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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*-phenylenebis(phosphinic chloride)s 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 $|D/hc| = 0.0120$ cm^{-1} and $|E/hc| = 0.0015$ cm^{-1}. Variable temperature ESR experiments reveal Curie behavior for the $\Delta m_s = 2$ 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 and 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.[2a] To investigate the possibility of ferromagnetic interactions between heavy-atom spin-containing substituents, we set out to prepare phosphoryl diradicals.

Phosphoryl radicals ($R_2\dot{P}O$) are closely related to nitroxyl radicals ($R_2\dot{N}O$), having the same number of valence electrons. In contrast to nitroxyl radicals, for which single or shallow double-well potential energy surfaces are found for out-of-plane distortions,[8] 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 **1** at 77 K produces the corresponding phosphoryl **1a** (Figure 1) that exhibits an enantioselective stereoinversion after annealing to 120 K. The large isotropic (A_{iso}) 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 sp^x hybridized molecular orbital with a p/s ratio of about 6. The remaining spin density is predominantly confined to the phosphoryl oxygen.[10]

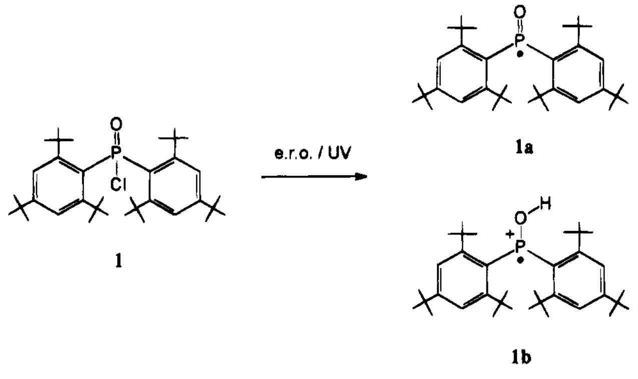

Figure 1. Structure of monophosphinic chloride **1** and radicals **1a,b** observed after a dissociative electron capture reaction of **1** induced by UV irradiation of ero in a 2MeTHF matrix.

It is clear that neither the pyramidal geometry at phosphorus, the reduced overlap of the phosphorus 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*-phenylenebis(phosphinic chloride)s **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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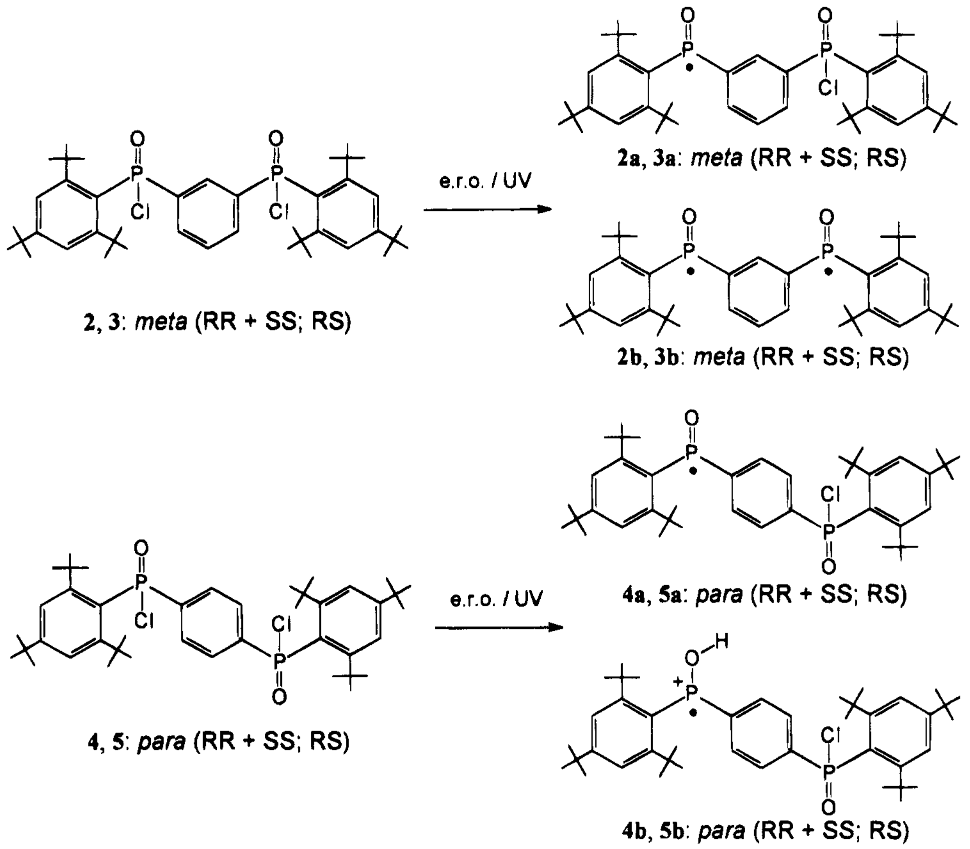


Figure 2. Structures of racemic (**2**, **4**) and *meso* (**3**, **5**) forms of *meta* and *para* isomers of *P,P'*-bis(2,4,6-tris(1,1-dimethylethyl)phenyl)phenylenebis(phosphinic chloride) and the mono- and diradicals observed after a dissociative electron capture reaction of **2**–**5** induced by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

Experimental Section

P,P'-Bis(2,4,6-tris(1,1-dimethylethyl)phenyl)phenylenebis(phosphinic chloride)s (**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 ^{1}H-, ^{13}C-, ^{31}P-NMR spectroscopy, elemental analysis, and X-ray crystallography (**2**, **3**, and **5**).[12]

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[13] to 100 μL of a 0.05 M solution of the phosphinic chloride precursor at room temperature.

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 between 100 and 150 K or by an Oxford 3120 temperature controller 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

Phosphoryl 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.[14] 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-dimethylethyl)phenyl)phosphinic chloride (**1**) in 2MeTHF at 77 K for 30 min and recording the ESR spectrum at 110 K affords an anisotropic ^{31}P doublet spectrum attributed to $Ar_2\dot{P}O$ (**1a**, Ar = 2,4,6-tris(1,1-dimethylethyl)phenyl), featuring well-resolved parallel ($A_\parallel$ = 1390 MHz) and perpendicular ($A_\perp$ = 868 MHz) transitions (Figure 3a). The isotropic and dipolar contributions to the hyperfine coupling tensor $A_{iso} = (A_\parallel + 2A_\perp)/3 = 1042$ MHz and $2A_{dip} = A_\parallel - A_{iso} = 348$ MHz (Table 1) are in good accordance with the values previously reported for radiogenically generated **1a** in glassy toluene and single crystals.[10]

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 ^{31}P hyperfine coupling (A_{iso} = 1210 MHz) together with an additional splitting of about 50 MHz by one $I = 1/2$ nucleus. A similar additional hyperfine coupling has been observed for $Ph\dot{P}(O)(OH)$ radicals, and we tentatively assign **1b** to the $Ar_2\dot{P}OH^+$ radical.[15] This anisotropic

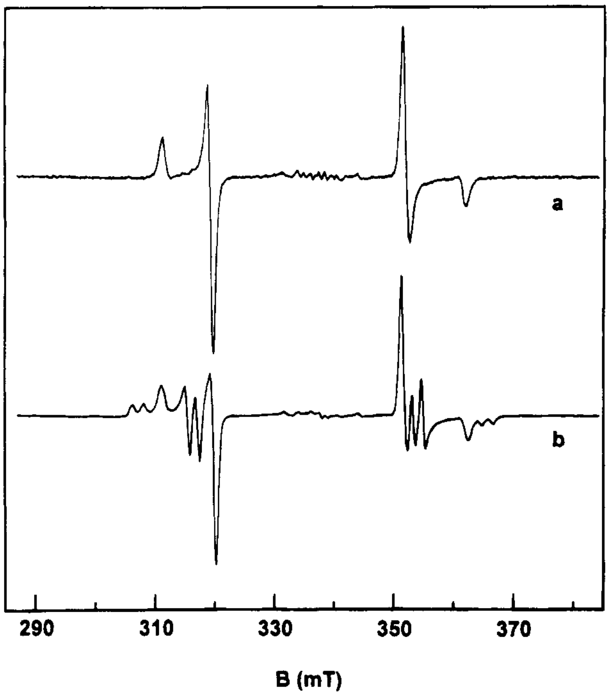


Figure 3. ESR spectra after reduction at 77 K of monophosphinic chloride **1** in 2MeTHF: (a) at 110 K; (b) at 120 K.

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

radical	host	T (K)	A_{iso} (MHz)	$2A_{dip}$ (MHz)
1a	2MeTHF	110	^{31}P 1042	348
1b	2MeTHF	120	^{31}P 1210 ^{1}H ≈50	371
2a	toluene	130	^{31}P 1123	346
2b	toluene	77	^{31}P 535[b]	186[b]
3a	toluene	130	^{31}P 1112	339
3b	toluene	77	^{31}P 535[b]	186[b]
4a	toluene	110	^{31}P 1095	338
4b	toluene	130	^{31}P 1068 ^{1}H ≈110	364
5a	toluene	110	^{31}P 1099	349
5b	toluene	110	^{31}P 1099 ^{1}H ≈110	332

[a] Isotropic and dipolar hyperfine couplings are corrected up to second-order. [b] For the diradical in the triplet state.

double-doublet ESR spectrum disappears irreversibly at 130 K, leaving the original doublet spectrum of $Ar_2\dot{P}O$, 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 ^{31}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 $\Delta m_s = 1$ 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 $\Delta m_s = 2$ 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 $Ar_2\dot{P}O$, a spectral simulation of the $\Delta m_s = 2$ signal (Figure 6b) has been obtained, which is in excellent agreement with the experimental spectrum. The fact that hyperfine coupling with two identical ^{31}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. $|J| \gg |A_{\parallel}|$, where $A_{\parallel} \approx 1500$ MHz (or 0.05 cm^{-1}). The zero-field splitting of triplet diradical **2b** is characterized by $|D/hc| = 0.0120\ cm^{-1}$, $|E/hc| = 0.0015\ cm^{-1}$, and $\beta = 90°$ (Euler angle of D and $A_{\parallel}$). The $\Delta ms = 1$ region of the spectrum is reproduced adequately by combining the simulations of mono- 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.

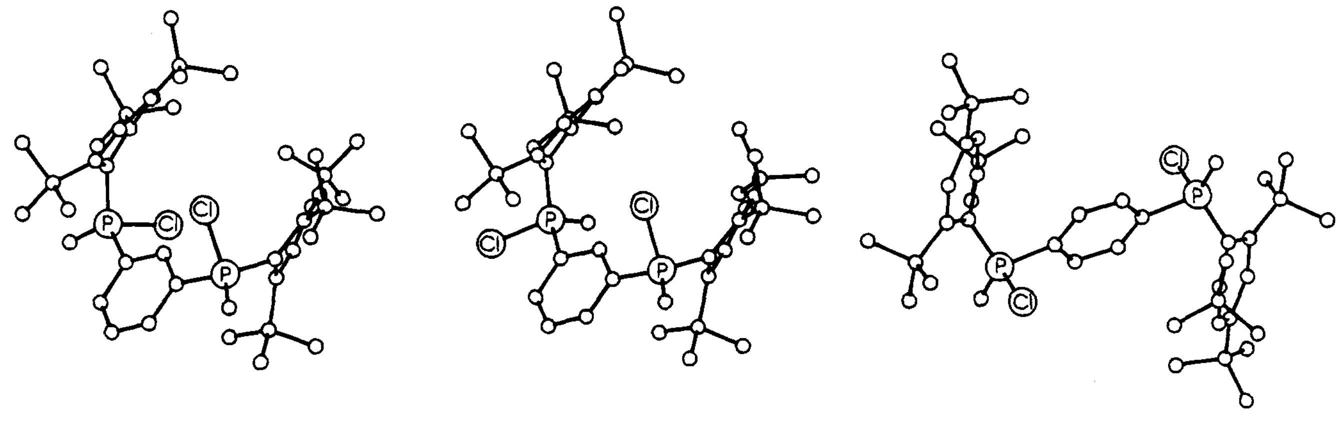
***Meso* 1,3-Phenylenebis(phosphinic chloride) 3.** The X-ray structure of **3** (*meso*, *RS*) (Figure 4) is very similar to the structure of **2** (racemic mixture, *RR* + *SS*). Due to the different stereochemistry of **3**, only one phosphoryl bond lies in the plane of the central *m*-phenylene ring, and, hence, the two phosphorus nuclei in **3** are not equivalent in this conformation. Variable temperature ^{31}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 $\Delta m_s = 2$ ESR spectrum of **3b** is identical to that of the racemic form (Figure 6c). The $\Delta m_s = 1$ 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-Phenylenebis(phosphinic chloride) 4. Variable temperature ^{1}H- and ^{31}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 $\Delta m_s = 1$ or $\Delta m_s = 2$ regions at various temperatures and/or irradiation times.

Slight annealing results in a complete conversion of phosphoryl radical **4a** to a secondary phosphorus-centered radical (**4b**) exhibiting an additional hyperfine splitting (Figure 7b). The ^{31}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**.



2 **3** **5**

Figure 4. Molecular structures of **2**, **3**, and **5** as determined by X-ray crystallography.

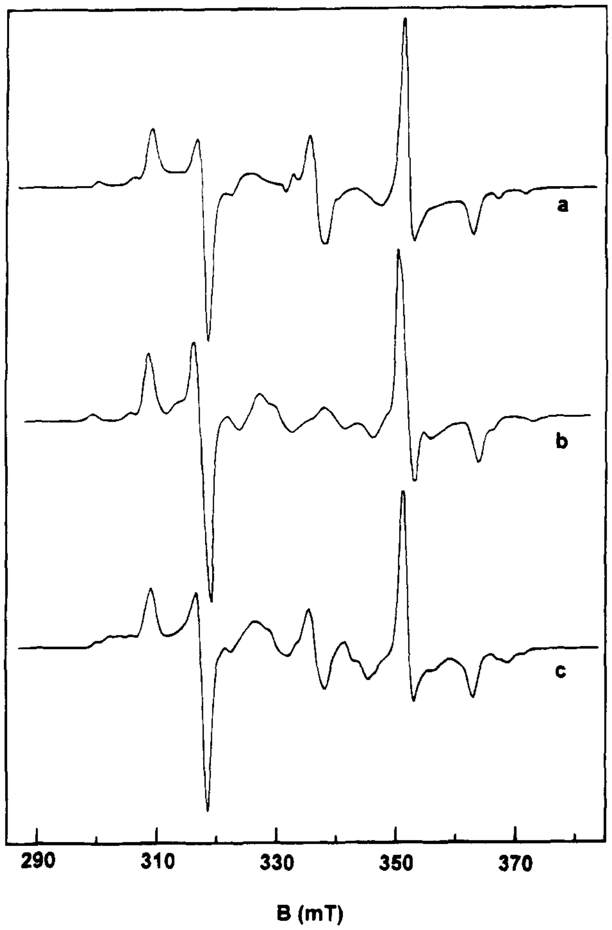


Figure 5. ESR spectra in the $\Delta m_s = 1$ region of radicals derived from bis(phosphinic chloride) precursors **2** and **3**: (a) **2a** and **2b** in a toluene matrix at 130 K; (b) simulation of a 5:2 mixture of the mono- and diradical; (c) **3a** and **3b** in a toluene matrix at 130 K.

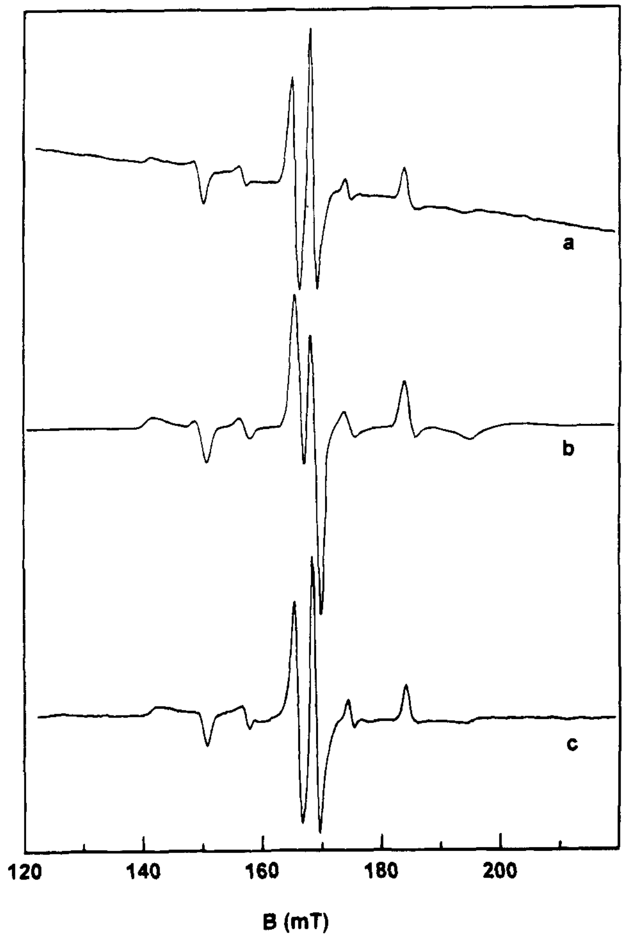


Figure 6. ESR spectra of diradicals in the $\Delta m_s = 2$ region: (a) **2b** in a toluene matrix at 77 K; (b) simulation; (c) **3b** in a toluene matrix at 77 K.

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 $Ar_2\dot{P}O$ (**5a**) and $Ar_2\dot{P}OH^+$ (**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.

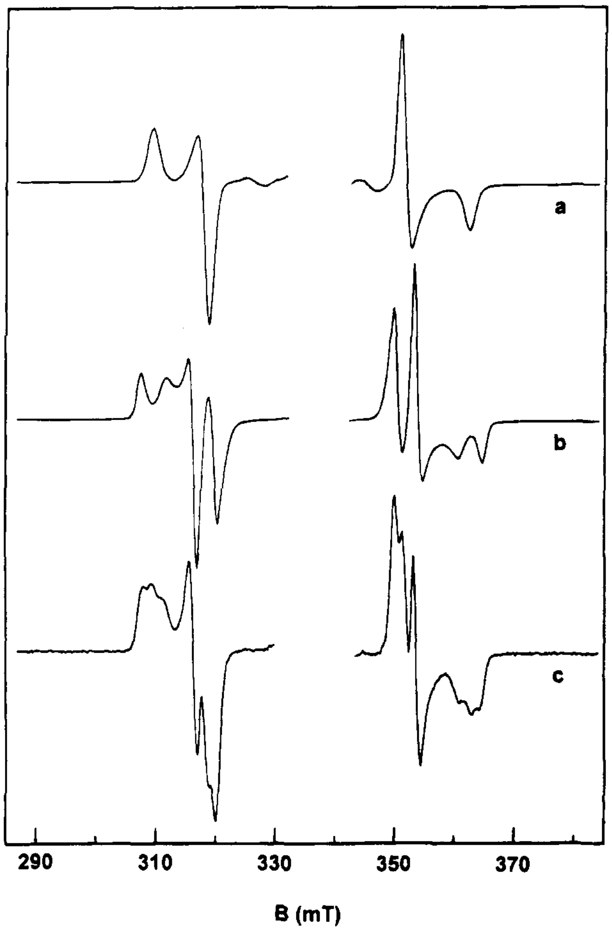


Figure 7. ESR spectra in the $\Delta m_s = 1$ region of radicals derived from bis(phosphinic chloride) precursors **4** and **5**: (a) **4a** in a toluene toluene matrix at 110 K; (b) **4b** after raising the temperature to 130 K; (c) **5a** and **5b** in a toluene matrix at 110 K. Central part of the 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, $H = -2J(S_1{\cdot}S_2)$, 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 $\Delta m_s = 2$ 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 $\Delta m_s = 2$ 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.[16] 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.[17] 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 couping unit, even for phosphorus-centered radicals.

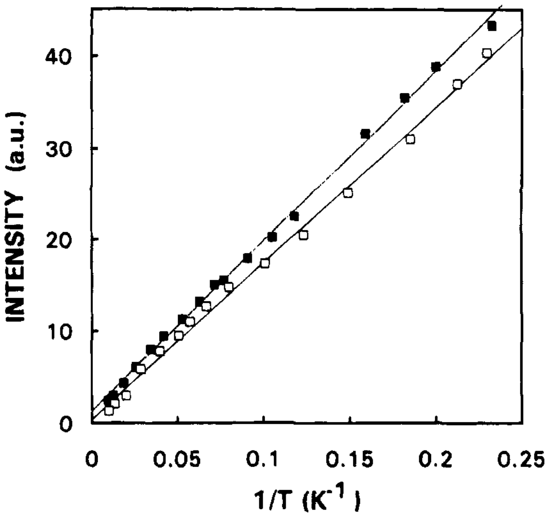


Figure 8. Temperature dependence of the $\Delta m_s = 2$ ESR signal intensity of biradicals **2b** (■) and **3b** (□). Solid lines are least-squares fits to the Curie law.

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 $|D/hc| = 2.6017d^{-3}$. The observed $|D/hc|$ 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 zfs 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 $|D/hc| = 0.0080$ cm^{-1}. The absence of corresponding signals in the $\Delta m_s = 1$ 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 stereoinversion 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 to the central phenylene ring. A stereochemical effect as discussed above cannot be excluded to explain the two triplet ESR spectra in the $\Delta m_s = 1$ region.

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 a first 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

(1) (a) *Proceedings of the Symposium on Ferromagnetic and High-Spin Molecular Based Materials*, 197th National Meeting of the American Chemical Society, Dallas, TX, April, 1989; American Chemical Society: Washington, DC; Miller, J. S., Dougherty, D. A., Eds. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 1–562. (b) Gatteshi, D., Kahn, O., Miller, J. S., Palacia, F., Eds. *Molecular Magnetic Materials*; Kluwer: Dordrecht, 1991. (c) *Proceedings of the International Symposium on Chemistry and Physics of Molecular-Based Magnetic Materials*, Iwamura, H., Miller, J. S., Eds. *Mol. Cryst. Liq. Cryst.* **1993**, *232*, 1–360.

(2) (a) Racja, A. *Chem. Rev.* **1994**, *94*, 871. (b) Miller, J. S.; Epstein, A. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 385. (c) Iwamura, H.; Koga, N. *Acc. Chem. Res.* **1993**, *26*, 346.

(3) Borden, W. T.; Iwamura, H. Berson, J. A. *Acc. Chem. Res.* **1994**, *27*, 109.

(4) (a) Nakamura, N.; Inoue, K.; Iwamura, H.; Fujioka, T.; Sawaki, Y. *J. Am. Chem. Soc.* **1992**, *114*, 1484. (b) Izuoka, A.; Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1987**, *109*, 2631. (c) Nakumara, N.; Inoue, K.; Iwamura, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 872.

(5) (a) Racja, A.; Utamapanya, S.; Thayumanavan, S. *J. Am. Chem Soc.* **1992**, *114*, 1884. (b) Utamapanya, S.; Racja, A. *J. Am. Chem. Soc.* **1991**, *113*, 2552.

(6) (a) Wasserman, E.; Murray, R. W.; Yager, W. A.; Trozollo, A. M.; Smolinsky, G. *J. Am. Chem. Soc.* **1967**, *89*, 5076. (b) Tukada, H.; Mutai, K.; Iwamura, H. *J. Chem. Soc., Chem. Commun.* **1987**, 1159. (c) Veciana, J.; Rovira, C.; Crespo, M. I.; Armet, O.; Domingo, V. M.; Palacia, F. *J. Am. Chem. Soc.* **1991**, *113*, 2552. (d) Azuma, N.; Ishiza, K.; Mukai, K. *J. Chem. Phys.* **1974**, *61*, 2294. (e) Yoshizawa, K.; Tanaka, K.; Yamabe, T.; Yamauchi, J. *J. Chem. Phys.* **1992**, *96*, 5516. (f) Yoshizawa, K.; Chano, A.; Ito, A.; Tanaka, K.; Yamabe, T.; Fujita, H.; Yamauchi, J.; Shiro, M. *J. Am. Chem. Soc.* **1992**, *114*, 5994.

(7) (a) Calder, A.; Forrester, A. R.; James, P. G.; Luckhurst, G. R. *J. Am. Chem. Soc.* **1969**, *91*, 3724. (b) Rassat, A.; Sieveking, H. U. *Angew. Chem.* **1972**, *84*, 353. (c) Mukai, K.; Nagai, H.; Ishiza, K. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2381. (d) Ishida, T.; Iwamura, H. *J. Am. Chem. Soc.* **1991**, *113*, 4238. (e) Dvoilaitzky, M.; Chiarelli, R.; Rassat, A. *Angew. Chem.* **1992**, *104*, 220. (f) Kanno, F.; Inoue, K.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1993**, *115*, 847.

(8) (a) Barone, V.; Grand, A.; Michino, C.; Subra, R. *J. Phys. Chem.* **1993**, *97*, 6355. (b) Pauzat, F.; Girtli, H.; Ellinger, Y.; Subra, R. *J. Phys. Chem.* **1984**, *88*, 4581. (c) Mikami, H.; Saito, S.; Yamamoto, S. *J. Chem. Phys.* **1991**, *94*, 3415.

(9) Nguyen, M. T.; Ha, T.-K. *Chem. Phys.* **1989**, *131*, 245.

(10) de Waal, B. F. M.; Aagaard, O. M.; Janssen, R. A. J. *J. Am. Chem. Soc.* **1991**, *113*, 9471.

(11) (a) Silverman, S. K.; Dougherty, D. A. *J. Phys. Chem.* **1993**, *97*, 13273. (b) Veciana, J.; Rovira, C.; Ventosa, N.; Crespo, M. I.; Palacia, F. *J. Am. Chem. Soc.* **1993**, *115*, 57. (c) Racja, A.; Utamapanya, S. *J. Am. Chem. Soc.* **1993**, *115*, 2396.

(12) Full details on synthesis, characterization, X-ray crystallography, and multinuclear variable temperature NMR studies will be published elsewhere. Wienk, M. M.; Schouten, A.; Kanters, J. A.; Janssen, R. A. J.; Meijer, E. W. In preparation.

(13) Winberg, H. E. U.S. Patent 3,239,519, 1966.

(14) (a) Winter, N. J.; Fossey, J.; Beccard, B.; Berchadsky, Y.; Villa, F.; Werbelow, L.; Tordo, P. *J. Phys. Chem.* **1986**, *90*, 6749. (b) Cetinkaya, B.; Hudson, A.; Lappert, M. F.; Golwhite, J. *J. Chem. Soc., Chem. Commun.* **1982**, 609. (c) Gynane, M. J. S.; Hudson, A.; Lappert, M. F.; Power, P. P.; Goldwhite, H. *J. Chem. Soc., Dalton Trans.* **1980**, 2428.

(15) Geoffroy, M.; Lucken, E. A. C. *Mol. Phys.* **1972**, *24*, 335.

(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.

(17) (a) Kanno, F.; Inoue, K.; Koga, N.; Iwamura, H. *J. Phys. Chem.* **1993**, *97*, 13267. (b) Ling, C.; Lahti, P. M. *J. Am. Chem. Soc.* **1994**, *116*, 8784. (c) Minato, M.; Lahti, P. M.; van Willigen, H. *J. Am. Chem. Soc.* **1993**, *115*, 4532. (d) Doi, T.; Ichimura, A. S.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1993**, *115*, 8928. (e) Matsumoto, T.; Ishida, T.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1992**, *114*, 9952. (f) Berson, J. A. In *The Chemistry of Quinoid Compounds*; Patai, S., Rapport, Z., Eds.; Wiley: New York, 1988; p 462 ff.

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