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

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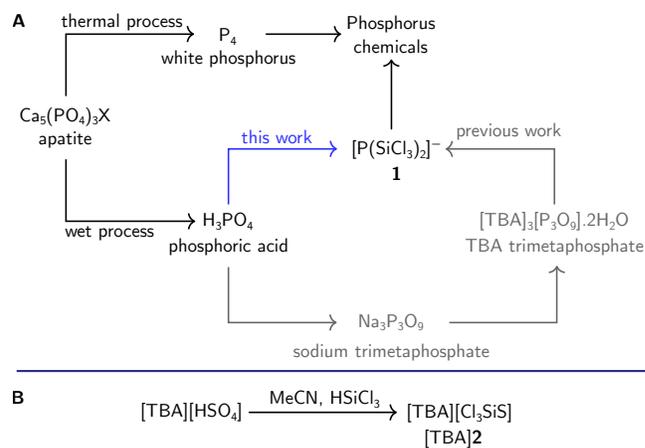
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Abstract: Reduction of phosphoric acid (H_3PO_4) or tetra-*n*-butylammonium bisulfate ($[\text{TBA}][\text{HSO}_4]$) with trichlorosilane leads to the formation of the bis(trichlorosilyl)phosphide ($[\text{P}(\text{SiCl}_3)_2]^-$, **1**) and trichlorosilylsulfide ($[\text{Cl}_3\text{SiS}]^-$, **2**) anions, respectively. Balanced equations for the formation of the TBA salts of anions **1** and **2** were formulated based on the identification of hexachloro-disiloxane 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 (*n*-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 theories; 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 non-fertilizer 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 are 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



Scheme 1. A: Synthetic routes to phosphorus-containing chemicals from phosphate rock. TBA = tetra-*n*-butylammonium. Most commonly, phosphate rock has the formula $\text{Ca}_5(\text{PO}_4)_3\text{X}$, where X is typically F, Cl or OH, collectively referred to as apatite. **B:** Application of trichlorosilane reduction to the chemistry of sulfur by preparation of $[\text{TBA}]\mathbf{2}$ from $[\text{TBA}][\text{HSO}_4]$.

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

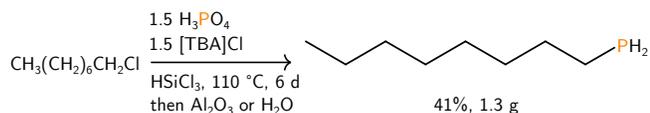
salt, by reduction of trimetaphosphate with trichlorosilane (Scheme 1A).¹⁰ [TBA]1 was shown to be a versatile reagent for the preparation of several phosphorus-containing products previously only available downstream of white phosphorus, such as Li[PF₆], RPH₂ and PH₃. We also demonstrated that [TBA]1 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 industry,¹⁶ 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 dihydrogenphosphate at 300–500 °C,⁵ 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.

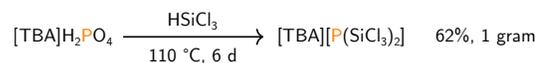


Scheme 2. Synthesis of *n*-octylphosphine from *n*-octylchloride and phosphoric acid.

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 *n*-octylchloride, anion 1 undergoes a key carbon-phosphorus bond forming reaction and, after workup, *n*-octylphosphine could be isolated in 41% yield based on *n*-octylchloride as the limiting reactant (Scheme 2).

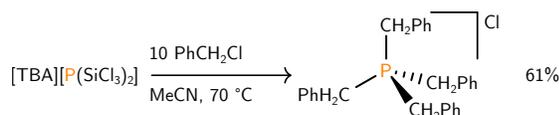
Although unactivated alkyl halides can be reduced with trichlorosilane in the presence of a halide catalyst to give trichlorosilyl-functionalized alkanes, such reactions typically require even more forcing conditions than we have employed here for P–C bond formation.³¹ In support of a mechanism in which 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 stannyphosphines,^{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}



Scheme 3. Preparation of [TBA]1 starting from [TBA][H₂PO₄].

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 dihydrogenphosphate, [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 [TBA][H₂PO₄] was subjected to the standard conditions for preparing anion 1 (Scheme 3). Importantly, we encountered no difficulties in the typical workup and purification procedure. Over the prolonged reaction times employed, decomposition of TBA to give tri-*n*-butylammonium ([Bu₃NH]⁺) was observed (S1.6.1), although based on the moderate yield of [TBA]1 from [TBA][H₂PO₄] (62%, Scheme 3) this process appears to be slow. [TBA]1 melts with slight decomposition at 105–108 °C; analysis of a sample of [TBA]1 that was maintained at 110 °C for 20 minutes partially redissolved in DCM to show the presence of anion 1 by ³¹P 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 [TBA]1 directly



4 **Scheme 4.** Synthesis of tetrabenzyl phosphonium chloride from
5 [TBA]1 and benzyl chloride.

6
7 from a source of orthophosphate, we set out to further explore the reactivity of **1** with carbon-based electrophiles. Heating [TBA]1 with an excess (10 equiv.) of benzyl chloride led to the formation of tetrabenzylphosphonium, identified by its ^{31}P NMR spectrum (δ 24.5 ppm, displaying coupling to 8 equivalent 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

22 Intermediates in the HSiCl_3 reduction of phosphate sources

23 With trimetaphosphate as the P source

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25
26
27 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 [TBA]₃[P₃O₉].2H₂O 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**, Fig. 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 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 [TBA]₂[Si(P₃O₉)₂].

46 This compound could be prepared independently by reaction of SiCl_4 with [TBA]₃[P₃O₉].2H₂O, allowing for its isolation in 27% yield. An X-ray diffraction study confirmed the connectivity of [TBA]₂[Si(P₃O₉)₂], featuring a six-coordinate central silicate moiety sandwiched between two trimetaphosphate ligands (Fig. 2). Anion [Si(P₃O₉)₂]²⁻ is a rare example of an entirely inorganic molecular silicophosphate; the majority of structurally characterized molecular silicophosphates contain organic substituents at silicon.⁴⁶ Like [TBA]₂[Si(P₃O₉)₂], silicophosphate materials generally feature silicon in an all-oxygen six-coordinate environment.⁴⁷ However, their syntheses generally proceed at higher temperatures⁴⁸ than we have found to be the case for [TBA]₂[Si(P₃O₉)₂].

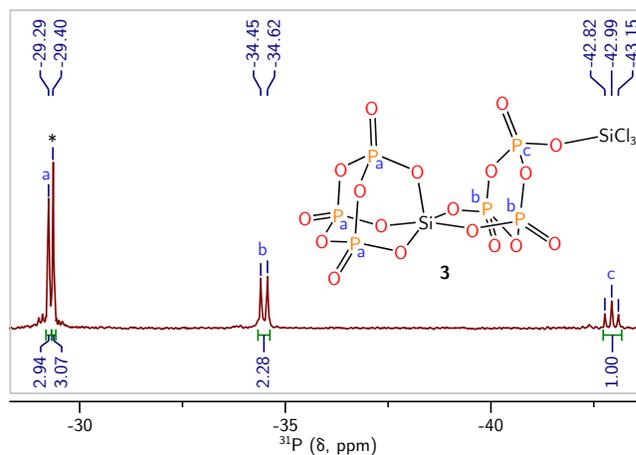


Figure 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture obtained when [TBA]₃[P₃O₉].2H₂O and SiCl_4 are mixed for 30 minutes in DCM at 23 °C. The resonances correspond to intermediate **3** (inset) in the synthesis of [TBA]₂[Si(P₃O₉)₂]. The asterisk (*) denotes [TBA]₂[Si(P₃O₉)₂].

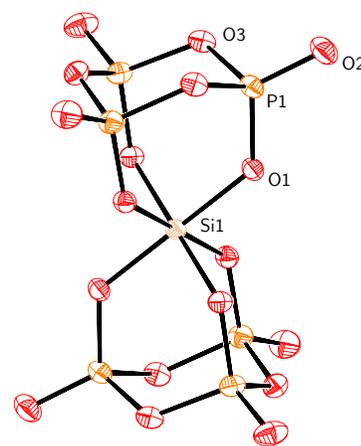


Figure 2. Molecular structure of [TBA]₂[Si(P₃O₉)₂] with the ellipsoids at the 50% probability level and the two TBA cations omitted for clarity. Color coding: phosphorus (orange), oxygen (red) and silicon (tan). Selected bond distances (given as the average of chemically equivalent bonds) (Å): Si1–O1: 1.7717(21), O1–P1: 1.5254(23), P1–O2: 1.4448(25), P1–O3: 1.6121(34).

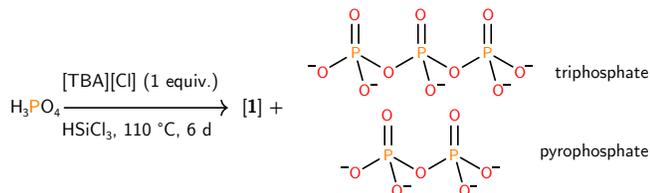
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Silicophosphate [TBA]₂[Si(P₃O₉)₂] forms quickly and quantitatively (≥ 20 min) when a DCM solution of [TBA]1 is treated with a large excess of trichlorosilane (23 equiv.) at room temperature. It was confirmed that the [Si(P₃O₉)₂]²⁻ anion can serve as a P-source in the generation of **1**, by subjecting an independently prepared sample of [TBA]₂[Si(P₃O₉)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 [TBA]₂[Si(P₃O₉)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, [SiCl₃]⁻,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 [TBA]1. 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 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 [TBA]**1**. Presumably, condensed phosphates formed under the dehydrative conditions employed are capable of acting as ligands towards 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

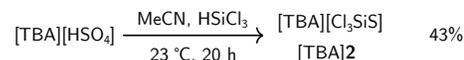


Scheme 5. Under the conditions used to prepare anion **1** in situ, pyrophosphate and linear triphosphate were observed by ^{31}P NMR spectroscopy. Line drawings of the polyphosphate products are shown in their fully deprotonated states for clarity.

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 di-

hydrogen 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, [TBA]**2** was prepared in moderate yield (43%) by stirring $[\text{TBA}][\text{HSO}_4]$ in an acetonitrile/trichlorosilane mixture at $23\text{ }^\circ\text{C}$ for 20 h (Scheme 6). Conditions leading to the formation of [TBA]**2** are notably milder than the conditions required for the corresponding preparation of [TBA]**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 [TBA]**2** was unambiguously identified as S_8 by comparison of its unit cell with previous literature reports.⁵⁹



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

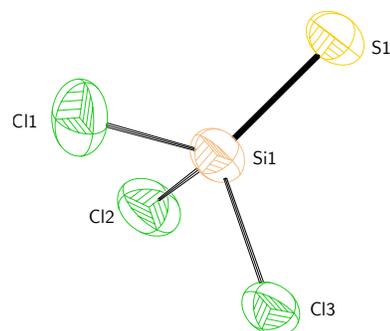


Figure 3. Molecular structure of [TBA]**2**, with ellipsoids at the 50% probability level and the TBA cation omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$): Si1–S1: 1.9756(14), Si1–Cl_{av.}: 2.073(7), S1–Si1–Cl_{av.}: 115.59(25), Cl–Si1–Cl_{av.}: 102.69(30).

[TBA]**2** was characterized by multinuclear NMR, IR, and Raman spectroscopies in addition to elemental analysis and X-ray crystallography (Fig. 3). The IR and Raman data are consistent with those provided in the single previous report of anion **2**, which had been isolated as the tetraethylammonium (TEA) salt.⁵⁷ The previous report also described the solid-state structure of $[\text{TEA}][\text{2}]$ 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 $\omega\text{B97X-D3/ma-Def2-QZVPP}$ level of theory.^{60,61} Anion **2** displays a Si–S bond of 1.9756(14) \AA , significantly shorter than the sum of the covalent single bond radii, 2.19 \AA .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 the conjugate acid of **2**, Cl_3SiSH , has

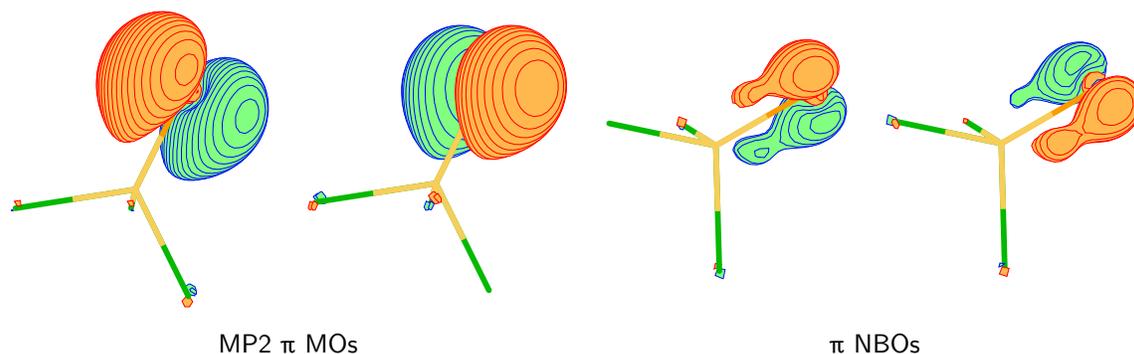
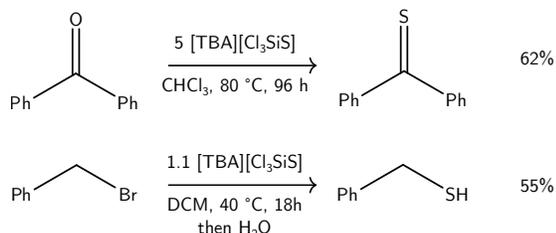


Figure 4. Comparison of the π interaction between silicon and sulfur in anion **2**. The MP2 π MOs resemble p-orbital lone pairs on sulfur, whereas the corresponding π NBOs suggest the presence of polar π bonds. Green: chlorine, tan: silicon, orange: sulfur.



Scheme 7. Use of [TBA]**2** as a thionation reagent to give benzyl mercaptan and thiobenzophenone from benzyl bromide and benzophenone respectively.

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**, [S–SiMe₃][–], recently prepared by desilylation of S(SiMe₃)₂ by ionic liquids⁶⁴ and thought to be an intermediate for thionation reactions employing S(SiMe₃)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, °): 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 wavefunction using GAMESS⁶⁷ gave a Mayer bond order of 1.784 for the S–Si linkage.⁶⁸ Submitting the same wavefunction 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 (Fig. 4) the MP2 π molecular orbitals (left) 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 valance bond (GVB) wavefunction (Fig. 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.

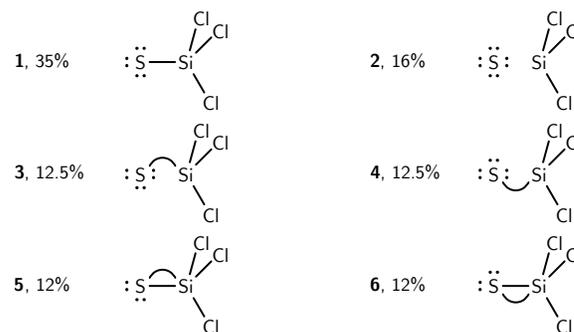


Figure 5. Summary of the generalized valance bond (GVB) wavefunction for anion **2** treating the Si–S bond at the CASVB(6,6)/6-31++G** level of theory. Analysis of the GVB wavefunction gives a Si–S bond order of 1.84.

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, °): P–Si, 2.145; Si–P–Si, 95.4). Analysis of the MP2/aug-cc-pVTZ wavefunction using 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 C_2 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 PSi_2 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 wavefunction. 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 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)) 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 ($R^2 = 0.98$, Eqn. 1):

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

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 $[P(SiH_3)_2]^-$. 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 $\sigma(P-Si)$ 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).

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	$^1J_{P-Si}$ / Hz		% s character ^a	
	Exp. ^b	Pred. ^c	$\sigma(P-Si)$ ^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 ⁷²	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

^a Determined by NBO analysis

^b Experimental value determined by ³¹P NMR spectroscopy

^c Predicted value determined by evaluation of the calculated

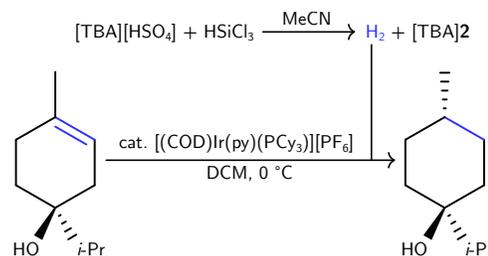
^d $^1J_{P-Si}$ value in Eqn. 1

^e Sum of the P and S s -orbital character in the P–Si bond

^f S s -orbital character in the P–Si bond

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 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.

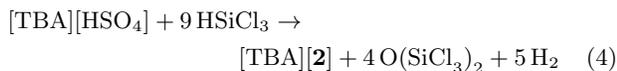
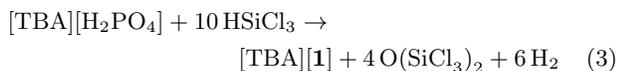
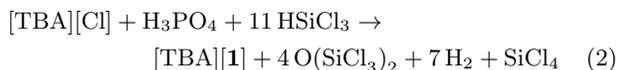


Scheme 8. Identification of the hydrogen produced from the reduction of [TBA][HSO₄] to [TBA]₂ using trichlorosilane; the hydrogen generated from the reduction was used to hydrogenate (−)-terpinen-4-ol using Crabtree's catalyst.

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 equivalents of hydrogen gas per mole of added [TBA][HSO₄], compared to the theoretical maximum of 5.0 (Eqn. 4). An analogous study to quantify the H₂ produced by the formation of [TBA]**1** from H₃PO₄ gave 5.0 equivalents of H₂, representing 71% of the theoretical maximum of 7 equivalents (Eqn. 2). Although not experimentally veri-

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fed, the corresponding balanced equation leading to the formation of [TBA]**1** from [TBA][H₂PO₄] is shown in Eqn. 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 ²⁹Si NMR spectroscopy confirmed the presence of hexachlorodisiloxane (Cl₃Si–O–SiCl₃) and pentachlorodisiloxane (Cl₃Si–O–SiCl₂H) (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 ²⁹Si 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 substoichiometric quantities of water.⁸⁴

Conclusions

The scope of P(V) reagents that can be used to prepare anion **1** has been extended to [TBA][H₂PO₄] and H₃PO₄. 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 P¹⁰ 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.

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Supplementary Information

Experimental details, characterization data, X-ray crystallographic information, computational details, and tables of Cartesian coordinates are provided in the Supporting Information document. This material is available free of charge via the Internet at <http://pubs.acs.org>. Crystallographic data are available from the Cambridge Structural Database under refcodes 1841573 and 1888218.

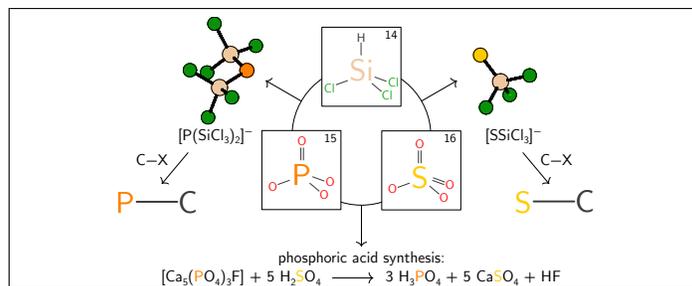
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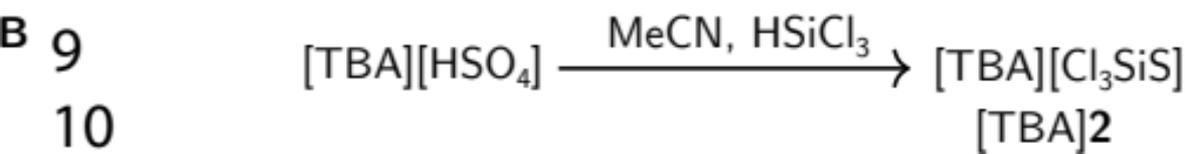
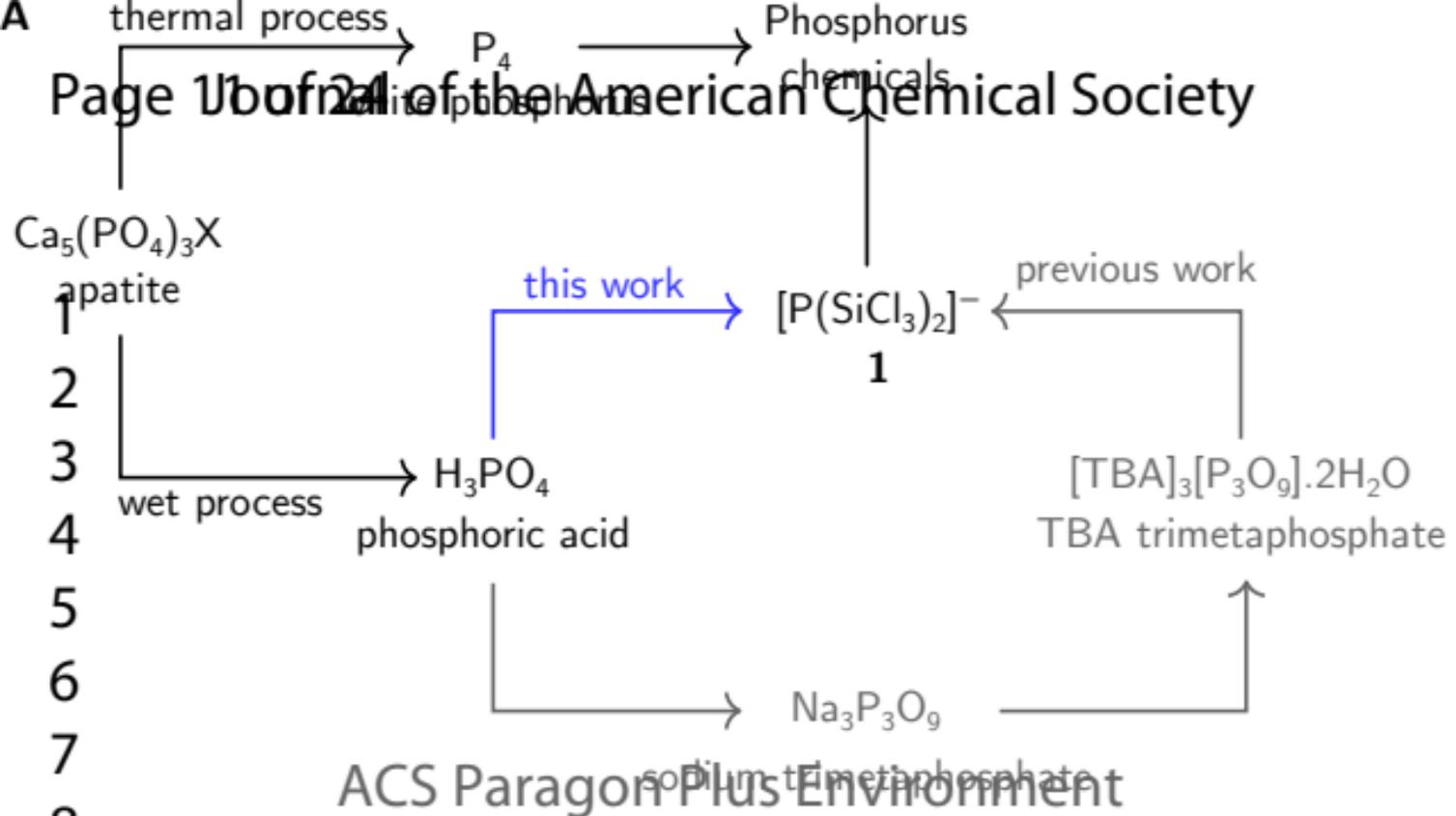
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Graphical TOC Entry





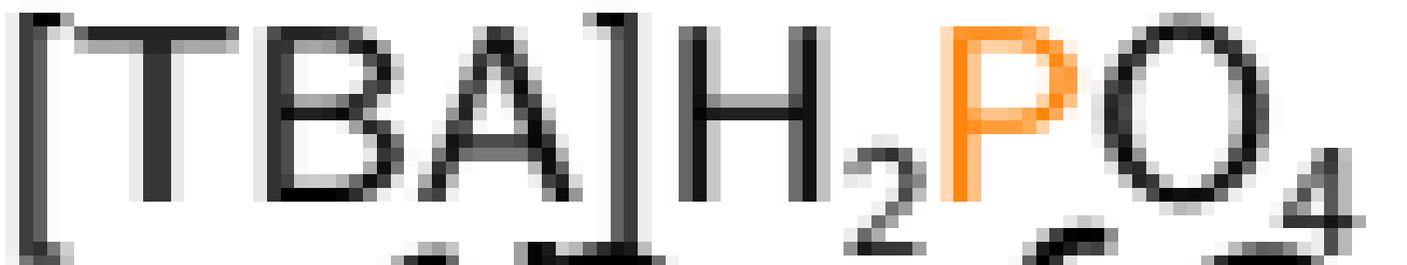
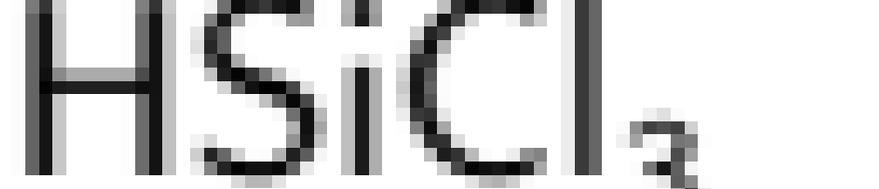
1 ACS Paragon Plus Environment

$\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{Cl}$ ~~1.5 g of the American Chemical Society of 24H_2~~

HSiCl_3 , 110°C , 6 d

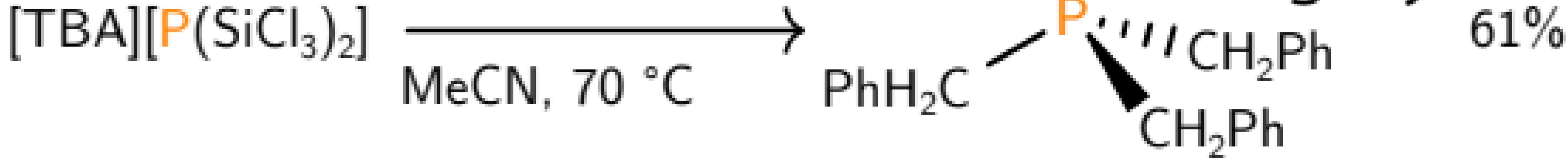
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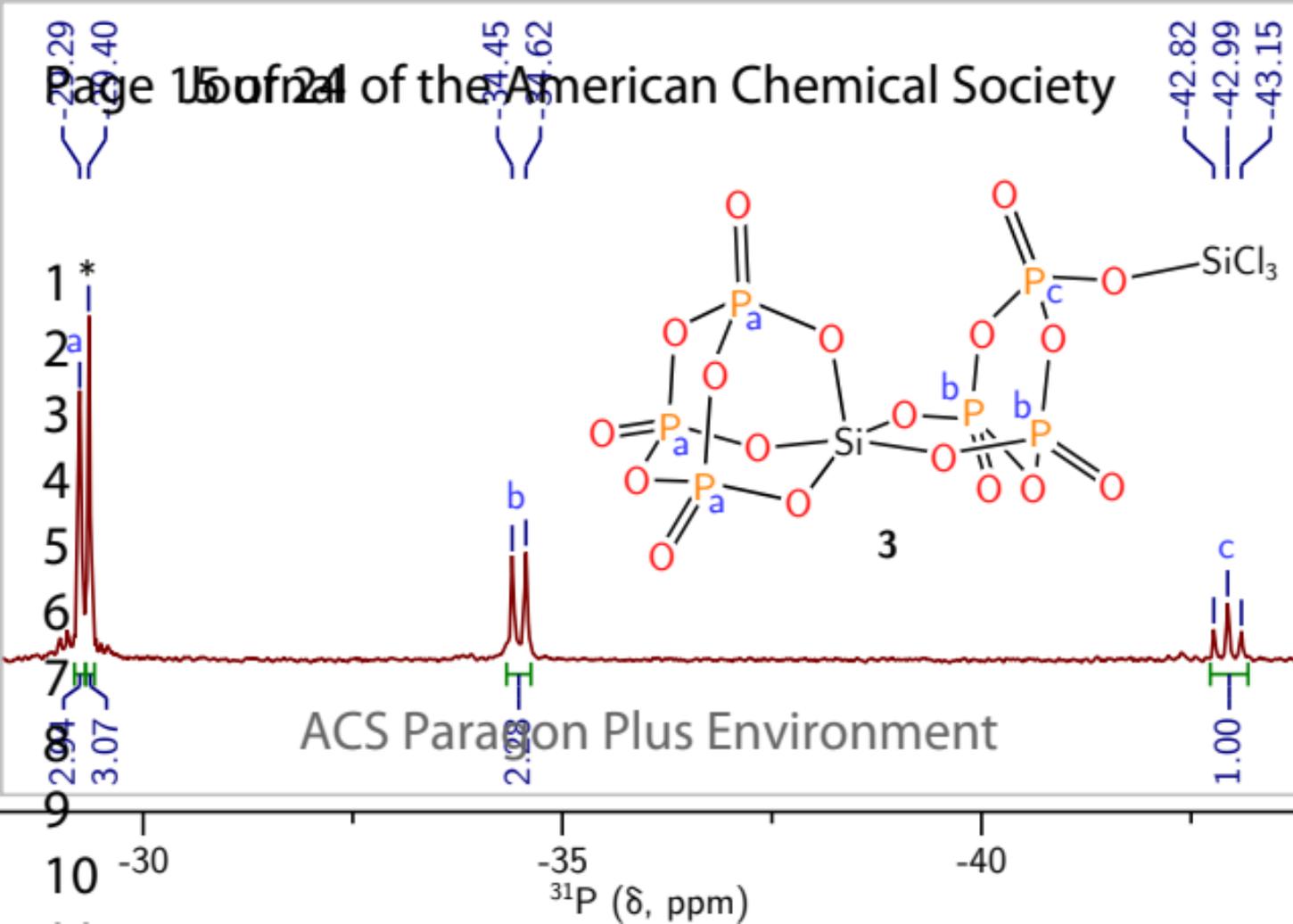
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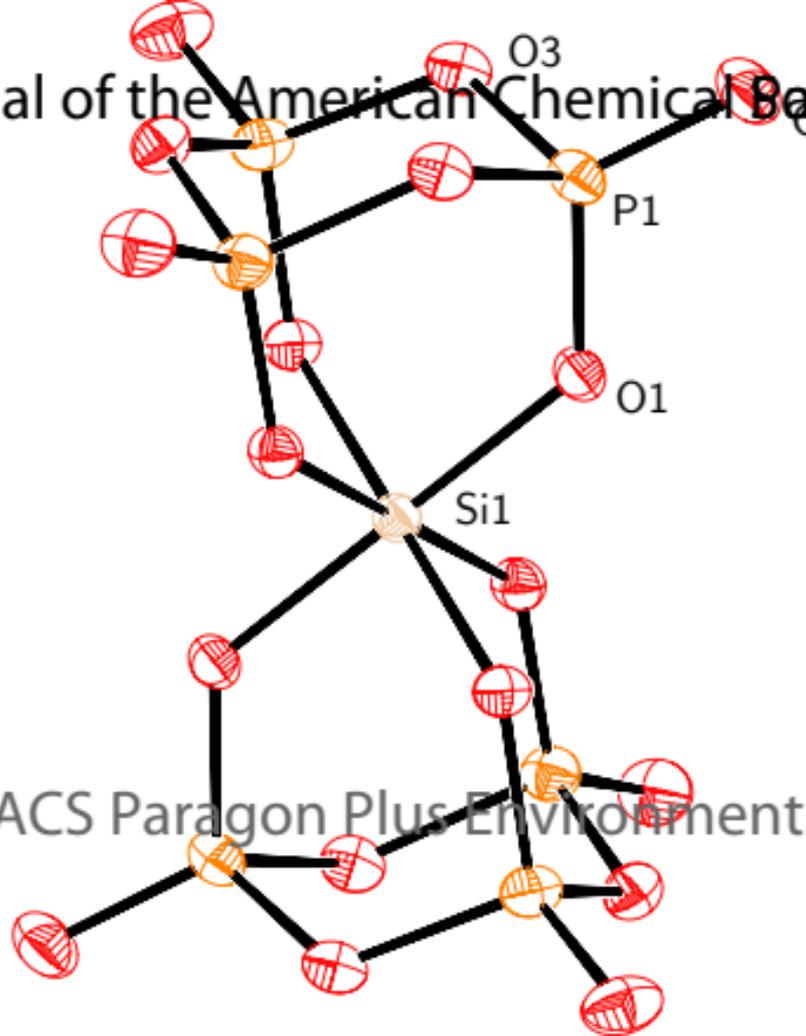
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Package 160 of ~~Ad~~ of the American Chemical Society





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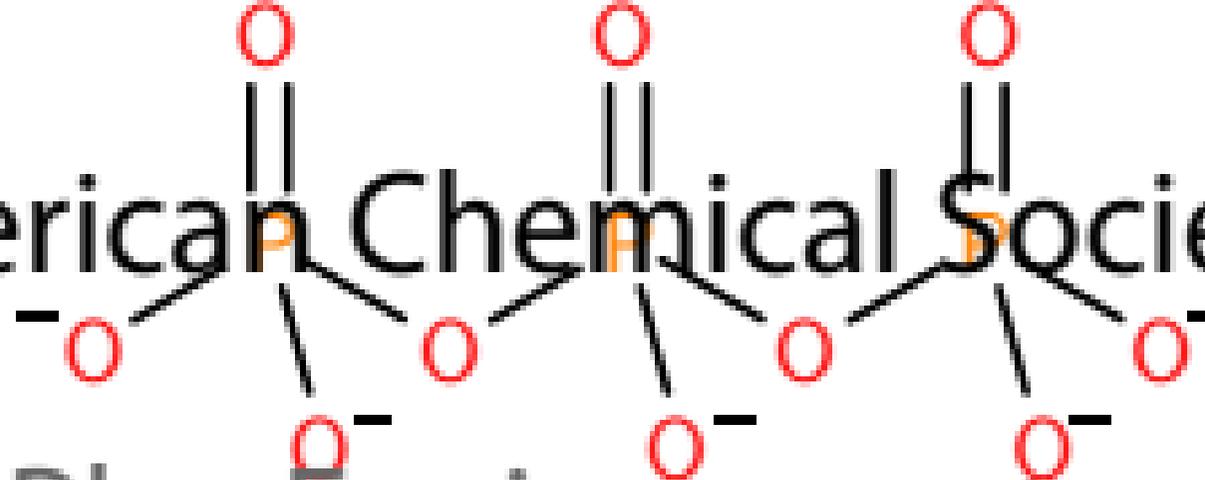
[TBA][Cl] (1 equiv.)

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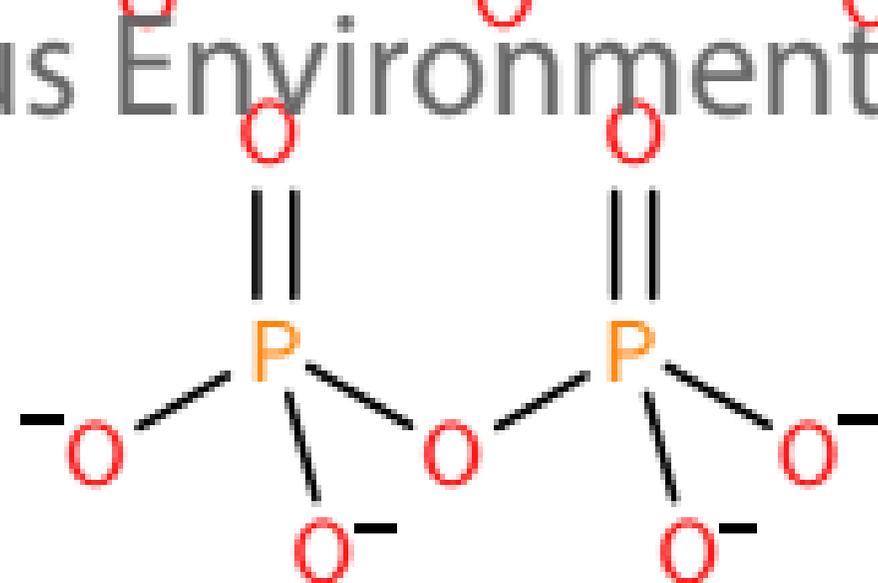
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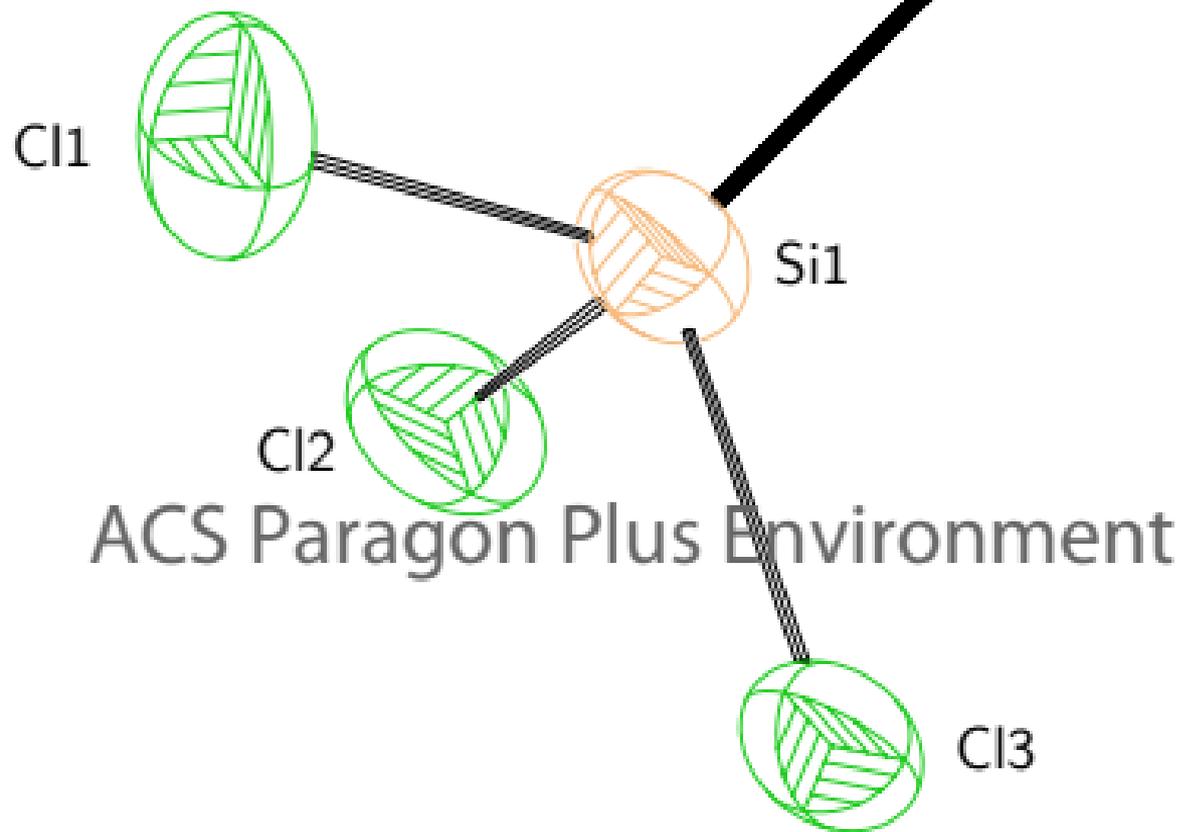


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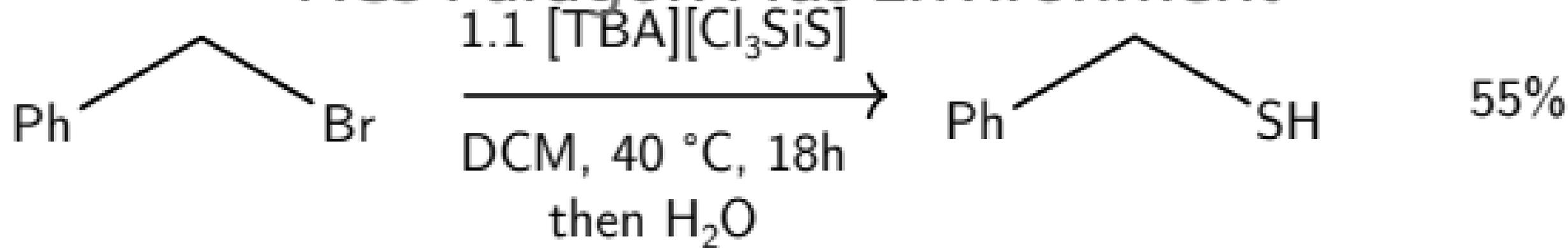
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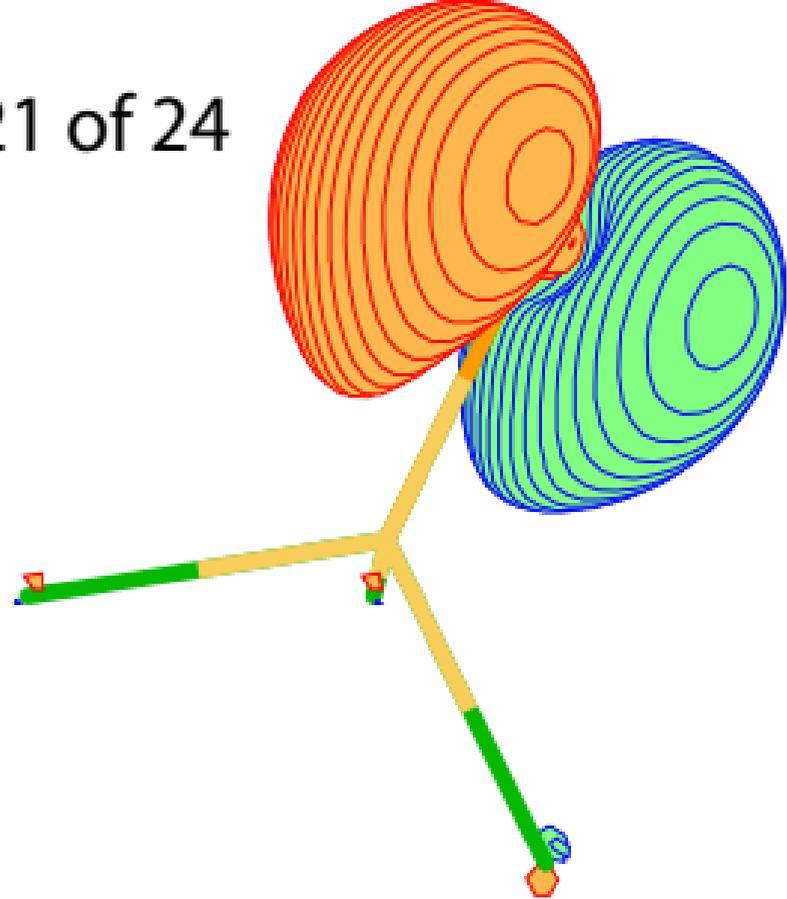
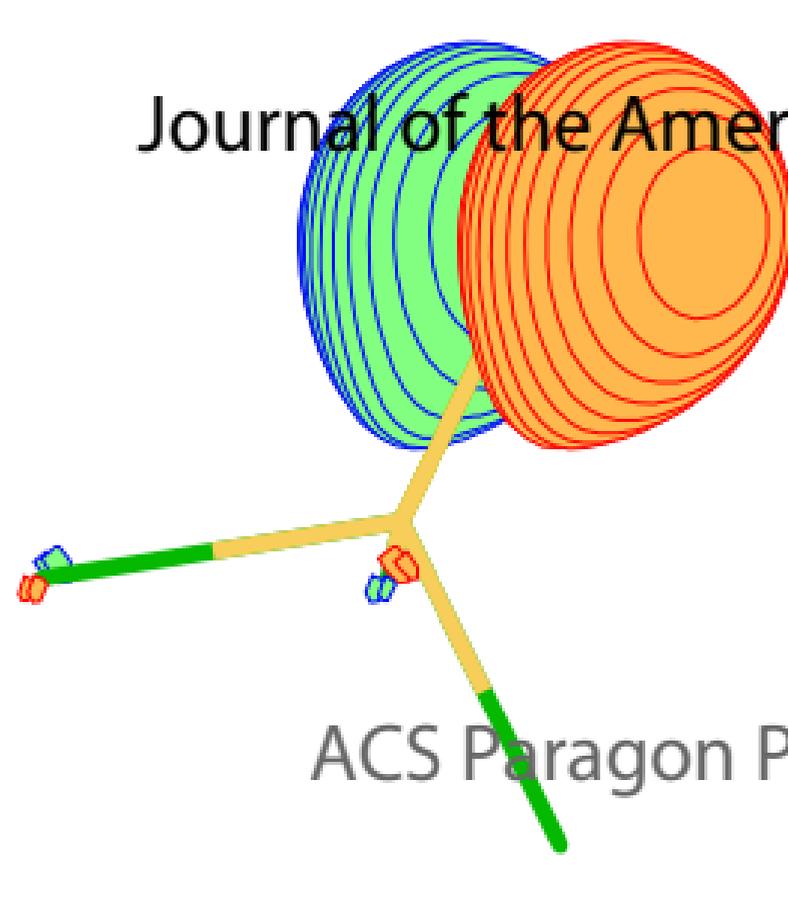




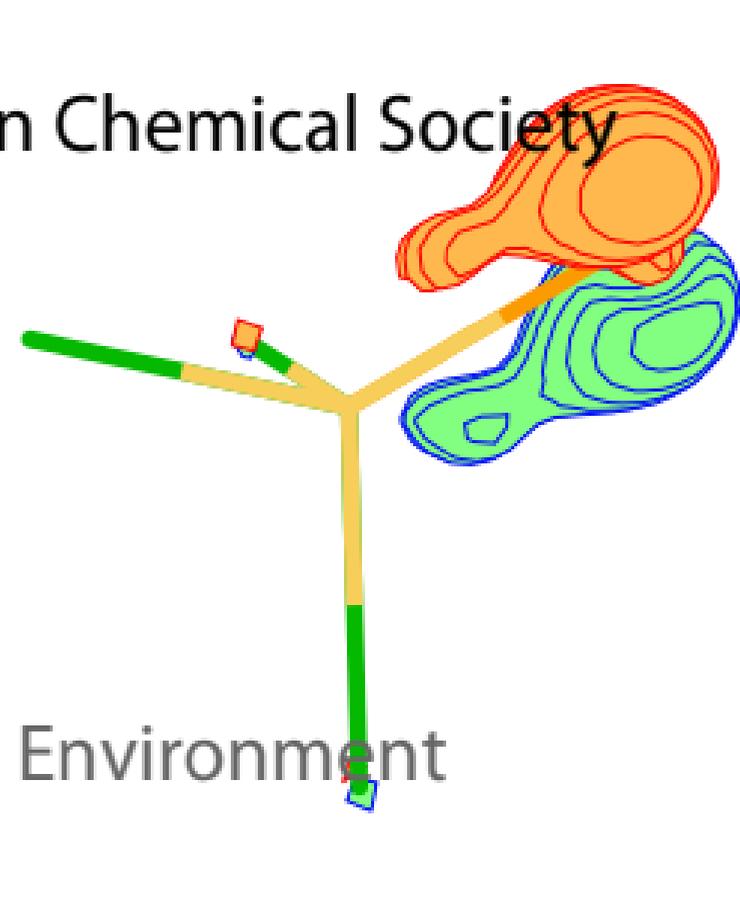


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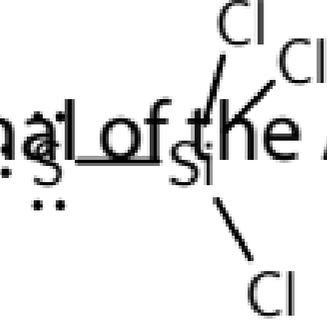


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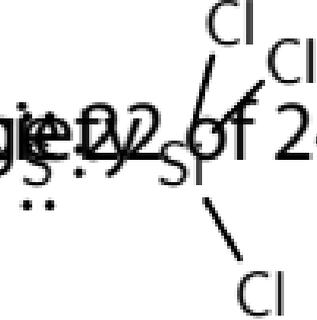
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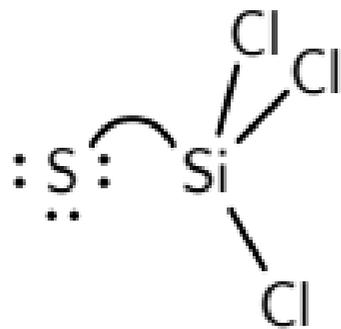
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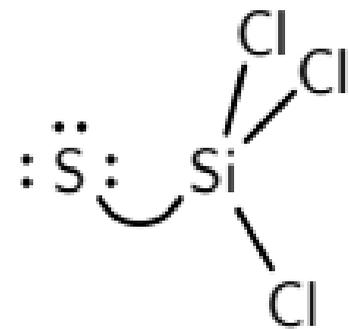
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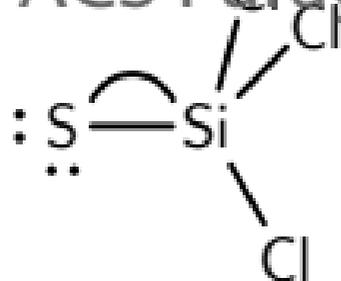
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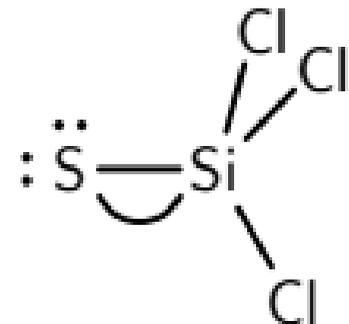
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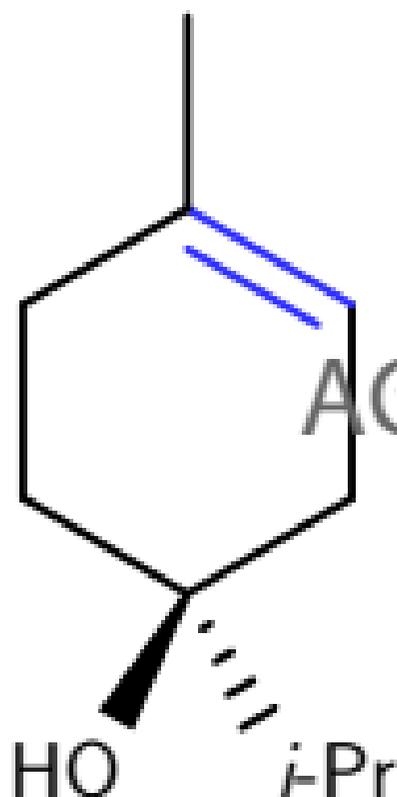
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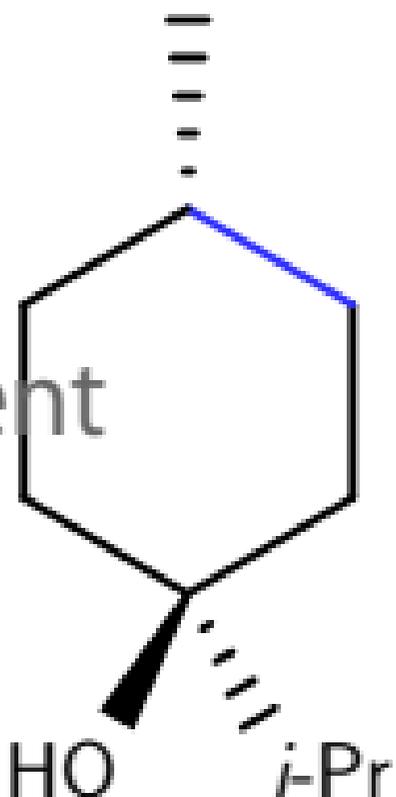


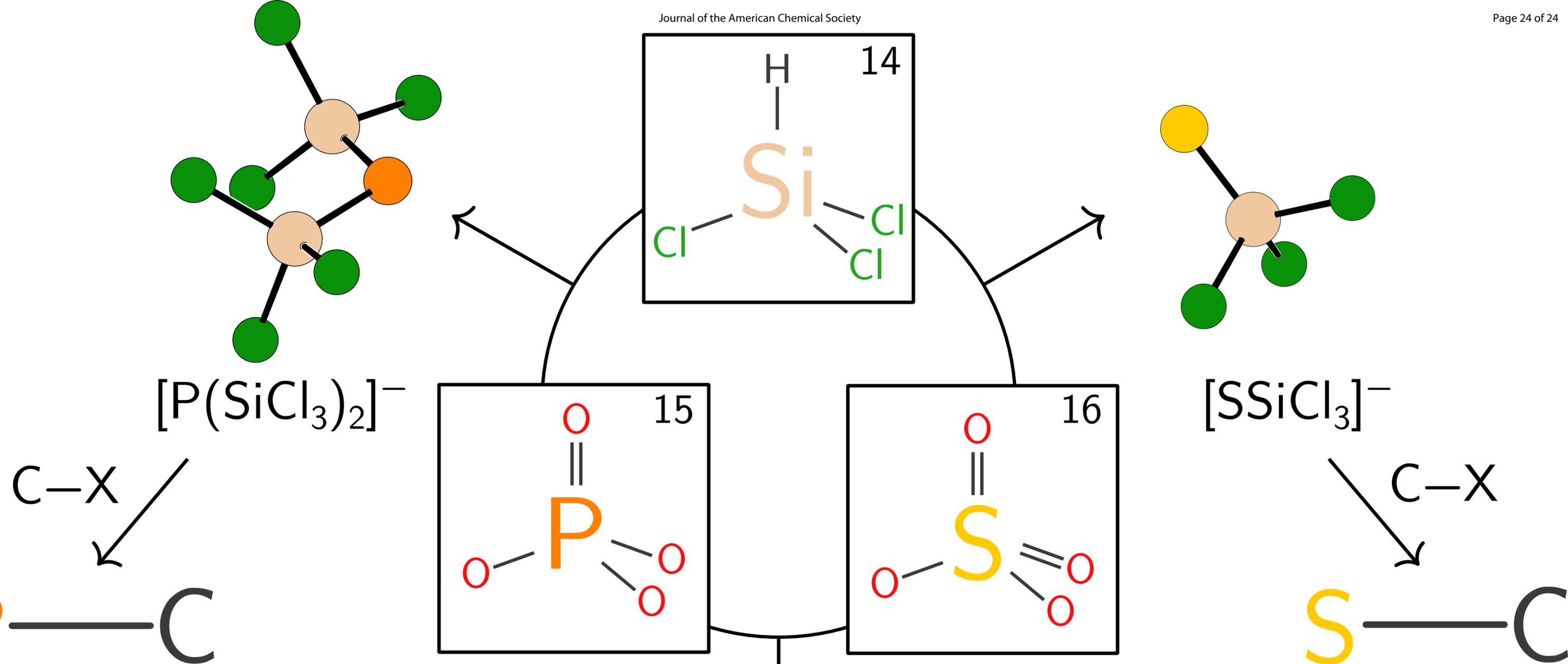
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