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Photocatalytic stannylation of white phosphorus†

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Organophosphorus compounds (OPCs) are highly important chemicals, finding numerous applications in both academia and industry. Herein we describe a simple photocatalytic method for the stannylation of white phosphorus (P_4) using a cheap, commercially-available distannane, $(Bu_3Sn)_2$, and anthraquinone as a simple photocatalyst. Subsequent 'one pot' transformation of the resulting stannylated monophosphine intermediate $(Bu_3Sn)_3P$ provides direct, convenient and versatile access to valuable OPCs such as acylated phosphines and tetraalkylphosphonium salts.

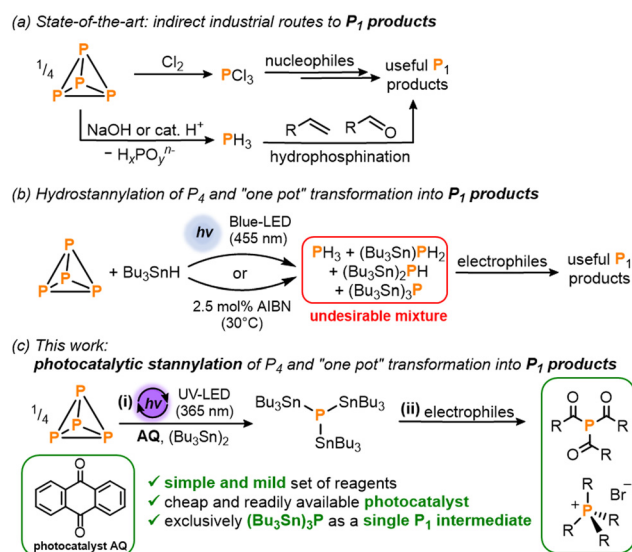
White phosphorus (P_4) – the most chemically important allotrope of this ubiquitous and abundant element – acts as the common precursor from which all commercially valuable and academically important organophosphorus compounds (OPCs) are prepared. The current methods used for the industrial synthesis of these myriad useful P_1 products include the oxidation of P_4 with toxic Cl_2 gas to generate PCl_3 which can subsequently be transformed into a variety of OPCs by reaction with nucleophiles (Scheme 1a). As an alternative route, initial acid- or base-mediated disproportionation of P_4 can be used to generate highly toxic PH_3 gas which is then employed for the hydrophosphination of unsaturated organic substrates.¹

Given the drawbacks of these methods, a highly prominent aim has long been to find ways of bypassing these multi-step procedures. In particular, there is a longstanding desire to develop more step-efficient *direct* – and, ideally, *catalytic* – methods to functionalize P_4 and generate OPCs in a single reaction.

As a result, for several decades comprehensive efforts have been made to better understand the fundamental reactivity of P_4 .² However, it is only very recently that it has finally become

possible to successfully transform P_4 directly into a variety of useful P_1 products.³ Moreover, and despite these extensive investigations, the number of successful examples remains extremely low, and those that do exist still suffer from substantial limitations.⁴ As such, there remains a clear need to expand the range of strategies available for direct, productive P_4 activation, with new catalytic methods being particularly desirable.^{4a}

In one of our own contributions to this area, we recently reported a simple 'one pot' method in which the classical radical reagent tri-*n*-butyltin hydride (Bu_3SnH) is used for initial hydrostannylation of



Scheme 1 (a) Current state-of-the-art industrial methods for the synthesis of valuable P_1 products.¹ (b) Recently reported hydrostannylation of white phosphorus (P_4) using Bu_3SnH followed by reaction with electrophiles to generate useful P_1 products in a 'one-pot' fashion.⁵ (c) This work: (i) photocatalytic stannylation of P_4 using the photocatalyst anthraquinone (AQ) and hexabutylstannane $(Bu_3Sn)_2$; and (ii) subsequent functionalization of the intermediate $(Bu_3Sn)_3P$ with electrophiles into products such as triacylphosphines and tetraalkylphosphonium salts.

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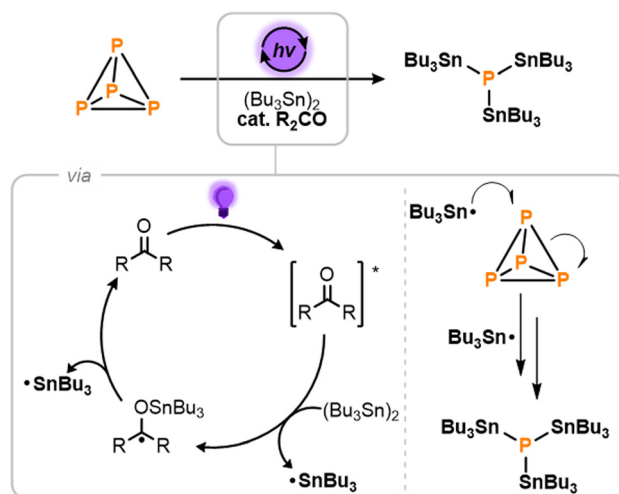
P_4 (Scheme 1b).⁵ This reductive P_4 activation is mediated either by light or by a chemical radical initiator such as AIBN (azobis(isobutyronitrile)) which can initiate a radical chain reaction that breaks down the P_4 tetrahedron, yielding a mixture of hydrostannylated phosphines $(Bu_3Sn)_xPH_{3-x}$ ($x = 0-3$). Key to this mechanism is the attack of stannyl radicals (Bu_3Sn^\bullet) on the P-P bonds of P_4 . The resulting $(Bu_3Sn)_xPH_{3-x}$ mixture can then be converted into a number of important and useful OPCs by reaction with electrophiles.⁵

Unfortunately, one significant disadvantage of this hydrostannylation strategy is the complexity of the $(Bu_3Sn)_xPH_{3-x}$ mixture, which complicates 'downstream' reaction development by requiring functionalization of two different types of bond (P-Sn and P-H), both of which are distributed over four distinct molecules. Moreover, the presence of gaseous PH_3 as a component of this mixture has been suggested to have a limiting effect on overall yields as it can easily be lost during subsequent manipulations,^{4a} and it is also problematic from a safety perspective.

These drawbacks would be overcome if the initial P_4 reduction step could instead furnish a single species with just one functionalizable motif, but with reactivity otherwise similar to $(Bu_3Sn)_xPH_{3-x}$. To achieve this, we describe herein a simple photocatalytic strategy for the atom-precise stannylation of P_4 using the cheap, commercially-available distannane $(Bu_3Sn)_2$ and simple benzophenone derivatives as photocatalysts (Scheme 1c). This new procedure generates exclusively the stannylated monophosphine $(Bu_3Sn)_3P$ and subsequent, simplified 'one pot' transformations with electrophiles afford valuable OPCs including acylated phosphines and alkylated phosphonium salts.

Based on the analysis above, we sought to develop a new method by which P_4 could be selectively transformed into $(Bu_3Sn)_3P$ as the sole product.⁶ It is worth noting that the closely related product $(Ph_3Sn)_3P$ has previously been prepared from P_4 using Ph_3SnCl as the stannylating reagent, but this required use of a relatively elaborate Ti(III) reagent as a halogen atom abstractor.^{3f} Instead, we imagined that an ideal reagent for such a reaction would be the distannane $(Bu_3Sn)_2$, which is cheap to purchase and could in principle provide the target phosphine with perfect atom economy.⁷ Indeed, Sn-Sn homolysis of $(Bu_3Sn)_2$ is known to furnish Bu_3Sn^\bullet radicals, which previous work has shown are capable of adding to P_4 .^{3f,5} However, achieving this homolysis directly requires extreme temperatures or very high energy UV light irradiation that is known to lead to unselective reactivity, and is also unlikely to be compatible with P_4 .⁸⁻¹⁰ Fortunately, it has been reported that simple ketones can be used as photocatalysts to access Bu_3Sn^\bullet radicals by Sn-Sn bond cleavage under much lower energy irradiation.¹¹

The light-driven photocatalytic stannylation of P_4 was therefore targeted, based on the mechanistic proposal outlined in Scheme 2.⁹ It was anticipated that photoirradiation of the ketone R_2CO would first provide an excited state, $[R_2CO]^*$,¹² capable of reacting with $(Bu_3Sn)_2$ to generate a stannylated ketyl radical and a free Bu_3Sn^\bullet radical.¹¹ The former could then



Scheme 2 Proposed mechanism for the light-driven, photocatalytic stannylation of P_4 in the presence of hexabutyldistannane, $(Bu_3Sn)_2$, and a ketone photocatalyst, R_2CO .

thermally release a second Bu_3Sn^\bullet radical to close the catalytic cycle. Once formed, these Bu_3Sn^\bullet radicals would then add to the P-P bonds of P_4 , ultimately breaking it down to generate $(Bu_3Sn)_3P$ as the only P_1 product.¹³

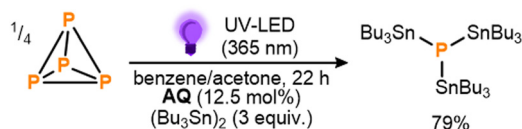
To begin, benzophenone (**BP**) was chosen as a proof-of-principle photocatalyst due to both its simplicity and the fact that its photoreactivity towards hexaalkyldistannanes has been studied previously.^{11d} Gratifyingly, after an initial optimization the photocatalytic stannylation of P_4 could successfully be achieved, with use of 25 mol% **BP** (all stoichiometries, in both equiv. and mol%, are defined per P atom) and a 3.3-fold excess (5 equiv.) of $(Bu_3Sn)_2$ providing 50% conversion to the target stannylated phosphine $(Bu_3Sn)_3P$ after stirring under near UV LEDs overnight (Scheme 3; see also ESI,† S3). Control experiments confirmed that all reaction components (P_4 , $(Bu_3Sn)_2$, **BP**, irradiation) were necessary for the reaction to proceed productively (see ESI,† S3, Table S1).

These initial results provided a clear proof-of-principle for the proposed mechanistic strategy. Notably, the observed conversion indicates the activation of at least three Sn-Sn bonds per available equivalent of **BP**,¹⁴ making this a rare example of a system where P_4 activation has been achieved catalytically, using an otherwise inert substrate.^{5,9a,9b,9e,15} Nevertheless, in order to improve the reaction outcome further, a broader range of benzophenone derivatives was subsequently screened, with several found to provide markedly improved performance (see ESI,† S5). Particularly impressive results were achieved using



Scheme 3 Initial conditions for the direct, photocatalytic stannylation of P_4 into $(Bu_3Sn)_3P$ optimized using benzophenone (**BP**) as photocatalyst. Stoichiometries in equiv. and mol% are defined per P atom.





Scheme 4 Optimized conditions for the direct, photocatalytic stannylation of P_4 into $(Bu_3Sn)_3P$ using anthraquinone (AQ) as photocatalyst. Stoichiometries in equiv. and mol% are defined per P atom.

anthraquinone (AQ) and following brief further optimization (see ESI,† S5 and S7) 79% conversion to $(Bu_3Sn)_3P$ could be achieved using significantly reduced loadings of both AQ (12.5 mol%) and $(Bu_3Sn)_2$ (3 equiv.) over the same timeframe (Scheme 4; see also ESI,† S7). Based on the catalytic cycle proposed in Scheme 2, this would correspond to a turnover number (TON) of 10.0 for AQ. Further reductions in catalyst loading to 6.3 mol% or 2.5 mol% were found to lead to even higher TONs (16.8 and 28.2, respectively), albeit at the cost of lower overall conversions (see ESI,† S7, Table S11).

With the stannylation of P_4 optimized, attention was then shifted to its subsequent, 'one pot' transformation into other useful P_1 products. Having previously developed procedures for the analogous transformation of the phosphine mixture $(Bu_3Sn)_xPH_{3-x}$, which includes $(Bu_3Sn)_3P$ as a minor component, it was anticipated that addition of electrophiles to photocatalytically-generated $(Bu_3Sn)_3P$ should be similarly productive,^{4,5} especially since neither the AQ photocatalyst nor the $(Bu_3Sn)_2$ starting material is expected to show appreciable reactivity towards such substrates. And, indeed, *in situ* addition of a variety of acid chlorides yielded the corresponding triacylphosphines $(R(O)C)_3P$ ($R = Ph, Cy, Ad, tBu, iPr, nBu, Me$) with good conversions of up to 75% (Scheme 5a(i)).^{5,16} Notably, and in comparison to our previously-reported hydrostannylation system, no exclusion of light and no additional base were required for this step, highlighting both the robustness and simplicity of $(Bu_3Sn)_3P$ as a " P^3- " synthon, relative to $(Bu_3Sn)_xPH_{3-x}$.

Similarly, reaction of $(Bu_3Sn)_3P$ with alkyl bromides RBr ($R = Bn, Et$) under moderate heating successfully provided

'one pot' access to the corresponding phosphonium salts, $[R_4P]Br$, including tetrabenzylphosphonium bromide, $[Bn_4P]Br$, which is a known precursor for useful Wittig chemistry (Scheme 5a(ii)).¹⁷ Again, no auxiliary base was required for these reactions, in contrast to the analogous procedures *via* $(Bu_3Sn)_xPH_{3-x}$ where the absence of base leads to a 50% reduction in yield.⁵

Finally, another industrially important class of P_1 products was targeted. Hydroxymethyl-substituted phosphine derivatives are used as flame-retardant materials (among a number of other applications),¹⁸ and could be accessed by reacting the stannylated monophosphine $(Bu_3Sn)_3P$ with paraformaldehyde in EtOH to furnish tris(hydroxymethyl)phosphine, THP (THP ; Scheme 5a(iii)).^{18a} Subsequent exposure to air then yielded the corresponding phosphine oxide, $(HOCH_2)_3PO$ ($THPO$; Scheme 5a(iv)),^{18b} while the phosphonium salt tetrakis(hydroxymethyl)phosphonium chloride, $[(HOCH_2)_4P]Cl$ ($THPC$),^{18c,18d} could be accessed by quenching the *in situ* generated THP with HCl, all in one pot (Scheme 5a(v)).

To demonstrate the viability of these reactions on a preparative scale the triacylphosphine $(Ph(O)C)_3P$ and the phosphonium salts $[Bn_4P]Br$ and $THPC$ were selected as representative examples for isolation (Scheme 5b; see ESI† S9). At 0.8 mmol scale $(PhC(O))_3P$ could be isolated in 55% yield,¹⁹ which compares well with our previously-reported hydrostannylation method (51%). $[Bn_4P]Br$ could also be isolated in good 56% yield, and $THPC$ in a more modest yield of 33%.¹⁹

For this last reaction, efforts were also made to recover the Sn-containing compounds present at the end of the reaction. We have previously shown that for the analogous synthesis of $THPC$ *via* $(Bu_3Sn)_xPH_{3-x}$ recovery of the Bu_3SnCl byproduct allows for convenient regeneration and recycling of the Bu_3SnH starting material, thus minimizing the formation of organotin-containing waste. Bu_3SnCl can also be used to regenerate $(Bu_3Sn)_2$ through a net one-electron reduction,⁸ meaning similar recycling should be feasible for this newer system, provided Bu_3SnCl can again be cleanly recovered. Satisfyingly, Bu_3SnCl could indeed be recovered during $THPC$ workup through simple washing with diethyl



Scheme 5 (a) One-pot synthesis directly from P_4 , via photocatalytically generated P_1 intermediate $(Bu_3Sn)_3P$, of (i) triacylphosphines $(R(O)C)_3P$ (4 equiv. $RC(O)Cl$, $R = tBu, Ph, Me, nBu, Cy, iPr, Ad$), (ii) phosphonium salts $[R_4P]Br$ (5 equiv. RBr , $R = Bn, Et$, 60–80 °C), (iii) tris(hydroxymethyl)phosphine, THP (EtOH, 3 equiv. paraformaldehyde), (iv) tris(hydroxymethyl)phosphine oxide, THPO (as for (iii) then air, 80 °C), and (v) tetrakis(hydroxymethyl)phosphonium chloride, THPC (as for (iii) using 12.5 equiv. paraformaldehyde, then 10 equiv. HCl); and (b) Isolated yields for reactions on preparative scale (0.8 mmol). Stoichiometries in equiv. are defined per P atom.



ether, being isolated as part of an otherwise clean mixture with unreacted $(\text{Bu}_3\text{Sn})_2$ in an excellent overall yield of 92% (1.3:1 molar ratio, see ESI† S9).

In conclusion, we have developed a simple, new method for the direct transformation of P_4 into a variety of commercially and academically interesting OPCs. The reaction proceeds through a photocatalytic stannylation of white phosphorus, which generates $(\text{Bu}_3\text{Sn})_3\text{P}$ with perfect atom economy as a single, convenient P_1 intermediate using an inexpensive, commercially available distannane and a simple photocatalyst. This method can be used to prepare a variety of different products through inclusion of a range of different electrophilic substrates, and we have demonstrated that the Sn-containing byproducts of the reaction can in principle be recovered and recycled. These results expand the currently very limited range of strategies that are available for the direct functionalization of P_4 , and suggest the intriguing possibility that P_4 activation might also be achievable by reaction with other weak E–E bonds under similar photocatalytic conditions.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

- (a) W. Gleason, *JOM*, 2007, **59**, 17–19; (b) G. Bettermann, W. Krause, G. Riess and T. Hofmann, *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley, 2000; (c) D. E. C. Corbridge, *Phosphorus: Chemistry, Biochemistry, and Technology*, CRC Press, 6th edn, 2013.
- (a) B. M. Cossairt, N. A. Piro and C. C. Cummins, *Chem. Rev.*, 2010, **110**, 4164–4177; (b) M. Caporali, L. Gonsalvi, A. Rossin and M. Peruzzini, *Chem. Rev.*, 2010, **110**, 4178–4235; (c) M. Scheer, G. Balázs and A. Seitz, *Chem. Rev.*, 2010, **110**, 4236–4256; (d) C. M. Hoidn, D. J. Scott and R. Wolf, *Chem. – Eur. J.*, 2021, **27**, 1886–1902; (e) L. Giusti, V. R. Landaeta, M. Vanni, J. A. Kelly, R. Wolf and M. Caporali, *Coord. Chem. Rev.*, 2021, **441**, 2139276–2139375; (f) Y. H. Budnikova, T. V. Gryaznova, V. V. Grinenko, Y. B. Dudkina and M. N. Khrizanforov, *Pure Appl. Chem.*, 2017, **89**, 311–330.
- (a) S. Reichl, E. Mädl, F. Riedelberger, M. Piesch, G. Balázs, M. Seidl and M. Scheer, *Nat. Commun.*, 2021, **12**, 5774; (b) M. Donath, K. Schwedtmann, T. Schneider, F. Hennersdorf, A. Bauzá, A. Frontera and J. J. Weigand, *Nat. Chem.*, 2022, **14**, 384–391; (c) Y. Mei, Z. Yan and L. L. Liu, *J. Am. Chem. Soc.*, 2022, **144**, 1517–1522; (d) D. H. R. Barton and J. Zhu, *J. Am. Chem. Soc.*, 1993, **115**, 2071–2072; (e) D. H. R. Barton and R. A. Vonder Embse, *Tetrahedron*, 1998, **54**, 12475–12496; (f) B. M. Cossairt and C. C. Cummins, *New J. Chem.*, 2010, **34**, 1533–1536; (g) S. K. Ghosh, C. C. Cummins and J. A. Gladysz, *Org. Chem. Front.*, 2018, **5**, 3421–3429.
- (a) D. J. Scott, *Angew. Chem.*, 2022, e202205019, DOI: [10.1002/anie.202205019](https://doi.org/10.1002/anie.202205019); (b) H. Grützmaier, *Nat. Chem.*, 2022, **14**, 362–364.
- D. J. Scott, J. Cammarata, M. Schimpf and R. Wolf, *Nat. Chem.*, 2021, **13**, 458–464.
- Previous work has shown that $(\text{Bu}_3\text{Sn})_3\text{P}$ can be prepared through stannylation of $(\text{Bu}_3\text{Sn})_x\text{PH}_{3-x}$ with Bu_3SnOMe . However, this requires addition of an extra stoichiometric reagent and results in formation of MeOH as a byproduct which could lead to competing reactivity upon subsequent addition of electrophiles, see ref. 5.
- (a) A. Darwish and J. M. Chong, *Synth. Commun.*, 2004, **34**, 1885–1890; (b) T. N. Mitchell, *Encyclopedia of Reagents for Organic Synthesis – Hexabutylidistannane*, Wiley, 2012; (c) T. N. Mitchell and G. Walter, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1842–1847.
- A. G. Davies, *Organotin Chemistry*, Wiley, 2004.
- For previous examples where photochemical methods have been used to functionalize P_4 , see: (a) U. Lennert, P. B. Arockiam, V. Streitferdt, D. J. Scott, C. Rödl, R. M. Gschwind and R. Wolf, *Nat. Catal.*, 2019, **2**, 1101–1106; (b) P. B. Arockiam, U. Lennert, C. Graf, R. Rothfelder, D. J. Scott, T. G. Fischer, K. Zeitler and R. Wolf, *Chem. – Eur. J.*, 2020, **26**, 16374–16382; (c) R. Rothfelder, V. Streitferdt, U. Lennert, J. Cammarata, D. J. Scott, K. Zeitler, R. M. Gschwind and R. Wolf, *Angew. Chem., Int. Ed.*, 2021, **60**, 24650–24658; (d) M. Till, V. Streitferdt, D. J. Scott, M. Mende, R. M. Gschwind and R. Wolf, *Chem. Commun.*, 2022, **58**, 1100–1103; (e) G. Lu, J. Chen, X. Huangfu, X. Li, M. Fang, G. Tang and Y. Zhao, *Org. Chem. Front.*, 2019, **6**, 190–194; (f) D. Tofan and C. C. Cummins, *Angew. Chem., Int. Ed.*, 2010, **49**, 7516–7518; (g) L. P. Wang, D. Tofan, J. Chen, T. V. Voorhis and C. C. Cummins, *RSC Adv.*, 2013, **3**, 23166–23171.
- Cleavage of P_4 under photoirradiation (256 nm) can generate highly reactive P_2 (ref. 9f and g). However, this requires very high energy UV light (256 nm) and so seems unlikely to be a major, relevant pathway for the reactivity reported herein, which uses significantly lower energy UV sources (365 nm). Nevertheless, the possibility that this could act as a minor competing pathway, for example leading to minor reaction side-products, cannot yet be fully excluded.
- (a) W. P. Neumann, H. Hillgärtner, K. M. Baines, R. Dicke, K. Vorspohl, U. Kobs and U. Nussbeutel, *Tetrahedron*, 1989, **45**, 951–960; (b) M. Harendza, J. Junggebauer, K. Leßman, W. P. Neumann and H. Tews, *Synlett*, 1993, 286–288; (c) D. J. Hart, R. Krishnamurthy, L. M. Pook and F. L. Seely, *Tetrahedron Lett.*, 1993, **34**, 7819–7822; (d) M. J. Tomaszewski and J. Warkentin, *J. Chem. Soc., Chem. Commun.*, 1993, **18**, 1407–1408.
- (a) J. A. Dantas, J. T. M. Correia, M. W. Paixão and A. G. Corrêa, *ChemPhotoChem*, 2019, **3**, 506–520; (b) B. Dinda, *Essentials of Pericyclic and Photochemical Reactions: Photochemistry of Carbonyl Compounds (Chapter 8)*, Springer, 2016; (c) B. König, *Chemical Photocatalysis*, de Gruyter, 2013; (d) W. A. Green, *Industrial Photoinitiators: A Technical Guide*, CRC Press, 2010; (e) J. P. Fouassier and J. Lalevée, *Photoinitiators: Structures, Reactivity and Application in Polymerization*, Wiley, 2021; (f) J. Cervantes-González, D. A. Vosburg, S. E. Mora-Rodriguez, M. A. Vázquez, L. G. Zepeda, C. V. Gómez and S. Lagunas-Rivera, *ChemCatChem*, 2020, **12**, 3811–3827.
- Alternative elementary steps such as “outer-sphere” energy transfer between $[\text{R}_2\text{CO}]^*$ and $(\text{Bu}_3\text{Sn})_2$ could also be possible, but would be expected to lead to the same overall outcome. For additional mechanistic discussion, please see ESI† S2.
- Since conversion to $(\text{Bu}_3\text{Sn})_3\text{P}$ requires activation of 1.5 Sn–Sn bonds per P atom.
- L. Riesel, M. Kant and R. Helbing, *Z. Anorg. Allg. Chem.*, 1990, **580**, 217–223.
- G. Becker, *Z. Anorg. Allg. Chem.*, 1977, **430**, 66–76.
- H. Schmidbaur, U. Deschler, B. Milewski-Mahrla and B. Zimmer-Gasser, *Chem. Ber.*, 1981, **114**, 608–619.
- (a) K. V. Katti, H. Gali, C. J. Smith and D. E. Berning, *Chem. Res.*, 1999, **32**, 9–17; (b) M. J. Chen, C. R. Chen, Y. Tan, J. Q. Huang, X. L. Wang, L. Chen and Y. Z. Wang, *Ind. Eng. Chem. Res.*, 2014, **53**, 1160–1171; (c) W. J. Vullo, *Ind. Eng. Chem. Process Des. Dev.*, 1966, **5**, 346–349; (d) W. J. Vullo, *J. Org. Chem.*, 1968, **33**, 3665–3667.
- Yields of isolated materials have not been corrected for the presence of trace impurities observable by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. See ESI† S9.

