

# VIP 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)Cu<sub>2</sub>(μ,η<sup>1</sup>:η<sup>1</sup>-MeCN)][X]<sub>2</sub> (X = weakly coordinating anion, NTF<sub>2</sub> (1 a), FAl[OC<sub>6</sub>F<sub>10</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (1 b), Al[OC(CF<sub>3</sub>)<sub>3</sub>]<sub>4</sub> (1 c)) was replaced by white phosphorus (P<sub>4</sub>) or yellow arsenic (As<sub>4</sub>) to yield [(DPFN)Cu<sub>2</sub>(μ,η<sup>2</sup>:η<sup>2</sup>-E<sub>4</sub>)]<sub>2</sub> (E = P (2 a–c), As (3 a–c)). The molecular structures in the solid state reveal novel coordination modes for E<sub>4</sub> tetrahedra bonded to coinage metal ions. Experimental data and quantum chemical computations provide information concerning perturbations to the bonding in coordinated E<sub>4</sub> tetrahedra. Reactions with N-

heterocyclic carbenes (NHCs) led to replacement of the E<sub>4</sub> tetrahedra with release of P<sub>4</sub> or As<sub>4</sub> and formation of [(DPFN)Cu<sub>2</sub>(μ,η<sup>1</sup>:η<sup>1</sup>-MeNHC)][X]<sub>2</sub> (4 a,b) or to an opening of one E–E bond leading to an unusual E<sub>4</sub> butterfly structural motif in [(DPFN)Cu<sub>2</sub>(μ,η<sup>1</sup>:η<sup>1</sup>-E<sup>Dipp</sup>NHC)][X]<sub>2</sub> (E = P (5 a,b), E = As (6)). With a cyclic alkyl amino carbene (E<sup>t</sup>CAAC), cleavage of two As–As bonds was observed to give two isomers of [(DPFN)Cu<sub>2</sub>(μ,η<sup>2</sup>:η<sup>2</sup>-As<sub>4</sub><sup>E<sup>t</sup>CAAC})][X]<sub>2</sub> (7 a,b) with an unusual As<sub>4</sub>-triangle + 1 unit.</sup>

## 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 PCl<sub>3</sub>/OPCl<sub>3</sub>.<sup>[1]</sup> Organophosphorus compounds are now invariably derived from the molecular form of elemental phosphorus, white phosphorus (P<sub>4</sub>) and its reaction with chlorine. In this regard, it is important to identify alternative, selective conversions of P<sub>4</sub> involving novel pathways. Indeed, P<sub>4</sub> 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.<sup>[2]</sup> A promising strategy for improving this selectivity is based on cooperative nucleophile/electrophile additions,<sup>[3–5]</sup> and such possibilities have increased interest in the coordination of P<sub>4</sub> units to transition metals that might provide catalytic routes<sup>[1a,c]</sup> to phosphorus compounds. Interesting, few examples to synthesize organo-phosphorus compounds from phosphates have been reported.<sup>[1e,6]</sup>

Coinage metals are known to readily bind intact P<sub>4</sub>, but little is known regarding the consequences for reactivity and the nature of bonding in the main group ligand.<sup>[7–11]</sup> Similar behavior has been observed for yellow arsenic (As<sub>4</sub>), but studies of this heavier pnictogen tetrahedron are even more scarce due to its extreme instability and limited availability. As with P<sub>4</sub>, As<sub>4</sub> can remain intact upon coordination to electrophilic metal centers,<sup>[7–9]</sup> and in some cases an As–As bond is cleaved as in insertion of Cp''<sub>2</sub>Zr into the As<sub>4</sub> tetrahedron (e.g. in [Cp''<sub>2</sub>Zr(As<sub>4</sub>)], Cp'' = 1,3-di-*tert*-butyl-cyclopentadienyl).<sup>[12]</sup>

Coordination of intact pnictogen tetrahedra to metal centers typically occurs in *end-on* (η<sup>1</sup>)<sup>[8,13,14]</sup> or *side-on* (η<sup>2</sup>) fashion,<sup>[4,5,9,15–18]</sup> to one or two metal centers. Interestingly, coinage metals as well as H<sup>+</sup><sup>[19]</sup> have been found to coordinate E<sub>4</sub> exclusively in η<sup>2</sup>-fashion. When E<sub>4</sub> 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(η<sup>2</sup>-E<sub>4</sub>)<sub>2</sub>]<sup>+</sup> structure (M = Cu, Au, E = P; M = Ag, E = P, As; Scheme 1, A).<sup>[7,15,17,18]</sup> Cationic coinage metal complexes bearing a single P<sub>4</sub> molecule have been obtained with an NHC co-ligand, as in [(DippNHC)M(η<sup>2</sup>-P<sub>4</sub>)]<sup>+</sup> (M = Cu, Au; Scheme 1, B)<sup>[4]</sup> whereas neutral bimetallic complexes with intact E<sub>4</sub> tetrahedra

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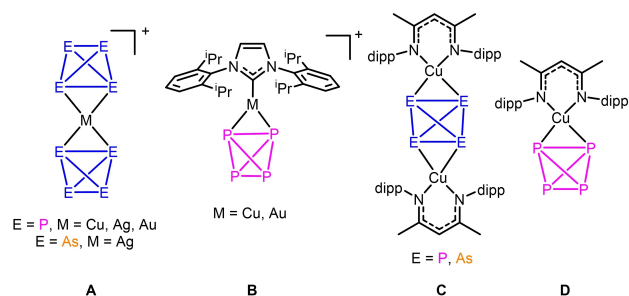
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**Scheme 1.** Selected coinage metal complexes with intact pnictogen tetrahedra.

were prepared by reactions of  $[(\text{nacnac})\text{Cu}(\text{MeCN})]$  with  $\text{P}_4$  and  $\text{As}_4$  to yield the binuclear  $[(\text{nacnac})\text{Cu}_2(\mu, \eta^2: \eta^2\text{-E}_4)]$  ( $\text{E} = \text{P}, \text{As}$ ; Scheme 1, C) or mononuclear  $[(\text{nacnac})\text{Cu}(\eta^2\text{-P}_4)]$  (Scheme 1, D).<sup>[9a]</sup>

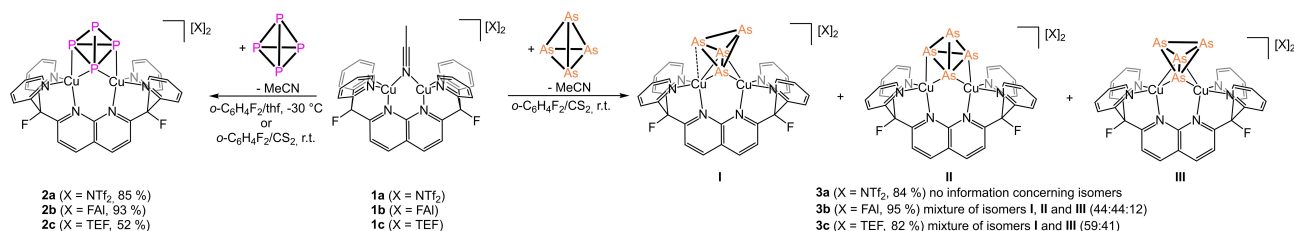
Notably,  $[(\text{nacnac})\text{Cu}_2(\mu, \eta^2: \eta^2\text{-E}_4)]$  (Scheme 1, C) complexes represent the only previous examples of binuclear coinage metal complexes of a pnictogen tetrahedron. There appears to be one example of a reaction involving an  $\text{E}_4$  unit ( $\text{E} = \text{P}, \text{As}$ ) with a bimetallic center, in the reductive cage opening of the tetrahedra across a dichromium quintuple bond to form bridging *cyclo*- $\text{E}_4^{2-}$  ligands.<sup>[9b]</sup> However, the coordination and subsequent reactivity of intact  $\text{E}_4$  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  $\text{E}_4$  tetrahedron within the coordination sphere of a coinage metal has only been reported for the reaction of  $[(\text{DippNHC})\text{Au}(\eta^2\text{-P}_4)][\text{TEF}]$  (B,  $\text{TEF} = \text{Al}[\text{OC}(\text{CF}_3)_3]_4$ ) with  $\text{ArLi}$  ( $\text{Ar} = \text{Dmp}, \text{Mes}$ ).<sup>[4]</sup> The first step represents the formation of a neutral complex with a  $\text{P}_4$  butterfly bonded to one aryl group and one  $\text{NHCAu}$  fragment, which is not stable and converts at room temperature to the cationic complex  $[(\text{DippNHCu})_2(\mu, \eta^1: \eta^1\text{-P}_4\text{Ar})][\text{TEF}]$ . Interestingly, addition of a neutral nucleophile (e.g., an N-heterocyclic carbene) to coordinated  $\text{E}_4$  species has not been reported, despite the intense study of analogous reactions of free white phosphorus.<sup>[20–26]</sup> The latter reactions proceed via multiple P–P bond cleavages, sometimes accompanied by fragmentation and/or aggregation.<sup>[22–26]</sup> Despite these investigations for  $\text{P}_4$ , no analogous reactivity studies have been reported for  $\text{As}_4$ .

The development of synthetically diverse transformations would perhaps best utilize a coordinated, intact  $\text{E}_4$  ligand activated toward further reactions. Thus, it was of interest to investigate the coordination of  $\text{P}_4$  and  $\text{As}_4$  to a preassembled and rigid bimetallic copper core that might impose unique binding modes. Thus, the dicopper complex  $[(\text{DPFN})\text{Cu}_2(\mu, \eta^1: \eta^1\text{-MeCN})][\text{X}]_2$  ( $\text{DPFN} = 2,7\text{-bis}(\text{fluoro-di}(2\text{-pyridyl})\text{methyl})\text{-}1,8\text{-naphthyridine}$ ) was chosen as a starting point, as this platform possesses two closely spaced copper centers that cooperate in their promotion of substrate transformations<sup>[27]</sup> and in the stabilization of reactive intermediates.<sup>[28,29]</sup> One question concerns the manner in which closely spaced copper centers might bind and activate  $\text{E}_4$  tetrahedra. A second line of inquiry concerned possible selective functionalizations of coordinated  $\text{E}_4$  units interacting with a bimetallic coordination site. Due to the greater extent of interactions between the metals and  $\text{E}_4$ , the bimetallic platform could promote higher selectivities and hinder uncontrolled degradation and/or aggregation as observed in reactions with free  $\text{E}_4$  or compounds containing loosely bound  $\text{E}_4$ . 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  $\text{E}_4$  units at a bimetallic copper core for the first time to give novel coordination modes of intact  $\text{E}_4$  entities. Moreover, subsequent reactions with neutral nucleophiles result in a selective opening of only one E–E bond for  $\text{P}_4$  and two for  $\text{As}_4$  to form unique butterfly-like and ring-opened complexes, respectively.

## Results and Discussion

The bridging acetonitrile ligand in  $[(\text{DPFN})\text{Cu}_2(\mu, \eta^1: \eta^1\text{-MeCN})][\text{X}]_2$  ( $\text{X}$ : weakly coordinating anion,  $\text{N}(\text{SO}_2\text{CF}_3)_2$  or  $\text{NTf}_2$  (**1a**),  $\text{FAI}[\text{OC}_6\text{F}_5(\text{C}_6\text{F}_5)]_3$  or  $\text{FAI}$  (**1b**),  $\text{TEF}$  (**1c**)) was readily replaced by  $\text{P}_4$  by treatment of a *o*-difluorobenzene solution of the corresponding copper complex with  $\text{P}_4$  in THF ( $-30^\circ\text{C}$ , **1a**) or in  $\text{CS}_2$  (room temperature, **1b,c**) to give  $[(\text{DPFN})\text{Cu}_2(\mu, \eta^2: \eta^2\text{-P}_4)][\text{X}]_2$  ( $\text{X} = \text{NTf}_2$  (**2a**),  $\text{FAI}$  (**2b**),  $\text{TEF}$  (**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  $\text{P}_4$  tetrahedra in **2a** and **2b** are disordered over two positions, while that in **2c** is located in only one position; nonetheless, all



**Scheme 2.** Reaction of **1a–c** with white phosphorus ( $\text{P}_4$ ) and yellow arsenic ( $\text{As}_4$ ). 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  $P_4$  tetrahedron are each bonded to a copper center, and notably this coordination mode has not yet been observed for an intact  $P_4$ . 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  $P_4$  (2.21 Å).<sup>[30]</sup> The coordinating P–P bonds are in the expected range for elongated single bonds<sup>[31]</sup> (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  $P_4$  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).

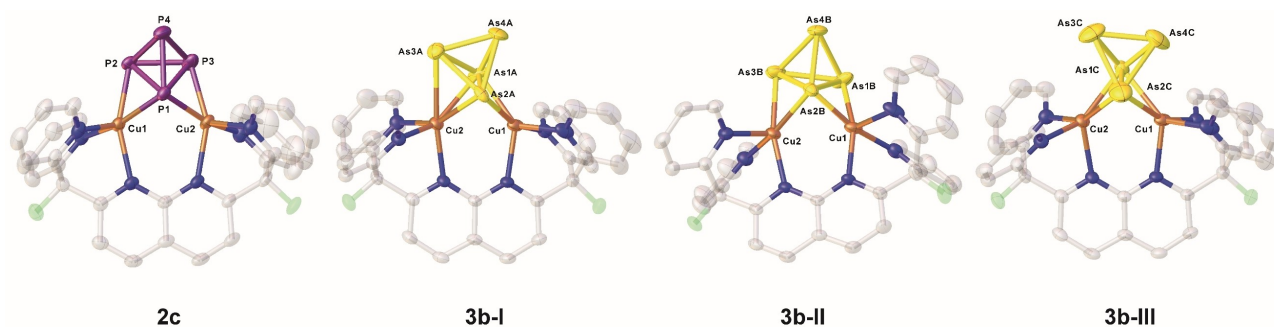
The Cu1–Cu2 distance (3.1993(5) Å) is significantly longer than that in the starting material **1c** (Cu1–Cu2 2.4963(5) Å, see Supporting Information). The observed binding mode of the  $P_4$  tetrahedra in **2a–c** is so far unique and differs from those found in systems such as  $[(\text{Nacnac})\text{Cu}_2(\mu, \eta^1: \eta^2\text{-P}_4)]^{[9]}$  or polymeric  $[\text{Cu}(\eta^2\text{-P}_4)_2][\text{GaCl}_4]^{[7]}$ . The  $P_4$  unit in **2a–c** can be described as an intact tetrahedron. Indeed, QTAIM analysis of the electron density in  $[(\text{DPFN})\text{Cu}_2(\mu, \eta^1: \eta^2\text{-P}_4)]^{2+}$  reveals bond critical points along all edges of the  $P_4$  ligand and high energy densities at these positions clearly indicate the presence of intact P–P bonds (see Supporting Information). The integrity of the  $P_4$  fragment is also supported by NMR spectroscopy. The  $^{31}\text{P}$  NMR spectra of **2a** in  $\text{THF-}d_6$  in the temperature range between  $-90^\circ\text{C}$  and  $20^\circ\text{C}$  contain only one singlet at  $-468.7$  ppm, significantly downfield shifted compared to that of free  $P_4$  ( $-527.5$  ppm).<sup>[32]</sup> This is consistent with rapid tumbling of the bound  $P_4$  fragment on the NMR timescale, even at  $-90^\circ\text{C}$ , such that the four phosphorus atoms appear equivalent in solution. In the ESI-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

$\text{As}_4$  can be enhanced when  $\text{CS}_2$  is used as a solvent. Fortunately,  $[(\text{DPFN})\text{Cu}_2(\mu, \eta^1: \eta^1\text{-MeCN})][\text{X}]_2$  ( $\text{X} = \text{NTf}_2$  (**1a**),  $\text{FAI}$  (**1b**),  $\text{TEF}$  (**1c**)) are stable enough in  $\text{CS}_2$  to allow reactions with a freshly prepared solution of yellow arsenic in  $\text{CS}_2$ , to yield  $[(\text{DPFN})\text{Cu}_2(\mu\text{-As}_4)][\text{X}]_2$  ( $\text{X} = \text{NTf}_2$  (**3a**),  $\text{FAI}$  (**3b**),  $\text{TEF}$  (**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 ( $\text{TEF}$ ), 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  $-30^\circ\text{C}$ , provided its molecular structure (Figure 1). In this structure the  $\text{As}_4$  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  $E_4$  tetrahedra. In **3b-I**, the  $\text{As}_4$  unit binds by donation of an edge to both Cu atoms in a  $\eta^2: \eta^2$  fashion, while a third As atom coordinates to one Cu atom in a  $\eta^1$  fashion. A second coordination mode, observed in **3b-II**, features symmetric,  $\eta^2: \eta^2$  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  $\mu, \eta^2: \eta^2$  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).<sup>[33]</sup> DFT



**Figure 1.** Molecular structure of the dication in **2c** and **3b**. Hydrogen atoms, solvent molecules and counterions omitted for clarity. Thermal ellipsoids are drawn with 50% probability level. The  $\text{As}_4$  unit in **3b** is disordered over three positions, revealing three isomers **3b-I**, **3b-II** and **3b-III** with site occupancies of 44, 44 and 12%.

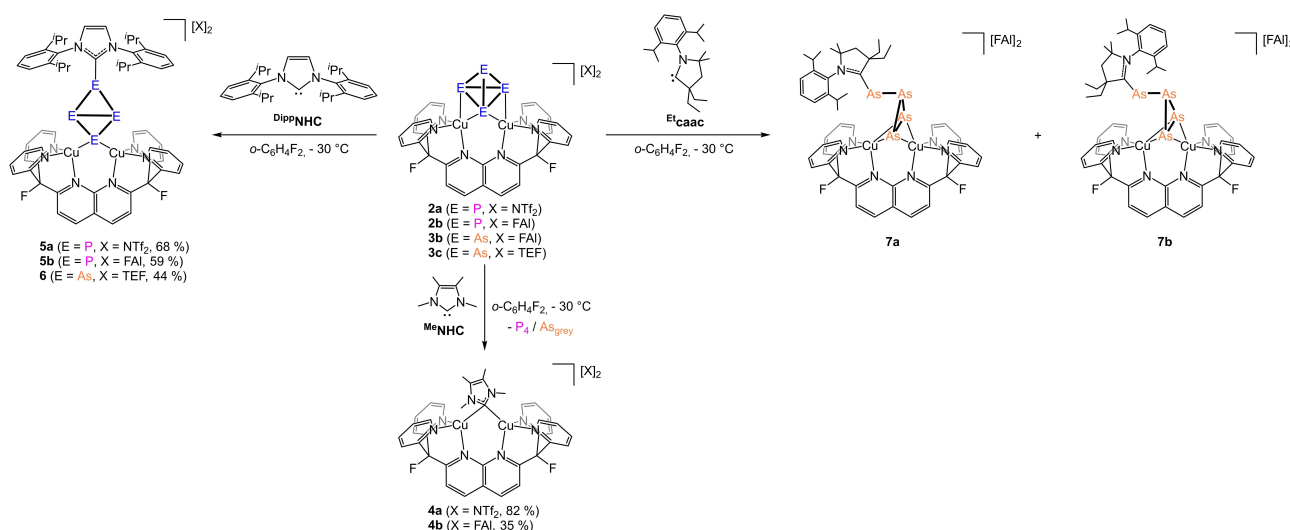
computations (BP86/def2-SVP level of theory)<sup>[34]</sup> show that all three isomers **3b–I–III** are almost equal in energy. The observed coordination modes differ substantially from those of known complexes, involving an intact As<sub>4</sub> tetrahedron coordinated in  $\eta^1$  fashion to a ruthenium fragment in [Cp\*Ru(dppe)( $\eta^1$ -As<sub>4</sub>)]<sup>+</sup>,<sup>[14]</sup> in an  $\eta^2$  fashion through one edge as in monometallic [Ag( $\eta^2$ -As<sub>4</sub>)<sub>2</sub>]<sup>+</sup>,<sup>[11]</sup> or through two opposite edges as in [((Nacnac)Cu)<sub>2</sub>( $\mu$ , $\eta^2$ : $\eta^2$ -As<sub>4</sub>)] (C in Scheme 1).<sup>[9]</sup> The topological analysis of the electron density in **3-II** was investigated by the QTAIM method. Bond critical points were located on all edges of the As<sub>4</sub> unit as well as along the Cu–As bonds. The properties of the electron density at these critical points are very similar to those of **2c** and indicate the presence of an intact As<sub>4</sub> unit in **3-II** (see Supporting Information). In the ESI-MS spectra of **3a–c**, molecular ion peaks are detected.

Having the complexes **2a–c** and **3a–c** at our disposal, it was of interest to determine whether the E<sub>4</sub> tetrahedra might be activated by the electron-deficient, cationic dicopper core to allow functionalization in a selective and controlled manner. For this purpose, carbenes appeared to be reasonable starting point, since the activation of white phosphorus with carbenes has been intensively studied.<sup>[20,21]</sup> Carbenes are known to cleave P–P bonds in P<sub>4</sub>; however, this is sometimes accompanied by fragmentation and/or aggregation processes to give compounds with P<sub>1</sub>,<sup>[22]</sup> P<sub>2</sub>,<sup>[22]</sup> P<sub>4</sub>,<sup>[22,24,25,26]</sup> P<sub>8</sub>,<sup>[26]</sup> or P<sub>12</sub>,<sup>[23]</sup> units. In most of the reported reactions, cyclic alkyl amino carbenes (CAACs) were used and only one reaction of P<sub>4</sub> with an N-heterocyclic carbene has been reported, namely the reaction of 1,3-bis-(2,6-diisopropylphenyl)-imidazolin-2-ylidene with P<sub>4</sub> to give a disubstituted P<sub>12</sub> cluster.<sup>[23]</sup> Remarkably, all isolated derivatives represent products of multiple reaction steps. On the other hand, <sup>Me</sup>NHC (1,3,4,5-tetramethyl-imidazol-2-ylidene) and <sup>Dipp</sup>NHC (1,3-bis-(2,6-diisopropylphenyl)-imidazol-2-ylidene) react with transition metal complexes including cyclic polynictogen (E<sub>n</sub>) ligands either by addition to the E<sub>n</sub> ligand<sup>[35]</sup> or by abstraction of one E atom with formation of [<sup>Me</sup>NHC<sub>2</sub>E]<sup>+</sup>.<sup>[35,36]</sup>

The rather small <sup>Me</sup>NHC was observed to react with both **2a** and **3b**. However, these reactions led to substitution of the E<sub>4</sub> tetrahedra to form [(DPFN)Cu<sub>2</sub>( $\mu$ , $\eta^1$ : $\eta^1$ -<sup>Me</sup>NHC)][X]<sub>2</sub> (X = NTf<sub>2</sub> (**4a**), FAI (**4b**)) (Scheme 3). The reactions were accompanied by release of the E<sub>4</sub> unit, as P<sub>4</sub> (detected by NMR spectroscopy) or grey arsenic (precipitation of a dark solid). This behavior is consistent with the intact nature of the E<sub>4</sub> units bound to the bimetallic platform. Compounds **4a,b** were also obtained by direct reaction of <sup>Me</sup>NHC with **1a,b**. Determination of the molecular structures **4a,b** in the solid state (see Supporting Information) revealed that the carbene binds simultaneously to both Cu atoms, and is aligned perpendicular to the Cu–Cu axis with a tilt of 40° to one side of the naphthyridine backbone. This tilting is consistent with that observed in bridging triazolidine and phosphalkyne complexes and reflects some degree of  $\pi$ -backbonding to <sup>Me</sup>NHC.<sup>[28,37]</sup>

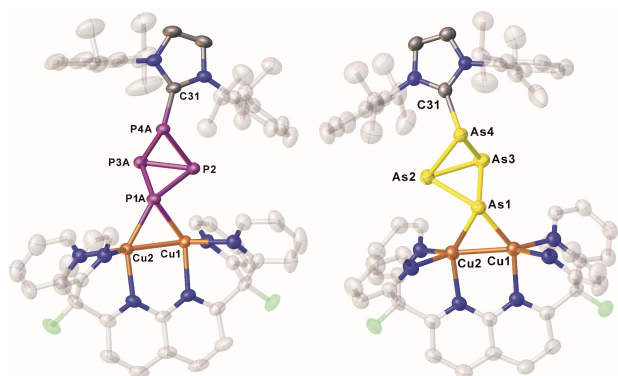
Interestingly, the bulkier <sup>Dipp</sup>NHC exhibits very different reactivity. The reaction of <sup>Dipp</sup>NHC with the phosphorus derivatives **2a,b** and the arsenic derivative **3c** yielded [(DPFN)Cu<sub>2</sub>( $\mu$ , $\eta^1$ : $\eta^1$ -E<sub>4</sub><sup>Dipp</sup>NHC)][X]<sub>2</sub> (E = P, X = NTf<sub>2</sub> (**5a**), FAI (**5b**); E = As, X = TEF (**6**)), isolated as crystalline solid in yields of 68, 59 and 44%, respectively (Scheme 3). For **5a**, 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 **5b**. For **5b** and **6**, crystals suitable for X-ray single crystal structure analysis were obtained from concentrated *o*-difluorobenzene solutions layered with toluene (**5b**) and pentane (**6**), respectively, at –30 °C.

The dication structures (see Figure 2) show that addition of the carbene led to an E<sub>4</sub> 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<sub>4</sub> fragment of **5b** is disordered over two positions with site occupancies of 70 and 30%. The addition of <sup>Dipp</sup>NHC to E<sub>4</sub> is accompanied by the cleavage of the



**Scheme 3.** Reactivity of [(DPFN)Cu<sub>2</sub>( $\mu$ , $\eta^2$ : $\eta^2$ -E<sub>4</sub>)]X<sub>2</sub> (E = P, X = NTf<sub>2</sub> (**2a**); E = P, X = FAI (**2b**); E = As, X = FAI (**3b**); E = As, X = TEF (**3c**)) towards carbenes.





**Figure 2.** Structures of the dications in **5b** (left) and **6** (right). Hydrogen atoms, solvent molecules and counterions omitted for clarity. Thermal ellipsoids are drawn with 50% probability level.

E1–E4 bond. Interestingly, the P1–P4 (P1–P4 A 2.7669(11) Å, P1–P4B 2.777(3) Å) and As1–As4 (3.0092(6) Å) distances are too long to be considered a bond, but are still less than the sum of van der Waals radii ( $\Sigma_{vdW}$  = 3.80 Å (P–P); 3.76 Å (As–As)).<sup>[38]</sup> However, a weak interaction cannot be excluded, and is supported by WBIs of 0.10 (E = P) and 0.09 (E = As). All other E–E bonds in **5b** and **6** are in the range of comparable single bonds (P–P distances in the range of 2.1268(12)–2.331(2) Å; WBIs 0.92–0.97 and As–As distances of 2.4003(6)–2.4898(6) Å; WBIs 0.91–0.97). The C–P and C–As bond lengths in **5b** (P4A–C31 1.891(3) Å) and **6** (As4–C31 1.996(4) Å), respectively, are in the range expected for single bonds.<sup>[31]</sup>

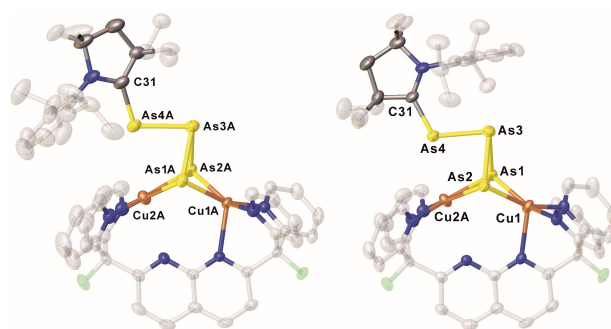
In principle, the ring-opening of an E<sub>4</sub> tetrahedron with formation of an E<sub>4</sub> butterfly represents the first step in derivatizations of these elemental allotropes. Similar transformations are achieved by reaction of P<sub>4</sub> with transition metal radicals to give [(Cp<sup>'''</sup>M)<sub>2</sub>(μ,η<sup>1</sup>:η<sup>1</sup>-E<sub>4</sub>)] (M = Cr, Fe; E = P, As),<sup>[39]</sup> by addition of organic radicals to produce organo-butterfly complexes R<sub>2</sub>E<sub>4</sub> (R = Mes, Ar<sup>Dipp</sup>, Cp<sup>BIG</sup>, Cp<sup>'''</sup>, Cp<sup>\*</sup>, Cp<sup>iPr</sup>),<sup>[40]</sup> or by reaction with a hindered nucleophile followed by trapping by a Lewis acid (e.g. Li[ArP<sub>4</sub>BAR<sub>3</sub>]).<sup>[41]</sup> The closest analogue to **5b** is [(DippNHCAu)<sub>2</sub>(μ,η<sup>1</sup>:η<sup>1</sup>-P<sub>4</sub>Ar)][TEF], reported by Lammertsma et al., which possesses a P<sub>4</sub> butterfly with one vertex carrying an aryl substituent with the opposite vertex coordinated to two unconnected gold fragments.<sup>[4]</sup>

While the As derivative **6** is thermally stable only to –30 °C, and decomposes in solution at room temperature within seconds, **5b** is stable at room temperature in solution. The <sup>31</sup>P {<sup>1</sup>H} NMR spectrum of **5b** in CD<sub>2</sub>Cl<sub>2</sub> reveals a slightly broadened quartet centered at –204.3 ppm and a very broad signal centered at –290.8 ppm with an integrated ratio of 1:2. Cooling the sample to –80 °C leads to a splitting of the signals into three multiplets centered at –202.9, –213.8 and –328.1 ppm, with an integral ratio of 1:1:2. However, at that temperature the pattern of the signals is too broad to obtain a useful simulation of the spectrum. For **5b** and **6**, molecular ion peaks are detected in the corresponding ESI-MS spectra from *o*-difluorobenzene solution.

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 <sup>Et</sup>CAAC (1-(2,6-diisopropylphenyl)-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 [(DPFN)Cu<sub>2</sub>P<sub>4</sub><sup>Et</sup>CAAC]<sup>2+</sup>. In contrast, reaction of the arsenic compound **3b** with <sup>Et</sup>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 [(DPFN)Cu<sub>2</sub>(μ,η<sup>2</sup>:η<sup>2</sup>-As<sub>4</sub><sup>Et</sup>CAAC)][FAl]<sub>2</sub> (**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<sub>3</sub> ring appended by an exocyclic As<sup>Et</sup>CAAC moiety. An As–As bond of the As<sub>3</sub> 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 <sup>Et</sup>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 DippNHC to the E<sub>4</sub> 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 isolate suitable amounts of pure **7a** and **7b**, respectively. Thus, analytical data were collected on mixtures of **7a** and **7b**. The <sup>1</sup>H NMR spectrum of a sample of **7a,b** in CD<sub>2</sub>Cl<sub>2</sub> solution contain two sets of signals in a ratio of 0.37:1.00, while no assignment as to which



**Figure 3.** Molecular structure of the dication in **7a** (left) and **7b** (right). Hydrogen atoms, solvent molecules and counterions omitted for clarity. Thermal ellipsoids are drawn with 50% probability level.

set belongs to which isomer can be made. The  $^1\text{H}$  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 1.00:0.51 ( $-80^\circ\text{C}$ ,  $\text{CH}_2\text{Cl}_2$ ), 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.<sup>[42]</sup> This is especially relevant for substrates that possess multiple potential reaction sites, as in the  $\text{E}_4$  tetrahedra ( $\text{E}=\text{P}$ , As). In the study presented here, a cationic dicopper core supported by a rigid binucleating ligand,  $[(\text{DPFN})\text{Cu}_2]^{2+}$ , provides a platform for the coordination of intact pnictogen tetrahedra in unprecedented coordination modes with coordination to both coppers through two adjacent  $\text{E}_4$  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  $^{\text{Me}}\text{NHC}$  simply displaces the  $\text{E}_4$  tetrahedra, the more sterically demanding  $^{\text{Dipp}}\text{NHC}$  selectively functionalizes the coordinated  $\text{E}_4$  unit to cleave an E–E bond with formation of the novel  $\text{E}_4$  butterfly complexes possessing  $\mu, \eta^1: \eta^1\text{-E}_4^{\text{DippNHC}}$  bridging ligands. This reaction behavior differs markedly from that of free  $\text{E}_4$ .<sup>[20–25]</sup> A simple change in the nucleophile, to  $^{\text{Et}}\text{CAAC}$ , results in a different type of activation for the  $\text{As}_4$  tetrahedron in **3b** involving selective functionalization with cleavage of two As–As bonds and formation of two isomeric complexes  $[(\text{DPFN})\text{Cu}_2(\mu, \eta^2: \eta^2\text{-As}_4^{\text{EtCAAC}})][\text{FAl}]_2$  (**7a,b**). This unique transformation produces a triangle + 1 arrangement of the initial  $\text{As}_4$  tetrahedron.

Significantly, these results illustrate the high potential of a bimetallic platform to coordinate and activate intact  $\text{E}_4$  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.

Deposition Numbers 2120551 (**1b**), 2120552 (**1c**), 2120553 (**2a**), 2120554 (**2b**), 2120555 (**2c**), 2120556 (**3b**), 2120557 (**4a**), 2120558 (**4b**), 2120559 (**5b**), 2120560 (**6**), 2120561 (**7a**) and 2120562 (**7b**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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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.

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