# *Notes*

## Synthesis and X-ray Crystal Structure of a Chlorobis(trimethylsiloxy)zirconium Silyl Derivative, $(Me_3SiO)_2Zr(SiPh_2Bu^t)Cl\cdot 2THF$

Zhongzhi Wu, Jonathan B. Diminnie, and Ziling Xue*

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

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*Summary: The chlorobis(trimethylsiloxy)zirconium silyl derivative $(Me_3SiO)_2Zr(SiPh_2Bu^t)Cl\cdot 2THF$ (**2**) and its precursor $(Me_3SiO)_2ZrCl_2\cdot 2THF$ (**1**) have been synthesized and characterized by X-ray crystallography. The Zr−Si bond distance of 2.848(3) Å in **2** is, to our knowledge, the longest reported Zr−Si bond to date.*

Group 4 metal silyl chemistry has been a subject of enthusiastic study for over a decade.[1,2] The interest in this area has been mainly focused on syntheses and studies of catalytic properties, including silane dehydropolymerizations[1e,f,2] and hydrosilation of alkenes.[2j,p,s] Most group 4 metal silyl complexes have $\pi$-anionic ancillary ligands, such as $\eta^5$-cyclopentadienyl ($C_5H_5$, $C_5Me_5$);[1] very few $d^0$ group 4 metal silyl complexes free of the Cp ligand have been reported.[3] The research in our group has recently focused on the chemistry of Cp-free early transition-metal silyl complexes,[3,4] and we have synthesized a series of alkyl silyl complexes with $d^0$ early transition-metal centers. These coordinatively and electronically unsaturated complexes were found to be very reactive toward many chemical substrates, such as silanes and isocyanides.[5] Unfortunately, the only stable alkyl silyl complexes of group 4 metals contain the bulky silyl ligand $Si(SiMe_3)_3$. Attempts to obtain other stable alkyl silyl complexes with smaller silyl ligands have been unsuccessful. Heyn and Tilley[3a] have reported the stable alkoxide silyl complexes $(Bu^tO)_3MSi(SiMe_3)_3$ (M = Zr, Hf) in which some degree of $O(p\pi)-Zr(d\pi)$ bonding is presumed. We thus assumed that partially replacing alkyl ligands with alkoxides would facilitate the isolation of stable alkyl alkoxide silyl complexes of $d^0$ group 4 metals containing less bulky silyl groups. In this paper, we describe the synthesis and structural characterization of the chlorobis(trimethylsiloxy)zirconium silyl complex $(Me_3SiO)_2Zr(SiPh_2Bu^t)Cl\cdot 2THF$ (**2**) as well as the bis(trimethylsiloxy)zirconium dichloride $(Me_3SiO)_2ZrCl_2\cdot 2THF$ (**1**).

### Experimental Section

**General Procedure.** All manipulations were performed under a dry, oxygen-free nitrogen atmosphere using standard Schlenk and glovebox techniques. Toluene, THF, and hexanes solvents were distilled from potassium/benzophenone prior to use. $ZrCl_4$ was purchased from Strem and resublimed before use. $NaOSiMe_3$ (Aldrich) was used as received. $Li(THF)_3SiPh_2Bu^t$ was synthesized according to the literature procedure.[6] All $^1H$ and $^{13}C$ NMR spectra were measured on a Bruker AC-250 spectrometer and referenced to solvent (residual protons in the $^1H$ spectra). $^{29}Si$ data were obtained on a Bruker AMX-400 spectrometer and referenced to TMS. Elemental analyses were performed by E+R Microanalytical Laboratory, Corona, NY.

**Synthesis of $(Me_3SiO)_2ZrCl_2\cdot 2THF$ (1).** A solution of $NaOSiMe_3$ (4.82 g, 43.0 mmol) in THF (30 mL) was added dropwise with stirring to a white slurry of $ZrCl_4$ (5.0 g, 21.4 mmol) in THF (30 mL) at 0 °C. After the solution was stirred

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**Table 1. Crystallographic Data for 1 and 2**

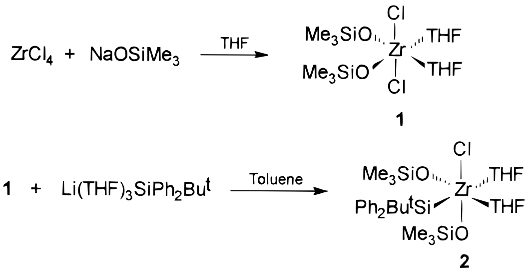
| | complex | |
|---|---|---|
| param | **1** | **2** |
| empirical formula | $C_{14}H_{34}Cl_2O_4Si_2Zr$ | $C_{30}H_{53}ClO_4Si_3Zr$ |
| fw | 484.71 | 688.66 |
| temp, K | 173 | 173 |
| cryst size, mm | 0.40 × 0.40 × 0.20 | 0.38 × 0.20 × 0.16 |
| space group | $P2_1/n$ | $P2_1/n$ |
| cell constants | | |
| *a*, Å | 12.554(3) | 13.213(4) |
| *b*, Å | 10.773(2) | 13.740(5) |
| *c*, Å | 17.897(5) | 20.552(7) |
| $\beta$, deg | 90.46(2) | 100.16(3) |
| *V*, Å$^3$ | 2420.4(10) | 3673(2) |
| *Z* | 4 | 4 |
| $D_{calcd}$, g/cm$^3$ | 1.330 | 1.245 |
| *F*(000) | 1008 | 1456 |
| $\lambda$(Mo K$\alpha$), Å | 0.710 73 | 0.710 73 |
| $\mu$, mm$^{-1}$ | 0.786 | 0.499 |
| $\theta$ range, deg | 1.97−22.55 | 1.79−22.55 |
| no. of reflns collcd | 3361 | 5077 |
| no. of unique reflns | 3189 | 4831 |
| abs corr | empirical | empirical |
| no. of variables | 204 | 352 |
| goodness of fit | 1.099 | 1.044 |
| R1 | 0.0503 | 0.0619 |
| wR2 | 0.1163 | 0.1418 |
| largest diff peak and hole, e/Å$^3$ | 0.458, −0.429 | 0.498, −0.579 |

for 12 h at room temperature, the THF solvent was removed in vacuo to yield a white solid which was extracted with hexanes and crystallized at −18 °C, affording colorless prisms (7.8 g, 75%). Due to the lability of the coordinated THF molecules in **1**, a satisfactory elemental analysis could not be obtained. The structural assignment for **1** follows from analysis of spectroscopic data and X-ray crystallography and its reaction with $Li(THF)_3SiPh_2Bu^t$ to form complex **2**. $^1$H NMR (23 °C, 250 MHz, benzene-$d_6$): $\delta$ 3.96 (m, 8H, $OCH_2$-$CH_2$), 1.30 (m, 8H, $OCH_2CH_2$), 0.36 (s, 18H, $OSiMe_3$). $^{13}C\{^1H\}$ NMR (23 °C, 62.9 MHz, benzene-$d_6$): $\delta$ 72.5 ($OCH_2CH_2$), 25.3 ($OCH_2CH_2$), 2.0 ($OSiMe_3$).

**Synthesis of $(Me_3SiO)_2Zr(SiPh_2Bu^t)Cl·2THF$ (2).** Complex **1** (1.24 g, 2.56 mmol) and $Li(THF)_3SiPh_2Bu^t$ (1.18 g, 2.56 mmol) were mixed together in a Schlenk flask and dissolved in hexanes at 0 °C. The reaction solution immediately turned deep brown. After the reaction was stirred overnight at room temperature, the supernatant solution was removed, and the deep brown precipitate was extracted with toluene to give a deep brown solution. Complex **2** crystallized as bright-yellow crystals at −20 °C from toluene (0.68 g, 38.6%). $^1$H NMR (23 °C, 250 MHz, benzene-$d_6$): $\delta$ 7.99−7.16 (m, 10H, $C_6H_5$), 3.69 (m, 8H, $OCH_2CH_2$), 1.50 (s, 9H, $SiCMe_3$), 1.11 (m, 8H, $OCH_2CH_2$), 0.29 (s, 18H, $OSiMe_3$). $^{13}C\{^1H\}$ NMR (23 °C, 62.9 MHz, benzene-$d_6$): $\delta$ 146.5, 137.9, 127.1, 126.9 ($C_6H_5$), 72.0 ($OCH_2CH_2$), 30.8 ($SiCMe_3$), 25.0 ($OCH_2CH_2$), 21.2 ($SiCMe_3$), 2.6 ($OSiMe_3$). $^{29}Si\{^1H\}$ (benzene-$d_6$, 79.5 MHz): $\delta$ 49.6 ($SiPh_2Bu^t$), 6.8 ($OSiMe_3$). Anal. Calcd for $C_{30}H_{53}ClO_4Si_3Zr$: C, 52.32; H, 7.76. Found: C, 52.14; H, 7.52.

**X-ray Crystallography.** Crystal data and a summary of intensity data collection parameters for **1** and **2** are given in Table 1. The crystal structures of **1** and **2** were determined on a Siemens R3m/V diffractometer fitted with a Nicolet LT-2 low-temperature device. The suitable crystals were coated with Paratone oil (Exxon) and mounted under a stream of nitrogen at −100 °C. The unit cell parameters and orientation matrix were determined from a least-squares fit of the orientation of at least 30 reflections obtained from a rotation photo and an automatic peak search routine. The structures were solved by direct methods. Non-hydrogen atoms were anisotropically refined, and one of the $Me_3SiO$ ligands in **1** is rotationally disordered. The methyl carbon atoms of the $SiMe_3$ group were refined as 2 rotamers with site occupation factors of 0.5. All hydrogen atoms were placed in calculated positions and introduced into the refinement as fixed contributors with an isotropic *U* value of 0.08 Å$^2$. All calculations were performed using the Siemens SHELXTL 93 (version 5.0) proprietary software package.

**Scheme 1**



## Results and Discussion

**Synthesis and Characterization.** Bis(trimethylsiloxy)zirconium dichloride $(Me_3SiO)_2ZrCl_2·2THF$ (**1**) was prepared by the reaction of zirconium tetrachloride with 2 equiv of $NaOSiMe_3$ in THF solution,[7] and colorless crystals of **1** were obtained from hexanes solution (Scheme 1). This complex is readily soluble in pentane, hexanes, benzene, toluene, $Et_2O$, and THF. The $^1$H and $^{13}$C NMR signals of the $Me_3SiO$ ligands in **1** are at $\delta$ 0.36 and 2.0 ppm, respectively, and the ratio of integrations between the signals of the $Me_3SiO$ ligands and THF molecules is consistent with the proposed formula. $(Me_3SiO)_2Zr(SiPh_2Bu^t)Cl·2THF$ (**2**) was prepared by reacting **1** with 1 equiv of $Li(THF)_3SiPh_2Bu^t$ in hexanes solution (Scheme 1). It was found that **2** could only be isolated by carrying the reaction out in aliphatic solvents, such as pentane and hexane, in which the complex has low solubility and readily precipitates out. We have tried to run the reaction in benzene or toluene and found that only reduced metal species and disilane $Ph_2Bu^tSiSiPh_2Bu^t$ were obtained instead of **2**. Because complex **2** is highly soluble in aromatic solvents, it could, once formed in the reaction solution, react further with $Li(THF)_3SiPh_2Bu^t$ to form unstable disilyl intermediates which could eliminate disilane and give reduced zirconium species. The $^1$H and $^{13}$C NMR signals of the $Me_3SiO$ ligands in **2** are at $\delta$ 0.29 and 2.6 ppm, respectively. Complex **2** is stable for hours in solution at room temperature, but over days it will decompose to $HSiPh_2Bu^t$ and uncharacterized species. Attempts to synthesize the $Si(SiMe_3)_3$ analogue by a similar reaction procedure were unsuccessful, and only red reduced metal species and disilane $(Me_3Si)_3SiSi(SiMe_3)_3$ were obtained.

The reaction of $(Me_3SiO)_2Zr(SiPh_2Bu^t)Cl·2THF$ (**2**) with $LiCH_2CMe_3$ has been investigated. The reaction was monitored by NMR, and the NMR spectra showed that the products formed in the reaction are $Zr(CH_2CMe_3)_4$, $LiOSiMe_3$, and $Li(THF)_3SiPh_2Bu^t$. Attempts with the relatively milder alkylating reagent $ClMgCH_2CMe_3$ gave similar results. Such metathesis reactions between metal alkoxides and alkyllithium or alkyl

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[7] Schindler, F.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 683.

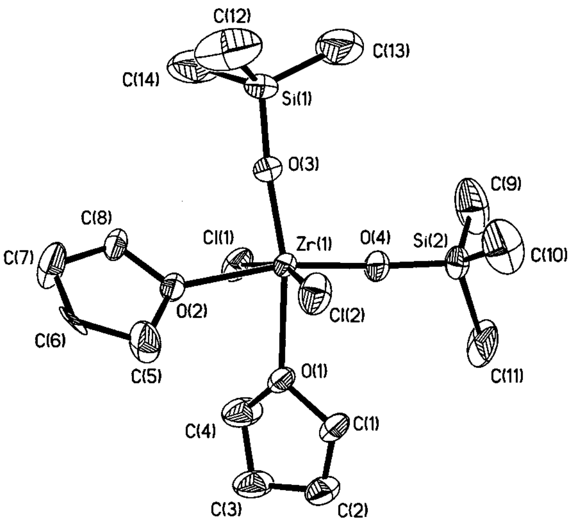

**Figure 1.** ORTEP view of the structure of $(Me_3SiO)_2ZrCl_2 \cdot 2THF$ (**1**), showing 35% thermal ellipsoids. The alternative rotamer of the $Si(2)Me_3$ group is omitted for clarity.

**Table 2. Selected Bond Distances (Å) and Angles (deg) for 1**

| | | | |
|---|---|---|---|
| Zr(1)−O(1) | 2.299(4) | O(3)−Si(1) | 1.614(5) |
| Zr(1)−O(2) | 2.293(4) | O(4)−Si(2) | 1.624(4) |
| Zr(1)−O(3) | 1.917(4) | Si(1)−C(12) | 1.830(11) |
| Zr(1)−O(4) | 1.923(4) | Si(1)−C(13) | 1.762(11) |
| Zr(1)−Cl(1) | 2.471(2) | Si(2)−C(9) | 1.74(2) |
| Zr(1)−Cl(2) | 2.472(2) | Si(2)−C(10) | 1.73(3) |
| Si(2)−C(11) | 1.89(3) | | |
| Cl(1)−Zr(1)−Cl(2) | 163.87(7) | O(1)−Zr(1)−O(2) | 79.5(2) |
| O(2)−Zr(1)−O(4) | 168.4(2) | O(1)−Zr(1)−O(4) | 89.2(2) |
| O(3)−Zr(1)−O(1) | 168.2(2) | O(1)−Zr(1)−Cl(1) | 83.64(12) |
| O(2)−Zr(1)−Cl(1) | 84.13(12) | O(1)−Zr(1)−Cl(2) | 84.25(12) |
| O(2)−Zr(1)−Cl(2) | 83.21(12) | O(3)−Zr(1)−O(2) | 89.0(2) |
| Zr(1)−O(3)−Si(1) | 171.4(3) | O(3)−Zr(1)−O(4) | 102.4(2) |
| Zr(1)−O(4)−Si(2) | 167.9(3) | O(3)−Zr(1)−Cl(1) | 92.5(2) |
| O(3)−Zr(1)−Cl(2) | 97.2(2) | | |

Grignard reagents have been observed in the synthesis of metal alkyl complexes.[8]

**Solid-State Structure of 1.** An ORTEP view of the solid-state structure of **1** is shown in Figure 1, and selected bond distances and angles are listed in Table 2. The Zr atom is coordinated by two $Me_3SiO$ ligands, two chlorine atoms, and two THF molecules to form a distorted octahedron. The two chlorine atoms are trans each other while both $Me_3SiO$ ligands and the two THF molecules are cis each other. A similar geometry has been observed in $(Me_2N)_2ZrCl_2 \cdot 2THF$.[9] The trans angles in **1** are 163.87(7), 168.2(2), and 168.4(2)°. As shown in Table 2, the cis angles between O(1) and the Cl(1), Cl(2), O(2), and O(4) atoms range from 79.5(2) to 84.25(12)°, while the angles between O(3) and the Cl(1), Cl(2), O(2), and O(4) atoms range from 89.0(2) to 102.4(2)°; the ligands cis to the siloxy ligand $O(4)-SiMe_3$ are bent away from it. Such distortion indicates that the $Me_3SiO$ ligand is more sterically demanding than the THF molecule. This is consistent with the fact that the angle between the two $Me_3SiO$ ligands, 102.4(2)°, is larger than that [79.5(2)°] between the two THF molecules. The Zr−O(siloxy) bond distances [1.917(4) and 1.923(4) Å] are similar to the corresponding distance found in the alkoxide complex $(Bu^tO)_3ZrSi(SiMe_3)_3$, 1.89 Å.[3a] The Zr−O−Si bond angles [167.9(3)° and 171.4(3)°] are also close to the Zr−O−C angle [166(1)°] in $(Bu^tO)_3ZrSi(SiMe_3)_3$. Both Zr−Cl [2.471(2) and 2.472(2) Å] and Zr−O(THF) [2.299(4) and 2.293(4) Å] bond distances are slightly shorter than the corresponding values found in $(Me_2N)_2ZrCl_2 \cdot 2THF$ [2.499(2) and 2.486(1) Å; 2.342(2) and 2.330(2) Å],[9] indicating that the complex $(Me_2N)_2ZrCl_2 \cdot 2THF$ is more sterically crowded than **1**.

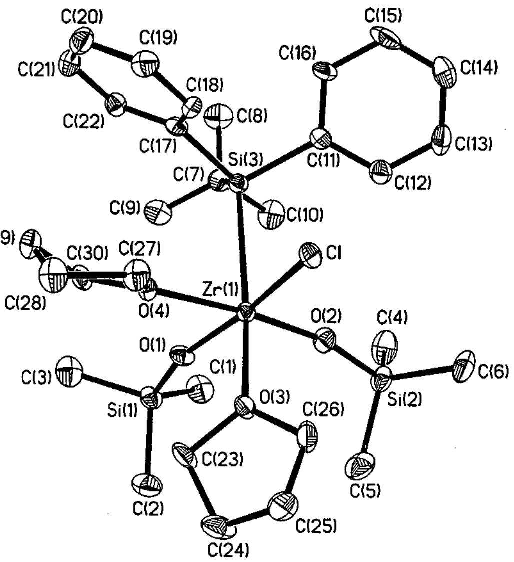

**Figure 2.** ORTEP view of the structure of $(Me_3SiO)_2Zr(SiPh_2Bu^t)Cl \cdot 2THF$ (**2**), showing 35% thermal ellipsoids.

**Table 3. Selected Bond Distances (Å) and Angles (deg) for 2**

| | | | |
|---|---|---|---|
| Zr(1)−Si(3) | 2.848(3) | Si(1)−O(1) | 1.641(5) |
| Zr(1)−Cl | 2.517(2) | Si(2)−O(2) | 1.643(6) |
| Zr(1)−O(1) | 1.952(5) | Si(3)−C(7) | 1.931(9) |
| Zr(1)−O(2) | 1.926(5) | Si(3)−C(11) | 1.924(8) |
| Zr(1)−O(3) | 2.292(5) | Si(3)−C(17) | 1.927(8) |
| Zr(1)−O(4) | 2.289(5) | $Si-C(Me)_{av}$ | 1.853(9) |
| O(1)−Zr(1)−Cl | 165.1(2) | O(2)−Zr(1)−O(1) | 98.1(2) |
| O(2)−Zr(1)−O(4) | 172.4(2) | O(2)−Zr(1)−O(3) | 94.4(2) |
| O(3)−Zr(1)−Si(3) | 161.2(2) | O(2)−Zr(1)−Cl | 95.1(2) |
| Zr(1)−O(1)−Si(1) | 163.2(4) | O(2)−Zr(1)−Si(3) | 98.8(2) |
| Zr(1)−O(2)−Si(2) | 166.8(4) | O(4)−Zr(1)−O(1) | 83.0(2) |
| O(1)−Zr(1)−O(3) | 90.8(2) | O(4)−Zr(1)−O(3) | 78.0(2) |
| O(1)−Zr(1)−Si(3) | 100.3(2) | O(4)−Zr(1)−Cl | 83.02(13) |
| O(3)−Zr(1)−Cl | 81.25(14) | O(4)−Zr(1)−Si(3) | 88.35(14) |

**Solid-State Structure of 2.** An ORTEP diagram of the molecular structure of **2** is shown in Figure 2, and selected bond distances and angles are given in Table 3. In **2**, the Zr atom is bonded to two $Me_3SiO$ ligands,two THF molecules, one chlorine atom, and one $SiPh_2Bu^t$ ligand to give a six-coordinate complex. The geometry around the metal center is similar to **1**, a distorted octahedron. However, the arrangement of the ligands around the metal center in **2** is different from **1**. Complex **2** was made by substituting one chlorine atom in **1** with a $SiPh_2Bu^t$ ligand. In **1**, two chlorine atoms are trans each other, but, in **2**, the chlorine atom and $SiPh_2Bu^t$ ligand are cis each other. The trans angle of O(2)(siloxy)−Zr−O(4)(THF) [172.4(2)°] is close to 180° while the other two are around 160°. As in **1**, the ligands cis to $O(2)-SiMe_3$ are bent away from it (see Table 3). The Zr−O−Si bond angles [163.2(4)° and 166.8(4)°] are slightly smaller than the corresponding

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(8) Schrock, R. R.; Clark, D. N.; Sancho, J.; Wengrovius, J. H.; Rocklage, S. M.; Pedersen, S. F. *Organometallics* **1982**, *1*, 1645.

angles in **1,** which may suggest a larger steric interaction between $Me_3SiO$ and $SiPh_2Bu^t$ ligands.

The Zr−Si bond distance of 2.848 Å is longer than those in $(Bu^tO)_3ZrSi(SiMe_3)_3$ [2.753(4) Å],[3a] $(Bu^tCH_2)_3ZrSi(SiMe_3)_3$ [2.74(2) Å],[5] $Cp_2Zr[Si(SnMe_3)_3]Cl$ [2.772(4) Å],[1b] and $Cp_2Zr(SiPh_3)(H)(PMe_3)$ [2.721(2) Å][2t] and close to those found in $Cp_2Zr(SiPh_3)Cl$ [2.813(2) Å][10] and $Cp_2Zr(SiMe_3)(S_2CNEt_2)$ (2.815 Å).[11] To our knowledge, the Zr−Si bond in **2** is the longest reported Zr−Si bond observed in Zr(IV) silyl complexes. The reason for the long Zr−Si bond in **2** is probably due to coordinative effects. Six-coordinated complexes are usually more sterically congested than four- and five-coordinated zirconium complexes. The Zr−O(siloxy) [1.952(5) and 1.926(5) Å] and Zr−O(THF) [2.292(5) and 2.289(5) Å] bond distances are similar to the corresponding values in **1**. The Zr−Cl bond distance of 2.517(2) Å is slightly longer than those found in **1** and $(Me_2N)_2ZrCl_2{\cdot}2THF$, which suggests a larger steric repulsion between ligands in **2**.

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**Supporting Information Available:** Complete listings of crystallographic data for **1** and **2** (12 pages). Ordering information is given on any current masthead page.

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(10) Muir, K. *J. Chem. Soc. A* **1971**, 2663.

(11) Tilley, T. D. *Organometallics* **1985**, *4*, 1452.