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Chapter 5

Brønsted Acid Promoted Reduction of Tertiary Phosphine Oxides

Abstract: Recently, Brønsted acids, such as phosphoric acids, carboxylic acids and triflic acid, were found to catalyze the reduction of phosphine oxides to the corresponding phosphines. In this study, we fully characterize the HCl, HOTf and Me₂SiHOTf adducts of triphenylphosphine oxide and find that the thermally stable adduct Ph₃POH⁺OTf⁻ is efficiently converted into triphenylphosphine at 100 °C in the presence of readily available hydrosiloxanes. Under the same reaction conditions, also Ph₃POSiMe₂H⁺OTf⁻ selectively affords triphenylphosphine indicating that silylated phosphine oxides are likely intermediates in this process.

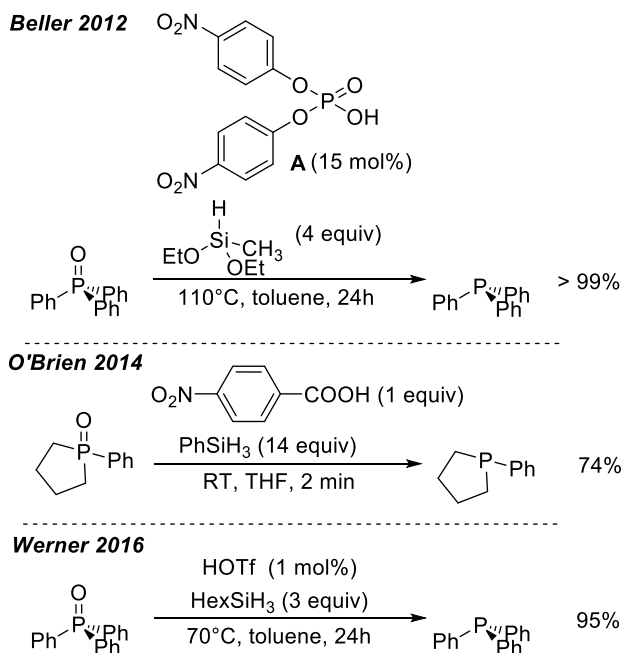
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5.1 Introduction

Phosphines and their derivatives have widespread application in organic synthesis. For example, triphenylphosphine (TPP), one of the most important organophosphorus compounds, is used in the industrial synthesis of vitamin A, carotenoids and many other alkenes via Wittig olefination.^[1] The by-product in these processes is triphenylphosphine oxide (TPPO), which is yearly produced in thousands of tons and has almost no industrial application.^[2] Currently, most of the TPPO is waste, and therefore the development of cheap and scalable methods for its recycling into TPP is of particular importance.^[3] The most widely employed reductants for the reduction of TPPO^[4] are hydrosilanes, chlorosilanes,^[5] aluminium hydrides,^[6] dialkylalanes,^[7] and boranes.^[8] Typically, these procedures are not functional group tolerant, require harsh reaction conditions and/or long reaction times, and utilize highly reactive reagents. Recently, catalytic procedures for phosphine oxide reduction have been developed that operate under considerably milder conditions due to the use of Lewis acids, such as $\text{Ti}(\text{O}i\text{Pr})_4$,^[9] InBr_3 ,^[10] $\text{Cu}(\text{OTf})_2$,^[11] Fe–H complexes,^[3h] $\text{B}(\text{C}_6\text{F}_5)_3$ and fluorophosphonium cations.^[12] Brønsted acids also catalyze this process. For example, Beller and co-workers have demonstrated that bis(4-nitrophenyl)phosphoric acid **A** catalyzes the chemoselective reduction of phosphine oxides to the corresponding phosphines by utilizing inexpensive hydrosilanes as the reductant (e.g., PMHS, $(\text{EtO})_2\text{MeSiH}$; Scheme 1).^[13] Subsequently, O'Brien *et al.* used simple carboxylic acids for the reduction of cyclic phosphine oxides at room temperature (Scheme 1), which was applied as key step in the catalytic Wittig reaction.^{[3c],[14]} Screening of different Brønsted acid additives by Werner and co-workers revealed that the $\text{p}K_{\text{a}}$ value has a significant impact on the reduction of the phosphine oxide to the corresponding phosphine.^[3j] Namely, weakly acidic benzoic acid derivatives led to low yields of TPP, while 1 mol% of the strong trifluoromethanesulfonic acid (HOTf) and phenyl- or hexylsilane afforded TPP in high yields (Scheme 1).^[15]

We envisioned that employment of a strong Brønsted acid will decrease the strength of the P=O bond by initial protonation, thereby facilitating the subsequent

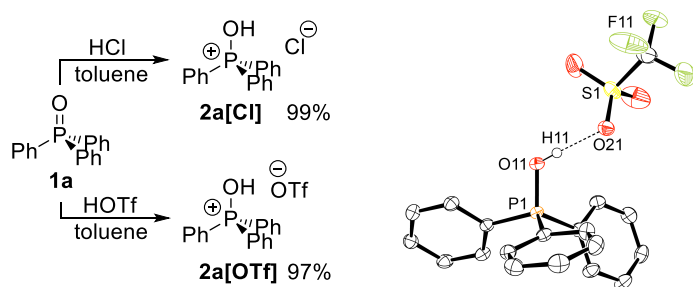
reduction. Herein, we report on the stoichiometric protonation of triphenylphosphine oxide with the commonly used hydrochloric and trifluoromethanesulfonic acid and fully characterize the formed products. Subsequently, we investigate the reduction of the protonated phosphine oxides with the readily available 1,1,3,3-tetramethyldisiloxane (TMDS) and polymethylhydrosiloxane (PMHS) and investigate the scope of this reaction.



Scheme 1. Examples of reduction of phosphine oxides promoted by Brønsted acids.

5.2. Results and Discussion

Treatment of triphenylphosphine oxide (**1a**) in toluene with 1.1 equiv of hydrochloric acid (2M in Et₂O) afforded Ph₃POH⁺Cl⁻ (**2a[Cl]**) as a colorless hygroscopic solid in 99% isolated yield (Scheme 2).^[16] **2a[Cl]** displays a ³¹P NMR resonance at δ = 38.7 ppm (in CDCl₃; TPPO (**1a**): δ³¹P: 28.9 ppm) and a characteristic downfield shift of the OH group in the ¹H NMR spectrum at δ = 12.32 ppm.



Scheme 2. Formation of the adducts **2a[Cl]** and **2a[OTf]** (left) and molecular structure of **2a[OTf]** (right; hydrogen atoms, apart from H11, are omitted for clarity, one crystallographic independent molecule is shown). Selected bond lengths [Å] and angle [°] for **2a[OTf]** (values for the other molecules in square brackets): P1–O11 1.5552(15) [1.5455(15), 1.5445(15)], O11–H11 0.78(3) [0.81(4), 0.76(3)], H11···O21 1.79(3) [1.71(4), 1.74(3)], O21–S1 1.4659(15) [1.4649(16), 1.4566(18)]; O11–H11···O21 176(3) [173(4), 169(4)].

Employing trifluoromethanesulfonic acid (HOTf) instead afforded $\text{Ph}_3\text{POH}^+\text{OTf}^-$ (**2a[OTf]**) in 97% isolated yield as a colorless, viscous oil, which crystallized upon standing.^[17] Interestingly, **2a[OTf]** features a ^{31}P NMR resonance at $\delta = 51.5$ ppm (in CDCl_3), which is shifted downfield by 12.8 ppm compared to that of **2a[Cl]**, and an OH resonance at $\delta^1\text{H}$ 13.39 ppm that is shifted downfield by 1.07 ppm; both can be attributed to the stronger acidity of HOTf, and consequently the higher ionic character of the corresponding TPPO salt.^[18] The molecular structure of **2a[OTf]**, established unequivocally by a single-crystal X-ray diffraction analysis (Scheme 2, right), confirmed its ionic nature as evidenced by the hydrogen bonding geometry with a short O11–H11 bond [0.78(3) Å], and long H11···O21 distance [1.79(3) Å]. Protonation of the O11 atom results in elongation of the P1–O11 bond [1.5552(15) Å] compared to TPPO [1.487(3) Å, orthorhombic; 1.484(1), monoclinic].^[19] This is in sharp contrast with the $\text{Ph}_3\text{PO} \cdot \text{HF}$ adduct (obtained using HF in excess),^[20] in which the P–O bond length [1.495(4) Å]^[20a] is similar to the one of free triphenylphosphine oxide, while $\text{Ph}_3\text{POH}^+\text{Cl}^-$ ^[16] and $\text{Ph}_3\text{POH}^+\text{Br}^-$ ^[21] feature intermediate values [1.517(2) and 1.550(6) Å, respectively]. Interestingly, it seems that P–O bond lengthening in these TPPOH^+X^- adducts is correlated with the $\text{p}K_a$ value of the corresponding acid (see Table 1).^[22]

Table 1. pK_a (HX) and selected crystallographic data of triphenylphosphine oxide and its HX adducts (X = F, Cl, Br, OTf).

Compound	pK_a (HX) in water ^[22]	pK_a (HX) in DMSO ^[22]	P–O (Å) ^[a]
Ph ₃ PO	–	–	1.487(3) ^[b] / 1.484(1) ^[c]
Ph ₃ PO·HF	3.2	15±2	1.495(4)
Ph ₃ POH ⁺ Cl [−]	−8	1.8	1.517(2)
Ph ₃ POH ⁺ Br [−]	−9	0.9	1.550(6)
Ph ₃ POH ⁺ OTf [−]	−14	0.3	1.5552(15)

[a] Bond distance in the molecular structure. [b] Orthorhombic form.^[19a] [c] Monoclinic form.^[19b]

The pK_a of the Brønsted acid also impacts the thermal stability of the acid adducts. While **2a**[OTf] is thermally stable at 100 °C, **2a**[Cl] decomposes already at 60 °C by eliminating HCl and reforming TPPO (**1a**).^[16] The weakly Brønsted acidic diphenylphosphoric acid ($pK_a = 3.88$ in DMSO^[23]) does not even react with TPPO, as was observed by Beller and co-workers.^[13] As the reduction of phosphine oxides with hydrosilanes typically proceeds at elevated temperatures, we decided to probe the follow-up chemistry of the thermally stable protonated triphenylphosphine oxide **2a**[OTf]. Gratifyingly, reaction of **2a**[OTf] with 3 equiv of TMDS in toluene for 2 hours at 100 °C afforded after work-up triphenylphosphine (**3a**) in 80% isolated yield (Table 2). Using 3 equiv of PMHS instead gave **3a** in 76% yield, but the reaction was slower (25 hours) due to the polymeric nature of the reductant. Interestingly, preforming **2a**[OTf] is not essential, as *in situ* addition of triflic acid to a mixture of TPPO (**1a**) and TMDS or PMHS gives similar results.^[24] However, no reaction was observed between TPPO and either TMDS or PMHS at

100 °C without Brønsted acid additives present, confirming that HOTf facilitates the reduction of TPPO.^[15]

Table 2. Triflic acid promoted reduction of TPPO.

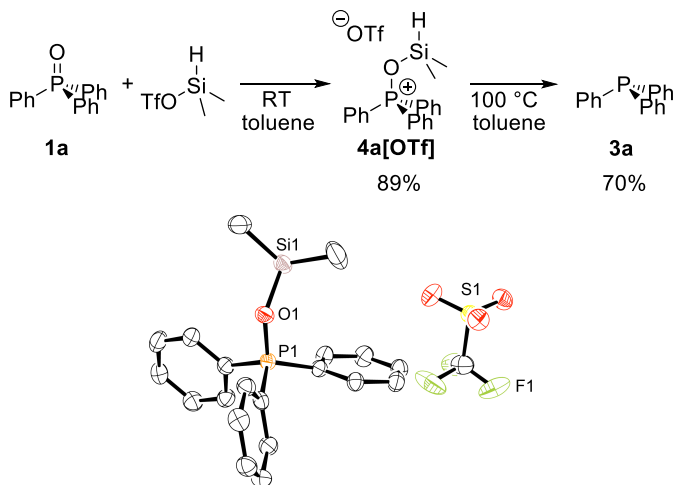
$$\text{Ph}^+\text{P}(\text{OH})(\text{Ph})_3 \text{OTf}^- \xrightarrow[\text{toluene, 100 } ^\circ\text{C}]{\text{silane (3 equiv)}} \text{Ph}-\text{P}(\text{Ph})_3$$

2a[OTf] **3a**

Silane	Time (h)	Isolated yield (%)
TMDS	2	80
PMHS	25 ^[a]	76 ^[b]

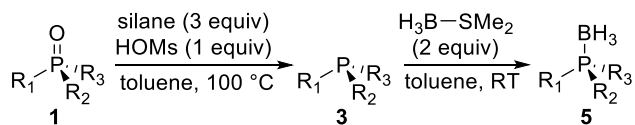
[a] Not optimized reaction time. [b] Product contains trace impurities of siloxane polymer according to ¹H NMR spectroscopy.

As the driving force of these reduction reactions is Si–O bond formation, we envisioned that silylated phosphine oxides could be plausible intermediates in the formation of triphenylphosphine (**3a**) from **2a[OTf]**. To verify this hypothesis we treated TPPO (**1a**) with 1 equiv of dimethylsilyl triflate^[25] in toluene at room temperature, which afforded **4a[OTf]** as a colorless solid in 89% isolated yield ($\delta^{31}\text{P}$: 53.5 ppm; Scheme 3, top). The molecular structure of **4a[OTf]**, determined by a single-crystal X-ray diffraction analysis (Scheme 4, bottom), displays a P1–O1 bond of 1.554(2) Å, a Si1–O1 bond of 1.701(2) Å and a P1–O1–Si1 angle of 134.58(15)° that compare well with the ones of the corresponding SiMe₃-substituted derivative Ph₃POSiMe₃⁺OTf[−] (1.545(4), 1.709(4) Å and 143.2(2)°, respectively) reported by Dutton and co-workers.^[26] Heating of **4a[OTf]** at 100 °C in toluene for 2 hours gave TPP (**3a**) in 70% isolated yield, which indicates that silylated phosphine oxides, such as **4a[OTf]**, are likely intermediates in the reduction of **2a[OTf]** with hydrosilanes. We postulate that the formation of TPP occurs via deprotonation of **4a[OTf]**, reforming HOTf, and elimination of dimethylsiloxane, which polymerizes to polydimethylsiloxane.



Scheme 3. Synthesis of **4a[OTf]** and its conversion into triphenylphosphine **3a** (top); molecular structure of **4a[OTf]** (bottom; hydrogen atoms are omitted for clarity, one crystallographic independent molecule is shown). Selected bond lengths [Å] and angle [°] for **4a[OTf]** (values for the second molecule in square brackets): P1–O1 1.554(2) [1.543(2)], O1–Si1 1.701(2) [1.710(2)]; P1–O1–Si1 134.58(15) [146.10(17)].

To broaden the substrate scope for this Brønsted acid promoted reaction, we studied the reduction of $\text{Ph}_2(\text{Me})\text{PO}$ (**1b**), $\text{Ph}(\text{Me})_2\text{PO}$ (**1c**) and $n\text{Bu}_3\text{PO}$ (**1d**) in the presence of triflic acid and TMDS as reductant. Unfortunately, only poor conversions were observed, most likely due to the considerably reduced solubility of the corresponding HOTf adducts **2b–d[OTf]** in toluene. To increase the solubility of the Brønsted acid adducts **2**, we used methanesulfonic acid (HOMs; $\text{pK}_a -0.06$ in water^[22]) instead that bears a more lipophilic anion. Satisfyingly, addition of 3 equiv of TMDS to an equimolar mixture of phosphine oxides **1b–d** and methanesulfonic acid in toluene at 100 °C afforded the phosphines **3b–d**, which were isolated as the corresponding BH_3 -adducts **5b–d** in 98, 89 and 97% isolated yield, respectively (Table 3). Also employing PMHS as reducing agent in the presence of HOMs was successful, which we tested for $n\text{Bu}_3\text{PO}$ (**3d**) that afforded $n\text{Bu}_3\text{P} \cdot \text{BH}_3$ (**5d**) in 78% isolated yield (Table 3).^[27]

Table 3. Methanesulfonic acid promoted reduction of phosphine oxides.

Phosphine oxide (1)	Product	Silane	Time (h) ^[a]	Yield (%) ^[b]
Ph ₃ PO (1a)	Ph ₃ P (3a)	TMDS	7	85
MePh ₂ PO (1b)	MePh ₂ P·BH ₃ (5b)	TMDS	7	98
Me ₂ PhPO (1c)	Me ₂ PhP·BH ₃ (5c)	TMDS	4.5	89
<i>n</i> Bu ₃ PO (1d)	<i>n</i> Bu ₃ P·BH ₃ (5d)	TMDS	4	97
<i>n</i> Bu ₃ PO (1d)	<i>n</i> Bu ₃ P·BH ₃ (5d)	PMHS	5	78

[a] Time at 100 °C. [b] Isolated yield of the corresponding product.

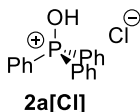
5.3. Conclusion

We have shown that the strong Brønsted acidic triflic acid and methanesulfonic acid can promote the reduction of tertiary phosphine oxides in toluene at 100 °C using the inexpensive hydrosiloxanes TMDS and PMHS. Our preliminary mechanistic investigations indicate that the Brønsted acid catalyzed reduction of phosphine oxides using hydrosiloxanes likely proceeds via silylated P oxide intermediates, of which we fully characterized **4a[OTf]** that afforded selectively triphenylphosphine (**3a**) at 100 °C in toluene.

5.4 Experimental Section

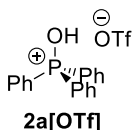
All syntheses were performed with the use of Schlenk techniques under an atmosphere of dry nitrogen. Solvents were distilled under nitrogen from sodium. NMR spectra were recorded at 25 °C. ¹H NMR: Bruker Avance 250 (250 MHz), Bruker Avance 400 (400 MHz), Bruker UltraShield™ 500 (500 MHz), referenced internally to residual solvent resonance of

CHCl₃: δ 7.27 ppm. ¹³C{¹H} NMR: Bruker Avance 250 (63 MHz), Bruker Avance 400 (100 MHz), referenced internally to residual solvent resonance of CDCl₃: δ 77.16 ppm. ³¹P{¹H} NMR: Bruker Avance 250 (101 MHz), Bruker Avance 400 (162 MHz) using 85% H₃PO₄ as an external standard: 0.00 ppm. ¹⁹F{¹H} NMR: Bruker Avance 250 (235 MHz) using CFC₃ as an external standard: 0.00 ppm. ¹H, ²⁹Si-geHMBC NMR: Bruker Avance 400 (79 MHz) using SiMe₄ as an external standard: 0.00 ppm. ¹¹B NMR: Bruker Avance 250 (128 MHz) using BF₃·OEt₂ as an external standard: 0.00 ppm. IR spectra were recorded on a Shimadzu FTIR-84005 spectrophotometer. High resolution electrospray ionisation-mass spectrometry (HR ESI-MS): Bruker MicroTOFQ, ESI positive mode, capillary voltage 4.5 kV. Melting points were measured on samples in unsealed capillaries on a Stuart Scientific SMP3 melting point apparatus and are uncorrected.



Synthesis of triphenylphosphine oxide adduct with hydrochloric acid

2a[Cl]: Hydrochloric acid (2 M in Et₂O, 0.55 mL, 1.10 mmol, 1.1 eq) was added dropwise to a solution of triphenylphosphine oxide (278 mg, 1.00 mmol, 1.0 eq) in toluene (3 mL) at 0 °C. After stirring for 1 h at 23 °C ³¹P NMR spectroscopy showed full conversion into **2a[Cl]**. The precipitate was isolated by filtration under nitrogen, washed with pentane and dried under reduced pressure to give **2a[Cl]**^[16] as a colorless hygroscopic solid in 99% yield (312 mg, 0.99 mmol). **MP**: 109–110 °C. **¹H NMR** (500 MHz, CDCl₃): δ 7.53–7.57 (m, 6H; *m*-PhH), 7.64–7.68 (m, 3H; *p*-PhH), 7.70–7.74 (m, 6H; *o*-PhH), 12.32 (s, 1H; OH). **¹³C{¹H} NMR** (63 MHz, CDCl₃): δ 128.7 (d, ¹J_{CP} = 106.5 Hz; *ipso*-PhC), 129.1 (d, ³J_{CP} = 13.4 Hz; *m*-PhC), 132.6 (d, ²J_{CP} = 10.9 Hz; *o*-PhC), 133.3 (d, ⁴J_{CP} = 2.8 Hz; *p*-PhC). **³¹P{¹H} NMR** (101 MHz, CDCl₃): δ 38.7 (s). **HR ESI-MS**: calcd for C₁₈H₁₆OP (M–Cl): 279.0933, found 279.0931. **IR**: 3051 (w), 1652 (m), 1183 (m), 1119 (s), 997 (w), 855 (m), 720 (s), 689 (s).



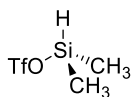
Synthesis of triphenylphosphine oxide adduct with triflic acid 2a[OTf]:

HOTf (97 μL, 1.10 mmol, 1.1 eq) was added dropwise to a solution of triphenylphosphine oxide (278 mg, 1.00 mmol, 1.0 eq) in toluene (3 mL) at 0 °C. After stirring for 1 h at 23 °C ³¹P NMR spectroscopy showed full conversion into the HOTf-adduct. Then, the solvent was removed under reduced pressure and the resulting oil was washed with pentane and dried, yielding **2a[OTf]**^[17] as a colorless oil (97%), which crystallized upon standing (**MP**: 63–67 °C). The compound is hygroscopic, and was stored under nitrogen. **¹H NMR** (400 MHz, CDCl₃): δ 7.62–7.67 (m, 6H; *m*-PhH),

7.69–7.74 (m, 6H; *o*-PhH), 7.67–7.82 (m, 3H; *p*-PhH), 13.39 (s, 1H; OH). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 123.3 (d, $^1J_{\text{CP}} = 109.2$ Hz; *ipso*-PhC), 129.69 (d, $^3J_{\text{CP}} = 13.3$ Hz; *m*-PhC), 132.8 (d, $^2J_{\text{CP}} = 11.7$ Hz; *o*-PhC), 135.0 (d, $^4J_{\text{CP}} = 2.9$ Hz; *p*-PhC). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ 51.5 (s). IR: 1700 (m), 1675 (w), 1560 (m), 1474 (s), 1305 (s), 1170 (s), 1121 (s), 1025 (s), 967 (s).

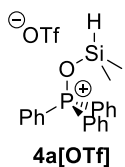
Reduction of 2a[OTf] with TMDS. TMDS (0.53 mL, 3.0 mmol, 3.0 eq) was added to a solution of **2a[OTf]** (0.43 g, 1.0 mmol, 1.0 eq)^[28] in toluene (5 mL) and the resulting mixture was heated at 100 °C for 2 h. Then, it was cooled to room temperature and a saturated sodium bicarbonate solution (10 mL) and Et_2O (15 mL) were subsequently added. The organic phase was separated and the aqueous phase was extracted twice with Et_2O (20 mL). The combined organic layers were dried over MgSO_4 , concentrated under reduced pressure, and purified by column chromatography (SiO_2 , pentane: Et_2O , 10:0.1), giving **3a**^[29] as a colorless solid in 80% yield (209 mg, 0.80 mmol). ^1H NMR (400 MHz, CDCl_3): δ 7.32–7.39 (m, 15H; PhH). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ 128.5 (d, $^3J_{\text{CP}} = 6.7$ Hz; *m*-PhC), 128.7 (s; *p*-PhC), 133.7 (d, $^2J_{\text{CP}} = 19.5$ Hz; *o*-PhC), 137.2 (d, $^1J_{\text{CP}} = 10.9$ Hz; *ipso*-PhC). $^{31}\text{P}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ -5.3 (s).

Reduction of 2a[OTf] with PMHS: PMHS (0.18 mL, 3.0 mmol of Si–H groups, 3.0 eq) was added to a solution of **2a[OTf]** (0.43 g, 1.0 mmol, 1.0 eq)^[28] in toluene (5 mL). The resulting mixture was stirred at 100 °C for 25 h (unoptimized reaction time), after which it was cooled to room temperature and Et_2O (15 mL) and a saturated sodium bicarbonate solution (15 mL) were subsequently added. **Note:** it is important to start with the addition of the diethyl ether, since in case of adding NaHCO_3 first the separation of two phases during the extraction is more difficult. The organic phase was separated and the aqueous phase was extracted twice with Et_2O (20 mL). The combined organic layers were dried over MgSO_4 , concentrated under reduced pressure, and purified by column chromatography (SiO_2 , pentane: Et_2O , 10:0.1), giving TPP **3a** as a colorless solid (199 mg, 0.76 mmol, 76%). Spectroscopic properties were identical to described above, however, the product also contained a small amount of siloxane polymers according to the ^1H NMR spectrum.



Dimethylsilyl trifluoromethanesulfonate was synthesized according to a literature procedure.^[25] Triflic acid (0.44 mL, 5.0 mmol, 1.0 eq) was added

dropwise to neat chlorodimethylsilane (0.57 mL, 5.0 mmol, 1.0 eq) at 23 °C, and the mixture was stirred for 10 min. Subsequent distillation (bp 50–53 °C/74–76 mbar) gave dimethylsilyl triflate as a colorless liquid in 60% yield (624 mg, 3.0 mmol). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 0.61 (d, $^3J_{\text{HH}} = 3.1$ Hz, 6H; CH_3), 5.03 (septet, $^3J_{\text{HH}} = 3.1$ Hz, 1H; SiH). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ -1.5 (s; CH_3), 118.4 (q, $^1J_{\text{CF}} = 317.5$ Hz; CF_3). $^{19}\text{F}\{^1\text{H}\}$ NMR (235 MHz, CDCl_3): δ -76.7 (s; CF_3). ^1H , ^{29}Si -geHMBC NMR (79 MHz): δ 24.6.



Synthesis of triphenylphosphine oxonium dimethylsilyl trifluoro-

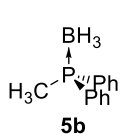
methanesulfonate 4a[OTf]: Dimethylsilyl trifluoromethanesulfonate (208 mg, 1.0 mmol, 1.0 eq) was added dropwise to a solution of triphenylphosphine oxide (278 mg, 1.0 mmol, 1.0 eq) in toluene (3 mL) at 0 °C. After stirring for 1 h at 23 °C, the mixture was filtered under nitrogen, washed with pentane

and dried *in vacuo* yielding **4a[OTf]** as a colorless solid (433 mg, 0.89 mmol, 89%). **MP:** 88–90 °C. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 0.47 (d, $^3J_{\text{HH}} = 2.8$ Hz, 6H; CH_3), 4.97 (septet, $^3J_{\text{HH}} = 2.8$ Hz, 1H; SiH), 7.67–7.76 (m, 12H; *o*-PhH, *m*-PhH), 7.85–7.89 (m, 3H; *p*-PhH). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ -0.61 (s; CH_3), 120.9 (q, $^1J_{\text{CF}} = 320.9$ Hz; CF_3), 121.6 (d, $^1J_{\text{CP}} = 111.1$ Hz; *ipso*-PhC), 130.5 (d, $^3J_{\text{CP}} = 13.7$ Hz; *m*-PhC), 132.8 (d, $^2J_{\text{CP}} = 12.6$ Hz; *o*-PhC), 136.1 (d, $^4J_{\text{CP}} = 2.71$ Hz; *p*-PhC). $^{31}\text{P}\{^1\text{H}\}$ NMR (235 MHz, CDCl_3): δ 53.5. ^1H , ^{29}Si -geHMBC NMR (79 MHz): δ 16.1. **IR:** 3063 (w), 29.63 (w), 1489 (m), 1312 (m), 1173 (m), 1119 (s), 972 (m), 725 (s), 687 (s), 532 (s).

Reduction of TPPO with TMDS in the presence of HOMs: TMDS (0.53 mL, 3.0 mmol, 3.0 eq) was added to a solution of TPPO (278 mg, 1.0 mmol, 1.0 eq) in toluene (5 mL) followed by the addition of methanesulfonic acid (HOMs; 0.07 mL, 1.0 mmol, 1.0 eq). The resulting mixture was stirred at 100 °C for 7 h. Then, the reaction mixture was cooled to room temperature and a saturated sodium bicarbonate solution (10 mL) and Et_2O (15 mL) were added. After separation of the organic phase, the aqueous phase was extracted twice with Et_2O (20 mL). The combined organic layers were dried over MgSO_4 , concentrated under reduced pressure, and purified by column chromatography (SiO_2 , pentane: Et_2O , 10:0.1), giving TPP (**3a**) as a colorless solid (223 mg, 0.85 mmol, 85%), spectroscopic properties were identical to described above.

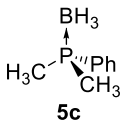
General procedure for reduction of MePh_2PO (1b), Me_2PhPO (1c), and $n\text{Bu}_3\text{PO}$ (1d) with TMDS in the presence of HOMs (isolation as BH_3 -adducts): TMDS (0.53 mL,

3.0 mmol, 3.0 eq) was added to a solution of the phosphine oxide (1.0 mmol, 1.0 eq) in toluene (5 mL) followed by the addition of methanesulfonic acid (0.07 mL, 1.0 mmol, 1.0 eq). The resulting mixture was stirred at 100 °C for the time indicated below. Then, the reaction mixture was cooled to room temperature and $\text{BH}_3 \cdot \text{SMe}_2$ complex (2 M in THF, 1.0 mL, 2.0 mmol, 2.0 eq) was subsequently added. The resulting mixture was stirred at 23 °C overnight followed by the addition of diethyl ether and water. The resulting mixture was extracted into Et_2O (3 x 20 mL), the combined organic phases were dried over MgSO_4 , filtered and concentrated under reduced pressure. Purification by column chromatography on silica gel (first pentane in order to remove unreacted TMSDS, and then – Et_2O :pentane, 1:10) afforded the phosphine-borane complexes as colorless liquids.



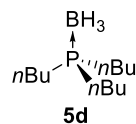
Methyl(diphenyl)phosphine borane 5b^[30]: Heating for 7h, isolated yield: 98%.

^1H NMR (250 MHz, CDCl_3): δ 1.02 (br. q, $^1J_{\text{HB}} = 98.1$ Hz, 3H; BH_3), 1.91 (d, $^2J_{\text{HP}} = 10.3$ Hz, 3H; CH_3), 7.44–7.56 (m, 6H; *m*-PhH, *p*-PhH), 7.66–7.74 (m, 4H; *o*-PhH). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (63 MHz, CDCl_3): δ 11.9 (d, $^1J_{\text{CP}} = 39.7$ Hz; CH_3), 128.8 (d, $^3J_{\text{CP}} = 9.9$ Hz; *m*-PhC), 130.6 (d, $^1J_{\text{CP}} = 56.3$ Hz; *ipso*-PhC), 131.1 (d, $^4J_{\text{CP}} = 2.4$ Hz; *p*-PhC), 131.7 (d, $^2J_{\text{CP}} = 9.5$ Hz; *o*-PhC). **$^{31}\text{P}\{^1\text{H}\}$ NMR** (101 MHz, CDCl_3): δ 10.6 (q, $^1J_{\text{PB}} = 54.0$ Hz). **^{11}B NMR** (128 MHz, CDCl_3): δ -38.0 (qd, $^1J_{\text{BH}} = 98.6$, $^1J_{\text{BP}} = 61.0$ Hz).



Dimethyl(phenyl)phosphine borane 5c^[31]: Heating for 4.5 h, isolated yield:

89%. **^1H NMR** (250 MHz, CDCl_3): δ 0.80 (br. qd, $^1J_{\text{HB}} = 96.7$ Hz, $^2J_{\text{HP}} = 15.2$ Hz, 3H; BH_3), 1.61 (d, $^2J_{\text{HP}} = 10.3$ Hz, 6H; CH_3), 7.47–7.58 (m, 3H; *m*-PhH, *p*-PhH), 7.73–7.81 (m, 2H; *o*-PhH). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (63 MHz, CDCl_3): δ 13.0 (d, $^1J_{\text{CP}} = 38.3$ Hz; CH_3), 128.9 (d, $^3J_{\text{CP}} = 9.8$ Hz; *m*-PhC), 131.0 (d, $^1J_{\text{CP}} = 54.9$ Hz; *ipso*-PhC), 130.9 (d, $^4J_{\text{CP}} = 9.4$ Hz; *o*-PhC), 131.3 (d, $^2J_{\text{CP}} = 2.9$ Hz; *p*-PhC). **$^{31}\text{P}\{^1\text{H}\}$ NMR** (101 MHz, CDCl_3): δ 2.9 (q, $^1J_{\text{PB}} = 63.5$ Hz). **^{11}B NMR** (128 MHz, CDCl_3): δ -30.1 (qd, $^1J_{\text{BH}} = 95.1$, $^1J_{\text{BP}} = 61.8$ Hz).



Tri-*n*-butylphosphine borane 5d^[10]: Heating for 4 h, isolated yield: 97%. **^1H**

NMR (250 MHz, CDCl_3): δ 0.73 (q, $^1J_{\text{HB}} = 99.6$ Hz, 3H; BH_3), 0.86 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3H; CH_3), 1.26–1.55 (m, 18H; CH_2). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (63 MHz, CDCl_3): δ 13.6 (s; CH_3), 22.9 (d, $^1J_{\text{CP}} = 34.6$ Hz; CH_2), 24.4 (d, $^2J_{\text{CP}} = 12.5$ Hz; CH_2), 24.7 (d, $^3J_{\text{CP}} = 2.2$ Hz; CH_2). **$^{31}\text{P}\{^1\text{H}\}$ NMR** (101 MHz, CDCl_3): δ 14.5 (q, $^1J_{\text{PB}} = 51.0$ Hz). **^{11}B NMR** (128 MHz, CDCl_3): δ -40.95 (m).

Synthesis of tri-*n*-butylphosphine borane by reduction of *n*Bu₃PO with PMHS in the presence of HOMs: PMHS (0.18 mL, 3.0 mmol of Si-H groups, 3.0 eq) was added to a solution of *n*Bu₃PO (0.28 g, 1.0 mmol, 1.0 eq) in toluene (5 mL) followed by the addition of methanesulfonic acid (0.07 mL, 1.0 mmol, 1.0 eq). The resulting mixture was stirred at 100 °C for 5 h, after which it was cooled to room temperature and BH₃·SMe₂ complex (2 M in THF, 1.0 mL, 2.0 mmol, 2.0 eq) was subsequently added. The resulting mixture was stirred at 23 °C overnight followed by the addition of diethyl ether and water. The resulting mixture was extracted into Et₂O (3 x 20 mL), the combined organic phases were dried over MgSO₄, filtered and concentrated under reduced pressure. Purification by column chromatography on silica gel (first pentane in order to remove unreacted PMHS, and then – Et₂O:pentane, 1:10) afforded tri-*n*-butylphosphine borane **5d** as a colorless liquid (0.22 g, 0.78 mmol, 78%).

X-ray crystal structure determination

2a[OTf]: [C₁₈H₁₆OP][CF₃O₃S], Fw = 428.35, colorless block, 0.30 × 0.24 × 0.15 mm³, monoclinic, P2₁/c (no. 14), a = 8.85807(10), b = 14.6779(3), c = 44.9508(9) Å, β = 99.771(1) °, V = 5759.63(18) Å³, Z = 12, D_x = 1.482 g/cm³, μ = 0.30 mm⁻¹. 51400 Reflections were measured on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator (λ = 0.71073 Å) at a temperature of 125(2) K up to a resolution of (sin θ/λ)_{max} = 0.61 Å⁻¹. The intensities were integrated with the Eval15 software.^[32] Multiscan absorption correction and scaling was performed with SADABS^[33] (correction range 0.81–0.95). 10725 Reflections were unique (R_{int} = 0.026), of which 9277 were observed [I > 2σ(I)]. The structure was solved with Direct Methods using SHELXS-97.^[34] Least-squares refinement was performed with SHELXL-2016^[35] against F² of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps. O-H hydrogen atoms were refined freely with isotropic displacement parameters. C-H hydrogen atoms were refined with a riding model. 769 Parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0395 / 0.0967. R1/wR2 [all refl.]: 0.0473 / 0.1018. S = 1.022. Residual electron density between –0.56 and 0.74 e/Å³. Geometry calculations and checking for higher symmetry were performed with the PLATON program.^[36]

4a[OTf]: [C₂₀H₂₂OPSi][CF₃O₃S], Fw = 486.50, colorless plate, 0.54 × 0.27 × 0.12 mm³, monoclinic, P2₁ (no. 4), a = 17.3344(2), b = 7.6327(1), c = 17.4473(2) Å, β = 93.3711(5) °, V = 2304.43(5) Å³, Z = 4, D_x = 1.402 g/cm³, μ = 0.31 mm⁻¹. 36246 Reflections were measured on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of (sin θ/λ)_{max} = 0.65 Å⁻¹. The intensities were integrated with the HKL2000 software.^[37] An absorption correction was not considered necessary. Scaling and merging was performed with Sortav.^[38] 10562 Reflections were unique (R_{int} = 0.055), of which 8917 were observed [I > 2σ(I)]. The structure was solved with Direct Methods using SHELXS-97.^[34] Least-squares refinement was performed with SHELXL-2016^[35] against F² of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps and refined with a riding model. 563 Parameters were refined with 1 restraint (shifting origin). R1/wR2 [I > 2σ(I)]: 0.0389 / 0.0896. R1/wR2 [all refl.]: 0.0488 / 0.0952. S = 1.038. Flack parameter^[39] x = 0.00(2). Residual electron density between -0.32 and 0.36 e/Å³. Geometry calculations and checking for higher symmetry were performed with the PLATON program.^[36]

CCDC 1543934 (**2a[OTf]**) and 1543935 (**4a[OTf]**) contain the supplementary crystallographic data for this chapter. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

5.5 References

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