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Review

Syntheses and properties of cyclosilazanes and cyclocarbosilazanes

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ABSTRACT

We present a review of synthetic methods and physico-chemical properties of cyclo(carbo)silazanes that could form the basis of composite ceramic materials of type $Si_x(C_y)N_z$, as well as polymeric materials. The review is compiled as a guide for the preparation of such compounds, which have the potential to be further modified to access novel derivatives. The review is subdivided according to ring size. Each section presents known synthetic methods to obtain various types of cyclo(carbo)silazanes and also highlights their possible functionalisation. The review also includes reactions of *N*-unsubstituted cyclic derivatives and data on the hydrolytic stability of such compounds.

Contents

1. Introduction

One of the current trends in the chemistry of materials represents the synthesis of silicon–carbon–nitrogen compounds, which are expected to form the basis of composite ceramic materials of type Si_xN_y as well as polymeric materials [1]. These compounds possess suitable material properties, which makes them utilisable in various industries such as materials for turbines, heat-resistant materials, various coatings and polymer fibres.

We present an overview of physico-chemical properties and synthetic methods for the preparation of selected types of monomeric precursors of such materials. The review is intended and compiled as a synthetic manual for the preparation of such compounds, which can be further modified to access novel derivatives.

The review is subdivided by ring size. Each section presents known synthetic methods to obtain various types of cyclocarbosilazanes, and also highlights their possible functionalisation. The review also includes reactions of *N*-unsubstituted cyclic

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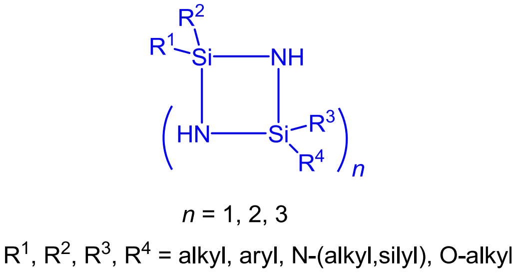


Fig. 1. General formula of cyclosilazanes.

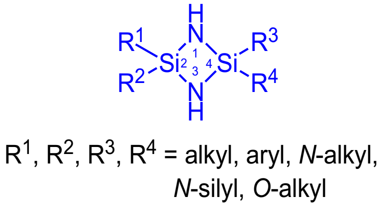


Fig. 2. General formula of cyclodisilazanes.

derivatives and important data on the hydrolytic stability of respective compounds.

2. Cyclosilazanes

Cyclosilazanes are silicon analogues of saturated carbon heterocycles – 1,3-diazetidine ($n = 1$), hexahydrotriazine ($n = 2$) and tetrazocine ($n = 3$) – while nitrogen and silicon atoms alternate in their structure (Fig. 1). This family of compounds has been widely studied [2], and apart from their properties, synthetic transformations towards various functionalised derivatives are of interest as well.

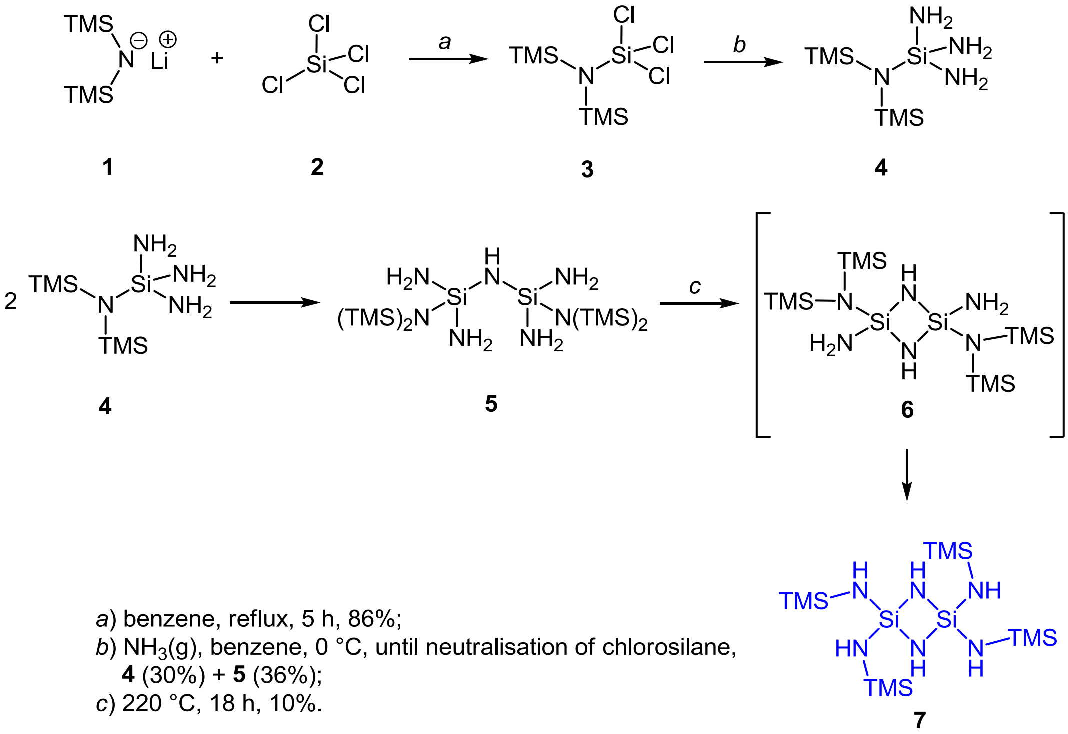
2.1. Cyclodisilazanes

Cyclodisilazanes form 4-membered rings with the basic structure shown in Fig. 2. The name of this group of compounds has been derived from the saturated azaheterocycle – 1,3-diazetidine. Carbon atoms in positions C-2 and C-4 have been replaced by silicon atoms; both carbon and silicon are group 14 elements of the periodic table, thus they have the same valence. Substituents are located in these positions, thus forming 2,2,4,4-tetrasubstituted cyclo-2,4-disiladiamines or 2,4-disila-1,3-diazacyclobutanes. The most common name for this group of compounds is cyclo-2,4-disilazanes. This section concentrates on the synthesis of cyclodisilazanes with an unsubstituted nitrogen atom, which could be capable of further functionalisation.

2.1.1. Preparation of cyclo-2,4-disilazanes

Cyclodisilazanes were first mentioned when NMR spectroscopy and X-ray analysis were in their infancy [3]. Until these two methods were available, such compounds could not be fully characterised or distinguished from the related 6- and 8-membered isomers. Since cyclo-2,4-disilazanes are sensitive to air moisture, all reactions had to be carried out under a blanket of dry argon or nitrogen.

2.1.1.1. Ammonolysis of chlorosilanes. The cyclosilazane skeleton was accessed in a step-wise fashion, but only very low yields of required products were obtained [4]. The first step of the sequence involved the reaction of lithiated hexamethyldisilazane **1** with tetrachlorosilane **2** which gave trisilazane **3** (Scheme 1). Trisilazane **3** further underwent an ammonolysis with a solution of ammonia in benzene which afforded compounds **4** and **5** in 66% combined yield. Compound **5** was assumed to be the product of a subsequent *in situ* de-aminative homocoupling of **4**. The branched disilazane **5** finally underwent thermal condensation under an argon atmosphere to yield cyclodisilazane **7** in very low yield (10%). Based on



a) benzene, reflux, 5 h, 86%;
b) NH_3(g), benzene, 0 °C, until neutralisation of chlorosilane, **4** (30%) + **5** (36%);
c) 220 °C, 18 h, 10%.

Scheme 1.