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Citation for published version (APA):

Wienk, M. M., & Janssen, R. A. J. (1997). Triplet-state di(cation radicals) of 1,3-phenylene-bis(methylene phosphorane). *Synthetic Metals*, 85(1-3), 1733-1734. [https://doi.org/10.1016/S0379-6779\(97\)80414-6](https://doi.org/10.1016/S0379-6779(97)80414-6)

DOI:

[10.1016/S0379-6779\(97\)80414-6](https://doi.org/10.1016/S0379-6779(97)80414-6)

Document status and date:

Published: 15/03/1997

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Triplet-state di(cation radicals) of 1,3-phenylene-bis(methylene phosphorane)

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Abstract

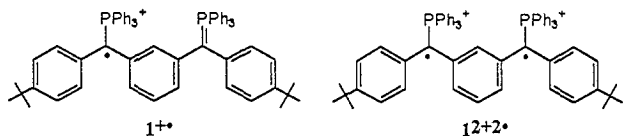
EPR spectroscopy is used to characterize a novel triplet ground state diradical obtained from oxidation of 1,3-phenylene-bis{[(4-*t*-butylphenyl)methylene]triphenyl phosphorane}

Keywords: High-spin molecules, Electron spin resonance

1. Introduction

Organic high-spin molecules continue to attract attention for future molecular ferromagnetic materials [1-3]. One approach to high-spin molecules is to link radical centers intramolecularly via ferromagnetic coupling units such as 1,3-phenylene. The meta substitution provides a non-Kékulé resonance structure in which the topological symmetry and in-phase periodicity of spin polarization favor intramolecular ferromagnetic coupling of the electron spins. In principle, this concept can be extended to prepare high-spin polyradicals. An important aspect of high-spin molecules is the nature of the radical site, which determines both the chemical stability and the spin density at the ferromagnetic coupling unit. Various pendant radicals have been tested for their applicability in combination with 1,3-phenylene, mostly with a carbon or nitrogen atom as the principal nucleus carrying spin density.

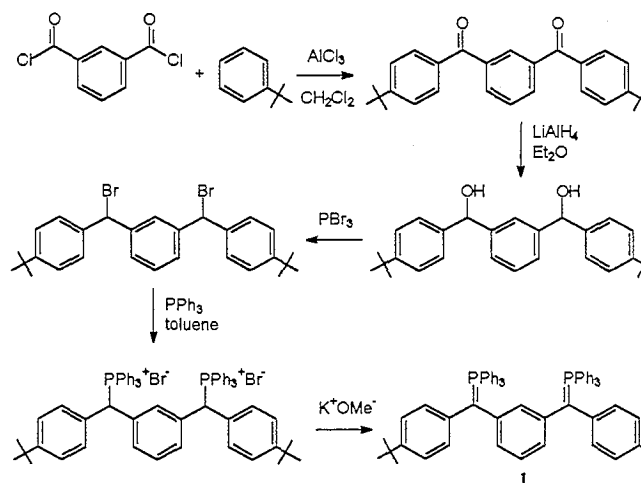
Compared to the well-known triarylmethyl radicals, diphenylmethylene phosphorane radical cations are expected to give a higher spin density at the methylene carbon atom directly linked to the 1,3-phenylene ring [4] which may be beneficial for a stronger ferromagnetic interaction. Here we describe the formation of a novel di(cation radical) $1^{2+2\cdot}$ obtained via oxidation of 1,3-phenylene-bis{[(4-*t*-butylphenyl)methylene]triphenyl phosphorane} 1.



2. Synthesis

The synthesis of **1** is outlined in Scheme 1. *t*-Butylbenzene is reacted in a Friedel-Crafts acylation with isophthaloyl dichloride to afford the 1,3-phenylene diketone which is reduced to the corresponding diol with lithium aluminium hydride. The diol is converted to the dibromide using phosphorus tribromide and reacted with triphenylphosphine to give the bis(phosphonium

bromide). Subsequent deprotonation with potassium methoxide or sodium amide affords the bis(methylene phosphorane) **1**.



Scheme 1.

3. Results and discussion

Cyclic voltammetry of **1** in tetrahydrofuran (THF) solution containing 0.1 M $n\text{-Bu}_4\text{N}^+\text{PF}_6^-$ at ambient temperature reveals two quasi-reversible one-electron oxidation waves at -0.14 and 0.23 V vs. SCE when recorded with at 100 mV sec^{-1} . This indicates that the doubly oxidized state of **1** is only moderately stable at room temperature. To prevent side reactions chemical oxidation was carried out at 200 K.

Chemical oxidation of **1** with Ag^+ at 200 K in THF initially produces the corresponding monocation radical 1^{1+} which is characterized by a partially resolved EPR spectrum. Hyperfine interactions with one ^{31}P nucleus ($A = 72.5$ MHz) and three different sets of two equivalent ^1H nuclei ($A = 11.5, 3.75,$ and 2.75 MHz) indicate appreciable spin delocalization over both the terminal and central benzene rings.

Further oxidation of 1^{1+} produces $1^{2+2\cdot}$. The EPR spectrum recorded at 120 K reveals a superposition of the spectra of the

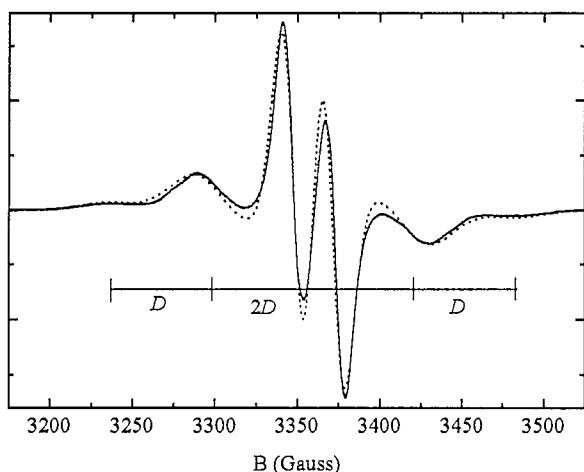


Fig. 1. EPR spectrum (solid line) of **1** in THF after oxidation with Ag^+ . The simulation (dashed line) is a 2:5 superposition of the spectra of monocation radical $1^{\cdot+}$ and a di(cation radical) $1^{2+\cdot}$ calculated using the parameters described in the text.

monocation radical and the triplet di(cation radical) (Fig. 1). The two strong central transitions are readily attributed to the monocation radical $1^{\cdot+}$ exhibiting an essentially isotropic ^{31}P hyperfine coupling constant. The broad lines in the lateral regions of the spectrum are the $\Delta M_s = \pm 1$ transitions of the di(cation radical) $1^{2+\cdot}$ exhibiting the zero-field splitting characteristic of a triplet state. Surprisingly, however, no ^{31}P hyperfine coupling is resolved for $1^{2+\cdot}$. Further evidence for the formation of di(cation radical) $1^{2+\cdot}$ in a high-spin state is obtained from the EPR spectrum recorded in $g = 4$ region where the formally forbidden $\Delta M_s = \pm 2$ transition of $1^{2+\cdot}$ is observed (Fig 2). The $\Delta M_s = \pm 2$ EPR spectrum exhibits a well-resolved 1:2:1 three-line pattern resulting from hyperfine interaction of the $S = 1$ spin with two equivalent ^{31}P nuclei with half the coupling constant observed for monoradical $1^{\cdot+}$. The identical hyperfine coupling to two ^{31}P nuclei directly relates the spectrum to the proposed structure of $1^{2+\cdot}$.

The EPR spectrum of monoradical $1^{\cdot+}$ can be simulated assuming an isotropic ^{31}P hyperfine coupling constant of $A = 65$ MHz and a Gaussian line width of 45 MHz. The hyperfine

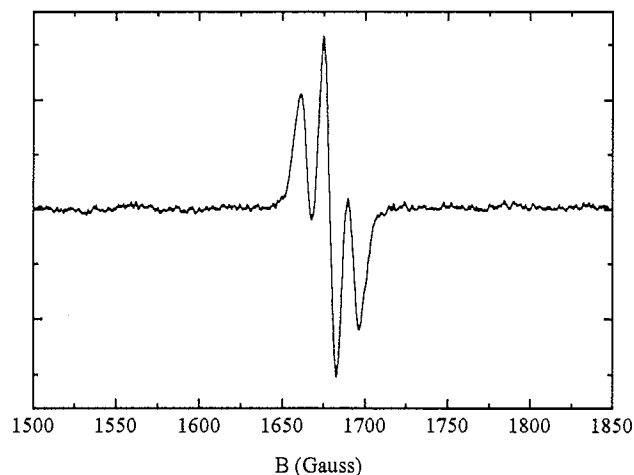


Fig. 2. $\Delta M_s = \pm 2$ EPR spectrum of $1^{2+\cdot}$

coupling constant of $1^{\cdot+}$ was then used as starting point to obtain a spectral simulation for $1^{2+\cdot}$. We find that the remaining transitions in the EPR spectrum attributed to $1^{2+\cdot}$ are reproduced satisfactorily by taking $D = 350$ MHz and $E = 0$ MHz for the zero-field splitting parameters, setting $A_{\text{iso}} = 32.5$ MHz (i.e. half the coupling constant of $1^{\cdot+}$), and using a Gaussian line width of 85 MHz (Fig. 1). The increased line width of $1^{2+\cdot}$ as compared to $1^{\cdot+}$ explains the loss of hyperfine structure in the $\Delta M_s = \pm 1$ triplet spectrum.

Adding the simulated spectra of $1^{\cdot+}$ and $1^{2+\cdot}$ in a 2:5 ratio provides a good agreement with the experimental spectrum (Fig. 1) and demonstrates the fairly efficient production of diradicals.

The zero-field splittings and hyperfine couplings obtained from the spectral simulation can be used to assess the electronic structure of $1^{\cdot+}$ and $1^{2+\cdot}$ in some detail. The isotropic hyperfine coupling $A_{\text{iso}} = 65$ MHz of $1^{\cdot+}$ when compared to $A_{\text{iso}} = 114$ MHz of the methylenetriphenyl phosphorane cation radical ($\text{Ph}_3\text{PCH}_2^{\cdot+}$) [5] suggests that the spin density at the methylene carbon is about 57%. The zero-field splitting of $D = 350$ MHz for $1^{2+\cdot}$ corresponds within the dipole approximation to a distance between the radical centers of about 6.1 Å. Standard bond lengths suggest a distance of only 4.85 Å between the two methylene carbon nuclei. The increase is consistent with delocalization of spin density into the terminal 4-*t*-butylphenyl rings.

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 $1^{2+\cdot}$ demonstrate that the signal intensity follows Curie's law ($I = C/T$). We conclude that the triplet state of $1^{2+\cdot}$ is the ground state, although an exact degeneracy with the corresponding singlet state cannot be excluded from this experiment.

4. Conclusion

We have shown that di(cation radical) $1^{2+\cdot}$ in which two methylene phosphorane cation radicals are linked by a 1,3-phenylene ring has a triplet ground state.

Acknowledgment

We thank Prof. E. W. Meijer for valuable discussions and Philips Research for an unrestricted research grant. This work has been supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

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