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# Disilene Fluoride Adducts versus $\beta$ -Halooligosilanides

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S Supporting Information

ABSTRACT: Extending the chemistry of disilene fluoride adducts studied earlier by us, we investigated the formation of 1,1-bis(trimethylsilyl)fluorodiphenylsilylsilanide, which was prepared by reaction of (Me<sub>3</sub>Si)<sub>3</sub>SiSiPh<sub>2</sub>F with KO<sup>t</sup>Bu. The formed FPh<sub>2</sub>SiSi(Me<sub>3</sub>Si)<sub>2</sub>K displays distinctively different structural and spectroscopic features compared to the earlier reported  $F(Me_3Si)_2SiSi(SiMe_3)_2K$ . While the latter eliminates metal fluoride upon reaction with MgBr<sub>2</sub>, the respective magnesium silanide is formed from FPh<sub>2</sub>SiSi(Me<sub>3</sub>Si)<sub>2</sub>K. Reaction of (Me<sub>3</sub>Si)<sub>3</sub>SiSiPh<sub>2</sub>Cl with KO<sup>t</sup>Bu proceeded similarly, but the formed ClPh<sub>2</sub>SiSi(Me<sub>3</sub>Si)<sub>2</sub>K easily undergoes



potassium chloride elimination to the disilene  $Ph_2Si=Si(SiMe_3)_2$ . Compared to  $F(Me_3Si)_2SiSi(SiMe_3)_2K$ , which can be regarded as a disilene fluoride adduct, structural, spectroscopic, and reactivity properties of FPh<sub>2</sub>SiSi(Me<sub>3</sub>Si)<sub>2</sub>K distinguish it as a  $\beta$ -fluorodisilanide.

#### INTRODUCTION

Over the last few years, the development of methods for the preparation of silanides<sup>1-5</sup> has promoted a tremendous progress of organosilicon chemistry. The availability of a wide variety of nucleophilic silicon compounds in combination with long known silvl electrophiles has brought us much closer to a mature organic chemistry of silicon, where Si-Si bond formation is not mainly restricted to Wurtz-type coupling of halosilanes.

A logical next step in this development is the introduction of functionalized silanides with the chemistry of  $\alpha$ -functionalized silyl anions (silylenoids) being pioneered by Kawachi and Tamao<sup>6-9</sup> as well as a few others.<sup>10–12</sup>

Our own contribution to this topic started out from the reaction of methoxytris(trimethylsilyl)silane with KO<sup>t</sup>Bu to bis(trimethylsilyl)methoxysilyl potassium,<sup>10</sup> which displays silylenoid character. This led us further to the synthesis of a  $\beta$ -fluorodisilanyl potassium compound (2a) from fluorosilane 1a, which forms via the condensation of two molecules of transient fluorosilylenoids (Scheme 1).13,14 Both of our synthetic approaches exploit silanide formation via Me<sub>3</sub>Si-Si bond cleavage with KO<sup>t</sup>Bu.<sup>15,16</sup>

In analogy to work by Wiberg and co-workers on Lewis base adducts of silenes,<sup>17</sup> we regarded the  $\beta$ -fluorodisilanides as fluoride adducts of tetrakis(trimethylsilyl)disilene. This view is supported by a rather short central Si-Si bond of 2.293(2) Å of 2a, indicating partial double bond character and very short Si-F bonds of 1.411(4)/1.437(4) Å.<sup>13</sup> Extending this chemistry to a case where one of the trimethylsilyl groups was replaced by a triisopropylsilyl group confirmed the transient formation of silvlenoid (Me<sub>3</sub>Si)(<sup>i</sup>Pr<sub>3</sub>Si)Si(F)K, which dimerized to  $(Me_3Si)(^{i}Pr_3Si)(F)SiSi(K)(SiMe_3)(Si^{i}Pr_3)$ (2b) (Scheme 1).<sup>14</sup>

An interesting feature of  $\beta$ -fluorodisilanyl potassium compounds 2a and 2b is that attempts to transmetallate by metathesis reaction with MgBr2 or Cp2ZrCl2 do not proceed as expected but lead via the elimination of metal fluorides to the formation of disilenes (Scheme 1), which depending on the bulk of substituents are either stable or undergo 2 + 2 cycloaddition.13,14

While condensation of fluorosilylenoids is a good and high yielding method to  $\beta$ -fluorodisilanides, it suffers from two disadvantages. First, it only works well starting out from a trisilylated silylfluoride. Our attempts to replace one of the silyl groups with other substituents were met only with very limited success. Reactions of  $R(Me_3Si)_2SiF$  (R = Me, Ph, <sup>t</sup>Bu) with KO<sup>t</sup>Bu gave the expected KR(SiMe<sub>3</sub>)SiSi(SiMe<sub>3</sub>)RF only for the R =  ${}^{t}$ Bu case with poor selectivity.<sup>14</sup> The second issue with the condensation reaction is that as a consequence of its nature, the substituents on the central silicon atoms are identical. To obtain access to  $\beta$ -fluorodisilanides with different substituents on the two silicon atoms, we decided to avoid the condensation step by introducing the Si-Si bond formed initially by silylenoid dimerization already into a substrate for silanide formation. The metalation then can occur in a separate step under conditions preserving the Si-Si bond.

#### RESULTS AND DISCUSSION

In a first attempt to implement this strategy, by reaction of  $(Me_3Si)_3SiSiMe_2Cl^{1.8}$  with  $ZnF_2$ . we prepared (Me<sub>3</sub>Si)<sub>3</sub>SiSiMe<sub>2</sub>F.<sup>18,19</sup> Treatment of the latter with KO<sup>t</sup>Bu was supposed to give (Me<sub>3</sub>Si)<sub>2</sub>(K)SiSiMe<sub>2</sub>F, but instead clean substitution of fluoride was observed to yield

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Scheme 1. Synthesis of Potassium  $\beta$ -Fluorodisilanides and Subsequent Disilene Formation upon Attempted Transmetallation



 $(Me_3Si)_3SiSiMe_2O^tBu$ . This outcome clearly indicates that the SiMe\_2F group is both sterically and electronically more susceptible to reaction with the alkoxides than the trimethylsilyl group. To suppress this reaction, the methyl groups of the SiMe\_2F substituent need to be replaced by bulkier groups.

A straightforward way to introduce the bulkier  $Ph_2SiX$  group and in addition avoid a subsequent halide exchange step is the reaction of silanide  $(Me_3Si)_3SiK$  with  $Ph_2SiX_2$  (X = F, Cl). We thus obtained  $(Me_3Si)_3SiSiPh_2X$  (X = F, Cl) (**3a**, **3b**) in excellent yields (Scheme 2).

Scheme	2.	Preparation	of	Oligosil	lanyl	Hal	ides	3a	and	31	b
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$Me_{3}Si$ $Me_{3}Si - Si - K + Ph_{2}SiX_{2}$ $Me_{3}Si - Si - K + Ph_{2}SiX_{2}$	
M8321	3a X = F 3b X = Cl

The solid-state structures in the crystals of **3a** and **3b** (Figure 1, Table 1) are inconspicuous with typical Si–F (1.6194(17) Å) and Si–Cl (2.0984(19) Å) distances and fairly short central Si–Si bonds of 2.3386(11) and 2.342(2) Å, respectively. Also, the NMR features of **3a** are rather predictable (Table 2). The <sup>29</sup>Si resonances at 21.1 (SiPh<sub>2</sub>F), -9.7 (SiMe<sub>3</sub>) and -134.8 ppm (Si<sub>q</sub>) are typical for a neopentasilane and so is the <sup>1</sup> $J_{Si-F}$  = 319 Hz for the SiPh<sub>3</sub>F<sup>20</sup> group.

Starting out from  $(Me_3Si)_3SiSiPh_2F$  (3a), reaction with KO<sup>t</sup>Bu in the presence of 18-crown-6 selectively cleaved off a trimethylsilyl group as silyl ether leading to the desired  $\beta$ -fluorodisilanide 4a (Figure 2, Scheme 3).

The solid state structure of **4a** (Figure 2) reveals a fairly typical silanide with the potassium ion in a crown-ether unit coordinating to the negatively charged silicon atom Si2 (Figure

2). Compared to the previously reported  $K(Me_3Si)_2SiSi-(SiMe_3)_2F$  (2a),<sup>13</sup> the bond distance between Si1 and Si2 (2.2970(15) Å) is very similar. This shortening of the central Si–Si bond by ca. 0.04 Å reflects the disilene contribution of the structure. The angles around the negative silicon atom sum up to 299.8 deg, thus exhibiting a more pronounced pyramidal silicon than the 333.2 deg observed for 2a.<sup>13</sup> This coincides with a Si–F bond length of 1.639(2) Å for 4a, featuring an elongation from the respective distance for 3a (1.6194(17) Å), which is surprising as the Si–F bond of  $K(Me_3Si)_2SiSi-(SiMe_3)_2F$  (2a) is very short (1.411(4)/1.437(4) Å).<sup>13</sup>

It can be assumed that the Si-F interaction is strongly connected to the polarity of the associated Si-Si double bond of the respective disilene. In their seminal paper, Wiberg and co-workers argue: "A prerequisite for adduct formation seems to be a polar Si=X double bond as neither Brook's sila enol ether  $(Me_3Si)_3Si = C(OSiMe_3)(1-adamantyl)_{,21,22}^{,21,22}$  which has a largely nonpolar silicon-carbon double bond nor West's<sup>23</sup> or Masamune's<sup>24</sup> (symmetrical) disilenes have been reported to form stable adducts." Despite the fact that our synthesis of K(Me<sub>3</sub>Si)<sub>2</sub>SiSi(SiMe<sub>3</sub>)<sub>2</sub>F (2a) has disproved Wiberg's argument, it is still reasonable that adducts of polar disilenes such as (Me<sub>3</sub>Si)<sub>2</sub>Si=SiPh<sub>2</sub> should be more stable. During their quest for the synthesis of a disilyne,<sup>25</sup> Wiberg et al. later reported some examples of  $\beta$ -halooligosilanides such as <sup>t</sup>Bu<sub>3</sub>Si-(H)(Br)SiSi(H)(Na)Si<sup>t</sup>Bu<sub>3</sub>, which however are very reactive even at low temperature and could not be rigorously characterized.26,27

The structural differences between 4a and 2a are consistent with the NMR spectroscopic analysis. The stronger silanide character, which is evident in the stronger pyramidalization of the anionic silicon atom of 4a, is reflected by a more shielded resonance at -201.6 ppm, which is decisively different from the -169.3 ppm observed for 2a (Table 2). Even more significant is the fact that for K(Me<sub>3</sub>Si)<sub>2</sub>SiSi(SiMe<sub>3</sub>)<sub>2</sub>F (2a) a



Figure 1. Molecular structures of 3a (left) and 3b (right) (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in deg). 3a: Si(1)-F(1) 1.6194(17), Si(1)-C(1) 1.873(3), Si(1)-Si(2) 2.3386(11), Si(2)-Si(5) 2.3508(12), Si(2)-Si(3) 2.3530(12), Si(2)-Si(4) 2.3535(12), F(1)-Si(1)-Si(2) 105.85(7), Si(1)-Si(2)-Si(5) 103.97(4), Si(1)-Si(2)-Si(3) 116.59(4). 3b: Si(1)-C(1) 1.876(5), Si(1)-Si(2) 2.342(2), Si(2)-Si(3) 2.353(2), Si(1)-Cl(1) 2.0984(19), C(1)-C(3) 1.386(7), Cl(1)-Si(1)-Si(2) 107.69(7), Si(1)-Si(2)-Si(3) 112.91(7).

compound	$Si^1 - F(X)$	Si <sup>1</sup> -Si <sup>2</sup>	Si <sup>2</sup> –SiMe <sub>3</sub>	Si <sup>2</sup> –M
3a	1.6194(17)	2.3386(11)	2.3508(12)/2.3535(12)	n.a.
3b	2.0984(19)  X = Cl	2.342(2)	2.353(2)/2.354(1)	n.a.
4a	1.639(2)	2.2970(15)	2.341(1)/2.347(1)	3.5609(14) M = K
4b	2.153(2) X = Cl	2.315(2)	2.356(2)/2.360(2)	n.a.
5	1.639(3)	2.3006(17)	2.339(2)/2.351(2)	n.a.
6	1.653(5)	2.318(3)	2.346(3)/2.345(3)	2.609(3) M = Mg
7	1.625(3)/1.621(3)	2.3593(19)/2.355(2)	2.361(2) - 2.378(1)	2.799(1)/2.803(1) M = Zr
$2a^{a}$	1.437(4)/1.411(4)	2.293(2)	2.350(2)	3.944(2)
AD to taken from a	f 12			

Table 1. Structural Bond Distances of Starting Materials 3a and 3b, as well as  $\beta$ -Halodisilanides 4a, 4b, 5, 6, 7 and Related Compound 2a

<sup>*a*</sup>Data taken from ref 13.

Table 2. NMR Chemical Shift and Coupling Data of 3a, 4a, 5, 6, 7 and the Related Compounds (Me<sub>3</sub>Si)<sub>3</sub>SiSi(SiMe<sub>3</sub>)<sub>2</sub>F, 2a, and 2b

	$\delta^{29}$ Si <sup>1</sup> –X	$\delta$ <sup>29</sup> Si <sup>2</sup>	$\delta$ <sup>29</sup> SiMe <sub>3</sub>			
compound	${}^{1}J_{\mathrm{Si}-\mathrm{F}}$	$^{2}J_{\rm Si-F}$	${}^{3}J_{\rm Si-F}$	$\delta$ $^{19}{ m F}$		
3a	21.1	-134.8	-9.7	-171.2		
	319 Hz	19 Hz	4 Hz			
3b	15.8	-127.3	-9.6	n.a.		
4a	41.4	-201.6	-4.4	-162.6		
	356 Hz	5 Hz	9 Hz			
4b	39.7	-195.7	-5.7	n.a.		
5	42.0	-202.5	-3.9	-164.5		
	358 Hz	n.d.	7 Hz			
6	32.1	-171.1	-7.4	-164.8		
	320 Hz	15 Hz	6 Hz			
7	25.1	-90.9	-6.5	-166.8		
	322 Hz	12 Hz	4 Hz			
$(Me_3Si)_3SiSi(SiMe_3)_2F^a$	41.3	-129.1	-12.1	-235.0		
	338 Hz	14 Hz	5 Hz			
<b>2a</b> •18-c-6 <sup><i>a</i></sup>	58.6	-169.3	-6.5	-213.5		
	314 Hz	79 Hz	18 Hz			
<b>2b</b> •18-c-6 <sup><i>a</i></sup>	62.3	-175.8		-200.1		
	342 Hz	53 Hz				
2 <b>b</b> •(THF) <sub>6</sub> <sup><i>a</i></sup>	72.3	-162.1		-195.8		
	292 Hz	91 Hz				
<sup>a</sup> Data taken from refs 13 and 14.						

rather pronounced  ${}^{2}J_{Si-F}$  coupling of 79 Hz was observed, whereas the  ${}^{2}J_{Si-F}$  coupling of 4a amounts only to 5 Hz.

While the crystal structure of 4a still reveals an interaction between the negatively charged silicon atom Si1 and the potassium ion, the reaction of 3a and KO<sup>t</sup>Bu in the presence of [2.2.2] cryptand gave product 5 as a separated ion pair. The structural properties of the anionic part of 5 (Figure 3) are quite similar to those of 4a (Table 1). The sum of angles around the negatively charged silicon atom (297.8 deg) is even slightly smaller than that for 4a. This picture is congruent with the NMR spectroscopic results. The diminished ionic interaction results in a slightly more shielded silanide chemical shift of -202.5 ppm, and the more pure silanide character is also reflected by other spectroscopic features such as  ${}^{1}J_{Si-F}$  and the chemical shifts of the SiPh<sub>2</sub>F and the SiMe<sub>3</sub> groups (Table 2).

Reactions of **2a** with MgBr<sub>2</sub>·Et<sub>2</sub>O and Cp<sub>2</sub>ZrCl<sub>2</sub> were found to cause the formation of disilene  $(Me_3Si)_2Si=Si(SiMe_3)_2$ .<sup>13,14</sup> Therefore, we reacted compound **4a** with these reagents in the expectation of an analogous disilene formation. However, reaction of **4a** with MgBr<sub>2</sub>·Et<sub>2</sub>O instead gave magnesium  $\beta$ -



Figure 2. Molecular structure of 4a (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in deg). K(1)-Si(2) 3.5609(14), Si(1)-F(1) 1.639(2), Si(1)-C(13) 1.888(3), Si(1)-Si(2) 2.2970(15), F(1)-Si(1)-Si(2) 120.26(9), Si(1)-Si(2)-Si(3) 97.89(5), Si(1)-Si(2)-K(1) 112.74(5).

Scheme 3. Reaction of  $(Me_3Si)_3SiSiPh_2F$  (3a) with KO<sup>t</sup>Bu in the Presence of 18-crown-6 or [2.2.2] Cryptand to Potassium  $\beta$ -Fluorodisilanides 4a and 5 and Subsequent Transmetallation to a Magnesium  $\beta$ -Fluorodisilanide (6)

	$\oplus$	
Me <sub>3</sub> Si Ph	Me <sub>3</sub> Si Ph	Me <sub>3</sub> Si Ph
Me <sub>3</sub> Si−Si−Si−F <u>KOƁu</u>		Br <mark>Mg-Si-S</mark> i-F
Me <sub>3</sub> Si Ph	Me <sub>3</sub> Si Ph	Me <sub>3</sub> Si Ph
3a	<b>4a</b> D = 18-crown-6	6
	5 D = cryptand	

fluorodisilanide 6 in a clean reaction (Scheme 3).<sup>28,29</sup> <sup>29</sup>Si NMR spectroscopic analysis of 6 shows rather typical chemical shifts for a trisilylated magnesium silanide of -171.1 ppm for the negatively charged silicon atom and -7.4 ppm for the trimethylsilyl groups.<sup>28,29</sup> This again is consistent with the structural data obtained from single crystal XRD analysis (Figure 4). The diminished silanide character of 6 is reflected by a less pyramidal silanide silicon atom with a sum of angles of 313.6 deg. The central Si–Si bond (2.318(3) Å) is also elongated compared to 4a and 5 but still shorter than that of 3a.

Reaction of **4a** with  $Cp_2ZrCl_2$  did also not give the expected disilene. Instead, clean formation of the silylzirconocene 7 (Scheme 4, Figure 5) was observed.<sup>30,31</sup> Again this outcome emphasizes the silanide character of **4a** compared to the disilene fluoride adduct character of **2a**. The <sup>29</sup>Si NMR



Figure 3. Molecular structure of 5 (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in deg). Si(1)-F(1) 1.639(3), Si(1)-C(1) 1.908(4), Si(1)-Si(2) 2.3006(17), K(1)-O(1) 2.802(3), K(1)-N(1) 3.066(4), F(1)-Si(1)-Si(2) 120.79(12), Si(1)-Si(2)-Si(3) 97.49(6), O(1)-K(1)-N(1) 121.06(10).



**Figure 4.** Molecular structure of **6** (thermal ellipsoid plot drawn at the 30% probability level). Only the anion part of the molecule is shown. All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in deg). Si(2)–Si(1) 2.318(3), Si(2)–Mg(1) 2.609(3), Si(1)–F(1) 1.653(5), Si(1)–C(1) 1.877(7), Mg(1)–O(1) 2.019(5), Mg(1)–Br(1) 2.460(3), Si(1)–Si(2)–Mg(1) 111.54(10), F(1)–Si(1)–Si(2) 112.11(18), O(2)–Mg(1)–O(1) 99.7(2), O(1)–Mg(1)–Br(1) 103.90(18), O(1)–Mg(1)–Si(2) 111.18(18), Br(1)–Mg(1)–Si(2) 122.41(11).

Scheme 4. Formation Fluorosilyl Zirconocene Chloride 7 by Reaction of 4a with Zirconocene Dichloride



spectrum of 7 features the Si-Zr resonance at -90.9 ppm, which is only slightly shifted to higher field compared to a number of related isotetrasilanyl zirconocene chlorides, which typically resonate close to -85 ppm.<sup>31,32</sup>

The solid state structure of 7 (Figure 5), which crystallizes in the triclinic space-group  $\overline{P1}$  with two crystallographically



Figure 5. Molecular structure of 7 (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in deg). Zr(1)-Cl(1) 2.4044(15), Zr(1)-Si(2) 2.7993(14), F(1)-Si(1) 1.624(3), Si(2)-Si(1) 2.3593(19), Si(2)-Si(3) 2.3641(18), Si(2)-Si(4) 2.3771(18), Si(1)-C(17) 1.868(5), Cl(1)-Zr(1)-Si(2) 94.28(5), Si(1)-Si(2)-Si(3) 101.62(7), F(1)-Si(1)-Si(2) 108.91(12).

independent molecules in the asymmetric unit was determined. The Si–Zr distance of 2.799(1)/2.803(1) Å is close to that of related oligosilanyl Zr(X)Cp<sub>2</sub> (X = Cl, Br) compounds,<sup>33–36</sup> and the Si–F bond length is close to that of **3a**. The Zr–Si–Si–F torsional angles of the two independent molecules of 7 are 145.6 and 162.56, indicating a transoid arrangement with no direct interaction between F and Zr. The sum of angles around the metalated of 7 is 310.5 deg, which is very close to what was found for **6**, whereas the central Si–Si bond (2.3593(19) Å) is substantially longer than what was observed for **3a** and **6**. However, this elongation might be caused not only by a less polar Si–Zr bond but also by the relatively large Cp<sub>2</sub>Zr(Cl) substituent.

When we studied the reaction of  $(Me_3Si)_3SiF$  with KO<sup>t</sup>Bu to **2a** (Scheme 1), it was evident that we ought to study also the analogous reaction with  $(Me_3Si)_3SiCl.^{13,14}$  However, this reaction is not clean at all, which we attribute to the propensity of the transient bis(trimethylsilyl)chlorosilylenoid to release bis(trimethylsilyl)silylene and maybe also the fact that the Si–Cl is weaker than the Si–F bond. In order to exploit the weaker Si–Cl bond we checked on the reaction of tris(trimethylsilyl)(chlorodiphenylsilyl)silane (**3b**) with KO<sup>t</sup>Bu. And indeed it was possible to detect the formation of  $\beta$ -chlorodisilanide **4b** (Scheme 5). As expected, the compound is

Scheme 5. Synthesis of  $\beta$ -Chlorodisilanide 4b, Followed by Chloride Elimination and Cyclotetrasilane (8) Formation



less stable than 4a. While the latter turned out to be stable in solution at temperatures up to 100 °C, compound 4b eliminates chloride slowly already at ambient temperature as well as under transmetalation conditions. The thus formed disilene  $(Me_3Si)_2Si=SiPh_2$  could not be observed directly as it undergoes head-to-tail [2 + 2] cycloaddition to give 1,1,3,3-



Figure 6. Molecular structure of 4b (thermal ellipsoid plot drawn at the 30% probability level). All hydrogen atoms are omitted for clarity (bond lengths in Å, angles in deg). Si(1)–Cl(1) 2.153(2), Si(1)–Si(2) 2.315(2), Si(2)–Si(4) 2.356(2), Si(2)–Si(3) 2.360(2), Si(3)–C(36) 1.889(7), K(1)–O(8) 2.665(5), K(1)–O(7) 2.695(5), K(1)–O(6) 2.792(4), Cl(1)–Si(2) 119.30(9), Si(1)–Si(2)–Si(4) 102.89(8), Si(4)–Si(2)–Si(3) 103.09(8), O(8)–K(1)–O(7) 166.80(17).

tetrakis(trimethylsilyl)tetraphenylcyclotetrasilane 8 (Scheme 5).

Crystal structure analysis of **4b** (Figure 6) revealed it to be another separated ion pair. The main structural properties are very similar to what was found for **5** (Table 1). Even more than was observed for the fluorosilanides, the Si–Cl distance of **4b** is elongated to 2.153(2) Å compared to the 2.0984(19) Å detected for **3b**. The central Si–Si bond (2.315(2) Å) is still shortened but to a lesser degree than was found for **4a** and **5** (Table 1).

NMR spectroscopic analysis of **4b** (Table 2) reveals the silanide signal (-195.7 ppm) to be distinctly less shielded compared to fluorosilanides **4a** and **5**. This is consistent with the chemical shifts of the trimethylsilyl groups of **4b** (-5.7 ppm) which are not shifted so far downfield as the ones of **4a** and **5** (-4.4 and -3.9 ppm, respectively).

# CONCLUSION

Some time ago, we encountered the formation of disilene fluoride adducts which form by condensation of two molecules of potassium bis(trimethylsilyl)fluorosilylenoid. These disilene adducts behave as nucleophiles in reactions with classical electrophiles such as silyl or alkyl halides. However, in attempts to transmetallate with metal halides such as MgBr<sub>2</sub>, LiCl, or Cp<sub>2</sub>ZrCl<sub>2</sub>, release of the disilene was observed. The current account deals with an extension of the chemistry of disilene fluoride adducts to compounds with different substituents in 1-and 2-positions.<sup>13,14</sup>

Starting from tris(trimethylsilyl)fluorodiphenylsilylsilane (3a), reaction with KO<sup>t</sup>Bu gave a disilene fluoride adduct with phenyl instead of trimethylsilyl groups at the fluoride bearing silicon atom.

Structural and spectroscopic characterization of the new adduct  $K(Me_3Si)_2SiSiPh_2F$  (**4a**, **5**) show surprising differences to  $K(Me_3Si)_2SiSi(SiMe_3)_2F$  (**2a**) with respect to the interaction between the disilene and the fluoride. The Si–F bond of **2a** is almost 0.2 Å shorter than a regular Si–F bond, in contrast to this, the Si–F bond of **4a** is slightly elongated compared to the starting material. This observation needs to be regarded in the context of  $J_{Si-F}$  coupling constants of **2a** and

4a. Whereas the  ${}^{1}J_{\text{Si-F}}$  coupling of 2a (314 Hz) is some 25 Hz reduced compared to the neutral analog (Me<sub>3</sub>Si)<sub>3</sub>SiSi- $(SiMe_3)_2F$ , the  ${}^1J_{Si-F}$  coupling constant of 4a (356 Hz) is almost 40 Hz larger than that of (Me<sub>3</sub>Si)<sub>3</sub>SiSiPh<sub>2</sub>F. Given the fact that J-coupling is strongly dependent on the s-orbital contribution, this behavior proves that the fluoride in 2a is bonded via  $\pi$ -type orbitals with a smaller s-orbital contribution than in 4a. This is further substantiated by the values of the  ${}^{2}I_{\text{Si-F}}$  coupling constants. While we observe an unusually large  ${}^{2}J_{\text{Si-F}} = 79$  Hz for **2a** the respective value is as small as 5 Hz for 4a and could not even be determined for the separated ion pair in 5. This clearly shows that the fluoride in 2a interacts with the disilene unit (i.e., the **two** doubly bound silicon atoms), whereas 4a and 5 can be categorized as  $\beta$ -fluorodisilanides with the fluorides interacting mostly with the directly attached silicon atoms. The stronger disilene character in 2a is also evident in its reactivity. Reactions of 2a with metal halides favor the elimination of metal fluorides with concurrent release of a disilene; analogous conversions with 4a cleanly lead to transmetalated compounds.

# EXPERIMENTAL SECTION

General Remarks. All reactions involving air-sensitive compounds were carried out under an atmosphere of dry nitrogen using either Schlenk techniques or a glovebox. All solvents were dried using column based solvent purification system.<sup>37</sup> Tetrakis(trimethylsilyl)silane,<sup>38</sup> 1-chloro-1,1-diphenyl-2,2-bis(trimethylsilyl)-trimethyltrisilane,<sup>39</sup> MgBr<sub>2</sub>·OEt<sub>2</sub>,<sup>40</sup> and [2.2.2] cryptand<sup>41</sup> have been prepared following published procedures. All other used chemicals were obtained from different suppliers and used without further purification. <sup>1</sup>H (300 MHz), <sup>13</sup>C (75.4 MHz), <sup>19</sup>F (75.4 MHz), and <sup>29</sup>Si (59.3 MHz) NMR spectra were recorded on a Varian INOVA 300 spectrometer. Spectra are referenced to tetramethylsilane (TMS) for <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si and to CFCl<sub>3</sub> for <sup>19</sup>F typically using the known positions of residual solvent signals.<sup>42</sup> If not noted otherwise, all samples were measured in  $C_6D_6$ . To compensate for the low isotopic abundance of <sup>29</sup>Si, the INEPT pulse sequence was used for the amplification of the signal.<sup>43,44</sup> Frequently, this does not allow observing diphenylsilyl Si signals; therefore, the Varian s2pul sequence (a simple inverse-gated single pulse experiment) was used for those cases. Elementary analysis were carried out using a Heraeus VARIO ELEMENTAR instrument. As potassium and magnesium

silanides usually give poor analysis data, the purity of these compounds is confirmed by  ${}^{1}$ H,  ${}^{13}$ C, and  ${}^{29}$ Si NMR spectra (see Supporting Information).

X-ray Structure Determination. For X-ray structure analyses, the crystals are mounted onto the tip of glass fibers, and data collection was performed with a BRUKER-AXS SMART APEX CCD diffractometer using graphite-monochromated Mo  $K_{\alpha}$  radiation (0.71073 Å). The data were reduced to  $F_{0}^{2}$  and corrected for absorption effects with SAINT<sup>45</sup> and SADABS,<sup>46,47</sup> respectively. The structures were solved by direct methods and refined by full-matrix least-squares method (SHELXL97).48 If not noted otherwise, all nonhydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles. All diagrams are drawn with 30% probability thermal ellipsoids, and all hydrogen atoms were omitted for clarity. Crystallographic data (excluding structure factors) for the structures of compounds 3a, 3b, 4a, 4b, 5, 6, and 7 reported in this paper are deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1920634 (3a), 1920635 (3b), 1920633 (4a), 1920637 (4b), 1920638 (5), 1920639 (6), and 1920636 (7). Copies of data can be obtained free of charge at http://www.ccdc.cam.ac.uk/products/csd/ request/. Figures of solid state molecular structures were generated using Ortep-3 as implemented in WINGX<sup>49</sup> and rendered using POV-Ray 3.6.50

**1-Fluoro-1,1-diphenyl-2,2-bis(trimethylsilyl)trimethyltrisilane (3a).** Tetrakis(trimethylsilyl)silane (200 mg, 0.623 mmol) and KO<sup>t</sup>Bu (73 mg, 0.654 mmol) were dissolved in THF (4 mL). After 6 h, MgBr<sub>2</sub>·OEt<sub>2</sub> (169 mg, 0.654 mmol) was added. Stirring was continued for 30 min after which precipitated KBr was removed by filtration. Difluorodiphenylsilane (0.654 mmol, 144 mg) was added dropwise within 3 min to the colorless solution, and the precipitated white MgBrF was removed again by filtration after 30 min. The solvent was removed in vacuo, and the yellow residue was crystallized from pentane yielding colorless crystalline 3a (252 mg, 90%). Mp.: 75–77 °C. NMR ( $\delta$  in ppm): <sup>1</sup>H: 7.73 (m, 4H), 7.10 (m, 6H), 0.21 (s, 27H, SiMe<sub>3</sub>). <sup>13</sup>C: 138.4 (d, <sup>2</sup>J<sub>C-F</sub> = 13 Hz), 134.0 (d, <sup>3</sup>J<sub>C-F</sub> = 3 Hz), 130.3, 128.3, 2.9. <sup>29</sup>Si: 21.1 (d, <sup>1</sup>J<sub>Si-F</sub> = 319 Hz, SiPh<sub>2</sub>F), -9.7 (d, <sup>3</sup>J<sub>Si-F</sub> = 4 Hz, SiMe<sub>3</sub>), -134.8 (d, <sup>2</sup>J<sub>Si-F</sub> = 19 Hz, Si<sub>q</sub>). <sup>19</sup>F: -171.2 (<sup>1</sup>J<sub>F-Si</sub> = 319 Hz). Anal. Calcd. for C<sub>21</sub>H<sub>37</sub>FSi<sub>5</sub> (448.95): C 56.18, H 8.31. Found: C 55.97, H 8.23.

1-Chloro-1,1-diphenyl-2,2-bis(trimethylsilyl)trimethyltrisilane (3b). Tetrakis(trimethylsilyl)silane (62.3 mmol, 20.0 g) and KO<sup>t</sup>Bu (65.5 mmol, 7.35 g) were dissolved in DME (40 mL) and stirred for 6 h. The solution was added dropwise within 2 h to dichlorodiphenylsilane (169.5 mmol, 17.6 g) in toluene (150 mL) and stirring was continued for 12 h. The solvent was removed in vacuo, and the residue was extracted with pentane three times. After removal of the solvent, **3b** was obtained as a colorless semicrystalline solid (28.7 g, 99%). Mp.: 175–176 °C. NMR (δ in ppm): <sup>1</sup>H: 7.80– 7.87 (m, 4H, Ph), 7.10–7.20 (m, 6H, Ph), 0.28 (s, 27H, SiMe<sub>3</sub>). <sup>13</sup>C: 137.4 (Ph), 135.0 (Ph), 130.3 (Ph), 128.2 (Ph), 2.9 (SiMe<sub>3</sub>). <sup>29</sup>Si (s2pul): 15.8 (SiPh<sub>2</sub>Cl), -9.6 (SiMe<sub>3</sub>), -127.3 (Si<sub>q</sub>). Anal. Calcd. for C<sub>21</sub>H<sub>37</sub>ClSi<sub>5</sub> (465.40): C 54.20, H 8.01. Found: C 54.19, H 8.12.

2-Fluoro-2,2-diphenyl-1,1-bis(trimethylsilyl)disilanyl potassium 18-crown-6 (4a). Method A. Compound 3a (300 mg, 0.668 mmol), 18-crown-6 (185 mg, 0.702 mmol), and KO<sup>t</sup>Bu (73 mg, 0.702 mmol) were dissolved in a minimum amount of benzene or DME. The color of the mixture immediately turned to yellow in DME and to orange in benzene/18-crown-6. After a few minutes, the reaction was finished as could be determined by NMR spectroscopic analysis. The solvent was removed, and pentane was added to the residue. The insoluble salts were removed by filtration. Tetrakis(trimethylsilyl)silane (in the case of both solvents) and tris(trimethylsilyl)silyl potassium (just when benzene/18-crown-6 was employed as solvent) were observed as byproducts. Sublimation at 60 °C to remove Si(SiMe<sub>3</sub>)<sub>4</sub> followed by crystallization of the residue from pentane yielded pure orange crystalline 4a (in case of DME: 258 mg, 65% (calculated with 2 DME); in benzene/18-crown-6:204 mg, 45%). NMR ( $\delta$  in ppm, in DME with a D<sub>2</sub>O capillary): <sup>1</sup>H: 8.44 (m, 2H), 8.24 (m, 4H), 7.40 (m, 4H), 3.76 (18-cr-6), 0.53 (s, 18H, SiMe<sub>3</sub>). <sup>13</sup>C: 148.5 (d, <sup>2</sup> $J_{C-F}$  = 19 Hz), 138.1 (d, <sup>2</sup> $J_{C-F}$  = 5 Hz), 134.8, 126.8, 70.2 (18-cr-6), 7.5. <sup>29</sup>Si: 41.4 (d, <sup>1</sup> $J_{Si-F}$  = 356 Hz, SiPh<sub>2</sub>F), -4.4 (d, <sup>3</sup> $J_{Si-F}$  = 9 Hz, SiMe<sub>3</sub>), -201.6 (d, <sup>2</sup> $J_{Si-F}$  = 5 Hz, Si<sub>q</sub>). <sup>19</sup>F: -162.6 (<sup>1</sup> $J_{F-Si}$  = 353 Hz).

*Method B.* Compound **3a** (280 mg, 0.623 mmol), 18-crown-6 (173 mg, 0.654 mmol), and KO'Bu (73 mg, 0.654 mmol) were dissolved in toluene (5 mL). The reaction mixture was stirred for 6 h, after which the solvent was removed in vacuo, and some byproducts were removed by sublimation. Product **4a** (204 mg, 45%) crystallized as deep orange crystals from THF/pentane at -60 °C.

**2-Chloro-2,2-diphenyl-1,1-bis(trimethylsilyl)disilanyl Potassium 18-Crown-6 (4b).** A precooled (-30 °C) solution of KO<sup>t</sup>Bu (112 mg, 1.00 mmol) and 18-crown-6 (265 mg, 1.00 mmol) in THF (5 mL) was added to a precooled solution of compound **3b** (466 mg, 1.00 mmol) in THF (3 mL). After vigorous shaking, the clear yellow reaction mixture was stored at -30 °C for 6 h. Reaction monitoring by NMR spectroscopy showed reaction completion. NMR ( $\delta$  in ppm, in THF with an acetone-*d*<sub>6</sub> capillary at 243 K): <sup>1</sup>H: 7.10 (d, 4H, *J*<sub>H-H</sub> = 6 Hz, PhH), 6.20–6.36 (m, 4H, PhH), 2.81 (s, 24H, 18-cr-6), 0.83 (SiMe<sub>3</sub>). <sup>13</sup>C: 146.3, 133.9, 125.5, 125.1, 69.4 (18-cr-6), 5.3. <sup>29</sup>Si: 39.7 (SiPh<sub>2</sub>Cl), -5.7 (SiMe<sub>3</sub>), -195.7 (Si<sub>0</sub>).

**2-Fluoro-2,2-diphenyl-1,1-bis(trimethylsilyl)disilanyl** Potassium Cryptand (5). Crypt[2.2.2] (377 mg, 1.00 mmol) and KO<sup>t</sup>Bu (113 mg, 1.00 mmol) were dissolved in benzene (2 mL) and added to a stirred solution of compound **3a** (449 mg, 1.00 mmol) in benzene (3 mL). After 2 h, stirring was discontinued upon which two liquid phases separated. The top layer was separated, and the orange ionic phase below was dried under a vacuum. The orange residue was washed with pentane, yielding the title compounds as an orange solid (351 mg, 43%). NMR (δ in ppm, C<sub>6</sub>D<sub>6</sub>): <sup>1</sup>H: 7.79–7.85 (m, 4H, Ph), 7.02–7.19 (m, 6H, Ph), 3.64 (s, 12H, cryptand), 3.60 (t, 12H, J<sub>H-H</sub> = 4 Hz, cryptand), 2.62 (t, 12H, J<sub>H-H</sub> = 4 Hz, cryptand), 0.00 (s, 18H, SiMe<sub>3</sub>). <sup>19</sup>F: -164.5 (<sup>1</sup>J<sub>Si-F</sub> = 359 Hz). <sup>29</sup>Si (s2pul): 42.0 (d, <sup>1</sup>J<sub>Si-F</sub> = 358 Hz, SiPh<sub>2</sub>F), -3.9 (d, <sup>3</sup>J<sub>Si-F</sub> = 6 Hz, SiMe<sub>3</sub>), -202.6 (Si<sub>q</sub>).

2-Fluoro-2,2-diphenyl-1,1-bis(trimethylsilyl)disilanyl Mag**nesiumbromide (6).** A cold solution of **3a** (1.00 mmol, 449 mg) (stored at -35 °C prior to the reaction) in THF (2 mL) was added to a cold solution of KO<sup>t</sup>Bu (1.05 mmol, 118 mg) in THF (2 mL), and the resulting yellow reaction mixture was kept cold for another 6 h. Then the silanide solution was added dropwise to a cold suspension of magnesium bromide etherate (1.05 mmol, 272 mg) in THF (6 mL) under vigorous stirring. The off-white suspension was stored at -35 °C for another 2 h followed by evaporation of the solvent under reduced pressure. The remaining off-white solid was extracted with benzene/pentane (1:2 ratio), and the combined extracts were concentrated under a vacuum to a volume of about 1 mL. Addition of pentane (10 mL) afforded precipitation of the magnesium silanide which was washed with pentane  $(2 \times 2 \text{ mL})$  and dried under a vacuum giving analytically pure 6 as a white microcrystalline solid (230 mg, 57%). Colorless single-crystals of 6 suitable for X-ray diffraction analysis were obtained from the pentane solutions used to wash the product. NMR ( $\delta$  in ppm, C<sub>6</sub>D<sub>6</sub>): <sup>1</sup>H: 8.04 (m, 4H, Ph), 7.22-7.32 (m, 4H, Ph), 7.15 (m, 2H, Ph), 3.63 (br s, 8H, OCH<sub>2</sub>CH<sub>2</sub>), 1.19 (br s, 8H, OCH<sub>2</sub>CH<sub>2</sub>), 0.49 (s, 18H, SiMe<sub>3</sub>). <sup>13</sup>C: 142.1 (d,  $J_{C-F}$  = 15 Hz, Ph), 134.5 (d,  $J_{C-F}$  = 3 Hz, Ph), 129.2, 69.8 (OCH<sub>2</sub>CH<sub>2</sub>), 25.0 (OCH<sub>2</sub>CH<sub>2</sub>), 5.6 (SiMe<sub>3</sub>). <sup>19</sup>F: -164.8. <sup>29</sup>Si (s2pul): 32.1 (d,  ${}^{1}J_{Si-F}$  = 320 Hz, SiPh<sub>2</sub>F), -7.4 (d,  ${}^{3}J_{Si-F}$  = 6 Hz,  $SiMe_3$ ), -171.1 (d,  $J_{Si-F} = 15$  Hz, SiMg).

**2-Fluoro-2,2-diphenyl-1,1-bis(trimethylsilyl)disilanyl Zirconocene Chloride (7).** A cold solution of **3a** (1.00 mmol, 449 mg) (stored at -35 °C prior to the reaction) in THF (2 mL) was added to a cold solution of KO<sup>t</sup>Bu (1.05 mmol, 118 mg) in THF (2 mL), and the resulting yellow reaction mixture was kept cold for another 6 h. Then, this silanide solution was added dropwise to a cold solution of Cp<sub>2</sub>ZrCl<sub>2</sub> (1.05 mmol, 307 mg) in THF (5 mL) under vigorous stirring. After the addition, the orange reaction mixture was kept at -35 °C for another 1 h, followed by evaporation of all volatiles under reduced pressure. The orange residue was extracted with benzene/ pentane (1:2 ratio), the combined solutions were evaporated to dryness, and the solid yellow residue was washed with pentane (3 × 5 mL). The remaining solid was taken up in benzene (3 mL) and the solution layered with pentane which afforded orange crystals of 7 (394 mg, 62%). NMR ( $\delta$  in ppm, C<sub>6</sub>D<sub>6</sub>): <sup>1</sup>H: 7.94 (m, 4H, Ph), 7.22 (m, 4H, Ph), 7.09–7.16 (m, 2H, Ph), 5.96 (s, 10H, Cp), 0.42 (s, 18H, SiMe<sub>3</sub>). <sup>13</sup>C: 140.7 (d,  $J_{C-F} = 13$  Hz, Ph), 134.4 (d,  $J_{C-F} = 3$  Hz, Ph), 129.9, 128.2, 111.8 (Cp), 5.1 (SiMe<sub>3</sub>). <sup>19</sup>F: -166.8 (d, <sup>1</sup> $J_{Si-F} = 323$  Hz). <sup>29</sup>Si (s2pul): 25.1 (d, <sup>1</sup> $J_{Si-F} = 322$  Hz, SiPh<sub>2</sub>F), -6.5 (d, <sup>3</sup> $J_{Si-F} = 4$  Hz, SiMe<sub>3</sub>), -90.9 (d, <sup>2</sup> $J_{Si-F} = 12$  Hz, SiZr). Anal. Calcd. for C<sub>28</sub>H<sub>38</sub>ClFSi<sub>4</sub>Zr (632.62): C 53.16, H 6.05. Found: C 52.90, H 6.21.

1,1,3,3-Tetrakis(trimethylsilyl)-2,2,4,4-tetraphenylcyclotetrasilane (8). Compound 3b (2.00 mmol, 931 mg) was dissolved in toluene (3 mL), and a solution of 18-crown-6 (2.10 mmol, 555 mg) and KO<sup>t</sup>Bu (2.10 mmol, 236 mg) in toluene (4 mL) was added. The mixture turned red immediately, and after vigorous shaking for some 10 s, it was left standing for 18 h. Then MgBr<sub>2</sub>·OEt<sub>2</sub> (2.10 mmol, 542 mg), a stirrer bar, and THF (5 mL) were added. The mixture was then stirred for another 18 h, after which it was quenched by transfer onto a mixture of THF (20 mL) and chlorotrimethylsilane (2 mL). The now colorless mixture was hydrolyzed using 1 M HCl. The organic layer was separated, and the aqueous layer extracted three times with toluene. The combined organic layers were dried over sodium sulfate, and all volatiles evaporated under reduced pressure yielding a colorless and highly viscous oil. The oil was taken up in benzene for crystallization yielding colorless crystals of 8 (480 mg, 69%) after slow evaporation at ambient temperature after 1 day. NMR  $(\delta \text{ in ppm, } C_6 D_6)$ : <sup>1</sup>H: 7.76 (m, 8H, Ph), 7.13 (m, 12H, Ph), 0.20 (s, 36H, SiMe<sub>3</sub>). <sup>13</sup>C: 139.2 (Ph), 137.2 (Ph), 129.2 (Ph), 128.1 (Ph), 3.7 (SiMe<sub>3</sub>). <sup>29</sup>Si (s2pul): -7.8 (SiMe<sub>3</sub>), -9.9 (SiPh<sub>2</sub>), -93.8 (Si<sub>q</sub>). Anal. Calcd. for C<sub>36</sub>H<sub>56</sub>Si<sub>8</sub> (713.52): C 60.60, H 7.91. Found: C 60.42, H 8.02.

## ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b02223.

Tabulated crystallographic data for compounds **3a**, **3b**, **4a**, **4b**, **5**, **6**, and 7. NMR spectra (<sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F, and <sup>29</sup>Si) for compounds **3a**, **3b**, **4a**, **4b**, **5**, **6**, 7, and **8** (PDF)

#### Accession Codes

CCDC 1920633–1920639 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

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