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# Radical Synthesis of Trialkyl, Triaryl, Trisilyl, and Tristannyl Phosphines from P<sub>4</sub>\*

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March 12, 2010

## Abstract

A reaction scheme has been devised according to  $3 \text{ RX} + 3 \text{ Ti(III)} + 0.25 \text{ P}_4 \rightarrow \text{PR}_3 + 3 \text{ XTi(IV)}$  wherein  $\text{RX} = \text{PhBr}$ ,  $\text{CyBr}$ ,  $\text{Me}_3\text{SiI}$ , or  $\text{Ph}_3\text{SnCl}$  with contrasting results in the case of more hindered  $\text{RX}$ ; the scheme accomplishes direct radical functionalization of white phosphorus without intermediacy of  $\text{PCl}_3$ .

It is known that P<sub>4</sub>, white phosphorus, has excellent properties as a trap for carbon-centered radicals in solution and under the mild conditions that are typical for organic synthesis. The most prominent example of this was the demonstration that phosphonic acids may be prepared from corresponding carboxylic acids by way of *O*-acyl derivatives of *N*-hydroxy-2-thiopyridone (Barton PTOC esters).<sup>1</sup> The latter provide carbon centered radicals in an oxygen-initiated chain reaction, and these are consumed upon combination with P<sub>4</sub> as the critical P–C bond-forming event; upon oxidative workup, any remaining P–P bonds are cleaved and the phosphonic acid  $\text{RP(O)(OH)}_2$  is the end product.<sup>2</sup> It is also known that P–P bonds *other* than those in P<sub>4</sub> may serve as traps for organic radicals. This has been shown by Sato et al. in a scheme for radical phosphination of organic halides wherein  $\text{ArX}$  serves as a source of  $\text{Ar}\cdot$  which in turn attacks  $\text{Ph}_2\text{P–PPh}_2$ , yielding  $\text{ArPPh}_2$ .<sup>3</sup>

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\*We dedicate this work to the memory of Sir Derek Barton.

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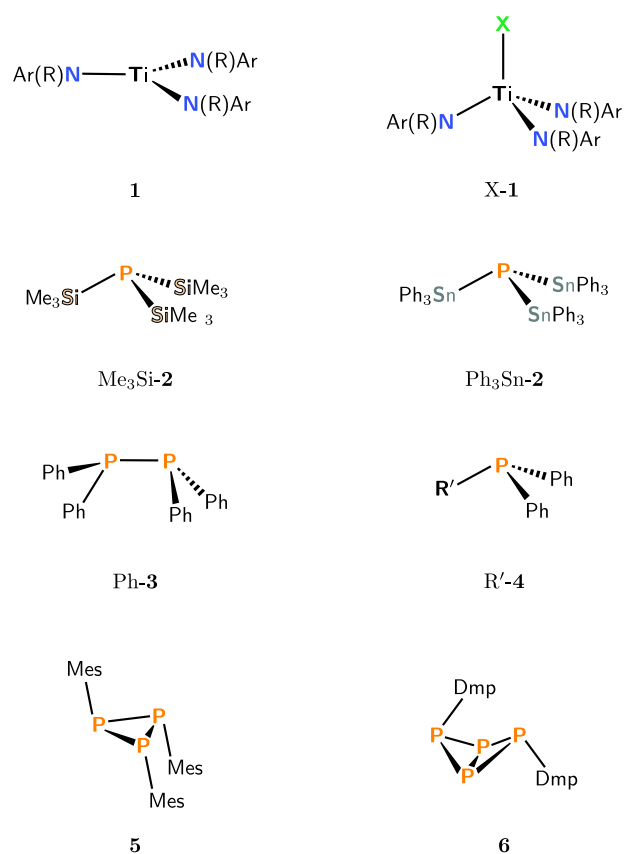
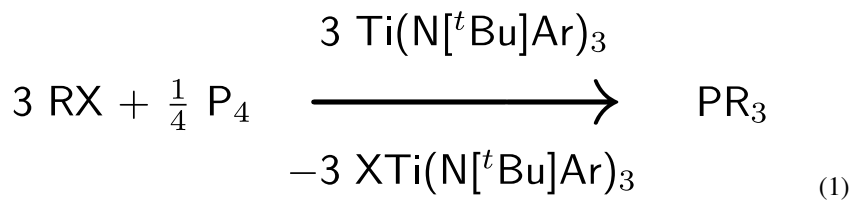


Figure 1:  $\text{Ti}(\text{N}[\text{tBu}]\text{Ar})_3$  together with various  $\text{P}_4$ -derived phosphanes and polyphosphorus products.  $\text{R} = \text{tBu}$ ;  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ;  $\text{R}' = \text{Ph}, \text{Mes}, \text{Cy}, \text{Ph}_3\text{Sn}$ ;  $\text{Mes} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ ;  $\text{Dmp} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ .

Such a vision for phosphine synthesis *via* homolytic substitution at a phosphorus center has also been developed by Vaillard et al., who employed  $\text{Me}_3\text{MPPh}_2$  ( $\text{M} = \text{Si}$  or  $\text{Sn}$ ) as the phosphorus substrate and  $\text{RX}$  as the carbon-radical source, together with a radical initiator, to produce  $\text{RP}(\text{O})\text{Ph}_2$  efficiently after an oxidative workup.<sup>4</sup> For our part, we have previously shown that the three-coordinate titanium(III) complex  $\text{Ti}(\text{N}[\text{tBu}]\text{Ar})_3$  ( $\text{Ar} = 3,5\text{-C}_6\text{H}_3\text{Me}_2$ ), **1**, is a potent halogen-atom abstractor, capable of abstracting  $\text{X}\cdot$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ , or  $\text{I}$ ) from various donor molecules at room temperature or below, in aprotic organic media (Figure 1). With the present work, we sought to develop a high-yield synthesis of phosphines  $\text{PR}_3$  from 3  $\text{RX}$  and 0.25  $\text{P}_4$ , using  $\text{Ti}(\text{N}[\text{tBu}]\text{Ar})_3$  as a halogen atom sink (see idealized Equation 1). Success in this arena would demonstrate that it is possible to synthesize valuable tertiary phosphanes  $\text{PR}_3$  through direct functionalization and complete consumption of  $\text{P}_4$  by a radical mechanism.



In the course of a prior study of radical cleavage of symmetrical 1,4-dicarbonyl compounds by  $\text{Ti}(\text{N}[\text{tBu}]\text{Ar})_3$ , the propensity was examined of  $\text{Ti}(\text{N}[\text{tBu}]\text{Ar})_3$  to abstract  $\text{X}\cdot$  from halobenzenes.<sup>5</sup> This study revealed that treatment of  $\text{Ti}(\text{N}[\text{tBu}]\text{Ar})_3$  with the stoichiometric amount of  $\text{PhBr}$  or  $\text{PhI}$  effected conversion to  $\text{XTi}(\text{N}[\text{tBu}]\text{Ar})_3$ . **1**, rapidly at room temperature, while conversion to  $\text{ClTi}(\text{N}[\text{tBu}]\text{Ar})_3$  upon treatment with  $\text{PhCl}$  was considerably slower. Dissolution of  $\text{Ti}(\text{N}[\text{tBu}]\text{Ar})_3$  in *neat* chlorobenzene and stirring overnight at room temperature did effect complete conversion to  $\text{ClTi}(\text{N}[\text{tBu}]\text{Ar})_3$ , however. A radical cyclization experiment using *o*-bromophenyl allyl ether as the  $\text{RX}$  substrate for  $\text{Ti}(\text{N}[\text{tBu}]\text{Ar})_3$  has been used to substantiate the hypothesis that phenyl radicals are indeed generated upon halogen atom abstraction from  $\text{PhX}$  by  $\text{Ti}(\text{N}[\text{tBu}]\text{Ar})_3$ .<sup>5,6</sup> On the basis of this information, together with the knowledge from recent independent work that  $\text{Ti}(\text{N}[\text{tBu}]\text{Ar})_3$  engages in negligible re-

action with  $P_4$ ,<sup>7</sup> we realized that  $Ti(N[{}^tBu]Ar)_3$  is an unusual reducing agent in that it could be selective for RX activation in the presence of  $P_4$ . This is unusual because most chemical reducing agents capable of  $X\cdot$  abstraction from RX would not be expected to be selective for this reactivity channel in the presence of  $P_4$ . An aspect of this type of special selectivity in reactions of  $Ti(N[{}^tBu]Ar)_3$  has been demonstrated previously wherein 7-chloronorbornadiene was treated with a 1:1 mixture of  $Ti(N[{}^tBu]Ar)_3$  and  $Mo(N[{}^tBu]Ar)_3$ ; in this instance  $Ti(N[{}^tBu]Ar)_3$  was entirely selective for Cl-atom abstraction giving  $ClTi(N[{}^tBu]Ar)_3$ , while exhibiting no propensity for trapping the 7-norbornadienyl radical which was seen to interact selectively with the molybdenum complex.<sup>8</sup> In addition, typical one-electron reducing agents that might be used for effecting  $X\cdot$  abstraction, e.g.  $CoCl(PPh_3)_3$ ,  $SmI_2$ , or  $Cp_2TiCl$ , simply give no reaction with a substrate such as PhBr.<sup>9,10</sup>

In a first reaction targeted at generating  $PPh_3$ , it was found that addition of 3 equiv of PhBr by microsyringe to a 0.04 M solution of 0.25 equiv  $P_4$  containing 3 equiv of **1** in benzene results in immediate formation of a bright orange solution containing  $BrTi(N[{}^tBu]Ar)_3$  (**Br-1**),  $PPh_3$  (**Ph-2**, 71% of the P-containing product), and  $P_2Ph_4$  (**Ph-3**, 29% of the P-containing product, Table 1).  $P_2Ph_4$  is one of the four possible stable intermediates en route to complete  $P_4$  degradation by  $P_4$  to give  $PPh_3$  and is present in this stoichiometric treatment because the trapping of the highly reactive phenyl radicals is not completely efficient in this system.<sup>11</sup> In order to convert the full equivalent of  $P_4$  to  $PPh_3$ , 5 equiv of PhBr and  $Ti(N[{}^tBu]Ar)_3$  are used, giving 95% conversion and an isolated yield of 72% (Table 1). We could also selectively target  $P_2Ph_4$  by treatment of 0.25 equiv of 0.04 M  $P_4$  in benzene with 2 equiv of **1** followed by 2 equiv of PhBr, which gives  $P_2Ph_4$  in 80% yield with small amounts of  $PPh_3$  and  $P_4Ph_4$  being observed as well. Evidence for the intermediacy of  $P_2Ph_4$  along the reaction pathway was provided by the use of  $P_2Ph_4$  itself as a starting material for  $PPh_3$  synthesis.<sup>10</sup> It was found that PhI can be used in place of PhBr with similar results, however PhCl does not lead to any  $PPh_3$  or  $P_2Ph_4$  formation as  $Ti(N[{}^tBu]Ar)_3$  reacts very slowly with PhCl under these conditions.<sup>5</sup>

This synthesis of phosphines from  $P_4$  and a burst of radicals was found not to be

Table 1: Synthesis of  $\text{PR}_3$  from  $n(\text{RX} + \text{Ti}(\text{N}[\text{tBu}]\text{Ar})_3)$  and  $0.25 \text{ P}_4$  in benzene solvent at  $20^\circ\text{C}$ .

Entry	$n^a$	R	X	$\delta \text{ PR}_3^b$	% yield <sup>c</sup>
1	3	Ph	Br	−4.9	71
2	3.75	Ph	Br	−4.9	82
3	5	Ph	Br	−4.9	95
4	3	Ph	I	−4.9	65
5	3	Ph	Cl	n/a	0
6	3	$\text{Ph}_3\text{Sn}$	Cl	−325 <sup>d</sup>	96
7	3	$\text{Me}_3\text{Si}$	I	−252	97
8	3	Cy	Br	10.5	64
9	3.75	Cy	Br	10.5	77
10	5	Cy	Br	10.5	95

<sup>a</sup> Number of equivalents per phosphorus atom.

<sup>b</sup>  $^{31}\text{P}$  NMR chemical shift for the  $\text{PR}_3$  product referenced to external 85%  $\text{H}_3\text{PO}_4$ .

<sup>c</sup> Phosphorus-based yield of  $\text{PR}_3$  as determined by  $^{31}\text{P}$  NMR spectroscopy *via* integration with respect to an internal standard using a single-pulse experiment.

<sup>d</sup>  $^1J_{^{119}\text{Sn}-\text{P}} = 442 \text{ Hz}$ ,  $^1J_{^{117}\text{Sn}-\text{P}} = 425 \text{ Hz}$ .

limited to aryl substituents. Treatment of a 0.04 M solution of 0.25 equiv  $P_4$  with 5 equiv of **1** and 5 equiv of CyBr results in formation of  $PCy_3$  (Cy-**2**) as the exclusive P-containing product (Table 1). The use of less than 5 equiv of CyBr resulted in mixtures of  $P_2Cy_4$  (Cy-**3**) and Cy-**2**, much like what was seen for PhBr. When the radicals produced were longer lived, it was possible to obtain stoichiometric conversion of  $P_4$  to the trisubstituted phosphine. For instance, treatment of a 0.04 M solution of 0.25 equiv  $P_4$  with 3 equiv of **1** and 3 equiv of  $Me_3SiI$  or  $Ph_3SnCl$  results in clean and quantitative formation of the known phosphines  $P(SiMe_3)_3$  or  $P(SnPh_3)_3$ , respectively, as the sole products (Table 1, Figure 1).<sup>12,13</sup> The  $P(SiMe_3)_3$  produced here is easily separated from the reaction coproducts by vacuum transfer from the crude reaction mixture in 86% yield, while the highly crystalline  $P(SnPh_3)_3$  can be isolated in 75% yield.

The ability of  $P_4$  to act as a radical trap in combination with the work of Sato and coworkers on the radical phosphination of aryl halides suggests that P–P bonds, generally, may be competent radical traps.<sup>3</sup> This was found to be the case using our radical method, opening up the potential for the synthesis of asymmetric phosphines. Treatment of 0.5 equiv of  $P_2Ph_4$  with 1 equiv of PhBr, MesBr, CyBr, or  $Ph_3SnCl$  and 1 equiv of **1** quantitatively produced 1 equiv of Ph-**2** ( $\delta$  4.9 ppm),  $P(Ph_2)Mes$  (Mes-**4**,  $\delta$  16.0 ppm),<sup>14</sup>  $P(Ph_2)Cy$  (Cy-**4**,  $\delta$  3.4 ppm),<sup>15</sup> or  $P(Ph_2)SnPh_3$  (Ph<sub>3</sub>Sn-**4**,  $\delta$  56.2 ppm,  $^1J_{119Sn-P} = 715$  Hz,  $^1J_{117Sn-P} = 682$  Hz),<sup>16</sup> respectively (Figure 1).<sup>10</sup> This striking attribute of P–P single bond chemistry has great potential for further synthetic development.

Based on our hypothesis that the radical-degradation of the  $P_4$  tetrahedron occurs in a stepwise manner, we thought that it might be possible to target intermediate structures by tuning the steric properties of the RX substrate. It was found that treatment of 0.25 equiv of 0.04 M  $P_4$  in benzene with 1.5 equiv **1**, followed by 1.5 equiv of MesBr gives  $P_3Mes_3$ , **5**, as the major product and small amounts of  $P_2Mes_4$  (Mes-**3**).<sup>17–19</sup>  $P_3Mes_3$  could be isolated from the reaction mixture in 61% yield. Increasing the steric pressure further, we found that treatment of 0.25 equiv of 0.04 M  $P_4$  with 1.5 equiv of **1** and 1.5 equiv of DmpI (Dmp = 2,6-Mes<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) gives cis,trans-Dmp $P_4$ Dmp, **6**, as the

exclusive product and isolated in 78% yield.<sup>10,20</sup> This latter reaction represents a facile approach for the synthesis of novel substituted tetraphosphabicyclobutane molecules directly from  $P_4$  in a single step. Many of the previously reported syntheses of stable tetraphosphabicyclobutanes involve coupling of two substituted diphosphanes,<sup>21</sup> or activation of  $P_4$  by some highly designed substrate.<sup>20,22–24</sup> Our synthesis is unique in that a large number of sterically hindered aryl or alkyl halides could be employed in a general synthesis.

In terms of recycling the titanium byproducts from these syntheses, it is worth noting that  $X-1$  ( $X = I, Br, Cl$ ) are cleanly reduced back to  $Ti(N[{}^tBu]Ar)_3$  by reduction with Na/Hg amalgam.<sup>25,26</sup> This ability to easily recycle the titanium-byproducts generates a closed cycle for the synthesis of trisubstituted phosphines from  $P_4$ . One might begin to contemplate a catalytic cycle using this system, however, the reduction of  $XTi(N[{}^tBu]Ar)_3$  is slow and  $P_4$  is itself susceptible to reduction to  $Na_3P$  by Na/Hg amalgam under such conditions. As such, other halogen atom abstractors are currently being screened as potential entry points into the catalytic generation of trisubstituted phosphines from  $P_4$  by this radical trapping method.<sup>10</sup>

The present day synthesis of organophosphorus compounds is a multistep process in which  $P_4$  is first chlorinated to generate  $PCl_3$ .<sup>27</sup>  $PCl_3$  is then functionalized via salt elimination reactions with appropriate Grignard or organolithium reagents, or with the organohalide and a harsh reducing agent.<sup>27</sup> For example, the industrial method for triphenylphosphine preparation is based on the high temperature reaction of chlorobenzene with phosphorus trichloride in the presence of molten sodium.<sup>28</sup> Manufacturers of organophosphorus compounds have recognized that the direct functionalization of white phosphorus is one of the major challenges in this field.<sup>28,29</sup> New studies are needed to work out alternative direct routes to organophosphorus compounds avoiding chlorination of white phosphorus. Strides have been made with regard to the electrosynthesis of trisubstituted phosphines directly from  $P_4$ ,<sup>30</sup> but facile solution methods are lacking. It is our hope that this work will inspire a renewed interest in the use of  $P-P$  bonds as efficient radical traps and will eventually lead to a robust catalytic system for the synthesis of organophosphorus compounds directly from white phosphorus.



Meanwhile, the syntheses reported herein represent novel methodologies for the direct functionalization of  $P_4$  and will themselves be the subject of further investigation.

## Experimental

### Representative protocol for reaction between $Ti(N[{}^tBu]Ar)_3$ , RX (RX = PhBr, MesBr, DmpI, CyBr, $Me_3SiI$ , and $Ph_3SnCl$ ), and $P_4$ : Synthesis of $PPh_3$

$Ti(N[{}^tBu]Ar)_3$  (279 mg, 0.484 mmol) was added to a 0.04 M solution of  $P_4$  in benzene (5 mg total  $P_4$ , 0.040 mmol).  $BrC_6H_5$  (76 mg, 0.484 mmol) was then added to the reaction mixture at room temperature by microliter syringe. Over the course of a minute, the originally green reaction mixture took on a bright orange color. The reaction mixture was analyzed by  $^1H$ ,  $^{13}C$ , and  $^{31}P$  NMR spectroscopies. Using  $OPPh_3$  (26 ppm) as an internal standard, a single pulse  $^{31}P$  NMR experiment showed 71% conversion to  $PPh_3$  (s,  $-4.9$  ppm) with the balance made up by  $P_2Ph_4$  ( $-14$  ppm). GC-MS analysis confirmed that assignment. A solvent screening (benzene, toluene, THF,  $Et_2O$ , *n*-hexane) and concentration screening (0.01 M  $P_4$ , 0.02 M  $P_4$ , 0.03 M  $P_4$ , 0.04 M  $P_4$ , and 0.05 M  $P_4$ ) indicated these conditions as optimal for conversion of 0.25 equiv  $P_4$  to 1 equiv  $PPh_3$  using 3 equiv  $Ti(N[{}^tBu]Ar)_3$  and 3 equiv PhBr.

In order to convert all of the  $P_4$  to  $PPh_3$ , the reaction was repeated using a 0.04 M solution of  $P_4$  (5 mg total  $P_4$ , 0.040 mmol, 0.25 equiv), 5 equiv (465 mg, 0.807 mmol) of  $Ti(N[{}^tBu]Ar)_3$  and 5 equiv (126 mg, 0.807 mmol) of  $BrC_6H_5$ . Again, over the course of a minute, the originally green reaction mixture took on a bright orange color. The reaction mixture was analyzed by  $^1H$ ,  $^{13}C$ , and  $^{31}P$  NMR spectroscopies. Using  $OPPh_3$  (26 ppm) as an internal standard, a single pulse  $^{31}P$  NMR experiment showed 98% conversion to  $PPh_3$  (s,  $-4.9$  ppm). GC-MS analysis confirmed that assignment. A screening of reaction stoichiometry showed 5 equiv of  $Ti(N[{}^tBu]Ar)_3$  and 5 equiv  $BrC_6H_5$  was necessary for the complete conversion of  $P_4$  to  $PPh_3$ ; when fewer equivalents were used, small amounts of  $P_2Ph_4$  were still observed. When the optimized

conditions are scaled up 10-fold, PPh<sub>3</sub> was isolated by repeated crystallizations at −35 °C in Et<sub>2</sub>O in 72% yield (304 mg).

These optimized conditions of 0.04 M P<sub>4</sub> (0.25 equiv), benzene, and 5 equiv of RX/Ti(N[<sup>t</sup>Bu]Ar)<sub>3</sub> are effective for both PPh<sub>3</sub> and PCy<sub>3</sub> syntheses. For P(SiMe<sub>3</sub>)<sub>3</sub> and P(SnPh<sub>3</sub>)<sub>3</sub> the same conditions are used but with only 3 equiv (stoichiometric) RX/Ti(N[<sup>t</sup>Bu]Ar)<sub>3</sub>. Starting with 50 mg of P<sub>4</sub>, P(SiMe<sub>3</sub>)<sub>3</sub> was isolated by vacuum transfer in 86% yield (348 mg) and P(SnPh<sub>3</sub>)<sub>3</sub> was isolated in 75% yield (1.30 g) by repeated recrystallization from Et<sub>2</sub>O. For the synthesis of P<sub>3</sub>Mes<sub>3</sub> and *cis,trans*-DmpP<sub>4</sub>Dmp, the same conditions are used but with only 1.5 equiv of RX/Ti(N[<sup>t</sup>Bu]Ar)<sub>3</sub>. P<sub>3</sub>Mes<sub>3</sub> was isolated by repeated crystallization from Et<sub>2</sub>O in 61% yield starting with 50 mg of P<sub>4</sub>. *cis,trans*-DmpP<sub>4</sub>Dmp was isolated by repeated crystallization from Et<sub>2</sub>O in 78% yield starting with 50 mg of P<sub>4</sub>.

In order to use P<sub>2</sub>Ph<sub>4</sub> as the starting material for PPh<sub>3</sub> synthesis, the same reaction protocol and conditions can be used. Treatment of a 0.04 M solution of P<sub>2</sub>Ph<sub>4</sub> (5 mg, 0.014 mmol, 0.5 equiv) with Ti(N[<sup>t</sup>Bu]Ar)<sub>3</sub> (93 mg, 0.16 mmol, 1 equiv) followed by BrPh (60 mg, 0.16 mmol, 1 equiv) resulted in a rapid color change from green to orange upon stirring. The reaction mixture was analyzed by <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectroscopies. Using OPPh<sub>3</sub> (26 ppm) as an internal standard, a single pulse <sup>31</sup>P NMR experiment showed 97% conversion to PPh<sub>3</sub> (s, −4.9 ppm). Similar results were found when 0.5 equiv P<sub>2</sub>Ph<sub>4</sub> was treated with 1 equiv of MesBr, CyBr, or Ph<sub>3</sub>SnCl, which produced 1 equiv of P(Ph<sub>2</sub>)Mes (−16.0 ppm), P(Ph<sub>2</sub>)Cy (−3.4 ppm), or P(Ph<sub>2</sub>)SnPh<sub>3</sub> (−56.2 ppm, <sup>1</sup>J<sub>119Sn-P</sub> = 715 Hz, <sup>1</sup>J<sub>117Sn-P</sub> = 682 Hz), respectively, each in greater than 95% yield.

Please see the Supporting Information accompanying this manuscript for additional synthetic and characterization details.

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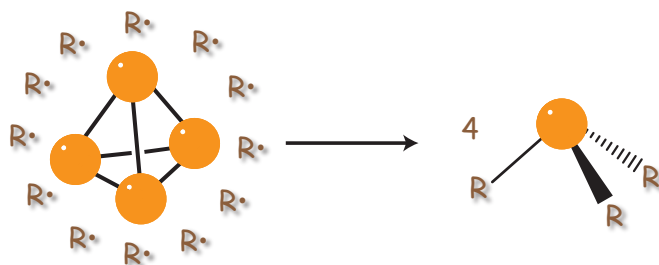
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A reaction scheme has been developed that accomplishes direct radical functionalization of white phosphorus without the intermediacy of  $\text{PCl}_3$ .