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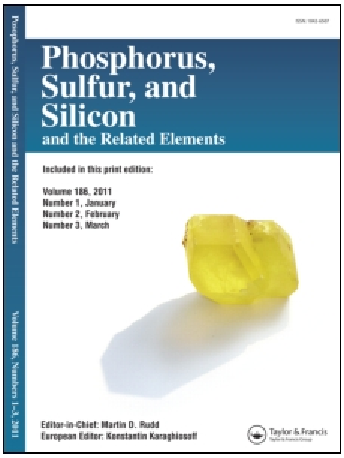

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1,3,6-Triphosphafulvene Bearing Three Low-Coordinated Phosphorus Atoms

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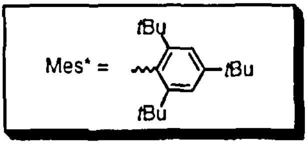
A kinetically stabilized 1,3,6-triphosphafulvene bearing three 2,4,6-tri-*tert*-butylphenyl (Mes^*) groups was formed as a trimer of phosphanylidene carbenoid generated from $Mes^*P{=}CBr_2$ with *tert*-butyllithium, and the corresponding pentacarbonyltungsten complex was analyzed by X-ray crystallography.

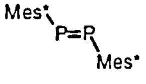
Keywords: Carbenoids; carbonyl tungsten complexes; phosphaalkenes; low coordinated phosphorus; 2,4,6-tri-*tert*-butylphenyl; fulvene

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,[2] diphosphinidenecyclobutene 3,[3] and diphospha[4]radialene 4.[4]



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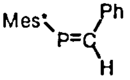

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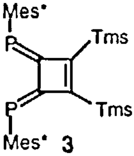

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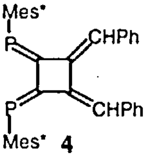

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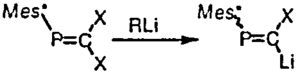
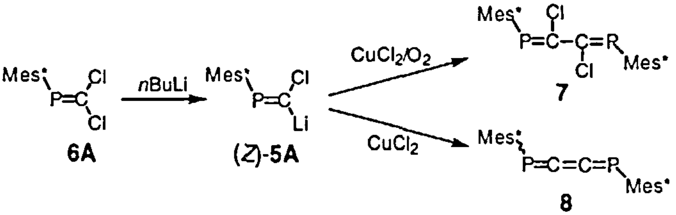
RESULTS AND DISCUSSION

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.



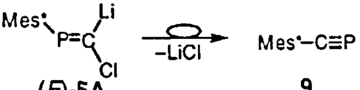
6A (X=Cl) **5A** (X=Cl)
B (X=Br) **B** (X=Br)

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 4-membered ring system.[6]



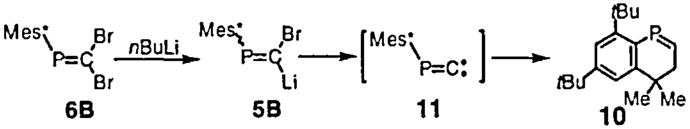
6A (*Z*)-**5A** **7** **8**

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

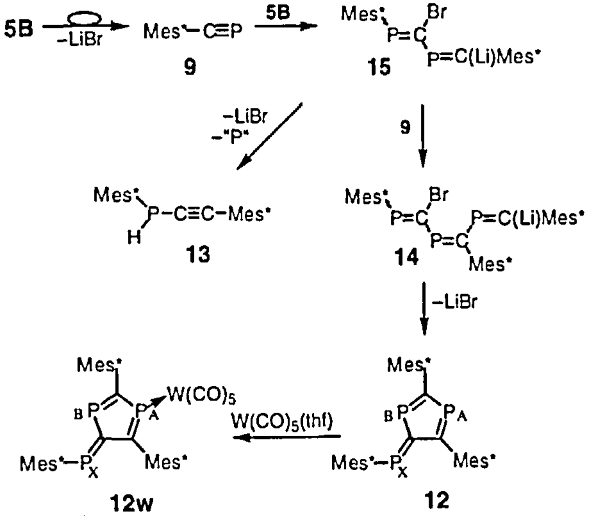


(*E*)-**5A** **9**

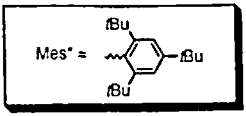
On the other hand, when dibromomethylenephosphine **6B** was used as a starting material together with *n*-butyllithium, the reaction gave mainly an intramolecular C-H insertion product, dihydrophosphanaphthalene **10**,[8] indicating generation of free phosphanylidene carbene intermediate **11** during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

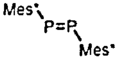


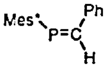
In contrast to the results above, a kinetically stabilized 1,3,6-triphosphafulvene **12**[10] bearing three Mes* groups was obtained as a trimer of phosphanylidene carbenoid **5B** generated from **6B** with *tert*-butyllithium, together with a small amount of phosphinoacetylene **13**, and traces of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


Mes* =
tBu
tBu
tBu


1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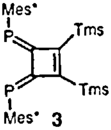
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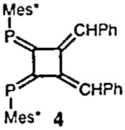
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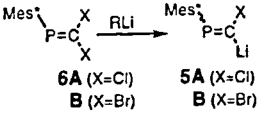
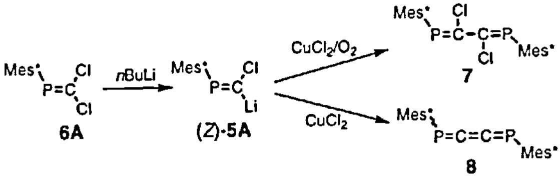
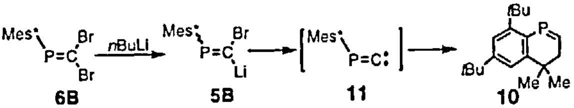
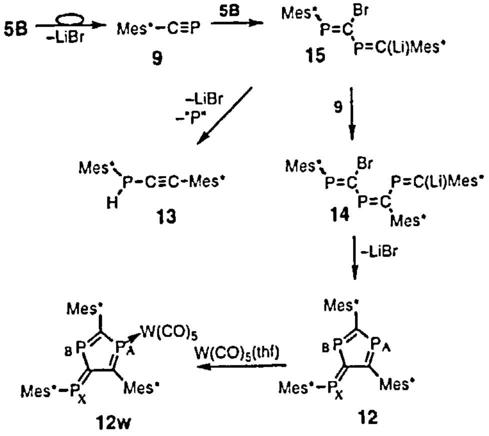

Mes*
P=C
X
X
RLi
Mes*
P=C
X
Li
6A (X=Cl)
B (X=Br)
5A (X=Cl)
B (X=Br)


Mes*
P=C
Li
Cl
(E)-5A
-LiCl
Mes*–C≡P
9


Mes*
P=C
Cl
Cl
6A
nBuLi
Mes*
P=C
Cl
Li
(Z)-5A
CuCl2/O2
CuCl2
Mes* Cl
P=C–C=P
Cl Mes*
7
Mes*
P=C=C=P
Mes*
8


Mes*
P=C
Br
Br
6B
nBuLi
Mes*
P=C
Br
Li
5B
Mes*
P=C:
11
tBu
P
tBu
Me Me
10


5B
-LiBr
Mes*–C≡P
9
5B
Mes*
P=C
Br
P=C(Li)Mes*
15
-LiBr
–"P"
9
Mes*
P–C≡C–Mes*
H
13
Mes* Br
P=C P=C(Li)Mes*
P=C
Mes*
14
-LiBr
Mes*
BP
PA
W(CO)5
Mes*–PX
Mes*
12w
W(CO)5(thf)
Mes*
BP
PA
Mes*–PX
Mes*
12

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 exclusively[8] 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

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References

[1] 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).