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Fixation and release of intact E4 tetrahedra (E = P, As)

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Inclusion and liberation of intact E₄ Tetrahedra (E = P, As)**

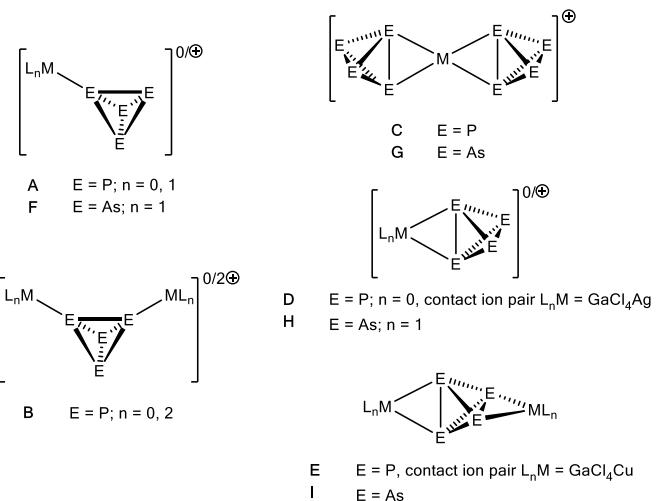
Fabian Spitzer, Marek Sierka, Mario Latronico, Piero Mastrorilli, and Manfred Scheer*

Dedication((optional))

Abstract: Abstract text.((Note: For every Communication, please supply an abstract as the first paragraph. In this abstract, the motivation for the work, the methods applied, the results, and the conclusions drawn should be presented (maximum 1000 characters)).

Since the first complex $[(np_3)Ni(\eta^1\text{-P}_4)]$ with an intact P₄ tetrahedron as ligand has been discovered by Sacconi *et al.* 1979,^[1] a huge progress has been made within the last decades in the synthesis and characterization of complexes containing an intact E₄ tetrahedron (E = P, As) as ligand. In the case of white phosphorus, terminal^[2] (η^1 , type **A**) and bridging^[3] ($\mu, \eta^{1:1}$, type **B**) coordination modes of the P₄ tetrahedra are known of ionic and neutral complexes as well. However, complexes containing terminal^[4] η^2 - or bridging^[5] $\mu, \eta^{2:2}$ -P₄ ligands have been only observed with coinage metal centers exclusively in ionic complexes or as part of a contact ion pair, respectively (types **C** - **E**).

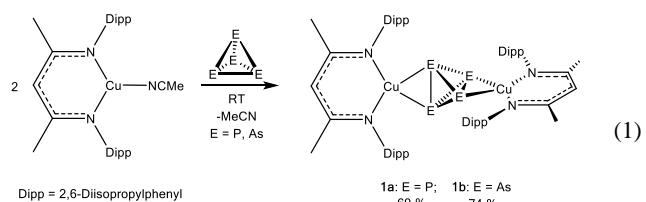
In stark contrast to the rich chemistry of P₄ containing complexes of this type, the As₄ derivatives are only sparingly studied. This is due to the high light sensitivity of yellow arsenic (As₄). In consequence, only few compounds have been published to date. Recently we reported about the synthesis of complexes containing As₄ as a ligand either in η^1 - or η^2 -bonding mode (types **F** - **H**).^[6] In these complexes, however, the central metal fragment is positively charged. The absence of neutral As₄ complexes of type **I** gave rise to the question, if a positively charged metal fragment is



necessary for the stabilization of a η^2 -coordination of intact As₄ tetrahedra to metal centers.

In the literature, there are two examples for neutral η^2 -P₄ ligand complexes. On the one side Ginsberg *et al.* reported on $[\text{RhCl}(\eta^2\text{-P}_4)(\text{PPh}_3)_2]$,^[7] for which the description as a P₄²⁻ ligand seems more appropriate, however. On the other side Scherer *et al.* reported on $[(\text{C}_5\text{HR}_4)\text{Cu}(\eta^2\text{-P}_4)]$ (R = CHMe₂),^[8] which recently could be revealed as incorrect by our working group.^[9] By this situation our motivation was to find a combination of ligand and coinage metal, which in fact could serve as a starting material for the synthesis of neutral E₄ containing complexes. We choose the sterically demanding, non-innocent β -Diketiminato ligand $[(\text{N}(\text{C}_6\text{H}_3\text{iPr}_2\text{-}2,6)\text{C}(\text{Me})_2\text{CH})]$ (Nacnac). When it coordinates to one metal center, the aromatic Dipp groups (Dipp = 2,6-Diisopropylphenyl) form a pocket, which size and shape is adequate to accommodate small molecules like E₄.

Herein we report on the synthesis and characterization of $[(\text{NacnacCu})_2(\mu, \eta^{2:2}\text{-E}_4)]$ (E = P (**1a**), As (**1b**)) the first neutral complexes containing an E₄ tetrahedron as bridging ligand in the $\mu, \eta^{2:2}$ -fashion. Furthermore we report on the treatment of **1a** with P₄, which results in the formation of $[\text{NacnacCu}(\eta^2\text{-P}_4)]$ (**2**). Its dynamic behavior in solution was investigated by VT $^{31}\text{P}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ EXSY NMR spectroscopy.



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Compound **1a** is formed by the stoichiometric reaction of [NacnacCu(NCMe)] with P₄. Conducting the reaction in acetonitrile, leads to the precipitation of the desired compound **1a** within minutes [Eq. (1)]. Compound **1a** is soluble in dichloromethane and even in nonpolar solvents like hexane or toluene. It is stable under ambient conditions and can be stored under argon. The synthesis of the arsenic analogue **1b** is comparably more difficult. Yellow arsenic (As₄) is a not storable compound, due to its sensibility to light, air and moisture. It needs to be prepared freshly in solution and therefore stoichiometric reactions are difficult. However, adding [NacnacCu(NCMe)] to an excess of a freshly prepared As₄ solution in toluene leads to the formation of the first neutral metal-arsenic complex **1b** containing an intact As₄ tetrahedron as ligand in good yields [Eq. (1)]. Removing the solvent leads to the conversion of remaining yellow arsenic into insoluble grey arsenic. As compound **1b** shows the same solubility like **1a**, As_{grey} can be removed by filtration. Compound **1b** can be stored under Argon at ambient conditions for months.

The ¹H NMR spectrum of **1a** and **1b** show the expected set of signals for the Nacnac ligands. Compound **1a** in CD₂Cl₂ shows a sharp singlet at -426.85 ppm in ³¹P{¹H} NMR spectrum. Complex **1b** in contrast does not show a signal in ⁷⁵As{¹H} NMR due to low molecule symmetry and to the quadrupole moment of ⁷⁵As.

Suitable crystals of **1a** and **1b** for single crystal X-ray diffraction could be grown from concentrated hexane solutions. The molecular structures show the side-on coordination of the E₄ tetrahedrons by two opposing edges to two NacnacCu fragments (**Figure 1** and **Figure 2**).

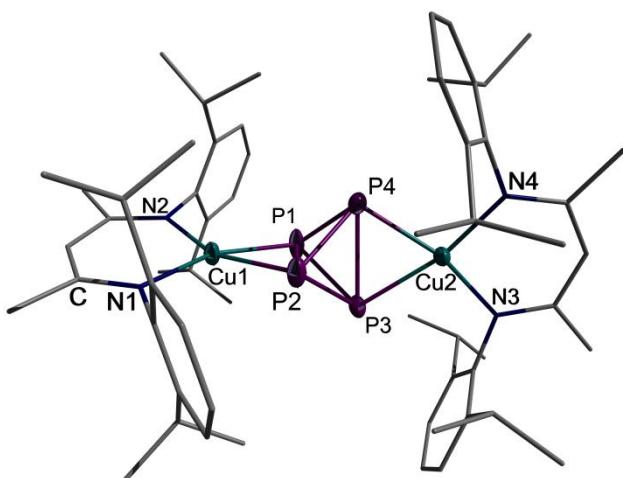


Figure 1. Molecular structure of compound **1a** in the crystal (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Cu1-P1 2.2629(4), Cu1-P2 2.2663(5), Cu2-P4 2.2589(5), Cu2-P3 2.2706(5), P1-P2 2.4119(6), P3-P4 2.4283(6), P1-P3 2.2115(6), P2-P3 2.2043(6), P1-P4 2.2006(7), P2-P4 2.2062(6), P2-P1-P3 56.75(2), P2-P1-P4 56.93(2), P3-P1-P4 66.79(2), P1-P2-P3 57.04(2), P1-P2-P4 56.70(2), P3-P2-P4 66.81(2), P1-P3-P2 66.21(2), P1-P3-P4 56.39(2), P2-P3-P4 56.63(2), P1-P4-P2 66.37(2), P1-P4-P3 56.82(2), P2-P4-P3 56.56(2), P1-Cu1-P2 64.35(2), N1-Cu1-N2 97.07(5), P3-Cu2-P4 64.84(2), N3-Cu2-N4 96.94(6).

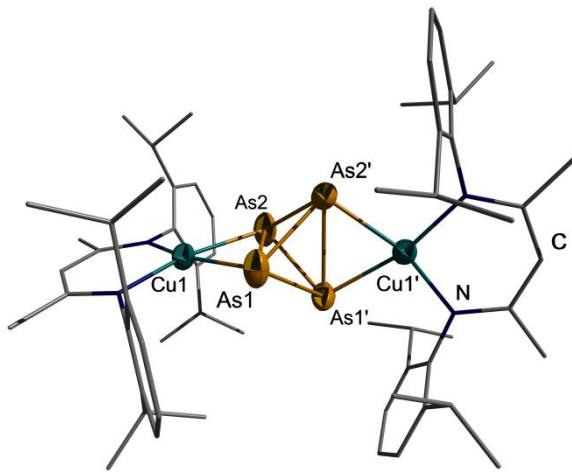


Figure 2. Molecular structure of compound **1b** in the crystal (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: As1-Cu1 2.3761(7), As2-Cu1 2.3879(8), As1-As2 2.6485(8), As1-As1' 2.4355(5), As1-As2' 2.4435(9), As2-As2' 2.4373(6), As1'-As1-As2 57.27(2), As2-As1-As2' 57.03(2), As1'-As1-As2' 65.75(2), As1-As2-As1' 56.98(2), As1-As2-As2' 57.25(2), As1'-As2-As2' 65.73(3), As1-Cu1-As2 67.55(2), N1-Cu1-N2 97.3(1).

The coordination geometry of Cu is almost quadratic planar in both cases. The maximum deviation from the coplanarity ($\Sigma_{\text{angles}} = 360^\circ$) is about 2° in **1a** and less than 0.1° in **1b**. As a result of the bridging E₄ ligands the planes build up from the two NacnacCu core are almost perpendicular to each other (torsion angle N-N-N-N = 94.19(5) ° (**1a**), 84.0(1) ° (**1b**)). The Cu-P distances in **1a** vary from 2.2589(5) Å to 2.2706(5) Å. They are slightly longer than the Cu-P distances found in compound [Cu(η^2 -P₄)₂][pftb] (pftb = [Al{OC(CF₃)₃}₄]^[10] (2.336(2)-2.345(2) Å), which also shows planar arrangement. To the best of our knowledge, there is no copper complex containing an As₄ ligand reported in the literature so far. The closest related known complex to **1b** is [Ag(η^2 -As₄)₂][pftb]^[11].

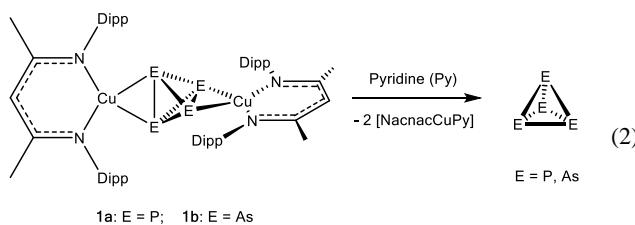
The distances between the coordinating atoms P1-P2 and P3-P4 in **1a** (2.4119(6) Å and 2.4283(6) Å, respectively) are elongated compared to the P-P bond lengths in white phosphorus (determined by electron diffraction^[12]: 2.1994(3) Å, Raman spectroscopy^[13]: 2.2228(5) Å, DFT calculations^[14]: 2.1994(3) Å). The distances between non-coordinating P-P edges are in the range of a P-P single bond (2.2006(7)-2.2115(6) Å). The P-P-P angles range from 56.39(2)° to 66.81(2)°, which deviated from the ideal tetrahedron angles of 60°.

Compound **1b** shows similar tendencies. The As1-As2 distance (2.6485(8) Å) is elongated compared to the As-As bond length in yellow arsenic (determined by electron diffraction: 2.435(4)^[15]-2.44(3)^[16] Å, DFT calculations^[17]: 2.437 Å). Distances between non-coordinating As-As edges are in the range of an As-As single bond (2.4355(5)-2.4435(9) Å). The As-As-As angles again are slightly different from the ideal tetrahedron angle, with values between 56.98(2)° and 65.75(2)°.

Enforcedly the question arises, whether the coordinating E-E edges (ratio P-P: **1a**/P₄, free = 1.0945, ratio As-As: **1b**/As₄, free = 1.0866) should be considered as elongated E-E bond or as cleaved? To get deeper understanding in the bonding situation of compound **1a** and **1b**, quantum chemical calculations have been carried out.

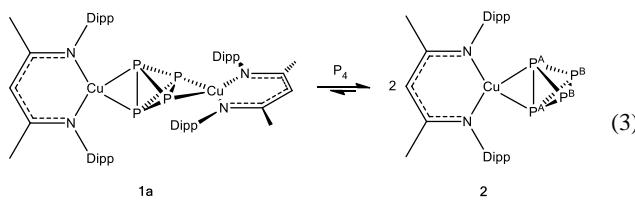
Conclusion of the DFT calculations and BCP analysis shows, that there should be assumed a bond/no bond between atoms of coordinating E-E edges (E = P, As).

To prove our theoretical assumptions, a simple and revealing experiment was carried out. If the bridging $\mu,\eta^{2:2}$ -E₄ tetrahedron in compound **1a** and **1b** could be substituted by a comparably stronger Lewis base, the E₄ tetrahedron ligand could be considered to be intact. The liberation of white phosphorus from **1a** and yellow arsenic from **1b** respectively, should be detectable by ³¹P{¹H} and ⁷⁵As{¹H} NMR investigation [Eq. (2)].



Indeed, adding pyridine (Py) to complex **1a** and **1b**, respectively leads to the liberation of the E₄ tetrahedron. Compound **1a** in CD₂Cl₂ shows a sharp singlet at -426.85 ppm in ³¹P{¹H} NMR experiments. After solving complex **1a** in pyridine, exclusively a singlet at -518 ppm could be detected. Without a doubt this signal is to be assigned to white phosphorous.^[X] Complex **1b** in contrast does not show a signal in ⁷⁵As{¹H} NMR spectrum due to low molecule symmetry and to the quadrupole moment of ⁷⁵As nucleus. However, adding an excess of pyridine-d₅ to a solution of **1b** in CD₂Cl₂ gives rise to the liberation of yellow arsenic, which was detected as broad singlet at -912 ppm in the ⁷⁵As{¹H} NMR spectrum.

The question arises, if a complex [NaCNacCu(η^2 -E₄)] (E = P, As) could be generated. Adding an excess of E₄ should give rise to the formation of complexes with an stoichiometry Cu:E₄ of 1:1. Since yellow arsenic cannot be applied in strict stoichiometry in reaction, the formation of the mononuclear complex is rather unfavorable. In the case of **1a** however, adding of P₄ gave rise to the formation of a second phosphorous containing species [NaCNacCu(η^2 -P₄)] (**2**) [Eq. (3)].



All attempts to isolate compound **2** in solid state failed so far. However, spectroscopic investigations of *in situ* prepared **2** could be carried out in CD₂Cl₂ solution. In the ³¹P{¹H} NMR spectrum at 300 K compound **2** showed a broad singlet at δ -475.1 ($\Delta\nu_{1/2} = 412$ Hz). Cooling the solution down to 273 K leads to the coalescence of the

signal. At temperatures lower than 263 K the spectrum showed two broad signals which progressively transformed into two mutually coupled triplets. At 193 K the triplets were centered at δ -450.5 (P^A) and δ -490.7 (P^B) and the direct coupling constant was $^1J_{PP} = 178$ Hz.^[XX] This behavior is indicative of a dynamic process involving the coordinated P₄ molecule. It has been now ascertained that η^1 -bonded P₄ complexes of type **A** are fluxional: in the case of Ru, Os[V. Mirabello, M. Caporali, V. Gallo, L. Gonsalvi, D. Gudat, W. Frey, A. Ienco, M. Latronico, P. Mastrorilli, M. Peruzzini, *Chemistry-A European Journal*, **2012**, *18*, 11238-11250] or Mn[ref2g] complexes the main dynamic process (beside the rotation about the metal-P axis) is a tumbling movement of the P₄ cage while remaining chemically coordinated to the metal; in the case of Cp*Fe(dppe)(η^1 -P₄) the main dynamic process is the dissociation of P₄. In order to shed light to the dynamic motion(s) responsible for the experimental ³¹P NMR behavior we have recorded ³¹P EXSY spectra of **2** in CD₂Cl₂ at various temperatures. The ³¹P EXSY spectrum of **2** at 213 K (Figure 3) showed exchange cross peaks between the triplets ascribed to P^A and P^B, indicating that, at low T, the main dynamic process is the tumbling of coordinated P₄.

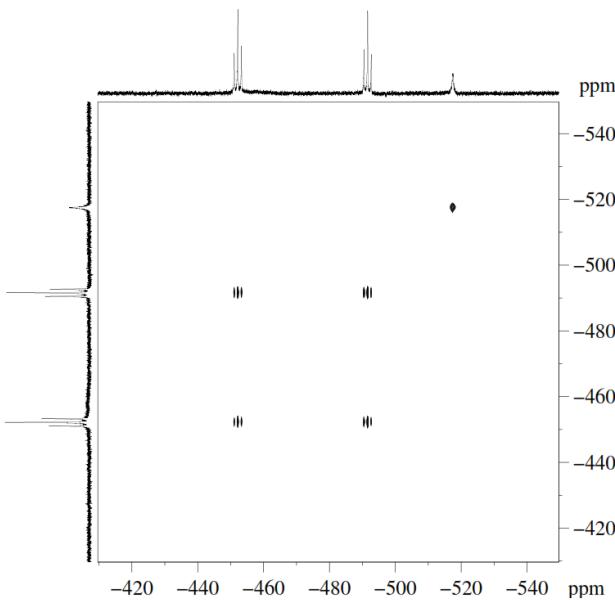


Figure 3. Portion of the ³¹P EXSY spectrum of **2** in CD₂Cl₂ at 213 K ($\tau_m = 0.200$ s)

However, on rising the temperature, the dissociative process begins to occur. In fact, at 243 K, besides the clear P^{A/B} exchange, a very weak cross peak between P^{A/B} and free P₄ becomes visible and, at 300 K, the exchange between P^{A/B} (now consisting of a single broad signal) and free P₄ becomes predominant. It is interesting to note that dissociation of P₄ from **2** results in an equilibrium between **1a**, **2** and free P₄, as indicated by the exchange cross peaks between **1a**, **2** and free P₄ (δ -518) in the ³¹P EXSY spectrum of **2** at 300 K (Figure 4).

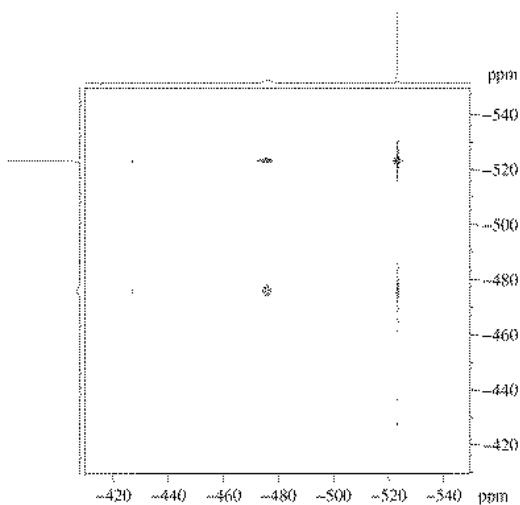


Figure 4. Portion of the ^{31}P EXSY spectrum of **2** in CD_2Cl_2 at 300 K ($\tau_m = 0.200$ s)

Given that “pure” tumbling occurs only at low T, we have carried out a line shape analysis of the $^{31}\text{P}\{\text{H}\}$ NMR spectra in the interval 213–253 K, obtaining the following activation parameters: $\Delta H^\# = 44.8$ kJ/mol; $\Delta S^\# = -41$ kJ/mol; $\Delta G^\# = 56.9$ kJ/mol. The activation free energy value is comparable to those obtained for the neutral Mn complex $[\text{Cp}^{\text{BIG}}\text{Mn}(\text{CO})_2(\eta^1\text{-P}_4)][\text{ref}2\text{g}]$ and for the cationic complexes $[\text{Ru}(\text{H})(\text{dpmm})_2(\eta^1\text{-P}_4)]^+$ and $[\text{Ru}(\text{H})(\text{dppe})_2(\eta^1\text{-P}_4)]^+.$ [V. Mirabello, M. Caporali, V. Gallo, L. Gonsalvi, A. Ienco, M. Latronico, P. Mastrolilli, M. Peruzzini, *Dalton Transactions*, **2011**, 40, 9668–9671]

$[(\text{NacnacCu})_2(\mu,\eta^{2:2}\text{-As}_4)]$ (**1b**) was characterized. Compound **1b** is the first example of a neutral complex, containing an intact As_4 tetrahedron as ligand at all. DFT- and AIM-calculations confirmed, that the E_4 ligands ($\text{E} = \text{P}, \text{As}$) should be considered as being intact. Furthermore, the liberation of the E_4 ($\text{E} = \text{P}, \text{As}$) ligands was achieved by substitution with pyridine. The liberated E_4 was proven by $^{31}\text{P}\{\text{H}\}$ and $^{75}\text{As}\{\text{H}\}$ -NMR spectroscopy, respectively. Furthermore, we reported on characterization of $[\text{NacnacCu}(\eta^2\text{-P}_4)]$ (**2**). The main dynamic behavior of **2** was examined by VT $^{31}\text{P}\{\text{H}\}$ and $^{31}\text{P}\{\text{H}\}$ EXSY NMR investigations. At low temperatures (up to 213 K) tumbling of the P_4 ligand takes place. On rising the temperature a dissociative process of the P_4 ligand starts to occur.

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Scheme 1. Scheme Caption.

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Figure 1. Figure Caption.

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Table 1. Table Caption.((Note: Please do not include the table in a textbox or frame.))

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Column 1	Column 2	Column 3	Column 4	Column 5

[a] Table Footnote) [b] ...

Experimental Section

Experimental Details.

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In conclusion, we reported on the $[(\text{NacnacCu})_2(\mu,\eta^{2:2}\text{-P}_4)]$ (**1a**), the first neutral complex containing an intact $\eta^2\text{-P}_4$ tetrahedron as ligand. Additionally the arsenic analogue complex

J. **2007**, *13*, 6682-6690; c) M. Caporali, M. Di Vaira, M. Peruzzini, S. Seniori Costantini, P. Stoppioni, F. Zanobini, *Eur. J. Inorg. Chem.* **2010**, *2010*, 152-158.

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[X] Control experiment: P₄ solvated in Pyridine

[XX] See Supporting information.

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