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Hydrogen-Halogen Exchange of Phosphines for the Rapid Formation of Cyclopolyphosphines

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ABSTRACT: The hydrogen-halogen exchange of phosphines has been exploited to establish a truly useable substrate scope and straightforward methodology for the formation of cyclopolyphosphines. Starting from a single dichlorophosphine, a sacrificial proton ‘donor phosphine’ makes possible the rapid, mild synthesis of cyclopolyphosphines: reactions are complete within 10 minutes at room temperature. Novel (aryl)cyclopentaphosphines (ArP)₅ have been formed in good conversion, with crystal structures presented. Use of catalytic quantities of iron(III) acetylacetonate provides significant improvements in conversion in the context of diphosphine (Ar₂P)₂ and alkyl-substituted cyclohexa- or cyclopentaphosphine formation (AlkylP)_n, n = 4 or 5. Both iron-free and iron-mediated reactions show high levels of selectivity for one specific ring size. Finally, investigations into the reactivity of Fe(acac)₃ suggest the iron species is acting as a sink for the hydrochloric acid by-product of the reaction.

INTRODUCTION

The preparation of P–P bonds remains a synthetic challenge, often relying on elaborate coupling partners, catalysts or forcing reaction conditions. Isolation is rarely trivial and often the products possess limited organic functionality.^{1–5} Cyclopolyphosphines ((PR)_n, n = 3 to 6) are a case in point; synthesis has predominantly been achieved by dehydrohalogenation reactions between phosphines and halophosphines (Scheme 1A) or Wurtz-type reduction reactions involving dihalophosphines and zinc, mercury, magnesium or alkaline earth metals (Scheme 1B).^{6–11} However, these synthetic routes have drawbacks: the former relies on forcing conditions (e.g. refluxing toluene) and necessitates access to both proteo- and halophosphines, with primary (proteo)phosphines being more challenging to access and handle. The latter route requires stoichiometric quantities of metal reagents thus generating a stoichiometric amount of metal halide salt by-product. Modern and catalytic routes to cyclopolyphosphines are also possible, most notably via dehydrocoupling reactions of phosphines (Scheme 1C). Transition metal catalysts for these reactions are scarce, with Zr,^{12–13} Fe,¹⁴ select examples of alkali metal,¹⁵ main group^{16–17} and Lewis acid¹⁸ catalyzed reactions all reported to yield cyclic products. Although the formation of hydrogen gas as the sole by-product of the reaction is attractive, this chemistry is not undertaken in the context of dehydrocoupling where H₂ is the desired product; dehydrocoupling of phosphines cannot compete with that of H₃N·BH₃, which can yield a high wt% of H₂; the purpose of P–P bond formation resides in materials, coordination, and synthetic chemistry.^{4–5} Stoichiometric carbene mediated reactions are also known,^{19–21} but in both cases long reaction times (up to 4 days¹⁶), high temperatures^{22, 20} (up to 120 °C^{23, 18}) and stoichiometric amounts of a hydrogen acceptor (e.g. carbene,

azobenzene, alkene) are often necessary to achieve good conversions. Dehydrocoupling and hydrogen atom abstraction methodologies can lack selectivity in the size of the ring formed in the reaction, with mixtures often formed. Furthermore, the product scope is limited to mainly phenyl- or cyclohexyl- substituted derivatives. Manners and co-workers have reported on the use of a simple catalytic system involving KOtBu with 1 equivalent of (*E*)-*N*,1-diphenylmethanimine or azobenzene being used to mop-up H₂ released.¹⁵ Pentaphenylcyclopentaphosphane, (PhP)₅ is formed at RT in 5 minutes. Tetracyclohexylcyclohexaphosphane, (PCy)₄, forms after heating at 130 °C for 1 h.

More recently, Hering-Junghans and co-workers presented a selective, stoichiometric route to aryl-triphosphiranes via the reduction of dichloro(aryl)phosphines with PMe₃ and Zn,²⁴ following early developments from Shah *et al* in 1998.²⁵ Additionally, Weigand and co-workers have built upon their P–N/P–P bond metathesis methodology of forming polyphosphines^{26–27} to achieve selective formation of cyclopentaphosphines.²⁸ These methods provide three examples of sterically bulky aryl phosphines (2,4,6-*i*Pr₃C₆H₂, 2,6-*i*Pr₂C₆H₃, 2,4,6-Me₃C₆H₂)²⁴ and two examples (2-pyridyl, 2-benzo[*d*]thiazolyl)²⁸ respectively.

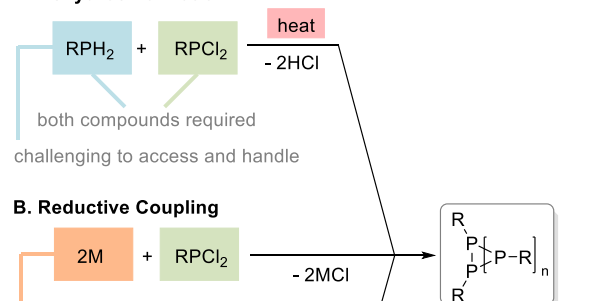
There is a lack of a generalized, single procedure to access an expanded array of cyclopolyphosphines. A universal route to form a more extensive range of novel cyclopolyphosphines is desirable; these species have synthetic applications, with examples including insertion of species (Se, Ga₄[C(SiMe₃)₃]₄)^{29–30} into the P–P bonds of triphosphiranes and the formation of metal phosphinidene clusters from cyclopenta- and cyclohexaphosphines.³¹ In addition, the ability of cyclopolyphosphines to coordinate to transition metal carbonyl complexes^{32–33} has been utilized to allow for insertion of acetonitrile into a P–P bond of

the coordinated ring.³⁴ These applications remain sparse but broadening the scope of available cyclopolyposphines should pave the way for further discoveries and applications.

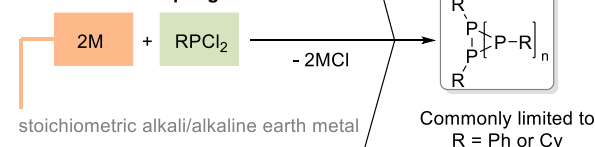
Scheme 1. Routes to cyclopolyposphines involve harsh reaction conditions when employing dehydrochlorination (A); stoichiometric solid waste and pyrophoric reagents (B); dehydrocoupling often requires forcing conditions and/or H₂ acceptor molecule and/or an elaborate catalyst (C). All reactions tend to be limited to the simplest cyclopolyposphine products. This work is mild (RT), rapid (10 minutes or less) and has allowed synthesis and isolation of 14 cyclopolyposphines (D).

Routes to cyclopolyposphines

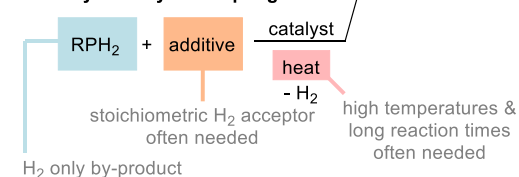
A. Dehydrochlorination



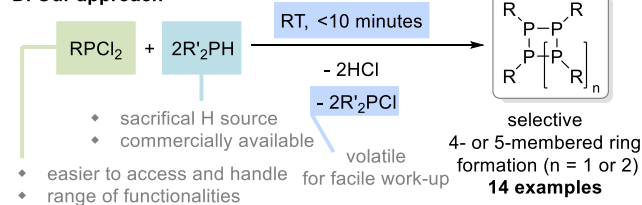
B. Reductive Coupling



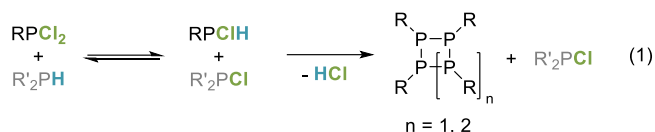
C. Catalytic dehydrocoupling



D. Our approach



Our approach was to exploit the natural and rapid process of hydrogen/halogen exchange between a phosphine and a halo-phosphine (Equation 1). We postulated that a mono-chlorophosphine (R'PClH) could form in situ from a more stable and easier to access chlorophosphine (R'PCl₂) by exchange with a sacrificial phosphine (R₂'PH) as a proton donor. A simple and similarly rapid dehydrochlorination of the mono-chlorophosphine would allow us to prepare a range of structurally diverse homocyclopolyposphines. Choice of proton donor would rely on the ability of that phosphine to facilitate hydrogen/halogen exchange with the chloro-substrate without undergoing any further reaction to form unwanted by-products.

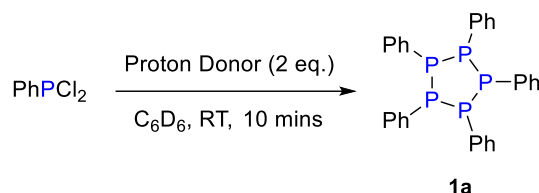


Our exchange/dehydrocoupling sequence method would allow the use of a commercially available sacrificial proton source negating preparation of otherwise challenging to access primary phosphines from more accessible and structurally varied R'PCl₂ i.e. a) avoiding reduction of R'PCl₂ to R'PH₂ and b) avoiding design of an active dehydrocoupling catalyst. It is remarkable that an H/Cl exchange/dehydrochlorination route has never been reported before.

RESULTS AND DISCUSSION

We initiated our study by focusing on optimizing the method for the preparation of pentaphenylcyclopentaphosphane, ((PhP)₅, **1a**). Reaction of PhPH₂ and PhPCl₂ produces a very modest conversion of 26% **1a** after 10 minutes at room temperature, with no increase in conversion seen after a further 2 h at RT. Clearly homocoupling of two phenylphosphane sources via H/Cl exchange is not efficient. Attention was then turned to other 'sacrificial donor phosphines'. To achieve this, dichlorophosphines were chosen as reagents with which to construct homocyclopolyposphines due to their ease of synthesis and handling in comparison to their primary phosphine counterparts. Therefore, a sacrificial proton donor phosphine is also necessary, and we opted to screen simple commercially available secondary phosphines for this purpose. Alcohols (e.g. EtOH) are not suitable due to their propensity to oxidize chlorophosphines³⁵⁻³⁶ and amines (e.g. *i*Pr₂NH) react with

Table 1. Formation of P₅Ph₅ (1a**) using a proton donor phosphine.^[a]**



Entry	Proton Donor	Conversion (%)
1	Ph ₂ PH	Trace
2	Cy ₂ PH	98
3	<i>i</i> Pr ₂ PH	93 (89)

[a] Conditions: 0.5 mmol PhPCl₂, 1.0 mmol proton donor, 0.6 mL C₆D₆, RT, 10 mins. [b] Conversion calculated by integration of product signals against starting material via ³¹P NMR spectroscopy. Isolated yield shown in parentheses.

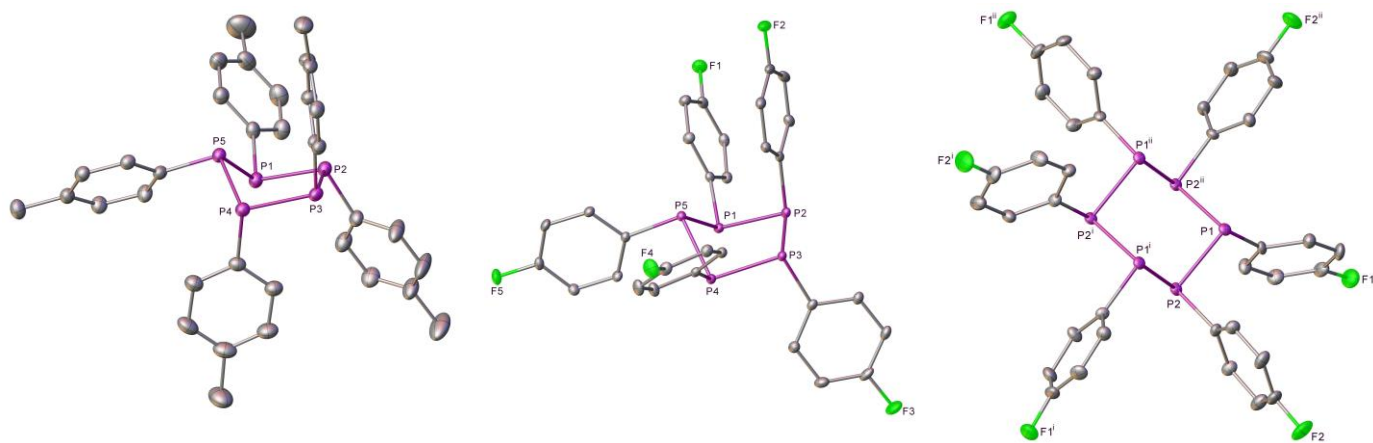
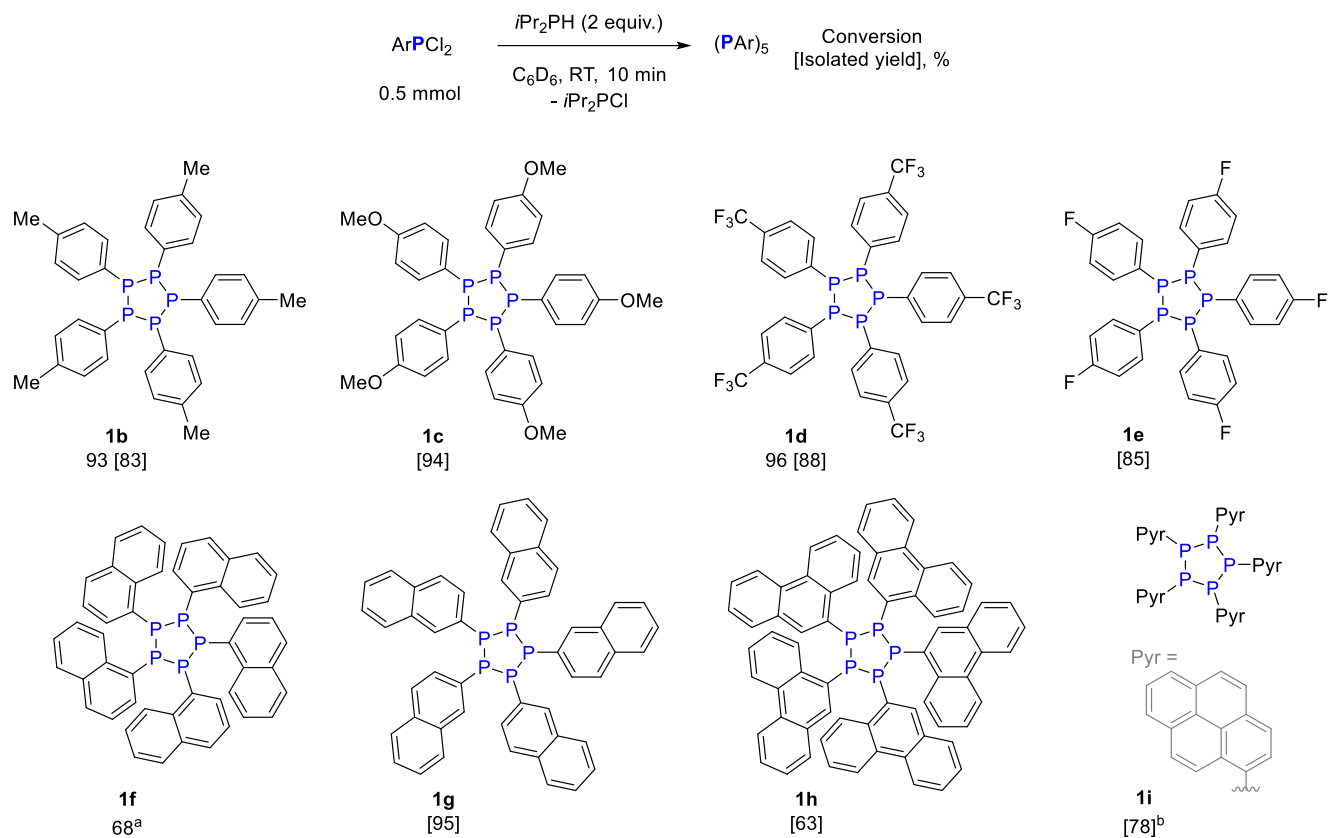


Figure 1. Substrate scope for formation of cyclopentaphosphines from dichloro(aryl)phosphines. Conversion calculated by integration of product signals against starting material via ^{31}P NMR spectroscopy. Total conversion shown, see supporting information for details of minor product components. ^a2.2:1P₅R₅:P₄R₄, not isolated; ^b1 mmol Cy₂PH. Single crystal X-ray structures (left to right) for **1b**, **1e** and (bottom) one of the two independent molecules present in **1e'**. Symmetry operations (**1e'**): ⁱ 1 - y, x - y, z; ⁱⁱ 1 + y - x, 1 - x, z. Ellipsoids are represented at the 30% probability level and H atoms have been omitted for clarity.

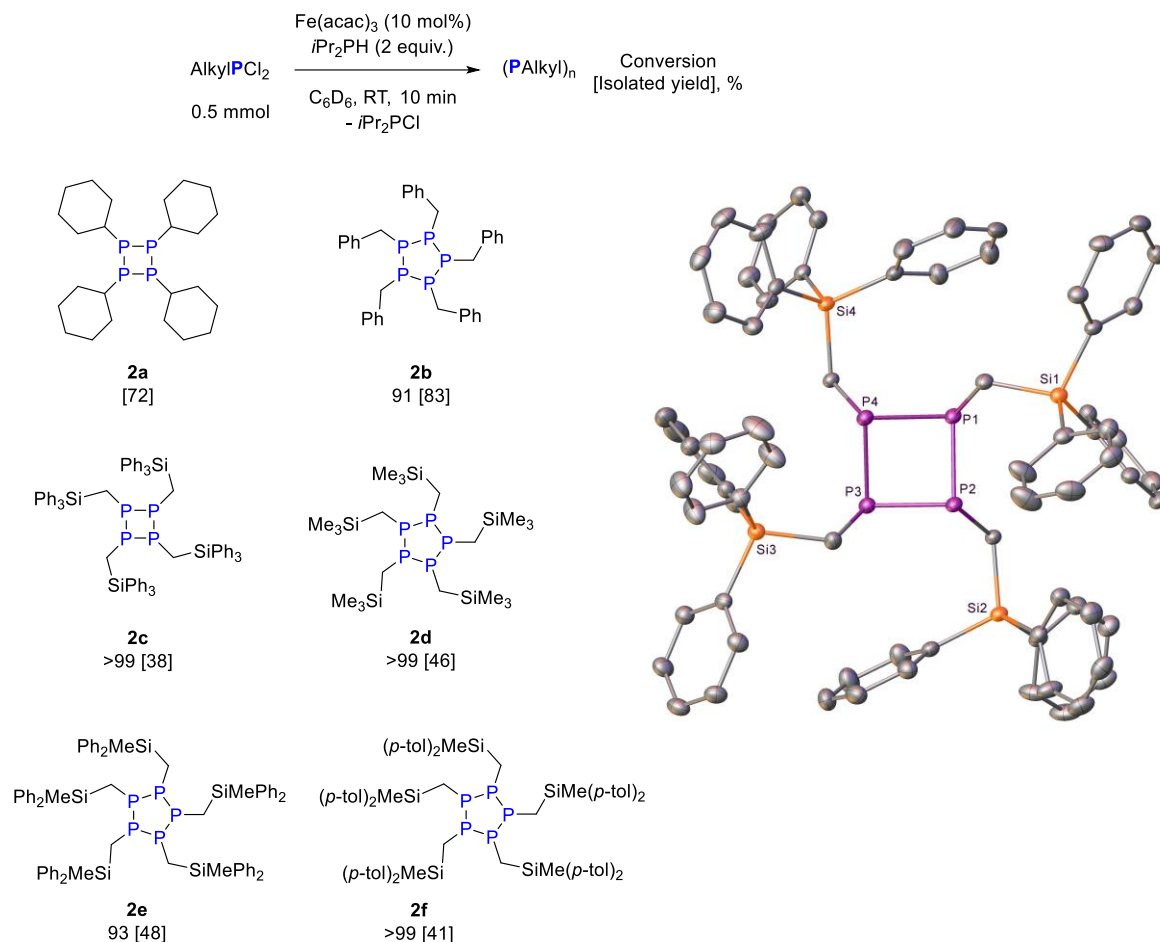


Figure 2. Substrate scope for formation of cyclopolyphosphines from alkyldichlorophosphines. Conversions calculated by integration of product signals against starting material via ^{31}P NMR spectroscopy. Total conversion shown, see supporting information for details of minor product components. Single crystal X-ray structure for **2b** (ellipsoids are represented at the 30% probability level and H atoms have been omitted for clarity).

chlorophosphines to give aminophosphines.³⁷⁻³⁸ Silanes (methylphenylsilane and phenylsilane) do not give any cyclopolyphosphine when reacted with PhPCl_2 or CyPCl_2 (the latter in the presence of $\text{Fe}(\text{acac})_3$, *vide infra*). Reaction of Ph_2PH with PhPCl_2 gives trace formation of **1a** after 10 minutes at room temperature, increasing to 13% after 1 hour at room temperature (Table 1, Entry 1). Remarkably, both Cy_2PH and $\textit{iPr}_2\text{PH}$ can mediate the formation of **1a** in excellent conversion within 10 minutes at room temperature without the need for heating or metal reagent (Table 1, Entries 2 and 3). Although the highest conversion is seen with Cy_2PH , difficulties arise in the isolation of **1a** from the resulting $\text{Cy}_2\text{P}Cl$. $\textit{iPr}_2\text{P}Cl$ is more volatile and can be removed by vacuum distillation making it more favorable in the context of isolating further cyclopolyphosphine compounds. Two equivalents of donor phosphine are needed to push the exchange process to completion. Encouraged by these results, scope for formation of other cyclopolyphosphines from dichlorophosphine moieties was investigated (Figure 1). Conversions and isolated yields were obtained using the optimized conditions (Table 1, Entry 3).

Dichloro(aryl)phosphines with both electron withdrawing and donating groups give good, selective conversion to the

corresponding cyclopentaphosphines (**1b** to **1e**) and can be isolated in excellent yields. Substrates containing polyaromatic units also produce 5-membered rings in good yield (**1f** to **1i**). **1f** is formed alongside the four-membered analogue (2.2:1 $\text{P}_5\text{R}_5\text{:P}_4\text{R}_4$) and therefore is not isolated. The formation of **1c** and **1g** have been mentioned briefly in the literature (via reaction of the respective perthiophosphonic anhydrides with $n\text{Bu}_3\text{P}$, 15 h, reflux in benzene).³⁹ **1d**, **1e**, **1h** and **1i** represent completely new cyclopolyphosphines that never been presented in the literature, isolated or characterized before.

1a was crystallized⁴⁰ and provides data comparable to the previous report from Radius.²⁰ The cyclic pentamer **1b** crystallizes as a skewed ring structure with asymmetric phosphorus environments, mirrored in solution in the ^{31}P NMR spectrum which displays multiple couplings between phosphorus atoms. P–P bond distances (Å) range between 2.2055(9) (P3–P4) to 2.2256(10) (P1–P2), while the P–P–P bond angles span a divergent range, in excess of 10° , as one would anticipate from the skewed envelope structure: (P2–P1–P5 94.29(3), P5–P4–P3 95.71(3), P1–P5–P4 96.67(3), P3–P2–P1 102.56(4), P4–P3–P2 105.47(4) $^\circ$). **1c** could be crystallized but the crystals displayed twinning to an extent that prevented a confidently assigned unit

cell. P–P bond distances in **1e** range from 2.2090(5) Å (P1–P5) to 2.2323(6) Å (P1–P2) and the bond angles have a narrower range than those for **1c** (P1–P5–P4 88.37(2), P5–P1–P2 95.25(2), P3–P4–P5 96.66(2), P3–P2–P1 98.52(2), P2–P3–P4 103.91(2)°). While **1e** is observed as the major species in solution by ³¹P NMR spectroscopy (89:4:7) P₃R₅:P₄R₄:P₆R₆, but the cyclic hexamer can also be crystallized (**1e'**, Figure 1, bottom). **1e'** contains two crystallographically distinct P₆ fragments and the P–P distances across both are similar, ranging from 2.226(2) to 2.235(2) Å. P–P–P bond angles vary such that one of the molecules returns values of 97.72(12)° for all angles in the P₆ ring, while the second species exhibits alternating values of 94.15(10) and 94.73(10)° around the P₆ core. This represents the rare example of an unsupported cyclohexaphosphine ring being crystallographically characterized.^{41, 20} Unfortunately, **1g** forms a powder as opposed to single crystals and **1h** and **1i** are highly insoluble, requiring analysis by solid state NMR spectroscopy (see Supporting Information).

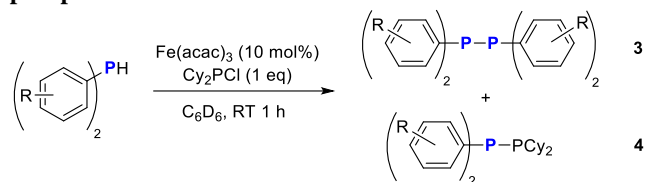
When the methodology was extended to alkyl-substituted dichlorophosphines, although the H/Cl exchange clearly takes place in an efficient manner, as evidenced by ³¹P NMR spectroscopy, the reaction stalls at the dehydrochlorination step. For example, only a 18% conversion to tetracyclohexylcyclotetraphosphane (**2a**⁴²) is achieved from reaction of Cy₂PCl₂ and *i*Pr₂PH. This is in line with reports from Seichter, who used refluxing toluene to force the dehydrochlorination of Cy₂PCl₂ and CyPH₂.⁶ We hypothesized that to achieve clean and efficient cyclization following H/Cl exchange, an additive was needed to facilitate the dehydrochlorination process. Simple bases do not give clean or high conversion to the desired product (see Supporting Information). However, use of inexpensive and commercially available Fe(acac)₃ in 10 mol% loading leads to efficient dehydrochlorination (other acetylacetonate complexes, such as vanadium and nickel-based complexes, also work but not as well, see Supporting Information). To investigate if this Fe-mediated dehydrochlorination could be extended to further substrates, a range of dichloro(alkyl)phosphines bearing silyl groups were synthesized and subjected to the reaction conditions (Figure 2). Selective formation of cyclopolyphosphine products is again observed after 10 minutes at RT, giving **2b** and novel compounds **2c** to **2f** in excellent conversion and good yield. The necessity for Fe(acac)₃ is again apparent for these additional alkyl substrates as poor conversions are obtained in absence of the iron species (see Supporting Information). Formation of the four-membered ring is favored in the case **2c**, with **2b**, **2d**, **2e** and **2f**, which bear less steric bulk, forming cyclic pentamers. AdamantylPCl₂ does not react cleanly and gives an intractable mixture postulated to be mixtures of linear oligomeric compounds. Crystallization is also readily achieved: novel tetramer **2c** shows a pseudo-4-fold symmetry axis, which is reflected by a singlet in the ³¹P NMR spectrum thereby confirming the equivalence of the phosphine environments.⁸ P–P bond distances (P1–P2 2.2269(11), P2–P3 2.2240(11), P3–P4 2.2375(10), P1–P4 2.2203(11) Å), are comparable with that observed for the original report of structure of **2a** (P–P' 2.224(2) Å⁴³), as are the bond angles (∠_{P–P–P(mean)} = 85.37° compared to ∠_{P–P–P'} = 85.47(6)°⁴³).

Finally, we extended the methodology to prepare diphosphines and used the synthesis of tetraphenyldiphosphane (P₂Ph₄, **3a**) for optimization purposes. Like cyclopolyphosphines, diphosphines sometimes rely on forcing or cryogenic reaction

conditions, long reaction times and/or stoichiometric amount of H₂ acceptor (or hydrogen atom abstraction agent) to enable preparation.^{44, 13, 45–46, 19, 18, 47–52} In the context of diphosphine reagent, preparation of R₂PH is readily achieved from the phosphine oxide,⁵³ and thus a range of secondary aryl phosphines were prepared and used in the dehydrochlorination methodology in the presence of a 'sacrificial chloride donor'. In the reaction of Ph₂PH and Cy₂PCl in C₆D₆ with no catalyst, a 14% conversion to **3a** after 1 h RT is observed.⁵⁴ Little to no conversion to the unwanted heterocoupled (Ph₂P–PCy₂, **4a**) or homocoupled (P₂Cy₄) side products is observed, proving Cy₂PCl is a good fit for use as a sacrificial chloride donor. As with (alkyl)cyclopolyphosphines of the form **2**, conversion can be improved by addition of 10 mol% Fe(acac)₃. Chloride donors were also varied, with *i*Pr₂PCl and *t*Bu₂PCl also considered as commercially available, viable options. Use of *i*Pr₂PCl gives similar conversion to the reaction with the cyclohexyl analogue, whereas *t*Bu₂PCl undergoes no hydrogen/halogen exchange with the substrate and so no conversion to **3a** is observed (see Supporting Information).

Using Cy₂PCl, we then investigated a brief scope for the formation of aryl-substituted diphosphines. ³¹P NMR spectroscopic analysis of the product mixture after isolation from iron residues shows minor quantities of heterocoupled product (**4** in Table 2) alongside the homocoupled diphosphine (**3**). Aryl rings with electron-donating substituents proceed well in the reaction (Table 2, **3b** and **3c**) whereas those with electron-withdrawing substituents exhibit reduced conversions (**3d** and **3e**), with the 4-trifluoromethyl-substituted derivative requiring 2 h to reach a desirable conversion (**3e**). The *ortho*-methoxy substrate gives reduced conversion (**3f**) which may be attributed to the additional steric bulk this substrate bears.

Table 2. Formation of P₂Ph₄ (3a**) using a chloride donor phosphine.^[a]**



Entry	Product	Substituent	Spectroscopic Yield (%) ^[b]	Product Ratio (3 : 4)
1	3a	H	93	9.7 : 1
2	3b	4-Me	>99	2.4 : 1
3	3c	4-OMe	88	28.9 : 1
4 ^[c]	3d	4-CF ₃	72	4.1 : 1
5	3e	4-F	61	17.1 : 1
6	3f	2-OMe	43	4.4 : 1

[a] Conditions: 0.25 mmol phosphine, 10 mol% Fe(acac)₃, 0.25 mmol Cy₂PCl, 0.6 mL C₆D₆, RT, 1 h. Product mixture isolated from iron residue via a silica plug eluting with toluene. [b] Calculated by integration of product signals against a triethylphosphite internal standard via inverse-gated ³¹P{¹H} NMR. [c] 2 h.

$\text{Fe}(\text{acac})_3$ is expected to act as a very efficient HCl sequestration agent. Qualitatively, reaction completion can be assessed by monitoring the complete loss of color in iron-mediated reactions: the solution changes from bright red to colorless within minutes, at which point the reaction is complete. Vacuum transfer of the product mixture of the reaction (using the formation of **3a** as a test reaction) shows the presence of free acetylacetonate, indicating the HCl formed is liberating the acac ligands of $\text{Fe}(\text{acac})_3$ whilst forming new FeCl bonds. This is confirmed by treating a solution of the iron complex with an ethereal solution of HCl, yielding an Fe(III) cation with two acac ligands bound alongside a Fe(III) tetrachloride anion (**5**, Figure 3).⁵⁵ This provides strong evidence that, under cyclopolyphosphine formation conditions, $\text{Fe}(\text{acac})_3$ is abstracting HCl from the system, and the removal of the acid in this manner may be the driving force of the reaction in the case of (alkyl)cyclopolyphosphine (**2**) and diphosphine (**3**) formation.⁵⁶ Taking isolated **2b** and exposing it to an atmosphere of HCl in the absence of $\text{Fe}(\text{acac})_3$ results in the reverse reaction; ring cleavage occurs and ((triphenylsilyl)methyl)phosphane is observed further supporting the thesis that the iron complex does not have any role beyond HCl sequestration.

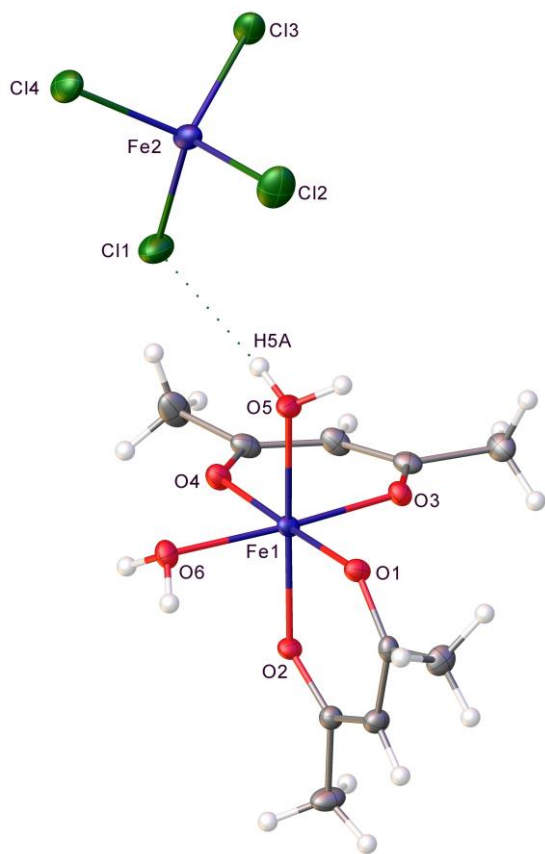


Figure 3. Complex **5** forms when $\text{Fe}(\text{acac})_3$ is exposed to HCl, indicating that protonation of the acetylacetonate ligands takes place along with formation of Fe–Cl bonds. Single crystal X-ray structure for **5** (ellipsoids are represented at 30% probability).

We therefore propose a mechanism for cyclopolyphosphine formation that starts from a dichlorophosphine (Figure 4), the proton donor ($i\text{Pr}_2\text{PH}$) can undergo an exchange reaction to form

$\text{R}'_2\text{P}(\text{Cl})$ and one of two intermediate species, the single exchange product (RPHCl , **I**) or double exchange product (RPH_2 , **I'**). In the case of aryl-substituted products, the dehydrochlorination reaction then proceeds from **I** (top reaction pathway), or from **I'** (bottom reaction pathway), without the need for Fe-mediated HCl abstraction. For alkyl-substituted products, the analogous $\text{Fe}(\text{acac})_3$ mediated HCl abstraction could occur via both pathways; liberated ligand and iron species are subsequently formed as by-products alongside the cyclopolyphosphine product. Unfortunately, due to the extreme speed of the reactions, the intermediate exchange products **I** and **I'** are not observable by ^{31}P NMR spectroscopy at RT. Low temperature studies are not viable due to precipitate formation hindering further study and reactivity, precluding confirmation of whether one or both pathways are active for a given substrate. The selectivity for the observed ring size simply originates from which ring size is thermodynamically favored. A reaction pathway involving the formation of a kinetic product and subsequent scrambling to the thermodynamic product cannot be ruled out,^{57, 28} however no evidence for this kind of reactivity has been observed in ^{31}P NMR analysis of the reactions. The formation of **2a** under standard conditions proceeds as usual in the presence of a (chloromethyl)cyclopropane radical trap (*see* Supporting Information), therefore a radical-mediated reaction pathway was ruled out.

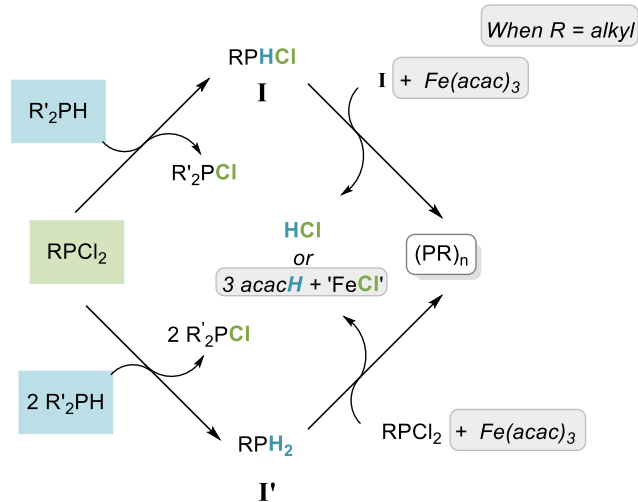


Figure 4. Proposed mechanistic pathway for the formation of cyclopolyphosphines via iron-mediated dehydrochlorination.

Conclusions

To summarize, utilizing the hydrogen-chlorine exchange of phosphines facilitates rapid, facile P–P bond formation via dehydrochlorination. A commercially available ‘sacrificial proton donor’ phosphine is used, allowing application of readily synthesized dichlorophosphines as building blocks for cyclic products. The by-product of the reaction is removed simply by evaporation. The reaction is complete within minutes at room temperature and gives access to otherwise synthetically challenging cyclopolyphosphines; this is highlighted by the fact that this remarkably simple P–P bond forming protocol has allowed the isolation and characterization of 8 novel cyclopolyphosphines.

We have crystallized four novel cyclopolyposphines: penta-*p*-tolylpentaphospholane (**1b**), pentakis(4-fluorophenyl)penta-phospholane (**1e**) the cyclic hexamer 1,2,3,4,5,6-hexakis(4-fluorophenyl)hexaphosphinane (**1e'**) and a silyl-substituted tetraphosphetane (**2b**). Use of a simple, inexpensive, and commercially available metal complex, Fe(acac)₃, is proven to expedite dehydrochlorination reactions to form alkyl-substituted cyclopolyposphines and diphosphines, whereas aryl-substituted cyclopolyposphines are formed without the need for this additive. Investigations into the role of Fe(acac)₃ in the reaction indicate that the iron complex is acting as a HCl sink, providing a driving force to reach higher conversions.

ASSOCIATED CONTENT

Supporting Information. Experimental details, analysis data and spectra for all products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

CCDC 2082082-2082086 contain the supplementary crystallographic data for structures **1b**, **1e**, **1e'**, **2b** and **5**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <https://www.ccdc.cam.ac.uk/structures/>

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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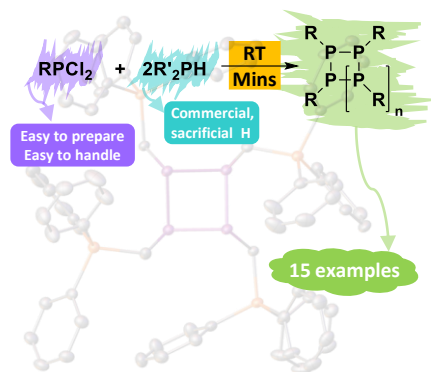
Maialen Espinal-Viguri, Andrew K. King and Kirstie Milne are thanked for preliminary optimization studies. The EPSRC is thanked for funding (fellowship to RLW, studentship to CJG), the University of Bath is thanked for a DTP studentship (ANB) and the EPSRC Centre for Doctoral Training in Catalysis (between Universities of Bath, Bristol and Cardiff) is thanked for a CDT studentship (CRW). The X-ray crystallography service at the University of Bristol is thanked for collection and refinement of data for compound **1e**.

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Rapid hydrogen-halogen exchange is exploited, using a commercially available sacrificial proton donor phosphine that can be readily removed from the product mixture, to yield an unprecedented range of functionalized cyclopolyphosphines from readily prepared di-chlorophosphine precursors. Reactions are complete within minutes at room temperature. Use of sub-stoichiometric $Fe(acac)_3$ allows P–P bond formation of more challenging phosphines.
