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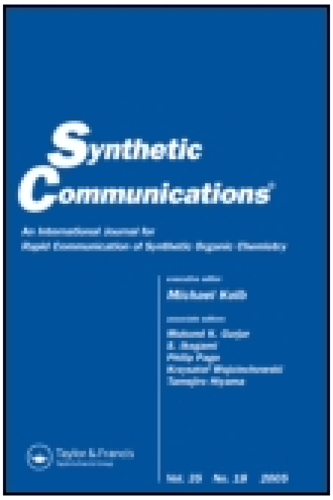

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FACILE SYNTHESIS OF 1,3-DICHLOROTETRAORGANODISILAZANES

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FACILE SYNTHESIS OF 1,3-DICHLOROTETRA-ORGANODISILAZANES

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Zhi-Jie Zhang, and Ze-Min Xie***

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ABSTRACT

A new 1,3-dichlorodisilazane, 1,3-dichloro-1,3-dimethyl-1,3-divinyldisilazane (DMDV), was prepared from the trans-silylation reaction of hexamethyldisilazane (MM^N) and methylvinyldichlorosilane. The reactions between MM^N and other dichlorosilanes, R_2SiCl_2 ($R = Me$, Ph) in the absence of catalyst were also investigated, and the expected, 1,3-dichlorosilazanes, $(ClSiMe_2)_2NH$ and $(ClSiPh_2)_2NH$ were obtained, respectively.

Silicon-based non-oxide ceramics, such as silicon nitride and silicon carbide ceramic materials, have attracted continuous interest for many years due to their excellent properties in extreme conditions.[1–3] Since the pioneering work of Verbeek in the mid 1970s,[4] intense research over the past 25 years has focused on the elaboration of Si_3N_4, SiC or Si/C/N-based materials from pyrolysis of organosilicon precursors. Compared with traditional technologies, the method from precursors offer many fabrication

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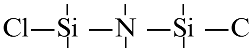
advantages in processing, especially in producing complex ceramic parts and composites. Properties of the final ceramic materials are strongly dependent on the structures and the chemical composition of precursors. According to the literatures,[1,5,6] the ideal preceramic polymer should contain rings or cages structure in molecule to decrease the polymer skeleton degradation; have latent chemical reactivity to obtain thermosetting or curing properties; and possess appropriate processibilities to apply the polymer in the desired shape before the pyrolysis process. In an attempt to prepare polysilazane that according with these rules, recently, we designed a new route to synthesize a class of new polysilazanes containing linear-cyclic structure as well as reactive groups.[7,8] It was shown that these polysilazanes could be thermally or catalyzed cross-linked and then pyrolysized to Si/C/N ceramics. In the new route, 1,3-dichlorodisilazanes were used as starting materials. In this paper, we report a facile synthesis route to 1,3-dichlorodisilazanes in the absence of any catalyst. Via the method, a new 1,3-dichlorodisilazane, 1,3-dichloro-1,3-dimethyl-1,3-divinyl-disilazane, $(ClSiMeVi)_2NH$, was obtained, which has not been synthesized and characterized before. In addition, the un-catalyzed reactions of hexamethyldisilazane with dimethyldichlorosilane and diphenyldichlorosilane were studied and the expected products, 1,3-dichloro-1,1,3,3-tetramethyldisilazane and 1,3-dichloro-1,1,3,3-tetraphenyldisilazane were synthesized, respectively.

In contrast with the alkyl-, aryl-substituted disilazanes, symmetrical 1,3-dichlorodisilazanes,  $\mathrm{Cl{-}\overset{|}{\underset{|}{Si}}{-}\overset{|}{\underset{|}{N}}{-}\overset{|}{\underset{|}{Si}}{-}Cl}$, were not obtained via condensation of Si-Cl bond of dichlorosilanes with ammonia, which generally prepared from equilibrium reaction between cyclosilazanes and diorganodichlorosilanes. Silbiger[9] first reported reaction of hexamethyldisilazane with dimethyldichlorosilane in the presence of $AlCl_3$ as the catalyst and 1,3-dichloro-1,1,3,3-tetramethyldisilazane were obtained. Bacqué and Pillot[10] also studied trans-silylation reaction between hexamethyldisilazane and dimethyldichlorosilane, results shown that no reaction occurred without catalyst. However, in the presence of $(^nBu_4N)F$, the reaction took place smoothly.

As important starting materials in the preparation of polysilazanes containing linear-cyclic structure, 1,3-dichlorodisilazanes were re-investigated in our work. We first examined the reaction between $(Me_3Si)_2NH$ and $MeViSiCl_2$ without a catalyst. As expected, $(ClMeViSi)_2NH$ was obtained in good yield after heating under reflux for a few hours. It is necessary to indicate that the another product, Me_3SiCl must be continuously distilled off during the reaction.

$$(Me_3Si)_2NH + 2MeViSiCl_2 \xrightarrow{\text{refl.}} (ClMeViSi)_2NH + 2Me_3SiCl \qquad (1)$$

Then we studied the reaction of $(Me_3Si)_2NH$ and Ph_2SiCl_2. To the best of our knowledge, there have been no available reports on this reaction. With the 1:2 ratios of $(Me_3Si)_2NH$ to Ph_2SiCl_2, no catalyst, the reaction occurred smoothly, and completed after 17 hours. A new synthetic way with good yields to $(ClPh_2Si)_2NH$ was given in our previous work.[11] However, the reaction needs long heated time (50 h) and a large excess of Ph_2SiCl_2, furthermore, another reactant, cyclosilazane, is much more expensive than $(Me_3Si)_2NH$.

Based on the above reactions, we assumed that it might be feasible to prepare $(ClMe_2Si)_2NH$ via this method. Thus, the reaction between $(Me_3Si)_2NH$ and Me_2SiCl_2 without catalyst was re-examined. In contrast with literature,[9,10] the reaction occurred under the condition that we adopted. There were resonance of the expected $(ClMe_2Si)_2NH$ and Me_3SiCl in ^{29}Si NMR spectra of the reaction mixture.

Bacqué[10] suggested that for the redistribution reaction between $(Me_3Si)_2NH$ and $HRSiCl_2$, the first trimethylsilyl-group exchange may be reversible. The analogous conclusion also can be inferred for the reaction of $(Me_3Si)_2NH$ and $RR'SiCl_2$.

$$(Me_3Si)_2NH + RR'SiCl_2 \rightleftarrows ClRR'Si\text{-}NH\text{-}SiMe_3 + Me_3SiCl \tag{2}$$

$$ClRR'Si\text{-}NH\text{-}SiMe_3 + RR'SiCl_2 \rightarrow ClRR'SiNHSiRR'Cl + Me_3SiCl \tag{3}$$

With Me_3SiCl distilled off, the equilibrium as depicted in eqn. (2) could be apt to transfer to right, which lead to more intermediate $ClRR'Si\text{-}NH\text{-}SiMe_3$. Then the trimethylsilyl group of the intermediate was substituted by another mixed-silicon ligand,[10] -SiRR'Cl, and the product $(ClRR'Si)_2NH$ was gained, which is more stable thermodynamically.

EXPERIMENTAL

IR spectroscopy was recorded on FT-IR spectrophotometer, PE-80. ^1H-NMR and ^{29}Si-NMR were performed on Unity 200 MHz, USA. Element Analysis was measured with Heraeus CHN-RAPID, systems, Inc (West Germany). Toluene and n-hexane were commercially available and of analytical purities, which were dried over sodium under reflux and distilled before used. Methylvinyldichlorosilane, dimethyldichlorosilane, diphenyldichlorosilane and hexamethyldisilazane were distilled and reserved in dry container before used. The samples were protected with dry nitrogen during the process of measurements. $CDCl_3$ used in ^1H-NMR and ^{29}Si-NMR was dried with CaO. Tetramethylsilane (TMS) was used as external reference for ^{29}Si-NMR.

General Procedure

RR′SiCl$_2$ (2 mol) and (Me$_3$Si)$_2$NH (1 mol) were mixed in a three-necked flask equipped with a stir-bar, a N$_2$ gas inlet tube, a thermometer and a fractionating column, which connected with a distillation apparatus. The mixture was heated under reflux, and at the same time, the by-product Me$_3$SiCl was removed by distillation. When the reaction was completed, for R = Me, R′ = Vi or R = R′ = Me, the fractionating column was then replaced by a short Vigreux column connected to vacuum line via a receiver and a liquid nitrogen trap, as the mixture was heated, (ClRR′Si)$_2$NH were collected in the receiver. For R = R′ = C$_6$H$_5$, the precipitated crystals were filtered off and washed with hexane, crude (ClPh$_2$Si)$_2$NH were obtained.

1,3-Dichloro-1,3-dimethyl-1,3-divinyldisilazane DMDV. According to the general procedure, a mixture of (Me$_3$Si)$_2$NH (35.9 g, 0.22 mol) and MeViSiCl$_2$ (62.5 g, 0.44 mol) was heated under reflux accompanied with Me$_3$SiCl distilled off. The reaction was completed after 20 hours. As the mixture was heated, DMDV was condensed in the receiver (35.5 g, 70%). ^{1}H NMR (CDCl$_3$), δ (ppm): 0.57 (s, 6H, $C\underline{H}_3$); 1.7 (broad, m, 1H, $N\underline{H}$); 5.9–6.2 (s, 6H, $C\underline{H}C\underline{H}_2$). ^{29}Si NMR (CDCl$_3$), δ (ppm): 1.20 (s, $N\underline{Si}$MeViCl). Anal. Cald. for $C_6H_{13}Cl_2NSi_2$: C, 31.86; H, 5.75; N, 6.19; Cl, 31.42. Found: C, 31.78; H, 5.76; N, 6.19; Cl, 31.22%.

1,3-Dichloro-1,1,3,3-tetraphenyldisilazane DCTPS. According to the general procedure, a mixture of (Me$_3$Si)$_2$NH (19.9 g, 0.12 mol) and Ph$_2$SiCl$_2$ (62.5 g, 0.24 mol) was heated under reflux accompanied Me$_3$SiCl distilled off. The reaction was completed after 17 hours. Then the precipitated crystals were filtered off at room temperature and washed with hexane. The crude product was recrystallized from the mixed solvent of hexane and toluene to give 43.5 g (78%) of pure DCTPS as white crystals. m.p. 117.1°C. ^{1}H-NMR (CDCl$_3$), δ (ppm): 2.5 (s, 1H, $N\underline{H}$); 7.2–7.6 (m, 20H, $(C_6\underline{H}_5)_4$). ^{29}Si-NMR (CDCl$_3$), δ (ppm): −7.5 (s, $N\underline{Si}(C_6H_5)_2Cl$). Anal. Cald. for $C_{24}H_{21}Si_2NCl_2$: C, 64.00; H, 4.67; N, 3.11; Cl, 15.78. Found: C, 63.70; H, 4.56; N, 2.91; Cl, 15.49%.

1,3-Dichloro-1,1,3,3-tetramethyldisilazane TMDS. According to the general procedure, a mixture of (Me$_3$Si)$_2$NH (32.2 g, 0.20 mol) and Me$_2$SiCl$_2$ (51.6 g, 0.40 mol) was heated under reflux accompanied with Me$_3$SiCl distilled off. The reaction was completed after 20 hours. As the mixture was heated, TMDS was condensed in the receiver (19.8 g, 49%). ^{1}H NMR (CDCl$_3$), δ (ppm): 0.27 (s, 12H, $C\underline{H}_3$); 1.2 (broad, m, 1H, $N\underline{H}$).

^{29}Si NMR ($CDCl_3$), δ (ppm): 13.70 (s, $N\underline{Si}Me_2Cl$). Anal. Cald. for $C_4H_{13}Cl_2NSi_2$: C, 23.76; H, 6.44; N, 6.93; Cl, 35.15. Found: C, 23.58; H, 6.36; N, 6.79; Cl, 34.92%.

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