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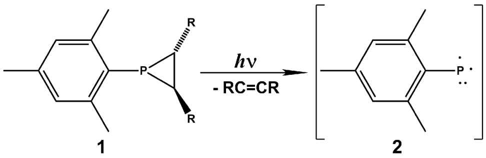
The EPR spectrum of triplet mesitylphosphinidene: reassignment a new assignment

Alexander V. Akimov,[a] Yulia S. Ganushevich,*[b] Denis V. Korchagin,[a, c] Vasili A. Miluykov, [b] and Eugenii Ya. Misochko*[a]

Abstract: Low temperature UV-photolysis of mesitylphosphiranes under strong anaerobic conditions leads to the formation of the triplet mesitylphosphinidene (MesP). The recorded X-band EPR spectrum of triplet MesP and the derived zero-field splitting parameter D = 4.116 cm^{-1} differ significantly from those reported previously for this intermediate. New magnetic parameters of mesitylphosphinidene are discussed along with the results of DFT calculations.

Among the great variety of organic compounds, there is a relatively small, but very important from practical and theoretical perspectives class of compounds that contain carbon, nitrogen, and phosphorus atoms in their extraordinarily low valence state. These are carbenes, nitrenes and phosphinidenes. Nitrenes and phosphinidenes are characterized by very strong (~> 10 kcal/mol) ferromagnetic exchange interactions between unpaired electrons and, as a result, mainly have high-spin ground states. Thus, nitrenes and phosphinidenes are model systems for investigations of magnetism in organic high-spin molecules. The scalar parameter *D* of the zero-field splitting (ZFS) tensor is an important magnetic parameter of such molecules. Nitrenes Ar-$(N^{\bullet\bullet})_x$, where X = 1, 2 and 3, have been used to study magnetic anisotropy in organic molecules for cases in which anisotropic spin-spin interactions are dominant.[1, 2, 3] In contrast to the widely studied high-spin nitrenes, the spin-orbit contribution to magnetic anisotropy is expected to be dominant in triplet phosphinidenes because the spin-orbit coupling constant of the phosphorus atom is approximately 16 times higher than that of the nitrogen atom.[4, 5] Therefore, organic phosphinidenes are attractive objects for studying "heavy atom" effects in magnetic anisotropy. In contrast to the thoroughly studied carbenes and nitrenes, it is a paradoxical situation. Although triplet phosphinidenes have been postulated as short-lived intermediates in numerous organophosphorus reaction systems,[6, 7, 8, 9, 10] few reports of the direct spectroscopic observations have been made to fully establish their formation.[11, 12, 13, 14] Several attempts have been made to observe triplet phenylphosphinidene directly using X-band EPR spectroscopy.[12 - 14] In fact, the only example in the literature, that involves an EPR observation of triplet phosphinidene (i.e. mesitylphosphinidene), was reported by Li et al.[12] The recorded broad structureless EPR line at a magnetic field of 1,150 T was assigned to this intermediate, and its ZFS parameter of *D* = 3.521 cm^{-1} was estimated from the recorded spectrum.[15] Afterwards, this *D* value and the recorded EPR spectrum were used as an experimental test for quantum chemical calculations[4] and cited in various papers and reviews[16] as an important magnetic parameter of triplet mesitylphosphinidene. It was also used as direct experimental confirmation of the triplet ground state for this intermediate.



1

2

R = H(1a), CH_3(1b)

Scheme 1. Photochemical generation of mesitylphosphinidene (**2**).

Our interest in the EPR spectra of organic phosphinidenes was motivated by the study of the "heavy atom" effect on magnetic anisotropy as a continuation of our previous studies.[17, 18, 19] Our first EPR measurements in photolyzed frozen solutions with precursors **1a** and **1b** showed that the spectrum of photolytic product **2** (Scheme 1) is significantly different from that previously reported in [12]. In the present work, we focused our attention on the assignment of the spectrum and magnetic parameters of the generated triplet intermediate.

The X-band cw EPR spectra of mesitylphosphinidene **2** were recorded after UV-irradiation of arylphosphiranes **1** in glassy methylcyclohexane (MCH) at 5 K. In a typical procedure, the arylphosphirane **1** was dissolved in freshly distilled MCH in the ratio of 1:1000, placed in a 4 mm o.d. quartz EPR tube, and sealed under vacuum. The sample tube was placed in the cavity of an EPR spectrometer equipped with a helium gas-flow thermostat. Then, the sample was cooled to 5 K to form glass and photolyzed at 60 K using a low-pressure mercury lamp (at λ = 254 nm).[20] EPR spectra were recorded using a standard 9 GHz spectrometer (*Bruker Elexsys 500*, the modulation frequency 100 KHz) at a sufficiently low microwave power to avoid the saturation effects.

Photolysis of **1a** and **1b** lead to the fully identical EPR spectra, demonstrating a strong EPR line at a magnetic field of 1.225 T with well resolved hyperfine structure on the ^{31}P atom, see Fig. 1. The recorded EPR line is assigned to the allowed EPR transition for (xy) canonical orientation of triplet species with a very large *D* (where the ZFS parameter *D* exceeds a quantum of microwave radiation hν (hν ≈ 0.33 cm^{-1} for X-band spectroscopy)). The

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parameter *D* derived from this spectrum equals 4.116 cm^{-1}, see Fig. 1. The obtained identical EPR spectra of the photolytic products of **1a** and **1b** with resolved hyperfine structure belong to the same product, namely, to mesitylphosphinidene **2** (Scheme 1).

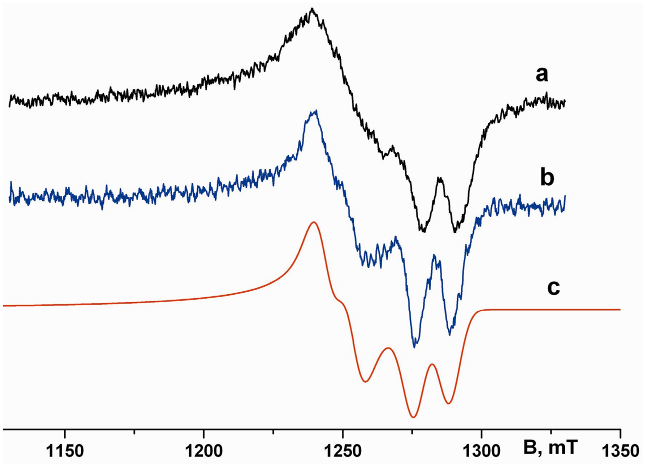

Figure 1. The EPR spectra recorded after photolysis of arylphosphirane **1b** (a) and **1a** (b) in glassy MCH. Microwave frequency 9.47135 GHz. Spectra were recorded at 5 K. The simulated spectrum for a triplet molecule with the ZFS parameters D = 4.116 $\mathrm{cм}^{-1}$, E = 0.004 $\mathrm{cм}^{-1}$ and the hyperfine components on ^{31}P atom A_x = 269 MHz and A_y = 356 MHz (c).

Initially, the recorded EPR spectra seemed surprising, since these spectra were significantly different from those previously assigned[12] to mesitylphosphinidene **2**, which was generated under similar experimental conditions. Our hypothesis on the nature of the spectrum, which was reported in the work [12] (parameter D = 3.521 cm^{-1}), was very close to that for triplet oxygen in solid nitrogen (D_{O2} = 3.572 cm^{-1}).[21], [22], [23] To verify this assumption, we performed measurements on the samples possessing a slow air leak from the upper tip of the quartz tube, see the Supporting Information for details. In these samples, there was slow air freezing over the top of the glassy solution of precursor **1a** in MCH. Figure 2 shows appearance of the well-resolved spectrum of **2** after 50 min of photolysis. Simultaneously, a new EPR line at 1.17 T appeared in the spectrum. Then, the intensity of this line continued to grow upon the subsequent sample aging in the dark at 5 K. The line shape, position (at magnetic field at 1.17 T), and parameter D = 3.521 cm^{-1}, that corresponded to this line, were very similar to those recorded in the previous work [12]. A similar EPR line at 1.17 T was registered in experiments, where an empty quartz tube with a slow air leak was placed in the cavity of the EPR spectrometer for a long time at 5 K, see Fig. S11 in the Supporting Information. These measurements definitely confirm that the previously reported EPR spectrum[12] belongs to triplet oxygen, whereas the spectrum in Figure 1 and that the derived from the spectrum parameter D = 4.116 cm^{-1} correspond to the triplet photolytic product, specially, triplet mesitylphosphinidene **2**.[24]

The magnetic parameters of **2** were determined by comparing the experimental and simulated spectra, see Fig. 1. The spectral simulation was performed using *EasySpin* program package,[25] which was operated with an exact numerical matrix diagonalization of the spin Hamiltonian

$$\mathrm{H} = g\beta BS + S\,D\,S + \hat{S}\,A\,I$$

for randomly oriented molecules with a total spin of S = 1, nuclear spin I = ½ for atom ^{31}P, isotropic value of g = 2.0023, and assuming similar orientations of the principal axes for the fine structure tensor ***D*** and the hyperfine structure tensor ***A***. Since only an EPR line for the perpendicular (xy) canonical orientation was detected in the recorded spectrum, only two perpendicular components of the hyperfine structure tensor ***A*** were derived from this spectrum: A_x = 269 MHz and A_y = 356 MHz.

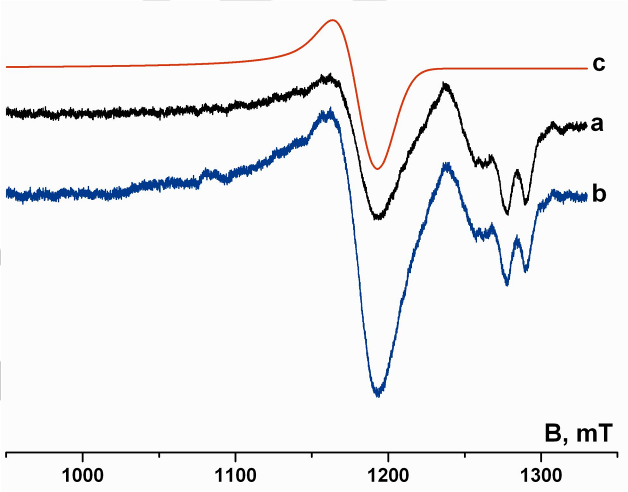

Figure 2. The EPR spectra recorded after 50 min photolysis of arylphosphirane **1a** in glassy MCH in the sample possessing slow air leak from the upper tip of the quartz tube (a) and after the subsequent aging of the sample for 60 min in dark at 5 K (b). The simulated EPR spectrum with D_{O2} = 3.572 cm^{-1} (data from Ref. [22]) for triplet oxygen in solid nitrogen (c).

The obtained new value of D = 4.116 cm^{-1} for triplet mesitylphosphinidene **2** is close to that of the simplest phosphinidene PH, (D_{PH} = 4.4 cm^{-1}).[26] DFT calculations for parameter *D* and hyperfine tensor ***A*** were performed to compare the theoretical and experimental values. The simulation results are shown in Tables 1 and 2 and Supporting Information. These calculations suggest the following preliminary conclusions:

1. The contribution of the spin-orbit coupling (SOC) to parameter *D* is one order of magnitude greater than the contribution of the spin-spin (SS) interaction. The main SOC contribution is the SOMO → SOMO spin flip interaction between excited singlet and ground triplet states (Table S3).
2. As proposed in this work, the PBE/Ahlrichs-DZ level of theory is universal and describes the experimental results for all known triplet phosphinidenes (Table 1), as well as for high-spin nitrenes[17, 18, 19].
3. The calculated components (A_x and A_y) of hyperfine structure tensor ***A*** are very similar to those obtained from the experimental spectrum, see Table 2.

Table 1. Calculated (PBE/Ahlrichs-DZ) and experimental ZFS parameters D (cm^{-1}) for triplet phosphinidenes R -P$^{\bullet\bullet}$.

R-P	DFT calculation			Expt.
R=	D_{SS}	D_{SO}	D_{SS+SO}	D
Mes	0.319	3.890	4.209	4.116[a]
H	0.414	3.951	4.365	4.4[b]
F	0.418	5.295	5.713	5.9[b]

[a] this work; [b] data from Ref. [26]

Table 2. The hyperfine components (MHz) on ^{31}P atom in triplet mesitylphosphinidene **2**.

	A_{xx}	A_{yy}	A_{zz}	A_{iso}
Experimental	269	356	-	-
Calculated (B3LYP/EPRIII)	242	339	-163	139

In summary, the experimental data obtained in the present work demonstrated that photolysis of arylphosphiranes **1a** and **1b** in glassy MCH leads to a fully identical EPR spectrum, which is assigned to the same product of triplet mesitylphosphinidene. **2**. The DFT calculations for parameter *D* and hyperfine coupling constants on phosphorous atom ^{31}P in mesitylphosphinidene **2** gave parameters very close to those obtained from the recorded spectra. The experimental EPR spectrum of triplet mesitylphosphinidene **2** and zero-field splitting parameter D = 4.116 cm^{-1} from this spectrum differ significantly from those of this intermediate that were previously reported in literature. Additional experiments confirmed that the previously reported EPR spectrum belongs to triplet oxygen in frozen air. Therefore, we consider the results of our work as the first experimental observation of the EPR spectrum of **2** and registration of its magnetic parameters. This study demonstrates that highly reactive intermediates, such as organic triplet phosphinidenes, can be effectively stabilized in low-temperature solids, if anaerobic conditions are met at all stages of the experiment. The detected doublet hyperfine structure in the EPR spectra provides reliable identification of these molecules in the complex chemical processes. This observation provides new opportunities for exploring the structure and chemical properties of these types of phosphinidenes under low temperature chemistry and matrix isolation conditions. In addition, these molecules may serve as a convenient model for the quantum chemical study of the magnetic anisotropy created by the spin-orbit interaction that is important for the molecular magnetism theory.

Experimental Section

Phosphiranes **1a** and **1b** were synthesized according to a previously published literature procedure[27] via reactions of mesitylphosphine[28] and ethylene glycol ditosylate[29] or (±)-2,3-butanediol ditosylate[12], respectively. Taking into account the high reactivity of **1**, all manipulations (synthesis, purification, and sample preparation) were performed under an atmosphere of purified nitrogen using standard high-vacuum Schlenk techniques. The synthesized compounds **1a** and **1b** were fully characterized via ^{1}H, ^{13}C, and ^{31}P NMR and MS, elemental analysis, see the Supporting Information in details.

Acknowledgements

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Keywords: Reactive intermediates • Phosphinidenes • High-spin molecules • EPR spectroscopy • Quantum chemistry

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Layout 1:

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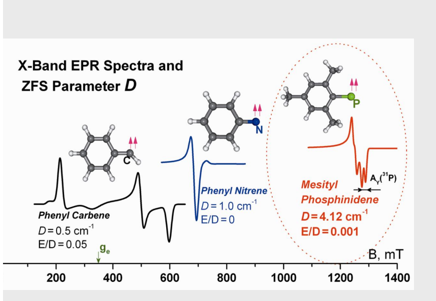
EPR spectra of triplet aromatic carbenes, nitrenes, and phosphinidenes – feel the difference: The recorded EPR spectrum of triplet mesitylphosphinidene and zero-field splitting parameter *D* from this spectrum differ significantly from those of this intermediate that were previously reported in literature. The presence of the doublet hyperfine structure in the EPR spectra provides reliable identification of these molecules in the complex chemical processes.



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