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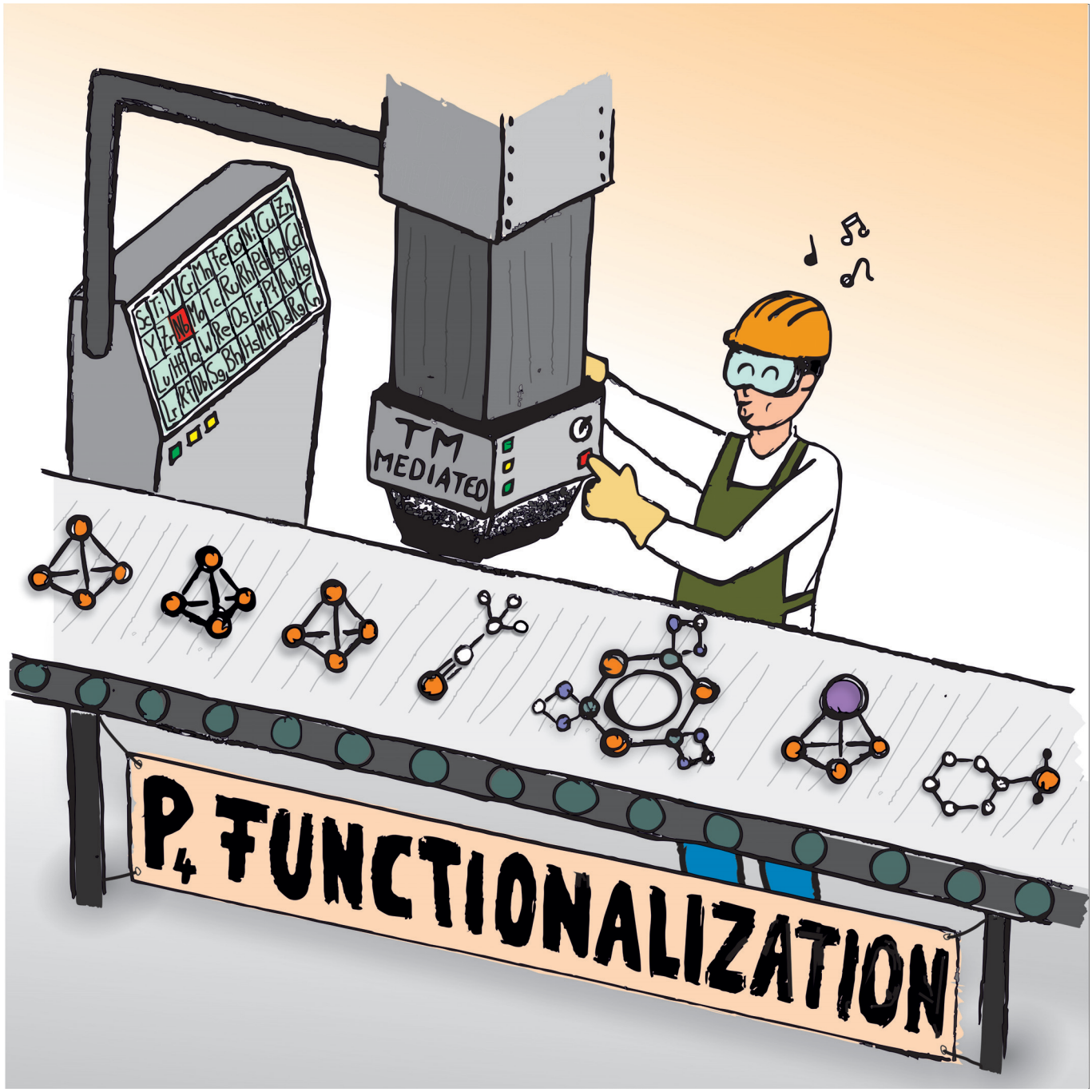
Transition-Metal-Mediated Functionalization of White Phosphorus

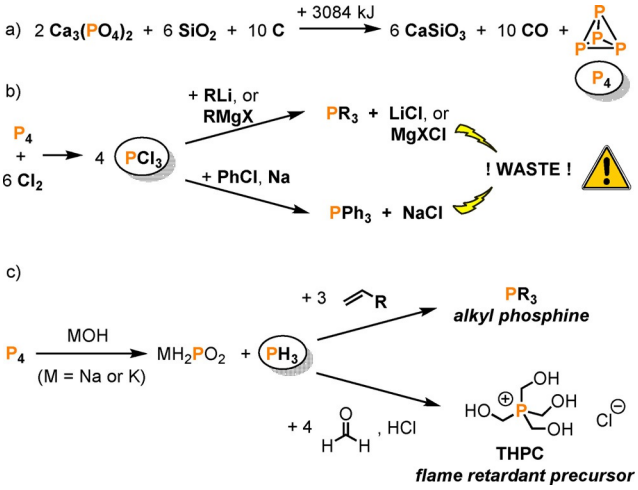
Christian M. Hoidn, Daniel J. Scott, and Robert Wolf*[a]



Abstract: Recently there has been great interest in the reactivity of transition-metal (TM) centers towards white phosphorus (P_4). This has ultimately been motivated by a desire to find TM-mediated alternatives to the current industrial routes used to transform P_4 into myriad useful P-containing products, which are typically indirect, wasteful, and highly hazardous. Such a TM-mediated process can be divided into two steps: activation of P_4 to generate a polyphosphorus complex TM-P_n, and subsequent functionalization of this complex to release the desired phosphorus-containing product. The former step has by now become well established, allowing the isolation of many different TM-P_n products. In contrast, productive functionalization of these complexes has proven extremely challenging and has been achieved only in a relative handful of cases. In this review we provide a comprehensive summary of successful TM-P_n functionalization reactions, where TM-P_n must be accessible by reaction of a TM precursor with P_4. We hope that this will provide a useful resource for continuing efforts that are working towards this highly challenging goal of modern synthetic chemistry.

1. Introduction

The element phosphorus is essential for life, serving as a building block for DNA and of the cellular energy carrier ATP in all living organisms.[1] In addition, synthetic phosphorus compounds have a huge impact on daily life,[1] being found in (among other things) detergents, fertilizers, insecticides, food products and flame retardants. Organophosphorus derivatives in particular play a crucial role in the chemical and pharmaceutical industries. The industrial precursor for these synthetic compounds is white phosphorus (P_4), the most reactive allotrope of the element, which is produced from phosphate rock on a megaton scale annually,[2,3] via reaction of the mineral apatite with quartz sand and coke in an electric arc furnace (Scheme 1a).[1] While most of the P_4 produced worldwide is re-oxidized to provide high-purity phosphate materials, a significant fraction (ca. 18%) is used to prepare the myriad valuable organophosphorus compounds that are required by modern society. Unfortunately, the synthesis of these target organophosphorus derivatives is a multistep process, almost always involving the initial chlorination of P_4 to PCl_3, followed by subsequent functionalization with Grignard or organolithium reagents (Scheme 1b).[2,3] Triphenylphosphane (PPh_3), for example, is one of the most synthetically important organophosphorus compounds, and is prepared industrially by high-temperature reaction of chlorobenzene with PCl_3 in the presence of molten sodium.[4] As well as requiring extremely toxic (Cl_2), corrosive (PCl_3) and pyrophoric (Na) reagents, this route also generates huge amounts of inorganic salt waste (NaCl), which is accumulated as a by-product. Thus, sustainability and safety concerns each provide a powerful impetus for the urgent overall improvement of such processes.[5]



Scheme 1. Production of white phosphorus (P_4) from the calcium phosphate part of apatite minerals (a) and the synthesis of organophosphorus compounds via PCl_3 (b) or PH_3 (c) (R = organic residue; X = Cl, Br, I; THPC = tetrakishydroxymethylphosphonium chloride).

In some specific cases alternative methods can be used to transform P_4; however, these often suffer from similar problems. For example, alkyl phosphanes and phosphonium salts can be prepared through hydrophosphination of alkenes and ketones (Scheme 1c), but this requires the intermediacy of extremely toxic PH_3 gas.[5] As such, the development of alternative routes that avoid the use of chlorine gas and circumvent the highly toxic intermediates PCl_3 or PH_3 is currently a topic of great interest.[6] In pursuit of this challenging goal, much emphasis has been placed on understanding the fundamental reactivity of P_4 towards reactive metal centers. It is hoped that studying these reactions may ultimately pave the way to effective catalytic methods for converting P_4 directly to organophosphorus derivatives.

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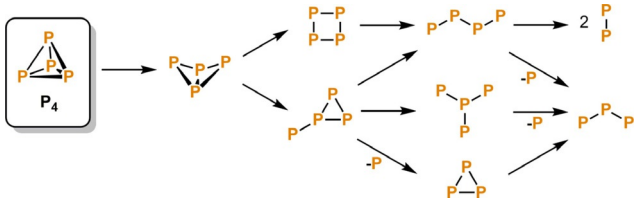
1.1. Activation of white phosphorus

The controlled and consecutive cleavage of P–P bonds within the P_4 tetrahedron (often referred to as P_4 activation) plays a crucial role in the formation of reactive P_n ($n = 1$–4) units, potentially suitable for further functionalization. As outlined in several reviews, a large number of reactive main group element or transition-metal compounds has been applied to the activation and degradation of the P_4 molecule.[3,7,8] Scheme 2 illustrates conceivable degradation pathways starting with the initial formation of "butterfly-P_4" species. The stepwise cleavage of further P–P bonds results in cyclic, branched and linear P_n fragments stabilized by transition metals or main group compounds.

The transition-metal-mediated activation of P_4 in particular has attracted considerable attention over the last several decades, and has given rise to a plethora of fascinating complexes bearing highly versatile P_n units.[3,7] A complete description of all the P_n ligands known in the literature would exceed the scope of this review. Nevertheless, an overview of common structural P_n motifs is illustrated in Figure 1. Monophosphido ligands, P_2 dumbbells or *cyclo*-P_3 rings can be derived from fragmented P_4 molecules ($n \leq 3$). Tetraphosphido ligands ($n = 4$) are typically observed either as intact, metal-bound P_4 tetrahedra, or as partially degraded "butterfly" species, P_4 rings and chains. Sometimes, the aggregation of multiple phosphorus atoms is also observed ($n \geq 5$), which may result in aromatic *cyclo*-P_5 and *cyclo*-P_6 ligands, or even extended polyphosphorus cages. In addition to the basic structures summarized in Scheme 2, bridging motifs, metal-phosphorus multiple bonding, and structures with varying hapticity may also be observed.



Scheme 2. A selection of possible reaction pathways for the activation of white phosphorus (P_4). Only the P_n backbones of the fragments are shown; charges and substituents are omitted for clarity.

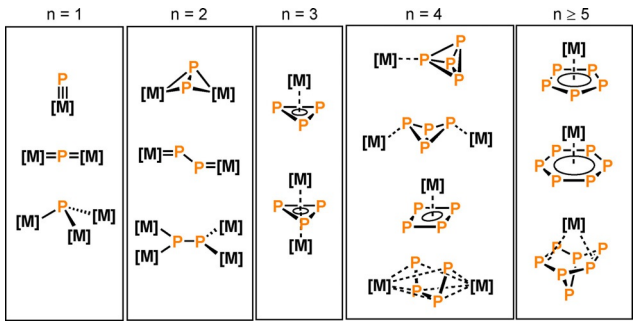


Figure 1. Structural motifs of selected transition-metal complexes bearing P_n ligands; [M] = transition-metal complex fragment.

2. Transition-Metal-Mediated Functionalization of White Phosphorus

If P_4 activation represents the first step of its transformation into potential organophosphorus products, then the second step is functionalization of the resulting P_n moieties through interaction with suitable reagents. However, whereas the activation of P_4 has now been extensively investigated, subsequent functionalization remains far less explored. In the last few years, interest in the transfer and incorporation of P_4-derived phosphorus atoms into organic or main group substrates has grown substantially, yet the controlled and selective functionalization of activated phosphorus units is still challenging. In this review, we aim to provide a comprehensive overview of these transition-metal-mediated functionalizations of white phosphorus. Throughout the review the term "functionalization" will be used to refer to reactions that involve formation of new chemical bonds between phosphorus and a non-metal

Christian M. Hoidn was born in Zwiesel, Germany, in 1991 and studied chemistry at the University of Regensburg, Germany, where he received his bachelor's degree in 2013 and his M.Sc. diploma in 2015. Recently, he completed his doctoral studies under the supervision of Prof. Dr. Robert Wolf, which focused on the synthesis and characterization of low-valent 3d metal complexes and their application for the activation and functionalization of white phosphorus. He was awarded with a Ph.D. scholarship of the Foundation of German Business (Stiftung der Deutschen Wirtschaft, sdw).

Daniel Scott earned his PhD from Imperial College London under the supervision of Dr. Andrew Ashley and Prof. Matthew Fuchter. He subsequently completed an EPSRC doctoral prize fellowship at the same institution, and is currently an Alexander von Humboldt fellow working at the University of Regensburg within the research group of Prof. Dr. Robert Wolf. His research interests revolve around the activation and functionalization of small molecules, mediated by both main group systems and low-valent transition-metal complexes.

Robert Wolf started his research career at the University of Cambridge, UK, under the guidance of Dominic S. Wright. He was awarded a PhD from Leipzig University for work in phosphorus chemistry supervised by Evamarie Hey-Hawkins. After postdoctoral research with Philip P. Power (UC Davis, USA) and Koop Lammertsma (VU Amsterdam, The Netherlands), he started his independent career at the University of Münster (mentor: Werner Uhl). He became Professor of Inorganic Chemistry at the University of Regensburg in 2011. In 2017, he received an ERC Consolidator Grant for the development of new methods for the functionalization of white phosphorus.

or metaloid element (c.f. P_4 "activation", where the P atoms only form new bonds to the transition metal). Reactions in which P_4 is functionalized by a main group reagent in the absence of a transition metal will not be discussed here, but have been reviewed previously.[8,9]

The main part of the review is divided into the following sections: section 2.1 discusses the activation and functionalization of P_4 in one step. The following sections discuss the functionalization of transition-metal coordinated P_n units. The functionalization of P_1, P_2, und P_3 moieties is described in sections 2.2. and 2.3. A large number of publications have focused on complexes with P_4 units, and these results are described in section 2.4. Section 2.5. describes the functionalization of larger P_n units with five or more P atoms. Finally, the functionalization of the P_4 molecules by transition-metal-generated *p*-block element radicals is described as an alternative for P_4 functionalization in section 2.6.

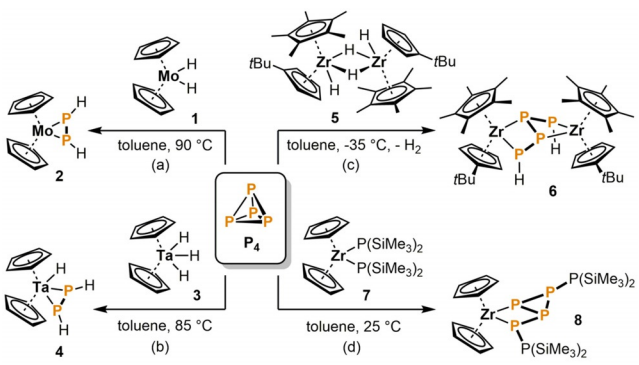
2.1. One-Step activation and functionalization

The first transition-metal-mediated P_4 functionalization reaction was reported in 1974 by Green and co-workers.[10] They described the reaction of $[Cp_2MoH_2]$ (**1**) with an excess of P_4 in hot toluene, affording the deep red diphosphene complex $[Cp_2Mo(\eta^2\text{-}P_2H_2)]$ (**2**), which was crystallographically characterized by Canillo et al. three years later (Scheme 3a).[11] This discovery represented a landmark in phosphorus chemistry, since not only P_4 activation, but also functionalization was observed. Specifically, four P–P bonds of the P_4 tetrahedron are cleaved and, simultaneously, new P–H bonds are formed by transfer of the hydride ligands from the metal center to phosphorus.

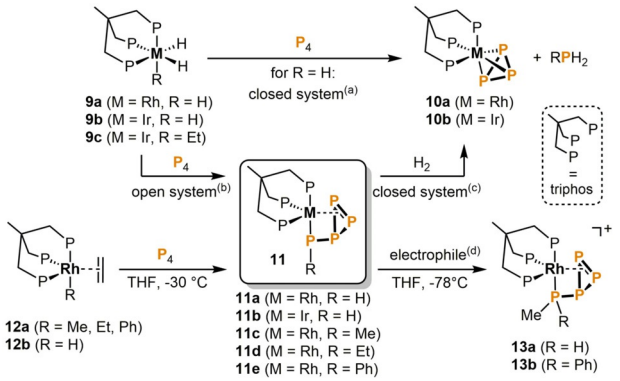
More than 20 years later, Stephan and co-workers provided a further example of such a fragmentation/hydrogenation process (Scheme 3 b). Reaction of the tantalocene trihydride complex $[Cp_2TaH_3]$ (**3**) with P_4 results in the hydridodiphosphene complex $[Cp_2Ta(H)(\eta^2\text{-}P_2H_2)]$ (**4**).[12] Interestingly, Chirik et al. found that an analogous reaction of the related zirconium dihydride complex $[Cp^*_2ZrH_2]$ with P_4 proceeds differently, and does not give a diphosphene complex. Instead, only P_4 activation to the [1.1.0]-tetraphosphabicyclobutane-1,4-diyl ("butterfly-P_4") complex $[Cp^*_2Zr(\eta^2\text{-}P_4)]$ occurs, along with reductive elimination of H_2.[13] They further described the treatment of the sterically more encumbered dinuclear complex $[Cp^*Cp'ZrH_2]_2$ (**5**, $Cp' = \eta^5\text{-}C_5H_4tBu$) with P_4 (Scheme 3 c). The product molecule $[\{Cp^*Cp'Zr\}_2(\mu_2,\eta^2\text{:}\eta^2\text{-}P_4H_2)]$ (**6**) features a bridging P_4 chain best described as a $P_4H_2^{4-}$ tetraanion. Lappert and co-workers used the zirconium diphosphido complex $[Cp_2Zr(P(SiMe_3)_2)_2]$ (**7**) for a related insertion of a rearranged P_4 scaffold into both Zr–P bonds to yield the hexaphosphane-3,5-diide complex **8** (Scheme 3 d).[14]

A related approach for the one-step activation and functionalization of P_4 using late transition metals was initially reported by Peruzzini et al. in 1998 (Scheme 4).[15] Rhodium(III) and iridium(III) hydride complexes $[(triphos)MH_3]$ (**9 a**: M = Rh, **9 b**: M = Ir; triphos = 1,1,1-tris(diphenylphosphanylmethyl)ethane) enable the direct hydrogenation of P_4 to PH_3, if conducted in a closed system. The stoichiometric by-products are the highly stable *cyclo*-P_3 compounds **10**. When carrying out the reaction of **9 a** with P_4 at lower temperature, or in an open system, the evolution of dihydrogen gas and an isolable intermediate species $[(triphos)Rh(\eta^1\text{:}\eta^2\text{-}HP_4)]$ (**11 a**) were observed. Further mechanistic studies performed with the kinetically more stable dihydridoethyl iridium complex $[(triphos)IrH_2(Et)]$ (**9 c**) revealed the initial formation of a butterfly compound $[(triphos)Ir(H)(\eta^2\text{-}P_4)]$, which slowly isomerizes to $[(triphos)Ir(\eta^1\text{:}\eta^2\text{-}HP_4)]$ (**11 b**).

Only a year later, Peruzzini et al. successfully extended this concept to P–C bond formation by reporting on analogous hydrocarbon-substituted tetraphosphido rhodium complexes $[(triphos)Rh(\eta^1\text{:}\eta^2\text{-}RP_4)]$ (**11 c**: R = Me; **11 d**: R = Et, **11 e**: = Ph) derived from the corresponding ethylene complexes $[(triphos)Rh(R)(\eta^2\text{-}C_2H_4)]$ (**12 a**) and P_4 (Scheme 4).[16] During the reaction the labile ethylene ligand is released while the alkyl and aryl moieties previously bound to the metal center in **12 a** selectively migrate to the activated P_4 scaffold. Notably, the reaction of P_4 with the corresponding hydrido-ethylene derivative $[(triphos)Rh(H)(\eta^2\text{-}C_2H_4)]$ (**12 b**) does not afford the expected product **11 a**. Instead, the ethylene ligand inserts into the Rh–H bond and successively gives the ethyltetraphosphido



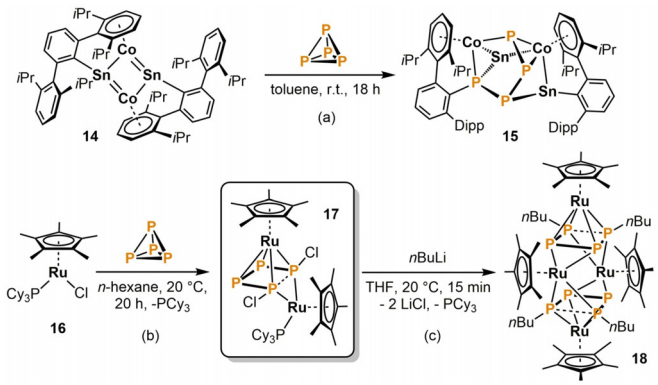
Scheme 3. Early transition metallocene-mediated activation of P_4 with concomitant functionalization.



Scheme 4. Functionalization of P_4 mediated by rhodium and iridium triphos complexes. Reaction conditions: (a) for **9 a**: THF, 70 °C; for **9 b** THF, 120 °C. (b) for **9 a**: open system, THF, 70 °C, -H_2 or closed system, THF, 40 °C, -H_2; for **9 c**: open system, THF, reflux, -C_2H_6. (c) for **11 a**, **11 b**: THF, 70 °C; for **11 c**, **11 d**, **11 e**: THF, 60 °C, 20 atm H_2. (d) for **11 a**, **11 e**: + MeOTf; for **11 c**: + $HBF_4{\cdot}OMe_2$.

species **11 d**. Moreover, the pressurization of **11 c**, **11 d** and **11 e** with H_2 at 60 °C induces the formation of **10 a** along with the phosphanes RPH_2 in moderate yields. The reactivity of complexes **11** was further explored through reactions with electrophiles.[17] The reaction of **11 a** and **11 e** with MeOTf or MeI gave the doubly functionalized and highly temperature sensitive cations $[(triphos)Rh(\eta^1{:}\eta^2\text{-}MeRP_4)]^+$ (**13 a**: R = H, **13 b**: R = Ph). The fact that **13 a** is also obtained by treating **11 c** with $HBF_4{\cdot}OMe_2$ supports the idea that in this system electrophilic attack generally takes place at the already-functionalized phosphorus atom.

More recently, a joint study by Power, Wolf and co-workers demonstrated that the low-coordinate cobalt-tin cluster **14** serves as a potent agent for one-step P_4 activation and functionalization (Scheme 5 a).[18] During the reaction, the P_4 tetrahedron is selectively inserted into the rhombohedral Co_2Sn_2 cluster core of **14**, during which one of the bulky, tin-bound terphenyl substituents undergoes a migration to phosphorus, thereby forming a new P–C bond. The product **15** bears a terphenyl-substituted P_4 chain and represented the first example of a molecular cluster compound containing phosphorus, cobalt and tin.

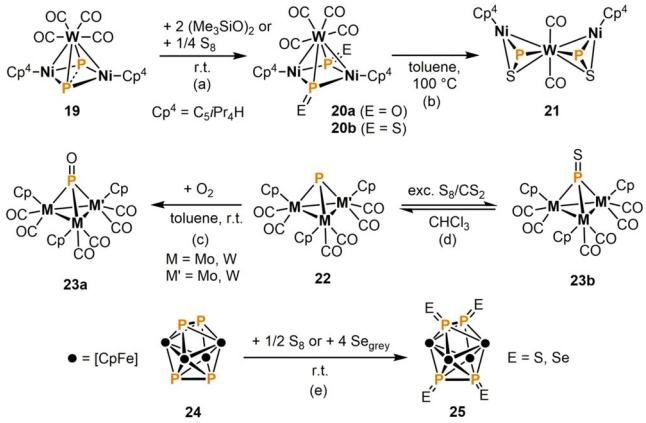


Scheme 5. Arylation of P_4 by a low-coordinate cobalt-tin cluster (a) and ruthenium-mediated halogenation (b) and subsequent alkylation of P_4 (c).

An even more recent collaboration by the groups of Caporali and Grützmacher dealt with the chlorination of P_4 by the 16 valence electron species $[Cp^*RuCl(PCy_3)]$ (**16**, Scheme 5b).[19] Promoted by two equivalents of **16**, migration of two chloride ligands from ruthenium to an activated P_4 unit yields the dinuclear complex $[Cp^*Ru(PCy_3)(\mu_2,\eta^2{:}\eta^4\text{-}P_4Cl_2)RuCp^*]$ (**17**), containing a planar and unsymmetrically bridging 1,4-dichlorotetraphosphabutadiene ligand. A selective exchange of the chloro substituents with alkyl groups was achieved by salt metathesis with *n*BuLi (Scheme 5 c). The product was the tetranuclear compound $[(Cp^*Ru)_4(\mu_3,\eta^2{:}\eta^2{:}\eta^4\text{-}P_4nBu_2)_2]$ (**18**), which features two coplanar $[P_4nBu_2]$ moieties.

2.2. Functionalization of P_1 and P_2 ligands

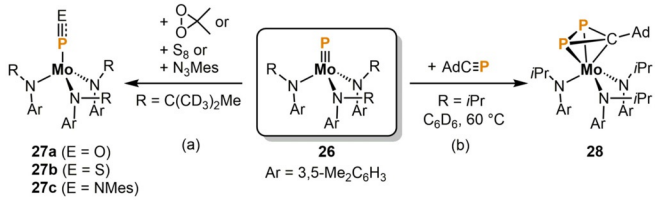
In comparison to the one-step reactions mentioned above, more versatile transformations can be made feasible by separating P_4 activation from the subsequent functionalization step. The following section deals with functionalizations of P_1 and P_2 ligands derived from P_4, which date back to the pioneering work of Scherer et al. in 1991. Oxidation of the Ni_2WP_2 complex **19** with $(Me_3SiO)_2$ affords **20 a**, the first complex of PO, the heavier congener of the ubiquitous nitric oxide (NO, Scheme 6a).[20] Oxidation of **19** with S_8 similarly affords the isoelectronic PS species **20 b**, which undergoes partial loss of CO and rearrangement from $\mu_3{:}\eta^1$ to $\mu_2{:}\eta^2$ coordination of the PS ligands when heated to 100 °C (**21**, Scheme 6 b).[21] Mays and co-workers found that a similar μ_3-PO compound (**23 a**) is formed if the trinuclear species **22** is exposed to atmospheric oxygen (Scheme 6 c).[22] The corresponding oxidation with elemental sulfur is fully reversible and leads to **23 b** in the presence of an excess of S_8 in CS_2 (Scheme 6 d).[23] The reverse reaction to produce **22** takes place in common organic solvents in the absence of an excess S_8. Scherer et al. also reported on the synthesis of E = P–P = E ligands in **25** by oxidation of the P_2 dumbbells in the Fe_4P_4 cluster **24** with elemental sulfur or grey selenium (Scheme 6 e).[24]



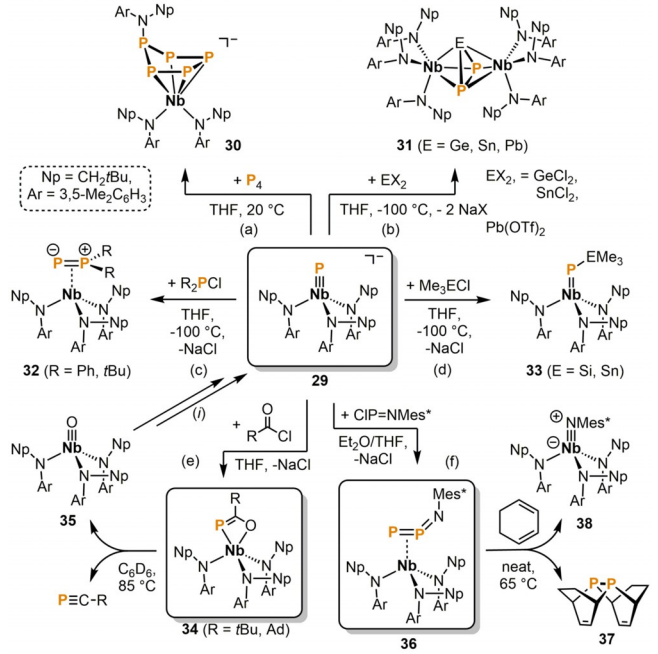
Scheme 6. Oxidation of P_4-derived P_1 and P_2 ligands in the coordination sphere of transition metals.

A series of remarkable functionalizations was performed by Cummins and co-workers using early transition metals triply bound to a terminal phosphido (P^{3-}) ligand. The molybdenum phosphide **26** was reacted with monomeric acetone peroxide, elemental sulfur and mesityl azide ($MesN_3$), giving complexes with terminally-bound phosphorus monoxide (**27 a**), phosphorus monosulfide (**27 b**) and iminophosphenium (**27 c**) ligands (Scheme 7 a).[25,26] In addition, the phosphaalkyne AdC≡P (Ad = 1-adamantyl) adds to the Mo≡P triple bond in **26** to yield the *cyclo*-CP_2 complex **28** (Scheme 7 b).[27]

Cummins and co-workers also subsequently demonstrated the impressive synthetic potential of the anionic niobium complex **29**, which is isoelectronic with **26** (Scheme 8). The Nb≡P triple bond in **29** participates in further solvent-dependent P_4 activation. Trapping of 0.5 equivalents of P_4 in weakly coordinating solvents affords $[(cyclo\text{-}P_3)Nb(N[Np]Ar)_3]^-$ (Np = CH_2tBu, Ar = 3,5-$Me_2C_6H_3$), which is structurally related and isolobal to **28**.[28] In THF, however, addition of the entire P_4 tetrahedron



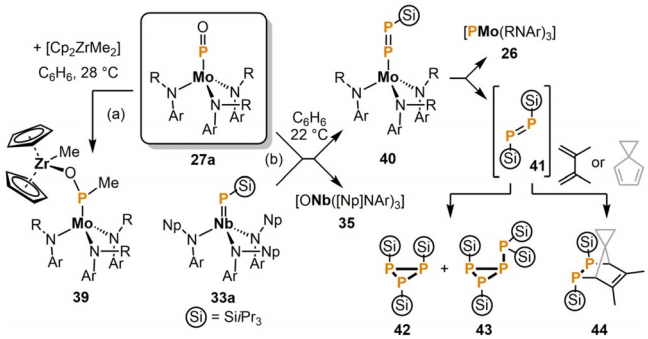
Scheme 7. P_1 functionalization mediated by the molybdenum phosphido complex **26**.



Scheme 8. Phosphorus functionalization mediated by the niobium phosphide anion **29**. (*i*) Recovery of starting material **29** from **35** proceeds by: 1. + Tf_2O in Et_2O at −35 °C; 2. + [Mg(thf)$_3$($C_{14}H_{10}$)]/-Mg(OTf)$_2$, -$C_{14}H_{10}$ in THF at −100 °C; 3. + 0.25 equiv P_4 in THF at r.t.; 4. + Na-amalgam/-Hg in THF at r.t.

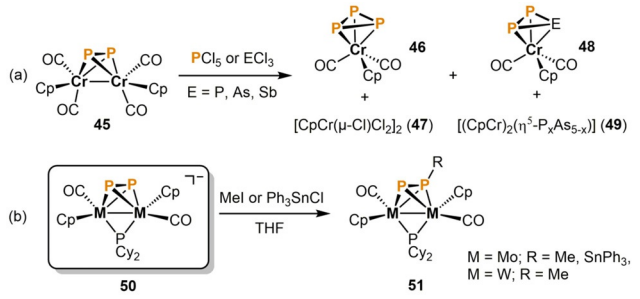
occurs and concomitant migration of one amide ligand onto phosphorus gives the amino functionalized *cyclo*-P_5 anion **30** (Scheme 8a). Moreover, the anionic nature of **29** opened up avenues to salt metathesis reactions with electrophiles. Treatment of **29** with divalent group 14 element salts at low temperatures provides the dinuclear compounds **31** containing bridging $\mu_2,\eta^3{:}\eta^3$-*cyclo*-EP_2 (E = Ge, Sn, Pb) triangles (Scheme 8b).[29] The η^2-phosphanyl phosphinidene complexes **32** were accessible by reacting **29** under similar conditions with chlorophosphanes (Scheme 8c).[30] Silylation and stannylation (compounds **33**) at the nucleophilic phosphorus atom were achieved by treating **29** with Me_3ECl (E = Si, Sn, Scheme 8d). Cummins and co-workers further reported that **29** enables the remarkable transformation of acyl chlorides into the corresponding phosphaalkynes (Scheme 8e).[31] In fact, the authors described a complete synthetic cycle involving an initially formed niobacyclic intermediate **34**, [2+2] fragmentation to give the phosphaalkynes P≡C-R (R = *t*Bu, Ad) and the niobium(V) oxo product **35**, and finally the recycling of **35** by step-wise deoxygenation, P_4 activation and reduction.[32] The reaction of **29** with the chloroiminophosphane ClP=NMes* (Mes* = 2,4,6-$tBu_3C_6H_2$) gives **36**, which bears the diphosphorus analogue of an organic azide ligand (P=P=N-Mes*) coordinating through the P=P unit in an η^2-fashion (Scheme 8f).[33] Remarkably, compound **36** serves as a precursor for the thermal release of formal [P≡P] units, which can be quantitatively trapped by using 1,3-cyclohexadiene to form the Diels-Alder adduct **37** via a double diene addition. The by-product of this process is the niobium imide complex [(Mes*N)Nb([Np]NAr)$_3$] (**38**).

Moreover, Cummins and co-workers also presented additional functionalizations of the terminal PO ligand in the above-mentioned molybdenum complex **27a**, mediated by addition of more oxophilic metal species. The nucleophilic attack of one methyl group in [Cp_2ZrMe_2] at phosphorus gives the Mo^{IV} complex **39** in up to 75% yield (Scheme 9a).[26] An uncommon phospha-Wittig reaction takes place upon treatment of **27a** with the silyl phosphinidene complex **33a** (Scheme 9b).[34] This O=P/Nb=PSi*i*Pr$_3$ metathesis generates the oxo niobium compound **35** along with the silyl substituted diphosphenido molybdenum complex **40**. In solution, **40** decomposes within days to the phosphido molybdenum complex **26** and the unstable diphosphene **41**. Elevated temperatures accelerate this decomposition reaction. The reactive intermediate **41** readily oligomerizes to a mixture of the phosphinidene trimer **42** and tetramer **43**, or can be trapped with dienes to form the [2+4] cycloaddition products **44**.



Scheme 9. Transformations of the phosphorus monoxide ligand P=O promoted by combinations of two metal complexes (Ar = 3,5-$Me_2C_6H_3$; R = $C(CD_3)_2Me$; Np = CH_2tBu).

In 2000, Scheer and co-workers described the functionalization of the chromium complex **45** with group 15 halides (Scheme 10a).[35] While reactions with PCl_5 and PCl_3 both lead to the *cyclo*-P_3 complex **46** and the dinuclear chromium chloride **47**, the reactions with ECl_3 (E = As, Sb) are very unselective. A complex mixture of products is obtained, including **46**, **47**, the *cyclo*-EP_2 complex **48** and various triple-decker compounds **49**. Interestingly, Ruiz and co-workers found that the closely-related heavier group 6 complex anions **50** can readily be functionalized with electrophiles affording the methyl- or stannyldiphosphenyl bridged species **51** (Scheme 10b).[36]

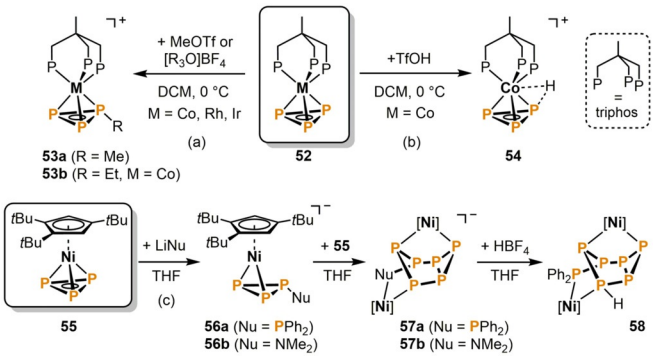


Scheme 10. Functionalization of P_2 units mediated by dinuclear group 6 complexes.

2.3. Functionalization of P_3 ligands

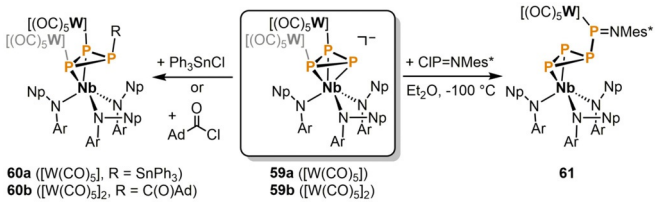
The first functionalization of a P_3 ligand was reported by Peruzzini and Stoppioni in 1986. Highly electrophilic alkylating agents MeOTf and $[Me_3O]BF_4$ were used for the methylation of the *cyclo*-P_3 moiety in the group 9 triphos complexes **52** (Scheme 11a).[37] The products **53a** contain methyltriphosphirene ligands coordinating in an η^3-mode. It is noteworthy that these alkylations represented the first examples of successful transition-metal-mediated functionalization of any polyphosphorus ligand with carbon-based electrophiles. Four years later, Huttner and co-workers performed the analogous reaction with $[Et_3O][BF_4]$, which gave the corresponding ethylated complex **53b**.[38] The protonation of **52** with HOTf gives a different outcome (Scheme 11b).[39] Spectroscopic and crystallographic investigations indicated that H^+ interacts weakly with the heteroatomic CoP_3 cluster core in **54** and is most likely located between both phosphorus and cobalt.

The reactivity of the *cyclo*-P_3 ligand toward main group *nucleophiles* was explored by Scheer and co-workers 30 years later using a related nickel complex (Scheme 11c).[40] According to variable temperature ^{31}P NMR studies, the reaction of the nickel *cyclo*-P_3 sandwich compound **55** with $LiPPh_2$ initially forms the intermediate triphosphirene species **56a**, which then rapidly incorporates a second equivalent of **55** and concomitantly rearranges to the heptaphosphane compound **57a**. Since crystallization and purification of **57a** was unsuccessful due to its high sensitivity, protonation with HBF_4 was investigated to afford the more stable neutral species **58**. The two nickel centers in **58** are bridged by a remarkable bicyclic P_6 ligand with an exocyclic PPh_2 substituent. By contrast, the reaction of **55** with $LiNMe_2$ gives the η^2-triphosphirene complex **56b** as isolable main product, and **57b** was detected only in minor quantities by ^{31}P NMR spectroscopy.



Scheme 11. Reactivity of neutral *cyclo*-P_3 complexes with electrophiles (top) and nucleophiles (bottom); [Ni] = [Ni($C_6H_2tBu_3$)] (triphos = 1,1,1-tris(diphenylphosphanylmethyl)ethane).

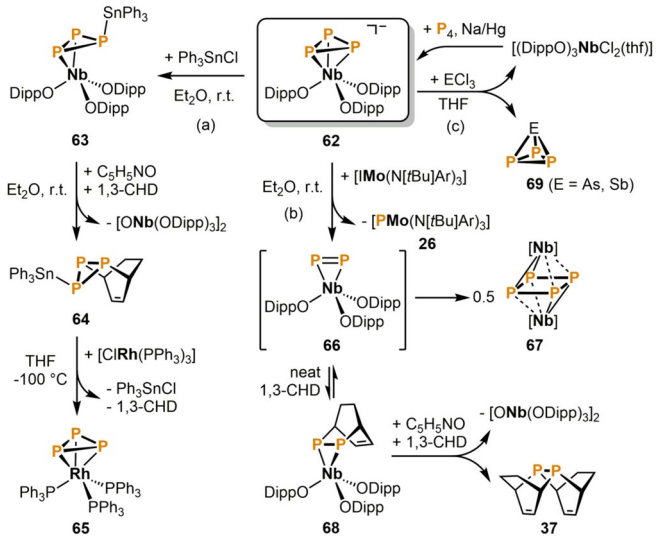
Further η^2-triphosphirene complexes were obtained by Piro and Cummins by reacting the di- and trinuclear *cyclo*-P_3 complex anions **59a** and **59b** with electrophiles (Scheme 12).[27] Treatment of dinuclear **59a** with Ph_3SnCl affords the P-stannylated compound **60a**, and the reaction of trinuclear **59b** with 1-adamantanecarbonyl chloride gives the analogous, yet thermally unstable, P-acyclated species **60b**. When **59b** is reacted with ClP=NMes*, one $[W(CO)_5]$ fragment is lost and a shift of the second $[W(CO)_5]$ moiety to the iminophosphane P is observed. The product **61** features a Mes*NP$[W(CO)_5]^+$ unit that circumambulates around the unsaturated triphosphorus cycle in solution at ambient temperature.



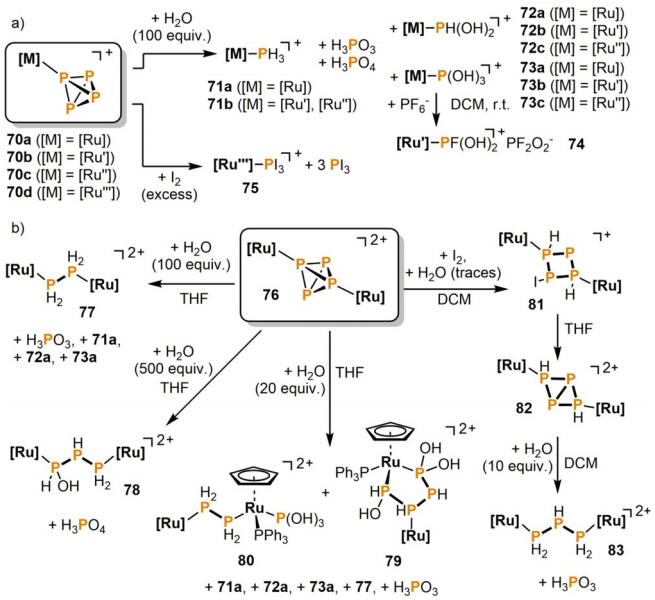
Scheme 12. Functionalization of *cyclo*-P_3 units with electrophiles mediated by oligonuclear complex anions (Ar = 3,5-$Me_2C_6H_3$; Np = CH_2tBu; Mes* = 2,4,6-$tBu_3C_6H_2$).

Cummins and co-workers further demonstrated the exceptional utility of anionic niobium complexes for phosphorus transfer by using the niobate **62** (Scheme 13), which bears phenolato instead of the more established anilido ligands (cf. **29**, **59**). The reaction of **62** with Ph_3SnCl yields the stannyltriphosphirene complex **63**, where the Ph_3Sn^+ moiety rapidly migrates around the *cyclo*-P_3 ring in solution even at −90 °C (Scheme 13a).[41] Subsequent liberation of the triphosphirene molecule from the metal center was achieved by converting **63** with the oxidant pyridine-*N*-oxide in the presence of the trapping agent 1,3-cyclohexadiene. This procedure gave the uncommon Diels-Alder adduct **64** along with the niobium oxo dimer $[ONb(ODipp)_3]_2$. Remarkably, **64** serves as a P_3^{3-} synthon and readily transfers its *cyclo*-P_3 unit onto $[ClRh(PPh_3)_3]$. This reaction involves chloride abstraction from rhodium to eliminate Ph_3SnCl, and the release of 1,3-cyclohexadiene from the diphosphene by [4+2] retrocycloaddition which ultimately affords the *cyclo*-P_3 rhodium complex **65**.

In a different approach, **62** was reacted with the iodo molybdenum(IV) species $[IMo(N[tBu]Ar)_3]$ (Ar = 3,5-$Me_2C_6H_3$, Scheme 13b), which acts as a P^- abstractor to form $[PMo(N[tBu]Ar)_3]$ (c.f. **26**, Scheme 7).[42] In this manner, the dinuclear *cyclo*-P_4 cluster **67** was quantitatively obtained, presumably via an irreversible dimerization of an intermediate P_2 species **66**. In the presence of the trapping agent 1,3-cyclohexadiene, an equilibrium with the Diels–Alder product **68** was detected by



Scheme 13. Phosphorus transfer reactions promoted by the anionic niobium *cyclo*-P_3 complex **62**; [Nb] = [Nb(ODipp)$_3$] (1,3-CHD = 1,3-cyclohexadiene).



Scheme 14. Hydrolysis and halogenations of P_4 in the coordination sphere of mononuclear (a) and dinuclear (b) ruthenium complexes; [Ru] = [CpRu(PPh$_3$)$_2$]; [Ru′] = [CpRu(dppe)] (dppe = 1,2-bis(diphenylphosphanyl)ethane); [Ru″] = [CpRu(TPPMS)$_2$] (TPPMS = Ph$_2$P(*m*-C$_6$H$_4$SO$_3$Na)); [Ru‴] = [Cp*Ru(dppe)].

^{31}P NMR spectroscopy. Complex **68** could not be isolated as a pure compound due to this equilibrium with **66**, which irreversibly dimerizes to **67**. However, upon addition of the oxidizing agent pyridine-*N*-oxide, liberation of the diphosphene ligand occurs, affording the above-mentioned double cycloaddition product **37** (c.f. Scheme 8). Cummins and co-workers also reported on the facile synthesis of the fascinating binary interpnictogen molecules EP_3 (**69**, E = As, Sb) via salt metathesis reactions of **62** with ECl_3 (Scheme 13c).[43] The niobium dichloride by-product [(DippO)$_3$NbCl$_2$(thf)] can easily be recycled to the *cyclo*-P_3 precursor **62** by reduction in the presence of P_4.

2.4. Functionalization of P_4 ligands

As the formation of P_4 ligands is the most common result of transition-metal-mediated P_4 activation,[3,7] it is not surprising that phosphorus functionalization has mostly been explored for these complexes. These reactions are particularly versatile, depending on the precise nature of the P_4 ligand. Thus, the following section is divided into four parts correlating with the successive degradation of the P_4 tetrahedron: tetrahedral P_4 ligands, [1.1.0]bicyclotetraphosphane-1,4-diyl compounds ("butterfly-P_4" ligands), *cyclo*-P_4 units, and *catena*-P_4 species.

2.4.1. Tetrahedral P_4 ligands

Stoppioni, Peruzzini and co-workers reported on the hydrolytic disproportionation of intact P_4 tetrahedra in the coordination sphere of ruthenium. Such reactivity is remarkable given that free P_4 is well known to be indefinitely stable in water at room temperature.[7] The authors found that [CpRu(PPh$_3$)$_2$(η^1-P$_4$)]$^+$ (**70a**) almost quantitatively forms the phosphane complex **71a** upon reaction with 100 equiv H_2O (Scheme 14a).[44] By-products are oxophosphorus species such as phosphorus acid (H_3PO_3) and phosphoric acid (H_3PO_4). Substitution of the triphenylphosphane ligands for bidentate 1,2-(bisdiphenylphosphanly)ethane (dppe), or the sodium salt of *meta*-sulfonated triphenylphosphane (TPPMS = Ph$_2$P(*m*-C$_6$H$_4$SO$_3$Na) (compounds **70b** and **70c**, respectively), resulted in formation of minor quantities of hydroxyphosphane complexes such as **72b,c** and **73b,c** as side-products.[45] The composition of the final mixtures strongly depends on the solvent, the temperature and the amount of H_2O used. When **73b** is dissolved in DCM, it reacts with its own PF_6^- counter anion and gives the fluorodihydroxyphosphane complex [CpRu(dppe){PF(OH)$_2$}]PF_2O_2 (**74**) by F/OH substitution. Lapinte, Peruzzini and co-workers also examined the reaction of the slightly bulkier complex [Cp*Ru(dppe)(η^1-P$_4$)]$^+$ (**70d**) with an excess of iodine in $CHCl_3$ at room temperature.[46] Three equivalents of PI_3 are released while one molecule of PI_3 remains bound to the metal center to form [Cp*Ru(dppe)(PI$_3$)]$^+$ (**75**).

The dicationic diruthenium complex **76** displays a very complex hydrolysis behavior. When treated with 100 equiv H_2O, in a similar manner to **70a**, a diphosphane complex **77** is obtained along with **71a**, **72a**, **73a** and H_3PO_3 as by-products (Scheme 14b).[47] With a much higher excess of water (500 equiv), the reaction becomes selective and gives rise to H_3PO_3 and the remarkable 1-hydroxytriphosphane complex **78** in 93% isolated yield.[48] Reducing the amount of water to only 20 equiv slows down the reaction rate significantly and affords two different compounds as major products:[49] the 1,1,4-tris-(hydroxy)tetraphosphane complex **79** and a dinuclear species **80**, which contains a bridging diphosphane and a P(OH)$_3$ ligand. The reaction mixture further contains small amounts of several other species, namely **71a**, **72a**, **73a**, **77** and H_3PO_3. A different reactivity is observed when **76** is first oxidized with iodine in the presence of traces of water.[50] The initial product

is the monocationic diruthenium complex **81**, which is stabilizing a cyclic $(P_4H_2I)^-$ anion. In THF, the iodide anion dissociates from the tetraphosphorus ligand, resulting in the ruthenium-substituted [1.1.0]bicyclotetraphosphane **82** that further hydrolyzes to the triphosphane complex **83** and phosphorous acid.

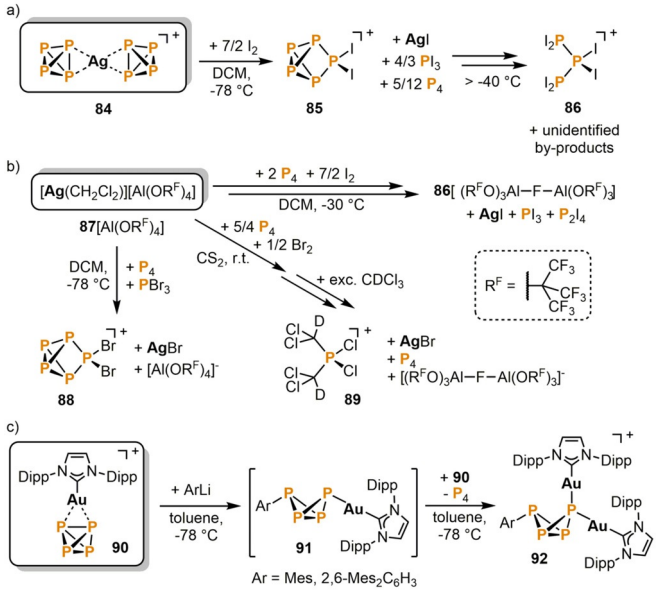
Krossing comprehensively studied the iodination of the homoleptic silver complex $[Ag(\eta^2\text{-}P_4)_2]^+$ (**84**), which features two intact P_4 tetrahedra bound in an η^2-fashion and is paired with the very weakly coordinating aluminate anion $[Al(OR^F)_4]^-$ ($R^F = C(CF_3)_3$, Scheme 15 a).[51] According to low temperature in situ ^{31}P NMR experiments, **84** reacts with 3.5 equivalents of iodine even at −78 °C to give the cationic pentaphosphorus cage $P_5I_2^+$ (**85**) along with AgI, PI_3 and P_4 as by-products. Quantum chemical calculations indicated that the formation of **85** may proceed via two different pathways: the insertion of an in situ generated PI_2^+ cation into one P–P bond of white phosphorus, or the intermediate formation of a naked P_5^+ cation, which then reacts with I_2. When the reaction mixture is warmed above −40 °C, **85** rapidly decomposes to the subvalent binary cation $P_3I_6^+$ (**86**) and several unidentified by-products. The Raman and ^{31}P NMR spectroscopic data support the intermediate formation of P_2I_4 from the remaining PI_3 and P_4, which reacts with $P_5I_2^+$ (**85**) ultimately affording $P_3I_6^+$ (**86**) and P_4.

In the same work, a different approach, namely the in situ reaction of $[Ag(CH_2Cl_2)][Al(OR^F)_4]$ (**87**$[Al(OR^F)_4]$), P_4 and various halogenating agents was also presented (Scheme 15 b). The lighter congener of **85**, $P_5Br_2^+$ (**88**), was synthesized almost quantitatively by stirring **87**$[Al(OR^F)_4]$ with equimolar amounts of P_4 and PBr_3 at −78 °C for 8 h. An NMR scale reaction of **87**$[Al(OR^F)_4]$ with white phosphorus and bromine in CS_2 at room temperature gave several colorless crystals after redissolving the crude mixture in $CDCl_3$ for an NMR experiment. XRD analysis revealed that these crystals consisted of a dichlorodiorganophosphonium cation $[Cl_2P(CDCl_2)_2]^+$ (**89**), as its $[(R^FO)_3Al\text{-}F\text{-}Al(OR^F)_3]^-$ salt. It must be noted that, in this case, the $[Al(OR^F)_4]^-$ anion present in the starting material decomposed to the fluoride bridged $[(R^FO)_3Al\text{-}F\text{-}Al(OR^F)_3]^-$ anion. **89** is suggested to form via double insertion of a very electrophilic intermediate P^+ unit into the C-Cl bond of $CDCl_3$. Finally, the reaction of **87**$[Al(OR^F)_4]$, P_4, and I_2 in a molar ratio of 1:2:3.5 resulted in a mixture containing P_2I_4 and **86**$[(R^FO)_3Al\text{-}F\text{-}Al(OR^F)_3]$. Both were identified by XRD analysis performed on single crystals, which were obtained from concentrated CS_2 extracts of the crude product.

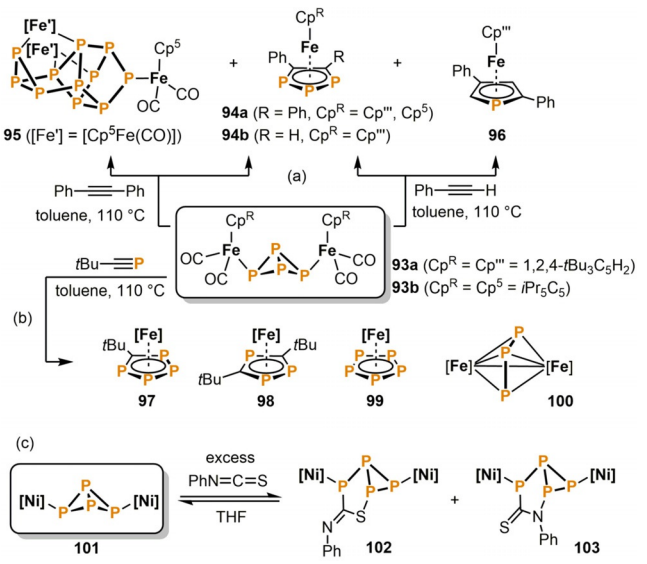
Lammertsma and co-workers recently reported that the *N*-heterocyclic carbene (NHC) gold complex **90** readily reacts with aryl lithium compounds at low temperatures (Scheme 15 c).[52] The controlled P–C bond formation and concomitant cleavage of one P–P bond gives rise to the proposed intermediate butterfly species **91**. Immediate addition of a second [(NHC)Au] fragment, derived through formal loss of P_4 from a second equivalent of **90**, affords the cationic complex **92** in high yield.

2.4.2. [1.1.0]Bicyclotetraphosphan-1,4-diyl ligands ("butterfly-P_4" ligands)

The first functionalizations of [1.1.0]bicyclotetraphosphan-1,4-diyl ("butterfly-P_4") ligands were reported by Scherer et al. Thermolysis of the diiron complexes **93** in the presence of diphenylacetylene affords the triphospholyl species **94 a** in moderate yields (Scheme 16 a).[53] In the case of the related compound containing a sterically more demanding pentaisopropylcyclopentadienyl ligand (**93 b**), the remarkable P_{11} cage compound **95** is also formed in small quantities. Scheer and coworkers later extended this concept to other alkynes. Phenylacetylene gives a mixture of the monophospholyl (**96**) and



Scheme 15. Halogenation of P_4 by silver complexes (a,b) and arylation of P_4 with organolithium compounds in the coordination sphere of *N*-heterocyclic carbene (NHC) gold cations.

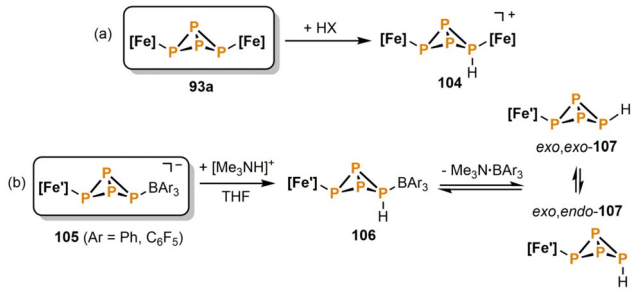


Scheme 16. Addition reactions of unsaturated organic molecules to P_4 butterfly complexes; [Ni] = [CpNi(IMes)] (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene); [Fe] = [Cp'''Fe].

1,2,3-triphospholyl species (**94b**).[54] The reaction of **93a** with the phosphaalkyne *t*BuC≡P produces several compounds (Scheme 16b).[55] While the tetraphospholyl (**97**) and the 1,2,4-triphospholyl (**98**) complexes are the main products, minor amounts of pentaphosphaferrocene **99** and the dinuclear triphosphaallyl complex **100** can also be isolated. It is proposed that key steps in these reactions are [3+1] fragmentation of the butterfly framework and subsequent addition of one or two equivalents of alkyne.

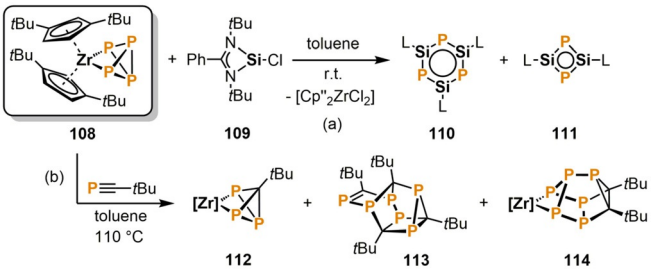
Wolf and co-workers found that the N=C and C=S bonds of the heterocumulene phenyl isothiocyanate (PhNCS) reversibly insert into a P–P bond of the P_4 butterfly scaffold of the dinuclear nickel complex **101** (Scheme 16c).[56] The products are the two isomeric bicyclo[3.1.0]heterohexane species **102** and **103**, which can be isolated as pure compounds, although they slowly equilibrate with the starting materials **101** and PhNCS in solution.

Protonation of the iron butterfly compound **93a** was also investigated by Scheer and co-workers. According to ^{31}P NMR and computational studies, the acidic proton selectively attacks the more nucleophilic, metal-bound ("wing tip") P atom to give the cation **104** (Scheme 17a).[57] A similar observation was made by Lammertsma and co-workers.[58] The reaction of the anionic Lewis acid-stabilized P_4-butterfly compound **105** with $[Me_3NH][BPh_4]$ initially forms the intermediate wing tip protonated species **106** (Scheme 17b). Immediate loss of the amine-borane adduct $Me_3N{\cdot}BAr_3$ (Ar = Ph, C_6F_5) leads to the formation of the neutral bicyclo[1.1.0]tetraphosphabutane isomers *exo,endo*-**107** and *exo,exo*-**107**. The two isomers were calculated to lie close in energy and readily undergo Lewis acid-catalyzed isomerization. Moreover, they decompose within one day due to a lack of kinetic stabilization.



Scheme 17. Iron-mediated protonation of P_4-butterfly ligands; HX = $[(Et_2O)H][BF_4]$, $[(Et_2O)_2H][Al(OC(CF_3)_3]$; [Fe] = $[Cp'''Fe(CO)_2]$; [Fe'] = $[Cp^*Fe(CO)_2]$.

As also reported by Scheer and co-workers, the reaction of $[Cp''_2Zr(\kappa^2P\text{-}P_4)]$ (**108**, Cp'' = 1,3-*t*Bu$_2$C$_5$H$_3$) with the monochlorosilylene **109** in toluene at room temperature gives compounds **110** and **111**, which are remarkable phosphorus/silicon analogues of benzene and cyclobutadiene, respectively (Scheme 18a).[59] Computational studies indicated that **110** possesses considerable aromatic character, whereas **111** is weakly antiaromatic. The aromaticity in both compounds is substantially influenced by the additional donating nitrogen lone pairs of the bidentate PhC(N*t*Bu)$_2$ substituents.

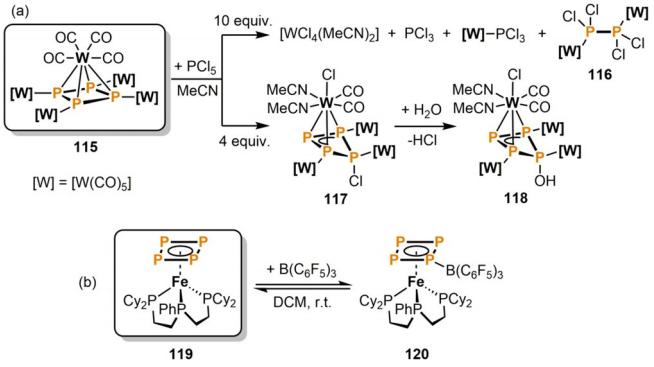


Scheme 18. Synthesis of phosphorus/silicon analogues of benzene (a) and phosphorus-rich cage compounds (b) by Zr-mediated P_4 functionalization (L = $[PhC(NtBu)_2]$, [Zr] = $[Cp''_2Zr]$, Cp'' = 1,3-*t*Bu$_2$C$_5$H$_3$).

Scheer and co-workers further reacted **108** with *t*BuC≡P in boiling toluene to access phosphorus-rich cage compounds (Scheme 18b).[60] According to ^{31}P NMR spectroscopic analysis the major product $[Cp''_2Zr(\kappa^2P\text{-}P_3CtBu)]$ (**112**) is formed along with minor amounts of the carbon/phosphorus cages **113** and **114**, which both incorporate a cuneane-like P_5C_3 or P_6C_2 subunit. The authors suggested that **112** is formed by elimination of a P_2 unit from **108** and subsequent reaction with *t*BuC≡P. The released P_2 species may be trapped by multiple phosphaalkyne molecules to give metal-free cages such as **113. 114** derives from the formal addition of two equivalents of *t*BuC≡P to the starting material **108**. The products were successfully separated by fractional crystallization and column chromatography.

2.4.3. *cyclo*-P_4 ligands

Functionalization at *cyclo*-P_4 ligands is less common than at tetrahedral and butterfly-P_4 ligands, and was first demonstrated by Scheer and co-workers (Scheme 19).[61] When a tenfold excess of PCl_5 is reacted with the pentanuclear *cyclo*-P_4 complex **115**, the main products in the reaction mixture are $[WCl_4(MeCN)_2]$, PCl_3, $[W(CO)_5(PCl_3)]$, and the dinuclear tetrachlorodiphosphane complex **116**. However, these species are only found in minor quantities when the reaction is performed with a smaller amount of PCl_5 (4 equiv). The main product in this case is **117**, in which a $[WCl(CO)_2(MeCN)_2]$ fragment is co-



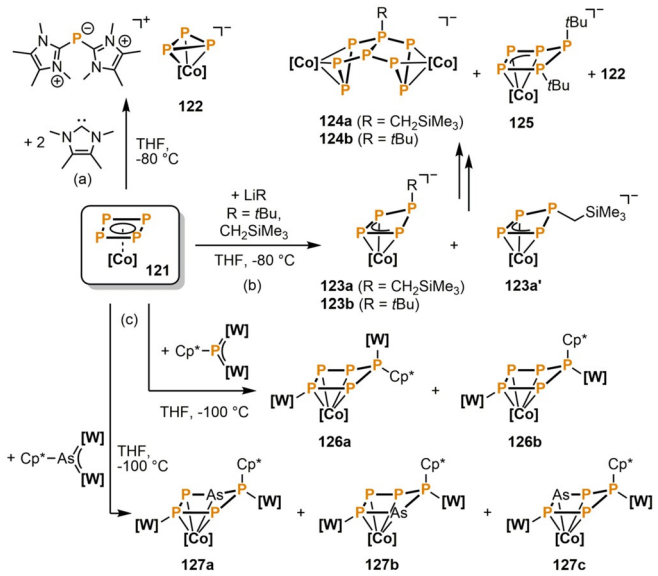
Scheme 19. Tungsten- and iron-promoted transformations of *cyclo*-P_4 ligands; [W] = $[W(CO)_5]$.

ordinated by a chlorinated *cyclo*-P_4 ligand through its triphosphaallyl subunit. The isolation of **117** as a pure compound was not successful, because it readily reacts with traces of moisture to give the corresponding hydrolysis product **118**.

Mézailles and co-workers investigated the reactivity of the end-deck *cyclo*-P_4 iron complex **119** toward electrophiles (Scheme 19b).[62] The P-borylated Lewis adduct **120** is formed in an equilibrium reaction upon treatment of **119** with $B(C_6F_5)_3$ in DCM.

Recently, Scheer and co-workers reported on the *N*-heterocyclic carbene-induced ring contraction of the end-deck *cyclo*-P_4 cobalt sandwich complex **121** (Scheme 20a).[63] The treatment of **121** with two equivalents of 1,3,4,5-tetramethylimidazol-2-ylidene (NHC) leads to selective abstraction of one phosphorus cation from the four-membered tetraphosphorus ring. The resulting ionic product consists of a $[(NHC)_2P]^+$ cation and a $[Cp'''Co(\eta^3\text{-}cyclo\text{-}P_3)]^-$ anion (**122**, $Cp''' = 1,2,4\text{-}tBu_3C_5H_2$). This methodology is also applicable to some triple-decker sandwich complexes bearing *cyclo*-P_6 middle decks (see Scheme 26, section 2.5).

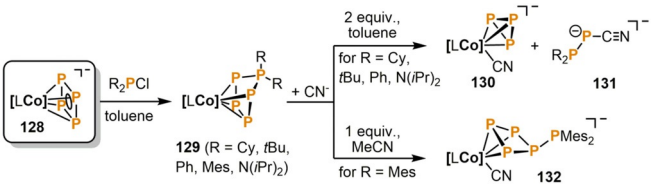
The reactivity of **121** towards carbon based nucleophiles was also studied, by the same group.[64] Treatment of **121** with *t*BuLi and $LiCH_2SiMe_3$ in THF at −80 °C gave the axially substituted tetraphosphido complexes $[Cp'''Co(\eta^3\text{-}P_4R)]^-$ (**123**, R = *t*Bu, CH_2SiMe_3), respectively as initial kinetic products (Scheme 20b). The anions **123** are metastable, however they can be sufficiently stabilized by trapping the Li^+ counter cations with 12-crown-4 or [2.2.2]-cryptand in the cold reaction mixture. By this manner, the authors were able to isolate the [Li(12-crown-4)$_2$]-salt of **123a** as a mixture with its equatorial isomer **123a′**, and pure **123b** as its [Li([2.2.2]-cryptand)]-salt at room temperature. Note that a corresponding equatorial isomer of **123b** was not detected. In the absence of complexing crown ethers, **123a** decomposes upon warming to room temperature to give a mixture of products including the abovementioned *cyclo*-P_3 sandwich anion **122**, and the dinuclear complex $[(Cp'''Co)_2(\mu,\eta^3{:}\eta^3\text{-}P_8CH_2SiMe_3)]^-$ (**124a**), which features an alkyl substituted bicyclo[3.3.0]octaphosphane ligand. Interestingly, a different product mixture is obtained from the decomposition of **123b**. Besides the analogous P_8tBu complex **124b** and **122**, in this case, $[Cp'''Co(\eta^3\text{-}P_5tBu_2)]^-$ (**125**) is also formed, which bears a 1,2-diorgano substituted *cyclo*-P_5 ligand.



Scheme 20. Functionalization of the *cyclo*-P_4 ligands in the cobalt sandwich complex **121**; [Co] = [(1,2,4-$tBu_3C_5H_2$)Co].

Scheer and co-workers also investigated ring expansions of **121** upon reaction with the pnictinidene complexes $[Cp^*E\{W(CO)_5\}_2]$ (E = P, As, Scheme 20c).[65] The insertion of the phosphinidene into the P_4 ring is followed by a shift of one $[W(CO)_5]$ unit and affords the two isomeric η^4-*cyclo*-P_5 species **126a** and **126b**, which differ only in the orientation of the tungsten pentacarbonyl and the Cp* substituents. Interestingly, when **121** is reacted with the analogous arsinidene, all substituents previously bound to arsenic migrate to phosphorus resulting in several η^4-*cyclo*-P_4As isomers (**127a-c**), which differ in the location of the arsenic atom within the five-membered ring.

Very recently, Wolf and co-workers described a highly selective P_4 functionalization and subsequent fragmentation in the coordination sphere of a cobalt α-diimine complex (Scheme 21).[66] The reaction of the *cyclo*-P_4 cobaltate anion $[LCo(\eta^4\text{-}P_4)]^-$ (**128**, L = bis(2,6-diisopropylphenyl)phenanthrene-9,10-diimine) with R_2PCl (R = Cy, *t*Bu, Ph, Mes, N(*i*Pr)$_2$) quantitatively gives the neutral *cyclo*-P_5R_2 complexes **129** in up to 77% isolated yield. Depending on the substituent R, different reaction outcomes are observed upon treatment of **129** with cyanide salts ([K(18-crown-6)]CN, $[Et_4N]CN$, $[nBu_4N]CN$). When R = Cy, *t*Bu, Ph or N(*i*Pr)$_2$ reaction with two equivalents of CN^- induces a remarkable [3+2] fragmentation, resulting in formation of the anionic cyclotriphosphido cobalt complex **130** and 1-cyanodiphosphan-1-ide anions **131**. By contrast, if **129** bears bulky mesityl substituents, the reaction reaches full conversion with only one equivalent of CN^-. The product in this case is **132**, which features a rearranged P_5Mes_2 ligand. The authors suggested that similar cyclotetraphosphido complexes may be key intermediates in the fragmentations that ultimately lead to **130** and **131**, but that the bulky mesityl substituent in **129** hinders such onward reactivity.

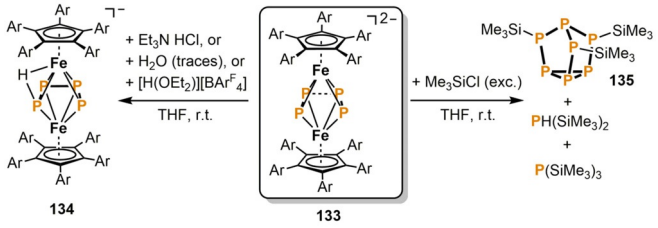


Scheme 21. Functionalization of a *cyclo*-P_4 ligand with diorganochlorophosphanes R_2PCl (R = Cy, *t*Bu, Ph, Mes, N(*i*Pr)$_2$) mediated by a low valent α-diimine cobalt complex, and subsequent rearrangement and fragmentation reactions (L = bis(2,6-diisopropylphenyl)phenanthrene-9,10-diimine).

2.4.4. P_4 chains

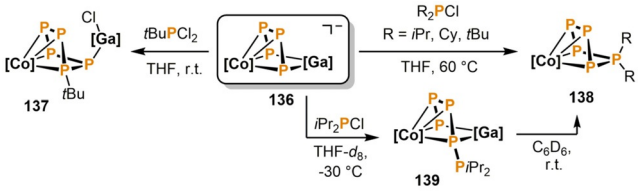
Wolf and co-workers demonstrated the first functionalization of P_4 chains in the coordination sphere of 3d metalate anions.

Reaction of the diiron compound **133** with one equivalent of $Et_3N{\cdot}HCl$ or $[H(Et_2O)_2][BAr^F{}_4]$ ($Ar^F = 3,5\text{-}(CF_3)_2C_6H_3$) affords the protonated ferrate **134** in moderate yields (Scheme 22).[67] Crystallographic, spectroscopic and computational investigations indicated that the proton is highly mobile, and simultaneously bound to both iron and phosphorus. Treatment of **133** with an excess of Me_3SiCl results in liberation of the phosphorus scaffold from the iron center to give a mixture of $PH(SiMe_3)_2$, $P(SiMe_3)_3$ and the nortricyclane compound $P_7(SiMe_3)_3$ (**135**) in a ratio of 1:1:10.



Scheme 22. Functionalization of the bridging P_4 chain in the ferrate **133** with electrophiles (Ar = 4-ethylphenyl; $Ar^F = 3,5\text{-}(CF_3)_2C_6H_3$).

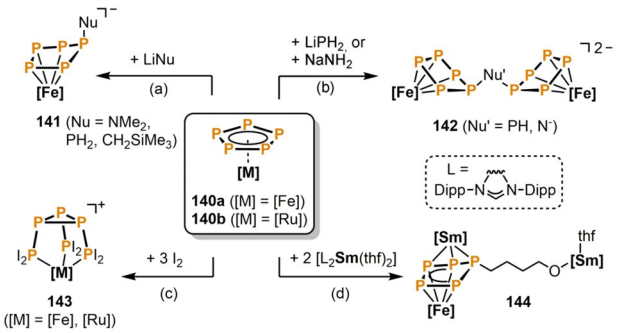
The heterodinuclear complex **136**, which features a *catena*-P_4 unit, readily undergoes P–P condensation reactions with chlorophosphanes (Scheme 23).[68] The reaction with *t*BuPCl$_2$ affords a *cyclo*-P_5 cobalt complex **137** with a concomitant chloride shift from P to Ga. By contrast, a different outcome is observed upon reaction of **136** with the dialkylmonochlorophosphanes R_2PCl (R = *i*Pr, Cy, *t*Bu). In this case, the *N*-heterocyclic gallylene [Ga(nacnac)] (nacnac = CH[CMeN(2,6-*i*Pr$_2$C$_6$H$_3$)]$_2$) is released, affording the mononuclear *cyclo*-P_5R_2 cobalt complexes **138**. Variable temperature NMR studies on the reaction with *i*Pr$_2$PCl revealed the formation of two intermediate species, likely being constitutional isomers, of which the more abundant could be crystallographically identified as the neutral *catena*-$P_5i Pr_2$ complex **139**.



Scheme 23. Functionalization of the *catena*-P_4 unit in the cobaltate complex **136** with chlorophosphanes; [Co] = [CoBIAN] (BIAN = bis(mesityl)iminoacenaphthene); [Ga] = [Ga(nacnac)] (nacnac = CH[CMeN(2,6-*i*Pr$_2$C$_6$H$_3$)]$_2$).

2.5. Functionalization of P_n ligands ($n \geq 5$)

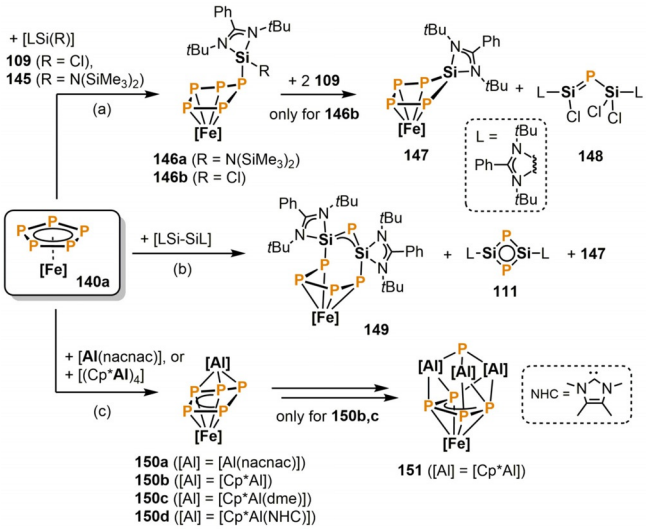
To date the functionalization of white phosphorus-derived P_n ligands with $n \geq 5$ has been only scarcely explored. Scheer and co-workers treated the pentaphosphaferrocene [Cp*Fe(η^5-P_5)] (**140a**) with a set of main group nucleophiles and thus obtained P-functionalized η^4-P_5 ferrate complexes.[69] Distinct reactivity was observed depending on the nucleophile. While $LiCH_2SiMe_3$, $LiNMe_2$, and $LiPH_2$ gave rise to mononuclear complexes **141** (Scheme 24a, minor product for $LiPH_2$), the formation of dinuclear complexes **142** (Scheme 24b) occurred upon reaction with $NaNH_2$ and $LiPH_2$ (major product). The iodination of **140a** and its heavier congener [Cp*Ru(η^5-P_5)] (**140b**) was also investigated by the same group (Scheme 24c).[70] Layering dichloromethane solutions of **140** with three equivalents of iodine dissolved in MeCN selectively gives the monocationic complexes **143** as insoluble crystalline solids. Compounds **143** feature a unique tripodal *cyclo*-$P_3(PI_2)_3$ ligand in an *all-cis* conformation.



Scheme 24. Functionalization of a *cyclo*-P_5 ligand by nucleophiles (a,b), iodination (c) and thf ring-opening (d); [Fe] = [Cp*Fe], [Ru] = [Cp*Ru], [Sm] = [L_2Sm], L = *N*,*N*′-bis(2,6-diisopropylphenyl)formamidinate).

Roesky and co-workers reported on the Sm^{II} induced reduction and concomitant functionalization of the *cyclo*-P_5 ligand in **140a** (Scheme 24d).[71] The trinuclear complex **144** was obtained in 59% yield by reacting **140a** with two equivalents of the bulky samarium complex [L_2Sm(thf)$_2$] (L = *N*,*N*′-bis(2,6-diisopropylphenyl)formamidinate) in refluxing heptane for seven days. During the reaction the P_5 unit is reduced and ring opening of a coordinated thf molecule occurs. The formation of a new P–C bond ultimately affords an oxidobutyl substituted pentaphosphido ligand bridging the [Cp*Fe], [L_2Sm] and [L_2Sm(thf)] fragments in an $\eta^4{:}\eta^3{:}\eta^1$-fashion.

Furthermore, the reactivity of **140a** was also investigated toward silylenes in a very recent collaboration between the groups of Scheer and Roesky.[72] Treatment of **140a** with one equivalent of the sterically encumbered silylene [LSi{N(SiMe$_3$)$_2$}] (**145**, L = [PhC(N*t*Bu)$_2$]) affords the Si-substituted η^4-P_5 compound **146a** in 79% isolated yield (Scheme 25a). A different reaction outcome is observed when the less bulky silylene [LSi(Cl)] (**109**, three equivalents) is reacted with **140a**. A simultaneous extrusion and insertion process results in the selective formation of the phosphasilene species **148** and [Cp*Fe(η^4-P_4SiL)] (**147**), which was formally described as a P_4^{4-} ligand bridging between $[Cp^*Fe]^+$ and $[LSi]^{3+}$ cations. According to a $^{31}P\{^1H\}$ VT-NMR experiment, in this case, **146b**, a *cyclo*-P_5 species analogous to **146a**, is formed only as an intermediate at −70 °C. The reaction of **140a** with an equimolar amount of the formal Si^I compound [LSi-SiL] gives [Cp*Fe{η^4-P_5(SiL)$_2$}] (**149**) via double ring expansion of the *cyclo*-P_5 ring to afford a remarkable seven-membered *cyclo*-Si_2P_5 ring (Scheme 25b). Consider-

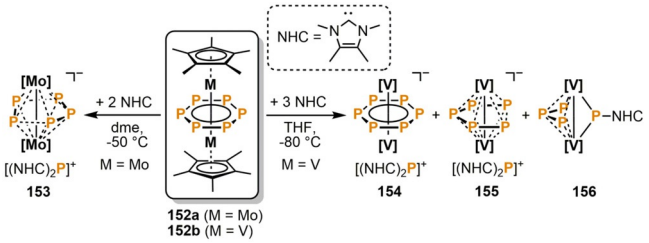


Scheme 25. Functionalization of the *cyclo*-P_5 ligand in pentamethylpentaphosphaferrocene **140 a** by heavy carbene analogues. [Fe] = [Cp*Fe], L = [PhC(N*t*Bu)$_2$, nacnac = CH[CMeN(2,6-*i*Pr$_2$C$_6$H$_3$)]$_2$), dme = dimethoxyethane, NHC = 1,3,4,5-tetramethylimidazol-2-ylidene.

able quantities of **147** and [$L_2Si_2P_2$] (**111**, see Scheme 18, section 2.4.2) were detected as by-products in the $^{31}P\{^1H\}$ NMR spectrum of the crude reaction mixture.

Roesky and co-workers also studied the reaction of **140 a** toward related low valent aluminium compounds.[73] Treatment of **140 a** with an equimolar amount of [Al(nacnac)] (nacnac = CH[CMeN(2,6-*i*Pr$_2$C$_6$H$_3$)]$_2$) at room temperature afforded the triple-decker type complex [(nacnacAl)(μ_2,η^3:η^4-P_5)FeCp*] (**150 a**), which features a bent *cyclo*-P_5 middle-deck (Scheme 25 c). By contrast, reacting **140 a** with [(Cp*Al)$_4$] led to the Al-Fe cluster compound **151**, containing a bridging monophosphido ligand (η^3-P) and a tetraphosphorus chain. A related [4+1] fragmentation of the *cyclo*-P_5 ring in **140 a** was also observed in the abovementioned reactions with silylenes (c.f. **149**). The authors suggest that the reaction proceeds via the intermediate formation of **150 b** and subsequent regioselective insertion of [Cp*Al] fragments into two adjacent P–P bonds. In fact, the donor stabilized compound **150 c** was detected by NMR spectroscopy in the presence of dimethoxyethane (dme) and **150 d** could even be successfully isolated and characterized by trapping with 1,3,4,5-tetramethylimidazol-2-ylidene (NHC).

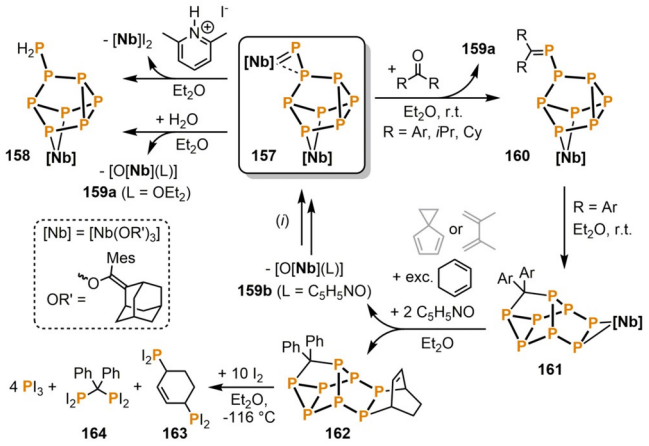
As mentioned in section 2.4.3 (Scheme 20), Scheer and co-workers have demonstrated that the *N*-heterocyclic carbene 1,3,4,5-tetramethylimidazol-2-ylidene (NHC) is a valuable reagent for the contraction of a *cyclo*-P_4 ring.[63] In the same work, this concept was also applied to the early transition-metal triple-decker sandwich complexes [(Cp*M)$_2$(μ,η^6:η^6-P_6)] (**152**, M = V, Mo, Scheme 26). Thus, the reaction of the dimolybdenum species **152 a** with two equivalents of NHC selectively extracts a phosphorus cation from the *cyclo*-P_6 middle deck, affording the bis(NHC)-supported P^I cation [(NHC)$_2$P]$^+$ and the molybdate anion **153**. According to the crystallographic data, the anticipated *cyclo*-P_5 ring in **153** is best described as separated P_3 and P_2 units. The reaction of the divanadium



Scheme 26. Functionalization of the *cyclo*-P_6 middle deck in early transition-metal triple-decker complexes; [Mo] = [Cp*Mo], [V] = [Cp*V].

complex **152 b** with NHC is less selective. The two ionic species [(NHC)$_2$P][(Cp*V)$_2$(μ,η^6:η^6-P_6)] (**154**) and [(NHC)$_2$P][(Cp*V)$_2$(μ,η^5:η^5-P_5)] (**155**) were isolated as a co-crystalline mixture from a THF extract. While **154** is probably formed by one electron reduction of the starting material **152 b**, **155** derives from phosphorus cation abstraction from **152 b**. The third identified product was the neutral complex **156**, which features two bridging ligands: a triphosphaallylic P_3 chain and an NHC-P phosphinidenide unit.

Separately, Cummins and co-workers found that the diniobium octaphosphide complex **157** possesses a reactive phosphinidene moiety, which readily hydrolyzes to give the mononuclear phosphanyl-substituted heptaphosphide complex **158** and the oxo niobium species **159 a** (Scheme 27).[74] The former compound could also be synthesized in a more selective manner by protonation of **157** with two equivalents of 2,6-dimethylpyridinium iodide. In this case, the corresponding niobium diiodide complex is the stoichiometric by-product. Remarkably, **157** also undergoes Nb = P/O = C metathesis with ketones.[75] While the resulting alkyl substituted phosphaalkene complexes **160** are stable for up to several days at ambient temperature, the corresponding aryl derivatives immediately undergo an electrocyclic rearrangement ultimately affording



Scheme 27. Niobium-mediated functionalization of a P_8 framework; [Nb] = [Nb(OR')$_3$] (OR' = (adamantane-2-ylidene)(mesityl)methanolate); Ar = Ph, 4-Cl-C$_6$H$_4$, 4-Me-C$_6$H$_4$, 4-OMe-C$_6$H$_4$, 4-NMe$_2$-C$_6$H$_4$, 4-CF$_3$-C$_6$H$_4$). (*i*) Recovery of starting material **157** (0.5 equiv) proceeds by: 1. + O(OCCF$_3$)$_2$, + 2 equiv Me$_3$SiI/-Me$_3$SiO(OCCF$_3$) in Et$_2$O; 2. + SmI$_2$/-SmI$_3$ in THF; 3. + P_4 in toluene.

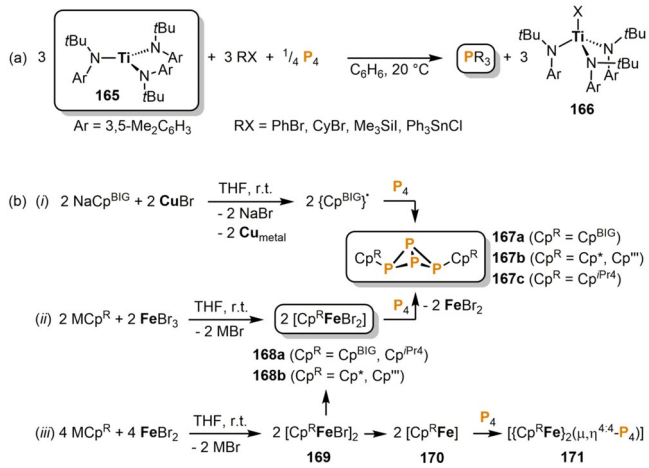
the saturated organophosphorus cluster compounds **161**. The carbophosphorus cluster can be liberated from niobium by treatment with two equivalents of pyridine-*N*-oxide in the presence of an excess of 1,3-cyclohexadiene, leading to the Diels–Alder product **162**.[76] Moreover, [4+2] cycloaddition with the niobium-bound diphosphene moiety in **161** also takes place when 2,3-dimethylbutadiene or spiro[2.4]hepta-4,6-diene are used as dienes, and the niobium oxo compounds **159 a** and **159 b** can be recycled by step-wise deoxygenation, reduction and P_4 activation. Furthermore, Cummins and co-workers described the remarkable reactivity of **162** towards ten equivalents of iodine, which cleanly affords four molecules of PI_3 along with the bis(diiodophosphanyl)-substituted hydrocarbons **163** and **164**.

2.6. Radical functionalization of P_4

While the reactions described thus far have all proceeded through direct coordination of P_n fragments, it has also proven possible for transition metals to mediate the functionalization of P_4 in an outer sphere manner, not necessarily involving the formation of intermediate (poly)phosphorus complexes. In particular, it has been found that transition metals can be used to induce the formation of free carbon- (or other main group element-) centered radicals, which induce successive, homolytic P–P bond cleavage reactions, resulting in stepwise degradation of the P_4 molecule. A related, metal-free concept was originally demonstrated by Barton and co-workers, using alkyl radicals generated by the decomposition of pyridine thione oxycarbonyl esters (Barton's PTOC esters).[77] Cummins and co-workers used the three-coordinate Ti^{III} complex $[Ti(N[tBu]Ar)_3]$ (**165**, Ar = 3,5-$C_6H_3Me_2$) for stoichiometric halogen radical abstraction from main group element halides RX (RX = PhBr, CyBr, Me_3SiI, Ph_3SnCl) to give the Ti^{IV} species **166** (Scheme 28 a).[78] The concomitantly-formed R· radicals successively break down the P_4 tetrahedron, ultimately affording the respective phosphanes PR_3 in certain cases. While quantitative conversion is observed for the heavier group 14 element halides Me_3SiI and Ph_3SnCl, considerable amounts of the diphosphanes P_2R_4 are found as by-products in the analogous reactions with CyBr and PhBr. However, with an excess (5 equiv) of **165** and RX, these reactions also become quantitative. When more sterically demanding aryl groups such as Mes and Ar* (2,6-$Mes_2C_6H_3$) are used, the stepwise P_4 degradation does not proceed to completion, but instead results in the triphosphirane P_3Mes_3 or the bicyclo[1.1.0]tetraphosphabutane (butterfly) species *exo,endo*-$Ar^*_2P_4$, respectively.

Scheer reported on the synthesis of the organic *exo,exo*-substituted P_4 butterfly compounds **167** by the one-pot reactions of P_4 with metal-generated cyclopentadienyl radicals (Scheme 28 b).[79] The required radicals were formed via three different pathways: (*i*) The treatment of $NaCp^{BIG}$ ($Cp^{BIG} = C_5(4\text{-}nBu\text{-}C_6H_4)_5$) with CuBr led to precipitation of metallic copper along with dark blue $\{Cp^{BIG}\}^\bullet$ radicals, which were detected by EPR spectroscopy and selectively give **167 a** upon addition of P_4. (*ii*) The reaction of the alkali cyclopentadienide salts MCp^R (= $NaCp^{BIG}$, NaCp‴, LiCp*, $NaCp^{iPr4}$) with $FeBr_3$ afforded the intermediate Fe^{III} complexes **168**, which readily transfer $Cp^{R\bullet}$ radicals onto the P_4 tetrahedron, giving **167** upon loss of $FeBr_2$. (*iii*) The corresponding Fe^{II} complexes **169** synthesized from MCp^R (= NaCp‴, LiCp*) and $FeBr_2$ resulted in the P_4 butterfly species **167 b** when reacted with P_4. The reaction mechanism in this case is suggested to involve disproportionation of **169** into the Fe^{III} complexes **168 b**, which undergo the abovementioned reaction with P_4, and Fe^{I} intermediates **170** that form the dinuclear species **171** bearing a bridging *catena*-P_4 ligand.

Furthermore, Yakhvarov and Budnikova have reported on electrochemical methods for radical functionalization of P_4.[80,81] Their work has recently been reviewed in detail.[82,83] The reaction principle is based on the electrocatalytic C–P bond formation mediated by bipyridine (bpy) nickel complexes. Figure 2 exemplifies a suggested schematic catalytic cycle for the nickel-promoted transformation of P_4 into organophosphorus compounds. The proposed mechanism involves the cathodic electrogeneration of active Ni^0 complexes from the corre-



Scheme 28. Radical functionalization of P_4 mediated by early (a) and late (b) transition metals. (*i*) only for Cp^{BIG}; (*ii*) MCp^R = $NaCp^{BIG}$, NaCp‴, LiCp*, $NaCp^{iPr4}$; (*iii*) only for MCp^R = NaCp‴, LiCp* ($Cp^{BIG} = C_5(4\text{-}nBu\text{-}C_6H_4)_5$; Cp‴ = $C_5H_2tBu_3$; Cp* = C_5Me_5; $Cp^{iPr4} = C_5HiPr_4$).

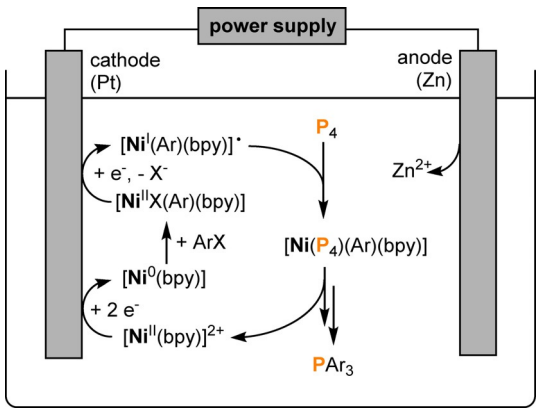
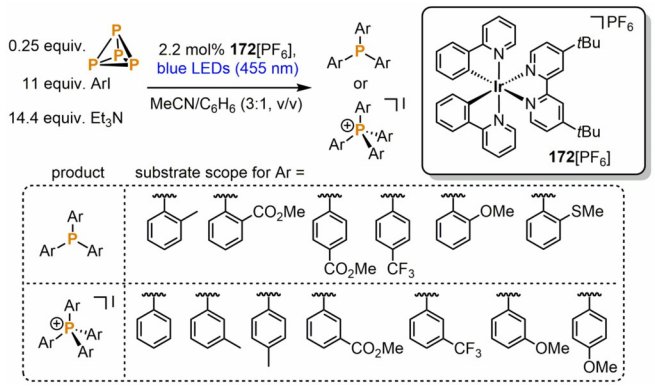


Figure 2. Proposed mechanism for nickel-electrocatalyzed arylation of white phosphorus in DMF or MeCN carried out in an undivided cell (bpy = 2,2′-bipyridine).

sponding Ni^{II} species, followed by the oxidative addition of aryl halides ArX.[81] The resulting organonickel aryl complex [NiX(Ar)(bpy)] is inert towards P_4. However, after electrochemical one-electron reduction, the radical species $[Ni(Ar)(bpy)]^{\cdot}$ immediately incorporates the P_4 molecule.[83] Subsequent aqueous work-up ultimately affords tertiary phosphanes and phosphane oxides. Note that the metal ions generated from the electrochemically soluble (sacrificial) anode are required to stabilize anionic phosphido intermediates and thus prevent undesired phosphorus polymerization processes. Depending on the anode material, different organophosphorus products are formed.[84] While a zinc anode mainly leads to the formation of tertiary phosphanes, an aluminium anode instead results in phosphane oxide formation. By contrast, use of a magnesium anode gives cyclic polyphosphorus compounds, such as $(PhP)_5$.

Very recently, Wolf and co-workers described the direct and photocatalytic synthesis of triarylphosphanes and tetraarylphosphonium salts from P_4, aryl iodides, and triethylamine as a terminal electron donor (Scheme 29).[85] Based on the phosphorus atoms (0.25 equiv P_4), the reaction uses an excess of aryl iodide (11 equiv) and Et_3N (14.4 equiv) and is catalyzed by the commercially available photocatalyst $[Ir(dtbbpy)(ppy)_2][PF_6]$ (**172**$[PF_6]$, 2.2 mol%, dtbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine, ppy = 2-(2-pyridyl)phenyl) under blue LED light (455 nm). Depending on the steric and electronic nature of the aryl iodide substrate the formation of either the triarylphosphanes or tetraarylphosphonium salts is favored (Scheme 29). The resulting organophosphorus compounds can be isolated in up to 71% yield. Both electron-withdrawing groups and additional steric bulk at the *ortho*-position support the formation of phosphanes over phosphonium salts. Further increase of the steric demand of the substrate gives even less substituted phosphanes: the secondary phosphane Mes_2PH is formed from mesityl iodide, and use of 2,6-dimesitylphenyl iodide (Ar*I) gives rise to the primary phosphane Ar^*PH_2. These observations are in line with mechanistic studies performed on the reaction using iodobenzene, which support a stepwise mechanism that sequentially produces primary phosphanes ($PhPH_2$), secondary phosphanes (Ph_2PH), tertiary phosphanes (Ph_3P) and finally the phosphonium salts (Ph_4P^+). According to emission quenching experiments and redox potential measurements it is likely that the excited state of the photocatalyst **172**$^+$ is reductively quenched by Et_3N, generating the neutral complex **172**, which in turn reduces PhI to the corresponding phenyl radical $Ph^{\cdot}$. White phosphorus is then rapidly consumed by these radicals. As well as aryl-substituted products, the same methodology could also be used to prepare the tin-substituted phosphane $P(SnPh_3)_3$, starting from Ph_3SnCl.



Scheme 29. Photocatalytic functionalization of P_4 to triarylphosphanes and tetraarylphosphonium salts.

3. Summary and Outlook

Building on the pioneering work of Green, Stoppioni and Peruzzini in the 1970s and 1980s, the transition-metal-mediated functionalization of white phosphorus has developed greatly over the past several decades. Scientists from around the globe have contributed to this branch of phosphorus chemistry, and demonstrated the synthetic potential of P_4 functionalization for the formation of diverse and unprecedented phosphorus compounds. A considerable number of transition-metal complexes bearing P_n ligands derived from P_4 activation have been used for subsequent P_4 functionalization (sections 2.2–2.5). By contrast, only a few hydrido or alkyl complexes have shown the potential to both activate and functionalize P_4 in a single reaction (section 2.1), and even fewer complexes are currently capable of promoting outer sphere, radical functionalization (section 2.6). To date, neutral complexes have been employed more often for P_4 functionalization than ionic ones. However, out of the charged systems, anionic complexes have generally proven to be better platforms than cations. This may be attributed to the fact that by far the most common reactants for P_4 functionalizations are electrophiles. Attack at nucleophilic phosphorus sites is often accompanied by metathetical halide abstraction, which provides the driving force for these reactions. Hydrolyses, oxidations, cycloadditions, and reactions with nucleophiles have been reported much less frequently. Many of these functionalizations have given rise to remarkable new mono- or oligophosphorus complexes. However, the liberation of these P-rich species from the complexing metal centers is challenging and thus far has seldom been achieved. Nevertheless, some fascinating compounds, such as EP_3 (E = As, Sb) prepared by Cummins and the P-Si analogue of benzene reported by Scheer have been synthesized via these approaches. It is worth noting that, while P_4 functionalization at both early and late transition metals has been established to similar extents, release from the metal has mostly been observed at early transition-metal systems. This is probably due to the higher oxophilicity of these metals, which can be exploited in ligand liberation reactions with oxidizing agents (e.g. pyridine-*N*-oxide).

Despite the growing number of successful phosphorus functionalization reactions, the ultimate goal, namely the general circumvention of chlorine gas and PCl_3 in the industrial formation of useful organophosphorus species, is still far from being reached. Nevertheless, we hope that careful evaluation of the above-mentioned literature may help chemists to begin to predict the outcome of their prospective functionalization reactions, and hence further accelerate the progress being made in this fundamental area of modern phosphorus chemistry.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: coordination compounds · P ligands · radicals · transition metals · white phosphorus

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