Diaminosilanes \((\text{CH}_3)_2\text{Si}(\text{NHR})_2\) 1a, b are obtained from dichlorodimethylsilane and primary amines (\(R = n\)-hexyl, iso-propyl) in good yields. Bis-insertion of CO\(_2\) into the Si–N bonds of the aminosilanes quantitatively gives the silylcarbamates \((\text{CH}_3)_2\text{Si}(\text{OCONHR})_2\), 2a, b. Oligo- and polydimethylsiloxanes 3a, b as well as \(N,N'\)-substituted ureas \(\text{CO(NHR)}_2\) 4a, b are formed upon heating the silylcarbamates 2a, b to \(\sim 150^\circ\)C. The results of comprehensive NMR analyses of the aminosilanes, the two novel bis-silylcarbamates, the siloxanes and the ureas, and of single-crystal structure analyses of 2a and 4b are presented. In the crystal the \(n\)-hexyl silylcarbamate 2a shows a similar molecular packing arrangement as the iso-propyl urea derivative 4b.

Key words: Polysiloxane, Silylamine, CO\(_2\) Insertion, Silylcarbamates, Crystal Structure