

Selective Si–O–Si Bond Cleavage as Synthetic Access to Functionalized, Hydrolysis-stable Zinc Silanolates

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

The selective cleavage of the strong and poorly reactive Si–O–Si bond in functionalized siloxanes under mild conditions is a decisive task for modern synthetic chemistry. Simple treatment of the aminomethyl-functionalized disiloxanes **1**, **6**, (*R,R*)-**7** and **8** ($[\text{R}_2(\text{CH}_2\text{NR}')\text{SiO}]_2$, R = Me or Ph, $\text{NR}' = \text{NC}_5\text{H}_{10}$, $\text{NC}_5\text{H}_8(\text{CH}_3)_2$ or $\text{NC}_4\text{H}_7(\text{CH}_3)$) with zinc(II) bromide and zinc(II) chloride, respectively, results in the formation of highly hydrolysis-stable, molecular zinc silanolates which were long time supposed to be unstable in the presence of water. Both, the selective cleavage of the Si–O–Si bond as well as the formation of the molecular zinc silanolates are independent of the substituents at silicon, the used zinc(II) salt or the aminomethyl side arm. Detailed structural studies showed that zwitterionic interactions are the reason for the high stability towards hydrolysis of the formed zinc silanolates **9**, **10**, (*R,R*)-**11** and **12**. NMR studies are indicative of the same structure of these molecular systems in solution as in the solid state.

Key words: Metallasilanolates, Zwitterionic Compounds, Zinc, Disiloxanes, Metal Complexes