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

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

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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, $Ca_{10}(PO_4)_6(X)_2$, X = OH, F, Cl, or Br) to white phosphorus, P_4, exceeds 500,000 tons annually as P_4 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 multi-step process in which P_4 is first chlorinated to generate PCl_3, 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 PCl_3 as an intermediate for the production of organophosphorus compounds is unpalatable and methods that circumvent its use are of great interest. This has provoked intensive investigations into the mild and controlled activation of P_4, a clear objective being the development of catalytic methods for phosphorus incorporation into organic molecules.

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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 through 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 through 7, and lanthanide and actinide metals are also included for comparison purposes. Sections two through four 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 five 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 either as terminal P$_3{}^{3-}$ ligands or as 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≡Mo(N[^{t}Bu]Ar)$_3$ (**1**; Ar = 3,5-C$_6$H$_3$Me$_2$).[10] Prior to this report and a concurrent report by Schrock and coworkers on the synthesis of P≡Mo(Me$_3$SiNCH$_2$CH$_2$)$_3$N and P≡W(Me$_3$SiNCH$_2$CH$_2$)$_3$N from reaction of the precursor chloro complexes and Li[P(H)Ph],[11] the M≡P functional group was virtually unknown.[12,13] Compound **1** was synthesized by Cummins and coworkers by treatment of three-coordinate Mo(N[^{t}Bu]Ar)$_3$ with 0.35 equiv of P$_4$ at 25 °C in diethyl ether.[10] Analogous terminal phosphide complexes, P≡Mo(N[^{t}Bu]Ph)$_3$, **2**, and P≡Mo(N[^{2}Ad]Ar)$_3$, **3**, obtained from reaction of white phosphorus with Mo(N[^{t}Bu]Ph)$_3$ and Mo(N[^{2}Ad]Ar)$_3$, respectively, have also been reported.[14,15] Interestingly, reaction of Mo(H)(η^2-Me$_2$C=NAr)(N[^{i}Pr]Ar)$_2$, a tautomer of Mo(N[^{i}Pr]Ar)$_3$, with P$_4$ does not directly give the terminal P≡Mo(N[^{i}Pr]Ar)$_3$, **4**, but instead, the bridging (Ar[^{i}Pr]N)$_3$Mo=P=Mo(N[^{i}Pr]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)(η^2-Me$_2$C=NAr)(N[^{i}Pr]Ar)$_2$.[16] Complex **4**, however, can be revealed by a re-

duction reaction 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[^{i}Pr]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^{t}Bu$_3$)$_3$ with 0.35 equiv of P$_4$ at 23 °C in diethyl ether results in clean formation of P≡Mo(OSi^{t}Bu$_3$)$_3$, **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≡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$_2$^{t}Bu)$_6$ was treated with P$_4$ in toluene at 75 °C with the stated goal of preparing the W≡P functional group. Obtained instead was the complex, (η^3-P$_3$)W(OCH$_2$^{t}Bu)$_3$(HNMe$_2$) (*vide infra*), together with the trimetallic monophosphide complex W$_3$-(μ_3-P)(μ-OCH$_2$^{t}Bu)$_3$(OCH$_2$^{t}Bu)$_6$, **7**.[20,21] It was postulated that **7** was formed by trapping of a sterically unprotected and highly reactive P≡W(OCH$_2$^{t}Bu)$_3$ intermediate by an equivalent of the starting material W$_2$(OCH$_2$^{t}Bu)$_6$.[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$_3$P tetrahedron are W–W–W = 60°, W–P–W = 71.3(1)°, and P–W–W = 54.3(1)° (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

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Ar = 3,5-C$_6$H$_3$Me$_2$, R = ^{t}Bu, **1**, 78%
Ar = Ph, R = ^{t}Bu, **2**, 79%
Ar = 3,5-C$_6$H$_3$Me$_2$, R = ^{2}Ad, **3**, 54%
Ar = 3,5-C$_6$H$_3$Me$_2$, R = ^{i}Pr, **4**, 84%

Ar = 3,5-C$_6$H$_3$Me$_2$, **5**, 74%

6, 65%

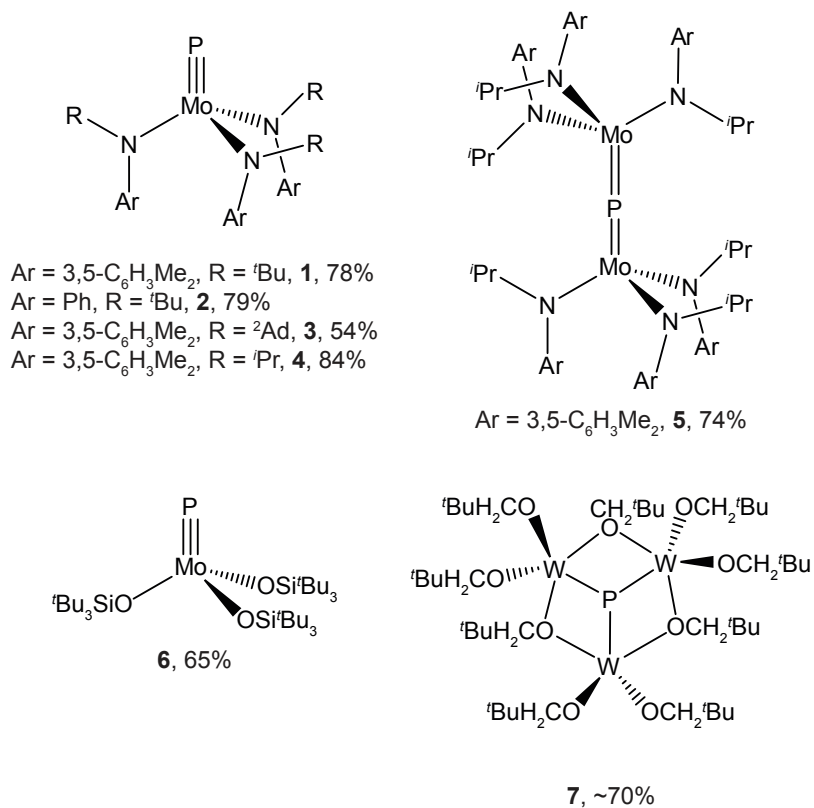**7**, ~70%

Figure 1: Monophosphide ligands derived from P$_4$ activation; yields given where available.
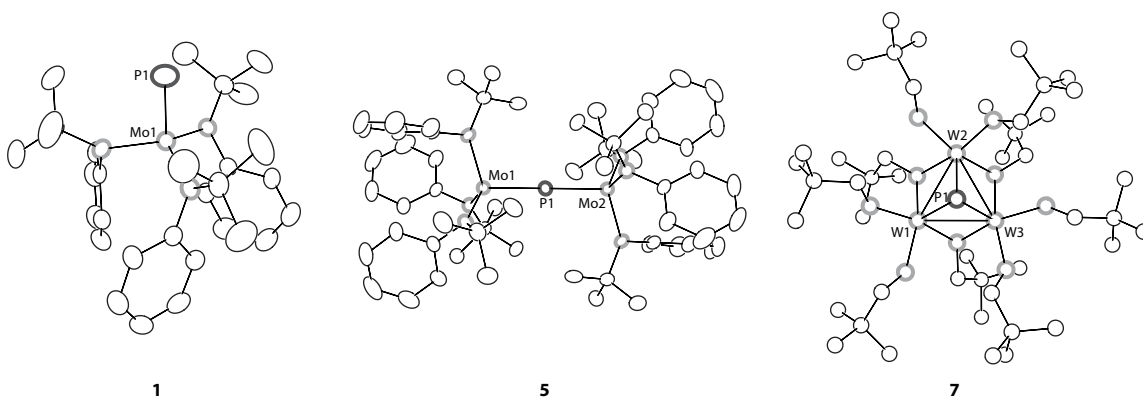

1   5   7

Figure 2: Structural diversity in monophosphorus ligands derived from P$_4$ activation.

metal fragments towards 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 coworkers.[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 coworkers. 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 $(\eta^3\text{-}P_3)Mo(CO)_2Cp$ (*vide infra*) and $Mo_2(CO)_4Cp_2(\mu_2 : \eta^2, \eta^2\text{-}P_2)$, **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 a typical 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 coworkers 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 $(\eta^3\text{-}P_3)Cr(CO)_2Cp$ (*vide infra*) and $Cr_2(CO)_4Cp_2(\mu_2 : \eta^2, \eta^2\text{-}P_2)$, **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 example, $[ReCp*(CO)_2]_2$ reacts with P_4 in toluene upon warming a chilled solution to 23 °C to give $Re_2(CO)_4Cp*_2(\mu_2 : \eta^2, \eta^2\text{-}P_2)$, **10**. Complex **10** adopts an M_2P_2 butterfly geometry with no

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direct metal-metal interaction.[27] If the reaction mixture leading to **10** is not cooled prior to addition of P_4, then **10** is formed only in trace quantities with the dominant reaction product being the tetranuclear complex, $[Re(CO)Cp^*]_4(P_2)$, **11**.[28] This diphosphinidine complex exhibits an unusual P_2 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 finding 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 coworkers involves the photolytic reaction of Cp"Ta(CO)$_4$ (Cp" = η^5-1,3-$C_5H_3{}^tBu_2$) with P_4 in toluene at 22 °C giving rise to three products including Cp"(CO)$_2$Ta(η^4-P_4) (*vide infra*), $(Cp"(CO)Ta)_2(\mu_2 : \eta^2, \eta^2$-$P_2)_2$, **12**, and $(Cp"(CO)Ta)_3(\mu_2 : \eta^2, \eta^2$-$P_2)_2$, **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 P_4 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 coworkers who showed that treatment of the dihydride complex Cp_2MoH_2 with an excess of P_4 in toluene at 90 °C leads to the red complex $Cp_2Mo(HP=PH)$, **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 coworkers of similar insertion behavior for the related trihydride complex Cp_2TaH_3. Specifically, it was found that treatment of Cp_2TaH_3 with white phosphorus overnight at 85 °C in toluene elicits formation of $Cp_2TaH(HP=PH)$, **15**.[32]

In addition to cyclopentadienyl-supported ETM complexes, the reactive niobaziridine hydride complex, $Nb(H)(\eta^2-{}^tBu(H)C=NAr)(N[CH_2{}^tBu]Ar)_2$, has also been shown to give a coordinated P_2 ligand upon reaction with white phosphorus. Treatment of the niobaziridine hydride complex with P_4 in diethyl ether gives rise quantitatively to $(\mu_2:\eta^2,\eta^2$-$P_2)[Nb(N[CH_2{}^tBu]Ar)_3]_2$, **16**.[33] This
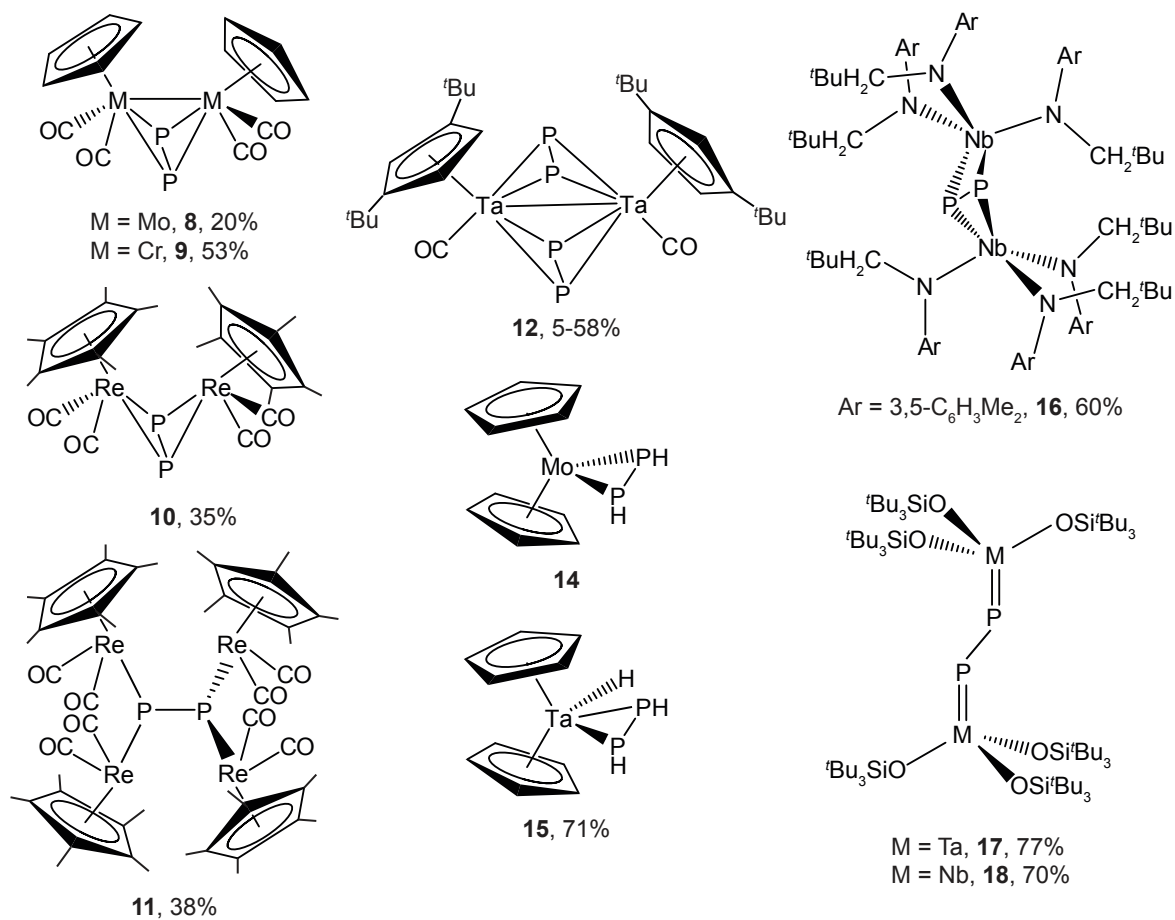
Figure 3: Bridging and side-on bound diphosphorus ligands derived from P_4 activation; yields given where available.
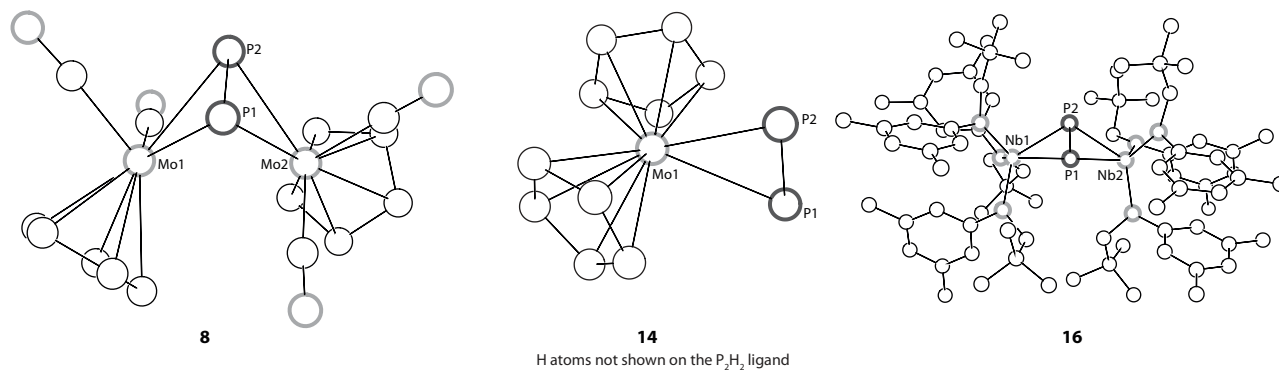

Figure 4: Structural diversity in diphosphorus ligands derived from P_4 activation.

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 P_4 tetrahedron and is reminiscent of the mild activation of P_4 reported for the molybdenum(III) *tris*-amide system discussed above.[10] Compound **16** displays the typical M_2P_2 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 P_2 ligands.

Recently, two examples of a rare end-on coordination mode for a P_4-derived diphosphorus ligand have been observed by Wolczanski and coworkers, these being demonstrated as a bridging component spanning a pair of three-coordinate niobium or tantalum metal fragments.[34] Treatment of $Ta(OSi^tBu_3)_3$ with P_4 in toluene gives rise to $(\mu_2{:}\eta^1,\eta^1\text{-}P_2)(Ta(OSi^tBu_3)_3)_2$, **17**. Interestingly, reaction of the related PMe_3-stabilized $Nb(OSi^tBu_3)_3$ with P_4 gave different major products depending upon the reaction conditions. When the reaction was run at 23 °C in toluene, the purple $(\mu_2{:}\eta^1,\eta^1\text{-}P_2)(Nb(OSi^tBu_3)_3)_2$, **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 $(\mu_2{:}\eta^2,\eta^2\text{-}P_6)(Nb(OSi^tBu_3)_3)_2$ could be isolated in good yield (*vide infra*). Complex **17** proved isomorphous to **18**, with both species displaying an end-on zig-zag coordination mode for the M_2P_2 core. The P–P interatomic distances in **17** and **18** are slightly longer than 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 coworkers have 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 $(\eta^3\text{-}P_3)Mo(CO)_2Cp$, **19**, and $(\eta^3\text{-}P_3)Cr(CO)_2Cp$, **20**, were isolated from product mixtures that resulted when the parent dimer complexes $[Cp(CO)_2Mo]_2$ and $[Cp(CO)_3Cr]_2$ were treated with P_4 in hot toluene solutions (Figure 5).[22,26] Similarly, Chisholm *et al.* found that 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 $(\eta^3\text{-}P_3)W(OCH_2{}^tBu)_3$, **21**, as a minor product.[20]
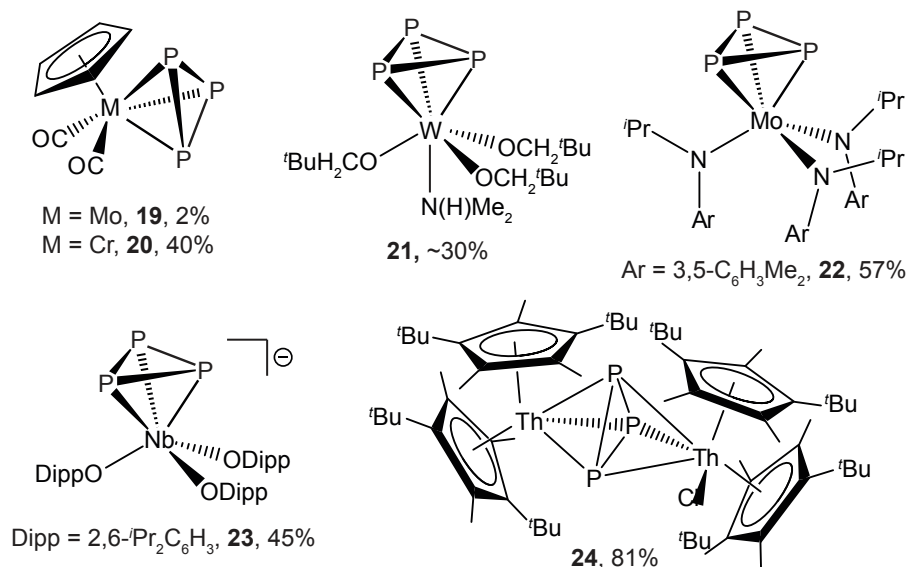

Figure 5: *Cyclo*-P_3 ligands derived from P_4 activation; yields given where available.

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)(η^2-Me$_2$C=NAr)(N[^{i}Pr]Ar)$_2$ (a tautomer of Mo(N[^{i}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)(η^2-Me$_2$C=NAr)(N[^{i}Pr]Ar)$_2$ to a toluene solution containing excess P$_4$, the *cyclo*-P$_3$ complex (η^3-P$_3$)Mo(N[^{i}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, [(η^3-P$_3$)Nb(ODipp)$_3$]$^{1-}$ (**23**, Dipp = 2,6-diisopropylphenyl, Figure 6). The complex anion **23** forms upon reduction of Cl$_2$Nb(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*).
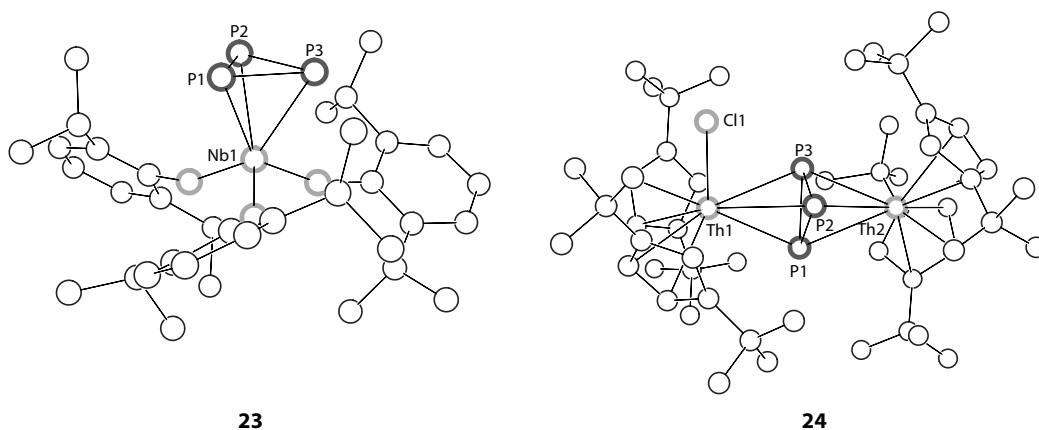

| **23** | **24** |

Figure 6: Structural diversity in *cyclo*-P$_3$ ligands derived from P$_4$ activation.

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 counter-cation 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"$_2$Th(η^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 complex Cp"$_2$Th(μ_2:η^3,η^3-P_3)Th(Cl)Cp"$_2$, **24** (Figure 6).[41] The average P–P distance in **24** was found to be 2.185 Å.

3 P_4 Activation Leading to P_4 Products

There is wide interest in understanding the nature of the metal-P_4 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 P_4 is observed to react with a transition metal complex, the integrity of the P_4 tetrahedron is not maintained and fragmentation and/or aggregation processes transpire. In some cases, the four atoms of the P_4 tetrahedron are each incorporated into the metal complex product affording derivatives containing tetraphosphabicyclobutane, tetraphosphabutadiene, or *cyclo*-P_4 coordination. In contrast, there are relatively few known coordination compounds featuring an intact P_4 tetrahedron. The earliest report of P_4 as a coordinated ligand on a transition metal was provided by Ginsberg and Lindsell in 1971 with the synthesis of $(P_4)Rh(PPh_3)_2Cl$,[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(np$_3$) (np$_3$ = N(C$_2$H$_4$PPh$_2$)$_3$), with P$_4$ in THF gave rise to the complex (P$_4$)Ni(np$_3$) with the P$_4$ 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(CH$_2$PPh$_2$)$_3$).[47] The chemical literature possessed these two as its only examples of an intact P$_4$ tetrahedron serving as a 2e ligand atop a transition metal complex for over twenty years despite a surge in the study of P$_4$ activation chemistry.

3.1 Coordination of P$_4$ Tetrahedra

The first reports of the coordination of intact P$_4$ molecules to an ETM center came in 1998 from Scheer and coworkers. They found that the electronically and coordinatively unsaturated compounds M(CO)$_3$(PR$_3$)$_2$ (M = Mo, W; R = ^{i}Pr, Cy), can serve as starting materials for coordination of the P$_4$ tetrahedron.[48,49] Slow addition of P$_4$ to a toluene solution of M(CO)$_3$(PCy$_3$)$_2$ at -78 °C followed by warming to -20 °C gives orange M(CO)$_3$(PR$_3$)$_2$(η^1-P$_4$) (M = Mo, R = Cy, **25**; M = W, R = Cy **26**; M = Mo, R = ^{i}Pr **27**, Figure 7). Complexes **25**, **26**, and **27** decompose in solution above 0 °C, but are stable as solids under argon at ambient temperatures.[49] Next, an example of an intact P$_4$ tetrahedron coordinated to an ETM came from the group of Peruzzini and in that report an intact P$_4$ ligand was observed as both a terminal and as a bridging entity.[50] The complex (triphos)Re(CO)$_2$(OTf), containing a weakly coordinated triflate ligand, was treated with a small excess of P$_4$ at 35 °C and was found to give, after work-up, the mustard colored [(triphos)Re(CO)$_2$(η^1-P$_4$)][OTf], **28**, in good yield.[50] Additionally, it was found that the "distal" P$_3$ face of the tetrahedro-P$_4$ ligand still maintained reactivity towards 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-P$_4$)][OTf]$_2$, **29**, which contains an intact P$_4$ tetrahedron and is the first report of such a ligand serving as a bridge between two metal centers.

M = Mo, R = Cy, **25**, 62%
M = W, R = Cy, **26**, 65%
M = Mo, R = ^{i}Pr, **27**, 58%

28, 76%

29, 90%

M = Zr, R = ^{t}Bu, **30**, 100%
M = Hf, R = ^{t}Bu, **31**, 100%
M = Zr, R = Me, **32**

33, 90%

34, 42%

M = Nb, R = Me, **35**, 3%
M = V, R = Me, **36**, 9%
M = Ta, R = ^{t}Bu, **37,** 6-35%

M = W, **38**, 67%
M = Cr, **39**

40, 8%

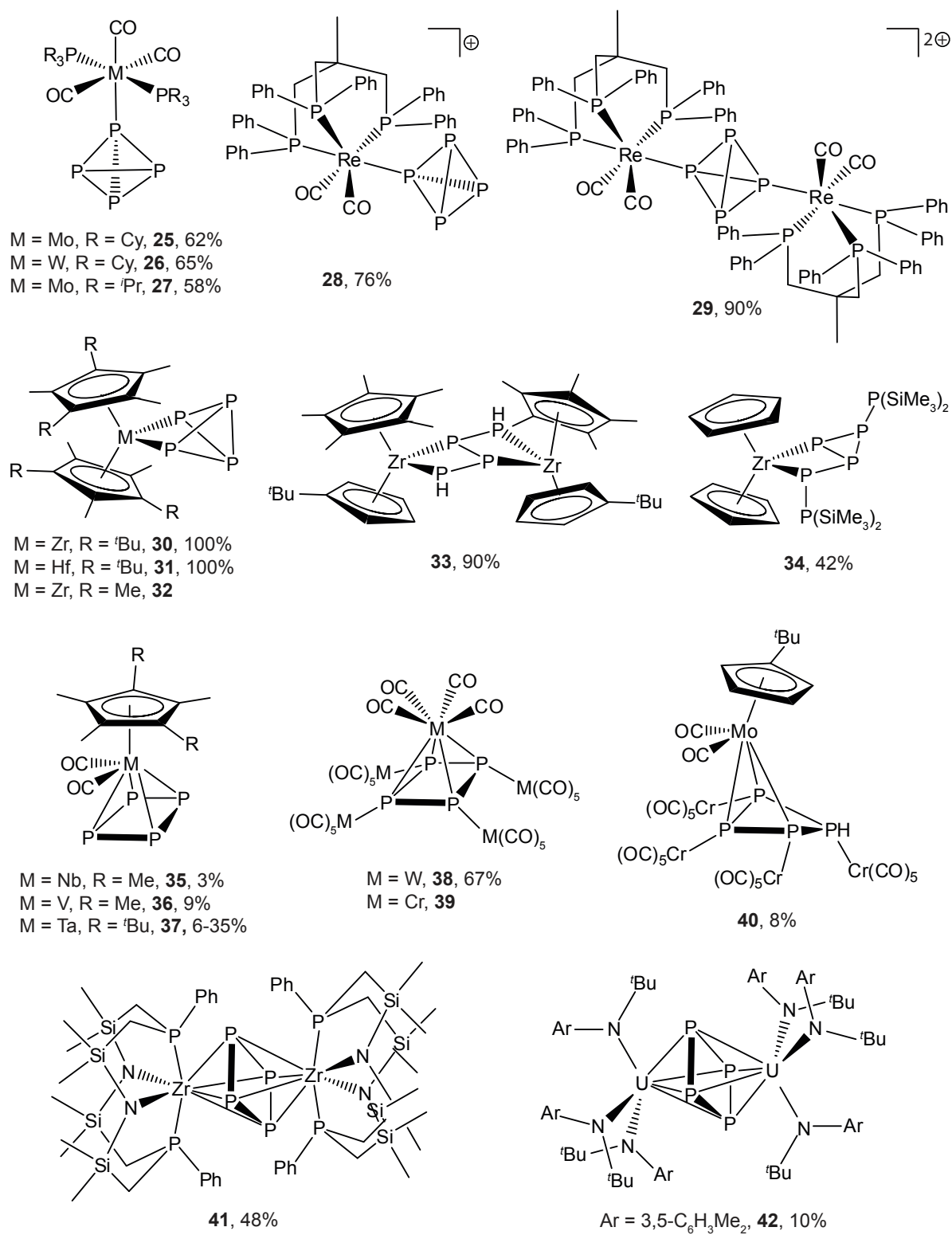**41**, 48%

Ar = 3,5-$C_6H_3Me_2$, **42**, 10%

Figure 7: Intact and rearranged P_4 ligands derived from P_4 activation; yields given where available.

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3.2 Rearranged P_4 Products

Rearranged P_4 units have also been observed as ligands attached to early transition metals; these ligands can display various geometries including the tetraphosphabicyclobutane and the *cyclo*-P_4 coordination modes. The reaction pathways that generate the various types of P_4 ligands have been speculated upon, but detailed mechanistic studies are essentially nonexistent.[8]

The structural motif involving the fewest bond cleavage events from intact P_4 is the tetraphosphabicyclobutane geometry (butterfly geometry). Only three examples of ETM P_4-butterfly complexes have been reported. Scherer and coworkers found that treatment of $Cp_2"M(CO)_2$ (M = Zr, Hf; Cp" = η^5-1,3-$C_5H_3{}^tBu_2$) with P_4 in refluxing xylene resulted in oxidative addition of the P_4 tetrahedron and clean formation of the air-stable complexes $Cp_2"M(\kappa^2$-$P_4)$ (M = Zr, **30**; M = Hf, **31**).[51] More recently, Chirik *et al.* reported on formation of a similar Zr product, $Cp^*{}_2Zr(\kappa^2$-$P_4)$ (**32**), which they obtained by treatment of $Cp_2{}^*Zr(H)_2$ with P_4 in toluene at $-35\,°C$.[52] Surprisingly, Chirik and coworkers also found that treatment of the related dihydride $Cp^*(\eta^5$-$C_5H_4{}^tBu)Zr(H)_2$ with P_4 under the same reaction conditions did *not* lead to the tetraphosphabicyclobutane structure, but instead to $(Cp^*(\eta^5$-$C_5H_4{}^tBu)Zr)_2(\mu_2{:}\eta^2,\eta^2$-$P_4H_2)$, **33**.[52] The phosphorus core of **33** is best viewed as a $(P_4H_2)^{4-}$ fragment resulting in two formally 16-electron Zr(IV) centers, and may be considered as a rare example of a hydrogenated $P_4{}^{4-}$ ligand (Figure 8). A related example of formation of a P_4 chain with concomitant functionalization has been provided by Lappert and coworkers who found that treatment of $Cp_2Zr(P(SiMe_3)_2)_2$ with P_4 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 $Cp_2Zr(\eta^1,\eta^1)$-$P_4(P(SiMe_3)_2)_2$, **34**, where the $P(SiMe_3)_2$ 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*-P_4 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]
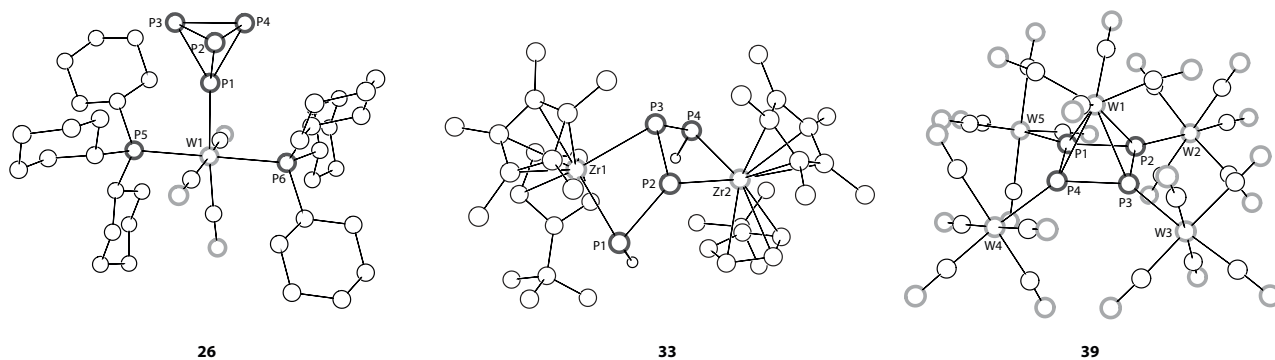
Figure 8: Structural diversity in P_4 ligands derived from P_4 activation.

The phosphorus NMR spectrum of **35** at room temperature consists of a broad singlet; at 223 K, 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. Alternative, 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 $Cp^*(CO)_2V(\eta^4\text{-}P_4)$ (**36**), and with tantalum to give $Cp''(CO)_2Ta(\eta^4\text{-}P_4)$ (**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 coworkers discovered that irradiation of THF solutions of $W(CO)_6$ and P_4 gave rise to $W(CO)_4(\eta^4\text{-}P_4)(W(CO)_5)_4$, **38**, in 67% isolated yield.[56] Similarly, Scheer *et al.* found that the photochemical reaction of $(Cp'Mo(CO)_3)_2$ ($Cp' = \eta^5\text{-}C_5H_4{}^tBu$) with white phosphorus in the presence of $Cr(CO)_5(THF)$ leads to a mixture of $Cr(CO)_4(\eta^4\text{-}P_4)(Cr(CO)_5)_4$ (**39**), $Cp'Mo(CO)_2(\eta^3\text{-}P_4)(Cr(CO)_5)_4(H)$ (**40**), and the diphosphorus complex $(Cp'Mo(CO)_2)_2(\mu_4{:}\eta^2\text{-}P_2)(Cr(CO)_5)_2$.[57] A further example of *cyclo*-P_4 ligand formation has been provided by Fryzuk and coworkers 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 $(Zr(P_2N_2))_2(\mu_2{:}\eta^4,\eta^4\text{-}P_4)$ (**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 $(THF)U(N[^tBu]Ar)_3$ with 0.5 equiv of P_4 results in clean formation of $(\mu_2:\eta^4,\eta^4\text{-}P_4)[U(N[^tBu]Ar)_3]_2$, **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 $P\bar{1}$, 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 was provided by Ellis and coworkers in 2002. A highly reactive naphthalene-stabilized titanate complex was first formed by reduction of $TiCl_4(THF)_2$ with six equiv of potassium naphthalenide in THF at 260 °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 $[K(18\text{-crown-}6)]_2[Ti(\eta^5\text{-}P_5)_2]$, **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 cowork-
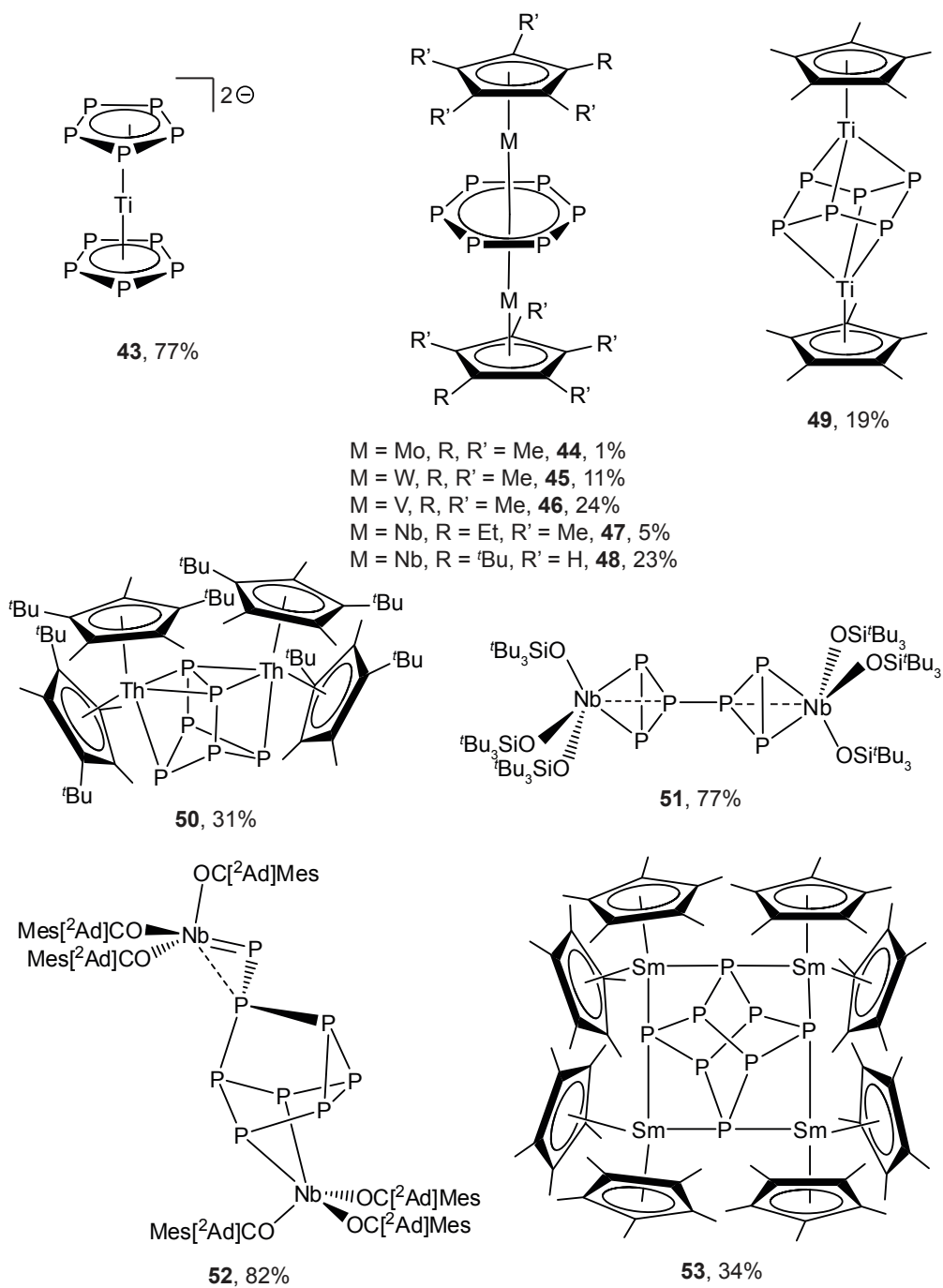
Figure 9: P–P aggregation products from P_4 activation; yields given where available.

M = Mo, R, R' = Me, **44**, 1%
M = W, R, R' = Me, **45**, 11%
M = V, R, R' = Me, **46**, 24%
M = Nb, R = Et, R' = Me, **47**, 5%
M = Nb, R = ^{t}Bu, R' = H, **48**, 23%

43, 77%

49, 19%

50, 31%

51, 77%

52, 82%

53, 34%

19

ers 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 °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 chair-like *cyclo*-hexaphosphido form occurs, and the P_6 ligand binds in a $\mu_2:\eta^3,\eta^3$ fashion as a P_6^{6-} ligand.
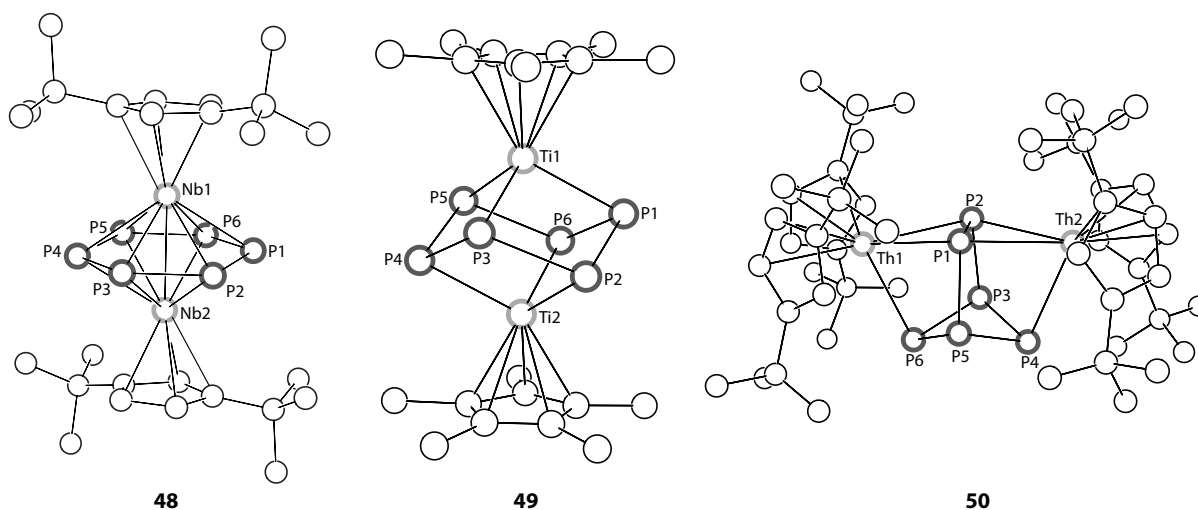

Figure 10: Structural diversity in P_6 ligands derived from P_4 activation.

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 °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 coworkers who found that if a reaction mixture containing $(^tBu_3SiO)_3NbPMe_3$ and P_4 was allowed to incubate at -78 °C for 7 h, followed by slow warming to 23 °C, then the red P_6-complex, $((^tBu_3SiO)_3Nb)_2(\mu_2:\eta^2,\eta^2-{}^cP_3-{}^cP_3)$, **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 sig-

nificantly shorter than the third (2.784(7) Å). The average P–P interatomic distance within each of the $^cP_3$ rings is 2.172(2) Å. The two $^cP_3$ 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 multimetallic arrangements with early transition metals. Cossairt and Cummins found that when 2 equiv of P_4 were combined with $INb(OC[^2Ad]Mes)_3$ in a weakly-coordinating solvent, a disproportionation reaction took place producing 0.5 equiv of $I_2Nb(OC[^2Ad]Mes)_3$ and the octaphosphorus complex $(Mes[^2Ad]CO)_3Nb=P(P_7)Nb(OC[^2Ad]Mes)_3$, **52**.[66] The P_8 core of **52** is closely related to that revealed by Wright and coworkers for the product of activation of P_4 by $[(18\text{-crown-6})K][Si(SiMe_3)_3]$.[67] What distinguished the octaphosphorus cluster in **52** from other related structural motifs seen in polyphosphorus ligands derived from P_4 was the fact that it incorporated a metal–phosphinidene bond, the reactivity of which was exploited, in one instance through phospha-Wittig chemistry.[61] Another example of ostensible P_4 dimerization comes from the lab of Roesky and coworkers who found that diffusion of P_4 vapor into a toluene solution of solvate-free permethyl samarocene, Cp^*_2Sm, over a period of several days resulted in the formation of $(Cp^*_2Sm)_4P_8$ (**53**) as red crystals.[68] Complex **53** can be described as containing a P_8^{4-} 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
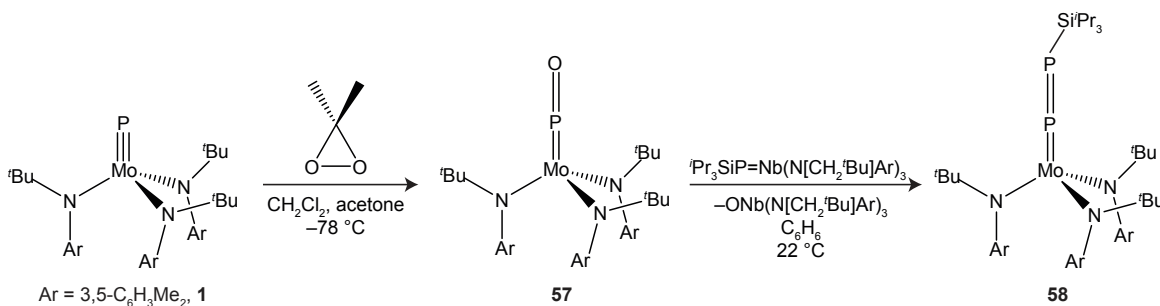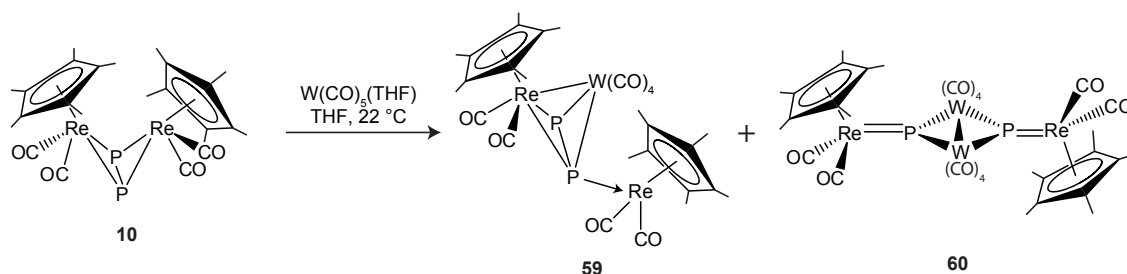

Scheme 1

The reason for the late development of the M≡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 $P≡Mo(N[^iPr]Ar)_3$ with $AdC≡P$ to afford the ($cyclo$-$AdCP_2$)$Mo(N[^iPr]Ar)_3$ complex, **54**, that is the product of combining an M≡P triple bond with a C≡P 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 Mo≡P triple bond remains intact during these transformations is remarkable as the steric protection at the metal center is reduced greatly in the ensuing alkoxide complexes. In one example, alcoholysis of **4** with 1-adamantanol affords P≡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 susbstitution 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[^{t}Bu]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[^{t}Bu]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$_2$ZrMe$_2$ to afford Cp$_2$ZrMeOP(Me)Mo(N[^{t}Bu]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 ^{i}Pr$_3$SiP=Nb(N[CH$_2$^{t}Bu]Ar)$_3$ to generate the oxoniobium complex ONb(N[CH$_2$^{t}Bu]Ar)$_3$ and the unusual diphosphenido complex ^{i}Pr$_3$SiP=PMo(N[^{t}Bu]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 coworkers have 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, $((Re(CO)_2Cp*)PW(CO)_4)_2$ (**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.

Scheme 2

Another striking example of the reactivity of P_2 units was demonstrated by Scheer and coworkers 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)-$P_3Cr(CO)_2Cp$, **61**, a *cyclo*-P_3 complex of chromium and the chlorinated byproduct $(CpCr(\mu\text{-}Cl)Cl)_2$ (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 that $AsCl_3$ 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 diniobium complex **16**. It was recognized that the P_2 unit in **16** could be further reduced by two electrons to afford a mono-anionic 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
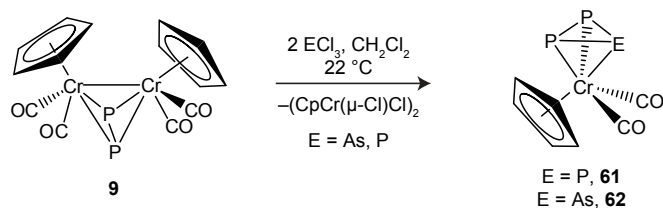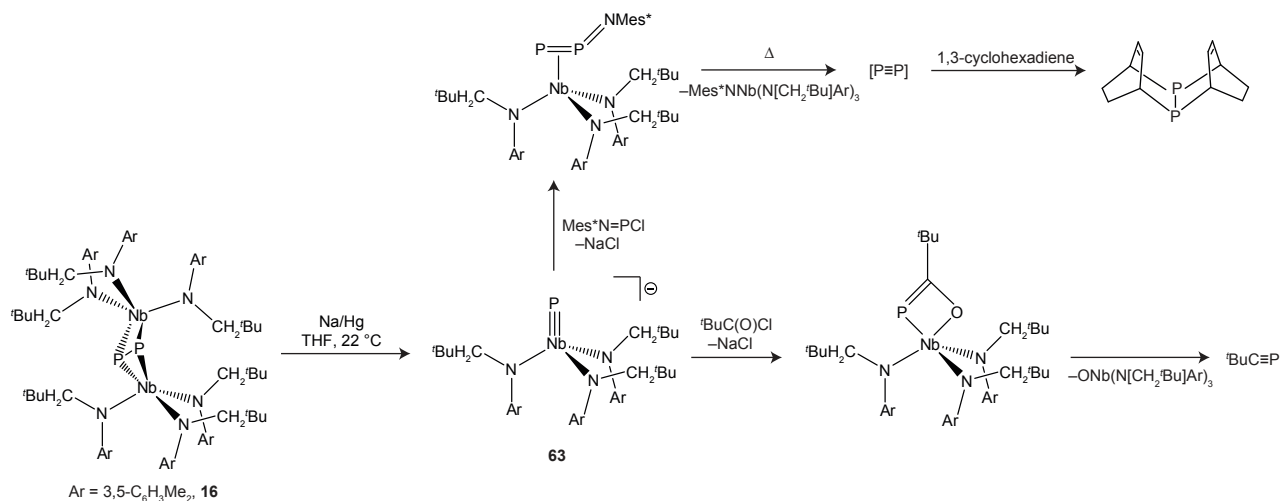
Scheme 3

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 reactions (Scheme 4). It was shown in 2004 that **63** gives rise to phosphaalkynes upon treatment with acid chlorides in a reaction that proceeds through a meta-stable NbPCO metallacycle. The niobium co-product 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 $C\equiv P$ 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=PCl to afford a diphosphaazide complex, $(\eta^2\text{-Mes*}N=P=P)Nb(N[CH_2{}^tBu]Ar)_3$ 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 $\mu_2:\eta^3,\eta^3\text{-}EP_2$ (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 $(P_3)M(triphos)$ (M = Co, Rh, Ir) and required the highly electrophilic reagents $[Me_3O][BF_4]$ or MeOTf to afford the
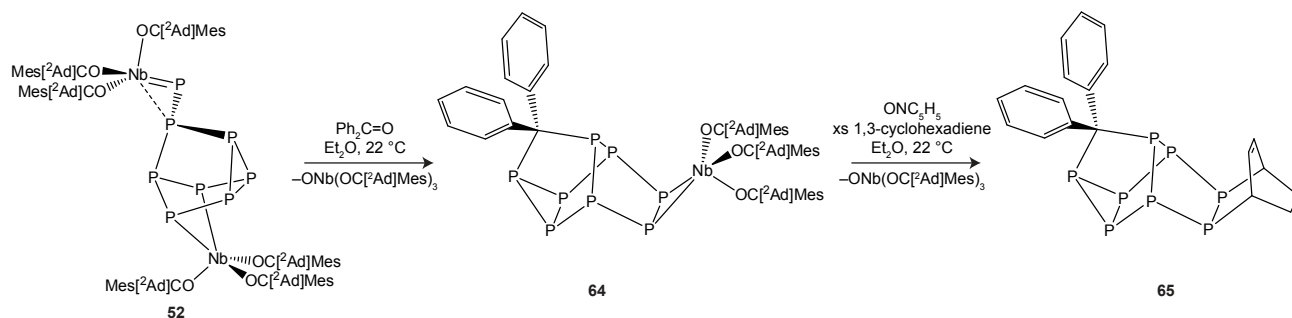
Scheme 4

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)$_5$P$_3$Nb(N[CH$_2^t$Bu]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] Though this anionic *cyclo*-P_3 complex was not obtained directly from P_4 activation, its reactivity provided inspiration for the study of the reaction chemistry of the anionic *cyclo*-P_3 molecule **23** which was derived from P_4 activation. Complex **23** was found to be capable of P_3^{3-} transfer to appropriate E^{3+} sources and this methodology provided the first selective synthesis of the tetraatomic interpnictide AsP$_3$ by reaction of **23** with 1 equiv of AsCl$_3$ with loss of NaCl and Cl$_2$Nb(ODipp)$_3$(THF) (Scheme 5).[39] The chemistry of AsP$_3$, which is synthetically available in two steps from P_4, is now being studied in detail.[39,93]

Scheme 5

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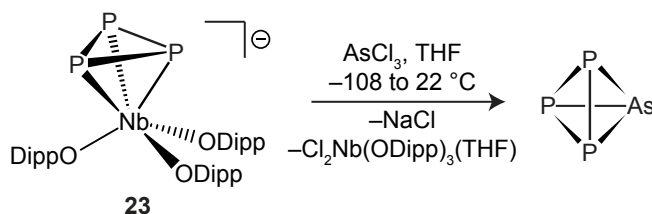
5.3 Functionalization and Transfer Chemistry of Polyphosphorus Ligands ($P_{\geq 4}$) Derived from P_4

The chemistry of P_4-derived polyphosphorus ligands (P_n, $n\geq 4$) in an ETM context has not been explored extensively. The sole example of transformation and transfer of P_n ligands ($n\geq 4$) from an ETM is confined to the chemistry of **52**. Notably, **52** was found to react with ketones (OCR_2) in a metathesis reaction to produce an equivalent of oxo $ONb(OC[^2Ad]Mes)_3$ and phosphaalkene complexes $R_2C=PP_7Nb(OC[^2Ad]Mes)_3$.[94] In cases where the ketone substituents R = aryl, the phosphaalkene complexes obtained via that phospha-Wittig reactivity were unstable with respect to a rearrangement that provided a saturated P_8 cluster containing an internalized R_2C unit (**64**, Scheme 6).[94] It was further found that the R_2CP_8 ligand could be transferred from the remaining niobium metal center by treatment with an equivalent of pyridine-*N*-oxide, ONC_5H_5, 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, $R_2CP_8(C_6H_8)$, **65**, was formed, isolated, and subjected to structural characterization (Scheme 6).[95]

Scheme 6

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 to 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 P_2 molecule, and the tetra-atomic AsP_3 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 P_4 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 P_4 transformation methodologies. With more than 30 years of chemistry documented between P_4 and ETM complexes, a library of P-ligands has emerged and general reactivity motifs have been revealed. The three strategies most commonly employed for P_4 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 P_4. 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 P_4 activa-

tion by an ETM complex versus n. Not surprisingly, formation of P_4 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 P_2 products. It is noteworthy, however, that nearly all of the P_2 complexes are bimetallic species, while most of the P_1 and P_3 complexes are monometallic in nature. One further observation is that P_n ligands with $n \geq 5$ occur far less frequently than ligands with $n \leq 4$. It is likely that these P_4 aggregation products are the result of kinetic trapping of highly reactive P_4 degradation products with themselves or with P_4 and cannot really be rationally predicted or anticipated. The relatively high frequency of P_6 ligands represents an exception here 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 help develop a greater understanding of that process.
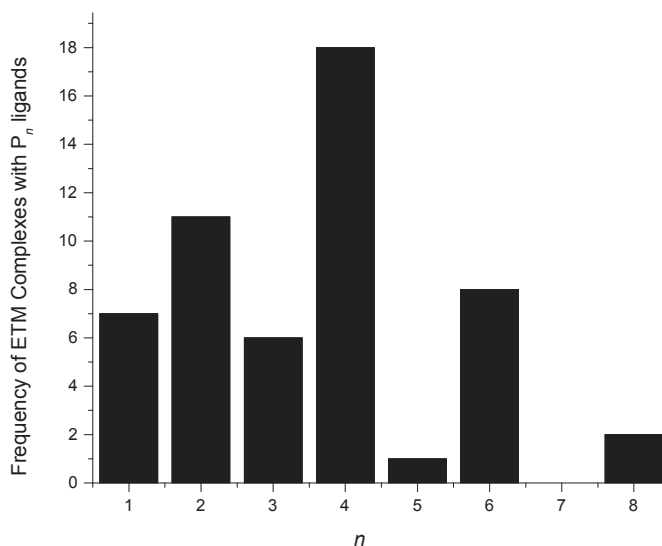

Figure 11: Frequency of P_n ligands formed from P_4 activation by ETM complexes as a function of n.

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 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 the potential goldmine 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.

Acknowledgement

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Biographies

Christopher C. Cummins, a.k.a. "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 Prof. 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 Prof. 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 triami-doamine 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≡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.

Figure 12: Christopher C. Cummins

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 P_4 reductive coupling by niobium enolate compounds, and subsequent synthesis of phosphorus-rich organic molecules. Moving from enolate to aryloxide supporting ligands, Brandi discovered an efficient *cyclo*-P_3 complex synthesis. The so-obtained anionic niobium *cyclo*-P_3 complex is effective as a P_3^{3-} transfer agent, leading in turn to the synthesis and isolation of AsP_3 as a pure substance. Brandi was an undergraduate at Caltech, where she co-authored papers in both physical and inorganic chemistry. Brandi grew up in Miami, Florida.

Figure 13: Brandi M. Cossairt

Nicholas Piro received his Ph.D. from MIT in June 2009. As a graduate student in the Cummins Group he studied the transformations of P_4-derived phosphorus ligands atop a niobium trisanilide platform. His research included the development of a solution phase source of a diatomic P_2 synthon that he later used in the synthesis of more phosphorus-rich coordination complexes, including

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cyclo-P_3 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 Prof. John Bercaw. Nick is currently a Miller Research Fellow at UC Berkeley.

Figure 14: Nicholas A. Piro