Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPORTING INFORMATION

Table S1. List of Chemicals.

chemical	**supplier**	**specifications**
ionic liquids		
tetrabutylammonium bromide, $[N_{4444}][Br]$	abcr	> 99 % 1)
tetrabutylammonium chloride, $[N_{4444}][Cl]$	abcr	> 97 % 2)
trihexyl(tetradecyl)phosphonium chloride, $[P_{66614}][Cl]$	Iolitec	> 97 % 3)
solids		
adipic acid	Sigma Aldrich	99 %
betaine	Sigma Aldrich	> 98 %
carbon	abcr	99.9995 %
copper 4)	abcr	99.9 %, 100 Mesh or 99.999 %
copper(II)-sulfate pentahydrate	Sigma Aldrich	> 98 %
poly(*N*-vinyl)-pyrrolidone	Sigma Aldrich	M_w = 40,000 g/mol
red phosphorous 5)	abcr	99.999 %
sodium hydroxide	Grüssing GmbH Analytica	99 %
sodium hypophosphite	Sigma Aldrich	
white phosphorous 6)	Thermphos International B.V.	
solvents		
diethyl ether	Th. Geyer	99.8 %
diethylene glycol	Sigma Aldrich	99 %
ethanol	Berkel	99 %

1) containing ≤ 0.5 wt.-% tributylamine hydrobromide, ≤ 0.5 wt.-% tributylamine (as specified by the supplier)

2) containing ≤ 0.5 wt.-% tributylamine hydrochloride, ≤ 0.5 wt.-% tributylamine (as specified by the supplier)

3) containing about 0.1–0.5 wt.-% HCl, 0.1–0.4 tetradecene isomers; 0.15 wt.-% H_2O; 0.1–0.2 wt.-% $[PR_3H]Cl$ (R = hexyl or tetradecyl)[S1,S2]

4) Copper was treated in H_2 at 400 °C before use.

5) Red phosphorus powder was washed with sodium hydroxide, rinsed with refluxing water, and finally vacuum dried in vacuum.[S3]

6) White phosphorus pieces were stored in water, dried with Me_3SiCl, and sublimated prior to usage. After sublimation the white phosphorus is pure according to ^{31}P NMR analyses.

Table S2. Elemental compositions determined by EDS analyses.
Note: Any signals of C, O, Na, Al, Si have been subtracted since they originate from the sample holder and the sample preparation.

sample description	**averaged element ratio in at.-%** [1]
activation of copper surfaces in [P_{66614}][Cl]	
copper particles[2] before heat treatment	Cu : P : S = 100 : b.d.l. : b.d.l. (3 spectra)
copper particles[2] after heat treatment in neutralized [P_{66614}][Cl], 200 °C, 24 h	Cu : P : S = 99.6(5) : b.d.l. : 0.4(5) (5 spectra)
copper particles[2] after heat treatment in as-received and dried [P_{66614}][Cl], 200 °C, 24 h	Cu : P : S = 95(2) : 0.1(2) : 5(2) (6 spectra)
diffusion experiment for the formation of $Cu_{3-x}P$ in [P_{66614}][Cl]	
phosphidized copper particles	Cu : P = 65(6) : 35(6) (3 spectra)
remaining phosphorus (at source)	Cu : P = b.d.l. : 100 (7 spectra)
exchange of [P_{66614}][Cl] with phosphorus-free ILs or DES	
$Cu_{3-x}P$ particles synthesized in [N_{4444}][Cl], 180 °C, 48 h	Cu : P = 74.6(2) : 25.4(2) (13 spectra) corresponds[3] to: $Cu_{2.93(3)}P$

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[1] "b.d.l." means "below detection limit"

[2] prepared by hot-injection method, small amounts of sulfur originate from the starting material copper(II)-sulfate pentahydrate

[3] range from minimal to maximal determined Cu content of $Cu_{3-x}P$

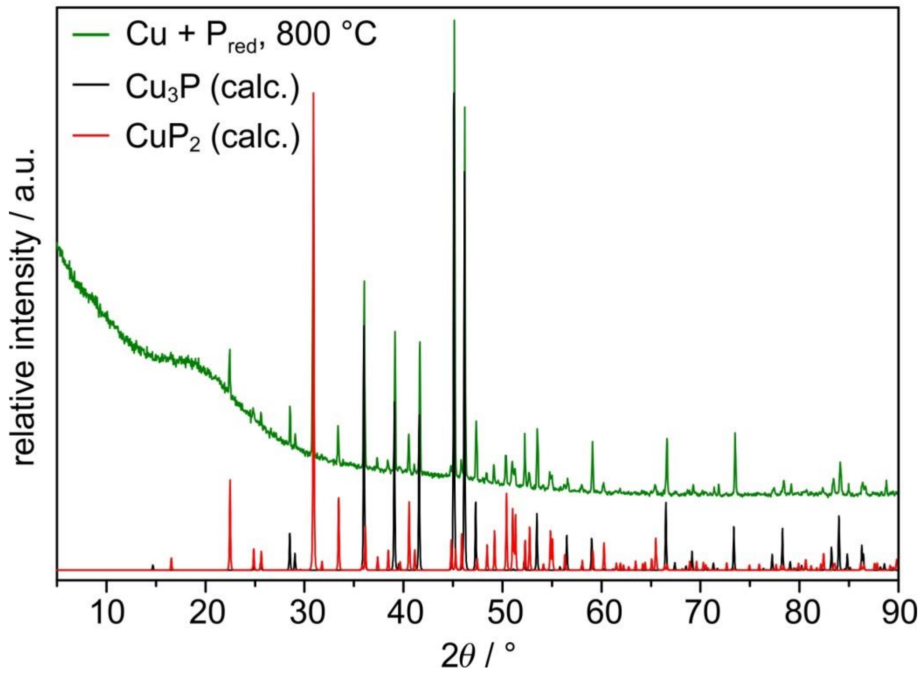

Figure S1. PXRD pattern of the product of the direct reaction of elemental copper and red phosphorus (P_{red}) (Cu : P = 2.95 : 1) at about 800 °C (green). The reference diffractograms were calculated from Inorganic Crystal Structure Database ICSD-15056 and ICSD-35282 for Cu_3P (black) and CuP_2 (red), respectively.[S4,S5]

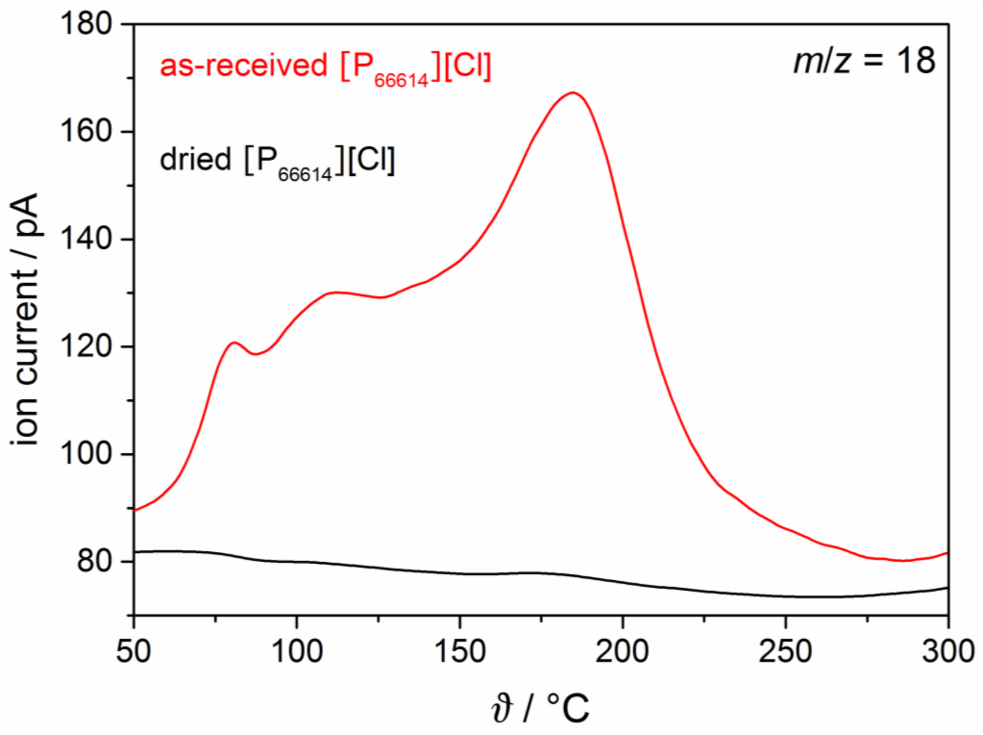

Figure S2. DTA/TG/MS results (Netzsch STA 409 PC Luxx and QMS 403C Aëolos; *m*/*z* = 18) for as-received (red) and dried (black) [P_{66614}][Cl]. Water release in a broad temperature range (about 50–250 °C) is detected for as-received [P_{66614}][Cl] while no signals are observed after the drying procedure.

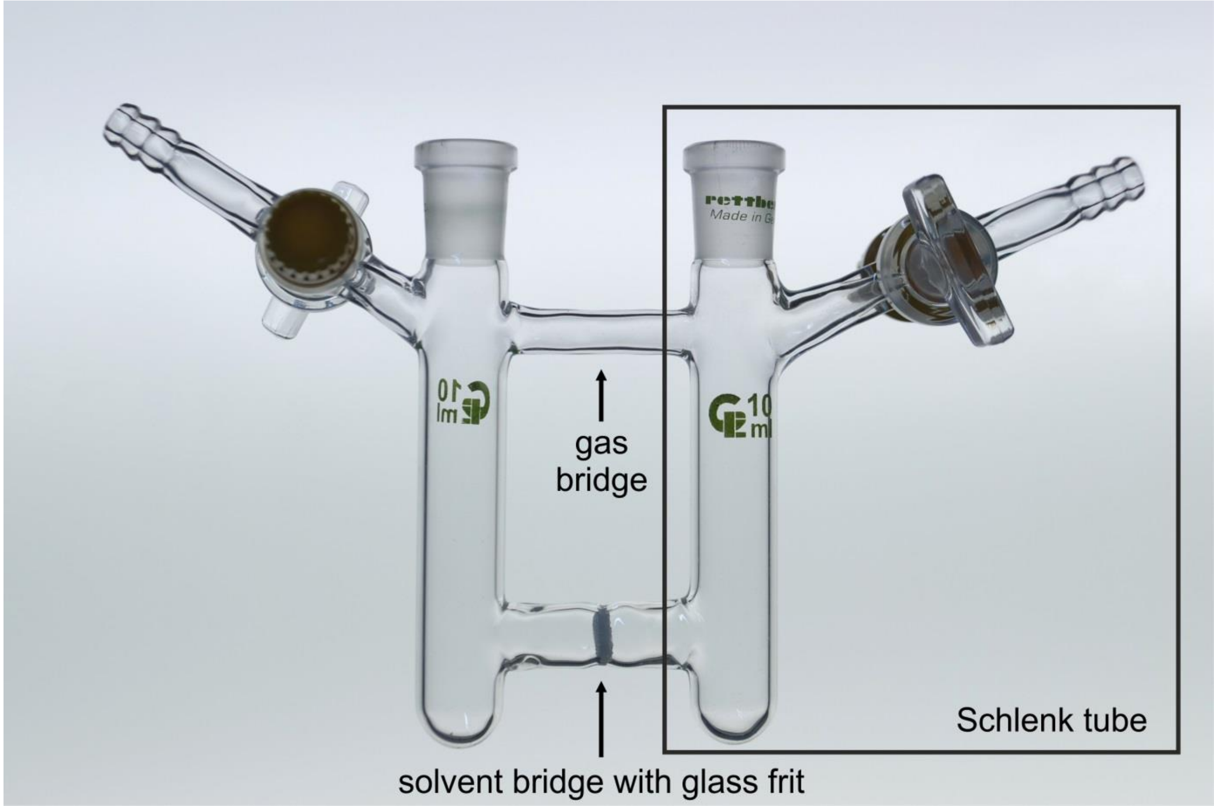

Figure S3. Diffusion tube for diffusion experiments.

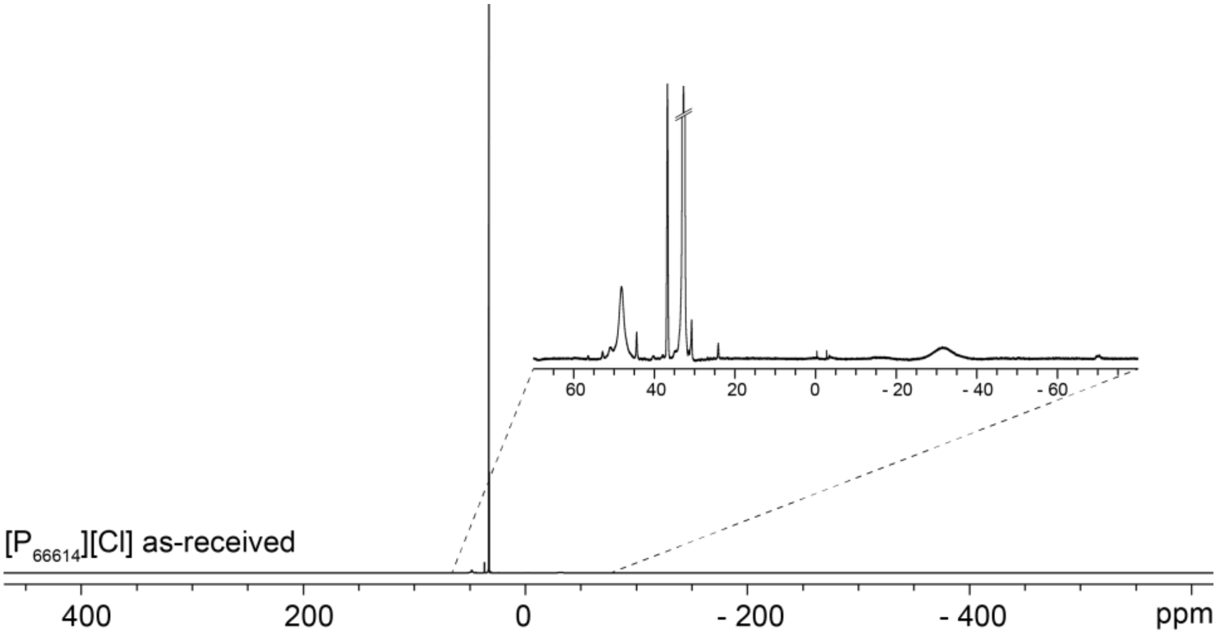

Figure S4. ^{31}P NMR spectrum of the as-received and neat [P_{66614}][Cl]. The inset shows an enlargement of the section with the most signals. The signal of the [P_{66614}]-cation is found at $\delta = 32.7$ ppm.

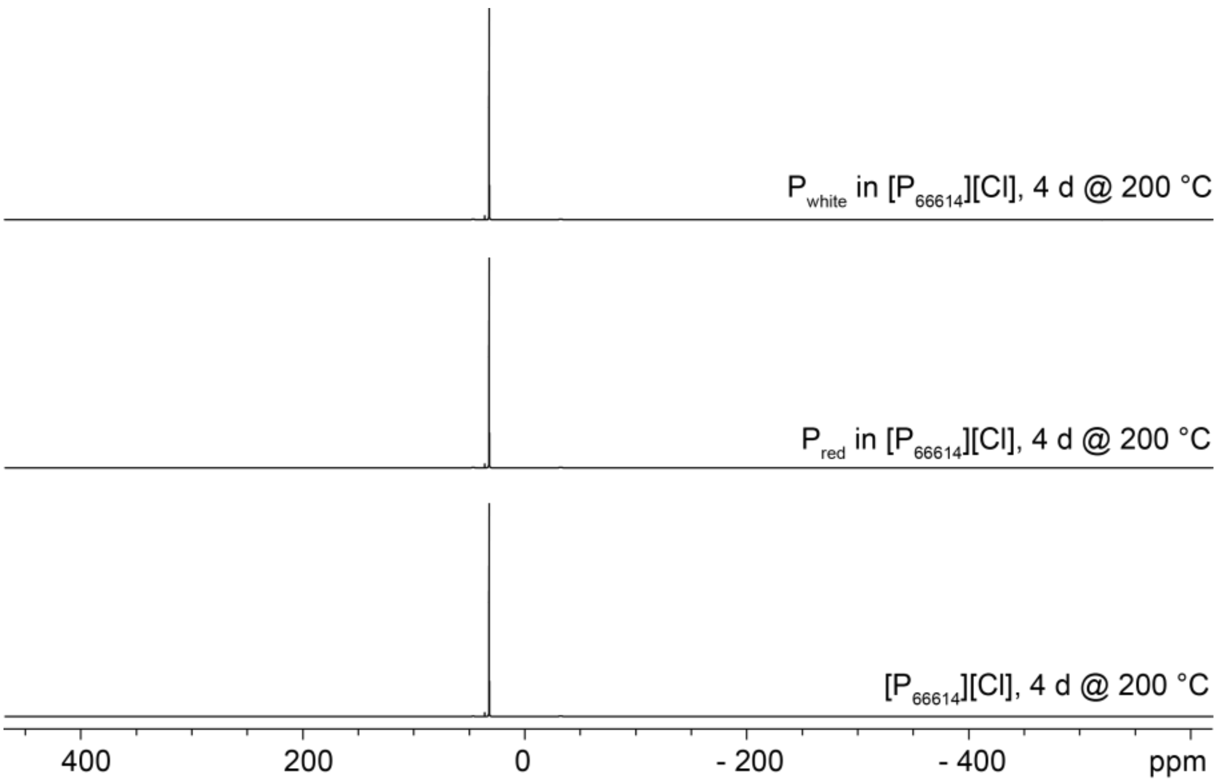

Figure S5. ^{31}P NMR spectra of [P_{66614}][Cl] after heating at 200 °C for 4 d without phosphorus (bottom), with P_{red} (middle), and with P_{white} (top). An amorphous solid was formed during the heating process of P_{white} in [P_{66614}][Cl], which reduces the P_4 signal intensity drastically compared to the dissolution experiment with P_{white} at 60 °C where no precipitation was observed. The amorphous solid was identified as P_{red} by solid state ^{31}P NMR investigations (condensation product of P_4 molecules).

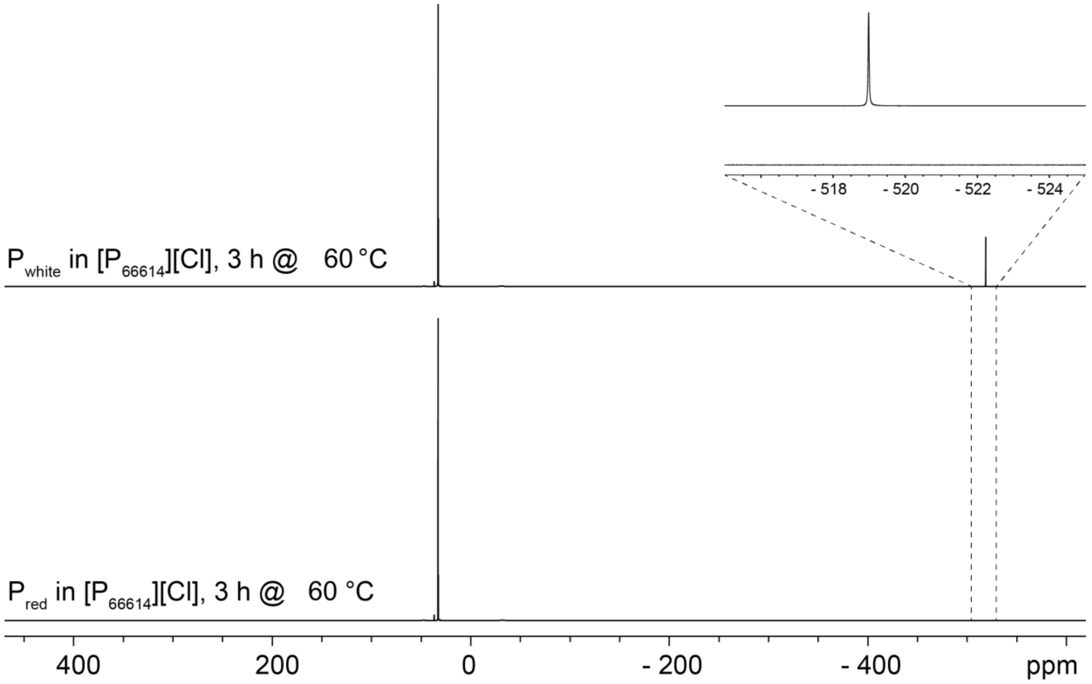

Figure S6. ^{31}P NMR spectra of [P_{66614}][Cl] after heating at 60 °C for 3 h with P_{red} (bottom) and P_{white} (top). The inset shows an enlargement of the section were the signal of P_4 emerges. The strong P_4 signal indicates a higher solubility of P_{white} at 60 °C compared to the dissolution experiments with P_{white} at 200 °C where precipitation of an amorphous solid (P_{red}, condensation product of P_4 molecules) was observed.

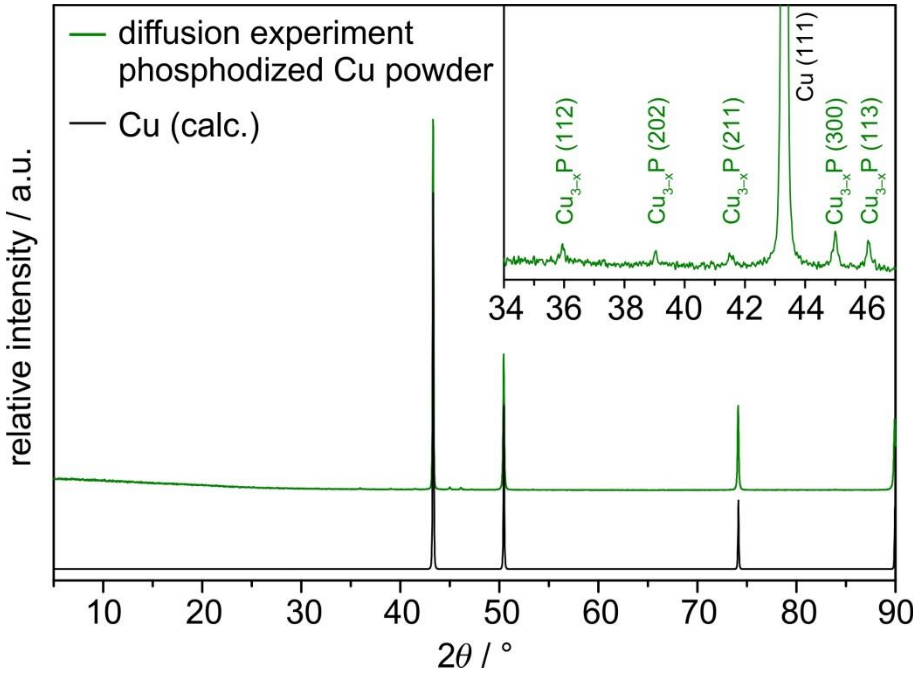

Figure S7. PXRD pattern of an intermediate mixture of copper and $Cu_{3-x}P$ particles (green) obtained in diffusion experiment at the copper compartment. Reflections of $Cu_{3-x}P$ and Cu are marked with *hkl* indices in green and black, respectively. The Cu reference diffractogram (black) was calculated from Inorganic Crystal Structure Database ICSD-627113.

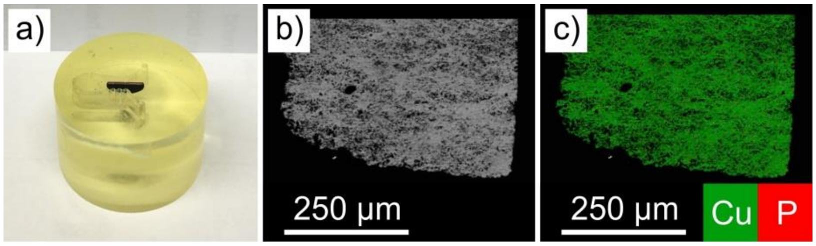

Figure S8. Diffusion experiment using pellets of elemental copper and P_{red} in $[P_{66614}][Cl]$ at 200 °C for several days: a) embedded copper pellet after the diffusion experiment. The phosphidization reaction yielded a black film at the surface; b) no elemental contrast is observed in the inner part of the pellet in SEM investigations using a detector for backscattered electrons; c) EDS map of the pellets cross section. The EDS measurements (99.65 at.-% Cu) as well as a mapping across the pellet clearly show that the inner part of the pellet only consist of elemental copper.

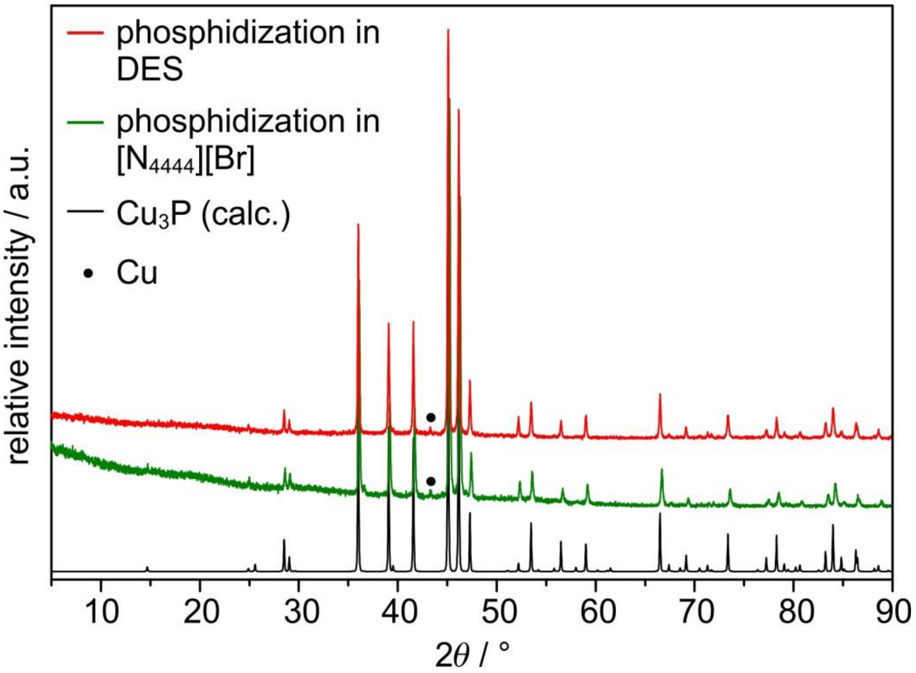

Figure S9. PXRD patterns of the products of the reaction of elemental Cu with P_{red} (Cu : P = 2.95 : 1) in $[N_{4444}][Br]$ at 180 °C in 48 h (green) and the DES consisting of betaine and adipic acid at 200 °C in 72 h (red). The Cu_3P reference diffractogram (black) was calculated from Inorganic Crystal Structure Database ICSD-15056.[S4]

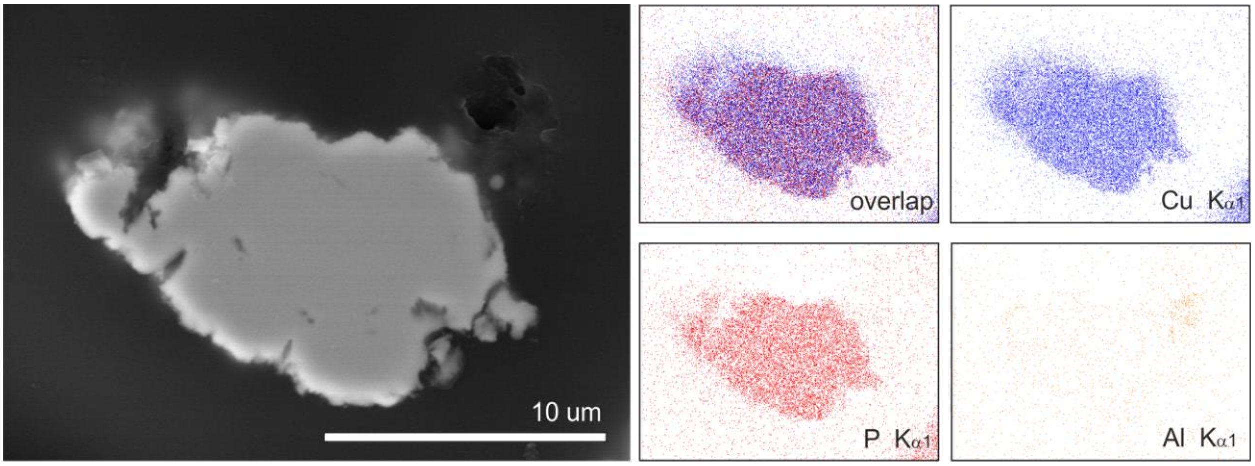

Figure S10. SEM image (detector for backscattered electrons) and EDS maps of a cross-section of homogenous $Cu_{3-x}P$ particles obtained by the reaction of elemental copper with P_{red} (Cu : P = 2.95 : 1) in $[N_{4444}][Cl]$ at 180 °C in 48 h.

Note: Small amounts of the suspension used for polishing adhere to voids of the $Cu_{3-x}P$ particles during sample preparation and appear bright in Z contrast at fissures and cracks. By-products of the phosphidization reaction, e. g. CuP_2, would appear as dark grey domains (as discussed in our previous work),[S6] but are not present. The homogeneity of the composition of the $Cu_{3-x}P$ particles was also verified by EDS measurements (see Table S2) and ^{31}P NMR spectroscopy (see Fig. S11).

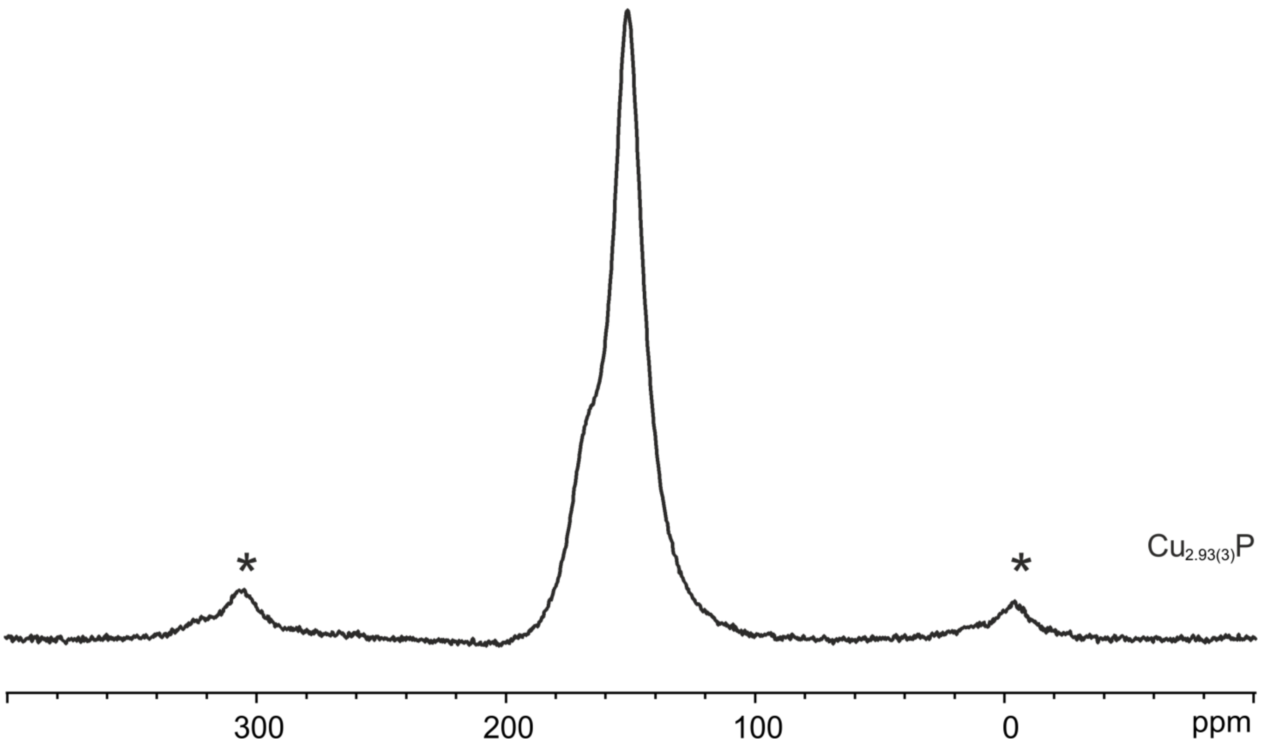

Figure S11. ^{31}P NMR spectra of single-phase $Cu_{2,93(3)}P$ powder (see Table S2) obtained by the reaction of elemental copper with P_{red} (Cu : P = 2.95 : 1) in $[N_{4444}][Cl]$ at 180 °C in 48 h.

SUPPORTING INFORMATION – REFERENCES

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(S2) C. J. Bradaric, A. Downard, C. Kennedy, A. J. Robertson and Y. Zhou, *Green Chemistry* 2003, **5**, 143–152.

(S3) G. Brauer, *Handbuch Der Präparativen Anorganischen Chemie*, 3rd ed.; F. Enke, Stuttgart, Germany, 1962.

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(S5) M. H. Möller and W. Jeitschko, *Z. Anorg. Allg. Chem.* 1982, **491**, 225–236.

(S6) A. Wolff, J. Pallmann, R. Boucher, A. Weiz, E. Brunner, T. Doert and M. Ruck, *Inorg. Chem.* 2016, **55**, 8844–8851.