



## Review

## Primary phosphine chemistry

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We dedicate this review to our respected late colleague Professor Roger J. Griffin.

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## ABSTRACT

In this review we will consider the developments in the field of primary phosphine chemistry over the past 10 years. A significant section is devoted to the number of newly developed air-stable primary phosphines, and a DFT-based model will be presented which aims to rationalise the oxidative resistance of certain primary phosphines. Chiral and fluorescent examples of primary phosphines will be reviewed, along with some interesting examples of reactivity. Finally, a collection of coordination compounds from across the periodic table which contain primary phosphines will be highlighted.

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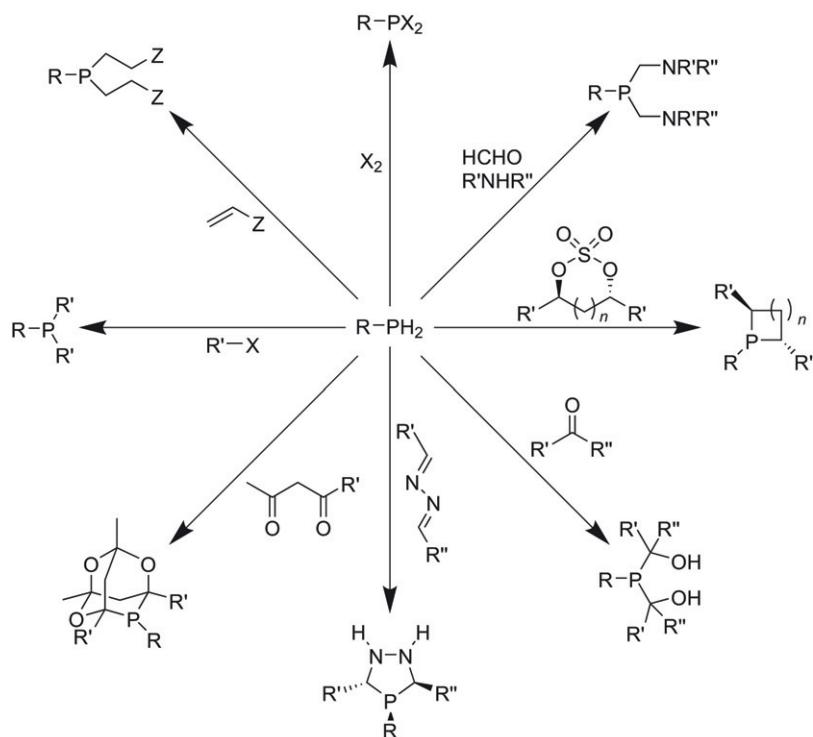
## 1. Introduction

Primary phosphines [1] are highly versatile precursors in the synthesis of functionalised phosphorus compounds due to the

high reactivity of the P–H bonds, and allow access to a range of molecules that are otherwise inaccessible or difficult to reach by other methods. **Scheme 1** provides a representation of reaction types which can be used to modify the phosphorus atom [2–4]. Primary phosphines have been used as starting materials in the fields of asymmetric catalysis [4], carbohydrate research [5], macrocyclic synthesis [6], medicinal chemistry [7] and polymer science [8]. Despite these diverse applications, there are still only a limited

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**Scheme 1.** Reactions to functionalise the P—H bonds in a primary phosphine ( $n$  = number,  $R/R'/R''$  = organic substituent,  $X$  = halogen and  $Z = R_2N, R_2P$ ).

number of reports on this functionality, in part due to certain pre-conceived ideas about their supposed high sensitivity to oxidation and noxious character, which lends them a reputation as being difficult to handle.

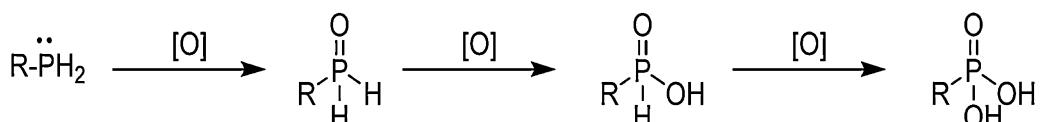
The reputation of primary phosphines as air-sensitive compounds, many of which are highly pyrophoric, is well deserved, especially those which are of a low molecular weight and lack steric encumbrance [9]. Decomposition occurs through an exothermic oxidation reaction which can be very rapid, even at room temperature (Scheme 2) [10]. This factor, in addition to other common characteristics of volatility, toxicity and unpleasant odour, appear to be the reasons why primary phosphines are not employed more routinely in the synthesis of organophosphorus compounds [11].

Brynda's review in 2005 cover those primary pnictanes which are found to be 'user-friendly' and focuses on the strategy of using bulky substituents in close proximity to the phosphino group to afford steric protection to air-oxidation – the review details the first examples of this approach dating back to the late 1960s. Some recently discovered examples of surprisingly air-stable primary phosphines containing heteroatoms or a ferrocenyl backbone were also introduced [1]. In the decade that has passed since Brynda's fascinating review, the number of "user-friendly" primary phosphines has steadily increased. While the air-stability of certain primary phosphines can be attributed to the well-known phenomenon of steric encumbrance, there have been a growing number of exam-

ples where the authors were unable to rationalise this unexpected stability. In this review, covering the period since Brynda's and also Katti's seminal works [1,3], we describe our efforts to synthesise air-stable enantiopure or fluorescent primary phosphines. In order to account for their resistance to air oxidation, we have developed a theoretical model of phosphine oxidation, and these DFT calculations have also proven to be a useful tool to rationalise the air-stability/sensitivity of other primary phosphines with previously unexplained air-stability; the model has also proven successful in predicting how novel primary phosphines behave towards air-oxidation [9,12]. We will discuss the salient features of this model, before moving on to report on some intriguing new primary phosphines, including chiral and fluorescent examples, and their applications. Finally, we move across the groups of the periodic table and highlight a number of interesting metal complexes of primary phosphines.

## 2. Air-stable primary phosphines

It is prudent at the outset to explain how we interpret 'air-stability'. For the purposes of this review, we mean the resistance of a primary phosphine to undergo oxidation by aerobic (or occasionally elemental) oxygen, in the absence of other oxidising agents. It is also worth noting that it is not always straightforward to compare literature examples of air-stability, as different authors judge this



**Scheme 2.** A simplified reaction showing the stepwise oxidation of primary phosphines.

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