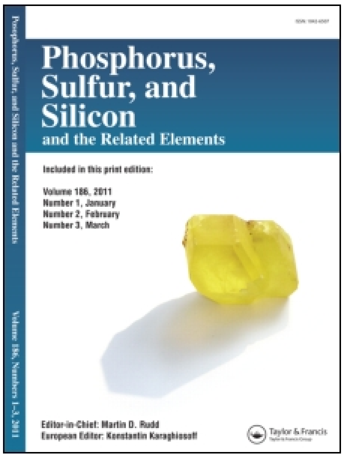

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Studies on Stable 1,3-Diphosphacyclobutane-2,4-diyls

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Studies on Stable 1,3-Diphosphacyclobutane-2,4-diyls

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Various kinds of stable 1,3-diphosphacyclobutane-2,4-diyls, sterically protected by bulky Mes (2,4,6-tri-t-butylphenyl) groups, were prepared from Mes*-phosphaethyne. The structures and physical and chemical characters were studied. They are discussed in terms of ground-state singlet biradicals and have been confirmed by spectroscopic analyses, X-ray crystallography and theoretical calculations. EPR studies were also carried out to validate the paramagnetic species related to the 1,3-diphosphacyclobutane-2,4-diyls. The reactions of the biradical species are described including oxidation and sulfurization.*

Keywords Biradical; radicals; phosphorus heterocycles; steric protection

INTRODUCTION

Radicals are highly reactive but can be stabilized by bulky substituents and/or by electronic factors. Biradicals are expected more reactive and are considered to be much more difficult to isolate. By use of a bulky Mes* group (2,4,6-tri-*t*-butylphenyl),

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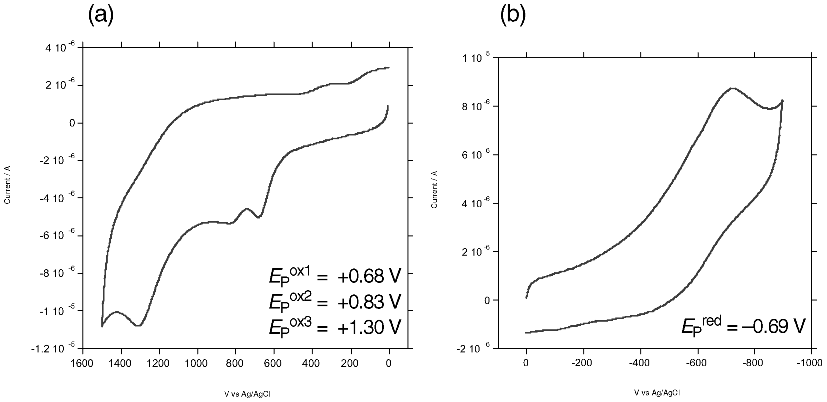


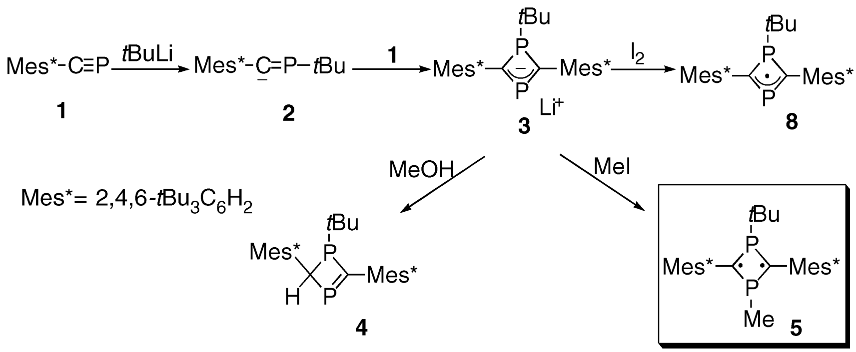
FIGURE 1 Cyclic voltammograms of **8**. (a): Oxidation waves. (b) Reduction waves. Conditions: 1 mM in dichloromethane; supporting electrolyte: 0.1 M tetrabutylammonium perchlorate (TBAP); working electrode: glassy carbon; counter electrode: platinum wire; reference electrode: Ag/AgCl ($E_{1/2}$ (ferrocene/ferricinium) = +0.60 V) at 20°C; scan rate: 50 mV s^{-1}.

however, unusually stable biradicals, 2,4-bis(2,4,6-tri-*t*-butylphenyl)-1,3-diphosphacyclobutane-2,4-diyls can be isolated and characterized.

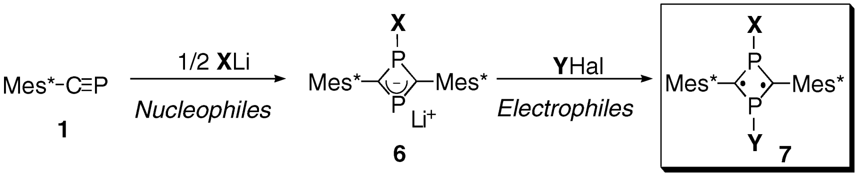
RESULTS

Reactions of Mes*-Phosphaethyne and Isolation of Stable Biradicals

As depicted in Scheme 1, asterically protected phosphaalkyne **1** reacted with 0.5 equiv of *t*-butyllithium to give a 4-membered ring anion **3**,



SCHEME 1



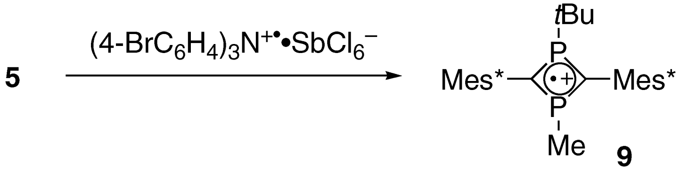
SCHEME 2

via intermediate **2**. When **3**, which was characterized by ^{31}P-NMR spectroscopy ($\delta_P = 268.5$, 87.6; $^2J_{PP} = 86.8$ Hz), was quenched with methanol as a proton source, 1,3-diphosphacyclobutene **4** ($\delta_P = 308.8$, 89.2; $^2J_{PP} = 94.1$ Hz)[1] was obtained and its structure was unambiguously confirmed by X-ray crystallography.[2]

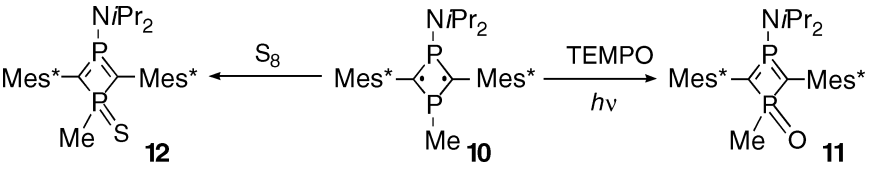
When anion **3** was quenched with methyl iodide, a stable dark blue biradical species **5** was obtained ($\delta_P = 55.9$, –11.3; $^2J_{PP} = 362.8$ Hz).[3] The structure of **5** was determined by X-ray analysis indicating that two Mes* groups efficiently protect two carbon atoms. Compound **5**, 1,3-diphosphacyclobutane-2,4-diyl, is a member of a new class of stable biradicals, on which Niecke [4] and Bertrand[5] recently reported.

Changing the identities of the nucleophile (from *t*–BuLi) and the electrophile (from MeI), various derivatized biradicals **7** (X = Me, *n*-Bu, *t*-Bu, Ph, and *i*-Pr_2N; Y = Me, Et, *n*-Bu, *t*-Bu, $PhCH_2$, *n*-$C_{18}H_{37}$, *n*-C_3F_7, PhC(O), $MeOCH_2$, and $MeOCOCH_2$) were formed via anions **6** (Scheme).[6–8] NMR, UV, and CV data for **7** were studied and several of these biradicals were characterized by X-ray crystallography.

Oxidation of **3** with 0.5 equiv of iodine resulted in the formation of a pink neutral radical **8**. Radical **8** is a stable crystalline compound and its structure was analyzed by X-ray diffraction and EPR spectroscopy.[9] Electrochemistry of **8** was examined and from the voltammograms, the compound showed three oxidation waves and one reduction wave (Figure 1). It is plausible that the first (lowest potential) oxidation occurs at the radical center and the following two waves correspond to the oxidation of phosphorus lone pairs. A relatively low reduction potential



SCHEME 3



SCHEME 4

indicates that the radical can be easily reduced to its radical anion. These phenomena are supported by calculations of a model compound.

Furthermore, **5** reacts with tris(4-bromophenyl)ammoniumyl hexachloroantimonate as an oxidant to give the corresponding cation radical **9**,[10] the structure of which was established by analysis of its EPR spectrum (Scheme 3).

Oxidation and Sulfurization of a Biradical

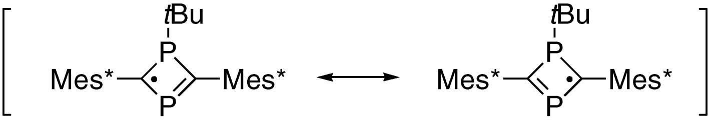
A biradical **10** (= **7**, where X = i-Pr_2N, Y = Me) was allowed to react with TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) on photo-irradiation to give the corresponding oxide **11** ($\delta_P = 121.8, 25.4$; $^2J_{PP} = 183.2$ Hz),[6] and the reaction with elemental sulfur gave the corresponding sulfide **12** ($\delta_P = 101.7, 45.7$; $^2J_{PP} = 194.2$ Hz).[8] Other chemical studies of **7** are in progress (Scheme 4).

DISCUSSION

Structures of Biradicals and Radicals

From the X-ray analysis of biradical species 5 and 7, two carbon atoms in the 4-membered ring have sp^2 configurations, while the two phosphorus atoms exhibit sp^3 configurations. In addition, the interatomic distance between the two carbon centers (2.50 Å) is too long to suggest a high degree of direct interaction between them. These considerations lead us to the conclusion that the structures of **5** and **7** should be drawn as biradicals as depicted in Schemes 1 and 2 .

The EPR studies of neutral radical **8** and cation radical **9** reveal the spin densities are localized on the carbons in the 4-membered ring showing spectra of typical carbon centered radicals. Computational modeling also explicates the hyper-fine coupling constants. Some important resonance contributors of **8** are shown in Scheme 5.[9]



8A **8B**

SCHEME 5

REFERENCES AND NOTES

[1] S. Ito, H. Sugiyama, and M. Yoshifuji, *Chem. Commun.*, 1744 (2002).

[2] The structure of **4** was misreported as a linear molecule. A.M. Arif, A.R. Barron, A.H. Cowley and S.W. Hall, *J. Chem. Soc.,Chem. Commun.*, 171 (1988).

[3] H. Sugiyama, S. Ito, and M. Yoshifuji, *Angew. Chem. Int. Ed.*, **42,** 3802 (2003).

[4] E. Niecke, A. Fuchs, F. Baumeister, M. Nieger, and W.W. Schoeller, *Angew. Chem., Int. Ed. Engl.*, **34,** 555 (1995).

[5] D. Scheschkewitz, H. Amii, G. Gornitzka, W.W. Schoeller, D. Bourissou, and G. Bertrand, *Science*, **295,** 1880 (2002).

[6] H. Sugiyama, S. Ito, and M. Yoshifuji, *Chem. Eur. J.*, **10,** 2700 (2004).

[7] M. Yoshifuji, H. Sugiyama, and S. Ito, *J. Organomet. Chem.*, **690,** 2515 (2005).

[8] S. Ito, M. Kikuchi, H. Sugiyama, and M. Yoshifuji, *J. Organomet. Chem.* **692**, 2761 (2007). DOI: 10.1016/j.jorganchem.2006.10.066.

[9] S. Ito, M. Kikuchi, M. Yoshifuji, A. J. Arduengo III, T .A. Konovalova, and L. D. Kispert, *Angew. Chem. Int. Ed.*, **45,** 4341 (2006).

[10] M. Yoshifuji, A. J. Arduengo III, T. A. Konovalova, L. D. Kispert, M. Kikuchi, and S. Ito, *Chem. Lett.*, **35,** 1136 (2006).