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A Trisilyl Zincate Containing Bidentate $[(Me_3Si)_2Si(CH_2)_2Si(SiMe_3)_2]^{2-}$ Ligands

Jaime B. Woods, Xianghua Yu, Tianniu Chen, and Zi-Ling Xue*

Department of Chemistry, The University of Tennessee, Knoxville, Tennessee 37996

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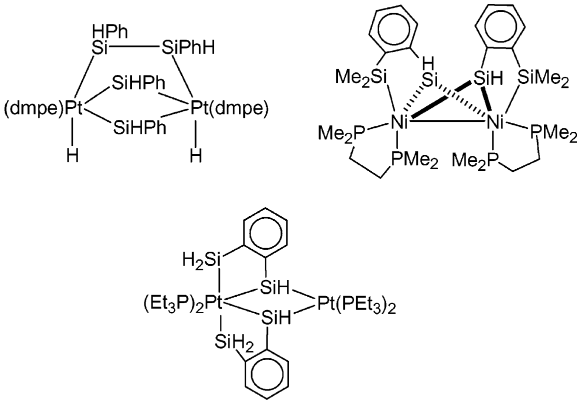
Summary: The trisilyl dimeric zincate $[K(18\text{-crown-}6)]_2\{[(Me_3Si)_2Si(CH_2)_2Si(SiMe_3)_2]_2Zn_2[\mu\text{-}(Me_3Si)_2Si(CH_2)_2Si(SiMe_3)_2]\}$ *(**1**) is reported. In the structure of **1**, each Zn center is bonded by one bridging disilyl ligand and one chelating disilyl ligand.*

The field of transition-metal silyl chemistry has experienced a period of rapid growth and proliferation in recent years.[1] Most known silyl complexes are monosilyl or disilyl complexes. Few transition-metal complexes containing three or more silyl/silylene ligands are known.[2] These complexes, with auxiliary phosphine ligands, include $(R_3P)_2Rh(SiR_3)(SiR'_3)(SiR''_3)$,[2a] $(R_3P)_2M(SiR'_3)_2(SiR''_3)(H)$,[2b−d] $L_2M(SiR'_3)_2(SiR''_3)_2$ (M = Ni, Pt; L = R_3P, R′NC),[2e,f] and those in Chart 1,[2b,c] and they are usually prepared from oxidative addition of hydrosilanes to phosphine complexes. The persilyl complexes $M(SiR_3)_n$ ($n \geq 3$), containing 3 or more silyl ligands per metal atom, are more difficult to prepare.[3]

Chart 1



Late-transition-metal disilyl complexes such as $Zn(SiR_3)_2$ [R_3 = Ph_3, $(SiMe_3)_3$, $^tBu_3$, H^tBu_2)][4] and $M[Si(SiMe_3)_3]_2$ (M = Cd, Hg) and base adducts such as $M[Si(SiMe_3)_3]_2(bpy)$ (M = Zn, Cd; bpy = 2,2′-bipyridine) and $Zn(SiPh_3)_2(PMe_3)_2$[5] have been reported. These complexes contained a nearly linear Si−Zn−Si geometry, and up to two silyl ligands were attached to the Zn centers.[4b−d] The zinc silyl complexes $Zn(SiR_3)_2$ have been prepared, in part, to study their reactivities as silylating reagents. The zinc alkyl complexes ZnR'_2 have often been used as alkylating reagents in organic and organometallic reactions, and the reactivities of these zinc complexes are usually milder than those of, for example, lithium alkyls and Grignard reagents.[6]

In the current work, $[K(18\text{-crown-}6)]_2[(Me_3Si)_2Si(CH_2)_2Si(SiMe_3)_2]$ (**2**), containing a hydrocarbon backbone, was chosen as a potential ligand precursor that may chelate to a transition-metal center. Such chelating ligands may serve to enhance the stability of the resulting metal complexes. Several dianionic bis(silyl) ligand precursors,[7] such as $Li(SiPh_2)_4Li$[7a] and $KSi(SiMe_3)_2(SiMe_2)_2Si(SiMe_3)_2K$[7b] containing an all-silicon backbone, have been reported. The reaction of 1.5 equiv of **2** with 1 equiv of anhydrous $ZnCl_2$ gives the unusual zincate $[K(18\text{-crown-}6)]_2\{[(Me_3Si)_2Si(CH_2)_2Si(SiMe_3)_2]_2Zn_2[\mu\text{-}(Me_3Si)_2Si(CH_2)_2Si(SiMe_3)_2]\}$ (**1**), containing Zn ions coordinated with *three* Si atoms.[8] This is a rare

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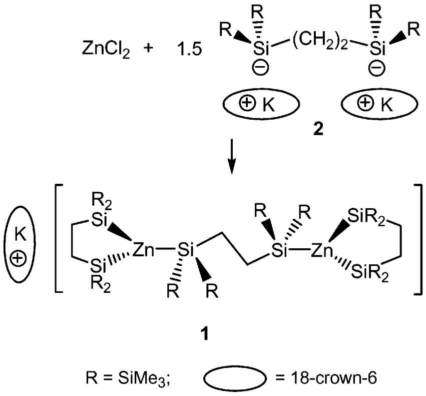
Scheme 1. Preparation of Trisilyl Zincate 1



trisilyl complex prepared from anionic substitution reactions. Recently, silyl-containing dianionic zincates were used in chemoselective silylzincation of functionalized terminal alkynes.[9] The current studies were conducted as part of our studies of metal silyl complexes.[1f,10] Our syntheses, characterization, and structure of **1** are reported here.

A slow addition of a freshly prepared solution of [K(18-crown-6)]$_2$[(Me$_3$Si)$_2$Si(CH$_2$)$_2$Si(SiMe$_3$)$_2$] (**2**)[11] (1.5 equiv) in mixed DME and toluene to a slurry of ZnCl$_2$ in Et$_2$O afforded an orange oil of **1** (Scheme 1).[12] Washing of the oil with pentane gave a yellow solid of **1**. In toluene, the solid turned into an oil, and cooling of the solution containing the oil at −20 °C gave crystals of the trisilyl zincate [K(18-crown-6)]$_2${[(Me$_3$Si)$_2$Si(CH$_2$)$_2$Si(SiMe$_3$)$_2$]$_2$Zn$_2$[μ-(Me$_3$Si)$_2$Si(CH$_2$)$_2$Si(SiMe$_3$)$_2$]} (**1**) containing toluene solvent in 53.1% yield.

ORTEP diagrams of **1**·(toluene)$_2$ and the anionic portion of **1** are given in Figures 1 and 2, respectively.

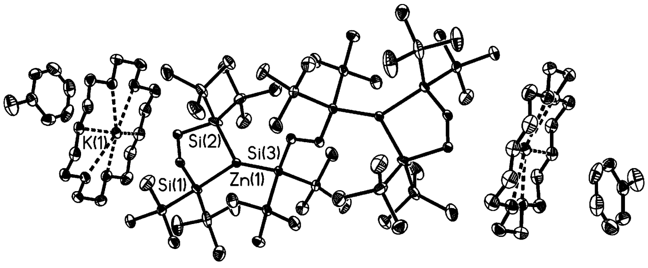


Figure 1. ORTEP diagram of **1**·(toluene)$_2$ showing 30% ellipsoids.

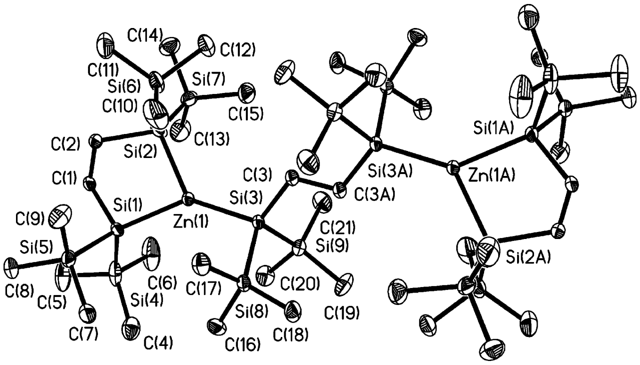


Figure 2. ORTEP diagram of the Zn dianion in **1** showing 30% ellipsoids. Selected bond distances (Å) and angles (deg): Si(1)−Zn(1) = 2.4368(8), Si(2)−Zn(1) = 2.4153(10), Si(3)−Zn(1) = 2.4076(8), C(1)−C(2) = 1.513(10), C(1)−Si(1) = 1.981(5), C(2)−Si(2) = 2.004(6), C(3)−C(3A) = 1.536(5), C(3)−Si(3) = 1.923(3), C(1A)−Si(1) = 2.008(5), C(1A)−C(2A) = 1.548(11), Si(1)−Si(4) = 2.3338(16); Si(2)−Zn(1)−Si(1) = 87.63(3), Si(3)−Zn(1)−Si(1) = 138.45(3), Si(3)−Zn(1)−Si(2) = 133.72(3), Si(5)−Si(1)−Zn(1) = 123.26(5), Si(4)−Si(1)−Zn(1) = 115.79(5), C(1)−Si(1)−Zn(1) = 102.97(15), C(1A)−Si(1)−Zn(1) = 100.62(16), C(2A)−Si(2)−Zn(1) = 104.86(19), C(2)−Si(2)−Zn(1) = 103.92(17), Si(7)−Si(2)−Zn(1) = 118.39(6), Si(6)−Si(2)−Zn(1) = 108.96(5), C(3)−Si(3)−Zn(1) = 114.83(8), C(2)−C(1)−Si(1) = 109.5(5), C(1)−C(2)−Si(2) = 108.7(5), C(3A)−C(3)−Si(3) = 117.7(2), C(2A)−C(1A)−Si(1) = 109.4(5).

The X-ray structure showed two three-coordinate Zn centers bridged by a disilyl ligand. Each Zn atom has one terminal, chelating disilyl ligand and one bridging disilyl ligand linking it to another Zn metal center. In other words, {[(Me$_3$Si)$_2$Si(CH$_2$)$_2$Si(SiMe$_3$)$_2$]$_2$Zn$_2$[μ-(Me$_3$Si)$_2$Si(CH$_2$)$_2$Si(SiMe$_3$)$_2$]}$^{2-}$ in **1** is a dianion. An 18-crown-6 molecule encapsulates a K$^+$ cation on each side of the dimer to balance the charge of the complex. These K(18-crown-6)$^+$ cations as two charge-separated ions have *no* direct interaction with the anionic Si centers in **1**, probably as a result of the steric crowding in the trisilyl Zn complex. In comparison, the two anionic Si atoms in [K(18-crown-6)]$_2$[(Me$_3$Si)$_2$Si(CH$_2$)$_2$Si(SiMe$_3$)$_2$] (**2**) have *direct* interactions with the K$^+$ cations surrounded by 18-crown-6 molecules.[11] Two toluene molecules are also found in the crystal structure. The Zn(1)−Si bond lengths in **1** are in agreement with those in other zinc silyl complexes such as Zn[Si(SiMe$_3$)$_3$]$_2$ (2.342(4) Å),[4b] Zn(Si^{t}Bu$_3$)$_2$ (2.384(1) Å),[4c] ^{t}Bu$_3$SiZnBr (2.377(2) Å),[4c] and Zn[SiH(Si^{t}Bu$_3$)$_2$]$_2$ (2.425(2)−2.449(2) Å).[4d] The lengths of the Zn−Si bonds for the chelating ligand (2.4368(8) and 2.4153(10) Å) are slightly longer than the Zn−Si bond length of the bridging ligand (2.4076(8) Å). The geometry around each Zn center is Y-shaped with two widened angles (Si(3)−Zn−

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[12] Preparation of **1**: all manipulations were performed under a dry nitrogen or argon atmosphere with the use of either a glovebox or standard Schlenk techniques. Degassed (Me$_3$Si)$_3$Si(CH$_2$)$_2$Si(SiMe$_3$)$_3$ (0.5168 g, 0.9874 mmol), ^{t}BuOK (0.2218 g, 1.977 mmol), and 18-crown-6 (0.5221 g, 1.975 mmol) were added to a Schlenk flask. This mixture of solids was then dissolved in DME and toluene (a 50/50 volume mixture) and stirred for 15 min to give [K(18-crown-6)]$_2$[(Me$_3$Si)$_2$Si(CH$_2$)$_2$Si(SiMe$_3$)$_2$] (**2**). This ligand solution was added dropwise to ZnCl$_2$ (0.0910 g, 0.668 mmol) suspended in Et$_2$O at room temperature. The mixture was stirred for 17 h, and the solution was filtered. Removal of volatiles from the filtrate yielded an orange oil which, after washing with two 10 mL portions of pentane, turned to a yellow solid. The solid was dissolved in toluene, and the resulting mixture of an oil and solution were placed in a freezer at −20 °C for crystallization. The supernatant was filtered, and the solid was washed with toluene to give 0.3585 g of crystalline **1**·(toluene)$_2$ (53.1% yield). See Table 1 for the NMR resonances of **1**. Anal. Calcd for C$_{80}$H$_{184}$K$_2$O$_{12}$Si$_{18}$Zn$_2$ (**1**·(toluene)$_2$): C, 46.81; H, 9.03. Found: C, 46.97; H, 9.10.

Table 1. Key NMR Data (ppm) of 1 and Relevant Complexes at 23 °C

	^{1}H	^{13}C	^{29}Si
1 THF-d_8	1.26 (CH_2 bridging) 1.13 (CH_2 terminal) 0.18 (SiMe_3 bridging) 0.03 (SiMe_3 terminal)	14.63 (CH$_2$ bridging) 12.17 (CH$_2$ terminal) 4.52 (SiMe_3 bridging) 3.77 (SiMe_3 terminal)	−9.95 (SiSiMe$_3$ terminal) −11.15 (SiSiMe$_3$ bridging) −85.15 (SiSiMe$_3$ bridging) −87.27 (SiSiMe$_3$ terminal)
Zn[Si(SiMe$_3$)$_3$]$_2$[4b] benzene-d_6	0.35 (SiMe_3)	4.54 (SiMe_3)	−7.18 (SiSiMe$_3$) −123.9 (SiSiMe$_3$)
Zn[Si(SiMe$_3$)$_3$]$_2$(bpy)[4b] benzene-d_6	0.27 (SiMe_3)	5.11 (SiMe_3)	−6.60 (SiSiMe$_3$) −150.8 (SiSiMe$_3$)
2 benzene-d_6	0.64 (SiMe_3)	5.74 (SiMe_3)	−6.8 (SiSiMe$_3$) −111.8 (SiSiMe$_3$)

Si(2) = 138.45(3)°; Si(3)−Zn−Si(2) = 133.72(3)°) and one narrow angle (Si(2)−Zn−Si(1) = 118.39(6)°). Zn−C bond lengths in alkyl zincates (>2.0 Å)[13] are usually longer than those in neutral complexes (1.946−1.988 Å).[14] It is not clear why the Zn−Si bond lengths in the current zincate **1** are similar to those in neutral Zn silyl complexes.[4b−d]

The X-ray structure of [K(18-crown-6)]$_2${[(Me$_3$Si)$_2$Si(CH$_2$)$_2$Si(SiMe$_3$)$_2$]$_2$Zn$_2$[μ-(Me$_3$Si)$_2$Si(CH$_2$)$_2$Si(SiMe$_3$)$_2$]} (**1**) showed that the anionic centers Zn(Si−)$_3^-$ in **1** are surrounded with the chelating as well as the bridging disilyl ligands (Scheme 1). This compound was found to be insoluble in benzene-d_6 and only sparingly soluble in toluene-d_8. **1** was, however, found to be soluble in THF-d_8, in which the ^{1}H, ^{13}C, and ^{29}Si NMR spectra of **1** at 23 °C were taken. These NMR spectra agree with the structure of **1**. NMR chemical shifts of **1** are listed in Table 1 along with those of related complexes. As expected, two sets of ligand peaks were observed in the ^{1}H, ^{13}C{^{1}H}, and ^{29}Si{^{1}H} NMR spectra, one for the chelating ligand and the other for the bridging ligand. The ^{29}Si NMR resonances of the α-Si atoms attached to the metal (−85.15 ppm, bridging; −87.27 ppm, terminal) are shifted downfield from those in Zn[Si(SiMe$_3$)$_3$]$_2$ (−123.9 ppm), Zn[Si(SiMe$_3$)$_3$]$_2$(bpy) (−150.8 ppm), and [K(18-crown-6)]$_2$[(Me$_3$Si)$_2$Si(CH$_2$)$_2$Si(SiMe$_3$)$_2$] (**2**; −111.8 ppm). Except for the ^{13}C NMR resonance of the −SiMe$_3$ group in the bridging silyl ligand, the −SiMe$_3$ NMR resonances of the terminal silyl ligands and bridging silyl ligands in **1** are shifted upfield from those in Zn[Si(SiMe$_3$)$_3$]$_2$ and Zn[Si(SiMe$_3$)$_3$]$_2$(bpy) (Table 1).[4b] It is not clear why these NMR shifts occur. It should be noted that the NMR spectra of **1** were taken in THF-d_8 solutions, while those of Zn[Si(SiMe$_3$)$_3$]$_2$, Zn[Si(SiMe$_3$)$_3$]$_2$(bpy), and **2** were obtained from their benzene-d_6 solutions. Only one 18-crown-6 resonance and one toluene resonance were observed in the ^{1}H and ^{13}C NMR spectra of **1**.

In summary, new zincate complex **1** has been prepared. The bidentate disilyl ligands in **1** perhaps play a critical role in the formation of this rare trisilyl complex.

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Supporting Information Available: Text giving details of the experiments and tables giving crystallographic data for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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