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Coordination chemistry and functionalization of white phosphorus *via* transition metal complexes

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The chemistry of phosphorus is nowadays rivalling that of carbon in terms of complexity and diversity. This *tutorial review* highlights the state-of-the-art in the field of metal-mediated activation and functionalization of white phosphorus. Particular attention is given to an illustration of the coordination abilities of the intact molecule as well as the disaggregating and reaggregating metal-mediated processes resulting in different polyphosphorus ligands from P_1 to P_{12}. The metal-promoted P–C and P–H bond forming processes are also reviewed showing that an ecoefficient catalytic protocol for transforming P_4 into high value organophosphorus compounds is a concrete possibility for chemical companies.

This *tutorial review* deals with the activation and functionalization of white phosphorus in the coordination sphere of transition metal complexes. Particular attention is given to the coordination abilities of the intact molecule as well as to the disaggregating and reaggregating metal-mediated processes yielding various polyphosphorus ligands from P_1 to P_{12}. The metal-promoted processes for P–C and P–H bond formation are also reviewed showing that an ecoefficient catalytic protocol for transforming P_4 into high value organophosphorus compounds offers good opportunities for chemical companies.

1 Introduction

During the last century, organophosphorus chemistry has become very important in many sectors of industry and everyday life. Phosphorus is present in most fertilizers, insecticides, detergents, foodstuffs and pharmaceutical products, in the form of inorganic and organic phosphates.[1] Thus,

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Maurizio Peruzzini was born in Florence, Italy, in 1955. After his "Laurea" cum laude (University of Florence 1979; advisors L. Sacconi and P. Stoppioni), he moved to ICCOM CNR in 1986, where he is currently Senior Research Associate. In 1993 he was awarded with the "Nasini" gold medal by the Inorganic Chemistry Division of the Italian Chemical Society in recognition of his contribution to the chemistry of non-classical hydrides. Together with R. Poli he edited the book Recent Advances on Hydride Chemistry. He has been the coordinator of several international projects (4–6th RFP, INTAS, NATO) and industrial contracts and is currently responsible for FIRENZE HYDROLAB (an integrated laboratory on hydrogen as energy carrier). His research interests are primarily in the field of organometallic chemistry and catalysis. He has authored over 200 papers and patents. He is married to Gianna and has a son, Riccardo.

Luca Gonsalvi

Luca Gonsalvi graduated in Chemistry in 1994 from the University of Parma under the supervision of G. Predieri and A. Tiripicchio. In 1996 he moved to the University of Sheffield (UK) as a PhD student with Anthony Haynes to study stereoelectronic ligand effects in Rh and Ir catalysed methanol carbonylation. In December 1999, he joined Roger Sheldon's group at Delft University of Technology (NL) as PDRA to develop a clean catalytic protocol to esters via selective oxidation of ethers and acetals. From December 2001, he has worked at ICCOM CNR as staff researcher to work on multiphase LTM-catalysed processes and mechanistic aspects of small molecules activation. He has authored more than 20 articles in refereed journals and 1 patent and presented his work at more than 20 international conferences.

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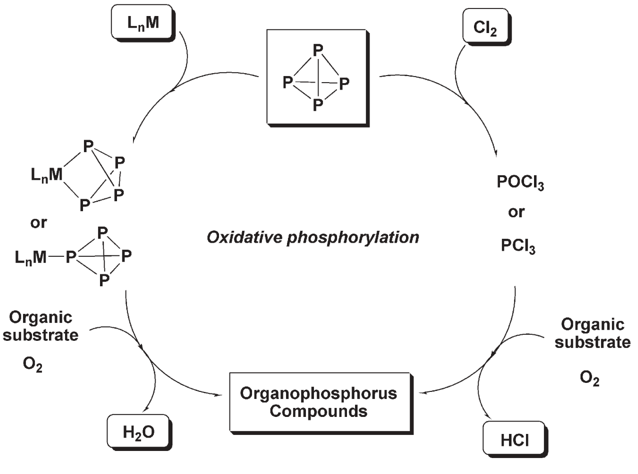
there is little doubt that the chemistry of organophosphorus compounds has nowadays grown to a level of complexity and development similar in many respects to that of carbon.[2]

White phosphorus, P_4, the most reactive allotrope of the element, is the starting material from which most of the organophosphorus compounds produced worldwide are synthesized. The traditional method used to convert white phosphorus into the target organophosphorus derivatives involves a two step process, namely the direct chlorination of P_4 using chlorine followed by the phosphorylation of the organic substrate by phosphorus chloride.[3] However, this industrial method is not environmentally benign as it involves the presence of chlorine and hydrogen chloride and therefore raises major costs for the purification of the oven gases from phosphorus plants.[4]

In order to meet the growing commercial interest in organophosphorus derivatives and the increasingly stringent environmental regulations, a green approach to convert white phosphorus directly into organophosphorus derivatives thus avoiding the use of chlorine is highly desirable. The ideal replacement would be a metal-mediated catalytic process that directly combines white phosphorus and organic molecules. The desired catalyst should be a suitable transition metal complex able to bring about the selective oxidative phosphorylation reaction of the organic substrate in an efficient way with high turnovers.

Scheme 1 (left) illustrates key steps of a possible homogeneous catalytic pathway, inspired by the principles of 'green chemistry'. In the process, an organophosphorus compound is assembled by combining P_4 and an organic substrate in the presence of oxygen as a cheap and environmentally benign oxidant. A comparison with the classical process (right) shows that the chlorine-free technology would offer far less pollution producing water instead of HCl as a by-product, with a consequent dramatic drop in the *E* factor (roughly expressed as kg by-product per kg product) of the process.[5]



Scheme 1

In order to develop an ecologically satisfying manufacturing process of organophosphorus compounds, it is however mandatory to achieve a deeper knowledge of the coordination chemistry of white phosphorus and to understand the molecular mechanisms governing the metal-mediated activation and the functionalization of the tetrahedral molecule once coordinated to a transition metal moiety.

Antonio Romerosa

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This *tutorial review* reports on this subject reviewing the current knowledge of the coordination chemistry of elemental phosphorus and highlights how the overall information in this area represents a mature discipline which could be attractive to chemical companies wishing to exploit innovative protocols for the green synthesis of organophosphorus compounds.

2 Coordination chemistry and reactivity of white phosphorus

The coordination chemistry of phosphorus was virtually neglected until thirty years ago when the first transition metal complex containing white phosphorus as a ligand, $[(PPh_3)_2ClRh(\eta^2\text{-}P_4)]$ (**1**), was obtained from the reaction of the Wilkinson complex, $[(PPh_3)_3RhCl]$, with white phosphorus at low temperature.[6] This breakthrough spearheaded a great interest in this chemistry lasting until now and providing a large body of information about the reactivity of P_4 towards a variety of transition metal fragments.[7–10] These studies have demonstrated that the P_4-tetrahedron can be easily activated within the coordination sphere of various unsaturated fragments of transition metals bearing adequate ancillary ligands, and have also pointed out that, once activated, the P_4 ligand may exhibit a rich chemistry with reactivity patterns different from those of the free molecule. Apart from sparse reports, almost all the studies dealing with this chemistry used harsh reaction conditions including either thermal reactions in high boiling point solvents, usually arenes, or photochemical activation under different conditions. The outcome of these reactions between P_4 and the metal moiety was hardly predictable generally resulting in fragmentation of the P_4 molecule with formation of metal compounds containing P_3 ligands, like the Sacconi's cyclotriphosphorus compounds $[(\text{triphos})M(\eta^3\text{-}P_3)]^{n+}$ (**2**) [$n = 0$, M = Co, Rh, Ir; $n = 1$, M = Ni, Pd, Pt; triphos = $MeC(CH_2PPh_2)_3$],[11] P_2 ligands, such as those found in the Scherer's polyrhenium species $[\{Cp^*Re(CO)_2\}_2(\mu,\eta^{2:2}\text{-}P_2)]$ (**3**)[12] and $[\{Cp^*Re(CO)_2\}_4(\mu,\eta^{1:1:1:1}\text{-}P_2)]$ (**4**)[13] or even terminal, bridging or encapsulated monophosphido ligands having coordination numbers ranging from one to ten.[7,8,14]

Whereas the degradation of P_4 into P_1, P_2 and P_3 ligands is, to a certain extent, an expected pathway in coordination chemistry and ligand reactivity,[15] alternative processes leading to aggregation to P_x units, which take place when white phosphorus is reacted with a metal fragment under harsh reaction conditions, were more surprising and largely unexpected. Polyphosphorus ligands with spectacular P_x topologies having up to twelve atoms, as in the trimetallic cluster $[\{Cp^{\#}Co(CO)\}_3(P_{12})]$ (**5**, $Cp^{\#} = 1,2,4\text{-}Bu^t_3C_5H_2$),[16] have been observed in mononuclear and polynuclear metal complexes. Generally, these species form as low-yield by-products through complicated and frequently unknown mechanisms. Examples of such kinds of compounds are the Scherer's complexes with cyclopentaphosphadienyl moiety, $[Cp^*Fe(\eta^5\text{-}P_5)]$ (**6**),[17] and hexaphosphabenzene, $[\{Cp^*Mo\}_2(\mu,\eta\text{-}^{6:6}\text{-}P_6)]$ (**7**),[18] which expand the P ↔ CH isolobal relationship to pseudoaromatic P_x rings. Another remarkable example is the carbon-free decaphosphatitanocene dianion $[Ti(P_5)_2]^{2-}$ (**8**) which has been isolated using bulky cations and is thermally robust and highly inert toward oxygen.[19] Impressive self-aggregation of polyphosphorus complexes forming giant cluster molecules have also been reported recently by Scheer *et al.* who described the inorganic fullerene-like molecule $[\{Cp^*Fe(\eta^{5:1:1:1:1:1}\text{-}P_5)\}_{12}\text{-}\{CuCl\}_{10}\{Cu_2Cl_3\}_5\{Cu(CH_3CN)_2\}_5]$ which incorporates 60 phosphorus atoms from 12 cyclo-P_5 ligands in the spherical molecule.[20]

3 Is white phosphorus a good ligand?

Four different topologies of the tetraphosphorus ligand may be envisaged in transition metal complexes depending on the increasing denticity of the P_4 assembly, that exhibit all the coordination modes from η^1- to η^4-P_4 (Chart 2). Several examples of complexes bearing a η^1- or η^2-P_4 ligand are known (I and II, respectively) and a pair of η^4-tetraphosphorus ligands (IV) have also been described, but no η^3-coordinated P_4 species (III) has been reported as yet.

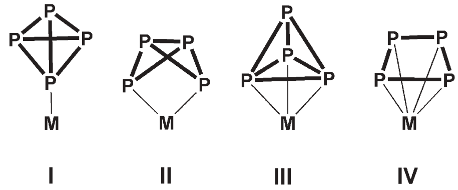
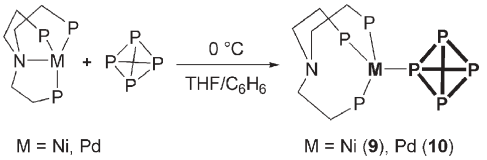


Chart 2



Scheme 2

Compounds with monohapto tetraphosphorus ligands are generally considered rare although this belief is somewhat unjustified. The first complexes of this type were described in 1979 by Sacconi and coworkers who prepared the nickel derivative $[\{N(CH_2CH_2PPh_2)_3\}Ni(\eta^1\text{-}P_4)]$ (**9**) by reacting white phosphorus in THF/benzene with the coordinatively unsaturated trigonal pyramidal complex $[\{N(CH_2CH_2PPh_2)_3\}Ni]$.[21] The related palladium compound $[\{N(CH_2CH_2PPh_2)_3\}Pd(\eta^1\text{-}P_4)]$ (**10**) was then obtained *via* a similar reaction.[22] Both compounds are moderately air sensitive and practically insoluble in all the common organic solvents (Scheme 2).

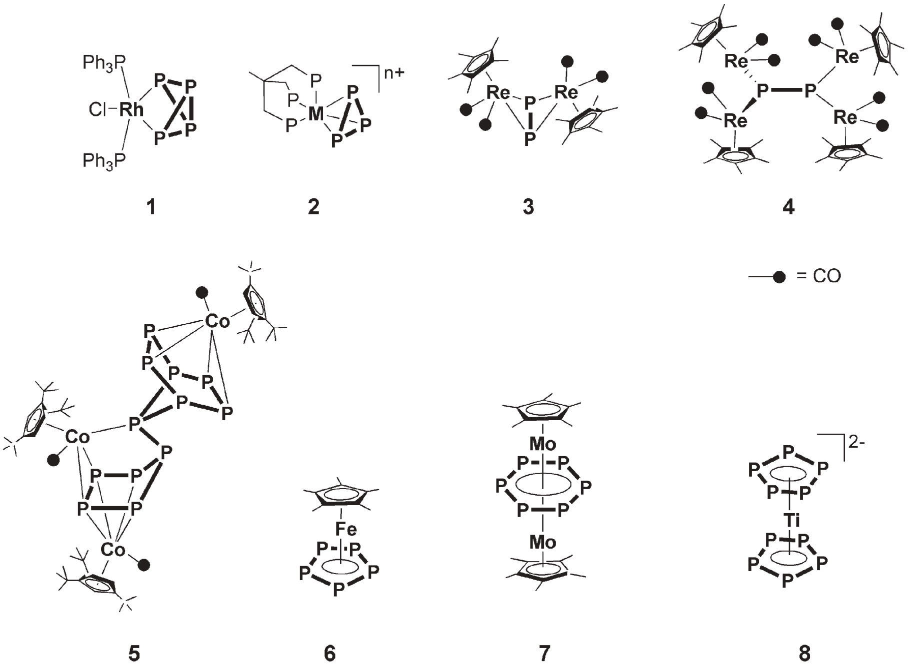
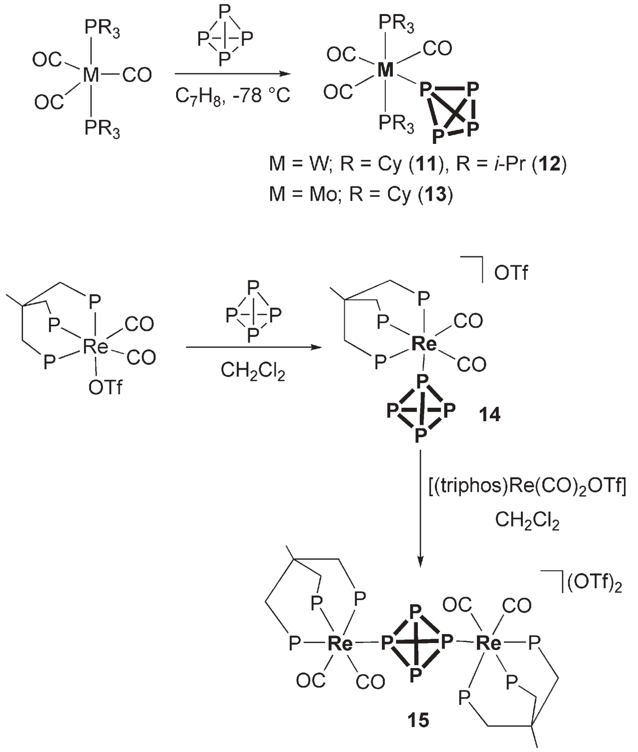


Chart 1

The structure of the nickel complex was determined by X-ray methods showing η^1-*P*-coordination with only modest deformations of the coordinated ligand in comparison to the free P_4 molecule. For many years the two Sacconi's derivatives remained the only known tetraphosphorus complexes giving the false belief that P_4 complexes were generally unstable, and hence difficult to synthesize or even to observe.[8a] In compounds **9** and **10** the unique shielding effect provided by the six phenyl rings wrapping around the metal–tetraphosphorus moiety was considered responsible for the stability of these compounds in the solid state.

In contrast to this popular misconception, the reaction of white phosphorus with transition metal fragments is much more controllable than was originally thought and, after reacting with a transition-metal system, the P_4 tetrahedron does not undergo the usually unpredictable activation and degradation processes that marked the first studies of P_4-coordination chemistry and which have been described in the previous section.[7,8]

Indeed, under mild reaction conditions white phosphorus may easily interact with metal centres, generating complexes in which the P_4-ligand behaves as a two-electron donor similarly to phosphines. Transition metal derivatives properly designed to interact with P_4 hold an easily accessible coordination vacancy made available either by displacement of an agostic interaction or by removal of a weakly coordinated ligand. Examples of both pathways are reported in Scheme 3 and refer to two different complexes synthesized by us and others recently. Thus, while Scheer and coworkers reported a small set of thermally sensitive molybdenum and tungsten compounds of formula $[M(CO)_3(PR_3)_2(\eta^1\text{-}P_4)]$ [M = W, R = Cy (**11**), *i*-Pr (**12**); M = Mo, R = Cy (**13**)] and verified by X-ray crystallography to be the η^1-P_4 tungsten derivative $[W(CO)_3(PCy_3)_2(\eta^1\text{-}P_4)]$ (**11**),[23] some of us described the rhenium complex $[(\text{triphos})Re(CO)_2(\eta^1\text{-}P_4)]OTf$ (**14**), which was the first P_4-complex stable enough to be isolated in the solid state at room temperature.[24] In both cases, the easy displacement of a weakly coordinated ligand by P_4 was an essential requirement for coordination. Remarkably, the rhenium–tetraphosphorus complex was able to bind a second metal fragment forming dinuclear species in which a $\eta^{1:1}$-P_4 ligand is bridging two metal–ligand moieties. For example, treatment of **14** with a second equivalent of $[(\text{triphos})Re(CO)_2OTf]$ afforded the dinuclear complex $[\{(\text{triphos})Re(CO)_2\}_2(\mu,\eta^{1:1}\text{-}P_4)](OTf)_2$ (**15**).



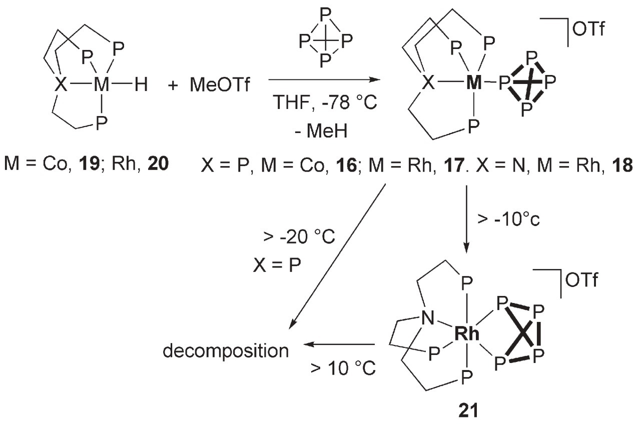
Scheme 3

An unstable dinuclear ruthenium(II) complex was obtained from the reaction of P_4 and $RuCl_2(PPh_3)_3$ in toluene at low temperature.[25] Trigonal bipyramidal cobalt[26] and rhodium[26] η^1-P_4-complexes stabilized by tetrapodal tetradentate ligands, namely $[\{P(CH_2CH_2PPh_2)_3\}M(\eta^1\text{-}P_4)]OTf$ [M = Co, **16**; Rh, **17**] and $[\{N(CH_2CH_2PPh_2)_3\}Rh(\eta^1\text{-}P_4)]OTf$ (**18**), were reported for the reaction of the monohydrides $[\{P(CH_2CH_2PPh_2)_3\}MH]$ [M = Co, **19**; Rh, **20**] and $[\{N(CH_2CH_2PPh_2)_3\}RhH]$ (**21**) with MeOTf in THF at −78 °C in the presence of white phosphorus (Scheme 4).

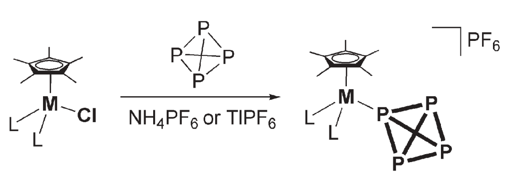
As for most of the white phosphorus complexes, also **16** and **17** are thermally unstable and quickly decompose when heated above −20 °C, in contrast to the rhodium(I) complex **18** which is stable up to *ca.* −10 °C, above which it undergoes an intramolecular rearrangement resulting in the oxidative addition of the P_4 ligand, that switches from η^1- to η^2-coordination to yield the rhodium(III) complex $[\{N(CH_2CH_2PPh_2)_3\}Rh(\eta^2\text{-}P_4)]OTf$ (**22**). The latter decomposes at about 10 °C.

We then prepared a family of amazingly stable pentamethylcyclopentadienyl derivatives of formula $[Cp^*M(L_2)(\eta^1\text{-}P_4)]Y$ (M = Fe, Ru; L = PR_3 or ½ diphosphine; Y = BPh_4, PF_6, BAr'_4) (Scheme 5).[27] Remarkably, the white phosphorus ligand in these Cp* complexes is stable to both hydrolysis and oxidation, and the products can be stored without apparent decomposition in the air and react neither with oxygen nor with organic peroxides in solution.

The structures of the iron and ruthenium complexes $[Cp^*M(dppe)(\eta^1\text{-}P_4)]BPh_4$ (M = Fe (**23**), Ru (**24**);



Scheme 4



M = Fe, Ru; L = PR_3, 1/2 dppe

Scheme 5

dppe = $Ph_2PCH_2CH_2PPh_2$) were determined by X-ray crystallography[27,28] and the crystal structure of the Fe derivative is shown in Fig. 1. This reveals that the P_4 tetrahedron is only slightly distorted with respect to the free molecule and that the amazing stability of the tetraphosphorus ligand does not depend on the steric shielding of the coordinated P_4 molecule, since three of four P atoms are not surrounded by the four phenyls of the ancillary diphosphine.

A survey of the metrical parameters exhibited by the known structural types containing η^x-P_4 ligands (x = 1, 2, 4) is available in the literature.[29]

Similar ruthenium derivatives, $[CpRu(L_2)(\eta^1\text{-}P_4)]PF_6$ [L = PPh_3, (**25**); ½ dppe, (**26**)], containing the less basic and less sterically demanding cyclopentadienyl ligand, have been recently synthesized and characterized by spectroscopic and crystallographic methods.[30] In contrast with the Cp* homologues, the Cp derivatives **25** and **26** show a surprising reactivity with nucleophiles as briefly mentioned below. The reaction with a second equivalent of $[CpRu(PPh_3)_2Cl]$ allowed us to exploit further the coordination abilities of **25** forming in quantitative yield the diruthenated-tetraphosphorus complex $[\{CpRu(PPh_3)_2\}_2(\mu,\eta^{1:1}\text{-}P_4)\}](PF_6)_2$ (**27**) whose bimetallic nature with only a slightly deformed P_4-ligand was validated by X-ray crystallography.[31]

In contrast with the η^1-adducts [23–26], the homoleptic bis(tetraphosphorus) silver complex, $[Ag(\eta^2\text{-}P_4)_2][Al\{OC(CF_3)_3\}_4]$ (**28**), which has been recently reported by Krossing *et al.*, is quite unstable and spontaneously ignites when exposed to air.[32] *Ab initio* calculations, supported by crystallographic data, showed that **28** is a true silver(I) species containing two unactivated side–on η^2-P_4 ligands ($d_{P\text{–}P(ave)}$ = 2.329 Å; see Fig. 2).[33]

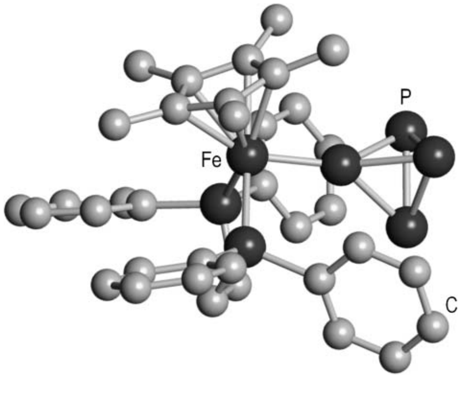


Fig. 1 Crystal structure of the complex cation in $[Cp^*Fe(dppe)(\eta^1\text{-}P_4)]BPh_4$ (**23**). Adapted from reference 27.

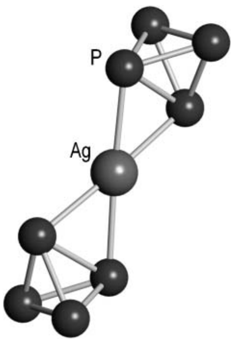


Fig. 2 Crystal structure of the complex cation in $[Ag(\eta^2\text{-}P_4)_2][Al\{OC(CF_3)_3\}_4]$ (**28**). Adapted from reference 32a.

The bonding and structure shown by the Krossing's silver salt are unprecedented with respect to the many other known η^2-P_4 complexes in which a metal-mediated P–P bond activation is usually attained.

These types of compounds contain the tetraphosphacyclobutadienyl P_4^{2-} dianion and show very different stability depending on the metal and coligands.[6,34,35] A few examples of this class of compounds are provided in Scheme 6 which include simple η^2-P_4 derivatives, such as $[(1,3\text{-}Bu^t_2Cp)M(\eta^2\text{-}P_4)]$ [M = Zr, (**29**); Hf (**30**)][34a] and multinuclear complexes with $\eta^{2:1}$- and $\eta^{2:1:1}$-bonding modes, like $[\{Cp^\#Cu\}_2(\eta^{2:1}\text{-}P_4]$ (Cp = $C_5MePr^i_4$; **31**)[34e] and $[(PPh_3)_2Pt(\eta^{2:1:1}\text{-}P_4)\{Cr(CO)_5\}_2]$ (**32**).[34d] Double metallation of the P_4 tetrahedron has also been reported for the dicobalt $[\{Cp^*Co(CO)_2\}_2(\mu,\eta^{2:2}\text{-}P_4)]$[36] (**33**) and, most recently, for the dialuminium $[\{HC(CMeNAr)_2\}_2\text{-}(\mu,\eta^{2:2}\text{-}P_4)]$[37] (**34**; Ar = 2,6-$i$$Pr_2C_6H_3$) derivatives (Scheme 6).

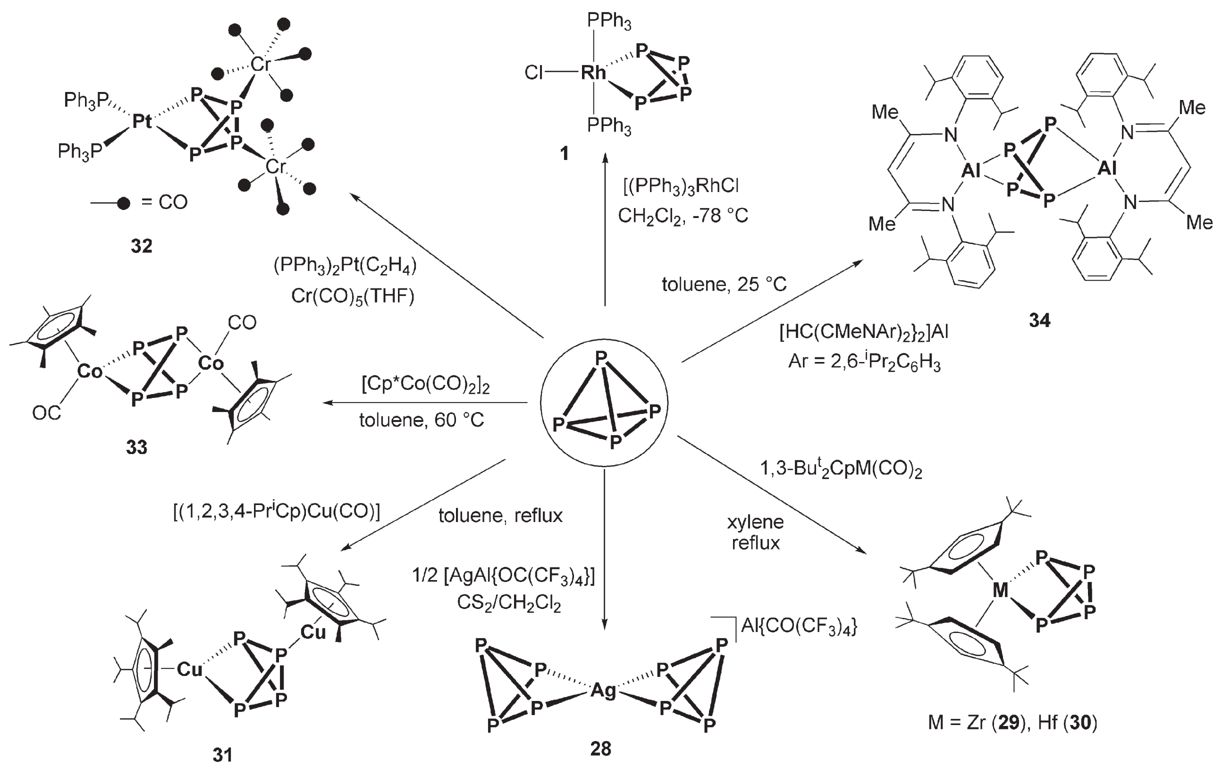
Whilst complexes with η^3-coordinated P_4 ligands have never been reported,[38] complexes $[Cp^*Nb(CO)_2(\eta^4\text{-}P_4)]$ (**35**) and $[(1,3\text{-}Bu^t_2Cp)Ta(CO)_2(\eta^4\text{-}P_4)]$ (**36**) containing a planar *cyclo*-P_4 ligand, have been synthesised by Scherer *via* photolysis of niobium[39] and tantalum[40] precursors with white phosphorus (Scheme 7).

4 Metal-mediated P_4 functionalization

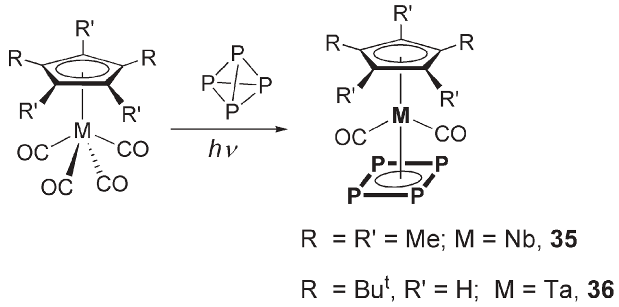
The synthesis of organophosphorus compounds directly from elemental phosphorus is a challenging process for chemists and chemical industries. In spite of this, the metal-mediated functionalization of white phosphorus resulting in the formation of P–C and/or P–H bonds is an uncommon reaction which usually involves reacting white phosphorus with electron-poor metals in the presence of organic substrates.[9,10,41]

The only example of P–C bond formation originating from the direct transfer of an organic group from an organotransition metal derivative to a metal-activated tetraphosphorus molecule, has been recently obtained by us and is shown in Scheme 8.

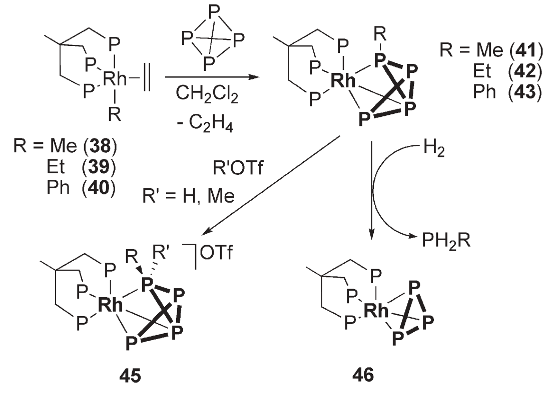
Ethylene labilization in the alkyl and aryl rhodium complexes $[(triphos)RhR(\eta^2\text{-}C_2H_4)]$ [R = H, (**37**); Me, (**38**); Et, (**39**); Ph, (**40**)], stabilised by the tripodal triphosphine *triphos*, reacts quickly with white phosphorus under extremely mild conditions (THF, −20 °C). The reaction affords the unprecedented rhodium(III) complexes $[(triphos)Rh(\eta^{2:1}\text{-}P_4R)]$ [R = Me, (**41**); Et, (**42**); Ph, (**43**)] where an alkyl or aryl



Scheme 6



Scheme 7



Scheme 8

tetraphosphido unit is coordinated to the metal as a six-electron donor.[42] The reaction with the hydrido-ethylene species **37** does not give the expected [(triphos)Rh($\eta^{2:1}$-P_4H)] (**44**), but results in the ethylphosphido derivative **42** *via* a remarkable double insertion process encompassing insertion of the ethylene ligand in the Rh–H bond followed by a migratory step transferring the ethyl ligand to the activated P_4 unit. In a separate experiment, pressurizing a THF solution of **37** with ethylene does not afford **42**, thus confirming the double insertion process. These organo-tetraphosphido derivatives are stable and can be isolated in the solid state, but are highly reactive towards electrophilic reagents and other simple molecules.[42b] The X-ray crystal structure of the doubly alkylated [(triphos)Rh($\eta^{2:1}$-P_4(Ph)Me]OTf (**45**) has been determined and a view of the cation is shown in Fig. 3.

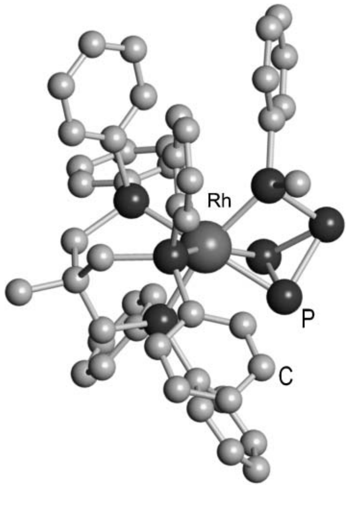


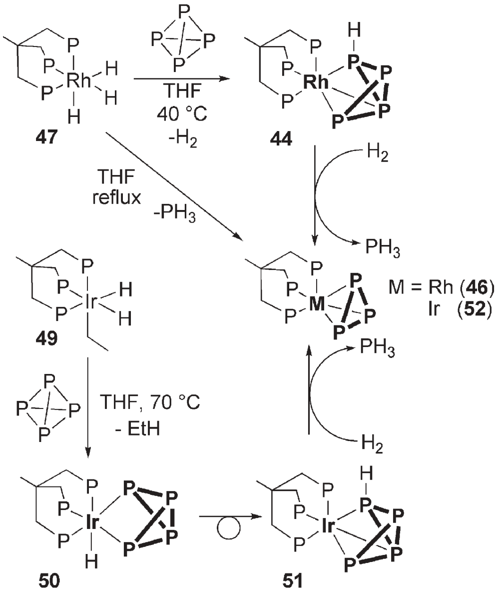
Fig. 3 Crystal structure of the complex cation in [(triphos)Rh($\eta^{2:1}$-P_4(Ph)Me]OTf (**39**). Adapted from reference 42b.

Of particular relevance is the reaction with hydrogen giving alkyl or arylphosphines PH_2R in moderate yields. The functionalization reaction involves one phosphorus atom while the three remaining P atoms are efficiently scavenged by the metal–triphos moiety to form the robust cyclo-P_3 complex [(triphos)Rh(η^3-P_3)] (**46**).

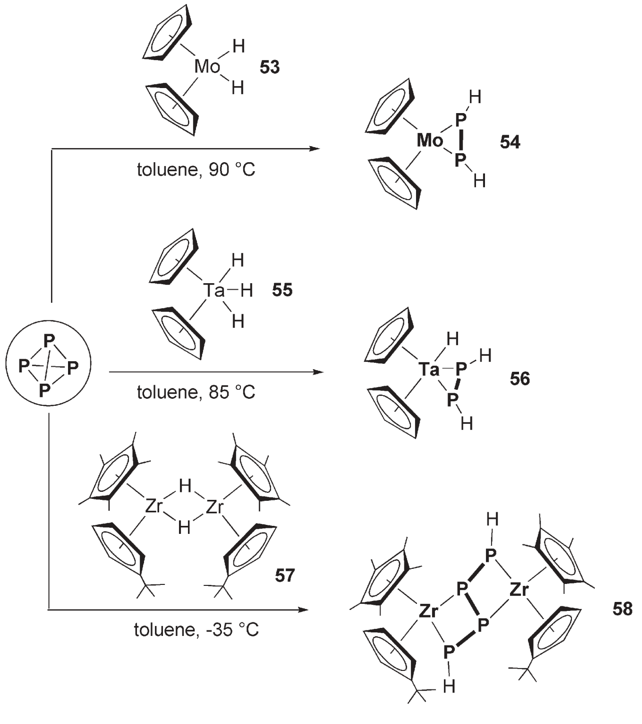
A similar behaviour is shown by [(triphos)RhH_3] (**47**) in the thermal reaction with P_4, which selectively gives the complex [(triphos)Rh($\eta^{1:2}$-P_4H)] (**44**).[35] This latter reacts with H_2 at atmospheric pressure yielding **46** and PH_3 in high yield. When the reaction between **47** and phosphorus was carried out in a closed system such as a sealed NMR tube, it afforded quantitatively PH_3 and the cyclo-triphosphorus complex **46** (Scheme 9).

The mechanism of these intriguing functionalization reactions has been investigated in depth by studying the behaviour of the kinetically more stable iridium complexes, [(triphos)IrH_3] (**48**) and [(triphos)IrH_2(Et)] (**49**). In particular, the dihydride–ethyl derivative releases ethane rather than H_2 when heated in THF at 70 °C, providing a simple way to the coordinatively unsaturated fragment [(triphos)IrH]. Thus, reaction of **49** with elemental phosphorus in refluxing THF allowed for the isolation of the hydrido-tetraphosphido species [(triphos)Ir(H)(η^2-P_4)] (**50**), which slowly isomerizes to [(triphos)Ir($\eta^{1:2}$-P_4H)] (**51**) by transfer of the metal bonded hydride to one of the metallated phosphorus atom of the P_4^{2-} ligand (Scheme 9). Addition of H_2 to **51** completes the reaction affording PH_3 and [(triphos)Ir(η^3-P_3)] (**52**).[35]

While the reaction highlighted in Scheme 8 represents the first clear account of the metal-mediated formation of P–C bonds, a few more examples dealing with the related hydrogenation of white phosphorus have been described, apart from the reaction of P_4 with [(triphos)MH_3]. In any case, these reactions involve metallocene dihydrides as precursors (Scheme 10).[9]



Scheme 9

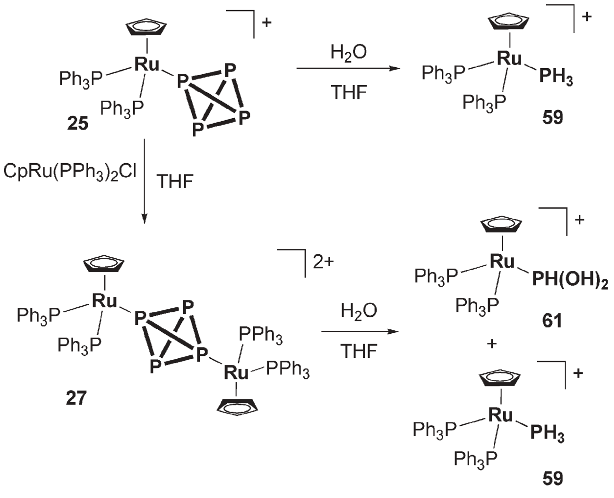


Scheme 10

Thus, the reaction of [Cp_2MoH_2] (**53**) with P_4 in toluene resulted in the formation of the diphosphene complex [Cp_2Mo(η^2-P_2H_2)] (**54**).[43] The related reaction of the tantalum trihydride [Cp_2TaH_3] (**55**) was studied by Stephan and coworkers, and provided a further example of a similar P_4 fragmentation/hydrogenation process yielding the hydrido-diphosphene [Cp_2Ta(H)(η^2-P_2H_2)] (**56**).[44] Both diphosphenes **54**[45] and **56**[44] were verified by X-ray methods which confirmed the presence of a transoid diphosphene unit coordinated to the metal originating from the partial hydrogenation of a degraded P_4 molecule. No mechanistic interpretation of these reactions has been provided.

In contrast to what was observed for **54**, [Cp^*_2Zr(η^2-P_2H_2)] was not obtained from the reaction of P_4 with [$Cp^*_2ZrH_2$], but instead gave [Cp^*_2Zr(η^2-P_4)] following the reductive elimination of H_2.[46] A completely different reaction took place by using a zirconium precursor with sterically more demanding cyclopentadienyl rings (**57**). Therefore, the dizirconium complex [{$Cp^*Cp'Zr$}$_2$($\mu,\eta^{2:2}$-P_4H_2)] (**58**; Cp′ = $Bu^tC_5H_4$) was obtained *via* a cooperative reductive elimination/insertion sequence involving the two metal centers. Noticeably, **58** is formed in toluene at −35 °C and does not decompose upon heating to 100 °C in benzene-d_6. The molecular structure of **58** contains a puckered $P_4H_2^{2-}$ dianion tethering two zirconocene units.

Phosphine (PH_3) is produced when the cyclopentadienyl ruthenium complexes [CpRu(L_2)(η^1-P_4)]PF_6 [L = PPh_3, (**25**); ½ dppe, (**26**)] are allowed to react with water (Scheme 11) yielding the highly stable PH_3 complexes [CpRu(L)$_2$(PH_3)]PF_6 [L = PPh_3, (**59**); ½ dppe, (**60**)].[30] Although the fate of the other three P-atoms deriving from the coordinated P_4 ligand in **25** or **26** has not been determined as yet, the formation of H_3PO_2 is likely accompanied by the hydrolysis of the η^1-P_4 complex because one equivalent of [CpRu(PPh_3)$_2${PH(OH)$_2$}]PF_6 (**61**) is formed together with



Scheme 11

59 when water is added to a solution of the dimetallated tetraphosphorus complex **27** in acetone.[47] As a whole, this astonishing hydrolysis, similar to the P_4-disproportionation occurring in a strong alkaline medium, sharply contrasts with the known inertness of white phosphorus in water and derives from the P_4 end-on coordination to ruthenium.

This result also shows that new and simple pathways for the functionalization of white phosphorus may be envisaged from a thorough exploration of the coordination chemistry of this ligand. Remarkably, the related Cp* derivatives does not react with H_2O even in refluxing THF or acetone solution indicating that the reactivity of these P_4 complexes may be finely tuned by a careful balance of the electronic and steric properties of the ancillary ligands. Although the process cannot be considered of industrial interest as only one phosphorus of the P_4 ligand is hydrogenated, the reaction clearly shows that the coordination chemistry of P_4 may open feasible ways to accomplish the so far elusive hydrogenation of the element.†

5 Towards the eco-efficient activation of P_4

The large amount of literature published so far on the reactivity of P_4 with transition metals should provide the fundamental understanding to attempt the catalytic functionalization of white phosphorus.

However, in spite of these achievements only modest steps have been made so far in accomplishing these goals, and a reliable process to bring about the direct catalytic phosphorylation of organic substrates using elemental phosphorus has not yet been found.

A few catalytic protocols for the preparation of oxyacids and esters of phosphorus may be found in the patent literature based on catalytic transformations of white phosphorus. Of relevance to the present review is a patent describing the palladium catalysed oxidation of white phosphorus with water which has been reported to yield a mixture of phosphorus oxyacids with good selectivity in the formation of P(III) derivatives.[48] However, the best catalytic process to carry out the chlorine-free oxidative alkoxylation of white phosphorus with organic substrates seems to be the one developed by Dorfman and co-workers[49] who described the mild catalytic chlorine-free oxidative alkoxylation of P_4 in arenes using CuX_2 or FeX_3 as catalyst and O_2 as a cheap oxidant. Depending on the reaction conditions, mixtures of alkyl phosphates and phosphites have been obtained by alcohol phosphorylation. The Dorfman's catalytic protocol is exciting from an environmental viewpoint as it removes both Cl_2 and HCl using dioxygen as efficient and ecobenign oxidant. On this basis, the process integrates in the catalytic synthesis of valuable organophosphorus compounds all the advantages typical of a homogeneous catalytic reactions with both P_4 and the catalyst dissolved in an arene/alcohol solution. The process has been successfully extended to phenols[50] and the oxidative P–S coupling of white phosphorus and thiols, affording esters of thiophosphorous and thiophosphoric acids, has been described.[51]

In spite of these brilliant perspectives, the Dorfman's process has not yet been exploited commercially due to poor cost effectiveness. Improvements in the removal of the aromatic solvent from the process and the recycling of the catalyst are necessary to render it appealing for chemical companies. Noticeably only simple metal ions have been used while no serious attempt has yet been made to use organometallic catalysts such as those described in the precedent sections of this review.

An alternative and very promising approach to catalyze the functionalization of P_4 in an eco-efficient way has been developed by Russian electrochemists who have published and patented several methods accounting for the electrosynthesis of a variety of organophosphorus compounds with P–C and P–E (E = O, S, N) bonds starting from white phosphorus under mild conditions. The products of the electrochemical functionalization depend on the nature of electrodes, electrolytes and substrates and involve the electrocatalytic activation of P_4 *via* oxidants produced anodically or reductants cathodically generated.[52] Remarkably and in contrast with the homogeneous processes described above, electrochemical methods may be applied not only to the synthesis of "oxygenated" organophosphorus compounds such as the esters and amides of phosphorus acids, but may bring about also the catalytic synthesis of low-valent phosphorus compounds, primarily phosphines. Tertiary phosphines have been indeed produced electrocatalytically from white phosphorus and organic halides.[52] The reaction is catalyzed by transition metal complexes such as $[Ni(bipy)]^0$ electrogenerated *in situ via* two-electron reduction of $[NiBr_2(bipy)]$ (bipy = 2,2′-bipirydine).[53] Organonickel compounds are indeed considered capable of oxidatively adding an RX molecule affording [NiR(X)(bipy)] which, in turn, may transfer the hydrocarbyl group to a molecule of P_4 once activated by the metal fragment. Altogether, the process results in the formation of P–C bonds well fitting the "green" catalytic protocol outlined in Scheme 1. Patents covering the electrocatalytic synthesis of tertiary phosphines from elemental phosphorus have been filed.[54]

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† The hydrogenation of N_2 has been known since 1913 and is applied to catalytically convert nitrogen into ammonia at massive industrial scale (Haber–Bosch process). In contrast, a similar process is unknown for phosphorus.[9]

Finally, before closing this section, it is worth mentioning the interesting photocatalytic procedure recently patented by some of us.[55] Solar irradiation of a suspension of white phosphorus in H_2O/THF in the presence of water soluble ruthenium complexes bearing *m*-monosulfonated triphenylphosphine, led to the catalytic formation of a mixture of H_3PO_4, H_3PO_3 and H_3PO_2. When alcohols were used instead of water the corresponding organophosphates were obtained, with light either from a commercially available incandescence bulb or by direct solar irradiation. The reactions were carried out at room temperature and atmospheric pressure of dioxygen.

Although many improvements are still necessary in terms of efficiency, recycling and safety to enhance the practical use of these processes for the manufacturing of organophosphorus compounds, the authors believe that the amount of knowledge gained on P_4-coordination and functionalization will be the foundations on which to build a green protocol for the controlled white phosphorus alkoxydation. It is indeed evident that the progress achieved in these fields[7–10] together with the astonishing development of the chemistry of low-valent phosphorus compounds[2] have the potential to foster further research which may lead to innovations in homogeneous catalysis and breakthroughs in the science of new materials.[20,56]

6 Conclusions

The results highlighted in this *tutorial review* clearly show that the molecule of white phosphorus exhibits rich and intriguing coordination abilities with both transition and main group metals. In summary, the tetrahedral molecule may behave as a terminal 2-e ligand towards a variety of different metal systems with only minor geometrical deformations or may coordinate as a side-on ligand to a metal cation, as in the silver complex **28**. Alternatively, the white phosphorus ligand may undergo a metal-promoted activation, formally resulting in single, double or triple P–P bond cleavage with stabilization of butterfly (P_4^{2-}), *zig-zag* (P_4^{4-}) and planar cyclic (P_4^{6-}) tetraphosphorus units, respectively (Chart 2). Less predictable are the disruptive pathways ending with multifaceted disaggregating and aggregating products derived from the four P-atoms under harsh reaction conditions. The first examples of eco-efficient catalytic, electrochemical or photo-induced activation of P_4 towards high value added products are presented.

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