Synthesis of a stable radical anion via the one electron reduction of a 1,1-bis-phosphinosulfide alkene derivative†

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A new type of stable radical ligand featuring a 1,1-bis-phosphinosulfide alkene backbone has been prepared and characterized on the basis of X-ray diffraction, EPR and DFT studies.

Organic π-conjugated oligomers or polymers have been extensively studied over the last 30 years, and some of these species show semi-conducting properties or even possess metallic behavior upon doping.1 The introduction of some hetero-elements such as N or S in these materials, either as end groups or part of the repeating monomeric unit, (such as in poly(thiophene), poly(aniline) or poly(pyrrole)) has proven highly beneficial.1,2 Surprisingly, the incorporation of phosphorus has seldom been done.3 Two different uses of phosphorus-containing groups may be envisaged. Firstly, it can be incorporated in the oligomeric (or polymeric) backbone, such as in polyphosphines. Or the phosphorus group may be incorporated as a terminal group and used to polarize the extended π-system: typically the push–pull systems found in NLO (Scheme 1). In this case, phosphine like moieties (R3P) acting as a σ-donor group should be less efficient than the corresponding amine groups, as “R3P” is pyramidal and the lone pair at phosphorus overlaps to a lower extent with the π-system.3 On the other hand, σ-bonded phosphorus fragments could be used as π-acceptors (via negative hyperconjugation).4,5 In fact, we have recently studied the potential of the phosphonium group to act as strong electron acceptor group for the polarization of a π-system and probed their ability to stabilize persistent radicals obtained by one-electron reduction.6 From another standpoint, the rare radical-bearing ligands, among which the nitronyl nitroxide ligand has been extensively studied, possess highly desirable properties.7 Namely, a strong direct exchange between the ligand and the metal center has been observed, depending both on the nature of the radical and on the electronic properties of the metal. A whole new area would then be opened if one could combine the two properties of chosen σ-bonded phosphorus fragments: the ability to stabilize radical species of an extended π-system and coordination to a metal center. We thus envisaged the stabilization of radical species of alkene derivatives bearing two P(V) fragments such as phosphine oxide, sulfide or iminophosphorane. These fragments indeed would also allow a fine tuning of the redox potential in the reduction of the alkene fragment. We present here our preliminary results in this endeavor, showing how the phosphine sulfide stabilizes efficiently the added electron density. A study of the electronic structure allows us to fully apprehend the electronic transfers occurring in these systems (Scheme 2).

The bis-sulfide 1 was chosen to test our hypotheses. Its synthesis is based on the Schrock type reactivity of the Zr carbene complex toward ketone derivatives, as reported recently (Scheme 2).8 This neutral species was crystallized which will allow for a structural comparison with the reduced species.9 The cyclic voltammetry revealed that this species may be reversibly reduced at −1.33 V (vs. SCE, CH3CN, RT) even at low scan rates (50 mV s−1). Not surprisingly, this potential is quite cathodically shifted compared to the analogous bis-phosphonium derivative (−0.54 V),8 this cationic moiety being a much stronger electron withdrawing group than the corresponding phosphine sulfide studied here. Anyhow, the reversibility of the reduction wave suggested that a persistent radical anion might be stable. The reduction of 1 was indeed performed equally well with either KC8 or Na/naphthalene in THF or DME at low temperature. The solution turned immediately purple and after warming to 25 °C, a 31P NMR spectrum showed the absence of any signal, pointing to the successful synthesis of the paramagnetic species 1+ M+ (M = Na or K). This species was isolated in an excellent 98% yield by crystallization relying on the slow diffusion of pentane into the crude reaction mixture.†

Use of phosphorus based groups as

Part of the π system

Polarizing end-groups

Electron donor end-group

Electron acceptor end-groups

Scheme 1

It was analyzed both by X-ray crystallography and EPR spectroscopy. The ORTEP plot of this radical anion is presented in Fig. 1. Several key aspects have to be highlighted. First and foremost, not only is this radical anion stable, but it also presents two phosphine sulfide moieties able to coordinate metal centers. Indeed, the two sulfur atoms bind to the K⁺ ion with different coordination modes: terminal and bridging. In terms of bond distances, compared to the neutral species, one notes a significant increase of the C1–C2 bond distance at 1.473(3) Å (vs. 1.368(3) Å in 1), the C–C bond being the site of reduction. In the radical anion the C–C bond has lost its double bond character. This is correlated to a decrease of both the P–C bond distances (1.754(2) Å and 1.767(2) Å vs. 1.836(2) Å and 1.845(2) Å in 1) and C–Ph bonds (vide infra). Apparent in the structure, the CPH₂ group is twisted from the plane denoted G, Aiso = 8.7 G) reasonably agree with the experimental ones; interactions with the protons of the two phenyl rings bound to carbon C2 (Aiso (Gauss) = −3.08 for Hortho, −2.65 and −2.38 for Hpara, 1.35 and 0.99 for Hmeta) are quite consistent with the observed hyperfine structure. These results are indicative of a spin density mainly localized on the C2 and C1 atoms and reveal the participation of the phenyl rings and the phosphinosulfide groups in the stabilization of the extra electron. The drastic effect of the presence of cryptand on the EPR spectra confirms the coordinating potential of these radicals ions in solution.

The electronic structure of 1⁺⁻ was analyzed with the aid of DFT calculations and NBO analyses. These were carried out on the real molecules 1 and 1⁺⁻, the geometry of the naked radical anion being optimized in the C2 point group. The neutral species 1 exhibits a (πC–C)² configuration, the anti-bonding π* C–C orbital being vacant (LUMO of 1, Fig. 3). The reduction of 1 to 1⁺⁻ leads to the addition of a single electron in the π* C–C orbital which is now described by the SOMO of the radical anion. Accordingly, the C1–C2 bond distance is significantly elongated and the corresponding Wiberg bond index is decreased from 1.72 to 1.21. The SOMO is also bonding between C1 and the phosphorus atoms, this accounts for the shortening of the P–C1 bond lengths observed in the X-ray structures. 1⁺⁻ finally possesses a (πC–C)²(π* C–C)²...
from the charge of the sulfur centers therefore increases upon reduction of the sulfide groups of the reduced species to the cation K⁺ both experimentally and theoretically. Moreover, the X-ray study and EPR experiments prove the coordination of the two phosphine NBOs of the radical anion. The capability of the ligand in the radical anion.

Due course.

Theoretical form but also are efficient in stabilizing the added electron in solution and in the solid. This opens the way to the use of such species as a new class of spin-bearing ligands for transition metal centers. Studies in this direction are currently underway in our laboratories and results will be reported in due course.

Notes and references

† DME (15 mL) was condensed onto a mixture of I (100 mg, 0.16 mmol) and KC₈ (22 mg, 0.16 mmol) at −78 °C. The solution was warmed to room temperature and stirred for 2 h. Graphite was removed from the crude mixture by centrifugation. A mixture of hexanes was then condensed at −78 °C onto the solution, which resulted in the formation of deep purple crystals of [I⁺,K⁺]-Et₂O within 12 h. The resulting crystals were isolated and washed with pentane (2 × 5 mL) to afford I⁺,K⁺ in 98% yield (116 mg). No NMR spectrum is available for this compound owing to its paramagnetic nature. CCDC 654637† contains the supplementary crystallographic data for this paper.


10 See Electronic Supplementary Information for further details.