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# UNUSUAL OXYGEN SHIFT DURING DIMERIZATION OF $\lambda^5\sigma^3$-PHOSPHAALKYNES [1]

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Summary: The phosphaalkynes 7 - generated by reaction of chlorophosphines 3 with the silver diazo compounds 4 - undergo spontaneous dimerization accompanied by a P → P O-shift to yield the $\lambda^5$-diphosphetes 9. Their structural assignment is based on an X-ray crystal structure analysis of 9a as well as on ring cleavage by water (9 → 10).

In contrast to $\lambda^3\sigma^1$-phosphaalkynes 1 [2,3], quinquevalent phosphaalkynes having coordination number 3 2 appear to be rather little known.

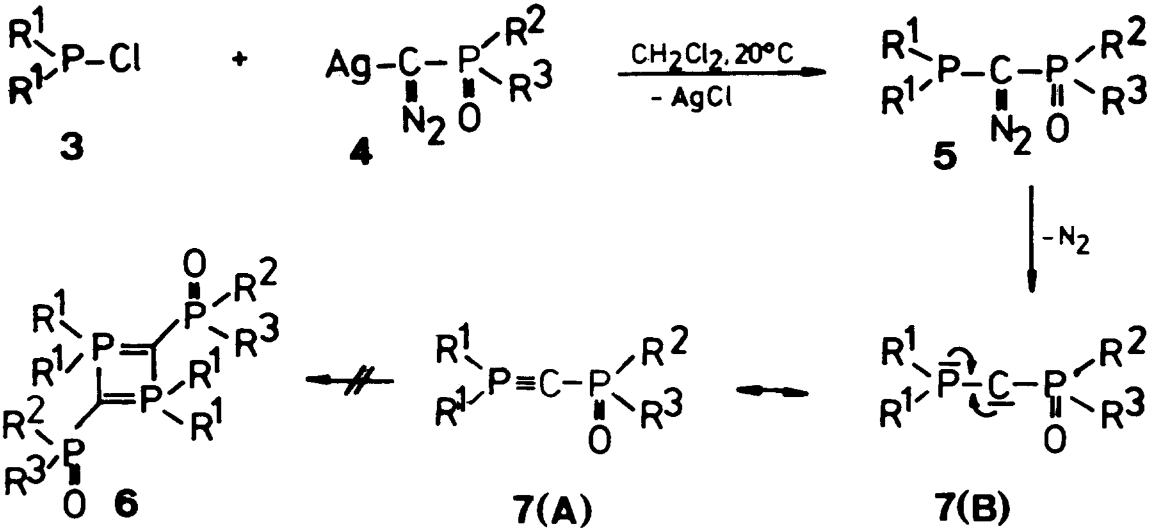
**$P\equiv C-$** **($\lambda^3\sigma^1$-Phosphorus)** **$>P\equiv C-$** **($\lambda^5\sigma^3$-Phosphorus)**

**1** **2**

Intermediates of type 2 may be responsible for the formation of the hitherto known $\lambda^5$-diphosphetes 11 [4] and 12 [5], starting from a chlorinated methylene phosphorane (thermally) or a difluorophosphorane (BuLi), respectively. Further evidence comes from the photolysis of a silylated phosphino diazomethane in which the intermediacy of a $\lambda^5\sigma^3$-phosphaalkyne could be proved by a trapping reaction with chloro trimethylsilane [6]. In this context we describe a simple access for phosphorylated $\lambda^5\sigma^3$-phosphaalkynes and report on their unusual dimerization.

When equimolar amounts of chlorophosphines 3a,b and silver diazo compounds 4a,b are reacted in dichloromethane at 20 °C and the reaction mixture is concentrated, high-melting crystals of the $\lambda^5$-1,3-diphosphetes 9a-c are isolated [m.p. 9a: 275 °C (decomp.) yellow; 9b: 268 °C (decomp.), colorless; 9c: 240 °C (decomp.), colorless].

In the first step of the one pot reaction, the phosphino diazo compounds 5 are formed [5b: $\nu(CN_2) = 2060\ cm^{-1}$] which decompose spontaneously with $N_2$-elimination yielding thus the phosphaalkynes 7 (A⟷B). Instead of [2+2] cycloaddition leading to $\lambda^5$-1,3-diphosphetes 6 or of carbene dimerization to give olefins, compounds 7 (A⟷B) form dimers 9 in which ring and exocyclic phosphorus atoms have apparently interchanged their substituents.



| 3 | $R^1$ |
|---|---|
| a | $N^iPr_2$ |
| b | Ph |

| 4 | $R^2$ | $R^3$ |
|---|---|---|
| a | Ph | Ph |
| b | Ph | OMe |

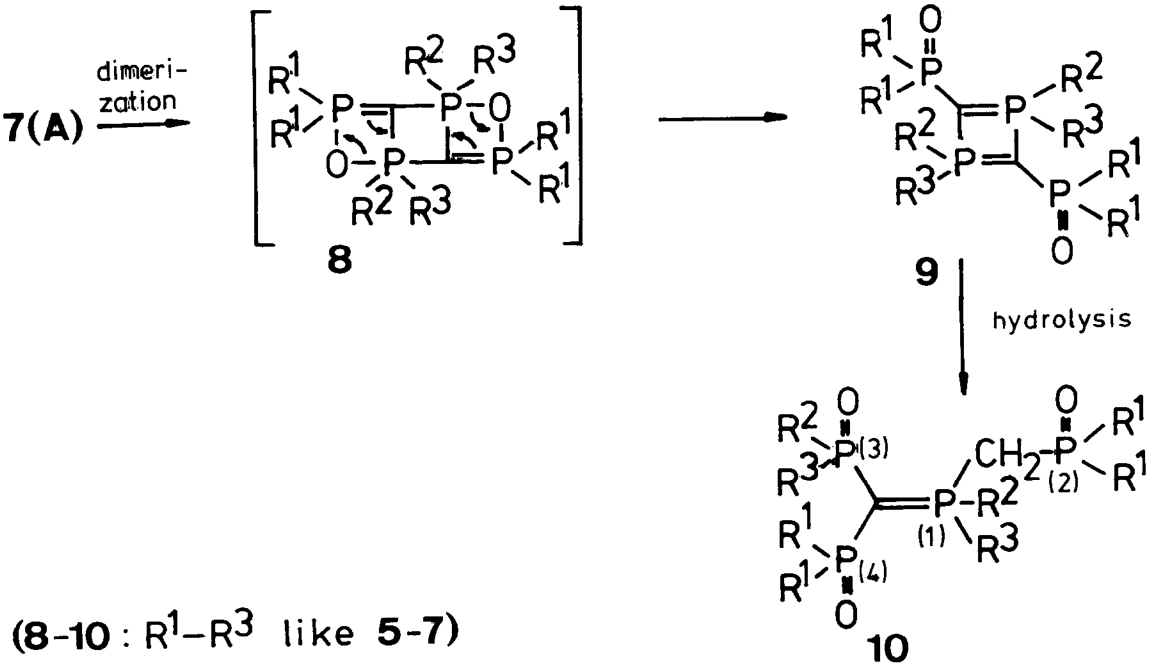
| 5-7 | $R^1$ | $R^2$ | $R^3$ |
|---|---|---|---|
| a | $N^iPr_2$ | Ph | Ph |
| b | Ph | Ph | Ph |
| c | $N^iPr_2$ | Ph | OMe |

A rationalization of this result is based on a cycloaddition process in which the P≡C bonds and PO-groups of two molecules 7(A) are involved. The formation of the heterotricyclic intermediates 8 is followed by ring opening giving rise to the final products 9. In the case of 7b ($R^1 = R^2 = R^3 = Ph$) identical $\lambda^5$-1,3-diphosphetes arise from both the 7 → 6 and the 7 → 8 → 9 route, rendering the two mechanistic pathways indiscernible.

From the mass spectra of compounds 9a-c it follows that they are dimers of 7a-c ($M^+$, 3-11%); furthermore the P → P oxygen shift in the case of 9a and c is indicated by the fragments $M^+-({}^iPr_2N)_2PO$ (28 and 78%, resp.). In the $^{31}$P-NMR-spectra ($CDCl_3$, 85% $H_3PO_4$), ring and exocyclic phosphorus atoms resonate within a very narrow range [9a: $\delta = 21.2$ and 20.8, 9b: $\delta = 31.6$ and 19.3, 9c: $\delta = 39.8$ and 24.3 ($^2J_{P,P} = 6.6$ Hz)], so that attempts of assignment remain doubtful.

The methylene phosphorane character of 9 is demonstrated by hydrolysis: If 9b and c are stored in methylene chloride without the explicit exclusion of moisture, hydrolytic ring cleavage occurs yielding 10b and c, resp. An analogous process is well established for open-chain acceptor-substituted phosphorus ylides [7]. Under these conditions, the diphosphete 9a is not attacked by water. The constitution of the hydrolysis products is based above all on the results of NMR and mass spectrometric investigations as is shown exemplarily for 10b

[$^1$H NMR(CDCl$_3$): δ = 4.04 (dd, $^2J_{P,H}$ = 12.85 and 12.93, 2H, CH$_2$); $^{31}$P NMR(CDCl$_3$, 85% H$_3$PO$_4$): δ = 28.5 (d, $^2J_{P-1/P-3,4}$ = 19.7 Hz, 2P, P-3 and P-4), 23.3 (d, $^2J_{P-1/P-2}$ = 15.1 Hz, 1P, P-2), 17.4-18.1 (m, 1H, P-1); MS: m/e = 815, 2% (M$^+$), 415, 19% (M$^+$-Ph$_2$PCH$_2$POPh$_2$), 400, 17% (Ph$_2$PCH$_2$POPh$_2$)].



**(8-10 : R$^1$–R$^3$ like 5-7)**

The structural assignment of the 1,3-diphosphetes was ascertained beyond doubt by an X-ray crystal structure analysis of 9a (Fig.1) [8]. In the crystalline state, 9a is centrosymmetric, i.e. the four-membered heterocycle is planar. P(1) is displaced from this plane by -0.085 Å. The exocyclic and endocyclic C-P bond lengths are equal within their standard deviations (Fig.2). Bond length equalization in the four-membered ring has also been observed in the other two known diphosphetes 11 [4,9] and 12 [5], and an explanation has been proposed by Fluck [5]. Comparison with the data for 11 and 12 suggests that the virtual identity of the exocyclic and endocyclic P-C distances in 9a is mainly due to contribution from a dipolar resonance structure, $Ph_2\overset{+}{P}-C{=}P(O^-)(N^iPr_2)_2$ [10].

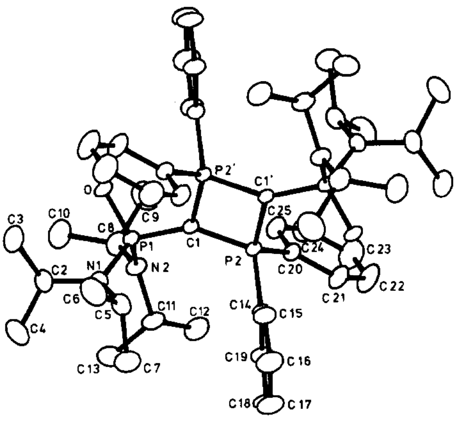
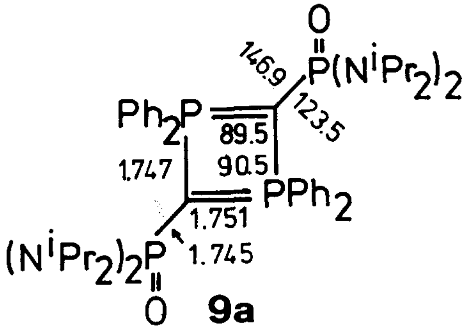
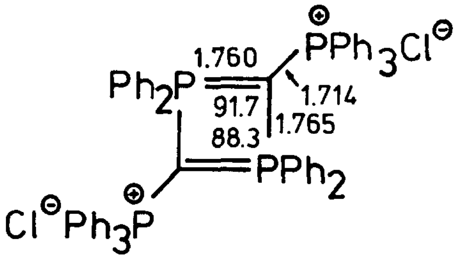


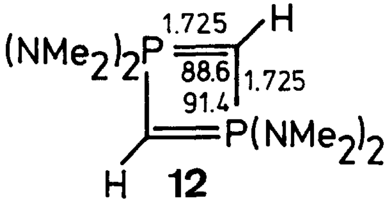
Figure 1. ORTEP plot of 9a. The size of the vibrational ellipsoids represents a 33% probability



**9a**



**11**



**12**

Figure 2. Comparison of bond lengths (Å) and angles (°) in 9a, 11 and 12. 9a: Esd's are 0.002-0.003 Å and 0.1-0.2°; P-C(phenyl) 1.817(3), 1.813(3); P-N 1.687(3), 1.672(3) Å.

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References:

[1] Unusually coordinated phosphorus compounds, Part 10; Part 9: J. Fink, W. Rösch, U.-J. Vogelbacher and M. Regitz, Angew. Chem. 97 (1986), in press.

[2] Review: R. Appel, F. Knoll and I. Ruppert, Angew. Chem. 93, 771 (1981); Angew. Chem., Int. Ed. Engl. 20, 731 (1981).

[3] Selected Papers: G. Becker, G. Gresser and W. Uhl, Z. Naturforsch. 36b, 16 (1981); W. Rösch, U.-J. Vogelbacher, T. Allspach and M. Regitz, J. Organomet. Chem. (1986), in press.

[4] R. Appel, F. Knoll and H. D. Wihler, Angew. Chem. 89, 415 (1977); Angew. Chem., Int. Ed. Engl. 16, 402 (1977).

[5] J. Svava, E. Fluck and H. Riffel, Z. Naturforsch. 40b, 1258 (1985).

[6] A. Baceiredo, G. Bertrand and G. Sicard, J. Am. Chem. Soc. 107, 4781 (1985).

[7] H.-J. Bestmann, Angew. Chem. 77, 609 (1965); Angew. Chem., Int. Ed. Engl. 4, 583 (1965).

[8] Crystal data of 9a: $C_{50}H_{76}N_4O_2P_4$; monoclinic space group $P2_1/n$; a = 13.019(7), b = 15.004(8), c = 13.177(6)Å, β = 101.99(8)°; Z = 2; $D_{calc}$ = 1.174 g cm$^{-3}$. Data collection: Enraf-Nonius CAD 4, Cu-$K_\alpha$ (monochromated), θ/2θ scan, scan range 0.95 + 0.14 tan θ, scan speed 2-5 ° min$^{-1}$; 4789 independent reflections (2.0 ≤ θ ≤ 65.0 °). Structure solution by MULTAN 82, structure refinement by full-matrix least-squares (3912 reflections having I > 3σ(I), unit weight, all hydrogen atoms located in a ΔF map and refined isotropically, R = 0.0475, $R_w = (\Sigma\Delta^2F/\Sigma F_o^2)^{1/2}$ = 0.0519).
Tables of atomic parameters, bond geometry and structure factors are available on request from the Director of the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW, England. Any request should be accompanied by the full literature citation for this communication.

[9] J. Weiss and B. Nuber, Z. anorg. allg. Chem. 413, 101 (1981).

[10] Comparison with the C-P bond distances in 12 suggests that a radialene-type resonance structure $(Ph_2\underset{|}{\overset{+}{P}}-\underset{|}{C}=PPh_3)$ contributes more to the bond state of 11 than the structure shown in Fig.2.

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