Intact P_4 and As_4 Complexes

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Fixation and Release of Intact E_4 Tetrahedra (E = P, As)**

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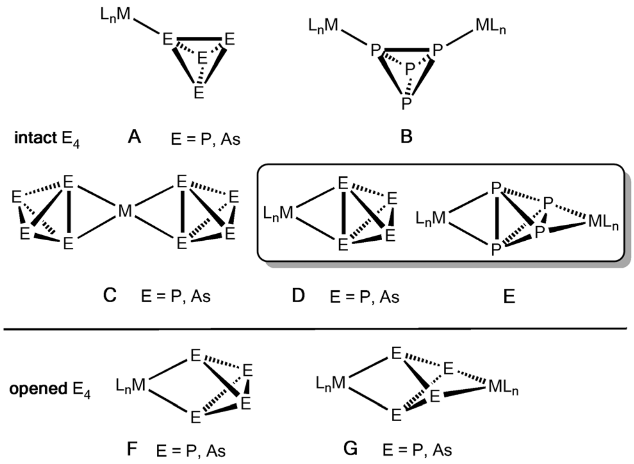
Dedicated to Professor Michael Veith on the occasion of his 70th birthday

***Abstract:** By the reaction of [NacnacCuCH_3CN] with white phosphorus (P_4) and yellow arsenic (As_4), the stabilization and enclosure of the intact E_4 tetrahedra are realized and the disubstituted complexes [(NacnacCu)$_2$($\mu,\eta^{2:2}$-E_4)] (**1a**: E = P, **1b**: E = As) are formed. The mono-substituted complex [NacnacCu(η^2-P_4)] (**2**), was detected by the exchange reaction of **1a** with P_4 and was only isolated using low-temperature work-up. All products were comprehensively spectroscopically and crystallographically characterized. The bonding situation in the products as intact E_4 units (E = P, As) was confirmed by theory and was experimentally proven by the pyridine promoted release of the bridging E_4 tetrahedra in **1**.*



Since the first complex [(np$_3$)Ni(η^1-P_4)] (np$_3$ = tris(2-diphenylphosphinoethyl)amine) with an intact P_4 tetrahedron as ligand was discovered by Sacconi et al. in 1979,[1] considerable progress has been made in the synthesis and characterization of complexes containing intact, that is, unopened, E_4 tetrahedra (E = P, As) as ligands. Such complexes reveal the first step of the E_4 activation by main-group and transition-metal complexes, respectively.[2] For the P_4 tetrahedron, single[1,3] (η^1, type **A**) and bridging[3c,f,4] ($\mu,\eta^{1:1}$, type **B**) end-on coordination modes are known in ionic and neutral complexes as well. However, to date complexes containing intact single coordinated[5] η^2-, or bridging[5c] $\mu,\eta^{2:2}$-P_4 ligands in a side-on coordination mode have been exclusively obtained for cationic coinage metal complexes (types **C**, **D**) or as part of ion-contacted coordination polymers (type **E**).

In contrast to the rich chemistry of P_4-containing complexes, As_4 derivatives have been only sparingly studied because of the extreme light sensitivity and handling problems with yellow arsenic (As_4). Recently, we reported the synthesis of cationic complexes of Ru, Ag, and Au containing intact As_4 as a ligand either in η^1- or η^2-bonding mode (types **A**, **C**, **D**).[6] The absence of neutral As_4 complexes of type **E** gave rise to the question as to whether a positively charged metal fragment is necessary for the η^2-coordination of an intact As_4 tetrahedron.

Few examples of neutral η^2-P_4 ligand complexes are known: Ginsberg et al. reported the complex [RhCl(η^2-P_4)(PPh$_3$)$_2$],[7] for which finally the bonding situation was later corrected to be a P_4^{2-} ligand containing an opened P–P edge (2.462(2) Å, type **F**).[5a] Something similar occurs with the Co complexes [Cp*Co(L′)(η^2-P_4)] and [{Cp*Co(L′)}$_2$($\mu,\eta^{2:2}$-P_4)] (Cp* = C_5Me_5; L′ = CO, *i*PrIm (1,3-di-isopropylimidazolin-2-ylidene)) of Scherer et al.[8] and Radius[9] et al. These compounds contain coordinated P_4 tetrahedra, also with short P–P edges (2.606(1) and 2.560(2)/2.597(2) Å and 2.6398(11) and 2.6161(16)/2.6282(18) Å), but calculations showed that the bonds are opened.[9b] Also, there are several neutral compounds known containing an E_4 unit with open E–E bond(s) (type **F** and **G**),[10] but no intact E_4 tetrahedra in η^2- or $\eta^{2:2}$-coordination mode have been described in neutral molecules to date (types **D** and **E**). Moreover, if the tetrahedron is intact, the release should be possible and furthermore, Scherer and Akbayeva reported the complex

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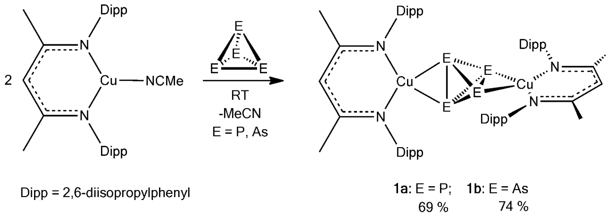
$[(Cp^{4iPr})Cu(\eta^2\text{-}P_4)]$ ($Cp^{4iPr} = C_5iPr_4H$),[11] which recently could be reviewed to be a doubly organo-substituted P_4 butterfly compound $(Cp^{4iPr})_2P_4$.[12] Thus, the quest for E_4 containing Cu complexes is still open.

To address these open topics, we searched for a combination of ligands and metals that could serve as a starting material for the synthesis of neutral E_4-containing complexes of types **D** and **E**. We chose the sterically demanding β-diketiminato ligand $[\{N(C_6H_3iPr_2\text{-}2,6)C(Me)\}_2CH]^-$. When it coordinates to a metal center, the aromatic Dipp groups (Dipp = 2,6-diisopropylphenyl) form a pocket, the size and shape of which is adequate to accommodate small molecules like E_4. Furthermore, we speculated that electron-rich metals would better serve as neutral metal centers to coordinate intact E_4 moieties accordingly. Thus, we chose copper(I) also to address the missing P_4 coordination compound.

Herein we report the synthesis and characterization of $[(LCu)_2(\mu,\eta^{2:2}\text{-}E_4)]$ ($L = [\{N(C_6H_3iPr_2\text{-}2,6)C(Me)\}_2CH]^-$; E = P (**1a**), As (**1b**)) the first neutral complex containing intact E_4 tetrahedra as bridging ligands in a $\mu,\eta^{2:2}$-coordination mode (type **E**) and the release of the E_4 tetrahedra by substitution with a stronger Lewis base. Furthermore, we report the formation of the mononuclear complex $[LCu(\eta^2\text{-}P_4)]$ (**2**) (type **D**) by the reaction of **1a** with P_4. Its dynamic behavior in solution was investigated by VT $^{31}P\{^1H\}$ and $^{31}P\{^1H\}$ EXSY NMR spectroscopy.



(1)

Compound **1a** is formed by the reaction of $[LCu(NCMe)]$[13] with P_4 in a stoichiometric ratio of 2:1 in CH_3CN or *n*-hexane [Eq. (1)]. Density functional theory (DFT) calculations reveal that this reaction is exergonic with free energy change of 115 kJ mol^{-1}. Despite higher free reaction energy of 126 kJ mol^{-1}, the synthesis of the arsenic analogue **1b** is more difficult. Yellow arsenic (As_4) is a not storable compound, owing to its sensitivity to light, air, and moisture. It needs to be prepared freshly in solution and therefore stoichiometric reactions are difficult to carry out. However, by adding [LCu(NCMe)] to a freshly prepared As_4 solution in toluene (large excess of As_4), **1b** is formed in good yields [Eq. (1)]. The remaining yellow arsenic is rapidly converted into insoluble grey arsenic and can be removed by filtration. Both compounds **1a** and **1b** are soluble in dichloromethane and even in less-polar solvents such as *n*-hexane or toluene. Solutions of **1a** and **1b** slowly decompose within several days indicated by a color change and precipitation of black solid. However, as a solid, they are stable under ambient conditions and can be stored under argon for months. Complex **1a** should be stored in the dark because of its light sensitivity. Surprisingly the arsenic compound **1b** is less sensitive to light. They are unprecedented neutral molecular complexes with an intact $\eta^{2:2}$-coordinated E_4 tetrahedron as a bridging ligand (type **E**, see below).

The ^1H NMR spectra of **1a** and **1b** show the expected sets of signals for the β-diketiminato ligands L. In $^{31}P\{^1H\}$ NMR spectrum of **1a** in CD_2Cl_2, a singlet at −426.9 ppm is observed. In contrast, **1b** does not show a signal in the $^{75}As\{^1H\}$ NMR owing to low symmetry of the molecule, as expected for the large quadrupole moment of the nucleus ^{75}As ($I = 3/2$). The Raman spectra of **1a** and **1b** are similar. Significant differences only can be obtained in the region between 500 and 150 cm^{-1}. For comparison, free white phosphorus and yellow arsenic show Raman modes at similar values.[14]

The molecular structures of **1a** and **1b** show the side-on coordination of the E_4 tetrahedra by two opposite LCu fragments (Figure 1 and 2).[24] The coordination geometry at Cu is almost square planar. The maximum deviation from the coplanarity is less than 0.5° and 0.1° in **1a** and **1b**, respectively. The Cu−P distances in **1a** vary from 2.2592(6) Å to 2.2707(6) Å. They are slightly shorter than the Cu−P distances found in $[Cu(\eta^2\text{-}P_4)_2][pftb]$ ($pftb = [Al\{OC(CF_3)_3\}_4]$)[5b] (2.336(2)–2.345(2) Å), the latter being a complex that also has a planar arrangement around Cu. The distances between the coordinating P atoms P1−P2 and P3−P4 in **1a** (2.4285(8) Å

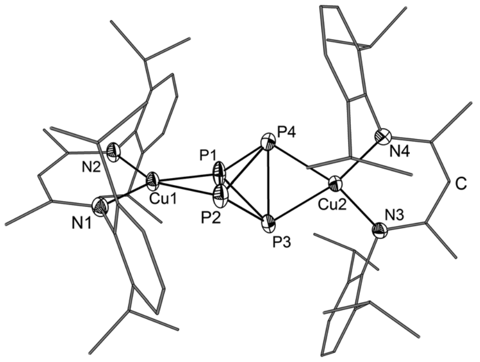


Figure 1. Molecular structure of **1a** in the crystal (hydrogen atoms are omitted for clarity; ellipsoids are set at 50% probability).

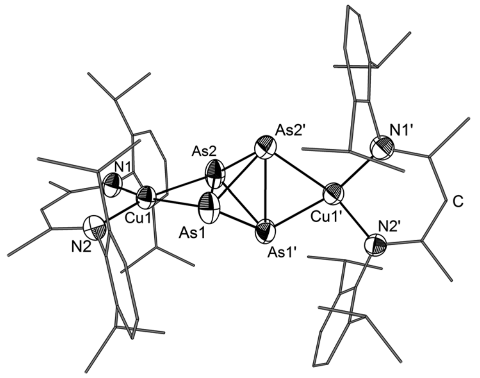
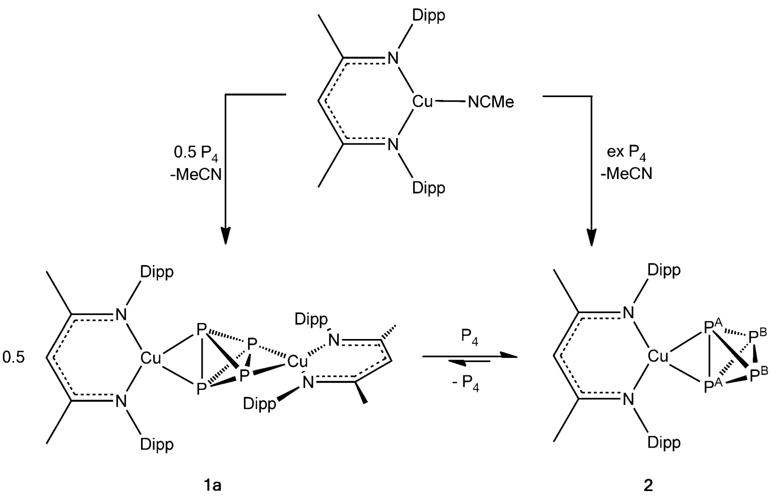


Figure 2. Molecular structure of $1b\cdot2C_6H_{14}$ in the crystal (hydrogen atoms and solvent molecules (*n*-hexane) are omitted for clarity; ellipsoids are set at 50% probability).



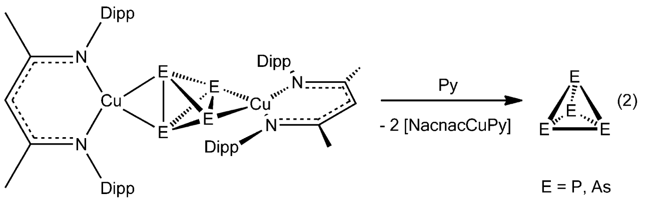
Scheme 1. Equilibria between [LCu(NCMe)], P_4, **1a**, and **2** in solution; labeling of the P atoms of **2** corresponds to the ^{31}P NMR data (see text for details).

and 2.4122(8) Å, respectively) are elongated compared to the P–P bond lengths in white phosphorus (determined by electron diffraction:[15] 2.1994(3) Å, Raman spectroscopy:[16] 2.2228(5) Å, DFT calculations:[15] 2.1994(3) Å).

Compound **1b** has similar features. The As1-As2 distance (2.6491(8) Å) is elongated compared to the As–As bond length in yellow arsenic (determined by electron diffraction: 2.435(4)[17] and 2.44(3)[18] Å, by DFT calculations:[19] 2.437 Å). The distances between non-coordinating As–As edges (2.4353(11)-2.4443(9) Å) are in the range of As–As single bonds. As no arsenic containing copper complex is so far reported, the closest known relative of **1b** is [Ag(η^2-As_4)$_2$][pftb],[6b] revealing coordinating As–As bonds of 2.585(2) and 2.569(2) Å, respectively.

In this context, the question arises as to whether the coordinating E–E edges should be considered as elongated but intact E–E bonds (ratio of E–E distance: **1a**/$P_{4,\text{free}} = 1.1005$; **1b**/$As_{4,\text{free}} = 1.0879$) or as cleaved ones. To gain deeper insight in the bonding situation of **1a** and **1b**, density functional theory (DFT) calculations were carried out. The calculation of the bond critical points (BCP), ring critical points (RCP), and the cage critical points (CCP) in **1a** and **1b** in comparison with that of the free E_4 tetrahedra confirm that the E_4 units (E = P, As) in these compounds can be considered as being intact and only a small depletion of the electron density of the coordinating E–E bond upon coordination to Cu occurred.[14]

To confirm the theoretical prediction experimentally, a displacement of the bridging μ,$\eta^{2:2}$-E_4 tetrahedra in **1a** and **1b** by a much stronger Lewis base, such as pyridine (Py), was performed and monitored by ^{31}P{^{1}H} and ^{75}As{^{1}H} NMR spectroscopy [Eq. (2)].



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

Compound **1a** shows a sharp singlet at −426.9 ppm in the ^{31}P{^{1}H} NMR spectrum in CD_2Cl_2. After dissolving **1a** in pyridine, a singlet at −518 ppm was exclusively detected, which reveals free white phosphorus.[20] Complex **1b** in contrast does not show a signal in ^{75}As{^{1}H} NMR spectrum, owing to low molecule symmetry and to the quadrupole moment of the ^{75}As nucleus. However, by adding an excess of pyridine to a solution of **1b** in CD_2Cl_2 a broad singlet at −912 ppm ($\omega_{1/2} = 5100$ Hz) was detected in the ^{75}As{^{1}H} NMR spectrum, which is characteristic for free yellow arsenic.[14,21]

Furthermore, the question arises for the existence of mononuclear copper complexes of the type [LCu(η^2-E_4)] (E = P, As). First evidence for the P derivative was obtained by monitoring a reaction between [LCu(NCMe)] and P_4 in a 1:1 stoichiometry by ^{31}P NMR spectroscopy. Here, besides traces of P_4 and the dinuclear complex **1a**, the desired complex [LCu(η^2-P_4)] (**2**) was also detected as a broad signal at −475 ppm. However, all attempts to isolate compound **2** failed (Scheme 1), instead **1a** could be isolated in yields much higher than initially indicated by the ^{31}P NMR spectrum. The calculated free energy for the reaction of **1a** to **2** indicates that it is slightly endergonic. Therefore, shifting equilibrium towards **2** requires considerable excess of P_4.

Indeed, by adding a solution of [LCu(NCMe)] to an excess of P_4 (3.5 equivalents) in *n*-pentane, **2** was generated quantitatively at room temperature. The reaction mixture was cooled to 77 K to precipitate the supernatant P_4. Filtration and evaporation of *n*-pentane were conducted at low temperatures of about 195 K. Light yellow crystals of [LCu(η^2-P_4)] (**2**) suitable for X-ray diffraction could be grown from concentrated *n*-pentane solution at that temperature. The molecular structure of **2** shows a P_4 tetrahedron coordinated to one LCu fragment (Figure 3). Despite the slightly exer-

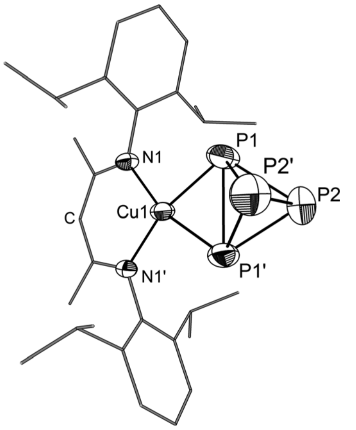


Figure 3. Molecular structure of **2** in the crystal (hydrogen atoms are omitted for clarity; ellipsoids are set at 50% probability).

gonic reaction, all attempts to isolate the arsenic analogue complex of **2** using a similar procedure failed. Instead of the mononuclear complex, compound **1b** was crystallized accompanied by the formation of black solid of grey arsenic. Although working at 195 K, the dinuclear compound **1b** seems to be more stable.

Complex **2** reveals a square-planar coordination geometry at the Cu atom ($\Sigma_{\mathrm{angles}} = 360.0(5)°$). The Cu−P distances are with 2.280(3) Å slightly longer than the Cu−P distances in **1a** (2.2592(6)–2.2707(6) Å). The distance between the coordinating P atoms P1 and P1′ of **2** (2.386(4) Å) are elongated compared to such P−P bond length in $[\mathrm{Cu}(\eta^2\text{-}\mathrm{P}_4)_2][\mathrm{pftb}]$[5b] (average $\mathrm{P{-}P}_{\mathrm{coordinated}}$: 2.342(2) Å) and for free P_4 (2.1994(3)–2.2228(5) Å),[15,16] but shorter than the coordinated P−P bonds in **1a** (2.4122(8) and 2.4285(8) Å). The distances P1−P2, P1−P2′, P1′−P2, and P1′−P2’ in **2** are between 2.180(4) and 2.192(4) Å, and thus longer than in $[\mathrm{Cu}(\eta^2\text{-}\mathrm{P}_4)_2][\mathrm{pftb}]$[5b] (average $\mathrm{P{-}P}_{\mathrm{non\text{-}coordinated}}$: 2.173(3) Å), but shorter than comparable bonds in **1a** (2.2010(9)–2.2114(8) Å). The P2−P2′ distance in **2** (2.141(6) Å) is smaller than the comparable distance in $[\mathrm{Cu}(\eta^2\text{-}\mathrm{P}_4)_2][\mathrm{pftb}]$[5b] (2.197(3) Å).

The bonding situation of **2** was investigated by DFT calculations. The P_4 unit in compound **2** shows a pattern of critical points very similar to **1a** and can therefore be considered as being intact. Crystals of **2** can be stored at 195 K. Slow decomposition occurs at higher temperatures indicated by the color change to black. Moreover, compound **2** easily can be prepared in solution by adding an excess of P_4 to **1a** or [LCu(NCMe)]. Such prepared solutions of **2** are stable even at room temperature and can be stored over months without decomposition if exclusion of light is ensured. Spectroscopic investigations of **2** prepared in situ could be conducted. Raman spectra of **2** in solution reveal one additional mode compared to **1a**.[14] Moreover, a freshly prepared solution of **2** in $\mathrm{CD_2Cl_2}$ was investigated in detail by variable-temperature $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectroscopy.[14] At 300 K a broad singlet at δ −475 ($\Delta\nu_{1/2} = 412$ Hz) for **2** is detected. Cooling the solution down to 273 K leads to breakdown of coalescence of the signal. At temperatures lower than 263 K two broad signals appear, which progressively transform into two mutually coupled triplets. At 193 K, the triplets centered at δ −450.5 ($\mathrm{P^A}$) and δ −490.7 ($\mathrm{P^B}$) reveal a coupling constant of $^1J_{\mathrm{PP}} = 178$ Hz. This behavior is indicative of a dynamic process involving the coordinated P_4 molecule. It should be noted that η^1-bonded P_4 complexes of type **A** are fluxional. For such Ru, Os,[22] or Mn[3a] complexes, the main dynamic process (apart from the rotation about the metal–phosphorus axis) is a tumbling movement of the P_4 cage while remaining chemically coordinated to the metal. For $[\mathrm{Cp^*Fe(dppe)}(\eta^1\text{-}\mathrm{P}_4)]^+$, the main dynamic process is the dissociation of the complex and temporary release of free P_4. To elucidate the dynamic process of **2**, which is responsible for the experimental ^{31}P NMR behavior, ^{31}P EXSY spectra of **2** (from **1a** and excess of P_4) in $\mathrm{CD_2Cl_2}$ at various temperatures were recorded. The ^{31}P EXSY spectrum of **2** at 213 K (Figure 4) showed exchange cross-peaks between the triplets ascribed to the atoms $\mathrm{P^A}$ and $\mathrm{P^B}$ (for assignment, see Scheme 1), indicating that at low temperature the main dynamic process is the tumbling of coordinated P_4.

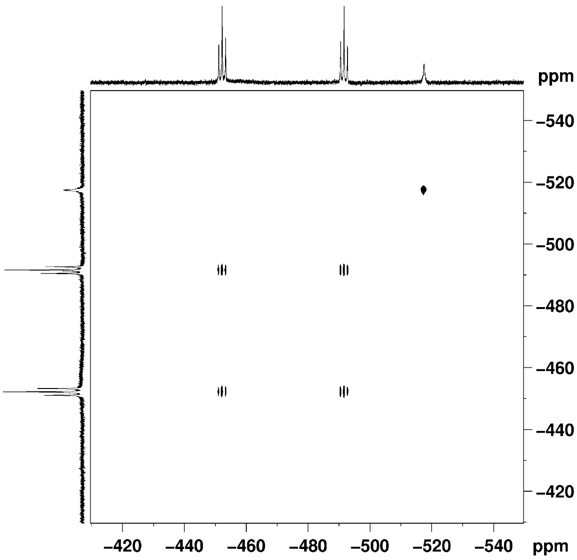


Figure 4. ^{31}P EXSY spectrum of **2** in $\mathrm{CD_2Cl_2}$ at 213 K ($\tau_{\mathrm{m}} = 0.200$ s).

However, on increasing the temperature, the dissociative process begins to occur. In fact, at 243 K, apart from the clear $\mathrm{P^A/P^B}$ exchange, a very weak cross-peak between $\mathrm{P^{A/B}}$ and free P_4 becomes visible and, at 300 K, the exchange between $\mathrm{P^{A/B}}$ (now consisting of a single broad signal), **1a** 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 −522) in the ^{31}P EXSY spectrum of **2** at 300 K (Figure 5).

Given that pure tumbling ($\eta^1 \rightarrow \eta^2 \rightarrow \eta^1$ walk down an edge of P_4)[22] occurs only at low temperatures, we have carried out a line shape analysis of the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra in the interval between 213 and 253 K, obtaining the following activation parameters: $\Delta H^{\#} = 44.8\ \mathrm{kJ\,mol^{-1}}$; $\Delta S^{\#} = -41\ \mathrm{kJ\,mol^{-1}K^{-1}}$; $\Delta G^{\#} = 56.9\ \mathrm{kJ\,mol^{-1}}$. The value of the free activation energy is comparable to those obtained for the

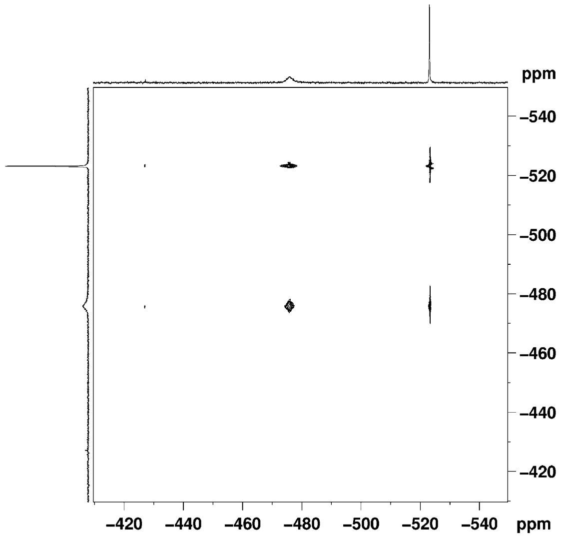


Figure 5. ^{31}P EXSY spectrum of **2** in $\mathrm{CD_2Cl_2}$ at 300 K ($\tau_{\mathrm{m}} = 0.200$ s).

neutral Mn complex $[Cp^{BIG}Mn(CO)_2(\eta^1\text{-}P_4)]^{[3a]}$ and for the cationic complexes $[Ru(H)(dppm)_2(\eta^1\text{-}P_4)]^+$ and $[Ru(H)(dppe)_2(\eta^1\text{-}P_4)]^{+[23]}$ (dppm = bis(diphenylphosphinomethane, dppe = 1,2-bis(diphenylphosphinoethane)).

In conclusion, we reported the synthesis of $[(LCu)_2(\mu,\eta^{2:2}\text{-}P_4)]$ (**1a**), the first neutral molecular complex containing an intact P_4 tetrahedron as a bridging side-on coordinated ligand. Additionally, the arsenic analogue $[(LCu)_2(\mu,\eta^{2:2}\text{-}As_4)]$ (**1b**) was synthesized as an unprecedented example of an intact As_4 tetrahedron as ligand fixed by two neutral complex fragments. Furthermore, $[LCu(\eta^2\text{-}P_4)]$ (**2**) was isolated, the first neutral molecular complex containing an intact P_4 tetrahedron in side-on coordination mode. The main dynamic behavior of **2** in solution was examined by VT $^{31}P\{^1H\}$ and $^{31}P\{^1H\}$ EXSY NMR spectroscopy. At low temperatures (up to 213 K) tumbling of the P_4 ligand takes place. By raising the temperature, dissociation of the P_4 ligand occurs. The existence of intact E_4 ligands (E = P, As) in **1a**, **1b**, and **2** was confirmed by DFT calculations, as well as experimentally by the liberation of the E_4 (E = P, As) molecules by substitution with pyridine.

Keywords: arsenic · density functional calculations · main-group chemistry · NMR spectroscopy · phosphorus

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[1] P. Dapporto, S. Midollini, L. Sacconi, *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 469–469; *Angew. Chem.* **1979**, *91*, 510–510.

[2] a) B. M. Cossairt, N. A. Piro, C. C. Cummins, *Chem. Rev.* **2010**, *110*, 4164–4177; b) M. Caporali, L. Gonsalvi, A. Rossin, M. Peruzzini, *Chem. Rev.* **2010**, *110*, 4178–4235; c) M. Scheer, G. Balázs, A. Seitz, *Chem. Rev.* **2010**, *110*, 4236–4256; d) S. Khan, S. S. Sen, H. W. Roesky, *Chem. Commun.* **2012**, *48*, 2169–2179; e) N. A. Giffin, J. D. Masuda, *Coord. Chem. Rev.* **2011**, *255*, 1342–1359.

[3] a) S. Heinl, E. V. Peresypkina, A. Y. Timoshkin, P. Mastrorilli, V. Gallo, M. Scheer, *Angew. Chem. Int. Ed.* **2013**, *52*, 10887–10891; *Angew. Chem.* **2013**, *125*, 11087–11091; 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**, 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; *Angew. Chem.* **2001**, *113*, 4028–4030; 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. S. Costantini, P. Stoppioni, F. Zanobini, *Eur. J. Inorg. Chem.* **2010**, 152–158.

[4] P. Barbaro, M. Di Vaira, M. Peruzzini, S. S. Costantini, P. Stoppioni, *Chem. Eur. J.* **2007**, *13*, 6682–6690.

[5] 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.

[6] a) C. Schwarzmaier, A. Y. Timoshkin, M. Scheer, *Angew. Chem. Int. Ed.* **2013**, *52*, 7600–7603; *Angew. Chem.* **2013**, *125*, 7751–7755; b) C. Schwarzmaier, M. Sierka, M. Scheer, *Angew. Chem. Int. Ed.* **2013**, *52*, 858–861; *Angew. Chem.* **2013**, *125*, 891–894.

[7] a) A. P. Ginsberg, W. E. Lindsell, *J. Am. Chem. Soc.* **1971**, *93*, 2082–2084; b) A. P. Ginsberg, W. E. Lindsell, K. J. McCullough, C. R. Sprinkle, A. J. Welch, *J. Am. Chem. Soc.* **1986**, *108*, 403–416.

[8] a) O. J. Scherer, K. Pfeiffer, G. Wolmershäuser, *Chem. Ber.* **1992**, *125*, 2367–2372; b) O. J. Scherer, M. Swarowsky, G. Wolmershäuser, *Organometallics* **1989**, *8*, 841–842.

[9] a) S. Dürr, D. Ertler, U. Radius, *Inorg. Chem.* **2012**, *51*, 3904–3909; b) B. Zarzycki, F. M. Bickelhaupt, U. Radius, *Dalton Trans.* **2013**, *42*, 7468–7481.

[10] a) G. Prabusankar, A. Doddi, C. Gemel, M. Winter, R. A. Fischer, *Inorg. Chem.* **2010**, *49*, 7976–7980; b) Y. Xiong, S. Yao, M. Brym, M. Driess, *Angew. Chem. Int. Ed.* **2007**, *46*, 4511–4513; *Angew. Chem.* **2007**, *119*, 4595–4597; c) Y. Peng, H. Fan, H. Zhu, H. W. Roesky, J. Magull, C. E. Hughes, *Angew. Chem. Int. Ed.* **2004**, *43*, 3443–3445; *Angew. Chem.* **2004**, *116*, 3525–3527; d) J. W. Dube, C. M. E. Graham, C. L. B. Macdonald, Z. D. Brown, P. P. Power, P. J. Ragogna, *Chem. Eur. J.* **2014**, *20*, 6739–6744.

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

[12] S. Heinl, S. Reisinger, C. Schwarzmaier, M. Bodensteiner, M. Scheer, *Angew. Chem. Int. Ed.* **2014**, *53*, 7639–7642; *Angew. Chem.* **2014**, *126*, 7769–7773.

[13] D. J. E. Spencer, N. W. Aboelella, A. M. Reynolds, P. L. Holland, W. B. Tolman, *J. Am. Chem. Soc.* **2002**, *124*, 2108–2109.

[14] See the Supporting Information.

[15] 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.

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

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

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

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

[20] Control experiment: P_4 solvated in pyridine; see the Supporting Information.

[21] C. Schwarzmaier, A. Schindler, C. Heindl, S. Scheuermayer, E. V. Peresypkina, A. V. Virovets, M. Neumeier, R. Gschwind, M. Scheer, *Angew. Chem. Int. Ed.* **2013**, *52*, 10896–10899; *Angew. Chem.* **2013**, *125*, 11097–11100.

[22] V. Mirabello, M. Caporali, V. Gallo, L. Gonsalvi, D. Gudat, W. Frey, A. Ienco, M. Latronico, P. Mastrorilli, M. Peruzzini, *Chem. Eur. J.* **2012**, *18*, 11238–11250.

[23] V. Mirabello, M. Caporali, V. Gallo, L. Gonsalvi, A. Ienco, M. Latronico, P. Mastrorilli, M. Peruzzini, *Dalton Trans.* **2011**, *40*, 9668–9671.

[24] CCDC 1035004 (**1a**), CCDC-1035006 ($\mathbf{1b}\cdot 2C_6H_{14}$), and CCDC 1035007 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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