

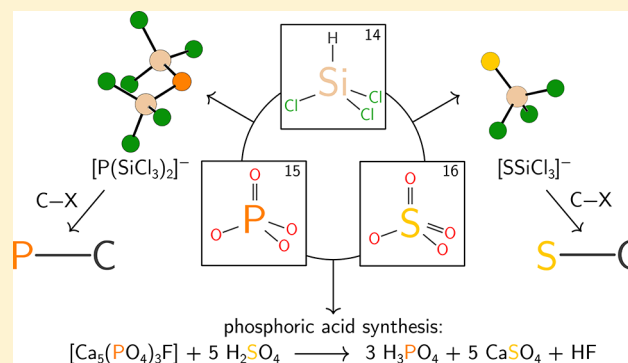
Orthophosphate and Sulfate Utilization for C–E (E = P, S) Bond Formation via Trichlorosilyl Phosphide and Sulfide Anions

Michael B. Geeson,^{1b} Pablo Ríos,^{1b} Wesley J. Transue,^{1b} and Christopher C. Cummins*^{1b}

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Supporting Information

ABSTRACT: Reduction of phosphoric acid (H_3PO_4) or tetra-*n*-butylammonium bisulfate ($[\text{TBA}][\text{HSO}_4]$) with trichlorosilane leads to the formation of the bis(trichlorosilyl)phosphide ($[\text{P}(\text{SiCl}_3)_2]^-$, **1**) and trichlorosilylsulfide ($[\text{Cl}_3\text{SiS}]^-$, **2**) anions, respectively. Balanced equations for the formation of the TBA salts of anions **1** and **2** were formulated based on the identification of hexachlorodisiloxane and hydrogen gas as byproducts arising from these reductive processes: *i*) $[\text{H}_2\text{PO}_4]^- + 10\text{HSiCl}_3 \rightarrow \mathbf{1} + 4\text{O}(\text{SiCl}_3)_2 + 6\text{H}_2$ for P and *ii*) $[\text{HSO}_4]^- + 9\text{HSiCl}_3 \rightarrow \mathbf{2} + 4\text{O}(\text{SiCl}_3)_2 + 5\text{H}_2$ for S. Hydrogen gas was identified by its subsequent use to hydrogenate an alkene ((-)-terpinen-4-ol) using Crabtree's catalyst ($[(\text{COD})\text{Ir}(\text{py})(\text{PCy}_3)][\text{PF}_6]$, COD = 1,5-cyclooctadiene, py = pyridine, Cy = cyclohexyl). Phosphide **1** was generated in situ by the reaction of phosphoric acid and trichlorosilane and used to convert an alkyl chloride (1-chlorooctane) to the corresponding primary phosphine, which was isolated in 41% yield. Anion **1** was also prepared from $[\text{TBA}][\text{H}_2\text{PO}_4]$ and isolated in 62% yield on a gram scale. Treatment of $[\text{TBA}]\mathbf{1}$ with an excess of benzyl chloride leads to the formation of tetrabenzylphosphonium chloride, which was isolated in 61% yield. Sulfide **2** was used as a thionation reagent, converting benzophenone to thiobenzophenone in 62% yield. It also converted benzyl bromide to benzyl mercaptan in 55% yield. The TBA salt of trimetaphosphate ($[\text{TBA}]_3[\text{P}_3\text{O}_9] \cdot 2\text{H}_2\text{O}$), also a precursor to anion **1**, was found to react with either trichlorosilane or silicon(IV) chloride to provide bis(trimetaphosphate)silicate, $[\text{TBA}]_2[\text{Si}(\text{P}_3\text{O}_9)_2]$, characterized by NMR spectroscopy, X-ray crystallography, and elemental analysis. Trichlorosilane reduction of $[\text{TBA}]_2[\text{Si}(\text{P}_3\text{O}_9)_2]$ also provided anion **1**. The electronic structures of **1** and **2** were investigated using a suite of theoretical methods; the computational studies suggest that the trichlorosilyl ligand is a good π -acceptor and forms σ -bonds with a high degree of *s* character.



INTRODUCTION

White phosphorus has long been the critical intermediate for the synthesis of nearly all phosphorus-containing nonfertilizer chemicals.^{1–3} The production of white phosphorus, in what is known as the “thermal process”, requires the energy-intensive reduction of phosphate rock and is conducted in an electric arc furnace at 1500 °C.³ White phosphorus is a toxic and pyrophoric substance that has been used as a chemical warfare agent, and its transport has led to high-profile catastrophes.⁴ The legacy thermal process for the production of P_4 has served a secondary role as a method of purification; the phosphorus volatilized from the electric arc furnace allows for it to be separated from chiefly sulfur- and silicon-containing impurities.⁵ However, it struggles to separate arsenic, which is toxic to humans,⁶ because As replaces P in the P_4 lattice.^{3,7}

In contrast, phosphoric acid, H_3PO_4 , is produced by the “wet process”, which involves treating phosphate rock with sulfuric acid.⁵ In this scheme, the industrial chemistry of sulfur and phosphorus is intimately intertwined; sulfur is a secondary product from the petrochemical industry, and the vast majority of it is used to make sulfuric acid, allowing the wet process to

operate.⁸ The scale of the latter is much larger than that of the thermal process, accounting for the fate of 95% of the phosphate rock mined annually.³ Improvements in the methods for purifying phosphoric acid have been such that, nowadays, the purity of H_3PO_4 produced by the wet process rivals that produced by the thermal process, allowing wet process phosphoric acid to be used in food-grade applications.⁹ The higher energy requirements of the thermal process, in addition to the toxicity and pyrophoric properties of P_4 , provide motivation for eliminating P_4 in favor of phosphoric acid as the key starting material for the production of P-containing chemicals.^{10,11} Along these lines, a microwave-assisted preparation of PCl_3 from calcium phosphate in a scheme that is thought to bypass elemental P has also been reported.¹²

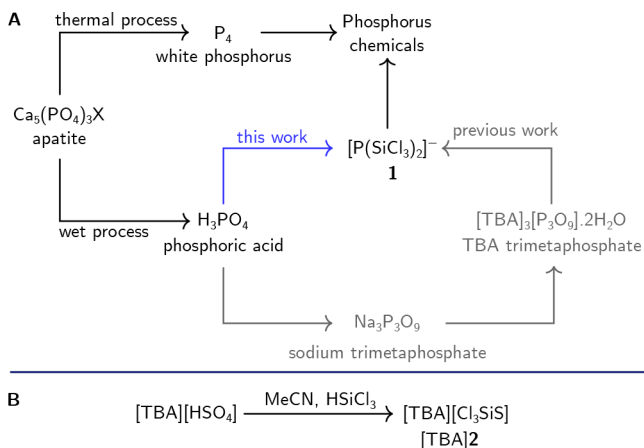
We recently reported the synthesis and characterization of the bis(trichlorosilyl)phosphide anion **1**, as its TBA salt, by reduction of trimetaphosphate with trichlorosilane (Scheme

Received: February 7, 2019

Published: March 22, 2019

1A).¹⁰ [TBA]1 was shown to be a versatile reagent for the preparation of several phosphorus-containing products pre-

Scheme 1. A: Synthetic Routes to Phosphorus-Containing Chemicals from Phosphate Rock^a and B: Application of Trichlorosilane Reduction to the Chemistry of Sulfur by Preparation of [TBA]2 from [TBA][HSO₄]



^aTBA = tetra-*n*-butylammonium. Most commonly, phosphate rock has the formula Ca₅(PO₄)₃X, where X is typically F, Cl, or OH, collectively referred to as apatite.

viously only available downstream of white phosphorus, such as Li[PF₆], RPH₂, and PH₃. We also demonstrated that [TBA]1 does not need to be isolated and purified and can instead be generated in situ for the conversion of a primary alkyl chloride to a corresponding alkyl phosphine.

Trichlorosilane, the reducing agent used to prepare anion 1, is manufactured on an industrial scale for the production of high-purity elemental silicon, which is in turn used to produce photovoltaic (PV) cells.¹³ It is listed as a high production volume (HPV)¹⁴ chemical, produced in the US in the range of 1–5 billion pounds (2016).¹⁵ The majority of trichlorosilane is produced by the reaction of hydrogen chloride gas and elemental silicon, the latter being derived from a similarly high energy process to thermal P₄ production.¹³ More recently, however, sustainable and less energy-intensive approaches for preparing trichlorosilane have been explored. One example, already practiced industrially, is the reaction of silicon(IV) chloride with hydrogen.^{16,17} Silicon(IV) chloride is a waste product of the PV industry¹⁶ or can alternatively be prepared in a redox-neutral process that involves converting silicate-containing minerals to a tetraalkyl orthosilicate¹⁸ and subsequent chlorination to silicon(IV) chloride.^{19,20} A method for producing silicon(IV) chloride from silica in a process that avoids elemental silicon entirely was described and patented in 2012.^{12,21} Finally, new methods for preparing silicon from silica using electrochemical techniques are areas of active investigation.²² These recent developments in the field of sustainable silicon chemistry hold promise for the use of trichlorosilane as a reducing agent for other element oxides.

RESULTS AND DISCUSSION

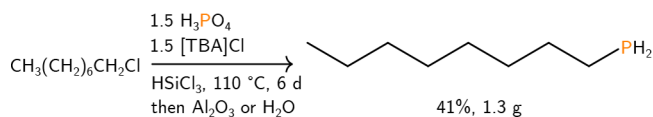
Reduction of Orthophosphate with Trichlorosilane.

Trimetaphosphate, the precursor to [TBA]1, is produced by the dehydration of monosodium dihydrogen phosphate at 300–500 °C⁵ or more recently by a similarly high-temperature dehydration of H₃PO₄ in the presence of sodium chloride.²³

We wondered whether it might be possible to obviate this dehydration step and instead prepare anion 1 more directly from a source of orthophosphate. Despite the well-documented reactivity of water and alcohols with Si–Cl bonds to give silanols,²⁴ our initial system tolerated the two equivalents of water present in the [TBA]₃[P₃O₉]·2H₂O starting material.²⁵ We therefore considered sources of orthophosphate containing acidic protons as potentially viable substrates for the preparation of [TBA]1.

Crystalline phosphoric acid, typically obtained from an aqueous 85% solution of H₃PO₄,^{26,27} accordingly was tested for its ability to serve as a precursor to anion 1. In order to target the stable TBA salt of 1, crystalline phosphoric acid was heated with [TBA]Cl in neat trichlorosilane. After heating at 110 °C for 86 h an aliquot was analyzed by ³¹P NMR spectroscopy; the characteristic signal for anion 1 was observed at –171.7 ppm. Despite several attempts, we were unable to obtain [TBA]1 as a pure compound using this preparative method due to the formation of byproducts, including [TBA]₂[Si₆Cl₁₄],^{28–30} which was identified by ²⁹Si NMR spectroscopy (S1.3.2). Instead, we used phosphoric acid to generate anion 1 in situ. In the presence of 1-chlorooctane, anion 1 undergoes a key carbon–phosphorus bond forming reaction, and, after workup, *n*-octylphosphine could be isolated in 41% yield based on 1-chlorooctane as the limiting reactant (Scheme 2).

Scheme 2. Synthesis of 1-Chlorooctane from 1-Chlorooctane and Phosphoric Acid

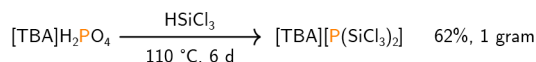


Although unactivated alkyl halides can be reduced with trichlorosilane in the presence of a halide catalyst to give trichlorosilyl-functionalized alkanes, such reactions typically require even more forcing conditions than we have employed here for P–C bond formation.³¹ In support of a mechanism in which a primary alkyl chloride undergoes nucleophilic attack by anion 1, we have previously shown that cleanly isolated [TBA]1 reacts with an alkyl chloride to give P–C bond-containing products in the absence of additional trichlorosilane.¹⁰ This method for the preparation of primary alkyl phosphines is attractive because it constitutes a one-step procedure from commercially available starting materials (Scheme 1A) and gives a primary alkyl phosphine in two steps from phosphate rock, the raw material that is mined from the ground. *n*-Octylphosphine is a useful precursor to stannylphosphines,^{32,33} as well as phosphacyclohexanes.³⁴ Octylphosphine can also be oxidized to octylphosphonic acid,³⁵ which finds applications as a ligand for nanoparticles^{36,37} and for heavy metal extraction processes.^{38,39}

Interested in having a reliable preparation of pure samples of [TBA]1 from a source of orthophosphate, we considered the possibility that tetra-*n*-butylammonium dihydrogen phosphate, [TBA][H₂PO₄],⁴⁰ might be a more suitable phosphate-containing starting material. By avoiding the introduction of additional chloride to the reaction, as was the case for the initial H₃PO₄/[TBA]Cl conditions, we sought to minimize the formation of byproducts such as [TBA]₂[Si₆Cl₁₄] which had impeded isolation of pure [TBA]1. Gratifyingly, [TBA]1 could

be isolated pure and in a moderate yield (62%) when $[\text{TBA}][\text{H}_2\text{PO}_4]$ was subjected to the standard conditions for preparing anion **1** (Scheme 3). Importantly, we encountered

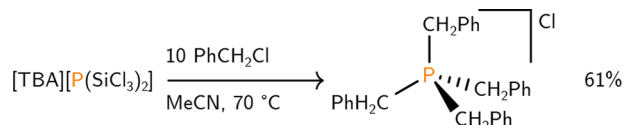
Scheme 3. Preparation of $[\text{TBA}]\mathbf{1}$ Starting from $[\text{TBA}][\text{H}_2\text{PO}_4]$



no difficulties in the typical workup and purification procedure. Over the prolonged reaction times employed, decomposition of TBA to give tri-*n*-butylammonium ($[\text{Bu}_3\text{NH}]^+$) was observed (S1.6.1), although based on the moderate yield of $[\text{TBA}]\mathbf{1}$ from $[\text{TBA}][\text{H}_2\text{PO}_4]$ (62%, Scheme 3) this process appears to be slow. $[\text{TBA}]\mathbf{1}$ melts with slight decomposition at 105–108 °C; analysis of a sample of $[\text{TBA}]\mathbf{1}$ that was maintained at 110 °C for 20 min partially redissolved in DCM to show the presence of anion **1** by ^{31}P NMR spectroscopy (S1.3.3). Nonetheless, future work will seek to determine which cations can be paired with anion **1** to provide salts with superior thermal stabilities.

With a method in hand for preparing $[\text{TBA}]\mathbf{1}$ directly from a source of orthophosphate, we set out to further explore the reactivity of **1** with carbon-based electrophiles. Heating $[\text{TBA}]\mathbf{1}$ with an excess (10 equiv) of benzyl chloride led to the formation of tetrabenzylphosphonium, identified by its ^{31}P NMR spectrum (δ 29.4 ppm, displaying coupling to 8 equiv protons to give a binomial nonet with $^2J_{\text{P-H}} = 14$ Hz), in line with previous literature reports.⁴¹ The phosphonium salt was separated from any TBA salts using water; while both the TBA and phosphonium salts were soluble in boiling water, only the TBA salts were soluble at 23 °C. Accordingly, recrystallization of the crude product from boiling water provided tetrabenzylphosphonium chloride in 61% yield (Scheme 4). Tetrabenzylphosphonium can be converted to the corresponding Wittig reagent and subsequently used to make carbon–carbon double bonds.⁴²

Scheme 4. Synthesis of Tetrabenzyl Phosphonium Chloride from $[\text{TBA}]\mathbf{1}$ and Benzyl Chloride



Intermediates in the HSiCl_3 Reduction of Phosphate Sources. With Trimetaphosphate as the P Source. Reduced P-containing species other than anion **1** were not observed upon trichlorosilane treatment of phosphate sources. However, a small but significant shift (10 ppm) of the trimetaphosphate resonance in the ^{31}P NMR spectrum was observed when the initial reaction of $[\text{TBA}]\mathbf{3}[\text{P}_3\text{O}_9]\cdot 2\text{H}_2\text{O}$ with trichlorosilane was monitored at 23 °C. Such changes in chemical shift are diagnostic of trimetaphosphate coordinating as a ligand.^{43,44} Diluting the reaction mixture in dichloromethane, thereby lowering the concentration of trichlorosilane and slowing the rate of reaction, led to the observation of an additional species (**3**, Figure 1), which by ^{31}P NMR spectroscopy was indicative of two trimetaphosphate units coordinated to two separate silicon centers. The connectivity of intermediate **3** was assigned based on the integration ratios and chemical shifts

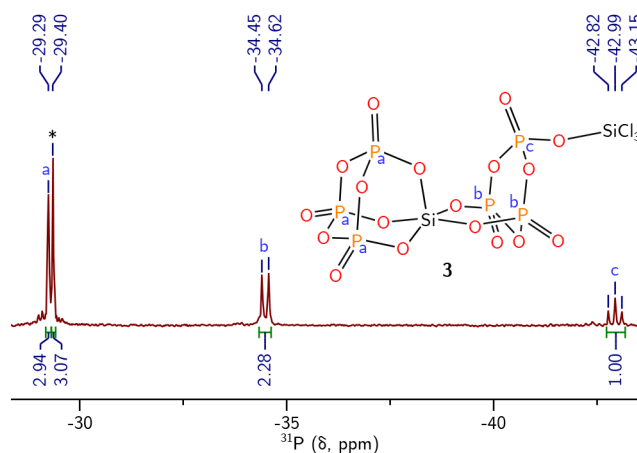


Figure 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture obtained when $[\text{TBA}]\mathbf{3}[\text{P}_3\text{O}_9]\cdot 2\text{H}_2\text{O}$ and SiCl_4 are mixed for 30 min in DCM at 23 °C. The resonances correspond to intermediate **3** (inset) in the synthesis of $[\text{TBA}]\mathbf{2}[\text{Si}(\text{P}_3\text{O}_9)_2]$. The asterisk (*) denotes $[\text{TBA}]\mathbf{2}[\text{Si}(\text{P}_3\text{O}_9)_2]$.

of the κ^3 coordinated⁴³ (P_a), ultraphosphate⁴⁴ (P_b), and branched⁴⁵ (P_c) polyphosphate regions, as well as the coupling pattern (AB_2 , $^2J_{\text{P-P}} = 27$ Hz) of P_b and P_c . After 48 h, this intermediate had converted to one having a single ^{31}P NMR resonance at δ 29.4 ppm, which is formulated as $[\text{TBA}]\mathbf{2}[\text{Si}(\text{P}_3\text{O}_9)_2]$.

This compound could be prepared independently by reaction of SiCl_4 with $[\text{TBA}]\mathbf{3}[\text{P}_3\text{O}_9]\cdot 2\text{H}_2\text{O}$, allowing for its isolation in 27% yield. An X-ray diffraction study confirmed the connectivity of $[\text{TBA}]\mathbf{2}[\text{Si}(\text{P}_3\text{O}_9)_2]$, featuring a six-coordinate central silicate moiety sandwiched between two trimetaphosphate ligands (Figure 2). Anion $[\text{Si}(\text{P}_3\text{O}_9)_2]^{2-}$ is a rare example of an entirely inorganic molecular silicophosphate; the majority of structurally characterized molecular silicophosphates contains organic substituents at silicon.⁴⁶ Like $[\text{TBA}]\mathbf{2}[\text{Si}(\text{P}_3\text{O}_9)_2]$, silicophosphate materials generally feature silicon in an all-oxygen six-coordinate environment.⁴⁷ How-

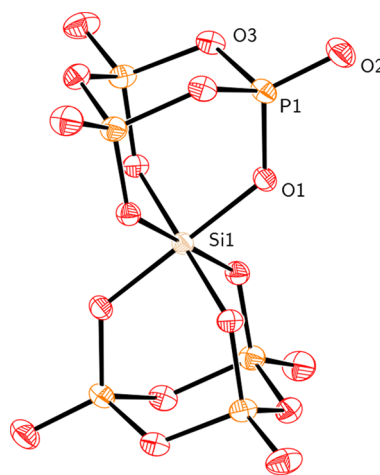


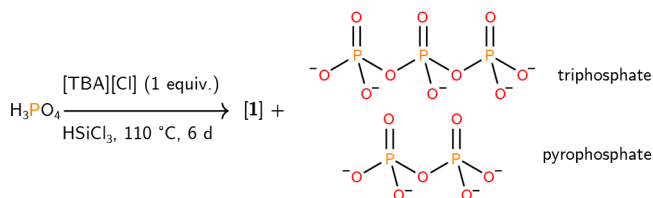
Figure 2. Molecular structure of $[\text{TBA}]\mathbf{2}[\text{Si}(\text{P}_3\text{O}_9)_2]$ with the ellipsoids at the 50% probability level and the two TBA cations omitted for clarity. Color coding: phosphorus (orange), oxygen (red), and silicon (tan). Selected bond distances (given as the average of chemically equivalent bonds) (Å): Si1–O1:1.7717(21), O1–P1:1.5254(23), P1–O2:1.4448(25), P1–O3:1.6121(34).

ever, their syntheses generally proceed at higher temperatures⁴⁸ than we have found to be the case for $[\text{TBA}]_2[\text{Si}(\text{P}_3\text{O}_9)_2]$.

Silicophosphate $[\text{TBA}]_2[\text{Si}(\text{P}_3\text{O}_9)_2]$ forms quickly and quantitatively (≥ 20 min) when a DCM solution of $[\text{TBA}]\text{I}$ is treated with a large excess of trichlorosilane (23 equiv) at room temperature. It was confirmed that the $[\text{Si}(\text{P}_3\text{O}_9)_2]^{2-}$ anion can serve as a P-source in the generation of **1**, by subjecting an independently prepared sample of $[\text{TBA}]_2[\text{Si}(\text{P}_3\text{O}_9)_2]$ to the standard synthesis conditions (neat HSiCl_3 , 110°C). Although no other intermediates were observed by ^{31}P NMR spectroscopy, the reduction of $[\text{TBA}]_2[\text{Si}(\text{P}_3\text{O}_9)_2]$ by trichlorosilane might proceed through mechanisms similar to those which have been proposed for related organic phosphine oxide reductions.⁴⁹ These have been postulated to proceed through either attack of the trichlorosilyl anion, $[\text{SiCl}_3]^-$,⁵⁰ at the phosphorus center or via a λ^5 phosphorane intermediate.⁵¹ Disproportionation and redistribution reactions of chlorosilanes by either a nucleophile or a base are well-known,^{28–30} and so a potentially large number of silicon-containing species could be responsible for reduction of the phosphate sources we have identified as precursors to $[\text{TBA}]\text{I}$. Given that we do not observe additional intermediates by ^{31}P NMR spectroscopy, the first reduction event at phosphate is likely rate-determining. Remarkably, anion **1** forms selectively under the reaction conditions; analogs in which a Cl is replaced by a hydrogen atom, a trichlorosilyl group, or a trichlorosiloxy group ($-\text{OSiCl}_3$) were not observed by ^{31}P NMR. Each of these three scenarios seems reasonable, given the facile redistribution of H for Cl in chlorosilanes,⁵² the ease at which chlorosilane oligomers are formed,^{29,53} and the existence of a related anion in which a phosphide features two dichloroaryloxysilyl functional groups ($[\text{P}(\text{SiCl}_2\text{OR})_2]^-$ ($\text{R} = 2,4,6\text{-}(t\text{-Bu})_3\text{C}_6\text{H}_2$)).⁵⁴

With Phosphoric Acid as the P Source. Condensed phosphates are observed (^{31}P NMR) to form under the reduction conditions for the preparation of **1** from phosphoric acid, demonstrating trichlorosilane must serve the role of the dehydrating agent in addition to its role as the reducing agent. At the end of the reaction used to prepare anion **1** in situ from H_3PO_4 , a white precipitate was seen to have formed that was insoluble in common organic solvents. The material dissolved completely in water and analysis of this aqueous solution by ^{31}P NMR spectroscopy revealed the presence of pyrophosphate and linear triphosphate (Scheme 5). Trichlorosilane is clearly capable of condensing orthophosphate into longer chain polyphosphates, and this may play a role in the mechanism governing the formation of $[\text{TBA}]\text{I}$. Presumably,

Scheme 5. Under the Conditions Used To Prepare Anion 1 in Situ, Pyrophosphate and Linear Triphosphate Were Observed by ^{31}P NMR Spectroscopy^a

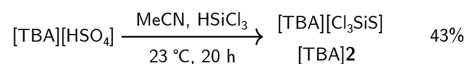


^aLine drawings of the polyphosphate products are shown in their fully deprotonated states for clarity.

condensed phosphates formed under the dehydrative conditions employed are capable of acting as ligands toward silicate centers, in a manner similar to the formation of $[\text{TBA}]_2[\text{Si}(\text{P}_3\text{O}_9)_2]$ from trimetaphosphate and trichlorosilane. The longer reaction times required for orthophosphate to be converted to anion **1**, versus trimetaphosphate, are in line with our previous arguments that metaphosphates are kinetically more prone to reductive processes.¹⁰

Sulfate Reduction by Trichlorosilane. The ability of trichlorosilane to effect the dehydration and complete deoxygenation of phosphate suggests a likely strategy for the reduction of other p-block oxoanions to give products containing the $\text{E}-\text{SiCl}_3$ group. Such compounds ($\text{E} = \text{C}, \text{Si}, \text{Ge}$) have received interest in recent years due to their potential applications in deposition processes⁵⁵ and chemical synthesis.⁵⁶ A survey of the literature returned the trichlorosilylsulfide anion ($[\text{Cl}_3\text{SiS}]^-$, **2**), which was prepared previously from tetraethylammonium hydrogen sulfide upon treatment with silicon tetrachloride in liquid hydrogen sulfide.⁵⁷ Given the above results for generation of **1** from dihydrogen phosphate and phosphoric acid, it follows that **2** might be accessed by reduction of bisulfate with trichlorosilane: a procedure that would avoid the use of liquefied H_2S , which is both extremely toxic and dangerous.⁵⁸ Accordingly, $[\text{TBA}]\text{2}$ was prepared in moderate yield (43%) by stirring $[\text{TBA}][\text{HSO}_4]$ in an acetonitrile/trichlorosilane mixture at 23°C for 20 h (Scheme 6). Conditions leading to the formation of

Scheme 6. Preparation of $[\text{TBA}]\text{2}$ from $[\text{TBA}][\text{HSO}_4]$



$[\text{TBA}]\text{2}$ are notably milder than the conditions required for the corresponding preparation of $[\text{TBA}]\text{1}$ (S1.3.6). We also found that reduction of $[\text{TBA}][\text{HSO}_4]$ with trichlorosilane leads to the formation of some elemental sulfur. A single crystal obtained from the crude reaction mixture in the preparation of $[\text{TBA}]\text{2}$ was unambiguously identified as S_8 by comparison of its unit cell with previous literature reports.⁵⁹

$[\text{TBA}]\text{2}$ was characterized by multinuclear NMR, IR, and Raman spectroscopies in addition to elemental analysis and X-ray crystallography (Figure 3). The IR and Raman data are consistent with those provided in the single previous report of

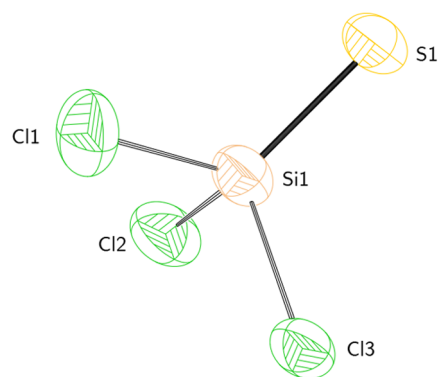
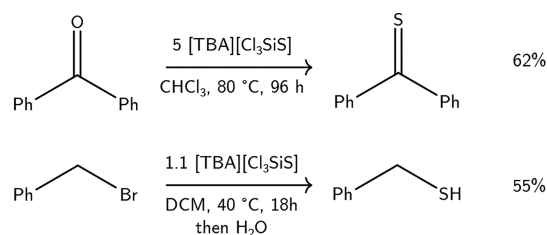


Figure 3. Molecular structure of $[\text{TBA}]\text{2}$, with ellipsoids at the 50% probability level and the TBA cation omitted for clarity. Selected bond lengths (\AA) and angles (deg): $\text{Si1}-\text{S1}: 1.9756(14)$, $\text{Si1}-\text{Cl}_{\text{av}}: 2.073(7)$, $\text{S1}-\text{Si1}-\text{Cl}_{\text{av}}: 115.59(25)$, $\text{Cl}-\text{Si1}-\text{Cl}_{\text{av}}: 102.69(30)$.

anion **2**, which had been isolated as the tetraethylammonium (TEA) salt.⁵⁷ The previous report also described the solid-state structure of [TEA][**2**], but the data were of insufficient quality to permit a detailed discussion of the bond metrics of the anion. Fortunately, our crystallographic study of [TBA]**2** permitted unambiguous assignment of the sulfur and chlorine atoms of anion **2**. The assignment of the sulfur and chlorine atoms is also supported by the different Si–S and Si–Cl lengths, which match well with those we calculated at the ω B97X-D3/ma-Def2-QZVPP level of theory.^{60,61} Anion **2** displays a Si–S bond of 1.9756(14) Å, significantly shorter than the sum of the covalent single bond radii, 2.19 Å.⁶² This bond length contraction is indicative of multiple bonding between silicon and sulfur, a phenomenon we have analyzed using a suite of theoretical methods (see **Electronic Structure and Bonding** section).

Carbon–Sulfur Bond-Forming Reactions. With [TBA]**2** in hand, we set out to test the value of this reagent for the preparation of organosulfur compounds (Scheme 7). Although

Scheme 7. Use of [TBA]**2** as a Thionation Reagent To Give Benzyl Mercaptan and Thiobenzophenone from Benzyl Bromide and Benzophenone, Respectively



the conjugate acid of **2**, Cl_3SiSH , has been known for half a century,⁶³ the use of this species in chemical synthesis seems to be largely unexplored. It seems reasonable to expect that formation of Si–X bonds (X = O, Cl, Br) from the reaction of anion **2** with C–X bond-containing substrates would provide a thermodynamic driving force for such reactions. Such is the case for an organic analog of **2**, $[\text{S}-\text{SiMe}_3]^-$, recently prepared by desilylation of $\text{S}(\text{SiMe}_3)_2$ by ionic liquids⁶⁴ and thought to be an intermediate for thionation reactions employing $\text{S}(\text{SiMe}_3)_2$.⁶⁵ Treatment of benzyl bromide with [TBA]**2** gave rise to a major new species in solution, identified as benzyl trichlorosilylsulfide by its NMR data (S1.9.1). A hydrolytic workup and purification by vacuum transfer allowed for the isolation of benzyl mercaptan in 55% yield. We also found that [TBA]**2** showed comparable reactivity to other thionating compounds, such as Lawesson's reagent, which can be used for the conversion of carbonyl to thiocarbonyl functional groups.⁶⁶ Accordingly, thiobenzophenone could be prepared from benzophenone using [TBA]**2** (5 equiv) in chloroform. An excess of [TBA]**2** was required in order to achieve a reasonable reaction time. Thiobenzophenone was extracted from the TBA-containing byproducts using hexanes and isolated in 62% yield.

Electronic Structure and Bonding. Electronic structure calculations on sulfide **2** at the MP2/aug-cc-pVTZ level of theory (C_{3v} -optimized metrical parameters (Å, deg): Si–S, 1.984; Si–Cl, 2.103; S–Si–Cl, 116.8) are indicative of multiple bonding between sulfur and silicon. Analysis of this wave function using GAMESS⁶⁷ gave a Mayer bond order of 1.784 for the S–Si linkage.⁶⁸ Submitting the same wave

function for natural bond orbital (NBO) analysis⁶⁹ provided via the natural resonance theory (NRT) routine an even larger estimate of this bond order, at 2.037, while indicating the presence of multiple resonance structures contributing greater than 10% to the overall electron density. The leading resonance structure, at ca. 22%, is the one corresponding to the NBOs and having a triple bond between sulfur and silicon together with three Si–Cl single bonds. The π bonds for this resonance structure are highly polar with 6% Si dp character and 94% S p character; thus, these π bonds are close to the NBO bonding/nonbonding cutoff. The S–Si σ bond is much more covalent with 35% Si $sp^{1.52}$ character and 64% S $sp^{3.1}$ character. The short nature of the Si–S bond is likely due to the large amount of s character used by silicon to form the σ interaction. This is in line with Bent's rule considerations that a central atom (here, Si) will accumulate s -orbital character in forming bonds to less electronegative elements. Accordingly, silicon uses majority p -orbital character, $sp^{2.5}d^{1.4}$, in forming the polar (19% Si, 81% Cl) Si–Cl bonds. In terms of their appearance (Figure 4), the MP2 π molecular orbitals (left)

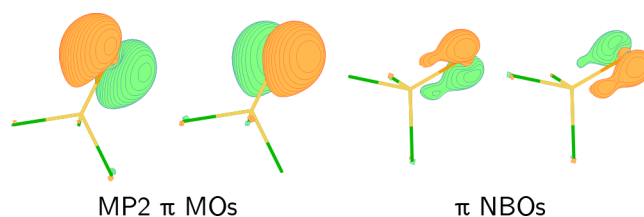


Figure 4. Comparison of the π interaction between silicon and sulfur in anion **2**. The MP2 π MOs resemble p -orbital lone pairs on sulfur, whereas the corresponding π NBOs suggest the presence of polar π bonds. Green: chlorine, tan: silicon, orange: sulfur.

look like p -orbital lone pairs polarized in the direction of silicon, while the corresponding S–Si π NBOs (right) do a better job of suggesting the presence of polar π bonds. Finally, analysis of the generalized valence bond (GVB) wave function (Figure 5) using the VB2000 program⁷⁰ as implemented in GAMESS,⁶⁷ treating the Si–S bond at the CASVB(6,6)/6-31++G** level of theory, gave a Si–S bond order of 1.84.

Analyzed similarly, there is some evidence of multiple bond character between phosphorus and silicon in phosphide **1**; the anion was geometry optimized with C_2 point group symmetry (key metrical parameters (Å, deg): P–Si, 2.145; Si–P–Si, 95.4). Analysis of the MP2/aug-cc-pVTZ wave function using

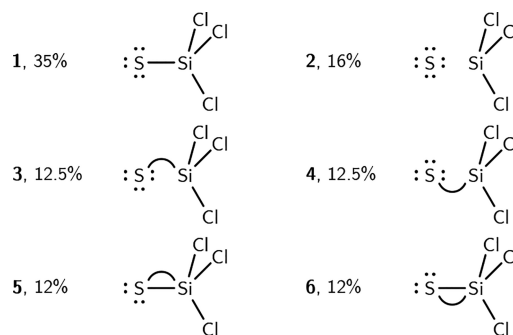


Figure 5. Summary of the generalized valence bond (GVB) wave function for anion **2** treating the Si–S bond at the CASVB(6,6)/6-31++G** level of theory. Analysis of the GVB wave function gives a Si–S bond order of 1.84.

GAMESS⁶⁷ gives a P–Si Mayer bond order of 1.318. In this case, NBO analysis indicates the presence of two lone pairs at the phosphorus atom, the first of which points along the C₂ rotational axis of symmetry and accumulates two-thirds *s*-orbital character (*sp*^{0.5} hybridization). The second P lone pair is contained in a pure *p*-orbital for which the PSi₂ plane is a nodal plane. The P–Si σ bonds are formed from overlap of *sp*⁵ and *sp*^{1.44} hybrids at P and Si, respectively, such that once again, silicon reserves much of its *p*-orbital percentage for bonding to the chlorine substituents, with *s*-orbital character being strong in silicon's contributions to the P–Si σ bonds. In anion **1**, the σ bonds are quite covalent (55% P, 45% Si). From inspection of the NBO second order perturbation theory analysis of the Fock matrix, the strongest delocalizations come from the π lone pair into the Si–Cl σ^* orbitals. The NRT analysis gives a natural bond order of 1.340 in this case, close to the value obtained from the GAMESS analysis of the MP2 wave function. Once again, due to the importance of multiple ionic resonance structures in which P–Si π bonds are formed at the expense of Si–Cl σ bonds, the leading resonance structure has a weight of only 22%.

Calculation of ¹J_{P–Si} Coupling Constants. Theoretical analysis of the electronic structure of anions **1** and **2** predicted the *s* character of the Si–E (E = P, S) bonds to be high, principally due to the electronegative chloride substituents on silicon. In the case of anion **1**, we sought to experimentally validate this analysis by interpretation of the ¹J_{P–Si} coupling constant, as measured by NMR spectroscopy. The magnitude of the ¹J_{P–X} coupling constant is dominated by the Fermi-contact interaction, proportional to the bond *s* character.⁷¹ Comparison to a series of related ¹J_{P–Si} values was approached with quantum chemical calculations (Table 1). These provided

Table 1. Comparison of the Experimental and Predicted Values for the ¹J_{P–Si} Coupling Constants and the % *s*-Orbital Character in the P–Si Bonds for a Series of Compounds

species	¹ J _{P–Si} /Hz		% <i>s</i> character ^a	
	exp. ^b	pred. ^c	σ (P–Si) ^d	Si ^e
Me ₃ SiPPh ₂ ·BH ₃	–44 ⁷⁵	–42	20	8
F ₃ SiPH ₂	15 ⁷⁶	22	21	15
HP(SiH ₃) ₂	35 ⁷⁷	20	17	9
Cl ₃ SiPH ₂	52 ⁷⁸	54	21	15
(<i>i</i> -Pr)P(SiCl ₃) ₂	73 ⁷⁹	85	21	15
[P(SiH ₃) ₂] [–]	77 ⁷⁹	76	22	14
(<i>i</i> -Pr)P(NPh ₂)(SiCl ₃)	125 ⁸⁰	115	23	18
[P(SiCl ₃) ₂] [–] , 1	158 ¹⁰	159	26	20

^aDetermined by NBO analysis. ^bExperimental value determined by ³¹P NMR spectroscopy. ^cPredicted value determined by evaluation of the calculated ¹J_{P–Si} value in eq 1. ^dSum of the P and S *s*-orbital character in the P–Si bond. ^eSi *s*-orbital character in the P–Si bond.

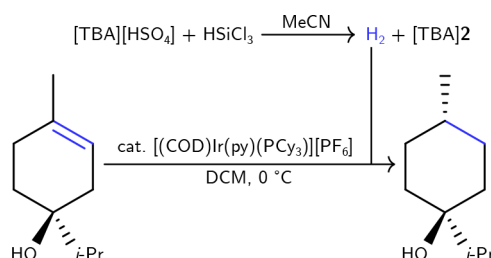
both the signs and magnitudes of the scalar couplings, as these can be difficult to determine in the presence of second-order coupling patterns.⁷² The geometry of each species was optimized at a low level of theory (B3LYP/6-31G(d,p)), and then the total nuclear spin–spin coupling constants (*J*) were calculated at the PBE/aug-cc-pVQZ level of theory.^{73,74} Linear regression between experimental and calculated scalar coupling constants⁷³ provided an excellent correlation (*R*² = 0.98, eq 1):

$${}^1J_{\text{P-Si}}(\text{calc.}) = 0.77 \times {}^1J_{\text{P-Si}}(\text{exp.}) - 38.57 \quad (1)$$

The species included in our study contained a range of different substituents on both phosphorus and silicon, as well as two-, three-, and four-coordinate phosphorus compounds (Table 1). Anion **1** exhibits the largest positive ¹J_{P–Si} value among all the species studied, consistent with a large amount of *s* character in its P–Si bonds, imparted by the trichlorosilyl groups. Trichlorosilyl groups consistently enhance P–Si scalar coupling, giving rise to four of the five largest constants in Table 1. The anionic charge of **1** may also increase ¹J_{P–Si} as suggested by the large value for [P(SiH₃)₂][–]. In order to determine the amount of *s* character of the phosphorus–silicon bonds, natural bond order (NBO) calculations were carried out. The *s* character of the σ (P–Si) bonds, and in particular the *s* character arising from silicon, correlated moderately well with the experimental ¹J_{P–Si} constants (*R*² = 0.54 and 0.76, respectively).

Balancing the Equations for the Formation of Anions **1 and **2**.** An important question we wished to address in these two reductive processes was the fate of the hydrogen atoms, originating from trichlorosilane and the protic substrates H₃PO₄ and [TBA][HSO₄]. H₂ or HCl would be the most likely gaseous hydrogen-containing byproducts with the former considered the more likely candidate given that P–Si and S–Si bonds of **1** or **2**, respectively, would be cleaved by HCl. Under the assumption of H₂ as the gaseous byproduct, we carried out a two-compartment experiment where the hydrogen generated from the reduction of bisulfate could be used to hydrogenate an alkene. We selected Crabtree's catalyst for the hydrogenation of (–)-terpinen-4-ol (Scheme 8) due to the high

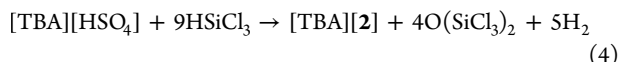
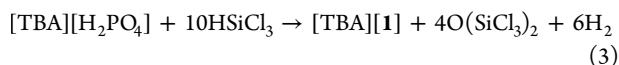
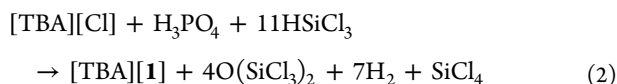
Scheme 8. Identification of the Hydrogen Produced from the Reduction of [TBA][HSO₄] to [TBA]₂ Using Trichlorosilane^a



^aThe hydrogen generated from the reduction was used to hydrogenate (–)-terpinen-4-ol using Crabtree's catalyst.

efficiency of this reaction at mild pressures and temperatures.⁸¹ Using a two-flask setup, we were able to confirm the formation of the hydrogenated product, *trans*-4-methyl-1-isopropylcyclohexan-1-ol, by ¹H NMR spectroscopy.

Control experiments showed that this method was unsuitable for the quantification of hydrogen (S1.11.3), so instead we turned to a simple gas collection experiment.⁸² The evolved hydrogen gas was collected by the displacement of water (S1.13), and this method indicated production of 4.45 equiv of hydrogen gas per mole of added [TBA][HSO₄], compared to the theoretical maximum of 5.0 (eq 4). An analogous study to quantify the H₂ produced by the formation of [TBA]**1** from H₃PO₄ gave 5.0 equiv of H₂, representing 71% of the theoretical maximum of 7 equiv (eq 2). Although not experimentally verified, the corresponding balanced equation leading to the formation of [TBA]**1** from [TBA][H₂PO₄] is shown in eq 3.



Analysis of the volatile liquid products at the end of the reaction was carried out to determine the fate of the oxygen atoms. Following the synthesis of [TBA]1, volatile material was removed under reduced pressure from the reaction vessel and collected in a liquid nitrogen cooled trap. Analysis of this material by ^{29}Si NMR spectroscopy confirmed the presence of hexachlorodisiloxane ($\text{Cl}_3\text{Si}-\text{O}-\text{SiCl}_3$) and pentachlorodisiloxane ($\text{Cl}_3\text{Si}-\text{O}-\text{SiCl}_2\text{H}$) (S1.3.8). Also observed was the formation of a white precipitate that was insoluble in common organic solvents, but which dissolved in aqueous sodium hydroxide solution to yield orthosilicate, as determined by ^{29}Si NMR spectroscopy.⁸³ These observations are consistent with the formation of some amount of silica, which is known to form when silicon tetrachloride is exposed to even sub-stoichiometric quantities of water.⁸⁴

CONCLUSIONS

The scope of P(V) reagents that can be used to prepare anion I has been extended to [TBA][H_2PO_4] and H_3PO_4 . Both present a significant advance over the use of trimetaphosphate, obtained by dehydration at elevated temperatures. Instead, trichlorosilane is employed to carry out both the dehydration and reduction of phosphate at 110 °C.

The present work opens the door for further reduction of p-block oxoanions using trichlorosilane as a viable strategy for the preparation of trichlorosilyl stabilized anions, which are known for the elements C,^{28,56} Si,⁸⁵ Ge,⁵⁵ N,⁸⁶ P,¹⁰ and S.⁵⁷ [TBA]1 and [TBA]2 are useful reagents for the preparation of phosphorus-carbon and sulfur-carbon bonds, respectively, with concomitant formation of Si-X (X = Cl, Br, O) bonds as a thermodynamic driving force for such reactions, demonstrating the utility of such trichlorosilyl substituted anions in chemical synthesis.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b01475.

Crystallographic data available from the Cambridge Structural Database under refcode 1841573 (CIF)

Crystallographic data available from the Cambridge Structural Database under refcode 1888218 (CIF)

Experimental details, characterization data, X-ray crystallographic information, computational details, and tables of Cartesian coordinates (PDF)

AUTHOR INFORMATION

Corresponding Author

*cummins@mit.edu

ORCID

Michael B. Geeson: 0000-0002-9228-7947

Pablo Ríos: 0000-0003-4467-4157

Wesley J. Transue: 0000-0001-7445-5663

Christopher C. Cummins: 0000-0003-2568-3269

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge financial and logistical support received through the UMRP, a partnership between UM6P and OCP Group in Morocco and MIT. Driss Dhiba (OCP) is thanked for his comments during the preparation of this manuscript.

REFERENCES

- (1) Schipper, W. Phosphorus: Too Big to Fail. *Eur. J. Inorg. Chem.* **2014**, *2014*, 1567–1571.
- (2) Borger, J. E.; Ehlers, A. W.; Slootweg, J. C.; Lammertsma, K. Functionalization of P₄ Through Direct P–C Bond Formation. *Chem. - Eur. J.* **2017**, *23*, 11738–11746.
- (3) Diskowski, H.; Hofmann, T. Phosphorus. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley: Weinheim, Germany, 2000; DOI: 10.1002/14356007.a19_505.
- (4) Emsley, J. *The 13th element: the sordid tale of murder, fire and phosphorus*; Wiley: New York, 2000.
- (5) Schrödter, K.; Bettermann, G.; Staffel, T.; Wahl, F.; Klein, T.; Hofmann, T. Phosphoric Acid and Phosphates. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley: Weinheim, Germany, 2008; DOI: 10.1002/14356007.a19_465.pub3.
- (6) Vahidnia, A.; van der Voet, G.; de Wolff, F. Arsenic neurotoxicity — A review. *Hum. Exp. Toxicol.* **2007**, *26*, 823–832.
- (7) Cossairt, B. M.; Diawara, M.-C.; Cummins, C. C. Facile Synthesis of AsP₃. *Science* **2009**, *323*, 602–602.
- (8) Müller, H. Sulfuric Acid and Sulfur Trioxide. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley: Weinheim, Germany, 2000; DOI: 10.1002/0471238961.1921120613211212.a01.pub2.
- (9) Gilmour, R. *Phosphoric acid: purification, uses, technology, and economics*; CRC Press/Taylor & Francis: Boca Raton, FL, 2014; DOI: 10.1201/b16187.
- (10) Geeson, M. B.; Cummins, C. C. Phosphoric acid as a precursor to chemicals traditionally synthesized from white phosphorus. *Science* **2018**, *359*, 1383–1385.
- (11) (a) Protasiewicz, J. D. From rock-stable to reactive phosphorus. *Science* **2018**, *359*, 1333–1333. (b) Slootweg, J. C. Sustainable Phosphorus Chemistry: A Silylphosphide Synthon for the Generation of Value-Added Phosphorus Chemicals. *Angew. Chem., Int. Ed.* **2018**, *57*, 6386–6388. (c) Slootweg, J. C. Zukunftsfähige Phosphorchemie: ein Silylphosphid-Synthesebaustein für die Entwicklung hochwertiger Phosphorverbindungen. *Angew. Chem.* **2018**, *130*, 6494–6496. (d) Swager, T. M.; Peeks, M. D. Trichlorosilane Paves the Way from Phosphoric Acid to Phosphorous Molecules. *Synfacts* **2018**, *14*, 0592.
- (12) Nordschild, S.; Auner, N. Direct Formation of Element Chlorides from the Corresponding Element Oxides through Microwave-Assisted Carbohydrochlorination Reactions. *Chem. - Eur. J.* **2008**, *14*, 3694–3702.
- (13) Simmler, W. Silicon Compounds, Inorganic. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley: Weinheim, Germany, 2000; DOI: 10.1002/14356007.a24_001.
- (14) A chemical is categorized as HPV if it is manufactured in, or imported into, the United States in amounts equal to or exceeding 1 million pounds a year. *Chemical Right to Know High Production Volume Chemicals Frequently Asked Questions*. <https://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=7000052X.txt> (accessed January 2019).
- (15) This figure was obtained from the Chemical Data Reporting tool. <https://www.epa.gov/chemical-data-reporting> (accessed January 2019).
- (16) Ding, W.-J.; Yan, J.-M.; Xiao, W.-D. Hydrogenation of Silicon Tetrachloride in the Presence of Silicon: Thermodynamic and

Experimental Investigation. *Ind. Eng. Chem. Res.* **2014**, *53*, 10943–10953.

(17) Knoth, J. F.; Eberle, H.-J.; Ruedinger, C. *Process for converting silicon tetrachloride to trichlorosilane*. 2017; US 9776878 B2.

(18) Goodwin, G. B.; Kenney, M. E. A new route to alkoxyxilanes and alkoxyxiloxanes of use for the preparation of ceramics by the sol-gel technique. *Inorg. Chem.* **1990**, *29*, 1216–1220.

(19) Roberts, J. M.; Placke, J. L.; Eldred, D. V.; Katsoulis, D. E. Synthesis of SiCl_4 via the Chloride Salt-Catalyzed Reaction of Orthosilicates with SOCl_2 . *Ind. Eng. Chem. Res.* **2017**, *56*, 11652–11655.

(20) Roberts, J. M.; Eldred, D. V.; Katsoulis, D. E. Synthesis of SiCl_4 from Gaseous HCl and $\text{Si}(\text{OMe})_4$. Reaction Development and Kinetic Studies. *Ind. Eng. Chem. Res.* **2016**, *55*, 1813–1818.

(21) Auner, N.; Bauch, C.; Deltschew, R.; Holl, S.; Mohsseni, J. *Method for the production of high-purity silicon*. 2012; WO 2012032129 A1.

(22) Dong, Y.; Slade, T.; Stolt, M. J.; Li, L.; Girard, S. N.; Mai, L.; Jin, S. Low-Temperature Molten-Salt Production of Silicon Nanowires by the Electrochemical Reduction of CaSiO_3 . *Angew. Chem., Int. Ed.* **2017**, *56*, 14453–14457.

(23) Pham Minh, D.; Ramarosan, J.; Nzihou, A.; Sharrock, P. One-Step Synthesis of Sodium Trimetaphosphate ($\text{Na}_3\text{P}_3\text{O}_9$) from Sodium Chloride and Orthophosphoric Acid. *Ind. Eng. Chem. Res.* **2012**, *51*, 3851–3854.

(24) (a) Cella, J. A.; Carpenter, J. C. Procedures for the preparation of silanols. *J. Organomet. Chem.* **1994**, *480*, 23–26. (b) Takiguchi, T. Preparation of Some Organosilane diols and Phenylsilane triol by Direct Hydrolysis Using Aniline as Hydrogen Chloride Acceptor. *J. Am. Chem. Soc.* **1959**, *81*, 2359–2361. (c) Kondo, S.-i.; Harada, T.; Tanaka, R.; Unno, M. Anion Recognition by a Silane diol-Based Receptor. *Org. Lett.* **2006**, *8*, 4621–4624.

(25) Besecker, C. J.; Day, V. W.; Klemperer, W. G. The trimetaphosphate ligand in organometallic chemistry. Isolation of tricarbonylmanganese(I), tricarbonylrhenium(I), (penta-methylcyclopentadienyl)rhodium(III), and (norbornadiene)rhodium(I) adducts. *Organometallics* **1985**, *4*, 564–570.

(26) Ross, W. H.; Jones, R. M. The Solubility and Freezing-Point Curves of Hydrated and Anhydrous Orthophosphoric Acid. *J. Am. Chem. Soc.* **1925**, *47*, 2165–2170.

(27) Smith, J. P.; Brown, W. E.; Lehr, J. R. Structure of Crystalline Phosphoric Acid. *J. Am. Chem. Soc.* **1955**, *77*, 2728–2730.

(28) Böhme, U.; Gerwig, M.; Gründler, F.; Brendler, E.; Kroke, E. Unexpected Formation and Crystal Structure of the Highly Symmetric Carbanion $[\text{C}(\text{SiCl}_3)_3]^-$. *Eur. J. Inorg. Chem.* **2016**, *2016*, 5028–5035.

(29) Tillmann, J.; Meyer, L.; Schweizer, J. I.; Bolte, M.; Lerner, H.-W.; Wagner, M.; Holthausen, M. C. Chloride-Induced Aufbau of Perchlorinated Cyclohexasilanes from Si_2Cl_6 : A Mechanistic Scenario. *Chem. - Eur. J.* **2014**, *20*, 9234–9239.

(30) Choi, S.-B.; Kim, B.-K.; Boudjouk, P.; Grier, D. G. Amine-Promoted Disproportionation and Redistribution of Trichlorosilane: Formation of Tetradechlorocyclohexasilane Dianion. *J. Am. Chem. Soc.* **2001**, *123*, 8117–8118.

(31) (a) Benkeser, R. A. Chemistry of trichlorosilane-tertiary amine combinations. *Acc. Chem. Res.* **1971**, *4*, 94–100. (b) Kang, S.-H.; Han, J. S.; Lee, M. E.; Yoo, B. R.; Jung, I. N. Phosphonium Chloride Induced Dichlorosilylene Transfer from Trichlorosilane. *Organometallics* **2003**, *22*, 2551–2553. (c) Kang, S.-H.; Han, J. S.; Yoo, B. R.; Lee, M. E.; Jung, I. N. Phosphonium Chloride-Catalyzed Dehydrochlorinative Coupling Reactions of Alkyl Halides with Hydridochlorosilanes. *Organometallics* **2003**, *22*, 529–534.

(32) Greulich, T. W.; Suzuki, N.; Daniliuc, C. G.; Fukazawa, A.; Yamaguchi, E.; Studer, A.; Yamaguchi, S. A biphenyl containing two electron-donating and two electron-accepting moieties: a rigid and small donor-acceptor-donor ladder system. *Chem. Commun.* **2016**, *52*, 2374–2377.

(33) Li, Y.; Chakrabarty, S.; Mück-Lichtenfeld, C.; Studer, A. *Ortho-Trialkylstannyl Arylphosphanes by C–P and C–Sn Bond Formation in Arynes*. *Angew. Chem., Int. Ed.* **2016**, *55*, 802–806.

(34) Mackewitz, T.; Ahlers, W.; Zeller, E.; Roper, M.; Paciello, R.; Papp, R.; Knoll, K.; Voss, H.; Roeper, M. *Phosphacyclohexanes and the use thereof in the hydroformylation of olefins*. 2004; CIB: B01J31/24; C07C45/50; C07F15/00; C07F15/04; C07F15/06; C07F9/6568; B01J31/28; (IPC1-7): B01J31/00.

(35) Buckler, S.; Epstein, M. The preparation and reactions of primary phosphine oxides. *Tetrahedron* **1962**, *18*, 1221–1230.

(36) Cozzoli, P. D.; Kornowski, A.; Weller, H. Low-Temperature Synthesis of Soluble and Processable Organic-Capped Anatase TiO_2 Nanorods. *J. Am. Chem. Soc.* **2003**, *125*, 14539–14548.

(37) Langley, S.; Helliwell, M.; Sessoli, R.; Teat, S. J.; Winpenny, R. E. P. Synthesis and Structural and Magnetic Characterization of Cobalt(II) Phosphonate Cage Compounds. *Inorg. Chem.* **2008**, *47*, 497–507.

(38) Lavaud, C.; Goettmann, F.; Causse, J.; Grandjean, A. *Procédé sol-gel pour séparer des ions métalliques d'une solution aqueuse*. 2014; FR 3001961 A1.

(39) Svara, J.; Weferling, N.; Hofmann, T. Phosphorus Compounds, Organic. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley VCH: Weinheim, Germany, 2006; DOI: 10.1002/14356007.a19_545.pub2.

(40) Julia, M.; Mestdagh, H.; Rolando, C. Une méthode simple de synthèse des phosphates terpeniques allyliques primaires et tertiaires. *Tetrahedron* **1986**, *42*, 3841–3849.

(41) Verstuyft, A. W.; Redfield, D. A.; Cary, L. W.; Nelson, J. H. Palladium(II) complexes of benzylphosphorus ligands. *Inorg. Chem.* **1977**, *16*, 2776–2786.

(42) McKenna, E. G.; Walker, B. J. The stereochemistry of Wittig reactions of ylide-anions derived from semi-stabilized phosphonium ylides. *Tetrahedron Lett.* **1988**, *29*, 485–488.

(43) Manna, C. M.; Nassar, M. Y.; Tofan, D.; Chakarawet, K.; Cummins, C. C. Facile synthesis of mononuclear early transition-metal complexes of κ^3 cyclo-tetrametaphosphate ($[\text{P}_4\text{O}_{12}]^{4-}$) and cyclo-trimetaphosphate ($[\text{P}_3\text{O}_9]^{3-}$). *Dalton Trans* **2014**, *43*, 1509–1518.

(44) Jiang, Y.; Chakarawet, K.; Kohout, A. L.; Nava, M.; Marino, N.; Cummins, C. C. Dihydrogen Tetrametaphosphate, $[\text{P}_4\text{O}_{12}\text{H}_2]^{2-}$: Synthesis, Solubilization in Organic Media, Preparation of its Anhydride $[\text{P}_4\text{O}_{11}]^{2-}$ and Acidic Methyl Ester, and Conversion to Tetrametaphosphate Metal Complexes via Protonolysis. *J. Am. Chem. Soc.* **2014**, *136*, 11894–11897.

(45) Shepard, S. M.; Cummins, C. C. Functionalization of Intact Trimetaphosphate: A Triphosphorylating Reagent for C, N, and O Nucleophiles. *J. Am. Chem. Soc.* **2019**, *141*, 1852–1856.

(46) (a) Styskalik, A.; Babiak, M.; Machac, P.; Relichova, B.; Pinkas, J. New Adamantane-like Silicophosphate Cage and Its Reactivity toward Tris(pentafluorophenyl)borane. *Inorg. Chem.* **2017**, *56*, 10699–10705. (b) Jähnigen, S.; Brendler, E.; Böhme, U.; Kroke, E. Synthesis of silicophosphates containing SiO_6 -octahedra under ambient conditions reactions of anhydrous H_3PO_4 with alkoxyxilanes. *Chem. Commun.* **2012**, *48*, 7675–7677. (c) Styskalik, A.; Skoda, D.; Moravec, Z.; Babiak, M.; Barnes, C. E.; Pinkas, J. Control of micro/mesoporosity in non-hydrolytic hybrid silicophosphate xerogels. *J. Mater. Chem. A* **2015**, *3*, 7477–7487.

(47) (a) Hesse, K.-F. Refinement of the crystal structure of silicon diphosphate, SiP_2O_7 AIV - a phase with six-coordinated silicon. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *35*, 724–725. (b) Poojary, D. M.; Borade, R. B.; Campbell, F. L.; Clearfield, A. Crystal Structure of Silicon Pyrophosphate (Form I) from Powder Diffraction Data. *J. Solid State Chem.* **1994**, *112*, 106–112. (c) Poojary, D. M.; Borade, R. B.; Clearfield, A. Structural characterization of silicon orthophosphate. *Inorg. Chim. Acta* **1993**, *208*, 23–29.

(48) Liebau, F.; Bissert, G.; Köppen, N. Synthese und kristallographische Eigenschaften einiger Phasen im System SiO_2 - P_2O_5 . *Z. Anorg. Allg. Chem.* **1968**, *359*, 113–134.

(49) Hérault, D.; Nguyen, D. H.; Nuel, D.; Buono, G. Reduction of secondary and tertiary phosphine oxides to phosphines. *Chem. Soc. Rev.* **2015**, *44*, 2508–2528.

(50) (a) Benkeser, R. A.; Voley, K. M.; Grutzner, J. B.; Smith, W. E. Evidence for the existence of the trichlorosilyl anion. *J. Am. Chem. Soc.* **1970**, *92*, 697–698. (b) Oehme, H.; Weiss, H. Reaction of 2,4,6-tributylphenyllithium with bromotrichlorosilane. Generation of trichlorosilyllithium, LiSiCl_3 . *J. Organomet. Chem.* **1987**, *319*, C16–C18. (c) Teichmann, J.; Bursch, M.; Köstler, B.; Bolte, M.; Lerner, H.-W.; Grimme, S.; Wagner, M. Trapping Experiments on a Trichlorosilanide Anion: a Key Intermediate of Halogenosilane Chemistry. *Inorg. Chem.* **2017**, *56*, 8683–8688. (d) Teichmann, J.; Wagner, M. Silicon chemistry in zero to three dimensions: from dichlorosilylene to silafullerene. *Chem. Commun.* **2018**, *54*, 1397–1412.

(51) (a) Krenske, E. H. Theoretical Investigation of the Mechanisms and Stereoselectivities of Reductions of Acyclic Phosphine Oxides and Sulfides by Chlorosilanes. *J. Org. Chem.* **2012**, *77*, 3969–3977. (b) Krenske, E. H. Reductions of Phosphine Oxides and Sulfides by Perchlorosilanes: Evidence for the Involvement of Donor-Stabilized Dichlorosilylene. *J. Org. Chem.* **2012**, *77*, 1–4. (c) Naumann, K.; Zon, G.; Mislow, K. Use of hexachlorodisilane as a reducing agent. Stereospecific deoxygenation of acyclic phosphine oxides. *J. Am. Chem. Soc.* **1969**, *91*, 7012–7023.

(52) Huang, X.; Ding, W.-J.; Yan, J.-M.; Xiao, W.-D. Reactive Distillation Column for Disproportionation of Trichlorosilane to Silane: Reducing Refrigeration Load with Intermediate Condensers. *Ind. Eng. Chem. Res.* **2013**, *52*, 6211–6220.

(53) Neumeyer, F.; Schweizer, J. I.; Meyer, L.; Sturm, A. G.; Nadj, A.; Holthausen, M. C.; Auner, N. Thermal Synthesis of Perchlorinated Oligosilanes: A Fresh Look at an Old Reaction. *Chem. - Eur. J.* **2017**, *23*, 12399–12405.

(54) Although we were unable to find a literature report associated with this compound, it can be accessed in the Cambridge Structural Database as a private communication under the refcode CCDC 183389.

(55) Teichmann, J.; Kunkel, C.; Georg, I.; Moxter, M.; Santowski, T.; Bolte, M.; Lerner, H.-W.; Bade, S.; Wagner, M. Tris-(trichlorosilyl)tetrelide Anions and a Comparative Study of Their Donor Qualities. *Chem. - Eur. J.* **2019**, *25*, 2740–2744.

(56) Georg, I.; Teichmann, J.; Bursch, M.; Tillmann, J.; Endeward, B.; Bolte, M.; Lerner, H.-W.; Grimme, S.; Wagner, M. Exhaustively Trichlorosilylated C_1 and C_2 Building Blocks: Beyond the Müller–Rochow Direct Process. *J. Am. Chem. Soc.* **2018**, *140*, 9696–9708.

(57) Müller, U.; Krug, V. Darstellung und Schwingungsspektren von Thiotrichlorosilicat und -germanat. Die Kristallstruktur von $\text{NEt}_4[\text{SiSiCl}_3]_2 \cdot 0.5\text{SCl}_4$. Preparation and Synthesis of Thiotrichloro Silicate and Germanate. Crystal Structure of $\text{NEt}_4[\text{SiSiCl}_3]_2 \cdot 0.5\text{SCl}_4$. *Z. Naturforsch., B: J. Chem. Sci.* **1985**, *40*, 1015–1019.

(58) *Chemistry of the elements*, 2nd ed.; Greenwood, N. N., Earnshaw, A., Eds.; Butterworth-Heinemann: Boston, MA, 1997; DOI: 10.1016/C2009-0-30414-6.

(59) Rettig, S. J.; Trotter, J. Refinement of the structure of orthorhombic sulfur, $\alpha\text{-S}_8$. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1987**, *43*, 2260–2262.

(60) Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.

(61) Chai, J.-D.; Head-Gordon, M. Systematic optimization of long-range corrected hybrid density functionals. *J. Chem. Phys.* **2008**, *128*, 084106.

(62) Pyykkö, P.; Atsumi, M. Molecular Single-Bond Covalent Radii for Elements 1–118. *Chem. - Eur. J.* **2009**, *15*, 186–197.

(63) Panckhurst, D. J.; Wilkins, C. J.; Brault, A. T.; Angelici, R. J. Trichlorosilanethiol. In *Inorganic Syntheses*; Kleinberg, J., Ed.; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 1963; Vol. 7; pp 28–30, DOI: 10.1002/9780470132388.ch8.

(64) (a) Finger, L. H.; Scheibe, B.; Sundermeyer, J. Synthesis of Organic (Trimethylsilyl)chalcogenolate Salts $\text{Cat}[\text{TMS-E}]$ ($\text{E} = \text{S}, \text{Se}$,

Te): the Methylcarbonate Anion as a Desilylating Agent. *Inorg. Chem.* **2015**, *54*, 9568–9575. (b) Finger, L. H.; Guschlbauer, J.; Harms, K.; Sundermeyer, J. N-Heterocyclic Olefin-Carbon Dioxide and -Sulfur Dioxide Adducts: Structures and Interesting Reactivity Patterns. *Chem. - Eur. J.* **2016**, *22*, 16292–16303.

(65) Degl'Innocenti, A.; Capperucci, A.; Castagnoli, G.; Malesci, I. Hexamethyldisilathiane-Based Thionation of Carbonyl Compounds: A Versatile Approach to Sulfur-Containing Heterocycles. *Synlett* **2005**, *13*, 1965–1983.

(66) Pedersen, B. S.; Scheibye, S.; Nilsson, N. H.; Lawesson, S.-O. Studies on organophosphorus compounds XX. syntheses of thioketones. *Bull. Soc. Chim. Belg.* **1978**, *87*, 223–228.

(67) (a) Schmidt, M. W.; Baldrige, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomery, J. A. General atomic and molecular electronic structure system. *J. Comput. Chem.* **1993**, *14*, 1347–1363. (b) Gordon, M. S.; Schmidt, M. W. Advances in electronic structure theory: GAMESS a decade later. In *Theory and Applications of Computational Chemistry: the first forty years*; Dykstra, C., Frenking, G., Kim, K., Scuseria, G., Eds.; Elsevier: Amsterdam, Netherlands, 2005; pp 1167–1189, DOI: 10.1016/B978-044451719-7/50084-6.

(68) Mayer, I. Charge, bond order and valence in the AB initio SCF theory. *Chem. Phys. Lett.* **1983**, *97*, 270–274.

(69) (a) Weinhold, F.; Landis, C. R. *Valency and bonding: a natural bond orbital donor-acceptor perspective*; Cambridge University Press: Cambridge, UK; New York, 2005; DOI: 10.1017/CBO9780511614569. (b) Glendening, E. D.; Badenhoop, J. K.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Landis, C. R.; Weinhold, F. *NBO 6.0*; 2013.

(70) (a) Li, J.; McWeeny, R. VB2000: Pushing valence bond theory to new limits. *Int. J. Quantum Chem.* **2002**, *89*, 208–216. (b) Li, J.; McWeeny, R. *VB2000 Version 2.7*, SciNet Technologies, San Diego, CA; 2013.

(71) “Theoretical Considerations: Spin-Spin Coupling” in Phosphorus-31 NMR spectroscopy in stereochemical analysis. In *Methods in stereochemical analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH Publishers: Deerfield Beach, Fla, 1987; Vol. 8, pp 211–217.

(72) Becker, G.; Eschbach, B.; Käshammer, D.; Mundt, O. Metallderivate von Molekülverbindungen. VII. Bis[1,2-bis-(dimethylamino)ethan-N,N']lithium-disilylphosphanid–Synthese und Struktur. *Z. Anorg. Allg. Chem.* **1994**, *620*, 29–40.

(73) Suardiaz, R.; Pérez, C.; Crespo-Otero, R.; García de la Vega, J. M.; Fabián, J. S. Influence of Density Functionals and Basis Sets on One-Bond Carbon–Carbon NMR Spin–Spin Coupling Constants. *J. Chem. Theory Comput.* **2008**, *4*, 448–456.

(74) Helgaker, T.; Jaszunski, M.; Ruud, K. Ab Initio Methods for the Calculation of NMR Shielding and Indirect Spin–Spin Coupling Constants. *Chem. Rev.* **1999**, *99*, 293–352.

(75) Whittell, G. R.; Balmond, E. I.; Robertson, A. P. M.; Patra, S. K.; Haddow, M. F.; Manners, I. Reactions of Amine- and Phosphane-Borane Adducts with Frustrated Lewis Pair Combinations of Group 14 Triflates and Sterically Hindered Nitrogen Bases. *Eur. J. Inorg. Chem.* **2010**, *2010*, 3967–3975.

(76) Fritz, G.; Schäfer, H.; Demuth, R.; Grobe, J. Das $\text{F}_3\text{Si}-\text{PH}_2$. *Z. Anorg. Allg. Chem.* **1974**, *407*, 287–294.

(77) Fritz, G.; Schäfer, H.; Hölderich, W. Zur Metallierung der PH_2 -Gruppe in Silylphosphinen. *Z. Anorg. Allg. Chem.* **1974**, *407*, 266–286.

(78) Driess, M.; Monsé, C.; Merz, K. Tetraphosphanysilane - A Mild PH_2 -Transfer Reagent and Building Block for the Synthesis of a Rhombododecahedral $\text{Li}_6\text{P}_6\text{Si}_2$ -Cluster Framework. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1225–1230.

(79) Müller, L.-P.; Zanin, A.; Jeske, J.; Jones, P. G.; du Mont, W.-W. Trichlorosilane/Triethylamine An Alternative to Hexachlorodisilane in Reductive Trichlorosilylation Reactions?. In *Organosilicon Chemistry Set*; Auner, N., Weis, J., Eds.; Wiley-VCH Verlag GmbH: Weinheim, Germany, 2005; pp 286–290, DOI: 10.1002/9783527620777.ch46b.

(80) Müller, L.-P.; Mont, W.-W. D.; Jeske, J.; Jones, P. G. Reactions at Silicon-Silicon Bonds, V. Selective Trichlorosilylation of Alkyl-(diorganylamino)chlorophosphanes with Hexachlorodisilane or with Trichlorosilane/Triethylamine. - Two Routes to New Functional Trichlorosilylphosphanes. *Chem. Ber.* **1995**, *128*, 615–619.

(81) Crabtree, R. H.; Davis, M. W. Occurrence and origin of a pronounced directing effect of a hydroxyl group in hydrogenation with $[\text{Ir}(\text{cod})\text{P}(\text{C}_6\text{H}_{11})_3(\text{py})]\text{PF}_6$. *Organometallics* **1983**, *2*, 681–682.

(82) Conley, B. L.; Williams, T. J. Dehydrogenation of ammonia - borane by Shvo's catalyst. *Chem. Commun.* **2010**, *46*, 4815–4817.

(83) Kinrade, S. D.; Swaddle, T. W. Silicon-29 NMR studies of aqueous silicate solutions. 1. Chemical shifts and equilibria. *Inorg. Chem.* **1988**, *27*, 4253–4259.

(84) (a) Chambers, D. W. S.; Wilkins, C. J. 982. Chlorosiloxanes from the reaction between oxygen and silicon tetrachloride. *J. Chem. Soc.* **1960**, 5088. (b) Schumb, W. C.; Stevens, A. J. The Partial Hydrolysis of Silicon Tetrachloride. *J. Am. Chem. Soc.* **1950**, *72*, 3178–3182.

(85) Olaru, M.; Hesse, M. F.; Rychagova, E.; Ketkov, S.; Mebs, S.; Beckmann, J. The Weakly Coordinating Tris(trichlorosilyl)silyl Anion. *Angew. Chem., Int. Ed.* **2017**, *56*, 16490–16494.

(86) (a) Schwarze, B.; Milius, W.; Schnick, W. Synthese und Kristallstruktur von $[(\text{Cl}_3\text{Si})_2\text{N}]_2\text{TiCl}_2$ -ein perchloriertes N-Silyltitanamid/Synthesis and Crystal Structure of $[(\text{Cl}_3\text{Si})_2\text{N}]_2\text{TiCl}_2$ -a Fully Chlorinated N-Silyl Titanium Amide. *Z. Naturforsch., B: J. Chem. Sci.* **1997**, *52*, 819–822. (b) Wannagat, U.; Schmidt, P.; Schulze, M. Reactions of Hexachlorodisilazane. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 447–448. (c) Moretto, H.-H.; Schmidt, P.; Wannagat, U. Beiträge zur Chemie der Silicium-Stickstoff-Verbindungen. CXII. Organylammonium-bis(trichlorosilyl)amide. *Z. Anorg. Allg. Chem.* **1972**, *394*, 125–132.