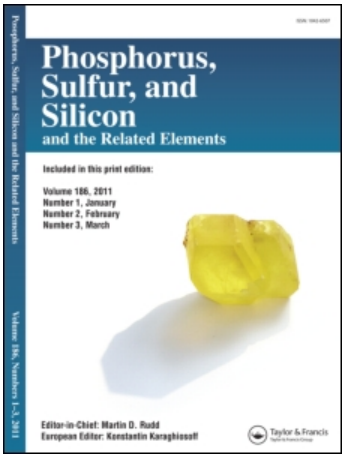

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SYNTHESIS OF 1*H*-DIPHOSPHIRENE, PHOSPHORUS-CARBON CAGE AND 2,3-DIHYDRO-1,2,3-TRIPHOSPHETE TUNGSTEN COMPLEXES

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Abstract: New 1*H*-diphosphirene and 2,3-dihydro-1,2,3-triphosphete tungsten complexes have been synthesized, by thermal decomposition of different 2*H*-azaphosphirene complexes in the presence of various phosphaalkynes. Novel phosphorus-carbon cage complexes were obtained, if a pentamethylcyclopentadienyl-substituted 2*H*-azaphosphirene complex and alkyl-substituted phosphaalkynes were employed.

Keywords: phosphorus heterocycles, 2*H*-azaphosphirene complexes, 1*H*-diphosphirene complexes, 2,3-dihydro-1,2,3-triphosphete complexes, phosphorus-carbon cage compounds.

INTRODUCTION

Although the first report of a 1*H*-diphosphirene was early as 1989,[1] knowledge about the reactivity of this heterocyclic system is still very limited. Recently, first reactions of a transiently formed electrophilic terminal phosphanediyl complex with phosphaalkynes yielding 1*H*-diphosphirene complexes were reported.[2,3] Quite interesting, exclusively a *C-tert.*-butyl-substituted 1*H*-diphosphirene complex displayed a subsequent ring opening, leading, after a multi-step reaction, to polycyclic heterocycles as final products. P-P bond cleavage followed by a dimerisation/rearrangement reaction, was given as an explanation.[2]

Interestingly, no evidence for a three-membered/four-membered ring enlargement had been obtained.

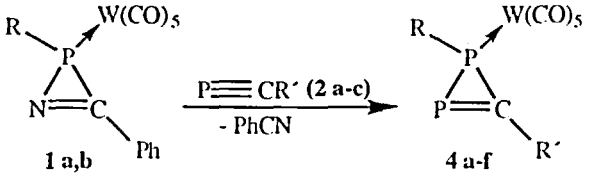
First synthesis of a 1,2-dihydro-1,2,3-triphosphete complex was achieved by thermal decomposition of a bis(trimethylsilyl)methyl-substituted 2*H*-azaphosphirene complex in the presence of *tert.*-butyl-phosphaalkyne.[4] Later on, a non-coordinated 1,2-dihydro-1,2,3-triphosphete was obtained by reaction of tetrakis(trifluoromethyl)cyclotetraphosphane or trimethyl(trifluoromethyl)-$\lambda^5\lambda^3$-diphosphene with phosphaalkynes.[5]

We now describe synthesis of new 1*H*-diphosphirene complexes, complexes of phosphorus-carbon cage compounds and of 1,2-dihydro-1,2,3-triphosphete complexes, which had been obtained by thermal decomposition of different alkyl-substituted 2*H*-azaphosphirene complexes (R = $CH(SiMe_3)_2$, C_5Me_5) and/or different phosphaalkynes (R'CP: R' = $N(SiMe_3)^iPr$, ^{t}Bu, adamantyl).

Results

Thermal decomposition of 2*H*-azaphosphirene complexes **1a**[7],**b**[8] in the presence of phosphaalkynes **2a**: R = $N(SiMe_3)^iPr$; **2b**: R = ^{t}Bu; **2c**: R = adamantyl), all of them are known by literature, yielded benzonitrile, 1*H*-diphosphirene complexes **4a**[4],**b**[8], novel phosphorus-carbon cage compounds **5a,b**[8] and 1,2-dihydro-1,2,3-triphosphete complexes **6a**[4],**b**[8] in good yields. Although the 1*H*-diphosphirene complexes **4c-f** could not be detected by ^{31}P NMR spectroscopy, their formation, which may proceed by [2+1] cycloaddition reaction of the transiently formed terminal phosphanediyl complexes [$(OC)_5W$=PR] (**3a**: R = $CH(SiMe_3)_2$, **3b**: R = C_5Me_5) with the phosphaalkynes **2a-c**, seems plausible (Scheme 1).

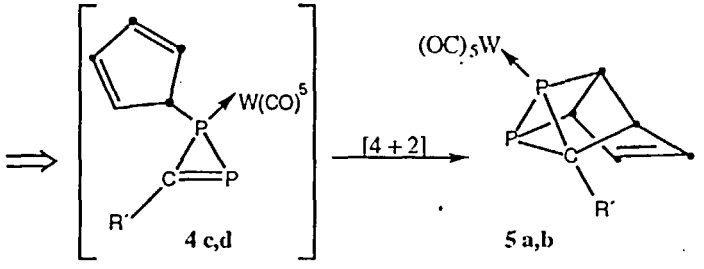
Very interesting was the observation, that the transiently formed 1*H*-diphosphirene complexes **4c-f** displayed different subsequent reactions.



SCHEME 1 Synthesis of 1*H*-diphosphirene complexes **4 a-f.**

R/R′	N(SiMe$_3$)^{i}Pr	^{t}Bu	adamantyl
PCR′	**2a**	**2b**	**2c**
CH(SiMe$_3$)$_2$	**4a**	**4e**	**4f**
C$_5$Me$_5$	**4b**	**4c**	**4d**

The formation of the phosphorus-carbon cage compounds **5a,b**[8] is explained, by an intramolecular [4+2] cycloaddition reaction of the pentamethylcyclopentadienyl-substituent with the P-C double bond of the transiently formed 1*H*-diphosphirene complexes **4c,d** (Scheme 2). Under these conditions, no formation of 1,2-dihydro-1,2,3-triphosphete complexes has been observed.



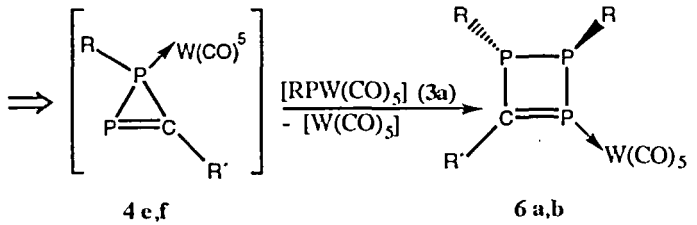
• = CMe, **4c**,**5a**: R′ = ^{t}Bu; **4d**,**5b**: R′ = adamantyl

SCHEME 2 Intramolecular [4+2] cycloaddition reaction of 1*H*-diphosphirenes **4c,d.**

The $^{31}P\{^1H\}$ NMR spectra of **4a,b** and **5a,b**, each having a spin system of the AB-type, display resonances at high field. This is known to be typical for phosphorus in a three-membered ring system. The magnitudes of the P-P coupling constants of **5a,b** are smaller compared to those of **4a,b**, a finding, which is quite astonishingly.

In the case of **4e,f** (R = CH(SiMe$_3$)$_2$) insertion of phosphanediyl complex **3a** into a P-C or P-P ring bond of the 1*H*-diphosphirene

complexes **4e,f** and subsequent loss of one pentacarbonyltungsten moiety lead formally to the 1,2-dihydro-1,2,3-triphosphete complexes **6a,b** (Scheme 3).



4 e,f **6 a,b**

4e, 6a: R′ = ^{t}Bu; R = CH(SiMe$_3$)$_2$ 4f, 6b: R′ = adamantyl; R = CH(SiMe$_3$)$_2$
3a: R = CH(SiMe$_3$)$_2$

SCHEME 3 Insertion of terminal phosphanediyl complex **3a** into a ring bond of **4e,f.**

The ^{31}P{^{1}H} NMR spectra of **6a,b** display each three distinct resonances and coupling constants, indicating four-membered ring systems with three types of phosphorus nuclei. Exclusively the P1 nuclei of **6a** and **6b** exhibit ^{183}W satellites, thus giving further support for the structural proposal of **6a,b** as mono-pentacarbonyl tungsten complexes.

Acknowledgment

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References

[1] E. Niecke, R Streubel, M. Nieger, D. Stalke, *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 1673.
[2] F. Mercier, L. Ricard, F. Mathey, M. Regitz, *J. Chem. Soc., Chem. Commun.* **1991**, 1305.
[3] R. Streubel, N. H. T. Huy, L. Ricard, F. Mathey, *Phosphorus, Sulfur, Relat. Elem.* **1993**, *77*, 229.
[4] R. Streubel, L. Ernst, J. Jeske, P. G. Jones, *J. Chem. Soc., Chem. Commun.* **1995**, 2113.
[5] H. Pucknat, J. Grobe, D. L. Van, B. Broschk, M. Hegemann, B. Krebs, M. Läge, *Chem. Eur. J.* **1996**, *2*, 208.
[7] R. Streubel, J. Jeske, P. Jones, R. Herbst-Irmer, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 80.
[8] R. Streubel, U. Rohde, unpublished results.