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Room-temperature reduction of sulfur hexafluoride with metal phosphides†

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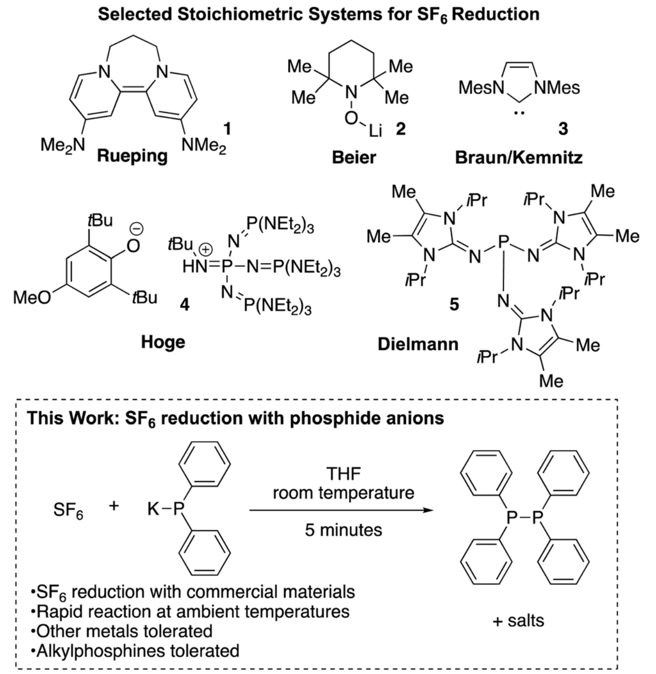
Upon treatment with sulfur hexafluoride, alkali metal diphenyl or dicyclohexyl phosphides are oxidized within seconds to tetraphenyl or tetracyclohexyl diphosphines. When bulky di-*tert*-butylphosphide is employed, fluorophosphine intermediates are detected. This is the first reported reaction of sulfur hexafluoride with metal phosphides, and a rare example of reactivity of sulfur hexafluoride at ambient temperature.

Sulfur hexafluoride (SF_6) is an industrially used gas, with many applications depending on its density, high dielectric constant, and relative inertness. An unfortunate side effect of this relative inertness is that SF_6 released into the atmosphere has a lifetime of thousands of years, resulting in it having the highest global warming potential (∼23 500 relative to CO_2 over a 100 year time-frame) of any commonly used industrial gas.[1] SF_6 is used most extensively in electrical equipment as an insulator and arc-quencher.[2] This application, involving the use of many thousands of tonnes of SF_6, mandates controls on its use and release.[3] Because of the high global warming potential of SF_6, and its common use, chemistry to decompose surplus SF_6 is a sought after goal. The stability of SF_6 arises from a kinetic barrier to decomposition, rather than high thermodynamic stability. The central sulfur is well shielded by the fluorides from nucleophilic attack. Harsh conditions, such as exposure to Lewis acids at high temperature and pressure, or electric-arc plasmas have been used to decompose sulfur hexafluoride.[4] More recently, several relatively mild solution-phase strategies resulting in stoichiometric reaction of SF_6 with a reductant have been disclosed. Low valent early metal complexes, and electron rich nickel complexes are fluorinated by SF_6.[5] SF_6 is reduced by solvated electrons in ammonia solutions.[6] The reaction of SF_6 with butyllithium has been reported in a patent, however limited analysis was provided.[7]

Select examples of main-group molecules that react with SF_6 are shown in Scheme 1. Rueping showed reduction of SF_6 in solution using Murphy's electron-donor reagent **1**.[8] Beier showed reduction of SF_6 using the lithium salt of the TEMPO anion **2**.[9] Braun and Kemnitz showed fluorination of N-heterocyclic carbene **3** by SF_6 under UV irradiation.[10] Hoge showed reduction of SF_6 with an electron rich phenolate anion/protonated phosphazene pair **4**.[11] Dielmann employed a nucleophilic super-basic phosphine complex for stoichiometric SF_6 activation.[12] While this manuscript was under revision, a manuscript from Crimmin appeared, showing the reaction of an aluminum(I) complex with SF_6.[13]

Catalytic reactions for functionalization of SF_6 have also been reported. Building on earlier stoichiometric work with



Scheme 1 Selected stoichiometric systems for SF_6 degradation.

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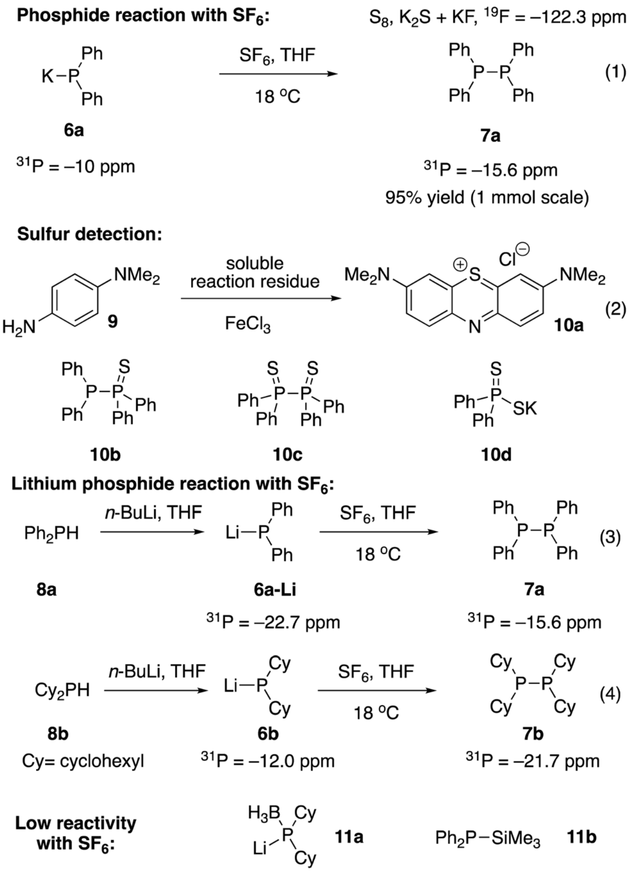
rhodium,[14] Braun reported rhodium-complex catalyzed decomposition of SF_6 with phosphines as sulfur scavengers and silanes as the terminal reductant.[15] Several photoredox systems that activate SF_6 have been reported. SF_6 has recently been used by Jamison as a fluorinating reagent for allylic alcohols employing ruthenium and iridium-complex photosensitizers.[16] Nagorny showed fluorination of carbohydrates using benzophenone-based photosensitizers.[17] Wagenknecht showed phenothiazine-derived photosensitizers allow addition of SF_5 radicals derived from SF_6 to substituted styrenes.[18] Despite the relative simplicity of the systems shown in Scheme 1, access to most of these SF_6-reactive examples require multi-step synthesis or relatively harsh conditions, so there is still much room for discovery of simple SF_6-reactive systems. Inspired by Dielmann's use of strongly basic phosphines for SF_6 functionalization, we explored if simply employing the conjugate base (*i.e.* metalation) of a secondary phosphine could afford reactivity with SF_6. Phosphides have been used in other small molecule activations, notably alkali di-*tert*-butylphosphides were shown by Stephan to activate H_2.[19]

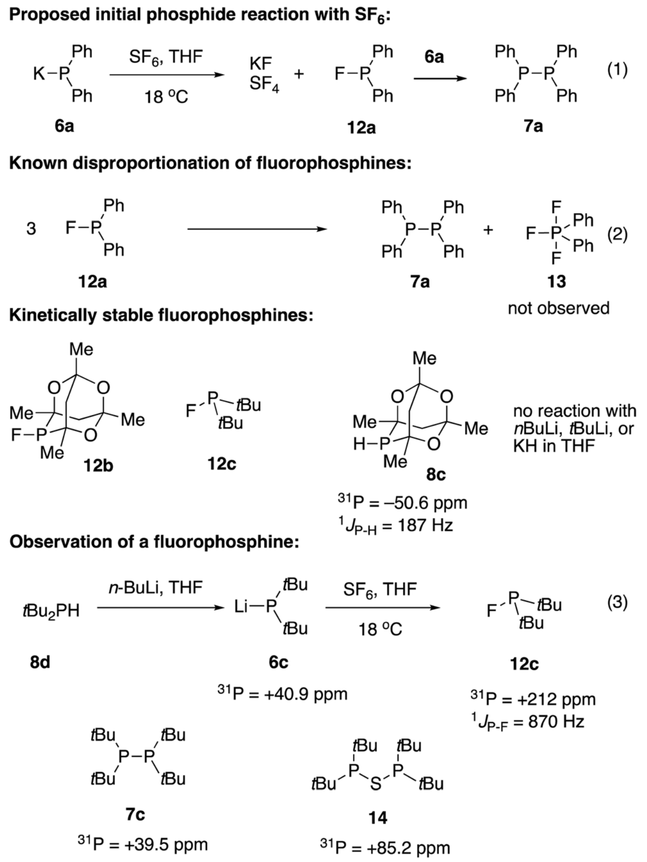
We found metal phosphides are highly reactive with SF_6. Bubbling SF_6 through a commercially available solution of potassium diphenylphosphide **6a** in THF resulted in disappearance of the deep orange colour within seconds (eqn (1), Scheme 2).[20] Analysis of the reaction mixture by ^{31}P NMR spectroscopy revealed complete consumption of phosphide, and the formation of tetraphenyldiphosphine **7a**. The reaction was relatively clean. Analysis of the reaction mixture by ^{19}F NMR spectroscopy revealed no sharp peaks associated with new products, however excess SF_6 is observed in solution. Despite this, we were able to account for the fate of the fluoride. The volatiles were removed, and the resulting solids were extracted with water and dichloromethane. ^{19}F NMR spectroscopy of the aqueous layer showed a strong signal attributed to KF. The sulfur had multiple fates. Testing the aqueous solution for sulfide with an acidic solution of **9** and ferric chloride resulted in the formation the characteristic colour of methylene blue **10a**, a classic test for sulfide ion (eqn (2), Scheme 2).[21] Inspection of the ^{31}P NMR spectra revealed minor products corresponding to phosphorus sulfides **10b** and **10c**.[22,23] Compound **10d** was observed in the NMR spectra acquired in THF, but was insoluble in chloroform or diethyl ether. Compounds **10b** and **10c** likely arose from reaction of **7a** with sulfur(0) during the reaction, while **10d** arose from corresponding reaction of phosphide **6a** with sulfur(0). We verified independently that **7a** and **6a** formed these compounds upon reaction with elemental sulfur in THF. We tested for remaining elemental sulfur by adding triphenylphosphine to a suspension of the reaction residue in acetonitrile, and also residue that was freed of soluble phosphines by extracting with solvent and centrifuging, but no formation of triphenylphosphine sulfide was observed in either case.[24] The reaction was conducted on a 1 mmol scale with no loss of efficiency, and **7a** was isolated from this reaction in 95% yield.



Scheme 2 Reaction of aryl and alkyl phosphides with SF_6.

A temperature rise was observed during this larger reaction. Metalation of diphenylphosphine **8a** with *n*-BuLi followed by introduction of SF_6 also resulted in formation of **7a** showing that other metals could be used (eqn (3), Scheme 2).[25] Dicyclohexylphosphine **8b** was also deprotonated by butyllithium and upon treatment with SF_6, oxidative dimerization to **7b** was observed within seconds, indicating the reaction was not limited to aryl phosphides (eqn (4), Scheme 2).[26] Other metalloids were unreactive, phosphide-borane adduct **11a** did not show appreciable reaction,[27] and silyl-phosphine $TMSPPh_2$ **11b** was also unreactive. These results indicate significant anionic character is necessary on the phosphorus centre for this reaction to proceed rapidly and cleanly. One mechanistic scenario involves polar activation of SF_6, where anion **6a** attacks a fluorine atom on SF_6, precedented by Dielmann's observation of nucleophilic reactivity of super-basic phosphines with SF_6.[12] While this would initially form fluorophosphine **12a**, which was not detected, **12a** could react with additional diphenylphosphide **6a** to form **7a** (Scheme 3, eqn (1)). Compound **12a** is also known to disproportionate into **7a** and phosphorane **13** (Scheme 3, eqn (2)).[28] We did not observe **13** in the reaction mixture, suggesting if **12a** is formed, the reaction with **6a** is faster than disproportionation.

This does not rule out the possibility of formation and subsequent reduction of **13** by additional phosphide. An alternate mechanistic possibility involves reduction initiated by single electron transfer from the phosphide to SF_6, generating the phosphinyl radical ($Ph_2P^\bullet$) and a SF_6 radical anion.[29]



Scheme 3 Further reactivity studies.

The SF_6 radical anion would undergo further fragmentation.[16] Most reported SF_6 reduction reactions invoke single electron transfer to SF_6 as the initial step, so this is a reasonable scenario, however the reducing agents used in those reactions were weak nucleophiles, in contrast to this system.[8,9,11,16,17] Alternatively, the phosphinyl radical could abstract a fluorine atom from a reduced sulfur fluoride intermediate, forming **12a**.[30] The radical scenarios would generate the same products in eqn (1), Scheme 3, as proposed for a polar mechanism, since phosphinyl radicals rapidly dimerize in solution to form **7a**.[31]

Lower oxidation state sulfur fluorides such as SF_4 were not observed by ^{19}F NMR spectroscopy. In general, highly reactive free lower fluorides of sulfur have not been observed in SF_6 reduction reactions, with the exception of the pentafluorosulfanyl anion (SF_5^-), which has been observed in Rueping's, Hoge's, and Dielmann's systems.[8,11,12] These systems have diffuse counterions that impart kinetic stability to SF_5^-, however instability of SF_5^- with simple cations such as potassium or lithium has been noted.[32] We did not detect SF_5^-, and it is unlikely this fragile anion would survive with the simple alkali metal cations originating from the phosphides used in this work.

In the reactions shown in Scheme 2, while **6a** did not produce any compounds that exhibited coupling to ^{19}F in the ^{31}P spectrum, traces of fluoride-containing phosphorus compounds were observed in the reaction that formed cyclohexyl compound **7b** (eqn (4), Scheme 2). Increased steric bulk is known to stabilize fluorophosphines. Unlike **12a**, fluorophosphines **12b** and **12c** are stable.[33] We sought to generate the appropriate phosphides to see if **12b** and **12c** could then be prepared by treatment with SF_6. Caged phosphine **8c** was resistant to deprotonation by *n*-BuLi, *t*-BuLi, or KH in THF over multiple hours, with the P–H bond remaining intact as ascertained by proton-coupled ^{31}P NMR spectroscopy.[34] Di-*tert*-butylphosphine **8d** was deprotonated with *n*-BuLi in THF to generate **6c**.[35] Upon exposure to SF_6, fluorophosphine **12c** was generated, and observed by ^{31}P and ^{19}F NMR spectroscopy, supporting our hypothesis that fluorophosphines are intermediate formed in the reactions of phosphides with SF_6.[36] The ability to stop at the fluorophosphine intermediate was presumably due to the greater steric hinderance of the *tert*-butyl groups relative to phenyl or cyclohexyl, however in addition to **12c**, dimer **7c** was still observed. Another prominent signal in the ^{31}P NMR spectrum at +85.2 ppm was observed, this closely matched that reported for compound **14** in an independent preparation.[37] Compound **14** could be expected to form from either the reaction of sulfide ion with **12c**, or the reaction of sulfur with **7c** followed by rearrangement.

In conclusion, these results represent rare examples of room-temperature reactivity of SF_6. In contrast to some previously reported systems, the reaction proceeds without the need for light irradiation. In addition, the reaction only takes seconds, and is to the best of our knowledge, the first example of a controlled reaction of a commercially available substance with SF_6 at ambient temperature. While this reaction conveniently generates diphosphines from the corresponding phosphides, its utility is limited by the high environmental burden of SF_6, so we did not conduct a large substrate scope. Of greatest conceptual importance is the discovery of a new example of an accessible reaction that consumes the potent greenhouse gas SF_6. While the high reactivity of potassium diphenylphosphide limits large scale application of this method for SF_6 remediation, one potential application could be use of this technique to dispose of small amounts of SF_6 residues from applications such as retinal surgery,[38] or in field-servicing electrical equipment,[2] that would otherwise be released into the atmosphere. The bleaching of the orange diphenylphosphide gives a convenient indication of when the reagent is exhausted. Investigation of phosphorus-based systems for remediation of SF_6 capable of catalytic turnover with appropriate terminal reductants is underway and will be reported in due course.[39]

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Conflicts of interest

There are no conflicts of interest to declare.

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