A Catalytic Method for the Reduction of Secondary and Tertiary Phosphine Oxides

Mikaël Berthod,[a] Alain Favre-Réguillon,[a,b] Jahjah Mohamad,[a] Gérard Mignani,[c] Gordon Docherty,[d] Marc Lemaire*[a]

[a] Laboratoire de Catalyse et Synthèse Organique, Institut de Chimie et Biochimie Moléculaires et Supramoléculaires (ICBMS), CNRS, UMR5246, Université Lyon 1, 43 Boulevard du 11 Novembre 1918, 69622 Villeurbanne, France
Fax +33(4)72448507; E-mail: marc.lemaire@univ-lyon1.fr

[b] Laboratoire de Chimie Organique, UMR 7084, Conservatoire National des Arts et Métiers, 2 Rue Conté, 75003 Paris, France

[c] Rhodia, Lyon Research Center, 85, Avenue des Frères Perret, BP 62, 69192 Saint-Fons Cedex, France

[d] Rhodia, Novacare, P.O. Box 80, Trinity Street, Oldbury, B69 4LN, UK

Received 26 March 2007

Abstract: TMDS has been found to be an efficient hydride source for the reduction of tertiary and secondary phosphine oxides using a catalytic amount of Ti(O*i*-Pr)$_4$. All classes of tertiary phosphine oxides, such as triaryl, trialkyl, and diphosphine, were effectively reduced.

Key words: phosphorus, reductions, titanium, hydrosiloxane, phosphine oxides

Transition-metal complexes incorporating phosphines and diphosphines as the ligands are frequently used catalysts in hydrogenation, hydroformylation, hydrocyanation, allylic substitution, hydrosilylations, and palladium- and nickel-catalysed coupling reactions.[1] The reduction of phosphine oxides in the final stage of a synthetic route constitutes a widely used synthesis of phosphine ligands. Indeed, because of the ease of interconversion of phosphine oxides and phosphines, it is possible to consider the oxo function as a protecting group on phosphorus.[2] Consequently, the search for safe and practical reducing reagents of phosphine oxides is of great importance.

A survey of the literature[3] showed a number of possible methods for the reduction of phosphine oxide. The existing reducing agents, though efficient in producing high yields of desired product, are pyrophoric such as metal hydride,[4] or harmful reagents such as silylhydride reagents.[5] Furthermore, these reagents, which have remained the reagent of choice for reduction of phosphine oxides, are used at temperatures far above their boiling points.[6] Thus, alternative reductions have been studied using an oxygen acceptor, such as chlorinated methyl disilanes,[7] hexachlorosilane,[8] POCl$_3$/(Et$_2$N)$_3$P,[9] or a CO/Cl$_2$/H$_2$ system.[10] It was shown that the deoxygenation step with sterically hindered or electron-deficient phosphine oxides can be improved using an oxygen acceptor, such as Ph$_3$P or (EtO)$_3$P in the presence of HSiCl$_3$.[11] Stoichiometric reagents, such as SmI$_2$/HMPA[12] or transition-metal-based systems[13] have also been used for the reduction of tertiary phosphine oxides.

Hydrosiloxane derivatives have emerged as potent reducing reagents. However, these compounds are not sufficiently potent hydride sources themselves and require activation. The combination of titanium(IV) isopropoxide with triethoxysilane efficiently converted esters to the corresponding primary alcohols.[14] The first example of catalytic reduction of phosphine oxides was described by Coumbe et al.[15] using this reducing system in THF. Two equivalents of triethoxysilane are needed for successful conversion. The proposed catalytic cycle involves reduction by a titanium hydride species generated by hydride transfer from the silane to titanium via a σ-bond metathesis process.[15,16] However, triethoxysilane can be disproportionated by titanium(IV) isopropoxide to form SiH$_4$, a pyrophoric gas.[17] Polymethylhydrosiloxane (PMHS)[18] (Figure 1) which is a free-flowing liquid polymer, soluble in most organic solvents and inert to air and moisture, can be a suitable substitute for (EtO)$_3$SiH, eliminating the risk of generating SiH$_4$, but involved the used of a stoichiometric amount of Ti(O*i*-Pr)$_4$.[15] The low reactivity of this system towards phosphine oxide reduction may be explained by the polymeric nature of the hydride source. Another disadvantage connected to the use of PMHS was the formation of a gel during the workup that may limit the recovery of the product.

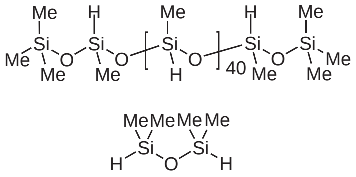
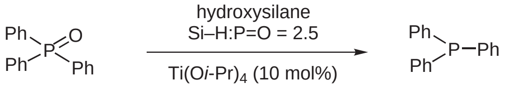


Figure 1 Structure of the polymethylhydrosiloxane (PMHS) and tetramethyldisiloxane (TMDS)

It therefore appeared reasonable that by using hydrosiloxane oligomers activated by an efficient catalyst we could significantly streamline the reduction of phosphine oxides. By switching to lower molecular weight commercially available hydrosiloxane, such as 1,1,3,3-tetramethyldisiloxane (TMDS, Figure 1) we could expect a more efficient catalytic process.[19] This idea was tested in a model study involving the reduction of triphenylphosphine oxide in the presence of catalytic amounts of Ti(O*i*-Pr)$_4$ in an aliphatic solvent (Table 1).

SYNLETT 2007, No. 10, pp 1545–1548
Advanced online publication: 07.06.2007
DOI: 10.1055/s-2007-982536; Art ID: G09407ST

Table 1 Reduction of Triphenylphosphine Oxide by Hydrosilane with a Catalytic Amount of $Ti(Oi\text{-}Pr)_4$



Entry	Hydrosiloxane	Solvent	Temp (°C)	Conditions	Yield (%)[a]
1	PMHS	THF	67	flask	25
2	TMDS	THF	67	flask	56
3	PMHS	THF	67	sealed tube	25
4	TMDS	THF	67	sealed tube	50
5	TMDS	methylcyclohexane	67	sealed tube	77
6	PMHS	methylcyclohexane	67	sealed tube	19
7	TMDS	toluene	100	sealed tube	100
8	PMHS	toluene	100	sealed tube	87
9	TMDS	methylcyclohexane	100	sealed tube	100[b]
10	PMHS	methylcyclohexane	100	sealed tube	90
11	TMDS	methylcyclohexane	100	flask[c]	100

[a] As calculated from ^{31}P NMR.
[b] Isolated yield.
[c] TMDS was added in four portions.

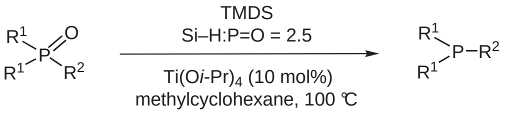
As a prelude to that goal, we re-examined the reduction of triphenylphosphine oxide using PMHS (Table 1, entry 1) according to Coumbe et al.[15] A 10 mol% catalytic amount of $Ti(Oi\text{-}Pr)_4$ refluxed in THF for 5 hours gave only moderate conversion (25%) justifying the use of the stoichiometric amount of $Ti(Oi\text{-}Pr)_4$.[15] Starting conditions using TMDS (Table 1, entry 2) revealed encouraging reaction features, i.e. moderate yields (56%) under the same conditions. Interestingly enough, no phosphinated side product or intermediary was detected during the course of the reaction. Moreover, the boiling point of TMDS (71 °C) is close to the reaction temperature and therefore suspected TMDS evaporation. Thus, the reaction was done in a sealed tube at 67 °C (Table 1, entries 3 and 4).[20] As expected, no improvement was noticed with PMHS (entry 3). The reaction appeared to be solvent- and temperature-driven (entries 5–10). Switching THF for methylcyclohexane (entry 5) improved the conversion and increasing the temperature to 100 °C (entry 9) yielded triphenylphosphine in five hours, using 10 mol% catalyst and a Si–H:P=O ratio of 2.5. The workup was straightforward. The reaction was cooled and concentrated in vacuum. The residue was suspended in pentane and insoluble triphenylphosphine was filtrated and washed with pentane.[21] Under those conditions, the conversion was 90% using PMHS (entry 10). Numerous types of catalysts have been used in combination with PMHS to reduce a wide range of organic functional groups.[16] The most frequently used catalyst are titanium species. We evaluated different titanium- and zirconium-based catalysts [Cp_2TiCl_2; $Zr(Oi\text{-}Pr)_4$–$HOi\text{-}Pr$; $Zr(OEt)_4$; $TiCl_4$) but from our work no reduction of triphenylphosphine oxides could be observed.

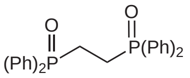
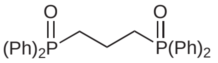
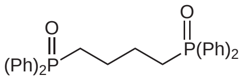
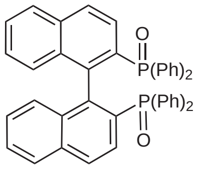
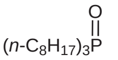
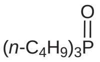
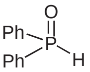
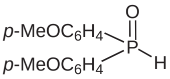
We decided to evaluate the scope of this new protocol with other phosphine oxides (Table 2).[22] Diphosphine oxides were effectively reduced to give diphosphine in excellent yields (Table 2, entries 1–3). We highlight the milder and safer conditions used for reducing phosphine oxides employing HMDS/$Ti(Oi\text{-}Pr)_4$ (110 °C) rather than $HSiCl_3/Et_3N$,[23] $PhSiH_3/HSiCl_3$[2] or $HSiCl_3/Ph_3P$ methods.[11]

This is particularly important in the reduction of the chiral BINAPO compound (Table 2, entry 4) where no racemisation was observed and the BINAP was obtained in high yield.[24] At the end of the reaction, the reaction mixture was cooled and filtered to give the diphosphine as a pure solid.[21]

Trialkylphosphine oxides[25] (Table 2, entries 5 and 6) and secondary phosphine oxides[26] (Table 2, entries 7 and 8) are also efficiently reduced by $Ti(Oi\text{-}Pr)_4$/TMDS. ^{31}P NMR analyses showed a completed conversion after 10 hours at 100 °C in methylcyclohexane. Pure trialkylphosphines and secondary phosphines could be recovered by distillation or could be isolated as borane complexes.[25,26] At the end of the reaction, the reaction mixture was cooled and BH_3–THF was added carefully and aqueous workup yielded pure borane complexes.[21]

Table 2 Reduction of Phosphine Oxides by TMDS with 10 mol% of Catalyst Ti(O*i*-Pr)$_4$



Entry	Phosphine	Conversion (%)[a]	Yield (%)[b]
1		100[c]	95
2		100[c]	91
3		100[c]	95
4		100[c]	92
5	 $(n\text{-}C_8H_{17})_3P{=}O$	100[d]	90[e]
6	 $(n\text{-}C_4H_9)_3P{=}O$	100[d]	95[e]
7		100[d]	85[e]
8		100[d]	89[e]

[a] As calculated from ^{31}P NMR.
[b] Isolated yield.
[c] After 7 h at 100 °C.
[d] After 10 h at 100 °C.
[e] Isolated as borane complexes.

In conclusion, we have shown that phosphine oxides are readily converted into the corresponding phosphine in high yield by the use of air-stable Ti(O*i*-Pr)$_4$ and TMDS. TMDS is more reactive than PMHS and could be proposed as a safer, easy-to-handle hydride source for the catalytic reduction of secondary and tertiary phosphine oxides.

References and Notes

(1) (a) *Comprehensive Asymmetric Catalysis I–III*; Jacobsen, E. N.; Pfaltz, A.; Yamamoto, H., Eds.; Springer: Berlin, **1999**. (b) Buchwald, S. L.; Mauger, C.; Mignani, G.; Scholz, U. *Adv. Synth. Catal.* **2006**, *348*, 23. (c) Berthod, M.; Mignani, G.; Woodward, G.; Lemaire, M. *Chem. Rev.* **2005**, *105*, 1801.

(2) (a) Berthod, M.; Mignani, G.; Lemaire, M. *Tetrahedron: Asymmetry* **2004**, *15*, 1121. (b) Berthod, M.; Saluzzo, C.; Mignani, G.; Lemaire, M. *Tetrahedron: Asymmetry* **2004**, *15*, 639.

(3) (a) For reviews of the literature on organophosphorus chemistry see all volumes of *Organophosphorus Chemistry*; Royal Society of Chemistry: Cambridge, UK, **1970-2006**. (b) Engel, R. *The Reduction of Quinquevalent Phosphorus to the Trivalent State*; Engel, R., Ed.; Marcel Dekker, Inc.: New York, **1992**.

(4) (a) LiAlH$_4$, see: Henson, P. D.; Naumann, K.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 5645. (b) LiAlH$_4$/CeCl$_3$, see: Imamoto, T.; Takeyama, T.; Kusumoto, T. *Chem. Lett.* **1985**, 1491. (c) LiAlH$_4$/MeOTf, see: Imamoto, T.; Kikuchi, S.-I.; Miura, T.; Wada, Y. *Org. Lett.* **2001**, *3*, 87. Alane (AlH$_3$) prepared in situ by addition of concd H$_2$SO$_4$ to a solution of LiAlH$_4$ in THF, see: (d) Griffin, S.; Heath, L.; Wyatt, P. *Tetrahedron Lett.* **1998**, *39*, 4405. (e) Bootle-Wilbraham, A.; Head, S.; Longstaff, J.; Wyatt, P. *Tetrahedron Lett.* **1999**, *40*, 5267. (f) DIBAL-H for *sec*-phosphine oxides: Busacca, C. A.; Lorenz, J. C.; Grinberg, N.; Haddad, N.; Hrapchak, M.; Latli, B.; Lee, H.; Sabila, P.; Saha, A.; Sarvestani, M.; Shen, S.; Varsolona, R.; Wei, X.; Senanayake, C. H. *Org. Lett.* **2005**, *7*, 4277. (g) Phosphine boranes can be obtained by treatment of the reaction mixtures with borane–THF or directly by reduction of phosphine oxides with borane in THF. For the reduction of tertiary phosphine oxides, see: Köster, R.; Morita, Y. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 593. (h) For the reduction of secondary phosphine oxides, see: Stankevic, M.; Pietrusiewicz, K. M. *Synlett* **2003**, 1012. (i) Phosphine boranes could be obtained directly from phosphine oxides by using a mixture of LiAlH$_4$/NaBH$_4$/CeCl$_3$, see: Imamoto, T.; Oshiki, T.; Onozawa, T.; Kusumoto, T.; Sato, K. *J. Am. Chem. Soc.* **1990**, *112*, 5244.

(5) (a) HSiCl$_3$: Horner, L.; Balzer, W. D. *Tetrahedron Lett.* **1965**, *21*, 1157. (b) HSiCl$_3$/NR$_3$: Cremer, S. E.; Chorvat, R. J. *J. Org. Chem.* **1967**, *32*, 4066. (c) PhSiH$_3$: Marsi, K. L. *J. Org. Chem.* **1974**, *39*, 265. (d) Ph$_2$SiH: McKinstry, L.; Livinghouse, T. *Tetrahedron* **1994**, *50*, 6145. (e) Me$_3$SiCl/LiAlH$_4$: Kyba, E. P.; Liu, S. T.; Harris, R. L. *Organometallics* **1983**, *2*, 1877.

(6) Trichlorosilane: fp –13 °C, bp 31 °C; phenylsilane: fp 8 °C, bp 120 °C; diphenylsilane: fp 98 °C, bp 97 °C.

(7) Deleris, G.; Dunogues, J.; Calas, R. *Bull. Soc. Chim. Fr.* **1974**, *3-4*, 672.

(8) Naumann, K.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 7012.

(9) Timokhin, B. V.; Kazantseva, M. V.; Blazhev, D. G.; Rokhin, A. V. *Russ. J. Gen. Chem.* **2000**, *70*, 1310.

(10) Masaki, M.; Kakeya, N. *Angew. Chem., Int. Ed. Engl.* **1997**, *16*, 552.

(11) Wu, H.-C.; Yu, J.-Q.; Spencer, J. B. *Org. Lett.* **2004**, *6*, 4675.

(12) Handa, Y.; Inanaga, J.; Yamaguchi, M. *J. Chem. Soc., Chem. Commun.* **1989**, 298.

(13) (a) Phosphine oxides have been reduced using stoichiometric amount of MgCp$_2$TiCl$_2$ in boiling THF: Mathey, F.; Maillet, R. *Tetrahedron Lett.* **1980**, *21*, 2525. (b) Phosphine oxides have been reduced using two equiv of Schwartz reagent: Zablocka, M.; Delest, B.; Igau, A.; Skowronska, A.; Majoral, J.-P. *Tetrahedron Lett.* **1997**, *38*, 5997.

(14) Berk, S. C.; Buchwald, S. L. *J. Org. Chem.* **1992**, *57*, 3751.

(15) Coumbe, T.; Lawrence, N. J.; Muhammad, F. *Tetrahedron Lett.* **1994**, *35*, 625.

(16) Lawrence, N. J.; Drew, M. D.; Bushell, S. M. *J. Chem. Soc., Perkin Trans. 1* **1999**, 3381.

(17) $(EtO)_3SiH$ should be used properly since it is volatile and is known to cause blindness. Furthermore, incident using this product have been reported, see ref. 12 in: (a) Berk, S. C.; Kreutzer, K. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1991**, *113*, 5093. (b) Berk, S. C.; Buchwald, S. L. *J. Org. Chem.* **1993**, *58*, 3221.

(18) PMHS has already been used to reduce tertiary phosphine oxides neat at 280–300 °C, see: Fritzsche, H.; Hasserodt, U.; Korte, F.; Friese, G.; Adrian, K.; Arenz, H. J. *Chem. Ber.* **1964**, *97*, 1988.

(19) **SAFETY:** TMDS is quite stable and not generally considered as a hazardous material, but under specific conditions, TMDS can generate high volumes of hydrogen gas in acid and basic conditions. Thus, all the necessary precautions for the safe handling of flammable gases should therefore be observed as mentioned in MSDS. Although TMDS proved to be stable up to 250 °C in a glass vessel, small exothermic reactions were observed with metallic ones. Furthermore, the use of glassware always gives rise to significantly higher conversion than the use of metal-containing reactors. This is probably due to the low stability of the titanium hydride intermediate. Further studies are being done to confirm this.

(20) Ace pressure tube Aldrich Ref. Z181099. We have checked that under those conditions the internal pressure does not exceed 1.2 bar.

(21) **CAUTION:** The TMDS remaining in the filtrate must be destroyed by slow addition of a 3 M alcoholic solution of KOH at r.t. TMDS decomposes on contact with bases, forming hydrogen.

(22) **General Procedure for the Reduction of dppe, dppp, and dppb Oxides**

In a 30 mL sealed tube with a magnetic stirrer were placed the diphosphine (2.32 mmol) and methylcyclohexane (5 mL). Then, TMDS (1.03 mL, 5.8 mmol, 2.5 equiv) was added to the reaction vessel followed by $Ti(Oi\text{-}Pr)_4$ (0.07 mL, 0.23 mmol). The flask was heated at 100 °C. After 7 h, the ^{31}P NMR analysis showed the complete conversion of the starting reagent. The heterogeneous mixture was cooled at 0 °C, filtrated over porous glass and washed with 4 × 5 mL of pentane. The resulting white solid was dried under vacuum, yielding the desired compound.

1,2-Bis(diphenylphoshino)ethane(dppe): yield 95%, mp 161 °C. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.32$ (20 H, m), 2.13–2.08 (4 H, m). ^{31}P NMR (81 MHz, $CDCl_3$): $\delta = -11.3$.

1,3-Bis(diphenylphosphino)propane(dppp): yield 91%, mp 63 °C. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.39$–7.33 (8 H, m), 7.30–7.28 (12 H, m), 2.21 (4 H, t, $J = 7.5$ Hz), 1.71–1.55 (2 H, m). ^{31}P NMR (81 MHz, $CDCl_3$): $\delta = -16.3$.

1,4-Bis(diphenylphosphino)butane(dppb): yield 95%, mp 135 °C. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.44$–7.34 (8 H, m), 7.33–7.30 (12 H, m), 2.04 (4 H, t, $J = 7.5$ Hz), 1.62–1.54 (4 H, m). ^{31}P NMR (81 MHz, $CDCl_3$): $\delta = -14.9$.

(23) Takaya, H.; Akutagawa, S.; Noyori, R. *Org. Synth., Coll. Vol. VIII* **1993**, *65-69*, 57.

(24) **(*S*)-2,2′-Bis(diphenylphosphino)-1,1′-binaphtyl (BINAP)** (a) In a tube with a magnetic stirrer was placed (*S*)-BINAP oxide (1.44 g, 2.2 mmol, 1 equiv) in 5 mL of methylcyclohexane. To this heterogeneous mixture was added TMDS (0.97 mL, 5.5 mmol, 2.5 equiv) and $Ti(Oi\text{-}Pr)_4$ (70 μL, 0,22 mmol, 0.1 equiv). The tube was sealed and the mixture stirred and heated at 100 °C overnight. The heterogeneous mixture was cooled at 0 °C and filtrated over porous glass, washing 4 to 5 times with cold pentane. The resulting white solid was dried under vacuum, yielding 1.26 g (92% yield, ee >98%). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.93$ (2 H, d, $J = 8.5$ Hz,), 7.88 (2 H, d, $J = 8.1$ Hz), 7.51 (2 H, d, $J = 8.5$ Hz), 7.39 (2 H, t, $J = 7.9$ Hz), 7.24–7.10 (20 H, m), 6.95 (2 H, dd, $J = 8.1$ Hz), 6.89 (2 H, d, $J = 8.5$ Hz). ^{31}P NMR (81 MHz, $CDCl_3$): $\delta = -14.3$. $[\alpha]_D^{25}$ –224 (*c* 0.365, benzene); lit. $[\alpha]_D^{25}$ –229 (*c* 0.31, benzene). The ee was determined after oxidation with H_2O_2 according to ref. 24b. Chiral column [Daicel Chiralpak AD, 0.46 cm ∅ × 25 cm, 254 nm UV detector, r.t., eluent 75:25 (*n*-heptane–2-PrOH), flow rate 0.5 mL/min], $t_R = 14.25$ min for *S* and 18.3 for *R*. (b) Sekar, G.; Nishiyama, H. *J. Am. Chem. Soc.* **2001**, *123*, 3603.

(25) **General Procedure for the Reduction of Trialkylphosphine Oxides**

In a 50 mL dried round-bottomed flask fitted with a magnetic stirrer and a condenser were placed the phosphine oxide (5.2 mmol) and methylcyclohexane (5 mL). Then, TMDS (1.14 mL, 6.5 mmol, 1.25 equiv) and $Ti(Oi\text{-}Pr)_4$ (154 μL, 0.52 mmol) were added to the reaction vessel. The heterogeneous mixture was stirred at 100 °C under an argon atmosphere. After 10 h, ^{31}P NMR analyses showed the complete conversion of the starting reagent. The mixture was cooled down to 0 °C and 1 M $BH_3\cdot THF$ (10.4 mL, 10.4 mmol, 2 equiv) was added dropwise to the solution. The mixture was allowed to warm to r.t. and stirred for 1 h. The solution was again cooled down to 0 °C and a 3 N alcoholic KOH solution (10 mL) was added dropwise to the reaction vessel (caution: abundant foaming). After gas formation has subsided, the resulting heterogeneous mixture was stirred at 50 °C under an argon atmosphere for 2 h. After cooling, the mixture was washed with H_2O (2 × 5 mL), a 10% aq solution of HCl (5 mL), and a sat. aq solution of $NaHCO_3$ (5 mL). The resulting solution was dried upon $MgSO_4$ and concentrated under vacuum, yielding a pale liquid containing only pure phosphine borane.

Tri-*n*-octylphosphine-borane (TOPB): yield 90%. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.61$–1.20 (42 H, m), 0.95–0.81 (9 H, m). ^{31}P NMR (81 MHz, $CDCl_3$): $\delta = 15.6$.

Tri-*n*-butylphosphine-borane (TBPB): yield 95%. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.54$–1.35 (18 H, m), 0.90 (9 H, t, $J = 7.1$ Hz). ^{31}P NMR (81 MHz, $CDCl_3$): $\delta = 15.6$.

(26) **General Procedure for the Reduction of Secondary Phosphine Oxides**

In a 50 mL dried round-bottomed flask fitted with a magnetic stirrer and a condenser were placed secondary phosphine oxide (2 mmol) and methylcyclohexane (5 mL). Then, TMDS (0.44 mL, 2.5 mmol, 1.25 equiv) and $Ti(Oi\text{-}Pr)_4$ (59 μL, 0.2 mmol) were added to the reaction vessel. The heterogeneous mixture was stirred at 100 °C under an argon atmosphere overnight. After 10 h, ^{31}P NMR analyses showed the complete conversion of the starting reagent. The mixture was cooled down to 0 °C and 2 M $BH_3\cdot DMS$ (3 mL, 6 mmol, 3 equiv) was added dropwise to the solution. The mixture was allowed to warm to r.t. and stirred for 2 h. The crude material was concentrated under vacuum and purified by flash chromatography EtOAc–cyclohexane (5:95) to give the product as a white solid.

Diphenylphosphine-borane: yield 85%. ^1H NMR (300 MHz, C_6D_6): $\delta = 7.44$–7.38 (4 H, m), 6.98–6.88 (6 H, m), 5.85 (1 H, d, $J = 378$ Hz), 2.40–1.36 (3 H, br m). ^{31}P NMR (81 MHz, C_6D_6): $\delta = 2.9$.

Bis(4-methoxyphenyl)phosphine-borane: yield 89%. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.57$ (4 H, dd, $J = 8.9$, 2.3 Hz), 6.96 (4 H, d, $J = 8.7$ Hz), 6.23 (1 H, d, $J = 378$ Hz). ^{31}P NMR (81 MHz, $CDCl_3$): $\delta = -1.54$.