Non-coordinated and Hydrogen Bonded Phenolate Anions as One-Electron Reducing Agents

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Abstract: In this work, the syntheses of non-coordinated electron-rich phenolate anions via deprotonation of the corresponding alcohols with an extremely powerful perethyl tetraphosphazene base (Schwesinger base) are reported. The application of uncharged phosphazenes renders the selective preparation of anionic phenol-phenolate and phenolate hydrates possible, which allows for the investigation of hydrogen bonding in these species. Hydrogen bonding brings about decreased redox potentials relative to the corresponding non-coordinated phenolate anions. The latter show redox potentials of up to $-0.72(1)$ V vs. SCE, which is comparable to that of zinc metal, thus qualifying their application as organic zinc mimics. We utilized phenolates as reducing agents for the generation of radical anions in addition to the corresponding phenoxyl radicals. A tetraacyanoethylene radical anion salt was synthesized and fully characterized as a representative example. We also present the activation of sulfur hexafluoride (SF$_6$) with phenolates in a SET reaction, in which the nature of the respective phenolate determines whether simple fluorides or pentafluorosulfanide ([SF$_5$]$^-$) salts are formed.

Introduction

Phenol and phenolates are key compounds in applied chemistry, as documented by the industrial Kolbe–Schmitt process.[1] Moreover, a variety of fundamental reactions within the biosphere, such as the photosynthesis, are strongly related to phenolic functionalities.[2,3] Phenol represents the simplest aromatic alcohol with a pronounced tendency for hydrogen bond formation, which strongly governs the acidity of the present OH functions.[4] Phenol derivatives with a higher acidity than phenol are deprotonated by tetraalkylammonium hydroxides, yielding the corresponding ammonium phenolates.[5] Interestingly, as reported by Reetz et al., all attempts to isolate the non-coordinated phenolate [H$_4$C$_6$O]$^-$ ([PhO]$^-$) anion by deprotonation with tetra-n-butylammonium hydroxide invariably led to a phenol-phenolate adduct featuring a moderately strong hydrogen bond (O–O distance of 247.1(5) pm).[6] Pronounced hydrogen bonding is also present in imidazolium phenolates, which feature strong C–H···O$^-$ cation-anion interactions.[7,8]

The investigation of hydrogen bonding in proton-coupled electron transfer processes is of growing interest, particularly because of its relevance towards the photosystem.[9,10] The high basicity of the tetrathiphosphazene base ([Et$_3$N]$_2$P=N$_2$P=NtBu) (1) is sufficient for the deprotonation of phenol, as discussed previously.[11] The proton of the corresponding phosphazenium cation [1H]$^+$ is well shielded towards nucleophilic attack, which allows the isolation of salts with non-coordinated phenolate anions. Thus, in the absence of cation-anion interactions, the effect of hydrogen bonding on the redox properties of phenolate anions can be investigated in detail. The presence of water also affects the oxidation potential of phenol,[8] which casts doubt on the reported phenolate redox data from the literature, which were obtained from phenolates generated by deprotonation with tetraalkylammonium hydroxide hydrides in acetonitrile solution.[11,12] The elucidation of the influence of hydrogen bonding requires uncharged phosphazene bases for the deprotonation of phenols to create a definite design of hydrogen bonded phenol-phenolate adducts or phenolate hydrates. Here, in contrast to the application of alkylammonium hydroxide hydrates, the degree of hydration can be controlled exactly by the added amount of water to the reaction. Furthermore, hydrogen bonding also strongly influences light absorption and emission of fluorophores.[13] This phenomenon is also observed for 2-naphtholate anions,[14] and the fluorescence of 2-naphtholate was investigated in more detail in the presence of imidazolium-based ionic liquids, which are able to form C–H···O$^-$ hydrogen bonds.[15] Therefore it is obvious to investigate light absorption and emission of the non-coordinated 2-naphtholate anion in comparison to its free 2-naphthole and its adduct with the anion.
Phenolate anions possess a pronounced tendency for single-electron transfer (SET) reactions, as the resulting phenoxyl radicals are well stabilized by electron delocalization. Obviously, we are interested in testing phosphazenium phenolates as electron donors in SET processes. As depicted in Scheme 1, neutral electrophiles are reduced under liberation of stable phenoxyl radicals, which are reluctant to further reactions, and by the generation of the corresponding phosphazenium salts of reactive radical anions [E]−.

Scheme 1. Application of phosphazhenium phenolates as reducing agent.

The applied phenolates should fulfill several prerequisites as a high electron density leading to a sufficiently negative redox potential. Bulky substituents in 2, 4 and 6 position are necessary for the stabilization of phenoxyl radicals by mitigating its nucleophilicity and by obstructing their dimerization.12 Consistently, we selected 2,6-di-tert-butyl substituted phenolates as the substrates of choice.

Results and Discussion

Syntheses of non-coordinated phenolate anions

The perethyl tetraphosphazene base 1 was synthesized on a multigram scale according to the procedure described previously.16 The reaction of 1 with phenols in ethereal solution affords the corresponding salts as microcrystalline solids in excellent yields (> 95 %, Scheme 2). Importantly, the products are devoid of significant cation-anion contacts.

Whereas salts [1H][PhO], [1H][MeBu2PhO] and [1H][Bu3PhO] are colorless, salt [1H][MeOBu2PhO] shows a deep yellow color. The deprotonation of 2-naphthol (C10H7OH, Scheme 2) afforded the saline naphtholate [1H][C10H7O] with the non-coordinated anions in nearly quantitative yield as fluorescent green crystals. All compounds are air sensitive and by oxidation change their color to yellow, purple, brown or rust-red, while the color of [1H][C10H7O] quickly fades. The salts deteriorate in Brønsted acids and solvents like chloroform, dichloromethane and acetone.

For the sake of a complete picture, we additionally tested the deprotonation of [MeOBu2PhOH] with tetra-n-butylammonium hydroxide (triacontahydrate) in a mixture of diethyl ether

Figure 1. Molecular structures of non-coordinated phenolate anions in [1H][MeBu2PhO] (left), [1H][Bu3PhO] (middle) and [1H][C10H7O] (right). Thermal ellipsoids are shown at 50% probability. The hydrogen atoms bonded at carbon atoms are omitted for clarity. Selected bond lengths [pm]: left: C1−O1 128.5(2), C1−C2 144.9(2), C1−C6 144.8(2); middle: C41−O1 129.8(2), C41−C42 144.3(2), C41−C46 144.8(2); right: C1−O1 128.4(2), C1−C2 142.1(2), C1−C10 145.8(2).
Table 1. Selected bond lengths, angles and redox potentials (E°) of non-coordinated and hydrogen bonded phenolate anions with [1H]⁺ as the counterion. For disordered molecules the values of the major representatives are depicted.

| Anion                  | Bond Distance [pm] | Angle [°] | E° [V] |
|------------------------|-------------------|-----------|--------|
| [PhO]⁻                  | C–O              | 128.7(2)  | 118.0(1) | 129.0(2) |
| [PhO]⁻                  | C–O              | 128.5(2)  | 118.4(1) | 128.4(2) |
| [PhO]⁻                  | C–O              | 129.0(2)  | 118.3(1) | 128.7(2) |
| [C₆H₅O]⁻                  | C–O              | 128.4(2)  | 114.3(1) | 128.4(2) |
| [PhO(H₂O)]⁻            | C–O              | 129.8(1)  | 114.8(1) | 129.8(1) |
| O(H)–O⁻                | 260.8(7)         | 265.2(7)  |        |
| [(PhO)⁻H]⁻             | C–O              | 131.9(2)  | 117.1(1) | 131.9(2) |
| O(H)–O⁻                | 243.7(2)         | 238.5(4)  |        |
| [(MeO₂Bu₃)O⁻PhO]⁻H⁺   | C–O              | 133.1(1)  | 118.0(1) | 133.1(1) |
| O(H)–O⁻                | 247.0(1)         | 238.5(4)  |        |
| [(C₆H₅O)H]⁻           | C–O              | 132.1(2)  | 118.1(1) | 132.1(2) |
| O(H)–O⁻                | 247.0(1)         | 238.5(4)  |        |
| [(NBu₃t)O⁻(MeO₂Bu₃)PhO]⁺ | C–O          | 133.0(6)  | 115.8(3) | 133.0(6) |

[a] The ortho-ortho-ortho carbon atom angle relative to the C–O⁻ function is depicted. (b) Voltammograms recorded in 0.1 m [NBu₃][PF₆]THF solution at 100 mV s⁻¹ under inert atmosphere with a glassy carbon working electrode (2.0(1) mm), a counter electrode (steel 18/8, 2.0(1) mm) and an Ag/AgCl reference electrode. All potentials were calibrated to the Fc/Fc⁺ couple (0.405 V vs. SCE). [c] Due to irreversible redox reaction, only the oxidation potential (E°[c]) is displayed.

and THF with a subsequent work-up. Since the in situ deprotonation leads to the formation of the hydrate [NBu₃][MeO₂Bu₃PhO(H₂O)], we focused on the investigation of a possible liberation of the free anion [MeO₂Bu₃PhO]⁻ by drying the hydrate in a high vacuum. The powdery pale yellow solid, which was obtained after removal of all volatiles, shows a signal of the C–O⁻ carbon atom at δ = 164.1 ppm in the ¹³C NMR spectrum, which is shifted upfield by about 4 ppm compared to [1H][MeO₂Bu₃PhO] (δ = 168.0 ppm). In the IR spectrum no OH stretching vibration is observed, which points to the absence of OH groups evoked by phenol or water. Recrystallization of the salt from a diethyl ether/THF solution at −28 °C afforded single crystals suitable for X-ray analysis. The investigation shows the free anion in [NBu₃][MeO₂Bu₃PhO], which is not hydrated and does not show any significant contacts to the cation with the shortest C–H–O⁻ contact of O1–C47⁺ with 340.6(2) ppm (symmetry code C47⁺ (−1/2 + X, 3/2 – Y, 1 – Z). The C1–O1 distance of 129.3(2) pm is not different from that in the phosphazene salt. However, air sensitivity evidenced by a color change from yellow to green is attenuated relative to that of the phosphazene analogue.

Syntheses of hydrogen bonded phenolates

A selective preparation of phenol-phenolate anions is effected by the deprotonation of phenol by half a molar equivalent of phosphazene 1, or in case of [1H][PhO(H₂O)] by deprotonation of phenol prior to the addition of one molar equivalent of water (Scheme 3).

Salt [1H][PhO(H₂O)] incorporates the anion with an asymmetric, moderately strong hydrogen bond with d(O1-O8) = 243.7(2) pm and therefore the ¹³C NMR resonance of the C-O⁻ carbon atoms of δ = 167.2 ppm is shifted upfield in comparison to free [PhO]⁻ (δ = 175.0 ppm).[10]

The monohydrate [1H][PhO(H₂O)] is accessible in excellent yields (95%). Figure 2 displays the aromatic regions of the ¹H NMR spectra of [PhO]⁻ and its adducts. Hydrogen bonding of [PhO]⁻ with water and phenol brings about significant low-field shifts of the signals and an improved resolution of couplings. The latter may be rationalized by a reduced delocalization of the negative charge over the aromatic system, evoked by charge withdrawing hydrogen bonding.

In accordance, the ¹³C NMR resonance of the C–O⁻ carbon atom in [PhO(H₂O)]⁻ (173.6 ppm) is slightly upfield shifted relative to [PhO]⁻ (175.0 ppm) and shielded relative to [PhO(H₂O)]⁻ (167.2 ppm).

Colorless [1H][PhO(H₂O)] deteriorates above 92 °C and thus, is more temperature sensitive than [1H][PhO] (dec. > 115 °C) with a non-coordinated [PhO]⁻ anion. The OH vibration modes are detected as a single sharp resonance at 3350 cm⁻¹. Single crystals for X-ray crystallography were grown from the ethereal reaction mixture at −28 °C. In the solid state the phenolate monohydrate anion forms a dimer, in which two phenolate hy-
drates are associated via hydrogen bonding (Figure 3). Interestingly, the water molecules do not show bridging between two phenolate anions, but are arranged linearly in a zigzag array. The water molecules are disordered in a 1:1 ratio due to symmetry. The hydrogen bonds with O1\(~\)O2 and O1\(~\)*\)O2B distances of 260.8(7) pm and 265.2(7) pm, respectively, are significantly elongated compared to phenol-phenolate hydrogen bonding in [1H][PhO(H2O)] (243.7(2) pm). The O2\(~\)O2B distance of 293.1(5) pm is remarkably long.

All attempts to crystallize hemi-, di- or trihydrates of [PhO] suitable for X-ray analysis by adding the respective amounts of water to [1H][PhO] resulted in the formation of amorphous solids. The investigation of diffracting crystals solely shows the presence of [1H][PhO(H2O)].

The naphthol-naphtholate salt [1H][[(C10H7O)2H]] is accessible in a 77% yield (Scheme 3) as a colorless solid with a melting point of 76 °C. Regarding the major representative of salt [1H][[(C10H7O)2H]] (Figure 4), the anion contains the strongest observed hydrogen bond within all phenolate adducts herein with an O–O separation of 238.5(4) pm. The respective OH vibration mode is detected at 3379 cm\(^{-1}\), and thus is slightly shifted to higher wavenumbers in comparison to [PhO(H2O)]\(^{−}\). In the IR spectra of all other hydrogen bonded phenolates this mode is not observed.

Interestingly, [1H][[(C10H7O)2H]] containing the hydrogen bonded anion appears colorless, which is in stark contrast to green [1H][C10H7O] featuring the non-coordinated anion. UV/Vis spectra in dry THF solution clearly reveal the bathochromic absorbance shift of [C10H7O] into the visible range with two local maxima at about \(\lambda = 412\) nm and 439 nm, while the absorbance of [(C10H7O)2H] is hypsochromically shifted and observed below 400 nm (Figure 5, left), which agrees with the lack of color. The influence of hydrogen bonding is also visible in fluorescence spectra (Figure 5, right). Fluorescence emission spectra were recorded in dry THF with an excitation wave-
length of $\lambda_{\text{em}} = 320$ nm. The fluorescence of the non-coordinated 2-naphtholate anion in [1H][C$_6$H$_5$O] is of high intensity and displays one strong fluorescence maximum at $\lambda_{\text{em}} = 462$ nm with a Stokes shift of 9605 cm$^{-1}$. The adduct in [C$_6$H$_5$O]$^-$ displays comparatively low intense fluorescence and exhibits four fluorescence maxima at $\lambda_{\text{em}} = 344$, 360, 427 nm and 458 nm (Stokes shifts of 2181, 3472, 7831 and 9416 cm$^{-1}$). It is remarkable, that the bands of [C$_6$H$_5$O]$^-$ at $\lambda_{\text{em}} = 462$ nm and of [(C$_6$H$_5$O)$_2$]$^-$ at $\lambda_{\text{em}} = 458$ nm are close together, which may suggest a dissociation of the hydrogen bonded adduct in the excited state prior to emission. However, mechanistic insights will be discussed elsewhere.

Bulky tert-butyl substituents in 2 and 6 positions of phenol do not prevent the formation of hydrogen bonded adducts, as shown for the phenol-phenolate anion in [1H][MeOPh$_2$PhO]$_2$, which can be easily obtained in a quantitative yield as a green solid (Scheme 3). However, the hydrogen bond with an O1-O3 distance of 247.0(1) pm is slightly elongated compared to [1H] [(PhO)$_2$H] (243.7(2) pm), which may result from steric repulsion (Figure 6).

![Molecular structure of the anion of salt [1H][MeOPh$_2$PhO]$_2$.](image)

Figure 6. Molecular structure of the anion of salt [1H][MeOPh$_2$PhO]$_2$. Thermal ellipsoids are shown at 50% probability. The hydrogen atoms bonded at carbon atoms are omitted for clarity. The cation is not shown. Selected bond lengths (pm): O1–O3 247.0(1), O1–C44 136.0(1), O3–C56 131.3(2).

The $^{13}$C NMR resonance of the C–O carbon atoms adjacent to the hydrogen bond are upfield shifted ($\delta = 158.5$ ppm) compared to free $^{[\text{MeO}]}$Ph$_2$O$^-$ ($\delta = 168.0$ ppm). Clearly, hydrogen bonding seems responsible for a reduced air-sensitivity, but increased thermal sensitivity (dec. $> 74$ °C, [1H][MeOPh$_2$PhO] dec. $> 118$ °C).

Cyclic voltammetry of phenolates

The non-coordinated and hydrogen bonded phenolates were analyzed by cyclic voltammetry (CV) measurements under inert conditions (Table 1, Figure 7). THF as the solvent and [NBu$_4$][PF$_6$] as the electrolyte were carefully dried prior to use. The substituted non-coordinated phenolate anions show the familiar trend of redox values, known from the literature.$^{[11, 12]}$

The determined redox potentials of substituted phenolates vary from $E^0 = -0.721$ (V vs. SCE for $^{[\text{MeO}]}$Ph$_2$O$^-$ to $-0.521$ (V vs. SCE for $^{[\text{Bu}]}$Ph$_2$O$^-$). These values exceed the reported literature data$^{[11]}$ in acetonitrile solution by about 0.3 V. The anion $^{[\text{MeO}]}$Ph$_2$O$^-$ has the most negative redox potential of the here prepared phenolates and reaches that of zinc, which qualifies the anion as an organic zinc mimic.$^{[19]}$ In contrast to the reversible redox reaction of the sterically encumbered phenolates

$^{[\text{MeO}]}$Ph$_2$O$^-$ and $^{[\text{Bu}]}$Ph$_2$O$^-$, the [PhO]$^-$ anion shows an irreversible oxidation at $E_{\text{ox}} = -0.121$ V vs. SCE due to a facile recombination of the formed radicals.$^{[20]}$ The anions $^{[\text{MeO}]}$Ph$_2$O$^-$ and $^{[\text{MeO}]}$Ph$_2$O$^-$ are irreversibly oxidized as well.

According to CV measurements, the anion of the salt [NBu$_4$][MeOPh$_2$PhO] exhibits the same redox potential of $E^0 = -0.721$ (V vs. SCE as [1H][MeOPh$_2$PhO]. However, the air sensitivity is reduced and the ease of color change upon air contact from yellow to green significantly decreases.

Since the reported potentials of phenolate salts in the literature were preferably determined in aqueous acetonitrile solution with alkylammonium hydroxide hydrates as the deprotonation agent, the influence of conceivable hydrogen bonding on the obtained potentials is neglected.$^{[11, 12]}$ The application of 1 enables the investigation with regard to the influence of hydrogen bonding on the oxidation potentials of phenolates.

In keeping with this, we now focused on the cyclic voltammetric investigation of the non-coordinated phenolate anion [PhO]$^-$, as well as of the adducts [PhO(H$_2$O)]$^-$ and [(PhO)$_2$H]$^-$.

We further looked at the influence of bulky substituents in 2 and 6 positions on the adduct formation and the resulting redox properties.

As described before, the oxidation potential of salt [1H][PhO]$_2$H$_2$O was determined to $E_{\text{ox}} = -0.121$ (V vs. SCE.$^{[19]}$ This value is significantly cathodically shifted compared to the reported literature data in acetonitrile solution (± 0.24 V vs. SCE)[$^{[12]}$]

Hydrogen bonding to water in the phenolate monohydrate salt [1H][PhO(H$_2$O)]$_2$ brings about an anodic shift of $E_{\text{ox}}$ to $-0.041$ (V vs. SCE (Figure 8). The potential of the anion in [1H][PhO]$_2$H$_2$O with a value of $E_{\text{ox}} = +0.221$ (V vs. SCE experienced an even stronger anodic shift. This trend is confirmed by calculated ionization potentials at the BP86/6-311+g(3df,2p) level of theory,$^{[21]}$ according to which the non-coordinated anion

![Cyclic voltammograms of non-coordinated phenolates.](image)

Figure 7. Cyclic voltammograms of non-coordinated phenolates: [1H][PhO] (red), [1H][MeOPh$_2$PhO] (green), [1H][MeOBu$_2$PhO] (blue) and [1H][MeOPh$_2$PhO] (black). Voltammograms recorded in 0.1 M [NBu$_4$][PF$_6$]THF solution at 100 mVs$^{-1}$ under inert atmosphere with a glassy carbon working electrode (2.01 mm), a counter electrode (steel 18/8, 2.01 mm) and an Ag/AgCl reference electrode. All potentials were calibrated to the Fc/Fc$^+$ couple (± 0.405 V vs. SCE).
The hydrogen bond donation capability of the 2-naphtholate anion is significantly influenced by hydrogen bonding to a water molecule in [PhO(H₂O)]⁻ (Eₒ = 267.42(1) kJ mol⁻¹). The hydrogen bond donation capability in [PhO(H₂O)]⁻ is characterized by a further increase of Eₒ to 314.90(1) kJ mol⁻¹.

The observations may be rationalized by a reduced charge density on the phenolate oxygen atom, which is affected by the strength of the formed hydrogen bond interaction. Moreover, the strength of the hydrogen bond influences the dissociation of the adduct in solution. Thus, assuming that excessive amounts of water displace phenol in [1H][MeO₂PhO]H⁺ in the equilibrium reaction, the increased oxidation potential points to the formation of phenolate-water aggregates (Figure 8).

The investigation of analogous 2-naphtholate anions delivers similar trends of the observed oxidation potentials as for [PhO]⁻ anions. The determined value of [1H][C₆H₅O]H⁺ with Eₒ = 0.15(1) V vs. SCE shifts significantly with formation of the hydrogen bond in [1H][C₆H₅O]H⁺ (Eₒ = 0.08(1) V vs. SCE, Figure 9). Also in this case, Eₒ of the non-coordinated phenolate in [C₆H₅O]⁻ is clearly shifted compared to the literature data (+0.10 V vs. SCE). As expected, the subsequent addition of water to the [1H][C₆H₅O]H⁺ electrolyte solution (0.1 M, 0.2 M, and 0.6 M H₂O) leads to gradually shifts of Eₒ (+0.00(1) V, +0.01(1) V, +0.03(1) V vs. SCE, Figure 9). The picture is completed by treatment of [1H][C₆H₅O]H⁺ with an excess of H₂O, which shifts the oxidation potential cathodically (Eₒ = +0.06(1) V vs. SCE).

Interestingly, CV measurements of the hydrogen bonded adduct in [1H][MeO₂Bu₂PhO]H⁺ reveal a similar redox potential (~0.70(1) V vs. SCE, Figure 10) as for the non-coordinated phenolate [MeO₂Bu₂PhO]⁻ (~0.72(1) V vs. SCE).

In comparison to phenolate [PhO]⁻ and [(PhO)H]⁻, the small redox shift between [MeO₂Bu₂PhO]⁻ and [(MeO₂Bu₂PhO)H]⁻ may be rationalized by weaker hydrogen bonding in [(MeO₂Bu₂PhO)H]⁻ relative to [(PhO)H]⁻. This fact could possibly lead to a more pronounced dissociation of [(MeO₂Bu₂PhO)H]⁻ in solution and could be responsible for the small redox shift between the coordinated and non-coordinated anion. Subsequent addition of water to the [1H][MeO₂Bu₂PhO]H⁺-electrolyte solution leads to further anodically shifted potentials of Eₒ = −0.68(1) V and −0.66(1) V vs. SCE (0.1 M and 0.2 M H₂O). Likewise, the addition of water (0.05 M, 0.1 M, 0.4 M and 1.9 M) to [1H][MeO₂Bu₂PhO] in the electrolyte solution lowers the observed redox potentials (Eₒ = −0.71(1) V, −0.70(1) V, −0.66(1) V and −0.58(1) V vs. SCE).

Phenolates for one-electron reductions

Having non-coordinated phenolate anions and their hydrogen bonded adducts in hand, the second part of this paper is focused on their reducing properties in SET reactions.

In general, radical anions are accessible by electrochemical reduction processes or by single-electron transfer reactions. Especially organic representatives featuring conjugated n-sys-
tems exhibit low lying π*-orbitals and enable the formation of stable radical anions. The "E. coli"[22,23] of electron transfer reagents is the well-known electron-acceptor tetracyanoethylene (TCNE), which is attracting considerable interest for applications in organic semiconductor materials or organic magnets.[26]

The reduction of tetracyanoethylene to its radical anion [TCNE]− is usually instrumented by the reaction with alkali or transition metals, like elemental potassium or copper, but can also be effected by potassium iodide.[27] The incorporated metal cations may be replaced by other cations via salt metathesis reactions.[26]

As discussed before, non-coordinated phenolate anions as one electron transfer reagents should be of low nucleophilicity and the formed phenoxyl radicals should not undergo any further reactions. For this purpose, salt [1H][MeO\textsubscript{2}Bu\textsubscript{2}PhO] is reacted with TCNE in ethereal solution (Scheme 4).

![Scheme 4. Synthesis of [1H][TCNE] by one electron reduction of TCNE applying phenolate salt [1H][MeO\textsubscript{2}Bu\textsubscript{2}PhO].](image)

A rapid electron transfer is observed, which is accompanied by an immediate color change from colorless to green-yellow. Advantageously, the formed radical anion salt [1H][TCNE] precipitates from the reaction mixture as a deep-orange solid in an 88% yield. The phenoxyl radicals can be completely removed by extraction with diethyl ether. The formation of [1H][TCNE] is ascertained by elemental analysis and X-ray investigation (Figure 11).

Although the formation of the dimeric [TCNE]− dianion is known,[28] the [TCNE]− radical anion in [1H][TCNE] is strictly monomeric. This anion is well separated from the counterion with the closest contact of N15-C9 with 326.6(1) pm. The C42-C45 bond in [1H][TCNE] of 141.7(1) pm well compares with that of calculated and isolated [TCNE]− radical anions.[23,28,30]

With the application of the "E. coli"[22,23] of electron transfer reagents we confirmed the proof of concept for the preparation of radical anion salts with a weakly coordinating phosphazenium cation, which originates from phosphazenium phenolates.

In view of the severe environmental pollution caused by our economy, which is evident in the climate change on our planet, we tried to find further practical applications for the newly synthesized phosphazenium phenolates.

Sulfur hexafluoride is the strongest greenhouse gas presently known. Its extreme chemical inertness has a dramatic impact on our climate.[31] Clearly, methods for the successful degradation of sulfur hexafluoride are urgently needed. Numerous papers are addressing SF\textsubscript{6} activation with transition metal complexes of titanium,[32] rhodium,[33] platinum,[34] chromium and vanadium,[35] as well as of nickel.[36] In all cases the principal reactions lead to corresponding sulfido and fluoride metal complexes. The activation of SF\textsubscript{6} can also be performed electrochemically[37] or by single-electron transfer reactions, as demonstrated by the reaction of SF\textsubscript{6} with alkali metals in liquid ammonia.[38] SET reactions of SF\textsubscript{6} with organic electron donors,[39,40] TEMPO,[41] and also photo-activated systems[42] have been described. The mechanism for the SF\textsubscript{6} degradation is not completely understood. While some papers claim that the activation proceeds via an SET prior to the disintegration of the corresponding [SF\textsubscript{5}]− radical anion,[39,41,42] DIELMANN et al. postulate a nucleophilic activation with the use of highly electron rich phosphines.[44]

As previously reported,[10] treatment of the strongest reducing reagent [1H][MeO\textsubscript{2}Bu\textsubscript{2}PhO] with SF\textsubscript{6} in ethereal solution leads to the spontaneous formation of the pentafuoroarsanide anion ([SF\textsubscript{5}]−) and a color change from yellow to deep red, for which the corresponding liberated phenoxyl radicals seem responsible.

The formation of the pentafuoroarsanide anion from SF\textsubscript{6} is reported to proceed via two single-electron transfer steps.

![Figure 11. Molecular structure of the radical anion salt [1H][TCNE]. Thermal ellipsoids are shown at 50% probability. The hydrogen atoms bonded at carbon and the minor occupied disordered N(C\textsubscript{6}H\textsubscript{5})\textsubscript{2} group are omitted for clarity.](image)
The intermediately formed radical anion $[\text{SF}_6]^{-}$ of the first reduction step disintegrates into $F^-$ and an $[\text{SF}_7]$ radical, and the latter is reduced by a second phenolate to obtain the $[\text{SF}_7]^{-}$ anion.

The reaction of $F^-$ with the borosilicate glass surface leads to the formation of several fluorides, mainly $[\text{HF}_3]^-$, as evidenced by $^{19}F$ NMR spectroscopy. Storage of the collected red ethereal $\text{MeO(OBu)}_2\text{PhO}$ phenoxyl radical solution at $-28^\circ$C and most likely diffusion of water and oxygen into the solution allowed green crystals of the corresponding decomposition product, 2,6-di-tert-butylbenzoquinone, which was authenticated by single-crystal X-ray diffraction. The reaction of the ammonium salt $[\text{NBu}_5]^+\text{MeO(OBu)}_2\text{PhO}^{-}$ with sulfur hexafluoride also leads to the formation of $[\text{SF}_7]^{-}$. However, the rate of the reaction seems significantly decreased compared to its phosphazene analogue, and the anion $[\text{SF}_7]^{-}$ was detected not before three days of reaction time.

The treatment of $\text{SF}_4$ with tri-tert-butyl phenolate $[\text{1H}]\text{[MeOBU}_2\text{PhO]}$ in THF as well enables the formation of the $[\text{SF}_7]^{-}$ anion and fluorides (mainly $[\text{HF}_3]^-$), as evidenced by $^{19}F$ NMR spectroscopy. The characteristic resonances of the pseudo square-pyramidal $[\text{SF}_7]^{-}$ anion$^{43,44,46}$ are observed in the $^{19}F$ NMR spectrum as a quintet at $\delta = 88.9$ ppm and a doublet at $59.5$ ppm, both showing the characteristic $J_{\text{FF}}$ coupling of 45 Hz.$^{45}$ The colorless reaction solution turns deep blue over time, which well agrees with the color of the free phenoxyl radical.$^{11}$ $^{19}F$ NMR spectroscopic investigations manifest the stability of the $[\text{SF}_7]^{-}$ anion in solution in the presence of phenoxyl radicals over weeks of storage at ambient temperature.

The phenolates $[\text{1H}]\text{[MeOBU}_2\text{PhO]}$ and $[\text{1H}]\text{[PhO]}$ are also utilized for $\text{SF}_4$ activation. However, in sharp contrast to the sterically encumbered 2,6-di-tert-butyl- and 2,6-di-tert-butyl-4-methoxy-substituted phenolates, the reactions of $[\text{1H}]\text{[MeOBU}_2\text{PhO]}$ and $[\text{1H}]\text{[PhO]}$ with $\text{SF}_4$ did not lead to the formation of the pentfluorosulfanide anion, but only afforded fluorides. Since $\text{[MeOBU}_2\text{PhO]}^{-}$ and $\text{[PhO]}^{-}$ show a chemical irreversibility in CV experiments, this observation may be rationalized by the reaction of phenoxyl radicals with intermediates prior to the generation of the $[\text{SF}_7]^{-}$ anion. The hydrogen bonded anionic adduct in $[\text{1H}]\text{[MeOBU}_2\text{PhO]}_2\text{H}^+$ was also reacted with $\text{SF}_4$. After stirring of the reaction mixture over three days, the solution turned red and the formation of $[\text{SF}_7]^{-}$ was monitored by $^{19}F$ NMR spectroscopy. In contrast to the reaction with the noncoordinated anion $\text{[MeOBU}_2\text{PhO]}^{-}$, the rate of the formation of $[\text{SF}_7]^{-}$ by $\text{[MeOBU}_2\text{PhO]}_2\text{H}^+$ was also significantly decreased. Presumably by the presence of phenolic OH functions, several unspecified fluorine containing products were further formed and detected by $^{19}F$ NMR spectroscopy.

Interestingly, the reducing agent tetrakis(dimethylamino)ethylene (TDAE) is reported to be not capable for the $\text{SF}_4$ activation$^{39}$ although TDAE is an even stronger reducing agent ($E^\circ = -0.78$ V vs. SCE) than all presented phenolate anions herein. This suggests the conclusion that the redox strength itself is not the only factor for a successful reduction of sulfur hexafluoride. In accordance with Dielmann et al.$^{44}$ one possible explanation for the success of the $\text{SF}_4$ activation with phenolates invokes a nucleophilic interaction of a phenolate anion with a fluorine atom of $\text{SF}_4$, which may support the subsequent activation by single-electron transfer.

**Conclusions**

We succeeded in high-yield syntheses of a series of non-coordinated phenolate anions by deprotonation of the corresponding alcohols with the tetraphosphazene base 1. The phenolate anions show significantly shortened C–O bonds (128.4(2) pm to 129.8(2) pm) compared to coordinated phenolate anions like in NaOPh (133(1) pm). With phosphazene 1 hydrogen bonded phenol-phenolate and phenol hydrides are accessible by the deprotonation of phenol in the presence of one equivalent of phenol or water, respectively. This renders the investigation of the influence of hydrogen bonding on the redox potentials of phenolate anions possible. The latter were studied by cyclic voltammetric measurements and reveal significant shifts of the oxidation potentials of $[\text{PhO}]^+$ (−0.12(1) V vs. SCE) by contact to a water molecule (−0.04(1) V vs. SCE) or to a phenol molecule (−0.22(1) V vs. SCE). The same trend was observed by comparison of the non-coordinated 2-naphtholate salt $[\text{1H}]\text{[C}_9\text{H}_8\text{O}^-]$ (−0.15(1) V) with the 2-naphthol adduct in $[\text{1H}]\text{[C}_9\text{H}_8\text{O}_2\text{H}^+]$ (−0.08(1) V). The latter anion displays the strongest observed hydrogen bond within all presented phenol-phenolates with an O–O separation of 238.5(4) pm, which results in a hypochromic shift of the absorption into the UV light relative to $[\text{C}_6\text{H}_5\text{O}^-]$, which displays two absorption bands in the visible light (412 and 439 nm). The strong hydrogen bond is also perceptible in fluorescence emission spectra. The non-coordinated anion displays a single fluorescence maximum at $\lambda_{\text{em}} = 462$ nm ($\lambda_{\text{ex}} = 320$ nm, Stokes shift 9605 cm$^{-1}$). In contrast, the fluorescence of the adduct is of less intensity and exhibits several maxima at $\lambda_{\text{em}} = 344, 360, 427, 475$ and 548 nm, respectively. The hydrogen bond in the phenol-phenolate adduct $[\text{1H}]\text{[MeOBU}_2\text{PhO]}_2\text{H}^+$ featuring bulky tert-butyl substituents in 2 and 6 position is slightly elongated (O–O distance 247.0(1) pm) compared to the non-substituted analogue $[\text{PhO}]_2\text{H}^+$ (243.7(2) pm). Consequently, the redox potential of the free phenolate $\text{[MeOBU}_2\text{PhO]}^{-}$ (−0.72(1) V vs. SCE) is only minor influenced by hydrogen bonding to the phenol with a difference of 20 mV.

We also disclosed the potential of non-coordinated phenolates as one-electron reducing agents. By application of tetraacyanoethylene as the “E. coli”$^{22,23}$ of electron transfer reagents, we presented the possibility for the preparation of radical anion salts from phosphazene phenolates and isolated the corresponding salt $[\text{1H}]\text{[TCNE]}$ in high yield (88%). We further described the reduction of the chemically inert sulfur hexafluoride with phosphazene phenolates, which in case of the sterically encumbered phenolates $\text{[MeOBU}_2\text{PhO]}^{-}$ and $\text{[Bu}_4\text{PhO]}^{-}$ resulted in the formation of pentfluorosulfanide anions. The reduction with other phenolates merely gave fluorides.

**Experimental Section**

Materials, instrumentation, methods: All chemicals were obtained from commercial sources and used without further purification. All
solvents were carefully dried and freshly distilled prior to use. Standard high-vacuum techniques were employed throughout all experiments. Non-volatile compounds were handled in a dry N2 atmosphere using Schlenk techniques. Syntheses of phosphazene 1,[19] phenolates 1H[PhO][2], 1H[4H/PhO][2] and 1H{[PhO][2]} were performed according to literature procedures.[10]

NMR spectra were recorded on a Bruker Avance III 500 spectrometer (1H: 500.01 MHz; 13C: 125.73 MHz; 19F: 470.48 MHz; 31P: 202.41 MHz) or on a Bruker Avance III 500 HD spectrometer (1H: 500.20 MHz; 13C: 125.78 MHz; 19F: 470.66 MHz; 31P: 202.48 MHz). Positive shifts are downfield from the external standards TMS (1H, 13C), CCl4F (19F) and H2PO4 (31P). The NMR spectra were recorded in the indicated deuterated solvent or in relation to D2J-acetone-filled capillaries.

IR spectra were recorded on an ALPHA-FT-IR spectrometer (Bruker) using an ATR unit with a diamond crystal for liquids and solids. Elemental analyses were performed by Mikroanalytisches Laboratorium Kolbe (Oberhausen, Germany). The elemental analyses of 1H{[4H/PhO][2]}, 1H{[PhO][2]} were performed in the element-analytical laboratory of the Universität Bielefeld using the EURO EA Element Analyzer 2010 (HEKtech GmbH).

Melting points were measured on a Mettler Toledo Mpm70 Melting Point System.

The UV/Vis spectroscopic investigations were performed using the UV/Vis-spectroscopy-system 8453 (Agilent) with a clasurable cuvette (d = 1 cm) containing a stirring bar (8 mm) under inert atmosphere at 20 °C. The cuvette was heated to 100 °C for 30 minutes prior to each measurement. All samples were prepared in flame-dried Schlenk flasks with concentrations of about 2 μM in THF, which was carefully dried over K and freshly distilled prior to use.

The fluorescence emission spectra were recorded on a RF-5301PC (Shimadzu) in a quartz glass cuvette (d = 1 cm) applying substance concentrations of 200 μM in THF. All samples were prepared in flame-dried Schlenk flasks using THF, which was carefully dried over K and freshly distilled prior to use. The samples were excited with a Xenon lamp at λex = 320 nm.

The cyclic voltammetric investigations were performed on a PGSTAT101 potentiostat (Metrohm) using a "three-electrode arrangement" in a flame-dried 25 mL Schlenk flask under inert atmosphere with a glassy carbon working electrode (2.0(1) mm diameter), a counter electrode (stainless steel 18/8, 2.0(1) mm diameter) and an Ag/AgCl reference electrode in a saturated ethanolic KCl solution (148 mV vs. SHE). The supporting electrolyte [NBu4][PF6] was carefully dried in a high vacuum (10−3 mbar). THF was dried over K and freshly distilled prior to use. For every run 0.1 mmol of the substrate and 15 mL of the electrolyte solution were used. The Fe/C≡C−Fe couple was used as internal standard by adding a small amount (spatula tip) of ferrocene after the measurements. The obtained redox potentials were finally recalculated based on the Fe/C≡C−Fe couple which was set at E°(Fe/C≡C−Fe) = +0.405 V vs. SCE. In case of 1H{[4H/PhO]} and 1H{[C6][H4][O]} the addition of ferrocene leads to changes in the observed oxidation potentials, and therefore E°(Fe/C≡C−Fe) = +0.673 V vs. Ag/AgCl was used as the external reference for the recalculation vs. SCE.

Nano-ESI mass spectra were recorded using an Esquire 3000 ion trap mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a nano-ESI source. Samples were dissolved in THF and introduced to static nano-ESI using in-house pulled glass emitters. Nitrogen served as nebulizer gas and dry gas. Nitrogen was generated by a Bruker nitrogen generator NGM 11. Helium served as cooling gas for the ion trap and collision gas for mass spectrometry experiments. The mass axis was externally calibrated with ESI-L Tuning Mix (Agilent Technologies, Santa Clara, CA, USA) as calibration standard.

The crystal data were collected on a Rigaku Supernova diffractometer (Cu-Kα radiation (λ = 1.54184 pm) or Mo-Kα radiation (λ = 71.037 pm) at 100.02 K). Using Olex2,[20] the structures were solved with the ShelXT [21] structure solution program using direct methods and refined with the ShelXL [22] refinement package using least squares minimization. All hydrogen atoms bonded to nitrogen or oxygen were refined isotropically including the 1:1 disordered ones in 1H{[PhO][2]}. Details of the X-ray investigation are given in Tables 2 and 3.

Deposition numbers 2035834, 2035835, 2035836, 2035837, 2035838, 2045902, and 2045903 contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Synthesis of 1H{[4H/PhO]}: Phosphazene 1 (4.17 g, 4.70 mmol) is dissolved in 20 mL of diethyl ether and the solution of 2,6-di-tert-butyl-4-methylphenol (0.48 g, 4.71 mmol) in 6 mL of diethyl ether is rapidly added. After 15 min a colorless solid separates. The suspension is stirred for additional 30 min (30 min are sufficient) and n-hexane (10 mL) is added. The slight purple supernatant is removed via a syringe and the colorless solid is washed with additional 10 mL of n-hexane. After drying in a high vacuum the product (5.11 g, 4.62 mmol, 98%, based on 2,6-di-tert-butyl-4-methylphenol) is isolated as a colorless solid (dec. > 111 °C). Suitable crystals for XRD were grown from the ethereal reaction mixture at −28 °C. 1H NMR (500 MHz, [D6]THF, rt): δ = 1.2 (t, JH,H = 7 Hz, 3H, NCH3), 1.4 (s, 9H, NC(CH3)2), 1.4 (s, 18H, C(CH3)2), 2.1 (s, 3H, CH3), 4.2 (d, JNC,H = 8 Hz, 2H, NH), 3.2 (d, JNC,H = 10 Hz, JNC,N = 7 Hz, 3H, NCH3,CH3), 6.4 ppm (s, 2H, meta H); 13C NMR (500 MHz, [D6]THF, rt): δ = 12.9 (d, JNC,N = 4 Hz, NCH3,CH3), 21.6 (s, CH3), 29.8 (s, CH3C), 31.1 (d, JNC,N = 5 Hz, NCH3,CH3), 34.8 (s, C(CH3)2), 39.1 (d, JNC,N = 6 Hz, NCH3,CH3), 50.5 (d, JNC,N = 4 Hz, NCH3,CH3), 105.7 (s, para C), 122.9 (s, ortho C), 134.0 (s, meta C), 170.2 ppm (s, ipso C); 31P NMR (500 MHz, [D6]THF, rt): δ = −33.7 (q, JPN = 70 Hz, 1H, 1H), 7.1 ppm (d, JPN = 7 Hz, 1H, P = NH), 7.7 ppm (d, tridec, JPN = 70 Hz, JPN = 10 Hz, 3 P, (Et4N)P); IR (ATR): ν = 2964 (w), 2932 (w), 2870 (w), 2160 (w), 1973 (w), 1595 (wv), 1465 (w), 1420 (w), 1377 (m), 1250 (w), 1177 (s), 1173 (vs), 1077 (w), 1054 (w), 1017 (wv), 1017 (wv), 942 (s), 887 (w), 848 (w), 793 (s), 741 (w), 700 (s), 612 (m), 508 (vs), 448 (s), 437 (s), 399 (m), 379 (m) cm−1; MS (ESI, pos.) [m/z (% assignment]): 886.7 (100) [1H+]; MS (ESI, neg.) [m/z (% assignment): 219.1 (100) [1H+]; elemental analysis calcd % for C33H25N3O2P2: C 59.70, H 11.20, N 6.46; found: C 59.74, H 11.13, N 6.34.

Synthesis of 1H{[4H/PhO]}: Phosphazene 1 (4.86 g, 5.49 mmol) is dissolved in 20 mL of diethyl ether and the solution of 2,4,6-tri-tert-butylphenol (0.44 g, 5.50 mmol) in 5 mL of diethyl ether is rapidly added. Immediately a colorless solid precipitates from the slightly yellow mixture. The suspension is stirred for additional 30 min (30 min are sufficient) and n-hexane (10 mL) is added. The slightly yellow supernatant is removed via a syringe and the solid is washed with additional 10 mL of n-hexane. After drying in a high vacuum the product (6.24 g, 5.43 mmol, 99%, based on 1H{[4H/PhO]} is isolated as a colorless solid (dec. > 196 °C). Suitable crystals for XRD were grown from the ethereal reaction mixture at −28 °C. 1H NMR (500 MHz, [D6]THF, rt): δ = 1.2 (t, JH,H = 7 Hz, 3H, NCH3,CH3), 1.2 (s, 9H, para C(CH3)2), 1.4 (s, 9H, NC(CH3)2), 1.5 (s, 18H, ortho C(CH3)2), 2.2 (d, JPN = 8 Hz, 1H, NH), 3.3 (d, q, JPN = 10 Hz, JNP,N = 7 Hz, JNP,P = 7 Hz, 3H, NCH3,CH3), 6.7 ppm (s, 2H, meta H);
| Compound | $[1H][\text{PhO}(\text{H}_2\text{O})]$, $[1H][\text{Bu}_2\text{PhO}]$, $[\text{NBu}_4][\text{fBuPhO}]$ | $[1H][\text{fBuPhO}]$ | $[\text{NBu}_4][\text{fBuPhO}]$ | $[1H][\text{fBuPhO}]$ |
|----------|------------------|------------------|----------------|------------------|
| empirical formula | $\text{C}_{25}\text{H}_{30}\text{N}_2\text{O}_2\text{P}_4$ | $\text{C}_{25}\text{H}_{30}\text{N}_2\text{O}_2\text{P}_4$ | $\text{C}_{25}\text{H}_{30}\text{N}_2\text{O}_2\text{P}_4$ | $\text{C}_{25}\text{H}_{30}\text{N}_2\text{O}_2\text{P}_4$ |
| $a$ (pm) | 1270.911(14) | 1570.493(16) | 919.264(10) | 4964.04(4) |
| $b$ (pm) | 1334.105(14) | 1952.776(17) | 1726.121(16) | 4964.04(4) |
| $c$ (pm) | 1772.395(17) | 2297.322(32) | 3817.73(3) | 2016.72(2) |
| $\alpha$ (°) | 81.8859(9) | 90 | 90 | 90 |
| $\beta$ (°) | 85.2605(9) | 103.50891(11) | 90 | 90 |
| $\gamma$ (°) | 79.5752(9) | 90 | 90 | 120 |
| $V$ ($10^{3}$ pm$^3$) | 2846.75(6) | 6850.55(12) | 6057.82(10) | 4303.7(58) |
| $Z$ | 2 | 4 | 8 | 18 |
| $\rho_{\text{calc}}$ (mg·mm$^{-3}$) | 1.165 | 1.114 | 1.048 | 1.098 |
| crystal system | triclinic | monoclinic | orthorhombic | trigonal |
| space group | $P1$ | $P2_1/c$ | $P2_12_12_1$ | $P3$ |
| crystal size (mm$^{-3}$) | 0.332×0.258×0.096 | 0.301×0.093×0.067 | 0.339×0.142×0.12 | 0.0424×0.381×0.247 |
| $\mu$ (mm$^{-1}$) | 0.180 | 1.365 | 0.476 | 1.145 |
| $f(000)$ | 1100.0 | 2544.0 | 2144.0 | 15768.0 |
| $\delta$ (angle) | 5.36 to 72.636 | 5.788 to 153.198 | 4.63 to 153.718 | 6.986 to 154.76 |
| index ranges | $-21 \leq h \leq 21$ | $-19 \leq h \leq 19$ | $-11 \leq h \leq 11$ | $-50 \leq h \leq 61$ |
| reflections | 275615 | 142644 | 125954 | 19943 |
| independent refl. | 27575 | 142644 | 125954 | 19943 |
| $R$ (int) | 0.0610 | 0.0418 | 0.0065 | 0.0490 |
| $R_{\text{wp}}$ | 0.0377/0.0913 | 0.0369/0.0931 | 0.0311/0.0768 | 0.0302/0.0909 |
| $R_{\text{wp}}$ (all data) | 0.0559/0.1005 | 0.0426/0.0969 | 0.0336/0.0786 | 0.0401/0.1006 |
| $\Delta\rho_{\text{max}}$ (e·Å$^{-3}$) | 0.59/−0.43 | 0.54/−0.42 | 0.21/−0.16 | 0.91/−0.42 |

The water molecule is disordered with a ratio of 1:1

Inversion twin with a ratio of 1:1

A solvent mask was calculated,

2154 electrons were found,

this is consistent with the presence of three molecules of diethyl ether per formula unit, which count 2268 electrons.

CCDC number | 2035834 | 2035835 | 2035836 |
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Synthesis of $[\text{NBu}_4][\text{fBuPhO}]$: Tetra-$n$-butylammonium hydroxide triacetatehydrolysis (641 mg, 0.80 mmol) is dissolved in diethyl ether (10 mL) and the solution is added to a solution of 2,6-di-tert-butyl-4-methylphenol (189 mg, 0.80 mmol) in 5 mL of diethyl ether. The product is dried in a high vacuum overnight. The product is isolated after drying in a high vacuum as a yellow fluorescent solid. The product is then isolated by column chromatography on silica gel. The yield is 65%.

Synthesis of $[1H][\text{C}_6\text{H}_{12}\text{O}]$: Phosphazene 1 (774 mg, 0.87 mmol) is dissolved in diethyl ether (15 mL) and the solution is added to a solution of 2-naphthol (126 mg, 0.87 mmol) in 5 mL of diethyl ether. The product is then isolated by column chromatography on silica gel. The yield is 65%.
Table 3. Structure refinement data of [1H][C₆H₄O₂], [1H][C₆H₄O₂·H] and [1H][TCNE].

| Compound | [1H][C₆H₄O₂] | [1H][C₆H₄O₂·H] | [1H][TCNE] |
|----------|---------------|-----------------|------------|
| empirical formula | C₆H₄O₂N⁺,OP₄⁻ | C₆H₄O₂N⁺,H⁺ | C₆H₄N⁺,O⁻ |
| a (Å) | 1321.29(3) | 1625.06(3) | 1111.08(6) |
| b (Å) | 1413.71(3) | 1804.57(3) | 2734.33(13) |
| c (Å) | 1630.93(3) | 2300.42(4) | 1927.36(13) |
| α (°) | 90 | 90 | 90 |
| β (°) | 95.9651(17) | 97.1688(15) | 97.907(6) |
| γ (°) | 105.357(2) | 90 | 90 |
| V (Å³) | 2901.55(12) | 6693.34(19) | 5799.81(6) |
| Z | 2 | 4 | 4 |
| ρ(000) | 1.179 | 1.166 | 1.163 |
| crystal system | triclinic | monoclinic | monoclinic |
| space group | P1 | P2₁/n | P2₁/n |
| crystal size (mg mm²) | 0.241 x 0.146 x 0.05 | 0.353 x 0.269 x 0.112 | 0.427 x 0.237 x 0.23 |
| μ (mm⁻¹) | 0.177 | 0.163 | 1.563 |
| F(000) | 1132.0 | 2568.0 | 2220.0 |
| 2θ range for data col. | 5.222 to 72.964 | 5.174 to 72.638 | 5.646 to 153.29 |
| index ranges | -21 ≤ h ≤ 22 | -27 ≤ h ≤ 27 | -13 ≤ h ≤ 13 |
| reflections | 91248 | 355625 | 104415 |
| independent refl. | 26937 | 32422 | 12103 |
| R(int) | 0.0347 | 0.0783 | 0.0650 |
| data/restraints/parameter | 26937/0/1123 | 32422/0/1236 | 12103/7/655 |
| goodness-of-fit on R² | 0.0417/0.0951 | 0.0438/0.1030 | 0.0380/0.0993 |
| R1/wR2 | 0.0427/0.237 | 0.0495/0.1151 | 0.0402/0.1027 |
| Δρ dicho-max. (e Å⁻³) | 0.89/−0.63 | 0.54/−0.38 | 0.53/−0.46 |

Remarks:
The anion and some ethyl groups are disordered with a ratio of 70:30. One naphthol molecule is disordered with a ratio of 59:41. Disordered atoms close together were constrained to have equivalent thermal parameters.

Disorder of one PhMe group over two sites (57:43). Bond lengths within this disorder were restrained to be equal.

CCDC number 2045902

2 J_{PH} = 8 Hz, 1H, NH), 3.2 (d, q, J_{PH} = 10 Hz, J_{NH} = 7 Hz, 36H, NCH₂CH₂), 6.1 (s, 1H, ary H), 6.3 (m, 1H, ary H), 6.5 (m, 1H, ary H), 6.7 (m, 1H, ary H), 7.0 (m, 1H, ary H), 7.1 (m, 1H, ary H), 7.1 ppm (m, 1H, ary H); ¹³C NMR (500 MHz, [D₆]THF, rt): δ = 13.0 (d, J_{C=O} = 4 Hz, NCH₂CH₂), 31.1 (d, J_{C=O} = 5 Hz, NC(CH₃)₂), 39.1 (d, J_{C=O} = 6 Hz, NCH₂CH₂), 50.5 (d, J_{C=O} = 4 Hz, NC(CH₃)₂), 107.5 (aryl C), 111.7 (aryl C), 122.0 (aryl C), 122.3 (aryl C), 126.3 (aryl C), 126.6 (aryl C), 129.0 (aryl C), 139.3 (aryl C), 173.7 ppm (C=O); ³¹P NMR (500 MHz, [D₆]THF, rt): δ = −33.7 (q, d, J₆₇ = 70 Hz, J₇₈ = 7 Hz, 1 P, P = NH), 7.7 ppm (d, tridec, J₆₇ = 70 Hz, J₇₈ = 10 Hz, 3 P, (Et₃N)₃P); IR (ATR): ν = 2967 (vw), 2931 (vw), 2868 (vw), 1602 (vw), 1585 (vw), 1543 (vw), 1490 (vw), 1462 (w), 1437 (w), 1375 (w), 1353 (w), 1278 (s), 1254 (s), 1227 (m), 1202 (s), 1172 (s), 1104 (m), 1054 (w), 1019 (vs), 941 (vs), 844 (w), 832 (m), 789 (m), 756 (w), 734 (m), 721 (w), 705 (s), 693 (s), 625 (w), 614 (m), 593 (w), 524 (s), 508 (vs.), 467 (vs.), 455 (s), 431 (s), 418 (s), 496 (m), 386 (m) cm⁻¹; MS (ESI, pos.) [m/z (%): 886.8 (100) [C₁₂H₂₂O₂⁺]; MS (ESI, neg.) [m/z (%): 143.0 (100) [C₆H₄O⁺]; elemental analysis calc for C₁₀H₁₀N₂O₂P: C 58.28, H 10.47, N 17.67; found: C 58.32, H 10.76, N 17.03.

Synthesis of [1H][C₆H₄O₂·H]: Phosphazene 1 (714 mg, 0.81 mmol) is dissolved in diethyl ether (10 mL) and the solution of 2-naphthol (C₁₄H₁₀O₂, 232 mg, 1.61 mmol) in 5 mL of diethyl ether is rapidly added to yield a strong green-blue fluorescent solution. The fluorescence disappears after the complete addition of 2-naphthol and a second light green phase forms. The emulsion is stirred for 5 min and is then cooled to −28 °C overnight. Since no precipitation of the desired product occurs, the upper phase is removed.
via a syringe and the lower phase is evaporated to dryness. After drying in a high vacuum the product (733 mg, 0.62 mmol, 77% based on 1) is isolated as a colorless crystalline solid (mp. 76 °C). Suitable crystals for XRD were grown from a concentrated ethereal solution at –28 °C. 1H NMR (500 MHz, D2THF, rt): δ = 1.1 (t, JPH = 7 Hz, 2H, NCH2CH2), 1.3 (s, 9H, N(CCH3)3), 1.2 (d, JPH = 8 Hz, 1H, NH), 3.2 (d, JPH = 10 Hz, JPH = 7 Hz, 2H, NCH2CH2), 1.3 (s, 9H, N(CCH3)3), 6.8 (m, 2H, aryl H), 7.0 (m, 2H, aryl H), 6.9 (m, 2H, aryl H), 7.4 (m, 4H, aryl H), 7.5 ppm (m, 2H, aryl H); 13C NMR (500 MHz, D2THF, rt): δ = 12.9 (δPCH ≈ 4 Hz, 4NCH2CH2), 31.0 (δPCH ≈ 5C(HCH3)3), 39.0 (δPCH ≈ 6N, 6NCH2CH2), 50.4 (δPCH ≈ 4H, 4NCH2CH2), 108.6 (αNCH), 117.7 (αaryl C), 123.5 (αaryl C), 124.7 (aryl C), 125.6 (aryl C), 126.9 (aryl C), 137.0 (aryl C), 165.1 ppm (C-O); 19F NMR (500 MHz, D2THF, rt): δ = -33.7 (q, JPH = 70 Hz, JPH = 7 Hz, 1P, P = NH), 7.7 ppm (d, tricd, JPH = 70 Hz, JPH = 10 Hz, 3P, (Et3N)F); IR (ATR): v = 3379 (vn), 3044 (vv), 2970 (w), 2929 (vv), 2870 (wv), 1621 (vw), 1597 (vvv), 1561 (vvv), 1499 (vvv), 1465 (vvg), 1453 (w), 1417 (tv), 1378 (m), 1349 (tv), 1295 (m), 1249 (s), 1226 (m), 1202 (s), 1171 (tv), 1112 (tv), 1074 (tv), 1055 (tv), 1017 (tv), 941 (s), 865 (w), 842 (s), 799 (s), 742 (s), 699 (s), 610 (s), 536 (s), 515 (s), 471 (s), 453 (s), 427 (s) cm⁻¹; MS (EI, pos.) (m/z [%]) [assignment]: 886.9 [100] [1H]; MS (ESI, neg.) (m/z [%]) [assignment]: 143.1 [%] (C6H5O), 287.1 (7) [C13H19O4Cl]; elemental analysis calcld for C36H31N7O6P4: C 61.36, H 9.87, N 15.50; found: C 61.32, H 9.78, N 15.05.

Synthesis of [1H][(4H-benzofuran-4-0xy)H]: Phosphazene 1 (131 g, 1.47 mmol) is dissolved in diethyl ether (10 mL) and the solution of 2,6-di-tert-butyl-4-methoxyphenyl (4H-benzofuran-4-0xy)Ph, 699 mg, 2.96 mmol in 5 mL of diethyl ether is rapidly added to yield a deep green-yellow solution. The solution is stirred for 5 minutes and then cooled to –28 °C overnight by which green crystals precipitate. The supernatant is removed via a syringe and the product (2.00 g, 1.47 mmol, 100% based on 1) is isolated after drying in a high vacuum as a fine green crystalline powder (mp. (dec.) >74 °C). Exposure to air results in a slow decomposition accompanied by a color change from green to brown-green. Suitable crystals for XRD were grown from the ethereal reaction mixture at –28 °C. 1H NMR (500 MHz, D2THF, rt): δ = 1.2 (t, JPH = 7 Hz, 5H, NCH2CH2), 1.4 (s, 9H, N(CCH3)3), 1.4 (s, 3H, 3H(CCH3)3), 2.2 (d, JPH = 8 Hz, 1H, NH), 3.2 (d, JPH = 10 Hz, JPH = 7 Hz, 2H, NCH2CH2), 1.3 (s, 9H, N(CCH3)3), 3.6 (s, 6H, OCH3), 6.5 (s, 4H, meta H), 10.5 ppm (s, br, OH); 13C NMR (500 MHz, D2THF, rt): δ = 12.9 (δPCH ≈ 4 Hz, 4NCH2CH2), 30.3 (5C(CCH3)3), 31.1 (δPCH ≈ 5C(HCH3)3), 35.0 (5C(CCH3)3), 39.1 (δPCH ≈ 6H, 6NCH2CH2), 50.5 (δPCH ≈ 4H, 4NCH2CH2), 55.5 (s, OCH3), 109.8 (s, meta H), 138.5 (s, ortho C), 147.6 (s, para C), 158.5 ppm (s, ipso C); 19F NMR (500 MHz, D2THF, rt): δ = -33.7 (q, JPH = 70 Hz, JPH = 7 Hz, 1P, P = NH), 7.7 ppm (d, tricd, JPH = 70 Hz, JPH = 10 Hz, 3P, (Et3N)F); IR (ATR): ν = 2961 (wv), 2934 (wv), 2869 (wv), 2143 (wv), 2123 (wv), 1465 (wv), 1414 (wv), 1378 (wv), 1350 (wv), 1267 (m), 1225 (wv), 1205 (s), 1175 (vs), 1108 (wv), 1054 (wv), 1018 (vs), 979 (m), 942 (s), 848 (m), 821 (wv), 795 (m), 740 (m), 699 (s), 614 (wv), 590 (wv), 513 (vs), 486 (s), 457 (s), 435 (s) cm⁻¹; MS (ESI, pos.) (m/z [%]) [assignment]: 886.9 [100] [1H]; MS (ESI, neg.) (m/z [%]) [assignment]: 127.8 (37) [TCNE]; HRMS (ESI, pos.) m/z calcd for C36H31N7O6P4: 886.71696; found: 886.7177; HRMS (ESI, neg.) m/z calcd for C36N7: calcld: 128.01284; found: 128.0128; elemental analysis calcld for C36H31N7O6P4: C 54.42, H 9.93, N 23.45; found: C 55.57, H 10.11, N 22.65.

Activation of SF6: General procedure: The phosphazene phenolate salt (60 mg) is filled into a Young NMR tube containing an [D3]acetone filled capillary. First THF or EtO (0.4 mL) as the solvent is condensed onto the salt at –196 °C prior to the condensation of an excess of SF6 (3 mbar, 0.075 mmol) onto the mixture. The reaction is allowed to warm to ambient temperature and the course of the reaction is monitored by 19F NMR spectroscopy.

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Conflict of interest

The authors declare no conflict of interest.

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