

DOI:10.1002/ejic.201500502

# Unexpected Reactivity of Red Phosphorus in Ionic Liquids

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Dedicated to Manfred Scheer on the occasion of his 60th birthday

Keywords: In situ spectroscopy / Ionic liquids / Nanoparticles / NMR spectroscopy / Phosphorus

Red phosphorus is far less reactive than the white allotrope. On the other hand, it is easier to handle and not as toxic as white phosphorus. In the Lewis-acidic ionic liquid (IL) [BMIm]Cl·2AlCl<sub>3</sub> ([BMIm] = 1-butyl-3-methylimidazolium), red phosphorus and elemental iodine form several iodides at moderate temperature. <sup>31</sup>P liquid- and solid-state NMR spectroscopy was used to rationalize the reaction at various tem-

Introduction

Various inorganic materials can be synthesized at or near ambient conditions with the help of ionic liquids (ILs).<sup>[1,2]</sup> This approach enables reduction of energy usage and technical efforts as well as better control of the reactions compared to commonly applied high-temperature processes.<sup>[2a]</sup> Moreover, syntheses in ILs provide great opportunities to discover new compounds with potentially outstanding and useful chemical and physical properties.<sup>[3]</sup> Still, the mechanisms of product formation are barely examined although this understanding would be crucial for the directed synthesis of a desired material. A (semi-)continuous reaction monitoring with high-resolution (HR) liquid-state NMR assisted by solid-state NMR is especially suitable for mechanistic investigations. Already in 1967, early <sup>31</sup>P NMR measurements had been applied successfully to follow the reaction of white phosphorus with iodine in CS<sub>2</sub>.<sup>[4]</sup> We decided to substitute white phosphorus by its more convenient red allotrope and the neurotoxic and highly reactive CS<sub>2</sub> with the comparatively inert and redox-innocent IL [BMIm]Cl·2AlCl<sub>3</sub> ([BMIm] = 1-butyl-3-methylimidazolium) in order to assess the viability of in situ investi-

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- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201500502.

peratures and ratios of the starting materials. Monitoring of the reaction revealed nanoscale red-phosphorus particles. In addition to this top-down formation, phosphorus nanoparticles were also obtained in a bottom-up synthesis by dissociation of  $P_2I_4$  in the IL. Depending on the ratio of red phosphorus and iodine, as well as the reaction temperature,  $P_2I_4$ ,  $PI_3$ , or  $P_2I_5^+$  dominate.

gations in ILs with NMR techniques. As we have shown previously, red phosphorus is reactive in [BMIm]Cl·*n*AlCl<sub>3</sub> if combined with a suitable reaction partner.<sup>[2a,2o]</sup> The chosen amount of AlCl<sub>3</sub> is the highest one for a homogeneous system at ambient conditions.

### **Results and Discussion**

To facilitate NMR signal assignment, the red phosphorus used as starting material as well as the potential reaction products PI<sub>3</sub> and P<sub>2</sub>I<sub>4</sub> were analyzed by using <sup>31</sup>P solid- and liquid-state NMR spectroscopy (see Supporting Information). The measurements were carried out between room temperature (RT) and 80 °C; the latter being the highest accessible temperature. Red phosphorus as an amorphous solid has a poorly defined structure.<sup>[5]</sup> Consequently, its physical and chemical properties are variable to some degree, and the linewidths and exact chemical shift of the NMR signals can vary for different batches and sources. Nevertheless, red phosphorus can easily be distinguished from the other common allotropes by its chemical shift. We observed a broad line centered at about 50 ppm (Figures S1 and S2, Supporting Information) in agreement with the literature, which reports values of 60 to 65 ppm.<sup>[6]</sup> Black phosphorus appears at  $\delta = 22.2 \text{ ppm}$ ,<sup>[7]</sup> Hittorf's phosphorus exhibits a broader and more complex spectrum ranging from -84.5 to 171.3 ppm,<sup>[8]</sup> and white phosphorus resonates at  $\delta = -527 \text{ ppm.}^{[9]}$  Crystalline fibrous phosphorus<sup>[10]</sup> has not yet been characterized by NMR spectroscopy, but owing to its structural similarity to Hittorf's phosphorus, one can expect a similarly complex spectrum.



One of the two non-crystalline, fibrous forms mimics the NMR signal of red phosphorus at  $\delta = 65$  ppm. However, this modification of phosphorus has only been obtained from a CuI matrix.<sup>[11]</sup>

For the monitoring of the first reaction, we chose a molar ratio  $P:I_2 = 1:2$ .  $PI_3$  forms upon mixing phosphorus and iodine in the IL. This is visible in the <sup>31</sup>P NMR spectrum at 25 °C (Figure 1, top), which is dominated by the CSAbroadened signal characteristic of PI<sub>3</sub> (Figure S3, Supporting Information). After heating to 80 °C inside the spectrometer, all PI<sub>3</sub> is in liquid phase. Ex situ conditioning at 100 °C results in the formation of a phosphorus iodide different from PI<sub>3</sub>. It gives rise to two rather broad signals at room temperature (provided the solution is quickly cooled). These signals at about 130 ppm and -150 ppm (Figure 1) are characteristic of P<sub>2</sub>I<sub>5</sub><sup>+</sup> (solid P<sub>2</sub>I<sub>5</sub>AlI<sub>4</sub>: 114 ppm for R- $PI_2$ , -142 ppm for R- $PI_3$ ;<sup>[12]</sup>  $P_2I_5[Al(OC(CF_3)_3)_4]$  in CD<sub>2</sub>Cl<sub>2</sub>: 127.4 and -156.3 ppm<sup>[13]</sup>). The P<sub>2</sub>I<sub>5</sub><sup>+</sup> cation dominates after conditioning at 120 °C (and subsequent fast cooling) and vanishes completely upon annealing at 55 °C, while PI<sub>3</sub> remains the only visible species. Therefore, we can propose a reaction scheme for the  $P:I_2 = 1:2$  case (Scheme 1).



Figure 1. Liquid-state <sup>31</sup>P NMR spectra of a reaction mixture P:I<sub>2</sub> = 1:2 (phosphorus batch 1). Top: at room temperature (black) and at 80 °C (red) after mixing. Middle: at RT (black) and at 80 °C (red) after ex situ annealing at 100 °C for 15 h and fast cooling. Bottom: at RT (black) and at 55 °C (red) after annealing at 120 °C for 24 h and fast cooling.

$2 \text{ P}_{\text{red}} + 3 \text{ I}_2 \rightarrow 2 \text{ PI}_3$	at 25 °C	(1)
2 $PI_3 \rightleftharpoons P_2I_5^+ + I^-$	at 100 °C	(2)

Scheme 1. Proposed reaction of red phosphorus and iodine at the molar ratio  $P:I_2 = 1:2$  in [BMIm]Cl·2AlCl<sub>3</sub>.

A molar ratio of the starting materials of  $P:I_2 = 1:1$  also leads to the formation of  $PI_3$  upon mixing of the elements in the IL at 25 °C, as indicated by the characteristic broad signal in the <sup>31</sup>P NMR spectrum (Figure 2, top). After heating the sample to 55 °C inside the spectrometer, an additional signal at about 50 ppm appears which intensifies at higher temperature (Figures 2 and S6, Supporting Information). The chemical shift is characteristic of red phosphorus (Figure S1, Supporting Information) but the signal is rather narrow. We assume that, in the course of etching of the red phosphorus with dissolved iodine, nanoparticles are cut off the solid. A rough estimation of the particle size based on the linewidth yielded diameters of  $20 \pm 10$  nm (see Supporting Information).



Figure 2. <sup>31</sup>P NMR spectra of the reaction mixture  $P:I_2 = 1:1$  (phosphorus batch 1). Top: liquid-state at room temperature (black) and at 80 °C (red) after mixing. Middle: liquid-state at RT (black) and at 80 °C (red) after ex situ annealing at 100 °C for 24 h. Bottom: 14 kHz MAS spectra at RT of the used red phosphorus (blue) and of the precipitate after conditioning at 120 °C (black). The asterisk marks the signal at  $\delta = 166$  ppm.

In addition, an unknown species with a chemical shift of 166 ppm is visible (Figure 2, marked with an asterisk). The latter must be either a monophosphorus or a symmetric diphosphorus species similar to PI<sub>3</sub>, P<sub>2</sub>I<sub>4</sub>, or the -PI<sub>2</sub> part of P<sub>2</sub>I<sub>5</sub><sup>+</sup>. Owing to strong spin-orbit coupling, the <sup>31</sup>P signals of four-coordinate phosphorus atoms bonded to iodine atoms are strongly shifted upfield (e.g. PI<sub>4</sub><sup>+</sup>, -PI<sub>3</sub> part of P<sub>2</sub>I<sub>5</sub><sup>+</sup>).<sup>[12-15]</sup> By quantum chemical calculations, the hypothetical ions PI<sub>2</sub><sup>+</sup> and P<sub>2</sub>I<sub>4</sub><sup>2+</sup> could also be ruled out. The chemical shift of 166 ppm resembles PI<sub>3</sub> dissolved in IL ( $\delta$  =187 ppm). Since this signal is rather broad, we assume it is related to PI<sub>3</sub> forming on the surface of the nanoparticles.

After conditioning the reaction solution at 100 °C for 24 h, the red phosphorus is completely converted into  $P_2I_4$  and  $PI_3$ , and the signals at  $\delta = 166$  ppm and 50 ppm have vanished (Figure 2, middle and bottom, Figure S7, Supporting Information). The annealing seems to reduce the solubility of the iodides by aggregation. Correspondingly, their NMR signals are broad. At the chosen element ratio, the reaction is limited by the equilibrium between PI<sub>3</sub> and  $P_2I_4$ . We propose a two-step reaction scheme (Scheme 2).

$$2 \mathsf{P}_{\mathsf{red}} + 3 \mathsf{I}_2 \rightarrow 2 \mathsf{PI}_3 \quad \text{at } 25 \ ^\circ \mathsf{C} \tag{3}$$

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4 PI_3 + 2 P \rightleftharpoons 3 P_2I_4 at elevated temperature (4)
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Scheme 2. Proposed reaction of red phosphorus and iodine at the molar ratio  $P:I_2 = 1:1$  in [BMIm]Cl-2AlCl<sub>3</sub>.

Exactly this two-step process was observed by Carroll et al. for white phosphorus in  $CS_2$ .<sup>[4]</sup> However, the reaction in  $CS_2$  proceeds to  $P_2I_4$  at room temperature. By increasing the phosphorus to iodine ratio in the reaction mixture to 2:1, the formation of PI<sub>3</sub> is disfavored, and  $P_2I_4$  becomes the only detectable reaction product at 70 °C (Figure S5, Supporting Information; keeping in mind that solid red phosphorus is virtually invisible).

We have used two batches of red phosphorus from different sources. The <sup>31</sup>P MAS NMR spectrum revealed a



minor difference between the two batches visible in an upfield "shoulder" of the signal of the first sample (Figure S2, Supporting Information). The intensity of the nanoparticle signal at about 50 ppm depends on the chosen batch (source) of red phosphorus as starting material. A second batch of red phosphorus yielded fewer nanoparticles under otherwise same conditions. Moreover, the second batch of red phosphorus enabled the synthesis of  $P_2I_4$  at lower temperature (<70 °C) and thus monitoring of the reaction in the spectrometer (Figure S8, Supporting Information; note the isosbestic point at  $\delta = 150$  ppm). The lower reaction temperature gives rise to much lower signal intensity for the nanoparticles because phosphorus is mainly transformed into iodides before appearing as a signal at  $\delta = 50$  ppm in the spectrum. Moreover, differences in the (micro-)structure of the amorphous solid seem to correlate with different etching behavior, perceived as the intensity of the nanoparticle signal. Together with the signal of the phosphorus nanoparticles at  $\delta$  = 50 ppm, the additional signal at  $\delta$  = 166 ppm – attributed to phosphorus iodides at the particle surface (Figure 2, top) - vanishes.

 $P_2I_4$ , taken as starting material, partly dissociates to  $PI_3$ and phosphorus in the IL at 80 °C (Figure S5, Supporting Information). Thereby, a small amount of yellowish powder is formed (Figures 3 and 4 and Figure S9, Supporting Information) and a narrow line at  $\delta = 50$  ppm, which indicates phosphorus nanoparticles (vide supra), appears in the NMR spectrum. This resembles the observations by Carroll et al. as well as Baudler et al. who described an iodinecontaining colloidal phosphorus polymer as one of the dissociation products of P<sub>2</sub>I<sub>4</sub> in CS<sub>2</sub>.<sup>[4,16]</sup> On the basis of the linewidth, we estimate particle sizes of  $22 \pm 10$  nm (cf. Supporting Information). We were unable to isolate these, owing to hindered sedimentation of very small particles, but detected massive (Figure 3) as well as hollow, spherical particles (Figure 4) of 60 to 500 nm in the scanning electron microscope (SEM). Chloridoaluminates originating from the IL cover the outer and inner surfaces of the particles



Figure 3. SEM images (SE detector) of phosphorus nanoparticles with diameters between 80 and 430 nm on a silicon wafer after washing with DCM and EtOH (96%).

(see EDX line scans and mapping, Figures S10 to S12, Supporting Information). Upon washing with dichloromethane (DCM) and ethanol (96%), the surfactants are either removed or converted into undefined compounds containing aluminum, carbon, and oxygen.



Figure 4. SEM image (SE detector, left) and STEM image (TE detector, right) of hollow phosphorus nanoparticles after washing with DCM and EtOH (96%). The insets show the EDX mapping for phosphorus (red, left) and aluminum (blue, right). Note the second wall formed by aluminum-containing surfactants within the particles.

### Conclusions

The following can be concluded: (i) The reactivity of red phosphorus is strongly increased by iodine in [BMIm]Cl-2AlCl<sub>3</sub>. (ii) The reaction pathways can be followed in detail by a combination of liquid- and solid-state <sup>31</sup>P NMR spectroscopy. (iii) Phosphorus nanoparticles, terminated by iodine on the surface, are formed in the course of the reaction (top-down). Similar nanoparticles are formed as a dissociation product of  $P_2I_4$  (bottom-up). The discovery of phosphorus nanoparticles may stimulate the development of a reactive form of phosphorus without the drawbacks of the white allotrope.

#### **Experimental Section**

Sample Preparation: All compounds were handled in an argonfilled glove box (M. Braun;  $p(O_2)/p^0 < 1$  ppm,  $p(H_2O)/p^0 < 1$  ppm). Starting materials: phosphorus "batch 1" (Sigma Aldrich, 99.95%), phosphorus "batch 2" (ABCR, 99.999%), iodine (Fluka, 98%), AlCl<sub>3</sub> (Fluka 98%, sublimated three times), and [BMIm]Cl (Sigma Aldrich,  $\geq 98\%$  HPLC, dried in dynamic vacuum). Both phosphorus samples were washed with sodium hydroxide, refluxed in water, and dried in vacuo.<sup>[17]</sup> PI<sub>3</sub> (ABCR, 98%) and P<sub>2</sub>I<sub>4</sub> (Aldrich, 95%) were used without further purification. To utilize the full range of the NMR probe, a minimum of 982 mg (5.6 mmol) of [BMIm]Cl and the corresponding amount of  $AlCl_3$  ( $n(AlCl_3) =$ 2n([BMIm]Cl)) was filled in a commercial 10 mm NMR glass tube. Owing to the high enthalpy of mixing of [BMIm]Cl and AlCl<sub>3</sub> as well as the absence of a stirring bar, the two compounds were alternatingly mixed before phosphorus (n(P) = 0.27-0.47n([BMIm]Cl))and iodine or  $P_2I_4$  (*n*(P) = 0.27*n*([BMIm]Cl)) were added. The glass tubes were sealed under dynamic vacuum. Subsequently, the reaction mixture was cautiously homogenized with a vortex mixer.

**NMR Spectroscopy:** All liquid-state NMR experiments were carried out on a Bruker Avance 300 spectrometer at a phosphorus resonance frequency of 121.5 MHz by using a commercial 10 mm HR probe. MAS NMR experiments were performed on a Bruker



Avance 300 spectrometer with commercial double resonance 2.5 and 4 mm MAS NMR probes operating at a resonance frequency of 121.5 MHz and a MAS frequency of 14 kHz. The phosphorus chemical shifts were referenced relative to  $H_3PO_4$ .

**SEM/STEM:** Scanning (transmission) electron microscopy was performed by using a SU8020 (Hitachi) with a triple detector system for secondary and low-energy backscattered electrons ( $U_a = 10-30 \text{ kV}$ ). Energy-dispersive X-ray (EDX) spectra were collected ( $U_a = 8-30 \text{ kV}$ ) using a Silicon Drift Detector (SDD) X-Max<sup>N</sup> (Oxford). Prior to the measurements, the samples were washed with dry DCM and subsequently with EtOH (96%), and in each washing step centrifuged and redispersed using a supersonic bath. Finally, the dispersed particles were transferred either on a TEM grid or a polished silicon wafer.

**XRD:** Data collection was performed at 296(1) K on an X'Pert Pro MPD diffractometer (PANalytical) equipped with a curved Ge(111) monochromator by using Cu- $K_{\alpha 1}$  radiation ( $\lambda$  = 154.056 pm). The air-sensitive samples were protected by a polyimide (Kapton®) film (Chemplex).

## Acknowledgments

We gratefully acknowledge J. Pallmann (TU Dresden) for her help with the MAS NMR measurements. This work was supported by the Deutsche Forschungsgemeinschaft (DFG).

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Published Online: June 3, 2015