Taming PH$_3$: State of the Art and Future Directions in Synthesis

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ABSTRACT: Appetite for reactions involving PH$_3$ has grown in the past few years. This in part is due to the ability to generate PH$_3$ cleanly and safely via digestion of cheap metal phosphides with acids, thus avoiding pressurized cylinders and specialized equipment. In this perspective we highlight current trends in forming new P−C/P−OC bonds with PH$_3$ and discuss the challenges involved with selectivity and product separation encumbering these reactions. We highlight the reactivity of PH$_3$ with main group reagents, building on the early pioneering work with transition metal complexes and PH$_3$. Additionally, we highlight the recent renewal of interest in alkali metal sources of H$_2$P$^-$ which are proving to be useful synthons for chemistry across the periodic table. Such MPH$_2$ sources are being used to generate the desired products in a more controlled fashion and are allowing access to unexplored phosphorus-containing species.

1. INTRODUCTION

There is an acute need to undertake drastic changes in the way we consume the Earth’s vital and finite resources, with much of this linked to changes needed to policies and practices of governments.$^1,2$ However, this should also bring into strong focus our need to undertake sustainable synthesis.$^3,4$ With this comes the need to develop new methods with which to undertake novel bond transformations; use reagents that avoid the generation of exogenous waste which requires protracted purification procedures; move away from harmful solvents; use feedstocks that are less activated (e.g., in the Earth’s crust); and use metals that are abundant (e.g., rock-forming metals) both in heterogeneous/homogeneous catalysis and in devices/materials.$^5$

Rather than providing prescriptive coverage of all reports on transformations involving PH$_3$, including the pioneering research into stoichiometric reactions with PH$_3$,$^6$ this perspective serves to highlight trends in the applications of PH$_3$, the “routine” P−C bond forming reactions that are base-mediated (i.e., reductive coupling) or involve the hydrofunctionalization of unsaturated bonds. This perspective will also cover more unusual transformations that form P−C bonds via other means, along with modern main group bond transformations and reactions with metals (Scheme 1).

The latter portion of this perspective goes beyond PH$_3$ and showcases the chemistry of the H$_2$P$^-$ anion. Recently, the use of alkali metal phosphides as a source of H$_2$P$^-$ has been receiving renewed interest. We will highlight some of the remarkable implementations of such salts, both in organic transformations and as promising reagents in the preparation of notable main group, transition metal, and f-block metal species.

We would be remiss not to briefly mention the numerous reports, during a prolific period of PH$_3$ research that took place between the late 1960s through to the early 1990s, on the reaction between PH$_3$ and transition metal (TM) complexes.$^7$−$^{15}$ Formation of TM complexes bearing the [TM]−PH$_3$ motif as well as formal oxidative addition/hydride abstraction to form [TM]−PH$_2$ and [TM]−(μ-PH$_3$)$_2$ motifs have been identified, with analysis ranging from multinuclear NMR and IR data only, through to those also reporting single crystal X-ray diffraction data. For example, Jones and co-workers reported the formation and isolation of a remarkably air-stable trans-[RuCl$_2$(PH$_3$)$_4$] complex.$^{16}$ However, further study into reactivity with these complexes has rarely been explored$^{17}$ and will therefore not be the focus of this perspective. However, this highlights the many seemingly...
simple areas of PH₃ research that are yet to be fully investigated.

2. AN IMPORTANT NOTE ON SAFETY

It would be irresponsible not to emphasize the dangers associated with handling PH₃, PH₃ is a highly toxic gas that is spontaneously flammable in air. The American Conference of Governmental Industrial Hygienists (ACGIH) places a time-weighted average limit on exposure at 0.05 ppm (which is the concentration of a substance to which most workers can be exposed without adverse effects), with a short-term exposure limit of 0.15 ppm (which means a 15 min time-weighted average exposure should not be exceeded at any time during an 8 h workday). The National Institute for Occupational Safety and Health (NIOSH) list 0.3 ppm as the time-weighted average limit and 1 ppm as the short-term exposure limit (10 h, 15 min respectively). The US Environmental Protection Agency lists 75 ppm as the 15 min TWA (time-weighted average limit) and 300 ppm as the short-term exposure limit (15 min respectively). The NIOSH short-term exposure limit for CO is 50 ppm.

To put these numbers into context, the NIOSH time-weighted average limit for CO is 35 ppm and the NIOSH short-term exposure limit for HCN is 4.7 ppm, while the 1 h LC₅₀ for HCN in rats is 139–144 ppm. In short, handling of PH₃ requires a robust risk assessment/COSHH assessment and rigorous safety protocols, not least a PH₃ monitor to ensure the safety of not only the chemist handling the substance but also other researchers in the lab. The fume hood setup must include NaOCl scrubbers or a PH₃ burner/H₂O spray to quench unreacted PH₃. Akin to our responsibility to study and develop more sustainable approaches to synthesis, safe use and quenching of this toxic gas, avoiding exposure of researchers and the environment to PH₃, this is paramount.

3. REACTING PH₃ TO FORM P−C/P−O C BONDS

PH₃ is the next downstream output from elemental phosphorus, which comes directly from industrial large-scale processing of phosphate rock. Numerous reviews on functionalization of P₂ exist, but the tetra-nuclear nature of this feedstock means that controlled, direct, or catalytic functionalization of P₂ into, for example, 4PR₃ is not well-documented. Instead, conversion of P₂ into PH₃ or PCl₃ and onward reaction to form organophosphines is the more traditional pathway. Onward reactions of PCl₃ with organic substrates to prepare P−C(sp³) bonds are well-documented, but wasteful in terms of atom economy.

P−C bond forming reactions with PH₃ range from stoichiometric-in-base-mediated reactions with alkyl halides through to hydroposphination in the presence of a metal catalyst, radical initiator, or a base. In many cases we invariably access products of the form Pr₄, although there are examples where HPR₃ and H₂PR are produced (vide infra). Even the hydroposphination literature has limitations: work on catalytic hydroposphination has routinely reported on the formation of the tertiary phosphine product as the major species, and only limited progress in diversifying the structure of the products, or the reaction selectivity, has been made. The reason that Pr₄ is formed preferentially can be linked to the enhanced reactivity of the product compared to the starting materials, i.e. PH₃ < H₂PR < HPR₃ and accessing H₂PR or HPR₃ tends to be achieved by limiting substrate stoichiometry rather than any greater form of reaction control. Stoichiometric-in-base transformations are simple to undertake and are well documented, but it could be argued that they serve to demonstrate the limitations in the organic transformations undertaken using PH₃; the reaction of RCl + base + PH₃ is simply the inverse of the classical method of using RH + base (or RCl + 2base) + PCl₃.

PH₃ is a reactive substrate, and the early work on the formation of phosphonium salts from PH₃ and formaldehyde dates back to at least 1888, with applications from this seminal study still very relevant today. Building upon work from Stiles et al. using photochemical initiation, an early report on catalytic functionalization of PH₃ came from Rauhut and co-workers where they disclosed the hydroposphination of acrylonitrile using PH₃ and aqueous KOH at room temperature. The reaction is mild, but is somewhat lacking in control, producing mixtures of primary, secondary, and tertiary cyanoethyl phosphines. Excess acrylonitrile allowed the formation of the tris-substituted product in 80% yield, and the secondary product could be formed in 58–63% when an excess of PH₃ is employed, while the primary cyanoethyl species is formed in 52% yield, but an autoclave operating at high pressure of PH₃ is needed (28–32 atm). The mono- and bis-substituted products were further employed in radical-mediated hydroposphination reactions. Rauhut and co-workers also employed azobis(isobutyronitrile) (AIBN) as a radical initiator to hydroposphinate with a range of alkenes in the presence of PH₃. Interestingly, although the ratio of primary/secondary/tertiary organophosphine product is often in the region of 1:1:1, reactions with unactivated systems such as 1-octene, 1-dodecene, cyclohexene, isobutylene, and butyl vinyl ether are reported (Scheme 2). In fact, 1-octene (1 mol), PH₃ (0.33 mol), and AIBN (5 mol %) is an exothermic reaction that generated a reaction temperature of 80–100 °C and produced 83% tris(octyl)phosphine cleanly after 6 h; this reaction is furthermore impressive as transformation of unactivated reagents has largely eluded modern hydroposphination catalysis.

Similar to the earlier work of Rauhut and co-workers, Trofimov and co-workers have recently reported base-mediated hydroposphination of 2 equiv. of styrene (or 4-fBu-styrene) with PH₃. The authors have published two possible onward transformations. The first is oxidation, to generate the anti-Markovnikov secondary phosphine oxide product, which is then used as a nucleophile to react with an aldehyde and finally, in the presence of FeCl₃, hydroxide abstraction to generate a carbocation in an SN1-type process. This then allows cyclization to form a phosphinoline oxide product (Scheme 3a). The second possible onward transformation is P−O or P−N bond formation at the para-position of azobenzenes, using a simple base to carry out the coupling

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Scheme 2. Rauhut and Co-workers’ Early Study into Radical Mediated Hydroposphination of Activated and Unactivated Alkenes

![Diagram of PH₃ reaction with PH₃ and AIBN to form RPH₂ + R₂P + PR₃](https://example.com/scheme2.png)
reaction (Scheme 3b).\textsuperscript{33} The UV/vis-mediated isomerization of the azo functionality was then investigated. Ragogna employed AIBN to prepare tertiary fluorinated alkyl phosphines which can then be transformed into phosphonium salts to attenuate the properties of UV-curable resins.\textsuperscript{34} Ragogna has also employed the early methods to prepare phosphinated lignin, which is effective as a metal scavenger. Compounds complexes for the reaction of formaldehyde with PH\textsubscript{2}Cl\textsubscript{2} salts, as well as tetrakis(phosphino) Pt, Pd, and Ni undertook the seminal work in this field and used platinum 1,2-shift step to generate the M=PR\textsubscript{3} hydrido phosphide species, and then insertion of the center, oxidative addition (OA) to generate a mixed metal(II) hydride transfer generates the M=PR\textsubscript{3} product (Scheme 4).\textsuperscript{36}

In contrast, many hydrophosphination reactions involving PH\textsubscript{3} have employed transition metal catalysts; Pringle undertook the seminal work in this field and used platinum as an example, cross-coupling reactions include SPhos (2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl), and XPhos (2-dicyclohexylphosphino-2',6'-triisopropylbiphenyl), and 2-yldiene as well as their complexes [(Me\textsubscript{3}Si)\textsubscript{2}N\textsubscript{3}M(NHC)\textsubscript{2}] (M = Ca, Yb, Sm) as precatalysts for hydrophosphination with PH\textsubscript{3}. Remarkably, they report the generation of primary phosphines based on the feedstock stoichiometry.\textsuperscript{37} A particularly intriguing reaction from this publication is the formation of tri(Z-styryl)phosphane; the acidic nature of both the phenylacetylene and PH\textsubscript{3} along with the selectivity for the kinetic all-Z product is remarkable. Transformations of this type warrant further investigation in terms of substrate scope (and with this E/Z selectivity) and onward functionalization with an eye toward applications.

Stoichiometric transformations are prevalent in the literature and follow similar trends in terms of the products formed and the makeup of the transformation. For example, Stelzer and Sheldrick report a KO\textsubscript{t}Bu route to prepare water-soluble phosphindoles/phosphindole oxides from PH\textsubscript{3}.\textsuperscript{38} Stelzer has also reported on exploiting the inherent equilibrium between PH\textsubscript{3} + OH\textsuperscript{-} \rightleftharpoons H\textsubscript{2}P\textsuperscript{3-} + H\textsubscript{2}O when aqueous DMSO/KOH solution (or with the inclusion of phase transfer catalysts such as (nBu\textsubscript{3})\textsubscript{3}NCl) is used, thus allowing generation of low concentrations of the highly nucleophilic H\textsubscript{2}P\textsuperscript{3-} ion for the selective reaction with organohalides forming (stoichiometry-driven) primary or secondary alkyl phosphines, bis(alkyl)-phosphines, and cyclic phosphines (Scheme 5a).\textsuperscript{39} Stelzer and co-workers have also employed iodine to prepare structurally exciting PH\textsubscript{2}—BINAP (1,1'-binaphthyl) and PH—BINAP systems (Scheme 5b).\textsuperscript{40}

Borangazieva and co-workers have reported an I\textsubscript{2}/pyridine system for the formation of trialkyl phosphates from PH\textsubscript{3} and methanol/ethanol/butanol/amyl alcohol/octanol.\textsuperscript{41} This methodology was further extended to the preparation of primary aminoaalkyl phosphines.\textsuperscript{42} A change to stoichiometric CuCl\textsubscript{2} in CCl\textsubscript{4} gives selective formation of the dialkyl phosphate (HP(O)(OiPr)\textsubscript{2}) when isopropanol is employed (Scheme 6).\textsuperscript{43} Further study into the reaction, and inclusion of quinone as a reductant, has also been reported.\textsuperscript{44}

However, in general, secondary and primary species are observed as side products in many reactions. Given the challenges associated with purification of reactive phosphines, particularly those that are the product of hydrophosphination reactions (where the product is invariably an alkyl phosphine and thus prone to oxidation), selective synthesis of a primary or secondary or tertiary phosphine is desirable. Moreover, when we look at commercial organophosphines, very few tertiary monophosphines are symmetrically substituted; there are key organophosphines such as PPh\textsubscript{3}, PCy\textsubscript{3}, and P(\textsuperscript{6}Bu)\textsubscript{3} but organophosphines routinely used in, for example, cross-coupling reactions include SPhos (2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl) and XPhos (2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl), and
bis(phosphines) such as dppf (1,1′-ferrocenediyl-bis(diphenylphosphine), XantPhos (4,5-bis(diphenylphosphino)-9,9-dimethylxanthene), and dppe (1,2-bis(diphenylphosphino)ethane) to name but a few. Here we raise another issue of a pure atom-economy-driven approach to PH$_3$ functionalization: that being that the preparation of P−Ar bonds is limited to work from Dorfman and Levina, and more recently Wolf (vide infra).

4. PH$_3$ REACTING WITH COMPOUNDS OF THE $p$-BLOCK

In the 1990s, Cowley and Jones undertook investigations into the reactivity of PH$_3$ with an alkyl gallium compound with a view to preparing precursors for OMCVD processes (organometallic chemical vapor deposition). The authors present a highly sensitive $\mu$-PH$_2$ cluster which undergoes slow decomposition at 200 °C (Scheme 7).

Further reports on reactions of PH$_3$, which we may consider being in the realm of main group bond transformations, are those involving NHCs and their heavier group 14 congeners. Grußmacher and Pringle reported the in situ generation of the SIPr (1,3-bis(2,6-diisopropylphenyl)imidazolidine-2-ylidene) NHC (1, Scheme 8) from the chloride salt, which forms the PH$_2$-imidazolidine product (2) from reaction with PH$_3$ and base (or the tert-butoxide adduct of NaPH$_2$). This product can then undergo hydrogen abstraction, driven by the aromatization of ortho-quinone, which allows the formation of the formal phosphinidine-carbene adduct (3). This latter species was shown to undergo complexation with HgCl$_2$.

Ragogna and Power have shown that PH$_3$ can oxidatively add to tetrylenes. The authors note a divergence in reactivity when comparing the chemistry of NH$_3$ and PH$_3$; the

The POV-Ray image of the single crystal X-ray structure (CCDC 1197532) shows a distorted 6-membered ring, but this is completely planar with no puckering. All H atoms removed for clarity.
former gives the OA product with Ge and the arene elimination dimeric product with the Sn congener (Scheme 9). However, when PH₃ is employed a mixture of the OA and

dimeric product is formed with both Ge and Sn (the OA product is the major species in both cases). ⁵⁷ Similar to the work of Ragogna and Power, where there is a discrepancy between the reactivity of the lighter and heavier pnictogens, Driess has demonstrated a difference in reactivity of PH₃ compared to AsH₃ when undertaking OA to silylene compounds. ⁵⁸ PH₃ generates the OA product, whereas with AsH₃, although OA takes place, there is an equilibrium between the arsenide product and the isomerized arsinidine species, making use of the ligand system to invoke this process.

Mitzel has employed both hydride sponge (4) and proton sponge (5, Scheme 10) as a frustrated Lewis pair (FLP) system to activate a range of small molecules, including PH₃. ⁵⁹ ⁶⁰ ⁶¹ ⁶² ⁶₃ ⁶₄ ⁶₅ ⁶₆ ⁶₇ ⁶₈ This hints that this could be a rich vein of research. Indeed, modification of the FLP structure could enable enantioselective transfer of the H₂P⁻ and H⁺ fragments to an organic substrate.

5. FUTURE TARGETS

At this stage it is useful to consider several aspects as we look toward future synthetic development targets with PH₃ or MPH₂. In an atom-economic, chemoselective manner, with wide-ranging functional group tolerance, key targets should include the following:

1. Controlled synthesis of primary or secondary or tertiary organophosphines. Reactions need to avoid the formation of mixtures that require complicated cleanup procedures or additional reduction steps to access the P(III) species from the P(V) phosphine oxide;
2. The synthesis of unsymmetrically substituted phosphines from PH₃ or MPH₂ and ultimately C₃ or P₃ sterogenic phosphines;
3. The preparation of P=Ar phosphines from PH₃ or MPH₂, e.g. PAR₃, through to P^Ar^Ar^Ar^ selectively;
4. Unique methods not only to activate PH₃ but also undertake onward functionalization, e.g. chemistry beyond hydrofunctionalization.

However, to make such advances PH₃ and MPH₂ needs to become more accessible to a wider range of researchers. Indeed, we envisage that many advances will be possible simply through PH₃ (or analogues of PH₃) being used more widely in research.

6. ALTERNATIVE SOURCES OF PH₃

The industrial standard for the production of PH₃ is the base-mediated disproportionation of white phosphorus, in the so-called Hoesch process. ⁶⁶ PH₃ is treated with sodium or potassium hydroxide at slightly elevated temperatures (50 °C). With very careful conditions the gas can be collected in ∼95% purity, though this procedure is not particularly practical for a research laboratory. The lab-scale synthesis of PH₃ has been achieved in a number of ways: by the treatment of PCl₃ with Na metal (followed by hydrolysis), ⁶⁷ the high-temperature treatment of black phosphorus in liquid hydrogen, ⁶⁸ and the pyrolysis of either hypophosphorous acid, phosphorous acid, or a salt of one of these acids. ⁶⁹ In 1967, the pyrolysis of phosphorous acid was described as the "most convenient" method for the generation of PH₃, ⁶⁹ however, in a modern...
research laboratory the idea of isolating PH$_3$ as a liquid by consecutive condensation and distillation is perhaps a barrier to implementation for many researchers. Additionally, Trofimov reported the generation of PH$_3$ from red phosphorus by treatment with aqueous KOH at 65−75 °C; however, this reaction is concomitant with the generation of dihydrogen and as such is limited to reactants that are inert toward dihydrogen and moisture.

6.1. Metal Phosphides for PH$_3$ Release. Handling pressurized gases, irrespective of toxicity, requires a level of rigor that is not necessarily required when handling solids. Recent reports on the use of metal phosphides, e.g., Zn$_3$P$_2$, AlP, and Mg$_3$P$_2$, for the in situ release of PH$_3$ by digestion using an acid, e.g., HCl, provide a route to PH$_3$ research that was previously inaccessible to many. However, PH$_3$ is still released from the metal phosphide; indeed these phosphides are routinely used as pesticides because of their ability to release PH$_3$ on ingestion, which is fatal. Therefore, although easy to obtain, inexpensive (approximately $74 per kg$), and easy to handle, the same level of care and safety assessment should be taken when handling these simple salts as handling PH$_3$ gas cylinders.

One of the earliest reports on the in situ generation of PH$_3$ from a metal phosphide (Zn$_3$P$_2$) for the preparation of high- value P−C bonds was reported by Dorfman and Levina in 1992. The authors employ stoichiometric CuCl$_2$ or Cu-(OAc)$_2$, which, in the presence of pyridine in the coordination sphere, is proposed to acidify the P−H bond in PH$_3$, forming a putative Cu-phosphide intermediate along with HCl/HOAc. It is postulated that the resonance structure of pyridine is such that it renders the ortho- and para- positions δ+, and this, coupled with the proximity of the ortho-position to the copper center, renders this position prone to attack by H$_2$P$^+$, generating the tris(pyridin-2-yl)phosphane product selectively (Scheme 11).

Scheme 11. Dorfman Provides a Rare Example of P−Arene Bond Formation Using PH$_3$

PH$_3$, generated by decomposition of Zn$_3$P$_2$, has been detailed more recently by Ball and Wolf. Ball has elegantly demonstrated the application of in situ generated PH$_3$ for the synthesis of tert-alkyl phosphonium triflates, where the byproduct of the reaction is TMSOAc. Due to the high levels of substitution these products cannot be formed using a hydrophosphination route, while the conventional route to secondary alkyl phosphines, R$_2$PH, would employ PCl$_3$ and organomagnesium or organolithium reagent, followed by reduction of the remaining P−Cl bond with a hydride reagent. Ball has shown that these phosphonium salts can then be converted into the secondary phosphine chloride on reaction with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and CCl$_4$, transformed into their BH$_3$ protected phosphine congeners (using DBU/BH$_3$·SMe$_2$), benzylated (BnBr then protected using BH$_3$·SMe$_2$) or oxidized to the phosphine oxide (using K$_2$CO$_3$ then H$_2$O$_2$), Scheme 12.

Scheme 12. Ball Has Demonstrated That in Situ Formation of PH$_3$ from Zn$_3$P$_2$ Can Be Used to Excellent Effect, Furnishing Otherwise Challenging To Access tert-Alkyl Phosphines via the Phosphonium Salt

Using a similar reaction setup to Ball, where Zn$_3$P$_2$ is digested using HCl in an H-tube and the in situ generated PH$_3$ can then react with substrate in the second chamber, Wolf employed iridium photocatalyst (6) NE$_3$PF$_6$, and blue LEDs to prepare Ph$_4$P$^+$I$^-$ in a 35% yield after 48 h (Scheme 13).

Scheme 13. Photocatalysis Has Been Used by Wolf and Co-workers To Prepare Arylphosphines from PH$_3$

However, use of NaPH$_3$ as an alternative to PH$_3$ was more successful, generating the product in 77% yield after 24 h. Extending the substrate scope beyond PhI, but continuing to use NaPH$_3$, the authors show selective triarylation using sterically encumbered 2-methylidobenzene (63% Ar,P with no other arylation products observed) and 2-methoxymidobenzene (42% Ar$_2$P$^+$ observed only). While 4-methylidobenzene gives 64% Ar$_3$P$^+$/<5% Ar$_2$P, 3-methylidobenzene gives 61%/<6% as Ar$_4$P$^+$/Ar$_3$P and 3-methoxymidobenzene gives 53%/<5% as Ar$_2$P$^+$/Ar$_3$P. The remaining ArI substrates give less attractive ratios of Ar$_n$P$^+$/Ar$_{n-1}$P and/or conversions below 50%. A change to an organophotocatalyst (7) can lead to modest adjustments in the ratio/conversion to product(s). The reaction mechanism is postulated to proceed via sequential
arylation steps, where a photogenerated Ar⁺ reacts with [P]⁻. Reaction profiling shows a rapid buildup of Ph₂PH as a major species, along with PhPH₂, which after 5 h are depleted as the onward reaction of these intermediates takes place, with Ar₂P⁺ eventually being the dominant product. The reaction requires 2 mol %; 11 equiv of ArI, and 15 equiv of NEt₃, (or 10 mol % 7, 13 equiv of ArI, 16 equiv of NEt₃); clearly elegant but, excitingly, with room for modification and diversification.

6.2. In Situ PH₃ Generation from P(OR)₃. Liptrot and co-workers recently presented a Cu-catalyzed route to generate PH₃ in 30 min from P(OR)₃ using HBpin as a reducing agent. PH₃ was generated in 89% conversion on a 0.1 mmol scale. The in situ generated PH₃ was then directly implemented in the quantitative catalytic hydrophosphination of phenyl isocyanate in a two-pot procedure.⁷⁷

7. THE PH₂ ANION

7.1. Reactions of MPH₂ with p-Block Compounds. Alkali metal sources of H₂P⁻, e.g., LiPH₂, NaPH₂, KPH₂, have been largely ignored in the literature until very recently, but given that they are prepared from PH₃ and clearly have the potential to act as an alternative source of PH₁ (cf., Wolf), they are an intriguing reagent that deserves further investigation. Their limited use until now may be linked to the routes of synthesis and the instability of these MPH₂ species. Joannis reported the first synthesis of Na and K dihydrogenphosphide in 1894;⁷⁷,⁷⁸ these compounds were further studied alongside the synthesis of LiPH₂.⁷⁹⁻⁸⁴ Later still, the rubidium⁸⁵ and cesium analogues were reported and the series of alkali metal dihydrogenphosphides were further characterized.⁸⁶ These species were prepared by condensing PH₃ in NH₄Cl and reacting with the metal or metal amide. Handling the Li and Na adduct is not trivial; LiPH₂ decomposes at room temperature while NaPH₂ is noted to decompose above 393 K. The KPH₂ and RbPH₂ species are noted to decompose above 476 K, making them a robust reagent, and it is thus surprising that KPH₂ has not been used more widely in the literature. The poor solubility of KPH₂ can be improved by the addition of 18-crown-6 (catalytic quantities can be used) and/or the preparation of phthalimide anion adducts.⁸⁷ It is worth noting that other routes to H₂P⁻ anion adducts (e.g., phthalate, alkoxide complexes) are known.⁸⁸,⁸⁹ Several rudimentary transformations of MPH₂ have been reported, where the products are often species that we could envisage as being useful building blocks ready for further reaction or functionalization. For example, Hänsgen reported the preparation of the planar 4-membered heterocycle [(tBu₂SnPH)] from tBu₂SnCl and NaPH₂ (Scheme 14a).⁹⁰ Driess has used a dehydrocoupling-type reaction to prepare a dihydrophosphido-aluminium compound [(tBu₂AlPH₂)] which also operates as an effective H₂P⁻ transfer agent, forming tris(phosphane) or tetrakis(phosphaneyl)silane/germane products from the trichlorosilane or tetrachlorosilane/germane precursor (Scheme 14b).⁹¹ Scheer has undertaken salt metathesis reactions of NaPH₂ with IPrGaHCl (8) and the Al analogue (8’) to generate the corresponding bis(dihydrophosphate) complexes (9/9’, Scheme 14c).⁹² Hassler undertook a study into hypersilyl substituted phosphanes and, as part of this investigation, employed PH₃ or NaPH₂ to prepare tris(trimethylsilyl)dihydrophosphide (10). This species can undergo deprotonation with KOtBu, forming (Me₃Si)₃SiPHK (11), which is remarkably stable at room temperature, and can undergo reductive coupling to generate a

Scheme 14. Various Main Group Bond Transformations Have Been Undertaken Using Metal Dihydrophosphides Including (a) the Formation of Sn−P Bonds; (b) Sn−PH₂; (c) Al− and Ga−NHC Complexes Functionalized with PH₃; (d) the Formation of Hypersilyl Substituted Phosphanes, Which Can Undergo Reductive Coupling, Forming 12

The Ga complex is depicted as the POV-Ray image (CCDC 2035403), with all H atoms, except the Ga−H fragment, removed for clarity.
mixture of the meso- and rac-isomers (12, Scheme 14d). This reductive coupling step involves reaction with tBu₂Hg or 1,2-dibromoethane; the latter indicates that the phosphide is not particularly nucleophilic in that a P−C bond is not formed between (Me₃Si)₃SiPHK and Br₂(CH₂)₂.⁹³ Again, this latter point is intriguing and could be further investigated.

In 1982 Issleib reported on the use of KPH₂ to form [3.3.1]-bicycle 14 by reaction with diallyl(chloromethyl)(methyl)silane (13) (Scheme 15a), and this type of protocol has since been used to access other phosphabicycles.⁹⁴,⁹⁵ A similar approach was taken to prepare a mixture of the cis- and trans-[4.4.0]-bicycle (15, Scheme 15b). These compounds were also complexed to Ni(CO)₄, and the resulting LcisNi(CO)₃ and LtransNi(CO)₃ have similar Tolman Electronic Parameters (2063 and 2062 cm⁻¹ respectively), which are very close to the σ-donor-only properties of PMe₃ (2064 cm⁻¹).⁹⁶ Both reports indicate that interesting, unique phosphorus architectures can be prepared in a controlled way using PH₃ derivatives.

Baulder employed KPH₂ in the degradation of red phosphorus to access the P₅⁻ anion, pentaphosphacyclopentadienide (the all-P analogue of the cyclopentadienyl anion) (16, Scheme 16a). With purification only requiring filtration and removal of PH₃ gas, this offers an attractive alternative to the controlled way using PH₃ derivatives.

An early report on potential applications in organic synthesis was provided by Liotta. Reaction of aryl or alkyl benzoates with KPH₂ in the presence of a catalytic amount of 18-crown-6 (10 mol %) generates potassium benzoyl phosphide (20, Scheme 17). This can undergo protonation with acid (trifluoroacetic acid, TFA) or methylolation with MeI, but in both cases the products are unstable and decompose to generate dibenzoylphosphines (21). As we might expect, based simply on atomic size, the authors note no further reactivity of Na(OCP) (and Lewis base/solvent adducts) has been studied by Grützmacher in terms of probing nucleophilia in the presence of group 14 compounds,⁹⁹ while Stephan has employed Grützmacher’s germanium compound, Ph₃GePCO, to prepare the phosphorus-containing analogue of N,N-dimethylformamide (18), which can undergo coordination chemistry with ruthenium forming 19 (Scheme 16d).¹⁰⁰

**Scheme 15.** Issleib Has Used KPH₂ To Install C−PH₂ Bonds, Which Can Then Undergo Hydrophosphination To Generate Highly Unusual Bicycles

**Scheme 16.** (a) An Improved Synthesis of Pentaphosphacyclopentadienide Was Achieved Using KPH₂ in the Presence of Red Phosphorus; (b) Grützmacher and Co-workers Use Na₅(OtBu)₄PH₂ as a H₂P⁻ Source to Prepare Elaborate Heterocycles; (c) Grützmacher’s Seminal Report on the Preparation of the Dme Adduct of NaOCP, Which Has Been Used to Great Effect in Main Group Synthesis (vide infra); (d) Stephan and Co-workers Prepare the Heavy Element Analogue of DMF and Demonstrate Elegant Coordination Chemistry of This Species

**Scheme 17.** One of the Earliest Examples of Reactions of Carbonyl Compounds with KPH₂ Was Presented by Liotta and Co-workers
partial double character due to P atom lone pair/carbonyl $\pi$-orbital overlap (as we normally see with amides); if decomposition pathways can be controlled it may be possible to develop useful chemistry that diverges from that of amides.

Goicoechea has reported the synthesis of Na(OCP) from the reaction of NaPH$_2$ with isocyanate Dipp-NCO (though notably the syntheses of Na(OCP) have been reported from NaPH$_2$ directly and PH$_3$ as a feedstock). Goicoechea goes on to react with isocyanates, generating structurally interesting main group compounds such as 22 (Scheme 18a).

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Interestingly, use of the potassium analogue, [K(18-crown-6)](OCP), gives a different product distribution compared to that obtained using Na(OCP) (Scheme 18b), while the products obtained using Na(OCP) vary based on the substituents on the isocyanate (compare Scheme 18a and 18b, bottom), hinting at the diversity of synthesis that could be achieved if these reagents were more widely studied.

Analogous to the work of Liotta on esters, reaction of NaPH$_2$ with CO$_2$ gives a phosphine carboxylate, which can then undergo onward reaction with silyl chlorides to form phosphine carboxylate silylesters (Scheme 19).

Goicoechea has also shown that NaPH$_2$ can react with dimethyl cyanocarbonimidate in one step to form the heteroallene anion species 23, or in a stepwise fashion via the (carboximidate)phosphide 24 (Scheme 20). 24 can undergo reaction with Ph$_3$GeCl to form a dimeric species product.

Many of the reactions discussed thus far are rooted in fundamental research, and therefore for many of the reactions that could be termed transformations of main group species, it may be difficult to envisage the relevance of these compounds to the organophosphorus, organic chemistry or applied chemistry communities. While these main group compounds are often challenging to prepare and handle, organic transformations of carboxylic acids and allenes are well-known: we have yet to discover if the aforementioned phosphorus-containing species undergo the same transformations, e.g. allenes undergoing a rich array of addition and cyclization reactions.

Gudat prepared a series of diazaboroles, including the PH$_2$ species (26) from KPH$_2$ and the bromodiazaborole precursor (25, Scheme 21a). The computational component of this study notes the covalent nature of the P–B $\sigma$-bond, along with the potential for these main group compounds to act as P-donor ligands. This ligand system has been incorporated into a scandium $\beta$-diketiminate complex, which can act as a phosphinidene transfer agent (Scheme 21b) similar to those

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Scheme 20. Goicoechea and Co-workers Demonstrate a Versatile Range of Main Group Transformations Using NaPH$_2$.

Scheme 21. (a) Gudat and Co-workers Prepared and Studied the Electronic Properties of Phosphino-Diazaboroles, While (b) Chen, Maron and Co-workers Employed the System in Coordination Chemistry.

"Dibenzo-18-crown-6 abbreviated for clarity. The Sc complex is depicted as the POV-Ray image (CCDC 2048477), with all iso-propyl groups and H atoms removed for clarity."
already reported using a bulky 2,4,6-\textit{t}Bu-phenyl phosphinidene Zr\textsuperscript{110} or Th\textsuperscript{111} complex, which operate in a stoichiometric fashion (akin to that possible with Tebbe’s reagent\textsuperscript{112}).

7.3. Reactions of MPH\textsubscript{2} with Compounds of the d- and f-Block. Using a triamidoamine ligand, but one that is less bulky than that used to activate N\textsubscript{2},\textsuperscript{113} Schrock was able to demonstrate the reactivity of a homologous series of Mo and W amido, phosphide, and arsenido complexes, employing LiPH\textsubscript{2} or LiEPhH (E = P, As) or trimethylsilylazide (TMSN\textsubscript{3}) to install the M=E bond (Scheme 22a).\textsuperscript{114} Their onward reaction with MeOTf to form the imido, phosphinidene, and arsinidene complexes (27) was studied, and the authors note that the Mo-phosphinidene complex decomposes in solution at room temperature whereas the W analogue does not. Similarly, the Mo arsinidene triflate was very unstable and could not undergo elemental analysis. The amido complex undergoes reduction in the presence of LiC\textsubscript{8}H\textsubscript{8} to generate the Mo(V) product (28, Scheme 22b). This chemistry is important, because of not only the analogies we can draw between phosphorus and carbon but also the wealth of chemistry undertaken on the activation and functionalization of metal nitrido complexes, in particular their conversion to amines.\textsuperscript{115-118}

If we consider the importance of metal–carbon double bonds in catalysis, e.g., in catalytic metathesis reactions, and the analogy between P and C, then it is vital that fundamental studies into bonding and reactivity of metal–P multiply bonded species are undertaken. In this regard, NaPH\textsubscript{2} has been used by Liddle to generate uranium and thorium phosphinidene (29/31) and phosphinidene (30/32) complexes (Scheme 23a and 23b).\textsuperscript{119,120} Liddle also presented a follow-up paper on the analogous Zr complex (33), which reacts in a similar way to the uranium and thorium analogues (forming the respective phosphane and phosphinidene compounds, 34 and 35, Scheme 23c).\textsuperscript{121} We can draw links to possible onward organic
transformation by looking at the insertion chemistry reported by Stephan, Walter, and Walensky, where benzenophene was shown to insert into the Th–P bond of a bulkier mesityl analogue, and from the work of Mindiola on Ti-phosphinidene complexes and their hydrophosphinination reactivity, although these species do require kinetic stabilization by use of a bulky organophosphine reagent.

Driess has further elaborated the silylene chemistry of PH₃ by taking a nickel-silylene species and demonstrating the coordination chemistry of PH₂ (derived from Li(dme)PH₂ or Li(tmeda)PH₂), generating 36 (Scheme 24) and subsequent isomerization chemistry of the η²-species to generate 37/38.

Considerable efforts have gone into the functionalization of Pₓ and PClₓ and adding PH₃ to the list of readily accessible phosphorus starting materials will grant access to a rich vein of research. The prospect of catalytically activating PH₃ to access useful phosphorus reagents is exciting, and with reports of M=PH and M–PH₂ species, this endeavor feels more attainable than ever. The question remains: how to take M=PH, M–PH₂ and undertake transformations of these species that go beyond hydrophosphinination chemistry reported in the 1980s and 1990s?

8. CONCLUSIONS AND OUTLOOK

The utilization of PH₃ in synthesis is undoubtedly an untapped well, and this is understandable owing to the significant challenges in manipulating pressurized cylinders of such a hazardous gas. However, the recent reports of in situ PH₃ generation offer a much safer alternative to its traditional manipulation. These new operationally simple methods have the potential to revolutionize phosphorus research (which is itself prevalent across a wide range of disciplines). More readily accessible PH₃ sources will also provide easier access to MPH₂ species (where M is an alkali metal), which are already experiencing a renaissance and are proving vital to access novel phosphorus-containing species (vide supra).

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Finally, Scheer has also employed NaPH₂ to generate a Mo dimer with a mixed P/As bridge (39, Scheme 25). A fundamental study, but one where we can envisage links to higher order main group polymer chains with unique properties.

Scheme 25. Scheer and Co-workers Prepare Mixed Group 15 Molybdenum Complexes Using NaPH₂ (or LiE(SiMe₃)₂/KE(SiMe₃)₂, where E = P, As, Sb, Bi)

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