



Phosphorus, Sulfur, and Silicon and the Related Elements

ISSN: 1042-6507 (Print) 1563-5325 (Online) Journal homepage: http://www.tandfonline.com/loi/gpss20

1,3,6-Triphosphafulvene Bearing Three Low-**Coordinated Phosphorus Atoms**

Masaaki Yoshifuji , Shigekazu Ito & Hiroki Sugiyama

To cite this article: Masaaki Yoshifuji , Shigekazu Ito & Hiroki Sugiyama (2001) 1,3,6-Triphosphafulvene Bearing Three Low-Coordinated Phosphorus Atoms, Phosphorus, Sulfur, and Silicon and the Related Elements, 168:1, 315-319, DOI: <u>10.1080/10426500108546574</u>

To link to this article: http://dx.doi.org/10.1080/10426500108546574

1	1	(1
Г			

Published online: 02 Apr 2008.



Submit your article to this journal 🕑

Article views: 10



View related articles 🗹



Citing articles: 2 View citing articles 🗹

Full Terms & Conditions of access and use can be found at http://www.tandfonline.com/action/journalInformation?journalCode=gpss20

1,3,6-Triphosphafulvene Bearing Three Low-Coordinated Phosphorus Atoms

MASAAKI YOSHIFUJI, SHIGEKAZU ITO and HIROKI SUGIYAMA

Department of Chemistry, Graduate School of Science, Tohoku University, Aoba, Sendai 980–8578, Japan

A kinetically stabilized 1,3,6-triphosphafulvene bearing three 2,4,6-tri-*tert*-butylphenyl (Mes[•]) groups was formed as a trimer of phosphanylidene carbenoid generated from Mes[•]P=CBr₂ with *tert*-butyllithium, and the corresponding pentacarbonyltungsten complex was analyzed by X-ray crystallography.

Keywords: Carbenoids; carbonyl tungsten complexes; phosphaalkenes; low coordinated phosphorus; 2,4,6-tri-tert-butylphenyl; fulvene

INTRODUCTION

Kinetically protected organophosphorus compounds have been of interest since 1981, when we found an enormously strong steric effect of the 2,4,6-tri-*tert*-butylphenyl group (Mes*) on the stability of phosphorus compounds in low coordination states.



We have been interested in a series of unusual organophosphorus compounds with coordination number 2, and among those, are involved sterically protected diphosphene 1, 1 phosphaalkene 2, 2diphosphinidenecyclobutene 3, 3 and diphospha[4]radialene 4.4



RESULTS AND DISCUSSION

During the course of our study, we became interested in the reactivities of phosphanylidene carbenoids 5 supposed to be generated from the reaction of dihalomethylenephosphines 6 with alkyllithium reagents. The reaction products depended on the conditions, as well as starting materials.



Either phosphabutadiene 7 or diphosphabutatriene 8 was obtained by use of copper salts depending on the reaction conditions,⁵ while without any additives the reaction has been reported to provide a 4membered ring system.⁶



Under certain conditions, phosphaalkyne 9 was obtained probably through [1,2]-rearrangement from phosphanylidene carbenoids, similarly to the Fritsch-Buttengerg-Wiechell rearrangement.⁷



On the other hand, when dibromomethylenephosphine **6B** was used as a starting material together with *n*-butyllithium, the reaction gave mainly an intramolecular C-H insertion product, dihydrophosphanaphthalene $10,^8$ indicating generation of free phosphanylidene carbene intermediate 11 during the reaction.



In contrast to the results above, a kinetically stabilized 1,3,6triphosphafulvene 12^{10} bearing three Mes* groups was obtained as a trimer of phosphanylidene carbenoid 5B generated from 6B with *tert*butyllithium, together with a small amount of phosphinoacetylene 13, and traces of phosphaalkyne 9 and 10.



As for 12, one of the valence isomers of triphosphabenzenes in the novel inorganic ring systems, the corresponding pentacarbonyltungsten complex 12w was analyzed by X-ray crystallography.¹⁰



A reaction mechanism has been postulated to involve the Fritsch-Buttenberg-Wiechell reaction type from 5B to phosphaalkyne 9^7 and elimination of LiBr from adduct 14, which might be formed from 5B and two equivalent amounts of 9. Phosphinoacetylene 13 might be formed from 15 followed by expulsion of one phosphorus atom. It should be noted that compound 10 was obtained almost exclusively⁸ if *n*butyllithium was used in place of *tert*-butyllithium. The present results also form a sharp contrast to those from the corresponding dichloro derivative forming 1,4-diphospha-1,3-butadiene 7^5 or 1,4-diphospha-1,2,3-butatriene $8,^9$ depending upon reaction conditions.

ACKNOWLEDGMENTS

This work was supported in part by a Grant-in-Aid for Scientific Research (No. 09239101) from the Ministry of Education, Science, Sports and Culture, Japan.

References

- M. Yoshifuji I. Shima, N. Inamoto, K. Hirotsu, and T. Higuchi, J. Am. Chem. Soc., 103, 4587 (1981); 104, 6167 (1982).
- [2] M. Yoshifuji, K. Toyota, I. Matsuda, T. Niitsu, N. Inamoto, K. Hirotsu, and T. Higuchi, *Tetrahedron*, 44, 1363 (1988).
- [3] M. Yoshifuji, K. Toyota, M. Murayama, H. Yoshimura, A. Okamoto, K. Hirotsu, and S. Nagase, Chem. Lett., 1990, 2195.
- [4] K. Toyota, K. Tashiro, and M. Yoshifuji, Angew. Chem. Int. Ed. Engl., 32, 1163 (1993).
- [5] S. Ito, K. Toyota, and M. Yoshifuji, Chem. Lett., 1995, 747.
- [6] E. Niecke, A. Fuchs, F. Baumeister, M. Nieger, and W. W. Schoeller, Angew. Chem., Int. Ed. Engl., 34, 555 (1995).
- [7] M. Yoshifuji, T. Niitsu, and N. Inamoto, *Chem. Lett.*, 1988, 1733; M. Yoshifuji, H. Kawanami, Y. Kawai, K. Toyota, M. Yasunami, T. Niitsu, and N. Inamoto, *Chem. Lett.*, 1992, 1053; R. Appel and M. Immenkeppel, Z. Anorg, Allgem. Chem., 553, 7 (1987).
- [8] S. Ito, K. Toyota, and M. Yoshifuji, Chem. Commun., 1997, 1637.
- [9] S. Ito, K. Toyota, and M. Yoshifuji, J. Organomet. Chem., 1998, 553, 135.
- [10] S. Ito, H. Sugiyama, and M. Yoshifuji, Angew. Chem., 112, 2892 (2000).