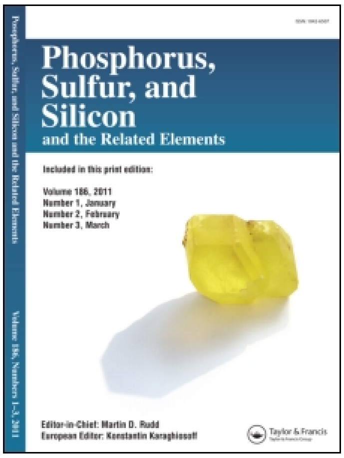

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Streubel, Rainer and Wilkens, Hendrik(1999) 'Generation and Reactions of Transient Nitrilium Phosphane Ylide Complexes', Phosphorus, Sulfur, and Silicon and the Related Elements, 144: 1, 473 — 476
To link to this Article: DOI: 10.1080/10426509908546284
URL: http://dx.doi.org/10.1080/10426509908546284

Phosphorus, Sulfur and Silicon, 1999, Vol. 144-146, pp. 473-476
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Generation and Reactions of Transient Nitrilium Phosphane Ylide Complexes

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Thermal decomposition of a 2*H*-azaphosphirene tungsten complex in the presence of *N*-piperidino nitrile and various trapping reagents (different nitriles, a ketone and an alkyne) yielded five-membered heterocycles, that are coordinated to pentacarbonyltungsten. These reactions are described as 1,3-dipolar cycloadditions of in situ generated nitrilium phosphane ylide complexes with the π-electron systems of the latter trapping reagents. The regioselectivity of this 1,3-dipol system is directed by the substituent attached to the dicoordinated carbon atom e.g. with phenyl the regioselectivity of such intermediates is nitrile sulfides-like, whereas with the *N*-piperidino substituent an Umpolung is achieved and it becomes nitrile ylides-like.

Keywords: nitrilium phosphane ylide complexes; phosphorus heterocycles; 1,3-dipolar cycloaddition reactions; N-ligands; P-ligands

INTRODUCTION

Recently, we described novel accesses to five-membered unsaturated nitrogen/phosphorus heterocycles, which were coordinated to a tungsten center, by using thermal ring opening of a 2*H*-azaphosphirene tungsten complex in the presence of dimethyl acetylenedicarboxylate[1] (DMAD) or dimethyl cyanamide.[2] Very recently, we ex-

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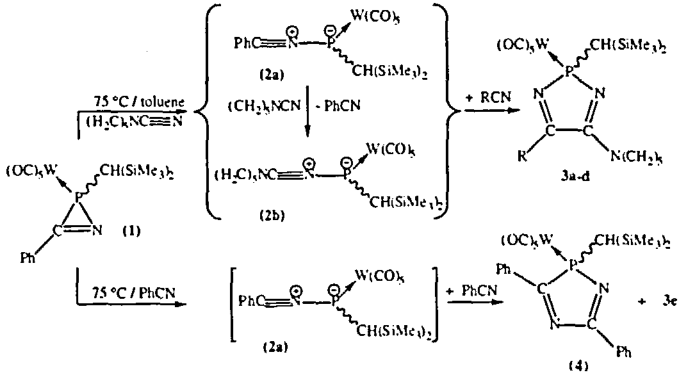
tended this three-component methodology for differently substituted nitriles, thus giving access to 4,5-substituted 2*H*-1,3,2-diazaphosphole complexes.[3] Transiently formed nitrilium phosphane ylide tungsten complexes - having a 1,3-dipole system - were assumed to be key intermediates in such reactions. In order to exploit the applications of this novel 1,3-dipole system as building block in heterocyclic syntheses, we studied the reactivity of precursor complex **1** towards a combination of *N*-piperidino nitrile as co-building block and various trapping reagents such as various nitriles, phenylglyoxonitrile, cyclohexanone and ethyl acetylenecarboxylate using the three-component methodology. Very recently, we described this concept for a combination of complex **1**, dimethyl cyanamide and DMAD.[4]

RESULTS

Stereoselective [3+2] cycloaddition reactions were achieved through thermal decomposition of the 2*H*-azaphosphirene complex **1** in the presence of *N*-piperidino nitrile and a second nitrile derivative, yielding the 2*H*-1,3,2-diazaphosphole complex **3a-d** as main products (Scheme 1).[3]

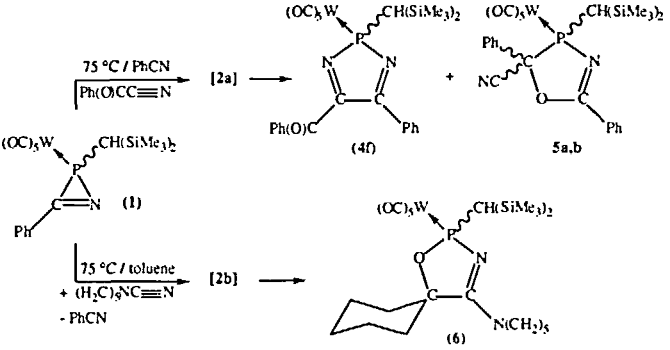


R = Ph (3a), Me (3b), ᵗBu (3c), ad (3d)

Scheme 1

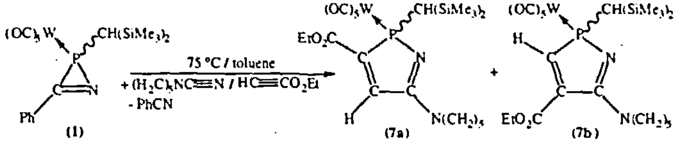
Their formation can be explained by a three step reaction mechanism: thermal induced ring opening of 2*H*-azaphosphirene complex **1** gives the corresponding phenyl-substituted 1,3-dipole **2a**, which then reacts with *N*-piperidino nitrile to yield the nitrilium phosphane ylide complex **2b** and the 2*H*-1,3,2-diazaphosphole complex **3a-d** via regioselective 1,3-dipolar cycloaddition reactions of **2b**. The synthesis of 2*H*-1,2,4-diazaphosphole complex **4** was achieved by heating 2*H*-azaphosphirene complex **1** in benzonitrile; the 4,5-diphenyl-substituted 2*H*-1,3,2-diazaphosphole complex **3e** was obtained as minor product (Scheme 1).[3] This finding suggested, that the regioselectivity of nitrilium phosphane ylide complexes can be changed (*umgepolt*) through changing the substituent at the two-coordinated carbon center.

Using **1**, benzonitrile as solvent and phenylglyoxonitrile, we obtained the 4-phenylcarbonyl-5-phenyl-2*H*-1,3,2-diazaphosphole complex **4f** and the two diastereoisomeric Δ^2-1,3,4-oxazaphospholene complexes **5a,b**, which represent the first examples of this heterocycle.[5] If **1**, *N*-piperidino nitrile and cyclohexanone was employed in toluene, the Δ^3-1,3,2-oxazaphospholene complex **6** was obtained in very good yields (85%) (Scheme 2).[5]



Scheme 2

The former reaction highlights the ambident reactivity and the regioselectivity of the nitrilium phosphane ylide complex **2a** towards a dipolarophile possessing two different multiple bond systems. The latter represents the first example for the regioselectivity of **2b** towards a ketone. As expected, thermolysis of **1** in the presence of *N*-piperidino nitrile and ethyl acetylenecarboxylate in toluene yielded 2*H*-1,2-azaphosphole complexes **7a** (73%) and **7b** (17%), but no phenyl-substituted 2*H*-1,2-azaphosphole derivatives (Scheme 3).[5]



Scheme 3

ACKNOWLEDGMENT

We grateful acknowledge F. Ruthe and Professor P. G. Jones for the X-ray crystal structure analyses and the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft for financial support.

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