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# Triplet-state phosphinyl diradicals

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**Photoinduced dissociative electron capture of a sterically hindered *m*-phenylenebis(phosphinous chloride) in the presence of an electron-rich olefin at 110 K affords a novel triplet ground-state phosphinyl diradical which is fully characterised using EPR spectroscopy.**

Intramolecular alignment of electron spins in oligo- and poly-radicals is considered as a promising route towards high-spin molecules and may eventually result in organic molecular ferromagnetic materials.<sup>1-3</sup> The general strategy for obtaining high-spin molecules is to couple radical centres *via* a ferromagnetic coupling unit such as *m*-phenylene. In *m*-phenylene the topological symmetry and in-phase periodicity of spin polarisation favours intramolecular ferromagnetic coupling of pendant radical centres over antiferromagnetic coupling. Although this strategy has been used successfully to align the electron spins of various carbon- and nitrogen-centred radicals, the use of other central atoms as radical centres has received less attention.<sup>4,5</sup>

Here we describe the formation of a novel phosphinyl diradical  $1^{\bullet\bullet}$  in which two phosphorus-centred radicals are coupled *via* *m*-phenylene. The diradicals are obtained *in situ* from a sterically hindered *m*-phenylenebis(phosphinous chloride) precursor **1** in the presence of an electron-rich olefin (ero) at 110 K *via* a photoinduced process (Fig. 1). In this reaction, UV irradiation of an ero in a toluene glass at low temperature produces free electrons which are reactive towards the P-Cl bonds. After electron capture, the resulting transient anion radical (with a  $\sigma^*$  three-electron P-Cl bond) dissociates into a phosphinyl radical ( $R_2P^\bullet$ ) and a chlorine anion. This dissociative electron capture reaction requires one free electron for producing a radical centre and formation of diradicals is expected to take place in two consecutive steps.

The precursor *P,P'*-bis[2,4,6-tris(1,1-dimethylethyl)phenyl]-1,3-phenylenebis(phosphinous chloride) **1** was prepared from

1,3-phenylenebis(phosphonous dichloride) by coupling with 2 equiv. of 2,4,6-tris-(1,1-dimethylethyl)phenyllithium at low temperature in tetrahydrofuran. Characterisation using  $^1H$ ,  $^{13}C$  and  $^{31}P$  NMR spectroscopy revealed that the phosphorus atoms are stereocentres, affording **1** as a mixture of *meso* (*R,S*) and *racemic* (*R,R* and *S,S*) diastereoisomers.<sup>5</sup> Samples for UV irradiation were prepared by freezing a 1:5 mixture of **1** and 1,1',3,3'-tetramethyl-2,2'-biimidazolidinylidene as ero in toluene at 77 K. UV irradiation was performed using a 500 W high-pressure Hg lamp (Müller Optik).

The EPR spectrum of a 1:5 mixture of **1** and ero in toluene at 110 K, obtained after UV irradiation, is a complex superposition of at least three different paramagnetic species (Fig. 2). The strong central line (partially omitted for clarity) is readily assigned to ero radical cations and trapped free electrons. The two strong signals (marked  $1^\bullet$ ) in the lateral regions of the EPR spectrum are attributed to phosphinyl monoradical  $1^\bullet$  and correspond to the  $A_{||}$  components of an axially symmetric  $^{31}P$  hyperfine tensor. The remaining lines in the spectrum are the  $\Delta M_s = \pm 1$  transitions of phosphinyl diradical  $1^{\bullet\bullet}$  in a triplet state exhibiting both zero-field splitting and  $^{31}P$  hyperfine coupling. Unambiguous evidence for the formation of a high-spin state in diradical  $1^{\bullet\bullet}$  is obtained from the EPR spectrum recorded in  $g = 4$  region where the formally forbidden  $\Delta M_s = \pm 2$  transition of  $1^{\bullet\bullet}$  is

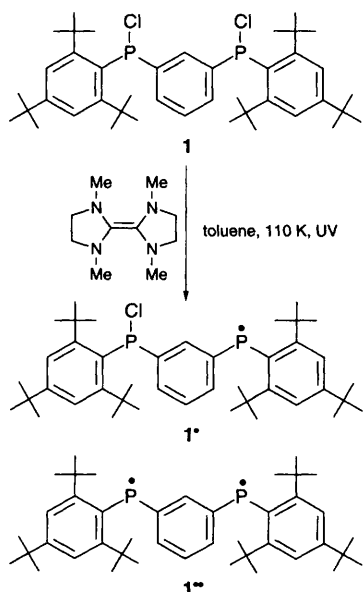


Fig. 1 Molecular structures of **1**,  $1^\bullet$ ,  $1^{\bullet\bullet}$  and ero

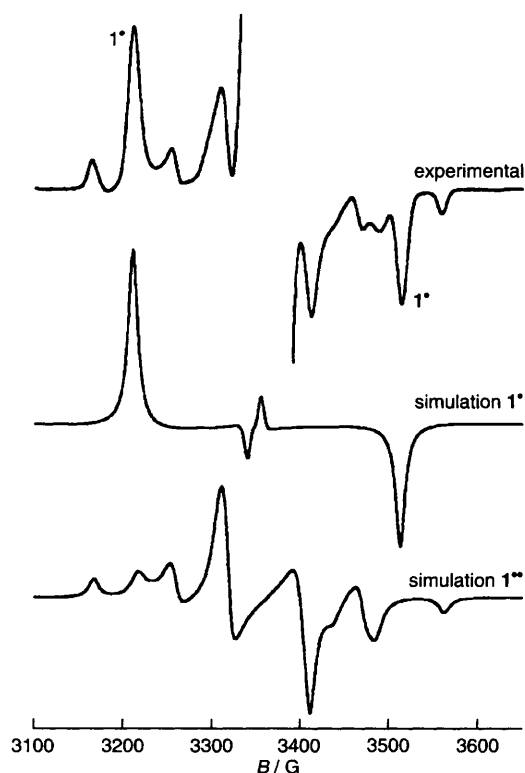


Fig. 2 EPR spectrum of a UV-irradiated **1**-ero mixture in toluene and simulations of mono- and di-radicals using parameters described in the text

observed (Fig. 3). The  $A_{\parallel}$  component in the wings of the  $\Delta M_s = \pm 2$  spectrum directly relates these transitions to  $\mathbf{1}^{\cdot\cdot}$ . No appreciable decay of phosphinyl monoradicals  $\mathbf{1}^{\cdot}$  or diradicals  $\mathbf{1}^{\cdot\cdot}$  is observed at 110 K in toluene. Above 130 K, their signals disappear irreversibly from the EPR spectrum.

The EPR spectrum of monoradical  $\mathbf{1}^{\cdot}$  can be simulated using an axially symmetric  $^{31}\text{P}$  hyperfine coupling tensor with  $A_{\parallel} = 850$  MHz and  $A_{\perp} = 20$  MHz (Fig. 2).<sup>6</sup> The hyperfine coupling tensor of  $\mathbf{1}^{\cdot}$  is then used to obtain a spectral simulation for  $\mathbf{1}^{\cdot\cdot}$ . We find that the remaining transitions in the EPR spectrum attributed to  $\mathbf{1}^{\cdot\cdot}$  are reproduced very satisfactorily by taking  $D = 260$  MHz and  $E = 0$  MHz for the zero-field splitting parameters, setting  $A_{\parallel} = 425$  MHz and  $A_{\perp} = 10$  MHz (*i.e.* half the coupling constants of  $\mathbf{1}^{\cdot}$ ) for the hyperfine coupling, and using  $\beta = 90^\circ$  (Euler angle of  $D$  and  $A_{\parallel}$ ) (Fig. 2). Using double integration and comparing with simulated spectra we find that the ratio of monoradicals to diradicals is about 5:4.

Variable-temperature experiments in the range from  $T = 3.8$  to 100 K on the  $\Delta M_s = \pm 1$  and  $\Delta M_s = \pm 2$  EPR transitions of  $\mathbf{1}^{\cdot\cdot}$  demonstrate that the signal intensity follows Curie's law ( $I = C/T$ ). We conclude that the triplet state of  $\mathbf{1}^{\cdot\cdot}$  is the ground state, although an exact degeneracy with the corresponding singlet state cannot be excluded.

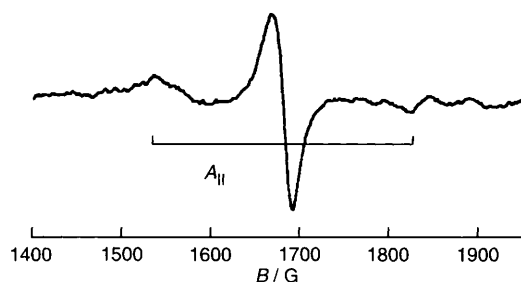


Fig. 3  $\Delta M_s = \pm 2$  EPR spectrum of  $\mathbf{1}^{\cdot\cdot}$

The zero-field splittings and hyperfine couplings obtained from the spectral simulation can be used to assess the electronic structure of  $\mathbf{1}^{\cdot}$  and  $\mathbf{1}^{\cdot\cdot}$  in some detail. From  $A_{\parallel} = 850$  MHz and  $A_{\perp} = 20$  MHz, the isotropic hyperfine coupling  $A_{\text{iso}} = (A_{\parallel} + 2A_{\perp})/3 = 297$  MHz and dipolar hyperfine coupling  $2A_{\text{dip}} = A_{\parallel} - A_{\text{iso}} = 553$  MHz can be obtained. These values can be used to approximate the spin density in the phosphorus 3s and 3p orbitals.<sup>7</sup> This analysis gives  $\rho_{3s} = 0.02$  and  $\rho_{3p} = 0.75$ , demonstrating that the unpaired electrons are mainly confined to the phosphorus p orbitals. The zero-field splitting of  $D = 260$  MHz for  $\mathbf{1}^{\cdot\cdot}$  corresponds within the dipole approximation ( $D = 7.8 \times 10^4 d^{-3}$ ) to a distance  $d$  between the radical centres of about 6.7 Å. This approximation is in fair agreement with the distance of 5.5 Å between the two phosphorus nuclei that has been obtained in the crystallographic X-ray structure of the oxidised form of  $\mathbf{1}^{\cdot\cdot}$ .

In conclusion we have shown that diradical  $\mathbf{1}^{\cdot\cdot}$  with two phosphinyl radicals linked by a *m*-phenylene ring has a triplet ground state.

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