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Minireview

Organophosphorus Compounds

# Functionalization of $P_4$ through Direct P−C Bond Formation

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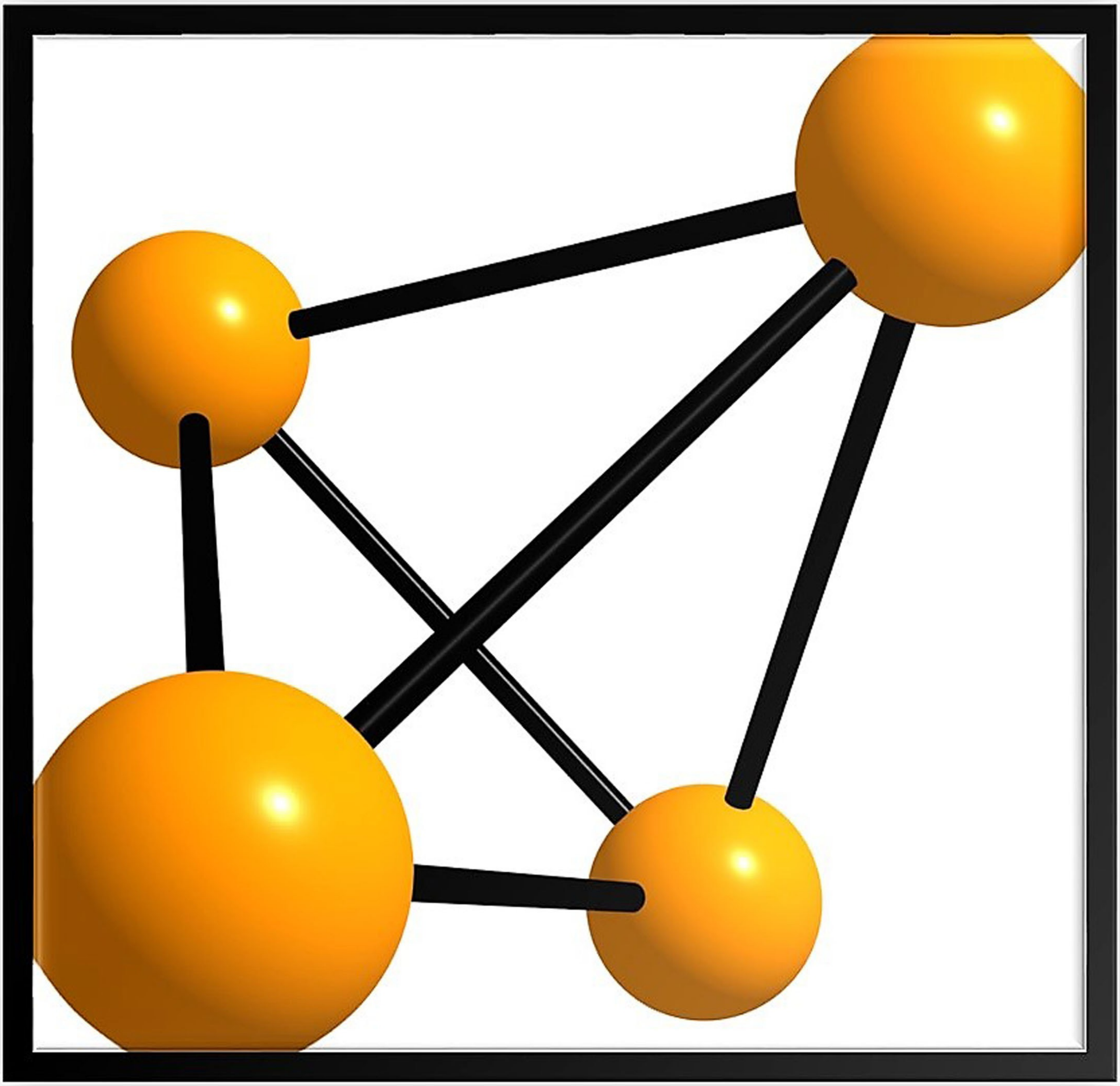

**Abstract:** Research on chlorine-free conversions of $P_4$ into organophosphorus compounds (OPCs) has a long track record, but methods that allow desirable, direct P–C bond formations have only recently emerged. These include the use of metal organyls, carbenes, carboradicals, and photochemical approaches. 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 ($P_4$), which is typically converted to $PCl_3$ 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.[1] Direct functionalization of $P_4$ could offer an attractive alternative (**B**), but this strategy is hampered by the unpredictable behavior of the $P_4$ 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,[3,4,5] an appealing approach based on direct P–C bond formation, resembling $PCl_3$ substitution,[6] has emerged only recently as a promising platform for the selective preparation of OPCs from $P_4$, which is the topic of this review.[7]

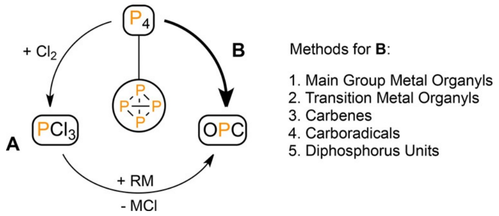

**Figure 1.** Preparation of organophosphorus compounds (OPCs) from $P_4$.

To understand how P–C bonds can be made using $P_4$ it is instructive to touch on its properties. Most pronounced is its electrophilicity,[8] which due to the acute (60°) bond angles of the $P_4$ 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 $P_4$ benefits from delocalization of the electrons in s, p, and d cluster orbitals (spherical aromaticity).[11] Whereas reduction of $P_4$ by means of cyclic voltammetry (CV) occurs readily, it is irreversible due to bond rupture and polymerization of the formed radical anion ($P_4^{\bullet -}$).[5b, 12] White phosphorus can also be "cracked" both thermally (> 1100 K)[13] and photochemically (UV irradiation)[14] into two transient $P_2$ molecules (P≡P) that polymerize rapidly to the more stable red phosphorus allotrope.[15]

In this Minireview we highlight recent breakthroughs in $P_4$ 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 $P_2$ fragments with organic substrates.

## 2. Functionalization of $P_4$ 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 $P_4$.[16] Quenching the resulting deep red suspensions with water or butylhalides afforded mixtures of mostly primary or tertiary phosphanes 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 organopolyphosphines.[17] Equally challenging with similar product mixtures are the reactions of $P_4$ with alkynyls (**II**)[18] or with *tert*-butyl- or methyllithium in combination with $Me_3SiCl$ as quenching agent (**III**).[19] The more bulky reagents allowed for formation of cyclotetraphosphanes (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-$t$Bu$_3$C$_6$H$_2$), Fluck et al. demonstrated that degradation of $P_4$ is stoppable after a single P–P bond cleavage. They isolated

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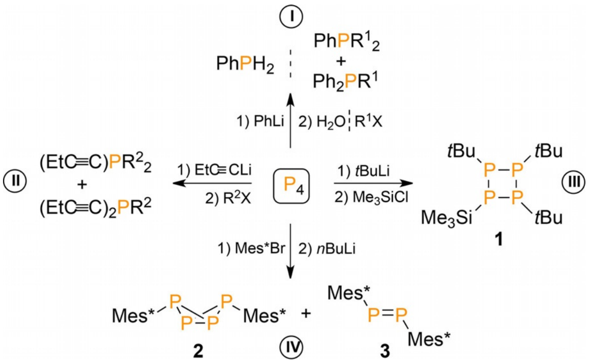


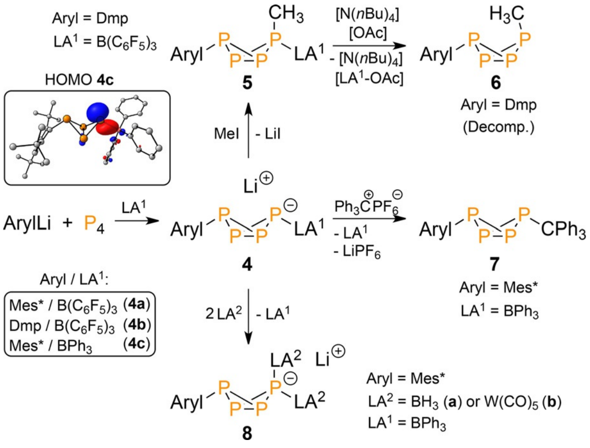
**Scheme 1.** Reactions of $P_4$ with organoalkali reagents. Mes* = 2,4,6-$tBu_3C_6H_2$, $R^1$ = Bu, $R^2$ = Et or Pr, X = Br or Cl.

in < 10 % yield the first example of a bicyclo[1.1.0]tetraphosphabutane (**2**) in addition to diphosphene **3**.[21]

The reactions of $P_4$ with organoalkali reagents proceed through a common highly reactive transient $[RP_4]^-$ butterfly anion, which is produced after nucleophilic addition and concomitant P–P bond cleavage [Eq. (1)].

(1)

In 2014, the formation of this elusive intermediate was confirmed by us.[22] We used sterically encumbered ArylLi reagents and Lewis acids (LA; $B(C_6F_5)_3$ or $BPh_3$) 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 $P_4$ core. For example, alkylation of **4b**, featuring the strong LA $B(C_6F_5)_3$, with MeI 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*-$R_2P_4$ butterfly **6**.[23] Conversely, alkylation of the more reactive $BPh_3$-stabilized anion **4c** with $Ph_3C^+PF_6^-$ 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]



**Scheme 2.** Synthesis of LA-stabilized $[RP_4]^-$ butterfly anions and subsequent substitution and transfer reactions. Mes* = 2,4,6-$tBu_3C_6H_2$, Dmp = 2,6-dimesitylphenyl.

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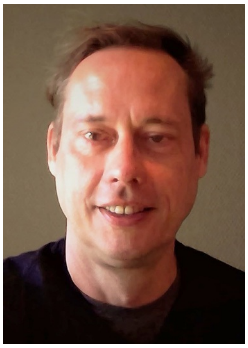
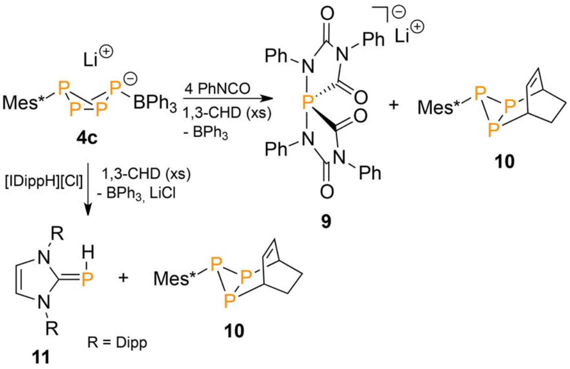


*Dr. A. W. Ehlers obtained his PhD at the Phillipps University of Marburg, Germany on ab initio calculations of Transition Metal-Ligand bond interactions. He joined the VU University in Amsterdam as Marie Curie Fellow and later as Assistant Professor to study organometallic and main group chemistry for 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.*

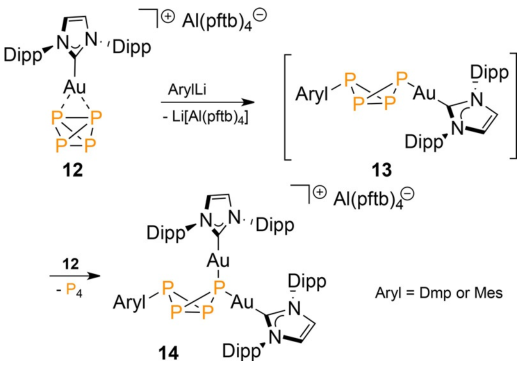
*Prof. Koop Lammertsma (born in 1949 in Makkum/the Netherlands) was educated at the Universities of Groningen (1974) and Amsterdam (Ph.D. 1979). After postdoctoral work with F. Sondheimer (London), P. v. R. Schleyer (Erlangen-Nürnberg), and Nobel laureate G. A. Olah (USC) he moved in 1983 to the University 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 $B(C_6F_5)_3$ group in **4a**,**b**, the less stabilizing $BPh_3$ 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).[24] Intriguingly, the high reactivity of **4c** also grants access to OPCs containing $P_1$ and $P_3$ entities through unprecedented [3+1]-fragmentation reactions using either phenylisocyanate or imidazolium chloride in the presence of an access of the $P_3$-trapping reagent 1,3-cyclohexadiene (1,3-CHD; Scheme 3).[25] The reactions proceed through "P" transfer from the LA-stabilized butterfly anions to the reagents to give spirophosphoranide **9** and carbene–phosphinidene adduct **11**, respectively, with concurrent trapping of the liberated diphosphene $Mes^*P_3$ by the organic diene that generates in both cases organotriphosphirane **10**.



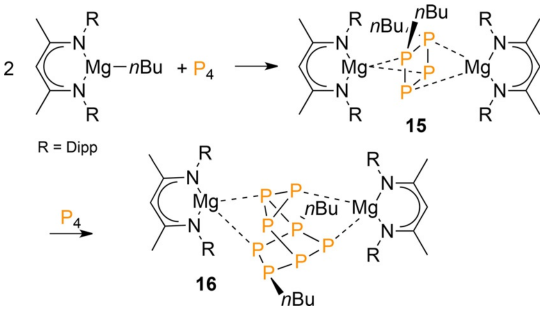
**Scheme 3.** Selective [3+1]-fragmentation reactions of LA-stabilized $RP_4^-$ butterfly **4c**. Mes* = 2,4,6-$tBu_3C_6H_2$, IDipp = 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene, CHD = cyclohexadiene.

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,[26] which is otherwise precluded due to rapid quenching with boron Lewis acids to Li[$MesBAr_3$]. Exemplary is the reaction of ArylLi with the $\eta^2$-$P_4$-coordinated cationic (NHC)$Au^I$ complex **12** (Scheme 4; Aryl = 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 $P_4$ molecule to give bimetallic **14**.

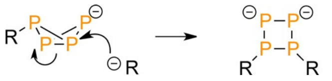


**Scheme 4.** Functionalization of $P_4$ in the coordinated sphere of a coinage metal cation. Dipp = 2,6-diisopropylphenyl, Dmp = 2,6-dimesitylphenyl, pftb = perfluoro-*tert*-butoxy.

In 2015, Hill and co-workers reported on the selective synthesis of the $Mg^{2+}$-stabilized cluster dianion $[nBu_2P_4]^{2-}$ **15** from $P_4$ and β-diketiminato *n*-butylmagnesium complex [($^{Dipp}$BDI)Mg*n*Bu] ($^{Dipp}$BDI = HC{C(Me)N(2,6-$iPr_2C_6H_3$)}$_2$; Scheme 5).[27] The disubstituted $P_4$-dianion likely results from 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 polyphosphide cluster $[nBu_2P_8]^{2-}$ (**16**), which is isolable due to the stabilizing bulky ($^{Dipp}$BDI)$Mg^{2+}$ 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.

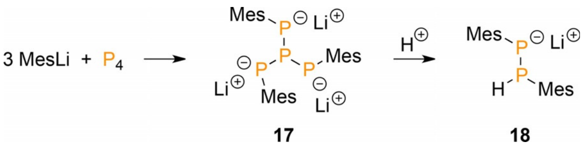


**Scheme 5.** Functionalization of $P_4$ by an *n*-butylmagnesium complex. Dipp = 2,6-diisopropylphenyl.

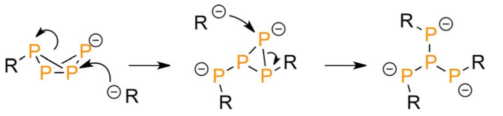


(2)

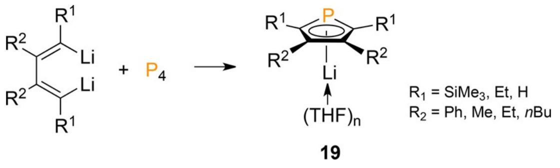
The group of Lerner reported on the synthesis of a trisanionic $[R_3P_4]^{3-}$ derivative (**17**, Scheme 6).[28] The complex is generated from $P_4$ and mesityllithium in benzene over the course of four days in 60% yield. Presumably, tetraphosphanetriide **17** results from nucleophilic attack on the 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 diphosphanide $[Mes_2P_2H]^-$ **18**, which on quenching with trifluoroacetic acid gave diphosphane Mes(H)P–P(H)Mes. This process hints toward a novel route to prepare lower nuclearity phosphanes.



**Scheme 6.** Functionalization of $P_4$ using solvent-free mesityllithium.

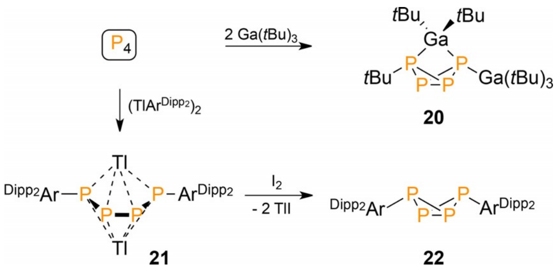


Recently, Zhang functionalized $P_4$ with dianionic 1,4-dilithio-1,3-butadienes to obtain phospholyl lithium derivative **19** in high yield (85 −99 %) and with a broad substrate scope (Scheme 7).[29] Computational analysis suggested a cooperative nucleophilic attack of two $C_{sp2}$–Li bonds on $P_4$ with concurrent cleavage of two P–P bonds and release of Li[$P_3$] 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 $P_4$.



**Scheme 7.** Direct preparation of phospholyl lithium derivatives from $P_4$.

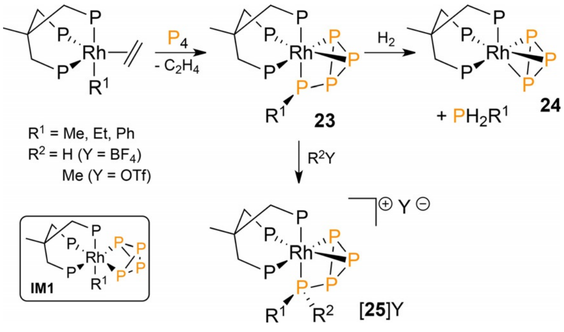
Two examples on p-block metals complement the work on the s-block metal organyls. In 1991, Barron reported on the formal insertion of $P_4$ into the Ga–C bond of Ga(*t*Bu)$_3$ to give an *endo*,*exo*-substituted bicyclo tetraphosphorus derivative, which coordinates an additional equivalent of gallium precursor to form the trifunctionalized $P_4$-butterfly **20** (Scheme 8).[30] Subsequently, Power showed related reactivity for the weak thallene dimer $TlAr^{Dipp2}$ ($Ar^{Dipp2}$ = 2,6-(2,6-*i*Pr$_2C_6H_3$)$C_6H_3$) that yielded instead a linear diaryl-substituted $Ar_2P_4$ chain capped by two thallium centers (**21**).[31] This doubly reduced $P_4$ derivative could be oxidized with iodine to the symmetrically substituted butterfly **22**.



**Scheme 8.** Functionalization of $P_4$ using p-block organometallic compounds. $Ar^{Dipp2}$ = 2,6-(2,6-*i*Pr$_2C_6H_3)_2C_6H_3$.

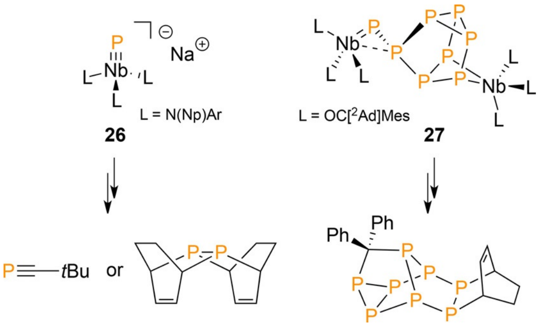
## 3. Functionalization of $P_4$ Using Transition Metal Organyls

Transition metal (TM) complexes have been widely applied for the functionalization of $P_4$,[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($R^1$)($\eta^2$-$C_2H_4$)]; $R^1$ = Me, Et or Ph, triphos = 1,1,1-tris(diphenylphosphanylmethyl)ethane) with $P_4$ to give the novel complexes [(triphos)Rh($\eta^1$:$\eta^2$-$P_4R^1$)] **23** (Scheme 9).[32] Their formation is believed to start by release of ethylene from the rhodium precursor with subsequent oxidative addition of a $P_4$ molecule to give [(triphos)Rh($R^1$)($\eta^1$:$\eta^1$-$P_4$)] (**IM1**) after which migratory insertion of $R^1$ affords the final products. The complexes are thermally labile and allowed extrusion of primary phosphanes by adding molecular hydrogen ($PH_2R^1$; albeit in low yield, < 15 %) with liberation of *cyclo*-$P_3$ complex **24**. The reaction illustrates an intriguing stepwise metal-mediated protocol for the preparation of OPCs from $P_4$.[33] Moreover, **23** ($R^1$ = Me or Ph) reacted with MeOTf (OTf = $SO_3CF_3$) or $HBF_4$ to undergo alkylation or protonation at the rhodium-coordinated PR-moiety to afford cations of the type [(triphos)Rh($\eta^1$:$\eta^2$-$P_4R^1R^2$)][Y] (**25**, Scheme 9)[34] in which the $\eta^1$:$\eta^2$-$P_4R$ ligand slowly tumbles with respect to the (triphos)Rh metal center.[35]



**Scheme 9.** Metal-mediated direct P–C bond formation using (triphos)rhodium alkyl and aryl ethene complexes. Triphos = 1,1,1-tris(diphenylphosphanylmethyl)ethane, Tf = $SO_3CF_3$.

Although not leading directly to P–C bonds from $P_4$, we note that Cummins' group reported on the use of $P_4$-derived terminal niobium phosphide [P≡Nb(N(Np)Ar)$_3$]$^-$ **26** (Ar = 3,5-$Me_2C_6H_3$)[36] and diniobium octaphosphorus complex ($P_8$)[Nb(OC-[$^2$Ad]Mes)$_3$]$_2$ **27** (Scheme 10),[37] which enabled access to a variety of organophosphanes through multistep processes. For example, a phosphalkyne (*t*BuC≡P) could be prepared by the reaction of **26** with pivaloyl chloride (*t*Bu-C(O)Cl) by P for (O)Cl metathesis,[38,39] and a diphosphane in a related fashion by reaction of **26** with chloroiminophosphane ClP=NMes*, which releases transient $P_2$ fragments that are

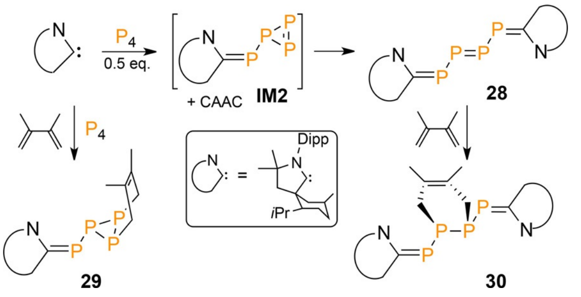


**Scheme 10.** Niobium-mediated P–C bond formation. Ar = 3,5-$Me_2C_6H_3$, $^2$Ad = 2-adamantylidene.

trappable by 1,3-CHD (see Section 6).[40] In addition, the niobium metal centers in **27** could be replaced by organic groups to furnish an organopolyphosphorus framework featuring a rearranged $P_8$ core with four new P–C bonds (see reference [37] for a detailed mechanism).

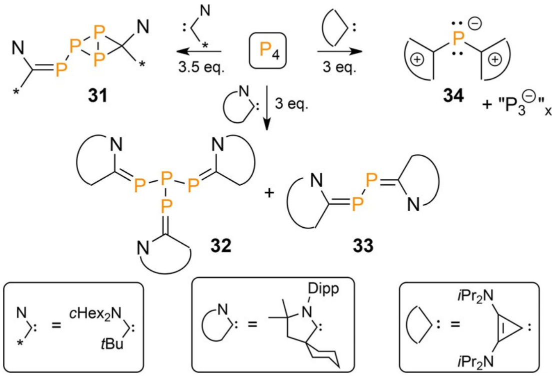
## 4. Functionalization of $P_4$ Using Carbenes

The ability to stabilize polyphosphorus intermediates along the $P_4$ 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 $P_4$ to afford the *E*- and *Z*-isomers of linear tetraphosphorus chain **28** (Scheme 11; only *E*-isomer shown).[41] The presumed transient triphosphirene (**IM2**) reaction intermediate could be trapped with 2,3-dimethylbutadiene to give **29**.[42] Likewise, the diphosphene core of **28** underwent a [4+2]-cycloaddition to yield **30** in which two additional P–C bonds have been introduced.



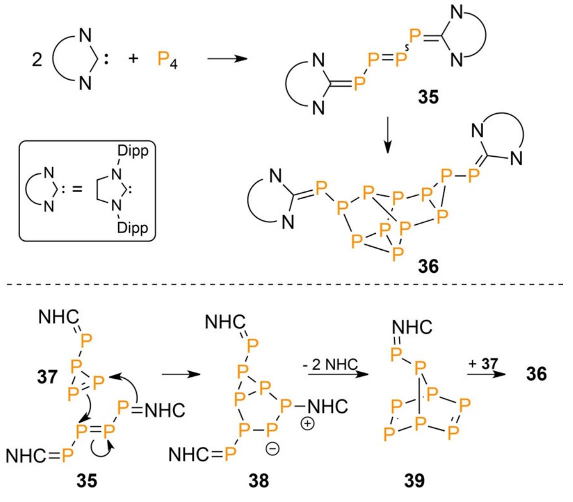
**Scheme 11.** Reactivity of $P_4$ with CAACs. Dipp = 2,6-diisopropylphenyl.

The nature of the carbene influences the fate of the $P_4$ 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).[43] On the other hand, a less bulky CAAC led instead to trisubstituted $P_4$-derivative **32** in addition to lower nuclearity $P_2$-diphosphaalkene **33**. Moreover, the small bis(diisopropylamino)cyclopropenylidene fragmented the $P_4$ tetrahedron even further to give $P_1$-cation **34**. These reactions reveal modular reactivity based on both the electronic and steric properties of the carbene.



**Scheme 12.** Reactivity of $P_4$ with various carbenes. Dipp = 2,6-diisopropylphenyl.

NHCs less π-acidic than CAACs react with $P_4$ in a related fashion but with different outcomes. For example, treating $P_4$ with two equivalents of 1,3-bis(2,6-diisopropylphenyl)-imidazolin-2-ylidene (SIDipp) gave **35** (Scheme 13), featuring the tetraphosphatriene structural motif, which over time aggregated to the neutral $P_{12}$ cluster **36**.[44] 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.

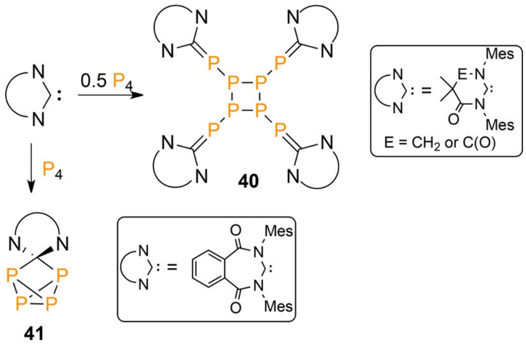


**Scheme 13.** Top: reactivity of $P_4$ with NHCs. Bottom: DFT computed mechanism for the formation of **36**. NHC = 1,3-bis(2,6-diisopropylphenyl)-imidazolin-2-ylidene, Dipp = 2,6-diisopropylphenyl.

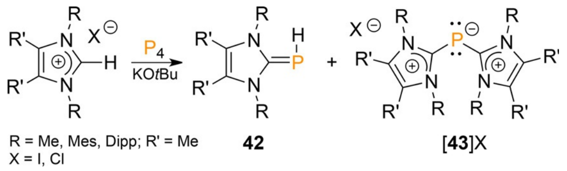
Remarkably, reacting $P_4$ with more electrophilic NHCs that bear carbonyl functional groups in the carbon backbones, allows isolation of $P_8$ clusters **40**, which are formed by [2+2]-cycloaddition of the linear $R_2P_4$ chains (Scheme 14).[45,46] Furthermore, a highly electrophilic benzamido carbene 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.[45,49]

A protocol to furnish OPCs containing $P_1$ units was reported in a joint publication by the groups of Gudat and Grützmacher who treated $P_4$ with equimolar amounts of imidazolium salts and KO*t*Bu.[47] The incipient carbene and the *t*BuOH by-product react with $P_4$ 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).[46]

Lastly, a frustrated Lewis pair (FLP) approach, based on the use of carbene I*t*Bu (I*t*Bu = 1,3-bis(*tert*-butyl)-imidazol-2-ylidene) and $B(C_6F_5)_3$, was reported by Tamm et al.[48] The NHC was

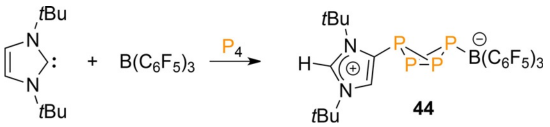


**Scheme 14.** Reactivity of $P_4$ with electrophilic NHCs.



**Scheme 15.** Three-component reaction of $P_4$ with imidazolium salts and KO*t*Bu. Dipp = 2,6-diisopropylphenyl.

found to bind "abnormally" (mesoionic) in the reaction with $P_4$ and induced a heterolytic P–P bond cleavage [Eq. (1)] to afford the labile zwitterionic *exo*,*exo*-bicyclo[1.1.0]tetraphosphabutane **44** in the presence of the Lewis acid, similar to anion **4** reported recently by our group (Scheme 16).[23,24]

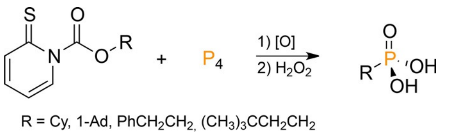


**Scheme 16.** Functionalization of $P_4$ using a carbene–borane Lewis pair.

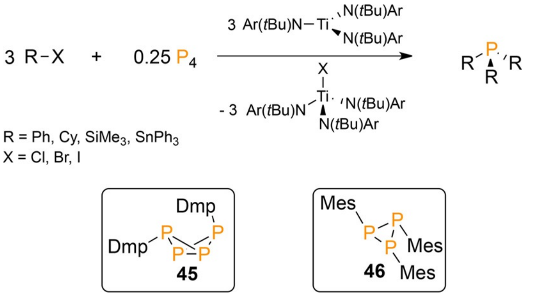
## 5. Functionalization of $P_4$ Using Carboradicals

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.[3] 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).[49]

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

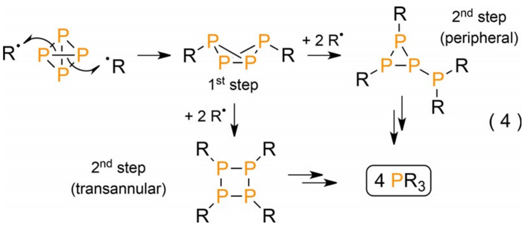


**Scheme 17.** Preparation of phosphonic acids from $P_4$ using Barton esters.

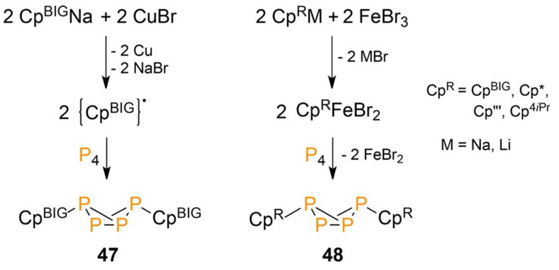


**Scheme 18.** Radical synthesis of tertiary- and cyclopolyphosphanes from $P_4$. Dmp = 2,6-dimesitylphenyl, Ar = 3,5-$Me_2C_6H_3$.

with titanium trisanilide $Ti(N(tBu)Ar)_3$ (Scheme 18; Ar = 3,5-$Me_2C_6H_3$).[50] 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-dimesitylphenyl), which impede complete substitution to afford bicyclo[1.1.0]tetraphosphabutane *exo*,*endo*-$Dmp_2P_4$ (**45**) and cyclotriphosphirane $Mes_3P_3$ (**46**), respectively. Notably, the oxidized titanium(IV) byproduct 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 + $P_4$ → $Na_3P$) 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.[5]



In 2014, the potential of reacting $P_4$ with metal-mediated radicals was further explored by Scheer and co-workers.[51] They showed that salt elimination from $Cp^{BIG}Na$ by CuBr afforded $\{Cp^{BIG}\}^\bullet$ radicals that interacted with $P_4$, as observed previously for the bulky $\{Dmp\}^\bullet$ by Cummins,[53] to give the *exo*,*exo*

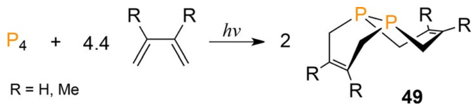


**Scheme 19.** Metal-mediated radical synthesis of organyl-substituted $P_4$ butterflies.

butterfly $Cp^{BIG}_2P_4$ (**47**, Scheme 19). The presence of free carboradicals was confirmed by EPR, whereas more reactive and less bulky $\{Cp^R\}^\bullet$ derivatives ($Cp^R$ = Cp, Cp*, Cp‴ and $Cp^{4iPr}$) were shown to undergo rapid decomposition, either through radical coupling or forming $Cp^RH$. They did react with $P_4$ via an iron-mediated route (with $Cp^RFeBr_2$ acting as radical transfer agent) to bicyclic tetraphosphanes **48**.

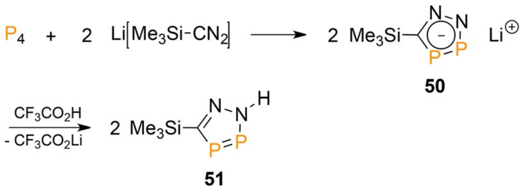
## 6. Functionalization of $P_4$ through $P_2$ Fragments

Cracking white phosphorus into two $P_2$ units has only been explored to a limited extent. The diatomic fragment features a highly reactive P≡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 = H, 2%; R = Me, 34%) due to their lability under the harsh irradiation conditions.



**Scheme 20.** Transfer of photochemically generated $P_2$ to1,3-dienes.

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 $P_4$, a formal [3+2]-cycloaddition reaction occurs to form diazadiphospholide anion **50** and neutral **51** after protonation (Scheme 21).



**Scheme 21.** Reaction of $P_4$ with (trimethylsilyl)diazomethanide.

The product is reminiscent to the recently described all-inorganic aromatic ion $P_2N_3^-$, prepared from reacting azide ($N_3^-$) with a thermally extruded $P_2$ unit from a transannular diphosphorus bisanthracene adduct, $P_2(C_{14}H_{10})_2$.[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).[29]

## 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, organometallic complexes, carbenes, carboradicals, and trapping of $P_2$ fragments with dienes. The product scope is varied and includes both industrially relevant phosphanes as well as unique OPCs that are essentially inaccessible through the use of $PCl_3$. These can serve as building blocks to access intriguing additional P-compound classes, like observed for the LA-stabilized $[RP_4]^-$ anions **4** and the $R_2P_4$ chains of the type **28**, or can be studied as ligands for coordination chemistry as displayed in $P_4$-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 dilithiobutadienes 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.

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## 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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