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Perfluoroalkyl Diphosphenes - Synthons for Diphospha Heterocycles

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Perfluoroalkyl Diphosphenes - Synthons for Diphospha Heterocycles

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Recent successful work in the field of $(2p-3p)\pi$ (P=C) and $(2p-4p)\pi$ (As=C) systems with F or R_F substituents led us to search for unsaturated $(3p-3p)\pi$ compounds using the stabilizing effect of perfluoroalkyl groups.

The result of our attempts is a simple one-pot procedure, in which, according to eq. (1), diphosphenes $R_F P = PR_F$ are formed from $R_F P I_2$ and $SnCl_2$ as reactive intermediates which can be trapped by 1,3-dienes in Diels-Alder type reactions (eq. 2).

$$2 R_{F}PI_{2} + 2 SnCl_{2} \longrightarrow R_{F}P=PR_{F} + 2 SnCl_{2}I_{2}$$
 (1)

$$R_{\rm F}P=PR_{\rm F}$$
 + 1,3-diene \longrightarrow (2+4) cycloadduct (2)

The cycloadducts obtained are generated in a stereospecific reaction; ^{31}P and ^{19}F NMR spectra establish the exclusive formation of the isomers with trans positions of the R_F groups. The observed stereoselectivity suggests a concerted mechanism for the (2+4) cycloaddition. The Diels-Alder compounds can be used as source for the diphosphenes as demonstrated by the retrodiene cleavage of the adduct of 1,3-cyclohexadiene and $\text{F}_3\text{CP=PCF}_3$ in the presence of 2,3-dimethylbutadiene.

Facts and arguments in support of the diphosphene intermediates will be presented and discussed on the poster. In addition, recent results with modified SnCl₂ reagents and substitutes for the production of phosphinidenes and diphosphenes will be produced.