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Synthesis, structure, bonding and reactivity in clusters of the lower phosphorus oxides

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Contents

Abstract

The chemistry of transition metal complexes of the lower phosphorus oxides has been reviewed with emphasis on cluster complexes of phosphorus monoxide (PO). Synthetic routes to complexes containing PO and related ligands are described, and spectroscopic and structural data for known PO complexes are reported and discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Phosphorus monoxide; Phosphorus oxides; Clusters; Synthesis; Structure

1. Introduction

That there are fundamental differences in the structures and chemistry of the oxides of nitrogen and phosphorus is well documented in general text books [1]. The simple nitrogen oxides N_2O (**1**), NO (**2**) and NO_2 (**3**) (Chart 1) are easily synthesised, well characterised di- or triatomic molecules which find industrial and medical use and are ubiquitous in our environment as the products of combustion or biological processes [2]. All three of these entities are well known as ligands (NO, NO_2) or reagents (N_2O) in inorganic and organometallic chemistry although perhaps more frequently recognised as nitrosyl (NO^+), nitro (NO_2^-) and nitrito (ONO^-) ligands. The co-ordination chemistry of NO is particularly well developed in organometallic compounds since CO and NO^+ are isoelectronic and there are structurally and electronically related families of carbonyls and nitrosyls [3]. Nitric oxide is also an important biological ligand [4]. The more complex oxides N_2O_3 (**4**), N_2O_4 (**5**) and N_2O_5 (**6**) (Chart 1),

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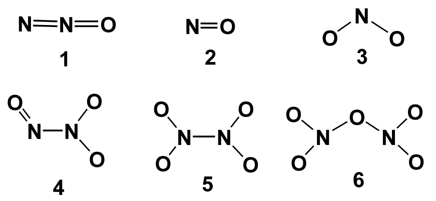


Chart 1. Oxides of nitrogen.

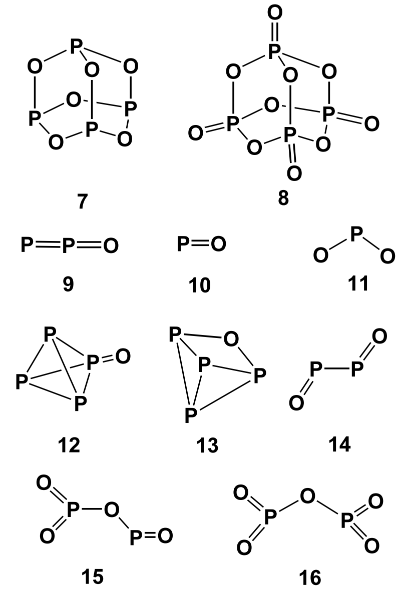


Chart 2. Oxides of phosphorus.

while less stable than their di- and triatomic counterparts, are nevertheless structurally well characterised [5].

In contrast, the stable and well known oxides of phosphorus are the cage-like molecules P_4O_6 (**7**) and P_4O_{10} (**8**) (Chart 2) which are themselves common laboratory reagents [6]. The direct phosphorus analogues of nitrogen oxides, namely the lower oxides of phosphorus P_2O (**9**), PO (**10**), and PO_2 (**11**), are observed only under carefully controlled experimental conditions such as in matrices, in vacuo or molecular beams and cannot be considered as chemical reagents in the normal sense of the term [7]. Nevertheless, these simple molecules and species derived from them have been well studied by spectroscopists and their molecular and electronic structures inferred [8,9], in large part because the species formed in the oxidation of elemental phosphorus have attracted scientific interest since the discovery by Boyle in 1680 of an internal green–white chemiluminescence which occurs when P_4 (white phosphorus) is oxidised [10,11].

Studies by Andrews [8], Davies [10], Hamilton [11], Hirota [12], and others have identified several species in the reactions of P_4 with oxygen atoms (Chart 2). These include a C_{3V} P_4O molecule (**12**) with a terminal P=O bond, the major initial product, P_2O (**9**) with a structure analogous to N_2O, an oxygen bridged isomer of P_4O (**13**), as well as the simple di- and triatomics PO (**10**) and PO_2 (**11**), the analogues of NO and NO_2. In addition, spectroscopic evidence for association products P_2O_2 (**14**), P_2O_4 (**15**) and stable P_2O_5 (**16**) has been adduced. Finally, it is worth noting that PO_2^-, the relative of nitrite NO_2^-, has been observed in solid KCl [13] and solid N_2 [14].

Of all of these lower oxides of phosphorus, PO has been particularly well investigated by chemical physicists since it is thought to be the dominant phosphorus-containing molecule in interstellar space. Thus vibrational and rotational spectroscopy has allowed for measurement of a stretching frequency for gaseous PO of 1220.25 cm^{-1} and a bond distance of 1.476370(15) Å [15,16]. Like NO, free PO is a radical having a valence electron configuration σ_p^2, π_x^2, π_y^2, π^{*1} with a single antibonding π electron giving a bond order of 2.5. Phosphorus monoxide differs significantly from NO in that low lying 3d orbitals on phosphorus are potentially available for bonding (vide infra).

Specifically, the development of PO co-ordination chemistry has been hindered by the fact that PO is not the stable oxide of phosphorus and no other suitable PO precursors exist analogous to the nitrosyl precursors NO^+ and NO_2^-. Indeed, the first phosphorus monoxide complex $[(\eta^5\text{-}C_5H^iPr_4)_2Ni_2W(CO)_4(\mu_3\text{-}PO)_2]$ (**18**) was reported by Scherer as recently as 1991 [17]. As a ligand, PO, like NO, is a net three electron donor. Although NO can also act as a net one-electron donor in bent nitrosyls [2b], this co-ordination mode has not been observed for PO. Nitrosyl ligands are also capable of a number of bridging bonding modes as illustrated in Chart 3. Most of these binding modes have now also been observed for PO. In a previous review [18] we discussed the two known routes to phosphorus monoxide, oxidation of naked phosphide and diphosphide ligands, and the hydrolysis of aminophosphinidenes. Since that review, there has been a significant increase in the number of PO and related compounds formed by both methods. This

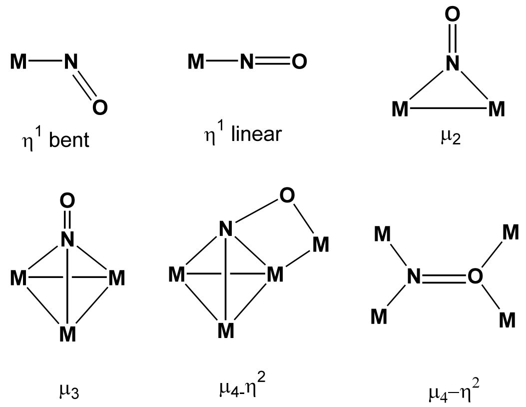


Chart 3. Nitrosyl bonding modes.

review will discuss the new PO complexes, their spectroscopic and structural properties, and their reactivity.

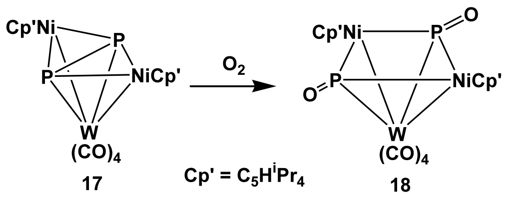
2. Synthesis of phosphorus monoxide and related complexes

2.1. Oxidation of phosphides by oxygen and heavier chalcogens

The first route to phosphorus monoxide complexes that will be discussed is the direct oxidation of a bare phosphorus ligand, either in the form of a phosphide (P) or a diphosphide (P_2) entity. This route was used to form the first phosphorus monoxide cluster complex $[(\eta^5\text{-C}_5\text{H}^i\text{Pr}_4)_2\text{Ni}_2\text{W(CO)}_4(\mu_3\text{-PO})_2]$ (**18**) which resulted from oxidation of the η^2-P_2 ligand in $[(\eta^5\text{-C}_5\text{H}^i\text{Pr}_4)_2\text{Ni}_2\text{W(CO)}_4(\eta^2\text{-P}_2)]$ (**17**) with molecular oxygen (Scheme 1) [17,19]. At the time of writing of our previous account [18], this was the only example of a PO complex formed by this method. Significant advances in the chemistry of bare phosphorus ligands [20] have provided precursors for the generation of PO ligands.

The most common application of the oxidation methodology is in the formation of μ_3-PO and related species by oxidation of μ_3-phosphide complexes. Chart 4 illustrates examples of complexes formed this way. In studies on the carbyne-phosphide cluster $[\text{Cp}'_3\text{Co}_3(\mu_3\text{-CCMe}_3)(\mu_3\text{-P})]$ (**19**, $\text{Cp}' = \text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{P}^t\text{Bu}_2$), reactions were carried out with elemental sulphur and atmospheric oxygen, resulting in oxidation of both the pendant phosphine arms and the μ_3-phosphide ligand to form the clusters $[\text{Cp}'_3\text{Co}_3(\mu_3\text{-CCMe}_3)(\mu_3\text{-PO})]$ (**20**, $\text{Cp}' = \text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{P(O)}^t\text{Bu}_2$) and $[\text{Cp}'_3\text{Co}_3(\mu_3\text{-CC}Me_3)(\mu_3\text{-PS})]$ (**21**, $\text{Cp}' = \text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{P(S)}^t\text{Bu}_2$). The mixed cluster $[\text{Cp}'_3\text{Co}_3(\mu_3\text{-CCMe}_3)(\mu_3\text{-PO})]$ (**22**, $\text{Cp}' = \text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{P(S)}^t\text{Bu}_2$), in which the phosphines are sulphurated and the phosphide ligand is oxidised, was also isolated from the reaction with sulphur [21]. Of these clusters, compound **22** has been structurally characterised. The selenium analogue $[\text{Cp}'_3\text{Co}_3(\mu_3\text{-CC}Me_3)(\mu_3\text{-PSe})]$ (**23**, $\text{Cp}' = \text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{P(Se)}^t\text{Bu}_2$) has also been synthesised and structurally characterised [22].

The molybdenum and tungsten clusters $[\text{Mo}_{(3-n)}\text{W}_n\text{Cp}_3(\text{CO})_6(\mu_3\text{-P})]$ (**24**–**27**, $n = 0$–3) react similarly with atmospheric oxygen to form the corresponding PO clusters $[\text{Mo}_{(3-n)}\text{W}_n\text{Cp}_3(\text{CO})_6(\mu_3\text{-PO})]$ (**28**–**31**, $n = 0$–3) [23]. The same phosphide clusters can also be oxidised using elemental sulphur to form the PS clusters $[\text{Mo}_{(3-n)}\text{W}_n\text{Cp}_3(\text{CO})_6(\mu_3\text{-PS})]$ (**32**–**35**) [24]. The reactions with sulphur are notable because they are reversible. The PS clusters lose sulphur in the absence of excess S_8.



Scheme 1.

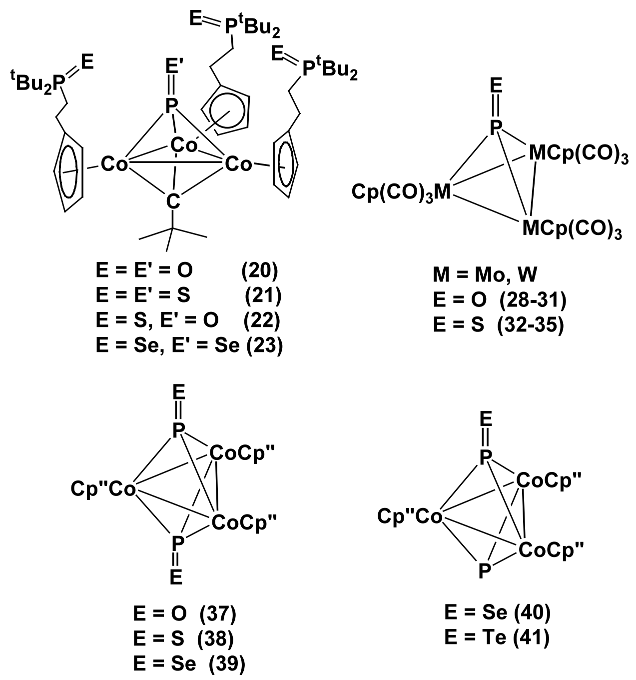
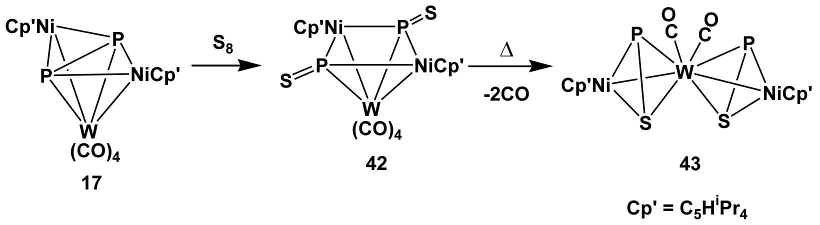


Chart 4. μ_3-Phosphorus monoxide and related complexes formed by oxidation of μ_3-phosphide complexes.

The bis-phosphorus monoxide cluster $[\{\text{Cp}''\text{Co}\}_3(\mu_3\text{-PO})_2]$ (**37**, $\text{Cp}'' = \text{C}_5\text{H}_3^t\text{Bu}_2\text{-1,3}$) can be formed by oxidation of the bis-phosphide cluster $[\{\text{Cp}''\text{Co}\}_3(\mu_3\text{-P})_2]$ (**36**) [25]. In the reactions with the heavier chalcogens, an interesting trend is observed. As in the reaction with oxygen, oxidation with sulphur results in sulphurisation of both phosphide ligands to form $[\{\text{Cp}''\text{Co}\}_3(\mu_3\text{-PS})_2]$ (**38**). Reaction with selenium, however, results in a mixture of the diselenated $[\{\text{Cp}''\text{Co}\}_3(\mu_3\text{-PSe})_2]$ (**39**) and mono-selenated $[\{\text{Cp}''\text{Co}\}_3(\mu_3\text{-PSe})(\mu_3\text{-P})]$ (**40**) products while tellurium gives only the mono-tellurated product $[\{\text{Cp}''\text{Co}\}_3(\mu_3\text{-PTe})(\mu_3\text{-P})]$ (**41**).

Oxidation by sulphur has also been used to form the sulphur analogue of the first PO cluster, $[(\eta^5\text{-C}_5\text{H}^i\text{Pr}_4)_2\text{Ni}_2\text{W(CO)}_4(\mu_3\text{-PS})_2]$ (**42**) which is structurally analogous to $[(\eta^5\text{-C}_5\text{H}^i\text{Pr}_4)_2\text{Ni}_2\text{W(CO)}_4(\mu_3\text{-PO})_2]$ (**18**), containing two PS ligands triply bridging three metal centres, but having only two metal–metal bonds. However, heating the PS analogue results in CO loss and transformation to a side-bound PS co-ordination mode to form $[(\eta^5\text{-C}_5\text{H}^i\text{Pr}_4)_2\text{Ni}_2\text{W(CO)}_2(\mu_2\text{-}\eta^2\text{-PS})_2]$ (**43**, Scheme 2) [26]. Here the P–S ligand functions as a 5-electron donor so that the cluster with two Ni–W bonds is electron precise. This co-ordination mode is unknown for PO, but a side-bound PS ligand was

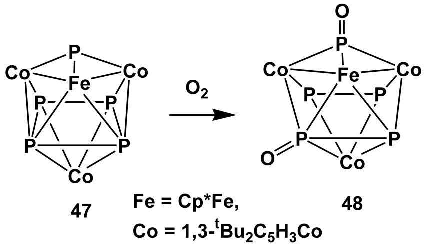


Scheme 2.

previously proposed for the structure of $[\{CpFeCO\}\{\mu\text{-}\eta^2\text{-}PS\}\{\mu\text{-}CO(CpFe(CO)_2)\}]$ (**45**) which was formed via photolytic decarbonylation of the triply bridging PS compound $\{\mu\text{-}CO(CpFeCO)_2\}\{CpFe(CO)_2\}P{=}S$ (**44**) (Scheme 3) [27]. Also reported is the related compound $\{CpFe(CO)_2\}_3P{=}S$ (**46**) in which the PS moiety forms a bridge between three non-bonded metal atoms. This binding mode has not been observed for PO. Compound **44** was the first structurally characterised PS complex, while the structures of **45** and **46** were deduced from spectroscopic measurements.

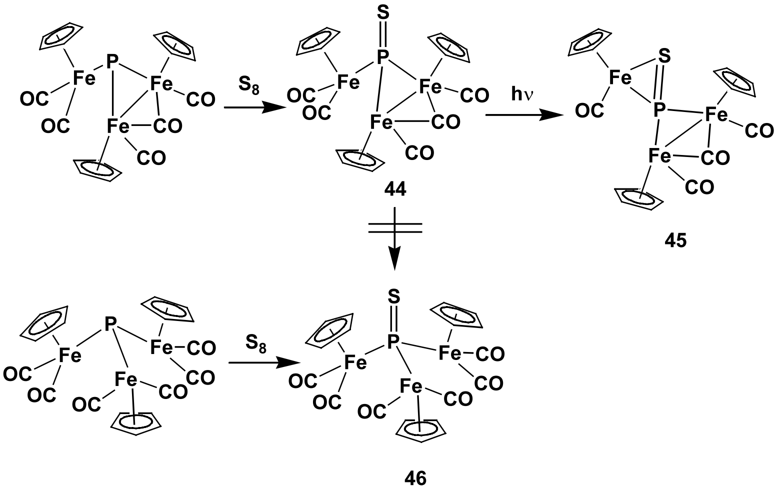
The novel cluster complex $[\{Cp^*Fe\}\{Cp''Co\}_2(P_2O)(PO)(P_2)]$ (**48**, $Cp'' = 1{,}3\text{-}{}^tBuC_5H_3$), which contains a μ_3-PO ligand as well as P_2 and a P_2O ligands, reported by Scherer et al. was formed by oxidation of the cluster $[\{Cp^*Fe\}\{Cp''Co\}_2(P_4)(P)]$ (**47**) which has a phosphide (P) and a P_4 ligand (Scheme 4) [28]. This is the first example of a P_2O ligand structurally analogous to N_2O, and differs from the isomeric POP ligand in the cluster $[Ru_4(CO)_{13}(\mu_3\text{-}POP\text{-}\mu_3)Ru_4(CO)_{13}]$ (**89**) described later.

In related work, the clusters $[\{Cp^RCo\}_4P_4]$ (**49**, $Cp^R = C_5H_4^tBu$; **50**, $Cp^R = C_5H_3^tBu_2\text{-}1{,}3$) were oxidised with sulphur or selenium to form clusters with various degrees of oxidation depending on the conditions and the steric bulk of the substituted Cp ligand as shown in Scheme 5 [29]. Oxidation of the cluster containing the less bulky $C_5H_4^tBu$ with sulphur or selenium results in oxidation of three out of four phosphide ligands forming $[\{Cp^RCo\}_4(PS)_3(P)]$ (**51**) and $[\{Cp^RCo\}_4(PSe)_3(P)]$ (**52**). With sulphur, the fourth phosphide ligand can also be oxidised by varying the conditions to form $[\{Cp^RCo\}_4(PS)_4]$ (**53**). When the more bulky ligand $C_5H_3^tBu_2\text{-}1{,}3$ is used, oxidation is limited to two of the phosphide ligands, forming $[\{Cp^RCo\}_4(PS)_2(P)_2]$ (**54**) and $[\{Cp^RCo\}_4(PSe)_2(P)_2]$ (**55**).

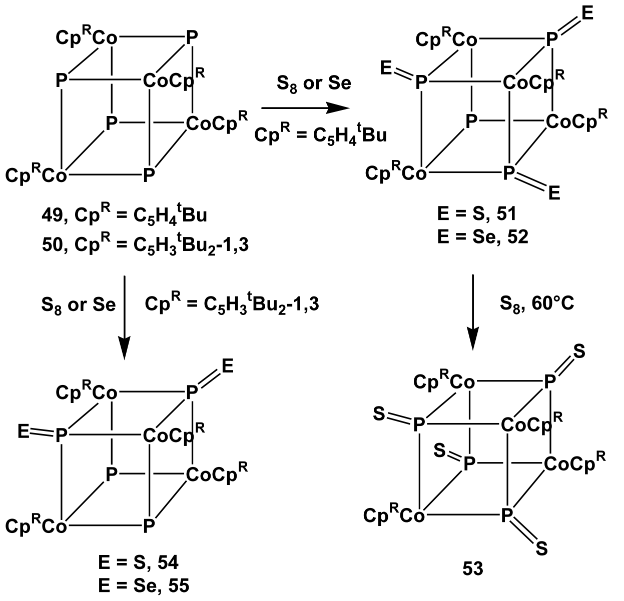


Scheme 4.

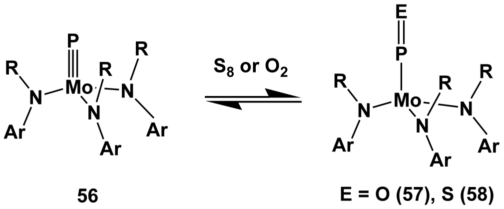
Perhaps the most significant application of this methodology is the formation of the only known terminal phosphorus monoxide complex. The complex $[PMo(N(R)Ar)_3]$ (**56**, $R = C(CD_3)_3Me$, $Ar = C_6H_3Me_2\text{-}3{,}5$) can be oxidised with dimethyldioxirane to form $[(OP)Mo(N(R)Ar)_3]$ (**57**) (Scheme 6). Remarkably, this oxidation reaction is reversible. In solution, the PO complex gradually reverts to the terminal phosphide complex, suggesting perhaps that strong Mo–P multiple bonding in the terminal phosphide is preferred over weaker Mo=P and P=O bonding [30]. The report of the



Scheme 3.



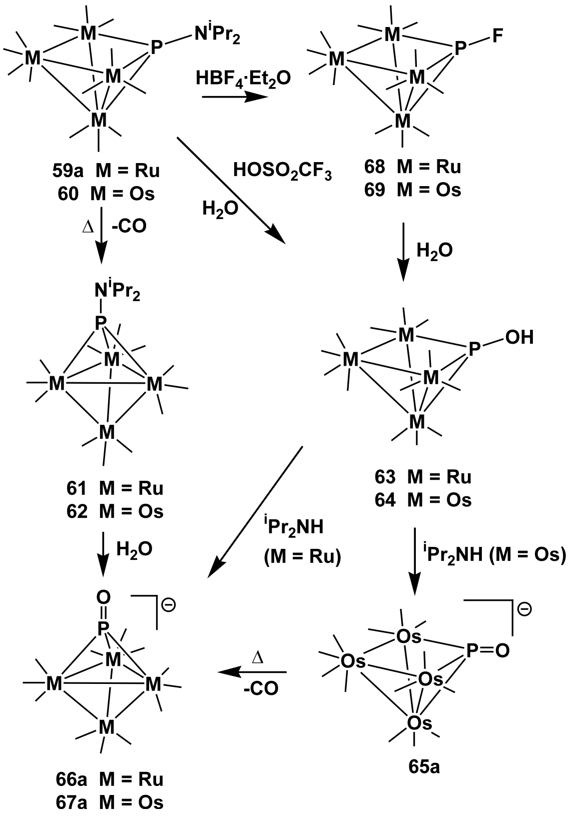
Scheme 5.



Scheme 6.

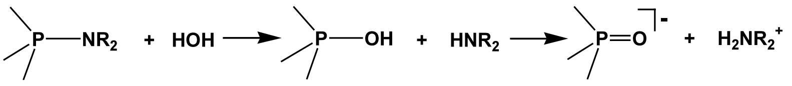
terminal PO complex was preceded by a report of the analogous terminal PS complex [(SP)Mo(N(R)Ar)$_3$] (**58**) [31]. Although reported in 1995 and 1997 these compounds remain the only examples of terminal PS and PO ligands to be characterised.

2.2. Hydrolysis of P–N bonds



Scheme 7.

In our previous account [18], we discussed a new route to phosphorus monoxide clusters which involves the acid hydrolysis of aminophosphinidene ligands. This route was discovered serendipitously when the anionic phosphorus monoxide complex [Ru$_4$(CO)$_{12}$(μ_3-PO)][H$_2$-N^{i}Pr$_2$] (**66a**) was formed from [Ru$_4$(CO)$_{12}$(μ_3-PN^{i}Pr$_2$)] (**61**) during an attempted chromatographic separation on silica gel [32]. A more rational route involving treatment with strong acid and hydrolysis, followed by deprotonation was then developed and used to synthesise Ru$_4$ and Os$_4$ clusters containing triply bridging phosphorus monoxide ligands [33].



The formation of the PO clusters in this synthetic strategy likely involves protonation at the nitrogen atom of the aminophosphinidene followed by nucleophilic displacement at the phosphorus by OH$^-$, formation of the hydroxyphosphinidene complex, and finally deprotonation by the secondary amine produced in the hydrolysis.

The chemistry described is summarised in Scheme 7. Two series of M$_4$ substituted-phosphinidene clusters have been investigated, the *nido* M$_4$(CO)$_{13}$PR clusters and the *closo* M$_4$(CO)$_{12}$PR clusters. In the *closo* M$_4$(CO)$_{12}$PR complexes, hydrolysis is facile and only the anionic PO complexes were isolated. However, in the *nido* M$_4$(CO)$_{13}$PR series, the hydroxyphosphinidene complexes [Ru$_4$(CO)$_{13}$(μ_3-POH)] (**63**) and

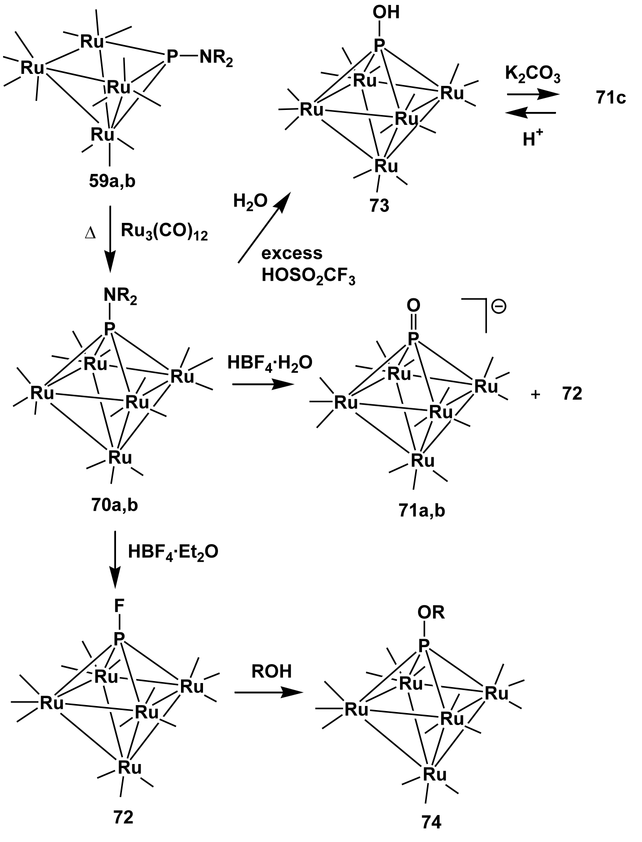
$[Os_4(CO)_{13}(\mu_3\text{-}POH)]$ (**64**) which are presumed intermediates in the formation of PO complexes were successfully isolated. Deprotonation then leads to the PO clusters. When $M = Ru$, deprotonation is accompanied by decarbonylation, leading directly to the *closo* $[Ru_4(CO)_{12}(\mu_3\text{-}PO)]^-$ anion (**66**). When $M = Os$, the carbonyl is less labile, allowing for isolation of the *nido* cluster $[Os_4(CO)_{13}(\mu_3\text{-}PO)]^-$ (**65**) as well as the *closo* $[Os_4(CO)_{12}(\mu_3\text{-}PO)]^-$ (**67**).

A complicating factor in these reactions is the formation of fluorophosphinidene clusters, which result from fluoride abstraction from the BF_4^- counterion if tetrafluoroboric acid is used. This discovery itself led to the synthesis of the first fluorophosphinidene clusters $[M_4(CO)_{13}(\mu_3\text{-}PF)]$ (**68**, $M = Ru$; **69**, $M = Os$) [18] However, hydrolysis of the fluorophosphinidene ligand leads to the hydroxyphosphinidene, and ultimately to a phosphorus monoxide ligand. The fluorophosphinidene cluster can be avoided through the use of trifluoromethanesulfonic (triflic) acid in the hydrolysis step.

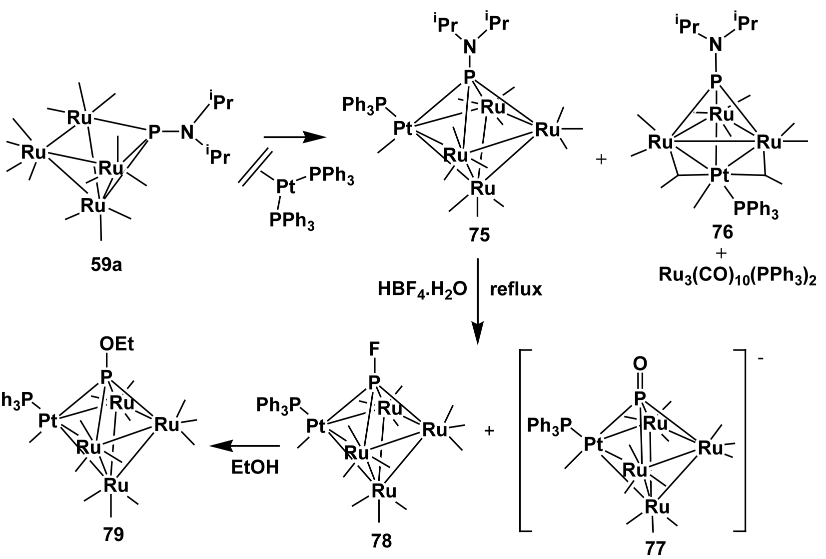
Since the initial account describing only the second known PO complex, developments in our laboratories using the P–N bond cleavage methodology have led to many new phosphorus monoxide and related clusters. This is in principle a much more versatile methodology for accessing PO complexes since phosphide or $\eta^2\text{-}P_2$ clusters are still relatively rare and difficult to access. In contrast $\mu\text{-}PNR_2$ clusters where R is a bulky electron releasing substituent such as $CH(CH_3)_2$ or C_6H_{11} are readily available via the reaction of a dichlorophosphine Cl_2PNR_2 with a carbonyl dianion. On the other hand, a limitation of the methodology is that the PO clusters generated in this way are anionic. Protonation of such anions generally occurs at the oxygen atom of the PO ligand, affording the neutral hydroxyphosphinidene compound.

An important extension of this methodology led to the formation of the first clusters containing μ_4-phosphorus monoxide ligands [34]. The molecule $[Ru_5(CO)_{15}(\mu_4\text{-}PO)][R_2NH_2]$ (**71a**, $R = Pr^i$, **71b**, $R =$ Cy) was accessed via the acid catalysed hydrolysis of $[Ru_5(CO)_{15}(\mu_4\text{-}PNR_2)]$ (**70a**, **b**). The latter aminophosphinidene clusters **70a**, **b**, which consist of a square pyramidal Ru_5 array with a phosphinidene ligand occupying an octahedral vertex, were synthesised from the 62-electron *nido* clusters $[Ru_4(CO)_{13}(\mu_3\text{-}PNR_2)]$ (**59a**, **b**) by capping the open Ru_3P face with a two electron donor $Ru(CO)_3$ fragment as shown in Scheme 8. One carbonyl group is lost from the $Ru(CO)_4$ fragment in this process. Direct formation of the phosphorus monoxide cluster via an analogous capping reaction on the cluster $[Ru_4(CO)_{13}(\mu_3\text{-}PO)]^-$ was not possible because this *nido* cluster readily loses CO to afford the *closo* 60e cluster $[Ru_4(CO)_{12}(\mu_3\text{-}PO)]^-$ (**66**). The fluorophosphinidene cluster $[Ru_5(CO)_{15}(\mu_4\text{-}PF)]$ (**72**) was also formed as a side product in the hydrolysis of **70** if tetrafluoroboric acid is used, and can be formed directly using anhydrous tetrafluoroboric acid. Of particular note in the above reaction sequences is the fact that the quadruply bridging hydroxyphosphinidene cluster $[Ru_5(CO)_{15}(\mu_4\text{-}POH)]$ (**73**) was not isolated from any of the reactions. This observation can be attributed to the relatively high acidity of the cluster acid **73** and the presence of amine in the reaction mixture. However, **73** can be generated by direct protonation of $[Ru_5(CO)_{15}(\mu_4\text{-}PO)][K]$ (**71c**) with triflic acid or by use of an excess of triflic acid in the hydrolysis reaction. In contrast to the reactions of NO complexes, electrophilic attack at oxygen does not appear to lead to cleavage of the PO bond. The μ_4-hydroxyphosphinidene cluster is acidic and readily reverts to the PO anion in the presence of base. Measurements of the acidities of these POH clusters relative to organometallic acids are currently underway. What is clear is that these new organometallic acids, which possess a strongly electron withdrawing cluster carbonyl centre of the $[M_4(CO)_{12-13}]$ or $[M_5(CO)_{15}]$ type, likely rank in acidic strength with mineral acids such as H_3PO_4 ($pK_1 = 2.15$) and are significantly stronger than organometallic hydrides such as $HCo(CO)_4$ and $H_2Fe(CO)_4$ [35].

The PF cluster **72** is also susceptible to nucleophilic attack, undergoing alcoholysis in its reactions with methanol, ethanol or isopropanol to form the alkox-



Scheme 8.



Scheme 9.

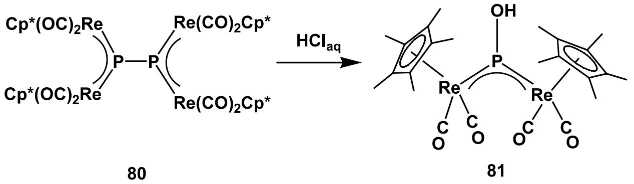
yphosphinidene clusters $[Ru_5(CO)_{15}\{POR\}]$ (**74**, R = Me, Et, ^{i}Pr). Alkoxyphosphinidene complexes are also accessible via alkylation of the anionic PO complexes with methyl trifluoromethanesulfonate.

Capping reactions have also been used advantageously in the formation of mixed metal clusters containing phosphorus monoxide or related substituted phosphinidenes. Thus, reaction of the 62-electron *nido* cluster $[Ru_4(CO)_{13}(\mu_3\text{-}PN^{i}Pr_2)]$ (**59a**) with the labile Pt(0) reagent $[(\eta^2\text{-}C_2H_4)Pt(PPh_3)_2]$ which delivers a $d^{10}\text{-}PtL_2$ fragment results in the capping of this face to form the mixed Pt–Ru cluster $[Ru_4(CO)_{12}Pt(CO)\text{-}PPh_3(\mu_4\text{-}PN^{i}Pr_2)]$ (**75**) along with the side product $[Ru_3Pt(\mu_3\text{-}PN^{i}Pr_2)(\mu\text{-}CO)_2(CO)_8(PPh_3)]$ (**76**) (Scheme 9). As mentioned above, a direct route to the PO cluster via a capping reaction is not available because of the lack of a suitable *nido* precursor. Thus, acid hydrolysis was used to form $[Ru_4(CO)_{12}Pt(CO)PPh_3(\mu_4\text{-}PO)][^{i}Pr_2NH_2]$ (**77**). If $HBF_4 \cdot Et_2O$ is used in the hydrolysis reaction, the fluorophosphinidene cluster $[Ru_4(CO)_{12}Pt(CO)PPh_3(\mu_4\text{-}PF)]$ (**78**) is observed as a side product. The cluster **78** can also be formed by the direct capping reaction of $[Ru_4(CO)_{13}(\mu_3\text{-}PF)]$ (**68**). The mixed metal alkoxyphosphinidene cluster $[Ru_4(CO)_{12}\text{-}Pt(CO)PPh_3(\mu_4\text{-}POEt)]$ (**79**) is also readily formed by reaction of the PF cluster (**77**) with ethanol.

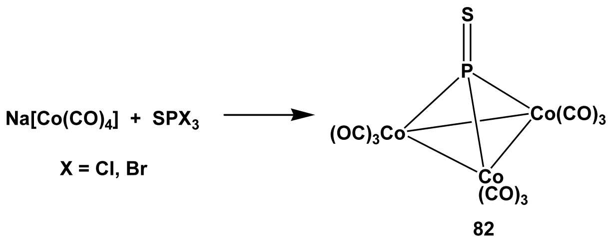
2.3. Related complexes formed by other routes

To date, the two routes described above are the only ones that have been successfully used to synthesise PO complexes. However, several related compounds have been formed by other routes. For example, the μ_2-hydroxyphosphinidene complex $[\{Cp^*Re(CO)_2\}_2(\mu_2\text{-}POH)]$ (**81**) was formed via acid hydrolysis of the P–P bond in $[\{Cp^*Re(CO)_2\}_4(\mu_4\text{-}\eta^1,\eta^1,\eta^1,\eta^1\text{-}P_2)]$ (**80**) (Scheme 10) [36]. Compound **81** is to our knowledge the only known doubly bridging hydroxyphosphinidene complex and might be a potential precursor of a doubly bridging PO ligand. No reports of deprotonation reactions of **81** have yet appeared.

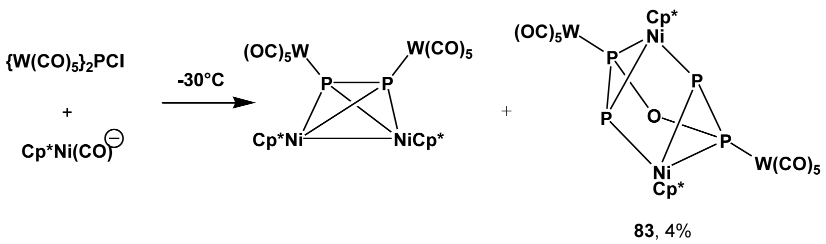
One possible route to PO complexes involves displacement of chloride from $O{=}PCl_3$ with an appropriate transition metal anion. Thus far this route has not been successfully applied to the formation of PO complexes. However, in a report [37] which predates the first PO complexes by many years, $S{=}PCl_3$ was used to form the complex $[\{(CO)_3Co\}_3(\mu_3\text{-}PS)]$ (**82**, Scheme 11). Unfortunately, compound **82** was not structurally characterised and the proposed structure was based solely upon infrared spectroscopy and microanalysis. In retrospect and with the knowledge we now have of μ_3-PO and



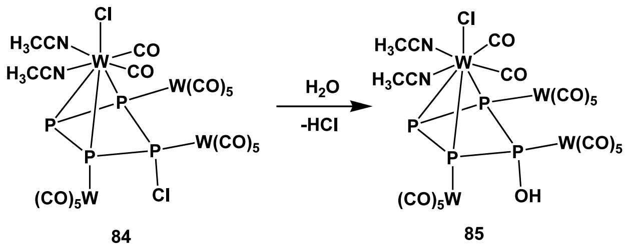
Scheme 10.



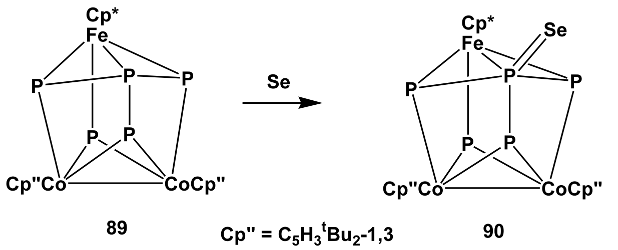
Scheme 11.



Scheme 12.



Scheme 13.



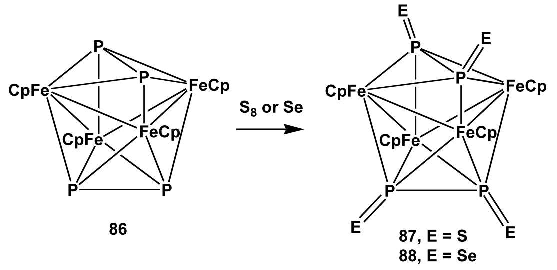
Scheme 15.

μ_3-PS ligands the formulation of this 48 electron cluster is likely correct.

The cluster [{W(CO)$_5$}$_2${Cp*Ni}$_2${η^1,η^3,η^3,η^1-P_2OP_2}] (**83**, Scheme 12) was formed as a minor side product in the reaction of {W(CO)$_5$}$_2$PCl with Cp*Ni(CO)$^-$ and contains an unusual PPOPP ligand which forms an η^1 interaction with each of two tungsten centres, and an η^3 interaction with each of two nickel centres [38]. This ligand is a structural isomer of the unstable phosphorus oxides P_4O (**12** and **13**) shown in Chart 2.

A similar phosphorus-rich ligand containing a hydroxy group was formed via hydrolysis of the P_4Cl ligand in [{W(CO)$_5$}$_3${(CH_3CN)$_2$(CO)$_2$WCl}{μ_4-η^3,η^1,η^1,η^1-P_4Cl}] (**84**) to form [{W(CO)$_5$}$_3${W-CO)$_2$Cl(CH_3CN)$_2$}{μ_4-η^3,η^1,η^1,η^1-P_4OH}] (**85**) (Scheme 13) [39]. The P_4OH ligand in this complex consists of a distorted square P_4 unit bearing a terminal OH group with η^3 co-ordination to one W centre, and η^1 co-ordination to three others.

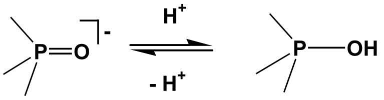
The oxidation of the P_2 ligands in the dodecahedral cluster [Cp_4Fe_4(μ_4-P_2)$_2$] (**86**) with sulphur or selenium led to the clusters [Cp_4Fe_4(μ_4-P_2E_2)$_2$] (**87**, E = S; **88**, E = Se) (Scheme 14) which contain E=P–P=E ligands, structurally analogous to the unstable phosphorus oxide O=P–P=O (**14**, Chart 2) [40]. Similarly, reaction of the cluster [{Cp*Fe}{Cp″Co}$_2$(P_4)(P)] (**89**) (Cp″ = $C_5H_3^tBu_2$-1,3) with selenium led to [{Cp*Fe}-{Cp″Co}$_2$(P_4Se)(P)] (**90**, Scheme 15) which contains a P_4Se ligand, analogous to the unstable phosphorus oxide P_4O (**12**, Chart 2) [25a].



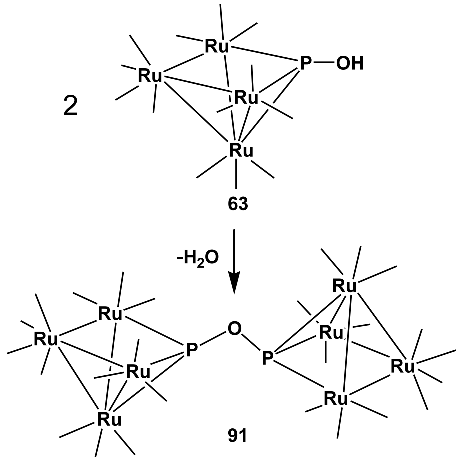
Scheme 14.

3. Reactions of phosphorus monoxide complexes

As alluded to above, phosphorus monoxide complexes are related to hydroxyphosphinidene complexes via Brønsted acid–base chemistry:

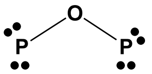


A clear structural parallel can be drawn between the



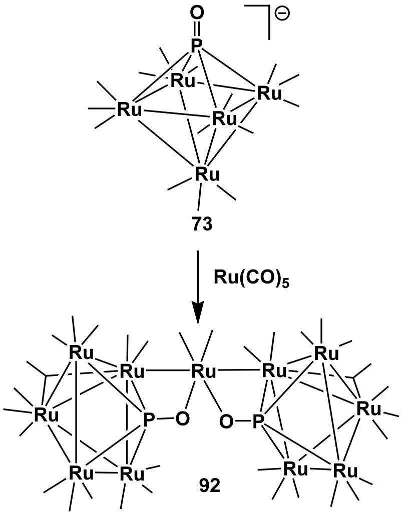
Scheme 16.

clusters and phosphorus oxy-acids. Indeed clusters such as **66** and **67** which have a μ_3-PO ligand could be described as trimetallated phosphine oxides, and corresponding hydroxyphosphinidene complexes such as **63** and **64** might be related to a monobasic organophosphorus acid $R_2P(O)OH$. In both cases the phosphorus atom is tetrahedrally coordinated. The analogy is reinforced by the dehydration reaction shown in Scheme 16 in which two molecules of the hydroxyphosphinidene cluster $[Ru_4(CO)_{13}(POH)]$ (**63**) eliminate water to form the cluster $[Ru_4(CO)_{13}(\mu_3\text{-POP-}\mu_3)Ru_4(CO)_{13}]$ (**91**) which contains an unprecedented POP ligand [41].

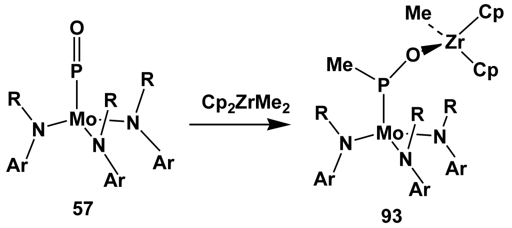


The POP ligand in **91** is a structural isomer of the P_2O molecule identified in beams and matrices (see Chart 2), and can be considered as an oxide of P(I) in which there are formally two lone pairs on each phosphorus atom. The POP ligand in **91** thus is able to donate eight electrons, four to each metal cluster, and acts much like two phosphinidene ligands with an oxygen bridge. This cluster can be considered as an organometallic analogue of inorganic acid anhydrides such as pyrophosphoric acid (the anhydride of phosphoric acid). Compound **91** can also be formed by elimination of HN^iPr_2 in the reaction of $[Ru_4(CO)_{13}(POH)]$ (**63**) with $[Ru_4(CO)_{13}(P\text{-}N^iPr_2)]$ (**59a**).

Another novel reaction of PO containing clusters is shown in Scheme 17. The thermal reaction of $[Ru_5(CO)_{15}(\mu_4\text{-PO})][^iPr_2NH_2]$ (**71a**) with $[Ru(CO)_5]$ led to the unusual cluster $[\{Ru_5(CO)_{15}(\mu_5\text{-}\eta^2\text{-PO})\}_2Ru(CO)_2]$ (**92**) [42]. An X-ray structural determination of **92** revealed two $Ru_5(CO)_{15}PO$ moieties bridged by an $Ru(CO)_2$ unit via oxygen co-ordination to the central Ru. Clearly from the reaction scheme, an oxidation–reduction process is occurring although it is not clear what the oxidant is. Unfortunately, this reaction has been difficult to consistently reproduce and as yet remains unreported. However, it does suggest the intriguing possibility of using phosphorus monoxide clusters as bulky oxygen based ligands for other metals, a concept we are currently investigating. Cummins and co-workers reported a related observation in the reaction of the terminal PO complex $[OPMo(N(R)Ar)_3]$ (**57**, $R = C(CD_3)_3Me$, $Ar = C_6H_3Me_2$-3,5) with Cp_2ZrMe_2 to form $[Cp_2Zr(Me)OP(Me)Mo(N(R)Ar)_3]$ (**93**) (Scheme 18). In this case, co-ordination of the PO oxygen atom to oxophilic zirconium was accompanied by methyl transfer from zirconium to phosphorus [30].



Scheme 17.



Scheme 18.

4. X-ray structural, spectroscopic, and theoretical studies

The bonding of PO ligands to transition metal fragments is interesting for several reasons: (i) PO is the heavy congener of NO and analogies between the bonding of these two diatomic molecules to transition metals would be expected; (ii) differences in M/PO and M/NO bonding might arise as a result of the availability of 3d orbitals in PO which are absent in NO and the possibility of higher co-ordination numbers at phosphorus in complexes of PO; (iii) there is a growing recognition that the chemistry of phosphorus may more closely resemble that of its diagonal neighbour carbon in the periodic table than that of nitrogen in its own Group 15 [43]. Hence comparisons of M/CO, M/PO and M/NO bonding are intriguing.

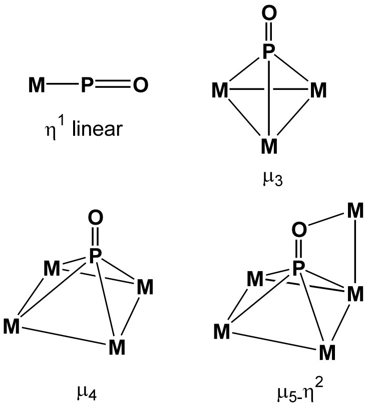


Chart 5. Phosphorus monoxide bonding modes.

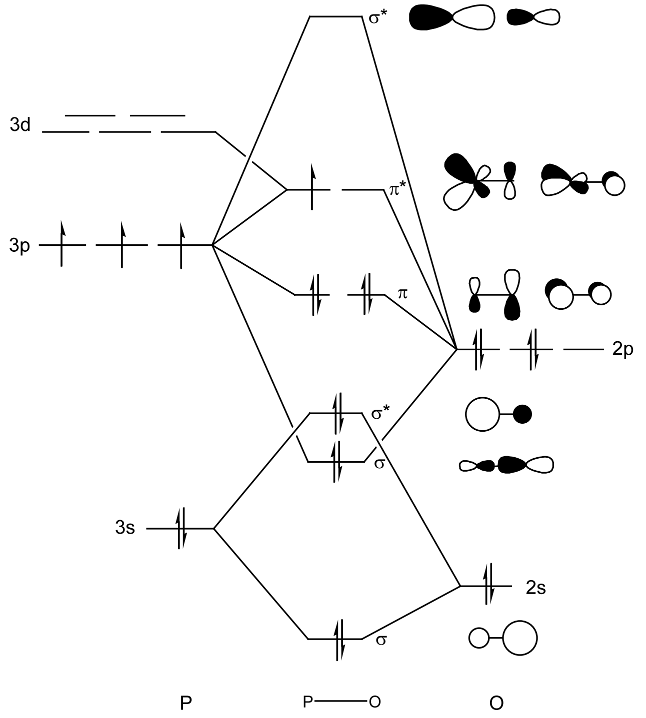


Fig. 1. A schematic representation of the molecular orbital diagram of PO.

Chart 5 shows observed bonding modes for PO. One notable difference between PO and NO bonding modes is the observation of μ_4-PO co-ordination, which is unknown for NO, and illustrates the possible involvement of phosphorus 3d orbitals. The other important difference is the absence of μ_2-PO co-ordination and bent terminal PO co-ordination. The absence of bent terminal PO co-ordination, in which the ligand would formally be PO^-, is not surprising, given the instability of low valent phosphorus. The lack of μ_2-PO complexes is more surprising and we feel that the synthesis of such compounds should be possible.

The electronic structures of PO and PO complexes have been studied using density functional theory calculations [44]. A schematic representation of the electronic structure of PO is shown in Fig. 1. Some important differences between the electronic properties of PO and isoelectronic NO were revealed by the calculations. For PO the s- and p-types σ orbitals do not separate into a pair of strongly antibonding and strongly bonding components, but are better described as sp hybrid orbitals of mainly non-bonding character. The nature of these orbitals is sensitive to the overlap between atomic orbitals and consequently to the PO bond length and the bonding character of the highest σ orbital increases with increasing PO bond length. Another key difference between PO and NO is the availability of the low lying 3d orbital of phosphorus. The π* orbital of NO is strongly antibonding. The π* of PO has a weaker antibonding character than that of NO due to mixing in of the d orbital. A consequence of these differences is that the strength of the PO bond is expected to be much less affected by either σ-donation or π-back donation upon interaction with a metal centre compared to NO.

An orbital interaction diagram for the model terminal PO complex $(NH_2)_3MoPO$ is shown in Fig. 2. The interaction of PO with the metal fragment is dominated by the π-interaction between the partially occupied PO π* orbital and the d_{xz} and d_{yz} metal orbital. The σ donation of the PO σ* orbital to the empty metal $d_z{}^2$ orbital is less significant. The interaction of PO with the metal clusters is more complex, but is also dominated by π interactions. As an example, the orbital interaction diagram for $[Ru_4(CO)_{12}(\mu_3\text{-PO})]^-$ is shown in Fig. 3. Unlike in the terminal PO complex, there is no single strongly stabilised orbital. Instead, filled (30E) and partly filled (31E) orbitals are stabilised by interaction with the PO π* orbital. Electrostatic effects also lead to a significant stabilisation of the non-bonding orbital $22A_1$.

4.1. Infrared spectroscopy of PO complexes

Infrared spectroscopy provides a useful probe of PO bond strength. The PO stretching band for free phosphorus monoxide occurs at 1220.25 in the gas phase and P–O stretching frequencies for known PO complexes are shown in Table 1. The values cover a relatively small range of 1266–1063 cm^{-1}. This compares with NO stretching frequencies in metal complexes which cover a range of over 650 cm^{-1} [45]. As expected, PO stretching frequencies show much smaller changes upon complexation.

Examination of Table 1 reveals that while ν(PO) in most PO complexes occurs at lower frequency than that of free PO, a few complexes have a ν(PO) at higher frequency. The high frequencies could be explained by a transfer of an electron from the π* orbital to the metal complex resulting in co-ordinated PO^+. However, as noted above, this orbital is essentially non-bonding in PO and calculations do not support extensive charge transfer. Instead, the high frequencies are attributed to electrostatic effects. The proximity of positively charged metals to PO has two effects. First of all, it changes the polarisation, increasing the relative electronegativity of phosphorus. The π orbital, which is strongly polarised towards oxygen becomes more evenly distributed and thus more bonding. The positive charge also increases the phosphorus d character in the π* orbitals, reducing its antibonding character. Both effects thus increase the PO bond strength.

An important point to note when considering PO distances and ν(PO) frequencies is the presence of hydrogen bonding contacts with the secondary ammonium counterions in the anionic PO clusters. The solid

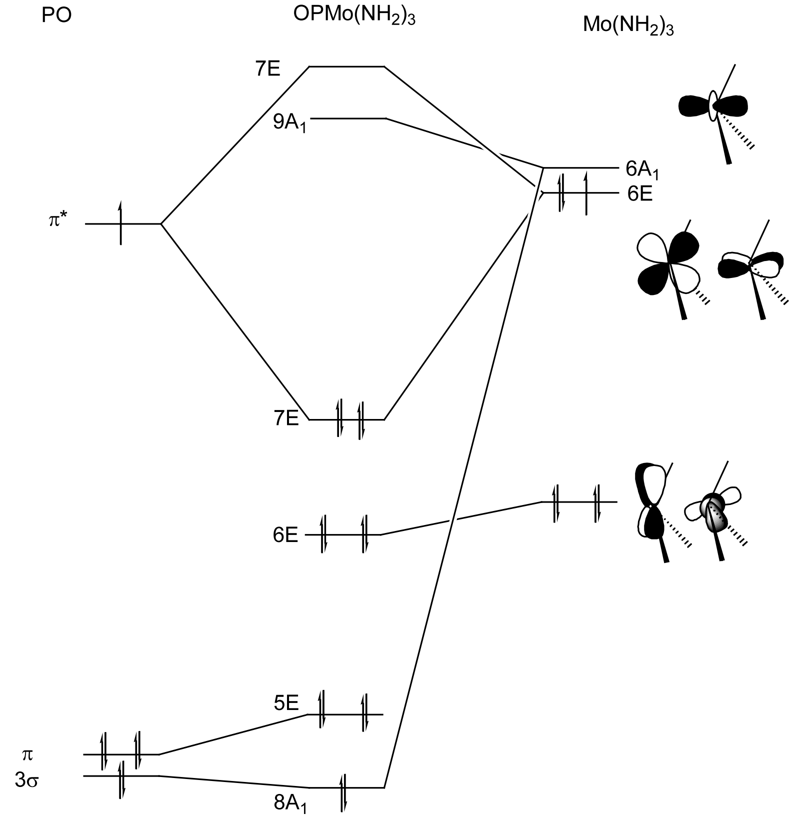


Fig. 2. Orbital interaction diagram of $(NH_2)_3MoPO$.

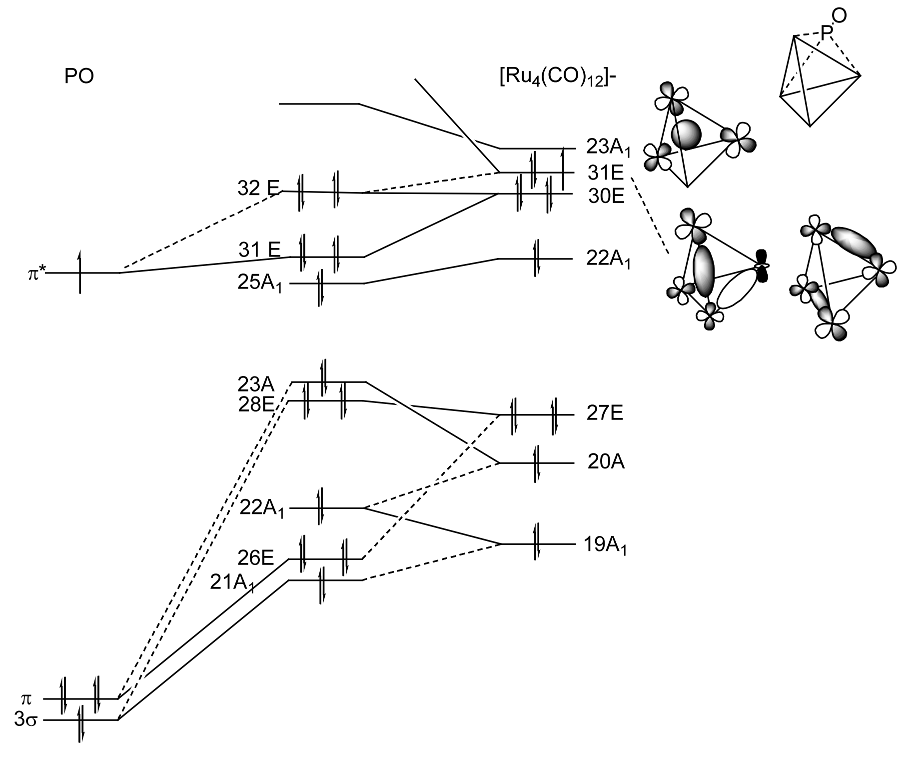


Fig. 3. Orbital interaction diagram of $[Ru_4(CO)_{12}PO]^-$.

Table 1
Spectroscopic parameters involving PO ligands

Compound	δ ^{31}P-NMR	ν(PO)
$[Cp_3Mo_3(CO)_6(\mu_3\text{-}PO)]$ (**28**)	345.5	1266
$[Cp_3Mo_2W(CO)_6(\mu_3\text{-}PO)]$ (**29**)	328.6	1266
$[Cp_3MoW_2(CO)_6(\mu_3\text{-}PO)]$ (**30**)	310.6	1265
$[Cp_3W_3(CO)_6(\mu_3\text{-}PO)]$ (**31**)	288.9	1265
$[(OP)Mo(N(R)Ar)_3]$ (**57**)	269.8	1232
PO		1220.25
$[\{Cp''Co\}_3(\mu_3\text{-}PO)_2]$ (**37**)	538.5	1182
$[\{Cp^*Fe\}\{Cp''Co\}_2(\mu_4\text{-}P_2O)(\mu_3\text{-}PO)(\mu_3\text{-}P_2)]$ (**48**)	558.8	1182
$[(Cp''Ni)_2W(CO)_4(\mu_3\text{-}PO)_2]$ (**18**)	354	1159
$[Cp'_3Co_3(\mu_3\text{-}CCMe_3)(\mu_3\text{-}PO)]$ (**22**)		1132
$[Ru_4(CO)_{12}(\mu_3\text{-}PO)][H_2N^iPr_2]$ (**66a**)	476.2	1075
$[Ru_4(CO)_{12}(\mu_3\text{-}PO)][Et_4N]$ (**66b**)	474.2	1169
$[Os_4(CO)_{12}(\mu_3\text{-}PO)][H_2N^iPr_2]$ (**67a**)	410.9	1156
$[Os_4(CO)_{12}(\mu_3\text{-}PO)][Et_4N]$ (**67b**)	403.8	1176
$[Os_4(CO)_{13}(\mu_3\text{-}PO)][Et_4N]$ (**65b**)	288.2	1095
$[Ru_5(CO)_{15}(\mu_4\text{-}PO)][H_2NCy_2]$ (**71b**)	515	1064
$[Ru_5(CO)_{15}(\mu_4\text{-}PO)][H_2N^iPr_2]$ (**71a**)	514	1063
$[Ru_4Pt(PPh_3)(CO)_{13}(\mu_4\text{-}PO)][H_2N^iPr_2]$ (**77**)	442.4	1096

state structure of anionic PO clusters with $H_2N^iPr_2$ or H_2NCy_2 counterions show O···H contacts of 1.814–2.09 Å. The presence of hydrogen bonding results in a considerable reduction in the PO stretching frequency. For example, compare $[Ru_4(CO)_{12}(\mu_3\text{-}PO)][H_2N^iPr_2]$ (**66a**, $\nu(PO) = 1075$) and $[Ru_4(CO)_{12}(\mu_3\text{-}PO)][Et_4N]$ (**66b**, $\nu(PO) = 1169$). Solution infrared spectra indicate that the hydrogen bonding is present in solution as well as in the solid state.

4.2. Structural features

Phosphorus–oxygen bond distances in PO complexes range from 1.462(9) to 1.547(4) Å (Table 2). This compares with typical values 1.489(6) Å ($(CH_3)_3P{=}O$) [46] and 1.484–1.491 Å ($Ph_3P{=}O$) [47] observed in phosphine oxides, and a gas-phase distance of 1.476370(15) Å for free PO. Complexes which exhibit hydrogen bonding to dialkyl ammonium counterions have longer PO distances (1.509(3)–1.518(3) Å), while co-ordination of the PO oxygen atom to another metal

Table 2
Structural parameters involving PO ligands

Compound	d(PO) (Å)	d(MP) (Å)	
PO	1.476370(15)		
$[(Cp''Ni)_2W(CO)_4(\mu_3\text{-}PO)_2]$ (**18**)	1.480(9) 1.462(9)	2.148(4) Ni 2.135(4) Ni 2.524(5) W	2.141(4) Ni 2.134(4) Ni 2.516(4) W
$[\{Cp'Co\}_3(\mu_3\text{-}CCMe_3)(\mu_3\text{-}PO)]$ (**22**)	1.489(13)	2.0959(13) 2.0964(13)	2.0941(13)
$[Cp_3Mo_3(CO)_6(\mu_3\text{-}PO)]$ (**28**)	1.479(11)	2.431(3) 2.399(3)	2.356(3)
$[\{Cp''Co\}_3(\mu_3\text{-}PO)_2]$ (**37**)	1.482(2) 1.480(2)	2.1309(8) 2.1251(8) 2.1156(8)	2.1242(8) 2.1233(8) 2.1171(8)
$[\{Cp^*Fe\}\{Cp''Co\}_2(\mu_4\text{-}P_2O)(\mu_3\text{-}PO)(\mu_3\text{-}P_2)]$ (**48**)	1.496(6)	2.190(3) Co 2.206(3) Co	2.161(3) Fe
$[(OP)Mo(N(R)Ar)_3]$ (**57**)	1.49(2)	2.079(5)	
$[Os_4(CO)_{13}(\mu_3\text{-}PO)][Et_4N]$ (**65b**)	1.503(8)	2.325(3) 2.498(3)	2.320(3)
$[Ru_4(CO)_{12}(\mu_3\text{-}PO)][H_2N^iPr_2]$ (**66a**)	1.509(3)	2.297(1) 2.282(1)	2.293(1)
$[Os_4(CO)_{12}(\mu_3\text{-}PO)][Et_4N]$ (**67b**)	1.476(10)	2.314(4) 2.294(4)	2.321(3)
$[Ru_5(CO)_{15}(\mu_4\text{-}PO)][H_2NCy_2]$ (**71b**)	1.512(5)	2.372(2) 2.369(2)	2.382(2) 2.372(2)
$[Ru_4Pt(PPh_3)(CO)_{13}(\mu_4\text{-}PO)][H_2N^iPr_2]$ (**77**)	1.518(3)	2.333(1) Pt 2.349(1) Ru	2.398(1) Ru 2.476(1) Ru
$[\{Ru_5(CO)_{15}(\mu_5\text{-}\eta^2\text{-}PO)\}_2Ru(CO)_2]$ (**92**)	1.547(4)	2.332(2) 2.339(2)	2.388(2) 2.377(2)

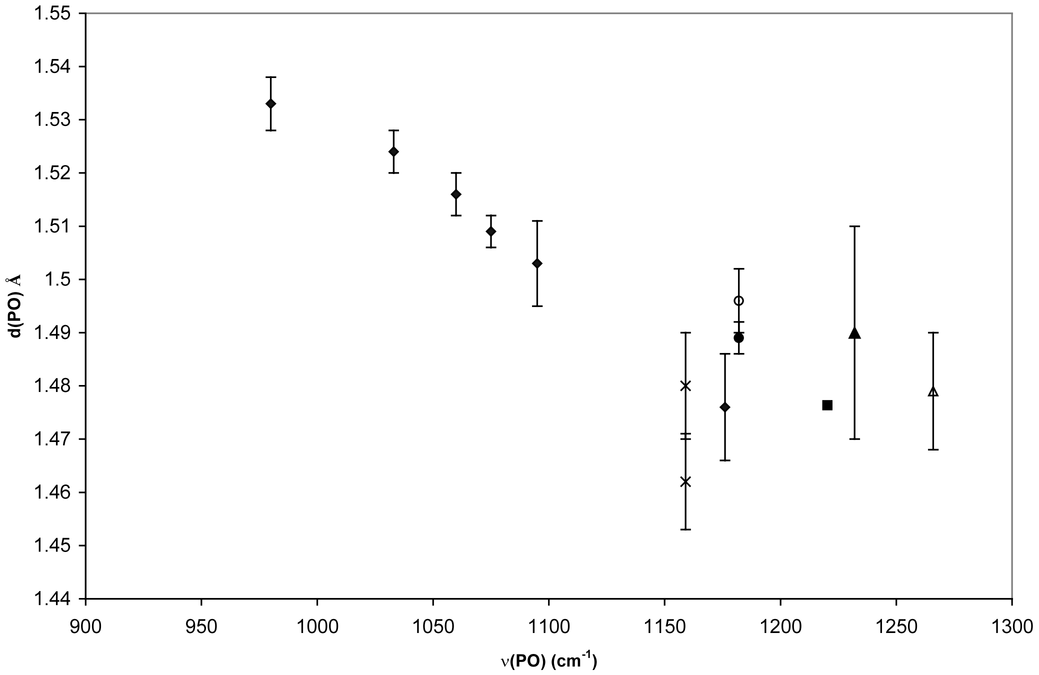


Fig. 4. Correlation between d(PO) (Å) and ν(PO) (cm^{-1}). The error bars correspond to the estimated standard deviations in the bond lengths. Legend: ◆, Ru and Os clusters, in order of increasing frequency: $[Ru_4(CO)_{12}Pt(PPh_3)(CO)(PO)][K]$, $[Ru_4(CO)_{12}Pt(PPh_3)(CO)(PO)][H_2N^iPr_2]$, $[Os_4(CO)_{13}PO][^iPr_2NH_2]$, $[Ru_5(CO)_{15}PO][^iPr_2NH_2]$, $[Os_4(CO)_{12}PO][Et_4N]$, $[Ru_4(CO)_{12}PO][^iPr_2NH_2]$; ×, $(\eta^5\text{-}C_5HPr^i_4)_2Ni_2W(CO)_4(PO)_2$; ^{B}s$[\{Cp''Co\}_3(\mu_3\text{-}PO)_2](Cp'' = \eta^5\text{-}C_5H_3Bu^t_2\text{-}1,3)$; ○, $[\{\eta^5\text{-}(CH_3)_5Fe\}\{Cp''Co\}_2(\mu_3\text{-}PO)(\mu_4\text{-}PO)(\mu_2\text{-}P_2)]$; ^{E}Q free PO, ^{G}S$(PO)Mo[N(R)Ar]_3(R = (RC(CD_3)_2Me_2)Ar = 3,5\text{-}C_6;H_3Me_2)$; $\Delta[\eta^5\text{-}C_5H_5(CO)_2Mo]_3PO$.

in $[\{Ru_5(CO)_{15}(\mu_4\text{-}PO)\}_2Ru(CO)_2]$ (**89**) results in the longest PO distance of 1.547(4) Å. The PO bond distances generally correlate well with the PO stretching frequencies (see Fig. 4), however, since the relative error in bond distances is much greater than in stretching frequencies, the stretching frequencies are a better indicator of bond strength. Phosphorus–metal distances are shown in Table 2, and as expected correlate to the hapticity of the PO ligand, increasing as the number of bonded metals increase.

Table 3
^{31}P chemical shifts of PO clusters and isostructural substituted phosphinidene clusters

$[Ru_4(CO)_{12}(\mu_3\text{-}PO)][H_2N^iPr_2]$ (**66a**)	476.2
$[Ru_4(CO)_{12}(\mu_3\text{-}PN^iPr_2)]$ (**61**)	467.0
$[Os_4(CO)_{13}(\mu_3\text{-}PF)]$ (**69**)	307.4
$[Os_4(CO)_{13}(\mu_3\text{-}POMe)]$ [18]	297.8
$[Os_4(CO)_{13}(\mu_3\text{-}PO)][Et_4N]$ (**65b**)	288.2
$[Os_4(CO)_{13}(\mu_3\text{-}POH)]$ (**64**)	275.5
$[Ru_5(CO)_{15}(\mu_4\text{-}PF)]$ (**72**)	548.6
$[Ru_5(CO)_{15}(\mu_4\text{-}POMe)]$ (**74**)	542.8
$[Ru_5(CO)_{15}(\mu_4\text{-}PO)][H_2NCy_2]$ (**71b**)	515
$[Ru_5(CO)_{15}(\mu_4\text{-}PNCy_2)]$ (**70b**)	490
$[Ru_5(CO)_{15}(\mu_4\text{-}PPh)]$ [48]	434
$[Ru_5(CO)_{15}(\mu_4\text{-}PMe)]$ [48]	417
$[Ru_4Pt(PPh_3)(CO)_{13}(\mu_4\text{-}PF)]$ (**78**)	485.1
$[Ru_4Pt(PPh_3)(CO)_{13}(\mu_4\text{-}POEt)]$ (**79**)	460.1
$[Ru_4Pt(PPh_3)(CO)_{13}(\mu_4\text{-}PO)][H_2N^iPr_2]$ (**77**)	442.4
$[Ru_4Pt(PPh_3)(CO)_{13}(\mu_4\text{-}PN^iPr_2)]$ (**75**)	439.8

4.3. NMR spectroscopy

The ^{31}P-NMR chemical shifts for known phosphorus monoxide complexes are shown in Table 1. Chemical shifts for μ_3-PO complexes cover a wide range from 288 to 559 ppm. Given the limited number and the structural diversity of the μ_3-PO clusters, it is difficult to discern any trends in the values. However, direct comparison of analogous Ru and Os clusters or analogous Mo and W clusters shows an upfield shift upon changing from a second to a third row metal. Phosphorus resonances for μ_4 clusters occur at δ 442–515 ppm, while the lone terminal PO complex has a ^{31}P resonance at δ 269.8. These values suggest that the chemical shifts move to lower field as the co-ordination number of phosphorus increases. However, the number of terminal and μ_4 examples is too small to draw firm conclusions.

Table 3 shows the ^{31}P chemical shifts of μ_3- and μ_4-PO clusters of ruthenium and osmium in the context of structurally analogous substituted phosphinidene complexes. In each series of isostructural compounds, a clear trend exists such that increasing the electronegativity of the phosphorus substituents increase the phosphorus chemical shift. In each case, the chemical shift of the phosphorus monoxide cluster places it between the electronegative phosphinidenes such as PF and POR and the more electropositive phosphinidenes PNR_2 and PR. Since π-bonding dominates the interaction of PO with metal clusters, the trend in the ^{31}P chemical shifts suggests that PO is intermediate in its π-acceptor abilities between the two types of phosphinidene ligands.

5. Conclusions

The number of phosphorus monoxide complexes continues to grow at a steady rate. As the number of phosphide and related ligands containing naked phosphorus atoms increases, the oxidation methodology will continue to provide new PO complexes, and perhaps new clusters containing other phosphorus oxide ligands such as P_2O, P_4O and P_2O_2, as well as PS, PSe and PTe and related complexes. The methodology involving hydrolysis of aminophosphinidenes, on the other hand, has the potential to provide a means of forming series of related clusters, allowing for systematic investigations of the co-ordination properties of phosphorus monoxide, via variation of the metal and ancillary ligand.

At the same time, a greater understanding of nature of this ligand is being developed. Although isoelectronic with NO, PO clearly has very different bonding properties. For example, PO forms μ_4 interactions, which are unknown for NO, while the common η^1- and μ_2-NO bonding modes are unknown for PO with the exception of a single example of a terminal PO complex. Density functional theory has provided a clearer picture of PO–metal complex bonding and reveals an interaction dominated by π-bonding.

One area which requires further study is the reactivity of PO complexes. The anionic clusters of ruthenium and osmium are weak conjugate bases to cluster acids which are capable of undergoing dehydration reactions leading to clusters linked by phosphorus oxide ligands. Preliminary studies show that PO clusters can act as oxygen-based nucleophiles toward metal centres. Phosphorus oxide ligands clearly have great potential utility in the formation of complex cluster structures.

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