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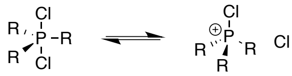
Electrophilic phosphonium cation-mediated phosphane oxide reduction using oxalyl chloride and hydrogen

Arne J. Stepen,[a][b] Markus Bursch,[c] Stefan Grimme,*[c] Douglas W. Stephan,*[b] and Jan Paradies*[a]

Abstract: The metal-free reduction of phosphane oxides with molecular hydrogen (H_2) using oxalyl chloride as activating agent was achieved. Quantum-mechanical investigations support the heterolytic splitting of H_2 by the *in situ* formed electrophilic phosphonium cation (EPC) and phosphane oxide and subsequent barrierless conversion to the phosphane and HCl. The reaction can also be catalyzed by the frustrated Lewis pair (FLP) consisting of $B(2,6\text{-}F_2C_6H_3)_3$ and 2,6-lutidine or phosphane oxide as Lewis base. This novel reduction was demonstrated for triaryl and diaryl phosphane oxides providing access to phosphanes in good to excellent yields (51-93%).

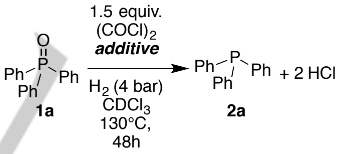
The reduction of phosphane oxides, in particular triphenylphosphane oxide (O=PPh$_3$, **1a**), is of great interest since it is produced on ton-scale in the industrial Wittig-reaction for the synthesis of vitamins.[1] Typical processes to recycle the phosphine oxides rely on the reductive deoxygenation with hydrosilanes at elevated temperatures in the presence of amines.[2] Only recently, a metal-free reduction of phosphane oxides using phosphites as reduction equivalent has been reported.[3] Alternative oxygen trapping reagents are phosgene derivatives and oxalyl chloride[4] which convert the phosphane oxides to the corresponding dichlorophosphoranes,[5] which are in equilibrium with the corresponding ionic chlorophosphonium chlorides (eq. 1).



eq. 1

Treatment of these electrophiles with elemental main-group metals (Si or Al) or sodium borohydride produces the corresponding phosphanes accompanied with stoichiometric amounts of aluminum/silicon chlorides or boron species.[4a, 6] The use of molecular hydrogen (H_2) as stoichiometric reductant would be highly desirable since only hydrochloric acid is produced. To date, no catalyst has been reported for such application. Only one patent details the reduction of phosgene-generate chlorotricyclohexylphosphane chloride with 150 bar H_2 at 160 °C. Neither further examples were presented nor the mechanism has been explored.[7]Boron-derived Lewis acids show outstanding reactivity in small molecule activation providing an unique catalytic access to hydride species directly from H_2.[8] Similarly, electrophilic phosphonium cations (EPCs) act as active Lewis acids and demonstrate high reactivity in bond activation[9] and in hydrogenations.[10] Both classes of main group-derived Lewis acids found wide application in hydrosilane reductions, reductive defluorinations[9a] and deoxygenations.[11] The reduction of phosphane oxides or derived chlorophosphoranes using H_2 as final reductant and main-group Lewis acid catalysts have so far not been precedented.

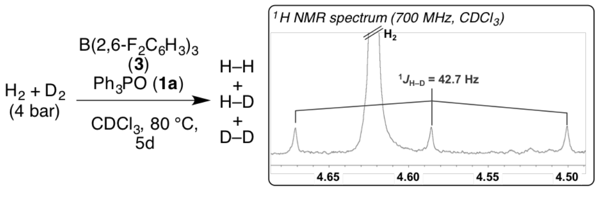
We initiated our investigations by pressurizing a mixture of **1a** and 1.5 equiv. oxalyl chloride in $CDCl_3$ with H_2 (4 bar). The typical ^{31}P NMR resonances of the phosphane oxide (38.3 ppm) vanished over a period of 30 min. with concomitant appearance of two new resonances, which were assigned to the dichlorotriphenylphosphorane (–46.2 ppm) and to the chlorophosphonium chloride (65.5 ppm) (lit. ref. –47.0 ppm; 65.5 ppm).[12][13] However, the reduction of these phosphorus species was not observed, potentially due to the absence of a suitable Lewis acid and/or Lewis base for H_2-activation (Scheme 1).



additive:	yield
no additive, 4 bar	0%
$B(2,6\text{-}F_2C_6H_3)_3$ (20 mol%) 2,6-lutidine (20 mol%), 4 bar	93%
$B(2,6\text{-}F_2C_6H_3)_3$ (20 mol%), 4 bar	98%
no additive, 80 bar	***93%***

Scheme 1. FLP-catalyzed reduction of triphenylphosphine oxide (**1a**) by $(COCl)_2/H_2$. Yields were determined after column chromatography.

This prompted us to use a FLP-catalyst consisting of the weak Lewis-acid $B(2,6\text{-}F_2\text{-}C_6H_3)_3$[14] (**3**) and 2,6-lutidine (**4**) to generate hydroborate species *in situ*. Indeed, the presence of 20 mol% of **3**/**4** and 4 bar H_2 resulted in 93% yield triphenylphosphine (**2a**). This result is remarkable, since 2 equiv. HCl are produced in the the reaction, which protonates 2,6-lutidine and should shut-down the hydrogenation. The control experiment with **3** (20 mol%) alone provided the product in almost quantitative yield of 98%. We identified triphenylphosphine oxide **1a** as the active Lewis base in the activation of H_2 (Scheme 2).



Scheme 2. Isotope exchange experiment with the FLP consisting of $B(2,6\text{-}F_2C_6H_3)_3$ (**3**) and Ph_3PO (**1a**) as Lewis base.

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The reaction of a 1:1 mixture of **3** and **1a** with H_2/D_2 (4 bar) at 80 °C resulted within 5d in the isotope scrambling to $HD/H_2/D_2$. These observations clearly indicate the ability of **3**/**1a** to act as hydrogenation catalyst.

Finally, we investigated the reaction at 80 bar H_2 in the absence of borane or amine. Surprisingly, under these conditions the product **2a** was obtained in 93% yield. The reduction proceeds presumably through the activation of H_2 by a Lewis pair consisting of Ph_3PO (**1a**) and of the electrophilic phosphonium cation $[Ph_3PCl]^+$. Careful consultation of the ^{31}P NMR spectra of the reaction revealed small quantities of phosphane oxide, most probably arising from water traces in the H_2 atmosphere. As control experiment, a sample of Ph_3PCl_2 was reacted with purified H_2 (4 bar) for 24 h at 130 °C in $CDCl_3$, but the formation of PPh_3 was not observed. After addition of phosphane oxide **1a** (20 mol%) to the sample, re-pressurization with purified H_2 (4 bar) and heating to 130 °C for 24 h, **2a** was produced in 25% yield. The reduced reaction rate must be attributed to the drastic pressure decrease. Nevertheless, these experiments strongly support the role of phosphine oxide as active Lewis base.

Quantum mechanical investigations at the double-hybrid PWPB95-D3(BJ, ATM)+COSMO-RS($CHCl_3$)/def2-QZVPP// PBEh-3c (COSMO($CHCl_3$))[15] level of theory with structure pre-optimizations applying GFN-xTB[16] revealed the ability of $[Ph_3PCl]^+$ to act as Lewis acid in combination with Ph_3PO as Lewis base (Figure 1).

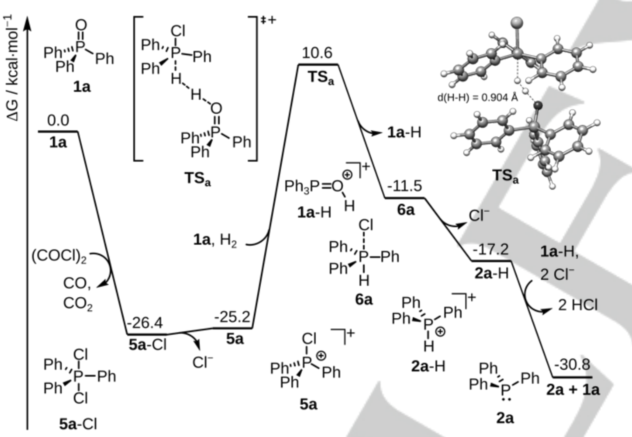
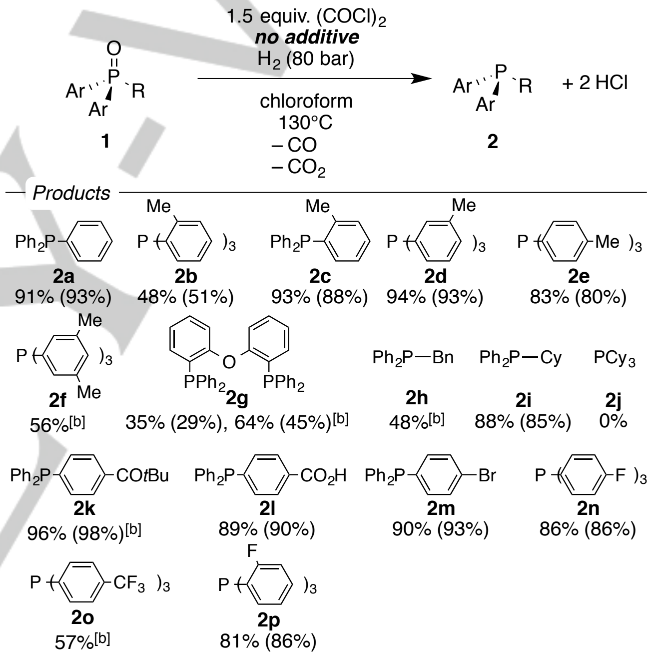


Figure 1. Relative Gibbs free energy diagram of the phosphane oxide reduction in $CHCl_3$. All energy values in kcal·mol^{-1} relative to **1a**. T = 130 °C.

The triphenylchlorophosphonium cation **5a** is obtained in a strongly exergonic reaction from the triphenylphosphane oxide (**1a**) and $(COCl)_2$. **5a** is in an almost barrierless equilibrium with the energetically slightly favoured triphenyldichlorophosphorane (**5a**-Cl) (ΔΔG = 1.2 kcal·mol^{-1}). An O-P coordinated, π-stacked adduct **1a/5a** (see Figure S1 in SI) of **1a** and **5a** is disfavoured by 4.2 kcal·mol^{-1} with respect to its isolated fragments in solution while the gas-phase association free energy amounts to −3.0 kcal·mol^{-1}. The heterolytic activation of H_2 by **5a** and the phosphane oxide **1a** requires 35.8 kcal·mol^{-1} with an overall reaction barrier of 37.0 kcal·mol^{-1} with respect to **5a**-Cl, which is in agreement with the required drastic reaction conditions. The transition state **TS₁** has an asymmetric, non-linear O-H-H-P unit (Angles / °: O-H-H = 176.1, P-H-H = 142.7; distances / Å: O-H = 1.337, P-H = 1.864) with a significantly elongated H-H bond distance of 0.904 Å. Some short intermolecular C-C interligand distances of approx. 3.5 Å in the structure of the transition state indicate the significance of attractive intermolecular interligand interactions, including π-π stacking for the stabilization of the transition state.[17] The subsequent conversion of the triphenylhydrochlorophosphorane (**6a**) into the protonated phosphane ([**2a**–H]) by chloride-loss is exergonic by –5.7 kcal·mol^{-1} leading to an overall exergonic process of –30.8 kcal·mol^{-1} after deprotonation of the protonated phosphane oxide intermediate (**1a**-H) and **2a**-H re-yielding **1a** and **2a**, respectively. According to this mechanistic model, the competence of the phosphine oxide/phosphonium Lewis pair to activate H_2 is strongly influenced by their electronic and steric properties.

Table 1. Reduction of phosphane oxides with oxalyl chloride/hydrogen.



[a] yields were determined by NMR spectroscopy, values in parentheses correspond to isolated yields after column chromatography; [b] reactions were performed in the presence of 20 mol% B(2,6-$F_2C_6H_3$)$_3$ (**3**) and 20 mol% 2,6-dimethylpyridine (**4**) at 4 bar H_2-pressure;

We investigated the reduction of a series of phosphane oxides (Table 1) at 80 bar H_2 (the results of the FLP-catalyzed low-pressure variant are summarized in Table S1 in the SI). Generally, triaryl and diaryl phosphane oxides were efficiently reduced. The diminished Lewis-acidity of more electron-rich chlorophosphonium ions is apparently counterbalanced by the increased Lewis-basicity of the corresponding phosphane oxides in the H_2-activation step. In detail, triphenylphosphane-oxide (**1a**) was reduced in excellent yield. Increase of steric bulk resulted in decrease of yields, as observed for P(*o*Tol)$_3$ (**1b**, 51%) and Ph$_2$P(*o*Tol) (**1c**, 88%). Methyl groups in meta or para position in **1d-f** were well tolerated and yields of 56% to 98% were obtained. The steric impact on the reactivity is also observed for bisphosphane derivatives. Although the dioxide derivatives of BINAP, xantphos and DPEphos (**1g**) were cleanly converted into the corresponding bis(chlorophosphonium chlorides, only the latter could be reduced in moderate yield of 45%. Next, we investigated the reactivity of alkyl-substituted phosphane oxides. Both, the benzyl and cyclohexyl derivatives **2h** and **2i** were reduced in 48% and 85% yield respectively, although differing methods were required. The low yield of **2h** may arise from a nucleophilic substitution on the chlorophosphonium intermediate by chloride. Steric hindrance in **1i** provides some kinetic stabilization and leads to significantly enhanced yield. Higher steric congestion in the tricyclohexyl derivative **1j** did not result in the formation of **2j** although quantitative formation of the corresponding chlorophosphonium chloride was observed. This is in agreement with a higher computed reaction barrier of 39.7 kcal·mol^{-1} and an endergonic reaction free energy of 6 kcal·mol^{-1} from **5j** to **2j** (For details see the Supporting Information). Finally, we investigated the impact of electron-withdrawing groups on the arene ring. Substituents in the 4-position of the arene ring in **1k-m** were well tolerated and the functionalized phoshanes were obtained in 90-98 % yield. Also, fluorinated triphenylphosphane derivatives **1n-p** were reactive. Whereas the 4-fluoro derivative **1n** was reduced in 86% yield, the corresponding CF_3-substituted derivative **1o** was only reactive in the presence of 20 mol% of the FLP. However, the 2-fluorophenyl derivative **1p** was obtained in high yield of 86%.

In summary, we have developed the metal-free reduction of phosphane oxides using oxalyl chloride and H_2. Quantum-mechanical calculations support the EPC-mediated heterolytic splitting of H_2 by the *in situ* generated chlorophosphonium ion followed by barrierless conversion to the phosphane and HCl. The applicability of the reduction was demonstrated for electron-donating and electron-withdrawing group substituted triaryl phosphane oxides providing the products in 51-98% yield.

Acknowledgements

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Keywords: hydrogenation • phosphane oxide • phosphane • frustrated Lewis pair • electrophilic phosphonium cation

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Layout 1:

COMMUNICATION

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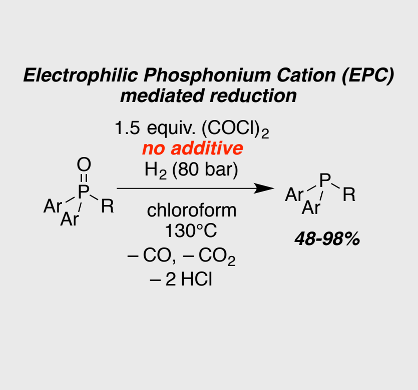

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