DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

Rapid Metal-Free Formation of Free Phosphines from Phosphine Oxides

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Received: ((will be filled in by the editorial staff))

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.((Please delete if not appropriate))

Abstract. A rapid method for the reduction of secondary phosphine oxides under mild conditions has been developed, allowing simple isolation of the corresponding free phosphines. The methodology involves the use of pinacol borane (HBpin) to effect the reduction while circumventing the formation of a phosphine borane adduct, as is usually the case with various other commonly used borane reducing agents such as borane tetrahydrofuran complex (BH_3·THF) and borane dimethyl sulfide complex (BH_3·SMe_2). In addition, this methodology requires only a small excess of reducing agent and therefore compares favourably not just with other borane reductants that do not require a metal co-catalyst, but also with silane and aluminium based reagents.

Keywords: Phosphine oxide; reduction; pinacol borane

Introduction

Phosphines are a vitally important class of compounds; found in the synthesis of a vast range of metal complexes,[1] as organocatalysts in their own right,[2] as auxiliaries in the ubiquitous Wittig reaction,[3] and as chemical intermediates for P-C, P-P and P-X bond formation to name but a few.[4]

Complexes using phosphine based ligands find extensive use in homogeneous catalysis due to the favourable solubility and stability which the phosphine ligand can confer, and the tuneable properties of the resulting complexes.[5] The predictable and profound influence of ligand sterics and electronics on the metal render phosphines one of the most flexible ligand families available. Moreover, chiral phosphines have demonstrated remarkable efficacy for facilitating asymmetric induction in catalytic reactions.[6]

Phosphines have also been used as nucleophilic organocatalysts for a profusion of C-X (X: C, N, O, S) bond forming reactions employing unsaturated substrates, in addition to the formation of cyclic and heterocyclic products.[2b] If the phosphines used are themselves chiral, then these transformations can be performed asymmetrically under the right conditions, producing a myriad of invaluable enantiomerically enriched products.[2c]

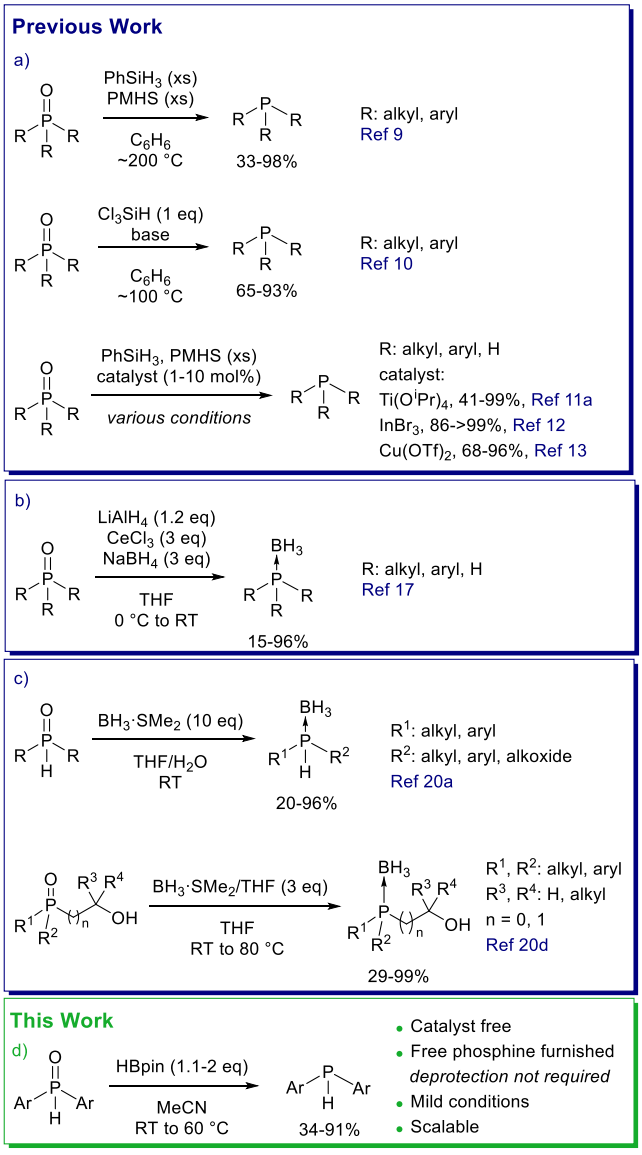
As a result of the diversity of uses for phosphines, their preparation has been the subject of academic and industrial interest for many decades. While tertiary phosphines are generally air stable as ligands in organometallic complexes, as free molecules they often demonstrate a tendency to oxidise to the P(V) phosphine oxides in the presence of air. Secondary phosphines are less stable to air than their tertiary analogues, while primary phosphines are even less stable; frequently demonstrating spontaneously pyrophoric behaviour on exposure to air. Often syntheses involving the use of secondary or primary phosphines therefore require scrupulously air-free techniques, which are difficult and expensive to maintain. Conversely, the phosphine oxides which these P(III) species so readily oxidise to are for the most part stable to both air and heat.[7]

The availability of effective and mild synthetic routes to P(V) phosphine oxides under air, and the comparative difficulty of performing the same sort of syntheses using less stable P(III) phosphines affords an opportunity; to perform the synthesis of a desired phosphine as the corresponding air-stable phosphine oxide, and only once this is complete, to reduce the P(V) centre to P(III) ready for whatever use is envisaged.

The stoichiometric reduction of P(V) phosphine oxides to P(III) phosphines was first discovered in the 1950s, and used relatively harsh reagents such as $LiAlH_4$ to reduce aryl and alkyl phosphine oxides, with concurrent production of H_2 at around 200 °C.[8] A variety of less onerous methodologies have been developed in the intervening years, notable among which are reductions using silicon and aluminium hydride sources, in addition to boranes.

A range of reductions using silane and siloxane based stoichiometric reductants have been

investigated. The first report from Fritzcsh *et al.* in 1964 used an excess of phenylsilane or polymethylhydrosiloxane (PMHS) at elevated temperatures and achieved yields of 33% to 98% for a variety of alkyl and aryl tertiary phosphine oxides.[9] Later work from the same group documented improved yields using equimolar chlorosilane in combination with triethylamine.[10] More recently high yields were achieved without the use of undesirable chlorosilanes by employing catalytic quantities of $Ti(O^iPr)_4$,[11] $InBr_3$,[12] $Cu(OTf)_2$,[13] $B(C_6F_5)_3$[14] or acid additives[15] in conjunction with much smaller excesses of an aryl silane and/or siloxane (*e.g.* TMDS, PMHS, DPDS) (Scheme 1a).



Scheme 1. Selected examples of phosphine reduction all of which require harsh conditions (a), excess reductant and a catalyst (a), a complex mixture of reagents in excess (b), or result in adduct formation (c). This work uses a catalyst-free method which generates the free phosphine (d).

As previously mentioned, $LiAlH_4$ was among the first reagents to be used in the reduction of the P(V) centre, although its utility ultimately proved to be limited to alkylphosphine oxides, with little activity in those with aryl substituents.[14] This was later mitigated using a Lewis acidic $CeCl_3$ auxiliary, which was theorised to activate the P-O bond and thereby facilitate the reduction in a much wider variety of substrates.[16] The addition of $NaBH_4$ to this system further improved the conditions required for the reduction, and also afforded the protected BH_3 adduct (Scheme 1b).[17] More recently, and rather elegantly, other aluminium based reductants have been shown by Tyler and co-workers to be effective in the gram-scale preparation of alkyl phosphines and primary phosphines.[18] Busacca *et al.* have employed 5 equivalents of DIBAL-H active in reducing sterically crowded secondary phosphine oxides in good to excellent yields under mild conditions.[19]

In addition to the myriad procedures for the reduction of phosphine oxides using silicon and aluminium based reagents, there are also ample examples in the literature of simple boranes being utilised for such reactions (Scheme 1c),[20] and these invariably afford the borane adduct of the P(III) species.[21] During recent studies into the homodehydrocoupling of secondary phosphines[22] we struggled to find a scalable reduction methodology with a simple work-up; many of the methods that employ aluminium reducing agents gel, meaning filtration and isolation procedures are laborious. We herein report a method for the reduction of phosphine oxides to the *free phosphines* using pinacol borane (HBpin) as the reducing agent (Scheme 1d). The work-up procedure is straightforward and rapid. While the free phosphine is less stable than the analogous borane adduct, this development allows the borane deprotection step to be avoided (which requires a stoichiometric or excess quantity of amine), and therefore synthetic procedures are significantly simplified.

Results and Discussion

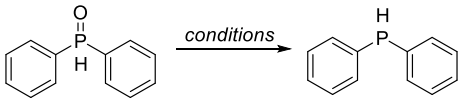
We rationalised that a simple, commercially available borane such as HBpin would be the ideal reagent with which to undertake the reduction of secondary phosphines: formation of the insoluble side product HOBpin (or pinBOBpin for tertiary phosphines[23]) would be a driving force allowing for only a slight excess of borane to be used and for facile work-up. The steric bulk of the borane, even if used in excess, should furnish the free phosphine on completion of the reaction.

We quickly established that this is indeed the case and work was undertaken to optimise the reduction of diphenylphosphine oxide by varying the solvent,

temperature and molar ratio of HBpin (Table 1). Despite there being a slightly higher isolated yield for Entry 5, 1.1 equivalents of HBpin was chosen as the standard conditions due to the difference in yield between Entries 5 and 6 being negligible. MeCN was chosen over toluene as it allows for a more straightforward work-up procedure. It is worth noting that catechol borane (HBcat) was tested but the conversion was not as good as that obtained with HBpin under identical conditions (compare Entry 1 and 3).

For the isolation of $HPPh_2$ wet, degassed $^{i}PrOH$ is added to the reaction mixture under an inert atmosphere, followed by filtration through a plug of alumina to remove pinBOBpin, eluting with MeCN. Removal of the solvent *in vacuo* furnishes the product in 72% yield.

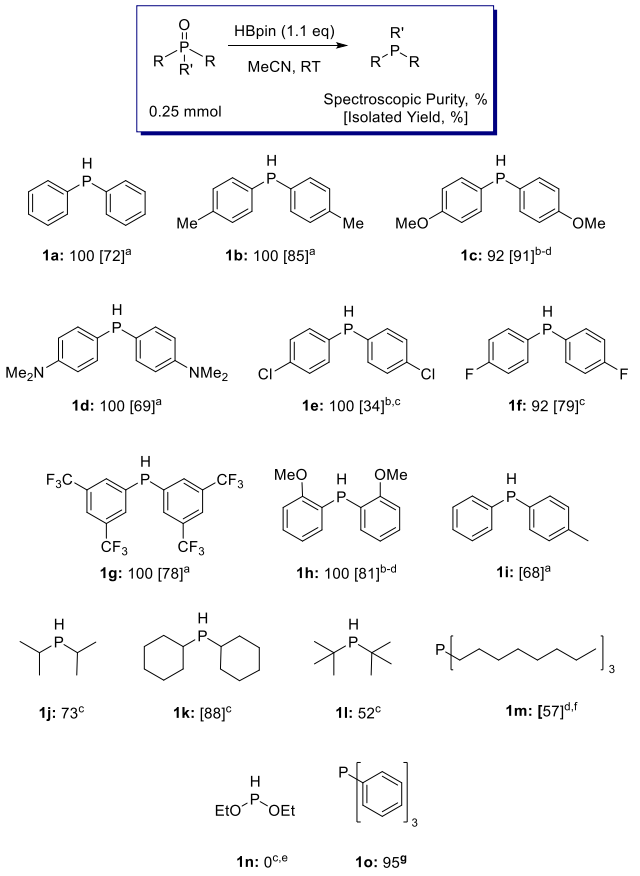
Table 1. Optimisation of reaction conditions.



Entry	Solvent	HBpin (eq.)	Conversion (%)[a]	Isolated yield (%)
1[b]	MeCN	1.0	84	-
2[c]	MeCN	1.0	95	-
3[c]	Toluene	1.0	90	63
4[b,d]	MeCN	1.0	40	-
5[c]	MeCN	1.2	100	75
6[b]	MeCN	1.1	100	72

[a] ^{31}P NMR data; [b] RT 2h; [c] RT, 20 h; [d] Catecholborane used rather than HBpin. Reaction did not proceed cleanly.

With these optimised conditions in hand, the substrate scope was explored. A variety of aryl secondary phosphine oxides were tested, as well as a tertiary phosphine oxide (Scheme 2).



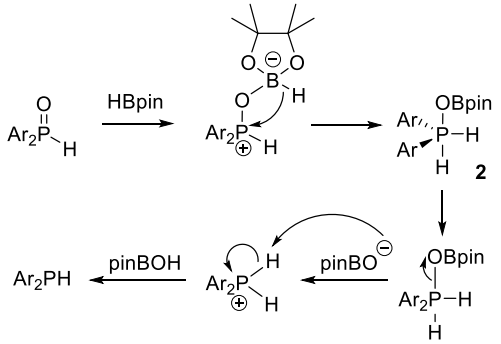
Scheme 2. Products of HBpin-mediated reduction of phosphine oxides. [a] 2h; [b] 60 °C; [c] 20 h; [d] 2 eq HBpin; [e] 80 °C; [f] 100 °C, 5 days; [g] 100 °C, 5 days.

The reduction of secondary aryl phosphine oxides proceeds well with quantitative or near quantitative spectroscopic yields obtained for all substrates tested. A variety of aryl phosphine oxides with electron withdrawing and donating substituents in the *para*-position are tolerated (**1b** to **1f**), with good isolated yields achieved in all cases with the exception of **1e**. In addition to this phosphine oxides containing both sterically and electronically challenging functionality can be readily reduced: 3,5-di-trifluoromethyl and *ortho*-methoxy substituted aryl phosphine oxides give excellent yields of the respective products (**1g** and **1h**). We also demonstrate that an unsymmetrical secondary phosphine oxide can be readily reduced at room temperature (**1i**) as can secondary alkyl phosphine oxides (to generate **1j** to **1l**). Unfortunately, no obvious reduction occurs with diethyl phosphite (to give phosphonite **1n**), but there is activity observed for the reduction of tertiary phosphine oxides (forming **1m** and **1o**), albeit under more forcing conditions (5 to 10 days at 100 °C).[23]

The reaction is scalable with 4.61 mmol (933 mg) $HP(O)Ph_2$ furnishing **1a** in 74% yield (636 mg). Even on this scale, the same straightforward work-up procedure can be followed and the resultant product is analytically pure.

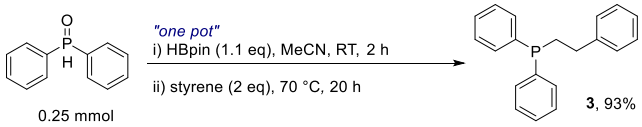
We propose that the reaction proceeds through the formation of a B–O adduct followed by a hydride shift,

affording the pentacoordinate trigonal bipyramidal species **2** (Scheme 3). Proton abstraction by the borolanolate can take place in an inter- (depicted) or intramolecular fashion.[24] This matches the generally accepted mechanism for borane-mediated reduction of phosphine oxides,[20d. 24] whilst avoiding phosphine-borane adduct formation that is inherent to other methodologies. The steric bulk of the pinacol and/or reduced Lewis acidity relative to BH_3 (due to hyperconjugation between the oxygen lone pairs and the empty *p*-orbital on boron) is hypothesised to disfavour the adduct formation, therefore affording the free phosphine. The analogous reaction performed using HBcat did not afford good yields of the free phosphine, so it may be that the HBpin has an optimal mix of Lewis acidic and steric properties which lend itself to this sort of reactivity.



Scheme 3. Postulated mechanism of phosphine reduction with HBpin.

A key transformation that uses secondary phosphines of the form **1a** is hydrophosphination. In order to show how useable the reduction procedure is, we employed a one pot procedure using first our reduction method followed by Alonso's catalyst-free hydrophosphination methodology[25] (Scheme 4). Hydrophosphination product **3** is obtained in excellent spectroscopic yield (93%).



Scheme 4. One pot reduction/ hydrophosphination.

Conclusion

We have developed a rapid and simple reduction method for secondary phosphine oxides which affords the free phosphine; a unique product for a borane reduction. This reaction has been shown to be fairly general and applicable to secondary phosphine oxides and to proceed slowly but inexorably in tertiary phosphine oxides. This allows the potential to expand the flexibility of phosphine synthesis generally, as it allows for phosphine oxides to be used as protected analogues for phosphines with a mild and efficient deprotection reaction.

Experimental Section

General method for reduction of phosphine oxides
Manipulations were carried out under an argon atmosphere in an M-Braun glove box. Phosphine oxides (0.25 mmol) and pinacolborane (1.1 - 2.0 equiv.) were added to a J. Young Schlenk tube along with 1 ml of dry MeCN or THF. The sealed tube was then maintained at the required temperature with stirring for the time specified. 200 µl of degassed isopropyl alcohol was then added to quench the residual HBPin, after which all the solvent was removed under vacuum. The residue was re-dissolved in MeCN or toluene under argon and passed through a plug of alumina into a pre-weighed vial inside a Schlenk tube. The solvent was then removed under vacuum and the vial re-weighed under argon to afford a yield.

Diphenylphosphane, 1a
Isolated yield: 72%. **^{1}H NMR (CD_3CN, 500 MHz):** δ 7.53-7.49 (m, 4H), 7.35-7.34 (m, 6H), 5.26 (d, 1H, J = 219.9 Hz); **^{13}C{^{1}H} NMR (CD_3CN, 126 MHz):** δ 136.1 (d, *i*-Ar, J = 10.0 Hz), 134.7 (d, *o*-Ar, J = 16.7 Hz), 129.7 (d, *m*-Ar, J = 6.0 Hz), 129.6 (s, *p*-Ar); **^{31}P NMR (CD_3CN, 202 MHz):** δ -39.7 (d, J = 220.0 Hz). Data comparable to previous reports in the literature.[19]

Di-*p*-tolylphosphane, 1b
Isolated yield: 85%. **^{1}H NMR (CD_3CN, 300 MHz):** δ 7.39-7.36 (m, 4H), 7.16-7.14 (m, 4H), 5.15 (d, 1H, J = 218.7 Hz), 2.30 (s, 6H); **^{13}C{^{1}H} NMR (CD_3CN, 126 MHz):** δ 138.7 (s, *p*-Ar), 133.8 (d, *o*-Ar, J = 17.1 Hz), 131.7 (d, *i*-Ar, J = 9.0 Hz), 129.4 (d, *m*-Ar, J = 6.3 Hz), 20.3 (s, Ar-CH_3); **^{31}P NMR (CD_3CN, 202 MHz):** δ –41.8 (d, J = 218.9 Hz). Data comparable to previous reports in the literature.[19]

Bis(4-methoxyphenyl)phosphane, 1c
Isolated yield: 91%. **^{1}H NMR (CD_3CN, 500 MHz):** δ 7.43-7.39 (m, 4H), 6.90-6.87 (m, 4H), 5.14 (d, 1H, J = 218.5 Hz), 3.95 (s, 6H); **^{13}C{^{1}H} NMR (CD_3CN, 126 MHz):** δ 161.2 (s, *p*-Ar), 136.3 (d, *o*-Ar, J = 18.4 Hz), 127.0 (d, *i*-Ar, J = 7.6 Hz), 115.3 (d, *m*-Ar, J = 6.7 Hz), 55.9 (s, O-CH_3); **^{31}P NMR (CD_3CN, 202 MHz):** δ –44.5 (d, J = 218.8 Hz). Data comparable to previous reports in the literature.[19]

4,4'-Phosphanediylbis(*N*,*N*-dimethylaniline), 1d
Isolated yield: 69%. **^{1}H NMR (C_6D_6, 500 MHz):** δ 7.67-7.65 (m, 4H), 6.63-6.61 (m, 4H), 5.61 (d, 1H, J = 212.2 Hz), 2.55 (s, 12H); **^{13}C{^{1}H} NMR (C_6D_6, 126 MHz):** δ 150.9 (s, *p*-Ar), 135.7 (d, *o*-Ar, J = 16.2 Hz), 125.0 (app. s, *i*-Ar), 113.0 (d, *m*-Ar, J = 2.8 Hz), 40.0 (s, N-(CH_3)$_2$); **^{31}P NMR (C_6D_6, 202 MHz):** δ -45.6 (d, J = 212.1 Hz). Data comparable to previous reports in the literature.[19]

Bis(4-chlorophenyl)phosphane, 1e

Isolated yield: 34%. **^{1}H NMR (CD_3CN, 500 MHz):** δ 7.47-7.44 (m, 4H), 7.36-7.34 (m, 4H), 5.22 (d, 1H, J = 222.4 Hz); **$^{13}C\{^1H\}$ NMR (CD_3CN, 126 MHz):** δ 135.4 (d, *o*-Ar, J = 17.5 Hz), 134.6 (s, *p*-Ar), 133.5 (d, *i*-Ar, J = 11.3 Hz), 128.8 (d, *m*-Ar, J = 6.2 Hz); **^{31}P NMR (CD_3CN, 202 MHz):** δ -42.8 (d, J = 222.3 Hz). Data comparable to previous reports in the literature.[19]

Bis(4-fluorophenyl)phosphane, 1f
Isolated yield: 79%. **^{1}H NMR (CD_3CN, 500 MHz):** δ 7.56-7.51 (m, 4H), 7.14-7.09 (m, 4H), 5.3 (d, 1H, J = 221.1 Hz); **$^{13}C\{^1H\}$ NMR (CD_3CN, 126 MHz):** δ 164.2 (d, *p*-Ar, J = 246.5 Hz), 137.0 (dd, *o*-Ar, J = 18.3, 8.1 Hz), 131.6 (dd, *i*-Ar, J = 10.8, 3.8 Hz), 116.7 (dd, *m*-Ar, J = 21.2, 6.9 Hz); **^{31}P NMR (CD_3CN, 202 MHz):** δ -44.2 (d, J = 221.0 Hz). Data comparable to previous reports in the literature.[19]

Bis(3,5-bis(trifluoromethyl)phenyl)phosphane, 1g
Isolated yield: 78%. **^{1}H NMR (CD_3CN, 500 MHz):** δ 8.14-8.12 (m, *o*-Ar, 4H), 7.97 (m, *p*-Ar, 2H), 5.58 (d, 1H, J = 230.1 Hz); **$^{13}C\{^1H\}$ NMR (CD_3CN, 126 MHz):** δ 138.6 (d, *i*-Ar, J = 16.6 Hz), 135.3 (dq, *o*-Ar, J = 17.7, 4.2 Hz), 132.4 (qd, *m*-Ar, J = 33.2, 5.7 Hz), 124.4 (q, CF_3, J = 272.2 Hz), 124.1 (app. hept, *p*-Ar, J = 3.8 Hz); **^{31}P NMR (CD_3CN, 202 MHz):** δ –41.7 (d, J = 229.9 Hz). Data comparable to previous reports in the literature.[19]

Bis(2-methoxyphenyl)phosphane, 1h
Isolated yield: 81%. **^{1}H NMR (CD_3CN, 500 MHz):** δ 7.34 (ddd, 2H, ^{4}Ar, J = 8.5, 8.1, 1.4 Hz), 7.19 (ddd, 2H, ^{3}Ar, J = 8.4, 7.4, 1.6 Hz), 6.96 (dd, 2H, ^{5}Ar, J = 8.2, 3.3 Hz), 6.89 (ddd, 2H, ^{2}Ar, J = 7.4, 1.3 Hz), 5.1 (d, 1H, J = 226.3 Hz), 3.80 (s, 6H); **$^{13}C\{^1H\}$ NMR (CD_3CN, 126 MHz):** δ 161.8 (d, ^{1}Ar, J = 9.6 Hz), 135.9 (d, ^{5}Ar, J = 9.5 Hz), 131.3 (s, ^{3}Ar), 123.1 (d, ^{6}Ar, J = 13.3 Hz), 121.9 (d, ^{4}Ar, J = 3.4 Hz), 111.5 (s, ^{2}Ar), 56.3 (s, O-CH_3); **^{31}P NMR (CD_3CN, 202 MHz):** δ –73.2 (d, J = 226.3 Hz). Data comparable to previous reports in the literature.[19]

Phenyl(*p*-tolyl)phosphane, 1i
Isolated yield: 68%. **^{1}H NMR (CD_3CN, 500 MHz):** δ 7.54-7.45 (m, 2H), 7.42-7.37 (m, 2H), 7.34-7.31 (m, 3H), 7.18-7.14 (m, 2H), 5.19 (d, 1H, J = 219.3 Hz), 2.31 (s, 3H); **$^{13}C\{^1H\}$ NMR (CD_3CN, 126 MHz):** δ 139.8 (s, ^{8}Ar), 136.6 (d, ^{5}Ar, J = 10.4 Hz), 135.0 (d, ^{3}Ar, J = 17.2 Hz), 134.5 (d, ^{6}Ar, J = 16.7 Hz), 132.2 (d, ^{4}Ar, J = 8.7 Hz), 130.4 (d, ^{2}Ar, J = 6.8 Hz), 129.6 (d, ^{7}Ar, J = 6.2 Hz) 129.4 (s, ^{1}Ar), 21.3 (s, Ar-CH_3); **^{31}P NMR (CD_3CN, 202 MHz):** δ –41.5 (d, J = 219.3 Hz). Data comparable to previous reports in the literature.[20a]

Dicyclohexylphosphane, 1k
Isolated yield: 88%. **^{1}H NMR (CD_3CN, 500 MHz):** δ 2.77 (dt, 1H, J = 195.0, 5.6 Hz), 1.88-1.13 (m, 27H); **$^{13}C\{^1H\}$ NMR (CD_3CN, 126 MHz):** δ 34.0 (d, J = 4.2 Hz), 33.1 (d, J = 18.9 Hz), 30.4 (d, J = 8.6 Hz), 27.8 (d, J = 3.1 Hz), 27.8 (d, J = 21.7 Hz), 27.1 (d, J = 0.7 Hz); **^{31}P NMR (CD_3CN, 202 MHz):** δ -28.1 (d, J = 198.1 Hz). Data comparable to previous reports in the literature.[19]

Trioctylphosphane, 1m
Isolated yield: 57%. **^{1}H NMR (C_6D_6, 500 MHz):** δ 1.36-1.20 (m, 42H), 0.82 (t, 9H, J = 6.8 Hz); **$^{13}C\{^1H\}$ NMR (C_6D_6, 126 MHz):** δ 32.1, 31.6 (d, J = 10.4 Hz), 29.5 (d, J = 12.0 Hz), 29.2 (d, J = 10.4 Hz), 27.6 (d, J = 13.2 Hz), 26.2 (d, J = 13.0 Hz), 22.8, 13.9; **^{31}P NMR (C_6D_6, 202 MHz):** δ -26.7. Data comparable to previous reports in the literature.[26]

Method for sequential reduction/hydrophosphination
Manipulations were carried out under an argon atmosphere in an M-Braun glove box. Diphenylphosphine oxide (0.25 mmol), pinacolborane (1.1 equiv.) and dichloroethane as an internal standard (1 equiv.) were added to a J. Young NMR tube and allowed to react without solvent at room temperature for 2 hours. Styrene (2 equiv.) was then added and the resulting neat mixture was heated at 70 °C for 20 hours to effect the hydrophosphination.[25]

Phenethyldiphenylphosphane, 3
Spectroscopic yield: 93% (1,2-dichloroethane used as an analytic standard). **^{1}H NMR (CD_3CN, 500 MHz):** δ 3.80 (s, 4H (DCE)), 2.73-1.68 (m, ^{1}C-H_2 1.76H), 2.42-2.38 (m, ^{2}C-H_2, 1.96H); **^{31}P NMR (CD_3CN, 202 MHz):** δ -16.7. Data comparable to previous reports in the literature.[27]

Acknowledgements

This research has been funded through an EPSRC Early Career Fellowship (EP/P024254/1) awarded to RLW. A PhD studentship has been awarded to CBPE as part of the Centre for Doctoral Training in Sustainable Chemical Technologies at the University of Bath (EP/L016354/1). Andrew King is acknowledged for provision of some phosphine oxide substrates that were used in this work.

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