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New Stable Diphosphenes

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New Stable Diphosphenes

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Since the isolation of the first stable diphosphene by YOSHIFUJI, some other diphosphenes have been prepared and stabilized by very bulky substituents. We have recently described the synthesis, via a germylated way, of the bis [bis(trimethylsilyl)methyl]diphosphene 1, one of the least crowded stable diphosphenes:

diphosphenes:

$$\frac{DBU}{RP(H)GeCl_{3}} \xrightarrow{DBU.GeCl_{2}}
\begin{bmatrix}
RP(H)Cl
\end{bmatrix} \xrightarrow{DBU.HCl}
\frac{RP=PR}{-DBU.HCl}
\xrightarrow{R}
R=(Me_{3}Si)_{2}CH$$

We present here two new routes to $\underline{1}$ involving fluorinated phosphines :

Reactivity of $\underline{1}$ towards protic reagents, dienes, selenium,... will be presented.

We have also synthesized the new diphosphenes $\underline{2}$ and $\underline{3}$ via the germylated route:

P(H)GeCl₃
$$\xrightarrow{DBU}$$
 $\xrightarrow{CF_3}$ $\xrightarrow{F_3C}$ $\xrightarrow{E_3}$ $\xrightarrow{F_3C}$ $\xrightarrow{E_3}$ $\xrightarrow{F_3C}$ $\xrightarrow{F_3$

The hexafluoro-m-xylyl substituent has been used for the first time in phosphorus chemistry; its influence on the changes in electronic structure and reactivity of these diphosphenes has been clearly evidenced.