*Inorg. Chem.* **1996,** *35,* 4391−4395

# Five- and Six-Coordinate 2-Methyl-2-propanethiolato Complexes of Zirconium(IV): Synthesis and Structures of $[Li(DME)_3][Zr(SCMe_3)_5]$ and $[(THF)Li]_2Zr(SCMe_3)_6$

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*Received September 15, 1995*[⊗]

Five-coordinate and six-coordinate 2-methyl-2-propanethiolato complexes of zirconium, $[Li(DME)_3][Zr(SCMe_3)_5]$ (**1**) and $[(THF)Li]_2Zr(SCMe_3)_6$ (**2**), were obtained from the $ZrCl_4/LiSCMe_3$ reaction system. The control of the Zr coordination number, by the ether ligands, THF or DME, bound to Li, is demonstrated by the conversion of **2** into **1** upon dissolution in DME. **1** and **2** were crystallographically characterized. The structures are extensively disordered. Crystal data follow: **1**, hexagonal $P6_3/m$, $a = b = 12.496(3)$ Å, $c = 17.561(9)$ Å, $Z = 2$, $V = 2375(1)$ Å$^3$, $R = 5.0\%$, $R_w = 6.8\%$; **2**, trigonal $R32$, $a = b = 11.813(3)$ Å, $c = 28.37(1)$ Å, $Z = 3$, $V = 3428(1)$ Å$^3$, $R = 5.2\%$, $R_w = 6.4\%$.

## Introduction

In the last 2 decades there has been a surge of interest in synthesizing electron deficient transition metal complexes with S-donor ligands, due to their relevance to bioinorganic chemistry, catalysis, and materials science.[1,2] Mononuclear species coordinated solely by thiolate ligands are the most fundamental class, and such homoleptic thiolato complexes of early transition metals are represented by those derived from benzenemonothiolate,[3] benzene-α, *β*-dithiolate,[4] 2-methyl-2-propanethiolate, and ethane-1,2-dithiolate.[5] We have isolated and structurally characterized $d^0$ metal complexes with aliphatic thiolate ligands, $[(TMEDA)Li]_3M(SCMe_3)_6$ (M = Yb, Sm),[6] $[(DME)Li]_4U(SCH_2CH_2S)_4$,[7] $(A)[M(SCH_2CH_2S)_3]$, $(A)[M(SCH_2CH_2CH_2S)_3]$,[8] and $(A)[M(ndt)_3]$ ($A = NEt_4$, $PPh_4$; M = Nb, Ta; ndt = norbornane-*exo*-2,3-dithiolate).[9] Other known homoleptic tert-butyl thiolato complexes are limited to $Ti(SCMe_3)_4$,[10] $V(SCMe_3)_4{}^{0,-}$,[11a] $M(SCMe_3)_4$ (M = Mo[11b], W[11c]), and $[Na(thf)_3]_2[U(SCMe_3)_6]$.[12]

Zirconium chemistry of thiolates is little explored, and the only fully characterized homoleptic thiolato complex known is $(NMe_4)_2\ [Zr(S_2C_6H_4)_3]$.[13] The reaction between $ZrCl_4$ and $Al(SPh)_3(Et_2O)$ was reported to give a blue complex formulated as $Zr(SPh)_4$, but no X-ray structure is available.[14] The synthesis of a zirconocene−thiolato complex, $[(C_5H_5)_2Zr(SCMe_3)(THF)](BPh_4)$ has appeared.[15] The reaction most closely related to the present study is protonolysis of $Zr(BH_4)_4$ by $Me_3CSH$ at room temperature to yield $Zr_3S_3(SCMe_3)_2(BH_4)_4(THF)_2$ and $Zr_6S_6(SCMe_3)_4(BH_4)_8(THF)_2$, reported by Coucouvanis et al.[16a] A similar reaction of $Zr(CH_2Ph)_4$ with $Me_3CSH$ also afforded a sulfido/thiolato cluster, $Zr_3(S)(SCMe_3)_{10}$.[16b] Obviously C−S bond cleavage took place even under mild reaction conditions. Coordination of aliphatic thiolate ligands to early transition metals is often followed by facile C−S bond cleavage, which hampers isolation of homoleptic thiolate complexes. For instance, the reaction of $NbCl_5$ with 6 equiv of $NaSCMe_3$ was found to generate $[Nb(S)_2(SCMe_3)_2]^-$ and $[NbS(SCMe_3)_4]^-$.[17]

As an extension of our study of the $d^0$ transition metal chemistry of aliphatic thiolates, we report in this paper the synthesis and structures of $[Li(DME)_3][Zr(SCMe_3)_5]$ (**1**) and $[(THF)Li]_2Zr(SCMe_3)_6$ (**2**). This is the first report of a homoleptic 5-coordinate complex in this family.

## Experimental Section

**General Procedures.** All manipulations were performed under an inert atmosphere of argon using standard Schlenck techniques. Solvents were purified by distillation from appropriate drying agents. $LiSCMe_3$

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[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1996.

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S0020-1669(95)01211-0 CCC: $12.00

was prepared from $Me_3CSH$ and *N*-butyllithium (1.53 M hexane solution) in THF or DME at 0 °C, and was used immediately for the reaction with $ZrCl_4$.

$^1H$ NMR spectra were measured on a JEOL JNM-GSX270 instrument. IR spectra were recorded as Nujol mulls between CsI plates on a Hitachi 295 spectrophotometer. Elemental analyses were performed on a LECO CHN-900 microanalyzer.

**[Li(DME)$_3$][Zr(SCMe$_3$)$_5$] (1).** To a suspension of $ZrCl_4$ (0.31 g, 1.33 mmol) in 30 mL of toluene, a DME (40 mL) solution of $LiSCMe_3$ (6.65 mmol) at 0 °C. The resulting yellow suspension was stirred at room temperature for 1 h. The reaction mixture was evaporated to dryness. The yellow solid was extracted with toluene (50 mL × 2) and centrifuged to remove LiCl. Solvent was removed from the yellow solution to give a yellow residue (0.98 g, 91%), which was recrystallized from DME to afford **1** as yellow crystals (0.70 g, 65%). $^1H$ NMR ($C_6D_6$): $\delta$ 3.22 (s, 12H, DME), 3.18 (s, 18H, DME), 1.96 (s, 45H, $SCMe_3$). IR (Nujol mull/CsI): 1190 m, 1160 s, 1121 s, 1082 vs, 1030 m, 870 s, 574 m, 416 m, 392 m, 330 m, 310 sh cm$^{-1}$. Mp: 129−133 °C dec. Anal. Calcd for $C_{32}H_{75}O_6S_5LiZr$: C, 47.19; H, 9.28. Found: C, 46.86; H, 8.93.

**[(THF)Li]$_2$Zr(SCMe$_3$)$_6$ (2).** A solution of 6 equiv of $LiSCMe_3$ (13.9 mmol) in THF (30 mL) was added to a toluene (40 mL) suspension of $ZrCl_4$ (0.54 g, 2.32 mmol) at 0 °C. The reaction mixture, which turned yellow immediately, was stirred at room temperature for 1 h. The mixture was then dried under vacuum to give a yellow solid which was extracted with $Et_2O$ (60 mL × 2) and centrifuged to remove the insoluble products. THF (1 mL) was added to the yellow solution, and the solution was concentrated to ca.10 mL and cooled to −35 °C. **2** was obtained as yellow crystals (0.33 g, 18%). Concentration of the mother liquor and addition of hexane gave a second crop; the total yield was 0.55 g (30%). $^1H$ NMR ($C_6D_6$): $\delta$ 3.84 (m, 8H, THF), 1.91 (s, 54H, $SCMe_3$), 1.47 (m, 8H, THF). IR (Nujol mull/CsI): 1210 m, 1160 vs, 1090 m, 1060 s, 1040 m, 898 m, 570 s, 404 s, 393 s, 319 m, 308 sh cm$^{-1}$. Mp: 141−144 °C dec. Anal. Calcd for $C_{32}H_{70}O_2S_6Li_2Zr$: C, 49.00; H, 8.99. Found: C, 48.77; H, 8.88.

**Conversion of 2 into 1.** **2** (0.53 g, 0.68 mmol) was dissolved in 20 mL of DME at room temperature, and the yellow solution was concentrated to 4 mL. Addition of hexane to the solution resulted in precipitation of yellow crystals. These were identified as **1** (0.26 g, 47%) by $^1H$ NMR and by determination of unit cell parameters. $^1H$ NMR ($C_6D_6$): $\delta$ 3.22 (s, 12H, DME), 3.17 (s, 18H, DME), 1.94 (s, 45H, $SCMe_3$). X-ray: crystal system, hexagonal; lattice, P; cell parameters, $a = b =$12.534(6) Å, $c$ = 17.53(2) Å, $V$ = 2386(3) Å$^3$.

**X-ray Data Collection and Structure Determination. [Li(DME)$_3$][Zr(SCMe$_3$)$_5$] (1).** A yellow block of **1** was sealed in a capillary and X-ray diffraction measurements were carried out using a Siemens P1 diffractometer with graphite-monochromated Mo Kα radiation at room temperature. The unit cell was determined from the coordinates of 28 reflections with 2$\theta$ values between 8.9° and 22.8°. Because the identity of the Laue group was unclear, a full one-third hemisphere of data for **1** was collected in the hexagonal unit cell. Friedel pairs were collected for a portion of the data set. The data were processed in the usual way using the SHELXTL PLUS system of programs and corrected for absorption based upon $\psi$ scans of five reflections spread throughout the 2$\theta$ range. The only systematic absence was 00*l*, $l = 2n + 1$, which indicates space group *P*6$_3$22 of Laue class 6/*mmm* or *P*6$_3$/*m* and *P*6$_3$, both of Laue class 6/*m*. The data intensities were roughly consistent with Laue class 6/*mmm*; however, detailed inspection showed that not to be the best assignment. This is illustrated by the merging *R* value, which was 12.7% for *P*6$_3$22 but only 3.4% for *P*6$_3$/*m* and *P*6$_3$. The structure of **1** presented in this paper is based on the centrosymmetric choice *P*6$_3$/*m* and the reasons for that choice are presented in Supporting Information. The structure was solved by the application of Patterson and direct methods and expanded using difference Fourier techniques using the SHELXTL PLUS system.

**Table 1.** Crystal Data for [Li(DME)$_3$][Zr(SCMe$_3$)$_5$] (**1**) and [(THF)Li]$_2$Zr(SCMe$_3$)$_6$ (**2**)

| | **1** | **2** |
|---|---|---|
| formula | $C_{32}H_{75}S_5ZrO_6Li$ | $C_{32}H_{70}S_6ZrO_2Li_2$ |
| fw | 814.43 | 784.37 |
| space group | *P*6$_3$/*m* (No. 176) | *R*32 (No. 155) |
| *a*, Å | 12.496(3) | 11.813(3) |
| *c*, Å | 17.561(9) | 28.37(1) |
| *V*, Å$^3$ | 2375(1) | 3428(1) |
| Z | 2 | 3 |
| $D_c$, g/cm$^3$ | 1.139 | 1.140 |
| $\mu$, cm$^{-1}$ | 4.66 | 5.37 |
| radiation; $\lambda$, Å | Mo Kα; 0.710 69 | Mo Kα; 0.710 73 |
| 2$\theta_{max}$, deg | 37.5 | 55.0 |
| transm factors | 0.87−1.00 | 0.93−1.00 |
| no. of unique rflns | 652 | 1015 |
| no. of observns | 528$^a$ | 846$^b$ |
| R | 0.050 | 0.052 |
| $R_w$ | 0.068 | 0.064 |
| GOF | 0.95 | 1.99 |
| function minimized | $\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$ | $\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$ |
| least-squares weights | $w = 1/\{\sigma^2(F) + 0.005F^2\}$ | $w = 1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$ |
| no. of refined params | 153 | 100 |

$^a$ $F > 4.0\sigma(F)$. $^b$ $I > 3.0\ \sigma(I)$.

**Table 2.** Atomic Coordinates and Equivalent Isotropic Thermal Parameters for [(THF)Li]$_2$Zr(SCMe$_3$)$_6$ (**2**) with Standard Deviations in Parentheses

| atom | *x* | *y* | *z* | $B_{eq}$$^a$ |
|---|---|---|---|---|
| Zr | 0 | 0 | 0 | 3.75(1) |
| S | 0.0246(3) | 0.1753(3) | 0.06295(9) | 5.79(6) |
| $S_X$ | 0.1573(4) | 0.1809(3) | 0.0549(1) | 4.35(6) |
| O | 0 | 0 | 0.1773(2) | 10.2(1) |
| C1 | 0.160(1) | 0.3399(5) | 0.0689(2) | 7.4(1) |
| C2 | 0.215(2) | 0.4216(8) | 0.0252(2) | 16.4(3) |
| C3 | 0.139(1) | 0.401(2) | 0.1136(5) | 9.7(4) |
| $C3_X$ | 0.044(3) | 0.368(3) | 0.071(2) | 24(1) |
| C4 | 0.285(1) | 0.319(1) | 0.0788(6) | 9.1(3) |
| $C4_X$ | 0.253(3) | 0.413(2) | 0.1030(8) | 15.5(6) |
| C5 | 0.110(1) | 0.098(1) | 0.2062(3) | 11.8(4) |
| C6 | 0.083(2) | 0.082(2) | 0.2507(4) | 18.2(8) |
| Li | 0 | 0 | 0.1109(5) | 9.0(2) |

$^a$ $B_{eq} = {}^8/_3\pi^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha]$.

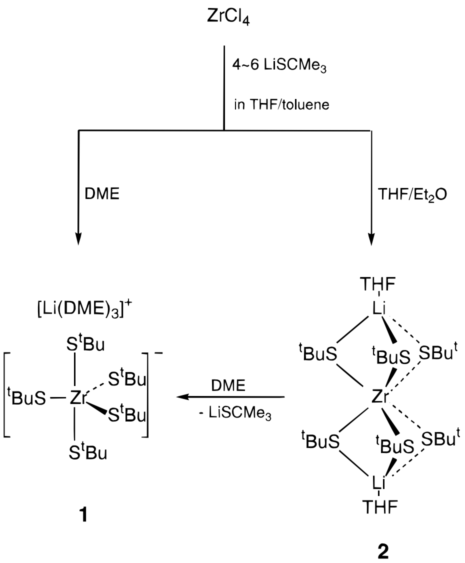
**[(THF)Li]$_2$Zr(SCMe$_3$)$_6$ (2).** A yellow prismatic crystal of **2** was sealed in a capillary, and a Rigaku AFC7R diffractometer with 12 kW rotating anode generator was used for data collection at room temperature. The unit cell was obtained from a least-squares refinement of the setting angles of 25 reflections with 2$\theta$ values between 25.05 and 28.30°. The resulting unit cell was rhombohedral, reported here on hexagonal axes, and the Laue class was determined to be 3*m*1. Data were collected under the *R* condition and no other systematic absences were observed. Intensity statistics indicated an acentric space group. Among acentric space groups which satisfy the *R* condition, only *R*32 and *R*3*m* belong to the correct Laue group. The structure is reported in *R*32 and is extensively disordered. The *R*3*m* choice would produce even further disorder and in particular would lead to unsuitable S−C distances, and was thus excluded. The structure was solved using direct methods and expanded using Fourier techniques by application of the teXsan crystallographic software package of the Molecular Structure Corp.

Crystal data and relevant information for **1** and **2** are summarized in Table 1. The final fractional coordinates of non-hydrogen atoms for **1** are available in the Supporting Information, and those for **2** are shown in Table 2.

## Results and Discussion

**Synthesis of Zr(IV) 2-Methyl-2-propanethiolate Complexes.** To prepare a neutral tetrakis(2-methyl-2-propanethiolato) complex of zirconium(IV), which is analogous to the known titanium congener $Ti(SCMe_3)_4$,[10] we first attempted the reaction of $ZrCl_4$ with 4 equiv of $LiSCMe_3$ in THF/toluene. Removal of solvent from the reaction system gave a yellow residue, from which $Zr(SCMe_3)_4$ or $Zr(SCMe_3)_4(THF)_n$ could not be isolated. Instead, recrystallization of this residue from

**Scheme 1**



DME afforded [Li(DME)3] [Zr(SCMe3)5] (**1**) as yellow crystals in low yield. A similar recrystallization from $Et_2O$ which contains a small amount of THF gave yellow crystals of $[(THF)Li]_2Zr(SCMe_3)_6$ (**2**), again in low yield. When the amount of $LiSCMe_3$ was increased to 5 or 6 equiv, **1** and **2** were produced in better yields, 65% for **1** and 30% for **2**, respectively. The isolable product is either **1** or **2** regardless of the stoichiometric relationship between $ZrCl_4$ and $LiSCMe_3$, which influences only their yields. The choice of DME or THF as the solvent for crystallization is a dominant factor in the generation of either **1** or **2**. Desolving **2** in DME and concentration of the DME solution gave rise to **1** in 47% yield, whereas conversion of **1** into **2** by treating **1** in THF/$Et_2O$ does not occur via a disproportionation process. The reaction system as described above is set out in Scheme 1.

The $^1H$ NMR spectrum of **1** in $C_6D_6$ at room temperature exhibits the $SCMe_3$ signal as a single peak at 1.96 ppm, as well as a set of the DME proton signals. Their relative intensities indicate that **1** contains three coordinated DME molecules. As shown later in this section, the solid-state structure of $[Zr(SCMe_3)_5]^-$ is that of a trigonal bipyramid, while in solution the axial and equatorial thiolate ligands exchange quickly on the NMR time scale. The $SCMe_3$ proton signal of **2** in $C_6D_6$ appears at 1.91 ppm, along with resonances attributable to coordinated THF. It seems that the principal coordination geometry of either **1** or **2** is retained in a nonpolar solvent which does not interact with the lithium cation. Their solid state IR spectra show bands at 330 and 319 $cm^{-1}$, with shoulders at 310 and 308 $cm^{-1}$, respectively, which are assignable to Zr−S stretching vibrations. However no structural information can be obtained from the IR spectra alone.

Most of zirconium/thiolato complexes reported so far were prepared from reactions of thiols with appropriate preformed halide-free zirconium compounds. For example, the acid−base reaction of $Zr(NR_2)_4$ with $H_2S_2C_6H_4$ and $HS_2C_6H_4^-$ gave $[Zr(S_2C_6H_4)_3]^{2-}$.[13] $Me_3CSH$ reacted with $Zr(BH_4)_4$ to give $Zr_3S_3(SCMe_3)_2(BH_4)_4(THF)_2$ and $Zr_6S_6(SCMe_3)_4(BH_4)_8(THF)_2$,[16a] while the reaction of $Zr(CH_2Ph)_4$ with $Me_3CSH$ generated $Zr_3(S)(SCMe_3)_{10}$.[16b] In these reactions with $Me_3CSH$, C−S bond cleavage took place, although the reactions were carried out under mild conditions. Interestingly, upon treating $ZrCl_4$ directly with $LiSCMe_3$ we were able to isolate the homoleptic thiolato complexes, **1** and **2**, in moderate yields without cleaving the C−S bonds.

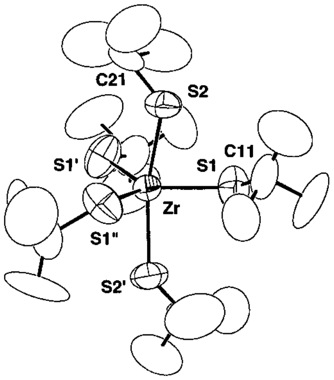


**Figure 1.** ORTEP drawing of the anion part of $[Li(dme)_3][Zr(SCMe_3)_5]$ (**1**). Only one set of the disordered $SCMe_3$ ligands is shown.

**Description of the X-ray Diffraction Crystal Structure of $[Li(DME)_3][Zr(SCMe_3)_5]$ (1).** The crystal structure of **1** is extensively disordered. There are two Zr atoms in the unit cell, located at Wyckoff position *c* of symmetry 6. The equatorial sulfur atom, S1, does not lie in the mirror plane, but is displaced about 0.5Å on either side of it. Likewise, none of the carbon atoms lie in the mirror plane and are therefore also 2-fold disordered. In addition, the equatorial $CMe_3$ group is rotationally disordered over two positions which refined to occupancies of 41.7(8)% for the one set carbon atoms and 8.3(8)% for the other. This rotational disorder, plus disorder across the mirror plane, means that the equatorial $CMe_3$ group is disordered over four sites. The sulfur atom of the axial $SCMe_3$ group, S2, does not lie on the 3-fold axis, and is thus 3-fold disordered around it. Therefore each of the carbon atoms of the axial $SCMe_3$ groups is also disordered over three positions around the 3-fold axis. All of the disordered positions for the $SCMe_3$ ligands of **1** are shown in Figure S1 in the Supporting Information.

The two $Li^+$ cations in the unit cell are located at Wyckoff position *b*, a site of 3 symmetry. Each $Li^+$ cation is coordinated to three DME molecules, so that a $M(AA)_3$ type chelate results. This arrangement is chiral with $\delta$ and $\lambda$ absolute configurations. However, since the $Li^+$ cation occupies a crystallographic 3 site, these two configurations must be 2-fold disordered. In either configuration, $[Li(DME)_3]^+$ has a normal octahedral geometry, and such a lithium cation carrying three DME molecules has been reported only three times.[18]

The structure of the anion of **1** is shown in Figure 1, where the three equatorial $SCMe_3$ groups are related to each other by crystallographic symmetry, while the two axial $SCMe_3$ groups are also crystallographically equivalent. The Zr is bound to five $SCMe_3$ ligands to form a $[Zr(SCMe_3)_5]^-$ anion which is trigonal bipyramidal. In Figure 1 only one of the three possible orientations of each axial $SCMe_3$ group is shown for clarity, and the disorder of the equatorial $SCMe_3$ groups is related to that of the axial groups. For instance, S2 is shown to the "right" of the 3-fold axis while S1 is in a "down" location with respect to the mirror plane. If S1 were placed at an "up" position, then the S1-S2 distance is too short, 2.43(1) Å, so that the "right" position for S2 and the "up" position for S1 cannot be occupied at the same time. By a similar reason, S1′ and S1″ are both placed in "up" locations, and S2′ is in a "right" location.

Selected bond distances and angles are listed in Table 3 and should be viewed with the following caveat. The thermal parameters in this structure are quite large, and, due to the

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**Table 3.** Selected Bond Distances (Å) and Angles (deg) for $[Li(DME)_3][Zr(SCMe_3)_5]$ (**1**) and $((THF)Li)_2Zr(SCMe_3)_6$ (**2**)

| | | | |
|---|---|---|---|
| | $[Li(DME)_3][Zr(SCMe_3)_5]$ (**1**) | | |
| Zr−S1 | 2.468(6) | C21−C22 | 1.52(5) |
| Zr−S2 | 2.539(8) | C21−C23 | 1.35(9) |
| S1−C11 | 1.77(1) | C21−C24 | 1.31(5) |
| S2−C21 | 1.70(4) | Li−O | 2.12(1) |
| C11−C12 | 1.62(7) | O−C1 | 1.58 |
| C11−C13 | 1.61(4) | O−C2 | 2.81(1) |
| C11−C14 | 1.48(6) | C2−C3 | 1.75(9) |
| C11−C15 | 2.0(3) | Ox−C3 | 1.48(4) |
| C11−C16 | 1.6(1) | Ox−C4 | 1.15(6) |
| C11−C17 | 1.2(1) | | |
| S1−Zr−S1′ | 116.6(1) | O1−Li−O1′ | 91(4) |
| S2−Zr−S2′ | 159.1(2) | Li−O1−C1 | 131(3) |
| S1−Zr−S2 | 91.8(3) | Li−O1−C2 | 113(2) |
| Zr−S1−C11 | 122.1(9) | Li−O1−C3 | 115(2) |
| Zr−S2−C21 | 129(2) | Li−O1−C4 | 135(3) |
| | $((THF)Li)_2Zr(SCMe_3)_6$ (**2**) | | |
| Zr−S | 2.638(3) | Li−S | 2.371(8) |
| Zr−$S_X$ | 2.545(3) | Li−$S_X$ | 2.563(9) |
| Zr−Li | 3.15(1) | Li−O | 1.88(1) |
| S−Zr−S′ | 79.2(1) | $S_X$−Zr−$S_X'$ | 86.4(1) |
| S−Zr−S″ | 79.2(1) | $S_X$−Zr−$S_X''$ | 86.4(1) |
| S−Zr−S‴ | 86.3(1) | $S_X$−Zr−$S_X'''$ | 76.6(1) |
| S−Zr−S⁗ | 147.2(1) | $S_X$−Zr−$S_X''''$ | 123.4(1) |
| S−Zr−S′′′′′ | 126.8(1) | $S_X$−Zr−$S_X'''''$ | 143.8(2) |

disorder, the geometry of the $CMe_3$ groups is quite distorted and inaccurate. It is not possible to ascertain the bonding within the disordered $CMe_3$ groups. For example S2 is 1.77(1) Å from C11, which we have selected as the bond. However it is also 1.87(2) Å from the alternate C11 site, which could also represent a S−C bond. The Zr−S−C angles associated with these two choices are 122.1(9) and 117.6(9)°, respectively. Again, either is possible, although the former set of values is more likely correct. There are many other examples of such ambiguities in the $CMe_3$ groups, so that their metric parameters we have selected to present in Table 3 are unreliable.

**Description of the X-ray Diffraction Structure of $[(THF)Li]_2Zr(SCMe_3)_6$ (2)**. The structure of **2** is presented in Figure 2, while selected bond distances and angles are given in Table 3. The structure consists of a Zr atom surrounded by six $SCMe_3$ ligands. There are two lithium cations each bound to those three sulfurs which form opposite trigonal faces, with charge-neutralizing of the complex dianion. The tetrahedral coordination of each $Li^+$ ion is completed by a terminal THF ligand.

The Zr atom occupies Wyckoff position *a*, i.e., a position of 32 ($D_3$) symmetry. Also located on the 3-fold axis at Wyckoff position *c* are the $Li^+$ cation and the oxygen atom of the THF molecule. Since the THF oxygen is located at this site, each of the carbon atoms of the THF is disordered over three positions around the 3-fold axis, as shown in Figure 2 (bottom) in which the methyl groups of the $SCMe_3$ ligands are omitted. The tertiary carbon atom C1 of the $SCMe_3$ ligand occupies a general position and is not disordered. However the sulfur atom does not occupy a single site, but is rather disordered over two sites, each of which is bound to the C1 atom of the $CMe_3$ group. The bond angles Zr−S−C1, 126.8(3)°, and Zr−$S_X$-C1, 127.0(3)°, are equivalent. The disorder amounts to bending the $ZrSCMe_3$ group at the sulfur atom either to the right or to the left. However instead of holding the sulfur position constant and moving the $CMe_3$ group, the $CMe_3$ group is held at the same general position and the sulfur atom is displaced to the right or left of the Zr−C1 line. Two of the three Me groups of the $CMe_3$ group are disordered, namely C3 and C4, while the third Me group, C2, occupies a position shared by both orientations of the $CMe_3$ group. The structure seems to be composed of $CMe_3$ groups packed closely together with a hollow space inside which is occupied by the Zr and S atoms, but which is large enough to accommodate two different orientations of the $SCMe_3$ ligands.

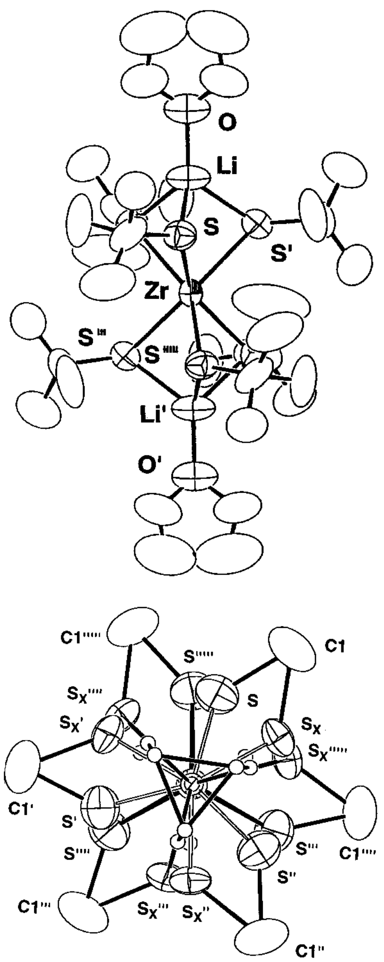

**Figure 2.** ORTEP drawings of the structure of $[(THF)Li]_2Zr(SCMe_3)_6$ (**2**). Top: A side view, where only one set of of the disordered $SCMe_3$ ligand is shown. Bottom: A top view, showing the disordered positions of sulfur, where the methyl groups of the $SCMe_3$ ligands are omitted for clarity.

The symmetry of the Zr position generates a set of six sulfur atoms for each sulfur position, i.e., six for S and six more for $S_X$. In each case a triangular set of three sulfur atoms is bridged by a $Li^+$ cation at both the top and bottom of the complex. In turn pairs of S atoms, one drawn from the top group and the second from the bottom, are related by one of the 2-fold axes which passes through Zr and is perpendicular to the 3-fold axis. This is also true for the $S_X$ atoms.

The Zr−S, 2.638(3)Å and Zr−$S_X$, 2.545(3)Å distances, are noticeably different. The reason for this seems to be related to the orientation of the THF group which is bound to Li. The $S_X$ sulfurs are eclipsed with respect to the THF carbons, and thus presumably experience some steric repulsion, while the THF carbons and the S sulfurs are staggered and thus would experience less or no such repulsion. As a result of this interaction between the THF carbons and $S_X$, the Li−$S_X$ distance is expanded to 2.563(9)Å compared to the Li−S distance of 2.371(8) Å. The stronger Li−S interaction in turn weakens the bond between Zr and S, thus accounting for the longer Zr−S distance compared to that of Zr−$S_X$.

Since both the Zr atom and $Li^+$ cation interact with S and $S_X$ so differently, one might expect the populations of S and

$S_X$ to be different. Indeed, refinement of occupancy of the two inequivalent sulfur positions yields 60% occupancy for S and 40% for $S_X$. Since it is $S_X$ which experiences the greater steric interaction with the THF carbons, one would expect it to have the lower occupancy. Indeed that is what is observed.

Unfortunately the coordination geometry about the Zr can be described as either trigonal prismatic or octahedral, and due to the disorder, we cannot tell which is the better description from the X-ray data alone. Each set of sulfur atoms, S and $S_X$ by itself, describes a trigonal prism with the 2-fold axis of the trigonal prism coincident with the crystallographic 2-fold axis. However if one selects one trigonal set of S and one trigonal set of $S_X$ then the coordination polyhedron is an octahedron, but in this case the 2-fold axis of the octahedron is not coincident with the crystallographic 2-fold axis. If the occupancies of S and $S_X$ are not equal, then we can rule out the octahedral description of the Zr coordination sphere since such a description requires the use of both S and $S_X$ within the same octahedron. The trigonal-prismatic structure of **2**, therefore, is presented in Figure 2 (top). While the refined occupancies are reasonable and are supported by the steric argument set forth above, they are not sufficiently strong evidence to completely rule out the octahedral case. Thus the steric argument and the occupancies of the disordered sulfur atoms support the assignment of a trigonal prismatic coordination sphere, but by themselves they do not firmly establish it.

Although transition metal six-coordination is dominated by octahedral geometries, substantial deviation from this polyhedral paragon is also established.[9,19] One such distortion is a trigonal twist from octahedron toward trigonal prism, which has occasionally been observed for $d^0$ $ML_6$ systems with chelating ($L_2$) ligands.[4,8b,9,20] In the case of monodentate ligands, occurrence of a trigonal prismatic arrangement is still rare, while molecular orbital analysis of the hypothetical $[TiH_6]^{2-}$ molecule predicted nonoctahedral ground states.[19c,21] The homoleptic methyl complex of zirconium [(tmeda)Li][$ZrMe_6$] is a single example of a fully-characterized mononuclear species which adopts a trigonal prismatic geometry.[22] The $TiS_6$ sphere of the central Ti atom in $Ti_3(SMe)_{12}$ approaches $D_{3h}$ symmetry (trigonal twist angle $\phi = 10.69(2)°$), where trigonal faces of $[Ti(SMe)_6]^{2-}$ are capped by $[Ti(SMe)_3]^+$ units.[23] Also in the dinuclear complex $[Zr_2(SPh)_7(CH_2Ph)_2]^-$, one Zr site is coordinated by six thiolates in a trigonal prismatic array.[24] While it was concluded that the choice of the trigonal prismatic structure is probably intrinsic to $[ZrMe_6]^{2-}$ anion,[22] capping a trigonal face or bridging a trigonal(or square) edge of $ML_6$ polyhedrons may enhance the preference for trigonal prismatic structures. This interpretation again supports the assignment of a trigonal prismatic structure for $[(THF)Li]_2Zr(SCMe_3)_6$ (**2**).

**Five vs Six Coordination of Zr(IV) by 2-Methyl-2-propanethiolato Ligands.** One would expect the Zr−S distances to be shorter in the five coordinate complex (**1**) as compared to the six coordinate one (**2**). In addition the equatorial Zr−S1 bond in **1** is expected to be shorter than the axial Zr−S2 bond for the usual steric reasons. This expectation is fulfilled by the distances, Zr−S1 = 2.468(6) Å and Zr−S2 = 2.539(8) Å. These bond distances compare with the Zr−S distances of $Zr_3S(SCMe_3)_{10}$ (terminal, 2.423(8) Å),[16b] $[(C_5H_5)_2Zr(SCMe_3)(THF)](BPh_4)$ (2.4618(13) Å),[15] $[(C_5H_5)_2Zr(SCH_2CH_2CH_2S)_2]_2$ (2.498 Å),[25] and$[(C_5Me_5)Zr(SEt)_2(\mu\text{-}SEt)]_2$ (terminal, 2.481 Å).[26]

In addition to the difference in coordination number, in the six-coordinate compound, the sulfur atoms are bound to $Li^+$ as well as Zr, causing additional lengthening of the Zr−S bonds (2.638(3) and 2.545(3) Å in **2**). Indeed the $Li^+$ cation seems to have a controlling influence on the course of the reaction which forms either the five- or six-coordinate complex. In the presence of DME, three of which chelate to $Li^+$, the Li coordination sphere is saturated and the Li does not coordinate to sulfur, and only five sulfurs coordinate to Zr. In the absence of DME, with only THF present to coordinate to $Li^+$, it chooses instead to coordinate to three sulfurs of a Zr complex, using a THF only as a terminal ligand. The coordination of the $Li^+$ to the sulfur atoms pulls them together, thus decreasing the steric demand of the $SCMe_3$ ligands which allows an additional ligand to coordinate to Zr producing the six coordinate complex. Coordination of the $Li^+$ cation also serves to neutralize the higher negative charge of the six-coordinate complex, and stabilizes the six-coordinate species. Thus, the Li cations are bound to THF and DME in a different way, which in turn controls the coordination geometry at the Zr(IV) center.

**Supporting Information Available:** Tables of atomic coordinates and isotropic thermal parameters, bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters of **1** and **2**, ORTEP drawings of the anion part of **1** showing the disordered positions, and text giving the details of determination of the space group of **1** (13 pages). Ordering information is given on any current masthead page.

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