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UNEXPECTED SYNTHESIS OF A 1,2 λ^3AZAPHOSPHIRIDINE

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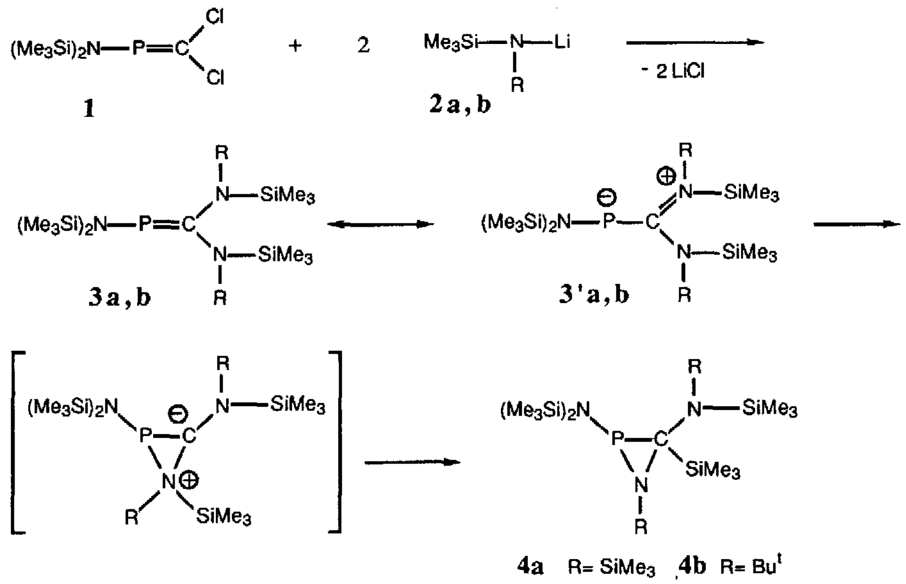
Abstract: 1,2 λ^3azaphosphiridines ***4a,b*** *are obtained by reacting a dihalogenated phospha-alkene $(Me_3Si)_2N\text{-}P{=}CCl_2$ with two equivalents of lithium silylated amides.*

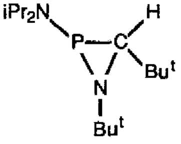
C substitution of dihalogenated phospha-alkenes $Ar\text{-}P{=}CX_2$ (X = Cl, Br ; Ar = 2,4,6-$Bu^t{}_3C_6H_2$) easily occurs after metallation with n-BuLi and treatment with a variety of reagents such as Me_3SiCl, Me_3SnCl, MeI or MeOH$^{1)}$. In contrast, metallation of Ar-P=CHCl affords the phospha-alkyne P≡C-Ar$^{2)}$.

We report here a new type of reaction involving the phospha-alkene **1** and lithium amides **2a,b**.



Addition of two equivalents of lithium bis-trimethylsilyl amide **2a** to the dihalogenated phospha-alkene **1** in THF at -70°C leads to the non isolated phospha-alkene **3a**, characterized by its ^{31}P chemical shift ($\delta\,^{31}P$ = +95 ppm) [3]. Surprisingly, **3** is not stable and is slowly converted into the 1,2 λ^3 azaphosphiridine **4a**, which is obtained as two isomers ($\delta\,^{31}P$ = -49.5 and -47.4 ppm). One of these isomers was isolated as an oil by extraction with hexane and fully characterized. **4a**: ^{31}P NMR ($CDCl_3$) δ: -49.5 ppm; ^1H NMR ($CDCl_3$) δ: 0.042 (d. J_{HP} = 6.3 Hz), 0.165 (s), 0.273 (s), 0.347 (s) ($SiMe_3$); ^{13}C NMR ($CDCl_3$) δ: 2.5 (m,($\underline{C}H_3)_3Si$) 49.08 (d. J_{CP}= 14.8 Hz $\underline{C}$-P). Mass spectrum: m/e : 254(M^+)

Up to now, only the 1,2 λ^3 azaphosphiridine **5** had been reported in the literature[4].



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It had been prepared by a valence isomerisation of an imino (methylene)phosphorane.The presence of bis(trimethylsilylamino) groups both on phosphorus and carbon atoms[5] might explain that **3a** can be better represented in its resonance form **3'a** which undergoes ring closure and 1,2-trimethylsilyl migration, giving rise to **4a**. Similarly, addition of lithium tert-butyl trimethylsilyl amide **2b** to **1** affords the 1,2 λ^3 azaphosphiridine **4b** (2 isomers $\delta\,^{31}P$ = -34.5 and -39.3 ppm).

It should be possible to extend the present new synthesis to other azaphosphiridines, provided the amides used bear an easily migrating group (TMS for instance).

References and notes :

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3. cf.: $\delta^{31}P$ $(Me_3Si)_2N$-P=C$(NMe_2)_2$: +98 ppm[6].
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