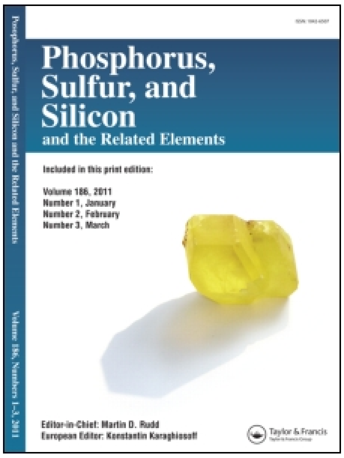

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RECENT RESULTS ON SYNTHESIS AND RING CLEAVAGE REACTIONS OF 2*H*-AZAPHOSPHIRENE DERIVATIVES

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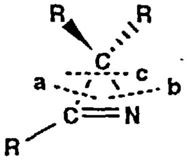
Abstract Reactions of [amino(aryl)carbene](pentacarbonyl)metal complexes with chlorophosphane derivatives under basic conditions yield 2*H*-azaphosphirene complex derivatives. Investigations of thermally induced ring-cleavage reactions of 2*H*-azaphosphirene tungsten derivatives in the presence of various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

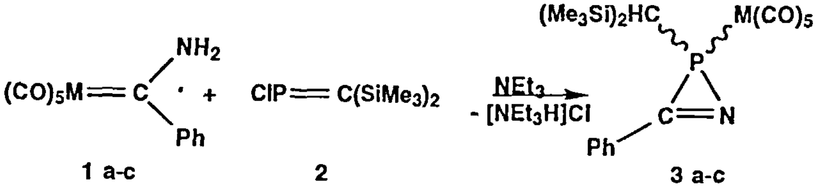
ceed by one- (a, b) or two-fold bond fission (c) (scheme).

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

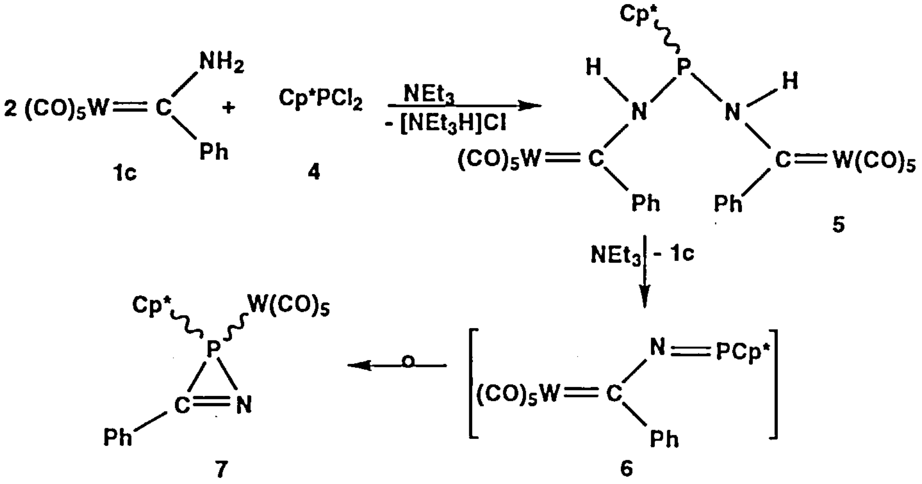
Syntheses of 2*H*-azaphosphirene complexes

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

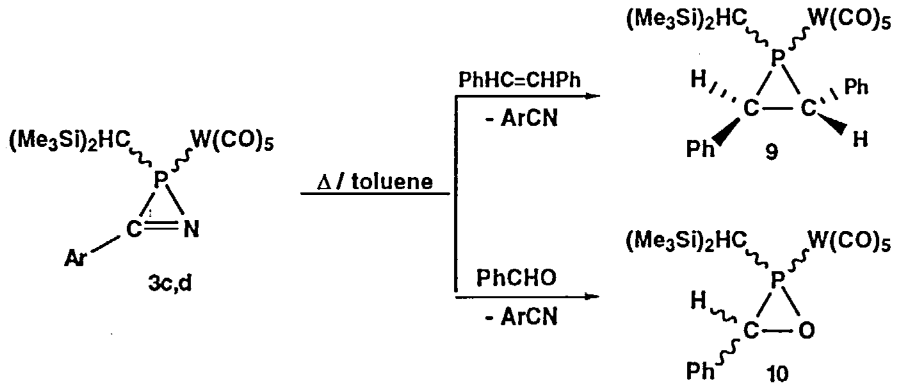
The employment of a *cis*-phosphane-substituted carbene tungsten complex showed that this rearrangement reaction proceeds stereospecifically with respect to the metal center.[3] A surprisingly selective base-induced condensation reaction of [amino(phenyl)carbene]-tungsten(0) derivative **1a** with the 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

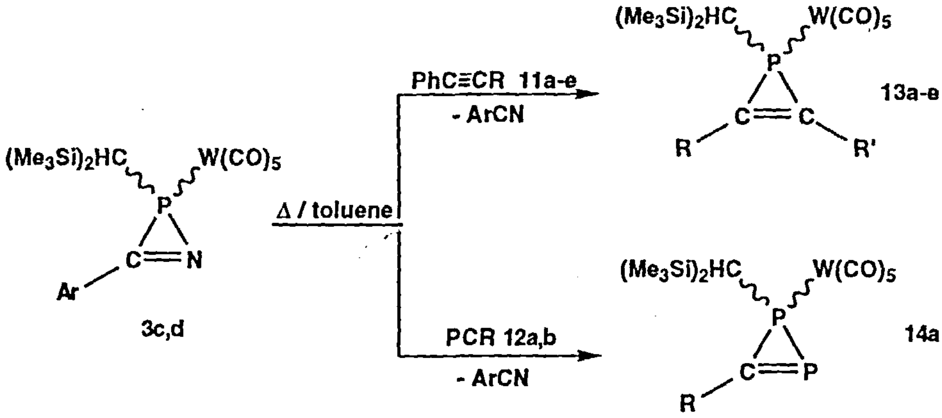
One of the most interesting aims in heterocyclic chemistry of small ring compounds is to explore their ring-opening behaviour.

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 t another oxaphosphirane complex.[5]

Further substantiation for the proposal of a phosphanediyl complex intermediate has been obtained using other trapping reagents Thermal decomposition of **3c,d** in toluene in the presence of acetylene 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_2Me) or phosphaalkynes **12a,b** (**a**: R = *i*Pr(Me_3Si)N; **b**: R = *t*Bu) afforded the corresponding 1*H*-phosphirene derivatives **13a,b**[4]**,c-e**[6] and the 1*H*-diphosphirene complex **14a**[6]; in the case of **12b** a 1,2-dihydro-1,2,3-triphosphete complex[6] is the final product.



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