

In search of stable lithium pentaorganosilicates; special role of five phenyl ligands and of ligands containing the 1,4-(1,3-butadienediyl) unit

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Abstract

Among several tetraorganosilanes tested, only 4–6, containing the 1,4-(1,3-butadienediyl) unit, have been found to form, by addition of a σ -organolithium, lithium pentaorganosilicates identifiable by characteristic ^{29}Si -NMR chemical shifts. Lithium silicates formed from 4 are of particular stability (and correspondingly low reactivity) and appear to have trigonal-bipyramidal structures that undergo stereomutation with ΔH^\ddagger ca. 50 kJ/mol, ΔS^\ddagger ca. -20 J/kmol. So far, lithium pentaphenylsilicate (3) is the only other lithium pentaorganosilicate that could be identified by ^{29}Si -NMR. © 1997 Elsevier Science S.A.

Keywords: Tetraorganosilanes; Lithium pentaorganosilicates; ^{29}Si -NMR; σ -organolithiums; Trigonal-bipyramidal structures; Stereomutation

1. Introduction

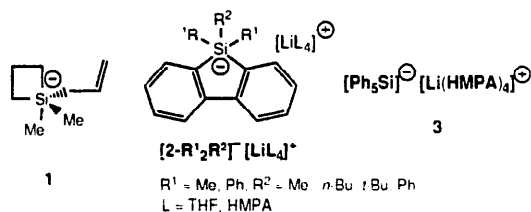
Calculations indicate practically all pentacoordinate silicon anions formed by addition of X^- to SiH_4 to be more stable than their separate components [1]. Consequently, within the framework of extensive studies of nucleophilic substitution on silicon and nucleophilic activation of organosilicon compounds, many pentacoordinate (and even hexa- and heptacoordinate) silicon compounds containing two or more ligands (Y, Z) that are more electronegative than carbon (e.g. Y(Z) = F, Cl, OR, NR_2) could be studied and characterized by X-ray crystallography and/or NMR spectroscopy [2]. By contrast, stable silicon anions containing four organic ligands and a single Y have only been identified in gas phase ion–molecule reactions [3] but never in a solution, although, e.g., ion pairs containing organyltrimethylfluorosilicate anions most probably [4] intervene in many synthetically important TBAF-induced desilylations¹ [2]. Likewise, for many years, 1, formed in a flowing afterglow experiment from 1,1-dimethylsila-

cyclobutane and allyl anion (in a reaction surely favored by relief of strain by allowing the four-membered ring to span one equatorial and one apical position in a trigonal-bipyramidal structure) [6] has been considered the only pentaorganosilicon species known. In solution chemistry, ion pairs containing pentaorganosilicate anions were supposed to be intermediates of intermolecular [7–12] and intramolecular [13,14] transfer of triorganosilyl groups from neutral to anionic carbon, but had never been reported. Species related to 1, arising from the addition of organometallics to silacyclobutane and silacyclopropane derivatives, were found to undergo instantaneous ring-opening [15–17] or rearrangement [18,19] under the conditions of their formation. Most probably, electrophilicity of the counter cation plays an important role among the factors inducing decomposition of pentaorganosilicon anions since many examples indicate that an increasing stability of the counter cation, e.g. by solvation, increases the stability of pentacoordinate silicon anions (vide infra and [2]). Recently, we have identified by the characteristic ^{29}Si -NMR chemical shift of pentacoordinate silicon compounds [20] the first pentaorganosilicates: several lithium 2,2'-biphenyldiyltriorganosilicates ($[\text{2-R}_1\text{R}_2]^-[\text{LiL}_4]^+$) and lithium pentaphenylsilicate (3) [21]. Under our conditions, lithium pentaorganosilicates are in equilibrium with their organolithium and tetraor-

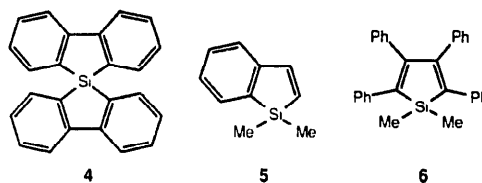
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¹ $[\text{n-BuAr}_3\text{SiOLi}]^- \text{Li}^+$ most likely intervenes in the cleavage of triarylsilanols with *n*-BuLi to give diaryl-*n*-butylsilanols and aryllithium [5].

ganylsilane components. In THF, silicates are the only species detectable at temperatures around -80°C , while, around ambient temperature, the tetraorganylsilane plus organolithium state dominates. In the more stabilizing medium THF/HMPA, $[2\text{-R}_2\text{R}^2]^{-}[\text{Li}(\text{HMPA})_4]^+$ is stable even beyond room temperature [21]. By contrast, in ether, at -80°C as well as at higher temperatures, neither $[2\text{-Me}_3]^{-}[\text{Li}(\text{Et}_2\text{O})_4]^+$ nor $[2\text{-Me}_2\text{Bu}]^{-}[\text{Li}(\text{Et}_2\text{O})_4]^+$ could be determined by ^{29}Si -NMR besides the respective organolithium and 9,9-dimethyl-9H,9-silafluorene. In the latter case, above



-14°C , silicon transfer leading to 9-butyl-9-methyl-9H,9-silafluorene [12] is observed to set in, strongly suggesting, as Ishikawa et al. [12] had already proposed, that $[2\text{-R}_2\text{R}^2]^{-}[\text{Li}(\text{Et}_2\text{O})_4]^+$ is accessible [4]. However, its thermodynamic stability is lower than that of the separate tetraorganylsilane and organolithium components, to a degree, that it cannot be detected anymore by ^{29}Si -NMR [21]. In the present paper, we report results of a study aimed at discovering further lithium pentaorganylsilicates using the conditions that had allowed us to identify $[2\text{-R}_2\text{R}^2]^{-}[\text{LiL}_4]^+$ and **3** [22].



2. Results

As shown by their low temperature ^{29}Si -NMR shifts, lithium silicates form from the silacyclopentadiene derivatives **4–6** when these are treated with approximately equivalent amounts of an alkyl lithium (RLi) in THF or THF/HMPA, respectively, at -80°C : $[4\text{-R}]^{-}[\text{Li}(\text{THF})_4]^+$ [23] ($\text{R} = \text{methyl} (\equiv \mathbf{7}), n\text{-butyl, phenyl, vinyl}$, ^{29}Si -NMR, THF- d_8 , -80°C : $-105.5, -101.7, -100.6, -106.0$, respectively); $[5\text{-Me}]^{-}[\text{Li}(\text{HMPA})_4]^+$ [23] (^{29}Si -NMR, THF/HMPA, 7.5 : 1 (vol.) [20], -80°C : -115.8); $[6\text{-Me}]^{-}[\text{Li}(\text{HMPA})_4]^+$ (^{29}Si -NMR, THF/HMPA, 7.5 : 1 (vol.) [24], -80°C : -107.13). Of the new lithium silicates, those from the spiro-silane **4** are most stable, forming already in the absence of HMPA. More details of the methyl derivative (**7**) will be given below. **5** and **6** reacted with methyl lithium only in the presence of HMPA. The conversion of **5** into $[5\text{-Me}]^{-}[\text{Li}(\text{HMPA})_4]^+$ appeared to be quantitative. In the purple solution arising from **6** and methyl lithium, ^{29}Si -NMR indicated only ca. 10% $[6\text{-Me}]^{-}[\text{Li}(\text{HMPA})_4]^+$ together with ca. 90% unreacted **6**. When **6** was treated with methyl lithium in the absence of HMPA, a dark blue solution resulted containing a source of an ESR signal (79.4 GHz, room temperature, $g = 2.0053$, $w(1/2) = 8.3$ G) which still has to be studied further.

According to NMR spectroscopy [25], $[4\text{-Me}]^{-}[\text{Li}(\text{THF})_4]^+$ ($\equiv \mathbf{7}$) is the only species present through the entire range of temperatures studied (-80 to 50°C). Whereas, even at -120°C , $[2\text{-Me}_3]^{-}[\text{LiL}_4]^+$ is fluxional, the slow-exchange limit is reached with the

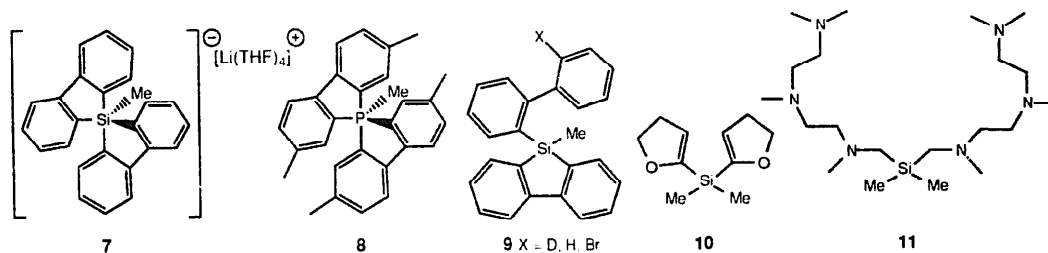
more sterically hindered $[4\text{-Me}]^{-}[\text{Li}(\text{THF})_4]^+$ ($\equiv \mathbf{7}$). At -80°C , twelve distinct NMR signals of the aryl ^{13}C -atoms and eight signals of the aryl protons are in line with the biphenyldiyl units occupying axial and equatorial positions in a trigonal bipyramidal structure **7**, as are different couplings with silicon: $^1J(^{13}\text{C}(\text{ar}_{ax}), ^{29}\text{Si}) = 70.1$ Hz and $^1J(^{13}\text{C}(\text{ar}_{eq}), ^{29}\text{Si}) = 33.4$ Hz [26]. The methyl group must be equatorial. Coupling between silicon and the methyl carbon atom at 25°C ($^1J(^{13}\text{C}(\text{Me}), ^{29}\text{Si}) = 57.4$ Hz) indicates that, at this temperature, reversible dissociation into free **4** + MeLi does not occur. On raising the temperature, signal broadenings and coalescences take place and, at around 50°C , five $^{13}\text{C}(\text{ar})$ and four $^1\text{H}(\text{ar})$ signals are observed. For $^{13}\text{C}(\text{ar})$, line-shape analysis between -65 and 50°C gave activation parameters of the axial \rightleftharpoons equatorial exchange: $\Delta H^\ddagger = 50$ kJ/mol, $\Delta S^\ddagger = -20$ J/kmol, which were independent, both of the concentration of **7** and that of methyl lithium (if an excess of the latter was used in the preparation of **7**). At 247 K, ΔG^\ddagger (55 kJ/mol) is nearly the same as that reported for the similar phosphorane **8** ($\Delta G^\ddagger = 52$ kJ/mol [27]).

At room temperature, **7** reacted with D_2O or CH_3OD by cleavage of a silicon–aryl bond to give **9** ($\text{X} = \text{D}$). With bromine, cleavage of a silicon–aryl bond gave **9** ($\text{X} = \text{Br}$). Even after prolonged times, no reaction was observed with dimethyl sulfate, paraformaldehyde, benzaldehyde and benzoyl chloride, respectively. In all cases, hydrolytic work-up gave **9** ($\text{X} = \text{H}$) besides the respective reagent or its hydrolysis product. Presumably, steric hindrance is responsible for this behavior. Since it is well documented that anionic pentacoordinate silicon species react with nucleophiles faster than the original tetra-coordinate silanes they are derived from [2], the reaction of **7** with butyllithium in THF was

² Even in the presence of HMPA, ethylmagnesium bromide did not react with **4**.

tried. However, no change was indicated by ^{29}Si -NMR and hydrolysis at room temperature gave **9** ($X = \text{H}$). Again, steric hindrance may be the reason of the inertness. Parenthetically, it is noted that the unreactivity of

7 constitutes an additional proof that reversible dissociation into minute amounts of methyllithium and **4** does not take place.



In THF/HMPA at -80°C , the reactivity of tetraphenylsilane towards phenyllithium [21] extends, to some degree, to methyltriphenylsilane and dimethyldiphenylsilane. However, $[\text{MePh}_4\text{Si}]^- [\text{Li}(\text{HMPA})_4]^+$ and $[\text{Me}_2\text{Ph}_3\text{Si}]^- [\text{Li}(\text{HMPA})_4]^+$, respectively, could not be identified by ^{29}Si -NMR. Their transitory existence is implied from the formation, from both silanes, of small amounts, both of Ph_4Si and of **3**, as indicated by their ^{29}Si -NMR signals whose intensities were about 5–10% of those of the starting materials. Apparently, in the reaction of Ph_3SiMe , methyllithium is lost from $[\text{MePh}_4\text{Si}]^- [\text{Li}(\text{HMPA})_4]^+$, followed, eventually, by addition of phenyllithium to Ph_4Si . In the reaction of Ph_2SiMe_2 , corresponding reaction sequences operate repetitively. Significantly, contrary to phenyllithium, methyllithium did not give with tetraphenylsilane a ^{29}Si -NMR signal characteristic of pentacoordinate silicon. In line with the results obtained with Ph_3SiMe and Ph_2SiMe_2 plus phenyllithium, respectively, this shows that the lower limit of lithium phenylsilicate detectability by ^{29}Si -NMR is reached when silicon binds five phenyl groups as in **3**. Next, efforts were directed to bis[2-(4,5-dihydrofuryl)]dimethylsilane (**10**) [11] known to be prone to carbanion exchange with σ -organolithiums. At -80°C , in THF/HMPA, carbanion exchange products were formed practically instantaneously, as shown by their ^{29}Si -NMR shifts and/or by conventional methods after work-up [28]. No NMR signal indicating lithium silicate was detected. We surmise that precoordination [29] of the organolithium reagent to the oxygens of **10** speeds up formation of the lithium pentaorganylsilicate ³, while, on the other hand, coordination of the lithium cation to the oxygens induces decomposition of the pentaorganylsilicate by loss of a relatively stable α -heteroorganolithium. The closely analogous behavior of bis(2,5,8-triaza-2,5,8-trimethyl-

nonyl)dimethylsilane (**11**) [30] supports this conjecture [28]. Finally, 1,1-dimethyl-1-silacyclobutane (**12**) was subjected to our reaction conditions. Again, reaction took place instantaneously, without any lithium pentaorganylsilicate being detectable [28]. Relief of strain undoubtedly governs the behavior of **12** and the transitory lithium pentaorganylsilicates formed from it. Under no circumstances could we observe any reactivity towards σ -organolithiums of tetramethylsilane.

3. Conclusion

So far, ordinary tetraorganylsilanes, lacking special features like **10**, **11** and the small ring silacycloalkanes [15–19], have failed to react with σ -organolithiums, i.e., under normal conditions, they are unable to form lithium pentaorganylsilicates. Only tetraorganylsilanes containing the 1-sila-2,4-cyclopentadiene unit and tetraphenylsilane, respectively, have been found to give, with σ -organolithiums, lithium pentaorganylsilicates that are stable at -80°C and, in some cases, higher temperatures (Fig. 1).

With **5** and **6**, formation of lithium silicate takes preference over addition of the organolithium to the vinylsilane unit [31] contained in these molecules (see also Ref. [22]). Calculations [32] have indicated that increasing the number of ligands increases the positive charge on silicon and, consequently, the negative charges residing on the ligands. It may well be that the special nature of the chelating (benzo-annulated or tetraphenyl-

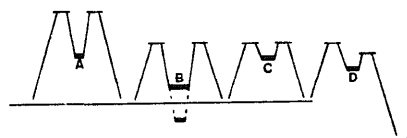


Fig. 1. Relative stabilities and activation barriers (schematically) of lithium pentaorganylsilicates. A: 'Ordinary' lithium pentaalkylsilicates (inaccessible); B: lithium pentaorganylsilicates detectable by ^{29}Si -NMR; C: lithium pentaorganylsilicates implied by triorganosilyl group transfer; D: lithium dimethylorganyl-1,3-propanediylsilicate from **12**. Baselines: Tetraorganylsilane plus RLi .

³ In the case of **10** + RLi , the large decrease of entropy as entailed by formation of $[2\text{-Me}_3]^- [\text{Li}(\text{THF})_4]^+$ from 9,9-dimethyl-9H,9-silafluorene and MeLi in THF [21] is attenuated if the two dihydrofuryl moieties of **10** take over the role of two molecules of THF.

substituted) 1,4-(1,3-butadienediyl) ligand and the combined action of five phenyl ligands, respectively, in stabilizing lithium pentaorganylsilicates is due to their (among carbon ligands) being especially well suited to accommodate negative charge [33]. We are continuing our search for stable pentaorganylsilicates along this guideline.

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