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Organohydridosilanes containing Y,C,Y-chelating ligands: Reactivity and vapour pressure studies

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ABSTRACT

The syntheses of organohydridosilanes containing Y,C,Y-chelating ligands of the general formula $PhL^{1-3}SiH_2$ (**1**, $L^1 = C_6H_3(CH_2O^tBu)_2$-2,6; **2**, $L^2 = C_6H_3(CH_2O^tBu)$-2-(CH_2NMe_2)-6; **3**, $L^3 = C_6H_3(CH_2NMe_2)_2$-2,6) are reported. The reactivity of compounds **1**–**3** towards elemental sulphur and selenium was studied. It depends on the identity of the donor atoms. While the ether-substituted organohydridosilane PhL^1SiH_2 (**1**) does not react, the amino-substituted organohydridosilanes PhL^2SiH_2 (**2**) and PhL^3SiH_2 (**3**) provide the N→Si-coordinated silathiones PhL^2SiS (**4**), PhL^3SiS (**6**) and the silaselenones PhL^2SiSe (**5**), PhL^3SiSe (**7**), respectively, all containing terminal Si–E bonds (E = S, Se). Compounds **1** and **2** do not react with water at ambient temperature whereas the hydrolysis of **3** yielded the diorganosilanediol $PhL^3Si(OH)_2$ (**8**). The compounds are characterized by ^1H, ^{13}C, ^{29}Si, (**1**–**8**) and ^{77}Se (**6**, **7**) NMR spectroscopy and single crystal X-ray diffraction analysis (**1**, **8**). In addition, the vapour pressures of compounds **2** and **3** were determined as well.

Introduction

It was demonstrated that the silicon atom in organohydridosilanes is able to expand its coordination number to become penta-or hexacoordinated [1] by formation of donor–acceptor interactions. Stable neutral penta- and hexacoordinated organohydridosilanes typically have a built-in ligand containing either a nitrogen, oxygen or sulphur donor atom that coordinates to the silicon center [2]. Moreover, "heptacoordination" at silicon has also been inferred from the molecular structures of organohydridosilanes established by X-ray diffraction analysis [3]. Important reactions of organohydridosilanes, such as the hydrosilylation of olefins [4], or Si–H/O–H coupling [5], are promoted by transition metals. Furthermore, in contrast to these catalytic hydrosilylation reactions, the silicon-bound hydrogen migrates *intra*molecularly through 1,2-shift, 1,3-shift or 1,5-shift in the hypercoordinated hydridosilanes [6]. As shown by the 1,3-hydride shift, hypercoordinated organohydridosilanes [7] can reduce carbonyl or related compounds by hydride transfer in the absence of a metal catalyst [8]. Even more, non-catalyzed hydrosilylation reactions provided the dioxasilacyclopentanes and dioxasilacyclopentenes with range of ΔG from 11 to 22 kcal mol^{-1} [8f]. The *intra*molecular 1,3-hydride shift to azobenzene moiety was also achieved by addition of fluoride anion, which increases the coordination number of initially tetracoordinated silicon atom [6c]. Kost et al. showed the facile and uncatalyzed *intra*molecular 1,3-hydride transfer from hexacoordinated silicon to imino carbon atom [9], and recently, Kano et al. reported on the ability of organosilanes to reduce phosphine imide moiety [10]. Wagler et al. showed 1,3-migration of an organic group initiated by the irradiation of hexacoordinated organosilanes [11]. The examples given above stimulate and justify further efforts concerning the synthesis and reactivity studies of various *intra*molecularly coordinated organohydridosilanes.

Herein, we report organohydridosilanes of the general formula $PhL^{1-3}SiH_2$ containing O,C,O–, N,C,O– and N,C,N–chelating ligands L^{1-3} ($L^1 = C_6H_3(^tBuOCH_2)_2$-2,6; $L^2 = C_6H_3(CH_2O^tBu)$-2-(CH_2NMe_2)-6 and $L^3 = C_6H_3(Me_2NCH_2)_2$-2,6) and study their reactivity towards

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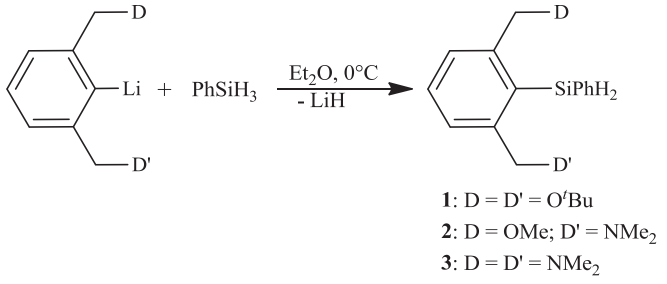
elemental sulphur and selenium, and water. We demonstrate that this reactivity is controlled by the character of donor atoms D (D = O, N) presented in the structures of **1**–**3**. In addition, the vapour pressures of two compounds were determined as well.

Result and discussion

*Synthesis and characterization of the organohydridosilanes **1**–**3***

Treatment of $L^{1-3}Li$ with $PhSiH_3$ provided the corresponding organohydridosilanes of general formula $PhL^{1\text{-}3}SiH_2$ [**1**, $L^1 = C_6H_3(CH_2O^tBu)_2$-2,6; **2**, $L^2 = C_6H_3(CH_2O^tBu)$-2-(CH_2NMe_2)-6; **3**, $L^3 = C_6H_3(CH_2NMe_2)_2$-2,6] (Scheme 1). While compound **1** is a white solid material being soluble in common organic solvents, compounds **2** and **3** are viscous oils. Compound **3** has been already published and the NMR data were identical with those reported in the literature [12].

The ^1H NMR spectra of compounds **1** and **2** show singlet resonances for the CH_3 protons at δ 1.02 (**1**), δ 1.67 (**2**, NCH_3) and δ 3.08 (**2**, OCH_3), respectively. Singlet resonances are also observed for the CH_2 protons at δ 4.51 (**1**), δ 3.28 (**2**, CH_2N) and δ 4.54 (**2**, CH_2O), respectively. The SiH_2 protons appear as singlet resonances flanked with $^1J(^{29}Si-^1H)$ satellites at δ 5.21 [$^1J(^{29}Si-^1H)$ 148 Hz, **1**] and δ 5.04 [$^1J(^{29}Si-^1H)$ 194 Hz, **2**], respectively. The ^{13}C NMR spectra of compounds **1** and **2** also show singlet resonances for the methylene CH_2 protons at δ 65.1 (**1**), δ 64.8 (**2**, CH_2O), and δ 75.6 (**2**, CH_2N), respectively. The ^{29}Si NMR singlet resonances of both **1** (δ −49.2) and **2** (−51.9) are shifted upfield as compared to tetracoordinated Ph_2SiH_2 (δ −33.6 ppm) [13] or to related intramolecularly coordinated organosilanes such as [{2,6-bis(dialkoxyphosphonyl)-4-tert-butyl}phenyl]dihydridophenylsilanes{4-*t*-Bu-2,6-$[P(O)(OR)_2]_2C_6H_2$}$SiPhH_2$ (R = Et, δ −41.0; R = *i*-Pr, δ −42.2) [13]. They are, however, comparable with pentacoordinated organohydrosilane **3** (−51.5, $^1J(^{29}Si-^1H)$ 200 Hz) [12] that can indicate the existence of D→Si (D = O, N) interaction in **1**–**3**. On the other hand, the literature reports of other diarylsilanes producing the upfield shifted ^{29}Si NMR signals in the range of −48.3 to −62.1 [13], although they do not contain additional donor atoms [13]. Therefore, the ^{29}Si NMR shift observed for compounds **1** and **2** can be a result of the different aromatic substituents only. In order to prove, if the ^{29}Si NMR shifts of compounds **1** and **2** arose from silicon hypercoordination, we perform both the variable temperature and solvent dependent NMR studies. Temperature dependence of ^{29}Si chemical shifts and $^1J(^{29}Si, ^1H)$ coupling constants were performed in the range from 240 to 330 K in deuteriochloroform (see Table S1 in supporting information). The differences in ^{29}Si chemical shifts as well as in $^1J(^{29}Si, ^1H)$ coupling constants are rather small. The most illustrative are the data for compounds **1** and **3**: both ^{29}Si chemical shift and $^1J(^{29}Si, ^1H)$ coupling constants are very similar supporting no coordination of donor groups D (O^tBu vs. NMe_2). The solvent dependent NMR studies showed the ^{29}Si NMR shifts of **1**–**3** are solvent independent. Thus ^{29}Si NMR spectra of **1**–**3** measured in $CDCl_3$ provided resonances at δ −48.9 for **1**, at δ - 51.8 for **2** and at δ - 51.7 for **3,** while the resonances at δ −49.3 for **1**, at δ - 52.8 for **2** and at δ - 52.3 for **3** were obtained in [D3]acetonitrile. These results suggest that upfield shifts of the ^{29}Si NMR signals found in **1**–**3** are a result of the different aromatic substituents only.



Scheme 1. Synthesis of organohydridosilanes **1**–**3**.

Single crystals of **1** suitable for X-ray diffraction analysis were obtained from *n*-hexane at −40 °C. The molecular structure of **1** is presented in Fig. 1. Selected interatomic distances and angles are given in the figure caption and crystallographic data are given in Table S2 (see supporting information).

The central Si1 atom can be seen as being [4+1]-coordinated. The distorted Si-centered C1C11H1H2 tetrahedron is face-attacked by O2 at a Si1−O2 distance of 2.984(2) Å that is only shorter than the sum of the van der Waals radii of silicon and oxygen (3.54 Å) [14] suggesting very weak O→Si interaction in the solid state of **1**. The O1 atom points away from the Si1 atom; the Si1−O1 distance being 4.559(2) Å. The Si1−H1 and Si1−H2 distances of 1.45(2) and 1.50(2) Å, respectively, are similar. They are slightly longer than the Si−H distances found for {4-*t*-Bu-2,6-$[P(O)(OR)_2]_2C_6H_2$}$SiPhH_2$ (1.348(15), 1.421(15) Å).[13] In contrast, presence of N→Si coordination was determined in related structurally characterized organohydridosilanes $L^3SiH_2(\mu\text{-}C_6H_4)SiH_2L^3$ and $(L^3)_2SiH_2$ (range of 2.681(2) - 3.008(2) Å) [15,16].

Since the complexes **2** and **3** are oily products, they have been characterized by the vapour pressure measurements. The experimental vapor pressures of complex **2** are listed in Table 1 (for more details see supporting information) [17]. A constantly increasing pressure during one measuring cycle of the vapor pressure measurements of compound **3** suggests that this compound is unstable in vacuum at given temperatures and therefore the vapor pressure could not be determined for this compound. The experimental vapor pressure data of **2** were fitted with the Clarke and Glew equation. [18]

$$R\ln\frac{p^{\mathrm{sat}}}{p^0} = -\frac{\Delta_l^g G_m^0(\theta)}{\theta} + \Delta_l^g H_m^0(\theta)\left(\frac{1}{\theta}-\frac{1}{T}\right), \qquad (1)$$

where p is the vapor pressure, p^0 is a selected reference pressure ($p^0 = 10^5$ Pa), θ is a selected reference temperature (θ = 298.15 K), R

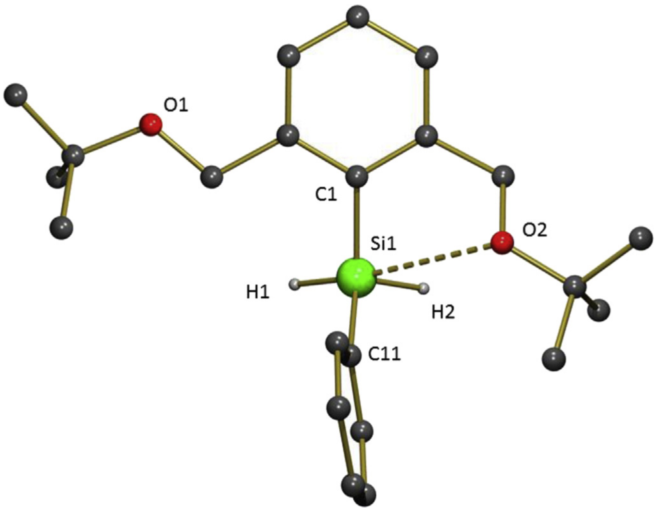


Fig. 1. Molecular structure of **1**. Selected interatomic distances (Å): C1−Si1 1.879(2), C11−Si1 1.858(2), H1−Si1 1.45(2), H2−Si1 1.50 (2), O2−Si1 2.984(2). Selected interatomic angles (°): C1−Si1−C11 116.22(10), C1−Si1−H1 107.3(6), C1−Si1−H2 108.6(6), C11−Si1−H1 109.2(7), C11−Si1−H2 111.0(6), H1−Si1−H2 103.7(9), O2−Si1−H1 169.7(7).