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Pentacoordinate hydrochlorosilanes with lactamomethyl ligand

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Abstract

The synthesis and reaction behavior of pentacoordinate hydrochlorosilanes $LCH_2SiRHCl$ (L- 2-piperidonyl ligand, R = Me, Ph, Bn) are described. The intramolecular O–Si and N–Si coordination is discussed on the basis of the NMR data. The strength of the O–Si coordinate bond is nearly the same for chelates **5**, **6**, **8** irrespective of the equatorial substituent R at the silicon atom. However, the nature of R substituent markedly affects the stability of the complexes with the N–Si intramolecular bond.

Keywords: Pentacoordinate silicon compounds; Silicon hydrides

1. Introduction

Pentacoordinate organosilicon compounds with amidomethyl or lactamomethyl ligands having the O–Si dative bond have been the subject of extensive synthetic and structural investigations [1–7]. The results of these studies made an important contribution to the understanding mechanism of the nucleophilic substitution at silicon [1,2,4,5,8]. It has been found that the extent of the O–Si intramolecular bonding in pentacoordinate monofunctional silanes LCH_2SiMe_2X (L – amido or lactamo donor group) depends on the nature of the donor amide group as well as the electronegativity and the leaving group ability of the axial ligand X (X = halogen, OAlk, OAr, OTf) [1,4]. The presence of the electronegative ligand in the equatorial position results in strengthening the oxygen-silicon coordination. Thus, the O–Si and Si–Cl axial bonds become shorter on going from *N*-(dimethylchlorosilylmethyl)- to *N*-(methyldichlorosilylmethyl)hexahydroazepinone-2 [9]. Nearly the same effect is observed by changing the methyl group by a methoxy group [9]. However the presence of a fluorine atom in the equatorial position has no profound effect on the Si–O hypervalent bonding in pentacoordinate chelates bearing acetamidomethyl or lactamomethyl ligands. Pentacoordinate (O–Si) complexes LCH_2SiMeF_2 derived from *N*-methylacetamide [10], *N*-(1-phenylethyl)acetamide [11], piperidone-2 [10] and hexahydroazepinone-2 [11] have similar ^{29}Si chemical shifts (55.5 ppm). The differences in the coordination shift $\Delta\delta^{29}Si$ for related pentacoordinate monofluoro and difluoro compounds are small (1–2 ppm). This indicates that the fluoro derivatives are not susceptible to changes in the amide ligand [12] and the presence of the second fluorine atom at silicon.

There are only few data for the variation in non-electronegative organic substituents at silicon in amide-type pentacoordinate complexes. By ^{29}Si NMR data, the O–Si interaction increases by changing the methyl group by the electron withdrawing phenyl group in monochloro derivative of *N*-methylacetamide [13,14] or monofluoro derivative of *N*-(1-phenylethyl)acetamide [14]. Introduction of a α-naphthyl group instead of the methyl one in the ligand environment at silicon results in shortening the O–Si bond length (by 0.02 Å) [15]. According to X-ray and ^{29}Si NMR data, replacing two equatorial methyl groups by two electron-donating trimethylsilyl groups in pentacoordinate chelate derived from *N*-methylacetamide does not affect

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the strength of the O–Si bond [16]. Although a broad range of pentacoordinate silicon hydrides were described [2,17–22], the amide-containing complexes having a Si–H bond are unknown until now. Meanwhile an additional Si–H bond provides further potential site for ligand substitutions that might lead to novel hypervalent silicon compounds.

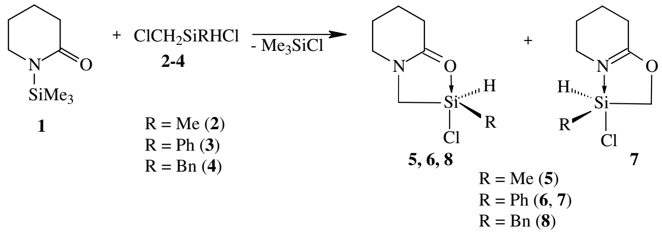
In this paper, we report synthesis, structure and some chemical transformations of new pentacoordinate hydrochlorosilanes obtained from piperidone-2. Variation in organic substituents at silicon allowed to study their effect on the formation of the intramolecular coordinate bond between the silicon atom and the oxygen or nitrogen atoms of the bidentate amide ligand.

2. Results and discussion

2.1. Synthesis

The pentacoordinate hydrochlorosilanes (**5–8**) were prepared by transsilylation reaction of *N*-trimethylsilylpiperidone-2 (**1**) by the appropriate (chloromethyl)silane derivatives $ClCH_2SiRHCl$ (**2–4**) (Scheme 1) using the method described previously [1,5–7]. The reaction product depends on the nature of R substituent. Thus, methyl(chloromethyl)hydrochlorosilane (**2**) reacts readily with (**1**) in hexane at room temperature to afford (O–Si) chelate (**5**) in high yield (65%). Reaction of (**1**) with phenyl substituted silane (**3**) gave a 4.5:1 mixture of isomeric pentacoordinate chelates (**6**) and (**7**) in 87% yield. It follows from the ^1H NMR spectrum of the crude reaction mixture which shows two sets of resonance with similar chemical shifts. The minor and major components were assigned to the (N–Si) and (O–Si) chelates (**7** and **6**, respectively) by comparison of their ^1H, ^{13}C and ^{29}Si NMR data with those for (N–Si) and (O–Si) dimethyl(chloro)silylmethyl chelates [23]. Compound (**8**) with the O–Si coordinate bond was obtained as the sole product from similar reaction of benzyl substituted silane (**4**) with (**1**).

To have a better understanding of the possible routes of the formation of complex (**6**), the reaction between *N*-silyllactam (**1**) and hydrochlorosilane (**3**) was monitored by ^1H and ^{29}Si NMR spectroscopy. When a 10% w/w solution of compound (**1**) in $CDCl_3$ was titrated with sufficient amount of (**3**) at room temperature, the simultaneous appearance of two sets of the chemical shifts in a 2.5:1 ratio for the chelates (**6**) and (**7**) are observed. Predominance of (**6**) over (**7**) became considerably higher (5.6:1) after heating the NMR sample at 40 °C for 1 h. The complete conversion of (**7**) into (**6**) occurs over 2 days at room temperature so that pure (O–Si) chelate (**7**) was isolated and characterized. The remained signals in the ^1H, ^{13}C, ^{15}N and ^{29}Si spectra of the crude product were assigned to (N–Si) chelate (**7**).

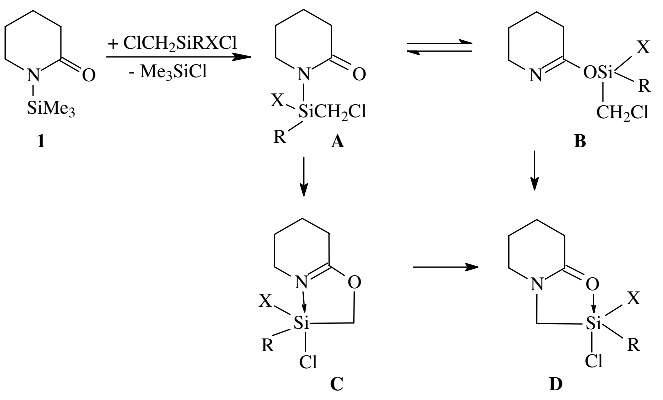


Scheme 1.

Mechanism of the formation of the (O–Si) chelates have been studied for the reaction of (**1**) with $ClCH_2SiMe_2Cl$ by ^1H, ^{13}C and ^{29}Si NMR monitoring at low temperature (Scheme 2) [1,4,5,23,24]. As was shown previously, silylated amides and lactams can exist in the N- and O-tautomer forms (Scheme 2, **A** and **B** structure, respectively). Their ratio depends on the electronic and steric effects of the substituents at silicon [25–27]. Compound (**1**) as well as the transsilylation product **A** (R = X = Me) have N-tautomer structure in CH_2Cl_2 and $CHCl_3$ solutions [4,23,28]. In this case the main reaction pathway involves rearrangement of **A** into *O*-silylmethylated compound **C** at low temperature (−20°C). The latter proved to be quite unstable at room temperature and readily converted into *N*-silylmethylated chelate **D** within 5-10 min [1,23,24]. Similar successive reaction sequence can be suggested for the formation of the (O–Si) pentacoordinate chelate (**5**).

Replacement of the methyl group by the electron-withdrawing phenyl group increases the population of *O*-silylated imidate (structure **B**) [27]. In this case the reaction proceeds via parallel conversions of the corresponding *N*- and *O*-transsilylated tautomers **A** and **B** into (N–Si) and (O–Si) chelates (**7**) and (**6**), respectively. Moreover, chelate (**6**) with the O–Si intramolecular bond arises mainly from *O*-silylated tautomer that is confirmed by appreciable stability of chelate (**7**) at room temperature. Such a way to the (O–Si) pentacoordinate complexes has been previously proposed as minor one for X = R = Me [1,23,24]. The imidate form, apparently, becomes more unfavorable on going from the phenyl to the benzyl derivative. As a consequence, benzyl substituted chelate (**8**) is formed via pathway **A** → **C** → **D** as in the case of chelate (**5**).

Compound (**7**) is the first example of stable at ambient temperature pentacoordinate complexes of the *O*-imidate structure. Previously related stable complexes were described for germanium and tin derivatives [5,29–31].



Scheme 2.