Binding, Release and Functionalization of Intact Pnictogen Tetrahedra Coordinated to Dicopper Complexes

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Dedicated to Professor Cameron Jones on the occasion of his 60th birthday

Abstract: The bridging MeCN ligand in the dicopper(I) complexes [DPFN]Cu₂(μ₂-η¹:η¹-MeCN)]X₂ (X = weakly coordinating anion, NTf₂ (1a), FAl[OC(CF₃)₃]₄ (1b), Al[OC(CF₃)₃]₄ (1c)) was replaced by white phosphorus (P₄) or yellow arsenic (As₂) to yield [DPFN]Cu₂(μ₂-η¹:η¹-X₂)]X₂ (E = P (2a–c), As (3a–c)). The molecular structures in the solid state reveal novel coordination modes for E₄ tetrahedra bonded to coinage metal ions. Experimental data and quantum chemical computations provide information concerning perturbations to the bonding in coordinated E₄ tetrahedra. Reactions with N-heterocyclic carbenes (NHCs) led to replacement of the E₄ tetrahedra with release of P₄ or As₄ and formation of [DPFN]Cu₂(μ₂-η¹:η¹-X₂NHC)]X₂ (4a,b) or to an opening of one E–E bond leading to an unusual E₄ butterfly structural motif in [(DPFN)Cu₂(μ₂-η¹:η¹-X₂NHC)]X₂ (E = P (5a,b), E = As (6)). With a cyclic alkyl amino carbene (CAAC), cleavage of two As–As bonds was observed to give two isomers of [(DPFN)Cu₂(μ₂-η¹:η¹-As₄CAAC)]X₂ (7a,b) with an unusual As₄ triangle + 1 unit.

Introduction

Direct functionalization of elemental phosphorus with carbon-based reagents is a promising approach to access compounds containing P–C bonds using atom-economical and non-toxic methods that avoid chemical intermediates such as PCl₅/OPCl₃.[1] Organophosphorus compounds are now invariably derived from the molecular form of elemental phosphorus, white phosphorus (P₄) and its reaction with chlorine. In this regard, it is important to identify alternative, selective conversions of P₄ involving novel pathways. Indeed, P₄ is known to undergo nucleophilic attack with formation of P–C bonds; however, such reactions are generally nonselective and produce mixtures of polyphosphorus cage compounds or oligomeric materials.[2] A promising strategy for improving this selectivity is based on cooperative nucleophile/electrophile additions,[3–5] and such possibilities have increased interest in the coordination of P₄ units to transition metals that might provide catalytic routes[6–10] to phosphorus compounds. Interesting, few examples to synthesize organo-phosphorus compounds from phosphates have been reported.[11–16]

Coinage metals are known to readily bind intact P₄, but little is known regarding the consequences for reactivity and the nature of bonding in the main group ligand.[17–20] Similar behavior has been observed for yellow arsenic (As₂), but studies of this heavier pnictogen tetrahedron are even more scarce due to its extreme instability and limited availability. As with P₄, As₂ can remain intact upon coordination to electrophilic metal centers,[7–9] and in some cases an As₂–As bond is cleaved as in insertion of Cp₂Zr into the As₄ tetrahedron (e.g. in [Cp₂Zr(As₄)], Cp₂Zr = 1,3-di-tertbutyl-cyclopentadienyl).[12] Coordination of intact pnictogen tetrahedra to metal centers typically occurs in end-on (η²) fashion, or side-on (η¹) fashion.[4,5,9,15–18] to one or two metal centers. Interestingly, coinage metals as well as H–[19] have been found to coordinate E₄ exclusively in η²-fashion. When E₄ is exposed to a naked coinage metal cation with a weakly coordinating anion (WCA), coordination of two tetrahedral units is observed to afford the generic [M(η²-E₄)]⁺ structure (M = Cu, Au, E = P; M = Ag, E = P, As; Scheme 1, A).[7,15,17,18] Cationic coinage metal complexes bearing a single P₄ molecule have been obtained with an NHC co-ligand, as in [(η⁴NHC)(M(η²-P₄))]⁺ (M = Cu, Au; Scheme 1, B)[20] whereas neutral bimetallic complexes with intact E₄ tetrahedra...
The development of synthetically diverse transformations would perhaps best utilize a coordinated, intact E₄ ligand activated toward further reactions. Thus, it was of interest to investigate the coordination of P₄ and As₄ to a preassembled and rigid bimetallic copper core that might impose unique binding modes. Thus, the dicopper complex [(DPFN)Cu₄(μ₁₋₄-E₄)][MeCN] [X]₂ (DPFN = 2,7-bis(fluoro-di(2-pyridyl)methyl)-1,8-naphthyridine) was chosen as a starting point, as this platform possesses two closely spaced copper centers that cooperate in their promotion of substrate transformations [27] and in the stabilization of reactive intermediates [28,29]. One question concerns the manner in which closely spaced copper centers might bind and activate E₄ tetrahedra. A second line of inquiry concerned possible selective functionalizations of coordinated E₄ units interacting with a bimetallic coordination site. Due to the greater extent of interactions between the metals and E₄, the bimetallic platform could promote higher selectivities and hinder uncontrolled degradation and/or aggregation as observed in reactions with free E₄ or compounds containing loosely bound E₄. Finally, it is of interest to identify any significant differences between the coordination and chemical behaviors of analogous phosphorus and arsenic tetrahedra.

Herein we report on the binding of E₄ units at a bimetallic copper core for the first time to give novel coordination modes of intact E₄ entities. Moreover, subsequent reactions with neutral nucleophiles result in a selective opening of only one E–E bond for P₄ and two for As₄ to form unique butterfly-like and ring-opened complexes, respectively.

Results and Discussion

The bridging acetonitrile ligand in [(DPFN)Cu₄(μ₁₋₄-E₄-MeCN)] [X]₂ (X: weakly coordinating anion, N(SO₂CF₂)₂ or NTf₂ (1a), FAI[OC(CF₃)₂]₂ or FAI (1b), TEF (1c)) was readily replaced by P₄ by treatment of a o-difluorobenzene solution of the corresponding copper complex with P₄ in THF (−30°C, 1a) or in CS₂ (room temperature, 1b,c) to give [(DPFN)Cu₄(μ₁₋₄-P₄)][X]₂ ([X] = NTf₂ (2a), FAI (2b), TEF (2c); Scheme 2), isolated as crystalline solid in yields of 85, 93 and 52 %, respectively. Crystals suitable for single crystal X-ray structure analysis were obtained for 2a–c (see Supporting Information). The P₄ tetrahedra in 2a and 2b are disordered over two positions, while in 2c the P₄ is located in only one position; nonetheless, all

Scheme 1. Selected coinage metal complexes with intact pnictogen tetrahedra.

were prepared by reactions of [(η²-naphthyl)Au(P₄)][TEF] with P₄ and As₄ to yield the binuclear [(η²-naphthyl)Au(P₄)] (E = P, As; Scheme 1, C) or mononuclear [(η²-naphthyl)Au(As₄)] (Scheme 1, D). Notably, [(η²-naphthyl)Au(μ₁,μ₂-E₄)] (Scheme 1, C) complexes represent the only previous examples of binuclear coinage metal complexes of a pnictogen tetrahedron. There appears to be one example of a reaction involving an E₄ unit (E = P, As) with a bimetallic center, in the reductive cage opening of the tetrahedra across a dichromium quintuple bond to form bridging cyclo-E₅⁻ ligands [30]. However, the coordination and subsequent reactivity of intact E₄ units at a bimetallic center, namely it includes bonds between the metals or metals in close contact, has not been reported. The functionalization of an intact E₄ tetrahedron within the coordination sphere of a coinage metal has only been reported for the reaction of [(η²-naphthyl)Au(μ₁,μ₂-E₄)][TEF] (B, TEF = [OC(CF₃)₂]₂) with ArLi (Ar = Dmp, Mes) [30]. The first step represents the formation of a neutral complex with a P₄ butterfly bonded to one aryl group and one NHCAu fragment, which is not stable and converts at room temperature to the cationic complex [(η²-naphthyl)Au(μ₁,μ₂-E₄)][ArLi] (TEF = Dmp, Mes) [30]. The latter reactions proceed via multiple P–P bond cleavages, sometimes accompanied by fragmentation and/or aggregation [30–32]. Despite these investigations for P₄, no analogous reactivity studies have been reported for As₄.

Scheme 2. Reaction of 1a–c with white phosphorus (P₄) and yellow arsenic (As₄). The given yields represent the yield of isolated crystalline material (2a–c, 3b,c) or the precipitated solid from the reaction mixture (3a). Given ratios of the isomers are related to the molecular structure in the solid state (3b) and to the connectivity structure in the solid state (3c).
three compounds exhibit the same coordination mode. Thus, metric parameters will only be discussed for 2c. In the molecular structure of 2c (Figure 1), adjacent edges of the Pa tetrahedron are each bonded to a copper center, and notably this coordination mode has not yet been observed for an intact Pa. The two coordinated P–P bonds are elongated (P1-P2 2.3731(9) Å, P1-P3 2.3775(10) Å) compared to the other P–P distances (2.1741(10)–2.1898(8) Å), which are slightly shorter than those observed in free Pa (2.21 Å).[30] The coordinating P–P bonds are in the expected range for elongated single bonds[31] (calculated Wiberg Bond Indices (WBIs) of 0.76 and 0.78) with all other P–P distances being in the range for normal single bonds (WBIs in the range between 0.91 and 0.98). The Pa unit is coordinated symmetrically between both Cu atoms with two slightly shorter Cu–P distances (Cu1-P1 2.2489(7) Å, Cu2-P1 2.2497(6) Å) and two somewhat longer Cu–P distances (Cu1-P2 2.3214(7) Å, Cu2-P3 2.306(8) Å).

The Cu1-Cu2 distance (3.1993(5) Å) is significantly longer than that in the starting material 1c (Cu1-Cu2 2.4963(5) Å, see Supporting Information). The observed binding mode of the Pa tetrahedra in 2a–c is so far unique and differs from those found in systems such as [[(Nacnac)Cu3(μ3-P2)]][32] or polymeric [Cu(μ2-P2)][GaCl4].[33] The Pa unit in 2a–c can be described as an intact tetrahedron. Indeed, QTAIM analysis of the electron density in [[DPFN]Cu3(μ1-η1-P2)]+ reveals bond critical points along all edges of the Pa ligand and high energy densities at these positions clearly indicate the presence of intact P–P bonds (see Supporting Information). The integrity of the Pa fragment is also supported by NMR spectroscopy. The 31P NMR spectra of 2a in THF-d8 in the temperature range between −90°C and 20°C contain only one singlet at −468.7 ppm, significantly downfield shifted compared to that of free Pa (−527.5 ppm).[32] This is consistent with rapid tumbling of the bound Pa fragment on the NMR timescale, even at −90°C, such that the four phosphorus atoms appear equivalent in solution. In the ESı-MS spectra of 2b,c, peaks for the molecular ions are apparent.

While white phosphorus can easily be used under inert conditions using standard preparation techniques, the handling of the heavier homolog yellow arsenic is much more challenging due to its extreme sensitivity to light and air. The stability of As4 can be enhanced when CS2 is used as a solvent. Fortunately, [[DPFN]Cu3(μ1-η1-As2)][MeCN]3 (X = NTf2) (1a), FAI (1b), TEF (1c) are stable enough in CS2 to allow reactions with a freshly prepared solution of yellow arsenic in CS2 to yield [[DPFN]Cu3(μ-As2)][X]3 (X = NTf2 (3a), FAI (3b), TEF (3c)).

Compound 3a was isolated as a yellow powder in 84% yield (precipitated with pentane from an o-difluorobenzene solution), whereas 3b and 3c were isolated as yellow crystals in yields of 95 and 82%. While all attempts to obtain single crystals of 3a failed (always giving oily residues), single crystals were successfully obtained for 3b and 3c. Although diffraction data were obtained for crystals of 3c, a satisfactory complete refinement could not be achieved due to the disorder in the anion (TEF), although the atom connectivity of the cation was unambiguously determined.

Crystals of 3b suitable for X-ray single crystal structure analysis, obtained from a concentrated o-difluorobenzene solution layered with hexane and cooled to −30°C, provided its molecular structure (Figure 1). In this structure the As4 tetrahedron is coordinated to the dicopper center, and is disordered over three positions with site occupancies of 44, 44 and 12% corresponding to the three different bonding isomers 3b-I, 3b-II and 3b-III, which are all unprecedented as coordination modes for E4 tetrahedra. In 3b-I, the As4 unit binds by donation of an edge to both Cu atoms in a η1:η1 fashion, while a third As atom coordinates to one Cu atom in a η1 fashion. A second coordination mode, observed in 3b-II, features symmetric, η1:η1 coordination of two adjacent edges to the Cu atoms in a manner analogous to that observed for 2a–c. Finally, 3b-III exhibits one As–As bond coordinated symmetrically in a μ1:η1:η1 fashion, and oriented perpendicular to the Cu–Cu axis. The connectivity in the structure of the cation 3c (see Supporting Information) is disordered over two sets of positions, which is in line with 3b-I and 3b-III in a ratio of 59:41. All coordinated As–As bonds in 3b are elongated, slightly for those coordinated to one Cu atom (As2B–As3B 2.597(3) Å, As1B–As2B 2.655(3) Å) and more strongly for those coordinated to two Cu atoms (As1A–As2A 2.680(3) Å, As1C–As2C 2.742(14) Å). All non-coordinating As–As bond lengths are in the range expected for single bonds and are comparable to those in free yellow arsenic (2.434(5) Å).[35] DFT

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computations (BP86/def2-SVP level of theory)\cite{56} show that all three isomers 3 b-I–III are almost equal in energy. The observed coordination modes differ substantially from those of known complexes, involving an intact As\textsubscript{4} tetrahedron coordinated in η\textsuperscript{1} fashion to a ruthenium fragment in [Cp\textsuperscript{R}Ru(dpp)(η\textsuperscript{2}-As\textsubscript{4}H\textsubscript{4})]\textsuperscript{+}\cite{19} or through two opposite edges as in [(\textit{Nacnac})Cu\textsubscript{2}(μ\textsuperscript{2}-η\textsuperscript{2}-As\textsubscript{4}H\textsubscript{4})]\textsuperscript{2+}\cite{20} or in an η\textsuperscript{1} fashion through one edge as in monometallic [Ag(η\textsuperscript{2}-As\textsubscript{4}H\textsubscript{4})]\textsuperscript{+}\cite{21} or through two opposite edges as in [(\textit{Nacnac})Cu\textsubscript{2}(μ\textsuperscript{2}-η\textsuperscript{2}-As\textsubscript{4}H\textsubscript{4})]\textsuperscript{2+}\cite{20} or through two opposite edges as in [(\textit{Nacnac})Cu\textsubscript{2}(μ\textsuperscript{2}-η\textsuperscript{2}-As\textsubscript{4}H\textsubscript{4})]\textsuperscript{2+}\cite{20} or through two opposite edges as in [(\textit{Nacnac})Cu\textsubscript{2}(μ\textsuperscript{2}-η\textsuperscript{2}-As\textsubscript{4}H\textsubscript{4})]\textsuperscript{2+}\cite{20}.

The reaction of \textit{Dipp}NHC with the phosphorus derivates 2 a,b and the arsenic derivative 3 c yielded [(DPFNC)Cu\textsubscript{2}(μ\textsuperscript{2}-η\textsuperscript{1}-E\textsuperscript{39}DippNHC)]\textsuperscript{2+}\textsuperscript{X}\textsuperscript{2} (E = P, X = NTf\textsubscript{2} (5 a, FAI (5 b); E = As, X = TEF (6)), isolated as crystalline solid in yields of 68, 59 \% and 44 \%, respectively (Scheme 3). For 5 a, only very poorly diffracting crystals could be obtained but the diffraction data provided a rough atom connectivity in the structure, which is similar to that of 5 b. For 5 b and 6, crystals suitable for X-ray single crystal structure analysis were obtained from concentrated o-difluorobenzene solutions layered with toluene (5 b) and pentane (6), respectively, at –30 °C.

The dication structures (see Figure 2) show that addition of the carbene led to an E\textsubscript{4} butterfly motif with one vertex bonded to the carbene while the opposite vertex occupies a bridging position between the copper atoms. Such a structural motif, with a bimetallic unit coordinated to one of the wingtip atoms, is so far unknown. The P\textsubscript{2} fragment of 5 b is disordered over two positions with site occupancies of 70 and 30 \%. The addition of \textit{Dipp}NHC to E\textsubscript{4} is accompanied by the cleavage of the

\textbf{Scheme 3.} Reactivity of [(DPFNC)Cu\textsubscript{2}(μ\textsuperscript{2}-η\textsuperscript{1}-E\textsuperscript{39}DippNHC)]\textsuperscript{2+}\textsuperscript{X}\textsuperscript{2} (E = P, X = NTf\textsubscript{2} (2 a); E = P, X = FAI (2 b); E = As, X = FAI (3 b); E = As, X = TEF (3 c)) towards carbenes.

\textbf{Scheme 3.} Reactivity of [(DPFNC)Cu\textsubscript{2}(μ\textsuperscript{2}-η\textsuperscript{1}-E\textsuperscript{39}DippNHC)]\textsuperscript{2+}\textsuperscript{X}\textsuperscript{2} (E = P, X = NTf\textsubscript{2} (2 a); E = P, X = FAI (2 b); E = As, X = FAI (3 b); E = As, X = TEF (3 c)) towards carbenes.
Cyclic alkyl amino carbenes (CAACs) were investigated for these reactions since they present a significant change in intrinsic electronic and steric properties relative to those of NHC nucleophiles. The reaction of the phosphorus complexes 2b,c with $^3$CAAC (1-(2,6-dipropylphenyl)-3,3-diethyl-5,5-dimethyl-2-pyrrolidinyl-idene) gave mixtures of unidentified species that could not be isolated or purified despite numerous attempts. The ESI-MS spectrum of the crude reaction mixture in o-difluorobenzene solution reveals the presence of an ion with the composition [(DPFP)Cu$_2$P$^3$CAAC]$^2+$. In contrast, reaction of the arsenic compound 3b with $^3$CAAC is more selective. Using a 1:1 ratio, the reaction solution changes color immediately from yellow to red-brown upon addition of the carbene at −30 °C. Layering the concentrated reaction solution with n-pentane at room temperature yielded a few single crystals of unreacted starting material 3b (dark yellow plates) and many crystals of two isomers of [(DPFP)Cu$_2$P$^3$CAAC][FAI], (7a,b) after a few days (Scheme 3). Both isomers crystallize as orange plates but can be distinguished by their unit cell parameters on the X-ray diffractometer.

The molecular structures of 7a and 7b (Figure 3) indicate formation of a cyclic As$_2$ ring appended by an exocyclic As$^5$CAAC moiety. An As—As bond of the As$_3$ ring is bonded to both copper atoms and coordinated perpendicular to the Cu–Cu axis. The isomers 7a and 7b differ only in the orientation of the $^3$CAAC. All As—As bonds are in the expected range for single bonds (2.4224(6)–2.4619(6) Å; WBIs 0.92 and 1.13). The two isomers differ in the As4-Cu2 distance (7a: 3.1246(8) Å; 7b: 2.8180(13) Å), probably due to the different steric demands of the carbene side groups.

The formation of 7a,b involves the formal cleavage of two As—As bonds, while the addition of $^3$DPFPNHC to the E$_2$ tetrahedron (formation of 5a,b and 6) leads to the cleavage of only one E—E bond. Isomers 7a and 7b have calculated energies that are essentially the same (within less than 1 kJ/mol). Since crystals of both isomers have the same shape and color and are quite small, it was not possible to isolated suitable amounts of pure 7a and 7b, respectively. Thus, analytical data were collected on mixtures of 7a and 7b. The $^1$H NMR spectrum of a sample of 7a,b in CD$_2$Cl$_2$ solution contain two sets of signals in a ratio of 0.37:1.00, while no assignment as to which...
set belongs to which isomer can be made. The $^1$H NMR spectrum of another batch of crystalline material, obtained by the same procedure, reveals the same sets of signals but with a different ratio of isomers (0.74:1.00; see Supporting Information). This indicates that the isomers 7a and 7b do not interconvert in solution, even after several days (by NMR spectroscopy). Notably, the ratio of both isomers is dependent on the reaction conditions and presumably reflect restricted rotation about the C31-As4 bond. Thus, for crude products precipitated from the reaction solution, the ratio varies from 1.00:0.69 (reaction at $-30^\circ \text{C}$, o-difluorobenzene), to 0.00:1.00 ($-80^\circ \text{C}$, CH$_2$Cl$_2$), to 0.60:1.00 (room temperature, o-difluorobenzene).

**Conclusion**

Bimetallic reaction centers have the potential to provide new pathways for activations and conversions of substrates, beyond what is possible with a single-metal site. This is especially relevant for substrates that possess multiple potential reaction sites, as in the $E_4$ tetrahedra ($E=P$, As). In the study presented here, a cationic dicopper core supported by a rigid binucleating ligand, [(DPFN)Cu$_2$]$_{3^{-\cdot}}$, provides a platform for the coordination of intact pnictogen tetrahedra in unprecedented coordination modes with coordination to both coppers through two adjacent $E_4$ edges. Studies of this unique binding mode, by X-ray crystallography, NMR spectroscopy and DFT calculations, reveal small electronic perturbations expected to play a role in subsequent functionalization chemistry. While the smaller nucleophile $^{15}$NHC simply displaces the $E_4$ tetrahedra, the more sterically demanding $^{15}$NHC selectively functionalizes the coordinated $E_4$ unit to cleave an $E=E$ bond with formation of the novel $E_4$ butterfly complexes possessing $\mu:1:1:1:1$-$E_4$-$^{15}$NHC bridging ligands. This reaction behavior differs markedly from that of free $E_4$.20–23 A simple change in the nucleophile, to $^{15}$CAAC, results in a different type of activation for the $As_4$ tetrahedron in 3b involving selective functionalization with cleavage of two As–As bonds and formation of two isomeric complexes [[DPFN]Cu$_2$($\mu:1:1:1:1$-$As_4$-$^{15}$CAAC)[$\text{FAI}$]$_2$ (7a.b). This unique transformation produces a triangle+1 arrangement of the initial $As_4$ tetrahedron.

Significantly, these results illustrate the high potential of a bimetallic platform to coordinate and activate intact $E_4$ units in an exceptional manner. The observed, subsequent reactivity represents selective functionalizations that are sensitive to the nature of the nucleophilic reagent. Further research will address the use of heterobimetallic platforms in search of new types of activations and transformations.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** carbenes · coordination modes · copper · metal-metal interactions · pnictogens

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The bridging MeCN ligand in the dicopper(I) complex \([\text{DPFN} \text{Cu}_2(\mu, \eta^1::\eta^1-\text{MeCN})][\text{X}]_2\) (X = WCA) can easily be replaced by white phosphorus (P₄) or yellow arsenic (As₄) to yield \([\text{DPFN} \text{Cu}_2(\mu, \eta^2::\eta^2-\text{E}_4)][\text{X}]_2\) (E = P, As). The coordinated intact E₄ tetrahedra can be further selectively functionalized with N-heterocyclic carbenes (NHCs) and cyclic alkyl amino carbenes (CAACs) under cleavage of E–E bonds, while using a small and strong NHC leads to the release of the pnictogen tetrahedra as P₄ and grey arsenic, respectively.