Synthesis, Reactivity and Structural Properties of Trifluoromethylphosphoranides

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In memoriam Alexander A. Kolomeitsev.

Abstract: Phosphoranides are interesting hypervalent species which serve as model compounds for intermediates or transition states in nucleophilic substitution reactions at trivalent phosphorus substrates. Herein, the syntheses and properties of stable trifluoromethylphosphoranide salts are reported. [K(18-crown-6)][P(CF₃)₃] and [K(18-crown-6)][P(CF₃)₃]F were obtained by treatment of trivalent precursors with sources of CF₃⁻ or F⁻ units. These [P(CF₃)₃]⁻ salts exhibit fluorinating (n = 1–2) or trifluoromethylation (n = 0) properties, which is disclosed by studying their reactivity towards selected electrophiles. The solid-state structures of [K(18-crown-6)][P(CF₃)₃] and [K(18-crown-6)][P(CF₃)₃]F are ascertained by single crystal X-ray crystallography. The dynamics of these compounds are investigated by variable temperature NMR spectroscopy.

Introduction

To date, a number of hypervalent phosphorus compounds has been studied, including phosphoranides which feature a formally negatively charged, tetracoordinated phosphorus atom. They turned out to be useful models for the intermediates or transition states in nucleophilic substitution reactions at trivalent phosphorus substrates.[1] In general, phosphoranides are accessible by three major approaches, namely the addition of X⁻ to a phosphorus(III) compound (Lewis acid-base interaction),[2] deprotonation of a pentavalent phosphorane PR₄=P=X,[3,4] or oxidation of an anionic and monovalent species, such as [P(CN)₃]⁻ by Cl₂ or Br₂.[5] As a rule of thumb, phosphoranides have to be stabilized by electron-withdrawing substituents X with a low tendency to function as leaving groups at the same time. The first phosphoranide to be isolated was [PBr₅]⁻, followed by the chloro- and fluoro-analogues [PCl₅]⁻ and [PF₅]⁻.[2,5,6] However, tetraiodo phosphoranide [PI₅]⁻ has eluded observation so far, which is in line with the decreasing acceptor properties of the phosphanes within the homologous series. In solution, the equilibrium between PX₅ and [PX₅]⁻ lies well on side of the educts for X = Br and to some extent on side of the educts for X = Cl, whereas it lies on side of the phosphorane for X = F.[2,5,6] Structurally, the phosphoranides are derived from a trigonal bipyramid, with the sterically active lone-pair in an equatorial position. Axial and equatorial substituents of the [PX₅]⁻ ion are interconverted via Berry pseudo rotation resulting in indifferent NMR resonances at room temperature. However, the exchange is slowed down at low temperatures, facilitating the differentiation of two types of substituents via NMR spectroscopy.[6] Apart from the aforementioned tetrahalophosphoranides, a few cyclic organophosphoranides have also been described.[2,7] Moreover, a few derivatives have been prepared containing both, organic residues and (pseudo-)halide groups at the phosphorus atom, for example [PR(CN)₅]⁻ with R = Me, Et, Ph, CF₃, and X = CI, Br, I.[6] Basically, halide substituents at [PX₅]⁻ may be replaced by perfluoroalkyl functionalities. Thus, trifluoromethylated phosphoranides had been predicted to be relatively stable, long before their verification by experiment.[1] The homoleptic tetrakis(trifluoromethyl)phosphoranide has been authenticated as an anion in the extremely unstable salt [(Me₃N)₅]⁺[P(CF₃)₃]⁻ and in a slightly more stable, but nevertheless still very reactive and pyrophoric, tetramethylammonium derivative, [(NMe₄)₅]⁺[P(CF₃)₃]⁻.[6] A similar increase in stability has been observed for the corresponding salts [(Me₃N)₅]⁺[P(CF₃)₃]F and [(NMe₄)₅]⁺[P(CF₃)₃]F. The difluorobis(trifluoromethyl)-phosphoranide [P-
(CF3)2F] results from difluorocarbene extrusion of [P(CF3)2F]+ or by addition of NMeF to the phosphine P(CF3)2F.[15] So far, detailed NMR-spectroscopic and crystallographic examinations of these compounds have been thwarted by their instability. The most suitable starting material for the preparation of trifluoromethyl-containing phosphoranes is P(CF3)2, which is well known as a ligand in transition metal coordination chemistry.[12] This phosphine may be prepared for example by treatment of CF3I with white phosphorus, by reaction of Cd(CF3)2 with Ph2 by reduction of the phosphorane (CF3)2PF3, or by combining CF3Br with P(NEt3)2 and P(OPh)3.[13] The aforementioned methods, however, all have significant drawbacks, since they are either inconvenient, cost-intensive or require the employment of toxic or environmentally harmful compounds. Thus, an alternate synthesis involving relatively non-hazardous, commercially available reagents was developed. The reaction of triphenyl phosphite with Me3SiCF3 in the presence of an equimolar amount of CsF afforded P(CF3)2 in 98% yield. Using only catalytic amounts of CsF, at least 90% yield were accomplished.[14]

Herein, we would like to report upon the synthesis, properties, and reactivity of stable trifluoromethyl phosphoranes derived from P(CF3)2.

Results and Discussion

P(CF3)2 (1) was obtained by treatment of P(OPh)3 with Me3SiCF3 in the presence of small amounts of NMeF or KOPh in ethereal solvents, after a modified literature procedure.[14] The reaction is performed in the temperature range 20 to 50 °C, affording phosphine 1 in yields of 80–85% (Scheme 1).[15] The starting materials are preferably used stoichiometrically to avoid contamination with by-products. An excess of the phosphite leads to the formation of (CF3)2P(OPh)3 and CF3H, whereas larger amounts of the silane mainly produce traces of CF3H. The product is easily pumped off and subsequently distilled at atmospheric pressure.

Treatment of P(CF3)2 (1) with Me3SiCF3 in the presence of fluoride salts leads to the formation of corresponding [P(CF3)2]+ salts. To obstruct the notorious tendency to decompose, the [NMe4]+ ion in [NMe4][P(CF3)2][15] should be replaced by more bulky cations, such as [K(18-crown-6)]+ which previously allowed synthesis and X-ray structural characterization of [K(18-crown-6)][P(CF3)2].[16] Therefore, we attempted the preparation of stable phosphoranes [P(CF3)2F]+ and [P(CF3)2]+ by combination of P(CF3)2 with KF/18-crown-6 or KF/Me3SiCF3/18-crown-6, respectively. Compounds [K(18-crown-6)][P(CF3)2] (2) and [K(18-crown-6)][P(CF3)2]+ (3) are accessible by this approach in 92% and 98% yield (Scheme 2).[15] Attempts to prepare pure salts of the difluorobis(trifluoromethyl)phosphorane ion, [P(CF3)2]+, failed when P(CF3)2 was reacted with NMeF or KF/18-crown-6. With large fluoride excess, a maximum of 60% phosphorane was achieved. In a consecutive reaction of [P(CF3)2]+ with the starting phosphine, [P(CF3)2F]+ (P(CF3)2) was formed as a by-product. The reaction is believed to proceed via an adduct formed by the phosphorane and phosphine, [P(CF3)2F][P(CF3)2]+, and subsequent fluoride transfer.

Interestingly, [NMe4][P(CF3)2]+ (4) is formed, when the mono-trifluoromethyl phosphine (CF3)2PF3 is allowed to react with NMeF in diethyl ether at room temperature (Scheme 2).[15] As a side product, PF3 is liberated, which implies a low affinity between PF3 and CF3+. Therefore, we investigated whether these differences between the mono-trifluoromethylated species and all other attempts to synthesize and detect this species failed. Thus, combination of (CF3)2PF3 with NMeF in CH2CN or treatment of PF3 with NMeF and Me3SiCF3 did not give unambiguous evidence for the transient existence of [NMe4][P(CF3)2F].

Next, we looked at the stability of the novel trifluoromethylphosphorane salts 2 and 3 in comparison to the related [NMe4]+ compounds. Disregarding the nature of the counter ion, most of the trifluoromethylated phosphoranes suffer from facial difluorocarbene elimination, leading to a mixture of (trifluoromethyl)fluoro derivatives.

The facile loss of a CF3 group may be due to the axial 3-center-4-electron bonding. Consistently, apical P–C bonds are weakened in comparison to 2-center-2-electron P–C bonds. In stark contrast to the corresponding [NMe4]+ salts, the decomposition of which commences at about −45°C in dimethoxyethane (DME) solution, derivative [K(18-crown-6)][P(CF3)2] (2) decomposes very slowly at ambient temperature. The stability of 2 is considerably improved in the presence of an equivalent amount of P(CF3)2 (1). Thus, 74% of 2 remained intact after 24 h in DME solution mixed with 1. A similar behavior was encountered for DME solutions of [K(18-crown-6)][P(CF3)2]+ (3)
Analytically pure compounds are only obtained by drying in vacuo at 0 to room temperature. The remarkable instability of the ammonium salt may be rationalized by the reaction of the strong base CF$_3^-$ with [NMe$_4$]$^-$ which would result in the formation of the very reactive and unstable ammonium ylide Me$_3$N$^-$→CF$_3$. Analysis of the decomposition products revealed only traces of P(CF$_3$)$_3$, but significant amounts of CF$_3$H and NMe$_4$. We also found, that CF$_3$ preferentially inserts into α-C–H bonds of ethereal solvents, as it has been described earlier.[16]

Clearly, all trifluoromethyl phosphoranides under discussion are thermally unstable and very reactive. The obtained products are colorless to pale yellow solids which are sensitive towards moisture and oxygen, the latter causing spontaneous ignition. Analytically pure compounds are only obtained by drying in vacuo at 0 to −30 °C. In contrast, drying at room temperature leads invariably to impure samples. Moreover, the phosphoranides are not characterized by sharp melting points, since they always suffer from decomposition prior to liquefaction. Thereby, the [NMe$_4$]$^-$ salts decompose and melt at lower temperatures than the corresponding compounds 2 and 3, featuring cation [K(18-crown-6)]$^+$. Pyrolysis of [NMe$_4$]$^-$ phosphoranides yields mixtures of PF$_3$, P(CF$_3$)$_3$, CF$_3$H and NMe$_4$ in addition to an intractable black solid, whereas [K(18-crown-6)]$^+$ salts mainly liberate P(CF$_3$)$_3$ as well as some PF$_3$ and CF$_3$H. Fast hydrolysis of the phosphoranides in wet DME yields [PH(CF$_3$)$_4$]−(O)(O)−, whereby [P(CF$_3$)$_3$F]$^-$ is slightly less readily hydrolyzed than [P(CF$_3$)$_3$]$_2$F$^-$.

The hydrolysis of [PH(CF$_3$)$_4$](O)(O)$^-$ is very slow, and requires a few drops of aqueous NaOH to produce CF$_3$H and HP(O)(OH)$_2$.

The remarkable reactivity of the phosphoranides under discussion is based upon the loss of an axial ligand which may be conveniently trapped by suitable electrophiles. In keeping with this, P(CF$_3$)$_3$F$^-$ is a powerful trifluoromethylating reagent, whereas the anions [P(CF$_3$)$_3$]$_2$F$^-$ and [P(CF$_3$)$_3$F]$^-$ behave as fluoride donors. This is nicely illustrated by the clean reaction of 2, 3, and 4 with Me$_3$SiCl which furnished products Me$_3$SiCF$_3$ and Me$_3$SiF, respectively.

The ammonium salt [NMe$_4$][P(CF$_3$)$_3$Cl] is generated in quantitative yield, if [NMe$_4$][P(CF$_3$)$_3$F]$_2$ is added to an equimolar amount of Me$_3$SiCl at −30 °C. On the other hand, reactions of the phosphoranides [P(CF$_3$)$_3$]$_2$F$^-$ and [P(CF$_3$)$_3$F]$^-$ with Me$_3$SiCl$_2$ yield [P(CF$_3$)$_3$]$_3$Cl$^-$.

Upon warming of the reaction mixture from −60 °C to room temperature, the phosphoranides also react with SO$_2$ and aryl sulfonyl chlorides Ar–SO$_2$Cl under formation of [X–SO$_2$]− and Ar–SO$_2$X, respectively (Scheme 3).[15] Moreover, boric esters and aldehydes are trifluoromethylated by [P(CF$_3$)$_3$]$_2$F$^-$ with CF$_3$H as a major side product. Thus, in the reaction of 2 with B(OMe)$_3$, [K(18-crown-6)][B(OMe)$_3$](CF$_3$)$_2$] is formed. Treatment of 2 with benzaldehyde and subsequent aqueous workup yields PhCH(CF$_3$)$_2$OH.

Interestingly, trifluoromethyl phosphoranides do not react with neutral 1,3-dimethyl-2,2-difluorimidazolidine (DFI). However, the corresponding imidazolium triflate is trifluoromethylated by [P(CF$_3$)$_3$]$_2$F$^-$ or fluorinated by [P(CF$_3$)$_3$F]$^-$ under liberation of P(CF$_3$)$_3$ (Scheme 3).

Furthermore, trifluoromethylated phosphoranides are prone to oxidation. Thus, high yields of sixfold coordinated trifluoromethyl phosphates [P(CF$_3$)$_4$XY]$_2$ (X = CF$_3$, F; Y = Cl, F) are generated upon oxidation of the phosphoranides with Cl$_2$ or Deoxo-Fluor® ([MeOCH$_2$]$_2$NSF$_2$) at low temperature. However, treatment of the phosphoranides with hexafluoroacetone does not lead to the oxidation of the phosphorus center. Transfer of CF$_3$- or F- anions to the ketone under formation of [F(FC)CO]$^-$ or [F(F$_3$C)$_2$CO]$^-$ was observed, instead.

Methylation of the phosphoranides yields pentavalent trifluoromethyl phosphates (Scheme 4). In case of [P(CF$_3$)$_3$]$_2$F$^-$, methyl transfer is achieved by MeOTf in DME at −40 °C. For the

Scheme 3. Fluorination and trifluoromethylation by trifluoromethylated phosphoranides.

Scheme 4. Methylation of trifluoromethylated phosphoranides and subsequent reaction with a second equivalent phosphoramide.
are strong Lewis acids, they cannot be isolated but immediately dimerize. Ellipsoids are at a probability level of 50%, hydrogen atoms are omitted for clarity.

**Figure 1.** Solid-state packing of [K(18-crown-6)][P(CF₃)₂]F (3) exhibiting zig-zag chains along the c-axis. The equatorial CF₃ groups are disordered. Ellipsoids are at a probability level of 50%, hydrogen atoms are omitted for clarity.

**Figure 2.** Extract of the solid-state packing of [K(18-crown-6)][P(CF₃)₂] (2) revealing zig-zag chains along the c-axis (left) and structure of a P(CF₃)₂⁻ anion (right). Ellipsoids are at a probability level of 50%, hydrogen atoms are omitted for clarity.

methylation of [P(CF₃)₂]⁺, MeI has been used in DME solution at room temperature. Since the initially formed phosphoranides are strong Lewis acids, they cannot be isolated but immediately dimerize. Ellipsoids are at a probability level of 50%, hydrogen atoms are omitted for clarity.

Elucidation of the solid-state structures of the compounds [K(18-crown-6)][P(CF₃)₂]F (3) (Figure 1) and [K(18-crown-6)][P(CF₃)₂] (2) (Figure 2) were effected by means of single crystal X-ray crystallography. [P(CF₃)₂]⁻ salt 3 crystallizes in the triclinic space group P-1, whereas [P(CF₃)₂]⁻ salt 2 crystallizes in the monoclinic space group P2₁/c with three geometrically non-equivalent anions, therefore average values of structural parameters of 2 are given hereinafter. In both cases, the coordination geometry of the phosphoranide anions is based on distorted trigonal bipyramids, where the lone pair at the phosphorus center is sterically active and occupies one of the equatorial positions. For both compounds, a few structural similarities are observed. The axial bonds in the phosphoranides

3: d(P-CF₃) = 1.97(2) Å, d(P-F) = 1.79(1) Å; 2: d(P-CF₃) = 2.049 Å) are elongated with respect to the neutral species PF₃ (d(P-F) = 1.570(1) Å, gas phase electron diffraction – GED) and P(CF₄) (1) (d(P-CF₃) = 1.93(2) Å, GED) due to the 3-center-4-electron bonding. The axial P–F bond is significantly shorter than the axial P–C bond in the [P(CF₃)₂]⁻ anion of compound 3, as could be expected. The equatorial P–F bonds of 2 are 1.894 Å on average and thus, comparable to the P–C bonds in the neutral compounds P(CF₃) (1) (1.93(2) Å, GED) or (F,Cp)P-P(CF₃) (1.886(4) and 1.880(4) Å via X-Ray; 1.90 Å via GED).

Furthermore, the CPC-angles between the two equatorial CF₃ groups are almost identical in 2 and 3 (104.06(2) to 105.05(1)°), but slightly larger than the corresponding CPC-angle in the neutral phosphine P(CF₃) (100(3)°, GED). The angles between the apical substituents are smaller than 180° and amount to 170.47(1)° for 3 and 174.74(1) to 176.02(1)° for 2. The reasons for this distortion are repulsive interactions of the axial substituents with the lone pair, which is especially pronounced for the apical fluorine substituent in compound 3. Thus, the CPC angles between axial and equatorial CF₃ groups in both anions are virtually identical (90.79(1)° and 89.94(1)° in 3 and on average, 89.1° in 2).

The phosphoranide salts 3 and 2 differ in their solid-state packing, since [P(CF₃)₂]⁻ in 2 forms zig-zag chains along the c-axis. The chains are composed of K⁺ centers which are symmetrically surrounded by 18-crown-6 and two phosphoranide anions. The bridging between two K-centers is realized by two fluorine atoms of each a single axial CF₃ group of the phosphoranide. In each cell, there are three geometrically inequivalent anions. In contrast, [P(CF₃)₂]⁻ in compound 3 has two ion-pairs per unit cell and exhibits a comparatively simple arrangement, resulting in zig-zag chains along the a-axis of the unit cell. Here, bridging between the cations is realized by the two axial substituents of the phosphoranide anion, i.e. the axial fluorine atom and one of the fluorine atoms of the axial CF₃ group. For both phosphoranide salts 2 and 3, the geometry of the cations and anions is determined by the pursuit for a maximum number of K–F contacts with preferably minimal distances. Since one observes rather large K–P distances of 4.454(3) to 5.436(7) Å (2) and 3.649(9) Å (3), respectively, this indicates in both cases a packing of well-isolated ions.

Furthermore, trifluoromethyl phosphoranides 2 and 3 were studied by variable temperature NMR spectroscopy. Their spectra are compared with those of the corresponding tetramethylammonium derivatives. Phosphoranides may undergo inter- and intramolecular exchange processes. They tend to form an equilibrium with their precursors in solution, and pseudorotation may lead to an exchange of equatorial and axial substituents. In keeping with this, the ³¹P NMR spectrum of [NMe₂]₂[P(CF₃)₂] shows a slightly broadened decept at –38 °C in acetonitrile solution, whereas the ³¹P NMR spectrum is characterized by a broad singlet and a doublet in the ratio 1:9. The lack of fine coupling implies a fast exchange process. Upon addition of excess NMe₃F this exchange is considerably slowed down, so that a doublet of quartets of septets can be distinguished in the ³¹P NMR spectrum. In contrast, the
exchange is very slow in DME solution, which allows differentiation of the axial and equatorial CF₃ groups. However, a slow exchange remains as evidenced by slightly broad signals. Again, these dynamics can be suppressed by addition of small amounts NMe₃F resulting in a well resolved ³¹P NMR resonance at room temperature. Cooling a DME solution of [NMe₃][PCF₃,F] to -60°C in absence of NMe₃F leads to the same observation. A fast exchange process takes place in DME above 60°C, which can be identified by variable temperature ³¹P NMR spectroscopy. At -50°C the ³¹P NMR signal is fully resolved (Figure 3), whereas a broad multiplet is found at about 50–60°C, finally resulting in a broad decet at 80°C. Consequently, the CF₃ groups give rise to two broad singlets in the ¹⁹F NMR spectrum at 50°C which fuse to one broad singlet at 60°C.

In contrast, ¹⁹F and ³¹P NMR spectra of [K(18-crown-6)][PCF₃,F] (3) in DME at -90°C do not allow a differentiation between axial and equatorial CF₃ groups. The appearance of the spectra points to a fast exchange process similar to that observed in MeCN solution. We investigated the influence of the counterions on the spectra in DME in greater detail. If a mixture of KF/18-crown-6 is added to a DME solution of [NMe₃][PCF₃,F], no changes in the NMR resonances take place. In contrast, the addition of NMe₃F to [K(18-crown-6)][PCF₃,F] (3) results in dramatic transformations in the spectrum. Exchange processes are significantly slowed down, so that partially resolved signals are observable in the same way as for [NMe₃][PCF₃,F] in MeCN at -60°C.

Presumably, [NMe₃][PCF₃,F] exists as a tight pair of contact ions in DME, which leads to decelerated exchange processes. The [NMe₃]⁺ cation probably interacts with the phosphorus atom, leading to the formation of P–F bonds. On the other hand, the [K(18-crown-6)]⁺ cation rather interacts with the axial fluorine atom of the anion than with the phosphorus atom, as evident from the molecular structure, facilitating a fast exchange process.

The resonances of the axial and equatorial CF₃ groups of [K(18-crown-6)][PCF₃,F] (2) are fully resolved at -50°C. Upon warming an intermediate behavior is observed at 0°C, whereas a fast exchange process occurs at 80°C. In comparison, [NMe₃][PCF₃,F] exhibits fully resolved spectra at -45°C but it cannot be observed above 10°C due to its thermal instability.

In solution, [PCF₃,F]⁺ and [PCF₃,F]⁻ are generally stabilized by the addition of P(CF₃)₃ (1). Since phosphoranides and their precursors form an equilibrium in solution, the addition of one of the reactants entails a shift of this equilibrium to the side of the phosphorane. Thus, [K(18-crown-6)][PCF₃,F] (2) already exhibits resolved ¹⁹F NMR spectra with fine splitting at -30°C in the presence of P(CF₃)₃ (1). The NMR resonances of [K(18-crown-6)][PCF₃,F] (3), on the other hand, are broadened, which might arise from interactions of the axial fluorine substituent of the phosphorane with the phosphine.

**Conclusion**

In conclusion, we have demonstrated that stable trifluoromethylated phosphoranides are accessible upon treatment of trifluoromethyl phosphines with a source of F or CF₃⁺, respectively. The anionic species are efficiently stabilized by crown ether-coordinated K⁺ cations. The [K(18-crown-6)]⁻ salts have been isolated as solids and are thus significantly more stable than the known [NMe₃]⁻ derivatives. As a general trend, trifluoromethylated phosphoranides tend to decompose under formal liberation of difluorocarbene, giving rise to mixed fluoro(trifluoromethyl)phosphoranides. The typical reactivity of [PCF₃,F]⁻ (n = 0–2) is determined by the tendency to donate one of the axial substituents, thus they serve as trifluoromethylation (n = 0) and fluorinating agents (n = 1–2) which has been demonstrated by reactions with several different electrophiles. Moreover, the trivalent phosphoranides are oxidized by chlorine or Deoxo-Fluor® to give pentavalent trifluoromethylphosphates. Solid-state structures of [K(18-crown-6)][PCF₃,F] and [K(18-crown-6)][PCF₃,F] have been elucidated. The examined phosphorane anions exhibit a distorted trigonal bipyramidal geometry, where the sterically active lone pair leads to a decrease of the bond angle between the axial substituents. Elongated distances to the axial substituents are evident, due to the 3-center-4-electron bonding. Finally, the solid-state packing of the trifluoromethyl phosphoranides [K(18-crown-6)][PCF₃,F] and [K(18-crown-6)][PCF₃,F] reveals zig-zag chains, which are formed by an alternating arrangement of anions and cations, bridged by K–F interactions. Apart from that, variable temperature NMR experiments in different solvents disclose exchange processes in the phosphoranides.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: fluorine · fluorination · hypervalent compounds · phosphorus · trifluoromethylation

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