

Coordination of hypervalent hexacoordinated Si in neutral and ionic complexes

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Silicon as a group 14 element is most often tetracoordinated, however, some hypervalent compounds are already known from the beginning of the 19th century [1]. These hypervalent Silicon compounds are remarkable because of their relative stability makes them important in the nucleophilic substitution reactions. Typically, they contain electronegative and/or multidentate ligands [2], furthermore, they are often charged species. It is also noteworthy, that SiO₅ or SiO₆ bonding motifs are rare among these compounds.

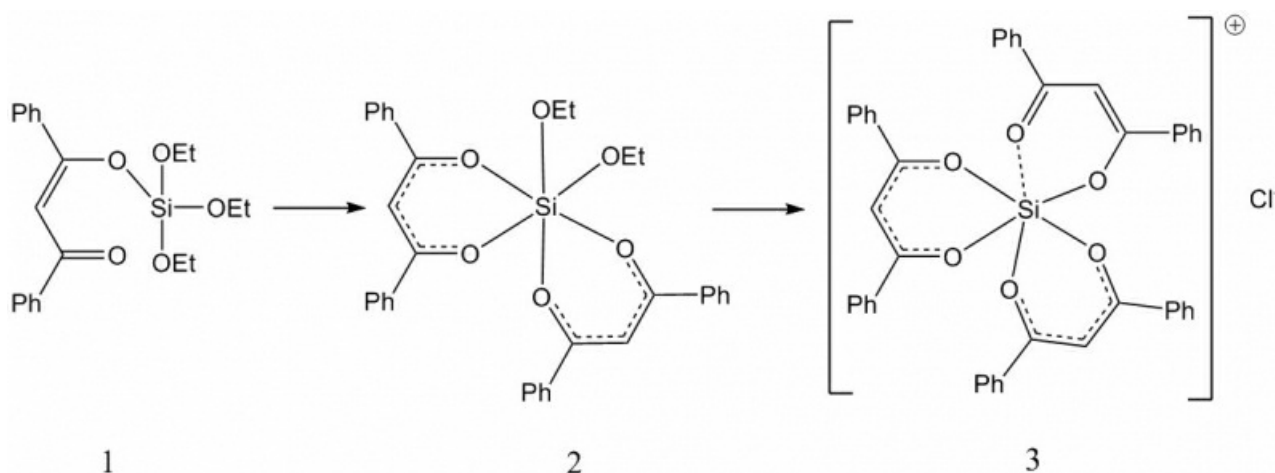
We previously reported the synthesis of a neutral pentacoordinated Germanium complex, which was selected for synthesis after thorough density functional calculations suggesting the use of three CF₃ groups and a bidentate 1,3-diphenylpropane-1,3-dione ligand [3]. Furthermore, computations suggested that germanium substituted by three -OEt moieties forms a stable pentacoordinate structure with beta-diketonato ligand, while the pentacoordinated Silicon analogue shows somewhat reduced stability compared to tetracoordinated one. Due to this small energy difference we examined the reaction between (EtO)₃SiCl and 1,3-diphenylpropane-1,3-dione. In this synthesis we could spectroscopically detect the tetracoordinated Si-complex (1) and structurally characterize two hexacoordinated compounds (2, 3). The existence of the pentacoordinated isomer of 1 could only be concluded from NMR spectroscopy. Computational mechanistic investigations show that the formation of 2 proceeds via this intermediate.

Two crystal structures of hypervalent hexacoordinated Silicon complexes will be reported. The neutral complex of (2) contains two bidentate beta-diketonato ligands and two ethoxy groups in cis position. Their oxygen atoms are bonded with strong Si-O bonds. In the six-membered rings formed by the beta-diketonato ligand and the silicon, the Si-O bonds are elongated compared to the ethoxy Si-O bonds and largely differ from each other in the same ring. The ¹³C NMR measurement suggests that (2) exists as cis-isomer in solution at lower temperature in accordance with the solid state structure. However, the cis/trans isomerization is so rapid at room temperature that the process is not detectable on NMR time scale, as could be concluded from DFT calculations. Complex (3) of hypervalent hexacoordinated Silicon contains three bidentate beta-diketonato ligands. There is one chloride salt and a water solvent in the asymmetric unit. The two Si-O distances in each beta-diketonato ligands are well balanced, as well the O-C and C-C distances. The delocalization of the electrons over the O-C-C-O bonds in the beta-diketonato ligands could be concluded from the distribution of the bond distances.

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