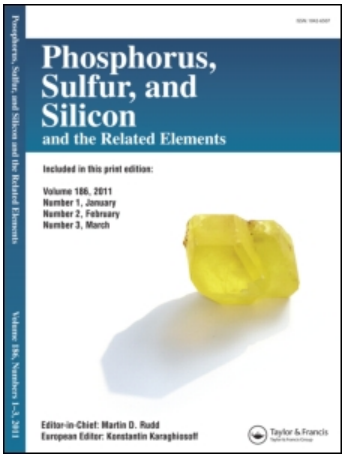

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Synthesis, Structure and Reactions of 2*H*-1-Aza-2-Phosphirene Derivatives

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SYNTHESIS, STRUCTURE AND REACTIONS OF 2*H*-1-AZA-2-PHOSPHIRENE DERIVATIVES

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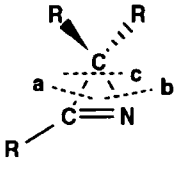
Abstract Reactions of amino(aryl)carbenepentacarbonylmetal complexes with chlorophosphane derivatives under basic conditions yield 2*H*-1-aza-2-phosphirene metal complex derivatives. First investigations of thermally induced ring-opening reaction of a 2*H*-1-aza-2-phosphirene tungsten derivative in the presence of various trapping reagents are presented.

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.

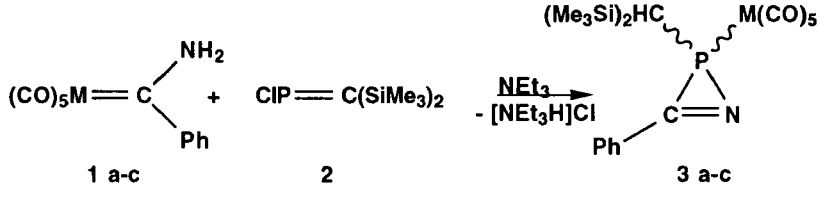
ceed by one- (a, b) or two-fold bond fission (c) (scheme).

The first synthesis of 2*H*-1-aza-2-phosphirene tungsten complexes has been achieved by reaction of amino(aryl)carbene-pentacarbonyltungsten(0) complexes with [bis(trimethylsilyl)methylene]-chlorophosphane under basic conditions.[2]

Results

Syntheses of 2*H*-1-aza-2-phosphirene complexes

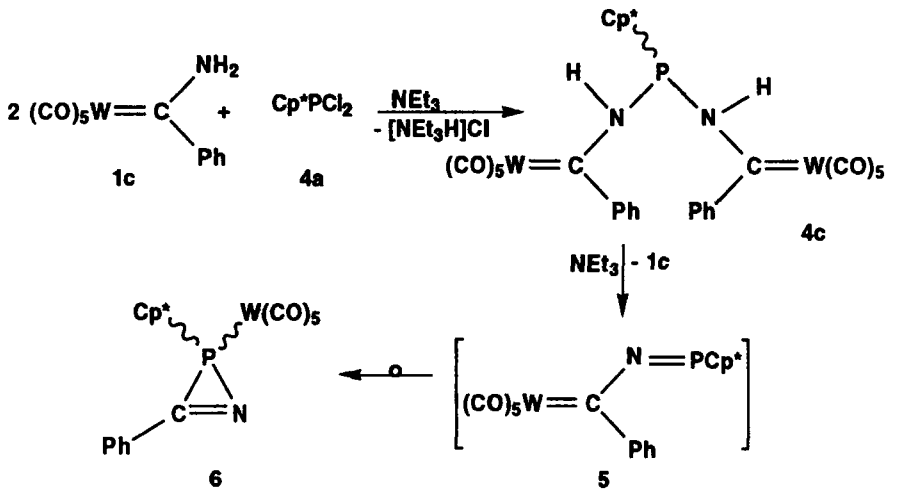
In order to exploit our synthetic approach to 2*H*-1-aza-2-phosphirene complexes, we decided to investigate the reaction of amino(phenyl)carbene metal complexes (M = Cr, Mo, W) **1a-c** towards methylene(chloro)phosphane **2**. In the presence of triethylamine a clean reaction occurred, affording 2*H*-1-aza-2-phosphirene metal complexes **3a-c** in moderate to good yields.[3]



1 a-c 2 3 a-c

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

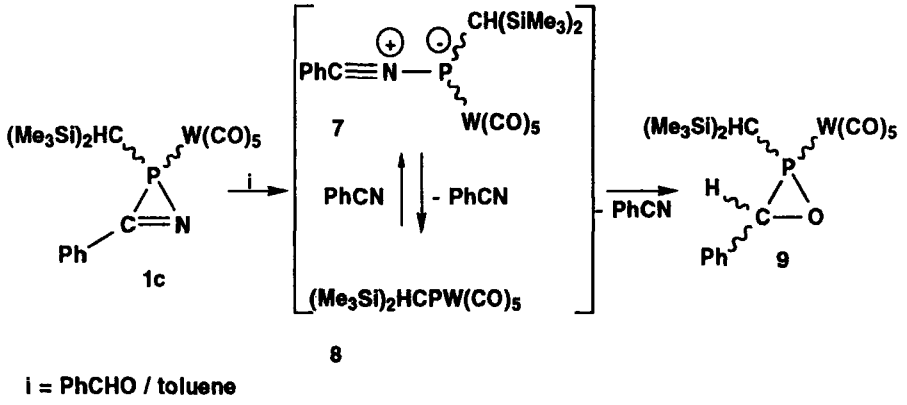
A surprisingly selective base-induced condensation reaction of amino(phenyl)carbenetungsten(0) **1a** with the bulky alkyldichlorophosphane derivative **4a** (R = Cp*) led to bisamino-substituted phosphane **4c**, instead of the expected alkyl(amino)chlorophosphane **4b**. Further reaction of base with the phosphane derivative **4c** afforded the 2*H*-1-aza-2-phosphirene complex derivative **6**, which has been purified and characterized.[3] As crucial reaction step a rearrangement of a transiently formed 2-aza-1-phospha-4-tungsta-1,3-butadiene derivative **5** to give **6** is proposed. The X-ray crystal sructure of **4c** shows two significantly different sets of W-C, C-N and N-P bond lengths, thus providing a starting point for the assumed consecutive reaction.



Investigations of thermally induced ring-opening of **3c**

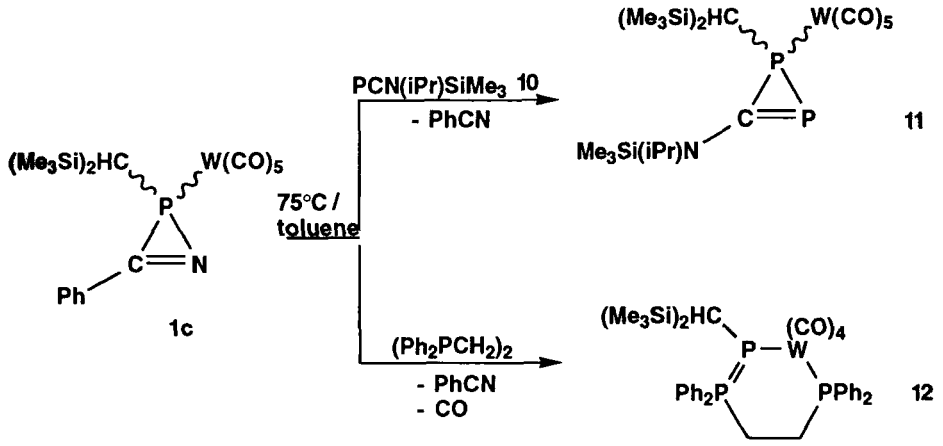
One of the most interesting aims in heterocyclic chemistry of small ring compounds is to explore their ring-opening behaviour.

The P-C-N ring system of the 2*H*-1-aza-2-phosphirene tungsten complex **1c** possesses very narrow ring angles, pointing to a strained ring system.[3] As first investigations of the reactions of **1c** have shown, it displays a remarkably low stability in solution. Thermal decomposition of **1c** in toluene in the presence of benzaldehyde afforded benzonitrile and the oxaphosphirane complex **9**.[4] The former is identified by IR-spectroscopy.



As depicted in the scheme, the formation of **9** can be rationalized by reaction of a transiently formed phosphanediyl complex **8** with benzaldehyde. Nevertheless a short living phospha-analogue of a nitrilylide **7** cannot be completely excluded. Compound **9** has been spectroscopically and structurally characterized.[4] The X-ray structure of **9** reveals a significantly widened P-C-O ring system in comparison to another derivative.[5]

Further substantiation for the proposal of an intermediate **8** has been obtained using other trapping reagents. Thermal decomposition of **1c** in toluene in the presence of aminophosphaalkyne **10** afforded the corresponding 1*H*-diphosphirene complex **11**, whereas with $(Ph_2PCH_2)_2$ compound **12** is obtained.[3] The novel six-membered ring system of **12** possesses a twisted boat conformation in the solid state.



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