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ARTICLE

Brønsted Acid Promoted Reduction of Tertiary Phosphine Oxides

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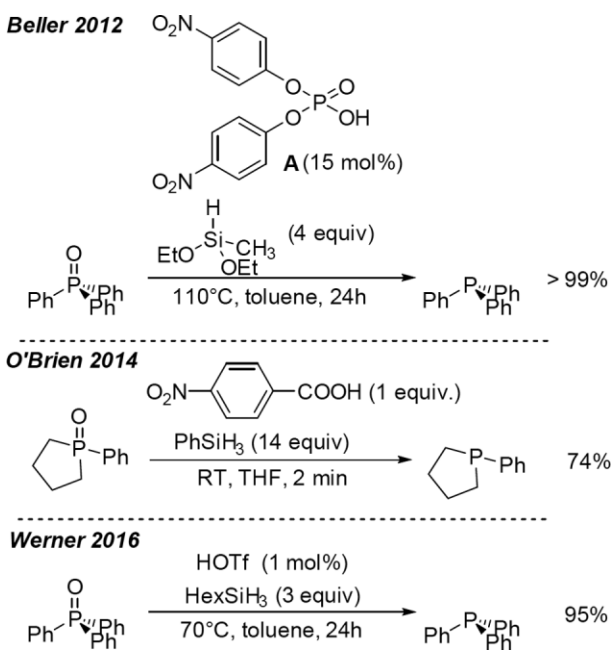
Dedicated to Professor Evamarie Hey-Hawkins on the Occasion of her 60th Birthday

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 $Me_2SiHOTf$ adducts of triphenylphosphine oxide and find that the thermally stable adduct $Ph_3POH^+OTf^-$ is efficiently converted into triphenylphosphine at 100 °C in the presence of readily available hydrosiloxanes. Under the same reaction conditions, also $Ph_3POSiMe_2H^+OTf^-$ selectively affords triphenylphosphine indicating that silylated phosphine oxides are likely intermediates in this process.

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 wasted, 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 $Ti(OiPr)_4$,[9] $InBr_3$,[10] $Cu(OTf)_2$,[11] Fe–H complexes,[3h] $B(C_6F_5)_3$ 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, $(EtO)_2MeSiH$; 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 pK_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 trifluoro-



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

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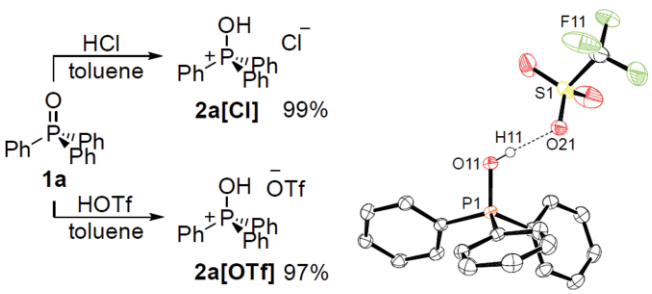
methanesulfonic acid (HOTf) and phenyl- or hexylsilane afforded TPP in high yields (Scheme 1).[15]

We envisioned that employment of a strong Brønsted acid will decrease the strength of 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.

Results and Discussion

Treatment of triphenylphosphine oxide (**1a**) in toluene with 1.1 equiv. of hydrochloric acid (2 M in Et_2O) afforded $Ph_3POH^+Cl^-$ (**2a[Cl]**) as a colorless hygroscopic solid in 99 % isolated yield (Scheme 2).[16] **2a[Cl]** displays a ^{31}P NMR resonance at δ = 38.7 ppm (in $CDCl_3$; TPPO (**1a**): $\delta^{31}P$: 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 H1, are omitted for clarity, one crystallographic independent molecule is shown). Selected bond lengths /Å and angles /° 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 $Ph_3POH^+OTf^-$ (**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 δ = 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 δ^1H 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 arrangement 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 Ph_3PO·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, whereas $Ph_3POH^+Cl^-$[16] and $Ph_3POH^+Br^-$[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 pK_a value of the corresponding acid (see Table 1).[22]

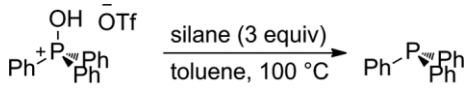
Table 1. pK_a (HX) and selected crystallographic data of triphenylphosphine oxide and its H*X* adducts (*X* = F, Cl, Br, OTf).

Compound	pK_a (H*X*) in water[22]	pK_a (H*X*) in DMSO[22]	P–O /Å[a]
Ph_3PO	–	–	1.487(3)[b] / 1.484(1)[c]
Ph_3PO·HF	3.2	15 ± 2	1.495(4)
$Ph_3POH^+Cl^-$	–8	1.8	1.517(2)
$Ph_3POH^+Br^-$	–9	0.9	1.550(6)
$Ph_3POH^+OTf^-$	–14	0.3	1.5552(15)

a) Bond length 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 coworkers.[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 h 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 h) 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.



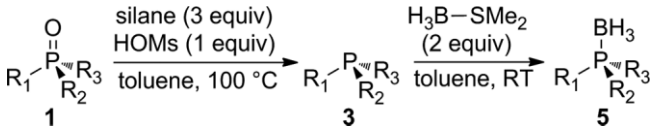
2a[OTf] **3a**

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]

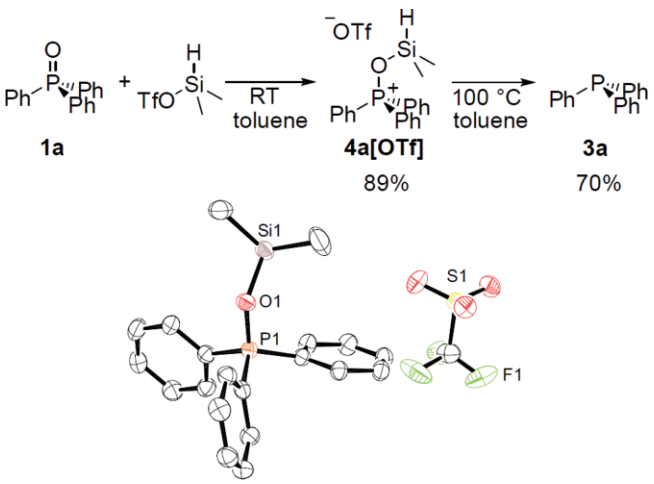
Table 3. Methanesulfonic acid promoted reduction of phosphine oxides.



Phosphine oxide (**1**)	Product	Silane	Time /h[a)]	Yield /%[b)]
Ph_3PO (**1a**)	Ph_3P (**3a**)	TMDS	7	85
$MePh_2PO$ (**1b**)	$MePh_2P{\cdot}BH_3$ (**5b**)	TMDS	7	98
Me_2PhPO (**1c**)	$Me_2PhP{\cdot}BH_3$ (**5c**)	TMDS	4.5	89
$n Bu_3PO$ (**1d**)	$n Bu_3P{\cdot}BH_3$ (**5d**)	TMDS	4	97
$n Bu_3PO$ (**1d**)	$n Bu_3P{\cdot}BH_3$ (**5d**)	PMHS	5	78

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

in toluene at room temperature, which afforded **4a[OTf]** as a colorless solid in 89 % isolated yield (δ^{31}P: 53.5 ppm; Scheme 3, top). The molecular structure of **4a[OTf]**, determined by a single-crystal X-ray diffraction analysis (Scheme 3, 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 $SiMe_3$-substituted derivative $Ph_3POSiMe_3{}^+OTf^-$ [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 h 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 angles /° 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 $Ph_2(Me)PO$ (**1b**), $Ph(Me)_2PO$ (**1c**), and $n Bu_3PO$ (**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**–**2d[OTf]** in toluene. To increase the solubility of the Brønsted acid adducts **2**, we used methanesulfonic acid (HOMs; 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**–**1d** and methanesulfonic acid in toluene at 100 °C afforded the phosphines **3b**–**3d**, which were isolated as the corresponding BH_3 adducts **5b**–**5d** 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 $n Bu_3PO$ (**3d**) that afforded $n Bu_3P{\cdot}BH_3$ (**5d**) in 78 % isolated yield (Table 3).[27]

Conclusions

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.

Experimental Section

Materials and Methods: All syntheses were performed with the use of Schlenk techniques in an atmosphere of dry nitrogen. Solvents were distilled under nitrogen from sodium. NMR spectra were recorded at 25 °C. ^{1}H NMR: Bruker Avance 250 (250 MHz), Bruker Avance 400 (400 MHz), Bruker UltraShield™ 500 (500 MHz), referenced internally to residual solvent resonance of $CHCl_3$: δ = 7.27 ppm. ^{13}C{^{1}H} NMR: Bruker Avance 250 (63 MHz), Bruker Avance 400 (100 MHz), referenced internally to residual solvent resonance of $CDCl_3$: δ = 77.16 ppm. ^{31}P{^{1}H} NMR: Bruker Avance 250 (101 MHz), Bruker Avance 400 (162 MHz) using 85 % H_3PO_4 as an external standard: 0.00 ppm. ^{19}F{^{1}H} NMR: Bruker Avance 250 (235 MHz) using $CFCl_3$ as an external standard: 0.00 ppm. ^{1}H, ^{29}Si-geHMBC NMR: Bruker Avance 400 (79 MHz) using $SiMe_4$ as an external standard: 0.00 ppm. ^{11}B NMR: Bruker Avance 250 (128 MHz) using $BF_3{\cdot}OEt_2$ as an external standard: 0.00 ppm. IR spectra were recorded with a Shimadzu FTIR-84005 spectrophotometer. High resolution electrospray ioniza-

tion-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 Et_2O, 0.55 mL, 1.10 mmol, 1.1 equiv.) was added dropwise to a solution of triphenylphosphine oxide (278 mg, 1.00 mmol, 1.0 equiv.) in toluene (3 mL) at 0 °C. After stirring for 1 h at 23 °C ^{31}P 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. **^{1}H NMR** (500 MHz, $CDCl_3$): δ = 7.53–7.57 (m, 6 H, *m*-Ph*H*), 7.64–7.68 (m, 3 H, *p*-Ph*H*), 7.70–7.74 (m, 6 H, *o*-Ph*H*), 12.32 (s, 1 H, O*H*). **^{13}C{^{1}H} NMR** (63 MHz, $CDCl_3$): δ = 128.7 (d, $^1J_{CP}$ = 106.5 Hz; *ipso*-Ph*C*), 129.1 (d, $^3J_{CP}$ = 13.4 Hz; *m*-Ph*C*), 132.6 (d, $^2J_{CP}$ = 10.9 Hz; *o*-Ph*C*), 133.3 (d, $^4J_{CP}$ = 2.8 Hz; *p*-Ph*C*). **^{31}P{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 38.7 (s). **HR ESI-MS**: calcd. for $C_{18}H_{16}OP$ (M–Cl): 279.0933, found 279.0931. **IR**: $\tilde{\nu}$ = 3051 (w), 1652 (m), 1183 (m), 1119 (s), 997 (w), 855 (m), 720 (s), 689 (s) cm^{-1}.

Synthesis of Triphenylphosphine Oxide Adduct with Triflic Acid (2a[OTf]): HOTf (97 µL, 1.10 mmol, 1.1 equiv.) was added dropwise to a solution of triphenylphosphine oxide (278 mg, 1.00 mmol, 1.0 equiv.) in toluene (3 mL) at 0 °C. After stirring for 1 h at 23 °C ^{31}P NMR spectroscopy showed full conversion into the HOTf adduct. Afterwards, 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 in a nitrogen atmosphere. **^{1}H NMR** (400 MHz, $CDCl_3$): 7.62–7.67 (m, 6 H, *m*-Ph*H*), 7.69–7.74 (m, 6 H, *o*-Ph*H*), 7.67–7.82 (m, 3 H, *p*-Ph*H*), 13.39 (s, 1 H, O*H*). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ = 123.3 (d, $^1J_{CP}$ = 109.2 Hz; *ipso*-Ph*C*), 129.69 (d, $^3J_{CP}$ = 13.3 Hz; *m*-Ph*C*), 132.8 (d, $^2J_{CP}$ = 11.7 Hz; *o*-Ph*C*), 135.0 (d, $^4J_{CP}$ = 2.9 Hz; *p*-Ph*C*). **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$): δ = 51.5 (s). **IR**: $\tilde{\nu}$ = 1700 (m), 1675 (w), 1560 (m), 1474 (s), 1305 (s), 1170 (s), 1121 (s), 1025 (s), 967 (s) cm^{-1}.

Reduction of 2a[OTf] with TMDS: TMDS (0.53 mL, 3.0 mmol, 3.0 equiv.) was added to a solution of **2a[OTf]** (0.43 g, 1.0 mmol, 1.0 equiv.)[28] in toluene (5 mL) and the resulting mixture was heated at 100 °C for 2 h. Afterwards, it was cooled to room temperature and a saturated sodium hydrogen carbonate 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 with $MgSO_4$, 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). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.32–7.39 (m, 15 H, Ph*H*). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 128.5 (d, $^3J_{CP}$ = 6.7 Hz; *m*-Ph*C*), 128.7 (s; *p*-Ph*C*), 133.7 (d, $^2J_{CP}$ = 19.5 Hz; *o*-Ph*C*), 137.2 (d, $^1J_{CP}$ = 10.9 Hz; *ipso*-Ph*C*). **^{31}P{^{1}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 equiv.) was added to a solution of **2a[OTf]** (0.43 g, 1.0 mmol, 1.0 equiv.)[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 hydrogen carbonate 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 with $MgSO_4$, 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 ^{1}H NMR spectrum.

Dimethylsilyl Trifluoromethanesulfonate was synthesized according to a literature procedure:[25] Triflic acid (0.44 mL, 5.0 mmol, 1.0 equiv.) was added dropwise to neat chlorodimethylsilane (0.57 mL, 5.0 mmol, 1.0 equiv.) 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}H NMR** (500 MHz, $CDCl_3$): δ = 0.61 (d, $^3J_{HH}$ = 3.1 Hz, 6 H, CH_3), 5.03 (septet, $^3J_{HH}$ = 3.1 Hz, 1 H, Si*H*). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ = –1.5 (s; *C*H_3), 118.4 (q, $^1J_{CF}$ = 317.5 Hz; *C*F_3). **^{19}F{^{1}H} NMR** (235 MHz, $CDCl_3$): δ = –76.7 (s; CF_3). **^{1}H, ^{29}Si-geHMBC NMR** (79 MHz): δ = 24.6 ppm.

Synthesis of Triphenylphosphine Oxonium Dimethylsilyl Trifluoro-methanesulfonate (4a[OTf]): Dimethylsilyl trifluoromethanesulfonate (208 mg, 1.0 mmol, 1.0 equiv.) was added dropwise to a solution of triphenylphosphine oxide (278 mg, 1.0 mmol, 1.0 equiv.) in toluene (3 mL) at 0 °C. After stirring for 1 h at 23 °C, the mixture was filtered in a nitrogen atmosphere, 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}H NMR** (500 MHz, $CDCl_3$): δ = 0.47 (d, $^3J_{HH}$ = 2.8 Hz, 6 H, CH_3), 4.97 (septet, $^3J_{HH}$ = 2.8 Hz, 1 H, Si*H*), 7.67–7.76 (m, 12 H, *o*-Ph*H*, *m*-Ph*H*), 7.85–7.89 (m, 3 H, *p*-Ph*H*). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$): δ = –0.61 *ppm*(s; *C*H_3), 120.9 (q, $^1J_{CF}$ = 320.9 Hz; *C*F_3), 121.6 (d, $^1J_{CP}$ = 111.1 Hz; *ipso*-Ph*C*), 130.5 (d, $^3J_{CP}$ = 13.7 Hz; *m*-Ph*C*), 132.8 (d, $^2J_{CP}$ = 12.6 Hz; *o*-Ph*C*), 136.1 (d, $^4J_{CP}$ = 2.71 Hz; *p*-Ph*C*). **^{31}P{^{1}H} NMR** (235 MHz, $CDCl_3$): δ = 53.5 ppm. **^{1}H, ^{29}Si-geHMBC NMR** (79 MHz): δ = 16.1 ppm. **IR**: $\tilde{\nu}$ = 3063 (w), 29.63 (w), 1489 (m), 1312 (m), 1173 (m), 1119 (s), 972 (m), 725 (s), 687 (s), 532 (s) cm^{-1}.

Reduction of TPPO with TMDS in the Presence of HOMs: TMDS (0.53 mL, 3.0 mmol, 3.0 equiv.) was added to a solution of TPPO (278 mg, 1.0 mmol, 1.0 equiv.) in toluene (5 mL) followed by the addition of methanesulfonic acid (HOMs; 0.07 mL, 1.0 mmol, 1.0 equiv.). The resulting mixture was stirred at 100 °C for 7 h. Afterwards, the reaction mixture was cooled to room temperature and a saturated sodium hydrogen carbonate 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 with $MgSO_4$, 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 the Reduction of $MePh_2PO$ (1b), Me_2PhPO (1c), and nBu_3PO (1d) with TMDS in the Presence of HOMs (Isolation as BH_3-Adducts): TMDS (0.53 mL, 3.0 mmol, 3.0 equiv.) was added to a solution of the phosphine oxide (1.0 mmol, 1.0 equiv.) in toluene (5 mL) followed by the addition of methanesulfonic acid (0.07 mL, 1.0 mmol, 1.0 equiv.). The resulting mixture was stirred at 100 °C for the time indicated below. Afterwards, the reaction mixture was cooled to room temperature and the BH_3·SMe_2 complex (2 M in THF, 1.0 mL, 2.0 mmol, 2.0 equiv.) 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 × 20 mL), the combined organic phases were dried with $MgSO_4$, filtered, and concentrated under reduced pressure. Purification by column chromatography on silica gel (first pentane in order to remove unreacted TMDS, and then – Et_2O:pentane, 1:10) afforded the phosphine-borane complexes as colorless liquids.

Methyldiphenylphosphine Borane (5b):[30] Heating for 7h, isolated yield: 98 %. **^{1}H NMR** (250 MHz, $CDCl_3$): δ = 1.02 (br. q, $^1J_{HB}$ = 98.1 Hz, 3 H, BH_3), 1.91 (d, $^2J_{HP}$ = 10.3 Hz, 3 H, CH_3), 7.44–7.56 (m, 6 H, *m*-Ph*H*, *p*-Ph*H*), 7.66–7.74 (m, 4 H, *o*-Ph*H*). **^{13}C{^{1}H} NMR** (63 MHz, $CDCl_3$): δ = 11.9 (d, $^1J_{CP}$ = 39.7 Hz; *C*H$_3$), 128.8 (d, $^3J_{CP}$ = 9.9 Hz; *m*-Ph*C*), 130.6 (d, $^1J_{CP}$ = 56.3 Hz; *ipso*-Ph*C*), 131.1 (d, $^4J_{CP}$ = 2.4 Hz; *p*-Ph*C*), 131.7 (d, $^2J_{CP}$ = 9.5 Hz; *o*-Ph*C*). **^{31}P{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 10.6 (q, $^1J_{PB}$ = 54.0 Hz). **^{11}B NMR** (128 MHz, $CDCl_3$): δ = –38.0 (qd, $^1J_{BH}$ = 98.6, $^1J_{BP}$ = 61.0 Hz).

Dimethyl(phenyl)phosphine Borane (5c):[31] Heating for 4.5 h, isolated yield: 89 %. **^{1}H NMR** (250 MHz, $CDCl_3$): δ = 0.80 (br. qd, $^1J_{HB}$ = 96.7, $^2J_{HP}$ = 15.2 Hz, 3 H, BH_3), 1.61 (d, $^2J_{HP}$ = 10.3 Hz, 6 H, CH_3), 7.47–7.58 (m, 3 H, *m*-Ph*H*, *p*-Ph*H*), 7.73–7.81 (m, 2 H, *o*-Ph*H*). **^{13}C{^{1}H} NMR** (63 MHz, $CDCl_3$): δ = 13.0 (d, $^1J_{CP}$ = 38.3 Hz; *C*H$_3$), 128.9 (d, $^3J_{CP}$ = 9.8 Hz; *m*-Ph*C*), 131.0 (d, $^1J_{CP}$ = 54.9 Hz; *ipso*-Ph*C*), 130.9 (d, $^4J_{CP}$ = 9.4 Hz; *o*-Ph*C*), 131.3 (d, $^2J_{CP}$ = 2.9 Hz; *p*-Ph*C*). **^{31}P{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 2.9 (q, $^1J_{PB}$ = 63.5 Hz). **^{11}B NMR** (128 MHz, $CDCl_3$): δ = –30.1 (qd, $^1J_{BH}$ = 95.1, $^1J_{BP}$ = 61.8 Hz).

Tri-*n*-butylphosphine Borane (5d):[10] Heating for 4 h, isolated yield: 97 %. **^{1}H NMR** (250 MHz, $CDCl_3$): δ = 0.73 (q, $^1J_{HB}$ = 99.6 Hz, 3 H, BH_3), 0.86 (t, $^3J_{HH}$ = 7.2 Hz, 3 H, CH_3), 1.26–1.55 (m, 18 H, CH_2). **^{13}C{^{1}H} NMR** (63 MHz, $CDCl_3$): δ = 13.6 (s; *C*H$_3$), 22.9 (d, $^1J_{CP}$ = 34.6 Hz; *C*H$_2$), 24.4 (d, $^2J_{CP}$ = 12.5 Hz; *C*H$_2$), 24.7 (d, $^3J_{CP}$ = 2.2 Hz; *C*H$_2$). **^{31}P{^{1}H} NMR** (101 MHz, $CDCl_3$): δ = 14.5 (q, $^1J_{PB}$ = 51.0 Hz). **^{11}B NMR** (128 MHz, $CDCl_3$): δ = –40.95 (m).

Synthesis of Tri-*n*-butylphosphine Borane by Reduction of *n*Bu$_3$PO with PMHS in the Presence of HOMs: PMHS (0.18 mL, 3.0 mmol of Si–H groups, 3.0 equiv.) was added to a solution of ***n*Bu$_3$PO** (0.28 g, 1.0 mmol, 1.0 equiv.) in toluene (5 mL) followed by the addition of methanesulfonic acid (0.07 mL, 1.0 mmol, 1.0 equiv.). The resulting mixture was stirred at 100 °C for 5 h, after which it was cooled to room temperature and BH_3·SMe_2 complex (2 M in THF, 1.0 mL, 2.0 mmol, 2.0 equiv.) 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 × 20 mL), the combined organic phases were dried with $MgSO_4$, filtered and concentrated under reduced pressure. Purification by column chromatography on silica gel (first pentane in order to remove unreacted PMHS, and then – Et_2O:pentane, 1:10) afforded tri-*n*-butylphosphine borane (**5d**) as a colorless liquid (0.22 g, 0.78 mmol, 78 %).

X-ray Crystallography of 2a[OTf]: [$C_{18}H_{16}OP$][CF_3O_3S], Fw = 428.35, colorless block, 0.30 × 0.24 × 0.15 mm^3, monoclinic, $P2_1/c$ (no. 14), a = 8.85807(10), b = 14.6779(3), c = 44.9508(9) Å, β = 99.771(1) °, V = 5759.63(18) Å^3, Z = 12, D_x = 1.482 g·cm^{-3}, μ = 0.30 mm^{-1}. 51400 Reflections were measured with 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 $(\sin\theta/\lambda)_{max}$ = 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 [$I > 2\sigma(I)$]. The structure was solved with Direct Methods using SHELXS-97.[34] Least-squares refinement was performed with SHELXL-2016[35] against F^2 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. R_1/wR_2 [$I > 2\sigma(I)$]: 0.0395 / 0.0967. R_1/wR_2 [all reflections]: 0.0473 / 0.1018. S = 1.022; residual electron density between –0.56 and 0.74 e·Å^{-3}. Geometry calculations and checking for higher symmetry were performed with the PLATON program.[36]

4a[OTf]: [$C_{20}H_{22}OPSi$][CF_3O_3S], Fw = 486.50, colorless plate, 0.54 × 0.27 × 0.12 mm^3, monoclinic, $P2_1$ (no. 4), a = 17.3344(2), b = 7.6327(1), c = 17.4473(2) Å, β = 93.3711(5) °, V = 2304.43(5) Å^3, Z = 4, D_x = 1.402 g·cm^{-3}, μ = 0.31 mm^{-1}. 36246 Reflections were measured with 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 $(\sin\theta/\lambda)_{max}$ = 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 [$I > 2\sigma(I)$]. The structure was solved with Direct Methods using SHELXS-97.[34] Least-squares refinement was performed with SHELXL-2016[35] against F^2 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). R_1/wR_2 [$I > 2\sigma(I)$]: 0.0389 / 0.0896. R_1/wR_2 [all reflections]: 0.0488 / 0.0952. S = 1.038; Flack parameter[39] x = 0.00(2); residual electron density between –0.32 and 0.36 e/Å^3. Geometry calculations and checking for higher symmetry were performed with the PLATON program.[36]

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1543934 (**2a[OTf]**) and CCDC-1543935 (**4a[OTf]**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): NMR spectra of all reported compounds.

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