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Triplet-State Phosphoryl Diradicals

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The first example of triplet-state phosphoryl diradicals is reported. Photoinduced dissociative electron capture of two diastereoisomeric m-phenylenediphosphinic chlorides in a glassy toluene matrix at 130 K using an electron-rich olefin affords the corresponding phosphoryl monoradicals and triplet-state diradicals in a 5:2 ratio. The triplet-state ESR spectrum gives zero-field parameters of |D/\hbar c| = 0.0120 cm⁻¹ and |E/\hbar c| = 0.0015 cm⁻¹. Variable temperature ESR experiments reveal Curie behavior for the Δm_s = 2 ESR signals between 3.8 and 100 K, consistent with a low-energy triplet state that either corresponds to the ground state or is degenerate with a singlet state. For the corresponding p-phenylene diastereoisomers, no triplet-state diradicals can be detected under identical experimental conditions and the ESR spectra only reveal the primary phosphoryl monoradicals and their protonated forms, as secondary species.

Introduction

Intramolecular ferromagnetic interaction within di-, oligo-, and polyradicals attracts considerable interest for the design of high-spin organic molecules and molecular ferromagnets.¹,² Taking advantage of the topological symmetry and the in-phase periodicity of spin polarization in alternant hydrocarbons, various high-spin molecules have been designed and characterized.³ One particular successful strategy to construct high-spin molecules is by coupling π and σ open-shell centers by a m-phenylene unit. Using m-phenylene, Iwamura et al. have prepared a series of high-spin oligocarbenes up to a branched nonacarbene possessing a nonadecet (S = 9) ground state.⁴ Linking triarylmethyl radicals via meta positions, Rajca et al. have obtained a S = 5 decaradical.⁵ In addition to these appealing examples, m-phenylene gives rise to high-spin ground-state molecules for various di-, oligo-, and polyradicals containing carbon and nitrogen radical centers,⁶ e.g. in di- and trinitroxyl radicals.⁷ However, all examples known up to now exclusively comprise light-element multiradicals. The possibility of incorporating heavy elements such as silicon or germanium has recently been suggested, but experimental examples have not been described so far.¹⁶ To investigate the possibility of ferromagnetic interactions between heavy-atom spin-containing substituents, we set out to prepare phosphoryl diradicals.

Phosphoryl radicals (R₂PO) are closely related to nitroxy radicals (R₃NO), having the same number of valence electrons. In contrast to nitroxy radicals, for which single or shallow double-well potential energy surfaces are found for out-of-plane distortions,³⁸ there is no doubt that phosphoryl radicals are nonplanar.⁹ The pyramidal geometry of phosphoryl radicals gives rise to stereoisomerism as was shown by de Waal et al.,¹⁰ X irradiation of single crystals of phosphinic chloride I at 77 K produces the corresponding phosphoryl 1a (Figure 1) that exhibits an enantioselective stereoinversion after annealing to 120 K. The large isotropic (A_iss) and dipolar (A_dip) hyperfine couplings observed for 1a indicate that more than half of the spin density is localized on phosphorus in a valence sp² hybridized molecular orbital with a p/s ratio of about 6.

Figure 1. Structure of monophosphinic chloride 1 and radicals 1a,b observed after a dissociative electron capture reaction of 1 induced by UV irradiation of e.r.o. in a 2MeTHF matrix.

remaining spin density is predominantly confined to the phosphoryl oxygen.¹⁰ It is clear that neither the pyramidal geometry at phosphorus, the reduced overlap of the phosphoryl valence 3p orbital with the 2p–π m-phenylene orbitals, nor the spin delocalization onto the phosphoryl oxygen are beneficial for a high-spin ground state in a phosphoryl diradical. On the other hand, m-phenylene is known to be a fairly robust ferromagnetic coupling unit, even for significantly twisted geometries.¹¹ In view of these conflicting arguments, one can speculate on the possibility of achieving a high-spin ground state for phosphoryl diradicals. In order to test this possibility we have prepared m-phenylenediphosphinic chlorides 2 and 3 and studied their conversion to the corresponding phosphoryl diradicals by P–Cl bond fission. For comparison we have studied the p-phenylene isomers 4 and 5 as well (Figure 2). All precursors possess two phosphorus stereocenters resulting in three possible stereoisomers (RR, SS, RS). Compounds 2 and 3 (as well as 4 and 5) represent the racemic mixture (RR + SS) and the meso (RS) compound, respectively.

Using these precursors, we were able to obtain spectral evidence of a first heavy-atom high-spin diradical linked via m-phenylene, and here we report the preparation and characterization of the low-energy triplet-state phosphoryl diradicals 2b and 3b and assess the multiplicity of their ground state.


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Experimental Section

P,P'-Bis(2,4,6-tris(1,1-dimethylethyl)phenyl)phenylenebis-(phosphinic chloride) (2-5) were prepared starting from 1,3- and 1,4-phenylenebis(phosphonous dichloride) by coupling with two equivalents of 2,4,6-tris(1,1-dimethylethyl)phenyllithium at low temperature, followed by oxidation using dimethyl sulfoxide. The stereoisomers were separated by column chromatography into the racemic (2, 4) and meso (3, 5) forms and characterized by 1H-, 13C-, 31P-NMR spectroscopy, elemental analysis, and X-ray crystallography (2, 3, and 5).

Toluene and 2-methyltetrahydrofuran (2MeTHF) were dried and degassed prior to use. Samples were prepared by adding 100 μL of a 0.25 M solution of 1,1',3,3'-tetramethyl-2,2'-biimidazolidinylidene, which are readily oxidized upon UV irradiation, yielding reactive free electrons. In this study we use a mixture of the appropriate phosphinic chloride precursor and an excess of ero in a frozen solvent matrix of either toluene or 2MeTHF in combination with in situ UV irradiation at cryogenic temperatures.

ESR spectra were recorded using a Bruker ER200D SRC spectrometer, operating with an X-band standard cavity and interfaced to a Bruker Aspect 3000 data system. Temperature was controlled by a Bruker ER4111 variable temperature unit combined with an ESR900 continuous flow cryostat in the range 3.8–100 K. Saturation of the ESR signal during variable temperature experiments on the \( \Delta m_s = 2 \) transitions was avoided by application of low microwave powers, typically 1 mW, which was well within the range where intensity followed the square root of microwave power at 5 K.

UV irradiation was performed by focusing unfiltered UV light from a Philips SP 500 W high-pressure mercury lamp on a sample in the cavity of the ESR spectrometer. ESR spectra were generally recorded with the UV light switched off.

Results and Discussion

Phosphonyl radicals can be prepared by X irradiation at cryogenic temperatures from a phosphinic chloride precursor. This process takes place via a dissociative electron capture reaction of the P–Cl bond, the electrons being provided by the indiscriminate ionization caused by X irradiation. An alternative free electron source is provided by electron-rich olefins (ERO), e.g. 1,1',3,3'-tetramethyl-2,2'-biimidazolidinylidene, which are readily oxidized upon UV irradiation, yielding reactive free electrons. In this study we use a mixture of the appropriate phosphinic chloride precursor and an excess of ero in a frozen solvent matrix of either toluene or 2MeTHF in combination with in situ UV irradiation at cryogenic temperatures.

Monophosphinic Chloride 1. UV irradiation of a 5:1 mixture of ero and bis(2,4,6-tris(1,1-dimethylphenyl)phosphinic chloride (I) in 2MeTHF at 77 K for 30 min and recording the ESR spectrum at 110 K affords an anisotropic 31P doublet spectrum attributed to Ar2PO (1a, Ar = 2,4,6-tris(1,1-dimethylethyl)phenyl), featuring well-resolved parallel (\( A_{||} = 1390 \text{ MHz} \)) and perpendicular (\( A_\perp = 868 \text{ MHz} \)) transitions (Figure 3a). The isotropic and dipolar contributions to the hyperfine coupling tensor \( A_{100} = (A_{||} + 2A_\perp)/3 = 1042 \text{ MHz} \) and \( 2A_{\text{dip}} = A_\perp - A_{100} = 346 \text{ MHz} \) (Table 1) are in good accordance with the values previously reported for radiogenically generated 1a in glassy toluene and single crystals.

Gradual warming of the sample to 120 K produces a secondary phosphorus-centered radical, 1b (Figure 3b). The ESR spectrum of 1b exhibits a large 31P hyperfine coupling (\( A_{100} = 1210 \text{ MHz} \)) together with an additional splitting of about 50 MHz by one I = 3/2 nucleus. A similar additional hyperfine coupling has been observed for PhPO(OH) radicals, and we tentatively assign 1b to the Ar2POH* radical. This anisotropic

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Figure 2. Structures of racemic (2, 4) and meso (3, 5) forms of meta and para isomers of P,P'-bis(2,4,6-tris(1,1-dimethylethyl)phenyl)phenylenebis-(phosphinic chloride) and the mono- and diradicals observed after a dissociative electron capture reaction of 2–5 induced by UV irradiation of ero in a toluene matrix.
Triplet-State Phosphoryl Diradicals

Figure 3. ESR spectra after reduction at 77 K of monophosphinic chloride 1 in 2MeTHF: (a) at 110 K; (b) at 120 K.

TABLE 1: Isotropic and Dipolar Hyperfine Couplings for Phosphoryl Mono- and Diradicals

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<tr>
<th>radical</th>
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<th>T (K)</th>
<th>$A_{31P}$ (MHz)</th>
<th>$2A_{31P}$ (MHz)</th>
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<td>348</td>
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<td>2MeTHF</td>
<td>120</td>
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<tr>
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<td>110</td>
<td>1099</td>
<td>332</td>
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</table>

* Isotropic and dipolar hyperfine couplings are corrected up to second-order. ** For the diradical in the triplet state.

double-doublet ESR spectrum disappears irreversibly at 130 K, leaving the original doublet spectrum of Ar$_2$PO, which remains up to the melting temperature of the host matrix.

Racemic 1,3-Phenylenebis(phosphinic chloride) 2. The X-ray crystallographic analysis of 2 shows that the two phosphoryl bonds are coplanar with the central m-phenylene ring (Figure 4). $^1$H- and $^3$P-NMR spectra are consistent with this structure and give no indication of other stable conformations in the temperature range from 193 to 293 K.12

The most favorable procedure for forming phosphoryl diradicals is UV irradiation of a 5:1 mixture of ero and 2 in toluene at temperatures around 130–135 K for several hours. The major transitions in the $\Delta m = 1$ region of the ESR spectrum (Figure 5a) show a strong resemblance to those obtained by irradiation of the monophosphinic chloride 1. Accordingly, they are attributed to a monoradical (2a), resulting from cleavage of only one of the P–Cl bonds in the precursor molecule. The central line is due to photo-oxidized ero (radical cation) and is slightly more persistent in frozen toluene than in 2MeTHF at the temperature at which the UV irradiation is performed. The most interesting features in the ESR spectrum (Figure 5a) are two pairs of transitions in the outermost low- and high-field regions.

These lines are assigned to a triplet-state phosphoryl diradical (2b), formed in two successive dissociative electron capture reactions of both P–Cl bonds of the bis(phosphinic chloride) precursor. Direct spectral evidence for the existence of a triplet species is obtained from the spectrum in the $\Delta m = 2$ region (Figure 6a), featuring a number of well-resolved transitions, that can only be attributed to a triplet state. Diradical 2b is stable in the toluene matrix up to the melting point of toluene.

By using the isotropic and dipolar hyperfine couplings of Ar$_2$PO, a spectral simulation of the $\Delta m = 2$ signal (Figure 6b) has been obtained, which is in excellent agreement with the experimental spectrum. The fact that hyperfine coupling with two identical $^3$P nuclei is observed while the isotropic and dipolar hyperfine coupling constants are halved indicates that the phosphoryl radicals are strongly coupled in 2b, i.e. $|J| > |A_{31P}|$, where $A_{31P} \approx 1500$ MHz (or 0.05 cm$^{-1}$). The zero-field splitting of triplet diradical 2b is characterized by $|D_{31P}| = 0.0120$ cm$^{-1}$, $|E_{31P}| = 0.0015$ cm$^{-1}$, and $\beta = 90^\circ$ (Euler angle of $D$ and $A_{31P}$). The $\Delta m = 1$ region of the spectrum is reproduced adequately by combining the simulations of monoradicals and diradicals in a 5:2 ratio (Figure 5b). This implies a significant concentration of diradicals as compared to monoradicals, possibly indicating that the second P–Cl bond within the same molecule is cleaved at a higher rate than the first.

**Meso 1,3-Phenylenbis(phosphinic chloride) 3.** The X-ray structure of 3 (meso, R,S) (Figure 4) is very similar to the structure of 2 (racemic mixture, RR + SS). Due to the different stereochemistry of 3, only one phosphoryl bond lies in the plane of the central m-phenylene ring, and, hence, the two phosphorus nuclei in 3 are not equivalent in this conformation. Variable temperature $^3$P-NMR spectroscopy indicates that at 203 K, in fact, two different stable conformations for 3 exist, each possessing magnetically nonequivalent phosphorus nuclei.12

UV irradiation of meso isomer 3 reveals essentially the same behavior as compared to racemic form 2 under identical experimental conditions. We conclude that monoradicals 3a and diradicals 3b are formed. The $\Delta m = 2$ ESR spectrum of 3b is identical to that of the racemic form (Figure 6c). The $\Delta m = 1$ ESR spectrum of 3b (Figure 5c), however, is somewhat different and reveals a total of eight lines in the outermost regions of the spectrum, in contrast to the ESR spectrum of 2b, which exhibits only four lines in this section. These eight transitions are likely to arise from two different conformations of the diradical, resulting from the two conformers of the precursor that exist at low temperatures, as inferred from variable temperature NMR spectroscopy studies.

**Racemic 1,4-Phenylenbis(phosphinic chloride) 4.** Variable temperature $^1$H- and $^3$P-NMR spectra indicate two possible conformations of 4 at low temperature, corresponding to the syn and anti orientations of the phosphoryl bonds in the plane defined by the p-phenylene ring. No X-ray structure has been obtained.12

The ESR spectrum of a UV irradiated 5:1 mixture of ero and 4 recorded at 110 K (Figure 7a) reveals the transitions of a phosphoryl monoradical (4a). No signals that can be attributed to a triplet state are observed in the $\Delta m = 1$ or $\Delta m = 2$ regions at various temperatures and/or irradiation times.

Slight annealing results in a complete conversion of phosphoryl radical 4a to a secondary phosphoryl-centered radical (4b) exhibiting an additional hyperfine splitting (Figure 7b). The $^3$P hyperfine splitting of 4b is similar to that of primary radical 4a. This behavior is similar to the formation of 1b from 1a in monophosphinic chloride 1. In this case, however, the extra hyperfine splitting is significantly larger: 110 MHz for 4b vs 50 MHz for 1b.
Figure 4. Molecular structures of 2, 3, and 5 as determined by X-ray crystallography.

Figure 5. ESR spectra in the $\Delta m_z = 1$ region of radicals derived from bis(phosphinic chloride) precursors 2 and 3: (a) 2a and 2b in a toluene matrix at 130 K; (b) simulation of a 5:2 mixture of the mono- and diradical; (c) 3a and 3b in a toluene matrix at 130 K.

The absence of a triplet state for 4 does not necessarily imply that no diradicals are formed, since the radical centers may couple antiferromagnetically to a singlet state ($J \ll 0$) which is not detected by ESR. In fact, this is to be expected when spin polarization does occur in the $p$-phenylene ring because the topology favors antiferromagnetic interaction by the out-of-phase periodicity of the spin polarization at the 1,4 positions.

*Meso 1,4-Phenylenebis(phosphinic chloride) 5.* The two phosphoryl bonds of 5 are in an *anti* coplanar conformation with the $p$-phenylene ring (Figure 4), as evidenced by X-ray crystallography. $^1$H-NMR spectroscopy at 193 K has shown that also a *syn* coplanar conformation of the phosphoryl bonds exists.12

No triplet state can be observed after UV irradiation of a 5:1 mixture of ero and 5 in toluene. The ESR spectrum recorded at 110 K (Figure 7c) exhibits signals of $\text{Ar}_2\text{PO}^-$ (5a) and $\text{Ar}_2\text{POH}^+$ (5b) monoradicals. Analogous to UV irradiation of 4, no conclusive evidence can be obtained whether diradicals are formed in 5. The absence of triplet-state diradicals for 4 and 5 under identical experimental conditions as for 2 and 3 suggests the presence of antiferromagnetic coupling.
Figure 7. ESR spectra in the $\Delta m = 1$ region of radicals derived from bis(phosphinic chloride) precursors 4 and 5: (a) 4a in a toluene matrix at 110 K; (b) 4b after raising the temperature to 130 K; (c) 5a and 5b in a toluene matrix at 110 K. Central part of the spectra is left out for clarity.

Determination of the Ground State for 2b and 3b. The results on phosphoryl radical formation in 2–5 suggest that spin polarization does occur in the central phenylene ring, stabilizing a high-spin state for meta and possibly destabilizing it for para isomers. The magnetic interaction within a diradical can be described by the Heisenberg exchange Hamiltonian, $H = -2J(S_1S_2)$, where $2J$ is the singlet–triplet energy gap. Several techniques have been used to determine $J$ (and hence the multiplicity of the ground state) for di-, oligo-, and polyradicals.\(^2\) Magnetization and magnetic susceptibility measurements cannot be used directly in the present case due to the inhomogeneity of the samples that contain various doublet species in addition to the triplet-state diradical of interest. ESR spectroscopy can be used in such a case, but will only give accurate values for $J$ when $|J|$ is on the order of the thermal energy.\(^2\)

Variable temperature ESR experiments were carried out in an attempt to assess the ground-state multiplicity of diradicals 2b and 3b. The intensity (I) of the $\Delta m = 2$ signal was measured as a function of temperature, between 3.8 and 100 K, with the UV light switched off. The temperature dependence of the $\Delta m = 2$ ESR signals of 2b and 3b follows Curie behavior, i.e. $I = C/T$ (Figure 8). This thermal behavior is completely reversible in the temperature range examined, indicating that irreversible loss of diradicals is negligible.\(^6\) The fact that linear Curie behavior is observed has two possible interpretations. Either the high-spin state (triplet) is the ground state and separated from an excited low-spin (singlet) state by a substantial energy gap of a few hundreds of calories/mole or an extremely small energy gap is present, resulting in a (near)

degenerate ground state.\(^7\) Without additional information, such as magnetization or magnetic susceptibility data, it is not possible to distinguish between either possibility. In principle, a linear variation of the spectral intensity as a function of the reciprocal temperature is also expected when a rapid equilibrium between the various states of different multiplicity is absent. In the present case, however, this criterion is readily met as a result of the relatively high spin–orbit coupling constants of the phosphorus atoms that enhance intersystem crossing rates. Therefore, we conclude that the triplet state of diradicals 2b and 3b is a low-energy state, either corresponding to the ground state or as part of a degeneracy with a singlet state. This demonstrates the versatility of m-phenylene as a ferromagnetic coupling unit, even for phosphorus-centered radicals.

The distance $d$ (Å) between the two radical sites in 2b and 3b can be estimated from the zero-field splitting under a point dipole approximation by $|D|/|h|c = 2.6017d^{-1}$. The observed $|D|/|h|c$ value of 0.0120 cm$^{-1}$ corresponds to a distance of about 6.0 Å, which is somewhat larger than the actual P–P distance of 5.6 and 5.5 Å for precursors 2 and 3, respectively, as determined by X-ray analysis. Similarly, we can estimate the $z$fs of a hypothetical diradical derived from 4 or 5 using the P–P distance of 6.40 Å given by the X-ray structure of 5. The expected separation of the two radical centers is 6.40 ± 0.50 Å and gives $|D|/|h|c = 0.0080$ cm$^{-1}$. The absence of corresponding signals in the $\Delta m = 1$ region gives unambiguous evidence for the absence of triplet-state diradicals for 4 and 5.

Although the spin density distribution on phosphorus indicates a pyramidal geometry, there is no conclusive evidence of stereoisomerism between diradicals 2b and 3b, formed from the racemic and meso precursors, respectively. It is well established that, in a frozen solvent matrix at cryogenic temperatures, intramolecular motional freedom of free radicals is sufficient to allow for monomolecular reactivity. Hence, it is very well possible that stereoisomerization takes place, not being observed experimentally in the randomly oriented matrix employed in this study. If this is the case, radicals 2b and 3b are identical, being the energetically favored diastereoisomer.

The additional pairs of lines observed in the spectrum of 3b are likely to arise from a different conformation of precursor 3, on the basis of low-temperature NMR studies. The conformational diversity of 3 is a result of the sterically crowded 2,4,6-tris(1,1-dimethylethyl)phenyl substituents and involves syn and anti conformations of the two phosphoryl bonds with respect

Figure 8. Temperature dependence of the $\Delta m = 2$ ESR signal intensity of biradicals 2b (■) and 3b (■). Solid lines are least-squares fits to the Curie law.
Conclusion

We have shown that phosphoryl diradicals 2b and 3b, coupled via a m-phenylene unit, possess a low-energy triplet state that is either the ground state or degenerate with a singlet state. This is another example of radical centers on heavy atoms ferromagnetically coupled by m-phenylene. In our opinion, this study demonstrates the potential application of second-row atoms as entities for newly designed high-spin molecules. Present research is focused on further exploring this proposition.

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Supplementary Material Available: Experimental details for the preparation, purification, and characterization of compounds 1-5 and variable temperature NMR spectra (7 pages). Ordering information is given on any current masthead page.

References and Notes


(16) In fact, diradicals 2b and 3b are persistent for at least 10 days without significant loss of ESR intensity when kept at 77 K.