Triplet-state phosphoryl biradicals

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Triplet-state phosphoryl biradicals

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Abstract

The preparation and characterization using ESR of a phosphoryl biradical is described as a first example of a triplet-state molecule consisting of a m-phenylene unit with pendant radical centers on second-row atoms.

1. INTRODUCTION

Increasing interest in exploring organic and organometallic molecules for ferromagnetic materials has recently resulted in a number of different molecular materials exhibiting ferromagnetic interactions.\textsuperscript{1} One approach towards ferromagnetic spin alignment is via the synthesis of high-spin molecules in which many radical centers are ferromagnetically coupled. A versatile ferromagnetic coupling unit is m-phenylene which provides spin alignment via an in-phase periodicity of spin polarization due to topological symmetry. A variety of carbon and nitrogen centered radicals have been shown to give rise to high-spin polyradicals when coupled via m-phenylene.

Here we report a first example of a m-phenylene coupled phosphoryl biradical, i.e. a second-row atom as a radical center. We show that racemic (Rp,Rp and Sp,Sp mixture) m-phenylene bis(phosphinic chloride) 1 (Figure 1) when subjected to reactive free electrons from a photo-oxidized electron rich olefin (ERO) gives rise to the corresponding triplet-state phosphoryl biradical (1**) in two consecutive dissociative electron capture reactions. Biradical 1** is fully characterized using ESR spectroscopy.

2. EXPERIMENTAL

The synthesis of bis(phosphinic chloride) 1 and the separation of racemic and meso stereoisomers will be described elsewhere.\textsuperscript{2} Compound 1 has been fully characterized using \textsuperscript{1}H, \textsuperscript{13}C, and \textsuperscript{31}P NMR spectroscopy. A crystallographic X-ray analysis confirmed that 1 is the racemic mixture of Rp,Rp and Sp,Sp stereoisomers. As ERO we used 1',3',5'-tetramethyl-2,2'-bi-imidazolidinylidene. ESR spectra were recorded using a Bruker ER 200D X-band spectrometer with variable temperature controls in the ranges 3\textdegree\text{K}-100\textdegree\text{K} and 90-300\textdegree\text{K}. UV irradiation was performed with a high-pressure mercury lamp (Philips SP 500).

3. RESULTS AND DISCUSSION

UV irradiation of a mixture of 0.025 M bis(phosphinic chloride) 1 and 0.125 M ERO in a frozen toluene matrix at 130-135 K for several hours results in the formation of phosphoryl mono- and bi-radicals as evidenced from the ESR spectrum (recorded with light switched off). The ΔM_s=1 region of the spectrum (Figure 2a) shows the signatures of three different radicals. The strong transitions in the lateral regions (marked 1*) are due to a phosphoryl monoradical, exhibiting the characteristic powder ESR pattern for an axially symmetric anisotropic \textsuperscript{31}P hfc tensor.\textsuperscript{3} The central line in the spectrum is due to the ERO photo-oxidation product and has a different temperature behavior than the other lines in the spectrum which can be detected up to the melting point of the matrix. The most interesting features in the ESR spectrum, however, are the two pairs of absorptions in the outermost regions of the spectrum which are attributed to biradical 1** in the triplet state. Direct spectral evidence for the triplet state of biradical 1** is obtained from the ESR spectrum at half field (Figure 3a). The ΔM_s=2 region shows a number of well-resolved transitions that can only be due to a triplet-state biradical.\textsuperscript{4}

Using the isotropic (A_{iso}=1039 MHz) and anisotropic (A_{aniso}=360 MHz) \textsuperscript{31}P hfc of phosphoryl monoradicals known

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Molecular structures of 1, 1*, and 1**.}
\end{figure}
from previous single crystal ESR studies on a closely related monoradical, it has been possible to determine the zero field splitting (zfs) parameters of $1^{**}$ via spectral simulation of the $\Delta M_s=1$ and $\Delta M_s=2$ regions. The resulting zfs values $\Delta E/\hbar c=0.0120 \text{ cm}^{-1}$, $\Delta E/\hbar c=0.0015 \text{ cm}^{-1}$, and $\gamma_{90^\circ}$ (Euler angle of D and A_{dip}) provide an excellent agreement with the experimental $\Delta M_s=2$ spectrum (Figure 3b). In addition to spectral simulation of the $\Delta M_s=2$ region, also the $\Delta M_s=1$ region can be reproduced with these hfc and zfs parameters when the spectra of mono- and bi-radicals are combined in a 5:2 ratio (Figure 2b). Since the photoinduced reduction and subsequent dissociation of the P-Cl bonds leading to $1^{**}$ is a 2-step process, we consider the 5:2 ratio to be an indication of an increased reactivity of the P-Cl bond once the monoradical has been formed.

The value $\Delta E/\hbar c=0.0120 \text{ cm}^{-1}$ corresponds within the dipole approximation to a distance between the radical centers of 6 Å, slightly longer than the distance of 5.5 Å between the two phosphorus nuclei as determined from the crystallographic analysis. Likewise, the $^{31}$P hfc's give information on the structure of the biradicals since they can be related to the spin densities in the valence 3s and 3p orbitals. This analysis results in $\rho_{3s}(P)=0.078$ and $\rho_{3p}(P)=0.497$ for each $^{31}$P nucleus. The $3p/3s$ ratio of about 6 indicates a non-planar phosphorus atom in the phosphoryl moiety. The $^{31}$P nuclei account for more than half of the total unpaired electron density (p=2). The remainder will be located on the two oxygen atoms and the aromatic ring(s), but goes undetected in absence of magnetic nuclei and resolvable $^1$H hfc's.

Variable temperature experiments in the range 3.8-100 K on the $\Delta M_s=2$ signal show that the intensity increases when going to lower temperatures. More experiments, however, are necessary to determine the type and strength of spin coupling in biradical $1^{**}$.

Similar results regarding triplet-state biradicals, have been obtained for the meso isomer of m-phenylene bis(phosphinic chloride) 1. No triplet-state biradicals were observed for the corresponding racemic and meso p-phenylene bis(phosphinic chloride) compounds under identical experimental conditions.

4. CONCLUSION

We have shown that phosphoryl biradical $1^{**}$ exhibits an ESR spectrum characteristic of a triplet state. Biradical $1^{**}$ is a first example of a m-phenylene ring carrying two second-row atom centered radicals with a low-energy triplet state.

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