Synthesis of Counteranion-Stabilized Bis(silylium) lons

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The preparation of a molecule with two alkyl-tethered silylium-ion sites from the corresponding bis(hydrosilanes) by two-fold hydride abstraction will be presented. The length of the conformationally flexible alkyl bridge is crucial as otherwise the hydride abstraction stops at the stage of a cyclic bissilylated hydronium ion. With an ethylene tether, the open form of the hydronium-ion intermediate is energetically accessible and engages in another hydride abstraction. The resulting bis(silylium) ion has been NMR spectroscopically and structurally characterized. In case of related systems based on rigid linkers, only bis(silylium) ions with naphthalene linker have been synthesized so far. The naphthalen-n,m-diyl platforms can only be converted into the dications when the positively charged silylium-ion units are remote from each other (1,8 versus 1,5 and 2,6). These superelectrophiles are potential candidate for various applications in the area of small molecules activation and Lewis acid catalysis. Among them, some of the recent progress on development of a new type of silicon-phosphorous frustrated Lewis pairs (FLP) system will also be described briefly.