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Deoxygenative Fluorination of Phosphine Oxides: A General Route to Fluorinated Organophosphorus(V) Compounds and Beyond

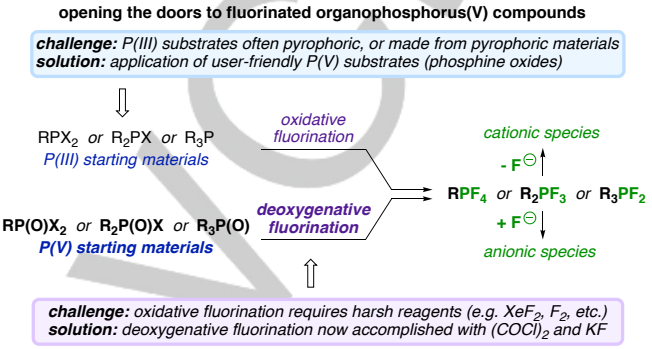
Dustin Bornemann, Cody Ross Pitts,[‡] Lionel Wettstein, Fabian Brüning, Sebastian Küng, Liangyu Guan,[‡] Nils Trapp, Hansjörg Grützmacher,* and Antonio Togni*

Dedicated to Professor Herbert Roesky

Abstract: *Fluorinated organophosphorus(V) compounds are a very versatile class of compounds, but the synthetic methods available to make them bear the disadvantages of 1) occasional handling of toxic or pyrophoric P(III) starting materials and 2) a dependence on hazardous fluorinating reagents such as XeF_2. Herein, we present a simple solution and introduce a deoxygenative fluorination (DOF) approach that utilizes easy-to-handle phosphine oxides as starting materials and effectively replaces harsh fluorinating reagents by a combination of oxalyl chloride and potassium fluoride. The reaction has proven to be general, as R_3PF_2, R_2PF_3, and RPF_4 compounds (as well as various cations and anions derived from these) are accessible in good yields and on up to a multi-gram scale. DFT calculations were used to bolster our observations. Notably, the discovery of this new method led to a convenient synthesis of 1) new difluorophosphonium ions, 2) hexafluorophosphate salts, and 3) fluorinated antimony- and arsenic- compounds.*

Either in neutral, anionic, or cationic forms, fluorinated organophosphorus(V) compounds have demonstrated remarkable applications in organocatalysis (e.g. in C-F bond functionalization,[1–3] carbonyl activation,[2,4] hydrosilylation,[2,5] CO_2 sequestration[3] and olefin hydrogenation[6]), as Lewis acids, in ^{18}F-radiolabeling,[7] as ionic liquids,[8] as well as electrolytes,[9] and may conceivably have untapped potential in other arenas. Yet, despite these known and prospective applications of fluorinated organophosphorus(V) compounds, there is a lack of synthetic methods available to access them in juxtaposition with other compound classes containing fluorinated heteroatoms. Generally, it may be stated that research in fluorine chemistry is notoriously dependent on reagents that are difficult to handle and frequently hazardous reaction conditions must be applied.

An assessment of the state of the art indicates there are two main challenges presented in modern synthesis of fluorinated organophosphorus(V) compounds: 1) the user-friendliness/scalability of the fluorination reaction itself and 2) the prerequisite of handling hazardous starting materials. For instance, the majority of compounds are synthesized via fluorination of substituted phosphines, many of which are either pyrophoric, prepared from pyrophoric materials, or otherwise toxic, and this is accomplished most commonly on a small scale with XeF_2 (although other equally, if not more, hazardous fluorinating reagents have been employed).[1,10–12]



Scheme 1. *The current two-fold accessibility problem surrounding fluorinated organophosphorus(V) compounds and one general solution using the oxalyl chloride/KF approach.*

Herein, we present a simple solution to these challenges in the form of a mild deoxygenative fluorination (DOF) strategy (see Scheme 1) using oxalyl chloride and potassium fluoride that employs phosphine oxides as starting materials. Phosphine oxides are usually bench-stable, easy to handle, and storable for longer times compared to their phosphorus(III) congeners. Harsh fluorination reagents such as XeF_2, HF, SbF_5, and SF_4 are replaced by an innocuous fluoride salt (KF) and oxalyl chloride (a cheap and commercially available reagent due to its applications, e.g., in acid chloride synthesis and Swern oxidation). This new method allows to perform the reactions safely on up to a multi-gram scale. Moreover, purification is often achieved through a straightforward filtration/evaporation procedure.

This oxalyl chloride/KF protocol proved to be general enough to afford alkyl-, aryl-, and heteroaryl-substituted phosphoranes with varying degrees of fluorination (anywhere from 1 to 6 P-F bonds), depending on the starting material employed. Additionally, we note the ability to access assorted neutral, anionic, and cationic P-F species either directly under our reaction conditions, by highlighting applications of established chemistry on new compounds, or by using workup alterations developed over the course of this study. As our reaction conditions have also expanded the scope of accessible products, this has presented additional opportunities to study new P-F species both through SC-XRD and DFT calculations and inspired the investigation of this deoxygenative fluorination strategy on molecules containing group 15 elements beyond phosphorus. Lastly, this study

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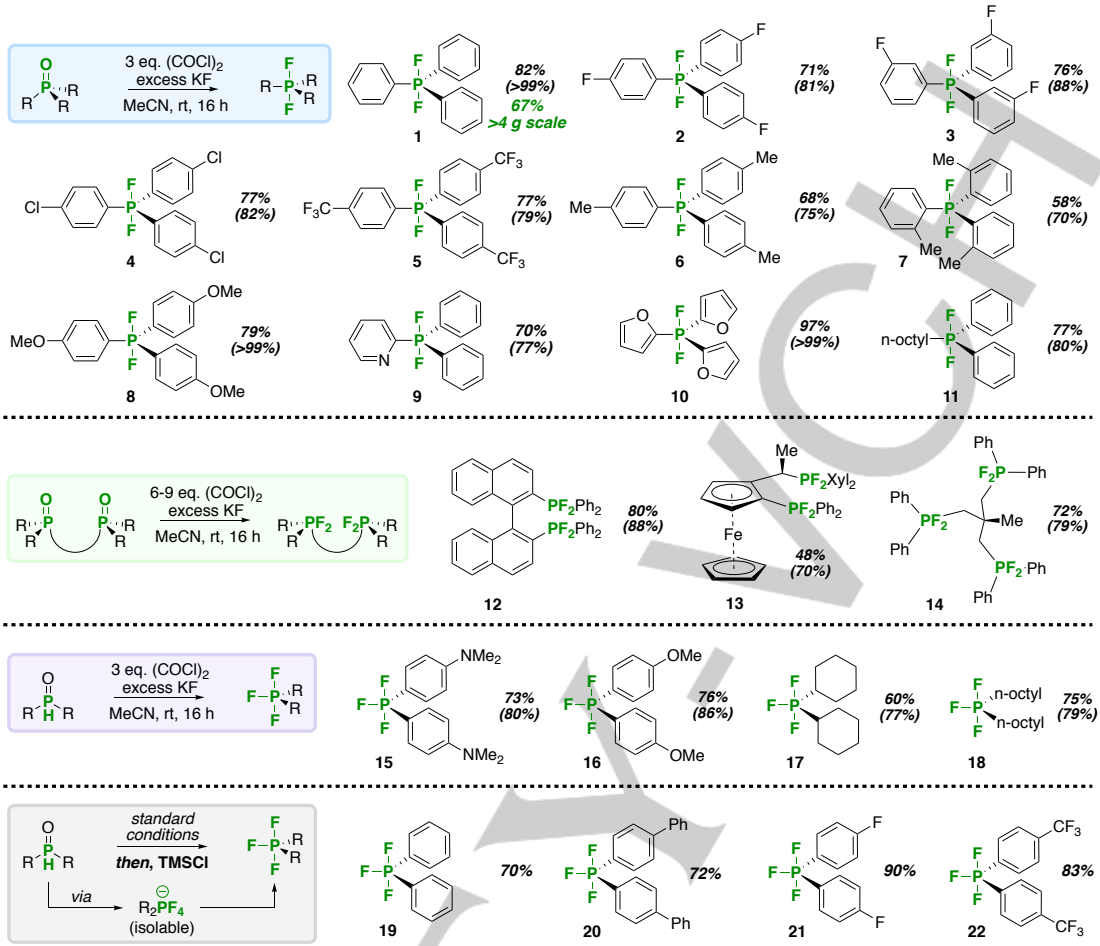


Figure 1. *Substrate scope of R_3PF_2 and R_2PF_3 compounds synthesized using oxalyl chloride/KF conditions. Isolated yields are reported with ^{19}F NMR yields in parentheses.*

facilitated the synthesis and characterization of new "R_2PF_2+" phosphonium ions.

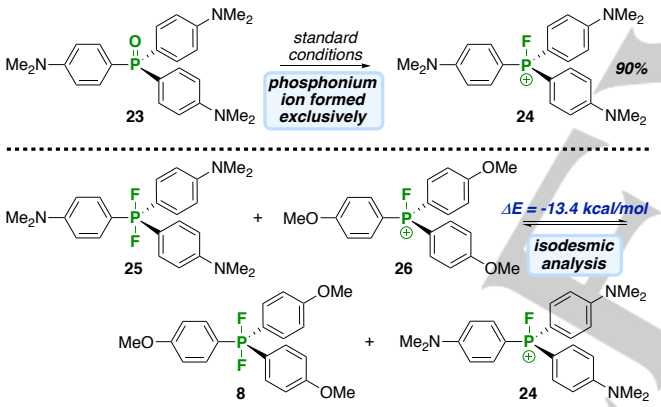
The initial inspiration for this transformation stems from our recent work involving oxidative fluorination of heteroatoms (i.e. S, Se, Te, and I) in organic frameworks using trichloroisocyanuric acid (TCICA) and KF.[13–16] Although in-depth mechanistic studies have not yet been conducted, the formation of heteroatom-chlorine bonds followed by Cl-F exchange processes is suspected to play an important role in these TCICA/KF-based reactions. In previous work by Masaki and Fukui,[17] and later Grimme and coworkers,[18] it was established that P-Cl bonds can be constructed concomitant with deoxygenation by exposing phosphine oxides to oxalyl chloride. Thus, it seemed logical to explore whether P-F bonds could be forged in a similar fashion in the presence of a fluoride source – either through putative generation of oxalyl fluoride *in situ*, Cl-F exchange processes, or otherwise direct fluorination of phosphorus.

Fortunately, we found that triphenylphosphine oxide underwent virtually quantitative conversion to difluorotriphenyl-λ^5-phosphorane (**1**) in the presence of 3 eq. $(COCl)_2$ and 6 eq. KF in MeCN at rt overnight, as assessed by ^{19}F NMR (Figure 1). Complete details of the reaction screening and optimization can be found in the Supporting Information. The chosen optimal conditions are characterized by the lowest possible amounts of $(COCl)_2$ and KF that still afford complete conversion of the starting material. However, the following observations are noteworthy: 1) other metal fluorides, such as CsF and CaF_2 may be employed in place of KF, 2) thionyl chloride may be a suitable surrogate for oxalyl chloride, 3) additives such as TFA and $ZnCl_2$, which have benefitted our TCICA/KF chemistry, only lowered product yields, 4) the reaction can also be performed in acetone, toluene, and EtOAc, though lower yields were observed in some instances, and 5) to circumvent etching of glassware by adventitious HF, polypropylene vessels can be used instead of borosilicate. Additionally, the reaction performed well on a >4-gram scale, providing **1** in 67% yield, thus demonstrating a level of scalability.

With optimized conditions in hand, we proceeded to explore the scope of the reaction with respect to trisubstituted phosphine oxides (Figure 1). Triarylphosphine oxides adorned with either electron withdrawing (**2**-**5**) or electron donating (**6**-**8**) substituents are well tolerated, and the representative examples indicate that *ortho*-, *meta*-, or *para*-substituted Ar_3PF_2 compounds may be accessed in good yields. However, an interesting departure from Ar_3PF_2 compound formation was observed in the presence of an even more potent electron donating group. That is, under standard reaction conditions, the *p*-NMe_2-substituted starting material **23** provided fluorophosphonium compound **24** exclusively in 90% yield (Scheme 2). No Ar_3PF_2 **25** formation was

observed – also not at longer reaction times (see SI for details). Conceivably, this phenomenon is easily rationalized by the increased ability of the *p*-NMe_2 groups to stabilize the positive charge on the phosphonium ion. At a glance, it is curious that no phosphonium ion formation was observed when employing other strong donating groups, such as *p*-OMe groups (hypothetically producing compound **26**), but the notable disparity in Hammett σ_{para} constants (σ_{para}(OMe) = -0.27 vs. σ_{para}(NMe_2) = -0.83) seems to account for the unique reactivity of compound **23**.[19] A calculation of the energy of the isodesmic reaction shown in Scheme 2 is consistent with the experimental observation and shows that the formation of phosphonium ion **24** is 13.4 kcal/mol more favorable than **26** (DFT ωB97XD/6-311++G**).[20,21]

Beyond substituted benzene derivatives, we also discovered that heteroaryl-substituted phosphine oxides are suitable substrates. Pyridine-substituted compound **9** and furan-substituted compound **10** were both formed in good yields, indicating both electron-rich and electron-deficient heteroaromatic substituents are compatible (Figure 1). (Note that compound **9** is a precursor to an established phosphonium ion catalyst used for Friedel–Crafts dimerization, hydrodefluorination, and hydrodeoxygenation, among other reactions).[22] Additionally, we found that alkyl substituents stay intact during deoxygenative fluorination (compound **11**).



Scheme 2. *Direct formation of a fluorophosponium ion under standard reaction conditions (top). Isodesmic reaction calculated with DFT (ωB97XD/6-311++G**) comparing NMe_2 vs. OMe substituent stabilizing effects (bottom).*

It is also possible to achieve deoxygenative fluorination at multiple phosphine oxide reaction sites simultaneously in one pot by scaling the amounts of oxalyl chloride and KF proportionately. For instance, tetra-fluorinated BINAP-derived compound **12** and Xyliphos-derived compound **13** were both obtained from substrates containing two phosphine oxide sites. These products also demonstrate the tolerance of naphthalene, xylene, and ferrocene substituents under standard reaction conditions. Likewise, hexa-fluorinated compound **14** can be formed cleanly from a substrate containing three phosphine oxide sites.

The structures of compounds **4**, **10**, and **14** in the solid state were determined with single-crystal X-ray diffraction methods (Figure 2). All three species exhibit an almost ideal trigonal bipyramidal structure around the central phosphorus atom with F-P-F, C-P-C and C-P-F angles only slightly deviating from the ideal 180°, 120°, and 90° angles, respectively (θ(F-P-F) = 176.23(5)°-179.43(7)°, θ(C-P-C) = 116.17(7)°-125.05(7)°, θ(C-P-F) = 87.95(6)°-92.03(6)°). The P-F and P-C bond lengths are in good agreement with previously characterized R_3PF_2 species (see SI for details). Notably, all furanyl groups in **10** are disordered around the P-C bonds indicating no preferential orientation of this group.

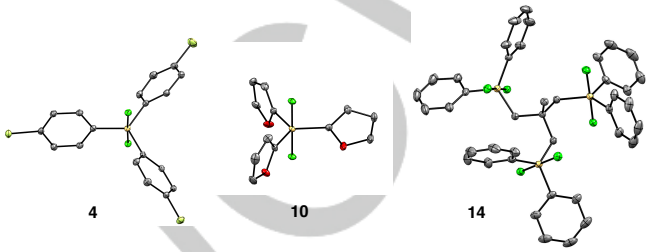
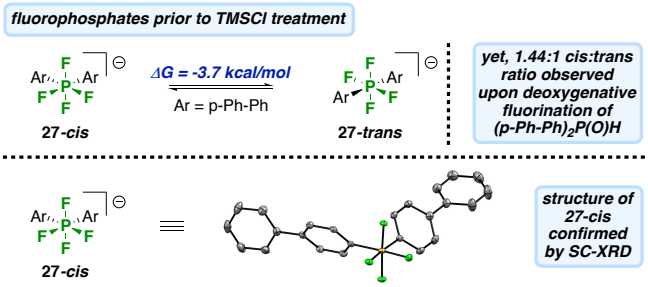


Figure 2. *Molecular structures of **4**, **10**, and **14**, determined by single-crystal X-ray diffraction methods (displacement ellipsoids depicted at 50% probability level; hydrogen atoms omitted for clarity).*

Limitations of the substrate scope are as follows: 1) alkenyl substituents on the central phosphorus atom promoted undesirable and unselective background reactivity, 2) alkynyl substituents were tolerated, but complete conversion of the starting material was often not achieved, and 3) the synthesis of Stephan's established fluorotris(perfluorophenyl)phosphonium catalyst was unsuccessful (see SI for details).[1]

Subsequently, we turned our attention to secondary phosphine oxides to find that either neutral or anionic fluorinated phosphorus(V) compounds are accessible depending on the nature of the starting material, using modified conditions (3 eq. $(COCl)_2$, 8 eq. KF). (Note that the reaction conditions were re-optimized for this substrate class using diphenylphosphine oxide; see SI for details.) The following trends were observed: Substrates with aryl- or alkyl-based electron rich substituents bound to the phosphorus atom provide R_2PF_3 compounds directly (e.g. **15**-**18**; Figure 1). Substrates with electron neutral or withdrawing substituents bound to phosphorus favor conversion to $K[R_2PF_4]$ compounds. The preference for fluorophosphate formation in the latter case is likely due to the enhanced Lewis acidity and lower steric encumbrance at the central atom in R_2PF_3 compared to R_3PF_2.



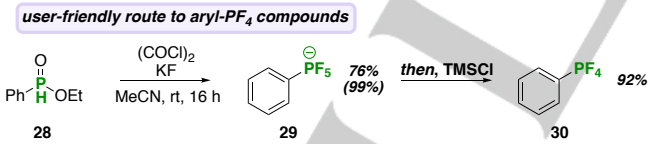
Scheme 3. *Top: Gibbs free energy analysis (DFT ωB97XD/6-311++G**) not in accordance with observed preference for **27-cis**. Bottom: Molecular structure of **27-cis** determined by SC-XRD (displacement ellipsoids depicted at 50% probability level; hydrogen atoms omitted for clarity).*

Accordingly, the role of electron donating substituents is to stabilize the neutral R_2PF_3 species over the anionic phosphate – a noteworthy parallel to the aforementioned ability to stabilize the cationic phosphonium over the neutral R_3PF_2 species by leveraging substituent effects.

The $K[R_2PF_4]$ compounds may be easily isolated. It is worth mentioning that coordination of the additional fluoride opens up the possibility of obtaining a mixture of isomers. (The geometry about the phosphorus atom changes from trigonal bipyramidal to octahedral.) For instance, bis(biphenyl)phosphine oxide provided the bis(biphenyl)tetrafluorophosphate isomers **27-*cis*** and **27-*trans*** in a 1.44:1 *cis:trans* ratio. While the *trans* isomer was calculated to be 3.7 kcal/mol lower in energy than the *cis* isomer (DFT ωB97XD/6-311++G**), this was not consistent with our observation (Scheme 3). In this light, it is possible that either the preference for **27-*cis*** is under kinetic control or the inconsistency could be attributed to limitations of the computational method.

Additionally, we were able to obtain single crystals suitable for an X-ray diffraction study of *cis*-di(biphenyl)tetrafluorophosphate **27-cis** (Scheme 3). The molecular structure exhibits the expected octahedral coordination sphere around the central phosphorus atom, with almost ideal bond angles (see SI for details). To the best of our knowledge, this is the only (diaryl)tetrafluorophosphate solid-state structure reported to date.

Although fluorophosphate(V) compounds may be of interest in their own right, we sought to address the limitation of accessing R_2PF_3 compounds with electron neutral or withdrawing R groups. Taking inspiration from the fluoride abstraction capabilities of silyl cations, we found that $K[R_2PF_4]$ compounds can be converted to their R_2PF_3 congeners by addition of TMSCl during the workup.[23] This TMSCl treatment is a simple and elegant solution, as 1) the resultant KCl precipitates out of solution rapidly and can be filtered off, 2) both TMSF and remaining TMSCl are volatile and can be removed *in vacuo*, and 3) TMSCl will not remove an additional fluoride from R_2PF_3 compounds, providing the neutral species exclusively. Using this approach, the previously inaccessible "electron-deficient" R_2PF_3 compounds in the presence of KF were isolated in good yields (e.g. **19**-**22**; Table 1).



Scheme 4. *Oxalyl chloride/KF approach with TMSCl treatment offers convenient access to both pentafluoro(aryl)phosphate(V) and tetrafluoro(aryl)-λ⁵-phosphorane (aryl-PF₄) compounds. Isolated yields are reported with ¹⁹F NMR yields in parentheses.*

Having successfully achieved the synthesis of R_3PF_2 and R_2PF_3 species, as well as to some of their phosphonium and phosphate congeners, with the DOF method, we next focused on the preparation of RPF_4 compounds. We examined the reactivity of ethyl phenylphosphinate (**28**), which, we hoped, would have a sufficiently labile ethoxy substituent that effectively could be displaced by fluoride (Scheme 4). Indeed, $K[PhPF_5]$ (**29**) formed quantitatively as indicated by ^{19}F NMR spectroscopy. Moreover, in a separate step, the TMSCl treatment was applied in order to obtain $PhPF_4$ (**30**). Notably, both steps must be carried out under meticulously dry conditions to avoid irreversible formation of $PhPOF_2$ by hydrolysis of either **29** or **30**. We also found that, instead of **28**, $PhPCl_2$ can be used as a convenient starting material to afford **29** and **30** (in 82% and 92% yield, respectively) analogously under standard reaction conditions (see SI for details). Tetrafluoro(organyl)-λ⁵-phosphoranes are generally more difficult to access than many of the fluorinated organophosphorus(V) compounds mentioned in Figure 1, with syntheses relying exclusively on hazardous reagents such as AsF_3, SbF_3, SF_5Cl, and PF_5, among others.[10,12,24,25]

This result stimulated a brief investigation of the lability of a number of P-X bonds under deoxygenative fluorination conditions, where, for instance, X = H, OR, NR_2, or SR (Figure 3). Interestingly, this study showed that P-OR bonds are converted to P-F bonds only under certain conditions in combination with hydride or amino substituents at the phosphorus center. For example, the P-OR bonds stay intact when the phosphorus-bound hydrogen substituent of **28** is replaced with another alkoxy substituent as in **31** and, furthermore, *the deoxygenative fluorination reaction shuts down entirely*. A similar trend was noted for diphenylphosphine oxide derivatives: When X = H as in **35**, the reaction proceeds to form $K[Ph_2PF_4]$ (**34**), though when X = OR as in **32**, no reaction occurs. However, when X = N of an amino substituent like in morpholinyl and present in **33**, $K[Ph_2PF_4]$ formation occurs in high yield. The behavior of P-S and P=S bonds under fluorination conditions was also studied using Lawesson's reagent **36**; we found that all phosphorus-sulfur bonds are readily cleaved to provide **37**.

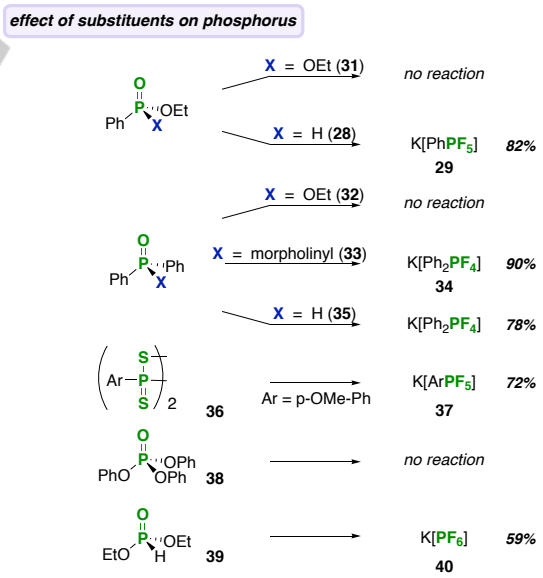
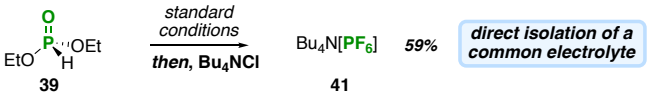


Figure 3. *Effects of phosphorus substituents on deoxygenative fluorination outcomes under standard reaction conditions. Isolated yields are reported.*

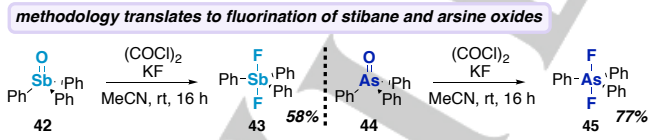
So far, these examples showed that various P-X bonds in phosphine oxides can be converted to P-F bonds in the presence of one or two P-C bonds. But will deoxygenative fluorination occur

in the absence of any P-C bonds? To investigate this, triphenyl phosphate $(PhO)_3P{=}O$ **38** was reacted with $(COCl)_2$/KF and, unsurprisingly, it was found to be unreactive (Figure 3). Conversely, diethyl phosphite **39**, in which one alkoxy substituent is replaced with a P-H bond, readily converts to K[PF_6] (**39**). As a complement to existing methodologies (e.g. fluorination of PCl_5), oxalyl chloride/KF conditions provide an alternative, viable approach to the synthesis of hexafluorophosphate salts (which have known applications as electrolytes in batteries and in electrochemistry) in addition to fluorinated organophosphorus(V) compounds.[9,26,27] Furthermore, the hexafluorophosphate ion can be readily precipitated and obtained in pure form as Bu_4NPF_6 (**41**) during the workup upon addition of Bu_4NCl (Scheme 5) from **39** and our standard conditions. This demonstrates a novel and straightforward route to Bu_4NPF_6 – a common electrolyte used in electrochemistry – via a deoxygenative fluorination approach.



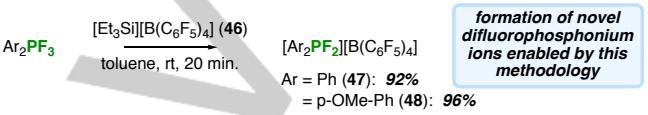
Scheme 5. *Direct conversion of diethylphosphate **39** to $Bu_4N[PF_6]$ **41** using standard oxalyl chloride/KF conditions followed by precipitation using Bu_4NCl. Isolated yield is reported.*

We also briefly entertained the extension of this fluorination chemistry to other group 15 elements, namely As and Sb. Notably, triphenylstibane oxide **42** and triphenylarsane oxide **44** undergo DOF to form **43** and **45**, respectively, in good yields (Scheme 6). Unlike many of their phosphorus congeners, difluorotriaryl-λ^5-stibanes may be subjected to purification via column chromatography and have found applications as precursors to pentavalent organoantimony compounds in main-group element chemistry.[28–31] As a consequence of harsh starting materials (AsF_3) and reagents (IF_5, HF, etc.), difluorotriaryl-λ^5-arsanes are less explored but have demonstrated some potential applications as fluorinating reagents.[32] Although a complete investigation of antimony- and arsenic-based substrate reactivity is beyond the scope of this study, these initial results serve as proof of concept that oxalyl chloride/KF-based deoxygenative fluorination can translate beyond phosphorus in group 15 elements.



Scheme 6. *Application of methodology to deoxygenative fluorination of triphenylstibane oxide and triphenylarsine oxide. Isolated yields are reported.*

Lastly, fluorophosphonium ions have a crucial role as catalysts in C-F bond functionalization, and we contemplated ways in which our deoxygenative fluorination chemistry could contribute to advancements in this field.[1–3,5] We were able to synthesize new "R_2PF_2+" difluorophosphonium ions as tetra(pentafluorophenyl)borate salts **47** and **48** (from **19** and **16**) using silyl salt **46** (Scheme 7) as fluoride abstraction reagent. Although **47** and **48** could not be obtained a single-crystals and their detailed structures are not yet known, some ^{19}F and ^{31}P NMR features are noteworthy. For instance, **47** and **48** exhibit very large $^1J_{F\text{-}P}$ coupling constants of 1131 and 1159 Hz respectively, in good agreement with the dimesityldifluorophosphonium ion with $^1J_{F\text{-}P}$ = 1204 Hz reported by by Olaru and coworkers. These values are larger than in R_3PF^+ fluorophosphonium ions such as $[(C_6F_5)_3PF][B(C_6F_5)_4]$ ($^1J_{F\text{-}P}$ = 1062 Hz), possibly indicating shorter P-F bonds in **47** and **48**.[1,33] The calculation of the enthalpy in an isodesmic reaction involving **47** and **48** shows that the latter is more stable by 8.1 kcal/mol [DFT ωB97XD/6-311++G** (see SI for details)], which we attribute to the electron donating effect of the p-OMe-substituents in the arene ring]. The efficacy of such difluorophosphonium ions as easily tunable Lewis-acidic catalysts shall be explored in future work.



Scheme 7. *Synthesis of novel difluorophosphonium cations **47** and **48**. Isolated yields are reported.*

In conclusion, this report discloses a new and highly versatile deoxygenative fluorination (DOF) protocol by which phosphine oxides are converted to fluorinated organophosphorus(V) compounds using the combination of oxalyl chloride and KF as relatively user-friendly reagents. This approach is practical and scalable, and can be applied to a wide range of substrates. This new method also allows the preparation of hexafluorophosphate salts and can be extended to fluorinated antimony- and arsenic-compounds. Moreover, the easy access to Ar_2PF_3 compounds now allows the synthesis and characterization of Ar_2PF_2+ ions which are largely unexplored

It is our hope that this method not only aids members of the synthetic community working in this field already but enables others who may not be willing to work with hazardous fluorinating reagents on scale.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Key words: fluorine, phosphorus, deoxyfluorination, fluorophosphates, phosphonium fluorides

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[34] CCDC 2013558 (**4**), 2013559 (**10**), 2013560 (**14**), 2015080 (**27-cis**).

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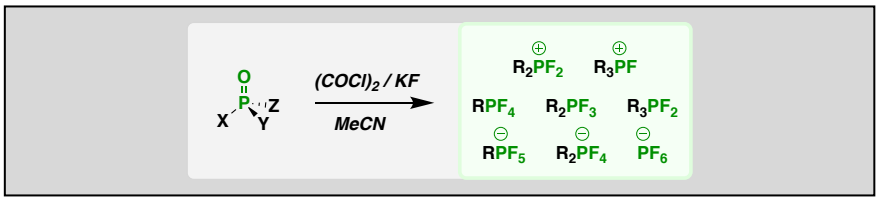
Entry for the Table of Contents



Fluorinating Phosphorus is No Fuss for Us! A mild, deoxygenative fluorination approach was developed using only oxalyl chloride and potassium fluoride to access a broad variety of fluorinated phosphorus(V) compounds in neutral, cationic, or anionic forms. The method circumvents working with both pyrophoric starting materials and hazardous fluorinating reagents, making fluorinated group 15 heteroatoms in organic frameworks more accessible.