

2-(Dimethylphosphinomethyl)- and 2-(methylthiomethyl)phenyl silicon compounds: higher coordination with soft donors

U.H. Berlekamp, A. Mix, B. Neumann, H.-G. Stämmler, P. Jutzi *

Faculty of Chemistry, Anorganische Chemie III, University of Bielefeld, Universitätsstraße 25; D-33615 Bielefeld, Germany

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Abstract

The synthesis of trimethoxy-, trifluoro-, trihydrido-, and hydrido(phenyl)chlorosilanes, and of hydrido(phenyl)silyltriflates bearing an additional 2-(dimethylphosphinomethyl)phenyl- or a 2-(methylthiomethyl)phenyl substituent is described. The coordination of the phosphorus and sulfur donor in the aryl side chain to the silicon center is discussed on the basis of NMR spectroscopic investigations. The trimethoxy and trifluorosilanes do not show any coordination. Weak donor–silicon interactions are found in the trihydrido- and in the hydrido(phenyl)chlorosilanes. The crystal structure of chloro-bis-[(2-(methylthiomethyl)phenyl)silane (**13**) [Angew. Chem. 111 (1999) 2071] features a distorted tetrahedral geometry at silicon with an additional weak donor–coordination. Different structural properties were found in the corresponding P- and S-donor functionalized phenylsilyl triflates. The S-donor compound **15** features a covalent structure with pentacoordination and a trigonal-bipyramidal geometry at the silicon atom. In the analogous P-donor derivative **14** the spectroscopic data indicate an ionic structure with a tetracoordinated silicon atom. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Silicon; 2-(Dimethylphosphinomethyl)phenylsilanes; 2-(Methylthiomethyl)phenylsilanes; 2-(Dimethylphosphinomethyl)phenylsilyl triflate; 2-(Methylthiomethyl)phenylsilyl triflate; Si-pentacoordination; X-ray structure

1. Introduction

It is well known that the coordination sphere at silicon in organosilicon compounds can be extended by the formation of donor–acceptor complexes [1]. A very successful approach to induce higher coordination is the integration of a donor into the side chain of an alkyl or an aryl substituent. By the use of this strategy a lot of higher coordinated neutral and cationic silicon compounds including low-valent silicon species [2–21] have been synthesized. In contrast to the well investigated amino-functionalized arylsilanes, only a few papers report on corresponding silicon compounds in which ether, thioether, and phosphino groups are intramolecularly coordinated at silicon [6,19–24]. In recent years, we have investigated the coordination behavior of silicon compounds bearing substituents with σ - or π -donor functions [6,23]. In this context, we are interested also in

silicon compounds bearing additional phosphorus and sulfur containing groups in order to study the potential of these donors to induce higher coordination at silicon. For this purpose we have synthesized exemplarily (2-dimethylphosphinomethyl)phenyl- and (2-methylthiomethyl)phenylsilicon compounds with further methoxy, hydrido, halogeno, and triflate groups. In order to elucidate structural parameters we investigated these compounds by X-ray crystal structure analysis, NMR and IR spectroscopic methods, and by conductivity measurements. We compared the obtained data with those of the analogous N- and O-donor functionalized derivatives.

2. Results and discussion

2.1. Syntheses

1-Bromo-2-(dimethylphosphinomethyl)benzene (**1**) and 1-bromo-2-(methylthiomethyl)benzene (**2**) were synthesized by standard procedures [24]. Lithiation

* Corresponding author. Tel.: +49-521-106-6181; fax: +49-521-106-6026.

E-mail address: peter.jutzi@uni-bielefeld.de (P. Jutzi).

was performed by reacting the bromo compounds **1** and **2** with *n*-butyllithium in hexane at low temperature. The resulting suspensions of the aryl lithium compounds **3** and **4** were used directly without further purification (Scheme 1).

Linkage of the side-chain functionalized aryl systems **3** and **4** to silicon was performed by reaction with tetramethoxysilane which gave the aryltrimethoxysilanes **5** and **6** in good yields as colorless viscous liquids fairly stable to air and moisture. The P-donor functionalized derivative **5** has been previously described by Müller et al. [22]. Treatment of **6** with one equivalent of the boron trifluoride diethylether complex gave the trifluorosilane **8** in good yields as a colorless air sensitive oily liquid. The corresponding reaction was performed also with compound **5**. After evaporation of all volatile components in vacuo a pale yellow viscous oil remained which consisted of the desired trifluorosilane **7** and of some unidentified by-products, according to NMR investigations. Attempts to purify **7** by distillation led to decomposition.

We used the alkoxysilanes **5** and **6** also as substrates for the synthesis of hydridosilanes. Thus, reduction of **5** and **6** with LiAlH_4 gave the corresponding trihydridosilanes **9**–**10**. Both compounds were isolated as colorless oily liquids in moderate yields. The S-donor functionalized compound **10** hydrolyses slowly in the presence of moisture. The P-donor functionalized derivative **9** ignites spontaneously when exposed to air.

Linkage of the side-chain functionalized aryl systems to silicon was carried out also by reaction of the aryllithium derivatives **3** and **4** with chlorosilanes. Thus, reaction with one equivalent of phenyldichlorosilane gave the corresponding arylchlorosilanes **11** and **12**

in moderate yields. Both compounds were obtained as moisture sensitive colorless oily liquids. The twofold S-donor functionalized chlorosilane **13** [6] was synthesized in good yields by reaction of **4** with trichlorosilane in a 2:1 stoichiometry and was obtained as a pale yellow viscous oil very sensitive to air and moisture.

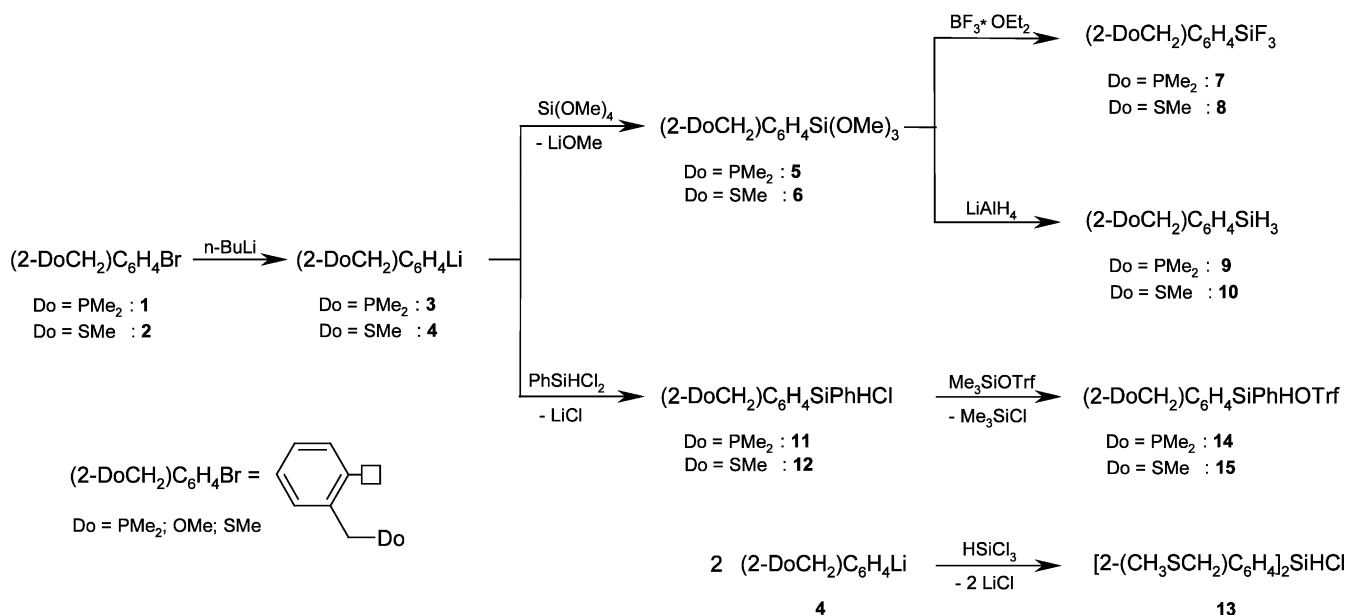
Treatment of the chlorosilanes **11** and **12** with trimethylsilyl trifluoromethanesulfonate in hexane yielded the P- and S-donor functionalized silyltriflates **14** and **15**. Compound **14** was isolated in moderate yields as a colorless powder. The corresponding triflate **15** was obtained as a colorless viscous oil. Both derivatives are sensitive to air and moisture and insoluble in non-polar solvents.

2.2. X-ray crystal structures

2.2.1. Chloro-bis-[(2-methylthiomethyl)phenyl]silane (**13**) [35]

Crystals of the chlorosilane **13** were grown from hexane. **13** crystallizes in the space group $P2_1/c$. The unit cell contains four crystallographically independent molecules. The coordination geometry at silicon is initially described here on the basis of a very distorted trigonal-bipyramidal arrangement (see Fig. 1).

The axial positions are occupied by the sulfur atom S(1) and the chloro substituent. The silicon sulfur S(1) distance of 313.3 pm is considerably shorter than the sum of the van der Waals radii of 390 pm [34]. This indicates at least a weak silicon sulfur donor interaction. In comparison to Si–Cl bonds in tetra-coordinated chlorosilanes [36], the Si–Cl bond in **13** is slightly elongated to 217.6 pm. The positions of the axial atoms deviate significantly from an ideal arrangement. The



Scheme 1.

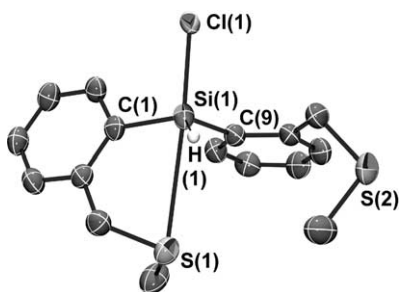


Fig. 1. ORTEP drawing of chloro-bis[2-(methylthiomethyl)phenyl]silane (**13**). The ellipsoids are at the 50% level probability. Except H(1), all hydrogen atoms are omitted for clarity. Selected bond lengths (pm) and angles ($^{\circ}$): Si(1)–C(1) 187.4(4); Si(1)–C(9) 186.6(4); Si(1)–H(1) 145 (5); Si(1)–S(1) 313.30(16); Si(1)–Cl(1) 217.60(14); C(9)–Si(1)–C(1) 112.60(17); C(9)–Si(1)–H(1) 116.4(18); C(1)–Si(1)–H(1) 114.7(18); C(9)–Si(1)–Cl(1) 105.71(13); C(1)–Si(1)–Cl(1) 104.57(13); Cl(1)–Si(1)–H(1); 100.8(18); C(9)–Si(1)–S(1) 85.69(12); C(1)–Si(1)–S(1) 76.32(12); S(1)–Si(1)–H(1) 67.5(18); Cl(1)–Si(1)–S(1) 166.76(6).

angle included by Cl(1), Si(1) and S(1) is reduced to 166.8° . The hydrogen atom H(1) and the aryl substituents represented by C(1) and C(9) form the equatorial plane of the trigonal-bipyramid. The silicon atom is placed 40 pm outside of this plane in direction to the chloro substituent. This deviation effects an increase of the angles included by the axial chlorine atom, the silicon atom, and the equatorial substituents. Simultaneously, the angles C(1)–Si(1)–S(1), C(9)–Si(1)–S(1) and H(1)–Si(1)–S(1) are decreased. The bond angles in the equatorial plane range from 112.6 to 116.4° and correspond more likely to values typical for a tetrahedral geometry. As a result of the described structural parameters for **13**, the coordination geometry at silicon might be better described as a distorted tetrahedron with an additional weakly coordinating donor.

2.2.2. [(2-Methylthiomethyl)phenyl]silyl trifluoromethanesulfonate (**15**) [35]

Crystals of compound **15** were obtained by storage of the oily product at 5°C . The compound crystallizes in space group $P\bar{1}$. The unit cell contains two independent molecules. The molecular structure of **15** is presented in Fig. 2.

The central silicon atom is pentacoordinated in a trigonal-bipyramidal fashion. The two phenyl substituents, represented by C(1) and C(9), and the hydrogen atom H(1) span the equatorial plane. The sum of the bond angles in the equatorial plane deviates with 357.9° only slightly from the ideal value of 360° . The silicon hydrogen bond is found to be rather short compared with other hydrosilanes. This reflects an enhanced s-character in the Si–H bond. The sulfur donor S(1) and the oxygen atom O(1) of the triflate substituent occupy the axial positions of the trigonal bipyramid. The arrangement of S(1), Si(1) and O(1) is nearly linear. The S–Si distance of 259.45 pm is much shorter than

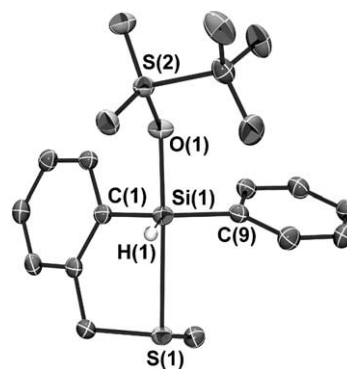


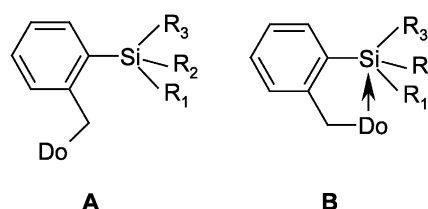
Fig. 2. ORTEP drawing of 2-[(methylthiomethyl)phenyl]silyl trifluoromethanesulfonate (**15**). The ellipsoids are at the 50% level probability. Except H(1), all hydrogen atoms are omitted for clarity. Selected bond lengths (pm) and angles ($^{\circ}$): Si(1)–C(1) 187.46(14); Si(1)–C(9) 185.96(14); Si(1)–H(1) 132.0 (17); Si(1)–S(1) 259.54(5); Si(1)–O(1) 183.93(11); S(2)–O(1) 150.27(10); S(2)–O(2) 142.43(11); S(2)–O(3) 142.86(11); C(9)–Si(1)–C(1) 117.11(6); C(9)–Si(1)–H(1) 122.3(7); C(1)–Si(1)–H(1) 118.5(7); C(9)–Si(1)–O(1) 94.64(6); C(1)–Si(1)–O(1) 96.06(5); O(1)–Si(1)–H(1); 93.8(8); C(9)–Si(1)–S(1) 88.32(4); C(1)–Si(1)–S(1) 83.90(4); S(1)–Si(1)–H(1) 83.3(8); O(1)–Si(1)–S(1) 176.69(4).

that found in **13** and in other sulfur-donor functionalized silicon compounds and indicates a rather strong interaction. Effected by the S-donor coordination, the Si–O bond in the silyl triflate unit is elongated to 183.93 pm.

2.3. Coordination behavior

Intramolecular donor-coordination in these types of silicon compounds should be identifiable by ^{29}Si -NMR spectroscopy. In comparison to the tetra-coordinated analogues without donor function, the resonances of type B compounds (Scheme 2) are expected to be shifted towards higher-field at least to a small extend [2].

In contrast, the resonances of open-ring derivatives (type A) should not differ significantly from those of the parent compounds. Beside chemical shift values, the coupling of silicon to adjacent nuclei should be sensitive for geometric changes. We used chemical shift values and coupling constants to assess the structure of the novel P- and S-donor functionalized silicon derivatives in solution. The important NMR spectroscopic data are presented in Table 1. The corresponding data of the N- and O-donor functionalized analogues are listed for



Scheme 2.

Table 1

²⁹Si-NMR data of N-, O-, P-, and S-donor functionalized arylsilicon compounds

	PhSi(OMe) ₃ [25]	Ph _N Si(OEt) ₃ ^a [26]	Ph _O Si(OMe) ₃ ^a [19]	Ph _P Si(OMe) ₃ ^a (5) [22]	Ph _S Si(OMe) ₃ ^a (6)
δ (²⁹ Si) (ppm)	−57.5	−57.17	−53.9	−53.2	−53.6
Δδ (Si) ^b (ppm)		+0.59 ^c	+3.6	+4.3	+3.9
	PhSiF ₃ [25]	Ph _N SiF ₃ [27]	Ph _O SiF ₃ [19]	Ph _P SiF ₃ (7)	Ph _S SiF ₃ (8)
δ (²⁹ Si) (ppm)	−73.2	−101.5	−88.0	−72.0	−71.9
Δδ (Si) ^a (ppm)		−28.3	−14.8	−1.3	−1.2
<i>J</i> (Si, F) (Hz)	268	236	240	268	266
	PhSiH ₃ [25]	Ph _N SiH ₃ [28]	Ph _O SiH ₃ [19]	Ph _P SiH ₃ (9)	Ph _S SiH ₃ (10)
δ (²⁹ Si) (ppm)	−60.1	−71.5	−61.8	−62.4	
<i>J</i> (Si, P) = 5.6 Hz	−65.0				
Δδ (Si) ^a (ppm)		−11.4	−1.7	−2.3	−4.9
<i>J</i> (Si, H) (Hz)	200	199	197	201	200
	Ph ₂ SiHCl [25]	Ph _N SiPhHCl [3]	Ph _O SiPhHCl [29]	Ph _P SiPhHCl (11)	Ph _S SiPhHCl (12)
δ (²⁹ Si) (ppm)	−5.4	−53.6	−22.6	−10.1	
<i>J</i> (Si, P) = 7.5 Hz	−12.4 Hz				
Δδ (Si) ^a (ppm)		−48.2	−17.2	−5.3	−7.0
<i>J</i> (Si, H) (Hz)	236	279	264	238	251
	Ph ₂ SiHTrf ^d [30]	Ph _N SiPhHTrf [5]	Ph _O SiPhHTrf [19]	Ph _P SiPhHTrf (14)	Ph _S SiPhHTrf (15)
δ (²⁹ Si) (ppm)	−2.1	−56.2	−48.7	−32.4	
<i>J</i> (Si, P) = 40 Hz	−42.8				
Δδ (Si) ^a (ppm)		−54.1	−46.6	−30.3	−40.7
<i>J</i> (Si, H) (Hz)	257	290	286	258	281

^a Ph_N, (2-dimethylaminomethyl)phenyl; Ph_O, (2-methoxymethyl)phenyl; Ph_P, (2-dimethylphosphinomethyl)phenyl; Ph_S, (2-methylthiomethyl)phenyl.

^b Shift difference to the analogous arylsilane without donor function.

^c In comparison with PhSi(OEt)₃.

^d Trf, trifluoromethanesulfonate.

comparison. In the following, we discuss the coordination behavior in the respective classes of arylsilicon compounds on the basis of the NMR data presented in Table 1.

In the class of the aryl(trimethoxy)silanes, the resonances of the P-donor and S-donor functionalized compounds **5** [22] and **6** show no upfield shift in comparison to phenyltrimethoxysilane and to the corresponding N-donor functionalized species. Thus, a formation of a donor–acceptor bond can be excluded, and compounds with structures of type A are present.

In the class of the aryl(trifluoro)silanes, the data of the P- and S-donor containing compounds **7** and **8** give no indication for a donor complexation. The observed ²⁹Si resonances are nearly identical with that of phenyltrifluorosilane. Furthermore, the ¹*J*(Si, F) coupling constants do not differ markedly from that found in the parent compound. In addition, no *J*(Si, P) coupling is observed for compound **7**. Thus, both compounds obviously behave like tetracoordinated silanes and form structures of type A. These results are in accordance with recently published theoretical investigations concerning the adduct formation behavior of SiF₄. In contrast to N- and O-donors, the tendency of P- and S-donors to form adducts with SiF₄ was found to be negligibly small [31].

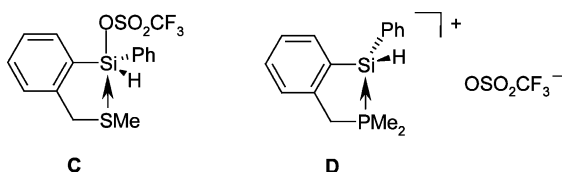
In the class of the aryl(trihydrido)silanes, the situation is more complicated. The ²⁹Si resonances of **9** and **10**

show only minor upfield shifts in comparison to phenylsilane. The Δδ values of −2.3 (**9**) and −4.9 (**10**) give no clear evidence for the existence of higher coordination at silicon. Also the ¹*J*(Si, H) coupling constants of **9** and **10** correspond to that of phenylsilane. On the basis of these data, a non-coordinating behavior is anticipated. However, for the P-donor derivative **9** a small *J*(Si–P) coupling of 5.6 Hz is observed. Based on a comparison of ^{*n*}*J*(Si, P) coupling constants (*n* = 1–4) [25], we exclude a ⁴*J* coupling via the aromatic ring and attribute this coupling to a rather weak P–Si interaction. Due to the comparable δ ²⁹Si and ¹*J*(Si, H) data found for **9** and **10**, we suppose a rather weak donor–silicon interaction also for the S-donor compound **10**. The comparatively strongest donor–silicon interaction is presumably present in the N-donor functionalized compound.

In the class of the chloro(aryl)(hydrido)phenylsilanes, the ²⁹Si resonances of the P- and S-donor containing derivatives **11** and **12** are shifted towards higher-field in comparison to that of chlorodiphenylsilane. Corresponding to the small Δδ values of −5.3 (**11**) and −7.0 ppm (**12**), compounds of type B (Scheme 2) with weak donor–silicon interactions are present. Additionally, a ¹*J*(Si, P) coupling of 7.5 Hz is observed in the P-donor functionalized silane **11**. The ¹*J*(Si, H) couplings of **11** and **12** show only minor differences in comparison with that of the parent compound, in accord with only

small changes in the hybridization of the respective silicon atoms. The NMR data of **13** confirm that the chelate structure of type B found in the solid state is also present in solution. Thus, the ^{29}Si resonance is shifted towards higher-field by 12.8 ppm. In the ^1H -NMR spectrum the benzylic protons appear as AB system. Only one set of signals is obtained for both aryl substituents. This finding implies a dynamic coordination of the two S-donors in **13** similar to that observed for other chlorosilanes with two donor groups [28]. The $^1J(\text{Si}, \text{H})$ coupling constant of 251 Hz corresponds to that found for **12** and is considerably smaller than that of the comparable N-donor functionalized compound $\text{Ph}_3\text{SiPhHCl}$ ($^1J(\text{Si}, \text{H}) = 279$ Hz), for which a trigonal-bipyramidal structure and thus a strong donor–silicon interaction has been found [3].

Donor-functionalized silyl triflates are of special interest with regard to their structure in the solid state and in solution [5,19]. The ^{29}Si resonance of the silyl triflate **15** is observed at higher-field ($\Delta\delta = -42.8$ ppm) in comparison to diphenylsilyl triflate, which indicates higher coordination at silicon induced by a silicon S-donor interaction [3,5,6,19]. Conclusions regarding the geometry at the silicon atom in **15** can be drawn from the coupling of the silicon atom to adjacent nuclei. The $^1J(\text{Si}, \text{H})$ coupling constant is significantly increased in comparison to that of the parent compound. This reflects an enhanced s-character of the Si–H bond [33] due to a sp^2 hybridization at silicon. Similar $^1J(\text{Si}, \text{H})$ coupling constants have been observed for N- and O-donor functionalized silyl triflates [3–6,23]. According to these data for **15**, a structure of type C (Scheme 3) with a trigonal-bipyramidal geometry at silicon comparable with that found in the solid state is also present in solution. Although **15** contains two chiral centers which should lead to the formation of diastereomers, only one set of signals is obtained in the NMR spectra even at low temperatures. Obviously, the energy barrier for the inversion at sulfur is small. In the ^1H -NMR spectrum below -10°C (T_c) the benzylic protons appear as an AB system, while at higher temperatures only one singlet is obtained. This finding indicates that the stereochemical rigidity at silicon is lifted either by a dynamic coordination of the donor or by dissociation–association of the triflate unit. The energy of activation for the observed process can be determined to $12.5\text{ kcal mol}^{-1}$ [32,6].



Scheme 3.

The ^{29}Si resonance of the P-donor functionalized silyl triflate **14** is also observed at higher-field but the shift difference $\Delta\delta$ for **14** (-30.3 ppm) is smaller than in **15** (-42.8 ppm). A $^1J(\text{P-Si})$ coupling of 40 Hz clearly indicates the existence of a silicon phosphorus bond. The ^{31}P resonance of **14** is shifted towards lower-field in comparison to other (2-dimethylphosphinomethylphenyl)silanes presented in this paper and is observed at -12.4 ppm. We attribute this shift to a significant transfer of electron density from phosphorus to silicon. In the ^1H -NMR spectrum of **14**, the benzylic protons in **14** remain chemically non-equivalent even at higher temperatures and appear as an AB system, due to a stereochemically rigid silicon center. The $^1J(\text{Si}, \text{H})$ coupling constant of 258 Hz is significantly smaller than that found for other donor-functionalized hydridosilyl triflates and corresponds nearly to the value found in diphenylsilyl triflate. This indicates an sp^3 -hybridized silicon atom in this derivative. Based on the NMR data of **14**, we assume a structure of type D (Scheme 3) with a tetracoordinated silicon center. The charge distribution might be similar to that in the ionic species $\text{Me}_{(4-n)}\text{P}(\text{SiMe}_3)_n^+$ ($n = 1-4$) [37,38]. However, dichloromethane solutions of **14** show no significant conductivity. Obviously, compound **14** exists as a contact ion pair. A comparable behavior in solution has been described for $\text{P}(\text{SiMe}_3)_4^+ \text{B}(\text{C}_6\text{F}_5)_4^-$ [38].

3. Conclusion

Our results concerning the intramolecular coordination of P- and S-donor functionalized arylsilicon compounds can be summarized as follows: In the aryltrimethoxy- and aryltrifluorosilanes **5** and **6** there is no evidence of a donor–silicon interaction. These compounds behave like tetracoordinated silanes. In the trihydridosilanes **9** and **10** the donor groups are supposed to be weakly coordinating to silicon. A more substantial donor silicon interaction is present in the chlorosilanes **11–12**. However, according to small $\Delta\delta(^{29}\text{Si})$ values, the interaction is significantly weaker than that in the N- and O-donor functionalized analogues. The S-donor bond in the chlorosilane **13** effects a distortion of the geometry at silicon in the solid state and presumably also in solution. The structure in side-chain functionalized (aryl)silyl triflates is obviously determined by a subtle balance of charge distribution between silicon and the donor atom. Thus, intramolecular donor–silicon interaction in the N-, O-, and S-donor containing derivatives leads to pentacoordination at silicon and formation of a type C structure (Scheme 3) with a trigonal-bipyramidal geometry at the silicon atom. In the corresponding P-donor compound the spectroscopic data imply the existence of an ionic

structure of type D with a tetrahedral geometry at the silicon atom.

4. Experimental

All manipulations were performed under a dry argon atmosphere using standard Schlenk techniques or a nitrogen fitted glovebox. Solvents were dried by standard methods and distilled prior to use. NMR spectra were recorded on a Bruker DRX 500 spectrometer operated at 500 MHz for ^1H , 470.6 MHz for ^{19}F , 202.5 MHz for ^{31}P , 125.7 MHz for ^{13}C and 99.3 MHz for ^{29}Si at ambient temperature unless otherwise noted. ^1H and ^{13}C chemical shifts were referenced to residual solvent resonances, ^{31}P chemical shifts to external 85% aqueous solution of H_3PO_4 , ^{19}F chemical shifts to external CFCl_3 , and ^{29}Si chemical shifts to external Me_4Si . All shifts are given in ppm. Mass spectra were recorded on a VG Autospec instrument at 70 eV EI, 200 mA emission unless otherwise noted. IR Spectra were recorded on a Bruker Vector 22 FTIR spectrometer. Wave numbers ($\tilde{\nu}$) are given in cm^{-1} . Conductivity measurements of the silyl triflates were carried out in CH_2Cl_2 solution at various concentrations. Elemental analyses were performed by the microanalytical laboratory of the University of Bielefeld or by the Mikroanalytisches Labor Beller, Göttingen. The X-ray structural data were collected on a Nonius KappaCCD instrument.

4.1. Synthesis of the aryllithium compounds 3 and 4

A 1.6 M solution of *n*-butyllithium (62.5 ml) in hexane (100 mmol) is slowly added at -50°C to 100 mmol of the corresponding arylbromide (**1** or **2**) solved in 50 ml hexane or Et_2O . The mixture is allowed to warm to room temperature (r.t.) and stirred for additional 4 h. The resulting suspensions of the aryllithium compounds **3** and **4** are used without further purification.

4.2. Synthesis of the aryltrimethoxysilanes (general procedure)

A solution of 100 mmol of the aryllithium compound **3** or **4** is added dropwise at -50°C to a solution of 18.3 g (100 mmol) of tetramethoxysilane in Et_2O . The mixture is warmed to r.t. After stirring for 20 h all volatile components are removed in vacuo, and hexane is added to the residue. After filtration the solvent is removed and the oily residue is purified by distillation.

4.2.1. Trimethoxy-[2-(dimethylphosphinomethyl)-phenyl]silane (**5**)

Colorless oil; yield 62.0 mmol (16.9 g, 62%); b.p. 86°C (0.02 mbar).

^1H -NMR (CDCl_3): 1.02 (d, $^2J(\text{P}, \text{H}) = 3.0$ Hz, 6H, $-\text{CH}_3$), 2.96 (s, 2H, $-\text{CH}_2-$), 3.60 (s, 9H, $-\text{OCH}_3$), 7.15 (pseudo-t, 1H, Ar-H), 7.25 (d, $^3J(\text{H}, \text{H}) = 8.6$ Hz, 1H, Ar-H), 7.33 (pseudo-t, 1H, Ar-H), 7.65 (d, $^3J(\text{H}, \text{H}) = 7.5$ Hz, 1H, Ar-H); $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3): 13.6 ($-\text{CH}_3$), 38.8 ($-\text{CH}_2-$), 50.2 ($-\text{OCH}_3$), 124.6, 127.7, 127.9, 136.3, 145.3 (C-arom); ^{31}P -NMR (CDCl_3): -39.9 ; ^{29}Si -NMR (CDCl_3): -53.2 ; MS m/z (relative intensity (%)): 272 (55), 181 (100); $\text{C}_{12}\text{H}_{21}\text{O}_3\text{PSi}$ (272.36), Anal. Calc. C, 52.92; H, 7.77. Found: C, 52.58; H, 8.12%.

4.2.2. Trimethoxy-[2-(methylthiomethyl)phenyl]silane (**6**)

Colorless oil, yield: 25.3 mmol (6.54 g, 25%); b.p. 68°C (0.02 mbar).

^1H -NMR (CDCl_3): 2.02 (s, 3H, $-\text{CH}_3$), 3.61 (s, 9H, $-\text{OCH}_3$), 3.88 (s, 2H, $-\text{CH}_2-$), 7.24 (pseudo-t, 1H, Ar-H), 7.41 (m, 2H, Ar-H), 7.68 (d, $^3J(\text{H}, \text{H}) = 7.5$ Hz, 1H, Ar-H); $^{13}\text{C}\{^1\text{H}\}$ -NMR (CDCl_3): 15.1 ($-\text{CH}_3$), 38.3 ($-\text{CH}_2-$), 50.7 ($-\text{OCH}_3$), 126.1, 128.8, 129.5, 136.5, 145.0 (C-arom); $^{29}\text{Si}\{^1\text{H}\}$ -NMR (CDCl_3): -53.6 ; MS m/z (relative intensity (%)): 258 (1), 226 (51), 211 (100), 181 (91), 151 (27), 121 (38), 105 (41), 91 (67), 84 (28), 59 (38), 45 (24); $\text{C}_{11}\text{H}_{18}\text{SSi}$ (258.42), Anal. Calc. C, 51.12; H, 7.02. Found: C, 53.44; H, 6.67% [39].

4.3. Synthesis of the aryltrifluorosilanes (general procedure)

At 0°C 10.6 mmol (2.66 ml) of the borontrifluoride diethylether complex are added dropwise to a solution of 10 mmol of the corresponding aryltrimethoxysilane in 20 ml diethylether. The cooling bath is removed and the mixture is stirred for 20 h. All volatile components are removed in vacuo.

4.3.1. Trifluoro-[2-(dimethylphosphinomethyl)-phenyl]silane (**6**)

Compound **6** was isolated together with by-products. A purification failed, due to its sensitivity. Accordingly, a correct assignment of ^1H - and ^{13}C -NMR resonances was not possible. Identification was performed by ^{29}Si -NMR.

^{29}Si -NMR (CDCl_3): -72.0 (q, $^1J(\text{Si}, \text{F}) = 268$ Hz).

4.3.2. Trifluoro-[2-(methylthiomethyl)phenyl]silane (**7**)

The crude was purified by distillation. Colorless oil, yield: 6.10 mmol (1.37 g, 65%), b.p. 30°C (0.2 mbar).

^1H -NMR (CDCl_3): 1.94 (s, 3H, $-\text{CH}_3$), 3.78 (s, 2H, $-\text{CH}_2-$), 7.35 (t, $^3J(\text{H}, \text{H}) = 7.5$ Hz, 1H Ar-H), 7.41 (d, $^3J(\text{H}, \text{H}) = 7.7$ Hz, 1H, Ar-H), 7.53 (t, $^3J(\text{H}, \text{H}) = 7.6$ Hz, 1H, Ar-H), 7.77 (d, $^3J(\text{H}, \text{H}) = 7.5$ Hz, 1H, Ar-H); ^{13}C -NMR (CDCl_3): 14.6 ($-\text{CH}_3$), 38.6 ($-\text{CH}_2-$), 127.0 (C-arom), 128.4 (C-arom), 130.2 (C-arom), 133.1 (C-arom), 136.6 (C-arom), 145.8 (C-arom); ^{19}F -NMR

(CDCl₃): –85.7; ²⁹Si-NMR (CDCl₃): –71.9 (q, ¹J(Si, F) = 265 Hz); MS *m/z* (relative intensity(%)): 222 (27), 207 (4), 175 (100), 146 (15), 138 (16), 105 (6), 84 (7), 65 (33), 45 (20), 39 (18); C₈H₉F₃SSi (222.30): Anal. Calc. C, 43.22; H, 4.08. Found: C, 43.27; H, 3.87%.

4.4. Synthesis of the aryltrihydrosilanes (general procedure)

At 0 °C a solution of 10 mmol of the corresponding trimethoxysilane in 10 ml of Et₂O is added slowly to a suspension of 30 mmol (1.14 g) of LiAlH₄ in 40 ml of Et₂O. After warming to r.t. and stirring for 20 h the solvent is removed in vacuo, and hexane is added to the residue. The mixture is filtered and after removing the solvent in vacuo the crude product is purified by distillation.

4.4.1. [2-Dimethylphosphinomethyl]phenyl]silane (**9**)

Colorless oil; yield: 4.9 mmol (0.89 g, 49%); b.p. 72 °C (1 mbar).

¹H-NMR (CDCl₃): 1.06 (s, 6H, –CH₃); 2.89 (s, 2H, –CH₂–), 4.30 (s, 3H, SiH₃), 7.18–7.20 (m, 2H, Ar–H); 7.36 (t, ³J(H, H) = 7.5 Hz, 1H, Ar–H), 7.60 (d, ³J(H, H) = 7.5 Hz, 1H, Ar–H); ¹³C-NMR (CDCl₃): 13.5 (–CH₃), 39.9 (–CH₂–), 125.1 (C-arom), 127.6 (C-arom), 128.2 (C-arom), 130.0 (C-arom), 137.4 (C-arom), 144.8 (C-arom); ³¹P-NMR (CDCl₃): –41.3; ²⁹Si-NMR (CDCl₃): –62.4 (¹J(Si, H) = 200.7 Hz, ¹J(Si, P) = 5.6 Hz), MS CI, *m/z* (relative intensity (%)): 181 (100), 121 (21), 117 (13), 105 (12), 91 (22); IR (liquid, CsI): 2155 (Si–H).

4.4.2. [2-(Methylthiomethyl)phenyl]silane (**10**)

Colorless oil; yield: 6.80 mmol (1.14 g, 67%); b.p. 83 °C (2 mbar).

¹H-NMR (CDCl₃): 1.97 (s, 3H, –CH₃), 3.77 (s, 2H, –CH₂–), 4.26 (s, 3H, SiH₃), 7.23–7.30 (m, 2H, Ar–H), 7.35 (t, ³J(H, H) = 7.3 Hz, 1H, Ar–H), 7.61 (d, ³J(H, H) = 7.4 Hz, 1H, Ar–H); ¹³C-NMR (CDCl₃): 14.7 (–CH₃), 39.2 (–CH₂–), 127.7 (C-arom), 128.3 (C-arom), 129.5 (C-arom), 130.9 (C-arom), 137.9 (C-arom), 144.4 (C-arom); ²⁹Si-NMR (CDCl₃): –65.0 (¹J(Si, H) = 200 Hz); MS *m/z* (relative intensity (%)): 167 (100), 121 (77), 105 (68), 91 (70), 77 (13), 65 (12), 53 (13), 45 (11); IR (liquid, CsI): 2157 (Si–H); Anal. Calc. for C₈H₁₂SSi C, 57.39; H, 7.19. Found: C, 57.08; H, 7.44%.

4.5. Synthesis of the arylphenylchlorosilanes (general procedure)

At –78 °C a solution of 100 mmol of in 100 ml of Et₂O is added slowly to a solution of 102 mmol (7.46 ml) of phenylchlorosilane in 120 ml of Et₂O. The mixture is warmed to r.t. and is stirred for 20 h. The solvent is

removed in vacuo, and hexane is added to the residue. After filtration and evaporation of the solvent the residue is purified by distillation.

4.5.1. Chloro-[2-(dimethylphosphinomethyl)-phenyl]phenylsilane (**11**)

Colorless oil; yield: 58.0 mmol (17.0 g, 51%); b.p. 145 °C (0.02 mbar).

¹H-NMR (C₆D₆): 0.69 (d, ²J(P, H) = 26.7 Hz, 6H, –CH₃), 2.58, 2.82 (AB-system, ²J(H, H) = 13.4 Hz, 2H, –CH₂–), 6.20 (s, 1H, Si–H), 6.98 (t, ³J(H, H) = 7.4 Hz, 1H, Ar–H), 7.07–7.15 (m, 5H, Ar–H), 7.66–7.67 (d, ³J(H, H) = 7.3 Hz, 2H, Ar–H); 8.74 (d, ³J(H, H) = 7.4 Hz, 1H, Ar–H); ¹³C-NMR (C₆D₆): 13.4 (d, ¹J(C, P) = Hz), 39.6 (d, ¹J(C, P) = Hz), 125.6 (C-arom), 128.4 (C-arom), 129.8 (C-arom), 130.9 (C-arom), 131.3 (C-arom), 133.2 (C-arom), 134.5 (C-arom), 136.8 (C-arom), 145.6 (C-arom); ²⁹Si-NMR (C₆D₆): –10.1 (¹J(Si–H) = 238 Hz, ¹J(Si, P) = 7.5 Hz); ³¹P-NMR (C₆D₆): –39.0; IR (liquid, CsI): 2177 (Si–H); Anal. Calc. for C₁₅H₁₈ClPSi (292.82): C, 61.53; H, 6.19. Found: C, 61.53; H, 6.19%.

4.5.2. Chloro-[2-(methylthiomethyl)phenyl]phenylsilane (**12**)

Colorless oil; yield: 38.0 mmol (9.98 g, 38%); b.p. 130 °C (0.02 mbar).

¹H-NMR (C₆D₆): 2.54 (s, 3H, –CH₃), 3.89, 3.98 (AB-system, ²J(H, H) = 12.1 Hz, 2H, –CH₂–), 6.14 (s, 1H, SiH), 6.98–7.14 (m, 6H, Ar–H), 7.61 (m, 2H, Ar–H), 7.87 (d, ³J(H, H) = 7.3 Hz, 1H, Ar–H); ¹³C-NMR (C₆D₆): 14.3 (–CH₃), 38.6 (–CH₂–), 127.1 (C-arom), 128.3 (C-arom), 128.4 (C-arom), 129.7 (C-arom), 130.0 (C-arom), 130.3 (C-arom), 131.7 (C-arom), 136.0 (C-arom), 144.9 (C-arom); ²⁹Si-NMR (C₆D₆): –12.4 (¹J(Si–H) = 251 Hz); IR (liquid, CsI): 2181 (Si–H); Anal. Calc. for C₁₄H₁₅ClSSi (278.88): C, 60.30; H, 5.42. Found: C, 60.95; H, 5.74%.

4.5.3. Chloro-bis[2-(methylthiomethyl)phenyl]silane (**13**)

At –78 °C a solution of 100 mmol of in 100 ml of Et₂O is added slowly to a solution of 51 mmol (5.16 ml) of trichlorosilane in 120 ml of Et₂O. The mixture is warmed to r.t. and is stirred for 20 h. The solvent is removed in vacuo and hexane is added to the residue. After filtration and evaporation of the solvent the product is purified by distillation. Compound **14** is isolated as a pale yellow oil. Yield: 34.2 mmol (11.6 g, 68%); b.p. 184 °C (0.02 mbar).

¹H-NMR (C₆D₆): 1.52 (s, 6H, –CH₃), 3.60, 3.68 (AB-system, ²J(H, H) = 13.6 Hz, 4H, –CH₂–), 6.39 (s, 1H, SiH), 6.97–7.00 (m, 2H, Ar–H), 7.07–7.08 (m, 4H, Ar–H), 7.80 (d, ³J(H, H) = 7.4 Hz, 2H, Ar–H); ¹³C-NMR (C₆D₆): 4.7 (–CH₃), 38.8 (–CH₂–), 127.0 (C-arom.), 129.0 (C-arom.), 130.0 (C-arom), 132.8 (C-arom), 136.6 (C-arom), 144.5 (C-arom); ²⁹Si-NMR (C₆D₆): –18.2

($^1J(\text{Si}-\text{H}) = 251 \text{ Hz}$); IR (liquid, CsI): 2189 (Si-H); Anal. Calc. for $\text{C}_{16}\text{H}_{19}\text{ClS}_2\text{Si}$ (238.00): C, 56.68; H, 5.64. Found: C, 56.57; H, 6.17%.

4.5.4. [2-(Dimethylphosphinomethyl)phenyl]phenylsilyl trifluoromethanesulfonate (**14**)

Thirteen millimole of trimethylsilyl triflate are added slowly to a solution of 13 mmol (3.80 g) of the chlorosilane **11** in 30 ml of hexane at -78°C . The mixture is allowed to warm slowly to r.t., and is stirred for 20 h. The liquid layer is removed. The colorless solid precipitate is washed three times with 25 ml of hexane and dried in vacuo. The product is isolated as a colorless powder. Yield: 6.40 mmol (2.60 g, 49%).

$^1\text{H-NMR}$ (CD_2Cl_2): 1.73 (s, 3H, $-\text{CH}_3$), 1.78 (s, 3H, $-\text{CH}_3$), 3.63, 3.65 (AB system, $^2J(\text{H}, \text{H}) = 14.3 \text{ Hz}$, 2H, $-\text{CH}_2-$), 5.78 (d, $^2J(\text{P}, \text{H}) = 32.6 \text{ Hz}$, 1H, SiH), 7.44–7.48 (m, 4H, Ar-H), 7.52–7.57 (m, 1H, Ar-H), 7.59–7.61 (m, 3H, Ar-H), 7.85 (d, $^1J(\text{H}, \text{H}) = 7.4 \text{ Hz}$, 1H Ar-H); $^{13}\text{C-NMR}$ (CD_2Cl_2): 15.7 ($-\text{CH}_3$), 16.0 ($-\text{CH}_3$), 31.8 (d, $^1J(\text{P}, \text{C}) = 36.9 \text{ Hz}$, $-\text{CH}_2$), 120.8 (q, CF_3), 126.0 (C-arom), 126.1 (C-arom), 129.1 (C-arom), 129.3 (C-arom), 129.7 (d, $^2J(\text{C}, \text{P}) = 12 \text{ Hz}$, C-arom), 131.2 (C-arom), 132.2 (C-arom), 135.0 (C-arom), 136.6 (C-arom), 143.1 (C-arom); $^{29}\text{Si-NMR}$ (CD_2Cl_2): -32.4 ($^1J(\text{Si}, \text{H}) = 257.5 \text{ Hz}$, $^1J(\text{Si}, \text{P}) = 40 \text{ Hz}$); $^{19}\text{F-NMR}$ (CD_2Cl_2): 131.3; $^{31}\text{P-NMR}$ (CD_2Cl_2): -12.4 ; IR (CsI): 2144.9 (Si-H); Anal. Calc. for $\text{C}_{16}\text{H}_{18}\text{F}_3\text{PSSi}$ (406.44): C, 47.28; H, 4.46. Found: C, 47.16; H, 4.77%.

4.5.5. [2-(Methylthiomethyl)phenyl]phenylsilyl trifluoromethanesulfonate (**15**)

Seven millimole (1.25 ml) of trimethylsilyl triflate are added slowly to a solution of 6.95 mmol (2.37 g) of the chlorosilane **12** in 20 ml of hexane. The mixture is stirred for 7 days. All volatile components are removed in vacuo. The product is isolated as a colorless oil contaminated with a small amount of the chlorosilane **12**. Yield: 6.73 mmol (2.86 g, 90%; $^1\text{H-NMR}$).

$^1\text{H-NMR}$ (CD_2Cl_2): 1.57 (s, 3H, $-\text{CH}_3$), 3.84 (br, 2H, $-\text{CH}_2-$), 6.01 (s, 1H, SiH), 7.33 (d, $^1J(\text{H}, \text{H}) = 6.0 \text{ Hz}$, 1H, Ar-H), 7.42 (m, 2H, Ar-H), 7.45 (t, $^1J(\text{H}, \text{H}) = 7.2 \text{ Hz}$, 1H, Ar-H), 7.50 (m, 2H, Ar-H), 7.63 (d, $^1J(\text{H}, \text{H}) = 6.5 \text{ Hz}$, Ar-H), 8.12 (d, $^1J(\text{H}, \text{H}) = 6.4 \text{ Hz}$, 1H Ar-H); $^{13}\text{C-NMR}$ (CD_2Cl_2): 14.8 ($-\text{CH}_3$), 39.3 ($-\text{CH}_2-$), 119.0 (q, $^1J(\text{C}, \text{F}) = 318 \text{ Hz}$, CF_3), 128.1 (C-arom), 128.4 (C-arom), 128.6 (C-arom), 129.3 (C-arom), 130.8 (C-arom), 131.7 (C-arom), 133.0 (C-arom), 133.3 (C-arom), 137.9 (C-arom), 144.7 (C-arom); $^{29}\text{Si-NMR}$ (CD_2Cl_2): -42.8 ($^1J(\text{Si}, \text{H}) = 281 \text{ Hz}$); IR (KBr): 2192.1 (Si-H).

Due to the oily consistence it was not possible to purify the compound in order to obtain a correct CH analysis.

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