

Politecnico di Bari

Repository Istituzionale dei Prodotti della Ricerca del Politecnico di Bari

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

This is a pre-print of the following article

Original Citation:
Fixation and release of intact E4 tetrahedra (E = P, As) / Fabian, S., Marek, S., Latronico, M., Mastrorilli, P., Alexander V., V., Manfred, S.. - In: ANGEWANDTE CHEMIE. INTERNATIONAL EDITION. - ISSN 1433-7851. - STAMPA. - 54:14(2015), pp. 4392-4396. [10.1002/anie.201411451]

Availability:
This version is available at http://hdl.handle.net/11589/5994 since: 2021-03-12

Published version
DOI:10.1002/anie.201411451

Publisher:

Terms of use:

(Article begins on next page)

27 November 2026

Angewandte Communications

Complexes with P_4 and As_4

DOI: 10.1002/anie.201((will be filled in by the editorial staff))

Inclusion and liberation of intact E_4 Tetrahedra (E = P, As)**

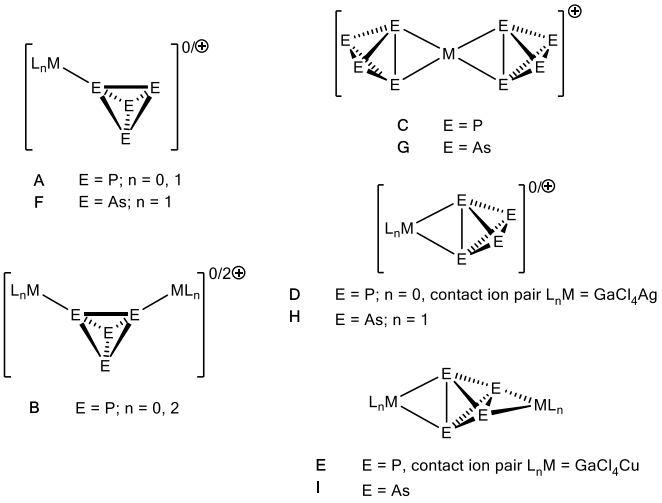
*Fabian Spitzer, Marek Sierka, Mario Latronico, Piero Mastrorilli, and Manfred Scheer**

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)).*

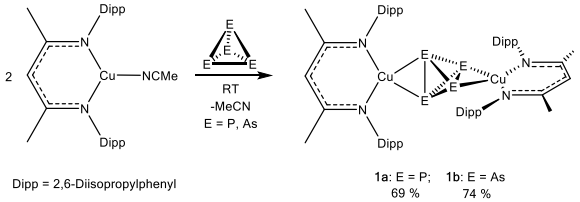
Since the first complex $[(np_3)Ni(\eta^1\text{-}P_4)]$ with an intact P_4 tetrahedron as ligand has been discovered by Sacconi *et al.* 1979,[1] a huge progress has been made within the last decades in the synthesis and characterization of complexes containing an intact E_4 tetrahedron (E = P, As) as 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 P_4 tetraheda are known of ionic and neutral complexes as well. However, complexes containing terminal[4] η^2- or bridging[5] $\mu,\eta^{2:2}$-P_4 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 P_4 containing complexes of this type, the As_4 derivatives are only sparingly studied. This is due to the high light sensitivity of yellow arsenic (As_4). In consequence, only few compounds have been published to date. Recently we reported about the synthesis of complexes containing As_4 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 As_4 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 As_4 tetrahedra to metal centers.



In the literature, there are two examples for neutral η^2-P_4 ligand complexes. On the one side Ginsberg *et al.* reported on $[RhCl(\eta^2\text{-}P_4)(PPh_3)_2]$,[7] for which the description as a P_4^{2-} ligand seems more appropriate, however. On the other side Scherer *et al.* reported on $[(C_5HR_4)Cu(\eta^2\text{-}P_4)]$ (R = $CHMe_2$),[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 E_4 containing complexes. We choose the sterically demanding, non-innocent β-Diketiminato ligand $[\{N(C_6H_3{}^iPr_2\text{-}2,6)C(Me)\}_2CH]^-$ (Nacnac). When it coordinates to one metal center, the aromatic Dipp groups (Dipp = 2,6-Diisoprylphenyl) form a pocket, which size and shape is adequate to accommodate small molecules like E_4.

Herein we report on the synthesis and characterization of $[(NacnacCu)_2(\mu,\eta^{2:2}\text{-}E_4)]$ (E = P (**1a**), As (**1b**)) the first neutral complexes containing an E_4 tetrahedron as bridging ligand in the $\mu,\eta^{2:2}$-fashion. Furthermore we report on the treatment of **1a** with P_4, which results in the formation of $[NacnacCu(\eta^2\text{-}P_4)]$ (**2**). Its dynamic behavior in solution was investigated by VT $^{31}P\{^1H\}$ and $^{31}P\{^1H\}$ EXSY NMR spectroscopy.



(1)

[*] M.Sc. Fabian Spitzer, Prof. Dr. Manfred Scheer
Department of inorganic Chemistry, University of Regensburg
93040 Regensburg (Germany)
E-mail: Manfred.scheer@chemie.uni-regensburg.de
Homepage: http://www.uni-regensburg.de/chemie-pharmazie/anorganische-chemie-scheer/
Prof. Dr. M. Sierka
Institute of Material Science and Technology
Friedrich-Schiller-University of Jena
Löbdergraben 32, 07743 Jena (Germany)
Prof. Dr. P. Mastrorilli, Prof. M. Latronico
Dipartimento di Ingegneria Civile, Ambientale, del Territorio Edile e di Chimica (DICATECh), Politecnico di Bari via Orabona 4, 70125 Bari (Italy) .
M. Sc. C. Koch, Prof. Dr. R. M. Gschwind
Department of organic Chemistry, University of Regensburg
93040 Regensburg (Germany)

[**] Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201xxxxxx.((Please delete if not appropriate))

© Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Compound **1a** is formed by the stoichiometric reaction of [NacnacCu(NCMe)] with P_4. 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 (As_4) 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 As_4 solution in toluene leads to the formation of the first neutral metal-arsenic complex **1b** containing an intact As_4 tetrahedron as ligand in good yields [Eq. (1)]. Removing the solvent leads to the conversation 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 CD_2Cl_2 shows a sharp singlet at -426.85 ppm in $^{31}P\{^1H\}$ NMR spectrum. Complex **1b** in contrast does not show a signal in $^{75}As\{^1H\}$ NMR due to low molecule symmetry and to the quadrupole moment of ^{75}As.

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 E_4 tetrahedrons by two opposing edges to two NacnacCu fragments (**Figure 1** and **Figure 2**).

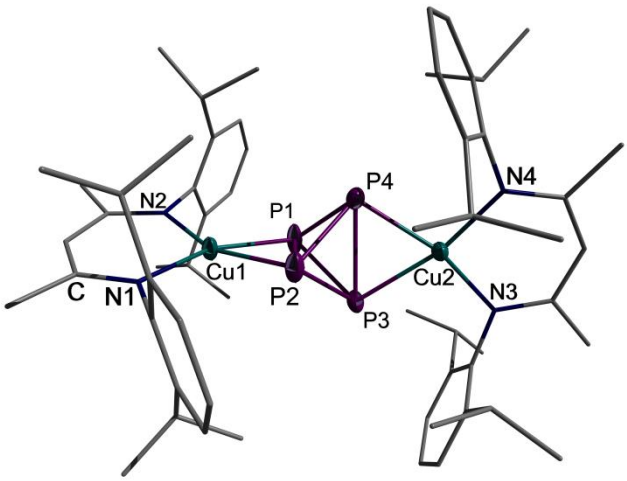


Figure 1. Molecular structure of compound **1a** in the crystal (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Cu1-P1 2.2629(4), Cu1-P2 2.2663(5), Cu2-P4 2.2589(5), Cu2-P3 2.2706(5), P1-P2 2.4119(6), P3-P4 2.4283(6), P1-P3 2.2115(6), P2-P3 2.2043(6), P1-P4 2.2006(7), 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).

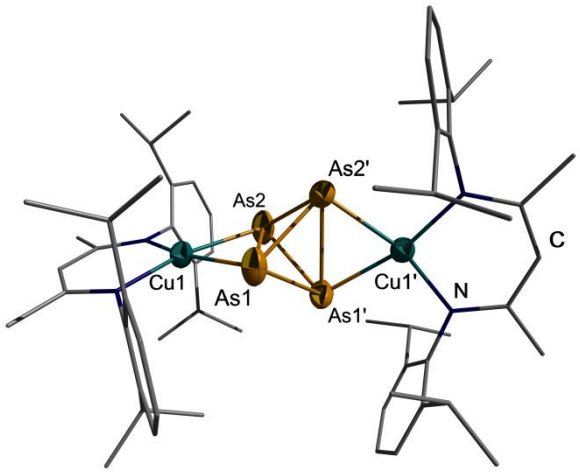


Figure 2. Molecular structure of compound **1b** in the crystal (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: As1-Cu1 2.3761(7), As2-Cu1 2.3879(8), As1-As2 2.6485(8), As1-As1' 2.4355(5), As1-As2' 2.4435(9), As2-As2' 2.4373(6), As1'-As1-As2 57.27(2), As2-As1-As2' 57.03(2), 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 (Σ_{angles} = 360°) is about 2° in **1a** and less than 0.1° in **1b**. As a result of the bridging E_4 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 $[Cu(\eta^2\text{-}P_4)_2][pftb]$ (pftb = $[Al\{OC(CF_3)_3\}_4]$)[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 As_4 ligand reported in the literature so far. The closest related known complex to **1b** is $[Ag(\eta^2\text{-}As_4)_2][pftb]$[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)°.

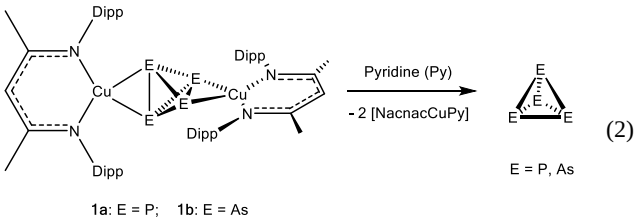
Enforcedly the question arises, whether the coordinating E-E edges (ratio P-P: **1a**/$P_{4,\ free}$ = 1.0945, ratio As-As: **1b**/$As_{4,\ free}$ = 1.0866) should be considered as elongated E-E bond or as cleaved? To get deeper understanding in the bonding situation of compound **1a** and **1b**, quantum chemical calculations have been carried out.

© Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Prof. Marek Stefaniak

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 $\mu,\eta^{2:2}$-E_4 tetrahedron in compound **1a** and **1b** could be substituted by a comparably stronger Lewis base, the E_4 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 $^{31}P\{^1H\}$ and $^{75}As\{^1H\}$ NMR investigation [Eq. (2)].

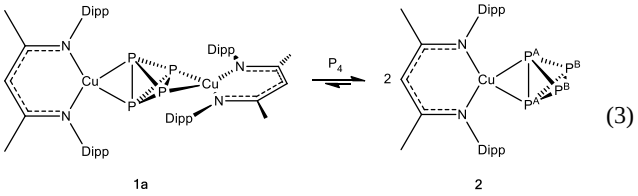


(2)

1a: E = P; 1b: E = As

Indeed, adding pyridine (Py) to complex **1a** and **1b**, respectively leads to the liberation of the E_4 tetrahedron. Compound **1a** in CD_2Cl_2 shows a sharp singlet at -426.85 ppm in $^{31}P\{^1H\}$ 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 $^{75}As\{^1H\}$ NMR spectrum due to low molecule symmetry and to the quadrupole moment of ^{75}As nucleus. However, adding an excess of pyridine-d_5 to a solution of **1b** in CD_2Cl_2 gives rise to the liberation of yellow arsenic, which was detected as broad singlet at -912 ppm in the $^{75}As\{^1H\}$ NMR spectrum.

The question arises, if a complex [NacnacCu(η^2-E_4)] (E = P, As) could be generated. Adding an excess of E_4 should give rise to the formation of complexes with an stoichiometry Cu:E_4 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 P_4 gave rise to the formation of a second phosphorous containing species [NacnacCu(η^2-P_4)] (**2**) [Eq. (3)].



(3)

1a 2

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 CD_2Cl_2 solution. In the $^{31}P\{^1H\}$ 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 P_4 molecule. It has been now ascertained that η^1-bonded P_4 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 P_4 cage while remaining chemically coordinated to the metal; in the case of Cp*Fe(dppe)(η^1-P_4) the main dynamic process is the dissociation of P_4. In order to shed light to the dynamic motion(s) responsible for the experimental ^{31}P NMR behavior we have recorded ^{31}P EXSY spectra of **2** in CD_2Cl_2 at various temperatures. The ^{31}P 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 P_4.

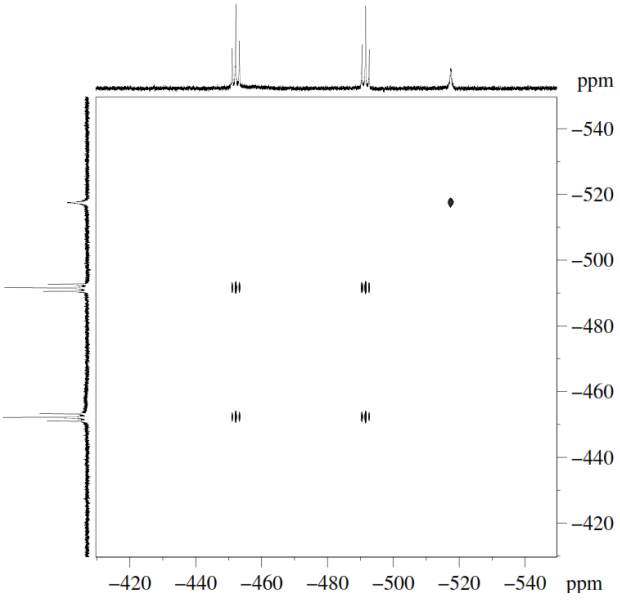


Figure 3. Portion of the ^{31}P EXSY spectrum of **2** in CD_2Cl_2 at 213 K (τ_m = 0.200 s)

However, on rising the temperature, the dissociative process begins to occur. In fact, at 243 K, besides the clear P^A/P^B exchange, a very weak cross peak between $P^{A/B}$ and free P_4 becomes visible and, at 300 K, the exchange between $P^{A/B}$ (now consisting of a single broad signal) and free P_4 becomes predominant. It is interesting to note that dissociation of P_4 from **2** results in an equilibrium between **1a**, **2** and free P_4, as indicated by the exchange cross peaks between **1a**, **2** and free P_4 (δ –518) in the ^{31}P EXSY spectrum of **2** at 300 K (Figure 4).

© Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

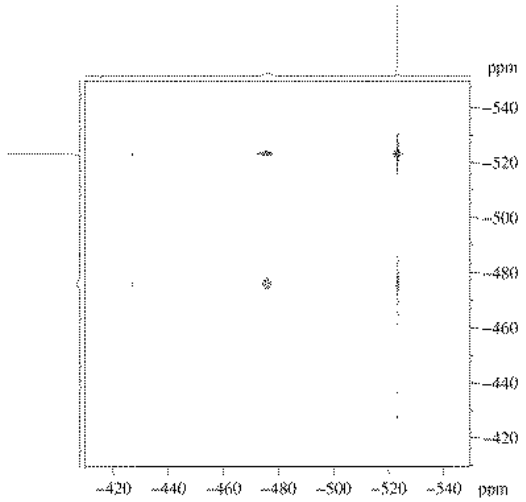


Figure 4. Portion of the ^{31}P EXSY spectrum of **2** in CD_2Cl_2 at 300 K (τ_m = 0.200 s)

Given that "pure" tumbling occurs only at low T, we have carried out a line shape analysis of the $^{31}P\{^1H\}$ 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 $[Cp^{BIG}Mn(CO)_2(\eta^1\text{-}P_4)]$[ref2g] and for the cationic complexes $[Ru(H)(dppm)_2(\eta^1\text{-}P_4)]^+$ and $[Ru(H)(dppe)_2(\eta^1\text{-}P_4)]^+$.[V. Mirabello, M. Caporali, V. Gallo, L. Gonsalvi, A. Ienco, M. Latronico, P. Mastrorilli, M. Peruzzini, *Dalton Transactions*, **2011**, *40*, 9668-9671]

In conclusion, we reported on the $[(NacnacCu)_2(\mu,\eta^{2:2}\text{-}P_4)]$ (**1a**), the first neutral complex containing an intact $\eta^2\text{-}P_4$ tetrahedron as ligand. Additionally the arsenic analogue complex $[(NacnacCu)_2(\mu,\eta^{2:2}\text{-}As_4)]$ (**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 (E = P, As) should be considered as being intact. Furthermore, the liberation of the E_4 (E = P, As) ligands was achieved by substitution with pyridine. The liberated E_4 was proven by $^{31}P\{^1H\}$ and $^{75}As\{^1H\}$-NMR spectroscopy, respectively. Furthermore, we reported on characterization of $[NacnacCu(\eta^2\text{-}P_4)]$ (**2**). The main dynamic behavior of **2** was examined by VT $^{31}P\{^1H\}$ and $^{31}P\{^1H\}$ 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. ((Insert Scheme here. **Note:** Please do **not** combine scheme and caption in a textbox or frame))

Scheme 1. Scheme Caption.

Main Text Paragraphs----with Indentation.

((Insert Figure here. **Note:** Please do **not** combine figure and caption in a textbox or frame))

Figure 1. Figure Caption.

Main Text Paragraphs----with Indentation.

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

Head 1[a]	Head 2	Head 3[b]	Head 4[c]	Head 5
Column 1	Column 2	Column 3	Column 4	Column 5
Column 1	Column 2	Column 3	Column 4	Column 5

[a] Table Footnote)) [b] …

Experimental Section

Experimental Details.

Received: ((will be filled in by the editorial staff))
Published online on ((will be filled in by the editorial staff))

Keywords: yellow arsenic • white phosphorus • main-group chemistry • DFT calculations • NMR spectroscopy

[1] P. Dapporto, S. Midollini, L. Sacconi, *Angew. Chem.* **1979**, *91*, 510-510.

[2] a) P. Dapporto, S. Midollini, L. Sacconi, *Angew. Chem.* **1979**, *91*, 510-510; b) T. Gröer, G. Baum, M. Scheer, *Organometallics* **1998**, *17*, 5916-5919; c) M. Peruzzini, L. Marvelli, A. Romerosa, R. Rossi, F. Vizza, F. Zanobini, *Eur. J. Inorg. Chem.* **1999**, *1999*, 931-933; d) I. de los Rios, J.-R. Hamon, P. Hamon, C. Lapinte, L. Toupet, A. Romerosa, M. Peruzzini, *Angew. Chem., Int. Ed.* **2001**, *40*, 3910-3912; e) M. Di Vaira, P. Frediani, S. S. Costantini, M. Peruzzini, P. Stoppioni, *Dalton Trans.* **2005**, 2234-2236; f) M. Caporali, M. Di Vaira, M. Peruzzini, S. Seniori Costantini, P. Stoppioni, F. Zanobini, *Eur. J. Inorg. Chem.* **2010**, *2010*, 152-158; g) S. Heinl, E. V. Peresypkina, A. Y. Timoshkin, P. Mastrorilli, V. Gallo, M. Scheer, *Angew. Chem., Int. Ed.* **2013**, *52*, 10887-10891.

[3] a) M. Peruzzini, L. Marvelli, A. Romerosa, R. Rossi, F. Vizza, F. Zanobini, *Eur. J. Inorg. Chem.* **1999**, *1999*, 931-933; b) P. Barbaro, M. Di Vaira, M. Peruzzini, S. Seniori Costantini, P. Stoppioni, *Chem. Eur.*

© Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

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.

[4] a) I. Krossing, L. van Wüllen, *Chem. Eur. J.* **2002**, *8*, 700-711; b) G. Santiso-Quinones, A. Reisinger, J. Slattery, I. Krossing, *Chem. Commun.* **2007**, 5046-5048; c) L. C. Forfar, T. J. Clark, M. Green, S. M. Mansell, C. A. Russell, R. A. Sanguramath, J. M. Slattery, *Chem. Commun.* **2012**, *48*, 1970-1972.

[5] L. C. Forfar, T. J. Clark, M. Green, S. M. Mansell, C. A. Russell, R. A. Sanguramath, J. M. Slattery, *Chem. Commun.* **2012**, *48*, 1970-1972.

[6] a) C. Schwarzmaier, A. Y. Timoshkin, M. Scheer, *Angew. Chem.* **2013**, *125*, 7751-7755; b) C. Schwarzmaier, M. Sierka, M. Scheer, *Angew. Chem., Int. Ed.* **2013**, *52*, 858-861.

[7] A. P. Ginsberg, W. E. Lindsell, K. J. McCullough, C. R. Sprinkle, A. J. Welch, *J. Am. Chem. Soc.* **1986**, *108*, 403-416.

[8] D. N. Akbayeva, O. J. Scherer, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1429-1430.

[9]

[10] G. Santiso-Quinones, A. Reisinger, J. Slattery, I. Krossing, *Chem. Commun.* **2007**, 5046-5048.

[11] C. Schwarzmaier, M. Sierka, M. Scheer, *Angew. Chem., Int. Ed.* **2013**, *52*, 858-861.

[12] B. M. Cossairt, C. C. Cummins, A. R. Head, D. L. Lichtenberger, R. J. F. Berger, S. A. Hayes, N. W. Mitzel, G. Wu, *J. Am. Chem. Soc.* **2010**, *132*, 8459-8465.

[13] N. J. Brassington, H. G. M. Edwards, D. A. Long, *J. Raman Spectrosc.* **1981**, *11*, 346-348.

[14] B. M. Cossairt, C. C. Cummins, A. R. Head, D. L. Lichtenberger, R. J. F. Berger, S. A. Hayes, N. W. Mitzel, G. Wu, *J. Am. Chem. Soc.* **2010**, *132*, 8459-8465.

[15] Y. Morino, T. Ukaji, T. Ito, *Bull. Chem. Soc. Jpn.* **1966**, *39*, 64-71.

[16] L. R. Maxwell, S. B. Hendricks, V. M. Mosley, *J. Chem. Phys.* **1935**, *3*, 699-709.

[17] H. A. Spinney, N. A. Piro, C. C. Cummins, *J. Am. Chem. Soc.* **2009**, *131*, 16233-16243.

[X] Control experiment: P_4 solvated in Pyridine

[XX] See Supporting information.

© Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

WILEY ONLINE LIBRARY © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

[1] P. Dapporto, S. Midollini, L. Sacconi, *Angew. Chem.* **1979**, *91*, 510-510.
[2] a) P. Dapporto, S. Midollini, L. Sacconi, *Angew. Chem.* **1979**, *91*, 510-510; b) T. Gröer, G. Baum, M. Scheer, *Organometallics* **1998**, *17*, 5916-5919; c) M. Peruzzini, L. Marvelli, A. Romerosa, R. Rossi, F. Vizza, F. Zanobini, *Eur. J. Inorg. Chem.* **1999**, *1999*, 931-933; d) I. de los Rios, J.-R. Hamon, P. Hamon, C. Lapinte, L. Toupet, A. Romerosa, M. Peruzzini, *Angew. Chem., Int. Ed.* **2001**, *40*, 3910-3912; e) M. Di Vaira, P. Frediani, S. S. Costantini, M. Peruzzini, P. Stoppioni, *Dalton Trans.* **2005**, 2234-2236; f) M. Caporali, M. Di Vaira, M. Peruzzini, S. Seniori Costantini, P. Stoppioni, F. Zanobini, *Eur. J. Inorg. Chem.* **2010**, *2010*, 152-158; g) S. Heinl, E. V. Peresypkina, A. Y. Timoshkin, P. Mastrorilli, V. Gallo, M. Scheer, *Angewandte Chemie International Edition* **2013**, *52*, 10887-10891.
[3] a) M. Peruzzini, L. Marvelli, A. Romerosa, R. Rossi, F. Vizza, F. Zanobini, *Eur. J. Inorg. Chem.* **1999**, *1999*, 931-933; b) P. Barbaro, M. Di Vaira, M. Peruzzini, S. Seniori Costantini, P. Stoppioni, *Chem. Eur. 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.
[4] a) I. Krossing, L. van Wüllen, *Chem. Eur. J.* **2002**, *8*, 700-711; b) G. Santiso-Quinones, A. Reisinger, J. Slattery, I. Krossing, *Chem. Commun.* **2007**, 5046-5048; c) L. C. Forfar, T. J. Clark, M. Green, S. M. Mansell, C. A. Russell, R. A. Sanguramath, J. M. Slattery, *Chem. Commun.* **2012**, *48*, 1970-1972.
[5] L. C. Forfar, T. J. Clark, M. Green, S. M. Mansell, C. A. Russell, R. A. Sanguramath, J. M. Slattery, *Chem. Commun.* **2012**, *48*, 1970-1972.
[6] a) C. Schwarzmaier, A. Y. Timoshkin, M. Scheer, *Angew. Chem.* **2013**, *125*, 7751-7755; b) C. Schwarzmaier, M. Sierka, M. Scheer, *Angew. Chem., Int. Ed.* **2013**, *52*, 858-861.
[7] A. P. Ginsberg, W. E. Lindsell, K. J. McCullough, C. R. Sprinkle, A. J. Welch, *J. Am. Chem. Soc.* **1986**, *108*, 403-416.
[8] D. N. Akbayeva, O. J. Scherer, *Z. Anorg. Allg. Chem.* **2001**, *627*, 1429-1430.
[9] ???????
[10] G. Santiso-Quinones, A. Reisinger, J. Slattery, I. Krossing, *Chem. Commun.* **2007**, 5046-5048.
[11] C. Schwarzmaier, M. Sierka, M. Scheer, *Angew. Chem., Int. Ed.* **2013**, *52*, 858-861.
[12] B. M. Cossairt, C. C. Cummins, A. R. Head, D. L. Lichtenberger, R. J. F. Berger, S. A. Hayes, N. W. Mitzel, G. Wu, *J. Am. Chem. Soc.* **2010**, *132*, 8459-8465.
[13] N. J. Brassington, H. G. M. Edwards, D. A. Long, *J. Raman Spectrosc.* **1981**, *11*, 346-348.
[14] B. M. Cossairt, C. C. Cummins, A. R. Head, D. L. Lichtenberger, R. J. F. Berger, S. A. Hayes, N. W. Mitzel, G. Wu, *J. Am. Chem. Soc.* **2010**, *132*, 8459-8465.
[15] Y. Morino, T. Ukaji, T. Ito, *Bull. Chem. Soc. Jpn.* **1966**, *39*, 64-71.
[16] L. R. Maxwell, S. B. Hendricks, V. M. Mosley, *J. Chem. Phys.* **1935**, *3*, 699-709.
[17] H. A. Spinney, N. A. Piro, C. C. Cummins, *J. Am. Chem. Soc.* **2009**, *131*, 16233-16243.

---

[1] ((Reference 1, **Example for Journals**:)) a) A. Author, B. Coauthor, *Angew. Chem.* **2006**, *118*, 1-5; *Angew. Chem. Int. Ed.* **2006**, *45*, 1-5; b) A. Author, B. Coauthor, *ChemBioChem* **2006**, *7*, 1-10.
[2] ((Reference 2: **Example for Books**:)) J. W. Grate, G. C. Frye, in *Sensors Update*, Vol. 2 (Eds: H. Baltes, W. Göpel, J. Hesse), WILEY-VCH, Weinheim, **1996**, pp. 10-20.
[3] …

© Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim