -catalysed hydrosilylation of aldehydes and ketones by Piers (examples 1–3) and Rosenberg (example 4).



Scheme 5 Hydrogenation of an alkene by Stephan (upper) and hydrogenations of carbonyl compounds using ether solvents as the Lewis base components by Stephan (lower, examples 1 and 2) and Ashley (examples 3 and 4).

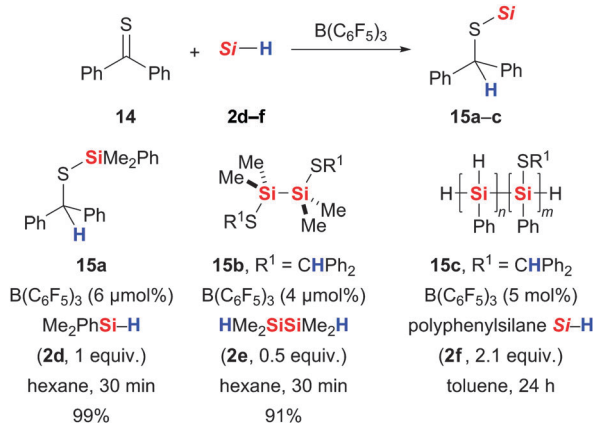
The related $B(C_6F_5)_3$ -catalysed hydrogenation of carbonyl compounds remained elusive for many years although its feasibility had been proposed in a computational study by Nyhlén and Privalov a few years ago.³⁰ Just recently, this gap was closed by the groups of Stephan³¹ and Ashley.³² Stephan and co-workers had already found that 1,1-diphenylethylene is reduced to the corresponding alkane when treated with dihydrogen in the presence of catalytic amounts of $B(C_6F_5)_3$ and Et_2O (**10a** → **11a**, Scheme 5, upper).³³ Inspired by this, the aforementioned groups were able to hydrogenate ketones as well as aldehydes to the corresponding alcohols with catalytic amounts of $B(C_6F_5)_3$ in ethereal solvents (**5/4** → **12/13**, Scheme 5, lower). It was shown that not the carbonyl substrate but the solvent acts as the Lewis-base component in the heterolytic splitting of dihydrogen. Subsequent proton and hydride transfers generate the alcohol. Hence, the mechanism is different from the case calculated by Nyhlén and Privalov and resembles a situation with an external Lewis base rather than the catalytic cycle described in Scheme 1.

The attempt to extend this carbonyl reduction chemistry to the thio ketone analogues was successfully accomplished by Rosenberg and co-workers.³⁴ This substrate class participates in the $B(C_6F_5)_3$ catalysis to form silyl thioethers with sterically accessible tertiary hydrosilanes and dihydrodisilanes such as $HMe_2SiSiMe_2H$ (**2e**) (**14** → **15**, Scheme 6). The mechanism proposed by Rosenberg and co-workers is the same as that of the carbonyl hydrosilylation (*cf.* Scheme 1).⁵ However, these authors showed that formation of Lewis adduct **II** is less

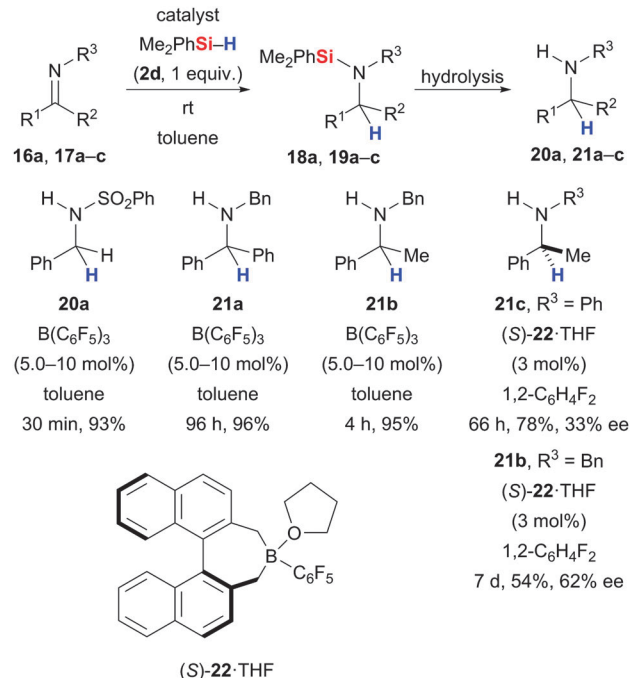
pronounced with thioketones than ketones. The hydrosilylation of benzophenone with Ph_3SiH (**2b**) is nevertheless faster than that of the corresponding thioketone; the ketone is chemoselectively reduced in the presence of the thioketone. Several years later, Rosenberg and co-workers applied the same hydrosilylation to the preparation of polymers containing Si-S linkages next to (unreacted) Si-H bonds (**14** + **2f** → **15c**, Scheme 6).³⁵ The Si-Si bonds in the polyphenylsilane reactant remained untouched. The use of other catalysts for this postpolymerisation modification, no matter if ionic or radical, would lead to Si-Si bond cleavage. Not all Si-H bonds were converted into Si-S linkages but Rosenberg and co-workers were not able to estimate the degree of the Si-H substitution.

Likewise, the $\text{B}(\text{C}_6\text{F}_5)_3$ -catalysed Si-H bond activation was applied to imines by Piers and co-workers (**16/17** → **18/19** → **20/21**, Scheme 7).^{20,36} Benzaldehyde-derived imines with representative substituents R^3 at the imine nitrogen atom were systematically subjected to the standard procedure with Me_2PhSiH (**2d**). As expected, the R^3 group had a profound influence on the reaction rate, and SO_2Ph and $t\text{Bu}$ were optimal requiring only 30 minutes at room temperature for completion. Imines derived from acetophenone, indan-1-one and benzophenone with benzyl protection were also successfully reduced.

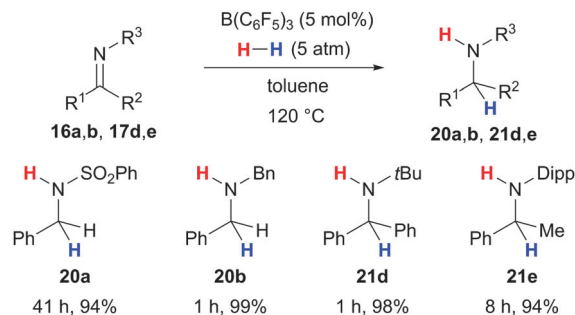
Mewald and Oestreich introduced the chiral electron-deficient borane (*S*)-**22**·THF^{29h} to render the imine hydrosilylation enantioselective (**17** → **19** → **21**, Scheme 7).²² The level of enantioinduction was in fact promising but the refined mechanistic picture of this reaction illustrates that it will be extremely difficult to achieve high enantiocontrol due to competing enantioselectivity-determining hydride transfer steps (cf. Scheme 3).²³ This was also illustrated by the work of Klankermayer and co-workers who utilised a chiral borane based on a functionalised camphor-derived backbone in the hydrosilylation of imines but could not detect any enantioinduction.^{36a} Only in combination with an external phosphine Lewis base substantial enantioinduction ($\leq 87\%$ ee) was observed albeit yields were relatively low (not shown). Zhu and Du were able to reach higher yields by applying chiral binaphthyl-based boranes as catalysts but enantiomeric excesses did not exceed 82% ee (not shown).^{36b}



Scheme 6 $\text{B}(\text{C}_6\text{F}_5)_3$ -catalysed hydrosilylation of thioketones by Rosenberg.



Scheme 7 $\text{B}(\text{C}_6\text{F}_5)_3$ -catalysed hydrosilylation of imines.

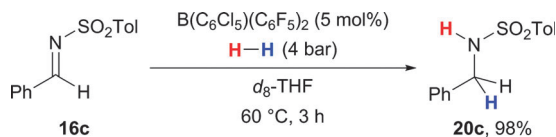


Scheme 8 $\text{B}(\text{C}_6\text{F}_5)_3$ -catalysed hydrogenation of imines by Stephan. Dipp = 2,6-(Me_2CH) C_6H_3 .

The related $\text{B}(\text{C}_6\text{F}_5)_3$ -catalysed hydrogenation of imines was independently discovered by the groups of Stephan²⁶ (**16/17** → **20/21**, Scheme 8) and Klankermayer.²⁸ Aldehyde- as well as ketone-derived imines **16–17** were successfully reduced to the corresponding amines **20–21**. Imine **16a** bearing an electron-withdrawing protecting group reacted significantly slower than more basic imines **16b**, **17d–17e**. The group of Stephan also extended this method to diastereoselective hydrogenations of chiral imines (not shown).³⁷

Ashley and co-workers were able to hydrogenate imines under milder reaction conditions (**16c** → **20c**, Scheme 9).³⁸ Similar to the hydrogenation of carbonyl compounds (cf. Scheme 5),^{31,32} the solvent d_8 -THF acts as the Lewis base in this system. To bypass its Lewis pair formation with the catalyst, the sterically more hindered $\text{B}(\text{C}_6\text{F}_5)_3$ congener $\text{B}(\text{C}_6\text{Cl}_5)(\text{C}_6\text{F}_5)_2$ was used.

Chen and Klankermayer had already observed 13% ee with (+)- α -pinene-derived $\text{B}(\text{C}_6\text{F}_5)_3$ -congener **23**^{39a} as chiral catalyst in the hydrogenation of phenyl-protected imine **17c** (**17c** → **21c**,

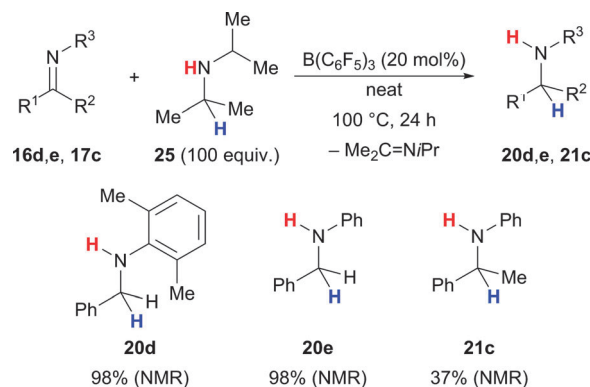


Scheme 9 Hydrogenation of imines using the solvent as the Lewis base component by Ashley.

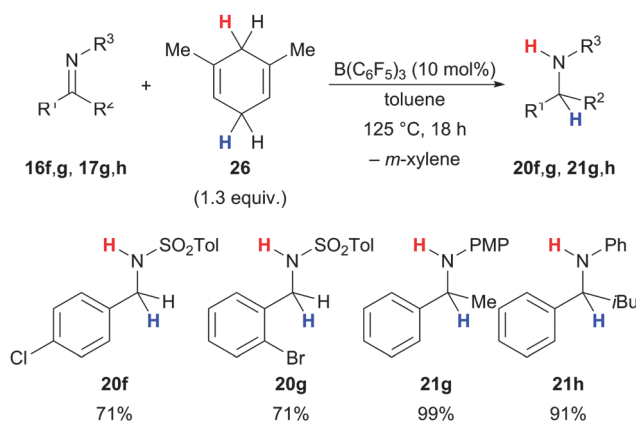
Scheme 10).²⁸ The same substrate **17c** was reduced with high enantiomeric excess by Liu and Du five years later.⁴⁰ The chiral borane **24a**, prepared *in situ* by hydroboration with Piers' borane $\text{HB}(\text{C}_6\text{F}_5)_2$,³⁹ induced high enantioselectivity in the reduction of a variety of alkyl aryl ketimines, including substrates bearing additional Lewis basic sites (**17** \rightarrow **21**, Scheme 10). However, *meta*-substituted substrates as well as diaryl and dialkyl ketimines showed poor enantioselectivities (not shown).

In addition to the direct hydrogenation of imines employing dihydrogen gas, methods for the transfer hydrogenation employing sacrificial dihydrogen sources were also developed. Stephan and co-workers treated various imines **16–17** with catalytic amounts of $\text{B}(\text{C}_6\text{F}_5)_3$ in $i\text{Pr}_2\text{NH}$ (**25**) (Scheme 11).⁴¹ A Meerwein–Ponndorf–Verley-type reduction resulted in the formation of the corresponding amines **20–21**. The excess of the dihydrogen source **25** is believed to shift the equilibrium toward the desired amine.

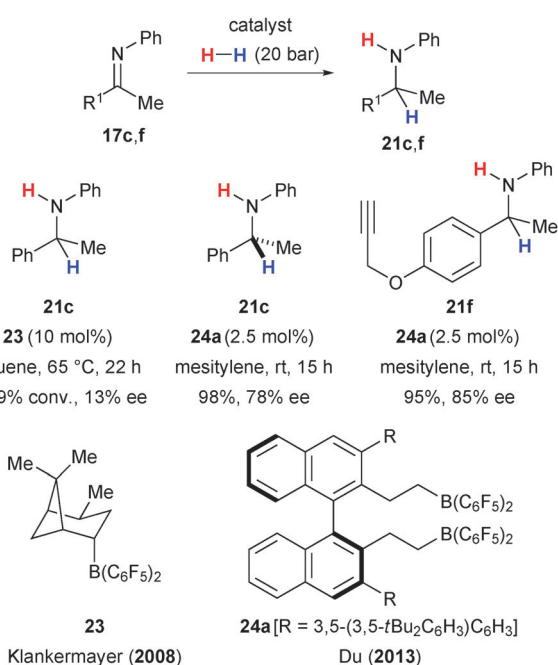
Chatterjee and Oestreich adopted a different approach toward imine reduction by employing cyclohexa-1,4-diene **26** as a dihydrogen surrogate (**16/17** + **26** \rightarrow **20/21**, Scheme 12).⁴² The net reaction is a transfer hydrogenation that was believed to be initiated by $\text{B}(\text{C}_6\text{F}_5)_3$ -mediated dihydrogen release from **26** followed by the pathways (including autocatalysis)^{26–28} of the $\text{B}(\text{C}_6\text{F}_5)_3$ -catalysed imine hydrogenation. However, monitoring



Scheme 11 $\text{B}(\text{C}_6\text{F}_5)_3$ -catalysed Meerwein–Ponndorf–Verley-type transfer hydrogenation of imines by Stephan.



Scheme 12 Transfer hydrogenation of imines by Oestreich.



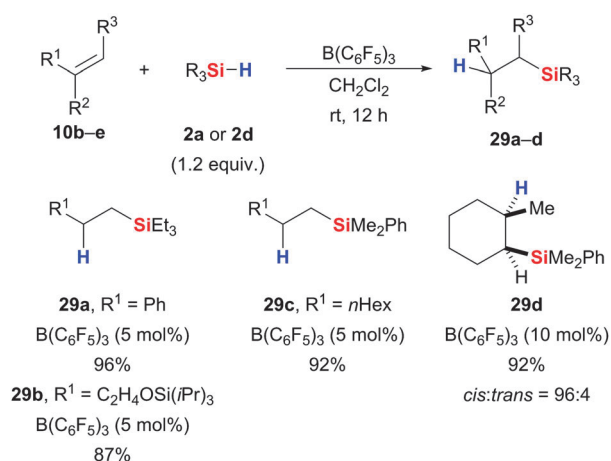
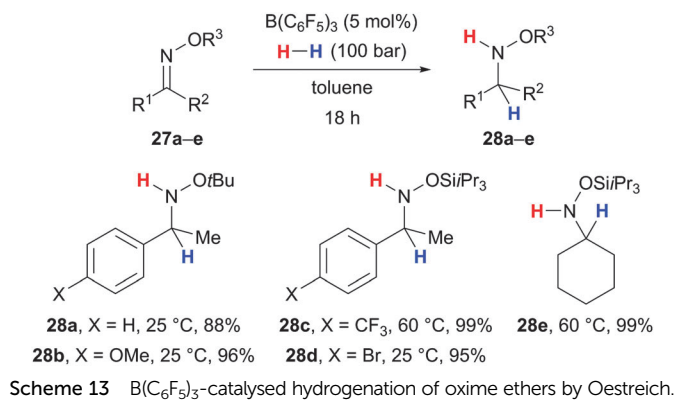
Scheme 10 Enantioselective imine hydrogenations catalysed by chiral electron-deficient boranes.

the reaction by ^1H NMR spectroscopic analysis suggested a different scenario that again involves hydride abstraction from **26** by $\text{B}(\text{C}_6\text{F}_5)_3$ (ref. 43) but no immediate dihydrogen formation. The high-energy Wheland intermediate is a strong Brønsted acid that protonates the imine substrate to arrive directly at the iminium ion–borohydride ion pair. Various tosyl-protected aldimines, *e.g.*, **16f** and **16g**, were successfully hydrogenated. Ketimines were less reactive but different phenyl-protected imines, *e.g.*, **17h**, or imine **17g** bearing the removable *para*-methoxyphenyl (PMP) group were reduced in excellent yield.

Recently, Mohr and Oestreich applied the $\text{B}(\text{C}_6\text{F}_5)_3$ -catalysed hydrogenation approach to the reduction of oxime ethers (Scheme 13).⁴⁴ Decoration of the basic oxygen atom with sterically demanding substituents (*t*Bu or $\text{Si}(\text{iPr})_3$) enabled the chemoselective reduction to the corresponding oxygen-protected hydroxylamines with leaving the weak N–O bond intact (**27** \rightarrow **28**). Although the method was largely unaffected by the electronic and steric properties of the substituents at the oxime carbon atom, it remained limited to ketone-derived oxime ethers.

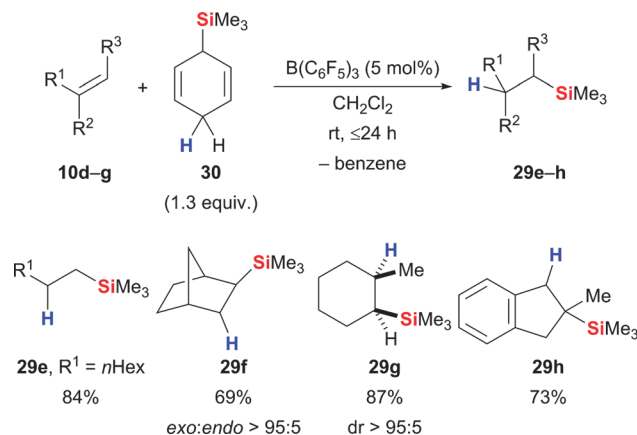
Another well-investigated transformation is the hydrosilylation of alkenes, tracing back to the pioneering work of Gevorgyan and co-workers (**10** \rightarrow **29**, Scheme 14).⁴⁵ The reaction follows the usual pattern of Si–H bond activation by $\text{B}(\text{C}_6\text{F}_5)_3$ with the π -basic alkene acting as nucleophile. A β -silylcarbenium ion is formed as an





intermediate, and the reaction is terminated by hydride transfer from the borohydride. Using various hydrosilanes (excluding sterically hindered ones such as iPr_3SiH), excellent yields were obtained with substituted styrenes (including polymerisable indene), aliphatic alkenes, cyclohexene as well as properly protected oxygen-containing alkenes. The addition across the C–C double bond is *trans*-selective since the hydride attack occurs from the less hindered face; e.g., 1-methylcyclohex-1-ene gives good *cis* relative configuration ($10\text{e} \rightarrow 29\text{d}$).

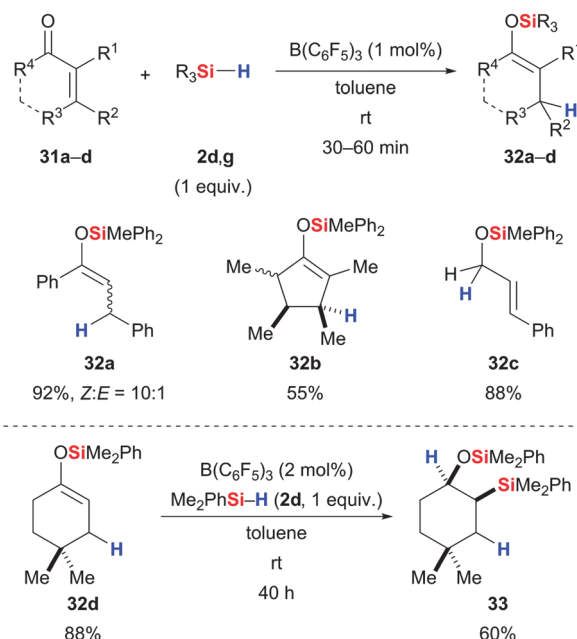
Recently, Simonneau and Oestreich introduced the new strategy of ionic transfer hydrosilylation where the hydrosilane is formed *in situ* by $\text{B}(\text{C}_6\text{F}_5)_3$ -promoted decomposition of easy-to-handle 3-silylated cyclohexa-1,4-dienes ($10 + 30 \rightarrow 29$, Scheme 15).⁴⁶ This approach is particularly beneficial in the case of gaseous hydrosilanes, e.g., highly flammable and explosive Me_3SiH (b.p. 6.7°C). As described for the $\text{B}(\text{C}_6\text{F}_5)_3$ -catalysed transfer hydrogenation of imines (cf. Scheme 12),⁴² the catalysis is initiated by abstraction of one of the bis(allylic) hydrides from the hydrosilane surrogate,⁴³ forming a silicon-stabilised Wheland complex with the borohydride as counteranion. We note here that the Wheland intermediate might also be described as a benzene-stabilised silicon cation. That ion pair readily transforms into Me_3SiH and benzene. Applied to alkenes, the *in situ*-generated Me_3SiH engages in the above $\text{B}(\text{C}_6\text{F}_5)_3$ -catalysed hydrosilylation (cf. Scheme 14).^{45a} Simonneau and Oestreich demonstrated the



Scheme 15 $\text{B}(\text{C}_6\text{F}_5)_3$ -catalysed transfer hydrosilylation of alkenes by Oestreich.

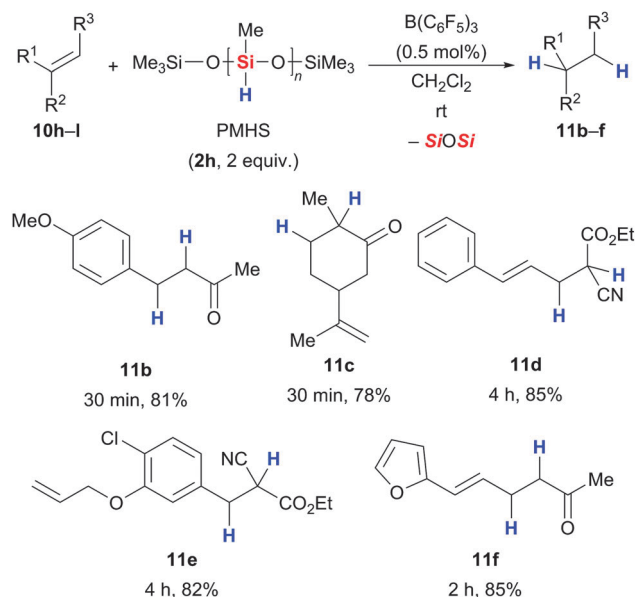
broad scope of this transfer hydrosilylation for terminal and internal alkenes (Scheme 15).⁴⁶ For instance, oct-1-ene ($10\text{d} \rightarrow 29\text{e}$) reacted with complete anti-Markovnikov selectivity, norbornene ($10\text{f} \rightarrow 29\text{f}$) underwent *exo*-selective hydrosilylation and 1-methylcyclohex-1-ene ($10\text{e} \rightarrow 29\text{g}$) featured *cis*-selective addition across its trisubstituted C–C double bond. Conversely, 2-methylindene shows opposite regioselectivity due to benzylic stabilisation of the carbenium ion, thereby overruling tertiary carbenium ion formation as well as steric factors.

Piers and co-workers extended the hydrosilylation of carbonyl functions to α,β -unsaturated acceptors (Scheme 16, upper).⁴⁷ The chemoselectivity is usually excellent with enones, favoring 1,4- over 1,2-reduction ($31\text{a,b} \rightarrow 32\text{a,b}$). Not surprisingly, 1,2-reduction becomes competitive with increased steric bulk at the β -carbon atom but in cases where the 1,2-pathway also suffers from steric



Scheme 16 $\text{B}(\text{C}_6\text{F}_5)_3$ -catalysed hydrosilylation of enones, enals, and silyl enol ethers by Piers.





Scheme 17 $B(C_6F_5)_3$ -catalysed hydrosilylation of α,β -unsaturated acceptors employing PMHS (**2h**) by Chandrasekhar.

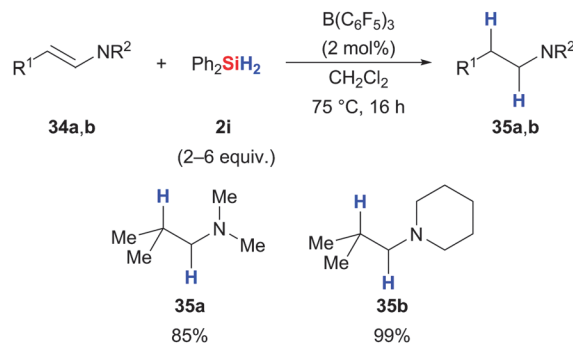
congestion the conjugate reduction still wins (**31a** \rightarrow **32a**). However, predominant 1,2-hydrosilylation is seen with enals (**31c** \rightarrow **32c**). These 1,4-hydrosilylations afford silyl enol ethers that participate in another hydrosilylation to yield β -silylated silyl ethers (**32d** \rightarrow **33**, Scheme 16, lower).⁴⁸ The diastereoselectivity of the addition of the Si-H bond across the C-C double bond is *trans* as a result of the sterically controlled borohydride reduction of the intermediate silylcarboxonium ion (*cf.* mechanistic discussion of the alkene hydrosilylation); the silyloxy and silyl groups are in a *cis* relationship.

Chandrasekhar and co-workers later employed polymethylhydrosiloxane (PMHS, **2h**) in this reduction (**10** \rightarrow **11**, Scheme 17).⁴⁹ The PMHS- $B(C_6F_5)_3$ system allowed for highly chemo- and regioselective reduction of various conjugated alkenes in excellent yields and was superior to other PMHS-Lewis acid combinations. The advantages of PMHS (**2h**), such as being inexpensive, environmentally friendly as well as air- and moisture-stable, make the procedure a practical alternative to the existing protocol.

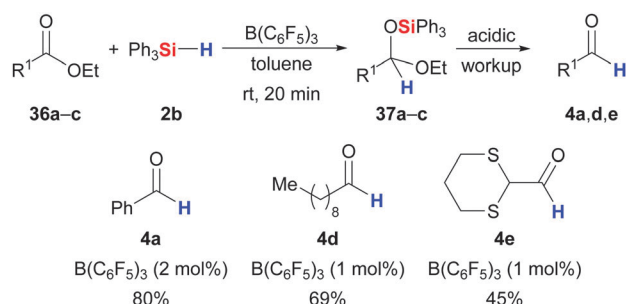
Similar to the hydrosilylation of silyl enol ethers (Scheme 16, lower), Tan and Zhang accomplished the reduction of enamines to afford the corresponding tertiary amines in excellent yields (**34** \rightarrow **35**, Scheme 18).⁵⁰ Only two examples have been reported to date but the related FLP-catalysed enamine hydrogenation is a popular application of this transformation.⁵¹

3.2 Reduction of carboxyl groups to the aldehyde oxidation level

The pioneering work of Piers and co-workers on carbonyl hydrosilylation also included carboxyl compounds as substrates (**36** \rightarrow **37** \rightarrow **4**, Scheme 19).^{3,5} Initially limited to aryl esters,³ the authors later extended the scope to (functionalised) aliphatic esters.⁵ Hydrolysis of the acetal **37** then affords the aldehyde **4**.



Scheme 18 $B(C_6F_5)_3$ -catalysed hydrosilylation of enamines by Zhang.



Scheme 19 $B(C_6F_5)_3$ -catalysed hydrosilylation of carboxylic esters to acetals by Piers.

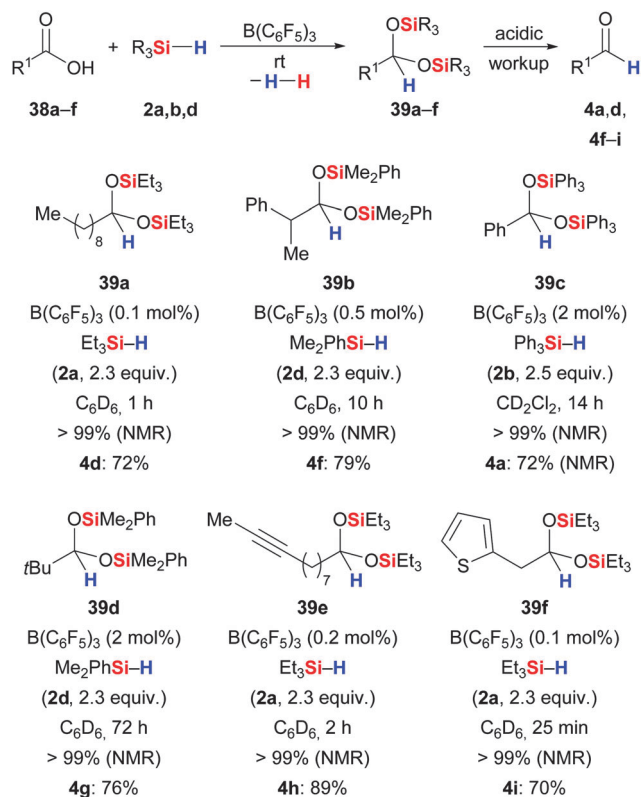
It is important to note that overstoichiometric amounts of the hydrosilane result in further degradation of the acetal **37**, yielding complex mixtures of various oxidation states.

The related hydrosilylation of carboxylic acids was recently elaborated by Brookhart and co-workers (**38** \rightarrow **39** \rightarrow **4**, Scheme 20).^{52,53} Again, the acetal is easily hydrolysed to the aldehyde (**39** \rightarrow **4**). Acetal formation was particularly effective with bulky tertiary hydrosilanes whereas smaller tertiary as well as secondary hydrosilanes led to overreduction. For example, hydrosilylation of phenylpropanoic acid with TMDS (1,1,3,3-tetramethyldisiloxane) cleanly produced fully reduced *n*-propylbenzene (not shown). The substrate scope ranges from linear and branched aliphatic to aromatic carboxylic acids with excellent tolerance of unsaturation (double and triple bonds). The difference between this and Piers' carboxyl hydrosilylation is that the present transformation begins with a $B(C_6F_5)_3$ -catalysed dehydrogenative Si-O coupling (see Section 7) that converts the free carboxylic acid into the corresponding silyl ester.

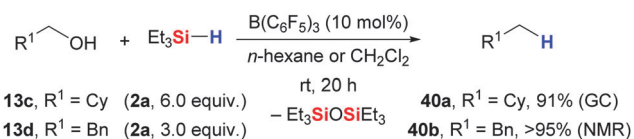
3.3 Deoxygenation

Another attractive application of the $B(C_6F_5)_3$ -catalyzed hydrosilylation was introduced by Gevorgyan, Yamamoto, and co-workers.^{54,55} These authors showed that alcohols, carbonyl as well as carboxyl compounds are fully reduced to the hydrocarbon at room temperature when treated with excess Et_3SiH (**2a**) in the presence of catalytic amounts of $B(C_6F_5)_3$ (Schemes 21 and 23). By this, primary alcohols are converted into the corresponding alkane (**13** \rightarrow **40**, Scheme 21). However, deoxygenation of secondary and tertiary alcohols failed. These alcohols undergo the initial dehydrogenative





Scheme 20 B(C₆F₅)₃-catalysed hydrosilylation of carboxylic acids to acetals by Brookhart.

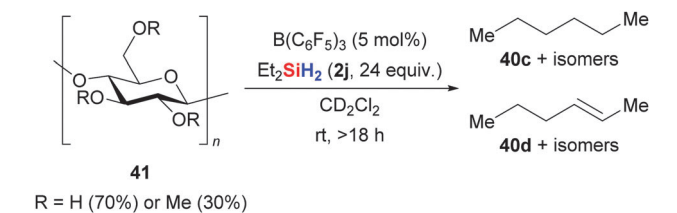


Scheme 21 B(C₆F₅)₃-catalysed deoxygenation of alcohols.

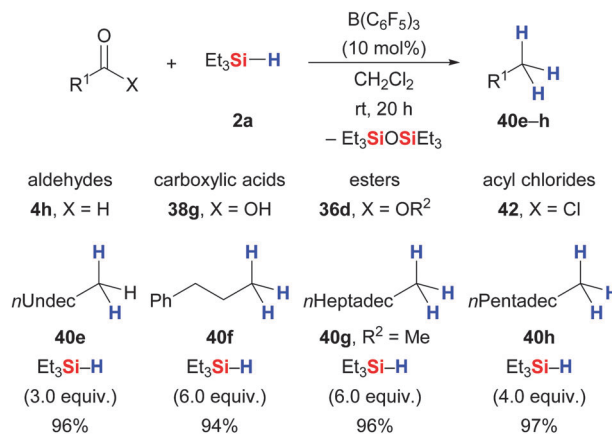
Si–O coupling (*cf.* Scheme 40) but the generated silyl ethers are too sterically hindered to react further with Et₃SiH–B(C₆F₅)₃ adduct. Chemoselective formation of silyl ethers from primary alcohols is possible with equimolar amounts of Et₃SiH (2a). Nimmagadda and McRae further advanced this methodology by utilizing less hindered *n*BuSiH₃ and Et₂SiH₂ (2j), respectively.⁵⁶ By this, secondary and tertiary alcohols were now susceptible to deoxygenation (not shown).^{57,58}

An intriguing application of this deoxygenation was reported by Gagné and co-workers by converting monosaccharides and polysaccharides into mixtures of saturated and unsaturated hydrocarbons, *i.e.*, alkanes and alkenes, respectively, with Et₂SiH₂ (2j) in the presence of catalytic amounts of B(C₆F₅)₃ (41 → 40, Scheme 22).⁵⁹

Defunctionalization of carbonyl and carboxyl compounds works equally well with excess Et₃SiH (2a) in the presence of B(C₆F₅)₃ (Scheme 23).⁵⁹ For example, *n*-dodecanal is converted into *n*-dodecane in high yield (4h → 40e). Similarly, the exhaustive reduction of aliphatic carboxylic acids (38g → 40f) as well as esters (36d → 40g) and acyl chlorides (42 → 40h)



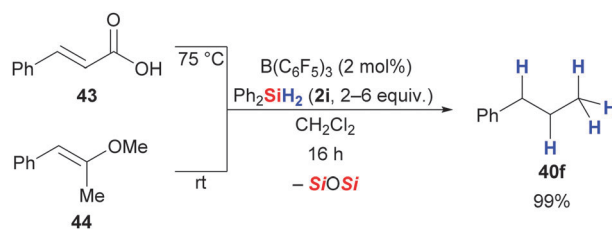
Scheme 22 B(C₆F₅)₃-catalysed deoxygenation of carbohydrates by Gagné.



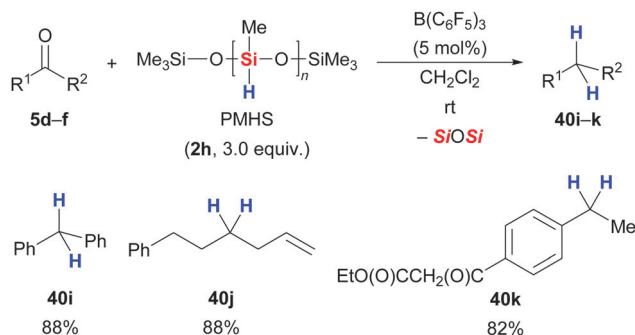
Scheme 23 B(C₆F₅)₃-catalysed deoxygenation of various carbonyl and carboxyl compounds by Gevorgyan and Yamamoto.

derived thereof proceeded smoothly at ambient temperature. Conversely, partial reduction was seen with aromatic carbonyl and carboxyl compounds, affording the corresponding TES-protected benzylic alcohols (not shown). Moreover, the authors indicate in the final paragraph of their publication that ketones, acetals and nitriles were also amenable to this procedure but no examples were reported. Tan and Zhang later showed that α,β -unsaturated carboxyl compounds, *e.g.*, cinnamic acid (43), undergo exhaustive reduction with Ph₂SiH₂ (2i) (43 → 40f, Scheme 24).⁵⁰ Their study also included an example of an enol ether that was reduced to the corresponding hydrocarbon (44 → 40f).⁵⁰

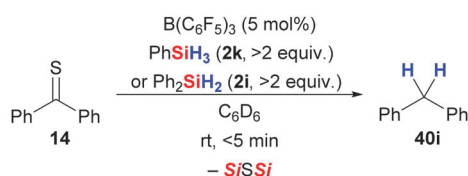
One year later, Chandrasekhar and co-workers found that PMHS (2h) can also be used as reductant in B(C₆F₅)₃-catalysed carbonyl deoxygenations.^{59b,60,61} Various aromatic and aliphatic carbonyl groups were rapidly reduced to methylene groups (5 → 40, Scheme 25). For example, benzophenone was cleanly defunctionalised to furnish diphenylmethane (5d → 40i). The



Scheme 24 B(C₆F₅)₃-catalysed exhaustive reduction of an α,β -unsaturated carboxylic acid and an enol ether.



Scheme 25 $B(C_6F_5)_3$ -catalysed deoxygenation of various carbonyl compounds using PMHS by Chandrasekhar.

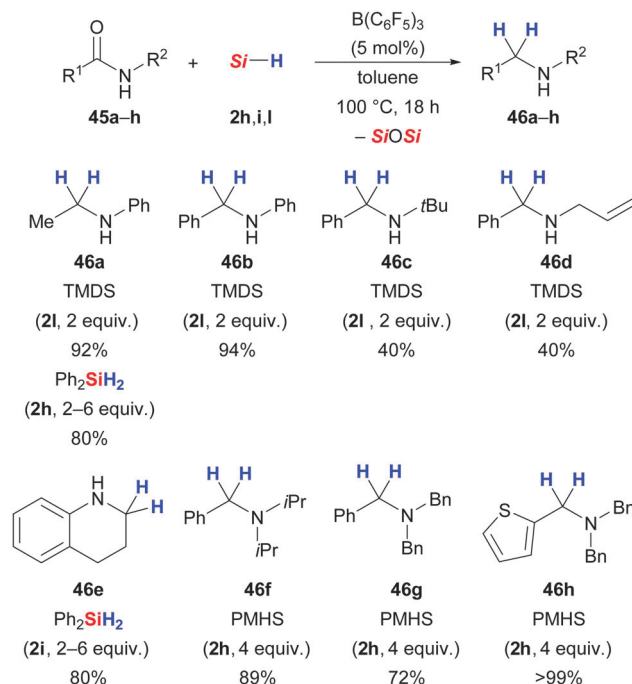


Scheme 26 $B(C_6F_5)_3$ -catalysed desulfurisation of a thioketone by Rosenberg.

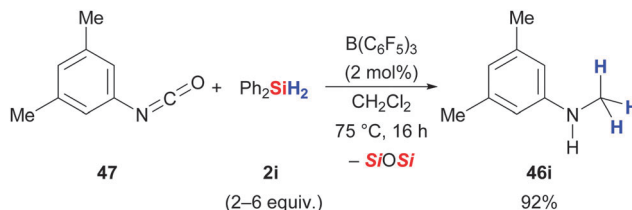
new hydrosilane–borane combination displays excellent scope. Alkyl and aryl halides remained untouched, and unsaturation in form of alkenes was tolerated as well (**5e** → **40j**). Remarkably, even carboxylic esters did not react (**5f** → **40k**). Rosenberg and co-workers demonstrated that defunctionalisation by $B(C_6F_5)_3$ -catalysed hydrosilylation is also applicable to thioketones (Scheme 26).³⁵ Thiobenzophenone underwent rapid desulfurisation with $PhSiH_3$ (**2k**) or Ph_2SiH_2 (**2i**) at room temperature to yield diphenylmethane quantitatively (**14** → **40i**).

Chandrasekhar and co-workers reported that the reduction of benzamide to benzylamine with the PMHS/ $B(C_6F_5)_3$ reducing agent failed (**45** → **46**, not shown).^{59b} In contrast, Tan and Zhang⁵⁰ as well as Blondiaux and Cantat⁶² identified a system that allows for the deoxygenation of primary, secondary and tertiary amides. Also, Tan and Zhang mentioned that the reduction of benzamide did not occur at temperatures as high as 120 °C, probably due to conjugation of the amide group with the phenyl ring.⁵⁰ Blondiaux and Cantat recently accomplished the challenging reduction of primary amides, with one example being benzamide. The “trick” is to protect one of the N–H bonds with Me_3SiCl , followed by $B(C_6F_5)_3$ -catalysed hydrosilylation with TMDS (not shown).⁶²

Tan and Zhang used various phenyl-substituted hydrosilanes in their amide reduction;⁵⁰ secondary and tertiary amides were reduced to the corresponding amines in good yields but *N*-phenylamides were limited to three examples: *N*-phenylacetamide, 1-methyl-2-indolinone and 3,4-dihydro-2(1*H*)-quinolinone (not shown). The deoxygenation of a broad range of aliphatic and aromatic amides was later presented by the groups of Cantat⁶² (**45** → **46**, Scheme 27) and Adronov⁶³ (not shown). Cantat and co-workers utilised cost-efficient, non-toxic and air-stable PMHS (**2h**) and TMDS (**2i**) as reducing agents. It is important to note that high temperatures are required to thermally cleave the relatively stable amide– $B(C_6F_5)_3$ adduct. Interestingly, in α,β -unsaturated



Scheme 27 $B(C_6F_5)_3$ -catalysed amide-to-amine reduction by Cantat.



Scheme 28 $B(C_6F_5)_3$ -catalysed deoxygenation of an isocyanate by Zhang.

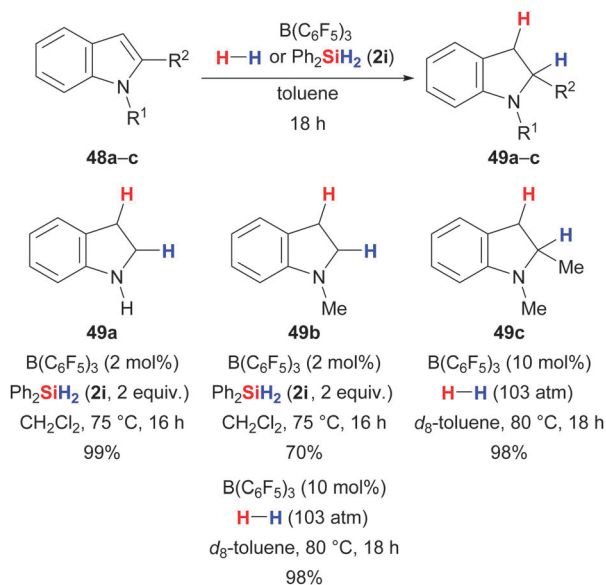
amides 1,4-reduction proceeds faster than the deoxygenation (not shown).

Tan and Zhang presented one example of an aryl isocyanate reduction to afford the corresponding aniline in quantitative yield (**47** → **46i**, Scheme 28).⁵⁰

3.4 Reduction of heterocycles

Tan and Zhang had also included an electron-rich heterocycle, namely indole, into their broad screening of substrates for the $B(C_6F_5)_3$ -catalysed hydrosilylation.^{50,64} Indole is reminiscent of the enamine motif that is indeed reduced to amines under the typical reaction setup (*cf.* Scheme 18). Consequently, free indole and *N*-methyl indole participate nicely in the reduction with Ph_2SiH_2 (**2i**) to yield the correspondings indolines (**48a,b** → **49a,b**, Scheme 29). Likewise, the hydrogenation of *N*-methyl protected indoles works equally well (**48b,c** → **49b,c**, Scheme 29).^{37c} Mechanistic investigations concerning Si–H and H–H bond activation in the presence of heteroarenes were undertaken by Ingleson and co-workers and these revealed a complex situation with multiple competing pathways that eventually lead to the reduced compounds (not shown).⁶⁵ In their *N*-silylation studies,





Scheme 29 B(C₆F₅)₃-catalysed reduction of indoles by Zhang (with hydrosilanes) and Stephan (with dihydrogen).

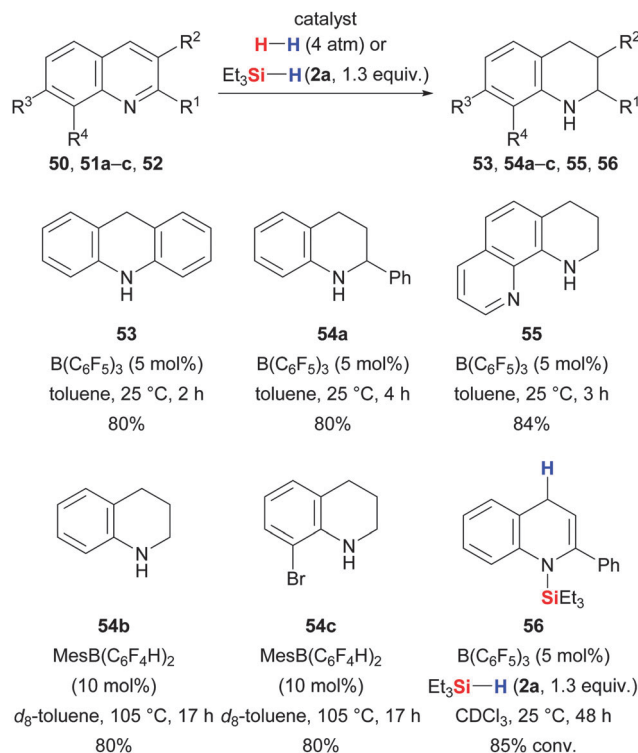
Paradies and co-workers also observed reduction of indoles to indolines (*cf.* Scheme 43).^{24b}

Moreover, imine-like heteroarenes are also reduced with dihydrogen in the presence of electron-deficient boranes (Scheme 30).⁶⁶ Examples include the hydrogenation of acridine (**50** → **53**), various quinolines (**51** → **54**) and 1,10-phenanthroline (**52** → **55**). Interestingly, 2-phenylquinoline was reduced to 1,2,3,4-tetrahydro-2-phenylquinoline with dihydrogen (**51a** → **54a**) but gave 1,4-reduction exclusively (**51a** → **56**) when treated with Et₃SiH (**2a**) in the presence of B(C₆F₅)₃.⁶⁶ The substrate scope of the quinoline hydrogenation was later extended by Soós and co-workers.⁶⁷ The use of a sterically more demanding and slightly less Lewis acidic catalyst, MesB(C₆F₄H)₂, prevented Lewis pair formation with the substrates, thereby even enabling the reduction of the free quinoline (**51b,c** → **54b,c**).

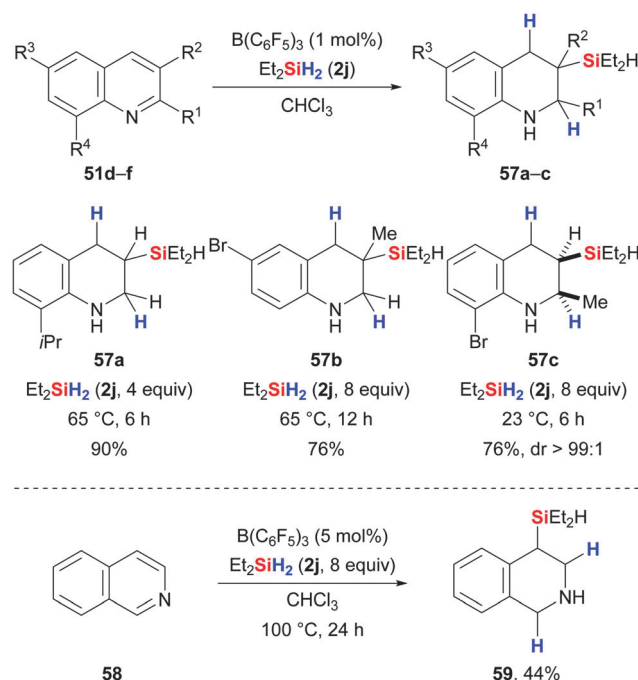
When quinolines are treated with an excess of dihydrosilane **2j** in the presence of B(C₆F₅)₃, 3-silylated 1,2,3,4-tetrahydroquinolines are formed as illustrated by the group of Park and Chang (**51** → **57**, Scheme 31, upper).⁶⁸ Mechanistic as well as computational studies revealed that an initial 1,4-reduction is followed by regioselective hydrosilylation of the thus formed *N*-silylated enamine.⁶⁹ For substrates bearing substituents in the 2-position, excellent diastereoselectivities were achieved (**51f** → **57c**). In the case of isoquinolines, reduction products with silylation in β-position with respect to the nitrogen atom were obtained (**58** → **59**, Scheme 31, lower).

A stereoselective hydrogenation method for 2,3-disubstituted quinoxalines was developed by Zhang and Du (**60** → **61**, Scheme 32).⁷⁰ Employing B(C₆F₅)₃ as catalyst resulted in the diastereoselective formation of *cis*-2,3-disubstituted 1,2,3,4-tetrahydroquinoxalines whereas the use of chiral borane **24b** afforded the same target molecules in enantioselective fashion.

A B(C₆F₅)₃-mediated exhaustive reduction of anilines⁷¹ and a few heteroarenes⁷² under hydrogen atmosphere to afford the



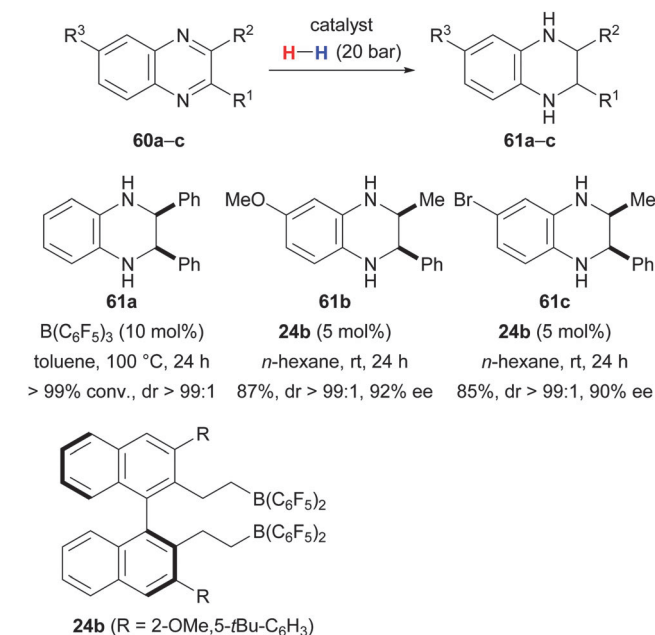
Scheme 30 Catalytic reduction of heterocycles by Stephan (with B(C₆F₅)₃) and Soós (with MesB(C₆F₄H)₂).



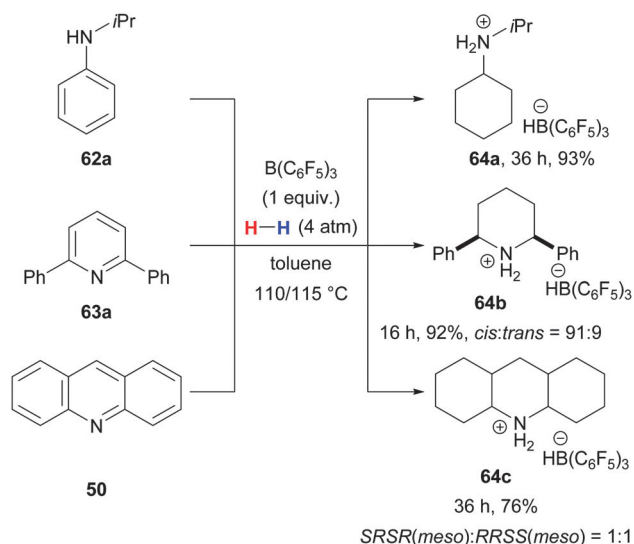
Scheme 31 B(C₆F₅)₃-catalysed reduction of quinolines (upper) and isoquinolines (lower) by Park and Chang.

hydridoborate salts was discovered by Stephan and co-workers (**62a/63a/50** → **64a-c**, Scheme 33). Although stoichiometric amounts of B(C₆F₅)₃ are required, multiple turnovers are achieved



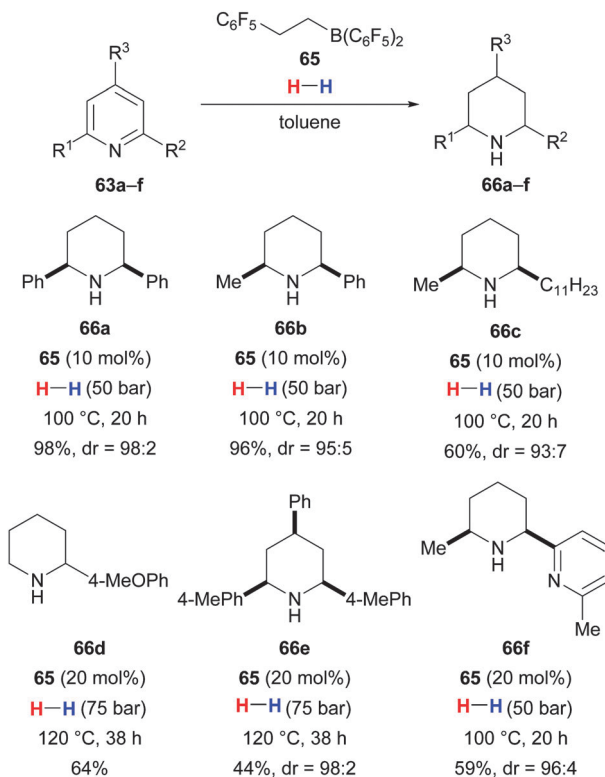


Scheme 32 Stereocontrolled reduction of quinoxalines by Du.

Scheme 33 B(C₆F₅)₃-catalysed reduction of anilines and heteroarenes to hydrioborate salts by Stephan.

before the final H-H bond activation by the formed amine and B(C₆F₅)₃ produces the hydrioborate salts.

Shortly thereafter, Liu and Du developed a truly catalytic method to reduce pyridines to piperidines with dihydrogen (**63** → **66**, Scheme 34).⁷³ These authors found that Piers' borane HB(C₆F₅)₂ (ref. 39b) was able to catalyse this reaction but its hydroboration products with electron-poor alkenes showed an even higher catalytic activity. *In situ*-formed borane **65** was used to promote the exhaustive reduction of pyridines with various alkyl or aryl substitution patterns with high levels of diastereoselection. 2-Bromopyridines were dehalogenated (not shown), and selective hydrogenation of one pyridine core was observed for bipyridine **63f**.



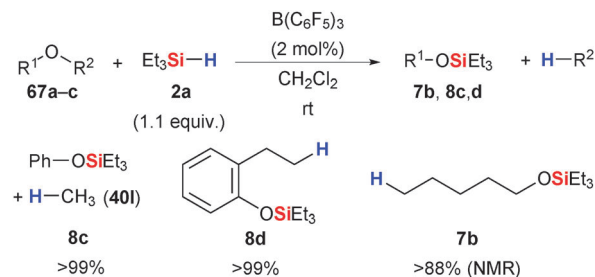
Scheme 34 Reduction of pyridines by Du.

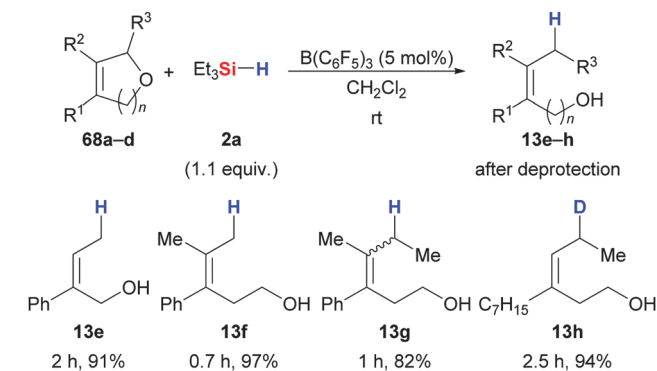
4. Transformations of ethers

4.1 Cleavage of dialkyl and aryl alkyl ethers

Gevorgyan, Yamamoto and co-workers had mentioned that Et₃SiH (**2a**) with B(C₆F₅)₃ reduces ethers to alkanes under mild conditions (*cf.* Section 3.3).^{54,55} Aryl methyl ethers yielded the corresponding silyl ethers and methane quantitatively (*e.g.*, **67a** → **8c**, Scheme 35). Likewise, 2,3-dihydrobenzofuran was ring-opened with Si-O and C-H bond formations (**67b** → **8d**). Primary ethers with linear alkyl chains, cyclic ethers such as tetrahydropyran (**67c** → **7b**) as well as secondary ethers such as iPr₂O were fully reduced to the respective hydrocarbons. Tertiary ethers did not react.

Njardarson and co-workers were inspired by this work and extended this mild ether cleavage to unsaturated cyclic ethers.⁷⁴ Their contribution is focused on 2,5-dihydrofurans and 3,6-2H-dihydropyrans (Scheme 36). The C-O cleavage in 2,5-dihydrofurans proceeded cleanly in high yield (**68** → **13**) but thermodynamically

Scheme 35 B(C₆F₅)₃-catalysed ether cleavage by Gevorgyan and Yamamoto.

Scheme 36 $B(C_6F_5)_3$ -catalysed cleavage of cyclic ethers by Njardarson.

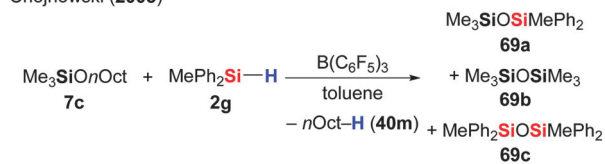
controlled alkene migration was seen in few cases. Homo-allylic alcohols were obtained from 3,6-2*H*-dihydropyrans, and scrambling of the double bond geometry occurred with selected substrates (**68c** → **13g**). The selective incorporation of deuterium in the allylic position was demonstrated with Et_3SiD (**68d** → **13h**, Scheme 36).

4.2 Cleavage of alkyl silyl ethers (Piers–Rubinsztajn reaction)

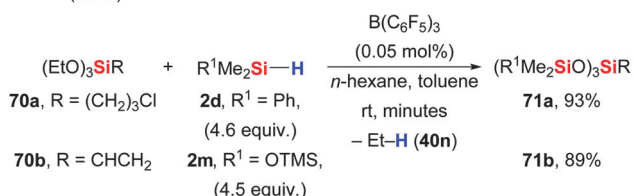
Alkyl silyl ethers, *i.e.*, alkoxyasilanes, convert into disiloxanes when reacted with hydrosilanes in the presence of catalytic amounts of $B(C_6F_5)_3$. This dehydrocarbonative condensation is commonly referred to as the Piers–Rubinsztajn reaction but might also be called a transesterification. This transformation is ideal for the rapid formation of 3D silicon structures for silicon-based polymers.

Chojnowski and co-workers described the preparation of disiloxanes along with hydrocarbons from alkoxyasilanes for the first time (**7** → **69**, Scheme 37, upper).⁷⁵ Their goal was to examine the mechanism of this reaction by means of kinetic and UV spectroscopic measurements. The reaction of $MePh_2SiH$ (**2g**) with $Me_3SiONOct$ (**7c**) was used as model reaction. Their kinetic analysis showed that the reaction rate is proportional to the catalyst concentration, and the reaction is 1st order in both reactants. The catalyst, $B(C_6F_5)_3$, is mainly available in free form

Chojnowski (2005)



Brook (2010)

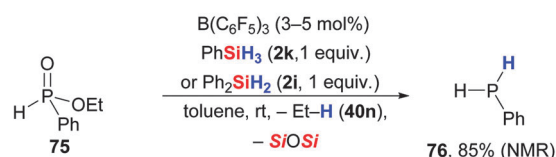
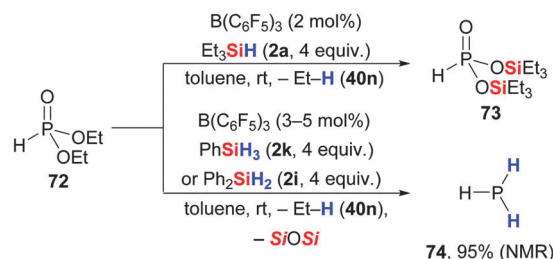
Scheme 37 $B(C_6F_5)_3$ -catalysed dehydrocarbonative condensation of alkoxyasilanes and hydrosilanes: the Piers–Rubinsztajn reaction.

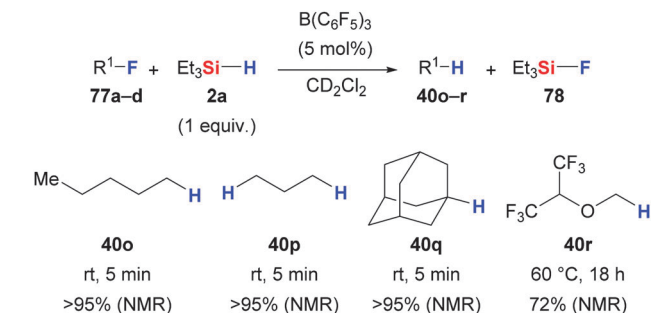
because Lewis pair formation with the alkoxyasilane **7** or disiloxanes **69** is relatively weak. The proposed mechanism passes through a complex of the hydrosilane, $B(C_6F_5)_3$ and the alkoxyasilane (*cf.* **V**, Scheme 1). Hydride transfer from the silicon to the boron atom generates an oxonium ion intermediate that can react with the borohydride in three different ways, that is hydride attack at either of the three groups attached to the oxonium ion oxygen atom. Out of these three options, the cleavage of the C–O bond will irreversibly form the disiloxane and the alkane. Breaking either of the Si–O bonds results in the backward reaction or a hydrosilane/alkoxyasilane metathesis.

Brook and co-workers became interested in the Piers–Rubinsztajn reaction for the preparation of silicon-based polymers and described the synthesis of oligosilicone building blocks from functionalized trialkoxyasilanes (**70** → **71**, Scheme 37, lower).^{76,77} For example, ω -haloalkyl- and vinyl-substituted trialkoxyasilanes were compatible with the reaction conditions of the dehydrocarbonative condensation. Neither hydrodehalogenation nor hydrosilylation of the alkenyl group occurred, thereby allowing for the generation of alkenyl-modified silicones.

5. Transesterification and deoxygenation of phosphonic and phosphinic esters

Denis and co-workers investigated the $B(C_6F_5)_3$ -catalysed C–O/Si–O metathesis (*cf.* Section 4) as well as the deoxygenation (*cf.* Section 3.3) of phosphonic esters (Scheme 38, upper).⁷⁸ The choice of hydrosilane determines the chemoselectivity. With tertiary hydrosilanes, phosphonic alkyl esters are converted into the corresponding silyl esters in high yields (**72** → **73**). Conversely, exhaustive reduction to free phosphines was achieved with excess of dihydro- or trihydrosilanes (**72** → **74**). In contrast, phosphinic alkyl esters are deoxygenated to the free phosphines already with one equivalent of dihydro- or trihydrosilane (**75** → **76**, Scheme 38, lower). The conversion to their corresponding silyl esters was not reported.

Scheme 38 $B(C_6F_5)_3$ -catalysed reaction of phosphonic (upper) and phosphinic esters (lower) with hydrosilanes.



Scheme 39 B(C₆F₅)₃-catalysed hydrodefluorination of (α-heteroatom-substituted) alkyl fluorides by Stephan.

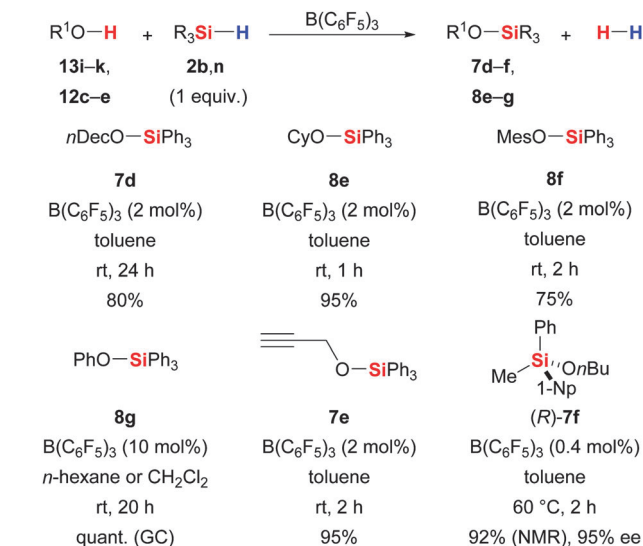
6. Hydrodefluorination with hydrosilanes

Caputo and Stephan introduced a simple protocol for the activation of C(sp³)-F bonds (Scheme 39).⁷⁹ The combination of Et₃SiH (2a) and catalytic amounts of B(C₆F₅)₃ was shown to convert (α-oxygenated) alkyl fluorides into the corresponding alkanes along with the formation of Et₃SiF (78). Quantitative yields were obtained for primary and tertiary fluorides within a few minutes (77 → 40). However, ether 77d required 18 h at 60 °C to afford hydrodefluorinated 40r in 72% yield; the CH(CF₃)₂ group remained intact.

7. Dehydrogenative Si-X couplings

The dehydrogenative coupling of alcohols,^{80–82} thiols^{35,80a} or amines²⁴ and hydrosilanes is, besides the hydrosilylation of C=X bonds, another major application of catalysis with B(C₆F₅)₃. These oxidations are generally high-yielding, releasing dihydrogen as the sole byproduct.

The methodology was introduced by Piers and co-workers, and their initial report was focused on the dehydrogenative silylation of primary, secondary, tertiary and phenolic hydroxy groups to afford the corresponding silyl ethers (13/12 → 7/8, Scheme 40).⁴ Interestingly, secondary and tertiary react faster than primary alcohols (1 h for 12c → 8e versus 24 h for 13i → 7d) but shorter reaction times are possible with higher catalyst loadings or at elevated temperatures. The functional-group tolerance of the method is excellent. Shortly thereafter, Gevorgyan, Yamamoto and co-workers reported similar observations in connection with their protocol for the deoxygenation of alcohols with Et₃SiH/B(C₆F₅)₃ (cf. Scheme 21).⁵⁴ Primary alcohols were defunctionalised after the Si-O coupling whereas the reaction stopped at this stage with the bulkier secondary and tertiary alcohols as well as phenols, even in the presence of excess of hydrosilane. Kawakami and co-workers applied Sommer's essentially enantiopure silicon-stereogenic hydrosilane 2n (>99% ee) to this dehydrogenative Si-O coupling and observed inversion of the stereochemistry at the silicon atom in (R)-7f with hardly any erosion of the enantiomeric excess (95% ee).¹⁴ The stereochemical course at the silicon atom is in agreement with the general mechanistic

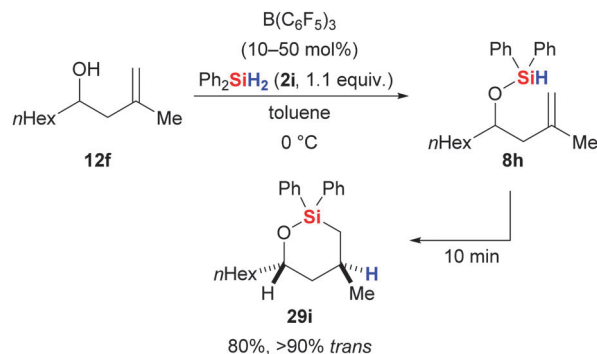


Scheme 40 B(C₆F₅)₃-catalysed dehydrogenative Si-O couplings.

picture (cf. V, Scheme 1). The hydroxy group attacks the silicon atom in the hydrosilane-borane adduct from the backside.

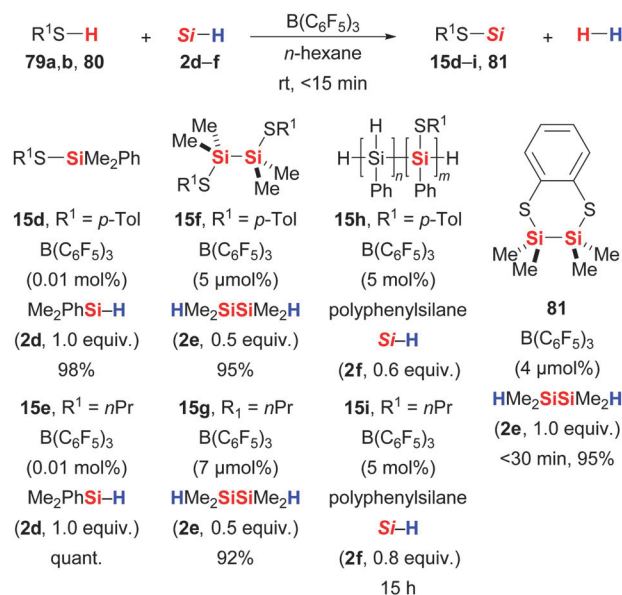
Dussault and co-workers merged the B(C₆F₅)₃-catalysed dehydrogenative Si-O coupling with the alkene hydrosilylation (cf. Scheme 14) promoted by the same catalyst into a one-pot procedure (Scheme 41).⁸¹ This domino process allows for the synthesis of cyclic siloxanes in regio- and stereoselective fashion. For example, chemoselective alcohol silylation of 12f with Ph₂SiH₂ (2i) generated alkoxy silane 8h that engaged in a rapid intramolecular hydrosilylation of the tethered alkene to yield siloxane 29i.

The potential of this methodology was further tested in the dehydrogenative coupling of aliphatic and aromatic thiols (79/80 → 15/81, Scheme 42).^{35,80a} It was Rosenberg and co-workers to elaborate the sulfur chemistry based on Piers' seminal work. These authors demonstrated that tertiary hydrosilane 2d as well as symmetrically substituted dihydrodisilane 2e and polyphenylsilane 2f are applicable to the Si-S coupling; the Si-Si bonds of the latter reactants were stable in the presence of B(C₆F₅)₃ (cf. Rosenberg's reduction of thioketones, Scheme 6). Reactions were generally fast, giving near-quantitative yields within minutes at room temperature. The clean coupling of HMe₂SiSiMe₂H (2e) and



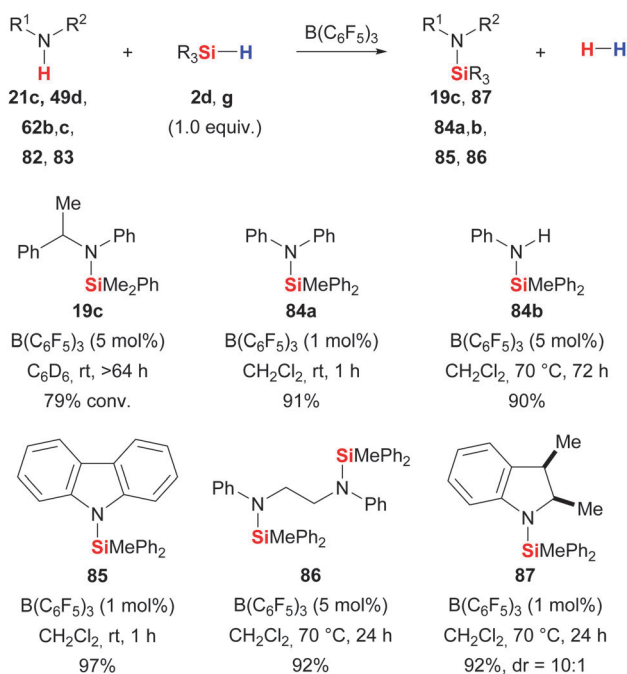
Scheme 41 B(C₆F₅)₃-catalysed dehydrogenative Si-O coupling followed by intramolecular alkene hydrosilylation.



Scheme 42 $\text{B}(\text{C}_6\text{F}_5)_3$ -catalysed dehydrogenative Si–S couplings.

1,2-benzenedithiol is particularly noteworthy as no acyclic oligomeric byproducts were formed (**80** → **81**).

The related dehydrogenative Si–N coupling had long been neglected. It was introduced by Oestreich and co-workers as part of their mechanistic investigation on the $\text{B}(\text{C}_6\text{F}_5)_3$ -catalysed imine hydrosilylation (**X** → **VII**, Scheme 3)²³ but the test reaction of Me_2PhSiH (**2d**) and 1-phenylethylamine was rather slow (**21c** → **19c**, Scheme 43). Shortly thereafter, Paradies and co-workers turned this into a useful methodology (**21/49/62/82/83** → **19/87/84/85/86**, Scheme 43).^{24b} Anilines **62** (including carbazole **82**) in any form

Scheme 43 $\text{B}(\text{C}_6\text{F}_5)_3$ -catalysed dehydrogenative Si–N couplings.

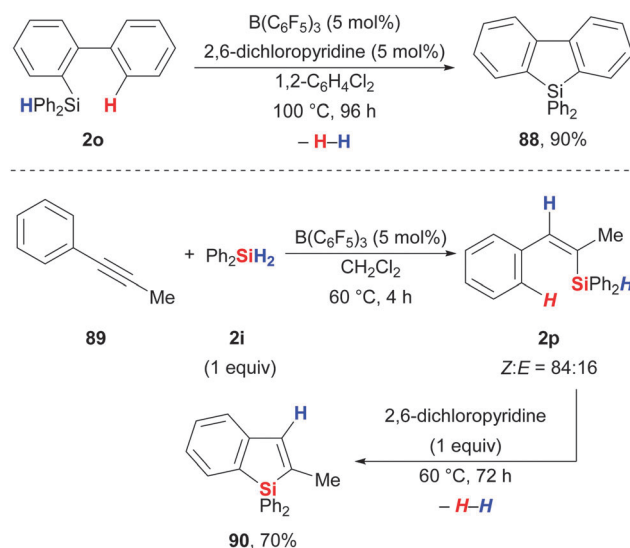
were amenable to this $\text{B}(\text{C}_6\text{F}_5)_3$ catalysis at elevated temperature. However, pyrroles were not participating and indoles were cleanly converted into the *N*-silylated indolines (cf. Scheme 29 for indole-to-indoline reduction). It is worth mentioning that these authors propose that anilines and carbazoles react by the same mechanism established for the Si–O coupling whereas indoles undergo silylation of the nitrogen atom followed by a rearrangement/reduction sequence to yield indolines.

8. Intramolecular sila-Friedel–Crafts-type reactions

Curless and Ingleson developed a method to perform intramolecular sila-Friedel–Crafts-type reactions catalytic in $\text{B}(\text{C}_6\text{F}_5)_3$ (Scheme 44).⁸³ Conventional activation of the Si–H bond in biphenyl-substituted hydrosilane **2o** with $\text{B}(\text{C}_6\text{F}_5)_3$ followed by intramolecular attack of the *ortho* arene at the silicon atom results in a silicon-stabilised Wheland intermediate that rearomatizes by deprotonation with 2,6-dichloropyridine to furnish silole **88**. The borohydride and the protonated pyridine base liberate dihydrogen as byproduct (Scheme 44, upper). A one-pot hydrosilylation/dehydrosilylation sequence starting from alkyne **89** via vinylsilane **2p** to access silaindene **90** was also reported (Scheme 44, lower). The initiation of this sequence constitutes the first example of a $\text{B}(\text{C}_6\text{F}_5)_3$ -catalysed hydrosilylation of an alkyne.^{46c} Moderate *trans*-selectivity in the hydrosilylation event (resulting in the *Z*-configured vinylsilane) was observed.⁸⁴

9. Short summary

It is evident from the enormous progress in recent years that catalysis with electron-deficient boranes is “alive and well”. Different from previous decades, the potential of these Lewis acids to contribute substantially to transition-metal-free

Scheme 44 $\text{B}(\text{C}_6\text{F}_5)_3$ -catalysed sila-Friedel–Crafts-type reactions by Ingleson.

catalysis matches the current zeitgeist of sustainable chemistry. $\text{B}(\text{C}_6\text{F}_5)_3$ -catalysed hydrosilylation and even more so hydrogenation are fundamental accomplishments. Of course, there are still problems, e.g., the limited functional group tolerance due to the strong Lewis acidity of the catalysts. Newly designed boranes where their Lewis acidity is finely balanced with their ability to mediate the bond activation will be required to address this issue. The same applies to the development of chiral catalysts for enantioselective variants. Again, the synthesis of such boron Lewis acids will be challenging but the work of Liu and Du nicely demonstrates that relatively simple solutions are indeed available.⁴⁰ We strongly believe that $\text{B}(\text{C}_6\text{F}_5)_3$ as well as FLP chemistry will continue to grow and that there is much more to be discovered.

Acknowledgements

This research was supported by the Cluster of Excellence *Unifying Concepts in Catalysis* of the Deutsche Forschungsgemeinschaft (EXC 314/2). Dr Sebastian Rendler (Freiburg/Münster) and Dr Marius Mewald (Münster/Berlin) deserve particular mention for their enthusiasm and commitment. M.O. is indebted to the Einstein Foundation (Berlin) for an endowed professorship.

Notes and references

- (a) A. G. Massey, A. J. Park and F. G. A. Stone, *Proc. Chem. Soc.*, 1963, 212; (b) A. G. Massey and A. J. Park, *J. Organomet. Chem.*, 1964, **2**, 245–250; (c) A. G. Massey and A. J. Park, *J. Organomet. Chem.*, 1966, **5**, 218–225.
- For early examples, see: (a) X. Yang, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1991, **113**, 3623–3625; (b) X. Yang, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1994, **116**, 10015–10031; (c) B. Temme, G. Erker, J. Karl, H. Luftmann, R. Fröhlich and S. Kotila, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1755–1757; (d) Y.-X. Chen, C. L. Stern, S. Yang and T. J. Marks, *J. Am. Chem. Soc.*, 1996, **118**, 12451–12452; for an overview, see: (e) E. Y.-X. Chen and T. J. Marks, *Chem. Rev.*, 2000, **100**, 1391–1434.
- D. J. Parks and W. E. Piers, *J. Am. Chem. Soc.*, 1996, **118**, 9440–9441.
- J. M. Blackwell, K. L. Foster, V. H. Beck and W. E. Piers, *J. Org. Chem.*, 1999, **64**, 4887–4892.
- D. J. Parks, J. M. Blackwell and W. E. Piers, *J. Org. Chem.*, 2000, **65**, 3090–3098.
- For overviews, see: (a) T. Robert and M. Oestreich, *Angew. Chem., Int. Ed.*, 2013, **52**, 5216–5218; (b) G. Erker, *Dalton Trans.*, 2005, 1883–1890; (c) W. E. Piers, *Adv. Organomet. Chem.*, 2004, **52**, 1–76; (d) K. Ishihara and H. Yamamoto, *Eur. J. Org. Chem.*, 1999, 527–538; (e) W. E. Piers and T. Chivers, *Chem. Soc. Rev.*, 1997, **26**, 345–354.
- (a) G. C. Welch, R. R. S. Juan, J. D. Masuda and D. W. Stephan, *Science*, 2006, **314**, 1124–1126; (b) P. A. Chase, G. C. Welch, T. Jurca and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2007, **46**, 8050–8053; (c) G. C. Welch and D. W. Stephan, *J. Am. Chem. Soc.*, 2007, **129**, 1880–1881.
- (a) P. Spies, G. Erker, G. Kehr, K. Bergander, R. Fröhlich, S. Grimme and D. W. Stephan, *Chem. Commun.*, 2007, 5072–5074; (b) P. Spies, S. Schwendemann, S. Lange, G. Kehr, R. Fröhlich and G. Erker, *Angew. Chem., Int. Ed.*, 2008, **47**, 7543–7546; (c) H. Wang, R. Fröhlich, G. Kehr and G. Erker, *Chem. Commun.*, 2008, 5966–5968.
- For overviews of frustrated Lewis pair chemistry, see: (a) D. W. Stephan, *Acc. Chem. Res.*, DOI: 10.1021/ar500375j; (b) M. Alcarazo, *Synlett*, 2014, 1519–1520; (c) D. W. Stephan and G. Erker, *Chem. Sci.*, 2014, **5**, 2625–2641; (d) *Top. Curr. Chem.*, ed. G. Erker and D. W. Stephan, Springer, Berlin, Heidelberg, 2013, vol. 332; (e) *Top. Curr. Chem.*, ed. G. Erker and D. W. Stephan, Springer, Berlin, Heidelberg, 2013, vol. 334; (f) D. W. Stephan and G. Erker, *Angew. Chem., Int. Ed.*, 2010, **49**, 46–76; (g) D. W. Stephan, *Org. Biomol. Chem.*, 2008, **6**, 1535–1539; (h) A. L. Kenward and W. E. Piers, *Angew. Chem., Int. Ed.*, 2008, **47**, 38–41.
- For an overview of applications of H–H and Si–H bond activations catalysed by electron-deficient boranes as well as frustrated Lewis pairs, see: X. Feng and H. Du, *Tetrahedron Lett.*, 2014, **55**, 6959–6964.
- For a comparison of Si–H and H–H bond activations catalysed by electron-deficient boranes, see: W. E. Piers, A. J. V. Marwitz and L. G. Mercier, *Inorg. Chem.*, 2011, **50**, 12252–12262.
- For reviews of hydrogenation reactions catalysed by electron-deficient boranes or frustrated Lewis pairs, see: (a) L. Shi and Y.-G. Zhou, *ChemCatChem*, 2015, **7**, 54–56; (b) Y. Liu and H. Du, *Acta Chim. Sin.*, 2014, **72**, 771–777; (c) L. J. Hounjet and D. W. Stephan, *Org. Process Res. Dev.*, 2014, **18**, 385–391; (d) J. Paradies, *Angew. Chem., Int. Ed.*, 2014, **53**, 3552–3557; (e) J. Paradies, *Synlett*, 2013, 777–780; (f) D. W. Stephan, *Org. Biomol. Chem.*, 2012, **10**, 5740–5746; (g) D. W. Stephan, *Chem. Commun.*, 2010, **46**, 8526–8533; (h) D. W. Stephan, *Dalton Trans.*, 2009, 3129–3136.
- S. Rendler and M. Oestreich, *Angew. Chem., Int. Ed.*, 2008, **47**, 5997–6000.
- For a previous attempt to verify this step by using a silicon-stereogenic silane as stereochemical probe, see: S. Shinke, T. Tsuchimoto and Y. Kawakami, *Silicon Chem.*, 2007, **3**, 243–249.
- K. Sakata and H. Fujimoto, *J. Org. Chem.*, 2013, **78**, 12505–12512.
- For reductions of carbonyl compounds with hydrosilanes and $\text{BF}_3\cdot\text{OEt}_2$, see: (a) M. P. Doyle, C. T. West, S. J. Donnelly and C. C. McOskey, *J. Organomet. Chem.*, 1976, **117**, 129–140; (b) J. L. Fry, M. Orfanopoulos, M. G. Adlington, W. R. Dittman, Jr. and S. B. Silverman, *J. Org. Chem.*, 1978, **43**, 374–375.
- A. Y. Houghton, J. Hurmalainen, A. Mansikkamäki, W. E. Piers and H. M. Tuononen, *Nat. Chem.*, 2014, **6**, 983–988.
- A. Y. Houghton, V. A. Karttunen, W. E. Piers and H. M. Tuononen, *Chem. Commun.*, 2014, **50**, 1295–1298.
- (a) S. P. Hoffmann, T. Kato, F. S. Tham and C. A. Reed, *Chem. Commun.*, 2006, 767–769; (b) S. J. Connelly, W. Kaminsky and D. M. Heinekey, *Organometallics*, 2013, **32**, 7478–7481.



- 20 J. M. Blackwell, E. R. Sonmor, T. Scoccitti and W. E. Piers, *Org. Lett.*, 2000, **2**, 3921–3923.
- 21 D. T. Hog and M. Oestreich, *Eur. J. Org. Chem.*, 2009, 5047–5056.
- 22 M. Mewald and M. Oestreich, *Chem. – Eur. J.*, 2012, **18**, 14079–14084.
- 23 J. Hermeke, M. Mewald and M. Oestreich, *J. Am. Chem. Soc.*, 2013, **135**, 17537–17546.
- 24 For dehydrogenative silylation of amines, see: (a) ref. 23; (b) L. Greb, S. Tamke and J. Paradies, *Chem. Commun.*, 2014, **50**, 2318–2320.
- 25 V. Sumerin, F. Schulz, M. Nieger, M. Leskelä, T. Repo and B. Rieger, *Angew. Chem., Int. Ed.*, 2008, **47**, 6001–6003.
- 26 P. A. Chase, T. Jurca and D. W. Stephan, *Chem. Commun.*, 2008, 1701–1703. This work also contains one example of a $B(C_6F_5)_3$ -catalysed reductive aziridine ring opening.
- 27 Computational models for the mode of dihydrogen activation by borane–imine and related borane–phosphine systems have been extensively discussed: (a) T. A. Rokob, A. Hamza, A. Stirling, T. Soós and I. Pápai, *Angew. Chem., Int. Ed.*, 2008, **47**, 2435–2438; (b) Y. Guo and S. Li, *Inorg. Chem.*, 2008, **47**, 6212–6219; (c) T. A. Rokob, A. Hamza, A. Stirling and I. Pápai, *J. Am. Chem. Soc.*, 2009, **131**, 2029–2036; (d) A. Hamza, A. Stirling, T. A. Rokob and I. Pápai, *Int. J. Quantum Chem.*, 2009, **109**, 2416–2425; (e) B. Schirmer and S. Grimme, *Chem. Commun.*, 2010, **46**, 7942–7944; (f) S. Grimme, H. Kruse, L. Goerigk and G. Erker, *Angew. Chem., Int. Ed.*, 2010, **49**, 1402–1405; (g) I. Bakó, A. Stirling, S. Bálint and I. Pápai, *Dalton Trans.*, 2012, **41**, 9023–9025; (h) D. M. Camaioni, B. Ginovska-Pangovska, G. K. Schenter, S. M. Kathmann and T. Autrey, *J. Phys. Chem. A*, 2012, **116**, 7228–7237; (i) T. A. Rokob, I. Bakó, A. Stirling, A. Hamza and I. Pápai, *J. Am. Chem. Soc.*, 2013, **135**, 4425–4437; (j) L. L. Zeonjuk, N. Vankova, A. Mavrandonakis, T. Heine, G.-V. Rösenthaller and J. Eicher, *Chem. – Eur. J.*, 2013, **19**, 17413–17424; (k) H. Zaher, A. E. Ashley, M. Irwin, A. L. Thompson, M. J. Gutmann, T. Krämer and D. O'Hare, *Chem. Commun.*, 2013, **49**, 9755–9757; (l) M. Pu and T. Privalov, *ChemPhysChem*, 2014, **15**, 2936–2944; (m) M. Pu and T. Privalov, *ChemPhysChem*, 2014, **15**, 3714–3719.
- 28 D. Chen and J. Klankermayer, *Chem. Commun.*, 2008, 2130–2131.
- 29 For further examples of hydrosilylation of carbonyls catalysed by electron-deficient boranes, see: ref. 14; (a) V. Gevorgyan, M. Rubin, J.-X. Liu and Y. Yamamoto, *J. Org. Chem.*, 2001, **66**, 1672–1675; (b) R. Roesler, B. J. N. Har and W. E. Piers, *Organometallics*, 2002, **21**, 4300–4302; (c) N. Asao, T. Ohishi, K. Sato and Y. Yamamoto, *Tetrahedron*, 2002, **58**, 8195–8203; (d) G. B. Bajracharya, T. Nogami, T. Jin, K. Matsuda, V. Gevorgyan and Y. Yamamoto, *Synthesis*, 2004, 308–311; (e) M. K. Skjel, A. Y. Houghton, A. E. Kirby, D. J. Harrison, R. McDonald and L. Rosenberg, *Org. Lett.*, 2010, **12**, 376–379; (f) P. Bach, A. Albright and K. K. Laali, *Eur. J. Org. Chem.*, 2009, 1961–1966; (g) K. Benda, W. Regenhart, E. Schaumann and G. Adiwidjaja, *Eur. J. Org. Chem.*, 2009, 1016–1021; hydrosilylation of acetophenone using a chiral binaphthyl-based borane, but with no enantioinduction: (h) M. Mewald, R. Fröhlich and M. Oestreich, *Chem. – Eur. J.*, 2011, **17**, 9406–9414; hydrosilylation of acetophenone using a $B(C_6F_5)_3$ congener: (i) J. Mohr, M. Durmaz, E. Irran and M. Oestreich, *Organometallics*, 2014, **33**, 1108–1111; for a catalytic hydrosilylation of oxalic acid, see: (j) E. Feghali, O. Jacquet, P. Thuéry and T. Cantat, *Catal. Sci. Technol.*, 2014, **4**, 2230–2234.
- 30 J. Nyhlén and T. Privalov, *Dalton Trans.*, 2009, 5780–5786.
- 31 T. Mahdi and D. W. Stephan, *J. Am. Chem. Soc.*, 2014, **136**, 15809–15812.
- 32 D. J. Scott, M. J. Fuchter and A. E. Ashley, *J. Am. Chem. Soc.*, 2014, **136**, 15813–15816.
- 33 L. J. Hounjet, C. Bannwarth, C. N. Garon, C. B. Caputo, S. Grimme and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2013, **52**, 7492–7495.
- 34 D. J. Harrison, R. McDonald and L. Rosenberg, *Organometallics*, 2005, **24**, 1398–1400.
- 35 P. T. K. Lee, M. K. Skjel and L. Rosenberg, *Organometallics*, 2013, **32**, 1575–1578.
- 36 For further examples of hydrosilylation of imines catalysed by electron-deficient boranes, see: ref. 21; (a) D. Chen, V. Leich, F. Pan and J. Klankermayer, *Chem. – Eur. J.*, 2012, **18**, 5184–5187; hydrosilylation by using a chiral binaphthyl-based borane: ref. 22 and 23; (b) X. Zhu and H. Du, *Org. Biomol. Chem.*, 2015, **13**, 1013–1016; hydrosilylation by using a $B(C_6F_5)_3$ congener: ref. 29i.
- 37 (a) Z. M. Heiden and D. W. Stephan, *Chem. Commun.*, 2011, **47**, 5729–5731 (diastereoselective); for further examples of imine hydrogenations catalysed by electron-deficient boranes, see: (b) C. Jiang, O. Blacque and H. Berke, *Chem. Commun.*, 2009, 5518–5520; (c) D. W. Stephan, S. Greenberg, T. W. Graham, P. Chase, J. J. Hastie, S. J. Geier, J. M. Farrell, C. C. Brown, Z. M. Heiden, G. C. Welch and M. Ullrich, *Inorg. Chem.*, 2011, **50**, 12338–12348; (d) J. W. Thomson, J. A. Hatnean, J. J. Hastie, A. Pasternak, D. W. Stephan and P. A. Chase, *Org. Process Res. Dev.*, 2013, **17**, 1287–1292.
- 38 D. J. Scott, M. J. Fuchter and A. E. Ashley, *Angew. Chem., Int. Ed.*, 2014, **53**, 10218–10222. Hydrogenation of several heteroarenes and alkenes are also included in this work.
- 39 Borane **23** was first prepared by Piers and co-workers: (a) D. J. Parks, W. E. Piers and G. P. A. Yap, *Organometallics*, 1998, **17**, 5492–5503; (b) D. J. Parks, R. E. von H. Spence and W. E. Piers, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 809–811.
- 40 Y. Liu and H. Du, *J. Am. Chem. Soc.*, 2013, **135**, 6810–6813.
- 41 J. M. Farrell, Z. M. Heiden and D. W. Stephan, *Organometallics*, 2011, **30**, 4497–4500.
- 42 I. Chatterjee and M. Oestreich, *Angew. Chem., Int. Ed.*, 2015, **54**, 1965–1968.
- 43 For a similar abstraction of hydrides from Hantzsch esters by $B(C_6F_5)_3$, see: (a) J. D. Webb, V. S. Laberge, S. J. Geier, D. W. Stephan and C. M. Crudden, *Chem. – Eur. J.*, 2010, **16**, 4895–4902; for an abstraction of hydride from an *N*-silyl dihydropyridine by $B(C_6F_5)_3$, see: (b) D. V. Gutsulyak, A. van der Est and G. I. Nikonov, *Angew. Chem., Int. Ed.*, 2011, **50**, 1384–1387.
- 44 J. Mohr and M. Oestreich, *Angew. Chem., Int. Ed.*, 2014, **53**, 13278–13281.



- 45 (a) M. Rubin, T. Schwier and V. Gevorgyan, *J. Org. Chem.*, 2002, **67**, 1936–1940; (b) for hydrostannation of unsaturated hydrocarbons with tributyltin hydride formed *in situ* from tributylchlorostannane and Et_3SiH , see: V. Gevorgyan, J.-X. Liu and Y. Yamamoto, *Chem. Commun.*, 1998, 37–38.
- 46 (a) A. Simonneau and M. Oestreich, *Angew. Chem., Int. Ed.*, 2013, **52**, 11905–11907; for a quantum-chemical treatment, see: (b) K. Sakata and H. Fujimoto, *Organometallics*, 2015, **34**, 236–241; for broad investigation of transfer hydrosilylation, see: (c) S. Keess, A. Simonneau and M. Oestreich, *Organometallics*, DOI: 10.1021/om501284a.
- 47 J. M. Blackwell, D. J. Morrison and W. E. Piers, *Tetrahedron*, 2002, **58**, 8247–8254.
- 48 For the defunctionalisation of enol ethers, see Scheme 24.
- 49 S. Chandrasekhar, G. Chandrashekar, M. S. Reddy and P. Srihari, *Org. Biomol. Chem.*, 2006, **4**, 1650–1652.
- 50 M. Tan and Y. Zhang, *Tetrahedron Lett.*, 2009, **50**, 4912–4915.
- 51 Ref. 8b; (a) V. Sumerin, F. Schulz, M. Atsumi, C. Wang, M. Nieger, M. Leskelä, T. Repo, P. Pykkö and B. Rieger, *J. Am. Chem. Soc.*, 2008, **130**, 14117–14119; (b) G. Erős, H. Mehdi, I. Pápai, T. A. Rokob, P. Király, G. Tárkányi and T. Soós, *Angew. Chem., Int. Ed.*, 2010, **49**, 6559–6563; (c) S. Schwendemann, T. A. Tumay, K. V. Axenov, I. Peuser, G. Kehr, R. Fröhlich and G. Erker, *Organometallics*, 2010, **29**, 1067–1069; (d) S. Schwendemann, R. Fröhlich, G. Kehr and G. Erker, *Chem. Sci.*, 2011, **2**, 1842–1849; (e) G. Erős, K. Nagy, H. Mehdi, I. Pápai, P. Nagy, P. Király, G. Tárkányi and T. Soós, *Chem. – Eur. J.*, 2012, **18**, 574–585; (f) K. Chernichenko, M. Nieger, M. Leskelä and T. Repo, *Dalton Trans.*, 2012, **41**, 9029–9032.
- 52 D. Bézier, S. Park and M. Brookhart, *Org. Lett.*, 2013, **15**, 496–499.
- 53 Partial reductions of carboxylic acids to silyl ethers were already mentioned by Gevorgyan and Yamamoto in ref. 29a.
- 54 V. Gevorgyan, J.-X. Liu, M. Rubin, S. Benson and Y. Yamamoto, *Tetrahedron Lett.*, 1999, **40**, 8919–8922.
- 55 For further examples of ether cleavages, see: (a) V. Gevorgyan, M. Rubin, S. Benson, J.-X. Liu and Y. Yamamoto, *J. Org. Chem.*, 2000, **65**, 6179–6186; (b) J. Heo, T. Kang, S. G. Jang, D. S. Hwang, J. M. Spruell, K. L. Killips, J. H. Waite and C. J. Hawker, *J. Am. Chem. Soc.*, 2012, **134**, 20139–20145; for an example of ether cleavages for formation of polymers, see: ref. 29b; for examples of $\text{B}(\text{C}_6\text{F}_5)_3$ -assisted intrachain ring-opening polymerization, see: (c) I. Perez-Baena, F. Barroso-Bujans, U. Gasser, A. Arbe, A. J. Moreno, J. Colmenero and J. A. Pomposo, *ACS Macro Lett.*, 2013, **2**, 775–779; for examples of $\text{B}(\text{C}_6\text{F}_5)_3$ -catalysed ether cleavages in natural product syntheses, see: (d) D. F. Taber and S. C. Malcolm, *J. Org. Chem.*, 2001, **66**, 944–953; (e) D. F. Taber, Q. Jiang, B. Chen, W. Zhang and C. L. Campbell, *J. Org. Chem.*, 2002, **67**, 4821–4827; (f) J. R. Vyvyan, J. M. Oaksmith, B. W. Parks and E. M. Peterson, *Tetrahedron Lett.*, 2005, **46**, 2457–2460; (g) N. A. McGrath, E. S. Bartlett, S. Sittihan and J. T. Njardarson, *Angew. Chem., Int. Ed.*, 2009, **48**, 8543–8546; for an application in lignin models, see: (h) E. Feghali and T. Cantat, *Chem. Commun.*, 2014, **50**, 862–865.
- 56 R. D. Nimmagadda and C. McRae, *Tetrahedron Lett.*, 2006, **47**, 5755–5758.
- 57 They successfully applied their methodology by the use of *n*-butylhydrosilane ($n\text{BuSiH}_3$) or diethylhydrosilane (**2j**) also to ketones and aldehydes.
- 58 For a reductive dehydroxylation of Baylis–Hillman adducts using PMHS (**2h**) and catalytic $\text{B}(\text{C}_6\text{F}_5)_3$, see: S. Chandrasekhar, G. Chandrashekar, K. Vijeender and M. S. Reddy, *Tetrahedron Lett.*, 2006, **47**, 3475–3478.
- 59 (a) L. L. Adduci, M. P. McLaughlin, T. A. Bender, J. J. Becker and M. R. Gagné, *Angew. Chem., Int. Ed.*, 2014, **53**, 1646–1649; for further examples of deoxygenation processes catalysed by electron-deficient boranes, see: ref. 29a, d and 56; (b) S. Chandrasekhar, C. R. Reddy and B. N. Babu, *J. Org. Chem.*, 2002, **67**, 9080–9082; for a catalytic deoxygenation of oxalic acid, see: ref. 29j.
- 60 For $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed reductive alkylation of alkoxybenzenes using aldehyde as alkylating agents in the presence of PMHS (**2h**), see: S. Chandrasekhar, S. Khatun, G. Rajesh and C. R. Reddy, *Tetrahedron Lett.*, 2009, **50**, 6693–6697.
- 61 For a $\text{B}(\text{C}_6\text{F}_5)_3$ -catalysed reductive coupling of carbonyl compounds with alkoxy-silanes in the presence of PMHS (**2h**), see: S. Chandrasekhar, G. Chandrashekar, B. Nagendra Babu, K. Vijeender and K. Venkatram Reddy, *Tetrahedron Lett.*, 2004, **45**, 5497–5499.
- 62 E. Blondiaux and T. Cantat, *Chem. Commun.*, 2014, **50**, 9349–9352.
- 63 R. C. Chadwick, V. Kardelis, P. Lim and A. Adronov, *J. Org. Chem.*, 2014, **79**, 7728–7733.
- 64 For a further example, see: G. T. Beng, R. Meesala, M. N. Mordi and S. M. Mansor, *Synth. Commun.*, 2014, **44**, 1291–1295.
- 65 L. D. Curless, E. R. Clark, J. J. Dunsford and M. J. Ingleson, *Chem. Commun.*, 2014, **50**, 5270–5272.
- 66 S. J. Geier, P. A. Chase and D. W. Stephan, *Chem. Commun.*, 2010, **46**, 4884–4886.
- 67 G. Erős, K. Nagy, H. Mehdi, I. Pápai, P. Nagy, P. Király, G. Tárkányi and T. Soós, *Chem. – Eur. J.*, 2012, **18**, 574–585.
- 68 N. Gandhamsetty, S. Joung, S.-W. Park, S. Park and S. Chang, *J. Am. Chem. Soc.*, 2014, **136**, 16780–16783.
- 69 J. Hermeke, H. F. T. Klare and M. Oestreich, *Chem. – Eur. J.*, 2014, **20**, 9250–9254.
- 70 Z. Zhang and H. Du, *Angew. Chem., Int. Ed.*, 2015, **54**, 623–626.
- 71 T. Mahdi, Z. M. Heiden, S. Grimme and D. W. Stephan, *J. Am. Chem. Soc.*, 2012, **134**, 4088–4091.
- 72 (a) T. Mahdi, J. N. del Castillo and D. W. Stephan, *Organometallics*, 2013, **32**, 1971–1978; (b) for a similar $\text{B}(\text{C}_6\text{F}_5)_3$ -mediated hydrogenation of carbodiimides, see: M. H. Holthausen, M. Colussi and D. W. Stephan, *Chem. – Eur. J.*, 2015, **21**, 2193–2199.
- 73 Y. Liu and H. Du, *J. Am. Chem. Soc.*, 2013, **135**, 12968–12971.
- 74 D. J. Mack, B. Guo and J. T. Njardarson, *Chem. Commun.*, 2012, **48**, 7844–7846.
- 75 J. Chojnowski, S. Rubinsztajn, J. A. Cella, W. Fortuniak, M. Cypryk, J. Kurjata and K. Kaźmierski, *Organometallics*, 2005, **24**, 6077–6084.



- 76 J. B. Grande, D. B. Thompson, F. Gonzaga and M. A. Brook, *Chem. Commun.*, 2010, **46**, 4988–4990.
- 77 Examples for the synthesis of silicon-based polymers with siloxanes: (a) S. Rubinsztajn and J. A. Cella, *Polym. Prepr.*, 2004, **45**, 635–636; (b) S. Rubinsztajn and J. A. Cella, *Macromolecules*, 2005, **38**, 1061–1063; (c) J. Chojnowski, W. Fortuniak, J. Kurjata, S. Rubinsztajn and J. A. Cella, *Macromolecules*, 2006, **39**, 3802–3807; (d) C. Longuet, C. Joly-Duhamel and F. Ganachaud, *Macromol. Chem. Phys.*, 2007, **208**, 1883–1892; (e) C. Xunjun, C. Yingde, Y. Guoqiang and L. Liewen, *J. Appl. Polym. Sci.*, 2007, **106**, 1007–1013; (f) J. Chojnowski, S. Rubinsztajn, W. Fortuniak and J. Kurjata, *J. Inorg. Organomet. Polym. Mater.*, 2007, **17**, 173–187; (g) D. B. Thompson and M. A. Brook, *J. Am. Chem. Soc.*, 2008, **130**, 32–33; (h) J. Cella and S. Rubinsztajn, *Macromolecules*, 2008, **41**, 6965–6971; (i) J. Chojnowski, S. Rubinsztajn, W. Fortuniak and J. Kurjata, *Macromolecules*, 2008, **41**, 7352–7358; (j) J. Kurjata, W. Fortuniak, S. Rubinsztajn and J. Chojnowski, *Eur. Polym. J.*, 2009, **45**, 3372–3379; (k) J. B. Grande, F. Gonzaga and M. A. Brook, *Dalton Trans.*, 2010, **39**, 9369–9378; (l) D. J. Keddie, J. B. Grande, F. Gonzaga, M. A. Brook and T. R. Dargaville, *Org. Lett.*, 2011, **13**, 6006–6009; (m) B. A. Kamino, J. B. Grande, M. A. Brook and T. P. Bender, *Org. Lett.*, 2011, **13**, 154–157; (n) F. Gonzaga, J. B. Grande and M. A. Brook, *Chem. – Eur. J.*, 2012, **18**, 1536–1541; (o) J. B. Grande, A. S. Fawcett, A. J. McLaughlin, F. Gonzaga, T. P. Bender and M. A. Brook, *Polymer*, 2012, **53**, 3135–3142; (p) M. J. Gretton, B. A. Kamino, M. A. Brook and T. P. Bender, *Macromolecules*, 2012, **45**, 723–728; (q) J. B. Grande, T. Ulrich, T. Dickie and M. A. Brook, *Polym. Chem.*, 2014, **5**, 6728–6739; for hydride transfer ring-opening polymerization of cyclic siloxanes catalysed by $B(C_6F_5)_3$, see: (r) J. Chojnowski, J. Kurjata, W. Fortuniak, S. Rubinsztajn and B. Trzebicka, *Macromolecules*, 2012, **45**, 2654–2661; for the synthesis of triarylamine-siloxanes using the Piers–Rubinsztajn reaction, see: (s) B. A. Kamino, B. Mills, C. Reali, M. J. Gretton, M. A. Brook and T. P. Bender, *J. Org. Chem.*, 2012, **77**, 1663–1674; (t) M. J. Gretton, B. A. Kamino and T. P. Bender, *Macromol. Symp.*, 2013, **324**, 82–94; for a polymerisation of phenylsilane catalysed by $B(C_6F_5)_3$ to form branched polysilanes, see: (u) A. Feigl, I. Chiorescu, K. Deller, S. U. H. Heidsieck, M. R. Buchner, V. Karttunen, A. Bockholt, A. Genest, N. Rösch and B. Rieger, *Chem. – Eur. J.*, 2013, **19**, 12526–12536; for an overview, see: (v) M. A. Brook, J. B. Grande and F. Ganachaud, in *Adv. Polym. Sci.*, ed. A. M. Muzafarov, Springer, Berlin, Heidelberg, 2011, vol. 235, pp. 161–183.
- 78 J.-M. Denis, H. Forintos, H. Szelke and G. Keglevich, *Tetrahedron Lett.*, 2002, **43**, 5569–5571.
- 79 C. B. Caputo and D. W. Stephan, *Organometallics*, 2012, **31**, 27–30.
- 80 For further examples of dehydrogenative silylation of alcohols, see: ref. 4, 14, 29a, h–j, 54, 55a, b and 56; (a) D. J. Harrison, D. R. Edwards, R. McDonald and L. Rosenberg, *Dalton Trans.*, 2008, 3401–3411; (b) T. Strašák, J. Sýkora, M. Lamač, J. Kubišta, M. Horáček, R. Gyepes and J. Pinkas, *Organometallics*, 2013, **32**, 4122–4129; (c) A. Simonneau, J. Friebe and M. Oestreich, *Eur. J. Org. Chem.*, 2014, 2077–2083.
- 81 R. Shchepin, C. Xu and P. Dussault, *Org. Lett.*, 2010, **12**, 4772–4775.
- 82 Examples for dehydrogenative silylation of alcohols for the synthesis of polymers: (a) D. Zhou and Y. Kawakami, *Macromolecules*, 2005, **38**, 6902–6908; (b) Z. Zhang, L. J. Lyons, J. J. Jin, K. Amine and R. West, *Chem. Mater.*, 2005, **17**, 5646–5650; (c) L. Xue and Y. Kawakami, *Polym. J.*, 2007, **39**, 379–388; (d) M. A. Hoque, Y. Kakihana, S. Shinke and Y. Kawakami, *Macromolecules*, 2009, **42**, 3309–3315; (e) Z. Zhang, J. Dong, R. West and K. Amine, *J. Power Sources*, 2010, **195**, 6062–6068; (f) N. Moitra, S. Ichii, T. Kamei, K. Kanamori, Y. Zhu, K. Takeda, K. Nakanishi and T. Shimada, *J. Am. Chem. Soc.*, 2014, **136**, 11570–11573.
- 83 L. D. Curless and M. J. Ingleson, *Organometallics*, 2014, **33**, 7241–7246.
- 84 For *trans*-selective hydrosilylations of alkynes using phosphonium salts, see: (a) M. Pérez, L. J. Hounjet, C. B. Caputo, R. Dobrovetsky and D. W. Stephan, *J. Am. Chem. Soc.*, 2013, **135**, 18308–18310; (b) M. H. Holthausen, M. Mehta and D. W. Stephan, *Angew. Chem., Int. Ed.*, 2014, **53**, 6538–6541.

