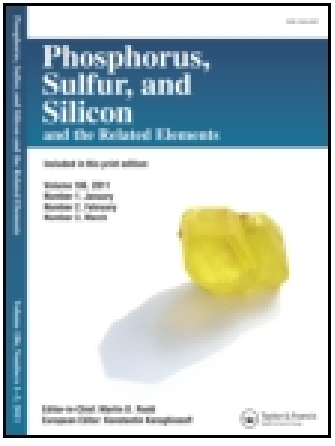

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First Synthesis and Structures of 2H-1,3,2-Diazaphosphole Tungsten Complexes

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FIRST SYNTHESIS AND STRUCTURES OF 2*H*-1,3,2-DIAZAPHOSPHOLE TUNGSTEN COMPLEXES

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Abstract: Thermal decomposition of a 2*H*-azaphosphirene tungsten complex in the presence of various nitrile derivatives yielded 2*H*-1,3,2-diazaphosphole tungsten complexes. The overall reaction may be described as a 1,3-dipolar cycloaddition of an in situ generated nitrilium phosphan eylide complex with a nitrile moiety. First evidence for a nitrile /nitrile substitution reaction leading to transiently formed nitrilium phosphane ylide complexes and a novel access to dialkylamino-substituted 2*H*-azaphosphirene tungsten complexes are reported.

Keywords: phosphorus heterocycles, cycloaddition reactions, diazaphosphole complexes, azaphosphirene complexes, nitrilium phosphane ylide complexes, phosphanediyl complexes.

INTRODUCTION

Very recently, novel accesses to three-membered unsaturated nitrogen heterocycles have been described. The first synthesis of a 2*H*-azirine via [2+1] cycloaddition of a carbene derivative to benzonitrile was published 1995[1] and, in 1996, the synthesis of a 2*H*-azasilirine was achieved, by reaction of an in situ generated silylene derivative with benzonitrile.[2] It

is noteworthy, that, up to know, [2+1] cycloaddition reactions of a nitrene or a phosphanediyl derivative to a C-N triple bond have not been reported. 2*H*-azirines and heteroanalogues thereof are potential precursors for nitrilium ylides (1,3-dipoles), which should be useful building blocks in heterocyclic syntheses. Interestingly, this has been established exclusively for 2*H*-azirines.[3]

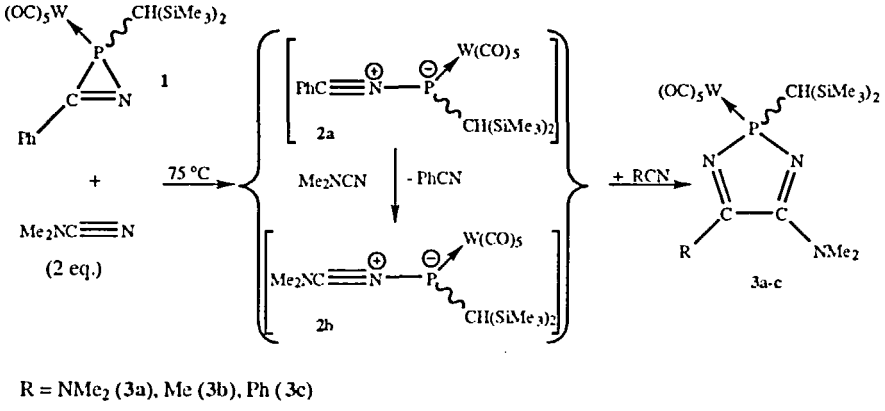
In recent years, we were interested in synthesis[4] and thermally induced ring opening reactions of 2*H*-azaphosphirene tungsten complexes. We have demonstrated, that they could be used as precursors for two different transiently formed species - a nitrilium phosphane ylide tungsten complex (a 1,3-dipole system)[5] or an electrophilic terminal phosphanediyl complex.[6,7] Here, we report on generation of transient nitrilium phosphane ylide complexes, which reacted with various nitrile derivatives to 2*H*-1,3,2-diazaphosphole complexes. Furthermore, a novel access to a 2*H*-azaphosphirene tungsten complex is presented.

RESULTS

Synthesis of 2*H*-1,3,2-diazaphosphole complexes via three-component reactions

Thermal decomposition of the 2*H*-azaphosphirene tungsten complex **1** in neat dimethyl cyanamide yielded the 2*H*-1,3,2-diazaphosphole tungsten complex **3a** as main product. The formation of the five-membered heterocycle can be explained by a three step reaction mechanism: thermal induced ring opening of 2*H*-azaphosphirene complex **1** gives the corresponding phenyl-substituted 1,3-dipole **2a**, which then reacts with dimethyl cyanamide in a nitrile/nitrile substitution reaction to the nitrilium phosphane ylide complex **2b**. Taken the description of **2a,b** as a donor stabilized terminal phosphanediyl complex into account, the formation of the 1,3-dipole **2b** should be thermodynamically favoured. The 2*H*-1,3,2-diazaphosphole complex **3a** is then formed by a 1,3-dipolar cyclo-

addition reaction of **2b** with dimethyl cyanamide. This subsequent [3+2] cycloaddition reaction is stereoselective, leading exclusively to the 2*H*-1,3,2-regioisomers (Scheme 1).



R = NMe_2 (3a), Me (3b), Ph (3c)

SCHEME 1 Synthesis of 2*H*-1,3,2-diazaphosphole tungsten complexes **3a-c**.

It should be pointed out, that the synthesis of the 2*H*-1,3,2-diazaphosphole complexes **3a-c** required the 2*H*-azaphosphirene metal complex **1** as precursor for the 1,3-dipolar system **2a**, a nitrile with a good donor ability as building block for the reactive intermediate **2b** and a trapping reagent for the [3+2] cycloaddition. Therefore, we suggest the term „three-component reaction" for those reactions. A remarkable finding was, that only two equivalents of dimethyl cyanamide (vs. **1**) were required for a selective reaction.

The structures of the 2*H*-1,3,2-diazaphospholes **3a,c**[8] were confirmed by X-ray crystallography. The structure of **3a**[9] is shown in figure 1. A remarkable feature of the molecular structure of complex **3a** is the five-membered ring system, which is approximately planar and has localized C-N double bonds, the latter being in contrast to aromatic 2*H*-1,2,3-diazaphospholes[10] or 2*H*-1,2,3-triazols.[11]

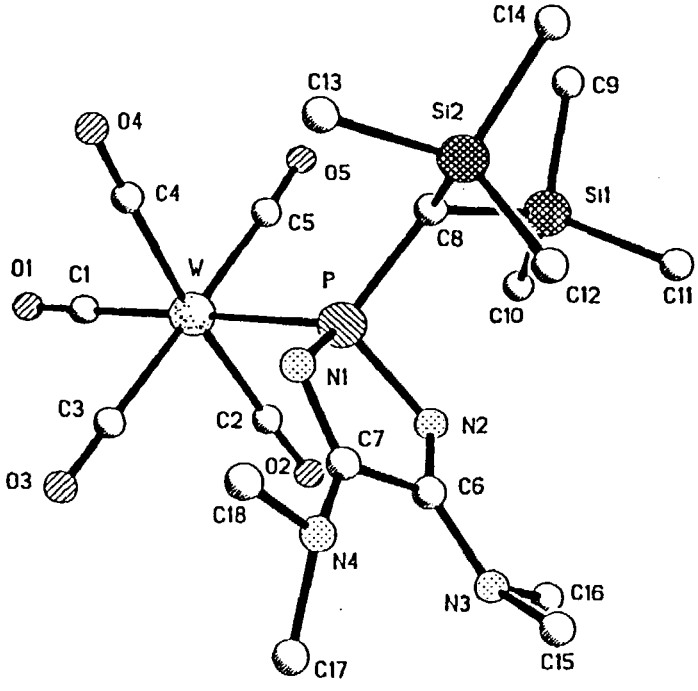
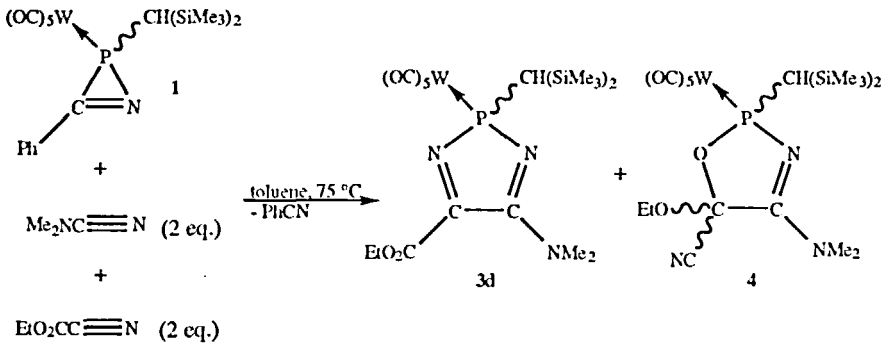


FIGURE 1 Molecular structure of complex **3a**, selected bond lengths [pm] and angles [°]: P-N1 170.7(2), N1-C7 129.6(3), C7-C6 152.4(4), C6-N2 129.2(3), N2-P 170.2(2); P-N2-C6 107.3(2), N2-C6-C7 113.6(2), C6-C7-N1 113.3(2), C7-N1-P 107.5(2), N1-P-N2 97.2(11).

Ambident reactivity of a nitrilium phosphane ylide complex towards ethyl cyanoformate

The use of ethyl cyanoformate as trapping reagent revealed an ambident reactivity of the nitrilium phosphane ylide tungsten complex **2b** towards a dipolarophile possessing two different multiple bond systems. Thermolysis of **1** in the presence of dimethyl cyanamide and ethyl cyanoformate yielded the corresponding 2*H*-1,3,2-diazaphosphole complex **3d** as main product and the two diastereomeric $\Delta^{2,3}$-1,3,2-oxazaphospholene tungsten complexes **4a,b** as by-products (Scheme 2).[9] The formation of

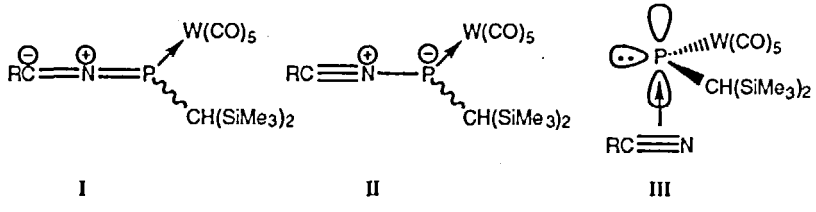
the complexes **4a,b** can be explained by a 1,3-dipolar cycloaddition reaction of **2b** (*cf.* Scheme 4) with the C-O double bond of the trapping reagent.



SCHEME 2 Ambident reactivity of a transiently formed nitrilium phosphane ylide complex towards ethyl cyanoformate.

Bonding description of nitrilium phosphane ylide complexes

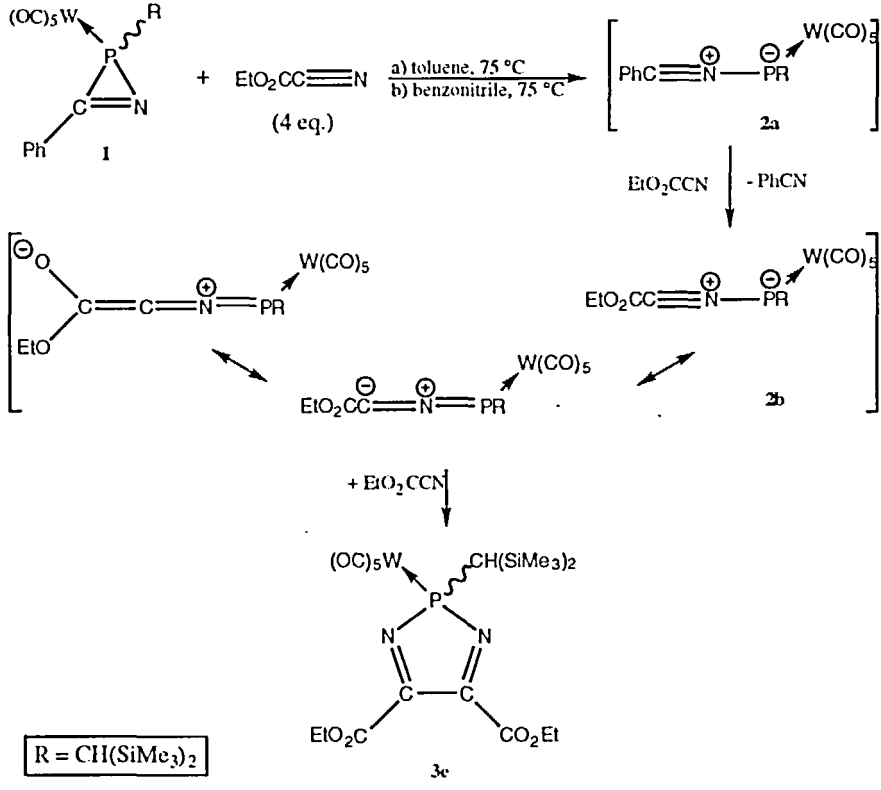
The bonding situation of nitrilium phosphane ylide complexes can be covalently described by two mesomeric forms - the allenyl type (**I**) and the propargyl type (**II**) - or as an Lewis acid/Lewis base adduct (**III**) (Scheme 3). In the latter, the nitrile nitrogen lone pair acts as a σ-donor towards the terminal phosphanediyl complex, which should have a singulett ground state and, therefore, a vacant p-orbital.[12]



SCHEME 3 Bonding description of nitrilium phosphane ylide complexes

Ethyl cyanoformate as donating nitrile and trapping reagent

The thermal decomposition of **1** in the presence of ethyl cyanoformate in toluene yielded the bis(ethylcarboxylate)-substituted 2*H*-1,3,2-diazaphosphole tungsten complex **3e** (Scheme 4).[9]

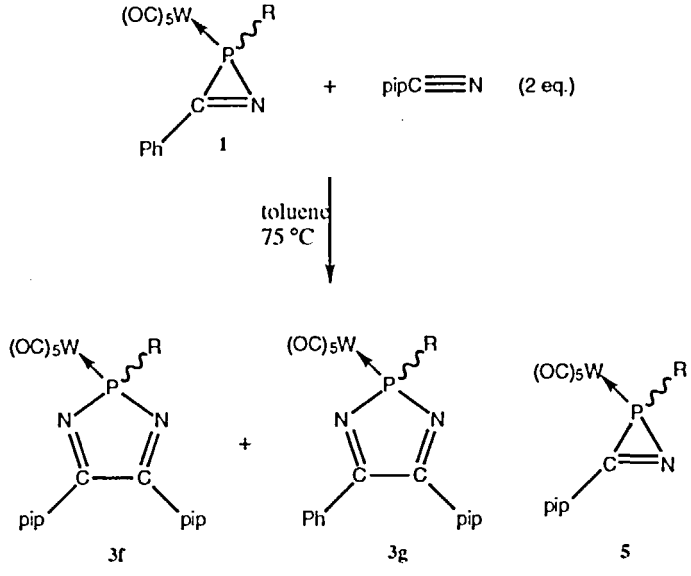


SCHEME 4 Thermal decomposition of **1** in the presence of ethyl cyanoformate.

Although benzonitrile should be the stronger donor compared to the electron poor ethyl cyanoformate, the reaction course was not influenced, upon changing the solvent from toluene (a) to benzonitrile (b). An efficient electron delocalisation in the nitrilium phosphane ylide complex **2c**, might be an explanation for this observation (*cf.* Scheme 4 and Scheme 3, type **I**).

***N*-piperidine carbonitrile as donating nitrile and trapping reagent**

Thermolysis of 2*H*-azaphosphirene complex **1** in the presence of *N*-piperidine carbonitrile led to 2*H*-1,3,2-diazaphosphole complexes **3f,g** and to 2*H*-azaphosphirene complex **1**, all of which have been isolated in pure form (Scheme 5).[9] It seems obvious, that the 2*H*-1,3,2-diazaphosphole complexes **3f,g** were formed by 1,3-dipolar cycloaddition reactions of the transient nitrilium phosphane ylide complex **2d**, either with *N*-piperidine carbonitrile (**2d** -> **3f**) or with benzonitrile (**2d** -> **3g**) (*cf.* Scheme 6). Noteworthy, that 2*H*-azaphosphirene complex **5** was surprisingly stabile under these reaction conditions.



R = $CH(SiMe_3)_2$; pip = $(H_2C)_5N$

SCHEME 5 Thermolysis of **1** in presence of *N*-piperidine carbonitrile.

The relationship between the 2*H*-azaphosphirene complex **5** and the acyclic isomer **2d** (*cf.* Scheme 6) in this reaction is not yet fully un-

derstood - probably, an equilibrium between **2d** and **5** has to be taken into account too. The product distribution (Table 1) strongly depends on the *N*-piperidine carbonitrile concentration and an increasing amount of complex **5** has been determined (by ^{13}P NMR spectroscopic means), if the concentration of *N*-piperidine carbonitrile was lowered.

TABLE 1 Estimated amounts of **3g,f** and **5** with respect the *N*-piperidine carbonitrile concentration.

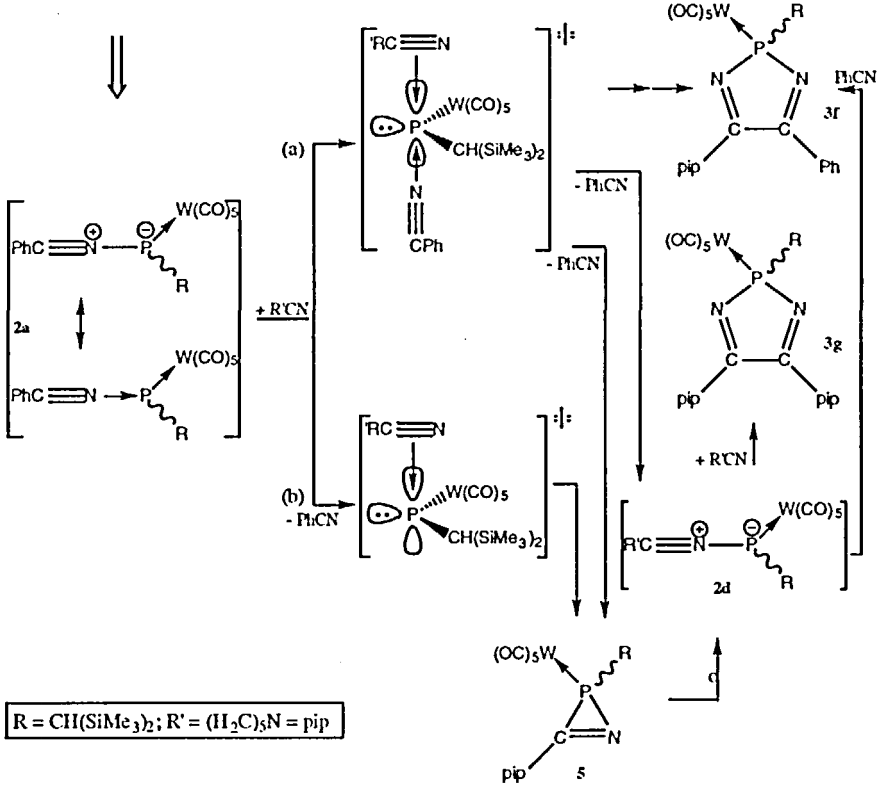
	3g[%]	3f [%]	5 [%]
2 eq. pipCN	30	50	20
4 eq. pipCN	50	40	10
neat pipCN	80	15	5

Proposed reaction mechanism of the nitrile/nitrile substitution reaction

We propose two mechanistic pathways of the nitrile/nitrile substitution reaction, which transforms one transient 1,3-dipole into the other. This proposal is consistent with the above described product formation (*cf.* Scheme 5) and relies on the observed product distributions in dilute solutions, having a low concentration of *N*-piperidine carbonitrile, and in neat *N*-piperidine carbonitrile. The two pathways have the transiently formed nitrilium phosphane ylide complex **2a** as starting-point in common (Scheme 6).

Assuming, that the HOMO of *N*-piperidine carbonitrile is the π-orbital, then two different transition states should be involved in the following steps (pathway a and b). One is that of an S_N^2-type reaction, in which two different nitriles are coordinating in a σ- and a π-type fashion to the terminal phosphanediyl complex (pathway a). The other is a π-type interaction of a nitrile with the terminal phosphanediyl complex (S_N^1-type

reaction, pathway b). The former transition state may lead finally to 2*H*-1,3,2-diazaphosphole complex **3f** or, by elimination of benzonitrile, to the 2*H*-azaphosphirene complex **5** and/or to the nitrilium phosphane ylide complex **2d**. The latter may be also formed directly via pathway b. Ring opening of **5** generates nitrilium phosphane ylide complex **2d**, which, by [3+2] cycloaddition with *N*-piperidine carbonitrile or benzonitrile, leads to the 2*H*-1,3,2-diazaphosphole complex **3g** or the 2*H*-1,3,2-diazaphosphole complex **3f**, respectively.



SCHEME 6 Proposed reaction mechanism for the formation of **3g,f** and **5** and transition states for the nitrile/nitrile substitution reaction.

ACKNOWLEDGMENT

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