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ScienceDirect
Journal of Organometallic Chemistry 692 (2007) 2160–2167
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Pentacoordinate hydrochlorosilanes with lactamomethyl ligand

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Received 14 November 2006; received in revised form 17 January 2007; accepted 22 January 2007
Available online 30 January 2007

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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✠ Prof. V.A. Pestunovich who inspired this work deceased July 4, 2004.

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doi:10.1016/j.jorganchem.2007.01.035

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

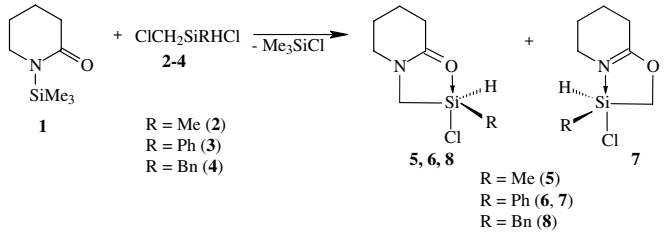
The pentacoordinate hydrochlorosilanes (**5–8**) were prepared by transsilylation reaction of *N*-trimethylsilylpiperidone-2 (**1**) by the appropriate (chloromethyl)silane derivatives $ClCH_2SiRHCl$ (**2–4**) (Scheme 1) using the method described previously [1,5–7]. The reaction product depends on the 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**).

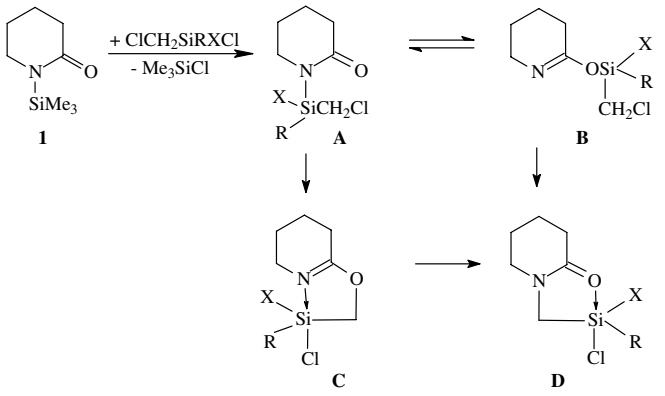
Mechanism of the formation of the (O–Si) chelates have been studied for the reaction of (**1**) with $ClCH_2SiMe_2Cl$ by ^1H, ^{13}C and ^{29}Si NMR monitoring at low temperature (Scheme 2) [1,4,5,23,24]. As was shown previously, silylated amides and lactams can exist in the N- and O-tautomer forms (Scheme 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 1.



Scheme 2.

2.2. Structure and coordination behavior

The structure of the novel (N–Si) and (O–Si) chelates (**5–8**) in solution was determined by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy. In the ^{1}H NMR spectra of chelates (**5–8**) the H–Si proton resonances are shifted to lower field (by 0.4–1.3 ppm) relative to those for initial silanes (**2–4**). The resonance of $SiCH_2N$ methylene protons for all chelates as well as silanes (**2–4**) appears as AB quartet due to the chirality of the silicon atom. Moreover, in the ^{1}H NMR spectra of all chelates coupling H(Si) proton with a *trans*-oriented methylene proton results in a further splitting high-field doublet of AB quartet into two doublets ($^{3}J = 2.5$–5.5 Hz).

^{1}H NMR spectrum of a 4.5:1 mixture of compound (**6**) and (**7**) shows the two signals at 2.93 and 4.08 ppm attributed to the $SiCH_2N$ and $SiCH_2O$ units. The H–Si proton resonance for (**7**) is observed at higher field relative to that for (**6**) (Fig. 1).

As the temperature of the solution of (**6**) in $CD_3C_6D_5$ increased to 80 °C no changes in the ^{1}H NMR signals of $SiCH_2N$ protons was observed. This suggests a high barrier for fluxional ligand exchanges at the chiral silicon atom.

The imidate structure for chelate (**7**) is supported by the ^{13}C and ^{15}N NMR spectral data. The ^{13}C NMR spectrum exhibits signals at 57.92 and 172.40 ppm for OCH_2Si and N=C–O groups, respectively. The difference in ^{13}C chemical resonances of a conjugate unit for chelates (**6**) and (**7**) is small (1 ppm) because of involving one or another heteroatom in the coordination bonding. The same difference for triorganosilylated amides and imidates is considerably greater (15 ppm) [27].

The ^{15}N NMR resonance for chelate (**7**) is shifted upfield relative to the range typical of *O*-silylated imidates [25] that is due to the formation of the N–Si intramolecular dative bond. For chelate (**6**) the ^{15}N signal (245.4 ppm) is shifted in lower field as compared with that of piperidone-2 (114 ppm) because of increased π-character of the N–C bond in amide-type chelates [13].

The important ^{29}Si NMR spectroscopic data are presented in Table 1. The corresponding data for the model tetravalent silanes are listed for comparison.

The ^{29}Si resonances of the chelates (**5–8**) are markedly shifted upfield from those of starting hydrochlorosilanes (**2–4**) as typical for pentacoordinate silicon compounds [32]. The J(Si–H) coupling constants for all compounds are significantly increased to those of the initial tetracoordinate silanes (**2–4**) that also suggests pentacoordination at silicon [32,33].

For $LCH_2SiMeRCl$ (L-2-piperidonyl ligand) the coordination shift is greater for R = H (**5**, $\Delta\delta^{29}Si = 68.05$ ppm) than that found for R = Me ($\Delta\delta^{29}Si = 59.98$ ppm) [5,6] indicating stronger O–Si intramolecular bonding in compounds having SiMeHCl fragment in comparison to those with $SiMe_2Cl$ unit. This is the result of the enhanced acceptor ability of the silicon atom on the replacement of the methyl group by a hydrogen atom [17,34,35].

The strength of the O–Si coordinate bond as measured by the $\Delta\delta^{29}Si$ values (Table 1) is nearly the same for chelates (**5**), (**6**) and (**8**) with SiCRHCl coordination framework irrespective of the R substituent at the silicon atom. However, the stability of the (N–Si) chelates is markedly affected by the nature of the equatorial R organic group.

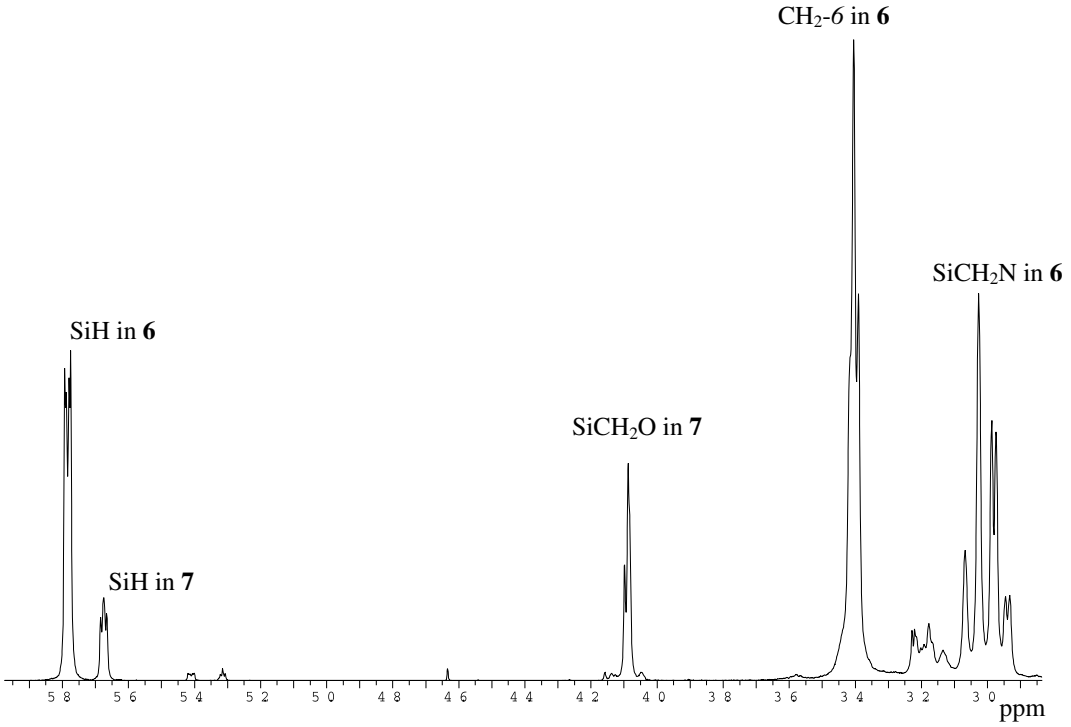


Fig. 1. Part of ^{1}H NMR spectrum for a 4.5:1 mixture of (**6**) and (**7**) in $CDCl_3$.

Table 1
^{29}Si NMR data for pentacoordinate complexes **5–8** and model compounds in $CDCl_3$ solution (δ, ppm; J, Hz)

Complexes	δ^{29}Si	J(SiH)	Initial silanes	δ^{29}Si	J(SiH)	$\Delta\delta^{29}$Si
5	−64.09	286.44	**2**	3.96	234.72	68.05
6	−74.35	298.7	**3**	−5.55	246.34	68.80
7	−83.30	286.90	**3**			77.75
8	−67.05	298.6	**4**	1.60	243.10	68.60

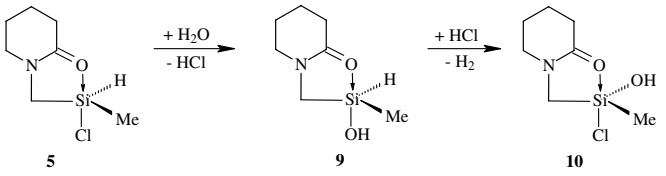
2.3. Chemical behavior

An enhanced reactivity of Si–Cl bond is typical for hypervalent silicon compounds compared to tetravalent derivatives [19]. As a consequence, pentacoordinate hydrochlorosilane obtained are susceptible to hydrolysis. Thus, complex (**5**) is very sensitive to moisture. Even trace amounts of H_2O in $CDCl_3$ solution results in its partial hydrolysis (~10%). ^{1}H NMR spectrum shows the additional resonance of the Me–Si protons (singlet at 0.69 ppm) and the excess integral intensity of the ring proton signals in reference to that of the Si–H signal. This points to the formation of hydrolysis product having no Si–H bond. The gradual decrease in intensity of the H(Si) resonance in the ^{1}H NMR spectrum of compound (**5**) is accompanied by appearance of a new signal at 6.70 ppm assigned to a silanol group.

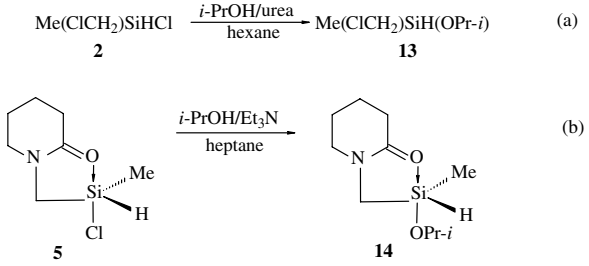
Complex (**8**) is hydrolytically highly unstable and decomposed rapidly on exposure to air moisture. As monitored by ^{1}H and ^{29}Si NMR spectroscopy, its hydrolysis proceeds much faster as compared to that of chelate (**5**). In the ^{29}Si NMR spectrum of $CDCl_3$ solution of (**8**) one new signal appears at −67.60 ppm assigned to hydrolysis product. To avoid hydrolysis in the NMR samples, it is necessary to use freshly distilled $CDCl_3$ or C_6D_6. Compared with (**5**) and (**8**) pentacoordinate hydrochlorosilane (**6**) appears to be more stable. When the latter complex was kept for one week under an argon atmosphere in a Schlenk flask with a rubber septum, rather intensive peak for H(Si) proton was still observed in its ^{1}H NMR spectrum.

We proposed that the first intermediate detected in the course of the hydrolysis of chelate (**5**) was pentacoordinate chlorosilanol (**10**). Evidence for this species was obtained from comparison of its ^{29}Si chemical shift with that for model pentacoordinate compound, *N*-(methylisopropoxychlorosilylmethyl)piperidone-2 (**12**). The latter was obtained by the reaction of (**1**) with $(ClCH_2)SiMeCl(OPr\text{-}i)$ (**11**) according to Scheme 1 [36]. Both compounds (**10**) and (**12**) have similar ligand environments at the pentacoordinate silicon atom and closely related ^{29}Si resonances (−48.66 and −52.50 ppm, respectively). Note that variations in the ^{29}Si chemical shifts from related silanols to alkoxysilanes are within limits of 2–10 ppm [37,38].

Chlorosilanol (**10**) is presumed to arise from initial conversion of (**5**) into hydrosilanol (**9**) followed by fast H–Cl exchange due to an enhanced reactivity of the hydrogen atom in pentacoordinate silicon complexes, as compared with tetravalent silanes [20,39,40]. Hypervalent hydrosil-



Scheme 3.



Scheme 4.

anes react rapidly with Brönsted acids without any catalyst [20]. Initial hydrolysis of the Si–H bond is less likely taking into account that chlorine is a better leaving group than hydrogen [17]. Further transformations of silanol (**10**) have not been studied (see Scheme 3).

It should be noted that hydrolysis of tetravalent silane (**2**) left the Si–H bond intact to give the corresponding disiloxane $[(ClCH_2)MeSiH]_2O$ (δ^{29}Si −9.32 ppm).

Like initial hydrochlorosilane (**2**), pentacoordinate chelate (**5**) reacts with one equivalent of isopropyl alcohol in the presence of triethylamine at 0 °C (Scheme 4a, b) to afford desired monosubstituted isopropoxysilane (**14**) in 40% yield. The ^{29}Si resonance of this compound shows small upfield shift ($\Delta\delta = 10$ ppm) relative to that of tetracoordinate silane $Me(ClCH_2)SiH(OPr\text{-}i)$ (**13**). Furthermore, the J(SiH) coupling for (**14**) is slightly increased in comparison to that for (**13**). According to these data, a weak O–Si intramolecular interaction exists in compound (**14**).

In summary, a series of new amide-type pentacoordinate silicon compounds with $SiOC_2HCl$ framework have been synthesized. The study of these complexes appears to be quite promising, because variations in organic substituents at silicon offer the possibility to prepare stable N–Si complexes unknown so far. Further studies to investigate this aspect are in progress.

3. Experimental

3.1. General comments

All reactions and other manipulations were carried out using standard Schlenk techniques under an argon atmosphere. Diethyl ether and tetrahydrofuran were purified by distillation from sodium/benzophenone ketyl; *n*-hexane, benzene, triethylamine were distilled from calcium hydride. $CDCl_3$ was distilled from calcium hydride and kept over 4 Å molecular sieves. NCS and piperidone-2 were pur-

chased from Lancaster and Merck, respectively, and used without further purification. Melting points were measured in sealed capillaries. The ^{1}H, ^{13}C, ^{15}N, and ^{29}Si NMR spectra were recorded on a Brucker DPX-400 spectrometer (^{1}H, 400.1 MHz; ^{13}C, 100.6 MHz; ^{15}N, 40.5 MHz; ^{29}Si, 79.5 MHz) at room temperature. $CDCl_3$ or C_6D_6 were used as the solvent. Chemical shifts (ppm) were determined relative to internal $CHCl_3$ (^{1}H, δ 7.27; $CDCl_3$), internal $CDCl_3$ (^{13}C, δ 77.0, $CDCl_3$), internal C_6HD_5(^{1}H, δ 7.28, C_6D_6), internal C_6D_6 (^{13}C, δ 128.0, C_6D_6), or external TMS (^{29}Si, δ 0; $CDCl_3$, C_6D_6). The ^{15}N chemical shifts are referred to resonance of CH_3NO_2 (^{15}N, δ 0.0). Analysis and assignment of the ^{1}H NMR data were supported by homonuclear (COSY) and heteronuclear (HSQC ^{13}C–^{1}H, HMBC ^{13}C–^{1}H) 2D correlation experiments.

3.2. Synthesis of organyl(chloromethyl)dichorosilanes

3.2.1. Methyl(chloromethyl)dichlorosilane was commercially available

3.2.2. Phenyl(chloromethyl)dichlorosilane

The compound was prepared following a common literature procedure [41,42].

Phenylmagnesium bromide prepared from magnesium powder (4.8 g, 200 mmol) and bromobenzene (34.42 g, 200 mmol) in anhydrous Et_2O (75 ml) was added dropwise to (chloromethyl)trichlorosilane (36.78 g, 200 mmol) in ether (50 ml) at room temperature. The mixture was refluxed for 4.5 h, magnesium salts were filtered and washed with anhydrous ether and benzene. Removal of the solvents by rotary evaporation followed by vacuum distillation gave a crude product (23.04 g, b.p. 104–110 °C/6 mm Hg) containing $Ph(ClCH_2)SiCl_2$ (by NMR, 96%, 22.04 g, 97 mmol, 49% yield). Lit. [42]: b.p. 110–118 °C/12 mm Hg. ^{1}H NMR ($CDCl_3$): δ 3.32 (s, 2H, $SiCH_2Cl$), 7.48 (m, 2H, H_m), 7.56 (m, 1H, H_p), 7.78 (m, 2H, H_o). ^{29}Si NMR ($CDCl_3$): δ 7.15.

Crude product was used without further purification for preparation of $Ph(ClCH_2)SiH_2$.

3.2.3. Benzyl(chloromethyl)dichlorosilane

The compound was prepared according to a modified literature procedure [41,43].

The Grignard reagent prepared from benzyl chloride (30.80 g, 197 mmol) and magnesium powder (4.80 g) in anhydrous Et_2O (150 ml) was added to (chloromethyl)trichlorosilane (29.00 g, 157 mmol) in ether (70 ml). The mixture was refluxed for 4.5 h, cooled, filtered, and fractionally distilled to give $Bn(ClCH_2)SiCl_2$ (18.87 g, 83 mmol, 42% yield), b.p. 102–106 °C/1 mm Hg. ^{1}H NMR ($CDCl_3$): δ 2.90 (s, 2H, CH_2Ph), 3.11 (s, 2H, $SiCH_2Cl$), 7.38 (m, 2H, H_m), 7.29 (m, 3H, H_o, H_p). ^{13}C NMR ($CDCl_3$): δ 6.84 (CH_2Ph), 28.83 ($SiCH_2Cl$), 126.27 (C_p), 128.87 (C_o), 129.06 (C_m), 133.03 (C_i). ^{29}Si NMR ($CDCl_3$): δ 6.22. Anal. Found: C, 41.64; H, 3.81; Si, 11.52. Calc. for $C_8H_9Cl_3Si$: C, 40.10; H, 3.79; Si, 11.72%.

3.3. Synthesis of organyl(chloromethyl)dihydrosilanes

3.3.1. General procedure: Methyl(chloromethyl)dihydrosilane

Methyl(chloromethyl)dichlorosilane (32.7 g, 0.2 mol) was added to $LiAlH_4$ (4.5 g, 0.12 mmol) in 100 ml dibutyl ether at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for additional 30 min. When the resulting white precipitate was settled, the upper ether solution was decanted to a dropping funnel and added to 400 ml of 10% aqueous HCl with cracked ice. After stirring for 30 min, the organic phase was separated and the aqueous layer was extracted with dibutyl ether (2 × 20 ml). The combined organic extracts were dried over anhydrous $MgSO_4$ and filtered off. A column distillation afforded methyl(chloromethyl)dihydrosilane in 40% yield (7.64 g, 0.08 mol) as a colorless liquid, b.p. 59 °C, n_D^{20} 1.4220. Lit. [44]: b.p. 60°C, n_D^{20} 1.4184. ^{1}H NMR ($CDCl_3$): δ 0.31 (t, 3H, $MeSi$, $^{3}J = 4.10$ Hz), 2.96 (t, 2H, $SiCH_2Cl$, $^{3}J = 3.05$ Hz), 3.97 (qt, 1H, SiH). ^{1}H NMR data are consistent with the literature data [45]. ^{13}C NMR ($CDCl_3$): δ−9.55 ($MeSi$), 25.91 ($SiCH_2Cl$). ^{29}Si NMR ($CDCl_3$): δ−33.80.

Phenyl(chloromethyl)dihydrosilane and *benzyl(chloromethyl)dihydrosilane* were obtained following the same procedure. Diethyl ether was used as a solvent.

3.3.2. Phenyl(chloromethyl)dihydrosilane

The compound (4.10 g, 26.3 mmol, 56% yield) was obtained from $Ph(ClCH_2)SiCl_2$ (9.54 g, 42.3 mmol) as a clear, colorless liquid, b.p. 71–73 °C/6 mm Hg. ^{1}H NMR ($CDCl_3$): δ 3.12 (t, 2H, $SiCH_2Cl$, $^{3}J = 3.32$ Hz), 4.54 (t, 2H, SiH, $^{1}J(SiH) = 206.08$ Hz), 7.40 (m, 2H, H_m), 7.46 (m, 1H, H_p), 7.64 (m, 2H, H_o). ^{13}C NMR ($CDCl_3$): δ 25.09 ($SiCH_2Cl$), 128.31 (C_m), 129.50 (C_i), 130.57 (C_p), 135.55 (C_o). ^{29}Si NMR ($CDCl_3$): δ−31.85. Anal. Found: C, 53.98; H, 5.88; Si, 17.09. Calc. for C_7H_9ClSi: C, 53.66; H, 5.79; Si, 17.93%.

3.3.3. Benzyl(chloromethyl)dihydrosilane

This compound was prepared from $Bn(ClCH_2)SiCl_2$ (2.41 g, 10 mmol) in 62% yield (1.06 g, 62.3 mmol). Colorless liquid, b.p. 73–74 °C/3 mm Hg. ^{1}H NMR ($CDCl_3$): δ 2.45 (t, 2H, CH_2Ph, $^{3}J = 3.42$ Hz), 2.91 (t, 2H, $SiCH_2Cl$, $^{3}J = 2.69$ Hz), 4.08 (tt, 2H, SiH, $^{1}J(SiH) = 203.2$ Hz), 7.17 (m, 2H, H_o), 7.18 (m, 1H, H_p), 7.30 (m, 2H, H_m) ^{13}C NMR ($CDCl_3$): δ 16.89 (CH_2Ph), 23.58 ($SiCH_2Cl$), 124.67 (C_p), 127.78 (C_o), 128.32 (C_m), 137.73 (C_i). ^{29}Si NMR ($CDCl_3$): δ−28.15. Anal. Found: C, 55.89; H, 6.54; Si, 16.25. Calc. for $C_8H_{11}ClSi$: C, 56.28; H, 6.49; Si, 16.45%.

3.4. Preparation of organyl(chloromethyl)hydrochlorosilanes

3.4.1. General procedure: Methyl(chloromethyl)hydrochlorosilane (**2**)

N-chlorosuccinimide (13.35 g, 100 mmol) was added to a solution of $Me(ClCH_2)SiH_2$ (9.39 g, 100 mmol) in

CH_2Cl_2 (20 ml) at 0 °C over a period of 1 h, and the resulting mixture was allowed to warm gradually to room temperature and stirred for 1.5 h. After the precipitate was filtered, the residue was fractionally distilled to give **2** (8.37 g, 65 mmol, 65% yield) as a colorless liquid, b.p. 94-95°C, n_D^{20} 1.4415. Lit. [46] b.p. 95–97 °C, n_D^{20} 1.4395. ^{1}H NMR ($CDCl_3$): 0.65 (d, 3H, *Me*Si, $^3J = 3.1$ Hz), 3.00, 3.08 (dd, 2H, SiC*H*$_2$Cl, $^2J = 13.83$ Hz, $^3J = 4.40$ Hz, $^3J = 1.28$ Hz), 4.86–4.90 (dqd, 1H, Si*H*, *J*(SiH) = 234.72 Hz). ^{13}C NMR ($CDCl_3$): δ−2.06 (*Me*Si), −28.50 (Si*C*H$_2$Cl).

Preparation of hydrochlorosilanes **3** and **4** was carried out at room temperature.

3.4.2. Phenyl(chloromethyl)hydrochlorosilane (3)

The compound was prepared from $Ph(ClCH_2)SiH_2$ (2.00 g, 12.8 mmol) in 81% yield. Colorless oil, b.p. 69–71 °C/2 mm Hg. ^{1}H NMR ($CDCl_3$): δ 3.21, 3.24 (dd, 2H, SiC*H*$_2$Cl, $^2J = 14.07$ Hz, $^3J = 3.32$ Hz, $^3J = 2.38$ Hz), 5.32 (dd, 1H, Si*H*, ^1J(SiH) = 246.34 Hz), 7.47 (m, 2H, H_m), 7.54 (m, 1H, H_p), 7.73 (m, 2H, H_o). ^{13}C NMR ($CDCl_3$): δ 27.72 (Si*C*H$_2$Cl), 128.36 (C_m), 129.12 (C_i), 131.33 (C_p), 133.86 (C_o). Anal. Found: C, 44.76; H, 4.36; Si, 14.42. Calc. for C_7H_8ClSi: C, 43.99; H, 4.22; Si, 14.69%.

3.4.3. Benzyl(chloromethyl)hydrochlorosilane (4)

This compound was obtained from the corresponding dihydrosilane (1.34 g, 7.8 mmol) in 49% yield (0.78 g). Colorless oil, b.p. 88–89 °C/3 mm Hg. ^{1}H NMR ($CDCl_3$): δ 2.60, 2.61 (AB quartet, 2H, C*H*$_2$Ph, $^2J_{AB} = 14.18$ Hz; $^3J = 2.2$ Hz), 2.90, 2.95 (dd, 2H, SiC*H*$_2$Cl, $^2J = 13.94$ Hz, $^3J = 1.22$ Hz, $^3J = 3.67$ Hz), 4.85 (dtd, 1H, Si*H*, *J*(SiH) = 243.1 Hz), 7.14 (d, 2H, H_o, $^3J = 6.85$ Hz), 7.16 (t, 1H, H_p, $^3J = 7.09$ Hz), 7.26 (dd, 2H, H_m). ^{13}C NMR ($CDCl_3$): δ 22.93 (*C*H$_2$Ph), 26.67 (Si*C*H$_2$Cl), 125.85 (C_p), 128.80 (C_o), 128.91 (C_m), 134.80 (C_i). ^{29}Si NMR ($CDCl_3$): δ 1.60. ^{1}H NMR (C_6D_6): δ 2.18, 2.20 (AB quartet, 2H, C*H*$_2$Ph, $^2J_{AB} = 14.43$ Hz; $^3J = 2.2$ Hz) 2.38 (d, 2H, SiC*H*$_2$Cl, $^3J = 2.69$ Hz), 4.65 (tt, 1H, Si*H*, *J*(SiH) = 242.33 Hz), 6.91 (d, 2H, H_o, $^3J = 7.58$ Hz), 6.96 (t, 1H, H_p, $^3J = 7.34$ Hz), 7.06 (t, 2H, H_m). ^{13}C NMR ($CDCl_3$): δ 22.08 (*C*H$_2$Ph), 25.71 (Si*C*H$_2$Cl), 125.18 (C_p), 128.15 (C_o), 128.24 (C_m), 134.21 (C_i). ^{29}Si NMR ($CDCl_3$): δ 3.31. Anal. Found: Si, 13.76; Cl, 34.33. Calc. for $C_8H_{10}Cl_2Si$: Si, 13.69; Cl, 34.56%.

3.5. Reactions of organyl(chloromethyl)hydrochlorosilanes with N-trimethylsilylpiperidone-2 (1)

3.5.1. General procedure: Preparation of N-(methylhydrochlorosilylmethyl)piperidone-2 (5)

A solution of (**2**) (1.29 g, 10 mmol) in hexane (10 ml) was added to a solution of (**1**) (1.71 g, 10 mmol) in hexane (15 ml) at room temperature. The resulting white suspension was stirred for 1 h. The solvent was decanted off and the residue was washed with hexane (2 × 5 ml) and dried under vacuum to yield (**5**) (1.14 g, 60%) as a white crystals, m.p. 53–54 °C (dec.). ^{1}H NMR ($CDCl_3$): δ 0.64 (d, 3H, *Me*Si, $^3J = 1.83$ Hz), 1.87-1.91 (m, 4H, C*H*$_2$-4,5), 2.46 (m, 2H, C*H*$_2$-3), 2.74, 2.80 (dd, 2H, NC*H*$_2$Si, $^2J = 16.16$ Hz, $^3J = 5.48$ Hz), 3.42 (t, 2H, C*H*$_2$-6, $^3J = 5.42$ Hz), 5.23 (dq, 1H, Si*H*, *J*(SiH) = 286.44 Hz). ^{13}C NMR ($CDCl_3$): δ 6.01 (*Me*Si), 19.48 (*C*-4), 19.64 (*C*-5), 27.76 (*C*-3), 41.43 (N*C*H$_2$Si), 48.76 (*C*-6), 173.70 (N*C*O). Anal Found: C, 43.56; H, 7.29; N, 7.39. Calc. for $C_7H_{14}ClNOSi$: C, 43.85; H, 7.36; N, 7.31%.

3.5.2. N-(phenylhydrochlorosilylmethyl)piperidone-2 (6)

A mixture of chelates (**6**) and (**7**) (0.262 g, 87%, 4.5:1 ratio) was obtained from (**3**) (0.204 g, 11.9 mmol) and (**1**).

Data for (**6**). White crystals, m.p. 89–92 °C. ^{1}H NMR ($CDCl_3$): δ 1.78 (m, 4H, C*H*$_2$-4,5), 2.42 (tt, 2H, C*H*$_2$-3, $^{gem}J \sim {}^{trans}J_{ax} = 18.5$ Hz, $^{trans}J_{eq} \sim {}^{cis}J = 6.0$ Hz), 2.93, 2.97 (dd, 2H, SiC*H*$_2$N, $^2J_{AB} = 16.33$ Hz, $^3J = 5.2$ Hz), 3.65 (m, 2H, C*H*$_2$-6), 5.74 (dd, 1H, Si*H*, *J*(Si*H*) = 298.7 Hz), 7.31 (m, 3H, H_m, H_p), 7.77 (m, 2H, H_o). ^{13}C NMR ($CDCl_3$): δ 18.39 (*C*-4), 21.44 (*C*-5), 26.55 (*C*-3), 39.83 (N*C*H$_2$Si), 47.56 (*C*-6), 126.45 (C_o), 127.36 (C_p), 133.30 (C_m), 138.89 (C_i), 173.40 (N*C*O). ^{15}N NMR ($CDCl_3$): δ−245.4. Anal. Found: C, 56.48; H, 6.56. Calc. for C_7H_8ClSi: C, 56.79; H, 6.36%.

3.5.3. O-(phenylhydrochlorosilylmethyl)piperidone-2 (7)

Data for (**7**). ^{1}H NMR ($CDCl_3$): δ 1.77 (m, 4H, C*H*$_2$-4,5), 2.44 (m, 2H, C*H*$_2$-3), 4.08, 4.11 (dd, 2H, SiC*H*$_2$O, $^2J = 15.58$ Hz, $^3J = 2.42$ Hz), 3.23 (m, C*H*$_2$-6), 5.68 (dd, 1H, Si*H*, *J*(Si*H*) = 286.9 Hz), 7.32 (m, 3H, H_m, H_p), 7.60 (m, 2H, H_o). ^{13}C NMR ($CDCl_3$): δ 17.73 (*C*-4), 20.36 (*C*-5), 24.34 (*C*-3), 57.92 (Si*C*H$_2$O), 40.43 (*C*-6), 126.91 (C_o), 127.36 (C_p), 132.12 (C_m), 138.13 (C_i), 172.40 (N*C*O). ^{15}N NMR ($CDCl_3$): δ−191.8.

3.5.4. N-(benzylhydrochlorosilylmethyl)piperidone-2 (8)

The compound was obtained from (**4**) (0.105 g, 0.51 mmol) in 87% yield as colorless crystals, m.p. 59–61 °C. ^{1}H NMR (C_6D_6): 0.71 (m, 2H, C*H*$_2$-4), 0.77 (m, 2H, C*H*$_2$-5), 1.61 (m, 2H, C*H*$_2$-3), 1.96, 2.11 (m, 2H, C*H*$_2$-6), 2.16, 2.51 (dd, 2H, C*H*$_2$Ph, $^2J = 16.63$ Hz; $^3J = 5.4$ Hz), 2.86, 3.05 (AB quartet, 2H, SiC*H*$_2$N, $^2J = 12.72$ Hz), 6.10 (d, 1H, Si*H*, *J*(SiH) = 295.2 Hz), 7.00 (m, 1H, H_p), 7.11 (m, 2H, H_m), 7.31 (m, 2H, H_o). ^{13}C NMR ($CDCl_3$): δ 19.15 (*C*-4), 21.39 (*C*-5), 27.17 (*C*-3), 31.97 (*C*H$_2$Ph), 39.99 (Si*C*H$_2$N), 47.56 (*C*-6), 124.52 (C_p, $C_6H_5CH_2$), 129.07 (C_o, $C_6H_5CH_2$), 129.57 (C_m, $C_6H_5CH_2$), 140.19 (C_i, $C_6H_5CH_2$), 173.07 (N*C*O). ^{29}Si NMR ($CDCl_3$): δ−66.36. ^{1}H NMR ($CDCl_3$): δ 1.55 (m, 2H, C*H*$_2$-4), 1.69 (m, 2H, C*H*$_2$-5), 2.29 (m, 2H, C*H*$_2$-3), 2.81, 3.11 (m, 2H, C*H*$_2$-6), 2.59, 2.66 (AB quartet, 2H, SiC*H*$_2$N, $^2J = 12.41$ Hz), 2.16, 2.26 (AB quartet, 2H, C*H*$_2$Ph, $^2J = 12.81$ Hz), 5.42 (d, 1H, Si*H*, *J*(SiH) =298.6 Hz), 7.06 (m, 1H, H_p), 7.14 (m, 2H, H_o), 7.19 (m, 2H, H_m). Anal. Found: Si, 10.84; N, 5.51. Calc. for $C_{13}H_{18}ClSiNO$: Si, 10.49; N, 5.23%.

3.6. Synthesis isopropoxysilanes

3.6.1. Methyl(chloromethyl)isopropoxychlorosilane (11)

This compound was prepared from $Me(ClCH_2)SiCl_2$ according to [36]. Physical data and ^1H NMR data are consistent with reported in [36]. ^{13}C NMR ($CDCl_3$): δ 0.82 (*Me*Si), 25.16 (*Me*$_2$CH), 29.25 (Si*C*H$_2$Cl), 67.55 (*C*HO). ^{29}Si NMR ($CDCl_3$): $\delta -1.09$.

3.6.2. N-(methylisopropoxychlorosilylmethyl)piperidone-2 (12)

A solution of (**1**) (0.22 g, 1.33 mmol) in hexane (1 ml) was added to a solution of (**11**) (0.262 g, 1.4 mmol) in hexane (5 ml). After stirring for 40 min, the upper layer was withdrawn by means of a syringe. Removal of the solvent in vacuo gave the crude product as white crystals. ^1H NMR ($CDCl_3$): δ 0.58 (s, 3H, *Me*Si), 1.17 (d, 6H, *Me*$_2$CH, $^3J = 6.12$ Hz), 1.85 (m, 4H, CH$_2$-4,5), 2.49 (m, 2H, CH$_2$-3), 2.72 (s, 2H, SiCH$_2$N), 3.36 (t, 2H, CH$_2$-3), 4.36 (hept, 1H, CHO). ^{13}C NMR ($CDCl_3$): 7.42 (*Me*Si), 19.68 (*C*-4), 21.98 (*C*-5), 25.37 (*Me*$_2$CHO), 27.65 (*C*-3), 42.70 (SiCH$_2$N), 48.66 (*C*-6), 65.75 (*C*HO), 172.65 (N*C*O). ^{29}Si NMR ($CDCl_3$): $\delta -52.5$.

3.6.3. Methyl(chloromethyl)isopropoxysilane (13)

A solution of *i*-PrOH (0.6 g, 10 mmol) in hexane (1 ml) was added to a mixture of (**2**) (1.30 g, 10 mmol), urea (0.61 g, 10 mmol), and hexane (3 ml), and the resulting mixture was stirred at room temperature for 6 h. After the upper layer was separated, the solvent was removed in vacuo and the residue was distilled to give (**13**) (0.4 g, 2.6 mmol, 26% yield), b.p. 132–135 °C. ^1H NMR ($CDCl_3$): δ 0.34 (d, 3H, *Me*Si, $^3J = 2.72$ Hz), 1.22 (d, 6H, *Me*$_2$CH, $^3J = 6.08$ Hz), 2.88, 2.86 (AB quartet, 2H, SiCH$_2$Cl, $^2J = 14.51$ Hz, $^3J = 2.42$ Hz), 4.12 (hept, 1H, *C*HO), 4.68 (qd, 1H, Si*H*, J(SiH) = 214.51 Hz). ^{13}C NMR ($CDCl_3$): $\delta -4.54$ (*Me*Si), 25.04 (*Me*$_2$CHO), 28.23 (Si*C*H$_2$Cl), 67.13 (*C*HO). ^{29}Si NMR ($CDCl_3$): $\delta -4.57$. Anal. Found: C, 39.24; H, 8.60, Si, 18.34. Calc. for $C_5H_{13}ClOSi$: C, 39.33; H, 8.58; Si, 18.39%.

3.6.4. N-(methylisopropoxysilylmethyl)piperidone-2 (14)

To the solution of (**2**) (1.311 g, 9.2 mmol) in heptane (3 ml) was added a solution of (**1**) (1.575 g, 9.2 mmol) in heptane (3 ml). The reaction mixture was stirred for 1.5 h at room temperature. The volatile compounds were removed under vacuum. To the residue was added heptane (5 ml) and a solution of isopropanol (0.553 g, 9.2 mmol) and triethylamine (0.937 g, 9.2 mmol) in heptane (5 ml) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C and the resulting ammonium salts were filtered. Evaporation of the solvent and volatile products under reduced pressure (1 mm Hg) gave crude product (0.787 g) as a colorless viscous oil containing 80% of (**14**). Data for (**14**). ^1H NMR ($CDCl_3$): 0.25 (d, 3H, *Me*Si, $^3J = 2.14$ Hz), 1.12, 1.13 (d, 6H, *Me*$_2$CH, $^3J = 6.08$ Hz), 1.78 (m, 4H, CH$_2$-4,5), 2.33 (m, 2H, CH$_2$-3), 2.41, 2.55 (dd, 2H, SiCH$_2$N, $^2J = 15.2$ Hz, $^3J = 4.4$ Hz), 3.30 (t, 2H, CH$_2$-6, $^3J = 5.24$ Hz), 3.92 (hept, 1H, *C*HO), 4.72 (narrow m, 1H, Si*H*, J(SiH) = 235 Hz). ^{29}Si NMR ($CDCl_3$): $\delta -15.51$.

Acknowledgment

Financial support from INTAS (Grant No. 03-51-4164) is gratefully acknowledged.

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