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SYNTHESIS OF DIPHOSPHIRENES BY [2+1]-CYCLOADDITION OF IMINO-PHOSPHANES TO A PHOSPHAALKYNE AND ISOMERIZATION TO AZADIPHOSPHETINES

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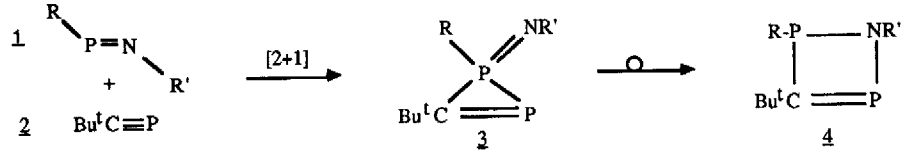
Summary: The reaction of iminophosphanes, RP=NR' 1 with P=CBu^t 2 affords diphosphirenes R(R'N=)P-P=CBu^t 3, and by isomerization the azadiphosphetines RP-N(R)-P=CBu^t 4.

The (2+1)-cycloaddition of phosphaalkynes with carbenes[1] or the heaviour carbene-analogues[2,3] is an elegant route to the three-membered ring systems containing the phosphaalkene-moiety (-P=CR-).
As we have demonstrated on the basis of spectroscopic and experimental results iminophosphanes containing the C-P=N - skeleton are exceptional candidates for carbenic reaction behaviour[4]. Here we report the synthesis of a novel three-membered ring system the diphosphirene 3 and its isomerization to the 1,2,4-azadiphosphetine-2 4.



R' = Mes*; R = Et_3C (a), Bu^t (b); R' = Bu^t, R = Et_3C (c)

Treatment of the P≡CBu^t[5] (5 mmol) 2 with one equivalent of the iminophosphanes (1a[4b,6], b[7]), at -30°C in n-hexane (10 ml) produces a cleanly deep red solution of the [2+1]-cyclodimers 3a,b, which can be separated as a deep red solid by evaporation of the solvent. The compositions of the thermal unstable air- and moisture sensitive diphosphirenes 3a,b have been confirmed by elemental analysis and mass spectrum. The mass spectrum shows the molecular ion peaks with low intensity (70 eV, m^+ m/z 489 3a, 448 3b (1%)). The loss of R and PCBu^t from this ion appears to be a strongly favoured process which gives the base peak ($PNMes^{*+}$ m/z 290). The constitution of 3a,b has been proven by means of their $^{31}P\{^1H\}$ n.m.r. spectra. Indicative for the two-fold coordinated phosphorus atom is the low field shift (δ 351.0 ppm 3a, 349.5 3b) while the coupling constants

of 182 Hz 3a, 180 Hz 3b are in good agreement with a one bond PP-interaction ($^1J_{PP}$ 140 - 230 Hz in azadiphosphiridines [4b]). While 3a[8] remained unchanged in solution at 25°C, 3b changed within hours (within few minutes at 50°C) under clear up in colour and formation of a new product 4b[8], which possesses the same molecular ion peak in the mass spectrum as 3b but a quite different fragmentation pattern (70eV, m/z 448 (m^+ 0.1%), 246 (Mes^{*+} 5%), 202 (m^+ - Mes* 18%), 57 (Bu^{t+} 100%). Furthermore in the $^{31}P\{^1H\}$-n.m.r. spectrum the highly shielded phosphorus nucleus in 3b (δ - 41.5 (-43.2 3a)) is shifted drastically to lower fields (δ 160.8), while the signal of the two coordinated phosphorus atom remains unchanged (δ 330.1). This together with the decrease in J_{PP} (68.5 Hz) is consistent with the formation of a 1,2,4-azadiphosphetine-2 the thermodynamically favoured product of the cycloaddition reaction.
The same ring system 4c[8] has been formed by reaction of 2 with the sterically less hindered iminophosphane 1c, without observation of the inter- mediate 3c. Isomerization of kinetically formed [n+1]- cycloadducts of iminophosphanes to the thermodynamically favoured ones has been observed recently in the case of a $1,2\lambda^3,3\lambda^5$-azadiphosphiridine[9] (the [2+1]-self-addition product of "carbenic" iminophosphane). Four-mem bered ring systems containing the -P=C< moiety are known so far as phosphacyclobutenes[10] and 1,3-diphosphacyclobutenes[11].

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[8] 3a: deep red crystals; m.p.102°C(dec.).4b: light yellow crystals; m.p. 190-192°C. 4c:orange oil; b.p. 68°C, 0.01 Torr, MS, m/z 301 (m^+ 2%), 147 (Bu^tCPNP^+ 100%). ^{31}P-NMR(C_6D_6):δ 126.0, 342.2 ($^2J_{PP}$ 57 Hz); ^{13}C-NMR(C_6D_6): δ 218.0 (d,d 31.2, 33.5 Hz) >P-C=P-.
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