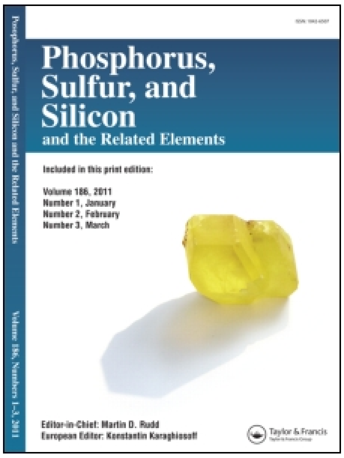

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Fluorophosphaalkenes $F_3CP{=}C\,(F)\,NR_2$, $HP{=}C\,(F)\,NR_2$ and Aminophosphaalkynes $P{\equiv}C\text{-}NR_2$-Synthesis, Structure and Reactivity

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FLUOROPHOSPHAALKENES $F_3CP{=}C(F)NR_2$, $HP{=}C(F)NR_2$ AND AMINOPHOSPHAALKYNES $P{\equiv}C{-}NR_2$ - SYNTHESIS, STRUCTURE AND REACTIVITY

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Abstract Electron-poor fluorophosphaalkenes of the type $F_3CP{=}C(F)NR_2$ (1) and $HP{=}C(F)NR_2$ (2) can be prepared in g-amounts by reacting $HP(CF_3)_2$ or H_2PCF_3 with secondary amines HNR_2. Due to their electronic structure (n/π-interaction) they show surprising differences to other PC (p-p)π-systems and to olefines. Similarly the phosphaalkyne $P{\equiv}C{-}N\textit{i}Pr_2$ (3) obtained from H_2PCF_3 and $HN\textit{i}Pr_2$, and the related labile compounds $P{\equiv}C{-}NR_2$ (R=Me, Et) generated *in situ* from $HP{=}C(F)NR_2$, exhibit chemical properties different from the known alkylphosphaalkynes.

INTRODUCTION

Phosphaalkenes and -alkynes are important synthons in organophosphorus and coordination chemistry and therefore have been thoroughly investigated by numerous research groups since more than 10 years [1]. Comparatively little is known about the properties of electron-poor PC double bond systems (e.g.fluorophosphaalkenes) and electron-rich phosphaalkynes with π-donor substituents like NR_2 on C.

RESULTS AND DISCUSSION

Recently we have found an effective one-pot procedure for the preparation of fluorophosphaalkenes of type 1 or 2. They are formed in a series of HF elimination and HNR_2 addition steps according to equations (1) and (2)[2].

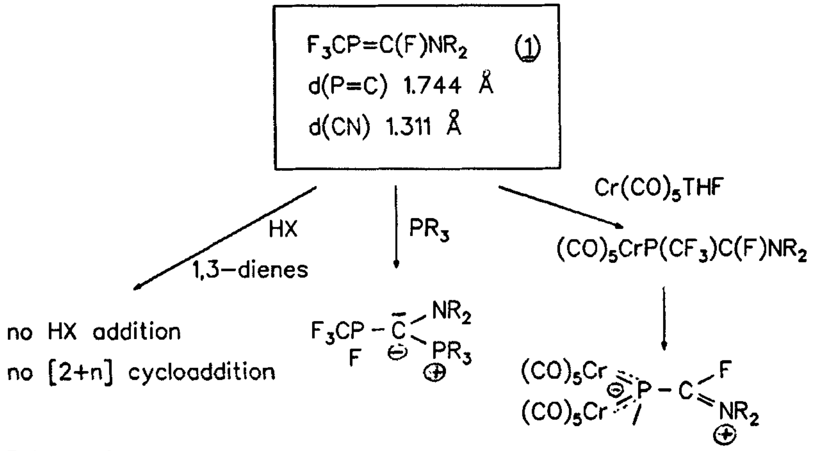
$$HP(CF_3)_2 \quad + \quad 3\ HNR_2 \quad \xrightarrow[-\ 2[R_2NH_2]F]{\qquad\qquad} \quad F_3CP{=}C(F)NR_2 \qquad (1)$$

$$H_2PCF_3 \quad + \quad 3\ HNR_2 \quad \xrightarrow[-\ 2[R_2NH_2]F]{\qquad\qquad} \quad HP{=}C(F)NR_2 \qquad (2)$$

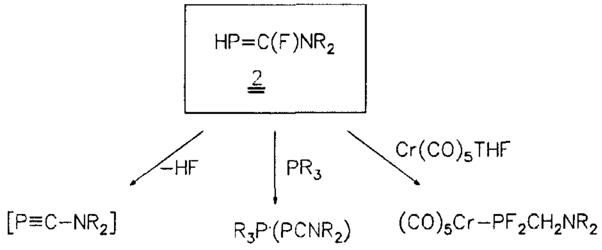
The analogous reaction of H_2PCF_3 with diisopropylamine, surprisingly, does not yield the expected phosphaalkene $HP{=}C(F)N\mathit{i}Pr_2$, but the novel aminophosphaalkyne $P{\equiv}CN\mathit{i}Pr_2$ (3). The spectrosopic data of 3 (^1H, ^{13}C, ^{31}P-NMR; IR, PES) are similar to those of Appel's silylamino derivative[3] $P{\equiv}CN(SiMe_3)\mathit{i}Pr$ and indicate a considerable n/π-interaction:

Compound	δ_P/ppm	δ(sp-C)/ppm	^1J(PC)/Hz	$\nu(P\equiv C)$/cm^{-1}	IP_1/eV
$P\equiv CNiPr_2$	- 99.6	152.2	14.7	1642	7.44
$P\equiv CN(SiMe_3)iPr$	- 140	154	18.3	1588	-

Investigations carried out to elucidate the chemical behaviour of 1 and 2 have shown that their reactivity greatly differs from that of alkyl- or arylphosphaalkenes, in particular with respect to the olefinic properties [4]. Some of the surprising results are shown in scheme I and II.



Scheme I



Scheme II

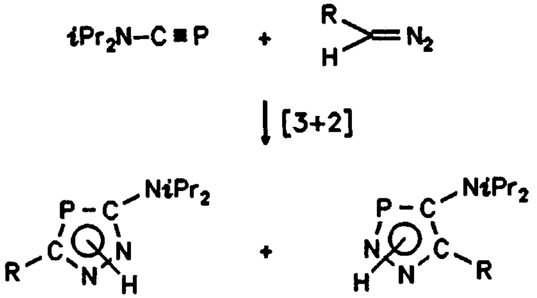
The unusual behaviour of 1 is due to the C-amino group and can be explained by a significant contribution of the zwitterionic form 1B to the electronic ground state of the molecules.

1A 1B

The reactivity of the related phosphaalkenes HP=C(F)NR$_2$ (2) is mainly governed by the ease of HF elimination leading to labile aminophosphaalkynes which undergo following reactions, for instance with PR$_3$ or Cr(CO)$_5$THF.

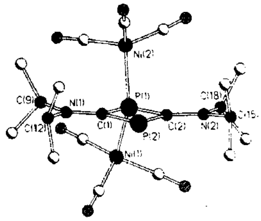
The important influence of the π-donor group NR$_2$ on the electronic structure is also demonstrated by surprising differences in the reactivity of P≡CN*i*Pr$_2$ (3) and the extensively studied P≡C^{t}Bu [1]. Thus 3 reacts with diazoalkanes to give a mixture of 1,2,4- and 1,2,3-diazaphospholes (scheme III), whereas P≡C^{t}Bu yields only the 1,2,4-isomer in a stereospecific [3+2]-cycloaddition [5a].

In addition, 3 acts as a suitable electron-rich partner for the electron-poor heteroalkenes F$_3$CP=CF$_2$ or "F$_3$CP=PCF$_3$" affording new diphospha- or triphosphacyclobutenes which formally can be described as [2+2] cycloadducts. Analogous products are obtained by applying the phosphaalkenes HP=C(F)NR$_2$ (R=Me, Et) as equivalents for P≡CNR$_2$.



3 also exhibits a surprising reactivity in reactions with transition metal carbonyls, e.g. an unusual binuclear complex of the 1,3-diphosphacyclobutadiene $(iPr_2NCP)_2$ is formed as the only product with $Ni(CO)_4$ [equation (3)]^{5b}:

$$\begin{array}{l} 2\ iPr_2NC\equiv P \\ \qquad \underline{\underline{3}} \\ \qquad + \\ 2\ Ni(CO)_4 \end{array} \xrightarrow{-\ 2CO}$$



(3)

Similar complexes are obtained with phosphine derivatives $Ni(CO)_3PR_3$ (R=Me, Ph), whereas with R = cyclohexyl (Cy) the novel 16e phosphaalkyne nickel complex $(iPR_2NCP)\,Ni(PCy_3)CO$ is produced with side-on coordination of $P\equiv CNiPr_2$.

REFERENCES:

1. Multiple Bonds and Low Coordination in Phosphorus Chemistry (Eds. M. Regitz, O. J. Scherer), Thieme-Verlag, Stuttgart, (1990).
2. (a) J. Grobe, D. Le Van, J. Nientiedt, B. Krebs, M. Dartmann, Chem. Ber., 121, 655 (1988); (b) J. Grobe, D. Le Van, B. Lüth, M. Hegemann, ibid., 123, 2317 (1990).
3. R. Appel, M. Poppe, Angew. Chem. Int. Ed. Engl., 28, 53 (1989).
4. J. Grobe, D. Le Van, J. Nientiedt, New. J. Chem., 13, 363 (1989);
   J. Grobe, D. Le Van, B. Krebs, R. Fröhlich, A. Schiemann, J. Organomet. Chem., 389, C29 (1990); J. Grobe, D. Le Van, U.
   Althoff, B. Krebs, M. Dartmann, R. Gleiter, Heteroat. Chem., 2, 385 (1991).
5. (a) J. Grobe, D. Le Van, M. Hegemann, B. Krebs, M. Läge, Chem. Ber., 125, 411 (1992); (b) Angew. Chem. Int. Ed. Engl., 31, 95 (1992).