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Weak interactions in Stabilized Silylium ions

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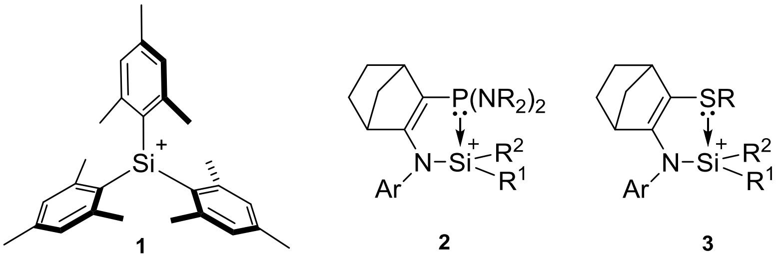
In contrast to carbocations, which existence was recognized and firmly established already in 1901, silylium ions (R_3Si^+) have remained for a long-time elusive species.[1] The major obstacle to the formation of silylium ions is their high reactivity towards any nucleophile. It was only in 2002 that the first tris(mesityl)silylium ion **1** was isolated by Reed and Lambert.[2] Recently, a series of weakly stabilized silyl cations were described offering the possibility to tune their Lewis acidity, and to develop their catalytic applications in: Diels-Alder cycloadditions, Mukaiyama aldol condensations, CO_2 reduction, hydrodefluorination reactions...[3]

In this context, we would like to present the synthesis and reactivity of a new class of base-stabilized silylium ions **2**, **3** using main group Lewis bases (P, S). Phosphines and sulfides being known to establish weak interactions, the new ligand systems provide a good balance between stability and reactivity of the related stabilized silylium ions.[4]



1 **2** **3**

$[Do \longrightarrow SiH_3]^+$

Do	Bond Energy (in kJ.mol^{-1})
H_3P	239
H_2S	194

Figure 1. First isolated silylium ion **1** and phosphine- or sulfide-stabilized silylium ions (**2**, **3**).

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