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## FLUOROPHOSPHAALKENES - NEW VERSATILE REAGENTS

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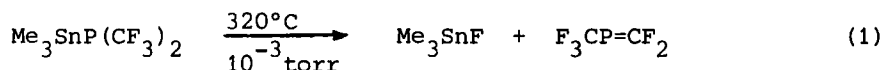
**Abstract** The synthesis of substituted fluorophosphaalkenes  $RP=CFR'$  with a variety of groups R and R' is discussed. The reactivities (self-addition, HX addition, [2+4] cycloaddition with 1,3-dienes) and the coordination chemistry of selected compounds have been explored.

### INTRODUCTION

Phosphorus carbon (p-p) $\pi$  compounds show a surprising similarity to alkenes<sup>1</sup>. The proof of this relationship faces some difficulties in case of sterically protected PC double bond systems, in particular for [2+4] cycloaddition reactions<sup>2</sup>. Some successful experiments with heterosubstituted phosphalkenes<sup>3</sup> demonstrate the influence of substituents, a result which led us to study the chemistry of fluorophosphaalkenes and related compounds.

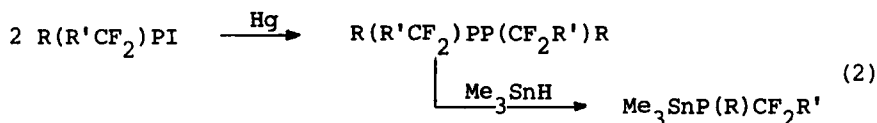
### PREPARATIVE ROUTES TO FLUOROPHOSPHAALKENES

$F_3CP=CF_2$  (1), a simple representative of this class of phosphalkenes was first prepared by Nixon et al. in 1979<sup>4</sup> by HF elimination from  $(CF_3)_2PH$  and later by Burg<sup>5</sup> by thermal cleavage of the dimer  $(CF_3PCF_2)_2$ . We recently discovered an optimal method of preparation, using the pyrolysis of  $Me_3SnP(CF_3)_2$  according to equ. (1)<sup>6</sup>.



This method is widely applicable to precursors of the general type  $\text{Me}_3\text{SnE(R)}\text{R}_\text{F}$  ( $\text{E} = \text{P}, \text{As}$ )<sup>7</sup> and  $\text{Me}_3\text{SnE'R}_\text{F}$  ( $\text{E}' = \text{S}, \text{Se}$ )<sup>8</sup>.

The preparation of substituted phosphaalkenes  $\text{RP}=\text{CFR}'$  demands suitable pathways to the trimethyltin precursors  $\text{Me}_3\text{SnP(R)CF}_2\text{R}'$ . Their synthesis involves a multistep procedure for the production of the iodophosphanes  $\text{R(R'CF}_2)_2\text{PI}$ , from which the required stannylphosphanes can be prepared according to equation (2).



The thermal stability of these compounds is strongly influenced by the nature of the substituents R and R'.

Depending on the aim of the actual investigation fluoro-phosphaalkenes are generated by thermolysis of the corresponding stannylphosphanes either at  $T > 300^\circ\text{C}$  and  $p \approx 10^{-3}$  torr<sup>6</sup> or in solution at  $70 - 120^\circ\text{C}$  in the presence of 1,3-dienes as trapping reagents<sup>9</sup>.

Alternatively, heterosubstituted derivatives of 1 ( $\text{F}_3\text{CP}=\text{CFX}$ ) have been prepared by HF elimination from the secondary phosphanes  $\text{HP(CF}_3)_2\text{CF}_2\text{X}$  produced by HX addition ( $\text{X} = \text{NR}_2, \text{OR}, \text{PMe}_2$ ) to 1<sup>10</sup>. Recent work established a simple one-pot procedure to the C-amino compounds  $\text{F}_3\text{CP}=\text{C(F)NR}_2$  by the reaction of  $\text{HP(CF}_3)_2$  with  $\text{HNR}_2$  in a 1 : 3 molar ratio.

In case of the trimethyltin precursors with two different fluoroalkyl groups  $\text{R}_\text{F}$  and  $\text{R}'_\text{F}$  in principle both can participate in the thermal elimination of  $\text{Me}_3\text{SnF}$ . A careful investigation of the thermolysis of  $\text{Me}_3\text{SnP(CF}_3)_2\text{CF}_2\text{H}$ ,  $\text{Me}_3\text{SnP(CF}_3)_2\text{CF}_2\text{F}$  and  $\text{Me}_3\text{SnP(CF}_3)_2\text{CF(CF}_3)_2$  demonstrates that 1,2-elimination preferably occurs with preservation of the  $\text{CF}_3$  and attack of the  $\text{CF}_2\text{X}$  or  $\text{CF(CF}_3)_2$  group. The same tendency is found for the HF elimination from  $\text{F}_3\text{CP(H)CF}_2\text{X}$  with  $\text{NMe}_3$ <sup>10</sup>. These results can be explained by the so-called "perfluoro effect"<sup>11</sup>.

REACTIVITY STUDIES

The isolation of the new phosphalkenes in preparative amounts offered the possibility of a systematic investigation of their reactivity. Of particular interest are reactions which can prove or disprove the expected relationship to alkene chemistry.

Self-addition of the fluorophosphalkenes ( $T \leq -78^\circ\text{C}$ ) leads to the trans 1,3-diphosphetanes as the main products. However, the cis isomers and the 1,2-diphosphetanes are formed, too, along with small amounts of tri- and polymeric species<sup>6</sup>. The self-addition reaction is strongly affected by the substituents on P and C.

In addition to the information recently published on reactions of 1<sup>10</sup> and  $\text{F}_5\text{C}_2\text{P}=\text{C}(\text{F})\text{CF}_3$  (2)<sup>12</sup> with HX compounds we studied (i) the addition of hexamethyldisilazane and (ii) the addition of primary amines  $\text{RNH}_2$  ( $\text{R} = \text{Bu}^t, \text{Pr}^i$ ) to 1. In both cases the phosphalkene undergoes a multistep reaction, involving the intermediates  $\text{F}_3\text{CP}^{\bar{1}}$  and  $\text{F}_3\text{CP}(\text{H})\text{CN}$  for (i) and  $\text{F}_3\text{CP}^{\bar{1}}$  and  $\text{F}_3\text{CP}=\text{C}=\text{NR}$  for (ii). The final products are the cyclic oligophosphanes  $(\text{F}_3\text{CP})_n$  ( $n = 4, 5$ ) and  $\text{Me}_3\text{SiF}$  (i) or  $\text{RNC}$  (ii).

The strong relationship between fluorophosphalkenes and alkenes has been proved by their pronounced dienophilicity in a series of [2+4] cycloaddition reactions with 1,3-dienes, performed either with the isolated monomers<sup>13</sup> or in a one-pot synthesis with the stannylphosphane precursors<sup>9, 12</sup>.

In the area of coordination chemistry our investigations concentrated on two types of reactions:

(a) The hydrometallation of 1, applying main group IV element hydrides  $\text{Me}_3\text{M}'\text{H}$  ( $\text{M}' = \text{Si}, \text{Ge}, \text{Sn}$ ) and the hydride complexes  $\text{HM}(\text{CO})_3\text{C}_5\text{H}_5$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ). With the exception of  $\text{Me}_3\text{SiH}$  all hydrides react with formation of  $\text{M}'\text{P}$  or  $\text{MP}$  bonds. In some cases following reactions are observed.

(b) The ligand properties of 1 and its derivative  $\text{F}_3\text{CP}=\text{C}(\text{F})\text{NMe}_2$  (3) have been studied using  $\text{Cr}(\text{CO})_5\text{L}$  complexes ( $\text{L} = \text{CH}_2\text{Cl}_2, \text{THF}$ ) as

precursors. The reaction of 1 with  $\text{Cr}(\text{CO})_5\text{CH}_2\text{Cl}_2$  at low temperature yields the  $\sigma$ -P complex as the primary product which at room temperature undergoes at least three following reactions: Rearrangement to the  $\pi$ -complex, dimerization to the 1,3-diphosphetane derivative  $[(\text{CO})_5\text{Cr}(\text{F}_3\text{CPCF}_2)]_2$ , and formation of a binuclear compound with 1 acting as a 4e ( $\sigma+\pi$ ) bridging ligand. 3 reacts with  $\text{Cr}(\text{CO})_5\text{THF}$  affording a yellow crystalline complex  $\text{Cr}(\text{CO})_5(\text{F}_3\text{CP}=\text{CFNMe}_2)$  for which the coordinating site of the ligand will be elucidated by an X-ray crystallographic study in the near future.

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