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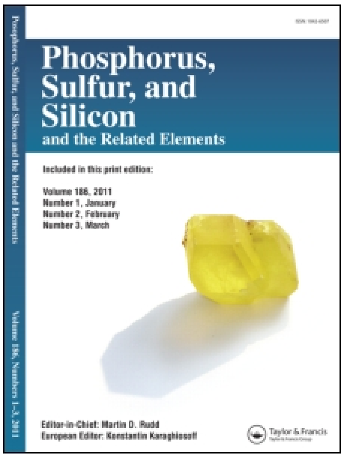

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Phosphanylcarbenes: From Unstable Intermediates to X-Ray Characterized Compounds

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PHOSPHANYLCARBENES: FROM UNSTABLE INTERMEDIATES TO X-RAY CHARACTERIZED COMPOUNDS

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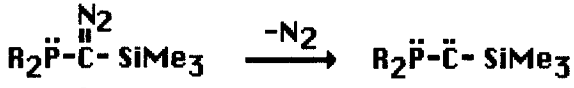
Abstract The synthesis of original (phosphanyl)diazo derivatives possessing either stannyl or phosphonio groups at the diazo carbon is described. The reactivity of transient (phosphanyl)(stannyl)carbenes as well as preliminary X-ray data concerning a (phosphanyl)(phosphonio)carbene are presented.

INTRODUCTION

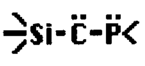
During the last decades, two of the most fascinating areas in chemistry have been the synthesis and reactivity of electron-deficient species and of p_π-p_π multiply bonded heavier main-group-element derivatives. In 1985, we reported that the photolysis of the α-diazophosphane **1a** led to the corresponding transient phosphanylcarbene **2a**.[1] Later on, we discovered that in fact phosphanylcarbene **2a** was stable, provided that it is prepared by flash thermolysis of **1a**.[2]



$$\underset{\textbf{1a}}{R_2\ddot{P}\text{-}\overset{\overset{N_2}{\|}}{C}\text{-}SiMe_3} \xrightarrow{-N_2} \underset{\textbf{2a}}{R_2\ddot{P}\text{-}\ddot{C}\text{-}SiMe_3}$$

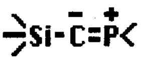
R: iPr_2N

The isolation of this (phosphanyl)(silyl)carbene **2a** has prompted considerable discussion of the best description of its ground state.[3]



A

B



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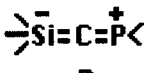

D

The absence of a crystal structure analysis[4] precludes a definitive answer. Calculations[5] led to the conclusion that phosphanylcarbenes were best formulated as multiply bonded λ^5-phosphaacetylenes, although these compounds featured both carbene and λ^5-phosphaacetylene reactivity.[2,6] Here we report our efforts to synthesize a crystalline phosphanylcarbene as well as the preliminary X-ray data concerning one of them.

RESULTS AND DISCUSSION

As precursors we chose diazo derivatives since they allow the generation of carbenes under several different experimental conditions. In a previous paper we have shown that the thermal stability of (phosphanyl)(silyl)diazomethanes and of (phosphanyl)(silyl)car- benes was strongly dependent on the nature of the phosphorus substituents, the diisopropylamino group being the best compromise.[6] Thus we decided to prepare bis(diisopropylamino)phosphanyldiazomethanes **1** with various substituents at the carbon center. Our first approach to get crystalline material was to increase the size of the silyl group. Unfortunately, the reaction of the lithium salt of the bis(diisopropylamino)phosphanyldiazomethane **3** with triphenyl or triisopropylchlorosilane did not lead to the desired substituted diazo derivative **1b** or **1c**, but to the isomeric nitrilimines **4b** and **4c**, respectively.[7] Although several examples of the rearrangement of nitrilimines into diazo derivatives have been reported,[8] we have not been able to obtain **1b** and **1c**.

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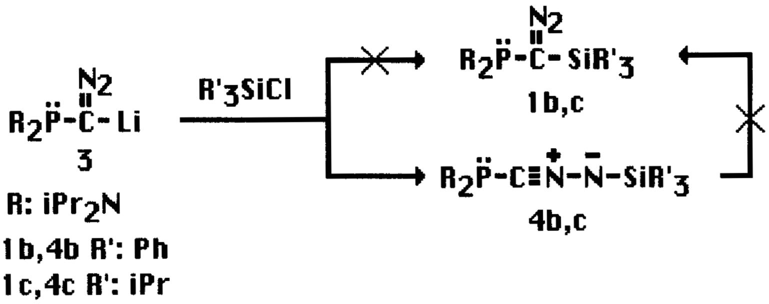
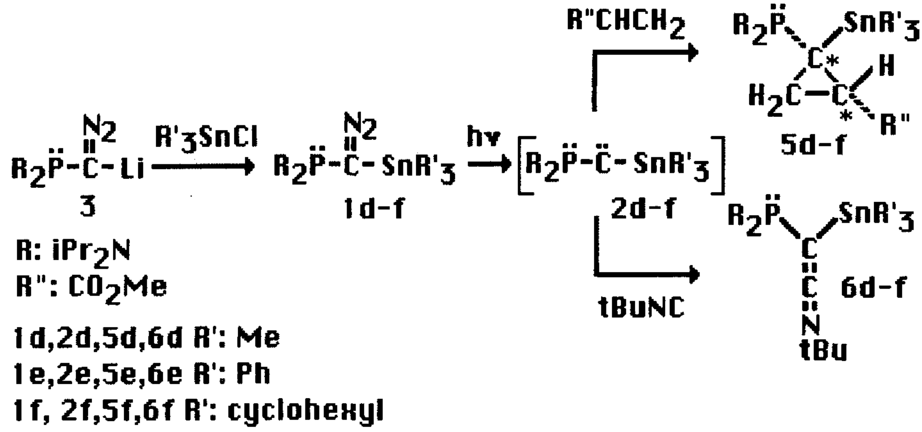
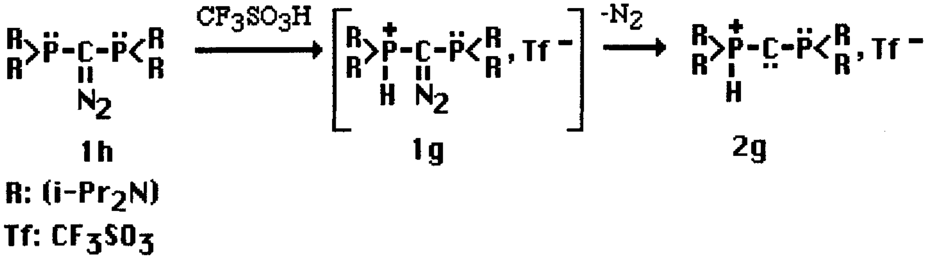


Therefore, we replaced the silyl group by stannyl substituents. Interestingly, we have been able to synthesize several (phosphanyl)(stannyl)diazomethanes **1d**, **1e** and **1f**.[9] Note that, in contrast to **1a**, the stannyl substituted diazo compounds, including **1f**, are only stable for a few hours at room temperature and decompose leading to a complicated mixture of products. In contrast, photolysis of these derivatives in the presence of methyl acrylate and tert-butylisocyanide led to the expected cyclopropanes

5d-f and ketene-imines **6d-f**, respectively, resulting from the trapping of carbenes **2d-f**, which are not observable. These results clearly demonstrate that even with relatively bulky substituents at the tin atom, (phosphanyl)(stannyl)carbenes are much less stable than the analogous silyl derivatives. This is probably due to the lengthening of the carbon-tin bond compared to a carbon-silicon bond, decreasing the steric protection of the carbene center.



Since silyl and phosphonio groups are isoelectronic and isovalent, we then tried to prepare the [bis(diisopropylamino)phosphanyl][bis(diisopropylamino)hydrogenophosphonio]diazomethane **1g**.[10] In fact, protonation of bis[bis(diisopropylamino)phosphanyl]diazomethane **1h**, with trifluoromethanesulfonic acid, directly led to the corresponding carbene **2g**.



Derivative **2g** was obtained as extremely air sensitive yellow crystals (mp 88 °C, dec; 76% yield). This compound was fully characterized by spectroscopy. Of particular interest, the ^{31}P NMR spectrum showed two doublet of doublet of quintets at +3.14 (J_{PP} = 120.8 Hz, J_{PH} = 530.3 and 17.4 Hz) and +27.16 (J_{PP} = 120.8 Hz, J_{PH} = 7.2

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and 19.2 Hz) proving the presence of two diisopropylamino groups on each phosphorus and a proton directly bonded to one of them. A ^{13}C NMR signal of a quaternary carbon appearing at 98.95 as a doublet of doublets ($J_{P(H)C}$ = 143.4 and J_{PC} =157.9 Hz) confirmed the PCP sequence. The single crystal X-ray diffraction study is of primary interest. Indeed, it appears that the σ^3P-C bond length is very short [1.548(4)Å], in the range expected for a phosphorus-carbon triple bond;[11] moreover, the geometry at the σ^3P is planar. From these values, it is clear that phosphanylcarbenes have a strong phosphorus-carbon multiple bond character.

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