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A stable crystalline triarylphosphine oxide radical anion

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Abstract: *Triarylphosphine oxides (Ar₃P=O) are ~~nowadays~~ being intensely studied as electron accepting (n-type) materials. ~~in organic electronics.~~ Despite the widespread application of these compounds as ~~versatile~~ electron conductors, experimental data regarding the structural and electronic situation in their negatively charged states remain scarce owing to their ~~pronounced~~ propensity for follow-up chemistry. Herein, a carefully designed triarylphosphine oxide scaffold is disclosed that is comprised of sterically demanding spiro-fluorenyl moieties to shield the central phosphoryl (P=O) moiety. The compound undergoes chemical one-electron reduction to afford an exceptionally stable radical anion, which was isolated and characterized by X-ray crystallography for the very first time. The experimental data corroborated by computational studies shall allow for the construction of phosphine oxide materials with enhanced stability.*

Due to the unique bonding situation at the pentavalent phosphorus center, the phosphoryl moiety acts as an electron accepting unit.[1] The formal double bond in the P=O fragment is significantly polarized and most appropriately described in terms of so-called negative hyperconjugation, i.e., the π back-donation from the lone pair at oxygen into the antibonding σ* orbital localized at the phosphorus.[2,3] These characteristics render the phosphoryl moiety a valuable building block for the construction of versatile electron acceptors, an aspect of vital importance in the context of the vigorously developing field of organic electronics.[4] Thus, triarylphosphine oxides have emerged as a promising class of electron-conducting (n-type) materials particularly suited for application in phosphorescent organic light-emitting diodes ~~(PHOLEDs)~~,[5] owing to their superior electron-transport ability, favorable morphological stability, and high triplet energy.[6] Although triarylphosphine oxides appear to almost meet all the key requirements to serve as ideal n-type semiconductors, their chemical instability during operation has recently been identified detrimental to the device lifetime.[7,8] ~~As demonstrated by theoretical and spectroscopic investigations,~~ The observed device decay mostly originates from the

considerably lowered P−C(sp²) bond dissociation energies in the negatively charged states, which are actively involved in the electron transport.[7] In fact, initial research activities on electrochemical[9,10] and chemical reductions of triarylphosphine oxides with alkali metals ~~to form the corresponding radical anions~~ date back to the 1950s[11–13] and were most likely conducted from chemical curiosity in analogy to the ketyl radical anion.[14] The electron paramagnetic resonance (EPR) spectra of the one-electron reduced triarylphosphine oxides indicated distribution of the unpaired electron spin density over the adjacent phenyl moieties.[9,10] However, the formed radical anions were prone to subsequent chemical reactions leading to numerous paramagnetic and non-paramagnetic secondary products, which hampered their isolation and characterization in the solid state.[11–13,15] Apart from these early spectroscopic studies and theoretical calculations later on,[16] to the best of our knowledge, no structural information regarding triarylphosphine oxide radical anions based on X-ray crystallographic analysis have been reported to date.
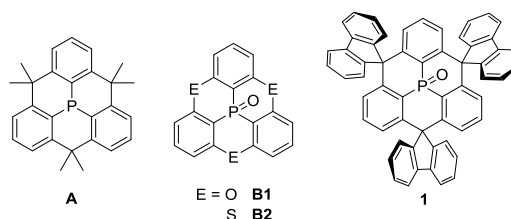

Figure 1. ~~Examples of~~ Bridged triarylphosphine **A**[17] and triarylphosphine oxides **B1**[18] and **B2**[19] reported previously. The spirofluorene-bridged scaffold **1** synthesized in this work.

In light of the continuously growing significance of organic phosphine oxide materials, structural characterization of the corresponding anionic radical species in the solid-state would be highly desirable as it could provide data essential for the molecular design of phosphine oxide scaffolds with enhanced stability. To this end, it is crucial to stabilize the vulnerable P−C(sp²) bonds in the negatively charged species and provide for sufficient steric protection of the phosphorus-centered radicals. Both requirements can be fulfilled by embedding the phosphorus atom into a π-conjugated polycyclic system akin to the previously reported dimethylmethylene-bridged phosphine **A**,[17] and its oxygen **B1**,[18] and sulfur-bridged phosphine oxide analogues **B2** (Figure 1).[19]

With this in mind, we realized triarylphosphine oxide scaffold **1**, in which the bridging C(sp³) spiro-junctions are decorated with rigid fluorenyl flanks to sterically protect the central phosphoryl moiety. We demonstrate the ability of **1** to undergo chemical reduction towards the corresponding radical anion **1·⁻** with unique stability, which enabled for the very first time the isolation and X-ray crystallographic characterization of the negatively charged state of a triarylphosphine oxide. Experimental and

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        the document.

computational studies enlightened the peculiar electronic situation in **1** and its anionic state **1**·⁻ resulting from the steric constraint around the phosphoryl moiety.
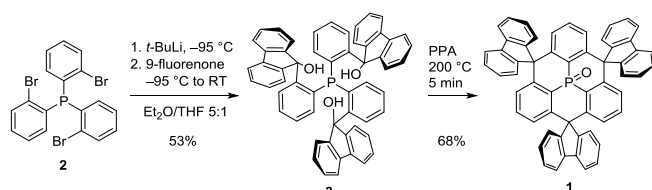
Scheme 1. Synthesis of the ~~spirocyclic~~ phosphine oxide **1**. PPA = polyphosphoric acid; THF = tetrahydrofuran.

As shown in Scheme 1, exhaustive lithiation of tris(2-bromophenyl)phosphine (**2**)[20] with *t*-BuLi in Et₂O/THF at –95 °C resulted in a yellow solution, stable for a few hours at this temperature. The lithiated species reacted readily with 9-fluorenone to afford **3** in 53% yield on a gram scale (for X-ray structural analysis and properties of **3**, see the Supporting Information). ~~crystallographic analysis of **3** revealed a unique intramolecular coordination of the three equivalent hydroxyl groups to the P(III) center with a distance of 1.906(2) Å, which is, in analogy to the previously reported *N,N*-dimethylamino-substituted triarylphosphines,[21] most likely facilitated by the rigid geometry of the peripheral fluorenyl moieties (Figure S19). Phosphine **3** was prone to oxidation yielding the P(V) species **S1**[22] after spontaneous intramolecular cyclocondensation of the initially formed phosphine oxide **S2** in analogy to the report of Hellwinkel and Krapp (see the Supporting Information).[23]~~ The final intramolecular Friedel-Crafts cyclization was achieved upon treatment of **3** with polyphosphoric acid, at 200 °C for 5 min, to deliver the trispirocyclic phosphine oxide **1**, after purification by column chromatography, as a white microcrystalline solid in 68% yield. The harsh reaction conditions were found to be crucial for the formation of **1** as at lower temperatures the reaction times were significantly prolonged and below 150 °C only partially cyclized products were identified in the reaction mixture. Interestingly, the ³¹P NMR (162.0 MHz, CD₂Cl₂) resonance of **1** appears dramatically upfield shifted at –21.0 ppm as compared to non-bridged triphenylphosphine oxide (Ph₃PO) at 27.5 ppm.
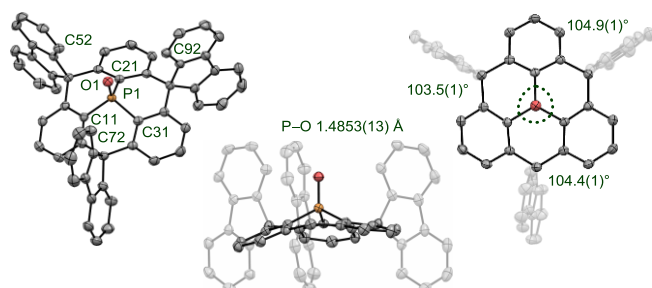

Figure 2. X-ray crystal structure of **1** (50% probability for thermal ellipsoids, H-atoms and solvent molecules are omitted for clarity).

X-ray crystallographic analysis of single crystals obtained by slow evaporation of an ethyl acetate solution of **1** at room temperature (RT) revealed a bowl-shaped structure of the triarylphosphine oxide core with a bowl depth of 1.50 Å surrounded by the three perpendicular fluorenyl flanks (Figure

2).[21] The steric congestion at the phosphorus center in **1** is reflected in the shortened average P–C bond length of 1.762(2) Å as compared to that of Ph₃PO 1.803(1) Å (Table 1.).[22] The phosphorus junction in **1** is characterized by an increased pyramidalization with a sum of the C–P–C angles of 312.8(3)° as compared to Ph₃PO with 318.6(3)°.[22] The bridging fluorenyl moieties are bent towards the phosphoryl unit denoting an intramolecular hydrogen bond interaction C(sp²)–H···O with an average C52/72/92···O1 distance of 3.21(6) Å. The observed elongation of the P–O bond distance in **1** (1.4853(13) Å) in comparison to Ph₃PO 1.479(2) Å[22] indicates a slight weakening of this bond. However, a direct assessment of the P–O strength in **1** in comparison to Ph₃PO by means of infrared spectroscopy was not accessible due to the pronounced dependency of the ν(P–O) stretching frequency on the environment,[23] that is, on the extent of intermolecular interactions in solution and in the solid state (see the Supporting Information).
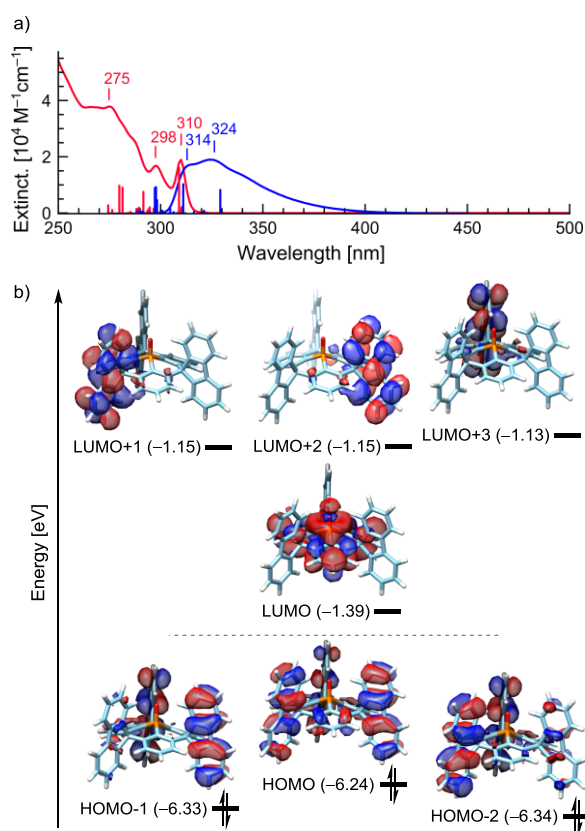

Figure 3. Photophysical properties and electronic structure of **1**. a) Experimental UV/vis absorption (red) and emission spectra (blue, λ_exc = 280 nm) in CH₂Cl₂ at RT along with the oscillator strengths (red and blue bars) obtained by TD-DFT calculations (B3PW91/def2-TZVP//PBE0/def2-TZVPP). For comparison purposes computed spectra are red-shifted by 20 nm. b) Kohn-Sham molecular orbitals (DFT, PBE0/def2-QZVP).

For a better understanding of the structural and electronic characteristics of **1**, density functional theory (DFT) calculations at the PBE0/def2-QZVP level of theory were performed. In the optimized structure of **1**, all the P–C and P–O bond lengths agree well with those observed for the molecular structure obtained by X-ray crystallography (Table 1). To elucidate the

considerable shielding of the phosphorus center, population, natural bond orbital (NBO), natural localized molecular orbital (NLMO), atoms in molecules (AIM), and electron localization function (ELF) studies were conducted, which all confirm the presence of negative hyperconjugation at the P–O moiety.[1–3] AIM analysis shows that the bond critical point (bcp) of the P–O bond is shifted towards the phosphorus atom with a P–bcp distance of 0.88 Å O–bcp distance of 0.61 Å and is characterized by positive Laplacian of electron density ($\nabla^2\rho$) as well as negative electronic energy density, which is in agreement with previous results (Figure S35a).[24] Moreover, Mayer's bond order of **1** is reduced to 1.59–1.76, compared to Ph$_3$PO with 2.05–2.10, depending on the level of theory. Reduced density gradient analysis clearly illustrates the weak intramolecular C(sp^2)–H···O interaction (Figure S35b). Together with the anisotropy of the induced current density (ACID) plot (Figure S32), these results provide a clear explanation for the unusual ^{31}P NMR upfield shift, i.e., strong electronic interaction with the adjacent aromatic rings locked in-plane by the C(sp^3)-tethers, effective π back-donation from the filled p orbital at the oxygen into the antibonding σ* orbital at the phosphorus (negative hyperconjugation), and steric effects in the phosphorus-containing six-membered rings.

The UV/vis absorption spectrum of **1**, recorded in CH$_2$Cl$_2$ at RT, features three bands at 275, 298 and 310 nm and the emission spectrum shows two maxima at 314 and 324 nm with a quantum yield of 0.07 (Figure 3a). As corroborated by time-dependent (TD) DFT computational studies, the observed UV/vis absorption and emission features originate from the electronic transitions from HOMO and HOMO–2 to the LUMO+1, LUMO+2, and LUMO+3, respectively, without involvement of the LUMO, which is localized exclusively at the triarylphosphine oxide core (Figure 3b). Hence, all transitions are of π–π* nature and occur at the electronically independent fluorenyl moieties connected through the C(sp^3) spiro-junctions (Table S5 and S6).

Cyclic voltammetry (CV) studies (CH$_2$Cl$_2$ with 0.1 M nBu$_4$NPF$_6$, RT, vs. Fc/Fc$^+$) provided further insight into the electronic nature of **1** (Figure 4c). S28 and S29). In THF the compound undergoes a reversible reduction event at –2.85 V (all potentials are reported vs. Fc$^+$/Fc) centered at the phosphoryl moiety. Furthermore, In agreement with the calculated HOMO energy level (–6.24 eV), compound 1 shows in CH$_2$Cl$_2$ two independent oxidation events are observed, which are ascribed to i) oxidation of the peripheral fluorenyl units at a half-wave potential of +1.44 V and ii) subsequent deposition of an electroactive polymer film on the working electrode as reported in the literature for other fluorenyl-containing compounds (see the Supporting Information).[25] However, under these conditions, no reduction waves could be observed; even at low potentials as negative as –2.80 V using different scan rates. Such behavior was previously reported for various phosphine oxide-based materials[29] and may be attributed to a lack of stabilization by the weakly coordinating tetra-n-butylammonium ion.

Despite the fact that phosphine oxide 1 could not be reduced by electrochemical methods, Treatment of **1** with an excess of potassium metal in THF in the presence of 18-crown-6 or [2.2.2]cryptand at RT resulted in a deep red solution of radical

anion **1**$^{•-}$ (Figure 4a). The color change was concomitant with the emergence of a UV/vis absorption maximum at 378 nm with a broad band centered at 485 nm, reaching saturation after 14 hours (Figure 4b). The spectral features remained largely unchanged even after prolonged treatment with excessive amounts of potassium for a time interval of 3 days indicating sufficient stability of the charged species under these conditions.[26]

While TD-DFT calculations completely failed to reproduce the UV/vis spectra of **1**$^{•-}$, the ZINDO/S approach with 150 roots was applied instead (Figure S33). Although the peak positions are still off by 40–60 nm, it is suggested that the absorption band around 485 nm corresponds to multiple excitations from the SOMO to LUMO and higher lying LUMO+n and the band around 378 nm originates from multiple HOMO–n to LUMO+n excitations.
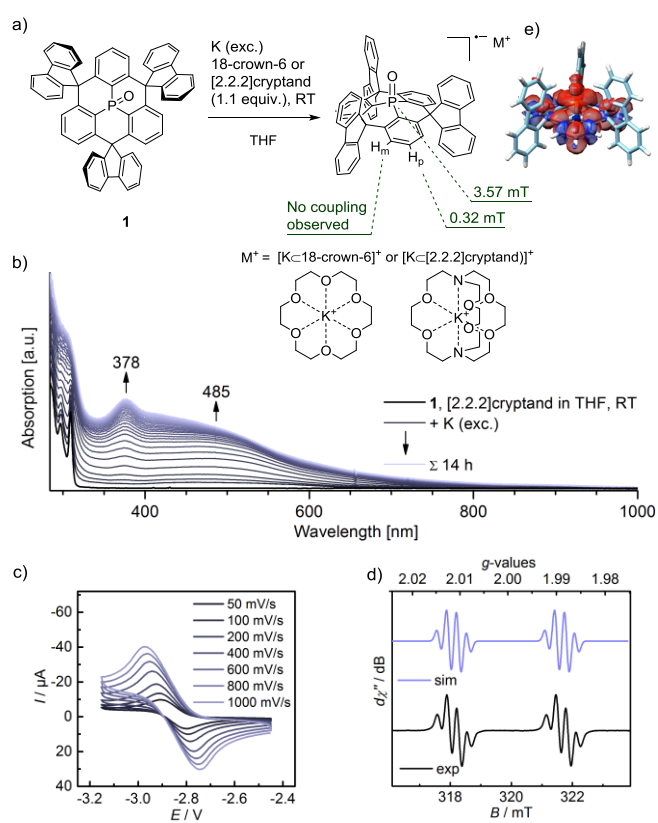

Figure 4. ~~Synthesis of radical anion 1$^{•-}$.~~ a) Chemical reduction of **1** with potassium and 18-crown-6 or [2.2.2]cryptand. b) The evolution of the UV/vis absorption spectra upon reduction of **1**. c) Cyclic voltammogram of **1** (in THF +0.1 M nBu$_4$NPF$_6$, RT, vs. Fc/Fc$^+$). d) EPR spectrum of **1**$^{•-}$ of [2.2.2]cryptand in THF at RT (black trace) and its simulation (blue trace).[27] d) Mulliken spin densities from DFT calculations (blue: "–", red: "+" spin density, isovalue – 0.0004).

The continuous wave X-band EPR spectrum of the deep red THF solution, obtained by the reduction of **1** with elemental potassium in the presence of [2.2.2]cryptand, recorded at RT, exhibits a sharp signal at $g \approx 2$ with a well resolved hyperfine structure (Figure 4d). The addition of [2.2.2]cryptand was found to significantly increase the resolution of the EPR spectra, most likely by interrupting the interactions between the radical anion

and the potassium cation through its incorporation within the cryptand (see the Supporting Information). The observed fine structure results from hyperfine coupling of the unpaired electron with the internal ^{31}P atom (I = 1/2, 100%) in addition to superhyperfine coupling to the three equivalent ^{1}H atoms (I = 1/2, 99.9%) in *para*-positions of the adjacent phenyl rings. The spectrum was simulated[27] with an effective *g*-value centered at g_{iso} = 2.0001, a linewidth W_{iso} of 0.10 mT, and hyperfine coupling constants $A(^{31}P)$ and $A(^1H_{para})$ of 99.9 MHz (3.57 mT) and 8.96 MHz (0.32 mT), respectively. These findings are in accordance with the EPR spectra reported previously for persistent radical anions derived from various acylphosphine oxides, in which, however, additional stabilization of the negative charge by delocalization into the electron-withdrawing carbonyls occurred.[28] In agreement with the literature, no coupling to *meta*-hydrogen atoms was observed.[9] Conclusively, the recorded EPR spectrum of **1**$^{•-}$ in the presence of [2.2.2]cryptand clearly indicates the formation of a discrete triarylphosphine oxide radical anion with the unpaired electron spin delocalized over the phosphoryl moiety and the three adjacent phenyl rings.[29] The experimental EPR data are supported by DFT calculated Mulliken spin densities, which confirm that only hydrogen atoms in *para*-position with respect to the phosphorus atom possess unpaired spin density (Figure 4e, Table S1). The calculated *g*-value of 2.0028 and the hyperfine coupling constants (–0.25, –0.30, and –0.32 mT) for the three *para*-hydrogen atoms are in satisfactory agreement with the experiment, although the calculations suggest very weak coupling of the unpaired phosphorus-centered electron with *meta*-hydrogens of the adjacent phenyl moieties (six values ranging from 0.03 to 0.08 mT).
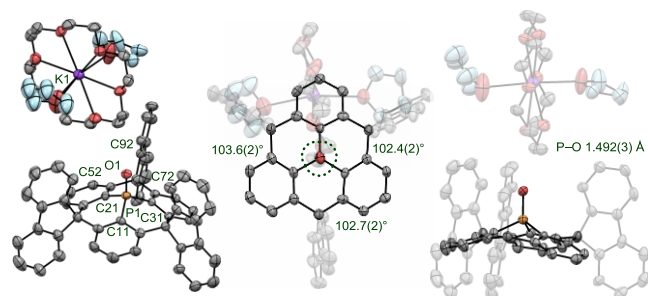

Figure 5. X-ray crystal structure of **1**$^{•-}$[K⊂18-crown-6]$^+$ and illustration of the C–P–C angles (50% probability for thermal ellipsoids, carbon atoms of THF colored light blue, disordered THF and hydrogen atoms omitted for clarity).

Single crystals of **1**$^{•-}$[K⊂18-crown-6]$^+$, obtained by slow diffusion of *n*-pentane into a THF solution of the compound at –35 °C under a nitrogen atmosphere, provide the very first opportunity to analyze the structural changes arising from the one-electron reduction of the triphenylphosphine oxide moiety (Figure 5, for further information, see the Supporting Information). The overall geometry of the spirocyclic scaffold in **1**$^{•-}$ is largely retained when compared to the neutral parent compound **1** (Table 1). However, significant deviations become apparent for the environment of the phosphorus center. The stronger pyramidalization of the phosphorus atom in the anionic state is illustrated by a lower sum of C–P–C angles 308.7(6)° for **1**$^{•-}$ as compared to 312.8(3)° for **1**, which, in turn, leads to an increased bowl depth of 1.71 Å for **1**$^{•-}$ in comparison to 1.50 Å measured for the neutral compound. Despite the increased pyramidalization of **1**$^{•-}$, the intramolecular hydrogen bond length C(sp^2)–H···O remains virtually unchanged (average C52/72/92···O1 distance of 3.21(6) Å for both compounds). More importantly, upon one-electron reduction of **1**, a slight shortening of the average P–C$_{av}$ bond length from 1.762(2) Å to 1.747(4) Å and concurrent elongation of the P–O bond from 1.4853(13) Å to 1.492(3) Å suggests delocalization of the unpaired electron over the central C(sp^2)$_3$P–O moiety, which is in agreement with the EPR results.

Table 1. Selected bond lengths [Å] and angles [°] of neutral **1** and radical anion **1**$^{•-}$[K⊂18-crown-6]$^+$ obtained from X-ray crystallographic analysis (black) and theoretical calculations (grey, see the Supporting Information).

	P–C$_{av}$[a]	P–O	∑C–P–C	Bowl depth[21]
1	1.762(2)	1.4853(13)	312.8(3)	1.50
	1.759(2)	1.487	310.2	1.60
1$^{•-}$	1.747(4)	1.492(3)	308.7(6)	1.71
	1.752	1.501	305.8	1.79

[a] Averaged values are shown with standard deviations calculated by the following equation: $\{\sum(x_i-<x>)^2/(n-1)\}^{1/2}$.

Comparable changes in the bonding situation were reported for the C–O moiety in benzophenone upon one-electron reduction to the corresponding potassium ketyl radical anion (Ph$_2$CO)$^{•-}$K$^+$, where an elongation of the C–O bond from 1.222 Å to 1.311(5) Å and concomitant shortening of the OC–C(sp^2) bond length from 1.496 Å to 1.460(6) Å was observed.[30]

Based on the orbital picture one can envisage that the addition of an extra electron to **1** to afford the corresponding radical anion should occur with an elongation of the P–O bond. Indeed, our computational studies of **1**$^{•-}$ are in a good agreement with the experiment, that is, the calculated P–O bond length is 1.501 Å, the average P–C bond length is 1.752 Å, and the C–P–C angles add to 305.8° (Table 1). The SOMO of **1**$^{•-}$ strongly resembles the parent LUMO of **1** with the unpaired electron localized on the central triphenylphosphine oxide fragment (Figure 3b). The Mulliken charge distribution in **1**$^{•-}$ indicates that the phosphoryl oxygen atom becomes more negatively charged (–0.66*e*) upon reduction, while, at the same time, the amount of the positive charge on the phosphorus atom decreases (0.39*e*) as compared to the neutral compound **1** with –0.62*e* (O) and 0.50*e* (P), respectively. In accordance with this charge evolution, Mayer's bond order decreases from 1.59 in **1** to 1.48 in **1**$^{•-}$, which corresponds well with the calculated elongation of the P–O bond length by 0.014 Å (Table 1, for calculated characteristics of Ph$_3$PO and its radical anion see the Supporting Information). In comparison to **1**, with P–bcp 0.88 Å and O–bcp of 0.61 Å, the AIM analysis shows that the bcp of the P–O bond in **1**$^{•-}$, with a P–bcp distance of 0.82 Å and an O–bcp distance of 0.68 Å, is shifted towards the phosphorus atom, which is also reflected in the observed shortening of the P–C bonds upon reduction.

Taken together, we have realized a new type of organophosphorus framework by the introduction of C(sp³)-hybridized spirofluorenyl-bridges into the triphenylphosphine oxide moiety. The incorporation of the electron-withdrawing phosphoryl moiety into a π-conjugated polycyclic framework – ~~together with~~most likely in conjunction with the sterically shielded environment provided by the bridging fluorenyls – efficiently stabilized the corresponding one-electron reduced species. Hence, this phosphine oxide radical anion could be isolated and characterized by X-ray crystallography for the very first time. On the basis of spectroscopic and computational studies, we provide fundamental insight into the structural and electronic situation in negatively charged triarylphosphine oxides, which are anticipated to occur during electron transport in organic electronics. We believe that the described molecular design will provide for the construction of phosphine oxide materials with enhanced operational stability as well as for the stabilization of other heteroatom-centered radical species, which are hitherto believed to be too unstable for isolation.

Acknowledgements

Keywords: phosphorus heterocycles• radical anions • • cyclization • polycyclic systems

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[22]   ~~The formation of compound **S1** was unambiguously confirmed by NMR spectroscopy, mass spectrometry and X-ray crystallography showing the P(V)-center with two covalent P–O bonds (1.773(3) Å and 1.745(3) Å) and a coordinated hydroxyl moiety with a P···O distance of 2.309 Å (see, the Supporting Information, Figure S20).~~

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[26]   While a THF solution of **1**˙⁻[K⊂18-crown-6]⁺ kept under Ar at –35 °C was stable for several weeks, at RT gradual decomposition towards EPR silent products was observed within several days. Decomposition of **1**˙⁻[K⊂18-crown-6]⁺ in the solid state was indicated by rapid decoloration of the crystals upon exposure to air.

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Entry for the Table of Contents

COMMUNICATION

The spin within: *A carefully designed triarylphosphine oxide scaffold with sterically demanding spiro-fluorenyl moieties undergoes chemical one-electron reduction at its phosphoryl moiety. The unique stability of the formed radical anion enables for the isolation and X-ray crystallographic characterization of this hitherto elusive species.*
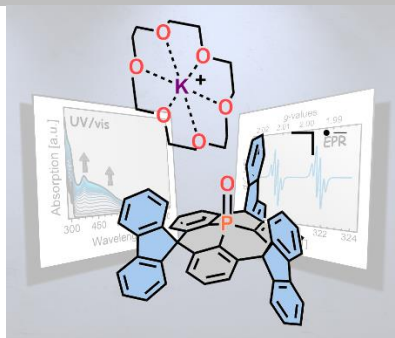
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A stable crystalline triarylphosphine oxide radical anion

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