This article was downloaded by: [Columbia University]
On: 09 December 2014, At: 02:12
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

Recent Results on Synthesis and Ring Cleavage Reactions of 2H-Azaphosphirene Derivatives

Rainer Streubel & Annette Ostrowski

[a] Institut für Anorganische und Analytische Chemie der Technischen Universität , Braunschweig Postfach 3329, D-38023, Braunschweig, Germany

[b] Institut für Anorganische und Analytische Chemie der Technischen Universität , Braunschweig Postfach 3329, D-38023, Braunschweig, Germany

Published online: 06 Aug 2008.

To cite this article: Rainer Streubel & Annette Ostrowski (1996) Recent Results on Synthesis and Ring Cleavage Reactions of 2H-Azaphosphirene Derivatives, Phosphorus, Sulfur, and Silicon and the Related Elements, 109:1-4, 153-156

To link to this article: http://dx.doi.org/10.1080/10426509608545113

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly

Phosphorus, Sulfur, and Silicon, 1996, Vols. 109–110, pp. 153–156
Reprints available directly from the publisher
Photocopying permitted by license only

RECENT RESULTS ON SYNTHESIS AND RING CLEAVAGE REACTIONS OF 2*H*-AZAPHOSPHIRENE DERIVATIVES

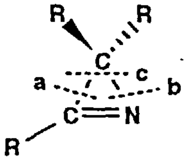
RAINER STREUBEL and ANNETTE OSTROWSKI
Institut für Anorganische und Analytische Chemie
der Technischen Universität Braunschweig
Postfach 3329, D-38023, Braunschweig, Germany

Abstract Reactions of [amino(aryl)carbene](pentacarbonyl)metal complexes with chlorophosphane derivatives under basic conditions yield 2*H*-azaphosphirene complex derivatives. Investigations of thermally induced ring-cleavage reactions of 2*H*-azaphosphirene tungsten derivatives in the presence of various trapping reagents are presented.

Keywords: phosphorus heterocycles, 2H-azaphosphirenes, carbene complexes, phosphanediyl complex.

Introduction

There are few known synthetic methods that give access to strained three-membered heterocycles containing a ring system with a C=N-moiety and a further heteroatom. These heterocycles are of interest because of their molecular structure and expected high reactivity. In contrast, the chemistry of 2*H*-azirenes has been investigated in detail, especially with respect to ring-opening reactions.[1] Several reaction pathways have been reported, including reactions that pro-



Scheme. Ring-opening reactions of 2*H*-azirenes.

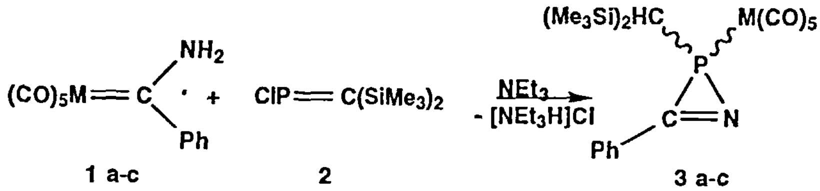
ceed by one- (a, b) or two-fold bond fission (c) (scheme).

The first synthesis of 2*H*-azaphosphirene tungsten complexes has been achieved by reaction of [amino(aryl)carbene](pentacarbonyl]-tungsten(0) complexes with [bis(trimethylsilyl)methylene]chlorophosphane under basic conditions.[2]

Results

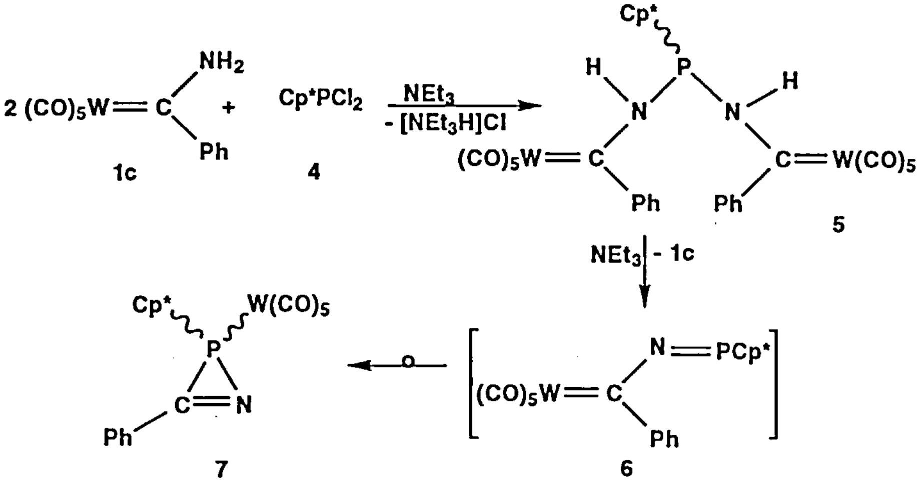
Syntheses of 2*H*-azaphosphirene complexes

In order to exploit our synthetic approach to 2*H*-azaphosphirene complexes, we decided to investigate the reaction of amino(phenyl)carbene metal complexes (M = Cr, Mo, W) **1a-c** towards methylene(chloro)phosphane **2**. In the presence of triethylamine a clean reaction occurred, affording 2*H*-azaphosphirene metal complexes **3b,c** in good yields, whereas compound **3a** showed a slow decomposition yielding diphosphene complex derivatives even at ambient temperature.[3]



1a, 3a: M = Cr; 1b, 3b: M = Mo; 1c, 3c: M = W

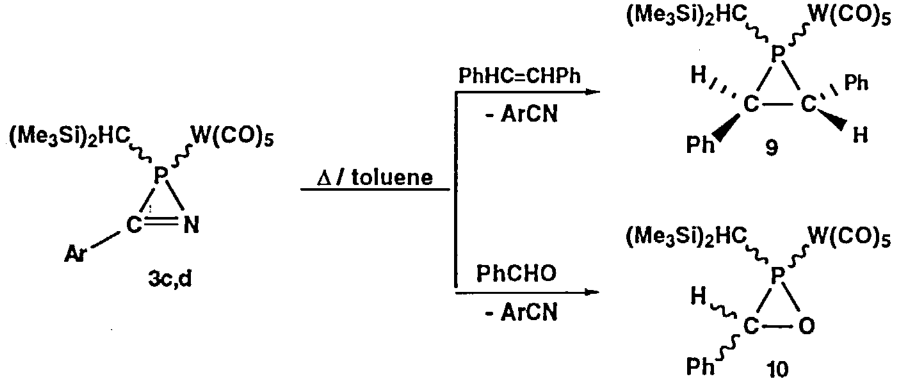
The employment of a *cis*-phosphane-substituted carbene tungsten complex showed that this rearrangement reaction proceeds stereospecifically with respect to the metal center.[3] A surprisingly selective base-induced condensation reaction of [amino(phenyl)carbene]-tungsten(0) derivative **1a** with the bulky alkyl(dichloro)phosphane derivative **4a** (R = Cp*) led to the 2*H*-azaphosphirene complex derivative **7** via the bisamino-substituted phosphane **4**.[3] As crucial reaction step a rearrangement of a transiently formed 2-aza-1-phospha-4-tungsta-1,3-butadiene derivative **6** to give **7** is proposed.



Investigations of thermally induced ring-opening of 3c,d

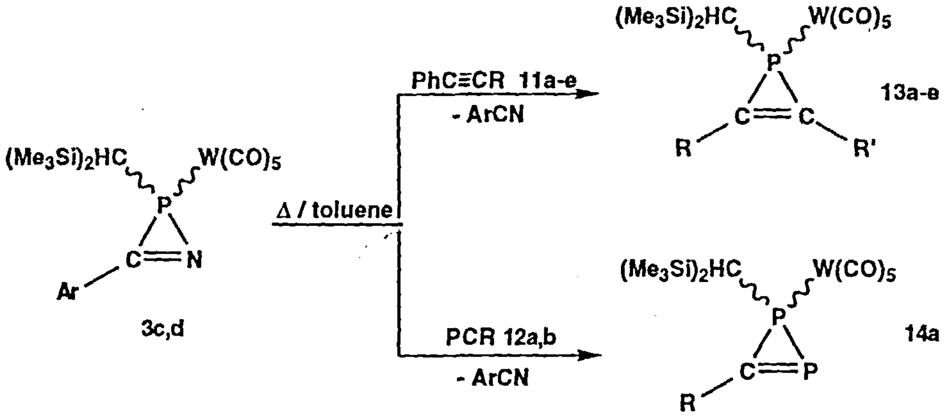
One of the most interesting aims in heterocyclic chemistry of small ring compounds is to explore their ring-opening behaviour.

The P-C-N ring system of the 2*H*-azaphosphirene tungsten complex **3d** possesses very narrow ring angles, pointing to a strained ring system.[2] As first investigations of the reactions of **3c,d** have shown, it displays a remarkably low stability in solution. Thermal decomposition of **3c,d** in toluene in the presence of *trans*-stilbene or benzaldehyde afforded the corresponding nitrile derivatives and the [2+1]-cycloaddition products **9**[3],**10**.[4] The nitrile derivatives have been identified by IR-spectroscopy. The formation of **9**,**10** can be rationalized by reaction of a transiently formed phosphanediyl complex with these multiple bond systems, nevertheless a short liv



ing phospha-analogue of a nitrile ylide - generated by ring-openi of **1c,d** - cannot be completely excluded. The X-ray structure an lysis of **10**[4] reveals a widened P-C-O ring system in comparison another oxaphosphirane complex.[5]

Further substantiation for the proposal of a phosphanediyl complex intermediate has been obtained using other trapping reagent Thermal decomposition of **3c,d** in toluene in the presence of acety lene derivatives **11a-e** (**11a**: R,R' = Ph; **11b**: R = Ph, R' = H; **11c**: R = Ph, R'' = Me; **11d**: R = H, R' = OEt; **11e**: R,R' = CO$_2$Me) or phosphaalkynes **12a,b** (**a**: R = iPr(Me$_3$Si)N; **b**: R = tBu) afforded the corresponding 1H-phosphirene derivatives **13a,b**[4]**,c-e**[6] and the 1H-diphosphirene complex **14a**[6]; in the case of **12b** a 1,2-dihydro-1,2,3-triphosphete complex[6] is the final product.



References

1. A. Pawda, A. D. Woolhouse in A. R. Katritzky, C. W. Rees (Eds.) Comprehensive Heterocyclic Chemistry, Vol. 7, Pergamon Press, Oxford, **1984**, p. 47.
2. R. Streubel, J. Jeske, P. G. Jones and R. Herbst-Irmer, *Angew. Chem..Int. Ed. Engl.* **1994**, *33*, 80-82.
3. R. Streubel, unpublished.
4. R. Streubel, A. Kusenberg, J. Jeske, P. G. Jones, *Angew. Chem.* Int. Ed. Engl. **1994**, *33*, 2427-2428.
5. S. Bauer, A. Marinetti, L. Ricard, F. Mathey, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 1166-1167.
6. A. Ostrowski, J. Jeske, P. G. Jones, R. Streubel, *J. Chem. Soc.,Chem. Commun.* submitted.