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

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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 triphenylphosphine(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.
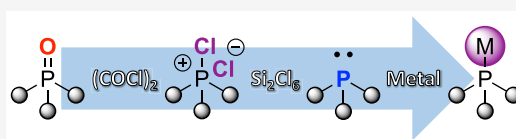
■ INTRODUCTION

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 Wittig[3,4] 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 ligands[6] 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 adducts[11,12] and phosphine(V) sulfides[13,14] but predominantly phosphine(V) oxides.[15−17] These precursors tolerate the reaction conditions necessary to construct more complex architectures[18] although the protection must be removed in the penultimate[12,19] or final[20,21] 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] Si₂Cl₆,[24,27] Si₂Me₆ with CsF/

Scheme 1. Phosphine Synthesis: Background and This Work[a]
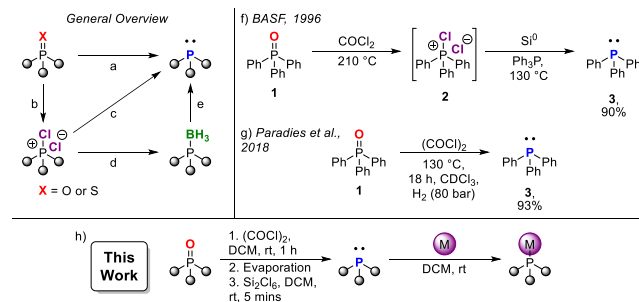
[a]Left: (a) direct reduction of P(V)=O or P(V)=S affording P(III); (b) conversion of P(V)=O or P(V)=S to activated phosphonium salt; (c) reduction of activated phosphonium salt to P(III); (d) conversion of activated phosphonium salt to phosphine−borane; (e) deprotection of phosphine−borane affording P(III). Right-top: (f) BASFs conversion of Ph₃PO to Ph₃P using phosgene and silicon. Right-bottom: (g) Paradies et al. recent conversion of Ph₃PO to Ph₃P using oxalyl chloride and pressurized hydrogen. Center-bottom: (h) this work.

TBAF,[28] HSi(OEt)₃/Ti(O-*i*-Pr)₄,[29] PhSiH₃,[30−32] 1,1,3,3-tetramethyldisiloxane (TMDS) with CuX₂,[33] polymethylhydrosiloxane (PMHS),[34,35] 1,3-diphenyldisiloxane
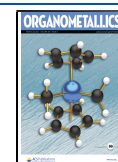
(DPDS),[36] and (EtO)$_2$MeSiH/(RO)$_2$P(O)OH;[37] aluminum hydrides such as LiAlH$_4$,[38,39] LiAlH$_4$/CeCl$_3$,[40] AlH$_3$,[41] and HAl(i-Bu)$_2$;[42] low-valent metals such as SmI$_2$/HMPA (hexamethylphosphoramide)[43] or Cp$_2$TiCl$_2$/Mg;[44] hydrocarbon/activated carbon;[45] and electrochemical reduction.[46−48] A mild iodine-catalyzed reduction of phosphine(V) oxides employing a sacrificial electron-rich phosphine was developed by Laven and Kullberg,[49] while Li et al.[50] employed less expensive phosphite, although in both cases P$^{(V)}$=O-containing contaminants must be removed from the final products. Thus, disadvantages of these procedures include harsh reaction conditions, toxic and/or highly reactive, potentially explosive reducing agents, narrow scope or undesirable side reactions, *e.g.*, C−P,[51,52] C−O,[52] or P−N[53−56] bond cleavage, and laborious column chromatography to purify the desired phosphine(III).

Reduction of Activated Chlorophosphonium Salts. The inherent stability of the P$^{(V)}$=O has compelled others to explore sequential activation reduction methods, *i.e.*, the conversion of the phosphine(V) oxide to more reactive chlorophosphonium salts (CPS) and subsequent reduction (Scheme 1b,c). Horner, Hoffmann, and Beck first published the reduction of chlorotriphenylphosphonium chloride (Ph$_3$PCl$_2$) in 1958,[57] with both LiAlH$_4$ and sodium. The following year a sequential activation and deprotection was published, converting triphenylphosphine(V) oxide (Ph$_3$PO) first to activated CPS, Ph$_3$PCl$_2$, before it was reduced to triphenylphosphine (Ph$_3$P) with sodium metal.[58] Being readily afforded *via* inexpensive chlorinating reagents,[59] CPSs have also been reduced with aluminum/metal salts,[60] alkali metals,[57,58] LiAlH$_4$,[57,61,62] thiols/Et$_3$N,[63] activated carbon,[45] Hantzsch ester/Et$_3$N,[64] electrochemically,[46−48,65,66] elemental aluminum[67,68] or silicon,[69] and hydrogenolysis,[70] which may be catalyzed by frustrated Lewis pairs (FLPs).[71,72] Harsh metal bases and Grignard reagents have even been used to deprotect certain CPSs.[73] Alternatively, CPS can be converted to phosphine−boranes by either NaBH$_4$[74,75] or LiBH$_4$,[76−79] although ultimately the borane "protecting group" itself requires removal (Scheme 1b,d,e).

Motivation to Develop a New Facile Reduction of Phosphine(V) Oxides. Our interest in phosphine(V) oxides reduction originates from our desire to explore bulky *N*-phosphinomethyl-functionalized *N*-heterocyclic carbene ligands (NHCPs)[80,81] as potential ligands for new olefin metathesis catalyst (Scheme 2).[19] Progress has been severely

Scheme 2. Problematic Reduction of NHCP Precursor[a]
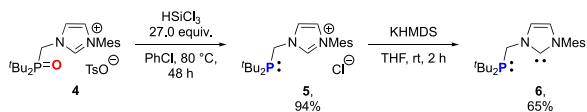
[a]Synthesis of NHCP **6** *via* the challenging reduction of phosphine(V) oxide in azolium salt **4** to phosphine(III) **5**.

hampered due to difficulties accessing azolium salt **5**, with the problematic reduction of **4** being achievable only with a large excess of trichlorosilane (27.0 equiv) in anhydrous degassed chlorobenzene at elevated temperature over 2 days.[19] As well as the lengthy reaction time, we experienced some reproducibility issues, with the unsuccessful reduction being accompanied by the decomposition of the precious azolinium **4**, previously obtained *via* a multistep synthesis.[19] In light of

this, a simple procedure for the conversion of **4** to **5** would be a great advantage. Such a process might also permit access to other challenging phosphine(III) and metal catalysts as well as permitting the recovery of the valuable phosphine(III) ligands: "closing the phosphorus cycle" is of increasing importance due to environmental and availability concerns.[82−84] Herein, we report a new activation/deprotection of phosphine(V) oxides without the use of harsh reaction conditions, metals, or sacrificial phosphanes. Intermediate CPSs are directly converted to desired phosphines by reaction with hexachlorodisilane. Mechanistic details have been elucidated by experimentation and supported by computation. The "one-pot" procedure affords excellent yields of pure phosphine(III) ligands that can be telescoped into formation of transition metal catalysts without the prior need for silica gel chromatography.

■ RESULTS AND DISCUSSION

Reduction of Activated CPSs with Disilane. In 1996, BASF reported the generation of tetrachlorosilane (SiCl$_4$) when the CPS, Ph$_3$PCl$_2$ (**2**), was heated with elemental silicon at 185 °C.[69] Not wanting to expose our ligand precursor to such harsh reaction conditions, we hypothesized that hexachlorodisilane might serve as a suitable surrogate for elemental silicon and similarly generate 2 equiv of SiCl$_4$ on reactions with a CPS. The abundant industrial byproduct Ph$_3$PO (**1**) appeared to be the ideal test substrate,[3,4] and was easily converted to activated Ph$_3$PCl$_2$ (**2**) with inexpensive oxalyl chloride.[59] Gratifyingly on reaction with 1.1 equiv of hexachlorodisilane (Si$_2$Cl$_6$) at room temperature, both ^{1}H NMR and ^{31}P NMR indicated the immediate, clean, and complete formation of Ph$_3$P (**3**), with ^{29}Si NMR showing only the formation of tetrachlorosilane, SiCl$_4$ (δ = −18.8 ppm). Motivated by the ability of Si$_2$Cl$_6$ to reduce **2**, we chose to explore other disilanes (Table 1, entries 2−10): 1,1,2,2-tetrachloro-1,2-dimethyldisilane (Si$_2$Me$_2$Cl$_4$), hexamethyldisilane (Si$_2$Me$_6$), and hexaphenyldisilane (Si$_2$Ph$_6$), which might generate the corresponding attractive byproducts

Table 1. Reaction of Phosphonium Salts with Disilanes

entry	CPS **2a−c**, X =	disilane	equiv	time	conv to **3** [%][a]
1	Cl	Si$_2$Cl$_6$	1.1	5 min	100
2	Cl	Si$_2$Me$_2$Cl$_4$	1.1	5 min	0
3	Cl	Si$_2$Me$_2$Cl$_4$	1.1	1 day	28
4	Cl	Si$_2$Me$_2$Cl$_4$	1.1	2 days	55
5	Cl	Si$_2$Me$_2$Cl$_4$	1.1	3 days	72
6	Cl	Si$_2$Me$_2$Cl$_4$	1.1	4 days	78
7	Cl	Si$_2$Me$_2$Cl$_4$	1.1	5 days	83
8	Cl	Si$_2$Me$_2$Cl$_4$	1.1	6 days	100
9	Cl	Si$_2$Me$_6$	1.0	1 day	0
10	Cl	Si$_2$Ph$_6$	1.0	1 day	0
11	OTf	Si$_2$Cl$_6$	1.1	10 min	7
12	OTf	Si$_2$Cl$_6$	1.1	1 day	80
13	OTf	Si$_2$Cl$_6$	1.1	2 days	100
14	BAr^{Cl}	Si$_2$Cl$_6$	4	2 days	0

[a]Conversion judged by ^{31}P NMR of **2a−c** relative to **3**.

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$_2$Me$_2$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$_2$Cl$_6$ was complete in under 5 min.[a] No reaction was observed for even more electron-rich and sterically shielded Si$_2$Ph$_6$ or Si$_2$Me$_6$.

Scope of the New Procedure. With Si$_2$Cl$_6$ proving to be the reductant of choice, we expanded the application of the procedure to other phosphine(III) compounds.[b] 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.[71] Cyclic alkene 2-phospholene 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;[53−56] while Gilheany et al. synthesized "protected" aminophosphine−borane 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 phosphepines permit structure elaboration,[86] and our new method rapidly afforded (*S*)-Ph-BINEPINE (**12**)[87] (96% yield). (*R*)-MeO-MOP (**13**)[88] was also readily synthesized (99%). It is of note that the direct reaction of MeO−MOP oxide with Si$_2$Cl$_6$ in acetonitrile led exclusively to scission of the C−O bond without reduction of P$^{(V)}$═O,[52] highlighting the divergence in the reactivity of the activated P$^{(V)}$Cl$_2$ 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 counteranions: 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).[c] 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 2. Conversion of Phosphine(V) Oxides to Phosphine(III) Ligands *via* CPS Intermediates

Entry	Phosphine(V) Oxide	CPS ^{31}P NMR [ppm]	Product #	Phosphine(III)	Yield [%]
1	PPh$_3$ (O)	60.2	**3**	PPh$_3$	99
2	PCy$_3$ (O)	107.1	**7**	PCy$_3$	97
3	(2-phospholene oxide, Me, Ph, P=O)	99.9	**8**	(2-phospholene, Me, Ph, P)	98
4	Ph$_2$P−N(^{i}Pr)$_2$ (O)	68.3	**9**	Ph$_2$P−N(^{i}Pr)$_2$	89
5	Cy$_2$P=O (biphenyl)	99.1	**10**	Cy$_2$P (biphenyl)	95
6	Cy$_2$P=O (biphenyl, Me$_2$N)	96.0	**11**	Cy$_2$P (biphenyl, Me$_2$N)	93
7	PhP=O (binaphthyl)	86.9	**12**	PPh (binaphthyl)	96
8	PPh$_2$ (binaphthyl, OMe, O)	66.4	**13**	PPh$_2$ (binaphthyl, OMe)	99
9[a]	^{t}Bu$_2$P=O (imidazolium, NMes, TsO$^-$)	108.7	**5**	^{t}Bu$_2$P: (imidazolium, NMes, Cl$^-$)	94
10[a]	^{t}Bu$_2$P=O (imidazolium, NDIPP, TsO$^-$)	108.5	**14**	^{t}Bu$_2$P: (imidazolium, NDIPP, Cl$^-$)	92

[a]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$_2$Cl$_6$.

presumably, the extra Cl$^-$ counterion of the imidazolium moiety also reacts with Si$_2$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,[89−93] while it has been demonstrated that Cl$^-$ (e.g., from ammonium
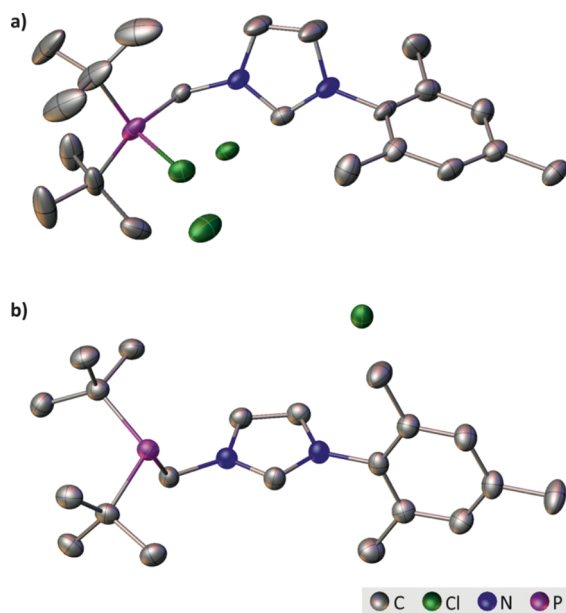
Figure 1. Graphical representation of molecular structure, where (a) CPS **15** and (B) azolium **5**. Displacement ellipsoids are drawn at the 50% probability level. The H atoms, the HCl molecule (CPS **15**), and the ionic pair "B" (azolium **5**) were omitted for clarity.

Scheme 3. Reaction Mechanism of Si₂Cl₆ with Dissociated Chloride Anions
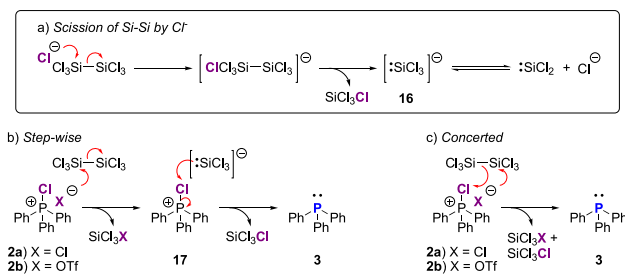
[a]Known formation of anion [:SiCl₃]⁻ from Si₂Cl₆. [b]Stepwise reaction mechanism (bottom left). [c]Concerted mechanism (bottom right).

salts) leads to scission of the Si—Si bond in Si₂Cl₆ (Scheme 3).[94−99] This lead us to surmise that the reaction is initiated by the attack of chloride anion at silicon of Si₂Cl₆ 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 triflate (Ph₃PClOTf) **2b** was synthesized.[100] The triflate anion is a superb nucleofuge, being a far more stable leaving group than chloride;[101] therefore, the dissociated triflate ion (TfO⁻) of **2b** would be expected to react much slower with hexachlorodisilane than Cl⁻ of **2a**. Indeed, after reaction for 10 min, ³¹P NMR indicated **5b** had generated only 7% Ph₃P **6**, 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 monotriflate **2b** with Si₂Cl₆ showed the generated of SiCl₄ (singlet at $\delta = -18.8$ ppm) but in addition a singlet at $\delta = -38.2$ ppm. ¹³C NMR spectra showed a quartet at $\delta = 118$
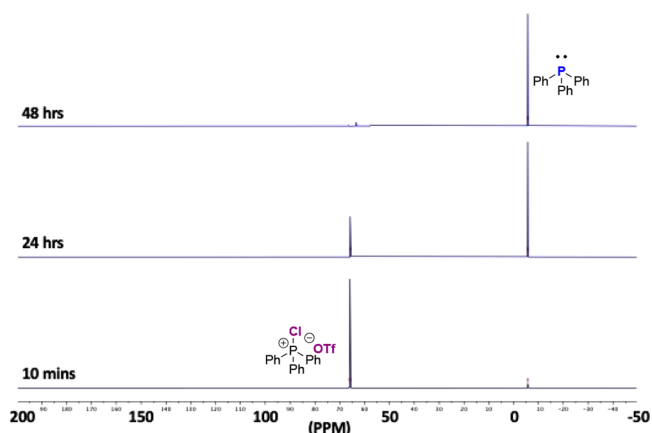
Figure 2. ³¹P NMR (CD₂Cl₂) of Ph₃PClOTf (**2b**) + Si₂Cl₆ → PPh₃ (**3**). Reaction times = 10 min (bottom), 24 h (center), and 48 h (top).

ppm ($J = 320$ Hz) and ¹⁹F NMR a singlet at $\delta = -75.6$ ppm; these signals are tentatively attributed to trichlorosilyl triflate, SiCl₃OTf (see the Supporting Information). Finally, CPS **2c** bearing the non-nucleophilic tetrakis(3,5-dichlorophenyl)-borate anion, [BAr^Cl]⁻, was mixed with Si₂Cl₆ in methylene chloride. As anticipated, no triphenylphosphine **3** was formed, even with an excess of Si₂Cl₆, 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):SiCl₂ by disproportionation of Si₂Cl₆ is also expected to be very unfavorable, $\Delta G = 107$ kJ/mol. However, the formation of the free phosphine with Si₂Cl₆ releasing two SiCl₄ molecules is thermodynamically favorable, $\Delta G = -246$ kJ/mol (Scheme 3b,c).

A Telescoped 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 telescope[110] 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 (η^3-allyl)palladium(II) dichloride to afford the versatile dichloro-(p-cymene)(triphenylphosphine)ruthenium(II) catalyst, **18**,[111] olefin metathesis catalyst Umicore M2 (Grubbs catalyst M202), **19**,[112] and the palladium Buchwald complex, CyJohnPhos(η^3-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 **21**[114] and tetradentate palladium complexes **22**[115] in good yields of 83% and 86%, respectively.

Table 3. Conversion of Phosphine(V) Oxides to Their Corresponding Phosphine(III) Ligands and Metal Complexes

Entry	Phosphine (V) Oxide	Metal Precursor	Product #	Complex	Yield [%]
1	$O=PPh_3$		**18**		98
2	$O=PCy_3$		**19**		96
3	$Cy_2P=O$		**20**		91
4[a]	Ph_2P—PPh_2 (dppe dioxide)		**21**		83
5[b]			**22**		86

[a]Activated with 3.0 equiv of $(COCl)_2$, deprotected with 2.1 equiv of Si_2Cl_6. [b]Activated with 6.0 equiv of $(COCl)_2$, deprotected with 4.1 equiv of Si_2Cl_6.

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 Si_2Cl_6 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 azolium 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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■ ADDITIONAL NOTES

[a]We believe the deprotection occurs immediately, although 5 min had elapsed between addition of Si_2Cl_6 and acquisition of NMR data.

[b]In the case of $Ph_3P{=}O$ **1**, we were able perform a one-pot process without removal of excess oxalyl chloride in vacou: as little as 1.01 equiv of oxalyl chloride was reacted with **1** in dry degassed methylene chloride before 1.04 equiv of Si_2Cl_6 was added to the intermediate CPS **2**, thus completely converting **1** to Ph_3P **3** in situ. However, for expediency we decided use 1.5 equiv of oxalyl chloride and then strip the excess chlorinating reagent and solvent in vacuo before the CPS salt was once again dissolved in dry methylene chloride and deprotected with 1.04–1.10 equiv of Si_2Cl_6 (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.

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

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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.