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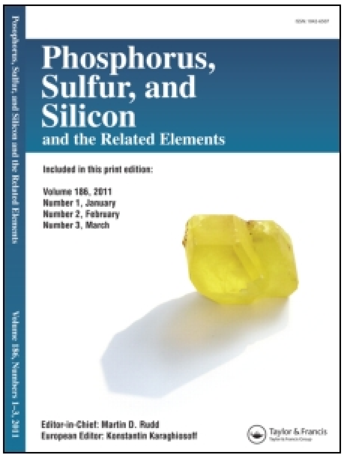

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To cite this Article Streubel, Rainer , Ostrowski, Annette , Wilkens, Hendrik , Priemer, Siegfried and Rohde, Udo(1997) 'Advances in 2*H*-Azaphosphirene Complex Chemistry', Phosphorus, Sulfur, and Silicon and the Related Elements, 124: 1, 93 — 102

To link to this Article: DOI: 10.1080/10426509708545614

URL: http://dx.doi.org/10.1080/10426509708545614

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Phosphorus, Sulfur, and Silicon, 1997, Vol. 124 & 125, pp. 93–102
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ADVANCES IN 2*H*-AZAPHOSPHIRENE COMPLEX CHEMISTRY

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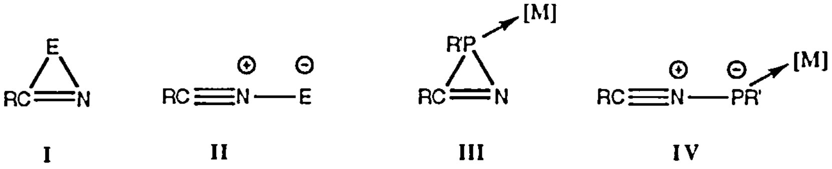
Abstract: Synthesis of a wide variety of 2*H*-azaphosphirene pentacarbonyl metal complexès is reported. The overall reaction of this heterocyclic synthesis was determined to be stereospecific, but no asymmetric induction has been observed. Generation, decomposition and trapping reactions of nitrilium phosphane ylide complexes, a zwitterionic acyclic isomer of 2*H*-azaphosphirene complexes possessing a novel 1,3-dipole system, are presented.

Keywords: phosphorus heterocycles, 2*H*-azaphosphirene complexes, carbene complexes, nitrilium phosphane ylide complexes, phosphanediyl complex.

Introduction

Three-membered heterocycles containing a ring system with a C=N-moiety and a further heteroatom (**I**) are of interest, because of their expected high reactivity. 1,3-dipoles (**II**), which are generated, by ring opening reactions of such heterocycles, are of great importance for the synthesis of five-membered heterocycles.[1] Apart from investigations on ring opening reactions of 2*H*-azirenes[2] and 1*H*-thiazirenes,[3] yielding nitrile ylides and nitrile sulphides, respectively, knowledge on the reaction behaviour of 1*H*-diazirenes[4] or 2*H*-azaphosphirenes is very limited (Scheme 1). Derivatives of the latter are still unknown.



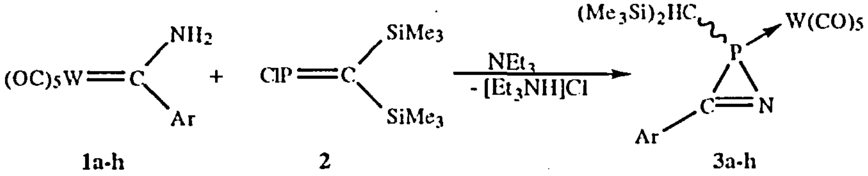
Scheme 1. Unsaturated heterocycles containing nitrogen and a second heteroatom and their 1,3-dipolar isomers (propargylic resonance structure); E = CR_2, S, NR, PR; R,R' = alkyl, aryl; [M] = metal complex fragment.

We have recently described, that coordinated 2*H*-azaphosphirenes (**III**) are easily accessible by rearrangement reactions of transiently formed metal carbene complexes.[5] Even more recently, we got the first evidence for the transient formation of a nitrilium phosphane ylide complex upon ring opening of a 2*H*-azaphosphirene complex.[6]

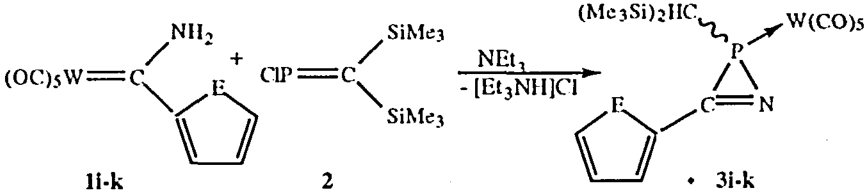
Results

Syntheses of 2*H*-azaphosphirene complexes

In order to exploit our synthetic route - reaction of [amino(aryl)carbene](pentacarbonyl]tungsten(0) complexes with [bis(trimethylsilyl)-methylene]chlorophosphane (**2**) under basic conditions[5] - we employed a wide variety of aryl- **1a-h** (Scheme 2) and heteroaryl-substituted aminocarbene tungsten complexes **1i-k** (Scheme 3).[7] The products **3a-k** were obtained after low-temperature chromatography in good yields.

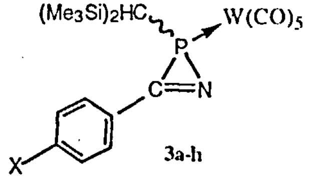


Scheme 2



Scheme 3. E = O, S, NMe.

Table 1 Selected NMR data of the 2*H*-azaphosphirene tungsten complexes **3a-h** and σ^{p}-Hammett constants.[8]

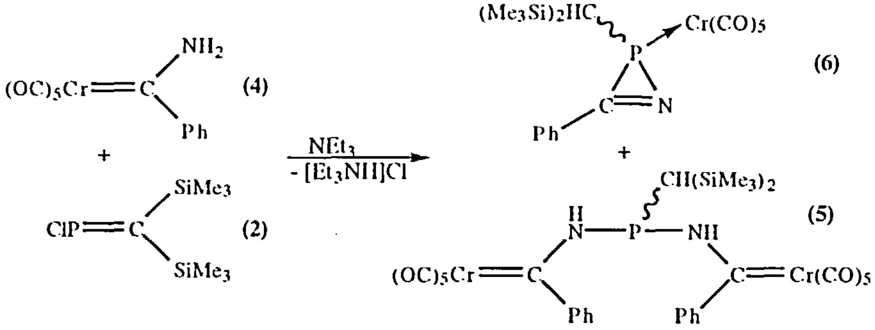
		d ^{31}P [ppm]	$^{1}J_{PW}$ [Hz]	d ^{13}C [ppm]	σ^{p}
X = CF_3	3a	- 102.0	297.5	193.1	0.54
Br	3b	- 105.2	296.8	192.2	0.23
Cl	3c	- 105.4	296.1	192.0	0.23
H	3d	- 108.8	294.7	192.3	0.00
F[*]	3e	- 109.1	295.6	190.8	0.06
Me	3f	- 111.2	293.1	191.4	-0.17
OMe	3g	- 115.1	292.5	190.2	-0.27
NMe_2	3h	- 117.6	291.5	187.8	-0.83

in $CDCl_3$, [*] in C_6D_6

The phosphorus and carbon NMR resonances as well as the P-W coupling constants clearly reflect the electronical influence of the *para* substituent. Moreover, the correlation of δ ^{31}P with the σ^{P}-Hammett constants[8] (*cf.* Table 1) is quite impressioning and may serve for an extrapolation of ^{31}P NMR chemical shift values of unknown 2*H*-azaphosphirene complexes.

The X-ray crystal structure analyses of the complexes **3d,f**[7] and **3k**[7] reveal coplanar arrangements of the two ring moieties, thus enabling effective p_π-p_π-electron interactions. The slight elongation of the C-N double bond of the three-membered ring in the molecular structure of **3k** most probably refers to this.

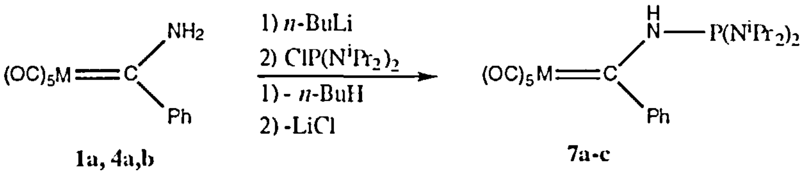
In a recent communication,[9] we reported the reaction of [amino(phenyl)carbene](pentacarbonyl)chromium(0) **4a** towards chloro(methylene)phosphane **2**, and mentioned, that the 2*H*-azaphosphirene complex **6** would slowly decompose, even at ambient temperature, yielding diphosphene complex derivatives. A reinvestigation has now shown, that lowering the reaction temperature led exclusively to chromium complex **6** and the bis(carbene)chromium complex **5**, the latter being a precursor for the former (Scheme 4).



Scheme 4

Low-temperature chromatography afforded complex **6**, which displays perfect stability in solution at ambient temperature.

We attempted to gain a novel access to 2*H*-azaphosphirene complexes by synthesis of [bis(diisopropyl)amino]phosphanyl-substituted aminocarbene complexes **7a-c** (Scheme 5)[10] and subsequent elimination/rearrangement reactions. But the latter have not been achieved, yet.



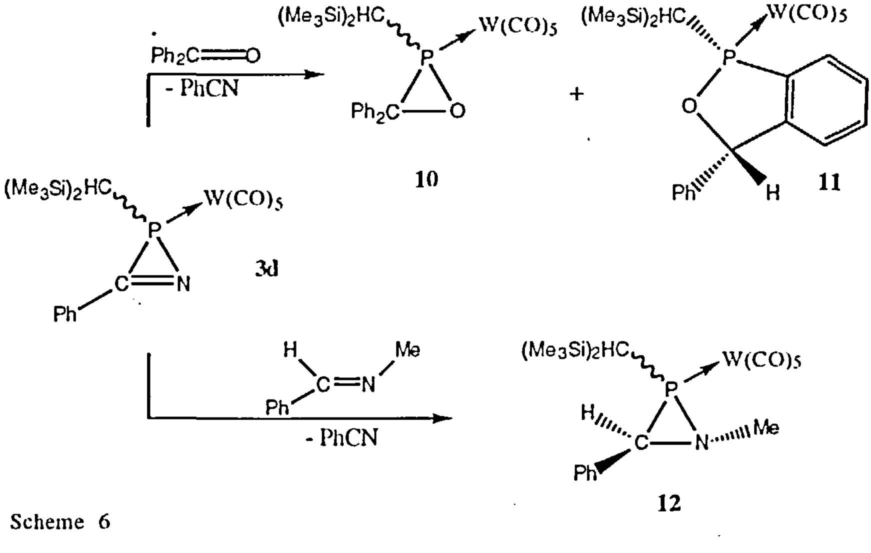
Scheme 5. **4a**,**7a**: M = Cr; **4b**,**7b**: M = Mo; **1a**,**7c**: M = W

Cis-triphenylphosphane[amino(phenyl)carbene](tetracarbonyl)tungsten(0) and *cis*-(-)-(*R*)-methyl(phenyl)propylphosphane[amino(phenyl)-carbene](tetracarbonyl)chromium (0) were reacted with the chloro(methylene)phosphane **2** in the presence of NEt_3 to yield stereospecifically the corresponding 2*H*-azaphosphirene complexes. Interestingly, the employment of the chiral phosphane-substituted metal carbene complex did not give rise to a significant enantiomeric excess.[7] Therefore we assume, that the transition state of this ring formation process has a butterfly type bicyclic structure and no bonding interaction between phosphorus and the metal center.

Investigations on generation and reactivity of nitrilium phosphane ylide complexes

If 2*H*-azaphosphirene tungsten complex **3d** was decomposed in toluene in the presence of benzophenone, we obtained benzonitrile, the oxaphosphirane complex **10** and the benz[*c*]-1,2-oxaphospholane complex **11**.[11] A Lewis acid/Lewis base interaction between benzophenone and the electrophilic terminal phosphanediyl complex **9** giving a phosphorus analogue of a carbonyl ylide, was proposed to be the first reaction step, after ring cleavage of **3d**.[11] 1,3 and 1,5 ring closure of the zwitterionic intermediates then afforded, after rearomatisation in the latter case, the final products **10** and **11**. Using *N*-methyl(benzylidene) amine as trapping reagent, the azaphosphiridine complex **12** was formed stereospecifically (Scheme 6).[11]

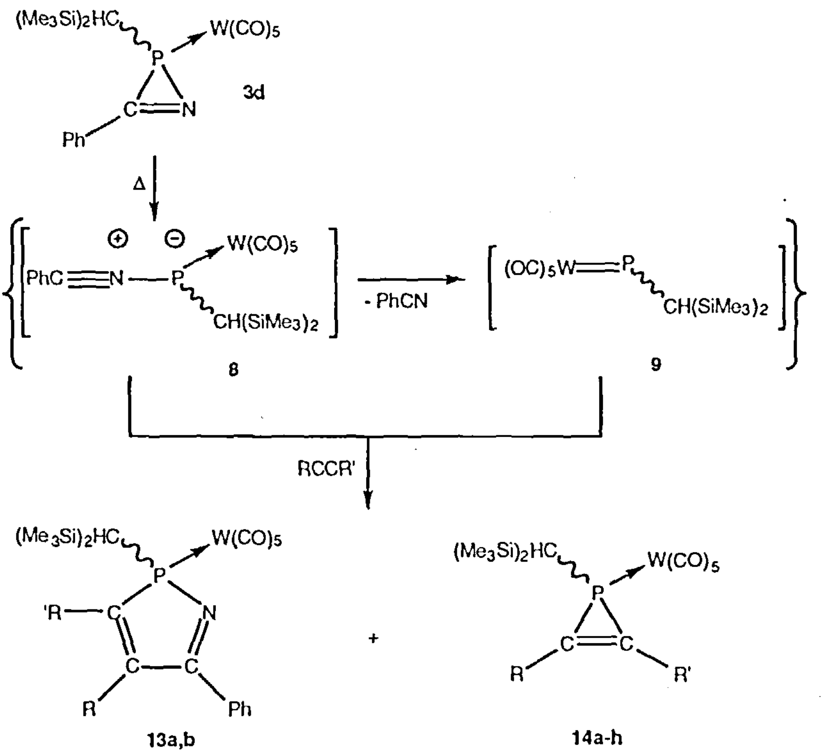
This latter observation underlines once more the singulett carbene type reactivity of the transiently formed terminal phosphanediyl complex **9** (*cf.* Scheme 7).



Scheme 6

In preliminary communications, we reported on the decomposition of **3d** in toluene in the presence of phenyl-[12] ethoxy-[13] or bis(methoxycarbonyl)-substituted[13] acetylene. We have now studied the thermally induced ring opening reaction of **3d** and the reactivity of the transiently formed species towards various acetylene derivatives. In all of these reactions the 1*H*-phosphirene complexes **14a**,[7] **b**,**c**,[13] **d**-**h**[14] were obtained as main and the 2*H*-1,2-azaphosphole complexes **13a**,[7] **b**[6] as by-products (Scheme 7). It has to be pointed out, that exclusively those acetylenes, which possesses one or two electron-withdrawing groups led to the formation of the five-membered heterocycles **13a**,[4]**b**. We propose the transient formation of the nitrilium phosphane ylide complex **8**, which may react either ina [3+2] cycloaddition reaction with the activated acetylene derivatives or decompose to yield benzonitrile

Scheme 7



13	a	b
R	H	CO_2Me
R'	CO_2Me	CO_2Me

14	a	b	c	d	e	f	g	h
R	H	CO_2Me	H	Ph	Ph	Ph	Ph	$SiMe_3$
R'	CO_2Me	CO_2Me	OEt	CO_2Et	Me	Ph	H	$SiMe_3$

and the terminal phosphanediyl complex **9**, which then gives the complexes **14a-h** by subsequent [2+1] cycloaddition reactions. It is remarkably, that exclusively one regioisomer of **13a** was obtained. According to the classification of Sustmann,[15] the process of these [3+2] cycloaddition reactions should be dipole-HOMO-dipolarophile-LUMO-controlled.

The molecular structure of complex **13b**[6] was elucidated by X-ray crystallography (Figure 1). The planar five-membered heterocyclic ring system is further characterized by approximately localized double bonds (C(13)-C(14) 134.3(6) and C(15)-N 129.1(6) pm) and a tetra coordinated phosphorus atom.

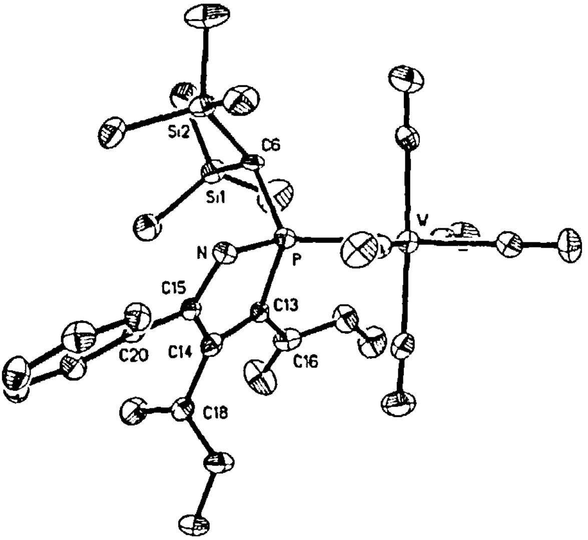
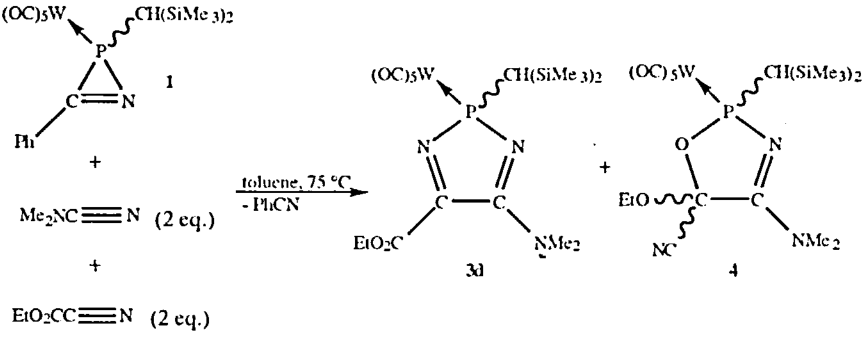


Figure 2. Molecular structure of **13a**.

Thermolysis of **3d** in the presence of dimethyl cyanamide and dimethylacetylenedicarboxylate (DMAD) yielded the corresponding 2*H*-1,3,2-diazaphosphole complex **13c** and the two diastereomeric $\Delta^{2,3}$-1,3,2-oxazaphospholene tungsten complex **16a,b**.[7] Formation of the complexes **13c** and **16a,b** can be explained by 1,3-dipolar cycloaddtion reactions of a transiently formed nitrilium phosphane ylide tungsten complex **15** with the C-C triple and the C-O double bond of the trapping reagent, thus revealing a surprising ambident reactivity of complex **15** towards the dipolarophile DMAD.



The molecular structure of complex **16a** was elucidated by X-ray crystallography (Figure 2). In comparison to **13a**, the five-membered heterocyclic ring system is characterized by slightly shortened P-N(1), P-C(6) and a P-W bonds, which might reflect the influence of the oxygen atom bonded to phosphorus.

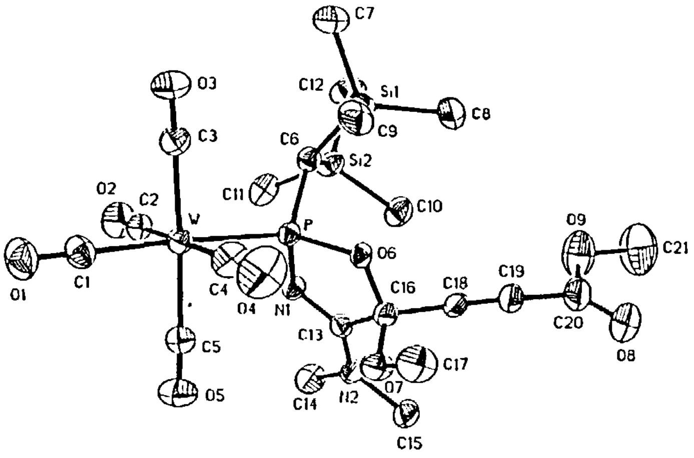


Figure 2. Molecular structure of **16a**.

Acknowledgment

Support of the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and Dipl.-Chemiker F. Ruthe and Professor Dr. P. G. Jones (X-ray structure analyses) is gratefully acknowledged.

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