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A NEW ROUTE TO λ^5-PHOSPHOLENES AND λ^5-PHOSPHIRENES via [n+1] CYCLOADDITION REACTIONS OF AN IMINOPHOSPHANE

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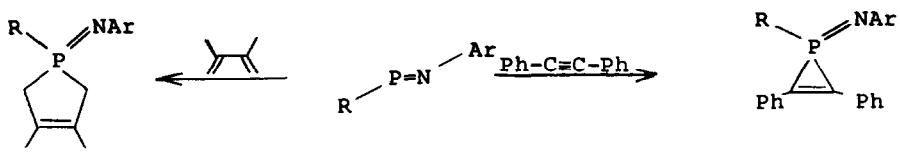
Summary: The title compounds have been synthesized by [n+1] cycloaddition reactions of an iminophosphane with 2,3-dimethylbutadiene or tolane, respectively.

According to quantum chemical calculations parent iminophosphane should show a carbenic reaction behavior[1] due to a sequence of frontier orbitals σ/π^*. In accordance with these predictions is the [2+1] selfaddition reaction of unstable iminophosphane[2] as well as the [2+1] cycloaddition reaction of silylated aminoiminophosphanes towards electrophilic carbonyl compounds[3]. Here we report on [n+1] cycloreactions of the stable iminophosphane Bu^t-P=N-Ar 1[4] with carbon-carbon multiple bond systems. Treatment of 1.0 g (2.9 mmol) 1 with an equimolar quantity of 2,3-dimethylbutadiene (tolane) in 4 ml n-hexane for 2 days (20 days) at room temperature formed during a change of colour a pale yellow solution of 2 (colourless solution of 3). After evaporation of the solvent the remaining solid residue is taken up with 3 ml n-hexane and recrystallized at -30°C. The resulting pale brown crystals 2 (mp. 108°C, yield 52%), colourless crystals 3 (mp. 126°C, yield 69%) were identified as the λ^5-phospholene 2 and λ^5-phosphirene 3 according to analytical and spectroscopic data[5].



2 1 3

Ar = 2,4,6-Tri-$Bu^tC_6H_2$; R = Bu^t

The formation of [n+1] cycloadducts is proved by $^{13}C\{^1H\}$-n.m.r. spectra which show one set of resonance signals for the single bonded 2 and doubly bonded carbon atoms 2, 3 only. The small value for $^1J_{PC}$ in 3 (14.8 Hz) reflects a stronger p-character of the P-C bond in comparison to 2 (56.4 Hz). This is in

accord with the high field ^{31}P-chemical shift for 3 (-68.7 ppm) which falls in a region typical for three-membered λ^5-phosphor-carbon ring systems[6]. In contrast to well known λ^5-phospholenes and λ^5-phosphirenes containing the phosphorus fragment X=P< (X = chalcogen) which were accessible via solvolysis of MacCormack[7] products or oxidation of λ^3-phosphirenes[8], this route allows a direct approach to iminosubstituted derivatives.

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5 Mass spectrum: (EI, 70eV): 2 m/e 429 (M,5%), 414 (M-CH_3, 1%), 372 (M-C_4H_9, 45%), 358 (M-CH_3,-C_4H_8, 5%), 316 (M-C_4H_9,-C_4H_8, 10%), 57 (C_4H_9, 100%), 3 m/e 525 (M, 4%), 510 (M-CH_3, 1%), 468 (M-C_4H_9, 1%), 347 (M-$(C_6H_5)_2C_2$, 4%), 290 (M-$(C_6H_5)_2C_2$,-C_4H_9, 39%), 178 ($(C_6H_5)_2C_2$, 60%), 57 (C_4H_9, 100%). - NMR spectra: δ<0 for downfield shifts in all cases, references H_3PO_4 or Me_4Si. - $^{13}C\{^1H\}$-NMR ($CDCl_3$): 2 δ= 16.1 (d, 10.8 Hz, =CCH$_3$); 26.1 (s, PCC$_3$); 31.9 (s, p-CC$_3$); 32.8 (s, o-CC$_3$); 34.5 (d, 51.6 Hz, PCH$_2$); 34.4 (s, p-CC$_3$); 36.8 (s, o-CC$_3$); 41.5 (d, 6.6 Hz, PCC$_3$); 121.2 (d, 4.1 Hz, C_3-Ar); 128.3 (d, 8.2 Hz, >C=); 137.6 (d, 4.2 Hz, C_4-Ar); 141.6 (d, 7.9 Hz, C_2-Ar); 146.7 (d, 4.8 Hz, C_1-Ar). - 3 δ= 28.8 (s, PCC$_3$); 31.8 (d, 1.5 Hz, p-CC$_3$); 32.2 (d, 1.8 Hz, o-CC$_3$); 34.4 (d, 2.0 Hz, p-CC$_3$); 36.6 (d, 2.3 Hz, o-CC$_3$); 38.0 (d, 22.1 Hz, PCC$_3$); 121.3 (d, 5.2 Hz, C_3-Ar); 128.5 (s, C_3-Ph); 129.0 (d, 4.3 Hz, C_2-Ph); 129.3 (s, C_4-Ph); 131.2 (d, 2.4 Hz, C_1-Ph); 138.9 (d, 6.0 Hz, C_4-Ar); 143.4 (d, 10.5 Hz, C_2-Ar); 144.1 (d, 14.7 Hz, C_1-Ar); 156.2 (d, 14.8 Hz, >C=). - ^{31}P-NMR ($CDCl_3$): 2 δ= 28.0; 3 δ= -68.7.
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