ORGANOMETALLICS

Synthesis and Structure of Zwitterionic Silylborates and Silylzincates with Pendant Polydonor Arms

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Supporting Information

ABSTRACT: The synthesis and structure of well-defined zinc- and potassium-containing heterobimetallic zwitterions that have pendant polydonor arms is reported. The zwitterionic complexes $[Me_2ZnSi(SiMe_2OCH_2CH_2OMe)_3Li]$ (Li-2), $[Cl_2ZnSi(SiMe_2OCH_2CH_2OMe)_3K]$ (K-3), and $[I_2ZnSi(SiMe_2OCH_2CH_2OMe)_3K]$ (K-4) were prepared from reactions of $[Si(SiMe_2OCH_2CH_2OMe)_3M]$ (M = Li, K) (M-1) with ZnCl₂, ZnI₂, and ZnMe₂, respectively. Reaction of K-1 with $B(C_6F_5)_3$ gave the potassium silyl borate $[(C_6F_5)_3BSi(SiMe_2OCH_2CH_2OMe)_3K]$ (K-5) in 90% yield.



Treatment of 2 equiv of K-1 with $ZnCl_2$ afforded the nonzwitterionic zinc silanide $Zn(Si(SiMe_2OCH_2CH_2OMe)_3)_2$ (6), as a liquid, which upon treatment with 1 equiv of $ZnMe_2$ and 4 equiv of $B(C_6F_5)_3$ could be converted into the zwitterionic zinc silyl borate $[(C_6F_5)_3BSi(SiMe_2OCH_2CH_2OMe)_3Zn][MeB(C_6F_5)_3]$ (7). The structures of the zwitterionic complexes K-4, K-5, and 7 were determined by X-ray crystallography.

■ INTRODUCTION

Zwitterionic silanides are a relatively new class of silyl anions¹ with dual functionalities that have the potential of being useful as spectator ligands for main group and transition metals.²⁻⁷ Interest in these zwitterionic silanide ligands primarily arises from the "naked" silyl anion that is rigidly locked and insulated from the metal cation by internal donor bridges. In striking contrast to tetracoordinate borate-based zwitterions,8 zwitterionic silanides are tricoordinated and bear a stereochemically active electron pair localized at the central silyl anion, which behaves as a Lewis base and can bind to electrophilic transition and main group metal centers. In fact, we have recently demonstrated that zwitterionic alkaline and alkaline earth metal silanides can efficiently be generated in high yields and used as precursors for the convenient synthesis of novel heterobimetallic zwitterions⁶ (Chart 1). Herein, we report the synthesis and structural characterization of well-defined zinc-containing monometallic and heterobimetallic zwitterions derived from





zwitterionic alkaline metal silanides with pendant polydonor arms.

RESULTS AND DISCUSSION

We first investigated the reaction of dimethylzinc with lithium silanide Li-1⁶ and isolated from the reaction mixture the zwitterionic Lewis acid—base adduct Li-2 as the only product (Scheme 1). Li-2, which was characterized by ¹H, ¹³C, ²⁹Si, and ⁷Li NMR spectroscopy, can be viewed as a heterobimetallic silylzincate in which the lithium cation is coordinated by the six neutral oxygen donors, while the zinc is being coordinated by the silyl anion to form a zincate structure. Li-2 is thermally unstable and decomposes slowly upon standing for longer periods of time at room temperature. It is soluble in most organic solvents (benzene, ether, toluene, THF), except hexanes and pentane, where it is insoluble.

When potassium silanide K-1 was reacted with $ZnCl_2$ in THF as solvent, a colorless microcrystalline material insoluble in pentanes and hexanes was isolated in 64% yield and identified by ¹H, ¹³C, and ²⁹Si NMR data and elemental analyses as the zwitterionic ZnCl₂ adduct K-3. The ¹H and ¹³C NMR spectra showed singlets for the SiMe₂ and OMe groups and triplets for the two chemically nonequivalent CH₂ groups, which is consistent with a structure of nearly C_3 symmetry in which the central potassium cation is equally coordinated by the three pendant OCH₂CH₂OMe donor arms. The reaction of K-1 with ZnI₂ in diethyl ether behaved similarly to that of K-1 with ZnCl₂ as the zwitterionic ZnI₂ adduct K-4 precipitated

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Scheme 1. Formation of the Zwitterionic Lewis Acid-Base Adducts Li-2, K-3, and K-4



from solution as a colorless crystalline material in 90% yield. Its composition was established by means of 1 H, 13 C, and 29 Si

NMR data and elemental analyses; the spectral features were similar to those of K-3.

In addition, the molecular structure of K-4 was determined by X-ray crystallography (see Figure 1). K-4 forms in the solid state a dimer composed of a square-planar Zn₂I₂ core. The zinc centers exhibit a distorted tetrahedral geometry with angles ranging from 96° to 119°. As expected, the Zn–I_{bridging} distances ranging from 2.741 to 2.768 Å are significantly larger than the Zn–I_{terminal} distances [Zn2–I4 2.592(1), Zn1–I3 2.614(1) Å]. The Si–Zn bond lengths [2.389 and 2.395 Å] are only slightly larger than those of the nonzwitterionic zinc silanides (Me₃Si)₃SiZnCl·TMEDA [2.367 Å],⁹ [(Me₃Si)₂SiZnCl·THF]₂ [2.365 Å],¹⁰ [(Me₃Si)₃Si]₂Zn [2.355 Å],¹¹ (Bu⁴₃Si)₂Zn [2.384 Å],¹² and [(Bu⁴₃Si)₂ZnBr]₄ [2.376 Å].¹² In the dimer the two potassium cations are each coordinated by the three OCH₂CH₂OMe donor arms, resulting in a distorted octahedral coordination environment for both potassium cations with O–K–O angles and K–O distances ranging from 61.7° to 141.7° and 2.63–2.78 Å, respectively.

Notably, both adducts K-3 and K-4 are stable at room temperature and do not spontaneously undergo elimination of KX (X = Cl, I) to generate salt-free zinc silanides. To the best of our knowledge, K-3 and K-4 represent the first stable ZnX_2 -silanide adducts.^{13,14} In fact, these adducts can be considered intermediates in the formation of zinc silanides of the general formula $R_3Si-Zn-SiR_3$ via an addition-elimination mechanism at the zinc center. The relative stability of K-3 and K-4 toward elimination of KX at room temperature can reasonably be explained by the potassium cation being sequestered within the cavity of the ligand with its three pendant donor arms resulting in a stable octahedral coordination environment for potassium.

In an attempt to generate zwitterionic zinc silanides, where the zinc dication would be exclusively coordinated octahedrally by the OCH_2CH_2OMe donor arms and charge separated from the anion, K-1⁶ was reacted with the strong Lewis acid



Figure 1. Solid-state structure of dimeric K-4 (the disordered MeOCH₂CH₂O group was omitted for clarity). Selected distances [Å] and angles [deg]: Zn1–Si1 2.389(2), Zn1–I3 2.614(1), Zn1–I1 2.741(1), Zn1–I2 2.756(1), Zn2–Si5 2.395(2), Zn2–I4 2.592(1), Zn2–I1 2.754(1), Zn2–I2 2.768(1), Si1–Zn1–I3 118.84(5), Si1–Zn1–I1 116.17(5), I3–Zn1–I1 103.55(3), Si1–Zn1–I2 111.84(5), I3–Zn1–I2 108.07(3), I1–Zn1–I2 95.60(3), Si5–Zn2–I4 118.71(5), Si5–Zn2–I1 112.78(5), I4–Zn2–I1 105.19(3), Si5–Zn2–I2 113.29(5), I4–Zn2–I2 109.04(3), I1–Zn2–I2 95.02(2), Zn1–I1–Zn2 84.89(2), Zn1–I2–Zn2 84.36(2), Si4–Si1–Zn1 108.95(7), Si3–Si1–Zn1 104.33(8), Si2–Si1–Zn1 111.45(7), Si6–Si5–Zn2 103.37(8), Si8–Si5–Zn2 109.98(7), Si7–Si5–Zn2 111.57(8).

 $B(C_6F_5)_3$ and subsequently treated with zinc halides. However, all attempts to generate such a zwitterionic zinc silylborate via salt metathesis (Scheme 2) failed primarily due to the very low

Scheme 2. Attempted Synthesis of a Zwitterionic Zinc Silylborate



solubility of K-5 in most organic solvents. Reactions of K-5 with ZnI₂ in THF gave several products, which could not be separated from each other due to their low solubilities in organic solvents. Despite its poor solubility, K-5 was isolated from the reaction of K-1 and $B(C_6F_5)_3$ in toluene as a microcrystalline material, and its structure determined by ¹H, ¹³C, ¹⁹F, ¹¹B, and ²⁹Si NMR data, elemental analyses, and X-ray crystallography (Figure 2).



Figure 2. Solid-state structure of K-5. Selected distances [Å] and angles [deg]: Si4–B1 2.167(4), K1–O2 2.666(3), K1–O4 2.679(2), K1–O6 2.680(3), K1–O5 2.704(2), K1–O3 2.720(2), K1–O1 2.736(2), O1–Si1 1.675(2), O3–Si2 1.671(2), O5–Si3 1.683(2), Si1–Si4 2.3821(12), Si2–Si4 2.3770(13), Si3–Si4 2.3813(12), Si1–O1–K1 123.36(10), Si2–O3–K1 126.78(11), Si3–O5–K1 125.57(11), O1–Si1–Si4 104.42(8), O3–Si2–Si4 104.35(9), O5–Si3–Si4 106.44(8), B1–Si4–Si2 115.68(10), B1–Si4–Si3 114.48(10), Si2–Si4–Si3 103.06(5), B1–Si4–Si1 115.59(10), Si2–Si4–Si1 102.81(4), Si3–Si4–Si1 103.51(4).

K-5, which represents one of the very few examples of silylsubstituted tris(pentafluorophenyl)borates,^{13,14} forms in the solid state a polymeric network held together by intermolecular H…F contacts. Close intramolecular H…F contacts are seen in the monomeric subunits: between the ortho- (F4, F6, and F11) and meta-fluorine (F5, F7, and F12) atoms and the next neighboring hydrogen atoms of the SiMe₂ groups ranging from 2.52 to 2.87 Å. The silicon boron distance [2.167 Å] of K-5 is somewhat larger than of the structurally related silvlene borate complexes $L \rightarrow SiCl_2 \rightarrow B(C_6F_5)_3$ [2.106 Å]¹⁵ and [Ph(NBu^t)-C=NBu^t]SiCl \rightarrow B(C₆F₅)₃ [2.108 Å]¹⁶ reported by Roesky and Stalke. The larger Si-B distance of K-5 perhaps is the result of significant steric repulsion occurring between the metal silanide and $B(C_6F_5)_3$ units, because the Si-B distance in the sterically less demanding potassium silvl borate [(Me₃Si)₃SiBH₃K·THF]₂ $[1.991 \text{ Å}]^{17}$ is significantly shorter. Steric repulsion in K-5 is also reflected by a lengthening of the Si-Si bonds to about 2.38 Å; zwitterionic K-1 has an average Si-Si distance of ca. 2.32 Å. Similar to K-4, the potassium cation of K-5 is coordinated by three OCH₂CH₂OMe donor arms, which gives rise to a distorted octahedral coordination environment for potassium with O-K-O angles and K-O distances ranging from 62.5° to 146.7° and 2.67-2.74 Å, respectively.

With the aim of synthesizing a zwitterionic disilyl zinc complex, reactions of various zinc salts with two equivalents of zwitterionic metal silanide, M-1 (M = Li, Na, K), were examined. In most cases mixtures of liquid products were obtained, which could not be separated. When two equivalents of K-1⁶ were treated at low temperatures with $ZnCl_2$ in THF, a mixture of two major products was obtained. Upon heating the mixture in hexanes, one of the two major products converted into the other one with elimination of KCl. By multinuclear NMR spectroscopy, the isolated liquid product was identified as the homoleptic zinc silanide of formula Zn-[Si(SiMe₂OCH₂CH₂OMe)₃]₂ (6) (Scheme 3).

Homoleptic zinc silanide 6 appears to be nonzwitterionic as judged by its good solubility in aliphatic hydrocarbons, its liquid nature, and the ²⁹Si NMR chemical shift of its formally anionic silicon (-146.3 ppm), a value that is within the range of structurally related and nonzwitterionic zinc silanides (see Table 1). Compared to the ²⁹Si NMR chemical shift of the silicon nuclei of the dicoordinated homoleptic zinc silanides [(Me₃Si)₃Si]₂Zn (123.9 ppm) and [(Me₃SiMe₂Si)₃Si]₂Zn (-116.4 ppm), however, the central silicon nucleus of 6 resonates at significantly higher field (-146.3 pm), more consistent with a tetracoordinated zinc center. In fact, the central silicon nuclei of tetracoordinated zinc silanides resonate within the relatively narrow range -150 to -157 ppm. Thus, it might be that the zinc center in compound 6 is additionally coordinated by one or more of the intramolecular OCH₂CH₂OMe donor arms.

Owing to its liquid nature, **6** could not be further purified, and consequently the results of combustion analysis were nonsatisfactory. However, **6** was sufficiently pure to perform reactivity studies. Although **6** was nonreactive in the presence of excess ZnMe_2 or BEt_3 , it reacted readily with one equivalent of ZnMe_2 after addition of four equivalents of the strong Lewis acid B(C₆F₅)₃ to form a colorless microcrystalline precipitate from toluene solutions. Multinuclear NMR spectroscopic studies, the results of elemental analysis, and single-crystal Xray crystallography revealed the isolated compound to be the zwitterionic zinc silylborate salt 7 (Scheme 3). Complex 7 is thermally stable, soluble in THF, poorly soluble in CD₂Cl₂, and



 Table 1. ²⁹Si NMR Chemical Shifts [ppm] of the Silyl Anion (shown in bold) of Selected Zinc Silanides

compound	solvent	Si NMR δ	ref		
(Me ₃ Si) ₃ SiZnCl·TMEDA	THF^{a}	-156.8	9		
(Me ₃ Si) ₃ SiZnBr·2THF	THF^{a}	-149.9	9		
$[(Me_3Si)_3Si]_2Zn$	C_6D_6	-123.9	11		
$[(Me_3Si)_3Si]_2Zn\cdot 2, 2$ -bipyridine	C_6D_6	-150.8	11		
$[(Me_3SiMe_2Si)_3Si]_2Zn$	$C_{6}H_{6}^{\ b}$	-116.4	18		
$\begin{array}{l} Me_{2}ZnSi(SiMe_{2}OCH_{2}CH_{2}OMe)_{3}Li\\ (Li-2) \end{array}$	THF-D ₈	-180.2	this work		
$I_2ZnSi(SiMe_2OCH_2CH_2OMe)_3K$ (K-4)	$THF-D_8$	-149.9	this work		
Cl ₂ ZnSi(SiMe ₂ OCH ₂ CH ₂ OMe) ₃ K (K- 3)	C_6D_6	-156.9	this work		
$\operatorname{Zn}[\operatorname{Si}(\operatorname{Si}\operatorname{Me}_2\operatorname{OCH}_2\operatorname{CH}_2\operatorname{OMe})_3]_2$ (6)	C_6D_6	-146.3	this work		
^{<i>a</i>} Measured with D_2O capillary. ^{<i>b</i>} Measured with DMSO- D_6 capillary.					

insoluble in aromatic and aliphatic hydrocarbons. The ¹¹B{¹H} NMR spectrum of 7 shows two distinct signals: one at -14.8 assigned to the MeB(C_6F_5)₃⁻ borate and a second one at -20.8 due to the SiB(C_6F_5)₃⁻ borate. The ¹⁹F{¹H} NMR of 7 is consistent with the presence of two tris(pentafluorophenyl)-

borate units, as it shows six signals in a 2:2:1:1:2:2 ratio due to the ortho-, para-, and meta-fluorine nuclei. Interestingly, the ortho-fluorine of the SiB(C_6F_5)₃⁻ unit appears as a broad signal at room temperature (-130.3 ppm), which upon cooling to -50 °C splits into two distinct but still broad signals at -121.8 and -135.9 ppm, indicative of a hindered rotation along the central B–C bonds in the SiB(C_6F_5)₃ unit with a calculated rotational barrier of ca. 9.6 kcal/mol (Figure 3). Also the signal of the meta-fluorine nuclei of the SiB(C_6F_5)₃ unit, which at room temperature appears as a quintet, changes into a broad featureless signal upon cooling to -50 °C, whereas the signal of the SiMe₂ group in the ¹H NMR spectrum splits into two distinct singlets at -50 °C (see also Supporting Information).

In the solid state, zinc salt 7 forms a polymeric network held together by intermolecular H…F contacts similar to what is seen in K-5 (Figure 4). Again, close intramolecular H…F contacts are seen in the monomeric subunits between the ortho- (F5, F10, and F11) and meta-fluorine (F4 and F9) atoms and the next neighboring hydrogen atoms of the SiMe₂ groups, ranging from 2.59 to 2.90 Å. The observation of close H…F contacts is consistent with variable-temperature ¹H and



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Figure 3. VT ¹⁹F NMR spectra of 7 in THF-D₈ as solvent.

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Figure 4. Solid-state structure of 7. Selected distances [Å] and angles [deg]: Zn1-O5 2.0720(15), Zn1-O1 2.0794(15), Zn1-O3 2.0945(15), Zn1-O4 2.1137(16), Zn1-O2 2.1317(16), Zn1-O6 2.1326(16), O1-Si1 1.7260(16), O3-Si2 1.7198(16), O5-Si3 1.7230(16), Si1-Si4 2.3505(10), Si2-Si4 2.3466(10), Si3-Si4 2.3630(10), Si4-B1 2.139(3), O5-Zn1-O1 95.93(6), O5-Zn1-O3 94.11(6), O1-Zn1-O3 91.95(6), O5-Zn1-O4 100.38(6), O1-Zn1-O4 161.00(6), O3-Zn1-O4 77.29(6), O5-Zn1-O2 164.16(6), O1-Zn1-O2 78.43(6), O3-Zn1-O2 100.82(6), O4-Zn1-O2 88.14(6), O5-Zn1-O6 77.99(6), O1-Zn1-O6 101.61(6), O3-Zn1-O6 164.87(6), O4-Zn1-O6 91.33(6), O2-Zn1-O6 88.57(6), Si1-O1-Zn1 125.35(8), Si2-O3-Zn1 128.54(8), Si3-O5-Zn1 126.66(8), O1-Si1-Si4 102.89(6), O3-Si2-Si4 101.82(6), O5-Si3-Si4 101.97(6), B1-Si4-Si2 119.26(8), B1-Si4-Si1 116.91(7), B1-Si4-Si3 116.77(8), Si2-Si4-Si1 99.96(3), Si2-Si4-Si3 99.44(3), Si1-Si4-Si3 101.20(3).

¹⁹F NMR studies in solution, which show at room temperature broad signals of the ortho-fluorine nuclei and the SiMe₂ protons due to a hindered rotation along the C-B bonds. The silicon-boron distance of 7 [2.139 Å] is slightly shorter than that of K-5 presumably due to the smaller size of the zinc dication forcing the central B-Si-Si angles to be larger and the Si-Si-Si angle to be smaller, which would reduce steric repulsion in the molecule. Similar to the potassium cations in K-4 and K-5, the zinc dication is octahedrally coordinated by three OCH₂CH₂OMe donor arms, with O-Zn-O angles and Zn-O distances ranging from 77.3° to 164.9° and 2.07-2.13 Å, respectively. Interestingly, the average Si-O distance [1.72 Å] is significantly larger than in K-1, K-4, and K-5 (see also Table 2 for comparison). Clearly, the elongation of the Si-O bonds in 7 is the result of an $O \rightarrow M$ donor-acceptor interaction, which is stronger for the small zinc dication $(M = Zn^{2+})$ than for the significantly larger potassium monocation $(M = K^{+})$.

Table 2. Selected Average Distances [Å] and Angles [deg] for K-1, K-4, K-5, and 7

	K-1 ⁶	K-4	K- 5	7
Si-Si	2.32	2.32	2.38	2.35
Si-O	1.68	1.67	1.68	1.72
O-M _(SiOC)	2.74	2.68	2.72	2.08
O-M _(COC)	2.74	2.73	2.68	2.13
Si-Si-Si	100	111	103	100
Si-Si-O	113	109	105	102
Si-O-M	125	120	125	127

Although the mechanism of formation of 7 remains unclear, the function of the added Lewis acid $B(C_6F_5)_3$ in this rather unusual multistep reaction appears to be twofold: (1) Replacement and release of the central zinc dication in 6, followed by its coordination by the OCH_2CH_2OMe pendant donor arms, to generate zwitterionic cation $[(C_6F_5)_3BSi(SiMe_2OCH_2CH_2OMe)_3Zn]^+$ (A) and anion $[(C_6F_5)_3BSi(SiMe_2OCH_2CH_2OMe)_3]^-$ (B) and (2) abstraction of the methyl groups from the added ZnMe₂ to produce two equivalents of anion $[MeB(C_6F_5)_3]^-$ and a zinc dication; the latter is picked up by anion A to generate a second equivalent of cation B (Scheme 4).



Scheme 4. Proposed Mechanism of the Reaction of 6 with $ZnMe_2$ and $B(C_6F_5)_3$

With the synthesized zwitterionic zinc salt 7 in hand we investigated its reactivity toward Lewis bases such as THF, pyridine, and dimethylaminopyridine (DMAP) and 2,2bipyridine. We were particularly interested in whether these donor molecules would be capable of competing with the pendant donor arms for the coordination sphere of the zinc dication. The addition of THF to a CD₂Cl₂ suspension of 7 had only a minor effect on the ¹H and ¹⁹F NMR chemical shifts due to slight changes in solvent polarity. Upon addition of 2.5 equivalents of 2,2-bipyridine to a CD₂Cl₂ suspension of 7, however, a complete set of new signals in the ¹H NMR spectrum (Figure 5) and three new fluorine signals in the ¹⁹F NMR spectrum appeared. Comparison of the integrals of the aromatic 2,2-bipyridine signals with those of the silanide signals in the ¹H NMR spectrum revealed three molecules of 2,2bipyridine to coordinate to zinc, suggesting the formation of the hexacoordinate zinc species $[Zn(2,2-bipyridine)_3]^{2+}$ along with the anionic species $[(C_6F_5)_3BSi(SiMe_2OCH_2CH_2OMe)_3]^-$ (A) and $[MeB(C_6F_5)_3]^-$ (Figure 5). As more than three equivalents of 2,2-bipyridine were added, the signals for 7 completely disappeared and signals arising from the aromatic protons of free 2,2-bipyridine appeared, indicating no exchange of free with coordinated 2,2-bipyridine. Similar results were found for



Figure 5. ¹H NMR spectra of the NMR tube reactions of 7 with 2,2-bipyridine (CD₂Cl₂) taken after adding various amounts of 2,2-bipyridine.

the addition of DMAP and pyridine to 7. After adding 4.5 equivalents of DMAP, clean formation of a single species that contains four molecules of coordinated DMAP consistent with the tetracoordinate zinc species $[Zn(DMAP)_4]^{2+}$ was observed according to the NMR data. In contrast, addition of 10 equivalents of the weaker Lewis base pyridine to 7 gave a complex mixture with compound 7 as the major species in solution. In the presence of 30 equivalents of pyridine, however, signals of 7 in the ¹H and ¹⁹F NMR completely disappeared, indicating the formation of $[Zn(pyridine)_4]^{2+}$ as the major cationic species along with the anions $[(C_6F_5)_3BSi-(SiMe_2OCH_2CH_2OMe)_3]^-$ (A) and $[MeB(C_6F_5)_3]^-$ (see Supporting Information for a detailed analysis of the NMR data).

From these preliminary NMR data it can be concluded that the silylborate ligand $[(C_6F_5)_3BSi(SiMe_2OCH_2CH_2OMe)_3]^-$ (A) with its three OCH₂CH₂OMe donor arms has a relatively high affinity to bind to metal dications and that only strong nitrogen-containing Lewis bases are capable of replacing $[(C_6F_5)_3BSi(SiMe_2OCH_2CH_2OMe)_3]^-$ (A) as supporting ligand for these dications.

CONCLUSION

In conclusion, we have reported the synthesis and structure of the first zwitterionic silvlborate silvlzincates of potassium and zinc. These zwitterions form discrete structures with the central metal cations being octahedrally surrounded by the pendant polydonor groups. The ZnX₂ adducts K-3 and K-4 are stable at room temperature and do not spontaneously undergo elimination of KX (X = Cl, I) due to the stable octahedral coordination environment of the potassium cation provided by the polydentate silvlborate ligand. The first stable zwitterionic zinc silvlborate (7) could conveniently be made in good overall yield via a two-step synthetic process involving the initial formation of the nonzwitterionic zinc silanide 6, derived from the reaction of K-1 with ZnCl₂ followed by the addition of $ZnMe_2$ and $B(C_6F_5)_3$. Further studies regarding the synthesis and structural characterization of transition metal-containing zwitterionic silanides and silvlborates are currently ongoing.

EXPERIMENTAL SECTION

The manipulation of air-sensitive compounds involved standard Schlenk line and glovebox techniques. THF, THF-D₈, toluene, and *n*-hexane were distilled under nitrogen from alkali metals and stored over molecular sieves prior to use. C_6D_6 and CD_2Cl_2 were dried and stored over molecular sieves prior to use. The compounds

 $Si(SiMe_2OCH_2CH_2OMe)_3K~(K-1),^6~Si(SiMe_2OCH_2CH_2OMe)_3Li~(Li-1),^6~and~B(C_6F_5)_3^{-19}~were~prepared~as~described~in~the~literature.$ All other chemicals were purchased from commercial sources and used without further purification. The ¹H, ⁷Li, ¹³C, ¹⁹F, ¹¹B, and ²⁹Si NMR spectra were obtained from a Varian Unity Inova 500 and JEOL ECS 400. All measurements, unless noted otherwise, were carried out at 298 K, and NMR chemical shifts are given in ppm. The ⁷Li NMR spectra were referenced to a 0.1 M solution of LiCl in D₂O ($\delta = 0$), the ¹¹B NMR spectra to H₃BO₃ in D₂O (δ = 36 ppm), the ¹⁹F NMR spectra to C_6F_6 in C_6D_6 ($\delta = -164.9$ ppm), and the ²⁹Si NMR spectra to TMS ($\delta = 0$ ppm). ²⁹Si NMR spectra were obtained by using the INEPT pulse sequence. The ¹H NMR spectra were referenced to the residual protonated solvent for ¹H, and the ¹³C NMR spectra were referenced to the deuterated solvent peaks. The following abbreviations were used to describe peak multiplicities in the reported NMR spectroscopic data: "m" for complex multiplet and "br" for broadened resonances. Elemental analyses were performed by Atlantic Microlab Inc. (Norcross, GA, USA).

Single crystals of K-4, K-5, and 7 suitable for X-ray diffraction were coated with polyisobutylene oil in a drybox and were quickly transferred to the goniometer head of a Bruker Apex II detector system equipped with a molybdenum X-ray tube ($\lambda = 0.71073$ Å). Data were collected at 150 K. Preliminary data revealed the crystal system. A hemisphere routine was used for data collection and determination of lattice constants. The space group was identified, and the data were processed using the Bruker AXS SHELXTL software (version 6.14) and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) completed by subsequent Fourier transformation and refinement by full-matrix least-squares procedures. The structure of K-4 contained a disordered MeOCH₂CH₂O group, which was modeled over two positions and refined isotropically."

Me₂ZnSi(ŠiMe₂OCH₂CH₂OMe)₃Li (Li-2). In a glovebox, a 1.2 M toluene solution of ZnMe₂ (0.15 mL, 0.18 mmol) was added to Li-1 (70 mg, 0.16 mmol) dissolved in 1 mL of toluene and allowed to stay for 4 h. Then the solvent was removed under vacuum, and the residue was washed with hexanes and dried under vacuum to give the title compound as a colorless solid (yield 70%). ¹H NMR (C₆D₆, 300 MHz): δ 0.23 (s, ZnMe₂, 6 H), 0.53 (s, SiMe₂, 18 H), 2.84 (s, OMe, 9 H), 2.84 (t, ³J_{H-H} = 4.8 Hz, CH₂OMe, 6 H), 3.22 (t, ³J_{H-H} = 4.8 Hz, SiOCH₂, 6 H). ¹³C NMR (C₆D₆, 125.7 MHz): δ -2.4 (ZnMe₂), 4.3 (SiMe₂), 58.5 (OMe), 61.0 (OCH₂), 73.2 (CH₂OMe). ²⁹Si NMR (C₆D₆, 99.3 MHz): δ 39.9 (SiMe₂O), -180.2 (SiS₃). ⁷Li NMR (C₆D₆, 194.2 MHz): δ -1.5. Due to the thermal instability of the title compound at room temperature, attempts to obtain satisfactory elemental analysis data failed.

Cl₂ZnSi(SiMe₂OCH₂CH₂OMe)₃K (K-3). In a glovebox a THF solution of ZnCl₂ (24 mg, 0.18 mmol) was added to K-1 (86 mg, 0.18 mmol) dissolved in 1 mL of THF, and the mixture was allowed to stir for 4 h. THF was removed under vacuum, and the product was extracted twice with toluene. After removal of solvent under vacuum, the residue was washed twice with hexanes and dried under vacuum to give 70 mg (64%) of the title compound as a white powder. ¹H NMR (C₆D₆, 300 MHz): δ 0.66 (s, SiMe₂, 18 H), 3.12 (s, OMe, 9 H), 3.19 (br, CH₂OMe, 6 H), 3.57 (br, SiOCH₂, 6 H). ¹³C NMR (C₆D₆, 125.7 MHz): δ 4.4 (SiMe₂), 58.5 (OMe), 61.9 (SiO<u>C</u>H₂), 74.3 (<u>C</u>H₂OMe). ²⁹Si NMR (C₆D₆, 99.3 MHz): δ 30.1 (SiMe₂O), -156.9 (<u>Si</u>Si₃). Anal. Calcd for C₁₅H₃₉O₆Si₄ZnKCl₂ (603.2): C, 29.87; H, 6.52; Cl, 11.76. Found: C, 29.60; H, 6.39; Cl, 11.48.

I₂ZnSi(SiMe₂OCH₂CH₂OMe)₃K (K-4). In a glovebox, ZnI₂ (60 mg, 0.18 mmol) was added to K-1 (86 mg, 0.18 mmol) dissolved in 1 mL of ether, upon which a white precipitate was formed. After stirring the resulting suspension for 4 h at room temperature, the precipitate was filtered, washed once with ether, and dried under vacuum to give 130 mg (90%) of the title compound as a white powder. ¹H NMR (THF-D₈, 300 MHz): δ 0.40 (s, SiMe₂, 18 H), 3.36 (s, OMe, 9 H), 3.47 (t, ³J_{H-H} = 4.6 Hz, CH₂OMe, 6 H), 3.74 (t, ³J_{H-H} = 4.6 Hz, SiOCH₂, 6 H). ¹³C NMR (THF-D₈, 125.7 MHz): δ 4.4 (SiMe₂), 59.0 (OMe), 62.6 (<u>C</u>H₂OSi), 75.2 (<u>C</u>H₂OMe). ²⁹Si NMR (THF-D₈, 99.3 MHz): δ

31.6 (SiMe₂O), -149.9 (SiSi₃). Anal. Calcd for $C_{15}H_{39}O_6Si_4ZnKI_2$ (786.1): C, 22.92; H, 5.00; Found: C, 22.77; H, 5.08.

(C₆F₅)₃BSi(SiMe₂OCH₂CH₂OMe)₃K (K-5). In a glovebox, a precooled toluene solution (ca. -20 °C) of B(C₆F₅)₃ (92 mg, 0.18 mmol) was added to a precooled toluene solution (ca. -20 °C) of K-1 (86 mg, 0.18 mmol). A precipitate was formed immediately, which after stirring for 30 min was centrifuged, washed several times with hexanes, and dried under vacuum to give the title compound as pale yellow powder in 90% yield (160 mg). ¹H NMR (CD₂Cl₂, 300 MHz): δ -0.01 (s, SiMe₂, 18 H), 3.35 (s, OCH₃, 9 H), 3.46 (t, {}^{3}J_{H-H} = 3.6 Hz, SiOCH₂, 6 H), 3.64 (t, ${}^{3}J_{H-H}$ = 3.6 Hz, SiOCH₂, 6 H). ${}^{13}C$ NMR (CD₂Cl₂, 125.7 MHz): δ 1.9 (SiMe₂), 59.0 (OMe), 61.6 (OCH₂), 74.7 (CH₂OMe), 125.6 (br, ipso-C), 137.1 (br d, J_{C-F} = 241.3 Hz, meta-C), 138.5 (br d, J_{C-F} = 245.0 Hz, para-C), 148.4 (br d, J_{C-F} = 237.5 Hz, ortho-C). ²⁹Si NMR (CD₂Cl₂, 99.3 MHz): δ 33.1 (SiMe₂O), (SiSi₃ not found). ¹¹B NMR (CD₂Cl₂, 160.3 MHz): δ -21.1. NMR (CD₂Cl₂, 376 MHz): δ –127.5 (br s, ortho-F), –163.2 (t, J_{F-F} = 19.1 Hz, para-F), -166.9 (m, $J_{F-F} = 19.1$ Hz, meta-F). Anal. Calcd for C33H39BF15KO6Si4 (978.9): C, 40.49; H, 4.02. Found: C, 40.43; H, 3.90.

 $Zn[Si(SiMe_2OCH_2CH_2OMe)_3]_2$ (6). In a glovebox a precooled THF solution (ca. -20 °C) of ZnCl₂ (31.3 mg, 0.23 mmol) was added to a precooled THF solution (ca. -20 °C) of K-1 (214 mg, 0.46 mmol) with stirring. The resulting suspension was stirred for 1 h, the solvent was removed under vacuum, and the oily residue was extracted twice with hexanes. The combined hexanes solution was heated at 55 °C for 4 h, upon which more precipitate was formed. After filtration of the suspension, solvent and other volatiles were removed under vacuum to leave 180 mg (85%) of the title compound as a colorless liquid that contained minor amounts of unidentified impurities. Therefore the results of elemental analysis were nonsatisfactory. ¹H NMR (C₆D₆, 300 MHz): δ 0.61 (s, SiMe₂, 18 H), 3.19 (s, OMe, 9 H), 3.43 (t, ${}^{3}J_{H-H}$ = 4.9 Hz, CH₂OMe, 6 H), 3.81 (t, ${}^{3}J_{H-H}$ = 4.9 Hz, SiOCH₂, δ H). ¹³C NMR (C_6D_6 , 125.7 MHz): δ 5.6 (SiMe₂), 58.9 (OMe), 63.0 (OCH₂), 74.9 (<u>C</u>H₂OMe). ²⁹Si NMR (C₆D₆, 99.3 MHz): δ 27.2 (SiMe₂O), -146.3 (SiSi₃).

 $[(C_6F_5)_3BSi(SiMe_2OCH_2CH_2OMe)_3Zn][MeB(C_6F_5)_3]$ (7). In a glovebox a solution of $B(C_6F_5)_3$ (220 mg, 0.45 mmol) in toluene was added at room temperature to a solution of 6 (100 mg, 0.11 mmol) in 15 mL of toluene, and the mixture was stirred for 5 min. Then, a 1.2 M toluene solution of ZnMe₂ (90 µL, 0.11 mmol) was added, and the resulting suspension was stirred overnight. A white precipitate was formed, which was filtered, suspended in CH₂Cl₂, and stirred rapidly for 2 h. The solid was collected by centrifugation and dried under vacuum to give the title compound as a microcrystalline material in 61% yield. ¹H NMR (THF-D₈, 300 MHz, 298 K): δ 0.31 (br, SiMe₂, 18 H), 0.49 (s, BMe, 3 H), 3.78 (s, OMe, 9 H), 3.97 (br, CH₂OMe, 6 H), 4.12 (br, SiOCH₂, 6 H); (THF-D₈, 500 MHz, 233 K): δ 0.03, 0.52 (2s, SiMe₂, 2 × 9 H), 0.47 (s, BMe, 3 H), 3.79 (s, OMe, 9 H), 3.93 (br d, CH₂OMe, 3 H), 4.22 (br d, CH₂OMe, 3 H), 4.03 (br quint, SiOCH₂, 6 H). ¹³C NMR (THF-D₈, 125.7 MHz, 298 K): δ 2.3 (SiMe₂), 10.5 (BCH₃), 62.2 (OMe), 63.2 (OCH₂), 72.5 (CH₂OMe), 123.8, 130.6 (br, ipso-C), 137.1 (br d, J_{C-F} = 243.8 Hz, C), 137.7 (br d, J_{C-F} = 237.5 Hz, C), 138.3 (br d, J_{C-F} = 242.5 Hz, C), 139.6 (br d, J_{C-F} = 235.0 Hz, C), 148.8 (br d, J_{C-F} = 236.6 Hz, ortho-C), 149.3 (br d, $J_{C-F} = 238.7$ Hz, ortho-C). ²⁹Si NMR (THF-D₈, 99.3 MHz): δ 26.2 (SiMe₂O), -159.1 SiSi₃). ¹¹B NMR (THF-D₈, 160.3 MHz, 298 K): δ –14.8 (BCH₃), –20.8 (BSi). ¹⁹F NMR (THF-D₈, 376 MHz, 298 K): δ -130.3 (br, ortho-F SiB(C₆F₅)₃), -134.7 (d, J_{F-F} = 19.1 Hz ortho-F, $CH_3B(C_6F_5)_3$), -163.8 (t, $J_{F-F} = 20.8$ Hz, para-F, $SiB(C_6F_5)_3)$, -168.0 (m, J_{F-F} = 20.8 Hz, meta-F, $SiB(C_6F_5)_3$), -168.5 (t, $J_{F-F} = 20.8$ Hz, para-F, CH₃B(C₆F₅)₃), -170.7 (m, $J_{F-F} = 20.8$ Hz, meta-F, $CH_3B(C_6F_5)_3$; (THF-D₈, 376 MHz, 233 K): δ -121.7, (br, ortho-F, SiB $(C_6F_5)_3$, -135.6 (br, ortho-F, SiB $(C_6F_5)_3$), -132.9 (d, J_{F-F} = 19.1 Hz ortho-F, $CH_3B(C_6F_5)_3$), -161.6 (t, J_{F-F} = 20.8 Hz, para-F, SiB(C₆F₅)₃), -165.8 (br, meta-F, SiB(C₆F₅)₃), -166.1 (t, J_{F-F} = 20.8 Hz, para-F, $CH_3B(C_6F_5)_3)$, -168.3 (t, J_{F-F} = 20.8 Hz, meta-F, $CH_{3}B(C_{6}F_{5})_{3}).$ Anal. Calcd for $C_{52}H_{42}B_{2}F_{30}O_{6}Si_{4}Zn$ (1532.2): C, 40.76; H, 2.76. Found: C, 40.18; H, 2.78.

Organometallics

Supporting Information

Crystallographic data for K-4 (CCDC 885796), K-5 (CCDC 885794), and 7 (CCDC 885795) including CIF files. This material is available free of charge via the Internet at http:// pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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