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Published in:
CHEMISTRY-A EUROPEAN JOURNAL

DOI:
10.1002/chem.201702067

Citation for published version (APA):

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Organophosphorus Compounds

Functionalization of P₄ through Direct P–C Bond Formation

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Abstract: Research on chlorine-free conversions of P₄ into organophosphorus compounds (OPCs) has a long track record, but methods that allow desirable, direct P–C bond formations have only recently emerged. These include the use of metal organyls, carbenes, carboradicals, and photochemical approaches. The versatile product scope enables the preparation of both industrially relevant organophosphorus compounds, as well as a broad range of intriguing new compound classes. Herein we provide a concise overview of recent breakthroughs and outline the acquired fundamental insights to aid future developments.

1. Introduction

Organophosphorus compounds (OPCs) are important reagents with widespread use in industry. Especially valuable are the compounds containing P–C bonds, which can be applied as ligands in catalysis or as auxiliaries in C–E coupling reactions (E = C, O, or N).[1] The required phosphorus atoms originate from white phosphorus (P₄), which is typically converted to PCl₅ through large-scale halogenation and subsequently functionalized by salt elimination reactions (A, Figure 1).[2] However, this process generates stoichiometric amounts of halide waste and often involves unselective multi-step synthetic routes.[3] Direct functionalization of P₄ could offer an attractive alternative (B), but this strategy is hampered by the unpredictable behavior of the P₄ tetrahedron as showcased in the diversity of currently known chemistry. While most of this work has been covered in a number of seminal reviews of the past decade,[4,5,6] an appealing approach based on direct P–C bond formation, resembling PCl₅ substitution,[6] has emerged only recently as a promising platform for the selective preparation of OPCs from P₄, which is the topic of this review.[7]

To understand how P–C bonds can be made using P₄, it is instructive to touch on its properties. Most pronounced is its electrophilicity[8] which due to the acute (60°) bond angles of the P₄ cage, is assumed to originate from ring strain (d(P–P) = 2.1994(3) Å, gas-phase electron diffraction),[9] even though the expected bending of the P–P bonds (>5°) is insignificant according to an AIM analysis (atoms in molecules).[10] The bonding in P₄ benefits from delocalization of the electrons in s, p, and d cluster orbitals (spherical aromaticity).[11] Whereas reduction of P₄ by means of cyclic voltammetry (CV) occurs readily, it is irreversible due to bond rupture and polymerization of the formed radical anion (P₄[−°°°°]).[10,12] White phosphorus can also be “cracked” both thermally (>1100 K)[13] and photochemically (UV irradiation)[14] into two transient P₃ molecules (P≡P) that polymerize rapidly to the more stable red phosphorus allotrope.[15]

In this Minireview we highlight recent breakthroughs in P₄ chemistry by focusing on reactions that directly create P–C bonds with main group and transition metal organyls, ambiphilic carbenes, and carboradicals as well as on trapping of P₄ fragments with organic substrates.

2. Functionalization of P₄ Using Main Group Metal Organyl

A common approach to introduce carbon atoms to electrophilic functional groups involves the use of organolithium or Grignard reagents. In 1963, Rauhut and co-workers were the first to report on the formation of P–C bonds by reaction of either phenyl- or n-butylithium (or MgBr salts) with ethereal solutions of P₄.[16] Quenching the resulting deep red suspensions with water or butylhalides afforded mixtures of mostly primary or tertiary phosphines as detectable products (I, Scheme 1);[16] only Ph shown), but with only low selectivity and poor yields (0–40%) in addition to large quantities of organophosphines.[17] Equally challenging with similar product mixtures are the reactions of P₄ with alkynes (II)[18] or with tert-butyl- or methyllithium in combination with Me₂SiCl as quenching agent (III).[19] The more bulky reagents allowed for formation of cyclotetraphosphines (e.g. 1; Scheme 1), indicating a more controlled degradation path through steric shielding.[20] Using the sterically encumbered Mes*Li (IV; Mes* = 2,4,6-iBu₃C₆H₃), Fluck et al. demonstrated that degradation of P₄ is stoppable after a single P–P bond cleavage. They isolated

Figure 1. Preparation of organophosphorus compounds (OPCs) from P₄.
in < 10% yield the first example of a bicyclo[1.1.0]tetraphosphabutane (2) in addition to diphosphene 3.[21]

The reactions of P₄ with organoalkali reagents proceed through a common highly reactive transient [RP₄]⁺ butterfly anion, which is produced after nucleophilic addition and concomitant P–P bond cleavage [Eq. (1)].

\[
\text{R}^+ + P_4 \rightarrow R^+P_3P^- \quad (1)
\]

In 2014, the formation of this elusive intermediate was confirmed by us.[22] We used sterically encumbered AryLi reagents and Lewis acids (LA; B(C₆F₅)₃ or BPh₃) to trap the incipient phosphide, thereby selectively obtaining the first examples of LA-stabilized bicyclo[1.1.0]tetraphosphabutanide anions (4, Scheme 2).[23,24] The HOMO of these species shows a lone pair on the boron-coordinated wing-tip P-atom, which allows for controlled subsequent functionalization of the P₄ core. For example, alkylation of 4b, featuring the strong LA B(C₆F₅)₃, with Mel afforded exclusively endo-methylated product 5 of which the exo P–B bond could be cleaved to furnish the labile, nonsymmetric organo-substituted exo,endo-R₃P₄ butterfly 6.[23] Conversely, alkylation of the more reactive BPh₃-stabilized anion 4c with Ph₄C⁺PF₆⁻ provided clean and direct access to LA-free exo,exo-7, which due to the steric shielding of the bulky trityl group proved kinetically inert.[24]

![Image](image.jpg)

**Scheme 1.** Reactions of P₄ with organoalkali reagents. Mes⁺ = 2,4,6-tBu₃C₆H₂, R₁ = Bu, R₂ = Et or Pr, X = Br or Cl.

Dr. Joop E. Borger was born in Wageningen, The Netherlands, in 1987 and obtained his B.Sc. in chemistry at the University of Applied Sciences Utrecht in 2009. After working as a research associate for Schering-Plough in Oss (currently MSD), he pursued an M.Sc. in chemistry at the VU University Amsterdam, where he graduated cum laude in 2013. Recently, he completed his doctoral studies under the supervision of Prof. Koop Lammersma, which focused on the controlled and direct conversion of white phosphorus into organophosphorus compounds. He is now working as a postdoctoral fellow in the group of Prof. Hansjörg Grützmacher at ETH Zürich in Switzerland.

Dr. A. W. Ehlers obtained his PhD at the Philipps University of Marburg, Germany on ab initio calculations of Transition Metal-Ligand bond interactions. He joined the VU University in Amsterdam as Marie Curie Fellow and later as Assistant Professor to study organometallic and main group chemistry for asymmetric homogenous catalysis by DFT. In 2016, he was also appointed as a Visiting Associate Professor in the Department of Chemistry at the University of Johannesburg. Finally, he accepted a position at the University of Amsterdam to study the activity of catalysts in sustainable processes theoretically and by NMR.

Dr. J. Chris Slootweg obtained his PhD degree at the Vrije Universiteit Amsterdam in 2005. As a post-doctoral researcher, he studied C–H activation at the ETH Zürich, for which he received a TALENT stipend from NWO. In 2006, he returned as an Assistant Professor to the VU, where he coordinated the Marie Curie Initial Training Network SusPhos on sustainable phosphorus chemistry. In 2013, he received a NWO VIDI grant on main-group chemistry and catalysis. He was promoted to Associate Professor in May 2014, and moved to the University of Amsterdam in November 2016 to continue exploring his interests in sustainable chemistry.

Prof. Koop Lammersma (born in 1949 in Makkum/the Netherlands) was educated at the Universities of Groningen (1974) and Amsterdam (Ph.D. 1979). After postdoctoral work with F. Wandelle (London), P. v. R. Schleyer (Erlangen-Nürnberg), and Nobel laureate G. A. Olah (USC) he moved in 1983 to the University of Alabama at Birmingham, USA, to become Full Professor in 1992. In 1996 he moved to the Vrije Universiteit Amsterdam, The Netherlands. Since 2015, he holds a Distinguished Visiting Professor position at the University of Johannesburg, South Africa. His physical organic chemistry has increasingly focused on computationally supported phosphorus chemistry.
In contrast to the strongly Lewis acidic $B(C_6F_5)_3$ group in 4a, b, the less stabilizing $BH_3$, in 4c departs immediately upon endo-cyclic substitution by BH$_3$ or W(CO)$_5$. In these cases the anionic [$RP_4$]$^-$ core transfers to the stronger Lewis acids to give the doubly coordinated anions 8a and b, respectively (Scheme 2). Intriguingly, the high reactivity of 4c also grants access to OPCs containing P$_1$ and P$_2$ entities through unprecedented [3+1]-fragmentation reactions using either phenylisocy- 
cane or imidazolium chloride in the presence of an access of the P$_2$-trapping reagent 1,3-cyclohexadiene (1,3-CHD; Scheme 3). The reactions proceed through “P” transfer from the LA-stabilized butterfly anions to the reagents to give spirophosphoranes 9 and carbene–phosphinidene adduct 11, respectively, with concurrent trapping of the liberated diphen- 
ephane Mes$_2$P$_3$ by the organic diene that generates in both cases organotriphosphane 10.

The isolation and versatility of the stabilized [RP$_4$]$^-$ anion 4 marks a significant step toward the controlled functionalization of P$_4$ with organolithium reagents. Interestingly, related RP$_4$ derivatives can also be generated from P$_4$ in the coordination sphere of a gold(I) cation, even with unencumbered MesLi,[24] which is otherwise precluded due to rapid quenching with boron Lewis acids to Li[MesBAr]. Exemplary is the reaction of AryLi with the $1^@$-P$_2$-coordinated cationic (NHC)Au complex 12 (Scheme 4; Ary = Mes or Dmp, NHC = N-heterocyclic carbene) initial formation of the $[nBuP_4]^-$ butterfly anion [Eq. (1)] with subsequent nucleophilic addition across the transannular P–P bond [Eq. (2)]. Product 15 reacts with P$_4$ to the polyphosphate cluster $[nBuP_4]^-$ (16), which is isolable due to the stabilizing $[nBuP_4]^{2-}$ centers. These results are in sharp contrast to the noted[16] unselective reactions with $n$-butylmagnesium bromide and demonstrates the large impact of the employed cation on the outcome of P$_4$ substitution.

The group of Lerner reported on the synthesis of a trisanionic [RP$_4$]$^-$ derivative (17, Scheme 6). The complex is generated from P$_4$ and mesityllithium in benzene over the course of four days in 60% yield. Presumably, tetraphosphanetriide 17 results from nucleophilic attack on the common [RP$_4$]$^-$ intermediate with simultaneous cleavage of a peripheral P–P bond, followed by a third addition [Eq. (3)]. Interestingly, partial protonation of 17 led to lithium diphosphane [Mes$_2$P$_2$H]$^-$, which on quenching with trifluoroacetic acid gave diphosphane Mes(H)P$_2$–P(H)Mes. This process hints toward a novel route to prepare lower nuclearity phosphanes.
Recently, Zhang functionalized P₄ with dianionic 1,4-dilithio-1,3-butadienes to obtain phospholyl lithium derivative 19 in high yield (85 – 99%) and with a broad substrate scope (Scheme 7).[29] Computational analysis suggested a cooperative nucleophilic attack of two Cₓ,y-Li bonds on Pₓ with concurrent cleavage of two P–P bonds and release of Li[P₂] to account for the formation of 19. Intriguingly, this mechanism differs from the noted stepwise routes for the direct preparation of the phosphorus anions from Pₓ.

Two examples on p-block metals complement the work on the s-block metal organyls. In 1991, Barron reported on the formal insertion of Pₓ into the Ga–C bond of Ga(ηBu₃) to give an endo,exo-substituted bicyclo tetraphosphorus derivative, which coordinates an additional equivalent of gallium precursor to form the trifunctionalized Pₓ-butterfly 20 (Scheme 8).[30] Subsequently, Power showed related reactivity for the weak thallene dimer TiArₓDipPh₂ (ArₓDipPh₂ = 2,6-(2,6-Pr₂C₆H₃)C₆H₄) that yielded instead a linear diaryl-substituted ArₓPₓ chain capped by two thallium centers (21).[31] This doubly reduced Pₓ derivative could be oxidized with iodine to the symmetrically substituted butterfly 22.

3. Functionalization of P₄ Using Transition Metal Organyls

Transition metal (TM) complexes have been widely applied for the functionalization of Pₓ,[4] but examples that involve direct P–C bond formation are scarce. In 1999, Peruzzini and co-workers reported on the reaction of rhodium alkyl or aryl ethylene complexes ([triphos]Rh(η¹,R²-P₂R³)) with concurrent oxidant addition of a Pₓ molecule to give ([triphos]Rh[Rₓ'(η¹,Pₓ)])IM1 after which migratory insertion of R² affords the final products. The complexes are thermally labile and allowed extrusion of primary phosphines by adding molecular hydrogen (PH₂R²; albeit in low yield, <15%) with liberation of cyclo-Pₓ complex 24. The reaction illustrates an intriguing stepwise metal-mediated protocol for the preparation of OPcCs from Pₓ.[33] Moreover, 23 (R² = Me or Ph) reacted with MeOTf ([OTf] = SO₂CF₂) to undergo alkylation or protonation at the rhodium-coordinated PR-moieties to afford cations of the type [(triphos)Rh(η¹,R²,PR′)]Y (25, Scheme 9)[34] in which the η¹,R²,Pₓ ligand slowly tumbles with respect to the (triphos)Rh metal center.[35]

Although not leading directly to P–C bonds from Pₓ, we note that Cummins’ group reported on the use of Pₓ-derived terminal niobium phosphide [PₓNb(N(np)Ar)]− (Ar = 3,5-Me₃C₆H₃) and diniobium octaphosphorus complex (Pₓ)[NbOC(η¹-Ad)Mes]₂ for access to a variety of organophosphines through multistep processes. For example, a phosphalkyne (ηBuC≡P) could be prepared by the reaction of 26 with pivaloyl chloride (ηBu-C(O)Cl) by P for (O)Cl metathesis,[38,39] and a diphosphane in a related fashion by reaction of 26 with chloroiminophosphane CIP=NMes*, which releases transient Pₓ fragments that are

![Scheme 7. Direct preparation of phospholyl lithium derivatives from Pₓ.](image)

![Scheme 8. Functionalization of Pₓ using p-block organometallic compounds. ArₓDipPh₂ = 2,6-(2,6-Pr₂C₆H₃)C₆H₄.](image)

![Scheme 9. Metal-mediated direct P–C bond formation using (triphos)rhodium alkyl and aryl ethene complexes. Triphos = 1,1,1-tris(diphenylphosphanyl)methyl)ethane, Tf = SO₂CF₂.](image)

![Scheme 10. Niobium-mediated P–C bond formation. Ar = 3,5-Me₃C₆H₃, 1Ad = 2-adamantyliden.](image)
In addition, the niobium metal centers in 27 could be replaced by organic groups to furnish an organopolyphosphorus framework featuring a rearranged P₄ core with four new P–C bonds (see reference [37] for a detailed mechanism).

4. Functionalization of P₄ Using Carbenes

The ability to stabilize polyphosphorus intermediates along the P₄ fragmentation pathway plays an important role in directing its functionalization, which can also be accomplished by ambiphilic carbenes. The first insights were reported by the group of Bertrand, who reacted two equivalents of a cyclic (alkyl)(aminocarbene (CAAC) with P₄ to afford the E- and Z-isomers of linear tetraphosphorus chain 28 (Scheme 11; only E-isomer shown). The presumed transient triphosphirene (IM2) reaction intermediate could be trapped with 2,3-dimethylbutadiene to give 29. Likewise, the diphosphene core of 28 underwent a [4+2]-cycloaddition to yield 30 in which two additional P–C bonds have been introduced.

The nature of the carbene influences the fate of the P₄ functionalization (Scheme 12). For example, a more electrophilic acyclic (alkyl)(amino)carbene (AAAC) generated bis(carbene) adduct 31 as the cyclopropanation reaction with the initially formed triphosphirene is more favorable compared to ring-opening (cf. IM2, Scheme 11). On the other hand, a less bulky CAAC led instead to trisubstituted P₄-derivative 32 in addition to lower nuclearity P₂-diphosphaalkene 33. Moreover, the small bis(dilisopropylamino)cyclopropenylidene fragmented the P₄ tetrahedron even further to give P₃-cation 34. These reactions reveal modular reactivity based on both the electronic and steric properties of the carbene.

NHCs less π-acidic than CAACs react with P₄ in a related fashion but with different outcomes. For example, treating P₄ with two equivalents of 1,3-bis(2,6-dilisopropylphenyl)-imidazolin-2-ylidene (SIDipp) gave 35 (Scheme 13), featuring the tetraphosphatreni structural motif, which over time aggregated to the neutral P₁₂ cluster 36. The mechanism was postulated to involve a [3+2]-cycloaddition of 35 with triphosphirene 37 to give intermediate 38, which rearranged to heptaphosphanorbonadiene 39 with loss of two NHCs to afford the final product upon an additional [4+2]-cycloaddition with 37. As such, the weaker P–C double bonds that are formed by NHCs over CAACs induce aggregation over fragmentation, because the former are better leaving groups.

Remarkably, reacting P₄ with more electrophilic NHCs that bear carbonyl functional groups in the carbon backbones, allows isolation of P₃ clusters 40, which are formed by [2+2]-cycloaddition of the linear R₂P₃ chains (Scheme 14). Furthermore, a highly electrophilic benzamido carbene was shown the insert into one P–P bond to give the expanded five-membered cage compound 41, which possibly also represents the initial product for other NHC-induced activations.

A protocol to furnish OPCI containing P₃ units was reported in a joint publication by the groups of Gudat and Grützmacler who treated P₄ with equimolar amounts of imidazolium salts and KOrBu. The incipient carbene and the tBuOH by-product react with P₄ to generate a phosphaalkene (42, Scheme 15) in addition to a small amount of cation 43 that resembles the CAAC-initiated fragmentation reported by Bertrand (cf. 34, Scheme 12).

Lastly, a frustrated Lewis pair (FLP) approach, based on the use of carbene tBu (tBu = 1,3-bis(tert-butyl)-imidazolin-2-ylidene) and B(C₆F₅)₃, was reported by Tamm et al. The NHC was
found to bind “abnormally” (mesoionic) in the reaction with $P_4$ and induced heterolytic $P@P$ bond cleavage [Eq. (1)] to afford the labile zwitterionic exo,exo-$\text{bicyclo}[1.1.0]$tetraphosphabutane 44 in the presence of the Lewis acid, similar to anion reported recently by our group (Scheme 16).

5. Functionalization of $P_4$ Using Carboradicals

Homolytic cleavage of the $P@P$ bonds with concomitant $P@C$ bond formation, all the way to monophosphanes ($PR_3$), can be accomplished with carboradicals. A key challenge is to cleanly generate the radicals in the presence of $P_4$. Illustrative is the early work by the group of Barton, who used $P_4$ as trap in trace oxygen-initiated radical chain reactions with Barton’s PTOC ester-derived carbon radicals (O-acyl derivatives of N-hydroxy-2-thiopyridone), which after oxidative work-up afforded phosphonic acids in high yield (71–86 %; Scheme 17).

The concept was later extended by the group of Cummins, who synthesized tertiary phosphanes from $P_4$ and radicals generated by halogen ($X$) abstraction from haloalkyls or halohydrins.

In 2014, the potential of reacting $P_4$ with metal-mediated radicals was further explored by Scheer and co-workers. They showed that salt elimination from $P_4$Na by CuBr afforded (Cp$^\text{RIG}$) radicals that interacted with $P_4$ as observed previously for the bulky (Dmp)$^*$ by Cummins to give the exo,exo-$

with titanium trisilanilide Ti(N(fBu)Ar)$_3$ (Scheme 18; Ar = 3,5-Me$_2$C$_6$H$_3$). Not only could PPh$_3$ and PCy$_3$ be generated, but also $P(SiMe$_3$)_3$ and $P(SnPh$_3$)$_3$ by splitting the higher congener Si–X and Sn–X bonds. Like Barton’s radical syntheses, the reactions involve consecutive homolytic $P@P$ bond breaking events and proceed through multiple cyclopolyphosphorus intermediates [Eq. (4)]. This was demonstrated for the more bulky substrates DmpI and MesBr (Dmp = 2,6-dimethylphenyl), which impede complete substitution to afford bicyclo[1.1.0]tetraphosphabutane exo,endo-Dmp$_2$P$_4$ (45) and cyclotriphosphirane Mes$_3$P$_3$ (46), respectively. Notably, the oxidized titanium(IV) by-product X@$^\text{III}$Ti(N(fBu)Ar)$_3$ can be easily reduced back to the Ti@$^\text{III}$ precursor with sodium amalgam, but due to the strong oxidizing properties of $P_4$ itself (Na/Hg + $P_4$ → Na$_3$P) this process cannot be conducted in situ, which prevents catalytic conversion. It is also of note that electrochemical methods have been employed to furnish related OPCs from $P_4$ which were recently outlined and discussed by Yakhvarov and Budnikova.

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Scheme 19. Metal-mediated radical synthesis of organyl-substituted $P_4$ butterflies.
butterfly \( \text{Cp}^\text{BG} \cdot \text{P}_4 \) (47, Scheme 19). The presence of free carboradicals was confirmed by EPR, whereas more reactive and less bulky \( \text{Cp}^\text{X} \) derivatives \( \text{Cp}^\text{X} = \text{Cp, Cp}^*, \text{Cp}^\text{e} \) and \( \text{Cp}^\text{Gr} \) were shown to undergo rapid decomposition, either through radical coupling or forming \( \text{Cp}^\text{XH} \). They did react with \( \text{P}_4 \) via an iron-mediated route (with \( \text{Cp}^\text{FeBr}_2 \) acting as radical transfer agent) to bicyclic tetraphosphanes 48.

6. Functionalization of \( \text{P}_4 \) through \( \text{P}_2 \) Fragments

Cracking white phosphorus into two \( \text{P}_2 \) units has only been explored to a limited extent. The diatomic fragment features a highly reactive \( \equiv \text{P} \equiv \text{P} \) triple bond that allows for Diels–Alder type chemistry. In 2010, the group of Cummins reported on photochemically\(^{[52]} \) generated \( \text{P}_2 \) that was captured in situ by DA reactions with 1,3-dienes (Scheme 20).\(^{[53]} \) The products formed after consecutive \( [4+2] \)-cycloadditions to afford unique organodiphosphanes 49, which have been shown to coordinate to Group 10 metals\(^{[54]} \) and undergo chalcogenation and alkylation reactions to allow further functionalization of the bicyclic structures.\(^{[55, 56]} \) Whereas this photochemical protocol transfers cleanly \( \text{P} \) atoms from \( \text{P}_2 \) into organic frameworks, the isolated yields are only moderate \( (R = \text{H}, 2\% ; R = \text{Me}, 34\% ) \) due to their lability under the harsh irradiation conditions.

The transfer of a \( \text{P}_2 \) fragment to an organic substrate was also achieved by Mathey and co-workers,\(^{[57]} \) who showed that upon mixing \( \text{Me}_3 \text{Si} \cdot \text{P} \equiv \text{P} \) with \( \text{P}_4 \) a formal \( [3+2] \)-cycloaddition reaction occurs to form diazadiphospholide anion 50 and neutral 51 after protonation (Scheme 21).

The product is reminiscent to the recently described all-inorganic aromatic ion \( \text{P}_2 \text{N}_3^- \) prepared from reacting azide \( (\text{N}_3^-) \) with a thermally extruded \( \text{P}_2 \) unit from a transannular diphosphorus bianthracene adduct, \( \text{P}_2 \text{C}_2(\text{H}_3) \text{H}_2 \),\(^{[58, 59]} \) Transient \( \text{P}_2 \) may be the intermediate in the formation of 50, but an ionic mechanism related to that observed for the dianions reported by Zhang is also feasible (see Section 2).\(^{[29]} \)

7. Summary and Outlook

The functionalization of \( \text{P}_4 \) through direct \( \text{P} \equiv \text{C} \) bond formation represents a versatile approach for the synthesis of OPCs, and shows potential to circumvent the current use of phosphorus halides. Forming the desired \( \text{P} \equiv \text{C} \) bonds can be accomplished by a number of methods, involving lithium organyls, organo-metallic complexes, carbenes, carboradicals, and trapping of \( \text{P}_2 \) fragments with dienes. The product scope is varied and includes both industrially relevant phosphines as well as unique OPCs that are essentially inaccessible through the use of \( \text{PCl}_3 \). These can serve as building blocks to access intriguing additional P-compound classes, like observed for the LA-stabilized \( |\text{RP}_2|^- \) anions 4 and the \( \text{R}_2 \text{P}_4 \) chains of the type 28, or can be studied as ligands for coordination chemistry as displayed in \( \text{P}_4 \)-butterflies 14 and 20, and explored for organodiphosphanes 49.

The chemistry surveyed reveals substantial progress in controlling \( \text{P}_4 \) functionalization and represents an encouraging entry point for further development. To translate the attained fundamental insights to practical substitution reactions using readily available reagents seems imperative. Exemplary are the protocols reported by Zhang, and Guidat and Grützmacher, using dithiolobutadienes or imidazolium chlorides, respectively, to directly produce phospholide anions 19 and carbene–phosphinidene adducts 42. Also the design of catalytic procedures to facilitate \( \text{P} \equiv \text{C} \) bonding is important. Cummins and Scheer showed Ti- and Fe-mediated radical processes to be potential platforms, and Peruzzini laid the foundation for a rhodium-assisted cycle. In this regard, photochemistry proves to be an equally promising tool to exploit the underdeveloped \( \text{P}_4 \rightarrow 2 \text{P}_2 \) fragmentation. While achieving these goals is ambitious and will require considerable effort, the recent advancements in this field are significant and continue to enable new avenues to be explored, which will hopefully spur the construction of a wealth of valuable new phosphorus products.

Acknowledgements

This work was supported by the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (NWO/ CW).

Conflict of interest

The authors declare no conflict of interest.

Keywords: main group chemistry · nucleophilic addition · organophosphorus compounds · phosphorus · phosphorus anions

[2] Hydrolysis of \( \text{P}_4 \) with \( \text{NaOH} \) leads to \( \text{NaH}_2\text{PO}_4 \) and \( \text{PH}_4 \) both of which can also be used to produce phosphorus compounds.
In 1988, Baudler et al. detected the anion \([\text{HP(CN)}]\)\(^{-}\) by PNMR spectroscopy, after reduction of \(\text{P}_3\) with chlorobenzene and sodium. See Ref. [1].

The reaction of potassium cyanide with \(\text{P}_3\) is selective, giving \(\text{K}[\text{P(CN)}_3]\)\(^{-}\). See Ref. [2].

In 1983, RSC reported on the reaction of \(\text{P}_3\) with chlorobenzene and sodium. See Ref. [3].

By 1985, a related set of reactions had been described by Baudler et al. See Ref. [4].

Similarly, the reaction of \(\text{P}_3\) with CO yields the phosphonylation anion, see: I. Krummenacher, C. C. Cummins, Polyhedron 2012, 32, 10–13.


Similarly, the reaction of \(\text{P}_3\) with CO yields the phosphonylation anion, see: M. Caporali, M. Serrano-Ruiz, M. Peruzzini. In Chemistry Beyond Chlorine (Eds.: P. Tundo, L.-N. He, E. Lokteva, C. Mota), Springer International Publishing, Cham, 2016, pp. 97–136.