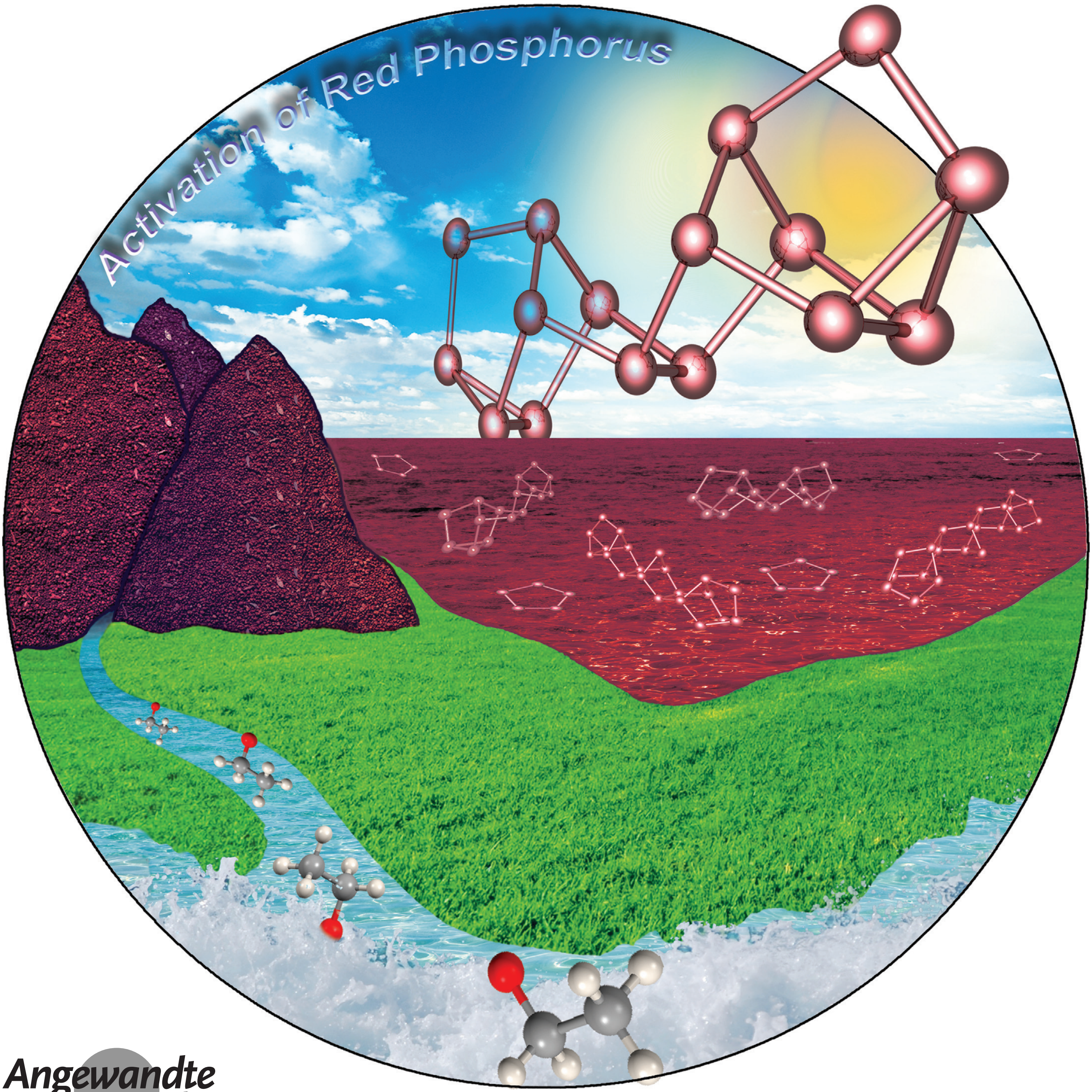
Red Phosphorus

International Edition: DOI: 10.1002/anie.201511186
German Edition: DOI: 10.1002/ange.201511186

Facile Conversion of Red Phosphorus into Soluble Polyphosphide Anions by Reaction with Potassium Ethoxide

Alina Dragulescu-Andrasi[+], *L. Zane Miller*[+], *Banghao Chen*, *D. Tyler McQuade*,* *and Michael Shatruk**



Abstract: *Soluble polyphosphide anions were successfully generated in a number of organic solvents by the reaction between shelf-stable red phosphorus and potassium ethoxide. The species were identified by* ^{31}*P NMR spectroscopy in solution and by X-ray crystal-structure determination of* $(Bu_4N)_2P_{16}$ *in the solid state. The reaction was scaled up to gram quantities by using a flow-chemistry process.*

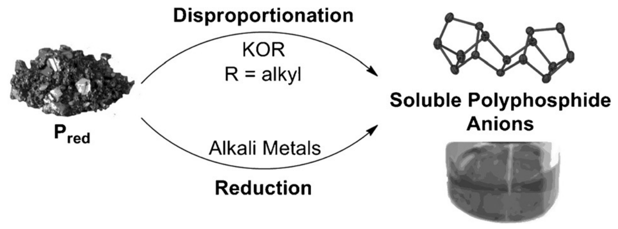
Polyphosphides are negatively charged clusters of phosphorus atoms that exhibit multifarious structural motifs. The diversity of these species was summarized by von Schnering, Hönle, and Pöttgen,[1] highlighting that the majority of polyphosphides had been obtained by direct solid-state reactions between metals and red phosphorus (P_{red}) or by iodine-assisted chemical vapor transport. The situation has not changed much since then. Only a handful of uncoordinated polyphosphide anions have been obtained by solution-based methods,[2–5] which can be explained by the difficulty in isolating these species. In general, the highly reactive polyphosphide fragments need to be captured with organic or organometallic reagents.

The long history of polyphosphides notwithstanding, there is currently a growing interest in the study of these species. Research efforts in polyphosphide chemistry have been fueled by aspirations to control the activation of the P_4 molecule,[6] known as the white allotrope of the element (P_{white}), and by the recent discovery of phosphorene as a promising graphene analogue with a finite direct band gap.[7]

Most polyphosphides prepared by solid-state methods are insoluble in common organic solvents and exhibit very high chemical stability.[1,8] In contrast, the solution methods furnish soluble and reactive polyphosphide fragments, many of which were not detected in the solid-state reactions. Therefore, the need for a broader exploration of solution-based routes cannot be overstated, as these synthetic methods provide access to different polyphosphide species as a result of kinetically controlled, rather than thermodynamically controlled, reaction pathways. Not only do these species exhibit fascinating reactivity[9] but they also might serve as precursors for high-performance materials, including 2D semiconductors[7] and lithium-ion battery anodes.[10]

The majority of solution-based routes for producing polyphosphides employ the toxic and flammable P_{white} allotrope, strongly reducing conditions, and/or cryogenic solvents.[2–5] Such methods, therefore, are difficult to scale up, which limits the potential uses of polyphosphides and hinders more extensive studies of their reactivity. There have been a few reports whereby P_{red} was used to prepare species such as K_3P_7, but the solvents were limited to liquid ammonia or ethylenediamine in combination with strongly reducing agents (Na or Na–K alloy).[5,11]

Herein we report a facile solution-based method for activating red phosphorus with nucleophilic reagents, yielding soluble polyphosphides by heating at reflux under mild conditions (Scheme 1). Moreover, by employing a solution-phase activator, we have been able to adapt this reaction to a flow-chemistry process to afford continuous production of soluble polyphosphides.



Scheme 1. Solution-based activation pathways for red phosphorus.

We began our investigation of P_{red} activation by surveying approaches that were previously used for the activation of P_{white} to form polyphosphides by using alkali metals,[12] $LiPH_2$,[13–16] or sodium naphthalenide.[17] By reacting P_{red} with potassium metal in refluxing THF/DME (1:1 v/v; DME = 1,2-dimethoxyethane), we were able to obtain orange/red solutions that contained a mixture of soluble polyphosphide anions, specifically P_5^-, P_{16}^{2-}, and P_{21}^{3-}, according to the ^{31}P NMR spectra (Figure 1 a). The chemical shift values of the corresponding resonance signals coincide well with previously reported values.

Earlier reports also described the activation of P_{white} by various nucleophilic reagents.[18–20] We set out to apply a similar approach to activate P_{red}, which is commonly thought of as a more inert phosphorus source. To this effect, we used a solution of potassium ethoxide (KOEt), which led to a remarkable activation of P_{red} in less than 2 h (Figure 1 b). Using this method, the same mixture of soluble polyphosphides was detected as that obtained in the aforementioned activation using the strongly reducing K metal (Figure 1 a).

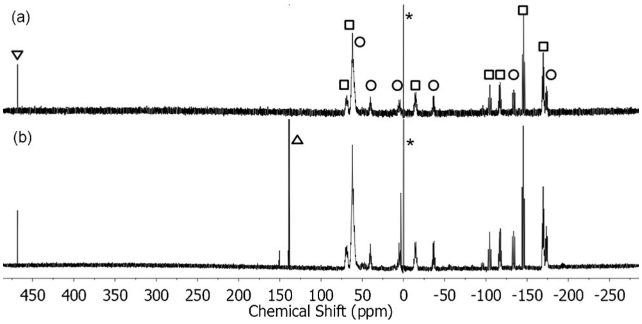


Figure 1. ^{31}P{^{1}H} NMR spectra of the reaction mixtures obtained from the activation of the P_{red} allotrope with a) K metal and b) KOEt. Symbols indicate resonance signals attributable to P_5^- (▽), P_{21}^{3-} (□), P_{16}^{2-} (○), $P(OEt)_3$ (△), and the external shift reference (*).

---

[*] Dr. A. Dragulescu-Andrasi,[+] Dr. L. Z. Miller,[+] Dr. B. Chen, Prof. D. T. McQuade, Prof. M. Shatruk
Department of Chemistry and Biochemistry
Florida State University
Tallahassee, FL 32306 (USA)
E-mail: mcquade@chem.fsu.edu
shatruk@chem.fsu.edu

[+] These authors contributed equally to this work.

Supporting information for this article can be found under http://dx.doi.org/10.1002/anie.201511186.

The activation by KOEt proceeded successfully in a variety of organic solvents, with the exception of low-boiling hydrocarbons (Table 1). The resonance signals detected in the ^{31}P NMR spectrum were assigned to the P_5^{-}, P_{16}^{2-}, and P_{21}^{3-} ions.

Table 1: Reaction of P_{red} with KOEt in various solvents.

Solvent	*T* [°C]	Reaction time [h]	Polyphosphides produced
Pentane	36.1	24	No reaction
Hexane	69	24	No reaction
MeCN	81.6	2	P_{16}^{2-}, P_{21}^{3-}, P_5^{-}
THF/DME (1:1)	85	2	P_{16}^{2-}, P_{21}^{3-}, P_5^{-}
DMF	153	24	P_5^{-} (major), P_{16}^{2-}, P_{21}^{3-}
DMSO	189	0.25	P_5^{-} (major), P_{16}^{2-}, P_{21}^{3-}

The activation of P_{red} with redox-inactive KOEt in THF/DME is drastically different from common approaches used for the synthesis of polyphosphides. We note, however, that the nucleophilic attack that initiates a cascade of disproportionation reactions and rearrangements was proposed as the mechanism for the conversion of P_{white} to organophosphorus compounds by p-block nucleophiles.[20] Indeed, in our case, the ^{31}P NMR spectrum of the crude mixture obtained from the activation of P_{red} with KOEt contains an intense signal at $\delta = 138$ ppm (Figure 1 b), which corresponds to $P(OEt)_3$, the main byproduct of the disproportionation reaction:

The observation of the formation of the $P(OEt)_3$ byproduct, which was not detected in the activation of P_{red} with K metal (Figure 1 a), corroborates the proposed nucleophilic initiation of the transformation as described by the equation above.

$$\mathbf{22}\ P_{red} + \mathbf{3}\ KOEt \xrightarrow[\text{reflux}]{\text{THF/DME}} (\mathbf{1\text{-}x})\ K_3P_{21} + \mathbf{x}\ K_2P_{16} + \mathbf{x}\ KP_5 + P(OEt)_3$$

To further probe the activation mechanism, we investigated the effects of the nucleophile strength, KOR, by varying the length and bulk of the alkyl substituent. As the R group was changed from ethyl to *n*-hexyl, the reaction rate decreased substantially; full conversion of P_{red} was achieved in 12–24 h for R = *n*-hexyl, whereas less than 2 h were required with R = ethyl. Full conversion was never reached for R = *t*-butyl, as judged by the observation of unreacted P_{red} in the reaction vessel even after 96 h. These results also provide strong support for the nucleophilic activation of P_{red} (see Figure S1 in the Supporting Information).

The crude mixture of polyphosphides obtained by the reaction of P_{red} with KOEt in THF/DME was evaporated to dryness. The residue was redissolved in EtOH, and the mixture was filtered to afford a dark-red solution. This solution was found to contain exclusively K_2P_{16}, as confirmed by the 2D ^{31}P–^{31}P COSY NMR spectrum (Figure 2). The P_{16}^{2-} polyphosphide ion was successfully crystallized by cation exchange with $(Bu_4N)Cl$ in EtOH. The X-ray crystal structure determination confirmed the formation of $(Bu_4N)_2P_{16}$. The compound can be redissolved in acetonitrile, with the P_{16}^{2-} polyanion remaining intact, as judged by the ^{31}P NMR spectrum (Figure S2). In this solution, a protonated $[HP_{16}]^{-}$ ion (*m*/*z* 496.6) was also detected using negative-mode electrospray ionization mass spectrometry (ESI-MS; Figure S3).

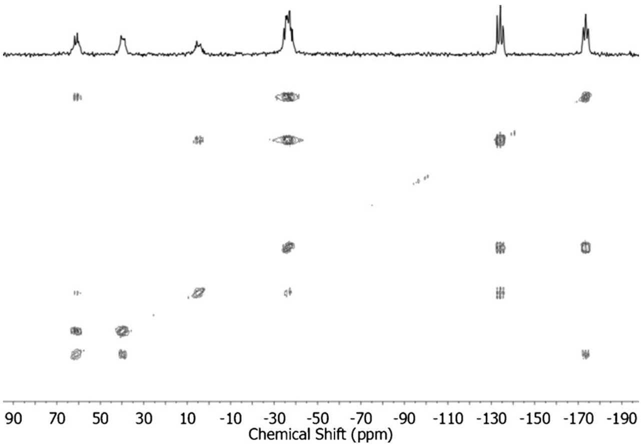


Figure 2. ^{31}P–^{31}P COSY NMR spectrum of K_2P_{16} in EtOH.

The crystal structure of $(Bu_4N)_2P_{16}$ contains the polycyclic hexadecaphosphide dianion P_{16}^{2-}, whose structure was also reported earlier as the $(Ph_4P)_2P_{16}$ salt.[4] The P_{16}^{2-} dianion can be viewed as two nortricyclene P_7 cages connected by a P_2 dumbbell (Figure 3). Each P atom forms 3 P–P bonds, except for the 2 two-bonded P atoms located at opposite ends of the P_{16} skeleton. According to the octet rule, each of the two-bonded atoms contributes one negative charge to the P_{16}^{2-} cluster. The P–P distances vary from 2.144(1) to 2.236(1) Å, with the exception of the 2.304(1) Å separation in the central dumbbell, which is significantly longer than that of a typical P–P single bond (2.20 Å).[1] The shortest P–P bond lengths are detected for the two-bonded P atoms, suggesting that the extra electron density on these atoms strengthens the P–P bonding interaction. It is important to note that, in contrast to the previous synthesis of $(Ph_4P)_2P_{16}$ from the sparingly soluble solid-state precursor K_3P_7, we obtained the highly soluble P_{16}^{2-} ion directly from the

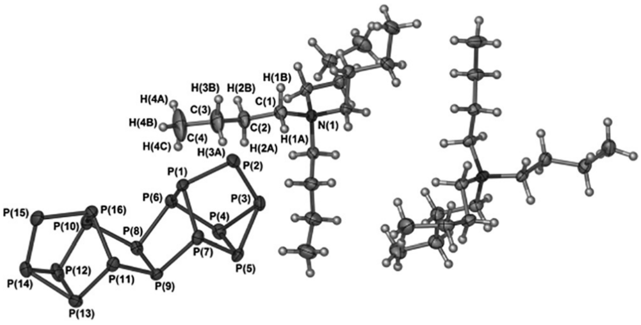


Figure 3. The crystal structure of $(Bu_4N)_2P_{16}$. Thermal ellipsoids are set at 50% probability.

P_{red} allotrope, thus circumventing the need for the intermediate synthetic step.

As an extension of this work, we realized that the use of shelf-stable P_{red} instead of highly reactive P_{white} should allow a straightforward scale-up of this new reaction through flow-chemistry approaches. Given our experience with solid reagents packed in flow reactors,[21] we anticipated that rapid conversion of P_{red} to form soluble polyphosphides could be achieved using a packed-bed method. To this end, P_{red} was loaded as a packed bed in a stainless steel column. Particles in a mesh range of about 14–25 (1.4–0.7 mm) were found to work better than smaller particles, which led to inconsistent flow profiles or channeling of the reagent solution around the packed bed and occasional clogging. A Phoenix flow reactor fitted with an automated back-pressure regulation unit (Figure S5) provided uniform heat and back pressure to the column. Figure 4 shows the flow process and conditions, starting from a homogeneous KOEt solution and progressing to a dark-red product solution upon exiting the packed bed. After 5 h of continuous operation, we obtained 150 mL of 0.03 M polyphosphide solution (the concentration calculated per P atom). The solution was collected under an inert atmosphere and sampled directly for characterization by ^{31}P NMR spectroscopy, which confirmed the presence of the same mixture of polyphosphides as detected in Figure 1 b. The solvent was removed under reduced pressure to yield solid products, which could be redissolved in EtOH to yield a solution of pure K_2P_{16}.

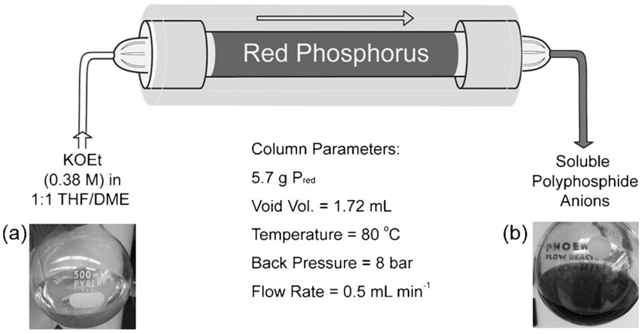


Figure 4. Flow-reactor diagram displaying a) the nearly colorless solution of KOEt in THF/DME flowing into the P_{red}-loaded reactor and b) the dark-red solution of polyphosphides exiting the column, followed by collection into a round-bottom flask.

In conclusion, we have demonstrated a new top-down approach for the activation of red phosphorus to afford a fast and convenient synthesis of soluble polyphosphides using shelf-stable reagents and common organic solvents. The mild nucleophilic activation of P_{red} with KOEt is in striking contrast to the previously reported activation of P_{red} which required the use of strong reductants, specifically alkali metals. This nucleophilic activation was also adapted to a flow-chemistry reactor, providing a method for the continuous multigram synthesis of polyphosphides. Our method has the potential to enable widespread access to these structurally diverse species, which could lead to rapid elucidation of their reactivity pathways. Current efforts in our labs are focused on expanding the range of nucleophiles and reaction conditions in order to achieve the conversion of the P_{red} allotrope into various polyphosphide anions.

Experimental Section

All manipulations with air- and moisture-sensitive compounds were performed under an inert-gas atmosphere by using standard Schlenk techniques or an Ar-filled glovebox. Red phosphorus (99.999 %, Alfa Aesar) and all anhydrous solvents (Sigma–Aldrich) were used as received. KOEt was freshly prepared from EtOH and K metal (99.5 %, Sigma–Aldrich) and dried under vacuum overnight. Reaction mixtures were sampled for analysis by ^{31}P NMR spectroscopy in air-free NMR tubes. Conversions were determined indirectly by isolation and weighing of unreacted P_{red} starting material. Elemental analyses (C, H, N, P) were performed by Midwest MicroLab, LLC.

Synthesis of $(Bu_4N)_2P_{16}$: Solid KOEt (136 mg, 1.6 mmol) was dissolved in DME/THF (3 mL; 1:1 v/v) and P_{red} (50 mg, 1.6 mmol) was added to the solution. The suspension was heated to reflux for 2 h. The resulting bright-orange suspension was allowed to cool to RT and was then evaporated to dryness under vacuum. The dark-red residue was dissolved in anhydrous EtOH to form a dark-red solution, which contained exclusively K_2P_{16} (as determined by ^{31}P NMR). Following cation exchange with $(Bu_4N)Cl$ in EtOH, the P_{16}^{2-} polyanion was isolated as the brown-red salt $(Bu_4N)_2P_{16}$. Yield = 62 mg (63 %). HRMS (ESI$^-$): m/z calcd for $[HP_{16}]^-$ ion 496.5880; found 496.5865. ^{31}P{^{1}H} NMR ([D$_3$]MeCN, 20 °C, 242.96 MHz): $\delta = 60, 39, 3.23, -37, -134, -175$ ppm. A satisfactory elemental analysis could not be obtained for this material, presumably because of the extreme sensitivity of the product. UV/Vis (MeCN): $\lambda_{max} = 338$ nm.

X-ray crystallography: Dark-red crystals of $(Bu_4N)_2P_{16}$ suitable for X-ray diffraction were obtained by layering ethanolic solutions of K_2P_{16} and $(Bu_4N)Cl$ in narrow glass tubes. Crystal data at 173 K: space group = $P\bar{1}$; $a = 12.815(5)$, $b = 13.664(5)$, $c = 16.069(6)$ Å; $\alpha = 73.301(4)$, $\beta = 75.741(3)$, $\gamma = 77.507(4)°$; $V = 2580(2)$ Å^3, $Z = 2$, $R1 = 0.0380$ [$I > 2\sigma(I)$] (see also Table S1). CCDC 1426921 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Continuous-flow synthesis of K_2P_{16}: A coarse 14–25 mesh (1.4–0.7 mm) powder of P_{red} (5.7 g, 2.25 mol) was loaded as a packed bed in a stainless steel column (internal diameter = 9 mm, length = 65 mm). A Phoenix flow reactor (ThalesNano) was used to apply heat (80 °C) and pressure (8 bar). A solution of KOEt (0.38 M) in THF/DME (1:1 v/v) was driven through the packed bed with micro HPLC pumps (ThalesNano) at a rate of 0.5 mL min^{-1} to yield a deep-red solution. A dark-red solid was isolated by removing the volatile compounds under reduced pressure. The solid was readily soluble in EtOH and yielded a spectroscopically pure solution of K_2P_{16} in nearly quantitative yield. ^{31}P{^{1}H} NMR (EtOH, 85 % H_3PO_4 external reference, 20 °C, 242.96 MHz): $\delta = 60, 40, 4.69, -37, -134, -174$ ppm.

Activation of P_{red} with K metal: Small pieces of K (30 mg, 0.8 mmol) and P_{red} (50 mg, 1.6 mmol) were suspended in DME/THF (3 mL; 1:1 v/v) and the mixture was heated under reflux for 3 h. The resulting bright-orange solution was allowed to cool to RT and was then evaporated to dryness under reduced pressure. The dark-red residue was dissolved in anhydrous EtOH to yield a dark-red solution, which contained exclusively K_2P_{16} (as determined by ^{31}P NMR spectroscopy).

Acknowledgements

The authors acknowledge the NSF (awards CHE-1152020 and CHE-1229021), the DoD (DOTC 13-01-INIT518) and

Chemring, Inc. for financial support. We thank Dr. Umesh Goli for assistance with the ESI-MS experiments and Thalesnano for access to the flow reactor (PFR) and micro HPLC pumps used in this study.

Keywords: flow chemistry · NMR spectroscopy · phosphorus allotropes · polyanions · structure elucidation

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 3904–3908
Angew. Chem. **2016**, *128*, 3972–3976

---

[1] a) H. G. von Schnering, W. Hönle, *Chem. Rev.* **1988**, *88*, 243; b) R. Pöttgen, W. Hönle, H. G. von Schnering in *Encyclopedia of Inorganic Chemistry*, *Vol. 8*, 2nd ed. (Ed.: R. B. King), Wiley, Chichester, **2005**, p. 4268.

[2] M. Baudler, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 419; *Angew. Chem.* **1987**, *99*, 429.

[3] M. Baudler, K. Glinka, R. A. Jones, *Inorg. Synth.* **1990**, *27*, 227.

[4] H. G. von Schnering, V. Manriquez, W. Hönle, *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 594; *Angew. Chem.* **1981**, *93*, 606.

[5] M. Miluykov, A. Kataev, O. Sinyashin, P. Lönnecke, E. Hey-Hawkins, *Z. Anorg. Allg. Chem.* **2006**, *632*, 1728.

[6] a) B. M. Cossairt, N. A. Piro, C. C. Cummins, *Chem. Rev.* **2010**, *110*, 4164; b) C. C. Cummins, *Angew. Chem. Int. Ed.* **2006**, *45*, 862; *Angew. Chem.* **2006**, *118*, 876.

[7] a) E. M. Reich, *Nature* **2014**, *509*, 19; b) F. Xia, H. Wang, Y. Jia, *Nat. Commun.* **2014**, *5*, 1; c) H. Liu, A. T. Neal, Z. Zhu, Z. Luo, X. F. Xu, D. Tomanek, P. D. D. Ye, *ACS Nano* **2014**, *8*, 4033; d) L. K. Li, Y. J. Yu, G. J. Ye, Q. Q. Ge, X. D. Ou, H. Wu, D. L. Feng, X. H. Chen, Y. B. Zhang, *Nat. Nanotechnol.* **2014**, *9*, 372; e) H. Liu, A. T. Neal, M. W. Si, Y. C. Du, P. D. Ye, *IEEE Electron Device Lett.* **2014**, *35*, 795.

[8] M. Bawohl, T. Nilges, *Z. Anorg. Allg. Chem.* **2015**, *641*, 304.

[9] R. S. P. Turbervill, J. M. Goicoechea, *Chem. Rev.* **2014**, *114*, 10807.

[10] L. Wang, X. He, J. Li, W. Sun, J. Gao, J. Guo, C. Jiang, *Angew. Chem. Int. Ed.* **2012**, *51*, 9034; *Angew. Chem.* **2012**, *124*, 9168.

[11] H. Schmidbaur, A. Bauer, *Phosphorus Sulfur Silicon Relat. Elem.* **1995**, *102*, 217.

[12] F. Guérin, D. Richeson, *Inorg. Chem.* **1995**, *34*, 2793.

[13] M. Baudler, O. Exner, *Chem. Ber.* **1983**, *116*, 1268.

[14] M. Baudler, R. Heumüller, J. Hahn, *Z. Anorg. Allg. Chem.* **1985**, *529*, 7.

[15] M. Baudler, D. Düster, *Z. Naturforsch. B* **1987**, *42*, 335.

[16] M. Baudler, D. Düster, G. Germeshausen, *Z. Anorg. Allg. Chem.* **1986**, *534*, 19.

[17] C. C. Cummins, C. Huang, T. J. Miller, M. W. Reintinger, J. M. Stauber, I. Tannou, D. Tofan, A. Toubaei, A. Velian, G. Wu, *Inorg. Chem.* **2014**, *53*, 3678.

[18] a) C. Brown, R. F. Hudson, G. A. Wartew, *Phosphorus Sulfur* **1978**, *5*, 121; b) C. Brown, R. F. Hudson, G. A. Wartew, *J. Chem. Soc. Perkin Trans. 1* **1979**, *7*, 1799.

[19] N. A. Giffin, J. D. Masuda, *Coord. Chem. Rev.* **2011**, *255*, 1342.

[20] M. Scheer, G. Balazs, A. Seitz, *Chem. Rev.* **2010**, *110*, 4236.

[21] a) S. M. Opalka, A. R. Longstreet, D. T. McQuade, *Beilstein J. Org. Chem.* **2011**, *7*, 1671; b) S. M. Opalka, J. K. Park, A. R. Longstreet, D. T. McQuade, *Org. Lett.* **2013**, *15*, 996; c) A. R. Longstreet, S. M. Opalka, B. S. Campbell, D. T. McQuade, *Beilstein J. Org. Chem.* **2013**, *9*, 2570; d) N. Alonso, L. Z. Miller, J. de Mata Muñoz, J. Alcázar, D. T. McQuade, *Adv. Synth. Catal.* **2014**, *356*, 3737.

Received: December 2, 2015
Revised: January 18, 2016