Metal-Free Reduction of Phosphine Oxides, Sulfoxides, and *N*-Oxides with Hydrosilanes using a Borinic Acid Precatalyst

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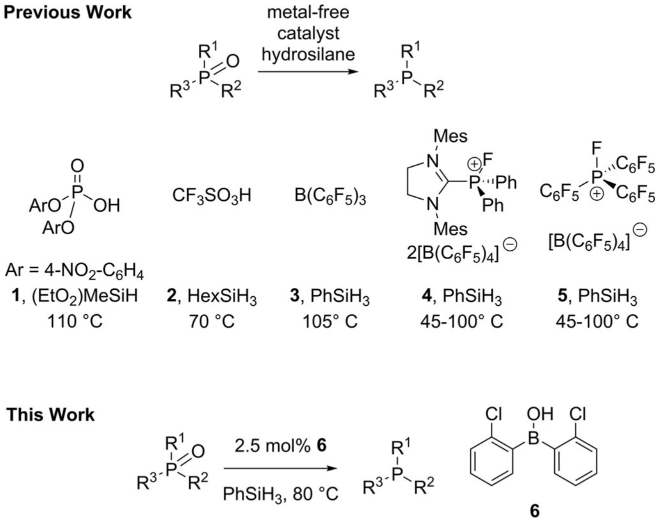
The general reduction of phosphine oxides, sulfoxides, and amine *N*-oxides was achieved by combining bis(2-chlorophenyl)borinic acid with phenylsilane. The reaction was shown to tolerate a wide range of substrates and could be performed under mild conditions, with only 2.5 mol% of the easily synthesized catalyst. Mechanistic investigations pointed to a key borohydride as the real catalyst and at bis(2-chlorophenyl)borinic acid as a precatalyst.

Phosphines have a central role in life science and in the chemical industries.[1] Besides their involvement in classical chemical transformations (e.g., Rauhut–Currier, Morita–Baylis–Hillman, Mitsunobu, Appel, and Wittig reactions[2]) and more recent synthetic applications,[3] they are an important class of transition-metal ligands that facilitate the development of useful arylation reactions. Since the pioneering work of Kagan in the development of *O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (DIOP) as a chiral diphosphine in 1971,[4a] the configurational stability of chiral phosphines has enabled their use in many enantioselective processes as ligands[4] and catalysts.[5]

Numerous methods for the synthesis of phosphines have been reported, including nucleophilic and electrophilic substitutions with phosphine derivatives, hydrophosphination, and Ullmann C–P coupling.[6] Still, the reduction of phosphine oxides remains the most straightforward way to synthesize phosphines.[7] However, mild reduction of the highly stable phosphorus–oxygen bond is much more challenging than the reduction of carbonyl compounds.

Most known reductions of phosphine oxides require an excess amount of air-sensitive or expensive boron, alumino hydrides, or chlorosilanes reagents such as $LiAlH_4$, diisobutylaluminum hydride (DIBAL-H), BH_3–SMe_2, and $HSiCl_3$.[8] In sharp contrast, hydrosilane derivatives are considerably more-stable and less-toxic reductants that usually require activation of the silicon–hydrogen bond by a nucleophile or a Lewis acid or Brønsted acid catalyst to promote the reduction at moderate temperatures. Lawrence introduced titanium(IV) catalysis[9] in combination with $(EtO)_3SiH$, whereas other catalysts based on copper, indium, and iron have also been occasionally reported.[10] More recently, Beller introduced phosphoric acid **1** as an efficient catalyst with significant chemoselectivity in the presence of ketones and aldehydes.[11a] Later, Werner reported the use of triflic acid (**2**) (Scheme 1).[11b] In 2016, Oestreich and Stephan jointly disclosed the use of $B(C_6F_5)_3$ and fluorophosphonium cations as efficient catalysts for the reduction of a range of phosphine oxides in the presence of phenylsilane[12] (Scheme 1).[13] Interestingly, the electrophilic cations allowed the use of a lower temperature than that required for $B(C_6F_5)_3$; and furthermore, a higher functional-group tolerance was achieved



Scheme 1. Catalytic metal-free reduction of phosphine oxides by using hydrosilanes.

This background associated with the important development of phosphine-catalyzed transformations relying on in situ reductive regeneration of the phosphine[14] appeared as an attractive basis for investigating alternative reductions conditions. In the context of our program devoted to developing general metal-free catalysts for challenging chemical transformations, we introduced bis(2-chlorophenyl)borinic acid (**6**) for difficult-to-achieve dipeptide-catalyzed synthesis, mild transamination reactions, and amide reductions.[15] Herein, we report a general and efficient method for the reduction of phosphine oxides, sulfoxides, and *N*-oxides under mild conditions with a low loading of **6**.

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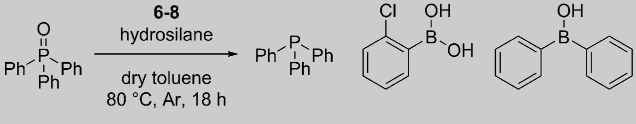
Triphenylphosphine oxide was selected as a model substrate to optimize the reaction conditions. First, a control experiment in the absence of **6** revealed no background reaction (Table 1, entry 1). 2-Chlorophenylboronic acid (**7**) as a catalyst was found to be inefficient, which is in line with similar observations made by Beller (Table 1, entry 2).[16] With simple diphenylborinic acid (**8**), the same inefficiency was observed (Table 1, entry 3). Remarkably, the use of **6** (5 mol %) led to total conversion at 80 °C after 18 h, whereas a lower temperature of 45 °C significantly slowed down the reaction (Table 1, entry 5). Decreasing the loading of **6** to 2.5 mol % did not alter the outcome of the reaction, and the product was isolated in 94 % yield (Table 1, entry 6).

Table 1. Initial screening of experimental conditions.



9a **10b** **7** **8**

Entry	Catalyst (mol %)	Hydrosilane (equiv.)	Yield[a] [%]
1	–	$PhSiH_3$ (2.4)	(0)
2	**7** (2.5)	$PhSiH_3$ (2.4)	(20)
3	**8** (2.5)	$PhSiH_3$ (2.4)	(24)
4	**6** (5)	$PhSiH_3$ (2.4)	95 (> 99)
5	**6** (2.5)	$PhSiH_3$ (2.4)	(18)[b]
6	**6** (2.5)	$PhSiH_3$ (2.4)	94 (> 99)
7	**6** (2.5)	$PhSiH_3$ (1.2)	(19)
8	**6** (5)	Et_3SiH (7)	(0)
9	**6** (5)	TMDS (3.5)	(0)
10	**6** (5)	$PhMe_2SiH$ (7)	(0)
11	**6** (5)	$Me(CH_2)_5SiH_3$	(61)
12	**6** (5)	$Me(CH_2)_{17}SiH_3$	(63)

[a] Yield of isolated product; conversion [%], as determined by ^{31}P NMR spectroscopy, is given in parentheses. [b] At 45 °C.

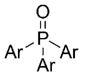
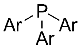
Interestingly, the reactivity was connected to the nature of the hydrosilane. A screening of other hydrosilanes such as tetramethyldisiloxane (TMDS), triethylsilane, and dimethylphenylsilane led to no detectable conversion (Table 1, entries 8–10), which thus pointed to a steric factor around the silicon atom. The electronic properties of the silane were further investigated: the use of alkyl primary hydrosilanes as reducing agents resulted in slower reactions (Table 1, entries 11 and 12), which suggested that the electrophilicity of the silicon atom was another relevant parameter. Finally, a loading of 2.5 mol % of borinic acid **6** with 2.4 equivalents of $PhSiH_3$ in toluene at 80 °C was retained as the optimal conditions (Table 1, entry 2).

Next, we investigated the scope of the reaction. Independent of the position of the methyl or methoxy group on the aromatic ring, yields in the range of 74 to 91 % were obtained with phosphine oxides **9 b**–d (Table 2). In the presence of electron-withdrawing substituents such as trifluoromethyl groups, the reaction afforded **10 e** with a decreased 65 % yield (Table 2). Increasing the steric hindrance by adding a naphthyl substituent led to a moderate 54 % yield from phosphine oxide **9 f** (Table 2), and exchange of a phenyl group with an allyl moiety gave 85 % conversion (determined by ^{31}P NMR spectroscopy). Electron-rich tricyclohexylphosphine (**10 h**) was also isolated successfully in 78 % yield. Our methodology was next applied to the reduction of diphosphine oxides, which are known to be more difficult substrates owing to the possible formation of complex mixtures of di- and monophosphines.[13] Nevertheless, under our conditions Xantphos (**10 i**) and ferrocene bis(diphenylphosphine) (**10 j**) were efficiently delivered in 71–89 % yield, and the formation of the monophosphine was not detected (Table 2). The bis-oxide of 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) required an extended reaction time to give **10 k** in an acceptable 61 % yield without detectable racemization (Table 2, see the Supporting Information for the related HPLC data).

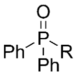
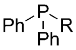
Having in hand a robust protocol for the reduction of tertiary phosphine oxides, we directed our efforts toward the reduction of secondary phosphine oxides (Table 3), a class of under-investigated substrates.[9b,17] The best result was observed with the trifluoromethyl-substituted phosphine oxide, which led to **10 l** with 81 % conversion, as determined by ^{31}P NMR spectroscopy, whereas phenyl and electron-rich aryl rings bearing a methoxy or *tert*-butyl group gave decreased conversions of 50–65 %.

Having covered the reduction of phosphine oxides by using bis(2-chlorophenyl)borinic acid (**6**), we turned our attention to the reductive cleavage of the other oxygen–heteroatom bonds present in sulfoxides and amine *N*-oxides.

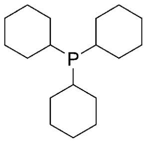
Table 2. Borinic acid catalyzed reduction of tertiary phosphine oxides.[a]

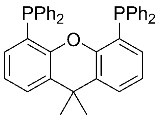



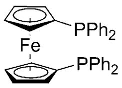
9	Ar	10	Yield[b] [%]
9 a	Ph	**10 a**	95
9 d	4-$MeOC_6H_4$	**10 d**	82
9 f	2-naphthyl	**10 f**	54

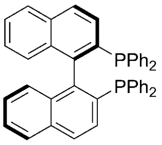



9	R	10	Yield [%]
9 b	4-MeC_6H_4	**10 b**	74
9 c	3-$MeOC_6H_4$	**10 c**	91
9 e	3,5-$(F_3C)_2C_6H_3$	**10 e**	65
9 g	allyl	**10 g**	(85)[c]


10h, (78)%[c]

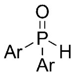
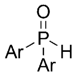

10i, 89%


10j, 71%


10k, 61%[d]

[a] Reaction conditions: phosphine, **6** (2.5 mol %), $PhSiH_3$ (2.4 equiv.), dry toluene, under an argon atmosphere, 80 °C, 18 h. [b] Yield of isolated product; conversion [%], as determined by ^{31}P NMR spectroscopy, is given in parentheses. [c] Reaction time: 36 h. [d] Reaction time: 24 h.

Table 3. Borinic acid catalyzed reduction of secondary phosphine oxides.[a]

9	Ar	10	Conv.[b] [%]
9 l	4-$F_3CC_6H_4$	**10 l**	81
9 m	Ph	**10 m**	53
9 n	4-*t*BuC_6H_4	**10 n**	65
9 o	4-MeOC_6H_4	**10 o**	50

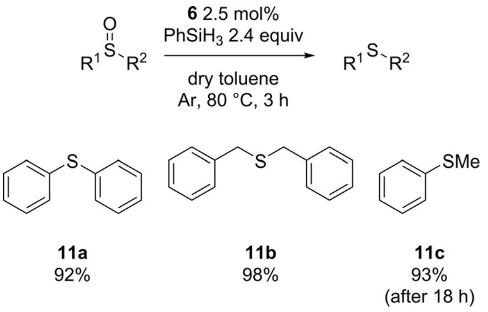
[a] Reaction conditions: phosphine, **6** (2.5 mol%), $PhSiH_3$ (2.4 equiv.), dry toluene, under an argon atmosphere, 80 °C, 18 h. [b] Conversions were determined by ^{31}P NMR spectroscopy.

Owing to their useful reactivity, amines *N*-oxides and sulfoxides are frequently encountered in synthetic organic chemistry,[18] and their use is usually related to efficient deoxygenation methods to obtain amines and sulfides.

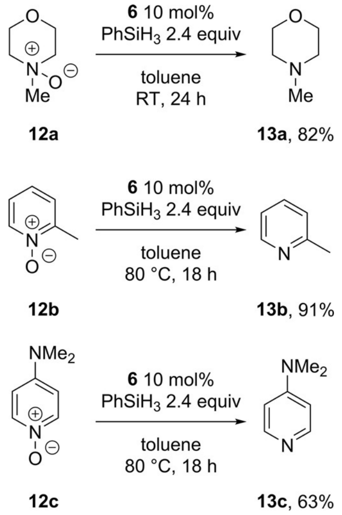
The reduction of sulfoxides and amine *N*-oxides is well known if methods involving the use of a stoichiometric amount of the reducing species are considered.[19] However, very few methods rely on the use of a catalyst to promote the mild deoxygenation of sulfoxides and amine *N*-oxides, as illustrated by the scarcity of metal-based procedures.[20] Moreover, only a few methods involving hydrosilanes have been reported to date.[21] Accordingly, a mild and catalytic method involving hydrosilanes was envisaged to be of high utility.

The scope of the reduction of sulfoxides was explored with the previously developed reaction conditions after a control experiment, which showed no conversion in the absence of borinic acid **6**. Rapid reduction at 80 °C was observed, which gave sulfides **11 a** and **11 b** in yields of 92 and 98 %, respectively (Scheme 2). In contrast, methyl(phenyl)sulfide (**11 c**) was obtained in 93 % yield after a longer reaction time of 18 h (Scheme 2).

Our reactions conditions were easily extended to the reduction of *N*-oxides. Then, the *N*-oxide derived from a tertiary alkylamine was markedly easier to reduce than pyridinium *N*-oxides. After controlling the absence of reactivity without borinic acid **6**, corresponding *N*-methylmorpholine (**13 a**) was obtained in 82 % yield at room temperature, whereas 2-methylpyridine (**13 b**) and 4-(dimethylamino)pyridine (DMAP, **13 c**) were obtained in yields of 91 and 63 %, respectively, at 80 °C (Scheme 3).



Scheme 2. Borinic acid catalyzed reduction of sulfoxides.



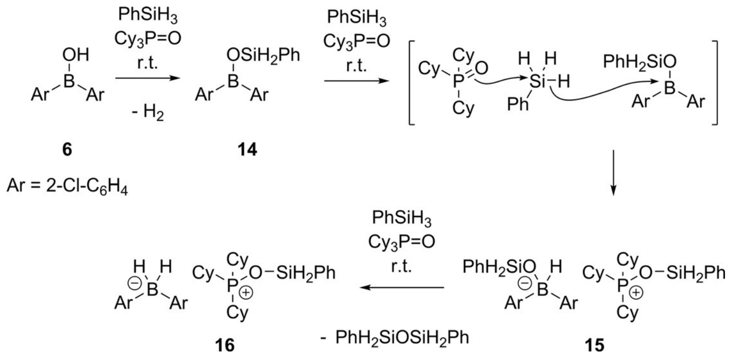
Scheme 3. Borinic acid catalyzed reduction of *N*-oxides.

First, the potential involvement of the Brønsted acidity of **6** was ruled out by a control experiment involving the use of 2,6-di-*tert*-butylpyridine (5 mol%) as a proton scavenger, which afforded 97 % conversion after 96 h.

As a consequence, the Lewis acid–base interactions between borinic acid **6** and various phosphine oxides were investigated: equimolar quantities of **6** and Ph_3PO or Cy_3PO (Cy = cyclohexyl) were mixed in deuterated toluene and heated at 80 °C for several hours, but careful analysis by ^{31}P NMR spectroscopy did not reveal any new signals, whereas analysis by ^{11}B NMR spectroscopy revealed minor protodeborylation leading to boronic acid **7**.[22]

Upon adding phenylsilane at room temperature, significant evolution of hydrogen was observed over 10 min. Whereas Ph_3PO gave puzzling NMR spectroscopy data, Cy_3PO delivered a clearer picture: a new ^{31}P singlet at $\delta = 69.8$ ppm (in [D$_8$]toluene) and complete conversion of the starting oxide ($\delta = 45$ ppm) were observed.[23] Additionally, the ^{11}B NMR spectrum of the mixture displayed complete conversion of borinic acid **6** associated with a new characteristic triplet at $\delta - 16.4$ ppm ($^1J = 85.0$ Hz), which matched previously characterized borohydride **16**.[15c] These observations likely suggest an ionic mechanism that involves fast dehydrogenative coupling between **6** and $PhSiH_3$ with the assistance of Cy_3PO to yield elusive boronate **14**, which very rapidly abstracts an additional hydride to observed borohydride **16** (Scheme 4). The nature of the phosphonium countercation was indicated by a significant upfield shift in the ^{31}P signal matching the structurally similar phosphonium ion and the existence of an indicative $^2J_{P,Si}$ coupling constant of 29 Hz.[22]

Upon aging the mixture at room temperature for 48 h, a new ^{31}P NMR signal characteristic of phosphine–borane complex **17**[23] [$\delta(^{31}P) = 15.4$ ppm, $\delta(^{11}B) = -28.8$ ppm, $^1J_{P,B} = 65$ Hz, $^2J_{H,P} = 18$ Hz] appeared very slowly.[24] After warming the mixture at 80 °C for 2.5 h, the conversion smoothly increased to 50 %. In the ^{11}B NMR spectrum, a second minor signal appeared {$\delta(^{11}B) = -42.9$ ppm, HSQC [^1H,^{11}B] correlation} and was tentatively attributed to intermediate borohydride **18**.[21] Final-

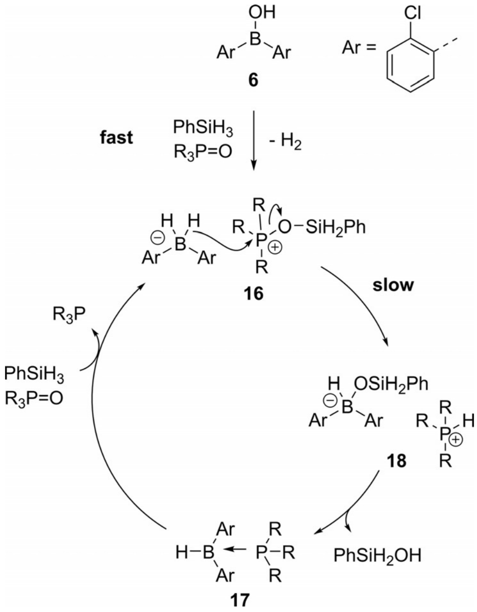


Scheme 4. Early stage of the reaction at room temperature.

ly, warming at 80 °C for 16 h led to the complete conversion of borohydride **16** to yield phosphine–borane **17** in equilibrium with free tricyclohexylphosphine (**10 h**) (Scheme 5).[22] Hence, those observations attribute to bis(2-chlorophenyl)borinic acid (**6**) the role of a precatalyst.

According to these observations, the following mechanism is proposed.[12c] After a dehydrogenative step and hydride abstraction from phenylsilane with the nucleophilic assistance of the phosphine oxide (or corresponding phosphine after one turnover), borinic acid **6** is converted rapidly into borohydride **16**. Then, a slow intramolecular hydride shift leads to phosphine–borane complex **17**, which upon interaction with an excess amount of phenylsilane delivers the free phosphine and regenerates borohydride **16**.

In summary we developed an efficient procedure relying on easy-to-synthesize and bench-stable bis(2-chlorophenyl)borinic acid (**6**) for the metal-free reduction of phosphine oxides; this method nicely complements the Brønsted acid catalyzed methods previously reported by Beller and Werner. The corresponding phosphines were obtained in good yields by using a low catalyst loading (2.5 mol%). Furthermore, our reaction conditions were easily extended to the reduction of representative sulfoxides and amine *N*-oxides.[25] Careful monitoring of the reaction by NMR spectroscopy revealed a borohydride as the key reducing species, and thus, **6** has to be considered a precatalyst.



Scheme 5. Mechanism of the reduction.

Experimental Section

General procedure for the reduction of phosphine oxides

Under an argon atmosphere, a dry tube was charged with borinic acid **6** (3.1 mg, 0.0125 mmol, 0.025 equiv.) followed by triphenylphosphine oxide (**9 a**; 139 mg, 0.5 mmol). The tube was flushed with argon (3×) and capped with a rubber septum; then, phenylsilane (0.150 mL, 1.2 mmol, 2.4 equiv.) was added, followed by previously degassed dry toluene (1 mL). The resulting mixture was stirred at 80 °C for 18 h. The crude mixture was concentrated under reduced pressure, and the residue was purified by flash column chromatography (cyclohexane/EtOAc) to yield corresponding phosphine **10 a**.

Acknowledgements

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Keywords: boron · hydrosilanes · oxides · reaction mechanisms · reduction

[1] a) L. D. Quin in *A Guide to Organophosphorus Chemistry*, Wiley, New York, **2000**.
[2] a) J. J. Li in *Name Reactions, 5th ed.*, Springer, **2014**. For related reviews see b) S. Fletcher, *Org. Chem. Front.* **2015**, *2*, 739–752; c) V. S. C. de Andrade, M. C. S. de Mattos, *Curr. Org. Synth.* **2015**, *12*, 309–327; d) B. E. Maryanoff, A. B. Reitz, *Chem. Rev.* **1989**, *89*, 863–927; e) M. Shi, F. Wang, M.-X. Zhao, Y. Wei in *The Chemistry of the Morita-Baylis–Hillman Reaction*, **2011**, RSC Catalysis Series.
[3] Phosphine catalysis of allenes with electrophiles: Z. Wang, X. Xu, O. Kwon, *Chem. Soc. Rev.* **2014**, *43*, 2927–2940.
[4] a) T. P. Dang, H. B. Kagan, *Chem. Commun.* **1971**, 481; b) T. Kégl, L. Kollár in *Comprehensive Inorganic Chemistry II, 2nd ed.* (Eds.: J. Reedijk, K. Poeppelmeier), Elsevier, Amsterdam, **2013**, pp. 271–308; c) L.-W. Ye, J. Zhou, Y. Tang, *Chem. Soc. Rev.* **2008**, *37*, 1140–1152.
[5] a) Y. Wei, M. Shi, *Chem. Asian J.* **2014**, *9*, 2720–2734; b) Y. Xiao, Z. Sun, H. Guo, O. Kwon, *Beilstein J. Org. Chem.* **2014**, *10*, 2089–2121.
[6] For a general review covering phosphines synthesis through C-P bond formation see: a) I. Wauters, W. Debrouwer, C. V. Stevens, *Beilstein J. Org. Chem.* **2014**, *10*, 1064–1093. For a review about hydrophosphination see: b) A. C. Gaumont, M. Gulea in *Science of Synthesis Houben-Weyl: Methods of Molecular Transformations*, Thieme, Stuttgart, **2007**, *33*, 711–725.
[7] For recent reviews see: a) T. Kovacs, G. Keglevich, *Curr. Org. Chem.* **2017**, *21*, 569–585; b) D. Hérault, D. H. Nguyen, D. Nuel, G. Buono, *Chem. Soc. Rev.* **2015**, *44*, 2508–2528.
[8] a) P. D. Henson, K. Naumann, K. Mislow, *J. Am. Chem. Soc.* **1969**, *91*, 5645–5646; b) T. Imamoto, T. Oshiki, T. Onozawa, T. Kusumoto, K. Sato, *J. Am. Chem. Soc.* **1990**, *112*, 5244–5252; c) S. Kobayashi, M. Suzuki, T.

Saegusa, *Polym. Bull.* **1982**, *8*, 417–420; d) C. A. Busacca, R. Raju, N. Grinberg, N. Haddad, P. James-Jones, H. Lee, J. C. Lorenz, A. Saha, C. H. Senanayake, *J. Org. Chem.* **2008**, *73*, 1524; e) For a BH_3 reduction of specifically hydroxyalkyl substituted tertiary phosphine oxides see: S. Sowa, M. Stankevič, A. Szmigielska, H. Małuszyńska, A. E. Kozioł, K. M. Pietrusiewicz, *J. Org. Chem.* **2015**, *80*, 1672–1688; f) H. Kawakubo, M. Kuroboshi, T. Yano, K. Kobayashi, S. Kamenoue, T. Akagi, H. Tanaka, *Synthesis* **2011**, 4091–4098; g) H.-C. Wu, J.-Q. Yu, J. B. Spencer, *Org. Lett.* **2004**, *6*, 4675–4678.

[9] a) T. Coumbe, N. J. Lawrence, F. Muhammad, *Tetrahedron Lett.* **1994**, *35*, 625–628. See also with TMDS as hydride b) M. Berthod, A. Favre-Réguillon, J. Mohamad, G. Mignani, G. Docherty, M. Lemaire, *Synlett* **2007**, 1545–1548.

[10] a) Y. Li, S. Das, S. Zhou, K. Junge, M. Beller, *J. Am. Chem. Soc.* **2012**, *134*, 9727–9732; b) C. Petit, E. Poli, A. Favre-Réguillon, L. Khrouz, S. Denis-Quanquin, L. Bonneviot, G. Mignani, M. Lemaire, *ACS Catal.* **2013**, *3*, 1431–1438; c) L. Pehlivan, E. Métay, D. Delbrayelle, G. Mignani, M. Lemaire, *Tetrahedron* **2012**, *68*, 3151–3155; d) S. Rommel, C. Belger, J.-M. Begouin, B. Plietker, *ChemCatChem* **2015**, *7*, 1292–1301.

[11] a) Y. Li, L.-Q. Lu, S. Das, S. Pisiewicz, K. Junge, M. Beller, *J. Am. Chem. Soc.* **2012**, *134*, 18325–18329. For the use of TfOH see: b) M.-L. Schirmer, S. Jopp, J. Holz, A. Spannenberg, T. Werner, *Adv. Synth. Catal.* **2016**, *358*, 26–29. See also c) K. Fourmy, A. Voituriez, *Org. Lett.* **2015**, *17*, 1537–1540. For a specific reduction at room temperature in the context of catalyzed Wittig olefination see : d) C. J. O'Brien, F. Lavigne, E. E. Coyle, A. J. Holohan, B. J. Doonan, *Chem. Eur. J.* **2013**, *19*, 5854–5858.

[12] Phenylsilane reduction of phosphine oxides with complete stereospecificity was shown earlier at high temperature. a) H. Fritzsche, U. Hasserodt, F. Korte, *Chem. Ber.* **1964**, *97*, 1988–1993. Lower temperatures are reported for dialkylaryl or trialkylphosphines b) K. L. Marsi, *J. Org. Chem.* **1974**, *39*, 265–267. See also c) O. M. Demchuk, R. Jasiński, K. M. Pietrusiewicz, *Heteroat. Chem.* **2015**, *26*, 441–448.

[13] M. Mehta, I. G. de la Arada, M. Perez, D. Porwal, M. Oestreich, D. W. Stephan, *Organometallics* **2016**, *35*, 1030–1035.

[14] a) A. Voituriez, N. Saleh, *Tetrahedron Lett.* **2016**, *57*, 4443–4451; b) Z. Lao, P. H. Toy, *Beilstein J. Org. Chem.* **2016**, *12*, 2577–2587.

[15] a) T. Mohy El Dine, J. Rouden, J. Blanchet, *Chem. Commun.* **2015**, *51*, 16084–16087; b) A. Chardon, T. Mohy El Dine, R. Legay, M. De Paolis, J. Rouden, J. Blanchet, *Chem. Eur. J.* **2017**, *23*, 2005–2009.

[16] In reference 11 a, M. Beller observed similar trend with benzene boronic acid.

[17] a) C. Petit, A. Favre-Réguillon, G. Mignani, M. Lemaire, *Green Chem.* **2010**, *12*, 326–330; b) C. A. Busacca, J. C. Lorenz, N. Grinberg, N. Haddad, M. Hrapchak, B. Latli, H. Lee, P. Sabila, A. Saha, M. Sarvestani, S. Shen, R. Varsolona, X. Wei, C. H. Senanayake, *Org. Lett.* **2005**, *7*, 4277–4280; c) J.-F. Pilard, G. Baba, A.-C. Gaumont, J.-M. Denis, *Synlett* **1995**, 1168–1170.

[18] For reviews see a) H. Pellissier, *Tetrahedron* **2006**, *62*, 5559–5601; b) S. Youssif, *ARKIVOC* **2001**, 242–268. Also see c) L.-C. Campeau, S. Rousseaux, K. Fagnou, *J. Am. Chem. Soc.* **2005**, *127*, 18020–18021; d) E. Nicolás, M. Vilaseca, E. Gilralt, *Tetrahedron* **1995**, *51*, 5701–5710.

[19] For reviews on deoxygenation of sulfoxides see a) M. Madesclaire, *Tetrahedron* **1988**, *44*, 6537–6580; b) H. Firouzabadi, A. Jamalian, *J. Sulfur Chem.* **2008**, *29*, 53–97. For selected method see c) Y. Jang, K. T. Kim, H. B. Jeon, *J. Org. Chem.* **2013**, *78*, 6328–6331; d) R. Ma, A.-H. Liu, C.-B. Huang, X.-D. Li, L.-N. He, *Green Chem.* **2013**, *15*, 1274–1279. And references cited therein. For reviews on deoxygenation of *N*-oxides see reference 17 b. See also e) H. P. Kokatla, P. F. Thomson, S. Bae, V. R. Doddi, M. K. Lakshman, *J. Org. Chem.* **2011**, *76*, 7842–7848; f) A. T. Londregan, D. W. Piotrowski, J. Xiao, *Synlett* **2013**, *24*, 2695–2700.

[20] a) R. Sanz, J. Escribano, R. Aguado, M. R. Pedrosa, F. J. Arnáiz, *Synthesis* **2004**, 1629–1632; b) R. Balicki, *Synthesis* **1989**, 645–646; c) M. Abbasi, M. R. Mohammadizadeh, Z. Moradi, *Bull. Chem. Soc. Jpn.* **2016**, *89*, 405–407; d) M. Abbasi, M. R. Mohammadizadeh, Z. Moradi, *Tetrahedron Lett.* **2015**, *56*, 6610–6613; e) J. Jeong, D. Lee, S. Chang, *Chem. Commun.* **2015**, *51*, 7035; f) S. Enthaler, *Catal. Lett.* **2012**, *142*, 1306–1311.

[21] a) S. Donck, E. Gravel, N. Shah, D. V. Jawale, E. Doris, I. N. N. Namboothiri, *RSC Adv.* **2015**, *5*, 50865–50868; b) A. C. Fernandes, C. C. Romao, *Tetrahedron* **2006**, *62*, 9650–9654.

[22] See supporting information.

[23] $[Et_3SiO\text{-}P(Et)_3]^+$ was previously reported : δ^{31}P 88.6 ppm, $^2J_{\mathrm{Si,\ P}} = 20$ Hz. However, in our case ^{29}Si NMR data were not recorded successfully. See H. Großekappenberg, M. Reißmann, M. Schmidtmann, T. Müller, *Organometallics* **2015**, *34*, 4952–4958.

[24] $[H_3B\text{-}{>}P(Et)_3]$ was previously reported : δ^{31}P 21.0 ppm, $^1J_{\mathrm{P,B}} = 64.4$ Hz. No $^2J_{\mathrm{P,H}}$ is reported with $BH_{3.}$ See reference 11 b.

[25] During the edition of this manuscript, a method appeared based on $B(C_6F_5)_3$. See: F. Ding, Y. Jiang, S. Gan, R. L.-Y. Bao, K. Lin, L. Shi, *Eur. J. Org. Chem.* **2017**, 3427–3440.

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