

Integrated process for the production of bifunctional monosilanes

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Production of methylchlorosilanes $\text{Me}_n\text{SiCl}_{4-n}$ ($n=0-4$) by the Müller-Rochow Direct Process^[1] is one of the main pillars in silicon chemistry. This process produces up to 10 wt% of a residue, mainly consisting of a disilane fraction of mixed methylchlorodisilanes, $\text{Me}_n\text{Si}_2\text{Cl}_{6-n}$ ($n=2-6$). A variety of procedures to recover valuable methylchlorosilane monomers by virtue of cleavage, redistribution or disproportionation reactions were conceived in the past to increase commercial benefit and to minimize environmental pollution. Historically, the preferred work up of the disilane residue by thermally induced rearrangements requires temperatures up to 600 °C, thus creating polymeric resins as by-products. To overcome polysilane formation and for simplification of disilane breakdown, hydrogen chloride is often used, but requires harsh reaction conditions. Recent results prove tetrabutylphosphonium chloride and 2-methylimidazole as efficient disilane cleavage catalysts that enhance monosilane formation under moderate reaction conditions.^[2] Monosilanes obtained from disilane cleavage reactions are then mainly reintroduced into the siloxane production chain. In a recent publication we reported on a single step reaction to directly form cyclic, linear and cage-like siloxanes upon treatment of the disilane residue with a HCl/ether solution at elevated temperatures, at first giving bifunctional monosilanes from disilane cleavage as intermediates.^[3] These Si(H)Cl containing monosilanes are key compounds in silicone technology, and the controlled installation of both functionalities at one silicon center has proved to be a synthetic challenge, despite the seeming simplicity of these compounds. Industrially important derivatives, such as MeSiHCl_2 and Me_2SiHCl , are formed as side-products of the Direct Process, but only in small amounts (1-4 wt% and 0.1-0.5 wt%, respectively). With this contribution an alternative, preparatively facile protocol for the synthesis of bifunctional monosilanes RMeSiHCl ($\text{R}=\text{Me}, \text{H}, \text{Cl}$) from methylchlorodi- and monosilanes is presented.

[1] E. G. Rochow, *J. Am. Chem. Soc.* **1945**, 67, 963-965; R. Müller, *Chem. Tech* 1950, 2, 41-50.

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[3] F. Neumeyer, N. Auner, *Chem. Eur. J.* **2016**, 22, 17165-17168.