A Mild One-Pot Reduction of Phosphine(V) Oxides Affording Phosphines(III) and Their Metal Catalysts

Łukasz Kapuściński, Philipp N. Plessow, Damian Trzybiński, Krzysztof Woźniak, Peter Hofmann, and Phillip Iain Jolly*

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ABSTRACT: The metal-free reduction of a range of phosphine(V) oxides employing oxalyl chloride as an activating agent and hexachlorodisilane as reducing reagent has been achieved under mild reaction conditions. The method was successfully applied to the reduction of industrial waste byproduct tripheynylphosphine(V) oxide, closing the phosphorus cycle to cleanly regenerate triphenylphosphine(III). Mechanistic studies and quantum chemical calculations support the attack of the dissociated chloride anion of intermediated phosphonium salt at the silicon of the disilane as the rate-limiting step for deprotection. The exquisite purity of the resultant phosphine(III) ligands after the simple removal of volatiles under reduced pressure circumvents laborious purification prior to metalation and has permitted the facile formation of important transition metal catalysts.

INTRODUCTION

Applications of Phosphine(III) Ligands and Synthesis. Phosphines and their derivatives are of significant importance to both academic and industrial chemistry. In particular, within organic chemistry phosphine(III) compounds have a distinguished history, mediating classical transformations such as the Appel,1 Mitsunobu,2 and Wittig3,4 reactions. Additionally, the ready modulation of electronic and steric properties of phosphine(III) has made them excellent ligands for the formation of well-defined transition metal complexes,5 although recalcitrant phosphine(V) oxides arise, when phosphine(III) compounds are employed as labile ligands6 or the metal complexes are simply decomposed, in the presence of a suitable oxidant.7 Arguably, the stoichiometric formation of phosphine(V) oxide waste from the above-named organic reactions presents an even greater issue, especially on the industrial scale,3,4 as the conversion of P(V)O to the P(III) oxidation state is nontrivial (vide infra).

Direct Reduction of Phosphine(V) Oxide. Given the significance of phosphine(III) compounds, a variety of anaerobic syntheses have been reported.8,9 However, the sensitivity of phosphine(III) to oxidation (requiring only minutes to hours) has led to the widespread use of “protected” phosphines,10 such as phosphine−borane adducts11,12 and phosphine(V) sulfoxides13,14 but predominantly phosphine(V) oxides.15−17 These precursors tolerate the reaction conditions necessary to construct more complex architectures18 although the protection must be removed in the penultimate12,19 or final10,12 step of the ligand synthesis. Thus, much attention has been focused on the conversion of P(V)=O to P(III)15,16 (Scheme 1a), including the use of silanes and siloxanes such as HSiCl3,22−25 HSiCl3/Ph3P,26 SiCl4,24,27 SiMe4, with CsF/

Scheme 1. Phosphine Synthesis: Background and This Work

TBAP,28 HSi(OEt)3/Ti(O-i-Pr)4,29 PhSiH3,30−32 1,1,3,3-tetramethylsiloxide (TMDS) with CuX2,33 polymethyl-hydroxiloxane (PMHS),34,35 1,3-diphenylsiloxane

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hydrides such as LiAlH4,38,39 LiAlH4/CeCl3,40 AlH3,41 and
be catalyzed by frustrated Lewis pairs (FLPs).71,72 Harsh metal
aluminum67,68 or silicon,69 and hydrogenolysis,70 which may
accompanied by the decomposition of the precious azolinium
cation/activated carbon;45 and electrochemical reduction.46
A mild iodine-catalyzed reduction of phosphine(V) oxides
published, converting triphenylphosphine(V) oxide (Ph3PO)
following year a sequential activation and deprotection was
accomplished by the challenges in the reduction of
inexpensive chlorinating reagents,59 CPSs have
disilanes (Table 1, entries 2–6) and hexachlorodisilane might serve as a suitable surrogate for
elemental silicon and similarly generate 2 equiv of SiCl4 on
reactions with a CPS. The abundant industrial byproduct
Ph3PO (1) appeared to be the ideal test substrate,3,4 and was
easily converted to activated Ph3PCl2 (2) with inexpensive
oxalyl chloride.59 Gratifyingly on reaction with 1.1 equiv of
hexachlorodisilane (Si2Cl6) at room temperature, both 1H
NMR and 31P NMR indicated the immediate, clean, and
complete formation of Ph3P(OC6H4Me2)3 (3) with inexpensive
chlorinating reagents,59 CPSs have
This work was supported by the National Science Foundation,
BASF, and the University of Wisconsin–Madison.

Table 1. Reaction of Phosphonium Salts with Disilanes

<table>
<thead>
<tr>
<th>Entry</th>
<th>CPS  2a–c</th>
<th>X =</th>
<th>Disilane</th>
<th>Equiv</th>
<th>Time</th>
<th>Conv to 3 [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cl</td>
<td>SiCl4</td>
<td>1.1</td>
<td>5 min</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Cl</td>
<td>SiMe2Cl4</td>
<td>1.1</td>
<td>5 min</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Cl</td>
<td>SiMe2Cl4</td>
<td>1.1</td>
<td>1 day</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Cl</td>
<td>SiMe2Cl4</td>
<td>1.1</td>
<td>2 days</td>
<td>55</td>
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<td>Cl</td>
<td>SiMe2Cl4</td>
<td>1.1</td>
<td>3 days</td>
<td>72</td>
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</tr>
<tr>
<td>6</td>
<td>Cl</td>
<td>SiMe2Cl4</td>
<td>1.1</td>
<td>4 days</td>
<td>78</td>
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<td>1.1</td>
<td>5 days</td>
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<td>Cl</td>
<td>SiMe2Cl4</td>
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<td>6 days</td>
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<tr>
<td>11</td>
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<td>1.1</td>
<td>10 min</td>
<td>7</td>
<td></td>
</tr>
<tr>
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<td>OTf</td>
<td>SiCl4</td>
<td>1.1</td>
<td>1 day</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>OTf</td>
<td>SiCl4</td>
<td>1.1</td>
<td>2 days</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>BaCl2</td>
<td>SiCl4</td>
<td>1.1</td>
<td>2 days</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

Conversion judged by 31P NMR of 2a–c relative to 3.

A mild iodine-catalyzed reduction of phosphine(V) oxides
published, converting triphenylphosphine(V) oxide (Ph3PO)
following year a sequential activation and deprotection was
accomplished by the challenges in the reduction of
inexpensive chlorinating reagents,59 CPSs have
trichloromethylsilane (MeSiCl$_3$), trimethylsilyl chloride (Me$_3$SiCl), or triphenylsilyl chloride (Ph$_3$SiCl). However, the more electron-rich and sterically hindered disilanes generated the desired phosphines in either lower yield, over extended reaction times or not at all. For instance, the addition of a single electron-donating methyl group to each of the silicon atoms in Si$_5$Me$_5$Cl$_4$ drastically decreased the rate of reaction, with only a 28% conversion to 3 after 24 h, eventually reaching completion after 144 h. In contrast, the reaction with Si$_5$Cl$_6$ was complete in under 5 min.$^6$ No reaction was observed for even more electron-rich and sterically shielded Si$_5$PH$_5$ or Si$_5$Me$_6$.

**Scope of the New Procedure.** With Si$_5$Cl$_6$ proving to be the reductant of choice, we expanded the application of the procedure to other phosphine(III) compounds.$^6$ Aliphatic tricyclohexylphosphine (7) was afforded in 97% yield, in contrast to the recently reported hydrogenation at 130 °C, which notably afforded none of the desired phosphine(III) complexes.$^7$ Cyclic alkene 2-phosphoxene oxide was also converted to P(III) 2-phospholene (8)$^{77}$ (98%) without the reduction or isomerization of the C=C bond. Reduction of phosphinamides without the P–N bond scission is particularly challenging,$^51$–$54$ while Gilheany et al. synthesized “protected” aminophosphinoborane adducts from CPSs in excellent yields,$^75$ we were able to furnish the free aminophosphine 9 directly (89%). The dimethylamino group in DavePhos 11 (93%) was also tolerated well, with fellow Buchwald ligand CyJohnPhos 10 being cleanly afforded in 95% yield. Chiral phosphines$^8$ are still of great significance, and we chose to explore binaphthyl systems as the CPSs of P-chirogenic phosphines are known to racemize.$^85$ The oxides of chiral phosphines permit structure elaboration,$^{46}$ and our new method rapidly afforded (S)-Ph-BINEPINE (12)$^{77}$ (96% yield). (R)-MeO-MOP (13)$^{86}$ was also readily synthesized (99%). It is of note that the direct reaction of MeO–MOP oxide with Si$_5$Cl$_6$ in acetonitrile led exclusively to scission of the C–O bond without reduction of P(V)O$_3$, highlighting the divergence in the reactivity of the activated P(V)O$_3$ compared to recalcitrant P(V)O. Moreover, we observed no racemization in the case of either 12 or 13.

Having established the optimal conditions for the generation of a range of phosphine(III) compounds, we turned our attention back to azolium 5. The reaction of 4 with excess oxalyl chloride yielded a new chlorophosphonium bearing azolium salt 15 (after removal of 4-toluenesulfonyl chloride produced by chlorination of the 4-toluenesulfonate; see the Supporting Information) which was readily transformed to the desired azolium 5 with hexachlorodisilane (1.5 equiv). The identity of both salts 5 and 15 was established by single-crystal X-ray diffraction analysis. Crystals suitable for this purpose were obtained by layering methylene chloride with hexane and storing at −30 °C. The salts crystallize in the monoclinic P2$_1$/c (CPS 15) and P2$_1$/n (azolium 5) space group, respectively. Graphical representation of molecular structure of both compounds is shown in Figure 1. The tetravalent phosphorus atom effectively means each molecule of CPS 15 has two dissociated chloride counterions: one for each of the cationic phosphonium and the azolium constituent parts. Interestingly, the asymmetric unit of the crystal lattice of 15 also contained a molecule of hydrochloride (Figure S2).$^7$ The additional chloride counterion has important implications for the deprotection of 15, which thus requires 1.5 equiv of hexachlorodisilane to fully convert the CPS to P(III) 5:

```
<table>
<thead>
<tr>
<th>Entry</th>
<th>Phosphine(V) Oxide</th>
<th>CPS</th>
<th>NMR [ppm]</th>
<th>Produ ct #</th>
<th>Phosphine net(III)</th>
<th>Yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>P$_2$O$_5$</td>
<td>60.2</td>
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<td></td>
<td>99</td>
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<tr>
<td>2</td>
<td>P$_2$O$_5$</td>
<td>107.1</td>
<td>7</td>
<td>P$_2$O$_5$</td>
<td></td>
<td>97</td>
</tr>
<tr>
<td>3</td>
<td>P$_2$O$_5$</td>
<td>99.9</td>
<td>8</td>
<td>P$_2$O$_5$</td>
<td></td>
<td>98</td>
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<td>4</td>
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<td>68.3</td>
<td>9</td>
<td>P$_2$O$_5$</td>
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<td>89</td>
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<tr>
<td>5</td>
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<td>99.1</td>
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<td>CyP$_5$</td>
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<td>95</td>
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<td>6</td>
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<td>CyP$_5$</td>
<td></td>
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<td>P$_2$O$_5$</td>
<td>86.9</td>
<td>12</td>
<td>P$_2$O$_5$</td>
<td></td>
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<td>9(x)</td>
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<td>P$_2$O$_5$</td>
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<td>10(x)</td>
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<td>14</td>
<td>P$_2$O$_5$</td>
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<td>92</td>
</tr>
</tbody>
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```

*The azolium salts were reacted with 5.0 equiv (COCl)$_2$. The resultant CPS was separated from TsCl and then reacted with 1.5–1.6 equiv of Si$_5$Cl$_6$.

Table 2. Conversion of Phosphine(V) Oxides to Phosphine(III) Ligands via CPS Intermediates

presumably, the extra Cl$^-$ counterion of the imidazolium moiety also reacts with Si$_5$Cl$_6$ (*vide infra*). Finally, mesityl-substituted 5 could be facilely synthesized in an excellent 94% yield, without implementing harsh reaction conditions. In addition, we further demonstrated the usefulness of the new procedure at generating phosphine-bearing azolium salts with the synthesis of the 2,6-diisopropylphenyl analogue 14, in a comparable 92% yield. More details concerning the crystal structure of CPS 15 and azolium 5 can be found in the Supporting Information (Figures S58–S66).

**Experimental and Computational Mechanism Studies.** CPSs in methylene chloride form a cationic phosphonium with a noncoordinated anionic chloride counteranion,$^{69$–$93}$ while it has been demonstrated that Cl$^-$ (*e.g.*, from ammonium...
Figure 1. Graphical representation of molecular structure, where (a) CPS 15 and (B) azolium 5. Displacement ellipsoids are drawn at the 50% probability level. The H atoms, the HCl molecule (CPS 15), and the ionic pair “B” (azolium 5) were omitted for clarity.

Scheme 3. Reaction Mechanism of Si2Cl6 with Dissociated Chloride Anions

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known formation of anion [SiCl3]− from Si3Cl6. bStepwise reaction mechanism (bottom left). cConcerted mechanism (bottom right).
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salts) leads to scission of the Si–Si bond in Si3Cl6 (Scheme 3).94-99 This lead us to surmise that the reaction is initiated by the attack of chloride anion at silicon of Si3Cl6 generating an equivalent tetrachlorosilane (SiCl4) and a reactive transient trichlorosilanide anion [SiCl3]− which then abstracts the remaining phosphorus bound chloride from intermediated 17 to generate the second and final equivalent of SiCl4.

To explore this mechanistic proposal, chlorotriphenyl-phosphonium trflate (Ph3PClOTf) 2b was synthesized.100 The trflate anion is a superb nucleofuge, being a far more stable leaving group than chloride,101 therefore, the dissociated trflate ion ([OTf]−) of 2b would be expected to react much slower with hexachlorodisilane than Cl− of 2a. Indeed, after reaction for 10 min, 31P NMR indicated 3b had generated only 7% Ph3P6, progressing to 80% and 100% after 24 and 48 h, respectively (Table 1, entries 11–13; Figure 2), significantly slower than the dichloride analogue 2a which appears to react instantly. As with 2a,29Si NMR analysis of the reaction mixture of monotrflate 2b with Si3Cl6 showed the generated of SiCl4 (singlet at δ = –18.8 ppm) but in addition a singlet at δ = –38.2 ppm. 13C NMR spectra showed a quartet at δ = 118 ppm (J = 320 Hz) and 19F NMR a singlet at δ = –75.6 ppm; these signals are tentatively attributed to trichlorrosilanyl trflate, SiCl4OTf (see the Supporting Information). Finally, CPS 2c bearing the non-nucleophilic tetrakis(3,5-dichlorophenyl)-borate anion, [BAR]+−, was mixed with Si3Cl6 in methylene chloride. As anticipated, no triphenylphosphate 3 was formed, even with an excess of Si3Cl6 demonstrating that the reaction is initiated by the attack of a dissociated anion at silicon.

To gain further insight, quantum-chemical calculations employing the TURBOMOLE program were performed to study the thermodynamics and kinetics of the reaction. By use of the harmonic oscillator and rigid rotator approximation with a reference pressure of 1 bar, Gibbs free energies are given at the PBE0-D3/def2-TZVPP//PBE-D3/dhf-SV(P) level of theory.102-109 Our calculations show that the disproportionation of CPS into free phosphine with liberation of chlorine is uphill in free energy by 94 kJ/mol; similarly, formation of (unstabilized) SiCl4 by disproportionation of Si3Cl6 is also expected to be very unfavorable, ∆G = 107 kJ/mol. However, the formation of the free phosphine with Si3Cl6 releasing two SiCl4 molecules is thermodynamically favorable, ∆G = −246 kJ/mol (Scheme 3b,c).

A Telescopied Synthesis of Metal Complexes from Their Corresponding Phosphine(V) Oxides. With the new method of generating phosphine(III) ligands with high yield and purity in hand, we attempted to telescope110 the procedure for the synthesis of organometallic catalysts. As such, after deprotection and removal of SiCl4 by evaporation, “intermediate” phosphine(III) compounds were filtered through Celite and then reacted with a suitable metal precursor to yield a selection of prominent phosphine-bearing catalysts. The resultant monodentate triphenylphosphine, tricyclohexyl-phosphine, and CyJohnPhos were reacted with the dichloro-(p-cymene) ruthenium(II) dimer, Umicore M31, and (η3-allyl)palladium(II) dichlorido to afford the versatile dichloro-(p-cymene)(triphosphine) ruthenium(II) catalyst, 18,11 olefin metathesis catalyst Umicore M2 (Grubbs catalyst M202), 19,112 and the palladium Buchwald complex, CyJohnPhos(η3-allyl)PdCl, 20,113 respectively, in excellent yields (91–98%). Moreover, the oxides of multidentate ligands where similarly reduced and successfully metalated, thus affording bidentate nickel 2114 and tetradeinate palladium complexes 2215 in good yields of 83% and 86%, respectively.
Table 3. Conversion of Phosphine(V) Oxides to Their Corresponding Phosphine(III) Ligands and Metal Complexes

<table>
<thead>
<tr>
<th>Entry</th>
<th>Phosphine (V) Oxide</th>
<th>Metal Precursor</th>
<th>Product #</th>
<th>Complex</th>
<th>Yield [%]</th>
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<tr>
<td>1</td>
<td>Ph₃PⱾ</td>
<td>CH₃Si₂Cl₆</td>
<td>18</td>
<td>(\text{CH₃Si₂P₃} )</td>
<td>98</td>
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<tr>
<td>2</td>
<td>Ph₃PⱾ</td>
<td>CH₃Si₂Cl₆</td>
<td>19</td>
<td>(\text{CH₃Si₂P₃} )</td>
<td>96</td>
</tr>
<tr>
<td>3</td>
<td>Ph₃PⱾ</td>
<td>CH₃Si₂Cl₆</td>
<td>20</td>
<td>(\text{CH₃Si₂P₃} )</td>
<td>91</td>
</tr>
<tr>
<td>4(c)</td>
<td>Ph₃PⱾ</td>
<td>CH₃Si₂Cl₆</td>
<td>21</td>
<td>(\text{CH₃Si₂P₃} )</td>
<td>83</td>
</tr>
<tr>
<td>5(c)</td>
<td>Ph₃PⱾ</td>
<td>CH₃Si₂Cl₆</td>
<td>22</td>
<td>(\text{CH₃Si₂P₃} )</td>
<td>86</td>
</tr>
</tbody>
</table>

*a Activated with 3.0 equiv of (COCl)₂, deprotected with 2.1 equiv of Si₂Cl₆. *b Activated with 6.0 equiv of (COCl)₂, deprotected with 4.1 equiv of Si₂Cl₆.

**CONCLUSIONS**

We have developed a simple mild one-pot activation/deprotection procedure in which phosphine(V) oxides are converted to their corresponding phosphine(III) ligands cleanly and efficiently at ambient temperature without the use of metals or the need for silica gel chromatography. The reduction of activated CPS 2 was investigated with a range of disilanes, and Si₂Cl₆ was demonstrated to be the best reductant. A reaction mechanism for the transformation has been elucidated through experimentation and supported by computation calculations, with the reduction being initiated by attack of the CPS’s dissociated chloride anion at the silicon of hexachlorodisilane. The new method was successfully applied to a range of aryl and alkyl phosphines, including state-of-the-art ligands, and found to be compatible with alkene, ether, and amine function groups. Challenging phosphine-bearing azo-lium salts were readily furnished. Furthermore, the high purity of resultant phosphine(III) compounds allowed the procedure to be telescoped for the formation of some prominent transition metal catalysts. We believe this research will facilitate the synthesis of both known and novel new phosphine(III) ligands as well as their corresponding complexes, while the catalytic use, reuse, or recycling of valuable phosphine(III)-based reagents is of importance for sustainability and is likely to be of only greater significance as increased demands or restrictions are placed upon finite phosphorus resources.82−84

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00788.

Experimental procedures and characterization data (PDF)

**Accession Codes**

CCDC 2023530–2023531 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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**Notes**

The authors declare the following competing financial interest(s): A patent on this research has been applied for. The Polish patent application number is P.426256.

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We believe the deprotection occurs immediately, although 5 min had elapsed between addition of Si2Cl6 and acquisition of NMR data.

In the case of Ph3P−O 1, we were able perform a one-pot process without removal of excess oxalyl chloride in vacuo: as little as 1.01 equiv of oxalyl chloride was reacted with 1 in dry degassed methylene chloride before 1.04 equiv of Si2Cl6 was added to the intermediate CPS 2, thus completely converting 1 to Ph3P 3 in situ. However, for expediency we decided use 1.10 equiv of Si2Cl6 (see the Supporting Information for details). It should be noted that residual oxalyl chloride appears to react vigorously with hexachlorodisilane leading to discoloration of phosphine(III) and even undesired byproducts.

The molecule of HCl is likely to arise from oxalyl chloride.

**REFERENCES**


(50) Kuroboshi, M.; Yano, T.; Kameneou, S.; Kawakubo, H.; Tanaka, H. Electroc reduction of Tetra-Coordinate Phosphonium...


■ NOTE ADDED AFTER ASAP PUBLICATION

This paper was published ASAP on March 5, 2021, with a typographical error in the title of the paper. The corrected version was reposted on March 9, 2021.