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DOI
10.1002/chem.201702067

Publication date
2017

Document Version
Final published version

Published in
Chemistry-A European Journal

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Citation for published version (APA):
Borger, J. E., Ehlers, A. W., Slootweg, J. C., & Lammertsma, K. (2017). Functionalization of P4 through Direct P-C Bond Formation. Chemistry-A European Journal, 23(49), 11738-11746. https://doi.org/10.1002/chem.201702067

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Organophosphorus Compounds

Functionalization of P₄ through Direct P–C Bond Formation

Jaap E. Borger,[a] Andreas W. Ehlers,[a, b, c] J. Chris Slootweg,[a, c] and Koop Lammertsma*[a, b]
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] 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⁺).[5a,12] White phosphorus can also be “cracked” both thermally (> 1100 K)[13] and photochemically (UV irradiation)[14] into two transient P₂ molecules (P₂=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 P₂ fragments with organic substrates.

2. Functionalization of P₄ Using Main Group Metal Organyls

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-butyllithium (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; only Ph shown), but with only low selectivity and poor yields (0–40%) in addition to large quantities of organopolyporphosphines.[17] Equally challenging with similar product mixtures are the reactions of P₄ with alkynyls (II)[18] or with tert-butyl- or methylithium in combination with Me₃SiCl 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 MesLi (IV; Mes⁺ = 2,4,6-iBu₃C₆H₂), 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.](image-url)
Versely, alkylation of the more reactive BPh$_3$-stabilized anion 4c with Ph$_3$C$^+$PF$_6$ 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.$^{[24]}$

Dr. Jaap 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 Lammertse, 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 Zurich 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 homo- and heteronuclear 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 Slookweg 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 Lammertse (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. Sondheimer (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(C₆F₅)₃ group in 4a,b, the less stabilizing BPh₃ in 4c departs immediately upon endo-cyclic substitution by BH₃ or WCO). In these cases the anionic [RP₃]⁻ 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 OCPs containing P₃ and P₄ entities through unprecedented [3+1]-fragmentation reactions using either phenylisocyanate or imidazolium chloride in the presence of an access of the P₃-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 spirophosphorane 9 and carbene–phosphinidene adduct 11, respectively, with concurrent trapping of the liberated diphosphine Mes₃P₃ by the organic diene that generates in both cases organotriphosphirane 10.

The isolation and versatility of the stabilized [RP₃]⁻ anion 4 marks a significant step toward the controlled functionalization of P₄ with organolithium reagents. Interestingly, related RP₃ derivatives can also be generated from P₄ in the coordination sphere of a gold(I) cation, even with unencumbered MesLi, which is otherwise precluded due to rapid quenching with boron Lewis acids to Li[MesBAR]. Exemplary is the reaction of AryLi with the η²-P₃-coordinated cationic (NHC)Au⁺ complex 12 (Scheme 4; Ary = Mes or Dmp, NHC = N-heterocyclic carbene) that afforded selectively the neutral bicyclic tetraphosphanes 13, which coordinates to an additional gold cation complex with displacement of a P₄ molecule to give bimetallic 14.

In 2015, Hill and co-workers reported on the selective synthesis of the Mg²⁺-stabilized cluster dianion [nBu₂P₄]²⁻ 15 from P₄ and β-diketiminato n-butylmagnesium complex [(POBDI)Mg(nBu)] (POBDI = HC(C(Me)N(2,6-iPr,C₆H₃))₃; Scheme 5). The disubstituted P₄-dianion likely results from initial formation of the [nBu₂P₄]⁻ butterfly anion [Eq. (1)] with subsequent nucleophilic addition across the transannular P–P bond [Eq. (2)]. Product 15 reacts with P₄ to the polyphosphate cluster [nBu₂P₄]²⁻ (16), which is isolable due to the stabilizing [POBDI]Mg²⁺ 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 P₄ substitution.

The group of Lerner reported on the synthesis of a trisanionic [R₂P₃]⁻ derivative (17, Scheme 6). The complex is generated from P₄ and mesityllithium in benzene over the course of four days in 60% yield. Presumably, tetraphosphanetriide 17 results from nucleophilic attack on the common [RP₃]⁻ 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 [Mes₃P-H]⁻ 18, which on quenching with trifluoroacetic acid gave diphosphane Mes₃P-H⁻ through a novel route to prepare lower nuclearity phosphanes.
nucleophilic attack of two C₄₋₂-Li bonds on P₄ with concurrent cleavage of two P–P bonds and release of Li[Li₄] 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 P₄.

Two examples on p-block metals complement the work on the s-block metal organyls. In 1991, Barron reported on the formal insertion of P₄ into the Ga–C bond of Ga(fBu)₃ to give an endo,exo-substituted bicyclo tetraphosphorus derivative, which coordinates an additional equivalent of gallium precursor to form the trifunctionalized P₄-butterfly 20 (Scheme 8).[30] Subsequently, Power showed related reactivity for the weak thallene dimer TIA[⁺⁺⁺⁺][⁺⁺⁺][(+++)⁺⁺⁺] that yielded instead a linear diaryl-substituted Ar:P₄ chain capped by two thallium centers (21).[31] This doubly reduced P₄ derivative could be oxidized with iodine to the symmetrically substituted butterfly 22.

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

give the novel complexes [(triphos)Rh(η⁴-P₄R²)] 23 (Scheme 9).[32] Their formation is believed to start by release of ethylene from the rhodium precursor with subsequent oxidative addition of a P₄ molecule to give [(triphos)Rh(R')(η¹-P₄)] (IM1) after which migratory insertion of R' affords the final products. The complexes are thermally labile and allowed extrusion of primary phosphines by adding molecular hydrogen (PH₃R)₂ albeit in low yield, <15% with liberation of cyclo-P₄ complex 24. The reaction illustrates an intriguing stepwise metal-mediated protocol for the preparation of OCPs from P₄.[33] Moreover, 23 (R' = Me or Ph) reacted with MeOTf (OTf = SO₂CF₂) or HBF₄ to undergo alkylation or protonation at the rhodium-coordinated PR-moiety to afford cations of the type [(triphos)Rh(η¹-P₄R²)][Y] (25, Scheme 9)[34] in which the η¹-P₄-R ligand slowly tumbles with respect to the (triphos)Rh metal center.[35]

Although not leading directly to P–C bonds from P₄, we note that Cummins’ group reported on the use of P₄-derived terminal niobium phosphide [P≡Nb(N(Np)Ar)]⁻ 26 (Ar = 3,5-Me₂C₆H₃)[36] and dinioibium octaphosphorus complex (P₄)[Nb(OC₁(²-Ad)Mes)]₂ 27 (Scheme 10),[37] which enabled access to a variety of organophosphines through multistep processes. For example, a phosphalkyne (fBuC≡P) could be prepared by the reaction of 26 with pivaloyl chloride (fBuCl) by P for (O)Cl metathesis,[38,39] and a diphosphene in a related fashion by reaction of 26 with chloroiminophosphane CIP=NMes*, which releases transient P₂ fragments that are

3. Functionalization of P₄ Using Transition Metal Organyls

Transition metal (TM) complexes have been widely applied for the functionalization of P₄,[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(η⁴-C₄H₈)]; R' = Me, Et or Ph, triphos = 1,1,1-tris(diphenylphosphanyl)methylethane) with P₄ to

Chem. Eur. J. 2017, 23, 11738 – 11746 www.chemeurj.org 11742 © 2017 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim
trappable by 1,3-CHD (see Section 6). 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)(amino)carbene (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 P₃-diphosphaalkene 33. Moreover, phosphahtiene structural motif, which over time aggregated to the neutral P₃₂ 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 P₄ clusters 40, which are formed by [2+2]-cycloaddition of the linear R₄P₄ 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 OPCs containing P₄ units was reported in a joint publication by the groups of Gudat and Grützmacher 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)-imidazol-2-ylidine) 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 a heterolytic P–P bond cleavage \[\text{Eq. (1)}\] to afford the labile zwitterionic $\text{exo,endo}$-$\text{bicyclo}[1.1.0]$tetraphosphabutane in the presence of the Lewis acid, similar to anion reported recently by our group (Scheme 16). \[\text{[23, 24]}\]

### 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). \[\text{[49]}\]

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 haloarylsl.

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 $\text{Cp}^{\text{PhNa}}$ by CuBr afforded $\text{Cp}^{\text{Ph}}$ radicals that interacted with $P_4$ as observed previously for the bulky (Dmp)$^+$ by Cummins, to give the $\text{exo,exo}$

### Scheme 18. Radical synthesis of tertiary- and cyclopolyphosphanes from $P_4$

with titanium trisanilide $\text{Ti(PhBu)Ar}_3$ (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)$_3$ 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 \[\text{Eq. (4)}\]. This was demonstrated for the more bulky substrates DmpI and MesBr (Dmp = 2,6-dimesitylphenyl), which impede complete substitution to afford bicyclo[1.1.0]tetraphosphabutane $\text{exo,endo}$-$\text{Dmp}_2$-$P_4$ (45) and cyclotriphosphirane $\text{Mes}_3$-$P_3$ (46), respectively. Notably, the oxidized titanium(IV) by-product $X@$-Ti(N(tBu)Ar)$_3$ can be easily reduced back to the Ti$^{III}$ 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. \[\text{[5]}\]

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### Scheme 19. Metal-mediated radical synthesis of organyl-substituted $P_4$ butterflies.
butterfly \( \text{Cp}^{\text{Bu}} \_P_4 \) (47, Scheme 19). The presence of free carboradicals was confirmed by EPR, whereas more reactive and less bulky (Cp\(^3\))\(^+\) derivatives (Cp\(^3\)=Cp, Cp\(*\), Cp\(^{\text{Bu}}\) and Cp\(^{\text{Bu}}\)\(^+\)) were shown to undergo rapid decomposition, either through radical coupling or forming Cp\(^{\text{Bu}}\)H. They did react with P\(_4\) via an iron-mediated route (with Cp\(^{\text{FeBr}}\) acting as radical transfer agent) to bicyclic tetraphosphanes 48.

6. Functionalization of \( P_4 \) through \( P_2 \) Fragments

Cracking white phosphorus into two \( P_2 \) units has only been explored to a limited extent. The diatomic fragment features a highly reactive \( P\equiv P \) triple bond that allows for Diels–Alder type chemistry. In 2010, the group of Cummins reported on photochemically \(^{[52]}\) generated \( P_2 \) 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 \( P \) atoms from \( P_4 \) 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 \( P_2 \) fragment to an organic substrate was also achieved by Mathey and co-workers, \(^{[57]}\) who showed that upon mixing (trimethylsilyl)diazomethanide with \( P_2 \) 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 \( P_2N_7^- \), prepared from reacting azide (\( N_3^- \)) with a thermally extruded \( P_2 \) unit from a transannular diphosphorus bisanthracene adduct, \( P_2(C_14H_{10})_2 \). \(^{[58, 59]}\) Transient \( P_2 \) 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). \(^{[60]}\)

7. Summary and Outlook

The functionalization of \( P_4 \) through direct \( P–C \) 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 \( P–C \) bonds can be accomplished by a number of methods, involving lithium organyls, organo-metallic complexes, carbenes, carboradicals, and trapping of \( P_2 \) 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 \( \left[ \text{RP}_2 \right]^- \) anions 4 and the \( \text{R}_2\text{P}_2 \) 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 \( P_4 \) 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 Gudat and Grützmacher, using diithiobutadienes or imidazolium chlorides, respectively, to directly produce phospholide anions 19 and carbene–phosphinidene adducts 42. Also the design of catalytic procedures to facilitate \( P–C \) 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 \( P_4 \rightarrow 2 P_2 \) 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

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Manuscript received: May 8, 2017  
Accepted manuscript online: May 11, 2017  
Version of record online: July 27, 2017