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Generation and Reactions of Transient Nitrilium **Phosphane Ylide Complexes**

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Thermal decomposition of a 2H-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 regionelectivity 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 2H-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. ¹³¹ 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]

$$(OC)_{s}W$$

$$(OC)$$

 $R \approx Ph (3a)$, Me (3b), ¹Bu (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-2H-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]

$$(OC)_{3}W Ph(SiMe_{3})_{2} (OC)_{3}W Ph(SiMe_{3})_{2}$$

$$Ph(OCC)_{5}W Ph(OCC)_{5}W Ph(OCC)_{5}W$$

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 2H-1,2-aza-phosphole complexes 7a (73%) and 7b (17%), but no phenyl-substituted 2H-1,2-azaphosphole derivatives (Scheme 3).^[5]

$$(OC)_{S}W \longrightarrow CH(SiMe_3)_2 \qquad (OC)_{S}W \longrightarrow CH(SiMe$$

Scheme 3

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