

Early-Transition-Metal-Mediated Activation and Transformation of White Phosphorus

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Brandi Cossairt is a graduate student in the Cummins research group at MIT. She has been studying the activation of white phosphorus by niobium complexes. Her studies have demonstrated P₄ reductive coupling by niobium enolate compounds and subsequent synthesis of phosphorus-rich organic molecules. Moving from enolate to aryloxy supporting ligands, Brandi discovered an efficient cyclo-P₃ complex synthesis. The so-obtained anionic niobium cyclo-P₃ complex is effective as a P₃³⁻ transfer agent, leading in turn to the synthesis and isolation of AsP₃ as a pure substance. Brandi was an undergraduate at Caltech, where she coauthored papers in both physical and inorganic chemistry. Brandi grew up in Miami, FL.



Nicholas Piro received his Ph.D. degree from MIT in June 2009. As a graduate student in the Cummins group he studied the transformations of P₄-derived phosphorus ligands atop a niobium trisanilide platform. His research included the development of a solution-phase source of a diatomic P₂ synthon that he later used in the synthesis of more phosphorus-rich coordination complexes, including cyclo-P₃ complexes and σ -complexed tetraphosphabenzenes. Prior to arriving at MIT, Nick was an undergraduate at Caltech, where he studied the group 10 chemistry of iso-bipyridyl and related ligands under the tutelage of Professor John Bercaw. Nick is currently a Miller Research Fellow at UC Berkeley.

1. Introduction

Phosphorus-containing molecules are ubiquitous in the world around us, and the synthetic and industrial utilization of phosphorus has prospered for over a century.^{1,2} The industrial reduction of phosphate rock (apatite, Ca₁₀(PO₄)₆(X)₂, X = OH, F, Cl, or Br) to white phosphorus, P₄, exceeds 500 000 tons annually as P₄ still represents the major commercial P-atom source for the production of organophosphorus compounds utilized by the food, detergent, specialty chemical, and pharmaceutical industries.³ The present-day synthesis of organophosphorus compounds is a multistep process in which P₄ is first chlorinated to generate PCl₃, which in turn is functionalized by reaction with an appropriate Grignard or organolithium reagent or by treatment with a halogenated organic compound and a powerful reducing agent.^{4,5} For example, the industrial method for triphenylphosphine preparation is based on the high-temperature reaction of chlorobenzene with phosphorus trichloride in the presence of molten sodium.^{4,6} From both a safety and a sustainability standpoint, the need for PCl₃ as an intermediate for the production of organophosphorus com-

pounds is unpalatable and methods that circumvent its use are of great interest. This has provoked intensive investiga-

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Christopher C. Cummins, aka "Kit", elucidated C–H bond activation and other chemistry of low-coordinate titanium and zirconium imido complexes while an undergraduate student in the laboratory of Professor Peter T. Wolczanski at Cornell University. Also while at Cornell, Kit was inspired by the theoretical chemistry teachings of Roald Hoffmann. For his Ph.D. studies, Kit joined the laboratory of Professor Richard R. Schrock at the Massachusetts Institute of Technology, where he divided his research between synthesizing semiconductor nanoparticles within block-copolymer microdomains and initiating a project on the transition-element coordination chemistry of triamidoamine ligands. Upon beginning his career as an independent investigator and faculty member, also in the MIT Department of Chemistry, Kit launched a program of research aimed at small-molecule activation, inorganic functional group synthesis, and group transfer reactions. Signature discoveries that have issued from this program include complete six-electron reductive cleavage of N_2 by three-coordinate molybdenum(III) complexes, selective cleavage of the nitrous oxide N–N bond, terminal phosphide $M\equiv P$ triple bond synthesis via P_4 activation, establishment of the terminal carbide functional group, structure and reactivity of a terminal PO complex, creation of a synthon for solution reactivity of the P_2 molecule, and the synthesis and isolation of AsP_3 as a pure substance. Ongoing research projects in Kit's laboratory are in the areas of group 15 element chemistry as mediated by early transition metals, uranium-element multiple bonding, carbon dioxide reduction, and ligand architectures for the molecular chemistry of renewable energy. For more information please visit <http://web.mit.edu/ccclab>.

tions into the mild and controlled activation of P_4 , a clear objective being the development of catalytic methods for phosphorus incorporation into organic molecules.

Sustained interest in the chemistry of low-valent, early-transition-metal (ETM) complexes arises from their propensity to reductively activate a wide variety of small molecule substrates.⁷ A combination of coordinative unsaturation, inherent Lewis acidity, and availability of chemically accessible d electrons endows low-valent, ETM fragments with a rich reaction chemistry. The ability to apply the reductive power of such reactive metal systems is therefore of great interest for applications ranging from organic catalysis to dinitrogen fixation, and it comes as no surprise that low-valent, ETM complexes have received considerable attention as agents for P_4 activation. The use of ETM complexes to study P_4 activation and functionalization is motivated by the wide array of P-containing ligands that can be obtained. P_1 – P_8 ligands have been isolated and studied from P_4 activation reactions of ETM complexes, and many of these metal–phosphorus systems have proven to be themselves reactive due to the hard–soft mismatch of ETM–phosphorus bonds. This bonding mismatch provides an underlying thermodynamic driving force by which assembled phosphorus ligands can be liberated from the metal center by exchange with preferred hard, anionic ligands, such as O^{2-} and X^- ($X = Cl, Br, I$).

The aim of this review is to highlight the wide array of results reported in the literature in the field of P_4 activation

and transformation with a particular emphasis on the special attributes of ETM utilization in such processes. For the purposes of this work we define "ETM" as any member of groups 3–7, and lanthanide and actinide metals are also included for comparison purposes. Sections 2–4 provide a general overview of the P_4 activation chemistry of this group of elements organized in terms of the phosphorus products that result. Section 5 details the strategies by which ETM chemists have gone about transforming white phosphorus in the coordination sphere of a metal en route to the synthesis of main-group phosphorus-containing molecules.

2. P_4 Activation Leading to P_1 , P_2 , and P_3 Products

ETM-mediated degradation of the white phosphorus tetrahedron to small P_n units has been observed frequently, and a variety of the possible P_4 degradation products have been characterized. Typical products include those incorporating a terminal or bridging phosphide (P^{3-}) ligand, bridging diphosphide ligand (P_2^{4-}), and cyclo- P_3 moieties serving as either terminal P_3^{3-} ligands or a $\mu_2:\eta^3,\eta^3$ bridge between two metal centers. Few mechanistic studies have been explicitly carried out on these P_4 degradation reactions; mechanistic proposals have been put forward in various cases,^{8,9} but these are not included in the coverage of the present review. The focus herein is on synthetic, structural, and spectroscopic details.

2.1. Terminal and Bridging P_1 Ligands from P_4

There are few examples of monophosphorus ligands derived directly from activation of P_4 that have been reported, and all of them involve group 6 metal complexes (Figure 1). The first terminal phosphide complex to be obtained from transition-metal activation of P_4 was $P\equiv Mo(N[^tBu]Ar)_3$ (**1**; $Ar = 3,5-C_6H_3Me_2$).¹⁰ Prior to this report and a concurrent report by Schrock and co-workers on the synthesis of $P\equiv Mo(Me_3SiNCH_2CH_2)_3N$ and $P\equiv W(Me_3SiNCH_2CH_2)_3N$ from reaction of the precursor chloro complexes and $Li[P-(H)Ph]$,¹¹ the $M\equiv P$ functional group was virtually unknown.^{12,13}

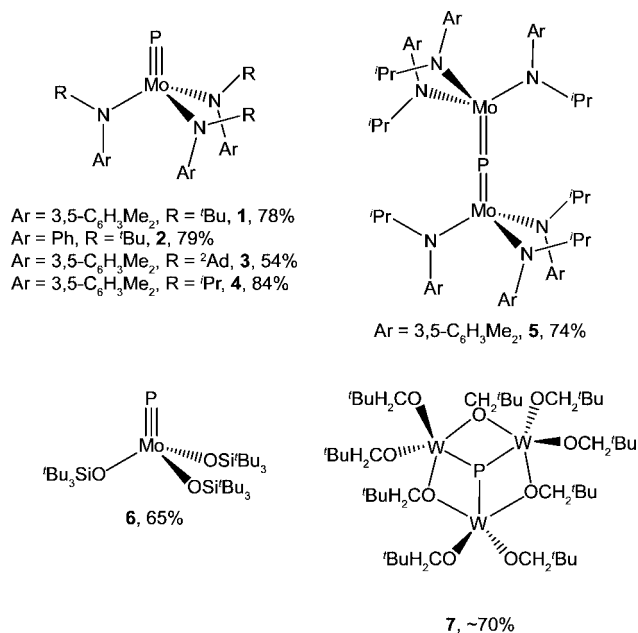


Figure 1. Monophosphide ligands derived from P_4 activation; yields given where available.

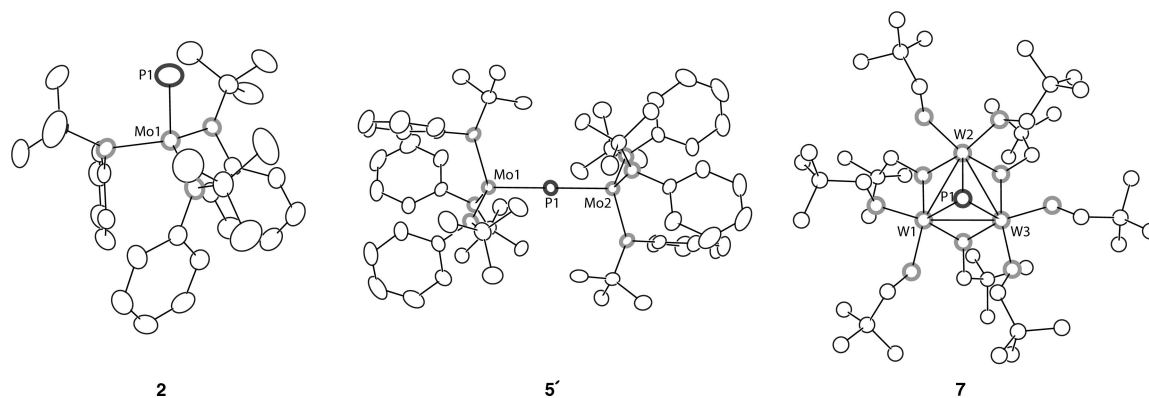


Figure 2. Structural diversity in monophosphorus ligands derived from P_4 activation.

Compound **1** was synthesized by Cummins and co-workers by treatment of three-coordinate $Mo(N[{}^iBu]Ar)_3$ with 0.35 equiv of P_4 at 25 °C in diethyl ether.^{14,15} Analogous terminal phosphide complexes, $P\equiv Mo(N[{}^iBu]Ph)_3$, **2**, and $P\equiv Mo(N[{}^iAd]Ar)_3$, **3**, obtained from reaction of white phosphorus with $Mo(N[{}^iBu]Ph)_3$ and $Mo(N[{}^iAd]Ar)_3$, respectively, have also been reported.¹⁶ Interestingly, reaction of $Mo(H)(\eta^2-Me_2C=NAr)(N[{}^iPr]Ar)_2$, a tautomer of $Mo(N[{}^iPr]Ar)_3$, with P_4 does not directly give the terminal $P\equiv Mo(N[{}^iPr]Ar)_3$, **4**, but instead, the bridging $(Ar[{}^iPr]N)_3Mo=P=Mo(N[{}^iPr]Ar)_3$, **5**, is obtained. This bimetallic complex is likely a result of quenching a transiently formed terminal phosphide complex with an additional equivalent of $Mo(H)(\eta^2-Me_2C=NAr)(N[{}^iPr]Ar)_2$.¹⁶ Complex **4**, however, can be revealed by a reduction of **5** to give the intact bimetallic complex monoanion followed by treatment with an equivalent of CO and 12-crown-4 with loss of the carbonyl anion salt $[Na(12-crown-4)]_2[(OC)Mo(N[{}^iPr]Ar)_3]$.¹⁶ Outside of the tris-anilide family of complexes, one other example of terminal phosphide formation from P_4 has been reported, and it too stems from a reactive three-coordinate molybdenum complex. Treatment of $Mo(OSi{}^iBu_3)_3$ with 0.35 equiv of P_4 at 23 °C in diethyl ether results in clean formation of $P\equiv Mo(OSi{}^iBu_3)_3$, **6**.¹⁷ Complexes **1**, **2**, **3**, **4**, and **6** each display a ^{31}P NMR resonance downfield of 1200 ppm. These signature low-field shifts are the result of a strong contribution from the paramagnetic shielding term, the origin of which is electronic circulations arising from field-induced mixing of the $M-P$ σ -bonding orbital with the $M-P$ π^* orbital.¹⁸ Structurally characterized molybdenum terminal phosphide complexes display very short $Mo\equiv P$ interatomic distances, averaging 2.11 Å, in accord with the interpretation that they incorporate a triple-bond functional group (triple-bond covalent radius for Mo is 1.13 Å and for P is 0.94 Å).¹⁹

In a reaction related to P_4 activation by three-coordinate molybdenum, the dimethylamine adduct of the tungsten dimer $W_2(OCH_2{}^iBu)_6$ was treated with P_4 in toluene at 75 °C with the stated goal of preparing the $W\equiv P$ functional group. Obtained instead was the complex $(\eta^3-P_3)W(OCH_2{}^iBu)_3(HNMe_2)$ (vide infra) together with the trimetallic monophosphide complex $W_3(\mu_3-P)(\mu-OCH_2{}^iBu)_3(OCH_2{}^iBu)_6$, **7**.^{20,21} It was postulated that **7** was formed by trapping of a sterically unprotected and highly reactive $P\equiv W(OCH_2{}^iBu)_3$ intermediate by an equivalent of the starting material $W_2(OCH_2{}^iBu)_6$.²¹ The phosphide resonance in **7** differs markedly from those of the terminal molybdenum phosphide species, consisting of a singlet at 275 ppm flanked by tungsten satellites. In the single-crystal X-ray structure of **7**, each tungsten atom resides in a square-pyramidal

coordination geometry with the $W-P$ bond occupying the axial site ($W-P = 2.365(4)$ Å). The average $W-W$ distance is 2.757(1) Å, and the angles within the distorted W_3P tetrahedron are $W-W-W = 60^\circ$, $W-P-W = 71.3(1)^\circ$, and $P-W-W = 54.3(1)^\circ$ (Figure 2).²¹

The observation of both bridging and terminal monophosphide ligands from P_4 activation by ETM complexes highlights the importance of steric factors in moderating the reactivity of such metal fragments toward P_4 and emphasizes the integral role of the ancillary ligands in P_4 activation chemistry. A thorough review of metal terminal phosphides originating from P_4 and from other P-containing substrates has been provided by Scheer and co-workers.^{12,13}

2.2. Bridging P_2 Ligands from P_4

The symmetrical degradation of the P_4 tetrahedron to P_2 units often results in diphosphorus ligands bridging two metal centers in a $\mu_2:\eta^2,\eta^2$ coordination mode (Figure 3). Many of the reports involving P_2 ligands have been documented by Scherer and co-workers. The first diphosphorus-containing metal complex was isolated and characterized in Scherer's laboratories in 1984. Treatment of the molybdenum dimer $[MoCp(CO)_2]_2$ with P_4 in toluene at 110 °C for 8 h gives a mixture of $(\eta^3-P_3)Mo(CO)_2Cp$ (vide infra) and $Mo_2(CO)_4Cp_2(\mu_2:\eta^2,\eta^2-P_2)$, **8**.²² This chemistry was found also to be available with substituted cyclopentadienyl complexes of Mo, including those containing Cp^* .^{23,24} Compound **8** exhibits a side-on-bound P_2 unit with a $P-P$ interatomic distance of 2.079(2) Å and a short $Mo-Mo$ distance of 3.022(1) Å. It is noteworthy that a common feature of bridging diphosphorus ligands is an incomplete reduction of the $P-P$ multiple-bonding character (relative to the free P_2 molecule) as signified by $P-P$ interatomic distances significantly shorter than those for a typical $P-P$ single bond, for which an appropriate example is the 2.21 Å $P-P$ interatomic distance in P_4 .²⁵ This type of transformation was extended to chromium by Goh and co-workers, who discovered that treatment of the chromium dimer $[CrCp(CO)_3]_2$ with P_4 for 3.5 h at 90 °C in toluene results in a mixture of $(\eta^3-P_3)Cr(CO)_2Cp$ (vide infra) and $Cr_2(CO)_4Cp_2(\mu_2:\eta^2,\eta^2-P_2)$, **9**.²⁶ Complex **9** exhibits a side-bound P_2 unit with a $P-P$ interatomic distance of 2.060(1) Å and a $Cr-Cr$ interatomic distance of 3.011(1) Å.

Since these initial reports, it has been found that a wide range of ETM carbonyl complexes supported by cyclopentadienyl and substituted cyclopentadienyl ligands do indeed give rise to side-on-coordinated diphosphorus ligands bridging two transition-metal centers in a butterfly format. For

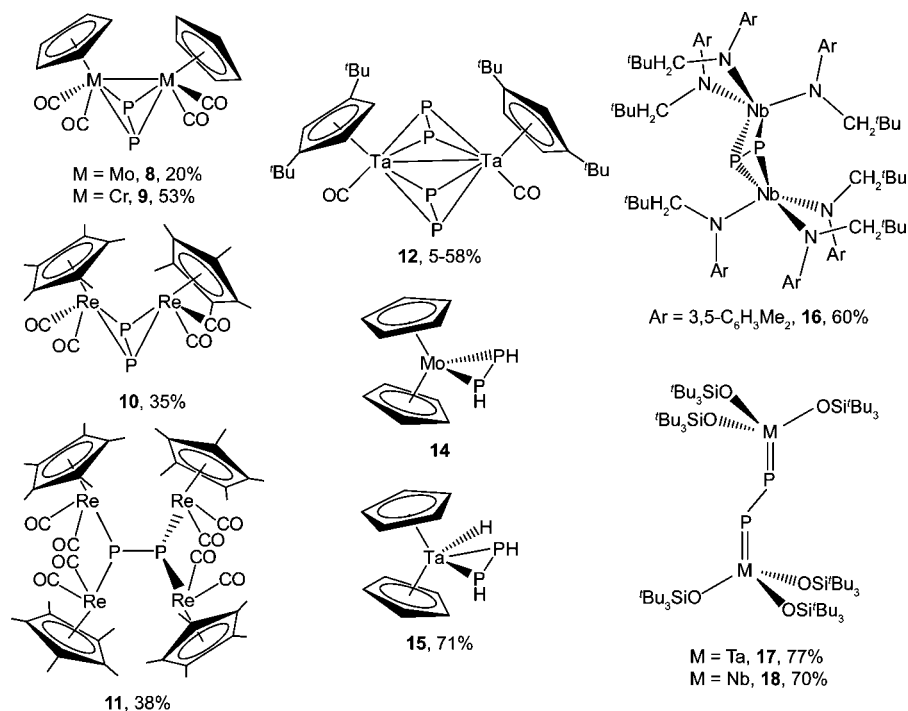


Figure 3. Bridging and side-on-bound diphosphorus ligands derived from P₄ activation; yields given where available.

example, [ReCp*(CO)₂]₂ reacts with P₄ in toluene upon warming a chilled solution to 23 °C to give Re₂(CO)₄Cp*₂-(μ₂:η²,η²-P₂), **10**. Complex **10** adopts an M₂P₂ butterfly geometry with no direct metal–metal interaction.²⁷ If the reaction mixture leading to **10** is not cooled prior to addition of P₄, then **10** is formed only in trace quantities with the dominant reaction product being the tetranuclear complex [Re(CO)₂Cp*]₄(P₂), **11**.²⁸ This diphosphinidine complex exhibits an unusual P₂ ligand stabilized as a formal 8 σ-electron donor. The P–P interatomic distance in **11** is a lengthy 2.226(3) Å, suggesting a P–P bond order of one, as compared with the short 2.032(8) Å interphosphorus distance exhibited by **10**. The synthesis of complex **11** illustrates the versatility of the diphosphorus ligand in being able to stabilize coordination complex clusters having two or more metals. A further example reported by Scherer and co-workers involves the photolytic reaction of Cp''Ta(CO)₄ (Cp'' = η⁵-1,3-C₅H₃Bu₂) with P₄ in toluene at 22 °C, giving rise to three products including Cp''(CO)₂Ta(η⁴-P₄) (vide infra), (Cp''(CO)Ta)₂(μ₂:η²,η²-P₂)₂, **12**, and (Cp''(CO)Ta)₃(μ₂:η²,η²-P₂)₂, **13**, in low yield.²⁹ Complex **12** was structurally characterized and found to contain short P–P interatomic distances (2.120(3) Å) in the coordinated diphosphorus ligands. No interaction between the two diphosphorus units was observed.

Cyclopentadienyl-supported ETM hydride complexes have also been shown to be viable reaction partners with P₄, leading to coordinated parent diphosphene, HP=PH, ligands resulting from transfer of hydride from the metal center to phosphorus. An early example of this type of transformation was provided by Green and co-workers, who showed that treatment of the dihydride complex Cp₂MoH₂ with an excess of P₄ in toluene at 90 °C leads to the red complex Cp₂Mo(HP=PH), **14**.³⁰ Subsequently, this compound was characterized crystallographically by Canillo et al.³¹ These reports were followed much later by the report by Stephan and co-workers of similar insertion behavior for the related trihydride complex Cp₂TaH₃. Specifically, it was found that

treatment of Cp₂TaH₃ with white phosphorus overnight at 85 °C in toluene elicits formation of Cp₂TaH(HP=PH), **15**.³²

In addition to cyclopentadienyl-supported ETM complexes, the reactive niobaziridine hydride complex, Nb(H)(η²-tBu(H)C=NAr)(N[CH₂tBu]Ar)₂, has also been shown to give a coordinated P₂ ligand upon reaction with white phosphorus. Treatment of the niobaziridine hydride complex with P₄ in diethyl ether gives rise quantitatively to (μ₂:η²,η²-P₂)[Nb-(N[CH₂tBu]Ar)₃]₂, **16**.³³ This reaction was found to be insensitive to the reaction conditions used, giving rise to **16** regardless of the P:Nb stoichiometry. The reaction can be viewed as a 2e per Nb reduction of the P₄ tetrahedron and is reminiscent of the mild activation of P₄ reported for the molybdenum(III) tris-amide system discussed above.¹⁰ Compound **16** displays the typical M₂P₂ butterfly geometry seen for coordinated diphosphorus units with a short P–P interatomic distance of 2.150(2) Å and no direct metal–metal interaction. The molecular structure of **16** is shown in Figure 4 along with examples of other molecular geometries for coordinated P₂ ligands.

Recently, two examples of a rare end-on coordination mode for a P₄-derived diphosphorus ligand have been observed by Wolczanski and co-workers, these being demonstrated as a bridging component spanning a pair of three-coordinate niobium or tantalum metal fragments.³⁴ Treatment of Ta(OSi^tBu)₃ with P₄ in toluene gives rise to (μ₂:η¹,η¹-P₂)(Ta(OSi^tBu)₃)₂, **17**. Interestingly, reaction of the related PMe₃-stabilized Nb(OSi^tBu)₃ with P₄ gave different major products depending upon the reaction conditions. When the reaction was run at 23 °C in toluene, the purple (μ₂:η¹,η¹-P₂)(Nb(OSi^tBu)₃)₂, **18**, could be isolated in 70% yield. However when the reaction mixture was kept at –78 °C for 7 h prior to warming to room temperature, the red hexaphosphorus complex (μ₂:η²,η²-P₆)(Nb(OSi^tBu)₃)₂ could be isolated in good yield (vide infra). Complex **17** proved isomorphous to **18**, with both species displaying an end-on zigzag coordination mode for the M₂P₂ core. The P–P interatomic distances in **17** and **18** are slightly longer than

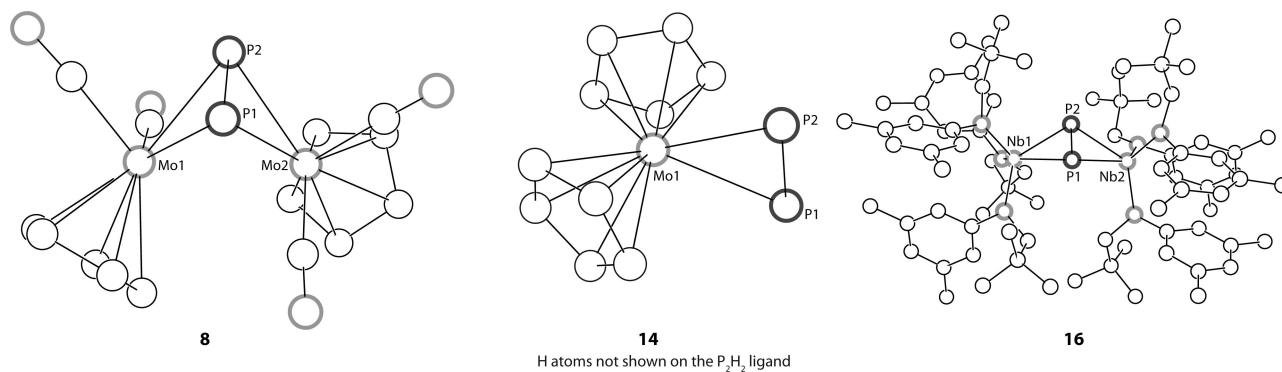


Figure 4. Structural diversity in diphosphorus ligands derived from P_4 activation.

those of the P_2 complexes discussed previously, at 2.171(2) and 2.143(1) Å, respectively; the structural features point to a diphosphinidene, i.e., $M=P=P=M$, Lewis picture for these systems that incorporates metal–phosphorus double-bond character. It is presumed that the end-on coordination observed in **17** and **18** may be due to the steric pressure provided by the bulky OSi^tBu_3 ligands surrounding the metal centers. To date, simple 1:1 complexes of a transition metal with a P_2 ligand have not been observed and remain sought-after targets.

2.3. Cyclo- P_3 Units Derived from P_4

The activation of P_4 in the coordination sphere of a metal complex to give a triphosphorus unit has been observed frequently, often as a pathway that competes with formation of a monophosphide complex.⁸ Triphosphorus ligands derived from P_4 appear generally as cyclo- P_3 units that bind to a metal in an η^3 coordination mode. Sacconi and co-workers provided the field with many examples of cyclo- P_3 ligands crowning various transition-metal centers, including the first structurally characterized example in both the terminal disposition (in a cobalt system) and as a symmetrical $\mu_2:\eta^3,\eta^3$ ligand connecting two nickel centers.³⁵ Much of this seminal late-metal work has been reviewed elsewhere.^{8,36–38}

The earliest cyclo- P_3 complexes in an ETM context were isolated as coproducts of P_4 activation chemistry. For example, the complexes $(\eta^3-P_3)Mo(CO)_2Cp$, **19**, and $(\eta^3-P_3)Cr(CO)_2Cp$, **20**, were isolated from product mixtures that resulted when the parent dimer complexes $[Cp(CO)_2Mo]_2$ and $[Cp(CO)_2Cr]_2$ were treated with P_4 in hot toluene solutions (Figure 5).^{22,26} Similarly, Chisholm et al. found that

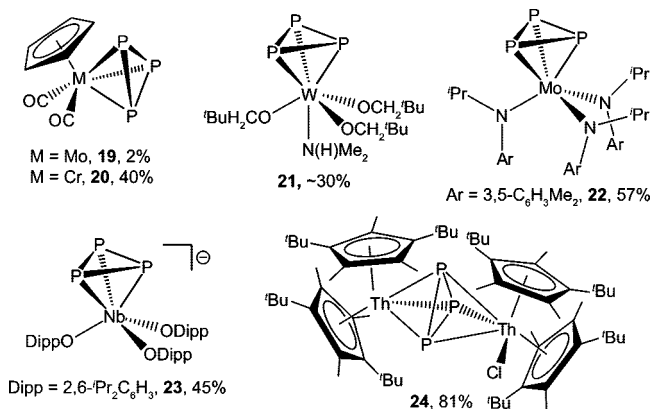


Figure 5. Cyclo- P_3 ligands derived from P_4 activation; yields given where available.

treatment of the dimethylamine adduct of the tungsten dimer $W_2(OCH_2^tBu)_6$ led to a trimetallic monophosphide cluster together with the cyclo- P_3 complex $(\eta^3-P_3)W(OCH_2^tBu)_3$, **21**, as a minor product.²⁰

Masked metal(III) ($M = Cr, Mo, W$) derivatives have been found to produce cyclo- P_3 complexes upon activation of white phosphorus. For instance, $Mo(H)(\eta^2-MeC=NAr)(N[Pr]Ar)_2$ (a tautomer of $Mo(N[Pr]Ar)_3$) reacts with P_4 to provide the μ -phosphide complex **5** in high yield (vide supra); this is the main reaction channel when diethyl ether, in which P_4 is not very soluble, is used as the solvent. However, upon adding a toluene solution of the molybdaziridine hydride complex $Mo(H)(\eta^2-Me_2C=NAr)(N[Pr]Ar)_2$ to a toluene solution containing excess P_4 , the cyclo- P_3 complex $(\eta^3-P_3)Mo(N[Pr]Ar)_3$, **22**, is favored as the reaction product.⁹

A recent addition to the family of cyclo- P_3 complexes derived from P_4 is the anionic niobium complex, $[(\eta^3-P_3)Nb(ODipp)_3]^{1-}$ (**23**, Dipp = 2,6-diisopropylphenyl, Figure 6). The complex anion **23** forms upon reduction of $Cl_2Nb(ODipp)_3$ with an excess of 0.5% sodium amalgam in the presence of 1 equiv of P_4 in THF.³⁹ The negative charge associated with this cyclo- P_3 complex evidently imparts it with nucleophilic character at phosphorus and thus leads to enhanced reactivity as compared with neutral group 6 metal- P_3 complexes (vide infra).

There are several unifying features to the small family of ETM terminal cyclo- P_3 complexes. The ^{31}P NMR resonance that is characteristic of cyclo- P_3 complexes coordinated to transition metals is a singlet found between -180 and -220 ppm. Such a high-field shift is characteristic of polyphosphorus units with small endocyclic bond angles, as found in a P_3 ring.⁴⁰ Structurally, each of the above-mentioned cyclo- P_3 complexes displays a symmetrical P_3 unit that can reasonably be viewed as a P_3^{3-} ligand. It should be noted that the P–P interatomic distances for structurally characterized P_3 complexes are not invariant. For instance, **20** and **21** both display somewhat short average P–P interatomic distances of 2.12 and 2.15 Å, respectively. The anionic complex **23**, on the other hand, displays average P–P interatomic distances of 2.20 Å, which are much closer to those found for the P–P single bonds of P_4 (2.21 Å),²⁵ but this may be due to interaction of the P_3 ring with a sodium counteraction in the solid state.³⁹ Such ostensible elongation of the P–P distances in a cyclo- P_3 ring is also observed for bimetallic P_3 complexes. Cyclo- P_3 as a bridging ligand is rare within the ETM regime, though examples do exist. For example, treatment of $Cp^*_2Th(\eta^4-C_4H_6)$ with P_4 in the presence of 0.5 equiv of $MgCl_2(OEt_2)$ in toluene at 100 °C for 20 h was reported to give the asymmetric bimetallic

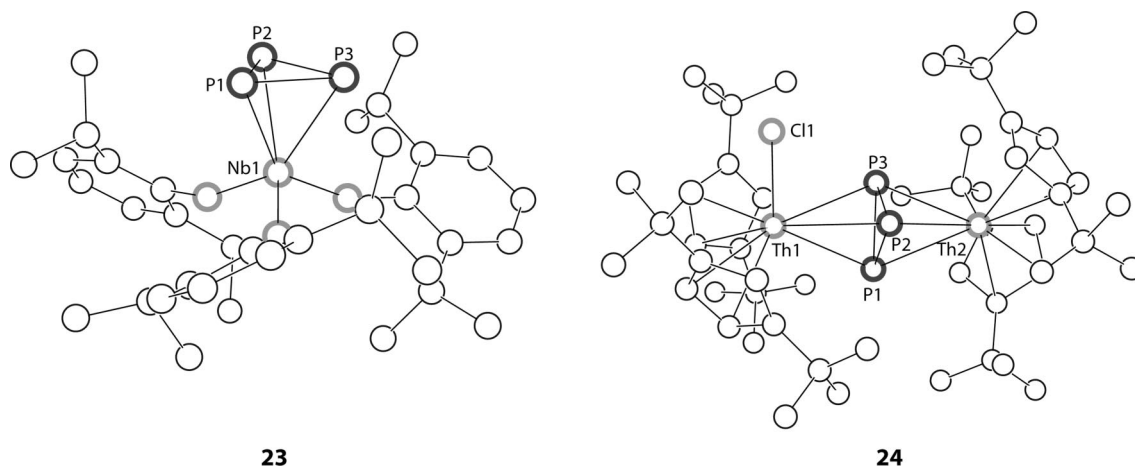


Figure 6. Structural diversity in cyclo-P₃ ligands derived from P₄ activation.

complex Cp''₂Th(μ_2 : η^3 , η^3 -P₃)Th(Cl)Cp''₂, **24** (Figure 6).⁴¹ The average P–P distance in **24** was found to be 2.185 Å.

3. P₄ Activation Leading to P₄ Products

There is wide interest in understanding the nature of the metal–P₄ interaction that precedes the P–P bond activation chemistry that is typically observed upon reaction of transition-metal complexes with white phosphorus.^{8,42,43} In most instances where P₄ is observed to react with a transition-metal complex, the integrity of the P₄ tetrahedron is not maintained and fragmentation and/or aggregation processes transpire. In some cases, the four atoms of the P₄ tetrahedron are each incorporated into the metal complex product, affording derivatives containing tetraphosphabicyclobutane, tetraphosphabutadiene, or cyclo-P₄ coordination. In contrast, there are relatively few known coordination compounds featuring an intact P₄ tetrahedron. The earliest report of P₄ as a coordinated ligand on a transition metal was provided by Ginsberg and Lindsell in 1971 with the synthesis of (P₄)Rh(PPh₃)₂Cl,⁴⁴ though the mode of coordination was not initially ascertained due to the lack of crystallographic or conclusive NMR analysis. The latter data were not reported until 1986 and were suggestive of an open edge, where a tetraphosphabicyclobutane coordinates to a metal(III) center.^{44,45} Sacconi deserves credit for the first full characterization of an intact tetraphosphorus ligand coordinated to a metal complex. His research group found that treatment of a nickel(0) complex, Ni(np₃) (np₃ = N(C₂H₄PPh₂)₃), with P₄ in THF gave rise to the complex (P₄)Ni(np₃) with the P₄ unit bonded to the metal atom by an apical P atom in an η^1 fashion.⁴⁶ Two years later Sacconi's group provided the second well-characterized example of a tetrahedro tetraphosphorus ligand, this time on Pd and supported by the related triphos ligand (triphos = MeC(CH₂PPh₂)₃).⁴⁷ The chemical literature possessed these two as its only examples of an intact P₄ tetrahedron serving as a 2e ligand atop a transition-metal complex for over 20 years despite a surge in the study of P₄ activation chemistry.

3.1. Coordination of P₄ Tetrahedra

The first reports of the coordination of intact P₄ molecules to an ETM center came in 1998 from Scheer and co-workers. They found that the electronically and coordinatively unsaturated compounds M(CO)₃(PR₃)₂ (M = Mo, W; R = ⁱPr, Cy), can serve as starting materials for coordination of the

P₄ tetrahedron.^{48,49} Slow addition of P₄ to a toluene solution of M(CO)₃(PCy₃)₂ at –78 °C followed by warming to –20 °C gives orange M(CO)₃(PR₃)₂(η^1 -P₄) (M = Mo, R = Cy, **25**; M = W, R = Cy **26**; M = Mo, R = ⁱPr **27**, Figure 7). Complexes **25**, **26**, and **27** decompose in solution above 0 °C but are persistent as solids under argon at ambient temperatures.⁴⁹ Next, an example of an intact P₄ tetrahedron coordinated to an ETM came from the group of Peruzzini, and in that report an intact P₄ ligand was observed as both a terminal and a bridging entity.⁵⁰ The complex (triphos)-Re(CO)₂(OTf), containing a weakly coordinated triflate ligand, was treated with a small excess of P₄ at 35 °C and found to give, after workup, the mustard-colored [(triphos)-Re(CO)₂(η^1 -P₄)] [OTf], **28**, in good yield.⁵⁰ Additionally, it was found that the “distal” P₃ face of the tetrahedro-P₄ ligand still maintained reactivity toward unsaturated transition-metal complexes and electrophiles. Accordingly, it was revealed that treatment of **28** with an additional equivalent of (triphos)Re(CO)₂(OTf) resulted in formation of the bimetallic complex, [((triphos)Re(CO)₂)₂(μ_2 : η^1 , η^1 -P₄)] [OTf]₂, **29**, which contains an intact P₄ tetrahedron and is the first report of such a ligand serving as a bridge between two metal centers.

3.2. Rearranged P₄ Products

Rearranged P₄ units have also been observed as ligands attached to early transition metals; these ligands can display various geometries including the tetraphosphabicyclobutane and the cyclo-P₄ coordination modes. The reaction pathways that generate the various types of P₄ ligands have been speculated upon, but detailed mechanistic studies are essentially nonexistent.⁸

The structural motif involving the fewest bond cleavage events from intact P₄ is the tetraphosphabicyclobutane geometry (butterfly geometry). Only three examples of ETM P₄-butterfly complexes have been reported. Scherer and co-workers found that treatment of Cp''₂M(CO)₂ (M = Zr, Hf; Cp'' = η^5 -1,3-C₅H₃^tBu₂) with P₄ in refluxing xylene resulted in oxidative addition of the P₄ tetrahedron and clean formation of the air-stable complexes Cp''₂M(κ^2 -P₄) (M = Zr, **30**; M = Hf, **31**).⁵¹ More recently, Chirik et al. reported on formation of a similar Zr product, Cp*₂Zr(κ^2 -P₄) (**32**), which they obtained by treatment of Cp*₂Zr(H)₂ with P₄ in toluene at –35 °C.⁵² Surprisingly, Chirik and co-workers also found that treatment of the related dihydride Cp*(η^5 -C₅H₄^tBu)Zr(H)₂ with P₄ under the same reaction conditions

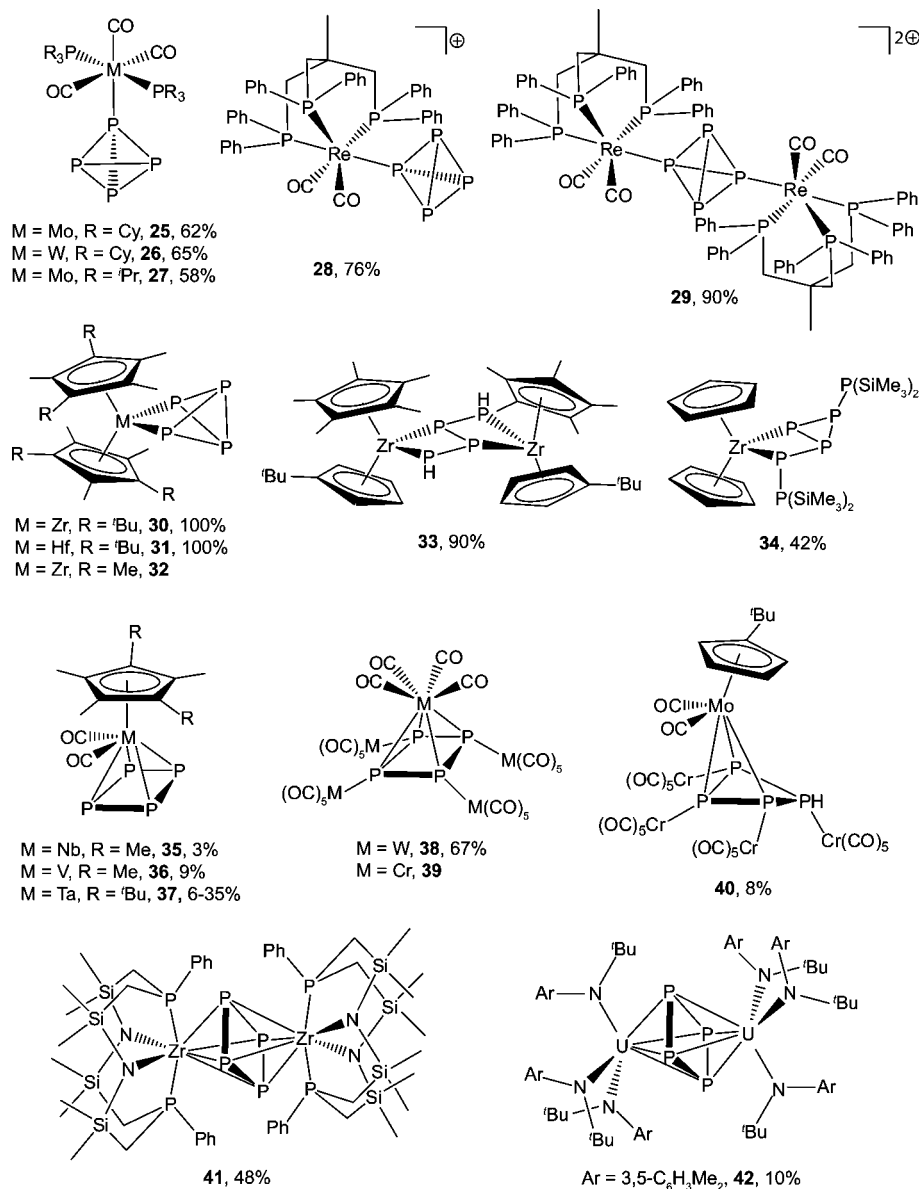


Figure 7. Intact and rearranged P₄ ligands derived from P₄ activation; yields given where available.

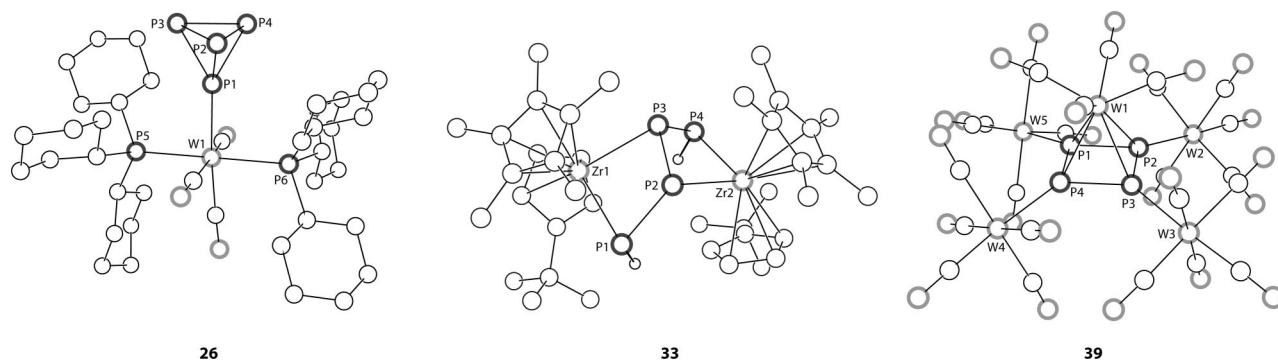


Figure 8. Structural diversity in P₄ ligands derived from P₄ activation.

did *not* lead to the tetraphosphabicyclobutane structure but instead to (Cp*(η^5 -C₅H₄/Bu)Zr)₂(μ_2 : η^2 , η^2 -P₄H₂), **33**.⁵² The phosphorus core of **33** is best viewed as a (P₄H₂)⁴⁻ fragment resulting in two formally 16-electron Zr(IV) centers and may be considered as a rare example of a hydrogenated P₄⁴⁻ ligand (Figure 8). A related example of formation of a P₄ chain with concomitant functionalization has been provided by Lappert and co-workers, who found that treatment of

Cp₂Zr(P(SiMe₃)₂)₂ with P₄ in toluene at 20 °C results in P–P bond scission, phosphido migration, and intramolecular rearrangement to yield the zircona(tetraphospha)bicyclo[2.1.0]pentane complex Cp₂Zr(η^1 , η^1)-P₄(P(SiMe₃)₂)₂, **34**, where the P(SiMe₃)₂ units are bonded to the two peripheral P atoms.⁵³

By 1989, of the possible cyclo-P_x compounds isoelectronic to the carbocyclic π systems, $x = 3-6$, only cyclo-P₄ had not been reported. It was in that year that Scherer reported

the photochemical synthesis of the first examples of cyclo- P_4 ligands. Irradiation of $Cp^*Nb(CO)_4$ in the presence of P_4 in hexane solution at room temperature gave rise to a mixture of products including $Cp^*(CO)_2Nb(\eta^4-P_4)$ (**35**), $(Cp^*(CO)Nb(\mu_2:\eta^2-P_2))_2$, and $(Cp^*Nb)_2(P_6)$ (vide infra).⁵⁴ The phosphorus NMR spectrum of **35** at room temperature consists of a broad singlet; at $-50^\circ C$, this resonance splits into the well-resolved signals of an AMX_2 spin system, suggestive of hindered rotation of the cyclo- P_4 ligand. The bonding in this system may be formally considered as a P_4^{2-} ring which consists of an allyl-like P_3^- monoanion and a phosphido-like anion. Alternatively, more symmetric bonding descriptions for cyclo- P_4 ligands include a neutral bis(diphosphene) ligand and a P_4^{4-} tetraphosphido ligand, but the bond lengths and NMR data for this particular compound are most consistent with the allyl-phosphido description. Similar reactions have been observed for vanadium to give $Cp^*(CO)_2V(\eta^4-P_4)$ (**36**) and with tantalum to give $Cp''(CO)_2Ta(\eta^4-P_4)$ (**37**).^{29,55}

The photochemical reaction of P_4 with group 6 metal carbonyl complexes has also been used to access cyclo- P_4 complexes. Dahl and co-workers discovered that irradiation of THF solutions of $W(CO)_6$ and P_4 gave rise to $W(CO)_4(\eta^4-P_4)(W(CO)_5)_4$, **38**, in 67% isolated yield.⁵⁶ Similarly, Scheer et al. found that the photochemical reaction of $(Cp^*Mo(CO)_3)_2$ ($Cp^* = \eta^5-C_5H_4Bu$) with white phosphorus in the presence of $Cr(CO)_5(THF)$ leads to a mixture of $Cr(CO)_4(\eta^4-P_4)(Cr(CO)_5)_4$ (**39**), $Cp^*Mo(CO)_2(\eta^3-P_4)(Cr(CO)_5)_4(H)$ (**40**), and the diphosphorus complex $(Cp^*Mo(CO)_2)_2(\mu_4:\eta^2-P_2)(Cr(CO)_5)_2$.⁵⁷ A further example of cyclo- P_4 ligand formation has been provided by Fryzuk and co-workers using a zirconium diamidodiphosphine macrocycle complex. They found that treatment of $ZrCl_2(P_2N_2)$ ($P_2N_2 = PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh$) with P_4 and 4 equiv of KC_8 in toluene gave rise to the D_{2d} symmetric bridging cyclo- P_4 complex $(Zr(P_2N_2))_2(\mu_2:\eta^4, \eta^4-P_4)$ (**41**).⁵⁸ The P_4 unit in **41** is nearly a perfect square and can be considered as a P_4^{4-} ligand.

A further example of a cyclo- P_4 ligand is found sandwiched between two uranium metal centers.⁵⁹ It was found that treatment of $(THF)U(N[{}^iBu]Ar)_3$ with 0.5 equiv of P_4 results in clean formation of $(\mu_2:\eta^4, \eta^4-P_4)[U(N[{}^iBu]Ar)_3]_2$, **42**, which displays a singlet in its phosphorus NMR spectrum at 794 ppm.⁵⁹ The square tetraphosphorus bridge in compound **42** represents the formal two-electron reduction of P_4 with concomitant formation of two $U(IV)$ fragments. Compound **42** crystallizes in the space group PI , and the two halves of the molecule are related by an inversion center located at the P_4 -square centroid. Density functional theory calculations show that the HOMO-1 orbital in **42** has δ symmetry, but there is minimal overlap between the bridging ligand and the two metal centers. As no other orbitals show appreciable overlap between the uranium centers, **42** is formulated as an ionic compound supported by a weak δ bond.⁵⁹

4. P_4 Activation Leading to $P_{\geq 5}$ Products

The divergent and fascinating reactivity of P_4 with ETM systems is highlighted particularly well by the cases in which polyphosphorus ligands with greater than four P atoms are formed. Instances of such aggregation are common in P_4 activation chemistry, and these reactions are important to developing a thorough understanding of structure and bonding in phosphorus chemistry. Perhaps one of the most intriguing examples of P_4 activation by an ETM complex

was provided by Ellis and co-workers in 2002. A highly reactive naphthalene-stabilized titanate complex was first formed by reduction of $TiCl_4(THF)_2$ with 6 equiv of potassium naphthalenide in THF at $-60^\circ C$ followed by addition of 2 equiv of 18-crown-6. The complex so obtained was found to react with 2.5 equiv of P_4 to give $[K(18-crown-6)]_2[Ti(\eta^5-P_5)_2]$, **43**, an all-inorganic analogue of the titanocene dianion (Figure 9).⁶⁰ Despite being isovalent with the group 6 metallocenes, **43** is both surprisingly air and moisture stable and chemically inert. This decaphosphametallocene remains the only such molecule and is a prime example of the isolobal analogy between P atoms and CH fragments.⁶¹

Both monocyclic and bicyclic P_6 ligands have been isolated when sandwiched between early transition metals. The first example of the cyclo- P_6 ligand was provided by Scherer and co-workers while exploring the chemistry of $[Cp^*(CO)_2Mo]_2$ with P_4 as mentioned above. Treatment of $[Cp^*(CO)_2Mo]_2$ with P_4 in xylene at $140^\circ C$ results in formation of a mixture of products including the Cp^* analogues of **8** and **19** as well as the triple-decker complex $[Cp^*Mo]_2(\mu_2:\eta^6, \eta^6-P_6)$, **44**.²³ As the all-phosphorus analogue of benzene, cyclo- P_6 has been stabilized by a variety of triple-decker complexes of early transition metals including those of W (**45**), V (**46**), Nb (**47**, **48**), and Ti (**49**) by thermolysis of a half-sandwich precursor (usually a cyclopentadienyl/carbonyl complex) with P_4 in a hydrocarbon solvent.^{54,62–65} Several of the P_6 triple-decker complexes adopt the expected D_{6h} configuration with a planar P_6 unit, but in the case of **49** a distortion to a chairlike cyclohexaphosphido form occurs and the P_6 ligand binds in a $\mu_2:\eta^3, \eta^3$ fashion as a P_6^{6-} ligand.

Several different geometries can be obtained for P_6 ligands as illustrated by the activation of P_4 by $Cp''_2Th(\eta^4-C_4H_6)$ in toluene at $100^\circ C$. The resultant $(Cp''_2Th)_2(\mu_2:\eta^3, \eta^3-P_6)$ complex (**50**) contains a bicyclic P_6^{4-} ligand, which resembles a reduced hexaphosphabenzvalene ligand sandwiched between two thorium metal centers (Figure 10).⁴¹ Yet another unique P_6 ligand geometry has been provided by Wolczanski and co-workers, who found that if a reaction mixture containing $({}^tBu_3SiO)_3NbPMe_3$ and P_4 was allowed to incubate at $-78^\circ C$ for 7 h, followed by slow warming to $23^\circ C$, then the red P_6 complex, $({}^tBu_3SiO)_3Nb(\mu_2:\eta^2, \eta^2-P_3-P_3)$, **51**, could be isolated in 77% yield.³⁴ In **51**, two of the niobium–phosphorus distances of 2.559(8) and 2.576(5) Å are significantly shorter than the third (2.784(7) Å). The average P–P interatomic distance within each of the tP_3 rings is 2.172(2) Å. The two tP_3 rings are linked via a 2.217(7) Å diphosphorus bond; thus, the parameters may be best represented by considering the interaction as that of a niobium center interacting with a triphosphirene ring and benefiting from substantial backbonding.

Polyphosphorus ligands up through P_{12} have been isolated by activation of white phosphorus by late-transition-metal fragments, but ETM systems to date have given ligands containing only up to as many as eight phosphorus atoms.⁸ Two examples of P_8 ligands have been isolated in multi-metallic arrangements with early transition metals. Cossairt and Cummins found that when 2 equiv of P_4 was combined with $INb(OC[{}^tAd]Mes)_3$ in a weakly coordinating solvent, a disproportionation reaction took place, producing 0.5 equiv of $I_2Nb(OC[{}^tAd]Mes)_3$ and the octaphosphorus complex $(Mes[{}^tAd]CO)_3Nb=P(P_7)Nb(OC[{}^tAd]Mes)_3$, **52**.⁶⁶ The P_8 core of **52** is closely related to that revealed by Wright and co-workers for the product of activation of P_4 by $[(18-crown-$

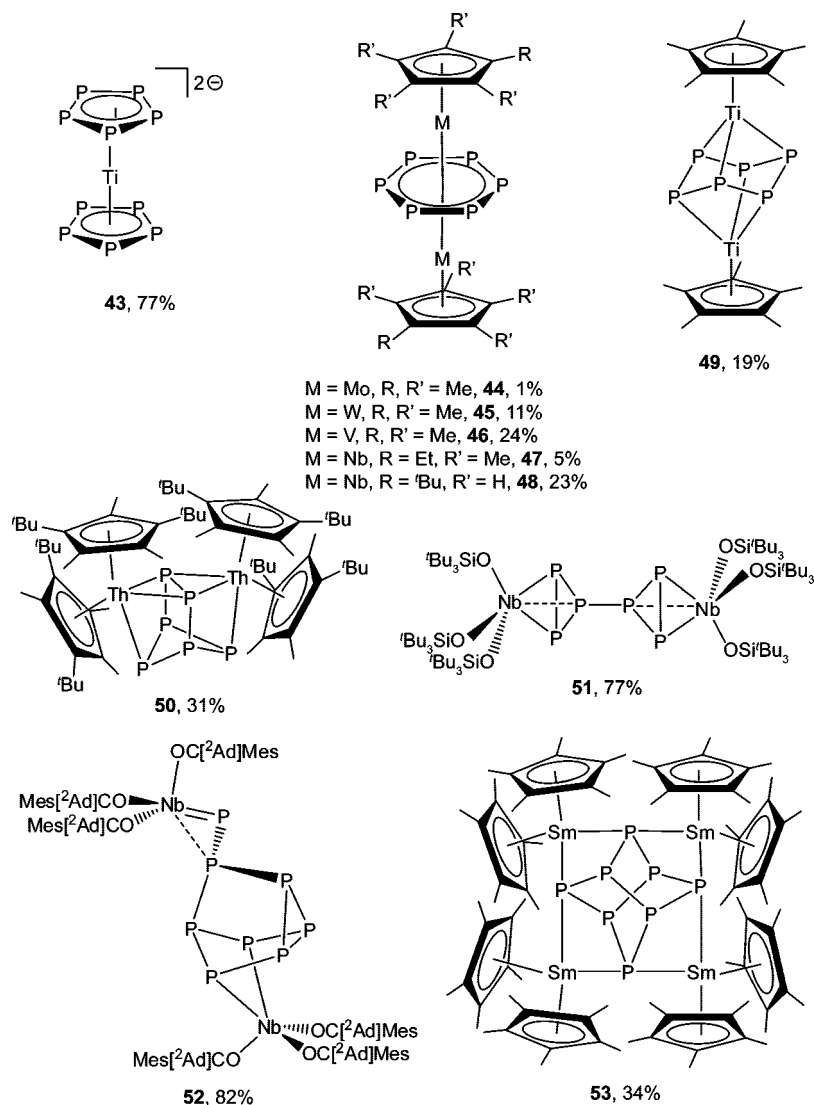


Figure 9. P–P aggregation products from P₄ activation; yields given where available.

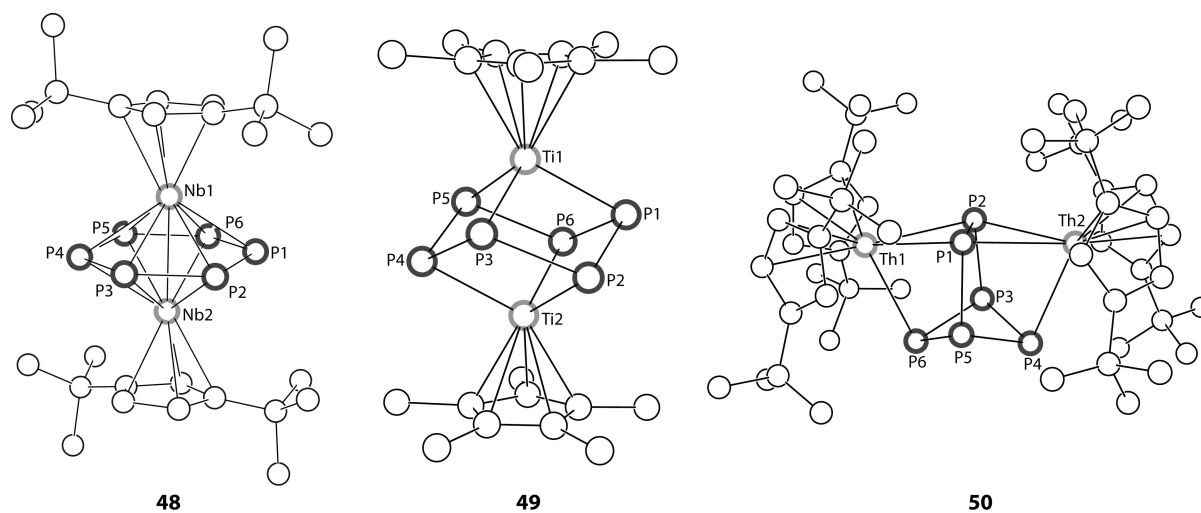


Figure 10. Structural diversity in P ligands derived from P₄ activation.

6)K][Si(SiMe₃)₃].⁶⁷ What distinguished the octaphosphorus cluster in **52** from other related structural motifs seen in polyphosphorus ligands derived from P₄ was the fact that it incorporated a metal–phosphinidene bond, the reactivity of which was exploited in one instance through phospho–Wittig chemistry.⁶¹ Another example of ostensible P₄ dimerization

comes from the lab of Roesky and co-workers, who found that diffusion of P₄ vapor into a toluene solution of solvate-free permethyl samarocene, Cp*₂Sm, over a period of several days resulted in the formation of (Cp*₂Sm)₄P₈ (**53**) as red crystals.⁶⁸ Complex **53** can be described as containing a P₈⁴⁻ ligand in a realgar-type homoatomic conformation supported

by four Sm(III) metal centers and represents the first example of a lanthanide-supported polyphosphide.

5. Functionalization and Transfer Methodologies

Much of the reaction chemistry of molecules derived from P_4 activation has remained confined to the protective coordination sphere of the metal complex; however, it is becoming increasingly evident that the transfer of such ligands is chemically feasible. While much research has been targeted at the direct incorporation of N_2 -derived nitrogen atoms into main-group molecules, the analogous chemistry with elemental phosphorus has been explored far less.^{69–74} The incorporation of P_4 -derived phosphorus atoms into organic frameworks by P-atom transfer reactions mediated by transition-metal complexes could circumvent the need for PCl_3 as an intermediate in the synthesis of organophosphorus molecules and open up a wide variety of new methodologies for main-group molecule synthesis.^{75,76} There are limited examples of such methods reported to date; however, this reaction base is continually expanding. It is the goal of this section to review the functionalization and, where available, transfer chemistry of P_4 -derived phosphorus ligands from ETM platforms.

5.1. Functionalization and Subsequent Reactivity of Terminal Monophosphide and Bridging Diphosphorus Complexes Derived from P_4

The reason for the late development of the $M\equiv P$ functional group lies in the high reactivity of these triple bonds, which exhibit “side-on” as well as “end-on” reactivity.¹³ Thus, before 1995, highly reactive intermediates containing a metal–element triple bond were the subject of much speculation.^{12,13,20}

Unfortunately, the stable terminal phosphide ligands that have been isolated via P_4 activation chemistry have the common feature of kinetic stabilization by protection of the triple bond through the use of bulky organic substituents which shut down most “side-on” reactivity of the multiple bond.⁷⁷ One exception to this has been the reaction of $P\equiv Mo(N[{}^iPr]Ar)_3$ with AdCP to afford the (cyclo-AdCP)₂- $Mo(N[{}^iPr]Ar)_3$ complex, **54**, which is the product of combining an MP triple bond with a CP triple bond.⁷⁸ It has also been shown that the same P_4 -derived terminal phosphide complex, **4**, will undergo clean ligand exchange reactions with alcohols to afford alkoxy-supported terminal phosphide complexes.⁷⁹ The fact that the MoP triple bond remains intact during these transformations is remarkable as the steric protection at the metal center is reduced greatly in the ensuing alkoxy complexes. In one example, alcoholysis of **4** with 1-adamantanol affords $P\equiv Mo(OAd)_3$, which itself undergoes

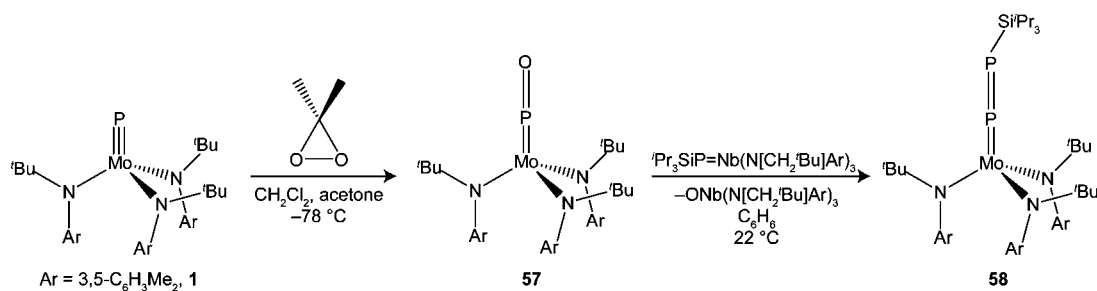
“side-on” dimerization to afford a bridging P_2 complex augmented by a Mo–Mo bond. Such terminal phosphide dimerization with P–P bond formation and reduction of the metal oxidation state is reminiscent of similar dimerization pathways that have been observed for group 8 metal nitrido systems, leading to bridging dinitrogen complexes.^{80–82} The concept of using ligand substitution in a post- P_4 activation step to open up new synthetic access to phosphide systems deserves more exploration.

The “end-on” reactivity of sterically protected terminal phosphides began to be demonstrated concomitant with their earliest isolation and structural characterization. The molybdenum complex **1** was shown early on to react with $MesN_3$ as well as S_8 and ethylene sulfide to afford the terminally functionalized complexes $(EP)Mo(N[{}^iBu]Ar)_3$ ($E = MesN$, **55**; S , **56**).¹⁰ In another oxidation of the terminal phosphide ligand, **1** was oxidized with a solution of dimethyldioxirane in acetone to the purple terminal PO complex $(OP)Mo(N[{}^iBu]Ar)_3$, **57** (Scheme 1).⁸³ Complex **57** is the only documented example of a molecule that contains a terminal PO substituent, and the chemistry of the $M=P=O$ functional group has been explored only to a limited extent. What is known is that the phosphoryl phosphorus in the PO complex is susceptible to nucleophilic attack. Complex **57** undergoes a facile reaction with Cp_2ZrMe_2 to afford $Cp_2ZrMeOP(Me)Mo(N[{}^iBu]Ar)_3$, in which a Zr–O bond has been formed and a methyl group transferred to the P center.⁸³ More recently, Piro and Cummins reported that **57** undergoes an O for $PSiR_3$ metathesis reaction with the niobium phosphinidene complex ${}^iPr_3SiP=Nb(N[CH_2{}^iBu]Ar)_3$ to generate the oxoniobium complex $ONb(N[CH_2{}^iBu]Ar)_3$ and the unusual diphosphenido complex ${}^iPr_3SiP=PMo(N[{}^iBu]Ar)_3$, **58**, that contains a “singly bent” diphosphenido moiety.⁸⁴

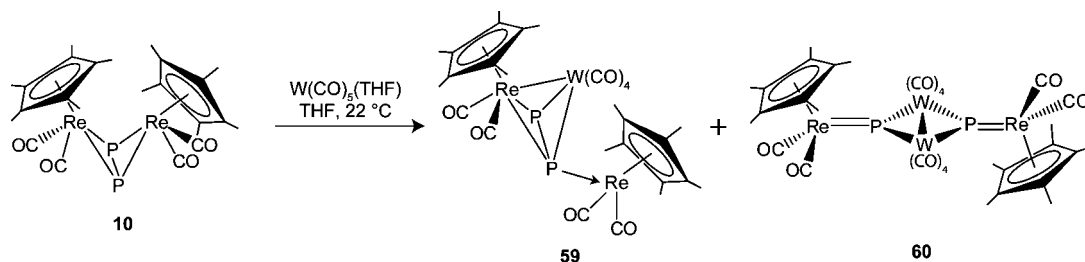
The reactivity of the P_2 functional group derived from P_4 activation has been explored to a reasonable extent and has led to the synthesis of a variety of new molecules. For example, Scherer and co-workers discovered that treatment of the dirhenium– P_2 complex **10** with excess $W(CO)_5(THF)$ leads to two new products (Scheme 2). The first isolated product is $(Re(CO)_2Cp^*)_2(P_2W(CO)_4)$, **59**, the first example of the transformation of an M_2P_2 butterfly complex to a complex with an M_2P_2 tetrahedrane framework. The second product of this reaction is a tetrametallic species $((Re(CO)_2-Cp^*)PW(CO)_4)_2$ (**60**), where the P–P bond has been broken with formation of new W–P and W–W bonds.²⁸ Complex **60** is notable for its downfield ${}^{31}P$ NMR chemical shift of 885 ppm as well as for its planar six-atom framework for the $Re_2P_2W_2$ core.

Another striking example of the reactivity of P_2 units was demonstrated by Scheer and co-workers with **9**. They discovered in their attempts to chlorinate the P–P bond in **9** that treatment with PCl_5 or PCl_3 leads to formation of η^3 -

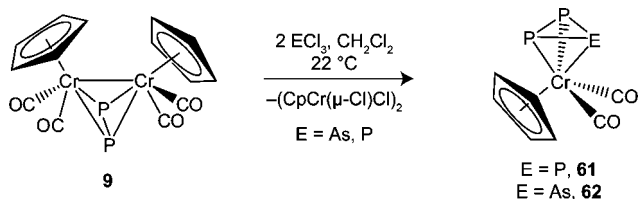
Scheme 1



Scheme 2



Scheme 3



$P_3Cr(CO)_2Cp$, **61**, a cyclo- P_3 complex of chromium and the chlorinated byproduct $(CpCr(\mu-Cl)Cl)_2$ (Scheme 3).⁸⁵ This is a potentially useful example of phosphorus ligand reactivity as it demonstrates a method for addition of a phosphorus atom to a P_2 ligand. Furthermore, in this report the authors show that not only can PCl_3 be used to make a P_3 complex but also $AsCl_3$ can be used instead, in which case the obtained product is $(\eta^3-P_2As)Cr(CO)_2Cp$, **62**, the first example of a cyclo- P_2As ligand complexed to a metal center.⁸⁵

Another progression of reactions derived from a bridging P_2 complex has stemmed from the dinobium complex **16**. It was recognized that the P_2 unit in **16** could be further reduced by two electrons to afford a monoanionic terminal phosphide complex. Reduction of **16** with an excess of sodium amalgam produced yellow $[Na][P\equiv Nb(N[CH_2^tBu]Ar)_3]$ (**63**) in 65% yield (Scheme 4).⁸⁶ This complex can also easily be synthesized without isolation of the intermediate bridging P_2 complex, making it readily accessible from P_4 in a one-pot synthesis. The phosphorus NMR spectrum of **63** displays a resonance at $\delta = 1010$ ppm that is diagnostic of early-transition-metal terminal phosphide complexes.

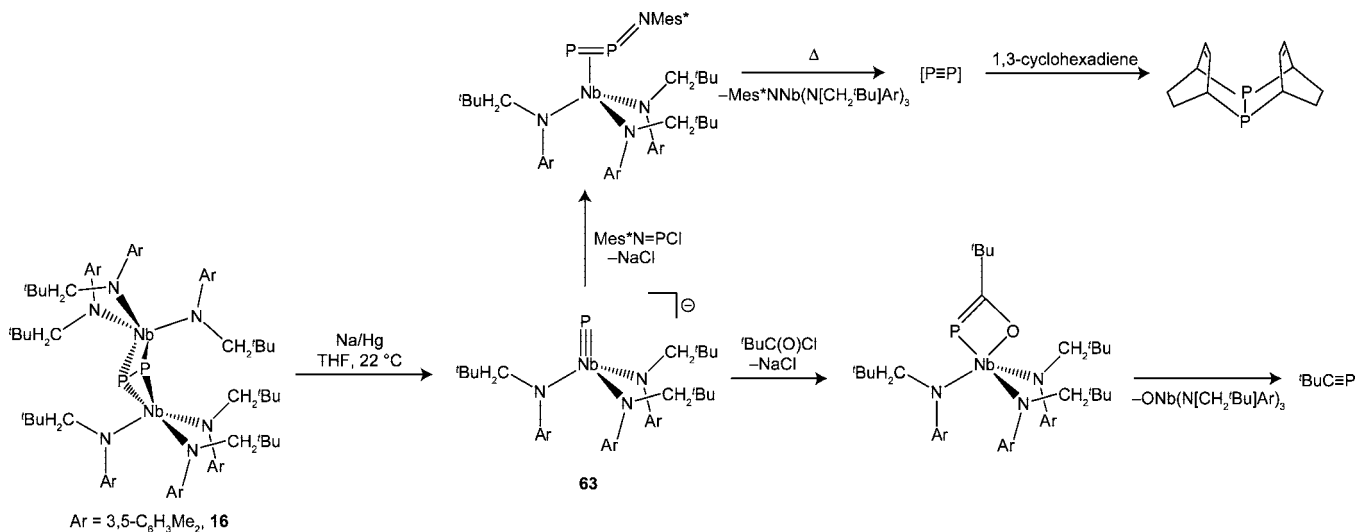
The terminal phosphide anion complex **63** has served as an entry to various phosphorus-element bond-forming reac-

tions (Scheme 4). It was shown in 2004 that **63** gives rise to phosphalkynes upon treatment with acid chlorides in a reaction that proceeds through a metastable $NbPCO$ metal-cycle. The niobium coproduct of this reaction, terminal oxo $ONb(N[CH_2^tBu]Ar)_3$, may be recycled back to the P_4 -activating starting material. As such, this reaction progression forms a closed synthetic cycle for the formation of a CP bond in only a few synthetic steps from P_4 .⁸⁶ The anionic terminal phosphide complex **63** was also shown to add to $Mes^*N=P=Cl$ to afford a diphosphaazide complex, $(\eta^2-Mes^*N=P=P)Nb(N[CH_2^tBu]Ar)_3$ that loses the P_2 unit upon gentle thermolysis or upon coordination of $W(CO)_5$. Therefore, this molecule serves as a synthon for diphosphorus or the $W(CO)_5$ complex of P_2 , allowing P_2 to be transferred to a variety of compounds including other terminal phosphide complexes which may themselves be derived from P_4 activation, organic dienes, and low-valent metal centers.^{78,87,88} In addition, reactions of **63** with main-group electrophiles have led to unusual phosphorus-containing ligands such as diorganophosphanylphosphinidenes and $\mu_2:\eta^3,\eta^3-EP_2$ ($E = Ge, Sn, Pb$) triangles.^{89,90}

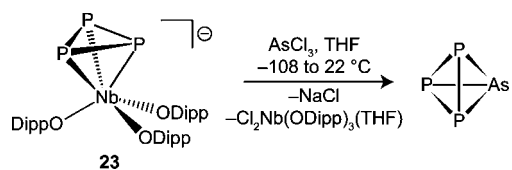
5.2. Reactivity and Transfer Chemistry of the Cyclo- P_3 Functional Group

Functionalizations of cyclo- P_3 complexes were first reported for the series $(P_3)M(\text{triphos})$ ($M = Co, Rh, Ir$) and required the highly electrophilic reagents $[Me_3O][BF_4]$ or $MeOTf$ to afford the methylated species.⁹¹ It was shown by Piro and Cummins in 2008 that the anionic nature of the cyclo- P_3 complex $[Na][W(CO)_5P_3Nb(N[CH_2^tBu]Ar)_3]$, derived from $P_2W(CO)_5$ trapping by **63**, imparts the molecule with greater nucleophilic character, allowing for functionalization using milder reagents to give a variety of products.^{78,92}

Scheme 4



Scheme 5



Though this anionic cyclo-P₃ complex was not obtained directly from P₄ activation, its reactivity provided inspiration for the study of the reaction chemistry of the anionic cyclo-P₃ molecule **23**, which was derived from P₄ activation. Complex **23** was found to be capable of P₃³⁻ transfer to appropriate E³⁺ sources, and this methodology provided the first selective synthesis of the tetraatomic interpnictide AsP₃ by reaction of **23** with 1 equiv of AsCl₃ with loss of NaCl and Cl₂Nb(ODipp)₃(THF) (Scheme 5).³⁹ The chemistry of AsP₃, which is synthetically available in two steps from P₄, is now being studied in detail.^{39,93}

5.3. Functionalization and Transfer Chemistry of Polyphosphorus Ligands (P_n ≥ 4) Derived from P₄

The chemistry of P₄-derived polyphosphorus ligands (P_n, n ≥ 4) in an ETM context has not been explored extensively. The sole example of transformation and transfer of P_n ligands (n ≥ 4) from an ETM is confined to the chemistry of **52**. Notably, **52** was found to react with ketones (OCR₂) in a metathesis reaction to produce an equivalent of oxo ONb(OC[²Ad]Mes)₃ and phosphalkene complexes R₂C=PP₇Nb(OC[²Ad]Mes)₃.⁹⁴ In cases where the ketone substituents have R = aryl, the phosphalkene complexes obtained via that phospho-Wittig reactivity were unstable with respect to a rearrangement that provided a saturated P₈ cluster containing an internalized R₂C unit (**64**, Scheme 6).⁹⁴ It was further found that the R₂CP₈ ligand could be transferred from the remaining niobium metal center by treatment with an equivalent of pyridine-N-oxide, ONC₅H₅, leading to release of another oxo equivalent, ONb(OC[²Ad]Mes)₃. In the presence of excess 1,3-cyclohexadiene the organic product of Diels–Alder trapping of the liberated diphosphene unit, R₂CP₈(C₆H₈), **65**, was formed, isolated, and subjected to structural characterization (Scheme 6).⁹⁵

6. Concluding Remarks

6.1. Conclusions

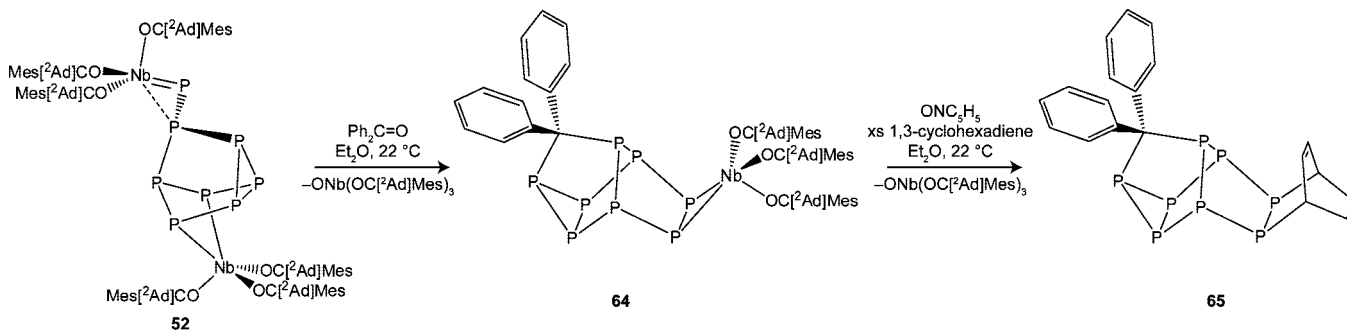
The activation of elemental phosphorus by ETM complexes has developed into a rich field rife with impressive structural motifs and transformation methodologies. ETM systems have the ability to promote the formation of and

stabilize a wide range of phosphorus ligands that can themselves act as a foundation for the synthesis of new transition-metal and main-group molecules. Transformation of white phosphorus mediated by early transition metals has opened doors permitting access to the chemistry of intriguing phosphorus-containing molecules including an all-inorganic analogue of titanocene, the diatomic P₂ molecule, and the tetra-atomic AsP₃ molecule, in addition to a host of monocyclic and polycyclic phosphides that allow for further cementing of the diagonal relationship between the HC functional group on the one hand and a P atom on the other.⁶¹

ETM systems have a proven ability to reduce the P₄ tetrahedron and stabilize reactive P–P bonds sufficiently to allow for further elaboration and manipulation while still maintaining the potential to transfer the newly built structures off of the transition-metal foundation. These abilities ensure a prominent place for early transition metals in the future development of new P₄ transformation methodologies. With more than 30 years of chemistry documented between P₄ and ETM complexes, a library of P ligands has emerged and general reactivity motifs have been revealed. The three strategies most commonly employed for P₄ activation include treatment with a low-valent, sterically hindered ETM complex, photolysis or thermolysis in the presence of an ETM carbonyl complex, and in situ reduction of an ETM precursor in the presence of P₄. Depending on the electronic and steric properties of the ETM complex, P ligands of different nuclearity can be obtained and we are beginning to understand the possible bonding motifs between phosphorus and ETM centers.

Careful study of the amassed library of information will now allow researchers to begin to predict what type of phosphorus activation products might be obtained from a given reaction. Figure 11 shows the frequency of occurrence of a given P_n (n = 1–8) ligand derived from P₄ activation by an ETM complex versus n. Not surprisingly, formation of P₄ ligands appears to be the most common outcome of ETM white phosphorus activation. It can be seen from this plot that phosphorus ligands with even numbers of P atoms occur more frequently than their odd-numbered counterparts. This suggests that phosphorus degradation more often occurs in a symmetric fashion, leading to many isolated P₂ products. It is noteworthy, however, that nearly all of the P₂ complexes are bimetallic species, while most of the P₁ and P₃ complexes are monometallic in nature. One further observation is that P_n ligands with n ≥ 5 occur far less frequently than ligands with n ≤ 4. It is likely that these P₄ aggregation products are the result of kinetic trapping of highly reactive P₄ degradation products with themselves or with P₄ and cannot really be rationally predicted or anticipated. The relatively high frequency of P₆ ligands represents an exception here

Scheme 6



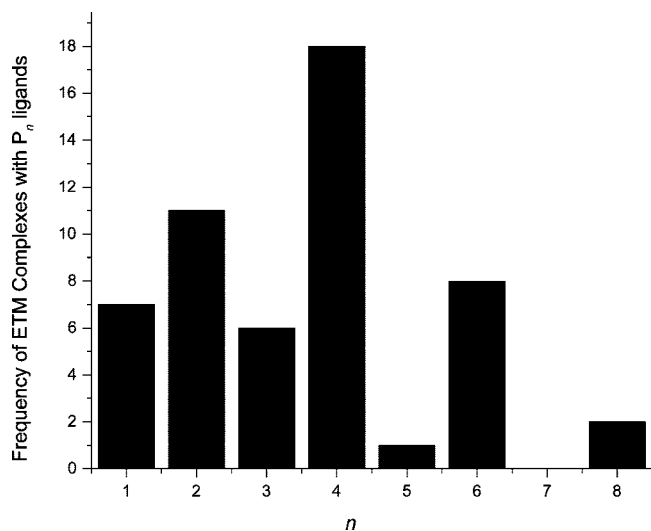


Figure 11. Frequency of P_n ligands formed from P_4 activation by ETM complexes as a function of n .

and would suggest that P_2 trimerization or P_2 trapping by P_4 ligands is favorable. The data set here is reasonably small, so it remains difficult to be able to use such information in an explicitly predictive way, but it does shine light on general principles of P_4 activation that are emerging and helps to motivate researchers to continue to study P_4 activation to develop a greater understanding of that process.

6.2. Future Prospects

Despite the resurgence of activity and growth in phosphorus activation and the chemistry promoted by it, there are still few processes capable of converting P_4 into organophosphorus molecules directly without going through PCl_3 as an intermediate, virtually no catalytic methods for the functionalization of P_4 have been documented, and consequently, no industrial-scale processes for the direct formation of P–C bonds from P_4 are in use. Researchers in the field are beginning to develop methods of P–C bond formation from P_4 , but these initial investigations have only just begun to scratch the surface of new methodologies left to be uncovered. Additionally, there has been little mechanistic work done to support the mass of synthetic research accomplished to date. Mechanistic investigations would greatly enhance our ability to predict the outcomes of and design new transformations in ETM P_4 activation chemistry. The significant recent advances in the field of ETM P_4 activation documented here show the breadth of chemistry that P_4 can undergo, and the unrealized goals of phosphorus chemistry support the need for continued work in this area. It is hoped that this review will not only inspire future researchers to new chemical discoveries but also drive others to employ molecular phosphorus as a synthon in their own research.

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8. References

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