



## UvA-DARE (Digital Academic Repository)

### Sustainable Phosphorus Chemistry: A Silylphosphide Synthon for the Generation of Value-Added Phosphorus Chemicals

Sloutweg, J.C.

**DOI**

[10.1002/anie.201803692](https://doi.org/10.1002/anie.201803692)

[10.1002/ange.201803692](https://doi.org/10.1002/ange.201803692)

**Publication date**

2018

**Document Version**

Final published version

**Published in**

Angewandte Chemie, International Edition

**License**

Article 25fa Dutch Copyright Act

[Link to publication](#)

**Citation for published version (APA):**

Sloutweg, J. C. (2018). Sustainable Phosphorus Chemistry: A Silylphosphide Synthon for the Generation of Value-Added Phosphorus Chemicals. *Angewandte Chemie, International Edition*, 57(22), 6386-6388. <https://doi.org/10.1002/anie.201803692>, <https://doi.org/10.1002/ange.201803692>

**General rights**

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

**Disclaimer/Complaints regulations**

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

UvA-DARE is a service provided by the library of the University of Amsterdam (<https://dare.uva.nl>)

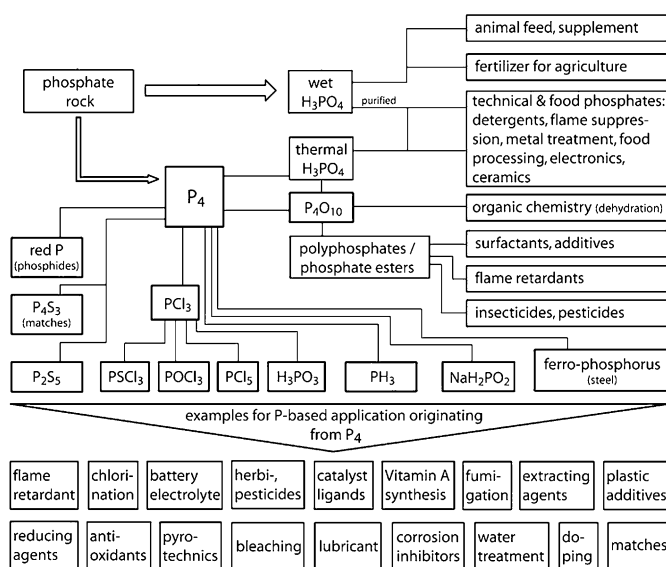
# Sustainable Phosphorus Chemistry: A Silylphosphide Synthron for the Generation of Value-Added Phosphorus Chemicals

J. Chris Slootweg\*

alternative synthesis · industrial chemistry ·  
phosphoric acid · sustainability · white phosphorus

The phosphorus chemical industry heavily depends on elemental, white phosphorus, which is produced in the energy-intensive Wöhler process (12.5–14 MWh per metric ton of  $P_4$ ) by reduction of phosphate rock in an electric arc furnace at 1500–1600 °C with coke (C; reducing agent) and silica ( $SiO_2$ ; for  $CaSiO_3$  slag formation).<sup>[1]</sup> This so-called “thermal process” functions as an element separator by removing impurities present in phosphate rock deposits (e.g., fluorine, cadmium, uranium, radium, mercury, lead, chromium, zinc, iron, copper, and rare-earth elements) and produces  $P_4$  in high purity.<sup>[2]</sup> The reduction of phosphates to white phosphorus ( $P_4$ ) is the route to many high-grade phosphorus products (Figure 1),<sup>[3]</sup> but now Cummins and Geeson provide an alternative pathway.<sup>[4]</sup> To date,  $P_4$  is thermally converted into its allotrope red phosphorus ( $P_{red}$ ),<sup>[1a]</sup> and reacts with sulfur to phosphorus sesquisulfide ( $P_4S_3$ ) and phosphorus pentasulfide ( $P_4S_{10}$ ).<sup>[1b]</sup> In addition, white phosphorus is oxidized by combustion using dry air to produce phosphorus pentoxide ( $P_4O_{10}$ ).<sup>[1b]</sup> Subsequent hydrolysis produces high-purity phosphoric acid ( $H_3PO_4$ ), which is applied as a food additive, for metal treatment, water treatment, and converted into phosphates for foodstuffs, pharmaceuticals, and animal feeds.<sup>[1a,d]</sup> Thermally generated phosphoric acid hardly contains any impurities; only arsenic (5–30 ppm; present in  $P_4$ ) is removed in a further purification step using hydrogen sulfide to precipitate arsenic sulfide.<sup>[1b,d,2]</sup>

Current industrial processes also rely on phosphorus trichloride ( $PCl_3$ ), which is obtained by treating molten white phosphorus with gaseous chlorine.<sup>[1b]</sup> Subsequent addition of chlorine, oxygen, sulfur, or water readily produces the key derivatives phosphorus pentachloride ( $PCl_5$ ), phosphoryl chloride ( $P(O)Cl_3$ ), thiophosphoryl chloride ( $P(S)Cl_3$ ), and phosphonic acid ( $H_3PO_3$ ; Figure 1).<sup>[1b]</sup> Phosphorus trichloride



**Figure 1.** Use of phosphorus in the chemical industry, an overview provided by Weigand and co-workers.<sup>[3]</sup> Reproduced (and slightly adapted) with permission from Springer Nature.

is an important intermediate in the production of, for example, the battery electrolyte lithium hexafluorophosphate ( $LiPF_6$ ; from  $PCl_3$ ), glyphosate (a herbicide), organophosphate triesters (phosphorus-based flame retardants), and a plethora of organophosphorus compounds, such as triphenylphosphine ( $PPh_3$ ; vitamin A synthesis).<sup>[3]</sup> Yet, in all cases, the production of these value-added phosphorus compounds is accompanied by the formation of copious amounts of Cl waste. An alternative approach that avoids the use of chlorine gas and the generation of Cl waste is the alkaline hydrolysis of  $P_4$  with sodium hydroxide, which affords phosphine ( $PH_3$ )<sup>[1b]</sup> and sodium hypophosphite ( $NaH_2PO_2$ ), which can both undergo atom-economic P–C bond formations (by hydrophosphination of alkenes and alkynes) to afford organophosphorus compounds<sup>[1c]</sup> and phosphinates,<sup>[5]</sup> respectively.

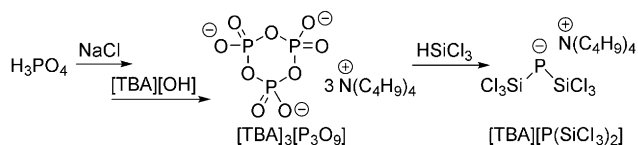
To further improve the sustainability of these chemical processes, it would be desirable to bypass the need for elemental white phosphorus (Figure 1).<sup>[6,7]</sup> Approximately 95 % of all phosphoric acid ( $H_3PO_4$ ; fertilizer for agriculture) is produced directly from phosphate rock in the “wet process”

[\*] Prof. Dr. J. C. Slootweg  
Van 't Hoff Institute for Molecular Sciences  
Research Priority Area Sustainable Chemistry  
University of Amsterdam  
Science Park 904, PO Box 94157, 1090 GD Amsterdam (The Netherlands)  
E-mail: j.c.slootweg@uva.nl

ID The ORCID identification number(s) for the author(s) of this article can be found under:  
<https://doi.org/10.1002/anie.201803692>.

by treatment with sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and subsequent removal of large amounts of gypsum ( $\text{CaSO}_4$ ) by filtration.<sup>[1d,2]</sup> Many of the impurities in the phosphate rock are still present in the wet phosphoric acid, which can be rigorously purified by several processes, the most common being extraction and precipitation. After intensive treatment, the purity of the phosphoric acid is comparable with the food-grade phosphoric acid produced by the thermal process.<sup>[1d,2]</sup>

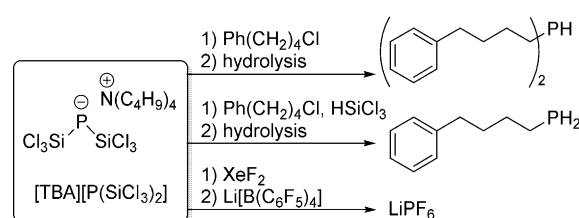
Cummins and Geeson have now unveiled that phosphoric acid is a suitable precursor for chemicals traditionally synthesized from white phosphorus ( $\text{P}_4$ ).<sup>[4]</sup> Their discovery is based on the use of commercially available sodium trimetaphosphate ( $\text{Na}_3[\text{P}_3\text{O}_9]$ ), which can be obtained in a one-pot procedure by the dehydration of phosphoric acid using sodium chloride (600 °C, 2 h), with hydrochloric acid (HCl) as the only byproduct.<sup>[8]</sup> Subsequent ion exchange with tetra-*n*-butylammonium hydroxide ([TBA][OH]) affords the more soluble cyclic phosphate trimer  $[\text{TBA}]_3[\text{P}_3\text{O}_9]\cdot 2\text{H}_2\text{O}$  (76 %;  $\delta(^{31}\text{P}) = -19.8$  ppm; Scheme 1), which was used by Cummins and Gleeson as the starting material.<sup>[4,8b]</sup>



**Scheme 1.** Synthesis of  $[\text{TBA}]_3[\text{P}_3\text{O}_9]\cdot 2\text{H}_2\text{O}$  and  $[\text{TBA}][\text{P}(\text{SiCl}_3)_2]$  from phosphoric acid. TBA = tetra-*n*-butylammonium,  $\text{N}(\text{C}_4\text{H}_9)_4$ .

Trimetaphosphate is an interesting anionic  $\kappa^3\text{-O}$  ligand for organometallic chemistry,<sup>[8b]</sup> and was recently applied, also by Cummins and co-workers, for the synthesis of cobalt and vanadium trimetaphosphate polyanions, which have favorable properties for non-aqueous redox-flow battery applications.<sup>[9]</sup> Cummins and Geeson now developed the direct conversion of trimetaphosphate,  $[\text{P}_3\text{O}_9]^{3-}$ , into valuable phosphorus compounds. Namely,  $[\text{TBA}]_3[\text{P}_3\text{O}_9]\cdot 2\text{H}_2\text{O}$  can be reduced in a steel pressure reactor with trichlorosilane as the solvent ( $\text{HSiCl}_3$ ; 33:1 Si/P molar ratio) at 110 °C for 72 hours to afford the novel bis(trichlorosilyl)phosphide anion in the form of its tetrabutylammonium salt  $[\text{TBA}][\text{P}(\text{SiCl}_3)_2]$  (65 %;  $\delta(^{31}\text{P}) = -171.7$  ppm,  $^1J_{\text{P,Si}} = 156$  Hz; Scheme 1).<sup>[4]</sup> Note that the industrial-scale production of  $\text{HSiCl}_3$  requires elemental silicon, which is, just like  $\text{P}_4$ , prepared in a high-energy process.<sup>[10]</sup> Cummins and Geeson discovered that the phosphorus–silicon bonds of  $[\text{P}(\text{SiCl}_3)_2]^-$  can be converted into phosphorus–carbon, phosphorus–hydrogen, or phosphorus–fluorine bonds by substitution (Scheme 2).<sup>[4]</sup>

Treatment of  $[\text{TBA}][\text{P}(\text{SiCl}_3)_2]$  with (4-chlorobutyl)benzene ( $\text{Ph}(\text{CH}_2)_4\text{Cl}$  (5 equiv), 105 °C, 108 h) in toluene afforded the corresponding dialkylsilylphosphine ( $\text{Ph}(\text{CH}_2)_4)_2\text{PSiCl}_3$ , which was converted into the desired bis(4-phenylbutyl)phosphine ( $\delta(^{31}\text{P}) = -69.2$  ppm,  $^1J_{\text{P,H}} = 199.5$  Hz; Scheme 2) by treatment with aqueous sodium hydroxide or basic alumina. Selective monoalkylation was also feasible and produced the primary phosphine  $\text{Ph}(\text{CH}_2)_4\text{PH}_2$  (Scheme 2), even by using trimetaphosphate



**Scheme 2.** Reactivity of  $[\text{TBA}][\text{P}(\text{SiCl}_3)_2]$ ; hydrolysis to  $\text{PH}_3$  not shown.

directly and in situ generation of the silylphosphide anion. Namely, heating a mixture of  $[\text{TBA}]_3[\text{P}_3\text{O}_9]\cdot 2\text{H}_2\text{O}$ ,  $\text{Ph}(\text{CH}_2)_4\text{Cl}$ , and trichlorosilane at 110 °C for 96 hours gave the alkylsilylphosphine  $\text{Ph}(\text{CH}_2)_4\text{P}(\text{SiCl}_3)_2\text{H}$ , which afforded the corresponding phosphine  $\text{Ph}(\text{CH}_2)_4\text{PH}_2$  (64 %;  $\delta(^{31}\text{P}) = -136.2$  ppm,  $^1J_{\text{P,H}} = 195$  Hz) after work-up (Scheme 2). Furthermore, Cummins and Geeson showed that this primary phosphine can be easily oxidized with hydrogen peroxide to afford (4-phenylbutyl)phosphinic acid ( $\text{Ph}(\text{CH}_2)_4\text{P}(\text{O})(\text{OH})\text{H}$ , 90 %;  $\delta(^{31}\text{P}) = 38.8$  ppm,  $^1J_{\text{P,H}} = 542$  Hz), which is a key building block in the reported synthesis of the prodrug fosinopril.<sup>[4]</sup>

$[\text{TBA}][\text{P}(\text{SiCl}_3)_2]$  can also be hydrolyzed directly to produce phosphine ( $\text{PH}_3$ ,  $\geq 63$  %;  $\delta(^{31}\text{P}) = -241.1$  ppm,  $^1J_{\text{P,H}} = 188$  Hz). Oxidation of the silylphosphide with a fluorine source is feasible, too. Treatment of  $[\text{TBA}][\text{P}(\text{SiCl}_3)_2]$  with xenon difluoride ( $\text{XeF}_2$ , 8 equiv) in dichloromethane gave  $[\text{TBA}][\text{PF}_6]$ , which yielded the prevalent electrolyte lithium hexafluorophosphate ( $\text{LiPF}_6$ , 70 %;  $\delta(^{31}\text{P}) = -144.6$  ppm,  $^1J_{\text{P,F}} = 706$  Hz) after salt metathesis with lithium tetrakis(pentafluorophenyl)borate ( $\text{Li}[\text{B}(\text{C}_6\text{F}_5)_4]$ , 1 equiv; Scheme 2).

The seminal work by Cummins and Geeson highlights the use of a novel silylphosphide synthon, which offers a route between phosphoric acid ( $\text{H}_3\text{PO}_4$ ) and value-added phosphorus chemicals that had previously only been available from white phosphorus ( $\text{P}_4$ ). This breakthrough will undoubtedly stimulate the development of more atom-economic synthetic methods that will safeguard our precious resources, and in particular promote the sustainable use of phosphorus.<sup>[5,6]</sup>

## Acknowledgements

This work was supported by the Council for Chemical Sciences of The Netherlands Organization for Scientific Research (NWO/CW and NWO/TTO) by a VIDI grant and an STW Take-off grant.

## Conflict of interest

The authors declare no conflict of interest.

**How to cite:** *Angew. Chem. Int. Ed.* **2018**, *57*, 6386–6388  
*Angew. Chem.* **2018**, *130*, 6494–6496

[1] a) “Phosphorus”: H. Diskowski, T. Hofmann in *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. 26, Wiley-VCH, Weinheim, **2012**, pp. 725–746; b) “Phosphorus Compounds,

- Inorganic”: G. Bettermann, W. Krause, G. Riess, T. Hofmann in *Ullmann’s Encyclopedia of Industrial Chemistry*, Vol. 27, Wiley-VCH, Weinheim, **2012**, pp. 1–18; c) “Phosphorus Compounds, Organic”: J. Svára, N. Weferling, T. Hofmann in *Ullmann’s Encyclopedia of Industrial Chemistry*, Vol. 27, Wiley-VCH, Weinheim, **2012**, pp. 19–49; d) “Phosphoric Acid and Phosphates”: K. Schrödter, G. Bettermann, T. Staffel, F. Wahl, T. Klein, T. Hofmann in *Ullmann’s Encyclopedia of Industrial Chemistry*, Vol. 26, Wiley-VCH, Weinheim, **2012**, pp. 679–724.
- [2] M. A. de Boer, L. Wolzak, J. C. Sloopweg in *Phosphorus Recovery and Recycling* (Eds.: H. Ohtake, S. Tsuneda), Springer Nature, Singapore Pte Ltd., **2018**, Chapter 5: Phosphorus: Reserves, Production, and Applications; [https://doi.org/10.1007/978-981-910-8031-9\\_5](https://doi.org/10.1007/978-981-910-8031-9_5).
- [3] O. Gantner, W. Schipper, J. J. Weigand in *Sustainable Phosphorus Management* (Eds.: R. W. Scholz, A. H. Roy, F. S. Brand, D. T. Hellums, A. E. Ulrich), Springer, Dordrecht, **2014**, pp. 237–242.
- [4] M. B. Geeson, C. C. Cummins, *Science* **2018**, 359, 1383–1385.
- [5] a) J.-L. Montchamp, *Acc. Chem. Res.* **2014**, 47, 77–87; for P–C(aryl) couplings, see: b) L. Botez, G. B. de Jong, J. C. Sloopweg, B.-J. Deelman, *Eur. J. Org. Chem.* **2017**, 434–437.
- [6] a) W. Schipper, *Eur. J. Inorg. Chem.* **2014**, 1567–1571; b) C. C. Cummins, *Daedalus* **2014**, 143, 9–20, and references therein.
- [7] Special issue on “Phosphates and Global Sustainability” (Eds.: E. Valsami-Jones, E. H. Oelkers), *Elements* **2008**, 4, 83–116; see in particular: a) E. H. Oelkers, E. Valsami-Jones, *Elements* **2008**, 4, 83–87; b) G. M. Filippelli, *Elements* **2008**, 4, 89–95; c) S. A. Parsons, J. A. Smith, *Elements* **2008**, 4, 109–112.
- [8] a) D. Pham Minh, J. Ramaroson, A. Nzihou, P. Sharrock, *Ind. Eng. Chem. Res.* **2012**, 51, 3851–3854; b) C. J. Besecker, V. W. Day, W. G. Klemperer, *Organometallics* **1985**, 4, 564–570.
- [9] J. M. Stauber, S. Zhang, N. Gvozdk, Y. Jiang, L. Avena, K. J. Stevenson, C. C. Cummins, *J. Am. Chem. Soc.* **2018**, 140, 538–541.
- [10] a) “Silicon Compounds, Inorganic”: W. Simmler in *Ullmann’s Encyclopedia of Industrial Chemistry*, Vol. 32, Wiley-VCH, Weinheim, **2012**, pp. 615–635; b) “Silicon”: W. Zulehner, B. Neuer, G. Rau in *Ullmann’s Encyclopedia of Industrial Chemistry*, Vol. 32, Wiley-VCH, Weinheim, **2012**, pp. 573–601.

Manuscript received: March 27, 2018

Version of record online: May 3, 2018