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Synthesis and Structure of Cyclic Trinuclear Zinc Disiloxides

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The synthesis and structure of the new disilane-1,2-diol $[(Me_3Si)_2SiOH]_2$ (**2b**) and the trinuclear zinc disiloxides of the formula $[Me_2Si\{(Me_3Si)_2SiO\}_2]_2Zn_3Me_2$ (**3a**), $[\{(Me_3Si)_2SiO\}_2]_2Zn_3Me_2$ (**3b**) and E-$[\{Me(Me_3Si)_3SiSiO\}_2]_2Zn_3Me_2$ (**3c**) are reported. Compounds **3a–c** were prepared by reactions of the corresponding silanedioles **2a–c** with $ZnMe_2$. The results of an X-ray structure analysis of **3b** reveal an almost perfectly planar spirocyclic Zn_3O_4 core with a square-planar geometry of the inner Zn^{2+} ion, whereas in **3a**,**c** the inner zinc ions are distorted tetrahedral. Upon treatment with $B(C_6F_5)_3$, compounds **3b**,**c** have been converted quantitatively into the complexes $[\{(Me_3Si)_2SiO\}_2]_2Zn_3(C_6F_5)_2$ (**4b**) and E-$[\{Me(Me_3Si)_3SiSiO\}_2]_2Zn_3(C_6F_5)_2$ (**4c**).

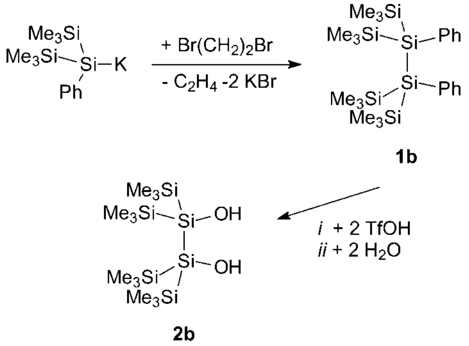
Introduction

There has been a considerable interest in recent years in the chemistry and structures of zinc siloxides as the steric hindrance of the ligand (R_3SiO^-) in such compounds can lead to novel structural features and unusual reactivity.[1] For example, some structurally well-defined zinc compounds have been found application as soluble precursors for zinc oxides and silicates.[2] Significant synthetic and structural studies of a variety of mainly monodentate zinc siloxides are reported from the Driess group. They could demonstrate that the degree of aggregation of the central $(ZnO)_n$ core decreases as the bulkiness of the attached siloxide ligand increases.[3] Bidentate cyclic zinc siloxides, however, are rare and the only example has been reported from the reaction of $ZnMe_2$ with $Ph_2Si(OH)_2$, which under self-condensation of the silanol affords a remarkable polycyclic hexanuclear zinc complex with two Zn_3O_4 cores.[4]

We have a long-term interest in the synthesis and structural characterization of cyclic five- and six-membered metal disiloxides, as these highly strained cycles might be useful for the selective ring insertion of metal species, which may form novel hetero- and homobimetallic complexes as we have shown recently for a dinuclear titanium disiloxide derived from a mononuclear cyclic species.[5] In this contribution we describe the preparation of a new disilane-1,2-diol and we report on the synthesis of polycyclic trinuclear zinc disiloxides from reactions of $ZnMe_2$ with various sterically congested vicinal silanediols together with their solid-state structures.

Results and Discussion

A rather straightforward strategy for the design of vicinal silanediols with an oligosilane backbone involves the use of phenyl-substituted metal silanides in salt metathesis reactions. In analogy to the synthesis of the trisilane-1,3-diol **2a** previously reported,[5] treatment of $Ph(Me_3Si)_2Si$-K with $BrCH_2CH_2Br$ provides easy access to the diphenyl oligosilane **1b** in high yields.[6] This compound was treated with two equivalents of trifluoromethanesulfonic acid (TfOH) and subsequently hydrolyzed to give almost quantitatively the silanediol **2b** as a colorless solid (Scheme 1). The compound slowly decomposes at room temperature within several days and must be stored in a freezer at ca. –40 °C. However, the structure of **2b** was unambiguously established by standard spectroscopic methods and elemental analysis. The synthesis of the racemic disilane-1,2-diol **2c** has been reported elsewhere.[7]



Scheme 1. Synthesis of **2b**.

As reported recently, differently aggregated zinc silanolates can be prepared by acid–base reactions of silanols R_3SiOH (R = Me, Et, *i*Pr, Ph) with ZnR_2 (R = Me, Et).

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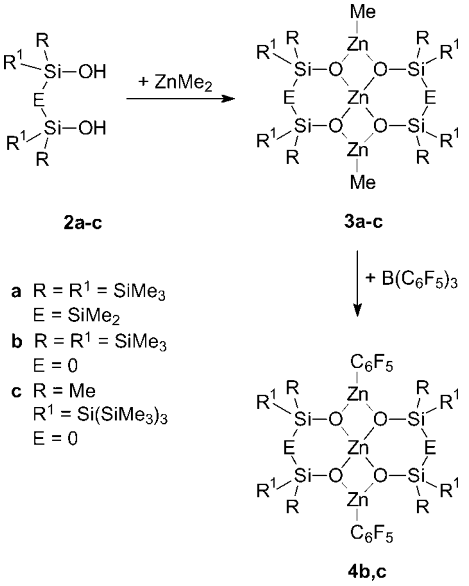
Employing $ZnMe_2$ as the reagent the trinuclear zinc complexes **3a**–**c** have been synthesized in good yields as outlined in Scheme 2. The NMR and MS data and the results of elemental analysis have confirmed the proposed structures of **3a**–**c**. The NMR (^{1}H, ^{13}C, ^{19}Si) spectra of all complexes are rather straightforward and show roughly the same features as observed for the corresponding free ligands **2a**–**c**. For example, the ^{1}H and ^{13}C NMR spectra of **3a** exhibit only one signal for the $SiMe_3$ and $SiMe_2$ groups, respectively, and also the ^{29}Si NMR spectra showed only one signal for the $SiMe_3$ silicon atoms.



Scheme 2. Synthesis of **3a**–**c** and reaction behavior toward $B(C_6F_5)_3$.

In addition, the solid-state structures of **3a**–**c** have been determined by X-ray crystallography; suitable single crystals were grown from pentane solutions at room temperature. The molecular structures along with selected bond lengths and bond angles are shown in Figure 1, 2, 3, and 4. Compounds **3a**–**c** crystallize in the triclinic space group $P\bar{1}$. All structures consist of fused polycyclic ring systems with central trinuclear Zn_3O_4 cores, which are coordinated in a chelate fashion by two diolate ligands, respectively. The coordination of the ligand to the inner zinc ion in **3a** results in the formation of a six-membered ring system with a distorted chair conformation. In **3b** and **3c**, however, five-membered rings are formed, which are either strongly twisted [**3b**; dihedral angle O1–Si2–Si3–O2 32.05(6)°] or almost planar [**3c**; dihedral angle O1–Si3–Si4–O2 2.70(10)°]. The outer zinc atoms of **3a** and **3c** are three-coordinate with trigonal-planar ligand environments, while the inner Zn^{2+} ions are four-coordinate with distorted tetrahedral geometries. Overall, the observed distorted geometries of the Zn_3O_4 cores are in good agreement with those of the monodentate zinc siloxides $[(i\mathrm{Pr}_3\mathrm{SiO})_4\mathrm{Zn}_3\mathrm{Me}_2]$ (**5**),[2a] $[(\mathrm{Ph}_3\mathrm{SiO})_4\mathrm{Zn}_3\mathrm{Me}_2]$ (**6**)[4] and $[(\mathrm{OSiPh}_2\mathrm{OSiPh}_2\mathrm{O})(\mathrm{OSiPh}_2)\mathrm{OZn}_2\mathrm{Me}_2\cdot\mathrm{THF}]_2$ (**7**)[4] (see Table 1).

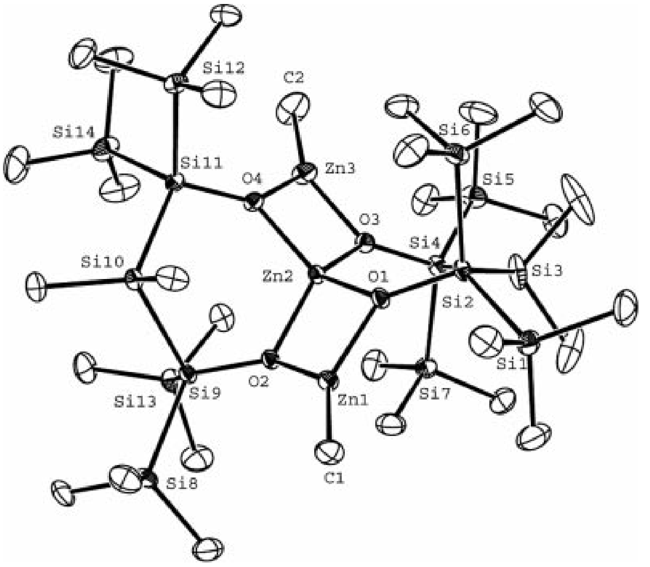


Figure 1. Molecular structure of **3a** in the crystal. The thermal ellipsoids correspond to 30% probability (hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Zn1–C1 1.942(4), Zn3–C2 1.934(5), Zn2–O1 1.975(2), Zn2–O2 1.968(2), Zn2–O3 1.959(2), Zn2–O4 1.973(2), Zn1–O1 1.952(2), Zn1–O2 1.954(2), Zn3–O3 1.953(2), Zn3–O4 1.959(2), Si2–O1 1.673(2), Si4–O3 1.673(2), Si9–O2 1.678(2), Si11-O4 1.679(2), Si2–Si3 2.3597(14), Si3–Si4 2.3775(14), O3–Zn2–O2 135.37(10), O3–Zn2–O4 85.50(9), O2–Zn2–O4 112.70(9), O3–Zn2–O1 110.92(9), O2–Zn2–O1 84.63(9), O4–Zn2–O1 135.80(10), O1–Zn1–O2 85.64(9), O3–Zn3–O4 86.03(9), C1–Zn1–O1 137.17(14), C2–Zn3–O3 140.12(19), Zn2–O3–Si4–Si3 45.43(18), O3–Si4–Si3–Si2 14.59(12), Si4–Si3–Si2–O1 23.79(12), Si3–Si2–O1–Zn2 43.74(19), Si2–O1–Zn2–O3 21.8(2), O1–Zn2–O3–Si4 34.34(19).

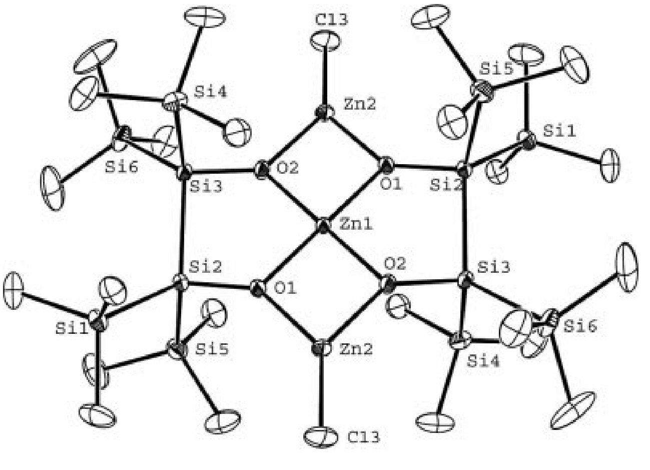


Figure 2. Molecular structure of **3b** in the crystal. The thermal ellipsoids correspond to 30% probability (hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Zn2–C13 1.9223(16), Zn1–O1 1.9721(9), Zn1–O2 1.9831(10), Zn2–O2 1.9438(10), Zn2–O1 1.9403(10), Si2–O1 1.6744(11), Si3–O2 1.6763(10), Si2–Si3 2.3832(5), O1–Zn1–O2 96.88(4), O1–Zn1–O1A 180.0, O1–Zn1–O2A 83.12(4), O2–Zn2–O1A 84.99(4), O1A–Zn2–C13 137.63(8).

The most remarkable feature of the zinc siloxide **3b**, however, is the unusual square-planar coordination geometry of the inner Zn^{2+} ion. To the best of our knowledge, this is the first completely planar structure with a spirocyclic

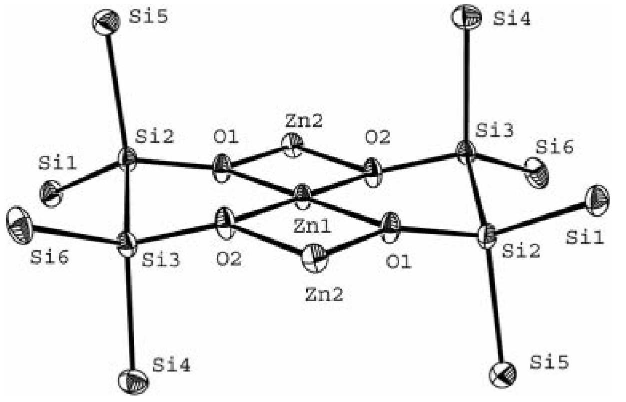


Figure 3. View along the Si2–Si3 axis of **3b**. Selected dihedral angles (all methyl groups are omitted for clarity): Si6–Si3–Si2–Si5 42.01(3)°, O1–Si2–Si3–O2 32.05(6), Si1–Si2–Si3–Si4 44.18(3), Si1–Si2–Si3–Si6 86.92(3), Si5–Si2–Si3–Si4 173.12(2).

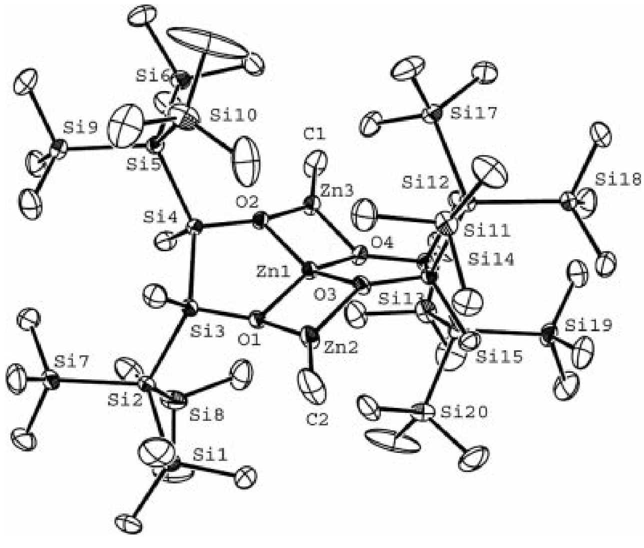


Figure 4. Molecular structure of **3c** in the crystal. The thermal ellipsoids correspond to 30% probability (hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: Zn2–C2 1.934(3), Zn3–C1 1.933(3), Zn1–O1 1.9665(17), Zn1–O2 1.9650(16), Zn1–O3 1.9677(16), Zn1–O4 1.9650(16), Zn2–O1 1.9687(17), Zn2–O3 1.9588(16), Zn3–O2 1.9644(16), Zn3–O4 1.9664(16), Si3–O1 1.6672(17), Si4–O2 1.6650(17), Si13–O3 1.6653(17), Si14–O4 1.6685(17), Si3–Si4 2.4229(9), Si13–Si14 2.4003(9), Si2–Si3 2.3891(10), O2–Zn1–O4 86.64(7), O2–Zn1–O1 101.54(7), O4–Zn1–O1 151.34(8), O2–Zn1–O3 147.62(7), O4–Zn1–O3 100.93(7), O1–Zn1–O3 86.84(7), O3–Zn2–O1 87.02(7), O2–Zn3–O4 86.62(7), C2–Zn2–O3 135.32(12), C2–Zn2–O1 137.66(12), C1–Zn3–O4 134.97(11), O1–Si3–Si4–O2 2.70(10), O3–Si13–Si14–O4 10.53(10).

Zn_3X_4 core (X = S, O, N, P). Apart from three planar mononuclear zinc complexes with bidentate phenolate type ligands,[8] only in porphyrin complexes the zinc ion has an almost perfect square-planar coordination environment. A view along the Si2–Si3 axis in **3b** (Figure 3) clearly reveals this arrangement to be mainly enforced by the steric repulsion of the adjacent trimethylsilyl groups. In fact, the steric interactions of the trimethylsilyl groups can be significantly minimized by adopting a staggered conformation along the Si2–Si3 axis, which results in the formation of a planar spirocyclic ZnO_2ZnO_2Zn core. This is not evident for **3a**, because the $SiMe_2$ spacer group, which reduces steric repulsions within the molecule, separates the vicinal trimethylsilyl groups. Consequently the bulky trimethylsilyl groups can adopt an eclipsed conformation, which enables the inner zinc ion to be coordinated in the energetically preferred tetrahedral geometry.

Table 1. Selected average bond lengths [Å] and angles [°] for trinuclear zinc disiloxides.

Compound	**3a**	**3b**	**3c**	**5**[a]	**6**[b]	**7**[c]
Zn–C	1.94	1.92	1.93	1.95	1.92	1.95
Si–O	1.68	1.68	1.67	1.65	1.64	1.61
Zn_{inner}–O	1.97	1.98	1.97	1.97	1.95	1.96
Zn_{outer}–O	1.95	1.94	1.97	1.98	1.96/2.01	2.02
O–Zn_{inner}–O	85/86	83	87/87	87/87	84/86	88/88
	86/111	97	101/102	117/120	112/120	114/104
	113/135	180	148/151	120/131	124/133	133/138
O–Zn_{outer}–O	86	85	87	86	84	84
Zn–Zn–Zn	177	180	177	166	159	176

[a] $[(i\text{Pr}_3\text{SiO})_4\text{Zn}_3\text{Me}_2]$. [b] $[(\text{Ph}_3\text{SiO})_4\text{Zn}_3\text{Me}_2]$. [c] $[(\text{OSiPh}_2\text{OSiPh}_2\text{O})(\text{OSiPh}_2)\text{OZn}_3\text{Me}_2\cdot\text{THF}]_2$.

For comparison, a summary of selected average distances and angles together with those of the complexes recently reported by Driess et al. is given in Table 1. As expected, the Zn–O distances and O–Zn–O angles of the inner zinc ions and also the Zn–C distances in all these complexes are rather similar to each other. It is worthy to note, however, that the Si–O distances in **3a–c** are markedly longer and the Zn–O distances for the outer zinc ions are shorter than those of the closely related complexes **5–7**. The longer Si–O distances can be attributed to the specific electronic situation in **3a–c**, in which the central silicon atoms possess electropositive silyl groups. These electron-donating groups clearly diminish the capability of silicon to act as strong π acceptor for oxygen, which gives rise to stronger electrostatic oxygen–zinc interactions and consequently to shorter Zn–O distances as compared to **5–7**.

Furthermore, we have investigated the reactivity of the highly strained trinuclear zinc complexes **3b**,**c** towards the Lewis acid $B(C_6F_5)_3$ that is known to abstract alkyl groups from the metal center to form cationic metal species. The reactions were performed at room temperature in a J-Young NMR tubes using [D$_6$]benzene as solvent, and the course of the reaction was monitored by ^1H NMR spectroscopy. The complexes **3b**,**c** reacted cleanly with $B(C_6F_5)_3$ (molar ratio 1:1) within minutes, resulting in the formation of $[\{(\text{Me}_3\text{Si})_2\text{SiO}\}_2]_2\text{Zn}_3(\text{C}_6\text{F}_5)_2$ (**4b**) and $[E\text{-}\{\text{Me}(\text{Me}_3\text{Si})_3\text{SiSiO}\}_2]_2\text{Zn}_3(\text{C}_6\text{F}_5)_2$ (**4c**), the quantitative products of a rapid C_6F_5 group transfer, as evidenced by multinuclear NMR spectroscopic data. The compounds **4b**,**c** could be isolated in a larger scale and the spectroscopic data obtained were identical to those from the NMR experiments (Scheme 2). Solutions of **4b**,**c** in C_6D_6 proved to be fairly stable over a prolonged period of time, and even at higher temperature no substantial decomposition occurred. Similar C_6F_5 transfer reactions have been observed for the reaction of $ZnMe_2$.[9] The fact that the C_6F_5 groups have replaced both methyl groups rapidly is somewhat surprising; however, it indicates an increased electrophilicity of the zinc centers caused by the electron-withdrawing disiloxide ligands.

Experimental Section

General Remarks: All manipulations of air- and/or moisture-sensitive compounds were carried out under argon using standard Schlenk and Glove Box techniques. THF, *n*-heptane and *n*-pentane were distilled under argon from alkali metals prior to use. CH_2Cl_2 was distilled from CaH_2 and stored over molecular sieves. [D_6]Benzene was dried with activated molecular sieves and stored in the glove box. $B(C_6F_5)_3$ was prepared as described previously.[10] NMR: Bruker AC 250, Bruker ARX 300. IR: Nicolet 205 FT-IR. MS: Intectra AMD 402, chemical ionization with isobutane as the reactant gas.

2,3-Dihydroxy-1,1,1,4,4,4-hexamethyl-2,3-bis(trimethylsilyl)tetrasilane (2b): Freshly distilled TfOH (0.97 mL, 0.011 mol) was added at –40 °C to a stirred solution of **1b** (2.51 g, 0.005 mol) in CH_2Cl_2 (25 mL) and the mixture was warmed to room temp. within 2 h. After changing the solvent from CH_2Cl_2 to diethyl ether, an aqueous solution of NH_4COONH_2 (10 mL, 1 M) was added dropwise and stirring was continued for 30 min. The organic phase was separated, dried with $MgSO_4$, and the solvent was evaporated. Drying under high vacuum afforded 1.76 g (92%) of the title compound, which was kept in a freezer. ^1H NMR (C_6D_6, 250 MHz): δ = 0.72 (br. s, OH, 2 H), 0.29 [s, $Si(CH_3)_3$, 36 H] ppm. ^{13}C NMR (C_6D_6, 62.9 MHz): δ = 0.1 [$Si(CH_3)_3$] ppm. ^{29}Si-INEPT (C_6D_6, 59.6 MHz): δ = 8.1 (SiOH), –15.0 [$Si(CH_3)_3$] ppm. MS (70 eV): *m/z* (%) = 383 (8) [M^+], 279 (8) [M^+ – 2Me – $SiMe_3$], 205 (20) [M^+ – Me – $2SiMe_3$ – OH], 131 (42) [M^+ – Me – $3SiMe_3$ – OH]. $C_{12}H_{38}O_2Si_6$ (382.94): calcd. C 37.64, H 10.00; found C 37.49, H 9.98. IR (Nujol): $\tilde{\nu}_{OH}$ = 3394.4 cm^{-1} (assoc.), 3641.6 cm^{-1} (non-assoc.).

[$Me_2Si\{(Me_3Si)_2SiO\}_2]_2Zn_3Me_2$ (3a): Solid **2a** (2.0 g, 4.5 mmol) was added to a vigorously stirred solution of $ZnMe_2$ (2 M, 3.6 mL, 7.2 mmol) in *n*-pentane (20 mL) at –78 °C. After stirring for 2 h at room temp., the solvent was removed under vacuum. Crystallization of a concentrated *n*-pentane solution in a freezer at –40 °C afforded the title compound as colorless crystals. Yield 1.75 g (65%). M.p. 115–117 °C. ^1H NMR (C_6D_6, 250 MHz): δ = 0.43 [s, $Si(CH_3)_2$, 12 H], 0.34 [s, $Si(CH_3)_3$, 72 H], –0.04 (s, $ZnCH_3$, 6 H) ppm. ^{13}C NMR (C_6D_6, 75.5 MHz): δ = 1.2 [$Si(CH_3)_3$], –0.4 [$Si(CH_3)_2$], –10.8 ($ZnCH_3$) ppm. ^{29}Si NMR (C_6D_6, 59.6 MHz): δ = 14.8 (SiOZn), –16.1 [$Si(CH_3)_3$], –37.1 [$Si(CH_3)_2$] ppm. $C_{30}H_{90}O_4Si_{14}Zn_3$ (1104.40): calcd. C 32.63, H 8.21; found C 32.47, H 8.24.

[$\{(Me_3Si)_2SiO\}_2]_2Zn_3Me_2$ (3b): A heptane solution of **2b** (0.5 g, 1.31 mmol) was added to a vigorously stirred solution of $ZnMe_2$ (2 M, 0.8 mL, 1.6 mmol) in *n*-pentane (20 mL) at –78 °C. After stirring for 2 h at room temp., the solvent was removed under vacuum. Crystallization of a concentrated *n*-pentane solution in a freezer at –40 °C afforded the title compound as colorless crystals. Yield 0.41 g (63%). M.p. 169–171 °C. ^1H NMR (C_6D_6, 250 MHz): δ = 0.30 [s, $Si(CH_3)_3$, 72 H], –0.13 (s, $ZnCH_3$, 6 H) ppm. ^{13}C NMR (C_6D_6, 75.5 MHz): δ = 0.1 [$Si(CH_3)_3$], –15.1 ($ZnCH_3$) ppm. ^{29}Si NMR (C_6D_6, 59.6 MHz): δ = 1.2 (SiOZn), –16.4 [$Si(CH_3)_3$] ppm. $C_{26}H_{78}O_4Si_{12}Zn_3$ (988.09): calcd. C 31.60, H 7.96; found C 31.42, H 7.84.

[E-$\{Me(Me_3Si)_3SiSiO\}_2]_2Zn_3Me_2$ (3c): A heptane solution of **2c** (0.5 g, 0.81 mmol) was added to a vigorously stirred solution of $ZnMe_2$ (2 M, 0.6 mL, 1.2 mmol) in *n*-heptane (15 mL) at –78 °C. After warming to room temp., the suspension was stirred overnight and refluxed until the colorless precipitate fully dissolved. Crystallization of the solution at room temp. afforded the title compound as colorless crystals. Yield 0.45 g (75%). M.p. 161–164 °C. ^1H NMR (C_6D_6, 250 MHz): δ = 0.94 (s, $SiCH_3$, 12 H), 0.41 [s, $Si(CH_3)_3$, 108 H], 0.04 (s, $ZnCH_3$, 6 H) ppm. ^{13}C NMR (C_6D_6, 75.5 MHz): δ = 11.0 ($SiCH_3$), 4.6 [$Si(CH_3)_3$], –10.3 ($ZnCH_3$) ppm. ^{29}Si NMR (C_6D_6, 59.6 MHz): δ = 15.8 (SiOZn), –10.0 [$Si(CH_3)_3$], –127.1 (*Si*Si_4) ppm. MS (70eV): *m/z* (%) = 1438 (2) [M^+ – Me], 1207 (22) [M^+ – $Si(SiMe_3)_3$], 1110 (8) [M^+ – $Si(SiMe_3)_3$ – 2Me – Zn], 247 (35) [$Si(SiMe_3)_3$]. $C_{42}H_{126}O_4Si_{20}Zn_3$ (1453.33): calcd. C 34.71, H 8.74; found C 34.51, H 8.74.

Table 2. Crystal data collection, and refinement details for crystal structures.[a]

Compound	**3a**	**3b**	**3c**
Formula	$C_{30}H_{90}O_4Si_{14}Zn_3$	$C_{26}H_{78}O_4Si_{12}Zn_3$	$C_{42}H_{126}O_4Si_{20}Zn_3\cdot C_6H_{14}$
Molecular weight	1104.39	988.07	1539.51
Crystal size [mm]	1.00 × 0.37 × 0.22	0.67 × 0.35 × 0.22	0.62 × 0.62 × 0.36
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	13.9735(4)	9.8213(6)	14.2317(6)
b [Å]	14.1182(3)	11.5149(7)	17.3635(7)
c [Å]	18.5569(5)	13.5301(13)	21.2325(8)
α [°]	81.7090(10)	102.830(4)	68.0030(10)
β [°]	68.8770(10)	97.107(4)	78.540(2)
γ [°]	65.2840(10)	111.836(3)	71.779(2)
V [Å]^3	3102.01(14)	1348.43(17)	4601.1(3)
Z	2	1	2
ρ [g/cm^3]	1.182	1.217	1.111
μ [mm^{-1}]	1.448	1.615	1.067
2Θ limit [°]	2.97–25.00	1.99–27.50	2.21–25.00
Measured reflections	56017	53729	82788
Independent reflections	10852	6125	15934
	[*R*(int) = 0.0696]	[*R*(int) = 0.0304]	[*R*(int) = 0.0246]
Data/restraints/parameter	10852/0/491	6125/0/218	15934/0/678
Final R^1/wR_2[b]	0.0661/0.1812	0.0210/0.0558	0.0367/0.1030

[a] All data sets were collected with a Bruker X8Apex diffractometer system with Mo-K_α radiation [λ = 0.71073 Å at 173(2) K]. [b] The value of R_1 is based on selected data with $F > 4\sigma(F)$; the value of wR_2 is based on all data.

Reaction of 3b,c with $B(C_6F_5)_3$ in C_6D_6: An NMR tube (equipped with J. Young valve) was charged in the glove box with **3b** or **3c** and $B(C_6F_5)_3$ (molar ratio 1:1) and dissolved in C_6D_6 (0.5 mL). The progress of the reaction was monitored by ^1H NMR spectroscopy and complete conversion of the starting materials into **4b** and **4c** and a mixture of the boranes $MeB(C_6F_5)_2$ (δ = 1.35 ppm), $Me_2BC_6F_5$ (δ = 0.98 ppm) and BMe_3 (δ = 0.74 ppm) was observed within 2 h at room temperature, according to the ^1H , ^{29}Si , ^{11}B and ^{19}F NMR spectra.

Isolation of 4b,c: A stirred mixture of $B(C_6F_5)_3$ and **3b** or **3c** (molar ratio 1:1) was dissolved in *n*-pentane at ca. –20 °C and stirring was continued for 2 h at room temperature. Crystallizations of concentrated solutions in a freezer afforded colorless crystals of the title compounds.

$[\{(Me_3Si)_2SiO\}_2]_2Zn_3(C_6F_5)_2$ (4b): Compound **3b** (0.15 g, 0.15 mmol), $B(C_6F_5)_3$ (0.08 g, 0.15 mmol) and *n*-pentane (10 mL). Yield 0.1 g (67 %). ^1H NMR (C_6D_6, 250 MHz): δ = 0.24 [s, $Si(CH_3)_3$, 72 H] ppm. ^{13}C NMR (C_6D_6, 75.6 MHz): δ = –0.1 [$Si(CH_3)_3$], 135.4–150.6 (C_6F_5) ppm. ^{29}Si NMR (C_6D_6, 59.6 MHz): δ = 7.9 (SiO), –16.0 [$Si(CH_3)_3$] ppm. ^{19}F NMR (C_6D_6, 235.4 MHz): δ = –169.5, –140.2, –116.2 (*o*-, *p*-, *m*-F, C_6F_5) ppm. $C_{36}H_{72}F_{10}O_4Si_{12}Zn_3$ (1292.11): calcd. C 33.46, H 5.62; found C 33.09, H 5.44.

$[E\text{-}\{Me(Me_3Si)_3SiSiO\}_2]_2Zn_3(C_6F_5)_2$ (4c): Compound **3c** (0.15 g, 0.1 mmol), $B(C_6F_5)_3$ (0.05 g, 0.1 mmol) and *n*-pentane (10 mL). Yield 0.09 g (61 %). ^1H NMR (C_6D_6, 250 MHz): δ = 1.00 (s, $SiCH_3$, 12 H), 0.31 [s, $Si(CH_3)_3$, 72 H] ppm. ^{13}C NMR (C_6D_6, 75.6 MHz): δ = 4.5 [$Si(CH_3)_3$], 10.9 ($SiCH_3$), 136.1–151.2 (C_6F_5) ppm. ^{29}Si NMR (C_6D_6, 59.6 MHz): δ = 21.0 (SiO), –9.9 [$Si(CH_3)_3$], –125.4 (*Si*Si_4) ppm. $C_{52}H_{120}F_{10}O_4Si_{20}Zn_3$ (1757.35): calcd. C 35.54, H 6.88; found C 35.18, H 6.79.

Crystal data collection see Table 2 for **3a**, **3b** and **3c** are deposited in the Cambridge Crystallographic Data Centre. CCDC-622651 (for **3a**), -622650 (for **3b**) and -622649 (for **3c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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