

## Oxygen vs Sulfur stabilized Silyl Cations – Which is the Better Lewis Acidic Catalyst

Sandra Künzler,\* and Thomas Müller

Carl von Ossietzky Universität Oldenburg, Institut für Chemie, 26129 Oldenburg,  
Germany, E-Mail: sandra.kuenzler@uni-oldenburg.de

The development of Lewis acidic catalysts is of current interest.<sup>[1]</sup> Silyl cations with their high Lewis acidity show a conspicuous capability to act as catalyst in e.g. hydrodefluorination, Diels Alder and Mukaiyama Aldol reactions.<sup>[2]</sup> In this context, a pronounced interest in the development of enantioselective catalysts has evolved. Here, we present the syntheses and structures of phenoxy and thiophenyl stabilized silyl cations **1** and **2**, in which the Lewis acidity of the silicon centre is defined by its intramolecular interaction with the donor substituent (OPh or SPh). NMR spectroscopy and X-ray diffraction analysis as well as the results of quantum mechanical calculations revealed remarkable structural differences between **1** and **2**. While in species **1** the oxygen atom shows a planar coordination sphere, the sulfur atom in species **2** exhibits a trigonal pyramidal coordination sphere (Fig. 1, 2).<sup>[3]</sup> Unsymmetrical substitution at the silicon atom as in **1b,c** and **2b,c** results in a Lewis acidic catalyst system in which not

only the Lewis acidity can be tuned but also the absolute stereo configuration can be controlled.<sup>[4]</sup>

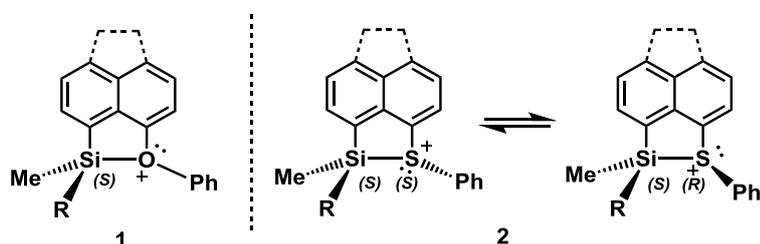


Figure 1. Silyl cations **1** and **2** (R = Me (a), Ph (b), t-Bu (c)).

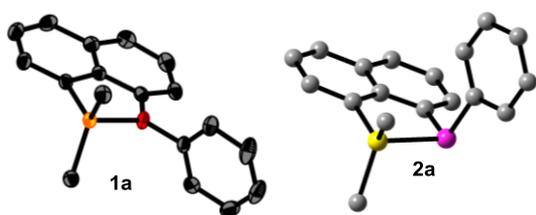


Figure 2. Molecular structure of phenoxy stabilized silyl cation **1a** in the crystal of **1a**[CB<sub>11</sub>H<sub>6</sub>Br<sub>6</sub>] (thermal ellipsoids at 50% probability level) and calculated structure of thiophenyl stabilized silyl cation **2a** (M062X/def2-tzvp) (in both structures, hydrogen atoms are omitted for clarity).<sup>[3]</sup>

[1] H. Yamamoto, *Lewis Acid in Organic Synthesis*, Wiley-VCH, Weinheim, 2000.

[2] (a) T. Müller, *Silylium Ions in Structure and Bonding*, 155, Springer, London 2014. (b) A. D. Dilman, S. L. Ioffe, *Chem. Rev.* **2003**, 103, 733.

[3] N. Kordts, S. Künzler, S. Rathjen, T. Sieling, H. Großbekappenberg, M. Schmidtmann, T. Müller, *Chem. Eur. J.* **2017**, 23, 10068.

[4] S. Künzler, Y. Landais, T. Müller, manuscript in preparation.