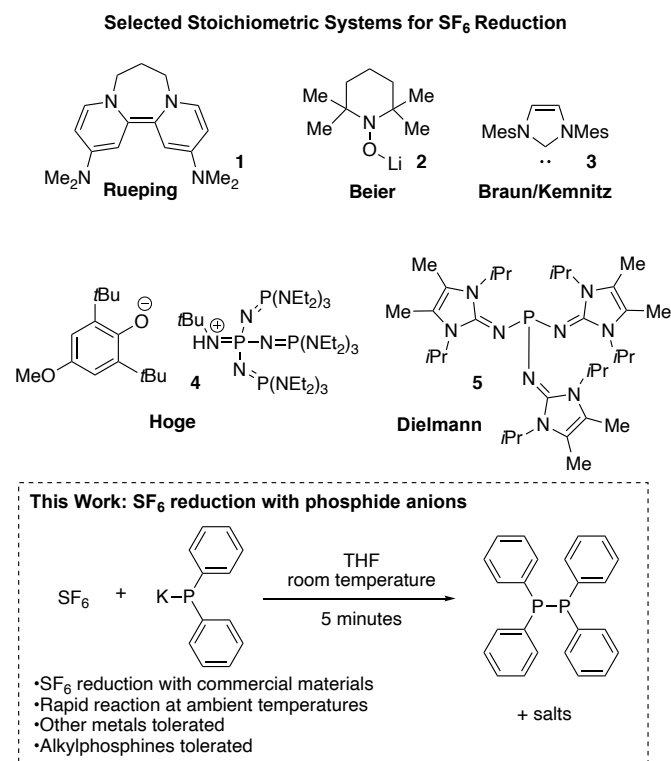


Room-Temperature Reduction of Sulfur Hexafluoride with Metal Phosphides

Blake S. N. Huchenski, Alexander W. H. Speed*

Upon treatment with sulfur hexafluoride, alkali metal diphenyl or dicyclohexyl phosphides are oxidized within seconds to tetraphenyl or tetracyclohexyl diphosphines. In a hindered example, di-*tert*-butylphosphide, 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 (~23500 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 remains 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 from nucleophilic attack by the fluorides. 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



Scheme 1. Selected stoichiometric systems for SF_6 degradation

Select examples of main-group molecules that react with SF₆ are shown in Scheme 1. Rueping showed reduction of SF₆ in solutions using Murphy's electron-donor reagent **1**.⁷ Beier showed reduction of SF₆ using the lithium salt of the TEMPO anion **2**.⁸ Braun and Kemnitz showed fluorination of N-heterocyclic carbene **3** by SF₆ under UV irradiation.⁹ During the course of this work, Hoge showed reduction of SF₆ with an electron rich phenolate anion/protonated phosphazene pair **4**.¹⁰ Dielmann employed a nucleophilic super-basic phosphine complex for stoichiometric SF₆ activation.¹¹

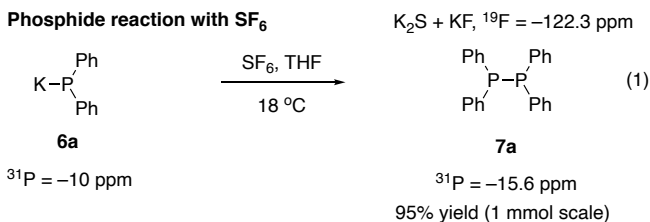
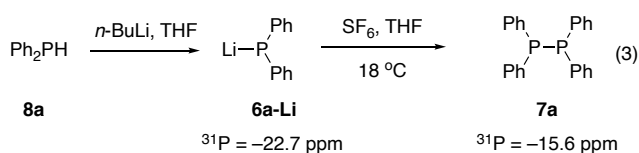
Catalytic reactions for functionalization of SF₆ have also been reported. Braun and coworkers have reported rhodium-complex catalyzed decomposition of SF₆ with phosphines as sulfur scavengers and silanes as the terminal reductant.¹² Several photoredox systems that activate SF₆ have been reported. SF₆ has recently been used by Jamison as a fluorinating reagent for allylic alcohols employing ruthenium and iridium complex photosensitizers.¹³ Nagorny showed fluorination of carbohydrates using benzophenone-based photosensitizers.¹⁴ Wagenknecht showed phenothiazine-derived photosensitizers have allowed addition of SF₅ radicals derived from SF₆ to 1,1-diphenylethylene.¹⁵

Despite the relative simplicity of the systems shown in **Scheme 1**, access to most of these SF₆-reactive examples require multi-step synthesis or relatively harsh conditions, so there is still much room for discovery of simple SF₆-reactive systems. Inspired by Dielmann's use of strongly basic phosphines for SF₆ functionalization, we explored if simply employing the conjugate base (ie metalation) of a secondary phosphine could result in an increase in basicity sufficient to afford reactivity with SF₆. Phosphides have been used in other small molecule activations, notably alkali di-*tert*-butylphosphides were recently shown by Stephan to activate dihydrogen.¹⁶

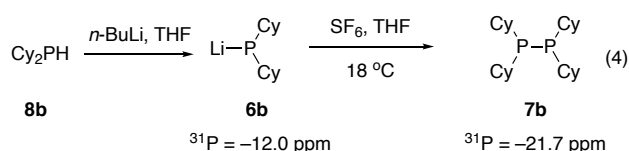
Gratifyingly, metal phosphides proved to be highly reactive with SF₆. Bubbling SF₆ through a commercially available solution of potassium diphenylphosphide **6a** in THF resulted in disappearance of the deep orange colour within seconds (Equation 1, Scheme 2).¹⁷ Analysis of the reaction mixture by ³¹P NMR spectroscopy revealed complete consumption of phosphide, and the formation of tetraphenyldiphosphine **7a**. The reaction was relatively clean. Analysis of the reaction mixture by ¹⁹F NMR spectroscopy revealed no sharp peaks associated with new products, however excess SF₆ 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 pentane and diethyl ether (toluene), resulting in removal of **7a**. The remaining solids were dissolved in water and ¹⁹F NMR spectroscopy showed a strong signal attributed to KF. To detect sulfide, exposure of the aqueous solution to acidic N,N-dimethylphenylenediamine **9** and ferric chloride resulted in the formation of the blue colour characteristic of methylene blue **10**, which is a classic test for sulfide ion (Equation 2, Scheme 2).¹⁸ This was not a quantitative test, and materials that were insoluble in both organic solvents and water were noted, which may be elemental sulfur or polysulfides.

The reaction was conducted on a 1 mmol scale with no loss of efficiency, and **7a** was isolated from this reaction in 95% yield, albeit with some inseparable phosphine oxide impurities. A temperature rise was observed during this larger reaction. Metalation of diphenylphosphine **8a** with butyllithium in THF followed by introduction of SF₆ also resulted in formation of **7a** showing that other metals could be used (Equation 3, Scheme 2).¹⁹

The sulfide detection test also gave a strong blue colour with material from this reaction. Dicyclohexylphosphine **8b** was also deprotonated by butyllithium and upon treatment with SF₆, a similar dimerization to **7b** was observed, indicating the reaction was not limited to aryl phosphides (Equation 4 Scheme 2).²⁰

Phosphide reaction with SF₆**Sulfide detection:****Lithium phosphide reaction with SF₆**

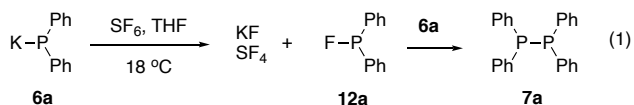
Cy = cyclohexyl

**Low reactivity with SF₆****Scheme 2. Reaction of aryl and alkyl phosphides with SF₆.**

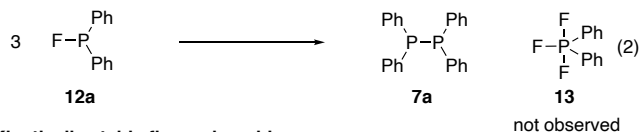
Complete consumption of the phosphide within seconds was again observed. Other metalloids were unreactive, phosphide-borane adduct **11a** did not show appreciable reaction,²¹ and silyl-phosphine, TMSPPH₂ **11** was also unreactive. These results indicate significant anionic character is necessary on the phosphorus centre for this reaction to proceed rapidly and cleanly.

Based on Dielmann's observation of nucleophilic attack by super-basic phosphines on SF₆, we speculated anion **6a** attacks SF₆. While this would initially form fluoride **12a**, which was not detected, electrophile **12a** would be expected to immediately react with additional diphenylphosphide **6a** to form **7a** (Scheme 3, equation 1). Furthermore, compound **12a** is not stable, and is known to disproportionate into **7a** and phosphorane **13** (Scheme 3, equation 2).²² We did not observe **13** in the reaction mixture, suggesting that attack from diphenylphosphide was the faster route to form **12a** though we could not rule out formation of **13** followed by reduction by **6a**.

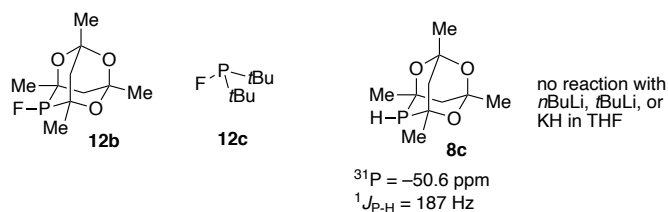
Proposed initial phosphide reaction with SF₆:



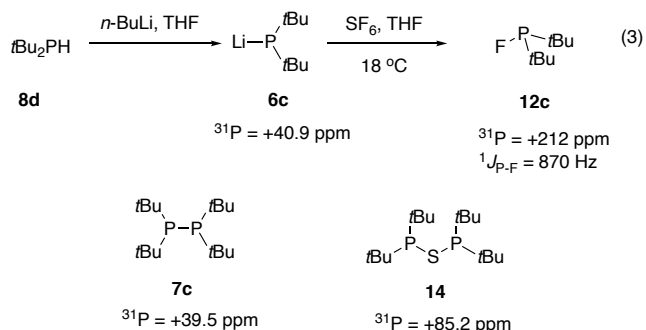
Known disproportionation of fluorophosphines:



Kinetically stable fluorophosphines:



Observation of fluorophosphines:



Scheme 3. Further reactivity studies

Lower sulfides of fluoride such as SF₄ would also be expected to form, however these reactive species were not observed by ¹⁹F NMR spectroscopy, and we expect they were rapidly reduced under these conditions. In general, free lower fluorides of sulfur have not been observed in SF₆ reduction reactions, with the exception of the pentafluorosulfanyl anion (SF₅⁻), which has been observed in Rueping's Hoge's, and Dielmann's systems.^{7,10,11} These systems all have counterions that impart kinetic stability to this anion, however instability of the pentafluorosulfanyl anion with simple cations such as potassium or lithium has been noted.²³ We did not detect SF₅ anion, and it is unlikely this fragile anion would survive the highly nucleophilic phosphides present in this reaction.

Detection of fluorophosphine intermediates would support this mechanistic hypothesis. In the reactions shown in Scheme 2, while the reaction of diphenylphosphides did not produce any compounds that exhibited coupling to ¹⁹F in the ³¹P spectrum, traces of fluoride-containing phosphorus compounds were observed in the reaction that formed cyclohexyl compound **7b** (Equation 4, Scheme 2). We speculated increasing the steric bulk of the phosphide would suppress dimerization. Increased steric bulk is also known to stabilize fluorophosphines. Unlike **12a**, fluorophosphines **12b** and **12c** are known to be stable.²⁴ We sought to generate the appropriate phosphides from the corresponding phosphines to see if **12b** and **12c** could then be prepared by treatment with SF₆. Surprisingly, caged phosphine **8c** was resistant to deprotonation by either *n*BuLi, *t*BuLi or KH in THF over multiple hours, with the P-H bond remaining intact as ascertained by proton-coupled NMR.²⁵ Our attention turned to di-*tert*-butylphosphine **8d**, which was deprotonated by *n*BuLi in THF to generate **6c**.²⁶ Upon exposure of phosphide fluorophosphine **12c** was generated, and observed by

³¹P and ¹⁹F NMR spectroscopy, supporting our hypothesis that fluorophosphines are an intermediate formed in the reactions of phosphides with SF₆.²⁷

The ability to stop at this intermediate, unlike previous examples was presumably due to the greater steric hinderance of the *tert*-butyl groups, however in addition to **12c**, dimer **7c** was still observed. Another prominent signal in the ³¹P NMR spectrum at +85.2 ppm was observed, this closely matched that reported for compound **14** in an independent preparation.²⁸ 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 a rare example of room-temperature reactivity of SF₆. In contrast to some previously reported systems, the reaction proceeds without the need for ultraviolet or violet 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 SF₆ at ambient temperature. While this reaction has potential as a rapid oxidative generation of diphosphines from the corresponding phosphides, its utility is limited by consideration of the high environmental burden of SF₆, accordingly we did not conduct a large substrate scope of phosphides. Of greatest conceptual importance is the discovery of a new example of a highly accessible reaction that consumes the potent greenhouse gas SF₆. While the relatively high reactivity of potassium diphenylphosphide would limit large scale application of this method for SF₆ remediation, one potential application could be use of this technique to dispose of small amounts of SF₆ residues from applications such as retinal surgery,²⁹ or in field-servicing electrical equipment,² that would otherwise be released into the atmosphere. In addition, the notable colour change of the diphenylphosphide reaction gives a good indication of when the reagent is exhausted.

Investigation of other phosphorus-based systems for remediation of SF₆ that are capable of catalytic turnover with appropriate terminal reductants is underway and will be reported in due course.

“There are no conflicts of interest to declare”.

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