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Reduction of tertiary phosphine oxides to phosphine-boranes using Ti(O*i*-Pr)$_4$/BH$_3$-THF

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ABSTRACT

A new method for reduction of tertiary phosphine oxides leading to the formation of tertiary phosphine-boranes has been developed. The BH$_3$-THF/Ti(O*i*-Pr)$_4$ reducing system enables conversion of triaryl, diarylalkyl and trialkylphosphine oxides directly to their borane analogues in good to high yields. In contrast to the previously reported protocols, the presence of activating groups in the structure of starting material is not necessary for the reaction to occur. The reaction is highly stereoselective and proceeds with predominant retention of configuration at the phosphorus atom. A plausible mechanism of reduction of the P═O bond by BH$_3$-THF/Ti(O*i*-Pr)$_4$ has been proposed.

1. Introduction

The reduction of phosphine oxides to phosphines, especially in a stereoselective way is still one of the most explored topics in the current organophosphorus chemistry [1]. Till now many different reducing agents were tested in transformation of phosphine oxides to phosphines including hydrides [2], silanes [3], metal complexes [4] and organoboron compounds [5]. Among them silanes are still considered as the most efficient in deoxygenation of phosphine oxides due to their chemo- and stereoselectivity [6]. In 1994, Lawrence et al. developed the first reduction of P═O bond by silanes catalysed by a Lewis acid [7]. They showed that the reduction of tertiary phosphine oxides using PHMS occurs under much milder conditions when run in the presence of stoichiometric amounts of Ti(O*i*-Pr)$_4$ and proceeds in a predominantly stereoretentive manner. At the same time, they also presented the first catalytic reduction of P═O bond using triethoxysilane assisted by the same Lewis acid and occurring with identical stereochemical outcome (Scheme 1, eq. A). Later, Ti(O*i*-Pr)$_4$ was employed in another catalytic reduction of P═O bond using 1,1,3,3-tetramethyldisiloxane (TMDS) [8], but in case of the reduction of (*S,S*)-DIPAMP(O)$_2$ the same group has observed a partial racemization of phosphorus center (Scheme 1, eq. B) [9].

More recently, reduction methods based on the silane/catalyst system have attracted even more attention. Not only Ti(O*i*-Pr)$_4$ but also other Lewis acids [InBr$_3$ [10], Cu(OTf)$_2$ [11], B(C$_6$F$_5$)$_3$ [12], electrophilic fluorophosphonium cations (EPCs) [12]] as well as Brønsted acids [bis(2-chlorophenyl)borinic acid [13], bis(*p*-nitrophenyl)phosphoric acid (BNPA) [14], TfOH [15], MsOH [15b]] have been reported to promote silane P═O reductions, when added in either catalytic or stoichiometric amounts. Among these protocols a significant advance in this field was the one developed by Beller's group on the use of strong Brønsted acid along with a large excess of diethoxymethylsilane [14a]. This new reducing mixture showed unprecedented tolerance to a number of sensitive functional groups present in the phosphine oxide structure, e.g., formyl, cyano, allyl, ester, and amide, and trimethylsilyl group, and was shown to proceed with inversion of configuration at phosphorus atom (Scheme 1, eq. C). The other use of BNPA with DPDS, reported by Aldrich, enabled also the reduction of (*S,S*)-DIPAMP(O)$_2$ in a stereoselective way also with inversion of configuration at the phosphorus atom (Scheme 1, eq. D) [14c].

In the meantime, methodologies offering direct transformations of phosphine oxides into easily handled and storable borane-protected phosphines without isolation of the intermediate free phosphines have also been developed and start to become practical

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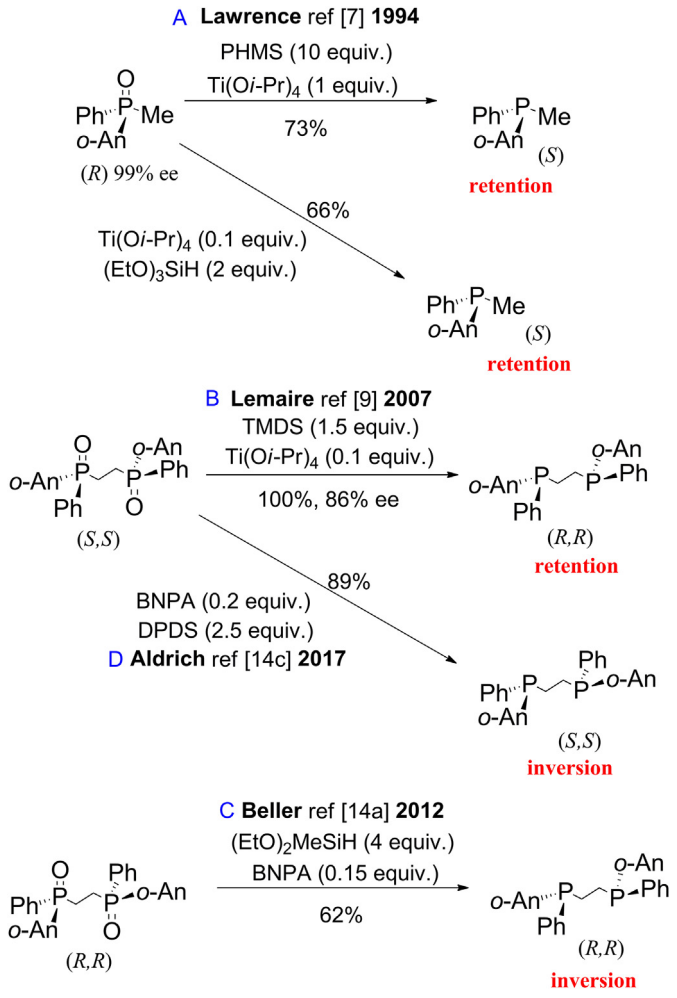


Scheme 1. Examples of reduction of P═O bond with silanes in presence of Ti(Oi-Pr)$_4$ proceeding in a stereoselective way.

alternatives to reductions stopping at the phosphine stage. Indeed, the method ($LiAlH_4$/$NaBH_4$/$CeCl_3$) [16] introduced by Imamoto and a family of reducing systems reported successively by Gilheany's group [17] provided phosphine-boranes with excellent yields directly from their phosphine oxide precursors. Two methods introduced by Gilheany at al., i.e., reduction of phosphine oxides using Meerwein salt/$NaBH_4$ [17a] and reduction of diastereomerically enriched menthoxyphosphonium salts [17b] using $LiBH_4$ or L-selectride [17c] provide phosphine boranes in the stereoselective manner.

Among methods enabling conversion of P═O bond to P–BH_3 moiety, those using BH_3 complexes as reducing agents (pioneered by Köster and Morita [5a], and continued by Keglevich [18] and our group [19]) have gained recently considerable importance. In case of secondary phosphine oxides [19] this transformation occur under mild conditions and with high stereoselectivity. It has been found especially successful in reductions of phosphine oxides possessing heteroatom activating groups in the α and β positions as demonstrated recently by Kiełbasiński [20], us [21], and others [22]. With a possible exception of five-membered ring phosphine oxides [18], the major limitation of this strategy has been its inefficiency in reductions of tertiary phosphine oxides which do not possess OH, NH or SH moiety in proximity to the P centre.

Therefore, we were interested in expanding the use of BH_3 on reduction of tertiary phosphine oxides which cannot be reduced by BH_3 complexes according to the existing protocols.

Herein, we wish to present the use of Ti(Oi-Pr)$_4$/BH_3-THF reducing system which combines the beneficial presence of a Lewis acid and reducing ability of BH_3 and enables the direct transformation of tertiary phosphine oxides to their P-borane derivatives. To our best knowledge such process has never been reported in the literature.

2. Results and discussion

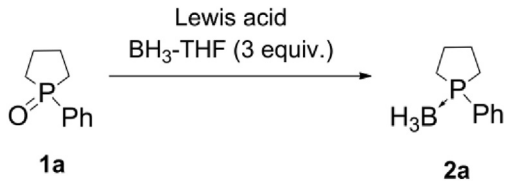
At the outset, we have investigated the influence of an added Lewis acid on BH_3 reduction of 1-phenylphospholane 1-oxide (**1a**) known already to undergo transformation into **2a** using BH_3 complexes alone, but only after prolonged heating at elevated temperature (60 °C, 2 d) [18]. The results of our screening experiments are listed in Table 1.

As the data collected in Table 1 indicate, this conversion can be effectively carried out at room temperature and in short reaction time when carried out in the presence of a Lewis acid. We focused our attention mainly on the use of Ti(Oi-Pr)$_4$ which was one of the most effective additives in the reported reductions by silanes [7–9].

First, we subjected **1a** to reduction by BH_3-THF in the presence of a catalytic amount of Ti(Oi-Pr)$_4$ (15% mol, Table 1 entries 1–2). These preliminary experiments revealed that conversion of starting material cannot be increased by prolonging the reaction time but that it was rather dependent on amount of added Lewis acid (Table 1, entries 1–3). However, even stoichiometric amount of Ti(Oi-Pr)$_4$ was not enough to transform **1a** into **2a** within expected time (Table 1, entry 4). It turned out that using 3-fold excess of Lewis acid was most beneficial and allowed to achieve complete conversion of **1a** to **2a** after 40 min (Table 1, entry 5). Briefly attempted use of other Lewis acids turned out to be much less effective (Table 1, entries 6–8). In case of $B(OMe)_3$ only 12% of expected product was obtained, even when the reaction was carried out at 60 °C for 24 h (Table 1, entry 6). In turn, BF_3*Et_2O complex under the same conditions has not provide **2a** (Table 1, entry 7). A catalytic amount of Yb(OTf)$_3$ used as an additive did not result in complete conversion of **1a** after 48 h at rt, and lead to desired **2a** in only 22% yield.

After this brief optimisation of the reaction conditions we turned then to check the possibility of similar reductions of representative tertiary phosphine oxides **3** which were known to be resistant to BH_3-THF alone. The results are summarised in Table 2.

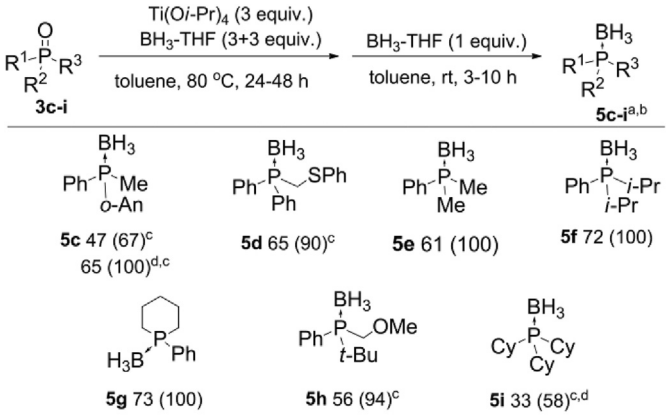
Table 1
Optimisation of reaction of **1a** in presence of different Lewis acids.



No.	Lewis acid (equiv.)	Conditions	Isolated yield of **2a** (%)
1	Ti(Oi-Pr)$_4$ (0.15)	rt, 55 min	37[a]
2	Ti(Oi-Pr)$_4$ (0.15)	rt, 4 h	37[a]
3	Ti(Oi-Pr)$_4$ (0.5)	rt, 55 min	50[a]
4	Ti(Oi-Pr)$_4$ (1.0)	rt, 55 min	70[a]
5	Ti(Oi-Pr)$_4$ (3.0)	rt, 40 min	98
6	$B(OMe)_3$ (3.0)	60 °C, 24 h	12[a]
7	BF_3*Et_2O (3.0)	60 °C, 24 h	0[a]
8	Yb(OTf)$_3$ (0.1)	rt, 48 h	22[a]

[a] Starting material present in the crude reaction mixture.

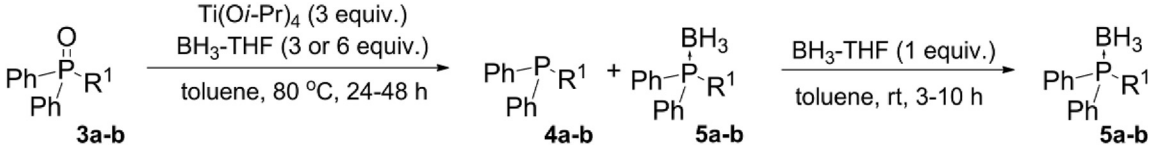
In the case of triphenylphosphine oxide (**3a**) it was quickly found that even with keeping the optimised stoichiometry of the reducing mixture, it was necessary to increase the reaction temperature to 80 °C in order to obtain a significant level of the reduction (Table 2, entry 1). Interestingly, in this case the product of the reaction was not the expected phosphine-borane **5a** but the corresponding phosphine **4a** which was isolated in 80% yield. When **3a** was subjected to a reaction with BH_3-THF/Ti(O*i*-Pr)$_4$ in a 6 equiv./3 equiv. ratio, we were pleased to find that **3a** was completely transformed into the corresponding tertiary phosphine-borane **5a** (91% isolated yield) after 24 h (Table 2, entry 2). The same conditions used for reduction of diphenylmethylphosphine oxide **3b** resulted in the formation of a mixture of **4b** and **5b** (isolated in 40% and 35% yield, respectively) (Table 2, entry 3). Lowering the amount of BH_3 complex failed to provide uncomplexed phosphine **4b** as the sole product, as it was observed in reaction of **3a**, but in this case we were able to isolate major free phosphine **4b** in 57% yield (Table 2, entry 4). For comparison, we also tried to use BH_3—SMe_2 (4 equiv.) as a hydride source in reductions of **3b**. In this case, **3b** was fully consumed and was converted directly to the expected phosphine-borane **5b**. No free phosphine **4a** was detected. However, **5b** was isolated in only 44% yield (Table 2, entry 5) due probably to the presence of another unidentified product detected in the crude reaction mixture by ^{31}P NMR (δ_P 48.0 ppm, broad peak) which could not be isolated.

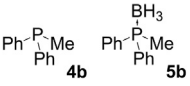
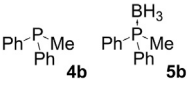


[a] Isolated yields of product. [b] Numbers in parentheses indicate yields according to ^{31}P NMR after additional complexation of phosphine with BH_3-THF. [c] Some amounts of the starting material were still present in the final reaction mixture. [d] Reaction was quenched without the additional boranation step. [e] Reaction was carried out with BH_3-SMe_2 (4 equiv.) at 80 °C for 24 h.

Scheme 2. Reduction of tertiary phosphine oxides **3c-i** with BH_3-THF/Ti(O*i*-Pr)$_4$.

Table 2
Optimisation of reduction of tertiary phosphine oxides **3a-b** with BH_3-THF/Ti(O*i*-Pr)$_4$.



Entry	Starting material	Conditions	Ratio of **4/5** after 24 h (^{31}P NMR)	Ratio of **4/5** after 48 h before addition of the second part of BH_3-THF (^{31}P NMR)	Product	Yield (%)[a,b]
1	 **3a**	BH_3-THF (3 equiv.), 24 h	**4a/5a** 80/0[c]	-	 **4a**	80 (80)[c,d]
2	 **3a**	BH_3-THF (6 equiv.), 24 h	**4a/5a** 0/100	–	 **5a**	91 (100)[d]
3	 **3b**	BH_3-THF (6 equiv.), 24 h	**4b/5b** 44/56	-	 **4b** **5b**	40 (44)[d,e] 45 (56)[d,f]
4	 **3b**	BH_3-THF (4 equiv.), 24 h	**4b/5b** 59/31	-	 **4b** **5b**	57 (59)[c,d,e] 20 (31)[c,d,f]
5	 **3b**	BH_3—SMe_2 (4 equiv.), 24 h	**4b/5b** 0/77	-	 **5b**	44 (77)[d]
6	 **3b**	BH_3-THF (3 + 3 equiv.), 48 h	**4b/5b** 33/63[c]	**4b/5b** 22/78	 **5b**	83 (100)

[a] Isolated yields of product.
[b] Numbers in parentheses indicate yields according to ^{31}P NMR after additional complexation of phosphine with BH_3-THF.
[c] Some amounts of the starting material were still present in the final reaction mixture.
[d] Reaction was quenched without the additional boranation step.
[e] The yield of **4b**.
[f] The yield of **5b**.

Therefore, to avoid this impediment, we focused our attention on application of BH_3-THF in the further study.

Because in case of **3b** addition of 6 equivalents of BH_3-THF at once did not result in effective transformation of P═O bond to P–BH_3 (Table 2, entry 3), we decided to add reagents initially in a 3 equiv./3 equiv. ratio and, after 24 h, add another 3 equiv. of BH_3-THF. We have found that under these modified conditions the selectivity of the reaction was markedly shifted towards the formation of **5b**, but still 22% of the produced phosphine **4b** remained uncomplexed in the reaction mixture even after 48 h (Table 2, entry 6). To complete the formation of **5b** additional portion of BH_3-THF (3 equiv.) was added and the reaction was stirred at room temperature until disappearance of **4b**. After this additional complexation, the reaction cleanly yielded phosphine-borane **5b** in 83% isolated yield.

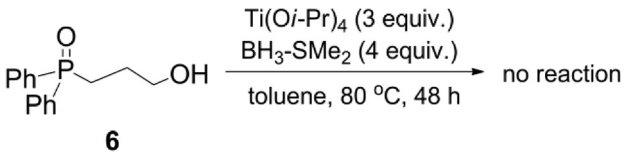
Next, the developed conditions were applied in reductions of a series of phosphine oxides of varied substitution pattern (Scheme 2). First we investigated another alkyldiarylphosphine oxide **3c** (PAMPO), possessing more crowded P═O centre. As expected, it exhibited low susceptibility to reduction under the studied conditions and even after 48 h the starting **3c** was consumed only in about 74%. Moreover, the phosphine **4c** appeared apparently the most resistant towards complexation by BH_3 among all the investigated cases and phosphine-borane **5c** was isolated in only moderate yield (47%). On the other hand, low complexation level (about 60% of **4c** and only 14% of **5c** in the crude reaction mixture after 48 h, see SI: Table 1) implies a reasonable access to **4c** under these reaction conditions. In addition, different reactivity of **3b** and **3c** points towards steric effects as an important factor influencing reduction rate of tertiary phosphine oxides. Interestingly, replacing BH_3-THF with BH_3–SMe_2 as a hydride source in reduction of **3c** resulted in complete conversion of **3c** into desired phosphine-borane **5c** which was finally isolated in 65% yield (Scheme 2, see also SI, Table 1).

Applying analogous reduction conditions to diarylalkylphosphine oxide **3d**, possessing protected sulfanyl moiety, resulted in nearly full consumption of **3d** as well as in much better selectivity towards formation of phosphine-borane and afforded **5d** in 65% isolated yield (Scheme 2).

Then, we investigated reductions of dialkylarylphoshine oxides **3e-h**. In all the four cases, we observed complete conversions of **3e-h** as well as the preferential formations of phosphine-boranes **5e-h** as the decidedly major products in the crude reaction mixtures. In the cases of **3e-g,** additional complexation step secured complete transformation of **4e-g** to the desired phosphine-borane **5e-g** what was confirmed by ^{31}P NMR. However, the isolated yields of **5e-g** fell in the range of 61–73%. Most probably, the applied water work-up must have lowered markedly the isolated yields in these cases. The highest amount of phosphine-borane **5** formed directly was observed in the case of **3h** where the ratio of phosphine **4h** to phosphine-borane **5h** equaled to 6/94 (see SI, Table 1). In this case additional complexation with BH_3 was omitted but isolated yield of **5h** was again lowered to 56%.

Finally, it is interesting to compare facility of reduction of cyclic phosphine oxides **1a** and **3g** by BH_3-THF/Ti(O*i*-Pr)$_4$. While at room temperature the five-membered phospholane oxide **1a** was swiftly reduced within 40 min (Table 1, entry 5), reduction of the six-membered ring phosphorinane oxide **3g** under the same conditions proceeded much more slowly to reach still incomplete 77% conversion after 24 h. This observation stays in line with early suggestion by Keglevich et al. that the five-membered ring strain facilitates the reduction of P═O bond with BH_3 [18].

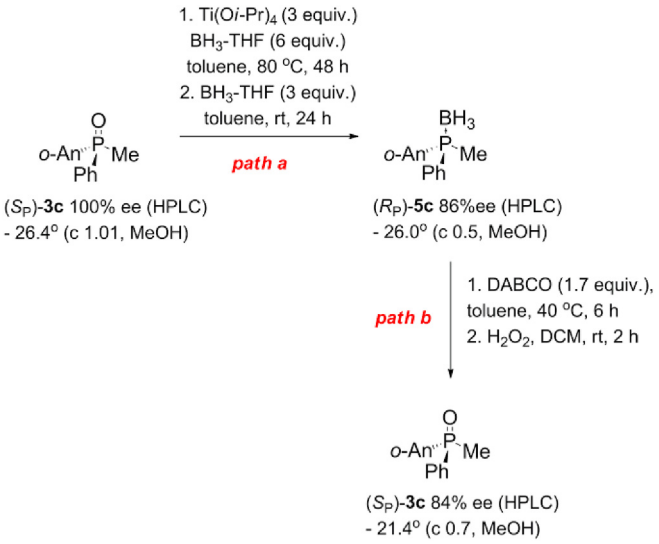
In contrast to **3a-h**, when tricyclohexylphosphine oxide (**3i**) was treated with BH_3-THF/Ti(O*i*-Pr)$_4$ system under the studied conditions the reaction was much slower and reached only 58% conversion in standard 48 h (see SI, Table 1). Nevertheless, the desired phosphine-borane **5i** was the only product formed and it was separated from the unconverted **3i** in 33% yield. Interestingly, the conversion of **3i** could not be improved by changing the borane reagent to BH_3–SMe_2, like it was observed for **3c** (Scheme 2). With this reagent the formation of only traces of **5i** was observed (not isolated).



Scheme 3. Attempted reduction of phosphine oxide **6** with BH_3–SMe_2/Ti(O*i*-Pr)$_4$.

We were also interested in checking whether phosphine oxides possessing free OH group in the γ-position (a position too distant to promote reduction by BH_3 according to our previously reported protocol [21a]) can be reduced with BH_3/Ti(O*i*-Pr)$_4$ reducing mixture. However, the attempted reduction of γ-hydroxyphosphine oxide **6** under the both studied conditions failed completely. In reaction of **6** with BH_3–SMe_2 only the starting oxide **6** was observed in the final reaction mixture (^{31}P NMR) (Scheme 3). In turn, use of BH_3-THF resulted in the formation of a mixture of phosphine oxides in which unreacted **6** was still the major constituent.

In the last part of this study, we investigated stereochemical outcome of the studied reduction. Toward this end, enantiomerically pure (S_P)-PAMPO (S_p)-**3c** was subjected to our optimised reduction protocol and gave **5c** in 58% yield (Scheme 4, path a). Then, the resulting **5c** was subjected to P-deprotection in the presence of DABCO at 40 °C for 6 h followed by oxidation of the resulting phosphine by H_2O_2 to afford optically active **3c** (Scheme 4, path b). Comparison of signs of the specific rotations of starting phosphine oxide (S_p)-**3c** with the one obtained in the correlation process revealed that both compounds possess the identical configuration at phosphorus. Hence, the absolute configurations of the newly formed oxide **3c** was assigned as S_P. These results indicated that the studied reduction had to occur with retention of configuration at phosphorus since the next two steps in the correlation i.e., deboranation of phosphine–borane by DABCO [16,23]

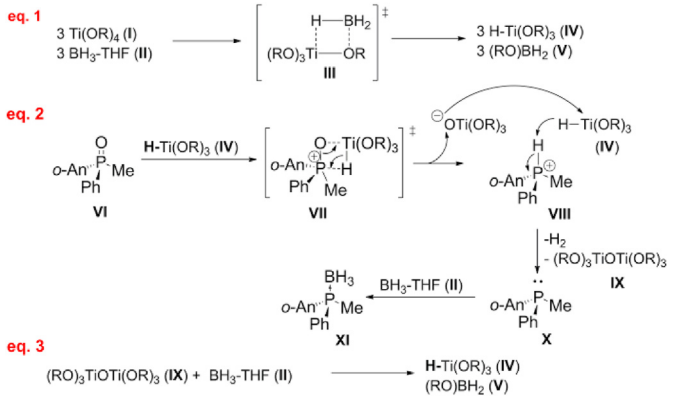


Scheme 4. Reduction of optically active phosphine oxide (S_p)-**3c** to phosphine-borane **5c** and its chemical correlation to (S_p)-**3c**.

and oxidation of phosphine by H_2O_2 [24], were already known to proceed with retention of configuration at the phosphorus atom. As evidenced by the HPLC analysis of the two oxides on a chiral stationary phase, the reduction took place with some loss of enantiomeric purity as the oxide obtained in the correlation process was found to be of 86% enantiomeric purity. This result closely resembles partial racemisations observed already by Lawrence [7] and by Lemaire [9] in their reductions of phosphine oxides by silanes promoted by Ti(O*i*-Pr)$_4$. Based on the early observation by Mislow et al. [25] that metal hydrides cause racemization of phosphines, it is tempting to assume that the involvement of the titanium hydride in the studied reductions mediated by Ti(O*i*-Pr)$_4$ may be responsible for the observed loss of enantiomeric purity of the produced phosphine.

A plausible mechanism of the studied reduction process which bears some resemblance to the mechanistic proposal reported for analogous reductions utilising (RO)$_3$SiH/Ti(O*i*-Pr)$_4$ system [7] is presented in Scheme 5. It commences with the formation of titanium hydride (**IV**) from Ti(OR)$_4$ (**I**) and BH$_3$-THF (**II**) via TS **III** (Scheme 5, eq. 1). The formation of titanium hydride **IV** is indicated by the development of a black colour (typically associated with the formation of titanium hydrides) which fades off when the reaction progresses. Then, triisopropoxytitanium hydride (**IV**) attacks the phosphoryl bond of **VI** with the formation of hydrophosphonium salt **VIII** via four-membered TS **VII**. Upon action of the second molecule of titanium hydride **IV**, assisted probably by triethyl titanoate anion, the hydrophosphonium salt **VIII** liberates free phosphine **X** and hydrogen, together with the formation of triethyltitanoate anhydride **IX**. Finally, added further equivalents of BH$_3$-THF (**II**) secure full conversion of **X** to **XI**, which with 3 or even 6 eq. of **II** originally applied has not always been complete (Scheme 4, eq. 2). Apparently, before this last protection stage, the free phosphine **X**, which according to this mechanism is formed with retention of configuration at P, can undergo partial racemization as it was observed in reduction of the optically active PAMPO (cf. Scheme 4). The proposed mechanism is fully consistent with the retention of configuration at phosphorus already evidenced in the correlation presented in Scheme 4.

Finally, the last equation (Scheme 5, eq. 3) presents the possible regeneration of titanium hydride (**IV**) in reaction of **IX** with another molecule of BH$_3$. This would explain why use of Ti(O*i*-Pr)$_4$ in only catalytic amounts could also be effective, and why it was necessary to add extra 3 equiv. of BH$_3$-THF to achieve complete boranation of the formed phosphine. However, the enhanced consumption of BH$_3$ in reductions of Ti—O bonds gives a possibility to obtain reduced phosphorus compound in either form, as free phosphine **4** or as phosphine-borane **5**, as confirmed in cases of **3a**, **3b**, and possibly also **3c** (cf. Table 2, entries 1–2, 3–4, and Scheme 2, respectively). This has not been optimised within the present work but apparently it may be used already to practical advantage at least in reductions of triarylphosphine oxides.



Scheme 5. Plausible mechanism of reduction of optically active phosphine oxide (S_p)-**3c** with BH$_3$-THF/Ti(O*i*-Pr)$_4$.

3. Conclusions

In summary, we have presented an efficient method for the direct one-pot conversion of tertiary phosphine oxides to the corresponding phosphine-borane derivatives using BH$_3$-THF in combination with Ti(O*i*-Pr)$_4$ as the reducing agents. The utility of the reduction process has been validated for triaryl, diarylalkyl, dialkylaryl and trialkylphosphine oxides. It is worth noting, that the developed reduction method expands the scope of the use of BH$_3$ as reducing agent also on simple tertiary phosphine oxides and thus, makes it complementary to previously reported reductions by this reagent which have been limited so far to five-membered ring phosphine oxides [18], secondary phosphine oxides [19], and tertiary phosphine oxides bearing proximal -XH (X = N, O, or S) activating groups [20–22]. The stereochemical course of the reduction process has been established by chemical correlation and a plausible mechanism of the reduction of the P═O bond by BH$_3$-THF/Ti(O*i*-Pr)$_4$ has been proposed.

It is also important to stress that the proposed use of BH$_3$ in combination with Ti(O*i*-Pr)$_4$ allows to avoid toxicity and potential hazard connected with the analogous use of silanes [7].

4. Experimental section

All reactions were performed under an argon atmosphere using Schlenk techniques. Only dry solvents were used, and glassware was heated under vacuum prior use. All chemicals were used as received unless noted otherwise. Solvents for chromatography and crystallization were distilled once before use and the solvents for extraction were used as received. Toluene were distilled from sodium/benzophenone ketyl under argon.

^{1}H NMR, ^{31}P NMR and ^{13}C NMR spectra were recorded on Bruker Advance 500 spectrometer at ambient temperature in CDCl$_3$ unless otherwise noted. Chemical shifts (δ) are reported in ppm from tetramethylsilane with the solvent as an internal indicator (CDCl$_3$ 7.27 ppm for ^{1}H and 77 ppm for ^{13}C). Mass spectra were recorded on Shimadzu GC-MS QP2010S in electron ionization (EI). Melting points were determined on Büchi Melting Point M – 560 in a capillary tube and were uncorrected. HPLC-HRMS was performed on Shimazu HRMS ESI-IT-TOF using reverse phase stationary phase with water/MeCN 65:35 as eluent, electrospray ionization (ESI), and IT-TOF detector. Optical rotations were measured on Perkin Elmer 341LC using a 1 mL cell with a 10 cm path length and are reported as follows: [α] [25]$_D$ (c: g/100 mL, in solvent). Elementary analyses were performed on PERKIN ELMER CHN 2400. Thin-layer chromatography (TLC) was performed with precoated silica gel plates and visualized by UV light or KMnO$_4$ solution or iodide on silica gel. The reaction mixtures were purified by column chromatography over silica gel (60–240 mesh).

4.1. Procedures

A. Procedure for the reduction of phospholane oxide **1a** using Ti(O*i*-Pr)$_4$/BH$_3$-THF (Table 1, entry 5)

In a Schlenk tube (25 mL) equipped with a magnetic stirrer and an argon inlet tertiary phosphine oxide **1a** (0.4 mmol) in anhydrous toluene (4 mL) was placed. Then, Ti(O*i*-Pr)$_4$ (0.355 mL, 1.2 mmol) was added followed by BH$_3$-THF complex (1.2 mL, 1.2 mmol, 1 M

solution in THF). After addition of BH_3 complex the reaction mixture was stirred at rt for 40 min. Reaction mixture was quenched with addition of 5% $NaHCO_3$ solution (5 mL). Then reaction mixture was transferred to separation funnel and extracted with $CHCl_3$ (4 × 10 mL). The collected organic phases were dried over Na_2SO_4, filtered off and evaporated to dryness. The residue was purified by column chromatography using silica gel hexane/AcOEt 6:1 as eluent.

1-Phenylphospholane-borane [26] **(2a). (Table 1, entry 4). 1a** (0.072 g, 0.4 mmol) was reacted according to general procedure **A** to afford **2a** (0.0697 g, 0.392 mmol, 98%) as a colourless oil; R_f 0.70 (hexane/AcOEt 2:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.50–1.20 (m, 3H), 2.00–2.29 (m, 8H), 7.46–7.53 (m, 3H), 7.72–7.75 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.7 (d, $J_{P\text{-}C}$ = 37.1 Hz, CH_2), 27.4 (s, CH_2), 128.7 (d, $J_{P\text{-}C}$ = 9.8 Hz, CH), 130.9 (d, $J_{P\text{-}C}$ = 2.3 Hz, CH), 131.3 (d, $J_{P\text{-}C}$ = 46.6 Hz, C), 131.3 (d, $J_{P\text{-}C}$ = 8.9 Hz, CH). ^{31}P NMR (202 MHz, $CDCl_3$) δ 28.60 (bm). *These data are consistent with those previously reported.* [26].

B. General Procedure for the reduction of tertiary phosphine oxides **3** using Ti(O*i*-Pr)$_4$/BH_3-THF (Table 2)

In a Schlenk tube (25 mL) equipped with a magnetic stirrer and an argon inlet, tertiary phosphine oxide **3** (0.2 mmol) in anhydrous toluene (1 mL) was placed. Then, Ti(O*i*-Pr)$_4$ (0.177 mL, 0.6 mmol) was added followed by BH_3-THF complex (0.6 mL, 0.6 mmol, 1 M solution in THF). After addition of BH_3 the reaction mixture was heated at 80 °C for 24 h. Then, another portion of BH_3-THF (0.6 mL, 0.6 mmol, 1 M solution in THF) was added and the mixture was left at 80 °C for 24 h to complete conversion of reaction and then reaction was again checked using ^{31}P NMR technique. Then, when necessary another portion of BH_3-THF (0.2 mL, 0.2 mmol, 1 M solution in THF) was added to transform free phosphine to phosphine-borane and reaction was left at rt until free phosphine was consumed (3–10 h). After this time reaction was checked using ^{31}P NMR technique. Then, the reaction mixture was quenched with addition of 5% $NaHCO_3$ solution (5 mL). Then reaction mixture was transferred to separation funnel and extracted with $CHCl_3$ (3 × 10 mL). The collected organic phases were dried over Na_2SO_4, filtered off and evaporated to dryness. The residue was purified by column chromatography using silica gel hexane/AcOEt 10:1 as eluent.

Triphenylphosphine [15b] **(4a). (Table 2, entry 1). 3a** (0.0556 g, 0.2 mmol) was reacted with BH_3-THF (0.6 mL, 0.6 mmol, 1 M solution in THF) according to modified general procedure **B** to afford **4a** (0.0419 g, 0.16 mmol, 80%) as a white solid; R_f 0.81 (hexane/AcOEt 6:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43–7.61 (m, 15H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 123.2 (d, $J_{P\text{-}C}$ = 7.2 Hz, CH), 123.6 (d, $J_{P\text{-}C}$ = 4.5 Hz, CH), 128.4 (d, $J_{P\text{-}C}$ = 1.8 Hz, CH), 128.6 (d, $J_{P\text{-}C}$ = 1.8 Hz, CH). ^{31}P NMR (202 MHz, $CDCl_3$) δ −5.36 (s). MS (70 eV): *m/z* (%): 263 (10), 262 (67) $[M]^+$, 261 (20), 184 (20), 183 (100). *These data are consistent with those previously reported.* [15b].

Triphenylphosphine-borane [27] **(5a). (Table 2, entry 2). 3a** (0.0556 g, 0.2 mmol) was reacted with BH_3-THF (1.2 mL, 1.2 mmol, 1 M solution in THF) according to modified general procedure **B** to afford **5a** (0.0503 g, 0.182 mmol, 91%) as a white solid; R_f 0.62 (hexane/AcOEt 6:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.70–1.40 (bm, 3H), 7.43–7.61 (m, 15H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 128.2 (d, $J_{P\text{-}C}$ = 10.0 Hz, CH), 129.2 (d, $J_{P\text{-}C}$ = 58.1 Hz, C), 131.2 (d, $J_{P\text{-}C}$ = 2.7 Hz, CH), 133.2 (d, $J_{P\text{-}C}$ = 10.0 Hz, CH). ^{31}P NMR (202 MHz, $CDCl_3$) δ 20.59 (bm). MS (70 eV): *m/z* (%): 263 (12), 262 (67) $[M\text{-}BH_3]^+$, 261 (21), 184 (21), 183 (100). *These data are consistent with those previously reported.* [27].

Diphenyl(methyl)phosphine-borane [2g] (**5b**). (Table 2, entry 6).

3b (0.0432 g, 0.2 mmol) was reacted according to general procedure **B** to afford **5b** (0.0355 g, 0.166 mmol, 83%) as a colourless oil; R_f 0.53 (hexane/AcOEt 6:1). HRMS (ESI) found: 427.2076. $C_{26}H_{31}B_2P_2$ requires 2 M^+, 427.2076). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.70–1.35 (bm, 3H), 1.88 (d, $J_{H\text{-}P}$ = 10.09 Hz, 3H), 7.43–7.52 (m, 6H), 7.65–7.69 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.8 (d, $J_{P\text{-}C}$ = 40.9 Hz, CH_3), 128.8 (d, $J_{P\text{-}C}$ = 10.0 Hz, CH), 130.4 (d, $J_{P\text{-}C}$ = 56.3 Hz, C), 131.1 (d, $J_{P\text{-}C}$ = 1.8 Hz, CH), 131.7 (d, $J_{P\text{-}C}$ = 10.0 Hz, CH). ^{31}P NMR (202 MHz, $CDCl_3$) δ 9.75 (bm). *These data are consistent with those previously reported.* [2g].

Diphenyl(methyl)phosphine [28] (**4b**). (Table 2, entry 4).

3b (0.0432 g, 0.2 mmol) was reacted with BH_3-THF (0.8 mL, 0.8 mmol, 1 M solution in THF) according to modified general procedure **B** to afford **4b** (0.0228 g, 0.114 mmol, 57%) as a colourless oil and **5b** (0.0086 g, 0.04 mmol, 20%).

4b

R_f 0.85 (hexane/AcOEt 6:1). HRMS (ESI) found: 217.0779; $C_{13}H_{13}OP$ $[M + O + H]^+$ requires: 217.0777. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.65 (d, $J_{H\text{-}P}$ = 3.47 Hz, 3H), 7.33–7.37 (m, 6H), 7.42–7.45 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.5 (d, $J_{C\text{-}P}$ = 13.6 Hz, CH_3), 128.35 (d, $J_{C\text{-}P}$ = 4.5 Hz, CH), 128.4 (d, $J_{C\text{-}P}$ = 1.8 Hz, CH), 132.8 (d, $J_{C\text{-}P}$ = 18.7 Hz, CH), 140.1 (d, $J_{C\text{-}P}$ = 11.8 Hz, C). ^{31}P NMR (202 MHz, $CDCl_3$) δ −26.82 (s). *These data are consistent with those previously reported.* [28]

***o*-Anisyl(methyl)phenylphosphine-borane** [29] **(5c). (Table 2, entry 7). 3c** (0.0492 g, 0.2 mmol) was reacted according to general procedure **B** to afford **5c** (0.0216 g, 0.094 mmol, 47%) as a white solid; R_f 0.40 (hexane/AcOEt 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.64–1.35 (m, 3H), 1.95 (d, $J_{H\text{-}P}$ = 10.56 Hz, 3H), 3.70 (s, 3H), 6.88–6.90 (m, 1H), 7.06–7.09 (m, 1H), 7.38–7.42 (m, 3H), 7.49–7.51 (m, 1H), 7.61–7.65 (m, 2H), 7.86–7.91 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.3 (s, C), 135.6 (d, $J_{P\text{-}C}$ = 14.5 Hz, CH), 133.7 (d, $J_{P\text{-}C}$ = 2.7 Hz, CH), 128.5 (d, $J_{P\text{-}C}$ = 59.0 Hz, C), 131.0 (d, $J_{P\text{-}C}$ = 10.0 Hz, CH), 130.3 (d, $J_{P\text{-}C}$ = 2.7 Hz, CH), 128.3 (d, $J_{P\text{-}C}$ = 10.9 Hz, CH), 121.1 (d, $J_{P\text{-}C}$ = 11.8 Hz, CH), 117.3 (d, $J_{P\text{-}C}$ = 54.5 Hz, C), 111.1 (d, $J_{P\text{-}C}$ = 4.5 Hz, CH), 51.3 (s, 3H), 10.5 (d, $J_{P\text{-}C}$ = 42.7 Hz, C). ^{31}P NMR (202 MHz, $CDCl_3$) δ 8.17 (bm). MS (70 eV): *m/z* (%): 230 (59) $[M\text{-}BH_3]^+$, 229 (44), 213 (13), 212 (10), 199 (62), 197 (37), 183 (51), 170 (11). *These data are consistent with those previously reported.* [29].

Diphenyl(phenylthiomethyl)phosphine-borane (5d). (Table 2, entry 8). 3d (0.0648 g, 0.2 mmol) was reacted according to general procedure **B** to afford **5d** (0.0419 g, 0.13 mmol, 65%) as a white solid; R_f 0.46 (hexane/AcOEt 10:1); m.p. = 75.5–76.5 °C; HRMS (ESI) found: 325.0818; $C_{19}H_{17}OPS$ $[M\text{-}BH_3{+}O + H]^+$ requires: 325.0810. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.76–1.48 (m, 3H), 3.72 (d, $J_{H\text{-}P}$ = 7.25 Hz, 2H), 7.20–7.29 (m, 5H), 7.45–7.56 (m, 6H), 7.73–7.77 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 33.8 (d, $J_{P\text{-}C}$ = 31.8 Hz, CH_2), 126.9 (s, CH), 127.8 (d, $J_{P\text{-}C}$ = 55.4 Hz, C), 128.8 (d, $J_{P\text{-}C}$ = 10.0 Hz, CH), 129.9 (s, CH), 131.6 (d, $J_{P\text{-}C}$ = 2.7 Hz, CH), 132.6 (d, $J_{P\text{-}C}$ = 9.1 Hz, CH), 135.8 (d, $J_{P\text{-}C}$ = 4.5 Hz, C). ^{31}P NMR (202 MHz, $CDCl_3$) δ 18.99 (bm). MS (70 eV): *m/z* (%): 308 (15) $[M\text{-}BH_3]^+$, 307 (7), 263 (13), 262 (50), 217 (14), 199 (54), 197 (10).

Dimethyl(phenyl)phosphine-borane [2g] **(5e). (Table 2, entry 9). 3e** (0.05 g, 0.324 mmol) was reacted according to general procedure **B** to afford **5e** (0.03 g, 0.198 mmol, 61%) as a colourless oil; R_f 0.55 (hexane/AcOEt 6:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.44–1.12 (bm, 3H), 1.58 (d, $J_{H\text{-}P}$ = 10.40 Hz, 6H), 7.46–7.51 (m, 3H), 7.71–7.77 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 12.9 (d, $J_{P\text{-}C}$ = 39.1 Hz, *C*H_3), 128.8 (d, $J_{P\text{-}C}$ = 10.0 Hz, *C*H), 130.8 (d, $J_{P\text{-}C}$ = 10.0 Hz, *C*H), 130.9 (d, $J_{P\text{-}C}$ = 54.5 Hz, *C*), 131.2 (d, $J_{P\text{-}C}$ = 1.8 Hz, *C*H). ^{31}P NMR (202 MHz, $CDCl_3$) δ 2.56 (bm). MS (70 eV): *m/z* (%): 151 (5) $[M]^+$, 150 (4), 149 (35), 148 (12), 139 (12), 138 (100) $[M - BH_3]$, 123 (39), 121 (37). *These data are consistent with those previously reported.* [2g].

Diisopropyl(phenyl)phosphine-borane [30] **(5f). (Table 2, entry 10). 3f** (0.042 g, 0.2 mmol) was reacted according to general procedure **B** to afford **5f** (0.0229 g, 0.144 mmol, 72%) as a white

solid; R_f 0.40 (hexane/AcOEt 10:1); m.p. = 35.9–36.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.26–0.93 (bm, 3H), 1.05 (dd, J_{H-H} = 6.94 Hz, J_{H-P} = 13.87 Hz, 3H), 1.17 (dd, J_{H-H} = 6.94 Hz, J_{H-P} = 15.45 Hz, 3H), 2.32–2.43 (m, 2H), 7.44–7.53 (m, 3H), 7.69–7.73 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 16.6 (d, J_{C-P} = 1.8 Hz, CH_3), 16.7 (s, CH_3), 21.7 (d, J_{C-P} = 34.5 Hz, CH), 125.2 (d, J_{C-P} = 48.1 Hz, C), 128.4 (d, J_{C-P} = 9.1 Hz, CH), 131.1 (d, J_{C-P} = 2.7 Hz, CH), 133.3 (d, J_{C-P} = 7.3 Hz, CH). ^{31}P NMR (202 MHz, $CDCl_3$) δ 33.71 (bm). MS (70 eV): *m/z* (%): 194 (39) [M-BH_3]$^+$, 152 (44), 151 (13), 110 (48), 109 (100), 108 (37), 107 (33).

1-Phenylphosphorinane-borane [31] **(5g). (Table 2, entry 11). 3g** (0.078 g, 0.4 mmol) was reacted according to general procedure **B** to afford **5g** (0.056 g, 0.292 mmol, 73%) as a colorless oil; R_f 0.53 (hexane/AcOEt 6:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.40–1.06 (m, 3H), 1.40–1.71 (m, 1H), 1.70–1.77 (m, 1H), 1.93–1.94 (m, 2H), 1.95–2.05 (m, 8H), 7.45–7.50 (m, 3H), 7.68–7.72 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.8 (d, J_{C-P} = 4.5 Hz, CH_2), 23.1 (d, J_{C-P} = 34.5 Hz, CH_2), 26.7 (d, J_{C-P} = 5.5 Hz, CH_2), 128.8 (d, J_{C-P} = 10.0 Hz, CH), 130.3 (d, J_{C-P} = 52.7 Hz, C), 130.9 (d, J_{C-P} = 2.7 Hz, CH), 131.0 (d, J_{C-P} = 8.2 Hz, CH). ^{31}P NMR (202 MHz, $CDCl_3$) δ 3.25 (bm). MS (70 eV): *m/z* (%): 179 (11), 178 (39) [M-BH_3]$^+$, 150 (44), 149 (42), 134 (10), 124 (16), 122 (11). *These data are consistent with those previously reported.* [31]

***t*-Butylphenyl(methoxymethyl)phosphine-borane** [21a] **(5h). (Table 2, entry 12). 3h** (0.0452 g, 0.2 mmol) according to general procedure **B** to afford **5h** (0.0251 g, 0.112 mmol, 56%) as a white solid; R_f 0.40 (hexane/AcOEt 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.27–0.92 (bm, 3H), 1.20 (d, J_{H-P} = 14.19 Hz, 9H), 2.93 (s, 3H), 4.13–4.25 (m, 2H), 7.43–7.47 (m, 2H), 7.52–7.54 (m, 1H), 7.91–7.94 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.2 (d, $^2J_{P-C}$ = 1.8 Hz, CH_3), 29.8 (d, J_{P-C} = 31.8 Hz, C), 61.7 (d, J_{P-C} = 9.1 Hz, OCH_3), 68.6 (d, J_{P-C} = 41.8 Hz, CH_2O), 126.5 (d, J_{P-C} = 49.9 Hz, C), 128.2 (d, J_{P-C} = 9.1 Hz, CH), 131.3 (d, J_{P-C} = 2.7 Hz, CH), 139.9 (d, J_{P-C} = 8.2 Hz, CH). ^{31}P NMR (202 MHz, $CDCl_3$) δ 28.90 (bm). MS (70 eV): *m/z* (%): 211 (2), 210 (12) [M-BH_3]$^+$, 180 (6), 154 (20), 125 (7), 124 (72), 123 (14), 122 (26), 121 (27). *These data are consistent with those previously reported.* [21a].

Tricyclohexylphosphine-borane [32] **(5j). (Table 2, entry 13). 3i** (0.059 g, 0.2 mmol) according to general procedure **B** to afford **5i** (0.0194 g, 0.066 mmol, 33%) as a white solid; R_f 0.76 (hexane/AcOEt 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ −0.04 -0.64 (bm, 3H), 1.18–1.44 (m, 15H), 1.68–1.96 (m, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 26.1 (s, CH_2), 27.2 (d, J_{C-P} = 9.9 Hz, CH_2), 27.8 (d, J_{C-P} = 1.8 Hz, CH_2), 30.8 (d, J_{C-P} = 30.9 Hz, CH). ^{31}P NMR (202 MHz, $CDCl_3$) δ 27.77 (bm). MS (70 eV): *m/z* (%): 281 (5), 280 (8) [M-BH_3]$^+$, 198 (10), 198 (26), 143 (8). *These data are consistent with those previously reported.* [32].

C. Reduction of optically active *o*-anisyl(methyl)phenylphosphine oxide (S_P)-(**3c**) [33] to *o*-anisyl(methyl)phenylphosphine-borane [2c] (**5c**) and its chemical correlation to *o*-anisyl(methyl) phenylphosphine oxide (S_P)-(**3c**) (Scheme 3)

(S_P)-3c[33]: $[\alpha]_D$ −26.4° (c 1.01, MeOH) (100% ee). HPLC OD-H: t_R = 17.91 min; 90:10 hexane/2-propanol; flow: 1.0 mL/min.

In a Schlenk tube (25 mL) equipped with a magnetic stirrer and an argon inlet, tertiary phosphine oxide (S_P)-**3c** (0.0589 g, 0.239 mmol) in anhydrous toluene (1 mL) was placed. Then, Ti(O*i*-Pr)$_4$ (0.177 mL, 0.6 mmol) was added followed by BH_3-THF (0.6 mL, 0.6 mmol, 1 M solution in THF). After addition of BH_3 complex the reaction mixture was heated at 80 °C for 48 h. After this time reaction was checked using ^{31}P NMR technique. Then, another portion of BH_3-THF (0.6 mL, 0.6 mmol, 1 M solution in THF) was added and the mixture was left at rt for 10 h to complete complexation with BH_3 of the free phosphine and then reaction was again checked using ^{31}P NMR technique. Then, the reaction mixture was quenched with addition of 5% $NaHCO_3$ solution (5 mL). Then, the reaction mixture was transferred to separation funnel and extracted with $CHCl_3$ (4 × 10 mL). The collected organic phases were dried over Na_2SO_4, filtered off and evaporated to dryness. The residue was purified by column chromatography using silica gel hexane/AcOEt (v/v = 10:1) as eluent affording (R_P)-**5c** as a white solid (0.0338 g, 0.139 mmol, 58%). $[\alpha]_D$ −26.0° (c 0.5, MeOH) (86% ee). HPLC IA: t_R = 15.555 min (minor enantiomer), t_R = 16.259 min (major enantiomer); 95:5 hexane/2-propanol; flow: 0.5 mL/min.

In a Schlenk tube (20 mL), (*o*-anisyl)(methyl)phenylphosphine–borane (**5c**) (0.0275 g, 0.113 mmol) in anhydrous toluene (2 mL) was dissolved. Then DABCO (0.021 g, 0.187 mmol) was added, and the mixture was stirred at 40 °C for 6 h. After cooling, solvent was removed under reduced pressure and 2 mL of DCM was added. Then 1 mL of H_2O_2 was added, and the mixture was stirred at room temperature for 1.5 h. The mixture was extracted with DCM (3 × 10 mL). The combined organic phases were dried over anhydrous MgSO4, filtered, and evaporated to dryness. The residue was purified by column chromatography (chloroform/ethyl acetate/methanol = 30:5:1) yielding **3c** (0.0147 g, 0.06 mmol, 53%). $[\alpha]_D$ −21.4° (c 0.7, MeOH) (84% ee). HPLC OD-H: t_R = 16.225 min (minor enantiomer), t_R = 18.228 min (major enantiomer); 90:10 hexane/2-propanol; flow: 1.0 mL/min.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2021.132057.

References

[1] (For reviews concerning the reduction of phosphine oxides see:). (a) L.D. Quin, In Guide to Organophosphorus Chemistry, Wiley-Interscience, New York, 2000;
(b) M. Zabłocka, K.M. Pietrusiewicz, Chem. Rev. 94 (1994) 1375–1411;
(c) D. Hérault, D.H. Nguyen, D. Nuel, G. Buono, Chem. Soc. Rev. 44 (2015) 2508–2528.
[2] (For examples, see:). (a) F. Hein, K. Issleib, H.Z. Rabold, Anorg. Chem. 287 (1956) 208–213;
(b) K. Issleib, G.Z. Grams, Anorg. Allg. Chem. 299 (1959) 58–68;
(c) T. Imamoto, S.-I. Kikuchi, T. Miura, Y. Wada, Org. Lett. 3 (2001) 87–90;
(d) T. Hanaya, H. Yamamoto, Bull. Chem. Soc. Jpn. 62 (1989) 2320–2337;
(e) S. Griffin, L. Heath, P. Wyatt, Tetrahedron Lett. 39 (1998) 4405–4406;
(f) 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. 7 (19) (2005) 4277–4280;
(g) 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. 73 (2008) 1524–1531;
(h) J.R. Pedroarena, B.P. Nell, L.N. Zakharov, D.R. Tyler, J. Inorg. Organomet. Polym. Mater. 30 (2020) 196–205.
[3] (For examples, see:). (a) H. Fritzsche, U. Hasserodt, F. Korte, Chem. Ber. 97 (1964) 1988–1993;
(b) H. Fritzsche, U. Hasserodt, F. Korte, Chem. Ber. 98 (1965) 171–174;
(c) L. Horner, W.D. Balzer, Tetrahedron Lett. 6 (1965) 1157–1162;
(d) K. Naumann, G. Zon, K. Mislow, J. Am. Chem. Soc. 91 (1969) 7012–7023;
(e) K. Naumann, G. Zon, K. Mislow, J. Am. Chem. Soc. 91 (1969) 2788–2789;
(f) A. Saare, L.Z. Dahlenburg, Naturforscher B 50 (1995) 1009–1017.
[4] (For examples, see:). (a) F. Mathey, R. Maillet, Tetrahedron Lett. 21 (1980) 2525–2526;
(b) M. Zabłocka, B. Delest, A. Igau, A. Skowronska, J.-P. Majoral, Tetrahedron Lett. 38 (1997) 5997–6000;

(c) Y. Handa, J. Inanaga, M. Yamaguchi, J. Chem. Soc., Chem. Commun. (1989) 298–299;
(d) A.-F. Pécharman, N.A. Rajabi, M.S. Hill, C.L. McMullin, M.F. Mahon, Chem. Commun. 55 (2019) 9035–9038.
[5] (For examples, see:). (a) R. Köster, Y. Morita, Angew. Chem. 77 (13) (1965) 589–590. Angew. Chem. Int. Ed. 1965, 4, 593-594;
(b) R. Köster, Y.-H. Tsay, L. Synoradzki, Chem. Ber. 120 (1987) 1117–1123;
(c) S. Hawkeswood, D.W. Stephan, Dalton Trans. (2005) 2182;
(d) C.B. Provis-Evans, E.A.C. Emanuelsson, R.L. Webster, Adv. Synth. Catal. 360 (20) (2018) 3999–4004.
[6] (a) F. Krech, K. Issleib, A. Zschunke, C. Mueggeand, S. Skvorcov, Z. Anorg. Allg. Chem. 594 (1991) 66–76;
(b) V. Ravindar, H. Hemling, H. Schumann, J. Blum, Synth. Commun. 22 (1992) 1453–1459;
(c) J.-F. Pilard, G. Baba, A.-C. Gaumont, J.-M. Denis, Synlett (1995) 1168–1170.
[7] T. Coumbe, N.J. Lawrence, F. Muhammad, Tetrahedron Lett. 35 (4) (1994) 625–628.
[8] M. Berthod, A. Favre-Réguillon, J. Mohamad, G. Mignani, G. Docherty, M. Lemaire, Synlett 10 (2007) 1545–1548.
[9] C. Petit, E. Poli, A. Favre-Réguillon, L. Khrouz, S. Denis-Quanquin, L. Bonneviot, G. Mignani, M. Lemaire, ASC Catal 3 (2013) 1431–1438.
[10] L. Pehlivan, E. Metay, D. Delbrayelle, G. Mignani, M. Lemaire, Tetrahedron 68 (2012) 3151–3155.
[11] Y. Li, S. Das, S. Zhou, K. Junge, M. Beller, J. Am. Chem. Soc. 134 (2012) 9727–9732.
[12] M. Mehta, I.G. de la Arada, M. Perez, D. Porwal, M. Oestreich, D.W. Stephan, Organometallics 35 (2016) 1030–1035.
[13] A. Chardon, O. Maubert, J. Rouden, J. Blanchet, ChemCatChem 9 (2017) 4460–4464.
[14] (a) Y. Li, L.-Q. Lu, S. Das, S. Pisiewicz, K. Junge, M. Beller, J. Am. Chem. Soc. 134 (2012) 18325–18329;
(b) C.J. O'Brien, F. Lavigne, E.E. Coyle, A.J. Holohan, B.J. Doonan, Chem. Eur J. 19 (19) (2013) 5854–5858;
(c) J.A. Buonomo, C.G. Eiden, C.C. Aldrich, Chem. Eur J. 23 (58) (2017) 14434–14438.
[15] (a) M.-L. Schirmer, S. Jopp, J. Holz, A. Spannenberg, T. Werner, Adv. Synth. Catal. 358 (2016) 26–29;
(b) T. Krachko, V. Lyaskovskyy, M. Lutz, K. Lammertsma, J.C.Z. Slootweg, Anorg. Allg. Chem. 643 (14) (2017) 916–921.
[16] T. Imamoto, T. Kusumoto, N. Suzuki, K. Sato, J. Am. Chem. Soc. 107 (1985) 5301–5303.
[17] (a) K.V. Rajendran, D.G. Gilheany, Chem. Commun. 48 (2012) 817–819;
(b) S.S. Al Sulaimi, K.V. Rajendran, D.G. Gilheany, Eur. J. Org Chem. (2015) 5959–5965;
(c) K.V. Rajendran, K.V. Nikitin, D.G. Gilheany, J. Am. Chem. Soc. 137 (29) (2015) 9375–9381.
[18] (a) G. Keglevich, T. Chuluunbaatar, K. Ludányi, L. Tőke, Tetrahedron 56 (2000) 1–5;
(b) G. Keglevich, M. Fekete, T. Chuluunbaatar, A. Dobó, V. Harmat, L. Tőke, J. Chem. Soc., Perkin Trans. 1 (2000) 4451–4455;
(c) T. Kovácsa, D. Cseresnyésa, L. Drahos, G. Keglevich, Phosphorus Sulfur and Silicon 192 (2017) 695–699.
[19] (a) M. Stankevič, K.M. Pietrusiewicz, Synlett 7 (2003) 1012–1016;
(b) K.M. Pietrusiewicz, M. Stankevič, Curr. Org. Chem. 9 (2005) 1883–1897.
[20] (a) P. Kiełbasiński, M. Albrycht, R. Żurawiński, M. Mikołajczyk, J. Mol. Catal. B Enzym. 39 (2006) 45–49;
(b) M. Kwiatkowska, G. Krasiński, M. Cypryk, T. Cierpiał, P. Kiełbasiński, Tetrahedron: Asymmetry 22 (2011) 1581–1590.
[21] (a) S. Sowa, M. Stankevič, A. Szmigielska, H. Małuszyńska, A.E. Kozioł, K.M. Pietrusiewicz, J. Org. Chem. 80 (2015) 1672–1688;
(b) S. Sowa, M. Stankevič, A. Flis, K.M. Pietrusiewicz, Synthesis 50 (2018) 2106–2118.
[22] (a) S. Lemouzy, D.H. Nguyen, V. Camy, M. Jean, D. Gatineau, L. Giordano, J. Naubron, N. Vanthuyne, D. Herault, G. Buono, Chem. Eur J. 21 (2015) 15607–15621;
(b) H.Y. Su, M.S. Taylor, J. Org. Chem. 82 (2017) 3173–3182;
(c) J. Chrzanowski, D. Krasowska, M. Urbaniak, L. Sieroń, P. Pokora-Sobczak, O.M. Demchuk, J. Drabowicz, Eur. J. Org Chem. (2018) 4614–4627;
(d) D. Gatineau, D.H. Nguyen, D. Hérault, N. Vanthuyne, J. Leclaire, L. Giordano, G. Buono, J. Org. Chem. 80 (2015) 4132–4141.
[23] H. Brisset, Y. Gourdel, P. Pellon, M. Le Corre, Tetrahedron Lett. 34 (1993) 4523–4526.
[24] L. Horner, Pure Appl. Chem. 9 (1964) 225–244.
[25] P.D. Henson, K. Naumann, K. Mislow, J. Am. Chem. Soc. 91 (1969) 5645–5646.
[26] S. Kobayashi, N. Shiraishi, W.W.-L. Lam, K. Manabe, Tetrahedron Lett. 42 (41) (2001) 7303–7306.
[27] S.E. Ashbrook, N.G. Dowell, I. Prokes, S. Wimperis, J. Am. Chem. Soc. 128 (21) (2006) 6782–6783.
[28] S. Rommel, C. Belger, J.-M. Begouin, B. Plietker, ChemCatChem 7 (8) (2015) 1292–1301.
[29] J. Mattiza, D. A, M. Stankevic, K. Dziuba, A. Szmigielska, K.M. Pietrusiewicz, H. Duddeck, Tetrahedron Asymmetry 17 (18) (2006) 2689–2696.
[30] P.W. Frost, J.A.K. Howard, J.L. Spencer, J. Chem. Soc., Chem. Commun. 20 (1984) 1362–1363.
[31] X.-M. Sun, K. Manabe, W.W.-L. Lam, N. Shiraishi, J. Kobayashi, M. Shiro, H. Utsumi, S. Kobayashi, Chem. Eur J. 11 (1) (2005) 361–368.
[32] A. Blumenthal, P. Bissinger, H. Schmidbaur, J. Organomet. Chem. 462 (1) (1993) 107–110.
[33] K. Dziuba, M. Lubańska, K.M. Pietrusiewicz, Synthesis 52 (6) (2020) 909–916.